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ATOMIC LAYER DEPOSITION OF
FERROELECTRIC COMPLEX
OXIDE THIN FILMS

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*For my parents and everyone
else who helped out along the way...*

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Abstract

Advanced technologies derive many of their capabilities from the advanced materials that they are made from. Complex oxides are a class of materials which are driving technological advancement in a host of different directions.

210 These highly functional materials have a great variety of useful properties, which can be chosen and even engineered through careful choice of material.

Advanced materials require advanced deposition methods. Atomic layer deposition (ALD), a variant of chemical vapor deposition (CVD), is gaining more use in industry for its ability to provide ultra-high film thickness resolution (down to 0.1 nm), capability to conformally coat three-dimensional structures, and its high uniformity across large surface areas. Additionally, ALD processes provide a possibility to improve economic and environmental viability of the process as compared to CVD by using and wasting less toxic reactants and expelling fewer nano-particulate byproducts.

220 ALD processes are highly mature for many binary oxides commonly used in the semiconductor industries, however processes for depositing heavy metal oxides and complex oxides — oxides containing two or more separate metallic cations — are sorely lacking in literature.

The primary focus of this work is the development of a process for depositing the complex perovskite oxide lead titanate ($PbTiO_3$), an end group of the lead zirconate titanate family ($PbZr_xTi_{1-x}O_3$), which has valuable technical applications as well as serves as a template for applying this research into other material systems.

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Sommario

In this study, a method is proposed for the development of a novel ALD thin-film deposition process. This involves the identification, testing, and selection of precursors; analysis of growth parameters and their effects on the produced films; and in-depth *ex situ* characterization of prepared films via a variety of techniques.

The material under consideration is lead titanate (PTO , PbTiO_3), which is an end group of the lead zirconate titanate family (PZT , $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$). Lead titanate is a complex perovskite oxide, which exhibits ferroelectricity at room temperature and has a high Curie temperature at which it transitions to paraelectric behavior. Ferroelectricity is an interesting material property, as it involves a hysteretic behavior with regard to the polarization of the material. This allows the material to switch from one state to another and recall this stored polarization even without the presence of an electric field. This property has a wide variety of applications in electronics and other physical sciences.

There are a large number of potential deposition techniques for thin film structures. Some, such as sol-gel processing, work on the principles of wet chemistry and allow for the formation of films with a tightly controlled composition. However, such techniques come with all of the drawbacks of solution based methods. Chemical vapor deposition (CVD) is another very common deposition method for thin films. It has a number of advantages, such as the capability to epitaxially deposit films (which greatly improves interface quality). However, it is not easy to precisely control film thicknesses and conformally coating non-planar structures is a very difficult task.

Atomic layer deposition (ALD) is a modification on standard CVD processes. It separates the reaction between the metallic precursor and the oxidant into two half reactions. These half reactions are only capable of occurring on the surface of the substrate, as opposed to occurring in the gas phase. By separating the reactions a number of important changes happen. One of the most critical, and a hallmark of an ALD deposition, is that the reaction becomes self-limiting. A half reaction can only deposit at most a single monolayer of material. This gives the incredibly high thickness resolution that can only be obtained by a very few processes. ALD is capable of resolutions down to the angstrom level ($1 \text{ \AA} = 0.1 \text{ nm}$). This self-limiting behavior also gives ALD some of its other advantages, such as the ability to precisely and conformally coat

a complex three-dimensional structure with the same high resolution. This is nearly impossible with any other deposition process.

ALD precursors are more particular than those for CVD. They must be reactive with the surface and with an oxidizer, but they cannot be capable of reacting with themselves. The temperature required to activate the reaction with the surface must be lower than the temperature required to pyrolytically crack the molecule. Finally, at the end of each pair of half reactions new surface sites capable of reacting with the precursor must be repopulated with the proper ligands.

A commonly used ALD precursor for titanium is readily available: titanium(IV) isopropoxide. However, there is no single ideal ALD precursor for lead. Of a number of different compounds two were chosen for further inspection: bis(2,2,6,6-tetramethyl-3,5-heptanedionato) lead(II) ($\text{Pb(TMHD}_2\text{)}$) and lead(II) hexafluoroacetylacetone ($\text{Pb(HFAC}_2\text{)}$).

The two selected precursors were analyzed using thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC). Between the two techniques it was possible to identify the regions of ideal volatility as well as a potentially viable temperature range where ALD reactions could take place. From this analysis, it was expected that $\text{Pb(TMHD}_2\text{)}$ would perform better in an ALD process than $\text{Pb(HFAC}_2\text{)}$.

A number of samples were prepared and analyzed. Variable angle spectroscopic ellipsometry was used to measure film thicknesses and growth rates, along with some optical and electronic properties. Calibrated X-ray fluorescence spectroscopy (XRF) was used to obtain quantitative compositional analyses on the samples. X-ray diffraction (XRD) was used to investigate the phases present and their relative concentration in the final samples.

In concluding this study, it was found that it is possible to grow complex perovskite oxides via ALD. However obtaining crystallized samples of pure perovskite phase was non-trivial and requires more investigation to fully accomplish. However, the study did manage to develop a valuable procedure for developing ALD processes of various materials.

Further work would include analysis of the ferroelectric behavior of the films, improving phase purity in the final samples, and extension of the method to creating depositions for other material systems such as $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ or barium strontium titanate (BaSrTiO_3).

Chapter 1

Introduction

Modern technology stands on the shoulders of modern materials, and the
305 two are inextricably linked together. Whenever a new material or property
has been discovered or engineered, applications of this new capability lie just
over the horizon.

One of the hotbeds of innovation and interest in novel applications of
material properties is the field of oxide chemistry. Such a seemingly simple class
310 of materials, examples of which are two of the most abundant compounds on
Earth (i.e. silica and alumina), has an incredibly rich set of capabilities derived
from the incredible variety of potential materials. One example is the field of
high-K dielectric oxides, such as hafnium oxide (HfO_2) and zirconium oxide
(ZrO_2), which are allowing the semiconductor industry to produce more capa-
315 ble devices while reducing power draw. Ferromagnetic and antiferromagnetic
oxides form the basis of the ubiquitous magnetic hard disk drive, advance-
ments in deposition and microstructure control allow for the steady increase
in capacities that consumers have become accustomed to.

The class of ferroelectric oxides comprises the family of materials that this
320 thesis will consider. One material in particular will be the primary subject:
lead titanate (PTO, PbTiO_3). Lead titanate is one end group of the lead
zirconate titanate family of ferroelectric oxides (PZT, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$). The PZT
family is of particular technical importance to many applications, especially
the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ form which exhibits exemplary piezoelectric, ferroelectric,
325 and pyroelectric behavior. PZT's piezoelectric capabilities allow for it to be
used as actuators and sensors in innumerable devices (e.g. tip actuators in
AFM microscopes and transducers in ultrasound imagers).

Other applications of such materials are found when they are created as
nanoscale thin films, where these capabilities are both more strongly exhibited.
330 One of the more prevalent methods of producing nanoscale films is chemical
vapor deposition (CVD), a powerful process that has been used to deposit a
vast number of material types and structures.

However, there are disadvantages to the CVD method of film deposition.
Great care must be taken to obtain highly regular film thicknesses, and the

335 method of producing most oxide films — a variation called metallorganic CVD (MOCVD) after the metallorganic compounds used as reactants — allows a significant amount of hazardous material to be released into the environment as toxic and nano-particulate byproducts.

340 Another deposition method, atomic layer deposition (ALD), is becoming popular in industry applications as an alternative to CVD. ALD provides the user with ultra-high resolution on film thickness, a lower operating temperature than nearly all CVD processes, amongst other features. In addition, due to the nature of the process, ALD is capable of consuming far less precursor material as well as utilizing a far larger percentage in depositing the film as 345 opposed to producing the types of byproducts caused by CVD.¹ This makes ALD, in situations where it can be applied, the more economical choice, as well as being more sustainable and environmentally friendly. To this end, the National Science Foundation (NSF) has awarded funding (under 2012 grant #1200940) toward the development of alternative ALD precursors, models, 350 and processes that will attempt to provide additional improvements to the sustainability of ALD.

355 However, well described processes for producing ALD films of many materials have not been developed. Binary oxides (A_xO_y) have been explored in a fair amount of depth, but there is a distinct lack of research work into processes for depositing complex oxide films via ALD.

1.1 Project Scope

360 This thesis will cover the main steps taken in developing a thin film deposition processes using ALD. In chapter 2 lead titanate as a material will be introduced, discussing its structure and some of the desirable properties that the oxide exhibits due to this structure.

Chapter 3 will be devoted to a few of the commonly used methods used to produce films of complex oxides, sol-gel and MOCVD, as well as introducing in detail the primary focus of this project: the deposition of thin films via ALD.

365 Following this, chapter 4 will go into detail of the various choices and parameters that go into the development of an ALD process. Concepts such as the choice of precursors from the various deposition parameters that must be carefully controlled and tuned to produce optimal results.

Chapter 5 will introduce and briefly discuss the topics involved in characterizing the various materials to be utilized in the deposition process, as well

³⁷⁰ as the various techniques used to analyze and quantify the properties of the produced samples.

Subsequently, chapter ⁶ will go into more detail of exactly how these analyses were performed, briefly mentioning various details of the standard measurement techniques as well as going into a bit more detail where analysis ³⁷⁵ procedures were developed for application to this project.

In chapter ⁷, the details of the results and data collected from the various measurements and experiments that were performed during this study will be discussed thoroughly.

Finally, chapter ⁸ will draw conclusions from the entirety of the work done ³⁸⁰ in the course of this project, as well as discuss possibilities for future experimentation and refinement of the process. A prime example of this would be to apply this research into the development of a procedure to produce films composed of the far more technically relevant PZT(52-48).

Chapter 2

³⁸⁵ Lead Titanate

2.1 Structure

Lead titanate (PbTiO_3 , PTO) naturally orders into the tetragonal perovskite crystal structure at room temperature (figure 2.1 on the following page). The structure can be affected by compositional changes, temperature, or strain (primarily in thin-film systems), allowing a transition to a cubic phase. In the perovskite crystal structure, the central cation (Ti^{4+} in the case of PbTiO_3) is encapsulated in a octahedral cage of anions (O^{2-}), with the remaining cations (Pb^{2+}) situated in the eight corners of the unit cell.²⁻¹⁰ If the material was doped (as in a mixed solid-solution), some of the cations would be replaced with the dopant ions, for example Zr^{4+} would be randomly distributed in Ti^{4+} sites in the $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ (PZT) system.²⁻¹⁰

2.1.1 Effect of Temperature

The transition from tetragonal to cubic perovskite is highly dependent on temperature. The critical temperature at which this transition occurs is referred to as the Curie temperature (T_C). If the material cools through this temperature, a lengthening of the ‘c’ axis of the unit cell spontaneously occurs via a first order phase transition. This creates anisotropy in the structure and allows for an anisotropic charge distribution to develop. In lead titanate this is caused by the shifting of the titanium ion, along with a slight shift of some of the oxygen ions as well (visible in figure 2.1b on the next page). Thus, a permanent dipole is created whose magnitude increases as the system cools further from T_C . This permanent dipole allows the system to exhibit ferroelectricity, implying an ability to semi-permanently switch the orientation of the dipole in the material. This switching can be reversed, but this will not occur spontaneously.^{2,6,8,10}

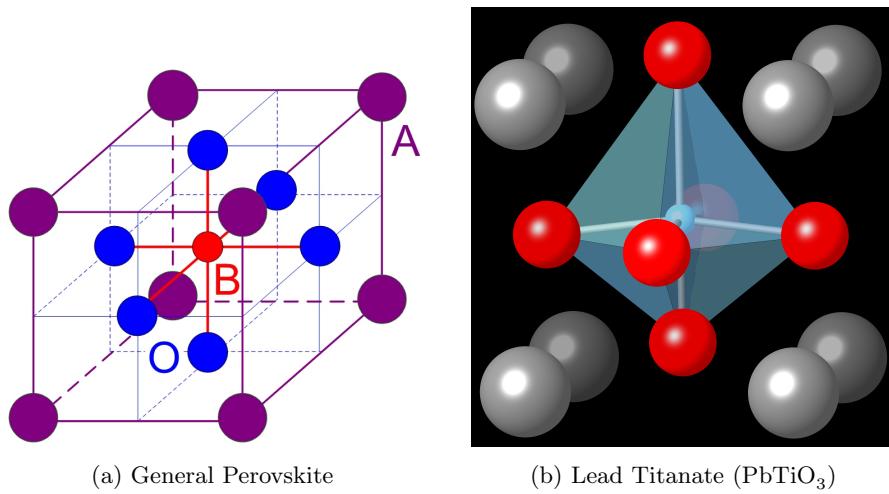


Figure 2.1: The perovskite (ABO_3) crystal structure.

(a) The general structure of perovskite oxides. (b) Tetragonal asymmetric perovskite structure of $PbTiO_3$. Grey, red, and blue spheres refer to Pb^{2+} , Ti^{4+} , and O^{2-} , respectively. Additionally, the octahedral oxygen cage is shown in pale blue.

2.2 Ferroelectricity

Ferroelectricity is the capability of a material to exhibit spontaneous electric polarization that requires external influence, such as an applied electric field, to be reversed. This is different from paraelectric (or even dielectric) materials, where there is no polarization without external field being applied. This can be seen in a plot of energy vs. polarization (fig. 2.2 on the facing page) for the two types of materials. In a ferroelectric material, the energy minima are found at non-zero levels of polarization.^{11,12}

The effect this has on the polarization of the material is profound, and is the hallmark of ferroelectricity. A ferroelectric material, once initially polarized, exhibits hysteresis with respect to its P-E curve (see fig. 2.3b). Thus a ferroelectric material essentially remembers the sign of its last polarization, and retains that even when no polarizing field is present. In comparison, a paraelectric material (fig. 2.3a) would exhibit no polarization without a polarizing field being present.¹¹⁻¹⁴

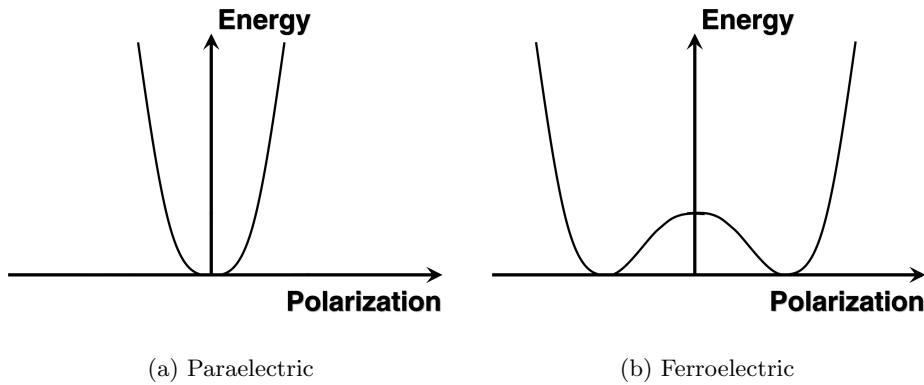


Figure 2.2: Example plots of the energy required to polarize a material. Ferroelectric materials (b) have non-zero polarization at the energy minima. Above T_C all ferroelectric materials transition to a paraelectric phase (a). As temperature increases, the energy minima will approach one another.

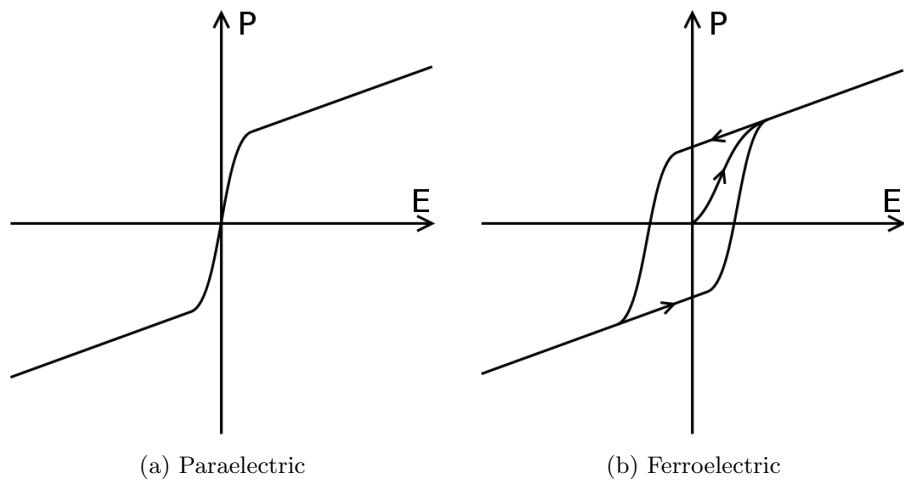


Figure 2.3: Example plots of the polarization as a function of applied field. (a) Paraelectric materials have two regions of polarizability; at low E the polarization increases quickly with the field, as E increases the rate of increase decreases. (b) Ferroelectric materials show similar behavior, but additionally have hysteresis. This means that the films are switchable between two states, but it is difficult to obtain zero polarization.

Chapter 3

Synthesis Methods

Synthesis of perovskite oxides has been demonstrated using a wide range of techniques. These range from solution-based processing methods (sol-gel approach), to physical vapor methods (molecular beam epitaxy and pulsed laser deposition), and gas phase chemical methods (chemical vapor deposition and atomic layer deposition). This review will briefly discuss sol-gel and CVD methodology, but will focus in more depth on films deposited via ALD.

