

AN ABSTRACT OF THE THESIS OF

Dylan R. Kearney for the degree of Honors Baccalaureate of Science in Mechanical Engineering presented on March 12, 2013. Title: Optimization of Pulsed Laser Deposited Piezoelectric Thin Films for Microelectromechanical Systems.

Abstract approved:

Brady J. Gibbons

Lead zirconate titanate (PZT) is well known to exhibit some of the strongest piezoelectric responses, explaining why it is at the heart of piezoelectric-based microelectromechanical systems (MEMS) research. The use of pulsed laser deposition (PLD) to synthesize PZT offers many advantages over alternative deposition techniques, mainly regarding its ability to maintain target to film stoichiometry, as well as *in-situ* crystallization of the deposited film. $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ was deposited onto platinized silicon substrates via PLD. PZT on platinized silicon was selected as a baseline for the thin film deposition optimization process due to the vast amount of work done in the research community regarding this system. As such, there is abundant data available for trend comparison. θ - 2θ x-ray diffraction scans verified the crystal structure of the films as phase-pure (001) PZT when deposited using a 30 mol% excess lead target, while film thicknesses were measured using variable angle spectroscopic ellipsometry (VASE). Electrical characterization revealed high-quality ferroelectric films, remanent polarization $\sim 30 \mu\text{C}/\text{cm}^2$, dielectric loss $\sim 1\%$, and dielectric constants up to 1370. Once the baseline for PZT deposition using PLD had been established, the potential to apply the same principles and methodologies to a more novel system was explored. Ion beam-assisted deposition (IBAD)-MgO offers a low-cost, flexible substrate that has a similar crystal

lattice to that of PZT, thus it can be used for epitaxial growth. However, the IBAD substrate requires the deposition of a conductive bottom electrode, the lattice structure of which must also match the underlying MgO and overlying PZT. LaNiO_3 (LNO) is often used as a bottom electrode in such systems, as it fulfills the aforementioned requirements. PZT/LNO/IBAD-MgO films were deposited, with in-plane orientation being measured via x-ray diffraction ϕ scans. Future work will focus on optimizing the epitaxial nature, as well as improving the ferroelectric responses of these films on IBAD substrates.

Key words: Pulsed laser deposition, piezoelectric, microelectromechanical systems, lead zirconate titanate, optimization

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Optimization of Pulsed Laser Deposited Piezoelectric Thin Films for
Microelectromechanical Systems
by

Dylan R. Kearney

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Dylan R. Kearney, Author

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1. Introduction

PZT is of particular interest due to its widespread use in piezoelectric-based microelectromechanical systems (MEMS) [1]. Piezoelectric materials provide a very useful alternative to electrostatic-based and other types of MEMS. It is well known that piezoelectric MEMS possess several advantages over their electrostatic counterparts, including: [2]

1. The coupling between electrical and mechanical properties means that piezoelectric MEMS are of interest for energy harvesting
2. Piezoelectric actuators have much higher energy densities than electrostatic actuators
3. Piezoelectricity scales well as an actuator technology

MEMS devices are attractive options as sensors, actuators, and resonators. Furthermore, they can offer levels of performance that can exceed their macroscale counterparts, while maintaining manufacturability to keep costs relatively low. For example, a MEMS pressure transducer will typically outperform a pressure sensor made using the most precise and advanced macroscale machining techniques available [3]. As MEMS technology becomes more pervasive in our everyday lives, whether it be in printers, cell phones, or a variety of other applications, the need to improve the materials and methods of manufacturing MEMS is at an all-time high.

This thesis will describe the fundamental concepts of piezoelectricity, the methodologies used to create and characterize thin films, and discuss the results of the piezoelectric thin film deposition process optimization.

1.1 Piezoelectricity

Piezoelectricity is a phenomenon exhibited by non-centrosymmetric crystalline materials, and is defined by the ability to generate an electric potential in response to applied mechanical stress or strain. This is known as the direct piezoelectric effect, expressed in the following equations [2]:

$$P_i = d_{ijk} \sigma_{jk} \quad (1.1)$$

Where:

P_i = polarization

σ_{jk} = stress

d_{ijk} = piezoelectric charge coefficient

Furthermore, piezoelectricity is reversible, meaning that the converse of the direct piezoelectric effect is also true. That is, by applying an electric field to a piezoelectric material a stress or strain is produced.

$$x_{ij} = d_{ijk} E_k \quad (1.2)$$

Where:

x_{ij} = strain

E_k = applied electric field

d_{ijk} = piezoelectric charge coefficient

The physical manifestation of these equations can be seen below in Fig. 1. Where Fig. 1 (a) shows an unstressed component, (b) shows a compressed component, and (c) shows a component in tension. An interesting observation of Fig. 1 (b) and (c) is that the polarity of the charge depends on the direction of the force.

The converse effect is also illustrated in Fig. 2: (a) has no electric field applied, and (b) and (c) show the component with electric fields of flipped polarities.

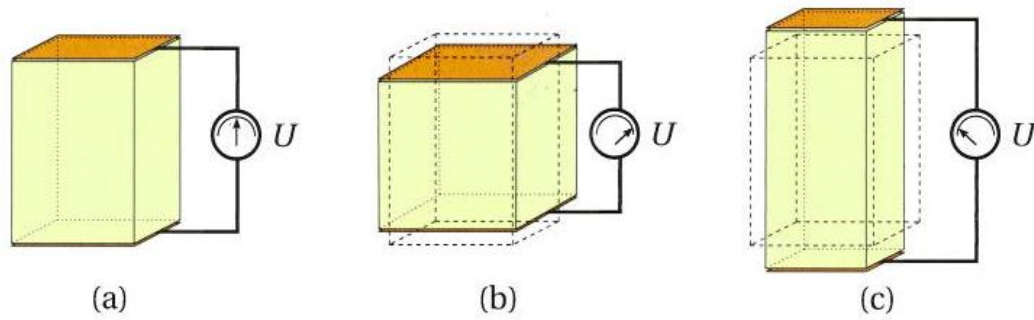


Figure 1: Direct piezoelectric effect [4]

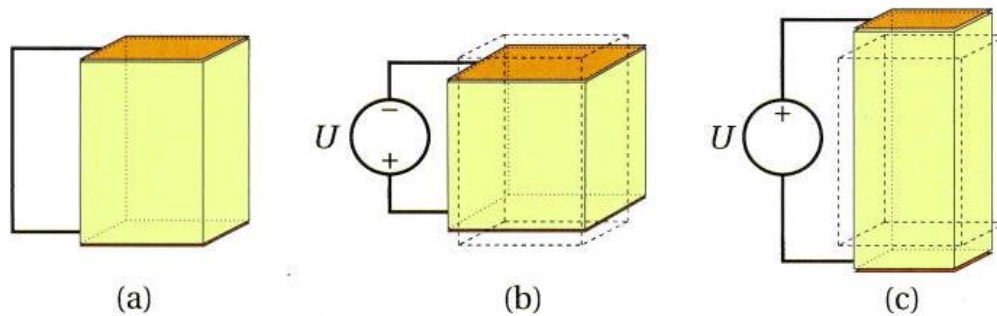


Figure 2: Converse piezoelectric effect [4]

1.2 Ferroelectricity and pyroelectricity

Two important subclasses of piezoelectrics are ferroelectrics and pyroelectrics. Ferroelectrics belong to the pyroelectric class of materials, which in turn belong to the piezoelectric class of materials. Ferroelectrics exhibit a spontaneous polarization below a critical temperature (Curie temperature), and this polarization can be reoriented with an applied electric field. Pyroelectrics have the ability to create an electric charge as a result of temperature change. All pyroelectrics are piezoelectric, but the converse is not true. Additionally, all ferroelectrics exhibit piezoelectricity and pyroelectricity, but once again the converse is not always true. Aluminum nitride (AlN) is an example of a piezoelectric material that does not exhibit ferroelectric behavior due to its Wurtzite crystal structure. The dipole formed in the Wurtzite structure cannot be reoriented with an applied electric field, meaning it does not display ferroelectric characteristics.

1.3 Perovskite structure

As previously mentioned, only non-centrosymmetric crystalline materials exhibit the piezoelectric effect. The significance of the absence of a center of symmetry is found in the ability of the bulk material to exhibit an electric charge at the end-faces. As seen in α -quartz below (Fig. 3), the mechanical deformation causes the atoms to shift in such a way that an electric dipole is present. This effect is carried out throughout the material, resulting in a measureable electric charge at opposing faces.

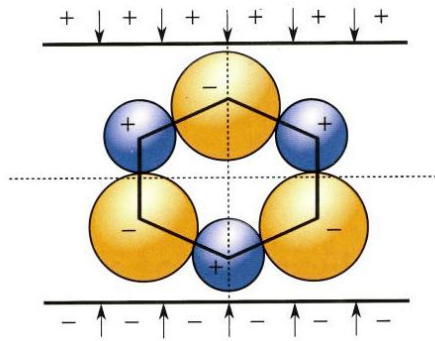


Figure 3: Example of direct piezoelectric effect in α -quartz [4]

One such non-centrosymmetric crystal structure is the perovskite structure; shown in Fig.4b. It is an ABO_3 structure, with the prototype being $CaTiO_3$. What makes this structure particularly relevant is that lead zirconate titanate ($Pb(Zr_x, Ti_{1-x})O_3$, PZT) has the perovskite structure. More specifically, PZT has tetragonal symmetry if Ti-rich and rhombohedral if Zr-rich, see Fig. 4b for details. In the PZT system, the A-ions are represented by $Pb(2^+)$, the B -ions are represented by $Ti/Zr(4^+)$, and the $O(2^-)$ can be found at the face centers. An electric dipole is created when equal and opposite charges are separated by some distance. In PZT this electric dipole occurs at temperatures below the Curie point, when the transition from symmetric cubic to non-centrosymmetric

tetragonal/rhombohedral occurs, Fig. 4. The dipole itself is caused by the movement of the Ti or Zr atom within the unit cell (see Fig. 4b). As the positively charged Ti/Zr atom moves to one end of the perovskite structure, it leaves behind a negatively charged region, resulting in a net polarization across the unit cell.

