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Thin film lithium niobate optical waveguides for integrated optics

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Rice University, 1992
RICE UNIVERSITY

THIN FILM LITHIUM NIOBATE OPTICAL WAVEGUIDES FOR INTEGRATED OPTICS

by

CHARLES HUNG-JIA HUANG

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

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THIN FILM LITHIUM NIOBATE OPTICAL WAVEGUIDES FOR INTEGRATED OPTICS

CHARLES HUNG-JIA HUANG

Abstract

Highly oriented polycrystalline thin films of lithium niobate on (012), (100), and (110) sapphire single crystal substrates, (111) silicon and SiO$_2$/(190)Si wafers were grown by magnetron rf sputtering and metallo-organic decomposition techniques. A novel technique of photo-induced metallo-organic decomposition (PIMOD) is proposed and implemented to eliminate inter-diffusion and cracking which are commonly observed in MOD-derived films. Results of XRD, TEM, and ion beam spectrometry confirm that highly oriented, polycrystalline, stoichiometric lithium niobate thin films have been successfully grown on a variety of substrates. Prism coupling has been used to excite the guided modes in the optical thin film waveguides. The optical and electrooptic properties, including the refractive index, propagation losses, and electrooptic coefficient, were investigated. Finally, an electrooptic phase modulator was implemented.
Acknowledgments

There have been so many people who have helped me throughout my studies at Rice. First of all I would like to thank my thesis advisor, Dr. Tom Rabson, for his guidance and valuable discussions on all aspects of this project. Thanks are also to Dr. Frank Tittel and Dr. Dan Callahan for serving on my committee. Thanks to these people again for their time spent reviewing my thesis. Many thanks are in order for Dr. He Lin, who has been a great coworker and my best friend at Rice. I am indebted to Dr. Tim Rost for teaching me how to use the sputtering system. Thanks are also due to Barbara Stone for helpful discussions. I'd like to thank Dr. W. K. Chu, Z. H. Zhang, and J. R. Liu in the Texas Superconductivity Center at University of Houston for teaching me the advanced aspects of ion beam spectrometry and for the use of the ion beam accelerator. Thanks are also in order for Dr. J. Stormer and Milton Peterson for letting me use the x-ray diffractometer, the electron microprobe, and the SEM. I need to thank Dr. K. Whitmire for preparing the metallo-organic compound precursors. I would also like to thank S. M. Wang for her help on the thermogravimetric analysis. I am very grateful to the ECE staff including Nora and Ida who took care of all the administrative details and Hubert who helped to solve technical problems.

This work is dedicated to my parents and my wife. Without their love and support, it would be very difficult for me to complete this work.
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Chapter 1

Introduction

The use of ferroelectric materials in computer memory devices has recently drawn very much attention because the ferroelectrics possess several important properties such as non-volatility, fast switching, and radiation hardness. Also, the need for high speed integrated optical devices has resulted in a great interest in the electrooptic and acoustooptic properties of ferroelectric materials. Ferroelectrics in the thin film form are particularly attractive because they offer integration with semiconductor electronic and optoelectronic devices. Moreover, the excellent light confinement in waveguide geometries allows for the use of the nonlinear properties of the materials.

LiNbO$_3$ is one of the most interesting ferroelectrics because of its excellent electrooptic, acoustooptic, and nonlinear properties. A variety of integrated optical devices, such as Mach-Zehender intensity modulators, total internal reflection (TIR) switch, directional couplers, Bragg deflection modulators, frequency shifter, and surface acoustic wave (SAW) modulators, have been proposed and implemented. In the early 1970's, a holographic optical memory system, utilizing the photorefractive effect of bulk LiNbO$_3$, was investigated [1, 2]. If LiNbO$_3$ thin films retain at least some magnitude of its bulk properties, a number of integrated thin film devices can be considered. For example, the research group at Rice University has recently developed a transistor based on thin film LiNbO$_3$, which can operate in two modes: the electrical and optical modes. The operation of the electrical mode involves the use of ferroelec-
tric switching, whereas that of the optical mode utilizes the bulk photovoltaic effect in LiNbO$_3$. The electrical properties of LinbO$_3$ has been fully characterized by Tim Rost [3], therefore, this thesis focuses more on the optical and electrooptic properties of the LiNbO$_3$ films.

For the development of integrated optics the fabrication of low loss waveguides on various substrates is essential. Processes of RF magnetron sputtering and metallo-organic decomposition (MOD) have been employed to grow epitaxial thin films on (012), (001), (100), and (110) sapphire (α-Al$_2$O$_3$) substrates and highly oriented polycrystalline films on (111) Si and SiO$_2$/(100)Si substrates. Sapphire was considered to be a suitable substrate because it is transparent in the visible light region, it has a similar lattice structure to LiNbO$_3$, the lattice mismatch between sapphire and LiNbO$_3$ is small (about 7%), and its much lower refractive index allows for excellent light confinement. Various silicon substrates were used to study the properties of LiNbO$_3$ thin film integrated on semiconductors.

The physical, optical, and electrooptic properties of the LiNbO$_3$ films have been investigated. A transmission type of electrooptic phase modulator has been built on a (110) sapphire substrate, and the performance of the device is satisfactory and very encouraging. A Bragg deflection electrooptic modulator, which can be used as an optical switch, is currently under investigation. Although optical waveguide devices can not be directly integrated on silicon substrates, other devices such as optically erasable memory disks are possible using the LiNbO$_3$/Si structure and have great potential in marketing.

The organization of this thesis is as following: Chapter 2 briefly gives the theory and properties of ferroelectrics. Chapter 3 discusses the growth of LiNbO$_3$ thin films. Modified versions of the two techniques of thin film growth are proposed and
implemented. Bragg x-ray diffraction (XRD) was used to characterize the physical properties of the deposited films. Chapter 4 describe the concepts of ion beam spectrometry, including Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA). These techniques of surface analysis have been very useful in obtaining information on the chemical composition, thickness, and depth profile of thin film. Chapter 5 includes the results of measurements of optical and electrooptic properties of the waveguide devices.
Chapter 2

Ferroelectrics

2.1 Dielectrics

When a conductor is placed in an externally applied electric field, all of the free charges will be driven by the electric field and their movement will depend on the direction of the field and their charge. What will happen if an ideal dielectric which contains no free charges is placed in an external electric field? Certainly, there will be no induced free charges moving to the surface to make the interior charge density and electric field vanish. However, one cannot conclude that the dielectric materials have no response to the electric field in which they are placed since there are still "bound charges" inside them. Instead of free charges, polarization of electric dipoles will be induced to "record" the effect on the electric field. Microscopically speaking, the polarization of dielectric materials is due to the electric dipoles caused either by the distortion of the electron clouds surrounding atoms (or ions) or by the relative displacement between the positive and negative ions. In addition, the asymmetry of the molecular structure of the crystal can also produce a dipole moment which tends to align with the direction of the applied electric field, thereby causing dielectric polarization. These three polarization mechanisms within dielectrics are commonly termed electronic, ionic, and dipolar polarizability, respectively.
Permittivity $\varepsilon$ is a very important physical quantity which reflects the polarization behavior of dielectrics in an applied electric field. The electric flux density $\mathbf{D}$ for a dielectric material is related to the applied electric field $\mathbf{E}$ by

$$\mathbf{D} = \varepsilon \mathbf{E} = \varepsilon_0 \varepsilon_r \mathbf{E} = \varepsilon_0 \mathbf{E}(1 + \chi), \quad (2.1)$$

where $\varepsilon_0$ is the free space permittivity, $\varepsilon$ is the absolute permittivity of the dielectric, $\varepsilon_r$ is a dimensionless constant known as the relative permittivity or the dielectric constant of the dielectric, and $\chi$ is the electric susceptibility of the material. Eq. 2.1 can be rewritten in terms of the polarization $\mathbf{P}$ by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}, \quad (2.2)$$

where

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E}. \quad (2.3)$$

### 2.2 Piezoelectric effect

From the least symmetrical geometry to the most symmetrical, crystals are commonly classified into seven systems: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic. These systems can be further divided into 32 point groups or crystal classes according to their symmetry with respect to a space point. A dipole moment or polarization will be induced in all of these dielectric materials by the application of an electric field. Twenty of the 32 crystal classes are non-centrosymmetric and thus piezoelectric materials which exhibit a linear, reversible electromechanical effect. For the piezoelectric materials, the polarization can be expressed as

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} + d \mathbf{X}, \quad (2.4)$$

where $d$ is the piezoelectric compliance and $\mathbf{X}$ is the applied strain. The piezoelectric effect was discovered by Pierre and Jacques Curie in 1880 [4]. Important
piezoelectrics include quartz, Rochelle salt, (NH₄)H₂PO₄ (ADP), LiTaO₃, LiNbO₃, PbZrO₃, PbTiO₃, and PZT [4].

The linearity of Eq. 2.4 implies that the piezoelectric effect is reciprocal. The direct piezoelectric effect is the production of an electric polarization by a strain, while the converse piezoelectric effect is the production of a stress by an electric field. The direct effect is linear in the strain, while the converse effect is linear in the electric field. Using the piezoelectric effects, devices such as pressure transducers, piezoelectric resonators, etc. can be made for many applications. Piezoelectricity also leads to indirect contributions to the electrooptic effect, the elastooptic effect, etc.

2.3 Pyroelectric effect

Only ten of the piezoelectrics classes have a unique polar axis, namely, 1, 2, m, 2mm, 3, 3mm, 4, 4mm, 6, and 6mm [5], and are often called polar materials [6]. Permanent polarization, commonly termed as spontaneous polarization, exists in the polar materials even in the absence of an applied electric field or mechanical stress. By adding the spontaneous polarization term, the total induced polarization of the polar materials can then be expressed by

\[ P = \varepsilon_0\chi E + dX + P_s, \]  

(2.5)

where \( P_s \) is the spontaneous polarization.

Since charge compensation rapidly happens within the dielectrics, the spontaneous polarization cannot be detected by measuring the surface charges of the materials. Spontaneous polarization in these materials, however, is temperature dependent and can be detected by monitoring the flow of the surface charges while rapidly changing the temperature of the material. This phenomenon is therefore called the pyroelectric
effect, and the ten polar materials are also referred to as the pyroelectric materials. The pyroelectric current is largest if the measurement is taken between the two faces of the polar axis of the material. Numerous devices using the pyroelectric effect have been designed, including infrared and millimeter wave detectors, temperature sensors, calorimeters, and thermal imagers [4]. Many pyroelectric materials have been considered for such device applications. Among the more widely used are triglycine sulfate (TGS), LiTaO₃, lead zirconate titanate (PZT), and polyvinylidene fluoride [4].

2.4 Ferroelectrics

A very important subgroup of the pyroelectrics is the ferroelectrics [7] in which there are two or more stable polarization states in the absence of an externally applied electric field. It is possible to apply a sufficiently large electric field to switch from one polarization state to another, and it won't automatically switch back to the original state when the applied field is removed. The variation of the electric polarization in an applied electric field for a linear dielectric, a polar material, and a ferroelectric is shown schematically in Fig. 2.1. In Fig. 2.1(c), the arrows indicate that as the applied electric field is decreased from its maximum positive value to zero, the polarization assumes the nonzero value $P_s$ ($P_s \approx P_r$), which is the spontaneous polarization, and is a true measure of the intrinsic electric moment of the material. As the field is reversed, it sweeps through a critical value $-E_c$, termed the coercive field, at which the ferroelectric switches into a new configuration which is then found, when the field is again removed, that the spontaneous polarization is in the opposite direction $-P_s$. The coercive field is the field needed to overcome the structural forces separating the charges and thereby to switch the spontaneous polarization.
Figure 2.1  Polarization vs. electric field characteristics for (a) a linear dielectric, (b) a polar dielectric, and (c) a ferroelectric. The hysteresis loop shows the behavior of the polarization induced by an applied field. The arrows indicate the direction in which the electric field is scanned.

In order to reverse the polarization, a ferroelectric material must pass through a unstable nonpolar state which is only slightly less stable than the polar state and can be stabilized by changing its environment such as temperature. For example, Fig. 2.2 shows the typical spontaneous polarization in a famous ferroelectric, BaTiO$_3$, measured at several temperature. At low temperature, there coexist two equally stable polar states $P_+$ and $-P_+$, while above a critical temperature, known as the Curie temperature $T_c$, the polar phases become less stable than the nonpolar phase and the spontaneous polarization normally drops to zero at $T_c$. In this case, the
Figure 2.2 Schematic phase diagram for BaTiO$_3$. Below its curie temperature, there are two stable polar states with the spontaneous polarization $P_s$ pointing in the opposite direction.

material is said to undergo a transition from its ferroelectric phase to the paraelectric phase.

Due to the non-volatility and the fast switching times, ferroelectric materials have received much attention for building computer memory systems [8, 9]. For example, using a ferroelectric capacitor structure, the PZT films have shown that they can withstand up to $10^{12}$ read-write cycles before fatigue (excitation aging) becomes intolerable. Retention time (self life) of 1 to 2 years has been predicted [10].

2.5 Birefringence

There are several other properties of ferroelectric materials that are directly related to the loss of symmetry associated with the transition from the nonpolar to polar phase. In the case of BaTiO$_3$, the unit cell in the nonpolar phase is cubic. Since it is
not possible for a cubic crystal to be polar, the cell must be distorted along the polar axis on passing into the polar phase. Therefore, the transition from the paraelectric phase to the ferroelectric phase develops not only a spontaneous polarization but a spontaneous noncubic lattice strain as well. The anisotropic structure makes a difference in the velocity of light propagating parallel and perpendicular to the polar axis. In the case of uniaxial crystals, a wave propagating along the polar axis (optic axis) will have one velocity \( v_1 \) associated with the so-called *ordinary index of refraction* \( n_o = c/v_1 \), while the one propagating perpendicular to the polar axis may have two different velocities. If the electric field vibrates in the plane normal to the polar axis, the wave has ordinary velocity and the ordinary refractive index applies. If the vibration of the electric field is along the polar axis, then the wave travels with a different velocity \( v_2 \) and the corresponding refractive index is called the *extraordinary index of refraction* \( n_e = c/v_2 \). The velocities \( v_1 \) and \( v_2 \) are given by

\[
\begin{align*}
  v_1 &= \sqrt{\frac{1}{\varepsilon_{11}\mu}}, \\
  v_2 &= \sqrt{\frac{1}{\varepsilon_{33}\mu}},
\end{align*}
\]  

(2.6)

where \( \varepsilon_{11} \) and \( \varepsilon_{33} \) are the elements in the dielectric tensor

\[
\begin{pmatrix}
  \varepsilon_{11} & 0 & 0 \\
  0 & \varepsilon_{11} & 0 \\
  0 & 0 & \varepsilon_{33}
\end{pmatrix},
\]  

(2.7)

and \( \mu \) is the permeability in free space. For LiNbO\(_3\) the low frequency dielectric constants \( (\varepsilon_{r,ij} = \varepsilon_{ij}/\varepsilon_0) \) are about \( \varepsilon_{r,11} = 30 \) and \( \varepsilon_{r,33} = 80 \) [11]. This birefringent effect in optical crystals has been tremendously used in making all kinds of polarizers such as the Nicol, Glan-Foucault, Rochon, and Wollaston prisms [12].

### 2.6 Electrooptic effect
Table 2.1  Linear electrooptic coefficient $r$ and half-wave voltage $V_{\lambda/2}$ for various polar materials at room temperature and 6328 Å wavelength for D.C. electric field. The half-wave voltages are calculated for a 1 cm cube of material.

<table>
<thead>
<tr>
<th>Material</th>
<th>$r \times 10^{10} , m/V$</th>
<th>$V_{\lambda/2} , (V)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ba$_2$(KNa)Nb$<em>5$O$</em>{15}$</td>
<td>0.4-0.52</td>
<td>1000-1400</td>
</tr>
<tr>
<td>Ba$_2$NaNb$<em>5$O$</em>{15}$</td>
<td>0.36</td>
<td>1500</td>
</tr>
<tr>
<td>KH$_2$PO$_4$</td>
<td>0.52</td>
<td>4000</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>0.31</td>
<td>2800</td>
</tr>
<tr>
<td>LiTaO$_3$</td>
<td>0.22</td>
<td>2800</td>
</tr>
<tr>
<td>PLZT</td>
<td>1.02-6.12</td>
<td></td>
</tr>
<tr>
<td>(SrBa)Nb$_2$O$_6$</td>
<td>2.1-14.0</td>
<td>37-250</td>
</tr>
<tr>
<td>Sr$_2$K Nb$<em>5$O$</em>{15}$</td>
<td>1.3</td>
<td>500</td>
</tr>
</tbody>
</table>

The birefringence can be induced or changed by an external electric field. This is called the *electrooptic effect*. In polar materials the two major electrooptic effects are the linear *Pockels effect* and the quadratic *Kerr effect*. In the Pockels effect the field-induced birefringence $\Delta n$ is proportional to the applied field and is given by

$$\Delta n = -\frac{1}{2} n^3 r E,$$

(2.8)

where $r$ is the linear electrooptic coefficient. Table 2.1 is a list of $r$ and $V_{\lambda/2}$ for some of the most promising electrooptic polar materials [6]. In the Kerr effect $\Delta n$ varies in a quadratic fashion with the polarization $P$ and can be expressed by

$$\Delta n = -\frac{1}{2} g n^3 P^2,$$

(2.9)

where $g$ is the quadratic electrooptic coefficient. A variety of electrooptic devices such as modulators, switches, and spectrum analyzers have been developed utilizing the electrooptic effects of the polar materials [13].
2.7 Photorefractive and photovoltaic effect

Change of refractive index can also be induced in certain spontaneously polarized materials by illuminating the sample with a strong optical radiation. This is the photorefractive effect which was first reported by Ashkin et al. [14] in LiNbO$_3$ and LiTaO$_3$ with focused laser beams in the blue or green regions of the spectrum, although unusual phenomenon observed earlier by Peterson et al. [15] can be ascribed to the same effect. The photorefractive effect shows promise for optical memories, and a great deal of effort has been devoted to both increasing and decreasing the susceptibility of materials to these index changes for the various applications.

The photovoltaic effect is another remarkable effect in some polar materials. An open circuit photovoltage or short circuit steady state photocurrent can be generated when the incident optical radiation has an energy which is high enough to create free carriers moving preferentially in one direction without an externally applied electric field. This effect is also very useful for building memory devices [3].

Since this research is mainly focused on LiNbO$_3$, various properties of bulk LiNbO$_3$ will be discussed in more detail in the following section.

2.8 Lithium niobate

Lithium niobate, first reported in 1949 by Matthias and Remeika [16] to be ferroelectric, is one of the most important and useful polar materials and has found many applications in the area of optoelectronics due to its excellent electrooptic, acoustooptic, and nonlinear optic properties. There are, to date, nearly six thousand literature references and a major book [17] on the subject of lithium niobate, therefore, only the properties related to this research will be summarized here.
2.8.1 Crystal structure

Crystal growth of lithium niobate by Czochralski pulling method was reported by Ballman [18] in 1965. The detailed structure was determined by S. C. Abrahams et al. in a series of papers [19, 20, 21] in 1966. Although LiNbO₃ does not have the perovskite structure [7], it is ABO₃ where A is a lower (mono- or di-) and B a higher (tetra- or penta-) valancy cation and O is oxygen. A perfect perovskite structure is shown in Fig. 2.3 in which the body-centered B cation is surrounded by an octahedra formed by the face-centered oxygen ions, and the A cations occupy the corners of the cubic structure. Below the Curie temperature, the perovskite structure is slightly deformed. In BaTiO₃, for example, the Ba²⁺ and Ti⁴⁺ are displaced relative to the O²⁻ ions, thereby developing the dipole moment. LiNbO₃ have a space group
Figure 2.4  A unit cell of LiNbO$_3$ structure with space group $R3_c$ viewed down the polar axis.

