To my loving wife
ACKNOWLEDGMENTS

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She is the proof that behind every good man, there is a better woman.
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<td>acac</td>
<td>2,4-pentandione, acetylacetonate, C₅H₇O₂</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscope/Microscopy</td>
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<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>ATO</td>
<td>Aluminum Titanium Oxide, Al₂O₃-TiO₂</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>GGG</td>
<td>Gadolinium Gallium Garnet</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Diffraction Standards</td>
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<tr>
<td>LED</td>
<td>Light-Emitting Diode</td>
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<tr>
<td>MOCVD</td>
<td>Metal-Organic Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal-Oxide-Semiconductor Field-Effect Transistor</td>
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<td>PET</td>
<td>Positron Emission Tomography</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TFEL</td>
<td>Thin Film Electroluminescence</td>
</tr>
<tr>
<td>thd</td>
<td>2,2,6,6-tetramethyl-3,5-dionate, C₁₁H₂₀O₂</td>
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<td>YAG</td>
<td>Yttrium Aluminum Garnet, Y₃Al₅O₁₂</td>
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<td>YAM</td>
<td>Yttrium Aluminum Monoclinic, Y₄Al₂O₉</td>
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<td>YAP</td>
<td>Yttrium Aluminum Perovskite, YAlO₃</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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The growth of thin films of selected phases from the pseudo-binary Al₂O₃-Y₂O₃ material system was demonstrated using atomic layer deposition (ALD). Specifically, ALD growth of Al₂O₃, Y₂O₃, Ce₂O₃, Y₂Al₄O₁₂ (Yttrium Aluminum Monoclinic - YAM), and Y₃Al₅O₁₂ (Yttrium Aluminum Garnet - YAG) was accomplished. All films were grown using the same precursors: AlCl₃ at 105°C and H₂O, Y(thd)₃ [thd = 2,2,6,6-tetramethyl-3,5-heptanedione] at 140°C and O₃, and Ce(acac)₃ [acac = acetylacetonate] at 140°C, and O₃. The Al₂O₃ films were grown at substrate temperatures from 295°C to 515°C. A surface-controlled growth temperature ‘window’ (ALD window) was found for Al₂O₃ between 365°C to 465°C using AlCl₃ and H₂O. The resultant films grown at all temperatures were amorphous as characterized by X-ray diffraction, and showed a rough surface morphology. The growth rate was determined to be 1 Å/cycle within the ALD ‘window’. The thickness of films grown in the ALD ‘window’ varied linearly with the number of cycles. Films up to 1 µm thick were grown (10,000 cycles).

The Y₂O₃ films were grown at substrate temperatures ranging from 200°C to 500°C. No surface-controlled growth temperature window could be determined using Y(thd)₃ and O₃. The resultant films were polycrystalline with a cubic structure and a
smooth surface morphology. The growth rate was determined to be 3 pm/cycle at 350°C. Films up to 30 nm thick were grown (10,000 cycles).

Atomic layer deposition of Ce$_2$O$_3$ thin films were also studied because Ce$^{3+}$ is often used as a luminescent rare earth dopant in YAG and YAM. The Ce$_2$O$_3$ films were grown at substrate temperatures from 200°C to 500°C. No surface-controlled growth temperature window could be found using Ce(acac)$_3$ and O$_3$. The resultant films had a rough surface morphology. Using X-ray photoelectron spectroscopy (XPS), it was determined that the Ce$^{3+}$ oxidation state was present in the as-deposited films rather than Ce$^{4+}$. When included in the growth process for YAG and YAM, Ce$_2$O$_3$ was found to create very rough surfaces.

The ternary oxide phases of YAM and YAG were produced by ALD growth of alternating nano-scaled multilayer stacks of Al$_2$O$_3$ and Y$_2$O$_3$ and subsequent calcinations of these thin nano-scale stack structures. By adjusting the ratio of Al$_2$O$_3$ deposition cycles to Y$_2$O$_3$ deposition cycles, stoichiometric amounts of material were deposited in an alternating fashion. A 300 nm YAG film was deposited using the ALD method at a substrate growth temperature of 350°C. X-ray diffraction data showed that these films were amorphous as-deposited, but they were transformed to a polycrystalline cubic garnet structure when calcined at 975°C for 12 hrs in air. The surface morphology was uniform and smooth. A 400 nm YAM thin film was also successfully deposited using the ALD method at a growth temperature of 350°C. X-ray diffraction of the YAM film showed an amorphous film as-deposited and a polycrystalline monoclinic structure after calcining at 975°C for 12 hrs in air. The surface morphology of this YAM film was rough and non-uniform.
Atomic layer deposition (ALD) [1] has emerged as a cost effective chemical vapor deposition alternative in the creation of very thin films. The advantages of ALD compared to other deposition methods are its excellent conformity, accurate thickness control at the smallest scales, large area uniformity, sharp interfaces, multilayer processing, and excellent quality films [2-5]. The applications for ALD films are numerous. The insulating material aluminum titanium oxide (ATO) is a commercially available thin film deposited via atomic layer deposition. Alumina and titania are deposited as alternating layers with thicknesses at the nanoscale. The result is a nanolaminate of the immiscible alumina and titania materials and is used as a dielectric layer in electroluminescent displays [6]. Thin film electroluminescent displays were among the first commercial applications for ALD. There is considerable interest in ALD with regards to the semiconductor industry and the creation of very thin, high-κ dielectric gate oxides in metal-oxide-semiconductor field-effect transistors (MOSFETs). As the transistor size continues to shrink, the oxide gate material thickness shrinks with it, thereby requiring a high-κ dielectric material [7, 8]. ALD is currently being used to deposit very thin, high-κ dielectric materials by companies such as Intel [9]. Numerous companies such as Applied Materials [10], Aixtron [11], Beneq [12], and Kurt J. Lesker [13], manufacture ALD systems for both commercial and research use. The pervasiveness of the semiconductor industry in modern life and the industries’ pursuit of very thin, conformal, high-κ dielectrics continue to be a large driving force for the growth in ALD research. Another area of application for ALD is in luminescent materials such as phosphors and scintillators. A scintillator’s resolution is inversely proportional to the
thickness of the scintillator [14], therefore, ALD can be used to make thin films of scintillator materials for higher spatial resolution, albeit with a lower sensitivity.

This research focuses on the atomic layer deposition of the pseudo-binary Al₂O₃-Y₂O₃ material system and two of its three primary phases: Y₄Al₂O₉ and Y₃Al₅O₁₂ [15]. In addition, ALD of Ce₂O₃ was investigated as a possible dopant for ALD deposited Y₄Al₂O₉ and Y₃Al₅O₁₂. The phases in this system are used as phosphors, scintillators, lasers, dielectrics, and optical waveguides. For example, Y₃Al₅O₁₂:Ce is a common phosphor material that converts some of the blue light from a GaN light-emitting diode (LED) into yellow light [16] that in turn complements the residual blue light to produce a white light. The Y₃Al₅O₁₂:Ce phosphor is typically synthesized from a solid state reaction of stoichiometric Y₂O₃, Al₂(OH)₃, and Ce₂O₃ at temperatures on the order of 1400°C [16]. In addition to a phosphor, Y₃Al₅O₁₂:Ce is used as a scintillator for radiation detection such as in Positron Emission Tomography (PET). With ALD, very thin Y₃Al₅O₁₂:Ce scintillators can be made for greater resolution. Chemical vapor deposition and physical vapor deposition methods are used for applications where these materials are integrated onto a device, such as a dielectric on a semiconductor. ALD provides a means for depositing these materials onto devices whereby very thin, uniform, and conformal films are needed. In addition, the deposition temperature for ALD processes are typically less than 700°C, approximately half the temperature used in solid state reactions. The low temperature process of ALD allows for integrating materials onto other more temperature sensitive materials.

This work demonstrates a novel low temperature process for the synthesis of Y₄Al₂O₉ and Y₃Al₅O₁₂ using atomic layer deposition. By varying the delivery sequence of
the precursor materials while keeping deposition temperature and pressure constant, the three different solid phases of the pseudo-binary \( \text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3 \) material system can be produced. These phases have different physical properties that can be taken advantage of either as a single thin film of one phase or in combinations of thin films using two or three phases. In addition, doping of these films is demonstrated, widening the number of potential applications for this process and material system. These materials can be formed at the nanoscale which can lead to new developments in optical devices such as quantum confinement of optical states, sub-wavelength optics, and photonics to name a few. Nanolaminates produced by ALD are shown to result in materials whose properties are different from the constituent materials [17,18]. As a material’s thickness (or characteristic length) decreases to length scales less than the characteristic length scale of a physical property, novel physical properties emerge. Light-emitting quantum dots, for example, are materials whose diameters are much less than the wavelength of light emitted. Quantum confinement of energy states in the quantum dot arise as the quantum dots size is reduced to the nano-scale in all three dimensions. ALD allows for quantum well structures in one dimension that can be further refined to three dimensions by careful patterning.

A literature review of the atomic layer deposition process and the atomic layer deposition of \( \text{Y}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) films are presented in Chapter 2 including a review of \( \text{Y}_4\text{Al}_2\text{O}_9 \) and \( \text{Y}_3\text{Al}_5\text{O}_{12} \) structure and properties. In Chapter 3 the experimental and characterization methods used to create the \( \text{YAlO}_3 \), \( \text{Y}_4\text{Al}_2\text{O}_9 \), and \( \text{Y}_3\text{Al}_5\text{O}_{12} \) films are discussed. Results and discussion are presented in Chapter 4. Conclusions and future studies conclude the dissertation in Chapter 5.
CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

The rare-earth doped materials of the pseudo-binary Al₂O₃-Y₂O₃ material system are important in optoelectronic devices such as scintillators (YAlO₃:Ce) [19], lasers (Y₃Al₅O₁₂:Nd) [20], and phosphors (Y₂O₃:Eu, Y₃Al₅O₁₂:Ce) [16,20], therefore improved fabrication methods have wide-ranging applications. Typically this material system is synthesized as bulk crystals using the Czochralski method [21-25] or as powders using a variety of chemical methods such as sol-gel [26], precipitation [27], rf-magnetron sputtering [28], and air or vacuum sintering [29] processes.

The Czochralski method for the growth of Y₃Al₅O₁₂:Ce is conducted at a temperature of ~1700°C and produces single crystals about 3 cm in diameter and 10 cm in length [30]. Czochralski growth of bulk crystals produces bulk stoichiometric materials and in regards to the Al₂O₃-Y₂O₃ material system, can produce bulk crystals of all phases. However, it is not possible to use the Czochralski method to deposit thin films onto a substrate.

The sol-gel method to synthesize Y₄Al₂O₉:Pr, Y₃Al₅O₁₂:Eu, YAlO₃, has been demonstrated and produces polycrystalline powders after annealing [26,31,32]. The products of the sol-gel method are powders and can be formed into films upon heat treatment. However, the conformity of sol-gel powders to substrates with high aspect ratios is difficult and accurate thickness control down to the nanoscale for thin film formation is an even greater challenge with the sol-gel method. Another wet chemistry method, the precipitation method, can produce products such as Y₃Al₅O₁₂:Ce from the
Al₂O₃-Y₂O₃ material system. The precipitation method produces powders and presents the same limitations for thin film formation as the sol-gel method.

Thin film deposition of Y₃Al₅O₁₂:Ce has been demonstrated for this material system using rf-magnetron sputtering [28] known for its advantages of low-temperature deposition and stoichiometric control, but with the disadvantage of poor surface conformation as it is a line-of-sight physical vapor deposition (PVD) process. In rf-magnetron sputtering, the target used is stoichiometric for the desired film, but effects such as re-sputtering of the film can lead to films that are non-stoichiometric.

Thin films by pulsed laser deposition (PLD) [33,34], is another PVD process used to grow thin films of Y₃Al₅O₁₂. PLD possesses many of the same advantages as rf-magnetron sputtering such as low-temperature processing and good stoichiometric control with some of the same disadvantages such as poor surface conformation and a problem with particulate deposition due to splashing of the ablated target. For example, the PLD of Y₃Al₅O₁₂ films produced were nanocrystalline particles embedded in an amorphous Y₃Al₅O₁₂ matrix [33] and presented a large degree of splashing onto the resultant thin film.

Metal organic chemical vapor deposition (MOCVD) of Y₃Al₅O₁₂ [35] has been demonstrated and possesses many advantages such as good uniformity, crystallinity, and large scale batch capability among others. For example, previous literature of heteroepitaxially grown Y₃Al₅O₁₂ on single crystal (111)-oriented Gd₃Ga₅O₁₂ (GGG) resulted in single crystalline Y₃Al₅O₁₂ films with the (111) orientation [35]. When the MOCVD technique is modified to operate in the surface-controlled regime, the result is
atomic layer deposition (ALD), also known as atomic layer chemical vapor deposition (ALCVD).

Atomic layer deposition (ALD) has received more attention in the semiconductor industry as films and interfaces approach the nanoscale. ALD is well known for its ability to deposit very thin conformal films. The semiconductor industry’s interest in ALD for thin film gate dielectrics used in MOSFETs has resulted in, improved reactor design, new precursors, and new applications of the technique are being developed. This work expands the state of the art of atomic layer deposition by demonstrating the growth of Y₂Al₄O₁₂ and Y₃Al₅O₁₂ by ALD for the first time.

2.2 Atomic Layer Deposition

2.2.1 Introduction

Atomic Layer Deposition (ALD), also known as Atomic Layer Epitaxy (ALE), was developed by Dr. T. Suntola and co-workers at Instrumentarium Datex in 1974 [36] and patented in 1977 by Suntola and Antson [1]. ALD is a chemical vapor deposition process in which film growth occurs in a surface controlled manner, layer by layer, also known as digital growth. Advantages of ALD are excellent conformity, accurate thickness control at the smallest scales, large area uniformity, sharp interfaces, multilayer processing, and excellent quality films [2-5]. A limitation is the low growth rate (~1Å/sec) which is significantly lower when compared to other growth processes (1-1000nm/sec). However, as demand for ever thinner films increases, this drawback becomes less important

Originally, ALD was developed to produce ZnS:Mn and amorphous Al₂O₃ thin films for alternating current thin film electroluminescent displays (ACTFELDs) [1]. Until the mid 1990’s, most films grown by ALD were of a binary character such as the
aforementioned ZnS, or oxides such as Al₂O₃. ALD growth of ternary oxides has also been demonstrated [37-40] and continued interest exists for more complex oxide film growth by ALD.

Figure 2-1. Schematic of an idealized surface reaction with AlCl₃ and H₂O precursors.

<table>
<thead>
<tr>
<th>a.) 1st Precursor</th>
<th>b.) 1st Exchange Rxn</th>
<th>c.) Purge</th>
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<td>d.) 2nd Precursor</td>
<td>e.) 2nd Exchange Rxn</td>
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</table>

Figure 2-1 is a schematic of the atomic layer deposition process that shows Al₂O₃ growth on a silica substrate. The substrate used in the process, shown in figure 2-1, is a hydrogen passivated silica surface on a silicon wafer. The first precursor, AlCl₃ in this case, is introduced to the heated substrate surface (figure 2-1a). The AlCl₃ chemisorbs onto the surface (figure 2-1b) in an exchange reaction. The Cl⁻ ligand is exchanged with a surface hydrogen atom to form a saturated chlorine terminated surface (figure 2-1b) and HCl by-products in the gas phase. The reaction chamber is then purged using an inert gas like N₂ (figure 2-1c). The second precursor, water, is then introduced to the chlorine terminated surface (figure 2-1d). The water is chemisorbed onto the surface...
(figure 2-1e) in a second exchange reaction. The OH molecule is exchanged with a surface chlorine atom to form a saturated hydroxide terminated surface and HCl by-products in the gas phase. The reaction chamber is again purged with N₂ (figure 2-1e) completing the growth of one molecular layer (∼0.2 nm) in times of ∼1-10 sec. The surface now resembles the original hydroxide passivated surface and the cycle can be repeated. With multiple cycles, the reactions result in a film with a thickness determined by the number of cycles. The precursors can also be switched in-situ to create new films.

Atomic layer deposition growth proceeds layer-by-layer in which each layer is a monatomic or monomolecular layer. In order to achieve monatomic or monomolecular layers, the dosing of a precursor, such as AlCl₃, needs to be uniformly delivered onto the substrate surface to achieve saturation of the substrate surface reaction sites. Saturation occurs when all available surface bonding sites are filled with new chemical species originating from the reaction between a precursor and a surface bonding site. The resulting surface does not create new bonding sites for the precursor being used, instead, bonding sites for the next precursor are formed. After saturation, the surface is then either exposed to a different precursor (e.g. water) or treated to re-create new bonding sites [41].

