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BARIUM STRONTIUM TITANATE THIN FILMS
FOR ELECTRO-OPTIC APPLICATIONS

Submitted by
WANG DANYANG

A thesis submitted in partial fulfilment of the requirements for
the Degree of Doctor of Philosophy

At
The Department of Applied Physics
The Hong Kong Polytechnic University

October 2005
CERTIFICATE OF ORIGINALITY

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ABSTRACT

This thesis presents the results of experiments on the deposition as well as the structural, electro-optic and optical properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) thin films. The applications of these thin films in rib waveguides and Mach-Zehnder electro-optical modulators are demonstrated.

Highly epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were deposited on single crystal substrates using pulsed laser deposition. Using X-ray diffraction, the structure of the thin films was studied with regard to the effects of the processing conditions (deposition temperature and oxygen partial pressure) and the substrate. It was found that both the processing conditions and the substrate had significant effects on the lattice deformation of the thin films. The surface morphology of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films was studied using atomic force microscopy. The grain size and surface roughness, which are related to the optical loss, depend strongly on the processing conditions. In order to achieve good crystalline quality, high degree of epitaxy, and low optical loss in the film, the optimum deposition temperature and oxygen partial pressure were found to be 750 °C and 200 mTorr, respectively.

The in-plane dielectric and ferroelectric properties were investigated in order to determine whether the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film was in the ferroelectric or paraelectric state at room temperature. The ferroelectric activity of the film was significantly modified by
the oxygen partial pressure and the substrate. For a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate at 750 °C under an oxygen pressure of 200 mTorr, the Curie temperature was upshifted to 88 °C, and a well-defined hysteresis loop was observed at room temperature.

The electro-optic properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film were investigated with regard to the effects of processing conditions (deposition temperature and oxygen partial pressure) and the substrate using the modified Sénarmont method. It was found that the processing conditions significantly affected the electro-optic properties of the films and different electro-optic behaviors were observed for films deposited on different substrates. Films grown on MgO and SrTiO$_3$ (STO) substrates exhibited a predominantly quadratic electro-optic effect, whereas films grown on LaAlO$_3$ (LAO) and (LaAlO$_3$)$_{0.7}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (LSAT) substrates showed linear electro-optic behavior. A high quadratic electro-optic coefficient of $10.0 \times 10^{-18}$ m$^2$/V$^2$ was achieved in the films grown on MgO (001) substrate under the optimum conditions. Since the BST/MgO structure led to good light confinement within the film, MgO was chosen as the substrate for waveguide fabrication.

The refractive indices, index profiles and optical losses of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO substrates were determined using the prism coupling technique. The step-like index profile indicated good optical homogeneity along the thickness direction of the film. The low optical losses of 0.93 dB/cm and 1.29 dB/cm at $\lambda = 1550$ nm.
observed for the TE\textsubscript{0} and TM\textsubscript{0} modes are within the acceptable range for optical waveguide applications.

The appropriate geometry of a single-mode rib waveguide based on Ba\textsubscript{0.7}Sr\textsubscript{0.3}TiO\textsubscript{3} thin film grown on MgO (001) substrate was found using the dispersion equation and the effective index method. A rib waveguide and a Mach-Zehnder electro-optic modulator were fabricated using photolithography and reactive ion etching techniques. Single mode (TE\textsubscript{00}) propagation at $\lambda = 1550$ nm was achieved in both the rib and Mach-Zehnder structures. A lightwave was effectively modulated by the Mach-Zehnder modulator by applying a voltage. The half-wave voltage $V_\pi$ and maximum modulation depth of the device were 60 V and 60 %, respectively. The effective quadratic electro-optic coefficient of this device was $R_{\text{eff}}^e = 0.983 \times 10^{-18}$ m\textsuperscript{2}/V\textsuperscript{2}.
LIST OF PUBLICATIONS


During my three years of Ph.D. study at the Hong Kong Polytechnic University, I enjoyed my research and personal life everyday because of all the people who gave endless support to me. First of all, I sincerely would like to express my gratitude to my supervisors, Prof. C. L Choy and Prof. H. L. W. Chan, for their invaluable guidance, support, encouragement and patience throughout the whole period of my research study.

I would like also to thank Prof. K. S. Chiang and Dr. H. P. Chan from the Optoelectronic Research Centre in the Department of Electronic Engineering at the City University of Hong Kong who have contributed resources and enlightening advices to the success of this research work. My thanks are also extended to the members of their research teams including Mr. K. P. Lor and Mr. K. K. Chung for their helpful assistance in waveguide fabrication and characterization.

I wish to acknowledge the academic members in our department: Dr. K. H. Wong and Dr. J. Y. Dai for their help in pulsed laser deposition, Dr. J. Wang for his insightful suggestions in the electro-optic measurements, Dr. Y. Wang for introducing the electrical characterization and photolithography to me. Thanks are due to Mr. M. N. Yeung of the Materials Research Centre for his assistance in the AFM and SEM investigations.
I would like to thank my former and present colleagues in our department for their assistance and discussions in the research work. They include (in no particular order): Dr. K. C. Cheng, Mr. K. H. Lam, Mr. S. H. Choy, Ms. Y. L. Cheng, Ms. C. Y. Lam, Ms. H. K. Lam, Dr. X. G. Tang, Dr. H. Y. Tian, Mr. X. Zhao and Ms. X. Y. Zhou.

I gratefully acknowledge the financial support from the Department of Applied Physics and the Centre for Smart Materials of the Hong Kong Polytechnic University.

Most of all, I would like to express my deepest appreciations to my parents for their continuous love, support, understanding and patience that inspired me to continue and to mature both as a person and as a professional.
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<tr>
<td>$B$</td>
<td>phase retardation</td>
</tr>
<tr>
<td>$c$</td>
<td>speed of light</td>
</tr>
<tr>
<td>$c_0$</td>
<td>speed of light in vacuum</td>
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<tr>
<td>$d_{hkl}$</td>
<td>interplanar spacing of the planes $(hkl)$</td>
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<td>$E$</td>
<td>electric field</td>
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<td>$\bar{E}$</td>
<td>electric field vector</td>
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<td>$H$</td>
<td>magnetic field</td>
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<tr>
<td>$\bar{H}$</td>
<td>magnetic field vector</td>
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<td>$k$</td>
<td>wavenumber of the light</td>
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<td>order of the mode</td>
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<td>$n$</td>
<td>refractive index</td>
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<td>$n_e$</td>
<td>extraordinary refractive index</td>
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<tr>
<td>$n_o$</td>
<td>ordinary refractive index</td>
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<td>$\Delta n$</td>
<td>birefringence, $n_e - n_o$</td>
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<td>$r_{hjk}$</td>
<td>linear electro-optic coefficient</td>
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<td>$R_{hjk}$</td>
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<td>$R_c$</td>
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<td>$V_\pi$</td>
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<td>$\chi^0$</td>
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<td>$\mu$</td>
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# LIST OF ACRONYMS

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<th>Acronyms</th>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BST</td>
<td>Barium strontium titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$</td>
</tr>
<tr>
<td>BTO</td>
<td>Barium titanate, $\text{BaTiO}_3$</td>
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<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>EIM</td>
<td>Effective index method</td>
</tr>
<tr>
<td>E-O</td>
<td>Electro-optic</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>IDE</td>
<td>Interdigital electrode</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>LAO</td>
<td>Lanthanum aluminate, $\text{LaAlO}_3$</td>
</tr>
<tr>
<td>LSAT</td>
<td>Lanthanum strontium aluminate tantalate, $(\text{LaAlO}<em>3)</em>{0.3}(\text{Sr}_2\text{AlTaO}<em>6)</em>{0.35}$</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>MZI</td>
<td>Mach-Zehnder interferometer</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>PLZT</td>
<td>Lanthanum modified lead zirconate titanate, $\text{Pb}_{1-x}\text{La}<em>x(\text{Zr}<em>y\text{Ti}</em>{1-y})</em>{1-0.25x}\text{O}_3$</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier</td>
</tr>
<tr>
<td>rf</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive ion etching</td>
</tr>
<tr>
<td>rms</td>
<td>Root mean square</td>
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<tr>
<td>STO</td>
<td>Strontium titanate, $\text{SrTiO}_3$</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse electric</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse magnetic</td>
</tr>
<tr>
<td>WKB</td>
<td>Wentzel-Kramers-Brillouin</td>
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<tr>
<td>XRD</td>
<td>X-ray diffractions</td>
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CHAPTER 1

INTRODUCTION

1.1 Background

The concept of integrated optics was initially proposed by S. E. Miller of Bell Laboratories in 1969 [Millier, 1969]. The introduction of integrated optics has triggered a tremendous growth in fibre-optics communication systems, especially in the last decade. Integrated optics is mainly developed in the direction of integration of waveguides and optoelectronic components on a single substrate to achieve creation of multifunction devices, thus ensuring the advantages of low cost, robustness, compactness, integration and compatibility with microelectronic systems [Palais, 1988].

Since the initiation of integrated optics in the early years, guided-wave optical devices, including waveguides, switches and modulators, have been intensively studied. Within the field of fibre-optics communication, the focus is on photonic devices, which are much faster than their electronic counterpart. To improve the device performance, the material used for these photonic devices has thus become a critical issue to be considered. Various materials are under investigation for use in integrated optics applications, including semiconductors [Walker, 1991], polymers [Steier, 1998], glasses [Marsh, 1990] and ferroelectric materials [Kaminov, 1974; Noda, 1975; Petraru, 2002;
Thapliya, 2003]. Among them, ferroelectric materials with high electro-optic coefficients are a leading class of materials for integrated optics applications. Bulk single crystals are already used, for instance, Ti-diffused bulk lithium niobate (LiNbO₃) channel waveguide structures are considered the best candidates for optical modulators because of the relative ease in fabrication into transparent waveguides [Alferness, 1990]. Mach-Zehnder electro-optic modulators based on LiNbO₃ single crystals are commercially available at operation frequencies of over 40 GHz and a driving voltage of 5 V [Lucent Technologies, 2000].

An optical modulator can modulate the intensity, frequency, phase or polarization of the output light at high speed. Intensity modulation is the most popular choice for fibre-optic communication systems, primarily due to the simplicity of envelope photodetection [Li, 2003]. Most of the modern broad bandwidth modulators are based on the electro-optic (E-O) effect, so they are voltage controlled devices. Significant achievements have been made over the past twenty years in the development of guided wave electro-optic modulator devices [Wang, 1995]. Reported waveguide intensity modulators include the following types: Mach-Zehnder interferometer modulators [Leonberger, 1980], directional coupler modulators [Alferness, 1981], x-switch modulators [Neyer, 1983], cutoff modulators [Chen, 1986], mode conversion modulators [Alferness, 1980], balanced-bridge modulators [Ramaswamy, 1978], planar Bragg grating diffraction modulators [Tangonan, 1978] and guide-to-radiation coupling modulators [Onodera, 1984]. However, many of the above modulators are based on bulk single crystals, there have been few modulators based on ferroelectric thin films.
Thin-film waveguide has become a key component in integrated optics, optical communications and optical interconnects. In particular, ferroelectric thin films are of interest for optical modulator applications. As integrated optics materials, high-quality ferroelectric thin films have advantages over bulk single crystals because they can operate at a higher modulation frequency and a lower driving voltage.

Although many challenges still remain before ferroelectric thin films can be used widely in optical waveguides, modern thin film technology is beginning to provide the tools and capabilities to make these concepts a reality. Epitaxial ferroelectric thin films are required for such integrated optics applications [Walker, 1996]. The fabrication of ferroelectric thin films by a variety of techniques, including sol-gel deposited [Zhai, 2001], metal organic chemical vapor deposition (MOCVD) [Moret, 2002], liquid phase epitaxy [Neurgaonkar, 1987], molecular beam epitaxy [Betts, 1985], pulsed laser deposition (PLD) [Kim, 1995] and sputtering [Blomqvist, 2003] has been explored.

1.2 Electro-optic Effect in Crystals

1.2.1 Refractive Index

The refractive index of an isotropic material is defined as:

\[ n = \frac{c_0}{c} \]  (1.1)
where \( c_0 \) is the speed of light in vacuum and \( c \) is the speed of light in the material [Nye, 1976]. Maxwell’s equations show that, if the relative magnetic permeability is taken as 1, \( c \) is given by:

\[
c = \frac{c_0}{\sqrt{\varepsilon}} \quad (1.2)
\]

where \( \varepsilon \) is the relative permittivity at optical frequency. Substituting Eq. (1.2) into Eq. (1.1) gives:

\[
n = \sqrt{\varepsilon} \quad (1.3)
\]

### 1.2.2 Optic Birefringence

In an anisotropic medium, Maxwell’s equations show that not one but two light waves, of different velocity, may in general be propagated through the medium with a given wave normal; moreover, these waves are plane polarized. The value of \( \frac{c_0}{c} \) for each wave may be called the refractive index \( n \) for that wave. The refractive indices of the two waves as functions of the direction of their common wave vector \( \vec{k} \) are obtained by drawing an ellipsoid (Figure 1.1) known as the indicatrix. If \( x, y, z \) are the principal axes of the relative permittivity tensor, the indicatrix is defined by the equation:

\[
\frac{x^2}{n_1^2} + \frac{y^2}{n_2^2} + \frac{z^2}{n_3^2} = 1 \quad (1.4)
\]

where \( n_1 = \sqrt{\varepsilon_x} \), \( n_2 = \sqrt{\varepsilon_y} \), \( n_3 = \sqrt{\varepsilon_z} \), and \( \varepsilon_x, \varepsilon_y, \varepsilon_z \) are the principal relative permittivities.
The indicatrix has the following important property. Draw through the origin a straight line along the wave vector $\vec{k}$. Draw the central section of the indicatrix normal to it. This will be an ellipse. Then the two waves with the wave vector $\vec{k}$ that can be propagated through the crystal have refractive indices equal to the semi-axis, OA and OB. The displacement vector $\vec{D}$ in the plane polarized wave with refractive index equal to OA vibrates parallel to OA. Similarly, the displacement vector in the wave with refractive index equal to OB vibrates parallel to OB. From this it follows, as a special case, that the two possible waves with wave vector in the $\hat{x}$ direction have refractive indices $n_2$ and $n_3$; and $\vec{D}$ in the two waves is parallel to $\hat{y}$ and $\hat{z}$, respectively. Similar arguments apply to the wave vectors in the $\hat{y}$ or $\hat{z}$ directions. For this reason, $n_1$, $n_2$ and $n_3$ are called the principal refractive indices.

![Figure 1.1 Optical indicatrix (index ellipsoid) for a positive uniaxial crystal, $n_1 = n_2 \neq n_3$. The optical axis is parallel to the z-axis.](image)

Figure 1.1 Optical indicatrix (index ellipsoid) for a positive uniaxial crystal, $n_1 = n_2 \neq n_3$. The optical axis is parallel to the z-axis.
The optical properties of a crystal are closely related to its crystal symmetry. For a cubic crystal, the indicatrix is a sphere and all central sections are circles, thus \( n_1 = n_2 = n_3 \). For hexagonal, tetragonal and trigonal crystals, the indicatrix is necessarily an ellipsoid of revolution about the principal symmetry axis \( \hat{z} \), as shown in Figure 1.1. The principal axis is called the optic axis and the crystal are said to be uniaxial. \( n_0 = n_1 = n_2 \) and \( n_e = n_3 \) are the ordinary and extraordinary refractive indices, respectively. The difference between the two indices, \( \Delta n = n_e - n_o \), is called the birefringence.

For a uniaxial crystal, the central section of the indicatrix that is perpendicular to the principal axis is a circle (radius \( n_0 \)). Hence there is no birefringence if the wave vector is parallel to the principal axis. However, if the wave vector \( \vec{k} \) makes an angle \( \theta \) with the principal axis as shown in Figure 1.1, the ordinary index is independent of \( \theta \), but the extraordinary index \( n_e(\theta) \) varies with the angle \( \theta \) as:

\[
\frac{1}{n_e^2(\theta)} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_e^2}
\]

For the three remaining crystal systems, the orthorhombic, monoclinic and triclinic, the indicatrix is a triaxial ellipsoid. There are two circular sections and hence two privileged wave vector directions for which there is no birefringence. These two directions are called the primary optic axes and crystals are said to be biaxial.
1.2.3 Electro-optic Effect and Electro-optic Coefficients

The electro-optic (E-O) effect refers to the change of optical refractive index in a crystal due to the presence of electric field. With the knowledge of the general optical indicatrix of the crystal, an understanding of the electro-optic effect can be realized. When an electric field is applied, both the size and the orientation of the indicatrix change. The equation of the indicatrix is generally modified to:

\[ \eta_{11}x^2 + \eta_{22}y^2 + \eta_{33}z^2 + \eta_{12}xy + \eta_{23}yz + \eta_{13}xz = 1 \]  

(1.6)

where \( \eta_{ij} \) is the impermeability tensor which is related to the relative permittivity tensor \( \varepsilon \) by:

\[ \eta_{ij} = [\varepsilon^{-1}]_{ij} \]  

(1.7)

Due to the presence of external electric field \( E \), the distribution of the charges in the crystal changes, resulting in a change of the impermeability tensor \( \Delta \eta_{ij} \):

\[ \Delta \eta_{ij} = \sum_k r_{ijk} E_k + \sum_{km} R_{hijkm} E_k E_m \]  

(1.8)

where the first term and second term are called the linear electro-optic effect (Pockels effect) and quadratic electro-optic effect (Kerr effect) and \( r_{ijk} \) and \( R_{hijkm} \) are the linear and quadratic electro-optic coefficients. Since \( \eta_{ij} \) is a symmetric tensor, the number of subscript indices in \( r_{ijk} \) and \( R_{hijkm} \) can be reduced. In the case of the third-rank tensor \( r_{ijk} \), the first and second indices are replaced by a single index running from 1 to 6:

11 → 1, 22 → 2, 33 → 3, 23 or 32 → 4, 13 or 31 → 5, 12 or 21 → 6.
In practice, the electro-optic effect is either predominantly linear or quadratic with respect to $E$ and is therefore characterized by either $r_{jk}$ or $R_{jkm}$. Although the linear electro-optic effect typically outweighs the quadratic effect in magnitude, the quadratic effect is present in all materials [American National & IEEE standard, 2003]. The quadratic electro-optic effect is the dominant effect in all materials with centrosymmetric structure, such as ferroelectric crystals in the paraelectric state. The change in the impermeability $\Delta \eta_{ij}$ in centrosymmetric crystals is independent of the sign of the electric field so that the linear component vanishes, resulting in the absence of linear electro-optic effect.

When only the linear E-O effect is considered, the change in the impermeability $\Delta \eta_{ij}$ induced by an electric field $E = (E_x, E_y, E_z)$ can be expressed as:

$$
\begin{pmatrix}
\Delta \eta_{11} \\
\Delta \eta_{22} \\
\Delta \eta_{33} \\
\Delta \eta_{23} \\
\Delta \eta_{13} \\
\Delta \eta_{12}
\end{pmatrix} =
\begin{pmatrix}
r_{11} & r_{12} & r_{13} \\
r_{21} & r_{22} & r_{23} \\
r_{31} & r_{32} & r_{33} \\
r_{41} & r_{42} & r_{43} \\
r_{51} & r_{52} & r_{53} \\
r_{61} & r_{62} & r_{63}
\end{pmatrix}
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix}
$$

(1.9)

where the $6 \times 3$ matrix $(r_{ik})$ is called the electro-optic tensor. For various crystals, due to the crystal symmetry, some of the E-O coefficients may be zero and some of them may be equal in value (or opposite in sign) [Yariv, 1984]. For example, the uniaxial BaTiO$_3$ crystal, which belongs to the point group 4mm, has an electro-optic tensor of the form:
\[
\begin{pmatrix}
0 & 0 & r_{13} \\
0 & 0 & r_{13} \\
0 & 0 & r_{33} \\
0 & r_{31} & 0 \\
r_{31} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

It is often possible to avoid the complication of the cross-terms by applying the external field parallel to one of the principal axes of the crystal. Applying the electric field along the \(z\)-axis of a uniaxial crystal \((E = (0, 0, E))\), Eqs (1.6) and (1.9) reduce to:

\[
\left(\frac{1}{n_o^2} + r_{13}E\right)\left(x^2 + y^2\right) + \left(\frac{1}{n_e^2} + r_{33}E\right)z^2 = 1
\]  

(1.11)

In this case, the principal axes of the indicatrix only change their lengths, but the indicatrix is not rotated (no cross terms are included). This new indicatrix gives for \(n_o(E)\) and \(n_e(E)\):

\[
\frac{1}{n_o^2(E)} = \frac{1}{n_o^2} + r_{13}E
\]

(1.12)

\[
\frac{1}{n_e^2(E)} = \frac{1}{n_e^2} + r_{33}E
\]

(1.13)

which, using the relation \(dn = \left(-\frac{n^3}{2}\right)d\left(\frac{1}{n^2}\right)\), gives

\[
n_o(E) = n_o - \frac{1}{2}n_o^3 r_{13}E
\]

(1.14)

\[
n_e(E) = n_e - \frac{1}{2}n_e^3 r_{33}E
\]

(1.15)

Thus, the electric field induced birefringence can be written as:

\[
n_o(E) - n_e(E) = \frac{1}{2}n_e^3 E[r_{33} - \left(\frac{n_o}{n_e}\right)^3 r_{13}] = \frac{1}{2}n_e^3 r_e E
\]

(1.16)
where \( r_c \) is the effective electro-optic coefficient, given by:

\[
r_c = r_{33} - \left( \frac{n_o}{n_e} \right)^3 r_{13}
\]  

(1.17)

In general, the electro-optic behavior of a material can be characterized by effective electro-optic coefficients. For materials exhibiting linear and quadratic electro-optic effects, the linear and quadratic electro-optic coefficients, \( r_c \) and \( R_c \), are defined by the following equations:

\[
\delta \Delta n = \frac{1}{2} n^3 r_c E
\]  

(1.18)

\[
\delta \Delta n = \frac{1}{2} n^3 R_c E^2
\]  

(1.19)

where \( \delta \Delta n \) is the change of birefringence induced by an electric field \( E \), \( n \) is the relevant refractive index; \( n^3 r_c \) and \( n^3 R_c \) are called the electro-optic figures of merit. If \( n^3 r_c \) or \( n^3 R_c \) is large, then a large change of refractive index can be achieved when a low electric field is applied to the material.

Refractive index changes due to the Pockels effect on the order of \( 10^{-6} \) to \( 10^{-4} \) are induced by a field of \( 10^6 \) V/m since the Pockels coefficients typically range from \( 10^{-12} \) to \( 10^{-10} \) m/V. Typical Kerr coefficients range from \( 10^{-18} \) to \( 10^{-14} \) m²/V² in crystals and \( 10^{-22} \) to \( 10^{-19} \) m²/V² in liquids. Therefore, changes in the refractive index on the order of \( 10^{-6} \) to \( 10^{-2} \) in crystals and \( 10^{-10} \) to \( 10^{-7} \) in liquids can be induced by a field of a \( 10^6 \) V/m [Saleh, 1991]. In practice, both the Pockels and Kerr effects are used to modulate the lightwave in telecommunication applications.
Another important figure of merit, the half-wave voltage $V_\pi$, is also used in the selection of materials for electro-optic modulation. The half-wave voltage $V_\pi$ is the voltage that is applied to a crystal in order to obtain a phase retardation of $\pi$. In the case of a uniaxial crystal, when an electric field is applied along of the optical axis ($z$-axis) and the light beam propagates in a direction perpendicular to this axis, the half-wave voltage is related to the linear electro-optic coefficient $r_c$ by [Günter, 1987]:

$$V_\pi = \frac{\lambda}{n^3 r_c} \cdot \frac{d}{L}$$

where $d$ is the electrode spacing and $L$ is the optical path length. In order to obtain a high efficiency in electro-optic modulation, $V_\pi$ should be as small as possible.

