Ferroelectric Thin-Film Waveguides in Integrated Optics and Optoelectronics

PROKHOROV, KUZ'MINOV & KHACHATURYAN

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# Ferroelectric Thin-Film Waveguides in Integrated Optics and Optoelectronics

A M Prokhorov, Yu S Kuz'minov, O A Khachaturyan (General Physics Institute, Russian Academy of Sciences, Moscow)

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## Contents

Prefac	e	ix
Symbo	ols	xi
Introd	luction	xiii
1	Epitaxial films of complex oxide compounds	1
1.1	Vacuum epitaxy	2
1.2	Gas-transport epitaxy	4
1.3	Films deposited by rf sputtering	8
1.3.1	Thin films of LiNbO deposited on a samphire substrate	ģ
1.3.2	Tungsten bronze ferroelectric K Li Nb O	13
1.3.3	KNbO thin films	14
1.3.4	KTa Nb O, thin films	16
1.3.5.	Thin films by pulsed laser deposition	17
1.3.6.	Wayeguides by MeV He ion implantation	20
1.3.7	Strip waveguides	21
1.3.8	Double waveguide	23
1.4	Autodiffused layers in lithium piohate and lithium tantalate	25
1.4.1	Out-diffusion kinetics	27
15	The diffusion method for metals and oxides	33
1.5.1	Diffusion of transition metals	37
1.5.2	Titanium diffusion	41
1.5.3	Conner diffusion	49
1.6	Proton-exchanged LiNbO waveguides	51
1.6.1	Ion-exchange processes in LiNbO	53
1.6.2	Sample preparation and experimental methods	54
1.6.3	Annealed proton-exchanged waveguides	56
1.6.4	Wayeguides fabricated using buffered melts	59
1.6.5	Proton diffusion	63
1.6.6	Wayeguides using cinnamic acid	64
1.6.7	Proton-exchange waveguides of MgO-doped and Nd:MgO-doped LiNbO.	66
1.7	Planar ion-exchanged KTiOPO waveguides	69
		••
2	Liquid-phase epitaxy of ferrolelectrics	74
2.1	The epitaxial growth by melting (EGM)	74
2.2	The capillary liquid epitaxial (CLE) technique	78
2.2.1	CLE growth procedure	79
2.2.2.	CLE growth and crystal quality	80
2.3	The liquid-phase epitaxy (LPE) technique	83
2.4	Physico-chemical basis of capillary liquid-phase epitaxy	87
2.4.1	The phase diagram of LiVO_LiNbO	91
2.4.2	Phase diagram of LiVOLi(Nb.Ta)O. pseudobinary system	92
2.4.3	The scheme of the growth cell	95
2.5	Kinetics of epitaxial growth of LiNbO.	97
2.5.1	The stationary crystallization model	97
2.5.2	Epitaxy under non-isothermic conditions	100
2.5.3	Determination of supersaturation U and diffusion coefficient D	101
2.5.4	Epitaxy under isothermal conditions	106
2.6	Crystallization of films from LiNb, Ta_O, solid solutions	109
2.6.1	Liquid-phase epitaxial growth of Li(Nb, Ta)O, films	112
2.7	Thin films of LiNbO3 doped with different elements	114
2.8	Epitaxial ferroelectric films with perovskite structure	119
2.8.1	Liquid-phase epitaxy of potassium niobate	119

2.8.2	Growth of potassium lithium niobate films on potassium bismuth niobate single crystals	122
2.9	Diffusion liquid-phase method of growing immersed waveguide channels	123
2.9.1	Strip line structures	124
2.9.2	Symmetric waveguides	124
2.10	Growth of epitaxial films in the KTiOPO family of crystals	127
3	Influence of electric current upon liquid-phase epitaxy of ferroelectrics	131
31	Electric field and crystallization	131
311	Bulk crystallization	131
312	Thin films	134
313	Liquid phase electroepitary	136
2.1.2	Dispute phase electrocytraxy	120
3.2	Physical dasis of inquid-phase electroephaxy (The theory of the method)	120
3.2.1	remperature distribution in a system under the action of an electric current	1.30
3.2.2	Film growth rate	141
3.2.3	Chemical composition control of the film	142
3.2.4	Initial stages of nucleation	143
3.3	The role of thermoelectric effects in the course of liquid-phase electroepitaxy of ferroelectrics	149
3.4	Electro-LPE growth of lithium niobate-tantalate films	151
3.4.1	Epitaxial growth	152
3.4.2	Electrochemical processes in the liquid phase	152
3.4.3	Growth kinetics of electro-LPE grown lithium niobate-tantalate films	155
3.5	Optimization of conditions of epitaxial growth of lithium niobate films with allowance for	
	Joule heat	158
4	Structure and composition of light guiding films	165
41	Structure and physico-chemical properties of lithium niobate and tantalate crystals	165
42	X-ray diffraction analysis of films	173
1.21	Laver composition	174
122	Monocrystallinity and interplanar distances	175
122	Measurement of strains in the diffused layer	178
4.2.5	Ti distribution in diffused layer	181
4.2.4	The structure of proton evolution of LiNkO	101
4.2.5	Chientetian relations	102
4.2.0	Orientation relations	104
4.3	Morphology and perfection of layers	102
4.3.1	Micromorphology of film surface for different crystallographic orientations of the substrate	180
4.3.2	Diffusion-induced defects in films	188
4.4	Substrate-film interface and transition region	190
4.5	Dislocation structure	191
4.6	Domain structure	196
4.6.1	Epitaxial film on a domain boundary of the substrate	197
4.6.2	Domain configurations in films	198
4.6.3	Microdomains in substrates and in epitaxial layers	199
4.6.4	Periodically inverted domain structures in LiTaO, and LiNbO, using proton exchange	200
4.6.5	Waveguide periodically poled by applying an external field	203
4.6.6	Domain inversion in LiNbO, using direct electron-beam writing	204
4.7	Annealing-induced variation of the phase composition and crystalline structure of the lithium	
	niobate crystal surface	206
471	Annealing-induced variation of the crystalline structure of the lithium nichate crystal surface	206
472	Annealing induced variation of the phase composition of the lithium nichate crystal surface	208
	Autoaning-induced variation of the phase composition of the nation module of ystar sarrace	200
5	Physical proparties of wavaguide layors	215
51	A hyperan properties of lithium nichote and tentalete single errorals	212
5.1	Optical properties of numum modale and lamatate single crystals	213
J.Z 5 2 1	Optical waveguide modes in single-crystal films	213
J.Z.I 5 0 0	waveguide and radiation modes	210
J.2.2	wave equation and netic distribution	221
5.2.5	Optical modes in epitaxial Li (NDTa)O <sub>3</sub> waveguides	223
5.2.4	Characteristics of out-diffused waveguides	229
5.2.3	roperues or diffused waveguides	254
5.3	Second harmonic generation in waveguides	237

5.3.1	Phase matching in an optical waveguide	239		
5.3.2	Overlap of fields of interacting modes	240		
5,3.3	Angular matching	241		
5.3.4	Temperature matching	244		
5,3.5	Second-harmonic generation in a waveguide with periodically domain-inverted regions	247		
5.3.6	Effect of proton exchange on the nonlinear optical properties	249		
5,3.7	Sum-frequency generation in waveguides	253		
5.4	Second harmonic generation in the form of Cherenkov radiation	255		
5,5	Electro-optic effects in optical waveguides	258		
5.6	Light resistance of light guides	260		
5.7	Photorefractive properties of light guides	264		
5.7.1	Holographic formation of gratings in optical waveguide layers	265		
5.7.2	Photorefractive effect in planar Ti-diffused guides	269		
5.7.3	Relaxation of index change	274		
5.7.4	Photorefractive effect in annealed proton-exchanged LiNbO, waveguides	275		
5.8	Energy loss in waveguides	279		
5.8.1	Losses in Ti-diffused LiNbO <sub>3</sub> waveguides	279		
5.8.2	Absorption loss in strip guides	282		
5.8.3	Loss in epitaxial waveguides	284		
5.9	Ferroelectric properties of waveguides	285		
5.9.1	Dielectric properties	285		
5.9.2	Pyroelectric properties	287		
5.9.2.1	The low-frequency sinusoidal temperature modulation method	287		
5.9.2.2	The thermal pulse method	287		
5.10	Temperature dependence of thermoelectric coefficients of lithium niobate and lithium tantalate	289		
6	Thin-film structure in integrated optics	293		
61	Principal characteristics of waveguiding electro-optic modulators	293		
611	Control voltage	293		
612	Bandwidth	295		
613	Modulation depth and insertion losses	297		
62	Photoinduced polarization conversion	298		
63	Waveguide modulators on the basis of Ti-LiNhO	300		
631	Electro-optic modulator on coupled channel waveguides with a variable AB	300		
632	Interferometric and perfect inner reflection modulators	304		
64	Practical examples of waveguide electro-optic modulators	308		
641	Ontical waveguide switch modulator	308		
642	Thin-film electro-optic light modulator	311		
643	Bragg diffraction modulator	315		
644	Ridge waveguide modulator	317		
645	Ti-diffused diffraction modulator	320		
646	Interferometric Mach-Zehnder modulator	326		
647	Electro-optic photorefractive modulator	328		
648	KNbO induced waveguide cut-off modulator	331		
65	Wavemide electro-ontic polarization transformer	334		
66	Light beam scanning and deflection in electro-ontic wayeguides	338		
67	Electro-optically tinable wavelength filter	342		
68	Flip-chin counting between fibres and channel waveguides	345		
69	KTiOPO waveguide devices and applications	349		
691	Phase matching in periodically segmented $KTiOPO$ wavequides	352		
Conclus	ions	356		
References				
Indev		371		
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## Preface

This book is a logical continuation of the two previous books by the authors' which were published in the Adam Hilger series. Altogether, these three books provide a complete enough picture of application of ferroelectric crystals and films in laser radiation control. This volume is devoted to ferroelectric thinfilm waveguides for integrated optics and optoelectronics. We deal here with the most well-known methods of obtaining thin-film structures. Our prime concern is liquid-phase epitaxy from a limited melt bulk with and without application of an electric field. A method is presented which combines liquid-phase and diffusion techniques for obtaining structures with a prescribed configuration of waveguide channels. A detained consideration is given to physico-chemical properties of thin ferroelectric layers, such as morphology, domain structure of a transition layer and ferroelectric properties. An important role for practical use as electro-optic modulators, deflectors and transducers is played by the optical properties, mode composition of propagating radiation, second harmonic generation, electro-optic properties, photorefraction, destruction threshold and light loss. All these aspects have found reflection in the book. Examples of practical use of optical waveguides are given.

The book may be instructive for experts in the field of integrated optics and optoelectronics, as well as for students interested in the corresponding topics.

A.M. Prokhorov Yu.S. Kuz'minov O.A. Khachaturyan

Moscow 1995

## LIST OF SYMBOLS

A.,,C.,	_	lattice parameters	$Q_{ii}$	_	electrostrictive coefficient
н'н В.,	_	dielectric impermeability tensor	r	_	radius
Č –		electrode capacitance	<b>r</b>	_	linear electro-optic coefficient
c	_	thermal conductivity	Ŕ		resistance
c	_	concentration	<i>R</i> .	_	reflectivity
d	_	interelectrode gap	s'	_	distance
d	_	nonlinear ontical coefficient	S	_	compliance
d d	_	thickness	S	-+	area
ds.	_	element of the light nath	S.	_	principal strain
D.	_	diameter	SAW	_	surface acoustic waves
ת ח		diffusion coefficient	t	_	time
ה ח	_	electric inductivity	T	_	temperature
0	_	electron charge	TE	_	wave modes
F		electric field strength	$\overline{U}$	_	supersaturation
с. с.с.	_	electric field components	v		velocity of zone motion
E <sub>x</sub> ,E <sub>y</sub>	_	components of quadratic electro.	v	_	voltage between electrodes
g <sub>ij</sub>	-	components of quadratic electro-	v W	_	electrode width
6		optic coefficient	~	-	effective particle charge
6	-		<sup>Z</sup> cf	_	energy of formation of unit surface
n ,	-	neight	a	_	cooling rate
1	-	light intensity	u n	-	insertion loss
J	-	charged particle flow	a	-	insertion loss
<i>J</i> ,	-	concentration gradient	$\alpha_i$	-	electronic polarisability
J	-	current density	a	-	evaporation coefficient
<i>J</i> ,	-	n <sup>th</sup> order Bessel function	$\alpha_0$	-	inverse accommodation coefficient
k	-	coefficient of segregation	α		number of atoms per unit volume
$k = 2\tau$	τ <i>n/</i>	$\lambda$ – propagation constant	α	-	overlap parameter
k	-	thermal conductivity	p	-	propagation constant in the guide
K(k)	-	complete elliptic integral	p,	-	wave vectors
KTP	-	KTiOPO₄	1	-	normalised overlap integral
1		length	δ <sub>ij</sub>	-	Kronecker symbol
L	-	path length	$\Delta n$	-	refractive index change
L	-	interaction length	Δμ	-	variation of chemical potential
Μ	-	molecular weight	$\Delta \lambda_{T}$	-	shift of the centre wavelength
М	-	number of modes	ε	-	dielectric permitivity
n <sub>o</sub> ,n	-	ordinary and extraordinary	e <sub>o</sub>	-	dielectric permitivity in a vacuum
		refractive indices	ξ	-	applied electric field
N,	-	molar fraction	η	-	phase modulation index
$P_L$	_	Langmuir vapour pressure	θ	-	diffracted angle
<i>p</i>	-	pressure	θ,	-	Bragg angle
P	÷	saturated vapour pressure	λ	-	wavelength
Р́	_	power of light	λο	-	free-space wavelength
P	_	output power	$\lambda_{LS}$	-	heat conductivities of source and
P	-	input power			liquid
<i>P</i> <sup>""</sup>	_	dielectric polarisation	λ	_	specific heat of crystallisation
Ρ.	_	spontaneous polarisation	٨	-	grating periodicity
P	_	photoelasticty tensor	μ	_	mobility
ijmi G	_	kinetic coefficient	v	_	mole fraction
<i>o</i> _	_	activation energy for diffusion	п	-	Peltier coefficient
Q.	_	activation energy for vaporisation	ρ	-	liquid-phase resistivity

### Introduction

An increased number of complicated electron and optical systems stimulates the development of optoelectronics. The analysis of tendencies in the development of applied physics points out the important role the dielectric materials and, first of all, non-centrosymmetric piezo- and ferroelectrics play in the formation of new trends in electronics (Lines and Glass 1981).

An inevitable increase in the variety of thin-film ferroelectric structures that are widely used in the new trends of applied physics brings about improvement in technology and detailed studies of the various physico-chemical properties of substances. This promotes further creation of materials with predetermined physical properties that are optimum for concrete applications in engineering (Miyazawa 1980; Tomashpol'sky 1984; Khachaturyan et al. 1984).

Single crystals of active dielectrics and ferroelectrics possessing an interesting combination of electro-, acousto- and nonlinear optical properties are promising materials for designing highly efficient discrete elements of integrated optics (modulators, deflectors, switches, *etc.*) and quick-operating schemes for computation, and can underlie the creation of hybrid optical integrated schemes (Kuz'minov 1975; Smolensky et al. 1971; Marcuse 1974; Burfoot and Taylor 1979; Smolensky et al. 1985).

The principal applications of ferroelectric materials are presented in Fig.1. As is seen from the figure, the widest range of application of ferroelectrics is optics. Ferroelectric crystals, usually clear and measuring from 0.35 to 4  $\mu$ m (ed. by Shaskol'sky 1982) are applied as phase and amplitude modulators of laser radiation, transducers, deflectors, *etc.* 

Ferroelectric films have been intensively investigated for the last 15 years due to the general tendency of microminiaturization, decrease in power capacity and increase in the sensitivity of devices. A number of phenomena (*e.g.* light switch-over in strip line waveguides) do not have bulk analogues at all. The possibility of using thin-film structures as control elements has led to the development of a large number of methods for obtaining films and coverings.

Depending on a concrete domain of applicability, thin-film ferroelectrics of different structural perfection are used, for instance, ferroelectric ceramics, polycrystalline and epitaxial single-crystal films. For small-size condensers, polycrystalline ferroelectric films with a high dielectric permittivity and low dielectric loss (BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, (Ba, Sr) TiO<sub>3</sub>) are used, an important role being played by the dependences of these parameters on temperature, frequency and



Fig.1 Recent advances in materials for communication devices (Miyazawa 1980).

electric field strength (Photonics, edited by Balkanski 1975). For stoichiometric polycrystalline films close to 1 µm in thickness, the low-frequency (1 kHz) dielectric permittivity exceeds 1000 and the high-frequency dielectric absorption leads to a strong frequency dependence of dielectric permittivity and the loss tangent. Slight violations from stoichiometry customarily induce a decrease of dielectric permittivity and an increase of losses. (Ba, Sr)Nb<sub>2</sub>O<sub>4</sub>, (Ba, Sr) TiO<sub>2</sub> and LiTaO, films of solid solutions of PbTiO, and PbZrO, with lanthanum (PLZT) and triglycinesulphate (TGS) are successfully used for high-frequency piezoelectric filters, transducers and pyroelectric thermal detectors. The requirement of these applications is a high electromechanical coupling or pyroelectric coefficient, as well as low dielectric losses. Polycrystalline films are suitable provided the crystallographic axes are appropriately oriented during film deposition or subsequent polarization. But the best characteristics can be expected from single-crystal films with oriented pyroelectric and piezoelectric axes because of their high coupling coefficient and the absence of influence of polarisation of intercrystal layers in polycrystalline films.

The use of ferroelectric films for recording IR radiation is of interest. Several papers are devoted to the study of pyroelectric effect in ferroelectric films (Okuyama et al. 1981; Nakagama 1979; Mukhortov et al. 1981; Petrosso et al. 1983; Schitt et al. 1984; Antsygin et al. 1986). Okuyama et al. (1981) described



Fig.2 Examples of the use of thin-film ferroelectrics (Okuyama, Hamakawa 1986).

a thin-film pyroelectric detector made of the ferroelectric PbTiO<sub>1</sub>.

Antsygin et al. (1986) investigated thin-film structures of ferroelectric bariumstrontium niobate. The experiments established that pyroelectric, electro-optic and electrophysical properties of the barium-strontium niobate (BSN) films are well described by the phenomenological relations typical of bulk ferroelectrics with a smeared phase transition. It was found that on the BSNelectrode boundary the length of a non-ferroelectric layer does not exceed about  $3 \times 10^{-8}$  m. The studies of BSN film repolarisation caused by an applied electric field, carried out by pyroelectric measurements using the thermal pulse method, repolarization currents and pulsed electro-optics, showed that the repolarization of BSN films is determined by nucleation near a positive electrode. Quick-operating and multielement radiation detectors employing BSN films as an active pyroelectric layer were created.

Thus, already early works on the application of thin ferroelectric films for IR radiation recording indicated that their sensitivity is close to that of pyroelectric crystals, although it should be noted that ferroelectric films were mostly polycrystalline.

Geary (1979) and Lemons et al. (1978) pointed to the possibility of employing ferroelectrics  $Pb_5Ge_3O_{11}$  and  $Gd_2(MoO_4)_3$  in devices with a moving domain boundary. They described optical shutters and analogue elements. Figure 2 gives examples of application of thin-film ferroelectric structures (Okayama and Hamakawa 1986). In the metal-ferroelectric-semiconductor (MFES) structure, the surface potential of the semiconductor can control the polarization of the ferroelectric film. When the MFES structure is used as a shutter of a field-effect transistor (FET), the outlet current of the transistor can be modulated by the surface potential due to film polarization. For example, PbTiO<sub>3</sub> films possess a dielectric hysteresis loop and a high remanent polarization and can therefore be used in MFES FET-type memory cells possessing stable states illustrated in Fig.2a.

Since a thin ferroelectric film has a very high dielectric constant, the applied voltage in devices can be lowered appreciably by using a ferroelectric rather than a dielectric film. Thin-film electroluminescent (EL) devices typically have a sandwich structure consisting of ZnS films and dielectric  $Y_2O_3$  films. An EL device using PbTiO<sub>3</sub> instead of  $Y_2O_3$  films (Fig.2b) has a low control voltage. The threshold voltage of an EL device is lowered from 210 to 50 V.

Films of  $PbTiO_3$  deposited onto thin  $SiO_2$  or Si membranes as strips several tens or hundred micrometers in length were used for the fabrication of ultrasonic transducers (Fig.2c). Thin membranes were made by seeding boron-doped silicon with the use of aqueous solutions of ethylenediamine and pyrocatechol which etched well the (100) and (110) facets but had a weak effect upon the (111) facets. Electrodes were deposited by photolithography. An ultrasonic wave induced mechanical oscillations of the membrane at several resonance frequencies, the shear stress in the film caused piezoelectric stress. In the 300–690 µm device, the second resonance harmonic had a frequency of 30–150 Hz.

Various IR transducers can be made in  $PbTiO_3$  films on the basis of the pyroelectric effect. MFES FET with an electrode absorbing IR light are sensitive transistors (Fig.2e). Infrared light increases the  $PbTiO_3$  film temperature and thus modulates the surface potential of Si which affects the outlet current of the transistor. The outlet voltage is inversely proportional to the light modulation frequency. The response to IR radiation is very quick and for a  $CO_2$  laser the time of pulse increase makes up 3.5 µs. The sensitivity of a silicon monolithic transducer can be increased by removing the silicon substrate from the sensitive area.

The properties and the way of preparation of thin films used in optical devices must satisfy higher demands.

The first experimental and theoretical studies of thin-film optical waveguides used in integrated optics were performed in the sixties (Deryugin et al. 1967; Goncharenko 1967; Goncharenko et al. 1969; Tien 1971). These papers investigated the main properties of thin-film dielectric waveguides of optical range and showed prospects of their application. Some progress made in this field in recent years is indicative of the necessity of growing thin single crystal epitaxial films for this purpose. In films of thickness comparable with the wavelength, one can obtain high intensities even with medium laser powers. Furthermore, the phase velocity of a light wave in a thin-film waveguide depends on the film thickness and the order of the wave mode, which suggests new prospects for creation of devices.

The theory of planar dielectric waveguides, which underlie the creation of the main elements for radiation control, is described in detail in a number of papers and monographs (Tien 1971; Zolotov et al. 1974; Kogelnik 1977; Tamir 1979; Hunsperger 1984; House 1988). The requirements of integrated optics in perfect thin-film structures necessitated a wide use of various methods of fabricating low-loss waveguide layers. All the known methods can be conditionally divided into two groups:

1. Refractive index increase in the near-surface layer of a bulk crystal.

2. Growth of a thin film with a higher refractive index on the substrate surface.

The first group includes the thermal diffusion of transition metal ions, outdiffusion, ion implantation and ion-exchanged diffusion. The second involves mainly epitaxial film growth.

Until recently, the liquid-phase heteroepitaxy has been, in fact, the only leader in producing heterostructures with predetermined physical characteristics, which was particularly clearly seen on an example of a wide range of  $A_3B_5$  compounds. For a number of devices, this situation will remain unchanged in the near future. Among the known liquid-phase epitaxy methods the most promising for composition, thickness and structure control is the liquid-phase electroepitaxy of films.

The existence of electro-, piezo- and nonlinear optical properties offers new opportunities for practical use of ferroelectric films. The use of epitaxial films of oxide ferroelectrics on the basis of niobates of alkaline metals in the elemental basis of optoelectronics shows their noticeable advantages over bulk analogues, first of all from the viewpoint of miniaturization, lowering of consumed energy and intensity of control fields. Lithium niobate and tantalate are widely used in integral electro-optic elements and in communication systems. Both passive integro-optic components (polarizers, couplers, filters) and active components (modulators, switchers, frequency shift, etc.) have found their application in communication systems. The above-mentioned ferroelectrics posses high electro-optic coefficients as compared with semiconducting compounds of the A<sub>3</sub>B<sub>5</sub> group widely used for creating radiation sources and detectors as well as various electronic devices. A special place in integro-optic devices is taken by 'dipped' optical waveguide channels. Obtaining symmetric waveguide channels by the film diffusion method provides a simple and convenient matching between the channel waveguide and optical fibres.

We have analyzed the epitaxial growth of ferroelectrics from a liquid phase, which made it possible to optimize the conditions for obtaining structurally perfect layers and film property control. The performed studies made it possible to improve technology to such an extent that the problems of vertical integration of multilayer ferroelectric structures for integro-optic devices can be solved completely using liquid-phase epitaxy and liquid-phase electroepitaxy. These techniques can also be applied to other oxide ferroelectrics and to high-temperature superconductors.

Chapter 1 presents the main methods of fabricating optical waveguides, except liquid-phase epitaxy, which is analyzed in chapter 2.

Epitaxial methods, which can now be used to produce layers with maximum proximity in their structural perfection to bulk crystals, are discussed in chapter 2.

Attention in this chapter is also given to the capillary method of liquid-phase epitaxy of ferroelectrics, to the growth kinetics of lithium niobate, potassium niobate and solid solutions of lithium niobate-tantalate. The crystallization models, describing the nature of mass transfer in the liquid phase for isothermal and non-isothermal epitaxy conditions, are considered. Analytical expressions are derived linking the film thickness with the growth system parameters. The film diffusion method of growing immersed waveguide channels in ferroelectrics is discussed.

Chapter 3 deals with theoretical and experimental results of investigating the influence of a direct electric current on the liquid-phase epitaxy processes. Materials of the original studies of the authors on growing thin-film ferroelectric structures are presented on an example of lithium niobate and solid solutions of lithium niobate-tantalate. An applied electric field inducing electric current is shown to have an appreciable effect on crystallization conditions, which guarantees control of the properties of the growing structures.

Chapter 4 is primarily concerned with the results of investigating epitaxial ferroelectric films: crystalline structure, composition, orientation, micromorphology of the surface and of the substrate-film boundary, domain and dislocation structures.

Chapter 5 is devoted to investigations of the ferroelectric, optical and waveguide properties of epitaxial films of lithium niobate, lithium tantalate and solid solutions of lithium niobate-tantalate. The dielectric and pyroelectric characteristics of layers and the temperature dependence of thermoelectric coefficients are presented. Optical resistance to laser radiation is examined. Refractive indices and the mode structure of radiation through epitaxial films are determined. Light attenuation under waveguide propagation and the electro-optic properties of structures are investigated.

The subject of chapter 6 is the application of optical planar and channel waveguides to laser radiation control. The parameters of various thin-film integrooptical modulators, deflectors and transducers of radiation are presented.

## 1 Epitaxial Films of Complex Oxide Compounds

The present-day development of solid state electronics is associated to a great extent with the development of the growth technique of single crystals and single-crystal films. This is connected with the fact that employment of single crystals and single-crystal layers excludes the influence of grain boundaries and structural defects typical of polycrystals and thus provides a more effective use of the physical properties inherent in a material.

In recent years, increasing attention has been paid to the problems of oriented growth of a single-crystal ferroelectric layer onto a single-crystal substrate, epitaxy, since the ferroelectric properties are most of all pronounced in singlecrystal layers.

Epitaxy of oxide ferroelectrics is now under particularly intense study, and in this chapter we examine this problem. The number of known ferroelectrics is increasingly large, reaching now several hundred. Particularly fruitful has been the search for new ferroelectrics among the perovskite-type structures (Lines and Glass 1977). The growth of perfect epitaxial ferroelectric films of a given thickness, with a controlled composition and a necessary impurity concentration, is one of the main tasks of thin-film technology and is stimulated by the requirements of integrated optics.

Single-crystal films are customarily obtained either by epitaxial growth onto oriented substrates or by stimulating oriented crystallization on non-oriented insulating substrates (Chernov et al. 1980; Sheftal 1983).

Table 1.1 gives a list of advantages and disadvantages of the main methods for obtaining films (ed. by Poate 1978). Comparative analysis of the methods for obtaining heterostructures shows the advantage of epitaxial methods.

The degree of film perfection is determined, in the first place, by the specificities of each method and, in the second place, by concrete film growth conditions (the degree of vacuum, temperature regimes, growth rates, impurity content).

There are now three basic ways of epitaxial growth of single-crystal films:

1. Vacuum epitaxy (involving molecular beam),

2. Gas-transport epitaxy (involving decomposition of volatile compounds and transport chemical reactions),

Method	Advantages	Shortcomings
Vacuum deposition with resistive heating of evaporator	Simple equipment for fusible materials	Fusion with evaporator materials
Vacuum deposition with electron-beam evaporator	Fit for most of the single-element metals and semiconductors	Refractory metals, carbon and oxides are difficult to evaporate
Ion sputtering	Fit for both conducting and insulating materials; composition is determined by that of the target. Permits obtaining amorphous films of metals and semiconductors. readily admits bias field	Ar or other atoms and molecules of sputtered gase re inserted into substrate; substrate is typically strongly heated, film material is mixed with substrate material and substrate surface can be damaged
Chemical precipitation from the vapour phase	Gives high-quality devices, epitaxial layers for active devices, polycrystalline layers can be deposited	Equipment is more sophisticated. requires exact prescription of gas flow velocity; high substrate temperature
Epitaxial growth from molecular beams	Guarantees high-quality films of compounds	Sophisticated equipment
Electrochemical precipitation	A wide range of films; uniformly thick large area	Can only be applied for metal films; problem of impurities
Epitaxial growth from the liquid phase	High-quality films of compounds	It is difficult to control concentration and guarantee reproducibility
Ion-beam method	Strict control over precipitation parameters	Low precipitation rate and sophisticated equipment

#### Table 1.1 Methods of producing films

3. Crystallization from a liquid phase or liquid-phase epitaxy.

We shall now consider each of these epitaxy methods.

#### 1.1 Vacuum epitaxy

Epitaxy from molecular beams suggests growth of an epitaxial layer when molecular beams or atoms fall onto a heated substrate surface in a ultrahigh vacuum. A beam is generated by sources located in the so-called effusive furnaces in which thermal equilibrium is maintained. The characteristic feature of this method is maintenance of a constant composition of the evaporating substance and its effusion rate. The process typically proceeds in high vacuum, which guarantees a sufficient purity of epitaxial layer growth. The method is commonly characterized by relatively low temperatures and growth rates. A layer on a substrate is formed under crystallization of components coming from different independent beams and, therefore, the composition of the growing layer and the level of its doping are easily controlled. This makes the method suitable for obtaining structures with a sharp variation in the composition and impurity concentration. A low growth rate enables the layer thickness to be rather accurately controlled. Low growth temperatures suppress the influence of the diffusion processes which level up the compositions of neighbouring layers.

During crystallization from a molecular (atomic) beam, vacuum in the reactor is maintained at such a level that the free path of the molecules (atoms) exceeds greatly the distance from the source to the substrate. Supersaturation above the substrate is determined by the pressure of the vapour of the crystallizing component and by the substrate temperature. Regulation of the source and substrate temperatures controls supersaturation and, therefore, the growth rate.

Layer growth by this method proceeds in the following steps:

1. transport of the component vapour to the substrate surface;

2. accommodation of atoms (molecules) on the substrate;

3. atom migration on the substrate surface, re-evaporation;

4. building-in of migrating atoms in active growth centres, stable nucleation;

5. coalescence of nuclei.

A molecular (or atomic) beam, emitted by the source, is directed onto a substrate. The vapour pressure above the source,  $P_{sour}$ , in the case of one-component vapour is equal to

$$P_{\text{sour}} = \alpha_0 P_0 \tag{1.1}$$

where  $P_0$  is the saturated vapour pressure at the source temperature,  $\alpha_0$  is the inverse accommodation coefficient equal to the ratio of the number of evaporated atoms to the number of atoms collided with the source surface.

In the case of a two-component (A and B) vapour, its pressure above the source containing both components is equal to (according to the Raoult law):

$$P_{\text{tot}} = P_{\text{A}} + P_{\text{B}} = \alpha_{0\text{A}} P_{0\text{A}} N_{\text{A}} + \beta_{0\text{B}} P_{0\text{B}} N_{\text{B}}$$
(1.2)

where  $P_A$  and  $P_B$  are the vapour pressures of the components A and B,  $\alpha_{0A}$  and  $\alpha_{0B}$  are inverse accommodation coefficients of the components A and B,  $P_{0A}$  and  $P_{0B}$  are saturated vapour pressures of the components A and B for  $T_{sour}$ ,  $N_A$  and  $N_B$  are molar fractions of the components A and B  $(N_A+N_B=1)$ .

In crystallization of a two-component vapour, special measures are taken to preserve its constant composition. Sometimes, evaporation is carried out from separate one-component sources. The vapour pressure of the crystallizing component is controlled by the source temperature.

It should be noted that even a small difference in the elasticity of vapours of the components of dissociating compounds can have an appreciable effect on both the structure and the properties of the condensates. The latter plays a great role for ferroelectric materials. The condensate composition also depends on the substrate temperature, which is explained by selective re-evaporation of components (Shimaoka 1985; Tomashpol'sky 1982).

In recent years, the method of pulsed laser deposition (PLD) has been intensely developed (Gaponov and Salashchenko 1976; Firtsak et al. 1984; Lushka et al. 1982). The idea of using laser radiation for substance evaporation in a vacuum for the purpose of thin-film sputtering appeared with the construction of initial powerful lasers.

Various researches using PLN have been carried out for obtaining oriented films of nearly twenty semiconducting compounds, such as germanium, silicon, gallium arsenide films, as well as films of oxygen-free ferroelectrics of the type of antimony sulphoiodide and tin thiohypodiphosphate (Gaponov and Salashchenko 1976; Firtsak et al. 1984; Luksha et al. 1982). In some cases, oriented growth of laser condensates exhibits a temperature lowering as compared with what we observe in thermal deposition methods. This fact cannot be explained consistently by the quantitative analysis of the layer formation mechanism. On the qualitative level, the specific features of epitaxial film growth under Q-mode laser deposition can be explained by bombarding the substrate by high-energy ions  $(10^2 - 10^3 \text{ eV})$  of laser-induced plasma, which strengthen the potential relief of the surface and provide an oriented growth already under insignificant atom motions, that is, at a lower substrate temperature.

The relationships between matter and energy transfer processes and phase and intraphase transformations in the condensate allow us to distinguish between two principal condensation mechanisms: vapour-liquid-amorphous metastable (glass-like) phase and vapour-amorphous metastable phase (with subdomains of polyamorphous modifications and their condensation through amorphous labile phases) which are typical of laser deposition (Firtsak et al. 1984).

Vacuum epitaxy, including high-frequency cathode sputtering (Takada et al. 1974), suggests an easy control of the process and enables pure films with a clearly pronounced interface to be produced. But in some cases, in particular, for ferroelectrics, these advantages are rather difficult to realize. Violations of stoichiometry, occurring when complex oxide films containing volatile components are formed in vacuum, restrict substantially the efficiency of the method. The films thus obtained are as a rule polycrystalline or have an imperfect structure, for example, films of bismuth titanate (Takei et al. 1969), lead titanate-zirconate (Philips 1971), lead-lanthanum titanate-zirconate (Ishida et al. 1977; Takada et al. 1974), BaTiO<sub>3</sub> and Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> (Mukhortov et al. 1981), lithium tantalate (D'Amico et al. 1984) and lithium niobate (Takada et al. 1977; Meek et al. 1986; Postnikov et al. 1973; Foster 1971; Ninomuka et al. 1978).

Lithium niobate films on a sapphire substrate were obtained by sputtering in vacuum (Foster 1971; Takada et al. 1974). Films 1800 Å thick were transparent and smooth but exhibited high optical losses, up to 9 dB/cm. It is noteworthy that the losses in films increased with increasing mismatch between the film and substrate lattice parameters.

Using vacuum epitaxy, Ninomuka et al. (1978) precipitated z-LiNbO<sub>3</sub> films onto a substrate of a single-crystal MgO oriented along the [111] axis. Such an orientational relationship is due to the identical position of oxygen ions in the indicated planes (the lattice parameter mismatch was about 0.2%). Films were precipitated at a rate of 0.1  $\mu$ m/h at a substrate temperature of 620– 660°C. This experiment gave single-crystal layers 6000 Å thick with a surface roughness of 100 Å. Nevertheless, losses in the films were in this case also an order of magnitude larger than in diffusion films (~10 dB/cm).

#### 1.2 Gas-transport epitaxy

Epitaxial film growth via a chemical reaction includes processes in which the crystallizing phase is due to reactions proceeding in a vapour-gas mixture.

The crystallization process, as any phase transition, is driven by the difference in the thermodynamic potentials of phases undergoing transformations, but in the case of crystallization by means of chemical reactions the gas phase supersaturation cannot be determined since the chemical reaction proceeds at the crystallization front – the elementary acts of chemical transformations and the elementary acts of crystallization are closely connected.

The epitaxial growth rate is determined by the yield of the chemical reactions resulting in the formation of a crystallizing substance and depends, therefore, on the concentration of interacting phases in the gas mixture, the speed of gas mixture passage over the substrate, the catalytic activity and the substrate temperature. These parameters can be controlled in the epitaxial growth process. The catalytic activity of the substrate, which depends on the method of surface treatment, is customarily assumed to be fixed in each series of experiments.

Film growth by means of chemical reactions undergoes the following stages:

1. transport of starting compounds to the substrate surface;

2. chemical reaction resulting in the formation of molecules of the growing crystal;

3. migration of molecules about the substrate surface due to reaction heat release, as well as spontaneous migration;

4. desorption of unreacted molecules;

5. building-in of migrating atoms into active growth centres, formation of stable nuclei;

6. coalescence of nuclei.

One of the modifications of the processes described above is the gas-transport reaction. Its main difference from the chemical reaction is that a chemical compound containing a crystallizing substance is formed straight in the reactor and then transported in a certain way onto a heated substrate where it is decomposed and crystallized.

The system in which the epitaxial film growth proceeds through gastransport reactions must have at least two temperature zones. In one of them, the transporting gas reacts with the substance source to form a volatile compound transported to the second zone where the substrate is located and where the substance or compound is segregated and crystallized. The stages of the process proceeding in the second temperature zone are similar to the stages of film growth by means of chemical reactions.

A widespread and constructive version of the gas-transport epitaxy is the so-called 'sandwich method' in which the substrate and the source are plates positioned fractions of a millimetre from one another and have different temperatures (Dorfman 1974).

In spite of the difficulties in creating steep temperature gradients, the 'sandwich method' has the following advantages:

a) the space where the reaction proceeds is separated from the remaining space of the reactor and, therefore, the purity of the precipitating layer is determined by the purity of the starting material only;

b) a high efficiency (90-98%) of mass transfer (the ratio of the substrate weight gain to the source weight loss);

c) a high crystallization rate (hundreds of microns per hour).

The chemical transport reaction underlying epitaxy from the gas phase can be represented in the following way on an example of a semiconducting compound AB:

$$(AB)_{sol} + C_{vap} \stackrel{T_{sour}}{\underset{T_{cryst}}{\leftrightarrow}} (AC)_{vap} + B_{vap}$$
(1.3)

where  $(AB)_{sol}$  is a material synthesized in advance, the so-called solid-state source, which is in most cases made of a polycrystalline powder;  $C_{vap}$  is a gaseous substance, the so-called transporter;  $(AB)_{vap}$  and  $B_{vap}$  are gaseous products of a forward chemical reaction.

Substance  $(AB)_{sol}$  is in the source zone at the temperature  $T_{sour}$  and the substrate is in the crystallization zone at the temperature  $T_{cryst}$ , where  $T_{cryst} < T_{sour}$ . When the source interacts with the transporters, gaseous products in the direct reactions  $(AB)_{vap}$  and  $B_{vap}$  go over to the crystallization zone where the reversed reaction (from right to left) proceeds and results in the formation of an epitaxial AB layer on the substrate. The transporter  $C_{vap}$  revealed in the reverse reaction goes over to the source zone, where it is again involved in a forward reaction.

When epitaxial films are grown by crystallization from a gas phase, uniformly doped layers can be obtained quite easily. A doping impurity is introduced into the operating space either in the form of a highly volatile compound or in the elemental state. The impurity concentration in the gas phase is controlled in this case by the gas mixture composition, and in the case of elemental additions by the source temperature.

The method of chemical gas-transport reactions has some advantages: the initial reagents can be subjected to purification, the crystallization process is readily controlled, the devices used in the method are simpler than those used in the molecular beam method (e.g. no devices for high vacuum are needed).

The shortcomings of the method are as follows:

a) difficulties in maintaining a constant concentration of gaseous reagents in the substrate zone;

b) rapid composition modulation cannot be carried out due to the diffusion character of gaseous reagent motion towards the substrate;

c) the absence of a clearly pronounced boundary between layers.

Curties and Brunner (1975) reported obtaining  $LiNbO_3$  films on a  $LiTaO_3$  substrate using gas-transport epitaxy. The propagation loss reached a value of 40 dB/cm, which is explained by the presence of scattering centres in the films. Single-crystal films obtained by the gas-transport epitaxy even under optimum conditions usually have a low structural perfection with numerous point defects of package and dislocations (Curties and Brunner 1975; Aleksandrov 1972; Nelson 1963).

Fushimi and Sugh (1974) reported on a study of the growth of LiNbO<sub>3</sub> single crystals by the closed-tube vapour transport technique and its application to the epitaxial growth of thin films of LiNbO<sub>3</sub> single crystals.

The transport experiments for LiNbO<sub>3</sub> were carried out using sealed, evacuated transparent quartz tubes. LiNbO<sub>3</sub> powder and a transport agent were loaded at one end of the tube, which was then evacuated to 10-5 mm Hg and sealed with a torch. The ampoules with starting materials were heated in an electric furnace. The temperature of both ends of each ampoule was controlled, and

the end containing the starting materials was always maintained at the higher temperature. The heating temperatures examined ranged between 650 and 1500°C. The cool end products were examined by X-ray diffractometry with  $CuK_{\alpha}$  radiation.

Transport agents examined in this study included sulphur, iodine, and a mixture of these elements.  $LiNbO_3$  could be transported by sulphur, but not by iodine. Transport of  $LiNbO_3$  by sulphur was retarded by adding iodine to the reaction system. The comparison was made between the starting composition of 1.00 g  $LiNbO_3$  and 0.40 g sulphur and that of 1.00 g  $LiNbO_3$ , 0.40 g sulphur, and 0.40 g iodine loaded in the ampoules 12 mm in diameter and 100 mm long. The hot and cool end temperatures were 1000°C and 910°C, and the heating period was seven days. The transport rates of  $LiNbO_3$  were 0.125 g/day for sulphur and 0.012 g/day for the mixture of sulphur and iodine.

The relations between the transport rate of  $LiNbO_3$  and the amount of the sulphur transport agent were examined at 1000°C hot end and 910°C cool end temperatures and are summarized in Fig.1.1. Although the measured transport rates are slightly scattered, the result was expressed as

$$(LN)_{\text{trans}} = a (S)^b \tag{1.4}$$

where b was found to be 2.0-2.5.

LiNbO<sub>3</sub> transported by sulphur, accompanied no by-products and crystallized in fairly well shaped tiny rhombs, covered by the facets parallel to the (102) planes, with dimensions up to  $0.5 \times 0.5 \times 0.5$  mm. The (102) planes correspond to the perfect cleavage plane of LiNbO<sub>3</sub>. The crystal habit was examined in a precession camera with MoK<sub>a</sub> radiation.

Even though the vapour transport technique was not suitable for obtaining bulk LiNbO<sub>3</sub> single crystals, the technique was applied to the epitaxial growth of LiNbO<sub>3</sub> on the LiTaO<sub>3</sub> substrate. Optically flat (102), (010) and (001) plates of LiTaO<sub>3</sub> were used as substrates for epitaxial growth. The conditions for epitaxial growth are listed in Table 1.2. Though the deposited layer thickness was not uniform, 2–10  $\mu$ m thick LiNbO<sub>3</sub> crystal layers were formed on the LiTaO<sub>3</sub> substrates. The surfaces of the LiNbO<sub>3</sub> layers deposited on the (102) LiTaO<sub>3</sub> plates were smooth, while those deposited on the (010) and the (001) plates were rough because they were covered by the (102) facets. Fairly good crystal

Ampoule size	15 mm diam., 170 mm long, 20 mm diam., 210 mm long		
Initial charge	LiNbO <sub>3</sub> : 1.00–1.40 g, S: 0.40–2.00 g		
Substrate	$LiTaO_{3}$ (102), (010), (001) plate		
Substrate-source distance	8.3–11.0 cm		
Source temperature	950–1000°C		
Substrate temperature	900–910°C		
Heating period	3-17 h		
Cooling rate	Furnace cooling, 60°C/h		

 Table 1.2 Conditions for the epitaxial growth of LiNbO<sub>3</sub> (Fushimi, Sugh 1974)



Fig.1.1 Relations between the transport rate of LiNbO $_3$  and the amont of sulphur (Fushimi and Sugh 1974).

**Fig.1.2** (right) Rocking curve of the LiNbO<sub>3</sub> layer deposited on a LiTaO<sub>3</sub> (001) plate (Fushimi and Sugh 1974).

quality of the LiNbO<sub>3</sub> layers and their excellent epitaxy on the LiTaO<sub>3</sub> substrates over the whole deposition area were revealed by X-ray topography. Figure 1.2 shows a rocking curve of the LiNbO<sub>3</sub> film deposited on a LiTaO<sub>3</sub> (001) plate, where  $K_{\alpha 1}$  and  $K_{\alpha 2}$  reflections from LiNbO<sub>3</sub> and LiTaO<sub>3</sub> are clearly separated.

#### 1.3 Films deposited by rf sputtering

Papers have been published on ion implantation for treatment of lithium niobate crystal surfaces, in particular, for producing light guiding layers. Townsend (1984) reported obtaining planar light guides in lithium niobate by implanting N<sup>+</sup>, B<sup>+</sup>, He<sup>+</sup> and Ne<sup>+</sup> ions. He also determined the dependence of the refractive index variation  $\Delta n$  on irradiation doses for each of these ions and showed the possibility of producing light guides with  $\Delta n > 0.1$  at low substrate temperatures and irradiation doses exceeding 10<sup>22</sup> cm<sup>-3</sup>. It is noteworthy that waveguides obtained by the ion-implantation method typically exhibit high losses. Sample annealing reduces the losses, but overannealing reduces the difference between the refractive indices of the waveguide and the substrate. Furthermore, under ion implantation, the surface layer of the single crystal becomes amorphous. In lithium niobate, implantation of Ar\* and Ne\* leads to distortions in the surface layer of the crystal lattice up to 10%. Damage in waveguide layers also impairs the electro-optical properties of crystals. This essential shortcoming of the ionimplantation method makes it effective only for producing passive elements of integrated optics.

The advantages of this method over the other methods of thin film precipitation are well known: the possibility of fabricating multicomponent compounds (the chemical elements in the compound composition can be qualitatively characterized by various physical properties, for example, partial vapour pressure); maintenance of a low growth rate (0.01-5 Å/s) during the whole film formation process under intense bombardment by secondary electrons and ions, which is in the end responsible for the high quality of its structure. But the main advantage of HF-sputtering, particularly important for producing multilayer structures, is the synthesis of grain-oriented and even single-crystal films on a non-orienting surface. This can be realized when the film is synthesized by the mechanism of final growth orientation (Bauer 1969). Film condensation in this case was the result of competing growth of differently oriented crystals rather than of the tendency to formation of configurations with a minimum of free energy, as is the case when the initial orientation (e.g. orientation caused by the influence of the substrate nature) determines nucleation and subsequent condensate growth. At different crystal surfaces, a different number of molecules is condensed per unit time, which determines the predominant growth of crystals with one of the orientations. It has been established that under HF-sputtering the determining factor in this growth mechanism is the difference in the re-evaporation rates of different crystalline grain facets under the action of electron and ion bombardment of the sample surface during ferroelectric layer synthesis (Margolin et al. 1983). Naturally, such mechanism is only possible at low growth rates comparable with the rates of particle re-evaporation from the crystal surface. HF-sputtering provides the indicated relation between the speed at which the material is fed to the condensation zone and the controlled speed of its removal. Choosing the target-substrate distance and the oxygen pressure creates conditions for plasmochemical reactions for oxide molecule formation due to two (and more) vapour atom collisions in the presence of ionizing electrons. Under such conditions, film thickness increases with increasing substrate temperature  $T_{\rm e}$ , which agrees with experiment. Samples thus obtained have a high degree of structure perfection and preserve initial stoichiometry.

Sapphire and silicon were used as substrates in such experiments. The ferroelectric films were 1–9  $\mu$ m thick. The substrate temperature maintained in the course of grain-oriented film synthesis was established to determine the grain size, which produces a qualitative effect on the principal electrophysical properties of samples. For example, a grain size of ~3  $\mu$ m suggests the occurrence of ferroelectric properties.

#### 1.3.1 Thin films of LiNbO, deposited on a sapphire substrate

Takada et al. (1974) were the first to succeed in feeding a laser beam into a single-crystal LiNbO<sub>3</sub> thin film deposited on a sapphire substrate by the rf sputtering method. The authors believe that the success is due to the use of an extremely low sputtering rate. It should be emphasized that, in their work, the above-mentioned polishing process was not essential to the rf-sputtered thin film, and the light beam could be easily fed into the film.

An rf diode sputtering apparatus was used to fabricate the thin film. The target used in the experiment was prepared in the following way: First, lithiumenriched pulled LiNbO<sub>3</sub> single crystals were crashed into grains. Then, a disc 9 cm in diameter and 8 mm thick was formed by the grains. Finally, the disc

9

Crystal	a <sub>H</sub> (Å)	$c_{\rm H}$ (Å)	$n_o$ ( $\lambda = 6$	n <sub>e</sub> 328 Å)
LiNbO <sub>3</sub> •	5.149	13.862	2.289	2.201
Sapphire**	4.758	12.991	1.766	1.758

Table 1.3 Lattice parameters and ordinary and extraordinary refractive indices of LiNbO<sub>3</sub> and sapphire at room temperatures (Takada et al. 1974)

\* K Nassau, H J Levinstein and G M Loiacono, J. Phys. Chem Solids, 27, 989 (1966); \*\* A Myron and J Jeppesen, J. Opt. Soc. Am., 48, 629 (1958).

Table 1.4 A typical sputtering adopted in the experiment (Takada et al. 1974)

Target-substrate spacing	4 cm
Gas contents	Ar (60%) + $O_2$ (40%)
Gas pressure	2×10 <sup>-2</sup> Torr
rf power	50 W
Magnetic field	100 G
Substrate temperature	500°C





Fig.1.3 (a) Laser beam in a single-crystal LiNbO<sub>3</sub> film deposited by the rf sputtering method, and (b) corresponding sample configuration (Takada et al. 1974).

was sintered. The c-plane of sapphire was used as substrate. Table 1.3 shows the lattice parameters and ordinary and extraordinary refractive indices of  $LiNbO_3$  and sapphire.

A typical growth condition of the film is shown in Table 1.4. The deposition rate under the condition of Table 1.4 is 250 Å/h, which is extremely low compared with the value used in the usual sputtering process. Films obtained are transparent and smooth, and show a homogeneous interference colour.

Figure 1.3 shows a photograph of a film with a thickness of 1800 Å and a trace of the 6328 Å He–Ne laser beam fed into the film by a rutile prism coupler at the left-hand side. The loss of the film is less than 9 dB/cm, which is comparable with the loss measured in an epitaxial ZnO film. The experimental value was obtained by using an optical fibre with a diameter of 0.5 mm. One end of the fibre was placed near the film surface and the other end was connected with a photodiode in order to measure the light intensity scattered by the surface. An example of experimental results is shown in Fig.1.4. The mode used in this experiment was TM<sub>o</sub>. In the experiment, the loss of the TE<sub>o</sub> mode was usually larger than that of the TM<sub>o</sub> mode.

The ordinary and extraordinary refractive indices of the film were obtained from the measured values of the coupling angles for the TE<sub>0</sub> and TM<sub>0</sub> modes and the thickness of the film by using the formulas from the paper by P.K.Tien. The results are  $n_o = 2.32 \pm 0.02$  and  $n_e = 2.18 \pm 0.04$ , where  $n_o$  and  $n_e$  are the ordinary and extraordinary refractive indices, respectively. These values are close to those of the bulk LiNbO<sub>3</sub> shown in Table 1.3.

It is very difficult to identify the film thickness less than 1  $\mu$ m to be a singlecrystal LiNbO<sub>3</sub> film because the film is too thin to be investigated by means of X-ray analysis. The films were therefore made thicker than 1  $\mu$ m, and the following patterns from the films were analyzed: (i) electron diffraction pattern, (ii) X-ray diffraction pattern by a diffractometer, (iii) X-ray Laue pattern, and (iv) pseudo-Kossel pattern by a divergent X-ray beam. Analysis showed that



**Fig.1.4** Surface-scattered light intensity as a function of distance along the laser beam in the film. The slope indicates that the loss of the film at 6328 Å is less than 9 dB/cm. The thickness of the film is 1800 Å. TM<sub>o</sub> mode is used (Takada et al. 1974).

**Fig.1.5** (right) Propagation loss of light as a function of the lattice constant  $c_{\rm H}$  of deposited films (Takada et al. 1974).

single-crystal  $LiNbO_3$  was really deposited epitaxially on the sapphire substrate over a wide area so that the *c*-plane of the film was parallel to the *c*-plane of the substrate.

Figure 1.5 shows the propagation loss as a function of the lattice constant of deposited films. It can be seen that the propagation loss of light in the film is strongly related to the increase of the discrepancy in the lattice constant of the film from that of the substrate.

The origin of the propagation loss of light is not clear in the given sample. It is, however, expected that the loss could be decreased up to about one-tenth of that of the present samples by purifying the target material and sputtering gases and by finding out a more adequate sputtering condition, even though the internal stress in the film caused by misfit in the lattice constant between the film and the substrate could not be completely eliminated.

In the work by N.F.Foster (1969), lithium niobate was deposited by triode sputtering in an argon-oxygen gas mixture containing 5-10% oxygen. The apparatus used is shown in Fig.1.6. The substrate holder assembly was mounted so that the substrate could be located above positions for the evaporation of metal films or for the sputtering of lithium niobate without breaking vacuum.

The substrates used were 1/4 in. square by 1/2 in. long bars of fused quartz, or sapphire with the c-axis coincident with the bar axis. After chemical cleaning, the bars were clamped in the substrate holder, heated to ~150°C in vacuum, and plated with a thin chromium underlayer followed by about 1000 Å of gold. The substrate temperature was then increased to the initial deposition temperature, the sputtering gas was admitted at a dynamic pressure of about 2  $\mu$ , and the primary discharge was struck and adjusted to 1.5 A at 60 V. The target voltage was applied and the substrate swung into place over the target. With a target voltage of 1 kV, the target current was 12 mA. A magnetic field parallel to the primary beam was produced by passing a current of 2 A through the 100 turn coils mounted on the filament and anode housings. Under these conditions, the substrate temperature increased during deposition to 30-50°C above the initial temperature. To permit optical rate monitoring, the substrate was tilted at 45° to the target, and under these conditions the film growth rate was approximately  $3/4 \mu/h$ . Films 2-4  $\mu$ m thick were deposited. The lithium niobate target was made of a powder pressed into a 2.5 cm diameter × 3 mm thick disc and



subsequently fired in air at 1200°C. Initially, the disc was white and highly insulating and sputtering was very slow. As the target became heated, however, it darkened, presumably through the loss of oxygen, and became sufficiently conducting for the dc sputtering process to proceed readily. The oxygen present in the sputtering gas assured that the deposited films were insulating.

14 films were deposited during this study. For the first four depositions the initial substrate temperatures were between 100 and 300°C. These films were clear and adherent but showed no X-ray structure or piezoelectric activity. The remaining ten films were grown at initial substrate temperatures of 325-380°C. These exhibited well defined X-ray patterns corresponding to trigonal lithium niobate. A typical X-ray Debye–Scherrer pattern shows that the film is partially oriented. Although the degree and the type of orientation varied from film to film, the (00.1) and/or (01.2) planes showed some tendency to align parallel to the substrate surface.

#### 1.3.2 Tungsten bronze ferroelectric K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub>

Among various families of ferroelectric materials, the tungsten bronze family is of interest for optical waveguides and SAW applications.  $K_3Li_2Nb_5O_{15}$  (KLN) is a tetragonal crystal with the point group 4 mm and is typical of completely filled tungsten bronze ferroelectrics. Single-crystal KLN has a large electromechanical coupling factor  $k_{15} = 0.34$ ,  $k_{31} = 0.18$  and  $k_{33} = 0.52$  and also has reduced zero-temperature coefficients of delay for SAWs. However, it is very difficult to obtain high quality and large KLN crystals. An approach to the solution of this problem is to grow epitaxial KLN films (Prokhorov and Kuz'minov, 1990).

An rf sputtering apparatus (ANELVA FP-21) was used by Shiosaki et al. (1982) to fabricate KLN thin films. The target used in the experiment was prepared by sintering the pressed powder with a potassium- and lithium-enriched composition of 33 mol.%  $K_2CO_3$ , 22 mol.%  $K_2CO_3$  and 45 mol.%  $Nb_2O_5$ . The optimum growth conditions for high-quality KLN single-crystal thin films sputtered on both  $K_3Bi_2Nb_5O_{15}$  (KBN) and sapphire substrates are a 50% Ar-50%  $O_2$  atmosphere at a pressure of  $9.0 \times 10^{-2}$  torr, an rf power input below 150 W and 500–630°C substrate temperature. The deposition rate under these conditions is ~800 Å h<sup>-1</sup> at an rf power of 100 W.

Both the KLN films epitaxially grown on KBN and those grown on sapphire substrates were transparent and their surfaces were smooth. Analysis of these KLN films by X-ray diffraction and RED measurements showed that the KLN films obtained were single crystals of fairly good quality.

A He-Ne laser beam was successfully fed into KLN films sputtered on the KBN (001) and sapphire (0112) substrates, using a prism coupler. By measuring coupling angles for three different TE modes, the effective refractive index  $\beta/k_0$  in a KLN film 2.1 µm thick sputtered on the KBN (001) substrate was determined to be 2.26, 2.25 and 2.23 for the TE<sub>0</sub>, TE<sub>1</sub> and TE<sub>2</sub> modes, respectively. The refractive index  $n_0$  in this KLN film was calculated to be 2.27 from the effective refractive indices given above. Measurements of the optical propagation loss in the KLN film grown on the KBN substrate were not attempted. The refractive index  $n_0$  in a KLN film ~2.7 µm thick sputtered on a sapphire

 $(01\overline{1}2)$  substrate was also determined to be 2.27 by measuring the coupling angles for eleven TE modes. The value of 2.27 obtained above is close to that for a bulk KLN crystal. Furthermore, the TE<sub>0</sub> mode propagation loss in the KLN film on sapphire was measured by the optical fibre probe method. The optical propagation loss in this film was determined to be 7.8 dB cm<sup>-1</sup>.

Some experiments were carried out on the SAW properties of the layered KLN/sapphire structure. The sample used in this study was a KLN film 9  $\mu$ m thick sputtered on a sapphire (01 12) substrate at a substrate temperature of 520°C. Interdigital transducers (IDTs) were normal electrodes with 25 finger pairs and a 100  $\mu$ m spatial period, which were evaporated on the film surface. The centre-to-centre propagation path length was 12.5 mm. Accordingly, the value of KH for this sample was 0.6. Since the delay time of SAW propagation is 2.3  $\mu$ s, the SAW velocity on this KLN film was determined to be 5430 m s<sup>-1</sup> which is in close agreement with the calculated value, 5500 m s<sup>-1</sup> at KH = 0.6.

#### 1.3.3 KNbO, thin films

The  $KNbO_3$  films were grown in a rf-diode sputtering system in which the cathode forms the bottom electrode. The system, described in detail by S. Schwyn and H.W. Lehmann (1992), is equipped with a load-lock and heated substrate platform (mounted on the top plate of the system), which allows substrate surface temperatures up to 700°C (Thony et al. 1992). This sputter up design turned out to be rather useful since this configuration also allows the use of home-made targets which do not always have the desired high density and cohesion.

The most important parameter in these experiments is the composition of the target. Sputtering from pure KNbO<sub>3</sub> target resulted in films which were severely deficient in potassium. In order to evaluate which composition is appropriate to obtain stoichiometric films,  $K_2CO_3$  and KNbO<sub>3</sub> powders were mixed in different molar ratios. Subsequently, the powder was pressed at room temperature at a pressure of  $5.6 \times 10^7$  N/m<sup>2</sup>. The discs obtained were solid enough to be transferred into a vacuum chamber. Although outgassing is much stronger compared to sintered material, the home-made targets proved to be useful if they are pumped and presputtered for a sufficiently long period of time (approximately 10 h). A target composition of 1:1 mole  $K_2CO_3$  and KNbO<sub>3</sub> finally yielded stoichiometric films. This means that the potassium concentration in the target was three times higher than the final concentration in the sputtered films. Table 1.5 summarizes the parameters with which crystalline stoichiometric KNbO<sub>3</sub> films were grown.

The optical properties are strongly related to the crystal structure and the crystallinity of the layers. To provide favourable conditions for the growth of highly ordered films, a relatively high substrate temperature ( $610^{\circ}$ C) and a very low deposition rate (6 Å/min) were chosen. The typical thickness of the layers obtained using these parameters is 200 nm.

Furthermore, lattice-matched substrates had to be found in order to obtain crystalline films. The two crystalline materials (MgO)  $(Al_2O_3)_{2.5}$  spinel and MgO were considered to be well suited as substrates for thin films of KNbO<sub>3</sub> bulk crystals. Moreover, the refractive index of these materials is considerably lower

than that of  $KNbO_3$  allowing monomode waveguiding in layers of only 100 nm thickness. The MgO substrates had atomic layer polished surfaces and both substrates were not specially cleaned prior to use.

The composition of the layers was determined by RBS using He<sup>4+</sup> ions with an energy of 2 MeV. These measurements showed that stoichiometric films could be grown from a  $(KNbO_3)(K_2CO_3)$  target sputtered in pure argon (Fig.1.7). The addition of oxygen results in a potassium deficiency of the films. As can be seen, the measurement results are in excellent agreement with the solid line of the simulated spectrum of a stoichiometric film with a thickness of 190 nm. Furthermore, the profile is flat topped indicating constant composition across the film thickness. The oxygen stoichiometry was investigated using nuclear reaction analysis and did not show any oxygen deficiency.

The X-ray diffraction spectra strongly depend on the composition of the films and deposition temperature. Layers with approximately stoichiometric composition (19.2–20 at%) deposited on MgO at a temperature of 500°C or below only show weak lines in the x-ray spectrum. Some of the small peaks could be identified as the (110) and (220) reflection of orthorhombic KNbO<sub>3</sub>, whereas it was not possible to identify the others unambiguously.

When the temperature was increased to 580-610°C, the film became single crystalline and on both substrates two lines were obtained which were close to the (0001) and (002) reflections of tetragonal KNbO<sub>3</sub> (Fig.1.8). The lattice constants obtained from the x-ray diffraction measurements for all the three lattice directions yielded a = b = 4.16 parallel and c = 4.10 perpendicular to the substrate plane for layers deposited on MgO. This means that the film is tetragonal within the measurement accuracy. Therefore, the tetragonal coordinate system will be used in the following. Compared with the lattice constants of the tetragonal phase (extrapolated to room temperature) of a = b =3.985 Å and c = 4.075 Å, this indicated a lattice mismatch of 4% and 0.7%, respectively. Tetragonal symmetry which in bulk material is assigned to the structural phase in the temperature range 22-440°C can be explained by the fact that the substrate is cubic and, therefore, forces the growing layer in both directions of the interface plane to the same lattice constant. The x-ray data showed that there is a close correlation between film stoichiometry and x-ray intensity: as the stoichiometry improves, the diffracted lines become narrower and their intensity increases.

Target composition		
K <sub>2</sub> CO <sub>3</sub> :KNbO <sub>3</sub>	1:1	mol
Gas	100%	Ar
Temperature	610	°C
Power	50	w
Process pressure	2×10-2	mbar
Gas flow	20	cm/min

Tabl	e 1.5 i	rf-sputtering p	parameters fo	or growing s	stoichiometrie	crystalline KN	lbO, films (1	Thony
et al	. 1992)	)					<b>3</b>	•



Fig.1.7 RBS spectrum of a KNbO<sub>3</sub> thin film of thickness d = 188nm deposited on MgO substrate from target composition of (KNbO<sub>3</sub>)(K<sub>2</sub>CO<sub>3</sub>) at 610°C (Schwyn et al. 1992).

#### 1.3.4 KTa<sub>x</sub>Nb<sub>1-x</sub>O<sub>3</sub> thin films

A Perkin Elmer 4400 sputtering machine was used for film deposition. A 4 in. diameter sputtering target (nominal composition:  $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ) with a 15 at% excess K and pressed to 90% of theoretical density, was prepared by standard ceramic procedures. Substrates used for film deposition were (a) Pt coated (3000 Å sputtered layer) Si wafers with a 1500 Å thick intermediate layer of SiO<sub>2</sub> and (b) GaAs(100) wafers with a heavily doped ( $n = 10^{18} - 10^{19}/\text{cm}^2$ ) surface layer. An excellent lattice match, within 0.3%, exists between KTN and GaAs surface sublattice (Sashital et al. 1993).

Under any chosen set of sputtering conditions, films were simultaneously deposited on  $Pt/SiO_2/Si$ , GaAs and sapphire substrates. The KTN synthesis conditions are similar to those for KNbO<sub>3</sub>, see Table 1.5. Films thus sputtered were completely colourless and transparent. Composition of a KTN film on sapphire was determined by Rutherford backscattering spectroscopy (RBS). RBS simulation spectra yielded a film composition of  $K_{0.94}Ta_{0.68}Nb_{0.4}O_3$ . X-ray diffraction analysis of the KTN film on sapphire shows only a single (100) peak and its two higher orders. The peak sharpness, referred to that of the (1012) sapphire substrate, indicates nearly single crystal epitaxial growth of the KTN layer. Bragg peaks from a KTN film on GaAs show only a single narrow (200) KTN reflection, indicative of large grains with a high (100) preferred orientation. The two weak peaks on the low 2 $\theta$  side of the GaAs reflection could not be attributed to any of the KTN related reflections.

The Curie temperature plot ( $\varepsilon$  vs T) for a KTN film on a Pt/SiO<sub>2</sub>/Si substrate (measured at 1 kHz, Fig.1.9a) peaks sharply at 6°C with a maximum  $\varepsilon$  of 2090, indicating almost a bulk single crystal-like behaviour. Figure 1.9b shows the capacitance (at 1 kHz) versus temperature behaviour of a Pt/KTN film/GaAs test capacitor. Again, the sharp peak at 3°C exhibits a bulk single crystal-like Curie–Weiss behaviour. Reflectance spectra of KTN films yielded refractive indices from 2.06 at 0.6 µm to 1.975 at 1.1 µm and low absorption characteristics. These are smaller than bulk KTN refractive indices, from 2.15 to 2.3. The quadratic EO effect in KTN films on Si and GaAs substrates was measured as the change in reflectance under an applied electric field at nearly 5°C above  $T_{c}$ . The lock-in signal, corresponding to the electric field induced reflectivity





change versus applied field, is shown in Fig.1.10. The differences in the plots for GaAs and Si substrates are apparently due to those of crystallinity and stoichiometry deviations of the two films.

The peak  $\varepsilon$  for these films (~2090) is significantly lower than that of bulk single crystal values. For a measured  $T_c = 3^{\circ}$ C, the corresponding film composition should be KTa<sub>0.63</sub>Nb<sub>0.37</sub>O<sub>3</sub>.

#### 1.3.5. Thin films by pulsed laser deposition

The laser sputtering method is demonstrated on an example of LiTaO<sub>3</sub> (J.A. Agostinelli, G.H. Braunstein 1993). The films were produced on (0001)-sapphire substrates by pulsed laser deposition (PLD) using KrF excimer laser radiation at 248 nm. Typical pulse energies were 400 mJ with pulse durations of about 30 ns. The beam was weakly focused onto a rotating target, giving a fluence between 1.0 and 2.0 J/cm<sup>2</sup>. The target was a sintered polycrystalline bulk ceramic disc of LiTaO, prepared from mixed powders of LiOH·H,O and Ta,O,. The target was produced with an excess Li content such that the Li/Ta atomic ratio was 1.1/1. The disc was mounted having the normal to its surface at an angle of 10° with respect to the rotation axis in order to improve the uniformity of deposited film thickness. The angle was chosen so that the normal to the target surface sweeps out a circle at the substance plane to give an optimum uniformity for the selected substrate-to-target distance, which was 6 cm. The substrate was mounted on the heater block using silver paint to provide good thermal contact. A reactive ambient of 85 mtorr of O2 was used. The thickness of deposited films ranged from about 100 to 800<sup>2</sup>Å, but most films were prepared with a thickness of 4000 Å. Film deposition rates in the vicinity of 1 Å/pulse were found and laser reprates of 4 Hz were commonly used.

Films grown at substrate-heater temperatures of 500°C were found to be amorphous whereas those grown at 525°C and above were crystalline. Films were found to improve with increasing temperature and substrate-heater temperature in the range 650-700°C, the produced films having excellent crystalline properties. Figure 1.11 is a coupled XRD scan of a LiTaO<sub>3</sub> film deposited on (0001) sapphire at 650°C. The data indicate that the film is single-phase, single-orientation LiTaO<sub>3</sub>. The presence of only the (001) lines of LiTaO<sub>3</sub> shows that the entire film is c-oriented, allowing easy use of the  $d_{33}$  coefficient.



Fig.1.9 a) Curie–Weiss behaviour of KTN on Pt/SiO<sub>2</sub>/Si and b) Curie–Weiss behaviour of KTN on GaAs (Sashital et al. 1993).



Fig.1.10 Electro-optic effect of KTN films (Sashital et al. 1993). Fig.1.11 (right) Coupled x-ray diffraction scan of a 4000 Å thin film of LiTiO<sub>3</sub> on (0001) sapphire prepared at 650°C (Agostinelli and Brainstein 1993).

Such an orientation is equivalent to 'z-cut' LiTaO<sub>3</sub> in the bulk. The measured c-lattice constant of 13.73 is close to the value of 13.755 Å for bulk LiTaO<sub>3</sub>. ICP analysis of these films indicated a Li/Ta atomic ratio of 48.5/51.5 with an uncertainty of about 2 at%. In-plane orientation was studied by x-ray pole figure analysis using the (012) plane of LiTaO<sub>3</sub>. For all substrate temperatures used between 525 and 750°C, the films were found to be twinned. At the lower temperatures, roughly equal proportions of each orientation were observed. For substrate-heater temperatures of 650°C and above, a major orientation (>90%) in exact alignment with the substrate was observed.

The degree of crystalline perfection was examined using ion channelling. From these investigations it follows that the quality of the film improves as a function of height above the interface. The lower quality of the near-interface region is likely to be related to a high density of misfit dislocations arising from a rather large lattice mismatch of about 8%.

Although a film that is strictly single crystal would be desirable, it is sufficient for nonlinear optical applications that the  $LiTaO_3$  film be *c*-oriented. Because the *c*-axis direction is the optical axis direction in this birefringent material, the effective index for light that is propagating in such a thin-film waveguide as either a transverse magnetic (TM) wave or a transverse electric (TE) wave will be independent of the propagation direction in the planar waveguide. Thus, a c-oriented film of LiTaO<sub>3</sub> with no in-plane orientation can in principle give an optical waveguide having low scattering loss. It is also of interest that the condition of c-orientation is sufficient to give a single  $d_{33}$  coefficient for the entire film. Thus, the well-oriented but somewhat twined films of LiTaO<sub>3</sub> meet the criteria for crystalline quality required for nonlinear optical/electro-optical devices. Although single crystallinity is not a necessary requirement for these applications, a single or controlled ferroelectric domain structure is essential. Some effort was made to elucidate the as-grown domain structure of the films by etching in hot HF:HNO<sub>3</sub> with a subsequent examination by scanning electron microscopy. The films appeared to etch uniformly, which suggests that the films are single domain as grown.

Measurements of the optical propagation loss for a LiTaO<sub>3</sub> film, ~3400 Å thick, grown at 650°C, are shown in Fig.1.12. A beam of 633 nm radiation was coupled into the film using a rutile prism. The data correspond to scattered light intensity for the  $TM_0$  mode. The best fit line through the data indicates a loss of about 0.6 dB/cm. However, the large scatter in the data places a considerable uncertainty in the loss factor. It is believed that the large deviations from the linear fit are the result of poor sampling statistics from a small number of strong scattering centres that are sampling the waveguide intensity. These centres are likely to be the particulate features discussed above. It is, however, apparent that these centres do not produce any serious waveguide loss.

Moreover, there are significant obstacles for the growth of epitaxial LiNbO<sub>3</sub> and LiTaO<sub>3</sub> films on GaAs for the blue light generation, because of the following reasons: (a) GaAs has the zinc blende structure with a lattice parameter of 0.5673 nm, while LiTaO<sub>3</sub> has the trigonal structure with a = 0.5153 nm and c = 1.3755 nm, (b) LiTaO<sub>3</sub> is reactive with GaAs and produced undesirable phases at interfaces, and (c) an intermediate oxide layer with low refractive index is required to form a waveguide.

L.S. Hung et al. (1993) report epitaxial growth of a  $LiTaO_3$  layer on a GaAs with a MgO buffer layer. The MgO layer acts as a diffusion barrier to impede film-substrate interactions, and forms a waveguide structure with the overlying  $LiTaO_3$ .

 $(NH_4)_2S_x$ -treated (111) GaAs wafers were used as substrates for epitaxial growth of MgO films. MgO was deposited directly on GaAs by electron-beam evaporation. The deposition process was carried out at  $3 \times 10^{-8}$  torr without introducing additional oxygen into the system, ensuring an undisturbed GaAs surface to the growth of epitaxial MgO films. The substrate was heated by a radiative heater. The growth temperature was  $450-550^{\circ}C$  and monitored by an infrared pyrometer. The deposition rate was 0.05-0.15 nm/s, and the thickness of the MgO films was about 100-500 nm.

LiTaO<sub>3</sub> films were grown by pulsed laser deposition. The parameters of the sputtering laser are presented above. Deposition was carried out at a rate of 0.1 nm/pulse, the sample was cooled to room temperature in oxygen at a pressure of 150 torr.

The thickness and composition of the resulting MgO and LiTaO<sub>3</sub> films were determined by Rutherford backscattering spectrometry. The spectrum can be best fitted by a simulation of a bilayered structure with the stoichiometric ratio
of Mg:O = 1.0:1.0 and Li:Ta:O = 1.15:0.97:3. The rear edge of the Ta profile and the front edge of the GaAs profile are abrupt, indicating limited interfacial reaction.

The standard  $\theta$ -2 $\theta$  diffraction pattern taken from a MgO film on GaAs reveals only the MgO (111) and GaAs (111) diffraction peaks. The full width at half maximum of the MgO (111) rocking curve measured at about 1.8°, indicating a highly [111]-axis oriented film. Epitaxial growth of MgO on GaAs was verified by x-ray pole figure analysis. A comparison of the results obtained from MgO and that from the underlying GaAs indicates that a single-crystal [111]-oriented MgO film is grown on (111) GaAs, and that the MgO lattice is rotated by 180° about the [111] surface normal with respect to the GaAs substrate.

The crystal quality of  $LiTaO_3$  can be substantially improved by increasing the growth temperature of 600-650°C.

## 1.3.6. Waveguides by MeV He ion implantation

Planar waveguides in KNbO<sub>3</sub> by MeV He ion implantation for optical waves with polarization parallel to the crystallographic *b*-axis were produced by F.P. Strohkendl et al. (1991). These guides consisted of the essentially undamaged surface layer which is separated from the bulk by a buried layer of a reduced refractive index. The ionic end of the damage range of the incident He ions was found to partially amorphize the crystal lattice (R. Irmscher et al. 1991). The waveguides are leaky, as light which is propagating in the undamaged surface layer can tunnel through the barrier with a lowered index into the substrate. The waveguides showed a minimum propagation loss for an implantation dose of  $5 \times 10^{14}$  cm<sup>-2</sup>. This dose was at least one order of magnitude below the doses which have been used so far to produce waveguides in KNbO<sub>3</sub> (T. Bremer et al. 1988 and L. Zhang et al. 1988).

F. P. Strohkendl et al. (1991) reported on a criterion of planar waveguides for optical waves with polarization parallel to the crystallographic *c*-axis with even lower implantation doses, that is, with doses of about  $10^{14}$  cm<sup>-2</sup>. Prism coupling, as well as end-fire coupling of a HeNe laser beam with a wavelength of 632.8 nm was used to characterize the TE modes propagating along the *a*-axis in the ion implanted planar waveguides.

KNbO, crystal samples were cut perpendicular to the b-axis and had dimen-



Fig.1.12 Intensity as a function of propagation distance for light scattered out of the  $TM_0$  mode LiTaO<sub>3</sub> thin film waveguide on sapphire (Agostinelli and Braunstein 1993).

sions of typically  $7\times2\times9$  mm<sup>3</sup>. The samples were irradiated at room temperature with He ions of either 1 or 2 MeV and doses in the range  $5\times10^{13}$  to  $5\times10^{14}$  cm<sup>-2</sup>. The angle of incidence of the He ions was slightly off normal to avoid channelling. The crystal samples were heat sinked and the ion flux was kept below  $5\times10^{15}$  cm<sup>-2</sup> h<sup>-1</sup> to prevent the crystals from heating. The doses were kept deliberately low because ion implantation is an inherently destructive process and leads in KNbO<sub>3</sub> already at doses of the order of  $2\times10^{15}$  cm<sup>-2</sup> to strong waveguide losses.

After implantation, the samples exhibited planar waveguiding. Prism coupling of an He-Ne laser with a wavelength of 632.8 nm was used to measure the mode spectra of the planar waveguides by darkline and brightline spectroscopy. Figure 1.13 shows two examples of darkline spectra which were taken by measuring the beam power reflected from the right-angle coupling prism as a function of the mode effective index  $N_{eff} = n \cos \alpha$ , where  $n_{\mu}$  is the refractive index of the coupling prism at a wavelength of 632.8 nm. The pronounced reflectivity dip in the darkline spectrum of the sample irradiated with 1 MeV He ions and a dose of  $5 \times 10^{13}$  cm<sup>-2</sup> indicates the successful production of a waveguiding structure and occurs due to resonant excitation of the lowest mode. The deeper the media in the darkline spectra the less light is reflected back from the coupling point, and hence, the better is the coupling of the laser beam to the waveguide mode. From the normalized intensity in the dip of the TE<sub>n</sub> mode of the 1 MeV waveguide, Strohkendl et al. (1991) calculated a coupling efficiency of ~33%. The TE<sub>o</sub> mode of the 2 MeV guide was only detected in the brigthline spectrum that is taken by measuring the power at the waveguide exit as a function of the coupling angle. The absence of a pronounced reflectivity dip in the corresponding darkline spectrum (Fig.1.13) indicates that the coupling efficiency of the incident laser beam to the TE<sub>o</sub> mode was less than ~1%.

The darkline and brightline spectra of the waveguides implanted with doses higher than  $1 \times 10^{14}$  cm<sup>-2</sup> exhibited several reflectivity dips.

Note that for a dose of up to  $1 \times 10^{14}$  cm<sup>-2</sup> nonleaky monomode waveguides were produced in KNbO<sub>3</sub>. The much weaker coupling efficiency for the 2 MeV guide gives evidence that the waveguiding layer with an increased refractive index is located deeper below the crystal surface than for the 1 MeV guide. Therefore, Strohkendl et al. (1991) have found that ion implantation creates a layer of increased refractive index buried below the crystal surface. There have been several reports on so-called 'anomalous' increases of the extraordinary refractive index in birefringent crystals (L. Chang et al. 1988).

## 1.3.7 Strip waveguides

Integrated optics applications, such as modulators or frequency doublers, which would benefit from the high figures of merit of  $KNbO_3$  demand for the fabrication of strip waveguides. Baumert et al. (1985) have reported for the first time on strip waveguides in  $KNbO_3$ . They achieved optical waveguiding and cut-off modulation by using the electro-optic effect for waveguide formation and modulation.

Fluck et al. (1991) reported for the first time on permanent optical strip

waveguides in  $KNbO_3$ . The one-dimensional waveguiding structures were produced by MeV ion implantation and appropriate masking.

The KNbO<sub>3</sub> crystals were cut perpendicular to the crystallographic *b*-axis. The size of the crystal samples was  $9.95 \times 1.97 \times 8.04$  mm<sup>3</sup>. The surface and the two end-faces perpendicular to the *a*-axis were carefully polished in order to allow efficient end-fire coupling of a laser beam. The fabrication of strip waveguides using He ion implantation was carried out by first producing a planar guide and then applying an implantation mask to form the vertical side walls (Fig.1.14). The planar waveguide was formed by irradiating the samples at room temperature with 3.2 MeV He ions and a dose of  $7.5 \times 10^{14}$  cm<sup>-2</sup>. The incidence of the ions was slightly off normal to avoid channeling. The dose was chosen deliberately low because for these conditions low attenuation planar waveguides have been produced. The thickness of the planar waveguides is given by the average ion penetration depth, which was calculated with the Monte Carlo method to be 7.7 µm for 3.2 MeV He ions in KNbO<sub>3</sub>.

To form one-dimensional waveguides, Fluck et al. (1991) masked the samples for further implantation by a set of parallel tungsten wires 13 µm in diameter and with a spacing of 400 µm (Fig.1.14). The wires were used as a simple mask of sufficient thickness to completely shield strips of the planar waveguides from further He ion bombardment, hence from further refractive index modification. The vertical side walls were formed with He ions of 2.9 MeV and varying angle implantation, respectively. Ideally, the implantation mask would possess vertical walls and uniform thickness. But because of using wires, there are ions which pass through the outer thinner part of the wires, therefore reducing the effective width of the strips. Because these ions lose part of their energy before reaching the crystal surface, they penetrate less deeply into the crystal, hence the side wall damage layers will continuously rise to the surface, reducing the waveguide width especially near the surface. The lateral straggling of the incident ions which is due to the interaction with the target ions leads also to narrowing of the width of the strip guides. The actual width of the strip waveguides formed by using tungsten wires 13 µm in diameter as an implantation mask is reduced to 11.4 µm.



**Fig.1.13** Reflectivity as a function of effective refractive index  $N_{eff}$  for waveguides created with 1 and 2 MeV ions and a dose of  $5 \times 10^{13}$  cm<sup>-2</sup>. (Strohkendlet al. 1991).



Fig.1.14 a) Creation of a planar waveguiding layer, b) formation of the optical strip waveguides by further implantation with appropriate masking of the sample which produces the sidewalls (Fluck et al. 1991).

The optical characteristics of the strip waveguides fabricated by the ion implantation process as described above are given in Table 1.6.

#### 1.3.8 Double waveguide

Planar buried double waveguides were produced in crystalline quartz and their convoluted profiles were determined by mode index measurements (Chandler et al. 1988). LiNbO<sub>3</sub> is of much greater interest and application than quartz and ion implantation is quite able to produce low-loss guides in this material (Al-Chalabi 1985). It is important, however, not to assume a simple profile summation process in LiNbO<sub>3</sub>. As the ion damage has been shown to anneal at a lower temperature (<400°C) (Glavas et al. 1988), it is quite likely to suffer partial annealing during successive irradiations, due to their thermal or ionization effects. An assessment of the seriousness of this problem is an important prerequisite to the consideration of any multiple waveguide construction.

The method of determining the double-waveguide profile is not immediately obvious. Simple waveguides are normally characterized by the spacing of their resonant mode spectra (bright or dark lines) using a quantum mechanical analogy such as perturbation theory, a phase-integral approximation, (Wentzel-Kramers-Brillouin), or a finite element method. Only the latter would be applicable to a double guide, and its implementation would be laborious.

Chandler et al. (1989) used LiNbO<sub>3</sub> samples obtained from 1 mm thick ycut wafers. They were clamped in good thermal contact with an aluminium block held at the required temperature. Beam heating was minimized by restricting the current to about 0.5  $\mu$ A and this was scanned over an area of nearly 0.5 cm<sup>2</sup> (for uniformity of dose). The shallow barrier was produced with 1.1 MeV He<sup>\*</sup> to a dose of  $1.5 \times 10^{16}$  ion/cm<sup>2</sup> and the deep barrier with 2.2 MeV He<sup>\*</sup> to a dose of  $3.0 \times 10^{16}$  ion/cm<sup>2</sup>. The energy ratio gave optical wells of approximately equal widths and the dose ratio was necessary for equal height barriers, because of the higher damage efficiency for the shallower implant. The implant areas for the two energies were overlapping but displaced from each other by several

	Planar implantation	
Energy		3.2 MeV
Dose	7.5	$\times 10^{14}$ cm <sup>-2</sup>
	Side wall implantation	
Energy		2.9 MeV
Angle	5	/22/34/45°
Total dose	3.5	×10 <sup>15</sup> cm <sup>-2</sup>
	Size of strip waveguide (µm)	
Width		11.4
Depth		7.7
	Propagation losses (dB/cm),	
	wavelength in nm	
514.5		4.3
632.8		1.4
860.1		2.9

Table 1.6 Characteristics of the optical strip waveguides in  $KNbO_3$  formed by He ion implantation (Fluck et al. 1991)

millimetres in order to give three distinct regions for profile measurements shallow barrier, deep barrier, and the composite guide. For each region, dark mode positions were measured with TE polarization using the z direction of propagation for both red (0.6328 µm) and blue (0.488 µm) light. All visible modes were measured - the sharp guiding modes within the wells, and the broad 'substrate modes' not confined by the guides. These were all used by the computer reflectivity simulation program to give the refractive index profiles in the different cases. The analytic function chosen to describe each refractive index barrier consisted of an exponential/Gaussian nuclear damage peak superimposed on a flat electronic plateau. This function is characterized by four variable parameters and has been found to describe adequately the experimental results for single-barrier profiles in LiNbO, (Glavas et al. 1988). For single-barrier implants the modes were spaced fairly evenly, but in the case of the double guides the spacing was very uneven, and also the line intensities varied considerably. The use of two wavelengths had the advantage of acting as a check against missing any of the very faint modes.

The first sample was implanted with a high-energy dose (2.2 MeV,  $3.0 \times 10^{16}$  ions/cm<sup>2</sup>) followed by the low-energy dose (1.1 MeV,  $1.5 \times 10^{16}$  ions/cm<sup>2</sup>) both at 300 K (Chandler et al. 1989).

Figure 1.15 shows the composite index profiles for this sample measured at 0.488 and 0.6238  $\mu$ m together with the real mode value. Both barriers are represented functionally by exponential/Gaussian nuclear damage peaks on flat plateaux. It appears that, in general, a direct summation of the damage has occurred from the two implants, with a few exceptions. The high-energy peak (which was implanted first) has been reduced, possibly by annealing during the second implant: the low energy peak height is not a summation because it is close to saturation and the low-energy peak position has been shifted to greater depth. This latter effect may be attributed to an increased ion range



Fig.1.15 Fitted profiles of experimental data measured at 0.488  $\mu$ m (upper) and 0.6328  $\mu$ m (lower). The mode levels and normalized mode curves are shown (0.488  $\mu$ m dotted) (Chandler et al. 1989).

 $(\sim 4\%)$  for the second implant (low energy) due to an overall reduction in density of the region during the first implant (high energy).

LiNbO<sub>3</sub> has been shown to be a good substrate for ion-implanted double waveguides. The profiles of the nuclear damage barriers are essentially additive, provided that account is taken of possible annealing during irradiation and ion range modification due to density changes. For barriers of equal height, it must also be remembered that the damage efficiency falls almost inversely with the ion range.

### 1.4 Autodiffused layers in lithium niobate and lithium tantalate

Kaminow and Carruthers (1974) developed a novel and simple out-diffusion technique for achieving thin positive index layers in LiNbO<sub>3</sub> or LiTaO<sub>3</sub> without degrading the original surface. The authors used diffusion of components out of a crystal. In this method, stoichiometric departures near the surface of lithium niobate and lithium tantalate crystals were achieved by vacuum heating the crystals causing out-diffusion of Li<sub>2</sub>O. It is known from previous work on bulk materials that extraordinary refractive index  $n_e$  increases as Li<sub>2</sub>O is removed from the crystal but the ordinary index is not affected (Carruthers et al. 1974). For (Li<sub>2</sub>O)<sub>v</sub>(Nb<sub>2</sub>O<sub>x</sub>)<sub>1-v</sub>

$$dn/dv = -1.6$$
 (1.5a)

in the 0.48  $< \nu < 0.50$  range; and for

$$dn/dv = -0.8 \tag{1.5b}$$

where the molar fraction v = 0.5 for a stoichiometric crystal. Thus, the outdiffusion produces a refractive index gradient that has a maximum positive index change at the surface and gradually approaches the bulk index in the interior of the specimen. These out-diffused layers serve as excellent low-loss optical waveguides that possess all the characteristics of the bulk crystal.

The out-diffused layers have the following advantages over epitaxial layers: (a) the processing is much simpler; (b) the surface remains smooth and need not be refinished; (c) the optical quality and properties of the layer are identical with those of the bulk crystal; (d) there is no abrupt lattice mismatch or imperfection at the film-substrate boundary to produce scattering; and (e) for out-diffusion below Curie temperature, the layers need not be poled. However, the out-diffused layers may be disadvantageous in some applications unless the index profile parameters can be controlled independently. Thus, the peak index change at the surface, a, and the characteristic diffusion depth, b, determine the number of modes the guide will support and the degree of confinement of optical energy to the surface.

The transmission interference microscope method was employed to measure the out-diffusion index profiles on a large number of specimens prepared under various conditions.

Refractive-index profiles normal to the surfaces were measured with a Leitz interference microscope. With this instrument, interference fringes, in polarized light, can be observed with a resolution of about 2 µm. Interferograms through the (a,c) facet of (1,2) are shown in Fig.1.16. The edge in Fig.1.16a is normal to the axis, and the light (a Hg lamp) is an ordinary wave. Only a very small ordinary index change  $\Delta n_o$  is observed. The index change  $\Delta n$  is given by  $\Delta n = p\lambda/d$ , where p is the number of fringes by which the interference pattern in the graded region is shifted from the unperturbed pattern,  $\lambda$  is the wavelength (0.546 µm), and d is the same thickness (2000 µm). The fringe shift depicts the index profile directly. A substantial positive index change is observed with extraordinary light as in Fig.1.16b, where the edge is again normal to the c-axis corresponding to out-diffusion along the c-axis. The extraordinary index change is greater than in Fig.1.16c, where the edge is parallel to the c-axis corresponding to out-diffusion normal to the c-axis. The interferogram of Fig.1.16d



FIg.1.16 Interferograms: a) ordinary wave, diffusion along c, b) extraordinary wave, diffusion along c, c) extraordinary wave, diffusion normal to c, d) extraordinary wave, diffusion normal to c (Kaminov and Carruthers 1973).

illustrates the still greater out-diffusion experienced by (1-3) under observation conditions comparable to those in Fig.1.16c for (1-2).

## 1.4.1 Out-diffusion kinetics

The out-diffusion components from the surface of a solid crystal involve three basic reaction steps: (i) diffusion of gaseous molecules away from the surface; (ii) desorption of molecules from the crystal surface; and (iii) diffusion of molecules through the crystal to the surface. The simple error function complement (erfc) solution to the diffusion equation to which the extraordinary index curves were fitted in the work by Kaminow and Carruthers (1973) is only valid for a constant surface concentration. More refined boundary conditions can be used to examine the nature of these approximations.

In the crystal, Fick's second law governing the diffusion is

$$(\partial C) / (\partial t) = D[(\partial^2 C) / (\partial x^2)], \ 0 < x < \infty$$
(1.6)

and is valid for cases where the diffusion coefficient D is independent of t and x. Here C is the concentration deficit of  $\text{Li}_2\text{O}$  in g cm<sup>-3</sup> at a distance x into the surface after diffusion time t.

The units of concentration are related to v by

$$C = -\Delta v \left\{ M(\text{Li}_2\text{O}) / M(\text{LiNbO}_3) \right\} \rho(\text{LiNbO}_3)$$
(1.7)

where M is the molecular weight and  $\rho$  the density (which varies slightly with v itself). The initial condition is

$$C = 0$$
 at  $t = 0$  for  $0 < x < \infty$  (1.8)

The diffusion constant varies with T

$$D = D_0 \exp(-Q_0/RT).$$
(1.9)

where  $Q_{\rm D}$  is the activation energy for diffusion, R = 1.99 cal K<sup>-1</sup>mol<sup>-1</sup>.

The boundary condition at the crystal surface equates the vaporization flux,  $J_{v}$ , to the concentration gradient at the surface as

$$J_{v} = D \left[ dC/dx \right]_{x=0}$$
(1.10)

This assumes implicitly that the solid-vapour interface is stationary with respect to the diffusion distance (*i.e.* there is no vapour etching of the crystal surface) and that the flux,  $J_{v}$ , does not change with surface concentration. For the outdiffusion problem, the surface concentration changes by very small amounts, so both these assumptions are valid, and the solution to equation (1.5) is (Carslaw and Jaeger, 1971)

$$C = 2J_{y} \left[ t/D \right]^{1/2} ierfc \left[ x/2(Dt)^{1/2} \right]$$
(1.11)

where *ierfc* is the integral of the error function complement and is evaluated by Carslaw and Jaeger (1971) and Crank (1970). The surface concentration can be written as

$$C(0,t) = (2J_y/D)(Dt/\pi)^{1/2}$$
(1.12)

The normalized functions erfc(x/b') and  $\pi^{1/2}erfc(x/b)$  are plotted in Fig.1.17 and can be seen to be similar. The exponential function exp (-x/b'') is also included for comparison.

The quantities  $\Delta n_e$  and C are related by equation (1.5) and equation (1.7) so that for LiNbO<sub>3</sub>:

$$\Delta n_{\rm r} = 1.75 \, C.$$
 (1.13)

Then equation (1.11) can be rewritten as

$$\Delta n_{\mu} = a\pi^{1/2} ierfc(x/b), \tag{1.14}$$

where

$$a = \Delta n_e (0, t) = (3.51 J_v) (t / \pi D)^{1/2}; \qquad (1.15)$$

$$b = 2(Dt)^{1/2}. (1.16)$$

The vaporization flux is related to the equilibrium vapour pressure of  $Li_2O$  over  $(Li_2O)_v(Nb_2O_s)_{(1-v)}$  by the Langmuir relation

$$J_{v} = \alpha p_{eq} \left\{ 2 \pi RT / M(\text{Li}_{2}\text{O}) \right\}^{-1/2}$$
(1.17)

or for computational purposes,



**Fig.1.17** Diffusion profiles – analytical curves for  $\pi^{t_{k}}$  ierfc (*x/b*), erfc (*x/b'*) and exp (*x/b''*). A typical set of experimental data is fitted as shown with a = a' = a'' and b = 1.36 b' = 1.97 b'' (Carruthers et al. 1974).

$$J_{v}(\text{gm cm}^{-2}\text{s}^{-1}) = 44.4 p_{L}(\text{atm}) / [TM(\text{Li}_{2}\text{O})]^{1/2}$$
 (1.18)

where the Langmuir vapour pressure  $p_L$  is related to the equilibrium saturation vapour pressure  $p_{ea}$  by

$$p_L = \alpha \, p_{eq} \tag{1.19}$$

and

$$p_{eq} = p_0 \exp(-Q_v / RT), \tag{1.20}$$

where  $Q_v$  is the activation energy for vaporization. Here the evaporation coefficient, *a*, may vary from unity, when molecules evaporate into a vacuum at the equilibrium rate, to near zero, when molecules evaporate at a kinetically determined rate with significant energy or entropy barriers. Experimentally, the evaporating geometry, total pressure and pumping speed influence  $J_v$  because of the partial confinement of the specimen surface by the furnace tube. This departure from ideal free evaporation will influence the value of *a* in an undetermined manner that does not depend on temperature. Consequently, this temperature dependence of *a* is ignored here, and the assumption will be justified later. The total surface concentration changes by  $\Delta v \leq 0.01$  (see Carruthers and Peterson, 1971), so we may regard  $J_u$  as constant at any given temperature.

The out-diffused specimens are observed by Kaminow and Carruthers (1973) under the interference microscope and the fringe displacements yielded  $\Delta n_e \leq 0.01(x)$ . The data are fitted to the *ierfc* distribution at  $\Delta n_e(0)$ , V and  $\Delta n_e(\infty) = 0$ . In Fig.1.17 it can be seen that  $\Delta n(0) = a$  and  $\Delta n(x) = 0.5a$  when x = 0.36b, which yields values for a and b. A typical set of data, measured by the intersection of each fringe with a line normal to the surface, is plotted in Fig.1.17 using the calculated normalization parameters a and b to obtain a comparison with the analytical curve for *ierfc*. To compare the same data with the *erfc* and exp functions, new parameters a', b' and a'', b'', respectively, are calculated to obtain a fit at  $\Delta n_e(0)$ ,  $\Delta n_e(0)/2$  and  $\Delta n_e(\infty)$  as before. Then

$$a=a'=a''; b=1.36, b'=1.97b''.$$

It can be seen in Fig.1.17 that the data are best represented by the *ierfc* curve as expected but that the *erfc* and exp curves give fair approximations to the data. The exp function is a convenient approximation for determining the waveguiding properties of these graded index layers. When the characteristic depth, b, obtained from such curve fitting is plotted against  $t^{1/2}$ , the slope is  $2(D)^{1/2}$ , allowing an accurate determination of D(T) for the temperature at which the specimen was treated.

The vaporization flux can be computed from the refractive index gradient at the surface. From equations (1.5a), (1.7) and (1.10) we have

$$\left\{ \left[ d(\Delta n_{e}) / (dx) \right]_{x=0} = -J_{v} / (0.57D).$$
(1.21)

It may be seen from equation (1.14) that

$$\left\{ \left[ d(\Delta n_{\epsilon}) / (dx) \right]_{x=0} = -\pi^{1/2} a / b.$$
(1.22)

Thus,  $J_{v}$  may be computed from the parameters *a* and *b* or from the gradient itself. Note from equations (1.15), (1.16) and (1.22) that the surface refractive index gradient is independent of *t*.

From equations (1.9), (1.17) and (1.20) we have

$$\left\{ \left[ d(\Delta n_e] / (dx) \right]_{x=0} = G_0 \exp\left[ -\left( Q_v - Q_D \right) / RT \right],$$
(1.23)

where  $G_0 = -\alpha p_0 / [0.57 D_0 (2\pi R T M)^{1/2}]$ . Taking the logarithm of equation (1.23) and differentiating with respect to 1/T, we come to

$$\partial \ln \left[ d(\Delta n_e) / dx \right]_{x=0} / \partial (1/T) = -(Q_v - Q_D) / R.$$
(1.24)

We have ignored the slight temperature dependence of  $G_0$  over the range of T employed. It can then be seen that the difference between the activation energies for vaporization and solid state diffusion determines the temperature dependence of the refractive index gradient at the surface.

The actual vaporization flux,  $J_{\nu}$ , can be calculated from equation (1.21) and provides a check against the measured weight loss.

The diffusion coefficients found experimentally by Carruthers (1974) are plotted against 1/T in Fig.1.18 for diffusion normal and parallel to the *c*-axis.





	$D_0, \ cm^2 \ s^{-1}$	$Q_{\scriptscriptstyle D}$ , kcal mol <sup>-</sup>
LiNbO,		
⊥ c-axis	(3.21±0.44)×10 <sup>2</sup>	68.21±0.48
c-axis	(3.32±1.19)×10 <sup>2</sup>	68.17±1.24
LiTaO,		
⊥ c-axis	(2.8±0.8)×10 <sup>-2</sup>	50,1±4.3
c-axis	(6.6±2.5)×10 <sup>-2</sup>	52.1±7.0

Table 1.7 Diffusion equation parameters (Carruthers, Kaminow, Stulz, 1974)

Table 1.8 Refractive index gradient equation parameters from regression analysis (Carruthers, Kaminow and Stulz, 1974)

	<b>G</b> <sub>0</sub> (μ <sup>-1</sup> )	$(Q_v - Q_p)$ (kcal/mol)	Q, (kcal/mol)	
Lindo,				
⊥ c-axis	3.69×10-5	2.38	70.6	
∥ c-axis LiTaO,	2.2×10-7	9.15	59.0	
$\perp c$ -axis	3.0×10 <sup>-3</sup>	13.6	64	
ll c-axis	1.5×10-3	11.2	63	

The straight lines were calculated by the least squares regression analysis. The residual variances are shown as parallel lines and can be seen to encompass the centroid of the *D*-values but not the error range in all cases. Also the residual variance is much larger for  $D_{\mu}$  than for  $D_{\perp}$  for not quite clear reasons. The calculated values of  $D_0$  and  $Q_D$  are shown in Table 1.7. It can be seen that both the pre-exponential factors and the activation energies are similar to each other, within experimental error, for diffusion normal.

The gradient of the refractive index change at the surface (given by  $\pi^{1/2} a/b$ ) may be very sensitive to a number of experimental variables such as surface condition, pumping speed, and pressure.

The gradients were averaged at each temperature and plotted against 1/T in Fig.1.19. The straight lines were drawn from a least squares regression analysis of the average values of the refractive index gradients at each temperature. The pertinent parameters are shown in Table 1.8.

The values of the activation energy for vaporization in Table 1.7 can be compared with the values obtained for the vaporization of  $Li_2O$ . (Berkowiz et al. 1959; Nesmeyanov and Belykh, 1969). For the reaction

$$(\text{Li}_2\text{O})_{\text{solid}} - 2(\text{Li})_{\text{gas}} + \text{O}_{\text{gas}}, \Delta H_T^0$$
(1.25)

a value for  $\Delta H_{1100C}$  of about 155 kcal/(mole Li<sub>2</sub>O) has been estimated. This gives an activation energy for vaporization of about 74 kcal/(mole LiNbO<sub>2</sub>),



**Fig.1.19** Variation of the gradient of the refractive index change at the surface of lithium niobate given as  $\pi^{1/2}a/b$  with temperature as 1/T, see Table 1.8 (Carruthers et al. 1974).

which is quite closed to the measured values in Table 1.8 for v = 0.48 and confirms this reaction as a probable realization mechanism.

There have been no equilibrium vapour pressure measurements of Li<sub>2</sub>O over lithium niobate, so it is not possible to determine *a* at this time. However, a comparison of the values of  $p_L$  calculated from equations (1.15) and (1.18) and shown in Table 1.9 with the range of equilibrium vapour pressures of pure Li<sub>2</sub>O over the same temperature range (Berkowiz et al. 1959; Nesmeyanov and Belykh, 1960) suggests that  $\alpha \le 10^{-4}$  and that  $\alpha_{\parallel}/\alpha_{\perp} \approx 3$ . Such anisotropic and low values of the evaporation coefficient suggest that evaporation occurs at a kinetically determined rate with significant surface energy or entropy barriers.

The diffusion data for lithium tantalate were obtained by out-diffusing one specimen at each of nine temperatures ranging from 930°C to 1400°C. The diffusion coefficients were calculated from the slopes of the *b* versus  $t^{1/2}$  relationships as before.

Since fewer specimens were used, these data are not as accurate as those for lithium niobate. As in the case of lithium niobate, the data for diffusion normal to the *c*-axis show less scatter than those for diffusion parallel to the *c*-axis. The diffusion coefficients are plotted against 1/T in Fig.1.20 for diffusion normal and parallel to the *c*-axis. The straight lines were calculated by least squares regression analyses, and the resulting values of  $D_0$  and  $Q_D$  are given in Table 1.7. As for lithium niobate, the pre-exponential factors and activation energies are similar, within experimental error, for diffusion normal and parallel to the *c*-axis. However, the differences between lithium niobate and lithium tantalate are significant; the values of  $D_0$  are lower by four orders of magnitude and  $Q_D$  is slightly smaller for lithium tantalate. The greater difficulty of diffusion in lithium tantalate may be associated with the more covalent nature of the bonding (as reflected, for example, in the higher melting point).

The gradient of the refractive-index change at the surface (given by  $\pi^{th} a/b$ ) is shown in Fig.1.21. The scatter is quite large, especially for diffusion parallel to the *c*-axis. The straight lines were calculated by least squares regression analyses, and the resulting values of  $G_0$  and  $Q_v - Q_D$  are shown in Table 1.8. The computed activation energies for vaporization are quite similar to those for lithium niobate and again suggest that the same vaporization reaction is occurring. Unlike lithium niobate, however, the gradient of the surface refractive-index change becomes higher at higher temperatures. This is a desirable

<i>T</i> (⁰C)	$J_{v}(g cm)$	n <sup>-2</sup> s)	$p_{L}$ (atm)		
	$\perp c$ -axis	c-axis	$\perp c$ -axis	$\perp c$ -axis	
930	1.95×10 <sup>-11</sup>	0.828×10-11	0.279×10-11	0.118×10-11	
1000	6.04×10-11	2.42×10-11	0.888×10-11	0.356×10-11	
1050	1.24×10-10	2.57×10-11	1.86×10-11	0.385×10-11	
1100	2.01×10 <sup>-10</sup>	5.18×10 <sup>-11</sup>	3.07×10-11	0.791×10 <sup>-11</sup>	
1125	1125 4.04×10 <sup>-10</sup> 2.6		6.22×10-11	4.05×10-11	

 Table 1.9 Calculated evaporation fluxes and kinetic vapour pressure for LiNbO<sub>3</sub> (Carruthers, Kaminow, Stulz, 1974)



**Fig1.20** Variation of diffusion coefficients with temperature as 1/T in lithium tantalate for diffusion normal and parallel to the o-axis. Straight lines have been fitted by least squares regression analysis, see Table 1.7 (Carruthers et al. 1974).

**Fig.1.21** (right) Variation of the gradient of the refractive index change at the surface of lithium tantalate given as  $\pi^{1/2}a/b$  with temperature as 1/T, see Table 1.7 (Carruthers et al. 1974).

feature for obtaining steeper index profiles and thinner waveguiding layers, provided the required diffusion times at 1400°C can be kept sufficiently short.

The evaporation coefficients,  $\alpha$ , are comparable with those for lithium niobate ( $\alpha \leq 10^{-4}$ ) and again suggest that evaporation is the kinetically rate-limiting reaction.

# 1.5 The diffusion method for metals and oxides

Among the most thoroughly investigated methods is now the diffusion method which is widely used for fabrication of planar and channel light guides on lithium niobate and lithium tantalate plates. However, this only refers in full measure to titanium diffusion. The method consists in depositing a film or a strip of metal or its oxide onto the substrate surface, after which the crystal is diffusionally distilled or doped in one or several stages. The characteristic diffusion time ranges between 1 and 10 h, the temperature being 800–1100°C for lithium niobate and 800-1300°C for lithium tantalate. The diffusion typically proceeds in a medium of inert gases – argon and hydrogen and in some cases in the air, in an oxygen flux or in its mixture with argon. In the presence of oxygen, processes typically proceed in two stages with a preliminary metal oxidation. Transition metals are most often employed as doping impurities.

The studies of metal diffusion method carried out in recent years in the technology of light guide fabrication involving lithium niobate and lithium tantalate have shown that in practice, titanium diffusion is more successful as being more intensive and providing higher  $\Delta n_o$  and  $\Delta n_e$  values as compared to other metals.

When this method is applied to creating channel and single-mode planar structures in lithium niobate and tantalate, allowance should be made for  $\text{Li}_2\text{O}$  outdiffusion in the regions adjoining those of channel formation. The out-diffusion process is known to cause an increase in  $n_e$ . Electro-optic devices are most often intended for modes of just this polarization since the element  $r_{33}$  (associated with  $n_e$ ) of the tensor of electro-optic coefficients of lithium niobate and tantalate crystals is the largest. Li<sub>2</sub>O out-diffusion may lead to increasing losses and to non-reproducibility of the mode composition in the channel structure and is therefore undesirable.

The specific features of background out-diffusion in the formation of Ti: LiNbO<sub>3</sub> light guides and the ways of its suppression are described by Chen and Pastor (1977), Jackel et al. (1981) and Noda et al. (1980). Chen and Pastor show that as a result of titanium diffusion (the metal film thickness 20  $\mu$ m, preliminary oxidation time 1 h at a temperature of 600°C, and the diffusion proper lasts six hours at 900°C) one 'titanium' mode (the effective light guide depth is 4  $\mu$ m) and two 'out-diffusion' modes (15  $\mu$ m) are excited. The latter modes were then removed by sample annealing in the powder mixture of Li<sub>2</sub>CO<sub>3</sub>+Nb<sub>2</sub>O<sub>5</sub>. Components of the mixture with 99% of the main substance were taken in proportion corresponding to LiNbO<sub>3</sub> composition with account taken of lithium carbonate. Samples were annealed at 900°C for 1–4 hours, and the 'titanium' mode was not suppressed.

We shall point out two ways of out-diffusion suppression: metal diffusion from films in a medium of lithium oxide or corresponding chemical compounds and lightguide channel formation in a gas flux containing water vapour.

The efficiency of this technique was proved by Jackel et al. (1981) using IR spectroscopy in the region of 3480 cm<sup>-1</sup> (bond -O-H-) of specimens which had undergone different treatment. Titanium diffusion in wet argon leads to a relative increase of hydrogen concentration in the surface layer of substrates as compared to the original crystal. The authors believe that this induces Li<sup>+</sup> ion migration suppression in the crystal and promotes the decrease of the out-diffusion rate.

Ziling et al. (1980) showed that as soon as  $Ti^{4+}$  is substituted for Nb<sup>5+</sup>, there occurs charge nonequilibrium which can be compensated by positioning the Li ion in the interstice. Refractive index variation in a LiNbO<sub>3</sub> crystal upon the substitution of titanium for niobium can, depending on the concentration of the latter, be caused by the difference in ion reactions and inner stresses due to diffusion. Taking into account a limited plasticity of LiNbO<sub>3</sub> crystals at the diffusion temperature, we can expect that the inner stresses will cause microcracking and relax partially with increasing dislocation density in the

near-surface layer. Both types of defects were observed experimentally and are likely to be the main factor determining optical losses of waveguiding layers. Similar results were obtained by Golubenko et al. (1980) and Zolotov et al. (1989) in the study of Ti diffusion into z-cut LiNbO<sub>3</sub> crystals in Ar atmosphere with a compensation of the back Li<sub>2</sub>O diffusion.

At the same time it should be noted that one of the most essential defects of  $Ti:LiNbO_3$ -waveguides is their liability to laser-induced damage known as 'optical' (Holman and Cressman, 1982).

An important role is played by the discussion of possible mechanisms of the refractive index increase on the crystal surface due to diffusion. Ziling et al. (1980), Sugii et al. (1978), Canali et al. (1986) and Fejer et al. (1986) point out three mechanisms of refractive index increase:

1. due to the photoelastic effect;

2. due to increase of electron polarizability;

3. due to decrease of spontaneous polarization in the doping region.