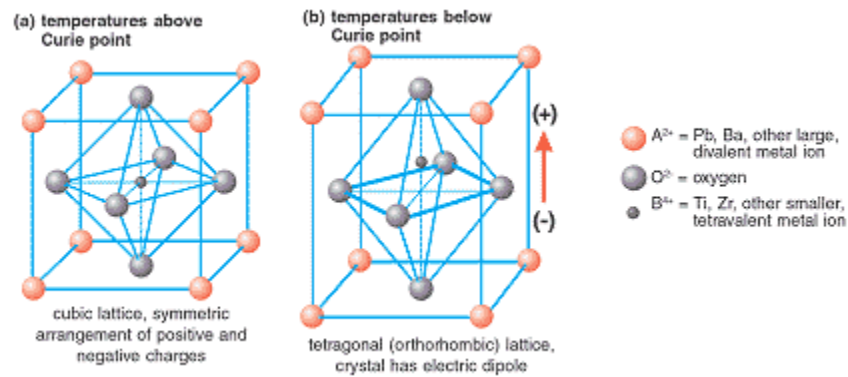


Figure 4: (a) symmetric cubic structure at temperatures above the Curie point, no electric dipole across unit cell; (b) non-centrosymmetric tetragonal structure at temperatures below the Curie point, resultant electric dipole caused by movement of Ti/Zr atom [5]

1.4 PZT thin films

The general formula for PZT is $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, however for this thesis all PZT films were processed using a $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ target with 30% excess lead.

PZT is a solid solution of PbTiO_3 and PbZrO_3 , with the resulting material properties depending on the specific composition and temperature. A morphotropic phase boundary (MPB) exists at approximately $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$, dividing the tetragonal Ti-rich region from the Zr-rich rhombohedral region. At compositions near the MPB, lead zirconate titanate exhibits its' highest piezoelectric, ferroelectric, and dielectric properties due to the multitude of directions the electric dipole can orient in the unit cell; see Fig. 5 [1].

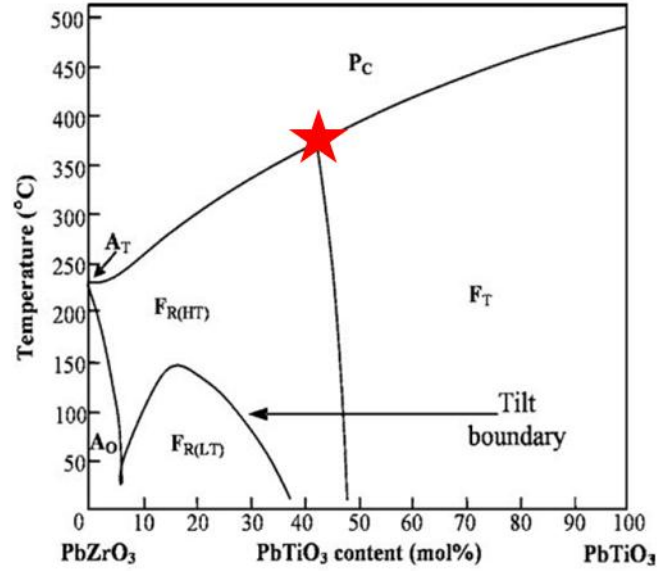


Figure 5: Morphotropic phase boundary for PZT, the star represents the composition of highest PZT properties [6]

PZT thin films have been widely researched, finding applications ranging from MEMS devices, energy harvesters, thin-film vibrators for micromotors, thin film capacitors, and a myriad others. Moreover, due to the widespread use of PZT, it has been synthesized using a multitude of methods, including chemical solution deposition, RF-magnetron sputtering, and pulsed laser deposition. While deposition parameters change depending on deposition method, PZT orientation is well known to drastically affect the observed properties. For example, remanent polarizations of $\sim 22 \mu\text{C}/\text{cm}^2$ have been observed for PZT deposited on Pt coated amorphous glass substrates [7], while values of $\sim 40 \mu\text{C}/\text{cm}^2$ have been measured for highly (001) oriented epitaxial PZT on IBAD substrates [8].

Lead is known to be a volatile element, meaning it has a high vapor pressure at normal temperatures. As such, Pb exhibits the tendency to vaporize from a surface if there is not sufficient ambient pressure. Furthermore, vapor pressure is known to increase

non-linearly with increasing temperatures according to the Clausius-Clapeyron relation [9].

$$\ln \frac{P_1}{P_2} = \frac{H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1.3)$$

Where:

P_1 = Vapor pressure at state 1

P_2 = Vapor pressure at state 2

T_1 = Temperature at state 1

T_2 = Temperature at state 2

H_{vap} = Enthalpy of vaporization

R = Gas constant

Deposition temperatures for films synthesized in this thesis ranged from 600°C to 700°C, while pressures were at low-vacuum conditions (~300 mTorr), so it is expected that Pb will evaporate from the surface of the substrate. To account for this, excess Pb was incorporated into the deposition target, mitigating the impact of Pb evaporation by providing an excess of Pb at the depositing film surface.

1.5 Thin film growth and epitaxy

In the scope of thin film growth it is generally accepted that there are three primary growth modes; shown in Fig. 6. The first mode is known as island, or Volmer-Weber, and is represented by the direct nucleation of small clusters on the substrate surface. These clusters then grow into islands as a condensed phase. Island growth occurs when the deposited atoms bind to each other more strongly than to the substrate [10].

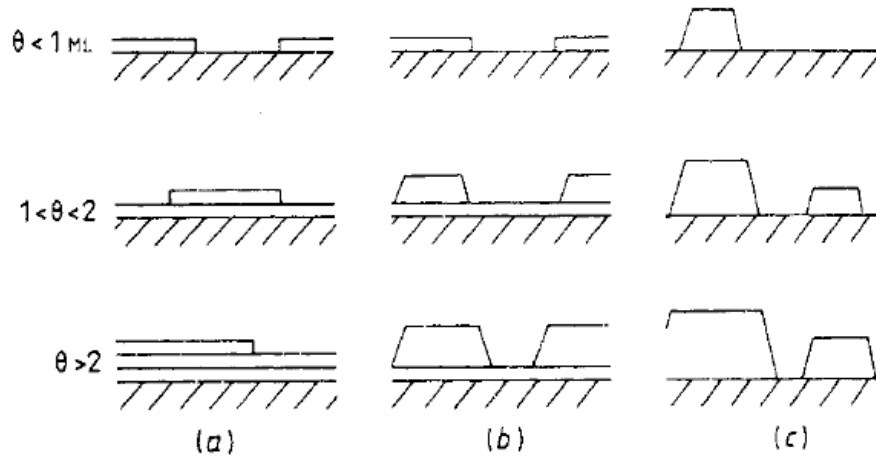


Figure 6: (a) Frank-van der Merwe growth, (b) Stranski-Krastanov growth, (c) Volmer-Weber growth [10]

The second mode, the layer-by-layer or Frank-van der Merwe mode, exhibits characteristics opposite to the island mode. In this case the atoms are more strongly bound to the substrate than to each other, causing the first atoms to reach the substrate to condense as a complete monolayer on the surface. This process continues, with the atoms forming layer after layer on top of each other. The third mode is an intermediate mode of the previous growth modes. The layer plus island, or Stranski-Krastanov, mode begins with the atoms forming a monolayer on the substrate. However, after this first (or sometimes several) monolayer further layer growth is unfavorable, giving rise to island growth on top of this ‘intermediate’ layer.

Epitaxy occurs when a film orients itself on the crystallographic scale to match a substrate, as seen in Fig. 7b. It is well known that crystallographically oriented ferroelectric films show improved electric properties, such as remanent polarization, over those with random crystallographic orientation. Furthermore, the tetragonal structure of PZT is such that (001) oriented films exhibit the best ferroelectric properties [11].

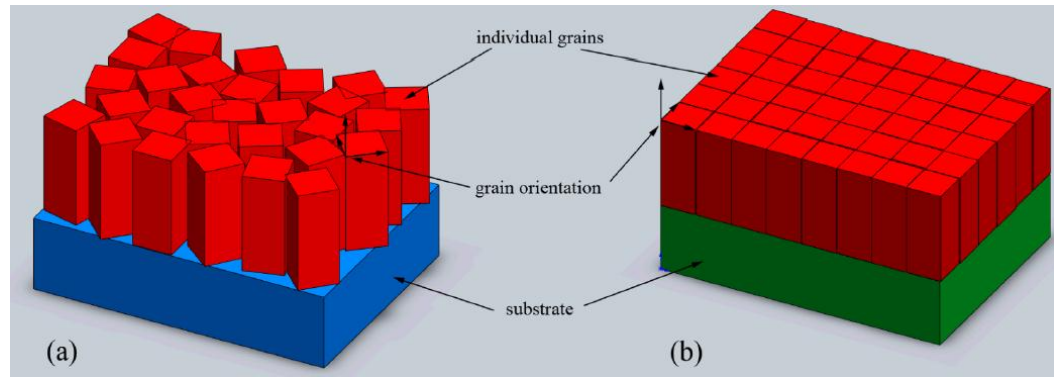


Figure 7: (a) Out-of-plane alignment, but in-plane random orientation, (b) both in-plane and out-of-plane alignment [1]

In order to obtain well-defined epitaxy there are a number of important variables to control: (1) substrate temperature; (2) deposition rate; (3) substrate preparation; and (4) deposit thickness [12]. It has been experimentally established that there is a critical substrate temperature, often referred to as the ‘epitaxial temperature’, above which epitaxy is well achieved and below which epitaxy is imperfect. While experimental evidence shows that a slower deposition rate usually leads to epitaxy, there is little systematic evidence. Conversely, higher deposition rates can mean higher substrate temperatures that would enhance epitaxy. Additionally, lower deposition rates lead to a higher contaminant-deposit ratio which could inhibit epitaxial growth. Surface preparation is important in that the topography of the substrate has a direct influence on the orientation of a deposit [12]. Furthermore, substrate preparation needs to be completed in such a way that the surfaces are not contaminated by chemical reagents. Orientation of a thin film can change appreciably with increasing thickness. It is not surprising that good film orientation can be maintained up to a certain thickness, but beyond that the film begins to exhibit more random orientation.

