

POLITECNICO DI MILANO  
Facoltà di Ingegneria dei Processi Industriali  
*Degree in Materials Engineering and Nanotechnology*



ATOMIC LAYER DEPOSITION OF  
FERROELECTRIC COMPLEX  
OXIDE THIN FILMS

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*For my parents...*



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# Abstract

As devices based on ferroelectric films become more commonplace, a commercially viable process for fabricating the material is needed; low cost and high  
155 volume are implied necessities for such a process. This work focuses on the application of atomic layer deposition (ALD) to this task. ALD is a standard fabrication process in the electronics industry, valuable for its high uniformity across large surfaces, capability to control film thickness with very high resolution, and conformality across three dimensional structures. The various  
160 tasks in designing and optimizing an ALD process, as well as characterization methods for analysis of the produced films, are discussed here in detail.

The primary focus of this work is the development of a process for depositing lead titanate ( $PbTiO_3$ ) thin films via an ALD process. Research focused on the application of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)lead(II)  
165 ( $Pb(TMHD)_2$ ) toward this end.

Work done towards the completion of this study was supported by the Army Research Office under Grant #W911NF-08-1-0067.



# **Sommario**

A detailed summary of the document to be presented solely in Italian.



<sup>170</sup> **Chapter 1**

# Introduction

## 1.1 Project Scope

The primary scope of this project involved the creation of a method to produce lead titanate thin films. To this end, a number of different steps <sup>175</sup> needed to be taken. Primarily,



# Chapter 2

## Lead Titanate

### 2.1 Structure

Lead titanate ( $\text{PbTiO}_3$ , PTO) naturally orders into the tetragonal perovskite crystal structure at room temperature (figure 2.1). 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 ( $\text{Ti}^{4+}$  in the case of  $\text{PbTiO}_3$ ) is encapsulated in a octahedral cage of anions ( $\text{O}^{2-}$ ), with the remaining cations ( $\text{Pb}^{2+}$ ) situated in the eight corners of the unit cell. If the material was doped (as in a mixed solid-solution), some of the cations would be replaced with the dopant ions, for example  $\text{Zr}^{4+}$  would be randomly distributed in  $\text{Ti}^{4+}$  sites in the  $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$  (PZT) system.

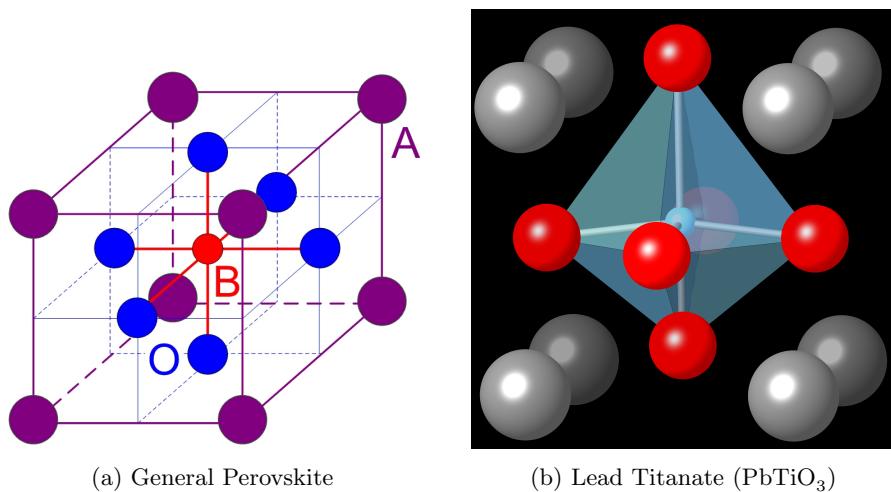


Figure 2.1: The perovskite ( $\text{ABO}_3$ ) crystal structure.

(a) The general structure of perovskite oxides. (b) Tetragonal asymmetric perovskite structure of  $\text{PbTiO}_3$ . Grey, red, and blue spheres refer to  $\text{Pb}^{2+}$ ,  $\text{Ti}^{4+}$ , and  $\text{O}^{2-}$ , respectively. Additionally, the octahedral oxygen cage is shown in pale blue.

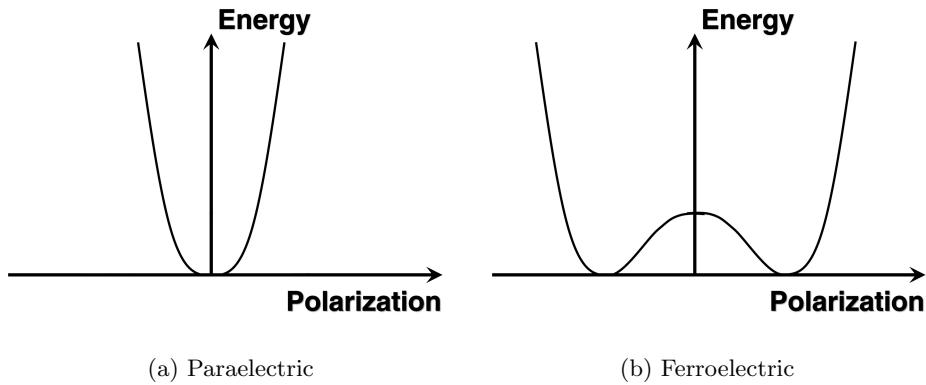
### 2.1.1 Effect of Temperature

190 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  
195 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 previous 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.  
200

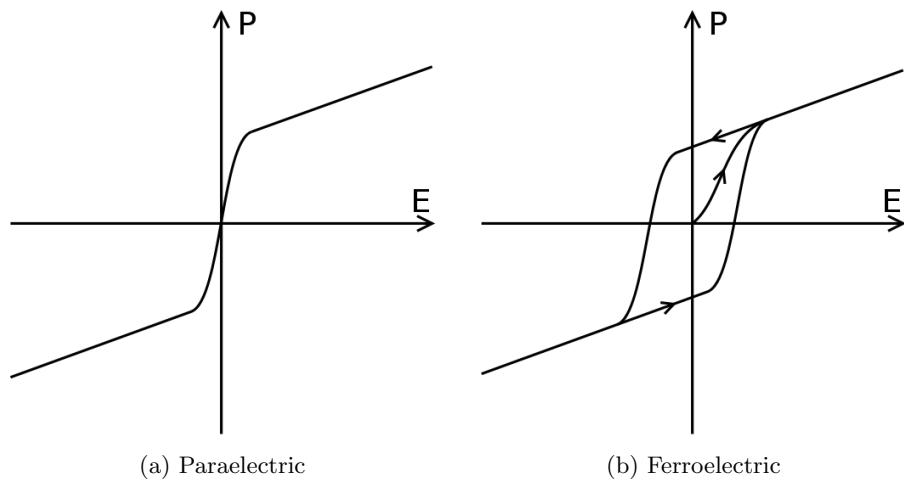
## 2.2 Ferroelectricity

205 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  
210 found at non-zero levels of polarization.

One of the most important effects of ferroelectric behavior is the exhibition of hysteresis in the polarization state of the material. Suboptimal explanations... Because additional energy is required to make the transition from one state to another, the original state endures for some amount of opposing field  
215 (see fig. 2.3b on the next page).



*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

### 225 3.2 Metallorganic Chemical Vapor Deposition

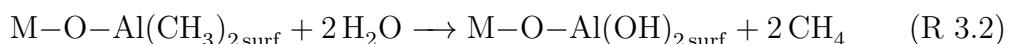
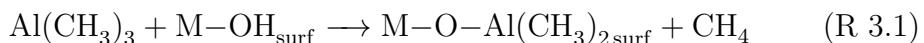
Metallorganic chemical vapor deposition (MOCVD) is a commonly used technique for depositing many different types of thin film materials. It is especially common for MOCVD to be used to deposit semiconductor films (a-Si, Ge, III-V, II-VI, etc.); these films can also be doped to varying degrees 230 with high precision.

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 235 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.

One advantage of CVD, partly due to the high deposition temperatures involved, is the ability to have the film deposit epitaxially to the substrate. 240 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.

