Fabrication and property study of plasma sprayed alumina coatings and magnetron sputtered multilayers

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FABRICATION AND PROPERTY STUDY OF PLASMA SPRAYED ALUMINA COATINGS AND MAGNETRON SPUTTERED MULTILAYERS

A Dissertation

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 Doctor of Philosophy

in

The Department of Mechanical Engineering

by

Ranran Liu
B.S., Nanjing University of Aeronautics and Astronautics, 2006
May 2011
DEDICATION

I would like to dedicate this dissertation to my parents and two younger brothers for their unconditional love and support.
ACKNOWLEDGMENTS

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ABSTRACT

In this study, air or atmospheric plasma spraying (APS), one of thermal spraying processes, was used to produce alumina coatings and single splats. Nanoindentation technique was used to measure the mechanical properties, such as hardness and elastic modulus, of APS alumina coatings and single splats. The detailed procedures to calculate elastic modulus and hardness, and testing parameters for nanoindentation have been provided. This study revealed that the phase combination of $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$ played an important role in the scattering distribution of nanoindentation results on APS alumina coatings.

In addition, nanoindentation technique was used to predict the phase information of the APS coatings in this study by elastic modulus comparison. Nanoindentation result confirmed disc-shaped alumina splats were $\gamma$ phase, which was also consistent with the XRD result that the bottom surface of APS alumina coating was almost pure $\gamma$-$\text{Al}_2\text{O}_3$.

An analytical model of nanoindentation on multilayered thin films was provided. Then, this analytical model was used to study nanoindentation response with APS alumina coatings. The analytical results were compared with experimental data and used to guide nanoindentation experimental parameters setup.

Reactive Al/Ni multilayered thin films were deposited by DC magnetron sputtering. Reactive Al/Ni multilayer foils can be used as local heat sources to melt solder or braze layers and thus bond different components. Performance of reactive Al/Ni multilayered thin films was studied under 1D, 2D and 3D configurations using multiphysics based numerical simulations. Temperature evolution during the reaction process was simulated. The simulation result showed both localized heating and rapid cooling during reaction.
Alumina thin films were fabricated by DC reactive magnetron sputtering. The hysteresis experiment has been carried out to find the suitable oxygen flow rate. The XRD analyses showed that the deposited aluminum oxide thin films were amorphous since no reflections of crystallized oxide could be observed. The stoichiometry of the aluminum oxide thin films was measured by XPS. The XPS analyses gave the O/Al ratio of 1.59, while the exact ratio is 1.50 corresponding to the stoichiometric Al$_2$O$_3$. 
CHAPTER 1. INTRODUCTION

1.1. Surface Coatings and Thin Films

Merriam-Webster’s dictionary defines a surface as “the exterior or upper boundary of an object or body.” For surface-engineering area, this concept needs to be extended, and a surface is defined as the interface between an object and its surroundings. Coatings are applied to the surfaces of substrates to protect them when they interface with other solids, liquids, or gases. Coating and surface modification technologies are commonly used to improve the performance, extend the life, and enhance the appearance of various substrates.

Surface engineering is to design a composite system of a coating and a substrate together to give a performance which cannot be achieved by either the coating or the substrate alone. Coatings can improve the appearance of surfaces; coatings can protect surfaces from adverse environment; and coatings can enhance many mechanical properties. This is possible by the application of any of the four main types of coating processes: 1) molten (thermal spraying, welding); 2) gaseous (vapor deposition, ionized plasma); 3) solution (electroless or electrolytic plating, resin bonding); 4) solid (friction welding, roll cladding) [1].

In industry, four major coating methods are commonly used: thermal spray (TS), physical vapor deposition (PVD), electro/electroless plating (EP/ElsP), and chemical vapor deposition (CVD). Although the initial equipment costs and the operating costs for EP/ElsP coatings are relatively low, the by-products are considered highly toxic and are subject to increasingly stricter government regulations, and the disposal of the waste stream may incur severe economic penalties. Equipment costs for CVD are moderate and the operating costs of CVD are dominated by gas costs and the frequent needs to clean the systems. The cost of thermal spray equipment
varies widely from simple manual combustion devices to computer-controlled plasma spray systems. The operating costs are mainly dependent on the cost of consumables such as powder, wire, or rod materials as well as the quantities and types of spray gases used. The cost of PVD coating equipment is very high, due to the need to maintain high vacuums in the chambers of PVD equipment. The EP/ElsP and CVD are omnidirectional coating processes, while TS and PVD are line-of-sight processes. With the exception of EP/ElsP, which is limited to metals and some alloys, the TS, CVD, and PVD coating process can apply a variety of metals, ceramics, cermets, and polymers [2].

1.2. Present Study

In this study, air or atmospheric plasma spraying (APS), one of thermal spraying processes, was used to produce alumina coatings and other ceramic coatings. The mechanical properties (hardness and elastic modulus) of APS alumina coatings were studied using nanoindentation testing, which is a widely used technique in the characterization of mechanical behavior of small scale bulk materials, thin films, coatings, and other nanomaterials. A detailed testing scheme, indentation control parameters, and corresponding data processing have been established in this study. Nanoindentation testing on APS alumina coatings and single splats were conducted. The influence of different phases of alumina on the nanoindentation results was investigated. An analytical model has been established to study nanoindentation testing on multilayered thin films. The analytical results of nanoindentation on APS alumina coatings were deduced based on this model, and the analytical results have a good agreement with the experimental results. In addition, this analytical model can be used to guide the experimental tests by predicting indentation parameters such as maximum load force and suitable indentation depth in order to get reasonable nanoindentation results.
DC magnetron sputtering technique was used to deposit reactive multilayered Al/Ni thin films, which could be used as a self-propagating heating source to melt solder layers and thus bond electrical components such as silicon wafer bonding applications. Performance of reactive Al/Ni nanofoils was studied under 1D, 2D and 3D configurations using multiphysics based numerical simulations. The flame speed was successfully modeled as a function of the chemical reaction rate. The detailed chemical compositions have been obtained for the Al/Ni multilayered foil. The performance of nanofoil was quantified in terms of temperature and species distributions, and the flame speed. The numerical simulation proved that the heating from a reactive nanofoil to the substrate was highly limited and localized. The use of a reactive nanofoil as a local heating source may eliminate the need for excess equipment, and dramatically reduce the total energy that is needed for bonding applications.

Reactive DC magnetron sputtering was used for the deposition of amorphous alumina thin films by adding reactive gas (oxygen) to the sputtering process. Hysteresis experiment was first performed to study the reactive sputtering process of alumina. The phase formation and surface structure of the as-deposited alumina films have been presented using XRD, XPS, and SEM.

1.3. Organization of Dissertation

This dissertation consists of a total of nine chapters to cover the research work that has been performed. Each chapter focuses on a specific topic. The following is a brief summary of each chapter’s content.

Chapter 2 introduces different thermal spray processes and compares these processes with other coating processes, such as physical vapor deposition (PVD), electro/electroless plating (EP/ElsP), and chemical vapor deposition (CVD). The merits and applications of thermal spray
technology, especially air plasma spraying process, are presented and discussed. The formation and structure of thermal sprayed coating are also included in this chapter.

Chapter 3 presents the theoretical background of indentation technology. The detailed procedures to calculate elastic modulus and hardness, and testing parameters for nanoindentation have been provided. Lastly, the substrates’ effect on the experimental results of thin coatings or multilayered thin films will be discussed.

Chapter 4 studies the splat formation and mechanical properties of APS alumina coatings and single splats. Using nanoindentation technique, the hardness and elastic modulus of APS prepared alumina single splats and alumina coatings have been studied. The load-displacement curves for the single splats and coatings are presented. The hardness and elastic modulus measured on alumina coatings showed a scattering distribution with an obvious peak corresponding to $\gamma$ phase.

Chapter 5 develops an analytical model of nanoindentation on multilayered thin films. Then, this analytical model is used to study nanoindentation on APS alumina coating. The analytical results are compared with experimental data and used to guide experimental parameters setup.

Chapter 6 introduces the principles of DC magnetron sputtering and describes the Denton Vacuum magnetron sputtering system used in this research. Experimental procedures and parameters to deposit Al/Ni multilayered thin films are given in this chapter.

Chapter 7 provides a numerical simulation study of Al/Ni multilayered thin films. Performance of reactive nanofoils is studied under 1D, 2D and 3D configurations using multiphysics based numerical simulations. The detailed chemical compositions have been obtained for the Al/Ni bi-layer foil. The performance of nanofoil is quantified in terms of
temperature and species distributions, and the flame speed.

Chapter 8 studies the reactive sputtering of alumina thin films. The hysteresis experiment has been carried out to find the suitable oxygen flow rate. The XRD analyses showed that the deposited aluminum oxide thin films were amorphous since no reflections of crystallized oxide could be observed. The stoichiometry of the aluminum oxide thin films was measured by XPS. The XPS analyses gave the O/Al ratio of 1.59.

Chapter 9 provides a summary of the conclusions achieved from this dissertation and recommendations for future research in this field.
CHAPTER 2. THERMAL SPRAY PROCESSES

2.1. Thermal Spray Processes versus Other Coating Processes

Thermal spray processes differ from other coating processes because they do not deposit materials onto surfaces as individual ions, atoms, or molecules. Instead, relatively massive particulates are deposited onto a surface in molten or semi-molten status. Coating feedstock materials are usually in the form of powder, wires, or rods. Feedstock materials are generally heated to their melting point by a plasma jet, electric arc, or flame. The molten material is then atomized, and propelled toward the substrate by processing gases. Upon impact, a bond forms with the surface, with subsequent particles causing thickness buildup and forming a lamellar structured coating. The coating process depends on several process conditions, such as spray power, mixtures of gases, spray distance and so on. The thin “splats” undergo very high cooling rates, typically in excess of $10^6$ K/s for metals [2]. Thermal spray is also a “light-of-sight” process-projected stream of droplets deposit onto surfaces that are directly in line with the droplets’ direction.

Because thermal spray processes are high-enthalpy (high energy density) processes, they are characterized as having high coating rates relative to other coating processes such as, CVD, PVD, and EP/ElsP. Additionally, thermal spray processes are capable of operating over a broad range of temperature, velocity, and different atmospheric conditions, enabling them to apply the greatest variety of materials.

Members of the thermal spray processes are typically divided into two major categories: thermal spray processes using electric energy and thermal spray processes using combustion. Each of these categories encompasses many more subsets, and each has its own characteristic
range of temperature, enthalpy, and velocity. For example, electric arc spraying and plasma spraying are thermal spray processes using electric energy; while flame spraying, detonation gun and high velocity oxy-fuel (HVOF) are using combustion [3]. These attributes in turn will determine coating characteristics and properties that are unique to other coating processes including coating bond strength, porosity, inclusions, hardness, and elastic modulus.

In general, there are two types of plasma spraying: conventional plasma spraying and vacuum plasma spraying. The conventional plasma spraying process is commonly referred to as air or atmospheric plasma spray (APS). The temperature within the plasma can be as high as 15,000 °C, significantly above the melting point of any known material, even ceramics [2].

In order to generate the plasma, the plasma gas, typically argon or gases mixtures are ionized and dissociated by a high frequency arc between an anode and a cathode in a plasma gun. The spray material is introduced in the powder feeder via a carrier gas and is heated and accelerated simultaneously onto the substrate surface by the high temperature and high speed plasma plume. Accordingly, spray deposition rates greatly depend on gun design, plasma gases, powder injection schemes, and materials properties. Also, coating properties and characteristics depends on the coating material, spray equipment configuration, and spray parameters.

Vacuum plasma spraying (VPS) is also commonly referred to as low-pressure plasma spraying (LPPS). Control of the chamber pressures during VPS process facilitates a reduction in the amount of impurities and contaminants, and results in high-quality deposits.

2.2. Thermal Spray: History and Applications

Thermal spray includes a group of coating processes in which finely divided metallic or nonmetallic materials are deposited in a molten or semi molten condition to form a coating on a substrate [4]. This process was first invented and patented in 1910 by Dr. Max Ulrick Schoop of
Zurich, who recognized the possibility that a stream of molten particles impinging upon themselves could create a coating. Plasma is the name given by scientists to describe vapors of materials which are raised to a higher energy level than the ordinary gaseous state and is considered a “fourth state of matter” besides solid, liquid, and gas. Irving Langmuir was the first to name plasma and wrote: “except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small” [5]. Thus, the name plasma is used to describe this region containing balanced charges of ions and electrons. Plasma is an ionized gaseous cloud of free electrons, positive ions, as well as neutral atoms and molecules.

Principally, the properties of a gas are primarily dependent upon the movement of its individual molecules. When the temperature of the plasma gas increases, the velocity of molecules will increase. When the velocity of the particles reaches a high level that, in case of a diatomic gas the molecules disintegrate into atoms due to mutual collision. This process taking place in plasma arc is called dissociation. When higher levels of energy are supplied, the velocity can achieve such a high level that not only molecules are dissociated but also electrons can be forced out from the electron envelope of atoms. This process is called ionization.

The final consequence of the whole dissociation and ionization processes is plasma as a state of mass containing the electrically charged particles. However, it must be noted that the plasma is, as a whole, neutral, since within it, the same number of electrically positive and negative charges must be evenly distributed [6].