Defining a monatomic layer via the ALD process is difficult. In general terms, Suntola defines a monatomic layer as, “a surface configuration formed by adatoms directly bonded to the underlying surface” and a ‘full monolayer’ as, “a layer of atoms identical to layers of corresponding atoms inside the lattice in the direction parallel to the surface studied” for a crystalline material [41]. Often, multiple ALD cycles are necessary
in order to produce a single full monolayer. For example, it has been previous reported that ZnS has a preferred growth rate of 1/3 monolayer (ML) per cycle when grown as a polycrystalline film using ZnCl$_2$ and H$_2$S as precursors [41]. This 1/3 ML per cycle rate for ZnS is explained as a steric hindrance from the two chlorine atoms on the surface after exposure to ZnCl$_2$ [41], effectively blocking ZnCl$_2$ from bonding sites on the surface. By comparison, CdS shows a 1 monolayer/cycle growth rate when using CdCl$_2$ and H$_2$S as precursors [41]. The explanation is that Cd has a larger ionic radius than Zn and CdS has a larger lattice constant than ZnS such that the chlorine ligands do not block (no steric hindrance) other surface sites as they are further apart than the ligand length [41].

2.2.2 ALD Precursors

The correct choice of precursor materials is important for ALD. The precursors need to be suitably volatile in order for sufficient vapor to be introduced into the reaction chamber [2]. They need to have about 0.1 torr equilibrium vapor pressure at a temperature where they do not decompose. However, the vapor pressure of the material doesn’t have to be very high. Solid precursors such as metal halides need only to provide enough flux for surface saturation. The precursors cannot react with an identical precursor and must be stable enough so as to not decompose on the surface or in the gas phase so as to achieve self-terminating surface reactions. The precursors can be solids, liquids or gases as long as they meet these requirements [2]. The precursors must chemisorb on the surface in question or react aggressively with surface groups in order to reach surface saturation quickly to ensure a reasonable growth rate [2] at lower ALD temperatures.
Metal halides are the most widely used precursors, especially chlorides [5]. Even though most metal halides are solids, their vapor pressures can be sufficient when heated for surface saturation when dosed into the reaction chamber. Homogeneity of the dose or a constant flux rate is typically unnecessary [2]. Metal alkyl compounds behave very well in making oxide and sulfide films, but do not behave well in making other types of films [2]. Metal alkoxides have been used successfully in several oxide processes [2]. For electropositive metals, such as rare earths, it is challenging to find suitable precursors that meet the necessary requirements of volatility and thermal stability for ALD from commercial sources as these are relatively new to ALD. Most precursors for rare-earth metals are expensive and available in limited quantities. β-diketonates are the most studied and show good results for rare-earth sulfides [2]. For reactions of β-diketonates to form oxides, ozone must be used as an oxygen source rather than water because β-diketonate anions are very weak Brønsted acids [42] and a strong oxidizer such as ozone is therefore needed to form the rare-earth oxide. H₂S, H₂O are the most common sulfide and oxide precursors. For reactions with halides, such as AlCl₃, H₂O is an effective oxygen source. Surface terminating hydroxyl groups from the surface metal halide and water reaction in ALD growth are an important intermediate surface chemical species. The hydroxyl groups are formed after the water exposure and act as bonding sites for the subsequent metal halide precursor [43,44]. A high density of surface hydroxyl groups can increase growth rates when compared to a low density hydroxide surface [44].

Precursor size plays a role in the size of the surface species formed at each step in an ALD cycle. For example, in growth of Ni films, Ni(acac)₂ (acac = acetylacetonate
or pentane-2,4-dionate) precursors have a projected surface area of 0.47 nm$^2$ whereas Ni(thd)$_2$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) has a projected surface area of 0.87 nm$^2$ which results in a calculated saturation density of 2.1 Ni/nm$^2$ and 1.1 Ni/nm$^2$, respectively [41]. Because of the large ‘footprint’ of the Ni precursor (acac or thd), many of the surface bonding sites are covered (sterically hindered) at saturation during a single pulse. The acac or thd ligands are removed by H$_2$O on the following ALD step to form H(acac) or H(thd), respectively, which then desorb from the surface. The new surface then has both Ni-O-H and R-O-H sites available for the next Ni(acac/thd) pulse (where R is the original substrate surface). The next few reaction cycles of Ni precursor are with either the Ni-O-H or R-O-H sites until after a few cycles only Ni-O-H sites are available as the substrate surface (R) is covered [41].

### 2.2.3 Nucleation and Growth

Atomic layer deposition has many similarities with other chemical vapor deposition (CVD) techniques. Nucleation and growth in ALD can use the same theoretical treatments as CVD techniques. The next few sections will briefly cover adsorption, nucleation, and growth of atomic layer deposition.

#### 2.2.3.1 Adsorption

The ALD process ‘window’ for a saturated surface (fractional or single monolayer) as a function of temperature is shown schematically in Figure 2-2 [41]. Figure 2-2 is an arbitrary plot of monolayer saturation (adsorption) versus temperature. The saturation (non-shaded) region shown in figure 2-2 represents a single monolayer or fractional monolayer. A fractional monolayer is simply a monolayer where full saturation has occurred and available bonding sites remain due to steric effects of the adsorbed precursor, i.e. a monatomic layer as described in section 2.21. ALD requires a sufficient
precursor flux for monolayer saturation unlike MOCVD which requires careful stoichiometric control of continuous precursor flux in the gas phase. Insufficient precursor flux in ALD results in a partially saturated surfaces. As precursors are alternatively introduced to the surface, growth proceeds only on those areas where the previous precursor saturated the surface and formed a selectively reactive chemical species (bonding site) for the next precursor. Insufficient flux effectively lowers the growth rate of the film as the reaction is starved of precursors.

Figure 2-2. Schematic of ALD process temperature window for saturation and rate limiting mechanisms at lower and higher temperatures [41].

Surface adsorption of a gaseous precursor at a constant temperature is described by the Langmuir Isotherm (equation 2-1) where $\theta$ is the fractional coverage of the
precursor on the surface, \( P \) is the partial pressure of the precursor, and \( K \) is the equilibrium constant [45].

\[ \theta = \frac{KP}{1+KP} \]  

(2-1)

The equilibrium constant, \( K \), is given by equation 2-2, where \( k_{ads} \) and \( k_{des} \) are the adsorption rate constant and desorption rate constant respectively. The rate constants have an Arrhenius relationship \( k \sim \exp \left(-\frac{E}{k_b T} \right) \) where \( K_b \) is Boltzmann’s constant, \( T \) is temperature and \( E \) is the energy of adsorption or desorption as the case may be.

\[ K = \frac{k_{ads}}{k_{des}} \]  

(2-2)

The Langmuir Isotherm describes surface coverage, or surface saturation. One can relate \( \theta \) to the monolayer saturation depicted in figure 2-2 (the y-axis). Within the saturation window (figure 2-2), once surface saturation has occurred no other saturation can take place until a new reactive precursor is introduced. This is the characteristic self-limiting mechanism characteristic of ALD. The shaded regions show deviations from this window.

If the temperature is too low, condensation of the precursor on the surface is a possible mechanism for deviating from monolayer saturation. From the Langmuir Isotherm one can see that if the partial pressure of a precursor is very large, \( \theta \) approaches one (full saturation). If the partial pressure of a precursor approaches zero then saturation also approaches zero. However, if the precursor gas has a partial pressure greater than its vapor pressure, supersaturation can occur resulting in condensation. In this case the precursor undergoes physisorption on the surface and lacks enough energy to overcome both the activation energy barrier to chemisorb and the energy barrier for desorption from the surface. Surface saturation increases with
decreasing temperature when condensation occurs. This growth regime is not strictly limited to surface saturation and therefore monolayer growth is not achieved [41].

Insufficient energy for a surface reaction to overcome the activation energy of a reaction is another possible mechanism for deviating from monolayer surface saturation at low temperatures. In this case, the surface reaction of the precursor with a bonding site lacks sufficient energy to overcome the activation for chemisorption. The rate of adsorption, \( r_{\text{ads}} \), of a precursor to a surface has an Arrhenius relationship given by equation 2-3.

\[
\frac{r_{\text{ads}}}{d} \propto e^{-E_a/kT} \quad (2-3)
\]

Surface saturation decreases with decreasing temperature in this regime as the precursor lacks sufficient activation energy, \( E_a \), for chemisorption.

For temperatures above the ALD window, two other mechanisms are possible: decomposition and desorption. Decomposition of the precursor into non-volatile material leads to an excess of available surface bonding sites for the precursor as the decomposed precursor material collects on the substrate [41]. Monolayer saturation may occur as desired, but in addition, the non-volatile decomposed products on the surface create new bonding sites for additional precursor adsorption. Surface saturation increases with increasing temperature as new bonding sites are being formed and an increase in saturation is observed (figure 2-2).

New surface species formed from chemisorption of the precursor onto the surface may also undergo desorption from the surface at higher temperatures. When the rate of desorption of the newly formed surface species begins to exceed the rate of adsorption...
of the precursor at higher temperatures, a decrease in surface saturation is observed (figure 2-2) [41].

Within the ALD window, saturation occurs such that all available surface bonding sites are filled with new surface species resulting from the reaction of the precursor and the available bonding sites [41]. In the window, neither an increase of bonding sites from decomposition or condensation occur, nor does insufficient energy for chemisorption or excess energy for desorption occur as a function of temperature. In other words, the available surface bonding sites remain constant as a function of temperature.

The temperature range of the saturation window varies for different precursor and surface combinations. For a multiple film process, such as an alternating Al₂O₃-Y₂O₃ process, the saturation windows of each film should overlap in order to make the desired film. If the windows do not overlap, one can either change the temperature between reaction processes or use extra energy to improve the saturation of one or more reaction sequences [41].

The density of the bound surface precursor molecules in a surface reaction is controlled by the density of available bonding sites and the size of the surface species formed at a particular reaction step in the ALD cycle [41]. Large ligands from the chemisorbed precursor block bonding sites on the surface from reacting with the precursor. The filling density of the surface species formed is dependent on the available bonding sites on the surface and on the size of the surface species formed [41]. Bonding sites can also be blocked or created by reconstruction or unwanted chemical groups, such as chlorine in figure 2-1f.
2.2.3.2 Nucleation

Alternating cycles of reactive precursors in ALD leads to the desired film formation. In traditional CVD methods, a gas phase reaction of the precursors occurs and the resultant molecular species adsorbs on the surface. These molecules then coalesce (nucleate) and grow. In ALD, the precursors react on the surface rather than the gas phase. The resultant molecular species is on the surface just as in traditional CVD. As such, treatment of nucleation and growth is similar.

Film growth begins with nucleation. The capillarity theory of heterogeneous nucleation provides a qualitative model of film nucleation [45]. This theory assumes that atoms or molecules impinge on the substrate surface and coalesce into a cap-shaped nuclei (film) of some mean dimension, d, on the substrate. The free-energy change of this nucleus formation is given by equation 2-4 [45].

\[ \Delta G = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{fv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv} \]  (2-4)

The first term is the volume of the nuclei and the free-energy change per unit volume and drives the coalescence of the nuclei. In the second term, \( \gamma_{fv} \) is the surface energy of the nuclei (film) surface at the nuclei-vapor interface. In the third term, \( \gamma_{fs} \) is the surface energy of the nuclei surface at the nuclei-substrate interface. And in the last term, \( \gamma_{sv} \) is the surface energy of the substrate at the substrate-vapor interface. This last term has the same area as the third term \( a_2 r^2 \). The last term is negative since the surface energy of this area of substrate-vapor interface has been ‘lost’. All the energy terms in equation 2-4 have units of J/m\(^2\).

A simple definition of surface energy is related to the change in work on a material when its surface area changes (equation 2-5). A surface can therefore alter its energy
by engaging in mechanical work to change its surface area. In solids, this involves surface stresses and therefore, surface energy is sometimes referred to as surface tensions. The surface energies in equation 2-4, therefore, can be equated to interfacial surface tensions between the film and the substrate. These surface tensions are in mechanical equilibrium parallel to the substrate surface and are described by Young’s equation (equation 2-6), where $\phi$ is the wetting angle.

$$dW = \gamma dA \quad (2-5)$$

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv}\cos\phi \quad (2-6)$$

In this work, we have already looked at the wetting of the precursors (section 2.2.3.1) in ALD. Monolayer saturation occurs in ALD when $\phi = 0$ (complete wetting of the surface). It is the reaction of surface saturated precursors with the underlying surface that produces a film in ALD. The resultant film wets the substrate no more than the precursor with the least surface saturation. The relative size of the surface tensions in equation 2-6, as well as the wetting angle, determine what type of growth occurs after nucleation.

**2.2.3.3 Growth modes**

There are three well known growth modes: Island (Volmer-Weber), layer (Frank-Van der Merwe), and a mixture of these two known as Stranski-Krastanov [45]. Island growth occurs when the deposited material preferentially attaches to growth material already present on the surface. Layer growth occurs when deposited material preferentially seeks the lowest (normal to the surface) unfilled bonding sites on the surface. The growth is two-dimensional and the material grows monolayer by monolayer. Stranski-Krastanov growth occurs when the substrate is first covered by a
few monolayers of growth in a layer growth mode and then proceeds to the island
growth mode. Finally, a fourth growth mode, random growth, has also been proposed
for ALD [46]. Random growth occurs when the deposited material settles with equal
probability to all surface bonding sites in an ALD reaction cycle [46].

For island growth, $\Phi > 0$ and therefore equation 2-6 becomes equation 2-7. If we
neglect $\gamma_{fs}$, equation 2-6 suggests that island growth occurs when the surface energy of
the film exceeds that of the substrate. In this growth mode, increased lattice mismatch
between the film and substrate increases the influence of island growth. In ALD, the
adsorbed precursors preferentially settle on top of material already deposited on the
surface.

$$\gamma_{sv} < \gamma_{fs} + \gamma_{fv} \quad (2-7)$$

For layer growth, the deposit wets the substrate ($\Phi \approx 0$) and equation 2-6
becomes equation 2-8. This suggests that layer growth occurs when the surface energy
of the substrate exceeds that of the film. In homo-epitaxy, the film is the same material
as the substrate and therefore $\gamma_{sf}$ vanishes. In ALD, the adsorbed precursors
preferentially settle in the lowest unfilled layer [46].

$$\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv} \quad (2-8)$$

Lastly, for Stranski-Krastanov growth, initially the film wets the substrate and layer
growth occurs. The transition from layer to island growth, occurring after approximately
5-6 monolayers, is not completely understood [45]. It is likely that after a few
nanometers of layer growth, a lattice mismatch between the film and the substrate
accumulates strain energy in the film surface and may trigger the onset of island growth.
In ALD, the adsorbed precursors initially settle in the lowest unfilled layer, but soon preferentially settle on material already deposited on the surface.

Another growth mode has been proposed for ALD referred to as “random deposition” [46]. This growth mode bears some similarity with the so-called “rain” model in continuous deposition processes like MOCVD [46]. In random deposition, the adsorbed precursors do not settle preferentially but instead settle randomly. This growth mode shows a dependence on the growth rate (Å/cycle) in ALD such that large growth rates result in a smoother film whereas a much smaller growth rate results in rougher films [46].

Figure 2-3. An ALD sequence illustrating the influence of steric effects on surface roughness.

Steric effects influence nucleation and growth in ALD as briefly discussed in section 2.2.3.1. An adsorbed precursor with large ligands can effectively block other
precursors from adsorption sites. If such a situation occurs, the surface reaction between an absorbed precursor and the next precursor in the cycle can produce an uneven surface. Figure 2-3 shows a simple cartoon of how this might occur. Frame ‘A’ shows a functionalized substrate and large ligand precursors (open box) about to absorb. Frame ‘B’ shows those large ligand precursors adsorbed (a fractional monolayer) on the surface and the second precursor (closed box) about to absorb. Frame ‘C’ shows the absorbed (reacted) second precursors and a new pulse of large ligand precursor about to absorb. Note that in frame ‘C’ the reaction of the two precursors produces a functionalized substrate similar to frame ‘A’, but with slight surface roughness. In Frame ‘D’ some of the large precursor has absorbed in the low spaces before those sites could be blocked. Upon reacting with the second precursor, frame ‘E’ shows further roughening of the surface. Frame ‘F’ shows multiple areas of steric hindrance occurring, with some of the original surface from frame ‘A’ still unsaturated. In frame ‘G’ we see the surface after 3 full cycles have occurred. Even if the surface tensions are such that layer growth is expected, large ligand precursors can result in some surface roughening.

Typically, growth of a binary film, such as Al₂O₃ or Y₂O₃, consists of multiple ALD cycles such that a monolayer of the binary material is formed. For ternary films using ALD, the common method is to grow alternating monolayers of the binary constituents and then post-calcine the multi-layered film to achieve the final structure [2, 38, 47, and 48]. For instance, it was shown that to grow a film of ternary LaGaO₃, alternating monolayers of binary La₂O₃ and Ga₂O₃ were grown and calcined to form LaGaO₃ [38]. For more complex stoichiometries, the monolayers were deposited such that the overall
stoichiometric ratio was maintained during growth and post-growth calcining for inter-diffusion. For growth of LaGaO$_3$ films, Nieminen [38] has shown that the pulsing sequence $5 \times [La(thd)_3 + O_3] + 2 \times [Ga(acac)_3 + O_3]$ produces stoichiometric LaGaO$_3$ films at 325°C-425°C. The pulsing ratio of La:Ga was 5:2 even though the stoichiometric ratio of the resultant film is 1:1.

