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Atomic Layer Deposition (ald) And Atomic Layer Etching (ale) Of Thin Films: Synthesis And Characterization Of A New Class Of Ald Precursors, Ald Of Pralo3 Thin Films, And Thermal Ale Of Cobalt Metal Films

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ATOMIC LAYER DEPOSITION (ALD) AND ATOMIC LAYER ETCHING (ALE) OF THIN FILMS: SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF ALD PRECURSORS, ALD OF PrAlO$_3$ THIN FILMS, AND THERMAL ALE OF COBALT METAL FILMS

by

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DEDICATION

TO MY LOVING BOYS
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LIST OF ABBREVIATIONS

AFM......................................................................................................Atomic Force Microscopy
ALD......................................................................................................Atomic Layer Deposition
ALE..............................................................................................Atomic Layer Etching
Cp.....................................................................................................Cyclopentadienyl
CVD...............................................................................................Chemical Vapor Deposition
DAD..................................................................................................Diazadiene
FWHM..................................................................................Full Width at Half Maximum
hfac.............................................................................................1,1,1,5,5,5-hexafluoroacetylacetonato
IR..............................................................................................Infrared Spectroscopy
ITRS.....................................................................................International Technology Roadmap for Semiconductors
MOSFET..................................................................................Metal Oxide Semiconductor Field Effect Transistor
NMR............................................................................................Nuclear Magnetic Resonance
PEALD................................................................................Plasma-Enhanced Atomic Layer Deposition
PVD...............................................................................................Physical Vapor Deposition
RF.............................................................................................Radio Frequency
SEM ..........................................................................................Scanning Electron Microscopy
TGA.............................................................................................Thermogravimetric Analysis
WDS-EPMA........................................................Wave Length Dispersive Electron Probe Micro Analysis
XPS.............................................................................................X-Ray Photoelectron Spectroscopy
XRR............................................................................................X-Ray Reflectivity
2DEG.....................................................................................Two-Dimensional Electron Gases
CHAPTER 1: INTRODUCTION

1.1 A Brief History and Evaluation of Semiconductor Industry

In 1948, with the first transistor invention in the Bell Laboratory, the development of the semiconductor industry had begun. After one decade of innovation of the transistor, the integrated circuit (IC) was developed with twelve transistors. Since then, the number of transistors in ICs are exponentially increasing. In 1965, Intel’s co-founder, Gordon Moore, predicted that the number of transistors in ICs doubles every 18 months. Later, the prediction identified as “Moore’s Law”. The exponential growth of the semiconductor industry is indicated according to increasing device density, increasing power efficiency, and decreasing device size. The International Technology Roadmap for Semiconductors (ITRS) predicts a reduction in feature size to 7 nm in 2018. However, achieving a 7 nm feature size is challenging due to some limitations in available thin film deposition techniques and processes. Uniform, conformal, and ultra-thin film deposition in high aspect-ratio features is required for modern device fabrication. Furthermore, the deposited films should be pinhole free, smooth, and high purity to enhance the performances and efficiency of devices.

Film deposition is a broad field which involves modern and traditional technologies. Therefore, there is an increasing demand for innovation of new film deposition strategies and chemistries to deposit new materials with a high level of quality. The rapid growth in the film deposition field directly contributes to the increasing number of research publications worldwide.

1.2 Thin Film Deposition Techniques

Many thin film deposition methods are mainly based on vapor phase precursors and co-reactants. Physical vapor deposition (PVD), chemical vapor deposition (CVD), and atomic layer deposition (ALD) are major thin film deposition techniques in the microelectronics industry. ALD plays a significant role because it enables the deposition of uniform, conformal films with
Angstrom-level thickness control.\textsuperscript{8–14} Figure 1 shows major differences between ALD and CVD/PVD when films are deposited in high aspect ratio features.

**Figure 1.** Difference between (a) CVD/PVD and (b) ALD

1.2.1 Physical Vapor Deposition (PVD)

PVD is a vacuum-based physical film deposition method which uses one or more precursors. PVD allows deposition of wide variety of materials with high levels of purity with a minimal level of environmental pollution.\textsuperscript{4,15} Sequential deposition is possible when multiple sources are available in the chamber to obtain alloy and multilayer films. PVD is sometimes challenging due to its need for highly qualified service technicians and requirements for special sample preparations. In PVD, evaporation or sputtering techniques are used to deposit thin films. The differences between these two methods are shown in Figure 2.\textsuperscript{4,15,16}
There are three different evaporation methods: 1. electron beam (e-beam) evaporation, 2. resistance-heated source, and 3. radio frequency (rf) induction heating. When the target material has a high melting point, heating is not enough to evaporate the material to the substrate. In such a case an e-beam is used to provide high thermal energy. Metals such as Al, Au, and alloys with Si, Ti, Mo, W, Pd, and Pt, as well as dielectric materials such as SiO$_2$ can be grown using e-beam evaporative PVD. Resistance-heated sources are used for metals such as tungsten which has higher melting points to wrap the lower melting metals such as Al. The heated W coil transfers thermal energy and facilitates the evaporation of the lower melting metal. This method is highly cost-effective. However, the resistance-heated sources cannot reach high enough temperatures to evaporate high melting point materials. Furthermore, contamination of depositing materials with heating filament is possible. rf Induction heating uses a strong magnetic field to change the temperature. The rf induction heating provides high volume capacitance.

The definition of sputtering is dislodging of atoms from the surface of a material due to the collision with high energy particles. Sputtering has several steps. 1. generated ions are directed to the target surface, 2. atoms are sputtered from the target surface, 3. the sputtered atoms get transferred through vacuum to the desired substrate, and 4. the transferred sputtered atoms condense on the substrate to form a thin film. There are several sputtering systems available including direct current (DC), reactive, rf, and magnetron sputtering. Sputtering PVD is used
to deposit a variety of materials and provides better step coverage and good adhesion to the substrate. Moreover, sputtering PVD has other advantages such as sputter cleaning before the film deposition, controlling of the film thickness, and alloy composition of the depositing material.\textsuperscript{4,15,16}

1.2.2 Chemical Vapor Deposition (CVD)

The history of CVD goes back to the early 1800s, after discovering the CVD of tungsten metal using WCl\textsubscript{6} and H\textsubscript{2}.\textsuperscript{17} CVD is a process which simultaneously uses one or more vapor phase precursors to deposit thin films.\textsuperscript{5,12–18} Figure 3 explains the basic steps in CVD using CH\textsubscript{4} and H\textsubscript{2} to deposit graphene.\textsuperscript{18} CVD precursors can be gases, liquids, or solids. CVD reactions are thermodynamically endothermic, thus require kinetic energy of activation.\textsuperscript{5} This activation energy is supplied as thermal energy from various methods such as direct heating of the substrate or substrate holder, rf induction heating, thermal radiation, or photo-radiation.\textsuperscript{5} High-temperature CVD processes may not be beneficial for temperature-sensitive substrates. Therefore, low-temperature CVD is preferable.\textsuperscript{5,12–19}

\textbf{Figure 3.} CVD of graphene using CH\textsubscript{4} and H\textsubscript{2}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{cVD_process}
\caption{CVD of graphene using CH\textsubscript{4} and H\textsubscript{2}}
\end{figure}

Plasma assisted or plasma enhanced CVD (PECVD) is an alternative method for low temperature CVD. PECVD uses electrical energy to activate vapor phase reactions. Therefore, the deposition temperature can be as low as ambient temperature for some CVD processes.\textsuperscript{5} Highly energetic plasmas which are generated from the electrical discharge in the gas phase provide inelastic collisions of the electrons with the precursor molecules to activate the reaction. Even
though PECVD offers low temperature CVD, there is a high possibility to damage the underlying substrates because of the highly energetic plasmas.\textsuperscript{5,12} When a CVD process uses metal organic precursors, the process is called metal-organic chemical vapor deposition (MOCVD).\textsuperscript{5} Metal-organic vapor phase epitaxy (MOVPE) is another type of MOCVD, which produces single crystal films on single crystal substrates.\textsuperscript{5} ALD is a different variation of CVD, which involves saturative surface reactions with an alternative exposure of precursors to the reaction chamber.\textsuperscript{5,7–10} A detailed description of ALD will be discussed later.

The growth rate of thermal CVD is determined by a few parameters such as substrate temperature, process pressure, and chemical nature of the gas phase precursors.\textsuperscript{5} The Arrhenius equation (Equation 1) describes the growth rate dependence parameters showing that the growth rate increases exponentially with substrate temperature.

\[
\text{Growth rate } \propto \exp \left( \frac{E_A}{RT} \right)
\]

Here, $E_A$ is the activation energy, $R$ is the gas constant, and $T$ is the temperature.

1.2.3 Atomic Layer Deposition (ALD)

ALD was developed by Suntola and Antson in the 1970s and was originally called atomic layer epitaxy.\textsuperscript{20} ALD is a thin film deposition technique mainly used in the semiconductor industry because of its simplicity, reproducibility, and capability of producing conformal thin films in high aspect ratio features with an Angstrom level thickness control.\textsuperscript{6–14} ALD has unique features compared with other vapor phase deposition methods, such as self-limited growth behavior and a linear growth of deposited films with increasing number of ALD cycles.

One ALD growth cycle has four steps.\textsuperscript{6–14} 1. the first precursor is exposed to the substrate in a reaction chamber, 2. the chamber is purged with a flow of inert gas to remove excess first precursor molecules and volatile reaction byproducts, 3. the second precursor is exposed and subsequently reacts with the surface-adsorbed first precursor molecules, and 4. purge with a flow
of inert gas to remove excess precursors and volatile reaction by-products. Figure 4 shows these four distinct steps using ALD of Al₂O₃ with trimethylaluminum (AlMe₃) and water. Nitrogen or argon is used in the purging step in between each precursor exposure and also as a carrier gas. In an ideal situation, one ALD cycle completes a monolayer growth of the material on substrates. Therefore, the thickness of the desired film can be controlled by changing the number of ALD cycles applied.⁵⁻¹⁴

**Figure 4.** Four basic steps in one ALD cycle
However, monolayer growth may not be observed in real ALD due to the steric bulk of precursors, or lack of surface-reactive sites on the substrate surface, which limits the monolayer growth.\textsuperscript{5} If the precursor molecule is large, it can cover more than one surface reactive site upon exposure of the precursor as shown in Figure 5, leading to sub-saturative film growth. Some substrates may not provide enough surface-reactive sites to adsorb precursor molecules. Thus, instead of a monolayer growth, less than monolayer growth is often observed in ALD.\textsuperscript{5–14} However, some ALD process show more than monolayer growth per cycle such as ALD of W metal using WF\textsubscript{6} and Si\textsubscript{2}H\textsubscript{6} (growth rate = 2.5 Å/cycle),\textsuperscript{20} and ALD of Al metal using AlCl\textsubscript{3} and Al hydride (growth rate = 3.5 Å/cycle).\textsuperscript{21}

**Figure 5.** Schematic diagram showing precursor molecules covering more than one surface active site

ALD can produce ultra-thin, conformal films due to self-limiting growth behavior. A plot of growth rate versus precursor pulse length is used to describe the self-limiting growth behavior of ALD as shown in Figure 6. When the surface reactive sites are completely saturated with the precursor molecules, self-limited growth behavior is observed.\textsuperscript{5–14} In such a situation, the growth rate becomes independent of the precursor pulse length (precursor saturation region). Below the point of precursor saturation, a lower growth rate is observed and is described as the precursor sub-saturative region.\textsuperscript{5–10} The lower growth rate is due to the insufficient dose of precursor molecules in shorter precursor pulse lengths, resulting in sub-saturation of surface reactive sites.\textsuperscript{5–14}
Another feature of ALD is the ALD window, which can be determined by plotting growth rate versus deposition temperature as shown in Figure 7. The ALD window is a temperature range where the growth rate is independent of the deposition temperature. At temperatures below the ALD window, the growth rate can be higher due to precursor condensation or lower because of low reactivity of precursors as a result of decreased thermal energy. At temperatures above the ALD window, an increased growth rate can be observed as a result of thermal decomposition of precursors or the growth rate may be decreased due to the precursor desorption from the substrate and loss of reactive sites on the surface due to the high temperature.  

Figure 6. The self-limited growth of ALD  

Figure 7. The ALD window plot
A linear relationship of film thickness versus number of cycles is a frequently observed feature of ALD as shown in Figure 8.\textsuperscript{5–10} The slope of the plot of film thickness versus number of cycles indicates the growth rate and the y-intercept provides information about nucleation delay. Nucleation delay occurs in some thermal ALD processes, as a result of island-type film growth during the first few ALD cycles or no growth may occur at all up to a certain number of cycles. Thus, a uniform thin film growth can be observed after a certain number of ALD cycles. Nucleation delay is a substrate-specific phenomenon and may be avoided by changing the substrate.\textsuperscript{5–10} Figure 8 illustrates the difference between ALD process with and without a nucleation delay.

**Figure 8.** The thickness versus number of ALD cycles plot (a) with a zero-nucleation delay and (b) with a nucleation delay

Finally, ALD can facilitate excellent control of the film composition. Deposition of complex materials with expected stoichiometric ratio can be obtained by applying an “ALD supercycle”. An ALD supercycle is used to deposit more than one material by changing pulse ratios of individual precursors as shown in Figure 9.\textsuperscript{6,22} Thus, the expected stoichiometric ratio of the final product can often be controlled. For instance, in the deposition of stoichiometric SrTiO\textsubscript{3}, 1:1 SrCO\textsubscript{3}:TiO\textsubscript{2} pulse ratios were used and 1:1 Sr:Ti atomic ratio was observed after annealing in the SrTiO\textsubscript{3} films.\textsuperscript{23a} In the deposition of Li\textsubscript{7}La\textsubscript{5}Zr\textsubscript{2}O\textsubscript{12} ceramic oxide garnet, 8:28:12:1
(Li:La:Zr:Al) pulse ratios were used and Li$_{6.28}$La$_3$Zr$_2$O$_{12}$Al$_{0.24}$ was observed in the deposited material.$^{23b}$ A detailed use of ALD supercycles is discussed in Chapter 3.

**Figure 9.** Schematic diagram of an ALD supercycle used to deposit two different metal oxides with controlled pulse sequences

Thermal ALD and plasma enhanced ALD (PEALD) are the major types of ALD. When temperature is used to provide the kinetic activation energy of surface reactions, the process is called thermal ALD and when the activation energy is supplied from plasma, the process is PEALD.$^{5,24,25}$ Typically H$_2$, N$_2$, O$_2$, and NH$_3$ plasmas are used in PEALD film depositions.$^{24,25}$ PEALD can be used to deposit varieties of materials because the highly energetic plasma is used to overcome the high thermodynamic and kinetic energy barrier of surface reactions. For instance, in the deposition of metal oxides, β-diketonate precursors are relatively unreactive towards water.$^{26-29}$ Use of PEALD is beneficial in such situations instead of use of ozone.$^{30-32}$ Due to the low-temperature deposition conditions in PEALD, the temperature range of the ALD window become broadened.$^{30}$ Meanwhile, plasma modifies the substrate surface and can enhance the surface reactive sites to mitigate the nucleation delay.$^5$ Highly reactive plasmas can improve material properties such as film density, impurity content, and electrical properties. However, thermal ALD is preferred over PEALD because plasma can damage the underlying substrates and
films. Moreover, radicals/ions which are generated from plasmas can recombine in walls of the trenches of high aspect ratio features and prevent conformal film growth.$^{5-14}$

### 1.3 Transition Metal Precursors for ALD/CVD

ALD precursor chemistry is very important in obtaining high quality thin films. Since ALD uses surface chemical reactions, precursors should be highly volatile. Volatility of precursors can be increased by minimizing the intermolecular interactions of the ligand system and tuning substituent on the ligand.$^{5,8}$ For instance, ligands which avoid intermolecular $\pi$-electron interactions and also contain nitrogen and oxygen donor atoms often result in highly volatile metal complexes.$^8$ Thermal stability of precursors is important to avoid unwanted vapor phase depositions (CVD like) and to obtain high-purity films. ALD precursors should be highly reactive towards co-reactants and the reaction by-products should be non-corrosive and volatile.$^{5-10}$ Design and development of new precursors is very important due to the limitations associated with currently available precursors such as poor reactivity, low volatility, and poor thermal stability. Chart 1 shows different ligand systems used to synthesize transition metal ALD/CVD precursors. Some of these ligands have been designed and synthesized by the Winter group at Wayne State University.$^{33-37}$
Chart 1. Selected ligand systems for transition metal precursors

Precursors containing metal halides are not always volatile. Volatile metal halides such as CuCl, TiCl₄, WCl₆, MoCl₅, TaCl₅, and WF₆ are used in ALD.⁵,⁸ Metal complexes containing fluorides can be more volatile than metal chlorides. However, there is a high risk of fluorine
contamination in the deposited film when fluorine-containing precursors are used.\textsuperscript{5,8} Also, metal halides potentially produce corrosive hydrogen halides as by products. However, due to the ease of handling and commercial availability, metal halides are often the preferred precursors for ALD.

Carbonyl-containing metal precursors are sufficiently volatile, reasonably air and moisture stable, and usually contain zero (M\textsuperscript{0}) oxidation state due to the neutral carbonyl ligand. Examples include Fe(CO)\textsubscript{5}, Co\textsubscript{2}(CO)\textsubscript{8}, Ni(CO)\textsubscript{4}, Mo(CO)\textsubscript{6}, and Ru\textsubscript{3}(CO)\textsubscript{12}.\textsuperscript{5} Heteroleptic metal complexes containing carbonyl ligands can demonstrate higher volatility than homoleptic metal complexes and the oxidation state of the metal center is no longer zero due to the attached anionic ligands.\textsuperscript{5,38} These carbonyl precursors are mostly used in metal CVD as single source precursors due to the ease of removing of CO groups from the metal center at high temperature.\textsuperscript{5–14,38} Metal carbonyl complexes are used to deposit single metal films, multilayer films, and alloy films.

Cyclopentadienyl (C\textsubscript{5}H\textsubscript{5}-Cp) complexes are sufficiently reactive and thermally stable for use in ALD and CVD. However, the volatility and the film growth rates are moderate for Cp precursors. The volatility and thermal stability of these Cp complexes can be tuned by changing substituents groups on the Cp ring and introducing different ligands to the metal center to produce heteroleptic complexes.\textsuperscript{5,39,40} Substituted derivatives of cyclopentadienyl titanium, zirconium, and hafnium complexes are widely used in ALD to deposit TiO\textsubscript{2} and high-k dielectric HfO\textsubscript{2} and ZrO\textsubscript{2} with water or ozone as the oxygen source.\textsuperscript{40}

β-Diketonate ligands are well-studied and widely used as ALD and CVD precursors. Metal complexes containing β-diketonate ligands show good thermal stability and sufficient volatility. Most of these compounds are stable upon exposure to air and moisture and can be prepared easily.\textsuperscript{5,41} β-Diketonate-containing precursors are used in metal oxide film depositions with ozone as an oxygen source. Water cannot be used as the oxygen source because β-diketonate ligands are weak Brønsted bases (pKa = 9.0 for acetylacetone) thus the reactivity with water (pKa = 15.7) is
endothermic.$^{42,43}$ $\beta$-Diketoiminate and $\beta$-diketiminate ligands are derived from $\beta$-diketonate ligands, allowing a high level of tunability. N-donor atoms on the $\beta$-diketoiminate and $\beta$-diketiminate ligands can be substituted with different groups to increase the steric bulk, which prevents oligomerization of metal complexes.$^{5,41}$ Furthermore, these $\beta$-diketonate, $\beta$-diketoiminate, and $\beta$-diketiminate-containing metal complexes can form adducts with different neutral donor molecules and can be used as ALD/CVD precursors.

Aminoalkoxide ligands form five-membered chelate rings, which are more stable than six-membered chelate rings. These aminoalkoxide-containing volatile metal precursors are available for late transition metal ions which have small ionic radii.$^5$ Early transition metal complexes form dimers or oligomers because the small aminoalkoxide ligands are not large enough to saturate the coordination sphere of early transition metal centers. Even though aminoalkoxide-containing metal complexes have high volatility, these complexes suffer from a lack of thermal stability.$^5$ Bis(dimethylamino-2-propoxy)copper(II) (Cu(dmap)$_2$) is well known and it has the highest reported volatility for a copper complex (sublimes at 65 °C) in CVD and ALD.$^{44}$

Diazadienyl ligands are redox non-innocent ligands and exist in three different forms (neutral, monoanionic, and dianionic) as shown in Chart 2.$^{37,45}$ This ligand makes a stable five-membered chelate ring with metal center, and due to the N-donor atoms on substituted groups, diazadienyl ligands are bulky enough to form monomers with late transition metals. Interestingly, monoanionic diazadienyl-containing transition metals complexes are decompose thermally to their metals at high temperatures.$^{37}$ This thermal self-decomposition is due to the reduction of the metal center by donation of electrons from the radical ligands.$^{37}$ As a result of good volatility, thermal stability, and reactivity, diazadienyl metal complexes are used to deposit many metals, metal oxides, and metal nitrides films using thermal ALD and CVD.$^{37,52,53,122}$
Chart 2. Three distinct forms of the diazadienyl ligand

Amidinate ligands are very versatile and have been used in almost all metals in the periodic table including main group, transition metals, and lanthanides to synthesize different metal complexes. Amidinate ligands can form monomeric, dimeric, trimeric, and tetrameric complexes with different metals depending on the steric bulk of the ligand and the atomic radii of the metal centers. Metal complexes containing amidinate ligands are highly reactive, thermally stable, and exhibit high volatility. Therefore, these metal complexes are promising for the ALD of metals, metal nitrides, and other forms.