### 1.3 Electro-optic Materials

In the past two decades, the rapid development of optical communication and optical computation technologies have triggered a large amount of research work on materials for realizing different types of photonic devices in optoelectronic and photonics applications. A variety of materials with promising electro-optic properties for integrated optics applications can be found in the literature. The common electro-optic materials can be mainly classified into three groups: ferroelectric materials, semiconductors and organic polymers. Some of these materials, together with their optical properties, are listed in Table 1.1.
1.3.1 Ferroelectric Materials

Ferroelectric materials are of great interest in integrated optics applications due to their superior optoelectronic properties such as the high electro-optic coefficients [Hu, 2004]. There are two types of electro-optic ferroelectrics, the perovskite type and tungsten-bronze type. Typical examples of these two types are given in Table 1.1.

Ferroelectric materials may exist in the form of single crystal, ceramic, film with randomly oriented crystallites or epitaxial thin film. The material properties strongly depend on the form of the materials. So far, practical ferroelectric waveguides are mostly limited to diffused or ion-exchanged waveguides fabricated by using lithium niobate (LiNbO₃) or lithium tantalate (LiTaO₃) single crystals. However, as shown in Table 1.2, high electro-optic coefficients together with low optical losses were observed in ferroelectric thin films, thus it is of interest to fabricate electro-optic devices using ferroelectric thin films instead of LiNbO₃ single crystals.

1.3.2 Semiconductors

Wide-band-gap III-V semiconductors are attracting a great deal of interest as possible candidates for use in photonic guided-wave devices for telecommunication and instrumentation applications [Long, 1995; Wang, 1988; Walker, 1991]. III-V semiconductors have the zinc blende ($\overline{4}3m$) structure and are not intrinsically birefringent. However, semiconductors promise ultrahigh response speed due to the
unique quantum confinement mechanism and they may also show high electro-optic response because of surface and quantum size effect. GaAs and GaN are typical electro-optic semiconductors and they have been used in high speed electro-optic modulators [Wang, 1988; Adams, 1994]. Because III – V materials offer the obvious advantage of monoclinic integration of active/passive photonic and electronic devices to form the foundation of optical electronic integrated circuits (OEIC) [Iwama, 1987], they may eventually replace lithium niobate, which is the most commonly used electro-optic crystal.

1.3.3 Polymers

In recent years, electro-optic polymers have been used to make various optical devices in the telecommunication field [Steier, 1999; Park, 2003a; Herminghaus, 1991; Faderl, 1995; Wang, 1994]. They have advantages such as low dispersion in the refractive index between infrared and millimeter-wave frequencies, and high and fast electro-optic response. They can be deposited and adhered to many substrates including semiconductors and they can be integrated into an optical circuit which contains other materials [Steier, 1999]. Among the disadvantages is the difficulty in chemical synthesis. Electro-optic polymers require optically nonlinear chromophores which can be incorporated into a polymer host, aligned by a poling electric field and finally fixed to maintain the alignment. Among the electro-optic polymers that have been studied, polyvinylidene fluoride (PVDF) and vinylidene fluoride-trifluorethylene copolymer [P(VDF-TrFE)] are commercially available.
Table 1.1 Summary of optical properties of promising materials for integrated optics applications.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electro-optic coefficient $r \left(10^{12} \text{m/V}\right)$; $R \left(10^{10} \text{m}^2/\text{V}^2\right)$</th>
<th>Refractive index</th>
<th>Half-wave voltage $V_\pi$ (V)</th>
<th>$\lambda$ (nm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ferroelectrics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>$r_{33} = 112$; $r_{13} = 11.7$</td>
<td>$n_0=2.44$; $n_e=2.37$</td>
<td>480</td>
<td>546.1</td>
<td>[Johnston, 1965]</td>
</tr>
<tr>
<td>Ce: BaTiO$_3$</td>
<td>$r_{33} = 207$; $r_{13} = 15$</td>
<td>$n_0=2.599$; $n_e=2.562$</td>
<td>202</td>
<td>632.8</td>
<td>[Chen, 1997]</td>
</tr>
<tr>
<td>PMN-0.33PT(001)</td>
<td>$r_{33} = 207$; $r_{13} = 15$</td>
<td>$n_0=2.599$; $n_e=2.562$</td>
<td>202</td>
<td>632.8</td>
<td>[Jeong, 2003]</td>
</tr>
<tr>
<td>PMN-0.30PT(111)</td>
<td>$r_{33} = 107$</td>
<td>$n_0=2.590$; $n_e=2.598$</td>
<td>347</td>
<td>632.8</td>
<td>[Wan, 2004]</td>
</tr>
<tr>
<td>PZN-0.08PT(001)</td>
<td>$r_{33} = 450$; $r_{13} = 15$</td>
<td>$n_0=2.57$; $n_e=2.46$</td>
<td>98</td>
<td>632.8</td>
<td>[Barad, 2000]</td>
</tr>
<tr>
<td>PLZT(8/65/35)</td>
<td>$r_5 = 612$</td>
<td>$n=-2.50$</td>
<td>---</td>
<td>546</td>
<td>[Haertling, 1971]</td>
</tr>
<tr>
<td>PLZT(9/65/35)</td>
<td>$R_c = 9.116$</td>
<td>$n=-2.50$</td>
<td>---</td>
<td>546</td>
<td></td>
</tr>
<tr>
<td><strong>Tungsten-Bronze</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr$<em>{0.75}$Ba$</em>{0.25}$Nb$_2$O$_6$</td>
<td>$r_{33} = 1300$; $r_{13} = 6.4$</td>
<td>$n_0=2.3117$; $n_e=2.2987$</td>
<td>37</td>
<td>633</td>
<td>[Xu, 1991]</td>
</tr>
<tr>
<td><strong>Semiconductors</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>$r_{41} = 1.43$</td>
<td>$n_0=3.41$</td>
<td>8</td>
<td>1300</td>
<td>[Wang, 1988]</td>
</tr>
<tr>
<td>GaN</td>
<td>$r_{33} = 1.91$; $r_{13} = 0.57$</td>
<td>$n_0=2.35$; $n_e=2.37$</td>
<td>---</td>
<td>632.8</td>
<td>[Long, 1995]</td>
</tr>
<tr>
<td><strong>Polymers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>$r_{51} = 0.1$; $r_{42} = 0.21$; $r_{33} = 0.38$</td>
<td>$n_1=1.444$; $n_3=1.436$</td>
<td>56000</td>
<td>632.8</td>
<td>[Broussoux, 1980]</td>
</tr>
<tr>
<td>PVDF-TrFE(75/25)</td>
<td>$r_{13} = 0.35$; $r_{23} = 0.30$</td>
<td>$n=-1.43$</td>
<td>---</td>
<td>632.8</td>
<td>[Ho, 2001]</td>
</tr>
</tbody>
</table>
Table 1.2 Summary of optical properties of promising ferroelectric thin films for integrated optics applications.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Substrate</th>
<th>Deposition method</th>
<th>Structure</th>
<th>Electro-optic coefficient $r$ ($10^{-12} \text{m/V}$); $R$ ($10^{16} \text{m}^2/\text{V}^2$)</th>
<th>Refractive index $n_o$; $n_e$</th>
<th>Optical loss (dB/cm)</th>
<th>$\lambda$ (nm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>MgO(001)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$R_c = 0.46$</td>
<td>$n_o = 2.378$; $n_e = 2.364$</td>
<td>2.9(TE$_{00}$)</td>
<td>632.8</td>
<td>[Kim, 1995] [Beckers, 1998]</td>
</tr>
<tr>
<td></td>
<td>Fused silica</td>
<td>RF Sputtering</td>
<td>Polycrystalline</td>
<td>$R_c = 0.00892$</td>
<td>$n = 2.2$</td>
<td>---</td>
<td>577</td>
<td>[Wu, 1990]</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$TiO$_3$</td>
<td>LAO(001)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$r_c = 70 - 115$ $R_c = 1.3$</td>
<td>---</td>
<td>---</td>
<td>632.8</td>
<td>[Li, 2000]</td>
</tr>
<tr>
<td>Ba$<em>{0.6}$Sr$</em>{0.4}$TiO$_3$</td>
<td>MgO(001)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$R^* c = 100$</td>
<td>---</td>
<td>---</td>
<td>632.8</td>
<td>[Kim, 2003]</td>
</tr>
<tr>
<td>Ba$<em>{0.7}$Sr$</em>{0.3}$TiO$_3$</td>
<td>LAO(001)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$r_c = 110 - 230$ $R_c = 0.55$</td>
<td>---</td>
<td>---</td>
<td>632.8</td>
<td>[Li, 2000]</td>
</tr>
<tr>
<td>(1-$x$)PMN-$x$PT ($x=0.25-0.35$)</td>
<td>LAO(001)</td>
<td>Sol-gel</td>
<td>Epitaxial</td>
<td>$R_c = 0.45-1.38$</td>
<td>$n_o = 2.5415$; $n_e = 2.4418$</td>
<td>4.1(TE$<em>{00}$); 4.8(TM$</em>{0}$)</td>
<td>632.8</td>
<td>[Lu, 1998] [Lu, 1999b]</td>
</tr>
<tr>
<td>PZT(53/47)</td>
<td>Glass</td>
<td>Sol-gel</td>
<td>Polycrystalline</td>
<td>$r_c = 315$ $R_c = 0.38$</td>
<td>$n = 2.10$</td>
<td>---</td>
<td>632.8</td>
<td>[Teowee, 1995]</td>
</tr>
<tr>
<td>PLZT(9/65/35)</td>
<td>Sapphire (0001)</td>
<td>RF Sputtering</td>
<td>Epitaxial</td>
<td>$R_c = 1.0$</td>
<td>---</td>
<td>---</td>
<td>632.8</td>
<td>[Adachi, 1986]</td>
</tr>
<tr>
<td></td>
<td>Sapphire (1102)</td>
<td>RF Sputtering</td>
<td>Epitaxial</td>
<td>$R_c = 0.7$</td>
<td>$n = 2.34$</td>
<td>---</td>
<td>632.8</td>
<td>[Tunaboylu, 1998]</td>
</tr>
<tr>
<td>Na$<em>{0.5}$K$</em>{0.5}$NbO$_3$</td>
<td>Sapphire (0112)</td>
<td>RF Sputtering</td>
<td>Polycrystalline</td>
<td>$r_c = 11$</td>
<td>$n_o = 2.247$; $n_e = 2.216$</td>
<td>---</td>
<td>632.8</td>
<td>[Blomqvist, 2003] [Blomqvist, 2005]</td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>MgO(001)</td>
<td>RF Sputtering</td>
<td>Epitaxial</td>
<td>$R_c = 0.009-0.03$</td>
<td>---</td>
<td>---</td>
<td>632.8</td>
<td>[Graettinger, 1991]</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>Sapphire (1120)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$R_c = 23.8$</td>
<td>$n_o = 2.26$; $n_e = 2.21$</td>
<td>3.0</td>
<td>632.8</td>
<td>[Kim, 1998]</td>
</tr>
<tr>
<td>Sr$<em>{0.5}$Ba$</em>{0.5}$Nb$_2$O$_6$</td>
<td>MgO(001)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$r_{33} = 844$</td>
<td>$n_o = 2.298$; $n_e = 2.311$</td>
<td>---</td>
<td>549</td>
<td>[Tayebati, 1996]</td>
</tr>
<tr>
<td>Bi$_2$Ti$<em>2$O$</em>{12}$</td>
<td>MgO(110)</td>
<td>PLD</td>
<td>Epitaxial</td>
<td>$R^* c = 38$</td>
<td>$n = 2.4 - 2.6$</td>
<td>---</td>
<td>632.8</td>
<td>[Jo, 1993]</td>
</tr>
</tbody>
</table>

$\delta(\Delta n) = R^* c (E - E_c)$, where $E_c$ is the coercive field.
1.4 Barium Strontium Titanate in Bulk and Thin Film Forms

1.4.1 Bulk Barium Strontium Titanate

Barium strontium titanate (Ba$_{1-x}$Sr$_x$TiO$_3$ or BST) is a solid solution of barium titanate (BaTiO$_3$ or BTO) and strontium titanate (SrTiO$_3$ or STO) and it can be formed over the entire range of concentration $x$. BST has a perovskite (ABO$_3$) structure (Figure 1.2) which may be regarded as being formed by the substitution of Sr atoms for the Ba atoms in the barium titanate lattice [Baumert, 1998]. The introduction of Sr atoms into the barium titanate lattice influences both the crystalline structure and the properties.

Figure 1.2 The lattice structure of Ba$_{1-x}$Sr$_x$TiO$_3$. Ba and Sr occupy the corner positions with Ti at the body center, surrounded by the oxygen octahedron.
The structure and properties of bulk Ba$_{1-x}$Sr$_x$TiO$_3$ have been reported in the literature [Landolt, 2002; Baumert, 1998]. The ferroelectric-to-paraelectric phase transition (Curie transition) occurs at about 120 °C for BaTiO$_3$ and -233 °C for SrTiO$_3$, and the Curie temperature for Ba$_{1-x}$Sr$_x$TiO$_3$ exhibits an approximately linear relationship with the content of SrTiO$_3$. Figure 1.3 shows the room-temperature lattice parameters and the Curie temperature $T_c$ of Ba$_{1-x}$Sr$_x$TiO$_3$ as a function of the SrTiO$_3$ content $x$, with $T_c$ taken as the temperature location of the peak in the relative permittivity versus temperature plot. Figure 1.3 (a) shows that, at room temperature (~25 °C), Ba$_{1-x}$Sr$_x$TiO$_3$ with $x < 0.3$ has a tetragonal (non-centrosymmetric) structure and is thus in the ferroelectric state. At $x > 0.3$, Ba$_{1-x}$Sr$_x$TiO$_3$ has a cubic (centrosymmetric) structure and is in the paraelectric state. However, Figure 1.3 (b) shows for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$, although the ferroelectric-to-paraelectric transition has already started at room temperature, the peak in the permittivity occurs at about 35 °C. Therefore Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ should exhibit ferroelectric behavior at room temperature.

Figure 1.3 (a) Room temperature lattice parameters [McQuarrie, 1955] and (b) Relative permittivity versus temperature for Ba$_{1-x}$Sr$_x$TiO$_3$ as a function of SrTiO$_3$ content [Smolenskii, 1954].
Studies on Ba$_{1-x}$Sr$_x$TiO$_3$ have been mainly focused on wireless telecommunication applications, because these materials show high tunability and low dielectric loss in the microwave regime at room temperature.

### 1.4.2 Barium Strontium Titanate Thin Films

The research interests in Ba$_{1-x}$Sr$_x$TiO$_3$ thin films have originated from their potential applications in integrated devices [Damjanovic, 1998]. For use in microwave devices, Ba$_{1-x}$Sr$_x$TiO$_3$ thin films are more attractive than bulk materials due to the lower operation voltage, smaller size and higher level of integration [Tseng, 1999; Chang, 1999]. Many thin film deposition techniques have been adopted in the fabrication of Ba$_{1-x}$Sr$_x$TiO$_3$ thin films and the properties of the films are strongly dependent on the processing techniques.

Most of the reports on Ba$_{1-x}$Sr$_x$TiO$_3$ thin films have focused on the dielectric properties; there has been no report on the electro-optic properties until the year 2000. The excellent dielectric properties of Ba$_{1-x}$Sr$_x$TiO$_3$ thin films motivated some researchers to investigate their electro-optic characteristics. Li et al. [Li, 2000] first studied the electro-optic effects in Ba$_{1-x}$Sr$_x$TiO$_3$ thin films deposited on LAO (001) substrates. Both the Pockels and Kerr effects were observed and the E-O coefficients were quite high. From then on, Ba$_{1-x}$Sr$_x$TiO$_3$ thin films were considered as promising candidates not only in microwave but also in electro-optic applications. Kim and co-workers [Kim, 2003] reported an extremely large quadratic electro-optic response in a Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ thin film.
grown on a MgO (001) substrate. The E-O coefficient of this film was one to two orders of magnitude higher than those of single crystals and ceramics. It should be noted, however, that they calculated the E-O coefficient by using an expression different from those used by other workers (see the footnote in Table 1.2).

The properties of Ba$_{1-x}$Sr$_x$TiO$_3$ thin films also depend on the composition. Thus it is necessary to investigate the compositional dependence of the electro-optic properties of Ba$_{1-x}$Sr$_x$TiO$_3$ thin films in order to select an optimum composition for detailed study and device fabrication. Therefore, we deposited Ba$_{1-x}$Sr$_x$TiO$_3$ ($x = 0, 0.1... 0.5$) thin films on MgO (001) substrates using pulsed laser deposition (PLD) under the same conditions for a quick E-O property screening. The E-O coefficient of the BST thin films was measured using the transmission ellipsometry method at room temperature. Details of electrode patterning and the measurement technique will be presented in Chapter 3.

The Ba$_{1-x}$Sr$_x$TiO$_3$ thin films exhibited a predominantly quadratic E-O behavior in the entire composition range and the highest E-O coefficient was found at $x = 0.3$ (Figure 1.4). Therefore, we chose this composition for detailed study and device development.
Figure 1.4 Electro-optic coefficient as a function of $x$ for $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films deposited on MgO (001) substrates at 650 °C.

1.5 Optical Waveguides

Optical waveguides, also known as “dielectric” waveguides, are the structures that are used to confine and guide the lightwave in guided wave devices and circuits of the integrated optics [Kogelnik, 1990]. A well-known optical waveguide is, of course, the optical fibre which usually has a circular cross-section. In contrast, the guides of interest to integrated optics are usually planar structures such as planar films or strips. Our work will focus on planar waveguides and the fundamentals of planar waveguides will be discussed in this Section.
The simplest dielectric guide is the planar slab waveguide shown in Figure 1.5, where a planar film of refractive index $n_f$ is sandwiched between a substrate and a cladding material with lower refractive indices $n_s$ and $n_c$ \((n_f > n_s \geq n_c)\). In integrated optics applications, slab waveguides are formed by various means, the simplest of which employs the deposition of dielectric thin films on substrates (single crystals, semiconductors or polymers). These films can be deposited by evaporation, sputtering, pulsed laser deposition or other epitaxial growth techniques. Another method of forming dielectric optical waveguides for integrated optics applications employs ion implantation techniques. By bombarding the substrate material with suitable ions, it is possible to alter the refractive index of the substrate so that a dielectric slab waveguide results [Prokhorov, 1996].

![Cross-section of a planar slab waveguide](image)

**Figure 1.5** Cross-section of a planar slab waveguide consisting of a thin film of thickness (or height) $h$ and refractive index $n_f$, sandwiched between substrate and cladding materials.
Two types of waveguide configurations classified based on the refractive index profile are shown in Figure 1.6. Figure 1.6 (a) depicts a graded-index waveguide as may be produced by diffusion processes such as metal in-diffusion [Schmidt, 1974], proton exchange [Jackel, 1982] and ion exchange [Giallorenzi, 1973]. In these processes, the waveguide region is achieved by doping the substrate surface to effectively raise its refractive index relative to the bulk. The refractive index profile in these cases tends to be a continuously changing function into the depth of the substrate. Relatively small refractive index modifications (small $n_f - n_s$) are normally achieved in these processes.

![Figure 1.6 Refractive index profiles of (a) graded-index waveguide and (b) step-index waveguide.](image)

A fundamentally different type of waveguide structure known as the step-index is shown in Figure 1.6 (b). In this case, a film of uniform and higher refractive index than the substrate is established such that there is an abrupt index discontinuity at the film-substrate interface. This type of structure is normally fabricated by depositing or
growing a thin film on a lower-index substrate. The layer thickness and the $n_f - n_s$ must be designed such that the structure is able to support the desired modes at the operating wavelength.

The optical properties of planar waveguides can be arbitrarily divided into two groups, the first responsible for waveguide propagation and the second for light control efficiency [Prokhorov, 1996]. The first group includes refractive indices, their profiles, mode composition and optical loss. The second involves electro-optic, acousto-optic and nonlinear optical parameters whose values depend on the way the waveguide is manufactured.

Many integrated optics applications use narrow dielectric strip waveguides, known as channel waveguides, instead of continuous two-dimensional films. For integrated optics devices, channel waveguides have advantages over planar ones, such as better light confinement and lower propagation loss. Such a waveguide is formed by the ion implantation technique or by the deposition of a thin film on a substrate. Part of the film is subsequently etched away so that only a narrow strip waveguide is left. Figure 1.7 shows sketches of the cross-section of six different types of channel waveguides [Kogelnik, 1990]. For simplicity, the figures show abrupt transitions of the refractive index. In all six examples, the lightwave is essentially confined in the film material with index $n_f$. It has been suggested that both the rib guide and the ridge guide use a “propagating surround” approach, i.e. the lateral guide layers can support at least one guided mode when they are operated as planar slab waveguides.
A large number of waveguide devices has been fabricated [Hutcheson, 1987; Boyd, 1990; Hunsperger, 2002] and most of them are used in three broad application areas: optical communication, optical signal processing and light sources. Devices used in these applications may either be passive (e.g. waveguides, couplers, gratings, lenses and mirrors) or active (e.g. modulators, switches, scanners, detectors, emitters and second harmonic generators) [Mir, 1994]. Active device components generally require the use of crystalline media exhibiting a high level of crystalline perfection. Passive functions are less demanding and may be achieved using either amorphous or crystalline thin film media. Because of the stringent requirements for crystalline media with highly crystalline perfection, active functions have been more difficult to accomplish using deposited films.
At present, only very few laboratories have succeeded to master the thin film processing technology for use in waveguide applications, but steady progress has been achieved. Buchal et al. have described the physics of thin-film optical modulators and have given examples of different modulator concepts [Buchal, 1999].

A few reports on E-O modulators based on ferroelectric thin films grown on single crystal substrates have appeared in recent years. Petraru et al. [Petraru, 2002] have described an epitaxial barium titanate (BaTiO$_3$) thin film Mach-Zehnder modulator integrated on a magnesium oxide (MgO) single crystal substrate. The modulator works well up to a frequency of 1 MHz at a wavelength of 1550 nm. The same group [Petraru, 2003] also reported on a Mach-Zehnder modulator based on a BaTiO$_3$ thin film without preferred orientation grown on a MgO substrate. Thapliya et al. [Thapliya, 2003] studied a Mach-Zehnder modulator of a lanthanum modified lead zirconate titanate (PLZT) thin film on a Nb-SrTiO$_3$ substrate.

A more promising idea is to use a ferroelectric thin film heterostructure integrated with silicon technology in the form of a Mach-Zehnder waveguide modulator, as shown in Figure 1.8 [Buchal, 1998]. In this modulator, a BaTiO$_3$ thin film is epitaxially grown on a silicon substrate coated with a MgO buffer layer, and then a SiO$_2$ cladding is deposited on top of the thin film. Although it is possible to carry out all the processing steps, such a device has not been fabricated so far.
Figure 1.8 Conceptual design of a Mach-Zehnder modulator based on BaTiO$_3$ thin film on silicon.

1.6 Scope of the Present Study

The main objective of the present research is to fabricate and characterize barium strontium titanate (Ba$_{0.7}$Sr$_{0.3}$TiO$_3$) thin films and to study their potential use as electro-optic waveguiding materials in telecommunication applications.

