The design and modification of a sputter system for DC reactive sputtering of alumina and zirconia thin films

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THE DESIGN AND MODIFICATION OF A SPUTTER SYSTEM FOR DC REACTIVE SPUTTERING OF ALUMINA AND ZIRCONIA THIN FILMS

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by

Diane Van Ho
B.S., Louisiana State University, 2008
August 2011
I would like to dedicate this thesis to
my parents, Nghia Thy Ho and Huong Thu Dinh,
my brother, Charlie Ho, my extended family, and
my boyfriend, Edward Scheuermann.
Through their love, support and encouragement,
I had the strength to pursue and complete my Master’s degree.
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ABSTRACT

Yttria-stabilized zirconia (7% YSZ) is the most used material for thermal barrier coatings (TBCs) to reduce the conductive heat transfer on turbine blades, but it is not resistant to infrared radiation. In order to reduce radiation heat transfer, alternating materials, such as alumina and zirconia, can be used to fabricate multi-layer coatings in which each layer is optimized to reflect a targeted range of wavelength. This research aims to fabricate these multi-layer coatings by reactive magnetron sputtering.

Reactive magnetron sputtering is the sputtering of an elemental target in the presence of a reactive gas that will react with the target material to form a compound on the substrate. Although reactive magnetron sputtering has high deposition rate, a major disadvantage of reactive magnetron sputtering is target poisoning, which leads to very low deposition rates.

In this research the flow control of reactive gas method has been used to complement the setup of the current sputtering system. First, pure aluminum and zirconium thin films are deposited and analyzed for film structure and properties. Then, alumina and zirconia thin films are reactively sputtered.

The films are analyzed using XRD and SEM to determine the crystallography and surface structure. The XRD results of the metallic thin films for aluminum and zirconium shows the peaks corresponding to FCC and HCP crystal structure, respectively. The XRD results of the alumina and zirconia films do not contain any peaks, indicating an amorphous structure. XPS results give elemental compositions for the films from which the stoichiometry can be determined. The composition of the films is analyzed for before
and after ion etching of the surface. The XPS results concluded that the films were under stoichiometric.

More experiments need to be performed to determine the best ratio of inert and reactive gas in order to produce stoichiometric films. Modifying the current system could help to improve the quality of the films by utilizing a pulsed-DC power source, an arc suppression system, the partial pressure control of the reactive gas, and other instruments to properly measure the film properties.
CHAPTER 1: INTRODUCTION

1.1 Motivation

Thermal barrier coatings (TBCs) are ceramic coatings applied to metal components in gas turbine engines or rocket engines that are exposed to high temperatures in order to extend the service life of that component. Even though research in this area began over 60 years ago, many researchers are still trying to find ways to improve TBCs for engines operating at even higher temperature ranges to achieve higher efficiencies. The current work aims to modify a sputter system to incorporate reactive sputtering capabilities and to fabricate alumina and zirconia thin films by reactive magnetron sputtering. Eventually, this process can be used to optimize the thickness of the individual layers of multi-layer thermal barrier coatings in order to reduce the infrared radiation passing through the TBCs.

1.2 Brief History of Thermal Barrier Coatings (TBCs)

This brief history was obtained from a NASA paper written by Robert A. Miller [Miller, 2007]. A form of thermal barrier coatings have been around since the 1940s when they were first introduced as frit enamel coatings for turbine blades by W.N. Harrison, D.C. Moore, and J.C. Richmond of the National Bureau of Standards in 1947. As early as 1948, one of the first frit coatings was tested on turbine blades in an engine. Bartoo and Clure tested a coating in an engine for 100 hours in 1953 (Figure 1.2.1). The Air Force led the development of frit coatings in the 40s, 50s, and 60s. Working with industrial partners, NACA, now NASA began using TBCs in the development of LH₂/LOₓ rocket engines in 1956. In 1960, the first flame sprayed coating used for rocket applications
was the Rokide™ thermal barrier coatings on the XLR99 rocket engine nozzles of the X-15 developed by L.N. Hjelm and B.R. Bornhorst. The Rokide™ TBC had a zirconia top coat and a nickel chrome bond coat. In the 1960s and early 1970s, Sal Grisaffe conducted materials-oriented thermal spray research using alumina, zirconia (calcia and possibly yttria stabilized), and hafnia for nuclear rocket applications.

![Image of engine test of coating on one blade for 100 hours by Bartoo and Clure in 1953](Miller, 2007)

Figure 1.2.1: Engine test of coating on one blade for 100 hours by Bartoo and Clure in 1953 [Miller, 2007]

Since 1970 plasma sprayed TBCs were used in commercial combustors. S. Stecura, C.H. Liebert, and F.S. Stepka played key roles in the development of the "modern" thermal spray coatings in the mid-1970s. These coatings, which survived a J-75 engine test, used yttria to stabilize zirconia and a MCrAlY type bond coat. Electron-beam
physical vapor deposition (EB-PVD) TBCs were introduced onto turbine blades in 1989 and remain the coating of choice for first-stage turbine blades (Figure 1.2.2).

1.2.1 Fabrication and Application of TBCs

TBCs are typically deposited using two common processes: air plasma spraying and electron-beam physical vapor deposition. As mentioned before, plasma spray technique, a form of thermal spray, was developed in the 70s, and EB-PVD was introduced in the early 90s. Nowadays it is more common to use EB-PVD for TBC deposition because it offers superior thermo-mechanical properties and lifetime performance over plasma spray process [Kelly, 2006]. A thermal barrier coating system usually consists of three layers: the ceramic top layer, a thermally grown oxide (TGO) layer, and a bond coat layer to the substrate (Figure 1.2.3).

Figure 1.2.2: Comparison of thermal spray and EB-PVD thermal barrier coatings [Miller, 2007].
The most common ceramic material for the top layer is yttria-stabilized zirconia, which has low thermal conductivity, a high coefficient of thermal expansion and is chemically inert to combustion atmospheres [Leyens, 1999].

Figure 1.2.3: Schematic of thermal barrier coating system [Padture, 2011].

The bond coat, typically made with MCrAlY-type compositions or aluminides, must provide sufficient bonding between the ceramic top coat and the superalloy substrate and should have corrosion resistance. The chromium and/or aluminum in the bond coat also provide oxidation protection to the metal blades by forming an oxide scale.

The first applications of ceramic coatings were used on aero turbine blades in the 1940s and then on rocket engines in the 1960s. They are commonly used on combustion liners, turbine vanes, and turbine blades to protect the components from the harsh environment. The TBCs have also found application in the automotive industry. They are used to coat components of the exhaust system, such as exhaust manifolds, turbocharger casings, exhaust headers, downpipes, and tailpipes. The most recent
research has been on the development of multi-layer TBCs to protect against radiation heat transfer as engine temperatures are rising to increase efficiency.

In order to fabricate these new multi-layer TBC structures using reactive sputtering, the process of sputter deposition needs to be studied. A brief sputtering history will be presented to give a full background on sputter deposition.

1.3 Brief Sputtering History

Cathodic sputtering is the phenomenon of the cathode electrode disintegration under the bombardment of the ionized gas molecules when an electrical discharge is passed between electrodes at a low gas pressure [Holland, 1956]. Over a century ago, early investigators of electrical discharges in gases observed that the wall of a glow discharge tube became coated with a metallic deposit in the negative electrode region [Mattox, 2003]. W.R. Grove was the first to study what came to be known as “sputtering” (and sputter deposition) in 1852 [Grove, 1852]. This film deposition from a glow discharge was also observed by M. Faraday in 1854 and Julius Plücker in 1858 [Plücker, 1858]. Prof. A.W. Wright of Yale University published a paper in the American Journal of Science and Arts in 1877 on the use of an “electrical deposition apparatus” to form mirrors and study their properties [Wright, 1878]. C.J. Overbeck reported the deposition of compounds by sputtering in a reactive gas (“reactive sputter deposition”) in 1933 for use as optical coating [Overbeck, 1933]. In 1936 F.M. Penning [Penning, 1936] proposed the “crossed field” (electric and magnetic) electron trap to enhance plasmas in sputtering from cylindrical-hollow (inverted) magnetrons and cylindrical-post magnetrons [Penning and Mobius, 1940].
Although our basic understanding of this complex subject is incomplete, sputtering is a very mature technology, as evidenced by the many applications of the process. Some examples given by Parsons of these applications are magneto-optical storage media, compact disks, planarized coatings for multilayer circuits, optical multilayer coatings for mirrors and filters, solar control and low emissivity window coatings, conductors and barrier layers for very large scale integrated circuits, solar cells, diamond-like coatings, transparent conducting electrodes, amorphous optical films for integrated optics devices, luminescent films, microcircuit photolithographic mask blanks, wear-resistant coatings for cutting tools, and decorative coatings [Parsons, 1991]. Parsons also gives some reasons for using sputtering: excellent film uniformity; surface smoothness and thickness control; deposition of films with nearly bulk-like properties; versatility; good adhesion; high rates, which are comparable to evaporation. For film deposition there are two categories of sputter sources: glow discharge (diode, triode, and magnetron) and ion beam. This research uses glow discharge sputter sources for the sputtering process.

1.4 Thesis Overview

In this chapter the motivation for the current work was presented. A brief history and the applications of thermal barrier coatings were discussed. Also, a brief sputtering history was presented.

Chapter 2 talks about the background of glow discharges and different sputtering techniques. Some sputter theories are presented. Various sputter deposition arrangements are revealed and comparisons made. Reactive sputtering is examined and compared with conventional sputtering techniques.
Chapter 3 goes into more details about DC reactive magnetron sputtering of alumina and zirconia thin films. The works of other authors are presented in order to compare their results with findings from the current work.

Chapter 4 introduces the sputtering system and modifications the author made on the system. The system maintenance is also reviewed to show the many obstacles the author faced during this research. The chapter concludes with the details of the experimental procedures for metallic and reactive sputtering.

Chapter 5 provides the experimental results from metallic sputtering of aluminum and zirconium and reactive sputtering of alumina and zirconia. These results are then compared to findings of other authors.

Chapter 6 summarizes the current research project and provides recommendations for future work.
CHAPTER 2: BACKGROUND ON SPUTTERING

Sputtering is a technology that was discovered in the 1850s, but was not widely used until the technology advanced in the 1940s. Sputtering stems from the investigations of glow discharges, which is why the basic principles of glow discharges are presented in this chapter. An understanding of the fundamental physics behind glow discharges will lead to greater comprehension of the sputtering process.

2.1 Glow Discharges

The glow discharge phenomena relevant to diode sputtering will be described in this section. The schematic in Figure 2.1.1 represents the characteristics for the applied voltage as a function of current for a DC discharge formed in a low-pressure gas with a high-impedance DC power supply.

Figure 2.1.1: The current density versus voltage in a DC glow discharge [Vossen and Cuomo, 1978].
Vossen and Cuomo [Vossen and Cuomo, 1978] described the four distinct regions of this process: Townsend discharge (1), normal discharge (2), abnormal discharge (3), and arc (4). Initially, a very small current flows when a voltage is first applied due to the presence of a small number of ions and electrons from some external source (i.e. radiation). Because all of the charge present is moving, the current is nearly constant, but as the voltage is increased, charged particles acquire sufficient energy to produce more charged particles by collisions with the electrodes and neutral gas atoms. The current steadily increases as more charge is created, but output impedance of the power supply limits the voltage. This describes the Townsend discharge (1) region.

As neutral gas atoms become charged ions, they strike the cathode releasing secondary electrons, which form more ions by colliding with neutral gas atoms. These ions then return to the cathode producing more electrons that, in turn, produce more ions. This avalanche effect continues until the number of electrons generated is just sufficient to produce enough ions to regenerate the same number of electrons, which yields a self-sustaining discharge. The normal discharge (2) is the region when the gas begins to glow, the voltage drops, and the current abruptly rises. In this region, the bombardment of the cathode is initially not uniform, but rather concentrated near the edges of the cathode or irregularities on the surface. The bombardment gradually covers the cathode surface as the power is increased until a nearly uniform current density is achieved.

Further addition of power increases both the voltage and current density in the discharge. This region is called the abnormal discharge (3), and it is the mode in which sputtering is operated. Thermionic electrons as well as secondary electrons are emitted
when the current density reaches about 0.1 A/cm², followed by further avalanche effect. Since the voltage is limited by the output impedance of the power supply, a low-voltage high-current arc (4) discharge forms.

Mahan [Mahan, 2000] also describes the various regions of the glow discharge but includes more mathematical details. He gives a combination of several classic diagrams for the representation of applied voltage as a function of current for a DC discharge in an argon pressure range of 0.1-1.0 Torr (Figure 2.1.2). Voltage is taken to be the dependent variable, whereas current is the independent variable.

![Diagram of current versus voltage in a DC glow discharge](image)

**Figure 2.1.2: An illustration of current versus voltage in a DC glow discharge [Mahan, 2000].**

The *ohmic conduction* and *saturation* (A) regime is described by low current density and a small free electron density due to an external agent. In this region the conditions of the discharge does not resemble the sputtering plasma. In the low current range at higher electric fields, the current saturates as a function of the applied voltage: \( I_{\text{sat}} = \)
constant. All available electrons are swept from the cathode to the anode by the electric field. During saturation the discharge is not yet self-sustaining.