$R3_c$ (point group $3m$, and in LiNbO$_3$ the oxygens are arranged in nearly hexagonal close-packed (HCP) planar sheet as shown in Fig. 2.4 [19, 20, 21]. The unit cell is rhombohedral (trigonal, a=$5.4944$ Å, $\alpha=55^\circ52'$) with two formula units per unit cell. The hexagonal cell ($a_H=5.1483$ Å, $c_H=13.8631$ Å, and $c/a=2.693$) has six formula units per unit cell [19, 20, 21, 22, 23]. The stacking sequence of cations in these octahedral sites is: Nb, Li, vacancy, Nb, Li, vacancy, and so on. The distance of the Li$^+$ ion from the nearest oxygen plane in the ferroelectric phase is 0.37 Å. The asymmetry of the lattice structure makes LiNbO$_3$ a polar material. As is illustrated in Fig. 2.5, the oxygens are expressed in terms of oxygen triangles and oxygen cages. To reverse the orientation of the polarization, the Li$^+$ ions have to be displaced to the other side of its nearest oxygen triangle, while the Nb$^{5+}$ ions can only move within the oxygen cages. The two stable positions (before and after reversal) define the two possible directions of the spontaneous polarization, thereby defining LiNbO$_3$ a one-dimensional ferroelectric.
At the Curie temperature of 1210°C [22], LiNbO₃ undergoes a structural phase transition from $R3_c$ (ferroelectric) to $R3$ (paraelectric). In its paraelectric phase (above the Curie temperature) the Li⁺ ions on average shift into their nearest oxygen plane while the Nb⁵⁺ ions go to the centers of the surrounding oxygen octahedra. The symmetry of the lattice structure in the paraelectric phase cancels the dipole moment, thus the spontaneous polarization drops to zero.

The density of LiNbO₃ is dependent on the Li content of the crystal. Abrahams and Marsh [24] reported the density in a congruent LiNbO₃ crystal (48.45 mole % Li₂O) to be 4.648 g/cm³ and that in a stoichiometric LiNbO₃ crystal to be 4.635 g/cm³.
Powder x-ray diffraction data of LiNbO$_3$ from $2\theta = 20^\circ$ to $90^\circ$ are tabulated in Table 2.2.

<table>
<thead>
<tr>
<th>$2\theta$ (deg)</th>
<th>(hkl)</th>
<th>I/I$_{\text{max}}$</th>
<th>$2\theta$ (deg)</th>
<th>(hkl)</th>
<th>I/I$_{\text{max}}$</th>
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<tr>
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<td>(125)</td>
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<tr>
<td>68.59</td>
<td>(208)</td>
<td>4</td>
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</tr>
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</table>

### 2.8.2 The Li$_2$O-Nb$_2$O$_5$ system

A recent version of the phase diagram of the Li$_2$O-Nb$_2$O$_5$ system was reported by Svaasand et al. [25] and that near the existence region of LiNbO$_3$ is reproduced in Fig. 2.6. As illustrated in Fig. 2.6, LiNbO$_3$ itself has a fairly large solid-solution range from about 44 to 50.5 mole percent of Li$_2$O, while the area narrows down to a small portion of the diagram at low temperature. As Svaasand et al. reported, transparent LiNbO$_3$ turns into milk-white opalescent after annealing at 700 to 900°C for 170 hours.

In another area of the phase diagram, LiNbO$_3$ may coexist with either LiNb$_3$O$_8$ or Li$_3$NbO$_4$. Ternary lithium niobium oxide (LiNb$_3$O$_8$) belongs to the $P2_1/c$ space...
Figure 2.6  Phase diagram in the existence region of LiNbO$_3$ [25].

group and is monoclinic (a=7.46 Å, b=5.03 Å, c=15.27 Å, and $\beta=107.4^\circ$) and centrosymmetric [26, 27], while lithium orthoniobate (Li$_3$NbO$_4$) has the $I23$ space group in its high temperature phase and the $Fm\bar{3}m$ space group in its low temperature phase such that both phases are centrosymmetric. The lattice structure of Li$_3$NbO$_4$ is cubic and the lattice constant $a=8.43$ Å[28]. Both of Li$_3$NbO$_4$ and LiNb$_3$O$_8$ are

<table>
<thead>
<tr>
<th>$2\theta$ (deg)</th>
<th>(hkl)</th>
<th>I/I$_{max}$</th>
<th>$2\theta$ (deg)</th>
<th>(hkl)</th>
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<td>(611), (532)</td>
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<td>(332)</td>
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<td>74.75</td>
<td>(541)</td>
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</table>
Table 2.4  Powder x-ray diffraction of LiNb<sub>3</sub>O<sub>8</sub>. s=strong, m=medium, w=weak, and vw=very weak.

<table>
<thead>
<tr>
<th>2θ (deg)</th>
<th>(hkl)</th>
<th>I/I&lt;sub&gt;max&lt;/sub&gt;</th>
<th>2θ (deg)</th>
<th>(hkl)</th>
<th>I/I&lt;sub&gt;max&lt;/sub&gt;</th>
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<td>s</td>
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</tr>
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<td>w</td>
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<td>30.77</td>
<td>(210)</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

not ferroelectric, hence, care must be taken to grow LiNbO<sub>3</sub> at low temperature since slight deviations can form either Li<sub>3</sub>NbO<sub>4</sub> or LiNbO<sub>3</sub> which will then degrade the ferroelectric properties of LiNbO<sub>3</sub>. The mass density of Li<sub>3</sub>NbO<sub>4</sub> is 3.8 g/cm<sup>3</sup>, and that of LiNbO<sub>3</sub> is 5.03 g/cm<sup>3</sup>. Powder x-ray diffraction data of Li<sub>3</sub>NbO<sub>4</sub> and LiNbO<sub>3</sub> are tabulated in Tables 2.4 and 2.3.

2.8.3 Chemical etching

For better observation of the grain boundaries in the SEM work, it is usually necessary to chemically etch the sample. LiNbO<sub>3</sub> is fairly chemically inert at room temperature. Nassau et al. [29] reported that single crystal LiNbO<sub>3</sub> can be etched by a boiling (110°C) solution of a mixture of one part HF and two parts HNO<sub>3</sub>. However, if the combination is used to etch a thin film sample make by the process of metallo-organic decomposition, the LiNbO<sub>3</sub> thin film peels off from the substrates after a few minutes
[30]. Vest et al. then determined that etching with 20% of the solution for six hours at room temperature had the best results for revealing grain structure in LiNbO₃ thin films [30].

2.8.4 Thermal expansion

For epitaxial growth of thin films thermal expansion data have been shown to be very useful for understanding the structural distortions of the lattices. Due to the symmetry of point group $\text{3m}$ there are two linear coefficients of thermal expansion: $\alpha_{11}$ describing the longitudinal effect in the $xy$ plane and $\alpha_{33}$ describing that in the $z$ direction. Kim and Smith [31] analyzed their experiment data by a power expansion

$$\frac{\Delta l}{l_R} = \alpha(T - T_R) + \beta(T - T_R)^2,$$

(2.10)

where $l_R$ is the length of the sample at 25°C and $T_R$ is the reference temperature of 25°C. The thermal expansion coefficients for LiNbO₃ are $\alpha_{11} = 15.0 \times 10^{-6}, \alpha_{33} = 7.5 \times 10^{-6}, \beta_{11} = 5.5 \times 10^{-9}$, and $\beta_{33} = -7.7 \times 10^{-9}$.

2.8.5 Dielectric constant

For making a computer memory, the dielectric constant of the thin film material is always the major concern. According to the axial symmetry of LiNbO₃, the dielectric permittivity tensor has only two independent elements as shown in Eq. 2.7. The low frequency dielectric constant arc about $\epsilon_{r,11} = 30$ and $\epsilon_{r,33} = 80$ [11]. Mitsuyu and Wasa [32] in 1981 and Kitabatake et al. [33] in 1984 measured the dielectric properties of amorphous LiNbO₃ thin film prepared by the sputtering technique. Their curve of dielectric constant vs. temperature is reproduced in Fig. 2.7.
2.8.6 Optical properties

Excellent optical properties and a large electrooptic effect have been the most attractive part of LiNbO$_3$ to optoelectronic engineers. Single crystal LiNbO$_3$ is a clear material. It is transparent from about 0.35 $\mu$m to about 5 $\mu$m where absorption due to lattice vibrations sets in.

Redfield and Burke [34] have studied the band edge absorption of pure LiNbO$_3$. They measured both congruent and stoichiometric materials and found that the stoichiometric material has a bandgap 0.1 eV higher than the congruent material. Fig. 2.5, as determined by Redfield and Burke, shows the temperature dependence of the absorption edge of congruent LiNbO$_3$. The edge is fairly broad and curved, which may be due to the large number of defects introduced by the deviation from the stoichiometric composition.
Figure 2.8  Temperature dependence of the absorption edge of congruent LiNbO₃ [34].

LiNbO₃ is a uniaxial crystal and exhibits birefringence which is characterized by an ordinary refractive index $n_o$ and an extraordinary refractive index $n_e$. Boyd et al. [35] first measured the wavelength dependence of the refractive indices of LiNbO₃. They demonstrated the nonlinear optical properties of LiNbO₃, which showed phase matching for second harmonic generation in the visible and near infrared is allowed by the large value of negative birefringence ($n_e - n_o \simeq -0.08$). This discovery has stimulated extensive studies on the refractive indices of LiNbO₃. Hobden and Warner [36] reported in 1966 the measurement of the refractive indices at temperatures between $19^\circ C$ and $374^\circ C$ and for wavelengths between 447 nm and 707 nm. They derived, from their data, two Sellmeier equations for $n_o$ and $n_e$:

$$n_o^2 = 4.9130 + \frac{1.173 \times 10^5 + 1.65 \times 10^{-2}T^2}{\lambda^2 - (2.12 \times 10^2 + 2.7 \times 10^{-5}T^2)^2} - 2.78 \times 10^{-8} \lambda^2$$  \hspace{1cm} (2.11)$$

and

$$n_e^2 = 4.5567 + 2.605 \times 10^{-7}T^2 + \frac{0.970 \times 10^2 + 2.70 \times 10^{-2}T^2}{\lambda^2 - (2.01 \times 10^2 + 5.4 \times 10^{-5}T^2)^2} - 2.24 \times 10^{-8} \lambda^2,$$
where $T$ is in degrees Kelvin and $\lambda$ is in nm. In general, $n_o = 2.289$ and $n_e = 2.201$ are used as the bulk values at 633 nm.

The refractive indices of LiNbO$_3$ may change if different composition of crystal is used. Bergman et al. [37] showed that the extraordinary index can change as much as $\Delta n \simeq 0.03$ with varying Li/Nb ratio while the ordinary index is almost independent on the composition.

2.8.7 Electrooptic effect

As a result having no inversion center in the crystal structure, LiNbO$_3$ exhibits a linear electrooptic effect [5, 13]. A rank three electrooptic tensor is used to describe the effect of the applied electric field on the two-dimensional index ellipsoid. The index ellipsoid can be expressed in a form given by

$$b_{11}x^2 + b_{22}y^2 + b_{33}z^2 + 2b_{23}yz + 2b_{13}xz + 2b_{12}xy = 1,$$  \hspace{1cm} (2.12)

where $b_{ij} = (n_{ij}^2)^{-1}$. The electrooptic tensor components are defined by

$$\Delta b_{ij} = r_{ijk}E_k,$$  \hspace{1cm} (2.13)

where $E_k$ are the components of the applied electric field. To simplify the notation, let's introduce the contracted indices: $(11) \rightarrow 1$, $(22) \rightarrow 2$, $(33) \rightarrow 3$, $(23) \rightarrow 4$, $(13) \rightarrow 5$, $(12) \rightarrow 6$. Eq. 2.13 can then be rewritten by

$$\Delta b_i = r_{ij}E_j = \sum_{j=1}^{3} r_{ij}E_j, \hspace{1cm} i = 1, 2, ..., 6,$$  \hspace{1cm} (2.14)

or

$$(\Delta n)_i = -\frac{n^3}{2} \sum_{j=1}^{3} r_{ij}E_j.$$  \hspace{1cm} (2.15)

Since LiNbO$_3$ belongs to point group $3m$, the number of independent coefficients can be reduced to four. The simplified $6 \times 3$ electrooptic tensor is given by
\[
\begin{pmatrix}
0 & -r_{22} & r_{13} \\
0 & r_{22} & r_{13} \\
0 & 0 & r_{33} \\
0 & r_{51} & 0 \\
r_{51} & 0 & 0 \\
-r_{22} & 0 & 0
\end{pmatrix}
\]

By inserting \( r_{ij} \), the six values of \( \Delta n \) can be written as the elements of a \( 3 \times 3 \) matrix:

\[
\Delta n_i = \frac{-n^3}{2} \begin{pmatrix}
-r_{22}E_y + r_{13}E_z & -r_{22}E_x & r_{51}E_x \\
-r_{22}E_x & r_{22}E_y + r_{13}E_z & r_{51}E_y \\
r_{51}E_x & r_{51}E_y & r_{33}E_z
\end{pmatrix}
\]

Use of the diagonal components 11,22, and 33 of the matrix results in an index and phase change for an incident optical wave polarized along the crystallographic \( x, y, \) and \( z \) axis, respectively. These diagonal components induce an index change, essential for modulators, for the optical wave polarized along the crystallographic \( j \) axis given an electric field applied in the appropriate direction. For instance, applying an electric field along \( E_z \), \( E_3 \), will induce an index change (to the extraordinary, \( j = 3 \))

\[
\Delta n_{33} = -\frac{n^3}{2}r_{33}E_z.
\]

Therefore, the electrode orientation depends on the orientation of the waveguide crystal used. The orientation is commonly specified by Miller indices or by the "cut" - the direction normal to the flat surface of the waveguide.

The electroo optic coefficients measured under constant strain, \( r_{ij}^S \) (high frequency, clamped), and under constant stress, \( r_{ij}^T \) (low frequency, free), have to be carefully distinguished since there is a large contribution of the photoelastic effect due to the strain induced by the converse piezoelectric effect. In 1966, Bernal et al. [38]
reported the low-frequency electrooptic coefficients and Turner [39] published the high-frequency coefficients. These data of \( r_{ij} \) are collected in Table 2.5, and they were measured at the He-Ne laser wavelength (6328 Å) and at room temperature or at 100°C.

<table>
<thead>
<tr>
<th>Table 2.5</th>
<th>Electrooptic coefficients of LiNbO₃, in units of 10⁻¹² m/V, measured at ( \lambda = 6328\text{Å} ).</th>
</tr>
</thead>
<tbody>
<tr>
<td>High freq.</td>
<td>( r_{33}^S )  ( r_{13}^S )  ( r_{22}^S )  ( r_{51}^S )</td>
</tr>
<tr>
<td>(25°C)</td>
<td>30.8     8.6     3.4     28</td>
</tr>
<tr>
<td>Low freq.</td>
<td>( r_{33}^T )  ( r_{13}^T )  ( r_{22}^T )  ( r_{51}^T )</td>
</tr>
<tr>
<td>(100°C)</td>
<td>32.2     10.0    6.8     32.6</td>
</tr>
</tbody>
</table>

2.8.8 Photorefractive effect

The photorefractive effect [40], as it is named, is the phenomenon that the refractive index change of a material is induced by irradiation. It was originally termed as optical damage because it was first observed by Ashkin et al. [14] as an undesirable light-scattering and decollimation of laser wave front in LiNbO₃ crystal in the blue and green region of the spectrum. However, this is neither a permanent damage of the optical material nor a irreversible change of the refractive index. The "damage" can be recovered by sufficiently intense homogeneous illumination or by heating the crystal to a certain temperature, depending on doping. This writability and erasability of LiNbO₃ make it possible to be used for information storage [1].

The process of the photorefractive effect can be considered in three steps: optical excitation, subsequent carrier transport, and retrapping of carriers at new sites. The optical excitation may be attributed either to a single photon effect or to a multiphoton absorption. The holographic intensity pattern produced by the photo-excited
space charges subsequently generates electric field that change the refractive index of the crystal via the electrooptic effect. The volume phase hologram may be erased by applying a strong homogeneous irradiation. The hologram provides an efficient way for storage of information with a theoretical limit of $10^{12}$ bits/cm$^3$ and a practical limit of $10^{10}$ bits/cm$^3$ [2].

2.8.9 Electrical properties

LiNbO$_3$ is an insulator at room temperature and has a resistivity of about $10^{18}$ $\Omega$·cm [41]. The dark conductivity of undoped LiNbO$_3$ is only about $10^{-17}(\Omega - cm)^{-1}$ [42]. The carrier transport is rather complicated being a combination of electronic and ionic conduction [43, 44, 45] The band structure of LiNbO$_3$ was calculated by Kam et al. in 1978 [46], and the smallest valence band-conduction band gap was given to be 3.47 eV which is in good agreement with the commonly accepted experimental value of 3.72 eV determined by Clark et al. [47]. The spontaneous polarization in LiNbO$_3$ was experimentally determined to be 71 $\mu$C/cm$^2$ by Wemple et al. [48] and was calculated to be 97 $\mu$C/cm$^2$ by Kam et al.
Chapter 3

Deposition of Ferroelectric Thin Films

3.1 Deposition techniques

The selection of an appropriate method for depositing ferroelectric thin films depends on the applications of the films. The application of thin films to optical devices poses much more stringent requirements on the properties and perfection of the thin films. Since the 1970’s, LiNbO₃ has been considered as an excellent optical material, and thus large effort has devoted to LiNbO₃ based integrated optical devices. High optical quality LiNbO₃ thin films have been successfully prepared in the past years using a variety of deposition techniques including epitaxial growth by melting (EGM) [49, 50], chemical vapor deposition (CVD) [51], liquid phase epitaxy (LPE) [52, 53, 54, 55], thermal out-diffusion of Li₂O from LiNbO₃ [56], in-diffusion of a dopant, almost exclusively titanium, into LiNbO₃ [56, 57, 58], proton exchange [59, 60, 61, 62, 63], ion implantation [64], sputtering [32, 33, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77], molecular beam epitaxy (MBE) [78], sol-gel [79, 80], metallo-organic decomposition (MOD) [30, 107], and ion plating [81]. More recently, ion-beam sputtering [82, 83], laser ablation [84, 85, 86], and jet vapor deposition [87] have been used for depositing high quality ferroelectric films, but LiNbO₃ films prepared by these methods have not yet been reported.

The idea of integrating ferroelectric and semiconductor materials together was first explored in the 1960’s. Combining of the unique properties of ferroelectrics (non-
volatile memory, electrooptic modulation, piezo- and pyro-electric sensing) with the powerful properties of integrated circuit semiconductor chips (microminiaturization, dynamic memory, and random accessing of a matrix array) will make the chips much more versatile. To implement the ferroelectric semiconductor devices, we can either deposit a thin film semiconductor on a bulk ferroelectric or deposit a thin film ferroelectric on a bulk semiconductor substrate. Early studies of the first structure proved the thin film semiconductor-bulk ferroelectric devices to be electrically unstable [89]. The retention problem results in a loss of memory in the device. Therefore, this research has been focusing on the second type of devices (thin film ferroelectric-bulk semiconductor).

To deposit a ferroelectric LiNbO$_3$ thin film on a semiconductor integrated circuit, not all of the previously described deposition methods are applicable. High temperature processes, in particular, have to be avoided to prevent the deformation of the p-n junctions. The methods such as EGM, CVD, LPE, and MBE are thus excluded because a temperature in excess of 900°C has to be used in these processes. Other methods such as ion implantation, proton exchange, in- and out-diffusion that need to start with a single crystal LiNbO$_3$ substrate are also not considered, although Ti:LiNbO$_3$ waveguides can have propagation losses as low as 0.03 dB/cm [90]. Films deposited by laser ablation are relatively inhomogeneous both in composition and in properties, however, Buhay et al. have recently developed a simple deposition configuration without laser beam scanning and have achieved spatial thickness uniformity over an area with approximately three inches diameter [85]. If the cost of processing by laser ablation can be further reduced, it seems to be a promising technique in the future. Neither electrical nor optical properties of the LiNbO$_3$ films deposited by the ion plating method have been reported although the method seems promising in
making epitaxial films. The jet vapor deposition has the advantages of low cost and high speed, however, the reproducibility is not as good as other processes. Among the rest of the deposition techniques, sol-gel is considered to be very promising and is currently attracting much attention. The MOD process, which is similar to the sol-gel method except there is no formation of a gel, has been relatively less investigated, and will be discussed here. In 1991, Ramtron put the first 256K non-volatile ferroelectric RAM chip on the market [88], in which the ferroelectric films were deposited by rf sputtering. This verifies that rf sputtering still possesses great potential for fabricating high quality ferroelectric films. We have successfully made LiNbO₃ thin film optical waveguides on sapphire substrates using rf sputtering [76, 77], and other waveguide devices made by the same technique will be examined in this study.