1.6 Film Characterization

While PLD was the sole method for film processing and growth, several methods were used for characterization. The importance of accurate and reliable thin film characterization cannot be understated, as it is by these means that the overall quality of the film is obtained. Moreover, the feasibility of the film's use outside of the laboratory setting is verified through the characterization process.

The critical electrical properties measured in the films were the remanent polarization, coercive field, dielectric constant, and dielectric loss. The remanent polarization (P_r) is the remaining spontaneous charge the film displays after an electric field has been applied (i.e. the measure of charge ($\mu\text{C}/\text{cm}^2$) seen with no applied electric field). Fig. 8 shows the how remanent polarization comes to exist within a ferroelectric material. The coercive field (E_c) is the applied field required to drive the polarization of the film to zero.

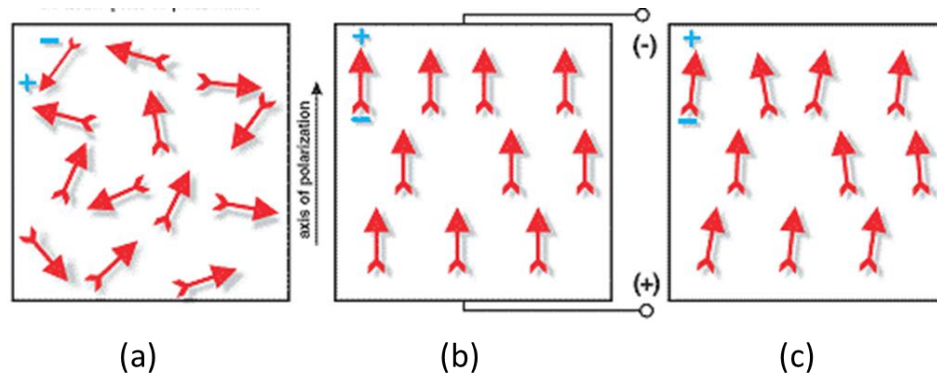


Figure 8: (a) random orientation of domains with no net polarization; (b) applied electric field aligning the domains; (c) remanent polarization of domains after electric field is removed [5]

Remanent polarization and coercive field are most easily visualized on a hysteresis loop; shown in Fig. 9. The loop is well-saturated, as shown by the near-zero slope at the maximum or minimum polarization values. This saturation means that all

available domains have switched, resulting in the maximum polarization the film can achieve. Any subsequent increase in polarization is from the intrinsic movement of the Ti/Zr atom within the unit cell. The area within a hysteresis loop is indicative of the dielectric losses in the film, therefore a thin, well-saturated loop is desirable [13].

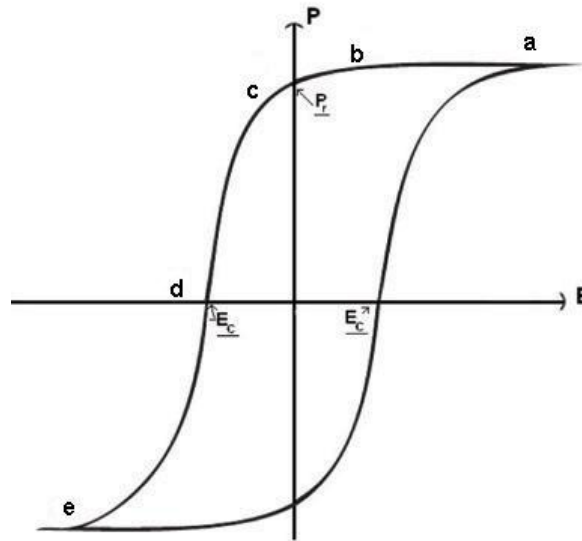


Figure 9: Example hysteresis loop with remanent polarization (P_r) and coercive field (E_c) labeled [14]

The dielectric constant (relative permittivity) is a measure of a material's ability to store charge and will be defined quantitatively later in this review (Eqn. 2.3). In ferroelectrics, very high dielectric constants are observed, reaching a peak at the Curie temperature [13]. Additionally, in dielectric materials there is a key property called the dielectric loss. The dielectric loss is denoted $\tan\delta$, and is a measure of dissipated energy within the dielectric when subjected to an AC electric field [13]. As the loss is indicative of unwanted energy dissipation within the film, it is desirable for thin films to have low $\tan\delta$ values (concomitant with slim hysteresis loops).

Thesis statement

The goal of this thesis is to optimize the synthesis parameters for Pulsed Laser Deposited (PLD) perovskite phase $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films for use in MEMS devices.

2. Materials and Methodology

2.1 Pulsed Laser Deposition

The synthesis of all thin films described in this thesis utilized pulsed laser deposition (PLD). PLD has increasingly been adopted as a method for thin film growth. Although studies concerning ablation plume dynamics were conducted as early as the 1960s, it wasn't until about the late 1970s, when laser pulses in the nanosecond regime (ns) became available, that the first films were deposited via PLD [15]. PLD is a method that has garnered significant interest in the scientific community due to its various advantages over other deposition techniques. Moreover, PLD is a preferred method for solid solutions of binary oxide systems, a relevant example of which being the lead zirconate titanate system [16]. The main advantages are as follows [15]: (a) complex stoichiometric thin films can be produced from bulk targets of similar stoichiometry; (b) PLD decouples process parameters (i.e. background pressure, background gas, type of substrate) from the ablation process, providing a greater degree of flexibility in terms of material use and geometric arrangements; (c) atoms and ions in the plume have excess energy, increasing the sticking and nucleation rate, as well as surface mobility; (d) due to the “pulsed” nature of PLD, the number of particles arriving at the substrate can be

precisely controlled, also allowing for highly perfect surface control in heterostructure systems.

Considering the aforementioned advantages, it is no surprise that PLD is regarded as one of the most promising methods for thin film growth [6]. What's more, the PLD process is surprisingly simple, consisting of five stages:

- (1) Light absorption in the solid
- (2) One-dimensional plume expansion of the ablated material during laser irradiation
- (3) "Free" three-dimensional expansion into vacuum or a dilute background gas
- (4) Slowing down and stopping of the plume in a background gas
- (5) Collection of ablated atoms on a substrate and subsequent film growth

A 20 ns long laser pulse is initially absorbed by the surface of the target (1) before an explosive evaporation of ions, electrons, and neutral atoms occurs. The ablation plume, initially one-dimensional (2) in the direction of the stage, changes to a three-dimensional plume, albeit still strongly directed in the forward direction of the substrate (3). The plume initially has high enough pressure to allow for "free" expansion, but in the presence of a background gas (4) this expansion is slowed. The plume stops within tens of microseconds, allowing atoms to transport across the chamber and collect on the substrate, growing the film (5) [15]. With all that in mind, it should be noted that PLD does have some drawbacks [16]:

- (1) Production of macroscopic particles ('boulders') during the ablation process
- (2) Target impurities

(3) Defects in film crystal structure caused by high kinetic energy ablation particles

(4) Angular energy distributions and inhomogeneous flux within the plume

In most cases these drawbacks can be overcome or avoided, leaving the advantages of PLD to outweigh the disadvantages. A schematic of a general PLD system is displayed in Fig. 10.

A Lambda Physik KrF excimer laser ($\lambda=248$ nm) with a pulse width of 20 ns was used for all PLD experiments. For each experiment the main parameters that could be adjusted were the laser energy (mJ), laser frequency (Hz), deposition time (minutes), target to substrate distance (cm), substrate temperature ($^{\circ}\text{C}$), chamber pressure (mTorr), and target composition (% excess Pb).

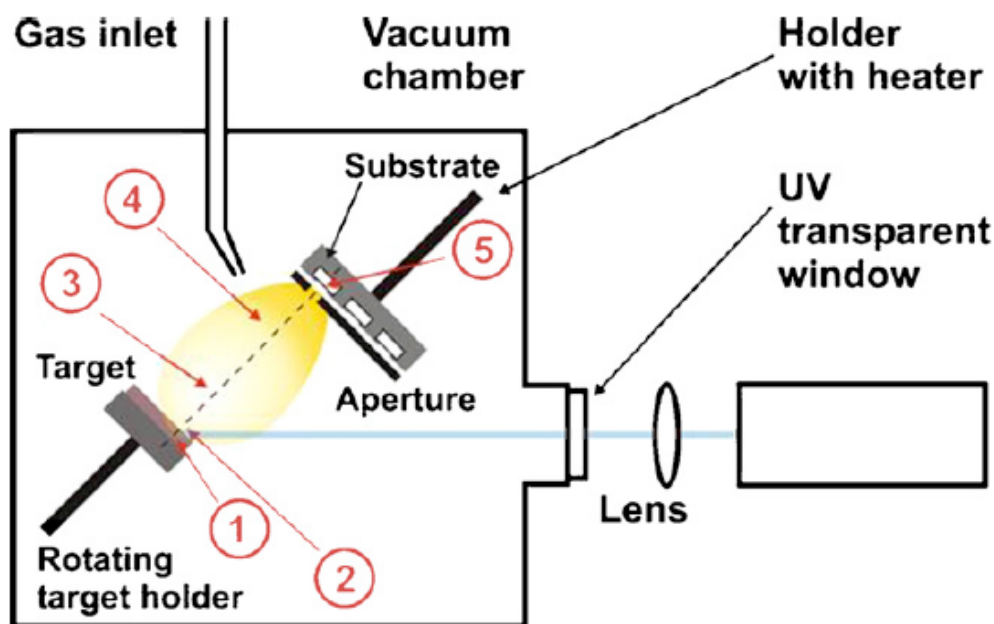


Figure 10: Schematic view of PLD system [15]

The majority of films synthesized here via PLD consisted of PZT on platinized silicon substrates (Si/SiO₂ substrates with a Ti adhesion layer and thin top layer of Pt for use as a bottom electrode in the final film).