## Mechanism 1

The relative dielectric impermittivity tensor  $\Delta B_{ij}$  and the strain tensor  $S_{ml}$  are known to be related through the photoelasticity tensor  $P_{iml}$ :

$$\Delta B_{ij} = P_{ijml} S_{ml}. \tag{1.26}$$

The components of the dielectric impermittivity tensor are equal to

$$B_{ij} = (n^{-2})_{ij} = (\varepsilon^{-1})_{ij},$$
  
$$\Delta B_{ij} = \left[ (n^{-2})_{ij} \right] = \Delta (\varepsilon^{-1})_{ij}.$$

The components of the tensors  $\varepsilon_n$  and  $\varepsilon_1^{-1}$  are related as

$$\varepsilon_{ni} \left( \varepsilon^{-1} \right)_{ij} = \delta_{nj}, \tag{1.27}$$

where  $\delta_{ii}$  is the Kronecker symbol.

Differentiating the expression (1.27), multiplying the result by  $\varepsilon_{ik}$  and making use of (1.26), we come to

$$\Delta \varepsilon_{nk} = -\varepsilon_{nl} P_{ijml} S_{ml} \varepsilon_{jk}. \tag{1.28}$$

In the case of thin layers it turns out to be sufficient only to consider the main strains  $S_x$ ,  $S_y$  and  $S_z$  along the x-, y- and z-axes, respectively. Making allowance for this and also for the estimate

$$\left|S_{x}\right| \approx \left|S_{y}\right| >> \left|S_{z}\right|$$

we obtain

$$\Delta n_o = -(n_o^3/2)(P_{11} + P_{12})S_y$$

$$\Delta n_e = -n_e^3/P_{31}S_y$$
(1.29)

where  $P_{im}$  is an abbreviated notation of the coefficients  $P_{iimm}$ .

Sugii et al. (1978) carried out a detailed calculation and reported  $\Delta n_o$  and  $\Delta n_e$  to be at least half the observed values and, besides, to exhibit a stronger temperature dependence.

## Mechanism 2

Here the direct cause of the refractive index increase is a relatively high polarizability of the impurity ions implanted into the composition of the medium. The relation between electron polarizability and the refractive index of the substance is given by the Lorentz-Lorenz formula

$$(n^2-1)/(n^2+2) = (4\pi/3)\sum_i N_i \alpha_i,$$
 (1.30)

where  $N_i$  is the number of *i*-type atoms in a unit volume and  $\alpha_i$  is the electron polarizability of these atoms.

According to Ziling et al. (1980), Holman and Cressman (1982) and Sugii et al. (1978), titanium ion diffusion in lithium niobate proceeds mostly through Li<sup>+</sup> and Nb<sup>+5</sup> sites of the crystal lattice. The crystallochemical radii of Ti<sup>4+</sup>, Li<sup>+</sup> and Nb<sup>5+</sup> ions are respectively equal to 0.061, 0.068 and 0.064 nm (Holman and Cressman 1982), and their coordination number in lithium niobate is equal to 6. The concentration of substitutional titanium ions under usual diffusion conditions amounts to approximately  $10^{21}$  cm<sup>-3</sup>. To provide the refractive index increase of the order of 0.001 for such concentrations, the  $\alpha_i$  values of Ti<sup>4+</sup> ions must exceed the corresponding values for the substituted ions by approximately  $0.0410^{-24}$  cm<sup>3</sup>. This requirement is in principle met by the substitution Ti<sup>4+</sup> $\leftrightarrow$ Li<sup>+</sup>. As far as the Nb<sup>5+</sup> ion is concerned, its  $\alpha_i$  values are higher than those of Ti<sup>4+</sup> since it has an additional occupied electron shell and its radius exceeds that of the Ti<sup>4+</sup> ion. In the qualitative respect, the action of this mechanism should obviously be thought of as disputable.

#### Mechanism 3

This mechanism reflects the relation between spontaneous polarization of a dielectric and its refractive index (the Kerr effect). This relation can be expressed in the form (Sugii et al. 1978)

$$\Delta n_o = -n_o^3 g_{13} P_s \Delta P_s, \ \Delta n_e = -n_e^3 g_{33} P_s \Delta P_s, \tag{1.31}$$

where  $\Delta P_s$  is variation of the quantity  $P_s$  due to impurity diffusion,  $g_{13}$  and  $g_{33}$  are tensor components of the quadratic electro-optic effect.

Calculations show (Sugii et al. 1978) that  $\Delta n_a \approx 0.0013$  and  $\Delta n_e \approx 0.0042$ .

On the other hand, it should be taken into consideration that polarization reversal in the bulk crystal induces deformations along the x-, y- and z-axes due to the electrostriction effect

$$S_{x} = S_{y} = 2Q_{31} P_{s} \Delta P_{s}, S_{z} = 2Q_{33} P_{s} \Delta P_{s}$$
 (1.32)

where  $Q_{ii}$  are electrostriction coefficients.

An increase of  $n_s$  and  $n_s$  is only possible provided that  $\Delta P_s < 0$ , and as a result of such polarization reversal we have

$$S_{x,y} > 0, \ S_z < 0.$$
 (1.33)

The signs of the required deformations are opposite to those observed in experiment.

Thus, the only satisfactory description of the factors responsible for the refractive index increase in the surface layer of lithium niobate due to titanium diffusion can be given exclusively in the framework of mechanism 1.

#### 1.5.1 Diffusion of transition metals

Three different transition metal ions have been diffused into crystals of LiNbO<sub>3</sub> to form low-loss TE and TM mode optical waveguides that confine the light to within a few microns of the surface. A thin layer of metal of thickness  $\tau$  is first evaporated onto a surface of the crystal and then the crystal is heated at temperature T in a nonreactive atmosphere for a time t. The important waveguide parameters – the number of modes M, the maximum index change a, and the effective guide thickness b can be independently controlled by the diffusion parameters  $\tau$ , T, and t.

Schmidt and Kaminow (1974) have shown that a wide variety of metals may be diffused into LiNbO<sub>3</sub> and LiTaO<sub>3</sub> to form guiding layers. One promising class of metals, which they studied, was the transition elements. They are known (Mc Clure, 1959) to contain *d*-electron orbitals that are polarizable in the visible spectrum. Representative members are Ti, V, and Ni containing respectively 2, 3, and 8 electrons in the unfilled *d* shells of the atoms. The number of *d* electrons in an ion depends upon its valence state.

Thin layers (200-800 Å) of the metals were evaporated onto the (010) or (001) facets of LiNbO<sub>3</sub> for diffusion perpendicular or parallel to the *c*-axis, respectively. The samples were heated in flowing Ar (to prevent oxidation of the metal) to temperatures in the range 850-1000°C (below the Curie temperature) in a time less than 1 h, and the diffusion time *t* was measured from that point. After time *t*, flowing oxygen was admitted (to reoxidize LiNbO<sub>3</sub>) and the oven switched off. For sufficiently long diffusion times, all the metal disappears from the surface. If the diffusion is stopped before all the metal enters the crystal, an oxide residue forms on the surface which is removed by very lightly hand polishing the surface.

Observations of the index profile by the interference microscope indicate the presence of positive-index layers for both  $n_o$  and  $n_e$  for diffusion of each of the three metals. Most of the layers, however, are too thin  $(1-3 \mu m)$  to permit measurements of the functional from the index profile. Electron microprobe measurements also lack the resolution to measure the metal concentration profiles of the thin layers. However, the microprobe was employed to measure the relative concentration profile for two thick Ni-diffused guides (Fig.1.22).



Fig.1.22 Electron microprobe measurement of waveguides formed by diffusion of a 400 Å Ni film: Ni/Nb count ratio vs depth x. ▲ are measured points for 6 h diffusion at 850°C. ● are measured points for 6 h diffusion at 950°C. The solid line is fit of the Gaussian function. The dashed line is fit of the erfc function (Schmidt and Kaminow, 1974).

For diffusion times long compared to the time required for the metal film to completely enter the crystal, the concentration profile should approach the Gaussian function (Shewmon 1963)

$$c(x,t) = (2\sqrt{\pi})(\alpha \tau / b) \exp(-x^2 / b^2)$$
(1.34)

where x is the depth below the surface,  $\alpha$  the number of atoms per unit volume in the deposited film of thickness  $\tau$ ,

$$b^2 = 4Dt \tag{1.35}$$

and the diffusion constant

$$D = D_0 \exp(-T_0/T)$$
(1.36)

(Strictly speaking, t in (1.35) should include a correction for the warm-up time.) For short diffusion times, where the metal is not completely diffused into the crystal, the concentration profile should be a complementary error function (erfc) with the surface concentration independent of time (Shewmon 1963). For diffusion times comparable with the time required for all the metal to enter the crystal, the concentration profile will be intermediate between the Gaussian and erfc profiles.

This behaviour is illustrated in Fig.1.22 where the Ni/Nb count ratios are plotted as functions of depth for diffusion perpendicular to the c-axis in two waveguides. The actual Ni/Nb concentration ratio is proportional to the count ratio with a proportionality factor greater than unity. The data were obtained by probing points on a plane normal to the plane of the evaporated layer. Measurements

of surface concentration c(0,t) were made on the evaporated facet itself. Gaussian and erfc profiles are fitted to the data at  $\Delta n(x) = a$  and (1/2)a in Fig.1.22. The waveguide formed by heating a 400 Å thick film at 850°C for 6 h has a functional shape well described by a complementary error function. The waveguide formed by heating a 400 Å thick film at 950°C for 6 h has the longtail characteristic of a complementary error function but it also has the belllike shape near the surface characteristic of a Gaussian function. In both cases the metal film appeared to be completely diffused into the crystal, but the diffusion rate is much greater at the higher temperature.

The values of b obtained for the two Gaussian profiles in Fig.1.22 show that the surface concentration c(0,t) is qualitatively proportional to  $\tau/b$ , as required by (1.34). In addition, the surface count ratio for a third sample with  $\tau = 250$  Å, which was treated for 6 h at 950°C, was also in agreement with the expected  $\tau/b$  dependence.

It is reasonable to assume that the refractive-index change  $\Delta n(t)$  is proportional to c(x) for small  $\Delta n$ . Then making allowance for the Gaussian profile (1.34), we have

$$a \equiv \Delta n(0) = \frac{2}{\sqrt{\pi}} \frac{dn}{dc} \frac{\tau}{b} \alpha, \qquad (1.37)$$

It is clear from (1.37) that a can be controlled by adjusting  $\tau$  and from (1.35) and (1.36) that b can be controlled by varying t and T. By analogy with a slab or exponential guide, the number of modes M should be proportional to (Carruthers and Kaminow 1974)

$$M \approx (b/\lambda)(na)^{1/2} \approx (n\tau b)^{1/2} / \lambda.$$
(1.38)

Thus, a single-mode guide can be fabricated with b/a and, hence, the optical mode depth quite small. In contrast, the b/a ratio for out-diffused guides was found to be relatively insensitive to the available diffusion parameters t and T (Carruthers and Kaminow, 1974).

Several metal-diffused waveguides have been examined. The number of modes and their prism coupling angles were measured and, from these measurements, the diffusion depth b and the index change at the surface  $\Delta n(0)$  were estimated by comparing the effective indices of the modes with those expected for an exponential waveguide (Carruthers and Kaminow 1974; Conwell 1973). The average results of these measurements for a number of Ti-, V-, and Ni-diffused samples are given in Table 1.10. It should be emphasized that since the profile is not exponential, all the effective mode indices in an experimental multimode guide could not be made coincident with those with an exponential guide for any set of a, b parameters. The highest- and lowest-order modes were matched for the estimates of Table 1.10, and it was assumed that b is about the same for TE and TM modes. It may be seen that a is as large as 0.04 and b as small as 1 µm for the Ti guides. The diffusion depths b are larger and the index changes a are smaller for Ni and V than for Ti for given t and T; however, reducing t and/ or T would bring a and b for Ni and V more into the line with the values for Ti. The change in refractive index with concentration may be calculated using the data of Table 1.10, equation (1.37) and the standard densities of the metals: for example, for Ti,  $dn_o/dc = 1.6 \times 10^{-23}$  cm<sup>3</sup>; for V,  $dn_o/dc = 0.8 \times 10^{-23}$  cm<sup>3</sup>; and for Ni,  $dn/dc = 0.6 \times 10^{-23}$  cm<sup>3</sup>.

The dominant sources of waveguide loss are scattering from crystal surface imperfections and, possibly, absorption by the metal ions. The losses at 0.63  $\mu$ m are estimated to be about 1 dB/cm.

The waveguides are superior to out-diffused guides in that a and b can be controlled separately to yield very thin single-mode layers. They have the advantage over guides formed by diffusion of Nb into LiTaO<sub>3</sub> at 1100°C that the crystals are not depoled since the Curie temperature of LiNbO<sub>3</sub> is 1125°C compared to 600 °C for LiTaO<sub>3</sub>. Diffusion into LiTaO<sub>3</sub> at temperatures below 600°C is feasible but very slow.

It seems likely that many other metals will produce effective guides when diffused into a variety of insulating crystals. Schmidt and Kaminow (1974) have made preliminary tests using various other elements on different substrates.

Metal	Thickness τ (Å)	Time t(h)	Temperat. T (°C)	Diffusion direction	Number of modes (M)	Effective b (µm)	e Effective $\Delta n_o(0)$	Effective $\Delta n_{e}(0)$
Ti	500	6	960	T	1 <b>TM</b>	1.1	0.01	•••
				Ť	4 TE	1.1	•••	0.04
				II	t TE	1.6	0,006	
				1	5 TM	1.6	•••	0.025
v	250	6	950	$\perp$	I TM	6.5	0.0005	
				Ţ	4TE	6.5	•••	0.002
v	500	6	970	$\perp$	1 TM	6.2	0.0005	
				T	4 TE	6.2	•••	0.004
Ni	270	6	800	T	2 TM	2.9	0.007	•••
				$\bot$	2 TE	2.9	•••	0.004
				Ш	2 TE	2.6	0.007	
				]	2 TM	2.6		0.006
Ni	270	6	960	$\bot$	3 TM	6.6	0.002	
				T	0 TE	6.6		••••
				1	2 TE	5.5	0.0015	•••
					0 TM	5.5		
Ni	500	6	800	T	3 TM	2.8	0.0095	•••
				Т	2 TE	2.8		0.006
				[]	3 TE	3.1	0.0085	
					2 TM	3.1	•••	0.0045
Ni	500	6	960	$\bot$	7 TM	11.6	0.0025	
				$\perp$	0 TE	11.6		
				ll -	4 TE	4.5	0.0045	
				11	0 TM	4.5		

Table 1.10 Average results for metal-diffused guides (Schmidt and Kaminow, 1974)

It has been found, for example, that Au-, Ag-, Fe-, Co-, Nb-, and Ge-diffused  $LiNbO_3$  and Ti-diffused  $LiTaO_3$  all yield good waveguides. Apparently, any valence electrons contributed by these elements increase the optical polarizability without a compensating increase in the lattice volume. Then, if the metal ions do not introduce excessive absorption at the operating wavelength, a satisfactory waveguide is produced.

## 1.5.2 Titanium diffusion

In the papers cited above, the back diffusion of  $Li_2O$  has not been used. But this diffusion is necessary for creating active elements of integrated optics (modulators, switches, *etc.*) on the basis of strip line waveguides since along with strip line waveguides the back diffusion provides the creation of a planar waveguide for an extraordinary wave. The data on the reverse diffusion compensation is due to Burns et al. (1978), Ranganath and Wang (1973) and Chen and Pastor (1977) and Miyasawa et al. (1977). These authors mainly considered diffusion in *y*-cut crystals. At present, *z*-cut LiNbO<sub>3</sub> crystals are of increasing importance for integrated optics, first of all because this cut allows a particularly simple 'Cobra' type electrode configuration to be used for modulators and switches (Papuchon and Combemale 1975) and, second, because the Ti diffusion rate in the Ar atmosphere along the *z*-axis of a LiNbO<sub>3</sub> crystal is several times greater than the rate along the *y*-axis (Fukuda et al. 1978). In view of this, *z*-cut LiNbO<sub>3</sub> crystals are very convenient for creating devices on the basis of strip line waveguides.

Golubenko et al. (1980) investigated Ti diffusion in z-cut LiNbO, crystals in an argon atmosphere with a back Li<sub>2</sub>O diffusion compensation. The methods of sample preparation are of practical interest. Polished z-cut LiNbO, samples were preliminarily annealed at 1000°C in an oxygen atmosphere to remove the surface layer damaged under mechanical polishing of crystals. Titanium layers of different thickness (200-600 Å) were deposited onto annealed plates by magnetron sputtering. The specimens were placed into a platinum crucible filled with LiNbO, powder prepared from shavings of the same crystals. The concentration of Li<sub>2</sub>O vapours formed by the powder and the sample is in equilibrium, and thus there is no need choosing the time when the back diffusion compensation must start. Diffusion was carried out in a furnace with an argon atmosphere. The heating rate was 50°C/min. As soon as the necessary temperature was established, the amount of Ar was decreased lest the flux should carry away Li<sub>2</sub>O vapours. When the diffusion was over, the specimens were cooled in the same Ar flux at a rate of 5°C/min. The waveguides obtained in this process had losses less than 1 dB/ cm and it was not necessary to cool the specimens in an oxygen atmosphere.

The EPR studies carried out by Ziling et al. (1980) showed that LiNbO<sub>3</sub> specimens that were not specially doped with titanium exhibited Fe<sup>+3</sup> and Mn<sup>+2</sup> ion spectra. After the specimens were annealed in a vacuum at 1000°C for 2 h, the Fe<sup>+3</sup> line disappeared while the Mn<sup>+2</sup> line remained unaltered. In the region  $g \approx 2$  there appeared a single line with an anisotropic g-factor. Analysis of the orientational dependence of the spectrum revealed that the paramagnetic centre observed has symmetry  $C_{iv}$ .

In specimens covered with a titanium layer 100 nm thick, for which the diffusion annealing was carried out in vacuum in regimes providing a Ti concentration



Fig.1.23 EPR spectra of (1) Ti-doped and (2) original vacuum-annealed crystals (Ziling et al. 1980).

of  $(0.5-2) \times 10^{-2}$  cm<sup>-3</sup>, the line intensity increases by more than an order of magnitude (Fig.1.23) and corresponds to the number of centres,  $6.5 \times 10^{15}$ . The paramagnetic centre responsible for the appearance of this line has an electron spin S = 1/2 and g-factors typical of the 3d-ion which in this case is titanium in the state Ti<sup>3+</sup>. EPR spectra of pairwise Ti<sup>3+</sup> ions were not observed.

When specimens are annealed in the air, the number of  $Ti^{3+}$  centres decreases rapidly with increasing temperature. At  $t \ge 600^{\circ}C$  the corresponding line disappears. No new lines except those belonging to Fe<sup>3+</sup> were observed, which suggests titanium transition to the non-paramagnetic state  $Ti^{4+}$ . The symmetry  $C_{3v}$  is indicative of the fact that a Ti ion can be in the position of either lithium or niobium, but the valence of the Ti ion and the change of this valence testify in favour of niobium substitution. For concentrations less than about  $6 \times 10^{19}$  cm<sup>-3</sup>, the conclusion of the position of Ti in the LiNbO<sub>3</sub> lattice is confirmed by the results reported by Pearsall et al. (1976).

These substitutional atoms also have activation energies of about 3.7 eV which are much higher than those of interstitial atoms, such as Li and Cu, of about 1 eV. Therefore, both the marked lattice contraction and the high activation energy found in the Ti diffusion into LiNbO<sub>3</sub> imply that Ti diffuses substitutionally into the LiNbO<sub>3</sub> crystal. Recently, it has been shown that Ti diffused into LiNbO<sub>3</sub> is all +4 valence and Ti ions sit not on vacancies or defects but on well defined sites (Pearsall et al. 1976). In LiNbO<sub>3</sub>, two possible sites remain for substitutional impurities, a Li site and a Nb site. The lattice contraction would occur if Ti ions replaced either the Li site or the Nb site, since the effective ionic radius of Ti<sup>+4</sup>, 0.605 Å, is smaller than those of Li<sup>+1</sup> and Nb<sup>+5</sup> of 0.68 and 0.64 Å, respectively, when the coordination number of all of them is six. However, the replacement of Nb ions by Ti ions is more favourable from the point of view of charge compensation, so it is assumed that Ti is diffused as substitutional ions for the Nb site in LiNbO<sub>3</sub>. Armenise et al. (1983) discussed the first step of the interaction between Ti and LiNbO<sub>3</sub>, occurring before, and subsequently leading to the formation of the (Ti<sub>0.65</sub>Nb<sub>0.35</sub>)O<sub>2</sub> compound layer. In particular, they started with the stresses eventually induced by Ti deposition, then described the kinetics of the Ti oxidation and its interaction with the O atoms of the annealing atmosphere and of the substrate. So, they showed the formation of LiNb<sub>3</sub>O<sub>8</sub> and (Ti<sub>0.65</sub>Nb<sub>0.35</sub>)O<sub>2</sub> compounds and the dissolution of TiO<sub>2</sub> and LiNb<sub>3</sub>O<sub>8</sub> phases, leading to a complete formation of the (Ti<sub>0.65</sub>Nb<sub>0.35</sub>)O<sub>2</sub> layer.

Optical grade and optically polished y- and z-cut LiNbO<sub>3</sub> single-crystal substrates were used. Ti films with thicknesses ranging from 150 to 600 Å, were dc sputter deposited on substrates from a pure (99.99% purity) Ti target in a pure Ar atmosphere ( $10^{-3}$  torr) with a deposition rate of about 80 Å/min. Before Ti deposition the Ti target was sputter etched, while no sputter etching was performed on the crystal substrates. On few samples, Ti was deposited in an evaporator equipped with an electron gun. Samples were then annealed in a flowing (120 litre/h) dry oxygen atmosphere at different temperatures and times. The heating and cooling rate was  $30^{\circ}$ C/min.

Sample morphology, compound formation, atomic composition profiles, and structural characterization of the formed phases were analyzed by a scanning electron microscope (SEM), equipped with an energy dispersive X-ray analysis, Rutherford back-scattering spectroscopy (RBS), by using a 1.8-MeV <sup>4</sup>He<sup>+</sup> beam, Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), and glancing angle X-ray diffraction performed with a Wallace–Ward cylindrical texture camera. The peculiarities and the reasons for the choice of these microanalytical techniques were discussed by Armenise et al. (1982). Nondestructive RBS and destructive AES and SIMS in-depth atomic composition profiling techniques were used to obtain complementary information and to ensure that measured compositions with AES and SIMS were not falsified by the eventual drift of mobile species, induced in the sample during the ion milling. In particular, to avoid electrical charge up during analyses, samples were coated with about 50–100 Å of carbon or gold.

The Ti oxidation process starts at temperatures higher than 300°C and may be directly observed from the colour of the specimen surface layer which changes from metallic-gray (300°C, 4 h) to white translucent in 500°C, 4 h annealed samples. Microanalytical techniques can help to understand the oxidation mechanisms and kinetics.

With increases in the annealing temperature, the complete formation of  $\text{TiO}_2$ , which occurs at 500°C, 4 h, is followed first by the growth of the  $\text{LiNb}_3\text{O}_8$  phase, and then by the formation of the  $(\text{Ti}_{0.65}\text{Nb}_{0.35})\text{O}_2$  phase.

The LiNb<sub>3</sub>O<sub>8</sub> compound can be clearly detected and identified by glancing angle X-ray diffraction patterns taken with the Wallace–Ward cylindrical texture camera.

The surface morphology of the sample annealed at  $750^{\circ}$ C for 2 h was examined in a SEM, operating with secondary electrons. On the surface, many white zones more than 100 µm in diameter appear and cover about 10% of the whole surface. Their typical shapes and morphologies are shown in the micrograph in Fig.1.24.

As already mentioned above, the growth of LiNb<sub>2</sub>O<sub>8</sub> is followed by the

44



Fig.1.24 SEM micrographs of white zones appearing on a z-cut sample, coated with a 400 Å thick Ti film and annealed in dry O<sub>2</sub> at 750°C for 2 h (Armenise et al. 1983).

appearance of the ternary compound  $(Ti_{0.65}Nb_{0.35})O_2$  whose spots become evident in glancing angle X-ray diffraction pattern taken with the Wallace–Ward cylindrical texture camera for annealing temperatures higher than 700°C and increase continuously in intensity up to 950°C for 30 min thermal annealing, when the LiNb<sub>3</sub>O<sub>8</sub> phase is already completely consumed and decomposed.

Armenise et al. (1983) fully characterized this ternary compound and identified it as the real source for Ti diffusion in  $LiNbO_3$ . It grows epitaxially on both y- and z-cut substrates.

Different microanalytical techniques were thus employed to study the first steps of the interaction between Ti and LiNbO<sub>3</sub> crystals occurring during the fabrication of Ti in diffused optical waveguides. The results obtained can be summarized as follows.

Ti sputtered or evaporated films grow oriented on the planes of the  $LiNbO_3$  substrate for all observed crystalline orientations. The crystalline quality of both the film and the substrate does not depend on the deposition techniques (evaporation or sputtering) if low voltage and sputtering rate are used.

The stresses induced by the Ti film are thus found to be independent of the deposition technique.

For low-temperature thermal treatments (300–500°C) the Ti film will form an amorphous Ti oxide layer. The oxidation mechanism was clearly determined as a capture of O atoms both from the surrounding atmosphere and from the LiNbO<sub>3</sub> substrate. This last effect gives rise to an accumulation of Nb at the Ti/LiNbO<sub>3</sub> boundary while, due to its high ionic ability, Li does not accumulate but diffuses through the Ti or Ti-oxide film. The change of the oxygen concentration in the annealing atmosphere (dry O<sub>2</sub> or dry Ar) will only produce an increase or decrease in the amount of the O atoms captured by Ti from

the bulk. Therefore, the first step of Ti in-diffused optical waveguide fabrication consists of the formation of a  $TiO_2$  layer at about 500°C. These results can also explain the formation of waveguides obtained by diffusing Ti at about 1000°C from deposited  $TiO_2$  films (Noda et al. 1975).

At increasing annealing temperature (greater than or equal to 600°C), the formation of the LiNb<sub>3</sub>O<sub>8</sub> phase was observed on both Ti coated and uncoated LiNbO<sub>3</sub> substrates. As sketched in Fig.1.25, on the Ti coated samples this compound grows as large crystallites characterized by a well-defined orientation relationship with respect to the underlying y- and z-cut substrates. From RBS spectra the epitaxial quality of the LiNb<sub>3</sub>O<sub>8</sub> phase shows up better on Ti uncoated samples.

The LiNb<sub>3</sub>O<sub>8</sub> compound continues to grow with increasing annealing temperature up to 750°C, while for higher annealing temperature it decomposes and finally vanishes ( $T > 900^{\circ}$ C). Fukuma et al. (1978) did not detect the presence of the LiNb<sub>3</sub>O<sub>8</sub> compound in samples annealed at high temperatures. This compound is still present and clearly detectable also in rapidly ( $\geq$ 30°C/min) cooled samples, when annealed at temperatures less than or equal to 800°C; nevertheless, the presence of flowing oxygen cannot inhibit the phase separation and the LiNb, Os growth. Moreover, LiNb<sub>3</sub>O<sub>8</sub> formation and dissolution appear not to be affected by the presence of Ti. Armenise et al. (1983) attribute the formation of this compound to Li or Li<sub>2</sub>O out-diffusion and to the consequent growth of a Li-deficient top layer. LiNb<sub>3</sub>O<sub>8</sub> is reported to be problematic: in fact, whenever this phase was detected the amount of the optical damage in waveguides increased dramatically (Holman et al. 1978). This phase was no longer detected in samples annealed at temperatures higher than 850°C, its formation induces large stress and microfractures in TiO, films (see Fig.1.25) and may be a source of Ti profile inhomogeneities in the diffused layers.

The growth of  $LiNb_3O_8$  is followed by the appearance of the  $(Ti_{0.65}Nb_{0.35})O_2$  compound which grows continuously up to 900–950°C, leading to a complete consumption of the  $TiO_2$  layer (Fig.1.25). This ternary compound is the only phase present at 900–950°C; it forms a uniform layer on top of the  $LiNbO_3$  substrate and constitutes the real source for Ti in-diffusion which takes place for longer annealing, as reported by Armenise et al. (1983). It should be pointed out that a decomposition of  $LiNb_3O_8$  occurs also in Ti uncoated samples, and consequently it appears as an intrinsic step of the  $LiNbO_3$  annealing process.

Results similar to those discussed above for annealing in a dry  $O_2$  atmosphere were obtained in LiNbO<sub>3</sub> samples annealed in dry N, Ar, and static air. Experiments are in progress on the presence and growth kinetics of the LiNb<sub>3</sub>O<sub>8</sub> phase in samples thermally treated with processes such as annealing in an atmosphere rich in Li or in a gas flowing through H<sub>2</sub>O, which were all reported as capable of preventing Li out-diffusion (Jackel, 1982).

Sugii et al. (1978) investigated the mechanism for generation of misfit dislocations and cracks. The diffusion of Ti into LiNbO<sub>3</sub> created stresses sufficient to generate both misfit dislocations and cracks within the diffused layer. In evaluating stresses, a positive sign for tensile stress and a negative one for compressive stress were used. By assuming that the stress  $\sigma_{\gamma}$  on the diffused layer in the direction normal to the surface plane is zero, the maximum impurity-induced stresses along the crystal surface inside the diffused layer



**Fig.1.25** Schematic of LiNb<sub>9</sub>O<sub>9</sub> and  $(Ti_{0.65}Nb_{0.35})O_2$  growth in LiNbO<sub>3</sub> after the formation of the TiO<sub>2</sub> top layer. Temperatures and times are only indicative for a 400 Å thick original Ti film (Armenise et al. 1983).

can be expressed as follows:

$$(\sigma_x)_{\max} = \left(S_{11}S_{33} - S_{13}^2\right)^{-1} \left\{-S_{33}\varepsilon_y + S_{13}\varepsilon_z\right\} \approx -S_{33}\varepsilon_y \left(S_{11}S_{33} - S_{13}^2\right)^{-1}$$
(1.39)

$$(\sigma_z)_{\max} = \left(S_{11}S_{33} - S_{13}^2\right)^{-1} \left\{-S_{13}\varepsilon_y - S_{11}\varepsilon_z\right\} \approx S_{13}\varepsilon_y \left(S_{11}S_{33} - S_{13}^2\right)^{-1}$$
(1.40)

where S is the compliance of LiNbO<sub>3</sub> (Warner et al. 1967) and  $\varepsilon$  is the stress along the x-, y- and x- axes. The calculated stresses for the samples are given in Table 4.3. These stresses were partially relieved by the generation of misfit dislocations near the boundary between the diffused and substrate regions, but the presence of cracks indicates that the density of the misfit dislocations was much lower than the one needed for complete accommodation of the impurity-induced stresses. Anisotropy of stresses,  $(\sigma_x)_{max} > (\sigma_z)_{max}$ , resulted in preferential generation of cracks.

The same authors also considered the mechanism causing refractive-index changes in the diffused layer. There are at least three possible mechanisms for refractive-index changes in the diffused layer: (i) due to a photoelastic effect

by diffusion-induced strains, (*ii*) due to an increase of the electronic polarizability by the in-diffusion of Ti, (*iii*) due to a decrease of the spontaneous polarization of LiNbO<sub>3</sub>,  $P_{\delta\pi}$ , by Ti diffusion.

The refractive index of a crystal is specified by the indicatrix, that is, an ellipsoid whose coefficients are the components of the relative dielectric impermittivity tensor  $B_{\mu}$ , namely,

$$B_{ij}x_ix_j = 1.$$
 (1.41)

Strains  $S_n$  deform the indicatrix through the photoelectric effect, and the change in  $B_{ii}$  is given by

$$\Delta B_{ij} = p_{ij,n} S_n, \tag{1.42}$$

where  $p_{ij}$  is the photoelastic coefficient.

In the case of a thin diffusion layer, it is sufficient to consider only principal strains  $S_1$ ,  $S_2$ , and  $S_3$ , in the x-, y-, and z-axes, respectively. Then equation (1.42) turns into

$$\Delta B_1 = \Delta B_2 = -(p_{11}S_1 + p_{12}S_2 + p_{13}S_3), \tag{1.43}$$

$$\Delta B_3 = -(p_{31}S_1 + p_{31}S_2 + p_{33}S_3) \tag{1.44}$$

where all the suffixes are abbreviated in the matrix form (Nye 1957). With allowance for  $|\varepsilon_x| = |\varepsilon_y| \gg \varepsilon_i$ , the changes in the refractive indices at the surface are approximated by

$$\Delta n_o \approx -(n_o^3/2)(p_{11}+p_{12})\varepsilon_y, \qquad (1.45)$$

$$\Delta n_e \approx -n_e^3 p_{31} \varepsilon_y. \tag{1.46}$$

For  $n_o = 2.306$ ,  $n_e = 2.220$  (refractive indices for Na D-lines) (Midwinter 1968), and  $p_{11} = 0.034$ ,  $p_{12} = 0.072$  and  $p_{13} = 0.178$  (O'Brien et al. 1970), the calculated values for the samples were compared with the values observed by Noda et al. (1975). It was found that the refractive index changes due to the photoelastic effect contribute to about half of the observed changes.

The second possible mechanism for index changes is by diffusion of impurity ions having larger electronic polarizability than that of the host ions to be substituted. As in most solids, the refractive index of a ferroelectric crystal should originate from electronic polarization. The relation between the refractive index, n, and electronic polarizability,  $\alpha$ , is given as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum N_i \alpha_i \text{ (electronic)}$$
(1.47)

where  $N_i$  is the number of ions of type *i* per unit volume and  $\alpha_i$  is the electronic polarizability of the ion. It was found that Ti ions replaced Nb ions of atomic fraction of about  $10^{21}$  cm<sup>-3</sup> in the LiNbO<sub>3</sub> crystal. In order to produce a refractive index change  $\Delta n = 10^{-3}$ , the electronic polarizability of Ti ion,  $\alpha$ (Ti), should be larger by  $0.04 \times 10^{-24}$  cm<sup>3</sup> than that of the Nb ion,  $\alpha$ (Nb). However, it is unreasonable since the electronic polarizability of ions has a tendency to decrease as the ionic radius becomes small (Kittel 1956).

The possibility of a third mechanism is now discussed. In the ferroelectric phase in LiNbO<sub>3</sub>, one of the characteristic features is the marked decrease in the refractive index due to spontaneous polarization  $P_s$  through the Kerr effect. They are given by

$$\delta n_o = (1/2) n_o^3 g_{13} P_S^2 \tag{1.48}$$

$$\delta n_e = (1/2) n_e^3 g_{33} P_S^2 \tag{1.49}$$

for the refractive indices  $n_o$  and  $n_e$ , respectively, where  $g_{ij}$  is the quadratic electrooptic coefficient. If Ti-diffusion into LiNbO<sub>3</sub> changed the spontaneous polarization by  $\Delta P_s$ ,  $\Delta P_s$  would produce refractive-index changes given as

$$\Delta n_o = -n_o^3 g_{13} P_S \Delta P_S \tag{1.50}$$

$$\Delta n_e = -n_e^3 g_{33} P_S \Delta P_S \tag{1.51}$$

when  $g_{13} = 0.043 \text{ m}^4 \text{ C}^{-2}$ ,  $g_{33} = 0.16 \text{ m}^4 \text{ C}^{-2}$  (Ivasaki et al. 1966) and  $P_s = 0.50 \text{ C} \text{ m}^{-2}$  (Savage, 1966),  $\Delta P_s$  of  $-0.005 \text{ C} \text{ m}^{-2}$  will cause refractive-index changes of  $\Delta n_o \approx 1.3 \times 10^{-3}$  and  $\Delta n_e \approx 4.2 \times 10^{-3}$ . On the other hand, a change of the spontaneous polarization will at the same time cause lattice strains in the *a*- and *c*-axes through the electrostrictive effect. Then, the strains due to  $\Delta P_s$ ,  $S_s$  are given by

$$S_1 = S_2 = 2Q_{31} P_S \Delta P_S \tag{1.52}$$

and

$$S_3 = 2Q_{33}P_S \,\Delta P_S \tag{1.53}$$

where  $Q_{31} = -0.0036 \text{ m}^4 \text{ C}^{-2}$ , and  $Q_{33} = 0.067 \text{ m}^4 \text{ C}^{-2}$  is the electrostrictive coefficient for LiNbO<sub>3</sub> (Iwasaki et al. 1968). If  $\Delta P_s < 0$  as required to increase the refractive indices, it should produce strains  $S_2 > 0$  and  $S_3 < 0$ . The signs of  $S_2$  and  $S_3$  are, however, opposite to those of the observed strains  $\varepsilon_y$  and  $\varepsilon_z$ , respectively. Thus, it is unlikely that the refractive index increments are caused by decreasing the spontaneous polarization.

It is concluded that the first mechanism proposed for refractive-index changes is more likely than the second and third.

## 1.5.3 Copper diffusion

Noda et al. (1974) attempted to diffuse many kinds of metals, such as Cu, Al, Ge, Cr, Fe, Nb, and Ti into  $LiTaO_3$ . Among them, Cu was easily diffused at relatively low temperatures, and as a result a large refractive index change was observed in the Cu-diffused layer. The authors reported the experimental results on Cu diffusion in  $LiTaO_3$ .

Two kinds of diffusion processes were examined: thermal diffusion, and diffusion under an electric field (electrodiffusion).

Polished LiTaO<sub>3</sub> Y-plates were deposited with Cu about 5000 Å thick and were heated in air and in an Ar atmosphere. For the specimens treated in air, the deposited Cu was oxidized during the heat treatment, and diffusion proceeded remarkably, while for the specimen treated in an Ar atmosphere diffusion scarcely occurred. These results indicate that Cu must be ionized in order to diffuse into the specimen and that ionization from the copper oxide is easier than that from the pure metal.

An interference fringe profile of the Cu-diffused layer observed along the xaxis is shown in Fig.1.26. Diffusion took place at 800°C for 10 h in air. The edge was normal to the y-axis and the light (a Na lamp) was an ordinary wave. The maximum increase in  $n_0$  is  $3\times10^{-3}$  and the diffusion depth is about 120 µm. The profile for the extraordinary wave was the same as that for the ordinary wave, and the diffused layer supported both TE and TM modes. A peak of the refractive index was always observed beneath the surface for all specimens diffused under different conditions. The reason for the phenomenon is not clear yet. In the thermal diffusion method, it is difficult to control the refractive index change and the diffusion depth. Moreover, the required temperature is higher than the Curie temperature of LiNbO<sub>3</sub>. Therefore, thermal diffusion is not suitable for fabricating the active and thin single-mode waveguiding layer.

The authors then examined the diffusion of Cu into LiTaO<sub>3</sub> under an electric field using the deposited Cu or CuO as electrodes. By applying an electric field, Cu ion diffused easily from the anode side in the lower-temperature region, that is, 500°C, at which no thermal diffusion was observed. Figure 1.27 shows an



**Fig.1.26** Interference fringe pattern on the Cu-diffused layer, indicating the change of the refractive index  $n_o$ . Cu was thermally diffused into a LiTaO<sub>3</sub> Y-plate at 800°C for 10 h (Noda et al. 1974).

**Fig.1.27** (right) Interference fringe pattern of the Cu electrodiffused layer in LiTaO<sub>3</sub> indicating the change of refractive index  $n_o$ . Diffusion was carried out at 500°C for 1 h in air and an electric field of 10 V/mm was applied (Noda et al. 1974).

49

interference structure for the Y-plate specimen diffused at 550°C for 1 h under an electric field of 10 V/mm. The structure was observed along the x-axis using the ordinarily polarized light. The profile for  $n_e$  was almost the same as that for  $n_o$  in this case also. The refractive index at the surface increases by about 5× 10<sup>-3</sup>, and the diffusion depth is 25 µm. The increase in the refractive index was found to be proportional to the applied field. With electric fields stronger than 30 V/mm, microcracks occurred at the surface of the diffused layer, and such a layer was not suitable for the waveguide.

Figure 1.28 shows the relation between the diffusion depth and the diffusion time for the specimens diffused in air at 550°C under an electric field of 10 V/mm. The changes in the refractive index were almost constant for the variation of the diffusion time. When the diffusion time was longer than 1 h, the crystallinity of LiTaO<sub>3</sub> was degraded. The electrodiffusion in an Ar atmosphere was also examined for the specimens deposited with CuO, and diffusion was found to proceed more slowly than that made in air.

Noda et al. fabricated successfully the waveguiding layer supporting only the fundamental modes  $TE_0$  and  $TM_0$  by the following conditions: temperature 550°C, electric field 10 V/mm, diffusion time 10 min, and in an Ar gas flow. The thickness of the diffused layer was about 4 µm. A He–Ne laser beam was fed into the layer with a prism coupler and propagated along the x-axis of LiTaO<sub>3</sub>. A photograph of the output spots of  $TE_0$  and  $TM_0$  modes decoupled with a gas prism is shown in Fig.1.29. The photograph shows that the spots have well-defined shapes and the *m* lines passing through the spots are faint. Furthermore, only a slight decay was observed in the strength of the scattered light over the 1 cm length of a light streak along the layer, and it can be concluded that the optical quality of the layer was satisfactory at 0.633 µm. However, a weak absorption peak was observed at a wavelength of 1 µm, and the use of the layer in this wavelength region may be somewhat limited.



**Fig.1.28** Relation between diffusion depth and diffusion time in Cu-diffused LiTaO<sub>3</sub>. Diffusion was carried out at 500°C in air under an electric field of 10 V/mm (Noda et al. 1974). **Fig.1.29** (right) Output spots with faint m line decoupled with a GaP prism for TE<sub>0</sub> and TM<sub>0</sub> modes. A He–Ne laser beam is fed into the Cu electrodiffused layer with the prism coupler, and is propagated along the *x*-axis of LiTaO<sub>3</sub> (Noda et al. 1974).

# 1.6 Proton-exchanged LiNbO<sub>3</sub> waveguides

The ion exchange method is based on treatment of a specimen in a salt melt or salt mixture so that as a result of chemical diffusion there occurs a partial replacement of mobile ions from the surface region of the specimen by ions from the melt. The most intensive ion-exchange processes proceed among univalent ions of alkaline metals Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Rb<sup>+</sup>, as well as Ti<sup>4+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup> and, possibly, Cu<sup>2+</sup> ions. The principal factors affecting the ion-exchange process are temperature, time, the state of the sample surface, the chemical composition and the melt properties. To form a light guide, it is necessary to provide a refractive index increase on the sample surface, and therefore the choice of appropriate ion-exchanged pairs is typically carried out by comparing the electron polarizabilities of ions or by establishing the ratio of electron polarizabilities to the cubes of their radii. The higher the values of electron polarizability, the larger the refractive index increase. This is in most cases valid for the ion exchange process in glasses. We also note that in developing this method one should not neglect a possible occurrence of some background processes, such as sample surface seeding, phase separation and others.

Lithium niobate and tantalate are the first crystalline objects for which ionexchanged doping was first realized. Substitutional ions in these processes are of course Li<sup>+</sup> ions.

Many recent reports are devoted to fabrication and investigation of the properties of light guides formed by the H<sup>+</sup> $\leftrightarrow$ Li<sup>+</sup> exchange method. As the source of H<sup>+</sup> ions, Jackel et al. (1982) used a melt of benzoic acid C<sub>6</sub>H<sub>5</sub>COOH at 160– 250°C. To avoid acid evaporation and decomposition, x- and z-cut lithium niobate plates were doped in a closed vessel without reach of air. The light guide samples exhibited propagation of TE-modes only, the distribution function of the refractive index of the light guide being a step function with  $\Delta n_e = 0.12$ . The values of the ion interdiffusion coefficients were  $3.8 \times 10^{-12}$  and  $1.0 \times 10^{-12}$  cm<sup>-2</sup>/s at 244 and 217°C, respectively. The proton-lithium exchange was observed to proceed somewhat slower along z than along x direction. The light loss in light guides was approximately 0.5 dB/cm. Channel light guides fabricated using masks (chromium films 10 nm thick and gold films 50 nm thick) were 1–20 µm thick (Jackel et al. 1982). Attempts to dope y-cut LiNbO<sub>3</sub> plate failed due to a strong destruction of the surface.

The possibility of obtaining waveguide layers on a z-cut LiTaO<sub>3</sub> using the ion-exchange reaction in a benzoic acid melt was reported by Atugin and Zakharyan (1984) and Kopylov et al. (1983). The profile of the refractive index increase n(x) at elevated temperatures was investigated by a numerical method (Kolosovsky et al. 1981) which allowed the authors to reconstruct the profile from a limited set of data both for a sharp (exponential) and a smooth (Gaussian) profile variation. Surface optical variations showed that the investigated interaction of LiTaO<sub>3</sub> with benzoic acid stimulates an increase of the extraordinary refractive index only. The profiles of  $\Delta n(x)$  are close to step-like ones, the depth of the waveguide region makes up about 2.5 µm. The observed jump in the refractive index variation is likely to be caused by the phase transition in Li<sub>1-x</sub>H<sub>x</sub>TaO<sub>3</sub> type compounds due to an increase of the order parameter x (Rice and Jackel 1982).

The experimental results (Reach et al. 1985; Boiko et al. 1985; Bashkirov et al. 1985; Gan'shin et al. 1985) suggest the following scheme of protonexchanged doping:

1. Proton-lithium exchange causes the formation on a crystal surface of a nearly constant hydrogen concentration, which is apparently due to a strong dependence of the interdiffusion coefficient D on ion concentration in the surface layer.

2. Experimental studies show that to nucleation and a further annealing-stimulated development in annealing the crystalline phases  $n - Nb_2O_5$  and  $LiNb_3O_8$  there corresponds a definite H<sup>\*</sup>-to-Li<sup>\*</sup> concentration ratio in the doped region. This ratio can be attained with the highest probability at the ion exchange front. The formation of the indicated phases is inevitably associated with the occurrence of significant structural distortions. This accounts, in particular, for the lowering of the refractive index  $\Delta n_o = 0.04$  which is larger than in the rest of the protonexchange region.

3. Mismatch of the lattice parameters of  $n-Nb_2O_5$ , LiNb $_3O_8$  and LiNbO $_3$  leads to considerable stresses, and the surface region goes over to a metastable state.

Reports have appeared on the development and successful application of a combined way of light guide fabrication on the basis of lithium niobate – the so-called TIPE (titanium-in-diffused-proton-exchange) process (Becker 1983). The process proceeds as follows: titanium diffusion forms a Ti:LiNbO<sub>3</sub> light guide in which modes of both ordinary and extraordinary rays can be excited. After this, the sample is treated in a benzoic-acid or in some other melt suitable for a proton–lithium exchange. The TIPE promotes the formation of structures with a high n on x-, y- and z-cuts of a crystal (after titanium diffusion the LiNbO<sub>3</sub>(Y) surface is not prone to destruction under the action of benzoic acid). TIPE light guides may have, depending on the preparation conditions, rather complicated refractive index profiles. Obviously, the Ti diffusion in TIPE structures should only be carried out at temperatures higher than 950°C. Diffusion at lower temperatures is fraught with a risk of formation on the crystal surface of a chemical compound containing Ti and Nb oxides which block lithium diffusion through the interface. This may result in blocking a subsequent proton–lithium exchange.

Being resistant to induced laser radiation, proton-exchanged waveguides exhibit the lowering of the electro-optic effect and a high instability of the refractive index. Ti-diffused waveguides degrade with time, while proton-exchanged waveguides age. Moreover, they possess a typical shortcoming – a weak restriction of the light wave, which is due to an essential impossibility of obtaining a sharp refractive index variation at the substrate-layer boundary.

## 1.6.1 Ion-exchange processes in LiNbO,

The proton-exchange technique involves chemical reaction between single crystal lithium niobate (LiNbO<sub>3</sub>) and a suitable protonic source, most commonly benzoic acid ( $C_6H_5CO_2H$ , m.p. = 122°C), at temperatures from 150°C to 300°C (Jackel et al. 1982). The overall reaction can be represented by the equation

 $LiNbO_3 + xH^+ \rightarrow Li_{1-x}H_xNbO_3 + Li^+$ .

Hydrogen is incorporated within the crystal in the form of hydroxyl groups

as the result of bonding between H<sup>+</sup> and O<sup>2-</sup> in the lattice. The extent of proton exchange depends on the reaction time and temperature, and only partial exchange is necessary for waveguide formation (Jackel et al. 1983; Rice 1986; Rice and Jackel 1984). A complete exchange can be observed in LiNbO<sub>3</sub> powder and results in the formation of the compound HNbO<sub>3</sub>, causing a structural (hexagonal to cubic) transformation (Rice and Jackel 1982; Fourquet et al. 1983; Weller and Dickens 1985). It is only the extraordinary refractive index that is increased by proton exchange, while the ordinary index is slightly decreased (Jackel et al. 1982). The nature of the single polarization means that TE modes are supported in x- and y-cut waveguides and TM modes are supported in z-cut waveguides.

The optical properties of proton exchange waveguides have been determined from prism-coupling data (Clark et al. 1983; Wong et al. 1986) and infrared spectroscopy has been used to follow the incorporation of hydrogen as hydroxyl groups (Jackel and Rice 1981; Loni et al. 1987). This approach has been extended to determine relationships between the extent of formation of OH groups and waveguide depths for x- and z-cut single-crystal lithium niobate. Improved optical properties for annealed waveguides and waveguides produced using buffered melts were reported many times (Jackel et al. 1983; Jackel and Rice 1984; Wong 1985; Minakata 1986), the term 'buffered' referring typically to benzoic acid containing small amounts of lithium benzonate. A systematic study of annealed and buffered melt waveguides was carried out in order to understand why the properties are improved. The room-temperature hydrogen isotopic exchange was shown to occur in proton-exchanges waveguides (De La Rue et al. 1987; Loni et al. 1987) indicating that these waveguides react with atmospheric water vapour. The isotopic exchange technique was used to investigate the behaviour of both annealed and buffered melt proton-exchanged waveguides towards atmospheric water vapour at temperatures up to 375°C.

High-index changes ( $\Delta n = 0.12$ ) were reported for ion exchange of LiNbO<sub>3</sub> in melts of AgNO<sub>3</sub> (Manhar and Shah 1975) and TlNO<sub>3</sub> (Jackel 1980) Unfortunately, the high-index change is not consistently reproducible and was found to be disconnected with the introduction of the heavy Ag<sup>+</sup> and Tl<sup>3,4+</sup> ions (Griffiths 1981; Chen et al. 1982). Rather it results from a proton exchange process similar to that reported by Jackel et al. (1982), with water impurities in the melt acting as the source of hydrogen (Jackel and Rice 1982). Since these processes cannot give consistent results, they are not as useful as had previously been hoped. Thus, proton exchange in benzoic acid fills the need for a means of producing large index changes in LiNbO<sub>3</sub>.

Jackel and Rice (1982) showed that immersion of LiNbO<sub>3</sub> in hot acids, or in certain hydrate melts, results in proton exchange, in which lithium ions are lost from the crystal and are substituted by an equal number of protons (Jackel and Rice, 1981; Rice and Jackel, 1982). In strong acids, such as HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, the substitution is complete and the new compound HNbO<sub>3</sub> is a cubic perovskite. The large structural and bulk change from the twisted perovskite LiNbO<sub>3</sub> structure precludes the formation of a surface layer on the LiNbO<sub>3</sub> substrate. However, in less acidic environments, such as Mg(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O or benzoic acid C<sub>6</sub>H<sub>5</sub>COOH), an incomplete exchange occurs. Studies of single-phase powder samples show that at least as much as 50% of the lithium can be replaced by protons without a major structural change. On macroscopic LiNbO<sub>3</sub> crystals, partially exchanged layers thicker than 10  $\mu$ m have been formed using benzoic acid.

Jackel and Rice (1982) choose benzoic acid as the most promising of the proton sources which produce partial exchange, primarily because of its high boiling point (249°C) and stability throughout its liquid range. The high boiling point permitted working at temperatures for which diffusion was rapid. Stability of the compound permitted obtaining consistent results. Secondary arguments in favour of benzoic acid were its low toxicity and low price.

Benzoic acid does not attack most metals, so metal masks can be used to define channel waveguides or other small features, such as gratings. Using a mask of approximately 100 Å Cr and 500 Å Au, Jackel et al. (1982) have made a series of channel waveguides 1–20  $\mu$ m wide. The use of a similar masking technique for making high-efficiency gratings is now under investigation.

Clark et al. (1983) confirmed that the use of y-cut substrates renders the surface of the substrate liable to severe etching. However, the problem can be overcome by using proton exchange in conjunction with Ti in-diffusion to produce waveguides on y-cut substrates which guide both TE and TM modes (De Michelli et al. 1982). Both active and passive optical waveguide devices can be fabricated using this technique; high efficiency beam deflectors (Pun et al. 1982), optical frequency translators (Wong et al. 1982), and second harmonic generators (De Michelli et al. 1983) have been demonstrated (see chapters 5 and 6).

## 1.6.2 Sample preparation and experimental methods

Loni et al. (1989) proposed the following way of preparation of light-guiding layers. Nominally identical congruent-composition x- and z-cut lithium niobate substrates (dimensions:  $1 \text{ cm} \times 1.5 \text{ cm} \times 0.1 \text{ cm}$ ) were polished on both facets for IR spectroscopic experiments. The samples in holders were placed in individual covered silica glass beakers which contained accurately weighed quantities of molten benzoic acid. The heating source was a high-temperature oil bath which was controlled to ±0.25°C. Temperatures were measured using a Pt-13% Rh/Pt thermocouple. The 'neat melt' x- and z-cut waveguides were fabricated at temperatures between 167°C and 211°C, for times ranging from 0.12 to 6 h. The fabrication procedure for the x-cut buffered melt proton-exchanged waveguides was identical, except that the waveguides were fabricated at 215°C and 135°C for times ranging from 1 to 8.5 h. The quantity of lithium benzoate added to the benzoic acid melts was defined in terms of the Li\* molar fraction, that is, [moles of lithium benzoate] / ([moles of lithium benzoate] + [moles of benzoic acid]). The molar fractions of lithium benzoate, for fabrication of the buffered melt waveguides, were between 0.28×10<sup>-2</sup> and 1.12×10<sup>-2</sup>.

Samples were annealed in a Pyrex tube mounted in a furnace whose temperature was controlled to  $\pm 2^{\circ}$ C. The atmosphere used was dioxygen saturated with water, obtained by bubbling O<sub>2</sub> through a column of warm (60°C) water. The waveguides were mounted in a stainless steel boat that allowed a uniform flow of gas over the surface of each waveguide. To avoid thermal shock at inlet and outlet, the waveguides were moved slowly along the furnace tube over a period of approximately one minute. The annealing time was defined as the interval between

the sample reaching the furnace hot spot and its subsequent removal. The wet  $O_2$  flow was maintained throughout the entrance and removal periods.

After processing, the waveguides were mounted in evacuable Pyrex infrared cells fitted with calcium fluoride windows for H/D hydrogen isotopic exchange studies. High-temperature hydrogen isotopic exchange was carried out by annealing the waveguides as above, except that D<sub>2</sub>O (99.8 percent) was used instead of H<sub>2</sub>O. The infrared spectra were recorded using a spectrometer and data station. The optical properties of the planar waveguides were assessed at  $\lambda = 0.6328$  µm using the prism coupling technique and assuming normalized step-index equations (Tien and Ulrich 1970). The refractive index profiles of the annealed waveguides were calculated using the IWKB method (Finak et al. 1982), a method particularly useful for waveguides with a graded-index profile.

Proton diffusion was controlled by the IR spectra. The x-cut spectra consist of two overlapping bands in the OH stretching region: a broad-band at  $v_{max} = 3250 \text{ cm}^{-1}$  due to hydrogen-bonded OH groups, and a sharp band at  $v_{max} = 3505 \text{ cm}^{-1}$  due to 'free' OH groups. Polarization measurements indicate that free OH is constrained to vibrate in the (x,y)-plane of the waveguide. A band at  $v_{max} = 3505 \text{ cm}^{-1}$  is also observed in the spectra of z-cut waveguides. However, the absorption due to hydrogen-bonded OH groups is discernible only as a shoulder on the lowfrequency site of the sharp band at  $v_{max} = 3505 \text{ cm}^{-1}$ .

The different spectra are presumably due to the different crystal orientation. The x- and z-cut infrared spectra, Fig.1.30(a,b), indicate that the OH absorbance increases with the waveguide fabrication time. It was reported (Wong et al. 1986) that for x-cut lithium niobate, the relationship between the OH absorbance at 3505 cm<sup>-1</sup> was nonlinear with temperature and time. The results due to Loni et al. (1989) were in agreement with these observations. However, to determine the extent of proton-exchange, the area of the OH bands should be used. The relationship between the absorption band area and waveguide fabrication temperature is linear, as depicted in Fig.1.31(a,b) for x- and z-cut proton-exchanged waveguides, respectively. The observed temperature dependence indicated that there is a minimum temperature required for proton-exchange, the values being  $T = (140.6 \pm 3.3)^{\circ}$ C for z-cut materials and  $T = (131 \pm 8.3)^{\circ}C$  for x-cut materials. Corresponding values obtained by plotting the waveguide depth (determined from prism coupling data) as a function of temperature were  $T = (148.5 \pm 7.5)^{\circ}C$  for z-cut materials and  $T = (145.4\pm 3.4)^{\circ}$  for x-cut materials. The data suggest that the minimum exchange temperature is slightly higher for z-cut materials.

The relationship between the OH absorption band area and  $(time)^{1/2}$  for x- and z-cut proton-exchanged waveguides is linear (the z-cut case in Fig.1.32(a)), which is consistent with a process in which the extent of OH group formation in the waveguide layer is governed by diffusion. The natural logarithm of the slope of each line (area versus  $t^{1/2}$ ) was plotted as a function of 1/T and the observed Arrhenius behaviour enabled apparent activation energies for the proton-exchange process to be calculated. The values obtained were  $Q_x = 60.4$  kJ mol<sup>-1</sup> and  $Q_{z} = 81.2$  kJ mol<sup>-1</sup>.

Since both the absorption band area and waveguide depth show a  $t^{1/2}$  dependence, the two quantities can be linearly related. This was verified by plotting the band area as a function of depth for the x- and z-cut waveguides, illustrated
in Fig.1.32(b) for the z-cut waveguides. Therefore, the depth of a protonexchanged waveguide can be estimated by calculating the area under the infrared absorption bands. With suitable recalibration, the method can also be used for waveguides produced using buffered melts. The method is particularly suited for single-mode proton-exchanged waveguides, where the usual IWKB and stepindex methods cannot be used.

## 1.6.3 Annealed proton-exchanged waveguides

The effect of annealing on the refractive index profile of an x-cut protonexchanged waveguide (Table 1.11) is shown in Fig.1.33a. Although the initial step-like index profile is substantially preserved after a short annealing time, a tail eventually forms at the waveguide-substrate boundary, indicating a change to a more graded-index profile. The waveguide (surface) index of the sample decreased by 0.04 (at  $\lambda = 0.6328 \mu m$ ) after annealing at 320°C for 3 h 11 min (Fig.1.33a), and the depth of the guiding region increased by 1.30  $\mu m$  (Table 1.11). As a consequence, the number of modes supported increased from three before annealing, to five. After further annealing at 400°C for 30 min, the tail on the step-like refractive index profile was more prominent.

The effect of annealing on the effective mode indices (at  $\lambda = 0.6328 \mu$ m) and waveguide depth of the same sample is illustrated in Fig.1.33b. The second-order mode (m = 1) and the third-order mode (m = 2) had maximum effective indices after annealing times of approximately 10 and 15 min, respectively. The fourthorder mode (m = 3) reached a maximum after approximately 1 h. After this, the effective mode indices all decreased gradually with increasing an-nealing time. No initial increase was observed for the fundamental mode (m = 0). The results obtained for the samples in Table 1.11 indicate that most of the changes in the refractive index profile occur, approximately, within the



**Fig.1.30** Infrared spectra of proton-exchanged waveguides. a) *x*-cut,  $T = 198^{\circ}$ C: i) 4.42 h, ii) 3 h, iii) 2 h, iv) 1 h, v) 0.25 h. b) *z*-cut,  $T = 211^{\circ}$ C: i) 6 h, ii) 4.42 h, iii) 3 h, iv) 2 h, v) 1 h, vi) 0.42 h, vii) 0.12 h (Loni et al. 1989).



Fig.1.31 Absorbance band area vs temperature: a) x-cut, b) z-cut (Loni et al. 1989).

first half to one hour of annealing and the smaller variations are observed after annealing for much longer periods.

After annealing the x-cut proton-exchanged waveguide at  $250^{\circ}$ C for 0.5 h, there was a significant decrease in the intensity of the infrared absorption band due to the hydrogen-bonded OH groups in the sample, but the band at 3505 cm<sup>-1</sup> was unchanged. A prolonged annealing at the same temperature produced further, but smaller, variations in the broad-band. This behaviour can be correlated with the observation that the major changes in the refractive index



**Fig.1.32** a) Absorbance band vs  $f^{\prime 2}$  (*z*-cut proton-exchanged waveguides). b) Absorbance band area vs depth (*z*-cut proton-exchanged waveguides) (Loni et al. 1989).

profile of sample X3 occurred within the first 0.5 h of annealing. No decrease in the effective mode indices was observed at room temperature (after annealing) over a measurement period of one year, in agreement with Jackel and Rice (1984).

The hydrogen isotopic exchange technique was used to test whether annealed proton-exchange waveguides react with atmospheric water vapour in a similar manner to annealed waveguides, at room temperature. The infrared absorption spectra indicated that, unlike in unannealed proton-exchange waveguides, no hydrogen isotopic exchange took place in the material. However, when the x-cut waveguides were subsequently annealed at 320°C for 0.5 h in a wet  $(D_2O)/O_2$  atmosphere, there was an uptake of deuterium. From the infrared absorption spectrum of the sample it can be seen that the hydrogen-bonded OH was markedly reduced by annealing. The sharp band at  $v_{max} = 3505$  cm<sup>-1</sup> decreased significantly, with the growth of an OD counterpart at  $v_{max} = 2590$  cm<sup>-1</sup>. The spectra of the absorption band structures indicated that, after annealing, the waveguides

Diffusion time, h	Annealing temperature, ℃	Annealing time, h	Waveguide (surface) index	Depth (µm)
	_	-	2.3281	0.40
	250	0.5	2.3082	0.70
1	250	1	2.3081	0.70
	250	2.62	2.3036	0.72
	_	_	2.3295	0.73
2	250	0.5	2.3168	1.14
3	250	1	2.3151	1.19
	250	2.62	2.3098	1.27
· · · ·		-	2.3307	1.09
6	250	0.5	2.3231	1.41
(T <b>−</b> 168°C)	250	1	2.3168	1.61
	250	2.62	2.3153	1.63
l	_	-	2.3244	0.63
	320	0.25	2.3072	1.02
	320	1	2.2862	1.34
	320	3.18	2.2763	1.50
	_	_	2.3286	1.12
3	320	0.25	2.3137	1.85
	320	1	2.3026	2.02
	320	3.18	2.2882	2.42
6	_	_	2.3281	1.60
	320	0.25	2.3191	2.35
(T <b>=</b> 175℃)	320	1	2.3021	2.72
	320	3.18	2.2992	2.54

Table 1.11 Optical waveguide measurements ( $\lambda = 0.6328 \ \mu m$ ) and annealing conditions for 'neat melt' x-cut proton-exchanged waveguides (Loni, Hay, De La Rue, Winfield, 1989)



**Fig.1.33** a) Refractive index profile ( $\lambda = 0.6328 \,\mu$ m) as a function of waveguide annealing; the same sample was proton-exchanged at 175°C for 3 h. b) Variation in effective mode indices with annealing time (the sample was annealed at 320°C) (Loni et al. 1989).

did not react with atmospheric water at room temperature. Similar results were observed when previously annealed  $(O_2/H_2 \text{ atmosphere})$  waveguides were reannealed using  $D_2O$  at a higher temperature of 375°C, although hydrogen isotopic exchange was not observed in these waveguides (before reannealing) at room temperature.

## 1.6.4 Waveguides fabricated using buffered melts

The optical properties of waveguides prepared in benzoic acid with added lithium benzoate were determined from prism coupling data, via mode angle measurements and calculations using the step-index model. The resulting waveguide depths were linearly related to the square root of the fabrication time. As the molar fraction of lithium benzoate increases, the effective diffusion coefficient (estimated from the depth versus  $t^{1/2}$  curves) decreases (Fig.1.34) indicating that the extent to which proton-exchange occurs depends strongly on the presence of lithium in the melt. A similar effect might be expected, in the absence of lithium benzoate, due to the presence of lithium in the melt resulting from the Li<sup>+</sup>-H<sup>+</sup> exchange process.

However, the lithium concentrations in benzoic acid determined by atomic absorption spectroscopy after proton exchange, are sufficiently small (Loni et al. 1987) and the equivalent lithium benzoate molar fraction is of the order of  $0.02 \times 10^{-1}$ . Therefore, the effective diffusion coefficient remains approximately constant throughout the exchange period.

The degree of optical stability in a proton-exchanged waveguide depends on the molar fraction of the added lithium ion (Fig.1.35a, x-cut). For example, the decrease in the fundamental mode (m = 0) index over a period of 410 h was 0.0045 for a sample containing Li<sup>+</sup> molar fraction = 0.09 ×10<sup>-2</sup>, and 0.001 for a sample containing Li<sup>+</sup> molar fraction = 1.10×10<sup>-2</sup>. Jackel and Rice (1984) showed that no measurable decrease in the effective mode index can be observed for waveguides produced from melts containing molar fractions of lithium ion greater than  $3.40\times10^{-2}$ .

Although the refractive index profiles are step-like, the value of  $\Delta n_{i}$ 

decreases as the lithium benzoate molar fraction increases (Fig.1.35b). The lowest value measured by Loni et al. (1989) was  $\Delta n_e = 0.085$  for a waveguide produced using Li<sup>+</sup> molar fraction equal to  $2.42 \times 10^{-2}$ . Infrared spectra of waveguides prepared in benzoic acid with added lithium benzoate are shown in Fig.1.36. Although the OH absorption bands at  $v_{max} = 3505$  cm<sup>-1</sup> and  $v_{max} = 3250$  cm<sup>-1</sup> are both present, the relative intensity of the latter band is much smaller than that for waveguides produced using benzoic acid alone under normally identical conditions. The larger Li<sup>+</sup> molar fraction, the smaller the relative magnitude of the absorption at  $v_{max} = 3250$  cm<sup>-1</sup>, indicating that the hydrogen-bonded OH groups are present to a lesser extent. No room temperature hydrogen isotopic exchange was observed in the waveguides which were fabricated using buffered melts (up to Li<sup>+</sup> molar fraction =  $1.04 \times 10^{-2}$ ), indicating that, like annealed proton-exchanged waveguides, they do not react with atmospheric water vapour.

Annealing the buffered melt waveguides in a wet  $(H_2O)$  dioxygen atmosphere had relatively little effect. For example, no measurable changes in the infrared absorption spectra were observed after the buffered melt waveguides were annealed. Small changes were, however, observed in the refractive index profiles, but these were of the same magnitude as the ones observed during the later stages of annealing neat melt proton-exchanged waveguides.

Since the presence of hydrogen-bonded OH in buffered melt waveguides is very much reduced, the changes in the refractive index profiles as a consequence of annealing must arise, in the main, from the diffusion of protons originating from 'free' OH into the substrate. It is unlikely that 'free' OH out-diffuses into the atmosphere since there would be an associated reduction in the absorption band.

The loss of hydrogen during the annealing process could arise by migration of the hydrogen-bonded OH to the surface of the guiding region followed by reaction of surface hydroxyl groups to give surface oxides and water. The latter process can either take place via route 2, or via route 4 followed by route 5, in the scheme:



Fig.1.34 Effective diffusion coefficients at215°C and 235°C versus Li\* mole fraction (x-cut) (Loni et al 1989).



**Fig.1.35** a) Variation in effective mode index with time for different Li<sup>\*</sup> mole fractions (*x*-cut). b) Step index change  $\Delta n_x$  versus Li<sup>\*</sup> mole fraction (*x*-cut) (Loni et al. 1989).



(where O-H-O represents hydrogen-bonded OH). The process is reversible, since it has been shown that D is incorporated into proton-exchanged waveguides from  $D_2O$  during annealing. This could occur either directly, via route 6, or via route 1 followed by route 4. The latter route requires hydrogen-bonded OH to be present and is likely to be important only during the early stages of annealing. Loni et al. (1989) demonstrated reversible H-D exchange at room temperature. However, this is not observed with annealed or buffered melt waveguides, arguing that H-D room temperature exchange involves route 1 then route 4 and route 3 then route 2, rather than the direct routes 5 or 6. The direct routes 5 and 6 do occur at high temperatures since, as mentioned above, D can be incorporated at high temperatures without the presence of hydrogen-bonded hydroxyl groups (O-H-O). It is





suggested that the annealing process can be represented by the following reaction steps:

$$O - H - O \rightarrow OH^{-} + O^{2-}$$
(1.54)

$$2OH^{-} \rightarrow O^{2-} + H_2O.$$
 (1.55)

The removal of hydrogen-bonded OH groups as  $H_2O$  preserved charge neutrality in the crystal and can take place via reaction (1.54) followed by reaction (1.55). Reaction (1.55) was first suggested by Bollmann (1987), although for a different situation.

Loni et al. (1989) believe that hydrogen-bonded OH groups are likely to be responsible, to a substantial degree, for the undesirable effects associated with proton-exchanged waveguides; for example, device instabilities, such as dc drift (Wong et al. 1982). Wong et al. (1982) reported that applying a dc voltage of approximately 5 V (either polarity) to a proton-exchanged strip waveguide phase modulator resulted in the extinction of the guided mode, with a time-constant of the order of 1 min. Removing the dc voltage led to a slow recovery whereas voltage reversal led to a much more rapid recovery. Such an effect may well be caused by the movement of hydrogen-bonded OH (protons) under the influence of an applied electric field. The distribution of hydrogen-bonded OH is, initially, likely to be approximately uniform within the guiding layer. However, on applying an electric field the electrostatic forces would redistribute the protons. Protons which are hydrogen-bonded will be more strongly attracted by a negative potential, since they are the more mobile hydroxyl groups. The consequent redistribution of the protons could result in a major modification in the waveguide refractive index profile. Removal of the electric field would give a charge imbalance and the protons would tend to migrate back to more favourable sites, recovering the original waveguide refractive index profile.

In addition to the removal of hydrogen-bonded OH and the diffusion of 'free' OH into the substrate, the annealing process may also involve migration of lithium ions from adjacent regions of the substrate into the waveguide region. In this situation, the distorted unit cell structure in the waveguide may tend to change back to that of virgin LiNbO<sub>3</sub>. As a consequence, the electro-optic effect would be restored and propagation losses reduced. It is widely accepted that the diamond (parallelogram) which appears in the (012) plane, based on the rhombic system, is related to the strong electro-optic effect in the LiNbO<sub>3</sub> crystal, as shown in Fig.1.37. After the exchange, the figure is slightly close to the square (perovskite, the cubic system) caused by the strain  $\Delta c/c$ . Since the square has the centre of symmetry, the linear electro-optic constant does not generally exist. Thus, it is estimated that  $r_{33}$  reduces because of the deformation of the diamond. However, in spite of no phase transition in the exchanged layer, the value of  $r_{33}$  seems to be very small. It is suggested that the HNbO<sub>3</sub> (system) composition of the exchanged layer should have a poor electro-optic effect.

## 1.6.5 Proton diffusion

Using the prism coupling technique, Clark et al. (1983) calculated the effective

refractive index of each observed mode. The values of effective refractive indices were then used as the input for a computer program based on normalized step index equations given by Kogel'nik and Romaswamy (1974), to calculate the surface refractive index and the depth of the planar waveguide. The step-index assumption was verified by modelling the diffusion profile of the planar waveguide by a finite difference solution of the one-dimensional ion exchange (equation (1.56)) (Wilkinson and Walker 1979)

$$\partial u / \partial t = D_a \frac{\partial}{\partial x} \left[ 1 / (1 - \alpha u) \frac{\partial u}{\partial x} \right], \tag{1.56}$$

where  $\alpha = 1 - D_a/D_b$ ;  $D_a$  is the in-diffusion coefficient for protons,  $D_b$  the outdiffusion coefficient for Li<sup>+</sup> ions, and u the concentration of protons to the total concentration of ions.

The equation takes into account the ratio of the diffusion coefficients of the species diffusing in and out of the substrate. It was found that the rate of protons diffusing in was very much smaller than that of the lithium ions diffusing out. From the model, theoretical values of the diffusion coefficients for lithium and proton ions were found to be 1.62 and 0.08  $\mu$ m<sup>-2</sup>/h at 200°C, respectively. Clark et al. (1983) used the above model in conjunction with a variational solution of the wave equation (Walker 1981) to calculate mode effective indices. The parameter  $\alpha$  in equation (1.56) was systematically varied to obtain a best fit to measured effective index values. The best-fit profile occurred when  $\alpha \approx 1$  indicating that the solution of equation (1.56) was a step function.

Plots of the diffusion depth versus  $(time)^{1/2}$  for various temperatures are shown in Fig.1.32(b). From the gradient of the curves, the values for the diffusion coefficient were calculated assuming that the proton source concentration did not vary during the exchange process. This gives values of the diffusion coefficient D(T), as shown in Table 1.12. The values were calculated assuming the diffusion depth d to vary as follows (Crank 1970):

$$d = 2[t \ D(T)]^{1/2}, \tag{1.57}$$



**Fig.1.37** Deformation of diamond appears in the  $(01\overline{2})$  plane of LiNbO<sub>3</sub> before and after exchange (Minakata et al. 1986).

where t is the exchange time. In equation (1.57), the temperature dependence of D is given by the Arrhenius law:

$$D(T) = D_0 \exp(-Q / RT),$$
(1.58)

where  $D_0$  is a constant for the proton exchange process in z-cut LiNbO<sub>3</sub>, R the universal gas constant, T the absolute melt temperature, and Q the activation energy for the exchange process. Figure 1.38 illustrates the relationship between 1/T and  $\ln D(T)$ . From this plot, the Q and  $D_0$  values have been obtained:  $Q = 94 \text{ kJ/mol}, D_0 = 1.84 \times 10^9 \text{ µm}^2/\text{h}$ . Equation (1.57) can therefore be rewritten as (1.59)  $d = 8.58 \times 10^4 \text{ (t)}^{1/2} \exp(-5.65 \times 10^3 \text{ T}) \text{ µm}$ . From Fig.1.38 one can read off the value of the diffusion coefficient within the working range for benzoic acid (150-230°C).

#### 1.6.6 Waveguides using cinnamic acid

Pun et al. (1991) have demonstrated the use of cinnamic acid ( $C_6H_5CH:CHCOOH$ ) and in particular transcinnamic acid, as a new proton source for the fabrication of high-index proton-exchanged (PE) waveguides in z-cut LiNbO<sub>3</sub>. The refractive index profile of the PE waveguides using this acid is a graded index function and is different from those obtained using organic acids which have step index profiles.

Z-cut y-propagating PE planar waveguides were fabricated in integrated optics grade LiNbO<sub>3</sub> substrates that were polished on one face. The substrates were precleaned thoroughly using a series of organic solvents and preheated before immersing into the acid melt. The analytical grade transcinnamic acid was contained in a covered quartz crucible and maintained at the set temperature for fabrication. After the exchange process, any residual acid was rinsed away with acetone. For annealing experiments, the waveguides were postbaked in a horizontal furnace at 350°C for times between 6 min and 5 h. A dry oxygen atmosphere flowing at 500 ml/min was used to prevent deoxidization of the waveguides.

The waveguide depths and index profiles were computed from the measured data using the continuous effective index function method (Chiang 1985).

Figure 1.39 shows the variation of waveguide depth d with exchange time t for different fabrication temperatures T. Assuming  $d = [t \times D(T)]^{1/2}$ , the effective diffusion coefficient D(T) can be calculated for each fabrication temperature. The temperature dependence of D(T) follows the Arrhenius law, that is,  $D(T) = D_0 \exp(-Q/RT)$ , where  $D_0$  is the diffusion constant, Q is the activation

Т (°С)	<i>D</i> ( <i>T</i> ) μm²/h
180	0.027
200	0.081
220	0.207

Table 1.12 Diffusion coefficients with respect to temperature (Clarc, Nutt, Wong et al. 1985)



**Fig.1.38** Plot of  $\ln D(T)$  versus 1/T (gradient of line = Q/R) (Clark, et al. 1983).

energy and R is the universal gas constant. From the Arrhenius plot, that is, ln [D(T)] versus 1/T, the values of  $D_0$  and Q were found to be  $9.78 \times 10^7 \,\mu m^2/$ h and 77.15 kJ/mol, respectively. Hence the diffusion depth of a PE waveguide using transcinnamic acid can be expressed as

$$d = 9.89 \times 10^3 \,\sqrt{t} \,\exp(-4.64 \times 10^3/T) \,\mu\text{m} \tag{1.59}$$

Figure 1.40 shows a typical variation of the index profile of the PE waveguide with annealing time as a parameter. The waveguide was initially exchanged at 235°C for 2 h. The index profile changes from a truncated-parabolic function to a step function after annealing for 16 min. With further annealing, an index tail forms at the guide-substrate boundary and the profile is Gaussian-like. Figure 1.41 shows the effect of annealing on the surface index change  $\Delta n$  and the waveguide depth increase  $\Delta d (= d - d_0)$ , where  $d_0$  is the initial waveguide depth before annealing. The linear dependence indicates that both  $\Delta n$  and  $\Delta d$ follow a power-law relationship with annealing time  $t_a$ , and could be given by

$$\Delta n = c_1 t^{-0.2} \tag{1.60}$$

$$\Delta d = d - d_0 = c_0 t^{0.41} \tag{1.61}$$

where  $c_1$  and  $c_2$  are constants. From the measured data,  $c_1$  and  $c_2$  have values of 0.082 and 1.81 respectively. Other waveguides prepared using different initial exchange times and temperatures have similar curves after annealing, but with different values of  $c_1$  and  $c_2$ . Annealed single-mode waveguides also exhibit a lower propagation loss (0.33 dB/cm) compared to that of the unannealed counterpart (0.81 dB/cm).

**1.6.7 Proton-exchange waveguides of MgO-doped and Nd:MgO-doped LiNbO**<sub>3</sub> It has been reported that proton-exchange waveguides formed in MgO-doped



**Fig.1.39** Waveguide depth d as a function of exchange time t using transcinnamic acid (Pun et al. 1991).

LiNbO<sub>3</sub> have a higher damage threshold than waveguides fabricated in undoped material (Digonnet et al. 1985). In order to use higher pump powers while avoiding effects associated with photorefractive damage, LiNbO<sub>3</sub> substrates doped with both neodymium (to provide the lasing medium) and magnesium oxide (to suppress photorefractive effects) can be used.

Both Jackel and Digoneet et al. (1985) have independently characterized proton-exchange waveguides fabricated in x- (Digonnet M. et al. 1985; Jackel J.L. 1985) and y-cut (Digonnet M. et al. 1985) LiNbO<sub>3</sub> doped with 5% MgO, whilst Li et al. (1988) characterized waveguides fabricated in x-cut LiNbO<sub>3</sub> doped with approximately 1% Nd. Jackel used neat benzoic acid melts for waveguide fabrication at 150 and 250°C and Digonnett et al. used neat and buffered benzoic-acid melts (1 and 2 mol.% lithium benzoate) at 249°C, whereas Li et al. used a 'double-exchange' technique (requiring 1 mol% followed by 3 mol% lithium benzoate) at 300°C. Loni et al. (1990) reported the first characterization of neat-melt, proton-exchanged waveguides in the x-cut substrate doped simultaneously with MgO and Nd.

Planar waveguides were fabricated on x-cut Nd MgO-doped (0.1-0.2%:4.5%)LiNbO<sub>3</sub> and on x- and z-cut MgO-doped (4.5%) LiNbO<sub>3</sub>. Planar waveguides were also produced in congruent LiNbO<sub>3</sub> and were used as a reference for the waveguides fabricated in the doped substrates. The waveguides were fabricated by immersion in neat benzoic acid at temperatures within the range of 182-235°C, with fabrication times ranging between 1 and 12.5 h. All the waveguides were multimode. Light propagation was along the y-direction.

The characteristic OH absorption bands were observed in the infrared spectra of all the MgO-doped and (Nd:Mg)-doped substrates and proton-exchanged waveguides. The relative intensitites of the bands were dependent on the waveguide fabrication parameters, in a manner similar to that observed for waveguides produced in congruent substrates, and the infrared spectra of waveguides produced in both types of doped substrates were identical. The only obvious dif-



ferences in the infrared absorption spectra, compared to those of waveguides formed by proton exchange in congruent  $LiNbO_3$ , were in the positions of the OH peaks before and after proton exchange.

In agreement with the results reported by Jackel (1985), the slightly different OH environments and behaviour before and after proton exchange may be indicative of slightly different waveguide material structures.

By plotting the exponential relationship between waveguide depth and  $t^{1/2}$ , and assuming  $d = [4D(T)t]^{1/2}$ , effective diffusion coefficients, D(T), for the proton-exchange process were estimated. Figure 1.42 shows the relationship

<b>Table 1.13</b> Diffusion parameters ( $Q$ and $D_0$ ) for proton exchange in doped (d) and undoped	d (c)
LiNbO <sub>a</sub> (Loni et al 1990)	

Sample description	Diffusion parameters		
	Q (kJ mol <sup>-1</sup> )	$D_0 ~(\mu m^2 h^{-1}) \times 10^9$	
x-cut, H*:LiNbO, (c)	81.24	0.234	
x-cut, H <sup>+</sup> :LiNbO, (d)	91.54	1.41	
(H*:Nd:MgO:LiNbO,) (d)			
z-cut, H <sup>+</sup> :LiNbO, (c)	90.40	1.472	
z-cut, H*:MgO:LiNbO, (d)	99.36	5.037	
H <sup>+</sup> :Nd:MgO:LiNbO, (d)			

obtained between the effective diffusion coefficients and temperature for protonexchanged waveguides fabricated in both the doped and undoped substrates. It can be seen from the relationships depicted in Fig.1.42 that the diffusion process in congruent LiNbO<sub>3</sub> is slower for z-cut substrates than for x-cut substrates. This relative slowness is also the case for the MgO-doped substrates and, presumably, for the Nd:MgO-doped substrates.

Although according to Fig.1.42, the proton exchange process proceeds more slowly in MgO:LiNbO, than in congruent material of the same orientation, in agreement with the results of Jackel (1985), there appear to be no measurable differences between the effective diffusion coefficients for proton-exchange in Nd:MgO:LiNbO, and MgO:LiNbO, The presence of MgO and Nd:MgO LiNbO, single crystals has also been shown to reduce the diffusion coefficients for titanium in-diffusion (Bulmer 1984). For proton exchange in congruent LiNbO, doped with 5% MgO, the effective diffusion coefficient estimated by Jackel (1985) for a waveguide fabrication temperature of 250°C was 0.81 m<sup>2</sup> h<sup>-1</sup>. Extrapolating the curve for the x-cut proton-exchange waveguides in MgO:LiNbO, to 250°C, Fig.1.42, yields as approximately identical diffusion coefficient of 0.80 m<sup>2</sup> h<sup>-1</sup>. This similarity is reasonable, given the probable level of precision in obtaining uniform MgO dopant concentrations in the solid. Taking the effective diffusion coefficients for proton exchange in MgO:LiNbO, (Nd:MgO:LiNbO,) as a percentage of the corresponding values for congruent, one finds that the reduction is of the order of  $50\pm5\%$  for x-cut waveguides and  $37\pm4\%$  for zcut waveguides (Table 1.13).

The observed Arrhenius-type relationships between D(T) and T (Fig.1.42), are typical of the proton-exchange process. By plotting  $\ln D(T)$  as a function of  $T^{-1}$ , a comparison of both the activation energy and preexponential factor was obtained for the waveguides fabricated in the doped and undoped substrates, Table 1.13. In congruent LiNbO<sub>3</sub>, both the activation energy and the preexponential factor are lower for x-cut substrates than for z-cut substrates and higher effective diffusion coefficients are evident for x-cut substrates (Loni et al. 1989, Clark et al. 1983). This relationship also applies for Nd:MgO-doped and MgO-doped substrates of x- and z-cut orientations. Comparing the waveguides produced in doped and undoped substrates (Table 1.13), one finds that lower effective diffusion coefficients are obtained for proton exchange in doped substrates. In addition, the activation energy and preexponential factor are higher for MgO-doped (Nd:MgO-doped) substrates. These differences are probably related to slight differences between the bulk and waveguide crystalline structures of congruent and MgO-doped (Nd:MgO-doped) LiNbO<sub>3</sub>.

# 1.7 Planar ion-exchanged KTiOPO<sub>4</sub> waveguides

Potassium titanyl phosphate (KTiOPO<sub>4</sub>, abbreviated as KTP below) has long been recognized as an outstanding material for many important optical and electro-optical applications (Zumsteg et al. 1976, Liu et al. 1984, Liu et al. 1986). Its high damage threshold, good mechanical and thermal stability, large optical nonlinearity, and broad temperature bandwidth have made it arguably the best material for frequency conversion in the visible and near infrared ranges. KTP also shows great promise in electro-optic applications due to its



Fig.1.42 Relationships between effective diffusion coefficient and temperature for a series of x- and c-cut proton exchanged waveguides fabricated in doped and undoped LiNbO<sub>3</sub> (Loni et al. 1990).

low dielectric constants and large Pockels coefficients (Bierlein and Arweiler 1986).

Despite the initial successes, the ion-exchange process has its drawbacks. Specifically, the ionic conductivity varies significantly with crystal growth methods and with impurities, making the device fabrication process difficult and with poor yields. This inherently diffusive and strongly anisotropic ion-exchange process often produces  $M_x K_{1-x} \text{TiOPO}_4$  (where M is Tl or Rb) guides with a broad poorly defined refractive index profile along the *c*-axis, and was believed to be responsible for the observed variations in the performance of these devices. Better understanding of the mechanism of ionic conduction and the underlying defects in KTP promises to reduce this problem (Morris et al. 1991).

The ion exchange conditions and waveguiding results are summarized in Table 1.14, where d is the diffusion depth and  $\Delta n$  the increase in the surface refractive index. An error function distribution is assumed for the refractive index profiles in the ion exchanged regions, a distribution which agrees well with the ion concentration profile and is shown in Fig.1.43 for a typical Rb-exchanged sample. The maximum increase in the surface refractive index observed for rubidium ( $\Delta n = 0.02$ ) is close to the value that would result in nearly complete ion exchange forming a RbTiOPO<sub>4</sub> surface on a KTP substrate (Zumsteg et al. 1976). The increase in the surface refractive index for all these ion exchanged guides generally scales with the electronic polarizabilities of the exchanged ions relative to potassium.

The ion exchanged waveguides are stable both at room temperature and, provided the diffusion temperature remains below about 450°C, the exchange process does not introduce any noticeable surface defects. Near and above 450°C, slight surface etching occurs in some samples during the exchange.

The results given in Table 1.14 show the ion diffusion in KTP to be highly anisotropic, being much greater along the z-axis (c or polar direction) and being



Fig.1.43 Depth profile for Rb ion exchange in KTP (Bierlein and Ferretti 1987).

higher on a negative z-surface (positive pyroelectric coefficient) than on a positive z-surface. The diffusion anisotropy correlates well with the large anisotropy of ionic conductivities and dielectric properties (Bierlein and Arweiler 1986). The variations in diffusion into the different polar surfaces result from differences in surface adsorption and reactivities. Additional variations in diffusion kinetics are observed along the z-axis from changes in local ionic properties depending on crystal defects, incorporated O-H, *etc.* The diffusion rate generally scales with ionic conductivity, a result which is expected since ionic conductivity and diffusion are closely related.

Diffusion constants and activation energies indicate that the Rb–K-exchange process does not obey simple diffusion kinetics. The effective waveguide thickness and  $\Delta n$  were found to be nearly independent of diffusion time from 0.25 to 4 h at a typical diffusion temperature of 350°C and also nearly independent of diffusion temperature from 350 to 400°C. Also, post-annealing a Rbexchanged guide in air from 300 to 350°C for 30 min to 2 h did not significantly change d or  $\Delta n$ . These results indicate that the effective exchange or the diffusion rate for the Rb–K system is initially high and then decreases significantly after some point in the exchange process. This large change in exchange or diffusion rate can be explained by assuming a very low diffusion constant for Rb and K in Rb-rich Rb<sub>x</sub>K<sub>1-x</sub>TiOPO<sub>4</sub> and a high constant in KTP. Single-crystal RbTiOPO<sub>4</sub> (RTP) shows a much lower (~100 times) ionic conductivity than KTP and hence ionic diffusion is also expected to be much lower. Exchanging K with the larger Rb ion in a KTP surface layer will also tend to block conduction channels which further lowers ionic conductivity. Hence, during ion exchange, as the

Ion	Surface type	Temperature (°C)	Time (h)	Number of modes	Mode type	d (µm)	Δn
Rb	x	450	3.3	0	TE		
				1	ТМ	1.3	0.02
Rb	z (+)	350	4	3	TE	4	0.019
				3	TM	4	0.018
Rb	z (–)	350	4	3	TE	6.5	0.008
				2	ТМ	6.5	0.008
Cs	z	450	4	11	TE	13	0.028
				8	ТМ	13	0.019
Tl	z	335	4	4	TE	1.6	0.23
				4	ТМ	1.6	0.18

Table 1.14 KTP waveguide characteristics (Bierlein, Ferretti, Brixner, Hsu 1987)

surface rubidium concentration increases, the diffusion constants at the surface decrease which will suppress further ion exchange and result in the equilibrium ion distribution shown in Fig.1.43. Although such an equilibrium distribution is unusual, it is consistent with diffusion theory. This type of behaviour is an advantage for optical waveguide devices since it allows to speed up waveguide fabrication at relatively low temperatures and also permits thermally stable properties.

Planar waveguides were fabricated on the z-surfaces (crystallographic c direction) of hydrothermally grown KTP crystals by immersing them in a molten mixture of RbNO<sub>3</sub> (80 mol%) and Ba (NO<sub>3</sub>)<sub>2</sub> (20 mol%). Diffusion times ranged from 2 to 20 min at 350°C.

Following diffusion, 633 nm light from a helium-neon laser was coupled into the waveguide using a prism. The effective indices of the waveguide modes travelling along the y-axis of the KTP crystal were measured and the refractive index profile of the waveguide was obtained by the inverse WKB method (Risk 1991).

A typical refractive index profile obtained in this manner is shown in Fig.1.44 for TE modes. The solid curves in Fig.1.44 are the best fits of the refractive index profile,  $n(z) = n_s + \Delta n$  erfc (z/d), where  $n_s$  is the refractive index of the KTP substrate,  $\Delta n$  is the refractive index change at the surface (z = 0)of the substrate, erfc is the complementary error function, and d is the depth of the waveguide. The experimentally measured refractive index distribution is well described by an erfc profile, as might be expected for simple diffusion, and this agrees with the microprobe measurements of Rb-ion concentration reported by Bierlein et al. (1987). It has been mentioned above that  $\Delta n$  and d are markedly different depending on whether the +c or -c side of the substrate is used (Bierlein et al. 1987). With the addition of Ba ions, the waveguide properties are essentially the same on both the +c and -c sides.

The waveguide depth d and surface refractive index change  $\Delta n$  were measured for several diffusion times. The depth of the waveguide was found to depend



Fig.1.44 Refractive index profile of KTP waveguide formed by ion exchange. Points were obtained by inverse WKB from measured mode indices. The solid curves are best fits of the profile  $n(z) = \Delta n_s + \Delta n \operatorname{erfc}(z/d)$ (Risk 1991).

**Fig.1.45** Effect of postbaking the KTP crystal. Solid curve shows refractive index profile of waveguide fabricated according to temperature cycledescribed. Dashed curve shows refractive index profile of the same waveguide after heating in air to 350°C for 10 min (Risk 1991).

on diffusion time t as  $d \sim \sqrt{t}$ . The depth obtained for a given diffusion time was similar for both TE and TM modes. The surface index change  $\Delta n$  obtained for TM modes was somewhat higher than for TE modes. This is possibly a consequence of inferring  $\Delta n$  from the mode indices using a simple WKB model that does not include the effect of the biaxial nature of the substrate on the TM modes. However, the TM mode indices are accurately modelled using this simple WKB approach with the values of  $\Delta n$  and d given, and this suffices for predicting the phase-matching characteristics for frequency doubling.

It is important to control the temperature of the KTP crystal before and after diffusion to prevent cracking of the substrate and unwanted migration of the Rb ions. It was found that immersing the KTP crystals directly into the melt from room temperature caused them to crack, so the substrates were first gradually heated in air to near the temperature of the melt before being immersed. This phenomenon is a result of the particular thermal and mechanical properties of KTP. The KTP crystal was held in a preheating furnace for about 1 h, to ensure that the temperature of the crystal had equilibrated to the furnace temperature. Then the crystal was dipped in the melt. After the prescribed diffusion time, the KTP crystal was removed from the melt and allowed to cool rapidly down to room temperature. Because the diffusion of the Rb ions is so fast for this Rb/Ba process, unwanted migration of the Rb ions further into the KTP crystal can occur if the substrate is not cooled rapidly, resulting in changes in the refractive index profile. This is illustrated in Fig.1.45, which shows the refractive index profile of a planar KTP waveguide immediately after the diffusion process and after an additional 10 min of baking in air at 350°C. It is evident that the additional heat treatment has resulted in a significant decrease in surface index change and an increase in the depth of the waveguide, and that the refractive index distribution no longer has an erfc profile.

# 2 Liquid-Phase Epitaxy of Ferroelectrics

The method of liquid-phase epitaxy from the flux is based on the following procedure (Nelson 1963; Andreev et al. 1975). The dissolved substance can crystallize on the substrate immersed in a supersaturated constant-temperature flux. In the course of crystallization, supersaturation of the solution decreases and the growth rate tends to zero. The maximum amount of the crystallized substance is proportional to the mass of solution and the magnitude of supersaturation.

The liquid-phase epitaxy has some advantages over other methods. Stoichiometry need not be maintained during growth from the melt, which permits any combination of temperatures and compositions near the liquidus line of the phase diagram. In many cases, a correct choice of the solvent allows crystallization at a temperature lower by several degrees than the melting point of the compound. This helps to lower the concentration of chemical and structural defects as compared to that in a crystal grown from a nearly stoichiometric melt. The lower the temperature, the less the possibility of contamination of the flux by impurities from the container (Alferov 1976; Dolginov et al.1976).

There are several modifications of the liquid-phase epitaxy of ferroelectrics, the most popular of which are epitaxial growth by melting (Miyazawa 1973; Adachi et al. 1979), liquid-phase epitaxy from the flux (Kondo et al. 1975; Baudrant et al. 1978 (a); Baudrant et al. 1978 (b); Ballman et al. 1975); Khachaturyan and Madoyan 1978; Miyazawa et al. 1978; Kondo et al. 1979; Khachaturyan and Madoyan 1980), capillary liquid-phase epitaxy (Khachaturyan et al. 1984; Fukuda and Hirano 1976; Fukuda and Hirano 1980), and liquid-phase epitaxy from a limited volume (Madoyan et al. 1983; Madoyan et al. 1985).

The application of liquid-phase epitaxy methods provides a clearly pronounced substrate-film boundary with step-like refractive indices and a relatively smooth surface of the structure.

# 2.1 The epitaxial growth by melting (EGM)

To obtain ferroelectric single crystal LiNbO<sub>3</sub> films, Miyazawa (1973) proposed the method of epitaxial growth by melting on LiTaO<sub>3</sub> substrates. For substrates, LiTaO<sub>1</sub> single crystals were used because the point group of LiNbO<sub>3</sub> and

LiTaO<sub>3</sub> has the same class,  $C_{3\nu}$ -3m, and the melting point of LiTaO<sub>3</sub> is higher by about 300°C than that of LiNbO<sub>3</sub>. This difference in the melting point is the key point for the EGM method, where the melting point of the substrate has to be higher than that of the film material, as will be described later.

Fortunately, it is obvious from many previous investigations on the refractive indices of LiNbO<sub>3</sub> single crystals (Tien 1972) that refractive indices for ordinary and extraordinary rays of LiNbO<sub>3</sub> single crystals with any solid-solution composition are larger than those of LiTaO<sub>3</sub> at room temperature. The refractive indices of LiNbO<sub>3</sub> and LiTaO<sub>3</sub> are given in chapter 5, indicating that a LiNbO<sub>3</sub> film on a LiTaO<sub>3</sub> substrate acts as a dielectric light waveguide.

The LiTaO, substrate, which was prepared from a single-crystal boule grown by pulling from a melt with a congruent melting composition of Li/Ta = 0.951 in mole ratio (Miyazawa 1971) was  $10 \times 15 \times 4$  mm in size in the x, y, and c directions, respectively. The c-plane was lapped and polished optically, and LiNbO, ceramics crushed into powder were laid on the polished c-plane of the substrate. The substrate with the powder on its top surface was heated to ~1300°C in a resistance furnace in order to melt the LiNbO, crushed powder alone, and it was then cooled slowly at ~20°C/h through the melting point of LiNbO, (1250°C). In this way, a LiNbO, film crystallized epitaxially on the LiTaO, substrate. As a matter of course, the substrate is not in a single ferroelectric domain. (The name EGM originates from the process described above.) For the composition of the LiNbO, ceramics a congruent melting composition of Li/Nb = 0.942 in mole ratio (Lerner et al. 1968) was used, since a compositional fluctuation did not occur during the growth run. Consequently, a fluctuation of the refractive index does not exist in the grown film. The refractive indices of congruent LiNbO<sub>3</sub> are  $n_e = 2.288$  and  $n_e = 2.207$ at 6328 Å.

The lattice parameters of congruent LiNbO<sub>3</sub> and LiTaO<sub>3</sub> single crystals at room temperature are given in chapter 4. The mismatch of the lattice parameters at room temperature between the LiNbO<sub>3</sub> film and the LiTaO<sub>3</sub> substrate is about 0.08% and 0.57% for  $a_{\rm H}$  and  $c_{\rm H}$ , respectively. The film thickness was measured by line analysis using an X-ray microanalyzer. An intensity distribution profile of characteristic X-ray spectra for Nb and Ta, as shown in Fig.2.1, was obtained by scanning the electron beam perpendicular to the filmsubstrate boundary over the cross section of the specimen. From Fig.2.1 the film thickness was measured to be about 6  $\mu$ m. The *c*-plane of the film was etched with a solution of a HF + 2HNO<sub>3</sub> mixture at its boiling point for 2 min to determine whether the LiNbO<sub>3</sub> single-crystal film was grown or not.

The ferroelectric domain of a LiNbO<sub>3</sub> single crystal is revealed more easily by chemical etching than that of LiTaO<sub>3</sub>. The etched top surface, shown in Fig.2.2, indicates the ferroelectric multidomain structure, which is very close to that of a LiNbO<sub>3</sub> single crystal where the areas with trigonal hillocks (black in colour) are at the negative end of spontaneous polarization and those without hillocks are at the positive one. It was concluded that the LiNbO<sub>3</sub> single-crystal film was grown on the LiTaO<sub>3</sub> substrate, since it is well known that the ferroelectric domain structure, as shown in Fig.2.2, is not revealed in a LiTaO<sub>3</sub> single crystal under the same etching condition. X-ray examination results



Fig.2.1 Intensity distribution profile of characteristics X-ray spectra for Nb and Ta, perpendicular to the film-substrate boundary (Miyazawa 1973). Fig.2.2 (right) Etch figure of the film surface, indicating the ferroelectric modulation pattern (Miyazawa 1973).

indicate that the LiNbO, single-crystal film was epitaxially grown on the substrate.

As the top surface of the as-grown film was relatively rough, it was hand polished first with diamond paste and then with 0.05  $\mu$ m Al<sub>2</sub>O<sub>3</sub> powder in order to demonstrate light wave propagation in the epitaxially grown film. Figure 2.3 shows a 6328-Å He–Ne laser beam which was fed into the film at the right-hand side by a prism coupler. A rutile prism was used as the input coupler. The light beam propagated through the entire length inside the film and then radiated into free space at the left-hand edge of the specimen, leaving a bright area which indicates the near-field structure. A few specks of light are observed along the light streak, and a large spot is observed near the left-hand edge. In other experiments, the single-crystal film was grown on the x- and y-planes of the substrate. The film grown on the x-plane included several cracks running along the perfect cleavage plane {102} of LiNbO<sub>3</sub>. From detailed observations of the film surface under a differential microscope, it was found that weakly observed scattering along the propagating light beam was caused by the roughness of the film surface.

Ballman et al. (1975) have modified the method developed by Miyazawa. Evidence is presented which suggests that the epitaxial growth by melting involves a diffusion mechanism between the melting liquid and the LiTaO<sub>3</sub> substrate. Although the growth process involves simple melting of LiNbO<sub>3</sub> powder on the surface of LiTaO<sub>3</sub> substrates, the successful production of a high quality film is especially dependent upon the manner in which the powder is applied to the substrate.

If the powdered layer is too thick or if the thickness varies appreciably over the surface area, puddles of LiNbO<sub>3</sub> form during the melting process. They produce a very uneven surface after recrystallization and make the fabrication of an optical waveguide quite difficult.





LiNbO<sub>3</sub> powders of about 30  $\mu$ m particle size were suspended in a lacquer. This LiNbO<sub>3</sub>-lacquer suspension was then 'painted' on the LiTaO<sub>3</sub> substrates. These painted layers were practically flat, and when dry, the suspended powders were firmly fixed to the substrate. The specimens were then brought up to the desired firing temperature (1260°C and 1320°C) in a resistance furnace. During the warm-up period, the organic lacquer is completely decomposed and leaves a very uniform layer of LiNbO<sub>3</sub> powder ready for the melt phase epitaxial reaction. After a 30 min soak period at the firing temperature the samples were cooled down to room temperature at a rate of 20 deg/h.

The film thickness can be controlled by varying the concentration of the  $LiNbO_3$ -lacquer suspension. Similarly, thickness can be built up by additional painting and firings. The films required light surface polish or buffing in order to couple laser light in or out via a rutile prism-film coupler. Figure 2.4 shows the phase diagram for LiNbO<sub>3</sub> (film) and LiTaO<sub>3</sub>(substrate) as to the two end members (Peterson et al. 1967). The shaded area represents the temperature range covered in this study and it includes the reaction temperature (1300°C) reported by Miyazawa in his work.



Fig.2.4 LiNbO<sub>3</sub>-LiTaO<sub>3</sub> phase diagram (Peterson et al. 1970).

It is evident that in a melt phase epitaxial process several factors combine to determine the final composition of the film. The phase diagram itself predicts the film composition one could obtain as a function of the reaction temperature. An additional, and important consideration is the rate at which  $LiTaO_3$ -lacquer will dissolve in the molten  $LiNbO_3$ -lacquer during the soak period. A further compositional grading can occur due to segregation which takes place as the molten layer crystallizes in accordance with the phase diagram. There is then the solid-solid diffusion process which occurs as the grown film is slowly cooled to room temperature.

The film thickness measurements were obtained by using an electron microprobe and tracking across the cleaved edge of a specimen. The electron beam tracked across the surface of the film and continued across the film-substrate boundary. As the beam first enters the film, both the niobium and tantalum counts rise and this is indicative of the solid solution nature of the film. As the beam leaves the film and enters the substrate region, the niobium intensity diminishes. The distance tracked while the niobium intensity is elevated is equal to the film thickness. Figure 2.5 shows the effect in a film  $\sim$ 3 µm thick.

The role of solid-solid diffusion and how it may be used to alter the properties of a grown film is shown in Fig.2.6. Curve A represents the index of the refraction profile for a solid solution film. Curve B represents the index profile for the same crystalline film after it has undergone an anneal at  $1200^{\circ}$ C for 48 h. It is clear from the lowering of the refraction index and the increased film thickness (3.7 µm to ~10 µm) that extensive diffusion has occurred in the solid state during the anneal.

The loss of the fundamental (m = 0) waveguide mode was determined by measuring the light lost in transmission between the input and the output coupler. Solid solution films of the type shown here gave losses of about 5 dB/cm. The same method was also used to obtain (K, Li) LiNbO<sub>3</sub> films (Adachi et al. 1979) up to several microns thick. The quality of the film depends on the choice of substrates and the way in which the ceramic powder is deposited onto the substrate surface.

## 2.2 The capillary liquid epitaxial (CLE) technique

The capillary liquid epitaxial technique is one of the new methods for obtaining





ferroelectric films. The method is a modification of the well-known Stepanov's technique (Stepanov 1963; Maslov 1977) which gives single crystals in the form of thin films (Fukuda and Hirano 1976; Fukuda and Hirano 1980).

## 2.2.1 CLE growth procedure

The growth setup used for CLE growth is the same as used in the preparation of  $LiNbO_3$  ribbon crystals (Fukuda and Hirano 1975). The growth setup comprises a 50 mm diameter×30 mm long Pt crucible, a gap-shaped Pt capillary with a 0.5 mm width and 30–50 mm height, a conical Pt afterheater, ceramic insulators and a substrate pulling mechanism. The growth geometry is shown in Fig.2.7. Growth is initiated when the tip of the substrate touches the liquid in the crucible, with about 0.5 mm separation between the substrate and the capillary plate. When the substrate is pulled, the solution is mixed with that in the capillary gap, on the top of the die. Therefore, the capillary die is used as a reservoir to feed the layer of liquid between the exterior of the die and an adjacent substrate. Temperature adjustment is accomplished by monitoring the liquid temperature.

Figure 2.8 shows the geometry for an improved CLE technique and a multilayer growth technique, proposed by Fukuda and Hirano (1980). In the improved CLE technique, the capillary die comprises two parallel vertical plates of different length suitably spaced to provide the capillary action (see Fig.2.8a). The liquid rises through the capillary die top and growth is then initiated. The substrate plate constitutes the die wall complementing the lower end portion of the shorter capillary plate. Figure 2.8b shows that a film (LiNbO<sub>3</sub>) or a ribbon (LiTaO<sub>3</sub>) crystal can be grown using the improved CLE and EFG techniques simultaneously.

LiNbO<sub>3</sub> thin films were grown from a LiNbO<sub>3</sub>-LiVO<sub>3</sub> molten solution. A mixture of 50 mol%  $Li_2CO_3$ , 10 mol%  $Nb_2O_5$  and 40 mol%  $V_2O_5$  was used as a starting material. The mixture was heated in a Pt crucible by rf heating and the solution temperature was adjusted to a value suitable for growth (850-900°C). The film thickness was controlled by solution temperature and pulling speed. After terminating growth, the furnace was cooled to room temperature at a rate of about 200°C/h. For LiTaO<sub>3</sub> substrates mirror-polished plates (typical dimensions 15×30×2 mm) were fabricated from Czochralski grown boules. The following orientations were used: (001) <100>, (100), <210>, (130° rotated Y plate) <210> and (170° rotated Y plate) <210>, where () and <> show the plate plane and pulling direction, respectively.

LiTaO<sub>3</sub> thin films were grown from a LiTaO<sub>3</sub>-LiVO<sub>3</sub> molten solution, as were LiNbO<sub>3</sub> films from a LiNbO<sub>3</sub>-LiVO<sub>3</sub> molten solution. For substrates, LiNbO<sub>3</sub> plate crystals were fabricated from Czochralski grown boules. Orientations were (001) <100>, (131° rotated Y plate) <210>, and (210)<112.1° rotated Y>.

For several advanced experiments, based on the CLE technique, multiplelayer structure films or striped films on substrates and multiple ribbons were grown. The following substrates were used: LiNbO<sub>3</sub> films on (001)<100> LiTaO<sub>3</sub> plates, LiTaO<sub>3</sub> films on (001) <100> LiNbO<sub>3</sub> plates, and (001)<100> LiTaO<sub>3</sub> substrates with 200 or 25  $\mu$ m width and 0.75  $\mu$ m depth along <100>



Fig.2.6 Index of refraction profile versus thickness for a film before and after 1200° anneal (Ballman et al. 1975).

Fig.2.7 (right) Geometry of CLE growth (Fukuda and Hirano 1980).

direction, as shown in Fig.2.9 (made by ion beam etching).  $LiNbO_3$  thick films were grown on (001)<100>LiTaO\_3 plates or as-grown ribbons, from a  $LiNbO_3$  melt instead of a  $LiNbO_3$ -LiVO\_3 solution. The film growth conditions are presented in Table 2.1.

#### 2.2.2. CLE growth and crystal quality

LiNbO<sub>3</sub> epitaxial thin films have been successfully grown onto LiTaO<sub>3</sub> substrates. The film thickness, when grown at 970°C and a 3 mm/min pulling rate, was about 2 µm and almost constant, except near the film edge. The film surface was smooth, clear and mirror-polished. The side view of the film-substrate boundary observed by optical microscopy was very sharp. An X-ray rocking curve from the (006) reflection showed clearly separated four peaks of CuK<sub>a1</sub> and CuK<sub>a2</sub> radiation from the film and substrate (Fukuda and Hirano 1976).



**Fig.2.8** Geometry for improved variations of the CLE technique (a) and multiple-layer growth technique (b) (Fukuda and Hirano 1980).

Film	Substrate	Solution temperature (°C)	Pulling rate (mm/min)	Film thickness (µm)	
LiTaO,	LiNbO <sub>3</sub>	1026	2	2	
LiNbO <sub>3</sub>	LiTaO <sub>3</sub>	995	1.8	0	
LiNbO <sub>3</sub>	LiTaO,	975	2.3	3.5	
LiNbO <sub>3</sub>	LiTaO,	970	3	3	
LiNbO <sub>3</sub>	LiTaO <sub>3</sub>	965	2.3	4.5	

Table 2.1 LiTaO, and LiNbO, th	hin-film growth conditions	(Fukuda, Hirano	1976)
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Fig.2.9 A (001)<100>LiTaO<sub>3</sub> substrate with 20  $\mu$ m wide and 0.75  $\mu$ m deep grooves etched with an ion beam, along the <100> direction (Fukuda and Hirano 1980).

These results suggest that the films obtained were of high quality.

The thickness of the film is a function of the solution temperature and pulling rate, as has been reported in detail (Fukuda and Hirano 1976). The lower the solution temperature, the thicker the film obtained. But as the temperature became lower, many small hillocks appeared on the film surface and slip boundaries were detected near the edge. Rapid pulling produced a gradual decrease in thickness within the crystal, while slower pulling produced a gradual increase in thickness.

LiNbO<sub>3</sub> films, which were grown onto the (100)<210>,  $(131^{\circ}$  rotated Y plate)<210>, and  $(170^{\circ}$  rotated Y plate)<210> using the same growth conditions as employed on the (001)<100> plates, were of poor quality having rough surfaces and many defects. The film quality was remarkably improved by adjusting the initiated temperature using dies of different lengths. It is assumed that the appropriate growth temperature was achieved after carving quickly the solution onto the substrate using capillary action so that the film did not suffer bad effects of large supercooling by lowering the solution temperature.

