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Growth of ferroelectric thin films through metallo-organic decomposition

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Rice University, 1992
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Growth of Ferroelectric Thin Films through Metallo-Organic Decomposition

by

Suresh Balaraman

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Master of Science

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Growth of Ferroelectric Thin Films through Metallo-Organic Decomposition

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Abstract

Metallo-Organic Decomposition (MOD) has been used in recent times to grow films with good material properties. The objective of this investigation is to grow films with good electrical and optical properties through the process of MOD and compare them with those made with other processes such as sputtering. Thin lithium niobate and lead zirconium titanate (PZT) films were made through the process of metallo-organic decomposition (MOD). Films were grown on Si(100), Si(111) and sapphire(012). The thickness of the films (as characterized through ellipsometry and reflectivity measurements) ranged from 750 $\text{nm} - 3000 \text{ Å}$. The films were characterized through XRD (x-ray diffraction), C–V (capacitance–voltage), I–V (current–voltage) and G–V (conductance–voltage) measurements. Switching studies were performed on LiNbO$_3$/Si films. Optical waveguiding were attempted on LiNbO$_3$ films grown on sapphire.

Thin films made via MOD yielded crystalline films with the absence of other phases other than LiNbO$_3$. The films were polycrystalline and often randomly oriented. Grain orientation along (104) was observed on Si(100). An attenuation of 2.8 dB/cm was observed on performing optical waveguiding on films grown on sapphire. C–V measurements yielded dielectric constants of about 28–32 for LiNbO$_3$ films on Si. The resistivity as measured from I–V tests was $10^{12}$ to $10^{13}$. 
The PZT films were crystalline and no particular grain orientation was found for films grown on silicon. MOD technique was found to yield films with good stoichiometry.
Acknowledgments

First of all, I would like to thank my advisor, Dr. Tom Rabson for the confidence that he has placed in me and for allowing me enough freedom to pursue my own manner of working. I am also grateful for his valuable guidance and insightful comments which helped a lot in tuning my approach to research. I would also like to thank Dr. Dan Callahan and Dr. Shiou-Jyh Hwu for their valuable comments on this dissertation. I am extremely grateful to Dr. Whitmire for helping me in the synthesis of the precursor solutions of LiNbO3 and PZT. Without his help it would have been very difficult for me to have got started on this project.

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To my parents
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Chapter 1

Introduction

The uses of a ferroelectric in the form of a thin film are quite numerous. Since ferroelectrics are also pyroelectric and piezoelectric, a thin film process which can promise good electrical and material properties can lead to advances in all related disciplines. Some of the direct applications of ferroelectric thin films are in non-volatile memories, high density capacitors, actuators, surface acoustic waves (SAW) and vast array of electro-optic, pyroelectric and piezoelectric devices. The ferroelectrics that have gained the most attention in recent past have been PZT, PLZT and LiNbO₃. Many researchers have been trying to obtain good quality ferroelectric thin films using dry processes like sputtering, MOCVD and laser deposition or wet processes like MOD and sol-gel.

The metallo-organic decomposition process was a technique developed primarily to produce ceramic powders. This has been used successfully in the recent past in making thin films of PZT and LiNbO₃ [28]. The process involves the mixing of essential components in a solvent and then depositing them on top of a substrate to provide a uniform coating. Subsequently the wet coating is pyrolysed to decompose metallo-organic compounds yielding the desired compound and to evaporate all of the solvent. Annealing is done to crystallize the film. The material parameters can be fine tuned during the annealing stage. The heating rate is decided contingent upon the nature of phase transformations, the volume changes and the microstructure that
is desired. If the film is too thick, cracks may result during heat treatment. In such cases, multilayers might be required to obtain the desired thickness.

The MOD process has assumed wider importance as it offers faster and inexpensive means of producing ferroelectric thin films. So far most of the research on MOD films has been focused on material properties.

A study has been made on producing good quality thin ferroelectric films of PZT and LiNbO$_3$ through MOD. The electrical properties studied were the C–V, I–V and G–V behavior. Switching was attempted on LiNbO$_3$/Si without much success. Ellipsometry and reflectivity measurements were used to gauge the thickness of the thin films. Waveguiding was attempted on LiNbO$_3$/sapphire. The influence of process parameters were also studied and comparisons were made with sputtered films in specific cases.
Chapter 2

General Theory of Ferroelectrics

A general discussion of ferroelectrics can be found in [13],[14],[17], [4],[8]. Dielectrics are insulators in which the conduction mechanism is non-electronic. When an external field is applied, a dielectric responds by polarizing itself. Polarization is effected when the center of positive and negative charges in a unit cell is separated. The magnitude of the dipole is the product of the charge and the distance of separation. Charge separation can be effected by the application of a mechanical stress, which distorts the lattice leading to asymmetry in charge distribution, as in piezoelectrics. All (except one) non-centrosymmetric crystal structures fit the definition of a piezoelectric. Of the twenty non-centrosymmetric crystal structures which exhibit piezoelectricity, ten have a unique polar axis. Such crystals are polar as they are said to possess a spontaneous polarization. However, such a spontaneous polarization cannot be detected by charges on the surface of a crystal as the depolarizing fields which are caused by such a charge distribution would be neutralized by flow of compensation charge from within the crystal and the surrounding medium. But, the spontaneous polarization is temperature dependent and its existence can be detected by observing flow of charge to and from the crystal surfaces on changing the temperature. This is the pyroelectric effect. Fig. 2.1 shows how polar and non-polar dielectrics respond to an applied field.

Ferroelectrics have two or more orientational states in the absence of an electric field and the dipoles can be shifted from one orientational state to the other by the
Figure 2.1: Effect of applied field on a dielectric material
application of an electric field. The orientational states are structurally similar and in the lack of external influence, the states are equally favored.

The electric field required to produce switch in the orientational states of the electric polarization vector is termed as the coercive field. Domain is a region within which all dipoles are aligned in a single direction. A domain wall is what divides one domain from another. A material doesn’t have a domain wall if all the dipoles are aligned in the same direction throughout the material. In a single crystal ferroelectric it is unusual to have a single domain after crystallization. Poling is the process of aligning all the dipoles along a single polar axis. This can be achieved by applying an electric field to the ferroelectric at elevated temperatures, usually past the curie temperature and then cooling it back to room temperature. The curie temperature is defined as the temperature beyond which the ferroelectric transforms into the paraelectric phase.

Often in practice, ferroelectrics exist as polycrystalline ceramics. In this case there might be many grains which have orientation of the crystals in arbitrary directions. Unlike domain walls, grains are physical realities. Not much can be done about them simply by applying an electric field. There are 90° grains which are grains whose domains are unaffected regardless of the direction of the applied field. Most of the grains would neither be a 180° nor a 90° domain but somewhere in between. These respond to the electric field according to the component strength along their respective orientational states. These factors reduce the effective polarization of a polycrystalline ferroelectric. It has been calculated that the fractions of the single-crystal polarization value that can be developed in polycrystalline material (without any specific grain orientation) cannot be more than 0.83, 0.91 and 0.87 for perovskites with tetragonal, orthorhombic and rhombohedral structures respectively [17]. Usually, the performance is much worse. The effective polarization can drop to
as much as half of the single crystal value. The need for grain orientation becomes very great in high performance ferroelectrics.
Chapter 3

Deposition of Thin Films

Deposition of ferroelectric thin films falls into two major categories – wet and dry [22]. The wet deposition techniques use low deposition temperatures, unheated substrates and usually have an annealing step to ensure crystallization. Two of the wet processes commonly used are MOD (metallo-organic decomposition) and Sol-Gel. The frequently used dry processes are rf-sputtering, magnetron sputtering, rf magnetron, MOCVD, laser deposition, ion beam sputtering and evaporation. The dry processes often use vacuum and higher deposition temperatures. Except for MOCVD, the dry processes use physical vapor deposition. The material is physically removed from a source and transferred to the substrate. The material then condenses on to the substrate without any chemical reaction in the gaseous phase or on the substrate surface. The deposition rates vary from 5 to 1000 Å/min. The sol-gel method of deposition is somewhat similar to that of MOD except that in MOD there is no formation of a gel. Another advantage that MOD offers is that the precursor solutions can be stored for months at a stretch without noticeable deterioration in quality. The processes discussed here viz. MOD and sputtering are inherently different and offer interesting insights into the nature of thin film depositions.
3.1 MOD

3.1.1 MOD Chemistry

The precursor solutions were selected according to the criteria given by Vest et al[28]. The lithium precursor compound used was lithium neodecanoate. This was synthesised from lithium methoxide and neodecanoic acid. Niobium tri-ethoxy di-neodecanoate was similarly obtained from niobium ethoxide and neodecanoic acid. Lead ethyl hexanoate and zirconium propoxide were bought from commercial sources. Titanium di-methoxy di-neodecanoate was synthesised almost identical to that of lithium and niobium precursors. The synthesis reaction is as follows:

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

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

\[
\text{Ti(OCH}_3\text{)}_4 + 2\text{C}_9\text{H}_{19}\text{COOH} \rightarrow 2\text{CH}_3\text{OH} + (\text{CH}_3\text{O})_2\text{Ti(C}_9\text{H}_{19}\text{COO})_2
\]

The TGA of these precursor solutions are given in Figs. 3.1, 3.2. The pyrolysis temperature for lithium niobate was at 500 °C and for PZT it was done at 400 °C. Films were also made with rapid thermal annealing.