J. S. Townsend investigated that impact ionization of neutrals by electrons occurs when the applied voltage is increased to the point where the current rises beyond the saturation value [Mahan, 2000]. These neutral gas atoms are ionized when the electrons are accelerated towards the anode. This process of producing more free electrons and ions is known as the Townesnd discharge \((B)\). The ionization potential of a neutral atom is the minimum kinetic energy required for the impact ionization process with an ionization cross section of \(S_i\). For kinetic energies below the ionization potential, the cross section is zero. The assumption made for the electron current coming off the cathode is \(I_{sat}\). The electron current increases due to the impact ionization with distance from the cathode \((x)\) according to the following relation:

\[
\frac{dl_{de}}{dx} = S_i \cdot n \cdot l_{de}, \tag{2.1}
\]

which leads to the relation:

\[
l_{de}(x) = I_{sat} e^{S_i n \cdot x}. \tag{2.2}
\]

\(l_{de}\) is the Townsend electron current, \(I_{sat}\) is the saturation current, and \(n\) is the neutral particle density in \(m^{-3}\). The electron current at any distance \(d\) between the cathode and anode can be used to calculate the total current, \(l_{td}\), in the discharge, which is constant and independent of \(x\):

\[
l_{td, total} = I_{sat} e^{S_i n \cdot d} \tag{2.3}
\]
The ion current is given by the difference in the total current and the electron current:

\[ I_{tdi}(x) = I_{sat} e^{S_i n \cdot d} \left[ 1 - e^{S_i n \cdot (x-d)} \right] \]  

(2.4)

At \( x=0 \) the maximum ion current occurs, and the ion current equals zero at the anode.

The Townsend discharge is not yet self-sustaining since the current would stop if the ionization radiation were removed.

In the previous region, ions did not have enough kinetic energy to ionize neutral gas atoms, but in the breakdown (C) region, they play a major role in creating charged particles by knocking out free electrons from the cathode. This process can be defined by the yield or secondary electron emission coefficient, \( \gamma \). The yield \( \gamma \) is the number of secondary electrons emitted per incident ion. An energy-independent, empirical expression for the yield has been provided by [Raizer, 1991]:

\[ \gamma \approx 0.016(E_i - 2W), \]  

(2.5)

where \( E_i \) is the ionization potential of the cathode atom and \( W \) is the work function.

Breakdown is described as the region where the sudden drop in voltage is necessary to maintain the discharge at a fixed current. The electron current at the anode is given by:

\[ I_{be}(d) = I_{sat} e^{S_i n \cdot d} + \gamma I_{bl}(0) e^{S_i n \cdot d} \]  

(2.6)

Equation 2.6 describes the original saturation current enhanced by electron impact ionization plus the secondary electron current, also enhanced by the electron impact ionization between the electrodes. The increase in original electron saturation current enhanced by impact ionization plus the increase in electron current due to the
secondary electron emission at the cathode also enhanced by impact ionization is equal to the ion current at the cathode. The ion current $I_{bi}(0)$ is defined as:

$$I_{bi}(0) = \frac{I_{sat}e^{s_i n d}}{1-\gamma[e^{s_i n d}-1]}$$

(2.7)

As stated before, the total current of the discharge is constant and can be evaluated as the electron current at some distance $d$ between the electrodes:

$$I_{b, total} = I_{be}(d) = \frac{I_{sat}e^{s_i n d}}{1-\gamma[e^{s_i n d}-1]}.$$  

(2.8)

In breakdown, the discharge no longer depends on any external ionizing source and transitions to a self-sustaining discharge.

The next regime after breakdown is the *normal glow* ($D$) in which discharge voltage is constant while current varies. The current density at the cathode is not uniform; rather, the secondary electron emission is localized at the edges and any irregularities on the cathode surface. The ion bombardment will spread over the entire cathode surface as the current increases at constant applied voltage. At this point the discharge begins to have the general characteristics of the sputtering plasma.

Once the entire cathode area is used, further increase in the current can only be achieved by increasing the yield $\gamma$ and/or the cross section $S_n$, which means that the applied voltage is increased. This regime is known as the *abnormal glow* ($E$) where most DC sputtering processes are operated. The final region in Figure 2.1.2 is the *arc* ($F$) regime, which occurs as a result of extreme heating of the cathode by ion bombardment, leading to the thermionic emission of electrons.
2.1.1 The DC Glow

Plasma is another name for a glow discharge, which is an electrical current flowing through a gas that glows by light emission from the excited gas atoms. A glow discharge has various luminous and dark characteristics observed by early researchers, which is illustrated in Figure 2.1.3.

Figure 2.1.3: The luminous and dark regions of a DC glow discharge [Mahan, 2000].

Mahan [Mahan, 2000] states that the Aston dark space is the region where electrons emitted from the cathode has very low energy and ions are rapidly accelerated towards the cathode. The electrons cannot excite or ionize any gas particles due to their low energy. According to Cobine [Cobine, 1941], the cathode glow “appears to cling to the cathode surface.” Brown described it as a “velvety coating [resulting from] the loss of excitation energy of the positive ions on neutralization” [Brown, 1966].

The next region is also known as the “cathode sheath” of processing plasmas, but it is
usually several times thicker than the actual sheath. This region, the *Crookes (or cathode) dark space*, is a “region of primary interest...its thickness is approximately the mean distance traveled by an electron from the cathode before it makes an ionizing collision” as explained by Maissel and Glang [Maissel and Glang, 1970]. High velocity electrons that have accelerated across the cathode fall and low velocity electrons from impact ionization of neutral gas atoms are both present in this region.

In the *negative glow* region, enhanced visible emission is due to the larger cross section of secondary electrons for excitation of neutrals. Electrons lose their energy in the negative glow region, so that when they arrive in the *Faraday dark space*, they are not able to neither excite or ionize any neutral gas atoms nor gain any more kinetic energy. The rest of the luminous region is called the *positive column*. Here electrons can gain enough kinetic energy from the small electric field in order to excite neutral gas atoms again as they move towards the anode. Ions with sufficient kinetic energy can also bombard the anode and emit secondary electrons, which then excite neutrals, producing the *anode glow*.

### 2.1.2 A DC Discharge Model

Consider a pair of electrodes in which the cathode is the electrode that attracts cations (positive ions) from the plasma and the anode is the electrode that attracts anions (electrons). (a) is a schematic representation of a DC discharge and (b) illustrates the potential profile.

To model a practical discharge, the current density to the cathode is taken to be $j_{\text{ion}}$, which may be enhanced by secondary electron emission, and the current density to the
anode is the negative of this value:

\[ j_{an} = -j_{cat} \]  

(2.9)

In order to achieve these currents, the following relations must be true:

\[ v_{cat} = -V_{DC} \ll V_f \]  

(2.10)

and

\[ V_f < v_{an} < V_p, \]  

(2.11)

where \(v_{cat}\) and \(v_{an}\) are the voltages of the cathode and anode respectively, \(V_{DC}\) is the applied voltage, \(V_f\) is the floating potential, and \(V_p\) is the plasma potential. Thus, this leads to the frequent observation that the plasma is the “most positive” body in the main current path of the discharge [Mahan, 2000].

Figure 2.1.4: (a) Schematic diagram of a DC sputtering discharge; (b) the electrostatic potential profile as a function of distance from the cathode [Mahan, 2000].
Using the expression for the current density for when the applied voltage is less than the plasma potential \( j_{an} = j_{\text{ion}} - qz^{-} \exp[-q(V_p - v_{an})/kT^{-}] \), the expression for the plasma potential relative to the anode can be obtained:

\[
V_p - V_{an} = \frac{-kT^{-}}{q} \ln \left[ \frac{j_{an} - j_{\text{ion}}}{-qz^{-}} \right]
\]  

(2.12)

When the anode is grounded, \( v_{an} = 0 \). In a practical model, the anode area is much larger than the surface area of the cathode, which increases the plasma potential. The potential drop across the cathode sheath is known as the cathode fall:

\[
\text{Cathode Fall} = V_p + V_{DC}.
\]  

(2.13)

This means that a value greater than the applied voltage is the maximum possible kinetic energy with which ions strike the cathode. Also, the sputtering power density is given by: \( p_{\text{ion}} = j_{\text{ion}} \cdot (V_p + V_{DC}) \).

The plasma body is separated from the cathode and anode by the sheaths, which are high-electric field regions. Figure 2.1.4(b) shows the resulting electrostatic potential as a function of position between the electrodes.

### 2.2 Sputter Yield

The most fundamental parameter of all sputtering processes is the sputtering yield, which was previously defined as the number of atoms emitted from the cathode surface per incident ion. The threshold for sputtering is approximately equal to the heat of sublimation, and the sputter yield increases with incident ion energy in the energy range of 10-5000 eV [Almen and Bruce, 1961]. The erosion rate of sputtering targets and
approximately the deposition rate of sputtered films can be determined by the sputtering yield. A compilation of sputtering yields for various elements is published in [Vossen, 1978]. Sputtering yields of metals rarely differ by more than a factor of 10 under similar conditions. However, over the years more recent developments and error corrections have led early data to be regarded as obsolete. Probably the most recent comprehensive compilation of sputter yield data for elemental targets was done by Matsunami et al [Matsunami et al, 1984]. They prepared graphs of yield as a function of energy using a database of all published sputter yield measurements available in early 1983. An empirical curve for the yield as a function of projectile energy \( Y(E) \) was plotted in addition to the actual data points obtained from literature. The empirical yield formula of Matsunami et al. is given by:

\[
Y(E) = 0.42 \frac{\alpha^* Q s_n(\varepsilon)}{U_s[1+0.35U_s s_e(\varepsilon)]} \cdot \frac{8.478Z_pZ_r m_p}{(Z_p^{2/3} + Z_r^{2/3})^{1/2} (m_p + m_r)} \cdot \left[1 - \left(\frac{E_{th}}{E}\right)^{1/2}\right]^{2.8}, \tag{2.14}
\]

where \( U_s \) is the sublimation energy, \( \alpha^*, Q, E_{th} \) are empirical parameters, \( s_e \) and \( s_n \) are the inelastic and nuclear reduced stopping cross section respectively, \( m_p \) and \( m_r \) are the projectile mass and recoil ion mass respectively, \( E \) is the projectile energy, and \( Z_p \) and \( Z_r \) are the atomic number of projectile and recoil ion respectively. The empirical parameters can be calculated using the following formulas:

\[
\alpha^* \left(\frac{m_r}{m_p}\right) = 0.08 + 0.164 \cdot \left(\frac{m_r}{m_p}\right)^{0.4} + 0.0145 \cdot \left(\frac{m_r}{m_p}\right)^{1.29} \tag{2.15}
\]

and
\[ E_{th}\left( \frac{m_r}{m_p} \right) = U_s \cdot \left[ 1.9 + 3.8 \cdot \left( \frac{m_r}{m_p} \right)^{-1} + 0.134 \cdot \left( \frac{m_r}{m_p} \right)^{1.24} \right]. \quad (2.16) \]

Lindhard’s nuclear, \( s_n \), (elastic) and the inelastic, \( s_e \), reduced stopping cross section are approximated by:

\[ s_n(\varepsilon) = \frac{3.441\sqrt{\varepsilon} \ln(\varepsilon + 2.718)}{1 + 6.355\sqrt{\varepsilon} + \varepsilon(-1.708 + 6.882\sqrt{\varepsilon})} \quad (2.17) \]

and

\[ s_e(\varepsilon) = 0.079 \cdot \frac{\left( \frac{m_p + m_r}{m_p} \right)^{3/2}}{m_p^{3/2} m_r^{1/2}} \cdot \frac{Z_p^{2/3} Z_r^{1/2}}{\left( Z_p^{2/3} + Z_r^{2/3} \right)^{3/4}} \varepsilon^{1/2}, \quad (2.18) \]

where the reduced energy is defined by

\[ \varepsilon(E) = \frac{0.03255}{Z_p Z_r \left( Z_p^{2/3} + Z_r^{2/3} \right)^{1/2}} \cdot \frac{m_r}{m_p + m_r} \cdot \frac{E}{m_r}. \quad (2.19) \]

### 2.3 Sputter Theory

One of the first theories of cathode disintegration was the belief that heated gas trapped in small cavities in the metal exerted sufficient pressure to blow particles out of the cathode. However, Baum disproved this theory by showing that sputtered material exited the cathode in atomic form with high thermal velocities [Baum, 1927]. Lamar and Compton [Lamar and Compton, 1934] believed in the momentum transfer theory and explain sputtering as a mechanical “bumping off of surface atoms by ions which have penetrated below the surface and rebounded.” While some may call sputtering “momentum transfer” process, it is really an energy transfer process in elastic collisions.
during which momentum must be conserved [Mahan, 2000]. In 1940 Penning and Mobius discovered that the sputtered atoms were sufficiently excited under intense ionizing conditions in a magnetic field to emit characteristic spectra [Penning and Mobius, 1940]. This was seen through the sputtering of copper where the discharge was a greenish hue. In modern sputtering theory discussion, there are two groups of such theories. One group of researchers, such as Blechschmidt and v. Hippel, state that at the point of impact of the positive ions, sputtering is due to local heating and thermal evaporation of the cathode atoms [Blechschmidt and Hippel, 1928]. Strong evidence against a universal thermal mechanism is due to the lack of yield dependence on target temperature [Bohdansky et al., 1987]. Another group of investigators argue that sputtering is due to the emission of atom-on-ion impact as seen in the same manner as secondary electron emission. Langmuir and Kingdon advanced this impact theory in order to describe the sputtering of thorium from a tungsten surface [Kingdon and Langmuir, 1923].