### 3.3 Atomic Layer Deposition

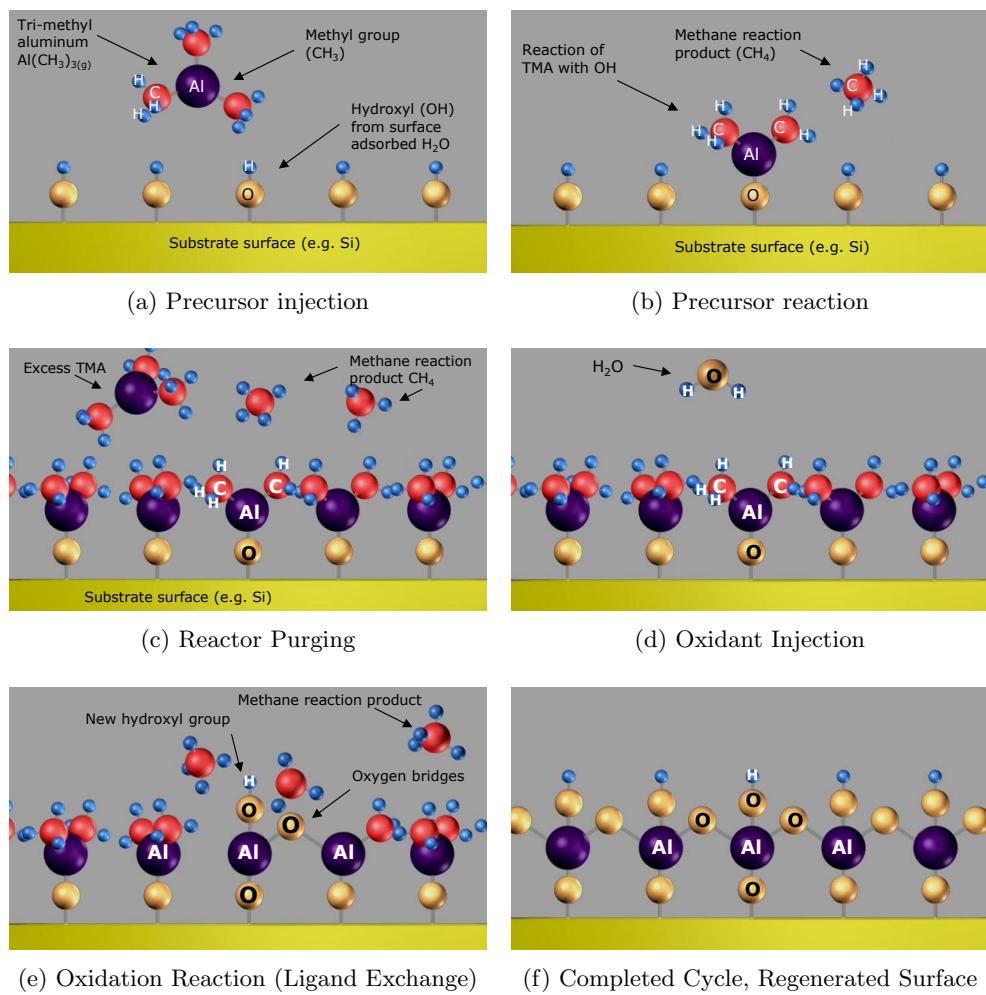
Atomic Layer Deposition (ALD) is a modification on standard CVD processes, with a few major differences. The defining aspect of an ALD process is the separation of the overall reaction into two steps: first the precursor is allowed to react with the substrate surface (see reaction R 3.1), excess reactant is purged from the chamber and an oxidizer is introduced to complete the reaction (see reaction R 3.2). These reactions show a very simple ALD reaction between trimethylaluminum (TMA,  $\text{Al}(\text{CH}_3)_3$ ) and water.



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 ( $\text{Al}_2\text{O}_3$ ), 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. 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 (at UHP grade) 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. If these are allowed to remain adsorbed they would react with the oxidant and negate the surface-limited aspects of ALD. The system would then again be evacuated, and the oxidant introduced and then pumped away to complete the cycle.

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



*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 ( $\text{Al}_2\text{O}_3$ ).*

*Graphic courtesy of Cambridge NanoTech, inc.*

275 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.

280 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. 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 285 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 thin layers of a high- $\kappa$  dielectric 290 (such as hafnia, HfO<sub>2</sub>) for use as the gate oxide in its transistors, with layer thickness generally less than 2 nm.

295 This method will produce a layer of a binary oxide material (AO<sub>x</sub>), 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<sub>3</sub>, one would begin by depositing a layer of TiO<sub>2</sub> and then depositing a layer 300 of lead oxide (PbO). Repeating this set of cycles — a super-cycle — would eventually form the PbTiO<sub>3</sub> film.

305 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 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. **Needs more here.**

310 ALD reactions are rather sensitive to a number of factors, such as temperature. The temperature must be high enough that the reactants have sufficient 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. This section needs more work. Primarily a relatively thorough review of other ALD depositions (binary films).



# Chapter 4

## <sup>315</sup> 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.<sup>320</sup> [Citation needed] 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-H<sub>2</sub>O reaction (see section 3.3 on page 8).

#### 4.1.2 Lead Source

<sup>325</sup> 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 <sup>330</sup> 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 ( $\text{Ph}_4\text{Pb}$ ), bis(2,2,6,6-tetramethyl-3,5-heptanedionato) lead(II) ( $\text{Pb(TMHD)}_2$ ), lead(II) hexafluoroacetylacetone ( $\text{Pb(HFAC)}_2$ ), and  $\text{Pb(mmp)}_3$  Be sure to find at least <sup>335</sup> one citation for each of these.

$\text{Ph}_4\text{Pb}$  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) and was thus discarded as a candidate.  $\text{Pb(TMHD)}_2$  was another commonly referenced precursor, as <sup>340</sup> was  $\text{Pb(HFAC)}_2$ .  $\text{Pb(mmp)}_3$  was seemingly a viable choice, with a very high vapor pressure at low temperatures, 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  
345 in detail as potential candidates for the lead precursor in the ALD deposition of  $\text{PbTiO}_3$ . Samples of both precursors were obtained from Strem Chemicals, inc. 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.

### 350 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  
355 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.

Based on literature reports, the two lead precursors under investigation do not undergo hydrolysis when exposed to water, and as such require the use  
360 of the combustion pathway. In addition, through the deposition of test films, it was found that the reaction proceeded more completely when the  $\text{O}_3/\text{O}_2$  mixture was used. For simplicity of the process, the  $\text{O}_3/\text{O}_2$  mix was used for both half-reactions.

## 4.2 Substrate Preparation

Fabrication and preparation of substrates was an important part of the  
365 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 platinum deposited on the surface, and strontium titanate (100) single crystal substrates.  
370

### 4.2.1 Si(100)

The silicon substrates were prepared in a simple manner. 4" diameter silicon wafers with 200 nm of thermally grown oxide were diced into 1.5 cm x  
375 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.

<sup>380</sup> **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 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. Then <sup>385</sup> a 15 nm layer of platinum was deposited via ALD (deposition recipe can be found in redacted). The substrates were then cleaved into smaller pieces for later 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 preceding page](#)).

<sup>390</sup> **4.2.3 STO(100) and Nb:STO(100)**

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.

<sup>395</sup> To prepare these samples, the substrates are first pre-cleaned in a three 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. Need to find reference and exact timings. Email Eric. The substrates were then dipped into buffered hydrofluoric acid to etch for <sup>400</sup> 35 seconds, then removed and flushed with copious DI water. Once the sample is thoroughly rinsed, the samples are dried using dry nitrogen.

After the etching process, the samples are annealed at  $1050^\circ\text{C}$  for two hours. Once the samples are cooled, they are ready for immediate use. AFM can be used to confirm the presence of atomic terraces.

<sup>405</sup> If the samples are stored, it is recommended to again clean the samples in the standard procedure (see [4.2.1 on the facing 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,  
410 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  
415 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.”

If the growth temperature is less than the lower bound of the ALD window,  
420 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  
425 energy limited regime, molecules of precursor lack sufficient energy to react with the surface. This is characterized by lower deposition rates.

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  
430 is not limited to the surface, and accounts for the extra material being deposited. Lower deposition rates indicate that the temperature is sufficient to cause desorption of previously-reacted material from the sample.

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  
435 difficult with reactions requiring multiple metal precursors (e.g.  $\text{PbTiO}_3$ , a combination of  $\text{TiO}_2$  and  $\text{PbO}$ ), 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  
440 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  
445 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  
450 choosing a potential compound for use in ALD (as discussed in section 4.1 on page 13).

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,  
455 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).  
460 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  
465 dose to the reactor.

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  $\text{N}_2$  flow to flush any remaining byproducts and excess reactants from the reactor zone. It also allows time  
470 between cycles which allows for low vapor pressure precursors to regenerate 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 course of the deposition.

<sup>475</sup> **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 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 accordingly to allow for byproducts to diffuse back out of the structure.  
<sup>480</sup>  
<sup>485</sup>

## 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 N<sub>2</sub>).  
<sup>490</sup>

### 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, 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.  
<sup>495</sup>

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 method most commonly used during this study.  
<sup>500</sup>

#### 4.4.2 Rapid Thermal Annealing

Rapid thermal annealing (RTA), as its name suggests, involves very high 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 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 45 in the appendix.



# Chapter 5

## <sup>515</sup> Film Characterization

### 5.1 Thermal Analysis

#### 5.1.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a very useful tool when attempting to determine the viability of a precursor in an ALD process. It allows for <sup>520</sup> 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 or time. A small sample (1–10 mg) of material is placed in a microgram balance <sup>525</sup> 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 by using a platinum pan in the microgram balance and constantly purging the <sup>530</sup> 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.

This technique was used to evaluate various precursor candidates for the lead oxide half of the PbTiO<sub>3</sub> deposition procedure. The instrument used was <sup>535</sup> a Q50 TGA device (fig. 5.1a on the next page). A detailed discussion of TGA procedures and the investigated chemicals can be found in subsequent chapters (see 7.1 on page 39).

#### 5.1.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique that allows for the <sup>540</sup> 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, 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 insulated chamber. The temperature of each is carefully monitored, and differing 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 energies.

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 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.

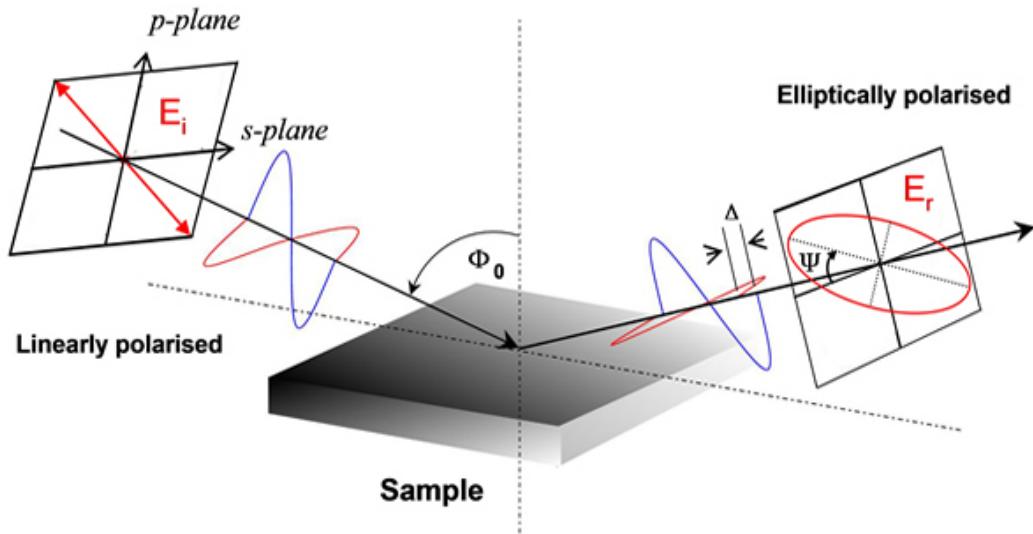


Figure 5.2: Schematic of the beam path during an ellipsometric measurement, critical parameters are indicated

## 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  $\Delta$ , while the amplitude change is given by  $\tan \Psi$  ( $\Psi$  is the angle between the *s*-plane and the major axis of the ellipse). The last major parameter is the incident angle, denoted by  $\Phi$ . A schematic diagram illustrating these parameters can be seen in figure 5.2.