Selecting a proper co-reactant is as important as selecting a metal precursor in ALD. Depending on type and dose of the co-reactants use in film depositions, the composition of the deposited film will be changed. For instance, deposition of low-resistivity Ru metal can be achieved by ALD using Ru(DMBD)(CO)$_3$ (DMBD = dimethylbutadiene) and short pulses (2 s) of oxygen as a co-reactant at 290–320 °C. When the oxygen pulse time increased up to 20 s, RuO$_2$ films are deposited at 220–240 °C. Moreover, Co metal films can be deposited by ALD using Co(tBuDAD)$_2$ (tBuDAD = 1,4-di-tet-butyl-1,3-diazabutadienyl) and formic acid or tert-butylamine. Co$_3$O$_4$ films can be deposited by ALD using the same Co-precursor with ozone as an oxygen source. Reducing agents such as hydrogen plasma, hydrazine, and its derivatives, boranes, formic acid, amines, and alcohols are often used in metal ALD in order to reduce the oxidized metal center to a corresponding metal. Water, molecular oxygen, hydrogen peroxide, and ozone are used as oxygen sources for metal oxide film growth. For the deposition of metal nitrides films, ammonia or hydrazine can be used.
1.4 ALD of Binary and Ternary Lanthanide Oxides

Lanthanide oxides are important potential gate dielectric materials to enhance the efficiency of metal oxide semiconductor field effect transistors (MOSFETs), as shown in Figure 10.\textsuperscript{58–62} SiO$_2$ has been a widely used dielectric material for three decades, and it has a 3.9 eV dielectric constant and 8.9 eV band gap.\textsuperscript{63} Through the continuous miniaturization of devices, it is important to deposit an ultra-thin layer of SiO$_2$ in MOSFETs.\textsuperscript{62,63} Extremely thin SiO$_2$ layers can cause large leakage currents which can reduce the device performance.\textsuperscript{62,63,66} Researchers attempted to incorporate N atoms in to SiO$_2$, which improved the dielectric constant.\textsuperscript{63} However, the dielectric constant of N-doped SiO$_2$ was not high enough to meet current requirements.\textsuperscript{63} Oxides of group II, III, IV, and some lanthanides such as Al$_2$O$_3$, Y$_2$O$_3$, La$_2$O$_3$, and Pr$_2$O$_3$ were then suggested.\textsuperscript{63} Due to some limitations, such as low power applications, scalability, and reactions with Si substrates, use of above-mentioned oxides have been limited. HfO$_2$ and ZrO$_2$ were then considered as potential replacements for SiO$_2$ and began to use HfO$_2$ as a gate dielectric material (dielectric constant = 25, band gap = 5.8 eV).\textsuperscript{63,64,66} However, the formation of the interfacial oxide layer during film deposition and the low crystallization temperature ruin the electrical properties of HfO$_2$ since such crystallized structures can create large leakage currents.\textsuperscript{66}

The rare earth oxides (REOs) have been identified as high dielectric constant materials ($k = 7–30$) with relatively high band gap (La$_2$O$_3$ = 5–6 eV).\textsuperscript{65,66} Also, REOs have other properties such as high breakdown electric fields, high resistivities, smooth surfaces, small lattice mismatches with silicon, and a high chemical and thermal stability.\textsuperscript{66} The enhanced electrical properties of REOs provides great potential for replacing SiO$_2$ in MOSFET.\textsuperscript{65,66} Early REOs, such as La$_2$O$_3$ and Pr$_2$O$_3$, show better electrical properties including high dielectric constant and band gap compared to late REOs.\textsuperscript{65–67} Therefore, these early REOs are potential candidates for replacing SiO$_2$. Further studies are essential to optimize film deposition, composition, and avoid reaction with Si.\textsuperscript{66}
Solids can exist in three different states as shown in Figure 11. In crystalline solids, atoms are arranged in a perfectly ordered manner. In amorphous solids, atoms are arranged randomly. In polycrystalline solids, atoms are arranged in an ordered manner but with different orientations or combinations of differently oriented single crystals.\textsuperscript{68,69} Depending on the way that atoms are arranged in solids, physical properties can change. For instance, crystalline solids have sharp melting points and anisotropic (anisotropic = properties are different in different directions) physical properties such as linear density and electrical transport.\textsuperscript{68,69} Due to the random orientations of atoms, amorphous solids do not have sharp (definite) melting points, instead, melt over a broad range of temperatures and isotropic physical properties (isotropic = physical properties are same in all directions) are observed. Polycrystalline solids display isotropic physical properties due to the different orientations of single crystals.\textsuperscript{68}

**Figure 10.** Schematic representation of the MOSFET

![MOSFET Diagram](image)

Monocrystalline  Polycrystalline  Amorphous

When a substrate acts as a template to grow a crystalline material with the same crystalline orientation as the substrate, the process is called epitaxial growth.\textsuperscript{69,70} Epitaxial growth can be
divided into two categories: 1. homoepitaxial and 2. heteroepitaxial. When the deposited material and the substrate is the same (Si on Si and SrTiO$_3$ on SrTiO$_3$),$^{70,71}$ growth is called homoepitaxy and when the deposited material is different from the substrate (LaAlO$_3$ on SrTiO$_3$ and BN on monolayer graphene),$^{67,72}$ growth is called heteroepitaxy. Solid phase epitaxy (SPE) is a method of converting metastable amorphous material which deposited on crystalline substrates, to a fully crystalized material by annealing or ion bombardment.$^{69,70}$ SPE can be achieved using different deposition methods such as molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), and metalorganic CVD (MOCVD).$^{66,70}$ Figure 12 demonstrates transformation of the atomic re-arrangement of an amorphous phase to a crystalline phase.$^{69}$ Annealing is a heating process used to obtain an ordered crystalline solid phase. The annealing processes can be carried out in different environments such as O$_2$, N$_2$, reduced atmosphere (N$_2$/H$_2$), or ambient atmospheric conditions.$^{69,70}$ It is very important to find the optimum annealing condition for a particular material, which can then be fully crystallized by varying the temperature and time.

**Figure 12.** Crystallization from amorphous solid (reproduced with permission from Journal of Current Opinion in Solid State and Materials Science. ref. 69)

Epitaxial growth of ternary lanthanide oxides (ABO$_3$) on SrTiO$_3$ substrates is used to create two-dimensional electron gases (2-DEG) at the heterointerface of the non-polar/polar system, as shown in Figure 13(a).$^{67,73-75}$ 2-DEGs at the heterointerfaces have specific properties such as
extremely high electron densities, magnetism, and 2D-superconductivity.\textsuperscript{73–75} To obtain epitaxial growth, deposition of Perovskite-type ternary lanthanide oxides on TiO\textsubscript{2}-terminated SrTiO\textsubscript{3} substrates and appropriate crystallization procedures should be followed. SrTiO\textsubscript{3} substrates are considered to be non-polar due to the zero charge of SrO and TiO\textsubscript{2}.\textsuperscript{73–75} LaAlO\textsubscript{3} or other ternary lanthanide oxides are polar due to the non-zero charge of LaO(+) and AlO\textsubscript{2}(−). A non-polar/polar interface is adopted due to a charge difference as shown in Figure 13(b) to create 2-DEGs.\textsuperscript{73–75} Thus, investigation of other systems such as PrAlO\textsubscript{3}/SrTiO\textsubscript{3} is beneficial for the field of nanomicroelectronics.

**Figure 13.** (a) Formation of 2-DEG in SrTiO\textsubscript{3}/LaAlO\textsubscript{3} system and (b) schematic diagram of resulting (LaO\textsuperscript{+}):(TiO\textsubscript{2}\textsuperscript{0}) interface

Lanthanide oxides readily react with water and form hydroxyl species as shown in Equation 2.\textsuperscript{65,76–79} The inherent hygroscopic nature of the lanthanide oxides can cause some undesirable outcomes to the film properties, such as reduction of electrical properties by causing increased leakage current, roughening of the surface of a gate dielectric, and increasing the film thickness due to the formation of additional hydroxyl species.\textsuperscript{76–80} In addition to reaction with water, lanthanide oxides also react with CO\textsubscript{2} according to Equation 3.\textsuperscript{65,76–80}
\[
\text{Ln}_2\text{O}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Ln(OH)}_3 + \text{LnO(OH)} \quad (2)
\]

\[
\text{Ln}_2\text{O}_3 + 3\text{CO}_2 \rightarrow \text{Ln}_2(\text{CO}_3)_3 \quad (3)
\]

The hygroscopic nature depends on the cation electronegativity and lattice energy of the lanthanide oxide. The combination of highest electronegativity and lowest lattice energy results in the highest reactivity with water and, therefore, La\(_2\)O\(_3\) has the highest reactivity. Lanthanide oxides such as Lu\(_2\)O\(_3\) show lower reactivity towards water.\(^{66}\) This undesirable reactivity with water and CO\(_2\) needs to be minimized in order to maintain good electrical properties and morphology of deposited lanthanide oxide films. When water is used as the oxygen source in the deposition of REOs, water can be absorbed by the REOs and act as water reservoirs.\(^{65,66}\) During the inert gas purge, this absorbed water desorbs slowly from the surface with remaining water able to react with subsequent lanthanide precursor, resulting in non-uniform film growth.\(^{60,65,66}\) Ozone or oxygen can also be used as an oxygen source to obtain oxide films. However, ozone and oxygen can react with the underlying silicon substrate, incorporating Si into the bulk film.\(^{60,66}\) Furthermore, ozone can damage underlying substrates and deposited films. In this thesis, Chapter 3 describes the ALD of Pr\(_2\)O\(_3\) and PrAlO\(_3\). Praseodymium can exist +3 and +4 oxidation states such as Pr\(_2\)O\(_3\), PrO\(_2\), and Pr\(_6\)O\(_{11}\), which is not common in other elements in the lanthanide series. When ozone is used as a co-reactant, different oxidation states of praseodymium oxides can also be formed due to the strong oxidizing nature of ozone.\(^{65}\)

Water is a mild co-reactant and does not damage many underlying substrates or the deposited films. Moreover, water is easier to handle, safer to use, and cheaper when compared to ozone or other oxygen sources. Therefore, the use of water as a co-reactant in film depositions is highly desired. At high temperatures (>380 °C), lanthanide hydroxide species are not stable and can decompose to their pure metal oxides.\(^{60,80}\) Therefore, high temperature depositions can minimize the hydroxyl-species contamination. In addition, incorporation of a stable binary oxide
such as Al$_2$O$_3$ with lanthanide oxides can act as a protective layer towards reactivity with water and CO$_2$.$^{30,60,66}$ In addition to Al$_2$O$_3$, other stable binary oxides can be used to deposit ternary oxides such as Lu$_2$O$_3$, which is more stable to water compared with early lanthanide oxides, Y$_2$O$_3$, and Sc$_2$O$_3$. A few processes have been developed using this strategy to deposit ALD of PrAlO$_3$, LaAlO$_3$, LaScO$_3$, and LaLuO$_3$.\textsuperscript{60,66,81,82}

The deposition of ternary and binary lanthanide oxides can be accomplished using PVD, CVD, and ALD.$^{58-61}$ PVD methods have been used widely for the deposition of almost all lanthanide oxides, which result in good electrical properties, good adhesion between film and substrate, and high deposition rates.$^{61}$ Also, the film depositions can be performed at low temperatures due to the use of high energy laser beam or electron beam. However, the target source can be damaged after exposure to highly energetic beams. CVD and ALD methods are essential in tuning the composition of films, especially in complex lanthanide oxide depositions.$^{60,66,67}$ The film morphology (amorphous or crystalline), composition, and the oxidation state of lanthanides metal can be controlled by varying the process temperatures, precursors, and co-reactants during the film deposition.$^{67,81,82}$

1.5 Atomic Layer Etching (ALE)

As a consequence of miniaturization of microelectronics devices, the materials which are deposited in devices may be only a few nanometers in thickness.$^{3,9,83}$ ALD allows a conformal ultra-thin film deposition in high aspect ratio features due to the self-limiting growth behavior.$^{5-14}$ As a counterpart of ALD, ALE has emerged to the microelectronics industry recently. ALE is essentially the reverse of ALD and removes films in a layer-by-layer self-limited manner.$^{83-88}$ The half reactions of ALE should be exothermic to facilitate spontaneous etching.$^{83}$ Figure 14 shows the differences between ALD and ALE.$^{83}$ ALE starts with a thicker film and removes material layer by layer until the desired thickness is observed.$^{83-88}$ In an ideal situation, the surface
roughness should be improved after etching. However, experimentally the film quality might not be improved as expected after etching if highly reactive reagents are used.\textsuperscript{84–88}

**Figure 14.** The ALD versus ALE (modified from ref. 83)

![ALD vs ALE diagram]

ALE was introduced by Yoder in 1988, and described etching of crystalline diamond using NO\textsubscript{2} and excited ions.\textsuperscript{89} After the discovery of crystalline diamond etching, there were many publications based on etching and termed differently, such as digital etching, layer by layer etching, molecular layer etching, and plasma atomic layer etching (PALE).\textsuperscript{90} In 1989, etching of GaAs was introduced using chlorination followed by ArF excimer laser pulses to remove halogenated species.\textsuperscript{91} Research expanded GaAs etching to ALE of group III and V semiconductors later.\textsuperscript{92} The first step of that type of ALE is halogenation using Cl\textsubscript{2} or F\textsubscript{2}. Then, as a second step, reactive ion bombardment is used.\textsuperscript{92} Specifically Ar\textsuperscript{+} or neutral Ar are used to remove weakly bound halogenated species from the surface. In parallel to Si etching, etching of oxide materials was also demonstrated.\textsuperscript{93} ALE of HfO\textsubscript{2} was reported by Yeom using BCl\textsubscript{3} and Ar neutral beam and enhanced electrical properties of the films were observed after etching.\textsuperscript{93} Later, using Ar plasma and C\textsubscript{4}F\textsubscript{8} ALE of SiO\textsubscript{2} was reported.\textsuperscript{94}

Many ALE processes have been reported using highly energetic plasmas for the removing of etched material such as Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, TiO\textsubscript{2}, GaAs, Ge, Graphene, Si\textsubscript{3}N\textsubscript{4}, etc.\textsuperscript{84,86} However, highly energetic plasmas may damage the underlying substrate and the film and may alter the film properties and give anisotropic etching.\textsuperscript{83–88,94} The Hess group at Georgia Tech has reported a
solution method to etch metals and metal oxides.\textsuperscript{95–97} This solution etching process was basically for the purpose of cleaning excess metals and metal oxides. The solution etching was based on two major steps: 1. oxidation of metal substrates and 2. reaction of oxidized metal substrates with a neutral ligand, in order to obtain water/solvent soluble metal complexes.\textsuperscript{95–97} From the perspective of microelectronics device fabrication, this solution-based etching has had little impact, therefore, developing an advanced etching method such as thermal ALE is important.

Similar to ALD, thermal ALE has four distinct steps (Figure 15).\textsuperscript{83–88} 1. modify the surface of the material to be etched, 2. purge with an inert gas to remove excess reactant and by-products, 3. a second reactant exposure, resulting in formation of a volatile species, and 4. purge with an inert gas to remove excess reactant and volatile products. The surface modification step can be an oxidation process or changing of the chemical nature without altering the oxidation state of the metal.\textsuperscript{83,98–109} The surface of the material can be oxidized using oxidizing agents such as oxygen, ozone, peroxide, halogens, or acids if the material is a metal.\textsuperscript{98,107,108,110} Step 1 is not always a monolayer surface modification. Depending on the reactivity of the reactants, it could be possible to modify a few layers of the material from the surface.\textsuperscript{83} Two basic reactions were identified for the formation of a volatile products in Step 3.\textsuperscript{98–110} When neutral ligands, such as $\beta$-diketonates, are used in the second half reaction of thermal ALE, a ligand exchange reaction occurs. When volatile metal complexes with labile ligands are used for the second half reaction, a ligand exchange transmetallation reaction mechanism then ensues.\textsuperscript{98–110}
Thermal ALE is an increasingly developing field and has been introduced recently by the George group at University of Colorado. The thermal ALE of $\text{Al}_2\text{O}_3$, $\text{AlN}$, $\text{AlF}_3$, $\text{ZnO}$, $\text{HfO}_2$, $\text{SiO}_2$, $\text{TiN}$, and $\text{WO}_3$ have been developed using fluorination followed by ligand exchange reactions. For the fluorination step, HF in pyridine was used.\textsuperscript{99–106} However, thermal ALE of transition metals is poorly studied. The first thermal metal ALE developed to etch tungsten metal was a three-step process using $\text{O}_2$/O\textsubscript{3}, BCl\textsubscript{3}, and HF at 207 °C.\textsuperscript{103} Thermal ALE of iron, cobalt, and copper metal were studied using hexafluoroacetaceton (hfacH) after the modification of metal surface using chlorine or $\text{O}_2$/O\textsubscript{3}.\textsuperscript{107–110} These processes required long pulse times of each reactant at relatively high temperatures. Long pulse and purge times will decrease the speed of these processes and limit their use in the semiconductor industry. Moreover, most of above-mentioned thermal ALE processes show poor self-limiting behavior.\textsuperscript{107–110} Therefore, the field of thermal ALE of transition metals is requires significant improvement in the future to develop robust processes which can be directly transferred to the microelectronics industry.
1.6 Thesis Problems

As a result of the challenges arising from the ever-growing microelectronics industry, researchers and scientists have to contribute enormously with new ideas and techniques. Among various thin film depositions techniques, ALD is important due to its unique features such as self-limiting growth with precise thickness control, which leads to conformal and uniform film deposition. The biggest limitation of the ALD is lack of chemistries to deposit a broad range of materials that affords high-quality thin film depositions for device fabrication. New metal precursors to deposit transition metal films have to be developed due to limitations in currently available precursors, such as lack of thermal stability, poor reactivity, low volatility, and sometimes difficult preparations. A thesis objective is to develop new classes of ALD precursors to deposit Cr, Mn, Fe, Co, and Ni metal thin films by low-temperature ALD to afford self-limited, smooth film growth. These precursors will be tested for film growth and deposited films will be analyzed using surface and bulk thin film characterization methods.

Furthermore, ALD of binary and ternary lanthanide oxides films is challenging because of the hygroscopic nature of lanthanide oxides. These lanthanide oxides have important applications as high-k dielectric materials to replace current gate oxide materials in MOSFETs. Also, ternary lanthanide oxides (ABO$_3$/SrTiO$_3$ system) are needed to create high density and high mobility 2DEGs in non-polar/polar interfaces. Although the LaAlO$_3$/SrTiO$_3$ system has been well studied, other systems such as PrAlO$_3$/SrTiO$_3$ are poorly studied in 2DEG. The other main problem in ALD of lanthanide oxides is the poor self-limited growth with current precursors and high level of impurity contamination. The development of precursors that enhance the self-limited growth with low impurity levels is crucial. Additionally, the selected precursors should react with a mild oxygen source such as water to minimize the strongly oxidizing nature of ozone.
ALE is the reverse of ALD in which thin films are etched in a layer by layer fashion. Most ALE processes have used highly energetic plasmas or ions to overcome the thermodynamic barriers in etching reactions, which can result in substrate and surface damage. Therefore, the use of thermal energy for ALE so-called thermal ALE is important. In thermal ALE processes, it is important to tune the basic chemistry to facilitate thermodynamically favorable spontaneous etching reactions. Thermal ALE of transition metal and other metals is poorly studied and challenging. Surface modification followed by ligand exchange reactions is a potential mechanism to achieve thermal ALE of metals and other materials. Thicknesses of the metal film before and after etching will be measured to obtain the etch rate. Additionally, change of surface morphology and change of chemical composition of the film before and after etching will be determined.
CHAPTER 2: VOLATILE, THERMALLY STABLE, AND REACTIVE MID-TO-LATE TRANSITION METAL COMPLEXES CONTAINING ENAMINOLATE AND CARBOHYDRAZIDE LIGANDS AS PROMISING ATOMIC LAYER DEPOSITION (ALD) PRECURSORS

2.1 Introduction

Thin film deposition techniques continue to be of great importance as the number of ICs in a device increases while the size decreases, following Moore’s Law. Deposition techniques such as PVD and CVD continue to be important in the microelectronics industry for the fabrication of devices. However, PVD and CVD methods require high process temperatures, which can damage the deposited thin films and underlying substrates. Deposition of uniform and conformal thin films in high aspect ratio features cannot be achieved from traditional PVD or CVD techniques. ALD is a thin film deposition technique which provides Angstrom level thickness control enabled by self-limited surface chemical reactions. ALD minimizes the additional vapor phase reactions by introducing each reactant separately, followed by a purge step. The controlled pulse and purge sequences in ALD provide uniform and conformal film deposition in high aspect ratio features. ALD can be used to deposit a wide variety of materials such as metals, metal oxides, metal nitrides, metal sulfide, alloys, etc. ALD precursors must be highly volatile in order to provide a saturative precursor dose to the reaction chamber. The precursors should be thermally stable at high temperatures to mitigate undesirable CVD growth, and thus improve the self-limiting growth behavior of the ALD. Reactions between precursor and the co-reactant must be thermodynamically and kinetically favorable or exothermic. Reaction byproducts must be volatile and non-toxic to the film growth process. The high reactivity of precursors leads to a rapid saturation of surface-active site which is important for high film growth rate. Design of new ligand containing metal complexes with desirable ALD precursor properties is a challenging process. Although a broad range of precursors is available, there is a considerably high demand for the development of new precursor chemistries to obtain high-quality thin films.
Mid-to-late transition metal thin films are important in the microelectronics industry in various applications. Copper is used as interconnects in microelectronics devices, chromium and manganese are used as copper diffusion barriers, and chromium and cobalt are used as seed layers for copper metallization. Iron, cobalt, and nickel are used in magnetoresistive random access memory devices due to their magnetic properties. Low temperature ($\leq 200$ °C) thermal ALD is a promising method to deposit smooth, defect free, and high purity transition metal thin films. The ALD of copper metal is the best developed process among transition metals with the use of a broad range of copper precursors: $\text{Cu(dmap)}_2/\text{ZnEt}_2$ (dmap = dimethylamino-2-propoxy) at 100–120 °C, $\text{Cu(thd)}/\text{H}_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanediolate) at 190–260 °C, $\text{Cu(sBuNCMeNsBu)}_2/\text{H}_2$ at 150–200 °C, and $\text{Cu(hfac)}_2/\text{isopropanol}$ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) at 300 °C. Recently, the Winter group has developed a three-step process, using $\text{Cu(dmap)}_2/\text{formic acid/hydrazine}$ to afford a self-limited ALD growth of copper metal films at 100–170 °C. Another three-step process, using $\text{Cu(dmap)}_2/\text{formic acid/BH}_3(\text{NHMe}_2)$ on Pt and Pd, and a two-step process, using $\text{Cu(dmap)}_2/\text{BH}_3(\text{NHMe}_2)$ on Ru, were developed to deposit copper metal films at 130–160 °C and exhibited self-limiting growth behavior. Thermal ALD of chromium, iron, cobalt, and nickel thin film was reported using $\text{M(RR'COCNtBu)}_2/\text{BH}_3(\text{NHMe}_2)$ (M = Cr, Fe, Co, Ni). ALD of manganese was also possible using the Mn analog, however, the films oxidized upon air exposure. Fe$_2$O$_3$ and metallic iron films were deposited using a three-step process of Fe(hfac)$_2$•TMEDA/water/oxalic acid (TMEDA = N,N,N’,N’ tetramethylethylenediamine) and a two-step process of Fe(hfac)$_2$•TMEDA/oxalic acid by using ALD and molecular layer deposition (MLD) respectively. The Winter group has developed a self-limited cobalt metal ALD using Co($^{\text{tBu}}$DAD)$_2$ ($\text{DAD} = 1,4$-di-$\text{tBu}$-1,3-diabutadienyl) and formic acid at 180–190 °C or tert-butylamine at 180–200 °C. tert-Butylamine was also used to deposit nickel metal films using Ni($^{\text{tBu}}$DAD)$_2$ at 180–200 °C.
Moreover, strong reducing agents are required to lower the film resistivity by decreasing the film deposition temperature.