3.2 Magnetron rf sputtering

3.2.1 Sputtering physics

Magnetron rf sputter deposition was employed to grow LiNbO₃ films. Detail description of the basic sputtering system used in this lab was given by R. C. Baumann [91]. The system was then modified to operate with a magnetron cathode and an automatic matching network by T. A. Rost [3]. The configuration of the system essentially remained unchanged afterward except the teflon coats of all the wires in the chamber were replaced by ceramic tubes for eliminating fluorine contamination.

Sputtering is a process that may be defined as the ejection of atoms or molecules from a target material by the bombardment with energetic gas ions. The ejected atoms or molecules are allowed to impinge on a nearby substrate, thus gradually building up a thin film layer on the surface of the substrate. Since sputtering is, in
nature, a physical process not a chemical process, it is suitable to grow a wide range of elements and compounds, independent of the individual element melting point and vapor pressure. However, sputtering yield may vary with different target composition, i.e., it is not guaranteed that the sputtered film will have the same composition as the target does. A powder target, instead of the traditional single crystal or hot pressed target, was used to allow for investigating different target compositions very easily. This was possible because of the sputter up geometry. It should be noted that the gas content is also an important parameter that affects the film properties.

The magnetron rf sputtering system is enclosed in a vacuum, which is normally pumped to below $10^{-6}$ Torr before introducing flowing gases and raised to the 1 to 10 mTorr range by introducing gases. A commonly used bombarding gas is argon, which is ionized by the electrons between the target electrode (cathode) and the substrate electrode (anode). As soon as the electrons have sufficient energy to ionize argon gas, a glow discharge (plasma) is initiated. In addition to argon, oxygen gas is used during sputtering to help oxidization of the ejected atoms or molecules and thus form an oxide compound with a desired composition, such as LiNbO$_3$, on the substrate.

Once depositing on the surface of the substrate, the target molecules are not simply "fixed" on a position. They can either atomically diffuse (the Gibbs-Thomson effect) or move as an entity (Brownion motion) along the substrate provided that they are not re-evaporated from the surface. The moving molecules will occasionally collide with other moving one and bind together, thereby forming a larger cluster. This is the so-called nucleation stage of thin film growth. As this process goes on, a continuous layer will eventually result.
3.2.2 Epitaxial growth

If the sputtering process is carefully controlled, epitaxy, i.e., oriented overgrowth of one crystal on another, is possible. Different materials have different bonding force such that the adhesion energy varies with different film-substrate combinations. Epitaxial growth can thus be classified into three different modes, namely, the modes of Volmer-Weber, Frand-Van der Merwe, and Stranski-Krastanov, [92] as shown schematically in Fig. 3.1.

In the Volmer-Weaver growth mode (Fig. 3.1(a)), small clusters are nucleated on the substrate surface and then aggregates into larger islands or crystallites, which coalesce eventually forming a continuous layer. This mode occurs when the depositing molecules are more strongly bound to each other than to the foreign substrate, thus corresponding to a weak adhesion of crystallites with the substrate. For example, semiconductors on insulators, both single-crystalline (e.g., sapphire, SiO$_2$, CaF$_2$) and amorphous (e.g., oxidized silicon, fused quartz, Si$_3$N$_4$), are related to this mode.

In the Frand-Van der Merwe growth mode (Fig. 3.1(b)), the depositing molecules are more strongly bound to the substrate than to each other, i.e., they condense onto the substrate surface monolayer by monolayer. For instance, pairs of isostructural
metals (e.g., Au/Ag, Pd/Au, Co/Cu) and some semiconductors (e.g., PbSe/PnS) belong to this case.

The Stranski-Krstanov growth mode (Fig. 3.1(c)) is an intermediate case. After the first few monolayers are formed, subsequent layer growth is not favorable, and islands are formed on top of the layer. This case happens in some metal-metal and metal-semiconductor systems [93].

In this research, only deposition of insulators onto insulators, semiconductors, or metals was concerned. Therefore, the Volmer-Weber (island) growth mode will be assumed in all cases.

In 1969, Dister and Vlasov [94] first reported that no orientation is observed at early stages of deposition, but appears when the deposit accumulates to a certain thickness. Puskeppel and Harsdorff [95], in 1976, found that the degree of epitaxial order is continuously improved with increasing thickness. These observations were confirmed by other researchers [96, 97]. These results strongly suggest that oriented growth is a postnucleation effect caused most possibly by mobility of crystallites on substrate surface. Having this idea in mind, Chadderton and Anderson [98] proposed the "pulse and anneal" technique to obtain a perfect epitaxial film, and Reiss [99] proposed a model that stated that the larger the crystallites (up to a certain size), the more possibly that they will align with the substrate lattice.

3.2.3 Three-stage sputtering

Although the real mechanisms leading to improvement of epitaxy are still unclear, the above concepts were utilized to modify the sputtering process. The substrate was first heated to 500°C, and a relatively high rf power (125-200 W) was used for 2 to 10 minutes to deposit large islands on the substrate. The high concentration
of crystallites favored early coalescence, and epitaxy was eventually improved while the crystallites were getting larger. At this first stage, the size of islands is expected to range from 50 to 150 Å. The deposition is then terminated before a continuous layer is formed. Since the islands produced at this stage were probably not oriented, an annealing temperature of 550-600°C was then applied for 1 hour to supply more energy to enhance mobility of the islands (crystallites), thereby allowing them to take an oriented position (minimum energy position) aligning with the substrate lattice. After the annealing stage, a very slow rate (50-75 W) was then used at the third stage both to fill any "holes" in the "discontinuous" film that occurred during rapid deposition and to provide a highly smooth film surface that satisfied the requirement for optical waveguide. Post-annealing was sometimes used to further improve the crystallinity and orientation.

3.2.4 Sputtered LiNbO₃ thin films

A variety of commercially available substrates, namely, (111) Si, (111)Pt/Si, SiO₂/(100)Si, and (012), (001), (100) and (110) sapphire substrates have been used to deposit LiNbO₃ films by magnetron rf sputtering. The substrate cleaning procedures were listed as follows:

1. The substrate was first placed in a solution of NH₄OH-H₂O₂-H₂O (1:1:5) at 80°C for 15 minutes, then in a deionized (DI) water bath at room temperature for 5 minutes, to remove metallic and organic residue.

2. If a bare silicon wafer was used, it was put into a dilute HF solution (1/50) at room temperature for 30 seconds to get rid of the native coating of silicon dioxide, then DI water bath for 5 minutes.
3. A HCl and H₂O₂ (1:1) solution at 80°C was used (1 min) to remove ionic contaminants, then DI water bath for 5 minutes.

4. The wafer was finally cleaned in methonal with an ultrasonic cleaner for 10 minutes followed by rinsing in DI water for 15 minutes.

5. The wafer was dried by a spinner (5000rpm, 1 min), then baked in a vacuum oven maintained at 120°C for 30 minutes.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Optimized parameters for depositing LiNbO₃ on Si substrate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target composition</td>
<td>99.99995% LiNbO₃ powder</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>Ar/O₂ (60%:40%)</td>
</tr>
<tr>
<td>Target-substrate spacing</td>
<td>5 cm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>600°C</td>
</tr>
<tr>
<td>Forward rf power</td>
<td>100 W</td>
</tr>
<tr>
<td>Reflected rf power</td>
<td>0 W</td>
</tr>
<tr>
<td>Sputtering pressure</td>
<td>2.3 mTorr</td>
</tr>
<tr>
<td>Growth rate</td>
<td>900 Å/hr</td>
</tr>
</tbody>
</table>

To optimize the sputtering process and to study the physical and electric properties of the sputtered LiNbO₃ thin films on semiconductors, (111) silicon substrates were used. Optimal sputtering parameters for depositing LiNbO₃ on Si substrates were determined by Rost [3] and are tabulated in Table 3.1. Bragg x-ray diffraction (XRD)* pattern of a LiNbO₃ thin film sputtered on a (111) Si substrate is shown in

*All of the XRD experiments, except the powder samples, were done using the x-ray diffractometer located in Geophysics Dept. at Rice University. The x-ray diffractometer consists of a Phillips Electronics Type 12045/3 x-ray generator fitted with a copper r-ray tube, an x-ray detector, and an x-ray goniometer equipped with a stepper motor. A computer was used to control the x-ray diffractometer and to analyze the detected data. A voltage of 35 kV and a current of 20 mA were used to excite radiation from the x-ray tube. A nickel filter was placed to absorb copper K₂ radiation and thus create a nearly monochromatic Cu Kα radiation with a wavelength of 1.5418 Å. The pulse height analyzer baseline was set to 1.0 V to reduce electronic noise.
Figure 3.2  XRD pattern of a sputtered thin film LiNbO₃/(111)Si.

Fig. 3.2. Only one LiNbO₃ diffraction peak, the (006), is observed. Since the axis normal to the LiNbO₃ (006) plane and that to the silicon (111) plane both possess three-fold rotational symmetry, film growth with this orientation is preferred. The film is thus considered to be highly oriented polycrystalline with its polar axis normal to the film plane. This orientation is particularly desired in the study of electrical switching in a metal-ferroelectric-semiconductor (MFS) structure. Note that a substrate temperature of 500°C has been used to sputter LiNbO₃ thin films on (111) silicon substrates, and good quality highly oriented films were able to grow under this lower temperature. The Ar/O₂ gas ratio of 60/40 is recommended for growing stoichiometric LiNbO₃ films on (111) Si substrate. Increasing the oxygen content to 50% or higher can produce Li₃NbO₄ coexisting with LiNbO₃, while decreasing the oxygen content to 30% or lower can cause the formation of LiNb₃O₈. The forma-
Figure 3.3  XRD pattern of a sputtered thin film LiNbO$_3$/(111)Pt/Si.

tion of either Li$_3$NbO$_4$ or LiNb$_2$O$_8$ should be avoid because they tend to degrade the ferroelectricity of LiNbO$_3$ films.

If a SiO$_2$ layer exists in a MFS structure, it will make electrical switching of spontaneous polarization more difficult because an extra electric field is needed to compensate the space charge within the oxide. However, a very thin (∼ 20-50 Å) amorphous SiO$_2$ layer was observed, via a high resolution transmission electronic micrograph, on the surface of the Si substrate, although a dilute solution of HF had been used to remove the native oxide layer. Since oxygen gas has been introduced into the vacuum chamber during pre-sputtering (normally 30 minutes), a thin oxide layer could have grown before sputtering, which seems unavoidable. Another type of substrate, (111)Pt/Si, was used to circumvent this problem. The evaporated Pt layer has an orientation of (111) and a thickness of about 1000 Å. The XRD pattern of a thin film LiNbO$_3$ sputtered on (111)Pt/Si is shown in Fig. 3.3. Substrate temperatures
in excess of 550°C were found to cause oxidation in the Pt layer, thus a substrate temperature of 500°C was recommended to use for depositing LiNbO$_3$ on Pt/Si. Other parameters were the same as in Table 3.1. Similarly, a preferred (006) orientation in LiNbO$_3$ thin film was found in this case although the film was slightly randomly oriented due to large lattice mismatch.

Highly oriented LiNbO$_3$ thin film optical waveguides have been sputtered on (100) Si substrates with a SiO$_2$ buffer layer ranging from 0.5 to 2.5 μm. Sputtering gas ratio (Ar/O$_2$) of 60/40 and a rf power of 50 W were utilized to deposit LiNbO$_3$ on SiO$_2$. Fig. 3.4 shows the XRD pattern of a thin film LiNbO$_3$ on a 2.5μmSiO$_2$/(100)Si deposited with a substrate temperature of 550°C. The as-sputtered film has a preferred (104) orientation although most of those sputtered with a higher rf power or at a lower substrate temperature were found to be randomly oriented. The broad feature at 2θ ~ 34° is due to the amorphous nature of the SiO$_2$ buffer layer.

![Graph](image_url)

**Figure 3.4** XRD pattern of a thin film LiNbO$_3$ sputtered on SiO$_2$/Si.
Figure 3.5  XRD pattern of a bare (100) (M-cut) sapphire wafer.

The optimized sputtering parameters for growing LiNbO$_3$ thin films on (111) Si were tried to grow LiNbO$_3$ optical waveguides on (100) sapphire substrates. However, the films turned out to be randomly oriented as shown in Fig. 3.6, and Li$_3$NbO$_4$ (211), (330), and (440) peaks accompanied with LiNbO$_3$ (012), (014), (110), and (300) peaks were observed, which means that the optimal condition for growing highly oriented LiNbO$_3$ films on (111) Si is no longer the case if the substrate is replaced to sapphire. A small matrix of sample was studied to optimize the sputtering conditions for epitaxial growth of LiNbO$_3$ films on (100) sapphire disks. Firstly, the rf power was reduced to 75 W, which totally eliminated the (211) peak of Li$_3$NbO$_4$ as shown in Fig. 3.7. The existence of the (330) and (440) peaks of Li$_3$NbO$_4$ suggests that Li$_3$NbO$_4$ is oriented in an epitaxial direction while LiNbO$_3$ is still slightly randomly oriented although the (012) and (104) peaks were highly suppressed by the preferred (300) peak.
Figure 3.6  XRD pattern of a sputtered (Ar/O$_2$=60/40, 100W) LiNbO$_3$ on (100)Al$_2$O$_3$.

To prevent from forming Li$_3$NbO$_4$, oxygen gas content was decreased to Ar/O$_2$=65/35 and 70/30 as shown in Figs. 3.8, 3.9, and 3.10. Reducing the oxygen concentration did exclude the formation of the undesired Li$_3$NbO$_4$ phase, yet, the LiNbO$_3$ film was still not perfectly epitaxial. The rf power was then further decreased to 50 W to slow down the deposition rate. By doing this, the optimal conditions were found, and an epitaxial LiNbO$_3$ film was successfully grown on (100) sapphire as shown in Fig. 3.11. The (300) peak is the only peak of reflection from LiNbO$_3$ in the XRD pattern, which indicates that the c axis of the LiNbO$_3$ film is highly oriented in the plane of the surface.

Post-annealing in air at 600°C has been used to improve the crystallinity of the assputtered LiNbO$_3$ films. The result is obvious by comparing Fig. 3.12 with Fig. 3.11.
Figure 3.7  XRD pattern of a sputtered (Ar/O₂=60/40, 75W) LiNbO₃ on (100)Al₂O₃.

Post-annealing was normally done in a conventional furnace (Lindberg Mark IV) which could provide a temperature range from room temperature to 800°C.

The results of the matrix of experiments to examine the optimal conditions for epitaxial growth of LiNbO₃ on (100) sapphire are tabulated in Table 3.2. Since LiNbO₃ is chemically very stable, while Li₃NbO₄ is soluble in H₂O₂, each of the films in the matrix was etched in a solution of 30% H₂O₂ solution at room temperature for 3 hours. The results of H₂O₂ etching are given in the last column of Table 3.2. A "yes" in the column menas that the film was either partly or totally removed from the substrate in the solution after 5 hours. A "no" means that the film was barely slightly etched or no sign of being etched was observed under a 400X optical microscope. The results of etching correlate with the XRD data. In particular, a pure and epitaxial LiNbO₃ film was very hard to etch in H₂O₂. Note that the (300) peak
**Figure 3.8** XRD pattern of a sputtered 
\((\text{Ar}/\text{O}_2=65/35, 75\text{W})\) \(\text{LiNbO}_3\) on \((100)\text{Al}_2\text{O}_3\).

of \(\text{LiNbO}_3\) is located at \(2\theta = 62.46^\circ\), while the \((440)\) peak of \(\text{Li}_3\text{NbO}_4\) is at \(62.32^\circ\). Moreover, because of lattice mismatch at the substrate-film interface, the distorted lattice has a shrunk \(c\) axis, and thus a stretched \(a\) axis which corresponds to a smaller Bragg angle \(\theta\). It is almost impossible to distinguish these two peaks in an XRD pattern. \(\text{H}_2\text{O}_2\) etching thus provides an easy way in aid of x-ray diffraction analysis for \(\text{LiNbO}_3\) identification. Also, if the peak is the \((440)\) reflection of \(\text{Li}_3\text{NbO}_4\), a \((330)\) peak at \(45.58^\circ\) should be observed as well. This is another place to check if \(\text{Li}_3\text{NbO}_4\) coexists with \(\text{LiNbO}_3\). Direct measurement of chemical composition of the as-sputtered epitaxial films via ion beam spectrometry, which will be discussed in next chapter, strongly shows that the films grown under the conditions in the last four rows of Table 3.2 are stoichiometric \(\text{LiNbO}_3\). The \(a\) axis of the \(\text{LiNbO}_3\) films
produced at 100, 75, or 50 W (Ar/O₂=70/30, T=500°C) was calculated, assuming a Hexagonal structure, by [100]
\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{3.1}
\]
where \(d\) is the distance between adjacent planes in the set (hkl), and \(a\) and \(c\) are the lattice constants. The value \(d\) can be calculated by the Bragg law \((n\lambda = 2d \sin \theta)\), where \(\lambda\) equals 1.5418 Å (Cu Kα radiation). The values of the \(a\) axis calculated from the XRD data are given in Table 3.3. The data of Tables 3.2 and 3.3 suggest that the crystallites did not have sufficient time to align with the substrate lattice if a high rf power, thus a fast deposition rate, was used, thereby having random orientations. Once the crystallites were randomly oriented, dislocations or defects could be easily created, which then released the interface stress due to lattice mismatch, and the lattice of the film was less distorted. On the other hand, if the film was epitaxial,
or highly oriented, there were less defects at the interface to release the stress, and hence the lattice of the film was more distorted.

Epitaxial LiNbO$_3$ films have been deposited via sputtering on (110) (A-cut) sapphire by other researchers [101] and in my previous work [76]. (110) sapphire substrates were thus used to study the three-stage sputtering process proposed in the last section. An XRD scan of an epitaxial LiNbO$_3$ film deposited on (110) sapphire using the three-stage sputtering is shown in Fig. 3.13. At the first stage (rapid deposition), the substrate was heated to 500°C, and a rf power of 125 W was used for 10 minutes to create large crystallites. The deposition time were carefully controlled such that a continuous layer had not yet been formed. The rf power was then turned off, and the sample was annealed at 580°C for 1 hour such that sufficient energy and time were given to allow for better lattice alignment of the crystallites. After
Figure 3.11 XRD pattern of a sputtered (Ar/O$_2$=70/30, 50W) LiNbO$_3$ on (100)Al$_2$O$_3$.

one hour, the substrate temperature was slowly decreased to 500°C with a cooling rate of 5°C/min. At the last stage (slow deposition), a rf power of 75 W was used to slowly fill up the vacancies between islands without resulting a significant stress at the interface and then to continue the film growth. As shown in Fig. 3.13, the only two reflection peaks, besides the sapphire (110) and (220) peaks, are LiNbO$_3$ (110) and its second harmonic, (220). The lattice constant $a_H$ was calculated to be 5.149 Å ($2\theta = 34.85^\circ$) which is in perfect agreement with the value of powder x-ray diffraction. For comparison, an XRD pattern of a bare (110) sapphire disk is shown in Fig. 3.14.

3.3 Metallo-organic decomposition process

3.3.1 Introduction
Figure 3.12 XRD pattern of a sputtered thin film LiNbO$_3$/(100)Al$_2$O$_3$. Rf power = 50 W, Ar/O$_2$=70/30, $T_{\text{substrate}} = 500^\circ$C, post-annealed at 600$^\circ$C in air for 5 hours, thickness = 200 nm.

The metallo-organic decomposition (MOD) process is a wet deposition technique for fabricating inorganic films without going through a gel step. The MOD process is attractive due to its simplicity of processing and suitability of mass production. Neither vacuum nor substrate-heating is needed. Any wet coating techniques available are useable for semiconductor processing. Moreover, inorganic films can be grown at a relatively low temperature although an annealing process is always used to ensure crystallization.