The thesis consists of seven Chapters. Following the introduction given in this Chapter, the fabrication of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films by pulsed laser deposition and the structural characterization of these films are described in Chapter 2. With the help of X-ray diffraction and atomic force microscopy measurements, the optimum deposition
conditions (substrate temperature and oxygen partial pressure) for preparing epitaxial 
Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films of high quality have been found. Using these optimum 
conditions, epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films have been deposited on four different 
substrates and their structures have been studied.

In Chapter 3, the in-plane dielectric and ferroelectric properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ 
thin films are measured after coplanar interdigital electrodes have been patterned on the 
film surface.

Chapter 4 describes the electro-optic properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films. Effects 
of the processing conditions, including deposition temperature and oxygen partial 
pressure on the electro-optic properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films are discussed and the 
effect of the substrate on the electro-optic properties is also discussed.

In Chapter 5, the prism coupling technique is employed to characterize the optical 
properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films, including the refractive indices, refractive index 
profile (refractive index as a function of depth) and optical loss.

Chapter 6 presents the design and fabrication of rib waveguide and Mach-Zehnder 
modulator based on Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films. The properties of the rib waveguide and 
modulator are measured.

Conclusions and suggestions for future work are given in Chapter 7.
1.7 Statement of Original Contributions

To the best of my knowledge, the present work has made the following original contributions:

1. The electro-optic properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were systematically studied with respect to the effects of processing parameters (deposition temperature and oxygen partial pressure) and different substrates. A high electro-optic response was achieved in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films prepared by using the optimum deposition conditions.

2. The refractive indices, refractive index profile and optical loss in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were determined using the prism coupling technique. A low optical loss at $\lambda = 1550$ nm was observed, which is within the acceptable range for optical guided wave devices.

3. Single-mode rib waveguide and Mach-Zehnder modulator based on Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films have been successfully fabricated. The Mach-Zehnder modulator can effectively modulate the intensity of light at $\lambda = 1550$ nm with a half-wave voltage $V_\pi = 60$ V.
CHAPTER 2

DEPOSITION AND STRUCTURAL CHARACTERIZATION OF BARIUM STRONTIUM TITANATE THIN FILMS

2.1 Introduction

Barium strontium titanate thin films have been successfully grown on various substrates via different deposition techniques, including pulsed laser deposition (PLD) [Chen, 2001], rf magnetron sputtering [Park, 2003b], sol-gel deposition [Adikary, 2003] and polymer-assisted deposition [Lin, 2004]. Among them, PLD is the most extensively used technique for growing epitaxial Ba$_{1-x}$Sr$_x$TiO$_3$ thin films. Pulsed laser deposition is chosen in this study because not only it can provide better stoichiometric control of the thin films but also it can give thin films of high quality at a lower deposition temperature than other techniques.

In the present work, Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films for electro-optic (E-O) studies and optical waveguide applications were prepared by pulsed laser deposition. Using the X-ray diffraction technique, the structure and crystalline quality of the films were studied with regard to the effect of substrate temperature and oxygen partial pressure during deposition in order to find the optimum deposition condition. The structure of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were also investigated in relation to the effect of lattice...
mismatch, thermal expansion mismatch and oxygen vacancies by depositing the films on various substrates including LaAlO$_3$ (001) [abbreviated as LAO (001)], (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (001) [abbreviated as LSAT (001)], SrTiO$_3$ (001) [abbreviated as STO (001)].

The optical loss due to light scattering resulting from surface roughness is a critical issue in thin-film optical waveguide applications. The size of the crystalline grains is also an important factor in optical applications [Fork, 1995]. Therefore, the surface morphology, surface roughness and grain size of the thin films were investigated by means of atomic force microscopy (AFM).

2.2 Pulsed Laser Deposition of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films

2.2.1 Description of the PLD Technique

Pulsed laser deposition (PLD) is a well developed method for producing thin films by utilizing a physical process called laser ablation. PLD is applicable to almost all materials, in particular to compounds that are difficult or impossible to produce in thin-film form by other techniques. Since its successful use for growing high temperature superconductors, this method has shown to be especially suited for the deposition of oxides and multi-component materials with highly epitaxial structures.

A schematic diagram of the PLD system used in our laboratory is shown in Figure 2.1. It consists of a target holder and a heated substrate stage housed in a vacuum
Laser pulses are focused through an optical system onto the target. In order to achieve high photon absorption by the oxide target, UV wavelengths are preferred. The laser used is a KrF excimer laser with a wavelength of 248 nm and pulse duration of 25 ns (Lambda Physik COMPex 205). The laser pulse repetition rate is fixed at 10 Hz. The laser energy is around 250 mJ (energy density of 2 - 3 J/cm² on the target surface) per pulse. During deposition, the target is rotated so that successive pulses do not hit the same point on the target surface.

Figure 2.1 Schematic diagram of the pulsed laser deposition system.
Before deposition, the system is pumped to a pressure of $10^{-5} - 10^{-6}$ Torr and oxygen (processing gas) is admitted so as to give a pressure of 100 - 300 mTorr. The laser beam enters the vacuum chamber through a quartz window and is directed at the solid target. The interaction of the pulsed laser beam with the target produces a plume of the target material containing energetic neutral atoms, ions and molecules, which are subsequently transported toward a substrate placed directly in line with the plume. The plasma reaches the substrate and a thin film is formed. Since sufficient ionic mobility is needed for the growth of epitaxial oxide thin films, the substrate is kept at a high temperature (550 °C to 750 °C) during deposition.

The PLD method offers a number of advantages in the formation of multi-component thin films. The distinct advantages of PLD include its simplicity of use since the laser is totally decoupled from the growth chamber. Also rather high deposition rates can be achieved by using PLD compared to other thin film deposition techniques [Tseng, 1996; Gaidi, 2004]. The most important feature of PLD is that the stoichiometry of the target can be retained in the deposited films. This is the result of the extremely high heating rate of the target surface (~10^8 K/s) due to pulse laser irradiation. It leads to the congruent evaporation of the target irrespective of the evaporation point of the constituent elements or compounds of the target. Because of the high heating rate of the ablated materials, laser deposition of crystalline films demands a lower substrate temperature than other film growth techniques.
In spite of the advantages of PLD, some shortcomings have been identified. One of the major problems is the splashing or the particulates deposition on the films. Homogeneous laser output is required to deposit high-quality films, but particulates or droplets formation is still present. The plume will not just contain atoms, ions and molecules, but also small droplets, which may cause rough film surface and thus strong optical scattering. Another problem of PLD is the narrow angular distribution of the ablated species. This feature limits the usefulness of PLD in producing large area uniform thin films, thus PLD has not been fully deployed in industry. Inserting a shadow mask in the front of the substrate is effective to block off the large particulates. Simultaneous rotation of the target and substrate can help to produce uniform films of large area.

### 2.2.2 Deposition of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films

Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were deposited on various substrates using our pulsed laser deposition system. The polished single crystal substrates were supplied by Heifei Kejing Materials Technology Co., Ltd. Details of the deposition conditions are summarized in Table 2.1. It has been reported that the main parameters determining the structural properties of ferroelectric thin films prepared using the PLD technique are the substrate temperature and the oxygen partial pressure during growth, whereas other experimental conditions like target-substrate distance and laser energy do not lead to measurable differences [Pons-Y-Moll, 2002]. Therefore, we first optimize the deposition conditions
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by changing the deposition temperature and oxygen partial pressure and then study the effects of different substrates on the lattice structure of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films.

Table 2.1 Conditions for the preparation of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films by pulsed laser deposition.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Deposition temperature ($^\circ$C)</th>
<th>O$_2$ partial pressure (mTorr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (001)</td>
<td>550</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td></td>
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<tr>
<td></td>
<td>650</td>
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<td>700</td>
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<td>750</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>300</td>
</tr>
<tr>
<td>LAO (001)</td>
<td>750</td>
<td>200</td>
</tr>
<tr>
<td>LSAT (001)</td>
<td>750</td>
<td>200</td>
</tr>
<tr>
<td>STO (001)</td>
<td>750</td>
<td>200</td>
</tr>
</tbody>
</table>

The substrate temperature was measured using a chromel-alumel thermocouple embedded in the heater block beneath the substrate. The pressure inside the vacuum chamber was monitored by a ZDF-I vacuum gauge system (Chengdu Chenghua electronic instrument factory), which combined a manometer and an ionization gauge for detecting low vacuum and high vacuum, respectively. The flux of the processing gas (O$_2$) was controlled by a D08-3B/ZM flow meter (Beijing Jianzhong Machinery factory). By using a 250 mJ laser pulse energy and a 10 Hz repetition rate, the typical deposition rate was estimated to be 15 - 18 nm/min. After deposition, the as-grown films were post-
annealed in a tube furnace at 1000 °C for 3 h in order to reduce the oxygen vacancies and to improve the crystallinity.

2.3 Structural Characterization of Ba_{0.7}Sr_{0.3}TiO_{3} Thin Films by X-ray Diffraction

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) is a versatile and non-destructive method for obtaining information on the crystalline structure of single crystals, ceramics and thin films. The basic geometry of XRD is shown in Figure 2.2. A beam of parallel X-rays impinges on the crystal surface at an angle \( \theta \) and is diffracted at an angle \( \theta \). The condition for constructive interference is that the path difference between the two rays shown in Figure 2.2 is equal to an integral number \( n \) of wavelengths:

\[
AB + BC = d \sin \theta + d \sin \theta = n \lambda
\]

Rewriting this gives the Bragg’s law:

\[
2d \sin \theta = n \lambda \tag{2.1}
\]

where \( d \) is the distance between the lattice planes and \( \lambda \) is the wavelength of the x-ray beam. The integer number \( n \) is called the order of diffraction. Eq. (2.1) can be rewritten as:

\[
2d_{hkl} \sin \theta = \lambda \tag{2.2}
\]

where \( d_{hkl} \) is the interplanar spacing of the planes \((hkl)\) and \(h, k, l\) are the Miller indices.
Bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics have a cubic structure at room temperature, but the structure of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films may be tetragonally distorted [Wang, 2005]. For a tetragonal structure, the lattice parameters $a$ and $c$ are related to the interplanar spacing $d_{hkl}$ by:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2 + c^2} \quad (2.3)$$

In this study, X-ray diffraction measurements on Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were carried out in a Bruker AXS D8 Discover X-ray diffractometer operating at 40 kV and 40 mA, and equipped with Cu K$\alpha$ radiation at a wavelength $\lambda = 1.540562$ Å. We have performed a standard set of XRD measurements for a full characterization of epitaxial thin films, including $\theta$- $2\theta$ scan, $\omega$-scan, and $\varphi$-scan. Figure 2.3 illustrates the scanning types of the XRD measurements.

Figure 2.2 Schematic diagram for Bragg diffraction of X-rays by a crystal.
Figure 2.3 Schematic diagram showing the X-ray diffraction measurements in a Bruker AXS D8 Discover X-ray diffractometer where the rotation about the typical axes is defined. Here $\omega$ and $\chi$ are the tilting angles of the sample, $2\theta$ is the angle of the detection position, $\varphi$ is the rotation angle of the film sample about its surface normal.

The most common mode of operation in XRD characterization is the $\theta$- $2\theta$ scan, which can give information about the crystalline structure and the orientation of the crystallites. As an example, the $\theta$- $2\theta$ scan pattern of a 300 nm thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film grown on a $\text{MgO}$ (001) substrate at 750 °C under an oxygen partial pressure of 200 mTorr is shown in Figure 2.4. Apart from the (002) and (004) reflections of the $\text{MgO}$ substrate, only the (00$l$) peaks of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film appear in the XRD pattern. Therefore the $c$-axes of the crystallites in the film are highly oriented along the film normal.
Figure 2.4 XRD $\theta$–$2\theta$ pattern of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate at 750 °C under an oxygen partial pressure of 200 mTorr.

Using the $\theta$–$2\theta$ scan pattern and the Nelson-Riley extrapolation function [Cullity, 2001], the out-of-plane lattice parameter can be determined with high accuracy. The Nelson-Riley function is given by:

$$c = c_0 - c_0k\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$$

(2.4)

where $c$ is the lattice parameter calculated from the position of the Bragg peak, $c_0$ the “true” fitted lattice parameter and $k$ is a fitting parameter. Eq. (2.4) yields $c = c_0$ at $\theta = 90^\circ$, thus in practice $c$ is plotted versus $\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ and linearly extrapolated to $\theta = 90^\circ$ to obtain $c = c_0$. The major errors in the determination of lattice parameter arise from the misalignment of the instrument, surface shape of the sample, absorption in the sample, displacement of the sample from the diffractometer axis (usually the largest
single source of error), and vertical divergence of the incident beam. The use of the Nelson-Riley function can effectively reduce the above systematic errors.

The out-of-plane lattice parameters $c$ were calculated from the position of the $(00l)$ peaks ($l = 1 - 4$) using:

$$c = l \cdot d_{(00l)}$$  \hspace{1cm} (2.5)

The out-of-plane lattice parameters $c$ are plotted against the function \( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \) as shown in Figure 2.5. The data points are least squares fitted to a straight line and the “true” out-of-plane lattice parameter $c_0$ of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film, obtained from the y-intercept, is 3.9718 Å.

![Figure 2.5](image.png)

Figure 2.5 The out-of-plane lattice parameters of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate fitted to the Nelson-Riley function.
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A $\theta$-2$\theta$ scan at $\chi = 0$ is only useful for investigating planes parallel to the film surface. To study other lattice planes, it is necessary to incline the sample at an angle $\chi$, as shown in Figure 2.3. These planes are often called oblique planes and we have to estimate the value of $\chi$ and then adjust the diffractometer accordingly. By investigating different oblique planes, the in-plane lattice parameter can be calculated. Figure 2.6 shows the $\theta$-2$\theta$ scan pattern of the oblique (202) plane for the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate by tilting the sample at an angle of $\chi = 45^\circ$. Since Ba$_1$-$x$Sr$_x$TiO$_3$ thin films grown on single crystal substrates usually have a tetragonal structure with symmetry axis along the film normal [Chen, 2002], the in-plane lattice parameter $a$ can be calculated using:

$$a = \frac{2}{\sqrt{d_{(202)}^{-2} - \frac{2}{c}^{-2}}}$$

(2.6)

For the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate, the in-plane lattice parameter $a$ was determined to be 4.0344 Å.

An $\omega$-scan, the so-called rocking curve, is performed to obtain information about the texturing or grain structure of the thin film. The 2$\theta$ angle is fixed at a value that corresponds to the position of a Bragg peak and the incident angle is varied by an amount $\omega$ around the angle $\theta$ as shown in Figure 2.3. The standard way of comparing rocking curves is to measure the full width at half maximum (FWHM). The smaller the value of FWHM, the better the crystalline quality of the thin film or the smaller the misorientation of the grains.
The $\varphi$-scan is performed by rotating the sample around its surface normal, with the position of the incident beam and detector kept fixed. It is usually used to examine the in-plane orientation relationship between the film and the substrate. A film is called epitaxial if the crystalline axes of the film coincide in orientation with the crystalline axes of the substrate at every position in the thin film. A thin film can be epitaxial but it is not a single crystal in the sense that grain boundaries are compatible with the notation of epitaxy. Even though neighboring grains often will include a small angle of misorientation, the film will still be called epitaxial.
2.3.2 Effect of Deposition Temperature

In pulsed laser deposition, deposition temperature has been found to have a significant effect on the crystalline growth of ferroelectric oxide thin films. Using the conditions given in Table 2.1, we have investigated the structure of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at substrate temperatures ranging from 550 °C to 750 °C.

Figure 2.7 XRD $\theta$- $2\theta$ scan patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) substrates at different temperatures.
The $\theta$-2$\theta$ scan patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at different temperatures are plotted in Figure 2.7. Only the (00$l$) peaks are observed, which implies that, in a broad range of deposition temperature, Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ films deposited on MgO substrates have a perovskite structure and are highly $c$-axis oriented. One important feature in the $\theta$-2$\theta$ scan patterns is that the intensity and sharpness of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (002) peaks increase with the increase of deposition temperature, indicating higher crystalline quality at higher deposition temperatures.

The grain orientation is a key factor that has been shown to be correlated with the optical loss of thin film waveguides [Kang, 1998; Siegert, 2000]. Therefore, the grain orientation must be controlled in order to avoid high optical losses due to light scattering at grain boundaries. The degree of grain misorientation in our Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films was evaluated by measuring the FWHM of the $\omega$-scan of the (002) diffraction peak and the result is shown in Figure 2.8. It is seen that the FWHM drops substantially with the increase of deposition temperature. The highest degree of grain orientation was achieved in the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film deposited at 750 °C, which has a FWHM of 0.48°.
It was reported that the crystalline quality of Ba\textsubscript{1-x}Sr\textsubscript{x}TiO\textsubscript{3} thin films would degrade if the deposition temperature was too high (> 800 °C) since the films suffered from the nonuniform strain that originated from point defects, such as oxygen vacancies [Park, 2000]. So we choose 750 °C as the “optimized” deposition temperature in subsequent experiments. More discussion to justify this choice will be given in Section 2.4.5.

Figure 2.8 FWHM of the rocking curve (ω-scan) of the (002) diffraction peak for Ba\textsubscript{0.7}Sr\textsubscript{0.3}TiO\textsubscript{3} thin film grown on MgO (001) substrate as a function of substrate temperature.
Off-axis $\varphi$-scans of the (202) diffraction of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films, as shown in Figure 2.9, were performed to determine the in-plane crystallographic relationship between the film and the substrate. It is seen that the four-fold symmetric diffraction peaks of all $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films coincide well with those of the MgO substrate, suggesting that $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films exhibit an epitaxial growth on MgO (001) substrates. It is noted that the diffraction peaks of the films grown at higher temperatures are sharper and stronger, implying a high degree of in-plane orientation. The broadening and weakening of the diffraction peaks for the films grown at lower temperatures indicate that there is crystalline disorder and poor in-plane orientation. The in-plane orientation relationship has been determined to be $<100>_{\text{BST}}/<100>_{\text{MgO}}$. The higher the deposition temperature, the higher the degree of epitaxy. Since good crystalline quality and high epitaxy were achieved in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films deposited at 750 °C, the out-of-plane lattice parameter $c$ and in-plane lattice parameter $a$ for films deposited at 750 °C were determined and will be discussed in the following Section.
Figure 2.9  Off-axis $\phi$- scans of the (202) diffraction of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films deposited on MgO (001) substrates at different temperatures: (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, (e) 750 °C. (f) is the $\phi$- scan of the (202) diffraction of the MgO (001) substrate.
2.3.3 Effect of Oxygen Partial Pressure

Ambient oxygen partial pressure plays an important role in the lattice deformation of ferroelectric oxide thin films grown by PLD at high substrate temperature [Navi, 2003]. To study the effects of oxygen partial pressure on the structural characteristics and crystalline quality, Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were deposited on MgO (001) substrates under different oxygen pressures (100, 200 and 300 mTorr) while keeping the other deposition parameters unchanged.

![XRD patterns](image)

Figure 2.10 XRD $\theta$- $2\theta$ patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates under different oxygen partial pressures. The deposition temperature is 750 °C.
Figure 2.10 shows the XRD θ- 2θ patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at different oxygen partial pressures. All the films have a perovskite phase; they are $c$- axis oriented and are epitaxial with respect to the substrate ($\phi$- scans are not shown here). The lattice parameters of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films are plotted as a function oxygen partial pressure in Figure 2.11. Moreover, the tetragonal $a/c$ ratio and the FWHM of the (002) peaks for these films are shown in Figures 2.12 and 2.13, respectively. It is seen that the structure of the films depends strongly on the oxygen partial pressure. The out-of-plane lattice parameter $c$ decreases as the oxygen pressure increases, and approaches the value for the bulk ceramic at an oxygen pressure of 200 mTorr and above. Compared to the bulk ceramic, the in-plane lattice parameter $a$ is compressed when the film is deposited at 100 mTorr oxygen pressure, but elongated when the oxygen pressure increases to 200 and 300 mTorr. The largest tetragonality ($a/c$) occurs in the film deposited at the oxygen pressure of 200 mTorr.

The changes of the lattice parameters can be explained in terms of the lattice mismatch and thermal expansion difference between the film and the substrate, and the presence of oxygen vacancies in the films. For the out-of-plane lattice parameter, the lattice mismatch and thermal expansion difference are expected to have comparatively little effect, so we will concentrate on the effect of oxygen vacancies. The presence of oxygen vacancies gives rise to a reduction of the Coulomb attractive force between the cation and anion atoms, thereby resulting in an increase of the lattice parameter and even of the unit cell volume [Kim, 2000]. Our result that the $c$ value for the film deposited under an oxygen pressure of 100 mTorr is higher than that of the bulk ceramic indicates
that the film contains a significant number of oxygen vacancies. As the oxygen partial pressure increases, the number of oxygen vacancies decreases and the $c$ value for the film is close to that of the bulk ceramic at an oxygen pressure of 200 mTorr and above. It should be noted that oxygen partial pressures around 300 mTorr are employed in the pulsed laser deposition of oxide film in order to reduce the formation of oxygen vacancies, but the films are still found to be oxygen-deficient [Knauss, 1996; Tarsa, 1996]. The presence of oxygen vacancies will lead to an increase in the optical absorption and scattering loss [Hiskes, 1994; Xie, 1995].

![Graph showing the out-of-plane and in-plane lattice parameters of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates as a function of oxygen partial pressure. The deposition temperature is 750 °C.](image)

Figure 2.11 Out-of-plane and in-plane lattice parameters of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates as a function of oxygen partial pressure. The deposition temperature is 750 °C.
Figure 2.12 Tetragonal distortion ($a/c$) of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films grown on MgO (001) substrates as a function of oxygen partial pressure. The deposition temperature is 750 °C.

Figure 2.13 FWHM of the (002) peaks of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films grown on MgO (001) substrates as a function of oxygen partial pressure. The deposition temperature is 750 °C.
To have a deeper understanding of the effect of oxygen partial pressure on the lattice parameter of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films, we assume that oxygen atoms in the films and in the deposition chamber are in equilibrium at a given deposition temperature $T$ (750$^\circ$C). The formation of oxygen vacancies in the film can be represented by [Kim, 2000]:

$$O_{BST} \rightleftharpoons V_O + \frac{1}{2}O_2 + 2e$$

(2.7)

where $O_{BST}$ and $V_O$ represent the oxygen atom and the oxygen vacancy in the film, respectively. Using a simple mass-action equation, the concentration of oxygen vacancies $[V_O]$ can be expressed as:

$$[V_O][e]^2 \propto \exp(-\Delta H / kT)P_{O_2}^{\frac{1}{2}}$$

(2.8)

where $[e]$ is the concentration of electrons, $\Delta H$ the enthalpy for generating oxygen vacancies and $P_{O_2}$ is the partial pressure of the oxygen gas in the chamber. $[O_{BST}]$ is constant because of the relatively small number of oxygen vacancies in the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film. Based on the assumption that $[V_O]$ is $1/2[e]$, the concentration of the oxygen vacancies at constant $T$ is:

$$[V_O] \propto P_{O_2}^{-\frac{1}{6}}$$

(2.9)

This relation indicates that, as the oxygen partial pressure increases, the concentration of oxygen vacancies decreases and thus the lattice parameter decreases, which is consistent with the data on the out-of-plane lattice parameter (see Figure 2.11). On the other hand, the observed in-plane lattice parameters increases as the oxygen partial pressure increases from 100 to 200 mTorr. Therefore, in this case, lattice mismatch and
difference in thermal expansion between the film and the substrate may play a more dominant role than oxygen partial pressure. The effects of lattice mismatch and difference in thermal expansion between the film and the substrate will be discussed in more detail in the following Section.