The various chemicals and the manufacturer from whom they were obtained are tabulated in Table 3.1.

3.1.2 Film Deposition

The usual form of depositing formulation solution are spinning, dipping or spraying. Spinning has been the most common technique. When the formulation solution is deposited on the substrate, the final thickness of the wet film is independent of the amount of solution injected (as long as the initial thickness well exceeds the final
Table 3.1: Sources of Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Manufacturer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium methoxide</td>
<td>Noah Technologies</td>
<td>99.99 %</td>
</tr>
<tr>
<td>Niobium methoxide</td>
<td>Noah Technologies</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Neodecanoic acid</td>
<td>Strem Chemicals</td>
<td>99.99 %</td>
</tr>
<tr>
<td>Lead 2 ethyl hexanoate</td>
<td>Alfa Chemicals</td>
<td>99.9 %</td>
</tr>
<tr>
<td>(in mineral spirits)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconium n-propropoxde</td>
<td>Noah Technologies</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Titanium methoxide</td>
<td>Strem Chemicals</td>
<td>99.99 %</td>
</tr>
</tbody>
</table>

thickness) onto it. The final thickness primarily depends on the viscosity, the spinning speed and the spinning time. The effect of secondary parameters like the nature of substrate surface (which might influence the adhesion of the formulation solution) and temperature of the substrate should not be overlooked if such conditions vary drastically.

The substrate is placed on a spinner. The formulation solution is dispensed onto the substrate from a syringe such that the solution covers the entire substrate area. For very viscous films, it’s often helpful to have an initial spinning at a slower rate before accelerating to the final spinning rate. It is essential that the environment is clean. Dust in the formulation solution causes radial streaks which affect the quality of the film along those streaks.

Spinning is one of the most critical steps in determining the thickness and uniformity of the ferroelectric thin film. Studies have been done on the flow of a viscous liquid on a rotating disk which are discussed in references [1],[15],[32],[29].

Bornside et al. [6], [3] divide spin coating into four stages: deposition, spin-up, spin-off and evaporation. During deposition, excess of liquid is dispensed on to the surface. In the spin-up stage, the liquid flows radially outward due to centrifugal
force. During spin-off, excess liquid is cast off the periphery of the spinning surface. But as spinning progresses, some of the volatile matter evaporates leaving the liquid more viscous and hence the flow of liquid to the periphery is greatly reduced. This is because, the thinner the liquid film, the higher the viscosity and the greater the resistance to flow. Thereafter, thinning is predominantly due to evaporation, which is the fourth stage. TGA curves used in this work are given in Figs. 3.1,3.2,3.3,3.4,3.5.

An advantage is spinning is the film becomes increasingly uniform with time of spinning. This is due to the fact that the rate of thinning is proportional to the thickness of the film and hence the thicker portions thin at a faster rate [1]. The thickness of an initially uniform film during spin-off can be described by

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

(3.1)

Where,

- \(h_0\) is the initial thickness of the film,
- \(\rho\) is the density of the ceramic,
- \(\omega\) is the spinning speed in rad/s,
- \(t\) is the time of spinning and
- \(\eta\) is the viscosity of the formulation solution

The spinning procedure creates a steady forced convection in the vapor above the substrate which causes the mass transfer coefficient to be uniform. Thus even during evaporation stage, uniform thinning is favored. Spinning rates used in this work varied from 1000 to 5000 rpm
3.1.3 Thermogravimetric Analysis

Thermogravimetry [31][7] forms one of the more widely used techniques in thermal analysis. The principles involved in TGA is rather simple. TGA involves the measurement of changes that occurs in the mass of a sample as its temperature is raised. A plot of mass as a function of temperature or time represents the thermogravimetric result. Thermogravimetry uses small amounts of sample and yields accurate results fairly quickly. It is often easy to interpret the curve. In the studies conducted, TGA was chiefly used as a means of determining the temperature at which pyrolysis or annealing was to be done, the rate of heating to be employed, the hold time at that temperature.

It is often critical to know the exact temperature at which a decomposition takes place. It is difficult to measure this from the TGA curve alone. A differential curve often proves useful in such a circumstance. In this, the variation of mass of the sample with respect to temperature is plotted against the temperature. Sharp peaks or dents on the differential curve indicates the temperature at which transformation/decomposition of a particular phase occurred. TGA was widely used in this study to make an initial estimate with regards to the composition of the precursor solutions and their decomposition temperature.

TGA was conducted in almost all cases in an atmosphere of nitrogen. In the initial stages of heating the metallo-organic solutions a substantial weight loss is observed. This is due to loss of volatile organic compounds like xylene. It can be seen that the fall in weight percent is steep owing to the large volume of xylene compound present. Xylene usually goes off almost completely by 150 °C. Around 150 - 350 °C, the metallo-organic compounds begin to decompose. A flat region on the TGA curve indicates stability over that temperature range. The residue can be later sent for
x-ray diffraction to verify if it matches with the powder diffraction spectrum of the compound which is expected to be left as the residue. For instance, in the case of the precursor solution of lithium neodecanoate, the residue would be lithium oxide. The TGA profiles of the various precursor solutions are shown in Figs. 3.1,3.2,3.3,3.4,3.5

3.1.4 Pyrolysis

Pyrolysis is the step in which the wet film is heated at a temperature high enough to ensure that all organic matter is volatalised and the metallo-organic compounds are decomposed into an organic film. Pyrolysis, is carried out in an oxidizing atmosphere to ensure that all carbonaceous material are removed from the film. Large volume changes, often as high as 10 to 30, might accompany this stage. Crack formation might result by improper pyrolysis. Thermogravimetric analysis (TGA) provide a convenient way of estimating the temperature at which pyrolysis is to be done. For the pyrolysis of thicker films, it is often advantageous to perform pyrolysis at different rates in the different temperature ranges. As is evident from Figs. 3.1 – 3.5, the heating rate should be the slowest between 30 - 150 °C. It is in this temperature range that the TGA curve often shows the steepest fall which implies a large volume change in the film. Such a procedure helps in minimizing crack formation to a great extent. But in some cases, slower heating rates can cause other problems. In the case of ITO [11] non-uniformities were reported for slowly heated films. This is because of the fact that the viscosity of the formulation solution decreased with increase in temperature. This caused the film to reach an equilibrium contact with its substrate and caused the formulation solution to form some regions more thicker than others. One way of circumventing this problem would be to heat the film at a faster rate. In that case the wet film would not have sufficient film for flowing non-uniformly in any particular direction. But such rapid heating can be used only in case of films which
Figure 3.1: TGA: Lithium Neodecanoate
Figure 3.2: TGA: niobium tri-ethoxy di-neodecanoate
Figure 3.3: TGA of lead 2-ethyl hexanoate
Figure 3.4: TGA of zirconium n-propoxide
Figure 3.5: TGA of titanium di-methoxy-di-neodecanoate
are relatively thin. The thermochemistry of the pyrolysis stage has been explained by Vest et. al.[28]. The pyrolysis temperature is chosen according to the constituents of the formulation solution. For LiNbO$_3$, pyrolysis was done at 450 – 500 °C. PZT films were pyrolysed at about 350 °C.

LiNbO$_3$ was pyrolyzed by placing the substrate directly into the furnace maintained at 500 °C. For PZT, the substrate was heated at a relatively slow rate, 10 °C till a temperature of 300 °C is reached. Then the furnace can be switched to a setting of 350 °C without bothering with the heating rates.