The improvement was observed as the result of changing the die length (l) (where *l* means the part of a gap-shaped capillary 0.5 mm wide) for growth on the (170° rotated Y plate)<210> plate.

Figure 2.10 shows typical etch patterns for LiNbO<sub>3</sub> films grown on (-Z)LiNbO<sub>3</sub> (i.e.(001)LiNbO<sub>3</sub>) plates (+Z)LiNbO<sub>3</sub> plates and (+Z) LiTaO<sub>3</sub> plate crystals, respectively. Etching was carried out for 15 minutes at the boiling point of the etchant (HF:HNO<sub>3</sub> = 2:1). For the crystals examined, it was observed that the film surface side was always (-Z) plane over the whole plate irrespective of substrate orientation. It is suggested that the film grown by the CLE technique is of the single domain type. This may be attributed to the fact that growth is initiated in the ferroelectric phase.

The lattice constant  $c_0$  of a LiTa<sub>x</sub>Nb<sub>1-x</sub>O<sub>3</sub> film on a (001)<100>LiTaO<sub>3</sub> plate, which was grown using the mixture of LiNbO<sub>3</sub> (10 mol%), LiTaO<sub>3</sub> (10 mol%) and V<sub>2</sub>O<sub>5</sub>(80 mol%), was measured by X-ray diffraction. The value of  $c_0$  was 13.80 Å, which was nearly the same as that of the bulk LiTa<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3</sub> crystal (Swartz et al. 1975). This suggests that  $K_{eff}$  of the CLE grown film from these systems approached unity, as is indicated in EFG growth (Fukuda and Hirano 1975).

 $LiTaO_3$  thin films could be also grown with good epitaxy onto  $LiNbO_3$  substrates, whose melting point was about 400°C lower than that of the film





**Fig.2.10** Typical etch patterns for a LiNbO<sub>3</sub> film (a) (-Z)LiNbO<sub>3</sub> plate (b) (+Z) LiNbO<sub>3</sub> plate and (c) (-Z) LiTaO<sub>3</sub> plate, respectively (Fukuda and Hirano 1980).

material. The thickness of the films grown at  $1026^{\circ}$ C at a pulling rate of 2 mm/min, was about 2 µm. The film surface and quality observed and measured by optical microscopy and X-ray diffraction were nearly the same as that of LiNbO<sub>3</sub> films on LiTaO<sub>3</sub> substrates.

Figure 2.11 shows the as-grown film surface and side view of LiTaO<sub>3</sub> and LiNbO<sub>3</sub> multiple-layer structure films on (001)<100> LiTaO<sub>3</sub> substrates. The film surface flatness is almost the same as that of the single layer films used as a substrate (see the dotted line in Fig. 2.11). The film are about 5  $\mu$ m thick. In particular, it is characteristic that the film-to-film boundary observed by a polarized microscope is very sharp.

 $LiNbO_3$  films were grown onto (001)<100>  $LiTaO_3$  substrates in which striped ditches 200 or 25 µm in width and 0.75 µm in depth along the pulling direction had been prepared (see Fig.2.9). It should be noted that striped ditches were completely buried under films and that the film surface was almost flat.

From the consideration of the CLE characteristics mentioned above it is suggested that a buried film or layer structure film, as depicted in Fig.2.12, can be grown by combining the CLE technique with etching and polishing. Shaped films can also be grown using a shaped die.

Using the die as shown in Fig.2.8,  $LiNbO_3$  thin films and  $LiNbO_3$  thick films were grown on (001)<100>  $LiTaO_3$  substrates. Thin films grown from the  $LiNbO_3$ - $LiVO_3$  system were essentially the same as those grown using the die shown in Fig.2.7. The film grown from a  $LiNbO_3$  melt was 200 µm thick. (001)<100> $LiNbO_3$  on  $LiTaO_3$  multiple ribbons were also grown. When grown from the  $LiNbO_3$  melt, the surface was not smooth and contained striations and ripples, as was seen in the EFG grown ribbon (Fukuda and Hirano 1975). The composition profiles perpendicular to the film-substrate boundary were determined using an X-ray probe microanalyzer. As shown in Fig.2.13, there is a sharp transition from the Nb- to the Ta-containing layer.

Capillary liquid epitaxy was used to grow ferroelectric films of  $LiNbO_3$  (Khachaturyan et al. 1984; Fukuda and Hirano 1976; Fukuda and Hirano 1980),  $Li(Nb,Ta)O_3$  and  $LiTaO_3$  (Fukuda and Hirano 1976; Fukuda and Hirano 1980), and KNbO<sub>3</sub> (Khachaturyan and Madoyan 1980; Khachaturyan and Madoyan 1984). The capillary liquid epitaxy method has the following advantages: the possibility of obtaining films from a high-temperature material on substrates from materials with a lower melting temperature, a smooth film surface and a clearly pronounced film-substrate boundary.

## 2.3 The liquid-phase epitaxy (LPE) technique

Analysis of experimental studies of the growth of thin-film ferroelectric structures shows that the most perfect epitaxial layers of  $LiNbO_3$ ,  $Li(Nb,Ta)O_3$ ,  $KNbO_3$  were obtained by the liquid-phase epitaxy technique. The optical losses in light propagation through the indicated structures lie within the range 0.5– 3 dB/cm.

The low growth rate typical of liquid-phase epitaxy makes it possible to control the size of epitaxial layers to an accuracy much higher than that attained





**Fig.2.11** As-grown film surface flatness and side view of a LiTaO<sub>3</sub> and LiNbO<sub>3</sub> multiple-layer structure film on a (001)<100>LiTaO<sub>3</sub> substrate (Fukuda and Hirano 1980).

in diffusion processes.

Kondo et al. (1975) applied the liquid-phase epitaxy method to growing  $LiNbO_3$  films. A mixture of 50 mol%  $Li_2O$ , 10 mol%  $Nb_2O_5$  and 40 mol%  $V_2O_5$  was chosen as a starting composition for LPE growth. The composition is equivalent to 20 mol%  $LiNbO_3$  in the pseudobinary system. After weighing the appropriate amount of  $Li_2CO_3$ ,  $Nb_2O_5$ , and  $V_2O_5$ , the mixture was heated at 1200–1250°C for more than 3 h in a resistance furnace. A Pt crucible 50 mm in diameter, 40 mm in height, and 1 mm in wall thickness was used. The furnace was divided into three heating zones. Each zone was controlled independently within an accuracy of  $\pm 0.5°C$ , so that the vertical temperature distribution was almost uniform up to 200 mm above the crucible base.

After achieving complete melt homogeneity, the molten solution was cooled to about 850°C at a rate of 30°C/h, and was held more than 3 h at this temperature.

A *c*-cut LiTaO<sub>3</sub> substrate, positioned slightly above the molten solution to be equilibrated with the solution temperature, was dipped in the molten solution. An appropriate dipping temperature was  $825-850^{\circ}$ C. The substrate was then removed from the molten solution and slowly brought to room temperature.



Fig.2.12 A buried film or layered structure film are shown, which can be grown by combining the CLE technique, etching and polishing (Fukuda and Hirano 1980).





The growth rate of the epifilm was examined by changing the dipping time, and it was estimated to be approximately  $0.1 \,\mu$ m/min. One end of the substrate was cut obliquely in order to drain the flux, and the flux was found to drain from the specimen upon removal from the molten solution. The residue of the flux adhering to the as-grown specimen was washed away with water.

The as-grown specimen thus obtained is shown in Fig.2.14a. The surface appears clear and smooth, and the film seems transparent and colourless. Figure 2.14b indicates a cross-sectional profile of the specimen near the film-substrate boundary. The film thickness was measured to be  $\sim$ 3.1 µm, except near the boundary. Protuberance at the boundary may be caused by 'wetting' of the molten solution onto the substrate.

The roughness of the as-grown surface depends on the film thickness. Small hillocks, which appear on the surface, are surrounded by  $\{10\overline{2}\}$  facets of LiNbO<sub>3</sub>. The hillocks on the growing surface are adjacent to a constitutional supercooled solution, and a preferential growth of the hillocks occurs. As a result, they may become larger and grow faster as the growth proceeds. Consequently, the film surface becomes rougher.







Diffraction angle



The crystallinity of the film was investigated by taking X-ray rocking curves. Figure 2.15 shows a (006) rocking curve. The four peaks, corresponding to  $CuK_{\alpha 1}$  and  $CuK_{\alpha 2}$  radiations from the film and the substrate, are well separated. This characteristic feature indicates that the film has a high single crystallinity with good epitaxy.

The film was also grown onto the y-plate substrate. The growth rate was 3-5 times faster than onto the c-plane. However, the film surface was rougher compared to the c-plane, and an X-ray rocking curve revealed that the film had poor epitaxy with many microcracks. This may be closely related to the lattice parameter mismatch between LiNbO<sub>3</sub> and LiTaO<sub>3</sub>. The mismatch for the c- and a-axes was about 0.7 and 0.1%, respectively. The anisotropy of the lattice mismatch in the y-plane results in the nonuniform growth of the film caused by mismatch dislocations.

Baudrant et al. (1978) has also used LiTaO<sub>3</sub> substrates for liquid-phase epitaxy of lithium niobate.

LiTaO<sub>3</sub> wafers were polished to a high degree of perfection, mounted horizontally on a platinum substrate-holder and slowly introduced into the vertical furnace for epitaxy. A solution obtained from a typical charge of 27 wt%  $Li_2CO_3$ -20 wt%  $Nb_2O_5$ -53 wt%  $V_2O_5$  had a saturation temperature of about 950°C. Growth temperatures were chose between 940 and 945°C. Under these conditions, the growth rate was about 0.5 µm/min.

In order to obtain smooth monolayer-type epitaxial films rather than islandtype films, several crystallographic orientations of the substrate were tested. Symmetry considerations and a good fit between the parameters suggested an attempt to try first epitaxial growth on the (00.1)basal planes.

Several LiNbO<sub>3</sub> films were isothermically grown from undercooled solutions during different growth periods in order to follow the successive growth steps of an epitaxial layer. The [00.1] oriented films become rapidly continuous

and from thickness of about 2  $\mu$ m are perfectly smooth and directly usable for light propagation experiments.

In fact, the profile of the transition layer could be determined by ionic analyser chemical control. This profile shows the existence of an ~2000 Å thick transient layer. This can be explained either by an interdiffusion  $Ta \leftrightarrow Nb$  on the LiTaO<sub>3</sub> matrix or, more probably, by a slight dissolution of the substrate before growth. Thus, the first growing layers will have composition of the type LiTa<sub>x</sub>Nb<sub>1-x</sub>O<sub>3</sub> varying rapidly from 1 to 0.

From an optical point of view, this LPE film profile can, however, be considered as a step interface compared to the melt phase epitaxial film profile which exhibits a graded index (Takada et al. 1974). It should be noted that too fast a cooling rate after epitaxy involved crack formation both in the film and in the substrate parallel to the cleavage planes (01.2).

In their earlier paper, Baudrant et al. (1975) used a substrate of lithium niobate crystals with orientation  $\perp c$ . The preparation and technology of epitaxial layers were identical with those described above.

The method of liquid-phase epitaxy from a limited volume of solution in a melt has been proposed recently by Madoyan et al. (1983) and Madoyan et al. (1985). Crystallization proceeds here from a limited volume of flux (solution in melt) contained in a capillary formed by two parallel substrates. When the gap between the substrates is small, the liquid-phase convection is absent and the growing surface is fed by diffusion of the dissolved component. The film thickness depends on the distance between the substrates (the capillary width), epitaxy temperature regime, material and substrate orientation. Low cooling rates provide precipitation of the layer onto the substrate surface without crystallization in the flux.

The liquid-phase epitaxy method is economical owing to the possibility of using the solvent material repeatedly. The basic shortcoming of the method, when applied to lithium niobate, is complicated control of obtaining layers with prescribed parameters. The tendency of the solution in melt to supercooling (to  $70-80^{\circ}$ C) hampers a precise location of the liquidus curve (the initial epitaxy temperature). Chemical activity of the liquid phase restricts strongly the choice of constructional material for crucibles and substrate-holders.

# 2.4 Physico-chemical basis of capillary liquid-phase epitaxy

Crystallization from a buffered melt exhibits functions of both the solution and melt methods, which accounts for the wide range of compositions employed, including the majority of melting compounds. Liquid-phase epitaxy is determined by thermodynamics, kinetics and technology (Andreev et al. 1975). The first of these factors is responsible for the character of phase equilibrium in the substrate-buffered melt-vapour system. These factors completely determine the process under equilibrium conditions only. The kinetic factors have a substantial effect upon the epitaxy process under nonequilibrium conditions. The growth kinetics are determined by the feed of the growing surface and by the activation energy of the process at the phase boundaries. The methodical factors include those connected with process technology.

Phase equilibrium in the substrate-solution system determines the nature of crystallization. A saturated liquid phase (i.e. a saturated solution of the compound under crystallization in a melt of another material) is brought in contact with the substrate, and under subsequent supersaturation (due to cooling or additional feed from the solid or gas phase) the epitaxial layer precipitates onto the substrate. The liquid-phase composition and the slope of the liquidus curve determine the composition, growth rate and thickness of the film. In reality, the process proceeds in nonequilibrium conditions for a simple reason that crystallization requires supersaturation, which in itself is a deviation from equilibrium. This explains why the crystallization process and the epitaxial layer parameters are characterized by other factors, namely, by a limited speed at which components approach the growing surface (typically, in a non-mixing and isothermic solution), by supersaturation of the solution during growth, by nucleation and the growth mechanism on the surface and by convection due to temperature and composition gradients. In addition, at an early stage of a new heterostructural layer, that is, in the heterotransition phase, there always exists a thermodynamic instability between the solution and the crystal surface.

Thermodynamic instability between the crystal surface and the liquid phase must exist provided the solid state composition, when in equilibrium with the liquid phase, differs from the composition of the crystal which is in contact with the solution (Bolkhovityanov and Chikichev 1982). Furthermore, the crystallization process depends on the relation between the crystallization rate of a given substance and the cooling rate of the solution for a definite state of the substrate surface, on the initial level of solution saturation and on other factors. The following versions of this relationship are possible. If the crystallization can alternate due to insignificant thermal fluctuations. Thus, the epitaxy process will have a fluctuational character, which can cause a distortion of the crystallization front shape. This effect is observed at minimum rates of induced cooling of the system.

Under epitaxy, the solution in melt is in contact with the substrate onto which the layer is crystallized. The epitaxy process and the properties of the precipitated layer are therefore also determined by the properties of the substrate. The substrate only has a direct effect upon the crystallization of the first layer (with the thickness of several lattice constants), when the epitaxy process is determined by the character of phase equilibrium at the substrate-solution boundary and by the kinetics of surface processes. Although the further growth proceeds on the epitaxial layer, part of the substrate parameters affect the crystallization during the whole process (e.g. the substrate orientation). In this connection, in the choice of material for a substrate, along with physical parameters, such as the refractive index, optical coefficients, etc., the crystallochemical specificities should be taken into account. The most important condition for obtaining perfect layers is uniformity of the crystalline structure of the film and substrate with a difference between the lattice constants not higher than 1%. The substrate must be chemically neutral with respect to the liquid phase and its solubility in the melt insignificant. Finally, substrate-film pairs should be chosen to have close thermal coefficients of expansion lest temperature variations should induce strong tensions along the interface.

The close values of the feed rates and crystallization promote conditions of approximate constancy of the buffered melt supersaturation. This provides a higher uniformity of crystallization layers. When the substance approaches the crystallization front at a rate exceeding the crystallization rate, the supersaturation of the solution in the melt gradually increases. Under these conditions, the various active centres have an increasing effect upon the layer growth. The role of such centres is most often played by defects of the substrate surface and atoms of impurities in the solution. When the induced cooling rate of the system differs only slightly from the optimum epitaxy conditions, the predominant substance crystallization on these centres can be seen as a slight worsening of the structural perfection of the layers. A faster cooling of the system leads to a stronger predominant role of defects of the orienting surface in the crystallization process. The extreme manifestation of this effect is the polycrystalline layer growth which takes place at considerable rates of induced cooling of the system. Thus, for the growth of layers with a perfect enough structure and morphology of the surface, the solution-substrate system should be so cooled that a strictly definite and constant amount of substance is fed to the crystallization front per unit time.

The basic requirements on solvents used in liquid-phase epitaxy are as follows (Andreev et al. 1975):

1. a low melting temperature of the solvent and a low vapour pressure at the epitaxy temperature;

2. a high solubility of material under crystallization, which makes it possible to obtain epitaxial layers at low temperatures;

3. stability of the solid phase of the dissolving substance under growth conditions;

4. solvent neutrality to the crucible material;

5. a low solvent solubility in the crystallized layer (the solvent contaminates the film less if the film and solvent material have identical ions).

Under LPE of ferroelectrics, the constituent liquid of the solution is most often one of the basic components of the solid state, and phase equilibriums are such that the liquid solution from which precipitation occurs is dilute with respect to all the components except one.

For instance, for growing ferroelectric films of lithium niobate from a solution in melt, the solvent should be nonvolatile and nonviscous, with a wide range of supercooling, and must not form compounds and solid solutions with the dissolved substance. The thermal coefficient of solubility must have values of the order of 0.1% g/grad in order that the solution in melt could be cooled slowly. To obtain films of high optical quality and structural perfection, it is necessary to optimize simultaneously all the technological parameters, namely, supersaturation and viscosity of the solution, saturation temperature, *etc.* 

For an adequate choice of solvent, the solubility of lithium niobate was investigated in various inorganic layers:  $PbO-PbF_2$ ,  $Li_2O-MoO_3$ ,  $Li_2O-V_2O_5$  (Kondo et al. 1975; Baudrant et al. 1975),  $Li_2O-B_2O_3$ ,  $Li_2O-WO_3$  (Kondo et al. 1975; Ballman et al. 1975), LiF, LiCl (Kondo et al. 1975), KCl (Baudrant et al. 1975), K<sub>2</sub>WO<sub>4</sub> and WO<sub>3</sub> (Khachaturyan and Madoyan 1978). The possibility

of LiNbO<sub>3</sub> precipitation from buffered melts  $Li_2O-V_2O_5$ ,  $Li_2O-B_2O_3$  and  $Li_2O-WO_3$  was revealed. All the three systems exhibited precipitation of lithium niobate without the formation of other phases in a wide range of concentrations.

Before any liquid-phase epitaxial technique was applied to film growth, several systems of interest,  $K_2WO_4$ -LiNbO<sub>3</sub>,  $KVO_3$ -LiNbO<sub>3</sub>,  $NaVO_3$ -LiNbO<sub>3</sub> and  $Li_{1-x}Na_xVO_3$ -LiNbO<sub>3</sub>, were investigated (Neurgaonkar et al. 1980) and the temperature and compositional boundaries over which LiNbO<sub>3</sub> crystallizes were established by the differential thermal analysis technique.

Examination of the phase diagrams in Fig.2.16 shows that the LiNbO<sub>3</sub> phase crystallizes in all the three systems when the concentration of LiNbO<sub>3</sub> is above 50 mol% and, hence, the dipping temperature had to be in the 1100 to 1150°C range. The LPE growth of the Nb-rich films was successful on the Y-cut LiNbO<sub>3</sub> substrates from the  $K_2WO_4$ -LiNbO<sub>3</sub> and  $KVO_3$ -LiNbO<sub>3</sub> systems, and the unit cell *a* varied from 5.148 Å for LiNbO<sub>3</sub> substrate to 5.153 Å for the Nb-rich LiNbO<sub>3</sub> films. Ballman et al. (1975) also studied the  $K_2WO_4$ -LiNbO<sub>3</sub> system, and their results were in excellent agreement with those of Neurgaonkar and Staples (1981). According to Neurgaonkar et al. (1978), K<sup>+</sup> does not prefer the sixfold coordinated Li<sup>+</sup>-site in the LiNbO<sub>3</sub> structure; the changes in the unit cell *a* are therefore considered to be due to changes in the Li:Nb ratio.

In the third system,  $NaVO_3$ -LiNbO<sub>3</sub>, the situation is completely different. Crystal chemistry (Neurgaonkar et al. 1980) shows that about 7 mol% sodium dissolves in the LiNbO<sub>3</sub> structure and, for this addition of sodium, the unit cell *a* changed from 5.148 Å for LiNbO<sub>3</sub> to 5.179 Å for Li<sub>0.93</sub>Na<sub>0.07</sub>NbO<sub>3</sub>. This



Fig.2.16 Partial phase diagram: a)  $K_2WO_4$ - LiNbO<sub>3</sub>; b) KVO<sub>3</sub>- LiNbO<sub>3</sub>; c) NaVO<sub>3</sub>-LiNbO<sub>3</sub> (Neurgaonkar and Staples 1981).

created a large lattice mismatch between the LiNbO<sub>3</sub> or LiTaO<sub>3</sub> substrate and the film, and the LPE growth was therefore unsuccessful.

## 2.4.1 The phase diagram of LiVO<sub>3</sub>-LiNbO<sub>3</sub>

The analysis of the results presented above shows that obtaining films is much more difficult from the borate and tungsten systems than from the vanadium one. The most suitable solvent for LiNbO<sub>3</sub> appeared to be the composition  $Li_2O-V_2O_5$  which satisfies the above-mentioned requirements. The excessive solvent is easily removed from the epitaxial structure surface by boiling in distilled water.

To choose optimum growth conditions and to study the growth kinetics, exact data are required on the phase diagram of the solvent-precipitate system. Since the data in the literature are very diverse, it became necessary to carry out systematic physico-chemical studies of the pseudo-binary system  $LiVO_3$ - $LiNbO_3$ .

The character of the interaction between LiNbO<sub>3</sub> and the flux  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$  was preliminarily investigated. Cooling the melted mixture with 10 to 100 mol% LiNbO<sub>3</sub> at a rate of about 1 grad/min resulted in the formation of small crystals which could be easily separated from the rest of the buffered melt by washing in distilled water. X-ray diffraction examination showed that the precipitated crystal powder corresponded to lithium niobate. It should be noted that, in some cases (LiNbO<sub>3</sub> concentration from 30 to 50 mol%), the crystal size reached 5 mm. So, the possibility of LiNbO<sub>3</sub> crystal growth by the spontaneous crystallization method has been shown.

Figure 2.17a shows the useful part of the pseudobinary phase diagram investigated by differential thermal analysis (DTA), direct observations of the melt and X-ray analysis (Baudrant et al. 1978).

Using heating and cooling rates of 10 or 5°C/min, thermal effects due to dissolution and crystallization can be detected. Thus, the appearance of the LiNbO<sub>3</sub> solid phase from various concentrated solutions is easily detectable and is represented by the dark line 2 in Fig.2.17a which is, in fact, the critical nucleation curve. Endothermal phenomena due to dissolution are less discernible at a low solution concentration and must often be completed by microscopic and weighing observations during liquid-phase epitaxy experiments. It is thus possible to draw the dotted line in Fig.2.17a which represents the liquidus curve.

The eutectic point has been localized at about 4 mol% of LiNbO<sub>3</sub> by accurate X-ray investigations of the primary largest crystals found in the bulk solid 'residue'. The primary crystals have been identified as  $LiVO_3$  on one side of the eutectic point and  $LiNbO_3$ , on the other side. This diagram shows that  $LiNbO_3$  can be crystallized over a wide composition range. Finally, Baudrant et al. (1978) point out that the domain of the slow growth rate is very narrow, extending no more than 10°C under the liquidus curve.

The liquidus curve was calculated using the Schröder equation:

 $\log N_i = -a \times 10^4/T + b$


**Fig.2.17** a) Pseudobinary LiNbO<sub>3</sub>-LiVO<sub>3</sub> phase diagram, (1) – liquidus curve. (2) – critical nucleation curve (Baudrant et al. 1978); b) Dependence of the mole fraction logarithm on inverse temperature (Madoyan et al. 1979).

where  $N_i$  is the molar fraction of the dissolved component. The linear dependence of the logarithm of the molar fraction on the inverse temperature (Fig.2.17b) suggests an ideal nature of the system solutions. The melting heat of an individual LiNbO<sub>3</sub>, determined from the slope angle, is equal to 13.2 kcal/mole.

Analysis of the phase diagram shows the possibility of obtaining films and crystals of lithium niobate within a wide temperature range of 700 to  $1200^{\circ}$ C. Within the range of 750–950°C (15–30 mol% LiNbO<sub>3</sub>), the slope of the liquidus curve permits an easy growth control since a slight temperature variation does not entail a variation of the solution composition. The growth rate of the layer can be estimated from the variation of the solution concentration at a given cooling rate.

### 2.4.2 Phase diagram of LiVO<sub>1</sub>-Li(Nb,Ta)O<sub>1</sub> pseudobinary system

Phase diagrams of the LiVO<sub>3</sub>-Li(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>3</sub> pseudobinary system, ranging from 0 to 1, were investigated, where x is the mole ratio of Ta<sub>2</sub>O<sub>5</sub>/(Ta<sub>2</sub>O<sub>5</sub>+Nb<sub>2</sub>O<sub>5</sub>) (Kondo et al. 1979). The temperature-composition range, in which Li(Nb,Ta)O<sub>3</sub> solid solution crystallizes, was determined by differential thermal analysis (DTA). Phase diagrams for Li<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>, Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub>-Nb<sub>2</sub>O<sub>5</sub> pseudobinary systems were reported on by Reisman and Holzberg (1965), Reisman and Mineo (1962) and Waring and Roth (1965), respectively.

Samples for DTA experiments were prepared by mixing chemical reagent grade LiCO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub> and V<sub>2</sub>O<sub>5</sub> powder in the desired ratios. The mixtures were placed in a platinum cell. DTA measurements were conducted in a hightemperature thermoanalyzer using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a reference. Heating-cooling cycles were carried out at a rate of 20°C/min, and were repeated several times. Heating or cooling rates below 20°C/min often resulted in a very weak response corresponding to thermal effects due to dissolution and crystallization. The temperature correction of DTA measurements was made by using LiVO<sub>3</sub> (616°C), NaCl (800°C) and LiNbO<sub>3</sub> (1250°C) as references at the same heating-cooling rate. Liquidus temperatures were determined from the heating curves, because the heating curves did not indicate significant overheating effects, while the cooling curves often indicated large supercooling effects. Furthermore, liquidus temperatures were also recognized by saturation temperatures. The saturation temperature is determined as the temperature where neither dissolution nor crystallization occurs when a substrate is dipped in the solution. The liquidus temperature from the heating cycle agreed with the saturation temperature within  $\pm 10^{\circ}$ C.

The results are given in Fig.2.18, where the end members are stoichiometric  $LiVO_3$  and specific solid-solution compositions of the pseudobinary system  $Li(Nb_{1-x}Ta_x)O_3$ , and liquidus temperatures for several values of x are shown. On the phase diagram of the  $LiVO_3$ -LiNbO<sub>3</sub> pseudobinary system, x = 0.0 in the Fig.2.18, the liquidus temperature decreases from 1250°C, the melting point of LiNbO<sub>3</sub> to 960°C at 20 mol% LiNbO<sub>3</sub>. A pseudoeutectic occurs at about 3 mol% LiNbO<sub>3</sub>.

The liquidus lines become higher and their slopes steeper as the parameter x increases. Figure 2.18 shows that the primary phase  $Li(Nb,Ta)O_3$  can crystallize at percentages higher than 3 mol%  $Li(Nb_{1-x}Ta_x)O_3$  for each x value.

Tamada et al. (1991) reported a LiNbO<sub>3</sub> thin-film optical waveguide grown by liquid phase epitaxy (LPE) using  $Li_2O-V_2O_5$  flux and a 5 mol% MgOdoped Z-plate LiNbO<sub>3</sub> substrate. Unfortunately, there was a large optical loss at blue-green wavelengths in spite of its high crystallinity and good surface morphology. This optical absorption which could not be completely removed by the heat treatment in a flowing oxygen with less than a few vol.% ozone after fabrication, was due to the  ${}^{3}F_{1}-{}^{3}F_{2}$  crystal field transition of V<sup>3+</sup> ions which were incorporated into the LiNbO<sub>3</sub> film from the Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> flux. Therefore, in order to realize a Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> thin film optical waveguide for blue wave-



80 Li(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>3</sub> **Fig.2.18** Phase diagram of LiVO<sub>3</sub>-Li(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>3</sub> O<sub>3</sub> mol % pseudobinary system (Kondo et al. 1979). lengths, another flux system which is free from transition metals must be developed.

 $Li_2O-B_2O_5$  was targeted as a likely candidate for this flux system for several reasons. First, it does not contain transition metals, so that optical absorption centres might not be introduced even if boron were incorporated into the film. Second, the reported eutectic reaction temperature of 800°C on the LiNbO<sub>3</sub>-LiBO<sub>2</sub> pseudobinary system (Ballman et al. 1975) is sufficiently low as compared with the Curie temperature of LiNbO<sub>3</sub> (1050–1200°C). Moreover, MgO-doped LiNbO<sub>3</sub> was considered to be more suitable as a substrate for obtaining a LiNbO<sub>3</sub> thin film with high crystallinity, because film properties were drastically improved when a MgO-doped LiNbO<sub>3</sub> substrate was used with Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> flux (Tamada et al. 1991).

Yamada and Tamada (1992) reported LPE growth of LiNbO<sub>3</sub> thin films on a 5 mol% MgO-doped Z-plate LiNbO<sub>3</sub> substrate using  $Li_2O-B_2O_3$  flux and presented a detailed characterization of the film properties.

LPE growth was tried from metals of various compositions in the LiNbO<sub>3</sub>-LiBO<sub>2</sub> pseudobinary system. Melt compositions appropriate for obtaining films with a perfect mirror surface were around 20 mol% LiNbO<sub>3</sub> in the LiNbO<sub>3</sub>-LiBO<sub>2</sub> pseudobinary system which corresponds to the point of 50 mol% Li<sub>2</sub>O, 10 mol% Nb<sub>2</sub>O<sub>5</sub> and 40 mol% B<sub>2</sub>O<sub>3</sub> in the ternary system. Thus, the Li<sub>2</sub>O/Nb<sub>2</sub>O<sub>5</sub> composition was also varied along the B<sub>2</sub>O<sub>3</sub> 40 mol% fixed line in the ternary system. The growth temperature was chosen to be about 5°C lower than the saturation temperature, which results in a growth rate of 1 µm/min. In this way, a LiNbO single-crystal thin film with a suitable thickness for an optical waveguide can be obtained by dipping the substrate into the melt for 3-4 min.

The film crystallinity was investigated by the x-ray double crystal method. A film grown from 52 mol% Li,O, 8 mol% Nb,O, and 40 mol% B,O, melt was used. The full width at half-maximum of 11.4 arcsec for a peak corresponding to the film is comparable to 10.2 arcsec for the substrate peak, which indicates that this film has extremely high crystallinity. The difference of the diffraction angle between the film and the substrate was 249 arcsec. The lattice mismatch along the *a* axis,  $\Delta a$ , calculated from this value, is 41.4×10<sup>-5</sup> nm, where Yamada and Tamada (1992) defined the substrate lattice constant minus the film lattice constant. The value of  $\Delta a$  was somewhat larger than that of films grown from Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> flux (3.7×10<sup>-5</sup>-40.3×10<sup>-5</sup> nm), which suggests that this film has a composition richer in Li. There exists an approximately 400 nm thick transient layer formed by Mg diffusion from the substrate to the film. However, if the thickness of a practical optical waveguide (typically 4-5  $\mu$ m) is taken into account, it can be said that the profile of this LPE film is almost step-shaped. Though boron could not be detected at all in this measurement, a very small amount might be included.

The ferroelectric domain structure was also investigated using a conventional etching method. The cross-section, which corresponds to the -Y surface of the substrate, was optically polished and then etched in a 1HF + 4HNO<sub>3</sub> solution at 90°C for 1 min. Polished surfaces were examined using a differential interference microscope. This showed that single-poled films were grown on both the +Z and -Z surface of the substrate. But the direction of spontaneous polarization of the film grown on the -Z surface is opposite to that of the substrate, whereas films grown on the +Z surface were single-poled along the same direction as the substrate. These phenomena form a striking contrast to the domain inversion at the +Z surface when the  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$  flux is used (Tamada and Yamada, 1991) and can be explained by an internal self-poling field produced by the difference of the spontaneous polarization between a film and a substrate (Miyazawa, 1979; Peuzin and Miyazawa, 1986). That is to say, due to the Li-rich composition of the film, the relationship of the spontaneous polarization of a substrate and a film at the growth temperature is contrary to that of the case using  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$  flux.

### 2.4.3 The scheme of the growth cell

Four basic ways of film crystallization from a flux onto a substrate are illustrated in Fig.2.19 on an example of the LiVO<sub>3</sub>-LiNbO<sub>3</sub> system:

1. growth by a slow solution cooling (the straight line A-B);

2. growth on a substrate located in the cold part of the crucible at a temperature  $T_{cold}$ , the excessive crystallizing substance being in contact with the solvent in a hotter zone at a temperature  $T_{hot}$ .

Convection and diffusion that take place in this method cause mass exchange which allows an excessive dissolved substance precipitate on the substrate. In the film growth region, the conditions are determined by the value of the constant temperature gradient and by the substrate growth regime (the straight line C-E);

3. growth under the condition of supersaturation due to solvent evaporation (the straight line A-D);

4. film growth by means of spontaneous crystallization from a supersaturated solution at a constant temperature.

Solution saturation is achieved by preliminary slow saturation of the solution. The method is based on the ability of the solution of some compounds to reach a stable and strong supersaturation within a wide temperature range and with a low temperature gradient, which permits rapid growth of epitaxial



**Fig.2.19** Phase diagram illustrating the methods of growing single-crystal films from solution in melt (on an example of the LiVO<sub>3</sub>-LiNbO<sub>3</sub> system).

films by spontaneous crystallization from a supersaturated solution.

The advantages of LPE are clearly seen on an example of obtaining a large series of semiconductor  $A_3B_5$  type compounds. To grow oxide ferroelectric films, this method should be modified.

The most promising is the method of capillary liquid-phase epitaxial growth of ferroelectrics, proposed by Khachaturyan and Madoyan (1985), which provides improvement of planarity and the quality of layer surfaces grown from a thin plane-parallel volume of a melt and permits some control over the growth parameters. This method also makes it possible to define with a high accuracy the parameters determining the film thickness and growth rate. Combination of the wide operational latitude of the capillary technique with the general procedural merits of LPE makes it the most promising method of obtaining integro-optical elements.

In a general case, the liquid-phase capillary (LPC) technique (Panish and Sumski 1971; Bolkhovityanov 1977; Malinin and Nevski 1978) suggests film growth from a buffered melt limited to two parallel substrates.

Figure 2.20 gives the scheme of substrate positions and the temperature regime for the liquid capillary epitaxy method.

Substrates are mounded vertically over a crucible filled with a liquid, and at a starting epitaxy temperature  $T_0$  are immersed in the buffered melt which is pulled into the gap between the substrates due to the action of capillary forces. The wetted substrates are then mounded horizontally in the operating zone of the reaction vessel, and the temperature in the crystallization cell starts to decrease. Films grow on the inner surfaces of the substrates, as shown in Fig.2.20. After the epitaxial thin-film structure is formed, the liquid phase is sucked off from the capillary gap by means of a liquid-phase absorber (Dudkin and Khachaturyan 1988). The liquid-phase absorber was made of microchannel slabs or kaolin cotton.

The temperature regime of the process is determined by the slope of the liquidus curve. For precipitation of perfect layers at a high-temperature coefficient of solubility, the cooling rate should be very low.



Fig.2.20 Temperature regime during the epitaxy process (left) and temperature distribution under capillary technology (right) (Khachaturyan and Madoyan 1984).

An important advantage of the liquid-phase capillary (LPC) technique is a constant thickness of the liquid zone over the whole substrate surface. This makes it possible to remove the wedge shape and obtain equally thick layers. The maximum gap is determined by the flux viscosity and by the wetting of the substrate surface.

The LPC technique permits easy control of the growth rate and the layer composition: the precipitation rate is determined by supersaturation near the front, which depends on diffusion and the temperature variation rate.

# 2.5 Kinetics of epitaxial growth of LiNbO<sub>3</sub>

Mass transfer plays an important role in the crystal and film growth. Having a direct effect upon the thickness and growth rate, these processes determine the structural perfection and properties of the grown crystals and films. The study of the regularities of processes in the liquid phase and at the interface suggests optimum versions of control over growth and obtaining epitaxial layers with prescribed properties.

The majority of papers devoted to kinetics of epitaxial film growth from a buffered melt are based on the diffusion approximation in which the film growth rate is limited by the diffusion mass transfer of the dissolved component to the crystallization front.

We have also considered the growth kinetics of  $LiNbO_3$  films in the diffusion approximation and established the domain of its applicability within which the influence of convective processes is inessential. Calculations have been carried out with allowance for specificities of a growing system for the capillary version of epitaxy, which permits a highly accurate reproduction of the calculated conditions of epitaxy (Madoyan and Khachaturyan 1983).

## 2.5.1 The stationary crystallization model

We shall consider a crystallization system in the form of two parallel substrates with a buffered melt between them. The gap between the substrates is much less than their size, which corresponds to the real conditions and allows us to proceed to a one-dimensional problem. The system is assumed to be isothermal without local supercooling, and the initial concentration  $C_0$  is the same throughout the entire thickness of the solution.

In real systems, phase and chemical equilibrium are displaced in oriented crystallization. The solution concentration differs from the equilibrium value, varies from one crystallographic facet orientation to another, and is connected with the properties of this facet. So, in our model the concentration near the substrate surface must be higher than the equilibrium one by a certain quantity U dependent on the material and substrate orientation.

We shall examine the concentration variation in a capillary consisting in the general case of different substrates (Fig.2.21). Cooling of the system leads to the formation of a concentration profile and to layer precipitation onto the substrates. At a point x = 0, which corresponds to the maximum supersaturation of the solution, the concentration gradient is equal to zero and, therefore, the particle flows through the plane x = 0 are equal on both sides. Then, for the liquid-phase region trapped between the plane x = 0 and the first substrate,



Fig.2.21 Schematic of distribution of concentrations in a capillary system: a) precipitation onto different substrates; b) precipitation onto identical substrates; c) concentration variation during crystallization in the bulk; d) dependence of the effective thickness of the liquid phase on the size of the opening in a capillary.

the concentration distribution satisfies the diffusion equation with the boundary conditions

$$C_1(\pm l_1, t) = C_0(1 - \alpha t/C_0 m) + U_1$$
(2.1)

where  $C_0$  is the initial solution concentration,  $C_1(x, t)$  is the concentration of the component between the first substrate and the plane x = 0, *m* is the slope of the liquidus curve, *t* is time,  $\alpha$  is the cooling rate,  $U_1$  is supersaturation near the substrate surface,  $(m = \tan \phi)$  is the slope angle of the liquidus curve.

Introduction of supersaturation does not alter the character of distribution but only leads to its displacement in time (retardation) by  $u_1m/\alpha$ . The solution of the diffusion equation gives the expression for concentration variation (Moon 1974):

$$\frac{\partial C_1}{\partial x} = \frac{\alpha \ell_1}{mD} \left\{ \frac{x}{\ell_1} - 2\sum_{n=0}^{\infty} \frac{(-1)^n}{\lambda_n^2} \exp\left[ \frac{-\lambda_n^2 D\left(t - \frac{U_1 m}{\alpha}\right)}{\ell_1^2} \right] \sin\left(\lambda_n \frac{x}{\ell_1}\right) \right\}$$
(2.2)

where  $\lambda_n = (n+1/2)\pi, \tau = t - \frac{U_1m}{\alpha}$ , D is the diffusion coefficient.

Under quasistationary conditions (for  $\frac{D\tau}{\ell_1^2} > 1$ ), integrating the expression (2.2), we obtain the value of the maximum relative supersaturation  $\Delta C_{ml}$ :

$$\Delta C_{m1} = (\alpha \ell_1^2 / 2Dm) + U_1 \tag{2.3}$$

We similarly obtain expressions for  $dC_2/dx$  and  $\Delta C_{m2}$  in the region between the plane x = 0 and the second substrate. The resulting supersaturation in the solution is equal to the sum of the relative supersaturation and the supersaturation at the substrate surface. Since the temperatures of both substrates are the same, it follows that in the absence of nucleation in the liquid-phase volume, there must hold the condition

$$\Delta C_{m1} + U_1 = \Delta C_{m2} + U_2. \tag{2.4}$$

From (2.4) we can readily derive the expression for  $\ell_1$  and  $\ell_2$ :

$$\ell_1 = (1/2)[\delta + (2DU_{21}m/\alpha\delta)]$$
(2.5)

$$\ell_2 = (1/2) \left[ \delta - (2DU_{21}m/\alpha\delta) \right]$$
(2.6)

where  $U_{21} = U_2 - U_1$  and  $\delta = \ell_1 + \ell_2$  is the gap between the substrates. Thus, film precipitation onto different substrates in a capillary comes from the liquid layer whose thickness is determined by the expressions (2.5) and (2.6).

Now we shall consider precipitation onto similar substrates, when  $U_1 = U_2$ . If the resulting supersaturation exceeds the critical supersaturation  $\Delta C_{m_0}$  under which crystallization occurs in the bulk, precipitation into each substrate comes from a layer thickness  $\ell = 1/2 \delta$  (Fig.2.21(b)). Supersaturation in the liquid phase increases,  $\Delta C_m + U$ , with increasing gap size and  $\delta$  appears to be equal to the critical value. From (2.3) it follows that

$$\delta_{cr} = \left[ (2Dm/\alpha) (\Delta C_{m} - U) \right]^{1/2} \tag{2.7}$$

Under such conditions nucleation occurs in the middle of the capillary, and a new crystallization front there appears. At this front, the supersaturation Ucan be assumed equal to zero since spontaneous non-oriented crystallization proceeds. In the centre of the capillary the concentration becomes equal to the equilibrium one at a given temperature, and a new concentration distribution occurs (Fig.2.21c). Precipitation onto the substrate comes from the layer

$$\ell_{\rm eff} = (1/2) \left[ \left( \delta / 2 \right) - \left( 4 DUm / \alpha \delta \right) \right].$$

A further increase of  $\delta$  leads to an increase of  $\ell_{\text{eff}}$  up to the critical value at which in the region between the substrate and the middle of the gap a crystallization front occurs again. Figure 2.21d shows the thickness variation of the liquid-phase layer from which increased precipitation comes onto the substrate. Thus, in the absence of convective flows and an induced mixture of the solution, precipitation of the layer comes from a limited volume of the liquid phase.

#### 2.5.2 Epitaxy under non-isothermic conditions

An important task of theoretical estimations is finding the epitaxial film thickness since this is, in fact, the only measurable parameter of the films. Typically, the thickness is evaluated from the amount of precipitate using the phase diagram and disregarding mass transfer.

Under the condition  $h \ll \ell$  (Fig.2.20), the layer thickness h is defined by the expression (Moon 1974)

$$h = \int_{0}^{t} \frac{D}{C_s - C(\ell, t)} \left(\frac{\partial C}{\partial x}\right)_{x=\ell} dt$$

If we substitute here the expression for concentration variation (Madoyan et al. 1988)

$$\frac{\partial C}{\partial x} = \frac{\alpha \ell_1}{mD} \left\{ \frac{x}{\ell_1} - 2\sum_{n=0}^{\infty} \frac{(-1)^n}{\lambda_n^2} \exp\left[\frac{-\lambda_n^2 D\left(t - \frac{U_1 m}{\alpha}\right)}{\ell_1^2}\right] \sin\left(\lambda_n \frac{x}{\ell_1}\right) \right\}$$

and  $C_s - C(\ell, t) \simeq C_0(k-1)$ , where  $C_s$  is the dissolved component concentration in the solid phase and k is the segregation coefficient, then replacing t by

$$\tau = t - \frac{U_1 m}{\alpha}$$

we obtain

$$h = \frac{\alpha}{C_0(1-k)m} \left\{ \ell \tau + \frac{2\ell^3}{D} \left[ \sum_{n=0}^{\infty} \frac{\exp(-\lambda_n^2 D \tau / \ell^2)}{\lambda_n^4} - \frac{1}{6} \right] \right\}$$
(2.8)

The whole crystallization process can be divided into two stages: nonstationary which forms the concentration profile, and stationary under which the profile remains unchanged (Zhovnir and Maronchuk 1980). The efficiency determined as the experimental-to-calculated thickness ratio increases with increasing cooling time or with decreasing gap size. To obtain LiNbO<sub>3</sub> films with a thickness corresponding to the equilibrium one, we can increase the soaking time at a constant temperature after the cooling process is over. The concentration in the solution levels up and becomes equal to  $U + C_k$ , where U is supersaturation at the crystallization front and  $C_k$  is the saturation concentration corresponding, according to the liquidus curve, to the final epitaxy temperature. In the formula

$$h_{\rm eq} = (\rho_L / 2\rho_S)\delta(C_0 - C_1)M_1 / (1 - C_1)[C_1(M_1 - M_2) + M_2]$$
(2.9)

 $C_1 = U_1 + C_2$ , and instead of  $\delta/2$  we have used the  $\ell$  value from Eq. (2.5).

#### 2.5.3 Determination of supersaturation U and diffusion coefficient D

Let a capillary with a gap  $\delta$  consist of two similar substrates with a characteristic supersaturation U.

The expression (2.9) determines the dependence of the film thickness on the final solution concentration. Substituting experimental film thickness values, we can find the final concentration value  $C_t+U$ . The difference between the

value obtained and  $C_k = C_0 - \frac{\alpha t}{m}$  is equal to the characteristic supersaturation.

For an exact determination of the U value it is necessary, as mentioned above, to proceed to soaking after cooling is over. As the soaking time increases, the thickness increment must decrease due to concentration levelling.

In a number of papers, diffusion was investigated on single-crystal samples with inclusions of drops from the mother liquor (Timofeeva 1978).

We have evaluated the diffusion coefficient on the basis of experimentally established film parameters.

When epitaxy proceeds onto different substrates, the film thickness depends on the position of the point of maximum supersaturation. From (2.5) it follows that

$$D = \alpha \delta(\ell_1 - \ell_2) / 2U_{21}m \tag{2.10}$$

The values  $\ell_1$  and  $\ell_2$  are determined from (2.9) on the basis of experimentally measured layer thicknesses (substituting  $\ell$  for  $\delta/2$ ).

In examining the relationship between the growth parameters and the mass transfer character, it has been established that, in buffered melt systems, the contribution of convective flows is insignificant if the gap between substrates is small and increases sharply with increasing  $\delta$  (Litvin and Maronchuk 1977; Mil'vidsky et al. 1980). The film growth rate is readily determined from (2.8) or (2.9). The linear dependence  $v = f(\delta)$  testifies to the fact that under these conditions mass transfer is limited to molecular diffusion. As  $\delta$  increases, a deviation from linearity in the solution is observed as a result of natural convection due to gravitation and the difference in the densities of the dissolved substance and the solvent. In the solution, crystallization centres may occur which are distributed throughout the entire liquid-phase volume by convective flows.

In addition to the value of the critical gap  $\delta^*$  determining the diffusion region, an important factor is the stationarity  $Dt/\ell^2$ . The time of appearance of a constant concentration profile for the gap  $\delta = 2\ell$  is defined by the condition  $Dt/\ell^2 = 1$ .

As the process time  $t > \ell^2/D$  increases, the process approaches the stationary one.



**Fig.2.22** Film thickness and growth rate as functions of growth system parameters: a,d: 1)  $\alpha = 0.2$  grad/min, 2)  $\alpha = 0.4$  grad/min, 3)  $\alpha = 0.6$  grad/min. b: 1) calculated values, 2) (0001) is orientation of LiTaO<sub>3</sub>, 3) (1120) is orientation of LiTaO<sub>3</sub>.

To calculate the thickness and the growth rate of a LiNbO, film, we should know the values of the diffusion coefficient of LiNbO, in the Li<sub>2</sub>O-V<sub>2</sub>O, melt and the characteristic supersaturation U depending on the material and substrate orientation. The experimental determination of these values on the basis of the constructed model requires realization of the growth processes under conditions very closely approaching the stationary ones. LiNbO, and LiTaO, plates of different orientations were used as substrates. Figure 2.22 presents the dependence of the LiNbO<sub>3</sub> film thickness on the size of the gap  $\delta$  between the substrates. In the absence of convective flows this dependence must be linear. The graph implies that at a cooling rate  $\alpha = 0.2$  grad/min, the contribution of convective mass transfer is insignificant up to the value  $\delta$  = 3 mm. For  $\alpha = 0.4$  grad/min, the value  $\delta^*$  decreases, which is evidently due to an increase of temperature gradients in the buffered melt and the associated density inhomogeneities of the liquid phase in the capillary. For  $\alpha = 0.6$  grad/ min, the film thickness does not alter substantially if  $\delta \ge 2$  mm, which is due to the beginning of crystallization in the bulk melt. For  $\delta = 3$  mm, the film thickness decreases less than expected within the proposed model. This can be caused by an incomplete covering of the surface of maximum supersaturation by bulk nuclei. In this case, the effective layer thickness  $\ell_{eff}$  from which precipitation comes onto the film must increase, and the mean concentration

in the centre of the capillary is somewhat higher than equilibrium. Thus, the analysis of the results obtained shows that at the cooling rate  $\alpha = 0.2$  grad/min and the gap size  $\delta \leq 3$  mm lithium niobate precipitates in accordance with the diffusion growth mechanism without crystallization in the bulk.

Precipitation of the entire excessive substance onto substrates is a long process. But when substrates are held for a long time in contact with the liquid phase at the final epitaxy temperature, the mass exchange between the liquid phase and the film surface leads to film roughness and thickness inhomogeneity. To determine the optimum soaking time  $\theta$ , the film thickness was investigated as a function of the soaking time for different cooling rates of the system. For  $\alpha = 0.2$  grad/min, precipitation stops 10 minutes after the cooling is over.

Further soaking leads to divergence between the film thicknesses on the upper and lower substrates, which must be associated with the downward gravitational flow of permanently occurring and decaying quasiparticles and, therefore, with concentration nonuniformity. For  $\alpha = 0.4$  grad/min, the thickness reaches its maximum value within 20 minutes and then does not change. Within 15–20 min, the thickness reaches its maximum value also at a cooling rate of  $\alpha = 0.6$  grad/min. In this case, further soaking leads to a decrease of film thickness, which must be associated with the redistribution of the substance between the film and small crystals in the liquid phase.

Under quasistationary conditions we have estimated the characteristic supersaturation for z- and y-planes of LiTaO<sub>3</sub>. We investigated the dependence of the film thickness on the gap size for identical substrates. The initial epitaxy temperature was 890°C, the final 860°C, the cooling rate  $\alpha = 0.16$  grad/min. The cooling time was three hours and the soaking time after the process was over was 15–20 min. The results obtained are presented in Fig.2.22a. The straight line I corresponds to the one calculated from formula (2.9). Since precipitation is assumed to proceed by the diffusion mechanism, the experimental dependences are linear. The film thickness on the y-plane of LiTaO<sub>3</sub> is somewhat higher than that on the z-plane. The lithium niobate concentration near the y- and z-substrates in this model exceeds equilibrium by 0.24 and 0.39 mol%, respectively.

Characteristic supersaturation has a strong influence on the thickness and the growth rate of the film under precipitation in a capillary which consists of different substrates. The asymmetric profile of the concentration distribution leads to the fact that precipitation onto substrates proceeds from solution layers of different thicknesses. Table 2.2 presents the thickness values under precipitation onto the y- and z-substrates of LiTaO<sub>3</sub>. For a precipitation rate of 0.16 grad/min, the thicknesses may differ by a factor of 3. On the basis of the results obtained, we have estimated, using formula (2.10), the diffusion coefficient  $D = (1.5\pm0.7) \times 10^{-5} \text{ cm}^2/\text{s}$ . The coefficient D determines the diffusion of concrete atoms (ions, molecules) in the medium. But in the framework of the model constructed, the estimated value characterizes conditionally the diffusion of molecular lithium niobate and simplifies appreciably the calculations of film parameters. The picture remains the same in the case of hyperepitaxy. Since the introduction of lithium tantalate into the buffered melt heightens the liquidus temperature of the system (Kondo et al. 1979), the liquid-phase supersaturation

δ mm	<i>h<sub>,</sub></i> µm	α deg/min	h <sub>x</sub> μm	h, μm	ℓ, mm	$\ell_2 \atop mm$	D×10 <sup>5</sup> cm <sup>2</sup> /s	$\frac{\Delta D \times 10^{5}}{\text{cm}^{2}/\text{s}}$
1.5	17.19	0.16	22.1±1.5	7.3±0.5	1.13	0.37	0.87	0.1
1.5	17.19	0.2	21.0±1.5	7.5±0.5	1.11	0.39	1.02	0.15
1.5	17.19	0.4	19.5±1.0	10.2±1.0	0.98	0.52	1,35	0.3
2	22.92	0.16	29.5±1.5	12.3±0.3	1.41	0.59	1.26	0.1
2	22.92	0.2	29.0±2.0	11.5±0.5	1.43	0.57	1.65	0.18
2	22.92	0.2	27.0±1.5	12.5±0.5	1.37	0.63	2.81	0.35
			$D_0 = (1.1)$	5±0.7)×10	-5 cm²/s			

**Table 2.2** Parameters of the growth system and LiNbO<sub>3</sub> film thickness in capillary growth on(0001) and (1120) LiTaO<sub>3</sub> substrate (Khachaturyan et al. 1984)

hampers dissolving of the substrate, its composition does not change and a layer of pure lithium niobate precipitates. The solid solution is formed in the narrow transition region at the expense of diffusion through the interface in the solid phase.

Figure 2.22 demonstrates the film thickness as a function of cooling rate. For  $\alpha \le 0.4$  grad/min the thickness does not practically change, while for  $\alpha = 0.5$  grad/min it falls sharply owing to the fact that the critical supersaturation is reached and crystallization proceeds in the bulk. Formula (2.3) implies

 $\Delta C_{m_0} = \left(\delta_{\rm cr}^2 \,\alpha \,/\, 2Dm\right) + U$ 

Substituting the value  $\delta_{cr} = 2.5 \text{ mm}$ ,  $\alpha = 0.5 \text{ grad/min}$ ,  $D = 1.5 \times 10^{-5} \text{ cm}^2/\text{s}$ , m = 11.6 grad/mole,  $v_z = 0.39$ , we obtain  $\Delta C_{m_0} = 1.89$ . From this we can determine the critical values of the gaps for various cooling rates.

In the capillary method of LPE for ferroelectric film growth with allowance for the above-mentioned restrictions, crystallization outside the substrate is absent and all the dissolved substance in the gap precipitates onto the substrate as a film. Knowing the thickness of the solution layer and the growth temperature range, we can calculate the expected film thickness using the state diagram.

For a computer calculation of the film thickness as a function of growth parameters in the framework of the capillary LPE method, there exists an algorithm, and the following methods of calculation are realized as a universal program (on an example of epitaxial films of lithium niobate (Madoyan et al. 1982)).

The calculations are based on the liquidus temperature of the phase diagram of the pseudobinary system  $LiVO_3$ -LiNbO<sub>3</sub> (Madoyan et al. 1979). The analytical expression (2.9) describing the dependence of the film thickness the growth parameters is obtained on the basis of calculating the amount of the precipitating crystallizing substance for a given system supercooling.

For convenience of programming, the phase diagram of the  $LiVO_3$ - $LiNbO_3$  system in the temperature range 800–870°C was approximated by the exponential function

$$C = a e^{bt} \tag{2.11}$$

where a and b are constants; c is the molar concentration of  $LiNbO_3$ . We have used the standard approximation program from the software of a Nairi-2 computer.

The algorithms for calculating the film thickness as a function of growth parameters were published in detail by Madoyan et al. (1982).

Thus, we obtain the complete set of values of  $LiNbO_3$  film thickness as a function of variable parameters. Figure 2.23 gives the graphs of the dependence of the film thickness on the parameters of the epitaxy process.



Fig.2.23 LiNbO<sub>3</sub> film thickness versus growth conditions: a) starting temperature, b) overcooling of the system, c) weight of the solution melt. Points are experimental values.

These dependences permits a rather accurate prediction of film thickness under concrete growth conditions. Points in Fig.2.23 indicate the film thickness values obtained under experimentally chosen optimum epitaxy conditions. The difference of 5-10% can be explained by additional precipitation from the melt of the substance remaining on the film surface after the epitaxy is over.

The satisfactory agreement between the experimental and theoretical data suggests a wide range of applicability of programming calculation of the epitaxial film width.

#### 2.5.4 Epitaxy under isothermal conditions

As distinguished from the nonisothermal case for which the diffusion processes determined by the system cooling rate are limiting, in isothermal epitaxy the rate of the diffusion processes varies with film growth, and the question of a relative contribution of diffusion and surface processes to the growth kinetics remains open. In view of this, we have considered the general case with allowance for the kinetic coefficient. Isothermal epitaxy is investigated under conditions of a quasistationary process which takes place in the indicated systems  $(D/\delta v \gg 1)$ .

As in the nonisothermal case, crystallization proceeds from a limited volume consisting of two identical parallel substrates mounted at a distance  $\delta$  (Fig.2.24a). The quantitative determination of the time dependence of film thickness at a given initial supersaturation consists of solving the differential equation describing the diffusion of a dissolved crystallizing material inside a capillary with corresponding initial and boundary conditions

$$\frac{\partial C}{\partial t} = \frac{2D}{\delta} \frac{\partial^2 C}{\partial y^2} + v \frac{\partial C}{\partial y}; \ 0 < y < 1 - \frac{2}{\delta} \int_0^t v \, dt$$
(2.12)

where y is a dimensionless distance (in the units  $\delta/2$ ) counted from the growth front. The range of y variation is due to the symmetry about the capillary centre. The initial and boundary conditions of the problem have the form

1. For t = 0  $C(y, 0) = C_0$ ;

2. In the capillary centre 
$$\frac{\partial C}{\partial y} = 0$$
; for  $y = 1 - \frac{2}{\delta} \int_{0}^{t} v dt$ ;

3. At the growth fronts there holds the mass conservation condition of the crystallizing material:

$$D\frac{\rho_L M_1}{\rho_s \left[C_1 (M_1 - M_2) + M_2\right]} \frac{\partial C}{\partial y} \bigg|_{y=0} = v \frac{\delta}{2} \left\{ \frac{\rho_L M_1}{\rho_s \left[C_1 (M_1 - M_2) + M_2\right]} C - 1 \right\}$$

where

$$v = q \frac{\rho_L}{\rho_S} \frac{M_1}{C_1(M_1 - M_2) + M_2} (C - C_1) \Big|_{y=0}$$

Here q is the kinetic coefficient. The boundary conditions disregard U since in real systems  $U_0 \ll \Delta C_0$ .

Under LPE conditions, the initial supersaturation  $\Delta C_0 = C_0 - C_1$  is so small that the maximum (final) film thickness is noticeably less than the capillary half width.

Solving equation (2.12) by the method of separation of variables, we obtain the time dependence of the film thickness h:

$$h(t) = \int_{0}^{t} v \, dt = \tau v_0 \sum_{h=1}^{\infty} \frac{2j}{(v_n^2 + j^2 + j)v_n^2} \Big[ 1 - \exp(-v_n^2 t / \tau) \Big]$$
(2.13)

where  $\tau = \delta^2/4D$  is the diffusion time,  $v_0 = v(t = 0)$ 

$$j = \frac{\delta q}{2D} \left\{ 1 - \frac{\rho_L}{\rho_S} \frac{M_1}{C_1 (M_1 - M_2) + M_2} C_1 \right\}$$

 $v_{j}$  are the roots of the equation and  $jv = \tan v$ .

The first summand in (2.13) is final film thickness  $h_0$  which is independent of t.

For  $j \gg 1$  and  $t \gg \Delta \tau / \pi$  we can retain one term in the series (2.13)

$$h = h_0 - \left[ \tau v_0 2 j / (v_1^2 + j^2 + j) v_1^2 \right] \exp(-v_1^2 t / \tau)$$
(2.14)

admitting here a relative error

$$\Delta h / h < \left[ (\mathbf{v}_1^2 + j^2 + j) / 6(j^2 + j) \right] \mathbf{v}_1^2 \exp\left[ -(\mathbf{v}_2^2 - \mathbf{v}_1^2)t / \tau \right]$$
(2.15)

It should be noted that for  $t = \tau$  the concentration profile variation due to diffusion reaches the point  $\delta/2$  (Fig.2.24a). For  $t \ll \tau$  the film increases in the same manner as in an infinite capillary, and the dependence  $h(t \ll \tau)$  is determined by the solution of equation (2.12) with the boundary conditions

$$\left( \frac{d\Delta C}{dy} \right)_{y=0} - j\Delta C = 0; \quad \Delta C = C - C_1$$
  
 
$$\Delta C_1(Z,0) = C_0 - C_1; \quad \Delta C(\infty; t) = C_0 - C_1$$
 (2.16)

leading to the following time dependence of supersaturation at the growth front

$$\Delta C(0,t) = \Delta C_1 \exp(j^2 t / \tau_k) \left\{ 1 - \Phi \left[ j(t / \tau_k)^{1/2} \right] \right\}$$
  
$$\tau_k = Dq^{-1} \left\{ 1 - \rho_L M_1 \rho_S^{-1} \left[ C_1 (M_1 - M_2) + M_2 \right]^{-1} \right\}$$
(2.17)

where  $\Phi$  is the probability integral. It should be noted that for  $t \ll \tau_k$  there holds a kinetic growth regime, that is, the film growth rate is only determined by the kinetic coefficient and initial supersaturation

$$v \equiv v_0 = q \rho_L M_1 (C_0 - C_1) / \rho_S [C_1 (M_1 - M_2) + M_2]$$
(2.18)

The expression (2.14) obtained above, which holds for j > 1,  $t \gg \tau/\pi$ , describes the diffusion regime in which the growth rate is determined by the diffusion



Fig.2.24 Concentration distribution (a) and film thickness h as a function of time (b).

coefficient and the capillary width and depends weakly on q.

To establish the character of LiNbO<sub>3</sub> crystallization from the buffered LiVO<sub>3</sub>-LiNbO<sub>3</sub> melt, the time dependences of the film thickness were measured for various  $\Delta C_1$  and  $\delta$  values.

The results of these measurements are presented in Fig.2.24b. The final thickness  $h_0$  is equal to the maximum film thickness value obtained under an increased soaking time. Measurements were carried out for  $h \ge 4 \mu m$  since for lower h the error is comparable with the film thickness. The linear character of the dependence h(t) in logarithmic coordinates is an evidence of predominance of the diffusion growth regime for  $h \ge 4 \mu m$ , that is, practically the whole of the film is growing in the diffusion regime. The results of experiments suggest estimates of the quantities entering (2.14) and show the error to which this formula holds. So, for curve 1 (Fig.2.24b)

$$v > 2 \times 10^{-6} \text{ cm / s},$$
  
 $\rho_L M_1 \rho_s^{-1} [C_1 (M_1 - M_2) + M_2]^{-1} (C_0 - C_1) > 1.7 \times 10^{-2}$ 

which corresponds to the kinetic coefficient

 $q > 1.2 \times 10^{-4} \text{ cm} / \text{ s}$ 

The best coincidence of (2.14) with experimental results takes place for  $D = 0.5 \times 10$  cm/s, which agrees in the order of magnitude with what we have obtained. To evaluate the error occurring in the use of formula (2.18), we shall employ (2.15), assuming

$$v > 2 \times 10^{-6} \text{ cm/s}, q > 2 \times 10^{-4} \text{ cm/s}$$
  
 $j > 2, v_2^2 - v_1^2 > (1 + \pi)\pi/2$ 

For  $t/\tau > \pi^{-1}$ , we obtain  $\Delta h/h_0 < 10^{-1}$ , which is within the experimental error for h. Thus, in the growth system under consideration we deal with the kinetic regime at  $t \ll \tau_{\perp} \simeq 5 \times 10^2$  s and with the diffusion regime at  $t \gg (2/\tau) \times 10^3$  s.

These estimates confirm the conclusion that the diffusion regime is prevailing for film growth.

# **2.6 Crystallization of films from LiNb\_{1-y}Ta\_yO\_3 solid solutions** Obtaining epitaxial films with a given composition is one of the important

Obtaining epitaxial films with a given composition is one of the important problems of applied physics since insignificant composition variations may have a considerable effect upon the physical properties of grown structures. It is very difficult to maintain a constant composition when layers of multicomponent dielectric materials are precipitated from a buffered melt, when introduction of each component is specified by an individual segregation coefficient, depends on the growth conditions and varies with local fluctuations of growth parameters (Timofeeva 1978).

To obtain films with a prescribed composition, it is necessary to establish a relationship between the composition and a complex of factors which determine the entering of components in the growing layer. In LPE, these factors are individual coefficients of segregation and the growth parameters, namely, the composition and thickness of the liquid phase, the initial temperature, the cooling rate of the system, *etc.* 

Lithium niobate and tantalate form  $\text{LiNb}_{1-y}\text{Ta}_yO_3$  solid solutions in the entire range of the compositions  $0 \le y \le 1$  (see Fig.2.4) (Madoyan and Khachaturyan 1985).

A specific feature of crystallization of films of solid solutions is the necessity to take into account the influence of the amount of precipitating components on the epitaxy temperature, composition, uniformity of component distribution and film thickness (Madoyan et al. 1985).

In precipitation from a high-temperature melt of multicomponent systems, the composition of the precipitating layer differs typically from the composition of the dissolved material since entering of each component into the layer is determined by an individual segregation coefficient. In epitaxy of lithium niobate-tantalate from the solution in the  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$  melt, the composition of the LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> film is shifted relative to the composition of the dissolved material LiNb<sub>1-x</sub>Ta<sub>x</sub>O<sub>3</sub> towards increasing tantalum, that is, y > x. Analysis of film compositions revealed a shift of the composition of the LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> layer relative to the liquid phase towards an increasing molar fraction of tantalate (y > x). Numerical estimates give a variation of the relation between niobium and tantalum by no more than 3% during precipitation of a layer about 10 µm thick. The corresponding liquidus temperature displacement does not exceed ±5° when the growth cell is cooled by about 40°. Thus, the equilibrium temperature variations during growth can be disregarded, but the error in predicting the film thickness increases up to 20%.

In the literature, the variation of the effective coefficient of segregation is customarily associated with mass transfer processes in the liquid phase, that is, with diffusion, convection, electromigration, *etc.* (Madoyan et al. 1985; Milvidsky 1986).



**Fig.2.25** The effective segregation coefficient of tantalum versus the growth rate of a  $Li(Nb,Ta)O_3$  film.

Figure 2.25 illustrates the dependences of the effective segregation coefficient, defined as the relation k = y/x, on the growth rate when the molar fraction of tantalum in the liquid phase is x = 0.2 and 0.4. The segregation coefficient assumes the values from 1.4 to 2.35 (x = 0.4) and from 1.5 to 2.75 (x = 0.2) as the growth rate varies from 0.4 to 0.1 µm/min. Making use of this dependence, we can control the film composition during growth and obtain LiNb<sub>1.2</sub>Ta<sub>2</sub>O<sub>3</sub> films with y ranging from 0.2 to 1.

When a Li(Nb, Ta)O<sub>3</sub> film grows from a saturated solution in the diffusion epitaxy regime, the growth rate is  $v \sim \alpha\delta$ , where  $\alpha$  is the cooling rate since the film thickness  $h \ll \delta$  (Avakyan et al. 1986). Thus, the change in the cooling rate of the system during growth leads to a variation of the growth rate and modulation in composition of the precipitating layer in line with the dependence k(v) (Khachaturyan et al. 1986). If the initial epitaxy temperature is below the phase equilibrium temperature  $T_i$ , the precipitation rate, which is maximum at the initial moment, will decrease till an equilibrium concentration is established, and the layer composition will change in a similar way. At  $T_o > T_i$ , the film does not precipitate and the substrate surface is slightly dissolved which causes an uncontrolled variation of the liquid-phase composition. Consequently, for an efficient composition control, it is necessary to start the precipitation process at a temperature equilibrium for a given concentration.

Independence of the segregation coefficient of mass transfer in the liquid phase provides an efficient layer composition control during growth. Figure 2.26 presents the graphs of a programmed temperature decrease (1) and the corresponding thickness distribution of structure components obtained by micro-X-ray spectral analysis (2). For a constant cooling rate and equilibrium initial temperature (a) the growth rate is constant and the composition remains unchanged throughout the entire layer thickness. Figure 2.26 (b,c) presents the graphs of the cooling rate at which films grow with a step-like and periodic distribution of components, which plays an important applied role, for instance, for maintaining a multiple-mode controlling integro-optic waveguide.

An important factor of structural perfection of Li(Nb,Ta)O<sub>3</sub> films is a low content of vanadium impurity. Analysis has shown that the concentration of a homogeneous vanadium impurity does not exceed 0.1 atom %. A predominant amount of niobium is explained by the equality of ionic radii of Nb<sup>5+</sup> and Ta<sup>5+</sup> (0.66 Å) as distinct from the ionic radius of V<sup>5+</sup> (0.4 Å). For an optimum range of growth rates, in which the composition was modulated relative

to niobium and tantalum  $(0.1-0.5 \,\mu\text{m/min})$  the vanadium concentration did not exceed 0.1 mol%, and with a further increase of the growth rate an inhomogeneous capture of the buffered melt was observed. Consequently, variation of growth conditions within the limits sufficient for obtaining films of different composition with respect to niobium and tantalum induces no substantial heightening of the content of vanadium impurity.

# 2.6.1 Liquid-phase epitaxial growth of Li(Nb,Ta)O, films

In this section, the liquid-phase epitaxial growth of  $Li(Nb,Ta)O_3$  solid-solution films on  $LiTaO_3$  y-plate substrates is described on the basis of the phase diagrams obtained by Kondo et al. (1979).

The vertical dipping technique was used for the experiment. A three-zone resistance heating furnace was used, to obtain an optimum vertical temperature distribution. The temperature difference between the melt surface and the bottom of the crucible was within 1°C. The starting material was put inside a platinum crucible. A thermocouple (Pt-Pt/Rh 13 %) was attached externally to the crucible.

The solution composition was fixed at 50 mol%  $Li_2O_5$ , 5 mol%  $(Nb_{1-x}Ta_x)O_5$  and 45 mol%  $V_2O_5$ , and the solution composition parameter x defined as  $Ta_2O_5/(Ta_2O_5+Nb_2O_5)$  in the solution was varied from 0.0 to 1.0. This composition corresponds to the point A, indicated by the arrow in Fig.2.18.

Approximately 1 mm thick y-plate substrates were cut from a LiTaO<sub>3</sub> single crystal, and their surfaces were mechano-chemically polished.

A typical temperature program for LPE growth is shown in Fig.2.27. The solution in the Pt-crucible was heated to 1300°C and was held at this tem-



**Fig.2.26** Programmed temperature decrease in LPE grown Li(Nb,Ta)O<sub>3</sub> (I) and the corresponding Nb and Ta distribution through the thickness of Li(Nb,Ta)O<sub>3</sub>/LiTaO<sub>3</sub> hyperstructure (II) (Khachaturyan et al. 1987).



Fig.2.27 Typical temperature programme for LPE growth.  $T_s$  shows the saturation temperature of the solution (Kondo et al. 1979).

**Fig.2.28** (right) Epilayer thickness as a function of growth time and several growth temperatures. The *x* of solution composition was 0.8 (Kondo et al. 1979).

perature for 2–4 days to make it homogeneous. Then the temperature was lowered to a growth temperature at which the solution was saturated. Prior to dipping, the substrate was thermally equilibrated just above the solution to bring it to the solution temperature. Then the substrate was inserted into the solution. After film growth, the substrate was withdrawn at a rate of 1 cm/min from the solution and slowly cooled to room temperature. The substrates were not rotated during the film growth. The flux adhered to the sample could be easily dissolved by dilute HCl solution.

A series of growth runs were carried out, with growth time and the growth temperatures as parameters, to determine their effects on the growth rate. Figure 2.28 shows a relationship between film thickness and growth time. The solution composition parameter x was fixed at 0.8, and the growth temperatures were 1120, 1125 and 1130°C. It can be seen that the film thickness increases approximately linearly with time up to about 30 min in growth time. The films were grown at 1120°C and the growth rate of these films was estimated to be 1  $\mu$ m/min.

The film thickness below 10  $\mu$ m yielded smooth surface. After 12  $\mu$ m growth, ripples appeared on the surface. At 50  $\mu$ m growth the ripples developed into a series of sharp ridges known as film faceting and the flux was trapped between the ridges. It can be said that a film thickness of less than approximately 10  $\mu$ m is adequate for obtaining a smooth as-grown surface.

Figure 2.29 shows the growth rate as a function of growth temperature for different solution compositions. The solution composition parameter x was 0.5, 0.7, 0.8, 0.9 and 1.0. Saturation temperatures for these compositions were estimated to be approximately 1020, 1095, 1135, 1165 and 1190°C, respectively, as were indicated in Fig.2.29. The growth time was fixed at 15 min in each case. The growth rates were directly proportional to the supercooling ranging from 0 to about 30°C, over which the growth rate departed from linear relationship. This can be explained in terms of both the curvature of the liquidus slope in the



Fig.2.29 Growth rate as a function of growth temperature and solution composition. Growth time was fixed at 15 min (Kondo et al. 1979).

 $LiVO_3-Li(Nb_{1-x}Ta_x)O_3$  system and the spontaneous nucleation of  $Li(Nb,Ta)O_3$  which occurred prior to or during the growth at large supercooling (Davies et al. 1974). Therefore, the magnitude of supercooling was chosen to be less than  $30^{\circ}C$ .

Electron probe microanalysis was used to monitor Nb, Ta and V concentrations in the film and the substrate. The solution composition parameter x of this film was 0.8 and the film thickness was about 30  $\mu$ m. The Ta concentration is constant not only in the substrate but also in the film and it varies discontinuously at the boundary between the film and the substrate. The ratio of Ta concentration in the film to that in the substrate is about 0.96. The Nb was detected only in the film and its concentration is constant in the film. The concentration of V ions, which is a flux element, is less than 0.2 mol% in the film.

The real film composition was defined as  $Li(Nb_{1-y}Ta_y)O_3$ , where y is the mole ratio of Ta/(Ta + Nb) in the film, and the results are given in Table 2.3. It is noted that the film contains a higher Ta concentration than the starting solution.

# 2.7 Thin films of LiNbO<sub>3</sub> doped with different elements

Neurgaonkar et al. (1979) reported the LPE growth of Na<sup>+</sup> and Co<sup>2+</sup>+Zr<sup>4+</sup>doped LiNbO<sub>3</sub> films from  $Li_2O-V_2O_5$  flux.

Li(Nb <sub>t-y</sub> Ta <sub>y</sub> )	O <sub>3</sub> (Kondon, Sugii,	Miyasawa, Uehai	ra, 1979)		
composition	was given as Li <sub>2</sub> O:(	Nb <sub>1-x</sub> Ta <sub>x</sub> )O <sub>5</sub> :V <sub>2</sub> O <sub>5</sub>	= 50:5:45 in ma	ol%, and the film	n composition
14010 2.0	The compositional	relationship the	solution and t	ne growin mini,	

Solution x	Film y
0.5	0.78
0.7	0.93
0.8	0.96
0.9	0.98
1	1

Before growing any epilayers of  $Li_{1-x}Na_xNbO_3$  and  $Li_{1-x}Co_xNb_{1-x}Zr_xO_3$  components, the crystalline solubility of these ions was first estimated in the LiNbO<sub>3</sub> phase. The substitutions were made as follows:

$$(1-x)$$
 LiNbO<sub>3</sub> + xNaNbO<sub>3</sub>  $\rightarrow$  Li<sub>1-x</sub>Na<sub>x</sub>NbO<sub>3</sub>,  
 $(1-x)$  LiNbO<sub>3</sub> + xCoZrO<sub>3</sub>  $\rightarrow$  Li<sub>1-x</sub>Co<sub>x</sub>Nb<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub>

All the ceramic phases were prepared by solid-state reactions  $(1000-1200^{\circ}C)$ and were checked by X-ray powder diffraction techniques in order to establish the solid solubility range of LiNbO<sub>3</sub> structure. NaNbO<sub>3</sub> has a pseudo-monoclinic unit cell (Wood 1951) at room temperature and belongs to the perovskite structural family. According to Le Comte et al. (1974), a maximum of 7 mol% Na<sup>+</sup> can be substituted for Li<sup>+</sup> in the LiNbO<sub>3</sub> phase. Although CoZrO<sub>3</sub> does not form a compound, it dissolves to a greater extent in the LiNbO<sub>3</sub> structure. About 22 mol% CoZrO<sub>3</sub> can be accommodated in the LiNbO<sub>3</sub> phase without altering its crystal symmetry. The substitution of Na<sup>+</sup> for Li<sup>+</sup>, and Co<sup>2+</sup> and Zr<sup>4+</sup> for Li and Nb, respectively, in the LiNbO<sub>3</sub> phase lowered the ferroelectric transition temperature.

The Li<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub> flux was used for LPE growth work, and mixtures containing 80 mol% LiVO<sub>3</sub> and 20 mol% Li<sub>1-x</sub>Na<sub>x</sub>NbO<sub>3</sub> and Li<sub>1-x</sub>Co<sub>x</sub>Nb<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub>, where 0.04 < x < 0.15, were prepared. Here, x = 0.15 (*i.e.* Na or Co = Zr) in both of the above compositions corresponds to about 3 mol% of the total of the mixtures. Since the phase diagram for the pseudobinary LiVO<sub>3</sub>-LiNbO<sub>3</sub> system is known (see Fig.2.17), it was relatively easy to establish the liquidus temperature for the Na<sup>+</sup> and Co<sup>2+</sup> + Zr<sup>4+</sup> containing phases by the DTA technique. The measurements showed no significant changes in the melting temperatures for either of the systems. The appropriate amounts of Li<sub>2</sub>CO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>CO<sub>3</sub> or CoCO<sub>3</sub> + ZrO<sub>2</sub> were thoroughly mixed, heated to 600°C and then melted in a 100 cc platinum crucible. A vertical platinum-wound resistance furnace was used, and the growth temperature was controlled within an accuracy of ±1°C. The mixture was heated to 1150–1200°C overnight, after achieving complete melt homogeneity, the molten solution was cooled to about 860°C at the rate of 30°C/h.

An y- or z-cut LiNbO<sub>3</sub> substrate, positioned slightly above the melt to equilibrate with the solution temperature, was dipped into the melt. An appropriate dipping temperature was 860-890°C for both the systems. After the required time for growth had elapsed, the sample was withdrawn and cooled very slowly to room temperature. The growth rate of the epifilms, which was examined by changing the dipping time, was estimated to be approximately 1.0  $\mu$ m/min. The residue of the flux adhering to the films was washed away with either water or dilute acids.

The surface for both the Na<sup>\*</sup> and Co<sup>2+</sup>+Zr<sup>4+</sup>-containing films was smooth and clear. Microscopic observations at high magnifications showed a slightly rougher aspect in the case of thicker films. Co<sup>2+</sup> + Zr<sup>4+</sup>-doped films were bluish tint in colour, indicating the inclusion of these ions in the films. Epitaxial films as thick as  $30-35 \mu m$  could be grown by this technique.

The crystallinity and the lattice constant a were studied for the substrate and



Fig.2.30 X-ray diffraction peak (300) taken for the film/substrate (Neurgaonkar et al. 1979).

the films by the X-ray diffraction technique. The y-cut LiNbO<sub>3</sub> substrate showed a reflection corresponding to (300). Figures 2.30(a)–(d) show the relative intensity of (300) as a function of film thickness. The peaks corresponding to  $CuK_{\alpha 1}$  and  $CuK_{\alpha 2}$  represent the LiNbO<sub>3</sub> substrate, while the film peak positions have been denoted by  $CuK'_{\alpha 1}$  and  $CuK'_{\alpha 2}$ . As can be seen from this figure, the relative intensity of  $CuK_{\alpha 1}$  and  $CuK'_{\alpha 2}$  gradually decreased with increasing film thickness and finally disappeared completely when the film thickness was more than 10 µm. The peaks from the substrate and films are well separated and reproducible under similar experimental conditions. This characteristic feature indicated that films have a high single crystallinity with good epitaxy.

The lattice constant *a* was established for the substrate and films. Although the lattice constant difference for the substrate and films was less than 0.1%, it was possible to identify these differences by the X-ray diffraction technique. The data showed that the films grown from the  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$  flux have the lattice constant *a* smaller than that usually observed in the bulk crystals of LiNbO<sub>3</sub>. The crystalline solid solubility of Na<sup>+</sup> and Co<sup>2+</sup> + Zr<sup>4+</sup> in the phase has been shown to be approximately 7 and 22 mol%, respectively. However, it was found difficult to raise their concentration in the films using the  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5$  flux. Based on these observations and the results reported by Baudrant et al. (1975) on the substitution of Ag<sup>+</sup>, Cu<sup>+</sup>, Fe<sup>3+</sup>, and Cr<sup>3+</sup> in the LiNbO<sub>3</sub> films, it would appear that the concentration of these ions is very low, ~1 mol% or less.

Table 2.4 summarizes the composition of a melt for Ag substituted films, and the results corresponding to different growth conditions on the *c*-axis LiNbO<sub>3</sub> substrates. The optical measurements were performed by using a 1.15-µm laser beam. Index variations in films containing Cu, Cr and Fe, were too small to be measured with accuracy. In Ag substituted films a refractive index of 2.2361 was found; with an account of the fact that the substrate index was 2.2300, this variation,  $\Delta n = 6 \times 10^{-3}$ , allowed the light propagation, for instance, to have Table 2.4 The composition of melt for Ag substituted films and results corresponding to different growth conditions on c axis LiNbO, substrates (Baudrant, Vial, Daval, 1975)

Melt composition (moles per cent) Nb <sub>2</sub> O <sub>5</sub> : 9.8, Ag <sub>2</sub> O : 2, Li <sub>2</sub> CO <sub>3</sub> : 49, V <sub>2</sub> O <sub>5</sub> : 39.2								
Epitaxial growth								
Temperature (°C)	Time (min)	Thickness (µm)	Growth rate (µ/min)	Observations				
952	-	0	0	T saturation				
950	10	2	0.2	Good quality films with flat				
945	10	6.5	0.65	and smooth surfaces				
945	30	22	0.7	Good quality film but hilly surface aspect				
942	10	14	1.4	Small rough parts				
935	10	-	_	Idem, with small crystals on the substrate edges				

a single mode in a 5  $\mu$ m thick film.

Neurgaonkar et al. (1987) reported the limit of stability of the LiM<sup>5+</sup>O<sub>3</sub> structure with respect to dopants and the LPE growth of modified LiNbO3 and LiTaO3 for SAW device applications.

To establish such a situation, the stability limit of the LiNbO<sub>3</sub> structure was determined by introducing various ions for the Li<sup>+</sup>, Nb<sup>5+</sup> or Ta<sup>5+</sup> sites. The substitutions were made as follows:

1)	LiM <sup>5+</sup> O <sub>3</sub> +M <sup>+</sup> M <sup>5+</sup> O <sub>3</sub>	Li <sub>1-x</sub> M <sup>+</sup> M <sup>5+</sup> O <sub>3</sub> ,
	M <sup>+</sup> = Na, Ag or K;	
<b>^</b> \	1 1 15 0 1 10 10 10	T 1

- 2)  $LiM^{5+}O_3 + M^{2+}M^{4+}O_3$ Li<sub>1-x</sub>M<sup>2+</sup>M<sup>5+</sup>M<sup>4+</sup>O<sub>3</sub>  $M^{2+}$  = Ca, Cd, Mg or Co,  $M^{4+}$  = Ti or Zr; 3)  $LiM^{5+}O_3 + M^{3+}M^{3+}O_3$ Li,\_M<sup>3+</sup>M<sup>5+</sup>M<sup>3+</sup>O,,
  - $M^{3+}=Al$ , Fe, Y or In.

All phases were synthesized by the solid state reaction technique, and were characterized by X-ray diffraction. Table 2.5 summarizes the site preference, solid solubility range and behaviour of  $T_c$  for the various solid-solution systems. Based on this work, the results may be generalized as follows:

(1) The size of substitutional ions should be close to Li<sup>+</sup> or M<sup>5+</sup> for complete solid solution in the LiNbO, or LiTaO, phase.

(2) The substitutions should be made on both the Li<sup>+</sup> and Nb<sup>5+</sup> sites simultaneously to obtain higher solid solubility in LiM<sup>5+</sup>O<sub>3</sub>-M<sup>2+</sup>M<sup>4+</sup>O<sub>3</sub>.

(3) The valence states of substitutional ions should be close to the host ions to achieve a substantial solubility, e.g. the solubility of Al<sup>3+</sup>, Fe<sup>3+</sup>, or Y<sup>3+</sup> is minimum in LiNbO<sub>3</sub> and LiTaO<sub>3</sub>.

The results of the present study show that the unit cell a increases and cdecreases for large cations in LiM5+O3. Larger ions such as Na<sup>+</sup> were used in

Dopant	Site prefe	erence	Solid so (mc	olubility ol%)	Lattice constar $T$ (°C)		nstants (Ă)
	Li site N	√1 <sup>5+</sup> site	LiNbO,	LiTaO <sub>3</sub>		а	с
Na+	Na⁺	-	7	9	Decreased	Increased	Decreased
Ag⁺	Ag⁺	-	4	6	Decreased	Increased	Decreased
Cd <sup>2+</sup> or Ca <sup>2+</sup> +Ti	4+ Ca <sup>2+</sup>	Ti⁴⁺	20	20	Decreased	Increased	Decreased
Cd <sup>2+</sup> , Ca <sup>2+</sup> +Zr <sup>4+</sup>	* <sup>a)</sup> Ca <sup>2+</sup>	Zr⁴⁺	20	-	Decreased	Increased	Decreased
Mg <sup>2+</sup> +Ti <sup>4+</sup>	Mg <sup>2+</sup>	Ti⁴⁺	30	35	Increased	Decreased	Increased
Co <sup>2+</sup> +Ti <sup>4+</sup>	Co <sup>2+</sup>	Ti⁴⁺	30	35	Increased	Decreased	Increased
Co <sup>2+</sup> +Zr <sup>4+</sup>	Co <sup>2+</sup>	Zr⁴+	30	35	Decreased	Increased	Decreased
Fe <sup>3+</sup> , Al <sup>3+</sup>	Fe <sup>3+</sup> , Al <sup>3+</sup>	Al³+, <b>I</b>	<sup>7</sup> e <sup>3+</sup> 1	1	_	_	-
Nd <sup>3+</sup> , Y <sup>3+</sup>	Y <sup>3+</sup> , Nd <sup>3+</sup>	Nd³+, `	Y <sup>3+</sup> 1	1	_	-	-
In <sup>3+</sup>	In³+	In <sup>3+</sup>	1	1	_	-185	_

Table 2.5 Crystal chemical data on LiM5+O3 phase, M=Nb or Ta (Neurgaokar et al. 1987)

<sup>a)</sup> Structural change was observed at x = 0.21.

the present LPE growth work to reduce the SAW velocity temperature coefficient.

Figure 2.31 shows the ternary phase diagram for the  $LiVO_3$ -NaVO\_3-LiTaO\_3 system. The  $Li_{1-x}Na_xTaO_3$  phase crystallizes over a large compositional range and is found to be useful for LPE work. As shown in Fig.2.31, two binary compositions,  $Li_{0.4}Na_{0.6}VO_3$ -LiTaO and  $Li_{0.5}Na_{0.5}VO_3$ -LiTaO<sub>3</sub>, were studied for LPE growth. Using these formulations, about 2 mol% of Na<sup>+</sup> in LiTaO<sub>3</sub> phase could be incorporated. The actual solid solubility according to the crystal chemistry work is approximately 9 mol% and 7 mol% in LiTaO<sub>3</sub> and LiNbO<sub>3</sub>, respectively. A similar phase diagram has also been constructed for the LiVO<sub>3</sub>-NaVO<sub>3</sub>-LiNbO<sub>3</sub> system by Neurgaonkar et al. (1980) and it exhibits a similar behaviour. The dipping temperature of the  $Li_{0.4}Na_{0.6}VO_3$ -LiTaO<sub>3</sub> system is much higher compared to the LiNbO<sub>3</sub> system as a result of a higher melting temperature of LiTaO<sub>3</sub>.



**Fig.2.31** LiVO<sub>3</sub>-NaVO<sub>3</sub>-LiTaO<sub>3</sub> system in air, at 1250°C (Neurgaonkar and Oliver 1987).

Flux	Substrate/film*	Growth	Lattice	constant Ă)	Temperature coefficient	
		(°C)	а	С	SAW velocity (ppm/°C)	
LiVO,	LiNbO <sub>3</sub> - S	700	5.148	_	_	
	LiNbO <sub>3</sub> – F		5.142	_	86	
Li <sub>1-x</sub> Na <sub>x</sub> VO <sub>3</sub>	LiNbO, – S	720	5.148		-	
	$Li_{1-x}Na_xNbO_3 - F$		5.156	-	56	
Li <sub>1-x</sub> Na <sub>x</sub> VO <sub>3</sub>	$LiTaO_3 - S^{b}$	720	5.152	13.785	-	
	Li <sub>1-x</sub> Na <sub>x</sub> NbO <sub>3</sub> – F		5.156	13.87	-	
LiVO,	LiTaO <sub>3</sub> – S	1050	5.152	-	35	
	LiTaO <sub>3</sub> – F		5.146	-	-	
Li <sub>1-x</sub> Na <sub>x</sub> VO <sub>3</sub>	LiTaO <sub>3</sub> – S	1050	5.152	_	_	
	Li <sub>1-x</sub> Na <sub>x</sub> TaO <sub>3</sub> – F		5.161	-	28	
Li <sub>1-x</sub> Na <sub>x</sub> VO <sub>3</sub> <sup>a)</sup>	LiNbO <sub>3</sub> – S	1050	-	-		
	$Li_{1-x}Na_{x}TaO_{3} - F$		-	-		

Table 2.6 Growth conditions and physical characteristics of LiM5+O3 films (Neurogaonkar et al. 1987)

\*) S = substrate, F = film; \*) Poling was problem, \*) Unsuccessful growth

The growth of Na<sup>+</sup>-doped LiTaO<sub>3</sub> and LiNbO<sub>3</sub> films by the LPE technique was successful and films 5 to 60 µm thick were grown. Table 2.6 summarizes the growth conditions and lattice parameters for these Na-modified LiNbO<sub>3</sub> and LiTaO<sub>3</sub> films. The results of X-ray diffraction studies showed that the lattice constant *a* increased for the Na<sup>+</sup>-doped LiNbO<sub>3</sub> and LiTaO<sub>3</sub> films, and based on the unit cell values, approximately 1.2 mol% and 1.8 mol% Na<sup>+</sup> is incorporated in the LiNbO<sub>3</sub> and LiTaO<sub>3</sub> films, respectively. The addition of more Na in these films was unsuccessful due to lattice mismatch and resultant cracking.

# 2.8 Epitaxial ferroelectric films with perovskite structure

# 2.8.1 Liquid-phase epitaxy of potassium niobate

Theoretical and experimental investigations on the application of ferroelectric thin films in the integrated optics (Ostrowsky and Vanneste 1978) and peculiarities of nonlinear optical properties of potassium niobate (Uematsu 1974; Ingle and Misshra 1977) make it one of the most interesting materials of optoelectronics. Potassium niobate crystal with melting temperature (T= 1039°C) enters the noncentrosymmetric space group mm2, with temperature decrease the cubic phase turns into a tetragonal (T = 435°C) then into a rhombic (T = 225°C) and, finally, into a rhombohedral one (T = 10°C) (Reisman and Holtzberg 1955).

The possibility of obtaining potassium niobate films by the liquid phase was investigated by the authors using the epitaxy non-stationary technique. They also discussed the results of  $K_2O-V_2O_5-Nb_2O_5$  triple system phase diagram study and the conditions for epitaxial film growth.

The phase equilibrium was studied by differential thermal analysis (DTA),

by visually polythermal analysis (VTA) and by X-phase analysis (XPA) (Khachaturyan and Madoyan 1984). Investigated compositions were chosen so that the mole ratio Nb/Nb + V could vary from 0 to 1 with an interval of 0.1.

The phase diagram of the three-component system  $K_2O-V_2O_5-Nb_2O_5$  was investigated along the straight line from 46 mol% of  $Nb_2O_5-54$  mol% of  $K_2O$  to 50 mol% of  $K_2-50$  mol% of  $V_2O_5$ .

Such a choice of investigated compositions is explained by KVO<sub>3</sub> synthesis under solidification of the melt of stoichiometric composition  $K_2O:V_2O_3$ = 1:1 (Holtzberg et al. 1956) while potassium niobate precipitation is possible with the mole ratio  $K_2O$  to Nb<sub>2</sub>O<sub>5</sub> = 54:46 (Reisman and Holtzberg 1955). Samples according to the indicated ratio were carefully mixed, heated in the furnace up to 1300°C, kept there for three hours and then cooled to room temperature.

XPA of transient compositions showed KNbO<sub>3</sub> to precipitate when the mole ratio of Nb/Nb + V in the charge varies from 0.1 to 1. If the Nb concentration is decreased from 0.3 to 0, other phases appear. The liquidus of the  $KVO_3$ -KNbO<sub>3</sub> pseudo-system is built (Fig.2.32), varying from 30 to 100 mol%.

The LPE of potassium niobate was realized in an industrial set 'Svet-3' by a non-stationary technique in a three-zone resistance furnace.

The temperature in the reactor was changed at a rate of 10-300 deg/h.

The  $K_2O-V_2O_5-Nb_2O_5$  flux was preliminarily melted for three hours at 1300°C in a platinum crucible and then mounted on a holder in the operating zone. Substrates were mounted on a quartz rod placed along the centre. Epitaxy was carried out by the capillary technique from the melt enclosed between two parallel substrates, due to good wetting. The slot was adjusted within 1–5 mm. The substrates were prepared of  $\{1\overline{2}10\}$  and  $\{0001\}$  plates of leucosapphire and of lithium niobate with dimensions  $1 \times 10 \times 15$  mm.

The system was heated up to 1100°C and after holding for a long period of time was cooled down to the initial temperature  $T_0$  of epitaxy (Fig.2.20a); the substrates were then wetted by the solution in melt and were slowly cooled down to  $T_1 = (850-875^{\circ}C)$ , the liquid zone temperature being 1–3° higher than that in the external side of the plates (Fig.2.20b). The system being cooled with the substrate dipped into the crucible, the layer precipitation was not observed (Khachaturyan and Madoyan 1980).

Cooling down to room temperature proceeded at a rate of not more than 80 deg/h. The solid charge between the plates was easily removed by boiling the substrates in distilled water.

The principal characteristics of potassium niobate liquid-phase epitaxy are presented in Table 2.7.

Homogeneously thick KNbO<sub>3</sub> films were obtained during epitaxy of 54 mol% of  $K_2O-23$  mol% of  $V_2O_5-23$  mol% of Nb<sub>2</sub>O<sub>5</sub> from the buffered melt. The epitaxy initial temperature of 920°C corresponds to the liquidus point of the present system. The initial temperature  $T_0$  being heightened to 930°C, the substrate surface is observed to dissolve.

 $KNbO_3$  films obtained by LPE from a  $K_2O-V_2O_5-Nb_2O_5$  buffered melt are colourless and transparent, their boundary with the substrate is sharp and their surface roughness is about 0.1 µm (Fig.2.33(a)). The transient region thickness

Substrate material	S r	olution melt, nol.%	Initial epitaxy temperature ℃	Cooling rate, dg min <sup>-</sup>	Layer thickness µm	Growth rate µm min <sup>-1</sup>	Remarks
{1210}A1203	54	ĸ,o	950	0.8	to 2	-	precipitation in separate areas
{1210}LiNbO3	46	Nb2O2	950	0.8	-	-	surface dissolution
{1210}AI2O3	54 23	K <sub>2</sub> O V <sub>2</sub> O <sub>5</sub>	920	0.5	5	-	single crystal in small volumes
{0001}A1203	23	Nb <sub>2</sub> O <sub>5</sub>	920	0.5	to 10	-	no precipitation
{1210}A1203			920	0.5	6	0.1	single crystal layer
{1210}A1203			925	0.5	-	0.05-0.1	single crystal layer
{1210}A1203	52	K₂O V O	930	0.5	-	-	surface dissolution
{1210}A1203	24 24	Nb <sub>2</sub> O <sub>5</sub>	930	0.2	-	-	surface dissolution
{0001}AI2O3			920	0.5	-	-	no precipitation
{1210}LindO3			920	0.5	-	_	surface intensive dissolution

Table 2.7 Principal characteristics of potassium niobate liquid phase epitaxy



Fig.2.32 Liquidus curve of KVO<sub>3</sub>-KNbO<sub>3</sub> pseudobinary system (Khachaturyan and Madoyan 1984).

is about 0.5  $\mu$ m (Fig.2.33(b)). An X-ray weak diffraction with an angle of 20-44.5° was observed from the sample surface, which corresponds to the KNbO<sub>3</sub> facet {200}.

The effect of the system cooling rate on the epitaxy process was found. With high rates KNbO<sub>3</sub> was crystallized only in the form of plate crystals. At a cooling rate of 0.2 deg min<sup>-1</sup> the substrate surface was observed to dissolve. The layer was precipitated at  $\delta T/\delta t \sim 0.5$  deg min<sup>-1</sup>.

In all experiments, plate crystals were separated in the solution in melt simultaneously with the film growth.  $KNbO_3$  films were obtained on leucosapphire substrates of  $\{1\overline{2}10\}$  orientation. On Al<sub>2</sub>O<sub>3</sub> (0001) substrates the layer precipi-



**Fig.2.33** Chipping of the KNbO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> epitaxial structure (a) and the distribution of Al and Nb along the thickness of the KNbO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> heterostructure (b) (Khachaturyan and Madoyan 1984).

tation was not observed. When an epitaxial layer grew on LiNbO<sub>3</sub> substrates, the plate surface dissolved in the buffered melt and became dulled.

# 2.8.2 Growth of potassium lithium niobate films on potassium bismuth niobate single crystals

Potassium lithium niobate (hereafter abbreviated as KLN crystal) is one of the most interesting materials for various applications because of its excellent electrooptic, nonlinear optic and piezoelectric properties (Prokhorov and Kuz'minov 1990). Accordingly, thin films of KLN single crystals have proved to be excellent active media for integrated optics. The typical crystallographic properties and refractive indices of KLN at room temperature are shown compared with those of potassium bismuth niobate (KBN) K15Bi10Nb51O15 crystal in Table 2.8. A single-crystal thin film of KLN can also be grown on a KBN substrate by the same technique as described above, because the crystalline structures of KLN and KBN are the same tungsten-bronze type structure, and because the melting point of KBN is higher by about 250°C than that of KLN, as shown in Table 2.8. The lattice mismatch between the KLN film and the KBN substrate is about 0.32% and 2.3% at room temperature for the a- and c-axes in the KLN coordinate system because the KBN crystal is orthorhombic, as opposed to the KLN crystal, which is tetragonal. Thus, it is expected that a single-crystal thin film of KLN grown on a KBN substrate will act as an optical waveguide, and it can be used as an optical waveguide modulator by coupled wave interaction between the guided and radiation modes (Adachi et al. 1979). In their previous paper, Adachi et al. (1978) described the epitaxial growth of KLN single-crystal films by the rf sputtering technique. In their 1979 paper they reported the epitaxial growth of KLN single-crystal films on KBN substrates by the EGM technique.

Single-crystals of KBN were grown by the rf heating Czochralski method.

	KLN	KBN
Symmetry	Tetragonal	Orthorhombic
Lattice constant, Å, a~b	12.58	17.85
С	4.01	7.84
Melting point, °C	1050	1312
Refractive index, n <sub>o</sub>	2.294	2.237
n <sub>c</sub>	2.156	2.253
Wavelength, $\lambda$ , nm	632.8	450

Table 2.8 Crystallographic properties and refractive indices of KLN and KBN at room temperature (Adachi, Shiasaki, Kawabata, 1979)

(001) or (100) KBN substrates were cut from as-grown crystals, and their top surfaces were lapped and optically polished. On the other hand, reagent grade carbonates of lithium and potassium, and 99.9% pure niobium pentoxide were used as starting materials for the fabrication of KLN single-crystal films. A material with composition 35 mol%  $K_2CO_3$ , 7.3 mol%  $Li_2CO_3$  and 47.7 mol% Nb<sub>2</sub>O<sub>5</sub> was mixed well with acetone in a ball mill, dried, pressed into a disc, and calcined at 800°C for three hours. The calcined material of KLN was then ground thoroughly. This powder of KLN was uniformly laid on the polished surface of the KBN substrate with a sprayer. The substrate, with the powder on its top surface, was heated to about 1120°C in a resistance furnace in order to melt the KLN crushed powder alone, and was then cooled slowly at a rate of 10°C/h through the melting point (1050°C) of KLN. In this way, the KLN film crystallized epitaxially onto the KBN substrate.

The top surface of the as-grown film was relatively rough, and the KLN film obtained was ~15 µm thick. In the X-ray diffraction patterns, the peaks corresponding to diffractions from the KLN films and KBN substrates are clearly separated. Further, the value obtained for the standard deviation angle  $\sigma$  of the X-ray rocking curve of KLN film is very small at 0.2. The lattice constants *a* and *c* of the KLN film obtained by X-ray diffraction measurement are 12.53 Å and 3.98 Å, respectively. These values agree fairly well with those of the KLN single crystal, as shown in Table 2.8. The electron diffraction patterns for KLN films epitaxially grown on KBN substrates and also the Kikuchi structure indicate that the films are of a single crystal of fairly good quality. These results show that a single-crystal film of (001) KLN is epitaxially grown on an (001) KBN substrate, and also that a single-crystal film of (110) KLN is epitaxially grown on a (100) KBN substrate by the EGM technique.

# 2.9 Diffusion liquid-phase method of growing immersed waveguide channels

Channel or strip line waveguides on the basis of LiNbO<sub>3</sub> are necessary elements for creation of electro-optic modulators, switches, directional couplers and other active devices of integrated optics (Photonics edited by Balkanski 1975; Tamir 1979; Hunsperger 1984; Yariv 1983; House 1988) suitable for joining with optical fibres.

The physico-chemical properties of buffered-melt systems, high temperatures of the processes, a limited choice of materials for solvent and container restrict strongly the possibilities of LPE in the creation of various device structures as compared with more technologically effective methods of diffusion, exchange reactions, ion implantation, *etc.* In spite of the obvious advantages in structural perfection of epitaxial layers, this method only serves for obtaining planar waveguide lithium niobate layers on LiTaO<sub>3</sub> substrates (Fukuda and Hirano 1980; Madoyan and Khachaturyan 1983; Ballman and Tien 1976).

To create effective integro-optic devices, we have proposed a combined method of liquid-phase epitaxy of LiNbO<sub>3</sub> films which uses the advantages of thermal diffusion and LPE and permits obtaining practically any prescribed waveguide configurations and refractive index profiles (Khachaturyan and Madoyan 1986).

#### 2.9.1 Strip line structures

To obtain a strip line structure, it is necessary to provide a variation of waveguide parameters along a LiTaO, substrate surface by a given scheme.

A mask with a given configuration is photographed onto a  $20\times30\times2$  mm substrate surface (Fig.2.34), after which a metallic layer is deposited onto this surface by spraying in vacuum (Avakyan et al. 1986). Of particular interest are waveguide layers obtained by titanium diffusion into a lithium tantalate substrate, since in these layers modes of both polarizations are possible (Ziling et al. 1980; Atugin et al. 1984; Sugii et al. 1980; Shashkin 1983).

Films, which are ion diffusion sources, are typically deposited onto the substrate surface by thermal evaporation in vacuum or by ion-plasma spraying of targets. According to requirements on the light guide parameters, diffusant-film thickness is varied from 50 to 80 nm. The diffusion temperature is 1150°C and the diffusion time 10–16 h.

The deposited metal diffuses into the growing layer thus increasing its refractive index along the photographed picture. The averaged metal concentration in the line  $\overline{c}$  is determined by the sputtered line thickness

$$h_m = \bar{c} h A_m \rho_f / M_f \rho_m \tag{2.19}$$

where  $h_m$  is the waveguide line thickness,  $A_m$ ,  $\rho_m$  and  $M_f$ ,  $\rho_f$  are atomic weights and densities of the metal and film material, respectively.

The diffusion depth (the height of the waveguide line) is determined by the diffusion coefficient of a given metal into a single-crystal film and by the epitaxy temperature. The refractive index variation along the direction  $(11\overline{2}0)$  perpendicular to the layer surface has the form (Ziling et al. 1980):

$$\Delta n_e(y) = \left[A_e m / (\pi \theta)^{\nu_2}\right] \exp\left(-y^2 / 2\theta\right), \qquad (2.20)$$

Here  $A_e = \Delta n_o/c$ ,  $m = \rho_m \times h_m$  is the diffusant specific mass,  $\theta = D\tau$ , where

 $\tau$  is annealing time,  $D = D_0 \exp(-U/kT)$ , U = 1.5 eV is the constant activation energy,  $D_0 = 4 \times 10^{-7}$  cm<sup>2</sup>/s (for titanium diffusion).

The expressions presented above allow us to calculate the necessary epitaxy temperature for obtaining any arbitrary refractive index profile.

For the refractive index variation  $\Delta n_{e}$  to be about 0.01 when the channel height *h* reaches approximately 2-4 µm, the annealing time should be of the order of 5-10 hours, which exceeds greatly the characteristic epitaxy times (1-3 hours). Consequently, the time  $\tau$  can be represented as  $\tau = \tau_{pr} + \tau_{an}$ , where  $\tau_{pr}$  is the layer precipitation time and  $\tau_{an}$  the additional annealing time.

## 2.9.2 Symmetric waveguides

Using the combined diffusion-film method, Khachaturyan and Madoyan (1986) obtained symmetric waveguide channels. The sequence of operations was the following. After removing the resist (Fig.2.34), an epitaxial  $\text{LiNb}_{0.1}\text{Ta}_{0.9}\text{O}_3$  layer was built up on the Ti:LiTaO<sub>3</sub> substrate by the capillary LPE method. The film composition was determined by the required refractive index distribution over the structure thickness. The growth rate variation in a wide range provided an optical epitaxy regime for obtaining perfect Li(Nb,Ta)O<sub>3</sub>/Ti:LiTaO<sub>3</sub>.

The film-diffusion waveguide was theoretically considered by Spikhal'sky (1984). He derived the dispersion equation for calculating the characteristics of multilayer waveguide structures. He also established the parameter characterizing the degree of the light-flux mode localization in the vicinity of a defined interface between media constituting the waveguide.

The study of the epitaxial growth of lithium niobate-tantalate films with titanium strips deposited onto a LiTaO<sub>3</sub> substrate has shown that for  $v_{e,g} < 0.2 \mu$ m/min the film surface is smooth with separate lines corresponding to dislocations. At such growth rates the layer growth is laminar.

Figure 2.34 shows the surface  $(11\overline{2}0)$  of a LiTaO<sub>3</sub> substrate with a deposited titanium strips (a) and the morphology of the epitaxial Li(Nb,Ta)O<sub>3</sub> film grown on this substrate. The epitaxial structures LiNbO<sub>3</sub>/Ti:LiNbO<sub>3</sub> can be readily grown in a similar manner (Khachaturyan and Madoyan 1988 (a), (b)).

Distler (1975) reported the possibility of epitaxial growth on substrates with preliminarily deposited thin (nearly 50 nm) metallic layers. The thickness of the strips investigated by Khachaturyan and Madoyan (1988 (a), (b)) lies within the range of approximately 100–500 nm. Structural information is not transmitted through titanium strips, and in the normal mechanism the film must surely be defective on these strips. In laminar growth the situation was different. The density of growth structures reflecting the defective layer structure is minimum just over the titanium strips. The metallic layer obviously 'screens' the structural defects of the substrate which on the remaining sites grow into the film. A low density of the nuclei guarantees an insignificant amount of small-angle boundaries which affect neither the structural perfection of the film nor the absence of disoriented sites caused by nucleation on titanium strips themselves.

As soon as the epitaxial growth process is over, the remaining solvent is removed from the surface of the epitaxial film using kaolin cotton plugs or micro-channel slabs as liquid-phase absorbent (Dudkin and Khachaturyan 1988).





A micro-channel slab is a set of regularly positioned microslits – channels with diameter from 7 to 25  $\mu$ m each and the length chosen within the range of 0.3 to 1.2 mm. The cross section of micro-channel slabs typically varies from 30 to 40 mm, which exceeds the standard dimensions of the working field of products fabricated using epitaxial technique. When microchannel slabs are used for a long time at temperatures exceeding 600–1200°C, the slabs are preliminarily wetted in liquid kaolin ('kaolin milk') and then dried. The microchannel slabs processed this way can be used to remove the remaining liquid-phase flux from the sample surface. To this end the microchannel slab is brought close to the gap between the substrates so that its surface touches simultaneously the entire layer surface, as shown in Fig.2.35. Under equivalent capillary forces the liquid residues are drawn off along all the channels, that is, uniformly along the entire surface.

Thus, the methods discussed above make it possible to obtain layers with various waveguide configurations in the film. Varying the growth rate and the annealing time, we can obtain surface and immersed waveguides, strip line structures and layers with metallic buffered layers on the substrate-film boundary.

# 2.10 Growth of epitaxial films in the KTiOPO, family of crystals

As an alternative to directly addressing the ionic conductivity problem, and as a means to more effectively confine the optical wave to yield higher power density, films with well-defined step-like refractive index profile can be grown



Fig.2.35 Schematic of the use of microchannel slabs to absorb the liquid-phase flux from the film surface: 1) microchannel slab, 2) single channel, 3) substrate, 4) liquid phase, 5) epitaxial film, 6,7) contacts of the melt with a microchannel slab.

directly by liquid-phase epitaxy. The KTP crystal family is highly versatile and readily forms solid solutions among its members (Bierlein and Gier 1976; Jarman and Grubb 1988). The monovalent cations (*i.e.* K, Rb, Cs and Tl) are found to be mobile due to their direct covalent linkage to the bridging oxygen in the lattice, the pentavalent P and As ions, and the tetravalent Ti ions are expected to have negligible mobility even at elevated temperatures. Thus, a thin film consisting of solid solution of these ions (*e.g.* KTiOAs  $_{x}P_{1-x}O_{4}$  or KTi  $_{x}Sn_{1-x}OPO_{4}$ ) grown on a pure KTP substrate is expected to have a well-defined abrupt refractive index profile along *c* direction.

Effective waveguiding is obtained by satisfying the condition that the film's refractive indices be higher than that of the substrate. Deep channel waveguides can be fabricated on these heteroepitaxial films by subsequent ion-exchange. As the evanescent wave barely penetrates into the substrate, fluctuation in the diffusive profile of these channel guides will not significantly affect their waveguiding properties, thereby avoiding the problem of ionic conductivity.