2.3. Gases in Thermal Spray Processes

In the APS process, the gases such as argon, helium, hydrogen, and nitrogen are brought to the plasma state. The plasma forming gases are divided into two basic groups: monatomic and
diatomic gases. Argon and helium belong to the first group, while nitrogen and hydrogen belong to the other. The physical and chemical characteristics of different gases are shown in Table 2-1.

Table 2-1. Plasma forming gases properties.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Argon</th>
<th>Helium</th>
<th>Nitrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative molar weight</td>
<td>39.94</td>
<td>4.00</td>
<td>28.02</td>
<td>2.02</td>
</tr>
<tr>
<td>Specific heat capacity $c_p$ at 20 °C</td>
<td>0.520</td>
<td>5.19</td>
<td>1.04</td>
<td>14.32</td>
</tr>
<tr>
<td>(kJkg$^{-1}$K$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity coefficient at 25 °C (Wm$^{-1}$K$^{-1}$)</td>
<td>0.016</td>
<td>0.14</td>
<td>0.024</td>
<td>0.17</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>14 000</td>
<td>20 000</td>
<td>7 300</td>
<td>5 100</td>
</tr>
</tbody>
</table>

Plasma flames for thermal spraying can produce temperatures around 7,000 to 20,000 K. The plasma forming gas is selected on the basis of the desired temperature, velocity, thermal conductivity, and specific heat of the plasma plume and the degree of inert material in the sprayed material and the substrate. The process of plasma formation of a diatomic gas differs from that of a monatomic gas. The difference is that the ionization of diatomic gas starts after dissociation of its molecules.

The enthalpies and plasma temperatures are also important parameters between the one atom and two atom gases. Nitrogen heated to 10,000 K going through dissociation and ionization forming a plasma is an effective heating media for thermal spraying, being able to supply about six times more energy than an equal volume of helium at 13,000K. This is because the great volume of energy gained by the diatomic gases is from dissociation of molecules into atoms, while the energy of monatomic gases is given by the specific heat and the ionization energy [6].

Argon plasma has been repeatedly studied while the dependence of ionization potential on the temperature was determined. Argon ionization starts at 9, 000 K and is completed at 22,
000 K [3]. Enthalpy of these one atom gases is considerably lower than the diatomic gases. Moreover, they have been preferred because of the following reasons:

- They are easy to transfer to plasma state than diatomic gases
- They can provide a stable electric arc
- Temperature of these plasmas is highest compared to the other plasmas
- They require low working voltage

As to their effects on the sprayed material, argon and especially helium have high inertness of environment. Because argon and helium do not dissociate, their beam is very bright, short, and constricted. Such a beam allows local deposit of the spraying layer, facilitating considerably higher spraying efficiency. Helium also has excellent thermal conductivity. But helium is a very expensive and precious gas.

2.4. Air Plasma Spray (APS) Process

Air plasma spray is a well-established process for preparing ceramic coatings and free-standing components. Figure 2-1 has shown several key components of the APS system used in this research. During APS process, powder particles injected into the plasma jet are heated and accelerated simultaneously in the plasma stream and deposited in molten or semi-molten droplet conditions onto a prepared substrate, as shown in Figure 2-2.

APS is a high-velocity impact deposition process in which melting, quenching, and consolidation of alumina take place in a single step. The properties of plasma sprayed ceramics, and especially the differences from conventionally sintered ceramics, are known to be dependent on their anisotropic, quasi-laminated, “splat” microstructures and non-equilibrium phase compositions [7]. The microstructure of splats is dependent on many spraying parameters, e.g.
arc current, carrier gas pressure, gun-substrate distance, etc. Variations in these parameters can lead to large changes in microstructure and phase system and hence lead to great variations in the properties of the deposited ceramic [8,9]. Depending on the feedstock powders, APS spray conditions, and splat cooling rates, some coatings exhibit a thin amorphous layer next to the substrate followed by various crystalline layers with non-equilibrium and even nonstoichiometric phases [10,11].

As shown in Figure 2-3, the droplets first strike the surface, flatten and form thin splats that adhere to irregularities of the surface and to each other. The droplets cool, solidify and build up on the substrate into a laminar structure to form a coating.

Figure 2-1. Key components of an APS system [12].
Figure 2-2. Cross-section of a typical plasma gun [12].

Figure 2-3. APS coating structure [12].
3.1. Indentation Testing

Indentation testing, also commonly known as hardness testing, is a simple, inexpensive and quick method of mechanically characterizing a sample. It consists of touching the material of interest whose mechanical properties such as elastic modulus and hardness are unknown with another material whose those properties are known [13]. The most important parameter determined by indentation testing is hardness. Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration. Hardness measurement can be defined as macro-, micro- or nano-scale according to the forces applied and displacements obtained.

Hardness is not an intrinsic material property dictated by precise definitions in terms of fundamental units of mass, length and time. A hardness property value is the result of a defined measurement procedure. Mohs first proposed a sufficiently precise and generally accessible method to determine the hardness parameters of minerals in 1822. Later, the more refined methods were developed including Brinell, Knoop, Vickers, and Rockwell tests in which the term “hardness” is quantified using one of a variety of scales that directly or indirectly indicate the contact pressure involved in deforming the test surface. The indenter used in different methods varies from spherical, pyramidal, conical, or Berkovich indenter, which are shown in Figure 3-1.

It should be noted that the indentations with pyramidal, conical, and even Berkovich indenters have geometric similarity. The principle of geometric similarity is widely used in hardness measurements. For example, due to geometrical similarity, hardness measurements made using a diamond pyramid indenter are expected to be the same for a large indentation and a
small indentation, which means that the measured hardness is independent of the load if the indentation size effects (ISE) are not considered.

![Indenter parameters for (a) spherical, (b) pyramidal, (c) conical, and (d) Berkovich indenters.](image)

Figure 3-1. Indenter parameters for (a) spherical, (b) pyramidal, (c) conical, and (d) Berkovich indenters.

The hardness value is expressed as the load divided by the actual contact surface area (e.g., Brinell hardness number BHN, Vickers hardness HV, and Knoop hardness KHN) or as the load divided by the projected contact area (e.g., Meyer hardness \( H_m \)). For example, Vickers hardness, HV, is determined as the load generating a fully developed plastic zone divided by the actual area of the surface of the residual impression as follows:

\[
HV = \frac{P}{A_{\text{actual}}}
\]  

(3-1)

where \( P \) is the load, and \( A_{\text{actual}} \) is the actual surface area of the residual impression. By contrast, the Meyer hardness is determined as the load divided by the projected area of contact:

\[
H_m = \frac{P}{A_c}
\]  

(3-2)

where \( A_c \) is the projected contact area. The Meyer hardness is a more physically meaningful concept which is well recognized now.
3.2. Nanoindentation

3.2.1. Measurement Techniques

Nanoindentation has become an increasingly popular mechanical characterization technique in the past decades. Nanoindentation, also named depth-sensing indentation (DSI) testing or instrumented indentation testing (IIT), is based on the theories of contact mechanics. In addition to measuring the hardness value, nanoindentation has been widely used to extract the elastic modulus of the specimen. Nanoindentation was developed in the early 1970s [14,15,16]. The technological developments have reduced the size of tips manufactured, and improved the accuracy and resolution of depth and load measurement of the indentation test.

This technique is widely used in the characterization of mechanical properties of small scale bulk materials, thin films, coatings, and other nanomaterials. Due to the micro/nano scale load and the resulting small residual impression left on the surface of the tested material, it can be regarded as a non-destructive testing technique. Nanoindentation is the combination of high resolution recording indentation and the accompanying data analyses for the determination of mechanical properties directly from the load-displacement data without measuring the area of the indentation.

There has been considerable interest during the last two decades in the mechanical characterization of thin film systems and small volumes of materials using depth-sensing indentation tests utilizing either spherical or pyramidal indenters. Usually, the principle goal of such testing is to obtain values for elastic modulus and hardness of the specimen material from experimental readings of indenter load and depth of penetration. The forces involved are usually in the millinewton range and are measured with a resolution of a few nanonewtons. The depths of penetration are in the order of nanometers, hence the term “nanoindentation”.
3.2.2. Nanohardness and Elastic Modulus

Many efforts have been made in developing nanoindentation equipment and nanoindentation techniques for probing the mechanical properties of coatings and thin films on nano-scale over the past decades. The most widely used method to determine the elastic moduli and hardness by nanoindentation was proposed by Oliver and Pharr [17]. During nanoindentation, an indenter with a known geometry and properties (e.g., Young’s modulus, Poisson’s ratio) is pressed into the flat surface of a material of unknown properties followed by unloading, while the load and indentation depth are continuously controlled and monitored through high resolution instrumentation. The mechanical properties of the material can be derived from the measured load-displacement curve. The length scale of the penetration is measured in nanometers (nm) rather than micrometers (μm) or millimeters (mm), the latter being in common in conventional indentation tests.

Compared with other mechanical experimental characterization methods, the advantages of nanoindentation include: 1) the contact area between the indenter and the specimen required to calculate the hardness is indirectly determined by measuring the depth of penetration of the indenter with the known geometry into the specimen surface, this overcomes the difficulties in directly measuring the nanoscale or microscale size of the residual impression which is commonly employed in conventional indentation tests; 2) the continuously recorded load-displacement data provide a wealth of information for characterizing a variety of mechanical properties such as elastic modulus [17], hardness, strain-hardening [18, 19, 20], cracking, phase transformations, creep, and energy absorption.
A schematic representation of a typical load-displacement curve for an indentation experiment is shown in Figure 3-2(b). Several assumptions are made to analyze the load-displacement curve [17]:

- Deformation upon unloading is purely elastic
- The compliances of the specimen and the indenter tip can be combined as springs in series
- The contact can be modeled using the analytical model developed by Sneddon for the indentation of an elastic half space by a punch that can be described by an axisymmetric solid of revolution.
Determination of hardness and elastic modulus by nanoindentation is based on the mechanics of elastic contact. An elastic parameter, named reduced modulus \( E_r \) or effective modulus of the indenter-sample contact, can be found from the measured stiffness \( S \) of the unloading curve and the contact depth \( h_c \) of the indentation load-displacement curve through the following relationship:

\[
E_r = \frac{\sqrt{\pi}}{2\beta\sqrt{A_c}} S
\]  

(3-3)

where \( \beta \) is a dimensionless correction factor for the indenter tip shape and \( \beta = 1.05 \) is commonly recommended [21]; \( A_c \) is the projected area between the indenter and sample; \( S \) is the elastic stiffness defined as the slope of the initial unloading curve at the maximum indentation depth \( (h_{\text{max}}) \) (Figure 3-2) and is usually determined by fitting the beginning portion of the unloading curve using a linear or power law relationship, depending on indenter geometry:

\[
S = \frac{dF}{dh}_{h=h_{\text{max}}}
\]

(3-4)

Equation 3-4 was initially developed by Sneddon for the penetration of a flat-surfaced, elastic half space by different probes of particular axisymmetric shapes (e.g., a flat-ended cylindrical punch, a paraboloid of revolution, and a cone) and experimentally verified thereafter suitable for conic and pyramidal indenters [22].

The reduced modulus can be obtained directly by following the above procedures. \( E_r \) actually reflects the elastic contact interaction between the indenter tip and sample and accounts for elastic deformation of both the indenter and the sample. To obtain the elastic modulus of the sample, the following relationship was used:
where $E_i$ and $E_c$ are the elastic modulus of the indenter and sample, respectively (for a diamond indenter, $E_i = 1141$ GPa); $\nu_c$ and $\nu_i$ are the Poisson’s ratio of the sample and indenter, respectively (for a diamond indenter, $\nu_i = 0.07$). $E_c$ is the elastic modulus of the sample if the sample can be described as a semi-infinite, elastic half space. If the tested sample is a thin film and the indented zone is affected by the underlying substrate, $E_c$ represents the “mean” response of the film-substrate composite.

In most cases, the depth to which the indenter is in contact with the material, or the contact depth ($h_c$) is less than the total depth of penetration ($h_{max}$) due to elastic deflection of the surface adjacent to the point of contact. The depth of contact is required for calculation of the projected contact area, and is calculated as follows:

$$h_c = h_{max} - \varepsilon \frac{F_{max}}{S}$$

where $\varepsilon$ is a constant that depends on indenter tip geometry (for Berkovich tip, a triangular pyramid, $\varepsilon = 0.75$), and $F_{max}$ is the maximum load of an indentation.

To quantify mechanical properties, the projected contact area $A_c$ must be known. For the perfect Berkovich geometry, the projected area will be expressed as a single geometric description of the tip, that is, $A_c=24.56h_c^2$. Since no tip is perfect, some function describing the geometry of the tip must be developed for diamond tip to be used. The function between the projected contact area $A_c$ and contact depth $h_c$ can be pre-established by performing independent indentation tests on a standard material (e.g., fused silica) with known properties. The indenter area function $A = f(h_c)$ was proposed by Oliver and Pharr as follows:
\[ A_c = C_0 h_c^2 + \sum_{i=1}^{8} C_i \left( \frac{1}{2} \right)^{i-1} \] (3-7)

where \( C_0, C_1 \cdots C_8 \) are constants for a specific indenter and are determined by curve-fitting procedure of a series of indentation tests with different indentation depth on a standard material.

Indentation hardness is determined as the mean contact pressure at maximum load:

\[ H = \frac{F_{\text{max}}}{A_c} \] (3-8)

It is evident that the indentation hardness here refers to the Meyer hardness.