3.1.5 Annealing

After pyrolysis, the film is essentially amorphous in nature. It is during annealing that crystallinity is developed. In many ways annealing is the step where the quality of the film is decided. The chief variables of this stage are (1) temperature, (2) time, (3) annealing atmosphere and (4) rate of heating/cooling. Parameters like flow rate of oxygen (if required) or partial pressure of oxygen are rather secondary in nature and is generally used for fine tuning.

The annealing temperature and the rate of cooling usually decides the phases that are to be present and the microstructure. Annealing temperature is chosen according to the final properties desired. As annealing temperature increases (up to about 800°C), better crystal structure can be achieved. However, higher temperature also brings along with it allied problems like greater porosity etc. Faster cooling yields a finer microstructure. Usually, the cooling rate is more important than the heating rate. The heating rate is controlled to ensure that cracking does not take place where as the cooling curve gives the final microstructure. The importance of these two parameters cannot be overemphasised as the microstructure controls many of the important electrical and material properties. The annealing time is not very critical.
Vest et al. [28] have used annealing time ranging from 1.5 – 11 hours. In this study it was found that much shorter annealing time is sufficient to produce good quality films. Not much difference in film nature has been observed for much longer annealing times. Annealing time should be sufficient to allow the film to be in equilibrium at the required temperature for long enough time for the oxygen in the atmosphere to diffuse freely throughout the fired film. It also should be long enough to allow proper bonding between the various species. The annealing temperature used in this study varied from 600 – 800 °C.

The atmosphere present during annealing depends on the type of film desired. For LiNbO$_3$ films, annealing in air was sufficient to produce good quality films whereas for PZT films oxygen atmosphere was required. The flow rate of oxygen for PZT should be sufficient to allow plenty of oxygen to the film. Oxygen content in these films are critical as they play a vital part in all electrical and optical applications. Slight deviations in stoichiometry would adversely affect switching properties. Care should be taken that the wet film is not in directly in the way of oxygen flow if the flow rate is relatively high. This might produce unwanted streaks or patches on the film.

3.1.6 Process Parameters

The processing parameters of the MOD process used in this work has been tabulated in Table 3.2. The spinning rate and spinning time are varied according to desired thickness.
Table 3.2: Process parameters for MOD process

| Precursors                          | LiNbO$_3$ : lithium neodecanoate and niobium tri-ethoxy di-neodecanoate  
|                                    | PZT : Lead 2 ethyl hexanoate, zirconium propoxide and titanium neodecanoate |
| Spinning rate                      | 1000 – 5000 rpm                                                            |
| Spinning time                      | 10 – 30 s                                                                   |
| Pyrolysis                          | 500 °C for LiNbO$_3$ and 350 °C for PZT                                      |
| Annealing temperature              | 750 °C                                                                      |
| Annealing time                     | 2 hrs. (2 min. for rapid thermal annealing)                                 |

3.2 Sputtering

The preparation method used has been due to Baumann, Rost et al[23],[2]. The main steps involved in making sputtered lithium niobate films on silicon are (i) cleaning the substrate, (ii) deposition and (iii) providing contacts to the film.

The substrates used were either sapphire or silicon. Both p-type and n-type silicon were used. The orientation were $<111>$ or $<100>$. The resistivities usually were 0.1, 1 or 10 $\Omega \cdot cm$.

The cleaning procedures were as follows: 1. To remove metallic and organic residue a solution of $H_2O - NH_4OH - H_2O_2$ in the ratio of 5:1:1 was used. The concentration of ammonium hydroxide was 29% and that of hydrogen peroxide was 30%. The water was filtered and deionised. The wafers were placed in a hot bath of cleaning solution at a temperature of 80 °C for a period of 10 min. The wafers were then removed and spray cooled by a jet of deionised water.

2. A solution of dilute HF (1:50) was used to strip the silicon of the thin coating of oxide that was invariably present. The wafer was placed in this solution for a minute or so.
3. A solution of HCl and H₂O₂ maintained at 80 °C was used to remove ionic contaminants.

4. The wafer was then quenched with a jet of deionised water spray.

The sputtering parameters used are given in Table 3.3[23].

Table 3.3: Sputtering parameters for LiNbO₃

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>13.56 MHz</td>
</tr>
<tr>
<td>Sputtering Gas</td>
<td>Ar/O₂ (60% : 40%)</td>
</tr>
<tr>
<td>Sputtering Pressure</td>
<td>2 - 3 mTorr</td>
</tr>
<tr>
<td>Forward RF power</td>
<td>100 W</td>
</tr>
<tr>
<td>Target-Substrate Spacing</td>
<td>5 cm</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>600 °C</td>
</tr>
<tr>
<td>Target Dimension</td>
<td>4 in</td>
</tr>
<tr>
<td>Growth Rate</td>
<td>900 Å/hr</td>
</tr>
</tbody>
</table>
Chapter 4

Characterization

4.1 X-Ray Diffraction

X-ray diffraction is a tool to study the structure of matter and is used chiefly for determining crystal structure, chemical analysis, stress measurement, phase equilibria and measurement of particle size, orientation of crystals and so on. In this study, x-ray diffraction has been used predominantly to study crystallinity and identify the existence of crystalline phases present in the thin films.

A crystal may be defined as a three dimensional array of atoms arranged periodically. A diffracted beam can be said to be composed of large number of scattered rays mutually reinforcing each other[5]. In common parlance, the diffracted beams are often called “reflections” and the planes which diffract are referred to as “reflecting planes”. When an x-ray beam is incident on a crystal, the beams get scattered. But planes of atoms that are parallel to each other scatter the x-ray beam in the same direction interfere constructively, thus reinforcing each other. In this case the diffracted x-ray beam that emerges out of the crystal is relatively more intense than a normally scattered beam. This condition is known as Bragg reflection. Bragg reflection occurs when

\[ n\lambda = 2d\sin\theta \]  \hspace{1cm} (4.1)

where \( \lambda \) is the wavelength of the x-ray, \( d \) is the spacing between the reflecting planes and \( \theta \) is the angle of incidence of the x-ray beam on the plane.
X-ray diffraction peaks and their relative intensities are characteristic of an element/compound. The peak positions are related to the lattice parameters and the crystal structure of a material. X-ray diffraction records of powder samples of various compounds and elements are cataloged in powder diffraction files[12].

4.2 Optical Characterization

4.2.1 Reflectivity Measurements

Reflectivity measurements are an easy and nondestructive way of estimating thickness. This can be done by shining white light on it. When a dielectric film is viewed through a microscope or an unaided eye, the interference effects give a characteristic color to the film which depends on the thickness of the film, its refractivity index and the nature of the spectral distribution of light. Using thickness charts, thickness can be measured within 200Å to 300Å. It is often advantageous to have calibrated samples as reference. Most common source of error occurs because of the fact that the colors repeat themselves due to different orders of interference. The color difference between two difference order is too small to detect without calibrated samples. The colors will not match exactly unless they are of the same order. It is also helpful to have a rough estimate of the thickness range (within 1000 Å). Piskin and Conrad [21] have estimated the color chart for SiO₂ on Si. This has been adapted to LiNbO₃ and is given in Table 4.1. The same chart can be used for any dielectric film of isotropic properties (under similar illuminating conditions) using the relation, \( n_1t_1 = n_2t_2 \), where \( n \) and \( t \) stand for the refractive index and the thickness of the film.
Table 4.1: Color Chart for LiNbO₃ Films Observed Perpendicularly under Daylight Fluorescent Lighting