The lattice constants for several end members of the KTP family are summarized in Table 2.9. Among the many possible film-substrate combinations, the KTA-KTP system was chosen in the experiments carried out by Cheng et al. (1991). There are two reasons for this. As the titanyl group is primarily responsible for the optical nonlinearity, replacement of titanium with other tetravalent ions is expected to lead to a significant loss in the nonlinearity, which in turn reduces the usefulness of these films in nonlinear frequency conversion. The arsenic for phosphorus substitution provides the desired refractive index increase without compromising on the nonlinearity. The optical and the crystal growth properties of KTP and KTA are better characterized than those of all other members of the KTP family (Bierlein et al. 1989). This allows for better correlation between experimental results and theoretical predictions.

Both the tungstate flux and the pure phosphate-arsenate self-flux were used in the experiments by Cheng et al. (1991). The self-flux used consists of the phosphate-arsenate along with the  $K_6P_4O_{13}$  flux (abbreviated as  $K_6$  below) used for bulk KTP growth (Gier 1980; Bordui et al. 1987). The relative crystal-flux compositions were chosen such that the growth temperatures were 850°C. Although significantly lower growth temperatures are possible using the tungstate, the  $K_6$  flux becomes far too viscous for growth below 750°C.

Crystal		]	Call voluma		
		<i>a b</i> (Å) (Å)		c (Å)	(Å)
KTiOPO4	(KTP)	12.822	6.4054	10.589	869.67
<b>RbTiOPO</b> ₄	(RTP)	12.964	6.4985	10.563	889.89
TlTiOPO₄	(TTP)	12.983	6.49	10.578	891.3
KTiOAsO₄	(KTA)	13.125	6.5716	10.786	930.31
RbTiOAsO₄	(RTA)	13.258	6.6781	10.766	953.2
CsTiOAsO₄	(CTA)	13.486	6.8616	10.688	989.02
T]TiOAsO₄	(TTA)	13.208	6.6865	10.724	947.09
KGeOPO₄	(KGP)	12.602	6.302	10.006	794.65
KSnOPO₄	(KSP)	13.146	6.528	10.727	920.56

Table 2.9 Lattice constants for several KTP isomorphs (Cheng et al 1991)

Variously oriented substrates, namely  $\{011\}$ ,  $\{110\}$ ,  $\{100\}$ ,  $\{111\}$  and  $\{201\}$  plates, have been successfully used to give as-grown films with highly specular surfaces. KTP and KTiOAs<sub>x</sub>P<sub>1-x</sub>O<sub>4</sub> substrates were primarily cut from flux-grown crystals.

The use of hydrothermally grown materials typically leads to optical degradation with the formation of fine white filaments in the substrate. Cheng et al. (1991) speculate that this degradation is due to the precipitation of fine water-based inclusions in these materials.

The substrates are  $-1\times1$  cm<sup>2</sup> × mm thick plates, cut parallel to the natural growth facets. All plates were polished with sequentially finer (3–0.25 µm) diamond based polishing powder, and finished with a 30 s chemical-mechanical polish in colloidal silica. A small (0.75 mm) hole, drilled at one corner of the substrate, allows it to be tied onto a crystal rotation-pulling head with a thin platinum wire. The substrate was held vertically to assist flux drainage after dipping. A slight etching of the substrate in warm dilute hydrochloric acid prior to the dipping was found to improve the equality of the epitaxial film.

The dipping setup is identical to the bulk growth furnace. It consists of a 250 ml crucible placed at the bottom of a short zone top-loading crucible furnace lined by a 4.5-inch quartz tube.

The melt (~200 ml) is homogenized at about 50°C above its liquidus temperature. A somewhat longer soak time is often needed when using the  $K_s$  flux. The substrate is introduced into the growth furnace slowly (~5-25 mm/min). The melt is then cooled to about 1.5-3°C below the saturation point and allowed to equilibrate for 30 min. The substrate is then dipped into the melt and spun unidirectionally at 10 rpm. The dipping time is varied depending on the desired film thickness, the degree of supersaturation used, the choice of flux and the growth temperature. Experimentally, Cheng et al. (1991) found that a slight back-etching of the substrate prior to growth results in significantly better quality films. This is accomplished simply by taking advantage of the thermal inertia of the system and submerging the substrate before the melt reaches the growth temperature.




Upon completion of the dipping, the plate is withdrawn from the melt and the furnace at approximately 5-25 mm/min. Any residual flux present is washed off with warm dilute hydrochloric acid. The thickness of the film is nearly  $\pm 5$  µm.

Using the dipping procedure outlined above, Cheng et al. (1991) have grown KTiOAs  $P_{1-v}O_4$  films between 4 and 20 µm on suitably chosen substrates of KTP or KTiOAs  $P_{1,y}O_4$  (where x < y). As an independent confirmation of the step-like of the step-like refractive index profile of these films, electron microprobe technique was used to map out the composition of a 50 µmthick KTiOP<sub>0.76</sub>As<sub>0.24</sub>O<sub>4</sub> film on a KTP substrate (Fig.2.36). The 'abrupt' increase in the arsenic content from the substrate to the film convincingly demonstrates that phosphorus-arsenic exchange is negligible under the growth conditions (~850°C). Since the as-grown film has the same morphology as that of KTP and the solid solution  $KTiOAs_v P_{1-v}O_4$  is the only stable phase in the melt, Cheng et al. (1991) conclude that the film is epitaxial and is structurally analogous to KTP. The refractive index of the film can be estimated from the known refractive indices of the end members, and is in excellent agreement with the *m*-lines spectrometry results. Cheng et al. (1991) have also grown thin films of  $Rb_{0,2}K_{0,8}TiOPO_4$  on KTP. The significant penetration of the Rb<sup>+</sup> into the substrate verified that the K<sup>+</sup> ions are highly mobile, and step-index films cannot be readily obtained from the cationic solid solutions.

Table 2.10 summarizes the partition coefficients for arsenic using the tungstate flux. The partition coefficient, k, is defined as:

 $k = [As]_{crystal} / [As]_{melt}$ 

where [As] is the mole fraction of As in the crystal or the melt. The greater than unity partition coefficient suggests that As is favoured in the  $KTiOAs_xP_{1-x}O_4$  lattice. Figure 2.37 plots the lattice constants of the  $KTiOAs_xP_{1-x}O_4$  system. The results indicate that, unlike the  $Rb_xK_{1-x}TiOPO_4$ 

[As] <sub>crystal</sub>	[As] <sub>melt</sub>	k
24	20	1.2
39.1	35	1.12
56.1	50	1.12
82.6	75	1.1
87.4	80	1.1

**Table 2.10** Partition coefficient, k, of arsenic from a tungsten melt; (As) is determined by ICP analysis of As and P in bulk crystals grown at the same temperature (Cheng at al 1991)



**Fig.2.37** Lattice constants of the KTiOP<sub>x</sub>As<sub>1-x</sub>O<sub>4</sub> system. Solid lines are predictions using Vegard's law (Cheng et al. 1991).

system, the lattice constants a, b and c, increase monotonically with arsenic content. The following Vegard laws fit the  $KTiOAs_{1}P_{1}O_{4}$  results very well:

```
a(x) = (0.32 \text{ Å})x + 12.822 \text{ Å},

b(x) = (0.1662 \text{ Å})x + 6.4054 \text{ Å},

c(x) = (0.197 \text{ Å})x + 10.589 \text{ Å},
```

where x is the mole fraction of As in the crystals. It was experimentally found that the maximum lattice mismatch for high quality film growth is about 1%, which corresponds to a 35% increase in arsenic content in the KTiOAs  $_{x}P_{1-x}O_{4}$  film and to an estimated refractive index increase of  $\Delta n_{b} \sim 0.0177$  at 1.064 µm. Film cracking and 'scaling' were observed for films with larger lattice mismatch.

Significantly different growth properties were observed for tungstate flux and the  $K_6$  flux. At about 850°C and with comparable supercooling (about 2°C), the growth rate was substantially slower in the  $K_6$  flux than in tungstate. To achieve a comparable growth rate using the  $K_6$  flux, a supercooling roughly twice that used in tungstate is needed. Films grown from the  $K_6$  flux tend to have film-substrate interfaces of poorer quality. It is likely that this is due to the slow dissolution kinetics of the  $K_6$  flux (Cheng et al. 1991), which makes the implementation of pre-growth etching difficult. The time linearity of film growth for a given supercooling was established.

The KTA processes were reported to have appreciably higher optical nonlinearity and lower optical scattering than KTP (Bierlein et al. 1989). The ideal film-substrate combination is therefore a pure KTA film on suitably chosen KTiOAs<sub>x</sub>P<sub>1-x</sub>O<sub>4</sub> substrate. This combination also eliminates any possible microscopic compositional fluctuation in the film due to the non-unity partition coefficient k of arsenic. Although compositional variations in KTiOAs<sub>x</sub>P<sub>1-x</sub>O<sub>4</sub> substrates can in principle occur, their effect on the waveguiding properties will be negligible. The film was shown to waveguide effectively at 0.632 µm, with no more than two optical modes.

Cheng et al. (1991) also explored the film growth of solid solutions involving the titanyl group. The growth of KTi, Sn, OPO, films, though preferred over KTi, Ge, OPO, proves difficult due to the anomalously slow dissolution of KSP. In contrast, using the procedure outlined above, Cheng et al. (1991) readily grew 10 µm KTi<sub>0.96</sub>Ge<sub>0.04</sub>OPO<sub>4</sub> films on {011} KTP substrates using a 20% {Ge} solution. Discouragingly, even with a low 4.3% Ge incorporation, numerous cracks perpendicular to c were observed in thicker (30 µm) films. Cheng et al. (1991) attribute this increased film-cracking tendency to the fact that, unlike the KTiOAs  $P_{1-x}O_4$  films, the KTi<sub>0.96</sub>Ge<sub>0.04</sub>O PO<sub>4</sub> films are under tensile stress. This interpretation is entirely consistent with the prediction, using Vegard's law and Table 2.9, that the cracks should be normal to c as observed. These experiments suggest that solid-solution films of either KTi<sub>1-x</sub>Sn<sub>2</sub>OPO<sub>4</sub> or KTi, Ge OPO, are of limited practical utility. The situation can however be improved significantly by reversing the film-substrate configuration, *i.e.* KTP film on KTi,\_,Ge,OPO, substrate - provided that the refractive indices condition for waveguiding can be satisfied.

# **3** Influence of Electric Current upon Liquid-Phase Epitaxy of Ferroelectrics

Progress of micro- and optoelectronics depends much on how successfully the existing methods for obtaining thin-film structures solve the problem of reproducible formation of perfect multilayer heteroepitaxial compositions based on multicomponent semiconductor solid solutions of A<sub>3</sub>B<sub>5</sub> and ferroelectrics manufactured from niobates and tantalates of alkaline and alkali earth metals. Requirements on the technology and crystallographic perfection of structures and on the properties of films have increased substantially. Among the known liquid-phase methods for obtaining epitaxial structures with predetermined properties, liquidphase epitaxy possesses the widest potentialities for film composition, thickness and structure control. In this chapter, we present theoretical and experimental results of studies of the influence of direct electric current upon the processes of liquid-phase epitaxy. We also present the results of original papers on growth and investigation of thin-film structures of ferroelectrics on an example of lithium niobate and solid solutions of lithium niobate-tantalate. We account for the fact that an electric field and, in particular, a direct electric current flowing through a crystal is one of the effective means for changing crystallization conditions that affect crystallographic perfection and some physical properties of grown structures (Khachaturyan et al 1987).

## 3.1. Electric field and crystallization

An electric field is a fairly strong energetic factor affecting the nucleation and growth of a new phase under first-order phase transitions. But the numerous reports on the influence of an electric field upon the crystallization process do not provide final unambiguous conclusions concerning a unified physical mechanism of field effect. In view of this we consider possible mechanisms of the influence of a direct electric field upon crystallization processes.

### 3.1.1 Bulk crystallization

In 1956, A.F. Ioffe gave a theoretical description of motion of a melted zone under the action of electric current in germanium bars (Ioffe 1956). This

motion was explained by the presence of temperature gradient in the liquid zone due to Peltier heat release (or absorption) at the liquid-solid interfaces. In 1957, W. Pfann (Pfann et al 1957) gave an experimental confirmation of the theory suggested by A.F. loffe. A whole number of new experimental results (Pfann 1970) on the direction of motion in a melted zone depending on its composition required specification of the theory.

The influence of an electric field on the formation of crystallization centres in supersaturated salt solutions was first discovered by Shubnikov (1956) who showed that a superposition of an external electric field causes a sharp increase in the number of crystallization centres.

Investigation of the action of electric current in a crystal-melt chain in germanium crystal growth using Czochralski and Stepanov methods has revealed variation in the intensity and striation period in crystals (Levinzon et al 1969; Dudnik et al 1973). Germanium single crystals were grown in the {111} direction and doped with antimony to obtain a resistivity of 5-10 ohm.cm.

The density of current increased from 0 to 50  $A/cm^2$  in the course of growth of one crystal. Stepanov grown ingots exhibited a decrease of the amplitude and pitch of striation, which does not depend on the direction of current and is only due to Joule heat release (*i.e.* the Joule heat exceeds the Peltier heat).

It should be noted that the parameters of inhomogeneity of control ingots grown in a similar manner by the Czochralski method remained practically unaltered when electric current was applied.

When germanium strips are grown by the Stepanov method, the transmitted electric current has an effect not only upon the nature of striation in single crystals. It was shown (Egorov et al 1971) that an application of a direct electric current through an interface provides control over the crystallization front shape during zone crystal growth. To choose the current density necessary for crystallization front shape control, one should take into account the relation between the Peltier and Joule heats which are respectively equal to

 $Q_p = \Pi J, \ Q_j = (1/2) \ RJ^2,$ 

 $\Pi$  is the Peltier coefficient, R is the resultant resistance of the portions of liquid and crystal adjoining the crystallization front and J is current density.

These effects can be summed up or subtracted depending on the direction of current.

In a region where the current density is such that  $Q_j > Q_p$ , the crystallization front rises, while for  $Q_j < Q_{p_s}$  it falls. When the Joule and Peltier heats are equal to each other,  $Q_j = Q_{p_s}$ , the applied current induces no variations of the crystallization front shape. The corresponding equilibrium density of current will be equal to

$$J_{\text{cauil}} = 2\Pi/R$$

The deviation of the impurity concentration from the equilibrium value ( $\Delta C$ ) at the solid-liquid interface can be represented in the general form as an

algebraic sum of the deviations of the concentrations from their equilibrium values, caused by electrothermal effects ( $\Delta C_1$  stands for the Joule effect, Peltier effect and others) and electric transfer ( $\Delta C_2$ )

 $\Delta C = \Delta C_1 + \Delta C_2$ 

In 1963–1964 two models were proposed (Tiller 1963; Hurle et al 1964) attempting allowance for migration of melt components under the action of an electric current in stationary conditions. Although the order of magnitude of differential mobility of a melted zone component was determined within these models, they were unable to explain the results of subsequent works on epitaxial growth.

The Peltier effect was applied to determine the crystallization rate of InSb in Czochralski type crystal growth (Singh et al 1968; Lichtensteiger et al 1971; Wargo and Witt 1984). Application of a pulsed current to a crystal-melt boundary resulted in the appearance of striation in the crystal structure, and variation of the frequency and pulse intensity caused variations in the width and intensity of these striae. The striae resulted from variation of impurity concentration due to a change of instantaneous growth rate caused by Peltier heating (or cooling). The authors noticed that the impurity concentration in a stria remains constant during all the time of application of a current, changes instantaneously at the end of a pulse and remains unchanged till a subsequent pulse. Changing the magnitude of electric current pulse and thus changing the impurity concentration in a stria, they established a direct dependence of impurity segregation on the density of the current flowing through the system. The electric transfer which accompanies the Peltier effect is observed to restrict its action in multicomponent systems.

Similar results were obtained for Ge (Vojdani et al 1975). The temperature distribution in a system to which an electric current is applied was shown to be a function of the Peltier effect.

The processes proceeding during the growth of potassium-tungsten bronze  $(Na_xWO_3)$  and lanthanum hexaboride  $(LaB_6)$  by the method combining electrochemical crystallization and Czochralski technique were investigated by Mattei et al (1976), Huggins and Elwell 1977) and DeMattei and Feigelson (1978). If in the usual crystal growth the motive force is supersaturation or thermal gradient, in electrochemical crystallization the kinetic and diffusion processes are activated by an external electric field whose potential exceeds the equilibrium potential value. Electrochemical crystallization is a Faraday effect, and the precipitation rate at the interface is readily controlled by the strength of current.

Problems connected with the influence of electric transfer and Peltier effect upon the impurity distribution coefficient were discussed on an example of growth of Bi-Sb crystals doped with Te, Se, Sn and Pb (Krylov and Ivanov 1980).

When growing chromium-doped lithium niobate crystals by Czochralski technique, Räber (1976) and Feisst and Räber (1983) examined the influence of the strength and direction of the electric current flowing through a crystal-

melt system upon the value of the chromium distribution coefficient.

Application of 50 mA pulses of against the background 5 mA current resulted in striation caused by a decrease of chromium concentration by about a factor of two, the current on the seed crystal having polarity '+'. The distribution coefficient ( $K_{eff}$ ) as a function of the strength and direction of current was estimated. As the electric current density varied within the range 15< j < 18mA/cm<sup>2</sup>, the distribution coefficient decreased linearly with an increase of the current density. Outside the indicated current density range the crystal growth became unstable. High values of the density of currents applied induced the appearance of gas bubbles in the crystal. The colour of the crystal changed with reversal of polarity, and the surface became rough.

Voskresenskaya et al (1985) reported the results of their investigation of the electric field effect upon the processes proceeding at the crystallization front of bismuth germanate grown by Czochralski method. Crystals were grown from a crucible with cathode and anode polarizations, the density of currents was varied within the range of (0÷20) mA. An electric current was shown to have a great effect on the impurity distribution coefficient and on the magnitude of remanent stresses in the crystal. In the case of cathode polarization, the growth process was stable, the resistance of the electric circuit increased monotonically with crystal growth. A change of polarization for an anode one led to a decrease in the electric resistance at the boundary by a factor of 25 and induced nonstationary processes at the crystallization front, which are connected with an unstable value of resistance in the crystal-meltcrucible chain. An analysis of the value of remanent stresses in different parts of crystals grown from a crucible with cathode polarization showed that the stresses fall down to 70% as compared with regions growing without any current being applied.

Thus, an analysis of the papers investigating the influence of a direct electric current upon crystallization of a bulk material revealed the possibility of controlling the impurity composition and structural perfection of grown single crystals.

#### 3.1.2 Thin films

The wide application of thin films in micro- and optoelectronics is explained by many factors. The most important here is obviously the fact that it is only thin films that permit obtaining compact schemes at a low consumed power and a high density of scheme elements. Furthermore, the methods of obtaining thin films provide highly pure substances or materials with a composition controlled with precision.

Researchers engaged in growing single crystals and films are interested in finding new ways of affecting a growing crystal, which would allow a more effective control over the growth rate, surface morphology, the distribution of alloying impurities in a crystallization medium and the concentration of structural defects.

A large amount of experimental material is available on the influence of an electric field upon epitaxial growth from the gas phase. The general chemico-physical considerations imply that superposition of the difference of electric potentials on the source and substrate may give the following principal effects:

1. Change of conditions of chemical equilibrium of heterogeneous reactions on the source and substrate surfaces. Indeed, the Gibbs expression for the free energy of a physico-chemical system in an electric field contains an additional term showing that the work of electric forces is proportional to the strength and depends on the direction of the electric field strength vector (Sychev 1970):

$$G = H - TS - \frac{\dot{E}}{4\pi}\vec{D},$$

where  $\vec{E}$  is the electric field strength,  $\vec{D} = \vec{E} + 4\pi \vec{P}$  the electric induction and  $\vec{P}$  the dielectric polarization.

2. Change of diffusion activation energy and diffusion rate in the gas phase on the source and substrate surfaces. The main effect is that the diffusive motion of particles is superposed by a directed drift of ions in the electric field (Boltaks 1972; Kolobov and Samokhvalov 1975):  $j = \mu EC$ , where j is a charged particle flow,  $\mu$  is mobility and C is concentration.

Electrodiffusion of charged vacancies can proceed simultaneously. The change in the diffusion activation energy under the action of electric field was reported by Gorsky (1969).

3. Change in the position of the Fermi level on the surface of a semiconductor caused by a transverse electric field. This results in displacement of equilibrium between a charged and uncharged forms of chemisorption on the surface, which leads to an additional adsorption or desorption of molecules depending on the sign of the field. This phenomenon was called electrosorption (Wolkenstein 1973). The relative change of adsorbtive ability is described by the formula

$$\Delta N / N_0 = \eta_0^{\mp} [\exp(\mp \Delta V_s / kT) - 1],$$

where  $N_0$  is adsorbtive ability in the absence of an electric field,  $\Delta N = N - N_0$  is the change of adsorbtive ability,  $\Delta V_s$  is the surface zone bend,  $\eta_0^{\pm}$  is a relative content of adsorbed particles on an uncharged semiconductor (the minus refers to acceptor molecules, the plus to donor molecules).

The near-surface zone bend  $\Delta V_s$  depends on the electric charge density on the superconductor surface caused both by the presence of electrically charged adsorbed particles and by superposition of an external field of strength E. For this reason  $\Delta N/N = f(E)$ , the external electric field affecting not only the relation between the evenly adsorbed donor and acceptor molecules, but also the sorption kinetics (Wolkenstein 1973). If the crystal lattice of a semiconductor is characterized by a substantial contribution of the ion component of chemical bond, an electric field can also produce a definite effect upon the stoichiometry of crystal composition

4. Change of critical supersaturation necessary for the appearance and stabilization of crystallization nuclei in the course of laminar crystal growth. As shown by Sirota (1971), in the simplest case, when the phase transition heat  $\Delta H = 0$ , the critical supersaturation  $\sigma_{crit}$  for crystallization nucleation is described, according to the generalized Thomson theory, by the Thomson formula

$$\sigma_{\rm crit} = V \left[ 2\gamma / r + \partial \gamma / \partial r - q^2 / 8\pi k r^4 \right],$$

where V and r are the volume and the radius of the crystallization nucleus, q is the electric charge of the crystallization nucleus,  $\gamma$  is the surface free energy and k is the constant dependent on the nature of the substance.

According to Chernov and Trusov (1969), the surface charges lower the nucleation activation energy by about 10%.

It is an experimentally established fact that an electric field has an effect upon the growth rate and alloy distribution between the gas phase and the growing films of germanium, silicon (Lyutovich et al 1971) and gallium arsenide (Palienko et al 1971). It was noticed that the threshold temperature of silicon epitaxial growth lowers under hydrogen reduction of  $SiCl_4$ , and the activation energy of precipitation and the morphology of the film surface also change (Chopra 1969).

The studies of the influence of an electric field under the chemical transport of substance from the near source onto the substrate, *i.e.* by the sandwich method (Ikonnikova and Ivleva 1974; Korobov et al 1977) reveal the possibility of controlling the gallium arsenide layer growth and of suppressing uncontrolled inhomogeneities in the bulk film (Korobov et al 1977).

Thus, the use of electric fields of different polarities and strength in the course of epitaxial growth from the gas phase is considered to be promising for an increase of integration and controlled local intensification of technological processes in microelectronics.

#### 3.1.3 Liquid-phase electroepitaxy

The method of liquid phase epitaxy in an electric field, called also liquidphase electroepitaxy, was first proposed for obtaining epitaxial films of semiconductors on an example of the compound GaSb (Golubev et al 1974a, b). This method is based on crystallization under the action of a direct electric current running through a source-buffered melt-substrate system. As opposed to electrocrystallization, where the crystallized substance is a product of the electrode reaction, crystallization in liquid-phase electroepitaxy is a secondary phenomenon, a result of the current-induced variation in the temperature and concentration of the substance.

The concentration and temperature gradients arising at the boundary are a consequence of a number of physical phenomena due to electric current in different parts of the growth cell, namely, it may be Peltier heat release or absorption at boundaries, electromigration of components in the liquid phase, Joule heat and some other effects.

Two types of liquid-phase electrocpitaxy were investigated (Fig.3.1). The first type is an equilibrium process, when in the course of film growth the liquid phase is permanently fed by precipitated components from the source (Fig.3.1a), and the second type when the liquid phase is not fed (Fig.3.1b).

Let us consider the essence of liquid-phase electroepitaxy (Gevorkyan et al 1977; Khachaturyan et al 1977). Prior to epitaxy, the temperature of the crystallization cell was  $T_0$ . In the initial state the system consists of a source and a substrate which are in contact with the buffered melt and with current-



FIg.3.1 Basic types of liquid phase electroepitaxy with indication of temperature and concentration distribution at the crystallization front: a) with liquid phase feeding; b) without liquid phase feeding.

conducting electrodes. An external heater maintains the constant temperature  $T_0$ . At this temperature, the liquid phase is saturated with the materials of the source and the substrate which are dissolved in the system, and the entire system is in the state of thermodynamic equilibrium yielding no material transport.

If a direct electric current of appropriate polarity runs through the crystallization cell, Peltier heat is released at the source-liquid phase boundary and is absorbed at the liquid phase-substrate boundary. As a result, the temperature at the boundaries changes, a temperature gradient occurs in the liquid phase leading to the appearance of a concentration gradient, the source is permanently dissolved and its material is transported to the substrate. Thus, liquid-phase electroepitaxy in fact combines elements of ordinary liquid phase epitaxy and elements of zone melting with a temperature gradient. A change in the current polarity is responsible for dissolution of the substrate, while the layer is precipitated onto the source. Reversibility and low inertia of heat release (Peltier heat releases within a characteristic time of excessive energy transfer to electrons by atoms of the main substance) provide a quick and convenient control over liquid-phase electroepitaxy.

It is also noteworthy that a flow of current through a crystallization cell is responsible for the substance transport onto substrate due to electromigration of liquid-phase components.

As soon as the electric current is off, the transport of substance particles stops practically instantaneously, a uniform distribution of components is established in the liquid zone, and thermodynamic equilibrium sets up in the system. The film grown on the substrate is not dissolved, and the liquid-phase composition remains exactly the same as before the current was switched on.

If a source is absent in the crystallization system then substance precipitation onto the substrate under the action of an electric current (under any mass transfer mechanism) may be only due to liquid-phase depletion, which leads to a nonequilibrium state of the crystallization system after the process is over.

Application of one or the other method should be coordinated with the purposes and tasks of a particular technological process.



138

Fig.3.2 Schematic of growth cell for liquid phase electroepitaxy. 1,5) electrodes, 2) substrate, 3) liquid phase, 4) source.

# 3.2 Physical basis of liquid-phase electroepitaxy (The theory of the method)

We shall consider the problem presented in Fig.3.2. The material of the liquid zone is not supposed to form chemical compounds or solid solutions with materials of the source and substrate. The theory of zone melting with a temperature gradient (ZMTG)\* (Lozovsky 1972) predicts two possible zone regimes: kinetic and diffusion.

We shall consider only the diffusion regime which is attained for a fairly small temperature gradient. In this case, the thermal equilibrium in the system will set in much quicker than the diffusion one since the liquid-phase diffusion coefficient of atoms, D, is much less than the thermal conductivity K. The times of establishing the diffusion  $\tau_{D}$  and thermal  $\tau_{T}$  equilibria are given by the relations

$$\tau_D = L^2 / \pi^2 D \tag{3.1}$$

$$\tau_{\tau} = L^2 / \pi^2 K. \tag{3.2}$$

Since  $D \ll K$ , from (3.1) and (3.2) it follows that  $\tau_D / \tau_T \gg 1$ . In as much as the stationary regime of zone melting with Peltier-induced motion was earlier considered by Tiller (1963) and Hurle et al (1964), the solution of the formulated problem falls into three parts analysed by Lozovsky (1972) and Khachaturyan (1974):

a. temperature distribution in a system to which a current is applied;

b. film growth rate as a function of current density;

c. time-dependent variation of film composition (composition distribution over thickness).

# 3.2.1 Temperature distribution in a system under the action of an electric current

We shall consider the simplest case when the materials of the source and substrate are the same. In the problem of temperature distribution such a consideration is almost always admissible.

In the general case, the following heat sources should be taken into account in the solution of the problem:

- 1. Peltier heat a surface heat source;
- 2. Joule heat a bulk heat source;
- 3. crystallization and dissolution heat a surface heat source;

<sup>\*</sup>It is obvious that the problem in indicated geometry is similar to ZTMG

4. Thomson effect – a bulk heat source;

5. Dufour effect - a bulk heat source.

When an electric current is applied to a source-solution-substrate system (Fig.3.2), Peltier heat is instantaneously released or absorbed at the boundaries (points z = 0 and z = L), with a surface power

$$Q_{n} = \Pi J, \tag{3.3}$$

where  $\Pi = |\alpha_1 - \alpha_2| T$  is the Peltier coefficient for the interfaces, J is the density of current through the system (mA/cm<sup>2</sup>),  $\alpha = (\alpha_1 - \alpha_2)$  is the difference between the thermoelectromotive forces of the solvent and source (substrate) material (in V/grad).

All calculations are carried out for the low-density regions of current, and therefore the Joule heat quadratic in J can be neglected.

The dissolution and crystallization heats have reverse signs of the Peltier heat. In the regions where Peltier heat is released the dissolution heat is absorbed, while in the region where Peltier heat is absorbed the crystallization heat is released. So, in the general case, this causes a decrease of absorbed and released Peltier heat, that is, a decrease of the temperature gradient. Under certain growth conditions the crystallization (dissolution) heat can completely compensate the Peltier heat and set in isothermal conditions of crystal growth. For the surface power of crystallization heat we can write

$$Q_i = H \times d \times \nu \tag{3.4}$$

where H is specific heat of crystallization (dissolution) (kcal/g), d is the density of substance under crystallization (dissolution) (g/cm<sup>3</sup>), v is the crystallization (dissolution) rate (cm/s).

The Thomson effect is due to the temperature dependence of current carrier concentration, and in our system it can be neglected (the zone material is a liquid metal). Moreover, it is also quadratic in J.

The Dufour effect in liquid systems is insignificant (De Groot and Mazur 1962). Thus, we can neglect bulk heat sources and only make allowance for surface sources, that is, Peltier and dissolution (or crystallization) heat. Under this assumption, the equation for thermal conductivity has the form

$$\frac{\partial T(z,t)}{\partial t} = K \frac{\partial^2 T(z,t)}{\partial z^2} + v \frac{\partial T(z,t)}{\partial z}; \ 0 < t < \infty; \ -L_1 < z < L_1 + L$$
(3.5)

where K is the thermal conductivity of the liquid-zone material, v is the velocity of zone motion.

We assume here the zone thickness to remain unaltered and the origin of coordinates to coincide with the interface (Petrosyan et al 1974). Since in a real technological regime the current does not change at all or changes very slowly, in the solution of the problem it can be thought of as constant.

The second term in the right-hand side of equation (3.5) describes the influence

of the interface motion upon temperature distribution. Since the growth rate in the system is very slow, its effect can be disregarded. Indeed, for this purpose it is necessary that the following should hold true

$$\frac{v L}{K} \ll 1.$$

140

If liquid Bi or Ga is used as solvent, then  $K_{\text{Bi}} = 1.1 \times 10^{-1} \text{ cm}^2/\text{s}$ ,  $K_{\text{Ga}} = 1.3 \times 10^{-1} \text{ cm}^2/\text{s}$ , and for the liquid zone thickness  $L = 100 \text{ }\mu\text{m}$  and the crystallization rate  $\nu \sim 10^{-6} \text{ cm/s}$  this inequality is satisfied.

Given this, a stationary temperature distribution sets in within the characteristic time  $\tau_r$  which is of the order of one millisecond. Thus, setting in of equilibrium temperature distribution actually appears to be high-speed and admits current pulses through the system of frequency up to tens of Hertz.

The diffusion processes in the system are characterized by a time constant  $\tau_p$ . Assuming the diffusion coefficient to be equal to  $5 \times 10^{-5}$  cm<sup>2</sup>/s, we find that it is of the order of a second and greatly exceeds  $\tau_r$ . In all further calculations, the temperature distribution can therefore be regarded as stationary and the time derivative in (3.5) can be neglected. The equation for thermal conductivity has the form

$$\partial^2 T(z) / \partial z^2 = 0, -L_1 \le z \le L_1 + L.$$
 (3.6)

This equation can be solved for each part of the system separately.

Kuznetsov et al (1983) solved the problem of temperature distribution for the system depicted in Fig.3.2 with the following boundary conditions. At the source-liquid zone and substrate-electrode interfaces, constant temperatures,  $T^{II}$  and  $T^{I}$ , are maintained. At the liquid zone-substrate boundary, the crystallization heat release is taken into account along with Peltier effect. Under these conditions, the temperature difference  $\Delta T$  at the liquid zone boundaries is equal to

$$\Delta T = \left[ T' - T'' + T' \Delta \alpha J (L_1 / \lambda_s) - Q_k (L_1 / \lambda_s) \right] / \left[ 1 + (\lambda_L L_1 / \lambda_s L) + (\Delta \alpha I L_1 / \lambda_s) \right],$$
(3.7)

where  $\lambda_s$ ,  $\lambda_L$ ,  $L_1$ , L are the temperature conductivities and thicknesses of the substrate (source) and liquid zone, respectively, and  $\Delta \alpha = (\Delta \alpha_2 - \Delta \alpha_3)$ . It is readily seen that at  $T^{T} = T^{TT} = T$ , disregarding the crystallization heat and taking into account  $\lambda_1 L_1 / L_2 \gg 1$ , we obtain from (3.7)

$$\Delta T/L = \prod 1/\lambda, \tag{3.8}$$

We can see that the temperature gradient is independent of the zone thickness and is determined by the magnitude of the density of current flowing through the system. We can estimate the temperature jump in the zone and the temperature gradient in the system GaSb-Bi(Ga). Taking the following values of the parameters (Khachaturyan 1974)  $\alpha_{GaSb} = 150 \ \mu V/grad$ ,  $\alpha_{Bi} = -20 \ \mu V/grad$ .  $\alpha_{Ga} = 3 \ \mu V/grad$ ,  $L = 10^{-2}$ cm,  $J = 25 \ A/cm^2$ ,  $\lambda_{Ga} = 27 \ W/mgrad$ ,  $\lambda_{Bi} = 14 \ W/mgrad$  and  $T = 723 \ K$ , we find the temperature difference in the zone

$$\Delta T = qL / \lambda_L = \left[ \left( \alpha_{\text{GaBb}} - \alpha_{\text{GaBi}} \right) / \lambda_L \right] T_0 J L \cong 0.2, \tag{3.9}$$

that is, the temperature gradient in the zone is grad  $T \approx 20$  grad/cm. It may be seen that this value varies within the range typical of ZMTG (Lozovsky 1972).

For the system presented in Fig.3.2, Gevorkyan et al (1983) found a temperature distribution with somewhat different boundary conditions: at the ends of the electrodes a constant temperature is maintained and at the electrode-substrate, substrate-liquid zone, liquid zone-source and source-electrode boundaries the Peltier effect is taken into account.

#### 3.2.2 Film growth rate

In the source-solution-substrate system considered above, a linear temperature distribution practically sets in after a direct electric current is switched on. At this stage the system is already not in the state of thermodynamic equilibrium. Our task is to determine the component concentration distribution in the zone and the film growth rate in a given temperature field.

The component concentration distribution in the liquid zone with allowance both for diffusion and electromigration is determined from the solution of the equation

$$\frac{\partial C}{\partial t} = D(\frac{\partial^2 C}{\partial z^2}) - \mu E(\frac{\partial C}{\partial z}) - \nu(\frac{\partial C}{\partial z}), \qquad (3.10)$$

where D is the diffusion coefficient,  $\mu E = eDz_{eff} J\rho /kT$  is the particle drift velocity in the electric field E,  $z_{eff}$  is an effective particle charge, e is the electron charge,  $\rho$  is resistivity of the liquid phase.

In experiments on liquid-phase electroepitaxy, the condition  $\mu E/\nu \gg 1$  is typically fulfilled. For this reason, the last term in (3.10) can be omitted. Equation (3.10) without the last term was solved by Gevorkyan et al (1983). Solving equation (3.10), we come to the final expression for  $\nu(t)$ :

$$v(t) = \frac{C_2 - C_1}{C_s - C_1} \cdot \frac{\mu E}{\exp(\mu EL / D) - 1} - \frac{\mu E C_1}{C_s - C_1} + \frac{2D}{L(C_s - C_1)} \sum_{n=1}^{\infty} \frac{\exp\left[-\left(1 + \mu^2 E^2 L^2 / 4\pi^2 n^2 D^2\right)n^2 t / \tau_{\nu}\right]}{1 + \mu^2 E^2 L^2 / 4\pi^2 n^2 D^2} \times [C_0 - C_1 + (-1)^n (C_2 - C_0) \exp(-\mu EL / 2D)],$$
(3.11)

where  $C_s$  is the concentration in the solid phase. As  $t \to \infty$ , from (3.11) we obtain the stationary velocity of growth,  $v_{et}$ 

$$v_{st} = (C_2 - C_1) / (C_s - C_1) \left\{ \mu E / \left[ \exp(\mu E L / D) - 1 \right] \right\} - \mu E C_1 / (C_s - C_1).$$
(3.12)

As might be expected, for E = 0 we obtain from (3.12)

$$v_0 = \left[ (C_2 - C_1) / (C_s - C_1) \right] \cdot (D / L).$$
(3.13)

From (3.12) we can see that  $v_{st}$  depends not only on the value, but also on the sign of *E*, that is, the type of substrate and source conductivities.

#### 3.2.3 Chemical composition control of the film

The liquid-phase electroepitaxy method permits obtaining films with composition controlled throughout the thickness by means of current density variation. Birulin et al (1984), Zhovnir and Zakhlenuk (1985), Zakhlenuk and Zhovnir (1985), Jastrebski et al (1978) and Bryskiewiecz (1985) showed the possibility of film composition control in liquid-phase electroepitaxy for a three-component system with account of Peltier and electric transfer. It is assumed that during the whole process the liquid zone at the boundary between phases is in local dynamic equilibrium with the source and substrate at a given temperature (the diffusion approximation), and the film composition is determined at each instant of time by the liquid phase composition at the boundary with the substrate. At each time moment, the film composition must be in proportional relation with diffusion fluxes at the surface, and the liquid phase composition is given by the liquidus curve.

As soon as the current through the crystallization cell is on and the transition process at the growth boundary is over, a certain value of the concentration of one of the components,  $C_x$ , sets in, which is determined on the one hand by the Peltier-induced temperature variation at the solid phase-buffered melt boundary and on the other hand by equilibrium of fluxes of particles of a given component coming to and from the boundary. At the other melt boundary (in the absence of convection) or at a distance of the  $\delta$ -layer (in the presence of convection) the initial concentration remains unchanged and equals  $C_0$ . The necessary condition is here the equality between the particle fluxes coming through the boundary of the  $\delta$ -layer and going away into the solid phase (Birulin et al 1984):

$$\mu E C_0 + D (dC/dz)_{rel} = k_0 \nu C_r$$

where  $k_0$  is the equilibrium segregation coefficient, v is the growth rate of the epitaxial layer.

Depending on the relation between the values of the buffered melt components  $\mu$  and D, two component concentration values near the substrate are possible, namely,  $C_x: C_{x_1} \ge C_0$  and  $C_{x_2} \le C_0$ . In the approximation that in the transition ( $\delta$ ) layer of the liquid phase the concentration varies linearly, Birulin at al (1984) derived the expression for particle concentration of the component in the epitaxial layer as a function of electric current density

$$C_r^s = (\mu \rho J + D/\ell) / (k_0 v + D/\ell), \qquad (3.14)$$

where  $\rho$  is the melt resistivity,  $\ell$  the  $\delta$ -layer thickness, J the current density.

The analysis of (3.14) shows that the dependence of crystallized layer composition on the current density may only be absent provided that the relation

$$\frac{\mu \rho J + D/\ell}{k_0 \nu + D/\ell}$$

remains unaffected by current density variation, which is possible under the conditions that

1) the transition layer thickness is very small, *i.e.* 

$$D/\ell \geq \mu \rho J, D/\ell \geq k_0 v,$$

2) the quantity  $\ell$  is very large and the growth rate depends linearly on the density of electric current;

3) v and  $1/\ell$  depend linearly on the current density.

Theoretically, when the dependence v = f(J) is nonlinear, the layer composition must always depend on the current density. The form of this dependence is determined for each particular case by the value of the relation between  $\mu E$  and  $k_o v$ . If the  $\mu E$  value increases faster than  $k_o v$  with increasing current (for example,  $k_o \ll 1$ ), the content of the component will increase, whereas if the  $\mu E$  value increases slower than  $k_o v$  ( $k_o \gg 1$ ) or if the dependence v = f(J) is linear, the component concentration will decrease.

On the basis of generalized equations of mass transfer and phase equilibrium, Zhovnir and Zakhlenuk (1985) gave a qualitative analysis of some situations occurring under liquid-phase electroepitaxy in three-component systems, making allowance for electromigration and Peltier effect.

#### 3.2.4 Initial stages of nucleation

The presence of charges and electric fields are known to speed up nucleation of a new phase (Chernov and Trusov 1969; Aleksandrov and Entin 1971). Chernov and Trusov (1969) estimated the probability of nucleation in a pointcharge field on the surface of a dielectric. They calculated the contribution of the electrostatic field to the critical nucleation energy and solved the following electrostatic problem: a point charge q is located under the crystal surface at a depth H. The dielectric permittivities of the crystal and medium are equal to  $\varepsilon_{\rm cr}$  and  $\varepsilon_{\rm med}$ , respectively. The supersaturation of the medium relative to the crystal is  $\Delta \mu$ . The nucleus of the new phase has the shape of a flat disc of height a (a is equal to the lattice constant), Fig.3.3 (Chernov and Trusov 1969).

The work of critical nucleation is equal to



Fig.3.3 Schematic of nucleation on the crystal-medium interface in the presence of an electric charge.

$$\Delta G_* = \pi r_* \, a \, \alpha - (a \, q^2 \, / \, 32 \, \pi \varepsilon_0 H^2) \Big[ r_*^2 \, / \, (r_*^2 + H^2) \Big]^2 (1 \, / \, \varepsilon_{\text{med}} - 1 \, / \, \varepsilon_{\text{cr}})$$

where  $\varepsilon_0$  is the dielectric permittivity of the vacuum, the critical radius  $r_*$  is determined from the equation

$$r_{*} = (V_{c}\alpha / \Delta\mu) \left\{ 1 - \left[ q^{2}r_{*} / 32\pi^{2}\varepsilon_{0}\alpha (r_{*}^{2} + H^{2})^{2} \right] (1 / \varepsilon_{\text{med}} - 1 / \varepsilon_{\text{cr}}) \right\}$$

where  $\alpha$  is the energy of the formation of a unit side surface,  $V_c$  is the volume of a single particle in the crystal.

Aleksandrov and Entin (1971) considered nucleation as a displacement of an infinite plane crystal-medium boundary towards the medium for a distance equal to the crystal lattice period a. Within such an approach, the work of critical nucleation  $\Delta G$ , does not depend on the critical radius r.

$$\Delta G_{\star} = -\left[g^2 a / 16\pi\varepsilon_0\varepsilon_{\rm cr} (H^2 - a^2)\right] \left[\left(\varepsilon_{\rm cr} - \varepsilon_{\rm mod}\right) / \left(\varepsilon_{\rm cr} + \varepsilon_{\rm med}\right)\right]^2.$$

So, according to Chernov and Trusov (1969) and Aleksandrov and Entin (1971), the presence of a charge on the substrate leads to a decrease of nucleation energy, which in turn speeds up the formation of crystallization centres.

Dhanasekaran and Ramasamy (1986) investigated the influence of an electric field upon a two-dimensional nucleation. He considered cases where the electric field is perpendicular and parallel to the nucleation and showed that subject to the relation between the dielectric permittivities of the nucleus and the medium, the nucleation can be either accelerated or decelerated.

We shall present the estimates of the influence of an electrostatic field upon the nucleation rate. We shall consider the case when a new phase is formed on an electrode. In the general case, between the electrodes there are two substances, A and B, in the same (say, liquid) phase. A new (solid) phase C can nucleate on the electrode either from the substance A or from B (see Fig.3.4).

To find out the effect of the electrostatic field on the nucleation rate, one should calculate the contribution of the electrostatic field upon the critical nucleation energy. We shall carry out this calculation for two cases: 1) when new nuclei on the electrode form a metal and 2) when they form a dielectric.

We proceed to the first case. Suppose the new nuclei make up half of the

metal sphere on the electrode. To calculate the electrostatic contribution to the nucleation energy, we should determine the energy variation of the condenser filled with dielectric A + B (with the dielectric constant  $\varepsilon$ ) when a protuberance, a hemisphere of radius *a* appears on the electrode. Since the protrusion and the electrode are metals, the electrode surfaces are equipotentials. This is schematically presented in Fig.3.5.

The change of the electrostatic energy upon the appearance on the electrode of a hemispherical nucleus, when  $a \ll d$ , is equal to

$$\Delta W = -\pi \varepsilon_0 \varepsilon E_0^2 a^3. \tag{3.15}$$

From (3.15) it is seen that  $\Delta W < 0$ , and, therefore, the appearance of a metallic nucleus on the electrode is energetically advantageous, that is, the presence of the field  $E_0$  must promote nucleation.

The non-electric part of the energy change upon nucleation in the form of a hemisphere is given by (Aleksandrov 1978)

$$\Delta W_1 = \pi a^2 \sigma - 2\pi a^3 \Delta \mu / 3V_c, \ \Delta \mu = (\lambda / T_0)(T_0 - T),$$
(3.16)

where  $\sigma$  is the surface tension at the interface,  $\Delta \mu$  is the chemical potential variation under phase change,  $V_c$  the particle volume in the phase C,  $\lambda$  specific heat of crystallization,  $T-T_0$  the supercooling,  $T_0$  the equilibrium temperature of phase transition.

Summing up (3.16) and (3.15), we obtain the total energy variation under nucleation

$$\Delta G = \pi a^2 \sigma - \left(2\pi a^3 \Delta \mu / 3V_c\right) - \pi \varepsilon_0 \varepsilon E_0^2 a^3.$$
(3.17)

From (3.17) we can easily determine the critical radius of the nucleus,  $a_{.}$ , and the height of the energy barrier under nucleation,  $\Delta G_{.}$ 

$$a_{\star} = 2\sigma / \left[ \left( 2\Delta\mu / V_c \right) + 3\varepsilon_0 \varepsilon E_0^2 \right]$$
(3.18)

$$\Delta G_{\bullet} = 4\pi\sigma^3 / 3\left[\left(2\Delta\mu / V_c\right) + 3\varepsilon_0\varepsilon E_0^2\right]^2$$
(3.19)



Fig.3.4 Schematic of nucleation on the electrode: 1) metallic electrodes; 2) energy source; A, B are initial substances; C is nucleus of the new phase.



**Fig.3.5** Distribution of electric potential in crystallisation. Horizontal lines are equipotential surfaces, vertical lines are electric field strengths,  $E_0$  is the field strength in a dielectric, *d* is the interelectrode gap.

From (3.17) and (3.18) it is readily seen that  $a_{\bullet}$  and  $\Delta G_{\bullet}$  decrease rapidly with increasing  $E_{0}$ . This is demonstrated in Fig.3.6.

The nucleation rate is given by the expression (Aleksandrov 1978)

$$I = A \exp(-\Delta G_* / kT), \tag{3.20}$$

where A is a pre-exponential multiplier. For this reason, we assume the preexponential function to be independent of  $E_0$ . Now, substituting (3.19) into (3.20), we come to the final expression for the nucleation rate as a function of the field strength

$$I = A \exp\left\{-4\pi\sigma^3 / 3kT\left[\left(2\Delta\mu / V_c\right) + 3\varepsilon_0 \varepsilon E_0^2\right]^2\right\}$$
(3.21)

The nucleation rate is thus seen to increase sharply with increasing field strength.

Now we turn to the case when the nucleus of the new phase is a dielectric. For simplicity of calculations assume the nucleus to have the shape of a cylindrical protrusion of area s and height h on the electrode. Figure 3.7 presents the scheme of nucleation in the system A + B.

We examined a case in which there was no external field, *i.e.*  $E_0 = 0$ . Surface tension of the surface boundary between the phases A + B and C is  $\sigma$ , at the boundary between the side surface of the nucleus and the phase A + B is  $\sigma_n$ , at the boundary between the electrode and the phase A + B it is  $\sigma_s$  and at the nucleus-electrode boundary  $\sigma_0$  (see Fig.3.7). Then the energy variation upon nucleation has the form

$$\Delta G = \pi r^2 (\sigma + \sigma_c - \sigma_0) + 2\pi r h \sigma_h - (\pi r^2 h \Delta \mu / V_c). \qquad (3.22)$$

It is of interest to determine the optimum size of the nucleus for a given volume, that is, for  $V = \pi r^2 h = \text{const.}$  It is equal to  $r = (V/\pi h)^{\frac{1}{2}}$ . In view of this fact we rewrite (3.22) as

$$\Delta G = \left[ V \left( \sigma + \sigma_s - \sigma_0 \right) / h \right] + 2\sigma_h (V \pi h)^{V_2} - V \left( \Delta \mu / V_c \right).$$
(3.23)



Fig.3.6 Energy variation upon nucleation as a function of parameter *a*.

Differentiating (3.23) with respect to h and equating  $\frac{\partial \Delta G}{\partial h}$  to zero, we obtain the equation from which we can find the optimum value of the height h of the cylindrical nucleus

$$h_{*} = \left[ V \left( \sigma + \sigma_{s} - \sigma_{0} \right)^{2} / \pi \sigma_{h}^{2} \right]^{1/3}$$
(3.24)

The dependence (3.24) has a simple physical meaning. As should be expected,  $h_{\star}$  increases with increasing  $\sigma_{s}$ . For the given volume, the nucleus acquires the form which corresponds to the minimum of surface energy.

Substituting (3.24) into (3.23), we obtain the following expression for  $\Delta G_{\star}$ 

$$\Delta G_* = 3 \left[ V^2 \sigma_h^2 \pi (\sigma + \sigma_s - \sigma_0) \right]^{1/3} - V \Delta \mu / V_c.$$
(3.25)

From (3.25) we can see that  $\Delta G_{\bullet}$  as a function of V has a maximum, that is, the appearance of small-volume nuclei leaves the system stable, but it becomes unstable as soon as large-volume nuclei occur. The critical nucleation energy can be readily obtained from (3.25)

$$\Delta G_{\bullet\bullet} = 4\sigma_h^2 \pi (\sigma + \sigma_s - \sigma_0) / (\Delta \mu / V_c)^2. \qquad (3.26)$$

The critical height  $h_{..}$  and the critical volume  $V_{..}$  have the form

$$h_{**} = 2(\sigma + \sigma_s - \sigma_0) / (\Delta \mu / V_c). \tag{3.27}$$

$$V_{**} = 8\sigma_h^2 \pi (\sigma + \sigma_s - \sigma_0) / (\Delta \mu / V_c)^3.$$
(3.28)

The coefficient of the form of the centre of the new phase  $h_{..}/V_{..}$  can be easily obtained from (3.27) and (3.28)



Fig.3.7 Schematic of formation of a cylindershaped crystal nucleus on an electrode.

$$h_{\bullet} / r_{\bullet} = (\sigma + \sigma_s - \sigma_0) / \sigma_h. \tag{3.29}$$

The results (3.26) and (3.29) were obtained by Bolkhovityanov and Yudaev (1986).

If a nucleus is formed in an external field  $E_0$ , the contribution of the electric energy into the nucleation energy for  $(h/d) \ll 1$  has the form

$$\Delta W = -\varphi^2 \varepsilon_0 \varepsilon(\varepsilon_c - \varepsilon) Sh/2d^2 \varepsilon_c, \qquad (3.30)$$

whence  $\varepsilon_c > \varepsilon$ ,  $\Delta W < 0$  and, therefore, the external field must promote nucleation. This fact has a clear physical meaning since, as is well known, a dielectric with a high dielectric permittivity value is always drawn into a condenser connected with the external voltage.

With allowance for the contribution of the electrostatic field, the energy variation is

$$\Delta G = \left[ V(\sigma + \sigma_0 - \sigma_0) / h \right] + 2\sigma_h (V \pi h)^{\frac{1}{2}} - V\left[ (\Delta \mu / V_c) + \phi^2 \varepsilon_0 \varepsilon(\varepsilon_c - \varepsilon) / 2d^2 \varepsilon_c \right]$$
(3.31)

From (3.31) and (3.23) one can see that a substitution of  $(\Delta m/V_c) + \varphi^2 \varepsilon_0 \varepsilon$  $\varepsilon (\varepsilon_c - \varepsilon)/2d^2 \varepsilon_c$  for  $(\Delta \mu/V_c)$  in formulae (3.26), (3.27) and (3.28) gives the dependence of  $\Delta G$  on  $\varphi$ .

The nucleation rate will be determined from the formula

$$I = A \exp\left\{-4\pi\sigma_{k}^{2}(\sigma + \sigma_{s} - \sigma_{0})/kT\left[(\Delta\mu/V_{c}) + \varphi^{2}\varepsilon_{0}\varepsilon(\varepsilon_{c} - \varepsilon)/2d^{2}\varepsilon_{c}\right]\right\}$$
(3.32)

which shows that for  $\varphi \neq 0$  the nucleation rate increases.

### 3.3 The role of thermoelectric effects in the course of liquidphase electroepitaxy of ferroelectrics

The application of a direct electric current in the control over crystallization

of epitaxial structures grown from a liquid phase are closely connected with thermoelectric effects observed during this process. We shall again turn to the crystallization cell showed schematically in Fig.3.2. The phenomena occurring in a crystallization cell under liquid-phase electroepitaxy are the following (digits refer to zones or interfaces where corresponding phenomena take place):

- (1-5) heat transfer,

-(1-5) Joule heat,

- (1-5) Thomson heat,

- (3) diffusion,

- (3) electric transfer.

These were heat exchange effects. Next come surface effects:

- (3-4) heterogeneous crystallization,

- (4-3), (3-2) crystallization (dissolution) heat,

- (4-3), (3-2), (5-4), (2-1) Peltier heat.

So, in the general case systems of liquid-phase electroepitaxy involve several mechanisms of heat absorption mechanisms. Electric transfer, crystallization and dissolution of solid phases leads to the appearance of concentration gradients of a crystallizing substance in the liquid zone and diffusion leads to levelling up these gradients.

The first question to be answered in the analysis of crystallization processes is how the motive forces of crystallization depend upon crystallization conditions. These motive forces are determined by the variations of temperature and concentration of a crystallizing substance at the crystallization front as compared to equilibrium values of these parameters.

When a direct current runs through interfaces, Peltier heat proportional to the product of current density by the Peltier coefficient is instantaneously released and absorbed.

Owing to this effect the temperature at the interface falls, this fall being equal to (Jastrzebski et al 1978):

$$\Delta T_{\Pi} = \Delta \alpha_{1,2} J T_0 L_1 / \lambda_s, \qquad (3.33)$$

where  $\Delta \alpha_{1,2} = \alpha_1 - \alpha_2$  is the difference of thermoelectromotive forces between the substrate and solvent,  $L_1$  is the substrate thickness,  $\lambda_s$  the thermal conductivity of substrate material,  $T_0$  the temperature in the system prior to application of current.

A consequence of temperature difference in the system is concentration variation in the liquid zone

$$\Delta C_{\Pi} = \Delta T_{\Pi} / m, \tag{3.34}$$

where m is the slope of the liquidus curve.

At the interface, Peltier heat is absorbed and crystallization heat released (since they have opposite signs).

Consequently, this leads in the end to a decrease of absorbed and released Peltier heat, *i.e.* to a decrease of the temperature gradient.

The results of comparison of theoretical and experimental data suggest that the crystallization heat can be neglected as compared to the Peltier heat. Then

$$\operatorname{grad} T = \Pi \ J/\lambda_L \tag{3.35}$$

where  $\lambda_i$  is the thermal conductivity of the melt.

Thus, the temperature gradient occurring at the interface is independent of the zone thickness and is determined by the value of the current density.

Since the time within which the temperature gradient is set in the system,  $\tau \approx 10^{-3}$  s, is comparatively small, the current runs through a nonuniformly heated system, that is, from the very start of the process an additional Thomson heat is released

$$Q_T = -\tau_T (J \Delta T), \tag{3.36}$$

where  $\tau_{\tau}$  is Thomson's coefficient.

Owing to the Thomson heat, the system can be additionally heated, the temperature increase being

$$\Delta T_{\tau} = -\tau_{\tau} (J \,\Delta T) / M \,c, \tag{3.37}$$

where M and c are respectively mass and thermal capacity of the substrate.

When a direct electric current is applied, Joule heat is simultaneously released in the system:

$$Q_{I} = 0.24 \ J^{2} R \tag{3.38}$$

where R is total system resistance and  $R_i$  is liquid phase resistance.

Since  $R_{L} \ll R$ , the Joule heat mainly affects the substrate.

Beginning from some instant of time  $(t_{\rm cr})$ , the Joule effect may become greater than the Peltier effect since a constant temperature gradient at the interface is maintained by the Peltier heat, while the Joule and Thomson heats are accumulated in the system. Consequently, the resultant temperature of the system starts exceeding the equilibrium temperature  $T_0$  and the system may appear to be undersaturated, which will result in dissolution of the crystallized layer.

As can be seen from the above formulae, the Joule heat is quadratic and the Peltier heat is linear in J. This means that there exists a certain optimum value  $J_{opt}$  when the Joule heat becomes predominant over the Peltier heat. The Joule heat can therefore be neglected if the applied current  $J < J_{opt}$ .

The Thomson effect is here due to temperature dependence of carrier concentration, and in such a system it can be neglected, provided the zone material is a liquid metal. Moreover, this effect is also quadratic in the current.

Gabrielyan and Khachaturyan (1984) investigated ferroelectric film growth using liquid-phase electroepitaxy and estimated the contribution of thermoelectric effects to this process on an example of lithium niobate. Figure 3.8 presents temperature versus current density under liquid-phase electroepitaxy of LiNbO<sub>3</sub> with allowance for Peltier, Joule and Thomson effects. The figure shows that at the initial instants of time temperature variations due to heat exchange effects are smaller by several orders of magnitude than temperature variations due to the surface Peltier effect and can, therefore, be neglected at early stages of growth. When the growth time is long, the resultant temperature of the system exceeds the equilibrium temperature  $T_0$  and the system may appear to be incompletely saturated, which leads to layer dissolution.

### 3.4 Electro-LPE growth of lithium niobate-tantalate films

The standard methods worked out for semiconductor materials cannot be used for current-induced liquid-phase electroepitaxy of ferroelectrics because of the physico-chemical specificities of oxide systems. We propose two ways of currentinduced liquid-phase electroepitaxy of ferroelectrics:

- current-induced liquid-phase capillary epitaxy

- liquid-phase electroepitaxy from an unlimited volume of the solution in melt.

Film growth in an electric field opens new horizons for growth of thin-film ferroelectrics with a current-controlled composition, thickness and structural perfection. Of particular interest is obtaining a single-domain (polarized) state of layers in the course of growth.

In this section we consider the use of current-induced liquid-phase epitaxial growth of films of lithium niobate-tantalate, electrochemical processes proceeding in the liquid phase and modulation in the composition of ferroelectric films under the indicated growth conditions. We also optimize conditions of epitaxial growth of Li(Nb,Ta)O, films with account of Joule heat.

#### 3.4.1 Epitaxial growth

The use of current-induced liquid-phase epitaxy for growing  $LiNbO_3$  and  $Li(Nb,Ta)O_3$  films from a limited liquid-phase volume contained between two substrates located close to each other was proposed by Khachaturyan et al (1986). Figure



Fig.3.8 Melt temperature variations due to thermal effects as a function of current density in the course of LEP of lithium niobate.

3.9 presents the scheme of a film growth device. The composition of 90%  $LiVO_3 + 10\% Li(Nb, Ta)O_3$  was chosen as solvent for liquid-phase electroepitaxy. (0001), (1120) plates of LiTaO\_3 served as substrates and crystalline plates of  $Li(Nb,Ta)O_3$  served as a source. The substrate and source size was  $20 \times 15 \times 1.5$  mm and the liquid-phase thickness was  $1.5 \div 2$  mm. The electrodes were manufactured using platinum blackening and a conducting high-temperature glue.

A preliminarily prepared platinum niello is deposited on inoperative substrate and source surfaces, then the plates are annealed for one hour at 400°C. After this a shining metallized surface is covered with a high-temperature conducting glue. The substrate and source plates with a fixed gap (intermediate planeparallel plates of a given thickness are used for fixation) are glued to a quartz holder with electrodes. The gap between plates is so chosen that under the action of capillary forces the buffered melt is uniformly drawn from the crucible into the space between the source and substrate. For oxide systems, the gap between the source and substrate is chosen within the range of 1-2 mm, which permits avoiding convective mixing. Then the system is mounted in a furnace over a crucible filled with buffered melt.

The furnace temperature is gradually increased till it becomes  $50-100^{\circ}$ C higher than the initial epitaxy temperature, which is maintained for 0.5-1 h until a complete homogeneity is attained, and then the temperature equal to the initial epitaxy temperature is established. After some holding, the plates are immersed 1-2 mm into the crucible containing the buffered melt, as a result of which the liquid phase affected by capillary forces is drawn into the gap between the plates. The moment of contact between the plates and the melt is fixed by an indicator lamp. Then the plates with liquid phase are separated from the crucible and return to the initial state. Constant (or pulsed) voltage is applied to the plates. The layer growth proceeds when the potential on the substrate is positive. As soon as the current is off, the layer growth ceases, and a liquid-phase absorber is taken to the gap between the plates (Dudkin and Khachaturyan 1986), after which the system is slowly cooled down to room temperature.

The essence of liquid-phase electroepitaxy from an unlimited buffered melt volume (Gabrielyan and Khachaturyan 1985) is illustrated in Fig.3.9b. This method differs from the one indicated above in that the liquid phase is not fed from the source, and the liquid-phase thickness  $\ell_{1,p} \gg \ell_{sub}$ .

#### 3.4.2 Electrochemical processes in the liquid phase

In the study of the process of liquid-phase electroepitaxy an important role is played by a correct estimate of the relative contribution of different stages of this process. The difference in the nature of charge carriers in oxide compounds leads to variation of the physical processes proceeding here as compared with liquid-phase electroepitaxy of semiconductor systems. As a consequence there occur a number of specific effects typical of liquid-phase electroepitaxy of complex oxides which are to be examined on an example of lithium niobate.

To specify the character of mass transfer under liquid-phase electroepitaxy of oxide systems, electrochemical processes at the interface between contacting phases were investigated and the layer growth rate was determined as a function of strength and time of the current applied to the crystallization cell (Khachaturyan 1988; Gabrielyan et al 1989).

Figure 3.10 shows the temperature dependence of the number of lithium ions transferred in lithium niobate single crystal of congruent composition. We can see that in the temperature range of 800–900°C single crystals are mixed conductors with comparable contributions of the ion and electron components of conductivity. As concerns melts of the system LiVO<sub>3</sub>-LiNbO<sub>3</sub>, we can assume, according to Pastukhov et al (1984) and Shumov (1984), that the conduction mechanism in them is completely ion and is due to lithium ion migration ( $\eta_{Li} \approx 1$ ). This implies that in the chain (Fig.3.2) the nature of the main charge carriers does change. As a consequence of ion conductivity of the melt LiVO<sub>3</sub>-LiNbO<sub>3</sub> and a mixed ion-electron conductivity of the crystal LiNbO<sub>3</sub>, electrochemical processes proceed in the chain when a direct electric current is applied to the crystallization cell.

In region 2-3 the most probable is the process

$$3\text{LiNbO}_{2} \rightarrow \text{LiNb}_{2}O_{2} + 2\text{Li}^{+} + 2e + 1/2 O_{2}$$
 (3.39)

with dissolution of released oxygen in the melt and accumulation of  $LiNb_3O_8$  at the boundary with the platinum electrode.

Through the boundary 2-3 the current can only be transferred by lithium ions, but through the boundary 1-2 comes only half ( $\eta_{ti} \approx 0.5$ ) the amount of lithium ions required for current transfer in the chain, while the rest of the ions are formed, according to (3.39), on the surface of a lithium niobate film.

Finally, at the boundary 3-4 there proceeds oxidation of oxygen dissolved



**Fig.3.9** Device for LPE film growth: 1) platinum crucible; 2) quartz holder; 3) a layer of current-conducting high-temperature glue; 4) substrate; 5) Li(Nb,Ta)O<sub>3</sub> source; 6) platinum conductors; 7) thermocouple; 8) liquid phase absorber; 9) quartz tube; 10) ceramic stand. **Fig.3.10** (right) Temperature dependence of the number of lithium ions transferred in a lithium niobate single crystal of congruent composition.

in the melt

$$1/2 O_{2} \text{ (melt)} + 2e \rightarrow O^{2} \text{ (melt)}$$
 (3.40)

which obviously leads to Li,O-enrichment of the melt near (4), by the reaction

$$2 \operatorname{Li}^* + \operatorname{O}^{2-} \to \operatorname{Li}_{2}\operatorname{O}$$
(3.41)

Thus, the kinetics of liquid-phase electroepitaxy will be determined by the ratio of crystallization rates due to Peltier heat absorption and to electrochemical film (or substrate) dissolution by the reaction (1) or the like.

The role of different effects under liquid-phase electroepitaxy of oxide systems can be conveniently illustrated using a fragment of the system state diagram (Fig.3.11). Suppose that the buffered melt has a composition corresponding to point 1. Peltier heat absorption corresponds to a shift of a figurative point of the system towards point 2. The solution appears to be supersaturated with LiNbO<sub>4</sub>, and the latter is crystallized on the substrate.

A long application of current may be responsible for heating of the entire system (Gabrielyan and Khachaturyan 1984), which leads to growth deceleration and then to film dissolution (the figurative point shifts towards point 3). It should be noted that in the course of crystallization the melt composition shifts in the direction '4' (liquid-phase electroepitaxy without feed maintenance), and in the presence of a source it can remain unaltered at the expense of equivalent feeding (Zhovnir and Zakhlenyuk 1985). According to the analysis carried out above, the ion transfer, causing variations in the melt composition, induces displacement of point 1 in the direction perpendicular to the plane of the picture, that is, a change of the Li,O/Nb,O, ratio.

The probable mechanisms considered above allow us to analyze the data on lithium niobate film growth by the liquid-phase electroepitaxy method.

When a Li(Nb,Ta)O<sub>3</sub> source is absent from the crystallization cell and current is applied for a time exceeding 50 min, the observed decrease of the growth rate or even dissolution of lithium niobate film is caused both by a decrease of supersaturation due to Joule heat release and by film electrolysis going by reaction (3.39) (Gabrielyan and Khachaturyan 1984). Film dissolution can also be stimulated by the fact that as a result of a limited amount of oxygen dissolved in the melt, its concentration falls when the current is applied, that is, the speed of the cathode reaction (3.40) necessary for charge transfer from the melt to the electrode decreases. Then, to maintain a constant current strength in the circuit, the speed of the reaction (3.39) which is the only molecular oxygen supplier of the melt, must obviously increase. A consequence of cathode reaction deceleration is an increased resistance of the circuit, which leads to the necessity of a higher voltage to be applied to the cell in order to maintain J = const.

Thus, the analysis of the available experimental data shows that the bufferedmelt system  $LiVO_3$ -LiNbO<sub>3</sub> is an ion-conducting medium with a clearly pronounced electric property. The degree of dissociation decreases with increasing content of lithium niobate in the buffered melt. The main charge carriers in





the liquid phase at the epitaxy temperature are lithium ions. Electrochemical and near-electrode processes in the liquid phase lead to the occurrence of  $Li_2O$  molecules and NbO<sub>3</sub>, VO<sub>3</sub> ions whose contribution to epitaxial precipitation of LiNbO<sub>3</sub> layers is insignificant.

3.4.3 Growth kinetics of electro-LPE grown lithium niobate-tantalate films To determine the character of mass transfer in electro-LPE of  $Li(Nb,Ta)O_3$ , we have analyzed the dependence of film thickness and growth rate on the time of application of current in an equilibrium electro-LPE consisting of substratebuffered melt-source. From the thermodynamic point of view, it would be more precise to think of this process as a liquid-phase electroepitaxy with feed maintenance or with a source.

Figure 3.12 presents the dependence of film thickness on the time of application of current to the crystallization cell for different values of current density. The rate of layer formation alters within the range of  $0.6-0.1 \mu m/min$  and the film surface appears to be mirror-smooth (Khachaturyan 1987). Micro X-ray spectral analysis showed an even distribution of the main components of tantalum and niobium over the heterostructure. The amount of vanadium coming to the epitaxial film from the liquid phase is minimum ( $0.005\div0.01$  at%).

A characteristic feature of electro-LPE of ferroelectric films and, in particular, of lithium niobate, is that simultaneously with layer growth the film is made single-domain (polarized). The method of polarization of  $Li(Nb,Ta)O_3$  films was



Fig.3.12 Thickness of a LiNbO<sub>3</sub> film versus the time of application of current to the crystallization cell.

worked out. For heterostructures, this process is characterized by a difference in the Curie temperatures of the substrate and the film and by the presence of transition regions with a smoothly varying composition.  $10 \times 15$  and  $40 \times 60$ mm containers with platinum contacts for six structures were made. Regimes were established that provide minimum potential and temperature differences, which is necessary for decreasing interdiffusion of film components, for palladium diffusion into the structure along the side contacts and for preventing sample cracking under the action of current.

Figure 3.13 presents the curves of the degree of polarization as a function of current density for various epitaxy times. When the time of application of current is increased from 10 to 35 min, single-domain films of lithium niobate are formed within the current density range of  $10-15 \text{ mA/cm}^2$ .

To grow films of solid solutions Li(Nb,Ta)O<sub>3</sub>, Khachaturyan et al (1987) applied opposite-polarity pulses to the crystallization cell. The control parameters were chosen from the following relations: current density in pulses  $J_{\text{direct}} = 3 J_{\text{rev}}$ ; the relation between pulse duration and pauses between them  $t_{\text{direct}} \ge 5t_{\text{rev}}$ ;  $t_{\text{rev}} \le 2 \tau_{\text{dif}}$ ;  $t_{\text{pause}} \le \tau_{\text{dif}}$ , where  $J_{\text{direct}}$  is current density in a direct pulse (mA/cm<sup>2</sup>);  $J_{\text{rev}}$  is current density in a reverse pulse (mA/cm<sup>2</sup>);  $t_{\text{direct}}$  is duration of a direct pulse (s);  $t_{\text{rev}}$  is duration of a reverse pulse (s);  $t_{\text{pause}}$  is pause duration (s);  $\tau_{\text{dif}}$  is the characteristic diffusion time (s).

The gap between the source and the substrate is diminished to 0.5 mm for the reason that in precipitation of layers of solid solutions  $Li(Nb,Ta)O_3$ . This reduces the time of diffusion, from the source to the substrate, of components dissolved in the liquid phase, which improves composition control in solid solutions.

The liquid phase composition corresponded to 90 mol.%  $LiVO_3 + 5 mol.\%$ LiNbO<sub>3</sub> + 5 mol.% LiTaO<sub>3</sub>. Initial epitaxy temperature  $T_{cpit} = 980^{\circ}C$ .  $J_{direct} = 10 mA/cm^2$ ,  $t_{direct} = 30 min$ ,  $t_{rev} = 3 mA/cm^2$ ,  $t_{rev} = 6 min$ ,  $t_{pause} = 1 min$ .

When a direct pulse is applied, an epitaxial layer precipitates on the substrate surface. Then, to neutralize the electrically induced state in the liquid phase and to prevent electric transfer, a 1 min pause is made, after which a reverse pulse is applied to mix ions in the liquid phase. Then again a 1 min pause and then the process is repeated. The layer composition determined by micro X-ray spectral analysis corresponded to  $LiNb_{0.5}Ta_{0.5}O_3$  and had a thickness  $h = 10 \mu m$  (see Fig.3.14a).

If we apply a unipolar pulsed current with amplitudes  $J_1$  and  $J_2$ , the composition of the growing film of the solid solution Li(Nb,Ta)O<sub>3</sub> changes according to applied pulses (Fig.3.14b).

Component distribution in a film was determined by a micro X-ray spectral analysis. The characteristic distribution spectra of the components Nb and Ta over the structure thickness are presented in Fig.3.15. As distinct from diffusion waveguides, epitaxial layers exhibit a sharp transition from the substrate to the film. Composition constancy of solid solutions of lithium niobate-tantalate over film thickness shows that the epitaxy process is stationary, that is, the concentration profile in the liquid phase and the effective coefficient of tantalum segregation remain unchanged. The calculation of the compositions corresponding to the microprobe curves has shown that the content of niobium and tantalum in a



Fig.3.13 Degree of LiNbO<sub>3</sub> film polarization as a function of current density. The time of application of current: 1 - 10 min; 2 - 20 min; 3 - 25 min; 4 - 35 min.

film of solid solution is constant and is determined by the layer growth rate. As the current density and, therefore, the growth rate decrease, the effective coefficient increases from 1.4 to 2.35 (Fig.3.15). The growth rate of the layer, v, changes with current density by a linear law within the indicated range of J values.

In precipitation of multicomponent systems from a solution in melt at a high temperature, the composition of the precipitated layer differs typically from the composition of the dissolved material since the presence in the layer of each component is specified by an individual segregation coefficient. In lithium niobate-tantalate epitaxy from the solution in the  $Li_2O-V_2O_5$  melt, the composition of the LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> shifts relative to the composition of the dissolved material LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> towards an increase of tantalum, that is, y > x.

The compositional shift is different under different growth conditions. Variations of the effective segregation coefficient are customarily associated with mass transfer in the liquid phase. A limited diffusion of dissolved components leads to the appearance of concentration profiles in the liquid phase and makes it practically impossible to control efficiently the composition of multicomponent



**Fig.3.14** Topogram of films of LiNb<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub> solid solutions of (1120) and (0001) orientations (a) and distribution of components along the Li(Nb,Ta)O<sub>4</sub>/LiTaO<sub>3</sub> heterostructure (b).



**Fig.3.15** Layer growth rate (1) and effective segregation coefficient (2) of Ta versus current density in LPE of  $Li(Nb,Ta)O_{a}$ .

films. Mass transition in liquid-phase electroepitaxy is due to diffusion and electric transfer of components to the crystallization front. The niobiumto-tantalum ratio in a film is determined by the kinetic processes of crystallization.

# 3.5 Optimization of conditions of epitaxial growth of lithium niobate films with allowance for Joule heat

One of the basic negative effects upon liquid-phase electroepitaxy is Joule heat. To prevent this effect in liquid-phase electroepitaxy of ferroelectrics, it is necessary to specify its role and contribution to the crystallization process (Avakyan et al 1988). We can conditionally distinguish between two main sources of temperature nonuniformity at the crystallization front associated with the Joule effect and leading both to preventing Peltier cooling and obtaining non-planar structures. The first of these sources is due to constructive imperfection of growth device, unsatisfactory quality of electric contacts between conducting elements (Jastrzebski et al 1978; Nikishin 1984a) and to inappropriate geometry of the elements (Barchuk and Ivaschenko 1982). The second source is of a more fundamental nature and is connected with the fact that the growth device is essentially inhomogeneous from the viewpoint of release and dispersion of Joule heat. By virtue of constructive variety of real growth devices for liquid-phase electroepitaxy of semiconductors and ferroelectrics, the role of one or another factor and their interrelations are not obvious (Milvidsky et al 1982).

The main unit of a device for equilibrium and nonequilibrium regimes of electro-LPE of ferroelectrics consists of growth cells depicted in Fig.3.16a, b. Conducting electrodes were made of platinum. Applying the method of equivalence of thermal and electric schemes (Stefanakos et al 1976) with allowance for Joule heating of the growth cell, the temperature variation of the crystal-lization front, T, is described by the expression

$$\Delta T = T_0 - T_1 = [\Pi_{14} J (G_1 G_3 G_4 + G_2 G_3 G_4) + \Pi_{23} J (G_1 + G_2) \cdot (G_1 G_4 + G_1 G_3 + G_3 G_4) - \Pi_{34} J (G_1^2 G_3 + G_1 G_2 G_3 + G_1 G_3 G_4 + G_2 G_3 G_4) - \Pi_{12} J (G_1 G_2 G_4 + G_1 G_2 G_3 + G_2 G_3 G_4) - (-1/2 J^2 R_2 G_1 (G_1 G_4 + G_1 G_3 + G_3 G_4) - J^2 R_2 (G_1 G_2 G_3 + G_3 G_4) - J^2 R_2 (G_1 G_1 G_2 G_3 + G_3 G_4) - J^2 R_2 (G_1 G_1 G_2 G_3$$

$$+G_{1} G_{2} G_{4} + G_{2} G_{3} G_{4}) - 1/2J^{2} R_{4} (G_{1}^{2} G_{3} + G_{1} G_{2} G_{3} + 2G_{1} G_{3} G_{4} + 2G_{2} G_{3} G_{4}] / (G_{1}^{2} G_{2} G_{4} + G_{1}^{2} G_{2} G_{3} + 2G_{1} G_{2} G_{3} G_{4} + G_{1}^{2} G_{3} G_{4})$$

$$(3.42)$$

where  $G_i = K_i / \ell_i$ , is the thermal conductivity of the *i*<sup>th</sup> element,  $\ell_i$  is the linear dimension of the *i*<sup>th</sup> element,  $R_2$  and  $R_4$  are resistances of the substrate and source, respectively.  $\Pi_{ik}$  is the difference of Peltier coefficients between the elements *i* and *k*, *J* is d.c. density,  $T_0$  is the temperature of external surfaces of the electrodes corresponding to the saturation temperature,  $T_1$  is the crystallization front temperature.

When deriving (3.42), the contact resistances were assumed to play an insignificant role under Joule heat release, which is confirmed by experimental measurements. The values of contact electrode-substrate and substrate-liquid phase resistances were respectively equal to  $5 \times 10^{-3}$  ohm/cm<sup>2</sup> and  $8 \times 10^{-3}$  ohm/cm<sup>2</sup>, which is much less than the substrate and source resistances,  $10^2$  ohm/cm<sup>2</sup>.

With account of experimental conditions  $\Pi_{12} = \Pi_{14} = \Pi_1$ ,  $\Pi_{23} = \Pi_{34} = \Pi_3$ ,  $G_2 = G_4 G_2$ ,  $R_2 = R_4 = R$ , formula (3.42) acquires the following simple form

$$\Delta T = G_1 G_2^2 \Pi_1 J + G_1 G_2 (G_1 + G_2) \Pi_3 J - J^2 R \times \times (G_1^2 G_3 + 3G_1 G_2 G_3 + 2G_2^2 G_3 + G_1 G_2^2 + G_1^2 G_2) / /G_1^2 G_2^2 + G_1^2 G_2 G_3 + 2G_1 G_2^2 G_3 + G_1^2 G_2 G_3$$
(3.43)

From (3.43) we can write the criterion for cooling the substrate-solution-melt boundary

$$d(\Delta T)/dJ > 0 \tag{3.44}$$

and therefore

$$J < \frac{G_1 G_2 \Pi_1 + G_1 G_2 (G_1 + G_2) \Pi_3}{2R \Big[ G_1^2 (G_2 + G_3) + G_1 G_2 (3G_3 + G_2) + 2G_2 G_3 \Big]}$$
(3.45)

The quantity

$$J_{0} = \frac{\prod_{1} + (G_{1} + G_{2}) \prod_{3}}{2R[G_{1} / G_{2}(G_{2} + G_{3}) + 3G_{3} + G_{2} + 2G_{3} / G_{1}]}$$
(3.46)

will correspond to the critical current of electro-LPE. With account of  $G_1 = \frac{\kappa_1}{\ell_1} \gg G_2$ and  $G_1 \gg G_4$ , formula (2.37) acquires the form

$$J_0 = \prod_3 / 2R$$
 for an equilibrium regime of electro-LPE (3.47a)

and

160

$$J_{a} = \prod_{a} / R$$
 for a nonequilibrium regime of electro-LPE (3.47b)

It is of interest to examine the physical nature of critical current under electro-LPE as a function of system temperature. The graph of the dependence for both regimes is constructed analytically (Fig.3.17).

As we can see from the graph, the critical current of electro-LPE depends on substrate material. The limit of a d.c.  $J_{epit}$  preventing the Joule effect increases with increasing temperature  $T_{o}$ .

Since the critical current of electro-LPE is a function of geometrical dimensions of the substrate, it follows that

$$J_0 = \prod_{T_0} S/2\rho_T l \tag{3.48a}$$

$$J_0 = \prod_{\tau_0} S / \rho_{\tau_0} l \tag{3.48b}$$

where  $\rho_{T_0}$  is resistivity, s and l are respectively the area and the thickness; therefore, increasing the substrate area and decreasing its thickness, we can increase the boundary value of  $J_0$ .

An increase of the area and a decrease of the thickness of the substrate and the source provide extension of the range of operating current densities for electro-LPE of ferroelectrics.

The thickness of epitaxial layers of LiNbO, grown on LiTaO, substrates is



**Fig.3.16** Schematic of a cell showing temperature distribution a) equilibrium regime of LPE; b) nonequilibrium regime of LPE. 1) platinum electrode; 2) LiTaO<sub>3</sub> or LiNbO<sub>3</sub> substrate; 3) solution in melt [N%LiNbO<sub>3</sub> – (100–N)%LiVO<sub>3</sub>]; 4) LiNbO<sub>3</sub> source; 5) thermal insulation.



**Fig.3.17** Temperature dependence of the critical LPE current  $(J_0)$ . 1) nonequilibrium regime, 2) equilibrium regime (dashed lines are for LiNbO<sub>3</sub>, solid lines for LiTaO<sub>3</sub>. **Fig.3.18** (right) Thicknesses of epitaxial layers of LiNbO<sub>3</sub> on LiTaO<sub>3</sub> substrates as functions of current density in equilibrium (+) and nonequilibrium (•) LPE regimes.

plotted against the current density variation in equilibrium and nonequilibrium regimes of liquid-phase electroepitaxy (Fig.3.18). The graph is divided into three regions. In region (1), layer growth proceeds and the film thickness increases linearly with increasing current density. This dependence deviates from linear when current density is close to  $J_0 = 10 \text{ mA/cm}^2$  in equilibrium regime and  $J_0 = 17 \text{ mA/cm}^2$  in nonequilibrium regime of liquid-phase electroepitaxy. Region (II) is characterized by a decrease of growing layer thickness due to the Joule effect, which results in a surface dissolution of the grown layer responsible for the appearance of etching patterns on the surface.

According to the expressions (3.19a, b), the Joule effect must exceed the Peltier effect with respect to the chosen parameters for  $J_0 = 9$  mA/cm<sup>2</sup> in equilibrium regime and  $J_0 = 17$  mA/cm<sup>2</sup> in nonequilibrium regime of liquid-phase electroepitaxy, and the formation of LiNbO<sub>3</sub> layers under such currents is explained by the above-said approximations. For current densities  $J_0 > 9$  mA/cm<sup>2</sup> in equilibrium regime and  $J_0 > 20$  mA/cm<sup>2</sup> in nonequilibrium regime there are no LiNbO<sub>3</sub> layers on the substrates, that is, the Joule heat completely overlaps the Peltier cooling (region (III).

Figure 3.19 presents the graph of the experimental dependence of epitaxial layer thickness on the substrate and source thickness both in equilibrium and nonequilibrium regimes. As the substrate and source thicknesses increase, the critical current of electro-LPE decreases and, therefore, the Joule heat increases, and for thicknesses d > 3 mm in equilibrium regime and d > 4 mm in non-equilibrium regime the growth process ceases. Consequently, proceeding from the solution of the system of equations of equivalent thermal and electric schemes





for equilibrium and nonequilibrium regimes and from comparison with experimental results, an optimum range of the process parameters is chosen which provides an epitaxial growth of LiNbO<sub>3</sub> layers of a LiTaO<sub>3</sub> substrate:

Nonequilibrium regime	Equilibrium regime
$J_{0} = (4 \div 17) \text{ mA/cm}^{2}$	$J_{0} = (4 \div 10) \text{ mA/cm}^{2}$
$S = 1 \text{ cm}^2$	$S = 1 \text{ cm}^2$
$\ell \leq 4 \text{ mm}$	$\ell \leq 3  \mathrm{mm}$
$t_{\text{cpit}} = (10 \div 25) \text{ min}$	$t_{\text{cnit}} = (10 \div 25) \text{ min}$

To simplify the analysis of temperature distribution at the crystallization front with allowance for Joule effect, we neglect the contact thermal effects assuming that the physical properties of cell elements are isotropic and that the isotropy of the properties and the geometry of the elements are temperature independent. From the solution of thermal conductivity equation in cylindrical coordinates we obtain, according to Barchuk and Ivaschenko (1982), the analytic expression for a stationary temperature distribution at the crystallization front

$$T(h,r) = T_0 - R_2(r^2 - a^2) + \sum_{\mu} j_0(\mu r) \left( A_{\mu} + \frac{B_{\mu}}{ch^2 \mu h} \right), \tag{3.49}$$

where  $A_{\mu}$  and  $B_{\mu}$  are coefficients defined by the boundary conditions of the problem,  $\rho_i$  is resistivity of the *i*-th element,  $R_i = J^2 \rho / 4k_i$ ;  $k_i$  are the coefficients of temperature conductivity of the *i*<sup>th</sup> element,  $\mu$  are the roots of the equation  $j_0(\mu a) = 0$ ,  $j_0(\mu r)$  is the zero-order first-class Bessel function. The explicit expressions for  $A_{\mu}$  and  $B_{\mu}$  are too cumbersome to be represented here, and we refer the reader to (Carslaw 1945) where the algorithm for their determination is given. From the expression presented above it is seen that in the general case the temperature field at the substrate-liquid phase interface is nonuniform. Because of complicacy of the explicit analytic expressions for  $\Delta T$  (*h*, *r*), the analysis of temperature distribution at the crystallization front has been per-



Fig.3.20 Temperature variation at the crystallization front for different current densities: 1) 4 mA/cm<sup>2</sup>; 2) 17 mA/cm<sup>2</sup>; 3) 10 mA/cm<sup>2</sup>.

163

Table 3.1 Growth cell parameters of LPE-grown lithium niobate

Cell element	ρ, ohm·cm <sub>W</sub>	K, cm <sup>-i</sup> grad <sup>-1</sup>	<i>k</i> , cm²/s <sup>-1</sup>	ℓ, cm	a, cm	J, mA/cm <sup>2</sup>
Platinum	1.05×10-4	0.71	1.4×107	10-2	5×10-'	4÷17
Substrate	4×10 <sup>-5</sup>	2×10 <sup>3</sup> 3×10 <sup>-2</sup>		10-1	5×10-1	4÷17
Liquid phase	$(T = 400^{\circ}\text{C})$ 148 $(T = 1200^{\circ}\text{C})$ $5 \times 10^{2}$ $(T = 890^{\circ}\text{C})$	1.5×10 <sup>-2</sup>		2×10-		
Source 5> (7 14 (7	$(T = 400^{\circ}C)$ $(T = 400^{\circ}C)$	4.2×10 <sup>-3</sup>		10 <sup>-1</sup> 2×10 <sup>-1</sup>	5×10-'	4÷17
	140 (T = 1200°C	2×10-3				

formed, in line with Barchuk and Ivashchenko (1982), on the basis of the numerical values of growth cell parameters listed in Table 3.1.

Figure 3.20 illustrates the calculation of  $\Delta T(h, r)$  at the crystallization front in the growth cell both in equilibrium and nonequilibrium regimes of liquidphase electroepitaxy for different current densities.

The temperature gradient along the radial axis for a current density of  $J = 10 \text{ mA/cm}^2$  is about six times the one for  $J = 4 \text{ mA/cm}^2$ , and for the current density  $J = 17 \text{ mA/cm}^2$  the same gradient increases by a factor of 17. According to (3.49), the gradient becomes three times smaller as the substrate diameter decreases by half. The 'boundary' effect is not observed experimentally for current densities  $J = (4 \div 6) \text{ mA/cm}^2$  and for the substrate radius of 0.5 cm. The epitaxial structures obtained are characterized by morphological uniformity and planarity.
Thus, using the method of equivalence of thermal and electric schemes for experimental cells in equilibrium and nonequilibrium electro-LPE regimes of ferroelectrics, we have introduced the concept of a critical current of electro-LPE and determined the optimum growth parameters for LiNbO<sub>3</sub> on LiTaO<sub>3</sub> and LiNbO<sub>3</sub> substrates, which permit planar structures to be produced under liquid-phase electroepitaxy.

## 4 Structure and Composition of Light Guiding Films

For an efficient use of epitaxial films of lithium niobate tantalate in optoelectronics, it is necessary to obtain layers homogeneous in thickness, possessing a high structural perfection, a low defect density and a low content of uncontrolled impurities, which substantially decreases attenuation in the course of wave propagation of light in the film. This has stimulated investigations of the crystalline structure, composition, orientation, surface morphology, substrate-film interface, domain and dislocation structures of the films. The influence of growth conditions upon these parameters has been established.

# 4.1 Structure and physico-chemical properties of lithium niobate and tantalate crystals

Lithium niobate (LiNbO<sub>3</sub>) is one of the most interesting and widely used ferroelectrics. First crystals were obtained by Lapitsky (1952) and Sue (1937). The study of the state diagram of the system  $\text{Li}_2\text{O}-\text{Nb}_2\text{O}_5$  has shown the possibility of formation of four compounds:  $\text{Li}_2\text{O}-14\text{N}_2\text{O}_5$ ,  $\text{Li}_2\text{O}-3\text{Nb}_2\text{O}_5$ , LiNbO<sub>3</sub> and  $\text{Li}_3\text{NbO}_4$  (Rusman and Holzberg 1958).

Crystallization of LiNbO<sub>3</sub> is possible in the region of 40-60 mol.% Nb<sub>2</sub>O<sub>5</sub> at temperatures between 1160 and 1253°C. Detailed studies of the phase diagram in this region have revealed distinction between congruent and stoichiometric compositions. To congruent composition there corresponds the ratio Li<sub>2</sub>O/Nb<sub>2</sub>O<sub>5</sub> = 0.946 and the melting temperature  $T_{melt} = 1170$ °C. Upon the liquid phase composition variation within the range of 45-58 mol.% Li<sub>2</sub>O, the crystal composition varies from 47 to 50 mol.% (Carruthers et al 1971). Thus, crystals of stoichiometric composition can be grown from a melt containing up to 58 mol.% Nb<sub>2</sub>O<sub>5</sub>, but because of the large difference in liquid and solid phase compositions this leads to the growth of inhomogeneous crystals.

X-ray and neutron diffraction analyses have revealed that lithium niobate has the structure related to ilmenite (Abrahams et al 1966). Both the structures are constructed following the pattern of high-density hexagonal packaging but differ in alternation of occupied and unoccupied octahedra. In room temperature  $LiNbO_3$ crystals, octahedral interstices formed by oxygen ions in an almost high-density hexagonal packaging are filled with niobium ions (1/3) and lithium ions (1/3), the remaining 1/3 being vacant. The succession observed was as follows:

$$- \text{NbO}_{6} - \text{LiO}_{6}^{-}$$
 (...)O<sub>6</sub>-NbO<sub>6</sub><sup>-</sup>

Figure 4.1 shows position of elementary cells in lithium niobate. The octahedron with Nb ions forms a common facet with the vacant octahedron which in turn forms a facet of the octahedron occupied with lithium ion. After a distance of c/2 (c is the lattice constant) the positioning of metallic ions is repeated: Nb occupies the fourth octahedron, the fifth remains vacant, Li occupies the sixth octahedron. Then the cell is repeated.

The symmetry of LiNbO<sub>3</sub> and LiTaO<sub>3</sub> crystals is tetragonal (class 3*m*). In the ferroelectric phase the space group is  $C_{3v}$ -R<sub>3</sub>C, in paraphase D3d-R3C. The rhombohedral cell contains two formula units and the hexagonal cell contains six. The lattice constants in the rhombohedral cell a = 5.4944 Å,  $\alpha = 55^{\circ}52$ ; in the hexagonal cell  $a = 5.14829\pm2\times10^{-5}$  Å,  $c = 13.8631\pm$  $4\times10^{-4}$  Å, c/a = 2.693. Interplanar spaces in the lattice are equal to 1.286 Å (*x*-cut), 1.489 Å (*y*-cut) and 1.15 Å (*z*-cut). The principal crystallographic directions (planes) of lithium niobate are presented in the stereographic projection of Fig.4.2. The [0001] axis corresponds to the special crystallographic direction.

The parameters of the crystallographic cells and ion positions in them in LiNbO<sub>3</sub> are tabulated in Table 4.1.

Ion positions in the crystal lattice are of interest from the point of view of



**Fig.4.1** Crystalline structure of LiNbO<sub>3</sub>; a) series of distorted octahedrals along the polar c-axis; b) real location of oxygen atoms relative to lithium and niobium atoms (Abrahams et al 1966).

Characteristic E	experimental data
Density of single crystals (g·cm <sup>-3</sup> )	4.612
Mohs's hardness	5
Melting point (°C)	1260
Curie point (°C)	1210
Parameters of a unit cell:	
Rhombohedral	
a (Å)	5,4920
Angle	55°53'
Hexagonal	
a (Å)	5.14829+0.00002
c (Å)	13 86310+0 00004
Number of formula units in cell	15:0051010100004
Rhombohedral	2
Hexagonal	5
Thermal expansion coefficient	0
a axis	16 7+10-4
c axis	2 0+10-6
Dielectric constant	$c_{1} = 44$ $c_{1} = 84$
Dielectric constant	$\epsilon_{11} = 44$ $\epsilon_{11} = 84$
	$\epsilon_{33} = 25  \epsilon_{33} = 50$
	$\mathcal{E}_{11} = 43  \mathcal{E}_{11} = 76$
	$E_{33}^{*} = 49  E_{33}^{*} = 32$
Refractive indices ( $\lambda = 0.023 \ \mu m$ )	$n_o = 2.286 \ n_e = 2.220$
Loss-angle tangent ( $v = 1 \text{ kHz}$ )	less than 0.02
Specific resistance ( $\Omega$ cm)	
200°C	over 10 <sup>14</sup>
400°C	5×10 <sup>8</sup>
1200°C	140
Water solubility (mol 1 <sup>-1</sup> )	
25°C	2.8±10-4
50°C	4.3±10⁴
100°C	7.4±10-4
Dissolution heat (kcal mol-1)	6.2
Diffusion activation energy $Q_D$ (kcal mol <sup>-t</sup> )	
$Q_{p}^{\perp}$	68.21±0.48
$Q_{D}^{"}$	68.17±1.24
$(\perp, \parallel \text{ to } c \text{ axis})$	
Evaporation activation energy $Q_v$ (kcal mol <sup>-1</sup> )	
$Q_v^{\perp}$	70.6
$Q_{v}$ "	59.0
$(\perp, \parallel to c axis)$	
Evaporation coefficient, $\alpha$	≤10-4
$\alpha_{1}/\alpha_{1}$	3
Thermoelectric coefficient of melt $\alpha$ (mV·K <sup>-1</sup> )	-0.4
Thermoelectric coefficient of crystal $\alpha$ (mV K <sup>-1</sup> )	0.76±0.02
Coefficient of crystallization emf $\alpha_v$ (mVs·m <sup>-1)</sup>	1.25±0.2

 Table 4.1 Physico-chemical constants of LiNbO3 crystals (Prokhorov, Kuz'minov, 1990)

168

the ferroelectric properties of lithium niobate. As distinct from other ferroelectric crystals, lithium and niobium exhibit a considerable ion shift from the symmetric position in the paraphase. The niobium ion is at a distance of 0.897 Å from the nearest plane of oxygen atoms and at 1.413 Å from the next plane. The Li ion shift makes up respectively 0.714 Å and 1.597 Å. So, appreciable shifts of lithium niobate ions are required for reaching a paraelectric state or polarization reversal. At a temperature exceeding the Curie point, lithium and niobium ions shift in the same direction so that Nb<sup>5+</sup> occupies the centre of the oxygen octahedron and Li<sup>+</sup> lies in the plane of oxygen layers (Fig.4.1(b)). In LiNbO<sub>3</sub> crystals, the shift on ions from positions they occupy in the paraelectric phase as the temperature lowers through the Curie point is responsible for the appearance of spontaneous polarization. Spontaneous polarization may be aligned either along positive or along negative direction of the third-order axis, both these states being energetically equivalent.

The largest and most perfect were Czochralski grown lithium niobate crystals (Fedulov et al 1965; Nassau et al 1966). Crystals obtained in other ways had smaller size and some structural imperfections.

The growth conditions of lithium niobate crystals are connected with the presence of controlled and uncontrolled impurities in the melt. When stoichiometry is violated, lithium and niobium ions may enter as impurities. Solvability of the Nb<sub>2</sub>O<sub>5</sub> component in the liquid phase is 45–58 mol.% and in the solid phase it narrows to 48–50 mol.%. This leads to stoichiometry violation and affects the Curie temperature, birefringence and phase matching temperature. The highest perfection of crystals is obtained for the ratio Li/Nb = 0.946 which corresponds to congruent composition.

The experimental data on the physico-chemical properties of lithium niobate (Kuz'minov 1975) are presented in Table 4.1 which shows that if imperfect crystals are disregarded, their density ranges between 4.6 and 4.7 g/cm<sup>3</sup>. The melting temperature of stoichiometric LiNbO<sub>3</sub> crystals is 1253°C. The phase transition temperature is  $1210\pm5$ °C. At a temperature of 1200°C, lithium niobate melt in vacuum and in air is nonvolatile, which is very important for the technology of this material. The surface tension of LiNbO<sub>3</sub> measured by the molten drop method at the vacuum-melt boundary at the melting temperature makes up 50–150 dyn/cm.

Refractive indices of lithium niobate are sensitive to stoichiometry violation, which leads to optical inhomogeneity in bulk crystal. Crystals grown from a melt with addition of Li<sub>2</sub>O and MgO has a lower refractive index, the decrease of  $n_e$  being substantial, which leads to an increase of birefringence. An excess Nb<sub>2</sub>O<sub>5</sub> has no effect upon  $n_e$  and a very little effect upon  $n_e$ .

An important role for liquid phase epitaxy is played by the phase diagram of solid solution LiNbO<sub>3</sub>-LiTaO<sub>3</sub> and the dependence of the Curie temperature on the composition.

The solidus and liquidus temperatures were determined up to  $1575^{\circ}$ C on thermoanalyser. The results of differential thermal analysis are illustrated in Fig.2.4. Both liquidus and solidus curves show a smooth variation from LiNbO<sub>3</sub> to LiTaO<sub>3</sub>. As expected, these curves do not meet at either end of this pseudobinary section since the stoichiometric and congruent melting composition do not coincide.



FIg.4.2 Stereographic projection of LiNbO3.

A wider spacing was found between the solidus and liquidus curves because of the lower homogeneity of the samples.

Curie temperatures were measured on powder specimens hydrostatically pressed at room temperature and sintered at 1100°C for 12 h. The straight line shown in Fig.4.3 was fitted to the data by least-square analysis. The standard deviation is 13°C, and the correlation coefficient of 0.9966 indicates that the straightline approximation is valid.

Abrahams et al (1966) have determined the crystalline structure of lithium niobate over the temperature range of 24–1200°C by means of a polycrystal X-ray diffraction analysis. The errors involved in high-temperature X-ray powder diffraction are frequently large, thus there is considerable scatter in the data for the oxygen positional parameters as functions of temperature.



**Fig.4.3** Variation in ferroelectric Curie temperature with solid composition in  $LiNbO_3$ - $LiTaO_3$  solid-solution system (Peterson et al 1970).

Peterson et al (1970) have therefore done a linear least-squares fit to the data with the constraint that the highly accurate single-crystal (Abrahams et al 1966; 1967) parameters should be reproduced at room temperature. The positional parameters so calculated were (Peterson et al 1970)

x = 0.005027 (T/1000) + 0.04908,

y = 0.3451 - 0.0207 (T/1000),

z = 0.00401 (T/1000) + 0.06460

and the temperature T was in degrees Centigrade.

Lithium niobate crystals grown by Czochralski method from a congruent melt possess the most homogeneous composition but are nonstoichiometric and lithium depleted (~1.4 mol.%  $Li_2O$ ) (Scott and Burns 1972; Peterson and Carnevale 1972). A wide enough homogeneity region, fluctuations of growth parameters in the course of crystal growth and other factors are responsible for the appearance of regions with local composition deviations in lithium niobate crystals (Holman 1978). Inhomogeneity of composition is observed both along the boule length and in radial direction. As shown by gravimetric measurements (Holman 1978), a deviation of lithium niobate composition from the mean value for specimens cut out of one crystal boule is in most cases equal to 0.2 and can even reach 0.66 mol.%  $Li_2O$ . Inhomogeneity of composition was identical for different regions of one and the same crystal cut. Congruent composition of lithium niobate makes up 48.6 ± 0.2 mol.%  $Li_2O$ (Holman 1978; Chow et al 1974).

The large width of homogeneity region of lithium niobate is due to the presence of intrinsic point defects such as interstice atoms and vacancies in cation and anion sublattices (Carruthers et al 1971). The nature of point defects of the crystal lattice of lithium niobate, which stem from crystal composition deviation from stoichiometry, is not exactly known. There exist models of the defect structure of lithium niobate, one of which is constructed on an ideal cation lattice of niobium with lithium vacancy charge compensation by the formation of oxygen vacancies (Fay et al 1968). But the dependence of lattice constants and density of lithium niobate on the composition cast doubt on the model of lithium vacancies. Lerner et al (1968) assume the excess niobium in the lattice of LiNbO, to occupy the vacant positions of lithium and thus to form antistructure  $Nb_{Li}$  defects. The  $Nb^{+5}$  ion charge in the place of Li<sup>+</sup> is compensated by the formation of four  $V_{Li}$  vacancies. Nassau and Lines (1970) proposed a model of extended cation packaging defect in the direction of z axis with alternation of lithium and niobium atoms. In extension of such defect complexes there occurs a complicated structural disorder. A more detailed review and analysis of the models of defect structure of lithium niobate is given by Ballman (1983) and Jarzebski (1974).

X-ray diffraction methods are inconvenient for the proof of the existence of niobium atoms occupying the position of lithium atoms in the crystal lattice because of their low concentration (~1%). Peterson and Carnevale (1972) discovered two types of signals from <sup>93</sup>Nb in the spectra of nuclear magnetic resonance from nonstoichiometric LiNbO<sub>3</sub> crystals. The authors ascribed the first and most intense line to the niobium that occupies crystallographically regular position in lithium niobate lattice and the second type of signal to excess niobium,  $Nb_{Li}$ . But the intensity of the second line made up 6% of the intensity of the first one, that is,  $Nb_{Li}$  concentration exceeded the expected one. The presence of an additional line in the NMR spectrum testifies to the existence of the second type of niobium atom position in the lattice of lithium niobate but proves neither of the defect structure models described above. The absorption spectra of <sup>7</sup>Li NMR also exhibited weak additional lines whose presence was associated (Yatsenko and Sergeev 1985) with dynamic disorder of lithium in the crystalline structure of lithium niobate.

So, lithium niobate crystals show appreciable composition variations, as well as a complicated point defect spectrum.

Peculiarities of constructing the phase diagram of lithium niobate and the observed deviations of crystal composition from stoichiometry may lead to precipitation of lithium triniobate as a second phase in these crystals under certain conditions of thermal treatment or under cooling of grown crystals. Few data in the literature testify to the fact that phase formation occurs both in the bulk (Scott and Burns 1972) and on the surface (Armenise et al 1983) of lithium niobate crystals.

The basic results on the formation of  $LiNb_3O_8$  in bulk lithium niobate crystals were obtained by Swaasand et al (1974). The X-ray phase analysis and measurements of optical transmission coefficients were used to examine the properties of lithium niobate crystals after a long-term annealing in the air within the temperature range of 600-1000°C for 100-1000 h. After the lithium niobate specimens of different composition were cooled down to room temperature, their optical transmission decreased considerably due to the appearance of milk-white opalescent regions. Transparency of the crystals decreased with increasing annealing time and decreasing Li,O content in the original specimens. So, lithium niobate crystals grown from a melt with less than 48 mol.% Li<sub>2</sub>O showed opalescence already after a 10 hour annealing at 800°C, whereas crystals grown from melts with a higher Li<sub>0</sub>O content required a 500-hour annealing at the same temperature. The authors believe that a change in the bulk crystal transparency under annealing is due to precipitation of a second phase – lithium triniobate  $LiNb_3O_8$  which borders upon LiNbO, on the side of niobium-enriched compositions. This assumption was fully confirmed in an X-ray phase analysis of annealed crystals.

Upon a second annealing at a temperature exceeding 1000°C and a rapid cooling to room temperature, in specimens of lithium niobate crystals containing the second phase the scattering centres disappeared and the crystals became clear again. The X-ray diffraction patterns of such specimens contained reflections only from lithium niobate. The temperature above that of back transformation depended on the specimen composition, and had a value of about 910°C for crystals grown from a congruent melt. On the basis of measurements of back transformation temperature for lithium niobate specimens of different composition, the authors traced out the line of LiNb<sub>3</sub>O<sub>g</sub>-LiNbO<sub>3</sub> phase equilibrium, found the width of the solid solution region and built the phase diagram for temperatures T < 100°C (Fig.4.25).

Thus, lithium niobate crystals are metastable at room temperature, unstable under a long-term thermal treatment and within a certain temperature range can contain the second phase  $LiNb_3O_8$ .

There are comparatively few data on the concentration and localization of  $LiNb_3O_8$  phase. Examination by optical microscopy and light scattering methods shows that upon annealing in the two-phase region, the submicroscopic particles (r < 10<sup>-5</sup> cm) of the phase are nucleated heterogeneously at block boundaries, on dislocations and, along with inclusions of platinum particles and other impurities, are light scattering centres in lithium niobate crystals.

In cooling annealed or grown crystals it is also necessary to take into account the temperature fall rate since this rate is responsible for the time during which the crystal will remain within the temperature range typical of precipitation of  $\text{LiNb}_3O_8$ . When the cooling rate increases to  $3-5^\circ\text{C/min}$ , the lithium niobate was less prone to cracking than crystals cooled at a rate lower than 1°C/min. Without denying the contribution of other mechanisms, Scott and Burns (1972) suppose that the precipitates of the second phase can serve as nuclei for the appearance and development of cracks in lithium niobate crystals. To prevent lithium triniobate from precipitating in bulk crystal of lithium niobate, the cooling rate should be > 20°C/min (Holman et al 1978).

Pioneering reports on variation of the phase composition of lithium niobate crystal surface caused by the formation of lithium triniobate appeared on 1983 as a result of analysis of titanium diffusion into lithium niobate crystals in the course of manufacturing optical waveguides (Armenise et al 1983; DeSario et al 1985). The compound LiNb<sub>3</sub>O<sub>8</sub> occurred on the surface of lithium niobate slabs covered with a titanium layer in the course of annealing within the temperature range of 550–900°C in oxygen atmosphere. Under a scanning electron microscope lithium niobate showed up as shapeless spots of more than 100 µm located in a TiO<sub>2</sub> layer. Analysis of atomic composition has shown that the content of titanium is decreased and that of niobium increased in such regions as compared to phase-free regions. As the annealing temperature heightened to T > 900°C, LiNb<sub>3</sub>O<sub>8</sub> was disintegrated and spots disappeared from lithium niobate slab surface.

Investigations of LiNbO<sub>3</sub> substrates (Armenise et al 1983) have shown that  $LiNb_3O_8$  is also formed in the absence of titanium layer, that is, phase formation on the crystal surface is a specific behaviour of lithium niobate itself in the course of annealing within the indicated temperature range. The presence of  $LiNb_3O_8$  phase orientation relative to (0110) and (0110)  $LiNbO_3$  substrates was discovered from Laue diffraction patterns taken in variable geometry and from the spectra of backward Rutherford helium ion scattering. Precipitation of  $LiNb_3O_8$  phase on crystal surface proceeds not only under annealing in oxygen atmosphere, but also in the air as well as in a N<sub>2</sub> or Ar flux. Addition of water vapors into the atmosphere of annealing prevents the formation of  $LiNb_3O_8$  and induces disintegration of the second phase if it has already been present on the specimen surface (DeSario et al 1985). Disintegration of  $LiNb_3O_8$  under annealing in moist atmosphere was hypothetically explained by the formation of the hydroxyl group OH<sup>-</sup> and ( $Li_{1-y}H_y$ )NbO<sub>3</sub> molecules due to proton diffusion into the crystal.

Phase formation on the surface of lithium niobate crystals was also observed under radiation damages of lithium niobate (Jetschke and Hehl 1985).

A change in the phase composition of LiNbO<sub>3</sub> surface irradiated by N<sup>+</sup> and P<sup>+</sup> ions was discovered by backward Rutherford scattering at a temperature of 279°C. Niobium concentration in the near-surface layer was found to be increased. Connection between phase precipitation and structural damage in the surface layer of lithium niobate substrates was reported by Gan'shin et al (1985, 1986) who observed the occurrence of the compound LiNb<sub>3</sub>O<sub>8</sub> after annealing at  $T = 450^{\circ}$ C for 3 h of proton-exchanged waveguides manufactured on (0001), (0110), (2110) and (0114) facets of lithium niobate.

The operation area of many acousto- and optoelectronic devices is the nearsurface layer, as well as the surface of lithium niobate substrates, and therefore of particular importance for the creation of effective devices is control over the state of lithium niobate crystal surface, its structure and phase composition. The study of phase formation in lithium niobate crystals plays a practical role since heat treatment of LiNbO<sub>3</sub> is a wide-spread technological operation in manufacturing various devices on the basis of lithium niobate crystals.

## 4.2 X-ray diffraction analysis of films

Investigations of film structure were carried out using the X-ray diffraction method. The analysis of patterns thus obtained allows us to judge of polarization, orientation and lattice constants. Polarization and lattice constants were also determined by the electron diffractometry and the composition by the X-ray diffraction method and laser microanalysis.

## 4.2.1 Layer composition

The distribution of components over the thickness of the light guiding layer was examined by microroentgen diffraction analysis (MRDA). Figure 4.4 presents



Fig.4.4 Distribution of components along the thickness of (a)  $LiNbO_3/LiTaO_3$ , (b)  $Li(Nb,Ta)O_3/LiTaO_3$  and (c)  $LiNbO_3/AI_2O_3$  heterostructure.

graphs of component distribution in films on LiTaO<sub>3</sub> (Fig.4.4(a,b)) and Al<sub>2</sub>O<sub>3</sub> (Fig.4.4 (c)). The concentration of the main component of the substrate (Ta or Al) at the interface decreases to zero while niobium concentration becomes maximum (Fig.4.4 (a,b,c)). In growing films of solid solution LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> on a LiTaO<sub>3</sub> substrate the Ta concentration at the interface decreases from 100% to equal the Ta concentration in the film Fig.4.4 (b). Analysis of concentrated profiles has shown that the composition does not change throughout the film thickness. The relative content of Nb and Ta in a film of solid solution is determined by their content in the liquid phase when the effective coefficient of tantalum concentration  $K_{eff} \sim 1.5$ .