As shown in Figure 2.13, the FWHM of the $\omega$-scan of the (002) peak is also significantly affected by the oxygen partial pressure. The larger FWHM for the film deposited at 100 mTorr can be attributed to the large number of point defects, mainly oxygen vacancies. However, a larger FWHM is also obtained for the film grown under a higher oxygen pressure of 300 mTorr, which is attributed to the decrease in kinetic energy of the ablated species reaching the growing film surface [Pons-Y-Moll, 2002]. It has been reported that in the PLD of oxide targets, the velocity of the ablated species decreases slowly from vacuum to a pressure of 75 mTorr, and then more significantly at higher pressure because of the collisions with the oxygen gas molecules in the chamber [Girault, 1990]. The decrease in the velocity of the ablated species leads to low surface diffusion and impedes the crystalline growth. Therefore, the optimum ambient oxygen partial pressure for growing epitaxial $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films is probably about 200 mTorr. Moreover, it has been reported that there is a possibility for the formation of a mixture of perovskite and pyrochlore phases if the oxygen pressure is higher than 200 mTorr [Tantigate, 1995].
2.3.4 Effect of Different Substrates

Oriented $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films deposited by PLD on (001) single crystal substrates with cubic structure show deviations from the expected cubic structure [Navi, 2003; Chen, 2002b; Canedy, 2000]. These deviations are caused by the strain generated as a result of the difference between the lattice parameters and difference between the thermal expansion coefficients of the film and the substrate, and the presence of oxygen vacancies. In this Section, we compare the crystal structures of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films deposited on MgO (001), LAO (001), LSAT (001) and STO (001) substrates under the same optimized conditions as shown in Table 2.1.

All of the four films have a pure perovskite phase with (001) orientation as shown in Figures 2.4, 2.14, 2.16 and 2.18, respectively. The in-plane alignment of the (100) crystal axis of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films with respect to the <100> axis of the single crystal substrate was also confirmed by the XRD off-axis $\phi$- scans of the (202) diffraction of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ film and the substrate as shown in Figures 2.9, 2.15, 2.17 and 2.19, respectively, indicating epitaxial growth of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films.

The lattice parameters of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ films were determined from the XRD $\theta$- $2\theta$ scan patterns and are listed in Table 2.2. The out-of-plane lattice parameters of the four films are slightly larger than that of bulk ceramic, which indicates that the films have more oxygen vacancies than the bulk ceramic. If we assume that the tetragonal structure
of the films arises from the distortion from the cubic structure of the bulk ceramic, then the in-plane strain $x^\parallel$ by:

$$x^\parallel = \frac{a_\parallel - a^0}{a^0}$$ (2.10)

where $a_\parallel$ is the in-plane lattice parameter of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film and $a^0$ is the lattice parameter of bulk ceramic. On the other hand, the ideal in-plane strain induced by lattice mismatch is given by:

$$x^0 = \frac{a_s - a^0}{a_s}$$ (2.11)

where $a_s$ is the lattice parameter of the substrate (also see Table 2.2).

Table 2.2 shows that the ideal in-plane strain $x^0$ of the films grown on LAO, LSAT and STO substrates have negative values, indicating that the films should be under in-plane compression, while $x^0$ of the film grown on MgO substrate has a positive value, indicating that the film should be under in-plane tension. However, a comparison of the actual and ideal in-plane strains indicates that the situation is not so simple. For MgO and STO substrates, $x^\parallel$ has the same sign as $x^0$ but has smaller magnitude, but for LAO and LSAT substrates, $x^\parallel$ and $x^0$ have opposite signs. The behavior for MgO and STO substrates may be explained as follows. Since the film thickness has greatly exceeded the critical value, the internal stress may have relaxed towards a zero-strain state by the formation of misfit dislocations. The large lattice mismatch energy induced by the lattice
mismatch at the interface can be released by creating a number of edge dislocations at the interface between the film and the substrate [Canedy, 2000; Chen, 2002a].

The situation for LAO and LSAT substrates are more complicated and more factors should be involved. It can be seen from Table 2.2 that lattice mismatch and difference in thermal expansion between the film and the substrate give rise to opposing effects on in-plane lattice deformation of the films grown on LAO and LSAT substrates. Moreover, oxygen vacancies may contribute to the in-plane lattice distortion, since these vacancies may increase, decrease or screen the overall film stress [Chang, 1999]. It is noted that the strain induced by thermal expansion difference is one order of magnitude smaller than that induced by lattice mismatch, implying that the thermal expansion mismatch could not be the dominant factor in this case. Therefore, elongation of the in-plane lattice parameters for the films grown on LAO and LSAT substrates results from the competition between the effects of lattice mismatch and oxygen vacancies. Since \( x^{\prime} \) and \( x^0 \) are opposite in sign, oxygen vacancies should be the dominant factor that is responsible for the in-plane lattice elongation.
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Figure 2.14 XRD $\theta$-2$\theta$ scan patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on LAO (001) substrate.

Figure 2.15 Off-axis $\varphi$-scans of the (202) diffraction of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on LAO (001) substrate.
Figure 2.16 XRD $\theta$-$2\theta$ scan patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on LSAT (001) substrate.

Figure 2.17 Off-axis $\varphi$-scans of the (202) diffraction of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on LSAT (001) substrate.
Figure 2.18 XRD $\theta$-2$\theta$ scan patterns of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on STO (001) substrate.

Figure 2.19 Off-axis $\phi$-scans of the (202) diffraction of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on STO (001) substrate.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thermal Expansion Coefficient ( \alpha \left( \times 10^{-6}/K \right) )</th>
<th>( \chi^0 ) (%)</th>
<th>FWHM of Rocking Curve of BST (002) Peak (deg)</th>
<th>FWHM of Rocking Curve of Substrate (002) Peak (deg)</th>
<th>Lattice Parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (001)</td>
<td>12.8</td>
<td>5.81</td>
<td>0.48</td>
<td>0.12</td>
<td>4.215 3.9718</td>
</tr>
<tr>
<td>LAO (001)</td>
<td>9.2</td>
<td>0.12</td>
<td>0.10</td>
<td>0.10</td>
<td>3.780 3.9702</td>
</tr>
<tr>
<td>LSAT (001)</td>
<td>10.5</td>
<td>0.13</td>
<td>0.13</td>
<td>0.10</td>
<td>3.9967 3.9706</td>
</tr>
<tr>
<td>STO (001)</td>
<td>10.3</td>
<td>-5.03</td>
<td>-2.64</td>
<td>-2.64</td>
<td>3.9365 3.9796</td>
</tr>
<tr>
<td>Ba(<em>{0.7})Sr(</em>{0.3})TiO(_3) Bulk Ceramics</td>
<td>10.5</td>
<td>-1.77</td>
<td>N.A.</td>
<td>N.A.</td>
<td>3.970</td>
</tr>
</tbody>
</table>

Table 2.2 Lattice parameters of Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin films, unrelaxed lattice misfit and actual in-plane lattice misfit strain on various substrates at room temperature.

\( \alpha \) data are quoted from [Hellwege, 1981].
The grain orientation of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on the four different substrates were studied using the XRD rocking curves of (002) diffraction peaks and the FWHM values are shown in Table 2.2. The smallest FWHM value was achieved in the film grown on STO substrate and this is probably because Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and STO have similar lattice parameters and thermal expansion coefficients. Films deposited on MgO substrates have a comparatively large FWHM of 0.48°, which may have resulted from the significant lattice mismatch between Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ and MgO. Therefore, MgO is not the best choice as a substrate if grain orientation is the only consideration. However, from the optical waveguide point of view, MgO is a desirable choice because it has a lower refractive index and higher optical transparency than the other three substrates. Furthermore, it has been reported that the dislocations that may result from the lattice mismatch do not cause significant optical losses since the light intensity at the interface in quite low especially when the film is thick enough (up to several hundred nanometers) [Siegert, 2000]. Details of the optical consideration for a thin film waveguide will be presented in Chapter 6.
2.4 Investigation of Surface Morphology by Atomic Force Microscopy

2.4.1 Atomic Force Microscopy (AFM)

Scanning probe microscopy (SPM) refers to all techniques which use a mechanism to scan a sharp tip across a sample surface to obtain 2- or 3-dimensional images of the surface at nanometer (or better) resolution both laterally and vertically. Atomic force microscopy (AFM) is one of these techniques and operates by probing the force between a tip mounted on a special spring and the sample surface. AFM provides topographic information down to Angstrom level. It is very sensitive in the vertical dimension and somewhat less sensitive in the lateral dimension.

AFM operates by measuring the atomic forces between a probe and the sample. These forces depend on the type of sample and probe, distance between probe and sample and sample surface contamination. AFM does not require conducting samples and is thus suitable for insulators, such as ferroelectric oxide thin films. The AFM instrument can give information on the grain size and surface roughness which will help us to optimize the processing of thin films for optical application.

The AFM instrument consists of a cantilever, usually formed from silicon, silicon oxide or silicon nitride, with a sharp tip mounted on its end. The surface of the sample is scanned by the very sharp cantilever tip (micron size). The cantilever is then affected by the interaction between the tip and the atoms in the sample. A laser beam is focused on
the tip and the movement of the tip is detected by the reflected laser beam. An AFM can operate in several different modes. In the contact mode the tip is brought in contact with the sample surface. More common one uses the tapping mode, where the tip is excited to perform vertical oscillation close to its resonance frequency. As the tip approaches the sample surface, the attractive forces increases, thereby causing a resonance frequency decrease. The probe exerts negligible frictional force on the sample and the surface damage is minimal.

2.4.2 Surface Morphology

Knowledge of the surface morphology of the films is important for optical waveguide applications. Surface scattering due to the surface roughness is one of the important sources of optical propagation losses in ferroelectric thin film waveguides [Tien, 1971; Fork, 1995]. In the case of single mode propagation in highly confined waveguides produced from heteroepitaxial films, scattering loss is magnified because the major portion of the guided light beam is confined near the surface of the films. Therefore, it is essential to produce thin films with very smooth surface to reduce the surface scattering loss. The grain size of the ferroelectric thin films also has a significant effect on the scattering loss in waveguides. It was reported that an average grain size smaller than $\lambda_0/10$ was well suited for optical devices operating at the vacuum wavelength $\lambda_0$ [Petraru, 2003]. Large grain size in thin films may lead to large optical scattering, which is another important reason for high waveguide losses [Lu, 1999a]. In this Section, the surface morphology, surface roughness and grain size of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$
thin films, which are strongly dependent on the deposition temperature and oxygen partial pressure, were studied using a Digital Instruments Nanoscope II atomic force microscope (AFM) operating in the tapping mode. All images were filtered using the flattening and plane fit functions provided with the AFM software. The root mean square (rms) roughness of the film surface and the grain size were determined also by using the software included in the instrument.

2.4.3 Effect of Deposition Temperature

Deposition temperature has a strong effect on the surface morphology and grain size of the thin films. Figures 2.20 and 2.21 show the typical AFM images in an area of $1 \times 1$ $\mu$m$^2$ of 300 nm thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films deposited on MgO (001) substrates under an oxygen partial pressure of 200 mTorr at 550 °C and 750 °C, respectively. Very fine grains with an average size of 25-35 nm were observed in the film grown at 550 °C while larger grains of size 80-90 nm were observed in the film deposited at 750 °C. The surface roughness increased from 1.2 nm to 2.3 nm with the increase of deposition temperature from 550 °C to 750 °C.
Figure 2.20 Surface morphology of a 300 nm thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ film deposited on MgO (001) substrate at 550 °C under 200 mTorr oxygen partial pressure.

Figure 2.21 Surface morphology of a 300 nm thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ film deposited on MgO (001) substrate at 750 °C under 200 mTorr oxygen partial pressure.
2.4.4 Effect of Oxygen Partial Pressure

Oxygen partial pressure also has a significant influence on the surface morphology of the films. AFM images are shown for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films (~300 nm thick) deposited under 100 mTorr (Figure 2.22), 200 mTorr (Figure 2.21) and 300 mTorr (Figure 2.23) oxygen partial pressure at 750 °C. A very smooth surface was obtained when the film was deposited under an oxygen pressure of 100 mTorr. The average grain size and surface roughness increase dramatically with the increase of oxygen partial pressure. The average grain size and rms surface roughness are shown in Table 2.3. The increase of the roughness with the increase of oxygen pressure is due to the decrease in the velocity and hence the surface mobility of the ablated species as a result of scattering by the ambient oxygen atoms. At low oxygen pressure, the ablated species have high velocities and hence high mobility when they reach the substrate. This will enhance the lateral growth of the nuclei, thereby giving a flat and smooth surface.

Table 2.3 Grain size and surface roughness of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ films grown under various oxygen partial pressures.

<table>
<thead>
<tr>
<th>Oxygen pressure (mTorr)</th>
<th>Average grain size (nm)</th>
<th>Surface roughness (rms) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>25-35</td>
<td>0.48</td>
</tr>
<tr>
<td>200</td>
<td>80-90</td>
<td>2.3</td>
</tr>
<tr>
<td>300</td>
<td>180-200</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Figure 2.22 Surface morphology of a 300 nm thick \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) film deposited on \( \text{MgO} \) (001) substrate at 750 °C under 100 mTorr oxygen partial pressure.

Figure 2.23 Surface morphology of a 300 nm thick \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) film deposited on \( \text{MgO} \) (001) substrate at 750 °C under 300 mTorr oxygen partial pressure.
2.4.5 Analysis of the Optical Scattering Loss due to Surface Roughness of Ferroelectric Thin Films

In order to analyze the optical loss in the films due to the surface roughness, the Rayleigh scattering formula developed by Tien [Tien, 1970] was employed to estimate the loss due to surface scattering [Siegert, 2000]. The Rayleigh scattering formula for waveguides is given by:

\[ \xi_{sc} = \left( \frac{4\pi\sigma}{\lambda} \right)^2 \frac{f(\theta)}{h} \quad (2.12) \]

where \( \sigma \) is the rms surface roughness, \( \lambda \) is the wavelength, \( f(\theta) \) is a geometric parameter associated with the angle of reflection \( \theta \) and \( h \) is the waveguide thickness. One can see from Eq. (2.12) that the scattering loss will increase significantly with the increase of surface roughness. Early calculations by Fork and Anderson [Fork, 1995] on the influence of surface roughness on light scattering in thin ferroelectric oxide films indicated that the films should have a roughness of less than 1 nm in order to achieve a loss of less than 1 dB/cm. This surface roughness requirement creates severe difficulty for the epitaxial growth of thin films, especially because surface roughness often increases with increasing film thickness. Calculations by Wessels’s group [Wessels, 1996], however, indicated that the surface roughness requirement may not be as restrictive as that reported by Fork and Anderson. They claimed that a surface roughness of 2 - 4 nm may be tolerated, since it leads to a low optical scattering loss of 1-2 dB/cm.

Grain size is also an important factor affecting optical scattering loss. Large grain size in films leads to more severe light scattering and thus higher losses in waveguides.
It was estimated that the optical loss in a film with a grain size of about 100 nm was 3 dB/cm [Lu, 1999a]. Since light is scattered at the grain boundaries, the scattering loss can be effectively reduced if the grain size is much smaller than the wavelength of the light. On the other hand, epitaxy is also an important requirement in order to diminish light scattering by grain boundaries. Since a substrate temperature of 750 °C and an oxygen partial pressure of 200 mTorr can give highly epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films with a grain size of about 80 nm and a rms surface roughness of 2.3 nm, these seems to be the optimized conditions for producing films with sufficiently low optical loss for waveguide applications.

2.5 Summary

Epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were produced by using pulsed laser deposition. Using X-ray diffraction the structural characteristics of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were studied with regard to the effects of deposition temperature, oxygen partial pressure and various substrates. The surface morphology of the films was observed using an atomic force microscope and the surface roughness and average grain size were determined from the AFM images. By considering the crystalline quality and epitaxy of the films, and the optical loss estimated from the surface roughness and grain size, the optimum conditions for depositing Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films for optical applications were found.
3.1 Introduction

As discussed in Chapter 1, crystals with a non-centrosymmetric structure exhibit a predominantly linear electro-optic behavior while crystals with a centrosymmetric structure show a quadratic electro-optic effect. It is known that barium strontium titanate transforms from the ferroelectric phase to the paraelectric phase at the Curie temperature ($T_c$), at which the structure changes from tetragonal to cubic. Therefore, it is important to know whether our Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films are in the ferroelectric state at room temperature, since this knowledge may lead to a better understanding of the electro-optic behavior. To determine whether the films are in the ferroelectric state, we have conducted relative permittivity measurements as a function of temperature and hysteresis measurements at room temperature.

3.2 Electrode Patterning on Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films

Before the dielectric and hysteresis measurements, surface electrodes were patterned on the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films. First, a 200-nm-thick gold layer was deposited
on the film surface by magnetron sputtering. Photolithography and wet etching techniques were then used to make the electrode patterns.

Optical lithography, with light as radiation source, is the most common type of lithography. A mask is usually utilized as the image control system. In this work, the lithography was conducted on a mask aligner (model JKG-2A, Shanghai Optical Machinery Works) with UV light source (λ=313.2 nm). An optical contact mask with a transparent carrier layer and an opaque absorber layer was used. The following steps in image reversal lithography and wet etching were performed in a Class 100 clean room environment:

1. **Cleaning.** The film surface was cleaned for 2 min in an ultrasonic bath of acetone, then rinsed in ethanol and finally dried in a stream of compressed air.

2. **Photoresist spinning and baking.** A positive photoresist (AZ 3100 PR, Clariant (China) Ltd.) was spin-coated on the film at 5000 rpm for 50 seconds, resulting in an approximately 1.0 -1.2 µm thick uniform layer. The photoresist-coated film was then soft-baked in an oven at 80 °C for 10 min.

3. **Exposure.** The pattern was defined using a mask inserted into a mask aligner and exposed to UV light for 18 seconds.

4. **Developing.** The exposed resist was developed in a developer (AZ 300, Clariant (China) Ltd.) for 30 seconds, then rinsed in de-ionized water and dried in a stream of compressed air. The pattern was checked in an optical microscope.
5. **Wet etching.** To remove the excess gold so as to leave the electrodes on the surface of the film, the photoresist-patterned film was immersed into a gold etching solution (KI and I₂ aqueous solution) for 20 seconds.

To remove the residual photoresist, the film was put into an ultrasonic bath of acetone for 5 min, then rinsed in ethanol and de-ionized water, and finally dried in a stream of compressed air. The final electrode pattern was inspected using an optical microscope. If all the photoresist had been removed and the contacts were good, the samples were ready for testing. The electrode was wire-bonded to a piece of PCB for easy handling and better electrical connection during the subsequent measurements.

As shown in Figure 3.1, the electrode pattern used for dielectric and ferroelectric characterization consisted of interdigital electrodes (IDE). The IDE had a total of 21 fingers with finger length of 925 µm and finger width of 5 µm. The finger gap spacing was 3 µm. The fingers of the IDEs were arranged to lie along the in-plane <010> or <100> crystallographic directions. The ferroelectric hysteresis loop was measured using a TF Analyzer 2000 equipped with a FE-Module (HV) (aixACCT). The relative permittivity of the film was measured using a HP 4194A impedance analyzer connected to a temperature-controlled chamber (Oxford). The calculation of the relative permittivity from the capacitance data was conducted by using a MATHEMATICA program we developed based on Gevorgian’s model, which gives the relationship among the capacitance, the electrode sizes and the material properties [Gevorgian, 1996; Wang, 2003].
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Figure 3.1 Schematic diagram showing the interdigital electrodes (IDE) used for dielectric and hysteresis measurements.

3.3 Relative Permittivity of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films as a Function of Temperature

3.3.1 Effect of Oxygen Partial Pressure

Figure 3.2 shows the temperature dependence of the in-plane relative permittivity $\varepsilon$ of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited under different oxygen partial pressures. For the films deposited under 200 and 300 mTorr oxygen pressure, the permittivity exhibits a maximum at $T_c \approx 88 \ ^\circ\text{C}$ and $80 \ ^\circ\text{C}$, respectively, which are higher than the Curie temperature ($\sim 35 \ ^\circ\text{C}$) of bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics (see Figure 1.3 (b)). The upward shift of $T_c$ to higher temperature in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films is believed to arise from the in-plane tensile strain induced by the lattice misfit. It has been reported that a biaxial tensile strain of the order of 1 % in ferroelectric thin films is enough to push the Curie temperature $T_c$ several hundred degrees higher than its inherent value [Choi, 2004;
Haeni, 2004]. The in-plane strain $\varepsilon_i''$ in our Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films, for instance, the film deposited under 200 mTorr oxygen pressure, was calculated to be 1.65%. However, the shift of $T_c$ in our tensile stressed Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film is not as high as expected probably because the film thickness (~300 nm) has greatly exceeded the critical value, thereby resulting in a relaxation towards a zero-strain state through the introduction of dislocations. The large lattice misfit energy induced by the lattice misfit at the interface can only be released by creating edge dislocations at the interface between the Ba$_{1-x}$Sr$_x$TiO$_3$ film and MgO substrate [Canedy, 2000; Chen, 2002a]. The high dislocation densities in epitaxial Ba$_{1-x}$Sr$_x$TiO$_3$ thin films (typically ~ $10^{11}$ cm$^{-2}$) may cause an inhomogeneous strain which will further smear the ferroelectric-paraelectric transition. Nevertheless, the fact that $T_c$ is much higher than room temperature for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited under 200 and 300 mTorr oxygen pressure imply that these films are in the ferroelectric phase at room temperature.

In contrast, the film deposited under 100 mTorr oxygen pressure exhibits a maximum in $\varepsilon$ at $T_c \approx -10 ^\circ$C, which is lower than that of bulk ceramics. In general, if there is a compressive stress in the film along the in-plane direction, then the Curie temperature of the film is likely to shift towards lower temperature [Haeni, 2004]. Figure 2.11 in Chapter 2 shows that the film grown under 100 mTorr oxygen pressure has a shortened in-plane lattice parameter, which is consistent with the downshift of the Curie temperature.
CHAPTER 3 DIELECTRIC AND HYSTERESIS BEHAVIOR OF BST THIN FILMS

Figure 3.2 In-plane relative permittivity $\varepsilon$ as a function of temperature for $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films deposited on MgO (001) at 750 °C under (a) 100 mTorr (b) 200 mTorr and (c) 300 mTorr O$_2$ pressure.
It is noted that the shape of the $\varepsilon - T$ peak of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films are much broader than that of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ bulk ceramics (see figure 1.3 (b)). The most probable reason for the broadening of the transition peaks in the films is the small grain size. Broadening of the transition has been observed in other ferroelectric thin films such as Pb(Zr, Ti)O$_3$ [Udayakumar, 1995] and BaTiO$_3$ [Troyler-McKinstry, 1995], which have grain size in the nanometer range. A correlation between the width of transition and the grain size (25 – 200 nm) has been found for PLZT films [Tyunina, 1998].

3.3.2 Effect of Different Substrates

Ba$_{1-x}$Sr$_x$TiO$_3$ thin films exhibit different dielectric behaviors when grown on different substrates [Carlson, 2000; Chen, 1999]. Substrates can modify the physical properties of thin films via the strains induced by the lattice misfit or difference in thermal expansion between the film and the substrate. As a result, the properties of the thin films can be markedly different than the intrinsic properties of the corresponding unstrained bulk materials [Choi, 2004; Haeni, 2004; Wang, 2005]. Although such strain sometimes leads to degraded film properties, if judicious use is made of substrates and growth parameters, strain offers the opportunity to enhance particular properties of a chosen material in thin film form, and this is called “strain engineering”. “Strain engineering” is a very hot topic in state-of-the-art thin film studies, since strain is an effective way to adjust the Curie temperature of ferroelectric thin films. In this Section, the temperature dependence of relative permittivity of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films
deposited on LAO (001), LSAT (001) and STO (001) substrates were investigated and compared with that of the film deposited on MgO (001) substrate.