### 3.2.3. Continuous Stiffness Measurement (CSM)

One of the most important improvements in nanoindentation is the continuous stiffness measurement (CSM) technique, in which dynamic contact stiffness is measured continuously during the loading portion of an indentation test by imposing a small dynamic oscillation on the force (or displacement) signal and measuring the amplitude and phase of the corresponding displacement (or force) signal by means of a frequency-specific amplifier [21]. The most important advantage is that it provides continuous results (modulus, hardness, stiffness, et.) as a function of indentation depth. In addition, the complicating effects of time-dependant plasticity and thermal drift could be reduced greatly if high frequencies are used.

The CSM device monitors the contact stiffness of the sample and indenter throughout the duration of the indentation test. This powerful technique enables the user to calculate the hardness and Young’s modulus continuously as a function of depth.

In the conventional techniques, the slope of the upper portion of an unloading curve is being used for stiffness calculation. This will generate one hardness and modulus per indentation
test. In CSM technique both hardness and elastic modulus are being measured as a function of depth of penetration; hence substrate effect becomes visible after certain depth.

Advantages of continuous stiffness measurement:

- Improved separation of a material’s elastic and plastic responses
- More accurate hardness and Young’s modulus
- Improved stiffness determination, especially for small contacts
- Accurate and independent determination of the indentation contact area as a function of indentation depth

3.2.4. Loading Modes

Conventional indentation test is a one point test in which the load is applied, held, and removed following a standard procedure with respect to the used method. The hardness is calculated as the load divided by the actual or projected area of the impression and is not significantly dependent upon the loading modes. Nanoindentation testing, however, provides continuous load-displacement data, and the mechanical properties (e.g., hardness and modulus) are derived from the curves instead of one point data. Therefore, the loading modes, which affect the curves’ features, are more critical in nanoindentation tests. There are two frequently used loading modes for nanoindentation testing: load control mode and displacement control mode. The first one is the load control mode with a constant loading rate [23]:

$$\frac{dF}{dt} = \frac{F_{\text{max}}}{t_L} = \text{const.} \quad (3-9)$$

where \(t_L\) is the loading time. In this mode, the load is applied from zero to the maximum load \(F_{\text{max}}\) at a constant loading rate determined by Equation 3-9 and \(F_{\text{max}}\) is held for a period of \(t_h\). This is followed by unloading to a certain percentage of \(F_{\text{max}}\) with a defined loading rate, and
then the load is kept constant to record the displacement for the correction of thermal drift. The other one is the displacement control mode with a constant indentation strain rate which is defined as [23,24]:

\[
\dot{\varepsilon} = \frac{dh/dt}{h} = \frac{1}{\beta} \left( \frac{dF/dt}{F} - \frac{dH/dt}{H} \right)
\] (3-10)

where \( \beta \) is a constant describing the shape of an idealized indentation tip. The determination of indentation strain rate originates from the assumption that the instantaneous change in contact area \( d(A_c)/dt \) divided by the instantaneous contact area \( A_c \) may be the most appropriate definition for the indentation strain rate and that the instantaneous displacement rate of the indenter \( (dh/dt) \) divided by the instantaneous displacement \( h \) is simply related to \( (dA_c/dt)/A_c \) [25].

Equation 3.10 suggests that an indentation conducted with an indenter with geometrical similarity, during which the loading rate is controlled so that the loading rate divided by the load \( (dF/dt)/F \) is constant, can be controlled with a constant value of the indentation strain rate if a steady-state value of the hardness can be reached. This advantage is widely used together with CSM technique in determination of mechanical properties versus indentation depth [23].

3.3. Data Analysis on Thin Films

The test techniques that are used to determine mechanical properties of bulk materials cannot be directly applied to measure the properties of thin films because the thin films of interest are usually extremely thin and are attached to a substrate. As a result, these techniques were modified and new techniques were devised to measure mechanical properties of thin films. Also, no single technique is capable of measuring all the properties. Some of the techniques used to determine the mechanical properties of thin films are substrate curvature, beam bending bulge testing, and nanoindentation. The advantage of nanoindentation over the other techniques is that
it is a relatively simple and direct technique. It does not require any complicated sample fabrication; and small-scale deformation can be made and measured. As a result, mechanical properties can be directly measured without having to remove the film from the substrate which simplifies the sample preparation. One can also test the film surface at many different locations and spatially map its mechanical properties [26].

The standard methods that are used for extracting properties from the measured load-displacement data were developed primarily for monolithic materials. These same methods are used for film/substrate systems for determining film properties without considering the substrate’s effect on the measurements. Since the film is attached to the substrate, the substrate can affect the measurement during the nanoindentation experiment. Figure 3-3 is a schematic representation of the deformation occurring beneath the indenter when a film/substrate composite is indented. As long as the plastic deformation volume and a significant portion of the elastic strain field are contained within the thickness of the film, as shown in Figure 3-3(a), “film-only” properties will be measured. However, once the elastic strain field or both the elastic strain field and plastic deformation volume extend into the substrate, as shown in Figure 3-3(b), the measured properties are those of the film/substrate composite. To measure the film-only properties, a commonly used rule is that the penetration depth is less than 10% of the film thickness [17,21]. Otherwise the stiffness contribution of the substrate to the indenter-sample contact should be taken into consideration.

Nanoindentation is widely recognized as an effective testing method to determine mechanical properties of not only small scale materials, but also thin films on substrates provided that the maximum indentation depth is limited to a certain portion of the film thickness. Much effort has been devoted to the methods of extracting film modulus and hardness from the
measured composite response of tip-film-substrate system.

Figure 3-3. Schematic representation of the elastic and plastic deformation beneath the indenter for a film on a substrate (a and b).

Although nanoindentation technique has been widely used to determine the hardness and
elastic modulus of small-scale materials, applications in plasma sprayed ceramic coatings are
very limited. The nanoindentation results of plasma sprayed ceramic coating, as compared with
metallic materials, have higher scatter and reduced reproducibility, which is caused by stochastic
indentation response [27].
CHAPTER 4. SPLAT FORMATION AND MECHANICAL PROPERTIES OF AIR PLASMA SPRAYED (APS) ALUMINA

4.1. Introduction

Atmospheric plasma spraying (APS) is a well-established process for preparing ceramic coatings and freestanding components. This technique is very versatile and virtually any material can be plasma sprayed. Among plasma sprayed ceramic and cermet coatings, alumina (Al$_2$O$_3$) is the most widely established coating material. These coatings have been used for many applications in textile, electronic, aerospace, and aircraft industries because of their dielectric and wear resistance properties. In APS process, alumina powder particles injected into the plasma jet are heated and accelerated simultaneously in the plasma stream, and then are deposited in molten or semi-molten droplets conditions onto a prepared substrate and are rapidly cooled at rates of about $10^6$ to $10^7$ Ks$^{-1}$ [28].

Under the assumptions that the alumina droplets impact perpendicularly onto the substrates and the splat solidification starts only when flattening is completed, the alumina liquid droplet can rebound, deposit, or splash based on the droplet velocity and substrate temperature. During droplet impingement, these molten droplets rapidly solidify to form single splats. The coating is built up by piling up the layers of splats. The alumina coatings piled up by disc-shaped splats have better mechanical properties compared with coatings consisting of fragmented splashing. The splat shape is usually controlled by altering the substrate temperature in real life applications. With an increase in substrate temperature, disc shape will be the splat pattern. According to Fukumoto et al. for APS alumina on AISI 304 stainless steel substrate, when the substrate temperature is above 318 K, disc-shaped splats can be obtained [29]. In order to get disc-shaped alumina splats, all the substrates in this study were preheated to more than 350 K.
Nanoindentation is a commonly used method to determine the mechanical properties of both small-scale bulk materials and thin films. The method was first introduced in 1992 by Oliver and Pharr [17] for measuring hardness and elastic modulus by instrumented indentation techniques. During nanoindentation, an indenter with a known geometry and properties (e.g., elastic modulus, Poisson’s ratio) is pressed into the flat surface of a material with unknown properties followed by unloading. The continuously recorded load $F$ and indentation depth $h$ for the loading and unloading processes offer an advantage that both hardness $H$ and modulus $E$ can be determined simultaneously in a single test.

Using nanoindentation, the mechanical properties of alumina coatings and alumina single splats, such as hardness and elastic modulus at the nanoscale, can be studied. The nanoindentation results of brittle materials are typically with higher scatter and reduced reproducibility. Other studies [30] have shown that the scattering data were mainly attributed to the brittle property of alumina. However, no attention has been paid to the effects of different alumina phases on the scatters of the nanoindentation data. The present work was designed to study the effects of different alumina phase combinations on the nanomechanical properties of the APS alumina coating. Studies on the mechanical properties of APS ceramic coatings, especially the single splats are very rare in open literature [31]. Therefore, one of the objectives of the present study is to carry out a detailed investigation on as-sprayed alumina splats using nanoindentation.

4.2. Experimental Procedures

4.2.1. Sample Preparation and APS Parameters

In current study, a Sulzer-Metco APS system with 9MB plasma spray gun was used for the deposition of the alumina coatings and single splats. Typical $\text{Al}_2\text{O}_3$ spraying parameters
recommended by Sulzer-Metco were used, as shown in Table 4-1.

Fused and crushed alumina powder (Figure 4-1) in the range of 5 to 45 μm (325 mesh, 99.5+\% purity) supplied by Inframat Advanced Materials USA was used as the feeding supply. Both smooth silicon wafer substrates with dimensions of 20×10×1 mm and grit-blasted mild steel substrates with dimensions of 40×30×4 mm were used. APS alumina coatings with thickness of about 300 μm were prepared on grit-blasted mild steel substrates. For collection of single splats, the plasma gun was quickly moved over the silicon wafer substrates for only one pass to minimize occurrences of two or more powder constituents depositing on the same location on the substrate surface and each other.

Figure 4-1. SEM micrograph of alumina powder.
Table 4-1. Plasma spraying parameters for Al$_2$O$_3$ coatings.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc current (A)</td>
<td>500</td>
</tr>
<tr>
<td>Arc voltage (V)</td>
<td>75</td>
</tr>
<tr>
<td>Primary gas Ar (l/min)</td>
<td>75</td>
</tr>
<tr>
<td>Secondary gas H$_2$ (l/min)</td>
<td>7</td>
</tr>
<tr>
<td>Power feed rate (g/min)</td>
<td>40</td>
</tr>
<tr>
<td>Spraying distance (mm)</td>
<td>60</td>
</tr>
</tbody>
</table>

4.2.2. Nanoindentation Testing

Nanoindentation experiments were performed on the single alumina splats and APS alumina coatings using an MTS Nanoindenter (MTS Nano Instruments, Inc., Oak Ridge, TN) equipped with a regular XP head and a dynamic contact module (DCM) head. The XP head has a load resolution of 50 nN while the DCM head has a load resolution of 1 nN. All the indentation tests presented in this study were performed at room temperature using diamond Berkovich indenters.

The indentation tests on the single alumina splats were conducted using DCM head with 350 nm depth limit. The XP head was used for nanoindentation tests on APS alumina coatings with 2000 nm depth limit. Continuous stiffness mode (CSM) module was used for both heads under constant indentation strain rate $(dh/dt)/h=0.05$ 1/s, where $h$ is the indentatin depth, and $t$ is the loading time.

For nanoindentation tests on APS alumina coatings, the distance between indents in a matrix of 5×5 was 50 µm to avoid the effects of stress fields on new nanoindentation where the
A depth limit of 2000 nm was applied. A total of 100 indentation tests were performed on two APS alumina coatings. The nanoindentation data will not be used if there is obvious defect in the load-displacement curve. For the disc-shaped splats on silicon wafer substrates, two indentations were made on each splat. In total, eight indentations were made on four splats.

4.2.3. Microstructure and Alumina Phase Characterization

The phase compositions of the coating samples were determined by X-ray diffraction (XRD) with CuKα (λ=1.54056 Å) radiation. The scanning speed of 2θ was 2°min⁻¹ in the XRD tests. The microstructure of the as-sprayed coatings and single splats were examined using scanning electronic microscopy (SEM) and field emission SEM (FESEM). Nano-Vision with nanoindentation equipment was also used to characterize the physical parameters of single splats.

4.3. Results and Discussion

4.3.1. Microstructure characterization

Figure 4-2 shows a disc-shaped splat on a silicon wafer substrate under SEM. The physical geometry of disc-shaped splats was measured using Nano-Vision function of the nanoindenter.

Figure 4-3 shows the result for a typical splat. The average diameter for those disc-shaped splats is about 60 µm and the thickness is around 1.5 µm. Figure 4-4 presents the top surface of plasma sprayed Al₂O₃ coating on a mild steel substrate prepared under the conditions listed in Table 4-1. The mild steel substrate was preheated to promote the disc-shaped splat formation. Pores in Al₂O₃ coating are shown as black areas in the microstructure. It has been reported that the porosity of Al₂O₃ coatings deposited by APS is about 5-10% [32] and depends on the surface roughness of substrate, substrate temperature, spraying parameters, and coating thickness [33].
Figure 4-2. SEM micrograph of a disc-shaped alumina splat.