3.1 Sol-Gel Processing

Sol-gel processing is a very commonly used technique for producing oxide films of a wide variety of types. It is rather straightforward in its method, but it is nonetheless a very powerful method for producing films with complex stoichiometries. Being a wet-chemical deposition technique, sol-gel has both advantages and disadvantages. It is a fairly low temperature deposition technique, but in order to obtain a fully dense and crystalline film a sintering and annealing step is often required. The solution-based nature of the chemistry lends itself to very close control of tolerances in the composition of the final film.^{15,16}

Sol-gel processing starts with the production of a colloidal solution containing all of the elemental precursors that are desired, in the precise ratios desired in the final film. Generally these precursors are metallic salts or metallic alkoxides, which are combined and then treated to undergo various co-reactions (hydrolysis, polycondensation, etc.) to form colloidal particles which become suspended in the solvent. By adjusting the pH and viscosity, the precursor sol can be converted into a gel which can be used to form a wide variety of structures such as fibers or powders.^{17,18}

For film synthesis, generally the sol is kept in a relatively low viscosity state and applied to a substrate via spin-coating techniques. Modulating the sol viscosity, rotor speed, and spinning time allows for relatively fine control over film thickness on planar structures, from the nanometer-scale to the micron-scale. The spun fluid is then heated to liberate any remaining solvent and catalyze

the formation of the fully gelled structure. This low-density structure can subsequently be heat treated at a much higher temperature to sinter and anneal the film, providing a much denser sample as well as control over crystallinity and phase. This improves the mechanical stability of the film, due to the densification, and can improve material properties by controlling phase purity by the anneal step.^{15–18}

Sol-gel films are very commonly used to produce many different types of high-tech oxide films. $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ¹⁹ is a very common ferroelectric material that is commonly produced in powder, film, and bulk forms via this technique. $\text{BaSr}_x\text{Ti}_{1-x}\text{O}_3$ is another.²⁰

Some of the disadvantages of sol-gel film deposition is the lack of truly precise control over the film thickness, its difficulty in evenly coating many types of 3-dimensional structures, as well as being somewhat difficult to integrate into conventional lithographic electronics processing.^{15–18}

3.2 Metallorganic Chemical Vapor Deposition

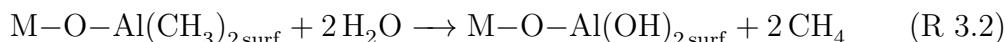
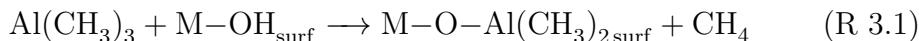
Metallorganic chemical vapor deposition (MOCVD) is a commonly used technique for depositing many different types of thin film materials. It is especially common for MOCVD to be used to deposit semiconductor films (a-²¹ Si, Ge, III-V, II-VI, etc.); these films can also be doped to varying degrees with high precision.^{21–23}

A CVD process begins with the introduction of reactant vapors into the reactant chamber. The chamber is heated to a temperature sufficient to cause pyrolysis — thermal cracking — of the reactant. This liberates the desirable element, the metallic portion of the compound, allowing it to adsorb to the substrate. Over time a thin film is deposited. Films of multiple elements are formed by introducing two different reactants into the chamber simultaneously; the same principle works for dopants, but at a much lower concentration.^{21–23}

One advantage of CVD, partly due to the high deposition temperatures involved, is the ability to have the film deposit epitaxially to the substrate. This allows for the creation of perfect, or nearly perfect depending on the lattice matching between film and substrate, interfaces. This is very desirable for a great number of applications, primarily in the semiconductor field.^{21–23}

3.3 Atomic Layer Deposition

490 Atomic Layer Deposition (ALD) is a modification on standard CVD processes, with a few major differences. The defining aspect of an ALD process is the separation of the overall reaction into two steps: first the precursor is allowed to react with the substrate surface (see reaction R 3.1), excess reactant is purged from the chamber and an oxidizer is introduced to complete 495 the reaction (see reaction R 3.2).¹ These reactions show a very simple ALD reaction between trimethylaluminum (TMA, Al(CH₃)₃) and water.



500 In this example, it is seen that the first stage allows the TMA to react with the hydrated substrate surface to form part of a layer of alumina (Al₂O₃), liberating a molecule of methane as a byproduct. In the next step, the remaining ligands are stripped away from the bound TMA molecule and replacing them with hydroxyl groups. This returns the system to the initial state — where the surface is presenting sites available to react with more TMA — and the cycle is completed. A graphical example of this process can be found in figure 3.1.

Having only surface reactions be permitted, as opposed to CVD where gas-phase interactions dominate, affords ALD a number of unique characteristics. One of these is the concept of the “self-limiting” growth mode.¹ This behavior arises from the limited number of available reaction sites; when all of these have either been reacted with or made unavailable by a blocking mechanism such as stearic hindrance from other local chemisorbed precursor the reaction can no longer proceed. At this point, additional available precursor is not going to be utilized, and instead will be removed and treated as waste material. The system is then evacuated, and a inert purge gas such as dry nitrogen or argon is flowed through the reactor. The purge gas serves both to push any remaining gases out of the reactor as well as to help desorb physisorbed species from the surface. The system would then again be evacuated, and the oxidant introduced and then pumped away to complete the cycle. Because of the self-limiting behavior of the reactants it is possible, in fact preferable, to utilize reactants that have highly energetic reactions with their corresponding surface site. For ALD, having fast and energetic reactions allows for rapid completion of the half-cycle, which allows for faster cycle times and thus higher 515 520

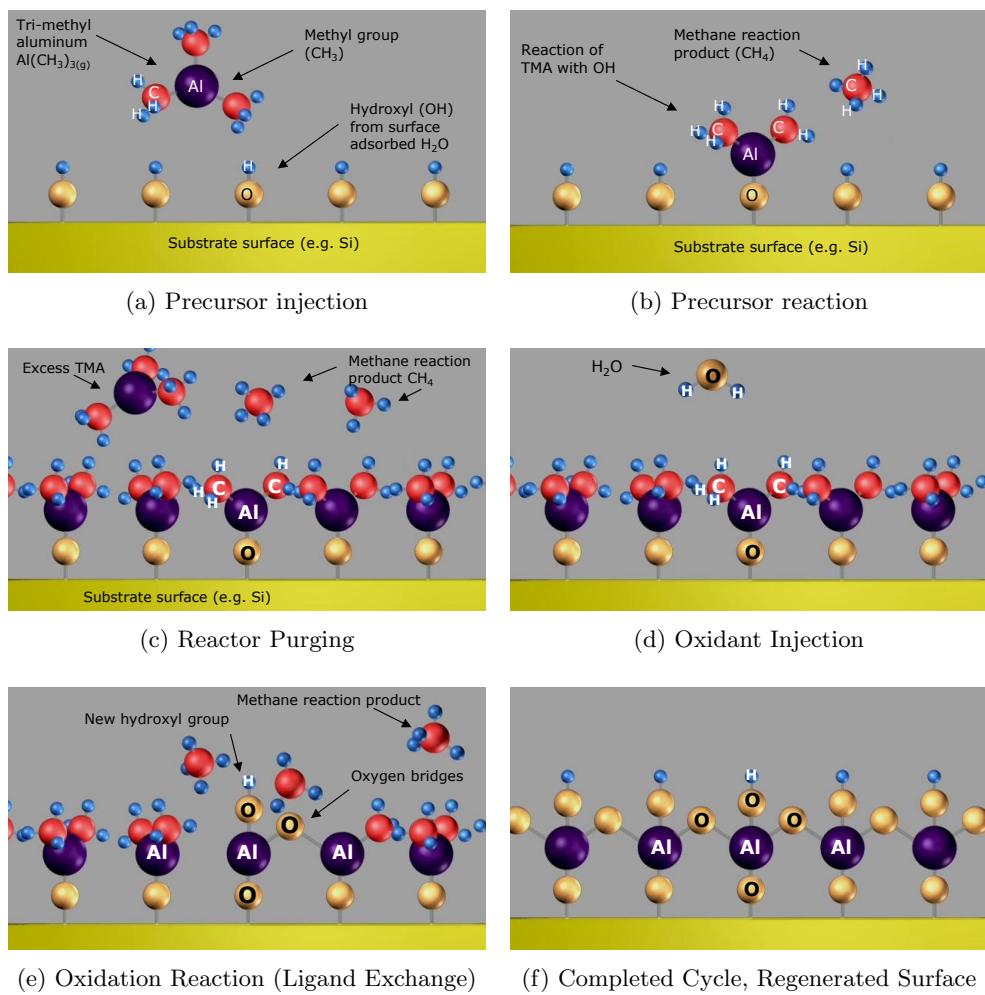


Figure 3.1: Example schematic of the process of an ALD deposition cycle. This example illustrates the reaction of TMA and water to form alumina (Al_2O_3).

Graphic courtesy of Cambridge NanoTech, inc.

throughputs. In CVD such energetic reactions are very difficult to control, and instead precursors that have only mild reactions — with a Gibbs free energy exchange as close to zero as possible while remaining negative — with each other are preferred. These require more effort to develop and require that the process be carefully controlled, as the reactions often can either easily extinguish themselves or rapidly accelerate in different conditions.¹

In the implementation of most ALD systems, the purge gas is also used as a carrier gas for the precursors. Thus a constant flow of gas is passed through the system, instead of having it occasionally fully evacuated, and the precursor is able to be delivered from its source to the reactor more effectively. For some precursor compounds, in particular those with a low vapor pressure, having carrier-assisted transportation can greatly improve the behavior of the system.¹

Because of the self-limiting behavior, each deposition cycle is limited to a theoretical maximum of one monolayer of material (in practice a much lower coverage per cycle is attained), which is far less than a unit cell.¹ Generally per cycle growth rates range between 0.03–1.5 Å, with the rate being nearly invariable during most of the deposition. This gives the second defining characteristic of ALD: very high (Å level) thickness resolution. The downside of this aspect is that growths are generally much slower than other types of depositions; ALD is generally slower by an order of magnitude or more than a similar CVD process, as an example. This has proved invaluable in many processes where high precision is critical, such as electronics manufacturing. Intel, for example, uses ALD to deposit extremely precise layer thicknesses of a high- κ dielectric (such as hafnia, HfO₂) for use as the gate oxide in transistors.^{24,25}

There are a wide range of binary oxides for which ALD processes have been developed. A deposition for alumina (Al₂O₃, one of the first ALD materials developed, was discussed briefly above and the method is common use.^{26,27} High- k gate oxides such as hafnia and zirconia (ZrO₂), along with some of their nitrides and silicides, are under intense research to develop industrial processes for their use in integrated circuitry.^{24,25} Other transition metal oxides, such as titania (TiO₂) and iron oxide (Fe₂O₃), have also had ALD deposition processes developed for their deposition.^{28,29}

The methods described above will produce a layer of a binary oxide material (AO_x); if more complex materials are desired the method must be changed. The basic principles remain the same; one would perform the procedure for depositing a cycle of a binary oxide and then change the precursor and deposit

another cycle of a different oxide material. For example, if one wished to deposit PbTiO_3 , one would begin by depositing a layer of TiO_2 and then 560 depositing a layer of lead oxide (PbO). Repeating this set of cycles — a super-cycle — would eventually form the PbTiO_3 film.

However, deposition of complex oxides is not this simple in practice. In many cases, running each oxide cycle in a 1:1 ratio will deposit a non-stoichiometric material. This makes it necessary to modify the method to deposit more of one 565 type of oxide than the other. For example, if a material is Ti-rich the super-cycle ratio would be modified to increase the number of lead oxide cycles as compared to the titania cycles. Careful tuning of the deposition conditions, which include a variety of different factors, is required to obtain a desired and consistent film stoichiometry.

570 In addition to lead titanate, there are other ternary oxide systems that are being investigated. Examples of which are bismuth ferrite (BiFeO_3) or barium strontium titanate ($\text{BaSr}_x\text{Ti}_{1-x}\text{O}_3$).³⁰

ALD reactions are rather sensitive to a number of factors, such as temperature. The temperature must be high enough that the reactants have sufficient 575 energy to drive the surface reaction but not so high as to allow undesirable reactions to activate (e.g. precursor cracking or surface material desorption). Precursor selection is also very important, for similar reasons. The precursors must also be incapable of reacting with themselves, to allow the self-limiting mechanism to work properly.¹

580 **Chapter 4**

Thin Film Growth

4.1 Precursor Selection

4.1.1 Titanium Source

The source of titanium that was used was titanium(IV) isopropoxide ($\text{Ti}-\text{o-}i\text{-Pr}$, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$). This compound is very commonly used in ALD literature.^{31–36} It is a liquid precursor with a high vapor pressure and reacts easily with most oxidizers; the most commonly used oxidant for this reaction is water vapor, similar to the TMA-H₂O reaction (see section 3.3 on page 11).

4.1.2 Lead Source

One of the primary tasks of this project was to identify viable ALD precursors for the deposition of lead into the thin films. Potential candidates needed to meet a few stipulations. First, it needed to have chemical and thermal properties compatible with the ALD reactor. It was also desired that previous studies had used it in other ALD processes. Finally, it was important that the compound was available in quantity from chemical suppliers.

To this end, there were four potential candidates that were investigated which were identified from previous literature reports: tetraphenyllead (Ph_4Pb),³ lead(II) bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ($\text{Pb}(\text{TMHD})_2$),⁵ lead(II) hexafluoroacetylacetone ($\text{Pb}(\text{HFAc})_2$),³⁷ and lead bis(3-N,N-dimethyl-2-methyl-2-propanoxide) ($\text{Pb}(\text{DMAMP})_2$).³⁸

Ph_4Pb was one of the commonly used compounds in both ALD and MOCVD references, but it was found to have insufficient volatility for use in the ALD (up to its maximum evaporation temperature of 200°C)³ and was thus discarded as a candidate. $\text{Pb}(\text{TMHD})_2$ was another commonly referenced precursor,⁵ as was $\text{Pb}(\text{HFAc})_2$.³⁷ $\text{Pb}(\text{DMAMP})_2$ was seemingly a viable choice, with a very high vapor pressure at low temperatures,³⁸ but it was not readily available from chemical suppliers and was very costly to purchase which also kept it from being considered further.

Thus, the two compounds $\text{Pb}(\text{HFAc})_2$ and $\text{Pb}(\text{TMHD})_2$ were investigated
610 in detail as potential candidates for the lead precursor in the ALD deposition
of PbTiO_3 . Samples of both precursors were obtained from Strem Chemicals,
inc.³⁹ and were analyzed to determine which would be most viable. Tests
included thermogravimetric analysis (TGA), differential scanning calorimetry
(DSC), as well as test depositions of ALD films.

615 **4.1.3 Oxidizer**

Three potential oxidants were considered; these included water, oxygen,
and an ozone/oxygen mix. The choice of oxidant depends heavily on the
reactivity with the potential precursors.

The choice of titanium(IV) isopropoxide as the titanium source allows for
620 any of the three selected oxidizers to be used. A hydrolysis reaction will occur
when exposed to water vapor; in the case of oxygen or ozone the ligands will
be consumed via a combustion reaction.^{1, 28, 40}

Based on literature reports, the two lead precursors under investigation do
not undergo hydrolysis when exposed to water, and as such require the use
625 of the combustion pathway. In addition, through the deposition of test films,
it was found that the reaction proceeded more completely when the O_3/O_2
mixture was used. For simplicity of the process, the O_3/O_2 mix was used for
both half-reactions.⁴¹

4.2 Substrate Preparation

630 Fabrication and preparation of substrates was an important part of the
deposition process. Some substrates were purchased and simply cleaned, others
needed to be fabricated or otherwise processed prior to cleaning and use in
deposition. Three main types of substrates were used: thermally oxidized
single-crystalline silicon (100) wafers, silicon wafers that had a thin layer of
635 platinum deposited on the surface, and strontium titanate (100) single crystal
substrates.

4.2.1 Si(100)

The silicon substrates were prepared in a simple manner. 4 in. diameter
silicon wafers with 200 nm of thermally grown oxide were diced into 1.5 cm x
640 1.5 cm pieces. When a sample was to be used for deposition, it was cleaned by

one minute of sonication in acetone, followed by isopropanol, with a subsequent 5 minutes of sonication in deionized (DI) water. These were then air dried with dry nitrogen. Finally, the substrates were cleaned in a oxygen plasma cleaning system to remove any remaining organic residues present on the surface.⁴²

⁶⁴⁵ **4.2.2 Platinized Si(100)**

Platinized silicon substrates were prepared in a similar manner to the Si(100) samples. For the initial platinization, a large piece ($5 \times 5 \text{ cm}^2$) of pre-cleaned silicon wafer with a thin layer of native oxide, as opposed to the 200 nm of thermally grown oxide, was prepared in the manner described above.⁴² Then a 15 nm layer of platinum was deposited via ALD.⁴³ The substrates were then cleaved into smaller pieces for subsequent use.

If the samples are stored, it is recommended to again clean the samples in the standard procedure prior to use (see [4.2.1 on the facing page](#)).

4.2.3 Single Crystal STO(100)

⁶⁵⁵ Oxide crystal substrates were prepared in such a fashion as to promote the formation of atomically flat terraces. This has the advantage of promoting a uniform surface species across the entire sample — the etchant used in this process leaves the sample titania-terminated.⁴⁴

To prepare these samples, the substrates are first pre-cleaned in a four step sonication process. The samples were cleaned for five minutes in each of acetone, methanol, and isopropyl alcohol. Subsequently, the samples were sonicated for fifteen minutes in DI water.⁴⁴ The substrates were then immersed into a commercially prepared buffered hydrofluoric acid (BHF) solution to etch for 30 seconds, then removed and flushed with copious quantities of DI water to purge any remaining BHF solution. Once the sample is thoroughly rinsed, the samples are dried using dry nitrogen.⁴⁴

After the etching process, the samples are annealed at 950°C for one hour.⁴⁴ Once the samples are cooled, they are ready for immediate use. AFM can be used to confirm the presence of well-defined atomic terraces.