A flow chart of the mod process is shown in Fig. 3.15. The processing starts with individual metallo-organic compound solutions of desired elements. The solutions are mixed in the appropriate ratio to give the desired cation stoichiometry. Thermogravimetric analysis (TGA) is performed to study the thermal chemistry of the individual solutions as well as the mixed one. The mixed solution is deposited
Table 3.2  Matrix of deposition parameters for growing LiNbO$_3$ on (100) sapphire. Pure LiNbO$_3$ powder was used as target, substrate temperature was retained at 500°C, chamber pressure was about 5 mTorr, and gas flow rate was 25 sccm.

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>Ar/O$_2$</th>
<th>RF power</th>
<th>XRD peaks</th>
<th>Can H$_2$O$_2$ etch?</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10304</td>
<td>60/40</td>
<td>100 W</td>
<td>LiNbO$_3$: (012), (104), (110), (300) Li$_3$NbO$_4$: (211), (330), (440)</td>
<td>yes</td>
</tr>
<tr>
<td>S10313</td>
<td>60/40</td>
<td>75 W</td>
<td>LiNbO$_3$: (012), (104), (300) Li$_3$NbO$_4$: (330), (440)</td>
<td>yes</td>
</tr>
<tr>
<td>S10320</td>
<td>65/35</td>
<td>75 W</td>
<td>LiNbO$_3$: (012), (104), (116), (300) Li$_3$NbO$_4$: none</td>
<td>no</td>
</tr>
<tr>
<td>S10312</td>
<td>70/30</td>
<td>75 W</td>
<td>LiNbO$_3$: (012), (104), (300) Li$_3$NbO$_4$: none</td>
<td>no</td>
</tr>
<tr>
<td>S10308b</td>
<td>70/30</td>
<td>100 W</td>
<td>LiNbO$_3$: (012), (104), (202), (024), (116), (018), (300) Li$_3$NbO$_4$: none</td>
<td>no</td>
</tr>
<tr>
<td>S10308a</td>
<td>70/30</td>
<td>50 W</td>
<td>LiNbO$_3$: (300) Li$_3$NbO$_4$: none</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 3.3  The lattice constant $a_H$ of the LiNbO$_3$ films sputtered at different rf power (Ar/O$_2$=70/30, $T$=500°C).

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>RF power (W)</th>
<th>$2\theta$ (deg.)</th>
<th>$a_H$ (Å)</th>
<th>Distortion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10308b</td>
<td>100</td>
<td>62.45</td>
<td>5.15</td>
<td>0.05</td>
</tr>
<tr>
<td>S10312</td>
<td>75</td>
<td>62.35</td>
<td>5.16</td>
<td>0.19</td>
</tr>
<tr>
<td>S10308a</td>
<td>50</td>
<td>62.20</td>
<td>5.17</td>
<td>0.41</td>
</tr>
</tbody>
</table>

on a cold substrate to produce a wet film which is then pyrolyzed to evaporate the solvent and to decompose the metallo-organic compounds to form an inorganic film. The deposition and pyrolysis steps can be repeated as many times until the film is of the required thickness. Since the inorganic films heated at a low temperature are normally amorphous, they are often subjected to a further annealing process to control features such as oxygen stoichiometry, crystallinity, or preferred orientation.
Figure 3.13 XRD pattern of a three-stage (125 W for 10 min, annealing at 580°C for 1 hr, then 75 W for 2 hr.) sputtered thin film LiNbO₃ on (110)Al₂O₃. Ar/O₂=65/35, T = 500°C.

3.3.2 Metallo-organic compound precursors

The selection of metallo-organic systems, synthesis of compounds, and considerations of solvent are discussed in great detail by Vest et al. [30]. The precursor solutions used in this study were chosen following the criteria given by Vest.

Lithium neodecanoate was synthesized from lithium nethoxide and neodecanoic acid. Niobium tri-ethoxy-di-neodecanoate was similarly prepared from niobium ethoxide and neodecanoic acid. The synthesis reactions are as follows:

\[
\text{LiOCH}_3 + 2\text{C}_9\text{H}_{19}\text{COOH} \rightarrow \text{C}_9\text{H}_{19}\text{COOLi} + \text{CH}_3\text{OH}
\]

\[
\text{Nb(OCH}_3\text{H}_2\text{)}_5 + 2\text{C}_9\text{H}_{19}\text{COOH} \rightarrow 2\text{C}_2\text{H}_5\text{OH} + \text{Nb(OCH}_3\text{H}_2\text{)}_3(\text{C}_9\text{H}_{19}\text{COO})_2
\]
3.3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to study the thermal chemistry of the metallo-organic compound solutions involved. TGA involves the measurement of weight losses as the sample solution is heated in certain atmosphere, such as air, O₂, or N₂, following a specific heating curve. Figs. 3.16 and 3.17 are the thermograms of xylene solutions of the metallo-organic precursor compounds used in this study. They were employed to accurately calculate the weight ratio of the final product to the original sample. From these ratio of individual precursor solutions, the amount of each precursor solution needed for mixing the stoichiometric formulation solution can be determined. Fig. 3.18 is the thermogram of LiNbO₃ formulation solution, from which the heating rate, the pyrolysis and annealing temperatures, and the hold time can be roughly determined although these parameters need to be optimized by characterizing the final films.
Figure 3.15 Flow chart for MOD processing.

The TGA curves can be divided into three stages according to their differential curve. Let us take the lithium precursor solution as an example. A heating rate of 10°C/min was used. From room temperature to about 175°C, the weight loss of the sample was due to evaporation of the xylene solvent. The precursor compound started to decompose at about 375°C and the decomposition was complete by 480°C. After 500°C, a flat stable region was observed, from which the residue (Li₂O) was then calculated to be about 0.90 wt.% of the sample. The residue of each decomposition reaction was in powder form, and x-ray powder diffraction was done to compare with the published powder diffraction data of the compound expected to be left as
the final product. An x-ray powder diffraction pattern of the residue after decomposition of LiNbO₃ formulation is shown in Fig. 3.19†, in which the first three strongest LiNbO₃ match the powder diffraction data. A summary of the TGA results is given in Table 3.4.

Table 3.4  Thermal decomposition behavior of metallo-organic compounds and formulations.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound in Xylene</th>
<th>Xylene loss</th>
<th>Decomposition</th>
<th>Residue</th>
<th>wt.% of residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₁₂H₂₅COOLi</td>
<td>25-175°C</td>
<td>175-480°C</td>
<td>480-800°C (Li₂O)</td>
<td>0.90%</td>
</tr>
<tr>
<td>2</td>
<td>NH(OC₃H₇)₃(C₆H₁₉COO)₂</td>
<td>25-150°C</td>
<td>150-360°C</td>
<td>360-800°C (Nb₂O₅)</td>
<td>14.44%</td>
</tr>
<tr>
<td>3</td>
<td>1 + 2</td>
<td>25-150°C</td>
<td>150-500°C</td>
<td>500-800°C (LiNbO₃)</td>
<td>6.21%</td>
</tr>
</tbody>
</table>

†The powder diffraction pattern was taken using the XRD machine in Chemistry Dept. at Rice University, and the curve was traced by hand from the original plot.
3.3.4 Film deposition

Since the viscosity and surface tension of the formulation solution can be changed by varying the concentration of the solvent and additives, almost any wet coating technique can be used to deposit the formulation solution on the substrate. A desirable feature of any deposition technique is the capability of controlling the thickness and the uniformity of the film because many physical and structural properties of MOD films are dependent on the single layer thickness. Spinning, dipping, printing, and spraying, etc. have been frequently used and recommended by researchers. Spin coating was used in this study since the film becomes more uniform with the time of spinning, and the thickness can be easily calculated if the solution viscosity, the spinning rate, and the spinning time are known. A fluid dynamics analysis of the spin coating process derived from the Navier-Stokes equation was given by Yanagisawa [102] who described the thickness of a spun-on film by
Figure 3.18  Thermogram of LiNbO$_3$ formulation solution.

\[ h(t) = \frac{h_0}{(1 + 4 \rho I \omega^2 h_0^2 t / 3 \eta)^{1/2}} \]  

(3.2)

where \( h_0 \) is the liquid film thickness at \( t = 0 \), \( \rho_I \) is the liquid density, \( \omega \) is the spinning rate in rad/sec, \( t \) is the time of spinning, and \( \eta \) is the viscosity of the liquid.

Spinning rate used in this study varied from 1000 to 4000 rpm and spinning time from 15 to 60 sec. The inorganic films produced under these conditions have a thickness from 1000 to 2500 Å.

Although the steps of solution preparation and spinning processing are commonly done in open circumstances, caution must be taken to minimize any contamination or defect sources. Since sodium ions can cause fatigue in ferroelectric films, all of the glasswares to be used in the processing were washed very carefully and rinsed in a deionized water bath for 30 minutes. To exclude any large particles existing in the formulation solution, which might form radial streaks on the film, a syringe and a filter with 0.2 μm filtering holes were used to transfer the formulation solution to the
spinner. After the formulation solution is placed onto the substrate, it is the time that dust particles are most easily to rest on the film. Therefore, a clean environment of processing is of primary importance.

3.3.5 Pyrolysis

After deposition of the wet film, the sample was then heated up to evaporate the solvent and to decompose the metallo-organic compounds into an inorganic material. Pyrolysis must always be carried out in an environment that is oxidizing to carbon to ensure all carbonaceous material are removed from the film. Pyrolysis is the most critical step in all of the MOD processing steps since the initial microstructure of the film is developed here. A large volume shrinkage happens during pyrolysis, therefore, the heating/cooling rate should be controlled at an appropriate rate to prevent crack formation. However, the heating rate must be fast enough to decompose
the metallo-organic compounds before they segregate. Thermogravimetric analysis was utilized to determine appropriate heating rates and pyrolysis temperatures for different formulation solutions.

3.3.6 Annealing

Since the films are often pyrolyzed at temperature slightly higher than the temperature that decomposition finishes, *e.g.*, \( \sim 500^\circ \text{C} \) for LiNbO\(_3\), decomposition temperature, they are usually amorphous to x-ray. As is well-known, several properties of the film are related to the film’s crystallinity. Annealing is a thermal treatment commonly used to improve crystallinity of the film. Although large grain size films are usually desired for their retaintion of certain bulk properties, the films become more porous as the grain size gets larger when the temperature increases. Therefore, the annealing temperature is determined according to the applications on particular properties of the thin film. In some applications such as optical waveguiding, the porosity can cause light to be highly absorbed or scattered, thereby enhancing the propagation loss in the waveguide. In addition to the annealing temperature, the grain size is also determined by the cooling rate. The faster the cooling rate is, the finer the microstructure results.

Annealing time ranging from 2 minutes to 10 hours has been tried to grow MOD films. No significant difference, except peak intensities, in x-ray diffraction has been observed. However, it was found by Rutherford backscattering spectrometry (RBS) that inter-diffusion at the film-substrate interface increases with the annealing time if the temperature is above the critical value. Therefore, rapid annealing processing is preferred as long as the annealing time is sufficient to allow the oxygen in the atmosphere to diffuse into and to equally distribute throughout the entire film. The
details of the RBS study in the diffusion problem will be discussed later in the chapter on ion beam analysis.

3.3.7 Photo-induced metallo-organic decomposition

Metallo-organic decomposition using a conventional furnace has been employed to successfully grow high quality ferroelectric LiNbO₃ films on various substrates. However, because high processing temperatures (> 600°C) and a relatively long processing time (> 30 min) were required by MOD for obtaining crystalline films with desired grain size, inter-diffusion was observed by ion beam spectrometry. Degradation of electrical properties of the films or performance of micron or submicron integrated circuits might be caused by this problem. Moreover, furnace annealing with a rapid heating/cooling rate may result cracks in the films, which is obviously a disadvantage for optical waveguide devices. By diluting the formulation solution, crack-free films could be produced. It is, however, very inefficient in making thick films due to large volume shrinkage after firing. An alternate method to rapidly induce the process of metallo-organic decomposition without cracking is thus needed. Some possible heating sources are incoherent lights, lasers, resistance heaters, electron beams, and ion beams. Among these, incoherent light sources seem to be more compatible with the MOD process because they produce continuous radiation which is essentially the same mechanism of energy transfer as in furnace processing. Lasers (monochromatic light sources) are inadequate in this case since both IR lights for thermal effects and UV lights for chemical effects are required in the MOD process. Resistance heaters may be inefficient if an insulator substrate is used. Electron and ion beams are expensive equipments and are thus not considered.
Nishiyama et al. [103] in 1980 were the first to use tungsten halogen lamps for annealing boron implanted silicon wafers. Up to date, the technique has been extensively applied in many processes such as silicide formation, gettering, formation and annealing of gate dielectrics, metal alloying, metal oxidation, etc [104, 105]. However, this was the first time, to the best of author's knowledge, that white light radiation generated from tungsten halogen lamps is employed to in the metallo-organic decomposition process. The process is termed "photo-induced metallo-organic decomposition" (PIMOD) from now on to distinguish from conventional furnace MOD process.

![Diagram of Tungsten Halogen Lamp with Reflector](image)

**Figure 3.20** Experimental setup for rapid photo-induced metallo-organic decomposition process.

A schematic of the experimental setup for the PIMOD process is given in Fig. 3.20. For example, a 100V-500W tungsten halogen lamp with a color temperature of 3000°K and a surface temperature of 550°C placed 3 cm above the sample can produce a
homogeneous chamber temperature of 500°C within five minutes, which is suitable for evaporating the solvent as well as for decompositing the metallo-organic compounds.

As discussed by Singh et al. [104], furnace processing at 400°C can be represented by a blackbody radiation at ~800°K, as shown in Fig. 3.21, assuming radiation as the dominant mechanism of energy transfer. Only photons with wavelengths shorter than 1.2 μm, which occupy simply a small portion of the radiation spectrum, could be available for possible chemical reactions including metallo-organic decomposition and oxidation, the efficiency of furnace processing is thus expected to be very low. On the other hand, in the case of PIMOD, the filament temperature (color temperature) can be higher than 3000°K, although the substrate temperature may be only 400°C as in furnace processing. A typical intensity vs. wavelength curve for tungsten halogen lamps is also plotted in Fig. 3.21 for comparison. Obviously, tungsten halogen lamps provide more short wavelength photons, and, hence, should be more efficient for inducing chemical reactions. Moreover, photons with wavelengths longer than 1.2 μm are not able to dissociate gaseous O₂ into atomic oxygen, which is more reactive and diffusive than the O₂ molecule and is of primary importance to the oxidation of solid state materials [106]. The high efficiency of the PIMOD process considerably decreases the processing time, thereby reducing the risk of being contamination during thermal treatment.

3.3.8 LiNbO₃ films by the MOD process

LiNbO₃ thin films have been deposited on a variety of substrates. Substrates of (012) and (110) sapphire single crystals, and thermally oxidized silicon wafers were used as substrates on which to grow optical waveguides for applications in integrated optics.
Figure 3.21 Relative intensity (not to the same scale) of tungsten halogen lamps (color temperature = 3000°K) and blackbody radiation of 800°K as a function of wavelength.

whereas (111) Si substrates were utilized to build ferroelectric capacitors for studies of non-volatile memories.

After finishing the regular wafer cleaning procedure, the substrates were rinsed with 99.9% xylene, spun twice with a spinning rate of 5000 rpm for 60 sec, and then dried by inert gas before deposition of the formulation solution. The formulation solution was stirred magnetomechanically overnight before it was used to ensure all of the metallo-organic compounds were mixed uniformly. A disposable syringe with a filter (hole size = 0.2 μm) was employed to deposit the formulation solution onto the substrate. A spinning rate of 500 rpm was first used for 2-3 sec in order to produce a roughly uniform initial liquid film, and then it was gradually increased to a "maximum" spinning rate and retained at this rate for 30 sec. The "maximum" spinning rates used in this study were in the range from 1000 to 4000 rpm. A Thermco
Figure 3.22 XRD patterns of MOD-processed LiNbO$_3$ films on (111) Si (fired in air at 600, 700, and 800°C).

diffusion furnace (up to 1400°C), or a Lindberg Mark IV furnace (up to 800°C), was used to fire the films. Different heating rates have been tried to study how the thermal treatment affects the microstructure of the films. Non-uniformity due to segregation of the metallo-organic compounds has found in the films grown at a heating rate less than 5°C/min. Therefore, in the first stage of pyrolysis (xylene loss) a heating rate greater than 10°C/min is required. In general, cracking in the LiNbO$_3$ films was not observed unless the wet films were directly transferred from room temperature into 500°C within an extremely short time, eg., 2 sec. To minimize diffusion of Li and Nb ions into the substrate, a rapid thermal treatment was used. The films directly, but slowly, inserted into and fired at a 500°C furnace were found to have quality as
good as those fired from room temperature to 500°C except the former did not suffer the problem of diffusion. The pyrolysis temperature of 500°C was determined by TGA and was considered to be adequate after a series of experiments using different temperatures had been carried out. Annealing temperatures ranging from 500 to 800°C have been tried to improve the crystallinity of the films.

XRD patterns of MOD LiNbO₃ films on (111) Si deposited at a spinning rate of 3000 rpm for 30 minutes and fired in air at 600, 700, and 800°C are shown in Fig. 3.22. The peaks match the powder diffraction data, however, there is no preferred orientation. The films annealed at 600°C have excellent transparency and uniformity. Those annealed at 700°C also have good optical quality, however, pores were observed for some of the films. The films fired at 800°C have large grain size and many pores such that they turned out slightly opaque.

XRD pattern of a LiNbO₃ film deposited on (100) Si by similar processing as described above is shown in Fig. 3.23. (104) seems to be the preferred orientation for LiNbO₃ grown on (100) Si, which greatly suppresses the (012) peak (the largest LiNbO₃ peak in powder x-ray diffraction data).

To make optical waveguides on silicon substrates, it is necessary to grow a buffer layer with a lower refractive index than the waveguide. Thermally oxidized (100) silicon substrates have been used to provide the required buffer layer with a thickness ranging from 0.1 to 2.5 µm. Fig. 3.24 is the XRD pattern of an MOD-derived LiNbO₃ film on SiO₂/(100)Si, which is very similar to Fig. 3.23 except there is a broad feature at around 2θ = 34° due to the amorphous nature of SiO₂.

LiNbO₃ films have been epitaxially grown on (012) sapphire, as shown in Fig. 3.25, by the MOD technique with a spin rate of 3000 rpm for 20 seconds. It was directly, but slowly, inserted into a 500°C air atmosphere, held for 15 minutes, then slowly
Figure 3.23  XRD pattern of an MOD-processed LiNbO$_3$ film on (100) Si.

Figure 3.24  XRD pattern of an MOD-processed LiNbO$_3$ film on SiO$_2$/(100)Si.
Figure 3.25 XRD pattern of an MOD-processed LiNbO$_3$ film on (012) sapphire.

pulled out. The temperature of the tube furnace was then increased to 650°C, and the sample was slowly inserted into the furnace and fired for 15 minutes. To avoid diffusion, the sample was then directly transported from the 650°C furnace to room temperature with an approximate cooling rate of 600°C/min. However, extremely rapid cooling may cause cracking in the film, therefore, caution must be taken that the sample should be slowly passing through the temperature barrier of the tube furnace.

For applications in integrated optics, it is usually desired that the thickness of the waveguide can be near the wavelength of the propagating wave, e.g., about 0.6 μm for He-Ne laser light. Thick single-layer films have been grown on sapphire substrates using slow spinning rate such as 1500 rpm for 10 second, but the rapid pyrolysis technique failed in producing crack-free thick LiNbO$_3$ films since the LiNbO$_3$ films
deposited on sapphire are in tension due to the relative large difference of the linear thermal expansion coefficient between the two materials. Multilayer techniques are thus necessary in this case for growing thick LiNbO₃ films, although defects may be introduced at the layer interface. Formation of cracks or multilayer interface defects are two problems that necessitate care in fabrication while making thick LiNbO₃ optical waveguides via the MOD process.