Lanthanum nickelate (LNO) films were also deposited using PLD. LNO films were deposited onto flexible ion-beam-assisted-deposition (IBAD) magnesium oxide (MgO) substrates. The intent is to eventually deposit PZT onto these flexible substrates, using LNO as the bottom electrode.

All PLD processed films discussed in this thesis were deposited using the same basic procedure:

- Substrates cleaned in small beaker of isopropyl alcohol (IPA) via ultrasonic cleaning (≈ 5 minutes)
- Cleaned substrates placed on edge of substrate heater
- Shake silver paint (*Ted Pella* Leitsilber 200 Silver Paint) bottle
- Paint a thin-layered area (slightly larger than substrate size) in middle of substrate heater
- Using tweezers, place substrate in middle of painted area, pressing lightly on edges of substrate with tweezers to ensure no air is trapped beneath
- Set the PLD temperature controller to 100°C, turn heater power supply on
- Observe substrate, press down on corners with forceps if any remaining air bubbles cause substrate to lift from the heater surface
- Let silver paint cure for 5 minutes
- Test adhesion of substrate to heater by pressing lightly on one corner of substrate with tweezers
- Turn the heater power supply off
- Start the laser by pressing the “**RUN/STOP**” button, followed by the “**EXE**” button
- Insert target holder into chamber, slide onto target rotation shaft
- Secure the target in the chamber by tightening the set screw on the target holder
- Check location of laser-target incidence using laser alignment paper
- Ensure that the top lid of the PLD chamber is closed
- Check that the gasket on the substrate heater flange is correctly seated in its’ groove
- Insert the heater into the deposition chamber at a slight angle, as to avoid the rotation switch stand
- Secure the heater in place by inserting and tightening the three screws, spaced evenly around the flange
- Put the rotation chain onto the small gear located on the rotation motor, then around the larger gear on the heater
- Insert the sheet metal shim to secure the rotation motor in place
- Close the foreline valve by switching it to the “up” position
- Turn the heater power supply on
- Open the roughing valve and wait until the chamber pressure reaches 40 mTorr

- Close the roughing valve
- Open the gate valve, allows turbo-pump to reduce chamber pressure further
- Wait until the chamber pressure reaches $\approx 7.5 \times 10^{-6}$ Torr on the ion gauge readout
- While the turbomolecular pumps down the chamber, set the laser parameters
 - **MODE:** EGY N
 - **EGY:** Desired laser energy
 - **REPRATE:** Desired laser frequency
- Once the ion gauge reads a pressure of 7.5×10^{-6} Torr or less, turn the ion gauge off
- Close the gate valve
- Close the foreline valve
- Open the oxygen valve
- Open the roughing valve
- Adjust the oxygen flow on the Mass Flow Controller (MFC) so that the Baratron displays the desired deposition pressure, keep within ± 0.002 Torr
- Set the PLD temperature controller to the desired deposition temperature
- Turn on the substrate heater rotation motor
- Turn on the target rotation motor
- Set a timer to the desired deposition time
- Once both deposition temperature and deposition pressure have been reached, don the laser goggles
- Flip open the beam shutter to allow the laser to reflect into the chamber, simultaneously start the timer
- Once the deposition time has elapsed, close the beam shutter
- Turn the laser off by pressing the “**RUN/STOP**” button
- Close the roughing valve
- Close the oxygen valve
- Partially vent the chamber for ≈ 7 seconds using the switch at the top of the chamber, allows the film to cool under near atmospheric pressure of oxygen
- Turn the heater power supply off
- Turn off substrate heater rotation motor
- Turn off target rotation motor
- Open foreline valve
- Set PLD temperature controller to 0°C
- Wait until substrate heater temperature cools to 200°C , vent the chamber to atmosphere using switch at top of chamber (until the top lid can be opened)
- Remove rotation chain and screws securing the heater in place
- Locate heater on its storage stand
- Using a razor blade, pry the sample from the substrate heater and store in labeled sample holder

The initial deposition conditions were determined from previous PLD experiments conducted in the Gibbons lab, as well as values obtained from literature. From these

initial conditions the various parameters were adjusted in such a way the sensitivity of film quality with respect to each parameter could be independently assessed.

2.2 Vacuum system basics

PLD uses a basic vacuum system consisting of a roughing pump and a high vacuum pump. In this system, the high vacuum pump (turbomolecular pump) is isolated via a gate valve and foreline valve, and the roughing valve is used to bring the chamber to a relatively low vacuum (40 mTorr). Once the chamber has been brought to the low vacuum, the valve connecting the roughing pump to the chamber is closed. The outlet of the high vacuum is opened to exhaust through the roughing pump, and thus to atmosphere. The gate valve exposing the inlet of the high vacuum pump to the chamber is then opened until it has reached a state of high vacuum ($\sim 7.5 \times 10^{-6}$ Torr). Upon reaching a high vacuum, the gate and foreline valves are closed to isolate the turbo pump once again, the mass flow controller is opened such that a defined amount of background gas (in this case O_2) is allowed to enter the process chamber, followed by the opening of the roughing valve. This process allows for a user defined background pressure in the chamber during deposition. A process flow diagram for the PLD system can be found in Fig. 11.

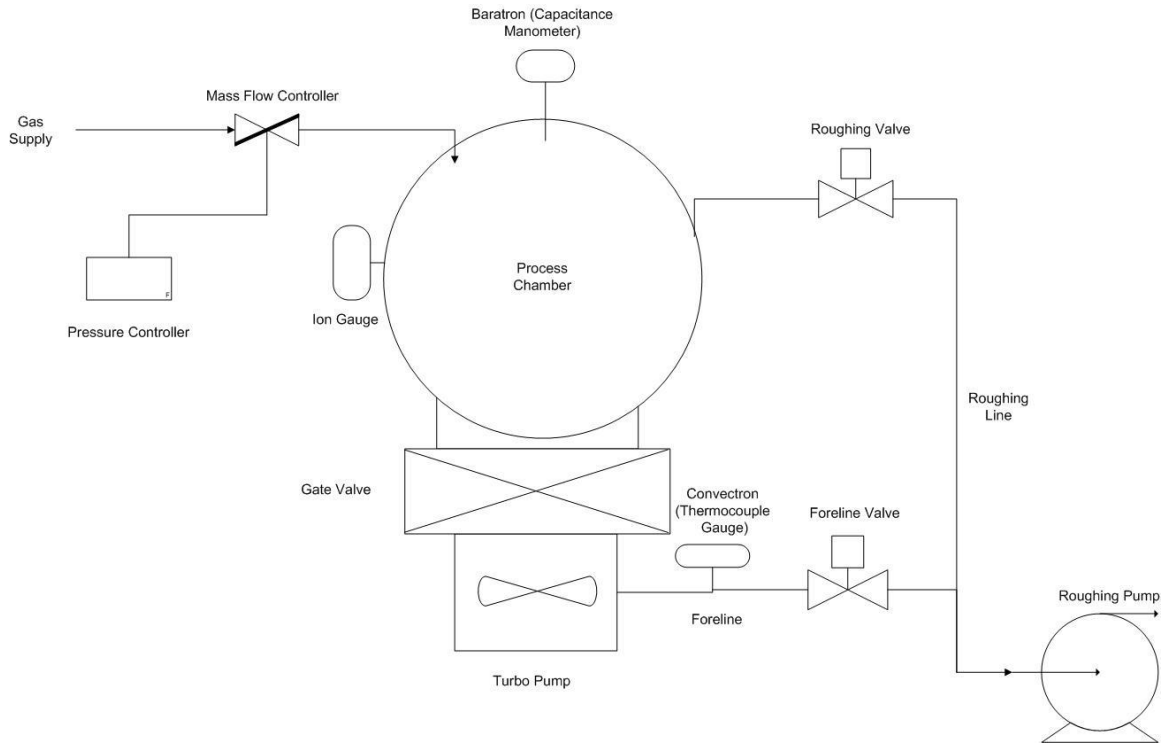


Figure 11: Typical vacuum setup for PLD system

2.3 X-Ray diffraction

X-ray diffraction (XRD) relies on the phenomenon of diffraction, which occurs when a wave encounters regularly spaced obstacles with spacing comparable in magnitude to the wavelength (i.e. crystalline solid) that are capable of scattering the wave. Diffraction is observed based on the interactions between two or more of these scattered waves [17]. XRD is used to obtain information about the structure, composition, and state of polycrystalline materials. A simple expression relating the x-ray wavelength (known) and interatomic spacing (unknown) to the angle of the diffracted beam (known) is given by Bragg's Law, see Equation 2.1. When Bragg's Law is not satisfied constructive interference will not occur, resulting in a very low-intensity of x-rays at the detector.

Bragg's Law: $n\lambda = 2d \sin\theta$ (2.1)

Where:

n = order of reflection

λ = x-ray wavelength

d = interatomic spacing

θ = angle of diffracted beam

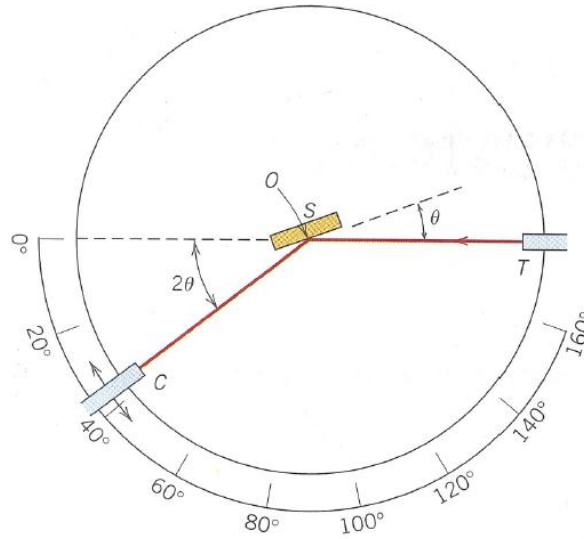


Figure 12: Schematic of XRD θ - 2θ setup [17]

A monochromatic x-ray beam is generated at T , Fig. 12, diffracts off the sample S , and the intensities of the diffracted beam are detected at C . The Bruker AXS D8 Discover utilized for this thesis has a configuration such that both T and C rotate by an angle θ for each measurement, resulting in the 2θ seen in all subsequent θ - 2θ plots. Using Eqn. 2.1 the interatomic spacing can be calculated at each diffraction angle. The significance of this is that these interatomic spacings depend solely on the dimensions of the crystal's unit cell. Furthermore, the intensities of the diffracted rays give an indication of the placement of the atoms within the unit cell [17].