⁶⁷⁰ If the samples are stored, it is recommended to again clean the samples in the standard procedure (see [4.2.1 on the preceding page](#)).

4.3 Deposition Parameters

There are four main parameters that can affect the behavior of an ALD deposition. These are the growth temperature, the dosage of each precursor,
675 the purge time between doses, and any extended precursor-surface exposure time.

4.3.1 Growth Temperature

The temperature of the growth chamber has a strong effect on reaction behavior. ALD reactions are sensitive to temperature, and will only proceed
680 properly within a certain range known as the ‘ALD window.’ Outside of this range, the reaction enters one of a number of different regimes; these are determined by comparing the growth rate of the deposition to that of a reaction in the self-limiting saturated “ALD mode.”^{1, 28, 40, 45}

If the growth temperature is less than the lower bound of the ALD window,
685 the two regimes are condensation limited and activation energy limited. Condensation limited growth occurs when the substrate temperature is low enough that precursor condenses onto the surface without reacting with the presented sites. This causes higher than expected growth rates, and a lack of self-limiting behavior. If the reaction instead proceeds into the activation
690 energy limited regime, molecules of precursor lack sufficient energy to react with the surface. This is characterized by lower deposition rates.^{1, 40}

Conversely, if the reactor temperature is excessive the reaction again become anomalous. Decomposition limited growth, characterized by excessive deposition, is a result of thermal cracking of the precursor materials. This reaction is not limited to the surface, and accounts for the extra material being deposited. Lower deposition rates indicate that the temperature is sufficient
695 to cause desorption of previously-reacted material from the sample.^{1, 45}

For an ALD run to be successful, the acceptable temperature window for all of the reactions should overlap in some temperature range. This can become
700 difficult with reactions requiring multiple metal precursors (e.g. PbTiO₃, a combination of TiO₂ and PbO), as these can have widely varying ALD windows for their respective reactions.

4.3.2 Precursor Dosage

The dosage of precursor or oxidant to the surface is another parameter of critical importance. An ALD reaction requires a minimal amount of precursor to sufficiently saturate the surface, while it is beneficial to minimize any excess precursor as it will be a wasted byproduct (minimizing costs, environmental impact, etc.).

The vaporization behavior of the precursor can have a dramatic impact on how simple or difficult it is to deliver a saturating dose to the surface. Some materials have readily available precursors with high vapor pressures; titanium isopropoxide and trimethylaluminum (TMA) are both liquids, and tetrakis(dimethylamido)hafnium ($\text{Hf}\{\text{N}(\text{CH}_3)_2\}_4$) is a low-melting temperature solid. These are commonly used precursors for depositing their respective oxides. This vapor pressure becomes an important consideration when choosing a potential compound for use in ALD (as discussed in section 4.1 on page 15).^{1,28,40,45,46}

Insufficient dosing is apparent in a deposition run by a slower than average growth rate, or also as a non-uniform deposition rate across the sample. However, overdosing is not readily apparent in an ALD-mode deposition. The dose must be lowered to a point where the dose is insufficient, and then increased back to a saturating level.

Controlling the dose is dependent on injection time (which is the time the valve between the process line and the precursor storage vessel is open), precursor temperature, and the cycle duration (time between precursor injections). By increasing either the injection time or the precursor's temperature the dose is increased, except in some cases with low vapor pressure materials. In this case, it can sometimes be found that the evaporation kinetics are slow and it takes additional time to build up a sufficient amount of vapor to provide a dose to the reactor.^{1,28,45}

If necessary, multiple doses of precursor can be delivered to the sample during each cycle to increase the total delivered dose.

4.3.3 Purge Time

Purge time is important as it gives time for the N_2 flow to flush any remaining byproducts, excess reactants, and physisorbed (as opposed to chemisorbed) species from the substrate surface and out of the reactor zone. It also allows time between cycles which allows for low vapor pressure precursors to regen-

erate evaporated material; if this time is too short to fully regenerate the dose in the cylinder the precursor will eventually appear to be depleted during the
740 course of the deposition.^{1,40}

4.3.4 Exposure Time

Exposure time denotes the time where the precursor is held in the reaction zone to increase the amount of time during which the surface reaction can occur. This is beneficial for two types of depositions. In the case of low-reactivity
745 precursors, it increases the amount of time that the precursor is available to the surface, greatly increasing the surface coverage per cycle. Exposure mode is also beneficial for depositing upon three dimensional structures, especially those with a high aspect ratio, e.g. nanotube templates. This extra dwell time of the precursor allows for diffusion of reactant into the structure, for a uniform coverage upon the entirety of the surface. Purge time must be increased
750 accordingly to allow for byproducts to diffuse back out of the structure.^{1,40,47}

4.4 Post-Deposition Annealing

Two types of annealing procedures were used in this study. Oven annealing, with the simple use of a furnace in ambient atmosphere; and rapid thermal annealing (RTA), characterized by very high heating and cooling rates and performed in an inert atmosphere (dry N₂).
755

4.4.1 Oven Annealing

In oven annealing, the samples to be processed are placed in a cold oven in the ambient atmosphere of the laboratory. The samples are then heated gradually at a rate of 10–25°C per minute up to the final annealing temperature,
760 which ranged from 600–900°C. The samples are then allowed to heat-treat for 120 minutes at the process temperature, and then the furnace is allowed to return to room temperature.

This conventional heating pattern allows the sample to obtain its equilibrium crystalline phase composition, be that a single crystalline phase, polycrystalline, or involve multiple phases or materials. This was the annealing
765 method most commonly used during this study.

4.4.2 Rapid Thermal Annealing

Rapid thermal annealing (RTA), as its name suggests, involves very high
770 heating and cooling rates. RTA systems can heat at rates over 10°C per second, allowing the chamber and sample to reach the process temperature very quickly. Similarly, processing times are generally much shorter, and are generally no longer than 10–15 minutes. Cooling, facilitated by a water cooling apparatus, also occurs rapidly. These sharp gradients can have different effects
775 on the crystal structure of the film, locking in different phases in the material that may otherwise dissociate given more time during heating or cooling.

In this study samples processed via RTA used a HeatPulse™ RTA system, which allowed for automatic control of the process. Sample processing conditions can be found in table [7.1 on page 49](#).

780 **Chapter 5**

Material Characterization

5.1 Thermal Analysis

5.1.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a very useful tool when attempting 785 to determine the viability of a precursor in an ALD process. It allows for estimation of vaporization rate at various temperature rates as well as indications of chemical breakdown (i.e. thermalization) which would hinder the precursor's usefulness.

At its core, TGA is a measurement of mass loss as a function of temperature 790 or time. A small sample (1–10 mg) of material is placed in a microgram balance pan and suspended inside a furnace. The furnace is then heated at a specified rate while the sample mass is carefully monitored. For the experiments used in this study (evaluation of thermal vaporization and thermal degradation) it is important to ensure that the testing environment is inert. This is accomplished 795 by using a platinum pan in the microgram balance and constantly purging the furnace with a small flow of dry nitrogen gas. The heating rate can be varied according to a pre-determined program to provide more information at various individual temperatures.^{48–51}

This technique was used to evaluate various precursor candidates for the 800 lead oxide half of the PbTiO₃ deposition procedure. The instrument used was a Q50 TGA device (fig. 5.1a on the following page). A detailed discussion of TGA procedures and the investigated chemicals can be found in subsequent chapters (see 4.1 on page 15 and 7.1 on page 43).

5.1.2 Differential Scanning Calorimetry

805 Differential scanning calorimetry (DSC) is a technique that allows for the determination of various critical temperatures for a material, and also can highlight changes in chemical structure due to degradation or other thermal processes.



Figure 5.1: Photograph of the thermal analysis instrumentation used during this study, made by T.A. Instruments, inc.

DSC is the analysis of energy absorption as a function of temperature,
810 which is the essence of calorimetry. DSC uses a sample and reference system
to isolate the energy absorbed by the sample from that of the holder pan.
Sample sizes usually range from 0.1–2 mg of material; as the samples used
in this study are volatile the sample pans are hermetically sealed to prevent
mass loss. The sample and reference pans are then placed inside a thermally
815 insulated chamber. The temperature of each is carefully monitored, and differ-
ing amounts of heat are applied to negate the temperature difference between
the sample and reference. The difference in absorbed heat as a function of
temperature is then given as the result. In general, experiments include both
heating and cooling curves to gain a complete understanding of the different
820 energies.^{51–53}

DSC was used to analyze the behavior of precursor chemicals around their
evaporation and reaction temperatures. The main goal was to determine if the
material underwent any thermally-activated degradation processes at either of
these two temperature ranges. At the evaporation temperature, the sample
825 was generally cycled multiple times to simulate actual use in the ALD. These
measurements were taken using a Q2000 DSC system (fig. 5.1b) made by T.A.
Instruments, inc.

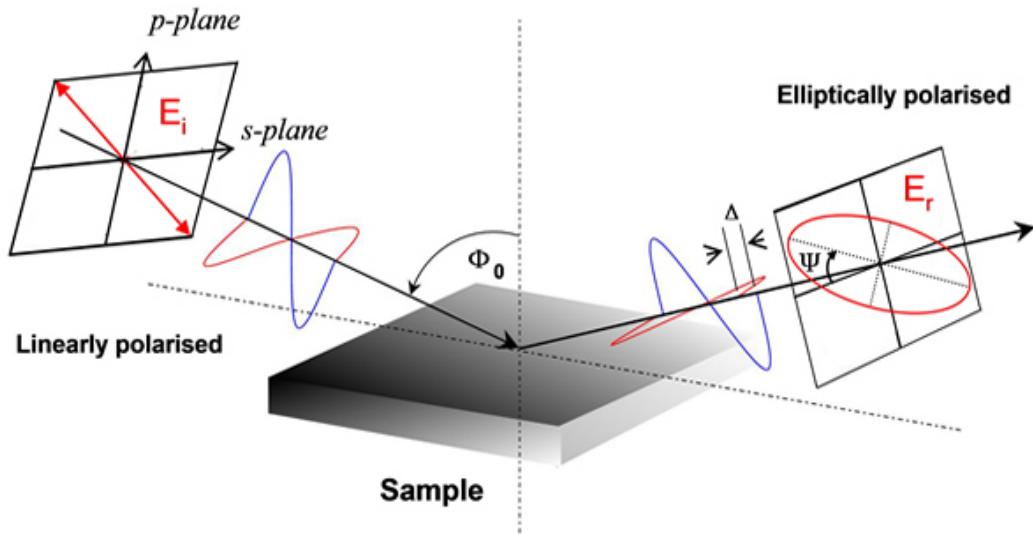


Figure 5.2: Schematic of the beam path during an ellipsometric measurement, critical parameters are indicated

5.2 Thin Film Characterization

5.2.1 Variable Angle Spectroscopic Ellipsometry

Ellipsometry is a powerful non-destructive optical technique that allows for the determination of a large number of properties of complex thin film structures. The basic tenet of ellipsometry relies on the analysis of the change in polarization state of a reflected light beam after interaction with the sample. The incident beam is generally linearly polarized, but upon reflection becomes elliptically polarized due to a phase shift in the components of the beam in the *s*- and *p*-plane, as well as a change in their relative amplitudes. The phase shift is correlated to the ellipsometric parameter Δ , while the amplitude change is given by $\tan \Psi$ (Ψ is the angle between the *s*-plane and the major axis of the ellipse). The last major parameter is the incident angle, denoted by Φ . A schematic diagram illustrating these parameters can be seen in figure 5.2.⁵⁴⁻⁵⁶

From these parameters, one can directly determine the ratio between the reflectance in the *p*-plane (r_p) and the reflectance in the *s*-plane (r_s) from the fundamental ellipsometric relation (eqn. 5.1 on the next page). Once this relationship is known, the Fresnel equations (eqn. 5.2 on the following page) can be used to numerically determine the value of the complex index of refraction at the specific wavelength of the incoming beam. The complex index of refraction (eqn. 5.3 on the next page) describes the nominal index of refraction but

additionally includes an imaginary term to describe absorption of light in the material (commonly referred to as the extinction coefficient, κ).^{54–56}

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (5.1)$$

$$r_p = \frac{\tilde{n}_1 \sqrt{1 - \left(\frac{\tilde{n}_1}{\tilde{n}_2} \sin \Phi \right)} - \tilde{n}_2 \cos \Phi}{\tilde{n}_1 \sqrt{1 - \left(\frac{\tilde{n}_1}{\tilde{n}_2} \sin \Phi \right)} + \tilde{n}_2 \cos \Phi} \quad (5.2a)$$

$$r_s = \frac{\tilde{n}_1 \cos \Phi - \tilde{n}_2 \sqrt{1 - \left(\frac{\tilde{n}_1}{\tilde{n}_2} \sin \Phi \right)}}{\tilde{n}_1 \cos \Phi + \tilde{n}_2 \sqrt{1 - \left(\frac{\tilde{n}_1}{\tilde{n}_2} \sin \Phi \right)}} \quad (5.2b)$$

$$\tilde{n} = n + i\kappa \quad (5.3)$$

This type of analysis is sufficient for thick, isotropic samples without any surface layers (e.g. surface oxides or adsorbed gases), and can directly provide the value of \tilde{n} . However, once layers are stacked upon one another, the system becomes very difficult to analyze directly due to interference effects between the layers. It becomes necessary to use modeling techniques to determine the correct values of \tilde{n} and thickness (t) for each layer.^{55,56}

The power of ellipsometry as a high-resolution optical analysis technique stems from the use of phase and polarization changes. This allows the analysis to overcome the diffraction limit, and can be accurate down to angstroms. Properly modeling the system is critical for this analysis to be as precise as possible. Thus, there have been refinements of the ellipsometric method to greatly increase the amount of experimental data points, allowing the overall system to be over-determined and thus letting all of the systems parameters to be calculated.

Variable angle spectroscopic ellipsometry (VASE) is one of these variants. Spectroscopic ellipsometry differs from single-wavelength ellipsometry by utilizing a broad-band light source as opposed to a monochromatic source. By performing ellipsometric analysis at each of the wavelengths, one can determine the wavelength (and thus photon-energy) dependence of n and κ . This not only helps to improve data analysis (as it can generally be safely assumed that the values of n and κ are smooth functions of λ), but allows for the determination of many other properties of the material. Of specific importance

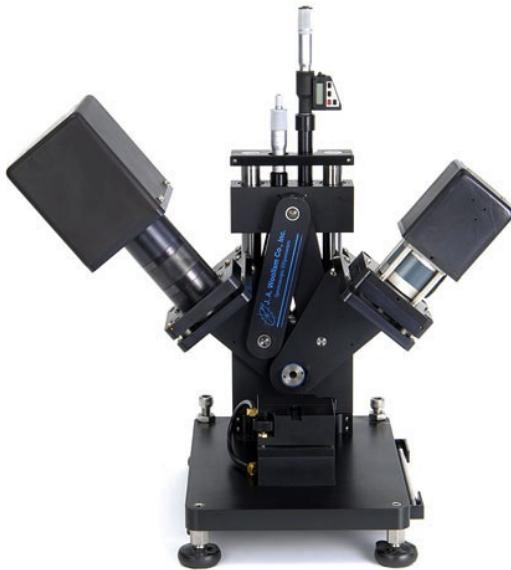


Figure 5.3: Photograph of the J.A. Woollam M-2000U variable angle spectroscopic ellipsometer (VASE)

is the complex dielectric function ($\tilde{\epsilon}$), which is related to \tilde{n} by the relation shown in equation 5.4. Knowing these functions can allow for determination of electronic properties such as the bandgap energy, the absorption coefficient,
875 amongst others. Finally, by obtaining spectra at a number of different incident angles, one directly provides additional data points across the entire wavelength spectrum. Even a small number of additional angles can quickly provide sufficient data points for the system to be over determined.^{54–56}

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2 = \tilde{n}^2 \quad (5.4)$$

During this project, a VASE M-2000U system (figure 5.3) built by J.A.
880 Woollam, inc. was used to collect all of the ellipsometric data. In addition, data analysis was performed using the WVASE32[©] package also provided by J.A. Woollam, inc. The system utilizes a rotating compensator and a CCD detector to greatly decrease data collection time by collecting data across the entire spectrum simultaneously. More information on this system is available
885 from the J.A. Woollam, inc. webpage.⁵⁷

5.3 Compositional Analysis

5.3.1 Energy-Dispersive X-Ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDXS) is a commonly used analysis technique for determining the composition of a sample. In this process, a sample is bombarded with high-energy electrons (2–30 keV) which interact with the sample. Some of these electrons will cause a core electron of an atom in the sample to be ejected. This leaves a vacant orbital in the inner shell, which a higher energy electron will fill. In the process of filling the vacancy, the electron will emit an X-ray photon equal to the energy difference between the two states. These energies are referred to using the common X-ray spectroscopy nomenclature (e.g. K_{α} , K_{β} , L_{α}). An illustration of this process can be found in figure 5.4 on the facing page.⁵⁸

Since the energies of the emitted photons are very specific to each element, the procedure can be used to identify the presence of the element in the sample. With some calibration, EDXS can also be used to quantify the relative amounts of each element in a sample using the different number of collected photons. However, this can sometimes be difficult due to some elements have overlapping spectrums as the peaks are not sharp and different elements can have similar energies for some transitions.⁵⁸

One of the downsides of EDXS is that the interaction volume of electrons is much larger deeper into the sample, so the surface sensitivity of the technique is smaller than with some other techniques. Additionally, Bremsstrahlung radiation, which is caused by high-energy electrons interacting with other charged particles, provides a large degree of background noise which can drastically interfere with the techniques ability to precisely measure, or even identify, trace elements such as those in a thin film.⁵⁸

5.3.2 X-Ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy (XRFS) is a similar technique to EDXS. In XRFS the excitation used is X-ray photons (often from a Cu K_{α} source with $\lambda = 1.54 \text{ \AA}$), as opposed to energetic electrons. In other considerations the techniques are equivalent.