2.3 Atomic Layer Deposition of Binary Oxides

2.3.1 Thermochemistry

Table 2-1. Thermodynamic properties of precursors and films grown in this study [49,50].

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Delta H_f$ (kJ/mol)</th>
<th>$S^\circ$ (J/mol K)</th>
<th>$C_p$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl$_3$(s)</td>
<td>-704.2</td>
<td>109.3</td>
<td>91.1</td>
</tr>
<tr>
<td>AlCl$_3$(g)</td>
<td>-583.2</td>
<td>314.4</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$(s)</td>
<td>-1675.7</td>
<td>50.9</td>
<td>79.0</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>-92.3</td>
<td>186.9</td>
<td>29.1</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>-241.8</td>
<td>188.8</td>
<td>33.6</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0</td>
<td>205.2</td>
<td>29.4</td>
</tr>
<tr>
<td>O$_3$(g)</td>
<td>142.7</td>
<td>238.9</td>
<td>39.2</td>
</tr>
<tr>
<td>(thd)$_3$(g)</td>
<td>-346.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YCl$_3$(s)</td>
<td>-1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YCl$_3$(g)</td>
<td>-750.2</td>
<td></td>
<td>75.0</td>
</tr>
<tr>
<td>Y(thd)$_3$(g)</td>
<td>-2269.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$_2$O$_3$(s)</td>
<td>-1905.3</td>
<td>99.1</td>
<td>102.5</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-393.5</td>
<td>213.8</td>
<td>37.1</td>
</tr>
</tbody>
</table>

Atomic layer deposition of binary oxides is a surface controlled chemical reaction. For ALD, chemical precursors that are highly reactive with each other are desired as discussed in section 2.2. The chemistries of the highly reactive precursors used in ALD are exothermic with large enthalpies of reaction. Table 2-1 shows thermodynamic data for the precursors used in this study and their products. In table 2-1, thd stands for 2,2,6,6-tetramethyl-3,5-heptanedionato and the enthalpy values for both thd and Y(thd)$_3$
come from Santos et. al. [49]. The other values are from the *Handbook of Chemistry and Physics* [50]. From these values, enthalpies of reaction are calculated for the ALD reactions in this work. In table 2-1, $\Delta H^\circ$ is the standard molar enthalpy of formation at 298.15K, $S^\circ$ is the standard molar entropy, and $C_p$ is the molar heat capacity at constant pressure at 298.15K.

### 2.3.2 Al$_2$O$_3$

The first known process for ALD of Al$_2$O$_3$ used AlCl$_3$ and H$_2$O at 250°C and was developed by Suntola, Pakkala, and Lindfors [51]. Deposition temperatures from 100°C to 660°C have been explored [39,51]. The deposition of ALD alumina films has primarily focused on using the metal sources of trimethylaluminum (TMA) and aluminum trichloride (AlCl$_3$) [39, 51, and 52]. Water is the primary source of oxygen used for alumina growth. In the present study for the ALD of Al$_2$O$_3$ thin films, AlCl$_3$ and H$_2$O precursors are used and the overall chemical reaction is shown in equation 2-8.

$$
2\gamma ACl_3(g) + 3H_2O(g) \rightleftharpoons \gamma Al_2O_3(s) + 6HCl(g)
$$

Equation 2-8 shows an ion exchange reaction where Al is exchanged for H. The enthalpy of reaction for the above chemical equation can be determined using Hess’s Law (equation 2-9) with the standard molar enthalpies of formation given in table 2-1. The calculation is given in equation 2-10 (the units have been dropped for clarity) and results in $\Delta H^\circ_{rxn} = -337.7kJ$.

$$
\Delta H^\circ_{rxn} = \sum \Delta H^\circ_{products} - \sum \Delta H^\circ_{reacts}
$$

$$
\Delta H^\circ_{rxn} = (6)(-92.3) + (1)(-1675.7) - (2)(-583.2) - (3)(-241.8)
$$

The large negative value for $\Delta H^\circ_{rxn}$ means this reaction is very exothermic. Likewise, using both the standard molar entropies from table 2-1 and Hess’s Law
(equation 2-9) the standard entropy of reaction for the above chemical reaction is
\[ \Delta S_{rxn}^o = -22.9 \text{ J/K}. \]
The calculation is given by equation 2-11 (the units have been dropped for clarity).
\[
\Delta S_{rxn}^o = (6)(186.9) + (1)(50.9) - (3)(188.8) - (2)(314.4) \tag{2-11}
\]
Therefore, the standard-state Gibbs energy of reaction at constant temperature and pressure is given by equation 2-12 and results in \( \Delta G_{rxn}^o = -330.9 kJ. \)
\[
\Delta G_{rxn}^o = \Delta H_{rxn}^o - T \Delta S_{rxn}^o \tag{2-12}
\]
A large negative \( \Delta G_{rxn}^o \) for this chemical reaction means that the reaction is very favorable to proceed spontaneously when at standard temperatures and pressures and occurs spontaneously. Raising the temperature of this reaction increases the \( \Delta G_{rxn}^o \) (less favorable), but at typical ALD temperatures the reaction remains favored with a large negative \( \Delta G_{rxn}^o \).

To grow \( \text{Al}_2\text{O}_3 \) by an ALD reaction between \( \text{AlCl}_3 \) and \( \text{H}_2\text{O} \), the incoming \( \text{AlCl}_3 \) vapor is introduced to the reaction chamber, adsorbs on the substrate surface, and reacts with surface hydroxyls to produce hydrochloric (HCl) gas as a byproduct in an exchange reaction leaving surface chlorides. Once all of the hydroxyl sites have reacted, no more \( \text{AlCl}_3 \) can be adsorbed on the surface. As discussed in section 2.2.3.1, this is known as surface saturation and is what makes the ALD process to be self-limiting. The remaining \( \text{AlCl}_3 \) and the HCl gas product are then removed from the reaction chamber by the nitrogen pulse. Next, \( \text{H}_2\text{O} \) is introduced into the reaction chamber, absorbs on the substrate surface, and reacts with surface chlorides to produce HCl gas as a byproduct in an exchange reaction that leaves surface hydroxyl groups. The reactor is again purged with nitrogen. This constitutes one cycle and the
process is repeated several thousand times to grow Al₂O₃ films ∼100-1000 nm thick. The temperature range for the AlCl₃ and H₂O ALD process is wide, 100°C-600°C with a growth rate of 0.5Å/cycle to 0.7Å/cycle [39, 53]. The AlCl₃ source temperature has been reported at 110°C [53].

The formation of Al₂O₃ from AlCl₃ and H₂O is not as simple as indicated by the above idealized reaction sequence. Surface reactions can proceed through a variety of different pathways. In the above idealized sequence, an adsorbed AlCl₃ may result in a surface terminated with a single bonded R*-AlCl₂, a double bonded R*=AlCl, or triple bonded R*=Al (where R* is the substrate surface bonding site). While all of these surface bonding configurations can lead to film growth, the growth rates as well as the density of the resultant films can be different.

The reverse of equation 2-8 is also possible. The gaseous HCl byproduct formed during the AlCl₃ pulse can etch the Al₂O₃ surface being formed (self-etching). The HCl and Al₂O₃ reaction produces gaseous water and AlCl₃. The gaseous water reacts with the AlCl₃ (either the by-product or the precursor flux) in the gas phase to form Al₂O₃: ie CVD rather than ALD. This reverse reaction forms particulate that deposits on the substrate as well “pits” where the etched material was removed leading to increased surface roughness in the final film.

2.3.3 Y₂O₃

Atomic layer deposition of Y₂O₃ using Y(thd)₃ [thd = 2,2,6,6-tetramethyl-3,5-heptanedione] and O₃ above 425°C was shown by Mölsä, Niinistö, and Utrianen [54]. The deposition of Y₂O₃ at temperatures of 200°C-425°C was then reported by Putkonen et. al. [55]. Putkonen also reported an ALD window of 250°C - 350°C for a Y(thd)₃ and
O₃ process with a growth rate of 0.23Å (cycle)⁻¹ [55]. However, Mölsä et. al. [54 did not show a saturation window and instead reported a linear increase in growth rate as a function of temperature. The films were crystalline and showed strong X-ray diffraction (XRD) (400) and (440) peaks [55] consistent with the cubic phase of Y₂O₃. The overall chemical reaction is shown in equation 2-13 [56].

\[ 2Y(\text{thd})_3(g) + 60O_3(g) \rightleftharpoons Y_2O_3(s) + 57H_2O(g) + 66CO_2(g) \]  

(2-13)

This is a combustion reaction with a very large enthalpy of reaction. Using the standard molar enthalpies of formation from table 2-1, the enthalpy of reaction for the above chemical equation can be determined using Hess’s Law in the same manner as for Al₂O₃ (section 2.3.2) and results in \( \Delta H_{\text{rxn}}^{\circ} = -22308.8 \) kJ. The calculation is shown in equation 2-14 (the units have been dropped for clarity).

\[ \Delta H_{\text{rxn}}^{\circ} = (66)(-393.5) + (57)(-241.8) + (1)(-1905.3) - (2)(-2269.1) - (60)(142.7) \]  

(2-14)

This chemical reaction assumes a complete reaction, but previously reported experimental results are not consistent with this reaction and a ligand exchange model is proposed [56,57]. This model assumes that only partial combustion occurs during the ozone delivery step. The H₂O from partial combustion during the O₃ pulse forms surface hydroxyl groups and oxygen bridges can then presumably form from dehydroxylation of these hydroxyl groups. In the following Y(thd)₃ delivery pulse a ligand exchange reaction then occurs between Y(thd)₃ precursors and the surface hydroxyl groups which remain on the surface during the previous O₃ delivery pulse. Partial combustion may result in the formation of CO and hydrocarbons in addition to the H₂O and CO₂ products. These may adsorb on the surface as well as provide possible ligand exchange bonding sites, further complicating the reaction mechanism.
The deposition by ALD of yttria films has primarily focused on using the β-diketonate precursors such as the aforementioned Y(thd)₃ as well as Y(thd)₃(bipyridyl), and Y(thd)₃(1,10-phenanthroline) with ozone [54,55]. The sublimation of Y(thd)₃ has been shown to be stable above 130°C [54]. The growth of Y₂O₃ using these precursors show only small differences in the growth rates, possibly due to steric hindrance [55]. In the present study, ALD was used to grow yttria thin films using Y(thd)₃ and O₃ as precursors.

In the idealized Y₂O₃ ALD reaction between Y(thd)₃ and O₃, the incoming Y(thd)₃ vapor is introduced to the reaction chamber, adsorbs on the substrate surface, and reacts with surface sites to produce a Y(thd)ₓ surface (where x=0,1, or 2). Once surface saturation is complete, the non-adsorbed Y(thd)₃ and the reaction by-products (H₂O, CO₂, and any thd fragments) are removed from the reaction chamber during the purge sequence using inert nitrogen gas. Next, O₃ is introduced to the reaction chamber, absorbs on the substrate surface, and reacts with the surface Y(thd)ₓ to produce a Y₂O₃ surface with some hydroxyl surface groups and combustion byproducts. The reactor is again purged with nitrogen. This constitutes one complete cycle which is repeated several thousand times to grow films ~100-1000 nm thick.

2.3.4 Ce₂O₃

Atomic layer deposition of CeO₄ using Ce(thd)₄ [thd = 2,2,6,6-tetramethyl-3,5-heptanedione] and O₃ with a temperature window of 175-250°C was shown by Jani Paivasaari, Matti Putkonen and Lauri Niinisto [58]. The growth rate of CeO₄ was found to be 0.32 Å/cycle [58]. The films were polycrystalline with no preferred orientation. The overall chemical reaction is shown in equation 2-15 [56].
This chemical reaction assumes a complete reaction, however, previously reported experimental results were not consistent with this reaction and a ligand exchange reaction with some thermal decomposition was observed [58]. A ligand exchange reaction occurs between Ce(thd)₄ precursors and the surface hydroxyl groups which remain on the surface during the previous O₃ delivery pulse.

In the idealized CeO₄ ALD reaction between Ce(thd)₄ and O₃, the incoming Ce(thd)₄ vapor is introduced to the reaction chamber, adsorbs on the substrate surface, and reacts with hydroxyl surface sites to produce a Ce(thd)ₓ surface (where x=0, 1, 2, or 3) and H(thd) as a byproduct. Once surface saturation is complete, the non-adsorbed Ce(thd)₄, H(thd), and any thd fragments are removed from the reaction chamber during the purge sequence using inert nitrogen gas. Next, O₃ is introduced to the reaction chamber, absorbs on the substrate surface, and reacts with the surface Ce(thd)ₓ to produce a CeO₂ surface with some hydroxyl surface groups and combustion byproducts. The reactor is again purged with nitrogen. This constitutes one complete cycle which is repeated several thousand times to grow films.

Atomic layer deposition of Ce₂O₃ has not been previously demonstrated. In this dissertation, ALD of Ce₂O₃ deposition is studied as a potential dopant for Y₄Al₂O₉ and Y₃Al₅O₁₂ using Ce(acac)₃ [acac = acetylacetonate or 2,4-pentanedionate] and O₃ as precursors. A possible combustion reaction is shown in equation 2-16.

\[
2Ce(acac)₃(g) + 25O₃(g) \rightleftharpoons Ce₂O₃(s) + 24H₂O(g) + 30CO₂(g)
\] (2-16)

This proposed chemical reaction assumes a complete combustion. It is suspected that much like the Ce(thd)₄ process above and that for Y(thd)₃ (section 2.3.2), a ligand
exchange reaction with some combustion is expected. In this manner, a ligand exchange reaction would occur between Ce(thd)$_3$ precursors and the surface hydroxyl groups which remain on the surface during the previous O$_3$ delivery pulse.

In the idealized Ce$_2$O$_3$ ALD reaction between Ce(thd)$_3$ and O$_3$, the incoming Ce(thd)$_3$ vapor is introduced to the reaction chamber, adsorbs on the substrate surface, and reacts with hydroxyl surface sites to produce a Ce(thd)$_x$ surface (where $x=0,1$, or 2) and H(thd) ligands as a byproduct. Once surface saturation is complete, the non-adsorbed Ce(thd)$_4$, H(thd), and any thd fragments are removed from the reaction chamber during the purge sequence using inert nitrogen gas. Next, O$_3$ is introduced to the reaction chamber, absorbs on the substrate surface, and reacts with the surface Ce(thd)$_x$ to produce a Ce$_2$O$_3$ surface with some hydroxyl surface groups and combustion byproducts. The reactor is again purged with nitrogen. This constitutes one complete cycle which is repeated several thousand times to grow films.

2.4 Pseudo-binary Oxides of the Al$_2$O$_3$-Y$_2$O$_3$ System

2.4.1 Introduction

The pseudo-binary Al$_2$O$_3$-Y$_2$O$_3$ material system has several well known solid phases. In order from least aluminum content to the greatest, these are: Y$_2$O$_3$, Y$_4$Al$_2$O$_9$, YAlO$_3$, Y$_3$Al$_5$O$_{12}$, and Al$_2$O$_3$. A pseudo-binary phase diagram is shown in figure 2-4. The solid phases continue as presented in figure 2-4 at temperatures below 1600°C. Both Al$_2$O$_3$ and Y$_2$O$_3$ are discussed in section 2.3. The other three phases of this material system are discussed in this section.

As can be seen from figure 2-4, the three solid phases of the Al$_2$O$_3$-Y$_2$O$_3$ material system have discrete phase boundaries between them that do not vary in concentration at temperatures below ~1800°C [10]. Mixtures of finely ground Al$_2$O$_3$ and Y$_2$O$_3$ particles
at high temperatures crystallize into one of the phases. The phases formed depend solely on the concentration of the mixture. In these solid-state reactions, repeated grinding of the material is necessary to provide intimate contact between Al$_2$O$_3$ and Y$_2$O$_3$ to facilitate their inter-diffusion into the new phases. Even with stoichiometric amounts of Al$_2$O$_3$ and Y$_2$O$_3$, it is difficult to get complete inter-diffusion and remnant Al$_2$O$_3$ and Y$_2$O$_3$ phases are often present.

Figure 2-4. Pseudo-binary phase diagram of the Al$_2$O$_3$-Y$_2$O$_3$ material system reprinted from [15].

At thermodynamic equilibrium, there are four solid-state regions present in the phase diagram in figure 2-4. In order of increasing Al$_2$O$_3$ content these are: a mixed
phase of $Y_2O_3$ and $Y_4Al_2O_9$, a mixed phase of $Y_4Al_2O_9$ and $YAIo_3$, a mixed phase of $YAIo_3$ and $Y_3Al_5O_{12}$, and a mixed phase of $Y_3Al_5O_{12}$ and $Al_2O_3$

Only by the precise mixing of $Al_2O_3$ and $Y_2O_3$ can pure phases $Y_4Al_2O_9$, $YAIo_3$, $Y_3Al_5O_{12}$ be synthesized. The relative amounts of each present can be determined by using the lever rule [59]. Tie lines in any given region in this phase diagram always correspond to the same concentrations at temperatures below 1800°C.

