

**NEW SURFACE CHEMISTRIES FOR THE
ATOMIC LAYER DEPOSITION OF OXIDES
AND NITRIDES**

By

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PREVIEW

A thesis submitted to the
Faculty of the Graduate School of the
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Burton, Beau Bernard (Ph.D., Physical Chemistry)

New Surface Chemistries for the Atomic Layer Deposition of Oxides and Nitrides

Thesis directed by Prof. Steven M. George

Abstract

The field of atomic layer deposition (ALD) has grown substantially over the past several decades. The development of ALD as a method to deposit materials has been predominantly led by the microelectronics industry, which continues to move to submicron dimensions. This momentum towards submicron dimensions has pushed conventional thin film deposition techniques to their limits. Atomic layer deposition is a thin-film deposition technique based on sequential, self-limiting surface reactions. The reactions are performed in an ABAB... binary reaction sequence to deposit a controlled and conformal film. A growing number of materials can be deposited by ALD including oxides, nitrides, sulfides, and metals. ALD has the ability to control numerous film properties such as thickness, morphology, crystallinity, conformality, and electrical properties.

This thesis studied the chemistry of reactions leading to the ALD of MgO, MnO, TaN, and SiO₂. Additionally, the novel chemistry for the rapid ALD of SiO₂ was investigated. *In situ* Fourier transform infrared (FTIR) spectroscopy and quartz crystal microbalance (QCM) were conducted to monitor surface species during each half reaction and verify saturation behavior. Once the surface chemistry was understood, the films were then deposited on Si(100) substrates using the optimal

deposition conditions. The films grown on Si(100) substrates were used for numerous *ex situ* thin film analysis techniques. X-ray reflectivity experiments were conducted to yield both film thicknesses and film density. X-ray diffraction experiments were used to determine film crystallinity. Four-point probe measurements were conducted to determine film resistivities. XPS sputter depth profiling, Rutherford backscattering measurements and in some cases SIMS measurements were also conducted to obtain the chemical composition of the films. Transmission electron microscopy and scanning tunneling microscopy were utilized to visualize the conformality of the films.

PREVIEW

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PREVIEW

Table of Contents

I. Introduction	1
1.1 <i>Thin Film Growth</i>	1
1.2 <i>Basic Concepts of Atomic Layer Deposition</i>	6
1.3 <i>Techniques for Studying Atomic Layer Deposition</i>	11
1.4 <i>Statement of Purpose</i>	13
1.5 <i>References</i>	16
II. Experimental	17
2.1 <i>Transmission FTIR and Mass Spectrometry Apparatus</i>	17
2.2 <i>Transmission FTIR</i>	20
2.3 <i>Sample Preparation for FTIR and QMS</i>	20
2.4 <i>Viscous Flow Reactor</i>	22
2.5 <i>Quartz Crystal Microbalance</i>	24
2.6 <i>Sample Preparation for Viscous Flow Reactor</i>	25
2.7 <i>References</i>	26
III. Atomic Layer Deposition of MgO Using Bis(ethylcyclopentadienyl)magnesium and H₂O.....	27
3.1 <i>Introduction</i>	27
3.2 <i>Experimental</i>	31
3.3. <i>Results and Discussion</i>	35
3.3.A <i>Quartz Crystal Microbalance</i>	35
3.3.B <i>X-ray Reflectivity</i>	40
3.3.C <i>X-ray Diffraction</i>	45
3.3.D <i>Fourier Transform Infrared Spectroscopy</i>	45
3.3.E <i>Transmission Electron Microscopy</i>	51
3.3.F <i>Rutherford Backscattering</i>	53
3.3.G <i>Proposed Growth Mechanism</i>	55
3.4 <i>Conclusions</i>	59
3.5 <i>Acknowledgements</i>	61
3.6 <i>References</i>	62
IV. Atomic Layer Deposition of MnO Using Bis(ethylcyclopentadienyl)manganese and H₂O	66
4.1 <i>Introduction</i>	66
4.2 <i>Experimental</i>	69
4.3. <i>Results and Discussion</i>	74
4.3.A <i>Quartz Crystal Microbalance</i>	74
4.3.B <i>X-ray Reflectivity</i>	79
4.3.C <i>X-ray Diffraction</i>	84
4.3.D <i>Fourier Transform Infrared Spectroscopy</i>	86
4.3.E <i>Transmission Electron Microscopy</i>	92