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) 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,  $\kappa$ ).

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

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

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

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

This type of analysis is sufficient for thick, isotropic samples without any  
585 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.

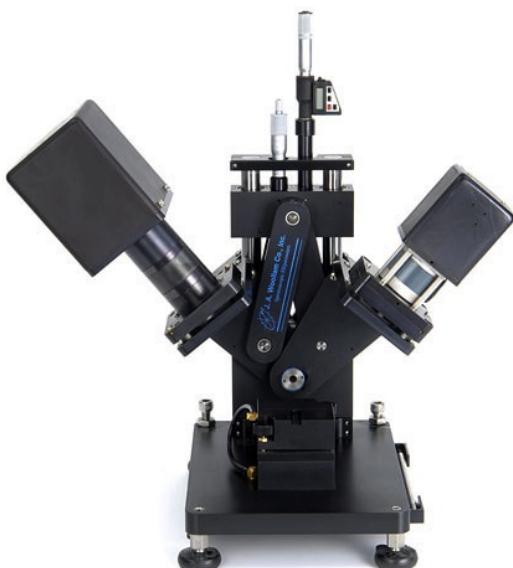
The power of ellipsometry as a high-resolution optical analysis technique stems from the use of phase and polarization changes. This allows the analysis to overcome the diffraction limit, and can be accurate down to angstroms. Properly modeling the system is critical for this analysis to be as precise as possible. Thus, there have been refinements of the ellipsometric method to  
595 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  $\kappa$ . This not only helps to improve data analysis (as it can generally be safely assumed

that the values of  $n$  and  $\kappa$  are smooth functions of  $\lambda$ ), but allows for the determination of many other properties of the material. Of specific importance 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, 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.

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

During this project, a VASE M-2000U system (figure 5.3) built by J.A. Woollam, inc. was used to collect all of the ellipsometric data. In addition, data analysis was performed using the WVASE32<sup>©</sup> 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 from the J.A. Woollam, inc. webpage.<sup>2</sup>



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

## 620 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 625 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 630 spectroscopy nomenclature (e.g.  $K_{\alpha}$ ,  $K_{\beta}$ ,  $L_{\alpha}$ ). An illustration of this process can be found in figure 5.4 on the facing page.

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 635 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.

One of the downsides of EDXS is that the interaction volume of electrons is 640 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.

### 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  $K_{\alpha}$  source with  $\lambda = 1.54 \text{ \AA}$ ), as opposed to energetic electrons. In other considerations the 650 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-

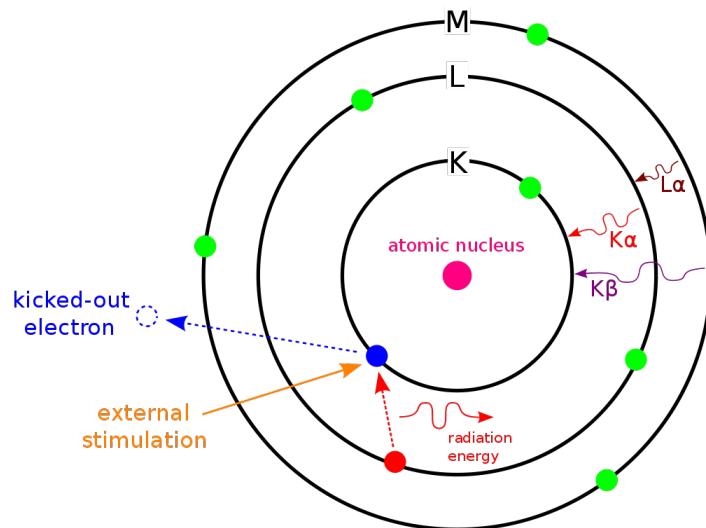


Figure 5.4: Graphic illustrating the basic mechanism for EDXS, along with the commonly used notation for the various energies. The external stimulation would be a high energy electron.

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.

X-ray fluorescence spectroscopy was performed using a fX-SEM analysis system from iXRF Systems, inc.<sup>1</sup> It was the primary method of composition analysis for the results presented in this thesis.

## 5.4 Phase Identification

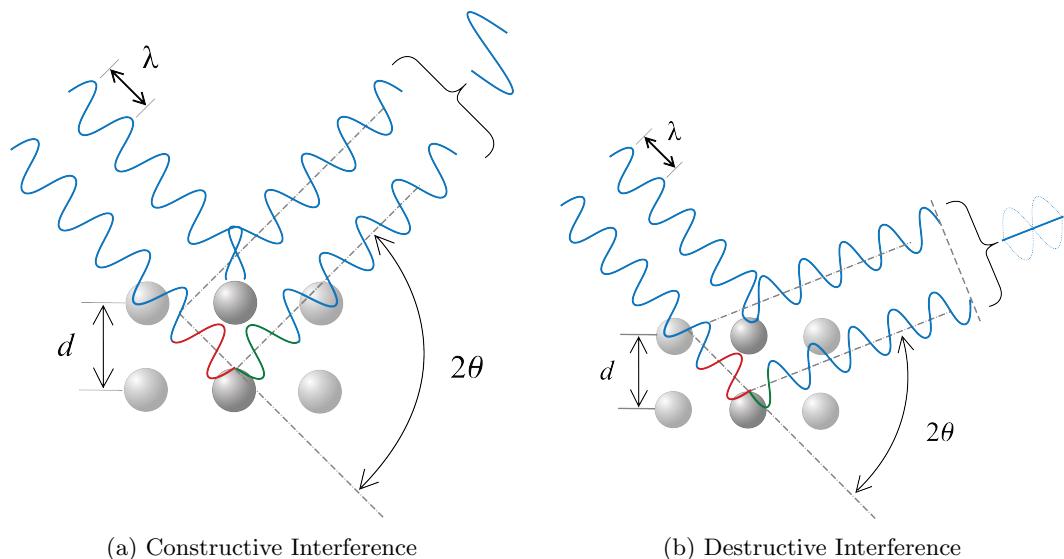
### 5.4.1 X-Ray Diffraction

Being able to identify the presence of various phases and materials was an important

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.

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

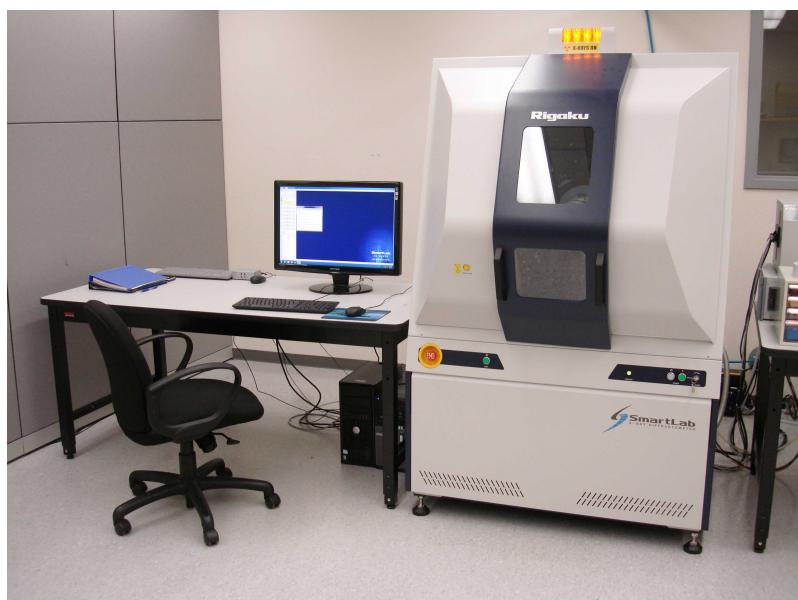
Figure 5.5 gives a graphical illustration of this principle. If the extra distance traversed by photons on the first path is equal to an integer number of wavelengths there will be constructive interference (see fig. 5.5a). However, if the  $\theta$  angle is slightly changed the interference rapidly 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.



*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.*

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  $2\theta$  can be converted to  $d$ -spacings via the relation  $d = \frac{\lambda}{2\sin\theta}$ . Individual materials 680 will have a specific pattern of reflections that allow them to be identified in the sample.

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



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



# Chapter 6

## <sup>685</sup> 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 <sup>690</sup> 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.

#### <sup>695</sup> 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. The use of hermetically sealed pans was important as the material was intended to vaporize, and the loss of material through escaped vapor would <sup>700</sup> change the results of the test. An additional sample pan was sealed with no contents to act as the standard. Both pans were weighed carefully and then loaded into the sample chamber of the Q2000. Again, the desired testing sequence was programmed into the instrument’s controller, and the experiment was run automatically.

### <sup>705</sup> 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 the film thickness, in order to be able to determine the film growth rate (in terms of Å per deposition cycle) of the process.

710    **6.2.1 Data Collection**

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

1. Optics alignment
2. Ambient light compensation (DC offset)
- 715    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.<sup>3</sup> 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 720 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 725 the equipment.