For example, in the first region of the phase diagram in figure 2-4, the fraction of $Y_2O_3$ in the mixture is given by equation 2-17 (lever rule), where $C_0$ is the initial concentration of $Al_2O_3$ in the first region (before thermodynamic equilibrium). The fraction of $Y_4Al_2O_9$ in the first region would then be 100% minus the % $Y_2O_3$ calculated by equation 2-17. At any given $C_0$, these relative amounts of $Y_2O_3$ and $Y_4Al_2O_9$ would remain the same for temperatures below 1800°C

$$\% Y_2O_3 = \frac{0.333 - C_0}{0.333} \times 100\% \quad 2-17$$

In ALD, intimate mixtures can easily be obtained by making alternating stacks of films, each of only a few nanometers or less in thickness. These nanolaminate stacks can then be calcined at high temperatures to facilitate self-diffusion into the desired solid phase. Stoichiometric amounts of deposited materials are made by noting that the number of moles of a film can be determined from the film thickness and area as shown in equation 2-18 as both density and molar mass are easily obtained values.

$$mol A = \frac{density \ A \times area \ A}{molar \ mass \ A} \times thickness \ A \quad 2-18$$

The stoichiometric ratio of a binary system is shown in equation 2-19. For an alternating stack of films, area $A$ is equal to area $B$ and therefore $C_x$ (where $x$ is $A$ or $B$) is a material constant equal to density over molar mass.
Solving equation 2-19 for \( t_A \) results in equation 2-20. For a desired stoichiometric ratio, the thickness of film \( A \) must equal to the stoichiometric ratio times a constant times the thickness of film \( B \) (equation 2-20).

\[
t_A = \frac{\text{mol } A}{\text{mol } B} \frac{c_B}{c_A} t_B \tag{2-20}
\]

Inter-diffusion such that complete homogenization is approached can be approximated from Fick’s second law [59]. A nanolaminate stack with very thin films approximates a diffusion couple that is approaching complete homogenization. A solution of Fick’s second law for the complete homogenization case is referred to as the long-time solution [59]. In this case, the long-time solution for a diffusion of solute out of a film (slab) leads to a result of \( L \approx 2 \sqrt{Dt} \), where \( L \) is the diffusion length, \( D \) is the constant diffusion coefficient, and \( t \) is time [59]. This solution provides an approximation for the extent of a diffusion-controlled process. For a nanolaminate stack, atoms of one layer will need to have diffusion distances no more than 1/2 the thickness of the other layer to transform the nanolaminate into a solid-solution in thermodynamic equilibrium.

In other words, the thickness of an individual film in a nanolaminate stack would need to be \( h \approx 4 \sqrt{D/t} \), where \( h \) is the film thickness, for thermodynamic equilibrium to be reached for some time, \( t \). Rearranging this equation in terms of \( D \) results in equation 2-21.

\[
D \approx \frac{h^2}{16t} \tag{2-21}
\]
Equation 2-21 can provide estimates of inter-diffusion constants between two films can be determined if the thickness of the nanolayer is known and the time to reach thermodynamic equilibrium at some temperature is determined.

2.4.2 Y₄Al₂O₉

Atomic layer deposition of the Y₄Al₂O₉ has not been previously demonstrated. The Y₄Al₂O₉ phase has a monoclinic structure [60] and is also known as yttrium aluminum monoclinic, or YAM. This phase is used as a luminescent material [61, 62] and as a thermal barrier coating [63]. In YAM, two of the Y ions are sevenfold coordinated and the other two are six fold coordinated, while all of the Al ions are tetrahedrally coordinated [64]. The Oxygen sites are more complex with four distinct arrangements among the nine sites [64]. YAM contains 13.3 atomic % Al and 26.7 atomic % Y. From the phase diagram (section 2.4.1) [15], YAM is 33.3 mol% Al₂O₃ in Y₂O₃. A mixture containing more than 33.3 mol% and less than 50 mol% Al₂O₃ in Y₂O₃ is a combination of YAM plus YAP at thermal equilibrium. Less than 33.3 mol% Al₂O₃ in Y₂O₃ results in a combination of YAM plus Y₂O₃ at thermal equilibrium.

2.4.3 YAlO₃

The YAlO₃ phase has a perovskite structure of the GdFeO₃ type [65] and is known as yttrium aluminum perovskite or YAP. This phase is often used as a scintillator material such as YAlO₃:Ce [63,64]. In YAP, the Y and Al are both octahedrally coordinated in a distorted octahedral formed by the O atoms [64]. YAP contains 20 atomic % Y and 20 atomic % Al. In terms of mol%, YAP is 50 mol% Al₂O₃ in Y₂O₃ according to the phase diagram (section 2.4.2) [15]. A combination of more than 50 mol% but less than 62.5 mol% Al₂O₃ in Y₂O₃ is a mixture of YAP plus YAG at thermal
equilibrium. When there is a combination of less than 50 mol% but greater than 33.3 mol% Al$_2$O$_3$ in Y$_2$O$_3$, a YAP plus YAM mixture is formed at thermal equilibrium.

2.4.4 Y$_3$Al$_5$O$_{12}$

Atomic layer deposition of Y$_3$Al$_5$O$_{12}$ has not been previously demonstrated. The Y$_3$Al$_5$O$_{12}$ phase has a cubic structure of the garnet type and is also known as yttrium aluminum garnet or YAG. The YAG phase is used widely as a phosphor, a scintillator, and as a laser host material. YAG has a complicated structure with 160 atoms in the cubic cell. In YAG, there are two Al sites, an octahedral and a tetrahedral, and Y is eightfold coordinated [64]. YAG contains 15 atomic % Y, and 25 atomic % Al or 62.5 mol% Al$_2$O$_3$ in Y$_2$O$_3$. From the phase diagram (section 2.4.1) [15] more than 62.5 mol% Al$_2$O$_3$ in Y$_2$O$_3$ is a combination of YAG and Al$_2$O$_3$ when at thermal equilibrium. A combination with less than 62.5 mol% but greater than 50 mol% Al$_2$O$_3$ in Y$_2$O$_3$ results in a mixture that is YAG plus YAP at thermal equilibrium.

2.4.5 Y$_3$Al$_5$O$_{12}$:Ce

The material Y$_3$Al$_5$O$_{12}$:Ce (YAG:Ce) is a phosphor utilized in the white light emitting diode (LED) market [16]. White light is produced by absorbing a fraction of the blue light from the LED, where the absorbed light stimulates emission of a broad band yellow light from the YAG:Ce crystal. The blue light emitted from the LED has a wavelength between \(\sim 450 \text{ nm-480 nm} \) [16] which corresponds well to the broad excitation band of YAG:Ce which peaks at about 470nm. In this material, Ce$^{3+}$ is substituted into the Y$^{3+}$ dodecahedral site of the Y$_3$Al$_5$O$_{12}$ host [66]. Ce$_2$O$_3$ is used in this work to demonstrate the ability to dope cerium into the YAG or YAM host material. As a dopant, very little material is needed. Concentrations on the order of 1% are typical for light-emitting dopants.
CHAPTER 3
EXPERIMENTAL PROCEDURE

3.1 Precursor Analysis

Atomic Layer Deposition (ALD) is a surface-limited chemical reaction, as discussed in Chapter 2, and typically consists of two sequential half-reactions on a substrate surface. The precursor chemistry determines surface-limited growth and therefore is an important factor in ALD. A precursor must be stable prior to delivery into the reaction chamber as well as be highly reactive with the other precursor when it is absorbed on the substrate (section 2.2.2).

The metal precursors used in this study were commercially available from Fisher Scientific. The precursors and their purity were as follows: AlCl₃ (99%), Tris(2,2,6,6-tetramethyl-3,5-heptanediolato)yttrium(III) or Y(thd)₃ (98%), and Tris(2,4-pentanediolato)cerium(III) or Ce(acac)₃ (99.9%), H₂O (10 MΩ conductivity) , and ozone. An oxygen source (99.994%) was purchased from Airgas inc., The oxygen passed through a corona discharge generated in-house using an Enaly HGOZ-1000 ozone generator. The ozone generator has a maximum output of 1% O₃ in an O₃/O₂ mixture. The solid precursors were characterized by thermogravimetric analysis (TGA) to determine volatility from 20°C to 600°C in a Seiko Instruments TG/DTA-320. The TGA results were used to determine the appropriate source temperature of the solid precursors to use during deposition. A small nitrogen flow was present during the analysis and all materials volatized completely.

3.2 Substrate Preparation

All ALD films were deposited onto boron doped Si (100) polished wafers with a ~100nm SiO₂ surface layer grown at 800°C for 12 hours in air? . Atomic layer deposition
results in amorphous or polycrystalline films. Post-growth calcining is needed to inter-diffuse the Al₂O₃ and Y₂O₃ films deposited in this work. Glass substrates would not be able to handle the post-growth calcining temperatures of ~1000°C. SiO₂ on silicon can handle the calcining temperatures used (975°C). ALD rare-earth oxide growth on silicon has been demonstrated [7]. The common chemistry uses a β-diketonate complex and ozone (section 2.4). In this work, a β-diketonate and ozone process is also used. The use of ozone would oxidize bare silicon to form an interfacial SiO₂ layer, therefore, SiO₂ on silicon is used in this work to both segregate the bare silicon from ozone and to prevent inter-diffusion between the ALD deposited films and bare silicon during the high temperature calcine. Gadolinium Gallium Garnet (GGG) could also be used rather than silicon if epitaxial growth of YAG was desired since the lattice parameter and structure of GGG has little mismatch with that of YAG. This work sought to investigate more than just the YAG phase, and using the same substrate for all films for comparative purposes was desired.

The oxidized silicon substrates were cleaned with Alconox (a commercially available powder detergent) and water, rinsed with de-ionized water, dried with nitrogen, and finally cleaned in an UVOCS Inc. ultraviolet light ozone cleaner for 10 minutes to remove organic contaminants.

3.3 Film Deposition

ALD oxide films were deposited onto the oxidized silicon substrates in a commercial (Planar Systems P400) hot-wall flow-type atomic layer deposition reactor. A schematic is provided in Figure 3.1 and photograph of the system in Figure 3.2. Deposition occurred at ~6 torr pressure with nitrogen (99.99% purity LN₂ source) as a carrier and purging gas. Precursors were alternately pulsed into the reactor using fast-
switching solenoid valves custom built by Planar Systems. The solid β-diketonate precursors (thd, acac) were evaporated from open glass crucibles inside the reactor with pulsed nitrogen to carry the precursors to the reaction chamber and substrate. The aluminum chloride precursor was heated (105°C) in an external aluminum container and transported into the reactor using fast-switching solenoid valves and heated (105°C) lines. Water was transported into the reactor through fast-switching solenoid valves from an external bottle at 20°C. Ozone was generated externally from oxygen (99.994%) in a corona-discharge ozone generator (Enaly HGOZ-1000). The 1% ozone in O₂ was pulsed into the reactor using fast-switching valves. The valves are normally closed valves. A pulse consists of opening the valve for 100ms-600ms.

The cleaned substrates were placed within a titanium reactor chamber that was previously coated with Al₂O₃. This reactor chamber has two openings, one which connects to the plenum on the exhaust side and one that connects to the precursor gas manifold (figures 3-1, 3-2). The chamber is inserted into another chamber, the hot-wall chamber, and connections made to the precursor gas manifold and the exhaust. The hot-wall is sealed and with the pumping unit on, both the reactor chamber and the hot wall chamber are pumped down to a base pressure of ~2 torr.

The schematic for the ALD reactor is given in Figure 3.1. The rough vacuum pumps are Leybold Trivac D65BCS wet rotary pumps with a Leybold RUVAC WSU251 Roots blower. A paper filter (Planar Systems, inc.) upstream from the pump was used to collect particulate with a size >0.1 μm generated in the plenum. The plenum (labeled in Figure 3-1) is a cold walled chamber where excess precursors from the half-reactions of the deposition process can combine to form less reactive chemical species, such as
oxides. But rather than being formed by surface-reactions, these oxides are formed in the gas-phase resulting in fine powders. The plenum is connected to the reactor chamber with the hot-wall chamber surrounding both the reaction chamber, and the gas manifold (figure 3-1).

The hot-wall chamber has a MKS Baratron pressure gauge (10 torr) attached to it and is kept at a slightly lower pressure than the reaction chamber, approximately 8 torr for the hot-wall chamber and 6 Torr for the reaction chamber during deposition. The hot-wall chamber is surrounded by heating coils, and the reaction chamber is heated by radiative heating from the hot-walls. The hot-wall chamber has a large door through which the reaction chamber can be removed and inserted into the hot-wall chamber (figure 3-2).

The reaction chamber is a rectangular “box” made of titanium. Two ports are built into the reaction chamber to allow gases to enter at one end from the gas manifold and for excess gasses to exhaust at the opposite end. The reaction chamber is coated with Al$_2$O$_3$ before any films are deposited onto substrates. The reaction chamber is sealed from the hot-wall reactor by a metal-to-metal seal at the two ports.

The gas manifold is under a constant purge of N$_2$ from the N$_2$ manifold. The N$_2$ manifold has a pressure gauge attached to it and with a 10 sccm flow reads 170 torr during deposition. The N$_2$ is constantly flowing through every precursor line purging them of any residual gases from the pulsing sequences. When a pulse occurs at one of the solenoid valves, the total flow of N$_2$ into the reactor remains constant as the N$_2$ flow is diverted through the solenoid valve.
It should be noted that according to the drawing there is a path for pulsed AlCl$_3$ to go directly into the exhaust. However, this drawing does not show the line diameters and the conductance of such lines. There is a N$_2$ pulse in addition to the AlCl$_3$ pulse such that the pressure differential favors the AlCl$_3$ to move towards the reaction chamber rather than directly towards the exhaust.

Atomic layer films were deposited using the following pulse sequence: metal precursor pulse, nitrogen purge, water or O$_3$/O$_2$ precursor pulse, and nitrogen purge. This sequence was repeated to grow a metal oxide to the desired thickness. Table 3-1 shows the pulse sequence for the binary oxide materials deposited in this study. The growth conditions for each material was determined separately in individual experiments and then the materials were grown together in order to form a polymorph of yttrium aluminum oxide.

<table>
<thead>
<tr>
<th></th>
<th>1$^{\text{st}}$ Pulse</th>
<th>2$^{\text{nd}}$ Pulse</th>
<th>3$^{\text{rd}}$ Pulse</th>
<th>4$^{\text{th}}$ Pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$</td>
<td>Y(thd)</td>
<td>N$_2$ Purge</td>
<td>O$_3$</td>
<td>N$_2$ Purge</td>
</tr>
<tr>
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<td>N$_2$ Purge</td>
<td>H$_2$O</td>
<td>N$_2$ Purge</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>Ce(acac)</td>
<td>N$_2$ Purge</td>
<td>O$_3$</td>
<td>N$_2$ Purge</td>
</tr>
</tbody>
</table>
Figure 3-1. Schematic of Atomic Layer Deposition vacuum system.
3.3.1 \( \text{Al}_2\text{O}_3 \) Deposition

Alumina (\( \text{Al}_2\text{O}_3 \)) was the first material grown in this study. The precursors used were \( \text{AlCl}_3 \) and \( \text{H}_2\text{O} \). The chemical reaction is shown in equation 3-1. Section 2.3.2 provides a discussion on this reaction.

\[
2\text{AlCl}_3(g) + 3\text{H}_2\text{O}(g) \rightleftharpoons \text{Al}_2\text{O}_3(s) + 6\text{HCl}(g) \quad (3-1)
\]

The water was maintained at room temperature, 20\(^\circ\)C, and the \( \text{AlCl}_3 \) was heated to 105\(^\circ\)C. The pulse sequence (alumina cycle) consisted of (in chronological order):

- 0.2s \( \text{N}_2 \) purge through the \( \text{AlCl}_3 \) line
- 0.2s of \( \text{AlCl}_3 \) and \( \text{N}_2 \) through the \( \text{AlCl}_3 \) line
- 0.2s \( \text{N}_2 \) purge through the \( \text{AlCl}_3 \) line

Figure 3-2. Photograph of the Planar Systems P400 hot-wall flow-type ALD reactor showing the gas manifold side of the reactor.
• 0.2s pause
• 0.2s N₂ purge through the H₂O line
• 0.2s of H₂O and N₂ through the H₂O line
• 0.2s N₂ purge through the H₂O line
• 0.2s pause

for a total alumina cycle time of 1.6 seconds.

The reactor temperature was varied from 200°C to 550°C with the number of alumina cycles fixed at 5000. For each run at a given temperature, the thickness was measured using a Tencor P2 Profilometer and the average growth rate determined by dividing the thickness by the number of cycles. A plot of the growth rate as a function of temperature reveals the so-called ALD window (section 2.2.3.1) [67]. X-Ray photoelectron spectroscopy (XPS) was used to verify the films composition. X-ray diffraction (XRD) was used to determine crystallinity of the film.