Figure 4-3. Surface scan of a disc-shaped Al$_2$O$_3$ splat using Nano-Vision.
4.3.2. Phase Information of APS Alumina Coatings

Alumina is a complex material and exhibits various phases such as the hard, stable trigonal $\alpha$ (corundum). This phase is often accompanied by a defective spinel cubic $\gamma$-$\text{Al}_2\text{O}_3$, a deformed tetragonal spinel $\delta$-$\text{Al}_2\text{O}_3$, a high temperature hexagonal phase $\varepsilon$-$\text{Al}_2\text{O}_3$, a monoclinic $\theta$-$\text{Al}_2\text{O}_3$, and some other phases. The properties of plasma sprayed ceramics, especially the differences from conventionally sintered ceramics, are known to be dependent on their anisotropic, quasi-laminated, splat microstructures and non-equilibrium phase composition [34,35]. Variations in these parameters can lead to large changes in microstructure and phase system and hence lead to great variations in the mechanical properties of the deposited ceramic [36]. The crystallographic phase compositions of APS alumina are strongly related to the cooling rate. Generally, a high cooling rate leads to a high composition of the $\gamma$-phase.

A summary of the phase development of the APS alumina coating is given in the X-ray
diffraction traces in Figure 4-5, which shows the diffraction patterns of the starting powder (a), the bottom surface (b), and the top surface (c) of as-sprayed coating. X-ray diffraction results showed that although the starting powder is pure $\alpha$-Al$_2$O$_3$, the bottom surface of as-sprayed coating is almost pure $\gamma$-Al$_2$O$_3$; the top surface of the as-sprayed coating consists of a mixture of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$. However, the main phase was the $\gamma$ phase, with $\alpha$ phase only occurring as a secondary phase.

The X-ray traces have been used to make a quantitative estimation of the phase composition of the top surface of the as-sprayed coating. Assuming that the integrated intensity under a given peak ($hkl$) in the trace of the starting powder gave the value for 100% $\alpha$-Al$_2$O$_3$, the fraction of $\alpha$-Al$_2$O$_3$ in the top surface of as-sprayed coating, $f_{\alpha}^{(hkl)}$, can be estimated by the relationship

$$f_{\alpha}^{(hkl)} = \frac{I_{\text{as-sprayed}}^{(hkl)}}{I_{\text{starting powder}}^{(hkl)}}$$

where $I^{(hkl)}$ is integral intensity under the peak ($hkl$). To reduce the errors, the values were averaged over a number of isolated peaks in a given trace. The results of these analyses are summarized in Table 4-2. The as-sprayed material was found to consist of approximately 68% metastable $\gamma$-Al$_2$O$_3$ phase, which is consistent with R.J. Damani’s result that the $\gamma$-Al$_2$O$_3$ phase is around 65% [37].

In view of nucleation kinetics, McPherson suggested that $\gamma$-Al$_2$O$_3$ tended to be nucleated from the melt in preference to $\alpha$-Al$_2$O$_3$ at high cooling rate because of lower interfacial energy between crystal and liquid [38]. For plasma spraying alumina coating, the phase of the bottom of coating tends to be $\gamma$-Al$_2$O$_3$ at the beginning of the spraying process due to high cooling rate of substrates. Under the typical spraying conditions, for the near substrate sublayer, $\gamma$-Al$_2$O$_3$
nucleates in preference to $\alpha$-Al$_2$O$_3$ and the cooling rate is sufficiently rapid to prevent transformation to $\alpha$-Al$_2$O$_3$. That is why the XRD results showed the bottom surface of APS alumina coating exhibited a thin layer of pure $\gamma$-Al$_2$O$_3$ next to the substrate. As the spraying process continues, the coating is built up by piling the splats onto the previously coated splats with higher temperature and lower cooling rate, so as a result a small portion of $\alpha$-Al$_2$O$_3$ will be formed.

Figure 4-5. XRD patterns of the alumina powder (a), bottom surface of APS alumina coating (b), and top surface of APS alumina coating (c).
**Table 4-2. Quantitative X-ray phase analysis of the top surface of as-sprayed alumina coating.**

<table>
<thead>
<tr>
<th>Phase α (hkl)</th>
<th>Fraction of α-alumina $F_{α}^{(hkl)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(012)</td>
<td>0.30</td>
</tr>
<tr>
<td>(104)</td>
<td>0.43</td>
</tr>
<tr>
<td>(113)</td>
<td>0.28</td>
</tr>
<tr>
<td>(024)</td>
<td>0.25</td>
</tr>
<tr>
<td>(116)</td>
<td>0.26</td>
</tr>
<tr>
<td>(300)</td>
<td>0.41</td>
</tr>
<tr>
<td>Averaged fraction of α-Al$_2$O$_3$ (fa)</td>
<td>0.32</td>
</tr>
<tr>
<td>Averaged fraction of γ-Al$_2$O$_3$ (1-fa)</td>
<td>0.68</td>
</tr>
</tbody>
</table>

**4.3.3. Load-Displacement Curves and Nanoindentation Results**

Figure 4-6 plots a typical load-displacement curve obtained on the APS alumina coating samples. The indentation depth limit is 2000 nm, which is much less than the overall alumina layer thickness of 300 µm. Thus, the alumina coatings’ hardness and elastic modulus can be obtained from these nanoindentation tests.

Most of the nanoindentation results are like the one displayed in Figure 4-6 with smooth force-displacement curves, so the Oliver-Pharr method gives reasonable results. However, due to the porosity and cracking of APS Al$_2$O$_3$ coatings with individual splat layers, small portions of load-displacement curves show giant steps which means the penetration displacement increases suddenly while there is little change in the load. The steps occurring during indentation loading are also called “serration” or “pop-in” [39]. The reason for these steps in Figure 4-7 is mainly due to the inconsistency of the material and the porosity. To present the reliable alumina hardness and elastic modulus, the load-displacement curves obtained on the alumina coating samples were carefully checked, and the curves with obvious cracking features, like Figure 4-7,
were discarded and only data with smooth load-displacement curves were used to calculate the average hardness and elastic modulus.

The nanoindentation results of APS alumina coatings exhibited a scattering distribution, which can be visible from the nanohardness histogram (Figure 4-8) and elastic modulus histogram (Figure 4-9). Here, the range of hardness is from 8 GPa to 18 GPa. The elastic modulus range is from 170 GPa to 410 GPa. The mean value for hardness is 12.7 GPa, and the mean value for elastic modulus is 236.0 GPa. Most studies simply attributed the wide distribution of nanoindentation results to the brittle property of alumina. However, different phase combinations have not been taken into account. As can be noted in Figure 4-5, the APS alumina coating mainly consists of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$. According to the nanoindentation test results in previous research [40,41,42], the elastic modulus of $\alpha$-alumina is 400±20 GPa and the elastic modulus of $\gamma$-alumina is 190±40 GPa. As can be seen in the experimental data (Figure 4-9), the lowest elastic modulus is around 170 GPa, which can be treated as experimental elastic modulus of $\gamma$-Al$_2$O$_3$. On the other hand, the highest elastic modulus is about 400 GPa, which can be viewed as the elastic modulus of $\alpha$-Al$_2$O$_3$. This is consistent with others’ results about elastic modulus of different alumina phases.

Therefore, when indented at different positions on the specimen surface, the response of the APS alumina coating to nanoindentation is different due to the fact that the load-induced deformation is dominated by the local phase composition rather than the bulk mechanical properties. As mentioned before, the APS alumina coating is composed of layers of single splats with the thickness around 1.5 µm. For one indentation test, the nanoindentation results depend on the local combination of single splats with different phases. Although the first layer has a dominant effect on the nanoindentation results, the under-layers also influence the results.
including hardness and elastic modulus. For example, if the top layer is $\alpha$-Al$_2$O$_3$ and the underneath layers were $\gamma$-Al$_2$O$_3$, the results would be a little smaller than the value of pure $\alpha$-Al$_2$O$_3$ case due to the soft layers underneath. Thus, the wide distribution on the APS alumina coating can be attributed to the presence of two different alumina phases, $\alpha$ and $\gamma$, in the top surface of the coating. In addition, there is an obvious peak for each of hardness and elastic modulus histograms. Because $\gamma$ phase is the dominant phase, the peaks with lower values corresponding to $\gamma$ phase in the histograms of hardness and elastic modulus have high percentage, as showed in Figure 4-8 and Figure 4-9.

Spatial resolution of X-ray diffraction techniques is not satisfactory for investigating phase formation of single splats. By comparing the elastic modulus of nanoindentation on single disc-shaped splats with the values of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, the phase of the single splats can be deduced. For nanoindentation tests on single splats, in order to reduce the silicon substrate’s influence on nanoindentation results, the displacement is much smaller than that on APS alumina coatings, which can be seen in Figure 4-10. The residual impression of the indents was examined and recorded using the scan mode of the nanoindenter (Figure 4-11). The average $H$ of the single alumina splats is 9.4 GPa, and the averaged elastic modulus $E$ is 151.6 GPa, averaged from eight nanoindentation tests.

The average elastic modulus, 151.6 GPa, from nanoindentation approximately equals the elastic modulus of $\gamma$-Al$_2$O$_3$. The conclusion that the phase of single splats on silicon wafer is $\gamma$ can be reached based on the elastic modulus comparison. The conclusion is also consistent with the XRD test result that the bottom part of the APS alumina coating is comprised of $\gamma$ phase because single splats themselves are actually the first layer deposited onto the silicon substrate with high cooling rate.
Figure 4-6. Typical load-displacement curve on alumina coatings.

Figure 4-7. Load-displacement curve on coating with giant steps.
Figure 4-8. Histogram of nanohardness for alumina coatings.

Figure 4-9. Histogram of elastic modulus for alumina coatings.
Figure 4-10. Load-displacement curve on single splats.

Figure 4-11. Alumina surface after nanoindentation.
4.4. Conclusions

This research studied mechanical properties of APS prepared alumina coatings and disc-shaped single splats. The disc-shaped single splats were prepared on smooth silicon wafers. In addition thick alumina coatings were prepared on mild steel substrates. X-ray diffraction results showed that although the starting powder is pure $\alpha$-$\text{Al}_2\text{O}_3$, the bottom surface of as-sprayed coating is almost pure $\gamma$-$\text{Al}_2\text{O}_3$, and the top surface of the as-sprayed coating consists of a mixture of $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$, in which $\gamma$ is the predominant phase. During the APS process, the first layer of alumina coating deposition experienced a very high cooling rate, which led to the almost pure $\gamma$ phase next to the substrate. The subsequent layers were deposited onto the previous deposited layers of high temperature under relatively low cooling rate; therefore, the rest of the coating showed a combination of $\alpha$ and $\gamma$ phases.

Using a nanoindenter, the hardness and elastic modulus of APS prepared alumina single splats and alumina coatings have been studied. The load-displacement curves for the single splats and coatings are presented. The hardness and elastic modulus measured on alumina coatings showed a scattering distribution with an obvious peak corresponding to $\gamma$ phase. Many previous publications simply attributed the scattering of nanoindentation results to the brittle property of alumina. This study revealed that the phase combination of $\alpha$-$\text{Al}_2\text{O}_3$ and $\gamma$-$\text{Al}_2\text{O}_3$ played an important role in the scattering distribution of nanoindentation results on APS alumina. In addition, nanoindentation technique was used to predict the phase information of disc-shaped splats in this study by elastic modulus comparison. Nanoindentation result confirmed disc shaped alumina splats were $\gamma$ phase, which is also consistent with the XRD result that the bottom surface of APS alumina coating is almost pure $\gamma$-$\text{Al}_2\text{O}_3$. 
5.1. Introduction

Considerable efforts have been devoted to studying the response of coating/substrate systems under indentation since the early 1950s [43]. These efforts include the finite element analysis (FEA), analytical modeling, and the empirical approach. The FEA is a powerful method to analyze the contact problems in coating/substrate (non-uniform) systems; however, it is a case-by-case study, and the simulation needs to be performed for any change in geometrical parameters and material properties. Even though analytical models start with analytical expressions of constitutive equations and boundary conditions for indentation on coating/substrate systems, it results in complex integral equations relating the unknown pressure to the displacement over the contact area, and numerical procedures are needed to solve this equation, which, in turn, result in an obstacle for its practical applications. However, analytical modeling is still a powerful tool to study nanoindentation so as to guide experimental parameters.

When the non-uniform system being investigated is a multilayered system, the measured indentation modulus will continually change with different indentation depth. This change is a function of the elastic properties and the relative thickness of different layers. However, the relationship between indentation modulus response and penetration of multilayered systems is not fully understood. Efforts have been made to understand the indentation modulus behavior of a single layered coating on a substrate. The various techniques for extrapolating the film modulus from experimental data have been described [44], and analytical equations that define indentation modulus with depth for a single layer on a substrate have been derived for cylindrical
and spherical indenters [43].

There are a few analytical studies on the nanoindentation of multilayered films. For example, experimental, analytical, and finite element analyses of nanoindentation of multilayer PZT/Pt/SiO₂ thin film systems on silicon wafers were studied by C. Chima-Okereke, et al [45].

The objective of this study is to investigate the modulus-depth behavior of multilayered thin film system by deriving approximate analytical equations that describe the modulus-displacement behavior of multilayered systems and compare that with nanoindentation experimental results of APS alumina coatings in Chapter 4.

5.2. Analytical Equations

The analytical study started with Hertz’s pioneering contribution on the contact between elastic bodies [46]. Boussinesq [47] subsequently studied the contact problem between two linearly elastic isotropic solids using methods of potential theory, which is a significant milestone to the understanding of the indentation problem. Sneddon [48] derived the load-displacement relationship for a rigid cone indenter using Boussinesq’s approach, and subsequently derived it for an arbitrary indenter with a body of revolution [49].