The synthesis and characterization of mid-to-late transition metal complexes containing carbohydrazide ligands (Figure 16) were recently reported. These metal complexes exhibited excellent thermal stability with high volatility. However, the reactivity of these mid-to-late transition metal complexes prepared using carbohydrazide ligands was not sufficient enough to use in ALD. Our goal was to increase the reactivity of these type of metal complexes while maintaining the favorable precursor properties, such as high volatility and high thermal stability. Herein we describe synthesis and characterization of enaminolate and a new type of carbohydrazide ligand, and their respective mid-to-late transition metal complexes. Thermal properties and reactivity of these newly synthesized metal complexes were investigated to assess their potential to use as ALD precursors.

2.2 Results and Discussion

2.2.1 Enaminolate Ligands Containing Mid-to-Late Transition Metal Complexes

The enaminolate ligand system has been selected to improve its reactivity compared to previously reported carbohydrazide ligand system. The carbohydrazide ligand system (Figure 16) does not containing an active proton to initiate any reactions with other co-reactants. Therefore, we hypothesize, the enaminolate ligand system should display enhanced reactivity compared to previously reported carbohydrazide ligand system.

Figure 16. General chemical structures of the carbohydrazide and enaminolate ligands

\[ \text{Reported carbohydrazide ligands} \quad \text{This work-enaminolate ligands} \]
Synthetic Aspects:

The enaminolate ligands (L\textsuperscript{1}–L\textsuperscript{3}) (Chart 3) were synthesized via treatment of 1-bromopinacolone with dimethylamine, piperidine, or pyrrolidine as described in the experimental section. Treatment of L\textsuperscript{1}H–L\textsuperscript{3}H with potassium hydride resulted in formation of KL\textsuperscript{1}–KL\textsuperscript{3}, which were subsequently treated with anhydrous MCl\textsubscript{2} (M = Cr, Mn, Fe, Co, Ni) at 23 °C in tetrahydrofuran (THF) to obtain 1–15 as crystalline solids (Scheme 1). Complexes 1–15 were purified by vacuum sublimation. The reported crystalline yields of 1–15 were obtained via sublimation between 90–180 °C at 0.05 Torr. Treatment of KL\textsuperscript{1}–KL\textsuperscript{3} with anhydrous CuCl\textsubscript{2} resulted in formation of copper metal. Therefore, enaminolate ligand-containing copper complexes could not be isolated.

**Chart 3.** Chemical structures of L\textsuperscript{1}–L\textsuperscript{3}
Scheme 1. Preparation of 1–15

The structures of 1–15 were determined by using X-ray crystallographic, spectroscopic, and analytical methods. X-ray crystal structures were obtained for 1, 5, 6, 8–10, and 15. Complexes 1–4, 6–9, and 11–14 were paramagnetic, displaying very broad peaks in their $^1$H NMR spectra. According to solution state magnetic moment experiments, 1–4, 6–9, and 11–14 exhibited high spin electronic configurations.

X-ray Crystallographic Data

X-ray quality crystals of 1, 5, 6, 8–10, and 15 were collected via sublimation, to determine the solid-state geometries. X-ray quality crystals could not be obtained for 2, 7, and 12, regardless of crystallization method (sublimation or solvent based). Tables 1 and 2 summarize experimental crystallographic data with selected bond lengths and angles for 1, 5, 6, 8–10, and 15 respectively. Figures 17–23 show representative perspective views of 1, 5, 6, 8–10, and 15 respectively.
According to the crystal structures of 1–5, only 1 and 5 were monomeric, presumably due to the high spin square planar geometry adopted by Cr$^{2+}$ and Ni$^{2+}$. Complexes 2, 3, and 4 were dimeric, most likely due to the large atomic radii of Mn$^{2+}$, Fe$^{2+}$, and Co$^{2+}$. In the dimeric complexes each metal atom was bonded to nitrogen and oxygen donor atoms in a $\kappa^2$-fashion. Each metal center was bound to two enaminolate ligands, with one oxygen donor serving as a bridge to the adjacent metal center in a $\mu-\kappa^1:k^2$-fashion. A low precision crystal structure of 4 revealed a dimeric structure with the connectivity shown in Scheme 1. According to the crystallographic and analytical data collected, 6–15 are monomeric. In monomeric structures, the ligands (L$^1$–L$^3$) are coordinated to the metal center in a $\kappa^2$-N,O fashion via terminal oxygen and nitrogen donor atoms, which resulted in stable five-membered chelate rings.

The M–O and M–N bond lengths decreased moving from left to right, across the periodic table. The M–O bond distances of 1, 6, 8, and 9 ranged from 1.9107(7) to 1.9599(8) Å, whereas the M–O bond distances of 5, 10, and 15 ranged from 1.8379(7)–1.8419(9) Å. This slightly elongated M–O bond in 1, 6, 8, and 9 is consistent with the larger ionic radii of Cr(II), Fe(II), and Co(II), compared to Ni(II). Following a similar pattern, the M–N bond distances of 1, 6, 8, and 9 (2.1893(7) to 2.0991(9) Å) were longer than the M–N bond distances of 5, 10, and 15 (1.9263(6) to 1.9371(10) Å). The core C–O (1.3274(14) to 1.3338(10) Å) and C–N (1.4528(12) to 1.4599(9) Å) bond distances of 1, 5, 6, 10 and 15 are slightly shorter than typical C–O (1.43 Å)$^{125}$ and C–N (1.47 Å)$^{125}$ bond distances, respectively. This slight shortening of bond distances could be due to the coordination of oxygen and nitrogen atoms with the metal center. The C=C bond length within the core was consistent with the typical C=C bond distance (1.34 Å)$^{125}$. In 1, 5, 6, 10, and 15, the intra-ligand N–M–O bond angles were between 83.73(4) and 88.20(2)$^\circ$, with inter-ligand N–M–O bond angles between 91.10(2) and 96.27(4)$^\circ$. Furthermore, the inter-ligand N–M–N and O–M–O bond angles were 180$^\circ$, consistent with the square planar geometry.
In 8 and 9, the intra-ligand N–M–O bond angles between 83.57(3) and 86.07(3)°, with inter-ligand N–M–O bond angles between 112.85(3) and 118.19(3)°. Moreover, the inter-ligand N–M–N and O–M–O bond angles were 123.42(4) and 146.12(12)°, consistent with distorted tetrahedral geometry.
Table 1. Experimental crystallographic data for 1, 5, 6, and 8

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aR (F) = ∑|F₀| - |F| / ∑|F₀|.  bRw(F²) = [∑w (F₀² - F²)² / ∑w (F₀²)²]¹/²
Table 1. Experimental crystallographic data for 9, 10, and 15

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^a R (F) = \sum ||F_o| - |F_o|| / \sum |F_o|.  
^b R_{w(F^2)} = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_c^2)^2]^{1/2}
Table 2. Selected bond lengths (Å) and angles (deg) for 1, 5, 6, and 8

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Table 2. Selected bond lengths (Å) and angles (deg) for 9, 10, and 15

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Figure 17. Perspective view of 1 with thermal ellipsoids at 50% probability level
Figure 18. Perspective view of 5 with thermal ellipsoids at 50% probability level
Figure 19. Perspective view of 6 with thermal ellipsoids at 50% probability level
Figure 20. Perspective view of 8 with thermal ellipsoids at 50% probability level
Figure 21. Perspective view of 8 with thermal ellipsoids at 50% probability level.
Figure 22. Perspective view of 10 with thermal ellipsoids at 50% probability level.
Figure 23. Perspective view of 15 with thermal ellipsoids at 50% probability level
**Thermal Properties**

Table 3 summarizes melting points, solid state thermal decomposition temperatures, sublimation temperatures, and percent recovery data for 1–15. As described in the experimental section, melting point and solid-state thermal decomposition temperatures were determined in sealed capillary tubes. The highest solid-state thermal decomposition temperature was observed for 2 and 7 at 303 °C. Overall, the thermal decomposition temperatures were highest for 6–10, lowest for 1–5, with 11–15 falling in between the two extremes. The thermal decomposition temperature increased as the ligand bulkiness increased (L₁< L₃< L₂). The decreased steric bulk of the ligand may not be sufficient enough to protect the metal center from intermolecular decomposition reactions. Excellent thermal stability is important in ALD to minimize additional CVD growth during film deposition. The sublimation temperatures for 1–15 were determined by heating ~1.0 g of the crude material for 4–5 h at 0.05 Torr. Observed sublimation temperatures were lowest for 1–5 (70–150 °C), highest for 6–10 (115–180 °C), with 11–15 residing in the middle. The highest sublimation temperatures were observed for the complexes with the highest molecular weight (6–10). The percent recovery values for all the complexes were between 80–98 %. Complexes 1–15 displayed high thermal stability and volatility, similar to previously reported metal complexes containing carbohydrazide ligands. The sublimation temperatures of 1–15 were slightly higher than previously reported carbohydrazide-containing metal complexes. The complexes with larger atoms, such a Cr²⁺, Mn²⁺, and Fe³⁺ bound to the carbohydrazide ligands, were non-volatile, due to the dimerization. However, in this work, 1–15 were volatile and sublimed below 180 °C at 0.05 Torr.
Table 3. Melting point, solid state thermal decomposition temperature, sublimation temperature, and percent recovery for 1–15

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<th>sublimation temperature (ºC/0.05 Torr)</th>
<th>% recovery</th>
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<td>3 (Fe)</td>
<td>243–244</td>
<td>250</td>
<td>130</td>
<td>98</td>
</tr>
<tr>
<td>4 (Co)</td>
<td>219–212</td>
<td>250</td>
<td>120</td>
<td>98</td>
</tr>
<tr>
<td>5 (Ni)</td>
<td>160–162</td>
<td>247</td>
<td>70</td>
<td>98</td>
</tr>
<tr>
<td>6 (Cr)</td>
<td>165–167</td>
<td>278</td>
<td>115</td>
<td>98</td>
</tr>
<tr>
<td>7 (Mn)</td>
<td>277–279</td>
<td>303</td>
<td>180</td>
<td>90</td>
</tr>
<tr>
<td>8 (Fe)</td>
<td>211–213</td>
<td>248</td>
<td>120</td>
<td>95</td>
</tr>
<tr>
<td>9 (Co)</td>
<td>238–241</td>
<td>290</td>
<td>145</td>
<td>95</td>
</tr>
<tr>
<td>10 (Ni)</td>
<td>212–214</td>
<td>274</td>
<td>155</td>
<td>98</td>
</tr>
<tr>
<td>11 (Cr)</td>
<td>158–160</td>
<td>230</td>
<td>115</td>
<td>98</td>
</tr>
<tr>
<td>12 (Mn)</td>
<td>289–291</td>
<td>303</td>
<td>170</td>
<td>80</td>
</tr>
<tr>
<td>13 (Fe)</td>
<td>236–237</td>
<td>256</td>
<td>130</td>
<td>98</td>
</tr>
<tr>
<td>14 (Co)</td>
<td>187–189</td>
<td>250</td>
<td>130</td>
<td>95</td>
</tr>
<tr>
<td>15 (Ni)</td>
<td>186–189</td>
<td>267</td>
<td>117</td>
<td>98</td>
</tr>
</tbody>
</table>

Thermogravimetric analysis (TGA) plots of 6–10 are shown in Figure 24. The TGA plots exhibited single-step weight loss, with a low percentage of non-volatile residues. Complex 7 displays the lowest volatility and the highest sublimation temperature. Complexes 6 and 8–10 have similar volatility according to the TGA plots. Complexes 1–5 and 11–15 should display similar TGA traces to 6–10, considering the similarity of spectral and analytical characterizations data. A clean evaporation, with a low percentage of non-volatile residual, is important in ALD, because the precursor can be delivered to the deposition chamber without decomposition, resulting in a high-quality thin film.119,120
Interestingly, 1–15 thermally decomposed to their respective metals at high temperatures. To evaluate the decomposition products, 6–10 were heated in a tube furnace, under flow of nitrogen, for 4 h at 400 °C. The resulting black residues were analyzed, using PXRD. PXRD patterns of cobalt metal and nickel metal were collected and shown in Figures 25 and 26. According to the XRD patterns, cobalt metal adopted a cubic phase and nickel metal adopted a hexagonal phase. PXRD patterns of other metals such as chromium, manganese, and iron were not observed, because, electropositive metal such as chromium, manganese, and iron may also oxidized upon exposure to air and result in amorphous oxides. The self-thermal decomposition of 1–15 can be associated with β-hydride elimination (Scheme 2). The β-hydride on the enaminolate ligand can be eliminated at high temperatures and coordinated to the transition metal center to form unstable transition metal hydride, which then reduced to metal.
Figure 25. PXRD patterns of cobalt metal after thermal decomposition of 9

Figure 26. PXRD patterns of nickel metal after thermal decomposition of 10
Precursor Reactivity

To evaluate the reactivity of 1–15, solution reduction experiments were undertaken. Table 4 summarizes the results obtained after treating the selected metal complexes with an excess amount of reducing agent (hydrazine monohydrate) at 23 ºC in THF. Immediate reactivity (color changed) was observed upon mixing the reactants, indicating high reactivity of 1–15. Figure 27 shows a PXRD pattern obtained for nickel metal (cubic phase) after treatment of 10 with hydrazine monohydrate.

**Table 4.** Summary of the solution reduction experiments using hydrazine monohydrate at 23 ºC in THF

<table>
<thead>
<tr>
<th></th>
<th>Immediate color change black solid after ~3 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Immediate color change black solid after ~24 h</td>
</tr>
<tr>
<td>4</td>
<td>Immediate color change, black solid after ~3 h</td>
</tr>
<tr>
<td>5</td>
<td>Immediate color change brown/green solid after ~2 h</td>
</tr>
<tr>
<td>6</td>
<td>Immediate color change clear solution</td>
</tr>
</tbody>
</table>

**Figure 27.** PXRD patterns of nickel metal after reacting 10 with NH₂NH₂

![PXRD pattern of nickel metal](image-url)
2.2.2 Carbohydrazide Ligands-Containing Cobalt and Nickel Metal Complexes

A new carbohydrazide ligand system has been also selected to improve its reactivity compared to previously reported carbohydrazide ligand system. The previously reported carbohydrazide ligand system (Chart 4) does not containing an active proton to initiate any reactions with other co-reactants. By contrast, the new carbohydrazide ligand system does contain an active proton on the nitrogen atom, which potentially can participate in initiating reactions. Therefore, we hypothesize, the new carbohydrazide ligand system should display enhanced reactivity compared to previously reported carbohydrazide ligand system.

**Chart 4.** General structures of carbohydrazide and enaminolate ligands

![Chart 4](image)

**Reported carbohydrazide ligands**  **This work-enaminolate ligands**  **This work-carbohydrazide ligands**

Moreover, there are two acidic protons attached on both nitrogen atoms, as shown in Scheme 3 (Hₐ and Hₐ) in the newly synthesized neutral carbohydrazone ligand. However, the acidity of the H₂ is higher than the acidity of the H₁ due to the resonance stabilization with adjacent carbonyl group. Therefore, Hₐ will selectively react with potassium hydride to result in an anionic carbohydrazide ligand.

**Scheme 3.** Formation of carbohydrazide
Synthetic Aspects:

L⁴H and L⁵H (Chart 5) were synthesized according to a modified published procedure. Treatment of L⁴H and L⁵H with potassium hydride resulted in formation of the anionic ligands (L⁴ and L⁵), which were treated with anhydrous CoCl₂ or NiCl₂·CH₃CN to afford 16–19 (Scheme 4). Complexes 16–19 are solids at 23 ºC, and isolated by vacuum sublimation. Complexes 16–19 decomposed upon exposure to ambient atmospheric conditions. According to ¹H NMR spectra and solid-state magnetic susceptibility measurements, 16 and 18 are paramagnetic with a high spin electronic configuration. Complexes 17 and 19 were diamagnetic by their ¹H NMR spectra.

Chart 5. Chemical structures of L⁴H and L⁵H

Scheme 4. Preparation of 16–19
X-ray Crystallographic Data

X-ray quality crystals of 16–19 were collected by sublimation, and crystal structures were analyzed to determine solid-state geometries. Crystallographic data, bond lengths, and angles for 16–19 are summarized in Tables 5 and 6 and Figures 28–31. Complex 16 is a dimer, consisting of typical $\kappa^2$-N,O coordination with terminal nitrogen and oxygen donor atoms of the first ligand. And complex 16 shows bridging bonds with oxygen and nitrogen atoms of the second and third ligands respectively, in a $\mu-\kappa^1$: $k^2$-fashion. The calculated geometry index of each cobalt centers is close to 1 (0.840). Therefore, the geometry of the cobalt metal center should be distorted tetrahedral. Complexes 17–19 are monomeric, and show $\kappa^2$-N,O coordination with terminal oxygen and nitrogen donor atoms of the ligand, resulting in five-membered chelate rings. Complexes 17 and 19 displays similar bond lengths and angles and adopt square planar geometry. N–M–N and O–M–O bond angles are close to 180° and 170° respectively with N–M–O bond angles of approximately 95° and 84°. Therefore, 17 and 19 adopt typical Ni$^{2+}$ d$^8$ square planar geometry by considering bond angles and lengths. Complex 18 afford a distorted tetrahedral geometry around the Co center, with two asymmetric ligands.

Interestingly, X-ray crystal structures reveal that 16 is a dimer and 18 is a monomer which contain the same cobalt metal center with different substituents. Instead of two tert-butyl substituents in 16, 18 has one tert-butyl and one isopropyl substituent. When considering the steric bulk of substituent groups tert-butyl is bulkier than isopropyl group, therefore, 18 is expected to be a dimer instead of 16. Preassembly, the energy difference between the dimeric and monomeric structures can be very small to differentiate 16 and 18.
Table 5. Experimental crystallographic data for **16**, **17**, **18**, and **19**

<table>
<thead>
<tr>
<th></th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C\textsubscript{36}H\textsubscript{72}CoN\textsubscript{8}O\textsubscript{4}</td>
<td>C\textsubscript{18}H\textsubscript{38}N\textsubscript{4}NiO\textsubscript{2}</td>
<td>C\textsubscript{16}H\textsubscript{34}N\textsubscript{4}CoO\textsubscript{2}</td>
<td>C\textsubscript{16}H\textsubscript{34}N\textsubscript{4}NiO\textsubscript{2}</td>
</tr>
<tr>
<td>fw</td>
<td>802.90</td>
<td>401.23</td>
<td>373.40</td>
<td>373.18</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>C 1/2/c 1</td>
<td>P-1</td>
<td>C 1/2/c 1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.9468(5)</td>
<td>13.6192(6)</td>
<td>10.5949(9)</td>
<td>15.0036(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.9338(6)</td>
<td>13.6762(6)</td>
<td>10.8154(8)</td>
<td>11.7984(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.3953(6)</td>
<td>11.9202(5)</td>
<td>10.8478(9)</td>
<td>11.6887(6)</td>
</tr>
<tr>
<td>α (deg)</td>
<td>65.322(2)</td>
<td>90</td>
<td>113.694(4)</td>
<td>90</td>
</tr>
<tr>
<td>β (deg)</td>
<td>81.315(3)</td>
<td>98.195(2)</td>
<td>116.578(5)</td>
<td>98.405(3)</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>88.012(3)</td>
<td>90</td>
<td>95.654(5)</td>
<td>90</td>
</tr>
<tr>
<td>V (Å\textsuperscript{3})</td>
<td>1112.66(10)</td>
<td>2197.57(17)</td>
<td>957.37(14)</td>
<td>2046.89(18)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>T (K)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.7103</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>ρ\textsubscript{calc} (g cm\textsuperscript{-3})</td>
<td>1.198</td>
<td>1.213</td>
<td>1.295</td>
<td>1.211</td>
</tr>
<tr>
<td>μ (mm\textsuperscript{-1})</td>
<td>0.788</td>
<td>0.900</td>
<td>0.911</td>
<td>0.961</td>
</tr>
<tr>
<td>R (F) (%)\textsuperscript{a}</td>
<td>2.77</td>
<td>4.15</td>
<td>4.57</td>
<td>3.26</td>
</tr>
<tr>
<td>R\textsubscript{w} (F) (%)\textsuperscript{a}</td>
<td>7.71</td>
<td>11.98</td>
<td>13.01</td>
<td>11.57</td>
</tr>
</tbody>
</table>

\textsuperscript{a}R (F) = \sum |F_\text{O}| - |F_\text{O}'| / \sum |F_\text{O}|. \textsuperscript{b}R\textsubscript{w}(F^2) = [\sum w (F_\text{O}^2 - F_\text{C}^2)^2 / \sum w F_\text{C}^2]^1/2
Table 6. Selected bond lengths (Å) and angles (deg) for 16, 17, 18, and 19

<table>
<thead>
<tr>
<th></th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>M–N</td>
<td>2.0644(6)</td>
<td>1.9129(19)</td>
<td>2.141(3)</td>
<td>1.9162(8)</td>
</tr>
<tr>
<td></td>
<td>2.0500(6)</td>
<td>1.9129(19)</td>
<td>2.278(3)</td>
<td>1.9162(8)</td>
</tr>
<tr>
<td>M–O</td>
<td>1.921(6)</td>
<td>1.8428(15)</td>
<td>1.931(2)</td>
<td>1.8419(8)</td>
</tr>
<tr>
<td></td>
<td>1.9272(6)</td>
<td>1.8428(15)</td>
<td>2.006(2)</td>
<td>1.8419(8)</td>
</tr>
<tr>
<td>C–O</td>
<td>1.3039(9)</td>
<td>1.304(3)</td>
<td>1.269(4)</td>
<td>1.3045(12)</td>
</tr>
<tr>
<td></td>
<td>1.3102(8)</td>
<td></td>
<td>1.298(4)</td>
<td></td>
</tr>
<tr>
<td>N–C</td>
<td>1.3051(9)</td>
<td>1.302(3)</td>
<td>1.334(4)</td>
<td>1.2931(12)</td>
</tr>
<tr>
<td></td>
<td>1.2984(9)</td>
<td></td>
<td>1.304(4)</td>
<td></td>
</tr>
<tr>
<td>N–N</td>
<td>1.4695(9)</td>
<td>1.475(2)</td>
<td>1.469(3)</td>
<td>1.4750(11)</td>
</tr>
<tr>
<td></td>
<td>1.4493(8)</td>
<td></td>
<td>1.470(3)</td>
<td></td>
</tr>
<tr>
<td>N–M–O</td>
<td>117.89(3)</td>
<td>95.29(7)</td>
<td>105.28(9)</td>
<td>94.95(3)</td>
</tr>
<tr>
<td></td>
<td>116.75(2)</td>
<td>95.29(7)</td>
<td>93.19(9)</td>
<td>94.95(3)</td>
</tr>
<tr>
<td></td>
<td>82.60(2)</td>
<td>84.79(7)</td>
<td>80.49(9)</td>
<td>84.90(3)</td>
</tr>
<tr>
<td></td>
<td>104.09(2)</td>
<td>84.79(7)</td>
<td>74.11(9)</td>
<td>84.90(3)</td>
</tr>
<tr>
<td>N–M–N</td>
<td>111.26(2)</td>
<td>179.07(10)</td>
<td>169.18(9)</td>
<td>178.08(4)</td>
</tr>
<tr>
<td>O–M–O</td>
<td>123.27(3)</td>
<td>170.31(10)</td>
<td>140.63(10)</td>
<td>171.40(5)</td>
</tr>
</tbody>
</table>
Figure 28. Perspective view of 16 with thermal ellipsoids at 50% probability level
Figure 29. Perspective view of 17 with thermal ellipsoids at 50% probability level
Figure 30. Perspective view of 18 with thermal ellipsoids at 50% probability level
Figure 31. Perspective view of 19 with thermal ellipsoids at 50% probability level
Thermal Properties

To understand the thermal properties of 16–19, melting points, thermal decomposition temperatures, sublimation temperatures, and percentage recovery values were collected and are summarized in Table 7. When both substituted groups on the ligand were tert-butyl (16 and 17), melting points of the complexes were higher than compared to the metal complexes with tert-butyl and isopropyl substituted ligands (18 and 19). The difference in the melting point can be due to the formation of asymmetric complex because of the isopropyl substituent, compared to the symmetric tert-butyl substituent. Furthermore, melting point values of the Ni complexes (17 and 19) were higher than the Co complexes (16 and 18). This contrast can be attributed to the symmetric square planar geometry of the Ni system that allows a dense-packing of molecules, whereas, distorted tetrahedral geometry of the Co system allows a less-dense packing resulting in lower melting point.

