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Thin Film Growth of Dielectric Materials by Pulsed Laser Deposition

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THIN FILM GROWTH OF DIELECTRIC MATERIALS BY PULSED LASER DEPOSITION

A thesis submitted in partial fulfillment of the Requirements for the degree of Master of Science

By

JASON CHRISTOPHER ANDERS
B.S., Tennessee Technological University, 2011

2014
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Jason Anders ENTITLED Thin Film Growth of Dielectric Materials by Pulsed Laser Deposition BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Anders, Jason Christopher. M.S. Department of Physics, Wright State University, 2014. Thin Film Growth of Dielectric Materials by Pulsed Laser Deposition.

Thin films of $\text{Sr}_x\text{Ca}_{1-x}\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$ (SCZT) with $x = 0.8$, $y = 0.01$, $\text{CaHf}_{1-x}\text{Ti}_x\text{O}_3$ (CHT) with $x = 0.8$, and $x\text{BiScO}_3 - (1-x)\text{BaTiO}_3$ with $x = 0.36$ (BSBT(36/64)) showing a high permittivity are useful in capacitor applications. These dielectric thin films with a $\text{SrRuO}_3$ (SRO) conductive bottom electrodes were prepared by using pulsed laser deposition on $<100> \text{La}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.65}\text{Ta}_{0.35}\text{O}_3$ (LSAT) single crystal substrates. In a search of optimal conditions to achieve epitaxially grown SCZT, CHT, BSBT(36/64), and SRO thin films, different substrate temperatures ($600^{0}\text{C}$, $650^{0}\text{C}$, $750^{0}\text{C}$, and $800^{0}\text{C}$) and different partial pressures of oxygen (50 mTorr, 100 mTorr and 300 mTorr) in the chamber were used during deposition onto LSAT substrates. The optimized deposition conditions for conductive buffer layer of SRO film required 300 mTorr of oxygen partial pressure and substrate temperature of $750^{0}\text{C}$. The thorough structural and chemical studies of SCZT, CHT and BSBT(36/64) films were done by using SEM (scanning electron microscopy), AFM (atomic force microscopy), and XRD (X-ray diffraction) measurements. Sputtered gold top electrodes were added to the samples, along with etching to the SRO conductive buffer layer. These conductive electrodes were used to generate an AC electric field between the top electrodes and conductive buffer layer. Electrical characterizations of thin films such as complex permittivity, resistance and capacitance of grains and grain boundaries were performed using AC impedance spectroscopy, with curve fitting using Z-View software.
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I. INTRODUCTION

Future technological advances in power electronics modules for electric vehicles and power distribution systems will depend on advances in dielectric materials with high energy density at elevated operating temperatures. The maximum capacity energy density depends on the relative dielectric permittivity $\varepsilon_r$ and the dielectric breakdown strength $E_b$ for these materials. The critical limitations of usage also strongly rely on their lowest losses and the lowest thermal coefficient of capacitance.

Polymers and ceramics dominate the solid-state capacitors industry, however, with the exception of fluorine-based polymers, most polymer dielectrics are limited to operating temperatures less than 105°C. Despite having large relative permittivity, BaTiO$_3$ has a low energy density due to its hysteretic and nonlinear behavior resulting in large-field losses. The linear dielectric materials have recently been shown to be competitive with polymer capacitors for small capacitive devices and can work up to 200 to 300°C. A typical composition is 0.8CaZrO$_3$ – 0.2CaTiO$_3$ (CZT) while having a high breakdown strength, this material has a low permittivity associated with CaZrO$_3$ ($\varepsilon_r = 30$) which limits the recoverable energy density. Substituting CaZrO$_3$ by the higher permittivity of CaTiO$_3$ ($\varepsilon_r \approx 171$) incipient ferroelectric and with addition of the small amount of Mn (0.5 mol %) to 0.8CaTiO$_3$ – 0.2CaHfO$_3$ (CHT) significant improvement of high-temperature breakdown stability, loss mitigation, and energy density takes place.

Another example of a linear type material with significant value of the permittivity is Sr$_x$Ca$_{1-x}$Zr$_{1-y}$Ti$_y$O$_3$ where for $x = 0$ and $y = 1$. It appears that the
permittivity increases with increasing x but it decreases with substitution of Ti by Zr. It was also shown that for fixed value of $y = 0.9$, the permittivity of $\text{Sr}_x\text{Ca}_{1-x}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ changes from $\varepsilon_r \approx 145 \ (x = 0)$ to $\varepsilon_r \approx 232 \ (x = 0.3)$ approaching to the value of $\varepsilon_r \approx 250$ for $\text{SrTiO}_3$.

Recently new reentrant dipolar or weakly coupled relaxor perovskite structured dielectrics in the $\text{xBiScO}_3 - (1-x)\ \text{BaTiO}_3$ solid solution system have shown high-energy density values of $\sim 15 \ \text{J/cm}^3$ at room temperature with a decrease to $\sim 5 \ \text{J/cm}^3$ value with increasing temperature to 200°C. This drop is due to an increase in the conductivity and the loss in the system. The values of the permittivity, the maximum capacitor energy density and the dielectric breakdown strength are listed for $\text{xBiScO}_3 - (1-x)\ \text{BaTiO}_3$ in Table I. The dielectric breakdown strength decreases with increasing value of x in contrast to the maximum capacitor energy density which increases with x. The permittivity, however, stays constant independent on x and its value is $\varepsilon_r = 1,000$. The voltage is also only weakly dependent on the applied field relative to classic ferroelectrics such as $\text{BaTiO}_3$.

The ceramics mentioned above have a cubic or an orthorhombic symmetry of the perovskite structure-based on displacements relative to a parelectric or paraelastic prototype and were made by the conventional solid state reaction method with average grain sizes spanning 2 μm to 12 μm. The reductions in grain sizes and in dielectric layer thicknesses will place these materials as strong candidates for integration into future power electronic applications.

The main objective of our study is to fabricate dielectric thin films by controlling their thicknesses using pulsed laser deposition (PLD). The choice of which thin films will
be deposited is based on those compositions from Table I that represent various types of dielectric materials. There are indications that the bulk properties of these materials are preserved with thin film thicknesses. For example, it has been found that a peak permittivity of 800 was obtained for a 230 nm thick film of $0.4\text{BiScO}_3 - 0.6\text{BaTiO}_3$ at $215^\circ\text{C}$ with the same high energy density as in a bulk ceramics of the same composition.

Our goal is to produce three different types of thin films by PLD for the following compositions: $\text{Sr}_{0.01}\text{Ca}_{0.99}\text{Zr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (SCZT), $0.8\text{CaTiO}_3 - 0.2\text{CaHfO}_3$ (CHT) and $0.36\text{BiScO}_3 - 0.64\text{BaTiO}_3$ (BSBT(36/64)) and thoroughly characterized them by using X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM).
II. THEORETICAL INTRODUCTION

DIELECTRIC THEORY

When a parallel plate capacitor is placed into an electrical circuit bound charges accumulate on the plates. An electric field will develop across the space between the plates. Dielectric materials resist the formation of an electric field by producing an opposite net polarization. Tiny dipoles in the material align with the electric field (Fig. 1).

The individual dipole response is proportional to the electric field with a constant of proportionality equal to the polarizability of the material. Polarization is the net effect caused by the sum of the individual dipole moments per unit volume. The polarization of the material generates an internal electric field, opposite to the direction of the external...
electric field. The resultant electric field in the medium is called a displacement field \( \mathbf{D} \) (Eq (1))

\[
\mathbf{D} = \varepsilon \mathbf{E}
\]  

(1)

where \( \mathbf{D} \) is the electric displacement, \( \varepsilon \) is the permittivity, and \( \mathbf{E} \) is the external electric field.