### 2.3.1 Evaporation Theory

Starr [Starr, 1939] has done an investigation of the evaporation theory of sputtering. He has reported that an empirical relation exists between the rate of sputtering of various metals and the total heat $W_H$ required to evaporate the metal [Holland, 1956]. Starr states that the sputtering rate for fixed glow discharge conditions follow:

$$Q = C/W_H^2$$

(2.20)

where $Q$ is the mass sputtered per ampere-hour and $C$ is a constant depending on the discharge conditions. He also argues that the theory of localized high temperature with
thermal evaporation predicts an exponential relationship, whereas a linear relationship is given by the theory of direct momentum transfer of the impinging ions with the metal atoms. Starr believed that sputtering is a double evaporation process. Initially, the sputter rate of emitted metal atoms by direct energy transfer due to ion bombardment is inversely proportional to the total heat of evaporation $Q \sim 1/W_H$. After leaving the cathode surface, the metal vapor condenses into a fine aggregate (metal powder). Additional exposure to the heat of ions and electrons near the cathode surface would cause re-evaporation into the residual gas. Starr does not give any experimental evidence of this theory.

### 2.3.2 Momentum Transfer Theory

Wehner’s research in the 1950s was one of the most important works on sputtering because it provided a satisfactory explanation of the energy exchange mechanism between the bombarding ions and cathode atoms [Wehner, 1954]. He argued that evaporation theory cannot explain the dependence of the sputtering rate on the angle of incidence of the positive ions. Wehner used Hg$^+$ ions impinging at normal incidence to bombard a target (of different metals) in order to measure the minimum ion energy for sputtering. He obtained that the heat of sublimation was proportional to the product of the momentum transferred at the threshold energy $V_c^*$ from the ion to the metal atom along with the bulk sound velocity of the metal. The threshold energies can be calculated from

$$V_c^* = \left( \frac{1.68 \times 10^5 (M_g + M_m) W_H}{1 \frac{3}{2} v_s M_m} \right)^2$$

(2.21)
where \( \nu_c^* \) is in eV, \( M_i \) and \( M_m \) are the atomic weights of the ion and metal respectively, \( v_s \) is the bulk sound velocity of the metal in cm/sec, and \( W_H \) is the heat of sublimation of the metal in Kcal/mol. Wehner states that [Holland, 1956]:

“The significance of the sound velocity here, although not yet fully understood, is obviously to introduce the elastic constants of the material, which determine what part of the transferred energy with the momentum directed to the inside of the material arrives at the surface with a momentum reversed in direction. This part has to be at least equal to the binding energy of a surface atom before sputtering ensues.”

Now that the sputtering background and theory have been introduced, the next sections will cover the different types of sputtering processes.

### 2.4 Diode Sputtering

The simplest sputter source is the planar diode. The diode electrodes are the target (cathode) and the substrate (anode) within a vacuum chamber. Typically, the target is disk-shaped with a diameter of about 5 to 10 cm and is thermally mounted to a water-cooled backing plate or directly water-cooled. The anode is the substrate or the chamber walls and is usually separated from the target by a few centimeters. A current flowing through a low pressure gas is called a discharge. Plasma, also known as the fourth state of matter, is a partially ionized gas, and some plasmas are also glow discharges, in that they glow with light emission from excited atoms [Mahan, 2000].

There are three fundamental sputtering arrangements: a direct-current (DC) diode discharge, a capacitive radio-frequency (RF) diode discharge, and a planar magnetron
with either a DC or RF discharge. In diode sputtering, energetic ions from the plasma of a gaseous discharge bombard the target and cause neutral target atoms to be ejected through momentum transfer. The ejected target atoms impinge on the substrate forming a coating. The target is the cathode of the discharge connected to either a DC or RF negative voltage supply, and the anode is usually grounded. Argon gas, which maintains a pressure on the order of 1 Torr, is typically the inert gas used as the medium for the plasma. As argon ions collide with the target surface, secondary electrons are emitted from the surface. These electrons are accelerated back across the sheath and gain significant energy, which is used to form more ions to sustain the discharge [Rossnagel, 2002]. The power supply can either be a high-voltage DC source or a high voltage RF source. The standard frequency used in the RF source is 13.56 MHz due to government communications regulations. The mean ion current density to the target is on the order of 1 mA/cm² for both DC and RF sources. However, for RF source, the amplitude of the total RF current is an order of magnitude (or more) higher. Generally, an RF discharge can operate in the same way as a DC discharge, but the difference is that the applied RF voltage oscillates with time. In addition, to develop the necessary DC self-bias, a blocking capacitor is placed in series with the powered electrode. A matching network is utilized to optimize power transfer from the RF source to the plasma [Mahan, 2000].

DC diode plasmas have typically been used for sputtering etching of samples placed on cathode surface or sputtering deposition of cathode material onto samples placed on the anode. However, DC plasmas are infrequently used because it is relatively slow compared to other deposition techniques and requires conductive electrodes to allow
the flow of the current. Using an RF source has some advantages over DC source, such as high deposition rates at lower voltages and lower sputter pressures and sputtering of insulating targets. Below shows the circuit schematics of DC (a) and RF (b) sputtering arrangements [Mahan, 2000].

The efficient use of target material is an advantage of diode sputtering since the diode electrodes can be large and the electric field between them is uniform, so the ion flux is nearly constant over the target. However, inefficient use of secondary electrons is a major disadvantage of diode sputtering. Also, the substrate temperature significantly increases due to the bombardment of the growing film, and diodes have low deposition rates compared to other sputter sources that are capable of low pressure operation [Parsons, 1991]. Although film deposition was discovered through investigations of glow discharges, diode sputtering is not commonly used since the development of the magnetron.

Figure 2.4.1: Circuit schematics of a sputtering system with DC (left) and RF (right) power supply [Mahan, 2000].
2.5 Magnetron Sputtering

As previously mentioned, Penning and Mobius [Penning and Mobius, 1940] first introduced the concept of cylindrical-hollow magnetrons in 1940. They found that sputtered atoms under the intense ionizing conditions obtained in a magnetic field were sufficiently excited to emit characteristic spectra. Since then many configurations have been developed to advance this technology. The most notable work on post cathode magnetron sputtering was done by A.S. Penfold and J.A. Thornton in the 1970s. The planar magnetron has been established as the embodiment of a high deposition rate sputtering source. J.S. Chapin first introduced the planar magnetron in 1974 even though this “obvious” solution eluded discovery and implementation for more than 30 years [Waits, 1978]. Several manufacturers had various versions of the planar magnetron sputtering source commercially available by early 1975. The planar magnetron is just the classical DC or RF diode sputtering arrangement with the addition of permanent magnets directly behind the cathode. There are various geometries but all magnets are arranged in such a way that the magnetic field lines are parallel to the cathode surface and perpendicular to the electric field lines (Figure 2.5.1). This causes the secondary electrons to drift in a closed path in the $-\vec{E} \times \vec{B}$ direction, also known as the Hall Effect, trapping the electrons near the cathode surface. This arrangement results in enhanced ion bombardment and sputtering rates for both DC and RF discharges.

A typical planar magnetron configuration is where a disk-shaped target (cathode) having a toroidal plasma ring facing and parallel to a fixed substrate holder (anode). RF planar magnetron sputtering allows the use of insulating targets and direct or reactive
deposition of dielectric films. However, due to the complexity of the RF power supply and the difficulty of ensuring an efficient RF ground, the choice for deposition of electrically conducting materials is DC planar magnetron sputtering.

**Figure 2.5.1: Depiction of the magnetic and electric field on a magnetron cathode [Mahan, 2000]**

Waits [Waits, 1978] reports that argon pressures of 0.5-30 mTorr and DC voltages of 300-700 V are typical operating parameters for DC planar magnetrons. RF planar magnetrons can operate at much lower voltages than their RF diode counterparts. Although RF magnetrons are necessary for sputtering insulating targets, they are about half as efficient as DC magnetrons. For a given power, RF planar magnetron deposition rate is constant (±10%) and independent of pressures ranging from 1-20 mTorr. Parsons lists typical magnetron characteristics: cathode current density of 20 mA/cm², discharge voltage 250 to 800 V, minimum pressure of about 1 mTorr, and target-to-
substrate distance vary from a few centimeters to 20 cm (about 6 cm is typical). One of the disadvantages of the planar magnetrons is poor utilization of the target material, which is typically 20-30% of the starting target material [Parsons, 1991].

Some applications listed by Waits for planar magnetron deposition are: decorative or functional coatings on plastic, anticorrosion or abrasion-resistant coatings on metals, large-scale integrated circuits, thermal printheads, and on a smaller scale, coating of heat sensitive biological samples.

2.6 Reactive Sputtering

G.A. Veszi introduced the term “reactive sputtering” in 1953 [Veszi, 1953]. The sputtering of a metal target in the presence of a reactive gas to form a compound is known as reactive sputtering (Figure 2.6.1).

Dielectric films can be sputtered from an insulating target comprised of the desired compound from an RF sputter source or by reactively sputtering a metal target with a suitable reactive gas using either DC or RF sputter sources. For example, reactive sputtering is commonly used for the deposition of oxides and nitrides. The disadvantages of directly sputtering dielectric films from a ceramic target using RF power is that the deposition rate is very low compared to elemental deposition and target cracking due to the poor physical stability of the compounds.

Reactive sputtering is usually the preferred method because of the following advantages [Parsons, 1991]:

- Metal targets can be machined;
- Metal targets have high thermal conductivity and, therefore, can handle high power densities without cracking;
- Different types of dielectrics can be fabricated by choosing different reactive gas mixtures; and
- High-rate techniques give deposition rates comparable to those of pure metals.

Figure 2.6.1: Simple reactive sputtering geometry [Rossnagel, 2002].
Another reason for using reactive sputtering with metal targets is the ability to use DC power instead of RF for high rate, controlled deposition. The disadvantage of using metal targets in reactive sputtering is that the target surface can also react with the gas to form an insulating thin film on the surface, which drastically alters the sputtering
process. During reactive sputtering, the target operates in two states: metallic mode and compound mode. Metallic mode is characterized by high target voltage and low gas pressure leading to high deposition rates. Compound mode is when a thin ceramic film forms on the target surface leading to low target voltage at high gas pressures. It is desirable to operate in the transition region between these two modes. In order to determine where this transition region lies, the hysteresis effect must be observed to determine the critical partial pressure of the reactive gas. Figure 2.6.2 below illustrates the hysteresis phenomena where deposition rate and discharge voltage are plotted as a function of reactive gas flow rate.

As reactive gas flow rate is increased, the deposition rate and discharge voltage are nearly constant as the reactive gas is being absorbed by the sample and chamber walls becoming partially oxidized. As the reactive gas is further increased, there is a certain point \( (f_c) \) where stoichiometric films are formed. This is the critical flow point \( (f_c) \), and it is also a point of unstable operation. Any further increase of reactive gas will cause an insulating film to form on the cathode surface since the saturated films will not be able to absorb any more reactive gas.

Even if the reactive gas flow rate is reduced, it will not return to the same path because now the target is operating in compound mode. Only when the reactive gas has been significantly reduced so that the oxide layer will be sputtered off, the target will return to metallic mode. That is why reactive sputtering should occur in the transition region between these two states just before the critical point at the knee of the curve. Because this point is unstable and difficult to control, there are several methods to fix this problem [Rossnagel, 2002]:
- Feedback control of the reactive gas;
- Increased pumping speed;
- Dual cathodes;
- Gas pulsing;
- Sample/cathode separation; and
- Oscillating deposition-oxidation.

Figure 2.6.2: Hysteresis loops for deposition rate and discharge voltage with increasing reactive gas flow [Rossnagel, 2002].
It is common to introduce a mixture of inert and reactive gas into the vacuum chamber at some arbitrary point during reactive sputtering. However, for high rate reactive sputtering, consideration of gas delivery pipe geometry can allow for better process control. There are two geometries that can be considered for deposition of nitrides and oxides. Figure 2.6.3 depicts these two gas geometries [Parsons, 1991].

In gas geometry (1), a mixture of inert and reactive gas is uniformly introduced over the cathode surface. This configuration is useful for high-rate deposition of nitrides because it utilizes the intense discharge region near the cathode to generate ions and other reactive species. Since oxygen is highly reactive with most metal surfaces, gas geometry (2) is better suited for oxide deposition. In this configuration the inert gas is uniformly introduced over the cathode surface while the reactive gas is distributed around the substrate region. This helps to minimize the oxygen partial pressure in the near-cathode region. The application of a negative substrate bias can maximize the reaction at the substrate surface.