3.3.9 LiNbO₃ films by the PIMOD process

A 5-layer (~0.7µm measured by α-step technique) epitaxial LiNbO₃ has been grown on a (110) sapphire substrate through the PIMOD process. To eliminate cracks, a spinning rate of 3000 rpm for 30 sec was used to deposit the first layer of wet film. After exposure at ~500°C (the wet film was exposed to a 500 W tungsten halogen lamp for 5 min), the second layer and other overlayers were deposited using a 1500 rpm spinning rate for 30 sec. Each deposition of wet film was followed by exposure at 500°C in air for 5 minutes. Finally, the sample was fired in a furnace (air atmosphere) at 650°C for 30 minutes with a heating rate of 30°C/min and a cooling rate of about 100°C/min. The XRD pattern of the LiNbO₃ film processed by PIMOD on (110) sapphire is shown in Fig. 3.26. Note that the final step of annealing can also be done by tungsten halogen lamps if more lamps are used simultaneously.
Figure 3.26  XRD pattern of a PIMOD-processed LiNbO₃ films on (110) sapphire.
Chapter 4

Ion Beam Spectrometry

4.1 Rutherford backscattering spectrometry

Both in its concept and in its elementary execution, Rutherford backscattering spectrometry (RBS) [108] is quite a simple experiment. It is, however, a very powerful tool for surface analysis in many branches of materials science. Fig. 4.1 shows a schematic of the major components of the RBS system. An ion beam is generated, accelerated, and then directed at the sample under investigation. The mono-energetic ions collide elastically with lattice atoms in the sample and are scattered into a detector which counts the number of scattered particles and measures their energy. The RBS energy spectrum gives information on the chemical composition, the depth profile of elements contained in the sample, and the thickness of the sample. Incorporated with the channeling technique, RBS can further determine crystallinity of the sample, interfacial strain, and concentration of the defects, etc.

4.1.1 Kinematic factor $K$

As shown in Fig. 4.1, an ion beam, typically 1-3 MeV $^4\text{He}^+$, is extracted from an accelerator and passed through a magnetic analyzer. The beam is collimated by two slits (pin holes) and incident onto the sample which is placed in a vacuum chamber maintained at a pressure of about $1 \times 10^{-6}$ Torr. Part of the scattered ions are collected by a solid state detector and analyzed by a multichannel analyzer. If the
scattering is treated as a two-body elastic collision (before scattering: $M_1 \ (E_0, \ v_0)$, $M_2$ (at rest); after scattering: $M_1 \ (E_1, \ v_1)$, $M_2 \ (E_2, \ v_2)$), as shown in Fig. 4.2, the ratio of the projectile energy after the collision to that before the collision can be defined as the \textit{kinematic factor} $K$ and the result, assuming $M_1 \leq M_2$, derived from conservation of energy and conservation of momentum is given by

$$K_{M_2} = \frac{E_1}{E_0} = \left\{ \frac{[1 - (M_1/M_2)^2 \sin^2 \theta]^2 + (M_1/M_2) \cos \theta}{1 + (M_1/M_2)} \right\}^2. \quad (4.1)$$

From Eq. 4.1, we notice that $K$ always decreases to its lowest value as the scattering angle increases to $\theta = 180^\circ$ for any value of $M_2/M_1$, i.e., the larger the scattering angle, the better the mass discrimination. Therefore, the "backscattered" particles, especially when $\theta$ near $180^\circ$, are of particular interest in RBS. The detector is normally
set at $\theta = 170^\circ$ since setting a detector at $180^\circ$ without blocking the incident beam is practically impossible.

4.1.2 Rutherford scattering cross section

If $Q$ is the total number of particles that have collided with the target and $dQ$ is the number of particles collected by the detector, then the differential scattering cross section $d\sigma/d\Omega$ is defined as

$$d\sigma/d\Omega = (1/Nt)(dQ/d\Omega)/Q,$$

(4.2)

where $N$ is the volume density of atoms in the sample and $t$ is its thickness and thus $Nt$ represents the areal density, and $d\Omega$ is the differential solid angle of the beam at the detector. For a uniform ion beam impinging at normal incidence on a uniform target which is larger than the cross section area of the beam, the total number of detected particles $A$, termed the backscattering yield, can be expressed as

$$A = \sigma \Omega \cdot Q \cdot Nt,$$

(4.3)

where $\sigma$ is the average differential scattering cross section and is defined as
\[ \sigma \equiv \frac{1}{\Omega} \int_\Omega (d\sigma/d\Omega) d\Omega. \]  

(4.4)

Darwin in 1914 derived a formula for calculating the Rutherford differential scattering cross section \cite{108}:

\[ \frac{d\sigma}{d\Omega} = \left( \frac{Z_1 Z_2 e^2}{4 E_0} \right)^2 \frac{4}{\sin^4 \theta} \frac{\left\{ 1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2 \right\}^{1/2} + \cos \theta}{\left[ 1 - \left( \frac{M_1}{M_2} \sin \theta \right)^2 \right]^{1/2}}, \]  

(4.5)

where \( Z_1 \) and \( Z_2 \) are the atomic number of \( M_1 \) and \( M_2 \), respectively. For 1 MeV ions, \((e^2/E_0)^2 = 2.0731 \times 10^{-26} \text{cm}^2 = 0.020731 \text{b} \) (barn). For \( M_1 \ll M_2 \), the angular dependence of the right-hand side of Eq. 4.5 can be expanded in power series as following \cite{109}:

\[ \frac{d\sigma}{d\Omega} \approx \left( \frac{Z_1 Z_2 e^2}{4 E_0} \right)^2 \left[ \sin^{-4} \frac{\theta}{2} - 2 \left( \frac{M_1}{M_2} \right)^2 + \cdots \right], \]  

(4.6)

which reveals the significant functional dependences of the Rutherford differential scattering cross section. These dependences are pointed out in the following to give a better understanding of ion beam spectrometry:

1. \( d\sigma/d\Omega \) is proportional to \( Z_1^2 \). The backscattering yield is higher for heavy incident ions.

2. \( d\sigma/d\Omega \) is proportional to \( Z_2^2 \). Heavy lattice atoms within the sample are more efficient scatterers than light ones, i.e., RBS is much more sensitive to heavy elements.

3. \( d\sigma/d\Omega \) is inversely proportional to the square of the projectile energy \( E_0 \). The incident ions with a high \( E_0 \) can penetrate more deeply into the sample than those with a low \( E_0 \), thereby rapidly lower the scattering yield.

4. \( d\sigma/d\Omega \) is approximately inversely proportional to \( \sin^{-4}(\theta/2) \). This indicates that the scattering yields increase rapidly as the scattering angle is decreased.
In some cases, the differential scattering cross section deviates from the Rutherford formula. For example, when the scattering angle approaches zero, the Rutherford scattering cross section goes to infinity, which is certainly not true. Small scattering angles correspond to large fly-by distances between the projectile and the target nuclei, at which the electrostatic interaction does not happen, and thus the Rutherford formula fails.

Another example of deviation of differential scattering cross section from the Rutherford equation is when the bombarding particle impinges with a sufficiently high energy to get so close to the target nuclei, the short-range nuclear interaction is induced and the collision is no more elastic. In such case, the scattering cross section will be greatly enhanced. Ion beam nuclear reaction analysis (NRA) is a very useful tool for analyzing the light elements beyond the detection limit of the standard RBS. Use of nuclear reaction in backscattering spectrometry will be discussed in a later section.

4.1.3 Energy loss and stopping cross section

When a particle penetrates through a solid sample, it loses energy. At a certain depth \( x \), the particle energy is reduced to \( E \) from its initial energy \( E_0 \) as expressed by

\[
E = E_0 - \int_0^x \frac{dE}{dx} \, dx.
\]  

(4.7)

Using RBS in surface analysis, we are only interested in the surface layers of the sample, and the rate of energy loss can be considered constant at the value \( dE/dx \mid_{E_0} \). This is the surface energy approximation described by Chu et al. [108], and Eq. 4.7 becomes

\[
E = E_0 - \frac{dE}{dx} \mid_{E_0} \cdot x.
\]  

(4.8)
The **stopping cross section** $\varepsilon$ is a more commonly used term in calculations concerning energy loss and is defined by

$$
\varepsilon = \frac{1}{N} \frac{dE}{dx},
$$

where $N$ is the target atomic density. Values of $^4He^+$ stopping cross section in all elements from 0.4 to 4.0 MeV are tabulated by Chu et al. [108].

When a target composed of many elements (e.g., $A_m B_n$) is encountered, the total energy loss can be calculated by **Bragg's rule** which is given by

$$
\varepsilon^{A_m B_n} = m \varepsilon^A + n \varepsilon^B,
$$

where $\varepsilon^A$ and $\varepsilon^B$ are the stopping cross section of the atomic constituents A and B. In a sample of LiNbO$_3$, for instance, the stopping cross section is given by

$$
\varepsilon^{LiNbO_3} = \varepsilon^{Li} + \varepsilon^{Nb} + 3 \cdot \varepsilon^O.
$$

Even though the bombarding ion beam is approximately mono-energetic, the energy loss process is subject to statistical fluctuations, and, therefore, identical particles do not travel with the same energy after penetrating into the same depth. This effect is called **energy straggling** which limits the precision of surface analysis using RBS.

### 4.1.4 Depth profiling

Fig. 4.3 shows a schematic of backscattering events at the surface and at a depth $x$ within the sample. If the rate of energy loss $dE/dx$ can be considered as a constant near the surface of the target, the incident particle passing through a distance $x$ suffers an energy loss $E_0 - E$ given by

$$
E_0 - E = \frac{x}{\cos \theta_1} \frac{dE}{dx} |_{E_0},
$$

and, after scattering, the particle loses another part of its energy before it can escape from the surface of the target. Similarly, this part of energy loss is given by
Figure 4.3  Schematic of backscattering events.

\[ K \cdot E - E_1 = \frac{x}{\cos \theta_2} \frac{dE}{dx} \bigg|_{KE_0} \]  \hspace{1cm} (4.13)

where the surface energy approximation is used. By combining Eqs. 4.12 and 4.13, we can calculate the energy difference between \( E_1 \) and \( KE_0 \) as following

\[ \Delta E \equiv KE_0 - E_1 = \left[ \frac{K}{\cos \theta_1} \frac{dE}{dx} \bigg|_{E_0} + \frac{1}{\cos \theta_2} \frac{dE}{dx} \bigg|_{KE_0} \right] \cdot x. \]  \hspace{1cm} (4.14)

The above equation can then be written as

\[ \Delta E = [S]x, \]  \hspace{1cm} (4.15)

where

\[ [S] \equiv \left[ \frac{dE}{dx} \bigg|_{E_0} + \frac{1}{\cos \theta_2} \frac{dE}{dx} \bigg|_{KE_0} \right] \]  \hspace{1cm} (4.16)

is the energy loss factor or \( S \) factor. An equivalent equation can be given in terms of stopping cross section:

\[ \Delta E = [\varepsilon]Nx, \]  \hspace{1cm} (4.17)

where

\[ [\varepsilon] = \left[ \frac{K}{\cos \theta_1} \varepsilon(E_0) + \frac{1}{\cos \theta_2} \varepsilon(KE_0) \right] \]  \hspace{1cm} (4.18)
is the stopping cross section factor or $\varepsilon$ factor. From Eq. 4.15 or Eq. 4.17, one can profile the depth distribution for each element in the sample. Tabulated data for both $[S]$ and $[\varepsilon]$ are given by Chu et al. [108].

![Diagram](image)

**Figure 4.4** Schematics of backscattering spectra for different type of self-supporting solid samples: (a) a thick solid element A, (b) a thick solid compound AB, (c) a thin foil of element A, (d) a thin foil of compound AB.

4.1.5 Some RBS examples

Let's now discuss some RBS examples for different type of samples. Figs. 4.4 and 4.5 show a few typical Rutherford backscattering spectra. If the sample is just a thick
solid of element A, the backscattering spectrum is as simple as shown in Fig. 4.4(a).
From the front surface energy $K_A E_0$, we can identify the element by calculating its mass using Eq. 4.1. Since energy $K_A E_0$ is measured from the particles scattered from surface of the sample, the energy scale can be converted to a depth scale by Eqs. 4.15 or 4.17.

If there are more than one element contained in the sample, then the spectrum from each element will superimpose on those from the others, and the resultant ($H = \sum H_i$, where $H_i$ is the spectrum height of element $i$) is shown in Fig. 4.4(b). By calculating the $K$ factor from each front surface energy $H_{i,0}$ (the vertical edges), we can identify the individual element in the sample.

For an $A_mB_n$ compound, the surface heights can be written as

$$H_{A,0} = \sigma_A(E_0)\Omega Qm(\varepsilon/|\varepsilon_0|_A^{AB} \cos \theta_1)$$

(4.19)

and

$$H_{B,0} = \sigma_B(E_0)\Omega Qn(\varepsilon/|\varepsilon_0|_B^{AB} \cos \theta_1),$$

(4.20)

where $\varepsilon$ is the energy width per channel. The ratio of these heights is

$$\frac{H_{A,0}}{H_{B,0}} = \frac{\sigma_A(E_0) m |\varepsilon_0|_B^{AB}}{\sigma_B(E_0) n |\varepsilon_0|_A^{AB}}.$$  

(4.21)

Eq. 4.21 can be used to determine the composition ratio $m/n$. However, one needs to know this ratio in order to calculate the stopping cross section factors $|\varepsilon_0|_A^{AB}$ and $|\varepsilon_0|_B^{AB}$. Fortunately, this ratio is actually very close to unity within 10% in most cases for He ions with energies of 1 to 2 MeV. One can then take a zeroth-order approximation, i.e.,

$$\frac{m}{n} \simeq \frac{H_{A,0}/\sigma_A(E_0)}{H_{B,0}/\sigma_B(E_0)}.$$  

(4.22)
From the zeroth-order approximation, a better estimate of the ratio $[\varepsilon_0]^A_B / [\varepsilon_0]^A_A$ is obtained and hence a first-order approximation to $m/n$. Normally, this first iteration is sufficient to get a value of $m/n$ within the experimental errors.

Fig. 4.4(c) shows a RBS spectrum of a thin foil of element A. Since the foil is so thin that part of the particles can penetrate through the foil without being scattered, another vertical edge representing the back surface energy appears on the low energy side, which allows to calculate the thickness of the thin sample by converting the energy difference $\Delta E_A$ between the front and the back surface energy to the depth scale.

If the thin foil is made from a compound, eg., $A_mB_n$ as shown in Fig. 4.4(d), the individual elements can be identified from the corresponding front surface energy, and the ratio of $m/n$ can be determined by comparing the area $A_i$ under each "peak" as well as by the ratio of surface heights, ie., Eq. 4.22 can be rewritten as

$$\frac{m}{n} \sim \frac{[A_A/\sigma_A(E_0)]}{[A_B/\sigma_B(E_0)]}.$$  \hspace{1cm} (4.23)

In some cases, integrating the peak area is a better way to calculate the ratio $m/n$ since overlapping of peaks might cause problem determining surface height correctly. The thickness of the thin foil can be calculated by

$$N^{AB}t = \begin{cases} \Delta E_A / [\varepsilon_A]^A_B & \text{peak } A \\ \Delta E_B / [\varepsilon_B]^A_B & \text{peak } B. \end{cases}$$  \hspace{1cm} (4.24)

Based on the understanding of RBS spectra of self-supporting solid samples as shown in Fig. 4.4, RBS spectra of thin film samples as shown in Fig. 4.5 now should become clear. Note that, whoever, the surface energy of the substrate is always shifted toward the low energy end since the incident ions have lost some energy in order to penetrate the film before they can reach the interface. The energy shift is quantitatively related to the film thickness.
Figure 4.5  Schematics of backscattering spectra for different type of thin film samples: (a) a thin film A on a light substrate B, (b) a thin film A on a heavy substrate B, (c) a double-layer thin film on a light substrate, and (d) a thin film of compound AB on a light substrate.

4.2 Nuclear reaction analysis

When a particle is incident at a solid target with a sufficiently high projectile energy so that it can overcome the Coulomb barrier of a lattice atom, a short-range, attractive, and charge-independent interaction occurs between the incident particle and the target atom. When nuclear reaction happens, the collision becomes inelastic, and the Rutherford formula can no more apply.
Figure 4.6 Schematic of kinematics of nuclear reaction and scattering.

A schematic of kinematics of nuclear reaction and scattering is drawn in Fig. 4.6. A nuclear reaction is commonly represented by an equation $a + A = B + b + Q$ or $A(a, b)B$ with a $Q$ value, where symbols $a$, $A$, $b$, and $B$ represent the elements with a mass of $M_1$, $M_2$, $M_3$, and $M_4$, respectively, and $Q$ is the energy released due to the total mass change in the nuclear reaction. Hence, according to relativistics, the $Q$ value can be given by

$$Q = [(M_1 + M_2) - (M_3 + M_4)]c^2,$$  \hspace{1cm} (4.25)

where $c$ is the speed of light. The emitted energy $E_3$ of the light scattered particle was derived by Marion and Young [109] and is given by

$$E_3 = [u \pm (u^2 + w^2)^{1/2}]^2,$$ \hspace{1cm} (4.26)

where

$$u = \frac{(M_1 M_3 E_1)^{1/2}}{(M_1 + M_4)^2} \cos \theta$$ \hspace{1cm} (4.27)

and

$$w = \frac{M_4 Q + E_1 (M_4 - M_1)}{M_3 + M_4}.$$  \hspace{1cm} (4.28)
Since the detection resolution of Rutherford backscattering spectrometry for light (low atomic number) elements is rather poor, ion-induced nuclear reactions are very useful in detecting light elements. Nuclear reaction analysis (NRA) is a highly sensitive technique, therefore, the choice of projectile and its energy, isotope to be analyzed, angle of detection, and detector arrangement need to be carefully considered. Many most encountered ion-induced nuclear reactions are tabulated in Table 4.1 [110], in which the detection angle was set at 150° with respect to incident beam direction. The operation and data analysis of NRA is very similar to that of RBS, hence, the concepts of energy loss and depth profiling described previously can still apply here.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Reaction</th>
<th>$Q$</th>
<th>$E_1$ (MeV)</th>
<th>$E_3$ (MeV)</th>
<th>$\sigma_{tot}(E_1)$ (mb/sr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6$Li</td>
<td>$^6$Li$(d,\alpha)^4$He</td>
<td>22.374</td>
<td>0.7</td>
<td>9.7</td>
<td>6</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>$^7$Li$(p,\alpha)^4$He</td>
<td>17.347</td>
<td>1.5</td>
<td>7.7</td>
<td>1.5</td>
</tr>
<tr>
<td>$^{11}$B</td>
<td>$^{11}$B$(p,\alpha)^8$Be</td>
<td>8.586</td>
<td>0.65</td>
<td>5.57($\alpha_0$)</td>
<td>0.12($\alpha_0$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.65</td>
<td>0.65</td>
<td>3.70($\alpha_1$)</td>
<td>90($\alpha_1$)</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>$^{12}$C$(d,p)^{13}$C</td>
<td>2.722</td>
<td>1.20</td>
<td>3.1</td>
<td>35</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>$^{13}$C$(d,p)^{14}$C</td>
<td>5.951</td>
<td>0.64</td>
<td>5.8</td>
<td>0.4</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>$^{14}$N$(d,\alpha)^{12}$C</td>
<td>13.547</td>
<td>1.5</td>
<td>9.9($\alpha_0$)</td>
<td>0.6($\alpha_0$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.146</td>
<td>1.2</td>
<td>6.7($\alpha_1$)</td>
<td>1.3($\alpha_1$)</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>$^{15}$N$(p,\alpha)^{12}$C</td>
<td>4.964</td>
<td>0.8</td>
<td>3.9</td>
<td>15</td>
</tr>
<tr>
<td>$^{18}$O</td>
<td>$^{18}$O$(p,\alpha)^{15}$N</td>
<td>3.980</td>
<td>0.730</td>
<td>3.4</td>
<td>15</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>$^{19}$F$(p,\alpha)^{16}$O</td>
<td>8.114</td>
<td>1.25</td>
<td>6.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### 4.3 Contamination

To determine the chemical composition of the thin film lithium niobate samples, both $\alpha$ particle RBS and proton RBS/NRA are needed since the detection resolution of RBS for lithium is rather poor. According to Table 4.1, a projectile energy $E_1$ of 1.5
MeV is recommended for observing the $^7Li(p,\alpha)^4He$ reaction. RBS/NRA spectra* of a few sputtered lithium niobate thin film samples have been taken using the same parameters described above and are shown in Figs. 4.7-4.10. The RBS/NRA spectrum for single crystal LiNbO$_3$ was used as a standard to easily identify the Li and Nb peaks although a standard is not necessary for backscattering spectrometry. From the spectrum, one can see that the $\alpha$ particles generated in the $^7Li(p,\alpha)^4He$ reaction and detected at $\theta = 150^\circ$ have a surface energy at channel 424, those generated in the $^{18}O(p,\alpha)^{15}N$ reaction has a surface energy at channel 53.5. The surface energy at channel 70.5 is due to standard Rutherford backscattering from Nb. After converting the energy into the $K$ factor, one can identify that the element is Nb.