3.3.2 Y₂O₃ Deposition

Yttria (Y₂O₃) was also grown in this study. The precursors used were Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III), also known as Y(thd)₃, and O₃ generated from an O₂ source. The chemical reaction is shown in equation 3-2. Section 2.3.3 provides a discussion on this reaction.

\[
2Y(thd)_3(g) + 60O_3(g) \rightleftharpoons Y_2O_3(s) + 57H_2O(g) + 66CO_2(g) \quad (3-2)
\]

The O₃ was delivered at room temperature, 20°C, and the Y(thd)₃ source was heated to 140°C. The pulse sequence (yttria cycle) consisted of (in chronological order):

• 0.2s N₂ purge through the Y(thd)₃ line
• 0.2s of Y(thd)₃ and N₂ through the Y(thd)₃ line
• 0.2s N₂ purge through the Y(thd)₃ line
• 0.2s pause
• 0.2s N₂ purge through the O₂/O₃ line
• 0.2s of O₂/O₃ and N₂ through the O₂/O₃ line
• 0.2s N₂ purge through the O₂/O₃ line
• 0.2s pause
for a total yttria cycle time of 1.6 seconds.

The reactor temperature was varied from 200ºC to 550ºC with the number of yttria cycles fixed at 10000. For each run at a given temperature, the thickness was measured using a Filmetrics F20 optical thin film measurement tool and the growth rate determined by dividing the thickness by the number of cycles. A plot of the growth rate as a function of temperature reveals the ALD window (section 2.2.3.1) [67]. X-ray photoelectron spectroscopy (XPS) was used to verify the films composition and X-ray diffraction (XRD) was used to determine crystallinity.

3.3.3 Ce2O3 Deposition

Ceria (Ce2O3) was another material grown in this study. Ce2O3 doped YAG is a well known phosphor material [16,19,20]. The precursors used were tris(2,4-pentanedionate) cerium(III), also known as cerium(III) acetylacetonate (Ce(acac)3), and O3. The chemical reaction is shown in equation 3-3. Section 2.3.3 provides a discussion on this reaction.

\[
2Ce(thd)_4(g) + 46O_3(g) \rightleftharpoons CeO_2(s) + 76H_2O(g) + 88CO_2(g) \quad (3-3)
\]

The O3 was delivered at room temperature, 20ºC, and the Ce(acac)3 source was heated to 140ºC. The pulse sequence (Ce2O3 cycle) consisted of (in chronological order):

- 0.2s N2 purge through the Ce(acac)3 line
- a 0.2s of Ce(acac)3 and N2 through the Ce(acac)3 line
- 0.2s N2 purge through the Ce(acac)3 line
- 0.2s pause
- 0.2s N2 purge through the O2/O3 line
- 0.2s of O2/O3 and N2 through the O2/O3 line
- 0.2s N2 purge through the O2/O3 line
- 0.2s pause
for a total Ce₂O₃ cycle time of 1.6 seconds.

The reactor temperature was varied from 200°C to 550°C with the number of Ce₂O₃ cycles fixed at 10000. For each run at a given temperature, the thickness was measured using Filmetrics F20 optical thin film measurement tool and the growth rate determined by dividing the thickness by the number of cycles. A plot of the growth rate as a function of temperature reveals the ALD window (section 2.2.3.1) [67]. XPS was used to verify the films composition and XRD was used to determine crystallinity.

### 3.3.4 Pseudo-binary Deposition

To grow a pseudo-binary oxide in ALD, the alumina and the yttria were grown sequentially as a multilayered stack of very thin films. The pulse sequences for each material were introduced sequentially in such a way as to achieve the desired stoichiometry for the bulk film. For example the Al₂O₃ pulse sequence was followed by the Y₂O₃ pulse sequence. The necessary thickness of these materials deposited by ALD to achieve a desired stoichiometry can be determined using methods described in section 2.4.1.

The density and molar mass of yttria are 5.010g/cm³ and 225.81g/mol, respectively. The density and molar mass of alumina are 3.97/cm³ and 101.96g/mol, respectively. The molar density of each is given by dividing density by the molar mass. This results in 2.219x10⁻² mol/cm³ Y₂O₃ and 3.894x10⁻² mol/cm³ Al₂O₃. The volume of each material can be expressed as the area of the substrate (A) times the film thickness: A·t. Let \( t_Y \) be the thickness of Y₂O₃ and \( t_{Al} \) be the thickness of Al₂O₃. Then the molar densities can be expressed as 0.219x10⁻² mol/A·\( t_Y \) Y₂O₃ and 3.894x10⁻² mol/A·\( t_Y \) Al₂O₃. If Yttrium Aluminum Garnet (YAG) with the chemical formula Y₃Al₅O₁₂
is desired, then 3 moles $Y_2O_3$ to 5 moles $Al_2O_3$ in a given volume are required. Setting the stoichiometric ratio equal to the ratio of molar densities results in equation 3-4 (a solved equation 2-19) and solving for $t_Y$ results in $t_Y = 1.04t_{Al}$.

$$\frac{3 \text{ mol } Y_2O_3}{5 \text{ mol } Al_2O_3} = \frac{(2.219 \times 10^{-2} \text{ mol } Y_2O_3) \times (A \times t_Y)}{(3.89 \times 10^{-2} \text{ mol } Al_2O_2) \times (A \times t_{Al})}$$

(3-4)

In other words, the thickness of the yttria layers needs to be 105% of the alumina layer thickness. Repeating this procedure for YAlO$_3$ and Y$_4$Al$_2$O$_9$ by setting the left side of equation 1 to the appropriate stoichiometric ratio and solving for $t_Y/t_{Al}$ results in the desired bi-layer thickness profile for a given phase and is summarized in Table 3-2.

Total film thickness, when in the ALD window [67], is determined by the number of cycles. Knowing the growth rate of each material in thickness per cycle, the required number of cycles of each constituent binary oxide needed to achieve stoichiometry can be determined.

Table 3-2. Necessary thickness ratios for $Y_2O_3$ to $Al_2O_3$ thin film bilayers to achieve stoichiometry for a given phase.

<table>
<thead>
<tr>
<th></th>
<th>$t_Y/t_{Al}$ ratio</th>
<th>Y/Al Stoichiometric ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_4Al_2O_9$</td>
<td>3.54</td>
<td>2/1</td>
</tr>
<tr>
<td>YAlO$_3$</td>
<td>1.77</td>
<td>1/1</td>
</tr>
<tr>
<td>$Y_3Al_5O_{12}$</td>
<td>1.04</td>
<td>3/5</td>
</tr>
</tbody>
</table>

Table 3-3. ALD sequences for Y-Al-O films.

<table>
<thead>
<tr>
<th>YAG Sequence #1</th>
<th>120 Al$_2$O$_3$ + 200 times (103 Y$_2$O$_3$ + 10 Ce$_2$O$_3$ + 103 Y$_2$O$_3$ + 6 Al$_2$O$_3$) + 120 Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG Sequence #2</td>
<td>120 Al$_2$O$_3$ + 175 times (315 Y$_2$O$_3$ + 32 Ce$_2$O$_3$ + 315 Y$_2$O$_3$ + 6 Al$_2$O$_3$) + 120 Al$_2$O$_3$</td>
</tr>
<tr>
<td>YAG Sequence #3</td>
<td>6 Al$_2$O$_3$ + 136 times (445 Y$_2$O$_3$ + 2 Ce$_2$O$_3$ + 445 Y$_2$O$_3$ + 3 Al$_2$O$_3$) + 3 Al$_2$O$_3$</td>
</tr>
<tr>
<td>YAM Sequence #4</td>
<td>3 Al$_2$O$_3$ + 100 times (612 Y$_2$O$_3$ + 122 Ce$_2$O$_3$ + 612 Y$_2$O$_3$ + 3 Al$_2$O$_3$) + 3 Al$_2$O$_3$</td>
</tr>
</tbody>
</table>
Multiple run sequences to achieve YAG and YAM were developed (Table 3-3). The pulse sequences show the number of cycles for each binary film and the order of deposition. The parenthetical sequence fragment was repeated a number of times equal to the number shown to the left of the parenthesis. The sequences will be described in greater detail in chapter 4. The reactor temperature for these experiments has to be such that the ALD windows for both materials overlap. This was determined to be true at 350ºC (chapter 4.5.1).

3.4 Heat Treatment

The films were calcined in a Barnstead/Thermolyne furnace (model F6010) in ambient air to inter-diffuse the Al, O, and Y into the desired polycrystalline YAM or YAG. For this study the calcining was performed at 975 ºC for 12 hours in air. The crystallinity of the as-deposited and calcined films was examined using x-ray diffraction.

Inter-diffusion such that complete homogenization is approached can be determined from Fick’s second law (section 2.4.1) [59]. In this case, the long-time solution for a diffusion of solute out of a film leads to a result of \( L \approx 2 \sqrt{Dt} \), where \( L \) is the thickness of the film, \( D \) is the diffusion coefficient, and \( t \) is time [59].

An element must diffuse at most a distance equal to one half of the film thickness of the constituent films. Concentration gradients prevent an element diffusing from near an interface through the entire film to another interface. In order to facilitate diffusion during heat treatment, the films are grown in multiple pairs such that the stoichiometric ratio (via bi-layer thickness ratio) is preserved while minimizing the thickness of the individual films. For example, rather than grow a 95nm \( \text{Y}_2\text{O}_3 \) film followed by a 100nm
Al₂O₃ film for a 195 nm film, fifty pairs of films are grown such that the thickness of each film is 1.9 nm Y₂O₃ and 2.0 nm Al₂O₃ for a 195 nm film.

### 3.5 Characterization

#### 3.5.1 X-Ray Diffraction (XRD)

The crystal structure of the as-deposited and calcined films were determined using a Philips APD 3720 X-Ray Diffractometer with Cu Kα radiation, λ = 1.54056Å. X-Ray Diffraction is a well known method for determining crystal structure [68]. Samples were scanned from a 2θ of 10° to 70° with a step size of 0.02°. XRD patterns were compared with powder diffraction files from the JCPDS-International Center for Diffraction Data to determine the crystalline phases present.

#### 3.5.2 X-Ray Photoelectron Spectroscopy (XPS)

The surface composition of the ALD films was determined by X-Ray Photoelectron Spectroscopy (XPS) [69]. The XPS measurements were performed on a Perkin-Elmer PHI 5100 XPS/ESCA spectrometer. Mg Kα radiation with an energy of 1253 eV was used to irradiate the sample with a spot size of 4 x 10 mm. Survey scans were taken from 0-1000 eV binding energy with a step size of 0.5 eV.

#### 3.5.3 Secondary Ion Mass Spectroscopy (SIMS)

Secondary Ion Mass Spectroscopy (SIMS) [70] was used to determine the relative concentration of the atomic species as a function of film thickness. SIMS is a characterization technique that is used to analyze the elemental composition of a thin film by sputtering the surface with energetic primary ions and analyzing the ejected secondary ions using a mass spectrometer. The SIMS measurements were performed on a Perkin-Elmer/Physical Electronics 6600 Quadrapole Dynamic SIMS system at 6
keV and 40-70 nA with a raster size of 250 \( \mu \text{m}^2 \) with electronic gating and Cs\(^+\) as the primary ion.

3.5.4 Thickness Measurements

The thickness of the Al\(_2\)O\(_3\) films was determined by masking a separate substrate with a permanent marker. Post-growth, the carbon residue of the mask is removed using methanol and gentle scrubbing. The thickness of the film is then measured using a Tencor P2 Profilometer. Multiple step heights were measured and the average of values was used to determine the thickness. For all other films, the ozone precursor prohibited the use of a permanent marker on a separate substrate. Instead, film thicknesses were measured using a Filmetrics F20 optical thin film measurement tool. This tool requires a materials library containing the indices of refraction for the material for a range of wavelengths. For the mixed, multilayer films of Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\), both the targeted material (YAM or YAG) as well as a double layered Al\(_2\)O\(_3\) Y\(_2\)O\(_3\) were used as models. To verify the Filmetrics results, the thickness of some ALD films was determined by using Secondary Ion Mass Spectroscopy depth profiling to locate the film-substrate interface and measuring the sputtered crater depth using the Tencor profilometer.

3.5.5 Scanning Electron Microscopy (SEM)

Surface morphology of films was investigated using a Phillips XL-40 field emission source scanning electron microscope (SEM) [71]. The entire chamber was vented to load or unload samples as this particular SEM does not possess a load lock. The chamber was evacuated using a turbomolecular high vacuum pump backed by a mechanical vacuum pump. An accelerating voltage of 30 kV was used and the probe
current set to a spot size of 3. The beam was stigmated and focused using a gold-on-
carbon standard sample.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

The results for the ALD growth of Al₂O₃, Y₂O₃, Ce₂O₃, and the pseudo-binary Al₂O₃-Y₂O₃ doped with Ce₂O₃ thin films are now summarized. The precursors used, the growth parameters, and characterizations of each material are discussed in Sections 4.2 to 4.5. In Section 4.5, the intermixing growth parameters and their relationship with the properties of the resultant films are also discussed.

4.2 Al₂O₃ Deposition

The first material studied in this work is Al₂O₃. First, the analysis of the AlCl₃ precursor is presented in Section 4.2.1. Next, data for the growth parameters are shown in Section 4.2.2 with emphasis on the ALD temperature window. The films are then characterized and the results are discussed in Section 4.2.3. The temperature window for ALD growth is determined and the films are characterized for crystallinity and surface morphology.

4.2.1 Al₂O₃ Precursors

As discussed in sections 2.2.2, the precursor chemistry plays an important role in surface-limited growth. The AlCl₃ used for Al₂O₃ growth was purchased from Fisher Scientific, and had a purity of 99%. The precursor H₂O was de-ionized water available on site with a conductivity of 10 MΩ cm and kept at ~20°C.

The AlCl₃ was characterized by thermogravimetric analysis (TGA) to determine the weight loss (volatility) from 20°C to 600°C to determine the appropriate deposition source temperature for the solid precursor. A small nitrogen flow was present during the analysis with a heating rate of 10°C/min, and all materials volatized completely. The
AlCl₃ precursor showed an onset of sublimation at 105°C, close to the reported source temperature of 110°C [53] (section 2.3.2), therefore 105°C was used for the AlCl₃ source temperature for Al₂O₃ growth. The source holder for AlCl₃ can hold approximately 30 grams of AlCl₃.

4.2.2 Al₂O₃ Growth Parameters

The temperature dependence of the growth rate of Al₂O₃ was studied to determine the ALD window (Section 2.2.3.1). In this work the number of cycles was fixed at 5000. The AlCl₃ source temperature was maintained at 105°C. The substrate temperature was varied from 295°C to 515°C at 25°C intervals. Growth temperatures lower than 295°C resulted in films too thin (< 20 nm) to accurately resolve thickness using the Tencor Profilometer, indicating a low growth rate. As discussed in section 2.2.3.1, a decreasing growth rate at decreasing temperatures is due to insufficient activation energy being provided for precursor dissociation and subsequent chemisorption. Growth temperatures higher than 515°C resulted in very thick films. This high growth rate is explained by decomposition of the AlCl₃ precursor as previously discussed in section 2.2.3.1.

All deposition was conducted at a pressure of ~6 torr. The films were deposited onto cleaned (section 3.2) glass substrates. The film thickness was measured for each temperature step and these values were divided by the 5000 cycles to determine a growth rate expressed as a thickness per cycle. As can be seen from figure 4-1, a substrate temperature window for ALD growth exists from about 365°C to 465°C with a growth rate of ~1Å/cycle. At this growth rate, films up to 2 μm can be grown in ~12 hours.
Figure 4-1. Growth rate of Al$_2$O$_3$ versus substrate temperature.

4.2.3 Al$_2$O$_3$ Characterization

X-Ray diffraction spectra for the as-deposited Al$_2$O$_3$ films show a very broad ‘peak’ at ~17 degrees and no sharp peaks indicating that the Al$_2$O$_3$ film was amorphous. Figure 4-2 shows the XRD spectrum for a 500 nm thick film deposited at 350°C on a SiO$_2$/Si substrate, and is typical for as-deposited films within the temperature window. The increased intensity in figure 4-2 at a 2-theta of 70 degrees is due to the Si substrates (002) diffraction peak. The SEM micrograph in figure 4-3 of a 1.0 µm thick (step profile) Al$_2$O$_3$ film deposited at 350°C shows a qualitatively rough surface morphology suggesting island growth of the film (section 2.2.3.3). Figure 4-4 shows an SEM micrograph of a fractured cross-section of that same film.

The rough morphology of the film can be attributed to self-etching (section 2.3.2). When self-etching occurs, the pits formed by self-etching as well as the CVD formed Al$_2$O$_3$ particulate result in a rough surface morphology. If we assume that self-etching
creates very shallow pits in a single AlCl₃ pulse, perhaps only two Angstroms in depth (~ the Al-O bond length), 5000 cycles would generate a pit about 1µm in depth. This assumes subsequent depositions do not fill the pit and that etching always occurs in the pit. Without these assumptions the effects would be less pronounced. This assumption does indicate that self-etching can have a significant impact on surface morphology. In addition, Al₂O₃ particulate would be falling on the surface in a random fashion rather than layer-by-layer, further disrupting the surface morphology.