Table 7. Melting point, solid state thermal decomposition temperature, sublimation temperature, and percent recovery for 16–19

<table>
<thead>
<tr>
<th>complex</th>
<th>melting point (ºC)</th>
<th>solid state thermal decomposition temperature (ºC)</th>
<th>sublimation temperature (ºC/0.05 Torr)</th>
<th>% recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 (Co)</td>
<td>198–200</td>
<td>245</td>
<td>140</td>
<td>92</td>
</tr>
<tr>
<td>17 (Ni)</td>
<td>266–268</td>
<td>276</td>
<td>140</td>
<td>99</td>
</tr>
<tr>
<td>18 (Co)</td>
<td>180–182</td>
<td>235</td>
<td>120</td>
<td>90</td>
</tr>
<tr>
<td>19 (Ni)</td>
<td>236–239</td>
<td>254</td>
<td>140</td>
<td>99</td>
</tr>
</tbody>
</table>

The TGA plots of 16–19 are shown in Figure 32. Complexes 16–19 display single step weight-loss, with nearly zero non-volatile residuals. The volatility of cobalt complexes (16 and 18) are higher than that of the nickel complexes (17 and 19), when considering the TGA onset
temperatures. The lower onset temperatures were observed for the higher volatility. A single step weight loss is important in ALD, because it provide a good vapor delivery.

Figure 32. TGA plots for 16–19

![TGA plots for 16–19](image)

Similar to the enaminolate ligand-containing metal complexes discussed earlier, these metal complexes decompose thermally to their respective metals. This property may be important in depositing metal thin films via ALD. PXRD patterns of cobalt and nickel after thermal decomposition at 400 °C for 4 h under flow of nitrogen are shown in Figure 33. According to the XRD patterns, both cobalt and nickel metal afforded hexagonal phases after thermal decompositions.
Figure 33. PXRD patterns of (a) cobalt metal and (b) nickel metal after thermal decomposition of 16 and 17, respectively.
Precursor Reactivity

To test the reactivity of $^{16–19}$, solution reduction experiments were performed, and the results are summarized in Table 8. Complex $^{16}$ and $^{19}$ were treated with an excess amount of reducing agent at 23 °C and/or under reflux conditions in THF. According to the results, these compounds are reactive at 23 °C toward reducing agents such as BH$_3$NHMe$_2$, BH$_3$(SMe$_2$), and NH$_2$NH$_2$•H$_2$O. After a refluxing, black precipitates/solids were observed and the resulted black solids could be metal oxides. Similar to enaminolate ligands-containing metal complexes ($^{1–15}$), these carbohydrazide ligands-containing metal complexes ($^{16–19}$) display good reactivity towards different reducing agents.

Table 8. Summary of the solution reduction experiments after reacting of each complex with different reducing agents (a) at 23 °C and (b) after refluxing in THF

<table>
<thead>
<tr>
<th>Reducing agent</th>
<th>$^{16}$</th>
<th>$^{19}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_3$(NHMe$_2$)</td>
<td>pink solution, a black precipitate$^b$</td>
<td>black precipitate$^b$</td>
</tr>
<tr>
<td>BH$_3$(SMe$_2$)</td>
<td>black precipitate$^b$</td>
<td>color change, a black precipitate$^b$</td>
</tr>
<tr>
<td>NH$_2$NH$_2$•H$_2$O</td>
<td>black solid: a sticks to stir bar</td>
<td>black solid: a sticks to stir bar</td>
</tr>
<tr>
<td>CH$_3$CONNH$_2$</td>
<td>color change$^b$</td>
<td>color change$^b$</td>
</tr>
<tr>
<td>Formic acid</td>
<td>color change$^b$</td>
<td>white precipitate$^b$</td>
</tr>
</tbody>
</table>

2.3 Conclusions

Treatment of KL$^1$–KL$^3$ with anhydrous metal chlorides affords $^{1–15}$. Crystal structures of $^{1, 5, 6, 10}$ and $^{15}$ displays square planar chromium and nickel complexes and distorted tetrahedral manganese, iron, and cobalt complexes. Paramagnetic chromium, manganese, iron, and cobalt complexes afford high spin electronic configurations according to solution-state magnetic susceptibility measurements. Complexes $^{1, 5}$, and $^{6–15}$ are monomeric, while $^{2, 3,}$, and $^{4}$ are dimeric in the solid-state according to crystallographic and other analytical data. Complexes $^{1–15}$
show promising thermal properties and reactivity for use as ALD precursors. Interestingly, 1–15 thermally self-decompose to their respective metals, allowing for the possibility to deposit transition metal thin films by ALD.

Treatment of KL\textsuperscript{4} and KL\textsuperscript{5} with anhydrous CoCl\textsubscript{2} and NiCl\textsubscript{2}•CH\textsubscript{3}CN afforded 16–19, which were isolated by vacuum sublimation. X-ray crystal structures revealed that 16 is a dimer, while 17–19 are monomers in the solid-state. These newly synthesized carbohydrazide ligand-containing metal complexes display similar structural and thermal properties to enaminolate ligand-containing metal complexes. Overall, the reactivity of 1–19 has been enhanced, without destroying thermal properties compared to previously reported metal complexes containing carbohydrazide ligands.

2.4 Experimental Section

General Considerations.

All metal-organic reactions were carried out in argon filled Schlenk line and glove box environments. Solvents were dried over activated molecular sieves and distilled from sodium prior to use. Anhydrous metal halides (CrCl\textsubscript{2}, MnBr\textsubscript{2}, FeCl\textsubscript{2}, CoCl\textsubscript{2}, and NiCl\textsubscript{2}) were purchased from Strem Chemicals and used as received. NiCl\textsubscript{2}•CH\textsubscript{3}CN was prepared according to a literature procedure.\textsuperscript{126} NiCl\textsubscript{2}•DME adduct was prepared by refluxing anhydrous NiCl\textsubscript{2} with excess dimethoxyethane for 4 h. Potassium hydride (in 30% mineral oil) was purchased from Sigma Aldrich and was washed with hexanes and dried before used. Pinacolone, bromine, dimethyl amine (40% W/W in water), piperidine, and pyrrolidine were purchased from Sigma Aldrich and used as received.

\textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra were obtained from an Agilent MR-400 MHz spectrometer using benzene-\textit{d}_6 or chloroform-\textit{d}. Solution state magnetic susceptibility values were determined according to the Evans method.\textsuperscript{127} Infrared spectra were obtained either in nujol mull or neat
(liquid/solid) using a Shimadzu IRTracer-100 spectrometer. Melting points were determined using an Electrothermal melting point apparatus in a flame sealed capillary tube. Thermogravimetric analysis was carried out on a Netzsch TG 209F1 Libra thermo-balance, that was housed in a nitrogen-filled glove box. Sublimation and percentage recovery experiments were carried out in 20 cm long glass tubes with an appropriate adaptor which was opened to 0.05 Torr vacuum. For the percentage recovery experiments, ~100 mg of pre-sublimed samples were used. For the thermal decomposition experiments, ~100 mg of sample was heated at 400 ºC under flow of nitrogen for 4 h in a tube furnace. The resulting black powders were analyzed using XRD. CHN elemental microanalyses were performed by Midwest Micro Laboratory, Indianapolis, IN.

**Preparation of 1-(dimethylamino)-3,3-dimethylbutan-2-one (L¹H)**

1-Bromopinacolone was synthesized according to published procedures.²⁸,²⁹ To a 250 mL round bottomed flask, a magnetic stir bar, 1-bromopinacolone (3.500 g, 19.00 mmol), triethylamine (8.2 mL, 58.0 mmol), and diethyl ether (100 mL) were added and cooled to 0 ºC. Then dimethylamine solution (40% W/W) (7.4 mL, 58.0 mmol) was slowly added and stirred for 16 h at 23 ºC. After overnight stirring, the organic layer was separated. The aqueous layer was extracted with two 20 mL portions of diethyl ether. Organic layers were combined and dried over anhydrous MgSO₄ and filtered through glass funnel a fitted to a fluted filter paper. The volatile components were removed under reduced pressure. The crude oil was filtered through a pad of silica gel filled in to a small disposable glass pipette. A pale yellow oil was obtained (2.400 g, 67%): IR (neat, cm⁻¹) 1707 (s, C=O); ¹H NMR (CDCl₃, 23 ºC, δ) 3.35 (bs, 2H), 2.24 (bs, 6H), 1.03 (bs, 9H); ¹³C{¹H} NMR (CDCl₃, 23 ºC, ppm) 211.66 (s, C=O), 62.71(s, N(CH₂)), 45.07 (s, N(CH₃)₂), 43.16 (s, C(CH₃)₃), 26.03 (s, C(CH₃)).
Preparation of 3,3-dimethyl-1-(piperidin-1-yl)butan-2-one (L²H)

L²H was synthesized according to modified published procedures.¹³⁰,¹³¹ To a 250 mL round bottomed flask, a magnetic stir bar, 1-bromopinacolone (5.000 g, 28.00 mmol), piperidine (8.3 mL, 84.0 mmol), K₂CO₃ (11.600 g, 84.00 mmol), and CH₃CN (100 mL) were added and stirred for 16 h at 23 ºC. Then a 1M NaOH solution (100 mL) was added. The organic and aqueous layers were separated and the aqueous layer was extracted with two 20 mL portions of ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄ and filtered through a glass funnel fitted to a fluted filter paper. Solvent was removed under reduced pressure. The crude oil was filtered through a pad of silica gel filled inside a small glass pipette using hexanes: ethyl acetate 1:1 mixture. Excess solvent was evaporated. A pale yellow oil was obtained (3.000 g, 60%): IR (neat, cm⁻¹) 1720 (s, C=O); ¹H NMR (CDCl₃, 23 ºC, δ) 3.26 (bs, 2H), 2.34 (bs, 4H), 1.16 (bs, 4H), 1.37 (bs, 2H), 1.01 (bs, 9H); ¹³C{¹H} NMR (CDCl₃, 23 ºC, ppm) 212.40 (s, C=O), 63.30 (s, CH₂CO), 54.90 (s, NCH₂), 43.60 (s, C(CH₃)₃), 26.63 (s, C(CH₃)₃), 25.96 (s, CH₂CH₂), 24.25 (s, CH₂(CH₂)₂).

Preparation of 3,3-dimethyl-1-(pyrrolidin-1-yl)butan-2-one (L³H)

Following the procedure similar to preparation of L¹H, L³H was prepared. To a 250 mL round bottomed flask, 1-bromopinacolone (2.570 g, 14.00 mmol), diethyl ether (60 mL), and triethylamine (6.0 mL, 43.0 mmol) were added and cooled to 0 ºC. Then pyrrolidine (3.6 mL, 43.0 mmol) was slowly added and stirred for 16 h at 23 ºC. A yellow oil was obtained (2.200 g, 90%): IR (neat, cm⁻¹): 1716 (s, C=O); ¹H NMR (CDCl₃, 23 ºC, δ) 3.46 (bs, 2H), 2.50 (bm, 4H), 1.72 (bm, 4H), 1.08 (bs, 9H); ¹³C{¹H} NMR (CDCl₃, 23 ºC, ppm) 212.27 (s, C=O), 60.06 (s, N(CH₂)CH₂), 54.06 (s, N(CH₂)CO), 26.29 (s, C(CH₃)₃), 23.51 (CH₂CH₂).
Preparation of Cr(L\textsuperscript{1})\textsubscript{2} (1)

A 100 mL Schlenk flask was charged with L\textsuperscript{1}H (0.500 g, 3.49 mmol) and THF (20 mL). To that flask, KH (0.154 g, 3.84 mmol) was slowly added inside the argon filled glove box. The reaction mixture was stirred for 16 h at 23 °C. The stirred solution was slowly cannulated to another Schlenk flask charged with anhydrous CrCl\textsubscript{2} (0.213 g, 1.75 mmol) in THF (20 mL) and was stirred for 16 h at 23 °C. A brown colored solution was observed, and solvent was removed under reduced pressure. The resulting brown solid was sublimed at 90 °C at 0.05 Torr to afford 1 (0.294 g, 25%) as brown-orange colored crystals: mp 153–156 °C; IR (nujol, cm\textsuperscript{-1}) 2755 (w), 1618 (s), 1377 (s), 1330 (s), 1136 (s); μ\textsubscript{eff} = 5.38 μ\textsubscript{B} in benzene solution. Anal. Calcd. for C\textsubscript{16}H\textsubscript{32}CrN\textsubscript{2}O\textsubscript{2}: C, 57.12; H, 9.59; N, 8.33. Found: C, 57.49; H, 9.90; N, 8.05.

Preparation of Mn(L\textsuperscript{1})\textsubscript{2} (2)

Following the procedure similar to preparation of 1, 2 was prepared. Anhydrous MnBr\textsubscript{2} (0.375 g, 1.75 mmol) was treated with KL\textsuperscript{1} (prepared from treating L\textsuperscript{1}H (0.500 g, 3.49 mmol) with KH (0.154 g, 3.84 mmol)) at 23 °C in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting yellow solid was sublimed at 150 °C at 0.05 Torr to afford 2 (0.237 g, 20%) as light yellow colored crystals: mp 251–254 °C; IR (nujol, cm\textsuperscript{-1}) 2727 (w), 1598 (s), 1377 (s), 1340 (s), 1259 (s); μ\textsubscript{eff} = 6.60 μ\textsubscript{B} in benzene solution. Anal. Calcd. for C\textsubscript{32}H\textsubscript{64}Mn\textsubscript{2}N\textsubscript{4}O\textsubscript{4}: C, 56.63; H, 9.50; N, 8.25. Found: C, 52.77; H, 9.35; N, 6.57.

Preparation of Fe(L\textsuperscript{1})\textsubscript{2} (3)

Following the procedure similar to preparation of 1, 3 was prepared. Anhydrous FeCl\textsubscript{2} (0.170 g, 1.34 mmol) was treated with KL\textsuperscript{1} (prepared from treating L\textsuperscript{1}H (0.770 g, 5.37 mmol) with KH (0.237 g, 5.91 mmol)) at 23 °C in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting brown solid was sublimed at 130 °C at 0.05 Torr to afford 3 (0.457 g, 25%) as brown-green colored crystals: mp 243–244 °C; IR (nujol, cm\textsuperscript{-1}) 2777 (w), 1604 (s), 1334
(s), 1215 (s), 1138 (s): $\mu_{\text{eff}} = 4.87 \mu_B$ in benzene solution. Anal. Calcd. for $\text{C}_{32}\text{H}_{64}\text{Fe}_2\text{N}_4\text{O}_4$: C, 56.47; H, 9.48; N, 8.23. Found: C, 56.03; H, 9.36; N, 7.91.

**Preparation of (Co(L$^1$)$_2$)$_2$ (4)**

Following the procedure similar to preparation of 1, 4 was prepared. Anhydrous CoCl$_2$ (0.226 g, 1.74 mmol) was treated with KL$^1$ (prepared from treating L$^1$H (0.500 g, 3.49 mmol) with KH (0.154 g, 3.84 mmol)) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting purple solid was sublimed at 120 ºC at 0.05 Torr to afford 4 (0.395 g, 33%) as red-purple colored crystals: mp 219–212 ºC; IR (neat, cm$^{-1}$) 2949 (w), 2860 (s), 1604 (s), 1460 (s), 1319 (s), 1120 (s); $\mu_{\text{eff}} = 3.43 \mu_B$ in benzene solution. Anal. Calcd. for $\text{C}_{32}\text{H}_{64}\text{Co}_2\text{N}_4\text{O}_4$: C, 55.97; H, 9.39; N, 8.16. Found: C, 55.98; H, 9.45; N, 7.97.

**Preparation of Ni(L$^1$)$_2$ (5)**

Following the procedure similar to preparation of 1, 5 was prepared. NiCl$_2$•DME (0.383 g, 1.74 mmol) was reacted with KL$^1$ (prepared from treating L$^1$H (0.500 g, 3.49 mmol) with KH (0.154 g, 3.84 mmol)) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting dark brown colored solid was sublimed at 70 ºC at 0.05 Torr to afford 5 (0.179 g, 30%) as dark brown crystals. X-ray quality crystals were grown in concentrated hexanes solution at −28 ºC: mp 160–162 ºC; IR (neat, cm$^{-1}$) 3248 (w), 2960 (s), 1636 (s), 1478 (s), 1365 (s), 1224 (s), 1130 (s); $^1$H NMR (C$_6$D$_6$, 23 ºC, $\delta$) 4.00 (bs, 1H), 2.32 (s, 6H) 1.15 (s, 9H); $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 23 ºC, ppm) 110.00 (s, N(CH), 69.90 (s, CH(C)O), 49.98 (s, C(CH$_3$)$_3$), 32.50 (N(CH$_3$)$_2$), 28.52 (s, C(CH$_3$)$_3$); Anal. Calcd. for C$_{16}$H$_{32}$NiN$_2$O$_2$: C, 56.01; H, 9.40; N, 8.16. Found: C, 55.99; H, 9.20; N, 7.95.

**Preparation of Cr(L$^2$)$_2$ (6)**

Following the procedure similar to preparation of 1, 6 was prepared. Anhydrous CrCl$_2$ (0.167 g, 1.36 mmol) was treated with KL$^2$ (prepared from treating of L$^2$H (0.500 g, 2.73 mmol)
with KH (0.120 g, 3.00 mmol)) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting purple solid was sublimed at 115 ºC at 0.05 Torr to afford 6 (0.143 g, 25%) as green-brown colored crystals: mp 165–167 ºC; IR (nujol, cm\(^{-1}\)) 2719 (w), 1629 (s), 1377 (s), 1095 (s); \(\mu_{\text{eff}} = 3.83 \ \mu_B\) in benzene solution. Anal. Calcd. for C\(_{22}\)H\(_{40}\)CrN\(_2\)O\(_2\): C, 63.43; H, 9.68; N, 6.72. Found: C, 62.92; H, 9.80; N, 6.55.

**Preparation of Mn(L\(^2\))\(_2\) (7)**

Following the procedure similar to preparation of 1, 7 was prepared. Anhydrous MnBr\(_2\) (0.293 g, 1.36 mmol) was treated with KL\(^2\) (prepared from treating L\(^2\)H (0.500 g, 2.73 mmol) with KH (0.120 g, 3.00 mmol)) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting yellow solid was sublimed at 180 ºC at 0.05 Torr to afford 7 (0.114 g, 20%) as light yellow colored crystals: mp 277–279 ºC; IR (nujol, cm\(^{-1}\)) 2783 (w), 1597 (s), 1340 (s), 1153 (s); \(\mu_{\text{eff}} = 2.56 \ \mu_B\) in benzene solution. Anal. Calcd. for C\(_{22}\)H\(_{40}\)MnN\(_2\)O\(_2\): C, 62.99; H, 9.61; N, 6.68. Found: C, 56.96; H, 9.26; N, 6.07.

**Preparation of Fe(L\(^2\))\(_2\) (8)**

Following the procedure similar to preparation of 1, 8 was prepared. Anhydrous FeCl\(_2\) (0.173 g, 1.36 mmol) was treated with KL\(^2\) (prepared from treating L\(^2\)H (0.500 g, 2.73 mmol) with KH (0.120 g, 3.00 mmol)) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting brown solid was sublimed at 120 ºC at 0.05 Torr to afford 8 (0.172 g, 30%) as blue-green colored crystals: mp 211–213 ºC; IR (nujol, cm\(^{-1}\)) 2355 (w), 1616 (s), 1444 (s), 1099 (s); \(\mu_{\text{eff}} = 4.19 \ \mu_B\) in benzene solution. Anal. Calc. for C\(_{22}\)H\(_{40}\)FeN\(_2\)O\(_2\): C, 62.85; H, 9.59; N, 6.66. Found: C, 54.97; H, 8.73; N, 5.02.

**Preparation of Co(L\(^2\))\(_2\) (9)**

Following the procedure similar to preparation of 1, 9 was prepared. Anhydrous CoCl\(_2\) (0.177 g, 1.36 mmol) was treated with KL\(^2\) (prepared from treating L\(^2\)H (0.500 g, 2.73 mmol) with
KH (0.120 g, 3.00 mmol)) at 23 °C in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting purple solid was sublimed at 145 °C at 0.05 Torr to afford 9 (0.127 g, 22%) as dark purple colored crystals: mp: 251–254 °C; IR (nujol, cm⁻¹) 2947 (w), 2850 (w), 1606 (s), 1454 (s), 1325 (s), 1099 (s); μₑff = 3.69 μB in benzene solution. Anal. Calc. for C₂₂H₄₀CoN₂O₂: C, 62.39; H, 9.52; N, 6.61. Found: C, 61.87, H, 9.68, N, 6.00.

**Preparation of Ni(L²)₂ (10)**

Following the procedure similar to preparation of 1, 10 was prepared. NiCl₂•DME (0.299 g, 1.36 mmol) was treated with KL² (prepared from treating L²H (0.500 g, 2.73 mmol) with KH (0.120 g, 3.00 mmol)) at 23 °C in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting dark brown solid was sublimed at 70 °C at 0.05 Torr to afford 10 (0.121 g, 21%) as dark brown colored crystals: mp 212–214 °C; IR (neat, cm⁻¹) 3248 (w), 2960 (s), 1636 (s), 1478 (s), 1365 (s), 1224 (s), 1130 (s); ¹H NMR (C₆D₆, 23 °C, δ) 4.84 (bs, 1H), 3.51 (m, 2H), 3.17 (m, 2H), 1.48 (q, 2H), 1.05 (m, 2H), 0.97 (m, 2H); ¹³C{¹H} NMR (C₆D₆, 23 °C, ppm) 173.70 (s, C(O)C), 102.06 (s, CH(N)C), 56.85 (s, CH₂(CH₂)), 34.08 (C(CH₃)₃), 28.78 (s, C(CH₃)₃), 24.27 (s, CH₂(CH₂) 20.08 (CH₂(CH₂)); Anal. Calcd. for C₂₂H₄₀NiN₂O₂: C, 62.43; H, 9.53; N, 6.62. Found: C, 62.32; H, 9.77; N, 6.44.