4.3.F Rutherford Backscattering	93
4.3.G Proposed Growth Mechanism	96
4.4 Conclusions	100
4.5 Acknowledgements	102
4.6 References	103
V. Tantalum Nitride Atomic Layer Deposition Using Tris(diethylamido)(tert-butylimido)tantalum and Hydrazine	106
5.1 Introduction	106
5.2 Experimental	109
5.3 Results and Discussion	113
5.3.A Quartz Crystal Microbalance	113
5.3.B X-ray Reflectivity and X-ray Diffraction	120
5.3.C X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy	128
5.3.D Resistivity Measurements	133
5.3.E Fourier Transform Infrared Spectroscopy and Quadrupole Mass Spectrometry	134
5.3.F Proposed Growth Mechanism Using TBTDET and Hydrazine	142
5.4 Conclusions	147
5.5 Acknowledgements	149
5.6 References	150
Atomic Layer Deposition of SiO₂ Using Tris(dimethylamino)silane and Hydrogen Peroxide Studied by <i>in situ</i> Transmission FTIR Spectroscopy	155
6.1 Introduction	155
6.2 Experimental	158
6.3 Results and Discussion	160
6.3.A SiO ₂ ALD with Various Silicon Precursors	160
6.3.A.i Vinyltrimethoxysilane (VTMOS), CH ₂ =CHSi(OCH ₃) ₃	160
6.3.A.ii Trivinylmethoxysilane (TVMOS), CH ₃ OSi(CH=CH ₂) ₃	162
6.3.A.iii Tetrakis(dimethylamino)silane (TKDMAS), Si(N(CH ₃) ₂) ₄	162
6.3.A.iiii (N,N-dimethylaminotrimethylsilane) (DMATMS), (CH ₃) ₃ SiN(CH ₃) ₂	163
6.3.B SiO ₂ ALD with Tris(dimethylamino)silane (TDMAS), SiH(N(CH ₃) ₂) ₃	164
6.3.B.i <i>In Situ</i> FTIR Studies of TDMAS and H ₂ O ₂ at 250°C	165
6.3.B.ii <i>In Situ</i> FTIR Studies of TDMAS and H ₂ O ₂ at 550°C	172
6.3.C Transmission Electron Microscopy of SiO ₂ ALD	179
6.3.D SiO ₂ ALD Growth Mechanism	183
6.4 Conclusions	187
6.5 Acknowledgements	189
6.6 References	190
VII. Rapid SiO₂ Atomic Layer Deposition Using Tris(<i>tert</i>-pentoxy)silanol	194
7.1 Introduction	194
7.2 Experimental	196
7.3 Results and Discussion	201
7.3.A Initial Studies with Different Silanol Precursors	201
7.3.B Single Exposure Experiments	202

7.3.C Multiple Exposure Experiments with Variable Delay Times.....	208
7.3.D Continuous Exposure Experiments.....	214
7.3.E Composition of Rapid SiO ₂ ALD Films.....	227
7.3.F Effect of Tris(<i>tert</i> -pentoxy)silylpyridine Impurity.....	230
7.3.G Position of the Al Catalyst.....	236
7.3.H Comparison between TBS and TPS for Rapid SiO ₂ ALD and Catalytic Polymerization.....	240
7.4 Conclusions.....	242
7.5 Acknowledgements.....	244
7.6 References.....	245
Bibliography.....	248

PREVIEW

I. Introduction

1.1 Thin Film Growth

Thin film growth has slowly permeated into a number of new technologies over the past several decades. The initial motivation for thin film growth was driven predominantly by the microelectronics industry. Thin films are used in the microelectronics industry as gate dielectrics, gate electrodes, metal interconnects, and diffusion barriers. Optics is another field that has utilized the advantages of thin film growth for applications such as anti-reflection coatings, optical filters, organic light emitting diodes (OLEDs), photonic crystals, and solar cells. The list of applications and industries utilizing thin film technology is ever expanding and continues to progress. This continued expansion has pushed thin film technology to its limits and has required thin film technology to evolve.