Every crystalline material has a distinct x-ray pattern, thus allowing the pattern to be used as a material identification or verification tool [18]. As could be expected, by

coupling the known XRD pattern for a material with the experimentally gathered XRD pattern any defects or undesired phases can be identified and addressed for future experiments.

In addition to its ability to identify crystal structures, XRD is also an effective tool to help determine if any preferred crystallographic orientation exists within a film. XRD ϕ scans allow for the in-plane orientation of a film to be measured. A typical ϕ -scan for the perovskite structure, with preferred in-plane orientation, will consist of four peaks separated from one another by 90° .

2.4 Electrical characterization

Electrical testing of each film utilized a metal-insulator-metal (MIM) structure. To contact the bottom electrode (Pt for the silicon substrates) a 10% molality HF solution was used to etch the PZT. Once etched, the films were then patterned with circular top electrodes of 0.0000785, 0.000314, and 0.000706 cm² using a shadow mask in an Ag evaporation system.

The relative permittivity and dielectric loss of each film was measured with an impedance analyzer (HP4192A). This system measures the capacitance of the film as a function of frequency, from 0.1 to 100 kHz, with a 50 mV oscillation voltage. Using Eqns. 2.2 and 2.3, the capacitance can be related to the permittivity of the film in terms of other known variables.

$$C = \epsilon_r \epsilon_o \frac{A}{d} \quad (2.2)$$

Where:

C = capacitance

ϵ_r = relative static permittivity

ϵ_o = electric constant

A = electrode area

d = film thickness

$$\epsilon_r = \frac{Cd}{A\epsilon_o} \quad (2.3)$$

The ferroelectric properties of each film were measured using a Radiant RT66B ferroelectric test system. This test produced a single-pass hysteresis loop, ranging from 9 kV up to the breakdown voltage of the measured film.

2.5 Spectroscopic ellipsometry

Variable angle spectroscopic ellipsometry (VASE, J.A. Woolam Co. Inc.) was used to determine film thicknesses. This method measures a change in polarization as light reflects or transmits from a surface. As this measured response depends both on material thickness and optical properties, ellipsometry is primarily used to ascertain those values [19].

It should be noted that film thickness is dependent on the optical properties of the film. The VASE uses the known wavelengths of the light in combination with a dispersion relationship to determine the optical constants n (index of refraction) and k (extinction coefficient). Physically, the index of refraction determines the light waves' velocity and diffracted angle, while the extinction coefficient is a measure of light absorbed by the material [19].

3. Results

3.1 Lead zirconate titanate

Initial films were deposited using a 20 mol% excess lead target with a $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ composition to account for the volatility of lead, as discussed previously. After exhaustive variation of deposition parameters (discussed in section 2.1) phase pure PZT was unable to be synthesized. $\text{CuK}\alpha$ x-ray diffraction revealed pyrochlore/second phase peaks in addition to the expected PZT, Pt, and Si/SiO_2 peaks. Fig. 13 below shows XRD plots for some of the non-phase pure films.

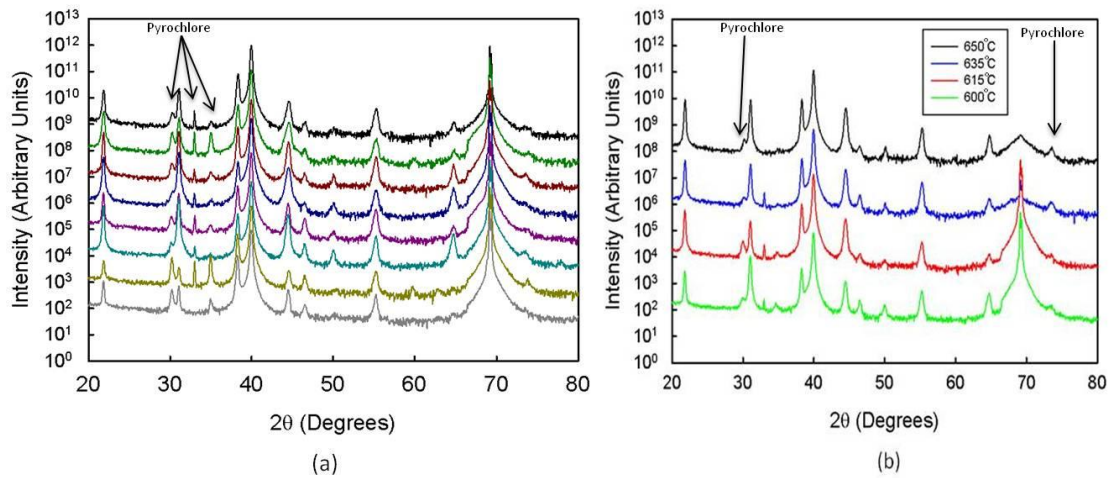


Figure 13: (a) θ - 2θ scan of PZT deposited with 20% excess lead target, oxygen partial pressure increases vertically, (b) θ - 2θ scan of PZT deposited with 20% excess lead target with varying deposition temperatures. Both figures show non-phase pure PZT, reference Fig. 14 for locations of PZT and substrate peaks.

To address this issue, a new target with 30 mol% excess lead was produced. Using a similar deposition optimization pattern as with the original target, phase pure PZT was synthesized with the new 30 mol% excess lead target. The improvement of phase-purity at higher mol% excess lead is observed in Fig. 14.

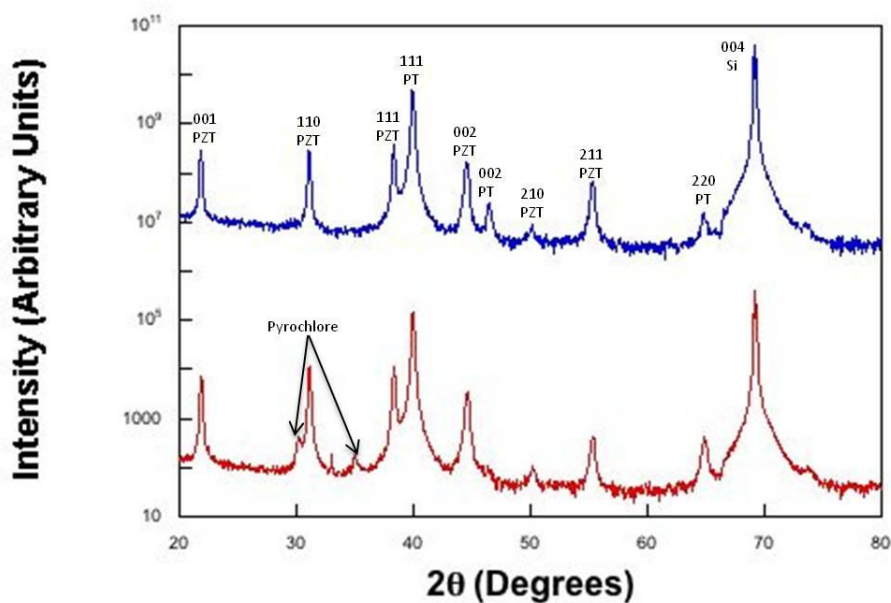


Figure 14: The top XRD pattern is phase-pure PZT using the 30 mol% excess lead target. The lower pattern has several pyrochlore phases, one appearing as a shoulder at approximately 30° and another at around 37°, this film used the 20 mol% excess lead. Both of these films were deposited at the same conditions (200 mTorr, 650°C, 250 mJ, 10 Hz, 7 minutes).

Optimized deposition conditions for the phase pure PZT were found to be at an oxygen partial pressure ranging from 150 to 340 mTorr at 650°C, see Fig. 15. In addition, the laser settings were 250 mJ and 10 Hz for 7 minutes.

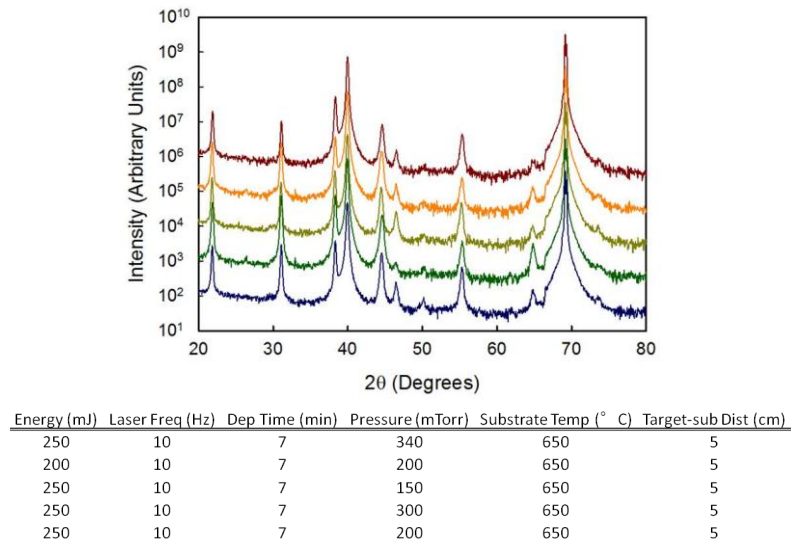


Figure 15: Consistently phase pure PZT deposited using 30% excess lead target. Deposition conditions in table align with XRD patterns.

Corresponding ferroelectric properties for these films were characterized. These measurements resulted in the hysteresis loops and dielectric constants and losses seen in Fig. 16. Referencing the ideal hysteresis loop seen in Fig. 9, it is clear that the hysteresis loop is not well-saturated. Common remanent polarizations (P_r) and coercive fields (E_c) for the films were $33 \mu\text{C}/\text{cm}^2$ and $80 \text{ kV}/\text{cm}$ respectively; all P_r and E_c reported were measured at 15 V drive voltage. Dielectric constants ranged from 450 to 1200, while dielectric losses were found to be approximately 4% (reported values at 1 kHz).