A peak at channel 393.5 was observed in all of the RBS/NRA spectra for the sputtered lithium niobate thin film samples as shown in Figs. 4.7-4.10 and does not belong to Li, O, Nb, Al, N, or Si, which means that it is probably due to some kind of contamination. From the emitted particle energy $E_3$ listed in Table 4.1, one can see that it could possibly attribute to $^{19}F(p,\alpha)^{16}O$ reaction, i.e., the contamination is due to F. To actually identify the element, a RBS/NRA spectrum of a teflon tape, which contains mostly F, was plotted in dashed line as shown in Figs. 4.7-4.10. The coincidence at channel 393.5 of the two spectra confirms that it is F contamination. A later experiment using single crystal CaF$_2$ instead of teflon is shown in Fig. 4.11, which also agrees with this conclusion.

Let's now calculate the concentration ratio of F to Li. From Fig. 4.12, the cross section ($E_{proton} = 1.5$ MeV, $\theta = 150^\circ$) for $^7Li(p,\alpha)^4He$ reaction is 1.74 mb/stc, and, from Fig. 4.13, that for $^{19}F(p,\alpha)^{16}O$ reaction is 0.38 mb/stc. Using Eq. 4.23, the

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*All of the RBS experiments were done by using the ion accelerator in Texas Superconductor Center at University of Houston with the help from Dr. W.K. Chu, Z.H. Zhang, and J.R. Liu.
Figure 4.7 1.5 MeV proton RBS/NRA spectrum of a thin film lithium niobate sputtered on Si$_3$N$_4$/Si. $\theta = 150^\circ$.

Figure 4.8 1.5 MeV proton RBS/NRA spectrum of a thin film lithium niobate sputtered on SiO$_2$/Si. $\theta = 150^\circ$. 
Figure 4.9 1.5 MeV proton RBS/NRA spectrum of a thin film lithium niobate sputtered on (100) Al₂O₃. θ = 150°.

Figure 4.10 1.5 MeV proton RBS/NRA spectrum of a thin film lithium niobate sputtered on (110) Al₂O₃. θ = 150°.
**Figure 4.11** Comparison of a RBS/NRA spectrum of a sputtered LiNbO$_3$/Si$_3$N$_4$/Si sample with that of a CaF$_2$ single crystal. 1.5 MeV proton energy, $\theta = 150^\circ$.

**Figure 4.12** Cross section vs. incident proton energy at $\theta = 150^\circ$ for $^7Li(p,\alpha)^4He$ reaction [110].
Figure 4.13  Cross section vs. incident proton energy at \( \theta = 150^\circ \) for \(^{19}F(p, \alpha)^{16}O\) reaction [110].

Figure 4.14  2.0 MeV He\(^+\) RBS spectrum of a sputtered LiNbO\(_3\)/Si\(_3\)N\(_4\)/Si sample. \( \theta = 170^\circ \).
ratio of F/Li can be calculated for the above samples, and the results are listed in Table 4.2. In some samples, *e.g.*, S10828, the concentration of F is so high that a clear edge (at $E \sim 845$ KeV) corresponding to F can be observed as shown in Fig. 4.14.

Table 4.2 Experimental data of the ratio of F/Li for some of the sputtered thin films. Proton energy is 1.5 MeV. Detection angle is set at 150°. $A_F$ and $A_{Li}$ represent the area under the F and Li peak, respectively.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Substrates</th>
<th>$A_{Li}$ (counts)</th>
<th>$A_F$ (counts)</th>
<th>$n_F/n_{Li}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S91106</td>
<td>(012) Al$_2$O$_3$</td>
<td>3412</td>
<td>11</td>
<td>0.015</td>
</tr>
<tr>
<td>S91201</td>
<td>(110) Al$_2$O$_3$</td>
<td>5592</td>
<td>20</td>
<td>0.016</td>
</tr>
<tr>
<td>S10426</td>
<td>(100) Al$_2$O$_3$</td>
<td>1061</td>
<td>9</td>
<td>0.039</td>
</tr>
<tr>
<td>S10827</td>
<td>SiO$_2$/Si</td>
<td>2880</td>
<td>927</td>
<td>1.549</td>
</tr>
<tr>
<td>S10828</td>
<td>Si$_3$N$_4$/Si</td>
<td>2852</td>
<td>1001</td>
<td>1.607</td>
</tr>
</tbody>
</table>

One possible source of F is HF solution which has been used in the wafer cleaning procedure. A bare silicon wafer was prepared by the same cleaning procedure and then a RBS/NRA spectrum was taken for the silicon wafer. No F peak was observed in this spectrum, which thereby excludes HF solution being the source of contamination. Since the substrate was clamped between a heater plate and a copper wafer holder and only the center of the wafer was exposed to the plasma during sputtering, the area near the edge of the wafer was still uncoated with film after sputtering. A RBS/NRA taken for the uncoated area did not show the F peak, which indicated that the film was contaminated during sputtering.

The sputtering system has been carefully examined to find the F source. Two suspects have been discovered: One is the teflon ring (electric isolator) inside the magnetron. It is, however, shielded by a stainless steel cover which should somewhat, if not absolutely, prevent the teflon ring from reaching and being vaporized by the plasma; The other is the teflon coats of the heater wires. Since they are directly
exposed in the plasma, they could be the source of F and needed to be replaced. After replacing the teflon coating with ceramic tubes, the concentration of F has dramatically decreased from more than 100% to less than 0.1% of Li. All of the components inside the vacuum chamber were then carefully cleaned with acetone and deionized water. After this was done, no F had been found.

Since 1990, the sputtered films made in this lab have suffered a severe aging problem that never happened before. When the existence of F was detected and its concentration was found to be greater than that of Li, we realized that the aging of the films was most probably due to F since F is very unstable when it exists in a LiNbO$_3$ system and very active such that it is easy to react with H$_2$O in air.

Contamination problems in surface analysis are ideal for RBS. The technique of NRA is particularly useful for detecting low atomic number contaminations. In comparison to other surface analysis techniques such as SIMS, as shown in Fig. 4.15, and ESCA,\textsuperscript{1} as shown in Fig. 4.16, RBS/NRA is more straightforward and simple.

### 4.4 Ion beam analysis of Lithium niobate thin films

Fig. 4.17 shows a 2.0 MeV $\alpha$ particle RBS (detection angle = 150°) spectrum of a sputtered LiNbO$_3$ on Si substrate (sample ID: S11231). From Eq. 4.22, the ratio of O/Nb is calculated to be 3.1. Since $\alpha$ RBS can not detect Li signal, therefore, a 1.5 MeV proton RBS/NRA (detection angle = 150°), as shown in Fig. 4.18, was implemented, and the ratio of Li/Nb was determined to be 1.1. By combining the two results, the chemical composition of the thin film is Li$_{1.3}$NbO$_{3.1}$, which indicates

\textsuperscript{1}The SIMS and ESCA spectra were done by Peter Sobol at Perkin Elmer
that the thin film sputtered under the optimal conditions is stoichiometric lithium niobate.

Let's now calculate the thickness of the film S11231 from the energy width of the Nb peak in the α RBS spectrum (Fig. 4.17). Assuming surface energy approximation, the stopping cross section factor can be rewritten, from Eq. 4.18, by

\[
[e]_{\text{LiNbO}_3}^{\text{Nb}} = \left[ \frac{K_{N_b}}{\cos \theta_1} \epsilon_{\text{LiNbO}_3}^{\text{Li}}(E_0) + \frac{1}{\cos \theta_2} \epsilon_{\text{LiNbO}_3}^{\text{Nb}}(K_{N_b} \cdot E_0) \right].
\]  

(4.29)

From Eq. 4.11, the stopping cross sections for LiNbO$_3$ can be calculated by Bragg's rule as

\[
\epsilon_{\text{LiNbO}_3}^{\text{Li}_1\text{NbO}_3\text{O}_3}(E_0) = 1.1 \cdot \epsilon_{\text{Li}}(E_0) + \epsilon_{\text{Nb}}^{\text{Li}}(E_0) + 3.1 \cdot \epsilon_{\text{O}}(E_0)
= (1.1 \times 15.35 + 98.1 + 3.1 \times 35.84) \times 10^{-15} \text{ eV} \cdot \text{cm}^2
= 226.1 \times 10^{-15} \text{ eV} \cdot \text{cm}^2,
\]

and
\[
\varepsilon^{{Li_{1.1}NbO_{3.1}}}(K_{Nb} \cdot E_0) = 1.1 \cdot \varepsilon^{Li}(K_{Nb} \cdot E_0) + \varepsilon^{Nb}(K_{Nb} \cdot E_0) + 3.1 \cdot \varepsilon^{O}(K_{Nb} \cdot E_0) = 248.5 \times 10^{-15} \text{ eV} \cdot \text{cm}^2,
\]

where \( K_{Nb} = 0.8514 \). Since the ion beam was normally incident on the sample and the detection angle was set at 150°, we have \( \theta_1 = 0^\circ \) and \( \theta_2 = 30^\circ \). By inserting these values into Eq. 4.29, the stopping cross section factor \([\varepsilon]_{Nb}^{Li_{1.1}NbO_{3.1}}\) can then be determined to be \( 4.8 \times 10^{-13} \text{ eV} \cdot \text{cm}^2 \). Now, we need to calculate the volume density \( N \) of LiNbO₃. The mass density of LiNbO₃ is about 4.64 g/cm³, and the molecular weight of 1 mole of LiNbO₃ is 147.847 amu. Therefore, \( N \) is equal to \( 2.0 \times 10^{22} \) molecules/cm³. From the width of the Nb peak, the energy loss \( \Delta E \) for He⁺ ions penetrating through the LiNbO₃ film is estimated to be about 185 KeV. Now, the thickness of the film can be computed, using Eq. 4.17, to be 0.19 \( \mu \text{m} \), which is in good agreement with the value (\( t_\alpha = 0.17 \mu \text{m} \)) measured by an \( \alpha \)-step profilometer. The reason that the thickness calculated from RBS spectrum is greater than the value.
Figure 4.17 2.0 MeV He\(^+\) RBS spectrum of a sputtered LiNbO\(_3\)/Si (sample S11231). \(\theta = 150^\circ\).

from \(\alpha\)-step measurement is because the surface energy approximation was used such that a smaller stopping cross section factor, thereby a larger thickness, was obtained.

A spectrum-fitting program was employed to calculate the depth profile for a thin film LiNbO\(_3\) sputtered on Si (sample S11231). By guessing the concentration of the elements layer by layer to fit the curve of the RBS spectrum, a depth profile, as shown in Fig. 4.19, can be obtained without destroying the sample, which is normally the case if other surface analysis techniques, eg., AES, SIMS, etc., were employed. An ESCA depth profile\(^\dagger\) is shown in Fig. 4.20 for comparison. Only the RBS spectrum can be used to simulate the depth profile. Spectra of proton nuclear reaction analysis involve much complicated reactions, and thus a simulation program is not yet available. Therefore, the depth profile does not show the concentration of Li element.

\(^\dagger\)The ESCA depth profile was done by Peter Sobol at Perkin Elmer
Figure 4.18 1.5 MeV H\(^+\) RBS/NRA spectrum of a sputtered \(\text{LiNbO}_3/\text{Si}\) (sample S11231). \(\theta = 150^\circ\).

2.0 MeV \(\alpha\) RBS and 1.5 MeV proton RBS/NRA spectra of a \(\text{LiNbO}_3\) thin film sputtered (\(\text{Ar}/\text{O}_2=70/30, 50\text{W}\)) on a sapphire substrate are shown in Figs. 4.21 and 4.22, respectively, from which the chemical composition of the film is determined to be \(\text{Li}_{0.9}\text{NbO}_{2.9}\) (stoichiometric lithium niobate). The top of the Nb peak is very uniform and the back surface edge (at \(\sim 180\) channel) is very steep, which indicates that the film is homogeneous and there is no significant inter-diffusion between the interface. Figs. 4.23 and 4.24 were the spectra used to determine the chemical composition (\(\text{Li}_{2.1}\text{NbO}_{3.8}\)) of another sample sputtered using different parameters (\(\text{Ar}/\text{O}_2=60/40, 100\text{W}\)). The result is as expected because the film grown under the described conditions coexists with \(\text{Li}_3\text{NbO}_4\) and is thus not stoichiometric lithium niobate.

Fig. 4.25 shows the 2.0 MeV \(\alpha\) RBS spectrum of an MOD-derived \(\text{LiNbO}_3\) thin film on silicon substrate. The thin film was annealed in air at 650\(^\circ\text{C}\) for 60 minutes.
As shown in Fig. 4.25, the back surface edge of the Nb peak and the front surface edge of the Si substrate are not as steep as those in Fig. 4.17, which indicates that there is inter-diffusion at the interface. Rapid annealing was implemented to overcome this problem. Fig. 4.26 shows the RBS spectrum of an MOD-derived LiNbO₃ film on Si annealed in air at 650°C for 10 minutes. Although the technique of rapid annealing has eliminated inter-diffusion, the elements in the film tend to distribute non-uniformly. Figs. 4.27 and 4.28 show RBS and RBS/NRA spectra for an MOD-derived LiNbO₃ film on sapphire annealed at 600°C in air for 15 minutes. Slight inter-diffusion is still found in this sample although the processing temperature was decreased to 600°C. It was found that, for MOD process, the annealing temperature should be higher than 500°C in order to form crystalline films. Therefore, inter-diffusion seems to be very difficult to circumvent if furnace processing is used in MOD deposition.
Figure 4.20 ESCA depth profile of a thin film LiNbO$_3$ sputtered (Ar/O$_2$=60/40, 100 W) on Si substrate.

A novel method of photo-induced metallo-organic decomposition (PIMOD) was then developed to solve the problem of inter-diffusion as described previously. The α RBS spectrum of a PIMOD-derived LiNbO$_3$ film on Si substrate is shown in Fig. 4.29. Neither inter-diffusion nor inhomogeneity was observed in these films made by the PIMOD process.

The results of ion beam spectrometry analysis for sputtered films are tabulated in Table 4.3 and those for MOD- or PIMOD-derived films are tabulated in Table 4.4. The chemical composition of the films agrees with the XRD data and the H$_2$O$_2$ etching test. The thickness of each film calculated from the RBS spectra are also in good agreement with those measured by α-step profilometer or by interferometer although the discrepancy gets larger when the film is thicker, which is attributed to the failure of the surface energy approximation.
Figure 4.21 2.0 MeV He ion RBS spectrum of a sputtered $(Ar/O_2=70/30)$ LiNbO$_3$ film on a sapphire substrate.

Figure 4.22 1.5 MeV proton RBS/NRA spectrum of a sputtered $(Ar/O_2=70/30)$ LiNbO$_3$ film on a sapphire substrate.
Figure 4.23  2.0 MeV He ion RBS spectrum of a sputtered
(Ar/O₂=60/40) LiNbO₃ film on a sapphire substrate.

Figure 4.24  1.5 MeV proton RBS spectrum of a sputtered
(Ar/O₂=60/40) LiNbO₃ film on a sapphire substrate.
Figure 4.25 2.0 MeV He ion RBS spectrum of an MOD-derived (long annealing) LiNbO$_3$ film on a Si substrate.

Figure 4.26 2.0 MeV He ion RBS spectrum of an MOD-derived (rapid annealing) LiNbO$_3$ film on a Si substrate.
**Figure 4.27** 2.0 MeV He ion RBS spectrum of an MOD-derived LiNbO$_3$ film on a sapphire substrate.

**Figure 4.28** 1.5 MeV proton RBS spectrum of an MOD-derived LiNbO$_3$ film on a sapphire substrate.
Figure 4.29  2.0 MeV He ion RBS spectrum of a
PIMOD-derived LiNbO$_3$ film on a Si substrate.

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>Substrate</th>
<th>Ar/O$_2$</th>
<th>RF power</th>
<th>Composition</th>
<th>$t_{RBS}$ ($\mu$m)</th>
<th>$t_\alpha$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10304</td>
<td>(100) Al$_2$O$_3$</td>
<td>60/40</td>
<td>100 W</td>
<td>Li$<em>{1.8}$NbO$</em>{3.7}$</td>
<td>0.67</td>
<td>0.60</td>
</tr>
<tr>
<td>S10313</td>
<td>(100) Al$_2$O$_3$</td>
<td>60/40</td>
<td>75 W</td>
<td>Li$<em>{2.4}$NbO$</em>{3.6}$</td>
<td>0.68</td>
<td>0.60</td>
</tr>
<tr>
<td>S10320</td>
<td>(100) Al$_2$O$_3$</td>
<td>65/35</td>
<td>75 W</td>
<td>Li$<em>{2.2}$NbO$</em>{3.5}$</td>
<td>0.33</td>
<td>0.30</td>
</tr>
<tr>
<td>S10312</td>
<td>(100) Al$_2$O$_3$</td>
<td>70/30</td>
<td>75 W</td>
<td>Li$<em>{1.1}$NbO$</em>{3.2}$</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td>S10308b</td>
<td>(100) Al$_2$O$_3$</td>
<td>70/30</td>
<td>100 W</td>
<td>Li$<em>{1.2}$NbO$</em>{3.2}$</td>
<td>0.18</td>
<td>0.15</td>
</tr>
<tr>
<td>S10308a</td>
<td>(100) Al$_2$O$_3$</td>
<td>70/30</td>
<td>50 W</td>
<td>Li$<em>{0.9}$NbO$</em>{3.0}$</td>
<td>0.35</td>
<td>0.30</td>
</tr>
<tr>
<td>S10401</td>
<td>(100) Al$_2$O$_3$</td>
<td>80/20</td>
<td>100 W</td>
<td>Li$<em>{2.7}$NbO$</em>{5.4}$</td>
<td>0.17</td>
<td>0.15</td>
</tr>
<tr>
<td>S20224</td>
<td>(110) Al$_2$O$_3$</td>
<td>70/30</td>
<td>50 W</td>
<td>Li$<em>{0.9}$NbO$</em>{2.9}$</td>
<td>0.65</td>
<td>0.50</td>
</tr>
<tr>
<td>S11216</td>
<td>(012) Al$_2$O$_3$</td>
<td>60/40</td>
<td>75 W</td>
<td>Li$<em>{2.1}$NbO$</em>{3.8}$</td>
<td>0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>S11231</td>
<td>(111) Si</td>
<td>60/40</td>
<td>100 W</td>
<td>Li$<em>{1.1}$NbO$</em>{3.1}$</td>
<td>0.19</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 4.4  RBS results of MOD- or PIMOD-derived LiNbO$_3$ films. $t_{RBS}$, $t_\alpha$, and $t_{\text{in}}$ are thickness measured by RBS, $\alpha$-step profilometer, and interferometer.