An example of one such application that fully illustrates the reliance on thin film technology is the gate dielectric in complementary metal-oxide-semiconductor (CMOS) technologies. Silicon dioxide (SiO_2) has been the gate dielectric in CMOS technologies over the past several decades and is the most common dielectric material in silicon microelectronic devices.¹ The demand for greater integrated circuit functionality and performance has translated to greater circuit density of transistors on a wafer.² This miniaturization has forced both the channel length and the dielectric thickness to decrease rapidly. Unfortunately, it has been demonstrated that the SiO_2 gate oxide can only be scaled to a thickness of 10–12 Å, which results in

unacceptably high leakage currents and low voltage dielectric breakdown.² Although thin film growth technology has allowed for the scaling of the SiO₂ gate oxide to at least 12 Å, future advances are required to obtain greater circuit densities of transistors on a wafer.³

The motivation for obtaining thin SiO₂ films was to increase the capacitance. The capacitance is defined by the following relationship:

$$C_{\text{ox}} = (\epsilon_0 * A * \kappa_{\text{ox}}) / t_{\text{ox}}$$

where C is the capacitance, A is the area of the film, κ is dielectric constant, and t is the thickness of the film.² The capacitance can be increased by decreasing the physical thickness, or increasing the area of the film. However, after the scaling of the SiO₂ to the fundamental limit has been achieved, the next option to increase the capacitance is to use a higher dielectric material. SiO₂, which only has a dielectric constant of 3.9, can be replaced with high- κ dielectrics such as Al₂O₃, HfO₂, or TiO₂ which have dielectric constants of 9, 25, and 80 respectively.² By replacing the SiO₂ gate dielectric with a high- κ dielectric, the gate dielectric can be made physically thicker for a required capacitance, while also lowering the tunneling current.

Recently, Intel announced that their 45 nm generation processors will include a high- κ HfO₂ gate dielectric deposited by atomic layer deposition (ALD), which Intel has announced will decrease leakage currents that occur with SiO₂ by 90%.³ However, the new high- κ dielectrics are not compatible with conventional silicon gate electrodes and have led to the use of metal gate electrodes, illustrating a trend away from silicon based technology. This use of a high- κ HfO₂ gate dielectrics will allow transistor sizes to be scaled far enough to allow for the doubling of transistors

on a chip.³ This doubling of transistors is commonly known as Moore's Law, which states the number of transistors on a chip will double roughly every two years.⁴ This has been a continuous challenge in the microelectronics industry and its success has been reliant on thin film technology.

A wide variety of vacuum based approaches are currently used for the deposition of thin films. The most basic of these techniques is physical vapor deposition (PVD). In this technique, a target containing the elements of the film is used as the source. The target can be heated and the desorbing film is then deposited on a sample facing the target. An electron beam can also be used to evaporate the source material to provide faster responses and reasonable fluxes. For materials with low vapor pressures, even at high temperatures, heavy ions can be accelerated toward the target to sputter material from the target. A problem with this method however, is that the technique results in line-of-sight deposition. Therefore, PVD techniques can only achieve aspect ratios of $<5:1$.⁵

Another thin film deposition technique currently available is molecular beam epitaxy (MBE). When using MBE, elemental sources of the desired film can be separately headed to produce precise fluxes of a material onto a surface. Thus, layer by layer growth is achievable using this technique and has been observed for a variety of systems. Similar to PVD, this deposition technique relies on a controlling a known flux onto a surface for a controlled exposure time. For this reason, the ability to grow films with both of these techniques is limited by the uniformity of the incoming flux, the time, and the rate the films are deposited.