As distinct from diffused waveguides, epitaxial layers are characterized by a sharp substrate-film interface. Epitaxial films of lithium niobate-tantalate are colourless.

The results obtained suggest some conclusions concerning the growth process. Since tantalum concentration in a growing lithium niobate film is zero, the solution-melt at the initial epitaxy temperature is in the metastable region, and the substrate surface is not additionally dissolved. The composition constancy of films of  $\text{LiNb}_{1-y}\text{Ta}_y\text{O}_3$  solid solutions implies that the concentration profile remains unaltered in the course of growth, which corresponds to the diffusion model.

Besides the distribution of macrocomponents, the uncontrolled impurity of vanadium atoms in the film and the content of iron ions, introduced in concentrations of 1 and 2 mol.% into the solution-melt in the form of  $FeCO_3$ , were determined. MRDA does not permit qualitative estimation of the content of low-concentration components. The presence of vanadium and iron impurities in the films was determined by laser emission microanalysis.

Analysis of the spectra of the examined patterns has shown that the films contain vanadium in concentration ranging under growth conditions between 0.005 and 0.1 atm.%. The spectra of LiNbO, films and LiTaO, substrate were measured for the second time using a four-step Gortman diaphragm under the same conditions. In this case, film spectra were investigated by comparison with the spectra of vanadium and iron oxides. The results confirmed the absence of vanadium spectral lines in the lithium tantalate substrate, whereas in the films they were clearly pronounced in the same wavelength region. Under optimum crystallization conditions (the growth rate  $v < 0.2 \,\mu$ m/min), a LiNbO, film on a LiTaO<sub>3</sub> substrate of (0001) orientation contains 0.005-0.01 atm.% of vanadium. The maximum concentration (0.01 atm.%) of homogeneous vanadium impurity was obtained at a precipitation rate of 0.6-0.8 µm/min. A homogeneous highly concentrated vanadium impurity was not observed with a further increase of precipitation rate. The upper limit of homogeneous vanadium impurity concentration is obviously due to the difference in V5+ and Nb5+ ion radii  $(R_v = 0.4 \text{ Å}, R_{Nb} = 0.66 \text{ Å})$ , which leads to strong lattice distortions under the Nb<sup>5+</sup>  $\rightarrow$  V<sup>5+</sup> substitution.

As distinct from vanadium, the radii of  $Fe^{3+}$  ions (0.67 Å) are close to those of Nb<sup>5+</sup> and Li<sup>5+</sup> (0.68 Å), which makes it possible to obtain lithium niobate crystals with iron impurity reaching 3 weight % (Gabrielyan 1978). Investigation of doped samples has shown that iron concentration in the sample depends

No	Film material	Lattice parameters (Å)		Orientation	Interplane
	Phili material	а	с	Orientation	distances (Å)
1	LiNbO <sub>3</sub>	5.137	13.828	(0001)	1.1523
				(1 <u>2</u> 10)	1.3884
				(1010)	1.2030
	LiNb <sub>0.7</sub> Ta <sub>0.3</sub> O <sub>3</sub>	5.1385	13.808	(0001)	1.1507
2				(1 <u>2</u> 10)	1.3888
				(1010)	1.2034
	LiNb <sub>0.5</sub> Ta <sub>0.5</sub> O <sub>3</sub>	5,1395	13.798	(0001)	1.1498
3				( <u>121</u> 0)	1.3891
<b>-</b>				(1010)	1.2036
4 I	LiNb <sub>0.2</sub> Ta <sub>0.8</sub> O <sub>3</sub>	5.1408	13.78	(0001)	1,1483
				( <u>121</u> 0)	1.3894
				(1010)	1.2040
5	LiTaO,	5.1421	13.772	(0001)	1,1477
				(1210)	1.3898
				(1010)	1.2042

Table 4.2 Lattice parameters and interplane distances of  $Li(Nb,Ta)O_3$  films and  $LiTaO_3$  substrate (Madoyan et al 1985)

on iron content in the liquid phase and remains essentially unchanged as the rate increases. The estimates of the effective iron segregation coefficient obtained by laser emission microanalysis lie within the range of 0.2-0.5.

## 4.2.2 Monocrystallinity and interplanar distances

X-rays incident on the crystalline structure surface diffract in the near-surface layer whose thickness is determined by the sample material and light beam intensity. X-rays incident on the surface of epitaxial structure can penetrate into the sample depth larger than the film thickness. In this case, X-rays diffract at two angles one of which corresponds to diffraction on the film and the other on the substrate. The relative intensities of these beams depend on film thickness and on the depth of the layers on which diffraction takes place. Superposition of beams is possible in the case of close diffraction angles, and the position of the diffraction lines cannot therefore be precisely determined. Figure 4.5 presents diffraction curves for LiNbO<sub>3</sub> and Li(Nb, Ta)O<sub>3</sub> films on LiTaO<sub>3</sub> substrates of (0001) and  $(11\overline{2}0)$  orientations. The difference in the diffraction angles of lithium niobate and lithium tantalate equal to 10' for the (0001) plane and 6' for the  $(11\overline{2}0)$  plane gives different peaks from the LiNbO, film and LiTaO, substrate. For a LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> film the diffraction maximum is displaced from the substrate with increasing y towards the maximum (Madoyan et al 1985; Madoyan 1984). The difference between the maxima from the film and substrate reaches y = 0.8. Further on, the presence of the film affects the asymmetry of the diffraction peak profile broadened, depending on the layer thickness, towards the film or substrate (Fig.4.5 (c,d)). The attempt to obtain separate peaks from films on (1010)-oriented substrates failed ( $\Delta \theta \sim 3'$ ). For close values of diffraction angles, investigations were carried out on very thick films (Fig.4.5 (e,f)). Since the diffraction depth makes up about 60 µm, for films thicker than



**Fig.4.5** X-ray diffraction patterns: LiNbO<sub>3</sub> films on LiTaO<sub>3</sub> substrates of (a) (0001) and (b) (1210) orientations, LiNb<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub> on a substrate of (c) (0001) and (d) (1210) orientations, LiNb<sub>0.2</sub>Ta<sub>0.8</sub>O<sub>3</sub> on a substrate of (e) (0001) and (f) (1210) orientations.



Fig.4.6 Hexagonal cell parameters versus  $LiNb_{1-v}Ta_vO_3$  film composition.

176

50  $\mu$ m X-rays do not practically reach the substrate, and the diffraction angle is determined by the film alone. The values of the diffraction angles and lattice constants were estimated for thick (1010)-oriented LiNbO<sub>3</sub> and LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> films (y < 0.8).

Table 4.2 presents the values of interplanar distances and lattice constants of  $Li(Nb, Ta)O_3$  films and  $LiTaO_3$  substrate.

There is controversy in the literature as to the character of the dependence of crystallographic parameters and Curie point of solid solutions  $\text{LiNb}_{1-y}\text{Ta}_y\text{O}_3$ on the amount of tantalum, y. Shapiro et al (1965) and Sugii et al (1976) point to the nonlinear dependence, whereas Shimura and Fujino (1977) show that the divergence is due to a lack of correspondence between the parameter y in the synthesized solid solution  $\text{LiNb}_{1-y}\text{Ta}_y\text{O}_3$  and the parameter x of the initial material  $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ . The constructed dependence of the lattice constants a and C on the tantalum content in the film is close to linear (Fig.4.6).

Analysis of X-ray diffraction patterns allows us to judge of structural perfection of epitaxial films. The existence of only one peak indicates that the film is single-crystal, and a small half width (not larger than that of the substrates) points to the lack of block structure of the film and to perfection not lower than that of bulk crystals.

Diffraction studies of films were also carried out by the electron diffractometry which provides a high accuracy in determination of lattice constants. It was established that films on substrates of (0001),  $(10\overline{1}0)$  and  $(11\overline{2}0)$  orientations are single-crystal, which fact accounts for the point-like character of the elec-



Fig.4.7 Electron diffraction from the LiNbO<sub>3</sub> film surface on a LiTaO<sub>3</sub> (1120) substrate, Kikuchi lines are observed.

tron diffraction pattern (Fig.4.7). Furthermore, high structural perfection of the near-surface layer of the film permit obtaining diffraction in the form of the Kikuchi-lines.





So far as electron diffraction pattern only provides information about a nearsurface layer, it permits determination of lattice constants of a film irrespective of its closeness to the substrate parameter. This is of particular importance for the diffraction study of homoepitaxial layers and films of LiNbO<sub>3</sub> on a  $(10\overline{10})$ aligned LiTaO<sub>3</sub> substrate. We should note that in all the cases the interplanar distances did not differ from the results presented in Table 4.1.

Homoepitaxial LiNbO<sub>3</sub> films are of interest in the case when they are doped with transition metal atoms. A detailed analysis of Fe atom distribution over crystallographic positions was given by Rubinina (1976) who showed that  $Fe^{2+}$  and  $Fe^{3+}$  ions substitute lithium or niobium ones. Such iron impurity must not lead to substantial lattice distortions. Variation of lattice constants of LiNbO<sub>3</sub> upon iron doping was not established within experimental error. The diffraction studies of LiNbO<sub>3</sub> films on a sapphire substrate showed film polycrystallinity.

Creation of light guiding layers in  $LiNbO_3$  using diffusion of metal (in particular titanium) ions necessitates determination of strains in the surface layer and the formation of misfit dislocations. To solve these problems, Sugii et al (1978) successfully applied X-rays.

### 4.2.3 Measurement of strains in the diffused layer

The X-ray rocking curve method was employed by Sugii et al (1978) for precise determination of strains in the diffused layer. Rocking curves were taken using a triple-crystal spectrometer as shown in Fig.4.8. It consists of two nearly perfect germanium single crystals  $C_1$  and  $C_2$ , and a simple crystal  $C_3$  arranged in the (+, +, -) position. For  $C_1$  and  $C_2$  the symmetric (333) reflection was used, the Bragg angle for CuK<sub> $\alpha_1$ </sub> radiation,  $\theta$ , being about 45°. The angular and wavelength distributions of the X-ray beam diffracted from the second crystal  $C_2$  were  $\omega = 2 \times 10^{-5}$  rad (4"arc) and  $\Delta \lambda \lambda_0 = 2 \times 10^{-5}$  ( $\lambda_0 = 1.5405$  Å), respectively. They were small enough to obtain an intrinsic rocking curve of the small sample for any lattice plane (*hkl*). In addition, the beam thus obtained is almost

Diffusion time, $t = 10$ h		Diffusion temperature, $T = 1000^{\circ}C$		= 1000°C
<i>T</i> (°C)	ε <sub>y</sub> ×10 <sup>3</sup>	<i>t</i> (h)	ε,×10 <sup>3</sup>	$\varepsilon_{z} \times 10^{3}$
1000	-1.3	1.25	-2.19	1.2
1050	-0.71	2.5	-1.66	0.75
1100	-0.39	3.75	-1.28	0.62
-	_	10	-0.759	0.52

Table 4.3 Strains in the Ti-diffused layer of LiNbO<sub>3</sub> (Sugii, Fukuma, Iwasaki, 1978)

 $\sigma$ -polarized (an electric field vector **E** perpendicular to the plane of incidence) because the scattering angle, 2 $\theta$ , is near 90°. A slit was placed between C<sub>2</sub> and C<sub>3</sub> to obtain a beam of width 0.5 mm and height 2.0 mm. Undiffused samples produced (030) rocking curves with width at half maximum intensity (WHMI) of about 12"arc, which is essentially the theoretical WHMI for the (030) reflection of a perfect LiNbO<sub>3</sub> crystal under these experimental conditions. On the other hand, the diffused samples produces (030) rocking curves accompanied by a diffraction satellite, displaced in angle with respect to the diffraction peak of the unperturbed region in the substrate. Precise determination of strains in the diffused layer is possible since a standard of lattice constant is available in the same trace as the diffused layer. The strain along the *a* axis,  $\varepsilon_r$  ( $\varepsilon_x$ ), is obtained from a shift in angle  $\theta_{030}$  of the satellite as

$$\varepsilon_{v} = \Delta a / a = -\Delta \vartheta_{030} / \tan \vartheta_{030}, \tag{4.1}$$

where  $\theta_{030}$  is the Bragg angle for the (030) reflection. However, strain along the *c* axis,  $\varepsilon_z$ , cannot be directly measured on the diffused layer, since the *c* axis is parallel to the surface in the *y*-plate crystal. If a shift  $\Delta \theta_{hkl}$  can be obtained for a  $(hk\ell)$  reflection with non-zero  $\ell$ , the strain  $\varepsilon_z$  is calculated from a pair of shifts  $\Delta \theta_{030}$  and  $\Delta \theta_{hkl}$  using the following expression

$$\varepsilon_{z} = \Delta C / C = (C^{2}/\ell^{2}) \times \left\{ (1/d) \left( -\Delta \vartheta_{hkl} / \tan \vartheta_{hkl} \right) - 4/3 \left[ (h^{2} + hk + k^{2}) / a^{2} \right] \left( (-\Delta \vartheta_{030} / \tan \vartheta_{030}) \right) \right\}$$

$$(4.2)$$



Fig.4.9 (a) Relationship between the (036) lattice plane and the incident X-ray beam. (b) Inclination in the (036) lattice planes between the substrate and the Ti-diffused layer. The dotted line represents a lattice plane parallel to (036), (Sugii et al 1978).



Fig.4.10 Family of (036) rocking curves for the samples of diffused LiNbO<sub>3</sub>:Ti (Sugii et al 1978).

where *d* is the (*hkl*) lattice spacing and  $\theta_{hkl}$  is the Bragg angle for the (*hkl*) reflection. A (036) reflection was used for this purpose. The geometrical relationship between the (036) lattice plane and the surface is shown in Fig.4.9. The angle  $\beta$  in the interplanar angle between the (036) plane and the surface. In the (036) asymmetric reflection, a shift  $\Delta \theta_{036}^{+}$  for an incident beam with a glancing angle ( $\theta_{036} + \beta$ ) is generally not equal to a shift  $\Delta \theta_{036}^{-}$  for one with a glancing angle ( $\theta_{036} - \beta$ ), since an inclination of the (036) lattice plane,  $\Delta\beta$ , is involved in both shifts (see Fig.4.9(b)). It is readily shown that ( $\Delta \theta_{036}^{+} + \Delta \theta_{036}^{-}$ )/2 gives  $\Delta \theta_{036}$  to be substituted in equation (4.2), which is a shift due only to the difference in the (036) lattice spacing between the diffused layer and the substrate.

The lattice constant *a* was observed in the diffused layers of all the samples investigated in this study. Figure 4.10 shows three pairs of (036) rocking curves  $\Delta \theta^+_{036}$  and  $\Delta \theta_{036}$  of the samples. The ratio of satellite to substrate peak intensity increases with diffusion time *t*, although the absolute intensity becomes small, due to the effect of asymmetric reflection. The substrate peaks could hardly be detected since they were absorbed by the thick diffused layers.

Using equations (4.1) and (4.2), Sugii et al (1978) could calculate strains  $\varepsilon_y$  and  $\varepsilon_z$ . A linear relationship is found between  $\ln(\varepsilon_y)$  and 1/T. The strains  $\varepsilon_y$  and  $\varepsilon_z$  for LiNbO<sub>3</sub>: Ti samples are given in Table 4.3. The strain  $\varepsilon_z$  is about one order of magnitude smaller than the strain  $\varepsilon_y$  in each sample. The strains  $\varepsilon_y$  are plotted against t. The slope  $\ln(\varepsilon_y)$  versus  $\ln(t)$  plot is calculated to be -1/2. These two relationships found between  $\varepsilon_y$  and 1/T, and between  $\varepsilon_y$  and t are similar to those between  $C_s$  and 1/T, and between  $\varepsilon_y$  and t, respectively. Therefore, it can be concluded that the strain  $\varepsilon_y$  in the diffused layer is proportional to the surface concentration  $C_s$ .

#### 4.2.4 Ti distribution in diffused layers

Figure 4.11 shows the Ti distributions of LiNbO<sub>3</sub> samples. Here, a position on the chart was regarded as the surface at which an EPMA response decayed to a value halfway between the maximum and background levels. All the diffused layers have bell-shaped Ti distributions characteristic of the Gaussian distri-



Fig.4.11 Ti diffusion as determined by EPMA of slices for the samples of LiNbO<sub>3</sub>:Ti (Sugii et al 1978).

Table 4.4 Titanium atomic fractions at crystal surface  $N_{\star}$  (Ti), and diffusion coefficients D, diffusion time t = 10 h, in LiNbO, :Ti (Sugii, Fukuma, Iwasaki, 1978)

<i>T</i> (°C)	$N_{\rm s}$ (Ti)×10 <sup>21</sup> cm <sup>-3</sup>	$D, 10^{-12} \text{ cm}^2 \text{ s}^{-1}$
1000	1.23	0.506
1050	0.82	1.06
1100	0.57	2.13

bution. The Gaussian distribution C(y) is expressed as follows

$$C(y) = C_s \exp(-y^2 / b^2)$$
(4.3)

$$C_s = \rho \tau / 2(\pi D t)$$

$$b^2 = 4Dt$$

$$(4.5)$$

where y is the depth below the surface, 
$$\rho$$
 is the number of atoms per unit

w volume in the deposited film of thickness  $\tau$ , and D is the diffusion coefficient given by

$$D = D_0 \exp\left(-Q_d/kT\right) \tag{4.6}$$

Values of EPMA response at the surface,  $R_s$ , corresponding to  $C_s$ , and of the diffusion coefficient D could be determined in such a way that the theoretical distribution calculated by Eqs. (4.3)-(4.5) was fitted to the measured one. Then, the Ti atomic fraction at the surface N<sub>(</sub>(Ti) was estimated from a ratio of  $R_{\rm c}$  to  $R_{\rm o}$  on the assumption that the EPMA response was proportional to C(y). The calculated values of  $N_{c}$ (Ti) and D are given in Table 4.4. It is to be noted that Ti has a remarkably high solubility in LiNbO, in the temperature range from 1000 to 1100°C. The diffusion data were calculated as  $D_0 = 2.19 \times$  $10^{-4} \text{ cm}^2 \text{ sec}^{-1}$  and  $Q_1 = 2.18 \text{ eV}$ .



Fig.4.12 Li depth profiles (a), H depth profiles (b) and ion chanelling results (c) for X-cut blink, after proton exchange in benzoic acid at 180°C for 1 h and after thermal annealing in air at 350°C for 10 h (Hsu et al. 1992).

### 4.2.5 The structure of proton-exchanged LiNbO,

Several studies have been reported on the structural characterization of LiNbO<sub>3</sub>. Rice (1986) reported an approximate phase diagram for the stoichiometric LiNbO<sub>3</sub>-HNbO, system. Depending upon composition, samples undergo one, two, or three phase transitions with temperature. Canali et al (1986) reported results of structural analysis of proton-exchanged lithium niobate optical waveguides fabricated in x, y, and z- cut substrates immersed in pure benzoic acid. They measured atomic composition profiles and noted a marked lattice distortion. H and Li concentration measurements indicated an exchange of about 70% of the Li atoms. The hydrogen depth profile measurements showed a steplike shape in agreement with the refractive index profile measured optically. They concluded that exchange includes a large crystal distortion strongly correlated to the presence of protons. Lee et al (1986) studied structural phase changes in proton-exchanged LiNbO, using transmission electron microscopy. Regions of diffuse intensity within the single crystal electron diffraction patterns of LiNbO, were observed. Minakata et al (1986) measured the lattice constants and electro-optic constants of z-cut proton-exchanged LiNbO, crystals by means of the x-ray rocking curve method and the phase modulation technique. They found that the strain along the c axis,  $\Delta c/c$ , was extremely large (+0.45%) whilst the strain perpendicular to the c axis,  $\Delta a/a$ , was negligibly small in proton-exchanged LiNbO, single crystals. The electro-optic coefficient value in the layer reduced to one-tenth of the bulk crystal value. Vohra et al (1989) measured the concentration profiles of proton and lithium proton exchanged LiNbO, crystals using secondary ion mass spectroscopy and found proton concentration profiles nearly rectangular in shape. Loni et al (1991) reported, using secondary ion mass spectrometry (SIMS) and an optical method, a direct comparison of

hydrogen depth distributions and refractive index profiles in annealed protonexchanged z-cut LiNbO<sub>3</sub> waveguides. Novak et al (1992) have reported SIMS depth profile measurements of H, Li, Nd, and Er in LiNbO<sub>3</sub> and LiTaO<sub>3</sub>. The above discussion indicates that extensive studies have been carried out on the characterization of the proton-exchange process. Some results have also been reported on the degradation of the electro-optic coefficient. To our knowledge, no results have been reported correlating the degradation of the nonlinear coefficient to its structural aspects. Hsu et al (1992) reported the results of x-ray rocking curves studies as well as depth profiles of H and Li and ion channeling measurements using forward recoil spectrometry (FRES), the ion induced nuclear reaction  $Li(p,a)He^4$  and Rutherford backscattering (RBS) techniques, respectively, that provide some structural characterization of proton-exchanged and annealed LiNbO<sub>3</sub> samples. These measurements are correlated with optical measurements of the refractive index and second harmonic generation.

Figure 4.12a shows the Li profiles from bulk LiNbO, crystal, a protonexchanged crystal and an annealed sample. These results indicate a significant loss of Li from the surface upon proton-exchange and recovery of it after thermal annealing (although a region of about 0.1 µm in thickness still remains Li deficient). Figure 4.12b shows the hydrogen profiles of the same set of samples. The hydrogen peak at the surface of the untreated LiNbO, crystal could be due to the moisture present at the surface. The simulation results indicate a steplike profile of hydrogen after proton-exchange in agreement with Loni et al (1991). After annealing, the hydrogen concentration falls, except for a small peak in the near-surface region of the sample. The RBS channeling results presented in Fig.4.12c show that the proton-exchange induces disorder in the Nb sublattice extending from the surface of the sample to a depth of approximately 0.7 µm. This disordered region coincides with the Li depleted and hydrogen-occupied regions shown in Fig.4.12a and b, respectively. In thermal annealing, most of the lattice disorder is recovered except for a narrow region, approximately 0.1 µm thick close to the surface of the sample. Figures 4.12a and b show that this region is also Li-deficient and presumably H-rich, respectively. In the second-harmonic reflectance technique, the second-harmonic signal is obtained only from the front surface since the skin depth for the wavelength employed is of the order of 0.1 µm. This implies that the reflectance technique does not provide a full characterization of the degradation in waveguides that are typically 1 µm deep. Also, since there is a marked recovery in deeper regions of sample, efficient second-harmonic generation is possible in LiNbO<sub>2</sub>, although conversion efficiencies smaller than theoretical values can be expected.

The RBS channeling results of an x-cut LiNbO<sub>3</sub> sample that was protonexchanged in benzoic acid for 30 min at 180°C and subsequently annealed in air for 2 h at 350°C, revealed disorder in the crystal lattice after protonexchange to a depth of about 0.35  $\mu$ m. However, in this case (short *p*-exchange time) there is almost complete recovery after thermal annealing. Indeed, an SHG signal was observed after thermal annealing, but not after proton exchange. Also, the prism coupling method indicated a waveguide in the sample after thermal annealing, but no waveguide was observed after proton exchange. The RBS channeling results of an x-cut LiNbO<sub>3</sub> sample that was proton-exchanged for 30 min at 230°C in pyrophosphoric acid and subsequently annealed in air for 1 h at 350°C, indicated disorder in the crystal lattice after proton exchange extending to a depth of 1.8  $\mu$ m, which partially recovers upon thermal annealing. Therefore, proton exchange with pyrophosphoric acid produces similar lattice disorder as proton exchange with benzoic acid.

The largest refractive index of LiNbO<sub>3</sub> is a result of the extreme polarizability of the Nb-O bonds. The proton exchange process induces a distortion of the crystal lattice and hence a distortion of the Nb-O bonds. This change of the niobate structure appears to cause the index increase. This effect appears to be also the source of the decrease in the nonlinear optical coefficient, a property that is also related to the polarizability of the Nb-O bond. Therefore, it appears that it is not the presence of the protons, but rather their effect on the Nb-O lattice, that affects the optical properties. A full recovery of the optical properties occurs not by removing the protons, but by restoring the crystal lattice.

## 4.2.6 Orientation relations

X-ray diffraction studies also determined the direction of the crystallographic axes of substrate and film surfaces. The results were most precise on samples the diffraction from whose surface gave two clearly separated maxima. In this case, the absolute loss of film and substrate orientation was measured by their orientation loss relative to the standard. It was established that crystallographic directions of the film of pure lithium niobate and solid solutions LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> coincide with identical directions of LiTaO<sub>3</sub> substrates up to 20' for (0001) and (1120) sample orientations irrespective of original orientation loss in the substrate surface.

Ninomura et al (1978) described the process of obtaining  $LiNbO_3$  films on a MgO substrate. Sputtering onto the (111) plane of the substrate resulted in crystallization of a (0001)-oriented  $LiNbO_3$  layer. Such orientation relation is explained by the fact that the position of oxygen ions in the indicated planes is identical and their coordinates in the plane do not differ by more than 0.2% of the oxygen sublattice period.

As distinct from MgO, the structure of LiTaO<sub>3</sub> is identical to that of LiNbO<sub>3</sub>, and their parameters differ by 4% in c and 1% in a.

Because of similarity of lattices, film orientation is preserved, as expected, and the substrate-to-film transition is due to formation of the transition layer of  $\text{LiNb}_{1-x}\text{Ta}_xO_3$  of variable composition, in the course of which the lattice constant changes from film to substrate parameter. In the absence of additional substrate dissolving, the width of the transition region appears to be small (1 µm) and is determined by the interdiffusion depth of substrate and film atoms after precipitation.

In growing homoepitaxial films with iron impurity no deviation of layer orientation from that of substrate was observed.

A lithium niobate film grown on a  $(1\overline{2}10)$  sapphire substrate exhibited no X-ray diffraction at an angle corresponding to the single crystal. The most intense scattering corresponded to the z plane of LiNbO<sub>3</sub>. It is most likely that

Ferroelectric Thin-Film Waveguides in Integrated Optics and Optoelectronics 185



Fig.4.13 Mechanisms of epitaxial growth of lithium niobate. a) model, b) photographs of surface morphology of LiNbO<sub>3</sub>.

a LiNbO<sub>3</sub> film precipitates onto an  $\{1\overline{120}\}$  Al<sub>2</sub>O<sub>3</sub> plate in the form of a polycrystalline layer or a layer consisting of regions with different orientations with predominance of the z direction. Such a conclusion is also confirmed by the fact that no point electron diffraction pattern corresponding to a single crystal could be obtained.

## 4.3 Morphology and perfection of layers

Attenuation of a light wave in a waveguide is the principal parameter responsible for efficiency of the epitaxial structure in integrated optics. In a zigzag propagation of light, attenuation is determined by two factors – by light scattering upon repeated reflection from substrate-film and air-film interfaces and by absorption in the bulk. The scattering loss typically increases with increasing order of the waveguide mode, whereas the bulk loss remains almost unchanged. In this connection, perfection of the film surface and of the substratefilm interface is of importance. The bulk loss is due to absorption and scattering of light on structural inhomogeneities of the films, which are determined by the film formation mechanisms.

According to modern concepts of the nucleation theory, the most important factor which determines basically the mechanism of single crystal nucleation and the kinetics of their subsequent growth is the structure of the real surface of the substrate (Veinstein et al 1979). One should bear in mind that the difference in the lattice periods of contacting materials affects the magnitude of the surface energy of the interface and, accordingly, the character of elementary growth processes at the early stage of heteroepitaxy establishing either two-or three-dimensional nucleation mechanism. The character of elementary growth processes essentially determines the structure perfection and the morphology of thin epitaxial layers near heteroboundary.

Figure 4.13 presents models of the layer growth mechanism for different supersaturations in the liquid phase and the corresponding surface micromorphologies

of heteroepitaxial structures LiNbO<sub>3</sub>/LiTaO<sub>3</sub> (Khachaturyan 1987; Khachaturyan et al 1987).

An analysis of recent publications on the mechanism of oriented growth of various substances shows that their common tendency is revision of conventional and generally accepted viewpoints. These works reject the dimensional geometric approach and make use of phase equilibrium as one of the criteria of the possibility of epitaxy (Chernov et al 1980; Bolkhovityanov and Yudayev 1986).

## 4.3.1 Micromorphology of film surface for different crystallographic orientations of the substrate

Morphological studies of lithium niobate and solid solutions  $LiNb_{1-y}Ta_yO_3$  have shown that surface morphology depends on the following factors: material and preparation of substrate surface, orientation, composition of precipitated layer, growth rate and temperature regime of epitaxy.

Plates of preferentially z and y cuts of single-domain single crystals are typically exploited to manufacture integro-optic elements. The state of their surface layer, which is of principal importance for technology of light guide formation, depends essentially on finish polishing.

The damaged surface layer is a developed system of structural defects and violation of chemical composition. Direct structural studies of reflection using electron diffractometry show that after mechanical polishing the surface layer of lithium niobate plates is completely disordered and amorphous (Sugii et al 1980; Rakova et al 1986). Its structural perfection can be improved by substrate annealing in oxygen atmosphere. Optimum annealing conditions are 1000°C and 1h. After such heat treatment, electron diffraction patterns of samples show Kikuchi lines, which is indicative of high perfection of crystal surface structure.

Figure 4.14 presents the photographs of surface morphology of LiNbO<sub>3</sub> films on LiTaO<sub>3</sub> substrates of *z*, *y* and *x* orientations. Perfectly smooth, mirror surfaces are typical whose roughness height on the *z* plane is not larger than 0.1  $\mu$ m (Fig.4.14 (Ia, IIa)). Introduction of iron impurity into solution leads to the formation of round figures of growth on the film surface. Heterolayers on LiTaO<sub>3</sub> substrate have morphology analogous to homolayers but the figures of growth have pronounced contours, the roughness height reaches 0.5  $\mu$ m (Fig.4.14 (Ib,c)).

The pictures show that the surface morphology of films is determined first of all by the substrate orientation. On the x plane of epitaxial LiTaO<sub>3</sub>, the figures of growth have the shape of a triangle and sometimes of a truncated pyramid 1 µm high. Long narrow hillocks directed along the x-axis are observed on y-oriented homo- and heterolayers (Fig.4.14 (1b, IIb, IIIb)). The morphology of epitaxial layers is substantially affected by interface instability. At high growth rates, the surface on which crystallization takes place becomes unstable and its roughness increases. At low cooling rates, the effect of gradients along substrates increases, which leads to the formation of layers with significantly different thickness. Investigation of the effect of growth rate upon surface morphology of LiNbO<sub>3</sub> films has shown that the smoothest layers correspond to the growth rate of not more than 0.6 µm/min. An increase in the growth rate has a special effect upon the morphology of z-oriented layers, at rates near



**Fig.4.14** Typical morphology of LiNbO<sub>3</sub> film surfaces of a) (0001); b) (10 $\overline{2}$ 0); c) (10 $\overline{1}$ 0) substrate orientations. I) y = 0.3,  $v \sim 0.2 \mu$ m/min; LiNbO<sub>3</sub> substrate; II) y = 0.8,  $v \sim 0.6 \mu$ m/min; LiTaO<sub>3</sub> substrate III) y = 0.3,  $v \sim 0.1 \mu$ m/min; LiTaO<sub>3</sub> substrate (Khachaturyan et al 1984).

1  $\mu$ m/min there appears mosaic structure of the surface, and above this value the film is completely covered with hillocks. An increase of precipitation rate on y and x planes entails an increase in the density of the figures of growth which somewhat increase in size and have a triangular shape (Fig.4.14 (IIIb,c)).

Thus, the surface morphology of LiNbO<sub>3</sub> films is basically determined by substrate orientation and growth conditions. The appearance of three-dimensional patterns is due to crystallographic specificities of lithium niobate structure: they are determined by the shape of cross-section of elementary rhombohedron with (0001),  $(10\overline{1}0)$  and  $(11\overline{2}0)$  planes.

Connection between the lattice parameter mismatch and the surface morphology also manifests itself in epitaxy of solid solutions  $\text{LiNb}_{1-y}\text{Ta}_yO_3$  on a  $\text{LiTaO}_3$  substrate. Figure 4.14 shows a decrease in surface roughness with increasing Ta content in the film and a decrease in the density and size of the growth patterns. The surface roughness does not exceed 0.2 µm. The result obtained testifies clearly to the fact that surface morphology is determined by the structure defects occurring at the interface due to mismatch of lattice constants. The film surface roughness is considerably influenced by the manner in which the substrate surface is prepared. Mechanical polishing leads to the appearance of a damaged near–surface layer. High-temperature annealing or chemical etching induce the appearance on the sample surface of some signs of polishing hidden by the near-surface layer. Scratches on the substrate occur on the surface of thin layers in the form of shallow grooves up to 3 µm wide. To obtain a perfect surface, the substrate was preliminarily treated in KOH at a temperature of 280–340°C for 2–3 min.

Examination of surface morphology has shown that to obtain smooth layers it is of importance to completely remove the residues of solution-melt from the film surface when the growth process is over. A rapid cooling to room temperature typically causes an uncontrolled additional crystallization from the remaining drops of liquid.

## 4.3.2 Diffusion-induced defects in films

The diffused layer and substrate can be diffracted separately by utilizing the diffraction angle corresponding to each lattice constant. Thus separate topographies can be recorded for the diffused layer and substrate. This technique is very useful for the investigation of defects generated by diffusion. Sugii et al (1978) took topographies of the Ti-diffused layer using the Lang camera applied to the reflection case with  $CuK_{\alpha 1}$  radiation.

Figure 4.15a shows topography of the diffused layers of the samples of group I. The excess diffraction constant observed in all the samples is due to a high density of defects. It is found that the higher the diffusion temperature, the less serious the degradation in crystallinity in the diffused layer. This corresponds to the result, obtained by the rocking curve measurement, that the mismatch decreased with increasing diffusion temperature from 1000 to 1100°C.

Figure 4.15b shows topography of the diffused layers of some samples of group II. Three types of defects are clearly observed: mismatch dislocations, cracks of type I running in the direction perpendicular to the x axis, and cracks of type II running in the direction perpendicular to the z-axis. All of the defects were induced by the Ti diffusion. Mismatch dislocations should be generated so as to relieve stresses in the diffused layer. The directions of the cracks suggest that the type I cracks must be generated by a stress along the a-axis and the type II cracks by a stress along the c-axis. Densities of the mismatch dislocations and of the type I cracks increase with diffusion time t, however, the density of type II cracks is almost independent of t.

When the Ti-diffused layer is utilized as an optical waveguide, the defects



**Fig.4.15** Diffusion-induced defects in Ti-diffused layers of samples of  $LiNbO_{s}$ :Ti group I (g = 030) (a) 1000°C, 10 h, (b) 1000°C, 2.5 h, group II (Sugii et al 1978).

may increase the scattering loss of optical guided waves as observed in the Nb-diffused LiTaO, waveguides (Ramaswamy and Standley 1975).

Applying the combined diffusion-film method, one can obtain channels of an 'immersed' or symmetric waveguide. Figure 4.16a shows a LiTaO<sub>3</sub> substrate of (1120) orientation with an 'Y'-shaped coupler preliminarily deposed by titanium thermodiffusion. The channel width was equal to 6 µm and the gap between the channels for depositing control electrodes to 10 µm. On this surface, an epitaxial LiNb<sub>0.1</sub>Ta<sub>0.9</sub>O<sub>3</sub> layer was grown. Figure 4.16 b shows the surface morphology of epitaxial structure LiNb<sub>0.1</sub>Ta<sub>0.9</sub>O<sub>3</sub>/Ti:LiTaO<sub>3</sub>. The channels and the 'Y'-shaped coupler are clearly seen.

Varying the layer composition, the substrate material, the thickness of titanium sputtered onto substrate and the time of the process we form different profiles of the refractive index with a maximum value on the substrate-film interface. The light transmitted through the waveguide has minimum scattering loss on the interface. The refractive index variation on the waveguide boundary, which determines scattering under complete internal reflection, is by an order of magnitude smaller than that on the film-air interface.

## 4.4 Substrate-film interface and transition region

The state and properties of the interface between the waveguiding layer and substrate have an effect upon the properties of the film as a whole and upon its structure. The influence of the substrate upon the interface structure depends on the layer growth conditions and determine the density and distribution of defects (inclusions, dislocations, impurity atoms and vacancies) and elastic stress in the transition layer.



Fig.4.16 The surface of a LiNbO<sub>3</sub> substrate with a Ti-diffused 'Y' coupler (a) and the surface of an epitaxial film grown on this substrate (b).

Epitaxial layers are characterized by a clearly pronounced substrate-film interface. The thickness of the transition region is determined by the growth conditions and materials, as well as by the initial epitaxy temperature at which the substrate is moistened by the solution-melt. The substrate surface dissolution increases with increasing initial temperature for the same solution composition. This leads to the fact that under epitaxy, before the beginning of precipitation at the LiTaO<sub>3</sub> crystallization front, this causes the formation of a thin liquid-phase layer enriched with Ta as compared to the rest of the liquid phase, and under a subsequent cooling a layer of variable composition is precipitated. Upon precipitation of a pure lithium niobate film, on the substrate-film interface there forms a solid solution LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub>. This obviously occurs due to substrate dissolution since in the indicated paper the concentration of Nb<sub>2</sub>O<sub>5</sub> in the solution-melt is by 5% smaller than in stoichiometric compositions.

Transition regions were examined on chips and polished cuts of the grown structures. Under ideal homoepitaxy the film-substrate interface is not pronounced. Figure 4.17 presents photographs of chips of LiNbO<sub>3</sub> and Li(Nb,Ta)O<sub>3</sub> films on LiNbO<sub>3</sub> and LiTaO<sub>3</sub> showing a clear and straight interface and a flat transition. Identity of crystalline structures of film and substrate and equal Nb<sup>5+</sup> and Ta<sup>5+</sup> radii lead to interdiffusion of niobium and tantalum atoms through the interface and to the formation of the transition region LiNb<sub>1-z</sub>Ta<sub>z</sub>O<sub>3</sub> where z varies from 0 to y.

The formation of the 'transition' region is an undesirable process which makes epitaxial layers closer in the properties and structure to the diffusion layers.

Films with a concentration profile close to rectangular can be obtained in







Fig.4.17 Boundaries between epitaxial structures: a)  $LiNbO_3/LiNbO_3$ ; b)  $Li(Nb,Ta)O_3/LiTaO_3$ ; c)  $LiNbO_3/LiTaO_3$  (Khachaturyan et al 1984).

different ways. Precipitation onto z-LiTaO<sub>3</sub> through a buffer layer substantially decreases interdiffusion, and the thickness of the transition region appears to be lower than the microprobe resolution (~0.2 µm). The concentration profile depends on the growth conditions. The interdiffusion depth is determined by the heat time and decreases with decreasing hold time after precipitation. For structures obtained at a growth rate of less than 0.2 µm/min and annealing for 3 h the transition region is typically wide (up to 3–5 µm) and the interface is only pronounced under selective etching as shown in Fig.4.17a. Precipitation at a rate  $v \sim (0.2-0.3)$  µm/min and holding for 1.5 h leads to the formation of structures with a transition region not wider than 0.5 µm, which is observed at chips without additional etching of the interface (Fig.4.17c).

## 4.5 Dislocation structure

To create effective waveguides with insignificant attenuation, films with low defect density, sharp substrate-film interface, mirror-smooth surface of the epitaxial layer and homogeneity of film properties throughout the thickness are necessary. Investigation of structural inhomogeneities and surface morphology plays an important role for growing films with prescribed parameters and low defect density (Madoyan and Khachaturyan 1987).

Morphological studies were carried out using scanning electron and light polarizing microscopes. Structural inhomogeneities were revealed by selective etching in a boiling 1:2 mixture of concentrated acids HF and  $HNO_3$  and in KOH. Etching time was varied from 1 to 40 min depending on the polarization vector direction.

The most typical inhomogeneities of epitaxial layers are dislocations. Analysis of experimental papers on examination of the dislocation structure of ferroelectrics shows that the most likely mechanism of the occurrence of dislocations is the following:

-penetration of dislocations from the substrate to the film in which they degenerate;

-nucleation of dislocations under stress caused by nonuniform impurity capture under laminar growth;

-occurrence of defects due to the nonuniform impurity distribution in a growing layer.

On the substrate-film boundary, defects may occur due to mismatch in lattice constants between the film and substrate. To minimize the mismatch between the two lattices, elastic deformation of films is energetically advantageous. If the mismatch is not compensated completely by the elastic stress, mismatch dislocations also occur (Milvidsky and Osvensky 1977). A relative contribution of elastic stresses and mismatch dislocations to the accommodation of crystal lattices depends on the difference in lattice constants, film thickness, geometry of dislocations, character of bonds on the interface and elastic constants of two intergrowing materials. Mismatch dislocations slide from the free surface into the interface region.

Places where dislocations appear on the film surface as conical etch pits with a clearly pronounced vortex shown in Fig.4.18e,f. But a mixture of hydrofluoric and nitric acids does not permit an exact location of dislocation etch pits on



**Fig.4.18** Dislocation structure and domain configurations in epitaxial films, successive etching of film surface with a tapered out positive domain (a,b); domain configurations in substrate (c) and in a film grown on this substrate (d); microdomains on (0001) (e) and (1120) (f) surfaces of LiNbO<sub>3</sub> structure inhomogeneities on the surface (1120) of a LiNbO<sub>3</sub> film (g) and etching-revealed dislocations and microdomains in a (0001) film (h) (Khachaturyan et al 1984).

the positive z-plane and, as analysis shows, does not at all possess properties of selective etching for the x-plane. The dislocation structure was unambiguously determined by etching in the KOH melt at a temperature of 400°C. Figure 4.18e and f shows z and y surfaces of LiNbO<sub>3</sub> after etching in KOH for 2 min.

Since substrate dislocations emerging on the surface under pseudomorphous film growth continue in the grown layer, the structural perfection of the layer depends on dislocation density in the substrate. A direct count of etching pits has shown that the density of dislocations emerging on the substrate surface is determined by the position of this surface relative to the growth axis of the original crystal. The number of dislocations on the y-plane of LiTaO<sub>3</sub> and z-plane of LiNbO<sub>3</sub> (that is, on the plane perpendicular to the crystal growth axis) makes up  $N\sim10^4$  cm<sup>-2</sup>, for the other planes it is by an order of magnitude smaller.

Selective etching of lithium niobate films in KOH has shown that growth hillocks on the film surface are of dislocation nature. In the place of hillocks

removed by polishing there typically appear dislocation etching pits (Fig.4.18c). Two mechanisms of this phenomenon are possible.

In mating two single-type lattices with interplanar distances  $a_1$  and  $a_2$  there occur mismatch dislocations with the linear density

$$N_{\rm mis,dis}=\frac{\Delta a}{a^2},$$

where

$$\Delta a = a_1 - a_2; \ a = \frac{a_1 + a_2}{2}. \tag{4.7}$$

For a pseudomorphously grown layer there exists a critical thickness

$$h_{\rm cr} = \frac{1}{2N_{\rm min,dis}}.$$
(4.8)

On reaching this thickness, the layer stops being pseudomorphous, and nets of mismatch dislocations appear on the boundary.

Dislocations of the substrate, that emerge on its surface upon pseudoamorphous film growth, stretch to the grown layer up to the critical thickness. After that, dislocations with the Burgers vector parallel to the substrate bend, become mismatch dislocations and then go to the grown layer. In this case there appear only separate regions, instead of a whole net, of mismatch dislocations. A substitution of the values of interplanar distances of lithium niobate,  $d_x = 1.284$  Å,  $d_y = 1.486$  Å,  $d_z = 1.152$  Å, and lithium tantalate,  $d_x = 1.286$  Å,  $d_y = 1.487$  Å,  $d_z = 1.147$  Å obtained by the X-ray diffraction method yields the values of linear dislocation densities  $N_y = 6.79 \times 10^4$  cm<sup>-1</sup>,  $N_x = 8.48 \times 10^4$  cm<sup>-1</sup>,  $N_z = 34.84 \times 10^4$  cm<sup>-1</sup> and correspondingly the values of pseudomorphous layer thickness  $h_{y,cr} = 0.074$  µm,  $h_{x,cr} = 0.059$  µm,  $h_{z,cr} = 0.014$  µm.

Thus, during crystallization on the z-plane of LiTaO<sub>3</sub> the mismatch dislocation density is minimum, and the surface morphology must be nearly isotropic. For y- and x-oriented layers the number of dislocations caused by mismatch between the interplanar distance along the z axis and aligned perpendicular to it is higher by an order of magnitude. Therefore, the segments of mismatch dislocations occurring on the growth dislocations that stretch to the film are expected to be perpendicular to the z-axis.

Such a model agrees with some of the experimental results. In particular, the surface morphology on the z plane is close to isotropic, and the direction of growth hillocks on y- and x-oriented films are perpendicular to the z-axis. Introduction of tantalum pentoxide to a lithium niobate film (*i.e.* mating the lattice constants of the film and substrate) decreases the number and size of the growth hillocks. But there exist essential contradictions. Because of small thickness of the pseudomorphous layers, the mismatch dislocation segments must occur at the initial instant of epitaxy (0.1  $\mu$ m) and must not have any effect upon the morphology further on. The figures of growth increase with increasing film thickness, whereas the effect of lattice mismatch decreases.

Under homoepitaxy onto a LiNbO<sub>3</sub> substrate the lattice mismatch is absent, but elongated hillocks occur on the film surface. Growth patterns on dislocations are obviously due to alien inclusions.

Analysis of crystallization from solution has shown that sheaf-shaped growth dislocations occur on inclusions concentrated for the most part along planes which are traces of termination or acceleration of a growing facet.

In epitaxial growth, such a plane is the substrate surface. The difference in ion radii of vanadium and niobium causes segregation of solvent in the form of inhomogeneous microinclusions. The direction of dislocations in a sheaf is connected with free energy anisotropy of unit dislocation length which is determined by the elastic moduli of the crystal. For lithium niobate and tantalate, anisotropy on y- and x-oriented planes is single-type relative to the z-axis. Divergence of the sheaves must lead to increase in the growth pattern size. Capture of the solvent may occur both under homo- and heteroepitaxy. The shape, size and concentration of inclusions are determined by surface processes. Introduction of tantalum oxide in the liquid phase, which stimulates an increase in the growth temperature and a decrease in the growth rate must result in a decrease in the solvent capture probability. The presence of sheaves of dislocations due to inclusions in a lithium niobate film is in agreement with the surface morphology. The structure of the interface is worsened by inclusions leading to a scattering of the waveguide mode.

The dislocation density in the film is thus of the same order as in the substrate or even higher. In addition to dislocations growth from the substrate, new dislocations occur in the film due to lattice mismatch and solvent inclusions. On the layer surface, dislocations appear as characteristic growth patterns whose shape is determined by orientation of the substrate and the size by the thickness and growth rate. Mismatch dislocations occur in pseudomorphous layers not thicker than 0.1 µm. Their density is minimum on the (0001) plane. On the (1120) and (1010) planes they appear as hillocks stretching perpendicular to the (0001) axis (Fig.4.18g). Introduction of tantalum pentoxide to the melt from which a lithium niobate film is grown (*i.e.* mating the lattice constants of the film and substrate) decreases mismatch dislocation density and the size of the growth hillocks in the places of dislocation occurrence.

During crystallization from solution, growth dislocations in the form of divergent sheaves occur on inclusions (Golubev et al 1982). Inclusions are largely concentrated along the planes which are traces of termination or acceleration of a growing facet (in particular, the substrate surface). The difference in ion radii of vanadium and niobium (0.4 Å and 0.66 Å) restricts solvent capture, and for high concentrations leads to segregation in the form of inhomogeneous microinclusions. For low vanadium concentrations, strong deformations and local stresses appear in the lattice that initiate the formation of dislocations and microdomains. Figure 4.18h) illustrates etching of a (0001) film of LiNbO<sub>3</sub> with a dislocation stretching through the entire length. The figure shows that dislocations occur along with microdomains aligned perpendicular to the surface. Dislocations aligned along the  $(10\overline{12})$  axis are generated at different depths of the film and are mostly concentrated near the interface.

Figure 4.19 presents a graph of the distribution of dislocation density over





the thickness of the epitaxial structure. Dislocations are basically generated in the transition region which is thicker by an order of magnitude than the calculated value of the pseudomorphous layer (0.1  $\mu$ m). Therefore, besides mismatch dislocations, other types of dislocations must develop in the film, which originate on the impurity centres that induce lattice deformation and microstrains. The latter lead, in turn, to the formation of microdomains coupled with dislocations.

Structural inhomogeneities of films affect essentially their optical properties. In particular, they cause scattering of channelled light on microinclusions and domain walls. The presence of domains with different polarization lowers the efficiency of electro-optic modulation.

We present the results of morphological studies of the film surface and substratefilm interface of lithium niobate structures grown by LPE and liquid-phase and electroepitaxy. Figure 4.20 presents typical pictures of surface morphology and transverse chips of these films grown by the two methods mentioned above.

In the figure one can see imperfections closed on the substrate-film transition region under liquid-phase electroepitaxy of lithium niobate (1b, IIb), thickness and planarity of epitaxial films, as well as regions of growth dislocation clusters and and occurrence of microdomains (III).

Figure 4.21 presents the dependence of the ratio of dislocation densities in lithium niobate under liquid phase electroepitaxy and liquid phase epitaxy (1) and film thickness (2) on the current density. As is seen from the figure, an increase in the current density  $(J > 15 \text{ mA/cm}^2)$  induces a sharp increase in the growth dislocation density as compared with liquid phase epitaxy of lithium niobate. This is apparently connected with a growing influence of Joule effect upon crystallization above the indicated current density range.

## 4.6 Domain structure

The most typical inhomogeneities in ferroelectrics are domain boundaries, growth dislocations and microinclusions of alien phases. In planar integro-optic waveguides on the basis of lithium niobate, these inhomogeneities lead to an additional scattering of channelled light and to lowering of the device efficiency.

Polydomain lithium niobate and tantalate crystals consist of  $180^{\circ}$  domains with polarization along the (0001) axis. Lithium tantalate used as substrate is a perfect structural analogue of lithium niobate, but the domain size is smaller by two orders of magnitude (10 µm). The dislocation density makes up ~ $10^4$ 



Fig.4.20 Photographs of transverse layers (I) and morphology of the surface (II) of lithium niobate films grown by liquid phase epitaxy (a) and liquid phase electroepitaxy (b) (Khachaturyan et al 1987).



Fig.4.21 Dislocation density ratios in lithium niobate films growth by liquid phase epitaxy and liquid phase electroepitaxy (1) and thickness of electro-LPE film as functions of current density (Khachaturyan et al 1989).

cm<sup>-2</sup>, most of the dislocations occurring during growth. Thin rods (up to 300 µm long) of needle-shaped microdomains were observed in lithium niobate along the (0001) axis with polarization reverse to that of the principal domain (Fig.4.22) (Prokhorov and Kuz'minov 1990). The presence of vacant oxygen octahedra in the structure promotes entrapment of impurity and first of all metal ions.

Defects typical of lithium niobate are oxygen vacancies which can be readily withdrawn by high-temperature annealing in oxygen atmosphere.

Lithium niobate crystals are highly sensitive to heat treatment which affects, besides oxygen vacancies, also dislocation migration, impurity distribution and the content of microdomains. (Rakova et al 1986; Bocharova et al 1985) pointed out the appearance of alien phases on the surface of LiNbO<sub>3</sub> under annealing at  $T = 900^{\circ}$ C, (Ohnishi and Yizuka 1974) reported repolarization of near-surface layers under mechanical treatment.



Fig.4.22 Needle-shaped domain structure of LiNbO<sub>3</sub> crystal (Prokhorov and Kuz'minov 1990).

Fig.4.23 (right) Growth rate of a lithium niobate film versus cooling temperature. The cooling rates 1) 0.3 deg/min; 2) 0.16 deg/min, O) on a negative domain; □) on a positive domain.

#### 4.6.1 Epitaxial film on a domain boundary of the substrate

Nonsymmetric position of ions in the ferroelectric phase is responsible for the difference in chemical activities of surfaces with different polarizations, which is observed in particular in selective etching.

Under epitaxy, when the growth rate is determined by surface processes (kinetic regime), the surface activity must tell upon the kinetics of crystallization processes. The Curie point of lithium tantalate (660°C) is lower than the epitaxy temperature, and precipitation under heteroepitaxy proceeds on substrates in the paraphase. The surface properties are identical throughout, and spontaneous polarization has no direct effect upon growth kinetics. Under epitaxy on (0001), a LiNbO<sub>3</sub> crystal is in the ferroelectric phase ( $T_c = 1210^{\circ}$ C), and precipitation may take place onto single- and polydomain substrates.

Crystallization from solution assumes that precipitated atoms come from the depth of solution to the crystallization front, are adsorbed onto the growing surface and built in the crystal lattice. For small supersaturations, the growth rate is limited by diffusion mass transfer and surface processes do not affect the precipitation rate. Film thicknesses on positively and negatively charged single-domain substrates are equal. In diffusion regime, the influence of domain structure is observed when precipitation takes place onto a polydomain substrate. On domains with different polarizations the film thickness is not at all uniform, but it becomes uniform far from domain boundaries. Such a picture can be easily explained if we take into account the fact that far from the boundaries the growth rate is only limited by mass transfer and near the domain boundaries a difference in surface activities leads to a faster concentration lowering on

the negative domain and, accordingly, to redistribution of the flux of precipitating atoms. Thus, the mass supply on the sides of the boundary is different, the growth rate on the negative z-surface is higher by a factor of 1.5 than that on the positive surface (Fig.4.23).

As the system cooling rate increases, crystallization is limited by buildingin of atoms into the lattice (kinetic regime). But there is no essential difference in the growth rates on positively and negatively charged surfaces of singledomain substrates since the breaking effect of the less active positive surface leads to an increase of supersaturation and growth rate. So, the growth rates on single-domain substrates are determined by the cooling rate of the solutionmelt (Fig.4.23) (Madoyan and Khachaturyan 1987; Madoyan et al 1985).

Under epitaxy on a polydomain substrate, a high activity of the negative surface leads to tapering out of the positive domain. When the film thickness exceeds 30  $\mu$ m, the growing films are typically single-domain and negatively polarized.

Figure 4.18b demonstrates successive etching of films about 25 µm thick. The dashed line indicates the regions of negatively polarized surface, on which positive domains appear after etching.

#### 4.6.2 Domain configurations in films

Analysis of domain structure of epitaxial films has shown that the configuration and size of domains depend on substrate material and orientation and on the thickness of the precipitated layer.

It has been established above that the boundary of a domain grows through the substrate-film interface. Investigations showed that when film thickness does not exceed 20 µm, the domain configurations of the substrate are fully inherited by the film both under homo- and heteroepitaxy. Under heteroepitaxy on LiTaO,, the substrate is in paraphase and the lithium niobate film is crystallized in the ferroelectric phase. The final formation of domain configurations proceeds when the sample is cooled through the Curie point of the substrate  $(T_c = 660^{\circ}\text{C})$ . The polydomain structures of film and substrate were found to be perfectly identical. Experiencing no action of the electric field of the substrate, a precipitated film obviously acquires the domain configuration which is energetically more advantageous. Taking into account the connection between polarization direction and growth kinetics, we may assume that the film must be negatively polarized or polydomain with predominance of negative domains. When the sample is cooled below 660°C, the polarization occurring in the substrate leads to film repolarization. This process is promoted by a large number of intergrain boundaries resulted from growth of nuclei at the crystallization front. These intergrain boundaries are places of point defect and dislocation pile-up along which newly formed domain boundaries can run. Moreover, the polarization effect of the substrate is strengthened due to the presence in epitaxial structures of transition regions with smoothly varying 2 µm-thick composition LiNb, Ta O,. To obtain single-domain LiNbO,/LiTaO, films, it suffices to carry out cooling in an electric field that provides substrate polarization.

Figure 4.18c and d presents the domain structure of homoepitaxial film and substrate of lithium niobate. The film naturally repeats the domain structure

of the substrate. Tapering out of the positive domain is observed, as mentioned above, for thicknesses of 30  $\mu$ m. On single-domain substrates the film is also single-domain and the polarization direction of the film is identical to that of the substrate.

## 4.6.3 Microdomains in substrates and in epitaxial layers

A typical feature of the domain structure of lithium niobate is the presence of thin needle-shaped micro-domains with a polarization reverse to that of the principal domain (Bocharova et al 1985; Ohnishi and Yizuka 1975). Upon selective etching of a negative (0001) plane, needle-shaped micro-domains appear as triangle pyramids with side-face orientation ( $10\overline{12}$ ). The vertices of these pyramids are places where microdomains emerge on the film surface (Fig.4.18d). On the positive z plane, in such places there form small irregular-shaped (up to 1 µm) etching pits corresponding to needle-shaped micro-domains. The size of the pits remains unchanged as the etching time increases. On the ( $11\overline{20}$ ) plane they appear as thin 300 µm strips running along the z-axis (Fig.4.18f).

The influence of alien factors upon the domain structure was investigated. Mechanical pressing with a diamond needle (P = 5, 10, 15 g, the diamond needle point curvature ~10 µm) on the (0001) plane of LiNbO<sub>3</sub> leads to the appearance of microdomain clusters with the density in the centre up to  $10^6$  cm<sup>-2</sup> and areas increasing with increasing pressure.

Laser radiation produces the same effect upon LiNbO<sub>3</sub> crystals. The densities of microdomains formed under near-threshold radiation intensity  $(\lambda = 1.06 \ \mu m, J_{thresh} = 6.5 \ GW/cm^2)$  reached  $10^9 \ cm^{-2}$  in the centre and  $10^5 - 10^6 \ cm^{-2}$  at the cluster boundaries. The size of the cluster areas decreases slightly with decreasing intensity, and on the whole the cluster diameter is determined by the diameter of the focal spot. Under selective etching a typical pattern is observed in the irradiated area.

This phenomenon can be interpreted in different ways. Levanyuk and Osipov (1975) showed the possibility of a photoinduced reversal of spontaneous polarization in ferroelectrics with occurrence of a 'frozen' bulk charge. But this mechanism does not account for the indicated phenomenon since the resultant charge of irradiated region is zero. Moreover, the polarization reversal region is strictly limited to the irradiated area, whereas irradiation-induced microdomains are observed outside the irradiated area as well. The mechanism of microdomain nucleation due to elastic strains, which was proposed by (Abul-Fadl and Stefenakos 1977) and confirmed by experiments with mechanical treatment, seems to be most realistic. Because of a short irradiation time and a low heat transfer coefficient, irradiation with a high-intensity laser beam induced a thermal shock which is responsible for high local strains and microdomain nucleation.

In epitaxial LiNbO<sub>3</sub> films microdomains are only observed in (0001)-aligned layers. The microdomain density varies from sample to sample (from 10 to  $10^5$  cm<sup>-2</sup>), but as a rule exceeds the microdomain density on the substrate. Thus, microdomains grow from the substrate to the film and emerge in the layer on local inhomogeneities and strains.
# 4.6.4 Periodically inverted domain structures in LiTaO<sub>3</sub> and LiNbO<sub>3</sub> using proton exchange

SHG by quasi-phase matching (QPM) of the fundamental and harmonic modes can release high conversion efficiency and is versatile for generation of shorter wavelength, QPM is based on the moodulation of nonlinear polarization by periodically domain-inverted structure, and thus it is possible to phase match an arbitary wavelength by an appropriate choice of period of modulation. By using this technique, blue light generation in LiNbO<sub>3</sub> waveguide has been realized (Lim et al 1989; Webjorn et al 1989). This device offers the advantage of efficient conversion of laser radiation, because the waveguide alllows long interaction length with strong modal confinement. However, as photorefractive damage is known to occur in LiNbO<sub>3</sub> its potential at higher powers may be limited.

LiTaO<sub>3</sub> was reported to be highly resistive against photorefractive damage and it also has the advantages of large nonlinear susceptibilities, and short wavelength transparency from 280 nm.

Several methods have been used to fabricate periodic domain inversion in  $LiNbO_3$  and  $LiTaO_3$ . Ti in-diffusion (Miyazawa 1979) or Li out-diffusion (Webjorn et al 1989) near the Curie temperature are well-known techniques to reverse the polarization in  $LiNbO_3$ , but the shape of the inverted domain is not rectangular. Electron beam bombardment (Keys et al 1991; Yomada and Kishima 1991; Ito et al 1991) has also been employed to make 'well'-shaped inverted domains, but it is difficult to fabricate short period patterns. Periodically poled structures in  $LiNbO_3$  can be realized through selective proton exchange (PE) followed by heat treatment near the Curie temperature (Mizuuchi et al 1991). A few micron deep semicircular-shaped domains with a first-order period has been fabricated using proton exchange and a quick heat treatment near the Curie temperature, generating 15 mW of blue light (Mizuuchi and Yamamoto 1991).

Makio et al (1992) reported on the formation of long (> 40  $\mu$ m), 'spikelike' inverted domains triggered by proton exchange with one-directional heating. These domains have straight walls and the same period as the proton exchanged grid, which are favourable conditions to achieve first-order QPM devices.

Authors described their fabrication process as follows; a 30 nm thick Ta mask was deposited on the  $c^*$  or  $c^-$  face of 0.5 mm thick LiTaO<sub>3</sub> or LiNbO<sub>3</sub> substrates using an electron beam deposition method. The first-order periodic pattern with a 3.2 µm period was fabricated on the Ta mask by conventional photolithography and CF<sub>4</sub> dry etching, forming windows to allow proton exchange. A small amount of pyrophosphoric acid was dropped on the Ta mask side of the substrate, which was then placed on an already heated (230–260°C) hot plate for several minutes, namely, one-directional heating from the rear surface of the substrate. After removal of the Ta mask, some specimens were cut into strips, polished, and etched with HF and HNO<sub>3</sub> to examine the proton exchange and the domain inversion.

They found that the polarization flipped during the proton exchange process, far below the Curie temperature. Figure 4.24 shows a cross-sectional view of a LiNbO<sub>3</sub> sample, proton exchanged at 260°C for 30min and without any post-PE annealing. Although the proton-exchanged layer is less than 1  $\mu$ m thick, inverted domains stemmed and stretched from the proton-exchanged region deep



Fig.4.24 Cross sectional micrograph of the periodically inverted spikeline domains fabricated on LiNbO<sub>3</sub> (Makio et al, 1992).

inside the substrate from more than 40  $\mu$ m. The domains look like spikes, with thin and sharp ends.

The spikelike domains can be formed on both  $c^+$  and  $c^-$  faces of LiNbO<sub>3</sub>, unlike other types of domains. Spike-like domains could be successfully fabricated on LiNbO<sub>3</sub> as well, in spite of its high Curie temperature.

These spikelike domains seen to be similar to the so-called 'needle-shaped' microdomains (Ohnishi and Iizuka, 1975) which are common in poled crystals as residual antidomains, usually being isolated and randomly distributed. The inversion mechanism is not clear, but the periodic stress due to proton exchange is likely to trigger the growth of the antidomains, which is accelerated by the thermal gradient caused by one-directional heating.

The thermal stability of the spikelike domains was examined during post-PE annealing. Heat treatment was carried out at 525°C for up to 2 min. Though the data are spread out over a wide range, they indicate the tendency for the domains to become shorter and finally vanish as the heat treatment time increases. At lower temperature, though, they survive longer treatment time. From the practical point of view, it is essential for the domains to survive the 350–





380°C heat cycle in order to fabricate waveguides on the substrate by the annealed proton exchange method.

The dependence of the inverted depth on the condition of proton exchange and heat treatment temperature was examined for the -c face substrate with a Ta mask of 20  $\mu$ m period. Only the -c face does produce inversion. The reason why inversion cannot be observed in +c face is not clear, and investigation of the formation process of domain inversion is being conducted to resolve the inversion mechanism. Figure 4.25 shows the inversion depth as a function of heat treatment temperature for a heat treatment time of 10 min. The inverted region became deeper with increasing temperature, but above 610°C a periodic structure cannot be observed, because it is above the  $T_{c}$  of pure LiNbO,. The figure also shows that the threshold temperature to cause domain inversion becomes lower with increasing proton-exchange time and saturates at a lower limit of 450°C. This saturation perhaps indicates the T of protonexchanged LiNbO,. Furthermore, the large difference between this lower limit and the  $T_{c}$  of pure LiNbO, shows the large extent to which the Li ions are exchanged by protons for the case of pyrophosphoric acid. By knowing this threshold temperature for domain reversal, Mizuuchi et al (1991) were able to carry out other processes, such as annealing, at any lower temperature without disturbing the domain-inverted regions.

### 4.6.5 Waveguide periodically poled by applying an external field

Yamada, et al, (1993) reported the fabrication of a periodically inverted domain structure in a  $LiNbO_3$  substrate by applying an external electric field, which yields an efficient first-order QPM-SHG device.

It was said that the domain inversion of  $LiNbO_3$  is difficult at room temperature.  $LiNbO_3$  is usually broken without domain inversion when an external field is applied at room temperature. The external field for domain inversion of  $LiNbO_3$  is close to that of the electron avalanche, so the  $LiNbO_3$  substrate is broken without its spontaneous polarization being inverted with the application of an external field.

Yamada et al, (1993) fabricated the periodic domain structure for first-order QPM-SHG devices in LiNbO<sub>3</sub> as follows. Figure 4.26 shows how external field is applied. They also used a z-cut LiNbO<sub>3</sub> crystal as the substrate. An Al thin film 200 nm thick was deposited on the positive and negative c-face of the



Fig.4.26 Schematic of applying voltage for periodically domain inversion (Yamada et al 1993).

LiNbO<sub>3</sub> substrate. The Al thin film on the positive *c*-face was periodically patterned with a 2.8  $\mu$ m period by wet etching. Electrodes were then fabricated on both *c*-faces.

Next, at room temperature, a negative pulse with a width of 100  $\mu$ s and a voltage of 24 kV/mm (the electric coercive force of LiNbO<sub>3</sub> is about 20 kV/mm) was applied on a plane electrode on the negative *c*-face and a periodic electrode on the positive *c*-face was grounded. After applying the voltage, the Al electrode was removed in an aqueous solution of NaOH.

The reason the periodic electrodes should be fabricated on the positive c-face is that the inverted domain nuclei appear on the positive c-face. The reason why pulsed external field should be applied can be understood if the process of domain growth is observed. When there exists a dependence of the domain growth on the time the external field is applied, first the domains grow along the c-axis, then grow under the electrodes. If the external field is applied too long, the domains spread out from under the electrodes and come into contact with each other. The external field must be shut off before the domains grow out form under the electrodes.

Using the above procedure, a z-cut LiNbO<sub>3</sub> substrate with a 2.8  $\mu$ m period laminar domain structure was obtained, which is similar to that illustrated in Fig.4.24. From the figure it is seen that the domains boundaries are parallel to the *c*-axis. This periodically inverted domain structure is ideal for first-order QPM-SHG devices.

## 4.6.6 Domain inversion in LiNbO<sub>3</sub> using direct electron-beam writing

Direct electron-beam writing was achieved using a scanning electron microscope (SEM) converted for this purpose (Nutt et al, 1992). Beam currents used were in the range of 3-7 nA and the beam voltage ranged between 20 and 30 kV. The electron-beam spot size was 0.5 µm. Patterns were written with saturated filament current at beam voltages of 20, 25, and 30 kV. The best grating resolution was obtained at 30 kV. Although surface cracking was observed at high voltages (30 kV) and at lower scan velocities (235  $\mu$ m/s) with a beam current of 7 nA, surface cracking was avoided by reducing the beam current whilst keeping the beam voltage high. Samples used in this study were 500 µm thick z-cut LiNbO<sub>3</sub>. The domain inversion process is controlled by the electric field created by electron bombardment. Hence, a 30 nm film of Ta metal was sputtered on the  $c^*$  face, which acted as a ground electrode. Samples were scanned on the  $c^$ face where the electron beam deposited a  $v \times e$  charge on the surface. The scan velocities were between 200 and 800 µm/s. Typical sheet resisitance of the metal film was 200  $\Omega/cm^2$ . Domain inversion was revealed by etching the LiNbO, sample in a solution of two parts HNO, and one part HF at 90°C for Smin since the etch rate for the  $c^-$  face is much higher than that of the  $c^+$  face.

To understand the domain inversion mechanism under direct electron-beam writing, metal lines were deposited on the  $c^+$  face that were 200 µm wide and spaced 280 µm apart. This gave a periodic ground plane. Single lines using different beam scan speeds (500, 250, 166.7, 71.4, and 33.3 µm/s with 30 kW beam voltage and 7 nA beam current) were written perpendicular to the metal lines on the  $c^-$  face. These results show that domain inversion can be achieved

between metal lines where there is no direct ground and, secondly, domain spreading occurs at the metal edges. These results imply that domain inversion is related to the electric field density, which is higher at the metal edges. No significant domain spreading was observed on the  $c^{+}$  face.

The width of the domain-inverted region on the  $c^*$  face was about twice the domain width on the  $c^-$  face. This spreading limits the fabrication of high-resolution gratings on the  $c^*$  face.

Surprisingly, domain inversion through the thickness of the sample was observed on LiNbO<sub>3</sub>, which had no metal film grounding whatsoever on the  $c^+$  face. However, high-resolution gratings on the  $c^+$  face showed distortion. This is possibly due to charging and discharging effects observed during the writing process. This implies that metal grounding is neccessary for high-resolution gratings although large-period gratings can still be written without direct grounding. More surface cracking was observed with samples without metal grounding.

Electron bombardment with focused beams (0.5 µm in diameter) on the  $c^{-1}$  face of LiNbO<sub>3</sub> with the  $c^{+}$  face as grounded can produce high electric fields near the surface. The distribution of the normal component of electric field, E(x), due to a point charge in a uniform dielectric medium near a conducting plane is given by (Becker, 1982)

$$E(x) = \frac{q}{4\pi\varepsilon} \left( \frac{a-x}{r^3} + \frac{a-x}{{r'}^3} \right)$$
(4.9)

where

$$r^2 = (a-x)^2 + y^2 \tag{4.10}$$

$$r'^2 = (a - x)^2 + y^2 \tag{4.11}$$

where x and y are the perpendicular distances of a point charge from the conducting plane as shown in Fig.4.27. The charge is q and  $\varepsilon$  is the dielectric constant of the medium. As expected, a high electric field is produced near



**Fig.4.27** Normalized electric field log  $(4\pi\epsilon a^2 E(x)/q)$  contours due to the point charge *q* near the conducting surface (Nutt et al 1992).

the point charge. Beam currents used in this study were of the order of a few nanoamperes and the typical scan velocity used was 300  $\mu$ m/s. The beam diameter was 0.5  $\mu$ m. This corresponds to a dwell time of about 1.5 ms per 0.5  $\mu$ m travel. Hence, the charge deposited is about 10<sup>-10</sup> C in 0.5  $\mu$ m. If we take this as a point charge q, then the field intensity at a depth of 5  $\mu$ m is about 10<sup>8</sup> V/m. This is in the vicinity of the breakdown voltage for dielectrics. Hence, very high-field intensities are produced near the point charge. The field intensity near the point charge is similar in magnitude to that of the polarization fields in the ferroelectric material. This field can produce reversed domains near the surface.

The role of electron energy in the domain-inversion process requires further investigation. Haycock and Townsend (1986) proposed a mechanism for domain inversion in LiNbO<sub>3</sub> and LiTaO<sub>3</sub> where excitation of the crystal lattice by an energetic beam of electrons is required while an external field is applied. In the experiments carried out by Nutt et al (1992), energetic electrons can provide excitation of the crystal lattice and at the same time an electric field is created due to a ground electrode on the  $c^+$  face. It is also possible that low-energy electrons (<10 keV) may not produce domain inversion due to surface conduction, while higher-energy electrons penetrate deeper in the crystal.

The domain-inversion process starts with nucleation of domains, with their polarization P orientation antiparallel to the original polarization field  $P_s$  at the surface. There is rapid growth of these nuclei into long domains through the thickness of the crystal. Finally, there is sidewise growth or expansion of domains. The initial shape of the domain may follow the field profile due to the point charge. There will be a critical field for nucleation. The inverted domains induce a depolarizing field that aids the external field in the further growth of inverted regions along the  $c^*$  axis of the crystal. So, the inverted domain shape will be essentially parallel to the c axis of the crystal as it grows further. The domain width on the  $c^*$  and  $c^-$  faces of the LiNbO<sub>3</sub> crystal increased as the scan speed decreased; this suggests that there is a field limit, which, when exceeded, allows domain reversal to occur spontaneously. When smaller-period metal lines (10 µm) were used, no lateral domain spreading was observed on the  $c^*$  face of the LiNbO<sub>3</sub> crystal. The 10 µm period grating obviously acted exactly like a continuous ground. Therefore, the sample thickness plays a part in the reversal mechanism because of the drop in field intensity across the sample.

# 4.7 Annealing-induced variation of the phase composition and crystalline structure of the lithium niobate crystal surface 4.7.1 Annealing-induced variation of the crystalline structure of the lithium niobate crystal surface

Electron diffraction studies have shown that the surface of mechanically polished x-, y- and z-cuts of lithium niobate substrates is covered with a layer with a damaged crystalline structure, which is formed due to brittle failure of the material in the course of mechanical treatment. The electron diffraction patterns containing only the diffusion background without any reflexes suggest amorphity of the thin near-surface layer of the crystal (Bocharova 1986).

To determine the damage depth in mechanically polished samples, the dam-

aged layers were etched one by one in a mixture of acids HF + HNO<sub>3</sub> at room temperature with simultaneous control of the surface structure. A portion of the surface was covered with picein which preserved the surface from the etching agent, and the height of the step was indicative of the etched layer thickness. The degree of structure perfection of the etched surface was controlled by electron diffractometry and the height of the step was determined using an optical interference microscope. The thickness of the amorphous layer varied within the range 5 nm  $\leq d \leq 30$  nm, was dependent on the quality of polishing and remained unaltered from sample to sample.

Between the amorphous layer and the perfect crystal there lies a damaged area. The depth of the damaged layer in lithium niobate can be estimated by ellipsometry and repeated total internal reflection. The ellipsometric measurements carried out on the y-cut lithium niobate have shown that the effective thickness of a damaged surface layer depends strongly on polishing quality and ranges between 35 and 160 nm (Yakovlev 1985). The method of repeated total internal reflection was applied to reveal an increase of light absorption in a 200 nm surface layer of lithium niobate, which is explained by a higher defect density in this layer (Zverev et al 1977).

Electron diffractometric and optical data suggest that near the lithium niobate surface there exists a thin strongly damaged amorphous layer (~30 nm) and a deeper-lying layer (~200 nm) of strained material. The real structure of lithium niobate crystals contains dislocations, block boundaries, microdomains and other types of defects. According to the results of selective chemical etching, the dislocation density was  $10^4-10^5$  cm<sup>-2</sup> and the linear dislocation density was  $~3\times10^4$  cm<sup>-2</sup>.

During annealing of mechanically polished crystals the following two processes proceed:

- damaged layer recrystallization,

- phase composition variation,

that can be recorded by high-energy electron diffraction by reflection. These processes are simultaneous and depend essentially on the annealing temperature.

Recrystallization in solid bodies consists of a change in their crystalline structure and removal of structural defects caused by preliminary mechanical treatment. The structure of matter is ordered by the nucleation and growth of grains as well as by enlargement of some grains at the expense of other grains. This procedure results in relief of internal micro- and macrostrains. The assembled (the assembled recrystallization) recrystallization may equally occur in strained and unstrained materials and typically follows the damaged layer recrystallization.

As shown by electron diffraction analysis, beginning with  $T = 300^{\circ}$ C recrystallization of the damaged layer induced by annealing proceeds at a rather high speed. Figure 4.28a-d presents a series of electron diffraction patterns of lithium niobate samples aligned parallel to the crystallographic (0001) plane and annealed at different temperatures during equal time intervals ( $\tau = 4$  h). Reflections from the samples, annealed at  $T = 300^{\circ}$ C, in the form of arcs and rings arranged concentrically near the primary beam (Fig.4.28a) characterize the change in the structure of the upper substrate layers. Moreover, the electron diffraction patterns

206





**Fig.4.28** Electron diffraction patterns of the base facet (0001) of lithium niobate versus annealing temperature (annealing time  $\tau = 4$  h): a) 300°C, b) 650°C, c) 750°C, d) 950°C (Bocharova 1986).

exhibit weak Kikuchi lines, far from the primary beam, formed deep inside the crystal. The presence of arc- and ring-shaped reflections is indicative of ordering of the surface-layer structure and of formation of small crystalline aggregates in this layer. The estimate of the size l of these crystallites obtained from the half width of reflexes B gives the range of 10–50 nm. The crystallites formed at  $T = 300^{\circ}$ C have basically random position, but show a tendency for texture formation.

An increase of annealing temperature from 300°C to 700°C causes a decrease of azimuthal disorientation and segregation of crystallites with preferential orientation parallel to a lithium niobate substrate surface.

The electron diffraction patterns of samples annealed at  $T \ge 650^{\circ}$ C (Fig.4.28b and c) show, together with arcs from the texture, also a system of point reflexes formed by a mosaic single crystal. With a further increase of temperature from 700°C to 900°C the reflections from the texture disappear, and the electron diffraction patterns only contain a net of point reflexes, which testifies to the presence of similarly aligned grains. Annealing of lithium niobate samples at  $T = 950^{\circ}$ C for 4 h suffices for a complete restoration of crystallinity of the near-surface layer. The electron diffraction patterns of such samples exhibit

Kikuchi lines (Fig.4.28d). The variation of the crystalline structure of lithium niobate facets  $(01\overline{1}0)$  and  $(2\overline{1}\overline{1}0)$  depending on the annealing temperature proceeds in a similar manner.

Thus, recrystallization of the damaged near-surface layer of crystals proceeds gradually in the entire temperature range beginning with 300°C. The surface structure changes from amorphous through texture (T = 300-650°C) and mosaic (T = 650-900°C) up to single-crystal. The final restoration of a single-crystal state of the near-surface layer is achieved at a temperature T > 900°C.

A specific feature of lithium niobate recrystallization is that within a certain temperature range it proceeds in the existence region of a two-phase system.

## 4.7.2 Annealing-induced variation of the phase composition of the lithium niobate crystal surface

Diffraction analysis of specimens annealed between 300 and 900°C reveals phase transformation proceeding on the surface of lithium niobate crystals simultaneously with recrystallization. This is also confirmed by the electron diffraction patterns showing a simultaneous diffraction from  $\text{LiNbO}_3$  and  $\text{LiNb}_3O_8$ , by which one can trace out annealing-induced variation of the crystalline structure and of the phase composition of substrate surfaces of different orientations.

Variations of the phase composition and crystalline structure of the lithium niobate surface are observed already at  $T = 300^{\circ}$ C. The system of ring- and arc-shaped reflections observed in electron diffraction patterns (Fig.4.28a) is induced in a monoclinic cell with parameters a = 15.26 Å, b = 5.033 Å, c = 7.46 Å,  $\beta = 107.33$  grad corresponding to lithium triniobate which belongs to the space group  $P 2_1/a$  (Lundberg 1971). Due to closeness of the interplanar distances of LiNb<sub>3</sub>O<sub>8</sub> and LiNbO<sub>3</sub> and reflex smearing, part of reflections from the matrix and phase are not separates, but a permanent strengthening of individual reflexes testifies to the presence of a two-phase system on the sample surface.

Reflexes from the monoclinic phase of lithium triniobate and from trigonal lithium niobate are seen more clearly in electron diffraction patterns as the annealing temperature increases. Within the temperature range  $T = 300-700^{\circ}$ C the newly formed crystals of the second phase get larger and acquire epitaxial orientation relative to the substrate. Point reflexes appear (Fig.4.28b), and at  $T = 700-900^{\circ}$ C two phases are formed connected with each other by certain orientation relations (Fig.4.28c). This suggests solid-phase epitaxial growth of a monoclinic phase on the lithium niobate surface.

The occurrence of the second phase is visualized as a typical thin dull coating on the substrate surface and can also be identified by light scattering in places of phase nucleation. The phase change  $LiNbO_3 \rightarrow LiNb_3O_8$  proceeds basically in the near-surface layer of a lithium niobate crystal damaged in the course of mechanical treatment. After the surface layer had been removed by etching in the mixture HF + HNO<sub>3</sub>, the electron diffraction patterns showed reflections only from lithium niobate, which is indicative of spatial limitation of nucleation and growth of the LiNb<sub>3</sub>O<sub>8</sub> phase. The rate of lithium triniobate nucleation on the crystal surface is rather high: the monoclinic phase appears on electron diffraction patterns after a 10 min stay of the substrate in the hot region at  $T = 750^{\circ}C$ .



Fig.4.29 Phase diagram of the  $Li_2O-Nb_2O_5$  system (Holman 1978).

Optical inhomogeneity of the bulk crystal before and after annealing in the two-phase temperature region was determined by comparing the Rayleigh  $I_{\rm R}$  and stimulated Brillouin  $I_{\rm SB}$  components of scattered light.

Under annealing at a temperature T = 750°C for 5-20 h, the number of scattering centres in the bulk crystal remains unchanged, whereas a layer of lithium triniobate phase forms on the crystal surface. A considerable increase in the number of scattering centres in the bulk crystal was only observed after annealing at the same temperature for 40 h.

An increase of the nucleation rate on a strongly damaged surface as compared with the crystal bulk is due to the lowering of the nucleation barrier and the higher diffusion rate of components in the amorphous layer. This conclusion is confirmed by the fact that the lithium diffusion activation energy in a single crystal, equal to  $68 \pm 1.2$  kcal/mol falls down to  $14.28 \pm 1.6$  kcal/ mol (Carruthers et al 1974; Jetschke and Hehl 1985).

Electron diffraction analysis shows that the variation of the phase composition of the lithium niobate surface due to monoclinic phase nucleation is a reversible process, and at T > 900°C the phase change LiNb<sub>3</sub>O<sub>8</sub> $\rightarrow$ LiNbO<sub>3</sub> is observed. The boundary of the existence region of two phases for crystals of congruent composition lies near T = 900°C, which agrees with the phase diagram. Above this temperature, only LiNbO<sub>3</sub> is present on the sample surface, and reflections from LiNb<sub>3</sub>O<sub>8</sub> disappear from electron diffraction patterns (Fig.4.28d). The phase change LiNbO<sub>3</sub>  $\leftrightarrow$ LiNb<sub>3</sub>O<sub>8</sub> on the surface of titanium-doped lithium niobate crystals proceeds in a similar manner.

We note that at  $T < 900^{\circ}$ C no monoclinic phase was observed on the substrate surface if annealing was carried out in a lithium-enriched atmosphere, that is, the presence of Li vapours in annealing and their absorption on the surface inhibits phase nucleation. In its nature, the indicated transition LiNbO<sub>3</sub> $\leftrightarrow$ LiNb<sub>3</sub>O<sub>8</sub> refers to solid-phase order-disorder type transitions occurring in solid solutions. The nucleation of the monoclinic phase LiNbO<sub>3</sub> corresponds to dissolving of excess solid-state niobium. Lithium niobate crystals of congruent composition are metastable at room temperature and contain point defects, due to lithium deficiency, in a concentration exceeding the equilibrium one. According to the phase diagram (Fig.4.29), at a temperature below 900°C, LiNbO<sub>3</sub> and LiNb<sub>3</sub>O<sub>8</sub> can exist simultaneously. The narrowing of the homogeneity region with lowering temperature leads to LiNb<sub>3</sub>O<sub>8</sub> phase segregation accompanying annealing of metastable nonstoichiometric lithium niobate crystals within the temperature range 300-900°C, which brings the system to a state energetically more advantageous and lowers the concentration of point defects in the crystals. The temperature range T > 900°C corresponds to the one-phase lithium niobate system and has a wide homogeneity region (up to 6 mol/ % Li<sub>2</sub>O) within which the existence of lithium niobate with widely different composition is energetically admissible. At annealing temperatures exceeding 900°C, the change LiNb<sub>3</sub>O<sub>8</sub>  $\rightarrow$  LiNbO<sub>3</sub> is observed, the monoclinic phase disappears and the sample surface becomes single-phase.

The physical and chemical properties of light guiding ferroelectric films are tabulated in Table 4.5.

Temperature variations affect not only the structure and phase composition, but also the surface morphology which is determined by crystallographic orientation of the sample surface.

The shapes of growing lithium triniobate crystals and the specificities of micro-crystal positions on the substrate surface in the monoclinic phase are best of all pronounced in the temperature range of 700-900°C that corresponds to an oriented growth of LiNb, Oe. The sizes and density of islands of the second phase depend on the annealing time and on the degree of damage of the near-surface sample structure. The thickness of the LiNb,O. layer was estimated by the height of the growth patterns on electron-microscopic pictures and ellipsometrically. After annealing at  $T = 750^{\circ}$ C for 4 h, the growth patterns of LiNb<sub>2</sub>O<sub>2</sub> ranged on the average within 150-500 nm, and the ellipsometrically measured thickness of the island layer of the phase made up 15-40 nm. The island density N of the phase varied from sample to sample within a range of 10<sup>7</sup> to 10<sup>10</sup> cm<sup>-2</sup>, the distribution of islands over the surface of one and the same island being nonuniform. Phase segregation are concentrated, in particular, in the vicinity of scratches resulting from sample polishing. The island density in such places makes up 10<sup>10</sup>-10<sup>11</sup> cm<sup>-2</sup>.

According to electron diffraction data, lithium triniobate is oriented relative to the (0001) substrate as follows:  $(\bar{3}01) [010]_{phases} \parallel (0001) \langle 2\bar{1}\bar{1}0 \rangle_{matrices}$ . The shapes of growing LiNb<sub>3</sub>O<sub>8</sub> crystals on the base facet of lithium niobate are basically represented by pinacoidal  $\{\bar{h}0l\}$  and  $\{h00\}$  type planes elongated along the [010] direction (Fig.4.30a). It should be noted that the pinacoid ( $\bar{3}01$ ) parallel to the substrate surface is not always present in the habitus of microcrystals of the new phase, and is occasionally tapered out with its other facets positioned at an angle to the surface. In Fig.4.30a phase islands with such facets are shown by the arrows 2; the arrow 1 indicates a LiNb<sub>3</sub>O<sub>8</sub> microcrystal whose habitus contains the ( $\bar{3}01$ ) facet. This is indicative of the difference in growth conditions of islands on one and the same substrate, which

	Crystal	Solvent	Mel poir	Melting Lattice parameters Refractive point					efractive dex	Electro-optic coefficient		
	Films-substrate		Т,	°C	а,	Å	с,	Å	$n_o = \lambda$	n, 0.63 μm	$r_{33}$ 10 <sup>-12</sup>	r <sub>13</sub> m/V
1	LiNbO,		1253	i.	5.1	48	13.8	62	2.289	2.201	30.8	8.6
2	LiNbO, - LiNbO,	LiVO <sub>3</sub>			5.1	42						
3	LiTaO,		1650	)	5.1	52	13.7	85	2.177	2.183	35.8	7.9
4	LiNbO <sub>3</sub> - LiTaO <sub>3</sub>	LiVO,					13.8	51				
5	LiNbO <sub>3</sub> - LiTaO <sub>3</sub>	LiVO <sub>3</sub>					13.8	5	2.288(	4) 2.191(4	4)	
6	LiNbO <sub>3</sub> - LiTaO <sub>3</sub>								2.200	2.184	12	2.3
7	LiNbO <sub>3</sub> - LiTaO <sub>3</sub>								2.29	2.20	28.5	
8	LiNbO3:Li+ - LiTaO3	Li2WO			5.1	43						
9	LiNbO3:Nb3+ - LiTaO	K,WO4			5.1	53						
10	Li <sub>1-x</sub> Na <sub>x</sub> NbO <sub>3</sub> - LiNbO	LiVO,			5.1	54						
11	$Li_{1-x}Co_xNb_{1-x}Zr_xO_3 - LiNbO_3$	LiVO <sub>3</sub>			5.1	44						
12	LiNbO,:Ag* - LiNbO,	LiVO,								2.2361		
13	LiTa Nb O, - LiTaO	LiVO,					13.8	0				
14	KNbO,		1039	1								
15	Sapphyre (Al,O,)		2030	i.	4.7	58	12.9	91	1.766	1.758		
16	KNbO <sub>3</sub> - Al <sub>2</sub> O <sub>3</sub>	KVO,										
17	LiNbO <sub>3</sub> :Cr <sup>3+</sup> (Fe <sup>3+</sup> , Cu <sup>2+</sup> - LiNbO <sub>3</sub>	LiVO <sub>3</sub>										
18	K289Li, 55Nb511O15		1050	1	12	.58	4.01		2.294(	8) 2.156(8	3)	
19	K, Bi, Nb, O,		1312	<u>}</u>	17	.85	7.84		2.237	2.253		
20	$\begin{array}{l}K_{2,39}Li_{1,55}Nb_{5,11}O_{15} - \\ - K_{1,5}Bi_{1,0}Nb_{5,1}O_{15}\end{array}$				12	.53	3.98					

Table 4.5 Physico-chemical parameters of crystals and films of oxide Ferroelectrics (Ivleva, Kuzminov, 1985)

Comments: 1. Prokhorov, Kuz'minov, 1990; 2. Baudrant et al, 1975; 3. Kuz'minov, 1975; 4. Miyasawa, 1973; 5. Miyasawa et al, 1975; 6. Fukunishi et al, 1974; 7. Tien et al, 1974; 8. Baudrant et al, 1975, Ballman et al, 1975; 9. Baudrant et al, 1975, Ballman et al, 1975; 10. Neurgaonkar 1981; 11. Neurgaonkar et al, 1979; 12. Baudrant et al, 1975; 13. Kosmina et al, 1983, Tien et al, 1974; 14. Prokorov, Kuz'minov, 1990; 15. Schaskolskaya 1982; 16. Khachaturyan et al, 1984; 17. Baudrant et al, 1975; 18,19,20. Adachi et al, 1979.

is evidently due to inhomogeneity of lithium niobate composition and inhomogeneity of strains in the surface layer of the crystal.

According to the symmetry of the base facet of lithium niobate,  $LiNb_3O_8$  micro-crystals occupy three equivalent positions on the substrate, making an angle of 120° (Fig.4.30b), which form dendrite-type adhesions (joints) shown in Fig.4.30a.



**Fig.4.30** (a) Surface morphology of the (0001) facet of lithium niobate after annealing at  $T = 750^{\circ}$ C for 4 h. (b) Positions of lithium triniobate islets on the (0001) facet of lithium niobate, (Bocharova 1986).

## **5** Physical Properties of Waveguide Layers

Practical use of various types of thin-film ferroelectric structures needs a detailed study of the physico-chemical properties of the substances involved, as well as technological perfection of obtaining these substances. This will permit creation of materials with the required physical properties optimum for a particular application.

In this chapter we describe the investigations of waveguiding, nonlinear optic and ferroelectric properties of epitaxial films of lithium niobate and lithium tantalate and their solid solutions. The dielectric and pyroelectric properties, and the temperature dependence of thermoelectric coefficients are presented. We also consider the optical properties of the thin-film structures: surface resistance and the effect of laser radiation, the refractive indices and the mode structure of films, light extinction upon waveguide propagation.

# 5.1 Optical properties of lithium niobate and tantalate single crystals

Lithium meta-niobate single crystals are uniaxial negative  $(n_o - n_e)$ , transparent from about 0.4 to 5 µm (Fig.5.1) (Boyd et al 1964). The nature of their transmission spectra depends on the conditions of heat treatment and polarization of crystals. Crystals prepared with no direct current maintained through them during the growth are clear and colourless.

The dispersion dependences of  $n_o$  and  $n_e$  over a wide frequency range for lithium niobate crystals grown from congruent melt compositions are collected in Table 5.1.

The temperature dependence of refractive indices was measured using a lithium niobate prism with the optical axis parallel to the two major facets. The prism was arranged in a small furnace on a spectrometer stage. The refractive indices were taken at eight temperatures between 19 and 374°C for eight lines of the helium metal vapour lamp at 447.1, 471.3, 492.2, 501.6, 587.6, 667.8, and 707.6 nm.

λ, nm	Laser	Stoichi (T =	ometric 25°C)	Congruently melting $(T = 24.5^{\circ}C)$			
		n	n,	n <sub>o</sub>	n <sub>e</sub>		
441.6	He-Cd	2.3906	2.2841	2.3875	2.2887		
457.9	Ar	2.3756	2.2715	2.3725	2.2760		
465.8	Ar	2.3697	2.2664	2,3653	2.2699		
472.7	Ar	2.3646	2.2620	3.3597	2.2652		
476.5	Ar	2.3618	2.2596	2.3568	2.2627		
488.0	Ar	2.3533	2.2523	2.3480	2.2561		
496.5	Ar	2.3470	2.2468	2.3434	2.2514		
501.7	Ar	2.3535	2.2439	2.3401	2.2486		
514.5	Ar	2.3370	2.2387	2.3326	2.2422		
530.0	Nd	2.3290	2.2323	2.3247	2.2355		
632.8	He-Ne	2.2910	2.2005	2.2866	2.2028		
693.4	Ruby	2.2770	2.1886	2.2726	2.1909		
840.0	GaAs	2.2554	2.1703	2,2507	2.1719		
1060.0	Nd	2.2372	2.1550	2.2323	2.1561		
1150.0	He–Ne	2.2320	2.1506	2.2225	2.1519		

Table 5.1 Refractive indices of lithium niobate crystals (Weiss and Gaylord 1985)



Fig.5.1 The dispersion spectrum of lithium niobate.

An analysis of the experimental data has yielded two equations for the temperature dependence giving the refractive indices between 400 and 4000 nm:

$$n_o^2 = 4.9130 + \frac{1.173 \times 10^{-5} + 1.65 \times 10^{-2} T^2}{\lambda^2 - (2.12 \times 10^2 + 2.7 \times 10^{-5} T^2)^2} + 2.78 \times 10^{-8} \lambda^2$$
(5.1)

$$n_e^2 = 4.5567 + 2.605 \times 10^{-7} T + \frac{0.97 \times 10^{-5} + 2.70 \times 10^{-2} T^2}{\lambda^2 - (2.01 \times 10^2 + 5.4 \times 10^{-5} T^2)^2}$$
(5.2)

 $-2.24\times10^{-8}\,\lambda^2$ 

where T is the temperature, K,  $\lambda$  is the wavelength, nm.

	y = 0.81		y = 0.92		y =	0.97	y = 1.00		
λ, Α	n	n,	n	n,	n <sub>o</sub>	n,	n <sub>o</sub>	n,	
5893	2.2057	2.1986	2.1984	2.1946	2.1902	2.1933	2.1862	2.1910	
6328	2.1954	2.1888	2.1888	2.1853	2.1800	2.1829	2.1766	2.1815	
8000	2.1702	2.1638	2.1643	2.1604	2.1561	2.1589	2.1531	2.1579	
8500	2.1666	2.1606	2.1598	2.1559	2.1516	2.1545	2.1484	2.1529	
9000	2.1615	2.1553	2.1557	2.1519	2.1478	2.1507	2.1446	2.1491	
10600	2.1517	2.1457	2.1460	2.1422	2.1385	2.1413	2.1351	2.1396	

**Table 5.2** Refractive indices,  $n_o$  and  $n_o$ , for mixed LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> crystals at 20 ± 0.5<sup>o</sup>C (according to Shimura 1977)

The standard deviation of 112 experimentally determined values of the refractive indices from those calculated according to formulae (5.1) and (5.2) is  $2.2 \times 10^{-4}$ .

The value of the negative birefringence decreases with a rising temperature and drops off to zero at 882°C for  $\lambda = 632.8$  nm and at 888°C for  $\lambda = 1152.3$  nm.

The change in  $(n_o - n_e)$  with temperature, as predicted by equations (5.1) and (5.2) differs by ±0.0010 from the experimental data for about 600°C. Above this temperature higher-order terms come into play. In the lithium niobate crystal, it is the extraordinary refractive index,  $n_e$ , that depends significantly on the melt composition ratio, while the ordinary refractive index,  $n_o$ , remains virtually at a constant level (Fig.5.2) (Bergman et al 1968). The composition of the melt and, hence, the composition of crystals grown therefrom may vary throughout the growth process. An isomorphic dopant of niobium is tantalum. The starting material may contain a certain amount of tantalum oxide. Sometimes, to reduce the Curie temperature and natural birefringence, mixed LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> crystals are grown. Such crystals have different refractive indices and their dispersions. Table 5.2 is a compilation of tantalum in mixed lithium niobatetantalate crystals. For practical applications refractive indices for various wavelengths are calculated according to the Sellmeier relation (Di Domenico and Wemple 1969):

$$n^{2}(\lambda) - 1 = S_{0}\lambda_{0}^{2} / \left[ 1 - (\lambda_{0} / \lambda)^{2} \right]$$
(5.3)

where  $\lambda_0$  is the average oscillator position and  $S_0$  is the average oscillator strength. The  $\lambda_0$  and  $S_0$ -values for various tantalum contents are listed in Table 5.3. The refractive indices  $n_0$  and  $n_e$  and the birefringence calculated using the relation are given in Figs.5.3 and 5.4, respectively.

## 5.2 Optical waveguide modes in single-crystal films

The optical properties of planar waveguides can be arbitrarily divided into



**Fig.5.2** Refractive indices  $n_{o}$  (upper curve) and  $n_{o}$  (lower curve) of lithium niobate versus molar ratio  $\text{Li}_2\text{O}/\text{Nb}_2\text{O}_5$  in the melt (Bergman et al 1968).

**Fig.5.3** (right) Refractive indices  $n_o$  (full circles) and  $n_o$  (open circles) versus Ta content in mixed LiNb<sub>1-v</sub>Ta<sub>2</sub>O<sub>3</sub> crystals for various light wavelengths (Shimura 1977).

**Table 5.3** Sellmeier constants  $\lambda_0$  and  $S_0$  for calculation of refractive indices of LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> crystals (according to Shimura 1977)

	S <sub>0</sub> ,10	<sup>-14</sup> m <sup>2</sup>	λ	μm
У	n <sub>o</sub>	n <sub>e</sub>	n <sub>o</sub>	n,
1.00	1.2195	1.2123	0.1687	0.1696
0.97	1.2121	1.2121	0.1695	0.1698
0.92	1.2036	1.2121	0.1709	0.1699
0.81	1.1905	1.2121	0.1724	0.1703

two groups, the first responsible for waveguide propagation and the second for light control efficiency. The first group includes refractive indices, their profiles, the mode composition and optical losses. The second involves electro-, acousto- and nonlinear optical film parameters whose values depend on the way in which the waveguide was manufactured.

#### 5.2.1 Waveguide and radiation modes

Tien (1971) gave a visual interpretation of the occurrence of modes in coplanar waveguides, which we represent below.

The film considered here has a thickness of the order of 1 µm or less; it is so thin that it has to be supported by a substrate. We thus consider three media: a film, an air space above, and a substrate below. As shown in Fig.5.5, the thickness of the film is in the X-Y plane. For a thin film to support propagating modes and to act as a dielectric waveguide for the light waves, the refractive index of the film  $n_1$  must be larger than that of the substrate no and naturally than that of the air space above  $n_2$ . Mathematically, the problem involves a solution of the Maxwell equations that matches the boundary conditions at the film-substrate and film-air interfaces. The solutions indicate



**Fig.5.4** Birefringence  $(n_p - n_p)$  in mixed LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> crystals versus  $1/\lambda^2$  for various Ta contents in the crystal (Shimura 1977).

**Fig.5.5** (Right) The light wave propagates in the film to the *x*-axis. The surface of the film is in the *xy*-plane and its thickness in the *z* direction (Tien 1971).

three possible modes of propagation. The light wave can be bound and guided by the film as the waveguide modes. It can be radiate from the film into both the air and substrate spaces as the air modes, or it can radiate into the substrate only as the substrate modes. The air and substrate modes are the radiation modes discussed by Marcuse (1969, 1970). The modes described above can be explained simply and elegantly by the Snell law of refraction and the related total internal reflection phenomenon in optics.

Let (Fig.5.6a)  $n_0$ ,  $n_1$ , and  $n_2$  be refractive indices and  $\theta_0$ ,  $\theta_1$ , and  $\theta_2$  be the angles measured between the light paths and the normals of the interfaces in the substrate, film, and air, respectively. Here  $n_1 > n_0 > n_2$ . We have then from the Snell law

$$\sin\theta_2 / \sin\theta_1 = n_1 / n_2 \tag{5.4}$$

and

$$\sin\theta_0 / \sin\theta_1 = n_1 / n_0. \tag{5.5}$$

Let us increase  $\theta_1$  gradually from 0. When  $\theta_1$  is small, a light wave, for example, starts from the air space above the film, can be refracted into the film, and is then refracted again into the substrate (Fig.5.6a). In this case, the waves propagate freely in all the three media – air, film, and substrate – and they are the radiation fields that fill all the three spaces (air modes). Next, as  $\theta_1$  is increased to a value larger than the critical angle  $\sin^{-1}(n_2/n_1)$  of the film-air interface as shown in Fig.5.6b, the impossible condition incurred in equation (5.4),  $\sin \theta_2 > 1$ , indicates that the light wave is totally reflected at the film-air boundary. Now the wave can no longer propagate freely in the air space. We thus describe a solution that the light energy in the film radiates into the substrate only (substrate modes). Finally, when  $\theta_1$  is larger than the critical angle  $\sin^{-1}(n_0/n_1)$  of the film-substrate interface, the light wave, as shown in Fig.5.6c,



**Fig.5.6** (a) When  $\theta_1 < \sin^{-1}(n_2/n_1)$ , the light wave shown represents the air mode. The light wave originated in the film is refracted into both the substrate and air space (b). As  $\theta_1$  increases so that  $\sin^{-1}(n_2/n_1) < \theta_1 < \sin^{-1}(n_2/n_1)$ , the light wave shown now represents the substrate mode. It is refracted into the substrate but is totally reflected at the film-air interface (c). When  $\theta_1$  increases further so that  $\theta_1 > \sin^{-1}(n_2/n_1)$ , the light wave shown is totally reflected at both the film-air interface at both the film-air and film-substrate interfaces. It is confined in the film as is to be expected in the wave guide mode (Tien 1971).

**Fig.5.7** (right) (a) Light wave in the wave guide mode can be considered as a plane wave which propagates along a zigzag path in the film. The wave can be represented by two wave vectors A, and B<sub>1</sub>. (b) The wave vectors A, and B, can be decomposed into vertical and horizontal components. The horizontal components  $kn_i \sin \theta_1$ , determine the wave velocity parallel to the film. The vertical components  $\pm kn_i \cos \theta_1$  determine the field distribution across the thickness of the film (Tien 1971).

is totally reflected at both the upper and lower surfaces of the film. The energy flow is then confined within the film; that is to be expected in the waveguide modes.

It is interesting to note that in the waveguide modes the light wave in the film follows a zigzag path (Fig.5.6c). The light energy is trapped in the film as the wave is totally reflected back and forth between the two film surfaces. This zigzag wave motion can be represented by two wave vectors  $A_1$  and  $B_1$ , as shown in Fig.5.7a. Then the wave vectors are divided into the vertical and horizontal components, as in Fig.5.7(b). The horizontal components of wave vectors  $A_1$  and  $B_1$  are equal, indicating that the waves propagate with a constant speed in a direction parallel to the film. The vertical component of the wave vector  $A_1$  represents an upward traveling wave; that of the wave vector  $B_1$ , a downward travelling wave. When the upward- and downward traveling waves are superposed, they form a standing wave field pattern across the thickness of the film. By changing  $\theta_1$ , we change the direction of the wave vectors  $A_1$  and  $B_1$  and thus their horizontal and vertical components. Consequently, we change the wave velocity parallel to the film as well as the standing wave field pattern across the film.

Since we discuss here a planar geometry, the waves described above are plane waves. They are TE waves if they contain the field components  $E_y$ ,  $H_z$ , and  $H_z$ ; they are TM waves if they contain the field components  $H_y$ ,  $E_z$  and  $E_z$ . Here x is the direction of the wave propagation parallel to the film. The wave vectors  $A_1$  and  $B_1$  discussed above have thus a magnitude  $kn_1$ , where  $k = \omega/c$ ,  $\omega$  and c are, respectively, the angular frequency of the light wave and the speed of



**Fig.5.8** (a) A light wave in the waveguide mode is an infinitely wide sheet of plane wave which folds back and forth in a zigzag manner between the top and the bottom surface of the film. (b) A light wave propagating inside the film is totally reflected at the two film surfaces. The figure shows that in order that the wave and its reflections could add in phase, the total phase change for the light wave to travel across the thickness of the film, up and down in one round trip, must be equal to  $2 m\pi$ . The figure also shows that the light wave suffers a phase change of  $-2\Phi_{12}$  and  $-2\Phi_{10}$  at the upper and lower film surfaces, respectively. These phase changes determine the field distribution across the thickness of the film, which is shown at the right of the figure for the m = 3 wave guide mode (Tien 1971).

**Fig.5.9** (right) Any radius of the quarter-circle at the right side of the figure represents a possible direction for the wave vector  $B_1$ . In the black region of the circle, the wave vector represents the substrate or air mode. In the white region of the circle, the wave vector represents the waveguide mode, but only a discrete set of the directions in this region satisfies the equation of the waveguide modes. Each direction of this discrete set represents one waveguide mode and each waveguide mode has its own field distribution as shown in the left side of the figure (Tien 1971).

light in vacuum. In the picture of wave optics, the wave vectors  $A_1$  and  $B_1$ are the normals of the wavefronts, when an infinitely wide sheet of plane wave folds back and forth in a zigzag manner between the two film surfaces (Fig.5.8a). Now consider an observer who moves with the wave in the direction parallel to the film. He does not see the horizontal components of the wave vectors. What he observes is a plane wave that folds upward and downward, one directly on top of the other as shown in Fig.5.8b. The condition, then, for all those multiple reflected waves to add in phase, as seen by this observer, is that the total phase change experienced by the plane wave for it to travel one round trip, up and down across the film, should be equal to  $2m\pi$ , where m is an integer. Otherwise, if after the first reflections from the upper and lower film surfaces, the phase of the reflected wave differs from the original wave by a small phase  $\delta$ , the phase differences after the second, third,..., reflections would be  $2\delta$ ,  $3\delta$ ,..., and then the waves of progressively larger phase differences would add finally to zero. As shown in Fig.5.8b, the vertical components of the wave vectors  $A_1$  and  $B_1$  have a magnitude  $kn_1 \cos \theta_1$ . The phase change for the plane wave to cross the thickness W of the film twice (up and down) is then  $2kn_1W\cos\theta_1$ . In addition, the wave suffers a phase change of  $-2\Phi_{12}$  due to the total reflection at the upper film boundary and, similarly, a phase change of  $-2\Phi_{10}$  at the lower film boundary. Here the phase  $-2\Phi_{12}$  and  $-2\Phi_{10}$  represent, in fact, the GoosHaenchen shifts (Lotsche 1968). Consequently, in order the waves in the film could interfere constructively, the condition

$$2kn_1W\cos\theta_1 - 2\Phi_{10} - 2\Phi_{12} = 2m\pi, \tag{5.6}$$

must hold, which is the condition for the waveguide modes. Here m = 0, 1, 2, 3, ..., is the order of the mode. According to Born and Wolf (1970) on the theory of total reflection,

$$\tan \Phi_{12} = (n_1^2 \sin^2 \theta_1 - n_2^2)^{1/2} / (n_1 \cos \theta_1);$$
  

$$\tan \Phi_{10} = (n_1^2 \sin^2 \theta_1 - n_o^2)^{1/2} / (n_1 \cos \theta_1)$$
(5.7)

for the TE waves, and

$$\tan \Phi_{12} = n_1^2 (n_1^2 \sin^2 \theta_1 - n_2^2)^{1/2} / (n_2^2 n_1 \cos \theta_1);$$
  
$$\tan \Phi_{10} = n_1^2 (n_1^2 \sin^2 \theta_1 - n_0^2)^{1/2} / (n_0^2 n_1 \cos \theta_1)$$
(5.8)

for the TM waves.

It is clear that in spite of the zigzag wave motion described above, the wave in the waveguide mode appears to propagate in the horizontal direction only; the vertical part of the wave motion simply forms a standing wave between the two film surfaces. To avoid confusion, it is desirable to use  $\beta$  and  $\nu$  exclusively for the phase constant and the wave velocity parallel to the film. Thus,

$$\beta = kn_1 \sin \theta_1, \quad v = c(k / \beta), \tag{5.9}$$

Another quantity which will also be used frequently is the ratio  $\beta/k$ . As shown in equation (5.9), it is the ratio of the speed of light in vacuum to the speed of wave propagation in the waveguide.

After substituting equations (5.7) and (5.8) into equation (5.6), Tien (1971) found that both (5.6) and (5.9) are transcendental equations. Fortunately, the transcendental functions involve  $\theta_1$  only. For a given  $n_0$ ,  $n_1$ ,  $n_2$ , and *m* one can readily compute both  $\beta/k$  and *W* for a common  $\theta_1$ , and then tabulate  $\beta/k$  and *W* by assigning different values for  $\theta_1$ . The curves showing *W* versus  $\beta/k$  using *m* as the parameter are the mode characteristics of the waveguide (see Fig.5.15 below).

To summarize, any radius of the quarter-circle shown in Fig.5.9 represents a possible direction for the wave vector  $B_1$  described above, and  $\theta_1$  is the incident angle measured between the wave vector and the vertical axis. The waveguide modes occur in the range  $\sin^{-1} (n_0/n_1) < \theta_1 < \pi/2$ . Within this range of  $\theta_1$  there is a discrete set of the directions which satisfies the equation of the modes (5.6). Each direction corresponds to one waveguide mode of the film. The horizontal component of the wave vector,  $kn_1 \sin \theta_1$ , determines the wave motion parallel to the film, while its vertical component,  $kn_1 \cos \theta_1$ , determines the standing wave field pattern across the film. As shown in the left side of Fig.5.9, when m = 0 the standing wave pattern has a form similar to a halfsine wave. When m = 1, it has a form similar to a full sine wave, and so on. The air and substrate modes occur in the range  $0 < \theta_1 < \sin^{-1}(n_0/n_1)$ ; they occupy the black region of the quarter circle. As  $\theta_1$  is varied continuously from 0 to  $\sin^{-1}(n_2/n_1)$  for the air modes and  $\sin^{-1}(n_2/n_1)$  to  $\sin^{-1}(n_0/n_1)$  for the substrate modes, the corresponding  $\theta_0$  and  $\theta_2$  sweep through the entire space of the substrate and the air space. It is thus possible to express any radiation field by superposing waves of the air and substrate modes. What has been discussed here is therefore simply an expansion of the solution of the Maxwell equation into plane waves of all possible directions.