XRFS has a lower noise floor than EDXS, due to the lack of signal from Bremsstrahlung radiation from the deceleration of electrons, allowing smaller signals to be more easily identified (such as in ultra-thin films). It does suf-

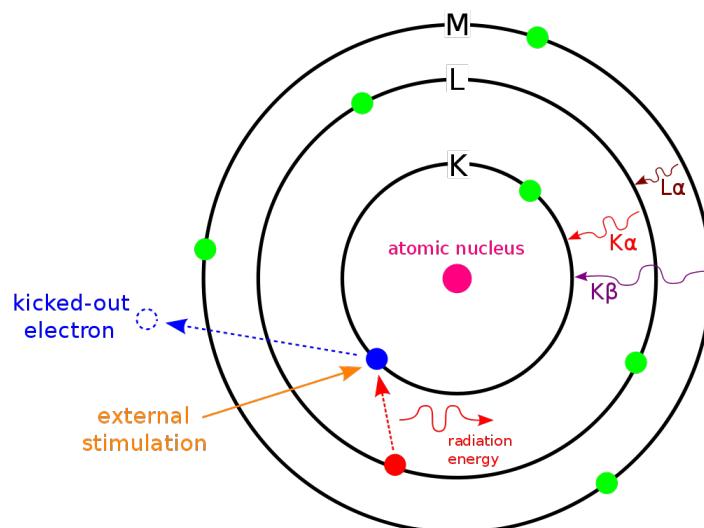


Figure 5.4: Graphic illustrating the basic mechanism for EDXS, along with the commonly used notation for the various energies. The external stimulation would be a high energy electron.

fer the same disadvantage of having overlapping peaks. This resolution issue can be alleviated to some degree by using wavelength dispersive XRFs (WD-XRFs), which uses diffraction techniques to analyze the emitted x-ray spectrum.⁵⁹

X-ray fluorescence spectroscopy was performed using a fX-SEM analysis system from iXRF Systems, inc.⁶⁰ It was the primary method of composition analysis for the results presented in this thesis.

5.4 Phase Identification

5.4.1 X-Ray Diffraction

X-ray diffraction (XRD) is a very commonly used technique for performing this identification. Utilizing the concepts of coherent interference, which leads to Bragg's law of diffraction given in equation 5.5. X-rays are utilized because their wavelengths are similar to the length scales between atomic planes in crystals (1–100Å). As the incident rays pass through the sample and are reflected by atomic planes, they can either constructively or destructively interfere.⁶¹

$$n\lambda = 2d \sin \theta \quad (5.5)$$

Figure 5.5 on the following page gives a graphical illustration of this principle. If the extra distance traversed by photons on the first path is equal to an integer number of wavelengths there will be constructive interference (see

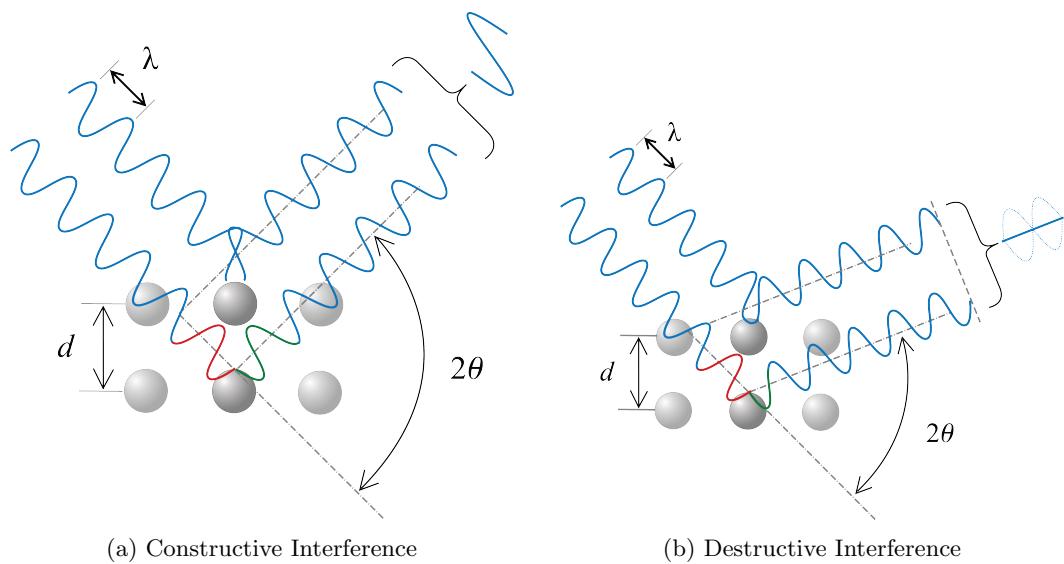


Figure 5.5: These two images illustrate the effect of interference on Bragg diffraction. In (a) the extra path length is exactly correct to allow coherence with the other ray; this causes constructive interference. (b) is the other condition, where the path length causes a phase shift of 90° and thus the rays interfere destructively.

fig. 5.5a). However, if the θ angle is slightly changed the interference rapidly obtains destructive character (see fig. 5.5b). In this manner, if the crystal is moved through a range of $\theta - 2\theta$ values, a pattern of angles where constructive interference occurred.⁶¹

The diffraction pattern can be used to determine a list of the interplane spacings (d-spacings) present in the sample. The values of peaks at various 2θ can be converted to d-spacings via the relation $d = \frac{\lambda}{2\sin\theta}$. Individual materials will have a specific pattern of reflections that allow them to be identified in the sample.⁶¹

This project used a Rigaku SmartLab XRD (see figure 5.6 on the next page), which utilized a Cu-K α X-ray source ($\lambda = 1.5418\text{\AA}$).

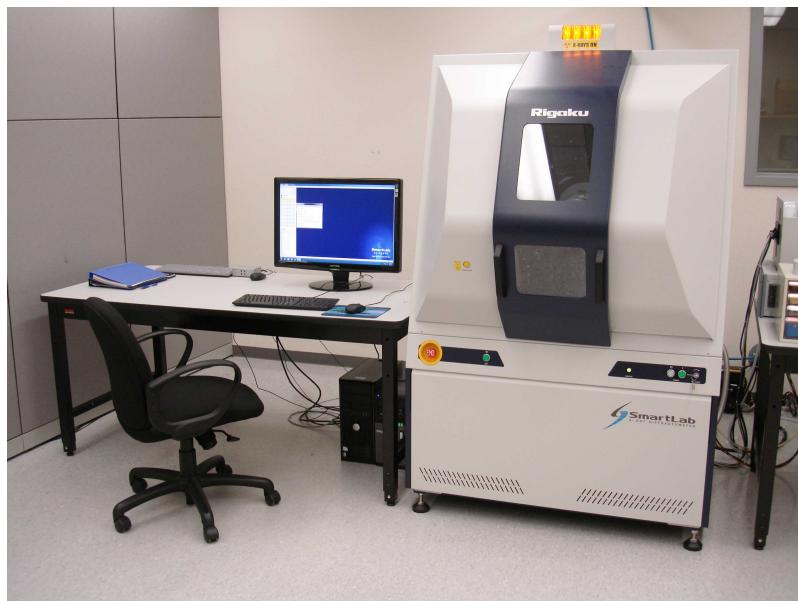


Figure 5.6: Photograph of the Rigaku SmartLab X-ray diffractometer

Chapter 6

⁹⁵⁰ Analysis Methods

6.1 Thermal Analysis

6.1.1 Thermogravimetric Analysis

Collection of TGA data was straightforward, and performed as described in the manual for the Q50 TGA. After initial calibration of the system, a small ⁹⁵⁵ sample (5–10 mg) of material was placed into a platinum sample pan. The pan was then loaded into the furnace of the TGA and a small flow of purge gas (N_2 at 50 mL/min) was started to isolate the sample from ambient atmosphere. At this point the desired test sequence was programmed into the controller and the instrument allowed to begin data collection.

⁹⁶⁰ 6.1.2 Differential Scanning Calorimetry

DSC experiments were performed in a similar method as those of TGA. Small samples of material (3–5 mg) were loaded into hermetically sealed sample pans inside of a glovebox containing an inert atmosphere. The use of hermetically sealed pans was important as the material was intended to vaporize, ⁹⁶⁵ and the loss of material through escaped vapor would change the results of the test. In addition, loading the material in inert atmosphere prevents the presence of oxidants within the sample atmosphere during the test. An additional sample pan was sealed with no contents to act as a reference. Both pans were weighed precisely on a high-resolution balance and then loaded into the sample ⁹⁷⁰ chamber of the Q2000. Again, the desired testing sequence was programmed into the instrument's controller, and the experiment was run automatically.

6.2 VASE and Modeling

Ellipsometry was used extensively to determine a variety of properties of the material. However, the primary goal of ellipsometric analysis was to determine ⁹⁷⁵ the film thickness, in order to be able to determine the film growth rate (in terms of Å per deposition cycle) of the process.

6.2.1 Data Collection

In order to collect the experimental data, the following series of steps were followed:

- 980 1. Optics alignment
2. Ambient light compensation (DC offset)
3. Data collection at multiple angles

Alignment of the optics of the system is performed in the manner described in the manual for the ellipsometer.⁶² The system can have focusing optics installed which diminish the spot size of the analysis, which is useful if inhomogeneity is expected in the sample as this is a major problem for analysis (two of the main assumptions made by ellipsometric models are that the layers have consistent thicknesses and optical behavior across the analysis area). This is done by manually adjusting the sample stage height and the sample surface plane. The system is designed so that when the incoming signal is maximized the sample is properly aligned with respect to the p- and s-planes defined by the equipment.⁶³

Once the system is aligned, the signal that is due to ambient light (not produced by the light source) must be compensated for. The M-2000U defines this as the “DC offset.”⁶² The offset is calibrated automatically by the system by blocking the light source and measuring the signal from the surroundings. As the light present in the room is generally randomly polarized, the signal will be invariant to the polarizer settings. Correctly setting this value greatly decreases the uncertainty during the analysis phase; it mainly affects the degree of light depolarization measured by the system. The ellipsometer includes the depolarization in its calculation of the confidence interval for the final measurement. If the degree of ambient unpolarized light is not determined before the measurement, the depolarization will be nearly completely unrelated to the actual depolarization by the sample. In addition, the depolarization can be used by non-idealized models to determine such parameters as layer thickness variation, or internal interface roughness. This process will not be used for the remainder of this discussion, but more information can be found in the manual for the M-2000U.⁶²

After the calibration steps have been completed, data collection can be performed. Three different incident angles were used for the data collection:

55°, 60°, and 65°. At each angle, the data was averaged over three hundred revolutions of the compensator to minimize noise in the experimental data. The system was set up to collect depolarization data simultaneously with the ellipsometric parameters.⁶²

If the sample is expected to be inhomogeneous, the focusing optics can be used and data collected at several different locations on the sample. This can provide data on how the growth process behaves spatially, such as if there is abnormal growth near the edges of the sample but homogeneous deposition as one moves nearer to the center of the substrate.

6.2.2 Model Definition

The definition of the model is a critical part of the analysis procedure. The model dictates how the software package will perform its various calculations to predict the overall optical behavior, which it iteratively compares to the experimentally determined Ψ and Δ .

Simply put, the model is defined as a bulk (semi-infinite) substrate layer, with a nominal number of nano- to micrometer thick layers stacked upon it. Each layer is modeled with a prediction of optical constants at each test wavelength. These optical constants can be provided as a table of experimentally determined results, which are available for many commonly used materials such as silicon, silica, titania, amongst others; they can also be predicted using a variety of different models. These can be empirical predictors, such as the Cauchy dispersion, or based upon physical properties of the material, oscillator-based models for example. The model types relevant to this work are discussed in more detail in subsequent sections.⁶³

The four different substrates require different material layer stacks to properly represent them, and each poses individual challenges for characterization. The Si(100) substrate that was most commonly used for this work was the simplest to model. It can be represented as a substrate layer of silicon, with a 200 nm layer of silica on top. The deposited film would be layered above the SiO_2 layer (see fig. 6.1 on the following page for a schematic representation). A large number of these substrates were analyzed for their oxide layer thickness, where the only parameter to be fit was the layer thickness. It was found that the nominal oxide layer was 200 ± 5 nm thick. This was consistent enough that 200 nm could be used for the initial thickness estimate for all samples using this substrate, and after the ALD layer was analyzed this thickness could also

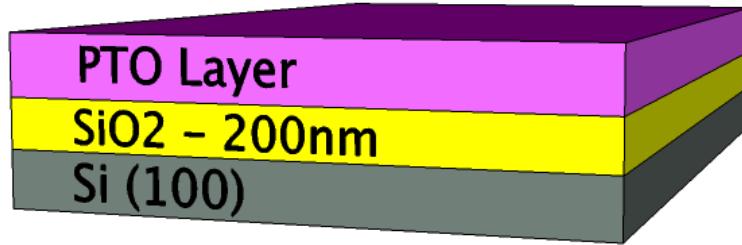


Figure 6.1: A simple graphical example of the model used for analysis of the film stack in the Si(100) samples. The parameters are t and the spectroscopic values of \tilde{n} for the PTO layer.

be included in the fit to confirm the true dimensions of the oxide layer. The substrate with thermally-grown oxide was preferred in comparison to silicon with only native oxide layer; this is because the thicker layer of transparent oxide helps to generate large oscillations in Ψ and Δ , which assists in the analysis (particularly the thickness, where the fringes are very closely related to this parameter).⁶³

6.2.3 Analysis Procedure

Once the data was collected, a specific series of steps was followed in order to obtain the highest degree of accuracy from the model. All steps were performed on the PTO layer. The modeling procedure went as follows:

1. High- λ Cauchy Model
2. Direct Calculation of n and κ
3. Conversion to Oscillator Model
4. Refinement of Oscillator Layer Parameters

This first step takes advantage of the transparency of the film at high wavelengths (low energies) where the photon energy is below the optical bandgap of the material. In this region, the Cauchy model can be used. The Cauchy model is empirical rather than physically descriptive, and best used for amorphous materials such as polymeric films, however the assumptions required for reasonable accuracy are met when absorption in the film layer is minimized (therefore $\kappa(\lambda) \approx 0$). The equations used in the Cauchy model are shown in equation 6.1. Generally, analysis during this step was performed in the spectral region where $\lambda = 600 - 1000$ nm ($E_{ph} = 2.06 - 1.24$ eV).

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} + \dots \quad (6.1a)$$

$$\kappa(\lambda) = A_\kappa e^{B_\kappa \left(\frac{hc}{\lambda}\right) - C_\kappa} \quad (6.1b)$$

Once reasonable estimates for n , κ , and the film layer thickness are obtained
1070 at the higher wavelengths, the second step of the analysis is to generate values of \tilde{n} for the rest of the spectrum. The film thickness parameter is fixed at the value determined from the Cauchy model. The values of n and κ are allowed to be determined freely without the use of a model (i.e. directly determined by use of the Fresnel relations). This type of modeling is not physical, but assists
1075 in the generation of the oscillator-based model in the next step. The software package is then instructed to run a point-by-point fit of the data from highest-to lowest- λ , attempting to minimize the change in n or κ between adjacent data points.

This model is then inputted into a oscillator model. For the analysis of
1080 these films, a Tauc-Lorentz oscillator model was utilized. The oscillator models used by WVASE32 are expressed in terms of the complex dielectric function $\tilde{\epsilon}$, which relates to \tilde{n} via the relationship in equation 6.2. The Tauc-Lorentz model changes the Lorentzian model by allowing for some absorption below the fundamental bandgap energy, which would be due to defect states and
1085 other intra-band transition mechanisms. The Tauc-Lorentz model uses the parameterization shown in equation 6.3.^{62,64} ϵ_1 is provided here in a condensed version (eq. 6.3a); the full expanded version, and its derivation via Kramers-Kronig integration (whose relations are shown in equation 6.4 on the next page) from ϵ_2 , has been presented by Jellison and Modine.⁶⁴

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2 = \tilde{n}^2 \quad (6.2a)$$

$$\epsilon_1 = n^2 - \kappa^2 \quad (6.2b)$$

$$\epsilon_2 = 2n\kappa \quad (6.2c)$$

$$\epsilon_1 = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \epsilon_2(\xi)}{\xi^2 - E^2} d\xi \quad (6.3a)$$

$$\left\{ \begin{array}{ll} \epsilon_2(E) = \frac{AE_0C(E - E_g)^2}{(E^2 - E_0^2)^2 + C^2E^2} \cdot \frac{1}{E} & E > E_g \\ \epsilon_2(E) = 0 & E \leq E_g \end{array} \right. \quad (6.3b)$$

$$(6.3c)$$

1090

$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (6.4a)$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega' \quad (6.4b)$$

The WVASE32 software package allows one to use a graphical interface to provide initial guesses for the various fit parameters. At times this required multiple oscillators to best fit the predicted ϵ_2 function. Once this has been set, all of the parameters affecting ϵ_2 (A, E_0, C, E_G) are marked to be included in the fit. The software is then instructed to perform a best-fit of the oscillator to ϵ_2 . Once this operation completes, the software is set to fit to ϵ_1 and only the value of the ϵ_1 offset is allowed to be fit. Finally, the software is set to optimize vs both ϵ_1 and ϵ_2 , and all parameters are included. This completes the initial setup of the oscillator model.