To avoid these issues observed when using either PVD or MBE, alternative approaches use molecular precursors containing some or all of the elements in the film. Chemical vapor deposition (CVD) is one such technique which uses these molecular precursors. Since molecular precursors can have much higher vapor pressures than elemental sources, films can be grown at higher rates than when using elemental precursors. Another advantage of CVD is that line-of-sight is not needed because stable gas precursors are used. By not being confined to a line-of-sight technique, much larger surfaces can be coated as well as the coating of higher aspect ratio structures. Unfortunately, this technique is dependent on the flux of the precursors to the surface and reaction kinetics which can lead to complications when depositing precise thicknesses or uniform films, especially in high aspect ratio structures.

In contrast to CVD, ALD is a technique that utilizes self-limiting surface reactions in a binary reaction sequence. This method is versatile because of its self-limiting nature. With ALD techniques, up to a monolayer of a thin film can be deposited every reaction cycle. The thickness is controlled by the number of reaction cycles as opposed to flux and time, thus extremely precise film thicknesses can be deposited. The use of a self-limiting binary reaction sequence also allows for extremely high aspect ratio structures to be coated. Conformal deposition in aspect ratios as high as 5000:1 have been achieved using ALD.⁶

As the previous CMOS example illustrated, the need for a thin film technology such as ALD is required. Moreover, a variety of other technologies are dependent on ALD to solve current technological boundaries. For this reason ALD

has grown dramatically since its first demonstration in 1981.⁷ As Figure 1.1 illustrates, the number of publications in the field of ALD has increased nearly exponentially since 1981.⁸ Since its induction, ALD has been used to deposit a variety of materials such as oxides, nitrides, sulfides, and various metals.⁹

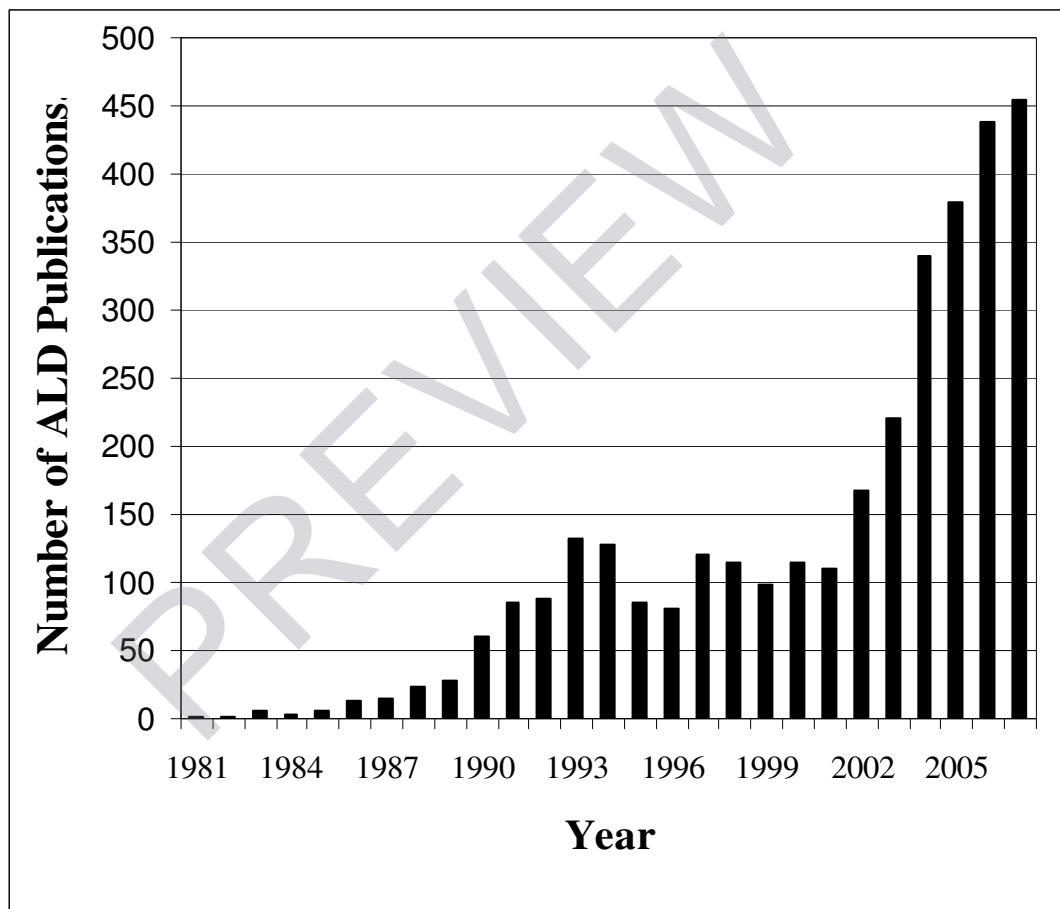
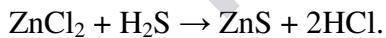