Figure 3.3 shows the temperature dependence of in-plane relative permittivity for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on different substrates under the optimum conditions (e.g. 750 °C and 200 mTorr O$_2$ pressure). Like the behavior of the film grown on MgO substrate, films grown on LAO and LSAT substrates show increased phase transition temperatures compared with that of bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics. The Curie temperature of the film grown on LSAT (001) is 105 °C, which is about ~ 70 °C higher than that of bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics ($T_c = \sim 35$ °C) [Smolenskii, 1954]. The shift of $T_c$ in the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film is believed to be due to the elongation of the in-plane lattice parameters (see $x''$ in Table 2.2). The film grown on STO shows a very broad peak and the Curie temperature is located at 40 °C, which is almost the same as that of bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics.
Figure 3.3  In-plane relative permittivity $\varepsilon$ as a function of temperature of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at 750 $^\circ$C under 200 mTorr O$_2$ pressure on (a) MgO (001) (b) LAO (001) (c) LSAT (001) and (d) STO (001).
3.4. Hysteresis Measurements of \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) Thin Films

### 3.4.1 Effect of Oxygen Partial Pressure

The hysteresis loops of \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) thin films deposited on MgO under different oxygen pressures are shown in Figure 3.4. As shown in Figure 3.4 (b) and (c), well-defined hysteresis loops are obtained for the films deposited under 200 and 300 mTorr oxygen pressure, which agree with the existence of the ferroelectric phase at room temperature found in \( \varepsilon-T \) measurements. The remnant polarization \( P_r \) for the films deposited under 200 and 300 mTorr oxygen pressure are 9.5 \( \mu \text{C/cm}^2 \) and 2.8 \( \mu \text{C/cm}^2 \), respectively. Bulk \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) ceramics have a cubic structure and do not exhibit an obvious hysteresis loop. In comparison with \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) ceramics, \( P_r \) of the film along the in-plane direction has been noticeably enhanced. It is believed that the increased tetragonality \( (a/c) \) contributes to the enhanced ferroelectricity. The higher \( P_r \) value for the film deposited under 200 mTorr oxygen pressure may be due to the larger tetragonal distortion (1.016) in comparison with the lattice distortion (1.004) in the film deposited under 300 mTorr oxygen pressure.

For the film deposited under 100 mTorr oxygen pressure, only a slim hysteresis loop was observed as shown in Figure 3.4 (a). Since the \( \varepsilon-T \) measurement shows a permittivity maximum at \( T_c \approx -10 \, ^\circ \text{C} \), it is reasonable that the film shows a slim hysteresis loop since it is in the paraelectric state at room temperature.
Figure 3.4 In-plane ferroelectric hysteresis loops of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) at 750 °C under (a) 100 mTorr (b) 200 mTorr and (c) 300 mTorr O$_2$ pressure.
3.4.2 Effect of Different Substrates

The hysteresis loops for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on different substrates under the same conditions are shown in Figure 3.5. Well-defined hysteresis loops were observed in thin films grown on MgO, LAO and LSAT substrates and the remnant polarizations $P_r$ are 9.5 μC/cm$^2$, 7.5 μC/cm$^2$ and 10.5 μC/cm$^2$, respectively. In comparison with bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics, $P_r$ of the films grown on MgO, LAO and LSAT substrate are significantly enhanced, which can be attributed to the increased tetragonality. A very slim hysteresis loop was obtained for the film grown on STO substrate. As seen from Figure 3.3(d), the $\varepsilon$-$T$ curve exhibits a very broad peak at about 40 °C. Therefore the ferroelectric-paraelectric phase transition has already started at room temperature and the film has lost most of its ferroelectric activity.
Figure 3.5 In-plane ferroelectric hysteresis loops for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at 750 °C under 200 mTorr O$_2$ pressure on (a) MgO (001), (b) LAO (001), (c) LSAT (001), and (d) STO (001).
3.5 Summary

Relative permittivity versus temperature and room-temperature hysteresis measurements were performed in order to determine whether Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin films deposited at 750 °C were ferroelectric or paraelectric at room temperature. The effects of oxygen partial pressure and different substrates on these physical properties were investigated and the results are summarized in Tables 3.1 and 3.2. It is seen that the Curie temperature \(T_c\) and the remnant polarization \(P_r\) depend on the oxygen partial pressure and the substrates.

When the films are deposited on MgO substrates under an oxygen pressure of 100 mTorr, the Curie temperature is -10 °C, which is significantly lower than the Curie temperature (35 °C) of bulk Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) ceramics. Higher oxygen pressures (200 and 300 mTorr) result in an upward shift of the Curie temperature, and the films are in the ferroelectric phase at room temperature. The hysteresis measurements show that the film deposited under an oxygen pressure of 100 mTorr exhibits almost no ferroelectric activity while the films deposited under higher oxygen pressures (200 and 300 mTorr) show ferroelectric behavior. The remnant polarization is higher for the film deposited under an oxygen pressure of 200 mTorr.

Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin films grown on different substrates under the optimum conditions (e.g. 750 °C and 200 mTorr oxygen pressure) exhibit different ferroelectric behavior at room temperature. Like the film grown on MgO substrate, films deposited
on LAO and LSAT substrates show significant ferroelectric activity at room temperature because their Curie temperatures have shifted to temperatures much higher than room temperature. However, the film grown on STO substrate has a Curie point close to room temperature, and exhibits almost no ferroelectric activity. Knowledge of whether the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film is in the ferroelectric state at room temperature may help us understand its electro-optic behavior.

Table 3.1 Curie temperature and remnant polarization of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates at 750 °C under different oxygen pressures.

<table>
<thead>
<tr>
<th>O$_2$ pressure (mTorr)</th>
<th>$T_c$ (°C)</th>
<th>$P_r$ (μC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-10</td>
<td>Hysteresis loop not well-defined</td>
</tr>
<tr>
<td>200</td>
<td>88</td>
<td>9.5</td>
</tr>
<tr>
<td>300</td>
<td>80</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 3.2 Curie temperature and remnant polarization of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on different substrates at 750 °C under 200 mTorr O$_2$ pressure.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$T_c$ (°C)</th>
<th>$P_r$ (μC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO(001)</td>
<td>88</td>
<td>9.5</td>
</tr>
<tr>
<td>LAO(001)</td>
<td>80</td>
<td>7.5</td>
</tr>
<tr>
<td>LSAT (001)</td>
<td>105</td>
<td>10.5</td>
</tr>
<tr>
<td>STO(001)</td>
<td>40</td>
<td>Hysteresis loop not well-defined</td>
</tr>
</tbody>
</table>
CHAPTER 4

ELECTRO-OPTIC PROPERTIES OF BARIUM STRONTIUM TITANATE THIN FILMS

4.1 Introduction

With the significant advance in the fabrication of high-quality single-crystalline ferroelectric thin films, these materials can now be considered for incorporation in thin-film devices such as waveguide modulators and optical switches [Potter, 1993]. For most devices in the field of optoelectronics or electro-optics, it is necessary to define and characterize the involved materials or components by means of the values of suitable parameters. In the case of electro-optic (E-O) materials this characterization is made by means of the induced birefringence, the E-O coefficient and the half-wave voltage [Aillerie, 2000]. In thin-film electro-optic devices, it is important to characterize the optical and electro-optic response of these films to provide feedback information for the optimization of thin film processing and design of devices.

Although the electro-optic properties of bulk ferroelectric materials, such as single crystals of LiNbO$_3$ and BaTiO$_3$, and PLZT transparent ceramics, are well identified, the identification of the E-O properties of ferroelectric thin films is not easy since they
exhibit process-dependent properties [Nashimoto, 1999]. The E-O properties of thin films are strongly affected by process-related factors such as deposition condition, crystallographic orientation, grain boundaries, film-electrode interfaces and residual stress. In this Chapter, we carried out a parametric investigation of the influence of the deposition conditions (e.g. deposition temperature and oxygen partial pressure) on the E-O properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) substrates at a wavelength of 632.8 nm. E-O behaviors of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on different substrates (MgO, LAO, LSAT and STO) were also studied.

### 4.2 Characterization Method of the Electro-optic Effect

Various experimental techniques have been used to measure the induced birefringence and electro-optic coefficients of electro-optic materials. Aillerie et al. have reviewed the experimental methods used to determine the electro-optic coefficients of bulk materials [Aillerie, 2000]. For thin films, the techniques have to be modified, although the general idea is similar, since the birefringence change is usually smaller than those of bulk materials. The methods used to measure the linear and quadratic E-O coefficients of thin films include modulation analysis of Bragg diffraction through ferroelectric (FE) waveguides [Griffel, 1989], Mach-Zehnder interferometer [Kawaguchi, 1984; Thapliya, 2003], transmission ellipsometry [Adachi, 1991], reflection ellipsometry [Wang, 1993] and waveguide refractometry [Potter, 1993]. In this Section, two methods used in this work for E-O measurements of thin films will be described. The first one is the transmission ellipsometry method and the other is the modified Sénarmont method.
4.2.1 Transmission Ellipsometry Method

In reflection ellipsometry, the ellipsometric angles $\psi$ and $\Delta$ are defined by the expression [Mak, 2001]:

$$
\rho = \frac{r_p}{r_s} = \tan \Psi \exp(j\Delta)
$$

(4.1)

where $r_p$ and $r_s$ are the complex Fresnel reflection coefficients for light polarized parallel ($p$ wave) and perpendicular ($s$ wave) to the plane of incidence, respectively. In a transmission ellipsometry measurement with the light beam traveling in a direction perpendicular to the principal axis of birefringence, a similar expression for the complex number $\rho$ can be written [Azzam, 1997]:

$$
\rho = \frac{t_p}{t_s} = \tan \Psi \exp(j\Delta)
$$

(4.2)

where $t_p$ and $t_s$ are the complex transmission coefficients for $p$ wave and $s$ wave, respectively. The transmission coefficients are complex functions of the refractive index $n$ and extinction coefficient $k$ and their explicit expressions can be found elsewhere [Azzam, 1997]. Eq. (4.2) can be rewritten as:

$$
\rho = \frac{t_p}{t_s} = \tan \Psi \exp(j\Delta) = \exp[-\frac{2\pi d}{\lambda}(k_e - k_o)]\exp[-j\frac{2\pi d}{\lambda}(n_e - n_o)]
$$

(4.3)

where $n_e$ and $n_o$ are the extraordinary and ordinary refractive indices, respectively. $k_e$ and $k_o$ are the extinction coefficients of the extraordinary and ordinary waves, respectively. The quantities $(n_e - n_o)$ and $(k_e - k_o)$ represent the birefringence and...
dichroism of the medium, and $d$ is the total distance traveled by the light beam through the medium.

From Eq. (4.3), it is clear that the ellipsometric angle $\Delta$ measured in transmission mode corresponds to the phase retardation between extraordinary and ordinary waves, i.e.:

$$\Delta = \frac{2\pi}{\lambda} d (n_o - n_e) = \frac{2\pi}{\lambda} d \delta n = \frac{2\pi}{\lambda} d (\delta n^{(o)} + \delta n^{(E)})$$

where $\Delta n = n_e - n_o$ is the total birefringence, and $\delta n^{(o)}$ and $\delta n^{(E)}$ denote the zero-field (natural) birefringence and electric-field induced birefringence, respectively.

Figure 4.1 Schematic diagram showing the transmission ellipsometry method for measuring the E-O coefficient of thin films.
The transmission ellipsometry measurements were carried out with a phase modulated ellipsometer (Jobin-Yvon UVISEL) at a wavelength $\lambda = 632.8$ nm as shown in Figure 4.1. The incident light beam was linearly polarized by a polarizer (P) and then modulated by a photoelastic modulator (M). The photoelastic modulator consisted of a rectangular fused silica block sandwiched between two piezoelectric quartz crystals oscillating at a resonant frequency of 50 kHz. After modulation, the light beam impinged normally on the surface of the thin film sample in the gap (20 $\mu$m wide) between two gold electrodes and an electric field was applied in the vertical direction. The transmitted beam then passed through an analyzer (A) and a monochromator set at 632.8 nm and was detected by a photomultiplier (PMT). The modulator generated a periodic phase shift $\delta(t)$ between the orthogonal amplitude components of the transmitted beam, and the detected light intensity can be described by:

$$I(t) = I_o + I_s \sin[\delta(t)] + I_c \cos[\delta(t)]$$  \hspace{1cm} (4.5)

The general expressions for $I_o$, $I_s$ and $I_c$ can be found elsewhere [Mak, 2001]. For the optical configuration shown in Figure 4.1, i.e. setting the polarization axes of P and A at 45° to the vertical, the ellipsometer angles $\Delta$ and $\Psi$ are related to $I_o$, $I_s$, and $I_c$ by:

$$I_o = K$$  \hspace{1cm} (4.6)

$$I_s = K \sin(2\Psi) \sin \Delta$$  \hspace{1cm} (4.7)

$$I_c = K \sin(2\Psi) \cos \Delta$$  \hspace{1cm} (4.8)

where $K$ is a constant. Therefore, $\Delta$ and $\Psi$ can be calculated from the measured $I_s$ and $I_c$. 
Figure 4.2 Recorded signals of (a) $I_s$ and $I_c$, (b) $\Delta$ and $\Psi$ in a transmission ellipsometry measurement of E-O coefficient for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film grown on MgO (001).

Figure 4.2 shows the typical measurement results obtained for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film grown on MgO (001). A jump of $I_s$ (or $\Delta$) can be clearly seen when a dc field of 10 V/µm was applied to the sample. But $I_c$ and $\Psi$ exhibit almost no change. Consequently, the electric field induced birefringence ($\Delta n$) can be deduced from the phase change $\delta\Delta$: 
\[(\Delta n) = \frac{\lambda (\Delta A)}{2\pi t} \quad (4.9)\]

where \(t\) is the thickness of the film.

### 4.2.2 Modified Sénarmont Method

This method made use of the well-know Sénarmont geometry but a PEM-90 photoelastic modulator (HINDS Instruments Inc., USA) was used in order to improve the sensitivity. A schematic diagram for the setup is shown in Figure 4.3.

![Figure 4.3](image)

Figure 4.3 Schematic diagram showing the modified Sénarmont method for the measuring E-O coefficient of thin films.
The thin film to be investigated was mounted on a sample holder. The light beam from a 2 mW stabilized He-Ne laser (Spectra-Physics model 117A, \( \lambda = 632.8 \) nm), after passing through a polarizer set at -45°, impinged normally on the film in the gap (20 µm wide) between two gold electrodes. The laser beam was then modulated at 50 kHz by the PEM-90 photoelastic modulator and then passed through an analyzer set initially at + 45°. The transmitted laser beam was detected by a photomultiplier tube (PMT). The electrical signal from the PMT was filtered by a band-pass filter and then fed to a SRS SR830 DSP lock-in amplifier.

The phase retardation in the optical components was eliminated by rotating the analyzer (computer controlled) to find its “true” cross position with respect to the polarizer. Figure 4.4 shows the variation of the detected light intensity with the analyzer angle for a Ba_{0.7}Sr_{0.3}TiO_3 film grown on MgO (001) without the application of an electric filed. The “true” cross position was found to be 54.8°.

![Figure 4.4 Relationship of the detected light intensity versus the analyzer angle for a Ba_{0.7}Sr_{0.3}TiO_3 film grown on MgO (001).](image-url)

Figure 4.4 Relationship of the detected light intensity versus the analyzer angle for a Ba_{0.7}Sr_{0.3}TiO_3 film grown on MgO (001).
An electric field was then applied. The general expression for the light intensity \( I \) at the detector is given by:

\[
I = 1 - \cos(B) \cos(A) + \sin(B) \sin(A)
\]

where \( B \) is the phase retardation in the film sample, \( A = A_0 \cos(\Omega t) \) is the phase retardation in PEM-90 photoelastic modulator. A Fourier series expansion yields:

\[
I = [1 - \cos(B)J_0(A_0)] + 2 \sin(B)J_1(A_0) \cos(\Omega t) + 2 \cos(B)J_2(A_0) \cos(2\Omega t) + ... (4.11)
\]

where \( J_n(A_0) \) are the Bessel functions and the first, second and third terms represent the DC term, the fundamental term and the first harmonic term, respectively. Therefore, the electrical signals corresponding to these three terms are:

\[
V_{DC} = G[1 - \cos(B)J_0(A_0)]
\]

\[
V_{1(peak)} = 2G \sin(B)J_1(A_0) \cos(\Omega t)
\]

\[
V_{2(peak)} = 2G \cos(B)J_2(A_0) \cos(2\Omega t)
\]

where \( G \) is a constant of proportionality. If \( A_0 \) is chosen such that \( J_0(A_0)=0 \), then the DC signal is independent of the sample retardation \( B \). This occurs for \( A_0=2.405 \) radians. The DC signal may therefore be used to “normalize” the fundamental term:

\[
\frac{V_{1(peak)}}{V_{DC}} = 2 \sin(B)J_1(A_0)
\]

In Eq. (4.15), \( V_{1(peak)} \) is the peak voltage of the signal. However, the lock-in amplifier only gives the rms voltage \( V_{rms} \). For sinusoidal waveforms, \( V_{rms} \) is given by:

\[
V_{rms} = \frac{V_{1(peak)}}{\sqrt{2}}
\]

If we define a ratio \( R_{1f} \) as:
\[ R_{1f} = \frac{V_{1rms}}{V_{DC}} = \sqrt{2} \sin(B)J_1(A_0) \] (4.17)

then the phase retardation \( B \) is given by:

\[
B = \sin^{-1}\left[\frac{R_{1f}}{\sqrt{2}J_1(A_0)}\right]
\] (4.18)

\[
= \sin^{-1}\left[\frac{R_{1f}}{\sqrt{2}J_1(2.405)}\right]
\]

\[
= \sin^{-1}\left[\frac{R_{1f}}{\sqrt{2} \cdot 0.5191}\right]
\]

Then the electric field induced birefringence change \( \delta(\Delta n) \) can be deduced from the phase change \( B \):

\[
\delta(\Delta n) = \frac{\lambda B}{2\pi \cdot t}
\] (4.19)

where \( t \) is the thickness of the film.

Both of the above two methods provide relatively simple and accurate ways to determine the change in the birefringence \( \delta\Delta n \) and thus the E-O coefficient under the application of a dc bias field. In this work, the transmission ellipsometry method was used to conduct a quick E-O property screening to determine the optimum composition of \( \text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3 \) material for E-O applications as presented in Chapter 1. The modified Sénarmont method was employed for a detailed study of the E-O effects of \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) thin films due to its relatively simple data acquisition and treatment.
4.3 Experimental Configuration for E-O Measurements

As shown in Figure 4.5, the electrode pattern used for electro-optic characterization consisted of two coplanar electrodes. The width of the gap between the two electrode stripes was 20 µm. The magnitude of the electric field was estimated using the relation \( E = \frac{V}{s} \), where \( V \) is the potential difference between the coplanar electrodes and \( s \) is the width of the gap.

As shown in Figure 4.5, the principal axes of the film were taken to lie along the \( \hat{x} \), \( \hat{y} \) and \( \hat{z} \) directions, with the optical axis lying along the \( \hat{z} \) direction. For the films grown on (001) substrates, the electrode stripes were aligned parallel to the <100> direction and the electric field was applied in the \( \hat{y} \) direction. The lightwave traveled in the \( \hat{z} \) direction and the polarization of the wave lay in the \( x-y \) plane making an angle of 45° with the \( y \) axis. Thus both the \( x \) and \( y \) axes correspond to ordinary polarization directions. During the E-O measurement, the electric field was first applied in the \( +\hat{y} \) direction and was increased in steps from zero to a maximum value. Then the field was decreased in steps down to \( E = 0 \). Then the field was applied in the \( -\hat{y} \) direction and the whole procedure was repeated.
4.4 Effect of Processing Conditions on the Electro-optic Properties

4.4.1 Effect of Deposition Temperature

Substrate temperature during deposition has been found to play one of the most important roles in determining the microstructure of deposited films. The electric field induced birefringence of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) at different temperatures were measured under an external dc electric field. All the films show a dominantly quadratic dependence of $\delta\Delta n$ on the applied electric field as shown in Figures 4.6 and 4.7. No hysteresis behavior in $\delta\Delta n$ versus $E$ was observed. When using coplanar type electrodes, it is possible that not only the thin film but also the substrate may contribute to the E-O response. Therefore, the substrate must have a very low E-O
coefficient in order not to contribute to the E-O response. MgO substrates are known for their very low E-O coefficient [Kim, 2003]. In order to confirm this, the E-O response of a blank MgO substrate was measured separately using the same electrode configuration. The E-O response of the MgO substrate is also shown in Figure 4.6. The birefringence change in MgO substrate was very low when compared with that of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film thus it was confirmed that the E-O effect originated entirely from the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film. Figure 4.8 shows the plot of the birefringence change $\delta \Delta n$ versus $E^2$ for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate under 200 mTorr O$_2$ pressure at 750 °C. It is seen that $\delta \Delta n$ varies linearly with $E^2$.

![Figure 4.6 Change in birefringence $\delta \Delta n$ as a function of applied dc electric field for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrates under 200 mTorr O$_2$ pressure at 650 °C.](image-url)
Figure 4.7 Change in birefringence $\delta\Delta n$ as a function of applied dc electric field for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrates under 200 mTorr O$_2$ pressure at 750 °C.

Figure 4.8 Change in birefringence $\delta\Delta n$ as a function of $E^2$ for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrates under 200 mTorr O$_2$ pressure at 750 °C.
The birefringence shift in a quadratic E-O effect (Kerr effect) is given by Eq. (1.19), from which the effective quadratic electro-optic coefficient $R_c$ can be deduced. The term \( \frac{1}{2} n^3 R_c \) in Eq. (1.19) is the slope of the $\delta \Delta n$ versus $E^2$ plot in Figure 4.8. Thus, $R_c$ can be determined if the refractive index $n$ is known. The refractive indices of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films were measured using the prism coupling technique (details will be presented in Chapter 5) and are plotted as a function of deposition temperature in Figure 4.9. There is a tendency for the refractive indices of the films to increase as the deposition temperature increases. This phenomenon is due to the improvement of the crystalline quality and the increase in the density of the films at higher deposition temperatures. The refractive indices of the films are close to the bulk values when the deposition temperature exceeds 650 °C. Similar results were also obtained in other ferroelectric thin films [Ono, 1998]. Using the known refractive indices, the effective quadratic electro-optic coefficients $R_c$ of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ films deposited at different temperatures were calculated.
Figure 4.9 Refractive index $n$ in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates under 200 mTorr O$_2$ pressure as a function of deposition temperature.

The effective quadratic E-O coefficients $R_c$ and the change in birefringence $\delta \Delta n$ under a 10 V/µm dc bias field of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates are plotted as a function of the deposition temperature as shown in Figure 4.10. It is seen that the E-O coefficient increases as the deposition temperature increases, which is attributed to the better crystalline quality. The highest quadratic E-O coefficient was $10.0 \times 10^{-18}$ m$^2$/V$^2$, which is achieved in the film deposited at 750 °C. This value is one order of magnitude lower than those of well-known bulk quadratic E-O materials such as PLZT (9/65/35) [Haertling, 1999], but higher than or comparable to those of ferroelectric thin films [Li, 2000; Kim, 1995; Wu, 1990; Graettinger, 1991; Lee, 1995; Blomqvist, 2005].
Figure 4.10 Effective quadratic E-O coefficient $R_c$ and change in birefringence $\delta \Delta n$ under a 10 V/\(\mu\)m dc field of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates under 200 mTorr O$_2$ pressure as a function of deposition temperature.