Capacitance \( C \) is given by Eq (2)

\[
C = \varepsilon_0 \varepsilon_r \frac{A}{d}
\]  

(2)

where \( \varepsilon_0 \) is the permittivity of free space, \( d \) is the space between the electrodes (plates), and \( A \) is the area of electrodes. The capacitance without dielectric medium between electrodes can be calculated by using the value for the relative permittivity \( \varepsilon_r = 1 \).

Solving for the dielectric constant \( (\varepsilon_r) \), we have (Eq (3))

\[
\varepsilon_r = \frac{C d}{\varepsilon_0 A}
\]  

(3)

Permittivity or the dielectric constant is related to susceptibility. This relation can be expressed as follows (Eq (4))

\[
\varepsilon = \varepsilon_r \varepsilon_0 = (1 + \chi) \varepsilon_0
\]  

(4)

where \( \varepsilon \) is the permittivity of the medium, \( \varepsilon_r \) is the relative permittivity (dielectric constant), \( \varepsilon_0 \) is the permittivity of free space, and \( \chi \) is the electric susceptibility. The electric susceptibility is a measure of the degree of the polarization response of a dielectric material to an external electric field. The dielectric constant can be composed of a real and imaginary part. The real part of the relative permittivity \( \varepsilon_r \)' is a measure of
the amount of the electric field stored as energy. The imaginary part of the relative permittivity \( \varepsilon_r'' \) is the loss factor. This loss factor includes dielectric loss, as well as conductivity.

Permittivity can be represented in a complex plane as a vector by plotting the real part of the permittivity on x-axis and the imaginary part along y-axis. Tangent delta (tan \( \delta \)) is an indicator of the “lossiness” of a material, where \( D \) is the dissipation factor, and \( Q \) is the quality factor (Eq (5) and Fig. 2)

\[
\tan \delta = \varepsilon_r'' / \varepsilon_r' = D = 1/Q = \text{energy lost per cycle/energy stored per cycle}
\]  

The relation of real to complex permittivity can be plotted as a function of frequency.

![Diagram of complex permittivity](image)

Figure 2: Geometrical Representation of Tan Delta.

\[
\tan \delta = \varepsilon_r'' / \varepsilon_r' = D = 1/Q = \text{energy lost per cycle/energy stored per cycle}
\]  

(5)
The peak in the imaginary part of the permittivity corresponds to dielectric loss due to a molecular, or dipolar polarizability contribution. Ionic polarizability dominates losses in the low frequency regime (see Fig. 4). Higher frequency loss contributions such as atomic and electronic polarizability are difficult to test in the laboratory with standard impedance spectroscopy methods.

Figure 4: Polarizability Contributions to Dielectric Losses.

Dipolar, or molecular, polarizability involves polar molecules with built in dipole moments. Some molecules, due to their geometry, have inherent charge separation. Water molecules are an example (see Fig. 5).

Figure 5: Molecular Polarizability of Water.
In the presence of an external electric field, these molecules tend to align themselves along the direction of the external electric field, from their originally random orientation in the material. This realignment process called orientational (rotational) polarizability $\alpha_0$ (Eq (5)). Increase in temperature tends to disrupt this process by thermally agitating the molecules out of position of the external electric field [1]

$$\alpha_0 = 2 \frac{p_0^2}{kT}$$

where $p_0$ is the permanent dipole moment parallel to the direction of the external electric field, $k$ is Boltzmann’s constant and $T$ is the temperature in degrees Kelvin.

Molecular dipoles are oriented in the external electric field, due to torque exerted by the electric field on the dipole (Fig. 6).

![Figure 6: Torque on Molecular Dipole in an External Electric Field.](image)

Friction between the dipoles during reorientation in the electric field can cause dielectric losses. Dielectric losses due to this molecular or dipolar polarizability tend toward a maximum when exposed to radio frequency AC fields.

Vibrational (atomic) polarizability occurs when the polar molecules are stretched by an external electric field. The field elongates the charge separation in the molecules into an energetic state. Upon removal of the external field, the molecules are subject to a
restoring force back toward their equilibrium values. The energy loss in the molecular vibrational motion is the atomic polarizability contribution to dielectric loss at high microwave frequency AC fields (Fig. 7).

Figure 7: Electronic Polarization.

Electronic polarizability tends to be the weakest and most uniform of the types of polarizability. The external electric field distorts the originally symmetric electron cloud. This drift of outer shell electrons creates an atomic dipole. Electronic polarizability ($\alpha_e$) is proportional to the atomic volume (Eq (6))

$$\alpha_e = 4\pi\varepsilon_0 R^3$$  \hspace{1cm} (6)

where the value $R$ is the Bohr radius, and $\varepsilon_0$ is the permittivity of free space [1].

The permittivity of the dielectric medium ($\varepsilon$) is composed of a real $\varepsilon'$ and imaginary part $\varepsilon''$. The dielectric constant (Eqs (7)-(8)) can be also calculated as a function of the impedance ($Z$), both real ($Z'$) and imaginary ($Z''$) parts, the frequency of the externally applied electric field ($\omega$), and the value for the capacitance in vacuum ($C_0$)

$$\varepsilon' = \frac{Z''}{\omega C_0 [ (Z')^2 + (Z'')^2 ]}$$  \hspace{1cm} (7)
Impedance \( Z \) is a generalization of resistance that includes complex values. The real part of impedance, \( \Re \{ Z \} \), is the resistance \( R \), from Ohm’s law \( V = IR \) (where \( V \) is the voltage, and \( I \) is the current). The imaginary part of impedance, \( \Im \{ Z \} \), can describe the “resistive” effect of a capacitor in a circuit. Ohm’s law can be rewritten by this generalization of resistance as function of frequency \( \omega \); \( V(\omega) = I(\omega)Z(\omega) \). The impedance of a resistor would be designated as \( Z_{\text{Resistor}} = R \) and the impedance of a capacitor (Eq (9))

\[
Z_{\text{Capacitor}} = \frac{1}{i\omega C} = \frac{-i}{\omega C}
\]

where \( C \) is the capacitance.

Impedance spectroscopy is an experimental technique of applying a small perturbing AC field to a capacitor to test its overall impedance response as a function of frequency. Modelling of the data according to a simplified equivalent circuit diagram is used to generate a value for each microscopic value, such as interface and grain boundary contributions to the overall measured impedance response. The model used to describe the contributions to impedance is the brick layer model (see Fig. 8).

Figure 8: Brick Layer Grain Boundary Model.
In an ideal capacitor, the impedance would have total imaginary contribution, and no real contribution. Equivalent circuit models are used to fit the complicated relations of frequency and impedance that emerge from impedance spectroscopy measurements. An equivalent circuit model for an ideal capacitor would consist of a single capacitor. In a plot of $\Im(Z)$ vs $\Re(Z)$, or imaginary vs. real impedance, an ideal capacitor would have frequency dependent values in a straight line. These relations can be expressed in a $Z^*$ plot. Figure 9 represents a plot of imaginary vs. real impedance. These are one of the standard plots of impedance spectroscopy.
Figure 9: Equivalent Circuit Models based on Impedance Measurement Results.