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>Substrate</th>
<th>Process</th>
<th>Temperature</th>
<th>Composition</th>
<th>$t_{RBS}$ ($\mu$m)</th>
<th>$t_\alpha$ ($\mu$m)</th>
<th>$t_{\text{in}}$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M10517</td>
<td>(111) Si</td>
<td>MOD</td>
<td>650°C</td>
<td>Li$<em>{1.3}$NbO$</em>{2.2}$</td>
<td>0.20</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td>M20123D</td>
<td>(012) Al$_2$O$_3$</td>
<td>MOD</td>
<td>600°C</td>
<td>Li$<em>{1.2}$NbO$</em>{3.1}$</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>P20124A</td>
<td>(111) Si</td>
<td>PIMOD</td>
<td>500°C</td>
<td>Li$<em>{1.1}$NbO$</em>{3.0}$</td>
<td>0.20</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td>P20124M</td>
<td>(110) Al$_2$O$_3$</td>
<td>PIMOD</td>
<td>500°C</td>
<td>Li$<em>{1.0}$NbO$</em>{2.9}$</td>
<td>0.19</td>
<td>0.18</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Chapter 5

Optical Waveguides and Electrooptic Effect

5.1 Optical waveguide

The dielectric planar slab waveguide \([111, 112]\) is the simplest light guide which is used to confine and guide the light in the devices and circuits of integrated optics. It is constructed by using at least three layers. The layer, which is usually a planar thin film, with the highest refractive index \(n_f\) is sandwiched between a cover and a substrate material with lower indices of refraction \(n_e\) and \(n_s\) \((n_f \geq n_s \geq n_e)\). In most cases the cover material is air \((n_c = 1.0)\). Since LiNbO\(_3\) \((n_c \approx 2.3, n_e \approx 2.2)\) is used as the waveguide in our work, a substrate with low refractive index, such as sapphire \((n \approx 1.77)\), is required. If the film is to be made on a material with a refractive index higher than that of the film (e.g., \(n_{\text{silicon}} = 3.83\)), a buffer layer (e.g., \(n_{\text{SiO}_2} = 1.46\) or \(n_{\text{Si}_3\text{N}_4} = 2.00\)) must be formed between the waveguide and silicon substrate.

5.2 Prism coupling

To evaluate the propagation characteristics of dielectric thin film waveguides, light coupling into waveguide is necessary. A variety of couplers, as shown in Fig. 5.1, have been utilized for converting the optical energy of the laser beam into one (or multi) guided mode in the thin film layer. End-fire coupling \([112]\) is the most intuitive method for mode launching, but a finely tunable micropositioner is required to correctly align the beam. The prism coupler, which has been discussed by Tien et
al. [113], has the advantage of versatility, one single unit being adaptable to many samples and to different type of films. The grating coupler, which was first discussed by Dakass et al. [114], is beautifully adapted to the integrated circuit format with superior ruggedness and stability. Prism coupling has been the primary coupling tool used in this study. A detailed discussion of prism coupling was given in my master's thesis [116], and is briefly reviewed here.

Fig. 5.2 shows a modified prism coupler used in this work. Thin film spacers have been used to create a linearly tapered air gap so that when the incident wave is totally reflected at the base of the prism, the evanescent wave can couple into the guided wave with a high coupling efficiency. The prism coupler is equipped with a goniometer to allow for fine-adjustment of the incident angle δ. If and only if the incident beam is in the synchronous direction, a guided mode can be build up due to phase matching, and a streak of guided light is observed.

### 5.3 Mode characteristics

The effective mode index $N_m$ can be calculated from the corresponding synchronous angle:

$$\delta_m = \sin^{-1}\left[\frac{n_p}{n_c} \sin(\sin^{-1}\left(\frac{N_m}{n_p}\right) - \alpha_c)\right],$$  \hspace{1cm} (5.1)

where $\delta_m$ is the synchronous angle of the $m$-th guided mode, $n_p$ and $n_c$ are the refractive indices of the prism and the cover (air), respectively, and $\alpha_c$ is the corner angle of the prism.

For a three-layer planar waveguide ($n_2 > n_3 > n_1$), the index $n_2$ and the thickness $t$ of the film can then be determined by the equations given as follows provided at least two effective mode indices are measured [117]:
Figure 5.1 Schematic of three techniques of transforming freely propagating wave into guided wave in thin film. (a) End-fire coupler. (b) Prism coupler. (c) Grating coupler.
Figure 5.2  Schematic of a modified prism coupler.
\[
\tan ht = \frac{p + q}{h(1 - pq/h^2)}
\] (5.2)

for TE modes, and
\[
\tan ht = \frac{h(\bar{p} + \bar{q})}{h^2 - \bar{p}\bar{q}}
\] (5.3)

for TM modes, where
\[
q = k\sqrt{N_m^2 - n_1^2},
\]
\[
h = k\sqrt{n_2^2 - N_m^2},
\]
\[
p = k\sqrt{N_m^2 - n_3^2},
\] (5.4)
\[
\bar{p} = pn_2^2/n_3^2,
\]
\[
\bar{q} = qn_2^2/n_1^2.
\]

Figure 5.3 Plot of effective mode index \(N_m\) vs. waveguide thickness \(t\) of a LiNbO\(_3\) film deposited on a thermally oxidized Si substrate, assuming the film is isotropic.

The plots of effective mode index vs. waveguide thickness for both TE and TM waves for some waveguide structures are shown in Figs. 5.3-5.5. In Fig. 5.3 the film
Figure 5.4  Plot of effective TE mode index $N_m$ vs. waveguide thickness $t$ of an epitaxial LiNbO$_3$ film deposited on a (110) or (100) sapphire substrate. The c axis of the film is in the plane of incidence.

is assumed to be isotropic, while in Figs. 5.4 and 5.5 it is assumed to be anisotropic, and the c axis of the film is in the plane of incidence such that $n_{TE}=n_o$ and $n_{TM}=n_e$. These curves are the mode characteristics of the waveguide, which will be outlined as follows:

1. The effective mode index $N_m$ is in the range from the refractive index of the substrate ($n_s$) to that of the film ($n_f$).

2. When the waveguide thickness $t$ is large, the effective mode index approaches the refractive index of the film ($n_f$). When $N_m \to n_f$, the film can be considered as thick as a bulk material, and all the optical energy is confined within the waveguide.
3. On the contrary, as $N_m \rightarrow n_s$, the guided mode is cut off, and $t$ is the minimum thickness of the waveguide that still support the guided mode. The cutoff thickness is thus an important factor to be considered in waveguide fabrication.

4. As $t$ decreases, the effective mode index also decreases from $n_f$ to $n_s$, and the optical fields more and more extend outside the waveguide. Hence, the propagation loss is expected to be higher as the film thickness decreases.

The mode equation (or eigenvalue equation) for four-layer planar waveguides is much more complex than Eqs. 5.2 and 5.3. For example, considering TE mode solutions, the mode equation is given by [118]

$$
(p+is)[(h^2-pq)\tan(ht)-h(p+q)]+e^{-2ptv(p-is)}[(h^2+pq)\tan(ht)+h(p-q)] = 0, \quad (5.5)
$$
where \( t_b \) is the thickness of the buffer layer, \( p, h, \) and \( q \) are the same as given in Eq. 5.4, and
\[
s = k \sqrt{n_4^2 - N_m^2} = \sqrt{k^2 n_4^2 - \beta^2}.
\] (5.6)

To the limit that the buffer layer is infinitely thick, the second addend disappears, leaving an equation exactly the same with Eq. 5.2, i.e., the four-layer planar waveguide can now be treated as a three-layer waveguide.

In practice, the thickness of the buffer layer is on the order of a few thousand angstroms. In the case that the buffer layer provides a good confinement to the optical field within the film, the evanescent field only slightly extends to the buffer layer such that the propagation constant \( \beta \) only slightly deviates from the value \( \beta_\infty \), which is a solution to the limit case of Eq. 5.5, i.e., Eq. 5.2. Stutius and Streifer [119] suggested that the change in propagation constant, \( \delta \beta \), from the three-layer solution due to the presence of the fourth layer can be expressed, using a first-order perturbation approximation in the propagation constant, by
\[
\delta \beta = \beta - \beta_\infty = \frac{2(p - is)h^2p}{(p + is)(h^2 + p^2)w}e^{-2pt_b},
\] (5.7)

where \( w \) is the effective waveguide thickness:
\[
w = t + \frac{1}{p} + \frac{1}{q}.
\] (5.8)

In cases of \( \text{Im}[s] \ll \text{Re}[s] \), Eq. 5.7 can be separated into two parts to first order
\[
\Re[\delta \beta] = \frac{2(p^2 - s^2)h^2p}{(p^2 + s^2)(h^2 + p^2)w}e^{-2pt_b}
\] (5.9)

and
\[
\Im[\delta \beta] = -\frac{4h^2ps}{(p^2 + s^2)(h^2 + p^2)w}e^{-2pt_b}.
\] (5.10)

Eq. 5.9 is a correction to the three-layer effective mode index \( N_m = \beta/k \), and Eq. 5.10 represents attenuation due to energy leakage through the buffer layer into the substrate. As a \( \text{SiO}_2 \) buffer layer thickness design guide, Nishihara et al. [120]
have given a plot, as shown in Fig. 5.6, of calculated minimum SiO$_2$ buffer layer thickness required to reduce the leakage loss of waveguides on SiO$_2$/Si substrate to 0.1 dB/$10^4\lambda$ ($\sim$ 0.1 dB/cm).

![Figure 5.6](image.png)

**Figure 5.6** Minimum SiO$_2$ buffer layer thickness required to reduce the leakage loss of waveguides on SiO$_2$/Si substrate to 0.1 dB/$10^4\lambda$ [120].

### 5.4 Optical characterization by prism coupling

The modified prism coupler shown schematically in Fig. 5.2 was implemented to measure refractive indices, thicknesses, and propagation losses of the waveguides. A polarized He-Ne laser beam with a wavelength of 6328 Å was coupled into the waveguide by a 45°-45°-90° rutile prism. The output of the laser was detected, after reflection through the bottom face of the prism, by measuring the current from a silicon photosensor. The rutile prism was mounted on a turntable equipped with a precision x-y micropositioner. The angles between the laser beam and the normal
to the prism face were read from the turntable to a precision of ± 1 minute of arc. The sample was pushed against the prism by a pneumatically-controlled piston. The pressure was adjusted by a pressure regulator. Measurements were made by loading the sample against the prism and rotating the turntable until coupling occurred as shown by a minimum in the power meter. The angle was recorded and the rotation continued until all the modes that the present system could couple into the film were found.

By properly choosing the incident angle, the phase matching condition can be achieved and therefore the propagation constant of the incident light can be made equal to that of the mode in the waveguide. The equation relating the incident angle and the propagation constant is given by Eq. 5.1. Since \( n_p, n_c, \) and \( \alpha_c \) are already known and \( \delta_m \) can be measured, the propagation constant can then be calculated by Eqs. 5.2 and 5.3. If two or more guided modes are observed, the thickness \( t \) and the refractive index \( n_f \) of the waveguides can be evaluated by these mode condition equations. For example, plots of the reflected intensity vs. incident angle (\( \delta \)) for a sputtered LiNbO\(_3\)/(012)Al\(_2\)O\(_3\) multi-mode waveguide and a sputtered LiNbO\(_3\)/(100)Al\(_2\)O\(_3\) single-mode waveguide are shown in Figs. 5.8 through 5.9, in which the bottoms of the dips correspond to the mode (or synchronous) angles. Since a single-mode waveguide does not provide enough data for simultaneously determining the thickness and the refractive index of the waveguide, the waveguide thickness has to be measured by other methods. In this case, the thickness of the films was either estimated by a color chart [115] or measured by a Tencor \( \alpha \)-step 200 profilometer*. The measured thickness was then used to calculated the refractive index of the single-mode

*Thanks are due to Dr. N.J. Wu (Space Physics and Epitaxy Center at University of Houston) for letting me use the \( \alpha \)-step profilometer
Figure 5.7  TM guided modes prism-coupled into a LiNbO$_3$/(012) Al$_2$O$_3$ waveguide.

Figure 5.8  TE guided modes prism-coupled into a LiNbO$_3$/(012) Al$_2$O$_3$ waveguide.
waveguide. The $\alpha$-step thickness profile of a sputtered LiNbO$_3$/(100) Al$_2$O$_3$ waveguide is shown in Fig. 5.10 as an example. From the thickness profiles, it was found that the surface of the films was very smooth, which greatly reduced the optical scattering loss at the surface of the films. The thickness and refractive indices corresponding to both TE and TM guided modes of various LiNbO$_3$ optical waveguides are tabulated in Table 5.1. The refractive indices and the thickness of the LiNbO$_3$ thin films measured by prism coupling technique are in good agreement with the values of the single crystal LiNbO$_3$ and the thickness measured by $\alpha$-step profilometer.

For evaluating propagation attenuation in the waveguide, both a fiber probe and a camera have been used to detect the surface scattered light from the waveguide. Discussion of the details of these techniques were given elsewhere [116]. Figs. 5.11 and 5.12 are pictures of waveguiding in the lithium niobate films on a sapphire and a SiO$_2$, respectively. Figs. 5.13 through 5.16 show the results of the attenuation measurement for several LiNbO$_3$ optical waveguides. The lowest value of propagation
Figure 5.10  The $\alpha$-step thickness profile of a sputtered LiNbO$_3$/(100) Al$_2$O$_3$ waveguide.

losses of each waveguide is given in Table 5.2, in which propagation losses published by other researchers are also listed for comparison.

5.5  Electrooptic effect

The electrooptic effect in the LiNbO$_3$ films has been observed and the electrooptic coefficient was calculated by measuring the birefringence shift of the LiNbO$_3$ films due to an applied electric field using a phase-modulation detection technique. Fig. 5.18 shows the experimental setup for the measurement of electrooptic modulation.

Planar interdigital electrodes of aluminum or gold have been tried to deposit by thermal evaporation on the film surfaces. However, these materials did not adhere well on the surface of LiNbO$_3$. Therefore, a chromium layer with a thickness of 40 nm was used to hold the gold electrodes and the LiNbO$_3$ thin films together. The thickness of the gold layer is about 100 nm. The electrode width and the spacing are
10 μm such that a sufficiently large electric field can be easily applied to the thin film without dielectric breakdown. A dc voltage was applied across the electrodes.

The electrode pattern was fabricated by photolithography as shown in Fig. 5.19. Shipley S1400-25 positive photoresist was uniformly spun on the surface of the gold layer with a spinning rate of 4000 rpm for 25 sec. The resist was dried by baking at 90°C for 30 minutes. After aligning the mask, the sample was exposed with a 100 W mercury vapor lamp (UV light) for 22 sec. Development was processed in a two-bath developer (Shipley MF 320). Post-baking was done at 100°C for 30 minutes to increase the strength of the photoresist. The gold layer was chemically etched by a solution of 40 g of KI and 10 g of I2 in 400 ml H2O with an etching rate of about 10 Å/sec and the chromium layer was etched by a solution of 150 g Ce(NH4)2(NO3)6 and 35 C2H4O2 in 1 liter of H2O with an etching rate of about 10 Å/sec. The sample was rinsed with DI water for 10 minutes to remove all the chemicals. The photoresist was then removed by Shipley S1165 remover.

The incident He-Ne light (λ = 6328Å) was linearly polarized at 45° with respect to the Z direction. The quarter wave plate was initially set at $\theta = 45^\circ$, where $\theta$ is the angle between the c axis of the quarter wave plate and the X axis, so that the two split beams had the same intensity, therefore the power meter of the lock-in amplifier (using differential mode) was preset to zero. The sample was then placed at the sample holder with the c axis of the film parallel to the Z direction. Since both the LiNbO3 film and the sapphire substrate are uniaxial crystals, a phase retardation results when the light wave passes through the sample. The quarter wave plate was rotate to an angle $\theta_1$ to balance the two split beams. The Cr(400Å)/Au(1000Å) electrodes were so deposited that the electric field can be applied along the c axis of the film. After application of the electric field, the quarter wave plate was rotate to
another angle $\theta_2$ to restore the polarization. The electrooptic retardation, $\Delta \phi$, in the film could be detected by the lock-in amplifier and calculated from $\Delta \theta (= \theta_2 - \theta_1)$ by the following equation

$$\Delta \phi = \frac{2 \sin 2\theta}{1 + \cos^2 2\theta} \Delta \theta.$$  \hspace{1cm} (5.11)

The relation between the electrooptic retardation and the field induced birefringence shift in the film, $\Delta(\Delta n) = \Delta n_o - \Delta n_e$, was discussed in detail by Yariv [124] and is given by

$$\Delta n = \frac{\lambda \Delta \phi}{2\pi t},$$  \hspace{1cm} (5.12)

where $\lambda$ is the wavelength of the incident light and $t$ is the film thickness. The change in birefringence, $\Delta(\Delta n)$, measured with and without the applied field can then be used to determine the linear electrooptic coefficients. Assuming the electrooptic effect in the substrate is negligible, the field-induced birefringence in the LiNbO$_3$ film can be given by

$$\Delta n_o = -\frac{1}{2} r_{13} n_o^3 E$$ \hspace{1cm} (5.13)

and

$$\Delta n_e = -\frac{1}{2} r_{33} n_e^3 E.$$ \hspace{1cm} (5.14)

Therefore, we have

$$(r_{33} n_e^3 - r_{13} n_o^3)E = 2\Delta(\Delta n).$$ \hspace{1cm} (5.15)

Because the smallest retardation which could be measured by the quarter wave plate was 5 seconds of arc, the film should be sufficiently thick to provide a phase retardation over the detection limit. A 5-layer PIMOD-processed LiNbO$_3$ film was deposited on a (110) sapphire substrate for the birefringence measurement. The thickness of the film was measured by an $\alpha$-step profilometer to be about 0.7 $\mu$m.
XRD data, as shown in Fig. 3.26, and x-ray Laue pattern show that the film is epitaxial with its c axis oriented along the c axis of the sapphire substrate.

The birefringence measurement as a function of applied electric field was made for the LiNbO$_3$ film and the experimental results were plotted in Fig. 5.20. The data show a very small hysteresis and parabolic curves instead of a straight line. The hysteresis might be due to stress strain [125] caused by lattice mismatch, and the parabolic curves might be attributed to the electrode heating effect. The birefringence shift was $-0.0008$ at an applied electric field of 20 kV/mm. Assuming the ratio of $r_{33}/r_{13}$ in the film equals that in the bulk material, the electrooptic coefficients $r_{33}$ and $r_{13}$ were calculated to be $10.7 \times 10^{-12}$ m/V and $3.0 \times 10^{-12}$ m/V, respectively. Although the EO coefficient $r_{33}$ of the LiNbO$_3$ thin film is only about one third of the bulk value, it is much higher than the published value ($1.34 \times 10^{-12}$ m/V in polycrystalline LiNbO$_3$ sputtered on Corning 7059 glass, [75]) attained to date. The LiNbO$_3$ thin films were found to be fine grained ferroelectrics by SEM and TEM analysis. For fine grained ferroelectrics, the ferroelectricity inside the grain is shielded by the field of interface charge, which decreases the efficiency of the applied field to the ferroelectricity. Therefore, a weaker electrooptic effect, which is based on polarization reversal, is expected for thin film (fine grained) ferroelectrics.
<table>
<thead>
<tr>
<th>ID</th>
<th>Substrate</th>
<th>Process</th>
<th>$n_f (\pm 0.002)$</th>
<th>$t (\pm 0.001 \mu m)$</th>
<th>$t_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0214</td>
<td>(012) Al$_2$O$_3$</td>
<td>sputtering</td>
<td>$n_{TE} = 2.224$</td>
<td>$t_{TE} = 0.578 \mu m$</td>
<td>$0.56 \mu m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$n_{TM} = 2.228$</td>
<td>$t_{TM} = 0.580 \mu m$</td>
<td></td>
</tr>
<tr>
<td>S11218</td>
<td>(110) Al$_2$O$_3$</td>
<td>sputtering</td>
<td>$n_o = 2.310$</td>
<td>$t_{TE} = 0.612 \mu m$</td>
<td>$0.60 \mu m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$n_e = 2.249$</td>
<td>$t_{TM} = 0.627 \mu m$</td>
<td></td>
</tr>
<tr>
<td>S10398ah</td>
<td>(100) Al$_2$O$_3$</td>
<td>sputtering</td>
<td>$n_o = 2.293$</td>
<td>$t_{TE} = 0.310 \mu m$</td>
<td>$0.30 \mu m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$n_e = 2.223$</td>
<td>$t_{TM} = 0.317 \mu m$</td>
<td></td>
</tr>
<tr>
<td>S20103</td>
<td>(100) Al$_2$O$_3$</td>
<td>sputtering</td>
<td>$n_o = 2.301$</td>
<td></td>
<td>$0.21 \mu m$</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>$n_e = 2.230$</td>
<td></td>
<td></td>
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<td>S01219</td>
<td>SiO$_2$/(100)Si</td>
<td>sputtering</td>
<td>$n_{TE} = 2.199$</td>
<td>$t_{TE} = 0.638 \mu m$</td>
<td>$0.62 \mu m$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$n_o = 2.156$</td>
<td>$t_{TM} = 0.302 \mu m$</td>
<td>$0.30 \mu m$</td>
</tr>
<tr>
<td>M10701</td>
<td>(012) Al$_2$O$_3$</td>
<td>MOD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P20214M</td>
<td>(110) Al$_2$O$_3$</td>
<td>PIMOD</td>
<td>$n_o = 2.271$</td>
<td></td>
<td>$0.18 \mu m$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$n_e = 2.206$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1  Thicknesses and refractive indices of the lithium niobate thin films deposited on various substrates. $t_o$ is the thickness measured by an $\alpha$-step thickness profilometer.