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.”<sup>3</sup> The offset is calibrated automatically by the system by blocking the light source and measuring the signal from the surroundings. 730 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 735 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 740 used for the remainder of this discussion, but more information can be found in the manual for the M-2000U.<sup>3</sup>

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.<sup>3</sup>

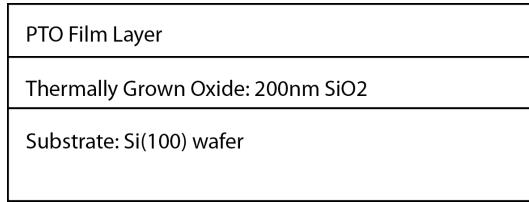
If the sample is expected to be inhomogeneous, the focusing optics can be used and data collected at several different locations on the sample. This can provide data on how the growth process behaves spatially, such as if there is abnormal growth near the edges of the sample but homogeneous deposition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

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.

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  $\text{SiO}_2$  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  $200 \pm 5$  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  
 780 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  $\Psi$  and  $\Delta$ , which assists in the analysis (particularly the thickness, where the fringes are very closely related to this parameter).

### 785 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- $\lambda$  Cauchy Model
- 790 2. Direct Calculation of  $n$  and  $\kappa$
- 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  
 795 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  $n$ ,  $\kappa$ , and the film layer thickness are obtained 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  $\kappa$  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 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- $\lambda$ , attempting to minimize the change in  $n$  or  $\kappa$  between adjacent data points.

This model is then inputted into a oscillator model. For the analysis of 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 other intra-band transition mechanisms. The Tauc-Lorentz model uses the parameterization shown in equation 6.3.<sup>3,4</sup>  $\epsilon_1$  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  $\epsilon_2$ , has been presented by Jellison and Modine.<sup>4</sup>

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

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

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

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

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

$$(6.3c)$$

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

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

825 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  $\epsilon_2$  function. Once this has been set, all of the parameters affecting  $\epsilon_2$  ( $A, E_0, C, E_G$ ) are marked to be included in the fit. The software is then instructed to perform a best-fit of the oscillator  
 830 to  $\epsilon_2$ . Once this operation completes, the software is set to fit to  $\epsilon_1$  and only the value of the  $\epsilon_1$  offset is allowed to be fit. Finally, the software is set to optimize vs both  $\epsilon_1$  and  $\epsilon_2$ , and all parameters are included. This completes the initial setup of the oscillator model.

835 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).

840 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  
 845 to proceed with the entire standard analysis procedure.

850 Further analysis can be performed to estimate the bandgap of the layer, via Tauc plot analysis. The method requires the calculation of the absorption coefficient ( $\alpha$ ) from the value of  $k$  for the layer (see equation [6.5 on the facing page](#)).  $\alpha$  is usually provided in terms of  $\text{cm}^{-1}$ , 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  $\alpha$  and the

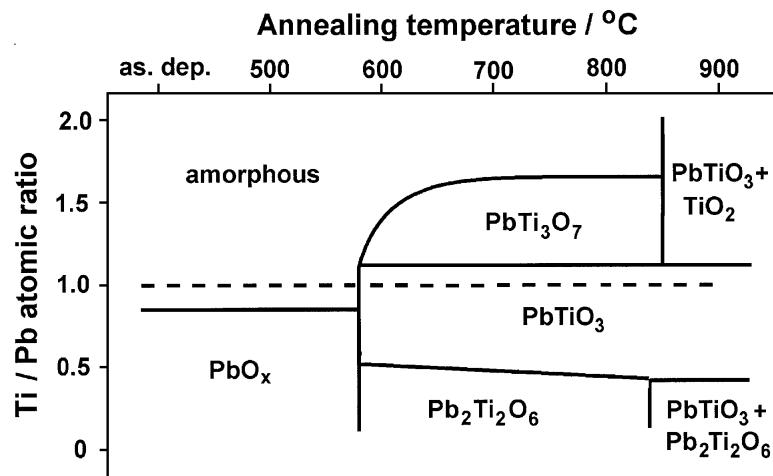


Figure 6.2: Graphic illustrating preferred phase of an annealed film at a range of stoichiometric ratios and annealing temperatures. A slight excess of Pb in the system is expected to help stabilize the perovskite  $\text{PbTiO}_3$  phase.<sup>5</sup>

855 photon energy. For direct bandgap materials the Tauc parameter is given by  $(\alpha E_{ph})^2$ . 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  
860 the layer, which may be a combination of multiple phases or materials.

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

Experimental data sets, the resulting fitted models, and Tauc analyses for selected samples are presented in appendix A.4 on page 59.

## 6.3 Composition Analysis

In order for the desired phase to be preferred, without any impurity phases  
865 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).<sup>5</sup>

### 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  $\text{PbTiO}_3$  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  $\text{SrTiO}_3$  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

900 **Chapter 7**

# Results

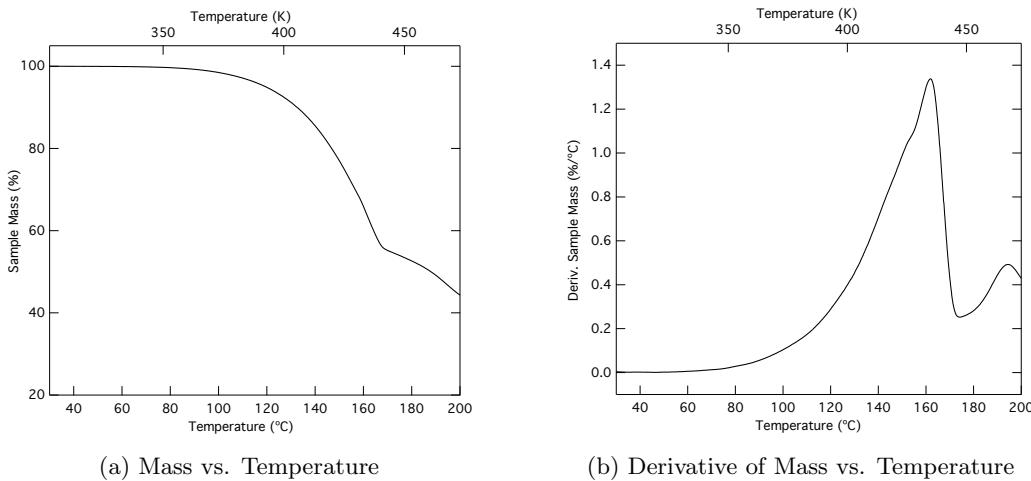
As discussed, the goal of this study was to determine methods for atomic layer deposition of ferroelectric oxides. In the process of realizing this goal there were a number of different areas of study. The first is the analysis of thermal and chemical behavior of the various potential precursors, during which TGA and DSC were primarily used (see [6.1 on page 31](#)). 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 31](#)). 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 37](#) 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 the facing page](#)).

## 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 13](#) for more details) in order to gauge the performance of these materials.

### 7.1.1 Thermogravimetric Analysis

925 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*

930 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, 940 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 945 and impacting the mass loss rate.

Comparing this data with that of  $\text{Pb}(\text{TMHD})_2$ , 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 on 950 the facing page, it is easier to see that there is basically smooth vaporization up

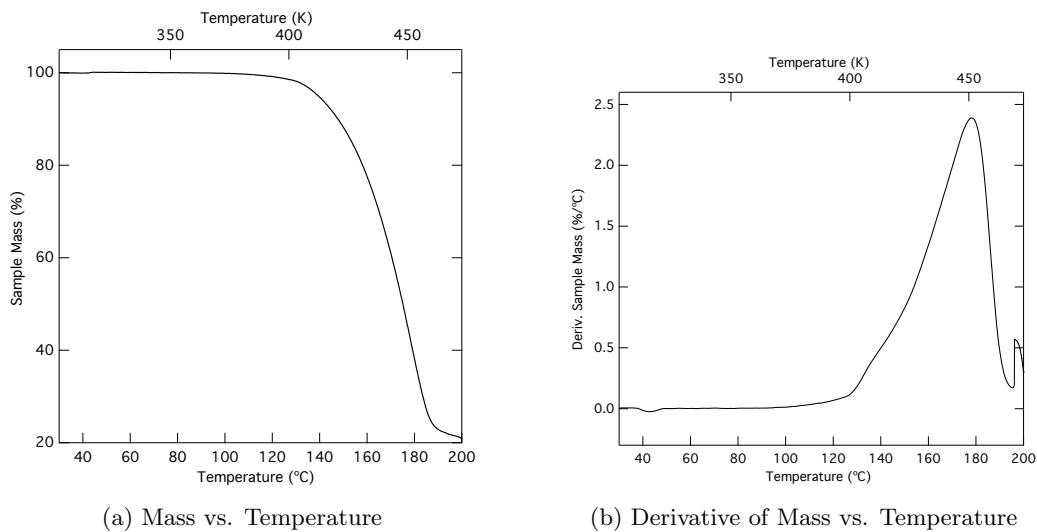


Figure 7.2: Plots of the results from TGA experiments on  $\text{Pb}(\text{TMHD})_2$ . As in figure 7.1 on the facing page, (a) presents the actual mass as a function of temperature, while (b) gives the derivative of that function. Initial sample mass: 3.719 mg

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

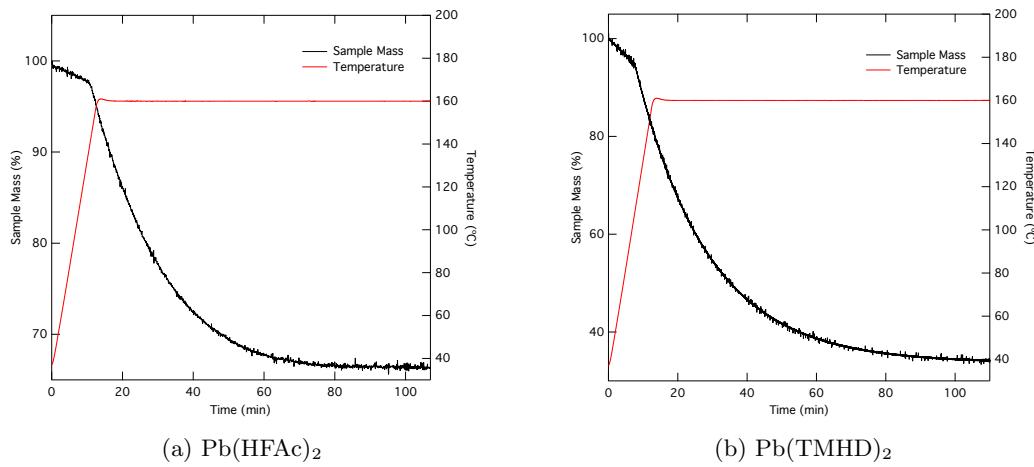
Neither of these precursors evaporated cleanly, leaving residues of more than 20% of their initial sample mass during the temperature scanning tests discussed above. When these were tested at moderate temperatures, such as those to be used for evaporation in the ALD system, both left even larger fractions 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 next page. From this test, it was found that  $\text{Pb}(\text{HFAc})_2$  left a much larger residue than  $\text{Pb}(\text{TMHD})_2$ , 63% and 34% respectively.