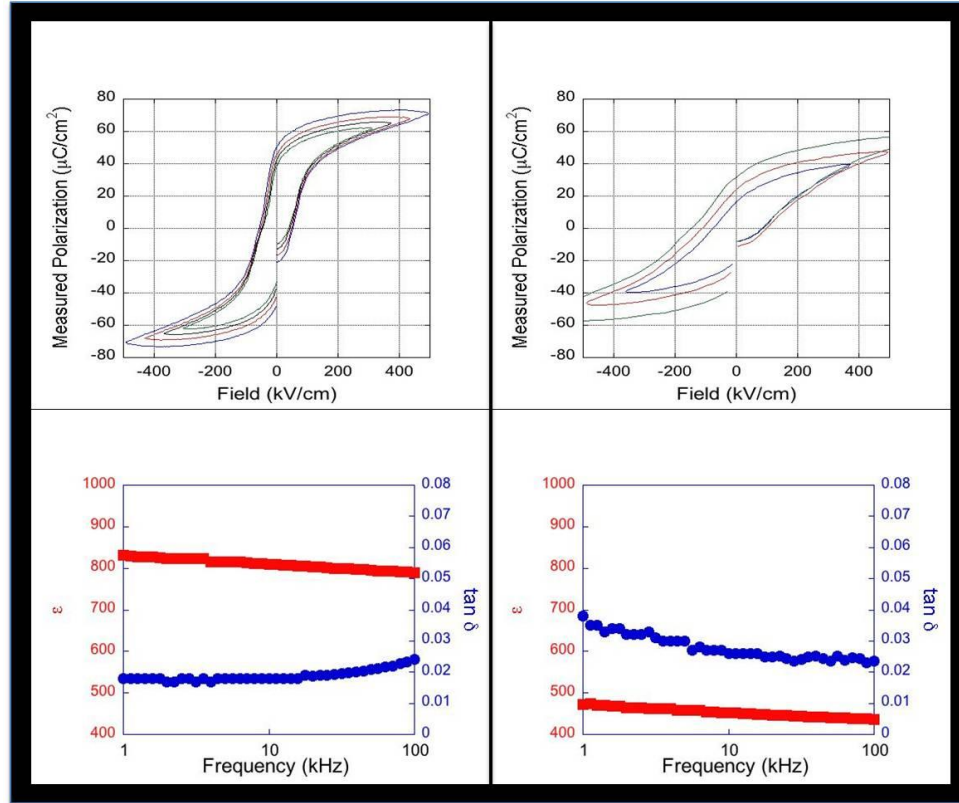


Figure 16: Electrical properties for two PZT thin films at differing deposition conditions

The best ferroelectric properties were found in a film deposited at an oxygen partial pressure of 340 mTorr, 650°C, at 250 mJ and 10 Hz for 7 minutes. This film had a high P_r , 29.2 $\mu\text{C}/\text{cm}^2$, and low E_c , 42.13 kV/cm. The specific dielectric constant and loss measurements for this film, at 1 kHz, were 1230 and 3.2% respectively.

To improve the electrical properties of the PZT, subsequent films were annealed in oxygen post deposition, while maintaining the deposition conditions at 340 mTorr, 650°C, at 250 mJ and 10 Hz for 7 minutes (laser settings were 250 mJ and 10 Hz for 7 minutes). After deposition was completed the chamber was partially vented to near-atmospheric pressure ultra-high-purity (UHP) oxygen. As the films cooled from their deposition temperature they were held at 400°C for 7 minutes. Films post-annealed in

this manner maintained their phase pure structure while improving their ferroelectric properties. Hysteresis loops, dielectric constants, and losses, Fig. 17, were more repeatable while also yielding higher P_r ($35.3 \mu\text{C}/\text{cm}^2$) and lower E_c ($36.5 \text{ kV}/\text{cm}$). The dielectric constant also improved to 1370 with loss values lower than the original films at 1.2% (reported values at 1 kHz).

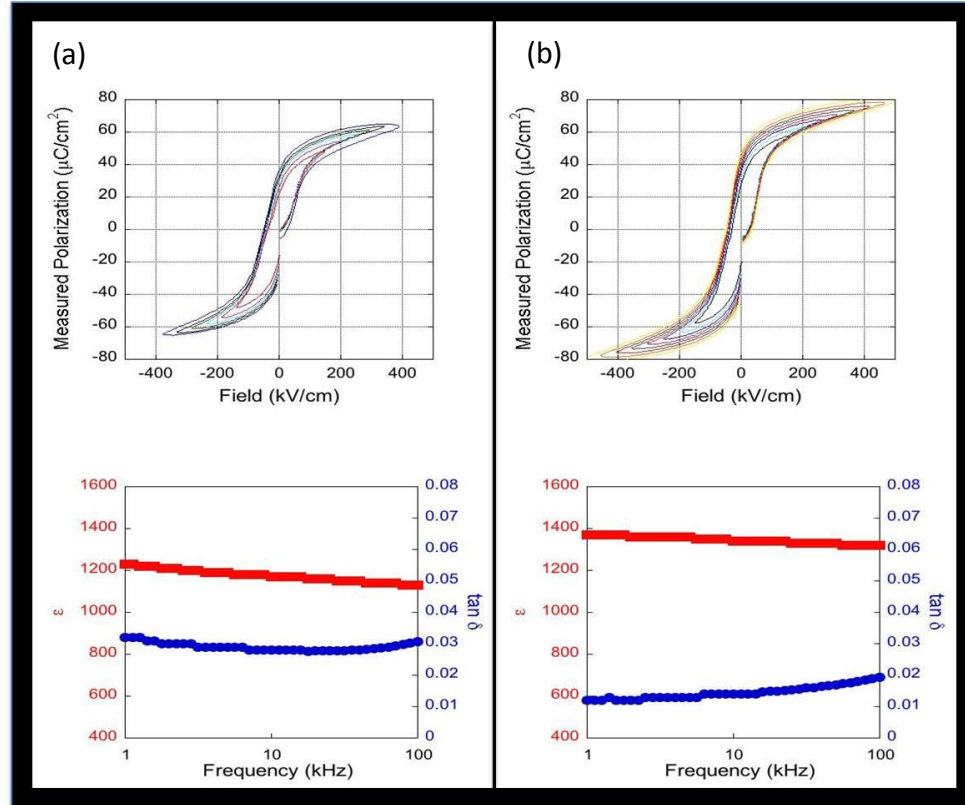


Figure 17: Electrical properties for two PZT films at identical deposition conditions, with (a) undergoing an anneal step, while (b) was not annealed

It should be noted that the remanent polarization and dielectric constant are dependent on electrode area size, the deposition of which is a process unto itself. The ideal areas are 0.0000785 , 0.000314 , and 0.000706 cm^2 but in reality the electrodes deviate some from these values. Every attempt was made to account for this by measuring deposited electrode diameters with an optical microscope camera system.

These measurements were then averaged and used to calculate all P_r , E_c , dielectric constant, and loss values.

Spectroscopic ellipsometry revealed that film thickness remained relatively similar with and without the anneal step. The film without the anneal step had a thickness of 600 nm while the film with the anneal step had a thickness of 561 nm (all other deposition conditions were the same). Surface roughness measured via atomic force microscopy (AFM) resulted in roughness values of 12 nm for the annealed film.

3.2 PZT/LNO/IBAD-MgO

Once PZT deposition was optimized on a more traditional platinized silicon substrate, the same methodology was applied to a more novel, flexible IBAD substrate.

IBAD-MgO offers a relatively inexpensive, flexible substrate with a similar crystal lattice to PZT to allow for epitaxial growth of thin films. But rather than deposit PZT directly onto IBAD-MgO, another layer is required to act as a bottom electrode in this MIM configuration. While the IBAD-MgO has a 50 nm layer of conductive $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ (LSMO), an additional layer was deposited to provide a more substantial bottom electrode, as well as to improve film texture. LaNiO_3 (LNO) is a conductive material that matches lattice structure well with both the underlying LSMO and overlying PZT. As such, a thin film of LNO was deposited onto IBAD-MgO/LSMO via PLD. Deposition conditions for LNO were adapted from values found in literature [8]. Optimized deposition parameters for LNO were 200 mTorr of oxygen, 650°C, at laser settings of 200 mJ and 10 Hz with a 3 minute deposition time.

X-ray diffraction was used to determine the phase purity and in-plane orientation of the resulting films. θ - 2θ scans revealed that PZT deposited at 200 mTorr oxygen,

650°C, at laser settings of 250 mJ and 10 Hz for 7 minutes shows phase-pure crystal structure. In addition, ϕ -scans of each layer were taken to measure the in-plane orientation of the films as subsequent layers were deposited, see Fig. 18b.

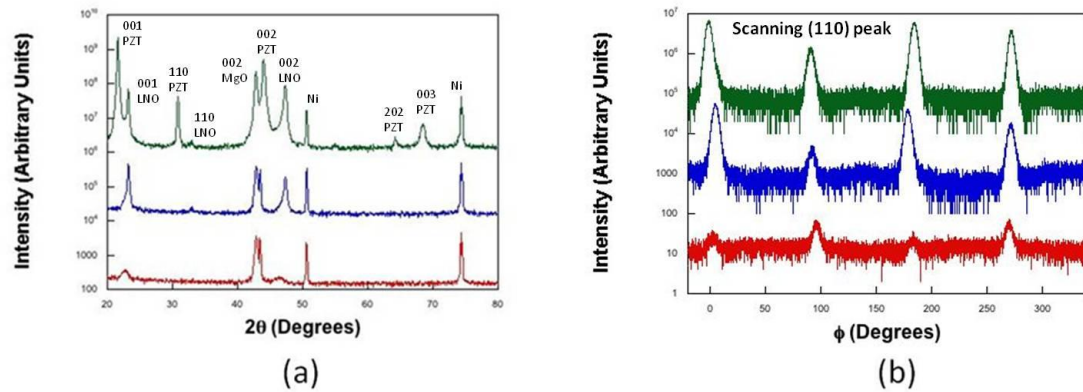


Figure 18: For both images the data progresses vertically from IBAD-MgO to LNO to PZT (a) θ - 2θ scan of the PZT/LNO/IBAD-MgO system; (b) ϕ scan of the (110) peak in the PZT/LNO/IBAD-MgO system

Electrical characterization was carried out using similar methods to PZT on platinized silicon. High remanent polarizations were observed in some films, 52.6 $\mu\text{C}/\text{cm}^2$, along with coercive fields of 42.2 kV/cm; see Fig. 19a. Initial dielectric constant and dielectric loss measurements, shown at 1 kHz in Fig. 19b, yielded values of 1150 and 5.2% respectively.