#### 5.2.2 Wave equation and field distribution

Having been described purely on an intuitive basis, the modes of light wave propagation can now be derived mathematically. For simplicity, assume the light wave in the film to be infinitely wide in the Y direction so that  $\partial/\partial y = 0$  (Fig.5.5). Let X be the direction of the wave propagation parallel to the film. The Maxwell equations in  $E_y$  for TE waves (or  $H_y$  for TM waves) can be reduced to the wave equation below

$$d^{2}E / dx^{2} + d^{2}E / dz^{2} = -(kn_{i})^{2}E, \quad j = 0, 1, \text{ or } 2$$
(5.10)

where  $n_j$  is the refractive index of the medium *j*. The subscripts j = 0,1, and 2 denote the substrate, the film, and the air space, respectively. A time dependence  $\exp(-i\omega t)$  is used in equation (5.10), where  $i = \sqrt{-1}$ . The solution of the wave equation is in the form of  $\exp(-ik_{xj}x) \exp(\pm ik_{zj}z)$ , which may be substituted into equation (5.10) to obtain

$$k_{xj}^2 + k_{zj}^2 = (kn)_j^2.$$
(5.11)

The boundary conditions at the film-air interfaces demand the same wave motion parallel to the film in all the three media considered; this can be written as

$$k_{x0} = k_{x1} = k_{x2} = \beta. \tag{5.12}$$

All the fields thus vary in time and x according to the factor  $\exp(-i\omega t + i\beta x)$ . This common factor will be omitted in all the later expressions for simplification. Combining equations (5.11) and (5.12) gives an important relation

$$k_{zj} = \left(k^2 n_j^2 - \beta\right)^{1/2}.$$
(5.13)

In the film,  $k_{x1}$  and  $k_{z1}$  are the horizontal and vertical components of the wave vector  $A_1$  or  $B_1$  discussed before. They are respectively  $k_{x1} = \beta = kn_1 \sin \theta_1$ 

and  $k_{z1} = kn_1 \cos \theta_1$ . In the waveguide modes, one can find from equation (5.13) and from the condition  $\sin^{-1} (n_0/n_1) < \theta_1 < \pi/2$  that  $kn_0 < \beta < kn_1$ ,  $kz_1$  is real, and  $kz_0$  and  $kz_2$  are imaginary. The field distribution in Fig.5.10a is thus a standing wave in the film and exponential in the substrate and in the air space. Next, for the substrate modes, there holds equation (5.13) and from the condition  $\sin^{-1}(n_2/n_1) < \theta_1 < \sin^{-1}(n_0/n_1)$  that  $kz_1$  and  $kz_0$  are real, but  $kz_2$  is imaginary. The fields in this case are standing waves in the film and in the substrate, but exponential in the air space (Fig.5.10b). Finally, for the air modes,  $0 < \theta_1 < \sin^{-1}(n_2/n_1)$ , and  $kz_0$ ,  $kz_1$ , and  $kz_2$  are real. The fields in all the three media are now standing waves (Fig.5.10c). It is convenient to denote  $kz_j$  by  $b_j$  when it is real and by  $ip_j$  when it is imaginary. For  $n_0 \neq n_2$  the waveguide is asymmetric. The upper and the upper and lower film surfaces are chosen to be  $z = W_{12}$  and  $z = -W_{10}$ . The thickness of the film is then  $W = W_{10} + W_{12}$ .

The field distributions are derived by choosing z = 0 at the position where  $E_y$  is maximum for any waveguide substrate, or even air mode, and  $E_y = 0$  for any odd air mode. It is important to note that these positions of z = 0 are different for different modes in an asymmetric waveguide. These choices are necessary to simplify mathematics so that the field distributions of various modes could be easily we can visualized. To avoid confusion,  $E_y$  of a TE wave only is considered below.

For the waveguide modes, as mentioned earlier, the wave suffers a phase change of  $-2\Phi_{12}$  at the upper film surface, and a phase change of  $-2\Phi_{10}$  at the lower film surface because of the inertial total reflections. The fields at the two film surfaces must therefore be  $\pm A \cos \Phi_{12}$  and  $\pm A \cos \Phi_{10}$ , respectively, where A is a constant. Let the field at z = 0 be a maximum value, A. Then one can choose  $kz_1W_{12}$  (or  $b_1W_{12}$ ) =  $\Phi_{12}$  so that the field at the upper film surface,  $z = W_{12}$ , can be A cos  $\Phi_{12}$ . Similarly one can choose  $b_1W_{10} = \Phi_{10} + m\pi$  so that the field at the lower film surface,  $z = -W_{10}$ , can be A cos  $\Phi_{10}$  if m = even and  $-A \cos \Phi_{10}$  if m = odds shown in Fig.5.10a. These choices give  $b_1W =$  $b_1W_{10} + b_1W_{12} = \Phi_{12} + \Phi_{10} + m\pi$ , which satisfies equation (5.6). The boundary conditions require  $E_y$  and  $\partial E_y/\partial z$  to be continuous at the two interfaces. Therefore,



Fig.5.10 The electric field distribution of (a) a TE waveguide mode; (b) a TE substrate mode; (c) a TE (even) air mode (Tien 1971).

$$E_{y} = A \cos \Phi_{12} \exp \left[-p_{2} \left(|z| - W_{12}\right)\right]$$

in the air space and

$$E_{y} = A\cos(\Phi_{10} + m\pi)\exp\left[-p_{0}(|z| - W_{10})\right]$$

in the substrate.

For the substrate modes, one again assumes a maximum field A at z = 0 and chooses  $b_1 W_{12} = \Phi_{12}$  (Fig.5.10b). The field at  $z = W_{12}$  is still A cos  $\Phi_{12}$  and that in the air space is still A cos  $\Phi_{12} \exp \left[-p(z-W_{12})\right]$ . The field at the lower field surface is then A  $\cos(b_1 W_{10})$  and that in the substrate is

$$\frac{1}{2A} \Big[ \cos(b_1 W_{10}) - i(b_1 / b_o) \sin(b_1 W_{10}) \Big] \exp \Big[ -ib_o (|z| - W_{10}) \Big]$$
  
+ the complex conjugate.

For the air modes, the even and odd modes must be treated separately. For an asymmetric waveguide, the z = 0 plane can be chosen anywhere between  $z = W_{12}$  and  $z = -W_{10}$ . However, once it is chosen, the same z = 0 plane should be used for all the air modes. For the even modes, the field is a maximum at z = 0 and the fields at the two film surfaces are  $A \cos b_1 W_{12}$  and  $A \cos b_1 W_{10}$ , respectively (Fig.5.10c). The boundary conditions require the fields in the substrate and in the air space in the form

$$\frac{1}{2A} \Big[ \cos(b_1 W_{1j}) - i(b_1 / b_j) \sin(b_1 W_{1j}) \Big] \exp \Big[ -i b_j (|z| - W_{1j}) \Big]$$

+ the complex conjugate,

where j = 0 and 2. For the odd modes the field is zero at z = 0 and is  $A \sin(b_1 W_{12})$  and  $-A \sin(b_1 W_{10})$  at the film surfaces. The films in the substrate and air space are then

$$\pm 1/2A \Big[ \sin(b_1 W_{1j}) + i(b_1 / b_j) \cos(b_1 W_{1j}) \Big] \exp \Big[ -i b_j (|z| - W_{1j}) \Big]$$

+ the complex conjugate,

where the plus sign is for j = 2 and the minus sign is for j = 0. The results discussed above are summarized in Table 5.4.

Mathematically, the field distributions described above are identical to those of the problem of a square potential well in quantum mechanics. Here the air space and the substrate are the potential barriers. The wave energy is divided here into the horizontal and vertical components, keeping the total energy constant. It is the vertical component of the wave energy that negotiates

		Waveguide mode
	sin <sup>-1</sup> ( <i>n</i>	$\mu_0/n_1) < \theta_1 < \pi/2; \ kn_0 < < kn_1$
Medium Film Substrate Air–space	$k_{xi} = \beta$ $= \beta$	$k_{ij} = k_{j} (TE wave)$ = $b_1 = A \cos b_1 z$ = $ip_0 = A \cos(\Phi_{10} + m\pi) \exp[-p_0( z  - W_{10})]$ = $ip_2 = A \cos \Phi_{12} \exp[-p_2( z  - W_{12})]$
		Substrate mode
sin- (n <sub>2</sub> /	$n_1 < \theta_1 < \sin^2 \theta_1$	$n_0'n_1$ ; $\sin^{-1}(n_2'n_0) < \theta_0 < \pi/2$ ; $\kappa n_2$
Medium Film	$\frac{k_{xj}}{\beta}$	$k_{ij} = E_{y} (\text{TE wave})$ = $b_{1} = A \cos b_{1} z$ = $b_{1} = b_{1} (A \cos b_{1} z)$
Air-space	= p = β	$= b_0  \sqrt{2} A [\cos(b_1 w_{10}) - 1(b_1 b_0) \sin(b_1 w_{10})] \\ \times \exp[-ib_0( z  - W_{10})] + c.c. \\ = ip_2 A \cos \Phi_{12} \exp[-p_2( z  - W_{12})]$
0< θ <sub>1</sub> < s	$E = \frac{1}{2} \sin^{-1}(n_2/n_1); 0 < 1$	ven and odd air modes $\theta_0 < \sin^{-1}(n_2/n_0);  0 < \theta_2 < \pi/2;  0 < \beta < kn_2$
Medium k <sub>sj</sub>	k <sub>zj</sub>	
Film = $\beta$	$= b_1 \begin{cases} Even \\ Odd \end{cases}$	$A \cos b_1 z$ $A \sin b_1 z$
Substrate = $\beta$	$= b_0 \begin{cases} Even \\ Odd \end{cases}$	$\frac{1}{2}A[\cos(b_1W_{10})-i(b_1/b_0)\sin(b_1W_{10})]\exp[-ib_0( z -W_{10})] + c.c. \\ -\frac{1}{2}A[\sin(b_1/W_{10})+i(b_1/b_0)\cos(b_1W_{10})]\exp[-ib_0( z -W_{10})] + c.c. $
Air-space = $\beta$	$= b_2 \begin{cases} \text{Even} \\ \text{Odd} \end{cases}$	$\frac{1}{2}A[\cos(b_1W_{12})-i(b_1/b_2)\sin(b_1W_{12})]\exp[-ib_2( z -W_{12})]+c.c.$ $\frac{1}{2}A[\sin(b_1W_{12})+i(b_1/b_2)\cos(b_1W_{12})]\exp[-ib_2( z -W_{12})]+c.c.$

 Table 5.4
 Electric field distribution in (a) a waveguide mode, (b) a substrate mode, and (c) the even and odd air modes (Tien 1972)

In deriving these expressions, we have chosen z = 0 at the position where  $E_y$  is either zero or maximum. These positions of z = 0 are therefore different for different modes.

the potential barriers mentioned above. The wave vector represents the momentum and its square, the wave energy. Within the interval  $\beta = kn_1$  and  $\beta = kn_0$ , because of the large horizontal component of the wave vector  $\beta$ , the vertical component of the energy is small enough so that the wave, or the particle, is trapped in the potential well. The mode spectrum or the energy level is thus discrete (waveguide modes). As the horizontal component of the momentum is reduced to a value  $\beta < kn_0$ , the vertical component of the wave energy is large enough to overcome the lower potential barrier. The wave function spills over the entire substrate space and one enters into the region of the substrate modes. The mode spectrum or the energy level is now continuous. As the vertical component of the wave energy is increased further by reducing  $\beta$  below  $kn_2$ , the wave can spill over the upper and the lower barriers. The mode spectrum remains continuous and it belongs to the air modes.

### 5.2.3 Optical modes in epitaxial Li (NbTa)O, waveguides

Solid-solution growth of  $(\text{LiNbO}_3)_{\alpha}$   $(\text{LiTaO}_3)_{1-\alpha}$  single-crystal films on LiTaO<sub>3</sub> substrates has been discussed above. These films are grown by EGM (epitaxial

growth by melting) method. However, the special process used by Tien et al (1974) permitted obtaining very thin films with a graded composition. The composition of each film is maximum at the air-film interface, and it decreases gradually to zero towards the substrate, as illustrates by curve A in Fig.5.11b. Because of this graded composition, any effect due to mismatch in lattice constant between the film and the substrate is minimized, and consequently films as grown are uniform and smooth. In Fig.5.11a, the z axis is normal to the surface of the film, and z = 0 and z = d are the air-film and filmsubstrate interfaces, respectively. All the optical measurements were performed by using a 0.6328-µm helium-neon laser, and the x axis was chosen as the direction of light wave propagation. Because of the differences in the refractive indices and the graded composition of the film, the refractive index varies inside the film as shown by curve A in Fig.5.11c. The solid-solution film has  $\Delta n = 0.0710$  and a thickness of 3.87 µm. The films formed excellent optical waveguides; all the waveguide modes observed are well separated, and they can be individually excited by a prism coupler. Moreover, several films had one TE and one TM waveguide mode only. Tien et al (1974) reported some interesting observations of the waveguide modes and discussed a simple method of calculation for the graded waveguides. This simple method can be used for calculation of the effective indices of the waveguide modes as well as for the evaluation of the index distribution in the film. The prism coupler (Tien 1971; Tien et al 1972) is an important tool for the study of the film properties.

To study the waveguide modes, a film with nine TE modes was chosen. The film was grown parallel to one of the cleavage planes of  $LiTaO_3$ . The c axis thus forms an angle of 33° from the surface of the film (Fig.5.11(a)). Let a be a projection of the c axis on the film and let b be normal to a. The TE wave is an ordinary wave when the light propagates along a, and



**Fig.5.11** (a) Position of the *c*-axis with respect to the geometrical axes in a solid-solution  $LiNbO_3-LiTaO_3$  film. (b) Curve A shows the graded composition in the film. (c) Curves A and B show, respectively, the index variation in a solid-solution film and that in a diffused film. (d) Photograph of the *m* lines of a solid-solution film. (e) Photograph of the *m* lines of a uniform waveguide made of a Ta<sub>2</sub>O<sub>5</sub> film on a glass substrate (Tien et al 1974).



Fig.5.12 (a) Mode indices calculated on the basis of an exponential distribution of refractive index. (b) Mode indices measured from one of the solid-solution films. (c) Mode indices calculated on the basis of an index distribution in the form of a Fermi function (Tien 1974).

it is an extraordinary wave when the light propagates along b. The m lines (Tien 1971; Tien et al 1969) observed for the case of the ordinary wave are shown in Fig.5.11(d). The TM wave is always an extraordinary wave. Consequently, as the direction of the light propagation varies from a to b, the effective indices (Tien et al 1972)  $\beta/k$  of the TE modes vary continuously, whereas those of the TM modes do not vary. To avoid confusion, one can use 'uniform waveguides' for those having a constant refractive index  $n_F$  throughout the film and 'graded waveguides' for those in which  $n_F$  varies in z. For comparison, the m lines observed in a uniform waveguide made of a Ta<sub>2</sub>O<sub>5</sub> film on glass are shown in Fig.5.11e. The difference between the mode patterns of a uniform and a graded waveguide is that the mode spacing increases with the mode number m in the former, whereas the opposite is true in the latter.

Modes in the graded waveguides have been calculated by many authors (Taylor et al 1972). In particular, an elegant theory has been developed by Conwell (1973). She used an index distribution for the film in the following form:

$$n_{\rm F}(z) = n_{\rm s} + \Delta n \exp(-z/d), \qquad (5.14)$$

where  $n_s$  is the refractive index of the substrate. Such a distribution is illustrated by curve B in Fig.5.11c. This theory was used to calculate the effective indices of the modes for the case of a TE wave propagating along *a*. For having nine modes, the argument (Conwell 1973) of the Bessel function X = 29,  $d = 2.23 \,\mu\text{m}$ ,  $n_s = 2.177$ , and  $\Delta n = 0987$  were chosen. The results of the calculations are plotted in Fig.5.12a and they should be compared with the measured values of Fig.5.12b. Obviously, the exponential distribution given by equation (5.14) does not apply to the solid-solution films, since the mode spacing shown in Fig.5.12a decreases much more rapidly with the mode number *m* than those observed in Fig.5.12b.

Search for a theory which applies to any distribution of the film has led

to the WKB method (Dicke and Wittke 1960). Recall that for a uniform waveguide the mode equations (Tien 1971) are

$$bd = \Phi_{10} + \Phi_{12} + m\pi \tag{5.15}$$

and

$$b^2 + \beta^2 = k^2 n_F^2. \tag{5.16}$$

Here we are considering a zigzag plane wave propagating in the film as exp  $(-i\omega t \pm ibz + i\beta x)$ , where b and  $\beta$  are respectively the z and x components of the wave vector, m and d are respectively the mode number and the film thickness,  $k = \omega/c$ , where  $\omega$  is the angular frequency and c is the velocity of the light wave in vacuum and, finally,  $-2\Phi_{10}$  and  $-2\Phi_{12}$  are respectively the phases advanced by the zigzag wave due to the total reflections of the wave at the film-substrate and film-air interfaces. On the basis of the WKB method, for a graded waveguide of any index distribution  $n_{c}(z)$ 

$$\int_{0}^{t_{1}} b(z)dz = \Phi_{10} + \Phi_{12} + m\pi, \qquad (5.17)$$

$$b^{2}(z) + \beta^{2} = k^{2} n_{F}^{2}(z), \qquad (5.18)$$

and

$$b(z_t) = 0.$$
 (5.19)

Here  $z_i$  is the turning point of the WKB method and, at  $z = z_i$ ,  $b(z_i) = 0$ and  $\beta = kn_r(z_i)$ . Consequently,  $z_i$  can be considered as a function of  $\beta$ . For



**Fig.5.13** Values of the integral *A* versus the mode indices,  $\beta/k$  for the two cases described in the text (Tien et al 1974).

	Case 1:9 modes	
m	Conwell's theory	Tien's method
0	2.2400	2.2399
1	2.2196	2.2192
2	2.2059	2.2057
3	2.1961	2.1959
4	2.1889	2.1888
5	2.1838	2.1835
6	2.1802	2.1800
7	2.1781	2.1778
8	2.1771	2.1771
	Case 2:2 modes	
m	Conwell's theory	Tien's method
0	2.1897	2.1898
1	2.1789	2.1790

Table 5.5 Mode indices,  $\beta/k's$  (Tien et al 1974)

all the films,  $\Delta n/n_{\rm r}$  is small and the index of the film is substantially larger than that of the air; one can take  $\Phi_{12} = \pi/2$ . According to the standard linear approximation of the WKB method (Dicke and Wittke 1960) at the turning point,  $\Phi_{10}$  is obviously  $\pi/4$ . Let the integral in (5.17) be A. With a given index distribution  $n_{x}(z)$ , Tien et al (1974) could compute b(z) from (5.18) and  $z_{z}$ from (5.19), and then evaluate the integral A for any value of  $\beta$ . In fact, we can plot A versus  $\beta/k$ , and the values of  $\beta/k$  corresponding to A = (m + 0.75) $\pi$  for m = 0, 1, 2, ..., are the effective indices of the waveguide modes. To substantiate this method, the distribution given by equation (5.14) was used and the calculations were performed for two cases. One case has nine modes and  $\Delta n = 0.0987$ ,  $n_r = 2.177$ , and  $d = 2.23 \mu m$ ; the other case has two modes only and  $\Delta n = 0.043$ ,  $n_c = 2.177$ , and  $d = 0.931 \,\mu\text{m}$ . The A-versus- $\beta/k$  curves for these two cases are shown in Fig.5.13. The results obtained by this method are then compared in Table 5.5 with those calculated from the exact theory of Conwell (1973). The agreement between the two methods is within ±2×10<sup>-4</sup>.

It is also possible to use equations (5.17)-(5.19) to evaluate the index distribution of the film from the measured  $\beta/k$ 's of the waveguide modes. As noticed earlier, the mode index  $\beta/k$  is the refractive index of the film at the turning point. The locations of the turning points for the waveguide modes can be solved in terms of the measured  $\beta/k$ 's by forming, based on (5.17), a set of simultaneous equations, one equation for each mode. Extensive calculations

of this nature have shown that the index distribution of the solid-solution films can be closely represented by a Fermi function

$$n_F(z) = n_s + \Delta n \left\{ 1 + \exp[(z - d) / a] \right\}^{-1}.$$
(5.20)

Such a distribution is shown by curve A in Fig.5.11b. There is a region near z = 0, in which the refractive index is relatively constant, indicating the beginning of the formation of a homogeneous epitaxial layer. This homogeneous region is followed by a broad transition region where the refractive index varies more rapidly. The parameters d and a determine, respectively, the thickness of the film and the sharpness of the transition region. Currently, these parameters are correlated with the growth process. For the particular film described above,  $\Delta n = 0.0710$ ,  $a = 0.286 \,\mu\text{m}$ , and  $d = 3.87 \,\mu\text{m}$ . Based on these constants, the calculated mode indices are shown in Fig.5.12c, which agrees with the measurement shown in Fig.5.12b within the experimental error of the order of  $5 \times 10^{-4}$ .

## 5.2.4 Characteristics of out-diffused waveguides

The asymmetric planar slab waveguide, produced by depositing a uniform guiding layer on a substrate, and the planar graded index guide are similar in their waveguiding properties but differ somewhat in detail. Carruthers et al (1974) compared two characteristics of the slab and graded guides, namely, the number of the modes N supported by the guide and the effective penetration depth w, for energy in the *i*-th mode.

The refractive index profiles for the slab and graded guides are illustrated schematically in Fig.5.14. For both guides, n = 1 for x < 0, and  $n = n_{\infty}$  for  $x \to \infty$ . For the slab,

$$n = n_{\infty} + A \text{ for } 0 < x < B$$

$$n = n_{\infty} \text{ for } B < x < \infty$$
(5.21)

and for the grade guide,

$$n(x) = n_{co} + \pi^{1/2} a \, \operatorname{ierfc} (x \,/ \, b). \tag{5.22}$$

The wave functions for the slab are sinusoidal in the range 0 < x < B and exponentially decaying outside this range. For modes sufficiently far from cutoff, most of the energy is confined within 0 < x < B. Thus, neglecting the evanescent tail, one can define an effective penetration depth for all TE slab modes as

$$w_i^s = B. \tag{5.23}$$



**Fig.5.14** Refractive index profiles for (a) an asymmetric planar slab wave-guide and (b) a planar graded index waveguide.  $TE_0$  and  $TE_1$  wave functions are indicated schematically along with turning points  $x_1$  (Carruthers et al 1974).

The various modes have propagation constants  $\beta_i$  that are plotted as index levels  $\beta_i/k$  in Fig.5.14(a), with  $k = 2\pi/\lambda$  and  $\lambda$  the optical wavelength. The number of TE modes that can be supported is the integer less than

$$N^{s} = (1/2) + (2B/\lambda)(2n_{m}A)^{1/2}$$
(5.24)

with a similar expression for TM modes (Nelson and Kenna 1967). The analogy with the quantum mechanical problem of a particle in a box having turning points at x = 0 and x = B is apparent. In the optical problem, the turning points represent reflecting surfaces for rays trapped in the guide.

The graded index problem, like most quantum mechanical potential-well problems, cannot be solved analytically without approximation except in special cases. Marcuse (1978) gives WKB solutions to a three-segment piecewise linear approximation to an arbitrary index profile. If equation (5.22) is approximated by linear segments that pass through the points  $(n_j, x_j):(n_{\infty} + a, 0), (n_{\infty} + a/3, b/2), (n_{\infty}, 5b/4)$  and  $(n_{\infty}, \infty)$ , then it is found that

$$N^{g} = 1/4 + (1.38b/\lambda)(2n_{\infty}a)^{1/2}.$$
(5.25)

The factor 1.38 is of course dependent on the choice of  $(n_j, x_j)$ , but it can be seen that  $N^s$  and  $N^g$  are similar for comparable A, B and a, b parameters. For example, if A = a, then  $N^s = N^g$  when B = 0.69 b for large N.

The wave functions and index levels for the  $TE_0$  and  $TE_1$  modes are shown schematically in Fig.5.14b. The intersection of the index level with the curve n(x) defines the turning point  $\tilde{x}_i$ , at which an equivalent optical ray or a quantum-mechanical particle in a similar potential well would reverse its direction. Most of the energy in a mode far from cut-off is confined to the region  $0 < x < \tilde{x}_i$ , so the penetration depth can be defined as

$$w_i^g = \widetilde{x}_i, \tag{5.26}$$

where  $\tilde{x}_i$  increases with increasing mode number *i*. The wave functions are oscillatory in the range  $0 < x < \tilde{x}_i$ , and increase in amplitude near  $\tilde{x}_i$ ; they decay exponentially outside this range (Marcuse 1978; Smithgall et al 1977; Conwell 1973).

To obtain an estimate for  $\tilde{x}_0$ , the quantity n(x) may be approximated crudely by a straight line tangent to n(x) at x = 0 as shown in Fig.5.14b. It can be seen that the value of  $\tilde{x}_0$  obtained from such an approximation will be smaller than the true value and will give a lower bound on  $w_0^s$ . For this approximation, Marcuse (1978) found

$$\widetilde{x}_0 = \left[ (81\lambda^2 b) / (512 n_{\infty} \pi^{1/2} a) \right]^{1/3}$$
(5.27)

with 86% of the TE<sub>0</sub> mode energy within  $0 < x < \tilde{x}_0$ . Combining equations (5.25) and (5.27) yields

$$\widetilde{x}_0 = 0.69 \, b \left( N - 0.25 \right)^{-2/3}.$$
(5.28)

Solutions for the wave functions of the  $\Delta n(x) = a' \operatorname{erfc} (x/b')$  profile (see Fig.1.9), which should be similar to those for  $a\pi^{-1/2}$  ierfc (x/b), have been computed numerically and compared graphically with those for the slab guide (Smithgall et al 1977). These results show clearly that the mode energy is buried more deeply for higher order modes. Here a' = a, b'' = 0.73b for coincidence at  $\Delta n = a$ , a/2, and 0.

The exponential function

$$n(x) = n_{\infty} + a'' \exp(-x/b'')$$
(5.29)

also gives a reasonably good fit to the data, as shown in Fig.1.9. For coincidence at  $\Delta n = a$ , a/2, and 0, Carruthers et al (1973) require a'' = a,  $b'' = 0.506 \ b$ . As shown by Conwell (1973), the exponential profile is one of the few that gives exact analytical solutions to the wave equation. These solutions also show an increase in the strength of the wave functions as x approaches the turning point, with deeper penetration for higher-order modes. Although the number of modes, wave functions and propagation constants can be calculated when a'' and b'' are known, simple expressions for N and w in terms of a'' and b'' are not given. However, useful expressions can be obtained in certain limits as follows.

Define the functions

$$\xi = 2kb''(2n_{\infty}a)^{1/2}, \tag{5.30}$$

$$\mu = 2 \left[ \left(\beta b''\right)^2 - \left(n_{\infty} k b''\right)^2 \right]^{1/2}$$
(5.31)

then, for  $2n a \ll n_{p}^{2}-1$ 

$$(\beta_i / k - n_{\infty}) / a = (\mu_i / \xi_i)^2,$$
(5.32)

where  $\mu_i$  and  $\xi_i$  are related so that the Bessel function

$$J_{\mu}(\xi_i) = 0; \ i = 0, 1, 2...$$
 (5.33)

Near cut-off,  $\mu_i \rightarrow 0$ , and in this limit the zero's in equation (5.33) are given approximately by

$$\mu_i = (2/\pi)\xi_i - 2i - (3/2). \tag{5.34}$$

The maximum  $\xi$  is given by equation (5.30); and the number of modes is the largest integer *i*+1 obtained from equation (5.34) at cut-off  $\mu_i = 0$ 

$$N^{e} = 1/4 + (4b''/\lambda)(2n_{\infty}a)^{1/2}, \qquad (5.35)$$

which may be compared with equation (5.25) for b = 1.97 b". Because of its extensive tail, the exponential profile overestimates both N and  $\overline{x_i}$ .

The turning point  $\overline{x}_i$  may be obtained by equating the right-hand side of equation (5.32) to  $\exp(-\overline{x}_i/b'')$ ; then

$$w_i^e = \bar{x}_i = -2b'' \ln[(2/\pi) - (4i+3)/(2\xi)].$$
(5.36)

In the other limit, far from cut-off,  $\mu_i$  and  $\xi_i$  are large; for i = 0, equation (5.33) is satisfied for

$$\mu_0 = \xi_0 - 1.856 \,\xi_0^{1/3}. \tag{5.37}$$

Equation (5.37) may be inserted into equation (5.32) to obtain the dispersion curve far from cut-off. The turning point may be estimated by equating the right-hand side of equation (5.32) to  $1-\overline{x_0}/b''$  for  $x_0/b <<1$ ; then



**Fig.5.15** Normalised guide index  $(\beta/k - n_{\perp})/a''$  versus normalised frequency  $\xi = 2kb'(2n_{\perp}a)^{1/4}$  (Carruthers et al 1974).

$$w_i^e = \bar{x}_0 = 0.659 \left[ \left( \lambda^2 \, b'' \right) / \left( n_\infty \, \pi^{1/2} \, a \right) \right]^{1/3} \tag{5.38}$$

which is nearly identical with equation (5.27) for b'' = 0.506 b.

Universal dispersion curves suitable for both TE and TM modes of the exponential profile in equation (5.29) calculated from computer solutions of equations (5.32) and (5.33) for  $2n_{\infty} a'' \ll n_{\infty}^2 - 1$  are plotted in Fig.5.15. The exponential TE<sub>0</sub> mode shows much less dispersion than the TE<sub>0</sub> mode for a slab having the same cut-off, that is, A = a'', B = 4b''/3.

It is clear from the preceding discussion that N and w for the graded guide can be adjusted just as for the slab guide provided a and b can be controlled independently. To assure single mode operation, it is necessary to restrict N to the range: 1 < N < 2. Such guides have been made in LiNbO<sub>3</sub> for  $\lambda = 0.63$ µm by restricting t to a few minutes. An example of a single mode guide is a sample for which t = 5 min and  $T = 1100^{\circ}$ C, yielding  $a = 1.65 \times 10^{-4}$ and b = 20 µm. From equations (5.25) and (5.27), respectively, it is calculated that  $N^g = 1.4$  and  $\overline{x}_0 = 12$  µm. On the other hand, using Conwell's exponential approximation (Conwell 1973), it is found that  $N^e = 1.95$  and  $\overline{x}_0 = 18$  µm.

From (5.27) and (5.38), the penetration depth  $w_0$  is limited by the range of surface gradient  $\pi^{1/2} a/b$  available by varying T. For LiNbO<sub>3</sub>,  $\pi^{1/2}a/b \approx 1.9 \times$  $\times 10^{-5} \ \mu m^{-1}$  is practically temperature independent because  $Q_v \approx Q_D$ , so  $\overline{x}_0 \approx$ 12 µm for the available range  $T < T_c$ . Therefore, it may be preferable to outdiffuse at lower temperatures where the required diffusion times are longer to maintain better control over the process, *i.e.* the heating and cooling transients will have a smaller effect on the profile. For LiTaO<sub>3</sub>, on the other hand,  $\pi^{1/2} a/b$  covers the range  $1.3 \times 10^{-4} - 7 \times 10^{-6} \ \mu m^{-1}$ , so  $\overline{x}_0$  covers the range 6– 16 µm as T varies from 1400°C to 930°C. Therefore, smaller penetration depths are achieved at higher temperatures; however, the short times required make control of the process difficult. An even greater change of penetration depth,  $w_0$  with T would be found in materials for which  $Q_v$  and  $Q_p$  differ more widely. Thus, very low-loss out-diffused layers can be fabricated with characteristics similar to those of a single mode slab guide thickness  $B \approx \bar{x}_0$ , where  $\bar{x}_0 \approx 12$  µm for LiNbO<sub>3</sub> and  $6 < \bar{x}_0 < 16$  µm for LiTaO<sub>3</sub>. These rather large effective widths may limit the operation of devices based on interactions with surface fields of short wavelength. On the other hand, the large width may prove advantageous in applications where the planar guide is converted to a ridge or strip guide by etching. In these cases, fields can be applied along edges of the ridge; and coupling can take place at the relatively large facets.

### 5.2.5 Properties of diffused waveguides

To establish the parameters of the refractive index profile in diffused waveguides, the following methods are used:

1) interferentional microscopy, 2) direct measurement of Ti concentration distribution in the waveguide cross-section (X-ray microanalysis, Auger spectroscopy), definition of the function n(y) from the observed spectrum of the effective  $n_m^*$  values (Naitoh et al 1977; Zolotov et al 1976).

In view of the fact that interferentional microscopy is only suitable for a study of thick enough (> 10 µm) diffused layers and the second group of methods requires sophisticated devices and a subsequent calibration, Zolotov et al (1980) used identification of diffused waveguide profiles from the spectrum of effective  $n_m^*$  values. The parameters of n(y) distribution over a diffused waveguide were identified from the spectrum of  $n_m^*$  values using the combination of the parabolic and exponential functions (Zolotov et al 1976) for which there exists an analytical solution of differential equations of the type

$$Y'' + k^2 \left( n^2(y) - n^{*2} \right) Y = 0, \tag{5.39}$$

that describe the electric field distribution in weak ( $\Delta n \ll n$ ) diffused waveguides.

The dependence of the waveguide parameters on the time of diffusion was determined using measurements for E- and H-waves (if the crystal orientation is fixed, the ordinary refractive index  $n_0(y)$  corresponds to E-waves while the extraordinary refractive index  $n_0(y)$  corresponds to H-waves). In the waveguides investigated by Sugii et al (1978), two-three E-modes and five-six H-modes could be excited at a wavelength of 0.63 µm, while at a wavelength of 0.44 µm four-five E-modes and six-nine H-modes were observed. The spectrum of  $n_m^*$  values changed with diffusion time. The analysis of the spectra obtained has shown that the waveguide profiles for ordinary and extraordinary polarizations are approximated fairly well by the combination of the parabolic and exponential functions

$$n^{o,e} = \begin{cases} n_1^{o,e} + \Delta n^{o,e} \frac{1 - (y - b)^2 / a^2}{1 - b^2 / a^2}, \ 0 < y < b + c, \\ n_1^{o,e} + \Delta n^{o,e} \frac{1 - c^2 / a^2}{1 - b^2 / a^2} \exp\left(-\frac{y - b - c}{h}\right), \ b + c < y < \infty. \end{cases}$$
(5.40)

Here a and b are parabola parameters, h is the exponent parameter, c is the distance from the parabola vertex to its conjugate point with the exponent.

The distributions of  $n_{o,e}(y)$  obtained for a waveguide with different diffusion times are represented in Fig.5.16 and Table 5.6 gives the numerical values of their parameters. The distributions of the refractive indices of Ti-diffused LiNbO<sub>3</sub> waveguides for waves with different polarizations differ practically only in the increment of the refractive index on the waveguide surface,  $\Delta n$ , and in the exponential function parameter *h*. The difference  $\Delta n$  can be explained by different proportionality coefficients between the titanium concentration  $C_{Ti}$ and the increments of the ordinary and extraordinary refractive indices. The assumption of direct proportionality between  $C_{Ti}$  and  $\Delta n_{o,e}$  is confirmed by the lack of dependence of the ratio  $\Delta n / \Delta n_{o}$  on the diffusion time (see Table 5.6).

The difference in the exponent parameter h in the distributions of  $n_{o}(y)$  and  $n_{o}(y)$  is due to the fact that the increment of the extraordinary refractive index is caused, besides titanium diffusion, also by the reverse diffusion of Li<sub>o</sub>O which increases substantially the waveguide length.

The mode fields in the above-mentioned waveguides are obtained from the solution of the wave equation (5.39) for ordinary waves (*E*-polarization) and

h		E	waves			H-waves					
I <sub>dif</sub> , n	$\Delta n_{0}$	lal-lbl µm	b/a	c/a	<i>h</i> , μm	$\Delta n_e$	lal-lb µm	b/a	c/a	h, μm	$\Delta n_{o} - \Delta n_{o}$
5	0.0161	2.99	-0.6	0.89	0.88	0.0374	2.99	-0.6	0.98	3.32	2.32
10	0.0127	4.27	-0.6	0.89	1.23	0.0296	4.00	-0.6	0.97	4.10	2.33
12	0.0115	4.56	-0.56	0.9	1.09	0.0259	4.56	-0,56	0.97	4.73	2.25
15	0.0112	5.20	-0.45	0.85	1.63	0.0231	4.95	-0.45	0.97	4.83	2.26
19	0.0088	6.27	-0.45	0.85	1.86	0.0192	6.17	-0,45	0.95	4.60	2.18

Table 5.6 Numerical values of diffused waveguide parameters ( $\lambda = 0.63 \ \mu m$ ) (Zolotov et al.1980)



**Fig.5.16** Distribution of ordinary (a) and extraordinary (b) refractive indices for Ti-diffused waveguides (dashed lines indicate calculated values). 1) diffusion time  $t_p = -5$  h; 2) 10 h; 3) 15 h (Zolotov et al 1980).
have the form

$$Y(y) = \begin{cases} C_1 \eta e^{-\eta^{2/2}} {}_1 F_1(3/4 - s_m/4, 3/2, \eta^2), -c \le y \le 0, \\ C_2 J_{\nu_m}(\alpha e^{\xi/\alpha}), -\infty < y < -c, \end{cases}$$
(5.41)

here  $_{1}F_{1}$  is a degenerate geometrical function,  $J_{ym}(\alpha, \xi)$  is the Bessel function

$$\overline{\alpha} = (2n_1 \Delta n)^{1/2} k a, \ \eta = \overline{\alpha}^{1/2} y / a$$

$$\gamma_m = (n_m^* - n_1) / \Delta n, \ S_m = \overline{\alpha} (1 - \gamma_m),$$

$$\xi = \left[2n_1 \Delta n (1 - c^2 / a^2)\right]^{1/2} k(y + c), \ \alpha = \overline{\alpha} \frac{a}{c} (1 - c^2 / a^2)^{3/2}$$

$$\nu_m = \overline{\alpha} (a / c - c / a) \gamma_m^{1/2}.$$

For extraordinary waves (H-polarization)

$$Y(y) = \left[C_{1\eta_{1}}F_{1}(3/4 - s_{m}/4, 3/2, \eta^{2}) + C_{21}F_{1}(1/4 - s_{m}/4, 1/2, \eta^{2})\right]e^{-\eta^{2/2}},$$
  
-c-b \le y \le 0,  
$$Y(y) = C_{3}J_{\nu_{n}}(\alpha e^{\xi/\alpha}), -\infty < y < -c-b.$$
(5.42)



**Fig.5.17** Dispersion of ordinary and extraordinary refractive index increment for waveguides with diffusion time  $t_p = 12$  h (dashed lines indicate calculated values – see the text) (Zolotov et al 1980).

Fig.5.18 (right) Optical waveguiding apparatus (Kaminow and Carruthers 1973).

$$\overline{\alpha} = \left(\frac{2n_1\Delta n}{1-b^2/a^2}\right)^{1/2} ka, \ \eta = \overline{\alpha}^{1/2} \frac{y+b}{a}, \ s_m = \left(1-\gamma_m(1-b^2/a^2)\right)^{1/2} kh, \ \xi = \left(2n_1\Delta n \frac{1-c^2/a^2}{1-b^2/a^2}\right)^{1/2} k(y+b+c),$$
$$\alpha = 2\left(2n_1\Delta n \frac{1-c^2/a^2}{1-b^2/a^2}\right)^{1/2} kh.$$

The constants  $C_1$ ,  $C_2$  and  $C_3$  are determined from the condition of equality to zero of the wave function at the boundary with air and continuity of the fuction at the sewing point

An important characteristic of optical waveguides is the dispersion of the refractive index increment. The data on the waveguide dispersion are necessary for creation of some integro-optical devices, in particular, nonlinear transducers. Zolotov et al (1980) investigated the dispersion of waveguide characteristics in a wide wavelength range: 0.44, 0.53, 0.63, 0.89, 1.06, 1.15  $\mu$ m. It is an experimentally established fact that as  $\lambda$  varies the shape of the profiles of  $n_o(y)$  and  $n_o(y)$  remains unaltered, and it is only the refractive index increments  $\Delta n_o$  and  $\Delta n_o$  that exhibit dispersion (Fig.5.17).

Guiding can be demonstrated (Tien 1971; Tien and Ulrich 1970) with the prism coupler arrangement shown in Fig.5.18, where crystals are oriented with a, b, and c along z, x, and y, respectively, and an incident beam is polarized as an extraordinary (TE) wave. A bright streak appears along the surface when  $\theta$  is adjusted near an angle  $\theta_0$  slightly less than the critical angle. There is no observable decay in the strength of the scattered light over a centimetre length of the streak, which suggests that the loss is  $\leq 1$  dB/cm. The modes radiates from the end of the guide, producing a far-field pattern narrow in the y direction but elongated in the x direction. Measurement of beam angle  $\alpha$  provides an estimate for the extent h of the field in the x direction in the guide:  $h \approx \lambda/\alpha$ . For sample I-3,  $h \approx 10 \,\mu\text{m}$  (Kaminow and Carruthers 1973), which indicates that, being coupled, the optical energy for the modes is confined to the neighbourhood of maximum  $\Delta n$ , near s = 0, where s is the depth.

An output prism coupler produces a well-defined spot at  $\theta' = \theta_0$  when  $\theta = \theta_0$ . A faint '*m*-line' passes through the spot, indicating only minor scattering into degenerate modes propagating in other directions in the plane. Waveguiding, as demonstrated by the coupled-out spot, exists over a range of angles  $\Delta \theta_0$ . Calculations show that  $\Delta \theta_0$  for each sample corresponds to a range of waveguide propagation constants  $\Delta \beta$  given approximately by  $2\pi A/\lambda$ . Thus, the waveguide supports a large number of unresolved modes. To produce guides that support only a few low-order modes, the product  $A^{1/2}B$  must be reduced by adjustment of t and T.

# 5.3 Second harmonic generation in waveguides

Integrated optics is a wide field for heightening the efficiency of nonlinear

interactions. The use of optical waveguides permits obtaining high intensities of light, in a film with thickness of the order of the light wavelength, from comparatively low-power sources, *e.g.* gas lasers. As distinct from the case when narrowing the light beam to small dimensions causes its large diffraction divergence, a small cross-section of the beam (and therefore its high density) in a waveguide remains unchanged throughout. Another advantage of thinfilm waveguides is the possibility to attain phase matching of interacting waves due to mode dispersion. This allows the use of isotropic media possessing high nonlinear coefficients. Anisotropic waveguides do not require temperature tuning for attaining a 90-degree matching that can be reached through the choice of the refractive index profile.

But in spite of the obvious advantages of optical waveguides for nonlinear conversion, the success in this field remains rather moderate. In particular, the efficiency of second harmonic generation reached experimentally in various materials was two or three orders of magnitude lower than the theoretically predicted one (Ito et al 1974; Van der Ziel et al 1975), which is obviously explained by a low quality of the guides. To obtain an effective nonlinear conversion, the film nonuniformity through the thickness must not exceed 0.01  $\mu$ m per 1 mm. Non-observance of this condition leads to phase mismatch and, therefore, to a lowering of the second harmonic power (Boyd 1972).

Planar waveguides on the basis of lithium niobate are now promising for the study and practical use of nonlinear second-order effects. This is connected with a large value of the nonlinear susceptibility tensor of the crystal as well as with the possibility of angular and temperature tuning of matched interaction.

We shall mention some most typical papers out of a comparatively small number of publications concerning nonlinear processes in planar waveguides.

Fejer et al (1986) obtained second harmonic generation (SHG) in a laser on a garnet with neodymium in a Ti:MgO:LiNbO<sub>3</sub> waveguide, in which a temperature-induced phase matching generated radiation at a wavelength of 532 nm with an efficiency of  $1.5 \times 10^{-2}$ . SH radiation of 22 mW was obtained in a non-stop regime; in a pulsed operation the conversion efficiency was of the order of 25%. Phase matching was reached both for the case  $TE_0^{\omega} \rightarrow TE_0^{2\omega}$ (the zeroth mode of fundamental radiation is converted into the zeroth mode of second harmonic) and for  $TE_0^{\omega} \rightarrow TE_0^{2\omega}$ .

The corresponding matching temperatures are equal to  $T = 102^{\circ}$ C and 21.7°C.

SHG in Ti:LiNbO<sub>3</sub> waveguides was obtained by Arvidsson and Laurell (1986) and Regener et al (1981) who reached, using an additional resonator for producing the fundamental frequency, a substantial increase of the field strength in the waveguide, which results in a sharp heightening of the efficiency of nonlinear optic conversion. In a similar way Regener et al (1981) reached an efficiency of the conversion into a second harmonic of the order of 10<sup>-2</sup> for a mean input radiation power of 1.5 mW.

Other nonlinear processes such as difference frequency generation (Uesugi 1980; Suche 1984), parametric amplification and generation (Suche et al 1985) were also attained in planar waveguides.

#### 5.3.1 Phase matching in an optical waveguide

As is well known, an effective second harmonic generation requires phase matching of interacting waves. In anisotropic crystals, dispersion at frequencies of first and second harmonics is compensated by exploiting different polarizations of interacting waves. The phase matching direction will coincide with the direction of intersection of indicatrices of their refractive indices  $n(\phi_0, \omega) = n(\phi_0, 2\omega)$ , which in the three-dimensional case is determined by birefringence and dispersion of the crystal. If the matching direction does not coincide with the optical axis, the interaction length will be limited to the divergence of waves of the first and second harmonics due to birefringence. Therefore, to obtain an effective nonlinear interaction it is preferable to use a 90-degree matching which gives no birefringence and in the three-dimensional case is reached by temperature tuning.

In optical waveguides, the refractive indices have increments  $\Delta n_a$  and  $\Delta n_e$ relative to the substrate. If these increments exceed dispersion of the refractive indices,  $n_{0} - n_{20}$  at the frequencies of first and second harmonics, then the  $n_{\omega} - n_{2\omega}$  can be compensated by mode dispersion. Isotropic media can well be used in this case, too. In the case of 'weak' waveguides in which the increment of the refractive index of the waveguiding layer is much less than the refractive index of the substrate  $(\Delta n \ll n_2)$ , phase matching is only due to birefringence. The use of mode dispersion widens significantly the region of phase matching. This can be readily seen from Fig.5.19 which shows possible positions of mode indicatrices at frequencies of the first and second harmonics in an anisotropic waveguide in a negative crystal. The regions which can contain indicatrices of ordinarily and extraordinarily polarized modes are dashed, and the overlap of these regions determines the range of possible matching. For each pair of modes, phase matching occurs at a certain angle at which mode indicatrices intersect. Varying the depth, shape of the profile or increment of the refractive index of a waveguide, we can vary the matching angles of nonlinear mode interaction. It should be noted that to perform such variations one should know the dependence of phase characteristics of a waveguide on its structure parameters and be able to control them during waveguide manufacturing. For



**Fig.5.19** Indicatrices of ordinary and extraordinary polarisation modes in LiNbO<sub>3</sub> (Zolotov et al 1979).

Ti-diffused waveguides in LiNbO<sub>3</sub>, the angles of possible mode matching lie within the range  $\phi \approx 75-90^{\circ}$ , that is, a 90-degree matching can be attained without temperature tuning.

#### 5.3.2 Overlap of fields of interacting modes

Phase matching in an optical waveguide is not a sufficient condition for obtaining an effective nonlinear conversion. The decisive role is played by the degree of overlapping of optical fields of interacting modes which is characterized by the overlap integral

$$I = \left(\int_{-\infty}^{0} Y_{\omega}^{2}(y)Y_{2\omega}(y)dy\right)^{2} / \left(\int_{-\infty}^{0} Y_{\omega}^{2}(y)dy\right)^{2} \left(\int_{-\infty}^{0} Y_{\omega}^{2}(y)dy\right)$$
(5.43)

where  $Y_{\omega}(y)$  and  $Y_{2\omega}(y)$  is the transverse distribution of mode fields at a frequency of the first and second harmonics. The overlap integral enters in the expression for the efficiency of second harmonic generation (derived for the case of phase matching in the plain wave approximation (Zernika and Midwinter 1973; Conwell 1973):

$$\eta = P_{2\omega} / P_{pum} = th^2 \left\{ \left( 8\pi^2 d / \lambda n \right) \left( 8\pi P_{pum} I / cnW \right)^{1/2} L \right\}$$
(5.44)

where d is a nonlinear coefficient,  $P_{pum}$  the pumping power,  $P_{2\omega}$  the second harmonic power, L the interaction length,  $\lambda$  the pumping wavelength, n the refractive index of the substance, W the beam width in the waveguide plane.

As is seen from the expression (5.41), the overlap integral depends on the field distribution of mode of both harmonics, which are very difficult to find for diffused waveguides since their profiles are not known in advance, but even if they were known, it is not always that there exists an analytic solution of the wave equation for them. If LiNbO<sub>3</sub> is used, the situation becomes even more complicated because an anisotropic crystal and waveguides have different profiles for ordinary and extraordinary polarizations. Moreover, in Ti-diffused waveguides of LiNbO<sub>3</sub> a waveguide forms not only due to Ti diffusion into a crystal, but due to a reverse diffusion of Li<sub>2</sub>O as well. These processes have different kinetics, and therefore the waveguide profile for extraordinary polarization is complex.

The method developed by Zolotov et al (1977) was used to determine  $Y_{\omega}(y)$ and  $Y_{2\omega}(y)$ . This method permits determination of the characteristics (including mode fields and dispersion dependences) of diffused waveguides with any profile of refractive index distribution. The method is based on approximation of the unknown waveguide profile by the functions that allow obtaining solutions of the wave equation in an analytic form. In Ti-diffused waveguides of LiNbO<sub>3</sub> (Y-cut), the profile of the transverse distribution  $n_0(y)$  for ordinary polarization is defined by the combination of a smoothly sewed parabola and exponent (5.40).



Fig.5.20 Overlap integrals for different interactions versus dimensionless thick-ness  $\alpha$  of a waveguide (dashed line corresponds to thickness of sample under investigation) (Zolotov et al 1979).

The overlap integrals  $I_{1m}$  (m = 1,2,3,4) for the interaction o + o = e were calculated using the obtained mode field distributions in a Ti-diffused LiNbO<sub>3</sub> waveguide. The dependences of  $I_{1m}$  on the value of dimensionless thickness  $\alpha = (2n_1^0 \Delta n_0)^{1/2} ka^0$  for typical parameters of the Ti-diffused waveguide (see Table 5.6) are shown in Fig.5.20. The calculations did not make allowance for insignificant variations of the structure parameter ratios c/a, h/a with varying  $\alpha$  since they did not practically affect the character of the dependences of the overlap integrals  $I_{1m}(\alpha)$ . The overlap integrals  $I_{nm}$  of modes in thicker waveguides ( $\alpha > 6$ ), where n > 1, is not considered since in these waveguides phase matching is attained for higher modes only (m > 3), and therefore the overlap integrals are small.

An analysis shows that for optimization of second harmonic generation in T-diffused waveguides, from the viewpoint of the overlap integral of interacting modes one should choose not very thick ( $\alpha \approx 3$ ) waveguides with the use of lower mode interaction.

#### 5.3.3 Angular matching

Second harmonic generated using a waveguide obtained by thermodiffusion of Ti into the Y-cut of LiNbO<sub>3</sub>. The waveguide mode spectrum  $(n_m^*)$  was measured on a goniometer by radiation output through a photoresistive grating  $(\lambda = 0.3462 \ \mu\text{m})$  deposited on the surface (Zolotov et al 1976). The results are shown in Fig.5.21. Modes  $H_1-H_4$ ,  $E_1$  and  $E_2$  were excited in a waveguide at a wavelength  $\lambda = 0.53 \ \mu\text{m}$  and modes  $E_1$  and  $H_1$  at a wavelength  $\Delta = 1.06 \ \mu\text{m}$ . Figure 5.22 presents indicatrices of refractive indices of waveguide modes at the frequencies of first and second harmonics. Phase matching conditions are only met for the following o + o = e type interactions:

 $\begin{array}{rcl} {\rm E_1} & (1.06) & \to & {\rm H_2} & (0.53), \\ {\rm E_1} & (1.06) & \to & {\rm H_3} & (0.53) \\ {\rm E_1} & (1.06) & \to & {\rm H_4} & (0.53). \end{array}$ 

The indicatrix of the mode  $H_1$  does not intersect the indicatrices of of modes of first harmonic, and therefore the phase matching for  $H_1$  is unattainable.



**Fig.5.21** Distribution of refractive indices and optical fields for ordinary and extraordinary waves of diffused waveguides: a)  $\lambda = 1.06 \ \mu m$ , b)  $\lambda = 0.53 \ \mu m$  (Zolotov et al 1979).



The profiles of refractive index distribution for ordinary and extraordinary polarizations, which were respectively characterized by the parameters  $n_i^o = 2.2335$ ,  $\Delta n_o = 0.0035$ ,  $a_o = 4 \ \mu m$ ,  $(c/a)_o = 0.7$ ,  $h_o = 1.5 \ \mu m$ ,  $n_2^e = 2.2308$ ,  $\Delta n_e = 0.015$ ,  $a_e = 14 \ \mu m$ ,  $(c/a)_e = 0.97$ ,  $(b/a)_e = -0.63$ ,  $h_e = 8.5 \ \mu m$  were found for the investigated waveguide on the basis of the obtained spectra  $n_{\pm}^{**}$ .

The mode fields of the investigated waveguide (Fig.5.21) were obtained and the overlap integrals  $I_{1m}$  (m = 2,3,4) were determined using the profiles. The integral  $I_{12}$  is maximum and close to the optimum value (Fig.5.20), and therefore



Fig.5.23 Theoretical (dashed line) and experimental (solid line) dependences of effective SHG on the pumping power (experimental) points correspond to CW laser pumping ( $\Delta$ ), a pulsed laser pumping in free generation regime (O) a pulsed Qswitching, ( $\bullet$ ) (Zolotov, et al, 1979).

the conversion  $E_1(1.06) \rightarrow H_2(0.53)$  was used. Pumping was realized by YAG:Nd<sup>3+</sup>-lasers operating in pulsed and non-stop regimes. A light beam was fed into (and out) with the help of rutile prisms in the direction of matching, the beam width being  $\approx 100 \ \mu m$ .

The efficiency of second harmonic generation as a function of pumping power is given in Fig.5.23. The maximum conversion efficiency was obtained through pumping of  $\approx 1$  kW and made up 16%.

The dependence of the efficiency of nonlinear conversion on the pumping power (see Fig.5.23) was noticeably overestimated in calculations as compared with experimental values which were saturated already for  $\approx 16\%$ . Such a difference is explained by nonuniformity of the waveguide over thickness ( $\Delta a \approx 0.1 \mu m$ ) and by the refractive index inhomogeneities, induced by second harmonic radiation, which were observed at a pumping power of  $\approx 1 kW$ . So, a further increase in the nonlinear conversion efficiency was due to the improvement of the waveguide surface quality as well as to the heightening of the threshold of the occurrence of optical inhomogeneities.

The dependence of second harmonic power on the angle between the pump-



Fig.5.24 Angular dependence of the output second harmonic power in a diffused waveguide (Zolotov et al 1979).

ing wave propagation direction and the optical axis of the crystal (Fig.5.24). The figure shows that this curve is nonsymmetric relative to the central maximum (the interaction  $E_1 \rightarrow H_2$ ) since its left side is overlapped by the maxima corresponding to the interactions  $E_1 \rightarrow H_3$  and  $E_1 \rightarrow H_4$ . The relative height of the maxima is in satisfactory agreement with the values of the overlap integrals. The width of the central maximum was four times the theoretical value, which is explained by inhomogeneity of the waveguide.

# 5.3.4 Temperature matching

Figure 5.25 shows the experimental setup used by Uesugi and Kimura (1976). The fundamental-frequency laser beam at a wavelength of 1.064  $\mu$ m, generated by a cw Nd:YAG laser, was fed into a single-mode fibre with a ×20 microscope objective. The core dimension of the fibre was equal to 5.5  $\mu$ m and the index difference  $\Delta n$  between the core and clad was 0.25%. The fibre was then butt-joined to a LiNbO<sub>3</sub> waveguide with a manipulator. Single-mode launching with a coupling loss as low as 1.4 dB was prepared with the butt-joined procedure. The LiNbO<sub>3</sub> optical waveguide was mounted on a copper block whose temperature was controlled with a thermoelectric element. The optical waveguide and the copper block were kept in a dry-nitrogen gas ambient to prevent water-vapour condensation. The waveguide temperature was measured at the crystal surface by a copper-constantan thermocouple (Uesugi et al 1976).

The three-dimensional LiNbO<sub>3</sub> optical waveguide was fabricated by Tiin-diffusion into a *c*-plate of LiNbO<sub>3</sub> crystal at 1050°C for 20 h. The index difference  $\Delta n$  was 0.002–0.003 and the core dimension was about 5 µm. The waveguide length was 1 cm. The refractive-index distribution was assumed to be Gaussian. It was estimated, from light transmission experiments, that the extraordinary refractive-index difference between the core and substrate is larger than that of an ordinary wave. This is attributed to Li<sub>2</sub>O out-diffusion during the fabrication process (Noda et al 1975). The guide can support only dominant TE<sub>00</sub> and TM<sub>00</sub> modes at 1.064 µm, and up to third-order modes at 0.532 µm.

Figure 5.26 shows the second harmonic power versus fundamental frequency power under a phase matched condition described in the sequel. Experimental results coincide with those shown by the solid line with a slope of 2. The





Fig.5.26 Dependence of second harmonic power on fundamental frequency power under phase-matching condition (Uesugi and Kimura 1976).

fundamental-wave polarization corresponds to the TE (ordinary) wave, and the generated second-harmonic wave is found to be linearly polarized with TM (extraordinary) polarization, which is induced by the second-order non-linear tensor element  $d_{31}$ . Optical damage was not observed in the experiment up to about 3 mW fundamental input.

The phase matching condition is satisfied by using the temperature dependence of LiNbO, birefringence. Figure 5.27 shows the temperature dependence of the harmonic power. In this measurement, the crystal was cooled at first to -29°C and the temperature was raised at a rate of about 1°C/min. Photographs showing typical near-field patterns of the second harmonic waveguide modes are depicted in Fig.5.27. The peaks at -2 and 15°C correspond to the second harmonic  $TM_{00}$  and  $TM_{20}$  modes, respectively. The peak at 10°C is estimated, from the near-field pattern, to be Cherenkov radiation. The Cherenkov radiation is generated when the nonlinear polarization propagation constant is larger than that of the harmonic wave in the bulk crystal (Tien et al 1973). For 2 mW fundamental frequency input power in the TE<sub>m</sub> mode, the conversion efficiency at -2°C was 1.5×10<sup>-4</sup>. A conversion efficiency as high as 0.1 is expected for an 1.4 W input. The conversion efficiency, calculated on the bulk-crystal data, is 3.1×10<sup>-4</sup> for a 2 mW fundamental plane-wave input, which is confined in a 5×5-µm cross-section for the length of a cm. The difference between the experimental and calculated values may be due to fractional spatial overlap of the nonlinear polarization and the harmonic waveguide mode, waveguide loss, and insufficient coherent interaction length between the fundamental and harmonic waves. The generated second harmonic light was easily observed on a screen and at the waveguide end surface with a naked eye.

The conversion efficiency of second harmonic power in the optical waveguide is proportional to the square of the overlap integral between the field distribution of the fundamental and second harmonic waves. The overlap integral is the largest when the fundamental and second harmonic waves are both in the dominant  $TE_{00}$  and  $TM_{00}$  modes, respectively. The harmonic  $TM_{10}$  mode was hardly observed. The  $TM_{20}$  mode was weaker than the dominant mode. The phase matching temperature of the LiNbO<sub>2</sub> optical waveguide depends



Fig.5.27 Harmonic power temperature dependence. Insetted photographs show typical nearfield patterns of second harmonic waveguide modes (Uesugi and Kimura 1976).



**Fig.5.28** Calculated phase-matching temperature difference between  $TM_{oo}$  and  $TM_{20}$  of a three-dimensional LiNbO<sub>3</sub> optical waveguide. Fundamental frequency mode is assumed to be  $TM_{oo}$ . The experimental temperature difference is shown on the ordinate. The waveguide height *b* is estimated to be about 5  $\mu$ m from an interference fringe measurement (Uesugi and Kimura 1976).

on the composition of  $\text{Li}_2\text{O}$  and  $\text{Nb}_2\text{O}_5$  and on waveguide dispersion. It is also affected by the pyroelectric effect when the crystal temperature is swept. However, the phase matching temperature difference  $\Delta T$  between the second harmonic dominant  $\text{TM}_{00}$  mode and the higher  $\text{TM}_{20}$  mode are insensitive to the composition and pyroelectric effect. Figure 5.28 shows the calculated temperature difference  $\Delta T$  as a function of the waveguide height *b*. Here it is assumed that the index profile is a step distribution over the cross-section. The propagation constant is calculated according to Marcatili's approximation (Marcatili 1969). Sellmeier's equation was used to express the temperature and wavelength dependence of refractive indices. Figure 5.28 serves to express several aspect ratios (*a/b*). The solid line corresponds to the refractive index difference  $\Delta n = 0.0025$ . The experimental result shown in Fig.5.27 is equal to  $\Delta T = 17^{\circ}$ C. LiNbO<sub>3</sub> has a pyroelectric coefficient as large as  $4 \times 10^{-9}$  C/cm<sup>2</sup> C at 25°C. When the crystal temperature is raised by 1°C and the spontaneous polarization remains uncompensated, the electric field along the *c*-axis becomes 1.67 kV/cm. This electric field induces birefringence, which corresponds to a temperature change of 0.4°C. In this experiment, the observed phase matching temperatures are higher than real phase matching temperatures, due to the pyroelectric effect. It was observed that when the crystal temperature is swept from high to low, the phase matching temperature is lower than that in the opposite situation. The hysteresis seems to result from the pyroelectric surface charge compensation. The pyroelectric effect could be avoided if a *b*-plate crystal with short-circuited electrodes on *c*-surfaces were used.

# 5.3.5 Second-harmonic generation in a waveguide with periodically domain-inverted regions

Second-harmonic generation (SHG) that uses a quasi-phase matching (QPM) in LiNbO<sub>3</sub> optical waveguide with periodically domain-inverted regions(PDR waveguide) is a promising approach (Lim et al 1989 (a)). Such waveguides possess a high power density and a large nonlinear coefficient. However, since the QPM condition is very difficult, the high-conversion experiments were made arranging suitable periods of domain-inverted regions precisely or using a tunable laser for the fundamental wave (Lim et al 1989 (b)).

Shinizaki et al (1991) described a self-quasi-phase-matched SHG that uses a PDR waveguide. The fundamental wave satisfying the QPM condition was generated by an LD (laser diode) which was lased by a feedback waves from the PDR waveguide. As the optical refractive index of the domain-inverted regions is slightly higher than the undoped region, the periodical domaininverted regions act as a distributed Bragg reflector (DBR). As the period of the domain-inverted regions was designed to satisfy the QPM conditions and the high-reflectance conditions of the quasi-phase matched fundamental wave, the LD was lased at the wavelength satisfying the QPM condition.

In the experimental arrangements, shown in Fig.5.29, the PDR waveguide and the LD with antireflection coating facets are optically connected by singlemode fibre (SMF). Periodical domain-inverted regions were formed by Tidiffusion. The Ti layer evaporated on a c-cut LiNbO, substrate was patterned by the lift-off technique. The Ti layer was 5 nm thick and the Ti lines were 4 um wide. Heat treatment consisted of a 2 h ramp up from room temperature to 1050°C and 1 h soak at 1050°C; after this the furnace was turned off. The domain-inverted period was  $\Lambda = 13 \ \mu m$ . The optical waveguide was fabricated to overlap perpendicularly on the periodical domain-inverted grating. The waveguide (6 µm wide, 2 mm long) was fabricated by proton-exchanged process (see Chapter 1). The LD was lased by feedback waves from the PDR waveguide. The period of domain-inverted regions, acting as DBR, is 13 µm. If the effective guide index for the radiated wave at 1.327 µm is equal to 2.195, the high reflectance condition is satisfied. When rgw LD lased at 1.327 µm in wavelength, the second-harmonic (SH) wave was observed. The SH spectrum which was measured is shown in Fig.5.30. The wavelength of the SH wave is 662.4 nm, which corresponds to the half wavelength of the fundamental wave. The



**Fig.5.29** Experimental arrangement of the self-QPM SHG. The SHG device is composed of PDR waveguide on the +c facet of the lithium niobate wafer. LDs with an antireflection coating facet are optically connected to the SHG waveguide by single-mode fibre (Shinozaki et al 1991).



FIg.5.30 SHG spectrum from the PDR waveguide. The fundamental wave was generated by the InP/ InGaAsP LD with AR-coated facets (Shinozaki et al 1991).

normalized SH conversion efficiency was 4.1%/W cm<sup>2</sup>.

The QPM conditions are satisfied if the half-period of domain-inverted regions,  $\Lambda/2$ , is equal to odd times of the coherence length. The coherence length  $\ell_c$  is given by

$$\ell_c = \lambda / 4 \left[ n(\lambda/2) - n(\lambda) \right], \tag{5.45}$$

where  $\lambda$  is the wavelength of the fundamental wave in vacuum,  $n(\lambda)$  is the optical index for wavelength  $\lambda$ . The condition for QPM is

$$k_2 - 2k_1 - 2\pi(2m - 1) / \Lambda = 0, \tag{5.46}$$



Fig.5.31 Length of domain inverted regions ( $L_c$ ) in first order of QPM and the half periods of 43rd order of DBR ( $L_w$ ) versus the fundamental wavelength. These lines intersect at 1.327 µm in fundamental wavelength, 6.5 µm in  $L_c$ or  $L_w$  (Shinozaki et al 1991).

where *m* is positive integer, and  $k_1$  and  $k_2$  are the wave vectors for the fundamental and SH waves, respectively. Then the period of the domain-inverted regions,  $\Lambda$ , is given by  $\Lambda = 2 (2m-1) \ell_c$  if the  $\Lambda$  satisfies the QPM condition given as equation (5.46). The periodical domain-inverted regions act as DBR. If the period  $\Lambda$  is designed to satisfy the high reflectance of the fundamental wave, the QPM condition is satisfied. That is, if the LD with an antireflectioncoated facet is lased by the feedback waves from the periodical domain-inverted regions, the radiated wave satisfies the QPM condition. The self-QPM conditions are as follows

$$\Lambda = 2(2m-1)\ell_c = p\lambda/2n(\lambda), \tag{5.47}$$

where p is positive integer. Figure 5.31 shows the relationships given by equation (5.47), the length of the domain-inverted regions,  $L_c$  ( $= \ell_c$ ), in the first order of QPM (m = 0) and the half-period of 43rd order of DBR (p = 43),  $L_w$  [=  $p\lambda/4n$  ( $\lambda$ )], against the fundamental wavelength. The dispersion function of the proton-exchanged LiNbO<sub>3</sub> material is given by n ( $\lambda$ ) =  $n'(\lambda)$  + 0.05 (De Micheli et al 1983), where  $n'(\lambda)$  is an optical index dispersion of congruent LiNbO<sub>3</sub>. These two lines intersect at 1.327 µm in fundamental wavelength, 6.5 µm in  $L_c$  or  $L_w$ , as shown in Fig.5.31. In the experiment, the wavelength of the fundamental wave was 1.327 µm, the half period of DBR,  $\Lambda/2$ , was 6.5 µm. The allowance of the DBR period  $\Delta\Lambda$  is equal to 0.039 µm. It is very difficult to design and fabricate a domain-inverted region to achieve a high SH conversion efficiency.

# 5.3.6 Effect of proton exchange on the nonlinear optical properties

Proton exchange using benzoic acid has been shown to be accompanied by a substantial reduction in the electro-optic coefficient (Becker 1983; Yan 1983); some decrease in the nonlinear optical coefficient (d) has also been observed (Suhara et al. 1989; Cao et al. 1991). Limited recovery of an electro-optical coefficient and a non-linear optical coefficient occurs under thermal annealing (Cao et al, 1991; Suchoski et al, 1988). Laurell et al (1992) have reported a 30-fold reduction in the optical nonlinearity for LiNbO<sub>3</sub>, they found that the optical nonlinearity cannot be effectively restored by thermal annealing. Bortz et al (1992) have measured the  $d_{33}$  nonlinear coefficient in protonexchanged LiNbO<sub>3</sub> using angle-depending reflected SHG and observed a reduction to  $\leq 1\%$  of the bulk LiNbO<sub>3</sub> value.

Recently, an improved proton exchange source using pyrophosphoric acid has been implemented because of its higher boiling temperature (300°C) and low vapour pressure. Low-loss (0.5 dB/cm) waveguides have been prepared in LiNbO<sub>3</sub> and LiTaO<sub>3</sub> using pyrophosphoric acid and efficient blue-light generation has been achieved (Mizuuchi et al.1991) However, the effect of the proton exchange process using pyrophosphoric acid on the nonlinear optical coefficient is not known. Hsu et al., (1992) reported the effect of the proton exchange process carried out using benzoic acid and pyrophosphoric acid on nonlinear optical properties of LiNbO<sub>3</sub> and LiTaO<sub>3</sub> and recovery of the nonlinear coefficient under thermal annealing. The nonlinear optical coefficient was evaluated using a reflection technique.

X-cut and Z-cut LiNbO<sub>3</sub> and LiTaO<sub>3</sub> crystals were used in this study. Waveguides were prepared by proton exchange in benzoic acid and in pyrophosphoric acid  $(H_4P_2O_3)$  with a heating rate of 10°C/min and cooling rate of 20°C/min.

If the incident beam makes an angle  $\theta_i$  with the surface normal, has a polarization angle  $\varphi$  with respect to the normal to the plane of incidence, and has an intensity *I*, then the nonlinear polarization for Z-cut LiNbO<sub>3</sub> with the Y-axis perpendicular to the plane of incidence can be written as (Dick et al. 1985)

$$\begin{split} P_x^{\text{NL}} &= I \Big( d_{31} f_z f_x \sin^2 \varphi \sin 2 \theta_i - d_{22} f_x f_y \cos \theta_i \sin 2 \varphi \Big), \\ P_y^{\text{NL}} &= I \Big[ d_{22} \big( f_y^2 \cos^2 \varphi - f_x^2 \cos^2 \theta_i \sin^2 \varphi \big) + f_y f_z d_{31} \sin \theta_i \sin 2 \varphi \Big], \\ P_z^{\text{NL}} &= I \Big[ d_{31} \big( f_x^2 \cos^2 \theta_i \sin^2 \varphi + f_y^2 \cos^2 \theta \big) + d_{33} f_z^2 \sin^2 \theta_i \sin^2 \varphi \Big], \end{split}$$

where  $d_{ij}$  are nonlinear coefficients and  $f_i$  are linear Fresnel coefficients. The measured intensity of the *s*- and *p*-polarized SHG in reflection (neglecting birefringence) is proportional to nonlinear polarization.

Figures 5.32 and 5.33 show results of such measurements at 1064 nm and theoretical calculations. The ratio of  $d_{33}/d_{31}$  and  $d_{22}/d_{31}$  was obtained as 6.2 and -0.30 by fitting the theoretical results with experimental data. These values are slightly different from the published values (7.0 and -0.53 from Nishihara et al 1989), but there appears to be quite a variation in the literature data (Yariv 1984).

Results of d-coefficient measurements at fundamental wavelengths of 532 nm for proton-exchanged LiTaO<sub>3</sub> using benzoic acid and pyrophosphoric acid are presented in Table 5.7. The incident beam powers used were below threshold for photorefractive effects to be observed as no change in signal was observed even for 1 h exposure to the incident beam. The shape of the pattern is related to the structural symmetry of the crystal and of the surface. The large scatter in the experimental data at the incident *p*-polarized light on *X*-cut crystal occurs because of possible small misalignments of the crystal.



**Fig.5.32** Variation of SHG intensity with incident polarization angle for a Z-cut LiNbO<sub>3</sub> crystal with the X axis perpendicular to the plane of incidence. Crosses are experimental points and the solid line is from theoretical calculations for (a) *p*-polarized and (b) *s*-polarized output beams (Hsu et al 1992).

**Fig.5.33** (right) Variation of SHG intensity with incident polarization angle for X-cut  $\text{LiNbO}_3$  crystal with the Z axis perpendicular to the plane of incidence. Crosses are experimental points and the solid line is from theoretical calculations for (a) *p*-polarized and (b) *s*-polarized output beams (Hsu et al 1992).

In situ measurement of recovery of  $d_{33}$  was made under thermal annealing. The saample was located in a heating furnace and the SH signal was continuously monitored whilst the sample was maintained at a temperature of 310°C. Figure 5.34 shows the recovery of the SH signal as a function of time. No recovery is seen for the initial 30 min during which the furnace was heated up from room temperature to the final annealing temperature (310°C). There is quick recovery of  $d_{33}$ , which begins at approximately 1.25 h into the annealing process, which saturates to a value of approximately 50% of the blank LiNbO<sub>3</sub> value.

Becker (1983) has shown that a proton exchange process using benzoic acid gives rise to a considerable reduction, by a factor of 2.7, in the electro-optic coefficient. If the nonlinear response is purely a result of electronic polarizations, the electro-optic and *d* coefficients are proportional (Yariv 1984), and any decrease in the electro-optic coefficient is necessarily accompanied by a corresponding decrease in *d*. However, the electro-optic coefficient for LiNbO<sub>3</sub> is known to have contributions form ionic polarizations. Such polarizations have no effect upon the SHG process. Hence, it is possible for the electrooptic and SHG processes to be affected differently by proton exchange. Suhara et al. (1989) reported a 50% reduction in the *d* coefficient at 1064 cm for proton exchange in benzoic acid. Similarly, Cao et al. (1991) have reported a 40% reduction, however annealing restored the *d* coefficient to 90% of the bulk value. In the experiments at 532 nm, Laurell et al. (1992) find that the optical nonlinearity cannot be effectively restored by thermal annealing. Bortz et al. (1992) suggest that the difference between their results and those reported **Table 5.7** Measured values of *d* coefficient for *x*-cut *p*-exchanged LiNbO<sub>3</sub> and LiTaO<sub>3</sub> relative to the blank crystal. Measurement error is  $\pm$  10%. Annealing temperature 350°C

	Proton exchange	LiNbO <sub>3</sub> , % recovery of $d_{33}$ compared to blank LiNbO <sub>3</sub>				npared	LiTaO <sub>3</sub> , % recovery of $d_{33}$ compared to blank LiTaO <sub>3</sub>	
Annealing time	time (h)	Üh	1 ከ	3 h	7 h	17 h	0	1 h
	0.5	0%	52%	51%	59%	54%		
	1		No recovery observed No recovery observed					
	1.5						69%*	56%*
	0.5	No recovery observed						
	1	No recovery observed					39%**	0%**

proton exchanged at 200°C

\*\* at 230°C



**Fig.5.34** Variation of SH signal with annealing time for an *x*-cut  $LiNbO_3$  sample that was proton-exchanged in benzoic acid for 0.5 h at 180°C. Annealing temperature was 310°C (Hsu et al 1992).

by Cao et al. (1991) is due to neglect of the reflected second-harmonic field on both the  $d_{33}$  discontinuity at the film-substrate interface and angular dependence of the non-linear polarization. The results reported by Hsu, et al. (1992) indicate that LiNbO<sub>3</sub> samples proton-exchanged for 0.5 h at 180°C showed some recovery of the nonlinear coefficient, whilst samples that were protonexchanged for 1 and 1.5 h did not show any measurable recovery under the thermal annealing conditions used.

The proton exchange process followed by annealing may produce higher lattice disorder at the top surface, which could explain why it is possible to see some waveguide SH conversion even though the nonlinear coefficient is degraded.

In contrast to LiNbO<sub>3</sub>, LiTaO<sub>3</sub> showed only partial loss of optical nonlinearity measured at 532 nm upon *p*-exchange using either pyrophosphoric acid or benzoic acid. Thermal annealing produced only small loss in nonlinearity of LiTaO<sub>3</sub> *p*-exchange in benzoic acid. Complete loss of nonlinearity was observed in the case of pyrophosphoric acid. These results also differ from annealing results for LiNbO<sub>3</sub> where some recovery of the optical nonlinear coefficient was observed. The LiTaO<sub>3</sub> index increases after annealing while the LiNbO<sub>3</sub> index decreases. Increase in the index may cause some distortion in the structure, which can affect the SH signal. To understand the degradation mechanism, structural characterization of proton-exchanged and annealed LiNbO<sub>3</sub> and LiTaO<sub>3</sub> is ongoing.

# 5.3.7 Sum-frequency generation in waveguides

There has been recent increased interest in compact short-wavelength light sources with the objective of realizing output powers in the mW range based on diode lasers. One of the most promising techniques to do this is to use nonlinear frequency upconversion in QPM waveguides (Lim et al. 1989; van der Poel et al. 1990; Mizuuchi, et al. 1991). By far the most widely used nonlinear process is second-harmonic generation (SHG) since only one light source is required. An alternative to SHG is sum-frequency generation (SFG), especially when fine tuning of the generated wavelength is required or fundamental light source for SHG is difficult to find. SFG can also be combined with SHG in such a way that two IR light sources generate three visible wavelengths simultaneously (Yamamoto et al. 1991). Waveguide SFG has been reported using birefringence phase-matching (Useugi et al. 1978). Cherenkov radiation (Sanford and Robinson 1989; Laurell et al. 1990). A major drawback with all these experiments has been the low-output powder obtained.

Laurell, et al., (1992) reported efficient SFG in segmented KTP waveguides (Bierlein et al. 1990) using QPM (van der Poel et al. 1990).

Two conditions have to be fulfilled to obtain quasi-phased-matched SFG, energy conservation

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} - \frac{1}{\lambda_3} = 0 \tag{5.48}$$

and momentum conservation,

$$\frac{N(\lambda_1)}{\lambda_1} + \frac{N(\lambda_2)}{\lambda_2} - \frac{N(\lambda_3)}{\lambda_3} + \frac{m}{\Lambda} = 0$$
(5.49)

where  $\lambda_1$  and  $\lambda_2$  are the fundamental wavelengths,  $\lambda_3$  the SF wavelength,  $N(\lambda)$  is the effective mode index at the corresponding wavelengths, and *m* and  $\Lambda$  are the order and the period of the QPM structure, respectively.

A 4.5 mm-long flux-grown z-cut KTP sample was masked with a titanium film with rectangular openings for ion exchange to form the waveguide in the x-direction. The sample was then end polished and immersed for 45 min in a 98 mol% RbNO<sub>3</sub>: 2 mol% Ba(NO<sub>3</sub>)<sub>2</sub> molten salt bath at 330°C for simultaneous ion exchange and domain reversal. The waveguides investigated on the sample were 4  $\mu$ m wide and has periods of 3, 4, 5 and 6  $\mu$ m. For these periods, the ratio between the exchanged and unexchanged regions was 2/1, 3/1, 4/1 and 5/1 respectively. These periods were chosen to give up



**Fig.5.35** Tuning curve for the sum frequency generation vs fundamental wavelengths in waveguides with (a)  $3 \mu m$ , (b)  $4 \mu m$ , (c)  $5 \mu m$  and (d)  $6 \mu m$  periods (Laurell et al 1992).

converted light from near UV to blue-green by first order (m = 1) QPM.

To analyze the nonlinear properties of the waveguide, two independently tunable Ti-sapphire lasers were used. The laser system consisted of an Ar ion laser which pumped two cw Ti:sapphire lasers to generate tunable radiation between 730 and 1070 nm. The radiation from lasers was combined using a birefringent beam splitter and used as the fundamental wavelengths for the sum-frequency generation experiment. The waveguides on the sample were first investigated in SHG experiements where the laser wavelength was tuned over the phase-matching peak and the SH intensity recorded. The wavelength of the fundamental and the SH wave was measured with a wavemeter and a monochromator, respectively, and the powers were measured with calibrated detectors. From the width and shape of the SH curves were of high homogeneity, so the full waveguide length was utilized for conversion. Both the mode at the fundamental and at the SH wavelengths were approximately circular in al waveguides. At degeneracy, the second-harmonic wavelength was 394, 425, 454, and 480 nm for the 3, 4, 5 and 6 µm period waveguides, respectively. A good agreement was obtained between the measured and the calculated phase-matching wavelengths.

The SHG measurements were followed by SFG experiments. Here, both lasers were first tuned to SHG and then the wavelength of the lasers tuned in opposite directions, maintaining the phase mathcing. The tuning range was limited by the wavelength region the lasers could cover. Figure 5.35 shows the tuning curve for the four periods. The accuracy (0.1 nm) of the monochromator was found to be insufficient to use in the plot of the tuning curve, and the SFG wavelength was therefore calculated from the fundamental wavelengths, Eq.(5.48). The largest tunability of the SF wavelength was 3 nm observed

for the 5 µm-period waveguide. This waveguide also gave the highest output power in the blue, 2.7 mW of the 454 nm radiation, generated with 149 mW at 942 nm and 106 mW at 875 nm coupled through the waveguide. The fundamental powers measured at the output of the lasers were approximately three times higher. Normalized at the output of the waveguide, this corresponds to a conversion efficiency of 84% W<sup>-1</sup>cm<sup>-2</sup> or 17%/W. The highest efficiency for SFG was 112%W<sup>-1</sup>cm<sup>-2</sup>, obtained with the 4 µm-period waveguide, but lower total-fundamental powers in this case resulted in lower SGF output.

# 5.4 Second harmonic generation in the form of Cherenkov radiation

Enhanced flux density of light and large interaction length explain an increasing interest in nonlinear optical effects in optical waveguide structures for realizing efficient functional devices (Stegeman and Stolen 1989). Among these effects, the second-order nonlinear effect permits observing frequency conversion such as SHG and sum- or difference-frequency generation. In particular, SHG in optical confinement structures such as optical fibres channel waveguides will find many applications that require a miniaturized visible light source with light coherence. An efficient guided-wave SHG device structure which can extract blue light has been demonstrated. It employs a Cherenkov radiation scheme to achieve phase matching at a 0.84 µm wavelength from a GaAs laser diode (Taniuchi and Yamamoto 1987, Sanford and Connors 1989), and blue power on the order of 1 mW from 50 to 100 mW input has been demonstrated with a 6 mm device length (Taniuchi and Yamamoto 1987). In this scheme, the phase matching condition between the fundamental (pumping) guided mode and the second harmonic radiation mode can be automatically satisfied by adjusting the waveguide parameters (Tien et al 1970). However, the second harmonic power generated depends on the parameters in a critical fashion, and therefore it is of great importance to determine optimum parameters for the guide structure, crystalline orientation, refractive index, etc. (Sanford and Connors 1989; Hayata and Koshiba 1989; Hayata et al 1990).

Another possibility for performance of Cherenkov type SHG devices by means of tailoring the transverse (y direction) nonlinear susceptibility profile in the guiding region is examined. More radiation efficiency is expected as a result of the increasing overlap between the nonlinear polarization wave (dividing source) and the generated SH wave (driven field) in analogy with the beam steering technique in a phased-array antenna. Linear and domaininverted (poled) channels embedded in a nonlinear substrate are considered, and the SHG efficiency for each case is compared with that for a conventional nonlinear channel without domain inversion (Sanford and Connors 1989). Numerical results obtained by a wave optics treatment show that a remarkable enhancement of the SHG is realizable, particularly with a domain-inverted channel.

The schematic illustrations are shown in Fig.5.36, where n is the builtin refractive index dependent on the wavelength and d is the thickness of the channel. In Fig.5.36b the value of the channel width (W) is implicitly included through an application of an effective refractive index approximation

λ, μm	n <sub>2x</sub>	n <sub>2y</sub>	n <sub>2z</sub>	n <sub>3x</sub>	n <sub>3y</sub>	n <sub>37</sub>
0.84 LD pumping	2.373	2.293	2.373	2.25	2.17	2.25
1.06 YAG pumping	2.352	2.276	2,352	2.232	2.156	2.232
λ,μm	n' <sub>2x</sub>	n' <sub>2y</sub>	n' <sub>22</sub>	$n_{3x}^{\prime}$	n' <sub>3y</sub>	n' <sub>3z</sub>
0.84	2.601	2.491	2.601	2.411	2.301	2.411
1.06	2.514	2.425	2.514	2.324	2.235	2.324

**Table 5.8** Parameters of LiNbO<sub>3</sub> waveguides  $n_1 = n_{11} = 1.0$  (air)

(Hayata and Koshiba 1989; Hayata and Sugawara 1990). Hayata and Yanagawa 1990) thus consider the slab waveguide as shown in Fig.5.36b in what follows.

Here, care must be taken to employ this reduced geometry. Algebraic manipulation of Maxwell's equations with nonlinear polarization yields the following equation for the y-polarized (TM) mode (Hayata and Koshiba 1989):

$$4 \overline{\gamma} \varepsilon_{y}^{\prime^{-1}} \frac{\partial h_{x}'}{\partial \overline{z}} = \frac{\partial}{\partial \overline{y}} \left( \varepsilon_{z}^{\prime^{-1}} \frac{\partial h_{x}'}{\partial \overline{y}} \right) + 4 \left( 1 + \varepsilon_{y}^{\prime^{-1}} \overline{\gamma}^{2} \right) h_{x}' + j Z_{0}^{-1} \left( 2 \overline{\gamma} \, \hat{y} [\varepsilon']^{-1} [d'] e^{2} + \frac{\partial}{\partial \overline{y}} \left( \hat{z} [\varepsilon']^{-1} [d'] e^{2} \right) \right),$$
(5.50)

where  $h'_x$  is the slowly varying envelope of the lateral component of the SH magnetic field,  $e = [e_x, e_y, e_z]^T$  is the pumping electric field (*T* stands for transposition),  $\overline{\gamma} = j\beta/k_0$ ,  $\beta$  is the propagation constant,  $k_0$  is the free-space wave number,  $\overline{y} = k_0 y$ ,  $\overline{z} = k_0 z$ ,  $Z_0 = 337 \ \Omega$ ,  $[\varepsilon']$  is the linear relative permittivity tensor whose diagonal elements are  $\varepsilon'_x, \varepsilon'_y$ , and  $\varepsilon'_z$  [d'] is the second-order nonlinear optical tensor, and the prime and the hat denote respectively the quantity for the second harmonic wave and a unit vector. In the derivation of equation (5.50), the slowly varying envelope approximation has been employed and pump depletion has been neglected, that is,  $\partial e/\partial \overline{z} = 0$ .

Consider the Z-cut LiNbO<sub>3</sub> (c axis/y axis) as a substrate material. Waveguide parameters used in the analysis are as in Table 5.8; the explicit value of [d'] has been obtained from the Table shown by Yarif A.Yehp (1984). The TM<sub>0</sub> mode is considered as a pumping condition onto z = 0.

As a nonlinear susceptibility profile in the film (|y| < d/2; the film centre is at y = 0), Hayata et al (1990) considered three cases: (A) linear film, *i.e.* all the elements in [d'] vanish anywhere in the film; (B) nonlinear film with the same sign of nonlinear susceptibility in the substrate; and (C) domaininverted film with opposite sign of nonlinear susceptibility in the substrate, that is,  $[d']_{film} = -[d']_{substrate}$ . Occurrence of the cases considered above depends on the actual fabrication process. For instance, case (A) may be observed in



Fig.5.36 Schematics of problem (a) 3D view; (b) side view (Hayata et al 1990).



**Fig.5.37** Total SH power versus guide thickness ( $w = 2.0 \ \mu$ m). Solid, dotted and dashed lines indicate domain-inverted (case (C)), linear [case (A)], and nonlinear channel without domain inversion [case (B)], respectively. (a)  $\lambda_0 = 0.84 \ \mu$ m, (b)  $\lambda_0 = 1.06 \ \mu$ m (Hayata et al 1990).

a situation in which degradation (damage) of the ideal crystalline structure in the channel cannot be ignored. On the other hand, case (C) can be realized by adequately poling a certain kind of ferroelectric crystal such as Z-cut LiNbO<sub>3</sub> (Lim et al 1989; Thaniyavarn and Miyazawa 1979).

Figure 5.37 shows a comparison between these cases, where the SHG efficiency is defined by  $P'/P^2$  with P' as the second harmonic power and P as the pumping power. These results are obtained from a stationary analysis  $\left[\frac{\partial}{\partial z} = 0\right]$  in equation (5.50), with which the optimum geometry of the guide is predictable. The validity of this approach has already been ensured in the literature (Noda et al 1975; Tien et al 1973) through a careful comparison with the results obtained by a more involved nonstationary analysis and with experimental results. The sharp minima occurring in the figures are due to interference effects across the film for grazing angles of the second harmonic wave (Tien et al 1973). It is evident from these results that the utmost second harmonic power is obtainable in case (C). In the vicinity of the optimum geometry,  $d = 0.35 \ \mu\text{m}$  for  $\lambda_0 = 0.84 \ \mu\text{m}$  and  $d = 0.53 \ \mu\text{m}$  for  $\lambda_0 = 1.06$ um, the efficiency of case (C) is an order of magnitude greater than that of case (B) (*i.e.* the order of 10 mW from a 50-100 mW input with  $\lambda_n = 0.84$ µm and a 5-10 mm device length). This significant enhancement of the SHG can mathematically be attributed to the increasing overlap quantified by the integral of the product between the nonlinear polarization term and the desired second harmonic mode propagating along the Cherenkov angle. In order to provide physical insight into the results, Fig.5.38 gives schematic illustrations for the relationship between the nonlinear polarization wave (source) and the

second harmonic wave (radiation). It should be noted that 1) a considerable part of the nonlinear polarization wave penetrates the substrate as a result of the extended evanescent tail of the pump field and 2) the wavefront of the second harmonic wave tilts with the Cherenkov angle against that of the nonlinear polarization (z-direction). As is seen from Fig.5.38, second harmonic waves generated at different locations (one in film the other in substrate) along the y-direction add partially out of phase and cancel each other in the conventional geometry (Fig.5.38a), whereas they add in phase by making the film domain inverted (Fig.5.38b). The linear film (case (A)) is intermediate between the two extreme cases. It is interesting to note that one can find an analogous mechanism to beam profiling in a phased-array antenna system in which the relative phase difference between adjacent dipole elements is tailored so that interference is in phase for the desired direction. This fact indicates that the use of homogeneously domain-inverted channel is very effective in enhancing Cherenkov-type SHG efficiency in LiNbO<sub>3</sub> optical waveguides.

# 5.5 Electro-optic effects in optical waveguides

Electro-optic coefficients in waveguides of solid solutions of lithium niobatetantalate were measured by the interferentional method. The scheme of measurements is presented in Fig.5.39.

A coherent light beam is separated by a separation prism into two independent light beams each of which is fed into a light guide by the prism



**Fig.5.38** Schematic illustrations for explaining the enhanced SHG, NLP and SH are abbreviations for nonlinear polarization and second harmonic, respectively. (a) Conventional geometry (case B), (b) domain-inverted film (case C) (Hayata et al 1990).



**Fig.5.39** Schematic illustration of a device for measuring electro-optic coefficients: 1) radiation source; 2)  $\lambda$ /4-plate; 3) focusing lens; 4,6) input-output prisms for optical radiation; 5) investigated sample; 7) objective; 8) screen; 9) microscope; 10) control electrodes; 11) mounting.

method. One of the beams is led in the interelectrode gap of the system of coplanar electric guides (10), the second beam propagates outside the electrode system in the direction parallel to the first one. The output of optical radiation from the specimen is realized using the second prism (6). The collecting lens (7) provides convergence of both light beams in the plane (8) in which interference is observed.

When control voltage is applied to the electrodes, the refractive index of the mode changes by a quantity  $\Delta n$  proportional to the electro-optic coefficients of the light guide material and to the applied voltage. This leads to a change of the optical pathlength of the light beam propagating in a film near the electrodes. This change is equal to  $\Delta L = \Delta nl$ , where *l* is the length of the control electrodes, which in turn induces a displacement of the interference pattern by M fringes ( $\Delta L = M\lambda$ ).

In the case of linear electro-optic effect, the change of the refractive index of a given mode,  $\Delta n$ , is given by the expression

$$\Delta n = n^3 r_{ij} E_z / 2 \tag{5.51}$$

where *n* is the refractive index of the film for a given light mode,  $r_{ij}$  is the electro-optic coefficient,  $E_z$  is the longitudinal component of the electrode field in the film.

In the case  $d_{el} \gg h$ ,  $d_{el} > 2\sigma$ , where  $d_{el}$  is the interelectrode distance, h is the film thickness,  $\sigma$  is half width of the light beam, the quantity  $E_z$  is determined by the expression  $E_z = 2U/\pi d_{el}$  (U is the voltage applied to the electrodes). Since the quantity  $\Delta n$  can also be expressed as  $\Delta n = M \times \lambda/\ell$ , the value of the electro-optic coefficient is determined by the expression

$$r_{ii} = \pi M \lambda \, d_{el} \,/ \, \ell n^3 U \tag{5.52}$$

When light propagates in the x-direction along the Y-cut of  $\text{LiNb}_{1-y}\text{Ta}_{y}\text{O}_{3}$ , we have  $r_{ii} = r_{33}$ .

The voltage applied to the structure of electric guides is changed in the course of measurements, and the displacement M is controlled visually. If to a measured M there corresponds the applied voltage U, then knowing the light wavelength  $\lambda$ , the electrode length  $\ell$ , the interelectrode gap  $d_{el}$  and the effective refractive index of the mode, one can calculate the electro-optic coefficient using the expression (5.52).

Investigations have shown that in epitaxial structures that have not been made single-domain the electro-optic coefficients are small, but the sensitivity of the device was not high enough to measure these coefficients. After films are polarized (and thus become single-domain), their electro-optic coefficients increase significantly. Measurements of the coefficient  $r_{33}$  for a number of single-domain specimens have shown that its value varies within the range  $(15-24)\times10^{-12}$  m/V, which is close to the value of this coefficient for lithium tantalate.

The dependence of induced birefringence on the electric field  $(3 \times 10^2 - 5 \times 10^5 \text{ V/m})$  is linear and is indicative of a high polarization of heteroepitaxial films.

The electro-optic constants of proton-exchanged LiNbO<sub>3</sub> optical waveguides were measured by Minakata et al (1986) by means of phase modulation technique (Yariv 1985) 633 nm laser light was fed into the waveguide from the end facet, and the propagation mode was the fundamental TM-like mode. The relevant electro-optic constant was  $r_{33}$ . The modulation characteristics were measured by applying a 50 MHz sinusoidal signal via electrodes. The modulation spectra were detected by using the scanning Fabry-Perot resonator. Figure 5.40 shows the experimental results. The power ratio (or peak value ratio) of the first side band frequency to the carrier frequency was given by the Bessel function as a parameter of a modulation index u as follows:

$$\frac{\text{Power of 1st side band freq.}}{\text{Power of carrier freq.}} = \left(\frac{J_1(u)}{J_0(u)}\right)^2, \ u = \frac{n_e^3 r_{33} \ell V \Gamma}{\lambda d} \propto r_{33} V,$$
(5.53)

where  $\lambda = 633$  nm and  $\ell$  and d are coplanar electrode length and the gap, respectively.  $\Gamma$ , determining the modulation efficiency, is given by the following equation (Minakata 1978):

$$\Gamma = \iint E^2(yz)E_z(yz)dy\,dz \Big/ E_0 \iint E^2(yz)dy\,dz \cong \frac{E_G}{E_0}$$
(5.54)

where E(yz),  $E_z(yz)$  are an optical electric field and an applied electric field of the z component, at point P(y z) in the crystal; x, y, z are the coordinates. A guided wave propagates along the x-axis. The y- and z-axes are parallel and perpendicular to the substrate surface, respectively.  $E_0 = V/d$  and  $E_G$  is the average applied electric field via electrodes, which is calculated by the successive over relaxation method (Minakata et al 1978). The calculated G value was 0.32 for the test samples. In Fig.5.40, open circles are experimental data, the three solid lines, as a parameter of  $r_{33}$ , are theoretical curves. When  $r_{33} = 3.3 \times 10^{-12}$  (m/V), the theoretical values are in good agreement with the experimental ones. Thus it is clear that the value of  $r_{33}$  reduced to one-tenth in comparison with the virgin crystal.

Figure 5.41 shows the relationship between the Li%, the strain  $\Delta c/c$ , the measured  $r_{33}$ , and the  $\Delta n_{e}$  quoted from DeMicheli et al (1983). It is clear that strain  $\Delta c/c$  and  $\Delta n_{e}$  are reduced, and  $r_{33}$  is increased with an increase in Li%.

# 5.6 Light resistance of light guides

The optical quality of light guides is basically characterized by the optical loss factor and by radiation resistance. The radiation resistance must be taken into account in work with lasers of power higher than 1 mW. At this and higher power, its density in the light guide can reach the value of  $10^5-10^6$ 





**Fig.5.41** Relation between Li%, strain  $\Delta c/c$ , measured  $r_{33}$ , and  $\Delta n_{2}$  quoted from De Michelli et al 1983 (Minakata et al 1986).

W cm<sup>-2</sup> at which nonlinear and thermal effects affect the refractive indices of the material.

As is known, the damage of the surface of oxygen-containing crystals (LiNbO<sub>3</sub>, LiTaO<sub>3</sub>, BaTiO<sub>3</sub>, etc.) possesses some specific features: the damage is due to accumulation which lowers the light resistance of the surface and leads to a characteristic temperature dependence of the damage threshold. Zverev et al (1977) hypothesized the existence in LiNbO<sub>3</sub> of an oxygen-depleted absorption surface layer containing two types of traps linked with oxygen vacancies and with reduced Nb<sup>4+</sup>. An increase of absorption, from pulse to pulse, in the surface layer is due to accumulation of electrons on shallow traps whose absorption cross-section is larger than that of deep traps. An increase of light resistance of the surface with increasing specimen temperature is caused by the emptying of shallow traps for the time between laser pulses due to their thermoionization.

Investigations of radiation resistance of LiNbO<sub>3</sub> films and their substrates have shown that the mechanisms of their damage are absolutely identical. A Q-switched garnet-neodymium laser ( $\lambda = 1.06 \mu m$ , pulse duration 10

No.	Material	Break-down threshold (GW/cm <sup>2</sup> )	Accumulation threshold (GW/cm <sup>2</sup> )	Maximum number of flares
1	LiNbO,	3.2	0.45	10-15
2	LiTaO,	12	4.1	8–12
3	Linbo,/Linbo	6.5	0.25	50
4	LiNbO <sub>3</sub> /LiTaO <sub>3</sub>	6.1	1	30–40
5	LiNbO <sub>3</sub> (Fe)/LiT	°aO <sub>3</sub> 4.5	0.3	50

Table 5.9 Damage threshold values for surfaces of epitaxial LiNbO, films on different surfaces

ns) was used as a radiation source. The radiation was focused by a shortfocus lens (f = 11 mm) onto film specimens under investigation. The neck diameter was 15 µm. The laser operated in a single-pulse regime, pulse recurrence rate being equal to 2 Hz (Khachaturyan 1980).

Table 5.9 presents averaged values of the damage threshold, as well as the damage threshold values determined by the accumulation effect both in films themselves and in their substrates.

It was established that the threshold intensity of the damage of a lithium niobate film increased several times as compared with a bulk crystal. Break-down thresholds of a homoepitaxial LiNbO<sub>3</sub> film and of a heterolayer on LiTaO<sub>3</sub> do not differ much, and an introduction of iron impurity (up to 0.5 at. %) lowers the threshold by  $\approx 30\%$ .

Analysis of the results obtains shows that the the breakdown threshold of lithium niobate films is determined by perfection of the specimen structure and surface. Zverev et al (1977) reported the presence in lithium niobate crystals of a surface absorption layer of about 2  $\mu$ m thick, but they did not describe the methods of sample surface preparation. As is known, mechanical polishing of the surface leaves a damaged layer of about 1  $\mu$ m. Mirror-smooth surfaces of epitaxial films require no additional treatment. The increase in the damage threshold of the film is evidently due to the lack of a damaged surface layer on it.

Investigation of the effect of laser radiation ( $\lambda = 1.06 \mu m$ ) upon lithium niobate films has shown that at 'under-threshold' radiation intensity a highly dense ( $\approx 10^9$  W cm<sup>-2</sup> at the cluster centre and  $10^5$ - $10^6$  W cm<sup>-2</sup> on the periphery) cluster of microdomains occurs at a place of irradiation. When the irradiated positive z-plane undergoes selective etching, because of their high density the etching holes merge to form a typical tracery. Cluster areas decrease with decreasing light intensity. These variations in the cluster areas are however insignificant, and the diameter of the cluster is mainly determined by the diameter of the focal spot.

This phenomenon can be interpreted as follows (Levanyuk and Osipov 1975; Holman and Gressman 1982). Levanyuk and Osipov (1975) have shown the possibility of a photoinduced change of spontaneous polarization in ferroelectrics. When a region of a crystal is exposed to light, polarization reversal in this region leads to the appearance of a depolarizing field which, acting on free carriers that interact under impurity ionization, causes the occurrence of free charge at the boundaries of this region. As soon as the light is off, the photoexcited states of impurities relax. The space charge may remain for a long time since its only clean-out channel in a low-conductivity crystal is a temperature-induced ejection of carriers trapped on donors into the conduction band, which is hardly probable at a low temperature. Thus, when a specimen is exposed to light, spontaneous polarization is reversed and the charge distribution over the bulk is 'frozen' after the light is off. This mechanism does not obviously correspond to the observed phenomenon since the occurrence of microdomains implies a decrease of the total polarization in the exposed region, and the 'frozen' volume charge is close to zero. Moreover, the polarization reversal region must be strictly limited by the exposed region, whereas the radiation-induced microdomains are also observed outside the exposed region.

The mechanism of occurrence of microdomains due to elastic strain is obviously closer to the real process. As mentioned above, local strain in a specimen leads to the appearance of a tense region of microdomain clusters. When a highly intense laser beam is used, a thermal shock is observed. Because of a short radiation treatment time and a small heat transfer coefficient, this thermal shock causes a high local tension and, as a consequence, the appearance of microdomains. The geometry of the observed pattern is determined by the crystal symmetry. The cluster area is determined by the diameter of the light spot. This limitation is not strict, and at high radiation intensities the tension near the spot may prove sufficient for the occurrence of microdomains.

We have carried out comparative studies of optical damage of single-mode light guides formed using autodiffusion, metal diffusion, ion-exchange doping (Goncharenko 1967) and liquid-phase epitaxy. The output power was measured as a function of exposure time and of the input light intensity. The latter was varied within the range of 0.5+7 mW, and the observation time reached 200 h. All the specimens exhibited lowering of the output signal with saturation. The dependence of output light intensity on the input intensity is depicted in Fig.5.42 which shows that Ti:LiNbO<sub>3</sub> light guides possess the lowest optical strength and epitaxial ones the highest.

Experiments on light resistance suggest that the optical strength of light guides is first of all determined by the concentration of traps the role of which can be played by oxygen vacancies in the crystal lattice (particularly for light guides formed in a vacuum). Important is also the impurity ionization energy variations in a crystal, trap depth and equilibrium concentration shift in oxidized and reduced forms of active impurities. Judging by the results reported by Holman and Gressman (1982), the low light resistance of Ti:LiNbO<sub>3</sub> is explained by the appearance in the light guide structure of a special type of traps for photo-induced electron-hole pairs occurring due to an uncompensated charge exchange under the Nb<sup>5+</sup> $\rightarrow$ Ti<sup>4+</sup>substitution in the crystal lattice sites in the course of diffusion.



**Fig.5.42** Dependence of the power loss T, at the saturation level, on the input power  $P_{in}$  in light guides: 1) LiNbO<sub>3</sub>:Ti; 2) LiNbO<sub>3</sub>:TI; 3) outdiffused; 4) epitaxial.

# 5.7 Photorefractive properties of light guides

The interferometric method is used to examine photorefractive properties of epitaxial structures, namely, refractive index changes under the action of photoactive radiation.

This method is realized in the same scheme as the study of electro-optic properties of films (see Fig.5.39). The part of the waveguide between electrodes is exposed to laser radiation perpendicular to the plane of the wave guide layer. Argon ( $\lambda = 488$ , 514 nm; P = 6 W) and krypton ( $\lambda = 647$  nm; P = 8 W) lasers were used for photorefractive recording.

The values of induced refractive index change  $\Delta n_e(t)$  were determined from the number of displaced fringes M in the interference pattern given by the formulae

$$\Delta l = \Delta n l \text{ and } \Delta L = M \times \lambda \tag{5.55}$$

The estimates of the maximum light-induced refractive index change show that within the experimental error ( $\approx 20\%$ ) the  $\Delta n_e$  value is practically independent of the wavelength of recording light and  $(\Delta n_e)_{max}$  makes up  $\approx 2 \times 10^{-3}$ . The limiting value ( $\Delta n_e$ )max does not practically depend on the Li (Nb, Ta)O<sub>3</sub> film composition either.

The change  $(\Delta n)$  max is a result of electro-optic effect in the bulk crystal. From its value one can estimate the stationary value of the internal electric field:

$$E_{\rm st} = \beta(\Delta n_e)_{\rm st}; \ \beta \equiv 2/n_e^3 r_{33}.$$
(5.56)

Using the values  $n_e = 2.187$ ,  $r_{33} = 2 \times 10^{-11}$  m/V and  $(\Delta n_e)_{st} = 2 \times 10^{-3}$  at the wavelength  $\lambda = 632.8$  nm, we obtain the lower estimate of the external electric field in the film,  $E_{st} \sim 191$  kV/cm which agrees with the values obtained for bulk materials (188 kV/cm for LiNbO<sub>3</sub> and 250 kV/cm for LiTaO<sub>3</sub> (Schwarz 1986)).

The obtained  $E_{st}$  value is indicative of a high electric resistance of the investigated epitaxial structures and is not limiting since the value  $(\Delta n_e)_{max}$  that can be reached in experiments is restricted by electric breakdowns along the film surface (which leads to a spontaneous lowering of  $\Delta n_e$ ).

Assuming the light absorption coefficient  $\alpha$  layer in the epitaxial layer to be close to the absorption coefficient in the substrate ( $\alpha < 5$  cm<sup>-1</sup> for  $\lambda = 488$  nm and  $\alpha < 1$  cm<sup>-1</sup> for  $\lambda = 647$  nm), one can estimate the photorefractive sensitivity  $S_{m}$ :

$$S = \Delta n_e / W = \Delta n_e / \alpha I t \tag{5.57}$$

where W is the absorbed energy, I is the incident light intensity, t is the exposure time.

Substituting typical experimental values  $(\Delta n_e) \approx 2 \times 10^{-4}$  for  $\lambda = 488$  nm,  $I \approx 400$  W/cm<sup>-2</sup> and t = 15 min, we obtain

 $S \approx 1.1 \times 10^{-10} \text{ cm}^2/\text{J}$ 

The obtained value ( $\lambda = 0.488 \mu$ ) is an overestimation. Since for lithium niobate the boundary of fundamental absorption lies at  $\lambda \le 0.4 \mu m$  and for lithium tantalate for  $\lambda \le 0.3 \mu m$  (ed. by Shaskol'sky 1982), one may assume that a Li(Nb,Ta)O<sub>3</sub> film has, in fact,  $\alpha_{layer}$  ( $\lambda$ ) >  $\lambda_{substr}(\lambda)$  for > 0.3  $\mu m$ . The S values obtained for Li(Nb,Ta)O<sub>3</sub> films are in close agreement with

The S values obtained for Li(Nb,Ta)O<sub>3</sub> films are in close agreement with the values of photorefractive sensitivity of lithium niobate,  $S = 2 \times 10^{-8}$ , and lithium tantalate,  $S = 6 \times 10^{-11}$  cm<sup>2</sup>/J (Kuz'minov 1982), and indicate that the waveguide structures obtained possess higher optical resistance than lithium niobate structures.

#### 5.7.1 Holographic formation of gratings in optical waveguide layers

The formation of thick phase (Bragg) gratings in optical waveguides by electrooptic (Hammer et al 1973) or acousto-optic (Kuhn et al 1970) effects is well known. Such gratings may find application in integrated optics devices such as switches (Kenan et al 1974; Taylor and Yariv 1974), modulators (Taylor and Yariv 1974), mirrors, beam splitters, *etc.* Gratings that are formed photorefractively, that is, through changes in the index of refraction occurring when a material is illuminated with light capable of altering the distribution or magnitude of the polarizabilities of its constituents, appear to offer the following advantages: (*i*) the grating spacing can be small enough so that arbitrarily large diffraction angles can be achieved; (*ii*) the refractive index changes produced can be quite large, consequently efficient diffraction gratings are possible; and (*iii*) no external structures are needed and no operating power is required.

Wood et al (1975) have produced such gratings by intersecting guided coherent beams of 0.488- $\mu$ m wavelength in waveguides formed on the surface of LiNbO<sub>3</sub> crystals by effusion of lithium and in a waveguide formed on the surface of a LiTaO<sub>3</sub> crystal by in-diffusion of a vapour-deposited layer of Nb,

by which means a varying-composition layer of  $\text{LiTa}_{1-x}\text{Nb}_xO_3$  was formed. Forming the grating this way is much superior to using external beams intersecting at the waveguide layer. The principal advantages of using intersecting guides beams are that the available writing power densities are high, the proper grating orientation is achieved automatically, and the grating is located in the region of maximum energy density of the guided wave.

A schematic top view of the experimental arrangement used to write and detect the gratings is shown in Fig.5.43. The LiNbO<sub>3</sub> or LiTaO<sub>3</sub> slab and the rutile prism couplers are rotatable as a unit about the axis AA which lies in the slab. This degree of freedom is required for the adjustment of the coupling angle. The grating is written by the photorefractive effect utilizing the 0.488  $\mu$ m line on an argon-ion laser. The power density in the waveguide is estimated to be about 1 W/cm<sup>2</sup>. Writing times for the gratings were in the 1–10 min range, depending upon the iron content of the sample.

After the grating was written, mirrors  $M_1$  and  $M_2$  were used to independently adjust the direction and position of the 0.633 µm beam to maximize the amount of 0.633µm light diffracted by the grating. Since the acceptance angle of the grating is  $\approx 0.5$  mrad, this adjustment is critical.

The gratings in effused waveguides were done using Y-cut crystals of undoped  $LiNbO_3$  heated in oxygen to form Li-deficient surface layers with higher extraordinary refractive indices than the bulk. Such layers can be produced to support anywhere from one to several hundred TE modes; TM modes are not guided. While it was not difficult to form gratings in such layers, and while a diffraction beam could be observed, its intensity was very low. This appeared to result from the low maximum diffraction efficiency (generally under 1%) obtainable in undoped or very lightly doped LiNbO<sub>3</sub>.