<table>
<thead>
<tr>
<th>Film Thickness (Å)</th>
<th>Color</th>
<th>Film Thickness (Å)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>Tan</td>
<td>4000</td>
<td>Violet-red</td>
</tr>
<tr>
<td>400</td>
<td>Brown</td>
<td>4350</td>
<td>Bluish (Not blue but borderline between violet and blue-green. It appears more like a mixture between violet-red and blue green and looks greyish)</td>
</tr>
<tr>
<td>600</td>
<td>Dark violet to red violet</td>
<td>4900</td>
<td>Blue-green to green (quite broad)</td>
</tr>
<tr>
<td>800</td>
<td>Royal Blue</td>
<td>5100</td>
<td>“Yellowish”</td>
</tr>
<tr>
<td>1000</td>
<td>Light Blue to metallic blue</td>
<td>5200</td>
<td>Orange (rather broad for orange)</td>
</tr>
<tr>
<td>1100</td>
<td>Metallic to very light yellow green</td>
<td>5400</td>
<td>Salmon</td>
</tr>
<tr>
<td>1300</td>
<td>Light gold or yellow (slightly metallic)</td>
<td>5500</td>
<td>Dull, light red-violet</td>
</tr>
<tr>
<td>1400</td>
<td>Gold with slight yellow orange</td>
<td>5550</td>
<td>Blue-violet</td>
</tr>
<tr>
<td>1600</td>
<td>Orange to mellow</td>
<td>5700</td>
<td>Blue</td>
</tr>
<tr>
<td>1700</td>
<td>Red-violet</td>
<td>5850</td>
<td>Blue green</td>
</tr>
<tr>
<td>1900</td>
<td>Blue to violet-blue</td>
<td>6050</td>
<td>Dull yellow-green</td>
</tr>
<tr>
<td>1950</td>
<td>Blue</td>
<td>6200</td>
<td>Yellow to “yellowish”</td>
</tr>
<tr>
<td>2000</td>
<td>Blue to blue-green</td>
<td>6300</td>
<td>Orange</td>
</tr>
<tr>
<td>2150</td>
<td>Green to yellow-green</td>
<td>6400</td>
<td>Carnation pink</td>
</tr>
<tr>
<td>2200</td>
<td>Yellow</td>
<td>6500</td>
<td>Violet-red</td>
</tr>
<tr>
<td>2300</td>
<td>Light orange</td>
<td>6700</td>
<td>Red-violet</td>
</tr>
<tr>
<td>2350</td>
<td>Carnation pink</td>
<td>6750</td>
<td>Violet</td>
</tr>
<tr>
<td>2500</td>
<td>Yellow</td>
<td>6800</td>
<td>Blue-violet</td>
</tr>
<tr>
<td>2550</td>
<td>Light-yellow</td>
<td>7000</td>
<td>Green</td>
</tr>
<tr>
<td>2600</td>
<td>Carnation pink</td>
<td>7100</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>2700</td>
<td>Yellow</td>
<td>7150</td>
<td>Green</td>
</tr>
<tr>
<td>2800</td>
<td>Red-violet</td>
<td>7300</td>
<td>Violet</td>
</tr>
<tr>
<td>2900</td>
<td>Violet</td>
<td>7500</td>
<td>Blue-violet</td>
</tr>
<tr>
<td>3000</td>
<td>Blue-violet</td>
<td>7600</td>
<td>Green</td>
</tr>
<tr>
<td>3050</td>
<td>Blue</td>
<td>7700</td>
<td>Yellow-green</td>
</tr>
<tr>
<td>3100</td>
<td>Blue-green</td>
<td>7900</td>
<td>Carnation pink to salmon</td>
</tr>
<tr>
<td>3200</td>
<td>Green (broad)</td>
<td>8000</td>
<td>Orange</td>
</tr>
<tr>
<td>3300</td>
<td>Red-violet</td>
<td>8200</td>
<td>“Yellowish”</td>
</tr>
<tr>
<td>3450</td>
<td>Yellow-green</td>
<td>8400</td>
<td>Sky blue to green-blue</td>
</tr>
<tr>
<td>3550</td>
<td>Carnation pink</td>
<td>8900</td>
<td>Orange</td>
</tr>
<tr>
<td>3600</td>
<td>Yellow to “yellowish” (not yellow but in the position where yellow is to be expected. At times it appears to be light creamy grey or metallic)</td>
<td>9200</td>
<td>Violet</td>
</tr>
<tr>
<td>3700</td>
<td>Light orange or yellow to pink borderline</td>
<td>9300</td>
<td>Blue-violet</td>
</tr>
<tr>
<td>3800</td>
<td>Carnation pink</td>
<td>9600</td>
<td>Blue</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9800</td>
<td>Dull yellow-green</td>
</tr>
</tbody>
</table>
4.2.2 Ellipsometric Measurements

The ellipsometers used conventionally are based on the null ellipsometric [24] principle. The Polarizer-Compensator-Sample-Analyzer configuration is the most common. A schematic figure of ellipsometer is shown in Fig. 4.1. A beam of unpolarized light from the laser source is allowed to pass through a polarizer. The light coming out of it is linearly polarized. The compensator, also known as retarder, changes the linearly polarized light to elliptically polarized light. The compensator has a fast and a slow optical axis perpendicular to the direction of transmitted light. The electric field component parallel to the slow axis is retarded with respect to the component of electric field parallel to the fast axis.

The polarizer and compensator angles can be adjusted to give any form of light ranging from linear to circular. The idea is to get linear polarization of the light that gets reflected off the sample. The analyzer angle suitably adjusted can completely extinguish the light. The operator is required to adjust the analyzer and polarizer angles alternately to achieve this end. The $\Psi$ and $\Delta$ [16] values are used to calculate the thickness and refractive index of the film. $\Psi$ is the phase shift between the parallel and perpendicular component of the electric field vector. $\tan(\Delta)$ is the ratio of the reflected components of perpendicular and parallel light. The $\Psi$ and $\Delta$ values are calculated from a set of P, C and A (the angles of the polarizer, compensator and the analyzer). There are 32 combinations of P, C and A that result in a pair of $\Psi$ and $\Delta$ values. By restricting all angles to less than $180^\circ$, the number of pairs of equations can be reduced to 16:

\[
\Psi : A, \quad 180^\circ - A \quad (4.2)
\]

\[
\Delta : 2P - 90^\circ, \quad 2P - 180^\circ, \quad (2n - 1)90^\circ \pm 2P \quad (4.3)
\]
where \( n = 1, 2, 3 \) or 4.

By fixing the compensator angle at, say, \( 45^\circ \), and the ranges of \( P \) and \( A \) to two zones:

Zone I: \(-45^\circ \leq P_2 \leq 135^\circ, \quad 0^\circ \leq A_2 \leq 90^\circ, \quad C = 45^\circ\) \hspace{1cm} (4.4)

Zone II: \(-135^\circ \leq P_4 \leq 45^\circ, \quad -90^\circ \leq A_4 \leq 90^\circ, \quad C = 45^\circ\) \hspace{1cm} (4.5)

Once \( P \) and \( A \) are determined in the above zones, they are related to \( \Psi \) and \( \Delta \) as:

\[
\Psi_2 = A_2, \quad \Psi_4 = -A_4 \hspace{1cm} (4.6)
\]

\[
\Delta_2 = 270^\circ - P_2, \quad \Delta_4 = 90^\circ - 2P_4 \hspace{1cm} (4.7)
\]

Error can be reduced by combining the average values of \( \Psi \) and \( \Delta \) measured in both the zones.

\[
\bar{\Psi} = \frac{\Psi_2 + \Psi_4}{2} = \frac{A_2 - A_4}{2} \hspace{1cm} (4.8)
\]
\[ \bar{\Delta} = \frac{\Delta_2 + \Delta_4}{2} = 180^\circ - (P_2 + P_4) \]  

(4.9)

A set of \( \Psi \) and \( \Delta \) can be used to calculate the refractive index and the thickness of the sample.

4.2.3 Coupling and Waveguiding

Prism coupling and waveguiding techniques are presented in greater detail by Huang[10]. Prism coupling, for sufficiently thick films, can yield the refractive index and thickness of the film. Thick films of optical quality cannot be obtained with a single layer deposition of MOD. The experiments were performed on films less than 2000 \( \AA \) thick. It is difficult to measure refractive index and thickness with such thin films. 2500 \( \AA \) or thicker films are required for this purpose.

4.3 Electrical Characterization

4.3.1 C–V Plots

One of the most useful electrical tests constitute the C–V plots[20],[27],[25],[26]. Its importance lies in the wealth of information that can be obtained from a single plot and the ease with which such tests can be carried out. A typical set up is shown in Fig. 4.2.