Figure 1.1 Graphical representation of the number of ALD publications each year from 1981-2007.

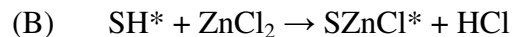
1.2 Basic Concepts of Atomic Layer Deposition

Atomic layer controlled growth is based on sequential, self-limiting surface reactions. The atomic layer controlled growth of conformal thin films can be obtained using ALD techniques.⁹⁻¹¹ A wide variety of materials including oxides, nitrides, sulfides and various metals have been deposited using ALD.⁹ The first demonstration of ALD was accomplished using elemental zinc and sulfur to deposit ZnS.¹¹ Self-terminating surface reactions were achieved because the bond strength of Zn-S is stronger than both the Zn-Zn and S-S interactions (physisorption). Self-terminating reactions were observed by heating the substrate high enough to desorb multilayers (either Zn-Zn or S-S) but low enough not to desorb the first chemically bonded Zn-S layer.

Subsequently, molecular precursors were used to yield similar results. Molecular precursors are advantageous over elemental precursors due to their increased vapor pressure. An example is the deposition of ZnS using molecular precursors. The thin film growth of ZnS can be accomplished using the binary CVD reaction:^{7,11,12}



This binary reaction can be divided into the following two surface half-reactions:



where the asterisks designate the surface species. During reaction (A), the Zn-Cl* surface species is exposed only to the H₂S molecular precursor. The result of the H₂S exposure is the formation of a Zn-SH* terminated surface and the release of HCl as a

reaction byproduct. A key in this reaction is that neither H_2S nor HCl further react with the Zn-SH^* surface species. After the reaction is complete, excess H_2S and the HCl byproduct are pumped out of the system. During reaction (B), an exposure of ZnCl_2 to the hydride terminated surface results in the formation of a Zn-S bond, while leaving a Zn-Cl^* terminated surface. Again, neither the precursor nor the HCl byproduct further react with the surface and can be pumped out of the system. The result of reactions (A) and (B) is the formation of a ZnS layer in which the surface is as it began, ready for the AB reaction cycle to repeat.

Typically, ALD works best for binary compounds since the binary CVD reaction can be separated into two half-reactions. The typical ALD process to form a binary compound consists of alternate exposures of two gas phase molecules onto a substrate in an ABAB... sequence. As illustrated in Figure 1.2, the (A) gas exposure reacts with surface species, adds the first desired atomic element, and changes the surface species. The subsequent (B) gas exposure reacts with the new surface species and adds the second desired atomic element. This second reaction also changes the surface species back to the original surface species. The ABAB... sequence can deposit thin and conformal films with atomic layer control.

Although ALD is generally used for the deposition of binary materials, ALD has also been developed for single element film growth. The general approach for single element film growth requires one surface reaction in the binary sequence to serve a sacrificial role to remove the surface functional groups without directly affecting the film composition. The ALD of W is one such system in which a sacrificial stripping reaction has been used.¹³ The W ALD film growth is