The ideal capacitor model demonstrates low leakage current and low contact resistance. The model for this impedance is $Z(\omega) = (-i)/\omega C$ (where $Z(\omega)$ is the total impedance mapped as a function of frequency $\omega$ and capacitance $C$). Another circuit model is the parallel resistor-capacitor model. In this model, a plot of imaginary vs. real impedance forms a semi-circle. The Parallel Resistor-Capacitor Model takes into account both leakage current and contact resistance. It is modeled as follows

$$Z(\omega) = R_C + \frac{R}{(\omega RC)^2 + 1} - i \frac{\omega R^2 C}{(\omega RC)^2 + 1} \quad (10)$$

where $R$ is the contact resistance and $R_C$ is the leakage.
Ferroelectrics are a special group of advanced electronic materials consisting of dielectrics which are spontaneously polarized and possess the ability to switch their internal polarization with an applied electric field [2]. The type of ferroelectric materials used in this paper share a perovskite crystal structure (see as an example unit cells of BaTiO$_3$ is presented in Fig.10). Perovskite mineral structures are crystal structures that adhere to a specific list of parameters [3]:

1. $ABO_3$ crystal structure ($A$ and $B$ are metals)
2. Total charge of the $A$ and $B$ ions must be +6
3. Significant difference in size between $A$ and $B$ ions
4. Larger ion must be a transition metal

![Figure 10: Unit Cell of BaTiO3 a) Cubic Phase b) Tetragonal Phase.](image)

The change in crystallographic orientation between paraelectric and ferroelectric can be illustrated (Fig. 11) by a transition of their quantum well potentials [4].
Perovskite material in cubic phase is paraelectric. The sum of the charges in the unit cell is balanced. An external electric field applied to a paraelectric material will cause a separation of charges, resulting in the development of a bulk polarization. When the field is removed, the cubic material will return to its lowest energy state. Net polarization returns to zero. Perovskite material in the tetragonal phase begins with a distortion of the crystal lattice. Charge separation is built in to the crystal structure itself through the shift in the molecular arrangement. This built in aspect of charge separation in the tetragonal crystal is known as spontaneous polarization.

In a perovskite material, the phase transition between cubic and tetragonal states is temperature dependent. This phase transition temperature is described by the Curie temperature. Many materials exhibit anomalous behavior along their phase transitions. In perovskites, the dielectric constant tends to become larger at temperatures just below the Curie temperature. This is described by the Curie-Weiss relation as follows (Eq (11))

\[ \varepsilon_r = \frac{C}{T - T_c} \]  

(11)
where $C$ is the Curie constant, $T$ is the temperature of interest, and $T_c$ is the Curie temperature.

![Figure 12: Thermal Transition from Ferroelectric to Paraelectric State.](image)

In terms of a free energy ($\Delta F$) vs. polarization ($P$) diagram (Fig. 12), the Curie temperature corresponds to the point at which the lower temperatures exhibiting strong energetically favorable polarization states switch to favor the central non-polarized state. The polarization of a material under an external electric field can be experimentally mapped by a hysteresis loop (Fig. 13) [5].

![Figure 13: Ferroelectric Hysteresis Loop.](image)
As an external electric field is applied in a direction, the material begins to polarize. At point A, individual polarized domains in the material are randomly aligned in such a way that there is no net polarization. As the electric field is increased, the net polarization begins to form (points A to D). The maximum polarization response reaches a maximum value at D, the saturation point. As the intensity of the electric field is lowered, the net polarization of the material decreases. A ferroelectric is said to have a non-linear response to an electric field. When the field is removed at point E, the material does not return to its original un-polarized state. It exhibits a remnant polarization. Total reversal of the electric field at point G corresponds with a reversal of the direction of the polarization in the material.

![Frozen Island of Micron Size](image)

Figure 14: Frozen Island (bright) of a Fatigued PZT Sample Imaged by PFM.

Ageing is the loss of polarizability due to being left in a polarized (poled) state. Stabilization of the ferroelectric domains constitutes ageing. This stabilization can occur by the effect of an internal bias within the material caused by the internal electric field
produced by remnant polarization. Defects in the material can cause the formation of anisotropic centers with preferred orientations that can also generate internal bias (Fig. 14).

Buildup of charges along grain boundaries can cause a preferential crystallographic orientation known as the grain boundary effect. Defects along grain boundaries, as well as lattice mismatch between the ferroelectric material and the electrodes used to inject the field into the material, as well as vacancies in porous material, and accumulation of trapped electron space charges all contribute to preferential orientation of the domains. Piezoelectric force microscopy (PFM) imaging is a method used to identify local polarization in a ferroelectric material. It can be used to create an image of stabilization of the polarization in specific domains.
III. GOALS

The goal of this project was to investigate the growth of epitaxial thin films of three composite materials, BSBT, CHT, and SCZT. Parameterization of deposition conditions such as laser energy, deposition back pressure, and temperature of substrate, were to be used in conjunction with characterization techniques to determine the conditions for best quality films. Epitaxial growth is a kind of uniform homogeneous growth model in which the entire surface of the growth can be considered close to that of a large, single crystal. Achievement of this kind of growth is more often considered with other atomic layer deposition systems, such as MBE (molecular beam epitaxy), or CVD (chemical vapor deposition) techniques. Due to this, our initial investigation into these materials concentrated around the search for parameterization of largest grain size. The assumption was that for larger grain size, the material would be more uniform and smooth.
III. EXPERIMENTAL

PULSED LASER DEPOSITION

In Pulsed Laser Deposition (PLD), a laser is used to generate energy in the form of monochromatic and coherent photons. This laser energy is directed through a guided optical train, including turning mirrors, focusing beams, and optical galvanometer. The controlled and focused laser beam is guided through a transparent optical window into a high vacuum chamber. Inside the chamber, the laser beam focuses on some target material. The energy from the beam causes localized vaporization (ablation) of the target material onto a substrate material. After the substrate material adsorbs the target material, a layer is formed. This adsorbed layer on top of the substrate is the thin film, in a stoichiometric ratio to the ablated bulk target material.

The light output from an excimer laser is derived from a molecular gain medium in which the lasing action takes place between a bound upper electronic state and a repulsive or weakly ground electronic state [6]. A reaction between gas pumped into the laser and injection of energy through avalanche electric discharge excitation creates an electronically exited species of molecules called “excimers.” These excimers spontaneously decay on the order of nanoseconds, producing the laser pulses.

The avalanche electric discharge circuit injects energy into the gas mixture inside the laser to create the conditions for lasing. The discharge circuit is composed of capacitors, inductor coils, and electrodes. First, the storage capacitors are charged to around 40kV. Second, the thyratron switch is fired, transferring energy to peaking
capacitors. A thyratron is a gas filled tube used as a high power electrical switch controlled through a rectifier (converter between AC and DC current device capable of handling high voltage DC). The energy in the peaking capacitors is then transferred to the discharge region. During this operation, voltages can reach up to 40kV, and currents up to 15kA. Magnetic-Switch-Control (MSC) was developed to partially insulate the thyratron from the discharge energies. This magnetic switch is an inductor, or device that can temporarily store energy in a magnetic field. When the current flowing through an inductor changes, the time-varying magnetic field can induce a voltage. This additional voltage can be used to supply some of the 40kV potential needed for laser discharge.

The excimer laser uses a blend of fluorine, krypton, helium, and neon. These gasses are injected into the laser from a ventilated gas cabinet, through ¼” copper gas lines, and through swagelok fittings with gas solenoid inlets. The gas is purged from the system through sealed ventilation. These gasses are mixed at a specific ratio for best lasing. The discharge circuit, coupled with the correct mixture and pressure of gas in the chamber, create the conditions for homogeneous uniform laser output necessary for good quality depositions.