Figure 4-2. X-Ray diffraction spectrum from an as-deposited 1.0 µm thick Al₂O₃ film deposited at 350°C.
Figure 4-3. SEM micrograph of an as-deposited Al₂O₃ film deposited at 350°C.

Figure 4-4. SEM micrograph of a fractured cross-section as-deposited Al₂O₃ film deposited at 350°C.
4.3 $Y_2O_3$ Deposition

The TGA analysis of the Y(thd)$_3$ precursor for $Y_2O_3$ is presented in Section 4.3.1, while the growth parameters are shown in section 4.3.2 with emphasis on the low $Y_2O_3$ growth rate. The film characteristics are discussed in Section 4.3.3. An ideal growth temperature was determined and the films were characterized for crystallinity and surface morphology.

4.3.1 $Y_2O_3$ Precursors

The Y(thd)$_3$ precursor used for $Y_2O_3$ growth was purchased from Fisher Scientific and had a purity of 98%. It was reacted with ozone generated in-house from 99.994% pure oxygen. The ozone was delivered in an O$_2$/O$_3$ mixture with approximately 1% O$_3$ (section 3.1).

The Y(thd)$_3$ precursor was characterized by thermogravimetric analysis (TGA) to determine volatility from 20°C to 600°C. The TGA data were used to determine the appropriate source temperature of the solid precursors. A small nitrogen flow (100 sccm) was used with a heating rate of 10°C/min. The Y(thd)$_3$ precursor shows a differential thermogravimetric (ΔTG) mass loss of 32.0 mg/min. at 140°C (Figure 4-5). The large peak at 64°C is due to desorption of methanol used to clean the sample holder. The cycle time for a yttria cycle is 1.6s (section 3.3.2) therefore 0.8 mg of Y(thd)$_3$ is consumed for every yttria cycle at this source temperature.
The following calculation was used to determine if a source temperature for Y(thd)$_3$ of 140°C was sufficient for Y$_2$O$_3$ deposition (equation 4-2). The reaction chamber has a total surface area of about 0.5 m$^2$ and a Y$_2$O$_3$ thickness of ~350 nm was desired, yielding a total Y$_2$O$_3$ volume of 175x10$^{-9}$ m$^3$. The density of Y$_2$O$_3$ is 5.01x10$^6$ g/m$^3$. The molar mass of Y$_2$O$_3$ and Y(thd)$_3$ are 225.81 g/mol and 638.72 g/mol, respectively. Therefore the amount of Y(thd)$_3$ needed for a 350 nm thick film is estimated to be 5 gms, assuming the growth rate was the same and constant for all parts of the substrate and reaction chamber and all the precursor is absorbed.

\[
(175 \times 10^{-9} \text{ m}^3) \left( \frac{5.01 \times 10^6 \text{ g} \ Y_2 \text{O}_3}{\text{m}^3} \right) \left( \frac{1 \text{ mol} \ Y_2 \text{O}_3}{225.81 \text{ g} \ Y_2 \text{O}_3} \right) \left( \frac{2 \text{ mol} \ Y}{1 \text{ mol} \ Y_2 \text{O}_3} \right) \left( \frac{1 \text{ mol} \ Y \text{(thd)}_3}{1 \text{ mol} \ Y} \right) \left( \frac{638.72 \text{ g} \ Y \text{(thd)}_3}{1 \text{ mol} \ Y \text{(thd)}_3} \right) = 5 \text{ g} \ Y \text{(thd)}_3 \tag{4-1}
\]
4.3.2 Y$_2$O$_3$ Growth Parameters

The temperature dependence of the Y$_2$O$_3$ growth rate was determined using 10000 cycles at a source temperature of 140°C. The substrate deposition temperature was varied from 200°C to 500°C at 25°C intervals. All depositions were conducted at a pressure of ~6 torr onto SiO$_2$/Si substrates with a 100 nm SiO$_2$ layer. The film thickness was measured and divided by the 10000 cycles to determine a growth rate expressed as thickness per cycle. Due to an extremely low growth rate for Y$_2$O$_3$, accurately measuring the thickness of the resultant films was problematic using the Filmetrics optical thin film measurement. The thickest Y$_2$O$_3$ film achieved was 30 nm at 350°C corresponding to a growth rate of only 3.0 pm/cycle. Without accurate thickness measurements at varying temperatures, an ALD temperature window could not be observed.

As discussed in the literature review (section 2.3.3), reported growth rates for Y$_2$O$_3$ at this temperature should be 0.23 Å/cycle, a factor of ten greater than the 3.0 pm/cycle reported here. The difference may be due to the use of a different ALD reactor, i.e. a ‘tooling’ factor. The reactor used in this study relies on careful placement of the solid source configuration and the balance of nitrogen flows around and through the solid-source crucible. The delivery of the Y(thd)$_3$ vapor is from an tube-shaped glass crucible (the Y(thd)$_3$ source in figure 3-1) with nitrogen used as a carrier gas. Reasonable assumptions and estimates were made as to the solid-source crucible design and placement. These are two important tooling factors that the flux of Y(thd)$_3$ vapor into the reaction chamber depend upon. A low flux can result in low growth rates if it is insufficient for monolayer saturation (section 2.2.3.1). While the temperature used for the Y(thd)$_3$ source were in agreement with both literature (section 2.3.3) and TGA data
(section 4.3.1 and figure 4-5), the crucible design influences the position of \( Y(\text{thd})_3 \) in the heating zones. If the \( Y(\text{thd})_3 \) was placed in lower temperature zones due to the crucible configuration, a low vapor pressure could result in a low flux as well. At higher temperatures the \( Y(\text{thd})_3 \) source would have a higher vapor pressure resulting in a high flux. There would be an excess flux of \( Y(\text{thd})_3 \) after surface saturation occurred and this excess flux would be removed from the reaction chamber. The rate of \( Y(\text{thd})_3 \) sublimation could result in the consumption of all the \( Y(\text{thd})_3 \) precursor before the entire ALD sequence is complete. All attempts were made to design the crucible such that it was placed in the correct zone. Due to the cost of the purchased \( Y(\text{thd})_3 \) at the time of this work, once \( Y_2O_3 \) growth was demonstrated further development and improvement of growth parameters ceased and is a topic for future work (section 5.2)

4.3.3 \( Y_2O_3 \) Characterization

The XRD spectrum for as-deposited \( Y_2O_3 \) films show several diffraction peaks from a polycrystalline film that matched the diffraction peaks reported on the Joint Committee on Diffraction Standards (JCPDS) card #43-1036 for the cubic phase of \( Y_2O_3 \). Atypical XRD spectrum is shown in figure 4-6 for a film deposited at 350°C. The peaks in figure 4-6 at 2-thetas of 34°, 62° and 69° are from the Si substrate. Using the Scherrer formula [49] an average crystallite size of 13.3 nm is calculated. This film had a smooth, uniform surface morphology indicating a layer-by-layer growth mode (figure 4-7) [45].
Figure 4-6. XRD spectrum from a 25 nm thick $Y_2O_3$ film as-deposited at 350°C. The lines show peaks from JCPDS Card #43-1036 for cubic $Y_2O_3$.

Figure 4-7. SEM micrograph of an as-deposited $Y_2O_3$ film deposited at 350°C.
4.4 Ce$_2$O$_3$ Deposition

Ceria (Ce$_2$O$_3$) was the third binary oxide studied. First, the analysis of the Ce(acac)$_3$ precursor is presented in Section 4.4.1. Next, the growth parameters are shown in Section 4.4.2. The films are then characterized and the results are discussed in Section 4.4.3. The films were characterized for crystallinity and surface morphology.

4.4.1 Ce$_2$O$_3$ Precursors

The cerium (III) acetylacetonate hydrate [Ce(acac)$_3$] used for Ce$_2$O$_3$ growth was commercially available from Fisher Scientific with a purity of 95%. It was reacted with ozone generated in-house from 99.994% oxygen, and delivered in an O$_2$/O$_3$ mixture with $\sim$1% O$_3$ (section 3.1). The Ce(acac)$_3$ was characterized by thermogravimetric analysis (TGA) from 20$^\circ$C to 400$^\circ$C to determine volatility, and all materials volatized completely. Figure 4-8 shows the $\Delta$TG plot for Ce(acac)$_3$ as a function of temperature, and a number of peaks are evident. From low temperature to high temperature, the first and second peaks at 64$^\circ$C and 78$^\circ$C result from volatilization of methanol (boiling point 64.6$^\circ$C [50] and ethanol (boiling point 78.3$^\circ$C [50] used to clean the sample holder prior to analysis. The third peak at 100$^\circ$C is attributed to water, consistent with the fact that the Ce(acac)$_3$ is a hydrated chemical and the boiling point of water is 100$^\circ$C. The fourth and sharpest peak at 134$^\circ$C is attributed to volatilization of Ce(acac)$_3$ and is in agreement with the literature reported value of 140$^\circ$C [58]. The sharp peaks at higher temperatures are attributed to thermal cracking of the (acac) ligands to produce organic fragments. The source temperature for the Ce(acac)$_3$ was chosen as 140$^\circ$C.
4.4.2 Ce₂O₃ Growth Parameters

The growth of Ce₂O₃ was investigated using 10000 cycles and a source temperature of 140°C. The substrate temperature was varied from 200°C to 500°C at 25°C intervals and at a pressure ~6 torr. The growth rate of Ce₂O₃ was so low that film thickness could not be measured at any substrate temperature (thickness < 20 nm).

4.4.3 Ce₂O₃ Characterization

Despite the lack of a film thickness measurable by the profilometer, X-ray photoelectron spectroscopy (XPS) spectra (figure 4-9) show that Ce₂O₃ is present on the SiO₂/Si substrate. As to the oxidation state (Ce³⁺ or Ce⁴⁺), the XPS spectra in figure 4-9 suggests Ce³⁺ is the dominant oxidation state. The Ce³⁺ 3d₃/₂ peak (904.5 eV) is larger than the Ce⁴⁺ 3d₃/₂ peak (917.0 eV) indicating a greater concentration of the Ce³⁺ valence state. Both valence states have a charge-transfer peak that appears as shoulders at lower binding energies in figure 4-10. It has been shown by Rack and
Holloway [73] that there is an increase in the Ce$^{3+}$ charge-transfer peak compared with the Ce$^{3+}$ ground state peak in XPS analysis as oxygen concentration increases. The large charge-transfer peaks for both Ce$^{3+}$ 3d$_{5/2}$ and 3d$_{3/2}$ compared with their corresponding ground state peak is another indicator that Ce$^{3+}$ is the abundant valence state. The 3d$_{3/2}$ for Ce$^{4+}$ is buried within the Ce$^{3+}$ 3d$_{5/2}$ peak. Typically, diamagnetic Ce$^{4+}$ show less shake-up and satellite peaks than does paramagnetic Ce$^{3+}$ [69]. The presence of silicon peaks in the XPS spectra (figure 4-9) suggests either that the Ce$_2$O$_3$ film is very thin and/or the uniformity of the Ce$_2$O$_3$ coverage on the SiO$_2$/Si substrate is non-uniform. The sodium (Na) Auger peaks are likely due to contamination (fingerprints) on the sample.

Figure 4-9. XPS spectrum showing that Ce and O were detected on SiO$_2$/Si substrate after 9000 cycles of growth at 350°C.
Figure 4-10. High resolution XPS spectrum showing the Ce\(^{3+}\) 3d peaks from figure 4-9: the intense charge-transfer peaks, and the small Ce\(^{4+}\) 3d\(_{3/2}\) peak. The Ce\(^{4+}\) 3d\(_{5/2}\) peak is buried beneath the Ce\(^{3+}\) 3d\(_{3/2}\) peak.

No XRD peaks were detected after the 10000 cycles of Ce\(_2\)O\(_3\) growth. However, SEM micrographs in figure 4-11 show that island growth dominated as evidenced by the island features (left) when compared to a feature-less bare Si/SiO\(_2\) substrate (right).

Since these films were to be used as a dopant rather than a “bulk” material, thick films were deemed unnecessary for this work. As will be seen (section 4.5), the inclusion of these films into the mixed Al\(_2\)O\(_3\)-Y\(_2\)O\(_3\) phases resulted in very rough films.
4.5 Al₂O₃-Y₂O₃ Pseudo-Binary Deposition

Alternating deposition of the components of the Al₂O₃-Y₂O₃ pseudo-binary system followed by heating can result in a ternary phase. By alternating the deposition cycles of Y₂O₃ and Al₂O₃, a stoichiometric mixture can be produced for the two phases discussed in section 2.4: monoclinic Y₄Al₂O₉ (YAM) and garnet Y₃Al₅O₁₂ (YAG). During calcining, the layered films inter-diffuse and crystallize into the appropriate phase. The different phases can be formed by changing the ratio of the number of cycles to grow Al₂O₃ to the number of cycles to grow Y₂O₃. The growth parameters used, including the number of cycles for each of the component phases, are reported in Section 4.5.1. The results and discussion of characterization of the as-deposited and calcined films are reported in Section 4.5.2.

4.5.1 Al₂O₃-Y₂O₃ Pseudo-Binary System Growth Parameters

The optimal growth temperature of Y₂O₃ was 350°C (section 4.3.3) and nearly overlaps the ALD temperature window for Al₂O₃ (365°C to 465°C-see section 4.2.2). Since Al₂O₃ exhibited high deposition rates, 350°C was chosen for the growth
temperature for the mixed deposition so as to optimize the very slow $Y_2O_3$ growth. This
temperature is slightly outside the $Al_2O_3$ ALD temperature window (figure 4-2). At this
temperature the $Al_2O_3$ growth rate begins to decline due to insufficient activation of the
precursors for adsorption and/or growth (section 2.2.3.1). With the $Al_2O_3$ growth rate
approximately 100 times greater than the $Y_2O_3$ at this temperature (sections 4.2.2 and
4.3.2), very few $Al_2O_3$ cycles are needed when combined with many $Y_2O_3$ cycles to
achieve stoichiometry. The pressure was ~6 torr, and all deposits were on cleaned
$SiO_2/Si$ substrates. After deposition, samples were calcined at 975°C for 12 hours to aid
in crystallization of the thin films. These ALD process conditions were used for both
$YAG$ and $YAM$ film growth

4.5.2 $Y_3Al_5O_{12}$ (YAG) Deposition

To achieve stoichiometric $Y_3Al_5O_{12}$ (YAG) phase, the thickness of the $Y_2O_3$ needs
to be 105% of the $Al_2O_3$ layer (section 2.4.1) or $t_Y = 1.04t_{Al}$. A single “thick” film of $Al_2O_3$
followed by a single “thick” film of $Y_2O_3$ followed by high temperature calcining for a long
time could result in the YAG phase. However, the inter-diffusion distances needed are
much too large for the given calcine temperature (975°C) and time (12 hours) and would
probably result in an inhomogeneous sample. As discussed in section 2.4.1, ALD is
capable of producing an intimate mixture that is near complete homogeneity for
stoichiometric solid solution of that mixture. This is achieved by creating a nanolaminate
stack of the constituent binary materials. In this case, alternating layers of nanoscale
$Al_2O_3$ and $Y_2O_3$ are made into a nanolaminate stack forming an intimate mixture. A pair
of films containing both $Al_2O_3$ and $Y_2O_3$ is called a bilayer and is a diffusion couple
during post-growth annealing. As a first approximation for reasonable diffusion
distances for an intimate mixture and therefore bilayer thickness, the lattice parameter
of the desired material was considered. For YAG, the lattice parameter is \( \sim 1.2 \) nm; therefore a reasonable thickness of the bilayer (\( \text{Al}_2\text{O}_3\)-\( \text{Y}_2\text{O}_3 \) couple) is 1.2 nm. Within this distance both \( \text{Al}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) need to be present or, \( t_Y + t_{Al} = 1.2 \) nm. In addition, \( t_Y \) must equal \( 1.04 t_{Al} \) in order to maintain stoichiometry, as discussed above. The calculated layer thicknesses for stoichiometry and intimate mixing are very small at \( t_Y = 0.62 \) nm and \( t_{Al} = 0.59 \) nm. These thicknesses maintain the 1.04:1 thickness ratio of \( Y:Al \) and sum up to 1.2 nm, providing both the necessary stoichiometric ratio and intimate mixing. The growth rate for \( \text{Al}_2\text{O}_3 \) was determined to be 1.0 Å/cycle at 350°C (section 4.2.2) and the growth rate for \( \text{Y}_2\text{O}_3 \) was determined to be 3.0 pm/cycle (section 4.3.2). Therefore, to achieve the above thicknesses of \( t_{Al} \) and \( t_Y \), 6 \( \text{Al}_2\text{O}_3 \) cycles and 207 \( \text{Y}_2\text{O}_3 \) cycles are needed and together maintain the proper mixture of \( \text{Al}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) for the stoichiometry of YAG. This pair of cycles can be repeated many times in order to create thicker films of YAG.