Finally, the model is set to also allow the layer thickness to be fit and a general fit to the entire experimental dataset is performed. This provides the best guess to the physical values of the film. The thickness calculated by this procedure matches very closely to measurements performed by other methods (e.g. SEM imaging or AFM measurement of a lithographically created step).

If similar deposition parameters are utilized, it is possible to save the parameterized model for later use. This allows the analysis to be streamlined when the material is expected to remain constant, for example if tests of deposition at different layer thicknesses are performed. In this case, the material would have optical behavior very similar to the initial sample, and the oscillator model would be sufficiently close to valid parameters to be used directly for fits. All that would need to be adjusted initially would be the estimated layer thickness. If the fit fails to produce useful data, such as unreasonable values for any of the parameters or very large confidence intervals, it is recommended to proceed with the entire standard analysis procedure.

Further analysis can be performed to estimate the bandgap of the layer, via Tauc plot analysis.^{63,65,66} The method requires the calculation of the absorption coefficient (α) from the value of k for the layer (see equation 6.5 on the facing page). α is usually provided in terms of cm^{-1} , so if the wavelength is provided in nanometers a corresponding factor of 10^7 must be incorporated as well. Subsequently, a Tauc plot is constructed using a combination of α

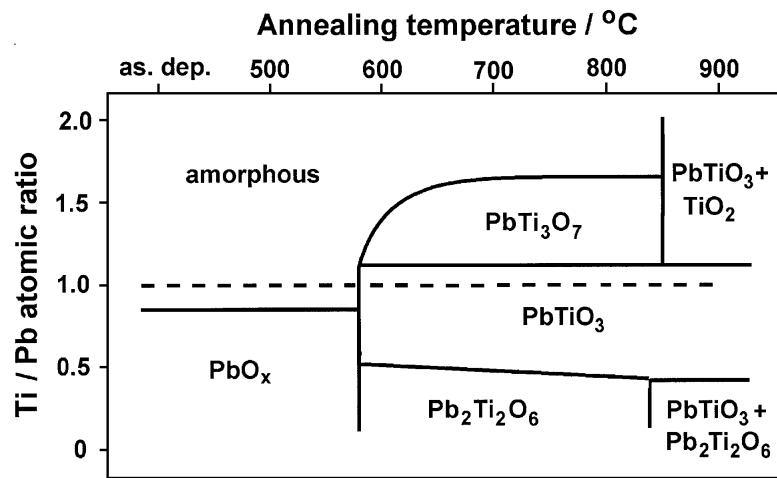


Figure 6.2: Graphic illustrating preferred phase of an annealed film at a range of stoichiometric ratios and annealing temperatures. A slight excess of Pb in the system is expected to help stabilize the perovskite PbTiO_3 phase.³

and the photon energy. For direct bandgap materials the Tauc parameter is given by $(\alpha E_{ph})^2$.^{63,65,66} If the bandgap is of the indirect type, the function is changed to $\sqrt{\alpha E_{ph}}$. The bandgap parameter matches well to literature values (when using standard samples of well defined materials, such as a thin layer of titania). It must be noted that the bandgap that is calculated is the overall bandgap of the layer, which may be a combination of multiple phases or materials.^{63,65,66}

$$\alpha = \frac{4\pi k}{\lambda} \quad (6.5)$$

Experimental data sets, the resulting fitted models, and Tauc analyses for selected samples are presented in appendix A.4 on page 70.

6.3 Composition Analysis

In order for the desired phase to be preferred, without any impurity phases precipitating, it is important to be able to control the stoichiometry of the produced film. Previous reports have shown that there is a close relationship between the composition of the film and the final resultant phase (see figure 6.2).³

6.3.1 X-Ray Fluorescence Spectroscopy

X-ray Fluorescence was the primary method used for determining the composition of the deposited films. Analysis was performed in a scanning electron microscope (FEI Strata DB235). The sample was imaged in order to identify the exact height of the sample within the chamber, via the microscope's focal length. After the sample had been properly positioned, the imaging beam was disengaged and the X-ray source activated. Then, in much the same manner as EDS, the emitted X-rays are collected and analyzed. A target X-ray count was around 20,000-50,000 for most samples. If the film on a particular sample was found to be very thin, more counts were often required to obtain well-defined peaks for the film elements.

Initial calibration of the system is critically important to acquiring accurate measurements. Calibration is performed using a pair of standard samples of known composition, which include all elements that are to be quantified. For this study, a pellet of commercially prepared PbTiO_3 powder and a thin film of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ were used as standards.

The only major issue with XRF — and composition analysis in general — that was encountered during the course of this work was the fact that it was not surface sensitive. In fact, many of the observed counts could be attributed to the substrate. In general this proved not to be problematic, but when the sample and film had elements in common this analysis was confounded and completely impossible to perform using XRF. This was the case with PTO films deposited on SrTiO_3 substrates, as both the film and the substrate had titanium content.

This issue could have been circumvented by using surface-sensitive techniques; examples of these methods include Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectroscopy (RBS). Unfortunately, none of these tools were available at the time and as such samples deposited on STO do not have associated composition information.

6.4 X-Ray Diffraction

X-ray diffraction (XRD) was used in this study to investigate the phases that crystallized in the samples after annealing treatments were performed. Sample alignment was an automated, preprogrammed process for film-type

structures; the system performed alignments on all available axes to ensure optimum sample placement and orientation. Calibration of the system was managed by lab technicians.

Data was collected in the standard $\theta - 2\theta$ orientation, and was programmed to sweep ranges between 10–90°. Varying time constants were used on different samples, as samples with thicker ALD films supplied a stronger signal.
1175

Chapter 7

Results

As discussed, the goal of this study was to determine methods for atomic layer deposition of ferroelectric oxides. In the process of realizing this goal there were a number of different areas of study. The first is the analysis of thermal and chemical behavior of the various potential precursors, during which TGA and DSC were primarily used (see [6.1 on page 33](#)). Secondly, the analysis of the film growth behavior under various conditions, this was primarily measured and analyzed using the ellipsometric techniques discussed earlier (see [6.2 on page 33](#)). Third, the film deposition needed to be tuned to produce films with a stoichiometric composition, as this was expected to produce films which would crystallize into the desired perovskite phase, see section [6.3 on page 39](#) for the methods used for this characterization. Fourth, the phase of the crystallized film was analyzed in detail to determine behavior of the films post-annealing. XRD was used extensively for this task (see [6.4 on page 40](#)).

7.1 Thermal Analysis

While a viable titanium precursor was well identified in literature as well as experimentally, as was the oxidizers that were used, there was no such universally accepted chemical used in ALD to provide a source of lead. The primary issue was either a lack of chemical stability or a undesirably low volatility in the compounds that currently were being used. TGA and DSC was performed on a number of potential candidates (see [4.1 on page 15](#) for more details) in order to gauge the performance of these materials.

7.1.1 Thermogravimetric Analysis

Thermogravimetric analysis allows for the estimation and comparison of volatility between multiple samples. It was used in this study primarily to compare properties of the two candidate precursors, $\text{Pb}(\text{HFAc})_2$ and $\text{Pb}(\text{TMHD})_2$. Of primary consideration was the volatility of the compound — evaluated qualitatively by analyzing the mass loss at various temperatures — and whether

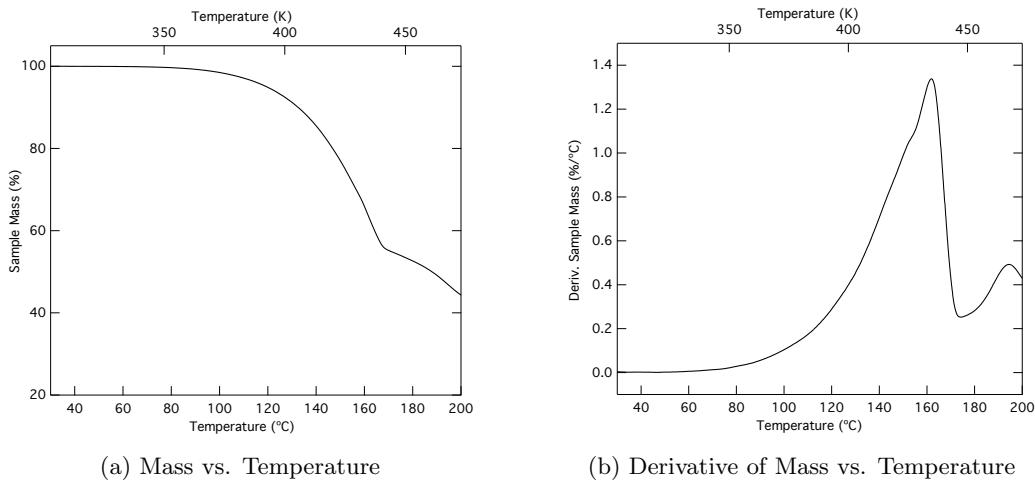


Figure 7.1: Plots of the results from TGA experiments on $\text{Pb}(\text{HFAc})_2$. The plot shown in (a) gives the raw data showing the current mass as a function of temperature. (b) gives the same data, transformed to show the derivative of mass. Thus (b) shows the rate of mass loss at a given temperature. Initial sample mass: 6.092 mg

or not there are indications of imperfect evaporation. The data collected for these materials can be found below.

By analyzing the TGA curve for $\text{Pb}(\text{HFAc})_2$, found in figure 7.1a, there are a number of features that are immediately noticeable. First of these is the presence of multiple stages of evaporation in the curve. These occur at approximately 170 and 190°C. A TGA curve for a material that is purely evaporative, e.g. pure water, will have a smooth curve. Additional steps indicate that other processes are activating, and causing changes to the compound affecting the mass loss.

More detail can be seen by performing a derivation on the TGA curve, giving the mass loss rate. This plot can be found in figure 7.1b. This plot shows a shoulder on the primary evaporative peak, and then another peak starting at around 170°C and peaking at 190°C. The shoulder indicates that even during the evaporation of the bulk of the material, before residues and other imperfections cause rate changes, a secondary mechanism is activating and impacting the mass loss rate.

Comparing this data with that of Pb(TMHD)_2 , it is immediately obvious that the evaporation mechanism for the latter is much smoother. There is no major visible step, apart from some slight changes nearing the upper end of the testing temperature range (185–200°C). With a closer look at figure 7.2b, it is easier to see that there is basically smooth vaporization up to approximately

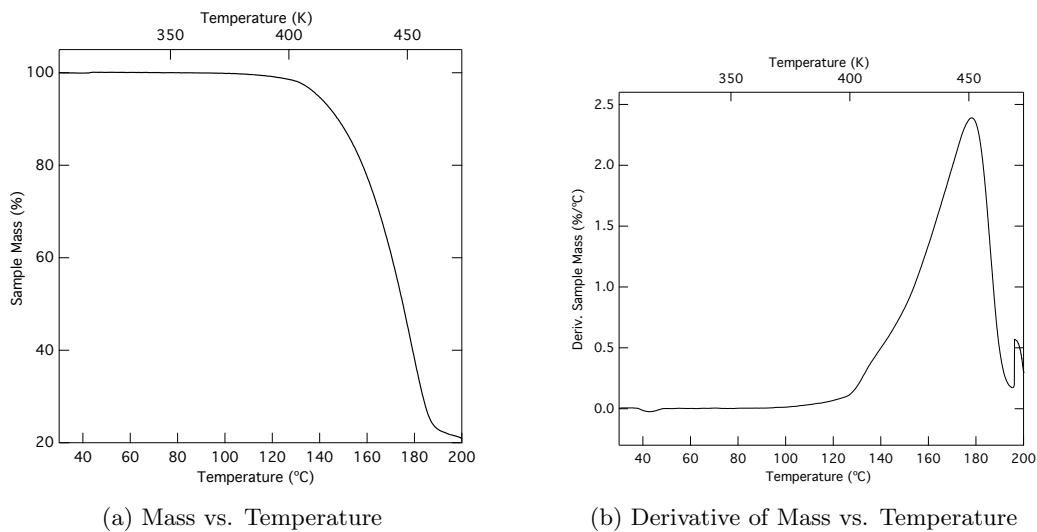


Figure 7.2: Plots of the results from TGA experiments on Pb(TMHD)_2 . As in figure 7.1 on the preceding page, (a) presents the actual mass as a function of temperature, while (b) gives the derivative of that function. Initial sample mass: 3.719 mg

180°C, at which point the evaporation is slowed dramatically due to residue buildup.

Neither of these precursors evaporated cleanly, leaving residues of more than 20% of their initial sample mass during the temperature scanning tests discussed above. When these were tested at moderate temperatures, such as those to be used for evaporation in the ALD system, both left even larger fractions of their initial masses behind. Testing at a constant temperature (160°C) over a longer period of time gives the plots shown in figure 7.3 on the following page. From this test, it was found that Pb(HF₂O)₂ left a much larger residue than Pb(TMHD)₂, 63% and 34% respectively.

Based on the results of these tests, the lower residual mass and the cleaner evaporative process, Pb(TMHD)_2 was predicted to have better performance as an ALD precursor.

7.1.2 Differential Scanning Calorimetry

As discussed in previous chapters, DSC is a powerful tool for analyzing the behavior of precursors. The data collected allows for the understanding of various energies in the material.

When considering the energetic behavior of $\text{Pb}(\text{HFAc})_2$ (see fig. 7.4 on page 47), there are a few minor features that can be noticed. Primarily at 25 and 150°C small peaks are visible that indicate changes in the material

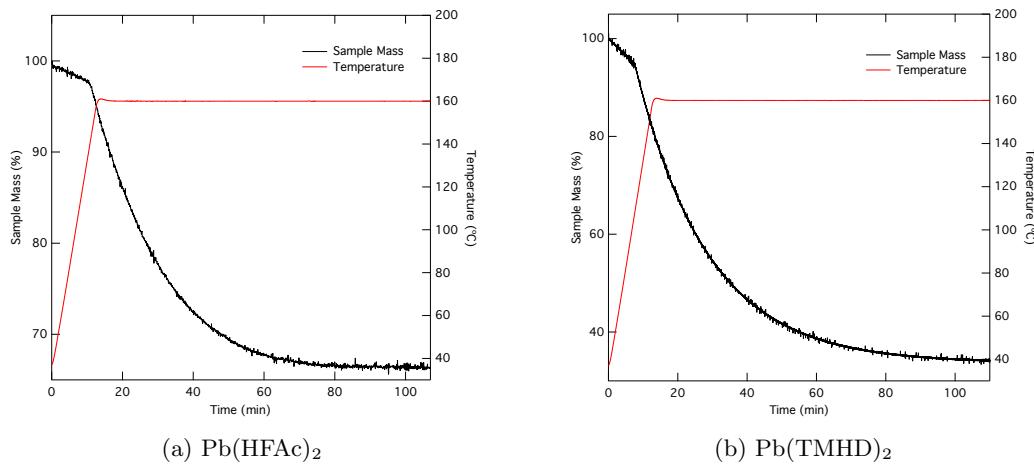


Figure 7.3: Plots of the results from ramp-and-hold TGA experiments designed to investigate residual material after complete evaporation at a given temperature. From the TGA experiments seen above (figs. 7.1 on page 44 and 7.2 on the preceding page), a common temperature of 160°C was chosen for this experiment. Sample masses were 3.921 mg and 4.381 mg for $\text{Pb}(\text{HFAC})_2$ and $\text{Pb}(\text{TMHD})_2$ respectively.

other than the solid to liquid phase change, which is the much larger peak seen around 155-160°C. However, these peaks appear to be negligible, as the 1250 total energy release by the sample is a mere 5.32 mJ (1.13 J/g), which is too low for any major chemical changes to be occurring.

Similarly, when $\text{Pb}(\text{TMHD})_2$ is heated to moderate temperatures (up to 200°C, see fig 7.5a on page 48), such as those used in the evaporation and transport stages of the ALD system, there are no irregularities in the data. 1255 There is also no net energy gain or loss during the test indicating that heating up to 200°C, along with the associated melting and freezing of the compound, is not detrimental to its structure.

If the test is again performed, but with a higher upper temperature bound, the data is drastically different (see fig. 7.5b on page 48). As the sample is 1260 heated up to 300°C, there are a number of significant energy releases that occur. These processes initiate at 234°C, and are due to the precursor undergoing pyrolysis reactions. As such, this sets the safe upper temperature range for the “ALD window” of $\text{Pb}(\text{TMHD})_2$ at 230°C. ALD reactions require that the precursor arrive to the surface intact and only react with surface species.

