DEPOSITION OF ALUMINUM OXIDE BY EVAPORATIVE COATING AT ATMOSPHERIC PRESSURE (ECAP)

BY

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THESIS

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ABSTRACT

Aluminum oxide is one of the most important ceramic oxides and has a wide range of uses, including high-temperature applications and microelectronics. Recently, the Center for Plasma-Material Interaction (CPMI) has developed innovative coating method of Evaporative Coating at Atmospheric Pressure (ECAP). This new idea is an atmospheric-pressure based process. By using the thermal energy of plasma, solid aluminum are evaporated and then produce a PVD-like alumina coating on a work piece. The aluminum rod is inserted in the center of the microwave torch feeding a melt pool and evaporates into the surrounding plasma plume. It can be deposits as $\text{Al}_2\text{O}_3$ if done in an oxygen environment or as AlN with nitrogen. A gas shield keeps the working gas pure. Following the same concept as the Laser Assisted Plasma Coating at Atmospheric Pressure (LAPCAP), the material captured by the plasma plume is atomic in nature (the evaporated metal atom) and should therefore end up deposited molecule-by-molecule as in a PVD fashion. A much higher thermal energy of the plasma plume will make a superior coating microstructure as compared to a purely evaporated film. On the contrary, aluminum evaporated in an oxygen environment will merely makes alumina dust.
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Chapter 1 : INTRODUCTION

1.1 Aluminum Oxide

Aluminum oxide (alumina) is one of the most important ceramic materials due to its many appealing properties. It is electrically insulating, optically transparent mechanically hard, chemically stable, and these properties make it suitable for many different applications. [1] This section will start by briefly describe the complexity of the many existing alumina crystalline phases, then move on to review properties of the three most important phases of aluminum oxide which have the most applications industrially.

1.1.1 Phases of Aluminum Oxide

Alumina could be found in a number of crystalline phases or polymorphs ($\alpha$, $\gamma$, $\eta$, $\delta$, $\kappa$, $\chi$ ...), and among all phases the three most important are the $\gamma$, $\theta$, and $\alpha$ phase. The $\alpha$ phase is thermodynamically stable at any temperatures up to its melting temperature at 2051 °C, but the other metastable phases like $\gamma$ or $\theta$ also appears frequently in alumina growth studies as well. [1]

All common alumina polymorphs can all be formed within typical synthesis temperatures from room temperature up to about 1000 °C. This makes the study and growth of alumina complicated, since it is sometime difficult to control the process to achieve the desired phase. However, this polymorphism also creates opportunities for applications in various areas of technical science, since the properties of one
alumina phase may differ from the properties of another, [2] as described in the following table. A summary of alumina properties is presented in Table 1.1 and 1.2.

**Table 1.1.: Selected properties of α-, θ- and γ-alumina at room temperature.[1]**

<table>
<thead>
<tr>
<th></th>
<th>α-Al₂O₃</th>
<th>θ-Al₂O₃</th>
<th>γ-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (GPa)</td>
<td>28[4]</td>
<td>28[47]</td>
<td>23.5[40]</td>
</tr>
</tbody>
</table>

**Table 1.2: Structures of stable alumina (corundum) and metastable aluminas[45,46]**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Structure</th>
<th>Lattice Parameters, angle (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha (Corundum)</td>
<td>Hexagonal</td>
<td>a = 4.75, b = 12.991, (rhombohedral 8</td>
</tr>
<tr>
<td>Eta</td>
<td>Cubic (spinel)</td>
<td>7.90</td>
</tr>
<tr>
<td>Gamma</td>
<td>Tetragonal</td>
<td>7.95, 7.97</td>
</tr>
<tr>
<td>Delta</td>
<td>Tetragonal</td>
<td>7.97, 23.47</td>
</tr>
<tr>
<td>Theta</td>
<td>Monoclinic</td>
<td>5.63, 2.95, 11.86, 103° 42’</td>
</tr>
<tr>
<td>Kappa</td>
<td>Orthorhombic</td>
<td>8.49, 12.73, 13.39</td>
</tr>
<tr>
<td>Beta</td>
<td>Hexagonal</td>
<td>5.59, 22.6</td>
</tr>
</tbody>
</table>