To dope with \( \text{Ce}_2\text{O}_3 \), the \( \text{Y}_2\text{O}_3 \) cycles were split into two equal parts with the \( \text{Ce}_2\text{O}_3 \) cycles between them. The cerium atom substitutes for yttrium in \( \text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce} \). Cerium is a large rare earth element with an ionic radius of 114 pm [59]. Using Pauling’s rules [59,72] for coordination with the oxygen anion shows that cerium has a coordination number of 8, and therefore sits in the dodecahedral site in the \( \text{Y}_3\text{Al}_5\text{O}_{12} \) lattice which is the yttrium site. Therefore, depositing \( \text{Ce}_2\text{O}_3 \) within the \( \text{Y}_2\text{O}_3 \) allows for \( \text{Ce}_2\text{O}_3 \) to readily occupy the dodecahedral sites. The number of \( \text{Ce}_2\text{O}_3 \) cycles was set at 5% of the \( \text{Y}_2\text{O}_3 \) cycles, so 10 \( \text{Ce}_2\text{O}_3 \) cycles were inserted between two sets of 103 \( \text{Y}_2\text{O}_3 \) cycles.

### 4.5.2.1 \( \text{Y}_3\text{Al}_5\text{O}_{12} \) sequence #1

With the theoretical justification from section 4.5.2 in mind, a complete ALD sequence for the deposition of \( \text{Y}_3\text{Al}_5\text{O}_{12} \) was determined. The total cycle sequence was:
120 Al$_2$O$_3$ cycles + 200 times (103 Y$_2$O$_3$ cycles + 10 Ce$_2$O$_3$ cycles + 103 Y$_2$O$_3$ cycles +
6 Al$_2$O$_3$ cycles) + 120 Al$_2$O$_3$ (YAG sequence #1). Sequence #1 includes 2 cladding
layers of Al$_2$O$_3$. Since YAG is the aluminum rich phase, the boundaries of the film were
made Al$_2$O$_3$ to provide a slight excess. Ideal atomic concentrations for Y$_3$Al$_5$O$_{12}$ are 15%
yttrium, 25% aluminum, and 60% oxygen.

Given the above growth rates for Al$_2$O$_3$ (section 4.2.2) and Y$_2$O$_3$ (section 4.3.2), a
film thickness of 270 nm was expected. The films deposited with YAG sequence #1
were measured to be 330 nm thick, and XRD data show they are amorphous both as-
deposited and after heat-treatment at 975°C for 12 hrs in air.

Quantification of XPS data in figure 4-12 show that growth sequence #1 produced
films with Y$_2$O$_3$ concentrations well below stoichiometry indicating a faster than
expected growth rate for Al$_2$O$_3$ and/or a slower growth rate for Y$_2$O$_3$ when compared to
their respective binary phase growth. The XPS data show 37.7% (atomic percent)
aluminum, 2.9% yttrium and 59.4% oxygen. Using these atomic percents and the
measured film thickness, the relative growth of Al$_2$O$_3$ and Y$_2$O$_3$ in this film can be
determined using the equations from section 2.4.1. The accuracy of the atomic percents
in XPS can be as high as 90% for high intensity peaks and as low as 50% for low
intensity peaks [69,74]. The oxygen concentration at 59.4% is close to the ideal of 60%.
The yttrium concentration, however, could be 1.5% to 6% due to the inaccuracy of XPS
at low peak intensities. As a first approximation, the XPS values indicate too much
aluminum and too little yttrium. New growth rates of 2.0 Å/cycle for Al$_2$O$_3$ and 1.0
pm/cycle for Y$_2$O$_3$ can be calculated and are consistent with the measured thickness
(330 nm) and the measured atomic percents of yttrium and aluminum in XPS (figure 4-
12). The XPS plot shows no cerium peaks. This is expected as very little cerium was added and XPS only detects those atoms within ~1 nm from the surface. It is possible that the excess Al$_2$O$_3$ on the surface did not completely diffuse upon calcining resulting in XPS results showing a higher than stoichiometric amount of aluminum. However, the phase diagram (section 2.4.1) shows that a mixed phase of Y$_3$Al$_5$O$_{12}$ and Al$_2$O$_3$ should occur when there is an excess of Al$_2$O$_3$. The films likely remained amorphous due to the excess Al$_2$O$_3$ and insufficient Y$_2$O$_3$ throughout the deposited film for transformation into Y$_3$Al$_5$O$_{12}$ rather than the film terminating in Al$_2$O$_3$. The increase in Al$_2$O$_3$ growth rate is attributed to an increase in the wetting of the AlCl$_3$ with the Y$_2$O$_3$ surface (section 2.2.3.3). A monolayer of Al$_2$O$_3$ formed on Y$_2$O$_3$ approaches a full monolayer in fewer cycles than a monolayer of Al$_2$O$_3$ formed on SiO$_2$. Therefore, for a given number of cycles, the growth rate will be larger.

![Figure 4-12. XPS of Y$_2$O$_3$-Al$_2$O$_3$ film grown using YAG sequence #1 (section 4.5.1.1).](image)

Min: 179 Max: 207363

- Al 2p: 37.7%
- Al 2s: 37.7%
- Y 3d: 2.9%
- Y 3p$_3$: 2.9%
- Y 3p$_1$: 2.9%
- Y 3s: 2.9%
- O 1s: 59.4%
- C 1s: 2.9%
- F 1s: 2.9%

O KVV

C KVV

F 1s

N(E)

Binding Energy (eV)
Figure 4-13 shows the SEM images of the film deposited using YAG sequence #1. The films are very rough as-deposited, in what appears to be ‘peeling’ sheets of material (the string shaped bright areas are edges of the peeled sheets). Upon calcining at 975°C, the materials coalesce into what appear to be rods.

4.5.2.2 Y$_3$Al$_5$O$_{12}$ sequence #2

These new growth rates of 2.0 Å/cycle for Al$_2$O$_3$ and 1.0 pm/cycle for Y$_2$O$_3$ were used for mixed film depositions. To improve the stoichiometry and produce a YAG film, the number of cycles of Y$_2$O$_3$ was increased in YAG sequence #2: 120 Al$_2$O$_3$ cycles + 175 times (315 Y$_2$O$_3$ cycles + 32 Ce$_2$O$_3$ cycles + 315 Y$_2$O$_3$ + 6 Al$_2$O$_3$) + 120 Al$_2$O$_3$ cycles. This sequence was expected to produce a film thickness of 375 nm. The growth cycles are such that Al$_2$O$_3$ thickness should be twice that of Y$_2$O$_3$. In addition, calculations show that the resulting mixture will contain 31.9% Al and 7.7% Y. Since YAG is an aluminum-rich phase (section 2.4.4), it should co-exist with Al$_2$O$_3$ if there is more than 25% Al (62.5 mol%, section 2.4.1). At twice the thickness of Y$_2$O$_3$, YAG plus
Al₂O₃ should be the case since the necessary condition for stoichiometry is roughly equally thick films (section 3.3.4, table 3-2).

The as-deposited films grown with YAG sequence #2 were ∼350 nm thick in reasonable agreement with the predicted thickness of 375 nm (section 4.5.1). The XRD spectra from as-deposited films using YAG sequence #2 did not contain any peaks from Y₂O₃ or YAG, and had a broad peak from an amorphous phase at a 2-theta of ∼17° and sharp diffraction peaks at 32°, 61°, and ∼70° from the Si substrate (figure 4-14).

However, after calcining at 975°C for 12 hrs in air, the XRD pattern consists of peaks from a YAG polycrystalline film (figure 4-15). The (420) peak is dominate with a smaller (400) peak showing. The peaks from the calcined film matched well with those reported on JCPDS card #33-0040. Using Scherrer's formula [71], an average crystallite size of 25 nm was calculated from XRD peak broadening.

Figure 4-14. XRD spectrum from an as-deposited film grown with YAG sequence #2 (see section 4.5.1).
Figure 4-15. XRD spectrum from a film grown with YAG sequence #2 and annealed at 975°C for 12 hrs in air.

Using equation 2-21, the coefficient for inter-diffusion of the Y₂O₃ and Al₂O₃ thin layers can be estimated. Crystalline YAG was obtained after a 12 hour (~43200 sec) calcine. The distance of inter-diffusion between Al₂O₃ and Y₂O₃ is calculated by multiplying the growth rate for Al₂O₃ by the number of cycles in a single cycle. In sequence #2 this is \( \frac{2.0 \text{Å}}{\text{cycle}} \times (6 \text{ cycles}) = 1.2 \text{ nm} \). Therefore, the diffusion coefficient for Y₂O₃ inter-diffusion with Al₂O₃ is \( 2.1 \times 10^{-24} \text{ m}^2/\text{s} \).

The diffusion coefficient for O in Al₂O₃ is \( \sim 10^{-14} \text{ cm}^2/\text{sec} \) at 1400°C [59]. At 975°C, the calcine temperature of these films, the diffusion coefficient for O in Al₂O₃ can be projected to be as low as \( 10^{-23} \text{ m}^2/\text{sec} \) [59]. The diffusion coefficient at 975°C for O in Y₂O₃ is \( \sim 5 \times 10^{-13} \text{ m}^2/\text{sec} \) [59]. Diffusion coefficients at 975°C for Y in Y₂O₃ and Al in Al₂O₃ are \( 10^{-18} \text{ m}^2/\text{sec} \) and \( 10^{-22} \text{ m}^2/\text{sec} \), respectively [59]. Complete homogenization is limited by the element with the slowest diffusion rate to the interface between Al₂O₃ and
Y$_2$O$_3$ where YAM, YAP, or YAG is then formed. This suggests that the diffusion mechanism is rate-limited by oxygen diffusion through Al$_2$O$_3$.

The XPS data from the as-deposited YAG sequence #2 films continue to show a low amount of yttrium (Figure 4-16). The Y concentration was higher at 7.5 atomic % from YAG sequence #2 versus 2.9% from YAG sequence #1 and is remarkably close to the expected value of 7.7 atomic % (section 4.5.1). There is also a reasonable match of the expected Al concentration at 31.9 atomic % Al with the XPS measured 29.4 atomic %. Note that the Al$_2$O$_3$ cap is still present in YAG sequence #2. The XPS spectra also show peaks from carbon and chlorine, even after a 10 min sputter with 4 keV Ar$^+$ to remove advantageous carbon from the surface. The carbon and chlorine appears to be incorporated throughout the film and is likely due to incorporation of ligands from the Y(thd)$_3$ and chlorine from the AlCl$_3$ precursors. In addition, there is no detectable XPS peak from Ce in this film (figures 4-16). XPS only detects elements within ~1 nm of the surface of a material with atomic concentrations > 1%, so a cerium signal is unlikely at dopant concentrations. In addition, there was a 120 cycle capping layer of Al$_2$O$_3$ with an expected thickness of 24 nm, therefore detection of yttrium by XPS was unexpected. However, a non-uniform surface coverage of Al$_2$O$_3$ on Y$_2$O$_3$ would allow detection of yttrium and the XPS data not being equal to the expected stoichiometry for YAG.

Indeed, the SEM images discussed below suggest that this hypothesis may be true.

The surface of this YAG film is very rough as seen by the SEM micrographs in figure 4-17. The figures 4-17a) and 4-17b) show the as-deposited surface (the scale bar shows 1 µm) and the calcined surface, respectively. The surface is rough both before
and after calcining at 975°C. As will be discussed below, it is believed that Ce₂O₃ incorporation into these films leads to the very rough surface morphologies.

![XPS spectrum from an as-deposited film grown with YAG sequence #2 after a 10 minute sputter with 4 keV Ar⁺.](image)

**Figure 4-16.** XPS spectrum from an as-deposited film grown with YAG sequence #2 after a 10 minute sputter with 4 keV Ar⁺.

![SEM images of YAG films via sequence #2. a.) as-deposited and b.) calcined at 975°C for 12 hours.](image)

**Figure 4-17.** SEM images of YAG films via sequence #2. a.) as-deposited and b.) calcined at 975°C for 12 hours.

Other depositions, using sequence #2, were made except that the number of Ce₂O₃ cycles was adjusted in an attempt to achieve dopant levels of cerium in the YAG
film that would result in photoluminescence (PL). It was found that the ratio of yttria cycles to Ce$_2$O$_3$ cycles (Y:Ce) influenced the roughness of the films. Figure 4-18 shows SEM images of 3 different films with increasing Y:Ce ratios. Panels a. and b. are from YAM sequence #4 (see below) and have a Y:Ce ratio of 10:1. Panels c. and d. are from YAG sequence #2 and have a Y:Ce of 20:1 and are the same as in those in figure 4-17. Panels e. and f. are from YAG sequence #3 (see below) and have a Y:Ce of 445:1. From the sequence of SEM images in figure 4-18, it is apparent that the number of Ce$_2$O$_3$ cycles plays a critical role in surface morphology. The Volmer-Weber growth mode (island growth) [45] occurs when the films’ surface energy is greater than the substrate (section 2.2.3.3). It is postulated that in this case the adsorbed Ce(acac)$_3$ on Y$_2$O$_3$ is such that the Ce(acac)$_3$ surface energy is greater than the underlying Y$_2$O$_3$ surface energy leading to island growth. Or perhaps the adsorbed Y(thd)$_3$ surface energy is greater than the underlying Ce$_2$O$_3$. In addition, crystalline Ce$_2$O$_3$ is hexagonal compared to the cubic structure of Y$_2$O$_3$. A lattice mismatch between the Ce$_2$O$_3$ and Y$_2$O$_3$ films could lead to island growth as well.

Figure 4-19 shows a SEM cross-section of a calcined YAG sequence #2 film. The cross-section shows that the film has a sharp interface with the SiO$_2$ layer of the Si substrate. The film shows either some porosity or more likely, inhomogeneity from the film mixture of Al$_2$O$_3$ and Y$_3$Al$_5$O$_{12}$. 
Figure 4-18. SEM images of as-deposited (top-a, c, e) and calcined (bottom-b, d, f) at 975°C YAG films with increasing Y:Ce ratios of (a. & b.) 10:1, (c. & d.) 20:1, and (e. & f.) 445:1.

Figure 4-19. Cross-section SEM image of calcined YAG sequence #2 film.
4.5.2.3 \textbf{Y}$_3$\textbf{A}l$_5$O$_{12}$ sequence #3

The XRD spectrum from the smooth, calcined film shown in figure 4-18f is shown in figure 4-19, and a strong (400) peak from polycrystalline YAG is observed (YAG Sequence #3). In addition a broad, diffuse peak at 18° could be a nascent (211) peak. The sharp peak at 33° is likely from silicon and not from the YAG (420) due to its very narrow shape. This film was grown with the following growth sequence: 6 Al$_2$O$_3$ cycles + 136 times (445 Y$_2$O$_3$ cycles + 2 Ce$_2$O$_3$ cycles + 445 Y$_2$O$_3$ cycles + 3 Al$_2$O$_3$ cycles) + 3 Al$_2$O$_3$ (YAG sequence #3). This sequence was expected to produce a film thickness of ~205 nm. The actual film thickness measured was 300 nm. Using Scherrer’s formula [71], a crystallite size of 13.3 nm was calculated by XRD peak broadening.

The deposited film was ~300 nm whereas the predicted value was ~205 nm. The growth rate for Al$_2$O$_3$ and/or Y$_2$O$_3$ must have changed. An increase in the Al$_2$O$_3$ growth rate such that an additional 100 nm of Al$_2$O$_3$ is deposited would imply a Al$_2$O$_3$ growth rate of 4.3 Å/cycle and the stoichiometry would favor YAG. Likewise, an increase in the growth rate for Y$_2$O$_3$ such that an additional 100 nm of Y$_2$O$_3$ is deposited would imply a growth rate of 1.8 pm/cycle for Y$_2$O$_3$ and the stoichiometry would favor YAM and YAP (~40 mol%, section 2.4.1). The XRD results in figure 4-19 show a YAG phase, suggesting an increase in the Al$_2$O$_3$ growth rate.

In section 2.3.2 it was noted that the AlCl$_3$ and H$_2$O water chemical reaction produces HCl which can etch the Al$_2$O$_3$ surface. A similar reaction can occur between HCl and Y$_2$O$_3$, etching the Y$_2$O$_3$ surface during the initial cycles of Al$_2$O$_3$ growth. Etching of Y$_2$O$_3$ can continue as long as there is an exposed Y$_2$O$_3$ surface. Once Al$_2$O$_3$ covers the Y$_2$O$_3$ surface, etching of Y$_2$O$_3$ by HCl ceases. This would result in a decrease of Y$_2$O$_3$ thickness. At constant temperature, pressure, AlCl$_3$ flux and surface coverage, the
amount of material removed will be constant. Assuming the bulk growth rate of 3 pm/cycle is reduced by etching such that there is an apparent growth rate of 1.8 pm/cycle, a difference of 1.2 pm/cycle, the amount of material apparently “lost” is 890 cycles x 1.2 pm/cycles = 1.1 nm. That is, the films would have been 2.7 nm without etching, but etching reduced them to 1.6 nm thick. The expected thickness total of Y\(_2\)O\(_3\) was 890 cycles x 1.0 pm/cycles = 0.89 nm. The thicker than expected Y\(_2\)O\(_3\) films resulted in the ~100 nm of overall film thickness. This explains the disparity in growth rates from bulk Y\(_2\)O\(_3\) to the nano-laminated Y\(_2\)O\(_3\) (section 4.5.2.1).