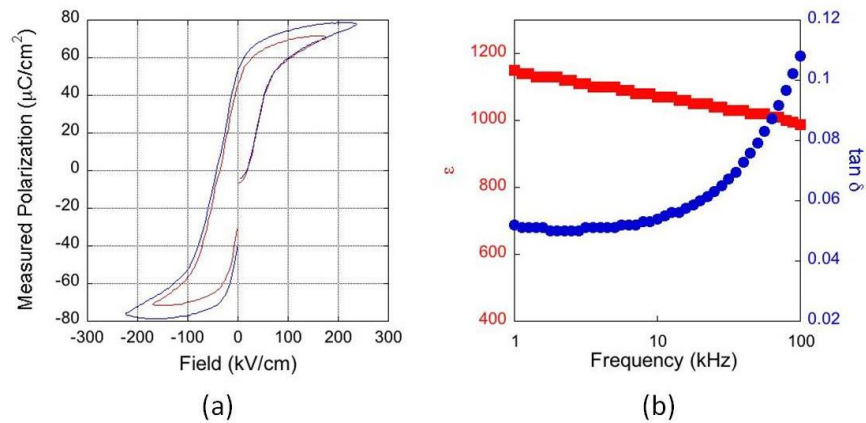


Figure 19: Electrical properties for PZT/LNO/IBAD-MgO system

4. Discussion

4.1 Lead zirconate titanate

Much work has already been completed regarding PZT on platinized silicon, as such it was a good way to verify the processes implemented. Furthermore, this research established a foundation for future work concerning flexible IBAD substrates in a PLD setting.

For all films discussed in this thesis, Volmer-Weber growth is the primary mode observed. This is in part due to the relative roughness of the substrates being used, with both Frank-van der Merwe and Stranski-Krastanov growth requiring much smoother surfaces. Also, it has been shown in a number of cases that isolated three-dimensional nuclei (i.e. islands) form at a stage where there is insufficient thickness to have formed an initial monolayer [12]. Moreover, the use of PLD as a processing method facilitates Volmer-Weber growth. In PLD, as the ablation plume expands into the background gas a resultant shock wave is formed. These shock waves work to dissipate the kinetic energy of the ablation species (i.e. target material), slowing them sufficiently to allow the nucleation of small nanoclusters in the plume. Meaning that the cluster growth described for the Volmer-Weber mode begins prior to even reaching the substrate [16].

Excess lead is known to promote formation of the perovskite phase, as well as reduce crystallization temperatures [20]. This behavior was evident for films synthesized using the 20 mol% excess lead target. Extensive parameter variation yielded no repeatable phase pure PZT samples, indicating that perhaps there was deficient Pb in the system to fully form the perovskite phase. The non-phase pure XRD plots showed several pyrochlore peaks, which should not be present in a phase pure perovskite structure. It

should be noted that the pyrochlore phase is part of the phase evolution of PZT films. During *ex-situ* crystallization, as seen in chemical solution deposition (CSD), amorphous PZT films first transform to a non-ferroelectric, metastable pyrochlore phase before transforming to the ferroelectric, stable perovskite structure [21]. This particular description of the PZT phase evolution describes chemical solution deposition, but the same basic principles hold true for PLD. Due to its non-ferroelectricity, minimizing the pyrochlore phase is necessary for high quality ferroelectric, phase pure films. Sufficiently high deposition temperatures are needed to accommodate the pyrochlore to perovskite transformation, which occurs around 550°C [22]. This was taken into consideration when selecting deposition parameters, even so the pyrochlore phases remained at temperatures well above the transformation temperature. The volatility of Pb is likely the root cause of not achieving phase purity. The theory being that Pb is evaporating from the substrate surface during deposition, resulting in Pb vacancies and pyrochlore development [23]. The solution was to increase the target composition to 30 mol% excess lead to ensure film stoichiometry.

Using the 30 mol% excess Pb target, phase pure PZT films were immediately obtained, as observed via XRD, validating the assumptions made about Pb vacancies. However, upon electrical characterization the majority of these phase pure films had poor properties, with unsaturated hysteresis loops, low dielectric constants, and high losses (reference Fig. 16).

Just as with the 20 mol% excess Pb target, the problem of non-stoichiometric PZT persisted. Non-stoichiometric films could give rise to Pb or oxygen vacancies, introducing the potential for space charge. Space charge is a behavior in which the space

created by an atomic vacancy takes on a charge, positive or negative. The net effect of space charges throughout a film is that they can lead to an internal bias, thus altering the ferroelectric properties of the thin film. The presence of space charge is often associated with unsaturated hysteresis loops [24].

In an attempt to improve the electrical properties of the films, a post-deposition anneal was performed, with films being deposited at the same conditions as previous phase pure samples. After deposition the chamber was partially vented to UHP oxygen (3 seconds), then cooled to 400°C where the films were held for 7 minutes. Subsequently, the chamber was vented for 4 more seconds and the film was allowed to cool to 200°C before being removed from the chamber. An example of the effect this anneal step had on the electrical properties can be seen above in Fig. 17. Comparing films at identical deposition conditions, one with anneal and one without, one can observe an increase in maximum polarization and dielectric constant and reduction in dielectric loss for the annealed film. The physical purpose of annealing was to allow the film to reside in a 100% O₂ environment, at a relatively high temperature, helping to fill any oxygen vacancies that are present. In doing so it should reduce the amount of space charge present in the film, thus improving the overall ferroelectric properties observed. Furthermore, holding at high temperatures helps the crystalline restructuring of the film, potentially mitigating any negative structural effects due to high laser frequency deposition [25].

While the post-annealed electrical properties of the PZT were improved, the hysteresis loops still exhibited a certain electrically lossy behavior, seen in the rounded

shape at higher polarizations. Fig. 9 displays a well-saturated hysteresis loop absent of this lossy characteristic. There are several theories as to why this behavior exists.

The first theory is that there is an excess of PbO at the grain boundaries of the film, which could be detrimental to the insulating nature of the PZT [26]. PbO is a moderately conductive oxide that occurs naturally in the deposition of the PZT. If conductive filaments of PbO reached across the film, as in Fig. 20, there would be a concomitant resistance degradation in the PZT. One solution to this problem would be to apply a DC voltage across the film which would cause the conductive PbO filaments to experience high levels of current. The high current would heat the region and ultimately vaporize the conductive PbO filaments.

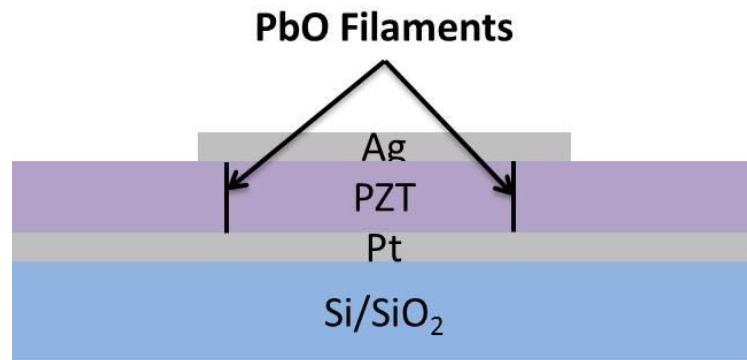


Figure 20: Diagram of PZT on platinized silicon substrate with Ag top electrodes, black lines indicate conductive lead oxide filaments that could lead to lossy behavior in film

However, after applying a ten second 3 V DC bias across the film in multiple locations no improvements in properties were observed [26]. As such, conductive PbO filaments creating localized shorts throughout the film are likely not the issue.

Another possibility is that Pb and O vacancies allow for space charges to exist, creating an internal bias and altering the ferroelectric properties of the film. Space charge would also result in a falsely high remanent polarization (especially at low frequencies),

meaning that the P_r of the film is artificially enhanced. In an attempt to reduce oxygen vacancies, films were re-annealed at 400°C for 15 minutes in flowing O_2 , the term ‘re-annealed’ is used here because these samples had already been annealed once in the deposition chamber. This resulted in a decrease in remanent polarization from 35.3 $\mu C/cm^2$ to 28.7 $\mu C/cm^2$, which could indicate a reduction in oxygen vacancies, reducing the space charge present within the film. Direct comparisons of the anneal in flowing O_2 can be found in Fig. 21. The annealed sample does appear to exhibit less lossy behavior in the hysteresis loop, showing slightly more saturation, as well as a marginal improvement in dielectric constant to 1440, but an increase in dielectric loss to 2.6%.