One of the capacitance meter used measures capacitance by applying a small (10 to 100 mV) ac voltage on top of a DC bias. The frequency of the small signal can be set anywhere between 20 Hz to 1 MHz. Fig. 4.3a shows a typical C–V plot at high frequencies. For a low frequency measurement, the C–V plot looks more like Fig. 4.3b. The curves shown are for an insulator on a \( p \)-type silicon [18]. For a negative bias in a \( p \)-type silicon, the majority carriers (holes) pile up against the insulator-semiconductor interface and causes a layer of accumulation. It is this layer
of accumulation that responds to the ac small signal applied and manifests itself as differential capacitance. But since the capacitance caused by this accumulation layer is much larger than that of the oxide capacitance, the net capacitance is that of just the oxide layer. As the bias voltage gets more positive, the accumulation layer decreases in magnitude as the majority carriers are pushed away from the insulator semiconductor interface. This leaves a depletion layer underneath the interface. The differential capacitance is due to the flowing in and out of the majority carriers at the edge of the depletion layer. But now, the differential capacitance caused is lower than that of the insulator. Hence the total capacitance is the equivalent of two capacitors $C_s$ and $C_i$. 

Figure 4.2: Experimental set-up for C–V measurements
Figure 4.3: C–V curves of an MIS Capacitor
When the applied DC bias exceeds a threshold voltage of $V_T$, an inversion layer is produced in the semiconductor. This is because, the bias voltage is large enough to pull the minority carriers from the bulk of the semiconductor. The minority carriers pile up against the metal-insulator interface. At low frequencies, the relaxation time of the minority carriers are much shorter than that of the applied ac signal. Hence the minority carriers are able to keep up with variation in applied signal. The differential capacitance caused due to this is very high which results in an increase in capacitance. The final capacitance reached is that of the insulator as this is again the case of two capacitors in parallel with the capacitance of the inversion layer much higher. Any further increase in voltage only serves to increase the inversion layer by bringing in more negatively charged particles from semiconductor bulk. This only serves to increase the differential capacitance of the inversion layer. The depletion region remains unaffected.

At higher frequencies, the C–V curve looks very similar to that of a low frequency curve until the inversion layer is formed. But from then on different mechanisms prevail. At higher frequencies, the relaxation time of the minority carrier is not sufficiently short. Due to this, the minority carriers at the interface are not able to respond to the fast varying ac. However, the majority carriers at the edge of the depletion layers can respond at much faster rates and the resulting differential capacitance is due to the charge (of majority carriers) flow at the depletion edge. This leads to a situation of two capacitances, $C_s$ and $C_i$, in series. Further increase in bias voltage brings more minority carriers to the interface but the capacitance is due to the majority carriers. The ac fluctuations and the way it affects charge layers are shown in Fig. 4.4. The dc biasing conditions correspond to (a) accumulation, (b) depletion, (c) inversion with $\omega \to 0$ and (d) with $\omega \to \infty$. In Fig. 4.4, $w_t$ stands for depletion width.
The C–V curve might exhibit hysteresis under the following circumstances: (1) presence of mobile positive charges in the insulator (2) switching of a ferroelectric due to the applied voltage and (3) charge injection. The effects of these factors for an insulator on silicon is shown in Fig. 4.5[24]. The C–V shift due to switching looks similar to that of charge injection, only the curve is traced in the clockwise (for ferroelectric on p-type silicon) direction.

Sweeping rates should be sufficiently low to allow the minority carriers to be generated fast enough to balance the changing gate voltage; else deep depletion would result owing to the ever increasing depletion region. However, the phenomena of deep depletion has applications in DRAM and CCDs.

It is essential that excellent contact is made to the substrate. The back of the substrate, which is usually the contact to the substrate, often has oxide and other form of impurities. Cleaning the surface and removing residual oxides by etching with dilute hydrofluoric acid helps. Better mechanical contact is achieved if the wafer is held in place with vacuum.

Moisture on the surface of the thin film doesn’t affect the capacitance measurement during accumulation or depletion. But once the threshold value of bias voltage is exceeded, and inversion sets in, the moisture on the insulator surface participates in inverting. This is because of an apparent increase in the area of the contact dot due to presence of moisture forming an annulus around the metallic contact. This causes an increase in capacitance of the depletion layer. This problem can be overcome by baking the device for an hour in a nitrogen atmosphere.

Miscellaneous problems exist too. Sometimes negative capacitance can be recorded. This is due to shorting of the insulator. There might be stray capacitances from cables in the set up. Also formation of dots by evaporating metal through a shadow
mask doesn’t yield as good results as does patterning metal dots with photoresist followed by an etching step.

Capacitance Measurement Technique

A simple schematic diagram of the C-V meter is given in Fig. 4.6. [18] The impedance of the device is calculated as the ratio of input voltage signal \( V_i \) to that of the current through the device \( I_i \). By using basic theory of operational amplifiers, we can calculate the impedance of the device as:

\[
Z = -\frac{R_F V_i}{V_o}
\]  
(4.10)

For a simple model of the device this can be interpreted as,

\[
Z = \frac{G}{[G^2 + (\omega C)^2]} - \frac{j\omega C}{[G^2 + (\omega C)^2]}
\]  
(4.11)

where \( \omega \) is the frequency of the input signal, \( V_i \) is the input signal and \( V_o \) is the output signal.

The first term stands for conductance and the second for susceptance. The voltages, \( V_i \) and \( V_o \) can be fed into a phase detector. The 0° phase angle gives the conductance \( G \) and the 90° phase angle gives the susceptance or the capacitance \( C \). It should be remembered that the conductance and capacitance that are measured are based on the circuit given in Fig. 4.7(c).

4.3.2 Conductance Measurements

To study the feasibility of the ferroelectric as a possible MFS configuration (Metal-Ferroelectric-Semiconductor), we need to study the presence of interface charges and their effects on the device. A lot of research has been done on MOSFETs and these apply to MFSFETs in a general sense. As the ferroelectrics are basically oxides, (e.g.
lithium niobate and PZT), the conditions of an oxide-semiconductor system discussed in Nicollian and Brews apply [18], [26]. There are usually four general types of charges that are associated with such systems. They are fixed oxide charge \((Q_f, N_f)\), mobile oxide charge \((Q_m, N_m)\), oxide trapped charge \((Q_{ot}, N_{ot})\) and interface trapped charge \((Q_{it}, N_{it}, D_{it})\). \(Q\) is the net charge per unit area and \(N\) is the net number of charges per unit area and \(D\) is density of interface traps.

Fig. 4.7(a) shows the equivalent circuit of a MFS with interface charges. A simple circuit conversion yields Fig. 4.7(b). We get,

\[
C_p = C_s + \frac{C_{it}}{1 + (\omega \tau_{it})^2}
\]

\[
\frac{G_p}{\omega} = \frac{q \omega \tau_{it} D_{it}}{1 + (\omega \tau_{it})^2}
\]

\(C_{it} = q D_{it}\) and \(\tau_{it} = C_{it} R_{it}\). A plot of \(\frac{G_p}{\omega}\) vs. frequency yields a maximum when \(\omega = \frac{1}{\tau_{it}}\). The measured conductance is different however. Appropriate circuit conversions have to be made.

\[
\frac{G_p}{\omega} = \frac{\omega G_m C_{ox}^2}{G_m^2 + \omega^2 (C_{ox} - C_m)^2}
\]

The conductance method has proved to yield much more accurate results as far as interface trapped charges are concerned. If we consider a simple capacitor without any trapped charges or interface states, we can define the admittance as:

\[
Y = j \omega C^*
\]

where \(C^*\) is the complex permittivity, and

\[
C^* = C_0 \epsilon^*
\]

and

\[
\epsilon^* = \epsilon' - j \epsilon''
\]
where $\epsilon'$ is the real part and $\epsilon''$ is the imaginary part of the complex permittivity.

A simple lossy capacitor of this nature can be be reduced to an equivalent circuit that is measured in normal capacitance set ups as given in Fig. 4.7 (c). In such cases the conductance is:

$$G = \omega \varepsilon_0 \varepsilon_r \tan(\delta)$$

which means,

$$G = \omega C \tan(\delta)$$

where $\tan(\delta)$ is the loss factor which arises from the fact that the resistance of the capacitor is not infinite. The current losses arise from two factors: (1) the long range migration of charges, e.g. dc Ohmic conduction and (2) the dissipation due to rotation or oscillation of dipoles.

These are of great importance in the study of the ferroelectric as a MFS structure. Detailed analysis of the conductance method can be found in Nicollian and Brews [18].