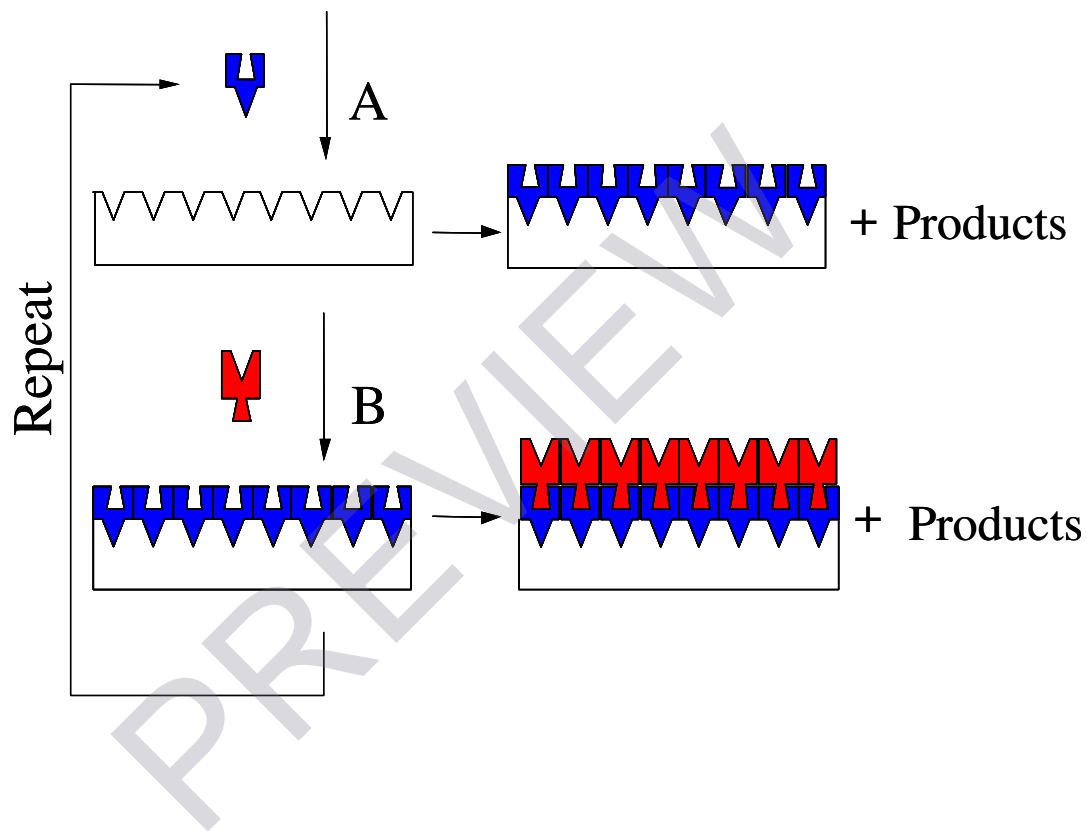
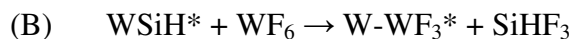
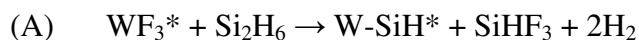


Figure 1.2 Schematic representation of atomic layer deposition using self-limiting surface chemistry in an AB binary reaction sequence.

accomplished by two self-limiting surface reactions that are described in previous work:¹³



where the asterisks denote the surface species. The W ALD growth occurs during alternating exposures to WF_6 and Si_2H_6 . In this case the sacrificial role to strip the fluorine from tungsten was accomplished using Si_2H_6 , which was not incorporated into the film.

The proposed model for binary reaction sequence chemistry illustrates a limiting case and the actual mechanisms may be much more complex. Factors such as steric hindrance between surface species may cause reactions to terminate before reaching completion. Moreover, surface functional groups may be unstable at a deposition temperature and desorb or decompose leading to further surface reaction. Reactions between neighboring surface groups may also occur during ALD.