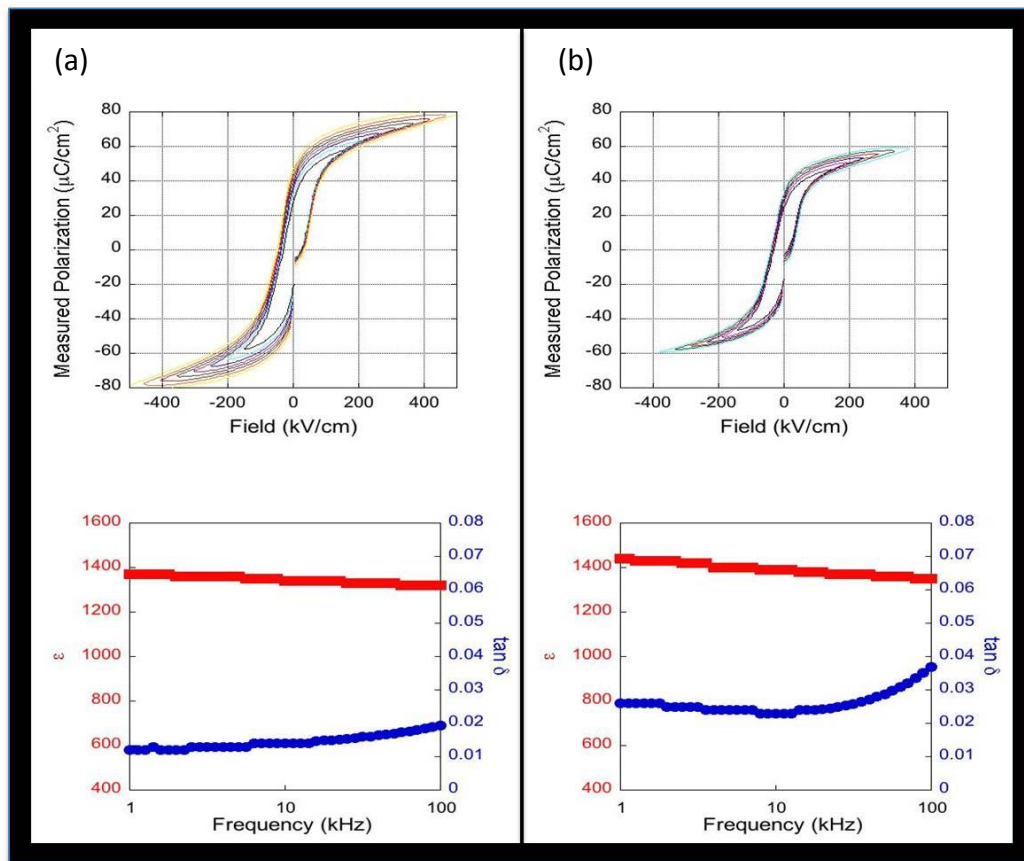


Figure 21: (a) shows electrical properties for a film with no anneal in flowing O_2 ; (b) shows electrical properties for a film deposited in identical conditions but underwent post deposition anneal in flowing O_2 (Deposition Conditions: 250 mJ, 650°C, 340 mTorr, 10 Hz, 7 minute dep. time, anneal in process chamber at 400°C for 7 minutes)

Several trends were observed in the data regarding film thickness as a function of laser energy, film thickness as a function of deposition pressure, and dielectric constant as a function of deposition temperature.

The first noticeable trend is also the most obvious, that film thickness will increase as laser energy increases (with all other deposition parameters remaining constant). In the previous description of the PLD process it was mentioned that the amount of ablated target material is dependent on the energy of the impinging laser beam. Thus, as the energy of the laser increases, so too will the amount of ablated material, leading to an increase in material reaching the substrate and an increase in overall film thickness.

Another relationship found was between deposition oxygen partial pressure and film thickness. It was found that, in general, film thickness increased with increasing oxygen partial pressure. As mentioned previously, the presence of a background gas has a direct effect on the plume behavior in PLD. As the pressure of the background gas increases it forces the plume to condense and terminate sooner. As such, at higher background pressures a more concentrated plume of ablated material is reaching the substrate, causing an increase in film thickness. That said, it is likely that the thickness would start to decrease at some point as the background pressure increases further. Due to the same phenomenon that increased film thickness, at high enough pressures it is imaginable that the plume would become too focused and terminate too quickly, meaning less and less material would actually reach the substrate.

Finally, the dielectric constant of the film was also found to increase as deposition pressures increased. This is an expected outcome as it was just shown that film thickness

increases as a function of increasing deposition pressure. As the film thickness increases it is likely that the ratio of high-to-low quality PZT is increasing, resulting in an increase in dielectric constant.. The relationship between deposition pressures, film thicknesses, and dielectric constants can be seen graphically below in Fig. 22.

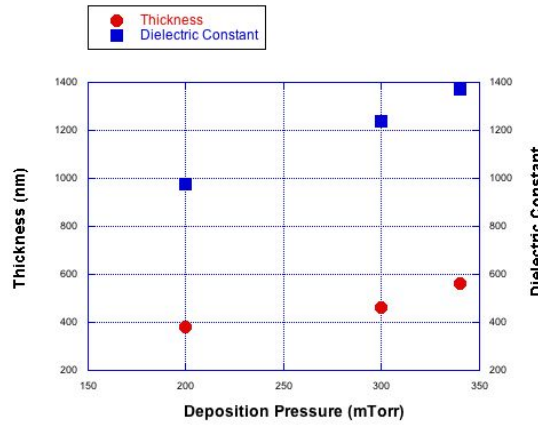


Figure 22: Effect of increasing deposition pressure on film thickness and dielectric constant

The nature of any optimization problem is found in the entanglements of tradeoffs, similar obstacles were not absent from this experiment. Finding the balance between deposition parameters and the manifested physical results was the key to ultimately producing high quality PZT films.

4.2 PZT/LNO/IBAD-MgO

The crystal structure of the PZT/LNO/IBAD-MgO system shows signs of epitaxy in Fig. 19b. The ϕ -scan reveals four distinct peaks, separated by $\sim 90^\circ$, that appear to be well aligned between each subsequent layer. This alignment indicates that there is an epitaxial in-plane relationship between the layers. Fig. 19(a) shows that there is a fair amount of lattice matching between the template substrate (IBAD-MgO) and the overlying LNO and PZT.

Measured values were similar in some aspects when compared to those found in literature, where remanent polarizations of $\sim 40 \mu\text{C}/\text{cm}^2$, E_c of 61 kV/cm and dielectric constants of between 350-400 with dielectric losses between 3-5% have been observed [8]. Remanent polarization was unexpectedly high at $52.6 \mu\text{C}/\text{cm}^2$, while coercive field was unexpectedly low at 42.2 kV/cm. As in the PZT on platinized silicon system, there is potentially space charge present in the film, causing these high P_r measurements. Furthermore, the hysteresis loop seen in Fig. 19 is clearly not saturated, and the thickness of the loop is an indicator of the expected lossy characteristics of the film. The methods of etching through the PZT to contact the bottom electrode are significantly different between the two systems discussed in this thesis. For the PZT-Si/SiO₂/Pt system the PZT layer was etched through using a 10 mol% solution of hydrofluoric acid (HF) to allow contact to the bottom Pt electrode. In the PZT/LNO/IBAD-MgO system this is not possible, as the HF will etch through the PZT as well as the LNO. The current method implemented was to “mask” a region of the film using silver paint. After the LNO layer was deposited, silver paint was applied to a corner area and cured at 100°C in a small mound, and the PZT was subsequently deposited. The small mound of silver paint was etched using a diamond-tipped scribe to remove any overlying PZT prior to top electrode deposition. Overall, this method has yielded inconsistent results. Due to this poor bottom electrode contact there were difficulties in obtaining multiple hysteresis measurements with the same top-bottom electrode combination. The electrodes would often short-circuit after multiple measurements were attempted with the same electrode pair. This issue will need to be addressed to accurately characterize these films.

5. Conclusion

The objective of this thesis was to obtain and demonstrate the optimized PLD conditions to successfully grow high-quality ferroelectric PZT thin films. Additionally, the potential for improved ferroelectric response was explored through epitaxial growth of PZT on IBAD-MgO substrates. This chapter will summarize the major findings of this research, as well as make recommendations for further work.

5.1 Lead zirconate titanate

$\text{Pb}(\text{Zr}_{0.52}, \text{Ti}_{0.48})\text{O}_3$ was deposited via pulsed laser deposition onto platinized silicon substrates. Films deposited with a laser energy of 250 mJ, repetition rate of 10 Hz at 340 mTorr oxygen partial pressure and 650°C for 7 minutes displayed phase-pure perovskite crystal structures after θ -2 θ x-ray diffraction analysis. Annealing these films post-deposition at 400°C for 7 minutes improved the ferroelectric behavior, resulting in remanent polarizations of 35.3 $\mu\text{C}/\text{cm}^2$ and coercive fields of 36.5 kV/cm. The dielectric constant and loss values for these films were 1370 and 1.2% respectively. An additional re-anneal (after the anneal carried out in the process chamber) at 400°C for 15 minutes in flowing O_2 reduced the remanent polarization to 28.7 $\mu\text{C}/\text{cm}^2$, which could indicate a reduction in space charge caused by a reduction in oxygen vacancies. The coercive field remained relatively constant at 36.0 kV/cm. This re-anneal also increased the dielectric constant to 1440 and dielectric loss to 2.6%.

5.2 PZT/LNO/IBAD-MgO

The work done on the PZT/platinized silicon system laid the foundation for work on the PZT/LNO/IBAD-MgO system. Phase pure LaNiO_3 was deposited at a laser energy

of 200 mJ, repetition rate of 10 Hz at 200 mTorr oxygen partial pressure and 650°C for 3 minutes. Initial films showed a nearly epitaxial structure when analyzed using XRD θ - 2θ and ϕ -scans. Electrical characterization revealed hysteresis loops with high P_r , 52.6 $\mu\text{C}/\text{cm}^2$, and low E_c , 42.2 kV/cm. Removal of space charge within the film will likely help to correct remanent polarization, as the P_r seems unexpectedly high when compared to values obtained by similar studies. Improvement of contact to LNO for subsequent ferroelectric testing is recommended for more repeatable results.

5.3 Future work

An improvement in electrical properties for the PZT/LNO/IBAD system is desirable and expected for future experimentation. The epitaxial nature of these films (as demonstrated through XRD ϕ -scans) indicates that the ferroelectric response should improve at the proper deposition parameters. Improvement in the epitaxy of the films will result in a decrease in the width of the peaks in the ϕ -scans (full width at half maximum, FWHM), thus improving the electrical properties. Different methods of contacting the bottom LNO electrode should be explored, potentially creating more consistent and repeatable measurement results. Much like the work done with PZT on Si/SiO₂/Pt, this optimization will involve balancing trade-offs and careful, documented parameter changes. Ultimately, the epitaxial deposition of PZT onto these flexible substrates could be linked to applications in sensor technology, energy harvesting, and charge storage devices.

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