The highest diffraction efficiency (defined as power coupled out in the diffracted beam divided by sum of powers coupled out in both the diffracted



**Fig.5.43** Schematic of apparatus used to write and detect gratings in a slab waveguide. The grating vector is parallel to the *c*-axis of the LiNbO<sub>3</sub> slab. All optical beam polarisations are parallel to the surface of the slab.  $P_{in}$  and  $P_{out}$  are prism imput and output couplers (Wood et al 1975).

and undiffracted beams) in an effused guide was obtained in a multimode guide in heavily iron-doped (1000 ppm in melt)  $LiNbO_3$ . An interference photograph showed that this guide had an overall extraordinary index change of about 0.004 and a diffusion length of about 140 µm; it should support around 60 TE modes at the 0.488 µm hologram writing wavelength (Kaminow and Carruthers 1973). A diffraction efficiency of 52% at 0.488 µm was attained.

Grating formation was also studied in a shallow guide produced by heating a LiNbO<sub>3</sub> plate for 14 min at 1118°C. Such a guide should support only about 5 TE modes at 0.633  $\mu$ m; individual modes could not be resolved experimentally. This plate was from a boule grown from a melt doped with just 50 ppm iron, and the maximum diffraction efficiency obtainable in the bulk sample (without the waveguide) for a grating written with 0.488- $\mu$ m light and read at 0.633  $\mu$ m was 2.4%. The maximum diffraction efficiency was obtained with the read-beam polarization parallel to the *c* axis, the same orientation as in the guide TE modes. The maximum diffraction efficiency at 0.633  $\mu$ m for a grating written with 0.488- $\mu$ m light in the waveguide was 3.1% greater than that obtainable in the bulk crystal. Neither the difference in grating thickness (extent in the direction of the incident beam) nor the difference in the angle between the writing beams is sufficient to account for the observed difference. Possibly the higher power density in the guided beam led to a higher maximum refractive index change.

Shallow waveguide layers with large index changes, supporting only a few modes, may be produced by diffusing Nb into  $LiTaO_3$  (see chapter 1).

TE modes propagating along the *a* axis were used to write (at 0.488  $\mu$ m) and read (at 0.633  $\mu$ m and at 0.488  $\mu$ m by blocking one write beam) a grating in the waveguide. An efficient grating with a period of 1.4  $\mu$ m formed readily despite the presumably unpoled state of the sample. The maximum diffraction efficiencies obtained were 28% at 0.633  $\mu$ m and 65% at 0.488  $\mu$ m. For comparison, no diffraction efficiency above 1.2% could be obtained at either wavelength for gratings formed throughout the bulk LiTaO<sub>3</sub> crystal, either with or without the infused Nb layer at the surface.

An alternative linear photorefractive technique is the use of short-wavelength light to form the holograms and long-wavelength light, for which the photorefractive sensitivity is negligible, as the operating wavelength. This technique is satisfactory only for simple plane-grating holograms since complex thick holograms suffer large losses in fidelity and efficiency if the read and write wavelengths differ.

A holographic writing technique which has the useful advantages of avoiding destructive readout, producing stable holograms, and retaining the low optical loss of out-diffused waveguides in undoped crystals is based upon the use of multiphoton absorption (van der Linde et al 1974) for initiating the photorefractive process. Veber et al (1977) have demonstrated that holograms may be recorded by a two-photon absorption process in out-diffused LiNbO<sub>3</sub> waveguides by intersecting two guided waves, and that the required energy and intensity are readily achieved in the waveguide using commercially available lasers. The absorption of a beam of light of intensity I (W/cm<sup>2</sup>) in a two-photon process is described by

$$dI = -\alpha_2 l^2(x) \, dx \tag{5.58}$$

where  $\alpha_2$  is the second-order absorption coefficient and x is depth in the crystal measured from the surface upon which the beam is incident. The index change associated with the photorefractive effect is proportional to the number of electrons excited into the conduction band. For the two-photon process, this number will be proportional to (1/2)N, where N is the number of photons absorbed per cm<sup>3</sup>. The index change is then

i

 $\Delta n = S(1/2N) \tag{5.59}$ 

where S is a proportionality constant characteristic of the material and the geometry. For an optically thin sample,  $\Delta n$  is not a function of x and

$$N(t) = -(\Delta I / \Delta x)(1 / hv)t = (\alpha_2 / hv)tI^2$$
(5.60)

where t is the time during which the sample is irradiated and hv is the photon energy. If the irradiation occurs in the form of M equal rectangular pulses of duration  $\Delta t$ , then

$$\Delta n = k I^2 M \Delta t \tag{5.61}$$

where all constants have been absorbed into k. The two-photon process is then indicated by a quadratic dependence of  $\Delta n/M$  upon I.

This quadratic dependence was observed using a Nd : YAG laser with an intercavity doubler which produced 140 ns pulses of 0.53 µ radiation. After reflection from a wedge beam splitter the laser output was prism coupled into an out-diffused waveguide in the surface of an undoped LiNbO, slab. The value of the induced  $\Delta n$  was monitored by measuring the diffraction efficiency of the holographic grating formed in the beam overlap region. The data shown in the log-log plot in Fig.5.44 clearly display the quadratic behaviour indicative of the two-photon effect. From the maximum power incident upon the coupling prism of 2 kW and estimates of the coupling efficiency and effective waveguide thickness, one can estimate a maximum power density of 106 W/cm<sup>2</sup> in the waveguide. Diffraction efficiencies of several percent were observed with no sign of saturation. Comparison of these results with the data (van der Linde et al 1974) obtained using the same wavelength but in a bulk configuration shows a far greater sensitivity for the waveguide case. The discrepancy is larger than can be accounted for by experimental errors or errors in estimating the power density in the waveguide. The discrepancy may be due to variations

Input power (µW)	Exposure time (s)	Energy density E in guide (J/cm <sup>2</sup> )	η	η/ <i>E</i> (cm²/J)	$\alpha S = \Delta n/E$ (cm <sup>2</sup> /J)
17	120	20	0.011	0.0052	1.3×10-?
120	20	24	0.1	0.013	3.0×10 <sup>-7</sup>
250	10	25	0.1	0.016	3.0×10-7

**Table 5.10** Diffraction efficiency  $\eta$  and photorefractive sensitivity  $\alpha S$  of planar Ti-diffused waveguides at 0.458  $\mu$ m (Glass, Kaminow, Ballman, Olson, 1980)



**Fig.5.44** Log–log plot of  $\Delta n$ /pulse versus power density for a grating written in an out-diffused LiNbO<sub>3</sub> waveguide with pulsed 0.53 µ radiation. The solid line has a slope of 2. The grating spacing is 0.55 µ (Veber et al 1977).

induced by the out-diffusion process or to other compositional differences in the samples used for the two sets of measurements.

# 5.7.2 Photorefractive effect in planar Ti-diffused guides

The formation of elementary holograms has been described above for outdiffused  $LiNbO_3$  waveguides (Glass et al 1980). A similar method is employed using a Ti-diffused planar guide. The technique involved coupling two beams into the planar guide, as shown in Fig.5.45 so that they form a thick hologram by means of the photorefractive effect. The magnitude of the index change can be measured from the diffraction efficiency of the hologram (Kogelnik 1969)

$$\eta = \sin^2(\pi \Delta \ell) / \lambda \cos \theta \tag{5.62}$$

where  $\ell$  is the interaction length and  $\theta$  is the angle between the two beams. The writing beams were coupled in and out of the waveguide using a single prism (Sarid et al 1978), and the diffraction efficiency was probed with a He-Ne beam by rotating the entire prism-waveguide assembly to obtain coupling at different wavelength.

Holograms could not be recorded at 0.633 µm, with 300 µW of optical



power. The results were the same within experimental errors at 0.515  $\mu$ m. Both the exposure and the diffraction efficiency could be measured with an accuracy of better than 5%, thus the major error lies in the estimate of the energy density in the guide. In Table 5.10 the energy density in the waveguide was estimated as follows. The width of the two beams was 0.3 mm, and the effective depth of the guide was taken to be 3  $\mu$ m. (Two modes could be launched in the guide.) At 0.458  $\mu$ m the total insertion loss of the entire prism-waveguide assembly was 15 dB (at 0.633  $\mu$ m, loss = 10 dB). This loss is considerably greater than that reported for optimized prisms (Sarid et al 1978) presumably because no special precautions were taken to optimize the taper between the prisms and guides for any wavelength. Glass et al (1980) assumed that 10 dB of the loss occurred at the input coupler giving an energy density in the guide of about 10<sup>4</sup> times the incident power. An error in estimating the coupling efficiency of  $\pm 5$  dB leads to an error in the estimated power density in the guide of a factor of 3.

The induced hologram was found to relax very rapidly after exposure. For this reason, long exposures were always found to be less efficient than short exposures for recording holograms. For short exposures the data in Table 5.10 gives

$$(\Delta n) / E = 0.3 \times 10^{-6} \,\mathrm{cm}^3 / J. \tag{5.63}$$

Using the value of  $\alpha = 0.08$  for  $\lambda = 0.633$  and 0.515 µm (Glass et al, 1980) the result is a photorefractive sensitivity of

 $S = (\Delta n) / (\alpha E) = 0.16 \times 10^{-5}.$  (5.64)

This result is even smaller than that obtained for the substrate crystal, and hence despite the experimental errors they provide conclusive evidence that Ti impurities do not contribute significantly to the photorefractive effect in  $LiNbO_3$  waveguides directly. The results of equation (5.63) and (5.64) are consistent with the interpretation that the photorefractive effect in Ti-diffused waveguides is due to residual  $Fe^{2+}$  impurities present in the LiNbO<sub>3</sub> substrate material before diffusion.

Fujiwara et al (1989) reported on a new novel method of quantifying the photorefractive sensitivity of Ti-indiffused LiNbO<sub>3</sub> waveguides. The proposed method is similar to the one by Becker and Williamson (1985) in using a waveguide Mach-Zehnder interferometer. By separating the irradiation light (including the index change) and probe light, the intensity and the wavelength of the irradiation light could be readily varied employing the same waveguide pattern. From measurements of the photorefractive sensitivity at various irradiation wavelengths, Fujiwara et al (1989) estimated the level of crosstalk degradation as a function of irradiation intensity and wavelength.

The waveguide pattern was designed and fabricated by Fujiwara et al (1989) as shown in Fig.5.46. It is basically a Mach-Zehnder (MZ) interferometer for the 1.3 µm wavelength in which the irradiation beam of wavelength  $\lambda_{ir}$  is fed into the upper arm. Light input from port A brought about a photoinduced index change and consequently an asymmetry of the optical path between the two interferometer arms. The phase retardation of the upper arm relative to that of the lower arm,

$$\Gamma = \frac{2\pi}{\lambda} \int_{0}^{L} \Delta n(z) \, \mathrm{d}z$$

caused the probe output to be modulated as

$$I_p(t) = I_p(0)\cos^2(\pi L \Delta n(t)/\lambda_p)$$
(5.65)

where <u>L</u> is the length of the interferometer arms,  $\lambda_p$  the probe wavelength, and  $\Delta n(t)$  the average index change

$$\overline{\Delta n}(t) = (1/L) \int_{0}^{L} \Delta n(z) \, \mathrm{d}z.$$

The probe light of 1.3  $\mu$ m was input from port B. Since optical waves of two wavelengths were mixed at output port C, the probe light was chopped at 270 Hz before entering port B and the probe output was measured by a lock-in amplifier placed after a photodetector. The probe light intensity was kept below 5  $\mu$ W to ensure that no photorefractive effect was caused by the probe (Fujiwara et al 1989). Port D monitored any temporal variation of the 1.3  $\mu$ m probe light due to input fibre-waveguide coupling.

In Fig.5.46, the waveguide width is 7  $\mu$ m and the angle  $\theta$  of waveguide bending is 1.7°. The length L of the interferometer arms is 16 mm.

Both the irradiation and probe beams were fed through optical fibres buttcoupled to input ports A and B. The quantities  $\Delta n_e$  and  $\Delta n_0$  can be determined separately by adjusting the input probe polarization to the TM and TE mode,


Fig.5.46 Configuration of the Tidiffused waveguide pattern fabricated in an LiNbO<sub>3</sub> substrate for the measurement of a photoinduced index change (Fujiwara et al 1989).

Fig.5.47 Typical time dependence of the probe output of the Mach–Zehnder interferometer after the onset of irradiation of wavelength 0.633  $\mu$ m (Fujiwara et al 1989).

respectively. The irradiation beam polarization was adjusted to be 45° from the optical axis of the substrate. The waveguides, designed to be single mode at  $\lambda = 1.3 \mu m$ , naturally support a few modes for  $\lambda = 0.63-1.06 \mu m$ .

A typical relation between probe output versus irradiation time t for  $\lambda_{ir} = 0.633 \ \mu\text{m}$  is shown in Fig.5.47. Since the MZ interferometer was initially symmetrical, the output  $I_p$  is at a maximum in the unirradiated state. In the figure, the intensity ratio of the first maximum and the first minimum corresponds to an extinction ratio of 18 dB, which was a typical level for all irradiation wavelengths. In the 'symmetric' Y branch in which the irradiation was fed into the upper arm, a 3 dB loss of the 1.3  $\mu$ m probe light was expected. Hence, unequal power in the two arms would limit the extinction ratio of the modulator to about 15 dB. However, since the irradiation in the upper branch induces an index change, the Y branch becomes asymmetric, reducing the branching loss from 3 dB. This optically induced asymmetry explains the extinction ratio higher than 15 dB. Further, the relatively high extinction ratio indicates that a spatially homogeneous index change was measured; scattering due to spatial inhomogeneity of index change was not appreciable.

A photoinduced index change of  $\Delta n \sim 10^{-5}$  was detected and a further improvement of the sensitivity should be feasible with design modifications such as modulating the probe light by an external field applied upon the lower arm of the interferometer.

Since the interferometer output can be expressed by equation (5.65), the observed temporal change of the output can be converted to the time evolution of  $\overline{\Delta n}(t)$ . For all wavelengths  $\lambda_{lr}$  and irradiation intensities  $I_{lr}$ , a good fit to an expression



**Fig.5.48** Photorefractive sensitivity *S* plotted as a function of irradiation intensity  $I_{\nu}$  for each wavelength (Fujiwara et al 1989).

$$\overline{\Delta n}(t) = \overline{\Delta n_s}(1 - e^{-t/\tau})$$

could be obtained, where the bar over n(t) denotes spatial averaging along the path  $I \rightarrow II \rightarrow III$ . The photorefractive sensitivity was defined as

$$S = \partial(\overline{\Delta n}(t)) / \partial(I_{i}t).$$

At the initial stage,

$$S(t \to 0) = \overline{\Delta n_e} / I_{\mu} \tau, \qquad (5.66)$$

where t is the irradiation time and  $\Delta n_s$  is the saturated index change. In obtaining  $I_{ir}$ , the waveguide was assumed to be uniformly illuminated inside the cross section of  $5 \times 10^{-7}$  cm<sup>2</sup> for all irradiation wavelengths. In determining the dependence of S on the irradiation intensity, the substrate was annealed at 180°C for 30 min after each measurement to erase the induced index change. The annealing temperature was found to completely revert the interferometer to a symmetric one.

The optical intensity dependence of S for each wavelength is shown in Fig.5.48. The irradiation intensity was measured at the arm of the MZ interferometer by cutback of the waveguide, and the spatially averaged irradiation intensity  $I_{ir}$  at the arm was calculated. The dependence of S on  $I_{ir}$  can be decomposed to the behaviour of  $\Delta n_s$  and  $\tau$  as is seen in equation (5.66). The  $\Delta n_s$  was found to be initially proportional to  $I_{ir}$  and then showed a slight saturation at higher  $I_{ir}$ , whereas the inverse time constant of buildup,  $1/\tau$ , was nearly constant up to  $I_{ir}$  of 40 W/cm<sup>2</sup> and then showed a sharp upturn at higher irradiation intensities (Izutzu et al 1982). In the first region where  $I_{ir}$  is small,  $\Delta n_s$  is proportional to  $I_{ir}$  while  $1/\tau$  is constant, rendering S to be nearly constant.

In the second region, the  $\Delta n_s$  vs  $I_{ir}$  relation deviates from linearity, while  $1/\tau$  is still constant, and therefore the ratio  $\Delta n_s/\tau$  gradually decreases with increasing  $I_{ir}$ . In the third region at still higher irradiation intensity levels, the sharp increase of  $1/\tau$  with  $I_{ir}$  predominates the behaviour of S ( $t \rightarrow 0$ ). A combined effect of the second and the third regions results in a dip in the three curves. The mechanism for the sharp increase of  $1/\tau$  is yet to be clarified.

In the intensity-independent region, S decreases with increasing wavelength for both TM and TE modes. The S for the TM mode,  $S_{TM}$ , is about three times greater than that for the TE mode for all  $\lambda_{ir}$  and  $I_{ir}$ . The ratio of the photoinduced phase changes for the TM and TE modes is  $\Gamma_{TM} n_e^3 r_{33} / \Gamma_{TE} n_0^3 r_{13}$ , where  $\Gamma_{TM}$  and  $\Gamma_{TE}$  are, respectively, the overlap integrals between the internally induced electric field and the TM and TE optical fields (Glass 1978). At 1.3 µm,  $n_e^3 r_{33} / n_0^3 r_{13}$  is about 3.2 (Holmes et al 1983). Although the overlap integrals could not at that stage be reliably estimated, taking the ratio  $\Gamma_{TM} / \Gamma_{TE} \approx 1.1$  accounts for the experimentally observed ratio  $S_{TM} / S_{TE}$  of 3.2–3.4.

### 5.7.3 Relaxation of index change

No relaxation of the induced index change was observed in bulk single-crystal Ti:LiNbO<sub>3</sub> over a period of days; the index change persists for a long time due to the high resistivity of crystals and the presence of deep trapping sites. In waveguides, on the other hand, the induced index change relaxes over a period of hours. The relaxation rate decreases with increasing time, as shown in Fig.5.49. The relaxation does not follow an exponential law or the sum of two exponentials.

This behaviour had been observed previously in the decay of X-ray induced centres in MgO. In that case the decay was shown to be hyperbolic not exponential. This behaviour occurs if thermally activated carriers have a high probability of being retrapped instead of recombining at the equilibrium sites (Searle and Glass 1968). In Ti-diffused LiNbO<sub>3</sub> the relaxation of the index change was found to be hyperbolic, *i.e.*  $\Delta n \sim 1/t$  (Glass et al 1980). A good fit to the experimental relaxation curve is shown in Fig.5.49. This behaviour



**Fig.5.49** Relaxation (at 300 K) of the induced refractive index change in planar LiNbO<sub>3</sub> waveguides. The points are calculated assuming a bimolecular decay  $\Delta n \sim \alpha/t$  (Glass et al 1980).

implies that the trapped carriers are in shallow traps (the nature of which is not known) and that probability of recombination at a similar trapping site is large compared with recombination at  $Fe^{3+}$  (excited  $Fe^{2+}$ ) centres. In any case the data do suggest a much lower density of deep trapping sites in the waveguides than in bulk crystals. Since it is known that  $Fe^{3+}$  ions are indeed deep traps in bulk LiNbO<sub>3</sub> crystals, the relaxation behaviour suggests a low density of  $Fe^{3+}$  ions in the Ti-diffused layers, that is, all unexpected Fe ions are in the reduced state. This would also account for a bimolecular relaxation if the density of  $Fe^{3+}$  ions.

It is probable that  $Ti^{4+}$  ions substitute for  $Nb^{5+}$  ions in the LiNbO<sub>3</sub> crystal in which case the Ti-ion site carries an effective negative charge. Compensation may be accomplished by reducing impurities such as  $Fe^{3+}$  to the bivalent state, *i.e.* the Ti in-diffusion tends to stabilize the reduced states of the impurities. The  $Fe^{2+}-Ti^{4+}$  complex is neutral if it compensates for a Li<sup>+</sup>-Nb<sup>5+</sup> pair. The reduced state of several ions ( $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Cu^{1+}$ ) is known to enhance the photorefractive effect in LiNbO<sub>3</sub> (Peterson et al 1971; Staebler and Phillips 1972).

Reduction of all multivalent impurities in the crystal is also likely to result in increased photoconductivity since it has been established that the free carrier mobility in Fe-doped LiNbO<sub>3</sub> single crystals is greatly increased in reduced crystals due to the reduction of the Fe<sup>3+</sup> trap density (Staebler and Phillips 1974). This fact may explain the high photoconductivity observed in Ti-diffused LiNbO<sub>3</sub> films compared with bulk crystals. It should be pointed out that in devices requiring an applied field, photoconductivity leads to space charge fields and index changes in the same way as the zero field photorefractive effect.

5.7.4 Photorefractive effect in annealed proton-exchanged LiNbO<sub>3</sub> waveguides Fujiwara, et al. (1992) presented a comparative study of the photorefractive effect in PE and APE LiNbO<sub>3</sub> waveguides at an irradiation wavelength  $(\lambda_{ir})$ of 488 nm. From a quantitative measurement of the temporal behaviour of the photoinduced index change due to irradiation at several intensities, the intensity dependence of the saturated index change as well as the build-up time constant in PE and APE LiNbO<sub>3</sub> waveguides are determined, and the photorefratory sensitivity in both waveguides is evaluated. The results indicate an increase in the saturated index change of the photorefractive effect due to annealing, a higher photorefractive sensitivity of APE waveguides than that of PE waveguides and a larger contribution of the dark conductivity to the photorefractive effect in the intensity range used in the experiments.

Seven micrometerwide PE and APE waveguides, sinlge mode at the wavelength of 1.3  $\mu$ m, were used in the modified Mach-Zehnder interferometer configuration. The waveguide pattern was delineated on an aluminium mask evaporated on the c face and LiNbO<sub>3</sub> substrate by etching. Proton-exchange was carried out in benzoic acid at 220°C for 88 min for PE and 20 min for APE LiNbO<sub>3</sub> waveguides. After removing the Al mask, the APE waveguides were formed by annealing at 350°C for 6 h.

By measuring the output intensity of the probe light during irradiation exposure, the authors obtained the time dependence of the photoinduced index change  $\Delta n(t)$ . Figure 5.50 shows the typical results for  $\Delta n(t)$  for irradiation intensities  $(I_{ir})$  of 65.4 and 105.3 W/cm<sup>2</sup> for APE LiNbO<sub>3</sub> waveguides. The above values of the intensity represent spatial averages across the waveguide cross-section, assuming uniform illumination and are estimated by taking into account the losses at the arm in the interferometer. The authors have used the values of  $7.0 \times 10^{-8}$  cm<sup>2</sup> for PE and  $2.7 \times 10^{-7}$  cm<sup>2</sup> and APE waveguide cross-sections in obtaining the irradiation intensity for all the experimental data. The build up of the index change shown in Fig.5.50 is exponential and is written as

$$\Delta n(t) = \Delta n_{\rm s} (1 - e^{-t/\tau}), \tag{5.67}$$

where  $\Delta n_s$  is the saturated index change, and  $\tau$  is the build-up time constant (Fujiwara, et al. 1989). The solid lines represent the fit of the data points to Eq.(5.67).

Based on the Glass model,  $\Delta n_s$  is proportional to the saturated space-charge field ( $E_s$  which is expressed as  $E_s = k \alpha I_{ir}(\sigma_d + \sigma_{ph})$  where k is the Glass constant,  $\alpha$  is the absorption coefficient, and  $\sigma_d$  and  $\sigma_{ph}$  are the dark and photoconoductivity respectively. Assuming that the photoconductivity is proportional to both the absorption and the irradiation intensity,  $\sigma_{ph} = a \alpha I_{ir}$ , the authors obtained

$$\Delta n_s(I_{ir}) = \frac{n_e^3 r_{33}}{2} \frac{k \alpha I_{ir}}{\sigma_d + a \, \alpha \, I_{ir}} = \frac{A \, I_{ir}}{1 + B I_{ir}},\tag{5.68}$$

where  $n_{1}$  is the extraordinary index,  $r_{13}$  is the electro-optic coefficient

$$A = n_e^3 r_{33} k \alpha / 2\sigma_d, \quad B = a\alpha / \sigma_d,$$

and a is a constant expressed as  $a = (e/hv)\mu\tau_0\phi$ , where e is the electron charge,



**Fig.5.50** Time dependence of refractive index change  $\Delta n(t)$  in APE LiNbO<sub>3</sub> waveguides for irradiation intensities of 65.4 and 105.3 W/cm<sup>2</sup> at an irradiation wavelength of 488 nm. Solid curves represent fit to Eq.(5.67) (Fujiwara et al 1992).

hv the photon energy,  $\mu$  the electron mobility,  $\tau_0$  the carrier lifetime and  $\phi$  the quantum efficiency. According to Eq. (5.68), in the lower intensity region where the dark conductivity is predominant, the saturated index change can be expressed approximately as  $\Delta n_s = AI_{ir}$ ; therefore, parameter A represents the response of the saturated index change in the lower intensity region dominated by the dark conductivity. In the high-intensity region, where the response is governed by the photoconductivity,  $\Delta n_s(\infty)$  approaches A/B, which is independent of both the irradiation intensity and optical absorption (Fujiawa et al 1989) and depends upon the ratio  $(r_{13}k/a)$  only.

On the other hand, the build-up time constant t can be expressed as  $\tau = \varepsilon_r \varepsilon_0 / (\sigma_d + \sigma_{ph})$ , where  $\varepsilon_r$  is the dielectric constant. The intensity dependence of  $1/\tau$  is given by

$$1/\tau = (1/\tau_d) + (a\alpha I_{ir} / \varepsilon_r \varepsilon_0), \qquad (5.69)$$

where  $1/\tau_d = \sigma_d/\varepsilon_r \varepsilon_0$ . Therefore, the intensity dependence of  $1/\tau$ , given by Eq. (5.69), yields the values of both dark-conductive  $(1/\tau_d)$  and the photo-conductive  $(a\alpha/\varepsilon_r \varepsilon_0)$  terms.

Moreover, if we write Eq. (5.69) as

$$1/\tau = \sigma_d (1 + BI_{ir}) / \varepsilon_r \varepsilon_0 \tag{5.70}$$

Fujiwara et al. (1992) have fitted the measured dependence of  $\Delta n_s$  on  $I_{ir}$  to Eq.(5.68) using A and B as adjustive parameters and the results are shown in Fig.5.51. The value of A is given in Table 5.11 for both PE and APE LiNbO<sub>3</sub> waveguides. In both cases, the saturated index change  $\Delta n_s$  varies linearly with intensity in the corner intensity region, and tends to deviate slightly from the linear behaviour in the higher intensity region. This almost linear behaviour indices that the dark-conductivity component is dominant in creating the space-charge field and the contribution of the photoconductivity is negligible. In other words, product  $BI_{ir}$  is still less than unity within the intensity range used in the experiments.  $\Delta n_s$  of APE LiNbO<sub>3</sub> waveguides is about eight times that of PE waveguides at irradiation intensity of up to 100 W/cm<sup>2</sup>. The almost linear behaviour of  $\Delta n_s(I_{ir})$  does not permit an accurate determination of B by the above fitting procedure.

Figure 5.51 also shows the fit of the intensity dependence of  $1/\tau$  to Eq.(5.69). From the intercept, the dark conductivity of the PE and APE waveguides is obtained, which is listed in Table 5.11. The ratio of the slope and the intercept of the  $1/\tau(I_{..})$  straight lines yields B. The values of B are listed in Table 5.11.

From Eqs. (5.68) and (5.70), the photorefractive sensitivity S (defined by  $S = \Delta n/I_{ir} \tau$ ) (Fujiwara et al 1989) is expressed as

$$S = n_e^3 r_{33} k \alpha / 2\varepsilon_r \varepsilon_0. \tag{5.71}$$

Figure 5.52 presents a plot of the dependence of irradiation intensity of  $\Delta n/\tau$  for PE and APE waveguides, and in the last column of Table 5.11 there is



**Fig.5.51** Intensity dependence of  $\Delta n_s$  and  $1/\tau$  for PE and APE LiNbO<sub>3</sub> waveguides at an irradiation wavelength of 488 nm. Solid and broken lines represent the best fit of the data to Eqs. (5.68) and (5.69), respectively.

**Fig.5.52** (right) Intensity dependence of  $\Delta n_s$  and  $1/\tau$  for PE and APE LiNbO<sub>3</sub> waveguides at an irradiation wavelength of 488 nm showing a linear behaviour. The slope of the lines gives the photorefractive sensitivity for the corresponding waveguide (Fujiwara et al 1992).

PE $0.88 \pm 0.04$ 1.5 $\pm 0.1$ 0.37 $\pm 0.08$ 2.6 $\pm 0.7$ 0.	
	.54 ± 0.01
APE $6.6 \pm 0.4$ $0.56 \pm 0.17$ $6.1 \pm 3.2$ $1.6 \pm 0.9$ $1.3$	.8 ± 0.06

Table 5.11 The values of parameters describing the photorefractive effect in PE and APE LiNbO, waveguides at an irradiation length of 488 nm (Fuyiwara et al 1992)

a list of values of the photorefractory sensitivity for PE and APE waveguides, obtained from the slop of two straight lines.

The effect of annealing on the photorefractive properties of proton-exchanged  $LiNbO_3$  waveguides will now be discussed. First of all, the parameters A increases by almost an order of magnitude as a result of annealing. This is caused by almost a factor of 3 increase in the  $r_{33}$  coefficient (Becker 1983) and a decrease in the dark conductivity by almost the same factor. While the reduced electro-optic coefficient in PE waveguides is attributed to the near-cubic symmetry of the proton-rich LiNbO<sub>3</sub>, the higher dark conductivity of PE LiNbO<sub>3</sub> waveguides may be a consequence of the presence of shallow donor levels (traps), probably resulting from the incorporation of protons at interstitial sites.

# 5.8 Energy loss in waveguides

# 5.8.1 Losses in Ti-diffused LiNbO, waveguides

An important consideration in the performance of any optical waveguide device is its insertion loss,  $L = -10 \log T$ , where T is the power transmission coefficient. A convenient method for obtaining the waveguide power attenuation coefficient a (in dB/cm) is to measure L as a function of guide length  $\ell$ . For a titanium-diffused LiNbO<sub>3</sub> strip guide, however, the problem is to change  $\ell$  without changing the coupling into and out of the guide through the end facets of the crystal. Polishing the ends without rounding requires great care; but cleaving has the potential for providing reproducible and rectangular ends with little difficulty (Hsu and Milton 1976). However, the cleaving method requires a special crystal orientation and, in addition, reflections from the parallel end facets lead to standing-wave behaviour that must be taken into account. Kaminow and Stulz (1978) described loss measurements in a cleaved crystal containing a 4-µm-wide single-mode Ti-diffused waveguide. In order to illustrate the isolation from metal electrodes provided by a dielectric buffer layer, the authors also measured a guide overcoated with a metal layer separated from guide by Al<sub>2</sub>O<sub>2</sub> or SiO<sub>2</sub>.

The experimental setup is illustrated in Fig.5.53. The power incident on the input microscope objective from the polarized He-Ne laser,  $P_{in}$ , is maintained at less than 2.5  $\mu$ W to avoid optical damage in the crystal and nonlinearity in the unbiased photodiode used to measure  $P_{in}$  and  $P_{out}$ . The output objective (×20, 0.57 N.A.) has a sufficiently large aperture to collect all the light from the guide. An iris is provided to isolate the waveguide mode from extraneous scattered light. The polarization of the output spot is observed to be the same as that of the input. A heater, shown schematically in Fig.5.53, tunes the Fabry-Perot formed by the cleaved end facets through maxima and minima by thermally varying the refractive index n. With  $n \approx 2.2$ , the Fresnel reflection coefficient R = 0.14, which is calculated by the formula  $R = [(n - 1)/(n + 1)]^2$ .

If  $T = P_{out}/P_{in}$ , the insertion loss L is the sum of three contributions: The two lenses introduce loss  $L_1$  which is measured in the absence of the crystal as 1.2 dB. The mismatch between the circular Gaussian input wave function and the strip-guide wave function introduces loss  $L_2$ . The crystal introduces loss  $L_3$  due to the wave loss,  $L_w = a \ell$ , and the effects of the Fresnel mirrors.

Burns and Hocker (1977) have shown that by choosing the Gaussian input spot radius w to be the geometric mean of the equivalent spot sizes  $w_1$  and  $w_2$  measured along the principal axes of the waveguide mode, the mismatch loss  $L_2$  may be as small as 0.8 dB. For the guide under investigation, the



Fig.5.53 Intersection loss measurement apparatus (Kaminow and Stulz 1978).

value  $w_1/w_2 \approx 3/4$ . The condition  $w \approx (w_1 w_2)^{1/2}$  was achieved by testing various microscope objectives in order to find one that gave minimum L. For an objective with nominal numerical aperture N and pupil diameter D focusing a laser beam of Gaussian diameter d, Kaminow and Stulz (1978) estimated w using paraxial Gaussian beam optics as

$$w \approx \lambda D (1 - N^2)^{1/2} / \pi d N.$$
 (5.72)

For the present measurements at  $\lambda = 0.63 \ \mu m$  with  $d = 1 \ mm$ , it was found that a ×10 lens with nominal N = 0.25 and  $D = 8 \ mm$  gave the minimum loss. The spot diameter 2w calculated from equation (5.72) was 12  $\mu m$ , which may be reasonable for a nominal 4  $\mu m$ -wide strip guide, allowing for lateral diffusion and small guide-substrate index difference.

The transmission through the crystal was

$$T_0 = (1 - R)^2 T_w$$
(5.73)

if the end facets do not provide coherent reflections, but with Fabry-Perot behaviour the transmission ranges between

$$T_{\max\min} = (1-R)^2 T_w / (1 \pm RT_w)^2.$$
(5.74)

In equations (5.73) and (5.74) the transmission through the waveguide was

$$T_{\rm sc} = 10^{-al/10},\tag{5.75}$$

where a is measured in dB/cm. It should be noted that by converting T to L, equations (5.73) and (5.74) give

$$1/2(L_{\max} + L_{\min}) = L_0 \tag{5.76}$$

for  $(RT_{u})^{2} \ll 1$ , so that  $L_{0}$  is also the average Fabry-Perot loss.

The orientation of the cleaved crystal is indicated in Fig.5.54. The 250  $\mu$ m thick plate is normal to the crystal x axis and contains the optic z axis at an angle of 32.75 Å from the cleaved edge. A scribe mark is made on the waveguide-containing surface at one edge of the plate; two pairs of tweezers on either side of the mark are used to make the break. As is usual on cleaved surfaces, a number of terraces appears, as indicated schematically in Fig.5.54. The edges of the terrace steps are indicated by the dotted curves in Fig.5.54. The character of the terraces and the nature of the cleaved end facet depend upon whether the break starts near the negative or positive end of the z axis.

The cleavage plane in LiNbO, was identified as a {102} plane. However,



Fig.5.54 Cleaved crystal orientation showing a 4  $\mu$ m wide guide and evaporated electrode spaces 9  $\mu$ m apart. The dotted curves on the cleaved face represent terrace steps; the first few of these steps start near the scribe mark on the surface of the plate (Kaminow and Stulz 1978).

there is some ambiguity in associating the generic {102} plane with either of the actual (102) or (012) planes in the crystal lattice. Nevertheless, examination of a crystal lattice model (Megaw 1973) reveals the likely plane as the one which contains the layer of vacant octahedral sites surrounded by a layer of Li on one side of the cleavage and a layer of Nb on the other (indicating possible charge neutrality). The atomic spacings across the proposed cleavage plane are relatively large, indicating weak bonding.

Light polarized normal to the crystal plate, parallel to the x axis, is an ordinary wave. The guide is oriented perpendicular to the end facets within  $1/4^{\circ}$ . Insertion loss L can be observed (with an oscilloscope connected to the photodiode) to pass through Fabry-Perot maxima and minima, as in equation (5.74), as the temperature varies over a few degrees of Centigrade. On the other hand, light polarized in the plane of the crystal plate is an extraordinary wave. In order that the Poynting vector be parallel to the guide axis, the incident beam must enter at about 4.5° from the normal (Burns and Warner 1974). The wave-normal vector is the guide is then about 2° from the guide axis and the wave fronts are no longer parallel to the cleaved facets. Then the loss behaviour corresponds to equation (5.73) and no maxima or minima are observed.

Waveguides were fabricated by diffusing 4 µm wide 180 Å thick Ti stripes in flowing O<sub>2</sub> using standard acoustic grade LiNbO<sub>3</sub> substrates. Ti was evaporated from a tungsten coil. The loss measurements on such a guide are plotted in Fig.5.55. A good fit to the data for the ordinary-wave maxima and minima was obtained for  $a_0 = 1.0$  dB/cm,  $L_1 = 1.2$  dB,  $L_2 = 0.8$  dB, and R = 0.14. The estimated accuracy of the loss measurements was  $\pm 0.2$  dB. Note from equation (5.74) that a measurement of  $L_{max}$  and  $L_{min}$  at one  $\ell$  is sufficient to obtain  $a_0$  for given  $L_1$ ,  $L_2$ , and R. However, measurements at several values of  $\ell$  give added precision. The extraordinary-wave data is fitted by a line with the slope  $a_2 = 1.5$  dB/cm, for the same  $L_1$ ,  $L_2$ , and R.

Metal electrodes (consisting of 300 Å of Ti plus 700 Å of Ag) 20 µm wide and spaced 9 µm apart, were evaporated alongside a similar 4 µm wide guide



**Fig.5.55** Insertion loss *L* versus waveguide length  $\ell$  for a 4-µm wide Ti:LiNbO<sub>3</sub> guide. Solid lines give maximum, minimum and average loss ( $L_{max}$ ,  $L_{min}$  and  $L_0$ ) of Fabry–Perot resonator calculated for  $a_0 = 1.0$  dB/cm and the dashed line gives the loss for  $a_p = 2.5$  dB/cm. Solid dots are measured for the ordinary wave and circles are measured for the extraordinary wave (Kaminow and Stulz 1978).

as in Fig.5.54. The attenuation coefficients measured in this case were  $a_0 = 3.0 \text{ dB/cm}$  and  $a_e = 2.5 \text{ dB/cm}$  indicating that some of the optical fields is in contact with the electrodes. The electrodes were then stripped off and the measured attenuation coefficients,  $a_0$  and  $a_e$ , were within experimental error of those obtained in Fig.5.55.

In a practical device, R can be reduced to zero by antireflection coating, and  $L_1$  and  $L_2$  could also be made small by coupling directly from a singlemode fibre with suitable circular-to-elliptical mode transformer or taper. Then only the waveguide insertion loss al will remain. The attenuation coefficient in bulk LiNbO<sub>3</sub> is very small: less than 0.1 dB/cm at  $\lambda = 1.15 \mu$ m. However, the source of the excess attenuation in these strip waveguides is not understood at present. The attenuation might be due to absorption by impurities in the LiNbO<sub>3</sub> substrate or by the diffused Ti, or it might be due to scattering from geometrical imperfections in the guide or on the crystal surface. Thus, Tidiffused LiNbO<sub>3</sub> waveguides with loss substantially less than 1 dB/cm are a real possibility.

#### 5.8.2 Absorption loss in strip guides

To measure the absorption loss in Ti-diffused LiNbO<sub>3</sub> (Kaminow et al 1980) the guides were prepared by depositing 300 Å of Ti onto the LiNbO<sub>3</sub> substrate followed by heating for 6 h at 980°C in oxygen and cooling to room temperature for several hours. The first arrangement was to use the electrode geometry shown in Fig.5.56, which has been used for electro-optic modulation. Coplanar electrodes spaced 9  $\mu$ m apart were deposited along the entire length of the crystal on each side of the 5- $\mu$ m wide waveguide. With about 100  $\mu$ W of light modulated at 150 Hz coupled into the end of the waveguide, the pyroelectric signal due to absorption of light in the guide could be easily measured with a lock-in amplifier. The pyroelectric response was very sensitive to the coupling efficiency into the waveguide and could be used as a more convenient means of coupling alignment than the far-field pattern of



**Fig.5.56** Experimental arrangement for pyroelectric measurement of absorption loss in  $LiNbO_3$  strip guides. The polar *c*-axis is in the plane of the waveguide at 32.75° from the cleaved ends (Glass et al 1980).

the transmitted light. This method of alignment would also lend itself to servo control of the coupling.

The coplanar electrode geometry was not satisfactory for absolute measurement of the absorption loss because of the geometrical correction factor for the field distribution between the electrodes and because thermal diffusion from the waveguide into the substrate was very rapid. The corresponding attenuation of the pyroelectric signal is also difficult to calculate because of the geometry. The attempt to use short optical pulses failed because twophoton absorption in the guides was dominant at the high intensities required to obtain a measurable signal (Glass 1978).

The preferred geometry for absolute measurements of absorption loss in the waveguide was to evaporate electrodes on the two sides of the substrate crystal along the entire length as shown shaded in Fig.5.56. Then the pyroelectric response of the entire waveguide and substrate was measured with the lockin amplifier. Equation (5.76) can be used for this geometry, and the thermal relaxation time to the surroundings is now long (~1 s) and can be neglected. To determine the loss in the Ti-diffused waveguide, the incident light is first injected into the substrate, and the value of the power absorbed in a crystal of good quality  $f(f - (1-R) [1- \exp (-\alpha d)] [1-R \exp (-\alpha d)])$ , where d is the optical path length through the crystal. Hence, the values of  $\alpha$  for the undoped substrate are measured. Then by coupling the light into the waveguide (with ordinary wave polarization) the change in pyroelectric response gives the change of absorption loss in the Ti-diffused region directly. In these experiments the signal-to-noise ratio allowed a change of 5% in the loss to be detected. The experimental data are summarized in Table 5.11.

The values of  $\alpha$  listed for the waveguide at 0.514 and 0.488 in Table 5.11 represent a lower limit since the following factors can act to decrease the difference between the pyroelectric signals for light coupled into waveguide and substrate modes. First, the intensity of light coupled into the waveguide mode may not be the same as that coupled into the substrate mode even though coupling was optimized (insertion loss minimized) using the far-field pattern of the transmitted light. With a similar experimental arrangement this factor has been measured to be 0.8 dB (Kaminow and Stulz 1978). Second, the intensity of the light in the guide may be decreased by scattering from the guide into the substrate. This can be corrected by measuring both the insertion loss and electrical response for two or more different waveguide lengths. (The total insertion loss of the 1.8-cm crystal was 5.5 dB at 0.633 µm, increasing

to 9 dB at 0.488  $\mu$ m). Another factor that can affect the accuracy of measurement of waveguide loss in this experiment is absorption of scattered light by the metal electrodes, which in turn heats up the crystal. This does not seem to have been significant in these experiments since this would give an increased pyroelectric response at 0.633 for light coupled into the waveguide where scattering is greater than in the substrates.

At 0.633  $\mu$ m, no increase of loss in the waveguide region could be detected. The pyroelectric signal was the same whether the light was coupled into the waveguide or the substrate. Thus at this wavelength the absorption loss is 0.3 dB/cm in the guide and is limited by the loss in the substrate. No additional absorption due to Ti could be detected at 0.633  $\mu$ m. At shorter wavelengths increased loss in the waveguide was measurable. At 0.515  $\mu$ m and 0.458  $\mu$ m pyroelectric signals increased by 50 and 60%, respectively, when the beam was coupled into the guide presumably due to the shift of the absorption edge to the visible.

### 5.8.3 Loss in epitaxial waveguides

The loss was calculated from the measured distribution of scattered light from the waveguide mode. The scattered light distribution was analysed using a microscope mounted on a micromanipulator, a photodetector and a selective microvoltmeter. The voltmeter reading U was proportional to the intensity of scattered light. Having measured the scattered light intensity at two points spaced by a distance L, one can calculate the attenuation coefficient by the formula

$$K = -\ln (U_2/U_1)/L$$
 (5.77)

Light loss measurements for several examined samples have shown that TMmode attenuation is as a rule higher than that of TE modes. This is evidently due to the fact that TM modes are more critical to interface nonuniformity than TE modes. It should be noted that some of the samples used in the experiment exhibited a decrease of loss to 0.7 dB/cm for TE modes.

In epitaxial layers of solid solutions of lithium niobate-tantalate the attenuation is equal to 1dB/cm for  $\lambda = 0.63 \mu m$  and 0.8 dB/cm for  $\lambda = 1.15 \mu m$ . The photorefractive film sensitivity studied by comparison was no higher than that of the substrate.

The lowest attenuation is observed in (0001)-oriented layers. In a LiNbO<sub>3</sub> film on a LiTaO<sub>3</sub> substrate losses do not exceed 2 dB/cm for lower modes. It is established that light propagation occurs in LiNb<sub>1-y</sub>Ta<sub>y</sub>O<sub>3</sub> films for  $y = 0.\div1$  for orientation (0001);  $y = 0.3\div0.99$  for  $(1\overline{1}20)$  and  $y = 0.4\div0.99$  for  $(10\overline{1}0)$ ; the light attenuation in the waveguide decreases with increasing tantalum content in the films (Fig.5.57). Attenuation in best samples does not exceed 1 dB/cm for y > 0.2, 0.6 and 0.9 for orientations (0001),  $(11\overline{2}0)$  and  $(10\overline{1}0)$ , respectively, and increases sharply with increasing order of the mode.

Absorption in lithium niobate-tantalate films is insignificant and does not exceed 0.3-0.5 dB/cm, which shows a high structural perfection of the layer.



Increase in light attenuation with increasing order of modes is a consequence of light scattering on substrate-film and film-air interfaces. The presence of irregularities on interfaces causes energy transfer from one waveguide mode to others. Inhomogeneity of the interface is an important factor determining efficiency of the practical use of structures. Periodic irregularities can be used (as a coupling element) for light output from a dielectric waveguide. But random inhomogeneities that occur in waveguide manufacturing weaken a propagating wave. The loss factor varies in proportion with root-mean-square roughness of the walls. Roughness on the inner film boundaries is apparently of a irregular nature. The indicated weak attenuation of low-order modes shows that waveguides obtained through liquid phase epitaxy of lithium niobate meet the strict requirements imposed on wall smoothness in integrated optics schemes.

### 5.9 Ferroelectric properties of waveguides

### 5.9.1 Dielectric properties

The capacity (c) and conductivity ( $\sigma$ ) of capacitors formed by the planar structure of platinum electrodes on the film surface were measured to determine the temperature dependence of dielectric permittivity ( $\epsilon$ ) of films. Measurements were carried out in the temperature range between 20 and 970°C in the 'weak' field regime ( $E_{\rm meas} < 10^4$  V/m) by the bridge method. Figure 5.58 represents typical temperature dependences of c and  $\sigma$  for a 6 µm LiNb<sub>0.1</sub>Ta<sub>0.9</sub>O<sub>3</sub> film on a LiTaO<sub>3</sub> substrate of orientation (1120).

Typical of the structures investigated is the presence of two peaks of c(T)and  $\sigma(T)$ , the first lying in the vicinity of 580°C for c(T) and at 575°C for  $\sigma(T)$ , the second, a more smeared one, at 770°C for c(T) and at 750°C for  $\sigma(T)$ . The peaks of c(T) and  $\sigma(T)$  near 580°C are due to phase transition in the substrate, which is clear from a smaller smearing and a rather small displacement of the maximum of c(T) relative to  $\sigma(T)$ . This fact is also confirmed by well known data indicating that for a single crystal LiTaO<sub>3</sub> the phase transition temperature lies within the range of 550÷680°C (ed. by Shaskol'skaya 1982). Since phase transition in LiNbO<sub>3</sub> crystals occurs at 1140÷1180°C, it is natural to expect the phase transition in LiNb<sub>0,1</sub>Ta<sub>0,9</sub>O<sub>3</sub> to occur within the range of 550÷1190°C, that is, smeared maxima in c(T) and  $\sigma(T)$  at 770 (750)°C



**Fig.5.58** Temperature dependence of dielectric properties of  $LiNb_{0,1}Ta_{0,9}O_3/LiTaO_3$ : a) capacity (1) and conductivity (2); b) dielectric permittivity of substrate (1) and film (2), calculated values.

may be due to phase transition in the film.

Assuming the dielectric permittivities of the film  $\varepsilon_1$  and substrate  $\varepsilon_2$  to have only one maximum (each) that corresponds to their phase transition, one can solve the problem of estimating  $\varepsilon_1$  (T) and  $\varepsilon_2$  (T) by measuring the capacity  $C_{st}$  of the structure. The following facts and assumptions are used to determine  $C_{st}$ .

1. It can be easily shown that

$$C_{\rm st} = \frac{1}{4\pi} \sum_{n=1}^{\infty} \frac{4}{\pi n} \sin^2\left(\frac{\pi na}{\ell}\right) \cdot \left\{ 1 + \varepsilon_1 \frac{\varepsilon_1 \mathrm{sh}\left(\frac{\pi \mathrm{nd}}{\ell}\right) + \varepsilon_2 \mathrm{ch}\left(\frac{\pi \mathrm{nd}}{\ell}\right)}{\varepsilon_2 \mathrm{sh}\left(\frac{\pi \mathrm{nd}}{\ell}\right) + \varepsilon_1 \mathrm{ch}\left(\frac{\pi \mathrm{nd}}{\ell}\right)} \right\},\tag{5.78}$$

where  $C_{\rm st}$  is the capacity of the structure,  $\ell$  the structure period (~300 µm), a the electrode width (100 µm), d the film depth (6÷20 µm).

2. In the range  $T > 750^{\circ}$ C,  $\varepsilon_1 \gg \varepsilon_2$  and, as follows from (5.78),  $\varepsilon_1(T)$  can be restored with a satisfactory accuracy.

3. Knowing the behaviour of  $\varepsilon_1(T)$  for  $T > 750^{\circ}$ C and  $\varepsilon_1(20^{\circ}$ C) = 46 (Wang Hong and Wang Ming 1986) one can interpolate  $\varepsilon_1(T)$  to the region  $T < 700^{\circ}$ C and, using this interpolation, restore  $\varepsilon_2(T)$  in this temperature range. For the relations between film thickness and lattice period,  $\varepsilon_2$  always restricts the structure capacity from above. The results of the calculations for the dielectric permittivity of the film and substrate is presented in Fig.5.58b.

The behaviour of the structure in strong electric fields was investigated for  $T > 750^{\circ}$ C, where the influence of the substrate is small, since at these temperatures it is in the paraelectric phase. A typical oscillogram of the dependence of spontaneous polarization  $P_s$  on the strength of the electric field E is presented in Fig.5.59.

Analysis of dielectric hysteresis loops shows that at 750-800°C the strength of the coercive field for  $\text{LiNb}_{0.1}\text{Ta}_{0.9}\text{O}_3$  films on  $\text{LiTaO}_3$  (1120) makes up ~(2-3)×10<sup>5</sup> V/m and  $P_s = 0.46$  C/m<sup>2</sup>. The observed effluent on hysteresis loops is obviously due to charge escape from small traps due to redistribution of the applied electric field caused by a decrease of ferroelectric impedance at the moment of repolarization (Lines and Glass 1977).



FIg.5.59 Oscillogram of a hysteresis loop of a LiNb<sub>0.1</sub>Ta<sub>0.9</sub>O<sub>3</sub> film.  $T = 750^{\circ}$ C, f = 60 Hz, P<sub>3</sub> $\cong 0.46$  C/m<sup>2</sup>,  $E_{o}\sim 2.3$  10<sup>5</sup> V/m.

### 5.9.2 Pyroelectric properties

The pyroelectric properties of films were measured by the thermal pulse and low-frequency sinusoidal temperature modulation methods (Antsygin 1987).

### 5.9.2.1 The low-frequency sinusoidal temperature modulation method

The absolute value of the pyroelectric coefficient  $\gamma$  was found using a setup shown schematically in Fig.5.60 (Antsygin et al 1986). The basic element of this device setup is a thermoelectric device enabling the sample temperature to change according to a strictly sinusoidal law with amplitude  $\Delta T$ . The temperature modulation frequency w is chosen to be such that it could provide a uniform temperature distribution throughout the entire sample thickness d, that is,  $2\pi/\omega > \tau_{\tau}$  where  $\tau_{\tau}$  is the thermal relaxation time of the sample. The nature of pyroelectric current is such that magnitude of pyroelectric current  $J_p$  is proportional to dT/dt. This is just what differs the pyroelectric effect from all other physical phenomena that are characterized by variation of current through a specimen with varying temperature and permits distinguishing the contribution of pyroelectric current into the total temperature-induced current. Temperature variation in a sample by sinusoidal law is responsible for the same law for variation of pyroelectric current  $J_p$  but with a phase shift  $\pi/2$ .

This method has been employed to investigate ferroelectric crystals (Carn and Sharp 1982). Uniform temperature distribution throughout the crystal thickness can be attained only at very low modulation frequencies  $\omega$  since  $\tau_{\tau} \sim d^2$ . Determination of the phase shift between pyroelectric and nonpyroelectric currents is characterized by low sensitivity. The phase shift  $\varphi$ , as can be readily shown (Carn and Sharp 1982), is equal to arc tan  $(J_{p \max}/J_{np \max})$ . Examination of thin ferroelectric films by this method has made it possible to single out the contribution of pyroelectric current and to measure  $\gamma$  values up to about 3%. The pyroelectric coefficient is found from the relation  $\gamma - J_{p, \max}/(s\Delta T\omega)$ , where s is the sample area.

### 5.9.2.2 The thermal pulse method

The direction of pyroelectric current in a ferroelectric is determined by the



Fig.5.60 Schematic of a device for measuring pyroelectric coefficient. 1) thermal bath; 2) sample; 3) temperature gauges; 4) mean sample temperature gauges; 5) heat conducting buffer layer; 6) thermocouple; 7) electrometer; 8,9) amplifiers; 10) two-coordinate x,y recorder; 11,12) units for thermocouple control; 13) printer; 14) crate 'Camak'; 15) computer; 16) display; 17) monitor.

spontaneous polarization vector  $P_s$ , which fact can be used in investigation of polarization distribution throughout the sample thickness.

The method consists in probing a sample by short radiation pulses that heat the thin absorbing electrode. Moving from the heated electrode in the sample towards the opposite electrode, the thermal flux induces the occurrence of pyroelectric signal. The initial polarity of this current is determined by the polarization direction in the vicinity of the absorbing electrode. If in a bulk ferroelectric the polarization direction reverses (head-on domain structure), this is expressed, beginning from some instant of time, as a sharp decrease in the magnitude of of pyroelectric current even reaching polarization reversal. The thermal pulse method shows a higher resolution in film studies than in crystal studies (Chynoweth 1956). This promoted investigation of pyroelectric processes directly near the electrode surface. The time resolution of about  $10^{-9}$  s attained in the measurements corresponds to the thickness resolution of 3-5×10-8 m. Analysis of the effect of radiation on both electrodes made it possible to directly discover the head-on domain structure in the sample. Such a structure causes opposite pyroelectric current polarity upon irradiation of each of the electrodes. Current polarity is determined only by the polarization direction and does not depend on the heat distribution direction.

Structures with the c axis normal to the substrate plane were used in measurements; chromium films ( $\sim 10^{-7}$  m in thickness and  $\sim (1-3) \times 10^{-6}$  m<sup>2</sup> in area) manufactured by the thermal sputtering method were used as electrodes.

A typical oscillogram of pulse pyroelectric signals is presented in Fig.5.61. Analysis of the behaviour of pulse pyroelectric current response of the structure to the light pulse both from the film and substrate has shown that spontaneous polarization of the film is aligned along the substrate polarization direction, and the pyroelectric coefficient of films estimated by the initial slope of the current response is  $\gamma \approx 1.4 \times 10^{-4} \text{ C/m}^2$  grad. This value agrees well with  $\gamma \approx 1.57 \times 10^{-4} \text{ C/m}^2$  grad obtained for solid solutions of the same composition (Wang Hong and Wang Ming 1986), which is indicative of high quality of the epitaxial structure.

The observed decrease of pyroelectric response with  $\tau \cong 3 \times 10^{-4}$  s, as well as the nonlinear dependence of pyroelectric stress on load impedance at subsonic temperature modulation frequencies indicate the existence of a nonferroelectric layer in the structure. The absence of current response delay relative to the light pulse (under  $10^{-8}$  s) upon light absorption by electrodes both on the side of the film and substrate implies that this layer is located on the filmsubstrate interface.

# 5.10 Temperature dependence of thermoelectric coefficients of lithium niobate and lithium tantalate

Thermoelectric effects in lithium niobate and lithium tantalate ferroelectrics affect greatly the film crystallization conditions.

Khachaturyan et al (1988) investigated thermoelectric Seebeck, Thomson and Peltier effects for LiNbO<sub>3</sub> and LiTaO<sub>3</sub> single crystals and their temperature dependence in the range of 300-1400 K.

The main results of the thermodynamic theory of thermoelectric phenomena come down to establishing relationship between various thermoelectric effects (Samoylovich and Korenblit 1953), namely:

$$\tau = \frac{\partial \Pi}{\partial T} - \alpha, \ \Pi = \alpha T,$$

where  $\tau$  is Thomson's coefficient,  $\Pi$  is Peltier's coefficient,  $\alpha$  is Seebeck's coefficient and T is temperature.

So, having measured the Seebeck coefficient for a particular material one can readily obtain the values of Peltier and Thomson coefficients. The experimental setup for determination of Seebeck coefficient included a main furnace, upper and lower microheaters, thermocouples and a specimen (Rekas and Wierzbicka 1983).



Fig.5.61 Oscillogram of a pyroelectric signal to light pulse. 1) light pulse, 2) pyroelectric response of the film, 3) response of the substrate.



Fig.5.62 Temperature dependence of Seebeck coefficients of LiNbO<sub>3</sub> and LiTaO<sub>3</sub>.

able 5.12 Thermoelectric coemclents of infinitin modale and tantalat	Table 5.12	Thermoelectric	coefficients of	f lithium	niobate	and	tantalate
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		Lindo,			LiTaO,	
<i>Т</i> , К	α mV/daa	П	τ mV/dea	α mV/deg	П	t mV/dea
	m v/ueg	111 V	in viueg		mv	in v/ueg
700	0.3	210	-5.2	0.04	28	1.2
750	0.05	37.5	-5.1	0.13	97.5	5.52
800	-0.65	-520	-5.0	0.91	728	6.9
850	-0.65	-552.5	-5.0	1.12	952	7
900	-0.2	-180	5	1.5	1350	7.1
950	0	0	5.1	1.69	1605,5	7.2
1000	0.2	200	5.1	1.66	1660	1.1
1050	0.35	367.5	5.2	1.6	1680	-1.6
1100	0.2	220	-2.5	1.44	1584	-1.5
1150	0.1	115	-2.4	1	1150	_9
1200	0.1	120	-0.37	0.8	960	-9.1
1250	0.1	125	-0.36	0.53	662.5	-9.1

Samples of LiNbO<sub>3</sub> and LiTaO<sub>3</sub> crystals  $(10\times10\times10 \text{ mm})$  were positioned between two platinum electrodes. The crystal surfaces contacting the electrodes was covered with platinum niello. Two inner microheaters were mounted on rods and enabled temperature gradients to occur throughout the specimen thickness. Temperature was controlled by three platinum-rhodium thermocouples, measurements were carried out by the compensation method in air at a constant normal pressure, the temperature gradient was 10 deg/cm. The thermo-electromotive force of crystals was measured within experimental error of 1-3%. Figure 5.62 presents the temperature dependence of the Seebeck coefficient (a) for LiNbO<sub>3</sub> and LiTaO<sub>3</sub> single crystals. Within the experimental error, no dependence of a on crystallographic orientation of the crystal was observed. The dislocation density of  $(2-4)\times10^4$  cm<sup>-2</sup> remained unaltered in all the specimens.

As is seen in Fig.5.62, the 300–1400 K temperature variation of the Seebeck coefficient for LiNbO<sub>3</sub> can be divided into three temperature ranges. In the range of 300–750 K the Seebeck coefficient starts increasing and then falls sharply, which suggests an intricate nature of conduction of LiNbO<sub>3</sub> single crystals in the indicated temperature range. At low temperatures there prevails the impurity conduction of LiNbO<sub>3</sub> (Kuz'minov 1987; Kuz'minov 1975). In the temperature range of 750–950 K,  $\alpha$  changes sign, which is indicative of the contribution of the electron component to the intrinsic conduction. A subsequent sign change in the Seebeck coefficient in the temperature range of 950–1400 K agrees with the fact that the main carriers are Li<sup>+</sup> ions (D'yakov et al 1985).

The values of the coefficient  $\alpha$  for LiTaO<sub>3</sub> are positive in the entire temperature range under examination. At the phase transition temperature (T = 933 K) a maximum is observed, which suggests the influence of the phase transition upon the character of conduction. It is obvious that the main carriers in LiTaO<sub>3</sub> single crystals are Li<sup>+</sup> ions. Comparing the values of Seebeck coefficients for lithium niobate and tantalate single crystals within the investigated temperature range one can assume that the higher the  $\alpha$  value, the higher the conduction of the material. For

 $\alpha_{\text{LiTaO_3}} > \alpha_{\text{LiNbO_3}}$  we have  $\sigma_{\text{LiTaO_3}} > \sigma_{\text{LiNbO_3}}$ 

The calculated values of Peltier and Thomson coefficients in the indicated temperature range are tabulated in Table 5.12 which shows that for lithium niobate the Peltier coefficient changes from -662.5 mV to 367.5 mV, while for lithium tantalate it changes from 28 mV to 1680 mV. At temperatures above 1200 K, Thomson coefficients for lithium niobate and tantalate do not change appreciably.

# **6** Thin-Film Structures in Integrated Optics

Integrated optics is mainly developed in the direction of integration of waveguide and optoelectronic components on a single substrate to the effect of creation of multifunctional devices.

Optical film waveguides are the basic components of integro-optical modulators, switchers, filters, nonlinear optical frequency converters, commutators, and light beam deflectors for correlation and spectral analysis of light signals during their processing. Hybrid bistable optical devices on the basis of channel waveguides operating at small levels of optical power are used as sensors of light intensity in automatic systems and optical multivibrators.

For integral nonlinear optical devices, channel waveguides are of great interest and have advantages over planar ones. Propagation of a light beam along a channel increases the luminous energy concentration and, accordingly, the efficiency of nonlinear conversion. The phase matching conditions can be maintained by varying the geometrical size of waveguides.

In this chapter, we are mainly concerned with devices based on waveguide lithium niobate and tantalate structures and involving electro-optic effect.

As distinct from the diffusion method, liquid-phase epitaxy for obtaining light guide structures in lithium niobate-tantalate systems is very flexible and suggests new possibilities for creating integro-optic schemes with integration of elements both in horizontal and vertical planes. In a vertically integrated structure, waveguide layers are separated by layers of a solid solution of lithium niobate-tantalate with a lower refractive index which plays the role of an optical insulator. No other insulating layers of other materials  $(SiO_2, Al_2O_3)$  applied in a number of integrated systems are needed here since separating layers are grown in a unified technological cycle of obtaining device structures.

We shall now carry out a comparison study of Ti-diffusion and epitaxial techniques of integro-optic devices on an example of electro-optic switching elements in crossing-channel waveguides or electro-optic X-switchers (Betts et al 1986). Single-mode switchers are of the utmost practical interest. In this case, for a sufficiently small width of waveguides, the operation of such a switcher is based on interference of even and odd modes in the intersection region and on electric control of their phase relations (Neyer 1984). Switchers of this type have a rather simple design and are fairly stable as compared to other types of switchers (Betts et al 1986). The control structure consists of two metallic electrodes with a gap of  $1\div3 \mu m$  positioned on the light guide structure and oriented along the long diagonal of a rhomb for an efficient even-mode control. To reduce the total losses this type of device, there is a buffer layer between metallic strips and the light guide layer.

The technological process of manufacturing such light guides using the diffusion method includes the following operations:

- deposition of a controlled width of titanium,
- photolithography for obtaining a picture of channel light guides,
- titanium diffusion for obtaining the light guide structure,
- deposition of a  $SiO_2$  or  $Al_2O_3$  insulating layer,
- surface metallization for the formation of a controlled structure,
- placing inside the device.

It should be noted that the diffusion process allows the formation of only nonsymmetric light guide structures, which suggests difficulties in a further matching of such a structure with fibres possessing axial symmetry. The calculations show (Lazarev 1986) that even upon a precision diffusion of Ti with the purpose of obtaining an optimal profile of a channel light guide for matching with axial-symmetric fibres there occur more than 10% of losses due to matching. Fibres are now typically face-adjusted to integro-optical devices, which requires polishing of device faces. The position of Ti-diffusive light guides directly in the near-surface region imposes strict requirements upon the processing of plate faces to remove or avoid possible chippings in the region of the light guiding structure.

When a device is made using epitaxial technique, then after titanium is deposed and photolithography is performed, the immersed light guiding structures are formed by the diffusion-film method. This yields symmetric light guiding structures allowing a decrease of losses in the course of fibre adjustment. It also lowers the requirements on the size of chippings during face polishing, and an insulating layer need not be specially deposited since it is formed in the technological process of obtaining immersed light guiding structures.

# 6.1 Principal characteristics of waveguiding electro-optic modulators

Modulators are characterized by a control voltage, by the band width, by the maximal modulation depth and by insertion losses (Tamir 1979; Mustel and Parygin 1970). We shall consider these characteristics following Alferness (1982).

# 6.1.1 Control voltage

An important characteristic of modulator is control voltage (a minimal voltage for which the modulation depth is maximal). In spite of the fact that the





magnitude of control voltage depends on a specific modulator scheme, the basic conclusions on the effect of the external field can be made on the basis of a simple phase modulator (Fig.6.1). If electrodes are placed on both sides of a waveguide, the horizontal component of the electric field  $\xi_{\parallel}$  is used, while if an electrode lies on the waveguide surface, the vertical component of the electric field  $\xi_{\perp}$  is used. In the latter case, to decrease light loss under the electrodes, especially for polarization of the perpendicular plane of the crystal (TM-modes), a buffer layer of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> should necessarily be deposited upon the waveguide surface (Uchara et al 1975). In both cases, crystal orientation is so chosen that the electrodes, the coefficient  $r_{33}$  has the highest value. When light propagates between the electrodes, the coefficient  $r_{33}$  is used for TE-modes on the y-cut, whereas when light propagates under the electrodes,  $r_{33}$  is used for TM-modes on the z-cut.

The refractive index variation under the action of the field due to electrooptic effect is given by the expression

$$\delta n^{*}(V) = -(n^{3}r/2)(V/d)\Gamma, \qquad (6.1)$$

where d is the interelectrode gap,  $\Gamma$  is the overlap integral of the electrode field and the mode field:  $\Gamma = (d/V) \iint \xi |E|^2 dA$ , where E is a normalized field of the mode,  $\xi$  is an applied electric field, V is voltage.

The condition for a 100 % modulation depth can be written as

$$\left|\Delta\beta L\right| = p\pi,\tag{6.2}$$

where  $\Delta\beta = (2\pi/\lambda)\delta n^*$ , L is the interaction length between the applied field

and the light, p = 1 and depends on the type of modulator. So,

$$VL = p\lambda d / n^3 r \Gamma.$$
(6.3)

The transmission band width can be shown to be inversely proportional to L (Alferness 1982). So, to broaden the band it is necessary to decrease the quantity  $V \times L$  by minimizing the geometric parameter  $d/\Gamma$ . To this end one should know how the overlap integral depends on the interelectrode gap, on the magnitude of the mode field, on the electric field component ( $\xi_1$ , or  $\xi_{\mu}$ ) and on the position of the waveguide relative to the electrodes. The dependence of the overlap integral on these parameters (for half-infinite electrodes) was considered by Marcuse (1982). The mode field distribution in width (with dimension  $\omega_{\mu}$ ) is assumed to be described by the Gaussian function and in depth (with dimension  $\omega_{i}$ ) by the Hermitian-Gaussian function. For a waveguide lying between the electrodes in a gap d equal to or slightly greater than the mode dimension, symmetric position relative to these electrodes is optimal. If the vertical component of the electrode field is used, then optimal is the case of coincident inner edge of the electrode with the mode field edge (with dimension  $\omega_{i}$  (Fig.6.1)). Figure 6.2 illustrates the dependence of the product of the field-induced change of the effective refractive index by the mode width  $\delta n^* \cdot \omega_{\mu}$  on the normalized gap size  $d/\omega_{\mu}$  for the case when both the vertical and horizontal field components are used (Marcuse 1982). These dependences show that an increase of  $\delta n^*$  requires a decrease of the waveguide mode and of a gap between the electrodes,  $d \le 0.5 \omega_{\mu}$ . For the case of the use of this  $\xi_{\perp}$  requirement is less critical than in the case of  $\xi_{\parallel}$  (Alferness 1982).

A photorefractive effect may result in a significant "increase of the control voltage (at a constant voltage) due to compensation of the applied field by photoelectrons. There are two reasons for this: first, the photoconductivity in the external field and, second, the photogalvanic effect (Schmidt et al 1980; Yamada and Minakata 1981).

### 6.1.2 Bandwidth

The width of the modulator frequency band is determined by electrode capacitance provided that the electrode length is much smaller than the wavelength of the radio frequency signal. It can be shown that the capacitance of the system of electrodes per unit length is equal to (Alferness 1982)

$$C/L = \varepsilon_{eff} \left[ K \left( 1 - r_s^2 \right)^{1/2} / K(r_s) \right], \tag{6.4}$$

where  $r_s = (d + 1)/2G$ ,  $\varepsilon_{eff} = (\varepsilon'_0/2)(1 + \varepsilon_s/\varepsilon'_0)$ , G is the electrode width,  $\varepsilon_s = \sqrt{\varepsilon_x \varepsilon_y}$ ,  $\varepsilon_x = 28$ ,  $\varepsilon_y = 43$  for (LiNbO<sub>3</sub>) is the dielectric constant and K is the elliptic integral.

The ratio C/L decreases and the bandwidth increases ( $\Delta f = (\pi RC)^{-1}$ , R is

296



**Fig.6.2** The product of the field-induced effective refractive index by the width of the mode  $\delta n^* \cdot \omega_{\parallel}$  and the overlap integral  $\Gamma$  as functions of normalised value of the gap for fields  $\xi_{\parallel}$  (a) and  $\xi_{\parallel}$  (b) (Alferness 1982).



**Fig.6.3** Capacity of an electrode system per unit length C/L and product of the band width by the electrode length  $\Delta f_{\rm RC}$ . L versus the value of the interelectrode gapelectrode widths ratio dG (Alferness 1982).

the load resistance) with increasing ratio d/G (Fig.6.3). Since the product of the critical frequency, which is determined by the signal passage time, by the electrode length  $f_c \times L = c/(\pi \sqrt{\varepsilon_{eff}}) = 2.2 \text{ GHz}$  cm (c is the speed of light), it is inexpedient to use d/G > 0.8.

It is known from the foregoing that to lower the control voltage, the gap between the electrodes should be small. Thus, to obtain a wide band, it is necessary to reduce the electrode width (since  $d/G \approx 1$ ). A reduction of the electrode width is, however, limited by two factors. First, it should not be made much less than the waveguide width lest the overlap of the electric and optical fields should be small. Second, when the electrode width is small, the resistance increases and the bandwidth decreases accordingly.

Since the control voltage and the band width are inversely proportional to the device length, the control voltage-to-the band width ratio can be though of as a figure of merit:

$$V / \Delta f = \pi R \left( \varepsilon_{eff} / n^3 r \right) (p\lambda) \left[ (d / \Gamma) K \left( 1 - r_s^2 \right)^{1/2} / K(r_s) \right], \tag{6.5}$$

The ratio  $V/\Delta f$  decreases with decreasing gap (down to  $d/\omega_1 \ge 0.5$ ) because C/L increases slower (Fig.6.3) than decreases the control voltage (Fig.6.2). But as the inequality  $d/\omega_1 \le 0.5$  decreases, an increase of C/L will not be compensated by the lowering of the control voltage. So,  $V/\Delta f$  has a minimum for  $d/\omega \le 0.5$  and  $d/G \simeq 0.5$ . In so far as C/L depends logarithmically on d/G, the electrode can be widened without a noticeable increase of  $V/\Delta f$ .

The smallest attainable gap is restricted by the smallest attainable mode dimension (Alferness 1982):  $\omega_{\min}/\lambda \sim 0.5(n\cdot\Delta n)^{1/2}$  and from  $d/\omega_{\parallel} \approx 0.5$  there follows

$$d_{\min} \sim 0.25 \lambda / (n \Delta n)^{1/2}$$
. (6.6)

For  $n \cong 2.2$ ,  $\Delta n \cong 0.01$ ,  $\lambda = 0.63 \ \mu\text{m}$ :  $d_{\min} = 1 \ \mu\text{m}$ . Thus,

$$(V / \Delta f)_{\min} \cong 0.5 \pi R \left( \varepsilon_{eff} / n^{7/2} r \Delta n^{1/2} \right) p \lambda^2 / \Gamma \sim \lambda^2$$
(6.7)

(since  $K(1-r_s^2)^{1/2}/(K(r_s) = 2$  for d/G = 0.5), where the overlap integral  $\Gamma = 0.3$  or 0.2 for modulators that employ  $\varepsilon_{\parallel}$  or  $\varepsilon_{\perp}$ , respectively. Assuming p = 1, R = 50 Ohm and neglecting the electrode resistance, one can obtain the minimal value V/ $\Delta f$ : 0.5 V/GHz and 1.5 V/GHz for  $\lambda = 0.63$  µm and 1.32 µm, respectively (Alferness 1982).

### 6.1.3 Modulation depth and insertion losses

Suppose that without an applied voltage the intensity of light coming out of the modulator is equal to  $I_0$ . Then the modulation depth is determined as (Barnoski 1974):

$$m = \left| I - I_0 \right| / I_0 \tag{6.8}$$

where I is the intensity of light at a corresponding voltage. When a control (half wave) voltage is applied, the modulation depth is called a maximal modulation depth. The action of the majority of modulators is based on the phase change ( $\Delta \phi = \Delta L$ ) which is transformed into the change of intensity. For interferentional modulators, the dependence of the modulation depth on the phase shift has the form (Barnoski 1974):

$$m = \sin^2 \left( \frac{1}{2\Delta\beta L} \right) \tag{6.9}$$

while for waveguiding devices employing phase change in the connection of two waveguides or two waveguide mode

$$m = 1 - 1 / \left[ 1 + \left( \Delta \beta / \kappa \right)^2 \right] \cos^2 \left( \kappa^2 + \Delta \beta^2 L \right)^{1/2} / \cos^2 \kappa L$$
(6.10)

where L is the interaction length and  $\kappa$  is the coupling constant.

The theoretically admissible modulation depth is 100%, while in experiment it is normally a little less (about 96%) due to light scattering on waveguide defects and on the electrode structure, and also due to conversion of light polarization. The first reason results from the technological difficulties of manufacturing a waveguide modulator (micron size, high class of surface polishing, *etc.*). The second is due to the photorefractive effect and the associated light polarization conversion. The dependence of the modulation depth of a waveguide modulator on the polarization of light is, in turn, a consequence of two facts. First, the electro-optic coefficients are not the same for TE- and TM-waves: in the case of z (y)-cut of lithium niobate, when the field is directed along the z axis for a TE (TM)-wave  $\Delta\beta \sim r_{13}V$ , and for a TM (TE)-wave  $\Delta\beta \sim r_{33}V$  and  $r_{33}/r_{13} = 3$ ; second, the increment of the refractive index,  $\Delta n$ , is not the same for TE- and TM-waves ( $\Delta n_e > \Delta n_o$ ), and therefore the magnitude of the mode field and the coupling coefficient depend, in the case of matched waveguides, on the polarization of light (Leonberger 1983).

A decrease in the modulation depth due to conversion of polarization of light on the passive part of the modulator (unaffected by the electric field) can be stopped by placing at the modulator exit an analyser allowing only one polarization of light (either a TM- or a TE-wave). But this will stimulate the insertion loss.

The insertion loss is determined as follows (Barnoski 1974):

$$\alpha = 10\log(1 - I_0 / I_{in}), \tag{6.11}$$

where  $I_{in}$  is the intensity of light entering the modulator. Insertion losses also include the input and output losses and those due to propagation along the modulating structure.

It should be emphasized that the insertion losses will also be increased by a photoinduced radiation output from the waveguides.

### 6.2 Photoinduced polarization conversion

If voltage is applied to electrodes placed on both sides of a waveguide (for the y-cut of lithium niobate), then along with the phase modulation the amplitude modulation of radiation may occur. Radiation intensity variation must be a result of phase mismatch between TE- and TM-waves and, therefore, of a change in the degree of polarization conversion. The estimation by formula (6.1) yields a control voltage of about 7 V for L = 10 mm, d = 10 µm,  $\lambda = 0.63$  µm and  $\Gamma = 0.3$ . Such amplitude modulation was experimentally discovered by Zolotov et al (1983).

The waveguides were manufactured by titanium thermodiffusion into lithium niobate crystals (the y-cut) from strips, 15  $\mu$ m wide and 300 Å thick, deposited along the x axis. The diffusion was carried out for 6 h in air at a temperature

of 960°C. Then the electrode structure (two parallel aluminium strips 15  $\mu$ m wide and 14 mm long were photolithographically deposited on both sides of the waveguide on the crystal surface. The distance between the electrodes was 10  $\mu$ m (Fig.6.1).

At the wavelength of laser radiation, 0.63 µm, an  $E_{11}^y$ -mode was excited whose polarization corresponded to that of an ordinary wave. With an increase of the power of light introduced to the waveguide, the  $E_{11}^y$ -mode power was lowered and an  $E_{11}^z$ -mode appeared which corresponded to an extraordinary wave. The degree of polarization conversion depended on the power of light introduced to the waveguide P, and for P  $\cong$  25 µW the conversion was practically complete ( $P_e/P_0 \cong 95\%$ ).

Then the potential difference was applied to the electrodes, and the power of the  $E_{11}^{z}$ -and  $E_{11}^{y}$ -modes was measured as a function of voltage V. The voltage at which the conversion stopped (the control voltage) and the  $E_{11}^y$ -mode only was observed at the output increased with increasing power of light fed into the waveguide. This is evidently associated with an increase in the modulation depth of the refractive index in the holographic grating and, therefore, with an increase of the coupling constant between the  $E_{11}^{y}$  and  $E_{11}^{z}$ -modes. When the light power was about 5  $\mu$ W, the degree of conversion ( $P/P_0 \sim 60\%$ ) was about 60% and the control voltage was equal to ~2.5 V. But after some time (~30 s) the polarization returned to its initial state which was likely due to the newly induced holographic grating restoring phase matching between the  $E_{11}^{y}$  and  $E_{11}^{z}$  modes and due to a compensation of the applied field by photoelectrons. If the potential difference of opposite polarity was applied to the electrodes, then with an increase of the voltage the power of the  $E_{11}^z$ -mode first grew (the maximum was observed for  $V \cong -3$  V) and then started falling. This is likely to suggest that when radiation polarization conversion is incomplete, the holographic grating does not yield a perfect matching between modes of the ordinary and extraordinary polarization in the absence of voltage between the electrodes. When the power of light was about 25 µW, the degree of conversion made up ~95% and the control voltage increased up to ~7 V. The modulation curve was observed on an oscillograph screen to the input of which a signal was sent from the photomultiplier that registered the power of light coming from the waveguide, and a sawtooth voltage with the amplitude of 8 V was applied to the electrodes during 1 µs. The power of the  $E_{11}^z$ -mode fell ( $P_{e} + P_{0} \simeq 25 \,\mu\text{W}$ ) as shown in Fig.6.4a, while the power of the



Fig.6.4 Extraordinary (a) and ordinary (b) wave polarization power vs voltage (Kazansky 1985).

 $E_{11}^{y}$  -mode grew as shown in Fig.6.4b. While at the initial instant of time the power of the  $E_{11}^{z}$ -mode fell to the minimum at a voltage of ~7 V, after a few seconds the modulation curve became more gentle (the control voltage increased) and its maximum was displaced towards the higher voltage. Such a behaviour of the dependence of the power on the voltage can be explained by the influence of the field of space changes induced by the effect of the constant component of the sawtooth voltage upon the polarization conversion mechanism. It should be noted that the modulation band was determined not by the slow photorefraction process caused by the change drift but rather by the electrode capacitance which in the given case made up 7 picofarads, which corresponds to the band width of ~900 MHz calculated for a lode of 50 Ohm.

The power of light coming from the waveguide after an analyser transmitting radiation polarized at an angle of  $45^{\circ}$  to the direction of polarization of the  $E_{1,-}^{y}$  and  $E_{1,-}^{z}$ -modes was measured as a function of the voltage. Here



**Fig.6.5** The power of light polarised at an angle  $\pi/4$  to the waveguide plane versus voltage (Kazansky 1985).

changed the character of polarization of light under the action of voltage which affected the phase difference between the  $E_{11}^{y}$ -mode and the  $E_{11}^{z}$ -mode transformed from the  $E_{11}^{y}$  by means of the photorefractive effect (Fig.6.5).

It is noteworthy that on the one hand the discovered amplitude radiation modulation is undesirable for the operation of a phase modulator, but on the other hand, the electro-optic control over a photoinduced radiation polarization conversion confirms the mechanism of this new effect based on phase matching of the ordinary and extraordinary polarization modes using a bulk phase grating; the electro-optic control can also be used for light modulation.

The phase modulator belongs to some types of amplitude integro-optic modulators using coupled waveguides (Papuchon et al 1975; Kogelnik and Schmidt 1976) and interferentional modulators (Papuchon 1977).

# 6.3 Waveguide modulators on the basis of Ti:LiNbO,

# 6.3.1 Electro-optic modulator on coupled channel waveguides with a variable $\Delta\beta$

The main shortcoming of the modulator on coupled waveguides is a low contrast of 90% (Bozhevil'ny et al 1981). To reach a high contrast, the coupling length between the waveguides should be equal to an integral (odd) number

of pumping lengths (Papuchon et al 1975), which is difficult from a practical point of view. To eliminate this defect, such electrodes were suggested that create in coupled waveguides the difference of propagation constants  $\Delta\beta = \beta_2 - \beta_1$  which reverses sign an integral number of times equal to the number of pumping lengths. Using this method in a two-section device gave an on-off ratio of ~27 dB for a control voltage of ~30 V (Schmidt and Kogelnik 1976).

The solution of the system of equations (Kazinsky 1985)

$$R' - i\delta R = -i\kappa S$$
  

$$S' + i\delta S = -i\kappa R$$
(6.12)

for coupled waveguides with a variable sign of  $\Delta\beta$  in the matrix form is (Kogelnik and Schmidt 1976)

$$\binom{R}{S} = M_2 \binom{R_0}{S_0} = M_1^+ M_1^- \binom{R_0}{S_0}$$
(6.13)

where  $M_{l}^{+} = \begin{pmatrix} A_{l} & -iB_{l} \\ -iB_{l}^{*} & A_{l}^{*} \end{pmatrix}$  is the matrix for the modulator region with  $\delta = \pm \Delta\beta/2$ ;

$$M_{1}^{-} = \begin{pmatrix} A_{1}^{*} & -iB_{1} \\ -iB_{1}^{*} & A_{1} \end{pmatrix} \text{ is the same for } \delta = -\Delta\beta/2; \quad M_{2} = \begin{pmatrix} A_{2} & -iB_{2} \\ -iB_{2}^{*} & A_{2}^{*} \end{pmatrix},$$

 $\begin{array}{l} A_2 = 1 - 2 \ B_1^2 ; \ B_2 = 2 \ A_1^* \ B_1 ; \\ A_1 = \cos \left[ x \left( \kappa^2 + \delta^2 \right)^{1/2} + i \ \delta \ \sin \left[ x \left( \kappa^2 + \delta^2 \right)^{1/2} / (\kappa^2 + \delta^2)^{1/2} \right] \\ B_1 = \kappa \sin \left[ x (\kappa^2 + \delta^2)^{1/2} \right] / (\kappa^2 + \delta^2)^{1/2}, \text{ where } \kappa = 2\pi/l \text{ is the coupling constant,} \end{array}$ 



Fig.6.6 Modulator on the basis of coupled waveguides with a variable  $\Delta\beta$ . 1, 2) waveguide (Zolotov et al 1982).



Fig.6.7 State diagram of a modulator on the basis of coupled waveguides (Kogelnik and Schmidt 1976).

x = L/2, *l* is the pumping length,  $R_0$  and  $S_0$  are the wave amplitudes at the waveguide input. If  $S_0 = 0$ , then the condition for the crosstalk, that is, for light pumping from waveguide 1 to waveguide 2 (Fig.6.6) can be obtained provided that  $A_2 = 0$ :

$$\left[\kappa^{2}/(\kappa^{2}+\delta^{2})\right]\sin^{2}(L/2)(\kappa^{2}+\delta^{2})^{1/2}=1/2.$$
(6.14)

For the straightforward state  $(B_2 = 0)$  one can accordingly write

$$L/2 = 2 (2\nu + 1) (A_1 = 0); (L/1)^2 + (\Delta\beta L/\pi)^2 = (4 \nu)^2 (B_1 = 0)$$

Figure 6.7 shows a state diagram for a system of coupled channel waveguides with a variable sign of  $\Delta\beta$ . In this diagram, the points  $\otimes$  lying on the curve correspond to the state in which the light is completely pumped over from waveguide I to waveguide 2 (Fig.6.6), while the points  $\ominus$  on the curve correspond to the state when the pumping is stopped.

The electro-optic modulator on the basis of coupled channel waveguides was manufactured on a z-cut lithium niobate plate (Fig.6.6) (Zolotov et al 1982). The system of waveguides was created by way of sputtering 300 Å of titanium onto the plate surface with a subsequent etching of titanium through a photoresistive mask and by diffusion in air at a temperature of 960° during 6 h. The bandwidth of the titanium made up  $3.5 \,\mu$ m, which provided obtaining single-mode waveguides at the radiation wavelength of 0.63. The distance between waveguides was  $4.5 \,\mu$ m. To decrease propagation losses under the electrodes, the waveguide surface was sputtered with a SiO<sub>2</sub> film 2000 Å thick. The electrode structure on the waveguides (Fig.6.6) was fabricated by etching the 2000 Å thick Al layer sputtered onto the crystal surface through a photoresistive mask. The length, width and the distance between the electrodes were respectively 8 mm, 20  $\mu$ m and 4.5  $\mu$ m.

To establish the pumping length, the He-Ne laser radiation was, using a



Fig.6.8 Modulation characteristic of modulator on the basis of coupled waveguides (Kazansky 1985).

×20 microlens, introduced in turn in each of the five systems of coupled waveguides, and the intensity of light at the waveguide output was registered by a photomultiplier. The maximum intensity of light in the case of the  $E_{11}^{y}$ (TE-) mode was observed at a coupling length of 7 mm. Light pumping between the waveguides was also observed as a mode track under a microscope. The pumping length thus determined was 3.5 mm. The experiment on light modulation was carried out on coupled waveguides with a coupling length of 7.5 µm. For zero voltage, the radiation after two pumpings was propagated in waveguide 1 (Fig.6.6). When a corresponding voltage was applied to the electrodes, the phase mismatch on the region 0 < x < L/2 of coupled waveguides was responsible for a division of the light intensity into two equal parts between the waveguides. In the region L/2 < x < L of coupled waveguides the electro-optically induced phase difference has a reverse sign as compared to the phase difference on the region 0 < x < L/2. This affects the variation in the energy pump direction and decreases the light intensity in waveguide 1.

To obtain the modulation characteristic of electrodes, a sawtooth voltage with an amplitude of 20 V was applied to the electrodes. The output radiation was applied to a photomultiplier whose signal was observed on the oscillograph screen (Fig.6.8). The maximal modulation depth was 14 dB and was reached at a voltage of  $\sim$ 9 V. The total light losses were 8 dB. The capacitance of the electrode system made up 4.4 picofarad.

When a constant control voltage is applied, the light power at the modulator output was first decreased, but after 10 s it increased up to the initial value; the relaxation time was independent of the light intensity. Such a relaxation is likely to be due to the conductivity of the buffer layer of  $SiO_2$  resulted from an incomplete oxidation of  $SiO_2$  (Tangonan et al 1978).

The basis of the effective refractive index method mode field distribution allowed calculation of the mode field distribution in a waveguide and pumping lengths were determined. For the  $E_{11}^y$ -modes the pumping length was 3.6 µm and for the  $E_{11}^z$ -mode it was 60 mm.

The large pumping length of the mode  $E_{11}^z$  as compared to the pumping length of the  $E_{11}^y$ -mode is explained by the fact that the increment of the refractive index  $\Delta n$  and, therefore, mode localization with an extraordinary polarization of  $E_{11}^z$  larger that the modes with an ordinary polarization of  $E_{11}^y$  (Alferness et al 1979). Thus, the experimental value of the pumping length in the case of  $E_{11}^y$ -mode is in close agreement with the theoretical value, while



Fig.6.9 Interferometer type modulator with an induced channel waveguide (Zolotov et al 1982).

in the case of  $E_{11}^z$ -mode the theoretical calculation is indicative of the practical lack of coupling between the waveguides, which was observed in experiment.

The overlap integral of the mode field with the field of electrodes was evaluated from the state diagrams of the system of coupled channel waveguides with  $\Delta\beta$  electrodes (Fig.6.7)

$$\Gamma = 0.75 \lambda d / \eta_o^3 r_{13} VL = 0.3. \tag{6.15}$$

When the light intensity increases up to ~5  $\mu$ W, the power of light at the modulator output was decreased, and no photoinduced polarization conversion was observed, which is likely due to large losses of light of extraordinary polarization (of the TM-mode) under the electrodes (~6 dB/cm) because of imperfection of the buffer layer of SiO<sub>2</sub>. A decrease of light intensity is evidently connected with the photoinduced variation of the refractive index of the waveguides, which leads to phase mismatch between modes of coupled waveguides.

#### 6.3.2 Interferometric and perfect inner reflection modulators

Zolotov et al (1982) considered the mechanism of the action of a technologically simple interferometer type modulator (Fig.6.9). When voltage is applied with a polarity corresponding to an increase of the refractive index in a crystal, in the region under the electrodes there forms a channel waveguide (Channin 1971). The mode of this waveguide has a small transverse dimension  $\omega$  in the waveguide plane and, therefore, a larger diffraction divergence  $-\lambda/\omega$ . In the farther region this mode must interfere with the mode of a planar Tidiffused waveguide (which belongs to the continuum of radiation modes of the channel waveguide) having a substantially larger transverse dimension W and a smaller divergence  $-\lambda/W$  (*i.e.* a small angular dimension in the far

region). The phase difference of these two waves (
$$\Delta \phi = \frac{2\pi}{\lambda} \delta n^*(V)$$
, where  $\delta n^*$ 

is the difference of effective refractive indices) depends on the magnitude of the applied voltage. In the case when waves are in the counterphase  $(\Delta \varphi = \pi)$ , in the centre of the interference pattern a minimum must be observed, whereas at the boundaries of this picture no complete mutual wave extinction will occur since their angular dimensions differ strongly from one another. By the estimates (6.1) the control voltage makes up (for  $\lambda = 0.63 \mu m$ ,  $d = 6 \mu m$ , L = 5 mm):

$$V = \lambda d / n_e^3 r_{33} L = 3V.$$
 (6.16)

To obtain the maximal modulation depth, we shall find the relation between the width of the Gaussian beam W incident on the modulator and the width  $\omega$  of the mode field of the induced channel waveguide. The normalized field of the incident beam has the form

$$E_{in} = 1/\left[\left(\pi/2\right)^{1/2}W\right]^{1/2} \exp\left(-y^2/W^2\right).$$
(6.17)

Accordingly, the normalized field of the mode of the channel waveguide we approximate by the Gaussian function

$$E_{\rm chan} = 1 / \left[ \left( \pi / 2 \right)^{1/2} \omega \right]^{1/2} \eta \exp(-y^2 / \omega^2), \tag{6.18}$$

where  $\eta = 2/[\omega/W] + (W/\omega)$  is the efficiency of light input into the channel waveguide.

For the light propagating outside the channel waveguide  $E_{\rm rad} = E_{\rm inc} - E_{\rm chan}$ . The intensity of light in the far region  $x \gg \lambda/\pi\omega^2$  is related to the field in

the near region as  $I(k) = \left[\int_{-\infty}^{\infty} E(y) \exp(-iky) dy\right]^2$ 

where  $k = \frac{2\pi}{\lambda x} y_1$ , (here  $y_1$  is the coordinate in the direction perpendicular to the light propagation direction at a distance x from the modulator. Then the interference pattern in the far region in the case of inphase wave interference has the form

$$I_{+}(k) = \left[\int_{-\infty}^{\infty} (E_{\text{rad}} + E_{\text{chan}}) \exp(-iky) \, dy\right]^{2} = \pi \left[ (2W / \pi)^{1/2} \exp(-k^{2}W^{2} / 4) \right]^{2}, \quad (6.19)$$

and in the case of counterphase subtraction, accordingly (Fig.6.11)



FIg.6.10 Modulation characteristic of an interference type modulator (Kazansky 1985).

**Fig.6.11** Interference patterns in the far region. Inphase wave interference  $(I_{i})$  and counter phase subtraction  $(I_{i})$  (Kazansky 1985).

$$I_{-}(k) = \left[\int_{-\infty}^{\infty} (E_{\text{rad}} - E_{\text{chan}}) \exp(-iky) \, \mathrm{d}y\right]^{2} = \pi \left[\frac{(2W/\pi)^{1/2} \exp(-k^{2}W^{2}/4) - (6.20)}{-2\eta(2\omega/\pi)^{1/2} \exp(-k^{2}W^{2}/4)}\right]^{2} \cdot (6.20)$$

From this we imply the condition when in the centre of the interference pattern the light intensity will be equal to zero

$$\frac{\omega}{W} = \frac{1}{\sqrt{7}}.$$

To perform an experiment on a substrate of lithium niobate (y-cut), a planar waveguide was manufactured by way of titanium diffusion (the Ti layer thickness 300 Å). The electrode structure was deposited photolithographically on the crystal surface, as shown in Fig.6.9. This electrode structure consisted of two parallel aluminium strips 5 mm long and 4  $\mu$ m wide. The distance between the electrodes was 6  $\mu$ m.

He-Ne laser radiation was introduced into the waveguide by means of a rutile prism. Beam focusing by a lense with a focus distance of 20 cm made it possible to obtain the dimension of the Gaussian beam W at the waveguide input equal to 60  $\mu$ m. As the potential difference on the electrodes changes from 0 to 5 V, the field pattern in the far region changes according to the model considered above, and the maximal modulation depth obtained for V = 5 V was 95% (Fig.6.10). Figure 6.11 presents the modulation curve of such a modulator observed on the screen of an oscillograph (the applied voltage varied from 0 to 20 V). The modulation curve has maxima and minima typical of interferential phenomena. It should be noted that a low value of the control



Fig.6.12 Total inner reflection modulator (Kazansky 1985).

voltage, a large modulation depth and the possibility of realizing a wide (~1 GHz) modulation band make this type of modulators fairly promising for practical use.

Tsai et al (1978) and Sheem (1978) considered the mechanism of operation of the total internal reflection modulator, shown schematically in Fig.6.12.

When voltage of an appropriate polarity is applied to the electrodes, in the region below the electrodes the electro-optic effect results in the formation of a layer in which the effective refractive index of the waveguide mode is decreased by the value determined by the relation (6.3). Making allowance for this relation one can calculate the reflection factor of the waveguide H-mode incident on the perturbed layer at an angle  $\theta_1$  (Born and Wolf 1979)

$$|R|^{2} = P_{\rm ref} / P_{\rm inc} = \left| R_{12} \left[ 1 - \exp(2i\beta) \right] / \left[ 1 - R_{12}^{2} \exp(2i\beta) \right] \right|^{2}$$
(6.21)

where

$$R_{12} = (n'^{*} \cos\theta_{1} - n^{*} \cos\theta_{2}) / (n'^{*} \cos\theta_{1} + n^{*} \cos\theta_{2}),$$
  

$$\cos\theta_{2} = (1 / n'^{*}) (n'^{*2} - n^{*2} \cos\theta_{1})^{1/2},$$
  

$$\beta = (2\pi / \lambda) n^{*} d \cos\theta_{2}, n'^{*} = n^{*} - \delta n^{*} (V)$$

Under the condition  $n'^* < n^* \sin \theta_1$  there occurs a total internal light reflection. So, varying the voltage applied to the electrodes one can change the  $\delta n^*$  value and, therefore, the light reflection coefficient.

Radiation with a wavelength of 0.63  $\mu$ m was introduced into the waveguide using a rutile prism and was directed to the electrodes at an angle of 89.5°. The dependence of the power of the reflected light,  $P_{ref}$  on the voltage applied to the electrodes within the range from 0 to 20 V is illustrated in Fig.6.13. For the potential difference of 15 V the reflection coefficient was 95%±3%. This value agrees closely with the 94% calculated by formulae (6.3) and (6.21). The capacitance of the electrode structure made up 2 pF, which admits


Fig.6.13 Modulation characteristic of the inner reflection modulator (Kazansky 1985).

in principle the bandwidth of > 1 GHz for the load resistance of 50 Ohm.

When light of power 1 mW was introduced into the modulators, in the waveguides there occurred a strong light scattering in the *m*-line (Tangonan et al 1977) caused by induced optical inhomogeneities, which is similar to the scattering without polarization reversal in bulk crystals (Magnusses and Gaylord 1974; Voronov et al 1980). Such a scattering was responsible for a decrease of the modulation depth (to ~50%). But no photoinduced radiation polarization conversion was observed, which is also associated with a photorefractive beam scattering in a planar waveguide and, therefore, with a decrease of of light intensity in this waveguide.

## 6.4 Practical examples of waveguide electro-optic modulators 6.4.1 Optical waveguide switch modulator

Fast waveguide optical switch modulators are important components for future wideband lightwave communication systems. High-speed switching may be especially useful for time division multiplexing. Several high-speed switches (Cross and Schmidt 1979; Mikami et al 1978) and modulators (Neyer and Sohler 1979; Auracher and Kiel 1980; Leonberg 1980) using Ti-diffused lithium niobate waveguides. Most of these devices have demonstrated modulation bandwidth of about 1 GHz (approximately 500 ps switching time) and require relatively long device length of 3 to 10 mm. High sinusoidal modulation rates have been achieved using a traveling wave geometry, again with long device length (Izutsu et al 1977). A uniquely designed and fabricated optical directional



Fig.6.14 Schematic drawing of optical waveguide directional coupler switch modulator (Alferness et al 1981).

coupler switch with a demonstrated switching time of 110 ps was described by Alferness et al (1981). High-speed switching was achieved by using very short (750  $\mu$ m) electrodes with a small (1 $\mu$ m) interelectrode gap (Fig.6.14). The small capacitance resulting from the short device length yields high-speed switching. At the same time, the small interelectrode gap allows a low switching voltage in spite of the short device length.

A schematic of the waveguide directional coupler switch is shown in Fig.6.14. The directional coupler was designed so that  $k \cdot L = \frac{1}{2} n\pi$ , where k is the coupling coefficient and n is the odd integer so that in the absence of an applied field most of the light incident in one waveguide crosses over to the other. For modulator applications, this condition need not be strictly satisfied. Application of an appropriate voltage sufficiently mismatches the two waveguides so that the light stays in the incident waveguide.

The optical switching time can be minimized by fixing the control voltage (power) at some acceptable low level. For the lumped electrodes considered here the switching time is given by the *RC* time constant, where *C* is electrode capacitance and R = 50 is a parallel resistance to match to an external driving circuit. The electrode capacitance is given approximately by (Kaminow and Stulz 1975)

$$C = (\varepsilon_0 / \pi) (1 + \varepsilon / \varepsilon_0) L \ln(4W / d), \qquad (6.22)$$

where L and W are the electrode length and width, respectively, and d is the interelectrode gap. Note that the capacitance increases linearly with L but it increases only logarithmically with decreasing gap.

Clearly for high-speed switching, short device length is desirable. However, the device length must be sufficiently large to yield an acceptably low switching voltage. The required electro-optically induced phase mismatch to switch the light back to the incident waveguide (assuming one coupling length) is

$$\Delta\beta L = (2\pi L/\lambda)\alpha n^3 r V/d = 2\pi, \qquad (6.23)$$

where the push-pull effect for electrodes placed on top of the waveguides (Fig.6.14) has been induced. V is the maximum admissible control voltage, n is the refractive index,  $\lambda$  the wavelength and  $\alpha$  the geometrical overlap between the optical and applied electric fields. The required length is therefore

$$L = \left(\lambda / \alpha n^3 r\right) d / V. \tag{6.24}$$

From equations (6.22) and (6.24) the RC switching time is

$$\tau = R(\varepsilon_0 / \pi)(1 + \varepsilon / \varepsilon_0)(\lambda d / \alpha n^3 r V) \ln(4W / d).$$
(6.25)





The results of equations (6.24) and (6.25) are shown in Fig.6.15, where the required L and the resulting modulation bandwidth  $\Delta f = 1/\pi\tau$  are plotted versus the interelectrode gap. It is assumed that V = 5V,  $r = r_{33}$  (lithium niobate) =  $30 \times 10^{-12}$  m/V,  $\lambda = 0.6328$  µm, W = 30 µm, and  $\alpha = 0.5$  and that in each case L corresponds to one coupling length. Clearly for fixed switching voltage the modulation bandwidth is maximized by using a small interelectrode gap d. A small d is desirable because although it results in a larger capacitance/ length, the resulting larger electric field (for a fixed applied voltage) allows a shorter device length. Because the electrode capacitance depends linearly upon length and only logarithmically upon d, the small gap makes possible a net enhancement of the switching speed. Of course, the resulting short length is also desirable for increased packing density in dc switching networks and results in lower optical and electrical loss.

Special fabrication care is required to achieve the desired one-micron electrode gap aligned over the waveguides. This limitation was overcome using the novel two-step alignment procedure outlined in Fig.6.16. First, the electron beam written electrode mask with 1  $\mu$ m gap was intentionally misaligned laterally by about 1  $\mu$ m. The pattern was exposed, developed and chrome/ aluminium electrodes patterned by lift off. The result is that while one electrode is properly aligned over one waveguide, because of line broadening, the other is not. The same electrode pattern is then aligned over the waveguides a second time, however with an intentional 1  $\mu$ m shift in the opposite direction. After a second evaporation and lift off, the desired 1  $\mu$ m interelectrode the desired 1  $\mu$ m gap, the double metal thickness obtained by this technique is beneficial to reduce the electrode resistance.

The device was evaluated at  $\lambda = 0.6 \,\mu\text{m}$  using the TM polarization which sees the  $r_{33}$  coefficient. Using dc conditions with a six-volt bias, an additional 6-V modulation results in an about -7 dB modulation in the light output from the crossover waveguide. The switching speed of this device when driven by a short electrical drive pulse was measured with a novel optical sampling technique reported in detail elsewhere (Alferness et al 1980). A sequence of



short electrical drive pulses from an electrical comb generator drives the modulator. These pulses are in synchronism with the picosecond optical pulses from a synchronously pumped mode-locked dye laser. The optical pulses are coupled into the device. The modulator response is mapped out via sampling by using an electrical phase shifter to sweep the optical pulse train temporally across the electrical pulse train and measuring the modulator output versus time shift.

### 6.4.2 Thin-film electro-optic light modulator

Kaminow et al (1973) demonstrated the utility of thin films by building and testing an efficient wide-band  $LiNbO_3$  phase modulator whose characteristics can be satisfactorily accounted for by the bulk electro-optic coefficient of  $LiNbO_3$ .

The power per unit bandwidth,  $P/\Delta f$ , required to drive a bulk modulator rod of length L and square cross section  $d^2$  was proportional (Kaminow and Turner 1966) to  $d^2/L$ . The minimum value of this factor is determined by diffraction of the laser beam passing through the modulator crystal. With the beam focused so that the waist occurs at the centre of the rod, the minimum value for  $d^2/L$  is  $4\lambda/n\pi$ , where  $\lambda$  is the optical wavelength and n is the refractive index. For this minimum condition, the power density at the edges of the aperture is less than  $1/e^2$  times the power density at the centre of the aperture. In order to alleviate the alignment problem, modulators are usually designed with a safety factor S (Kaminow and Turner 1966) such that

$$d^{2}/L = S^{2}(4\lambda/n\pi), \tag{6.26}$$

with  $S \geq 3$ .

In a planar waveguide, there is no beam spreading normal to the plane, but diffraction in the plane still limits electrode spacing according to (6.26). However, since alignment is simpler and reflections from crystal surfaces are not a problem, one may employ the minimum value  $S \approx 1$  in the planar structure.

Kaminow et al (1973) have used the simple modulator structure illustrated in Fig.6.17: a LiNbO<sub>3</sub> planar waveguide with aluminium electrodes evaporated on the surface, and input and output rutile prism couplers. The out-diffused crystal has dimensions of  $15 \times 2 \times 5$  mm along the *a*, *b*, and *c* crystal axes, respectively. The extraordinary index profile is given by

$$\Delta n_e = A \operatorname{erfc}\left(-x/B\right), x < 0, \tag{6.27}$$

where x is the depth below the surface,  $A = 4 \times 10^{-3}$ , and  $B = 530 \,\mu\text{m}$ . The guide, which can support about 198 modes, is excited in TE modes via the input coupler by a 0.633  $\mu\text{m}$  laser polarized along the crystal c axis.

The electrodes were formed photolithographically with dimensions chosen so that

$$b^{2} / L = S^{2}(4\lambda / n_{e}\pi), \tag{6.28}$$

where b is the electrode spacing and  $S \approx 1$ . The extraordinary index,  $n_e$ , measured on a sample at  $\lambda = 0.633 \,\mu\text{m}$ , is 2.214.

As indicated in Fig.6.18, the width of the electrodes, a, is chosen so that  $a \approx b$ . The capacitance C for a coplanar condenser with a = b on a uniaxial crystal like LiNbO, having dielectric constants  $\varepsilon_a = 43$  and  $\varepsilon_c = 28$  along



Fig.6.17 Thin-film LiNbO<sub>3</sub> electro-optic phase modulator (Kaminov et al 1973).



Fig.6.18 Coplanar electrode on LiNbO<sub>3</sub> guiding layer (Kaminov et al 1973).

the a and c axes, respectively, is given approximately by (Prokhorov and Kuz'minov 1990)

$$C = \varepsilon_0 \Big[ 1 + \left( \varepsilon_a / \varepsilon_c \right)^{1/2} \Big] L.$$
(6.29)

The modulating field components just below the surface of the crystal are

$$E_x(0, y) = 0$$
 and  $E_y(0, y) = V/b$ ,  $|y| < b/2$ . (6.30)

where V is the voltage between electrodes. The  $E_y$  component decreases with depth at least as fast as (Engan 1969)  $\exp(x/x_0)$ , where

$$x_0 = \left(\varepsilon_a / \varepsilon_c\right)^{1/2} (2b / \pi). \tag{6.31}$$

For most effective use of the modulating field, the penetration depth of the optical beam should be comparable with  $x_0$ . The electrode dimensions were L = 6.2 mm, a = 44 µm, and b = 57 µm, yielding S = 1.22,  $x_0 = 45$  µm, and C = 2.0 pF. The measured capacitance at 50 MHz was about 3 pF.

If a load resistance R is placed in parallel with C and the combination is driven by a matched voltage generator with impedance R, the base bandwidth is given by (Kaminow and Turner 1966)

$$\Delta f = \left(\pi R C\right)^{-1}.\tag{6.32}$$

For  $R = 50 \ \Omega$  and the calculated  $C = 2 \ pF$ , the maximum bandwidth is  $\Delta f = 3.2 \ \text{GHz}$ . Transit-time limitations are above 3.2 GHz for  $L = 6.2 \ \text{mm}$ .

For the crystal c axis oriented along y, the phase modulation index is

$$\eta = \pi n_e^3 r_{33} \overline{E}_y L / \lambda, \tag{6.33}$$

where  $r_{33}$  is the electro-optic coefficient and  $\overline{E}_y = uV/b$  is the effective modulating field. The factor u is a number less than unity that takes account of the fact



Fig.6.19 Apparatus for heterodyne measurement of the phase modulation index (Kaminov et al 1973).

that  $E_y$  varies across the beam. With  $r_{33} = 31 \times 10^{-12}$  m/V, the calculation yields  $\eta/V = 0.18$  u/V.

The modulation index can be measured by using the heterodyne system (Kaminow 1965) illustrated in Fig.6.19. The stabilized He-Ne laser oscillate in only one longitudinal mode because of their restricted length. The local-oscillator laser can be swept over a 500-MHz range without appreciable variation in amplitude by varying the mirror spacing. The spectrum of the modulated carrier laser mixes with the local oscillator in a photodiode; the photocurrent is passed through a 70-MHz-i.f. amplifier and is detected and displayed on an oscilloscope. The ratio of sideband to carrier amplitudes is  $J_1(\eta)/J_0(\eta)$ , where  $J_n$  is the  $n^{th}$  order Bessel function. The amplitude ratio is measured with the aid of calibrated optical attenuators placed in front of the local oscillator, and  $\eta$  is calculated from the result. The use of input and output prisms, rather than focusing the beam into and out of the edges of the layer, ensures that only guided light is detected.

In the experiment, a General Radio oscillator feeds a miniature 50  $\Omega$  coaxial cable leading to a panel connector adjacent to the modulator crystal. Thin gold wires from the connector connect the voltage to the electrodes on the crystal. The capacitance of the connector, leads, and electrodes measured at the connector is about 4 pF. In order to obtain a correct reading of V at high frequency, it is necessary to place the voltmeter probe in direct contact with the electrodes.

The measurements yield  $\eta/V = 0.13 V^{-1}$ , constant to within 10% over the available measuring range of the apparatus, 50-500 MHz. Voltage was also varied from 0.7 to 7 V without altering  $\eta/V$ . The measured and calculated values of  $\eta/V$  agree if the effective field factor u is set equal to 0.7, which is reasonably close to unity. Thus, Kaminow et al (1973) confirm that the beam passes cleanly between the electrodes in the x = 0 plane and does not penetrate much deeper than  $x_0$ , justify the assumption that the electro-optic coefficients in the guiding layer and bulk crystal are practically the same, and demonstrate experimentally a base bandwidth at least as great as 500 MHz.

The observed value of u may seem surprisingly close to unity in view of the fact that the penetration of the modulating field is approximately  $x_0 = 45 \ \mu m$  while the thickness of the guiding layer is approximately

 $B = 530 \ \mu\text{m}$ . The likely explanation is that, by adjusting the input angle to the prism coupler for maximum modulation, only the shallow low-order modes are selectively excited. The experimental error in the measurement of  $\eta/V$  is probably less than 15%. The peak voltage required to obtain  $\eta = 1$  rad is 7.7 V. The corresponding power  $P = V^2/2R$  consumed in the 550  $\Omega$  load is 590 mW, and, for  $\Delta f = 3.2$  GHz,  $P/\Delta f = 0.19$  mW/MHz. If one uses the capacitance measured at the connector rather than the calculated C,  $\Delta f$  will be halved and  $P/\Delta f$  doubled.

In order to improve  $P/\Delta f$ , the optical beam and modulating fields must be confined to smaller cross sections over their interaction length. Optical confinement in the y = 0 plane can be improved by reducing the out-diffusion time and/ or temperature in order to reduce the layer thickness (Kaminow and Carruthers 1973). Other schemes are being considered that will guide the optical beam in the x = 0 plane in order to eliminate diffraction effects; then  $b^2/L$  may be reduced indefinitely. In order to use the modulating field most effectively, the modulating field distribution should be tailored to just overlap the optical beam; for the closely confined optical beam, this can be achieved by reducing the electrode spacing.