### 4.3.3 Switching

The two most common ways of studying the switching properties of ferroelectrics is through hysteresis loops and pulse switching.[4, 8, 13, 14]. Ferroelectric hysteresis loops are reminiscent of their magnetic counterparts. Almost all ferroelectrics exhibit hysteresis. Fig 4.8(a) shows a

simple Sawyer-Tower circuit used to study large signal application to a ferroelectric. The linear capacitor placed in series with the ferroelectric integrates the charge that flows into it and this is proportional to the voltage developed across the linear dielectric. The value of the reference capacitor is chosen large enough such that most of the voltage drop is across the ferroelectric. The charge flow across the ferroelectric
is simply CV where V is the voltage across the ferroelectric and C is the capacitance of the linear dielectric.

\[ P = q/A \]  \hspace{2cm} (4.20)

\[ E = V/d \]  \hspace{2cm} (4.21)

As P and E are independent of extraneous factors like size of test spot plot of P-E is more meaningful than q-V. Typical hysteresis loops are shown in Fig. 4.9.

The parameters usually measured from a hysteresis loop are: (i) the coercive field, \( E_C \), (ii) the remanent polarization \( P_R \) and (iii) the saturation polarization \( P_S \). The loop parameters vary according to the frequency of the input signal.

Pulse switching is another way of studying ferroelectric behavior. These have been widely used to study the prospect of ferroelectric memories. A square wave pulse is applied to the ferroelectric in the manner shown in Fig. 4.8(b). The X plates of the oscilloscope are connected to the time base. The resistor is chosen small (usually about 10Ω - 10kΩ) such that most of the voltage applied drops across the ferroelectric.

The switching transient is observed only during pulses that cause switching. In Fig. 4.10, the first pulse causes a complete switching of the thin film. The spike is the non-switching transient and is produced for any pulse. The charge displacement \( D \) in a dielectric under an applied field is given by:

\[ D = \varepsilon E + P \]  \hspace{2cm} (4.22)

Where \( E \) and \( P \) are applied electric field and the polarization respectively.

In Fig. 4.10, the first positive pulse has caused switching. When a second positive pulse is applied, all dipoles have been switched and the material behaves effectively a linear dielectric for a pulse of the same polarity. When a reverse pulse is applied, switching occurs again when dipoles reverse their orientation. The double pulse method has many advantages. It is non-destructive, easy to measure and
simulates the conditions that exist during memory read/write cycles. It should be ensured that the duration of pulse far exceeds the switching time of the ferroelectric. Otherwise, switching might only be partial, unstable or non-existent [4, 8]. The amount of switched charge can be calculated from the area under the switching transient curve for a given pulse. For better accuracy, the area under a spike (which is due to the linear dielectric part) should be subtracted from the total charge switched. But in ferroelectrics of relatively low permittivity like lithium niobate, the error caused due to this is very small. But that is not so in the case of PZT or PLZT, which have a much higher dielectric constant and a lower remnant polarization.
Figure 4.4: ac charge fluctuations in a p-type MIS capacitor
Figure 4.5: (a) Flat band voltage shifts due to no charge [curve (a)], injected charge [curve (b)], and mobile charge [curve (c)], (b) C–V curves due to injected charge, (c) C–V curves due to mobile charge.
Figure 4.6: Circuit diagram of a C-V measurement set up
Figure 4.7: Equivalent circuits for capacitance and conductance measurements: (a) a MIS capacitor with interface state time constant, (b) simplified circuit of (a), (c) measured circuit
Figure 4.8: Sawyer–Tower Hysteresis Loop Circuit
Figure 4.9: Polarization Vs. applied characteristics for (a) a polar dielectric (b) a linear dielectric; (c) a ferroelectric; (d) a ferroelectric with poorly contacting electrodes
Figure 4.10: Switching transients
Chapter 5

Results and Discussion

5.1 Physical Characterization

5.1.1 X-Ray Diffraction

The objectives of characterization through x-ray was to study the crystallinity, orientation and stoichiometry of the film.

The x-ray peaks of the LiNbO$_3$ films show a grain orientation along (01.2) for the film grown on sapphire (012) as shown in Fig. 5.1. Vest et al. [28] have reported orientation along (11.0) on sapphire(11.0). On Si(100) there was a preferred growth of (10.4) planes$^1$ direction thereby suppressing the strongest peak of LiNbO$_3$ viz. (01.2). On Si(111), there was no particular orientation that was preferred. The x-ray plots of LiNbO$_3$/Si are shown in Fig. 5.2 and 5.3. The noise present for 2$\theta$ values of 40 to 50$^\circ$ is due to the Si(111) substrate.

In MOD films the processing conditions were similar in nature for all the films presented here, yet the films have shown preferential growth in different directions. It has been found that epitaxy is favored in certain orientational relationships [9]. Some of the favored orientational relationships include related or similar lattice structures, lattice parameter matching (the mismatch of lattice parameters should be less than 10 - 15 %).

$^1$Means that the direction of preferred growth is the direction normal to the plane (10.4). A similar convention has been followed throughout this book. In HCP, the $<10.4>$ and normal to the (10.4) do not coincide
Thus, for the films made via MOD, the substrate seems to have been the single dominating factor in deciding grain orientation. The reason for such an excellent grain orientation on sapphire can be attributed to the similarity of the structure of sapphire and LiNbO$_3$ as seen from Table 5.1.

<table>
<thead>
<tr>
<th>Features</th>
<th>Sapphire</th>
<th>LiNbO$_3$</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>R3c</td>
<td>R3c</td>
<td>cubic $Fd3m$</td>
</tr>
<tr>
<td>a (in Å)</td>
<td>4.758</td>
<td>5.149</td>
<td>5.4301</td>
</tr>
<tr>
<td>c (in Å)</td>
<td>12.991</td>
<td>13.862</td>
<td></td>
</tr>
</tbody>
</table>

Thus we can see that some grain orientation can be achieved if the substrate is properly chosen. In many applications, it might be necessary to grow the thin film on Si or SiO$_2$. In such cases compromises have to be made on orientation. Further research is being conducted at Rice to get induced grain orientation of ferroelectric thin films. Two of them are:

1. Grow a buffer layer of a metal which induces grain orientation in the desired direction. However it must be ensured that the intervening metallic monolayer does not adversely affect the performance of the device. Another way is to grow a buffer layer of LiNbO$_3$ via some other technique like sputtering or MOCVD (which are time consuming but yield high quality films) and then grow the film with MOD. The advantage of the latter method would be that it can be used to grow virtually any thin film which has been grown by these two methods.

2. A high electric field can be applied to the MOD grown film during the annealing stages. The advantage of this method is that it poles the crystals along the switching direction and the final film will have polycrystalline structure but with a strong c-axis orientation. This might produce films with better switching capabilities.
The films made via MOD were invariably polycrystalline and did not have any other crystalline phase apart from LiNbO$_3$. Thus one can be reasonably certain that the stoichiometry of the films was excellent. In MOD, the mixing of the precursors were done on a macroscopic scale with an accuracy of 0.2 % and a true solution was formed even before the deposition process. Either during spinning or annealing, there are no physical factors that favor segregation or localized compositional variations. Hence there was no presence of other phases like Li$_3$NbO$_4$ and LiNb$_2$O$_8$

The sputtered films had characteristics of a larger grain size or a single crystal. Fig. 5.4[23] shows the x-ray scan of a sputtered lithium niobate film. In the powder diffraction [12] of LiNbO$_3$, the (00.6) peak has a relative intensity of about 6%. The films grown by sputtering show virtually no other peak apart from (00.6). This leads us to conclude that there is an excellent grain orientation along the c - axis of LiNbO$_3$. Such a strong orientation was obviously not substrate induced as the orientation was the same for virtually any substrate. The reason could most probably be due to the high electric fields which prevail during the deposition stage of the sputtering. As the temperature of substrate during sputtering deposition is as high as 600 °C, a poling effect is created in the film and at any instant the electric field ‘pulls’ the dipole along the direction of the field. This causes the atoms to align accordingly.

In sputtering, great care had to be taken to ensure proper stoichiometry. Many factors like oxygen partial pressure, temperature, gas flow rate and rf power had to be controlled carefully [23]. Improperly controlled parameters indicated presence of Li$_3$NbO$_4$ and LiNb$_2$O$_8$.