<table>
<thead>
<tr>
<th>Group</th>
<th>Year</th>
<th>Substrate</th>
<th>Process</th>
<th>Ref. indices (633 nm)</th>
<th>Losses (633 nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huang</td>
<td>1991</td>
<td>(100) sapphire</td>
<td>sputtering</td>
<td>$n_o = 2.293, n_e = 2.223$</td>
<td>0.9 dB/cm</td>
<td></td>
</tr>
<tr>
<td>Huang</td>
<td>1991</td>
<td>(110) sapphire</td>
<td>sputtering</td>
<td>$n_o = 2.310, n_e = 2.249$</td>
<td>1.0 dB/cm</td>
<td></td>
</tr>
<tr>
<td>Huang</td>
<td>1990</td>
<td>(001) sapphire</td>
<td>sputtering</td>
<td>$n_o = 2.322, n_e = 2.263$</td>
<td>1.1 dB/cm</td>
<td>[77]</td>
</tr>
<tr>
<td>Huang</td>
<td>1989</td>
<td>(012) sapphire</td>
<td>sputtering</td>
<td>$n_{TE} = 2.312$</td>
<td>1.7 dB/cm</td>
<td>[77]</td>
</tr>
<tr>
<td>Huang</td>
<td>1989</td>
<td>2.5 µm SiO$_2$/Si</td>
<td>sputtering</td>
<td>$n_{TE} = 2.199$</td>
<td>1.9 dB/cm</td>
<td></td>
</tr>
<tr>
<td>Huang</td>
<td>1991</td>
<td>(012) sapphire</td>
<td>MOD</td>
<td>$n_{TE} = 2.156$</td>
<td>2.8 dB/cm</td>
<td></td>
</tr>
<tr>
<td>Huang</td>
<td>1992</td>
<td>(110) sapphire</td>
<td>PIMOD</td>
<td>$n_o = 2.271, n_e = 2.206$</td>
<td>2.2 dB/cm</td>
<td></td>
</tr>
<tr>
<td>Sohler</td>
<td>1989</td>
<td>LiNbO$_3$</td>
<td>Ti in-diffusion</td>
<td></td>
<td>0.03 dB/cm</td>
<td>[90]</td>
</tr>
<tr>
<td>Buchal</td>
<td>1987</td>
<td>LiNbO$_3$</td>
<td>ion implantation</td>
<td>$\Delta n = +0.030$</td>
<td>1 dB/cm</td>
<td>[121]</td>
</tr>
<tr>
<td>Miyazawa</td>
<td>1975</td>
<td>LiTaO$_3$</td>
<td>Nb in-diffusion</td>
<td>$n_{TE} = 2.188$</td>
<td>1 dB/cm</td>
<td>[122]</td>
</tr>
<tr>
<td>Griffel</td>
<td>1989</td>
<td>Corning 7059</td>
<td>sputtering</td>
<td>$n = 2.1 - 2.3$</td>
<td>&lt; 2 dB/cm</td>
<td>[75]</td>
</tr>
<tr>
<td>Hewig</td>
<td>1982</td>
<td>Corning 7059, 7740</td>
<td>sputtering</td>
<td>$n = 2.1 - 2.3$</td>
<td>3 dB/cm</td>
<td>[69]</td>
</tr>
<tr>
<td>Miyazawa</td>
<td>1975</td>
<td>LiTaO$_3$</td>
<td>LPE</td>
<td>$n_o = 2.2884, n_e = 2.1914$</td>
<td>5 dB/cm</td>
<td>[122]</td>
</tr>
<tr>
<td>Okada</td>
<td>1976</td>
<td>LiTaO$_3$</td>
<td>sputtering</td>
<td>$n = 2.318$</td>
<td>8 dB/cm</td>
<td>[68]</td>
</tr>
<tr>
<td>Takada</td>
<td>1974</td>
<td>(001) sapphire</td>
<td>sputtering</td>
<td>$n_o = 2.32, n_e = 2.18$</td>
<td>9 dB/cm</td>
<td>[66]</td>
</tr>
<tr>
<td>Tien</td>
<td>1974</td>
<td>LiTaO$_3$</td>
<td>EGM</td>
<td>$n_o = 2.288, n_e = 2.207$</td>
<td>10 dB/cm</td>
<td>[123]</td>
</tr>
<tr>
<td>Betts</td>
<td>1985</td>
<td>Z-cut sapphire</td>
<td>MBE</td>
<td>$n = 2.2 - 2.3$</td>
<td>16 dB/cm</td>
<td>[78]</td>
</tr>
<tr>
<td>Curtis</td>
<td>1975</td>
<td>LiTaO$_3$</td>
<td>CVD</td>
<td></td>
<td>40 dB/cm</td>
<td>[51]</td>
</tr>
</tbody>
</table>

Table 5.2  Comparison of optical properties of various LiNbO$_3$ optical waveguides.
Figure 5.11  A 633 nm laser light was guided in a sputtered LiNbO$_3$ film on a (100) Al$_2$O$_3$ substrate.

Figure 5.12  A 633 nm laser light was guided in a sputtered LiNbO$_3$ film on a SiO$_2$/Si substrate.
Figure 5.13 Surface-scattered light of the guided mode in a sputtered LiNbO$_3$/(110)Al$_2$O$_3$ waveguide vs. the waveguide length.

Figure 5.14 Surface-scattered light of the guided mode in a sputtered LiNbO$_3$/(100)Al$_2$O$_3$ waveguide vs. the waveguide length.
Figure 5.15 Surface-scattered light of the guided mode in a sputtered LiNbO$_3$/SiO$_2$/Si waveguide vs. the waveguide length.

Figure 5.16 Surface-scattered light of the guided mode in an MOD-processed LiNbO$_3$/(012)Al$_2$O$_3$ waveguide vs. the waveguide length.
Figure 5.17 Surface-scattered light of the guided mode in a PIMOD-processed LiNbO$_3$/(110)Al$_2$O$_3$ waveguide vs. the waveguide length.

Figure 5.18 Experimental setup for measuring electric-field-induced birefringence shift in a thin film.
Figure 5.19  Photolithographic process for making electrodes.
**Figure 5.20** Electric-field-induced birefringence shift in a PIMOD-processed LiNbO$_3$/(110)Al$_2$O$_3$ thin film.
Chapter 6

Conclusions

In optical computing, information is carried by optical waves and stored in holographic form, and logical operations are carried out by optical logic gates. Is it possible to integrate holograms with other optical elements on a single wafer, especially a semiconductor substrate, such that optical computers can be implemented in a reasonable size? Today, millions of different electronic logic gates can be integrated on a single chip. Design of optical computers should take account of the experience obtained from electronic computer engineering. Before 1960, building an optical computer seemed impossible because of no appropriate light source. The invention of the laser made light propagation in solid materials without significant power consumption realizable, and the concept of "integrated optics" was then developed. In the early 1970's, a number of integrated waveguide devices were implemented. However, fabrication of these devices by the in-diffusion and proton exchange techniques had to start with transparent single crystal substrates, such as LiNbO$_3$ and LiTaO$_3$, and was not compatible with the semiconductor microelectronic technology. Recently, significant progress has been reported on several thin film coating techniques, and it is now possible to deposit high optical quality thin films on semiconductor substrates, on which light sources, photodetector arrays, and integrated waveguide devices can be integrated together.
Integration of thin film lithium niobate on various substrates, such as sapphire, silicon, and silicon dioxide on silicon wafers, gives the possibility of numerous devices. An MFS structure transistor has been implemented by Rost [3] in this research group, which can operate either electrically (based on ferroelectric switching) or optically (based on bulk photovoltaic effect). Electrical properties of the lithium niobate thin films sputtered on silicon substrates have been fully investigated by Rost. This work has concentrated more on fabrication and characterization of lithium niobate thin film optical waveguide devices.

For the development of integrated optics the fabrication of low loss waveguides is of primary importance. Single crystal sapphire disks were used to grow epitaxial lithium niobate films in which the electrooptic effect can be observed using a transmission phase modulation geometry. Silicon wafers were used for depositing low loss optical waveguides which offer the possibility of combining integrated optic and microelectronic devices on a single wafer. The use of magnetron rf sputtering and metallo-organic decomposition methods for the deposition of high optical quality thin films of lithium niobate has been investigated.

Magnetron rf sputtering is a rather complex process involving control of several parameters. The properties of thin films of lithium niobate grown by sputtering are very parameter-dependent. Formation of other undesirable lithium niobium oxide compounds was found if sputtering parameters deviate from certain values. Optimal sputtering parameters were determined by a matrix of experiments. The optimal conditions for making stoichiometric lithium niobate thin film optical waveguides on silicon, including silicon dioxide, substrates were tabulated in Table 6.1 and those for making lithium niobate optical waveguides on sapphire substrates were in Table 6.2. Although 100 W was generally used in making lithium niobate films for electrical
devices, 50 W is recommended for growing low loss waveguides. A low deposition rate (low rf power) gives the deposited crystallites sufficient time to relax to the epitaxial orientation. Moreover, the films made with a low rf power have a smaller grain size and less defects, and thus have a more uniform surface which results less optical scattering in the waveguides. A lower processing temperature of 500°C (compared to 600°C which was previously used before) has been used to be more compatible with the molybdenum liftoff process used in fabrication of the transistor, and good quality film could still be made under this condition.

A three-stage sputtering process is proposed to modify the regular sputtering process for better epitaxial growth. Thin films of lithium niobate grown by the three-stage sputtering show that epitaxial growth via this modified version of sputtering process is more repeatable than the regular method although more experiments have to be performed before the conclusion can be made.

Grain orientation of the as-sputtered lithium niobate thin films has been examined by Bragg x-ray diffraction and Laue method. The films sputtered on (012), (001), (100), and (110) sapphire substrates were epitaxial, and those on (111) silicon were oriented with the c axis normal to the surface. The films grown on SiO₂/(100)Si substrates were normally slightly random-oriented, but have a preferred orientation along the (104) direction, which is probably due to the amorphous nature of the SiO₂ buffer layer and the significant lattice mismatch. Laue pattern was very difficult to observe for most of the films because the film thickness was too thin. In this case, prism coupling can be used to determine the orientation of the optical axis since the birefringence shift reaches maximum if the c axis of the film is in the plane of incidence.
Table 6.1  Optimized parameters for sputtering LiNbO$_3$ optical waveguides on SiO$_2$/Si substrates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target composition</td>
<td>99.99995% LiNbO$_3$ powder</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>Ar/O$_2$ (60%:40%)</td>
</tr>
<tr>
<td>Target-substrate spacing</td>
<td>5 cm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>500°C</td>
</tr>
<tr>
<td>Forward rf power</td>
<td>50 W</td>
</tr>
<tr>
<td>Reflected rf power</td>
<td>0 W</td>
</tr>
<tr>
<td>Sputtering pressure</td>
<td>2-3 mTorr</td>
</tr>
</tbody>
</table>

Table 6.2  Optimized parameters for sputtering LiNbO$_3$ optical waveguides on sapphire substrates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target composition</td>
<td>99.99995% LiNbO$_3$ powder</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>Ar/O$_2$ (70%:30%)</td>
</tr>
<tr>
<td>Target-substrate spacing</td>
<td>5 cm</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>500°C</td>
</tr>
<tr>
<td>Forward rf power</td>
<td>50 W</td>
</tr>
<tr>
<td>Reflected rf power</td>
<td>0 W</td>
</tr>
<tr>
<td>Sputtering pressure</td>
<td>2-3 mTorr</td>
</tr>
</tbody>
</table>

The sputtered films were stoichiometric and homogeneous as shown by RBS, SIMS, and ESCA. The grain size was determined by TEM to be in the range of 0.01-0.05 $\mu$m [3]. The dielectric constant and the resistivity of the sputtered lithium niobate films were 34.5 and $5 \times 10^{12}$ $\Omega$-cm calculated from C-V and I-V measurements, respectively.

Prism coupling has been demonstrated, and the optical properties including refractive index and propagation losses have been determined for every optical waveguide structure. The refractive index of the films was determined to be in the range of 2.1 to 2.3 which is very close to the bulk value. The lowest propagation loss in the lithium niobate waveguides on sapphire substrates has been measured to be 0.9 ± 0.1 dB/cm and that in the waveguides on SiO$_2$/Si substrates has been determined to be 1.9 ± 0.1 dB/cm. The values of the propagation loss are the lowest attained so far.
in the literature. Waveguides with such a low loss fulfill the requirement for signal transmission and thus can be readily used to satisfactorily interconnect optoelectronic and microelectronic devices in an integrated technology.

The MOD process is a relatively simple process in comparison with sputtering. Since the formulation solution is a true solution, the stoichiometry of the lithium niobate films made with MOD has been very good as measured by ion beam spectrometry. However, inter-diffusion and cracking have been the two major problems which are difficult to overcome if a conventional furnace processing is used to induce the decomposition. A novel technique termed photo-induced metallo-organic decomposition (PIMOD) has been developed to solve these problems. Using tungsten halogen lamps, the PIMOD process can supply more of the required UV and IR photons and thus evaporation of solvent, decomposition of metallo-organic compounds, oxidation of films, and even crystallization can all be done very efficiently in one single shot. Low processing temperature (500°C) and short processing time (5 min) make PIMOD an ideal method for mass production.

XRD data show that the lithium niobate films made by either MOD or PIMOD were epitaxial on sapphire and randomly oriented on silicon. For the MOD-derived films fired at 600°C, the microstructure was very uniform and dense with grain size of approximately 0.09 μm*, and the transmittance was greater than 95% in the visible light region. For those fired at 700°C or higher, porosity began to develop due to grain growth into a large size of approximately 0.13 μm, and the films began to look opaque and milk-white. The PIMOD-derived films processed at 500°C have similar properties as the MOD films fired at 650°C, except the transparency is better for the PIMOD films.

*The grain size of the LiNbO₃ was estimated by Y. Tao at University of Texas at Austin using SEM.
The dielectric constant and the resistivity of the MOD- or PIMOD-processed films were measured to be 34 and $5 \times 10^{13}$ Ω·cm. The resistivity of the MOD and PIMOD films is one order higher than the sputtered films. It is probably because that the sputtered films have more ions which could be easily driven by an applied electric field.

This is the first time that waveguiding has been successfully demonstrated in the MOD- and PIMOD-derived lithium niobate thin film optical waveguides. Prism coupling was utilized to couple a He-Ne laser light into the waveguides. The refractive index of the waveguides made by MOD or PIMOD was determined to be in the range of 2.1 to 2.3, and the propagation loss in the waveguide deposited on sapphire was estimated to be $2.2 \pm 0.1$ dB/cm. Prism coupling into lithium niobate optical waveguides MOD-deposited on SiO$_2$/Si has not yet observed, and the investigation is still proceeding. Optical quality of MOD or PIMOD films was found to be comparable to that of sputtered lithium niobate films. However, the prism coupling discussed here was performed using single layer MOD (or PIMOD) films. Multilayer MOD films have a more non-uniform surface and thus prism coupling is not easy on these thick samples.

The electrooptic coefficients $r_{33}$ and $r_{13}$ of a PIMOD-derived lithium niobate thin film on a sapphire substrate were determined using a transmission phase modulator to be $10.7 \times 10^{-12}$ m/V and $3.0 \times 10^{-12}$ m/V, respectively. They are again the highest EO coefficients of lithium niobate in the thin film form when compared to the published values. Although the value of $r_{33}$ is only one third of the bulk value, it is feasible to build an optoelectronic devices using thin film lithium niobate. For example, the applied voltage required to operate an electrooptic Bragg modulator for maximum deflection is calculated to be about 30 V if the as-grown film (0.6 μm) is used.
Table 6.3  Comparison of three thin film coating processes: sputtering, MOD, and PIMOD.

<table>
<thead>
<tr>
<th></th>
<th>Sputtering</th>
<th>MOD</th>
<th>PIMOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>$1 \times 10^{-6}$ Torr</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Processing temperature</td>
<td>500°C</td>
<td>650°C</td>
<td>500°C</td>
</tr>
<tr>
<td>Control of stoichiometry</td>
<td>difficult</td>
<td>easy</td>
<td>easy</td>
</tr>
<tr>
<td>Control of processing</td>
<td>complicated</td>
<td>simple</td>
<td>simple</td>
</tr>
<tr>
<td>Processing time</td>
<td>long</td>
<td>short</td>
<td>extremely short</td>
</tr>
<tr>
<td>Mass production</td>
<td>fair</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Thickness uniformity</td>
<td>good (to 0.7 μm)</td>
<td>good (to 0.5 μm)</td>
<td>good (to 0.5 μm)</td>
</tr>
<tr>
<td>Film homogeneity</td>
<td>good</td>
<td>poor</td>
<td>good</td>
</tr>
<tr>
<td>Inter-diffusion</td>
<td>no</td>
<td>yes</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 6.4  Comparison of properties of films made by sputtering, MOD, and PIMOD.

<table>
<thead>
<tr>
<th>Properties</th>
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<th>MOD and PIMOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain orientation</td>
<td>(006) on Si(111)</td>
<td>random on Si(111)</td>
</tr>
<tr>
<td></td>
<td>(104) on Si(100)</td>
<td>random, but prefer (104) on Si(100)</td>
</tr>
<tr>
<td></td>
<td>(001) on Al₂O₃(001)</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>(100) on Al₂O₃(100)</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>(012) on Al₂O₃(012)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110) on Al₂O₃(110)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>random, but prefer (104) on SiO₂/(100)Si</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.1 - 2.3</td>
<td>2.1 - 2.3</td>
</tr>
<tr>
<td>Attenuation in waveguide</td>
<td>0.9 dB/cm</td>
<td>2.2 dB/cm</td>
</tr>
<tr>
<td>Resistivity</td>
<td>$5 \times 10^{12}$ Ω-cm</td>
<td>$5 \times 10^{13}$ Ω-cm</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>34.5</td>
<td>34</td>
</tr>
</tbody>
</table>

The decrease of the electrooptic coefficient in the lithium niobate thin films is because it is a fine grain ferroelectric, and the ferroelectricity inside the grain is shielded by the field of interface charge, which decreases the efficiency of the applied field field to the ferroelectricity. If a film with a larger grain can be made, a higher electrooptic coefficient is expectable.

Comparison of different thin film deposition processes and various properties of the films grown by these methods are compared and listed in Table 6.3 and 6.4.
Low loss LiNbO$_3$ waveguides have been made on silicon substrates and electrooptic modulation has been demonstrated. Semiconductor lasers (light source) and photodetector array can be easily fabricated on the same wafer using the microelectronic integration techniques. Optical logical operations can thus be implemented in a single chip. If holographic storage, which is another particular application of LiNbO$_3$, can also be made in thin film form, building of optical computers is no more a dream in the near future. Optical memories based on LiNbO$_3$ thin films is thus very attractive, and study of the photorefractive effect in LiNbO$_3$ thin films is of particular importance and should be the subject of much work. Other applications using the photorefractive effect in LiNbO$_3$ including making holographic gratings for beam coupling or beam deflection are currently under investigation and the results will be discussed elsewhere.

Besides electrooptic effect, acoustooptic effect is another interesting property of LiNbO$_3$ and various type of thin film LiNbO$_3$ based optical switches and modulators, such as Mach-Zehender intensity modulators, total internal reflection switches, directional couplers, Bragg deflection modulators, and surface acoustic wave modulators, should also be investigated in order to design different functional components for logic gates or logic arrays.
Bibliography