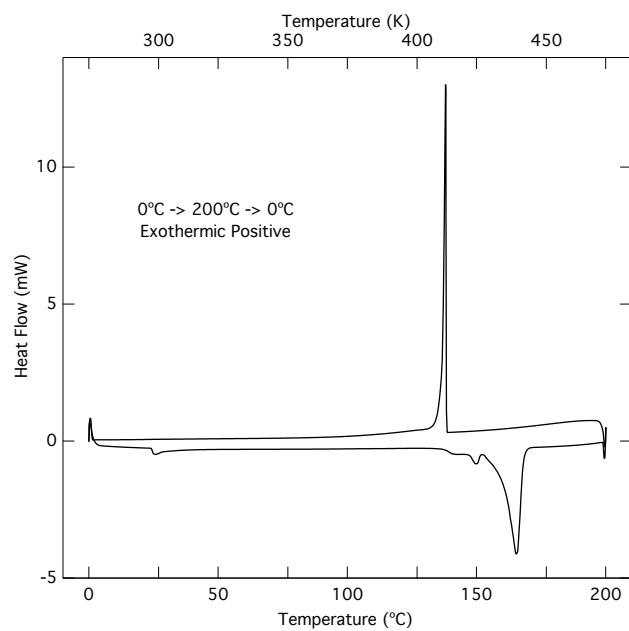
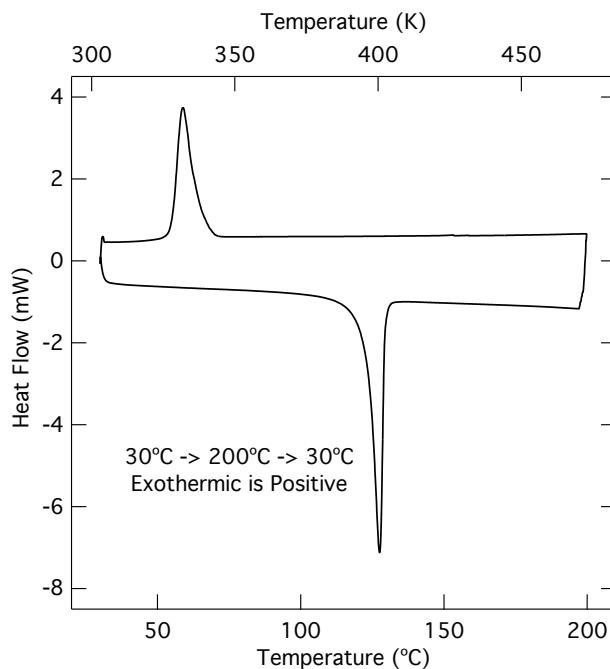
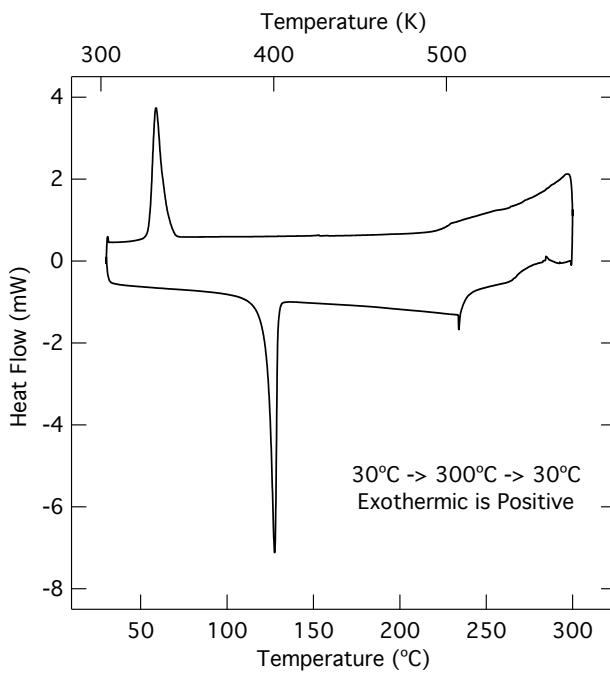


Figure 7.4: Plot of the DSC scan of $\text{Pb}(\text{HFAc})_2$. In this plot exothermic behavior, where the sample releases heat, is considered positive. Thus, the first sweep of the scan (from 0°C to 200°C) is negative. Sample mass: 4.7 mg.



(a) Low Temperature Test (30–200–30°C)



(b) High Temperature Test (30–300–30°C)

Figure 7.5: Results from the DSC scans of $Pb(TMHD)_2$. (a) Temperatures up to 200°C show no change in the material other than that of melting and freezing. (b) As temperatures increase, features start to appear indicating chemical reconfiguration of the molecule.

₁₂₆₅ **7.2 List of Samples**

Based on the results from the thermal analysis, a number of samples were deposited with various deposition parameters. Information on the deposition parameters for each of the samples used in this study can be found in the following table 7.1. A small number of samples were attempted at 200°C, but ₁₂₇₀ it was quickly determined that 225°C provided better growth behavior without risking thermal cracking of the precursor.

Table 7.1: A list of samples produced during the course of this project.

| Temp. (°C) | Run # | Pb:Ti Ratio | Cycles | Subs. Type | Annealing | | |
|---------------|-------|----------------|--------|---------------|-----------|---------------|---------------|
| | | | | | Type | Temp. (°C) | Time (min) |
| 200 | 3 | 1:1 | 250 | Si | None | N/A | N/A |
| | 2 | 1:2 | 250 | Si | None | N/A | N/A |
| | 30 | 3:1 | 160 | Si | None | N/A | N/A |
| | | | | Pt-Si | None | N/A | N/A |
| 225 | 0 | 1:1 | 625 | Si | Oven | 650 | 120 |
| | | | | | Oven | 900 | 120 |
| | | | | | RTA | 900 | 10 |
| | 1 | 1:1 | 475 | Si | None | N/A | N/A |
| | 6 | 1:2 | 250 | Si | None | N/A | N/A |
| | 13 | 3:1 | 250 | Si | None | N/A | N/A |
| | 16 | 3:1 | 150 | Si | RTA | 650 | 1 |
| | 19 | 3:1 | 100 | Si | None | N/A | N/A |
| | | | | Pt-Si | None | N/A | N/A |
| | 20 | 3:1 | 200 | Si | None | N/A | N/A |
| | | | | Pt-Si | Oven | 650 | 90 |
| | | | | STO | Oven | 650 | 90 |
| 21 | 3:1 | 150 | Si | None | N/A | N/A | N/A |
| | | | Pt-Si | Oven | 650 | 90 | |
| | | | STO | Oven | 650 | 90 | |
| 22 | 3:1 | 150 | Si | None | N/A | N/A | N/A |
| | | | Pt-Si | Oven | 650 | 90 | |
| | | | STO | Oven | 650 | 90 | |
| 23 | 3:1 | 200 | Si | None | N/A | N/A | N/A |
| | | | Pt-Si | Oven | 650 | 90 | |
| | | | STO | Oven | 650 | 90 | |
| 28 | 3:1 | 120 | STO | Oven | 650 | 90 | |

7.3 Ellipsometry

Ellipsometry was a valuable tool during the course of this study. As discussed previously, it is capable of quickly, accurately, and non-destructively determine various properties of thin film layer stacks. Of primary importance is the ability of the tool to provide a rapid method of determining the thickness of a deposited layer. In ALD the growth rate is one of the primary markers of a well-tuned deposition process. An uncontrollably high growth rate is nearly as detrimental as having minimal growth. Varying deposition parameters and noting their effects on the growth rate of the process provided valuable insight into how best to tune the process.

Given in table 7.2 is information on various samples and their as-deposited layer thicknesses, along with some relevant deposition parameters. One can also see from the plot of the sample thicknesses with respect to the number of deposition cycles (fig. 7.6 on the next page) the consistency of a growth rate given a certain set of parameters. There is a small number of initial cycles required to initiate growth, referred to as “incubation” cycles, and then the film thickness follows a close linear dependence to the number of deposition cycles. This is indicative of a deposition that is operating within the ALD window and behaving well. From figure 7.6 it was found that films deposited on silicon required approximately 10 cycles to initiate layer growth and subsequently grew at a rate of 3.78 Å/cycle. For platinum coated silicon the incubation time was longer, an average of 36 cycles, but the films grew at a faster rate of 4.12 Å/cycle. On STO crystals a 21 cycle incubation period was followed by a growth phase with a rate of 4.08 Å/cycle. This varies greatly from values reported in table 7.2 as the growth rates reported here do not take into account the incubation time. The relatively constant number of initiation cycles has a seemingly greater effect on samples with low cycle counts; the incubation cycles take up a greater percentage of the total run and lower the growth rate accordingly.

An additional piece of information that can be extracted from ellipsometric analysis is an estimation of the band gap energy of the deposited layer. Because the final model used in the analysis method (see section 6.2.3 on page 36) is physically descriptive of the optical properties of the material, it is possible to extract such information from the model. By transforming the plot of the extinction coefficient, k , into that of the absorption coefficient, α , it becomes possible to use the method developed by Tauc, *et.al.* to determine the band

Table 7.2: Table of the film thicknesses and associated growth rates as measured by ellipsometry. Growth rates do not take into account any incubation times for the films.

| Pb:Ti Ratio | Sample # | Cycles | Substrate Type | Thickness (nm) | Growth Rate (Å/cycle) |
|-------------|----------|--------|----------------|----------------|-----------------------|
| 1:1 | 0 | 625 | Si | 85.9 | 1.37 |
| | 1 | 475 | Si | 63.4 | 1.33 |
| 3:1 | 13 | 250 | Si | *32.9 | *1.31 |
| | 16 | 150 | Si | 51.2 | 3.41 |
| | 19 | 100 | Si | 34.3 | 3.43 |
| 20 | | | Pt-Si | 27.5 | 2.75 |
| | | 200 | Si | 71.8 | 3.59 |
| | | | Pt-Si | 64.4 | 3.22 |
| 21 | | | STO | 73.6 | 3.68 |
| | | 150 | Si | 53.2 | 3.54 |
| | | | Pt-Si | 45.8 | 3.05 |
| 22 | | | STO | 52.9 | 3.53 |
| | | 150 | Si | 53.3 | 3.55 |
| | | | Pt-Si | 46.5 | 3.10 |
| 23 | | 200 | Si | 72.0 | 3.60 |
| | | | Pt-Si | 64.6 | 3.23 |
| 28 | 120 | | STO | 41.0 | 3.42 |

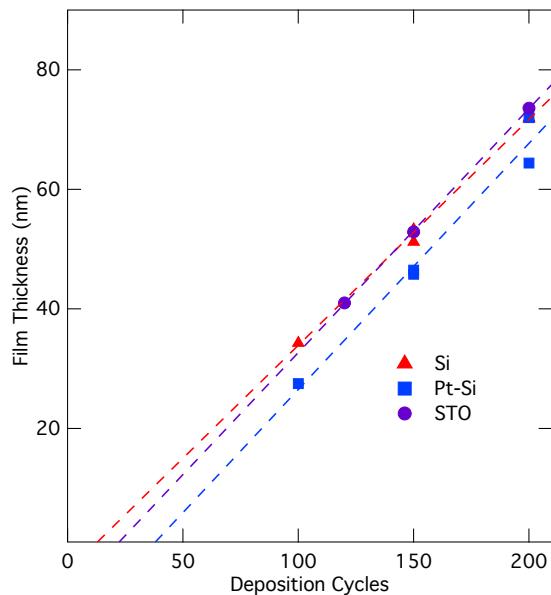


Figure 7.6: A plot of film thicknesses determined by ellipsometry. Growth rates and average incubation times are extrapolated from this data. All films were deposited with a 3:1 Pb:Ti ratio and at 225°C

gap energy of the material.^{65,66} However, such analysis does not take into account presence of multiple phases in the layer; when multi-phase layers are present the resulting band gap can only be used as a rough estimate. Tauc analysis also requires that the sample be properly crystallized, and thus must have undergone an annealing treatment before the analysis method becomes valid. As samples produced here had low phase purity, which will be discussed in subsequent sections, this analysis was of little use as a film benchmark.

Some results from these analyses can be found in section [A.4 on page 70](#).

7.4 Composition

Controlling the composition of the film was another primary task during the course of this project. Controlling the stoichiometry of the deposited films was of critical importance in obtaining films that presented the perovskite phase. If the balance of the two cations (Pb^{2+} and Ti^{4+}) was allowed to stray away from unity, other phases would be preferred or a mixture of phases would precipitate during a crystallizing heat treatment.

As discussed previously, X-ray fluorescence was the method used for performing the composition analysis of the film structures. Through testing it was found that a deposition ratio of 3:1 in favor of the lead half-reaction provided the best film composition; there were a pair of samples deposited at an even 1:1 ratio that also provided near unity compositions (sample #0 and #1). A list of samples and their compositions, measured via XRF, can be found below (see [table 7.3 on the facing page](#)).

As mentioned in section [6.3.1](#), samples deposited on STO were unable to have their compositions accurately measured using this technique. This was due to the confounding influence of the titanium content in the STO substrate, and there were no surface sensitive characterization methods available.

*Table 7.3: Calculated compositions of selected samples, determined via XRF.
Composition percentages are all $\pm 1\%$.*

| Run # | Substrate | Composition (%) | | |
|-------|------------------|-----------------|----------|-------------|
| | | Lead | Titanium | Ti:Pb Ratio |
| 0 | SiO ₂ | 56.0 | 44.0 | 0.786 |
| 1 | SiO ₂ | 55.0 | 45.0 | 0.809 |
| 13 | SiO ₂ | 54.0 | 46.0 | 0.853 |
| 16 | SiO ₂ | 49.4 | 50.6 | 1.022 |
| 19 | SiO ₂ | 65.9 | 34.1 | 0.518 |
| | Pt-Si | 42.9 | 57.1 | 1.333 |
| 20 | SiO ₂ | 56.6 | 43.4 | 0.769 |
| | Pt-Si | 51.5 | 48.5 | 0.944 |
| 21 | SiO ₂ | 69.6 | 30.4 | 0.437 |
| | Pt-Si | 56.1 | 43.9 | 0.783 |
| 22 | SiO ₂ | 67.7 | 32.3 | 0.478 |
| | Pt-Si | 56.1 | 43.9 | 0.784 |
| 23 | SiO ₂ | 66.9 | 33.1 | 0.495 |
| | Pt-Si | 49.1 | 50.9 | 1.038 |
| 24 | SiO ₂ | 69.0 | 31.0 | 0.450 |
| | Pt-Si | 62.2 | 37.8 | 0.609 |

7.5 X-Ray Diffraction

¹³³⁵ XRD was performed on a number of samples that had indicated composition ratios near unity. After an annealing treatment, generally performed in a regular ambient environment furnace but occasionally through use of the RTA, the XRD data was taken. . However, samples processed using the RTA tended to obtain a unique and very rough surface texture, as opposed to the ¹³⁴⁰ smooth mirror appearance of samples processed in the standard furnace. This observation lead to the adoption of the standard furnace as the main method of heat treatment.

¹³⁴⁵ Analysis of XRD spectra made on the samples indicated a significant variety of phases present in the crystallized films. For example, figure 7.7 gives the result from the sample #0 deposited on a platinized silicon substrate. There are three major phases present: PbO_2 , PbO , and PbTiO_3 . The reflections from PbTiO_3 and lead(IV) oxide are much weaker than those from the lead(II) oxide.

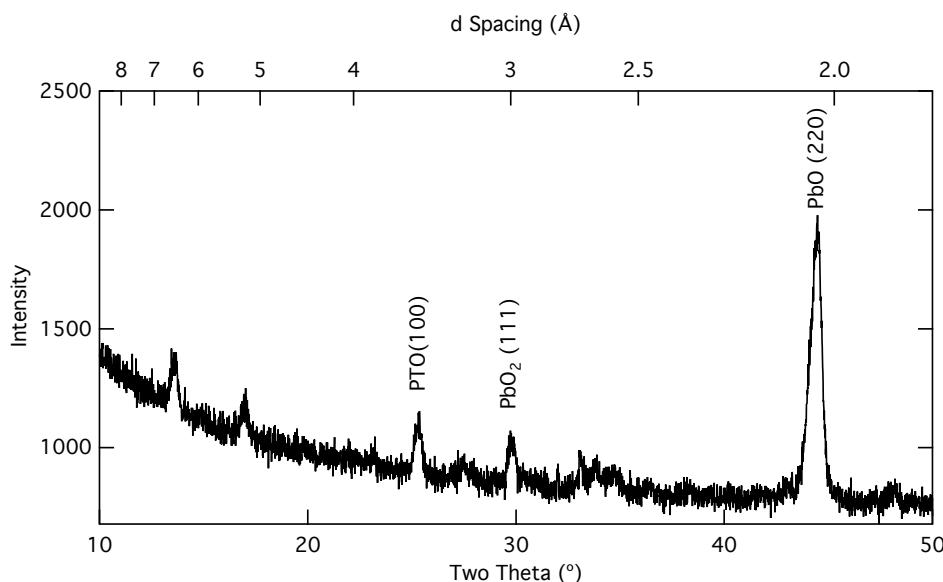


Figure 7.7: This data shows the result of diffractometry on sample #0 Pt-Si. From this, the PTO(100) reflection can be identified, as well as some other lead oxide phases.

¹³⁵⁰ However, other samples produced more interesting films. For example, sample #23 on Pt-Si (see figure 7.9 on page 56), has strong reflections from the PbTiO_3 (110) and (101) planes. There was a significant number of impurity phases present, often in significant amounts, such as the pyrochlore phases

Pb₂Ti₂O₆ and PbTi₃O₇, which indicates issues during the crystallization phase of the sample processing. However, the presence of the desired perovskite phase 1355 marked an important point in the course of this study, as it showed that the process is capable of accomplishing the goal of PbTiO₃ via ALD methodology.