Boussinesq’s solution for the problem of a point force acting on the surface of a semi-infinite elastic body is used in this study. This classical solution shows that the stress field at a certain point is a function of the applied force and Poisson’s ratio of the body, but is independent of elastic modulus. When the semi-infinite body is replaced by a coating/substrate composite, the stress field is perturbed [43]. Continuity condition requires that both the axial stress and the in-plane shear stress are continuous at the coating/substrate interface. Compatibility conditions at the interface require that the in-plane strains are the same in each material; however, because of different elastic moduli between different layers, both the radial and hoop stress become
discontinuous across the interface [43]. Hence, the major perturbation occurs in the radial and the hoop stress components in the region close to the interface. The axial stress is modified as well in the interfacial region because of the equilibrium condition. Although the perturbed stress field in a layered system has been analyzed, numerical procedures are needed to obtain its result. There is not a closed-form analytical expression for such a perturbed stress field, so the point force-induced stress field in a homogeneous semi-infinite elastic body is adopted for the multilayered system to obtain an approximate analytical solution for indentation depth.

Because the displacement component of interest is the one in the loading (i.e., \(z\)) direction, which is dominated by the axial stress component, the simplification is expected to be reasonable. According to Boussinesq’s results, the derivative of the axial displacement, \(h\), with respect to \(z\) (i.e., the axial strain) is given by

\[
\frac{\partial h}{\partial z} = \frac{F(1+\nu)}{2\pi E \left[ 3r^2 z(r^2 + z^2)^{-\frac{5}{2}} - (3 - 2\nu)z(r^2 + z^2)^{-\frac{3}{2}} \right]}
\]

(5-1)

where \(F\) is the indentation force, and \(r\) is the horizontal axis.

As mentioned before, in order to measure the multilayered thin film properties, a commonly used rule is that the penetration depth is less than 10% of the film thickness. This rule will determine how many layers would be used in the analytical analysis. For example, if the thickness of one layer is 1.5 \(\mu\)m and if the displacement is less than 900 nm, six layers with 9.0 \(\mu\)m of total thickness will be adequate for analysis based on the 10% rule. To make sure the analytical solution is accurate enough; eight layers will be used in this study, as shown in Figure 5-1.
The Herztian relationship for calculating the force ($F$)-depth ($h$) characteristics will now be extended to include equations for an eight-layer system in closed form. To calculate the surface displacement for 8 layers on a substrate, the equation for one layer

$$h_B = \int_{t_f}^{t_f} \frac{\partial h}{\partial z} \, dz + \int_{t_f}^{\infty} \frac{\partial h}{\partial z} \, dz$$

(5-2)

(where $t_f$ is the film thickness and $z$ is the vertical coordinate) is extended to

$$h_B = \int_{t_1}^{t_1} \frac{\partial h}{\partial z} \, dz + \int_{t_1}^{t_1+t_2} \frac{\partial h}{\partial z} \, dz + \int_{t_1+t_2}^{t_1+t_2+t_3} \frac{\partial h}{\partial z} \, dz + \cdots + \int_{t_1+t_2+t_3+t_4+t_5+t_6+t_7+t_8}^{t_1+t_2+t_3+t_4+t_5+t_6+t_7+t_8} \frac{\partial h}{\partial z} \, dz +$$

$$\int_{t_1+t_2+t_3+t_4+t_5+t_6+t_7+t_8}^{\infty} \frac{\partial h}{\partial z} \, dz$$

(5-3)

where $t_1$, $t_2$, $t_3$, $t_4$, $t_5$, $t_6$, $t_7$, $t_8$ are the thickness of the layers. In order to simplify the equation and calculation, $d_1 = t_1$, $d_2 = t_1 + t_2$, ..., $d_8 = t_1 + t_2 + t_3 + t_4 + t_5 + t_6 + t_7 + t_8$.

Therefore the general equation for a multilayer material with $n-1$ layers can be written as

$$h_B = \sum_{i=1}^{d_i} \int_{d_{i-1}}^{d_i} \frac{\partial h}{\partial z} \, dz \quad i = 1, 2, 3, \ldots n, d_0 = 0, d_n = \infty$$

(5-4)
Substituting Equation 5-1 into Equation 5-4 gives

\[ h_B = \]

\[ F \left( \int_{d_1} (1+v_1) \frac{\beta}{2E_1 \pi} dz + \int_{d_2} (1+v_2) \frac{\beta}{2E_2 \pi} dz + \int_{d_3} (1+v_3) \frac{\beta}{2E_3 \pi} dz + \int_{d_4} (1+v_4) \frac{\beta}{2E_4 \pi} dz + \int_{d_5} (1+v_5) \frac{\beta}{2E_5 \pi} dz + \int_{d_6} (1+v_6) \frac{\beta}{2E_6 \pi} dz + \int_{d_7} (1+v_7) \frac{\beta}{2E_7 \pi} dz + \int_{d_8} (1+v_8) \frac{\beta}{2E_8 \pi} dz + \int_{d_9} \frac{\beta}{2E_9 \pi} dz \right) \]  

\[ (5-5) \]

\[ \beta = \left[ 3r^2 z (r^2 + z^2)^{\frac{5}{2}} - (3 - 2v_i) z (r^2 + z^2)^{-\frac{3}{2}} \right] \]

where \( v_1, v_2, v_3, v_4, v_5, v_6, v_7, v_8, v_9, E_1, E_2, E_3, E_4, E_5, E_6, E_7, E_8, E_9 \) are the Poisson’s ratios and elastic moduli of the 1\(^{st}\) through 8\(^{th}\) layer and the substrate, respectively. This integration gives the intermediate equation

\[ h_B = F \left( -\frac{1-v_i^2}{E_1 \pi r} - \frac{(1+v_1)[2r^2(-1+v_1)+d_1^2(-3+2v_1)]}{2E_1 \pi (r^2+z^2)^2} + \frac{(1+v_2)[2r^2(-1+v_2)+d_2^2(-3+2v_2)]}{2E_2 \pi (r^2+z^2)^2} \right. \]

\[ \left. + \frac{(1+v_3)[2r^2(-1+v_3)+d_3^2(-3+2v_3)]}{2E_3 \pi (r^2+z^2)^2} + \frac{(1+v_4)[2r^2(-1+v_4)+d_4^2(-3+2v_4)]}{2E_4 \pi (r^2+z^2)^2} \right. \]

\[ \left. + \frac{(1+v_5)[2r^2(-1+v_5)+d_5^2(-3+2v_5)]}{2E_5 \pi (r^2+z^2)^2} \right. \]

\[ \left. + \frac{(1+v_6)[2r^2(-1+v_6)+d_6^2(-3+2v_6)]}{2E_6 \pi (r^2+z^2)^2} \right. \]

\[ \left. + \frac{(1+v_7)[2r^2(-1+v_7)+d_7^2(-3+2v_7)]}{2E_7 \pi (r^2+z^2)^2} \right. \]

\[ \left. + \frac{(1+v_8)[2r^2(-1+v_8)+d_8^2(-3+2v_8)]}{2E_8 \pi (r^2+z^2)^2} \right. \]

\[ \left. + \frac{(1+v_9)[2r^2(-1+v_9)+d_9^2(-3+2v_9)]}{2E_9 \pi (r^2+z^2)^2} \right) \]  

\[ (5-6) \]

Recalling that the equation for the pressure distribution \( q \) on the contact area of a spherical indenter is given by

\[ q = \frac{3F\sqrt{(a^2-r^2)}}{a^3} \quad 0 \leq r \leq a \]  

\[ (5-7) \]

where \( a \) is the contact radius. The surface displacement at \( r = 0 \) due to the above loading stress is given by

\[ h_{\text{Herztain}} = \int_0^a \frac{3r\sqrt{(a^2-r^2)}}{a^3} h_B dr \]  

\[ (5-8) \]
Integrating the above equation gives

\[
\begin{align*}
\frac{h_{\text{Herztain}}}{a^3 E_0 n d_0 \sqrt{(a^2 + d^2)}} &= \frac{3}{8} \left( -2 (1 - v_i^2) \right) \left( \frac{a}{E_1} \right) - \frac{\alpha}{a^3 E_1 \pi d_1 \sqrt{(a^2 + d^2)}} + \frac{\gamma_i}{a^3 E_2 \pi d_1 \sqrt{(a^2 + d^2)}} - \frac{\varphi_i}{a^3 E_2 \pi d_2 \sqrt{(a^2 + d^2)}} + \ldots \\
&= \frac{\delta}{a^3 E_0 \pi d_0 \sqrt{(a^2 + d^2)}} \tag{5-9}
\end{align*}
\]

where

\[
\begin{align*}
\alpha &= (1 + v_1) \left( a \left( a^2 \pi d_1 \sqrt{1 + \frac{d_1^2}{a^2}} (-1 + v_1) + \left( -4 d_1^2 \sqrt{(a^2 + d_1^2)} + \pi d_1^3 \sqrt{1 + \frac{d_1^2}{a^2}} \right) v_1 \right) - \\
&\quad 2d_1 \sqrt{(a^2 + d_1^2)} (a^2 (-1 + v_1) + d_1^2 v_1) \text{ArcCot} \left[ \frac{2a d_1}{-a^2 + d_1^2} \right]
\end{align*}
\]

\[
\begin{align*}
\gamma_i &= (1 + v_i) \left( a \left( a^2 \pi d_{i-1} \sqrt{1 + \frac{d_{i-1}^2}{a^2}} (-1 + v_i) + \left( -4 d_{i-1}^2 \sqrt{(a^2 + d_{i-1}^2)} + \pi d_{i-1}^3 \sqrt{1 + \frac{d_{i-1}^2}{a^2}} \right) v_i \right) - \\
&\quad 2d_{i-1} \sqrt{(a^2 + d_{i-1}^2)} (a^2 (-1 + v_i) + d_{i-1}^2 v_i) \text{ArcCot} \left[ \frac{2a d_{i-1}}{-a^2 + d_{i-1}^2} \right]
\end{align*}
\]

\[
\begin{align*}
\varphi_i &= (1 + v_i) \left( a \left( a^2 \pi d_i \sqrt{1 + \frac{d_i^2}{a^2}} (-1 + v_i) + \left( -4 d_i^2 \sqrt{(a^2 + d_i^2)} + \pi d_i^3 \sqrt{1 + \frac{d_i^2}{a^2}} \right) v_i \right) - \\
&\quad 2d_i \sqrt{(a^2 + d_i^2)} (a^2 (-1 + v_i) + d_i^2 v_i) \text{ArcCot} \left[ \frac{2a d_i}{-a^2 + d_i^2} \right]
\end{align*}
\]

where \(i = 2, 3, \ldots, 8\)

\[
\begin{align*}
\delta &= (1 + v_9) \left( a \left( a^2 \pi d_9 \sqrt{1 + \frac{d_9^2}{a^2}} (-1 + v_9) + \left( -4 d_9^2 \sqrt{(a^2 + d_9^2)} + \pi d_9^3 \sqrt{1 + \frac{d_9^2}{a^2}} \right) v_9 \right) - \\
&\quad 2d_9 \sqrt{(a^2 + d_9^2)} (a^2 (-1 + v_9) + d_9^2 v_9) \text{ArcCot} \left[ \frac{2a d_9}{-a^2 + d_9^2} \right] \tag{5-10}
\end{align*}
\]

The above formula is the closed form of the Hertzian relationship for the eight-layer system. The full equation is obtained by substituting \(a = (Rh_{\text{Herztain}})^{1/2}\) into the above equation. Setting the Poisson’s ratio and elastic modulus of all layers including the substrate to the same value (e.g. \(v=0.28\) and \(E=150\) GPa) returns the Herzian solution for an isotropic half space.
5.3. Analytical Study of Nanoindentation on APS Alumina Coatings

Nanoindentation technique has been established as a powerful means of characterizing the near-surface mechanical properties of thin films and coatings, such as hardness, $H$, and the elastic modulus, $E$. Due to the unique laminar and porous microstructures with different alumina phases, APS coated ceramic coatings have a wide range scattering of $H$ and $E$ under nanoindentation testing. It is commonly believed that the scattering data on APS coatings are attributed to the brittle property of the ceramic materials, such as alumina. However, not much attention has been paid to the effects of different phases of alumina on the scattering of the nanoindentation data.

As mentioned before, the APS alumina coating is composed of layered single splats with the thickness around 1.5 µm per layer. For one indentation test, the nanoindentation results depend on the local combination of single splats with different phases. Although the first layer has a dominant effect on the nanoindentation results, the underlying layers also influence the results of the measured hardness and elastic modulus.

It is well known that the APS alumina coating consists of two main alumina phases, $\alpha$ and $\gamma$. Therefore, when indented at different positions of the specimen surface, the response of the test material to nanoindentation is different due to the fact that the load-induced deformation is dominated by the local phase composition rather than the bulk mechanical properties.