Based on the results of these tests, the lower residual mass and the cleaner evaporative process,  $\text{Pb}(\text{TMHD})_2$  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 43), 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 40 and 7.2 on the previous 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 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 44), such as those used in the evaporation and transport stages of the ALD system, there are no irregularities in the data. 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 44). As the sample is 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 present.

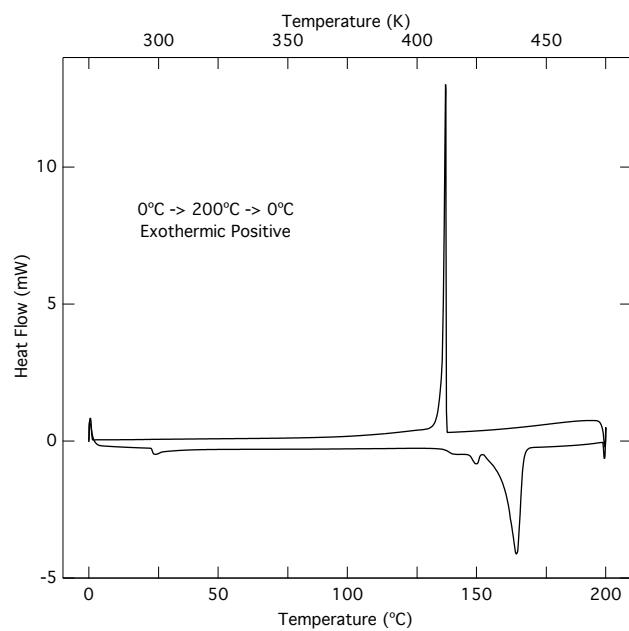
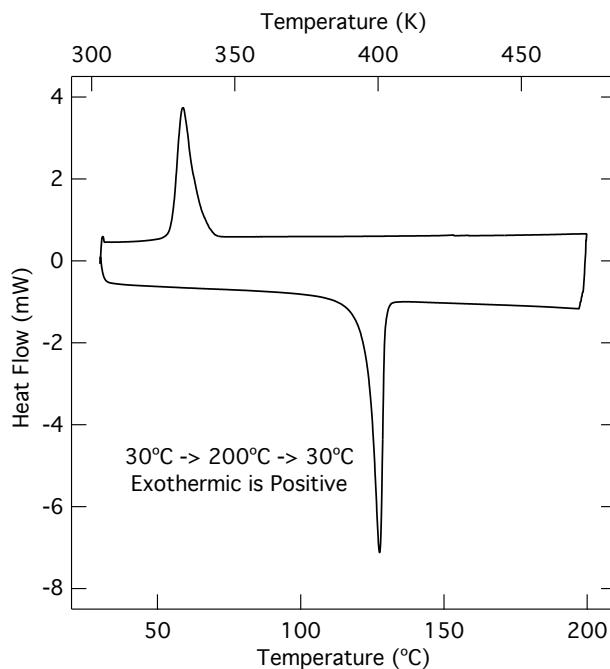
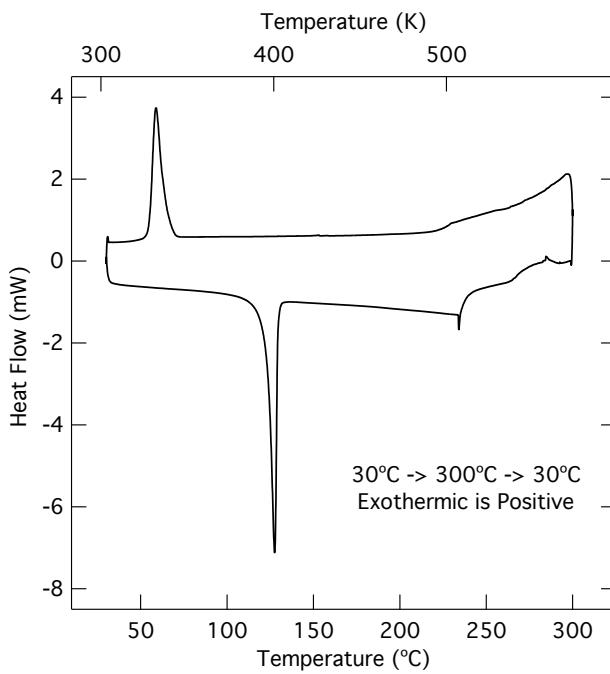


Figure 7.4: Plot of the DSC scan of  $\text{Pb}(\text{HFAc})_2$ . In this plot exothermic behavior, where the sample releases heat, is considered positive. Thus, the first sweep of the scan (from  $0^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ ) is negative. Sample mass: 4.7 mg.



(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.*

## 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 it was quickly determined that 225°C provided better growth behavior without risking thermal cracking of the compound.

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

Temp. (°C)	Run #	Pb:Ti Ratio	Cycles	Subs. Type	Annealing			XRD
					Type	Temp. (°C)	Time (min)	
200	3	1:1	250	Si	None	N/A	N/A	No
	2	1:2	250	Si	None	N/A	N/A	No
	30	3:1	160	Si	None	N/A	N/A	No
				Pt-Si	None	N/A	N/A	No
225	0	1:1	625	Si	Oven	650	120	Yes
					Oven	900	120	Yes
					RTA	900	10	No
	1	1:1	475	Si	None	N/A	N/A	No
	6	1:2	250	Si	None	N/A	N/A	No
	13	3:1	250	Si	None	N/A	N/A	No
	16	3:1	150	Si	RTA	650	1	No
	19	3:1	100	Si	None	N/A	N/A	No
				Pt-Si	None	N/A	N/A	No
	20	3:1	200	Si	None	N/A	N/A	No
				Pt-Si	Oven	650	90	Yes
				STO	Oven	650	90	No
	21	3:1	150	Si	None	N/A	N/A	No
				Pt-Si	Oven	650	90	No
				STO	Oven	650	90	No
	22	3:1	150	Si	None	N/A	N/A	No
				Pt-Si	Oven	650	90	Yes
	23	3:1	200	Si	None	N/A	N/A	No
				Pt-Si	Oven	650	90	Yes
	28	3:1	120	STO	Oven	650	90	Yes

### 7.3 Ellipsometry

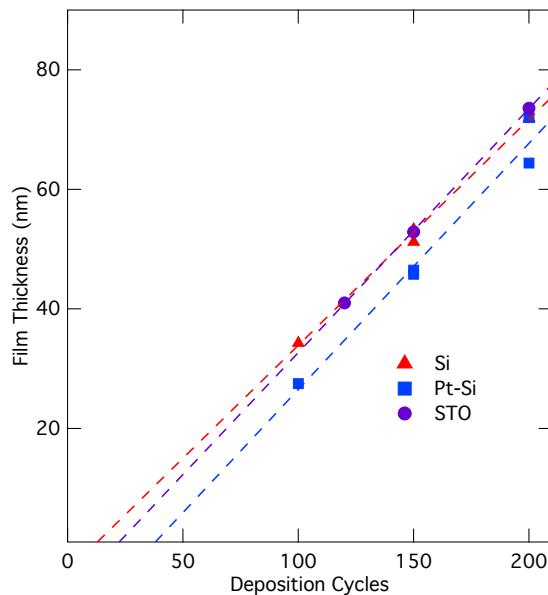
Ellipsometry was a valuable tool during the course of this study. As discussed previously, it is capable of quickly, accurately, and non-destructively determine various properties of thin film layer stacks. Of primary importance 1000 is the ability of the tool to provide a rapid method of determining 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 1005 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 1010 of deposition cycles (fig. 7.6 on the facing 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 1015 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.

1020 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 34) 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 1025 extinction coefficient,  $k$ , into that of the absorption coefficient,  $\alpha$ , it becomes possible to use the method developed by Tauc, *et.al.* [citation needed] to determine the band gap energy of the material. However, such analysis does not take into account presence of multiple phases in the layer and takes a weighted average of the bandgaps. It also requires that the sample be properly 1030 crystallized, and thus must have undergone an annealing treatment before the analysis method becomes valid. However, since the samples produced here had

*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*

low phase purity, which will be discussed in subsequent sections, this analysis was of little use as a film benchmark.

## 7.4 Composition

1035 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 ( $\text{Pb}^{2+}$  and  $\text{Ti}^{4+}$ ) was allowed to stray away from unity, other phases would be preferred or a mixture of phases would 1040 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 1045 even 1:1 ratio that also provided near unity compositions (sample #0 and #1). Table 7.3 provides a list of samples and their compositions measured via XRF.

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, 1050 and there were no surface sensitive characterization methods available.