The optics pathway, or optical train (see Fig. 15), connects the output from the front of the laser, to the laser window facing the target assembly inside the vacuum sealed deposition chamber. The laser output from the front of the laser (248 nm wavelength) is beyond the visible spectrum. It is necessary to take special precautions when working with these invisible, high energy beams.

There are three primary optics used to guide the beam. First are mirrors. Mirrors with coated surfaces specifically made to reflect the 248 nm wavelength are used to
change the direction of the beam. Often a 45° turning mirror is used. This type of mirror changes the direction of the beam by 90°. Second are lenses. Lenses are made of a material that allows the UV wavelength of the laser to pass through with minimal loss or absorption. UV light is highly absorptive with materials such as glass and plexiglas. The optical lens is often made with a specific spherical focal length. 1 meter focusing lens is a common focal length. The laser light itself does not completely focus spherically, some lenses with cylinder power are designed to capture laser focus more completely. Third are beam splitters. They are optics that split the beam into two separate pathways. One application of beam splitters are the front optic on the excimer laser. A beam splitter separates a small portion of the beam to a photomultiplier. The PMT takes the measurement, next it scales up the measured value according to the percentage of splitting, to make an estimate for the total beam energy going through the front of the laser.

One other component of the optics train is the galvanometer. The galvanometer is inserted into the optics train, following the initial focusing of the beam by the focusing lens, and before the tightening beam passes through the target window through one of the deposition chamber ports. The galvanometer is controlled through computer software. It is used to raster the beam back and forth across the face of the target located inside the deposition chamber. The optics train is completed inside the deposition chamber as the beam is focused on the surface of the target.
The deposition chamber is one of the most crucial components in a PLD system (Fig.16). It is composed of a spherical metal shell, with round ports open to the outside used for attachment of sensors and devices, as well as windows to allow viewing and entry of laser beam. Inside the chamber the target is mounted on a target carousel which rotates the target itself, and allows multiple targets to be brought into position of alignment with the laser coming through the laser window. Across and parallel to the target, is the sample, or substrate holder. As the laser energy vaporizes the material from the target, this material travels across the distance to the substrate, and is adsorbed onto the surface of the substrate. Often, it is necessary for the substrate to be heated during this process. Situated behind the substrate holder is a resistive style heating puck that allows heating from room temperature to over 800°C [7].
Other components attached to the chamber are baritron pressure gauges. These gauges, operating at different ranges of pressure, allow visual inspection of the operating pressure during different stages such as: bringing up and down pressure to/from atmosphere to vacuum, base pressure, and oxygen back pressure. A gate valve, or manual valve that opens or closes the chamber at UHV, is situated between the chamber and the two stage pumping used in bringing the chamber to vacuum.

Two stage pumping consists of a roughing pump, connected in series with a turbomolecular pump, through the gate valve, into the deposition chamber. The roughing pump pulls the pressure in the system down to around 20 mTorr (760 Torr atmospheric pressure). At this pressure, the turbomolecular pump is activated. The turbo pump consists of a series of rotating vanes that push air molecules through a one-way channel.
This allows the pressure inside the chamber to be brought to around $10^{-8}$ Torr. In order to maintain consistent vacuum in the deposition chamber, all component connections through the open ports are designed with UHV fittings. The UHV fittings consist of metal flanges with knife edges. These knife edge flanges are bolted together with one time use copper gaskets sandwiched between. The knife edges bite into the copper, creating a high pressure seal.

When deposition is desired at a known gas pressure instead of vacuum, the butterfly valve is used. The butterfly valve is a side channel from the two-stage pumping to the deposition chamber, circumventing the closed gate valve on the bottom of the chamber. The butterfly valve connects the chamber to pumping through an electronically controlled valve. The valve is controlled through software connected to the baratron pressure gauges. First, the software notes the base pressure of the chamber. Secondly, the software operates solenoids connected to the gas input. Opening the solenoids allows the pressure to rise, as the gas enters the chamber. A specific back pressure is set in mTorr. The difference between the base pressure and the current rising pressure due to the injection of gas into the chamber is the dynamic estimate of the given gas back pressure. Once the difference between the back pressure and the stream of gas into the chamber reaches the set point, the butterfly valve opens, allowing the pressure in the chamber to be maintained dynamically. Through the process, the software continually updates the gas pressure, opening and shutting the valve.

Pulsed laser deposition is often described by a three stage process. This process consists of vaporization of target material, transport of the vapor plume, and film growth
on the substrate material. Ablation, or complete vaporization of the target material in response to the impinging laser pulse, addresses the first of these.

The arrangement of the focusing lens is such that it is inserted into the optics train a distance from the surface of the target located inside the deposition chamber at a length equal to its focal length. That is, the focusing lens collimates the focus, as well as the energy footprint of the beam into the smallest possible square area on the surface of the target (Fig. 17). This increases the energy imparted to the target from the laser in terms of the fluence.

![Figure 17: Beam Focus in Chamber.](image)

The incident laser beam onto the target induces a basic thermal cycle consisting of:

1. Absorption of laser pulse.
2. Melt front and vaporization propagation into target material.
3. Melt front recedes, causing partial re-solidification along the solid-liquid Interface (Fig. 18).
4. Completion of re-solidification with frozen in capillary waves.

[6]
Source angular distributions of the ablating material forming plume generated from the laser, follow a source angular distribution function (Eq (12))

\[ f(\theta) = \cos(\theta) \]  

where \( \theta \) is the polar angle of the ejected material from the target surface normal. This is to say that when the laser hits the target at some angle, often close to 45° due to common geometry of the systems, the ejection of the plume from the surface of the target is perpendicular to the surface of the target. Because of this, the substrate is often situated parallel and directly across from the target at some target to substrate distance on the order of 10 centimeters or less, even though the laser is oriented to strike the surface of the target at an angle.

The optimum conditions for deposition are complete ablation or vaporization of the target material, along with absorption of the material onto the substrate at energy levels that maximize development of largest grain boundaries, and minimize formation of separate regions of island growth. One obstacle in reaching these ideal conditions is the formation of particulates in the plume.

Ablation is the complete vaporization of the material from the energy imparted into the molecular bonds of the target material from the laser. This complete evaporation occurs when the transfer of laser energy into heat is enough to evaporate a mass volume
depth equal to half the skin depth [6]. This parameter for laser intensity \( I_{\text{max}} \), can be describes as follows (Eq (13))

\[
I_{\text{max}} \approx \alpha^{-1} \rho H_v / 2t_r
\]  

(13)

where \( \alpha \) is the absorption coefficient, \( \rho \) is the solid mass density, \( H_v \) is the heat of vaporization, and \( t_r \) is the relaxation time of the hot electrons in the surface layer. When the laser energy is greater than this optimum value, the heat energy transfer from the laser is not contained solely in imparting energy into breaking the bonds of the molecules in the target material causing vaporization, but also begin to melt the material, causing the formation of molten droplets that can splash from the molten surface of the target material, onto the substrate. These molten droplets can splash onto the substrate to form debris on the surface of the substrate. This debris can be on the scale of microns, affecting the roughness of the substrate. The laser fluence, or energy imparted by laser onto the target surface, per area of the laser footprint on the surface, is the primary source determining the vaporization vs. melting of the target during deposition (Fig. 19) [8].
Ambient gas pressure can be injected dynamically into the deposition chamber. This gas pressure can cause changes in the overall dynamics from the ablation stage to the nucleation stage of deposition, that is, the state of the system as the vaporized plume from ablation crosses the distance in the chamber from the target to the surface of the substrate. Ambient gas in the chamber tends to scatter, attenuate, and thermalize the plume. These effects can change deposition parameters such as the spatial distribution of atoms, deposition rate, and the kinetic energy of the plume. Also, when oxygen is used as an ambient background gas, the oxygen molecules can be incorporated into the growing film. This is an added benefit of the gas when dealing with deposition of metallic oxides. In fact, one additional technique is to post anneal the sample at elevated temperature after deposition in elevated oxygen backpressure to encourage further oxidation of the material.