**Preparation of Cr(L³)₂ (11)**

Following the procedure similar to preparation of 1, 11 was prepared. Anhydrous CrCl₂ (0.182 g, 1.49 mmol) was treated with KL³ (prepared from treating L³H (0.500 g, 2.95 mmol) with KH (0.130 g, 3.25 mmol)) at 23 °C in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting purple solid was sublimed at 115 °C at 0.05 Torr to afford 11 (0.108 g, 19%) as brown-green colored crystals: mp 158–160 °C; IR (neat, cm⁻¹) 2958 (w), 1614 (s), 1465 (s), 1097 (s); μₑff = 4.00 μB in benzene solution. Anal. Calcd. for C₂₀H₃₀CrN₂O₂: C, 61.83; H, 9.34; N, 7.21. Found: C, 61.79; H, 9.36; N, 7.30.
Preparation of Mn(L₃)₂ (12)

Following the procedure similar to preparation of 1, 12 was prepared. Anhydrous MnBr₂ (0.317 g, 1.47 mmol) was treated with KL₃ (prepared from treating L₃H (0.500 g, 2.95 mmol) with KH (0.130 g 3.25 mmol) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting yellow solid was sublimed at 170 ºC at 0.05 Torr to afford 12 (0.092 g, 16%) as light yellow colored crystals: mp 289–291 ºC; IR (nujol, cm⁻¹) 2725 (w), 1597 (w), 1377 (s), 1261 (s), 1099 (s); μₑff = 3.20 μB in benzene solution. Anal. Calcd. for C₂₀H₃₆MnN₂O₂: C, 61.37; H, 9.27; N, 7.16. Found: C, 60.67; H, 8.90; N, 6.49.

Preparation of Fe(L₃)₂ (13)

Following the procedure similar to preparation of 1, 13 was prepared. Anhydrous FeCl₂ (0.187 g, 1.47 mmol) was treated with KL₃ (prepared from treating L₃H (0.500 g, 2.95 mmol) with KH (0.130 g, 3.25 mmol)) at 23 ºC in 40 mL of THF and was stirred for 16 h. Excess solvent was evaporated and the resulting brown solid was sublimed at 130 ºC at 0.05 Torr to afford 13 (0.214 g, 37%) as green-brown colored crystals: mp 236–237 ºC; IR (neat, cm⁻¹) 2949 (w), 1622 (s), 1604 (s), 1475 (s), 1321 (s); μₑff = 3.43 μB in benzene solution. Anal. Calcd. for C₂₀H₃₆FeN₂O₂: C, 61.22; H, 9.25; N, 7.14. Found: C, 55.58; H, 9.70; N, 7.41.

Preparation of Co(L₃)₂ (14)

Following the procedure similar to preparation of 1, 14 was prepared. Anhydrous CoCl₂ (0.191 g, 1.47 mmol) was treated with KL₃ (prepared from treating L₃H (0.500 g, 2.95 mmol) with KH (0.130 g, 3.25 mmol)) at 23 ºC in THF (40 mL) was stirred for 16 h. The solvent was evaporated and the resulting dark purple solid was sublimed at 130 ºC at 0.05 Torr to afford 14 (0.100 g, 17%) as dark purple colored crystals: mp 187–189 ºC; IR (nujol, cm⁻¹) 2947 (s), 2860 (w), 2158 (w), 2027 (w), 1604 (s), 1321 (s); μₑff = 3.12 μB in benzene solution. Anal. Calcd. for C₂₀H₃₆CoN₂O₂: C, 60.75; H, 9.18; N, 7.08. Found: C, 58.49; H, 9.28; N, 6.04.
Preparation of Ni(L³)₂ (15)

Following the procedure similar to preparation of 1, 15 was prepared. NiCl₂•DME (0.324 g, 1.47 mmol) was treated with KL³ (prepared from treating L³H (0.500 g, 2.95 mmol) with KH (0.130 g, 3.25 mmol)) at 23 ºC in THF (40 mL) and was stirred for 16 h. The solvent was evaporated and the resulting dark brown solid was sublimed at 117 ºC at 0.05 Torr to afford 15 (0.100 g, 17%) as dark brown colored crystals: mp 186–189 ºC; IR (neat, cm⁻¹) 2947 (w), 2881 (s), 1624 (s), 1452 (s), 1381 (s); ¹H NMR (C₆D₆, 23 ºC, δ) 4.36 (bs, 1H), 3.42 (m, 2H), 2.87 (m, 2H), 1.34 (m, 4H), 1.16 (bs, 9H); ¹³C {¹H} NMR (C₆D₆, 23 ºC, ppm) 172.95 (s, CH(C)O), 108.16 (s, N(CH), 59.60 (s, CH₂(CH₂)), 33.80 (C(CH₃)₂), 28.67 (s, C(CH₃)₃), 21.89 (s, CH₂(CH₂)); Anal. Calcd. for C₂₀H₃₆NiN₂O₂:  C, 60.78; H, 9.18; N, 7.09. Found: C, 54.43; H, 8.26; N, 5.03.

Preparation of N’-(tert-butyl)pivalohydrazide (L⁴H)

The L⁴H was synthesized according to a published procedure with minor modifications.¹²³ To a 500 mL three necked flask, equipped with condenser, addition funnel, glass stopper, and magnetic stir bar, tert-butylhydrazine hydrochloride (40.800 g, 330.00 mmol) and distilled water (300 mL) were added. To that flask, Na₂CO₃ (24.300 g, 225.00 mmol) was added and the flask was then immersed in an ice bath to control the temperature below 10 ºC. Then, pivaloyl chloride (18.900 g, 150.00 mmol) was slowly added to a vigorously stirred solution using an addition funnel. The solution was further stirred for 3 h at 23 ºC. The white product was filtered with a Buchner funnel fitted to a filter paper and dried (major isomer, 17.600 g). The aqueous layer was then extracted with five 20 mL portions of dichloromethane and the combined organic layers were dried over anhydrous Na₂SO₄ and filtered with a glass funnel fitted to a fluted filter paper. Solvent was evaporated under reduced pressure and the white product was collected (minor isomer, 5.600 g). Both major and minor isomers were showed similar IR and NMR spectra. Total crude yield was 23.200 g, 86%. The crude product was purified by sublimation at 0.05 Torr. The major isomer
sublimed at 95 ºC and the minor isomer sublimed at 45 ºC. mp 102–105 ºC (major isomer, lit. 97–
105 ºC); IR (neat, cm⁻¹) 3293 (w); 2964 (s), 1640 (s), ¹H NMR (CDCl₃, 23 ºC, δ) 7.00 (bs, 1H),
4.29 (bs, 1H), 1.21 (s, 9H), 1.07 (s, 9H); ¹³C {¹H} NMR (CDCl₃, 23 ºC, ppm) 177.71 (s, C=O),
55.39 (s, C(CH₃)₂CO), 38.32 (s, C(CH₃)₃NH), 27.56 (s, C(CH₃)₃), 27.23 (s, C(CH₃)₃).

Preparation of N'-(tert-butyl)isobutyrohydrazide (L⁵H)

In a similar fashion to synthesis of L⁴H, L⁵H was prepared with minor modifications. tert-
Butylhydrazine hydrochloride (13.700 g, 110.00 mmol), distilled water (100 mL), and Na₂CO₃
(7.950 g, 75.00 mmol) were mixed below 10 ºC. Then isobutyryl chloride (5.330 g, 50.00 mmol)
was slowly added to a vigorously stirred solution using an addition funnel. The solution was further
stirred for 3 h at 23 ºC. The white byproduct was filtered off with a Buchner funnel fitted to a filter
paper. The aqueous layer was then extracted with five 20 mL portions of dichloromethane. The
combined organic layers were dried over anhydrous Na₂SO₄ and filtered with a glass funnel fitted
to a fluted filter paper. Excess solvent was evaporated under reduced pressure. A white product
was obtained (3.000 g, 42.5% yield). The crude product was purified by sublimation at 60 ºC at
0.05 Torr: mp 88–90 ºC; IR (neat, cm⁻¹) 3192 (w), 2962 (s), 1627 (s); ¹H NMR (CDCl₃, 23 ºC, δ)
6.87 (bs, 1H), 4.00 (bs, 1H), 2.37 (pentet, 1H), 1.18 (d, 6H), 1.09 (s, 9H); ¹³C {¹H} NMR 176.39
(s, C=O), 55.23 (s, C(CH₃)₂), 34.35 (s, C(CH₃)₃), 27.26 (s, C(CH₃)₃), 19.75 (s, CH(CH₃)₂).

Preparation of Co(L⁴)₂ (16)

In a 100 mL Schlenk flask, L⁴H (1.00 g, 5.80 mmol) was dissolved in THF (20 mL) and
was brought into an argon filled dry box. Inside the dry box, KH (0.255g, 6.38 mmol) was slowly
added to the flask which contained L⁴H, and was stirred for 16 h at 23 ºC. A pale-yellow solution
was observed. Then, anhydrous CoCl₂ (0.377 g, 2.90 mmol) was slowly added to the deprotonated
ligand solution (KL⁴). The dark purple solution was stirred for 24 h at 23 ºC. The solvent was
removed under vacuum and the resulting blue-purple solid was sublimed at 140 ºC at 0.05 Torr to
afford 16 (0.436 g, 40.4%) as dark purple colored crystals: mp 198–200 °C; IR (neat, cm\(^{-1}\)) 3145 (s), 2953 (w), 2343 (s), 1558 (s); \(\mu_{\text{eff}} = 5.88 \mu_B\) in chloroform solution. Anal. Calcd. for C\(_{36}\)H\(_{76}\)Co\(_2\)N\(_8\)O\(_4\): C, 53.85; H, 9.54; N, 13.96. Found: C, 53.58; H, 9.31; N, 13.55.

**Preparation of Ni(L\(^4\))\(_2\) (17)**

Following a procedure similar to preparation of 16, 17 was prepared. NiCl\(_2\)•CH\(_3\)CN (0.490 g, 2.90 mmol) was slowly added to a KL\(^4\) solution (prepared by treating L\(^4\)H (1.000 g, 5.80 mmol) with KH (0.255 g, 6.38 mmol)) in THF (40 mL). A pale orange solution was stirred for 24 h at 23 °C. The solvent was removed under vacuum and the resulting pale orange solid was sublimed at 140 °C at 0.05 Torr to afford 17 (0.236 g, 20.4%) as dark orange colored crystals: mp 266–268 °C; IR (neat, cm\(^{-1}\)) 3116 (s), 2950 (s), 2360 (s), 1564 (s); \(^1\)H NMR (CDCl\(_3\), 23 ºC, \(\delta\)); 4.03 (bs, 1H), 1.45 (s, 9H), 1.01 (s, 9H); \(^{13}\)C\{\(^1\)H\} (CDCl\(_3\), 23 ºC, ppm) 166.57 (s, CO), 70.40 (s, C(CH\(_3\))\(_3\)), 61.05 (s, C(CH\(_3\))\(_3\)), 28.46 (s, C(CH\(_3\))\(_3\)), 27.64 (s, C(CH\(_3\))\(_3\)); Anal. Calcd. for C\(_{18}\)H\(_{38}\)N\(_4\)NiO\(_2\): C, 53.88; H, 9.55; N, 13.96. Found: C, 54.01; H, 9.30; N, 13.89.

**Preparation of (Co(L\(^5\))\(_2\))\(_2\) (18)**

Following a procedure similar to preparation of 16, 18 was prepared. Anhydrous CoCl\(_2\) (0.376 g, 2.90 mmol) was slowly added to a KL\(^5\) solution (prepared by treating L\(^5\)H (1.000 g, 6.32 mmol) with KH (0.278 g, 6.95 mmol)) in THF. The brown-green solution was stirred for 16 h at 23 °C. The solvent was removed under vacuum and the resulting dark purple solid was sublimed at 120 °C at 0.05 Torr to afford 18 (0.385 g, 35.6%) as dark purple colored crystals: mp 180–182 °C; IR (neat, cm\(^{-1}\)) 2965 (w), 2329 (s), 1537(s); \(\mu_{\text{eff}} = 4.28 \mu_B\) in chloroform solution Anal. Calcd. for C\(_{16}\)H\(_{34}\)N\(_4\)CoO\(_2\): C, 51.47; H, 9.18; N, 15.00. Found: C, 50.79; H, 9.18; N, 14.77.

**Preparation of Ni(L\(^5\))\(_2\) (19)**

Following a procedure similar to preparation of 16, 19 was prepared. Anhydrous NiCl\(_2\)•CH\(_3\)CN (0.540 g, 3.16 mmol) was slowly added to a KL\(^5\) solution (prepared by treating L\(^5\)H
(1.000 g, 6.32 mmol) with KH (0.278 g, 6.95 mmol) in THF. The brown solution was stirred for 16 h at 23 °C. The solvent was removed under vacuum and the resulting brown solid was sublimed at 140 °C at 0.05 Torr to afforded 19 (0.483 g, 41.2%) as dark orange colored crystals: mp 236–239 °C; IR (neat, cm⁻¹) 2983 (w), 2961 (w), 2134 (s), 1576 (s); ¹H NMR (CDCl₃, 23 °C, δ); 4.04 (bs, 1H), 2.35–2.30 (m, 1H), 1.48 (s, 9H), 0.98–0.92 (dd, 6H); ¹³C {¹H} (CDCl₃, 23 °C, ppm) 61.18 (s, C(CH₃)₃), 29.84 (s, C(CH₃)₃), 27.86 (s, CH(CH₃)₂), Anal. Calcd. for C₁₆H₃₄N₄NiO₂: C, 51.50; H, 9.18; N, 15.01. Found: C, 51.59; H, 8.90; N, 15.09.
CHAPTER 3: ATOMIC LAYER DEPOSITION OF PrAlO$_3$ FILMS: (001) HIGHLY ORIENTED GROWTH ON SrTiO$_3$(001) SUBSTRATES

(This project was carried out as a part of a collaboration with the Material Research Science and Engineering Center (MRSEC), University of Wisconsin-Madison (NSF-DMR-1720415))

3.1 Introduction

Early lanthanide oxides, such as lanthanum and praseodymium oxides, are becoming increasingly interesting materials due to their enhanced electrical properties compared with late lanthanide oxides.$^{58-60,65}$ Owing to the improved electrical properties such as high dielectric constant and band gap, early lanthanide oxides are useful in the semiconductor industry as gate oxide materials replacing SiO$_2$, in metal oxide semiconductor field-effect transistors (MOSFET), and dynamic random-access materials (DRAM).$^{58-64}$ The hexagonal cubic structure of early lanthanide oxides results in high permittivity values ($\varepsilon = 25$) and large band gap ($E_g \approx 3.5$ eV), leading to a high charge density and low leakage current in MOSFETs.$^{63,65,134}$ PrO$_x$ ($x = 1.5, 2$) has a wide spectrum of applications, such as a photocatalytically active anode coating in organic light emitting diodes.$^{132,133}$ Similarly, ternary lanthanide oxide materials are used as 2-dimensional electron gases (2-DEGs), since they create a high density 2-DEGs at the hetero-interface upon depositing on single crystal SrTiO$_3$ substrates.$^6-8$ The interface between the polar LaAlO$_3$ and nonpolar SrTiO$_3$ layers has been studied extensively due to various interesting properties such as 2DEGs.$^{58,59,74,75}$ Moreover, other combinations of polar/nonpolar oxide (NdAlO$_3$/SrTiO$_3$, PrAlO$_3$/SrTiO$_3$, and NdGaO$_3$/SrTiO$_3$) interfaces, which are similar to the LaAlO$_3$/SrTiO$_3$ interface, can also produce 2DEGs at their hetero-interfaces.$^{67,81,135–138}$

The deposition of lanthanide oxides including PrO$_x$, is challenging due to the hydrophilic nature of these materials as explained in introduction.$^{65,78–81}$ The incorporation of a stable binary oxide such as Al$_2$O$_3$ stabilizes the lanthanide oxide towards reaction with water and CO$_2$.$^{65,142,143}$ Furthermore, Al$_2$O$_3$ exhibits excellent electrical properties such as a high dielectric constant, thus,
incorporation of Al$_2$O$_3$ does not affect the electrical properties of the binary lanthanide oxides. ALD is an attractive method to deposit thin films with Angstrom level thickness control with high film conformality. Moreover, ALD is distinctive from CVD because of the independent exposure of each reactant to the reaction chamber that subsequently results in self-limiting growth. One study has reported the ALD of Pr$_2$O$_3$ using tris(dimethylsilylamide)praseodymium and water. This Pr$_2$O$_3$ process established ALD growth behavior, however, films were highly contaminated with Si, C, and H impurities. The ALD of Pr$_2$O$_3$ was studied using tris(N,N’-diisopropylamidinato)praseodymium and water and resulted in non-uniform films. Then, ALD of PrAlO$_3$ was studied by incorporating stable Al$_2$O$_3$ and uniform films were then observed. When tris(tetramethyl-3,5-heptanedionate)praseodymium (Pr(thd)$_3$) was used as the praseodymium precursor, ozone was required as the co-reactant due to the low reactivity of β-diketoiminates with water. Both Pr$^{3+}$ and Pr$^{4+}$ oxides were formed during film deposition due to the strong oxidizing nature of ozone. Furthermore, lanthanide-containing N,N-dimethylaminodiboranates, donor functionalized alkoxides, and heteroleptic cyclopentadienyl-amidinate precursors have been used to deposit rare earth oxides including PrO$_x$. In a recent study, the Kondo group reported an ALD process to deposit Pr$_2$O$_3$ using tris(ethylcyclopentadienyl)praseodymium and water. They established the self-limiting growth behavior for both praseodymium and water at 180 ºC. Moreover, Pr$_2$O$_3$ films grown on Si(111) substrates were crystalline by grazing incident X-ray diffractometry (GI-XRD). Additionally, the ALD of PrAlO$_3$ was studied using tris(N,N’-diisopropylamidinato)praseodymium, AlMe$_3$, and water at 300 ºC. In that work, the composition of Pr:Al was determined by changing the Pr:Al pulse ratio and it was found that the ratio of Pr:Al ratio increased non-linearly with an increased Pr:Al pulse time. Furthermore, the PrAlO$_3$ films grown on Si(100) were amorphous even after annealing at 800 ºC. In this study we demonstrate a new ALD process to deposit Pr$_2$O$_3$ and
PrAlO$_3$ using tris(isopropylcyclopentadienyl)praseodymium (1). Cyclopentadienyl compounds readily react with water thus preventing the need to use ozone as oxygen source.$^8,^{157}$

3.2 Results and Discussion

Precursor Properties

Selecting a good lanthanide precursor is a crucial factor to obtain a thin film with low impurity levels, as it directly affects the electrical properties of the deposited material. In addition, the precursor should be thermally stable at the deposition temperature to limit film growth from decomposition of the precursor.$^8,^{157}$ Usually, Cp compounds have high thermal stabilities and high melting points. Early lanthanide Cp complexes can afford dimeric or oligomeric structures due to the large atomic radii of lanthanide metal ions.$^{157c}$ Therefore, a reduced volatility can be expected. For instance, Pr(Cp)$_3$ melts around 427 °C which makes it difficult to deliver, as the vapor pressure is low.$^{157b}$ Introducing substituents groups to the Cp ligand can change the aggregation state, thus increasing volatility.

Precursor 1 has isopropyl substituent groups on Cp, which can decrease the aggregation, thus, 1 melts at 53–54 °C. Furthermore, 1 decomposes thermally around 353 °C. Precursor 1 is a liquid at the delivery temperature (150 °C) and provides constant vapor pressure to the deposition chamber during the film deposition. Liquids do not change the exposed surface area when the material is being evaporated, whereas solids gradually increase the exposed surface area with sublimation, resulting in continuously increase vapor pressure during the deposition, as explained in Figure 34.
Figure 34. Delivery of liquid versus solid precursors

The thermogravimetric analysis (TGA) plot of 1 in Figure 35 shows a single step weight loss. The percent of non-volatile residue was less than 10% of the total mass. The clean evaporation of 1 is important to obtain high purity films. Because of these structural and thermal properties, 1 can be considered as a good ALD precursor.28

Figure 35. Thermogravimetric analysis plot of 1

3.2.1 ALD of Pr$_2$O$_3$

First, Pr$_2$O$_3$ film growth behavior was studied using 1 and water by varying precursor pulse lengths, deposition temperatures, and a number of deposition cycles on Si(100) with a native oxide layer (2–2.5 nm) and SiO$_2$ substrates. As discussed in the introduction, due to the high reactivity of lanthanide oxides with water, a thickness gradient was observed in the Pr$_2$O$_3$ films, starting from
the precursor inlet. The Pr$_2$O$_3$ film thickness gradient is previously also reported by the Gordon group at Harvard University. Therefore, for the determination of Pr$_2$O$_3$ thickness, the center of the wafer was selected, and an average of four to five ellipsometry measurements was considered as a thickness. Ellipsometry measurements were confirmed by cross-sectional SEM image measurements.

The self-limiting growth behavior of 1 was determined at 300 °C using the following sequences for 250 cycles: 1 (varied), N$_2$ purge (10.0 s), water (0.1 s), and N$_2$ purge (10.0 s). Precursor 1 demonstrates saturation after ≥3.0 with a constant 0.85 Å/cycle growth rate (Figure 36). Water did not show self-limiting behavior, instead, a high thickness gradient was observed with increasing water pulses. Therefore, thickness measurement was not successful. The increased of absorption of water by Pr$_2$O$_3$ with longer water pulses may increase the thickness gradient of the Pr$_2$O$_3$ films.

**Figure 36.** Plot of growth rate of Pr$_2$O$_3$ films versus pulse length of 1 after 250 cycles with a deposition temperature of 300 °C on SiO$_2$

![Figure 36](image)

Experiments were conducted to explore the temperature dependency of the film growth. Growth rate versus deposition temperature was plotted using a saturated pulse sequence of 1 (4.0 s), N$_2$ purge (10.0 s), water (0.1 s), and N$_2$ purge (10.0 s) for 250 cycles (Figure 37). An ALD
window with constant growth rate of a 0.85 Å/cycle was observed at 275–325 °C, possibly up to 350 °C. At temperatures below the ALD window, increased growth rate was observed due to precursor condensation. At temperatures above the ALD window, increased growth rate was observed due to precursor decomposition as evidenced by the solid-state thermal decomposition of 1 at 353 °C.