## 7.5 X-Ray Diffraction

*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 <sub>2</sub>	56.0	44.0	0.786
1	SiO <sub>2</sub>	55.0	45.0	0.809
13	SiO <sub>2</sub>	54.0	46.0	0.853
16	SiO <sub>2</sub>	49.4	50.6	1.022
19	SiO <sub>2</sub>	65.9	34.1	0.518
	Pt-Si	42.9	57.1	1.333
20	SiO <sub>2</sub>	56.6	43.4	0.769
	Pt-Si	51.5	48.5	0.944
21	SiO <sub>2</sub>	69.6	30.4	0.437
	Pt-Si	56.1	43.9	0.783
22	SiO <sub>2</sub>	67.7	32.3	0.478
	Pt-Si	56.1	43.9	0.784
23	SiO <sub>2</sub>	66.9	33.1	0.495
	Pt-Si	49.1	50.9	1.038
24	SiO <sub>2</sub>	69.0	31.0	0.450
	Pt-Si	62.2	37.8	0.609



# Chapter 8

## Conclusions

The final result of this study was to show that it is certainly possible to  
1055 grow perovskites using an ALD process, but the exact processes are sensitive  
and require much attention and further analysis.

### 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 in-  
1060 cluding the topic of discussion of this thesis, there is much left to be inves-  
tigated 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). Be-  
1065 ing able to consistently produce films of constant quality would make this work  
applicable to a myriad of 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  
1070 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); more standard ferroelectric measurements could likely be  
utilized with improved film quality.

Following this path of discussion quickly leads to the question of doping  
1075 the films in order to improve properties. As an example, it is well known [ci-  
tation needed] that a solid solution of  $\text{PbTiO}_3$  and  $\text{PbZrO}_3$  greatly improves  
polarizability as well as the energy required to switch the film (???).

Finally, it would be useful to extend this method to completely novel mate-  
rial systems.  $\text{BaSrTiO}_3$  is another commonly used ferroelectric material (and  
1080 valuable due to its lack of lead content), and  $\text{BiFeO}_3$  is another interesting  
perovskite as it presents multiferroic behavior as opposed to simply ferroelec-  
tricity.



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# Appendix A

## Supplemental Information

### A.1 List of Chemicals

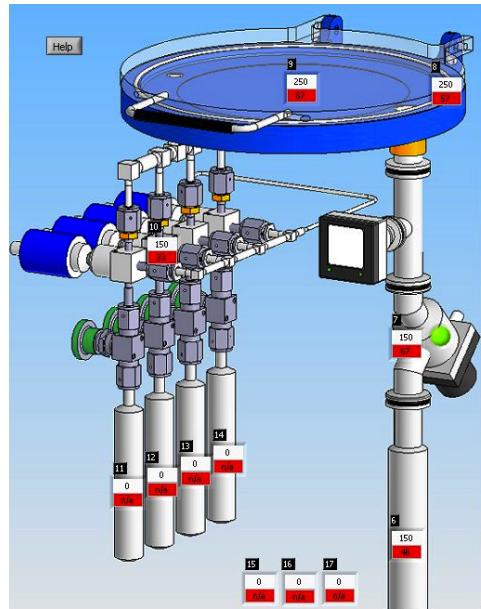
*Table A.1: List of chemical compounds used during the course of this study.*

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

## 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

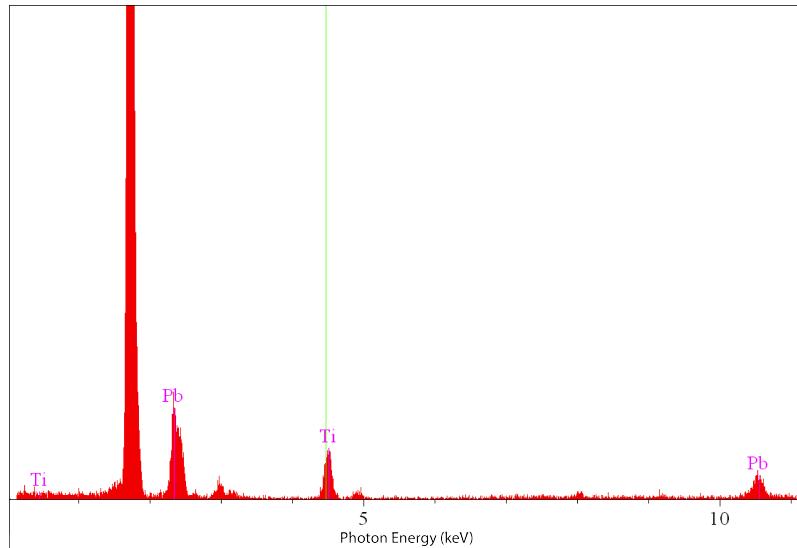


Figure A.2: The XRF spectrum collected from deposition run #0.

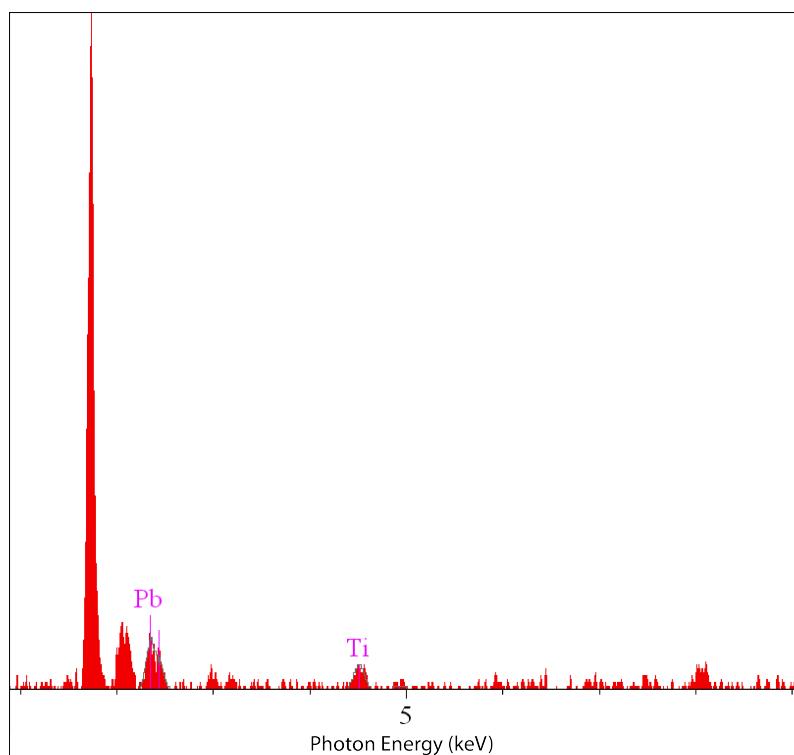


Figure A.3: The XRF spectrum collected from deposition run #20 deposited on platinized silicon. The peak between the substrate and Pb is that of Pt.

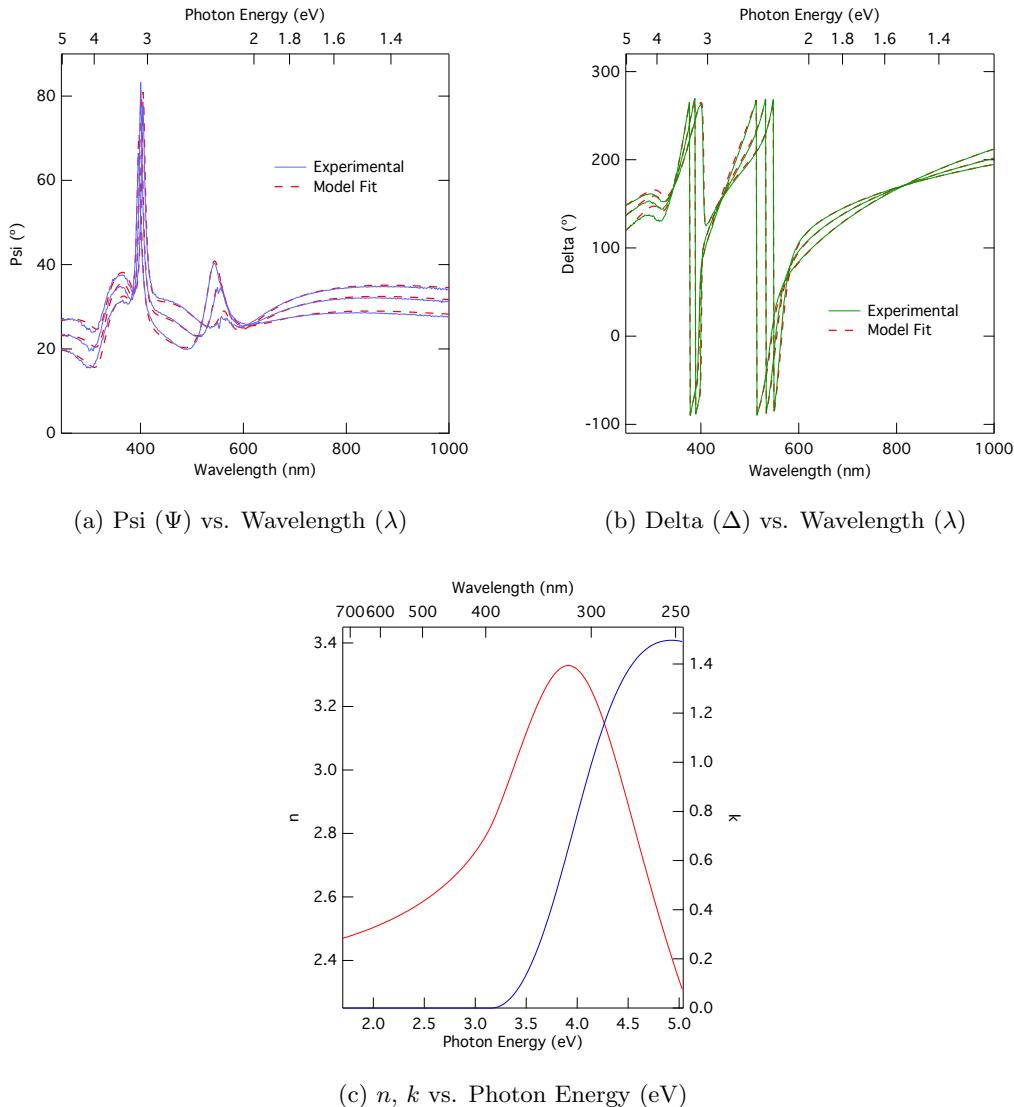
<sub>1100</sub> A.4 Ellipsometry Results