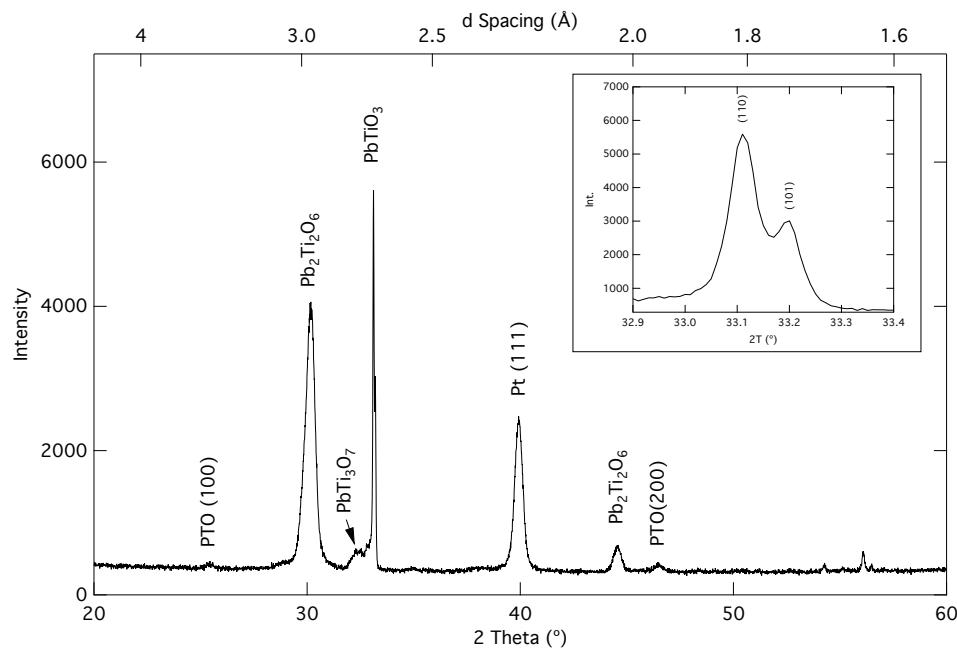


Figure 7.8: This data shows the result of diffractometry on sample #23 Pt-Si. In this sample there are present a variety of phases. The inset shows the splitting of the PbTiO₃ peak, due to the tetragonal nature of the unit cell.

Additional samples provided similar results. For example, #20 on Pt-Si (fig. 7.9 on the next page), has similar impurities but again exhibits an abundance of the PbTiO₃ phase. This sample has a slightly higher concentration 1360 of PbTi₃O₇, and a slightly weaker reflection from the dominant PTO planes.

Finally, investigation of a sample deposited on strontium titanate crystal (see figure 7.10 on the following page) showed a strong preference of the PTO phase to orient with the orientation of the substrate. In this sample was also seen presence of titania phases (rutile, α -TiO₂) as composed to samples 1365 deposited on Si and Pt-Si substrates. However, since the precise composition of films on STO is unknown the reason for finding TiO₂ is unclear, likely due to an excess of titanium in the deposited film.

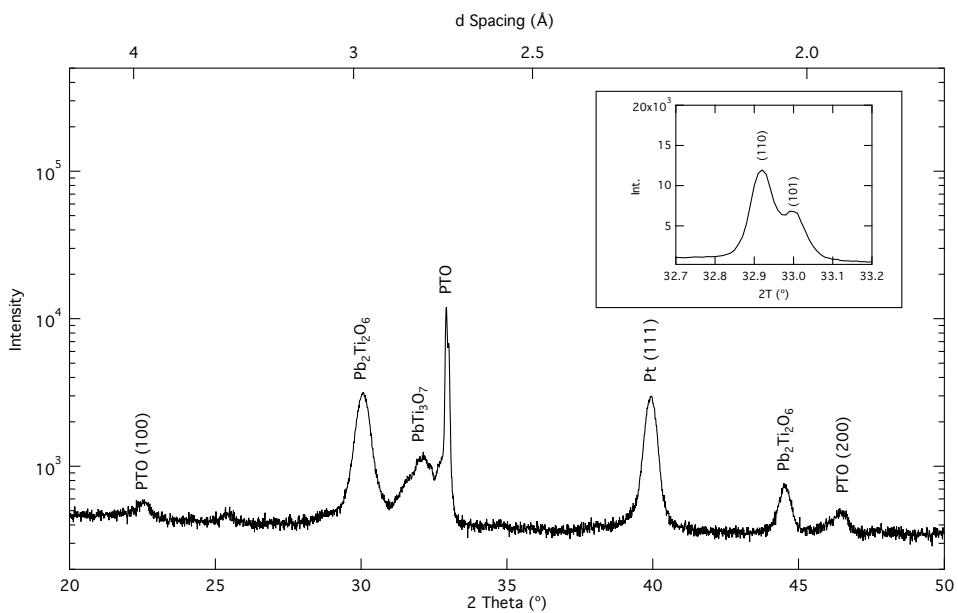


Figure 7.9: This data shows the result of diffractometry on sample #20 Pt-Si. There are some impurity phases present, however the strongest signals are due to the PbTiO₃ (101) and (110) reflections (see inset).

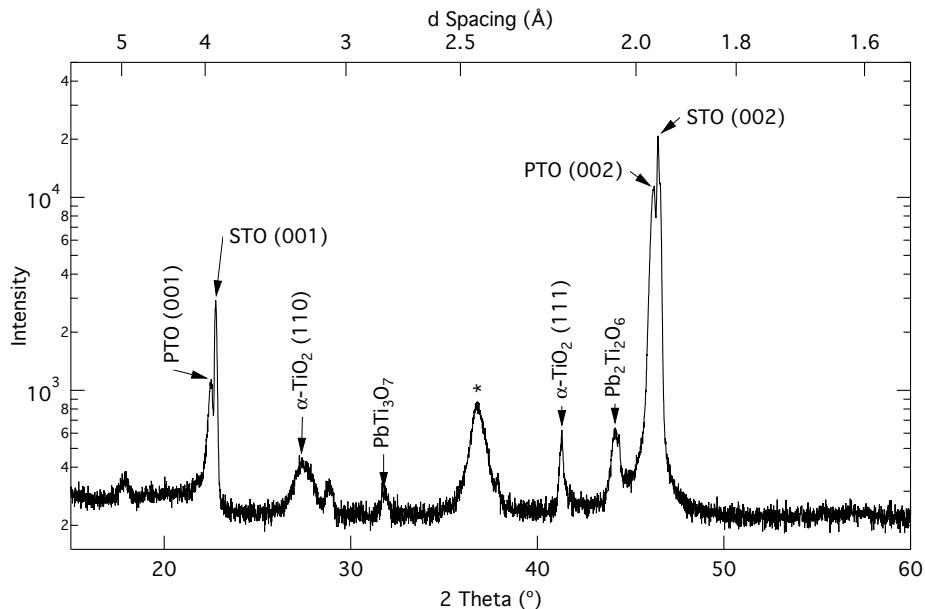


Figure 7.10: This data shows the result of diffractometry on sample #28 STO. Impurity phases were present (particularly α-TiO₂ and pyrochlore). It was also notable that the PTO phase preferentially oriented itself with the STO (001) substrate.

Chapter 8

Conclusions

1370 The final result of this study was to show that it is certainly possible to grow perovskites using an ALD process, but the exact processes are sensitive and require much attention and further analysis.

At the completion of this project, it can be said that the following goals have been met. A method for analyzing and predicting the behavior and operating windows of potential ALD precursors using standard thermal analysis techniques (TGA and DSC) has been proposed and shows good promise for applicability towards other material systems and precursor.

1380 A reliable method of analyzing film thicknesses and growth rates has been developed utilizing ellipsometry, which allows for rapid and non-destructive testing (and possibly incorporation as an *in situ* testing mechanism to monitor film growth during deposition). In addition, the method described is capable of extracting additional information about film properties (e.g. band gap energies and other electronic characteristics) that could be applied given a higher degree of phase purity in the final crystallized film.

1385 Use of XRF, in place of the more common EDS, allowed for the quantitative analysis of film composition even at ultra thin thicknesses. This rapid and non-destructive tool was of significant utility to this project. However, the ability to perform surface sensitive measurements would have made analysis of films grown on strontium titanate crystals more complete.

1390 It was found that phase identification was possible using XRD with the thin films produced in this study. However, utilization of grazing incidence XRD — a technique used to improve surface sensitivity of XRD — would likely improve upon the results seen here, and would likely prove necessary if films of lower thicknesses were to be analyzed.

1395 It proved to be non-trivial to produce films which, upon annealing, crystallized into phase-pure perovskite PbTiO_3 . Instead, the films often degrade into a mixture of PTO, pyrochlore forms (PbTi_3O_7 and $\text{Pb}_2\text{Ti}_2\text{O}_6$), various lead oxides (PbO_x), and rutile tania. At this time it is unclear exactly what causes this behavior. Additional research into the thermodynamics and crystallization behavior of these films would be of great value.

8.1 Future Work

While the work presented herein is noteworthy, and lays a framework for further investigation and refinement of ALD deposited perovskite oxides including the topic of discussion of this thesis, there is much left to be investigated in this line of research. Next steps would serve to further refine the process to improve the reliability of deposition, improving the phase purity and improve the degree of epitaxy of the grown film, or better conserve and deliver precursor (issues that plagued this project throughout its course). Being able to consistently produce films of constant quality would make this work applicable to a myriad of material systems.

Additionally, there is one aspect of film characterization that had not been investigated thoroughly during the course of this project: the ferroelectric character of the films. Verification of ferroelectric behavior, even initially in isolated grains, would greatly improve the value of the method. Initial tests would likely require the use of microscopy techniques, e.g. piezoelectric force microscopy (PFM), to measure response of isolated grains of ferroelectric material; more standard ferroelectric measurements could likely be utilized with improved film quality and phase purity.

Following this path of discussion quickly leads to the question of doping the films in order to improve properties. The obvious example here would be the development of an ALD process for $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. Lead titanate as a material is rather uncommonly used in applications, however as a simplified example of this family it was a prime candidate for the primary research. This project thus serves as a gateway to exploring the more valuable and technically relevant materials via ALD.

Finally, it would be useful to extend this method to completely new material families. BaSrTiO_3 is another commonly used ferroelectric material. Use of this material is gaining interest not only due to its intrinsic properties, but also due to its lack of lead content which makes it a far more environmentally conscious choice. BiFeO_3 and corresponding doped materials, are another interesting perovskite. This set of materials presents multiferroic — a combination of (anti)ferromagnetism and ferroelectricity — behavior, making it a prime target for such novel technologies as spintronics.

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Appendix A

Supplemental Information

A.1 List of Chemicals

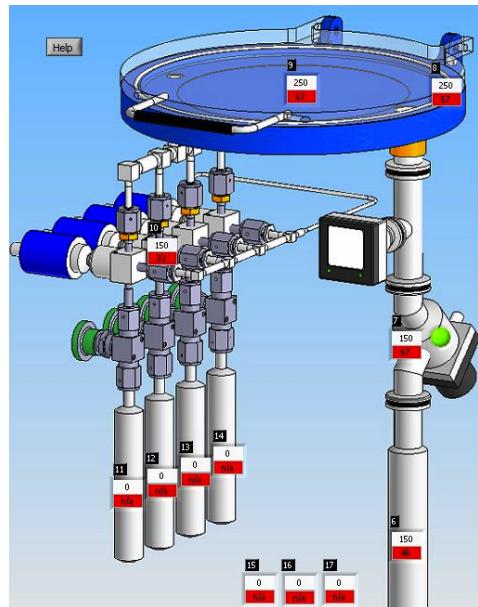
Table A.1: List of chemical compounds used during the course of this study.

| Chemical Name | Chemical Formula | CAS # | Molec. Weight | Source |
|--|--|------------------------|---------------|-----------------------|
| Lead(II) hexafluoro-acetylacetone | Pb(C ₅ O ₂ HF ₆) ₂ | 19648-88-5 | 621.29 | Strem Chemicals, Inc. |
| Bis(2,2,6,6-tetramethyl -3,5-heptanedionato) | Pb(C ₁₁ H ₁₉ O ₂) ₂ | 21319-43-7 | 573.50 | Strem Chemicals, Inc. |
| Lead(II) | | | | |
| Titanium(IV) i-propoxide | Ti[OCH(CH ₃) ₂] ₄ | 546-68-9 | 284.25 | Strem Chemicals, Inc. |
| Isopropyl Alcohol (IPA) | (CH ₃) ₂ CHOH | 67-63-0 | 60.10 | Alfa Aesar |
| Acetone | C ₃ H ₆ O | 67-64-1 | 58.08 | Alfa Aesar |
| Buffered Hydrofluoric Acid (BHF) | NH ₄ F-HF | 7664-39-3 & 12125-01-8 | N/A | Alfa Aesar |
| Ozone | O ₃ | 10028-15-6 | 48.00 | |

1635 A.2 ALD Reactor Diagram



(a) Photograph



(b) Schematic Diagram

Figure A.1: Cambridge NanoTech, inc. Savannah S100 ALD reactor. Precursors are stored in heated cylinders, flow up to the reaction zone, and byproducts are pumped out of the vacuum line on the right side. Each zone can be individually temperature controlled.

A.3 Composition Results

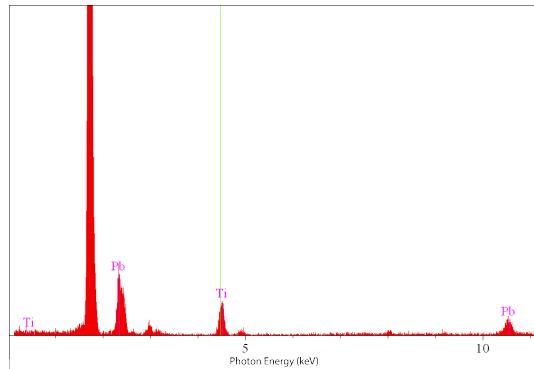


Figure A.2: The XRF spectrum collected from deposition run #0.

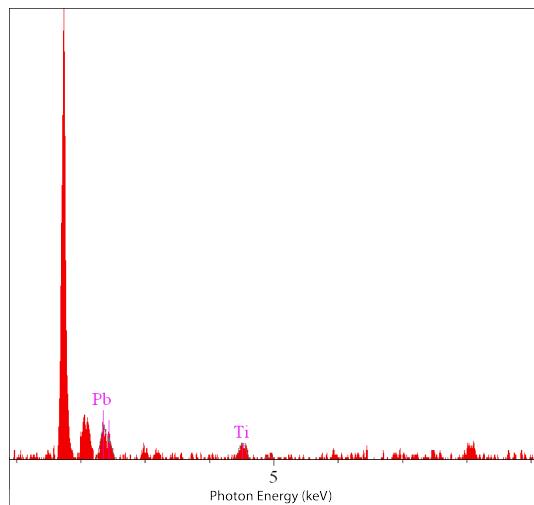


Figure A.3: The XRF spectrum collected from deposition run #20 deposited on platinized silicon. The peak between the substrate and Pb is that of Pt.