Figure 37. Plot of growth rate of Pr₂O₃ films versus deposition temperature using 1 and water after 250 cycles on (a) SiO₂ and (b) Si(100) substrates

The linearity of the plot of Pr₂O₃ film thickness versus number of cycles was analyzed at 300 °C using following pulse sequence: 1 (4.0 s), N₂ purge (10.0 s), water (0.1 s), and N₂ purge (10.0 s) on SiO₂ substrates. This resulted in a linear plot with a slope of 0.771, which corresponds to the growth rate of Pr₂O₃ films. The y-intercept close to zero indicates an absence of a nucleation delay (Figure 38).
**Figure 38.** Plot of thickness versus number of cycles of Pr$_2$O$_3$ on SiO$_2$ substrates with a deposition temperature of 300 ºC using 1 and water

![Plot of thickness versus number of cycles](image)

\[ y = 0.0771x + 1.359 \]
\[ R^2 = 0.9872 \]

Figure 39 shows the SEM images of Pr$_2$O$_3$ films deposited on Si(100) and SiO$_2$ at 300 ºC after 250 cycles with saturative doses of 1 and water, which show similar growth rate on both substrates. The morphology of films deposited at 300 ºC was explored using GI-XRD and it was found to be nanocrystalline with reflections from Pr$_2$O$_3$(100) and Pr$_2$O$_3$(101) as shown in Figure 40.

**Figure 39.** Cross-sectional SEM images of (a) a 23.1 nm thick Pr$_2$O$_3$ film deposited on Si(100) and (b) a 21.6 nm thick Pr$_2$O$_3$ film deposited on SiO$_2$, using 1 and water after 250 cycles at 300 ºC.
3.2.2 ALD of PrAlO$_3$

Incorporation of a binary oxide can be used to stabilize the lanthanide oxides from reactivity towards water. Al$_2$O$_3$ was used as the binary oxide in this study, since Al$_2$O$_3$ is stable towards CO$_2$ and water and thus acts as a protective layer for the Pr$_2$O$_3$. Moreover, incorporation of Al$_2$O$_3$ prevents additional reactivity toward atmospheric water and CO$_2$, thereby enhancing the film uniformity. An ALD supercycle was established to deposit PrAlO$_3$ films, keeping the Pr:Al precursor pulse ratio 1:1 as shown in Chart 5.

**Chart 5.** Pulse and purge sequences chart for the deposition of PrAlO$_3$ films

The self-limiting behavior of the film growth was investigated using plots of growth rate versus precursor pulse lengths (Figure 41). The saturation of 1 was explored using the following pulse sequence: 1 (varied), N$_2$ purge (10.0 s), water (0.1 s), N$_2$ purge (10.0 s), AlMe$_3$ (0.1 s), N$_2$
purge (10.0 s), water (0.1 s), and N₂ purge (10.0 s) for 250 cycles at 300 °C. After a ≥ 3 s pulsing of 1, a constant growth rate was observed, thus 1 was saturated. The precursor consumption increased with the precursor pulse length as shown in Figure 41, indicating a saturative dose of precursor 1.

**Figure 41.** Plot of growth rate of PrAlO₃ versus pulse length of 1 on (a) Si(100) and (b) SiO₂, after 250 cycles of 300 °C.

![Figure 41](image-url)

(a)                                                                    (b)

The saturation of AlMe₃ was explored using 1 (4.0 s), N₂ purge (10.0 s), water (0.1 s), N₂ purge (10.0 s), AlMe₃ (varied), N₂ purge (10.0 s), water (0.1 s), and N₂ purge (10.0 s) for 250 cycles at 300 °C. After a ≥0.1 s pulse of AlMe₃, a constant growth rate was observed up to 0.2 s pulse as shown in Figure 42. At a 0.3 s pulse of AlMe₃, the growth rate dropped to a 1.2 Å/cycle. Presumably, AlMe₃ poisons the surface reactions and consequently results in a lower growth rate.
The saturation of water was explored using 1 (4.0 s), N₂ purge (10.0 s), water (varied), N₂ purge (10.0 s), AlMe₃ (0.1 s), N₂ purge (10.0 s), water (varied), and N₂ purge (10.0 s) for 250 cycles at 300 °C. The water saturation was observed after a ≥ 0.1 as shown in Figure 43. With increasing water pulse time, a slight thickness gradient was observed across the film due to the reactivity of Pr₂O₃ with water. The thickness gradient can be eliminated with a longer purge time after the water pulse. A longer purge time (20.0 s) might desorb comparatively higher percentage of water than a shorter purge time (10.0 s), which was adsorbed by the Pr₂O₃. Therefore, additional reactivity of 1 with absorbed water may minimize and results in uniformly thick films.
Experiments were conducted to explore the temperature dependency of the film growth (Figure 44). The growth rate versus deposition temperature was plotted. An ALD window was observed for temperatures between 275–300 °C. At temperatures below 275 °C, the growth rate was higher perhaps due to precursor condensation or due to the higher Al₂O₃ growth rate at lower temperatures.²⁴ At temperatures above the ALD window from 325–350 °C, the growth rate was decreased. The lower growth rate can be due to AlMe₃ decomposition around 350 °C.²⁴ At 375 °C, the growth rate again increased, which can be attributed to the decomposition of 1. A similar pattern of growth behavior was observed in the Pr₂O₃ ALD window plot at temperatures above the ALD window (Figure 36). In Figure 45, selected SEM images of PrAlO₃ films deposited on Si(100) and SiO₂ substrates at 275 °C are shown and the same thickness was observed for PrAlO₃ films deposited on both substrates.
**Figure 44.** Plot of growth rate of PrAlO$_3$ versus deposition temperature using 1, water, and AlMe$_3$, on (a) Si(100) and (b) SiO$_2$, after 250 cycles

![Plot of growth rate of PrAlO$_3$ versus deposition temperature](image)

**Figure 45.** Cross-sectional SEM image of a 41 nm thick PrAlO$_3$ films deposited on (a) Si(100) and (b) SiO$_2$, deposited at 275 ºC after 250 cycles

![Cross-sectional SEM image of PrAlO$_3$ films](image)

A plot of film thickness versus number of cycles was explored with a saturated pulse of each precursor (Figure 46) for the PrAlO$_3$ films, deposited on Si(100) and SiO$_2$ substrates at 300 ºC. A linear plot was observed with approximately 60 ALD cycles of nucleation delay for the films grown on Si(100). Similarly, a linear plot was observed for the films grown on SiO$_2$ with approximately 25 cycles of nucleation delay. Figures 47 and 48 show selected SEM images of PrAlO$_3$ films deposited at 300 ºC after 150 and 750 cycles respectively.
Figure 46. Plot of thickness of PrAlO$_3$ films versus number of cycles on (a) Si(100) and (b) SiO$_2$ at 300 °C using 1, AlMe$_3$, and water

(a) ![Graph](image1)

(b) ![Graph](image2)

Figure 47. Cross-sectional SEM images of (a) a 15.9 nm thick PrAlO$_3$ film on Si(100) and (b) a 14.4 nm thick PrAlO$_3$ films on SiO$_2$, deposited at 300 °C after 150 cycles

(a) ![SEM Image](image3)
Figure 48. Cross-sectional SEM images of (a) a 139 nm thick PrAlO$_3$ film on Si(100) and (b) a 127 nm thick PrAlO$_3$ film on SiO$_2$, deposited at 300 ºC after 750 cycles.

Furthermore, in the ALD of Pr$_2$O$_3$, we did not observe a nucleation delay. However, the presence of the nucleation delay for the PrAlO$_3$ process can be due to the delaying of growth of Pr$_2$O$_3$ on Al-O terminated surface reactive sites.$^{134b}$ The Al-O surface sites may be less favorable for the absorption of 1. A similar growth behavior was observed by the Niinistö group, for the atomic
layer epitaxy of LaAlO$_3$ films.$^{134c}$ In the LaAlO$_3$ study, they observed a decrease of growth rate of LaAlO$_3$ at higher La:Al ratio and according to their explanation, the reason for the lower growth rate was the lowering of surface adsorption reactions of upcoming La precursor due to the Al-O layer.$^{134b,c}$

**X-ray Reflectivity Study**

We would like to thank Ms. Yajin Chen, University of Wisconsin-Madison for conducting these experiments. Film thickness, surface roughness, and mass density were determined using X-ray reflectivity measurements (XRR). A 41.1 nm thick (by SEM) PrAlO$_3$ film deposited on Si(100) substrate at 275 °C was used for the XRR measurements (Figure 49). The film thickness value obtained from the SEM measurement (Figure 45) was confirmed from the XRR fitting results (41.9 nm). The surface roughness was 1.2 nm for the 41.9 nm thick PrAlO$_3$ film, with a density of 5.07 g/cm$^3$ (Table 9). The low surface roughness value indicates smooth film deposition on both Si(100) and SiO$_2$ substrates.

**Figure 49.** XRR fitting results of 41.9 nm thick PrAlO$_3$ film on Si(100) deposited at 275 °C
Table 9. Summary of XRR data for the PrAlO$_3$ films deposited on Si(100) substrate at 275 °C

<table>
<thead>
<tr>
<th></th>
<th>Fitting result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of PrAlO$_3$ (nm)</td>
<td>41.9</td>
</tr>
<tr>
<td>Thickness of native SiO$_2$ (nm)</td>
<td>2.1</td>
</tr>
<tr>
<td>PrAlO$_3$ surface roughness (nm)</td>
<td>1.2</td>
</tr>
<tr>
<td>PrAlO$_3$ density (g/cm$^3$)</td>
<td>5.07</td>
</tr>
</tbody>
</table>

**X-ray Photoelectron Spectroscopy Study**

We would like to thank Ms. Yajin Chen, University of Wisconsin-Madison for conducting these experiments. X-ray photoelectron spectroscopy (XPS) measurements were conducted on 41 nm thick PrAlO$_3$ films deposited on Si(100) and SiO$_2$ substrates at 300 °C to determine the composition and purity of the PrAlO$_3$ films. Similar results were obtained with XPS study for the PrAlO$_3$ films deposited on both Si(100) and SiO$_2$ (Figures 50, 51, and 52). The binding energies for Al 2p, O 1s, and Pr 3d$_{5/2}$ were 73.25, 529.38, and 933.31 eV, respectively, and matched well with reported values.$^{158-161}$ In the Pr 3d$_{5/2}$ plot, there is an additional ionization around 928 eV (Figure 52) which is attributed to a satellite ionization and is a common phenomenon for the Pr 3d$_{5/2}$.$^{158-161}$ The ionization corresponding to the Pr 3d$_{3/2}$ should be above 950 eV.$^{158-160}$
Figure 50. XPS aluminum 2p ionization region of a 41 nm thick PrAlO$_3$ film deposited on (a) Si(100) and (b) SiO$_2$, at 300 ºC

(a)                                                                 (b)

Figure 51. XPS oxygen 1s ionization region of a 41 nm thick PrAlO$_3$ film deposited on (a) Si(100) and (b) SiO$_2$, at 300 ºC

(a)                                                                 (b)
XPS depth profile (Figure 53) shows a uniform distribution of each atom throughout the film. Carbon, nitrogen, and silicon were below the detection limit of XPS, thus conforming the high purity of PrAlO$_3$ films. Lanthanide oxides have high affinity towards silicon to form lanthanide silicates.$^{70b}$ The absence of silicon in the bulk film can be due to the Al$_2$O$_3$ protection. Because the films are slightly rich in Al$_2$O$_3$ and this excess Al$_2$O$_3$ may be act as a silicon diffusion barrier. According to the XPS depth profile, the Pr:Al ratio was 1:2.33 which was slightly higher than the expected Pr:Al ratio in the PrAlO$_3$ films (calculation of expected Pr:Al ratio is explained in detail in the electron probe microanalysis section). The XPS depth profile experiment uses highly energetic Ar ions, which can preferentially remove Pr atoms from the bulk film, resulting in a high amount of surface aluminum. Therefore, use of a non-destructive method such as electron probe micro analysis is useful to determine Pr:Al ratios.
**Figure 53.** XPS depth profile of a 41 nm thick PrAlO$_3$ film deposited on (a) Si(100) and (b) SiO$_2$, at 300 °C

(a) ![XPS depth profile for Si(100)](image)

(b) ![XPS depth profile for SiO$_2$](image)

**Electron Probe Microanalysis: Determination of Pr:Al Ratio**

We would like to thank Dr. J. H. Fournelle, Department of Geology and Geophysics, University of Wisconsin-Madison for conducting these experiments. Electron probe microanalysis with X-ray wavelength dispersive spectroscopy (WDS-EPMA) was performed as a non-destructive method to investigate the Pr:Al ratio of the PrAlO$_3$ films. Different temperatures in the ALD window plot were selected for the experiment with 1:1 Pr:Al precursor pulse length as shown in Table 10. The outcome of this study reveals that the films are Al rich, most likely due to the independent growth rates of binary oxides of Pr$_2$O$_3$ and Al$_2$O$_3$. The growth rate of Pr$_2$O$_3$ and Al$_2$O$_3$ at 300 °C were 0.85 Å/cycle and 1.0 Å/cycle. Comparing growth rates of the two oxides, there is a possible Pr:Al ratio of 1:1.18. The Pr:Al ratio is slightly higher at 250 °C, compared to other temperatures for the 1:1 Pr:Al pulse ratio, possibly due to the slightly higher growth rate of PrAlO$_3$ at 275 °C as shown in ALD window plot (Figure 44). At temperatures of 300, 325, and 350 °C, the Pr:Al ratio remains approximately the same for the 1:1 Pr:Al pulse ratio. At 375 °C the Al content is slightly lower, compared to other temperatures, which might be due to the decomposition of AlMe$_3$ at higher temperatures which can result in lower Al$_2$O$_3$ growth rate.
Table 10. Pr:Al ratio for the PrAlO$_3$ film deposited on Si(100) at different temperatures using electron probe microanalysis measurements

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Pr:Al precursor pulse ratio</th>
<th>Pr:Al atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1:1</td>
<td>1:1.71</td>
</tr>
<tr>
<td>300</td>
<td>1:1</td>
<td>1:1.34</td>
</tr>
<tr>
<td>325</td>
<td>1:1</td>
<td>1:1.39</td>
</tr>
<tr>
<td>350</td>
<td>1:1</td>
<td>1:1.26</td>
</tr>
<tr>
<td>375</td>
<td>1:1</td>
<td>1:1.23</td>
</tr>
<tr>
<td>300</td>
<td>2:1</td>
<td>1:1.25</td>
</tr>
</tbody>
</table>

We attempted to increase the Pr:Al ratio by increasing the Pr:Al pulse ratio in the ALD supercycle. No significant enhancement of the Pr content was observed after 2:1 Pr:Al precursor pulses as shown in last row of Table 10. Instead, a thickness gradient was observed for the deposited PrAlO$_3$ film. To overcome the thickness gradient, a 20 s purge time was used after each water pulses. After a longer purge time, a uniform film was observed. Figure 54 shows the cross-sectional SEM image of the PrAlO$_3$ film deposited on SiO$_2$ substrate using 2:1 Pr:Al pulse ratio.

Figure 54. Cross sectional SEM image of a 56.3 nm thick PrAlO$_3$ film deposited on SiO$_2$ at 300 ºC after 250 cycles using 2:1 Pr:Al pulse ratio.
Figure 55 shows the XPS depth profile for the corresponding PrAlO$_3$ film. The elemental distribution of the PrAlO$_3$ film deposited using a 2:1 Pr:Al pulse was not as uniform as the PrAlO$_3$ film deposited using a 1:1 Pr:Al pulse ratio. In the Pr:Al 2:1 depositions, two consecutive cycles of Pr$_2$O$_3$ were used with one cycle of Al$_2$O$_3$ and the amount of water being used for one ALD supercycle can be high. The excess water can be adsorbed by the Pr$_2$O$_3$ and react with subsequent exposure of 1 resulting in a thickness gradient. At the substrate/film interface, a high aluminum content is observed, which may be due to the absence of nucleation delay for the Al$_2$O$_3$ growth. However, a low praseodymium content is observed, indicating a lower growth rate at the interface presumably due to the presence of nucleation delay of the PrAlO$_3$ film growth. A high level of silicon can be observed due to the formation of interfacial silicon layer. In the bulk of the film, the praseodymium content is higher than the aluminum content. Presumably, praseodymium hydroxyl species which can be generated after the water reaction can be delayed the Al$_2$O$_3$ growth. There is a significant silicon contamination throughout the film, which can be attributed to the diffusion of silicon from the substrate. The silicon diffusion is a common feature of lanthanide oxides. At the surface, Al$_2$O$_3$ can only be observed with absence of praseodymium oxide, which can be due to the gradual depletion of 1 in the last few ALD cycles.
**Figure 55.** XPS depth profile for a 56.3 nm thick PrAlO$_3$ films deposited on SiO$_2$ using Pr:Al 2:1 pulse ratio

**PrAlO$_3$ films: Annealing and Crystallization**

We would like to thank Ms. Yajin Chen, University of Wisconsin-Madison for conducting these experiments. PrAlO$_3$ film deposited on Si(100) substrates at 275 °C were amorphous by GI-XRD (Figure 56). Even after annealing at 1000 °C for 5 h, the film remained amorphous. After annealing at 1200 °C for 5 h, PrAlO$_3$ films were damaged due to the melting of silicon. The as-deposited PrAlO$_3$ film grown on Si(111) at 300 °C is also amorphous as shown in Figure 57. A PrAlO$_3$ film was grown on Si(111) substrate to investigate the epitaxial growth on differently oriented Si. However, no significant difference was observed for the PrAlO$_3$ film deposited on Si(100) or Si(111).
Figure 56. GI-XRD patterns for an as-deposited PrAlO$_3$ film on a Si(100) substrate at a deposition temperature of 275 ºC with a corresponding 2D detector image.

Figure 57. GI-XRD pattern of PrAlO$_3$ film deposited on Si(111) at 300 ºC after 500 cycles.

Single crystal SrTiO$_3$ substrates were used to investigate the epitaxial growth of PrAlO$_3$ films. SrTiO$_3$ substrates were treated according to a previously established procedure to obtain a
TiO\textsubscript{2}-terminated phase.\textsuperscript{70} For the crystallization experiments, a 206 nm thick PrAlO\textsubscript{3} film was deposited using 1000 ALD supercycles with saturative doses of I, AlMe\textsubscript{3}, and water at 300 °C (Figure 58). As-deposited films were amorphous by GI-XRD pattern with a broad reflection (Figure 59(a)). Investigation of optimum annealing conditions for the complete crystallization is very important. The PrAlO\textsubscript{3} films deposited on TiO\textsubscript{2}-terminated SrTiO\textsubscript{3} substrates were amorphous as-deposited, as mentioned above, and different annealing conditions were tested. After annealing at 1000 °C for 5 h, polycrystalline PrAlO\textsubscript{3} was observed (Figure 60). Then, annealing at lower temperature for a shorter time was studied, and a highly (001) oriented, fully crystallized PrAlO\textsubscript{3} film was obtained at 800 °C after 3 h annealing. Figure 59(b) shows the XRD of the crystalline PrAlO\textsubscript{3} thin film, indicating that the PrAlO\textsubscript{3} film is highly (001)-oriented. However, polycrystalline grains in other directions are also present as minor components in the crystallized PrAlO\textsubscript{3} film. The reflections were indexed based on the pseudo-cubic structure of PrAlO\textsubscript{3} with a lattice parameter of 3.772 Å.

**Figure 58.** Cross sectional SEM image of a 206 nm thick PrAlO\textsubscript{3} film deposited on SrTiO\textsubscript{3}(001) at 300 °C after 1000 cycles
Figure 59. (a) GI-XRD patterns for the as-deposited PrAlO$_3$ film on SrTiO$_3$(001) substrate at 300 °C. The 2D detector image of the diffraction from the as-deposited amorphous PrAlO$_3$ is shown on the right. (b) GI-XRD patterns for the PrAlO$_3$ film deposited on SrTiO$_3$(001) crystallized at 800 °C for 3 h. The right side shows the corresponding 2D detector image.

Figure 60. GI-XRD pattern of PrAlO$_3$ films deposited on SrTiO$_3$(001) after annealing 1000 °C for 5 h.
The epitaxial relationship between the crystallized PrAlO\(_3\) film and SrTiO\(_3\)(001) substrate was determined by conducting a \(\theta\)-2\(\theta\) scan along the \(Q_z\) direction of SrTiO\(_3\) substrate, as shown in Figure 61(a). The PrAlO\(_3\) 00L and SrTiO\(_3\) 00L reflections appeared on the same rod of reciprocal space, confirming that the amorphous PrAlO\(_3\) film converted into an epitaxial layer. The full width at half maximum (FWHM) of the PrAlO\(_3\)(001) reflection from the rocking curve was 9° (Figure 61(b)) and indicates the 001 highly oriented growth of PrAlO\(_3\) films on SrTiO\(_3\)(001). However, the growth of PrAlO\(_3\) films on SrTiO\(_3\) substrates is not perfectly epitaxial as evidenced by the relatively high FWHM. For perfect SPE growth, the FWHM, calculated from the rocking curve of the deposited film, should be very small.

**Figure 61.** (a) XRD patterns along \(Q_z\) direction and (b) rocking curve scan of PrAlO\(_3\)(001) reflection, of the PrAlO\(_3\) film on SrTiO\(_3\)(001) crystallized at 800 °C for 3 h.

### 3.3 Conclusions

ALD of Pr\(_2\)O\(_3\) was studied using \(\text{1}\) and water and self-limiting growth behavior was observed for the Pr-precursor with a growth rate of 0.85 Å/cycle at 300 °C. Since the Pr\(_2\)O\(_3\) films are unstable upon water and CO\(_2\) exposure, a new ALD process was developed using \(\text{1}\), AlMe\(_3\), and water to deposit stable PrAlO\(_3\) films with a growth rate of 1.6–2.0 Å/cycle at 300 °C. The process showed a typical ALD growth behavior including precursor saturation, ALD window, and a linear relationship with the thickness versus number of cycles, were observed for the PrAlO\(_3\)
films deposited on both Si(100) and SiO₂ substrates. As-deposited PrAlO₃ films were amorphous and smooth by GI-XRD and XRR, respectively. An XPS study displayed a low level of impurity contamination and presence of Pr³⁺, Al³⁺, and O²⁻ with a uniform distribution of each atom throughout the film. The PrAlO₃ films were Al-rich for 1:1 Pr:Al pulse ratio. PrAlO₃ films grown on TiO₂-terminated SrTiO₃ substrates showed epitaxial film growth, and the films can be fully crystallized at 800 °C for 3 h annealing to afford a (001) preferred orientation. Annealing at 1000 °C results in polycrystalline PrAlO₃. Epitaxial film growth was not observed for the PrAlO₃ film grown on Si(100) substrates.