The next chapter studies the works of other investigators on reactive sputtering of alumina and zirconia in order to compare sputter systems, sputter parameter, and sputtered film results with the results of this investigation.
Figure 2.6.3: Gas geometries for (1) mixed inert and reactive gas at target and (2) inert gas at target and reactive gas at substrate.
CHAPTER 3: LITERATURE SURVEY

Reactive sputtering was studied for the fabrication of alumina and zirconia thin films because it offers many advantages for high deposition rates and good film properties. The cost effectiveness of using reactive sputtering of metal targets over direct sputtering of ceramic targets was a major constraint for this research.

3.1 Reactive Sputtering

Reviews [Holland, 1956; Parsons, 1991; Vossen and Cuomo, 1978; Mahan, 2000; Rossnagel, 2002; Schwartz, 1963] of various deposition processes of thin films including sputtering and reactive sputtering have been compiled to cover many investigations in this field. This author aims to incorporate reactive sputtering capability into an existing vacuum sputter system in order to produce ceramic thin films.

Schwartz [Schwartz, 1963] describes the important characteristics of reactive sputtering and why it is being utilized more in industry, especially for integrated electronic circuitry. Schwartz also points out some mechanisms of reactive sputtering, gives details on experimental techniques, and compiles experimental investigations on using reactive sputtering for resistive films, insulating films, and semiconductor films.

Hollands and Campbell [Hollands and Campbell, 1968] sputtered thin films of tantalum in mixed argon/oxygen atmosphere (total pressure of $3.0 \times 10^{-4}$ Torr) and found that oxygen partial pressure was the controlling factor for other film parameters, such as deposition rate, density, electrical properties, and electron diffraction. They concluded that there exists a critical oxygen pressure in which below this point, tantalum metal is sputtered and reaction occurs at the substrate and above this point, reaction at the
target forms an oxide surface from which tantalum oxide is sputtered. Through experiments, they found that the deposition rate was independent of oxygen concentration up to an oxygen pressure of approximately 1.25 x 10^{-4} Torr at which the deposition rate fell from 2.6 x 10^{-5} to 6.0 x 10^{-6} g/min. Using a target of 1 cm² area, the growth rate was measured and recorded. At room temperature in 100% argon, the growth rate was 14 Å/min and rose to a maximum rate of 32 Å/min at 6.0 x 10^{-5} Torr, and then it significantly declined in 100% oxygen to 4 Å/min. They formulated that with increasing partial pressure of oxygen, at any given temperature and constant deposition rate, the degree of oxidation of the sputtered films will increase. Therefore, they came to the conclusion that chemisorption equilibrium precedes the rate-determining step of oxide growth. They found that at a constant temperature the rate of oxidation will be approximately proportional to the square root of the oxygen pressure [Hollands and Campbell, 1968]. The following equation expresses this statement:

$$[O^-]_{chemisorbed} = \frac{K P_{O_2}^{1/2}}{(RT)^{1/2}}, \quad (3.1)$$

where $K$ is the chemisorption equilibrium constant and $R$ is the gas constant. They also studied the effects of substrate temperature above and below the critical pressure, and also presented supporting evidence for their conclusions.

Sproul et al. [Sproul et al., 2005] gives a more comprehensive review of the control of reactive sputtering processes by comparing different methods of reactive gas control. The simplest method is flow control of the reactive gas; however, the deposition rate can be very low and film properties are not optimal. The more desirable method is partial pressure control, but this is more complex since it requires active feedback
control. This method allows the target to be operated in the transition region between metallic mode and compound mode. The authors state that using a pulsed DC or mid-frequency AC power supply can prevent arcing during the sputtering of insulating films.

In order to obtain high deposition rates and optimum film properties, reactive sputtering must take place in the transition region between the metallic and compound states of the target. The process is unstable in the transition region for flow control of the reactive gas. Observing the hysteresis effect for flow control, a sudden transition region can be seen on a graph with increasing reactive gas flow rate. Using partial pressure control, there are three basic feedback signals that have been used since the mid-1980s: optical emission spectrometer, mass spectrometer, and cathode voltage. There is a continuous transition between the metallic mode and compound mode when using partial pressure control of the reactive gas. Therefore, there is an advantage in using partial pressure control over mass flow control. Sproul et al. illustrated this difference by showing the hysteresis curves for flow control (Figure 3.1.1) and partial pressure control (Figure 3.1.2).

Shinoki and Itoh [Shinoki and Itoh, 1975] investigated the mechanism of RF reactive sputtering by mass spectrometry. They modeled the reactive process and found that there was an abrupt step-like decrease in the sputtering rate at a definite partial pressure of reactive gas. They concluded that the reaction process in RF reactive sputtering is highly influenced by the gettering action of sputtered atom deposits. Gettering is the process by which unwanted impurities are removed by providing an alternative location (“a getter”) where they prefer to reside [http://dunham.ee.washington.edu/ee528/notes.getter.pdf].
Figure 3.1.1: Hysteresis curve for mass flow control of reactive gas [Sproul et al., 2005].

Figure 3.1.2: Hysteresis curve for partial pressure control of reactive gas [Sproul et al., 2005].
3.1.1 Alumina Reactive Sputtering

Aluminum oxide (Al$_2$O$_3$) films have been produced for many applications in the mechanical, optical, and electronics industries due to their excellent properties, such as chemical inertness, mechanical strength and hardness, transparency, high abrasive and corrosion resistance, and insulating and optical properties [Deshpanday and Holland, 1982; Koski et al., 1999].

Deshpanday and Holland investigated the reactive magnetron sputtering of aluminum in Ar-O$_2$ mixtures to determine the conditions for preparing oxide films with low optical absorptance using both DC and RF power sources [Deshpanday and Holland, 1982]. They used an aluminum target (99.9% purity) of 75 mm (~ 3") diameter, a target to substrate distance of 40 mm (1.6") and an erosion track mean diameter of 52 mm (2"). The chamber pressure was vacuumed to 10-5 Torr with a gas pressure of 20 mTorr when O$_2$ was increased to 10% of total pressure. The presented tables for both DC and RF reactive magnetron sputtering of aluminum target with values for deposition rate, optical reflectance, transmittance, and absorptance of the Al$_2$O$_3$ films. They found that with increasing O$_2$ concentration, the deposition rate decreases in both DC and RF reactive magnetron sputtering. Alumina films with absorptance less than 1.0% by DC magnetron sputtering were possible in a 10% Ar-O$_2$ mixture. The absorptance decreased with increasing power at 10% O$_2$ concentration. However, with RF magnetron sputtering, the film absorptance increased with increasing O$_2$ concentration as well as power input. They used the Abelès method to measure the refractive index of the films, which considers the film to have negligible absorptance. Since all the films had some absorptance, they found that the films with the highest transmittance had a
refractive index of 1.61-1.62 for films evaporated using electron beam heating. They concluded that for most oxidized films deposited stoichiometry was not completely achieved.

Sproul et al. [Sproul et al., 1995] showed that it was possible to deposit aluminum oxide coatings by DC reactive magnetron sputtering when using an arc suppression system. They state that "Coatings such as aluminum oxide (Al₂O₃) are almost impossible to deposit by conventional reactive DC magnetron sputtering because of the strong interaction of the oxygen with the target surface that leads to very rapid oxide compound formation on the target surface." Arcing is very common and particularly violent for reactive DC sputtering, and it can result in damage to the power supply. Some investigators have used RF power to overcome the issue of arcing, but the deposition rate is very slow, typically 2%-3% of the metal deposition rate at the same power. Some researchers have also found that pulsed DC power supplies work well in reactive sputtering; however, they can be quite expensive. Therefore, Sproul et al. investigated a cheaper alternative – an arc suppression unit placed between the DC magnetron power supply and the target. They also used this arc suppression unit in conjunction with an automatic feedback control of the reactive gas.

For their experimental methods, the following system parameters were used: base pressure of 5 x 10⁻⁷ Torr, argon as inert gas, etching pressure of 8 mTorr and sputter pressure of 4 mTorr. The substrates used were glass slides and M2 tool steel, and they were at a floating potential during deposition. The glass slides were etched for 1 minute, and M2 tool steel were etched for 5 minutes with 1.5 kW of RF power. The target power was set to 2 kW for all deposition runs. An Advanced Energy SPARC-LE 20 kHz unit
was used for the arc suppression. Partial pressure control of the reactive gas is used to overcome poisoning of the target surface. They characterized the alumina films by measuring the film hardness, film thickness and roughness, crystallographic structure, and transmittance and absorbance of the film. Very clear, insulating films were deposited at a partial pressure of 0.08 mTorr and showed very little difference between the glass slide and the coating. The average refractive index of the film was found to be 1.6.

Koski et al. [Koski et al., 1999] also deposited aluminum oxide films using DC reactive magnetron sputtering on glass slide, silicon wafer, stainless steel, and polycarbonate substrates. The main disadvantages of reactive sputtering are poor deposition rate due to target poisoning, hysteresis phenomena, arcing and inhomogeneity. To reduce target poisoning and arcing, they controlled target voltage rather than power during deposition. A pulsed DC power supply was used to minimize arcing.

Koski et al. [Koski et al., 1999] used an Alcatel reactive physical vapor deposition (PVD) apparatus for depositing the films. They chemically cleaned the substrates in an ethanol ultrasonic bath for 5 to 15 minutes to remove organic contaminants. The target was pre-sputtered in a pure argon atmosphere of 1.0 Pa (7.5 x 10^{-3} Torr) for 10-20 minutes in order to remove any oxide contaminants. They used a 6-inch diameter aluminum (99.999 at.%) target. The system also contained a differentially pumped quadrupole mass spectrometer for leak detection, residual gas analysis, and deposition control. Argon gas was introduced in the target housing, while oxygen was introduced in the immediate vicinity of the substrate holder using a home-made circular gas inlet located 1-2 cm from the substrates. The substrate bias voltages were between 0 V and -200 V.
The target voltage was between 310 V and 405 V, and the power was between 1000 and 1500 W. An Advanced Energy SPARC-LE V Accessory was used to handle arcing.

A Taylor-Hobson profilometer was used to measure film thickness right after deposition. Stoichiometric aluminum oxide films were transparent, while metal-rich films were black or brown. SEM (Scanning Electron Microscope) was used to study the surface structure, and AFM (Atomic Force Microscope) was used to image the surface topography and detect surface roughness. XRD was used to gather information on crystallographic structure, and a RBS (Rutherford Backscattering Spectrometer) was used for composition analysis and density measurements. Nanoindentation was used to measure the nanohardness and elastic modulus of the thin films.

At a voltage of 405 V, the deposition rate of the transparent film was 215 nm/min, which is 77% of the metallic deposition rate. All deposited films had an amorphous structure since the deposition temperature is lower than the crystallization temperature of aluminum oxide, 400ºC. The surface roughness on silicon substrates as measured by AFM were between 0.72 and 2.64 nm. As substrate bias increased and sputtering gas pressure increased, the surface roughness increased. The O/Al ratio, which depends on the target voltage, was between 1.30 and 1.72. The density decreased with increasing target voltage, and it is also dependent on sputtering gas pressure and substrate bias voltage. Hard thin films occur at low pressures and have higher compressive stress levels. The authors concluded in their findings, "Low sputtering gas pressures and low bias voltages led to aluminum oxide thin films with a high hardness and low intrinsic stress. High sputtering gas pressure, high substrate bias voltage and low target voltage led to dense aluminum oxide thin films."
3.1.2 Zirconia Reactive Sputtering

Zirconium oxide (ZrO\textsubscript{2}) films have been used in a wide range of applications that include laser mirrors, broadband interference filters, ionic conductors, oxygen ion conductors for sensor and fuel cell applications and thermal barrier coatings. The properties of zirconium oxide that make them desirable for these applications are high melting point, oxidation resistance, excellent thermal stability, high refractive index, and good ionic conductivity in the Y-stabilized cubic phase [Venkataraj et al., 2002].

Venkataraj et al. [Venkataraj et al., 2002] deposited zirconium oxide thin films by DC reactive sputtering onto silicon substrates at room temperature from a metallic zirconium (Zr) target in an argon-oxygen atmosphere. Sputtering was performed using a 3" Zr target at room temperature with constant cathode current of 900 mA and a pressure of 0.8 Pa (6 mTorr). Oxygen flow was varied between 0 and 4 sccm. The target to substrate distance was maintained at 70 mm (2.75 inches). The substrates used were glass slide and silicon wafer. Various methods were used in order to characterize the thin films, such as Rutherford backscattering spectroscopy, X-ray diffraction, X-ray reflectometry, atomic force microscopy, and optical spectroscopy.