Since the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO substrate is in a strain induced ferroelectric phase at room temperature, the field-induced birefringence change is expected to depend linearly on the field, i.e. a linear E-O effect (Pockels effect) should be exhibited. Therefore, the observed quadratic E-O behavior seems to be inconsistent with the ferroelectric nature of the film. In fact, anomalously large quadratic E-O effects have been frequently observed in ferroelectric thin films [Lee, 1995; Lee, 1996; Kim, 1995; Lu, 1999b; Jo, 1992], and the possible reason are given below.
Lee et al. [Lee, 1996] claimed that the large electric field in the transverse configuration (coplanar electrodes) plays an important role in the quadratic E-O effects observed in ferroelectric thin films. Electric field may induce domain realignment, anisotropy change, nonlinear electronic or ionic polarization change or phase transition, so various orders of E-O effects may appear [Wu, 1990]. As presented in Chapter 2, the narrowest FWHM of (002) peak for BST films grown on MgO (001) substrates is 0.48°, which implies that the film contains not only $c$- domains but also a small amount of $a$-domains. As the films studied are multidomain materials and domain reversal may occur, quadratic-like dependence of birefringence change on applied field may be observed [Graettinger, 1991].

Another possible reason for the quadratic E-O behavior in ferroelectric films may lie in the electrode configuration used in the measurement. Reitze et al.[Reitze, 1993] demonstrated totally different E-O behaviors in PLZT films by using different electrode configurations. A linear E-O response was observed when coplanar electrodes were used, while a quadratic E-O effect with hysteresis was obtained in longitudinal geometry (parallel capacitor electrodes). It is possible that various mechanisms, such as constrained electrostriction between the film and the substrate, might be involved. Therefore, further studies are required to resolve this issue.
4.4.2 Effect of Oxygen Partial Pressure

Oxygen pressure during deposition has a significant effect on the lattice structure and the dielectric and ferroelectric properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films and the results have been presented in Chapters 2 and 3. It was reported that the E-O performance of ferroelectric thin films was greatly affected by oxygen partial pressure [Gaidi, 2004]. In this Section, the effects of oxygen partial pressure on the E-O properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films are discussed.

Figures 4.11 and 4.12 show the birefringence change as a function of the applied electric field for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrate at 750 °C under 100 and 300 mTorr O$_2$ pressures, respectively. Both of the films show predominantly quadratic E-O response which is slightly asymmetric with respect to the applied field. The effective quadratic E-O coefficients were calculated and summarized in Table 4.1. The E-O properties of the BST film deposited under 200 mTorr oxygen pressure are also listed in the same table for comparison. It was found that the E-O coefficients for the films deposited under 100 and 300 mTorr oxygen pressures were smaller than that of the films deposited under 200 mTorr. This phenomenon could be explained in terms of a larger number of point defects, such as oxygen vacancies, or a poorer domain alignment since the films deposited under 100 and 300 mTorr oxygen pressure have larger FWHM values for the rocking curves of the (002) X-ray diffraction than that of the films deposited under 200 mTorr oxygen pressure. The weak E-O effect observed in the film deposited under 100 mTorr oxygen pressure may also result from the smaller grain size in the film [Gaidi, 2004] as revealed by our AFM measurement.
Figure 4.11 Change in birefringence $\delta \Delta n$ as a function of applied dc electric field for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrates under 100 mTorr O$_2$ pressure at 750 °C.

Figure 4.12 Change in birefringence $\delta \Delta n$ as a function of applied dc electric field for a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrates under 300 mTorr O$_2$ pressure at 750 °C.
Table 4.1 E-O properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates at 750 °C under different oxygen pressures.

<table>
<thead>
<tr>
<th>O$_2$ pressure (mTorr)</th>
<th>$n$ @ 632.8 nm</th>
<th>$R_c$ $(\times 10^{-18})$ m$^2$/V$^2$ @ 10 V/µm dc</th>
<th>$\delta\Delta n$ $(\times 10^{-3})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.1515</td>
<td>1.21</td>
<td>0.95</td>
</tr>
<tr>
<td>200</td>
<td>2.1737</td>
<td>10.0</td>
<td>6.12</td>
</tr>
<tr>
<td>300</td>
<td>2.2429</td>
<td>2.29</td>
<td>1.50</td>
</tr>
</tbody>
</table>

4.5 Effect of Different Substrates

The nature of the substrate is another important factor that will influence the E-O properties of the thin films. Different substrates may result in different E-O behaviors even for the same film material [Adachi, 1986; Gaidi, 2004; Kim, 2003; Li, 2000]. Thus, it is essential to study the substrate effect on the E-O properties of the BST thin films. In this Section, the E-O properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on LAO (001), LSAT (001) and STO (001) substrates were investigated and compared with that of the film deposited on MgO (001) substrate.

The E-O responses of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on LAO (001), LSAT (001) and STO (001) are shown in Figures 4.13, 4.14 and 4.15, respectively. As compared to
the film grown on MgO (001) under the same conditions (see Figure 4.7), films deposited on LAO and LSAT substrates exhibit predominantly linear birefringence change with respect to dc electric field. However, a quadratic and slightly asymmetric E-O behavior is observed for the film grown on STO (001) substrate. Generally, the birefringence shift due to linear E-O effect (Pockels effect) is given by Eq. (1.18) and the effective linear electro-optic coefficient $r_c$ can be deduced from the slope of the $\Delta n$ versus $E$ plots. The effective E-O coefficients were calculated and shown in Table 4.2.

As shown in Table 4.2, all the films show promising E-O properties. Among them, the best E-O properties were found in the films grown on LSAT and STO substrates with $\Delta n$ values of $7.48 \times 10^{-3}$ and $7.41 \times 10^{-3}$, respectively, under a 10 V/µm dc electric field. The linear E-O coefficient $r_c$ of the film grown on LSAT substrate is $125 \times 10^{-12}$ m/V, which is over six times higher than that of LiNbO$_3$ single crystal [Xu, 1991]. The quadratic E-O coefficient $R_c$ of the films grown on STO substrate is $12.9 \times 10^{-18}$ m$^2$/V$^2$, which is slightly larger than that of the film deposited on MgO (001) substrate under the same conditions. It is believed that the better crystalline quality of films grown on LSAT and STO substrates may contribute to their better E-O performance. The presence of twins in films grown on LAO substrates may be an important reason for inferior E-O properties.
Figure 4.13 Change in birefringence $\delta \Delta n$ as a function of applied dc electric field for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at 750 °C under 200 mTorr O$_2$ pressure on LAO (001) substrate.

Figure 4.14 Change in birefringence $\delta \Delta n$ as a function of applied dc electric field for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at 750 °C under 200 mTorr O$_2$ pressure on LSAT (001) substrate.
Figure 4.15 Change in birefringence $\delta\Delta n$ as a function of applied dc electric field for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at 750 °C under 200 mTorr O$_2$ pressure on STO (001) substrate.

Table 4.2 E-O properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited at 750 °C under 200 mTorr O$_2$ pressure on various substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$n$ @ 632.8 nm</th>
<th>Effective E-O coefficient</th>
<th>$\delta\Delta n$ ($\times$ 10$^{-3}$) @ 10 V/μm dc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Substrate</td>
<td>Film</td>
<td>$R_c$ ($\times$ 10$^{-18}$) m$^2$/V$^2$</td>
</tr>
<tr>
<td>MgO(001)</td>
<td>1.735</td>
<td>2.1737</td>
<td>10</td>
</tr>
<tr>
<td>LAO (001)</td>
<td>2.020</td>
<td>2.2858</td>
<td>---</td>
</tr>
<tr>
<td>LSAT(001)</td>
<td>2.058</td>
<td>2.2820</td>
<td>---</td>
</tr>
<tr>
<td>STO(001)</td>
<td>2.388</td>
<td>2.2908</td>
<td>12.9</td>
</tr>
<tr>
<td>Ba$<em>{0.7}$Sr$</em>{0.3}$TiO$_3$ Bulk Ceramics</td>
<td>$\sim$ 2.20*</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

*datum is taken from [Landolt, 2002].
Films grown on LAO (001), LSAT (001) and STO (001) substrates exhibit E-O behaviors which depend on whether they are in the ferroelectric or paraelectric state. The film grown on STO shows almost no ferroelectric activity at room temperature, thus a quadratic E-O behavior appears. The films deposited on LAO and LSAT show reasonably strong ferroelectric characteristics at room temperature, therefore a linear E-O behavior occurs.

4.6 Summary

Two techniques for the measurement of electro-optic properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films, transmission ellipsometry method and modified Sénarmont method, were introduced in this chapter. The E-O properties of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were investigated with regard to the deposition conditions (i.e. substrate temperature and oxygen partial pressure) and nature of the substrates. The E-O effect of the films grown on MgO (001) substrates was found to be predominantly quadratic and the E-O coefficient increased with the increase of deposition temperature. The highest E-O coefficient of $10.0 \times 10^{-18} \text{ m}^2/\text{V}^2$ was found in the film deposited at 750 °C under 200 mTorr oxygen partial pressure.
The E-O performance of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were significantly affected by the substrates. Films grown on LAO (001) and LSAT (001) substrates showed linear E-O behavior with high E-O coefficients of $82.7 \times 10^{-12}$ m/V and $125 \times 10^{-12}$ m/V, respectively. A quadratic E-O effect was observed in the film deposited on STO (001) substrate and the quadratic E-O coefficient was calculated to be $12.9 \times 10^{-18}$ m$^2$/V$^2$. It was found that, except the film grown on MgO (001) substrate, all the films exhibited E-O behaviors which were consistent with their ferroelectric states.

If only the E-O property is taken into consideration, the film deposited on MgO (001) may not be the best candidate. From the waveguiding point of view, however, the large difference in refractive index between the film and substrate (see Table 4.2) will lead to good light confinement within the film, thereby improving the device efficiency. Consequently, Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ films deposited on MgO (001) substrates at 750 °C under 200 mTorr oxygen pressure were used for the fabrication of optical waveguides.
5.1 Introduction

The development of optical thin films for waveguide applications will enable a variety of new and highly useful optoelectronic functions [Zhai, 2001]. Besides the electro-optic properties presented in the last Chapter, there are other optical properties of thin films which are related to waveguide applications, such as the refractive index, optical homogeneity and optical loss. Therefore, characterization of these optical properties of thin films is very important in order to realize good device performance. To measure the refractive indices and optical loss in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films grown on MgO (001) substrates at 750 °C under 200 mTorr oxygen pressure, the prism coupling technique was employed. In this method, the thin film acted as a planar waveguide, so no further processing of the film was needed.

Prism coupling is an advanced optical waveguiding technique for the rapid and accurate measurements of both the thickness and the refractive index/birefringence of dielectric films [Tien, 1969; Ulrich, 1973]. For many thin film and optical waveguide applications, the prism coupling technique offers unique advantages over conventional
instruments based on ellipsometry or spectrophotometry. One major advantage of the prism coupling method is that the thickness of the films needs not be known in advance. Moreover, a resolution in refractive index of about ± 0.0005 can be achieved, which is an order of magnitude better than other techniques. The prism coupling technique also allows great flexibility of the film/substrate combinations. For simultaneous measurements of the thickness and the refractive index using the prism coupling technique, the film must be sufficiently thick to support two or more propagation modes.

The thickness of the film to be studied is the single most important factor determining whether ellipsometry or prism coupling is the preferred technique. In general, ellipsometry is the clear choice for investigating the thin films with a thickness smaller than a few hundred nanometers. For studying moderate-to-thick films, the prism coupler is usually superior. Consequently, ellipsometry and prism coupling can be viewed as complementary techniques.

5.2 Basic Principles of the Prism Coupling Technique

Measurements of the refractive indices and optical loss in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were carried out using a Metricon Model 2010 prism coupler equipped with a 45°-45°-90° rutile (TiO$_2$) prism (Metricon Corporation, Pennington, USA). The schematic diagram for the instrument is shown in Figure 5.1.
Two laser systems were used to generate the light beam. The first one was a He-Ne laser with a wavelength of 632.8 nm, which is the commonly used wavelength for the optical characterizations of ferroelectric thin films. Since the optical waveguide may have potential to be used in the near infrared (IR) region for telecommunication applications, measurements were also conducted using a laser diode with a wavelength of 1550 nm. In the measurement, the film was brought into contact with the base of the rutile prism by means of a pneumatically-operated coupling head, creating a small air gap between the film and the prism. The laser beam struck the base of the prism and was totally reflected at the prism base onto a photodetector. At certain discrete values of the
incident angle, called mode angles ($\theta_m$), photons can tunnel across the air gap into a guided optical propagation mode, causing a sharp drop in the intensity of light reaching the detector as illustrated in Figure 5.2. The mode angle $\theta_m$ is given by:

$$\sin \theta_m = \frac{n_p}{n_1} \sin \sigma = \sin \alpha_p - \sin^{-1}\left(\frac{\sin \alpha}{n_p}\right)$$

(5.1)

where $n_p$ is the refractive index of the prism, $n_1$ the refractive index of the film, $\sigma$ the incident angle of the laser beam at the prism-film interface (internal incident angle), $\alpha$ the incident angle of the laser beam at the air-prism interface (external incident angle) and $\alpha_p$ is the base angle of the prism ($\alpha_p = 45^\circ$).

Figure 5.2 Intensity of reflected light versus internal angle of incidence showing the TE guide modes.
The laser beam is polarized with the electric field in the plane of the film (transverse electric or TE mode) or perpendicular to the film surface (transverse magnetic or TM mode). In normal operation, the Metricon 2010 prism coupler uses a TE polarized incidence with electric field vibrating transverse to the plane of incidence. In Figure 5.3, for the sample on the left, with TE incidence the electric field is vibrating parallel to an arbitrary reference line so the index is being measured in a direction parallel to this line. Actually, the film can be manually rotated with respect to the prism by any arbitrary angle and the electric field vector can be made to assume any orientation within the plane defined by the surface of the film, yielding index along any direction in the plane of the film. In addition, with TM incidence, the magnetic field is transverse to and the electric field parallel to the plane of incidence. This makes the electric field perpendicular to the film surface at the critical angle since the refracted ray must propagate parallel to the surface at the critical angle. Since the refractive index is measured along the direction of electric field vibration, the TM incidence yields the index perpendicular to the plane of the film.
Figure 5.3 Schematic diagrams showing TE and TM mode propagations in prism coupling measurements. In the TE mode, the electric field (\( \vec{E} \)) vector is in the plane of the film. In the TM mode, the electric field vector is perpendicular to the plane of the film. \( \vec{B} \) is the magnetic field vector and \( \vec{S} \) is the direction of the refracted laser beam and is parallel to the film surface plane.

Refractive index and thickness of the film are the two parameters that can be measured using the prism coupling technique. For a given substrate type, the angular location of the modes depends only on the refractive index and thickness of the film. Thus, once two mode angles are measured, the refractive index and thickness of the film can be calculated by an appropriate computer algorithm. For the \( m^{th} \) mode, the light propagation in the waveguide layer follows the eigenvalue equation, commonly referred to as the “dispersion equation” [Tien, 1971]:

\[
2kn_i^2 \cos \theta_m d - 2\Phi_{12} - 2\Phi_{13} = 2m\pi
\]  

(5.2)
where \( d \) is the thickness of the film, \( n_1 \) the refractive index of the film, \( k = \frac{2\pi}{\lambda} \) the free-space wavenumber with \( \lambda \) the wavelength of the incident light, \( m = 0, 1, 2, 3, \ldots \), the order of the mode and \( \Phi_{12} \) and \( \Phi_{13} \) are the Fresnel phase shift at the film-substrate and film-air interfaces. According to the theory of total internal reflection [Born, 1975], the terms \( \Phi_{12} \) and \( \Phi_{13} \) can be evaluated by considering the total internal reflections at the film-substrate and film-air interfaces:

\[
\Phi_{12} = \arctan\left(\frac{n_1}{n_2}\right)^{2i} \sqrt{n_1^2 \sin \theta_m - n_2^2} \quad \text{(5.3)}
\]

\[
\Phi_{13} = \arctan\left(\frac{n_1}{n_3}\right)^{2i} \sqrt{n_1^2 \sin \theta_m - n_3^2} \quad \text{(5.4)}
\]

where \( n_1, n_2, n_3 \) are refractive indices of the guiding layer, the substrate and the air gap, respectively, \( i = 0 \) for TE modes and \( i = 1 \) for TM modes. The above equations are complex transcendental equations which must be solved numerically, but simultaneous solution of the equations for two modes yields the refractive index \( n_1 \) and thickness \( d \) of the film. If more than two modes are observed, the problem is overspecified and it is possible to calculate the independent refractive index and thickness of the film from each pair of modes and then the mean and standard deviation of all the pairs of modes are obtained.
Using the software incorporated in the prism coupler system, the guided mode spectra against both the internal angle $\sigma$ and external angle $\alpha$ were displayed and the refractive indices and thickness were calculated.

### 5.3 Guided Modes in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films

Figures 5.4 and 5.5 show the guided mode spectra of a 620 nm thick Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate obtained when the light beam travels along the $<100>$ direction. Three TE and three TM modes were observed at 632.8 nm, while only one TE and one TM mode were found at 1550 nm. The reflectivity dips of each guided mode are very sharp, indicating that good confinement of lightwave is achieved and the film is potentially useful for making waveguide devices. At the end of the spectra in both TE and TM polarization (Figures 5.4 and 5.5), a sharp fall of the reflected intensity is observed, which is associated with the substrate mode (or knee position).
Figure 5.4 Guided mode spectra excited at $\lambda = 632.8$ nm in the (a) TE and (b) TM polarization for a $\sim$620 nm thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ film deposited on MgO (001) substrate.
Figure 5.5 Guided mode spectra excited at $\lambda = 1550$ nm in the (a) TE and (b) TM polarization for a $\sim 620$ nm thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ film deposited on MgO (001) substrate.
Using the mode equations (Eqs. 5.2-5.4) and the observed angular positions of the TE and TM modes at $\lambda = 632.8$ nm (see Figure 5.4 (a) and (b)), the refractive indices and thickness were computed. The calculated film thickness of $626.0 \pm 2$ nm is in good agreement with that determined by an $\alpha$-step profiler. The ordinary refractive index ($n_0$) obtained from the TE mode data is $2.1737 \pm 0.0011$ and the extraordinary refractive index ($n_e$) obtained from the TM mode data is $2.2185 \pm 0.0007$, giving an index difference of $0.0448$. The large index difference observed cannot be fully explained by the intrinsic birefringence in the film and may be due to the strain induced by lattice mismatch as presented in Chapter 2. With the known thickness of $626.0$ nm, refractive indices of the film at $\lambda = 1550$ nm were determined to be $2.0618$ and $2.1033$ for the TE and TM mode, respectively.

To show the high degree of epitaxy in the film, the positions of the guided modes were also measured after rotating the film by $90^\circ$ about the film surface normal ($<001>$ direction). Whatever the state of light polarization used, no change in the position of the guided modes was detected and the calculated refractive indices remained constant. The fact that the indices of the TE modes remain stationary implies that the film is optically equivalent along the $<100>$ and $<010>$ directions. Furthermore, the fact that the indices of the TM modes are not affected by the rotation of the film implies the uniaxial nature of the film with the optical axis perpendicular to the film surface.

Because the reflectivity dips in guided mode spectra appear well-defined and relatively sharp, the optical loss in the film is expected to be rather low since it is related
to the FWHM of the reflectivity dip [Vilquin, 2003; Dogheche, 2003]. Since the observed FWHM of the reflectivity dip at 1550 nm is smaller than that at 632.8 nm, a lower optical loss is expected at 1550 nm.

5.4 Determination of the Refractive Index Profile of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films

In order to investigate the optical homogeneity of the film, we have determined the refractive index profile in the film. From the knowledge of the effective mode indices, it is possible to determine the refractive index profile along the film thickness direction for either TE or TM modes by using the inverse Wentzel-Kramers-Brillouin (i-WKB) method. This method was first used by J. M. White [White, 1976] to study the propagation characteristics of single crystal LiNbO$_3$ waveguides, and then improved by K. S. Chiang [Chiang, 1985] for use in the study of Cu diffused MgO film waveguides. Details of this method were described by Dogheche et al [Dogheche, 2000]. The index profile $n(x)$ can be determined by solving the following characteristic equation for $m^{\text{th}}$ order,

$$2k \int_0^{x_{(m)}} \sqrt{n^2(x) - N_m^2} \, dx = 2m\pi + 2\Phi_a + 2\Phi_s$$

(5.6)

where $n(x)$ and $N_m$ are, respectively, the refractive index profile and the effective index of the $m^{\text{th}}$ order mode. The effective index $N_m$ is related to the angular position of the TE or TM modes by:

$$N_m = n_p \sin[\alpha_p - \sin^{-1}\left(\frac{\sin \alpha}{n_p}\right)]$$

(5.7)
$x_t(m)$ is defined as the “turning point” at which the refractive index is equal to the effective index and is given by:

$$n[x_t(m)] = N_m$$  \hspace{1cm} (5.8)

Generally, the phase shift $\Phi_s$ at the turning point is taken as $\frac{\pi}{4}$ and $\Phi_a$ is approximately equal to $\frac{\pi}{2}$ at the surface boundary according to Chiang et al [Chiang, 1985].

From the angular positions of the modes given in Figure 5.4, the refractive index profiles of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film at $\lambda = 632.8$ nm as a function of depth were determined and are shown in Figure 5.6. Both of the extraordinary refractive index ($n_e$) and ordinary refractive index ($n_o$), exhibit a maximum at the film surface and remain almost constant within the guiding region. This behavior implies good optical homogeneity along the thickness direction of the film. The indices decrease rapidly near the substrate surface. This type of index profile is commonly observed for step-index thin film structures. The change near the film-substrate interface in the profile is indicative of a problem in the growth process. In fact, during the early stage of growth, many dislocations induced by the lattice misfit are introduced into the film [Chen, 2002a], which can lead to the islanding and columnar growth. This behavior results in large distortion of the crystal structure at the interface. The interface containing defects manifests itself through the changes of the optical properties of the samples. As a consequence, the index becomes lower in the region near the interface. Nevertheless,
the film has an index which is fairly uniform in the thickness direction and is thus useful for making step-index waveguide structures [Boudiombo, 1998].

Figure 5.6 Refractive index profile at $\lambda = 632.8$ nm of a Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film (620 nm thick) epitaxially grown on MgO (001) substrate.

5.5 Optical Loss in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Thin Films

Optical clarity is a requirement for thin film waveguides and the optical loss is a major barrier for using ferroelectric thin film in waveguide applications. A loss of about 2 dB/cm will reduce the efficiency of an optical device (e.g. frequency doublers) by over 50% [Fork, 1995]. Achieving a low loss of this magnitude in conjunction with other essential film properties is a very challenging issue. Nevertheless, there have been few investigations of the optical losses in ferroelectric thin films.
An understanding of the origins of the optical losses is essential to optimizing waveguide performance. The optical losses in dielectric waveguides originate from several factors, including absorption, mode leakage, internal scattering, surface scattering and interface scattering. Table 5.1 lists the sources of propagation loss and provides some of the causes and their dependence on wavelength, thickness and the order of the mode. Interestingly, certain types of loss are more important in some regimes than in others.