Raising the background pressure increases the fluorescence of the material in the plume due to collisions between the ablated material and the gas molecules. It sharpens
the plume boundary. It also slows the velocity of the plume, lowering the kinetic energy of the material as it reaches the surface of the substrate (Fig. 20) [9].

![Image of Deposition Gas Back Pressure](image)

Figure 20: Deposition Gas Back Pressure.

The luminous shock front created during deposition in high background gas pressures is described by a blast wave model. This model describes the explosive release of energy through the gas in terms of a time dependent shock wave. Initially, the mass of the plume exceeds the mass of the displaced gas in the chamber. The plume experiences a viscous force by the gas during its time of flight. As the plume continues to travel toward the target material, a shock wave begins to form. At this time, the plume begins to separate into a fast component, followed by a delayed component that arrives at a later time (Fig. 21) [9].
Ablation in PLD tends to be stoichiometric. The ratio of molecules in the target material tends to be the same as that of the film growth. This aspect is helpful in heteroepitaxial growth of multicomponent metal oxides. Deposition of multiple species occurs simultaneously at the film growth site as the plume of vaporized particles comes into contact with the substrate, or with a conductive layer sputter deposited onto the substrate such as Strontium Ruthenate (SRO).
NUCLEATION

Atoms form (nucleate) through a complicated interaction between the interfacial energies on the substrate surface as well as the kinetic energy of the plume along the vaporization-to-adsorption path of the particles from target to substrate (Fig. 23) [7].

Figure 22: Illustration of Three Growth Modes a) Volmer-Weber (island), b) Frank-Van der Merwe (layer-by-layer), and c) Stranski-Krastanov Growth.

The Volmer-Weber equation describes the formation of atomic cluster on the surface of the substrate during deposition. Atoms can deposit from vapor onto the substrate and re-evaporate from the surface back into the vapor form. On the surface of the substrate, the atoms continue to be mobile (ad-atoms). These mobile atoms move across the surface of the substrate to nucleate into clusters.

Due to energy considerations occurring on the surface of the substrate, nucleation can continue across the surface of the substrate in a two-dimensional manner, growing a
homogeneous crystalline thin film. Nucleation can also occur in the development of three
dimensional structures, called island growth.

This process is governed by the total free energy of the cluster, and the energy of the
individual atoms. This free energy $\Delta G$ can be written in Green’s notation (Eq (14))[6].

$$\Delta G = a_1 r^2 \Gamma_{c-v} + a_2 r^2 \Gamma_{s-c} - a_2 r^2 \Gamma_{s-v} + a_3 r^3 \Delta G_v$$  \hspace{1cm} (14)$$

where $r$ is the radius of the cluster, $\Gamma$ are the interface energies, $a_n$ are constants, $\Delta G_v$ is
the change in volume free energy on condensation, and $c, s, v$ describe the cluster,
substrate, and vapor. If the derivative of the change in free energy of a forming cluster is
positive, then the cluster becomes instable and the atoms tend to separate. If the
derivative is negative, then the cluster will tend to grow. These growing clusters tend to
collect together to form “islands.” From Eq (14) island growth occurs when the following
inequality takes place (Eq (15)) [6]

$$a_1 \Gamma_{c-v} + a_2 \Gamma_{s-c} > a_2 \Gamma_{s-v}$$ \hspace{1cm} (15)$$

where these are the conditions for positive surface free energy on the substrate during
deposition. When this ratio does not hold, and the surface free energy on the surface is
negative, then perfect, crystalline, monolayer growth occurs (Fig. 22b) [10].
Growing perfect monolayers of crystal growth on the surface of the substrate using the PLD technique is difficult (Fig. 23). One roadblock is a voltage/energy minimum required for lasing in the excimer laser. The voltage limit (16 kV) sets a minimum to the overall energy of the target material as it ablates onto the surface of the substrate, below which, the nucleation tends toward layer-by-layer growth. The excess energy imparted from the laser in our case, helped in creating conditions favorable for island growth.

One model of atomic nucleation during deposition involves Young’s equation (Eq (16)) [7]

\[ \gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta \]  

(16)

where γ is the interfacial energy, the subscripts s, f, and v stand for the substrate, film, and vapor, respectively, and θ is the contact, or wetting angle.
For values of $\theta > 0$ (Volmer-Weber) $\gamma_{sv} < \gamma_{fs} + \gamma_{fv}$. That is, the interfacial energies involving substrate are lower than the energies of the film. This relation represents the state in which the surface tension of the film is greater than that of the substrate. This creates conditions favorable for island growth. Energetically, the clusters tend to clump together on the film surface.

For values of $\theta \approx 0$ (Frank-Van der Merwe) $\gamma_{sv} > \gamma_{fs} + \gamma_{fv}$. Under these conditions, layer-by-layer growth dominates the formation of the film layer.

For the final type of growth (Stranski-Krastanov), the interface between the layer and the substrate are similar enough that $\gamma_{fs}$ basically equals zero at $\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv}$ [7] (Fig. 24)

![Figure 24: Atomistic Nucleation Process during Deposition.]

The structure of the grain boundary network in polycrystalline solids has characteristics similar to those of soap froth. One topological model of grain formation is the soap-froth model (Figs 25-27) [10].
Figure 25: Microstructural Evolution during Grain Growth.

Figure 26: SEM Image of Thin Film Island Growth on BSBT.
Figure 27: Nucleation on Substrate during Deposition: a) Pre-deposition b) Initial Adatom Motion into Aggregates c) Island Formation d) Final Film after Deposition e) Coverage by Top Electrode.
ATOMIC FORCE MICROSCOPY

AFM consists of a laser source, flexible cantilever of known spring constant, four quadrant photodiode, and a detector with feedback electronics (Fig. 28) [11].

AFM operates by scanning a probe tip across the surface of a sample, line by line, in a raster pattern. The tip itself does not come into actual contact with the surface. As the tip approaches the surface, Coulomb and Van der Waals forces become strong enough to cause deformation of the cantilever (Fig. 29). Coulomb forces are strong, short-ranged repulsive forces that arise from the electrostatic repulsion of the electron clouds of the tip and the sample. Van der Waals forces are longer range attractive forces between molecules. Van der Waals forces can describe forces between two permanent dipoles, the force between a permanent dipole and an induced dipole, as well as the force between two instantaneously induced dipoles.
As the cantilever is lowered toward the surface of the sample, Van der Waals forces tend to bow the cantilever toward the sample. As the cantilever is moved closer to the surface, the Coulomb forces tend to bow the cantilever in the opposite direction, away from the surface. It is necessary for the cantilever to be flexible to respond to the atomic interaction between tip and sample. As the tip moves across the surface of the sample, the cantilever can be deflected along three directions. A scanner is used to move the probe tip over the surface. The scanner consists of a tube of piezoelectric material connected to the probe tip. Piezoelectric material constricts and expands upon application of an electric field. This piezoelectric response controls the position of the tip with high accuracy.
The AFM feedback cycle begins with positioning the laser source onto the reflective top of the cantilever. The laser reflects from the cantilever onto a small, highly sensitive photodiode. The photodiode is composed of four quadrants. The laser is originally aligned in the center of the quadrants. As the cantilever is brought close to the surface of the sample, the deflection of the tip is translated to the top of the cantilever. In this way, the laser is scanned across the four quadrant photodiode. This information is fed to a control system on a computer. As the cantilever tip is deflected upward, this translates to an increase in the height measurement. Information about the deflection of the cantilever is collected by the photodiode into the computer, then through software that is used to control the parameters of the scanning such as deflection set points that control maximum deflection of the cantilever, feedback gains for cycle times, and scan rates. As the cycle iterates during the probe tip raster across the surface, a three dimensional image of the material is scanned into the computer. From this the overall surface topology of the material is obtained, as well as information such as surface roughness.