Deposition rate was plotted against oxygen flow, which was increased from 0 to 4 sccm. It can be seen that there is a sudden drop between 2.7 and 2.8 sccm. This indicates the transition region between metallic and compound mode of the target. In metallic mode (below 2.7 sccm O\textsubscript{2}) the films have a nearly constant deposition rate of 1.6 nm/s, while the sputter rate of the films sputtered in compound mode drops to 0.2 nm/s. The stoichiometry of the films was determined by Rutherford backscattering experiments. It was found that films sputtered in the metallic mode were under-stoichiometric.
sample sputtered in the transition region had an O/Zr ratio of 1.75, which is approaching stoichiometric zirconia. Films sputtered in compound mode (above 2.8 sccm) were fully oxidized with a stoichiometry of $\text{Zr}_2\text{O}_{2.1\pm 0.3}$. The films were observed to have a well-ordered crystalline phase of $\text{ZrO}_2$ with monoclinic structure rather than an amorphous structure.

Koski et al. [Koski et al., 1999] deposited zirconium oxide thin films by pulsed DC reactive magnetron sputtering on glass slide, silicon wafer, and stainless steel substrates using an ALCATEL PVD system. The substrates were cleaned in an ethanol ultrasonic bath for 15 minutes, and the target was pre-sputtered in argon for 15 minutes to remove any contaminants from the surface. A 6 inch diameter zirconium target was used in argon pressures between 0.30 and 1.0 Pa ($2.25 \times 10^{-3}$ and $7.5 \times 10^{-3}$ Torr). Oxygen was the reactive gas introduced near the substrate holder. The target to substrate distance was 70 mm (~2.76 inch). Target power controlled deposition process was used while arcing was suppressed by using an Advanced Energy SPARC-LE V Accessory with a pulsing frequency of 30 Hz.

Koski et al. [Koski et al., 1999] used the same instruments to measure the thin film properties that were used in the measurement of aluminum oxide thin films. The partial pressure of oxygen was between 0.07 and 0.10 Pa ($5.25 \times 10^{-4}$ and $7.5 \times 10^{-4}$ Torr), and the power density was 1000 W ($5.48$ W/cm$^2$). As the sputtering gas pressure was increased, the deposition rate increased from 35 to 135 nm/min/kW. Deposition rate was also affected by substrate bias voltage. As the substrate bias voltage was increased from a floating to -150 V, the deposition rate was increased from 50 to 95 nm/min. The deposition rate is also dependent on the target power, and as the target
power increased from 500 to 2000 W, the deposition rate increased from 50 to 455 nm/min. Below a power of 1500 W, the thin films were colorless and transparent; however, at higher powers of 1750 and 2000 W, they films were partly brown and totally black, respectively. They also found that the surface roughness was inversely proportional to the nanohardness, and the roughness was lower for biased samples versus floating bias samples. At lower pressures, the thin films were found to have high hardness and low surface roughness. For example, at 0.50 Pa the nanohardness and surface roughness was found to be 17.8 GPa and 2.9 nm, respectively. The nanohardness of thin films of thicknesses 500 nm to 1µm increased up to 19 GPa. With increasing substrate bias voltage and decreasing sputtering gas pressures, the elastic modulus was found to increase from 210 to 231 GPa. The black thin films had an O/Zr ratio of 1.6. The differences in the crystallization of thin films could be related to the argon ion energy. The stoichiometric transparent films had a preferred monoclinic structure whereas the under-stoichiometric black films had a preferred tetragonal phase. Reactive sputter deposited zirconium oxide films with an amorphous structure can be annealed for crystallization of the monoclinic phase.

In summary, the authors concluded that the deposition rate of the thin films increased as a function of target power density as well as increasing sputter pressure and substrate bias voltage. Zirconium oxide films with low nanohardness, rough surfaces, and low elasticity were observed with increased sputter pressure. Hard, elastic, stoichiometric and dense thin films with smooth surfaces were produced when the substrate was biased during deposition.

Sethi et al. [Sethi et al., 2009] produced zirconium oxide films on silicon and glass
substrates by reactive sputtering using pulsed-DC and radio frequency (RF) power sources. The chamber was evacuated to a base pressure of 1 x 10^{-4} Pa (7.5 x 10^{-7} Torr) using a turbomolecular pump. A zirconium target 3” diameter was pre-sputtered for 5 minutes with 50 W in pure argon at 0.7 Pa (5.25 x 10^{-3} Torr). The total pressure was kept constant at 0.7 Pa. Two power sources were used: pulsed direct current at 150 kHz and radio frequency at 13.56 MHz. The substrates were mounted on a copper base plate, and substrate temperature was measured using a chromel-alumel thermocouple. The target to substrate distance was fixed at 89 mm (3.5 inches). The target voltage was measured using an oscilloscope. Film thickness was measured using a Tencor Alpha-Step 500 surface profiler. XRD, SEM, and EDS were used to characterize the properties and structure of the film.

The structure of the zirconia films were compared for the two power sources from XRD results. Both sources produced films with the monoclinic ZrO$_2$ phase; however, the RF sputtered films had the presence of a minor phase of tetragonal ZrO$_2$ as well as larger crystallite size at the same power and pressure. Crystallite size increases with increasing pressure except for films that are prepared at lower powers and higher pressures. Deposition rate was also observed to increase with increasing power. Films prepared at 0.2 and 0.3 are oxygen deficient, which was confirmed by EDS. The Zr:O ratio was 1.3 instead of the desired 0.5 of Zr:O. However, a Zr:O ratio of 0.6 was found for films prepared at 6.0 Pa. A liquid N$_2$ substrate-cooling system was implemented in order to determine the effect of substrate temperature on crystallization. The crystallite size at room temperature was larger than that at low temperatures for high power. The deposition rates for pulsed DC sputtering dropped from 117 to 37.8 Å/min at 400 W and
from 25.2 to 15.6 Å/s at 200 W at a constant pressure of 0.7 Pa. The growth mode, which defines the crystallization and stoichiometry of the films, is controlled by sputtering pressure, power, and oxygen content. The thickness of the films was found to be critical; zirconia films under 50 nm were mainly amorphous.
CHAPTER 4: EXPERIMENTAL METHODS

4.1 The Sputter System

This chapter will describe the maintenance and modification of the current sputter system. It will also focus on the experimental procedures done to obtain thin film coatings. Finally, a discussion of a mini chamber design for separating inert and reactive gas will conclude this chapter. Metallic thin films were produced by direct current (DC) planar magnetron sputtering of metal targets while oxide thin films were produced by introducing oxygen as a reactive gas.

4.1.1 Current Sputter System

The sputter system used in this work is a Denton Vacuum Explorer 14 planar magnetron sputtering system shown in Figure 4.1.1.

![Figure 4.1.1: Denton Vacuum Explorer 14 sputtering system.](image)
The vacuum chamber is a cylinder of 30.5” ID x 18” high made from stainless steel. The top plate of the chamber lifts open to allow access to the targets and substrates. Attached to the center of the top plate is a rotating, water-cooled substrate fixture designed to mount 4” to 6” wafers. The chamber can be mounted with up to six cathodes, as shown in Figure 4.1.2, but the system used only has four cathodes, which are in a cross configuration.

Figure 4.1.2: Top view of schematic representation of Denton Vacuum sputter system [Denton Vacuum manual].

The sputter source configuration consists of a planar cathode (target) that is parallel to an anode surface, which is usually grounded, that serves as a substrate holder. All four sputter sources are manufactured by Angstrom Sciences and are 4” diameter, indirect-cooled, internal “stalk-mount” planar magnetron sputter sources optimized for straight-on deposition. However, three of the sputter sources have standard magnetics and one has enhanced magnetics for magnetic targets. Two kinds of power supplies were used:
three Advanced Energy MDX 1.5 kW DC power supplies and one Seren 600W RF power supply and matching network. Typical target sizes are 4” diameter and ¼” or ⅛” thickness. The chamber is pumped down by a CTI Cryogenics CryoTorr® 8 cryogenic pump connected to an Edwards XDS 10 dry scroll pump for rough pumping. The chamber base pressure reaches less than 1.0e-7 Torr, which is detected by an Inficon BPG400 vacuum gauge. The sputter pressure is detected by an MKS 627B Baratron® absolute capacitance monometer. An MKS Type 2179A mass-flo® controller (MFC) regulates argon gas flow into the chamber. The system includes a programmable logic controller with a color touch panel. The experimental parameters, such as gas flow rate, power, and sputtering pressure can be controlled and viewed on this panel. (Figure 4.1.3).

Figure 4.1.3: Computer-controlled touch panel on sputter system.
4.1.2 Modified Sputter System

In order to do reactive sputtering, the current system had to be modified to introduce reactive gases into the vacuum chamber. The current system had a 4-way manifold for the addition of other gases. Argon was already connected to the system, but oxygen and nitrogen need to be added. Argon and oxygen/nitrogen will be mixed inside the chamber via single tubing during reactive sputtering. An MKS Type 247D four-channel power supply/readout and two MKS Type 2179A mass-flo® controllers were purchased to control the reactive gases. The Type 2179 MFCs have a positive shutoff valve solenoid valve, which is opened with compressed air. Plastic tubing was used to route compressed air to the MFCs and ¼” stainless steel tubing was used for gas flow into the chamber (Figure 4.1.4).

Figure 4.1.4: Additional gas lines on modified sputter system.
4.2 System Maintenance

The system maintenance is not known for these previous years since the previous professor has left the university. During the modification and initial experimentation phase, the author has come across many components that needed to be replaced or repaired. The water filters for the cooling system had not been replaced for at least three years. The once clear filter housing was completely black, and filter particulates were getting into the water lines. The cryogenic compressor adsorber is recommended to be replaced every 12 months but had not been replaced since the system was purchased. The Inficon BPG400 was not properly detecting the vacuum pressure because the filament of the hot cathode was broken and needed to be replaced. Cathode shields and shutters needed to be sand/bead blasted to remove the layers of deposition after a long time of sputtering. An additional viewport was added in order to see the sputtering process on the RF gun. Also, a gas feed through was installed in order to separate argon and reactive gas inside the chamber. These maintenance issues did not all occur at the same time. They were discovered gradually over time as the author was doing experiments with the machine. Due to wait time for parts and repair, experimental results have been delayed longer than the author had wished. Because the machine was not up to par for operation, any coatings produced during this time could not yield accurate results.

4.3 Experimental Procedures

This section will describe the procedures carried out for metallic and reactive sputtering of thin films. In both cases the substrates used were microscope glass slides and silicon wafers. Pure aluminum and zirconium targets (99.999 % and 99.2% purity, respectively)
were used. Argon is used as the inert gas, and oxygen is used as the reactive gas. The user must follow the check list and operating procedures posted on the sputter system before beginning any experiment to ensure that the system will not be damaged during sputter operation.

4.3.1 Metallic Sputtering

For metallic sputtering, the desired metal target is installed on a sputtering gun with the desired power source (DC or RF). The substrates are cleaned with ethanol or acetone in an ultrasonic bath for 10-15 minutes. They are dried off with compressed air from an aerosol can. Then, the substrates are mounted on the substrate holder depending on how many tests will be performed. The system is allowed to vacuum for a minimum of two hours but is usually vacuumed overnight. Once the base pressure is below 1e-7 Torr, the vacuum pressure is low enough for sputtering to take place. Then argon flow rate is set, and gas is introduced to the chamber, which will increase the chamber pressure. The sputter pressure is determined by the flow rate of the gas and can be set to a desired pressure using the high vacuum valve in pressure control mode (PCM). Typical sputter pressures are around 5-10 mTorr, and in order to decrease the sputter pressure, the high vacuum valve should be opened. After the pressure is fixed, the power for the corresponding gun is turned on. Viewports allow the user to see the plasma inside the chamber. In an argon atmosphere, the color of the glow is typically purple. The target is usually pre-sputtered for at least 10 minutes to remove any oxide layer that might have formed when opening the chamber. Pre-sputtering means that a sputtering process with the shutter closed or on a facet that does not contain any substrates so that the coatings are not contaminated.
This system allows for multiple guns to be used at the same time in order to do multi-layer coatings. Usually, this can be programmed to run automatically. If the user is only making single layer coatings, the system can be run in manual mode. The current and voltage is monitored throughout the experiment to make sure it stays constant. The deposition rate varies depending on the material system. By varying the time, the thickness of the coating can be changed. When the desired thickness has been achieved, the power and gas are turned off. The system is allowed to pump for about 30 minutes before opening the chamber so that the coating will be cooled down to mitigate the formation of oxide layer from reacting with the air. The samples are then analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS).