Table 5.1 Selected sources of propagation loss, some causes and their dependence on thickness, wavelength and mode order [Fork, 1995].

<table>
<thead>
<tr>
<th>Source of Loss</th>
<th>Cause</th>
<th>Trend vs. increasing guide thickness</th>
<th>Trend vs. increasing ( \lambda )</th>
<th>Trend vs. increasing mode order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption (in guided layer)</td>
<td>point defects, grain boundaries, vacancies</td>
<td>increase</td>
<td>decrease</td>
<td>decrease</td>
</tr>
<tr>
<td>Leakage</td>
<td>cladding layer not thick enough</td>
<td>decrease</td>
<td>increase</td>
<td>increase</td>
</tr>
<tr>
<td>Internal Scatter</td>
<td>grain boundaries, second phases, misorientation</td>
<td>increase</td>
<td>decrease</td>
<td>decrease</td>
</tr>
<tr>
<td>Surface Scatter</td>
<td>roughness, outgrowths, grain grooves</td>
<td>increase, then decrease</td>
<td>decrease</td>
<td>increase</td>
</tr>
<tr>
<td>Interface Scatter</td>
<td>surface polish, cladding, roughness</td>
<td>increase, then decrease</td>
<td>decrease</td>
<td>increase</td>
</tr>
</tbody>
</table>
For a transparent ferroelectric thin film, the dominant loss mechanism is scattering [Fork, 1995; Lu, 1998; Wessels, 1998]. Scattering is, in essence, the coupling of one mode to other guide modes and/or radiation mode. The surface scattering loss is directly related to the surface roughness. When the film surface morphology is accurately known, it is possible to estimate the surface scattering component of the loss. Since our films have a rather smooth surface as shown in the AFM images, the surface scattering loss seems not the major source of the optical loss. Variation in refractive index will induce internal and interface scattering in the waveguide. This can occur through material inhomogeneities or grain misorientation in a thin film. In order to lower the internal scattering and interface scattering, highly oriented thin films are needed [Nashimoto, 1995]. Grain boundaries in optically anisotropic media may induce refractive index discontinuities among grains which can scatter the guided mode. Any polycrystalline medium that is not optically isotropic will scatter light if the crystalline orientation varies among grains. A difference in refractive index at a grain boundary will therefore give rise to refraction of the propagating lightwave at an angle given by Snell’s law and thus scattering of the lightwave from the direction of propagation. The nature and degree of scattering will depend on the statistics of the grain orientation [Zhai, 2001]. Our Ba_{0.7}Sr_{0.3}TiO_3 thin films were epitaxially grown on MgO single crystal substrates, implying a high degree of grain orientation with respect to the substrate normal. Thus the optical scattering loss is expected to be very low in Ba_{0.7}Sr_{0.3}TiO_3 thin films.
In this study, a “moving fibre method” (built-in option of Metricon 2010 prism coupler) was employed to determine the scattering loss in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film (620 nm thick). The measurement setup is shown schematically in Figure 5.7. In the moving fibre method, the light scattered perpendicular to the waveguide surface was measured by a fibre sensor as it was translated along the propagation streak. The optical fibre method is identical in concept to the CCD camera approach for measuring the decay of the propagating streak as described in previous work [Walker, 1994; Kang, 1998]. The loss was derived for the film from measurements of the out-of-plane scattered light intensity for the specified guiding modes.

Figure 5.7 A schematic diagram of the experimental arrangement for scattering loss measurements (moving fibre method).
Figure 5.8 shows the variation of scattered light intensity as a function of propagation distance for TE\(_0\) and TM\(_0\) modes at both 632.8 nm and 1550 nm. A least square fit to an exponential function gives optical losses of 2.64 dB/cm and 3.04 dB/cm for the TE\(_0\) and TM\(_0\) modes at 632.8 nm, respectively and 0.93 dB/cm and 1.29 dB/cm for the TE\(_0\) and TM\(_0\) modes at 1550 nm, respectively. It is seen that the losses in TM modes are slightly higher that those in TE modes.

Losses of similar magnitudes were measured for the other guided modes of Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin film as summarized in Table 5.2. For modes of higher order, higher scattered losses were observed. It is noted that the scattered losses at 1550 nm, the commonly used wavelength in telecommunication, are rather low, which is consistent with our measurement results of surface roughness and the FWHM of the reflectivity dip in guided mode spectra. The accuracy of our loss results is limited due to the small sample area and thus the short scanning length along the light propagation direction. However, the results are reasonably accurate and are comparable with previously reported data for ferroelectric thin films [Beckers, 1998; Kang, 1998; Dogheche, 1998; Lu, 1998; Eknoyan, 1992; Zhai, 2001].
Figure 5.8 Scattered intensity from the $\text{TE}_0$ and $\text{TM}_0$ modes of a 620 nm thick Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film epitaxially grown on MgO (001) substrate at (a) $\lambda = 632.8$ nm and (b) $\lambda = 1550$ nm.
Table 5.2 Scattering losses in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film epitaxially grown on MgO (001) substrate.

<table>
<thead>
<tr>
<th>Guided mode</th>
<th>Losses at 632.8 nm (dB/cm)</th>
<th>Losses at 1550 nm (dB/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE$_0$</td>
<td>2.64</td>
<td>0.93</td>
</tr>
<tr>
<td>TE$_1$</td>
<td>6.43</td>
<td>--</td>
</tr>
<tr>
<td>TE$_2$</td>
<td>8.33</td>
<td>--</td>
</tr>
<tr>
<td>TM$_0$</td>
<td>3.04</td>
<td>1.29</td>
</tr>
<tr>
<td>TM$_1$</td>
<td>5.39</td>
<td>--</td>
</tr>
<tr>
<td>TM$_2$</td>
<td>8.85</td>
<td>--</td>
</tr>
</tbody>
</table>

5.6 Summary

The waveguide related optical properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) substrates were characterized using the prism coupling technique and the optical properties were found to be very promising for optical waveguide applications. The reflectivity dips of each guided mode at $\lambda = 632.8$ nm and $\lambda = 1550$ nm are very sharp, indicating good confinement of light propagation in such a planar waveguide structure. The refractive index and thickness of the film were derived from the guided mode spectra. The refractive index profile of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film was determined using the i-WKB method. The step-like index profile indicates good optical homogeneity along the thickness direction of the film. The scattering loss in the film was evaluated using a moving fibre method. At a wavelength of 1550 nm, the scattering
losses were found to be 0.93 dB/cm and 1.29 dB/cm for TE\(_0\) and TM\(_0\) modes, respectively. For telecommunication applications involving fibre optics, it is important that the films have a loss around 1 dB/cm at 1.3 \(\mu\)m and 1.5 \(\mu\)m. Our results, including low propagation loss and strong electro-optic effect, show that Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin film is a good material candidate for optical waveguide device applications.
CHAPTER 6

BARIUM STRONTIUM TITANATE THIN FILM OPTICAL WAVEGUIDES

6.1 Introduction

Since the idea of integrated optics has been proposed, intense research has been carried out in order to improve the materials and techniques used for waveguide fabrication. Numerous experiments were performed by which active and passive devices were demonstrated [Hunsperger, 2002]. Thin-film ferroelectrics offer unique physical characteristics that could dramatically improve the performance of many integrated optic devices. The large refractive index difference between the film and the substrate leads to strong confinement of light, thus allowing a great reduction in the dimensions of the devices. Moreover, it is easier to integrate thin films into existing semiconductor technologies than developing bulk hybrid technologies.

Ferroelectric thin films for waveguide-modulator applications should exhibit low optical loss, low surface roughness and high electro-optic response [Moret, 2002]. The realization of active thin-film devices has been hindered by the difficulty of fabricating low-loss films and channel waveguides before the last decade [Gill, 1997]. Advances in the processing of epitaxial oxide thin films have now made it possible to synthesize
layers of sufficient optical quality to form low-loss waveguides [Jo, 1996; Wessels, 1998; Petraru, 2002; Thapliya, 2003]. Barium strontium titanate (BST) is a promising thin film material for optical waveguide devices due to its outstanding properties, such as a high electro-optic coefficient and low optical scattering loss. BST/MgO is a favorite structure for use in waveguide applications. There is a large refractive index difference between the film and the MgO substrate ($\Delta(n) \sim 0.44$ at $\lambda = 632.8$ nm), thus lightwave is expected to be highly confined in the film.

In this Chapter, we first present the basic theory for lightwave propagation in a slab waveguide, and then we describe how the geometry of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin-film rib waveguides can be optimized using the effective index method. The fabrication and characterization of rib waveguides and Mach-Zehnder modulators based on $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films are then discussed.

6.2 Lightwave Propagation in Slab Waveguides

6.2.1 Basic Concepts of Slab Waveguides

Dielectric slabs are the simplest optical waveguides. The study of slab waveguides and their properties will help us gain an understanding of the waveguide properties of more complicated dielectric waveguides. This Section will focus on a slab waveguide, which has finite dimension in the thickness direction but infinite dimension in the length
and width direction. We will consider a step-index waveguide (Figure 6.1), in which the refractive index changes abruptly along the thickness direction at the surface of the core.

![Figure 6.1 A step-index slab waveguide of thickness d with a guided mode.](image)

The core region of the waveguide, with a refractive index $n_1$, is deposited on a substrate with refractive index $n_2$. The refractive index of the medium (cladding) above the core is $n_3$. The refractive index $n_3$ may be unity if the region above the core is air, or it may have some other value if the core is surrounded by dielectric materials on both sides. In order to achieve true mode guidance, it is necessary that $n_1$ is larger than $n_2$ and $n_3$. In order to have a specific example in mind we shall assume that $n_1 > n_2 \geq n_3$. A slab waveguide is called symmetric if $n_2 = n_3$ and is called asymmetric if $n_2 \neq n_3$. The modes of symmetric slab waveguides are simpler than those of asymmetric slab because they can be expressed either as even or odd field distributions. The lowest-order mode of a
symmetric slab waveguide does not have a cutoff frequency, which means that, in principle, this mode can propagate at arbitrarily low frequencies. By contrast, all modes of asymmetric slabs become cutoff if the frequency of operation is sufficiently low.

Consider the situation shown in Figure 6.1. The light waves are confined in the core region by suffering total internal reflection at the dielectric interfaces. From Snell’s law, the critical angles, $\theta_1$ and $\theta_2$, for total reflection at the upper and lower interfaces are given by:

$$\sin \theta_1 = \frac{n_3}{n_1}$$  \hspace{2cm} (6.1)

$$\sin \theta_2 = \frac{n_2}{n_1}$$  \hspace{2cm} (6.2)

Most commonly the cladding layer is air, thus $n_2 > n_3$ and $\theta_2 > \theta_1$. When $\theta_2 < \theta < 90^\circ$, the lightwave is confined in the core layer by total internal reflection at both interfaces and it propagates along a zig-zag path. This is called a guided mode. The plane wave propagation constant in the wave-normal direction is defined as $k n_1$ (see Figure 6.1), where $k = \frac{2\pi}{\lambda}$ and $\lambda$ is wavelength of light in free space. For a slab waveguide, the propagation constant $\beta$ along the z-direction is defined as:

$$\beta = k z n_1 = kn_1 \sin \theta$$  \hspace{2cm} (6.3)

The speed of the lightwave parallel to the waveguide $v$ is given by:

$$v = c_0 \left( \frac{k}{\beta} \right)$$  \hspace{2cm} (6.4)

where $c_0$ is the speed of light in free space.
Another quantity which is frequently used is the effective index of refraction of a slab waveguide \( N_m \), which is the ratio of the speed of light in free space to the speed of the lightwave in the waveguide:

\[
N_m = \frac{c_0}{v} = \frac{\beta}{k} \tag{6.5}
\]

### 6.2.2 Guided Modes of Slab Waveguides

An optical mode refers to a discrete solution of Maxwell’s equations, such that it satisfies all the boundary conditions and has the property that its spatial distribution does not change with propagation. Maxwell’s equations for plane waves in an isotropic, lossless dielectric medium can be written in the form [Agrawal, 2004],

\[
\nabla \times \vec{E} = i \omega \mu_0 \vec{H} \tag{6.6}
\]

\[
\nabla \times \vec{H} = -i \omega \varepsilon_0 n^2 \vec{E} \tag{6.7}
\]

where \( \vec{H} \) and \( \vec{E} \) are the magnetic and electric field vectors. \( \varepsilon_0 \) and \( \mu_0 \) are the dielectric permittivity and magnetic permeability of free space, respectively. \( \omega = \frac{2\pi \cdot c_0}{\lambda} \) is the angular frequency and \( c_0 = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \) is the light speed in free space. We now use the geometry of slab waveguides to simplify the two curl equations. Assuming that the \( x \) axis is normal to the waveguide plane and that the waveguide is infinitely wide along the \( y \) axis, we note that both \( E \) and \( H \) are independent of \( y \). Moreover, both of them vary with \( z \) as \( \exp(i \beta z) \). Then the electromagnetic fields vary as:
\[ \tilde{E} = E(x, y)e^{i(\kappa x - \beta z)} \quad (6.8) \]
\[ \tilde{H} = H(x, y)e^{i(\kappa x - \beta z)} \quad (6.9) \]

where \( E \) and \( H \) are electric and magnetic fields in the plane perpendicular to the propagation direction. We can thus remove the \( y \) and \( z \) derivatives from Eqs. (6.6) and (6.7) using:

\[ \frac{\partial E}{\partial y} = 0, \quad \frac{\partial H}{\partial y} = 0, \quad \frac{\partial E}{\partial z} = i\beta E, \quad \frac{\partial H}{\partial z} = i\beta H \quad (6.10) \]

The resulting set of six equations, when written in Cartesian coordinates, has two distinct sets of linearly polarized solutions, known as the transverse electric (TE) and transverse magnetic (TM) modes, depending on whether we choose \( E_z = 0 \) or \( H_z = 0 \).

In the case of TE modes, \( E_x = E_z = 0 \), while \( E_y \) satisfies:

\[ \frac{\partial^2 E_y}{\partial x^2} + (k^2 n^2 - \beta^2)E_y = 0 \quad (6.11) \]

where \( k = \frac{2\pi}{\lambda} = \omega \sqrt{\varepsilon_0 \mu_0} \). The magnetic field components are related to \( E_y \) as:

\[
\left\{
\begin{align*}
H_x & = -\frac{\beta}{\omega \mu_0} E_y \\
H_y & = 0 \\
H_z & = -\frac{i}{\omega \mu_0} \frac{\partial E_y}{\partial x}
\end{align*}
\right. \quad (6.12)
\]

In the case of TM modes, \( H_x = H_z = 0 \), while \( H_y \) satisfies:

\[ \frac{\partial^2 H_y}{\partial x^2} + (k^2 n^2 - \beta^2)H_y = 0 \quad (6.13) \]
The electric field components are now related to $H_y$ as:

$$
E_x = -\frac{\beta}{\omega \varepsilon_0 n_z^2} H_y
$$

$$
E_y = 0
$$

$$
E_z = -\frac{i}{\omega \varepsilon_0 n_z^2} \frac{\partial H_y}{\partial x}
$$

The two orthogonal TE and TM modes must be distinguished in order to discuss the dispersion characteristics of the guided modes. Here we consider the TE mode first. The same analysis can be made for TM mode. Assuming that the core layer has a thickness $d$, Eq. (6.11) can be solved within each layer using $n = n_3$, $n_1$, or $n_2$ for the three layers shown in Figure 6.1. Since the refractive index is constant in each layer, the general solution can be written in terms of sinusoidal and exponential functions as:

$$
E_y = \begin{cases} 
A e^{-\delta x} & \text{for } x \geq 0 \\
A \cos \kappa x + B \sin \kappa x & \text{for } 0 \leq x \geq -d \\
(A \cos \kappa d - B \sin \kappa d) e^{\gamma (x + d)} & \text{for } x \leq -d 
\end{cases}
$$

with the abbreviations:

$$
\kappa = \sqrt{n_i^2 k^2 - \beta^2} = n_i k \cos \theta_i
$$

$$
\gamma = \sqrt{\beta^2 - n_i^2 k^2} = \sqrt{(n_i^2 - n_2^2) k^2 - \kappa^2}
$$

$$
\delta = \sqrt{\beta^2 - n_3^2 k^2} = \sqrt{(n_3^2 - n_1^2) k^2 - \kappa^2}
$$
The constants $A$ and $B$ can be determined from the boundary conditions at the two interfaces requiring the tangential components of $E$ and $H$ being continuous across them. In the case of TE modes, these boundary conditions are satisfied if $E_y$ and $H_z$ are continuous at $x = 0$ and $x = -d$, provided:

$$\delta A + \kappa B = 0$$

$$\bigl(\kappa \sin \kappa d - \gamma \cos \kappa d\bigr) A + (\kappa \cos \kappa d + \gamma \sin \kappa d) B = 0$$

This homogeneous equation system has a solution only if the system determinant vanishes. We thus obtain the eigenvalue equation:

$$\delta(\kappa \cos \kappa d + \gamma \sin \kappa d) - \kappa(\kappa \sin \kappa d - \gamma \cos \kappa d) = 0$$

This eigenvalue equation can be written in a different form:

$$\tan \kappa d = \frac{\kappa(\gamma + \delta)}{\kappa^2 - \gamma \delta}$$

Similarly, the eigenvalue equation for TM mode can be derived as:

$$\tan \kappa d = \frac{n_2^2 \kappa(n_3^2 \gamma + n_2^2 \delta)}{n_2^2 n_3^2 \kappa^2 - n_1^4 \gamma \delta}$$

### 6.2.3 Cutoffs of Asymmetric Slab Waveguides

In the case of an asymmetric slab with $n_2 \neq n_3$, cutoff frequencies exist in the waveguide. Thus, one must solve the eigenvalue equations (6.22) and (6.23) to find the cutoff points for the TE and TM modes supported by the waveguide. We can obtain some information about the solutions of the TE mode eigenvalue equation (6.22) by considering Figure 6.2. The solid lines in this figure are the branches of the tangent as a
function of $\kappa d$. The dashed lines represent the function $F(\kappa d)$ that represents the right-hand side of Eq. (6.23). From Eq. (6.17) to (6.19) we obtain:

$$F(\kappa d) = \frac{kd(\gamma d + \delta d)}{(\kappa d)^2 - (\gamma d)(\delta d)}$$

$$= \frac{\kappa d \left[\sqrt{(n_i^2 - n_z^2)(k d)^2 - (\kappa d)^2} + \sqrt{(n_i^2 - n_z^2)(k d)^2 - (\kappa d)^2}\right]}{(\kappa d)^2 - \sqrt{(n_i^2 - n_z^2)(k d)^2 - (\kappa d)^2} \sqrt{(n_i^2 - n_z^2)(k d)^2 - (\kappa d)^2}}$$

(6.24)

Figure 6.2 was drawn for $\sqrt{n_i^2 - n_z^2} \cdot k d = 11$, and $\sqrt{n_i^2 - n_z^2} \cdot k d = 24$. The pole in the $F(\kappa d)$ curve occurs at the point where the denominator of Eq. (6.24) vanishes. The $F(\kappa d)$ curve ends at the point:

$$\sqrt{n_i^2 - n_z^2} \cdot k d = \kappa d$$

(6.25)

since one of the square root expression in Eq. (6.24) becomes imaginary as $\kappa d$ exceeds the value given by Eq. (6.25). The $\kappa d$ coordinates of the crossing points of the solid and dashed lines give the solutions of the eigenvalue Eq. (6.22). Each solution gives one TE mode of the slab waveguide. As shown in Figure 6.2, four guided modes were obtained for the conditions that were used to draw this figure.
We define a parameter $V$ that combines the difference of the squares of the refractive indices of the core and substrate with information about the operating wavelength and the thickness of the core:

$$V = \sqrt{n_1^2 - n_2^2} \cdot k \cdot d$$

(6.26)

As the value of $V$ decreases, the endpoint of the dashed lines moves to the left, so that it crosses fewer braches of the tangent function. For decreasing values of $V$, the number of guided modes is reduced. The total number of modes that can be supported by a waveguide depends on the thickness $d$, the refractive indices ($n_1$, $n_2$, and $n_3$) and wavelength $\lambda$ of the propagation light. For sufficiently thin cores, low frequencies, or sufficiently small refractive index difference, no guided modes can exist.
The cutoff value of $V$ for each guided TE mode can be obtained from Eq. (6.22). The cutoff points occur when $\gamma = 0$. We thus can obtain from Eqs. (6.16), (6.18) and (6.22),

$$V_c = \arctan\left(\frac{n_1^2 - n_3^2}{n_1^2 - n_2^2}\right) + m\pi$$

(6.27)

where the integer $m$ is the mode number with $m = 0, 1, 2, 3\ldots$

Similarly, the cutoff value of $V_c$ for the TM mode is,

$$V_c = \arctan\left(\frac{n_2^2 - n_3^2}{n_1^2 - n_2^2}\right) + m\pi$$

(6.28)

A waveguide will support a single TE and a single TM mode when its thickness is chosen such that $V_c|_{m=0} < V < V_c|_{m=1}$. This is the single-mode condition for slab waveguides. A single propagation mode is generally required in a practical waveguide device since this mode possesses the lowest optical loss. The field distribution for each TE mode is completely specified in terms of $E_y(x)$ as given in Eq. (6.15). Figure 6.3 shows, as an example, the mode profiles for the first four TE$_m$ modes ($m = 0, 1, 2$ and $3$) for an asymmetric slab waveguide. The value of $m$ denotes the number of nodes within the core layer at which the field amplitude vanishes. For the fundamental modes, TE$_0$ and TM$_0$, there are no nodes within the core.
6.3 Design of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ Rib Waveguide Using the Effective Index Method

In this work we wish to fabricate rib waveguides, so we have to find the appropriate geometry for this type of waveguides. This can be done by using the effective index method (EIM) proposed by Knox and Toulios [Knox, 1970]. This method is one of the most popular methods for the analysis of rib waveguides in millimeter-wave and visible lightwave integrated circuits because the mathematics is not too complicated [Chiang, 1986].

We start by rewriting the dispersion equation Eq. (5.2) for a slab waveguide by using the parameters defined in Eqs. (6.16)-(6.18) [Suhara, 2003]:

$$\kappa l - \Phi_{12} - \Phi_{13} = m\pi$$  \hfill (6.29)
where $\Phi_{12} = \arctan[\left(\frac{n_1}{n_2}\right)^2 (\frac{\gamma}{\kappa})]$ and $\Phi_{13} = \arctan[\left(\frac{n_1}{n_3}\right)^2 (\frac{\delta}{\kappa})]$, $m = 0, 1, 2, 3, \ldots, i = 0$ for TE mode and $i = 1$ for TM mode. According to Eq. (6.5), the effective refractive index of a slab waveguide is $N_m = \frac{\beta}{k}$. By substituting this relation into Eqs. (6.16) - (6.18), we obtain:

$$\kappa = \sqrt{n_1^2 - N_m^2} \cdot k$$

$$\gamma = \sqrt{N_m^2 - n_2^2} \cdot k$$

$$\delta = \sqrt{N_m^2 - n_3^2} \cdot k$$

Eqs. (6.29) - (6.32) gives the dispersion relation in terms of the effective refractive index $N_m$:

$$N_m = N(n_1, n_2, n_3, d, \lambda, m, i)$$

In the effective index method of Knox and Toulios, a rib waveguide (Figure 6.4(a)) is regarded as consisting of three regions: the rib region in the centre and the two regions on the left and right sides. The rib region is regarded as a slab waveguide of thickness $d$ and each of the other two regions is considered as a slab waveguide of thickness $d-h$ (Figure 6.4(b)). Using the dispersion equation as given by Eqs. (6.29) - (6.32), the effective index of the rib region, $N_{eff1}$, and the effective index of the region on each side, $N_{eff2}$, can be calculated. Finally, the whole system is considered as a symmetric waveguide of thickness $W$, with the “core” having an effective index $N_{eff1}$ and the “substrate” and “cladding” having the same effective index $N_{eff2}$ (Figure 6.4(c)). Then the effective index for the whole system can be calculated.
Figure 6.4 Application of the effective index method to a rib waveguide. (a) The original rib waveguide. (b) Solving the problem of three slab waveguides to define $N_{\text{eff}1}$ and $N_{\text{eff}2}$. (c) Solving the problem of an equivalent slab waveguide to determine the effective index $N_{\text{eff}}$ of the whole structure.