AFM contact mode brings the probe sample close enough to the surface of the sample to measure a resistive force of $10^{-9}$ N (Coulomb force). This small force is measured by the compression of a piezoelectric crystal. Piezoelectric materials deform under an electrical signal. Conversely, these materials generate a small electric signal when they are deformed. As the crystal is deformed by the small movement of the cantilever, an electric signal is sent through a DC feedback amplifier. This information is used to adjust the voltage to the controller as the tip scans laterally across the surface. AFM non-contact mode hovers the probe above the surface around 50-150 Angstroms. The attractive Van der Waals force is detected at this distance. Due to the fact that Van
der Waals forces are weak, the cantilever is set to vibrate at a certain frequency. AC
detection methods are then used to detect changes in the amplitude, phase, or frequency
of the oscillating cantilever, in response to the interaction with the sample surface.
AFM tapping mode the cantilever is oscillated at a high frequency, between 50,000 to
500,000 cycles per second. The oscillation is held constant through the feedback loop. As
the cantilever nears a surface, the probe tip contacts the surface and immediately lifts off.
This contact causes a change in the operating amplitude, and measured as height [12].
X-RAY DIFFRACTION SPECTROSCOPY

X-rays have short wavelengths comparable to the size of atoms, on the order of angstroms. The X-rays are generated by a focused electron beam accelerating across a potential, incident on a solid. The sudden change in velocity of the electrons in the beam creates an array of X-rays. In the XRD unit used in our characterization, radioactive isotope of copper is used as the solid material, yielding X-rays of a specific wavelength. The X-rays travel along a grazing angle to the lattice planes of the sample. In elastic scattering between the X-ray source and the electrons in the sample, an angle is formed between the X-ray source, the sample, and a detector on the other side. The X-rays can penetrate different lattice planes in the sample. As the X-rays reflect from the sample, wave-like interference pattern emerge. This interference can be constructive, or destructive, amplifying the intensity of the X-rays as they reach the detector, or damping the intensity. This occurs at each angle of the incident X-rays with respect to the grazing angle across the sample. The relation of this angle, the spacing of the lattice planes, and the intensity given by the diffraction pattern is given by Bragg’s Law (Eq (17))

\[ 2d \sin(\theta) = n\lambda \]  \hspace{1cm} (17)

where \( d \) is the lattice spacing, \( \theta \) is the grazing angle, \( n \) is an arbitrary integer number, and \( \lambda \) is the X-ray wavelength (Fig. 30) [13].
Figure 30: Bragg’s Law.

Powder X-ray diffraction is a technique for characterizing materials with randomly oriented grain structures. Concentric rings of scattering peaks are formed according to the spacing in the crystal lattice. These concentric rings are used to determine the underlying structure of the material. In this way, information is gathered from the intensities of the diffracted conic sections (Fig. 31) [14].

Figure 31: X-Ray Powder Diffraction.
These intensities are plotted as intensity vs. θ-2θ plot. Peaks in θ-2θ, correspond to known lattice parameters of materials. In this way, knowledge of crystal structure, as well as constituent molecular makeup of the material can be gained.

SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy is a high resolution imaging system. SEM can generate images at around 100x magnification. A beam of electrons are generated in an electron column above the sample chamber. The electrons are focused into a tight beam by a series of electromagnetic lenses. Scanning coils direct and focus the beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface of the sample.

As the incident electron beam scans across the surface of the sample, electrons are emitted from the sample due to elastic and inelastic scattering. The high energy electrons emitted from the sample due to elastic scattering are called backscattered electrons. Lower energy emitted electrons resulting from inelastic scattering are called secondary electrons. These emitted electrons are captured by an electron detector. The intensity of the measured electrons is represented in the SEM image in terms of brightness of the image. In this way, SEM is able to represent the morphology of the surface of the sample. Scintillator detectors provide secondary imaging by applying a positive voltage to assist in attracting the electrons to the detector. Backscatter imaging uses scintillator detectors, or solid state detectors. Chamber vacuum is also used to allow the electrons to move freely between from the sample to the detector (Fig. 32).
Generally, SEM is used to determine the surface morphology of electrically conductive materials. Incident electrons on the surface of a conductive material can be drawn toward ground. For non-conductive materials, excess charge buildup can occur, causing divergence in the electron beam. This results in “charging effects” or destabilization of the image as it appears on the screen during the raster process. To combat charging effects of non-conductive material, samples can be coated with a thin conductive carbon surface layer. This layer is thin enough so that the morphology of the material is identifiable.
V. RESULTS

MATERIALS

Our investigation of perovskite-type thin films centered around three target materials for PLD ablation:

1. (SCZT) $\text{Sr}_y\text{Ca}_{1-y}\text{Zr}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.8$, $y = 0.01$

2. (CHT) $\text{CaHf}_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0.8$

3. (BSBT) $x\text{BiScO}_3-(1-x)\text{BaTiO}_3$ with $x = 0.36$ (BSBT(36/64))

These target materials were deposited by PLD onto a substrate with a conductive layer on top. The substrate material was single crystal $\text{La}_{0.3}\text{Sr}_{0.7}\text{Al}_{0.65}\text{Ta}_{0.35}\text{O}_3$ (LSAT). The conductive layer on top of the substrate was $\text{SrRuO}_3$ (SRO). In this way, after deposition, the conductive SRO layer acted as a bottom electrode, with the deposited dielectric material on top. Gold discs sputtered on top of the dielectric material were used as top electrodes (Fig. 33).

![Figure 33: Thin Film Layers.](image)

The laser used during deposition was a Lambda Physik excimer laser with a 248 nm (UV) wavelength. The CHT and SCZT targets were prepared by the University of Pennsylvania. The LSAT substrates were prepared by MTI Corporation, Richmond, CA.
The SRO conductive buffer layer was prepared under the conditions of 300 mTorr partial oxygen pressure, a substrate temperature of 750°C, and a laser repetition rate of 10 Hz.

DEPOSITION CONDITIONS

The depositions were performed with the use of a LabVIEW program which monitored and controlled all growth conditions. Parameters that were monitored during the depositions included: laser voltage, pulse energy, background gas pressure, laser repetition rate, total deposition time, substrate temperature, and time of flight (TOF) for ablated species from targets. The repetition rate of the laser was set for 10 Hz in all depositions. The LabVIEW program was designed to adjust the laser voltage and energy in order to maintain a set TOF. The TOF for all depositions was between 3.5 μsec and 8.0 μsec which had been shown to provide good quality thin films. The background gas pressure was applied by evacuating the chamber to 10^{-7} Torr and back filling it with O₂ during deposition. After each deposition was completed an oxygen annealing was done to ensure an optimal amount of oxygen and guarantee its stoichiometry. This was done by cooling slowly under oxygen pressure used at the given deposition condition to 550°C and then dwell at this temperature and at the elevated partial oxygen pressure of 500 Torr for 0.5 hours. Finally, the samples were cooled down to room temperature.