3.4 Experimental Section

A Picosun R–75 SUNALE ALD reactor was used for the Pr₂O₃ and PrAlO₃ thin film depositions. The chamber pressure was maintained at 2–4 Torr. The ALD reactor was equipped with one Pico-solid booster to deliver low vapor pressure precursors at elevated temperatures and two liquid delivery bubblers. Ultrahigh purity nitrogen (99.999%, Airgas) was used as carrier gas to deliver precursors and co-reagents to the deposition chamber. Si(100) with a ~2 nm native oxide and SiO₂ substrates were used for the film depositions without further cleaning. One side polished single crystal SrTiO₃(001) substrates were cleaned prior to the film deposition according to the literature procedure. Precursor 1 was synthesized according to the modified literature procedure or was purchased from Strem Chemicals and used without further purification. Precursor 1 was delivered at 150 ± 2 °C and AlMe₃ and water were delivered at 23 °C in separate liquid delivery bubblers. The film deposition temperatures ranged from 250–375 °C and an ALD supercycle was (Pr:Al 1:1 pulse) used to control the Pr:Al ratio in the PrAlO₃ films. Film thicknesses were measured from cross-sectional SEM (JEOL-6510LV) in a minimum of three different positions in the film and were confirmed by X-ray reflectivity and ellipsometry (J. A. Woollam Co. Alpha-SE) measurements.
Grazing-incidence X-ray scattering measurements were obtained using a Bruker D8 Advance diffractometer with Cu Kα radiation at a wavelength of 1.54 Å, running at a tube voltage of 50 kV and current of 1 mA. A 2D area detector subtending an opening angle of 32° was used to record the scattered X-ray intensity. Integrating the 2D detector images along the scattering ring azimuthal angle offers measurements of the scattered intensity as a function of 2θ. The incident angle of the X-ray beam was obtained based on the beam width and sample size to optimize the amorphous reflection signal by maximizing the X-ray footprint on the sample surface. The incident angles for the film of PrAlO₃ on SrTiO₃ and PrAlO₃ on SiO₂/Si were 2.9° and 3° respectively. The 2θ angle at the center of the detector was 30° for all measurements. X-ray diffraction along the Q_z direction for the PrAlO₃ on SrTiO₃ (001) annealed at 800 °C for 3 h was conducted using a PANalytical Empyrean diffractometer with Cu Kα₁ radiation (λ = 1.54 Å) at a generator voltage of 40 kV and emission current of 40 mA. XRR data were collected using a Panalytical X’Pert MRD at a wavelength of 1.5406 Å with monochromatic Cu Kα₁ X-ray radiation. The data were interpreted using the interdiff model of the GenX software package.¹⁶⁶ XPS was collected with a Thermo Scientific K-alpha XPS spectrometer using a micro-focused monochromatic Al Kα X-ray source. The XPS depth profile was determined using a monoatomic Ar⁺ ion source. Infrared spectra of thin films were obtained using Shimadzu FT-IR Tracer 100. TGA was performed using a TGA Instrument (TGA Q-50) placed inside a nitrogen-filled glove box with a ramping rate of 10 °C/min. The melting point and the thermal decomposition temperature were determined using an Electrothermal-IA 9000 series melting point apparatus with a heating rate of 10 °C/min. Annealing experiments were performed under an oxygen environment at different temperatures inside a tube-furnace.
Dicyclopentadiene was cracked to obtain monomeric cyclopentadiene at 180 °C nitrogen atmosphere. 6,6-dimethylfulvene and 2-isopropylcyclopenta1,3-diene were prepared following literature reported procedures. 163–165

**Synthesis of tris(isopropylcyclopentadienyl)praseodymium (1)**

All the manipulations were carried out under inert conditions either in Schlenk line or glove box environments. A 250 mL Schlenk flask was charged with magnetic stir bar, 2-isopropylcyclopenta-1,3-diene (7.000 g, 64.70 mmol), and anhydrous diethyl ether (50 mL) and was cooled to 0 °C. To that flask, n-BuLi (26 mL, 64.7 mmol, 2.5 M in hexanes) was slowly added and was stirred for 2 h. Excess solvent was removed under vacuum, and the resulting crude was dissolved in anhydrous THF (40 mL). To a separate 250 mL Schlenk flask, anhydrous PrCl$_3$ (5.330 g, 21.56 mmol) and anhydrous THF (50 mL) were added and stirred for 30 min. To the stirred solution of PrCl$_3$, the lithium salt of 2-isopropylcyclopenta1,3-dienyl was slowly cannulated at 0 °C. The resulting light green solution was stirred for 24 h at 23 °C, and all the volatile materials were removed under vacuum. The light green paste was extracted with anhydrous diethyl ether (100 mL) and filtered through a filter frit which contained a 2 cm pad of Celite. The light green filtrate was concentrated under vacuum and purified by vacuum distillation at 120 °C at 0.05 Torr. A light green solid was obtained (1.990 g, 20% yield). mp: 53–54 °C.
CHAPTER 4: THERMAL ATOMIC LAYER ETCHING OF COBALT METAL FILMS

4.1 Introduction

Atomic layer etching (ALE) is the reverse of ALD, which removes material in a layer by layer, self-limited manner. ALE half reactions are exothermic similar to ALD and consist of four basic steps as explained in Figure 15 of Chapter 1. The importance of ALE in the microelectronics industry is directly related to device miniaturization. Moore’s Law dictates that the number of transistors in ICs doubles every 18 months while device size halves. ALD has emerged in the microelectronics industry and has taken over an extensive portion of the device fabrication due to the self-limiting conformal film growth. Furthermore, because of the self-limiting growth behavior, ALD can enable film depositions with Angstrom level thickness control. ALD is used to deposit a variety of materials including metals, metal oxides, metal nitrides, metal sulfides, and various alloys. Sometimes, ALD processes require a nucleation step before starting the actual film growth and result in non-uniform films with high surface roughness. Due to the roughness caused by the nucleation delay, it is necessary for the process to run an additional number of cycles to develop a smooth film, thus leading to thicker films. Therefore, ALE becomes important in the microelectronics industry. Removal of films in a layer by layer manner can be applied to obtain a desired thickness of the film with a minimum damage to the properties of the deposited material as explained in Figure 14 of Chapter 1.

Due to the high activation energies of half reactions, ALE has been introduced recently using plasma assisted or energetic ion bombardment methods. One of the oldest plasma ALE processes is GaAs etching using Cl₂ followed by electron bombardment to achieve self-limited etching. Later there were many studies seeking a less corrosive process. Furthermore, ALE of Si has been studied extensively using Cl₂ or F₂, followed by plasma or neutral ion bombardment. Various oxides such as Al₂O₃, SiO₂, HfO₂, TiO₂, and ZrO₂ have been etched using plasma or ion
assisted ALE.\textsuperscript{167,168} The Hess research group at Georgia Tech has reported plasma and halogen assisted etching of tungsten, molybdenum, aluminum, silver, gold, and copper.\textsuperscript{169–177} However, use of plasma or energetic ions can damage or modify the underlying film and substrate. Therefore, it is critical to find an alternative method which prevents the use of plasma or energetic ions.\textsuperscript{83–88} Furthermore, plasma ALE provides anisotropic etching, which limits its use in designing gate-all-around (GAA) architectures.\textsuperscript{167}

Unlike plasma ALE, thermal ALE provides isotropic and damage free etching via thermally driven surface chemical reactions. The George research group at the University of Colorado Boulder has recently discovered thermal ALE of Al\textsubscript{2}O\textsubscript{3} and HfO\textsubscript{2} using fluorination reactions followed by treatment with Sn(acac)\textsubscript{2} (acac = acetylacetonate) or AlMe\textsubscript{3}.\textsuperscript{177–182} The concept behind the Al\textsubscript{2}O\textsubscript{3} or HfO\textsubscript{2} ALE is the modification of Al\textsubscript{2}O\textsubscript{3} surface with HF, followed by metal-exchange transmetallation reaction with fluorine-modified surface species, which produces volatile byproducts.\textsuperscript{177–182} The ALE half-reactions including fluorination and transmetallation are exothermic, thus, the overall etching reaction is spontaneous.\textsuperscript{83,99–102,177–182} Moreover, thermal ALE of AlF\textsubscript{3}, ZnO, SiO\textsubscript{2}, TiO\textsubscript{2}, TiN, and WO\textsubscript{3} were studied using the same concepts as explained above.\textsuperscript{99–102}

Thermal ALE of metals has been minimally studied due to the lack of appropriate chemistry which can overcome the thermodynamic barrier in etching reactions.\textsuperscript{83–88} The Hess group has reported several solution-based etching processes to etch transition metals and their oxides such as copper and iron using hfacH (hfac = hexafluoroacetylactonate).\textsuperscript{95,96} Furthermore, using acetic acid, only copper oxide can be etched.\textsuperscript{97} The Masel group has reported chemical vapor etching (CVE) of copper using oxygen and hfacH.\textsuperscript{182} The etching process occurs via an oxidation followed by hfacH reaction to produce volatile Cu(hfac)\textsubscript{2}. Another process was developed using liquid vaporized supercritical carbon dioxide and hfacH to etch copper, nickel, cobalt, and iron.
metals. Supercritical carbon dioxide can be used to dissolve magnetic metals due to its tunable solvent properties. Thermal dry-etching of copper metal was demonstrated using H₂O₂ and hfacH, which results in isotropic etching and a high etch rate. In that study, H₂O₂ was used as an oxidizing agent, to oxidize the metal surface before the reaction with hfacH and different etch rates were observed by varying temperature, flow rate, and pressure. A halogen-based ALE of iron was reported with an in situ XPS study. In that study, Cl₂ was used to modify the iron surface at room temperature, after which acacH was used to react with the chlorine-modified iron surface at temperature above 135 °C. Another study focused on surface chemistry of thermal etching of cobalt metal films using hfacH, however, a high process temperature was required for the hfacH reaction, which can destroy the cobalt film. Moreover, the cobalt surface was oxidized using long pulse of oxygen, prior to the reaction with hfacH, which can destroy the self-limiting behavior of ALE. Therefore, the demand for transition metal ALE is rapidly growing. This chapter will discuss thermal ALE of cobalt using formic acid and two different neutral ligands (carbohydrazone-L₆H or acetylacetone-L₇H), applying the concept of surface oxidation followed by formation of volatile metal complexes after ligand exchange reactions, thus, resulting in etched cobalt.

4.2 Results and Discussion:

For etching experiments, cobalt metal films were deposited using Co(tBuDAD)₂/formic acid process on ~10 nm Pt substrates or Co(tBuDAD)₂/tert-butylamine process on ~40 nm Cu substrates (tBuDAD = 1,4-di-tert-butyl-1,3-diazadienyl) using ALD. Formic acid was used to oxidize the cobalt metal surface to cobalt formate (Co(HCOO)₂). Then L₆H or L₇H (Chart 6) was introduced to react with the oxidized cobalt surface (Co(HCOO)₂) to produce volatile cobalt by-products and formic acid according to equations (4) and (5), thus resulting in cobalt etching.
Chart 6. Chemical structures of L\textsuperscript{6}H and L\textsuperscript{7}H

\[
\text{Co(s)} + 2 \text{HCOOH(g)} \rightarrow \text{Co(HCOO)}_{2(s)} + \text{H}_{2(g)} \quad (4)
\]

\[
\text{Co(HCOO)}_{2(s)} + 2 \text{LH(g)} \rightarrow \text{Co(L)}_{2(g)} + 2 \text{HCOOH(g)} \quad (5)
\]

Formic acid (pKa = 3.74) is strong enough to oxidize the cobalt metal. The deprotonation of formic acid to form bidentate formate is an exothermic reaction with \(-72\) kJ/mol of formation energy\textsuperscript{184}. Furthermore, the thermal decomposition of cobalt formate is around 237 °C\textsuperscript{185} and it is well above the anticipated Co ALE process temperature (180–200 °C), which avoids the re-deposition of cobalt metal due to the thermal decomposition of cobalt formate. Additionally, L\textsuperscript{6}H and L\textsuperscript{7}H are simple organic bidentate ligands, and can bind to the Co\textsuperscript{2+} center. Ligand L\textsuperscript{6}H is a volatile solid and L\textsuperscript{7}H is a liquid at room temperature.

Thermal decomposition temperatures of Co(L\textsuperscript{6})\textsubscript{2} and Co(L\textsuperscript{7})\textsubscript{2} are 245 °C\textsuperscript{36} and 250–300 °C\textsuperscript{186} respectively, and Co(L\textsuperscript{6})\textsubscript{2} sublimes at 75 °C\textsuperscript{36} at 0.05 Torr and Co(L\textsuperscript{7})\textsubscript{2} sublimes at 140 °C\textsuperscript{186}. Additionally, Co(L\textsuperscript{6})\textsubscript{3} is also reported and sublimes around 170 °C\textsuperscript{187}. Complex Co(L\textsuperscript{6})\textsubscript{2} and Co(L\textsuperscript{7})\textsubscript{2} have high enough thermal decomposition temperatures to avoid the re-deposition of cobalt metal films, and low enough the sublimation temperatures to purge from the deposition chamber with an inert gas during the Co ALE process. Chart 7 represents the chemical structures of Co(L\textsuperscript{6})\textsubscript{2} and Co(L\textsuperscript{7})\textsubscript{2}. 

4.2.1 ALE of Co Metal Films Using Formic Acid and L^6H

To investigate the temperature dependency, the “ALE window” plot was explored using 0.1 s formic acid, 10.0 s purge, 5.0 s L^6H, and 10.0 s purge for 1000 cycles (Figure 62). The etch rate was plotted with the temperature range from 140–240 °C. An ALE window was observed at 180–200 °C. At temperatures above the ALE window, cobalt film growth was observed instead of etching. This film growth may be due to the thermal decomposition of cobalt formate or Co(L^6)_2. At temperatures below the ALD window, a higher etch rate was observed, which may be due to the highly favorable exothermic half reactions at lower temperatures. However, more experimental details are needed to prove the concept. Cross-sectional SEM images of cobalt films obtained from the ALE window are shown in Figures 63–69.

Figure 62. The ALE window plot using formic acid and L^6H after 1000 cycles
**Figure 63.** Cross-sectional SEM image of (a) a 62 nm thick Co film before etching and (b) a 23 nm thick Co film after etching at 150 °C after 1000 cycles

(a) ![Image](image1.png)  (b) ![Image](image2.png)

**Figure 64.** Cross-sectional SEM image of (a) a 97 nm thick Co film before etching and (b) a 71 nm thick Co film after etching at 160 °C after 1000 cycles

(a) ![Image](image3.png)  (b) ![Image](image4.png)
**Figure 65.** Cross-sectional SEM image of (a) a 40 nm thick Co film before etching and (b) a 21 nm thick Co film after etching at 170 °C after 1000 cycles

(a) ![Image](image1.png)  (b) ![Image](image2.png)

**Figure 66.** Cross-sectional SEM image of (a) a 63 nm thick Co film before etching and (b) a 52 nm thick Co film after etching at 180 °C after 1000 cycles

(a) ![Image](image3.png)  (b) ![Image](image4.png)
Figure 67. Cross-sectional SEM image of (a) a 44 nm thick Co film before etching and (b) a 34 nm thick Co film after etching at 200 °C after 1000 cycles

(a) ![SEM image](image1.png) (b) ![SEM image](image2.png)

Figure 68. Cross-sectional SEM image of (a) a 44 nm thick Co film before etching and (b) a 59 nm thick Co film after etching at 220 °C after 1000 cycles

(a) ![SEM image](image3.png) (b) ![SEM image](image4.png)
Figure 69. Cross-sectional SEM image of (a) a 82 nm thick Co film before etching and (b) a 108 nm thick Co film after etching at 240 °C after 1000 cycles

In Table 11, thermal ALE of cobalt etch characteristics are shown. The bulk resistivity of the cobalt film did not change drastically after etching at temperatures from 150–200 °C. However, at temperatures 220 °C and 240 °C the bulk resistivity increased, presumably due to the re-deposition of cobalt metal may changes the bulk density of cobalt.

Table 11. Thickness differences, bulk resistivity changes before and after etching, and etch rate of Co ALE at different temperatures ((+) film growth and (−) film etch)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thickness difference (nm)</th>
<th>Bulk resistivity (μΩ.cm)</th>
<th>Etch rate/Growth rate (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>150</td>
<td>(−)39</td>
<td>23.14</td>
<td>13.09</td>
</tr>
<tr>
<td>160</td>
<td>(−)25</td>
<td>18.39</td>
<td>17.59</td>
</tr>
<tr>
<td>180</td>
<td>(−)12</td>
<td>12.43</td>
<td>16.71</td>
</tr>
<tr>
<td>200</td>
<td>(−)11</td>
<td>25.83</td>
<td>24.20</td>
</tr>
<tr>
<td>220</td>
<td>(+)14</td>
<td>25.50</td>
<td>31.62</td>
</tr>
<tr>
<td>240</td>
<td>(+)23</td>
<td>16.22</td>
<td>20.56</td>
</tr>
</tbody>
</table>
The changes in thickness (before and after etching) versus number of ALE cycles plot was plotted to examine the linearity of the cobalt ALE process using 0.1 s formic acid, 10.0 s purge, 5.0 s L₆H, and 10.0 s purge at 180 °C (Figure 70). The etch rate increases linearly with the number of ALE cycles. Figures 71–74 represent SEM images of cobalt metal film after different number of ALE cycles.

**Figure 70.** Thickness difference versus number of ALE cycles plot using formic acid and L₆H at 180 °C

![Graph showing linear relationship between thickness difference and number of cycles with equation and R² value](image)

**Figure 71.** Cross-sectional SEM image of (a) a 63 nm thick Co film before etching and (b) a 52 nm thick Co film after etching at 180 °C after 1000 cycles

(a)  
(b)
Figure 72. Cross-sectional SEM image of (a) a 105 nm thick Co film before etching and (b) a 86 nm thick Co film after etching at 180 °C after 1500 cycles

Figure 73. Cross-sectional SEM image of (a) a 90 nm thick Co film before etching and (b) a 70 nm thick Co film after etching at 180 °C after 2000 cycles
The bulk resistivity of the cobalt metal films before and after etching slightly increased (Table 12). This minor increase may be caused by the surface oxidation reaction of formic acid. An image by atomic force microscopy (AFM) was collected for the 52 nm thick etched Co film at 180 °C after 1000 cycles (Figure 75). The root mean square (RMS) surface roughness was 2.37 nm for 52 nm thick film, which indicates a slight increase of surface roughness after etching. The surface roughness of ALD Co film before etching was 1.24 nm for a 105 nm thick film.52

**Table 12.** Thickness differences, bulk resistivity changes before and after etching, and etch rate of Co ALE after different number of cycles

<table>
<thead>
<tr>
<th>Number of cycles</th>
<th>Thickness difference (nm)</th>
<th>Bulk Resistivity (μΩ.cm)</th>
<th>Etch rate (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>1000</td>
<td>12</td>
<td>12.43</td>
<td>16.71</td>
</tr>
<tr>
<td>1500</td>
<td>16</td>
<td>12.49</td>
<td>15.12</td>
</tr>
<tr>
<td>2000</td>
<td>18</td>
<td>14.2</td>
<td>14.2</td>
</tr>
<tr>
<td>2500</td>
<td>25</td>
<td>13.59</td>
<td>19.84</td>
</tr>
</tbody>
</table>
4.2.2 ALE of Co Metal Film Using Formic Acid and L\textsuperscript{7}H

Cobalt metal films were deposited on ~40 nm thick copper substrates using Co(\textsuperscript{tBu}DAD\textsubscript{2}) and tert-butylamine by ALD and used for ALE experiments. The etch rate as a function of temperature was plotted (Figure 76) to investigate the ALE window. For the etching experiment, 0.3 s formic acid pulse, 15.0 s N\textsubscript{2} purge, 0.2 s L\textsuperscript{7}H pulse, and 15.0 s N\textsubscript{2} purge sequence was used for 250 cycles. An ALE window was observed at temperatures between 200–210 °C with a constant etch rate of 0.45 Å/cycle. At temperatures below the ALE window, the etch rate decreased, presumably due to the low thermal energy slowing down the rate of the ALE half reactions. At temperatures above the ALE window, the etch rate increased at 220 °C and then dropped, possibly because of the decomposition of Co(II)formate. However, the exact reason for the variation of etch rate at high temperatures is still unclear. Figures 77–84 show selected SEM images of cobalt films before and after etching, represent the ALE window plot. After etching, the bulk resistivity of cobalt decreased (Table 13). The low resistivity of cobalt film after etching may be due to the removal of surface oxide or displaying the resistivity of the underlying copper substrate.
Figure 76. The ALE window plot for the Co ALE using formic acid and L^7H after 250 cycles

![Graph showing etch rate vs. temperature](image)

Figure 77. Cross-sectional SEM image of (a) a 57 nm thick Co film before etching and (b) a 58 nm thick Co film after etching at 150 °C for 250 cycles

(a) ![SEM image of Co film before etching](image)

(b) ![SEM image of Co film after etching](image)
Figure 78. Cross-sectional SEM image of (a) a 46 nm thick Co film before etching and (b) a 42 nm thick Co film after etching at 160 °C for 250 cycles.

(a) [Image of a 46 nm thick Co film before etching]  (b) [Image of a 42 nm thick Co film after etching]

Figure 79. Cross-sectional SEM image of (a) a 57 nm thick Co film before etching and (b) a 49 nm thick Co film after etching at 180 °C for 250 cycles.

(a) [Image of a 57 nm thick Co film before etching]  (b) [Image of a 49 nm thick Co film after etching]
**Figure 80.** Cross-sectional SEM image of (a) a 49 nm thick Co film before etching and (b) a 40 nm thick Co film after etching at 190 °C for 250 cycles

(a) ![Cross-sectional SEM image of a 49 nm thick Co film before etching](image1)

(b) ![Cross-sectional SEM image of a 40 nm thick Co film after etching](image2)

**Figure 81.** Cross-sectional SEM image of (a) a 50 nm thick Co film before etching and (b) a 37 nm thick Co film after etching at 200 °C for 250 cycles

(a) ![Cross-sectional SEM image of a 50 nm thick Co film before etching](image3)

(b) ![Cross-sectional SEM image of a 37 nm thick Co film after etching](image4)
**Figure 82.** Cross-sectional SEM image of (a) a 44 nm thick Co film before etching and (b) a 34 nm thick Co film after etching at 210 °C for 250 cycles

**Figure 83.** Cross-sectional SEM image of (a) a 50 nm thick Co film before etching and (b) a 33 nm thick Co film after etching at 220 °C for 250 cycles
Figure 84. Cross-sectional SEM image of (a) a 47 nm thick Co film before etching and (b) a 37 nm thick Co film after etching at 250 ºC for 250 cycles

![Cross-sectional SEM images](image)

(a)  
(b)

Table 13. Thickness differences, bulk resistivity changes before and after etching, and etch rate of Co ALE at different temperatures

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Thickness difference (nm)</th>
<th>Bulk resistivity (µΩ.cm)</th>
<th>Etch rate/Growth rate (Å/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>150</td>
<td>0.3</td>
<td>16.6</td>
<td>14.7</td>
</tr>
<tr>
<td>160</td>
<td>4.8</td>
<td>17.7</td>
<td>12.5</td>
</tr>
<tr>
<td>180</td>
<td>8</td>
<td>13.1</td>
<td>9.6</td>
</tr>
<tr>
<td>190</td>
<td>9</td>
<td>20.0</td>
<td>13.0</td>
</tr>
<tr>
<td>200</td>
<td>11</td>
<td>20.0</td>
<td>13.0</td>
</tr>
<tr>
<td>210</td>
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<td>9.7</td>
</tr>
<tr>
<td>250</td>
<td>9</td>
<td>15.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>

The saturation behavior of L²H and formic acid was then explored. Figure 85 shows the plot of etch rate versus L²H pulse length using a sequence of 0.3 s formic acid pulse, 15.0 s N₂
purge, L\textsuperscript{7}H pulse (varied), and 15.0 s N\textsubscript{2} purge at 220 °C for 250 cycles. However, the self-limiting behavior was not clearly observed for the L\textsuperscript{7}H. A 0.2 s L\textsuperscript{7}H pulse with an etch rate of 0.62 Å/cycle was selected for studies.