In order to determine the appropriate thickness of the rib which is required to maintain single-mode wave propagation, we first plot the effective index $N_m$ as a function of $d$ at $\lambda = 1550$ nm (Figure 6.5) and $\lambda = 632.8$ nm (Figure 6.6). It is seen from Figure 6.5 that only the first TE mode (TE$_0$) will propagate if $d$ is between 190 nm and 870 nm for our rib waveguide. Therefore, an intermediate value of $d$ is chosen to be 620 nm for our rib waveguide to be used at $\lambda = 1550$ nm. For this chosen $d$ value, we can obtain from Figure 6.5 the corresponding $N_m$, which is in fact $N_{\text{eff}1}$. 
Figure 6.5 Effective index $N_m$ as function of thickness for a BST/MgO slab waveguide at a wavelength of $\lambda = 1550$ nm.

Figure 6.6 Effective index $N_m$ as function of thickness for a BST/MgO slab waveguide at a wavelength of $\lambda = 632.8$ nm.
To determine the appropriate width of the rib which is required to maintain single-mode propagation we need to calculate the effective index for the whole system. As an example, take \( h = 50 \text{ nm} \), then \( d-h = 570 \text{ nm} \). Then \( N_{\text{eff}2} \) can be read from Figure 6.5 and Figure 6.6 as the \( N_m \) values at a thickness of 570 nm. With the value of \( N_{\text{eff}1} \) and \( N_{\text{eff}2} \) known, Eqs. (6.29) - (6.32) then give the effective index of the rib waveguide as a function of \( W \). Similar calculations can be performed for other values of \( h \) and the results are shown in Figures 6.7 and 6.8 for \( \lambda = 1550 \text{ nm} \) and \( \lambda = 632.8 \text{ nm} \), respectively.

Figure 6.7 shows that, for \( h = 50 \text{ nm} \), single-mode propagation can be maintained if \( W \) is smaller than 2.4 \( \mu \text{m} \). The required rib width for single-mode propagation becomes smaller as \( h \) increases and must be smaller than 1.3 \( \mu \text{m} \) for \( h = 300 \text{ nm} \). To ensure that only a single TE\(_{00} \) (the first and second subscripts are the mode numbers along the thickness and rib width direction, respectively) propagates in our rib waveguides at an operation wavelength \( \lambda = 1550 \text{ nm} \), \( h \) and \( W \) are chosen to be 60 nm and 2 \( \mu \text{m} \), respectively.
Figure 6.7 Effective index $N_m$ versus rib width $W$ for various rib heights $h$ of a BST/MgO rib waveguide at $\lambda = 1550$ nm. Thickness of the film is 620 nm.

Figure 6.8 Effective index $N_m$ versus rib width $W$ for various rib heights $h$ of a BST/MgO rib waveguide at $\lambda = 632.8$ nm. Thickness of the film is 620 nm.
6.4 Microfabrication Processes for Preparing Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Rib Waveguides

To fabricate a rib waveguide from the BST film/MgO structure, photolithographic patterning and dry etching were used [Schneider, 1998; Kang, 2003]. The microfabrication flow chart is shown in Figure 6.9. In order to remove the particulates on the film surface, the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film was immersed consecutively in an ultrasonic bath of acetone, ethanol and deionized water for 15 minutes and then dried in a stream of compressed air. After cleaning, a 150 nm thick chromium film was deposited on the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ film by rf magnetron sputtering to serve as the etch barrier layer. A positive photoresist (AZ 3100 PR supplied by Clariant China Ltd.) was then deposited on the chromium layer by spin coating at a spinning speed of 5000 rpm for 50 seconds, resulting in a photoresist layer of 1 µm thickness. After baking at 100 °C for 10 min, the photoresist layer was exposed under a mask to high intensity ultraviolet light for 12 seconds in a Model JKG-2A mask aligner (Shanghai Optical Machinery Works). The exposed photoresist was then immersed in a developer (AZ 300 supplied by Clariant China Ltd.) for 30 seconds. Using an etching solution of Ce(NO$_3$)$_4$ in aceric acid, the chromium layer without the protection of photoresist was removed, leaving the bare waveguide patterns of the undeveloped photoresist covering the chromium barrier layer on the film surface.
In order to fabricate the desired rib pattern with a smooth etched surface, a reactive ion etching (RIE) process was carried out in a Plasma Therm 790 series RIE system (at the Optoelectronic Research Centre, Department of Electronic Engineering of the City University of Hong Kong) to etch away the unprotected region of the film. Because of its high degree of anisotropy, RIE is a better choice for patterning features in the submicron range compared to isotropic wet chemical etching [Schneider, 1998]. In this dry etching process, a gas mixture of CF\(_4\) and Ar in the ratio of 1:4 was used as the
etchant gas. A rf power of 200 W was used and the gas ambient pressure was kept at 35 mTorr. A 30-min etching resulted in a 60 nm etching depth as measured using an α-step surface profiler. Finally, the input and output endfaces of the waveguide were cleaved and the waveguide was ready for light coupling tests.

Figure 6.10 shows the SEM image of a cleaved BST/MgO rib waveguide. It is seen that the cleaved Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ face has a higher roughness than that of the MgO substrate. Thus there will be a light scattering at the junctions of the input and output optical fibres and the waveguide because of the roughness of the cleaved faces [Petraru, 2003].
6.5 Characterization of Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) Rib Waveguides

The near-field output pattern of the BST film/MgO rib waveguide was measured (at the Optoelectronic Research Centre, Department of Electronic Engineering of the City University of Hong Kong) at a wavelength of 1550 nm using the end-fire coupling technique. Figure 6.11 shows the schematic diagram of the end-fire coupling method. The light source is a TE-polarized diode laser operating at a wavelength of 1550 nm (Amonic ALS-15CL, C+L band ASE broadband source). The laser beam was butt-coupled to the cleaved endface of the waveguide by a polarization-maintaining single mode optical fibre (\(D \sim 8 \mu m\)). The near field optical distribution at the output facet of the waveguide was measured using an IR charge-coupled device (CCD) camera after the light beam had passed through a micro-objective lens. Since the size of the waveguide is very small, the positions of the fibre, waveguide and lens are carefully adjusted using three \(xyz\) micro-positioners mounted on an optical vibration isolator.

Figure 6.11 Schematic diagram showing the measurement of the near-field output pattern by the end-fire coupling method.
Figure 6.12 shows the near-field optical distribution pattern of the rib waveguide captured by an IR camera. The output spot is sharp and is slightly elliptical in cross-section, showing that a strong light beam is propagating along the rib structure. The light beam is almost completely confined within the rib. The intensity of the output light spot exhibits a single peak along the $y$ direction as shown in Figure 6.12, indicating a single mode confinement in the $y$ direction. Figure 6.13 shows that the intensity exhibits a Gaussian profile in the $x$ and $y$ directions, implying that the single-mode lightwave is confined in both directions. No high-order modes have been observed.

Figure 6.12 The near field optical output image and the intensity as a function of $y$ for a BST/MgO rib waveguide operating at a wavelength of 1550 nm.
6.6 Characterization of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ Mach-Zehnder Electro-optic Modulator

6.6.1 Geometry of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ Mach-Zehnder Electro-optic Modulator

In integrated optics, interferometric devices such as optical sensors and electro-optic amplitude modulators are often of the Mach-Zehnder interferometer (MZI) type [Krijnen, 1995]. The structure of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ Mach-Zehnder modulator investigated in this work is shown schematically in Figure 6.14. The modulator consists of an input waveguide that branches out into two separate parallel waveguides that are
finally recombined into the output waveguide. All the waveguides in the modulator are of the rib type and the geometry of the rib is chosen based on the numerical calculation described in previous Sections in order to achieve single mode propagation at a wavelength of 1550 nm.

Using photolithography and wet etching techniques, two gold coplanar electrodes with a spacing of 10 µm are fabricated such that they are parallel to one branch waveguide (Figure 6.14(a)). By applying a voltage to the electrodes, the phase of the guided light in this branch can be changed. The active arm length and the device length are set at 5000 µm and 9000 µm, respectively, to assure smooth curvatures at the Y-branches. In practice, the branching angle is usually kept below 1° in order to reduce the insertion loss because the loss increases with branching angle [Agrawal, 2004]. However, due to the limited length (1 cm) of our thin film samples, the branching angle is set at 3°.

The truncation at the tip of a Y-branch gives rise to radiation loss. The truncation is related to the resolution limit of the fabrication process, which depends on the lithography equipment and etching process. In a perfect Y-branch, the gap between the two arms can be smoothly reduced to zero (i.e. zero truncation) such that the radiation loss is almost zero. In reality, however, there is a resolution limit which inevitably causes the formation of a truncation.
It has been reported that if the truncation can be reduced to 1 µm, the radiation loss is estimated to be 1 dB [Thapliya, 2003]. As shown in Figure 6.15, the truncation of the Y-branch in the BST/MgO Mach-Zehnder is around 1 µm, thus a low radiation loss is expected in our Mach-Zehnder modulator.
6.6.2 Near Field Output Distributions

In the Mach-Zehnder interferometer, one power-splitting Y-junction at the entrance of the structure is used for equal division of the incoming power over two single mode branches. During passage through these branches the two beams undergo phase changes which depend on the phase velocity of the beams. At the output end of the structure the modes in both arms are combined by means of a symmetric Y-junction. This combination of modes will in general produce both the fundamental and first-order modes in the output section with a distribution that depends on the phase difference of the two combining modes [Auracher, 1980]. When the output end is a single mode
waveguide, the first order mode is converted to radiation modes. As the radiation modes are strongly attenuated, only the fundamental mode emerges from the device as shown in Figure 6.16.

![Active arm (E-O effect) Reference arm](image)

Figure 6.16 Mode propagations in an optical Mach-Zehnder interferometer [after Krijnen, 1995].

The Mach-Zehnder modulator was tested without applying electric field using the end-fire coupling method at a wavelength of 1550 nm. Figure 6.17 shows the near-field intensity pattern of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Mach-Zehnder modulator captured by an IR CCD camera. The output spot appears clear and sharp, indicating relatively low propagation loss along the MZI structure. As seen from Figures 6.17 and 6.18, the intensity of the light beam exhibits a Gaussian profile, implying that only the TE$_{00}$ mode propagates in the modulator.
Figure 6.17 The near field optical output image and the intensity as a function of $y$ for a BST/MgO Mach-Zehnder E-O modulator operating at a wavelength of 1550 nm.

Figure 6.18 The output light intensity exhibits a Gaussian beam profile, showing that only a single TE$_{00}$ mode propagates along the BST/MgO Mach-Zehnder E-O modulator at a wavelength of 1550 nm.
6.6.3 Intensity Modulation Produced by \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) Mach-Zehnder Electro-optic Modulator

Figure 6.19 shows the experimental setup (at the Optoelectronic Research Centre, Department of Electronic Engineering of the City University of Hong Kong) for investigating the modulation of intensity by the \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) Mach-Zehnder modulator. A light beam \((\lambda = 1550 \text{ nm})\) from a laser diode was coupled into a single-mode optical fibre. A fibre polarizer was used for defining the polarization state of the input light (TE). The light beam was end-fire coupled into the Mach-Zehnder modulator. The output of the waveguide was butt-coupled into another single mode fibre, which was fed to an optical spectrum analyzer (Agilent 86140 B). Two \( xyz \) micro-positioning systems were used to position the optical fibres at the input and output of the modulator. Contact needles, supported by micromanipulators, were used to apply the voltage to the coplanar electrodes. The transmitted optical intensity was recorded by an oscilloscope (HP 54645A).

Figure 6.19 Experimental setup for the characterization of Mach-Zehnder E-O modulator.
As shown in Figure 6.19 the intensity of light beam can be modulated by applying a dc voltage to one branch of the Mach-Zehnder modulator. The half-wave voltage $V_\pi$ was determined to be 60 V if the device operates in the ranges of 80 to 140 V. The value of $V_\pi$ in our device is much lower than those of LiNbO$_3$ and PMN-PT single crystals [Salvesrini, 1994; Wan, 2004] as shown in Table 1.2, but higher than the reported data for Mach-Zehnder modulators based on other ferroelectric thin films [Petraru, 2002]. Petraru and co-workers reported that a Mach-Zehnder E-O modulator based on $a$-axis oriented BaTiO$_3$ thin film epitaxially grown on MgO substrate had a half-wave voltage of 9.5 V at a wavelength of 1550 nm.

![Figure 6.20 Intensity change generated in the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film Mach-Zehnder modulator versus dc applied voltage at a wavelength of 1550 nm.](image-url)
Another important parameter of a modulator is the modulation depth, $\eta$. In the case of an intensity modulator in which the applied electrical signal acts to decrease the intensity of the transmitted light, $\eta$ is given by:

$$
\eta = \frac{I_0 - I}{I_0}
$$

where $I$ is the transmitted light intensity and $I_0$ is the transmitted light intensity without applied electric field. It is noted that the maximum modulation depth of our device is about 60%, which is not as high as those achieved by other workers [Petraru, 2002]. The moderate modulation depth is probably due to the short length of the straight waveguide at the output end so that the radiation mode is not totally attenuated.
Figure 6.21 Response of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film Mach-Zehnder modulator when an ac voltage is applied. (a) Applied voltage versus time; (b) Intensity output at a wavelength of 1550 nm.
To evaluate the electro-optic modulation under an ac electric field, a triangular voltage with a frequency of 25 Hz and peak voltage of 120 V was applied to the Mach-Zehnder modulator. The device exhibited good response to the applied ac voltage as shown in Figure 6.21. A frequency doubling phenomenon was observed in the output signal as compared with the driving voltage. The performance of the device was very stable up to a frequency of 1 MHz. The response time of the device cannot be determined due to the frequency limitation of our photodetector.

The E-O coefficient of the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film Mach-Zehnder modulator operating at a wavelength of 1550 nm can be calculated from the half-wave voltage $V_\pi$. Since Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate exhibits the Kerr E-O effect, the phase change $B$ in the device can be derived from Eqs. (4.19) and (1.19):

$$B = \frac{2\pi L_\delta n}{\lambda} \delta(\Delta n) = \frac{2\pi L_\delta}{\lambda} \cdot \left(\frac{1}{2} n^3 R_{\text{eff}} E^2\right) = \frac{\pi \cdot n^3 \lambda V^2}{\lambda d^2} R_{\text{eff}}$$

where $L$ is the activation length of the device, $d$ is the coplanar electrode gap width, $\lambda$ the wavelength of the light, $V$ the applied voltage, and $R_{\text{eff}}$ is the effective quadratic E-O coefficient. Putting $B = \pi$,

$$R_{\text{eff}} = \frac{\lambda \cdot d^2}{n^3 \lambda V^2 \pi}$$

Therefore, the effective quadratic E-O coefficient of the device at $\lambda = 1550$ nm is calculated to be $R_{\text{eff}} = 0.983 \times 10^{-18}$ m$^2$/V$^2$. The value is one order of magnitude smaller than that measured for our Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film at a wavelength of 632.8 nm (see Chapter 4).
6.7 Summary

Rib waveguides and Mach-Zehnder electro-optic modulators based on epitaxial Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films grown on MgO (001) substrates were fabricated. The appropriate geometries of rib Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film waveguides and Mach-Zehnder modulators were found by using the dispersion equation and the effective index method. Single mode (TE$_{00}$) propagation at $\lambda = 1550$ nm was observed in both the rib and Mach-Zehnder structures using the end-fire method and the results were consistent with our numerical calculations. The modulation of light intensity produced by the Mach-Zehnder modulator by applying a dc or ac voltage was measured. The half-wave voltage and the maximum modulation depth of the device were found to be 60 V and 60 %, respectively. The Mach-Zehnder modulator showed stable performance up to a frequency of 1 MHz. The effective quadratic E-O coefficient of this device was calculated to be $R_z^{eff} = 0.983 \times 10^{-18}$ m$^2$/V$^2$. 
CHAPTER 7

CONCLUSIONS AND SUGGESTIONS
FOR FUTURE WORK

7.1 Conclusions

The present research focused on the investigation of the electro-optic and optical properties of epitaxial $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films with the aim of evaluating their potential in active waveguide applications.

Epitaxial $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films were deposited on single crystal substrates by using pulsed laser deposition. The structural properties of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films were studied with regard to the effects of processing conditions (deposition temperature and oxygen partial pressure) and various substrates using X-ray diffraction. It was found that the crystalline quality of thin films was enhanced when the deposition temperature was increased. Oxygen partial pressure had a significant effect on the lattice parameters of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films. The lattice distortion in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films deposited on various substrates is believed to arise from the lattice mismatch and difference in thermal expansion between the film and the substrate, and oxygen vacancies.
The surface morphology of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films depended strongly on the processing conditions. Both the grain size and surface roughness increased with an increase of deposition temperature or oxygen partial pressure. The grain size and surface roughness had a significant effect on the optical loss in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films. To achieve good crystalline quality, high degree of epitaxy and low optical loss in Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films, the optimum deposition temperature and oxygen partial pressure were 750 °C and 200 mTorr, respectively.

The Curie temperature and hysteresis behavior of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were significantly modified by both the processing condition (oxygen partial pressure) and the substrate. For Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) substrates, a low oxygen pressure (100 mTorr) resulted in a depressed Curie temperature (-10 °C), as compared to the Curie temperature (35 °C) of bulk Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ ceramics. High oxygen pressures (200 and 300 mTorr) gave rise to an upshifted $T_c$ of around 80 °C, implying that the film is in the ferroelectric phase at room temperature. This film also exhibited a well-defined hysteresis loop, indicating strong ferroelectric activity at room temperature. Films grown on LAO (001) and LSAT (001) substrates also showed significant ferroelectric activity because their Curie temperature were well above room temperature. However, the film deposited on STO (001) substrate had a Curie temperature that was close to room temperature and thus showed a very slim hysteresis loop.

Using the modified Sénarmont method, the electro-optic properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were studied with regard to the effects of processing conditions (deposition
temperature and oxygen partial pressure) and different substrates. The E-O behavior of the film grown on MgO (001) substrates was predominantly quadratic and both the deposition temperature and oxygen partial pressure had a significant effect on the electro-optic properties. Using the optimum deposition conditions, a high E-O coefficient of $10.0 \times 10^{-18} \text{ m}^2/\text{V}^2$ was achieved in films grown on MgO (001) substrates. The E-O performance of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films were significantly affected by the substrates. Films grown on LAO (001) and LSAT (001) substrates showed linear electro-optic behavior with high E-O coefficients of $82.7 \times 10^{-12} \text{ m/V}$ and $125 \times 10^{-12} \text{ m/V}$, respectively. A quadratic E-O effect was observed in the film deposited on STO (001) substrate and the quadratic E-O coefficient is $12.9 \times 10^{-18} \text{ m}^2/\text{V}^2$. From the viewpoint of waveguide fabrication, the large difference in refractive index between the film and MgO substrate will lead to good light confinement within the film, thereby improving the device efficiency. Therefore, Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ films deposited on MgO (001) substrates at 750 °C under 200 mTorr oxygen pressure were used for the fabrication of optical waveguides in our subsequent work.

Waveguide related optical properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin films deposited on MgO (001) substrates were measured using the prism coupling technique. The ordinary refractive index $n_o$ and extraordinary refractive index $n_e$ of a 620 nm thick Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film were determined to be $n_o = 2.1737 \pm 0.0011$ and $n_e = 2.2185 \pm 0.0007$ at $\lambda = 632.8 \text{ nm}$, and $n_o = 2.1737 \pm 0.0011$ and $n_e = 2.2185 \pm 0.0007$ at $\lambda = 1550 \text{ nm}$, respectively. The refractive index profile in the Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film was determined using the i-WKB method. The step-like index profile indicated good optical
homogeneity along the thickness direction of the film. The scattering loss in the film was measured using the moving fibre method. At a wavelength of 1550 nm, the scattering losses were found to be 0.93 dB/cm and 1.29 dB/cm for TE$_0$ and TM$_0$ modes, respectively, which were sufficiently low for optical waveguide applications.

The appropriate geometry for a single-mode rib waveguide based on Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film grown on MgO (001) substrate was determined using the dispersion equation and the effective index method. Rib and Mach-Zehnder waveguides were successfully fabricated using photolithography and reactive ion etching techniques and single mode (TE$_{00}$) propagation at $\lambda = 1550$ nm was observed in these two waveguides. A lightwave can be effectively modulated by the Mach-Zehnder modulator by applying a dc or ac voltage. The maximum modulation depth and half-wave voltage $V_\pi$ of this device were 60 % and 60 V, respectively, and the effective quadratic E-O coefficient is $R_c^{\text{eff}} = 0.983 \times 10^{-18}$ m$^2$/V$^2$. Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ thin film Mach-Zehnder electro-optic modulators seem to have potential to be used in telecommunication applications.
7.2 Suggestions for Future Work

Ferroelectric thin films show great promise as electro-optic materials for integrated optics applications, but so far there have been only a few reports on waveguides based on ferroelectric thin films. The following are some suggested topics for future research which may be regarded as an extension of the present work.

The electro-optic properties of the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films in this work may be improved since our E-O coefficients are not as high as the published data [Li, 2000]. It is believed that, in pulsed laser deposition, deposition temperature is a key factor that will affect the crystalline quality and thus the properties of thin films. If the deposition temperature can be increased, better electro-optic properties in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films may be achieved. Furthermore, to realize better electro-optic properties, we may attempt to use other thin film deposition techniques such as sputtering, metalorganic chemical vapor deposition and molecular beam epitaxy.

Besides the material properties, the geometry of a waveguide is also a critical factor that will affect its performance. In a Mach-Zehnder electro-optic modulator, the branching angle should be as small as possible in order to reduce the insertion loss. To reduce the half-wave voltage, a smaller gap spacing in the coplanar electrodes and a longer activation length are preferred. To increase the modulation depth, the length of
the waveguide in the output end should be made long enough to ensure complete attenuation of the radiation mode.

Although the concept of waveguide devices based on ferroelectric thin films grown on single crystal substrates has been realized both in our work and in several reports [Petraru, 2002; Petraru, 2003; Thapliya, 2003], so far there has been no report on ferroelectric thin film electro-optic modulator integrated on semiconductor substrates. The demand for high speed transfer of huge data volumes is increasing rapidly. In parallel, the requirement of lowering the production costs is becoming more and more important, so the optoelectronics community is longing for a break-through where the high-speed, low-loss integrated electro-optic modulator is a key component. The long term goal in this area is the production of high-quality epitaxial films on large diameter semiconductor substrates (Si, GaAs), which may involve oxide buffer layers to prevent leakage of the lightwave into the substrate [Xiong, 1998; Liang, 2004; Chen, 2004]. Such films would offer a large surface for device development and a compatibility to integrate with microelectronic systems.
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