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

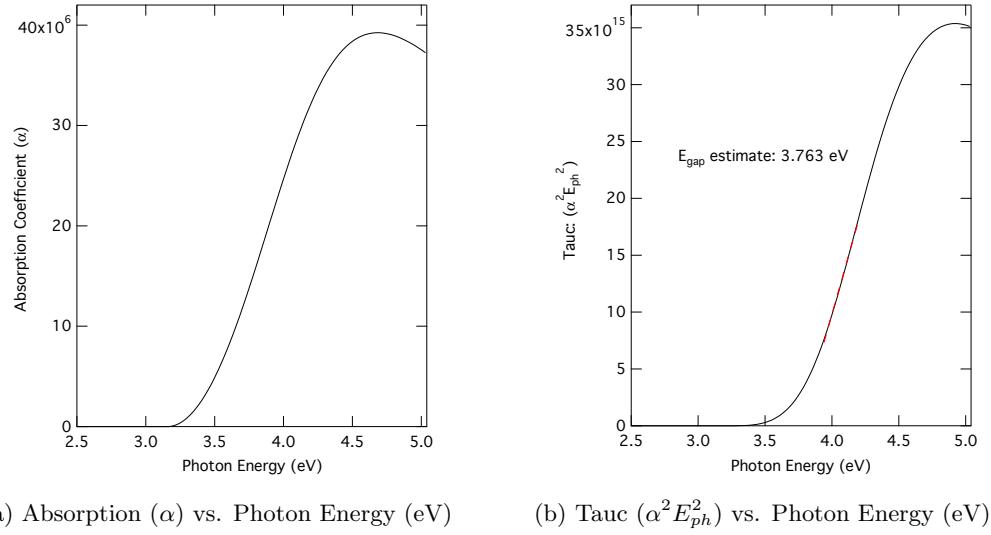
Layer	Variable	Thickness (nm)	Value
2. T-L Osc.		88.7	
	$\epsilon_1$ offset		2.49
	Amp		12.66
	$E_n$		4.60
	C		1.35
	$E_g$		0.86
1. SiO <sub>2</sub>		203.7	
0. Si		Substrate	

*Table A.3: Variables used to produce the model fit for PTO #20 seen in fig. A.6 on page 62.*

Layer	Variable	Thickness (nm)	Value
3. T-L Osc.		75.6	
	$\epsilon_1$ offset		3.62
	Amp		36.54
	$E_n$		4.51
	C		1.30
	$E_g$		2.07
2. Pt		15.1	
1. SiO <sub>2</sub>		1.1	
0. Si		Substrate	



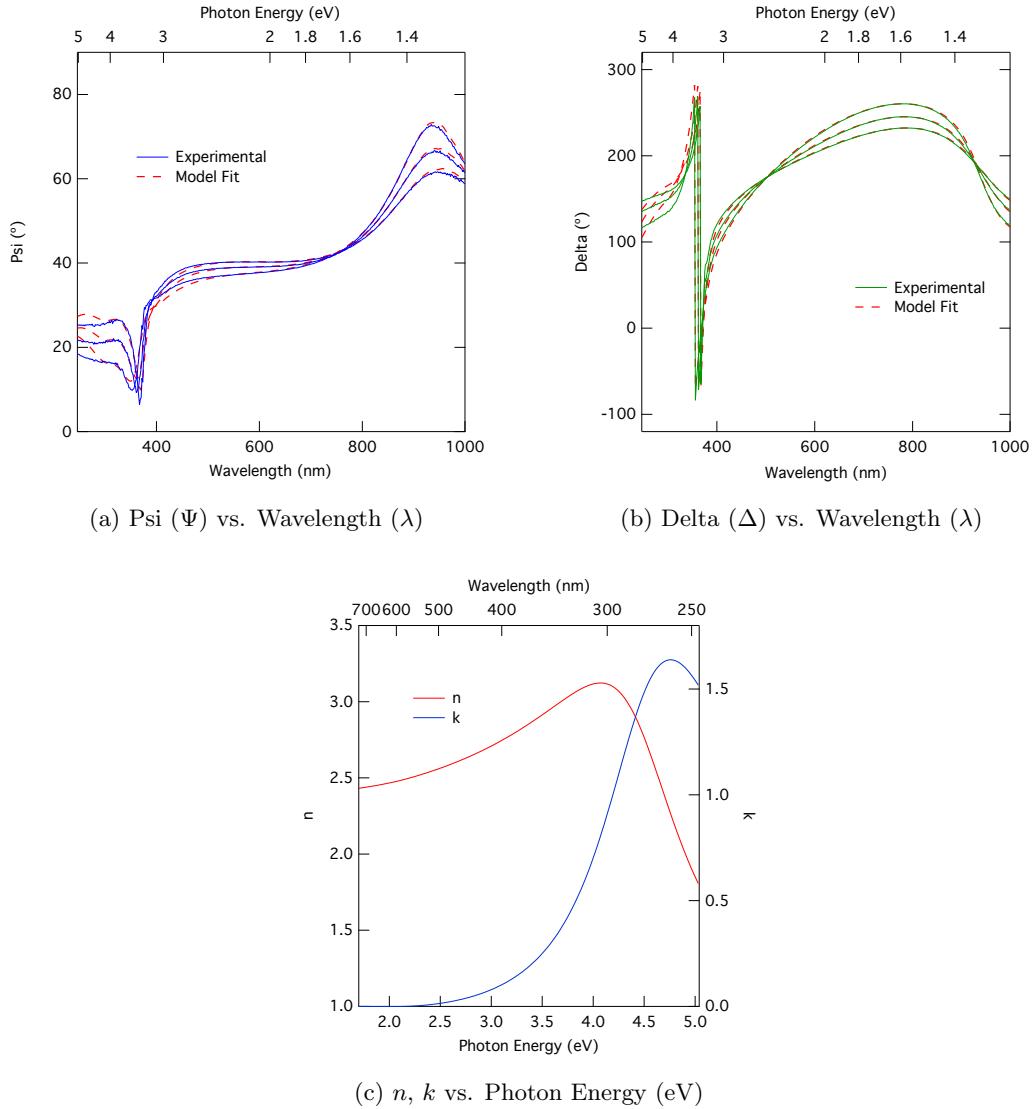
*Figure A.4: The set of plots shown above show the results from ellipsometric analysis on sample #0 (see table 7.1 on page 45) grown on a silicon wafer and subsequently annealed. (a) and (b) show the data and the modeled fit from the experiment. (c) shows the components of the complex index of refraction ( $\tilde{n}$ ),  $n$  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 ( $\alpha$ ) calculated from  $k$  (seen in figure A.4c on the preceding page). (b) shows the Tauc plot, the linear region can provide an estimate of the bandgap of the material.*

*Table A.4: Variables used to produce the model fit for PTO #28 seen in fig. A.8 on page 64.*

Layer	Variable	Thickness (nm)	Value
1. T-L Osc. (2)			49.2
	$\epsilon_1$ offset		1.42
	Amp <sub>1</sub>		64.71
	E <sub>n1</sub>		3.69
	C <sub>1</sub>		4.44
	E <sub>g1</sub>		1.55
	Amp <sub>2</sub>		1.55
	E <sub>n2</sub>		2.12
	C <sub>2</sub>		0.76
	E <sub>g2</sub>		0.001
0. STO			Substrate