In section 4.5.2.2, YAG sequence #2 showed a slight decrease from the expected thickness to the measured thickness. In that case, assuming a 3 pm/cycle growth rate for Y\(_2\)O\(_3\) and then subtracting 1.4 nm for etching effects explains the lower than expected film thickness.

Using equation 2-21, the inter-diffusion coefficient for Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\) can be estimated as in section 4.5.2.2. Crystallinity of YAG was obtained after a 12 hour (~43200 sec) calcine. The diffusion distance of Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\) was determined by multiplying the growth rate for Al\(_2\)O\(_3\) by the number of cycles in a single cycle. In sequence #3 this is \((2.0 \text{Å/cycle}) \times (3 \text{ cycles}) = 0.6 \text{ nm}\). Therefore, the diffusion coefficient for Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\) is \(2.1 \times 10^{-24} \text{ m}^2/\text{s}\). Again, oxygen diffusion in Al\(_2\)O\(_3\) is discussed in section 4.5.2.2 and has a value of \(\sim 10^{-23} \text{ m}^2/\text{s}\) at 975°C. This reinforces the hypothesis that the diffusion mechanism is limited by oxygen diffusion.
Both YAG sequence #2 and #3 resulted in a polycrystalline YAG material after calcining at 975°C in air. The thicknesses of these films were correctly predicted from the calculated growth rates including etching effects. Stoichiometric thickness values for the constituent Al₂O₃ and Y₂O₃ bilayers resulted in the YAG phase after calcining at 975°C for 12 hrs in air.

4.5.3 Y₄Al₂O₉ (YAM) Deposition

For the stoichiometric Y₄Al₂O₉ (YAM) phase, the thickness of the Y₂O₃ needs to be 354% of the Al₂O₃ layer (section 3.3.4) or \( t_Y = 3.54t_{Al} \). As a first approximation for reasonable diffusion distances, the lattice parameters of the desired material were considered. For YAM, the monoclinic lattice parameters are 0.74 nm, 1.0 nm, and 1.1 nm; therefore a reasonable thickness of the bilayer (Al₂O₃-Y₂O₃ couple) is 1.1 nm.
Within this distance both Al$_2$O$_3$ and Y$_2$O$_3$ need to be present or, $t_Y + t_{Al} = 1.1$ nm. In addition, $t_Y$ must equal or be greater than $3.54t_{Al}$ in order to maintain stoichiometry, as discussed above. Therefore, the layer thicknesses can be determined to be $t_Y = 0.86$ nm and $t_{Al} = 0.24$ nm. These thicknesses maintain the 3.54:1 thickness ratio of Y:Al and sum up to 1.1 nm. These thickness values for Al$_2$O$_3$ and Y$_2$O$_3$ are also smaller than twice the calculated diffusion length (2.6 nm) for O in Al$_2$O$_3$ (section 3.4) therefore calcining should produce a homogenous film. The growth rate for Al$_2$O$_3$ was determined to be 2.0 Å/cycle at 350°C and the growth rate for Y$_2$O$_3$ was initially determined to be 1.0 pm/cycle for the multilayered deposition (section 4.5.2). In section 4.5.2 it was found that a larger number Y$_2$O$_3$ cycles can lead to greater than expected growth rates for Y$_2$O$_3$, namely 1.8 pm/cycle. The growth rate for Y$_2$O$_3$ remains 3.0 pm/cycle for the nano-laminate stack as in the bulk. However, in the nano-laminate stack, HCl from the initial Al$_2$O$_3$ cycles etches the Y$_2$O$_3$ surface. For YAM sequence #4, the 3.0 pm/cycle is assumed for the Y$_2$O$_3$ growth and a 1.1 nm etch is factored in.

In order to achieve the monoclinic phase (YAM), the following sequence was used: 3 Al$_2$O$_3$ cycles + 100 times (612 Y$_2$O$_3$ cycles + 122 Ce$_2$O$_3$ cycles + 612 Y$_2$O$_3$ cycles + 3 Al$_2$O$_3$ cycles) + 3 Al$_2$O$_3$ (YAM sequence #4). The cycles of Y$_2$O$_3$ are such that a slight excess of Y$_2$O$_3$ is present. This sequence should result in a film ~340 nm thick and with the stoichiometry of the YAM phase. The number of Ce$_2$O$_3$ cycles was set to 10% of the Y$_2$O$_3$ cycles. The measured thickness of the as-deposited film was ~400 nm, ~60 nm greater than the predicted thickness. The deposited film was ~400 nm whereas the predicted value was ~340 nm, This suggests that there was less than 1.0 nm of etching.
Assuming an etch of 0.4 nm rather than 1.0 nm explains the discrepancy in film thickness.

Figure 4-20 shows the XRD plot for the film grown using YAM sequence #4 after being calcined at 975°C for 12 hrs in air. Multiple peaks indicate a polycrystalline YAM phase. The (122) and (112) peaks from the YAM phase are the dominant peaks. The crystallite size of the YAM phase was calculated to be 20 nm using Scherrer’s formula [49].

Using equation 2-21, the inter-diffusion coefficient for Y₂O₃ and Al₂O₃ can be calculated as in sections 4.5.2.2 and 4.5.2.3. Crystalline YAM was obtained after a 12 hour (~43200 sec) calcine. The thickness of Al₂O₃ is calculated by multiplying the growth rate for Al₂O₃ by the number of cycles. In sequence #2 this is 

\[ \frac{2.0 \text{Å/cycle} \times 3 \text{ cycles}}{12 \text{ hrs}} = 0.6 \text{ nm} \].

Therefore, the inter-diffusion coefficient for Y₂O₃ and Al₂O₃ is 2.1x10⁻²⁴ m²/s. Oxygen diffusion in Al₂O₃ is discussed in section 4.5.2.2 and has a value of ~10⁻²³ m²/s at 975°C. This suggests that the diffusion mechanism is limited by oxygen diffusion.

The number of growth cycles for Ce₂O₃ was the greatest in this film (YAM sequence #4). The surface morphology was rough (figure 4-18a and 4-18b) for both as-deposited and calcined samples respectively. As discussed above (section 4.5.1.1), inclusion of a larger number of Ce₂O₃ growth cycles results in a rough surface morphology. The 10:1 ratio of Y₂O₃ to Ce₂O₃ cycles in this film is the highest Ce₂O₃ concentration attempted.

The XPS results are shown in figure 4-21. This figure shows a Y concentration of 20.7% and no apparent Al. There is a significant Si peak resulting in an 11.5%
concentration. The presence of Si in the XPS spectrum is likely due to the very rough surface as shown in figure 4-18b. Non-uniform surface coverage of the film could allow the underlying substrate to be detected in XPS. The XRD spectrum for YAM sequence #4 is strong evidence for the formation of polycrystalline YAM. Stoichiometric thickness values for the constituent Al₂O₃ and Y₂O₃ bi-layers resulted in the YAM phase after calcining at 975°C for 12 hrs in air.

Figure 4-20. XRD spectrum from a film grown with YAM sequence #4 and calcined at 975°C for 12 hrs in air.
Figure 4-21. XPS spectrum from an as-deposited film grown with YAM sequence #4 after a 10 minute sputter with 4 keV Ar⁺.
5.1 Conclusions

Atomic layer deposition (ALD) of Al$_2$O$_3$, Y$_2$O$_3$, and Ce$_2$O$_3$ films has been demonstrated as well as ALD of pseudo-binary Y$_3$Al$_5$O$_{12}$ (YAG), and Y$_4$Al$_2$O$_9$ (YAM) films. YAG and YAM are two of three phases in the pseudo-binary Al$_2$O$_3$-Y$_2$O$_3$ system. By alternating deposition of very thin films of Al$_2$O$_3$ and Y$_2$O$_3$ to create a nanolaminate stack in stoichiometric amounts, the yttrium aluminum garnet (YAG-Y$_3$Al$_5$O$_{12}$) and yttrium aluminum monoclinic (YAM-Y$_4$Al$_2$O$_9$) phases can be produced after calcining in air at 975°C for 12 hours. The proper stoichiometry for a particular phase can be achieved by varying the ratio of the Al$_2$O$_3$ and Y$_2$O$_3$ thicknesses.

In this work, the ALD precursors for Al$_2$O$_3$, Y$_2$O$_3$, and Ce$_2$O$_3$ were AlCl$_3$/H$_2$O, Y(thd)$_3$/O$_3$, and Ce(acac)$_3$/O$_3$ respectively. As is typical for ALD, a layer growth cycle consisted of a metal precursor pulse, a N$_2$ purge pulse, an oxygen precursor pulse, and a final N$_2$ purge pulse. The growth rate at 350°C for Al$_2$O$_3$ was found to be 1.0 Å/cycle and films up to 1μm thick were grown. Al$_2$O$_3$ was found to be amorphous as-deposited when grown at substrate temperatures of 295°C to 515°C. The growth rate for Y$_2$O$_3$ was found to be 3.0 pm/cycle and films up to 30 nm thick were grown. Y$_2$O$_3$ deposited at 200°C to 500°C was found to be a polycrystalline cubic phase as-deposited. Alternating layered deposition of Al$_2$O$_3$ and Y$_2$O$_3$ was found to be amorphous as-deposited. Attempts to dope the samples by inserting Ce$_2$O$_3$ cycles in the middle of Y$_2$O$_3$ cycles resulted in rough films. The growth rate for Ce$_2$O$_3$ was too low to be determined when using Ce(acac)$_3$ and 1% O$_3$ in O$_2$/O$_3$ as precursors. The Ce$^{3+}$ oxidation state was found
to be present in greater amounts than the Ce\textsuperscript{4+} oxidation state using X-ray photoelectron spectroscopy for Ce\textsubscript{2}O\textsubscript{3} films.

Films with the YAG phase were produced from a multilayer film consisting of sub-nano-scale Al\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} layers. The films were deposited using a pulsing sequence that consisted of YAG sequences #2 & #3. These films were amorphous after deposition at 350°C. Post growth calcining at 975°C for 12 hrs in air transformed the amorphous as-deposited multilayer film into a polycrystalline YAG film. It was shown that polycrystalline YAG was detected when using a thickness ratio of Y\textsubscript{2}O\textsubscript{3} to Al\textsubscript{2}O\textsubscript{3} of 1.04 to maintain the proper stoichiometry.

Similarly, a YAM thin film was produced from an Al\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} sub-nanoscale multilayer film. These films were also deposited at 350°C and were calcined at 975°C for 12 hrs in air. The YAM phase required a Y\textsubscript{2}O\textsubscript{3} to Al\textsubscript{2}O\textsubscript{3} thickness ratio of 3.54 to maintain the proper stoichiometry.

Both of these phases have been accomplished by growth of sub-nanoscale multilayered binary oxides. It was found that the growth rates for the individual binary oxides are different from the growth rates for multilayered structure oxides. The Al\textsubscript{2}O\textsubscript{3} growth rate in mixed deposition with Y\textsubscript{2}O\textsubscript{3} was found to be 2.0 Å/cycle rather than the 1.0 Å/cycle for bulk Al\textsubscript{2}O\textsubscript{3} growth. The Y\textsubscript{2}O\textsubscript{3} growth rate in mixed deposition with Al\textsubscript{2}O\textsubscript{3} was found to effectively vary from 1.0 pm/cycle to the 3.0 pm/cycle for bulk Y\textsubscript{2}O\textsubscript{3} growth due to etching effects from HCl byproducts produced during the initial Al\textsubscript{2}O\textsubscript{3} cycles. The layer thickness of Al\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} was less than the crystalline lattice parameter (either for YAG or YAM) in order to reduce inter-diffusion distances and therefore the times and temperatures for achieving homogeneous samples.
This approach resulted for the first time the synthesis of $Y_3Al_5O_{12}$ and $Y_4Al_2O_9$ thin films by atomic layer deposition. This work allows for novel and unique developments in optical devices such as phosphors, photonics, quantum confinement of optical states, scintillators, sub-wavelength optics, and waveguides. Some specific examples of using ALD to deposit $Y_3Al_5O_{12}$ include: deposition into high aspect ratio trenches to act as a laser waveguide in a monolithic films, very thin film deposition to increase the resolution of a scintillator, and as organic-free thin film complementary phosphor for light emitting diodes.

5.2 Future Studies

This work allows for novel and unique developments in optical devices such as phosphors, photonics, quantum confinement of optical states, scintillators, sub-wavelength optics, and waveguides. Some specific examples of using ALD to deposit $Y_3Al_5O_{12}$ include: deposition into high aspect ratio trenches to act as a laser waveguide in a monolithic films, very thin film deposition to increase the resolution of a scintillator, and as organic-free thin film complementary phosphor for light emitting diodes.

Future work on atomic layer deposition of the $Al_2O_3-Y_2O_3$ pseudo-binary system is needed for both the formation of yttrium aluminum perovskite (YAP-$YAlO_3$) phase as well as the doping of rare-earth materials such as cerium. In addition, continued improvements to the formation of YAG and YAM can be made. With a stable YAG process, and improved cerium incorporation, the synthesis of light-emitting $Y_3Al_5O_{12}$:Ce can be realized. Furthermore, substituting gallium for aluminum and/or gadolinium for yttrium in $Y_3Al_5O_{12}$:Ce can alter the crystal field around cerium. The formation of pure YAP phase will be difficult. Any deviation from the stoichiometric ratio of unity for Y to Al should result in the formation of either YAM or YAG in addition to YAP based on the
phase diagram (section 2.4.1). Such a balancing act requires very precise thickness control. Thus, process improvements for the formation of Y$_2$O$_3$ and Al$_2$O$_3$ can aid in the development of the YAP phase. Specifically, the very low growth rate for Y$_2$O$_3$ should be increased. There are reports in the literature [39,54] of growth rates on the order of 0.25 Å/cycle (section 2.3.2). It is believed that the design of the solid source manifold configuration in the ALD reactor used in this could be improved in order to achieve higher Y(thd)$_3$ flux into the reactor. Different precursors could also be used. The highly corrosive nature of AlCl$_3$ may be leading to etching of the Y$_2$O$_3$, yielding a lower than expected growth rate. Other ALD studies of Al$_2$O$_3$ films have used trimethylaluminum (TMA). Re-tooling of the ALD reactor used in this study for TMA delivery would be more in-line with best practices in the field.

It would be desirable to dope YAG and YAM with Ce$_2$O$_3$. The use of Ce(thd)$_3$ as a precursor may be more compatible for Y(thd)$_3$ chemistry and surface saturation of the Y$_2$O$_3$ films. In addition, dependable growth would allow for accurate determination of the Ce$_2$O$_3$ growth rate. Reliable Ce$_2$O$_3$ growth rate information would aid in depositing the appropriate film thickness needed to achieve the correct Ce$^{3+}$ concentration for photoluminescence.

Further development could further explore the concept of multilayered diffusion couples. Using radioactive ions in some layers and examining the position of the radioactive ions in the as-deposited and calcined films could be used to determine the dominate diffusion species and pathways. The use of Fick’s second law assumes semi-infinite films in a diffusion couple, but clearly the boundary conditions in nano-scaled
films are much different. Indeed, defining a concentration gradient in a sub-nanoscale multilayer stack is difficult and would be a very interesting line of research.

Finally, epitaxial deposition of the pseudo-binary $\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$ phases would be an interesting avenue to explore. It may be possible to achieve epitaxial crystalline films without post-growth annealing as the “thickness” of an individual film approaches bond lengths, literally building a crystal one atomic plane at a time.
LIST OF REFERENCES


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BIOGRAPHICAL SKETCH

Jason C. Rowland was born in Arcadia, California, on June 11th 1972. He graduated from Etiwanda High School in 1990. He attended the California Polytechnic University, Pomona from 1990-1991 as an English major. From 1991-1997 he took time to work and explore the world. During this period he worked as a ski lift operator, a customer service representative, and as a fisherman in Alaska, among other odd jobs.

In 1997 Jason re-enrolled at California Polytechnic University, Pomona. In 2002 he graduated with a Bachelor of Science degree in Physics with a minor in Chemistry. During his undergraduate studies, he worked full time at Tecstar Inc., Applied Solar Division, as a Production Technician, a Senior Process Control Technician, and eventually promoted to Engineer. At Tecstar, he performed Metal Organic Chemical Vapor Deposition of AlGaAs solar cell devices and their post-processing into a working solar cell.

Jason was admitted into the University of Florida, Department of Materials Science and Engineering in August 2002 as a University of Florida Alumni Graduate Fellow in Dr. Paul Holloway's research group. He earned a Master of Science degree in Materials Science and Engineering in 2004. Jason's work focused on the development of Atomic Layer Deposition and the growth of pseudo-binary Al$_2$O$_3$-Y$_2$O$_3$ materials for optoelectronic applications. He received his Ph.D. from the Department of Materials Science and Engineering at the University of Florida under the advisement of Dr. Paul Holloway in May 2010.