Temperature is also a critical factor for ALD reactions. For most ALD systems an “ALD window” is observed. This window is a temperature region in which the growth rate is constant. This region is depicted in Figure 1.3 as well as the regions outside of this window in which non-ALD behavior is observed. At temperatures above this ALD window, the process can suffer from either the decomposition of precursor (pyrolysis) or desorption of precursor from the surface. The decomposition of precursor leads to the observation of higher growth rates due to continuous reaction of precursor with the surface. Decomposition of precursor typically leads to higher levels of film impurities. In the case of precursor desorption

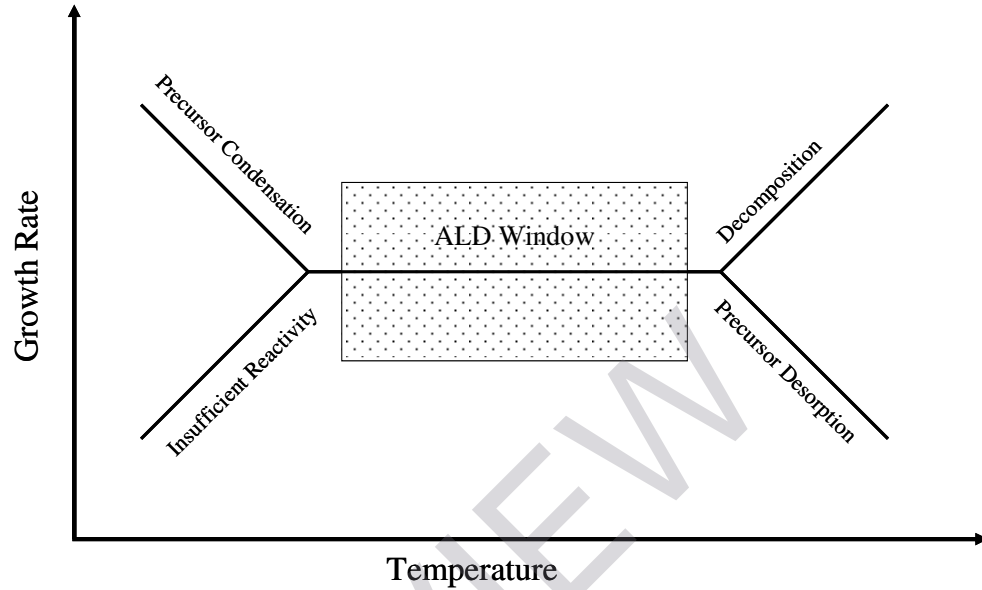


Figure 1.3 Effect of temperature on the ALD growth rate, and the constant growth ALD temperature region.

at higher growth temperatures, the growth rate observed is lower due to the loss of reactive surface sites. In contrast, at temperatures below the ALD window there is the possibility of either precursor condensation or insufficient reactivity (kinetically limited). Precursor condensation translates into higher growth rates due to the abundance of precursor on the surface while the latter results in lower growth rates being observed. As Figure 1.3 illustrates, there is a balance between precursor stability and reactivity which must be understood in order obtain reproducible film thicknesses and to avoid film contamination.

1.3 Techniques for Studying Atomic Layer Deposition

Surface science techniques have been the predominant means of studying ALD over the past several decades. There are a number of both *ex situ* and *in situ* techniques which can be used to study ALD. The *in situ* techniques provide information related to the reaction mechanism during the ALD reactions. *Ex situ* techniques on the other hand, are used to obtain film properties such as elemental composition, thickness, or crystallinity. Each single technique provides some insight into the ALD process of a material. However, when using multiple techniques in conjunction with each other, a full understanding of an ALD system can be achieved.

Some of the *in situ* techniques for studying ALD include Auger electron spectroscopy (AES), quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), and Fourier transform infrared (FTIR) spectroscopy. Techniques such as QMS and AES require high vacuum environments. While other techniques such as FTIR spectroscopy and QCM for example can be accomplished at higher pressures in flow type ALD reactors. Some of the *ex situ* techniques for studying ALD films are ellipsometry, X-ray reflectivity (XRR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), Rutherford backscattering (RBS), atomic force microscopy (AFM), four point probe, and transmission electron microscopy (TEM). The techniques can be grouped in four primary categories: film composition techniques, thickness measurement techniques, surface chemistry techniques, and film characterization techniques.