4.3.2 Reactive Sputtering

Reactive sputtering procedures are similar to metallic sputtering with the addition of the reactive gas into the chamber. However, it is difficult to perform reactive sputtering when using DC power since it is easy to poison the target surface. Poisoning means that an oxide layer forms on the surface and prevents target atoms from sputtering off. Therefore, the maximum oxygen flow rate before poisoning occurs must be determined and a hysteresis test must be performed. Before any oxygen is introduced into the chamber, the target is pre-sputtered in a pure argon atmosphere for a minimum of 15 minutes to the clean the target surface of contaminants or any oxide layer. The sputter pressure, current and voltage are recorded as a baseline to determine when poisoning occurs. While the target is sputtering in pure argon, 1.0 cm²/min of oxygen is sent into the chamber via the MFC. The target is allowed to sputter in the argon-oxygen mixture
for 5 minutes. Again, the sputter pressure, current and voltage are recorded. Oxygen flow rate is slowly increased in increments of one until there is a sudden change in the voltage. For example when using an aluminum target, there is a sudden decrease in voltage when the target is poisoned. The point just before this decrease is the optimum flow rate for reactive sputtering. Once the optimum flow rate has been determined, the oxygen is turned off and the target is sputtered in pure argon for 10-15 minutes. Then, oxygen is re-introduced into the chamber, mixed with argon, and reactive sputtering takes place. The plasma can be seen through the viewports. For the case of aluminum oxide, the plasma glow is purple when in a pure argon atmosphere but changes to a white color when oxygen is mixed in. The plasma should be carefully watched for any discontinuities (flashing or turning off and on), which can be a sign of arcing or poisoning of the target. If this happens the system should be turned off so that the sputtering guns do not get damaged. If the current and voltage stays approximately constant throughout the duration of the test, then there is a possibility of a good coating. In order to determine the components of the coating, the sample should be analyzed using EDS or X-ray photoelectron spectroscopy (XPS) for elemental composition. XRD was also used to determine the crystallographic structure.

Various tests were done with reactive sputtering in order to improve the stoichiometry of the thin films. The target to substrate distance was varied using a rod and plate apparatus to move the substrates closer to the target. Also, a separate gas line for oxygen was installed in order to introduce oxygen closer to the substrate holder to reduce oxidation on the target surface.
4.4 Mini-chamber Design

During reactive sputtering, the formation of stoichiometric films on the substrate occurs during the transition of the target from metallic mode to compound mode. This means that the deposition rate is determined by the sputter yield of the compound, which is much lower than the sputter yield of most elemental metals. In order to remedy this problem, researchers have investigated separate control of target and substrate processes. Schiller et al. proposed using rapid motion of the substrate between the deposition and oxidation regions in the sputtering system [Schiller et al., 1979]. For the sputtering indium tin oxide from a metal target, Maniv et al. used a combination of a geometric baffle between the target and the substrate and an auxiliary RF discharge coupled to the substrate to support the reactive process [Maniv et al., 1983]. For the deposition of non-absorbing oxides, such as Al_2O_3 and SiO_2, at high deposition rates, Scherer and Wirz used a similar set up to Maniv et al. with the exception of the RF discharge. Instead, they used an additional DC discharged produced between the baffle and the substrate by electrodes working at positive voltages of about 40 V [Scherer and Wirz, 1984]. The schematic representation of their reactive DC sputtering arrangement is shown in Figure 4.4.1.

The experimental details explaining the schematic is provided in Scherer and Wirz's [Scherer and Wirz, 1984] paper. The shield (12) is about 20 mm from the target surface (2) and also has variable apertures. Argon (5) is introduced near the cathode surface while oxygen (7) is introduced between the shield and the substrate (13). Using this configuration the authors observed very stable process conditions for the deposition of Al_2O_3 and SiO_2. They found the static deposition rate of Al_2O_3 to be 36 Å/sec at a
dissipated power of 12 W/cm². The theoretical deposition rates of Al₂O₃, SiO₂, and Ta₂O₅ compared well with the measured values.

Figure 4.4.1: Schematic of mini chamber setup by Scherer and Wirz.

The configuration for this research was based loosely on the design by Scherer and Wirz [Scherer and Wirz, 1984]. It contains a stainless steel mini-chamber around the sputtering gun with an interchangeable shield of varying aperture sizes. The stainless steel shield will be about one inch from the target surface. There will also be a fixed port on the mini-chamber wall for argon gas to be introduced near the target surface. Stainless steel, quarter-inch tubing will be bent into a circular shape of about 4" in
diameter for the reactive gas inlet system. It will also contain 0.5 mm holes spaced every 20 mm on the inside of the circular tubing. The gas inlet will be placed about 2 cm from the substrate holder.

Before manufacturing the test chamber, a temporary test chamber was mocked up using the cathode shield already on the gun and heavy duty aluminum foil for the shield (Figure 4.4.2). The cathode shield was extended 1” past the target surface. Plastic tubing was used to route the argon gas inlet to the cathode shield. A 37 mm diameter hole was cut out of a sheet of aluminum foil and then placed over the cathode shield to imitate the shield with an aperture. A separate gas line for oxygen was installed and mounted on the chamber lid so that the reactive gas would be introduced near the substrate holder (Figure 4.4.3). Metallic and reactive sputtering tests were done to see if any plasma formed and deposition would still occur using the mini-chamber design.
Figure 4.4.2: Mock-up of a mini chamber design using aluminum foil and shield.

Figure 4.4.3: Separate oxygen nozzle placed closer to substrate holder.
CHAPTER 5: EXPERIMENTAL RESULTS

5.1 Metallic Sputtering

Aluminum and zirconium films were sputtered on glass slide and silicon wafer from 4” metallic targets in DC magnetron sputtering. The films were analyzed using a Rigaku MiniFlex benchtop XRD machine. The following data was collected over the range of 20° to 110° to determine the crystal structure of the as-sputtered aluminum film (Figure 5.1.1).

![Figure 5.1.1: XRD result for aluminum film on glass slide.](image)

Figure 5.1.1: XRD result for aluminum film on glass slide.
The aluminum film is shown to have peaks that correspond to a face-centered cubic (FCC) crystal structure belonging to the space group Fm-3m. The three peaks with the highest intensity are found at 38.5° (1 1 1), 44.7° (2 0 0), and 78.2° (3 1 1). The lattice parameters can be calculated using the Miller Indices; however, XRD software called MDI Jade Easy Quant XRD was used to find the Miller Indices and lattice parameters. Since aluminum is a cubic structure, the lattice parameters \( a = b = c = 4.050 \, \text{Å} \). The XRD result for an as-sputtered zirconium film on glass slide over the range of 30° to 90° is shown in Figure 5.1.2. The three peaks with the highest intensity are found at 35.5° (1 1 0), 63.8° (3 0 0), and 50.9° (2 0 1), where the angle is 2\( \theta \) and the Miller Indices are in parentheses. These peaks correspond to a hexagonal closed-packed (HCP) crystal structure with a space group of P6/mmm. The corresponding lattice parameters are \( a = 5.039 \, \text{Å}, b = 5.039 \, \text{Å}, \) and \( c = 3.136 \, \text{Å} \).

**Figure 5.1.2:** XRD result for zirconium on glass slide.
An FEI Quanta 3D FEG SEM system was used to characterize the film surface structure and to measure the film thickness. Figure 5.1.3 is an SEM micrograph of the surface structure of an as-sputtered aluminum film on silicon wafer. The surface shows large, faceted grains in a porous structure. This image was taken at 25,000X magnification.

![SEM micrograph of as-sputtered aluminum film on silicon wafer.](image)

**Figure 5.1.3: SEM micrograph of as-sputtered aluminum film on silicon wafer.**

The as-sputtered zirconium film on silicon wafer can be seen in Figure 5.1.4. This film shows a denser surface with smaller, faceted grains as compared to the aluminum film. This film was also taken at 25,000X magnification. The cross section of both aluminum and zirconium films were captured in the SEM. The deposition rate was calculated based on the average thickness of the film divided by the deposition time. Figure 5.1.5 and Figure 5.1.6 show the cross section of aluminum and zirconium films, respectively. Table 5.1.1 gives the average deposition rate for each film with a target to substrate distance of about 10 cm.
Figure 5.1.4: SEM micrograph of as-sputtered zirconium film on silicon wafer.

Figure 5.1.5: SEM micrograph of cross section of aluminum film on silicon wafer.
Figure 5.1.6: SEM micrograph of cross section of zirconium film on silicon wafer.

Table 5.1.1: Average deposition rate for metallic thin films.

<table>
<thead>
<tr>
<th>Material</th>
<th>Power (W)</th>
<th>Sputter Pressure (mTorr)</th>
<th>Film Thickness (µm)</th>
<th>Deposition Time (min)</th>
<th>Deposition Rate (nm/min)</th>
<th>Average Deposition Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>200</td>
<td>5.0</td>
<td>1.015</td>
<td>30</td>
<td>33.8</td>
<td>33.53</td>
</tr>
<tr>
<td>Al</td>
<td>200</td>
<td>11</td>
<td>3.99</td>
<td>120</td>
<td>33.25</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>150</td>
<td>4.8</td>
<td>3.83</td>
<td>120</td>
<td>31.92</td>
<td>31.74</td>
</tr>
<tr>
<td>Zr</td>
<td>150</td>
<td>4.8</td>
<td>3.786</td>
<td>120</td>
<td>31.56</td>
<td></td>
</tr>
</tbody>
</table>

There are many factors that can influence the deposition rate such as power density in the erosion area, size of erosion area, cathode surface condition, cathode temperature, target to substrate distance, target material, applied voltage and current density, gas density, and sputter pressure. Some of these parameters are interrelated, such as pressure, power density, and size of the erosion area. Holland [Holland, 1956] writes that voltage and current density controls the deposition rate, which in turn is depended
on the gas density. He states, “Since the temperature of the residual gas may increase appreciably as the sputtering proceeds, *the gas pressure must be adjusted to maintain a constant gas density and hence constant voltage and current density* [Holland, 1956].”

In a water-cooled cathode, Penning and Moubis [Holland, 1956] found that the sputtered material on the substrate increased, meaning the deposition rate increased, when the current density was increased to increase the discharge temperature. As stated by Waits [Waits, 1978] in the chapter on Planar Magnetron Sputtering, the deposition rate is directly proportional to the target power. He also writes that “if all the factors affecting deposition rate can be held constant, then the rate will be constant and reproducible.”

From Table 5.1.1 this statement is proven true for zirconium. All the parameters were kept the same and the film thickness and deposition rate remained nearly constant around 32 nm/min. For the aluminum case, the sputter pressure and deposition time were changed to see if there would be a change in deposition rate. However, it can be seen that the deposition rate is also nearly constant around 34 nm/min.

### 5.2 Reactive Sputtering

For reactive sputtering, a quick hysteresis test should always be performed prior to sputtering in order to determine the critical reactive gas flow rate. The critical reactive gas flow rate indicates the transition region between the metallic and compound states of the target. Many investigators have observed the hysteresis phenomena in reactive sputtering. Koski *et al.* [Koski *et al.*, 1999] indicates that in a typical hysteresis curve (Figure 5.2.1) for power controlled deposition, the target voltage and total pressure were
depended on the oxygen gas flow rate. When the oxygen flow rate reached the value of $f_1$, the target voltage dropped dramatically and the total pressure increased.

![Figure 5.2.1: Typical hysteresis curve for reactive magnetron sputtering [Koski et al., 1999].](image)

As seen in Figure 5.2.2 and Figure 5.2.3, the hysteresis curves for power controlled deposition agree with the findings of Koski et al [Koski et al., 1999]. The parameters for this experiment are 300 W DC, starting sputter pressure of 5 mTorr in argon, and oxygen flow rate from 0 to 10 sccm. The critical point occurs at 3 sccm where the voltage drops drastically and the pressure starts to increase. Upon decreasing the oxygen flow rate, the voltage and pressure take a slightly different path but goes back to the initial voltage and pressure values.
Figure 5.2.2: Hysteresis curve for reactive sputtering of aluminum oxide, presented as reactive gas flow rate versus target voltage.

Figure 5.2.3: Hysteresis curve for reactive sputtering of aluminum oxide, presented as reactive gas flow rate versus sputter pressure.
Venkataraj et al. [Venkataraj et al., 2002] demonstrated the behavior of mass deposition rate, voltage, and partial pressure of reactive gas with respect to reactive gas flow for zirconium oxide thin films. Figure 5.2.4 presents the hysteresis behavior of these parameters that are dependent on reactive gas flow. In all three graphs the critical point is between 2.7 and 2.8 sccm O₂ flow. The voltage (b) and partial pressure of oxygen (c) suddenly increase at this point transitioning into the oxide mode.

Figure 5.2.4: Hysteresis curves for (a) mass deposition rate of zirconium oxide, (b) target voltage, and (c) partial pressure of oxygen as a function of oxygen flow rate [Venkataraj et al., 2002].

The parameters for the zirconium hysteresis test are 150 W DC, starting pressure of 5 mTorr in argon, and oxygen flow rate from 0 to 8 sccm. Figure 5.2.5 displays the oxygen flow rate versus target voltage. From this plot, it can be seen that the voltage suddenly
increases at the critical flow of 2.0 sccm. A similar trend for the sputter pressure can be seen in Figure 5.2.6 where the pressure increases rapidly at 2.0 sccm entering into the compound mode.