#### 6.4.3 Bragg diffraction modulator

In their work, Hammer and Phillips (1974) reported the production of lowloss  $\text{LiNb}_x \text{Ta}_{1-x}O_3$  optical waveguides and their use as the basis of electrooptic modulators with over 80% modulation at voltages below 5 V.

A simple technique of diffusing metallic niobium into the LiTaO<sub>3</sub> substrates produces a high-index surface layer of LiNb<sub>x</sub>Ta<sub>1-x</sub>O<sub>3</sub> which acts as an optical waveguide. The effective thickness and index can be controlled to readily produce single-mode waveguides. Losses of about 1 dB/cm at 6328 Å have been measured on a single-mode guide of this type.

Using a periodic electrode structure, Bragg diffraction modulation (Hammer et al 1973) is obtained which switches over 80% of the guided light at voltages of 3.5, 4.5, and 6.5 V for laser lines at 4976, 5592, and 6323 Å, respectively. These results hold for both operation at dc and with pulse rise times of less than 3 nsec. Frequency response in the microwave range with power requirements below 0.2 mW/MHz is expected.

The low power and voltage requirements of these optical waveguide modulators are compatible with integrated circuit technology. This, plus the excellent and controllable waveguide properties, makes these devices extremely attractive for use in a variety of optical communication and integrated optic applications.

Laser light is coupled into the film with  $SrTiO_3$  prism couplers. The effective index for the guided light may be calculated from the coupling angle (Tien et al 1969). The values found fall in the range expected for optical waveguides with indices between those of LiNbO<sub>1</sub> and those of LiTaO<sub>3</sub>.

For example, in a single-mode x-z plane sample the effective index for the TE<sub>0</sub> mode propagating at 51° to the z axis is measured to be 2.188 at  $\lambda = 6328$  Å. This falls in the range between 2.179 and 2.237 which are the indices in this direction for pure LiTaO<sub>3</sub> and LiNbO<sub>3</sub>, respectively. Propagation at 51° is chosen to optimize the electro-optic coefficient and retain relatively strong guiding as described below. For a guide of this type to have only one mode the thickness at which the graded index difference between film and substrate falls to 10% of its maximum value is  $0.7-1.6 \mu m$  (Marcuse 1973).

The loss is determined by measuring the intensity of light scattered out of the waveguide as a function of distance using a fibre optic probe. At 6328 Å the loss in the solitary  $TE_0$  mode is less than 1 dB/cm. At the 5592- and 4845-Å He-Ne laser lines the losses are 4.3 and 6.7 dB/cm. This represents a more rapid increase in loss than the  $\lambda_0^{-4}$  dependence expected for Rayleigh scattering ( $\lambda_0$  is the free-space wavelength). It is possible that impurity ion absorption, particularly Fe<sup>2+</sup>, is responsible.

Hammer and Phillips (1974) noted that for the x-z substrates and transverse electric fields used in the modulator, propagation of a TE mode in the c direction gives rise to the largest index difference between lithium niobate and lithium tantalate ( $\Delta n_o = 0.113$ ) but an electro-optic coefficient is equal to zero. Propagation along the x direction reverses the situation with  $\Delta n_e =$ 0.021 and  $r_{33} = 3 \times 10^{-12}$  m/V. Propagation in the plane at an arbitrary angle  $\phi$  with respect to the z axis gives an index differential  $\Delta n'$  such that  $\Delta n_e < \Delta n' < \Delta n_o$  and an effective electro-optic coefficient r' which is a linear combination of  $r_{13}$ ,  $r_{33}$ , and  $r_{51}$ . may be chosen to maximize r'. The resulting values for LiNbO<sub>3</sub> can be shown to be  $\phi = \pm 51^{\circ}$ ,  $r' = \pm 34.4 \times 10^{-12}$  m/V, and  $\Delta n' = 0.058$ . Thus, the operating angle can be chosen to maximize the electrooptic coefficient without minimizing the index differential required for waveguiding.

The waveguide modulator is produced by applying a voltage to an interdigital electrode pattern deposited on the waveguide surface as shown in Fig.6.20a.

Application of a voltage to the electrodes results in an electro-optically induced Bragg diffraction grating. Light entering the grating at an angle  $\theta_B$ is diffracted through an angle  $2\theta_B$  in the waveguide plane where  $\sin\theta_B = \lambda_0/4Sn_g$ .  $n_g$  is the effective refractive index for the guided mode being considered. The fraction of the entering light diffracted is  $I/I_0 = \sin^2(\Delta\phi/2)$  and to first order in r',  $\Delta\phi = -\pi r'(n_g)^3(L/\lambda_0)E$ , where E is the average in plane field component caused by the voltage  $V_0$ . Thus,  $I/I_0$  has the form  $\sin^2(BV_0)$ .

The percentage diffraction as a function of voltage for three laser wavelengths is shown in Fig.6.20b. The squares, crosses, and circles are the data points for 4976, 5592 and 6328 Å laser lines, respectively. The solid curves are plots of  $\sin^2(BV_0)$  normalized to the data  $I/I_0 = 75\%$ . The functional agreement is good. No variation was observed in these percentages from dc up to pulses with rise times below 3 nsec. The observed variation of voltage with wavelength, however, is greater than the first-order theory predicts if dispersion in the electro-optic coefficients is ignored. This dispersion for LiNb<sub>x</sub>Ta<sub>1-x</sub>O<sub>3</sub> is under study. The measured capacitance of this sample is 20 pF which gives indicated capacitive power requirements below 0.2 mW/MHz. The total loss introduced by the electrodes is under study but appears to be less than 1 dB.

The LiNb<sub>x</sub>Ta<sub>1-x</sub>O<sub>3</sub> optical waveguides described in this report are relatively simple to make, have excellent and controllable waveguide properties, and can be oriented to make optimal use of the strong electro-optic effect of both LiNbO<sub>3</sub> and LiTaO<sub>3</sub>. The high efficiency and low voltage and power requirements of the grating modulator formed on this type of guide represent at least



**Fig.6.20** (a) Schematic of grating modulator in LiTa<sub>x</sub>Nb<sub>1-x</sub>O<sub>3</sub> waveguide. Guided light is diffracted through an angle  $2\theta_{g}$  when a voltage is applied to the interdigital electrodes. *S* is 7.6 µm and *L* is 0.3 cm. (b) The curve shows the percentage of light diffracted as a function of voltage. Open squares 4976 Å (He–Se laser), crosses 5598 Å (He–Se laser), and solid circles 6328 Å (He–Ne laser). The solid curves are plots of sin<sup>2</sup>(*BV*<sub>0</sub>) normalised to the data at 75% (Hammer and Phillips, 1974).

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an order-of-magnitude improvement in performance over bulk devices and earlier waveguide grating modulators. Similar improvements may be expected for other forms of electro-optic and possibly acousto-optic waveguide modulators and switches if the LiNb<sub>x</sub>Ta<sub>1-x</sub>O<sub>3</sub> guide is employed.

#### 6.4.4 Ridge waveguide modulator

Kaminow et al (1974) reported an experimental LiNbO<sub>3</sub> ridge waveguide modulator requiring a modulating power of only 0.02 mW/MHz/rad.

A LiNbO<sub>3</sub> crystal having dimensions 25 mm×6 mm×3 mm along the crystallographic X, Y, and Z axes, respectively, was out-diffused to produce a planar guide with extraordinary index profile based on the integral error function complement

$$n(x) = n_{\infty} + \pi^{1/2} a \operatorname{ierfc}(x / b), \tag{6.34}$$

where  $n_{\infty} = 2.214$ . In order to approach single-mode operation; the resultant coefficients were  $a = 2 \times 10^{-4}$ ,  $b = 33 \,\mu\text{m}$ . If the profile (equation (6.34)) is approximated by an exponential function

$$n(x) = n_{m} + a \exp(-2x/b)$$
(6.35)

then calculations (Conwell 1973) indicate that the planar guide will support just two modes. For the  $TE_0$  and  $TE_1$  modes, respectively,

$\left(\beta / k - n_{\infty}\right)a^{-1} = 0.36$	(6.36a)
$(\beta / k - n_{\infty}) a^{-1} = 0.09$	(6.36b)

where  $\beta$  and k are the propagation constants in the guide and in free space, respectively.

A ridge was produced by ion-beam etching the  $6\times25$  mm surface of the crystal everywhere except for a narrow central strip along the 25 mm dimension. A quartz fibre of square cross section adhered to the crystal surface with photoresistor serving as the mask. An ion gun fired argon ions at 30° from the normal onto the crystal surface. With 100 µA ion beam current, the etching rate for this configuration was approximately 1 µm/h for both the LiNbO<sub>3</sub> crystal and quartz fibre. After ion etching and with the fibre mask still in place, the sample was coated with Cr (250 Å) and Al (3000 Å) electrodes by evaporation. In order to ensure coating the side walls of the ridge, the sample was tilted first to one side and then the other during evaporation. After examination of the completed ridge, the best region was selected and the remainder of the crystal was ground off and the ends polished.

A scanning electron micrograph of the sample shows that the walls of the ridge are smooth and rectangular. Although the cross-section dimensions may vary by  $\pm 1 \ \mu m$  along the length of the ridge, the average height h is 7.5  $\mu m$  and average width w is 19  $\mu m$ . The length L of the ridge is 11.5 mm.

A heterodyne measuring set was used to determine the phase modulator. A 0.633-µm laser beam was injected into the end of the ridge with a  $\times 20$  microscope objective; a  $\times 40$  objective was used to image the output end onto a screen and later to collimate the beam in the measuring set. The beam appears to be single-mode, slightly elliptical in cross section, and is almost completely confined within the ridge itself, rather than penetrating into the planar waveguide region below the ridge.

If one assumes the exponential index profile (6.35) for the original planar guide and then removes 7.5 µm to form the ridge, the planar guide outside the ridge will have an exponential profile with coefficients  $a_p = a \exp(-2h/b) = 1.3 \times 10^{-4}$  and  $b_p = b$ . Then using the curves of Fig.5.15 (Carruthers et al 1974) one obtains for TE<sub>0</sub> and TE<sub>1</sub> modes, respectively,

$$\left(\beta_p / k - n_{\infty}\right) a_p^{-1} = 0.26 \tag{6.37a}$$

$$\left(\beta_p / k - n_{\infty}\right) a_p^{-1} = 0.04.$$
 (6.37b)

Then the effective index approximation can be used (Ramaswamy 1974) to determine the confinement within the plane. The effective index change for the symmetrical guide within the plane is (from equations (6.36) and (6.37))



Flg.6.21 Schematic diagram of the LiNbO<sub>3</sub> ridge waveguide modulator (Kaminov et al 1979).

$$(\beta / k - \beta_p / k) = 3.6 \times 10^{-5}$$
 (6.38a)

 $(\beta / k - \beta_p / k) = 1.3 \times 10^{-5}$  (6.38b)

for  $TE_0$  and  $TE_1$  modes, respectively. In either case, computation shows that only the fundamental mode is guided in the plane. The planar  $TE_1$  mode is probably not strongly excited nor is it tightly confined in the ridge guide. Other approaches to the analysis of ridge guide (or equivalently rib guide) modes give similar results.

The ridge waveguide modulator is shown schematically in Fig.6.21. The electrodes are attached by thin wires to a miniature coaxial connector. A voltmeter and 50  $\Omega$  load are placed in parallel with the crystal at the connector and the modulation index  $\eta$  is measured at frequencies between 50 and 200 MHz. The series inductance of the leads and stray capacitance of the connector interfere with the measurement of peak modulating voltage V at high frequency. However, these unwanted impedances can be eliminated or reduced in a practical device.

The capacitance measured at the connector is 19 pF, while the capacitance C of the modulator crystal alone, obtained by subtracting the capacitance measured when the leads are disconnected at the crystal, is 10 pF. The calculated capacitance of the ridge capacitor in parallel with the associated planar capacitor is only 5 pF, so that a further reduction of C and an increased bandwidth must be possible.

The measured value of  $\eta/V$  is 0.85 V<sup>-1</sup>. The value calculated assuming the beam to be completely confined within a ridge of width  $w = 19 \mu m$  is 0.98 V<sup>-1</sup>. This excellent agreement is further evidence that the beam is well guided within the ridge. For a planar modulator,  $\eta/V$  was 0.13 V<sup>-1</sup>. That device was diffraction limited so that the safety factor S was unity. For the ridge guide, if w = d in equation (6.26), then S = 0.28. Since modulating power P per unit bandwidth per unit modulation index is proportional to  $S^2$ , the ridge guide modulator represents a potential thirteenfold improvement in efficiency over the diffraction-limited planar modulator and an additional order-of-magnitude improvement over bulk modulators for which the safety factor is usually greater than 3.

The modulator bandwidth is  $\Delta f = (\pi R C)^{-1}$  and, with  $R = 50 \Omega$  and measured C = 10 pF,  $\Delta f = 640 \text{ MHz}$ . Then using the measured  $\eta/V$  and  $P = V^2/2R$ , Kaminow et al (1974) obtained  $P/\Delta f = 20 \mu W/MHz$  for  $\eta = 1$  rad.

The optical attenuation due to absorption by the metal walls on the ridge guide may be estimated from calculations for a planar symmetrical metal-clad guide operating in the  $TM_2$  mode (Kaminow et al 1974). The calculated losses were 4 and 3 dB/cm for Cr and Al electrodes, respectively. Ag electrodes would introduce a loss of only 0.2 dB/cm. The major source of transmission loss in the devise at present, however, is imperfect input coupling into the dominant metal-clad ridge guide mode. The ridge waveguide phase modulator is well suited to incorporation in a balanced bridge arrangement in an integrated optical circuit for use as switch or amplitude modulator.

#### 6.4.5 Ti-diffused diffraction modulator

Tangonan et al (1978) described the design and fabrication of thin-film Bragg diffraction modulators in Ti-diffused LiTaO<sub>3</sub> waveguides. The modulator performance was adequate for near-term systems applications with a demonstrated diffraction efficiency of 98% at the visible and near IR wavelengths, a high extinction ratio (< 250:1), and a design bandwidth of  $\approx 1$  GHz. LiTaO<sub>3</sub> was switched as the waveguide material because of the much higher image threshold of waveguides formed by Ti-diffused in LiTaO<sub>3</sub> than in LiNbO<sub>3</sub> (Tangonan et al 1977).

Beam diffraction, as a mechanism for intensity modulation by electro-optic means in the thin films, is achieved by producing an electrically controlled phase grating in the path of the propagating beam. The diffraction process results from a periodic perturbation of the refractive index transverse to the beam propagation direction. A useful method for electro-optically generating the desired phase grating is shown in Fig.6.22. The mechanism for interaction relies on the fringing electric fields extending below the surface between interdigital strip electrodes formed on the crystal surface. The local fringing field strength should be reasonably uniform across the guided beam and approximately sinusoidal in the plane of the guiding layer, transverse to the beam. This may be most readily achieved by applying an isolating lower-index layer above the guiding layer. This serves the added function of minimizing interaction of the optical beam evanescent tail with the lossy metallic surfaces. Bragg





diffraction involves introducing the input beam at a specific angle  $\theta_{g}$ , the Bragg angle, with respect to the electrode array (Hammer and Phillips 1974; Noda et al 1974). Diffraction occurs reflectively in a single output at twice the input angle when the Bragg condition is satisfied.

The phase change  $\phi$ , in radians, induced by the electrical signal field over a pathlength L is

$$\phi = \left[2\pi L / \lambda_0\right] \Delta n, \tag{6.39}$$

where  $\Delta n$  is the refractive-index increment caused by the electro-optic effect,  $\lambda_0$  and is the free-space wavelength. The strongest interaction in LiTaO<sub>3</sub> and LiNbO<sub>3</sub> occurs when the applied electric field and optical electric polarization are both parallel (or nearly parallel (Hammer and Phillips 1974)) to the crystalline c axis (the optic axis). For this condition, the refractive-index increment is

$$\Delta n_3 = 1/2 \, n_3^3 r_{33} E_3,\tag{6.40}$$

where  $n_3$  is the extraordinary refractive index,  $r_{33}$  is the appropriate electrooptic coefficient, and  $E_3$  is the applied electric field (Chen 1970). Thus, the crystal must be cut with its c axis in the plane of the waveguide essentially transverse to the beam propagation direction, and the propagating optical mode must have TE polarization. This polarization has the least loss characteristics in proximity to the metal electrode surfaces. Hence, this minimizes the insertion loss of the modulator caused by absorption.

Combining equations (6.39) and (6.40) yields

$$\phi = \left(\pi L n_3^3 r_{33} E_3\right) / \lambda_0. \tag{6.41}$$

Assume that the c axis-oriented electric field in the region of the guided layer is approximately sinusoidal in the transverse direction (a reasonable assumption for a region about a distance s below the surface). For Bragg diffraction, the zero- and the first-order powers are proportional, respectively, to  $\cos^2(\phi/2)$  and  $\sin^2(\phi/2)$ . For modulation, corresponding to 100% depletion of the zero-order beam in the idealized case, the maximum required value of  $\phi$  is  $\pi$ .

To design a suitable diffraction modulator, one has to determine the allowable dimensions of the electrode array, based on bandwidth requirements and driver power limitations. This can be done in a fairly straightforward manner, and both the power and the capacitance can be easily expressed in terms of the ratio of the electrode spacing to electrode length, s/L.

With optimized video peaking, the power required to drive a capacitance C over a bandwidth B with peak driver voltage  $V_m$  is

$$P = \left(V_m^2\right) / (2R_s) = (\pi/2)BCV_m^2$$
(6.42)

where  $R_s \simeq 1/\pi BC$  is the shunt resistance needed to dissipate the power and provide an *RC*-limited bandwidth *B*. The capacitance of an interdigated electrode array having *N* finger pairs on an *x*- or *y*-cut uniaxial crystal such as LiTaO<sub>3</sub> is (Joshi and White 1969)

$$C = \left[\varepsilon_0 + \left(\varepsilon_1 \varepsilon_3\right)^{1/2}\right] K L N, \qquad (6.43)$$

where K is a correction factor (Barros and Wilson 1972) determined from the ratio of electrode width to spacing w/s. For LiTaO<sub>3</sub> in the clamped condition (which is expected to obtain over most of the operating band), the capacitance is

$$C = 3.8 K L N \text{ (pF)}$$
 (6.44)

The number of electrode pairs is readily determined from the total width of the electrode array. For an input laser beam having a  $1/e^2$  diameter D equal to about 1 mm, it turned out to be sufficient to assume an electrode array width of 1.5 D, which yields

$$N = (1.5D) / S = (0.15) / S, \tag{6.45}$$

where S is the periodicity (expressed in centimeters).

The applied electric field  $E_3$  in the active region of the beam is estimated to be approximately (Joshi and White 1969; Barros and Wilson 1972)

$$E_3 = (V_m)/(2s) \tag{6.46}$$

when the distance below the surface is comparable to s. This is the assumed design condition that leads to a reasonably uniform field strength across the optical beam. It is convenient to express  $V_m$  in terms of the commonly used electro-optic parameter  $E_3L$ , the field-length product

$$V_m = 2(E_3 L)(s/L), \tag{6.47}$$

where

$$E_{3}L = (\phi \lambda_{0}) / (\pi n_{3}^{3} r_{33}).$$
(6.48)

Table 6.1 lists the relevant electro-optic and dielectric characteristics of LiTaO<sub>3</sub> and LiNbO<sub>3</sub> at 0.53  $\mu$ m and 1.06  $\mu$ m. These data are useful in the design of a doubled Nd:YAG communication link. The changes in  $\varepsilon_1$  and  $\varepsilon_2$  for LiNbO<sub>3</sub> in going from the unclamped to clamped condition are quite large,

Quantity	LiTaO3			LiNbO <sub>3</sub>	
	0.53 µm		1.06 µm	0.53 µm	1.06 µm
<i>n</i> <sub>3</sub>	2.21		2.14	2.23	2.16
$r_{33}^{T} \cdot 10^{-10} \text{ cm/V}$	~31		~29	32.2	~32
r <sup>s</sup> <sub>33</sub> 10 <sup>-10</sup> cm/V	30.3		~29	30.8	~30
$n_3^3 r_{33}^T \cdot 10^{-10} \text{ cm/V}$	33.5		~28.4	35.7	~32
$n_1^3 r_{31}^8 \cdot 10^{-10} \text{ cm/V}$	32.7		~28.4	34.1	30
$(\varepsilon_1 / \varepsilon_0)^T$		51		78	
$(\epsilon_1/\epsilon_0)^s$		41		43	
$(\varepsilon_3/\varepsilon_0)^T$		45		32	
$(\epsilon_3/\epsilon_0)^s$		43		28	
<ul><li>(T) = unclamped</li><li>(S) = clamped</li></ul>					

Table 6.1 Properties of electro-optic materials (Tangonan et al 1978)

Table 6.2 Results of design calculations (Tangonan, Persechini, Lotspeich, Barnoski, 1978)

	$0.53\mu m,3$ W drive	1.06 µm, 24 W drive	
rarameter	B = 0.7  GHz	B = 1.4  GHz	
K = 1, s = w			
$E_3 \times L$ , V	1606	3732	
L, mm	2.5	5	
s, µm	4.6	6.9	
S, µm	18.4	27.5	
N	81	54	
C, pF	77	104	
<i>R</i> <sub>s</sub> , Ω	6	2.2	
Q	11	20	

a fact which adversely affects the frequency response characteristics. Similarly, the change in  $r_{33}$  is substantially greater than that of LiTaO<sub>3</sub>, thus producing a stronger effect on the electro-optic frequency response.

For w/s = 1, a maximum interaction length of 2.5 mm was chosen 0.53 µm to keep within reasonable limits of optical loss. It was found that the waveguide loss at 5145 Å for Ti-diffused LiTaO<sub>3</sub> guides was 3–5 dB/cm. For the 1.06-µm case, where optical losses are substantially lower ( $\approx 1$  dB/cm), a length of 5 mm was arbitrarily chosen as a reasonable upper limit.

Table 6.2 gives the results derived from the preceding equations for the two wavelengths of interest. The Table includes a parameter Q defined by

$$Q = \left(2\pi\lambda_0 L\right) / \left(n_3 S^2\right),\tag{6.49}$$

#### Thin-Film Structures in Integrated Optics



Fig.6.23 Series electrode modification for Bragg diffraction grating (Tangonan et al 1978). Fig.6.24 (right) Split electrode pattern of modulator (Tangonan et al 1978).

which describes the same nature of the diffraction. Bragg diffraction occurs most efficiently when Q > 10.

Examination of the values of shunt resistance  $R_{i}$  for the two cases shown clearly indicates the need for impedance matching from a 50  $\Omega$  driver source. Some developments in the design of wideband rf impedance transformers have led to very wideband devices capable of operating from below 1 MHz to well above 500 MHz with insertion losses of 0.5 dB and less, provided the impedance ratios do not exceed about 3 or 4 to 1. For larger step-down ratios, the insertion losses are substantially higher. As an alternative, a different electrode design may be used to provide matching to a 50  $\Omega$  driver. For the case of 0.53 um design, the modification follows a scheme proposed by Noda et al (1974) in which the electrode array is divided into several sections, say 3, each of length L/3, arranged in series both electrically and optically. This device reduces the capacitance by a factor of 9, which increases shunt resistance in the same proportion. This modification is shown in Fig.6.23. For the case of the 0.53  $\mu m$  modulator design, this clearly yields a shunt resistance of 0.54  $\Omega$  and a capacitance of 8.6 pF. The penalty paid by this approach is that the driver voltage is increased by a factor of 3.

Optical waveguides were formed in y-cut LiTaO<sub>3</sub> wafers by Ti in-diffusion following the processing technique described in chapter 1. Interdigital electrodes employing the design parameters in Table 6.2 for 0.53  $\mu$ m operation were fabricated on the wafers with the field directions aligned with the *c* axis. Diffraction efficiency measurements were made at 6328 Å (He-Ne), 5145 Å (Ar), and at 10.640 Å (Nd:YAG). Diffraction measurements indicate that these are the most efficient electro-optic Bragg modulators to date: 98% efficiency with extinction ratios as high as 300:1.

For the modulator structures fabricated, the electrode patterns were formed by photoetching 1500 Å Al films that had been evaporated directly on the

324

waveguide sample or on a buffer film of SiO<sub>2</sub> (1500 Å). This thickness of the buffer layer has been found to be effective in providing the necessary isolation to prevent direct interactions of the optical field with the metal grating. Figure 6.24 is a photograph of a portion of a split electrode design used to reduce the effective capacitance by a factor of 9. The width-to-spacing ratio achieved was close to 0.5 for all the samples studied.

The diffraction efficiency of modulators with and without electrode buffer layers was studied to determine the degree of energy transfer from the m = 0 undiffracted beam to the different grating orders. Electrical leakage can hinder device evaluation, and severe leakage currents were observed in several samples. The leakage currents originate from incomplete oxidation of the SiO<sub>2</sub>. The applied voltage was simply turned on and kept on. It is clear from the trace that the effective field over the waveguide structure goes to zero in a short time. These results were obtained for modulators with a sputtered SiO<sub>2</sub> buffer layer. These same samples were stripped of the Al electrode pattern and placed in an oven in an oxygen atmosphere at 500°C for a few hours. The samples were then reprocessed and new modulator patterns fabricated on them. These samples were found to exhibit good dc properties: no leakage was observed, and modulation tests could be carried out.

Diffraction efficiency measurements were made at 5145 Å. This modulator had no buffer layer on it and was used to determine the effects of the metal grating. The metal grating induced a deflected spot at twice  $\theta_{g}$  of intensity equal to 15–25% of the undeflected (m = 0) spot. The measured voltage for maximum diffraction was 17.5 V, which is quite close to the calculated value of 17.0 V for 5145 Å operation. The calculated value for doubles Nd:YAG operation (0.53 µm) is 17.7 V. The diffraction efficiency measured in this experiment was 95.3%.

The results of measurements made at 1.06  $\mu$ m are plotted in Fig.6.25. The measured diffraction efficiency was 98% with an extinction ratio of 300:1, or 24.7 dB.



Fig.6.25 Results of diffraction measurements at 1.06  $\mu$ m showing 98% maximum first order diffraction and a 300:1 extinction ratio (Tangonan et al 1978).

Control voltage	2 V
Operating frequency bands	50 Hz – 500 MHz
Operating wavelength	0.85 µm
Optical insertion loss, not more than	12 dB
Control input capacity	10 pF

Table 6.3 Characteristics of electro-optic interference type modulator

#### 6.4.6 Interferometric Mach-Zehnder modulator

An optical interferometer-type modulator was realized in practice using the epitaxial thin-film technique.

The modulator was manufactured by the Mach-Zehnder interferometer scheme on an Y-LiTaO<sub>3</sub> substrate. Single-mode channel light guides with the distribution profile  $\Delta n$  close to a cylindrical one were formed by the film diffusion method. The size of the mode spot at a wavelength of 0.85 µm made up ~9 µm. An aluminium electrode structure with dimensions *l* (length) 20 mm, *d* (width) 5 mm was formed on the film surface.

The Li(Nb, Ta)O<sub>3</sub> film thickness was h = 13 µm, L = 20 mm, the interelectron gap width d = 3 µm,  $\lambda = 0.85 \text{ µm}$ , n = 2.18,  $r = 20 \times 10^{-12} \text{ m/V}$ . Under such conditions the overlap integral  $\Gamma = 0.8$ . The calculations show that the value of the control voltage will be equal to V = 1 V, while experimental values were 2 V. The experimental modulation depth *m* (equation (6.8)) was equal to 82% when we worked with linearly polarized radiation at the input.

A 100% modulation depth which is theoretically admitted is typically somewhat less in experiment due to light scattering on waveguide defects and on the electrode structure. In our experiments m was equal to 82% when we worked with linearly polarized radiation at the input.

The insertion losses include input and output radiation losses to propagation about the modulating structure. The measured value of  $\alpha$  was 12 dB. For linearly polarized radiation this value falls down to 9 dB. The losses of light scattered from channel light guides on the structure were 6 dB, and the losses on 'Y' branches were equal to 2 dB.

The modulators were manufactured integro-optically on a lithium tantalate substrates measuring  $20 \times 30 \times 2$  mm<sup>3</sup> on which two Mach-Zehnder interferometers were placed. The modulators are distinguished in that their light guide structure is formed in an epitaxial film of a solid solution of lithium niobate-tantalate and represents channel light guides obtained by the combined film diffusion method. Such light guides, as compared with lithium niobate, are highly resistant to optical damages. The control structure of the modulator is well protected from the influence of the atmosphere.

The modulators are mounted into a metallic frame measuring  $75 \times 15 \times 35$  mm<sup>3</sup>. The control voltage is applied through joints. There exists two versions of adjustment with external optical chains.

The modulator can be fabricated in two modifications. First, a semicon-



Fig.6.26 Thin film integro-optic modulator (general view).

ductor laser mated with a modulator may serve as a light source. The light is transmitted through a single-mode fibre adjusted immediately to the modulator end. In the second version the light is put in and out of the modulator through a single-mode fibre joined to the substrate ends.

The principal parameters of the modulator are presented in Table 6.3.

Figure 6.26 gives a picture of the modulator (Dubrovennaz et al 1988). Significant interest lies in producing optical waveguide devices in material with a higher electro-optic coefficient which could be used for making compact low-voltage electro-optic modulators and switches (Eknoyan and Swenson 1991). A suitable choice for this is  $Sr_{0.6}Ba_{0.4}Nb_2O_6$  (SBN : 60), because its  $r_{33}$  electrooptic coefficient ( $420 \times 10^{-12}$  m/V) is more than an order of magnitude larger than that for LiNbO<sub>3</sub> and LiTaO<sub>3</sub> (Prokhorov and Kuz'minov 1990 (a)). Other relevant parameters of SBN:60 are its relevant dielectric constant values  $\varepsilon_{11} = 470$  and  $\varepsilon_{12} = 880$ , and refractive indices which at 0.83 µm wavelength (Prokhorov and Kuz'minov 1990 (b)) are  $n_e = 2.2435$  and  $n_o = 2.2375$ . The interest in this material is particularly attractive due to major advances in its growth techniques, which now makes it possible to produce crystals in large sizes (2–3 cm in diameter) of excellent quality (Neurgaonkar 1989).

Optical waveguides have been produced in SBN:60 by Zn diffusion from vapour phase. Using electron microprobe wavelength-dispersive spectroscopy, the Zn distribution was determined and a value of 7.3  $\mu$ m for the diffusion depth was obtained. The best waveguides were realized by diffusion at 1000°C for 30 min followed by annealing at 600°C for ~100 h.

The optical waveguides were produced by Zn diffusion from the vapour phase into 1 mm thick Z-cut SBN substrates, in a process similar to one described earlier with LiTaO<sub>3</sub> crystals. Tungsten bronze SBN:60 is tetragonal at room temperature and exhibits the Curie point  $T_c$  at 78°C. The crystals were grown by the Czochralski technique and the surfaces were prepared according to current needs. Waveguiding was observed for both TE and TM polarizations by end-fire coupling at 0.83 µm wavelength. Electro-optic modulation at a wavelength of 0.83 µm on a Mach–Zehnder interferometer was demonstrated for the first time in this material. With electric field applied to both arms of the interferometer, a voltage–length product of 0.48 V cm was obtained. Lower values of  $V_{\pi}$  can be expected by further optimizing the poling procedure or using material of higher electro-optic coefficient like SBN:75. Electro-optic

327



**Fig.6.27** (a) Geometry used for writing a holographic grating into a Ti-diffused LiNbO<sub>3</sub> waveguide with 0.5145  $\mu$ m light; (b) beam splitting of a guided wave ( $\lambda = 0.6328 \ \mu$ m) by a holographic grating; (c) modulation of a guided beam by the application of an electric field across a holographic grating (1.59 mm gap electrodes) (Goruk et al 1981).

modulators and switches in SBN are attractive as they might pave the way to compact low-voltage devices.

#### 6.4.7 Electro-optic photorefractive modulator

Goruk et al (1981) described a novel modulator based on a combination of the photorefractive and electro-optic effects. It is essentially an integrated optics version of the electro-optic switch first demonstrated in bulk LiNbO<sub>3</sub> by Kenan et al (1974). Light incident onto a photorefractive grating at and near the appropriate Bragg angle is first split into two beams whose relative intensity varies with the exposure time used in writing the grating. The electrooptic effect is then used to modulate temporally these beams via an input electrical signal. The resulting modulator is a useful low cost laboratory tool which does not require elaborate fabrication. Furthermore, by using standard holographic techniques, various optical elements such as lenses and couplers may be written into the waveguide and switched on and off by this method.

The photorefractive method of writing grating holograms in planar optical waveguides has been reported by Chen et al (1968) and Wood et al (1981). Goruk et al (1981) made use of the large photorefractive effect known to occur in LiNbO<sub>3</sub> when light in the blue-green region of the spectrum is incident. Two guided waves (writing beams at  $\lambda = 0.5145 \,\mu\text{m}$  from an Ar+ laser) with wave vectors  $\beta_1$  and  $\beta_2$  interfere to produce a grating with periodicity  $\Lambda = 2\pi/\beta_g$  ( $\beta_g = \beta_1 - \beta_2$ ). For the case illustrated in Fig.6.27a,  $\beta_g = 2 \beta_0 \sin \theta_0$ , where  $\beta_0 = 1 \beta_1 1 = 1 \beta_2 1$ ,  $\theta_0$  is the angle between  $\beta$  (or  $\beta_2$ ) and the x axis, and  $\beta_g$  lies along the z axis. The effective waveguide refractive index is given by

328

$$n' = n_o + \Delta n \sin\left(\beta_g r\right), \tag{6.50}$$

and the modulation depth  $\Delta n$  depends on the numerous factors such as the writing beam intensities and duration, waveguide, and mode parameters.

Consider now a set of electrodes deposited onto the waveguide surface as indicated in Fig.6.27c. When a voltage V is applied to the electrodes which are separated by a distance d, an effective index (Marcuse 1975) change  $\Delta N$ ,

$$\Delta N = 1/2 n_a^3(\theta) r_{33}(2V/\pi d), \tag{6.51}$$

is superimposed onto the photorefractive grating via the electro-optic effect. (There is an additional effect due to the material piezoelectricity, but this is believed to be a secondary mechanism here.) The parameter  $r_{33}$  is the appropriate electro-optic coefficient for the geometry shown in Fig.6.27(c). Hence, the total refractive index

$$n' = n_o + \Delta n \sin\left(\beta_g r\right) + \Delta N. \tag{6.52}$$

A similar phenomenon has been analysed previously via a coupled mode approach by Kenan et al (1974). (In their case a surface corrugation instead of a holographic grating was used to obtain the initial division of the incident guided wave into two beams.) They showed that the diffracted light intensity  $I_d$  is given in terms of the incident guided wave light intensity  $I_i$  by

$$I_d / I_i = \left[k_e^2 / \left(k_e^2 + \delta^2\right)\right] \sin^2 \left[L_g \left(k_e^2 + \delta^2\right)^{1/2}\right].$$
(6.53)

Here  $L_g$  is the length of the grating with periodicity  $\Lambda$ , and  $\delta$  is the phase mismatch term due to both the electro-optic effect and (or) misalignment  $\Delta \theta$  of the incident beam from the Bragg angle  $\theta_B$ , i.e.

$$\delta = (\delta \Delta N / \lambda) + (\pi / \lambda) \Delta \theta. \tag{6.54}$$

The parameter  $k_i$  is given by

$$k_e = k \cos(2\theta_B), \tag{6.55}$$

where k is the coupling coefficient which appears in the coupled wave equations (Kenan et al 1974). Maximum diffraction occurs when  $\delta = 0$ , which is usually obtained by ensuring that the guided wave is incident at the Bragg angle. It is also useful to note that a misalignment in the direction of the incident light can be compensated for by applying an appropriate voltage. Furthermore,

the voltage  $\Delta V$  which must be applied to go from the  $m^{\text{th}}$  to the m+1 minimum is given approximately  $(k, L < \pi/2)$  by

$$\Delta V = \left\{ 1 + k_e^2 L^2 / 2 \pi^2 m(m+1) \right\} \pi \lambda d / n_0^3 r_{33} L_g.$$
(6.56)

The waveguides studied were y-cut and x-propagating Ti in-diffused LiNbO<sub>3</sub> waveguides characterized approximately by exponential refractive-index profiles (equation (6.35)). Gratings were written into the waveguide as indicated in Fig.6.27 by coupling two cw laser beams from an argon-ion laser  $(\lambda = 0.5145 \,\mu\text{m})$  into TE<sub>0</sub> waveguide modes via rutile prisms. Two separate gratings were studied; the angles between the writing beams which were symmetric about the x axis were 3° (1.59 mm spacing between electrodes) and 4° (0.3 mm spacing). Typically the incident powers in each beam were 1 mW, and the grating were written in 1 s exposures. These parameters were adjusted to produce approximately a 50:50 splitting ratio when He-Ne guided wave light was incident at the appropriate Bragg angle. The first set of electrodes consisted of two strips separated by 1.6 mm painted on with silver paint. The second had a set of evaporated 1500 Å thick aluminium electrodes with a 0.3 mm spacing.

The modulator characteristics were studied with 0.1 mW of He-Ne laser light. Light was coupled into and out of the  $TE_0$  mode via rutile prisms. The gratings were studied within a few months of their fabrication, and it was verified six months later that the gratings were still present. Modulation was obtained by applying a voltage varying with time across the electrodes, and the deflected and undeflected beam intensities were measured with a calibrated photodiode.

Some of the pertinent operating characteristics of the modulator are shown in Figs. 6.27c and 6.28. When the incident and deflected beams were kept away from the electrode edges, the quality of both beams was good, as indicated



Flg.6.28 Modulator efficiency (100% = complete extinction) versus applied voltage across the 1.59 mm electrode gap. Solid line corresponds to theory (see the text) (Goruk et al 1981).

in Fig.6.27c. For light incident at the Bragg angle, the output signal is the harmonic of the fundamental. Away from the Bragg angle, the output can be chosen to be either in phase or out of phase with the modulation signal.

Detailed measurements of the modulator response function (modulator efficiency are reproduced in Fig.6.28. (100% efficiency corresponds in this case to a complete extinction of the diffracted beam.) As is evident from Fig.6.28, the agreement between experiment and theory is excellent. The best extinction ratio obtained was 20 dB, and the applied voltage corresponded to an applied electric field of  $0.22 \times 10^6$  V/m.

The beam quality displayed anomalous behaviour whenever the incident and (or) deflected beams were propagated near the electrode edges. Goruk et al (1981) hypothesized that the fields at the electrode edges are sufficiently high to cause the waveguide to approach the cutoff condition, and hence the beam quality is much more susceptible to laser damage.

Based on these observations, it was important to keep the guided wave beams away from the electrodes to maintain reasonable beam quality.

# 6.4.8 KNbO<sub>3</sub> induced waveguide cut-off modulator

Potassium niobate (KNbO,, point group symmetry mm2 at room temperature) is a very interesting electro-optical material for both bulk and waveguide applications, because of its large electro-optic and nonlinear optic coefficients, good photorefractive properties, and high damage threshold (60 MW/cm<sup>2</sup> pulsed at  $\lambda = 0.86 \ \mu m$ ) (Prokhorov and Kuz'minov 1990). These properties make KNbO, attractive for thin-film waveguides, such as electro-optic modulators, which would benefit from high figures of merit  $n r_{33} = 680 \text{ pm/V}$  and n $r_{42}$  = 4350 pm/V ( $n_3$  = 2.1683 is a principal refractive index,  $n_4$  = 2.254 is an average refractive index in the bc plane, and  $r_{42} = 380 \text{ pm/V}$ ) compared to  $n r_{33} = 341 \text{ pm/V}$  for LiNbO<sub>3</sub>, or an efficient frequency doubler for Al<sub>x</sub>Ga<sub>1-x</sub>A<sub>s</sub> semiconductor lasers, allowing collinear phase-matched type I interaction around room temperature within this wavelength range. Tucker et al (1974) observed optical waveguiding in naturally formed planar sheet domains in KNbO,. More useful waveguides would request structures with controllable parameters in preferred orientations of single domain crystals. Baumert et al (1985) reported on the first waveguides in KNbO, induced by the electro-optic effect. KNbO, needs low-temperature processing (Curie temperature around +220°C) and careful handling, otherwise ferroelectric domains may appear. Up to now, it has not yet been possible to prepare optical waveguides by indiffusion of Ti ions from the crystal surface.

In order to use the electro-optical coefficient  $r_{33}$  in KNbO<sub>3</sub>, a crystal plate was cut normal to the b axis, and two electrodes with a width of  $(s-h) = 100 \mu m$ , separated by a gap of width  $2h = 10 \mu m$ , were deposited on the polished b face (see Fig.6.30). The edges of the electrodes were parallel to the a axis. The horizontal (parallel to the c axis) component  $E_x(x, y)$  of the applied electric field yields an increase of the refractive index  $n_c$  of the crystal in the gap region given by

$$\Delta n_c(x, y) = 1/2 n_c^3 r_{33} E_x(x, y) = A E_x(x, y), \tag{6.57}$$

with  $A = 3.262 \times 10^{-4} \text{ µm/V}$  for  $\lambda = 0.63 \text{ µm}$ . The refractive index change  $\Delta n_{b^3}$  due to the vertical electric field  $E_y(x, y)$ , has been neglected because of the small electro-optic coefficient  $r_{23} = 1.3 \text{ pm/V}$  (Prokhorov and Kuz'minov 1990). Therefore, with this type of waveguide only TE modes propagating along the *a* axis are guided. In order to evaluate the working voltage and the light field distribution of the propagating modes Baumert et al (1985) have calculated the refractive index distribution  $n_c + \Delta n_c(x, y)$  as a function of the applied voltage. The electric field components  $E_x(x, y)$  and  $E_y(x, y)$  inside the crystal, below the electrode gap, were obtained by solving the Laplace potential equation using the conformal mapping technique (Vandenbulcke and Lagasse 1976; Wei 1977) and are given by

$$E_{x} = -U/2 K(k) \operatorname{Re}(dw/dz),$$
  

$$E_{y} = \left(\varepsilon_{x}/\varepsilon_{y}\right)^{1/2} (U/2 K(k)) \operatorname{Im}(dw/dz),$$
(6.58)

where z = x + iy, k = h/s, K(k) is the complete elliptic integral of the first kind, and

$$\frac{\mathrm{d}w}{\mathrm{d}z} = \frac{h}{\left[ \left( h^2 - k^2 z^2 \right) \left( h^2 - z^2 \right) \right]^{1/2}}.$$
(6.59)

*U* is applied voltage,  $\varepsilon_x = \varepsilon_{33}^T = (55\pm 5)$  and  $\varepsilon_y = \varepsilon_{22}^T = (1000\pm 80)$  are the free dielectric constants (at 25°C) of KNbO<sub>3</sub> along the *c*- and *b*-axes, respectively.

A preferentially single domain KNbO<sub>3</sub> crystal was grown by a top seeded high-temperature melt pulling technique (Fluckiger and Arend 1978). Chips with a size of  $4\times3.4\times0.7$  mm were cut from the crystal and oriented by x-ray and preferential etching methods (Wiesendanger 1973). After surface polishing the remaining domains were removed in a strong polarizing dc field near the Curie temperature. Opposite ends of the single crystals were polished in order to allow for end-fire coupling of laser light. This process, however, has caused stress-induced microdomains along the edges of the facet that could not entirely be removed by poling. For electrode preparation, a thin chrome/ gold film was deposited by electron beam evaporation on the *b*-cut surface. A positive electric field was applied and the surface was baked very carefully to prevent creation of new domains (heating/cooling cycle with  $dT/dt < 2^{\circ}C/$ min). The electrode structure was patterned and the metal film etched. The electrodes had a length of 3 mm (Fig.6.29). The samples were mounted on a ceramic substrate and contacted using copper wire and silver paste.

Light of a TE-polarized He-Ne laser beam was coupled into the electrooptically induced waveguide. For the end-fire in- and out-coupling, two 20x



microscope lenses were used. With no electric field applied, only some light spots caused by diffraction at stress-induced domains at the crystal endfaces were observed. Increasing the applied voltage up to 30 V, an on-off ratio of 12 dB could be measured, clearly demonstrating a field-induced increase of the refractive index  $n_c$  between the two electrodes. Baumert et al (1985) measured

333

the wavelength dependence of the near-field light distribution. The following laser light sources were used: InGaAsP/InP diode (1.3  $\mu$ m), Nd : YAG (1.064  $\mu$ m and 0.532  $\mu$ m), argon pumped dye (0.86  $\mu$ m), and He–Ne (0.633  $\mu$ m). Figure 6.30 shows the near-field light distributions at 0.633  $\mu$ m for an applied voltage of 0 and 35 V. For a voltage of 35 V the intensity distribution of the fundamental mode of the electro-optic induced waveguide was calculated (Fig.6.31). Good agreement between calculated (Fig.6.31, 10  $\mu$ m) and measured (Fig.6.30, 3.8±0.5  $\mu$ m) width of the intensity profiles was found despite the microdomains at the edges.

### 6.5 Waveguide electro-optic polarization transformer

Polarization transformation is an essential function for optical signal processing. It is especially important for single-mode fibre systems because, although short lengths of specially fabricated polarization preserving birefringent fibres have been reported (Ramaswamy et al 1978a; Stolen et al 1978), typical singlemode fibres do not maintain linear polarization (Ramaswamy et al 1978b; Kapron et al 1972). For many communication application, the polarization independent switch (Alferness (1979) and on/off modulator (Burns 1978) can be effectively used in spite of an incident signal of unknown and temporally changing polarization. However, for interferometric signal processing applications such as, for example, heterodyne detection or fibre sensors, a received signal of fixed polarization identical to that of some reference signal is required. In these cases, active polarization stabilization (Ulrich 1979) may be necessary. Polarization transformation suitable for such stabilization has been achieved by bulk mechanical elements which squeeze (Johnson 1979) or twist (Ulrich and Johnson 1979) the fibre to induce linear birefringence or optical activity, respectively. These devices are bulky and may result in fibre fatigue. However, because it relies solely upon changing the birefringence, two electrooptical crystals with proper relative orientation are required. Furthermore, because it is a bulk device, a large control voltage (~425 V) is required. The waveguide electro-optic polarization transformer described by Alferness and Buhl (1981) is compact, nonmechanical, capable of fast response, has high fidelity and needs only low control voltage.

The polarization state of an optical wave can be defined by two parameters,  $\theta$  and  $\phi$ . In terms of these parameters the relative TE and TM field components of an optical guided wave are

$$\begin{pmatrix} A_{\rm TE} \\ A_{\rm TM} \end{pmatrix} = \begin{pmatrix} \cos \theta \\ \sin \theta \, e^{,i\theta} \end{pmatrix}.$$
 (6.60)

Thus,  $\theta$  defines the magnitude of the relative TE and TM amplitudes and  $\phi$  the relative phase between these components. For  $\phi = 0$ , the light is linearly polarized at an angle  $\theta$ ;  $\theta = 0$  represents pure TE polarization and  $\theta = \frac{1}{2}\pi$  pure TM. Right circular polarization is given, for example, by  $\theta = 0.25 \pi$  and  $\phi = 0.5 \pi$ .



The demonstrated polarization transformer, which under electrooptical control provides any desired  $(\theta_i, \phi_i) \rightarrow (\theta_0, \phi_0)$  transformation, is shown schematically in Fig.6.32. It is comprised of a single-mode waveguide with three electrode regions. The outer two electrode pairs (Fig.6.32) provide the E/O change of the birefringence. For the crystal orientation shown the electrically induced phase shift between the TE and TM modes is

$$\Delta \phi = (\pi / \lambda) (VL / d_1) (n_e^3 r_{33} - n_0^3 r_{13}), \qquad (6.61)$$

where V is the applied voltage,  $d_1$  the interelectrode gap, L the electrode length,  $\lambda$  the optical wavelength,  $n_{o,e}$  the ordinary and extraordinary refractive indices and r the e/o coefficients. The centre electrode provides TE $\leftrightarrow$ TM mode conversion by utilizing an off diagonal element of the e/o tensor to couple the otherwise orthogonal TE and TM modes (Alferness 1980). The effect of the mode converter upon the amplitude components in equation (6.60) is given by the matrix



Fig.6.33 Calculated output polarization angle  $\theta_o$  vs the mode converter coupling strength kL for various input polarization angles  $\theta_i$ . The incident relative TE/TM phase is assumed to be zero (Alferness and Buhl 1981).

$$\begin{pmatrix} \cos kL & -j\sin kL \\ -j\sin kL & \cos kL \end{pmatrix}$$
(6.62)

where the coupling coefficient is

$$k = (\alpha \pi / \lambda) n^3 r_{51} (V / d_2), \tag{6.63}$$

where  $d_2$  is the interfinger separation and  $\alpha$  the overlap parameter (Alferness 1980). Periodic electrodes are required because of the material birefringence of lithium niobate.

Alferness and Buhl (1981) outlined some key features of the device operation before presenting experimental results. First, the mode converter was essential because the relative TE/TM amplitudes cannot be altered by simple changing the birefringence. However, the mode converter alone was, in fact, also insufficient to produce general TE/TM amplitude changes, that is the arbitrary change  $\theta_i \rightarrow \theta_0$ . This fact is demonstrated in Fig.6.33, where the calculated output polarization angle  $\theta_0$  is plotted versus the electrically induced mode converter coupling strength (proportional to  $V_{2}$ ) for several input polarization angles  $\theta_i$ . The results were calculated using the transformation matrix of equation (6.62) with the assumption that the relative TE/TM phase upon incidence to the mode converter  $\phi'_i$  is zero. Of course, for either pure TE or TM input ( $\theta_1 = 0$  or  $\frac{1}{2}\pi$ , respectively) with proper voltage, an arbitrary angle  $\theta_0$  can be achieved. However, as the angle  $\theta_1$  increases from 0 or decreases from  $\pi$ , the results of Fig.6.33 show that the range of achievable  $\theta_0$  becomes greatly limited. Indeed, for  $\theta_i = \frac{1}{4\pi}$ , regardless of the voltage  $(V_{2})$  applied to the mode converter, the angle  $\theta_0$  remains equal to  $\frac{1}{4\pi}$ .

The key to overcoming this limitation is the use of the e/o phase shifter before the mode converter to adjust the relative TE/TM phase of the signal incident upon the mode converter to  $\pm \pi$ . In these cases, a proper value of the mode converter voltage can be shown to exist, so that any  $\theta_i \rightarrow \theta_0$  change is possible. Indeed, only for these special relative phase values can such arbitrary transfomations be achieved. Fortunately, for these cases the mode converter acts as a linear rotator with respect to the polarization angle. For  $\phi'_i =$ -0.5  $\pi$ , for example,

$$\theta_0 = \theta_i + k L_2, \tag{6.64}$$

where  $k\alpha V_2$  is the subject of the equation (6.62). Thus, control over  $\theta$  is achieved by the combination of the first phase shifter and the mode converter.

The desired overall relative phase transformation is then achieved with the final phase shifter. It should be noted that if the relative TE/TM input phase to the mode converter is  $-0.5\pi$ , then the output phase from the mode converter is also  $-0.5\pi$ . Furthermore, the birefringent substrates there is a relative phase shift  $\phi_f - (2\pi/\lambda) \times |N_{\text{TE}} - N_{\text{TM}}| L_{\text{T}}$ , where  $L_{\text{T}}$  is the total crystal length, and  $N_{\text{TE}}$  and  $N_{\text{TM}}$  are the effective indices of the TE and TM modes, respectively. Thus,

336



**Fig.6.34** Measured results of the device as a linear polarization rotator, the required mode converter voltage to achieve an output TE field vs input polarization angle  $V_1 =$ -4.1 V and  $V_3 =$  0 (Alferness and Buhl 1981).

to achieve the desired value of  $\phi_0$  the voltage of the second phase shifter must be adjusted to obtain a phase shift  $\Delta \phi_2$ , so that,

$$\phi_0 = \phi_i + \phi_f + \Delta \phi_1 + \Delta \phi_2, \tag{6.65}$$

where  $\Delta \phi_2$  is the change induced by the first phase shifter. The value of  $\Delta \phi_2$  does not affect  $\theta_2$ .

The device was tested in several modes of operation. First, the necessity of the first phase shifter was verified; for  $V_1 = 0$  arbitrary  $\theta_i \rightarrow \theta_0$  transformations could not be achieved regardless of the mode converter voltage. Next, the device was operated as a linear rotator with the goal of transforming an arbitrary input linear polarization to an output wave, that is, pure TE. To find the proper value of  $V_1$  to achieve a  $\frac{1}{2}\pi$  TE/TM phase shift at the mode converter, the angle  $\theta_i$  was set to  $\frac{1}{4}\pi$  and  $V_1$  adjusted to maximize the output TE component. Once determined, this value of  $V_1$  was fixed. The required mode converter voltage to achieve a pure TE output polarization versus the input polarization angle was then measured. The results are shown in Fig.6.34. As predicted (equation (6.63)), a linear rotation is observed and, indeed, any value of  $\theta_i$  can be transformed. The rotation rate is 15°/V. The orthogonal polarization component (TM) was typically greater than 23 dB down from the desired one. With care in voltage adjustment values of -27 dB could be achieved.

Because the large birefringence of lithium niobate necessitates periodic electrodes for the mode converter, the demonstrated device is effective only over a limited spectral bandwidth of ~10 Å (Alferness and Buhl 1980). However, the device can be broadbanded either by shortening the mode converter electrode length or by linearly varying the electrode period. Effective spectral bandwidths of several hundred angströms should be readily achievable. Alternately, the device can be fabricated using a less birefringent substrate like lithium tantalate or a nonbirefringent one. Although three control voltages are required for the most general polarization transformation, for many applications only output light that is pure TE or TM is required. In this case, only the first phase shifter and the mode converter are required.

# 6.6 Light beam scanning and deflection in electro-optic waveguides

Tien et al (1974) reported a method of light beam scanning and deflection in which the angle of deflection varies with the applied field. In one of the experiments the authors were able to scan a light beam continuously up to  $4^{\circ}$  in the plane of the film. The experiments were carried out in an electrooptic waveguide of a single-crystal LiNbO, film grown epitaxially in LiTaO<sub>1</sub>.

The theory and experiment for the light beam deflection and the conditions that optimize the deflection efficiency are discussed below.

A general equation of a light path in a medium of variable index of refraction is considered. The equation (Born and Wolf 1959; Tien et al 1965) is

$$\frac{\mathrm{d}}{\mathrm{d}s} \left( n \frac{\mathrm{d}\rho}{\mathrm{d}s} \right) = \nabla n. \tag{6.66}$$

Here ds is an element of the light path and  $\rho$  is the position vector of ds. Let the film lie in the yx plane. The refractive index of the film varies in x and y as it is excited by the electro-optic effect. The origin of the coordinates are chosen to lie on the x axis (Fig.6.35(a)), and the light path is considered which deviated from the x direction by an angle  $\theta$  not more than 10°. Then tan  $\theta = \theta$  and  $\theta$  is small. Thus,

$$ds \cong dx, \rho = y\hat{y} + x\hat{x}, \tag{6.67}$$

where x and y are the unit vectors along the x and y directions, respectively. Equation (6.66) now becomes



**Fig.6.35** (a) Light beam in a medium of variable refractive index n(x,y). (b) Diagram showing the process of optimising the deflection of a light beam. (c) Experimental arrangement used to deflect a light beam through refractions. (d) Experimental arrangement used to deflect a light beam through incomplete reflection  $(\Delta \theta_r)$  and refractions  $(\Delta \theta_n)$  (Tien et al 1974).

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(n\hat{x}+n\frac{\mathrm{d}y}{\mathrm{d}x}\hat{y}\right) = \frac{\partial n}{\partial x}\hat{y} + \frac{\partial n}{\partial x}\hat{x}$$

After simplification, we have

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right) = \frac{1}{n}\left(\frac{\partial n}{\partial y} - \frac{\partial n}{\partial x}\frac{\mathrm{d}y}{\mathrm{d}x}\right).$$
(6.68)

Since dy/dx (- tan  $\theta = \theta$ ) is small, equation (6.68) becomes

$$\Delta \theta = \theta_2 - \theta_1 = \int_{y_1}^{y_2} \frac{1}{n} \frac{1}{\tan \theta} \frac{\partial n}{\partial y} dy + \int_{x_1}^{x_2} \frac{1}{n} \tan \theta \left(\frac{\partial n}{\partial x}\right) dx.$$
(6.69)

Here, in the first integral, dx is replaced by (dx/dy)dy which is  $(1/\tan \theta)dy$ . Equation (6.69) is a general equation for deflecting a light beam and  $\Delta \theta$  is the deflection angle occurring after the light beam has traced a path from  $(x_1, y_1)$  to  $(x_2, y_2)$ . The angles  $\theta_1$  and  $\theta_2$  are the entrance and exit angles of the light beam at  $(x_1, y_1)$  and  $(x_2, y_2)$ , respectively. The quantities *n*, tan  $\theta$ ,  $\partial n/\partial x$ , and  $\partial n/\partial y$  are evaluated along the light path. Equation (6.69) has several intersecting features: First, the first integral involves  $(\partial n/\partial y)$  whereas the second integral involves  $(\partial n/\partial x)$ . Next, the first integral contains a factor of  $(1/\tan \theta)$  and the second integral contains a factor of tan  $\theta$ . Since tan  $\theta$ is small, the first integral in (6.69) is usually much larger than the second one. To demonstrate the process leading to the optimization of  $|\Delta \theta|$ , let us consider in Fig.6.35b a light beam which is deflected by passing through a rectangular region of refractive index  $(n + \Delta n)$  surrounded by a uniform medium of the refractive index n. To be specific, the case where dx, dy,  $\tan\theta$ ,  $\Delta n$  and  $\Delta \theta$  are all positive. For optimizing  $\Delta \theta$  in the portion of the light path where the refractive index is increasing, the conditions are  $\partial n/\partial x = 0$ ,  $\partial n/\partial y$  is positive, and tan $\theta$  should be small. By placing  $\partial n/\partial x = 0$ , the entire amount of  $\Delta n$  has to be contributed by  $\partial n/\partial y$  alone. Consequently,  $\partial n/\partial y$  can have the largest possible value for a given  $\Delta n$  and so is the first integral in (6.69). Moreover, because  $\partial n/\partial x = 0$ , the second integral in (6.69) is zero. Otherwise, this integral would be negative and would reduce the value of  $\Delta \theta$ . Using a similar argument, Tien et al (1974) found that for the portion of the light path where the refractive index is decreasing, the conditions are  $\partial n/\partial y = 0$ and  $\partial n/\partial x$  is negative. As illustrated in Fig.6.35b, all the above conditions are satisfied, if a light beam which enters into the region of  $(n + \Delta n)$  through the bottom leaves it at the right without touching the top side of the rectangle. The same light path (Fig.6.35b) optimized a negative  $\Delta \theta$ , if  $\Delta n$  is negative.

To produce a proper distribution of electric field on the film, Tien et al (1974) used the circuit shown in Fig.6.35d. It consists of two main electrodes, A and B, and four parallel fingers each 5  $\mu$ m wide. The spacings between the fingers are 20  $\mu$ m and the total spacing between A and B is 120  $\mu$ m. The electrodes and the fingers are L = 2.7 mm long along  $\hat{x}$ . By applying



**Fig.6.36** The dots are the measurement of  $\Delta \theta$  vs the intensity of the applied field using the experimental arrangement shown in Fig.6.35 (c). Solid line indicated the result calculated from equation (6.71) using  $r_{33}$ =28.5×10<sup>-12</sup> m/V (Tien et al 1974).

proper voltages to the electrodes and the fingers, a variety of electric field distributions can be produced between A and B. The circuit is fabricated on a glass substrate by the usual photolithographic technique and is then attached on top of the epitaxial LiNbO<sub>3</sub> film. A coat of EUKITT is applied between the film and the circuit in order to avoid electric breakdown in air. The film has the c axis parallel to  $\hat{y}$  and the refractive indices of the film are  $n_o = 2.290$  and  $n_e = 2.220$ . In the experiments, a  $\lambda = 0.6328$  µm He-Ne laser beam was coupled into the film by a rutile prism coupler. The light beam in the film was 60 µm wide and propagated nearly parallel to  $\hat{x}$  in the TE (m = 0) waveguide mode (Tien 1971). To simplify the computation, the mode index was taken to be equal to  $n_e$  of the film.

The first experiment is illustrated in Fig.6.35c. By applying a voltage across A and B, a uniform electric field  $E_y$  is excited between the electrodes. The electric field distribution is illustrated in this Fig.by dashed lines. Due to the electro-optic coefficient  $r_{33}$  of LiNbO<sub>3</sub>, the refractive index (extraordinary) of the film in the space between A and B is increased by an amount  $\Delta n$  such as

$$\Delta n = -1/2 n_e^3 r_{33} E_y. \tag{6.70}$$

This was a reproduction of the situation shown in Fig.6.35b – a region of  $(\Delta n + n_e)$  surrounded by a medium of  $n_e$ . Here,  $\Delta n$  is positive or negative depending upon the sign of  $E_y$ . When  $E_y$  varies from 7.0 to -6.7 V/µm, the light beam scans first over  $\Delta \theta_{-} = 1.06 \times 10^{-2}$  rad (when  $\Delta n$  is negative) and then over  $\Delta \theta_{+} = 0.62 \times 10^{-2}$  rad (when  $\Delta n$  is positive), as shown in figures 6.35c and 6.36. To calculate these deflections, it can be shown from equations (6.68) and (6.69) that

$$\theta_2 = \left[\theta_1^2 + (2\Delta n / n)\right]^{1/2} \tag{6.71}$$

where  $\theta_1$  and  $\theta_2$  are expressed in radians. From the experimental values of  $\Delta \theta$  and using (6.70) and (6.71) Tien et al (1974) obtained  $r_{33} = 28.5 \times 10^{-12}$  m/V for their film, which was substantially larger than that reported by Fukunishi et al (1974) for their LiNbO<sub>3</sub> films. In fact, the value of  $r_{33}$  obtained by Tien et al (1974) was only about 10% less than that of bulk LiNbO<sub>3</sub>. Using the experimental value  $r_{33}$  of the film, the measured values of  $\Delta \theta$  are compared in Fig.6.36 with those computed from equations (6.70) and (6.71); the agreement is excellent.

Tien et al (1974) discussed a phenomenon of refraction. The light wave was refracted as it entered into the region of  $(n_e + \Delta n)$  and was refracted again as it left the region. For optimizing  $|\Delta \theta|$  the authors arranged the light path so that these two refractions added. It is evident from (6.71) that this mode of operation applies only for  $(2\Delta n/n) > -\theta_1^2$ . Otherwise, the light beam would be totally reflected.

The second experiment is illustrated in Fig.6.35d. Consider again the gap between the electrodes A and B. By applying proper voltages to the fingers and the electrodes an index distribution was excited, such that  $\Delta n (= \Delta n)_{-}$  was negative in the top part of the gap and  $\Delta n (= \Delta n)_{+}$  was positive in the lower part. The overall variation of the refractive index in the gap was  $\Delta n = -(\Delta n_{+} + |\Delta n_{-}|)$ . A light beam with an entrance angle  $\theta_{1}$  faces a negative gradient of the refractive index which causes the light path to bend. If the negative  $\Delta n$  is large enough, the light beam traces a circular arc inside the gap and finally emerges at the right with an exit angle  $\theta_{2} = \theta_{1}$ . This is what one would expect for a total integral reflection. However, when  $\Delta n$  is less negative, the arc traced by the light beam becomes larger. Soon, one finds that the gap is not long enough for the light beam to complete this arc. This



**Fig.6.37** Schematic diagram of the polarization-independent optical filter ( $V_{\rm Mc}$ , polarization converter voltage;  $V_{\tau}$  birefringence tuning voltage;  $V_c$ , polarization splitter tuning voltage) (Waransky et al 1988).

341

incomplete total reflection makes  $\theta_2$  again vary with  $\Delta n$  which of course depends on the intensity of the applied electric field. It can be shown further that, for values of  $(2\Delta n/n)$  much less than  $-\theta_1^2$ , the light beam inside the gap is deflected through the incomplete total reflection (illustrated in Fig.6.35(d) by  $\Delta \theta_7$ ). In this mode of operation the deflection is linear with  $|\Delta n|$  from  $\theta_2 = 0$  to  $\theta_2 = -\theta_1$  and then stays at  $\theta_2 = -\theta_1$  for a further increase of  $|\Delta n|$ . On the other hand, in the range between  $(2\Delta n/n) = -\theta_1^2$  and 0 (or positive), the light beam is deflected by refractions as discussed earlier in the first experiment (illustrated in Fig.6.35d by  $\Delta \theta_R$ ). The separating line between these two modes of operation,  $(2\Delta n/n) = -\theta_1^2$ , is simply the condition of the critical angle.

### 6.7 Electro-optically tunable wavelength filter

Wavelength division multiplexing (WDM) is a very attractive scheme to increase the information bandwidth of fibreoptic communication systems and networks. Wavelength demultiplexing and channel selection in such WDM systems require tunable narrow-band optical filters that are compatible with single-mode fibres. Furthermore, applications with fibres that do not preserve polarization require optical filters that operate independently of the input polarization. Various schemes of tunable optical filters have been demonstrated with single-mode waveguides, such as wavelength selective integrated optical directional couplers (Alferness and Schmidt 1978) and interferometers (Rottman and Voges 1987) or fibreoptic Bragg reflectors (Whalen et al 1986) and Fabry-Perot resonators (Stone and Stulz 1987). Waransky et al (1988) proposed and demonstrated the first polarization-independent electro-optically tunable wavelength filter with single-mode waveguides. The LiNbO, wavelength filter has a bandwidth of only 12 Å and a tuning range of at least 110 Å. It had two output ports serving as a bandpass and a notch filter, and it can be used for wavelength demultiplexing as well as for multiplexing.

The polarization-independent filter employs two identical wavelength-dependent TE  $\leftrightarrow$ TM polarization converters and two identical TE/TM polarization splitters in the input and output of the polarization converters. The input polarization splitter demultiplexes the quasi-TE and quasi-TM polarized components of input light and routes each component separately through one of the two parallel TE + TM polarization converters, where the two polarization components experience the same wavelength-dependent TE ↔TM polarization conversion before they are recombined at the output polarization splitter. Figure 6.37 shows a schematic diagram of the filtre implemented with single-mode strip waveguides on x-cut y-propagating LiNbO<sub>3</sub>. The two electro-optic TE  $\leftrightarrow$ TM polarization converters are wavelength tunable and consist of a cascade of short sections of polarization converter electrodes alternating with short sections of birefringence tuning electrodes (Alferness and Buhl 1985). The two polarization splitters are identical waveguide directional couplers with  $\Delta\beta$ -reversal tuning electrodes and are designed to couple TM- polarized light completely into the crossover waveguide while leaving TE-polarized light in the input (straight-through) waveguide (Alferness and Buhl 1984).

The filter operates as follows. Arbitrarily polarized light enters the filter

in the input waveguide (No.1 in Fig.6.37) of the first polarization splitter, where all TM-polarized light is completely coupled into the crossover waveguide (No.2 in Fig.6.37), while all TE-polarized light stays in the straight-through waveguide (No.1). The two separated polarization components pass through identical narrow-band TE $\leftrightarrow$ TM polarization converters. If their wavelength is at the centre wavelength of the polarization converters, then the TE-polarized light of waveguide No.1 is completely converted into TM-polarized light, and likewise, the TM-polarized light in waveguide No.2 is completely converted into TE-polarized light. The output polarization splitter couples the now TM-polarized light of waveguide No.1 completely into the crossover waveguide (No.2) while leaving the now TE-polarized light in waveguide No.2. Thus the two polarization components are recombined and exit the filter in waveguide No.2 (the crossover waveguide).

On the contrary, of the wavelength of the input light is outside the bandwidth of the polarization converters, then the two polarization components pass the polarization converters without change in polarization, and the output polarization splitter couples the TM-polarized component of waveguide No.2 completely back into input waveguide (No.1), where it is recombined with the TE-polarized input light. In this case, both polarization components exit the filter in waveguide No.1 (the input waveguide).

Thus light at a wavelength within the bandwidth of the polarization converters exits the filter in waveguide No.2, whereas light at other wavelengths exits the filter in waveguide No.1. The device therefore acts as a bandpass filter when the output is taken from waveguide No.2 and as a notch filter when the output is taken from waveguide No.1. Note that both output ports can be used simultaneously, thus allowing applications as a wavelength tap in a bus-type network or as a wavelength multiplexer.

The details of the electro-optic TE $\leftrightarrow$ TM polarization converters and the TE/TM polarization splitters used in the filter were described by Heismann and Alferness (1988), Habara (1987), Heismann and Buhl (1987). In the waveguide orientation of Fig.6.37, the TE- and TM-polarized modes have different propagation constants because of the large birefringence of LiNbO<sub>3</sub>, thus requiring periodic coupling for efficient TE  $\leftrightarrow$ TM polarization conversion. Periodic coupling of the two modes is achieved electro-optically by inducing a periodic grating of index perturbations in the waveguide via a spatially alternating electric field  $E_x$  and the  $r_{51}$  electro-optic coefficient ( $r_{51} \approx 28 \times 10^{-12}$  m/V). Most efficient TE  $\leftrightarrow$ TM polarization conversion is obtained at a free-space wavelength  $\lambda_0 \approx \Lambda | \Delta n_{ph}(\lambda_0)|$ , where  $\Lambda$  is the spatial period of the applied electric field  $E_x$ , and  $\Delta n_{ph} \approx n_o - n_e$ ). The optical bandwidth of the efficient TE  $\leftrightarrow$ TM conversion is determined by the overall interaction length L (Heismann and Alferness 1988):

$$\Delta \lambda_{\rm FWHM} \approx 0.8 \frac{\lambda_0^2}{\left|\Delta n_{gr}(\lambda_0)\right| L},\tag{6.72}$$
where  $\Delta n_{gr}(\lambda_0) = \Delta n_{ph}(\lambda_0) - \lambda_0 [\partial \Delta n_{ph}(\lambda) / \partial \lambda]_{\lambda=\lambda_0}$  is the group index difference of the two modes at  $\lambda_0$ .

Tuning of the centre wavelength  $\lambda_0$  is accomplished electro-optically by changing the birefringence  $\Delta n_{ph}$  in the waveguide via a spatially uniform electric field  $E_i$ , and the  $r_{33}$  and  $r_{13}$  electro-optic coefficients ( $r_{33} \approx 30 \times 10^{-12}$ m/V and  $r_{13} \approx 10 \times 10^{-12}$  m/V). Here the fields for polarization conversion,  $E_i$ , and for birefringence tuning,  $E_i$ , are applied alternately over a large number of short sections. In this device, 45 sections of uniform birefringence tuning electrodes are periodically interleaved between 46 sections of periodic polarization converter electrodes, where all birefringence tuning electrodes are driven by a common voltage  $V_{T}$  and all polarization converter electrodes by a common voltage  $V_{MC}$ . The tuning rate of the centre wavelength  $\lambda_0$  is given by (Heismann and Alferness 1988)

$$\frac{\Delta\lambda_T}{V_T} \approx \left(n_e^3 r_{33} - n_0^3 r_{13}\right) \frac{\Gamma}{2G} \frac{\ell_T}{\ell_{\rm MC} + \ell_T} \frac{\lambda_0}{\left|\Delta n_{gr}(\lambda_0)\right|},\tag{6.73}$$

where  $\Delta\lambda_{\tau}$  is the shift of the centre wavelength,  $\Gamma$  is the normalized overlap integral of the applied electric field  $E_{z}$  with the optical fields, G is the gap of the birefringence tuning electrodes, and  $\ell_{MC}$  and  $\ell_{\tau}$  are the lengths of a single polarization converter and birefringence tuning section, respectively.

Operation of such tunable TE ↔TM polarization converter as a wavelength filter requires linear TE- (or TM-) polarized input light and a linear TMpass (TE-pass) polarization filter in the output beam. Note that the wavelength dependence of electro-optic TE  $\leftrightarrow$  TM conversion is independent of the direction, i.e. TE  $\leftrightarrow$  TM conversion has the same centre wavelength, bandwidth, and tuning rate as TM $\leftrightarrow$ TE conversion. This TE $\leftrightarrow$ TM symmetry of the wavelength response is essential for the operation of the polarization independent filter. Here identical wavelength responses for TE- and TM-polarized input light are obtained by using identical polarization converters in the two branches of the filter. In the present device, the two polarization converters share the same interdigital finger electrodes, as shown in Fig.6.37, to obtain the same centre wavelengths for TE- and TM-polarized input light. The birefringence tuning electrodes of both converters are designed to have exactly the same lengths to obtain identical tuning rates. The tuning electrodes are arranged in such a way that no cross connections are needed within the electrode structure. However, this electrode layout requires two tuning voltages,  $V_{\tau}$  and  $2V_{\tau}$  to obtain an effective tuning voltage of  $V_{\tau}$  for both polarization converters.

The polarization splitters are conventional waveguide directional couplers designed to have coupling coefficients of  $k_{TM} L_c \approx 1.5(\pi/2)$  for TM-polarized light and  $k_{TE} L_c \approx 0.45(\pi/2)$  for TE-polarized light, where  $L_c$  is the coupling length. Polarization splitting with low crosstalk is achieved by detuning the couplers via two-section  $\Delta\beta$ -reversal electrodes utilizing the  $r_{33}$  (for TE) and  $r_{13}$  (for TM) electro-optic coefficients so that TM-polarized light is completely coupled into the crossover waveguide, while TE-polarized light stays in the input waveguide (Habara 1987).



**Fig.6.38** Normalized filter transmission of the untuned ( $V_{\tau} = 0$  V, solid and thin dashed lines) and tuned bandpass filter ( $V_{\tau} = +100$  and -100 V, bold dashed lines) measured for TE- and TM-polarized input light (Waransky et al 1988).

The filtre is realized in x-cut and y-cut propagating LiNbO<sub>3</sub> using standard fabrication techniques. The TE $\leftrightarrow$ TM polarization converters are designed for operation around  $\lambda_0 = 1.52 \ \mu$ m. The basic period of the interdigital finger electrodes is  $\Lambda = 21 \ \mu$ m ( $\Delta n_{ph} \approx 0.072$ ), and the total interaction length is 19 mm. The polarization splitter/directional couplers have a centre-to-centre waveguide separation of 17.5  $\mu$ m and a total coupling length of 8 mm. Polarization splitting with crosstalk of less than -18 dB is achieved by applying voltages of -37 and +40 V to the two sections of the  $\Delta\beta$ -reversal electrodes. The overall length of the filtre is 52 mm.

Polarized light from a tunable color centre laser is used to test the filter response separately for TE- and TM-polarized input light. Fig.6.38 shows the transmission of the bandpass filtre (output port No.2) versus wavelength for TE as well as for TM input light. For both input polarizations the centre wavelength of the untuned filtre ( $V_T = 0$ ) is 1.5254 µm and the optical bandwidth is 12 Å, as expected for the 19 mm long polarization converters ( $\Delta n_{gr} \approx 0.08$ ). The voltage for complete TE $\leftrightarrow$ TM conversion is  $V_{MC} = +37$  V. Also shown in Fig.6.38 is the filtre transmission when tuning voltages of  $V_T = -100$  and  $\pm 100$  V are applied to the birefringence tuning electrodes. Here the centre wavelength is shifted by 55 Å to shorter and longer wavelength, respectively, where identical results are obtained for both input polarizations. Thus the filtre can be tuned over a range of at least 110 Å.

#### 6.8 Flip-chip coupling between fibres and channel waveguides

Efficient coupling between single-mode fibres and Ti-diffused LiNbO<sub>3</sub> channel waveguides is essential for the inclusion of LiNbO<sub>3</sub> waveguide devices in single-mode fibre systems. Such coupling is difficult to achieve because of critical positioning and preparation tolerances. Micromanipulators can be used for the fibre/channel alignment for end-fire coupling (Noda et al 1978; Keil and Auracher 1979; Fukuma and Noda 1980). Hsu et al (1978) demonstrated fibre/channel end-fire coupling using the flip-chip approach where V-grooves are preferentially etched in a Si wafer. The LiNbO<sub>3</sub> end-faces were cleaved. In fibre/fibre coupling, improved altitudinal alignment has been demonstrated with tapered fibres positioned in grooves at right angles to the input and output



Fig.6.39 Schematic of Si V-groove/flip-chip coupling structure (Bulmer et al 1980).

fibre grooves (Sheem and Giallorenzi 1978). Bulmer et al (1980) used tapered fibres in transverse grooves in Si V-groove/flip-chip coupling method and have consistently measured coupling efficiencies of >70%, corresponding to an  $\sim$ 3 dB total throughput loss (Bulmer et al 1980) for TE- and TM-mode polarizations. The coupling structure is indicated schematically in Fig.6.39. It is compact and can be made rigid.

There are several very stringent requirements for efficient coupling: (i) accurate horizontal, vertical, and angular positioning; (ii) planar, defect-free waveguide and surfaces, normal to the propagation direction; and (iii) for complete coupling, matching of the waveguide field distributions. Bulmer et al (1980) aimed to achieve translational alignment of <1  $\mu$ m and angular alignment of <1°. Only LiNbO<sub>3</sub> waveguide orientations were used in order to avoid anisotropic leaky-mode (Sheem et al 1978) and double refraction effects (Kaminow and Stulz 1978) which occur when waves are propagating along a nonaxial direction, and so achieve polarization-independent propagation losses and coupling efficiencies. As LiNbO<sub>3</sub> has only one cleavage plane, along a nonaxial direction, it is necessary to prepare the cubic and faces of the LiNbO<sub>3</sub> substrates by polishing. The LiNbO<sub>3</sub> substrate edges should have minimal rounding.

Accurate positioning in the horizontal plane is achieved by aligning matching registration lines (grooves and channels) which are registered along the coupling fibre V-grooves in the Si wafer and along the channel waveguides in the  $\text{LiNbO}_3$ . The registration lines are several microns wide and are registered with an accuracy better than 0.5 µm. Accurate vertical positioning is provided by tapered alignment fibres, with diameters tapered by 0.5–1 µm/mm, placed under the coupling fibres in deep V-grooves, at right angles to the coupling fibre grooves. The hight of the input or output fibre is continuously adjusted by pushing or pulling the tapered fibre in its transverse groove so that the coupling is maximized. Without such fine altitudinal alignment, a high coupling efficiency could be achieved only with coupling grooves precisely to the depth appropriate for a fibre of known o.d. (optical damage) and perfect concentricity.

Bulmer et al (1980) used high-resistivity (100) Si wafers, with an 1 µm thick masking layer of SiO<sub>2</sub>, and aligned the photolithographic groove mask

to the wafer axes to better than 1°. The mask has two registration grooves along either side of each coupling groove. In the alignment of the flippedover LiNbO<sub>3</sub> on top of the Si wafer, a corresponding Ti-diffused line in the LiNbO<sub>3</sub>, to either side of each channel waveguide or waveguide device, is arranged to lie between these two registration grooves. In the central region where LiNbO<sub>3</sub> substrate is to be laid, only halfway through the SiO<sub>2</sub> mask layer was etched so that the registration lines are not overetched during the Si V-groove etching process. The coupling and alignment coupling grooves were then etched in the Si using an ethyl-enediamine-pyrocatechol-water mixture (Finne and Klein 1967). If the registration grooves are etched in the Si, they deteriorate greatly owing to undercutting and the finite preferential etch ratio, which makes exact alignment very difficult. The complete pattern on the Si wafer consisted of six coupling grooves with deeper transverse alignment grooves to either side of substrate region. Coupling in turn to each of six different channel waveguides is therefore possible with a single unit.

The LiNbO, end surfaces were prepared by an optical contact polishing method. The Ti-diffused LiNbO, substrate was optically contacted to a dummy LiNbO, substrate, the input and output edges were polished, and the substrates were then separated by mild thermal shock. To allow optical contact, Ti was diffused over the entire LiNbO, substrate except close to the channel waveguide pattern. As there is no gap between the substrates, chip-free edges with no rounding are obtained. Very flat fibre ends, with little or no lip, normal to the fibre axis, were obtained using the conventional cleaving technique. If the waveguide field distributions are perfectly matched, 100% coupling is possible (neglecting reflection losses which can be minimized with antireflection coatings). However, perfect matching is not possible because the channel waveguide field distribution has a non-unity aspect ratio, is asymmetric perpendicular to the surface, and is not exactly Gaussian either parallel or perpendicular to the surface, whereas the fibre field is essentially Gaussian (Burns and Hocker 1977). The channel waveguide field can be optimized somewhat by an appropriate choice of Ti diffusion conditions (Fukuda et al 1979).

Bulmer et al (1980) defined 3 and 4 µm wide straight channel waveguides and 3 µm wide channel waveguide Mach-Zehnder interferometers in 170-220 Å Ti on z-cut, x-propagating LiNbO, substrates. The diffusion was performed in O, for 6 h at 1000°C, and in some cases in the presence of LiNbO, powder to reduce  $Li_2O$  out-diffusion. The channels were perpendicular, to ~1°, to the edges which were then polished. An ~4000 Å SiO, layer was sputtered on each substrate and then oxidized for ~9 h at 600°C. It was needed to isolate the optical waveguides from the Al electrodes later deposited along the interferometer. To obtain polarization-independent behaviour, authors used horizontal and vertical field electrodes. The authors used single-mode fused-silica fibre with NA ~0.1 and core and cladding diameters of 4.5 and 88 µm, respectively. The outer plastic jacket was removed in the coupling region and along sections of the input and output fibres where cladding modes were stripped. The fibre beat length was ~20 m. Measurements were made at 633 nm, separately for each optical polarization. The polarization was rotated with a half-wave plate at the input to the 0.5 m long input fibre and it was checked at the fibre

output. The polarization was maintained to ~99%.

Bulmer et al (1980) entirely neglected any mode propagation losses in calculations of flip-chip coupling efficiencies. Using the flip-chip arrangement described above, the authors obtained 76 and 72% coupling between the same input fibres and the 3 and 4  $\mu$ m channels, respectively, for each optical polarization. Thus, the flip-chip coupling efficiencies were as high as those measured with the micropositioner. The coupling could be smoothly varied between maximum and near zero by moving the tapered alignment fibre. If the coupling fibre grooves were etched too deeply (by several  $\mu$ m), there was some friction between the two fibres, resulting in appreciable horizontal motion of the coupling fibre, which aids coupling if the LiNbO<sub>3</sub>-Si wafer transverse alignment is imperfect.

With 3 and 4  $\mu$ m wide channels on each substrate cemented to a Si wafer, and with fibre/channel separation of <10  $\mu$ m, Bulmer et al (1980) have measured TE- and TM-mode coupling efficiencies of 70-88%, corrected for reflection losses. Provided that the initial Si/LiNbO<sub>3</sub> alignment is accurate to 1  $\mu$ m, the measurements were repeatable within 10% and the same coupling efficiencies were obtained for coupling with one input fibre or with input and output fibres. The values for substrates were determined allowing for small Fabry-Perot resonances (Born and Wolf 1970) using the expression

$$P_{\max(\min)} = \frac{(1-R_1)(1-R_2)}{\left[1\mp (\gamma_1\gamma_2 R_1 R_2)^{1/2}\right]^2} k P_{in}.$$
(6.74)

Here  $P_{\max(\min)}$  is the maximum (minimum) output power,  $P_{in}$  is the input power, k is the fibre/channel coupling efficiency, and  $R_i$  (i = 1,2) are the reflectivities at either end of the Fabry-Perot cavity;  $\gamma_i$   $(0 \le \gamma_i \le 1)$  represents the fraction of power reflected at either end of the cavity which remains guided in the channel waveguide ( $\gamma_i = 0$  indicates complete loss on reflection because of nonperpendicular channel end facets). In the cases under consideration,  $(\gamma_1, \gamma_2)^{1/2} \approx 0.2$ . Equation (6.74) was derived in the assumption of zero mode attenuation in the cavity and with disregard of any effect of the 7.5 cm laser coherence length. For one of the samples, from comparisons of the outputs with index matching oil and air between the fibre and LiNbO<sub>3</sub>, the LiNbO<sub>3</sub> itself appeared to be acting as a resonant cavity. This was verified by heating and cooling the LiNbO<sub>3</sub> to vary the optical pathlength and observing the resultant oscillatory variation in output of up to 7% due to thermal expansion and refractive index change.

In order to estimate the maximum coupling efficiency for perfect alignment limited only by the mode field mismatch (Burns and Hocker 1977), mode distributions were measured by scanning with a 100  $\mu$ m diam. pinhole in the horizontal (x) and vertical (y) directions across the magnified near-field images of the channel waveguide and fibre outputs. All the profiles were extremely smooth, and showed no indication of imperfections in the channel and surfaces. From the 1/e points of these intensity profiles, the Gaussian mode field half width was determined (see Table 6.4). For the channel, these were  $w_r$ ,

Mode	<i>w<sub>x</sub></i> (μm)	w <sub>,</sub> (μm)	k <sub>m</sub> (%)	k' <sub>m</sub> (%)
$3\mu m$ channel $\begin{cases} TE \\ TM \end{cases}$	2.9	2.2	88	92
	3.6	3	91	93
(TE	2.9	2	86	89
4 µm channel {TM	3.2	2.3	89	92

**Table 6.4** Measured channel mode field half-widths  $w_r$ ,  $w_r$  and corresponding theoretical maximum coupling efficiencies  $k_m$  and  $k'_m$  from numerical overlap of beam profiles (Bulmer, Sheem, Moeller 1980)

 $w_y$  of the rectangular Gaussian (Burns and Hocker 1977) (where, e.g.,  $E_x \propto \exp(-x^2/w_x^2)$ ) which approximates the waveguide mode electric field ( $w_x$  is parallel and  $w_y$  perpendicular to the surface). For the fibre, assuming a circular Gaussian field, the mode radius was  $a = 3.0 \,\mu\text{m}$ . Then for a perfect alignment, a zero separation and no reflection losses, the power coupling coefficient was estimated as

$$k_{m} = 0.93 \times 4 / (w_{x} / a + a / w_{x}) (w_{y} / a + a / w_{y}).$$
(6.75)

where the factor 0.93 is a correction for the deviation of the real mode fields from their Gaussian approximations. Table 6.4 presents the  $k_m$  values corresponding to the measured mode widths. They are a few percent higher than the experimental coupling efficiencies. The maximum coupling efficiencies were also estimated by a numerical overlap of the normalized mode profiles and are shown as  $k'_m$  in Table 6.4. The values are 2-4% higher than the corresponding  $k_m$  values. Since theory intends  $k_m \cong k'_m$ , it can be concluded that the correction factor 0.93 is slightly conservative for this case.

#### 6.9 KTiOPO, waveguide devices and applications

KTP has several potential advantages for optical waveguide device compared with other materials in addition to having a much larger modulator figure of merit. Its high optical damage threshold suggests that KTP waveguide devices could be used to control or convert high-intensity optical beams with input wavelengths extending from the visible to the IR. KTP waveguide devices should be much less susceptible to piezoelectric and pyroelectric instabilities because these effects have not been observed in bulk device applications, and hence device thermal and mechanical stability should be much better.

Several demonstration electro-optic and nonlinear optic devices have been fabricated by using KTP with the waveguide fabrication process described in chapter 2. The measured  $V_{\pi}$  for several single-channel phase modulators indicates that the waveguide fabrication process does not alter the electro-optic coefficient. Using a 6 µm wide channel waveguide and a 0.2 µm MgF<sub>2</sub> buffer layer, and coupling to the electro-optic coefficient  $r_{c2}$ , Bierlein and Vanherzeele

(1989) observed a  $V_{\pi}\ell$  of 6 V cm at 6328 Å, which is close to the theoretically predicted value for KTP's bulk electro-optic and dielectric constants (Bierlein et al 1989). These devices are dc stable for both hydrothermally and fluxgrown substrates. The  $V_{\pi}\ell$  was lower than 6 V cm at low frequencies and increased to 6 V cm at high frequency. The occurrence of ionic-conduction effects suggests that the dc conductivity of the Rb-rich optical waveguide is lower than that of bulk KTP. Limited data on the dielectric properties of bulk RbTiOPO<sub>4</sub> indicate such a lower conductivity, a result that is not totally unexpected because Rb has a larger ionic radius compared with K, giving a lower ion hopping rate.

A Mach-Zehnder modulator was also fabricated on a 1 mm thick, z-cut KTP substrate by using 6 µm wide Rb-exchanged waveguides and travelingwave electrodes that show a bandwidth of nearly 16 GHz (Laubacher et al 1988). This modulator was fabricated with a 0.4 µm SiO<sub>2</sub> buffer layer, a 1 cm electric field interaction length, and a 25 µm electrode gap and had a  $V_{\pi}$  of 10 V at a 1.3 µm input wavelength and 5 V at 0.633 µm. This modulator did not show any instabilities due to optical damage or photorefraction, which are commonly observed in other materials, even with inputs of as great as 1 mW.

The nonlinear-optical properties of KTP waveguides have also been evaluated by measuring the SHG output, using a diode-pumped Nd:YAG input at 1.064 and 1.31  $\mu$ m. Using a 6  $\mu$ m wide Rb-exchanged channel waveguide, Bierlein (1989) measured conversion efficiencies to the green in the 4% W<sup>-1</sup> cm<sup>-2</sup> range. This conversion efficiency is close to the best values measured (4.8%) for Ti:LiNbO<sub>3</sub> waveguides. At 1.31  $\mu$ m input conversion efficiencies of approximately 1% W<sup>-1</sup> cm<sup>-2</sup> were obtained.

For frequency doubling experiments conducted by Risk (1991) a waveguide was fabricated on the c-side of a KTP substrate with a depth of  $d \sim 2 \mu m$ and found to be single mode at the infrared wavelength used for SHG. In bulk KTP, type II nonlinear processes are used, since these have high effective nonlinear coefficients. These processes, such as frequency doubling of 994 nm light (Risk et al 1989), or sum-frequency mixing of 809 and 1064 nm light (Baumert 1988), require both x- and z-polarized fields at the IR wavelengths for propagation along the y-axis. The generated SH field is polarized along x. The phase matching condition for SHG is thus  $1/2 [n_x(\omega) + n_z(\omega)]$  $= n_z(2\omega)$ . In the waveguide, the analogous interaction corresponds to  $TE_m^{\omega} + TM_m^{\omega} \Rightarrow TE_p (2\omega)$ , where m, n, and p are mode numbers. The most desirable interaction is for m = n = p = 0, which involves only the lowest-order modes. Interactions involving lowest-order modes at the fundamental (m = n = 0)and higher-order modes at the second-harmonic  $(p \neq 0)$  permit generation of blue/green wavelengths shorter than those obtained using the bulk material.

Figure 6.40 shows calculated values for the refractive indices involved in the bulk interaction and for effective mode indices in the guided-wave interaction. The bulk refractive index values are calculated from Sellmeier equations. The effective mode indices have been calculated by the WKB method using the parameters of the waveguide measured by prism coupling at 633 nm. The dashed curves represent  $1/2 [n_{c}(\omega) + n_{c}(\omega)]$ , corresponding to fundamental



Fig.6.40 Phase-matching characteristics for frequency doubling in a planar KTP waveguide. Lower horizontal scale refers to fundamental wavelengths; upper horizontal scale refers to corresponding second-harmonic wavelengths (Risk 1991).

Interaction	Calculated wavelength	Measured wavelength
$TE_0^{\omega} + TM_0^{\omega} \Rightarrow TE_0^{2\omega}$	1130 nm	N/A
$TE_0^{\omega} + TM_0^{\omega} \Rightarrow TE_1^{2\omega}$	966 nm	969 nm
$TE_0^{\omega} + TM_0^{\omega} \Rightarrow TE_2^{2\omega}$	913 nm	923 nm
$TE_0^{\omega} + TM_0^{\omega} \Rightarrow Cherenkov$	905 nm	906 nm

Table 6.5 Wavelengths of phase-matched interactions (Risk 1991)

wavelengths on the lower horizontal scale and  $n_x(2\omega)$ , corresponding to secondharmonic wavelengths on the upper horizontal scale. At the intersection of these two curves, the bulk phase-matching condition given above is satisfied; this corresponds to SHG with a fundamental wavelength of 994 nm (Risk et al 1989). The solid curves in Fig.6.40 show the dispersion of the effective indices for waveguide modes. The intersections of the curve representing the average of the TE<sub>0</sub><sup> $\omega$ </sup> and TM<sub>0</sub><sup> $\omega$ </sup> mode indices with the curves representing the mode indices for the TE<sub>p</sub><sup> $2\omega$ </sup> modes define wavelengths for which guided-mode SHG interactions are phase matched. As can be seen from the figure, blue/ green light can be generated at wavelengths considerably shorter than that obtained by SHG in the bulk crystal.

Light from a titanium-sapphire laser in the 900-1000  $\mu$ m range was used to simultaneously excite the TE<sub>0</sub> and TM<sub>0</sub> modes of the waveguide. As the wavelength of the laser was tuned, SHG interactions involving excitation of higher-order TE modes at the second harmonic were observed. The measured wavelengths at which these interactions occurred are shown in Table 6.5, along with the calculated values from Fig.6.40. The measured and expected wavelengths for the various interactions are in good agreement. Excitation of the TE<sub>0</sub> mode at the second harmonic was expected to occur for a fundamental wavelength of 1130 nm, but could not be observed since this wavelength was outside the tuning range of the titanium:sapphire laser. For wavelengths shorter than 905 nm, excitation of radiation modes at the second harmonic (Cherenkov doubling) was observed.

6.9.1 Phase matching in periodically segmented KTiOPO, waveguides Bierlein et al (1990) described a new technique used for achieving phase matching in KTiOPO<sub>4</sub> (KTP) waveguides but equally applicable for both bulk and other waveguide systems. This scheme can not only give phase-matched second-harmonic conversion efficiencies but can significantly extend processing latitude which is particularly important for practical nonlinear optical channel waveguide devices.

In the conventional phase matching involving the nonlinear interaction of three beams in a crystal where the frequencies of the three beams are related as  $\omega_1 + \omega_2 = -\omega_3$ , either the direction of propagation or the temperature is tuned so that the propagation constants  $k = 2\pi n/\lambda$  of these beams obey the relation  $k(\omega_i) + k(\omega_2) = k(\omega_3)$ , or  $\Delta k = [k(\omega_1) + k(\omega_2)] - k(\omega_3) = 0$ . Here the  $k(\omega_i)$ 's are the beam propagation constants, n's the refractive indices, and  $\lambda$ 's the corresponding wavelengths. The crystal or waveguide is divided into segments, each segment consisting of sections of length  $\ell_i$  and propagation constant mismatch  $\Delta k_i$  such that for each segment  $\Sigma \ell_i \Delta k_i = 0$ , where the sum is over all sections. The length of each section is less than its corresponding coherence length, that is  $\ell_i < 2\pi / \Delta k_i$ . When these conditions are met, even though the beams are not phase matched is the sections individually, they are phase matched at the end of each segment and the generated output power will increase as the square of the number of segments.

Each segment could in principle consist of many sections, might differ in structure from the previous segment, or could even be a single section with continuously varying properties such that  $\int \Delta k(z) dz = 0$ . To illustrate the method, the simplified case was considered, where the second-harmonic generation in a periodic waveguide structure consisted of two sections per segment as shown in Fig.6.41. For this case, a fairly simple quantitative relation for the generated output power can be obtained. In the structures considered, the length of the sections deviated strongly from the Bragg condition and the refractive index differences between the sections were small. Therefore, the reflection effects from the subsequent sections and the fundamental beam depletion could be ignored. With these approximations and extending this analysis



Fig.6.41 Segmented waveguide structure (Bierlein 1990).

to include ferroelectric domain reversals, the second-harmonic power generated from the segmented structure, P, normalized to the power generated in a perfectly phase-matched uniform waveguide of equal length,  $P_0$ , is given by

$$P/P_0 = G^{2*} I^2, (6.76)$$

where G describes the effects of the periodic grating and I the internal SHG within a single period. The effects of overlap between fundamental and harmonic guided modes were assumed to be identical for both P and  $P_0$ .

The grating function, G, in equation (6.76) is given by

$$G = \frac{1}{N} \frac{\sin(Nq/2)}{\sin(q/2)},$$
(6.77)

where N is the total number of periods in the waveguide and

$$q = \Delta k_1 \ell_1 + \Delta k_2 \ell_2, \tag{6.78}$$

is the phase matching between the fundamental and second-harmonic waveguide modes in a single period. The  $\ell_i$ 's and  $\Delta k_i$ 's are the lengths and corresponding propagation constant mismatches of the two segments. The function G will peak if the second harmonic waves from subsequent periods add in phase, that is, at  $q = 2\pi M$ , where  $M = 0, \pm 1, \pm 2, etc.$  and the phase-matching condition becomes

$$\Delta k_1 \ell_1 + \Delta k_2 \ell_2 = 2\pi \mathcal{M}. \tag{6.79}$$

The internal function, I, in equation (6.76) describes how, within a single period, the second-harmonic fields of neighbouring segments interfere. At phase matching, I is given by

$$I = \frac{1}{\pi} \frac{\ell_{1c} \pm \ell_{2c}}{\ell_1 + \ell_2} \sin \pi \frac{\ell_1}{\ell_{1c}},$$
(6.80)

where  $\ell_{ic} = 2\pi/\Delta k$  are the coherence lengths of the two sections. The + sign in equation (6.80) corresponds to the case where adjacent segments have inverted ferroelectric domains, the - sign corresponds to a pure refractive index grating. With the low index steps usable in practice, it can be readily shown from equation (6.80) that the latter situation leads to much lower conversion efficiencies as compared to the domain inverted case.

Balanced phase matching (BPM) occurrs when M = 0 in equation (6.79) and is limited to phase-matched SHG in KTP for a wavelength longer about that 1 µm (Bierlein, et al. 1990). With  $M \neq 0$  the blue region of the visible



**Fig.6.42** Second-harmonic generation in 5 mm Rb/Ba flux KTP segmented waveguides. (a) Absolute conversion efficiency at 850.5 nm for a 4  $\mu$ m period, 4  $\mu$ m waveguide. (b) Wavelength scan for a 5  $\mu$ m period, 4  $\mu$ m waveguide.  $P_w$  is the guided fundamental power (Poel et al 1990).



Fig.6.43 Phase-matching wavelength vs segment period of 4  $\mu$ m-wide waveguides. Solid lines and (•) are for TM  $\rightarrow$ TM interactions, dashed lines and (×) are for TE  $\rightarrow$ TM interactions. *M* is defined in equation (6.79) (Poel et al 1990).

spectrum becomes available for phase-matched second-harmonic generation. The waveguide depth can be chosen to minimize the effects of depth variations on the refractive index mismatch such that optimum fabrication tolerances for phase function result. This property of the segmented structure constitutes a major advantage over uniform waveguides, where this degree of freedom in fabrication is absent. In the experiments, one segment was bulk KTP and the other was an ion-exchanged waveguide. With this mask 24 different waveguide width/segment period combinations can be fabricated on a single substrate. In a typical example segmented y-propagating waveguides were fabricated on the z-surface of a flux-grown KTP substrate. Using a tunable Ti:Al<sub>2</sub>O<sub>3</sub> laser, the phase-matching wavelengths and conversion efficiencies for these waveguides are given in Fig.6.42. Overall fundamental beam throughput from the laser to the waveguide output (including lenses, coupling and waveguide losses)



**Fig.6.44** Phase-matched wavelength bandwidths for segmented KTP waveguides. (a) M = 0, type II, 5 µm period, 5 µm width. (b) M = 1, type I TM  $\rightarrow$ TM, 4 µm period, 5 µm width. (c) M = 2, type I TE  $\rightarrow$ TM, 4 µm period, 4 µm width (Poel et al 1990).

is about 40%. Two waveguide modes are observed to give phase-matched SHG. From the near- and far-field distributions, these modes correspond to couplings between the lowest order guided fundamental mode and, respectively, the lowest and first-order guided harmonic modes, as indicated in Fig.6.42.

A typical efficiency plot is also shown in Fig.6.42 which, at low fundamental powers, indicates an efficiency of  $80\pm5\%/W$  cm<sup>2</sup>. Depending on waveguide processing conditions, significantly lower phase-matched type I efficiencies can also occur with both hydrothermal and flux-grown substrates. For example, lowering the exchange temperature by 20°C decreases the conversion efficiency by nearly three orders of magnitude.

For a waveguide width of 4 µm, the SHG phase-matching wavelengths were measured for four different segment periods present on the same KTP substrate. In Fig.6.43, the measurements are compared with theoretical predictions for various phase-matching M values and nonlinear interactions. The interactions include type I coupling through the  $d_{33}$  nonlinear optical coefficient (TM  $\rightarrow$  TM) and through the  $d_{32}$  coefficient (TE  $\rightarrow$  TM). Efficient SHG phase-matched output is observed from deep purple at 0.38 µm to bluegreen at 0.48 µm. For KTP, this wavelength range is normally not addressable by conventional phase-matching techniques. For periods of 3, 4, 5 and 6 µm, the observed phase-matching wavelengths for these various combinations are in good agreement with those predicted from equation (6.79) using bulk KTP refractive indices (Bierlein and Vanherzule 1989). The differences between the calculated and experimental wavelengths are quite small considering that in the calculation bulk refractive indices rather than effective waveguide indices were used in equation (6.79).

The wavelength bandwidths, as measured in 5 mm segmented waveguides, are summarized in Fig.6.44 and compared to a typical result using BPM. From

a Taylor's expansion of equation (6.77), using equation (6.79) and the Sellmeier equations for bulk KTP (Bierlein et al 1989), wavelength bandwidths full width at half maximum of 0.67 nm cm for type II at 1.06 µm and 0.06 nm cm for type I, TM  $\rightarrow$  TM at 0.80 µm are predicted. The close agreement between the predicted and measured bandwidths indicates that nearly perfect phase matching occurs over the full 5-mm sample length. This also accounts for the high absolute conversion efficiency observed (3 % at 100 mW fundamental power for M = 1). The measured temperature bandwidth is about 3°C. Also shown in Fig.6.44 is the type I TE  $\rightarrow$  TM phase-matched peak. This peak corresponds to phase matching for M = 2, with an expected wavelength bandwidth of 0.05 nm cm.

Preliminary results from low-temperature electrostatic tuning and from surface SHG experiments indicate that the origin of these large type I conversion efficiencies is ferroelectric domain reversal induced by the waveguide processing when Ba is present in the exchange bath. Assuming that the depth of the ferroelectric domain correlates with the Ba ion concentration in the waveguide and, since the effective SHG mode overlap is expected to vary strongly with domain depth (Arvidsson and Jaskorzynskii 1989), this mechanism would also explain the large changes in conversion efficiency that occur with changes in ion-exchange temperature. Ion-exchange experiments with different substrate materials, different surface polarities, and a variety of molten salt compositions are in progress to clarify the mechanism for domain reversal in these materials and to gain improved understanding of and control over the fabrication process.

#### Conclusions

In a single book, even of this volume, it is difficult to embrace all aspects of ferroelectric thin-film waveguides, from a large number of methods of fabrication to even a larger number of possible applications in devices for laser radiation control. As indicated by the contents, the book examines mainly the effect of the physico-chemical factors on the optical and wave properties of thin films which are of primary importance for practical application. We have also presented several methods of examining the thin films and theoretical conclusions regarding the variation of the refractive indices and the laws of light propagation in the film. Only in the final chapter we have examined, as examples, several devices for electro-optical light modulation., deviations and transformations to the second harmonics. In this period characterized by the appearance of a large number of publications in many scientific journals the authors sometimes omit initial studies in which the fundamental results for the examined problem were obtained. We have therefore tried to stress the role of initial publications in which the phenomenon under examination is often studied in considerable detail. We hope the book will be useful for experts working in the area of producing and applying thin lightguide films for laser radiation control.

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#### INDEX

### A

absorption loss 282 activation energy for vaporization 29 actual vaporization flux 30 angular matching 241 annealed proton-exchanged waveguides 56 autodiffused layers 25

#### B

bandwidth 295 Bragg diffraction modulator 315 Bragg reflector 247 buffered melts 59 Bulk crystallization 131

### С

capillary liquid epitaxial technique 78 channel width 255 Cherenkov radiation 245 cinnamic acid 64 coherence length 248 control voltage 293 conversion efficiency 245 copper diffusion 49 coupled channel waveguides 302 critical supersaturation 135 crystallization from a gas phase 6 Curie temperature 16 Curie-Weiss behaviour 16 Czochralski method 132

### D

degree of film perfection 1 dielectric impermittivity tensor 35 dielectric properties 285 diffusion depth 123 diffusion of transition metals 37 diffusion-induced defects 188 direct electron-beam writing 203 dislocation structure 191 domain configuration 198 domain inversion 203 domain structure 195 double waveguide 23 double-exchange' technique 66 Dufour effect 139

### E

effective segregation coefficient 110

electro-optic coefficient 259 electro-optic effects 258 electro-optic modulators 293 electro-optic photorefractive modulator 328 electro-optic X-switchers 292 electro-optically tunable wavelength filter 342 electrodiffusion 49 electron polarizability 36 electrostriction effect 36 energy loss in waveguides 279 epitaxial ferroelectric films 118 epitaxial growth 151 epitaxial growth of LiNbO, 97 equilibrium segregation coefficient 142 evaporation coefficient 33 exchange time 66 extraordinary refractive index 215

### F

Fabry-Perot loss280Fabry-Perot resonator260Fermi function229Fermi level135ferroelectric films210Fick's second law27film growth rate141flip-chip coupling345

## G

gas-transport epitaxy 1 gas-transport epitaxy 6 Gaussian nuclear damage 24 Gaussian profiles 39 Glass constant 276 Glass model 276 Grating formation 267 gratings 266

## H

holographic writing 267 homoepitaxial LiNbO<sub>3</sub> films 178 hydrogen isotopic exchange 58

### I

in-diffusion coefficient 65 index change 274 insertion losses 293 interferometric Mach-Zehnder modulator 326 isothermal epitaxy 105

### J

Joule effect 133

## K

Kerr effect 48 Kikuchi lines 207 KLN crystal 121 KNbO<sub>3</sub> induced waveguide cut-off modulator 331

### L

Langmuir relation 28 Langmuir vapour pressure 29 laser sputtering method 17 layer composition 173 layer precipitation time 124 light resistance 2601 LiNbO<sub>3</sub> birefringence 245 liquid-phase electroepitaxy 136 liquid-phase epitaxy 74 liquid-phase epitaxy (LPE) technique 83 lithium niobate 165 Lorentz-Lorenz formula 36

## M

Mach-Zehnder interferometer 271 Marcatili's approximation 246 maximal modulation depth 293 MFES structure xvi micro-channel slab 125 microdomains 199 micromorphology of film surface 186 mode number 231 modulation index 260 monocrystallinity 175

### N

negative birefringence 215 nucleation rate 146

## 0

one-dimensional waveguides 22 optical modes 224 optical properties 213 optical switching time 309 optical waveguide switch modulator 308 ordinary refractive index 215 out-diffused layers 26 out-diffusion coefficient 65 out-diffusion index profiles 26 out-diffusion kinetics 27 out-diffusion suppression 34

### P

partition coefficient 128 PDR waveguide 247 PE waveguide 65 Peltier coefficient 132

perovskite 118 phase matching 239 photoelastic coefficient 47 photoinduced polarization conversion 298 photorefractive effect 269 photorefractive properties 264 photorefractive sensitivity 270 planar ion-exchanged KTiOPO, waveguides 68 planar waveguides 20 Pockels coefficient 68 potassium lithium niobate 121 prism coupling technique 65 propagation constant 230 propagation loss 12 proton diffusion 62 proton-lithium exchange 52 proton-exchanged LiNbO, 182 proton-exchanged LiNbO, waveguides 51 pseudo-Kossel pattern 11 pulsed laser deposition 17 pumping power 240 pumping wavelength 240 pyroelectric properties 287

# Q

QPM-SHG device 202 quasi-phase matching 200

### R

Raoult law 3 refractive index gradient 31 rf sputtering 8 ridge waveguide modulator 317 Rutherford backscattering spectroscopy 16

## S

'sandwich method' 5 scheme of the growth cell 95 Schröder equation 91 second harmonic generation 237 Seebeck coefficient 289 Selfmeier relation 215 Snell law 217 spikelike domains 201 stationary crystallization model 97 Stepanov method 132 strip line structures 123 strip waveguides 21 substrate modes 222 sum-frequency generation 253 supersaturation 101 surface index 72 symmetric waveguides 124

### Т

 $TE \leftrightarrow TM$  polarization conversion 345

TE wave 226 temperature matching 244 tensor of electro-optic coefficient 34 thermal diffusion 49 thermal pulse method 287 thermoelectric effects 289 thin films 134 thin-film electro-optic light modulator 311 Thomson effect 139 Thomson's coefficient 150 Ti oxidation 43 Ti-diffused diffraction modulator 320 TIPE 52 titanium diffusion 41 titanium-in-diffused-proton-exchange 52 TM wave 226 total internal reflection modulator 307 tungsten bronze ferroelectric 13

#### V

vacuum epitaxy 1

vaporization flux 29 vapour pressure 3 Vegard law 129 vertical dipping technique 111

#### W

Wallace-Ward cylindrical texture camera 43
waveguide depth 64
waveguide electro-optic polarization transformer 334
waveguide line thickness 123
waveguide modes 222
wavelength division multiplexing 344
WKB method 227

### X

X-ray Laue pattern 11





Academician A M **PROKHOROV** received the Nobel Prize for Physics (1964) for fundamental investigations in quantum electronics leading to the development of masers and lasers. He is well known as an outstanding expert on quantum electronics, radiospectroscopy, laser science and technology. He founded and is now the Director of the General Physics Institute of the Russian Academy of Sciences. His pioneering work in the theory of nonlinear oscillations, nonlinear optical processes, fibre and integral optics, solid-state physics and other areas of physics has contributed significantly to the development of a number of areas of modern physics.



Professor Yu S **KUZ'MINOV** is a Corresponding Member of the Engineering Academy of Sciences of the Russian Federation, Principal Research Associate of the General Physics Institute of Russian Academy of Sciences, a specialist in the field of nonlinear optical crystals for laser radiation control. He has published more than 150 publications in Russian and foreign journals and three monographs, two of which (published jointly with Prof Prokhorov) were translated into English (Physics and Chemistry of Crystalline Lithium Niobate and Ferroelectric Crystals for Laser Radiation Control).



Professor O A **KHACHATURYAN** graduated in 1968 from the Leningrad Polytechnic in the field of semiconductors and dielectrics. In 1989 he received his PhD in solid state physics and since 1990 he has been a Professor at the Chair of Microelectronics of the Erevan Technical University. He has authored more than 100 scientific publications in the field of thin-film micro- and optoelectronics. He has developed technologies for growing complex epitaxial structures of semiconductor and ferroelectric materials used in optical communication and information processing systems.

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