Included in the film composition techniques are AES, XPS, SIMS, and RBS. All of these techniques require high vacuum. AES and XPS are very sensitive to the surface and near surface region and yield elemental composition of thin films. Additionally, when sputtering in combination with AES or XPS, elemental composition through a film can be monitored. RBS on the other hand is used to determine the structure and composition of the entire thin film. Lastly, SIMS is the most sensitive surface analysis technique, being able to detect elements present in the parts per billion range. SIMS can be used with sputtering to analyze impurity concentrations through a thin film.

The thickness measurement techniques are profilometry, ellipsometry, XRR and TEM. Surface profilometry obtains the film thickness by measuring the step height between the deposited film and an area that was masked using tape or photoresist. Ellipsometry can measure both the film thickness and film refractive index. Ellipsometry has the ability to measure the thickness of a thin film within $\pm 1 \text{ \AA}$ on an optically flat sample. XRR is a sensitive technique and can be used to obtain the film thickness, film density, and the interfacial surface roughness for thin films on flat substrates. TEM is primarily used to determine the film thickness on particles by the contrast between the underlying particle and the thin film coating on the particle but can also be used to visualize the conformality and morphology of a thin film.

Techniques for monitoring surface chemistry include FTIR spectroscopy, QCM, and QMS. FTIR spectroscopy monitors the surface species during ALD. High surface area particles provide sufficient surface sensitivity for transmission FTIR

experiments. Vibrational spectroscopy reveals the gain and loss of surface species during the two surface half-reactions. The vibrational spectrum of the deposited material also grows with AB reaction cycles. QCM is used to monitor ALD growth in viscous flow reactors. The QCM has exceptional mass sensitivity and the mass changes for each half-reaction are able to unravel the surface reactions. The growth of the film is also determined by the linear mass increase versus the AB reaction cycles. QMS can be used to monitor the reaction byproducts during and ALD reaction. Moreover, when using both FTIR spectroscopy and QMS, the byproducts can be related back to the reaction mechanism during the ALD.

Last are the various film property techniques which include AFM, Hg-probe, four-point probe, and XRD. The film topography and surface roughness can be obtained using AFM. For electrical characterization the current-voltage (IV) and capacitance-voltage (CV) properties of insulating films can be characterized using a Hg-probe. While thin film conductivity can be measured using a four-point probe. Finally, XRD can be used for structural characterization and crystalline alignment of thin films deposited by ALD.

1.4 Statement of Purpose

As the field of ALD continues to expand, the optimization of the precursor chemistry is required. Some general requirements for a good ALD precursor include: high vapor pressure, temperature stability, sufficient reactivity, availability, and non-toxicity. Many of the initial ALD systems for oxides and nitrides involve the use of

halogenated precursors. Halogenated precursors generally suffer from low volatility, and low reactivity. In addition, the use of halogenated precursors results in byproducts such as HCl or HF which are corrosive. However, these precursors are some of the cheapest and most commercially available.

These precursor requirements led to the primary goal of this thesis which was to develop novel chemistries for the ALD of MgO, MnO, TaN, and SiO₂ using organometallic precursors as opposed to the conventional metal halides. Organometallic precursors offer the advantages of higher volatility, higher reactivity, and non-corrosive byproducts. Utilizing organometallic precursors allows for lower deposition temperatures as well as lower precursor exposures.

Another goal of this thesis was to study the ALD of MgO, MnO, TaN, and SiO₂ using the *in situ* techniques of FTIR spectroscopy and QCM. These techniques were conducted to monitor surface species during each half reaction and verify saturation behavior. Once the surface chemistry was understood, the films were then deposited on Si(100) substrates using the optimal deposition conditions. The films grown on Si(100) substrates were used for numerous *ex situ* thin film analysis techniques. XRR experiments were conducted to yield both film thicknesses and film density, XRD experiments were used to determine film crystallinity, and four-point probe measurements were conducted to determine film resistivities. XPS sputter depth profiling, RBS and in some cases SIMS were also conducted to obtain compositional analysis. TEM and SEM were utilized to visualize the conformality of the films and confirm growth rates.