![Zirconium Oxide V vs O₂](image)

**Figure 5.2.5: Hysteresis curve for reactive sputtering of zirconium oxide, presented as reactive gas flow rate versus target voltage.**

X-ray diffraction was used to determine the crystallography of the films. Figure 5.2.7 shows the XRD result for the aluminum oxide sample as well as the standard peaks for γ-Al₂O₃. Since no distinguishing peaks can be seen, the film has an amorphous structure. The XRD result for the zirconium oxide sample with peaks for monoclinic-ZrO₂ can be seen in Figure 5.2.8. This result also shows no identifying peaks, which correlates to an amorphous structure of the zirconia film. It can be concluded that thin films deposited by reactive sputtering have an amorphous structure. Some investigators have post-heat treated or annealed their samples in order to obtain a crystalline structure. C.M. Chiang and L.S. Chang found that the alumina thin films have a more
crystalline structure with increases in RF power density due to the bombardment of secondary electrons and ions. The growth of crystallites is enhanced by the increase in surface diffusivity of atoms when the film is heated up [Chiang and Chang, 2005].

Figure 5.2.6: Hysteresis curve for reactive sputtering of zirconium oxide, presented as reactive gas flow rate versus sputter pressure.

SEM was used to capture the surface structure of the alumina and zirconia thin films. Images of the cross section were also taken in order to measure the thickness and determine the deposition rate for DC reactive magnetron sputtering of metallic targets. The surface images of alumina thin film samples on silicon wafer with different oxygen flow rates of 1.8 sccm O₂ (Figure 5.2.9), 2.0 sccm O₂ (Figure 5.2.10), and 2.1 sccm O₂ (Figure 5.2.11) during reactive sputtering are depicted below. The images are all taken at 50,000X magnification, and all films sputtered with 200 W DC power at 5 mTorr sputter pressure. From XRD results, the alumina films were found to have an
amorphous structure, which is commonly seen in thin films. This can also be confirmed by the dense, continuous surface structure of the films compared with the faceted, grains of the aluminum film.

Figure 5.2.7: XRD result of aluminum oxide on glass slide.

Figure 5.2.8: XRD result of zirconium oxide on glass slide.
Figure 5.2.9: SEM surface image of alumina thin film with 1.8 sccm O₂.

Figure 5.2.10: SEM surface image of alumina thin film with 2.0 sccm O₂.
There is a difference seen from the films increasing oxygen content form 1.8 sccm to 2.0 sccm. A more porous structure with cracks can be seen in the surface structure of the film with 2.0 sccm O₂. As noted by findings from Chiang and Chang [Chiang and Chang, 2005], “the effects of target poisoning and plasma reduction with increasing oxygen flow rate over 3 sccm become dominating. The outcome of both is the porous structure of aluminum oxide thin films.” This means that once the target transitions from metallic to compound state, target poisoning effects the deposition rate and also the crystallinity of the target material. For 2.1 sccm O₂ in Figure 5.2.11, the film is very dense with very small grains, similar to the surface structure of the film with 1.8 sccm O₂. There is an explanation for the difference in the surface structure of the film with 2.0 sccm O₂. If the target surface was poisoned, this could explain the difference in surface structure and why the film with 2.0 sccm O₂ is more porous. The oxygen flow rate of 2.1 sccm was chosen because it was around the critical point during the hysteresis test.
The objective is to sputter at the maximum flow rate first in order to get the most oxygen reaction to produce stoichiometric films.

Below in Figures 5.2.12 - 5.2.14 the surface structure of zirconia thin films on silicon wafer were captured by SEM for varying oxygen flow rates of 1.8 sccm O₂ (Figure 5.2.12), 2.0 sccm O₂ (Figure 5.2.13), and 2.2 sccm O₂ (Figure 5.2.14). All images were captured at 50,000X magnification, and all films were sputtered at 150 W DC power at 4.8 mTorr sputter pressure.

![SEM micrograph of zirconia thin film surface with 1.8 sccm O₂.](image)

*Figure 5.2.12: SEM micrograph of zirconia thin film surface with 1.8 sccm O₂.*

Figure 5.2.12 exhibits varying grain sizes, which indicates that smaller grains agglomerate to form bigger clusters. These clusters then form a continuous film over the substrate surface. In the film with 2.0 sccm O₂, the surface structure appears porous with individual small grains forming a continuous film. Then when oxygen flow is increased to 2.2 O₂, the film is denser but with the same approximate grain size. Again, the porosity of the film may or may not be attributed to the poisoning effect of the target.
Figure 5.2.13: SEM micrograph of zirconia thin film surface with 2.0 sccm $O_2$.

Figure 5.2.14: SEM micrograph of zirconia thin film surface with 2.2 sccm $O_2$. 

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However, the author cannot definitely say that this is the reason for the difference in surface structure due to lack of knowledge and reference from other investigators. The author believes that these films may have been deposited in the different modes of the target. The lowest oxygen content is closer to the metallic mode while the highest content is just before the compound mode. The middle oxygen content is most likely to be in the transition region between the two modes, which may account for the porosity of the films. However, Sethi et al. [Sethi et al., 2009] investigated the crystallization of zirconia films with RF sputtering. They found a porous structure consisting of tapered crystallites separated by voids at high sputtering pressures and low power (Figure 5.2.15). Gao et al. [Gao et al., 2000] also sputtered zirconia thin films using RF power with varying O\textsubscript{2} concentrations. The SEM image shows a porous structure with small grains (Figure 5.2.16). The grain size and surface structure from findings of Sethi et al. and Gao et al. look similar to the findings of this author.

![Figure 5.2.15: SEM micrograph of the surface structure for zirconia film sputtered at 150 W with RF power [Sethi et al., 2009].](image)
The samples above were analyzed using EDS in order to determine the composition of the films. Table 5.2.1 gives a summary of the ratios found for each sample. For the alumina films, the ratio of oxygen to aluminum increases with increasing oxygen content. The zirconia films also show increasing oxygen to zirconium ratio with increasing oxygen content; however, there is a slight error between 2.0 and 2.2 sccm O₂. This is a very small difference and could be attributed to human error as well and inaccuracy of EDS to measure oxygen content. The main point here is that the ratio is increasing with increasing oxygen content. Although none of these films are stoichiometric alumina or zirconia, they are a form of alumina and zirconia films that are under stoichiometric. The difficulty in obtaining stoichiometric films is determining the correct ratio of inert to reactive gas as well as other interrelated parameters, such as the target power, sputter pressure, substrate to target distance, and target voltage and current density. This analysis just provides the conclusion that reactive sputtering can
be achieved even though the process is unstable using DC power. Other system configurations and parameters must be modified and properly controlled in order to obtain stoichiometric films with good film structure and properties.

Table 5.2.1: EDS results of alumina and zirconia thin films at varying O₂ flow.

<table>
<thead>
<tr>
<th>EDS Analysis for Film Composition</th>
<th>O:Al ratio (Al₂O₃ = 1.5)</th>
<th>O:Zr ratio (ZrO₂ = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8 sccm O₂</td>
<td>0.627</td>
<td>1.8 sccm O₂</td>
</tr>
<tr>
<td>2.0 sccm O₂</td>
<td>0.772</td>
<td>2.0 sccm O₂</td>
</tr>
<tr>
<td>2.1 sccm O₂</td>
<td>0.931</td>
<td>2.2 sccm O₂</td>
</tr>
</tbody>
</table>

Figure 5.2.17 and Figure 5.2.18 show the SEM micrographs of the cross section of alumina and zirconia films, which were used to measure the thickness and determine deposition rates.

Figure 5.2.17: SEM micrograph of alumina thin film cross section for 1.8 sccm O₂.
From the SEM images of the film cross section, thicknesses were measured and then divided by the deposition time in order to determine the deposition rates of alumina and zirconia from metallic targets at different oxygen flow rates.

Figure 5.2.18: SEM micrograph of zirconia thin film cross section with 2.0 O$_2$.

The average deposition rate of alumina is around 43 nm/min. It would be closer to 42 nm/min if the deposition rate of the film with 2.0 sccm O$_2$ were not 44 nm/min. This increase could be due to human error in measuring the film thickness. Overall, the deposition rate seems to stay nearly constant for alumina films with increasing oxygen flow. The average deposition rate of zirconia film was calculated to be 22 nm/min; however, there is a large error in this calculation. This is probably due to the cross section image captured for the film with 2.2 sccm O$_2$. The cross section must have been tilted at an angle so that the true thickness was not measured and the deposition rate was much lower. The deposition rate for the film with 2.0 sccm O$_2$ seems more accurate and corresponds to the deposition rate of metallic zirconium.
X-ray photoelectron spectroscopy was used to analyze the chemical composition of alumina and zirconia films of varying \( \text{O}_2 \) content. Using analysis software XPSpeak 4.1, the spectrum peaks can be separated based on the binding energy to determine the chemical composition.

Table 5.2.2: Deposition rates for alumina and zirconia thin films at different \( \text{O}_2 \) flow.

<table>
<thead>
<tr>
<th>Material</th>
<th>Power (W)</th>
<th>Sputter Pressure (mTorr)</th>
<th>( \text{O}_2 ) Flow (sccm)</th>
<th>Film Thickness (µm)</th>
<th>Deposition Time (min)</th>
<th>Deposition Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>200</td>
<td>5.0</td>
<td>1.8</td>
<td>2.5454</td>
<td>60</td>
<td>42.42</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>200</td>
<td>5.0</td>
<td>2.0</td>
<td>3.9732</td>
<td>90</td>
<td>44.15</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>200</td>
<td>5.0</td>
<td>2.1</td>
<td>5.085</td>
<td>120</td>
<td>42.38</td>
</tr>
<tr>
<td>( \text{ZrO}_2 )</td>
<td>150</td>
<td>4.8</td>
<td>2.0</td>
<td>1.8979</td>
<td>60</td>
<td>31.63</td>
</tr>
<tr>
<td>( \text{ZrO}_2 )</td>
<td>150</td>
<td>4.8</td>
<td>2.2</td>
<td>1.106</td>
<td>90</td>
<td>12.29</td>
</tr>
</tbody>
</table>

Figure 5.2.19: XPS aluminum spectrum for alumina sample without ion etching.
Figure 5.2.19 is a graph of the aluminum spectrum detected from an alumina sample with 2.0 sccm O₂ content. The blue solid line is the original raw spectrum from the XPS machine, and the red dotted line is the baseline. After separating the spectrum, there are two peaks. The green dashed line corresponds to Al-Al, 2p, which has a binding energy of 72.65 eV based on the *Handbook of X-ray Photoelectron Spectroscopy* [Wagner, 1979]. The purple dot-dashed line has a peak that corresponds to the binding energy of 74.7 eV for Al-O, 2p. This means the aluminum detected in this peak comes from alumina and not metallic aluminum.

![Zirconium (2.2 O₂)](image)

**Figure 5.2.20: XPS zirconium spectrum for zirconia sample without ion etching.**

The XPS spectrum for zirconium in a zirconia sample is shown in Figure 5.2.20. The blue solid line is the original spectrum, and the red dotted line is the baseline. According
to the XPS handbook, there are two peaks for zirconium orbitals 3d$_{5/2}$ and 3d$_{3/2}$ with binding energies of 178.7 and 181.1 eV, respectively. The peaks in the plot are slightly shifted. This was noticed during the XPS analysis and was caused by an option in the system analysis not being checked at the start of the analysis. The spectrum for aluminum and zirconium were analyzed for the highest oxygen content only; however, six samples were analyzed at the same time for their chemical composition without ion etching the surface. Table 5.2.3 summarizes the oxygen to aluminum/zirconium content. For both the alumina and zirconia, the samples with the lowest oxygen content seem to be over stoichiometric. This may be due to oxidation of the sample surface or error in the system analysis. However, for the next two samples in each set, the oxygen to aluminum/zirconium increases with increasing oxygen content. For zirconia film with 2.2 sccm O$_2$, the film has a ratio corresponding to stoichiometric zirconia. Although this is only a quantitative analysis in XPS, other methods should be used to verify the composition, such as the Rutherford backscattering spectrometer. EDS analysis also indicates an increase in ratio with increasing oxygen content (Table 5.2.4). For the alumina sample with 2.0 sccm O$_2$, silicon was also detected in the quantitative measurements and was not left out. Therefore, the ratio in the table is higher than what the actual would be without silicon.

Table 5.2.3: XPS results for alumina and zirconia samples at varying O$_2$ flow without ion etching.

<table>
<thead>
<tr>
<th>O:Al ratio (Al$_2$O$_3$ = 1.5)</th>
<th>O:Zr ratio (ZrO$_2$ = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6 sccm O$_2$</td>
<td>1.81</td>
</tr>
<tr>
<td>1.8 sccm O$_2$</td>
<td>1.26</td>
</tr>
<tr>
<td>2.0 sccm O$_2$</td>
<td>1.35</td>
</tr>
</tbody>
</table>
Table 5.2.4: EDS results for the same alumina and zirconia samples as in Table 5.2.3.

<table>
<thead>
<tr>
<th>EDS Analysis for Film Composition</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O:Al ratio (Al₂O₃ = 1.5)</td>
<td>O:Zr ratio (ZrO₂ = 2)</td>
</tr>
<tr>
<td>1.8 sccm O₂</td>
<td>0.691</td>
</tr>
<tr>
<td>2.0 sccm O₂</td>
<td>1.09*</td>
</tr>
</tbody>
</table>

Figure 5.2.21: XPS spectrum for alumina sample after ion etching.