This research describes a study on the effects of alumina phases to the nanoindentation results. Although large scattering of $H$ and $E$ were observed on APS alumina samples, these two mechanical properties generally show only one obvious peak. The X-ray diffraction (XRD) results showed that the APS alumina coating samples consisted of about 68% $\gamma$ phase. To assist the development of APS coating microstructure analytical model, the microstructure of the APS
alumina coating and single splats were first characterized. It is found that the coating was built up by single disc shaped splats with the thickness around 1.5 μm, with the diameter around 60 μm. For simplicity, the laminated APS alumina coating was taken to consist of alternating layers of α and γ alumina phases in the analytical model. This model was used to derive an approximate closed-form solution for nanoindentation of APS alumina coating comprised of both α and γ phases. The elastic modulus distribution is then deduced from this model based on the experimental data. The analytical solutions revealed that the phase combination plays an important role in the material response to nanoindentation. The model agreed with the experimentally observed scattering in modulus distribution of APS alumina coating.

As can be noted in Figure 4-9, the peak value of elastic modulus from nanoindentation testing is around 210 GPa. Another method to find the peak is to first fit the experimental data with polynomial function of degree 4, shown in Figure 5-2, and then the slope function of the fitted polynomial function is calculated accordingly. The reverse of each slope value at each point (Figure 5-3) can be viewed as the relative possibility as noticed in Figure 5-3, which also showed that the experimental peak value of elastic modulus is 212.4 GPa, and is in good agreement with the result (around 210 GPa) from the histogram of elastic modulus in Figure 4-9.

XRD results have shown that the APS alumina coatings consist of two different phases of alumina as a non-uniform composite. As mentioned before, eight layers were used to derive the analytical solution for APS alumina coating. Therefore, theoretically there will be $2^8$ (256) different combinations of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ for eight layers. For non-uniform samples, the elastic modulus will change with the increase of penetration depth. First of all, the loading force must be determined in order to measure or simulate the elastic modulus of thin films or coatings. If the loading force is too low, the measured or calculated elastic modulus mainly depends on the
alumina phase of the first layer of APS alumina coating or the first few layers, so that it cannot represent the mechanical properties of the complete coating. On the other hand, if the loading force is too large which means that the corresponding penetration depth will also be increased; the substrate will have a noticeable effect on the results if the thin films or coatings are not thick enough.

Figure 5-2. Polynomial function of experimental elastic modulus data.
Figure 5-3. Relative possibility of elastic modulus.

Figure 5-4. Variations in elastic modulus with penetration depth for different combinations.
Figure 5-4 presents the elastic modulus values obtained from the analytical results as a function of the penetration depth for eight different combinations under conditions in Table 5-1. Although the first layer has a dominant effect on the nanoindentation results, the underlying layers will also influence the results. If the first layer is alpha alumina, the elastic modulus have a higher value, which is around 380 GPa, but if the first layer is gamma alumina, the results will have a lower value, which is around 200 GPa as shown in the figure. It is obvious that the elastic modulus will be stabilized when the indentation force is larger than 600 mN. Figure 5-5 shows the elastic modulus distribution with different loading forces for 8-layered alumina coating. When the loading force is small, the phase of the first layer of the alumina coating will determine the elastic modulus result. As a result, there is a big gap between 230 GPa and 290 GPa for 50
mN loading force. The elastic modulus gap will decrease with increased loading forces. Also, the elastic modulus distribution will also become very uniform once the force is larger than 600 mN. This further proves that 600 mN is large enough to obtain accurate results.

Table 5-1. Elastic modulus peaks calculated from analytical model.

<table>
<thead>
<tr>
<th>Ratio of α phase</th>
<th>Ratio of γ phase</th>
<th>E_{alpha} (GPa)</th>
<th>E_{gamma} (GPa)</th>
<th>E_{sub} (GPa)</th>
<th>F (mN)</th>
<th>Peak (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>900</td>
<td>232</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>800</td>
<td>231</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>700</td>
<td>232</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>600</td>
<td>231</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>500</td>
<td>228</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>400</td>
<td>222</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>300</td>
<td>218</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>200</td>
<td>213</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>100</td>
<td>206</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>290</td>
<td>50</td>
<td>201</td>
</tr>
</tbody>
</table>

Though the loading force is not set in the nanoindentation experiments, the penetration depth is set to be less than 2000 nm. From the load-displacement curve, the maximum loading force is around 650 mN which is larger than 600 mN. Thus, reasonable results can be obtained from nanoindentation testing.

What should be mentioned is that the foregoing analytical results were based on the condition that the ratio between of α-Al₂O₃ and γ-Al₂O₃ is 1:1, as noted in Table 5-1. For
different phase ratios, the peak values were presented in Table 5-2. The experimental part has shown that the ratio of $\gamma$-Al$_2$O$_3$ is around 68%, and the corresponding elastic modulus peak is about 210 GPa. The analytical results have demonstrated that when the phase ratio of $\gamma$-Al$_2$O$_3$ is 2/3, the calculated elastic modulus peak is 212 GPa, which is consistent with the experimental result (Figure 5-3). In conclusion, the analytical modeling in this study agrees well with the nanoindentation testing results.

Table 5-2. Peak values corresponding to different phases ratios.

<table>
<thead>
<tr>
<th>Ratio of $\alpha$ phase</th>
<th>Ratio of $\gamma$ phase</th>
<th>$E_{\text{gamma}}$ (GPa)</th>
<th>$E_{\text{alpha}}$ (GPa)</th>
<th>$F$ (mN)</th>
<th>Peak (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4</td>
<td>3/4</td>
<td>170</td>
<td>410</td>
<td>650</td>
<td>184</td>
</tr>
<tr>
<td>1/3</td>
<td>2/3</td>
<td>170</td>
<td>410</td>
<td>650</td>
<td>212</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>170</td>
<td>410</td>
<td>650</td>
<td>230</td>
</tr>
</tbody>
</table>
6.1. Introduction

As partly mentioned in the introduction, one type of choice in making surface coatings and thin films has been PVD, in which sputtering is a widely used and highly versatile vacuum coating system used for the deposition of a variety of coating materials. The attractive features of this method include its wide area coating capabilities, automation, and deposition of adhesive and homogeneous films among others.

For sputtering, the energized particles are present as plasma. Plasma is a partially ionized gas consisting of positively charged particles (ions), negatively charged particles (electrons and anions), and neutrals. The overall charge of the plasma is neutral. In the plasma, the ionization of the gas generally occurs between a cathode and an anode. In a sputtering system the sputtering target is the cathode. The anode is usually the vacuum chamber wall or the substrate. Within the sputtering process gas ions are accelerated towards a sputtering target. Material is sputtered from the target and afterwards deposited on a substrate.

Sputter deposition systems are generally categorized by different types of power sources used to generate the plasma. The most common sputtering systems are the magnetron sputtering systems. An important note is that multiple targets can be used simultaneously in order to create complex compositional or multilayered coatings. The common used sputtering deposition technologies include:

- DC Diode Sputtering
- Magnetron Sputtering
6.1.1. Direct Current Diode Sputtering

The simplest sputtering system is the direct current diode system (DC diode). The DC diode sputtering system consists of two electrons within the vacuum chamber and an external high-voltage power supply. A glow discharge is formed by application of a potential between two electrodes (target and substrate). A negative potential $U$ up to several hundred volts is applied to the target. When the first electron strikes a gas atom (usually argon), it will create an ion as well as secondary electrons within the sputtering chamber. These electrons will cause further ionization of the gas. Depending on the pressure $P$ of the gas and the distance $d$ between the electrodes a breakdown voltage is required for a self-sustaining discharge. The breakdown voltage [50] can be derived in the form of

$$V_B = \frac{A(Pd)}{(C + \ln(Pd))}$$  \hspace{1cm} (6-1)

where $A$ and $C$ are constants that depend on the gas. For a sufficient ionization rate, stable plasma is required so that sufficient amount of ions is available for sputtering of the material.

6.1.2. Direct Current Magnetron Sputtering

To increase the ionization rate by emitted secondary electrons even further, the original DC diode sputtering systems have mostly been replaced by magnetron sputtering systems. A basic magnetron sputtering system uses a magnetic field below the target to trap secondary electron emission near the surface of the target. From longer dwell time in the gas, a higher ionization probability can be accomplished and hence form a plasma ignition at low pressures, which can be up to one hundred times smaller than the diode sputtering process. In addition, the
The trapping of the secondary electrons will also allow the magnetron sputtering system to surpass traditional diode sputtering systems in many regards including: increasing deposition rate, decreasing impurities in coatings, and achieving depositions at lower substrate temperatures.

The setup of the magnetron sputtering system, as shown in (Figure 6-1), is very similar to the diode sputtering system. To overcome the problem of low ionization at low pressures a magnetron source is used at the diode target. The electrons are trapped close to the surface of the target by a magnetic field and move in cycloidal curves immediately above the target as shown in the figure. This magnetic field is used to control the density and location of the secondary electrons above the target. Through this increased path length ionization efficiency is vastly increased.

![Figure 6-1. Basic principles of sputter deposition. Ions generated in plasma and accelerated towards a target sputter material, which condenses at the substrates.](image)

One of the disadvantages of traditional magnetron sputtering is the localization of the plasma over the substrate. The electrons are trapped in a specific area above the target, so the
ionization of the carrier gas tends to be more heavily concentrated in the regions of the trapped electrons. The concentrated plasma preferentially wears down the source material over the target area where the magnetic lines are parallel to the target face.

DC magnetron sputtering is restricted to conducting materials like metals or doped semiconductors. There are two ways to produce dielectric films: RF sputtering and reactive sputtering.

6.1.3. Radio Frequency Magnetron Sputtering

Since the cathode of a magnetron sputtering system is also the target, only electrically conductive materials can be used as targets for deposition. Radio frequency (RF) power is often applied to the electrodes in a diode discharge to allow sputtering from a dielectric or electrically insulating target material.

The basis for the use of radio frequency is the large mass difference between the ionized gas particles and the electrons in the plasma. If the frequency of the alternating frequency is high enough, plasma can be sustained by continually accelerating and reversing the direction of the electrons through long enough distances that they gain the kinetic energy required to ionize the sputter gas through collisions. The frequency required to sustain the plasma is generally in the range of 0.5-30 MHz, but RF sputtering systems are generally operated at 13.56 MHz which is the maximum allowed frequency in the United States because of government communication regulations [50]. This eliminates the need for secondary electrons from the target to sustain the plasma. The main disadvantages of RF sputtering are the decrease in deposition rate due to lack of secondary electrons for gas ionization, and the expense associated with radio frequency power supplies and the tuning systems required to couple the alternating potential to the plasma.
6.1.4. Reactive Sputtering

Dielectric coatings, such as oxides and nitrides, can also be deposited by reactively sputtering a metal target with RF or DC power instead of sputtering from a dielectric substrate using radio frequency magnetron sputtering, in a mixture of an inert and a reactive gas. [51]. One benefit of reactive sputtering as opposed to RF magnetron sputtering is that high purity targets of one material can be used for deposition. Reactive sputtering involves reaction between reactive gas and with the target material as it travels between the substrate and the target. The partial pressure of the gas in the chamber will directly impact the stoichiometry of the coating composition. One problem with reactive sputtering is that the target can build up a thin layer of dielectric on the surface if the partial pressure of the reactive gas is too high. This can lead to decreased deposition rates.

6.2. The Sputtering System and Experimental Procedures

In this chapter the experimental methods used in film preparation and characterization are discussed. Films were produced by direct current magnetron sputtering of metal targets. The sputter system used in this work is a Denton Vacuum Explorer 14 magnetron sputtering system shown in Figure 6-2. It can be mounted with up to six cathodes in the cylindrical vacuum chamber, as shown in Figure 6-3. A rotating water-cooled substrate fixture with six facets designed to mount 4” to 6” wafers is installed in the chamber. Typical sizes of targets are 4” diameter and 1/4” or 1/8” thickness. The sputtering guns are water-cooled. The chamber is pumped down by a CTI Cryogenics CryoTorr® 8 cryogenic pump connected to an Edwards XDS 10 dry scroll pump for pre-pumping. The chamber has a base pressure less than 1.0E-7 Torr. Gas flows into the chamber are regulated via three mass flow controllers (MFCs). Two types of sputter sources optimized for straight-on deposition are used: three internal “stalk-mount” planar
magnetron sputter sources with standard magnetic and one Mag II, internal “stalk-mount” planar magnetron sputter sources with enhanced magnetic for magnetic targets. Also, two kinds of sputter power supplies were also used: three DC power supplies and one RF power supply. The plasma power supply is operated in constant power mode. The experimental parameters such as gas flow rate, power, and sputtering pressure, can be viewed and controlled from the digital control panel (Figure 6-4).

Figure 6-2. Denton Vacuum magnetron sputtering system.
Figure 6-3. Structure of sputtering system (magnetron sputtering manual).

Figure 6-4. Digital control panel of sputtering system.
6.3. Films Preparation

After loading the system with prepared substrates, the system was pumped down to the base pressure less than 1.0E-7 Torr. Argon was used as the sputter gas. The targets were pre-sputtered in Argon for a minimum of 15 minutes to remove any surface oxide, which may be formed during system venting. The substrates used included ordinary microscope glass slides, silicon wafers (100), copper sheets, stainless steel sheets, and aluminum sheets.

Al/Ni multilayered foils were prepared at 10 mTorr argon (99.99%) chamber pressure from pure Al and Ni targets (99.99% and 99.98% pure, respectively) onto stainless steel substrates mounted on a rotating holder. The base pressure prior to deposition was below 8e-7 Torr and the substrates were mounted on a thick steel block, which acted as a heat sink.