The choice of appropriate deposition conditions produced the best quality thin films which ensure both good stoichiometry and smooth surfaces keeping in mind, their possible future applications as a part of the electronic devices. From our previous experience, we have concluded that, for example, in the case of 0.2BiScO₃ – 0.8BaTiO₃ (BSBT(20/80)) thin films (Table 1 and Fig. 34), the best results have been achieved for
depositions at the low oxygen partial pressures (50 mTorr or 100 mTorr) and elevated temperatures between 700°C and 750°C.

<table>
<thead>
<tr>
<th>RMS SURFACE ROUGHNESS (AFM)</th>
<th>BSBT(20/80)/SRO750C(300 mTorr)/LSAT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Film No.</strong></td>
<td><strong>3485</strong></td>
</tr>
<tr>
<td>100 mTorr</td>
<td>600 C</td>
</tr>
<tr>
<td>5x5 μm²</td>
<td>15.4 nm</td>
</tr>
<tr>
<td>1x1 μm²</td>
<td>10.7 nm</td>
</tr>
<tr>
<td><strong>Film No.</strong></td>
<td><strong>3435</strong></td>
</tr>
<tr>
<td>300 mTorr</td>
<td>600 C</td>
</tr>
<tr>
<td>5x5 μm²</td>
<td>14.1 nm</td>
</tr>
<tr>
<td>1x1 μm²</td>
<td>10.8 nm</td>
</tr>
</tbody>
</table>

Table 1: RMS Surface Roughness (AFM) of BSBT(20/80).

![SEM Micrographs for BSBT(20/80) Thin Films.](image)

Figure 34: SEM Micrographs for BSBT(20/80) Thin Films.
We have also concluded that the conductive buffer layer SrRuO$_3$ deposited first on a single crystal buffer layer of LSAT has the best crystallinity at the following deposition conditions: deposition temperature of 750$^0$C and oxygen partial pressure of 300 mTorr (Fig. 36).

![XRD Graphs](image)

Figure 35: XRD Graphs for SrRuO$_3$ (SRO) Thin Films Deposited at Three Different Temperatures 650$^0$C, 700$^0$C and 750$^0$C and at the Partial Pressure of Oxygen 300 mTorr.

Most of the thin films were deposited under lower oxygen pressure of 50 mTorr or 100 mTorr and at elevated temperatures up to 800 C. All films including buffer layer were 0.5 μm thick. However, the SrRuO$_3$ buffer layer was deposited at previously known optimized conditions of 300 mTorr oxygen pressure and the substrate temperature of 750$^0$C or 800$^0$C. The deposition of buffer layer took place at 800$^0$C when thin films of CNT, SCZT and BSBT(36/64) were deposited at 800$^0$C also in order to avoid additional stresses or strains imposed on the substrate. In Appendix B, the deposition conditions of buffer layers are listed next to their thin film conditions. The time of flight (TOF) was set to be between 3.5 μsec and 8 μsec for all of them and as a result the laser power and voltage have been automatically adjusted to meet this requirement.
Two different LSAT substrate attachment options on the PLD resistive heater were checked. One of them requires a hastelloy sheet which was attached to the resistive heater directly with the LSAT substrate on it in order to avoid overheating of substrates during thin film deposition. These series of thin films we called “OLD”. Other depositions had the LSAT substrate pasted directly to the heater and we named them “NEW”.
AFM MEASUREMENTS

The surface morphology of the thin films was given by AFM measurements.

These AFM measurements were grouped together for comparison by deposition temperature. On inspection, the conditions for largest grain size according to AFM occur at 700°C (Figs 36-38 and Table 2).

Figure 36: BSBT (36/64)_NEW at the Constant Pressure of 50 mTorr.
Figure 37: CHT_NEW at the Constant Pressure of 50 mTorr.

Figure 38: SCZT_NEW at the Constant Pressure of 50 mTorr.
<table>
<thead>
<tr>
<th>Film No.</th>
<th>T(C)</th>
<th>RMS (nm)</th>
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<td></td>
<td></td>
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<tr>
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<td>3553</td>
<td>800</td>
<td>1.1</td>
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Table 2: AFM Roughness Measurements of Dielectric Thin Films.

AFM roughness measurement gave an idea of the relative smoothness of the deposition layer. Deposited samples with greater roughness values correlate to deposition conditions more favorable for island growth and smaller grain size.

Values for grain size were plotted for the samples for optimization of deposition temperature (Fig. 39).
At the same time, roughness measurements were performed by AFM over an area of 5 μm x 5 μm. These showed relatively smooth surfaces in a range of a few nanometers (RMS) with the best result of 0.6 nm for SCZT_NEW film deposited at 800°C and 50 mTorr oxygen partial pressure. However the average smoothness is the best for films deposited at 700°C exactly where grain sizes are large. BSBT(36/64) and CHT films deposited at 700°C have identical values of 1 nm with the SCZT film of 0.9 nm at the same temperature.
XRD characterization (Fig. 40) reveals the substrate, conductive buffer layer, and deposition layer of the dielectric thin film. The angular position of the peaks yields information about the crystallographic structure of each of the layers. Information about the grain size of the layer is embedded into the XRD data. This information was calculated using the Scherrer equation.

The Scherrer equation relates the mean grain size ($\tau$) to the line broadening of the XRD peak ($\beta$) at the full width, half maximum (FWHM) intensity (Eq (18))

$$\tau = K \lambda / \beta \cos(\theta)$$ (18)

where $K = 0.94$, a dimensionless shape factor, $\lambda = 0.15405$ nm is the X-ray wavelength, and $\theta$ is the Bragg angle.
Some thin films did not have clear separation of the XRD peaks. Figure 42 shows two overlapping intensity peaks along a $\theta$-2$\theta$ range of approximately 100 to 103 degrees. For samples with overlapping intensity peaks, it was necessary to approximate the contributions of each peak (one for the CHT film, and one for the buffer layer of SRO) using Gaussian fitting curves, then fit their sum to the overall XRD peak. This was done using XRD peak deconvolution software.

Gaussian fitting curves used to approximate the intensity peaks of the deposition layer of CHT and the buffer layer of SRO, respectively. Their sum was used to fit the original XRD curve. In this way, the position and FWHM value of the deposition layer intensity peak CHT could be separated from the position and FWHM values of the buffer layer. This allowed Scherrer’s equation grain size calculations.

Curve fitting of the XRD deposition intensity peak gives FWHM or its peak width (Fig. 41). Gaussian decomposition is necessary to resolve individual overlapping peaks.

Figure 41: Deconvolution of CHT_NEW for 750$^\circ$C.
DIELECTRIC MEASUREMENTS

BSBT(36/64) samples of two grain size (23 and 38 nm) were evaluated using impedance spectroscopy on a Solartron 1296 Dielectric Interface system, running off a Solartron SI 1260 Impedance gain-phase analyzer. Frequency values were scanned from 100 Hz through $10^6$ Hz. Values were given by the software for frequency, AC level, DC level, real and imaginary impedance, real capacitance, and tan delta. The real and imaginary plots were used to produce Cole-Cole plots. The values for tan delta vs. frequency were used to create the Bode plots.

Information is embedded into the values for impedance. Total impedance, consisting of the real and imaginary part, can be transformed into other information about the electrical properties of the material, such as admittance, permittivity, and electric modulus. The key to making these transformations is in calculating the value of the capacitance of the system of electrodes used to measure the film, as if there was only nothing between the terminals. This is done by setting the value for the dielectric constant in the capacitance equation equal to one, the constant for vacuum.