One alumina and one zirconia sample was selected to do another XPS analysis with ion etching of the surface since XPS can only analyze the first 10 nm of the top surface of the sample. Because it was thought that the surface of the samples may have had some oxidation, which increased the oxygen content, the surfaces were etched in order to get a reading from the bulk material underneath the surface layer. Only one sample of each was chosen due to money and time constraints. The author thought to analyze
the sample with the highest oxygen content; however, after the analysis was done, it was realized that the alumina sample was for the lowest oxygen content.

Figure 5.2.21 shows the XPS spectrum for aluminum in the alumina sample after ion etching of the surface. Once again the spectrum was separated into two peaks. The green dashed line corresponds to the aluminum content from metallic aluminum, whereas the purple dot-dashed line is the aluminum content from aluminum oxide. Comparing the relative intensities of the Al₂O₃ sample before and after etching, it can be concluded that the ratio of Al-Al, 2p to Al-O, 2p increases, and that the film is comprised of both metallic and ceramic material.

Figure 5.2.22: XPS spectrum of zirconia sample after ion etching.
The separated spectrum for zirconium in a zirconia sample after ion etching is seen in Figure 5.2.22. This time there are four peaks, two corresponding to metallic zirconium and two corresponding to zirconium oxide, since zirconium has two orbitals shown in the spectrum. The yellow and orange lines correspond to Zr-Zr, 3d\(_{5/2}\) and Zr-Zr, 3d\(_{3/2}\), respectively. Zr-Zr, 3d\(_{5/2}\) and Zr-Zr, 3d\(_{3/2}\) have binding energies of 179.2 and 181.6 eV, respectively. Zr-O, 3d\(_{5/2}\) and Zr-O, 3d\(_{3/2}\) are represented by the green and purple lines, respectively. The binding energy of ZrO\(_2\)-3d\(_{5/2}\) is 183.1 eV and ZrO\(_2\)-3d\(_{3/2}\) is 185.5 eV. Based on the relative intensities, there is more zirconium content coming from zirconium oxide than pure zirconium.

Table 5.2.5: XPS results for one sample of alumina and zirconia with ion etching.

<table>
<thead>
<tr>
<th></th>
<th>O:Al ratio (Al(_2)O(_3) = 1.5)</th>
<th>O:Zr ratio (ZrO(_2) = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.6 sccm O(_2)</td>
<td>2.2 sccm O(_2)</td>
</tr>
<tr>
<td>With Etching</td>
<td>1.079</td>
<td>1.34</td>
</tr>
<tr>
<td>Without Etching</td>
<td>1.81</td>
<td>2.06</td>
</tr>
</tbody>
</table>

For both the alumina and zirconia sample, the oxygen to aluminum/zirconium ratio decreased meaning that the oxygen content decreased. This analysis is probably a more accurate measurement of the composition of the samples. In order to have a more conclusive result, analysis should have been done for all the samples to see if the trend does follow the previous conclusion of increasing ratio with increasing oxygen content. Access to a Rutherford backscattering spectrometer would have allowed the author to gather more results for comparative purposes and to obtain a valid conclusion on the composition of the constituent materials in the as-sputtered films.
5.3  Sputtering with Mini-Chamber

During experimentation the author had problems deposition stoichiometric films using regular DC reactive magnetron sputtering. Many investigators have stated that this is an unstable process and other methods must be employed to control the process. The author came across a design by Scherer and Wirz [Scherer and Wirz, 1984], who incorporated a mini chamber around the sputtering gun inside the sputter chamber. The idea was to separate the reaction of oxygen from occurring on the target surface leading to target poisoning. This author produced a mock up design to test whether plasma would still be produced using Scherer and Wirz’s idea.

Metallic sputtering was performed to deposit aluminum and zirconium films using the mini chamber mock up (Figure 4.4.2). Then reactive sputtering was performed to deposit alumina and zirconia films. XRD was performed on the metallic films. In the aluminum film, no distinguishing peaks were observed indicating an amorphous structure. This could mean that the deposition rate was greatly reduced with the mini chamber and thus, the film was too thin to form crystal structures. The author did not have access to any instruments that could measure these thin films, such as a thickness profilometer, ellipsometer, or a quartz crystal microbalance. For the zirconium sample, there was one peak corresponding to (1 1 2) plane at \(2\theta = 70.8^\circ\). XRD was not done on the ceramic samples because it was assumed to also have an amorphous structure. However, SEM was used to view the surface structure of the ceramic films. The alumina film shows a continuous surface with a porous structure, and the zirconia film has a smooth surface with small amounts of grain formations.
5.4 Sputtering with Ceramic Target

The author attempted to sputter alumina films from a ceramic target using RF power in order to compare the films to those deposited by reactive sputtering of a metallic target. One sample was deposited using 300 W RF at 3 mTorr sputter pressure for three hours. The second sample was deposited using 300 W RF at 3 mTorr sputter pressure with the addition of 0.5 sccm O₂ for two hours. SEM was used to study the surface structure of the two alumina samples at 50,000X magnification. The surface of the alumina film from the ceramic target showed a smooth surface with no distinguishing defects. However, the alumina film, which had the addition of oxygen flow, showed a continuous surface structure with small grain formations. Although the deposition rate was not measured, it is known from literature that the deposition rate for RF reactive sputtering is much lower than DC reactive sputtering. The film with the additional oxygen has the same size grains as the films from DC reactive sputtering of alumina but not as dense. If sputtered for longer time, the film deposited would have become denser and look similar to the reactive sputtered alumina films. More samples should have been deposited in order to have comparative results and make a better conclusion as to whether the alumina films had the same structure. Also, XPS or EDS should have been used to determine the composition of the film sputtered from a ceramic target. Although, the target should be stoichiometric alumina, some investigators have said the films may come out under stoichiometric without the addition of oxygen. Since the author did not spend much time researching the sputtering of ceramic targets, the experiments did not yield good alumina thin films.
CHAPTER 6: DISCUSSION AND FUTURE WORK

6.1 Discussion

New materials are being investigated in order to enhance and improve current thermal barrier coatings, which in turn will help increase the efficiency of gas turbines and jet engines. Presently, an old technology, reactive sputtering, was utilized in order to research new designs for TBCs. In this work the author's goals were to modify an existing sputter system for reactive sputtering capabilities and to produce multilayered ceramic thin films. The most challenging part of this research was to understand the theory, to modify system, and to control the process. Regular maintenance of the various components on the system was an obstacle that delayed, but did not hinder, experimental work. Gas lines were added for nitrogen and oxygen reactive gases to be used for reactive sputtering. Mass flow-controllers and a 4-channel power supply were installed to control the flow of reactive gas into the sputter chamber.

Metallic sputtering was performed using both DC and RF power in order for the author to understand the system and how the process works. Aluminum and zirconium thin films were deposited on glass slide and silicon wafer at room temperature. XRD analysis was utilized to determine the crystallography of the films. Aluminum was found to have peaks consistent with FCC crystal structure with lattice parameter $a = 4.05 \, \text{Å}$. Zirconium had peaks corresponding to HCP crystal structure with lattice parameters $a = b = 5.0309 \, \text{Å}$ and $c = 3.136 \, \text{Å}$. SEM micrographs displayed the surface structure of the thin films. Aluminum had large, faceted grains with a porous surface structure. Zirconium had small, faceted grains with a continuous, dense surface. The cross section was measured for the film thickness in order to calculate the deposition rate.
Aluminum had a deposition rate of 34 nm/min, whereas zirconium’s deposition rate was 32 nm/min.

Reactive sputtering from metallic targets was then employed to deposit aluminum oxide and zirconium oxide thin films on glass slide and silicon wafer at room temperature using DC power. XRD results concluded that the ceramic films were amorphous. SEM surface images depicted films with continuous surface and small grains. One sample from alumina and zirconia showed a porous structure, which could be attributed to target poisoning. The average deposition rate of alumina was found to be 43 nm/min, and the average deposition rate of zirconia was found to be 22 nm/min. However, the author believes there was an error in the cross section image taken in SEM, and that the deposition rate is closer to 32 nm/min, which is similar to metallic zirconium. Although the deposition rate for the alumina ceramic films was calculated to be greater than the metallic films, it is more accurate to conclude that the high rate was due to deposition in metallic mode of the target. XPS analysis of the elemental composition found that the films were under stoichiometric.

Over the course of this research, the author has learned much about sputtering and reactive sputtering processes. Many investigators have utilized DC reactive sputtering because of its advantages; such has high rate deposition, metal target utilization, and multiple dielectric combination fabrication. Through discussions with other researchers in industry, the author learned that fabrication of stoichiometric films in this sputter system would not be viable. Sproul et al. has stated that, for most cases, it is not possible to operate in the transition region of the target with flow control of the reactive gas. They also state that it is not possible to optimize rate, reproducibility, and film
properties with flow control of the reactive gas. The Denton Vacuum Explorer system is likely capable of reactive sputtering, but not able to achieve stoichiometric films without modification to the system. There are many parameters that are interdependent, which makes it harder to determine the exact parameters that would produce the best films.

The author recommends the incorporation of a pulsed-DC power supply in order to suppress arcing and prevent target poisoning if DC power is desired. Partial pressure control can also prevent target poisoning by precisely controlling the reactive gas flow since it has an active feedback control. Flow control of the reactive gas is very unstable, and some investigators have said that it is impossible to achieve stoichiometric films.

The author also recommends acquiring the proper instruments to characterize the structure, thickness, and properties of the sputtered thin films. Also, it was not an objective of the author to obtain films with quality properties, but it would be required when fabricating multi-layer coatings for new TBCs. A mass spectrometer was used by other investigators for leak detection, residual gas analysis, and deposition control. Substrate bias and substrate heating improved the properties of the sputtered films.

### 6.2 Future Work

Since the overall objective of this research group is to design and fabricate multi-layer coatings for TBCs in gas turbines and jet engines, more experimental work needs to be done in order to produce stoichiometric ceramic coatings. A majority of the experiments performed by this author held most sputter parameters constant and varied only the oxygen flow rate. However, if more experiments were to be done, the power, sputter pressure, and target to substrate distance should be varied and compared to find the
right combination of sputter parameters for stoichiometric films. Also, more discussions with other researchers, who have already accomplished this feat, should be done to gain more knowledge about the dependency of the sputter parameters and to restrict the number of experiments that need to be performed to find optimum films.

More time should be spent experimenting with sputtering from ceramic target in order to determine the quality of the thin films and to have a comparison for reactive sputtering of thin films from a metal target.

Although it was encouraged by the author’s major professor to manufacture a mini chamber to incorporate in the sputter chamber, this was not completed due to the limited time the author had to finish the current experiments. However, from the mock up the author can conclude that films can be sputtered using this design if properly installed. The author has created some drawings to represent a preliminary design for the mini chamber. This is not a completed design and should be engineered to work with the Denton Vacuum system. The dimensions in the picture are not true or concrete dimensions. They are there only for scaling purposes.

The mini chamber is a concentric cylinder that will go over the sputter gun (inside cylinder) and will be held in place with four set screws (Figure 6.2.2). A shoulder will be milled into the wall of the mini chamber in order to hold the shield in place with hex screws. This design is for ease of changing the aperture size in the shield. The shield has a two-part role: one is to close the chamber off and the second is to prevent the reactive gas from reaching the target surface. The red circle in the left image indicates a port hole for argon gas to be introduced inside the chamber.
Figure 6.2.1: Various views of the mini chamber over the sputter gun.

Figure 6.2.2: (Left) View of mini chamber over sputter gun, (Right) view of mini chamber with shield
The reactive gas will be introduced over the substrate holder and placed about 2 cm from the substrate surface. Figure 6.2.3 is a representation of ¼" stainless steel tubing gas outlet. Small holes will be drilled on the inside of the tube at an angle directed towards the substrate.

Figure 6.2.3: Representation of reactive gas inlet made of stainless steel tubing.

Further experiments should be carried out with the mini chamber design in place to see if stoichiometric films can be produced. If this design does not work, modifications to the system using one of the other recommendations would most likely help further the research in obtaining stoichiometric ceramic thin films. After stoichiometric ceramic films have been fabricated, the researcher should begin design for multi-layer coating. Simulation to calculate the necessary thickness of each layer to reflect a targeted wavelength should be done in order to reflect the whole spectrum of infrared radiation.
REFERENCES


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VITA

Diane Ho was born in October 1985 in Marrero, Louisiana. She was Valedictorian of Immaculata High School, Class of 2004. She received her Bachelor of Science in Mechanical Engineering from Louisiana State University (LSU) in December 2008. After graduating from her undergraduate studies, she traveled to Hong Kong, Australia and New Zealand for six weeks. She joined the graduate program at LSU in August 2009 and will receive her Master of Science in Mechanical Engineering in August 2011. Diane has accepted a job with Air Liquide’s ALLEX program. She will be starting her job in Houston, Texas in August 2011. She is the elder daughter of Nghia Thy Ho and Huong Thu Dinh and has a younger brother, Charlie Ho.