**Figure 85.** Plot of etch rate versus L\textsuperscript{7}H pulse length at 220 °C after 250 cycles

![Plot of etch rate versus L\textsuperscript{7}H pulse length at 220 °C after 250 cycles]

Figure 86 shows the plot of etch rate versus formic acid pulse length using the sequence of formic acid pulse (varied), 15.0 s N\textsubscript{2} purge 0.2 s L\textsuperscript{7}H pulse, and 15.0 s N\textsubscript{2} purge at 220 °C for 250 cycles. Similar to the observation of L\textsuperscript{7}H saturation experiment, a clear saturation was not observed for the formic acid. At long formic acid pulses, we assume that the formation of Co(II)formate is much higher than the formation of Co(L\textsuperscript{7})\textsubscript{2}. Therefore, lower etch rate can be due to the longer formic acid pulses. However, for the rest of the experiments, 0.3 s formic acid pulse length was selected as a saturated dose with an etch rate of 0.62 Å/cycle.
A plot of thickness difference versus number of cycles was explored using 0.3 s formic acid pulse, 15.0 s N\(_2\) purge, 0.2 s L\(^7\)H pulse, and 15.0 s N\(_2\) purge at 200 °C and a constant etch rate of 0.45–0.46 Å/cycle (Figure 87) was observed. The lower etch rate (0.45–0.46 Å/cycle) compared with 0.62 Å/cycle which observed for the saturation study, was due to the temperature difference. The thickness versus number of cycle plot was performed at 200 °C, whereas, saturation plots were performed at 220 °C. The bulk resistivity of the cobalt films did not change significantly (Table 14). For 150 and 500 ALE cycles, the bulk resistivity decreased, however, after etching for 750 ALE cycles the bulk resistivity increased possibly due to the enhanced surface oxidation. Figures 88 and 89 show SEM images of cobalt metal films before and after etching, at different number of ALE cycles.
**Figure 87.** Plot of thickness differences versus number of cycles at 200 °C

![Plot](image)

\[ y = 0.0457x + 0.1601 \]

\[ R^2 = 0.9998 \]

**Table 14.** Thickness differences, bulk resistivity changes before and after etching, and etch rate of Co ALE after different number of cycles

<table>
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<th>Number of cycles</th>
<th>Thickness difference (nm)</th>
<th>Bulk Resistivity (μΩ.cm)</th>
<th>Etch rate (Å/cycle)</th>
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<tr>
<td></td>
<td></td>
<td>Before</td>
<td>After</td>
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<tr>
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<td>13.59</td>
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</table>

**Figure 88.** Cross-sectional SEM image of (a) a 58 nm thick Co film before etching (b) a 50 nm thick Co film after etching at 250 °C after 150 cycles

(a) ![Image](image)  
(b) ![Image](image)
Figure 89. Cross-sectional SEM image of (a) 41 nm thick Co film before etching (b) 21 nm thick Co film after etching at 250 °C after 750 cycles

The RMS surface roughness was measured using AFM for a 39 nm thick cobalt metal film after etching (Figure 90). The RMS surface roughness was 6.38 nm and it was slightly higher than RMS surface roughness of cobalt metal film deposited using Co(\textsuperscript{t}BuDAD)\textsubscript{2} and tert-butylamine ALD process which was 3.07 nm for a 98 nm thick Co film.\textsuperscript{53}

Figure 90. AFM image of a 39 nm thick cobalt metal film after etching at 200 °C after 250 cycles
Dummy pulse experiments were carried out using one of the reactants at a time to demonstrate the proposed mechanism for Co ALE. No etching was observed in experiments pulsing exclusively formic acid or L⁷H, indicating the need of both formic acid and L⁷H to complete the etching reaction. Figure 91 shows that the thickness of the cobalt film remains the same before and after a formic acid only run. However, the film morphology has changed, and the film turned to a red color after the formic acid only run, is likely due to the formation of red colored Co(II)formate. Figure 92 shows the SEM images of cobalt metal film before and after an L⁷H only run. There was no significant thickness difference observed. As a result of these two observations, it is clear for the need of both formic acid and L⁷H for the Co ALE. Thus, formic acid oxidation of cobalt metal followed by ligand exchange reaction of L⁷H is expected as the etching mechanism.

**Figure 91.** Cross-section SEM image of (a) a 40 nm thick cobalt film before and (b) a 40 nm thick cobalt film after formic acid only run at 200 °C after 250 cycles
**Figure 92.** Cross-sectional SEM image of (a) a 56 nm thick cobalt film before and (b) a 56 nm thick cobalt film after L^6H only run at 200 °C after 250 cycles

(a)                                                      (b)

4.3 ALE of PVD Co metal films

About 50 nm thick, PVD cobalt films provided by Intel Corporation were used for etching experiments using formic acid and L^6H or L^7H. Compared to cobalt films deposited by ALD, cobalt films deposited by PVD showed a slower etching rate, presumably due to the density of the sputtered cobalt being greater than that of ALD cobalt. Figures 93 and 94 show ALE of PVD cobalt with L^6H and L^7H with formic acid, respectively. The etching of PVD cobalt metal is possible up to ~10 nm with an etch rate of 0.05 Å/cycle for L^6H and 0.11 Å/cycle for L^7H. This ~10 nm removal of cobalt metal film may be due to the lower density packing of cobalt and surface oxidation.
Figure 93. Cross-sectional SEM image of (a) a 50 nm thick cobalt film before (b) a 40 nm thick cobalt film after using formic acid and L¹H at 180 °C for 2000 cycles

(a)                                                                 (b)

Figure 94. Cross-sectional SEM image of (a) a 50 nm thick cobalt film before (b) a 37 nm thick cobalt film after using formic acid and L⁷H at 180 °C after 1000 cycles

(a)                                                                 (b)

4.4 Conclusions

Thermal ALE of cobalt metal films has been demonstrated using formic acid oxidation followed by ligand exchange mechanism. ALD grown cobalt metal films were used for the etching experiments. Two different classes of ligands (L⁶H and L⁷H) were used to react with the oxidized
cobalt surface and resulted in volatile cobalt species (Co(L\textsuperscript{6})\textsubscript{2} and Co(L\textsuperscript{7})\textsubscript{2}), which can be removed after inert gas purges. The etch rate is 0.10 Å/cycle for the formic acid/L\textsuperscript{6}H process and 0.45 Å/cycle for the formic acid/L\textsuperscript{7}H process. Formation of Co(L\textsuperscript{7})\textsubscript{2} may be thermodynamically favorable at high temperatures in order to result in higher etch rate compared to formic acid/L\textsuperscript{6}H process. Additionally, it can be possible to form both Co(L\textsuperscript{7})\textsubscript{2} and Co(L\textsuperscript{7})\textsubscript{3} during the second half reaction which may give a higher etch rate. Moreover, L\textsuperscript{7}H has a higher vapor pressure than L\textsuperscript{6}H, which may provide high amount of L\textsuperscript{7}H dose to the reaction chamber, which can increase the rate of conversion of Co(II)formate to volatile Co(L\textsuperscript{7})\textsubscript{2}. ALE of sputtered cobalt film has a lower etch rate. The lower etch rate may be due to the higher density of sputtered cobalt than ALD cobalt. Dummy pulse experiments suggest a proposed mechanism for the cobalt ALE process, i.e. surface oxidation followed by ligand exchange reaction to produce volatile cobalt complexes.

4.5 Experimental Section

Co ALE Using Formic Acid and L\textsuperscript{6}H

A Picosun R-75 ALD reactor was used with the chamber pressure of 4-6 Torr and 99.999% ultra-high pure N\textsubscript{2} was used as a carrier gas. Cobalt metal films were deposited on 10 nm Pt substrates using Co(\textsuperscript{\textau}DAD)\textsubscript{2} and formic acid by ALD and used for the etching experiments.\textsuperscript{52} SEM images were obtained from a JEOL-6510LV instrument, to determine the thickness of the cobalt metal films before and after etching experiments. To calculate the thickness differences of cobalt metal films, before and after etching, at least three different spots were measured by SEM and averaged. Then the thickness difference was calculated by subtracting the averaged values obtained before and after etching. L\textsuperscript{6}H was prepared according the literature procedure\textsuperscript{36} and delivered from the Pico-solid booster at 75 ± 5 °C. Formic acid (>99%) was purchased from Sigma Aldrich and used without further purification and delivered from stainless steel bubbler at 23 °C. Substrate temperatures for Co ALE ranged from 150–250 °C. The general ALE recipe included a
0.2 s formic acid pulse, 10.0 s \( \text{N}_2 \) purge, 5.0 s L\(^6\)H pulse, and 10.0 s \( \text{N}_2 \) purge for 1000 ALE cycles at 180 °C. Sheet resistivity was measured before and after etching of cobalt metal films and then bulk resistivity was calculated.

**Co ALE Using Formic Acid and L\(^7\)H**

The cobalt metal films were deposited on ~40 nm copper substrates using Co\((^{18}\text{Be})\text{DAD})_2\) and \textit{tert}-butylamine by ALD and used for etching experiments.\(^{53}\) Formic acid (>99%) and L\(^7\)H were purchased from Sigma Aldrich and used without further purification and delivered from stainless steel bubbler at 23 °C. Substrate temperatures of Co ALE ranged from 150–250 °C. The general ALE recipe included a 0.3 s formic acid pulse, 15.0 s \( \text{N}_2 \) purge, 3.0 s L\(^7\)H pulse, and 10.0 s \( \text{N}_2 \) purge for 250 ALE cycles at 200 °C. The sheet resistivity was measured before and after etching of cobalt metal films and then calculated the bulk resistivity.
CHAPTER 5: CONCLUSIONS

Continuous miniaturization of device size in the microelectronics industry is requiring new methodologies and chemistries to overcome current problems in film deposition techniques. Among many existing film deposition methods, ALD plays a vital role due to the conformal film growth with Angstrom-level thickness control. However, many ALD processes require high process temperatures, hazardous co-reactants or reactive ions/plasmas, and post-deposition treatments. Furthermore, many available ALD precursors have limitations such as low reactivities, poor thermal properties, and poor volatilities. This research work attempted to address some of these limitations associated with ALD processes and precursor chemistries in order to obtain high quality thin films.

Chapter 1 provides an overview of thin film deposition techniques such as PVD, CVD, and ALD. Furthermore, unique features inherent to ALD and different types of ALD were discussed with appropriate examples. Next, a detailed discussion about mid-to-late transition metal precursors, their thermal properties, reactivities, and film depositions characteristics were introduced. Then, alternative gate oxide materials to replace SiO$_2$ in MOSFETs were discussed. Among several alternative gate oxide materials, lanthanide oxides are important because of their excellent electrical properties such as high dielectric constant and band gap. Additionally, a discussion about epitaxial growth of ternary lanthanide oxides on SrTiO$_3$ substrates and creation of 2DEGs at the polar/non-polar heterointerfaces were discussed. Finally, an evaluation of ALE of different metals, metal oxides, and metal nitrides was introduced. Use of highly energetic plasmas or ions is not beneficial for etching experiments, due to their destructive nature. Therefore, the need for self-limited thermal ALE processes, as non-destructive methods, was discussed. Oxidation followed by ligand exchange reactions can be proposed as a mechanism for the thermal ALE of metals.
Chapter 2 describes the synthesis, characterization, and investigation of the thermal properties of mid-to-late transition metal complexes containing enaminolate and carbohydrazide ligands. Three different types of enaminolate ligands and their transition metal complexes were synthesized and characterized (L\textsuperscript{1}–L\textsuperscript{3}, M = Cr, Mn, Fe, Co, and Ni). All of the new complexes were solids at 23 °C and purified by sublimation under vacuum (90–180 °C at 0.05 Torr). Metal complexes containing chromium, manganese, iron, and cobalt were paramagnetic and nickel complexes were diamagnetic. Chromium and nickel complexes adopted square planar geometry, while iron and cobalt complexes adopted distorted tetrahedral geometry according to the X-ray crystal structures. Magnetic susceptibility measurement values for paramagnetic complexes in benzene indicate high spin electronic configurations. Similar to enaminolate metal complexes, new carbohydrazide-containing metal complexes were synthesized (L\textsuperscript{4} and L\textsuperscript{5}, M = Co and Ni)) and were also demonstrated to have good thermal properties and volatilities.

Interestingly, at high temperatures, these metal complexes decomposed thermally to their respective metals. Solution reduction experiments demonstrated rapid reactivity toward different reducing agents. Meanwhile, synthesis of corresponding copper complexes was not successful due to the reduction of CuCl\textsubscript{2} to copper metal, thus indicating the high reactivity of both enaminolate and carbohydrazide ligands. The enhanced reactivity compared to metal complexes with previously reported carbohydrazide ligands, can be associated with presence of extra protons in the anionic enaminolate and carbohydrazide metal complexes, respectively. Considering excellent thermal properties, volatilities, and reactivities, these newly synthesized metal complexes are considered to be promising ALD precursors and can potentially be used for metal ALD. As an immediate future direction, ALD of Co and Ni metal films can be tested using cobalt and nickel precursors which were introduced in Chapter 2, with dimethylhydrazine as a reducing agent.
Additionally, the thermal ALD of Mn, Cr, and Fe are poorly studied. Therefore, testing of these newly synthesized precursors for deposition of Mn, Cr, and Fe metal is also suggested.

Chapter 3 describes a new ALD process to grow PrAlO$_3$ thin films using 1, AlMe$_3$, and water. The ALD growth of PrAlO$_3$ films deposited on both Si(100) and SiO$_2$ followed a similar trend. The self-limiting behavior of each of the precursors was demonstrated at 300 ºC and the ALD window ranged between 275–300 ºC. Film growth of PrAlO$_3$ followed a linear trend with the number of ALD cycles, with a small nucleation delay. The growth rate of PrAlO$_3$ films grown on Si(100) substrates was 1.6–1.8 Å/cycle. PrAlO$_3$ films are stable upon exposure to air and moisture. As-deposited PrAlO$_3$ films were amorphous, smooth, and contained low impurity levels according to the GI-XRD, XRR, and XPS. With a 1:1 Pr:Al precursor pulse ratio, films were Al-rich by WDS-EPMA. As deposited PrAlO$_3$ films grown on TiO$_2$-terminated SrTiO$_3$(001) substrates at 300 ºC were amorphous and after annealing at 800 ºC for 3 h resulted in fully crystallized PrAlO$_3$ films. Crystallized PrAlO$_3$ showed a (001) preferred orientation. PrAlO$_3$ films deposited on Si(100) remained amorphous at temperatures greater than 1000 ºC, over 5 h. After 1200 ºC, melting of silicon substrate was occurred.

The ALD of PrAlO$_3$ resulted in Al-rich films, which can be a problem in epitaxial growth on SrTiO$_3$ as we observed a 001-highly oriented PrAlO$_3$ growth, instead of epitaxial growth. Therefore, as future directions, selecting a different Pr-precursor which can provide a higher Pr$_2$O$_3$ growth rate may avoid the sub-stoichiometric Pr:Al ratios in PrAlO$_3$ growth. In addition, our study revealed a small nucleation delay for the PrAlO$_3$ ALD process. Presumably Al$_2$O$_3$ delays the Pr$_2$O$_3$ growth as discussed in Chapter 3. Therefore, selecting a different stable binary oxide such as TiO$_2$, Y$_2$O$_3$, and Lu$_2$O$_3$ may enhance the Pr$_2$O$_3$ growth and may provide stoichiometric film growth while retaining other electrical properties. Meanwhile, tuning the ALD supercycle to obtain stoichiometric PrAlO$_3$ films is also suggested. Our attempt to increase the Pr:Al ratio to 2:1 was
not successful as described in Chapter 3. Varying the purge times after water pulse and discovering a good combination of Pr:Al pulse ratio may result in enhanced Pr content with a better film uniformity. Furthermore, studying the crystallization mechanism and kinetics of PrAlO$_3$ on SrTiO$_3$ and investigation of electrical properties of PrAlO$_3$ films deposited on SrTiO$_3$(001) for use as 2DEGs can also be proposed.

Chapter 4 discusses thermal ALE of cobalt metal films. Cobalt metal films were grown by ALD and used for ALE experiments. Formic acid oxidation of surface cobalt metal followed by a ligand exchange reaction which produces volatile cobalt complexes, results in cobalt etching. Two different ligand systems (carbohydrazone (L$_6^6$H) and acetylacetone (L$_7^7$H)) were used with formic acid and different etch rates were observed with different ligands. Formic acid/L$_6^6$H resulted in a 0.12 Å/cycle etch rate at 180 ºC, and formic acid/L$_7^7$H resulted in a 0.45 Å/cycle etch rate at 200 ºC. Precursor saturation was minimally observed in any of the two processes. Presumably, ALE half reactions may not self-limiting, and may etch underneath layers upon exposure to precursor pulses. Both of the Co ALE processes observed a linear relationship with a plot of thickness difference versus number of ALE cycles. The resistivities of Co films were not changed significantly before and after etching. The surface roughness of the cobalt metal film increased when L$_7^7$H was used as the ligand with formic acid pulse. Sputtered cobalt films showed a lower etch rate compared to ALD cobalt, which may be due to the higher density packing of cobalt atoms in sputtered film compared to lower density packing of cobalt atoms in ALD cobalt film. Thus, result in lower etch rates occur in sputtered cobalt films.
APPENDIX

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REFERENCES


42. Ripin, D. H.; Evans, D. A. pKa Table.


ABSTRACT

ATOMIC LAYER DEPOSITION (ALD) AND ATOMIC LAYER ETCHING (ALE) OF THIN FILMS: SYNTHESIS AND CHARACTERIZATION OF A NEW CLASS OF ALD PRECURSORS, ALD OF PrAlO$_3$ THIN FILMS, AND THERMAL ALE OF COBALT METAL FILMS

by

WATHSALA LAKMALI IWADUNNA WADUGE

May 2019

Advisor: Dr. Charles H. Winter
Major: Chemistry (Inorganic)
Degree: Doctor of Philosophy

ALD is an attractive thin film deposition technique due to its unique self-limiting growth behavior and the ability to achieve Angstrom level thickness control. Alternative thin film deposition techniques such as CVD and PVD are unable to attain the conformal and Angstrom level film growth which are of great significance to future microelectronics device fabrication demands. Because ALD proceeds by surface reactions, the precursors which are used for ALD should have unique properties. Therefore, the design and synthesis of these ALD precursors are challenging. Transition metal ALD has not been well developed due to a lack of good ALD precursor chemistry. Herein, mid-to-late transition metal complexes containing enaminolate and carbohydrazide ligands have been synthesized and characterized. Additionally, the thermal properties and reactivity of these complexes were determined. Enaminolate ligand-containing chromium, manganese, iron, cobalt, and nickel complexes were isolated as pure solids by vacuum sublimation. TGA of these metal complexes shows a single step weight loss with minimum non-volatile residuals. Manganese complexes show lower volatility compared to the other metal complexes. However, the highest thermal stability (303 °C) was observed for manganese complexes. Interestingly these metal complexes thermally decompose to their metals at high
temperatures and show high reactivity towards reducing agents. Similar to enaminolate containing metal complexes, newly synthesized carbohydrazide-containing metal complexes also display promising thermal properties and reactivity to use as ALD precursors. Detailed synthesis procedures, precursor characterizations of these metal complexes are reported in this thesis, Chapter 2.

Following Moore’s Law, the device size in the microelectronics industry is dramatically shrinking. SiO$_2$ has been used as the gate dielectric material in MOSFETs until recently, and it has been partially replaced with HfO$_2$. However, the need for replacing SiO$_2$ with an efficient high-k material is increasingly growing. Binary and ternary lanthanide oxides are potential candidates to use as high-k materials on MOSFETs. Additionally, a polar non-polar system containing ABO$_3$/SrTiO$_3$ is important in creating 2-DEGs. Herein ALD of Pr$_2$O$_3$ and nearly stoichiometric PrAlO$_3$ are developed and discussed. Characterization of the Pr$_2$O$_3$ films was difficult due to their hygroscopic nature. Incorporation of stable Al$_2$O$_3$ minimizes the Pr$_2$O$_3$ film degradation. Additionally, I, AlMe$_3$, and water were used for the film deposition with 1:1 Pr:Al precursor pulse ratio. The growth rate of Pr$_2$O$_3$ is 0.85 Å/cycles, and PrAlO$_3$ is 1.6–2.0 Å/cycles at 300 ºC on both Si(100) and SiO$_2$ substrates. The PrAlO$_3$ films contain low impurity levels by XPS measurements, and as-deposited films are amorphous by GI-XRD. The PrAlO$_3$ films deposited on TiO$_2$-terminated SrTiO$_3$ substrates can be fully crystallized by annealing at 800 ºC for 3 h to result in (001) highly oriented PrAlO$_3$. Detailed film morphology and properties are discussed in this thesis, Chapter 3.

ALE is a method of removing films in a layer-by-layer manner, in contrast to ALD, which deposits films layer-by-layer manner. Thermal ALE of transition metal films is poorly studied due to the lack of chemistries to overcome thermodynamic and kinetic barriers of etching half reactions. Therefore, scientists have used highly energetic ion bombardment or plasmas to initiate
etching reactions. For the Co metal ALE, surface chemical modification followed by ligand exchange reaction mechanism is used. In our Co ALE study, formic acid is used as an oxidant to oxidize the cobalt metal and carbohydrazone or acetylacetone is used for the ligand exchange reactions. The volatile cobalt complexes are formed after ligand exchange reactions and can then be removed with an inert gas purge resulting in etched cobalt films. Different etch rates are observed for different ligands. Etch rates, changes in film resistivities and surface roughness of before and after etching of the cobalt films, are discussed in detail in this thesis, Chapter 4.
AUTOBIOGRAPHICAL STATEMENT

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