The deposition rates for both Al and Ni under specific sputtering parameters are shown in Table 6-1. By altering the sputtering time, Al/Ni multilayer films with different modulation period can be fabricated. Figure 6-5 shows a cross section of Al/Ni multilayer, which has 6 bilayers of 1.6 µm period (half thickness of Al and half thickness of Ni).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition Time (s)</th>
<th>Power (Watt)</th>
<th>Sputtering Pressure (mTorr)</th>
<th>Film thickness (µm)</th>
<th>Average deposition rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>7200</td>
<td>200</td>
<td>10</td>
<td>3.99</td>
<td>34.7</td>
</tr>
<tr>
<td>Ni</td>
<td>7200</td>
<td>100</td>
<td>10</td>
<td>2.16</td>
<td>18.8</td>
</tr>
</tbody>
</table>
Figure 6-5. SEM cross-section of Al/Ni multilayered thin films with 1.6 µm period.
CHAPTER 7. NUMERICAL SIMULATION OF AL/NI MULTILAYERED THIN FILMS

7.1. Introduction

Nanostructured thin film materials have recently attracted a great deal of interest due to their unique mechanical, thermal, electrical and optical properties. Schematics of such a foil are shown in Figure 7-1. Individual nanofoils with alternate layers of two materials can be easily fabricated using sputtering deposition [52] or electron beam evaporation [53]. Hence, the nanofoil consists of many hundreds of individual layers arranged in the form of a periodic lamina. The overall thickness of a typical nanofoil is in the order of 10–100 µm, and the multilayer period is in the order of nanometers.

It is well known that intermetallics and other compounds formed from transition metals and Boron (B), Carbon (C), or Silicon (Si) can be synthesized from their pure constituents via highly exothermic reactions. Examples include Al/Ni and Al/Monel (a Ni–Cu alloy in the ratio 7:3). The compounds form when the Al/Ni or Al/Monel constituents undergo intermixing as a result of thermally induced atomic diffusion. Once the reaction has been initiated with a pulse of heat or energy, such as an electric spark, the large amount of energy released by the intermixing causes the temperature to rise sharply; hence, the reactions can become self-propagating. Self-propagating formation reactions in multilayer foils are driven by a reduction in atomic bond energy. In the Al/Ni multilayer system, with a small thermal pulse, atoms diffuse into the companion layers, and Al-Al and Ni-Ni bonds are exchanged for Al-Ni bonds. This local bond exchange produces a large quantity of heat that is conducted down the foil and facilitates more atomic mixing and compound formation, thus establishing a self-propagating reaction.
One potential application of reactive nanofoils is to use the reactive foils as a controllable, localized heating source for joining applications, which will enable soldering and brazing of materials at room temperature. Another potential application of reactive nanofoils is in near-net shape forming.

![Schematic of reactive nanofoils](image)

Figure 7-1. Schematic of reactive nanofoils.

Note that the flame is taken to move in the negative x direction. In front of the flame the composition is that of the unreacted foil and behind the flame the foil is taken to be fully intermixed.

Figure 7-2(a) shows a cross-sectional transmission electron micrograph of an as-deposited Al/Ni foil with nanoscale bi-layers [54]. The nanofoils contain hundreds of nanoscale layers that alternate between aluminum and nickel. When a small spark is applied to one end of such a free-standing foil (Figure 7-2(b)), a self-propagating reaction is ignited that travels across the full length of the foil and raises the temperature of the foil from room temperature to over 1200 °C within several milliseconds [55]. The speed at which a reaction propagates along a reactive nanofoil depends on how rapidly the atoms diffuse normal to the coupling layer and how rapidly heat is conducted along the foil. It has been theoretically predicted and experimentally demonstrated that the velocities, heats, and temperatures of the reactions can be controlled by
varying the thicknesses of the alternating layers.[56,57]

Figure 7-2. (a) Cross-sectional TEM micrograph of an as-deposited Al/Ni multilayer foil showing nanoscale layers. (b) A self-propagating formation reaction that travels across the Al/Ni multilayer foil.

In this chapter, the multiphysics-based numerical simulations of reactive nanofoil heat and mass transfer using COMSOL [58] are presented. The conductive heat transfer and mass diffusion equations are solved for 1D, 2D and 3D cases.

7.2. Numerical Modeling

This study presents the numerical simulation of heat transfer behavior of reactive nanofoils. Three levels of modeling, namely 1D, 2D and 3D, were performed to simulate the heat transfer and chemical reaction in the nanofoil and substrate.

For a typical reactive nanofoil, the width (z) is larger than its thickness (y) and the width is small in comparison to the length (x). As a result, it is reasonable to make the assumption that the reaction front, or flame front, is uniform, lying parallel to the yz-plane. The reactive nanofoil can therefore be treated as a two-dimensional structure with the composition varying periodically in the y-direction while the flame propagates along the x-direction, as shown in Figure 7-1. This forms the base for the 2D modeling and simulation.

As the thickness of nanofoil (y) is considerably smaller than the length (x), the bi-layer
thickness effects can be modeled by adjusting the reaction rates. Thus, a 1D simulation can be explored to study the flame speed and axial direction temperature/composition variations.

To study the transient heating of the reactive nanofoil to the bonding substrate, such as a silicon wafer, a 3D simulation must be performed.

### 7.2.1. 1D Simulation

The goal of the 1D simulation is to find out the flame speed as a function of chemical reaction rate. Since the temperature variation through the foil (in the $y$-direction) is negligible when compared to that along the direction of the flame’s propagation, the 1D assumption is justified. A reactive nanofoil of 0.6 m in length was simulated. The chemical composition variation due to reaction can be modeled using the diffusion equation.

\[
\frac{\partial C}{\partial t} + \nabla \cdot (-D \nabla C) = Rw
\]

(7-1)

where $R$ is the reaction rate (reaction constant times chemical composition $C$, when $T > 500^\circ$C, was used in the simulation); and $D$ is the diffusion coefficient in m$^2$s$^{-1}$. In the simulation, the atomic diffusion coefficient, $D$, is taken to obey an Arrhenius relationship: $A \times \exp(-E/RT)$, where $A$ is the Arrhenius prefactor, $R$ is the gas constant (8.31434 kJ/kmol-K), $T$ is the temperature, and $E$ is the activation energy for atomic diffusion. The Arrhenius prefactor $A$ depends on the mole fractions and diffusion coefficients of the two constituents in the nanofoil. The values $E = 137$ kJ/mol and $A = 2.18E-6$ m/s$^2$ were used in the present study following Jayaraman et al. [59]. The initial composition value was set to be 1.

The heat conduction equation is used to simulate the temperature field in the reactive nanofoil. The heat conduction equation and the mass diffusion equation are coupled together using the local temperature and concentration, as shown below.
\[ \rho \times c_p \times \frac{\partial T}{\partial t} - \nabla \cdot (k \nabla T) = \dot{Q} \]  

(7-2)

where \( C_p \) denotes the specific heat capacity, \( T \) is temperature, \( k \) is the thermal conductivity, \( \rho \) is the density, and \( \dot{Q} \) is related to the changing rate of the nanofoil composition. \( \dot{Q} \) provides the coupling between the thermal transport and atomic diffusion. In the simulation, the heat release rate, \( \dot{Q} \) is related linearly to the local concentration when the temperature is above an activation temperature of 500 °C. The left side boundary was set to be a fixed temperature of 600K, high enough to trigger the reaction, and thermal insulation \( q \cdot n = 0 \) was used for the right side boundary.

7.2.2. 2D Simulation

The 2D case has a focus on the temperature and composition distributions in the bi-layer of reactive nanofoil. To model the Al/Ni bi-layer, two mass diffusion equations were used to track the local composition of Al and Ni respectively within the nanofoil. The reaction rate was set to be linearly proportional to the product of Al concentration and Ni concentration along the Al/Ni interface.

\[
\text{Rate} = \text{constant} \times C_{\text{Al}} \times C_{\text{Ni}}
\]

(7-3)

when \( T > 500 \) °C.

7.2.3. 3D Simulation

The objective of the 3D simulation is to study the transient heat transfer and localized heating effect to the substrate, thus a heat conduction equation with a prescribed flame speed along the nanofoil surfaces is used. Under a preset flame speed, the transient temperature distribution on a silicon wafer substrate was obtained.
7.2.4. Numerical Schemes

The simulations were performed using COMSOL Multiphysics package. COMSOL is a powerful interactive environment for modeling and solving the coupled heat transfer and mass diffusion equations. To solve the coupled partial differential equations (PDEs), COMSOL Multiphysics uses finite element method (FEM). The software runs the finite element analysis together with adaptive meshing and error control using a variety of numerical solvers. In this study, the time-dependent solver was used. This solver was developed by Linda Petzold at the University of California, Santa Barbara [60]. The solver uses variable-order variable-step-size backward differentiation formulas. Thus, the solver is an implicit time-stepping scheme, which implies that it solves a possibly nonlinear system of equations at each time step.

To control the accuracy and calculation performance, both absolute and relative tolerance parameters were set for the time-dependent solver in the simulations. The absolute and relative tolerances control the error in each integration step. For the 3D geometry, the mesh contains both tetrahedral elements for the silicon wafer substrate, and the swept mesh (prism elements) for the nanofoil.

7.3. Numerical Simulation Results

Transient heat transfer and composition calculations were performed for the 1D case first. Starting from time zero, the reactive nanofoil was ignited at the left side boundary. Heat was generated due to the prescribed chemical reaction in the reactive nanofoil. As no heat loss is considered in the 1D simulation, after the flame front passes, the nanofoil reaches and maintains a constant elevated temperature. To study how the flame speed could be adjusted in the simulation, the reaction rate constant is altered from 1 to 200,000. Figure 7-3 shows the flame speed variation as a function of the reaction constant. By adjusting the reaction constant, both
heat conduction and mass diffusion characteristics can be altered.

Armstrong and Koszykowski [61] presented an analytical solution for bi-layered nanofoils with an ideal composition profile. They found that the flame speed was proportional to \(1/\delta\), where \(\delta\) was the foil bi-layer thickness. The flame speed also depends strongly on the maximum reaction temperature. As reported by Gavens et al. [62], Figure 7-4, for a nanofoil with 200 nm bi-layer thickness, flame speed was in the order of 1 m/s, and corresponding to the reaction constant of 3000 in our simulation; for a thin bi-layer thickness of 30 nm, a flame speed of 10 m/s could be achieved, which would corresponding to a reaction constant approximately 60,000.

Figure 7-3. The flame speed versus the reaction rate.
Figure 7-4. The measured and predicted flame speed as a function of bi-layer thickness and anneal time [62].

Figure 7-5. (a) Temperature (b) Species concentration in the nanofoil under a reaction constant of 50.
Figure 7-5 shows the typical temperature and concentration distribution in the nanofoil at different time steps, under the reaction constant of 50. A sharp flame front is observed. For a larger reaction constant, a faster flame speed, and a steeper rise of temperature and composition, interfaces around the flame front are expected.

For a 2D case, the calculation domain includes a layer of Al and a layer of Ni, and two mass diffusion equations are used. For the Ni/Al system considered here, the physical properties are listed in Table 7-1. These values are the typical weight averaged values of those for pure reactants at room temperature. Note that because these properties are assumed constant, the thermal diffusivity is constant as well.

The Al/Ni bi-layer is assumed to have a perfect interface initially, with no heat loss being considered in the simulation. As it takes both Al/Ni to trigger the reaction, the temperature change starts from the Al/Ni interface (Figure 7-6). The composition diffusion is controlled by
the local temperature, and only heat conduction is modeled here. It is evident that the thinner the
bi-layer, the faster the mixing, and the faster the flame speed. Two diffusion equations were
used, for mass transfer simulation. Taking the Al diffusion equation as an example, initially the
Al side is set to be one and the Ni side is set to zero. After the reaction, the Al concentration
decrease to zero.

Table 7-1. Thermophysical properties of silicon and Al/Ni nanofoil.

<table>
<thead>
<tr>
<th></th>
<th>Unreacted Foil</th>
<th>Reacted Foil</th>
<th>Silicon Wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>152</td>
<td>25</td>
<td>163</td>
</tr>
<tr>
<td>Heat capacity (J/KgK)</td>
<td>830</td>
<td>610</td>
<td>703</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.5</td>
<td>5.86</td>
<td>2.33</td>
</tr>
<tr>
<td>Heat of reaction (kJ/mol)</td>
<td>59</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 7-6. The 2D case: temperature distribution in the Al/Ni bi-layer.
The 3D simulation targets the major industrial application of reactive nanofoils, namely the bonding of electronic components and devices. The current wafer bonding techniques, such as anodic bonding and fusion bonding, are conducted at high temperature, 1000°C for the conventional fusion bonding and 300-500°C for anodic bonding. These high temperature processes may cause thermal damage to components. Dissimilar materials may debond on cooling due to the coefficient of thermal expansion (CTE) mismatch. In contrast, reactive multilayer Al/Ni nanofoils can be used as novel localized heating sources to melt solder layers and bond silicon wafers. In the 3D simulation, reactive nanofoils are applied onto a substrate block of silicon, 0.05x0.05x0.01m. Four sections of nanofoils, with a width of 2 mm and a length of 30 mm, are arranged as the four edges of a square box. The physical properties used in the simulation are shown in Table 7-1. Figure 7-7 shows the mesh of the 3D model. A flame speed of 0.02 m/s is prescribed with a heat flux density of 5x10^7 W/m^2, which represents the heating value of an Al/Ni nanofoil.