*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.3 on page 59*

*Table A.5: 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

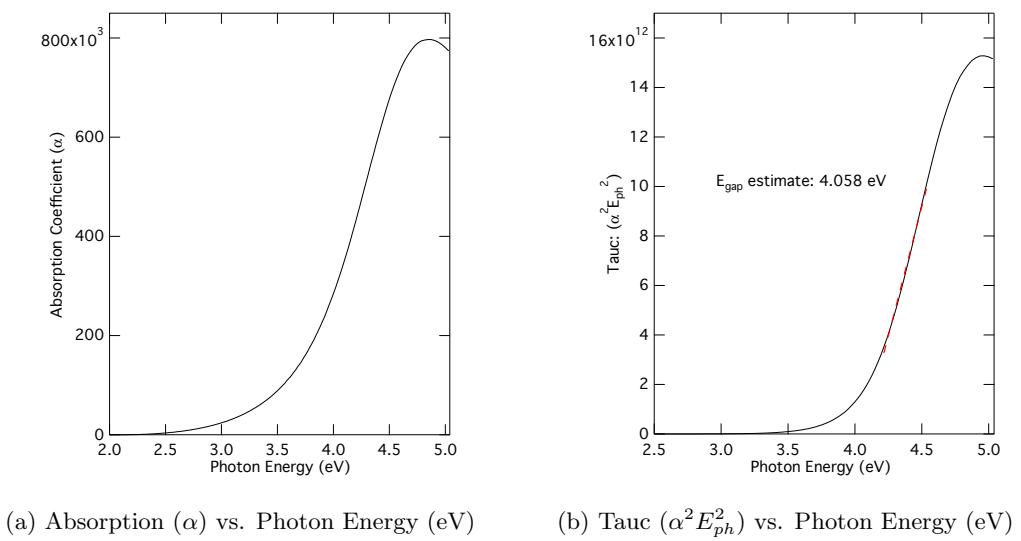
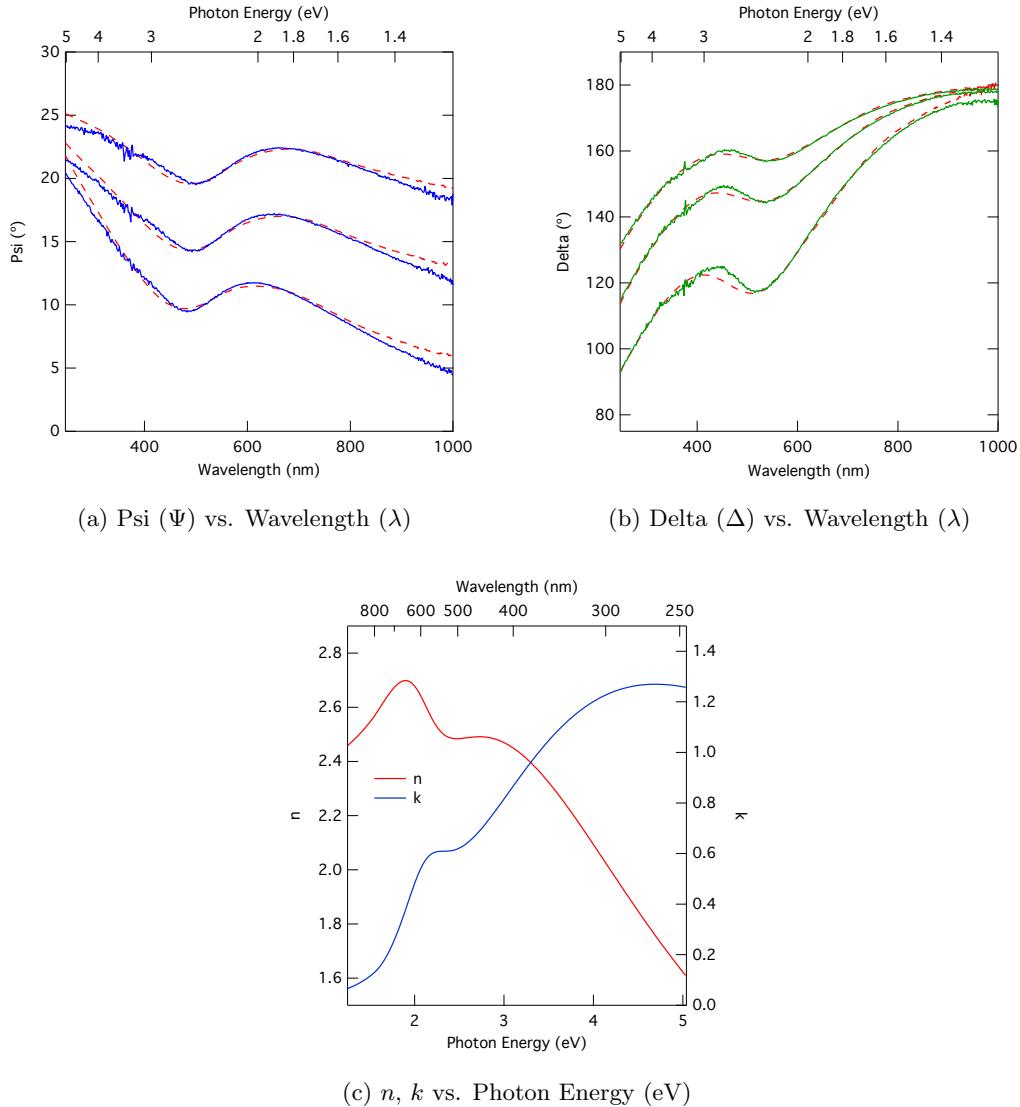
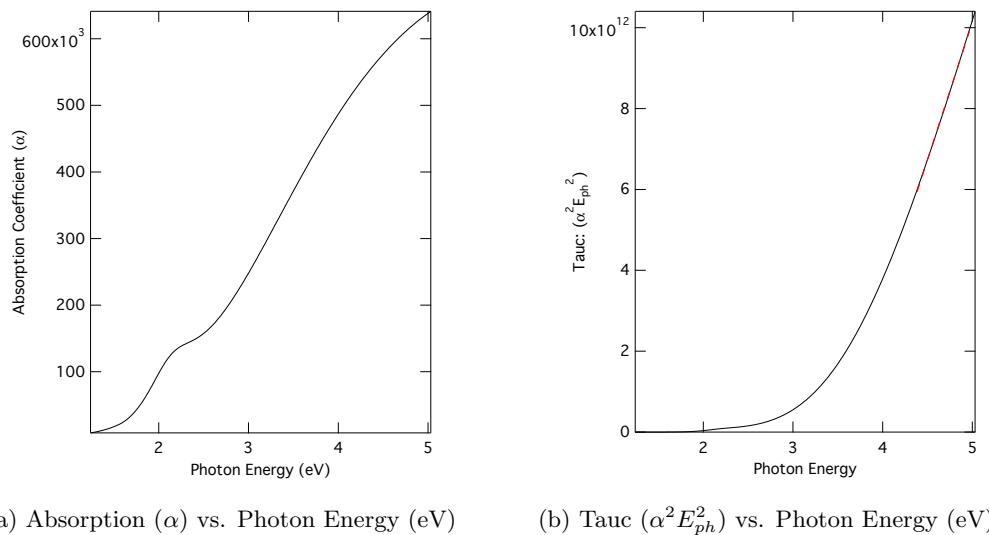


Figure A.7: Tauc analysis of sample #20 on Pt-Si



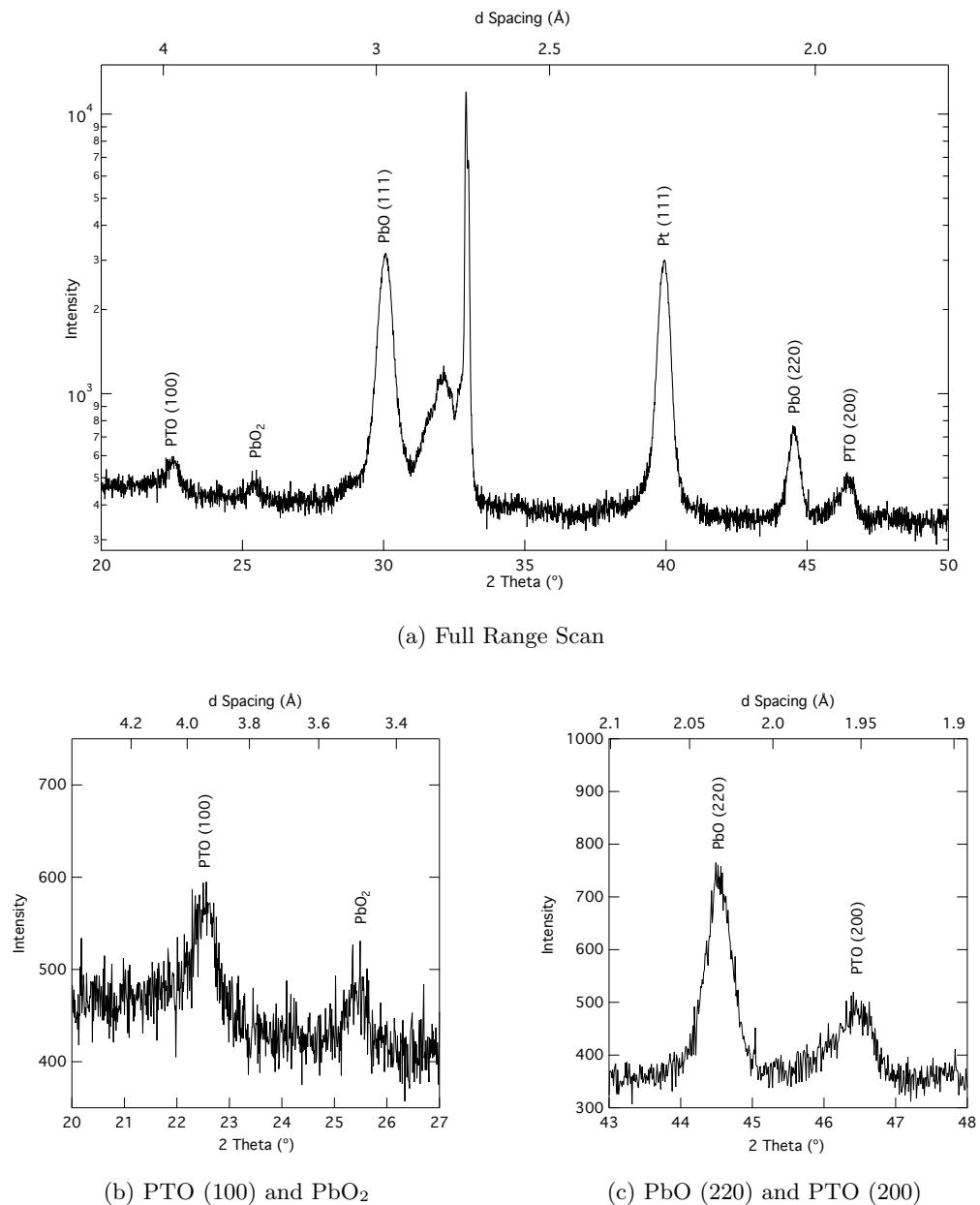
*Figure A.8: Results of ellipsometric analysis on sample #28, deposited on a strontium titanate  $\text{SrTiO}_3(100)$  single crystalline substrate. As in fig. A.4, (a) and (b) show the experimental data and model fits of psi and delta (respectively). (c) gives the plot of calculated  $n$  and  $k$ . This sample would not model well without a second oscillator, which gives rise to the secondary peaks in the  $n$ ,  $k$ , and  $\alpha$  plots (see fig. A.9a on the facing page). For model parameters, see table A.4 on page 61.*



(a) Absorption ( $\alpha$ ) 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.*

### A.5 XRD Results



*Figure A.10: XRD of #20 Pt*