A.4 Ellipsometry Results

Table A.2: Variables used to produce the model fit for PTO #0 seen in fig. A.4 on page 72.

| Layer | Variable | Thickness (nm) | Value |
|---------------------|---------------------|----------------|-------|
| 2. T-L Osc. | | 88.7 | |
| | ϵ_1 offset | | 2.49 |
| | Amp | | 12.66 |
| | E_n | | 4.60 |
| | C | | 1.35 |
| | E_g | | 0.86 |
| 1. SiO ₂ | | 203.7 | |
| 0. Si | | Substrate | |

Table A.3: Band gap energies, determined via Tauc analysis of ellipsometric data

| Run # | Subs. | Type | Band Gap (eV) |
|-------|-------|------|---------------|
| 0 | Si | | 3.763 |
| 20 | Pt-Si | | 4.058 |
| 28 | STO | | 3.506 |

Table A.4: Variables used to produce the model fit for PTO #20 seen in fig. A.6 on page 74.

| Layer | Variable | Thickness (nm) | Value |
|---------------------|---------------------|----------------|-------|
| 3. T-L Osc. | | 75.6 | |
| | ϵ_1 offset | | 3.62 |
| | Amp | | 36.54 |
| | E_n | | 4.51 |
| | C | | 1.30 |
| | E_g | | 2.07 |
| 2. Pt | | 15.1 | |
| 1. SiO ₂ | | 1.1 | |
| 0. Si | | Substrate | |

Table A.5: Variables used to produce the model fit for PTO #28 seen in fig. A.8 on page 76.

| Layer | Variable | Thickness (nm) | Value |
|-----------------|---------------------|----------------|-------|
| 1. T-L Osc. (2) | | 49.2 | |
| | ϵ_1 offset | | 1.42 |
| | Amp_1 | | 64.71 |
| | E_{n1} | | 3.69 |
| | C_1 | | 4.44 |
| | E_{g1} | | 1.55 |
| | Amp_2 | | 1.55 |
| | E_{n2} | | 2.12 |
| | C_2 | | 0.76 |
| | E_{g2} | | 0.001 |
| 0. STO | | Substrate | |

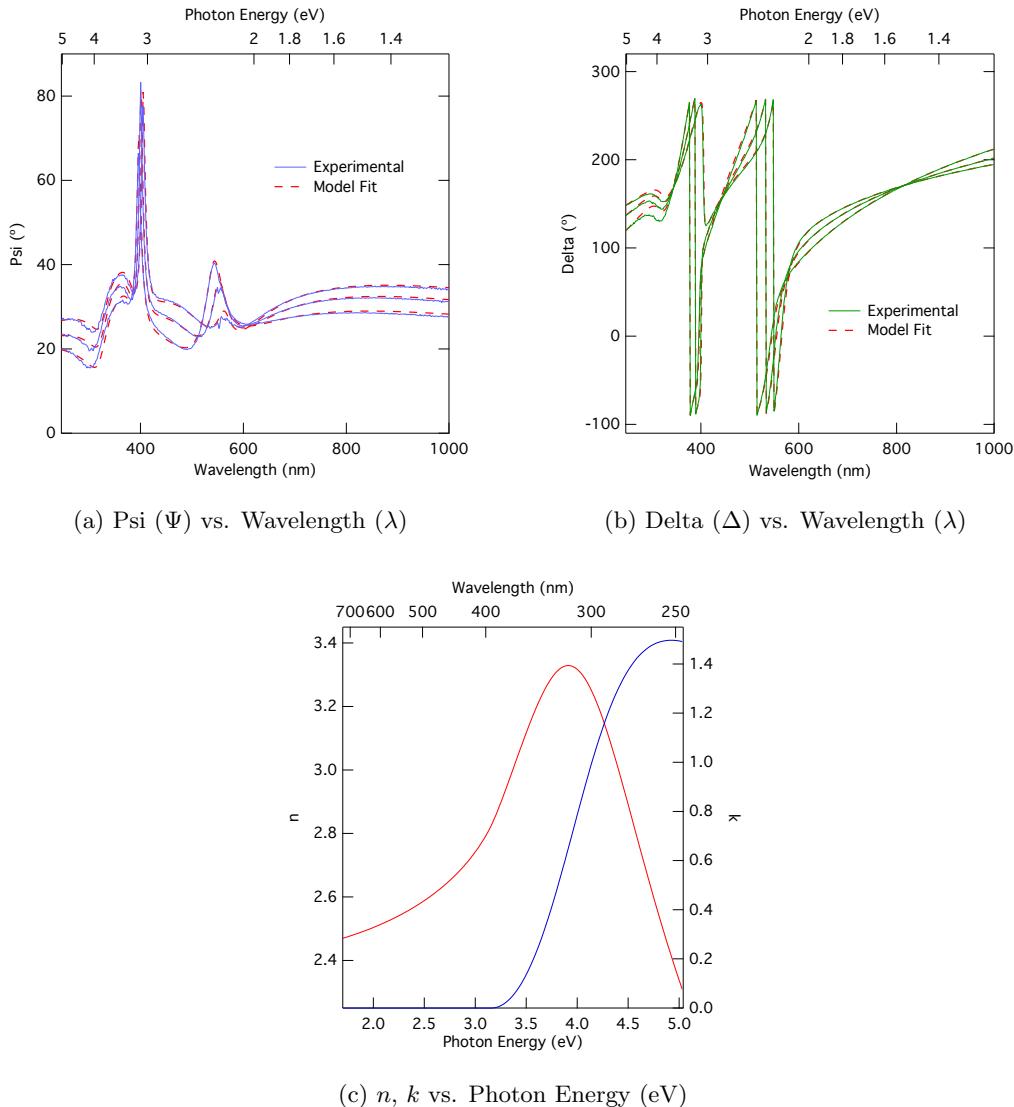


Figure A.4: The set of plots shown above show the results from ellipsometric analysis on sample #0 (see table 7.1 on page 49) grown on a silicon wafer and subsequently annealed. (a) and (b) show the data and the modeled fit from the experiment. (c) shows the components of the complex index of refraction (\tilde{n}), n and k . Band gap estimation was performed using the values of k . The highlighted portion of k is the nearly linear region used in this analysis.

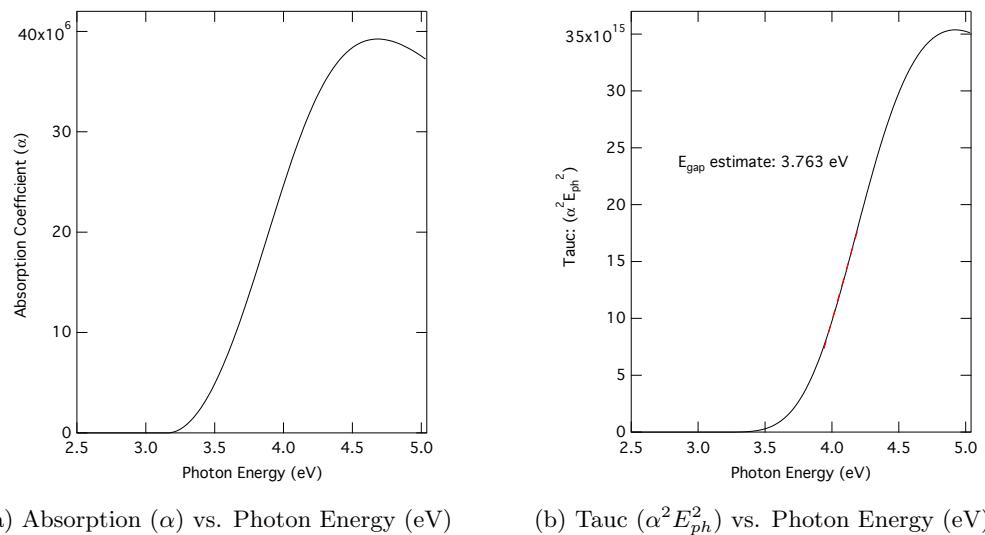


Figure A.5: Tauc analysis used to determine the bandgap of PTO #0. (a) shows the values of the absorption coefficient (α) calculated from k (seen in figure A.4c on the facing page). (b) shows the Tauc plot, the linear region can provide an estimate of the bandgap of the material.

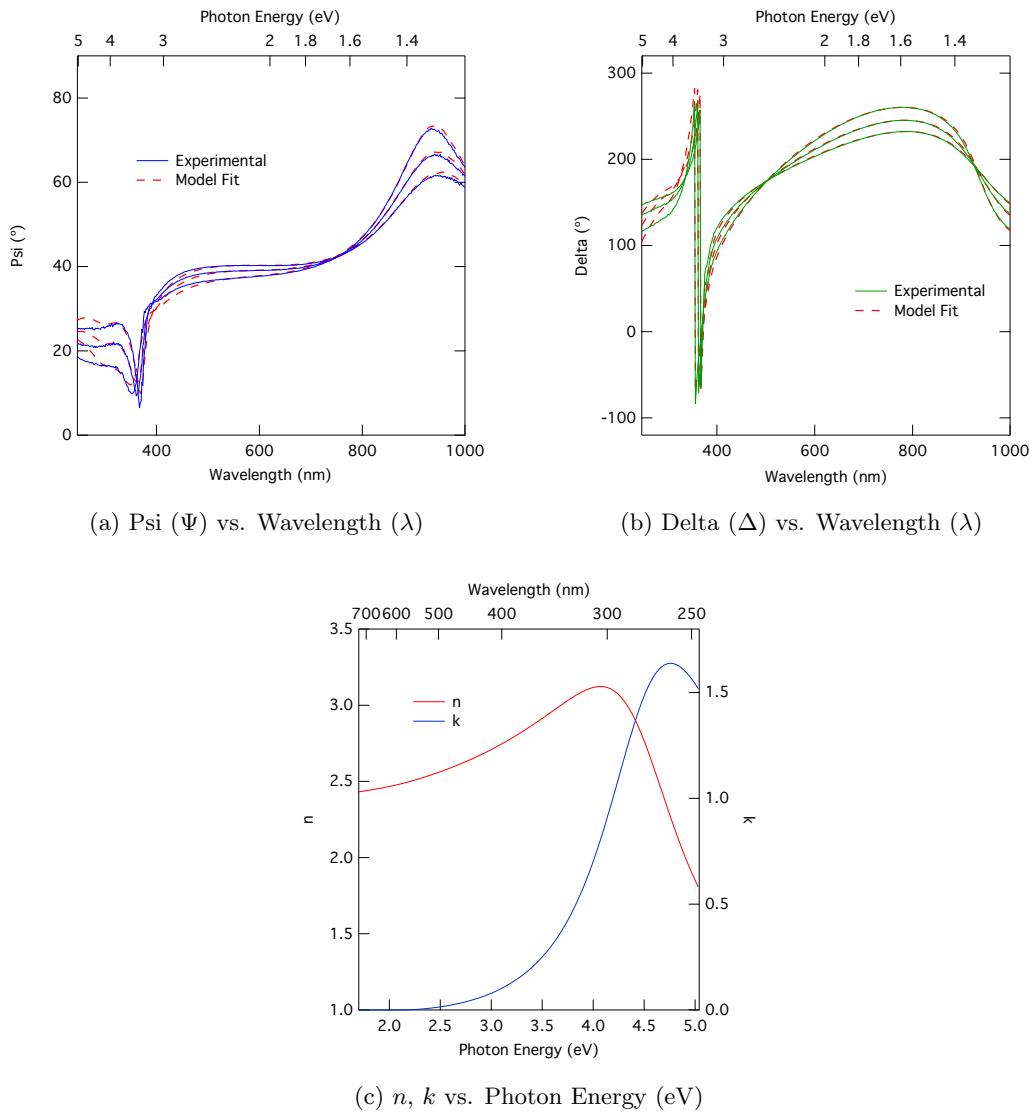


Figure A.6: Results of ellipsometric analysis on sample #20, deposited on a platinized silicon substrate. As in fig.A.4, (a) and (b) show the experimental data and model fits of psi and delta (respectively). (c) gives the plot of calculated n and k . For model parameters, see table A.4 on page 71

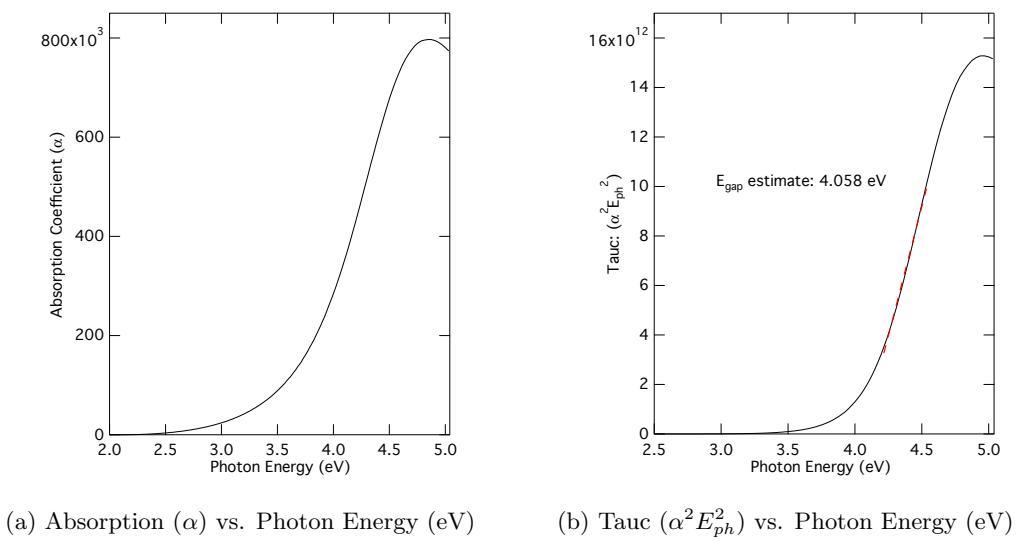


Figure A.7: Tauc analysis of sample #20 on Pt-Si

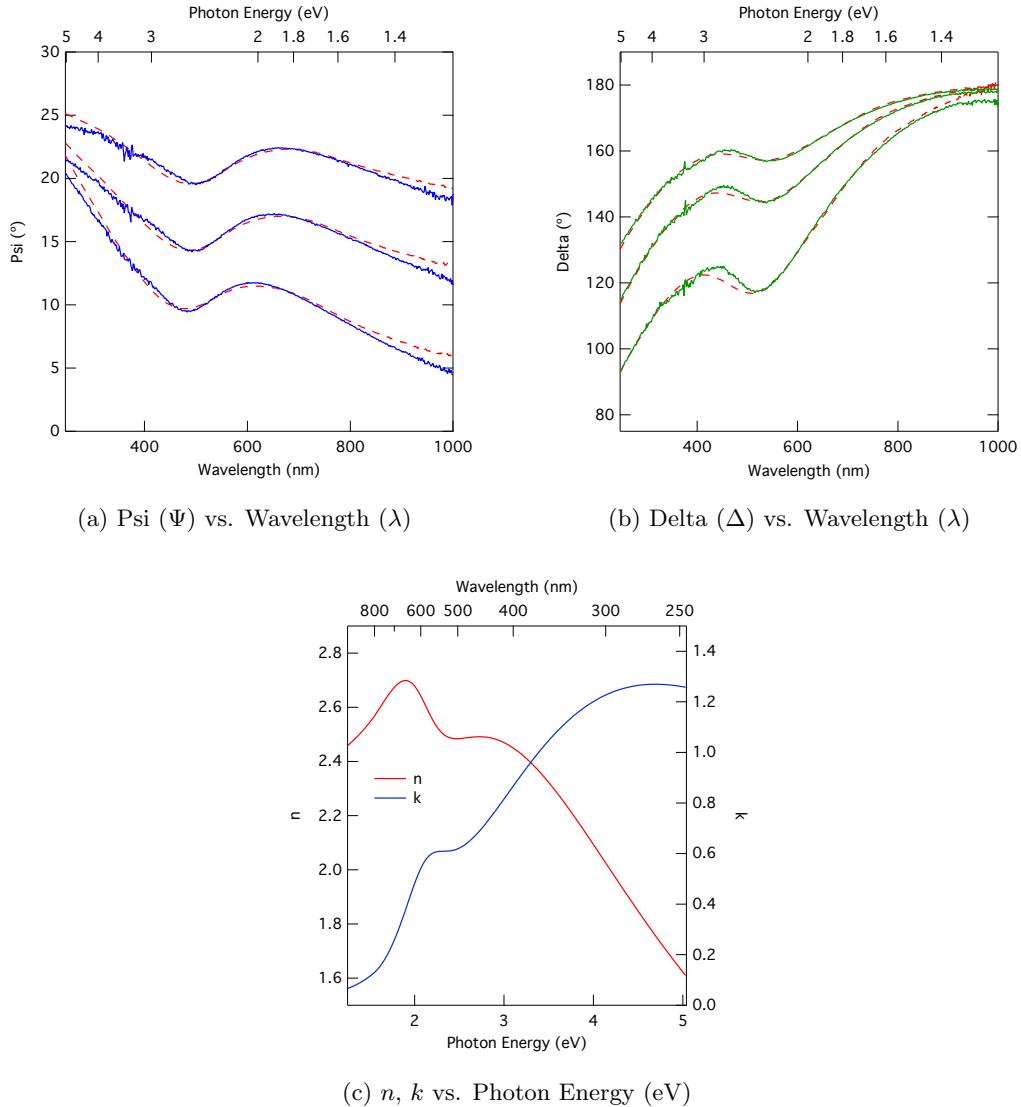
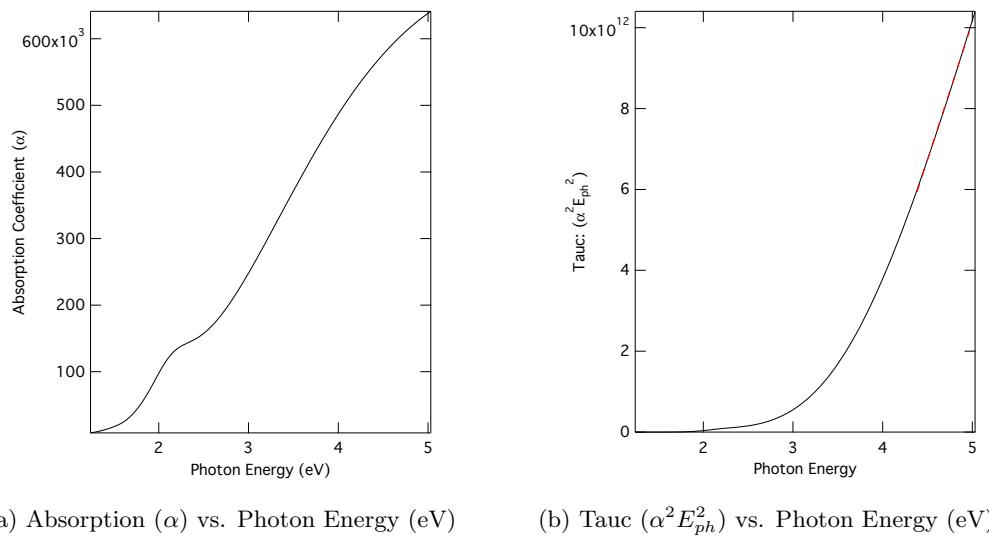


Figure A.8: Results of ellipsometric analysis on sample #28, deposited on a strontium titanate $\text{SrTiO}_3(100)$ single crystalline substrate. As in fig. A.4, (a) and (b) show the experimental data and model fits of psi and delta (respectively). (c) gives the plot of calculated n and k . This sample would not model well without a second oscillator, which gives rise to the secondary peaks in the n , k , and α plots (see fig. A.9a on the next page). For model parameters, see table A.5 on page 71.



(a) Absorption (α) vs. Photon Energy (eV) (b) Tauc ($\alpha^2 E_{ph}^2$) vs. Photon Energy (eV)

Figure A.9: $E_g = 3.506$. Tauc analysis of sample #28 - STO. Notice that the second oscillator can be seen in the absorption coefficient (a), but does not affect the shape of the Tauc plot (b) and thus does not interfere with bandgap estimation.