5.1.2 Adhesion

A problem was observed in etching LiNbO$_3$ on silicon. There is reason to believe that an oxide interface layer between silicon and LiNbO$_3$ enables stronger adhesion of the
film. Etching in a solution which also contains hydrofluoric acid removes the oxide layer and this effectively removes the film from the silicon even though the film itself doesn’t get affected. The film on gold caused no such problems. Vest et al.[28] report no problems for etching LiNbO$_3$ on sapphire. Future directions include the study of the necessity of an intermediate oxide layer to grow a film of LiNbO$_3$ on Si.

### 5.2 Electrical Characterization

#### 5.2.1 I-V Measurements

The I-V measurements were intended to measure photocurrents and the resistivity of the films. The films made through both the processes had good resistivity. Most films made had films of resistivity of the order of $10^{12}$ to $10^{13}$ Ω-cm. Photocurrent were measured when green laser light was shined on the film during I–V measurements. Fig. 5.5 shows a typical plot. The plot of I Vs. V shows a linear region between 0 to 0.4 V. Beyond 0.4 V, the curve assumed a parabolic nature. This could be due to space charge effects as discussed by Sze [26]. The I-V curve was symmetrical about the y-axis. The regression coefficient for a parabolic fit was about 0.99 for both the positive and the negative voltages. For a voltage of magnitude less than 0.4 V, the curve is linear and conduction mechanism is believed to be ohmic [26]. A study is underway to study the thickness dependence of the conductivity which goes as $1/d^3$ at a constant voltage.

In Fig. 5.5, photocurrents were observed on illuminating the film with green laser. A photocurrent of 10 pA was observed on a film of about 1500 Å thick\(^2\). This generates an equivalent electric field of 5 kV across the film. For sputtered films, a

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\(^2\)the spotsize number indicates the area of a spot. Nos. 1 – 5 have an area of .0081 cm\(^2\), #6 – # 10 have an area of 0.0046 cm\(^2\) and #11 – #15 have an area of 0.002 cm\(^2\)
photocurrent of 4 pA has been reported on a 3300 Å[23]. In iron doped LiNbO$_3$, Glass et al. [14] report fields up to 100 kV on a single crystal. The observed effect in our case could be due to microscopic inhomogeneity at the absorbing center as discussed by Glass et al. [14]. The C-V measurements indicate the possibility of mobile Li$^+$ ions which might be causing this effect.

5.2.2 C-V Measurements

The C-V measurements made in the accumulation region were used to calculate the dielectric constant of the ferroelectric. The dielectric constant measured for the films made by both the processes agreed well with established bulk values. The sputtering process yielded films with a dielectric constant of 34.5 whereas the one from MOD yielded films of dielectric constant from 23 to 32.5. The variation in the observed dielectric constant can be attributed to the grain size variation due to different annealing conditions. The C-V curves for LiNbO$_3$ is shown in Figs. 5.6 and 5.7.

A plot of the C-V curve of PZT/Si shown in Fig. 5.9 looks similar to a MOSFET in its profile but the dielectric constant that was measured from it was much too low for PZT. This apparent reduction in dielectric constant could be due to a thin layer of (perhaps non-stoichiometric) oxide of silicon between the PZT and Si. Such a configuration can bring down the effective capacitance measured between the metallic contact and the silicon wafer.

An interesting hysteresis was observed in C-V plots (Fig. 5.6 & 5.7). There's a perceptible shift of the C-V curve towards the left during the reverse sweep of the voltage.

Polarization charge is the charge buildup on the Si/ferroelectric interface because of oriented dipoles in the ferroelectric. If the polarization charge is a major component of surface charge, then the C-V curve will be strongly affected by the orientation of
polarization. For polarization directed into the film, the polarization charge, $Q_p$, is negative. Hence the accumulation region starts at a more negative voltage (for a p-type substrate). The reverse is true for a positive polarization charge. The effect of polarization charge on C–V curve is given in Fig. 5.8.

Fig. 5.8 shows a schematic sketch of an MFS structure under a C-V test. When the voltage goes from negative to positive, the accumulation region dwindles and an inversion layer builds up as shown in Figs. 4.4c & d. But while the voltage becomes more positive, it also serves to move the positive mobile charges to the interface. This leads to positive charge buildup at the ferroelectric/silicon interface and a negative charge at the metal (contact)/ ferroelectric interface. The positive charges at ferroelectric/Si attract (in this case) minority carriers from the bulk of silicon and cause a buildup of negative charges as shown in the Fig. 5.8a.

When the voltage sweep reverses, there's already a fair amount of negative charges that have to be neutralized before accumulation begins. This causes the shift of the C-V curve towards the left for a C-V curve of LiNbO$_3$/Si. There might be aligning of the dipoles of the ferroelectric which can also cause a shift in C–V curve. But in this case the ionic movement might be masking the effect.

Another interesting observation in C-V curves is the deep depletion characteristics. A typical curve is shown in Fig. 5.7. By the time the reverse sweep begins, the minority carriers are regenerated and are able to flood to the interface reducing the depletion zone, thereby increasing the total capacitance. This phenomena is exploited in CCDs.[18, 19, 27]

Unlike those of LiNbO$_3$, there was no effect of switching on the C – V curve. Deep depletion was observed in a somewhat reduced manner on the PZT films. A major problem with PZT was that there was a fine network of cracks criss crossing the entire surface of the film. A C–V and G–V curve of PZT/Si is given in Fig. 5.9. Studies
are being conducted on PZT regarding switching and would be presented in future papers.

5.2.3 Conductance Measurements

In an earlier discussion (Sec. 4.3.2) it was mentioned that the measured circuit and actual circuit are different. To get the right interpretations of the conductance measurements it is essential that a rough idea of the nature of the interface traps and charges. The conductance measurements are a good way of estimating the losses of a dielectric. Again it must be ensured that what is measured is what is actually modeled. Appropriate conversions must be made. In Fig. 5.10, a plot of measured capacitance and measured conductance versus frequency is given for lithium niobate films. Assuming a simplistic model of the ferroelectric being a capacitor in parallel with a resistor, the dielectric loss factors can be calculated. But this yields unusual magnitudes of loss factors (or loss tangents) varying from 0.6 to 0.2 for frequencies varying from 1 KHz to 1 MHz. Another model that it doesn't fit is a that of a pure capacitor with extremely high dc resistance. Further studies are underway to develop better models.

5.2.4 Switching

Pulse switching was tried in both MOD films. Switching was observed in some cases for sputtered films. This was in films with good (006) orientation. The studies are reported in [23]. Switching of about 8 μC/cm² has been observed with sputtered films [23]. In MOD films not much switching was observed through this set up. This could be due to the inherent random orientation of the grains which vastly diminish switching behavior (as discussed in Chap. 3). Another reason could be due to lack of
good contact or surface defects. Study is underway on switching in the ferroelectric films (PZT and LiNbO$_3$).

5.3 Optical Measurements

As mentioned in Chapter 4, reflectivity and ellipsometric measurements were used to measure the thickness of the ferroelectric thin film. Waveguiding was attempted on the MOD films using the prism coupling method discussed by Huang [10]. Fig. 5.11 shows the plot of attenuation in a thin lithium niobate film on sapphire. The attenuation comes to about 2.8 dB/cm. The attenuation on sputtered films has been reported to be as low as 1.1 dB/cm. The attenuation of LiNbO$_3$ on sapphire made from MOD is much larger owing to (1) random orientation of the grains and (2) polycrystallinity of the grains causing scattering at grain boundaries and (3) much thinner films used for studying. All the aforementioned factors increase scattering during transmission of the wave [10]. Studies are underway to investigate waveguiding in multilayered LiNbO$_3$ coating on sapphire.

5.4 Thickness Measurements

The thickness of the thin films were measured three fold. An initial estimate of the thickness was made based on rheology of spinning process [1, 32]. The color code chart was used to narrow down the range of thicknesses to within 300 - 500 Å. Finally, the ellipsometric measurements were used to narrow down the thickness to within 50 to 100 Å. A color code chart is given in Table 4.1.
5.5 Annealing

Vest et al. [28] have used annealing time ranging from 11 hours to 1.5 hours. In MOD the longest time is often taken by annealing. In part of our experiments, the heating rate was increased to rapid thermal annealing rates. The sample was inserted into the furnace at 700 °C and annealed for two minutes. Thereafter it was removed from the furnace and allowed to air cool. The crystallinity was unaffected. There was even a slight improvement in observed (01.2) peak. The x-rays are shown in Fig. 5.3. The film did not show any porosity or cracking when viewed under optical microscope. When similar annealing procedure was conducted for a thin film (lithium niobate) on gold, the film cracked. This may be attributed to much higher thermal expansivity of gold. Further studies are being conducted as to the importance of annealing time as far as optical and electrical properties are concerned.