The temperature distributions on the nanofoil and the silicon substrate at different times are shown in Figure 7-8. The peak temperature on the nanofoil, around 820 K, is high enough to melt the solder. Figure 7-9 shows the temperature history for the region under the nanofoil on the silicon substrate. The flame front hits the region at a time of 4.7s, as shown in Figure 7-9. The substrate temperature increases quickly by ~320 K with the reactive foil in action. The heat is then absorbed by the silicon substrate, and the temperature quickly drops to about 175 K above the initial block temperature. From the simulation, it is evident that when using reactive nanofoils for microchip bonding, the heat affected region is localized. The wafer temperature decreases to a low bulk temperature in less than one second.
Figure 7-7. 3D simulation mesh.

Figure 7-8. Temperature distributions on the nanofoil/silicon block (a, b, c, and d).
(Figure 7-8 continued)

(b) Time = 1.7  Boundary: Temperature [K]

Max: 795.645
Min: 298.168

(c) Time = 3.5  Boundary: Temperature [K]

Max: 793.59
Min: 305.494
Figure 7-9. Temperature history on the silicon wafer block underneath the nanofoil.
7.4. Conclusions

Nanostructured reactive foils have attracted a great deal of interest recently due to their unique mechanical and thermal properties. Reactive nanofoils can be used as a controllable, localized heating source for joining applications, which enable soldering and brazing of materials at room temperature. In this study, multiphysics-based numerical simulations were performed to simulate reactive nanofoils.

Performance of reactive nanofoils is studied under 1D, 2D and 3D configurations using multiphysics based numerical simulations. The flame speed is successfully modeled as a function of the chemical reaction rate. The detailed chemical compositions have been obtained for the Al/Ni bi-layer foil. The performance of nanofoil is quantified in terms of temperature and species distributions and the flame speed. The numerical simulation proves that the heating from a reactive nanofoil to the substrate is highly limited and localized. The use of a reactive nanofoil as a local heating source eliminates the need for excess equipment and dramatically reduces the total energy that is needed for bonding applications. With localized heating, temperature sensitive components, such as microelectronic devices can be joined without thermal damage. It is also advantageous for joining materials with very different coefficients of thermal expansion, e.g. joining metals and ceramics.
8.1. Introduction

Magnetron sputtering is a very widely used technique to fabricate thin film coatings and is usually carried out in an argon atmosphere. By adding a reactive gas to the sputtering process, it is possible to form a compound between sputtered metal atoms and reactive gas molecules. In this way, dielectric films are formed, such as oxides, nitrides, carbides, by reactively sputtering a metal target [63,64] in the presence of a reactive gas, usually mixed with argon gas.

Aluminum oxide thin films are widely used in different industrial applications from micro-electronic and optical applications to wear resistant coating because of its excellent properties, chemical inertness, mechanical strength and high hardness, high abrasive and corrosion resistance, as well as insulating and optical properties [65].

Reactive direct current (DC) magnetron sputtering of dielectric coatings is very hard to deposit because of the strong interaction of the oxygen with the target surface that leads to very rapid oxide compound formation on the target surface. To overcome these problems, radio frequency (RF) power can be used, but RF reactive sputtering usually is very slow. Typically the deposition rate for reactive RF deposited alumina is only 2-3% of the metal deposition rates for the same sputtering parameters [66].

Alumina films can also be deposited by sputtering an insulating ceramic target using RF power source. However, reactive sputtering is usually the preferred method because of the following advantages [67]:

- Metal targets can be machined, so they are much less expensive;
Metal targets have high thermal conductivity and, therefore, can handle high power densities (e.g., 50 W/cm²) without cracking;

Different types of dielectrics can be fabricated by choosing different reactive gas mixtures;

High deposition rates comparable to those of pure metal

The main advantage of DC magnetron sputtering is the high deposition rate. In contrast, the deposition rate of reactively sputtered oxide from a ceramic target is about 10 times lower. The nature of reactive magnetron sputtered alumina film depends on parameters such as sputtering rate of the metal, target-to-substrate distance, substrate temperature [68], and the pressures of the sputtering and reactive gas. The main disadvantages of reactive sputtering are target poisoning, and arcing resulting in defects in the thin film.

Two different operating modes of the reactive magnetron sputtering discharge exist: the metallic mode and the reactive mode. The metallic mode is characterized by a high sputtering rate and therefore a high reactive gas consumption and low partial pressure of the reactive gas. The transition between these two discharge modes occurs abruptly at two critical values of the reactive gas flow depending on the direction of the transition. This general phenomenon is qualitatively known as a hysteresis effect.

8.2. Experimental and Results

8.2.1. Hysteresis Effect

Many problems encountered in the preparation of alumina films by reactive sputtering are due to a hysteresis effect. This effect arises in consequence of two competitive processes: the sputtering of the target surface and the covering of its surface by reaction products. The transition between these two processes occurs abruptly at two critical values of the reactive gas
flow depending on the direction of the transition. This general phenomenon is qualitatively known as a hysteresis effect.

The main cause of the hysteresis effect has been attributed to the formation of a ceramic layer on the surface of the target. Conversion back to the metal mode occurs only when the flow of reactive gas is reduced to the point where it can no longer maintain the ceramic layer [63]. The poisoning of the target surface causes problems, like a decrease in the deposition rate and arcing.

Hysteresis experiment was first performed to study the reactive sputtering process: the plasma is ignited in pure argon at a given pressure by introducing a certain amount of argon flow to the vacuum chamber. Keeping the sputtering power constant, the oxygen flow rate is stepwise increased from zero. Between each step the process parameters (sputtering pressure, current, and discharge voltage) are recorded until the sputtering process is steady (around 2 minutes). When the aluminum target is completely poisoned, the measuring procedure is reversed, i.e. the oxygen flow is stepwise decreased to zero. Although the discharge voltage value is negative, one generally plots and discusses its absolute value. Figure 8-1 and Figure 8-2 show the result of a hysteresis experiment for the reactive sputtering of aluminum. The curve takes different pathways for increasing the oxygen flow than for decreasing the oxygen flow, as shown in the figure. There are avalanche-like transitions when increasing or decreasing oxygen flow rates.

From Figure 8-1, when the target is poisoned, the discharge voltage will drastically decrease about 60 V. It is also noticed that, when still in metallic mode, the discharge voltage slightly increases as indicated in the figure. Severe hysteresis could be observed in the voltage-reactive gas flow cycle. With constant sputtering power, the target voltage dropped dramatically when oxygen flow was introduced into the chamber. The target turned to the compound mode
from metallic mode. By decreasing the gas flow, the target voltage increased close to the original value and the target was again in the metallic mode. The critical condition for deposition of the aluminum oxide thin film was 3 sccm, immediately before the target voltage started to decrease.

Figure 8-1. Discharge voltage as a function of the oxygen flow rate during DC reactive sputtering of an aluminum target. The power is adjusted to a constant value of 300 W.
8.2.2. Deposition of Alumina Thin Films

The thin film processing procedure begins with chemical cleaning of the glass slides and silicon wafer substrates by ethanol for 15 min in ultrasonic bath. The substrates, blown dry by air, were placed on the substrate holder which was water cooled. Prior to deposition, the target was pre-sputtered in argon for 15 min in 4 mTorr pressure with a 200 W target power, argon flow rate of 25 SCCM and oxygen flow rate of 2.5 SCCM. The process parameters used are given in Table 8-1.

The same Denton magnetron sputtering system was used for this reactive sputtering. The processing chamber was pumped by a mechanical pump and a cryogenic pump to a pressure in the range of 10^{-7} Torr prior to the experiments. The 99.999% Aluminum target of 4-inch diameter was used. Ar and O_{2} gas flows were controlled by independent mass flow controllers and MKS gas 4-channel readout.
Table 8-1. The reactive sputtering process parameters for aluminum oxide thin films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>Al, purity of 99.99%</td>
</tr>
<tr>
<td>Target size (diameter)</td>
<td>4-inch</td>
</tr>
<tr>
<td>Substrate</td>
<td>Glass, Si</td>
</tr>
<tr>
<td>Power</td>
<td>200W</td>
</tr>
<tr>
<td>Voltage</td>
<td>440 V</td>
</tr>
<tr>
<td>Sputtering pressure</td>
<td>4 mTorr</td>
</tr>
<tr>
<td>Argon flow rate</td>
<td>25 SCCM</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>2.5 SCCM</td>
</tr>
<tr>
<td>Sputtering distance</td>
<td>4-inch</td>
</tr>
</tbody>
</table>

8.2.3. Characterization of Alumina Thin Films

First, electrical conductivity of all deposited films were analyzed after the deposition to test whether it is alumina or aluminum thin film. SEM was used to study the surface structure of the as-deposited alumina film and X-ray diffraction (XRD) for structure analysis. EDS and XPS were used to study the stoichiometry of the alumina films.

Figure 8-3 shows a denser coating structure without large faceted grains or pores, which mean the sputtered alumina films are amorphous which is consistent with the XRD results. Compared to Figure 8-3, the surface structure of magnetron sputtered aluminum metal films with the same sputtering parameters except without oxygen flow is shown in Figure 8-4.

The XRD results showed that the deposited aluminum oxide thin films were amorphous since no reflections of crystallized oxide could be observed. The SEM analyses also showed that the films were dense with a columnar structure. The stoichiometry of the aluminum oxide thin films was measured by XPS. The XPS analyses gave the O/Al ratio of 1.59. The exact ratio is 1.50 corresponding to the stoichiometric Al$_2$O$_3$. 
Figure 8-3. SEM of the surface of the reactive sputtered alumina coatings on silicon wafer.

Figure 8-4. SEM of the surface of the magnetron sputtered aluminum coating on silicon wafer with same sputtering parameters.
8.3. Conclusions and Summary

The following conclusions could be drawn: (1) Sputtering parameters are tested to deposit aluminum oxide thin films rapidly without a strong hysteresis effects. (2) The aluminum oxide thin films deposited are amorphous. The O/Al ratio of the films is around 1.59, while the exact ratio of O/Al corresponding to the stoichiometric Al₂O₃ is 1.50.
CHAPTER 9. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

9.1. Conclusions

In the present study, the mechanical properties (hardness and elastic modulus) of APS alumina coatings and single splats were first investigated by nanoindentation technique. A detailed testing scheme, indentation control parameters, and corresponding data processing are established. Nanoindentation tests on APS alumina coatings and single splats are conducted. SEM and FESEM were used to characterize the microstructure of the samples. XRD was used to study the phase information of APS alumina coating. The influence of different phases of alumina on the nanoindentation results has been investigated.

An analytical comprehensive model to estimate the elastic modulus of multilayered thin films has been successfully developed. Because APS alumina coatings were built with layered disc-shaped alumina splats which could be viewed as the multilayered structure, this analytical model was used to study nanoindentation testing on APS alumina coatings. The analytical results have a good agreement with the experimental results. In addition, this analytical model can guide the experimental tests by predicting indentation parameters such as maximum load force and suitable indentation depth in order to get reasonable nanoindentation results.

DC magnetron sputtering technique was used to fabricate reactive multilayered Al/Ni thin films, which can be used as a self-propagating heating source to melt solder layers and thus bond electrical components, such as silicon wafer bonding applications. Performance of reactive nanofoils is studied under 1D, 2D and 3D configurations using multiphysics based numerical simulations. The flame speed is successfully modeled as a function of the chemical reaction rate. The detailed chemical compositions have been obtained for the Al/Ni bi-layer foil. The
performance of nanofoil is quantified in terms of temperature and species distributions and the flame speed. The numerical simulation proves that the heating from a reactive nanofoil to the substrate is highly limited and localized.

Reactive magnetron sputtering was used to fabricate amorphous alumina thin films. Hysteresis effect of reactive deposition of alumina in a mixture of argon and oxygen with DC power source was presented. Suitable reactive sputtering parameters were found to deposit alumina films.

9.2. Recommendations for Future Work

9.2.1. Nanoindentation Study of Magnetron Sputtered Thin Films and Multilayers

Magnetron sputtering has been used to synthesize thin films and multilayers of different metals, alloys, and ceramics. Single metallic films, multilayered metal films, metal-ceramic layered composites, and ceramic-ceramic layered composite have been investigated in the past decades. These single and multilayered films exhibit higher strength than that of bulk materials. Nanoindentation can be used to study the hardness and elastic moduli of magnetron sputtered thin films and multilayers including Al, Ni, Al/Ni, alumina, zirconia, and alumina/zirconia with different thickness or layer thickness.

9.2.2. Install Oxygen Gas Inlet System

Introducing the oxygen gas immediate to the substrate will improve the oxidation of the aluminum. Such as feeding arrangement, introducing oxygen flow separately in the vicinity of the substrate, has been demonstrated by other researchers. There are three reasons leading to the improved oxidation. First, the target is less poisoned when the reactive gas is introduced directly in front of the substrates. The target is then possible to maintain partially in the metallic mode. Second, the plasma contains more ionized oxygen radicals when the oxygen gas is introduced
into the plasma. The highly reactively oxygen radicals react with the aluminum atoms to oxidize them. Thirdly, when the oxygen gas was introduced in the vicinity of the substrates by a separate gas inlet system, less oxygen will be needed to obtain fully oxidized aluminum oxide films.
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