The equation for capacitance for the arrangement of electrodes in our experiment is given by Eq (2) where $\varepsilon_0$ is the permittivity of free space (8.85x10$^{-12}$), d is the space between the electrodes (3.0x10$^{-7}$m), and A is the area of the sputtered gold top electrode (1.188x10$^{-6}$m$^2$). Solving Eq (2) for the dielectric constant ($\varepsilon_r$) we ended up with Eq (3). The value for capacitance in vacuum where there is no dielectric medium between the electrodes, ($C_0$) can be calculated (Eq (19)) by using the value for the relative permittivity of free space ($\varepsilon_r = 1$).
The dielectric constant was shown to be higher for larger grain sizes (Fig. 42).

![Dielectric Constant vs. Frequency](image)

**Figure 42:** Dielectric Constant for BSBT(36/64).

Both samples showed tan delta loss at the lower frequencies (Fig. 43). They had a corresponding peak at higher frequency due to a relaxation process caused from frictional losses from molecular polarization contribution to the overall polarization.

![Tan delta vs. Frequency BSBT(36_64)](image)

**Figure 43:** Tan Delta vs. Frequency.
ZVIEW software was used in analysis of the raw impedance information. ZVIEW was used to create plots of imaginary vs. real impedance. The software was used to fit this plot. ZVIEW was also used to generate data set fitting from equivalent circuit models. Impedance is a broad term that covers the real and imaginary parts of resistors, capacitors, and as well inductors (Figs 44-45). Equivalent circuit diagrams are useful in generating concrete data about the electrical properties of the material (Fig. 46).

![Impedance Plot and AFM for BSBT(36/64) 23 nm Grain Size.](image)

The value for estimated capacitance C increases as grain size increases. The values for estimated real resistance of grains and grain boundaries (in Ohms) decrease as grain size increases. The values for both real and imaginary impedance decrease with increasing grain size (Fig. 43).
Figure 45: Impedance Plot and AFM for BSBT(36/64) 38 nm Grain Size.

![Impedance Plot](image1.png)

![AFM Image](image2.png)

ZVIEW was used to model the samples using a series resistance in line with a parallel resistor-capacitor circuit.

Values for 23 nm grain size were: \( R(S) = 921.3 \, \Omega \), \( R(p) = 64.5 \, \Omega \), and \( C = 30.5 \, \text{nF} \).

Values for 38 nm grain size were: \( R(S) = 128.6 \, \Omega \), \( R(p) = 15.7 \, \Omega \), and \( C = 77.8 \, \text{nF} \).

The values for estimated capacitance \( C \) from equivalent circuit (Fig. 47) were on the same order of magnitude as the values calculated by the Cole-Cole plot fit for capacitance \( (C_{gb} - \text{capacitance of grain boundaries}) \) given in Figs 44-45. The values for
the parallel resistance $R(p)$ are close to those of estimated resistance ($R_{gb}$ – resistance of grain boundaries) given in those figures. Finally, the large series resistance $R(s)$ given by the equivalent circuit diagram is equivalent to $R_g$ (resistance of grains) described by Cole-Cole plot as intersection of semicircle with $Z'$ axis (see Figs 44-45).
VI. CONCLUSION AND FUTURE WORK

Comparing the AFM RMS surface roughness measurements from Table 1, with visible inspection of the surface morphology of the grains by SEM in Fig. 34, the connection between surface roughness and grain size was seen. Deposition conditions of 50 to 100 mTorr, and temperature between 700 and 750 °C showed best results for largest grain size. Relative grain size was also compared using AFM images from Figs 36-38. The comparison of largest grain size also corresponded with smallest AFM RMS surface roughness from Table 2.

The Scherrer equation estimate for grain size gave qualitative information about relative grain size of the samples. This estimate came from Gaussian curve fitting of the XRD peaks for the crystalline deposition layer. Using the overlap of these three methods, we were able to identify the optimum deposition parameters for largest grain size formation.

Our study suggested that the best dielectric films of SCZT, CHT, and BSBT(36/64) fabricated by PLD in terms of the smallest roughness of the surface and the largest grains were obtained at 700°C deposition temperature and at 50 mTorr oxygen partial pressure.

These results concluded the initial part of our work. We were able to determine the deposition parameters that led to the largest grain size in our materials. We were also able to correlate larger grain size in the materials with smoother surface roughness of the films.
In the second part of our work, we began the initial investigation into the
dielectric properties of the films using impedance spectroscopy. A comparative analysis
of BSBT(36/64) for two grain sizes showed a higher value for the dielectric constant for
the larger grain. Using the equivalent circuit model suggested by literature for the shape
of our Cole-Cole impedance data, we were able to fit physical parameters for the grain
and grain boundary (resistance and capacitance). These values closely matched the
approximations based on a second and independent method, curve fitting of the
semicircle plot. These fitting parameters were important tools to extract tangible values
about the grain and grain boundary, from the complicated real and imaginary components
involved in impedance only measurements.

Future work will involve a more detailed theoretical evaluation of the capacitance
and resistance of the grain and grain boundaries for all thin films fabricated by PLD
system in AFRL. Our current results show a higher contribution of both resistance
contributions for smaller grain size, and a higher capacitive element for larger grain size.
Important topics to be covered will be determining the activation energies of the grain
boundaries, and their contributions toward resistance to conduction through the dielectric
on one end, and possible contribution to accumulation of space charges leading to
anisotropy in the overall polarization, on the other. These electrical effects based on film
morphology will be important in understanding pulsed laser deposition’s contribution to
the development of thin film dielectrics.
VII. REFERENCES


## APPENDIX A

Properties of Dielectric Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>ε&lt;sub&gt;r&lt;/sub&gt;</th>
<th>E&lt;sub&gt;b&lt;/sub&gt; (MV/cm)</th>
<th>U&lt;sub&gt;vol&lt;/sub&gt; (J/cm&lt;sup&gt;3&lt;/sup&gt;)</th>
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<td>Nanocomposite polyvinylidene fluoride (PVDF)</td>
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<tr>
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<td>0.73</td>
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</tr>
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<td>8</td>
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<td>SrTiO&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>Sr&lt;sub&gt;x&lt;/sub&gt;Ca&lt;sub&gt;1-x&lt;/sub&gt;Ti&lt;sub&gt;0.9&lt;/sub&gt;Zr&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (0 ≤ x ≤ 0.3)</td>
<td>(145–232)</td>
<td>–</td>
<td>–</td>
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<td>(34–75)</td>
<td>(0.65–1.75)</td>
<td>≤ 5</td>
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<tr>
<td>0.8CaTiO&lt;sub&gt;3&lt;/sub&gt; – 0.2CaHfO&lt;sub&gt;3&lt;/sub&gt; (CHT)</td>
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<td>1.20</td>
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Table 3: Bulk Properties of Dielectric Materials.
### APPENDIX B

Deposition Conditions

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<th>Film No.</th>
<th>T(C)</th>
<th>P(mTorr)</th>
<th>TOF(µsec)</th>
<th>Power(mJ/P)</th>
<th>Voltage(kV)</th>
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Table 4: SCZT_NEW Deposition Conditions.

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<th>Power(mJ/P)</th>
<th>Voltage(kV)</th>
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Table 5: BSBT(36/64)_NEW Deposition Conditions.
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Table 6: CHT_NEW Deposition Conditions.
Table 7: CHT_OLD Deposition Conditions.

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Table 8: BSBT(36/64)_OLD Deposition Conditions.
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<th>TOF(µsec)</th>
<th>Power(mJ/P)</th>
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Table 9: SCZT_OLD Deposition Conditions.