The TGA curve is often a good guideline to follow to control the heating and cooling rate. The behaviour of the substrate under the heating cycle is an important factor to be considered too. Figs. 3.1,3.2,3.3,3.4,3.5 show the TGA curves of the various precursor solutions used in this work.

5.6 Multicomponent Systems

One of the advantages of the MOD process is the ease with which multicomponent systems can be fabricated without having to make too many changes in the infrastructure. PZT films were grown on silicon using MOD. Studies are underway to characterize them. Initial results show that MOD has promise as an easy way of making PZT films. An XRD plot of PZT/Si is shown in Fig. 5.1b. A C–V curve is shown in Fig. 5.9
Figure 5.1: XRD plots: (a) LiNbO₃/Sapphire(012), (b) PZT/Si(111) grown via MOD process
Figure 5.2: XRD plots: (a) LiNbO$_3$/Si(111), (b) LiNbO$_3$/Si(100) grown via MOD process
Figure 5.3: XRD plots: (a) LiNbO₃/Si(111) annealed, (b) LiNbO₃/Si(111) with shorter annealing time; grown via MOD process.
Figure 5.4: XRD plot of sputtered LiNbO$_3$/Si(111)
Figure 5.5: I-V plot of LiNbO₃/Si
Figure 5.6: C–V curve of a 2800 Å LiNbO$_3$/Si film
Figure 5.7: C – V curve of a 1500 Å LiNbO₃/Si film
Figure 5.8: Effect of polarization charge on high frequency C–V curves
Figure 5.9: C–V curve of a 1500 Å PZT/Si film
Figure 5.10: Frequency dependence of capacitance and conductance on a 1500 Å thick LiNbO₃ film
Figure 5.11: Attenuation of a wave guide in LiNbO$_3$ film made via MOD
Chapter 6

Conclusions

The objective of the research was to grow films of LiNbO$_3$ and PZT through the process of MOD, study their material, electrical and optical properties and compare specific properties with the films obtained through sputtering. Many of the specific information regarding the sputtering process and properties has been obtained from Rost [23]. So far it has been concluded that both have their merits. Sputtering has yielded excellent films with grain orientation along the c-axis regardless of the substrate orientation. This could be due to the enormous electric fields that are present due to deposition that may force the film to grow along the c-axis. In MOD no such field exists and the substrate orientation plays a major part in determining the orientation.

The stoichiometry of the films made with MOD has been very good. This is because the mixing of the precursor solutions on a macroscopic level yields a true solution. No segregation or polymerization occurs with the formulation solution even after prolonged storage. In the case of sputtering, factors like oxygen flow rate, amount of Li$_2$O to compensate for lithium loss, temperature and rf power must be controlled very carefully in order to achieve the necessary stoichiometry [22, 23]. The dielectric constant, resistivity and switching behavior has been good for sputtered films. With MOD films satisfactory switching behaviour could not be observed. This could be due to the fact that the grains in MOD films are randomly oriented.
MOD films were uniform, crystalline and had good electrical properties comparable to that of sputtered films. The finer grain size in MOD could account for lower dielectric constant observed in some cases.

The I-V curve Fig. 5.5 became quadratic at higher fields. This could be due to space charge effect discussed by Sze [26]. Further investigations are being conducted to study dependence of conduction on thickness. The I-V curve was linear for smaller electric fields. The resistivity yielded was satisfactory - about $10^{12}$ to $10^{13}$ $\Omega$-cm. Photocurrents were measured when green laser light was incident on the metal contacts. This could probably be due to localized inhomogeneity. The sputtering process reportedly [23] has yielded films with resistivity of $5 \times 10^{12}$ $\Omega$-cm.

C-V curves were used to study the thin film in an MFS (Metal-Ferroelectric-Semiconductor) configuration. The dielectric constant in the case of MOD was comparable to what was obtained by other researchers [28] and varied from 28 to 32.5. The sputtered films yielded films with a dielectric constant of 34.5. The variation in observed dielectric constant of MOD grown films could be due to grain size effects.

A hysteresis behaviour was noticed in some of the C-V curves. This could be due to the mobility of Li$^+$ ions. This could not be due to charge injection as discussed by Wu [30], in which case the curve would have been swept in the reverse direction.

Conductance measurements were used to study the existence of traps or charges in the interface. Such measurements could also be used to estimate losses in the dielectric if a suitable model was found. A satisfactory model wasn't found to explain the conductance curves. Further studies are underway in this area.

It was found that even by reducing the annealing time to a fraction of what has been done by other researchers, good quality MOD films can be made. It was found that an annealing time of 2 minutes was sufficient for LiNbO$_3$ on silicon. LiNbO$_3$ on
gold/Si cannot be processed with short times as the expansivity of gold and LiNbO$_3$ vary considerably and such an attempt would result in cracked films.

Optical quality of MOD films was found to be comparable to that of sputtered LiNbO$_3$. The attenuation of a guided laser wave in MOD made LiNbO$_3$ was about 2.8 dB/cm, whereas sputtered LiNbO$_3$ had an attenuation as low as 1.1 dB/cm. The difference could be attributed to the fact that the MOD films tested were much thinner than those of sputtered films and that the MOD films were polycrystalline.

The advantages of MOD are many. The most significant being the reduced time taken, the inexpensive equipment used, and the ease of handling. The essential differences in the two processes have been tabulated in Table 6.1.

The sputtered films manufactured at Rice have immediate applications in capacitors, memory cells, electro-optic devices, actuators, surface acoustic waves, pyrodetectors and IR detectors. There are many more future applications in related disciplines. The LiNbO$_3$ made through MOD cannot be used in all of the above applications. The optical and switching properties have to be of superior quality before such applications could be made. At present MOD made films can be used safely in high density capacitors, actuators and pyrodetectors where the performance requirements are not as stringent [22]. Effort is being made to make MOD films of better optical and electrical quality. The properties obtained through the two different processes are tabulated in Table 6.2. The properties and process information of sputtered films are taken from Rost [23].
Table 6.1: Sputtering Vs. MOD

<table>
<thead>
<tr>
<th>Sputtering</th>
<th>MOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent grain orientation along c-axis</td>
<td>Randomly oriented grains</td>
</tr>
<tr>
<td>Single crystals can be produced</td>
<td>Invariably polycrystalline</td>
</tr>
<tr>
<td>Difficult to control stoichiometry esp.</td>
<td>Easy to control stoichiometry</td>
</tr>
<tr>
<td>in multicomponent systems</td>
<td></td>
</tr>
<tr>
<td>Processing time is long</td>
<td>Extremely short processing time</td>
</tr>
<tr>
<td>Extreme care is required</td>
<td>Simple processing and amenable to mass</td>
</tr>
<tr>
<td>in process control</td>
<td>production</td>
</tr>
<tr>
<td>Low temperature processing,</td>
<td>High temperature annealing</td>
</tr>
<tr>
<td>Vacuum to be maintained</td>
<td>No vacuum or special atmosphere</td>
</tr>
<tr>
<td>Excellent optical quality</td>
<td>Films too thin and hence excessive</td>
</tr>
<tr>
<td>scattering</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2: Properties of films made by sputtering and MOD

<table>
<thead>
<tr>
<th>Properties</th>
<th>Sputtering</th>
<th>MOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>1000 – 6000 Å</td>
<td>800 – 3000 Å</td>
</tr>
<tr>
<td>Resistivity</td>
<td>5 x 10&lt;sup&gt;12&lt;/sup&gt;</td>
<td>10&lt;sup&gt;10&lt;/sup&gt; to 10&lt;sup&gt;13&lt;/sup&gt;</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>34.5</td>
<td>28 to 34</td>
</tr>
<tr>
<td>Attenuation of wave guide</td>
<td>1.1 dB/cm</td>
<td>2.8 dB/cm</td>
</tr>
<tr>
<td>Grain Orientation</td>
<td>(00.6)</td>
<td>random on Si(111) (10.4) on Si(100) and (01.2) on sapphire(01.2)</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>single crystals and large grained polycrystals</td>
<td>polycrystalline</td>
</tr>
<tr>
<td>Switching</td>
<td>8 μC/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>not observed</td>
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Bibliography