All alumina phases (except the α phase) has a transformation sequences, and the common characteristic in which all they have in common are that they all transform to the α phase at high temperature, since α phase is the only thermodynamically stable phase of alumina. It has the highest density, elastic modulus, hardness and band gap among all phases of alumina and these properties
make it the material of choice for many applications industrially such as chemical and wear protection. Figure 1.1 and 1.2 illustrates some phase transition relations for the common metastable alumina phases. The transformations to the α phase from other metastable phases typically take place at above 1000 °C and all are irreversible. [2][8]

**Figure 1.1:** Commonly accepted transition sequences of the aluminas from the hydroxides to corundum (α-Al₂O₃) during thermal treatment. [9, 10]
1.1.2 Properties of $\alpha$-alumina

The $\alpha$ form of aluminum oxide is also called corundum (its name came from the naturally occurring mineral, corundum, which consists of pure $\alpha$-$\text{Al}_2\text{O}_3$). Its transparent and uncolored crystal form is known as sapphire. The polycrystalline form can be made from powder by sintering. It is used not only in industrial applications, but also occurs naturally as gemstones. The gemstone sapphire is actually $\alpha$-alumina doped with trace amount of iron and titanium, while the other gem, ruby, is $\alpha$-alumina doped with small amounts of chromium. Like all other alumia phases, the $\alpha$ phase is highly ionic, with a theoretical charge of $+2.63e$ and –
1.75e for aluminum and oxygen, respectively. [13] Thus, the chemical bonds between ions are almost purely ionic; this is also similar in the case for θ-alumina.

The corundum structure is also formed in a number of other metal sesquioxides, such as Cr₂O₃, Ti₂O₃, and Fe₂O₃. [14] The structure of corundum belongs to space group R₃c and is rhombohedral with two formula units (10 atoms) in the primitive unit cell. However, the hexagonal representation containing six formula units is more often used. [14] The c axis of the hexagonal cell in this case is along the (111) direction of the rhombohedral lattice. This structure can be further described as a hexagonal close-packed (HCP) oxygen sublattice, in which the aluminum atoms, or ions, occupy two thirds of the octahedral interstices, i.e., they have six nearest oxygen neighbors. [1]
The thermodynamic stability of α-alumina makes it the most suited phase for many high-temperature applications, although the κ phase can also be used due to its high transformation temperature. Other important characteristics of α-alumina include chemical inertness and high hardness. The elastic modulus and hardness are measured to be ~440 and ~28 GPa, [4] respectively. These numbers are comparable to diamond, which have values of ~1100 and ~100 GPa, [15] and to TiN, with values similar to those of α-alumina, [16] and much higher than metallic aluminum, which has values of ~70 and ~0.3 GPa. [4, 15] All these properties made α-alumina thin films important for application in use for wear-resistant [17] and high-temperature
diffusion barrier [18] coatings. Other uses of α-alumina are found in electronics, where it is used as an insulator due to its wide band gap of 8.8 eV, [6] and in optics, due to its optical transparency in the visible range and stability at high temperature. [1]

1.1.3 Properties of θ-alumina

The θ phase of alumina is a metastable phase and it will transform into the α phase as low as 1050 °C. [2] It has a lower density than the α phase with a density of about 3600 kg/m³, compared to 4000 kg/m³ for α-alumina. [2] Properties of θ-alumina are also shown in Table 1.1.

The structures of all alumina phases are built up around a slightly distorted close-packed oxygen lattices. While the α phase has an HCP framework, the θ structure is based on a FCC oxygen lattice. [19] Within this oxygen framework, half the aluminum ions occupy the octahedral interstitial sites and half occupy the tetrahedral (with four oxygen neighbors) sites. Thus, each oxygen ions have three different possible surrounding sites, and each of which is occupied by one third of the oxygen ions. Two of these oxygen sites there have three nearest aluminum neighbors and the third has four. The overall structure is monoclinic and belongs to the space group C_{2m}, and the unit cell contains four formula units (20 atoms). θ-alumina is a structural isomorph of β-Ga2O3, and gallium oxide can also form this corundum structure as well. There are not as many investigations made on the θ phase as on α phase, although it is clear that it is highly ionic [20] and is insulating with a band gap of 7.4 eV. [21].
1.1.4 Properties of γ-alumina

γ-alumina has a low surface energy, and hence high surface area, and it is extensively used as catalyst supports.[2, 22] The low surface energy also indicates that the γ phase is surface energy stabilized, since the surface area is relatively high compared to the bulk volume, especially in the case with small grain sizes.[23] In high-temperature applications, a problem with the use of the γ phase is that it will transform into θ phase at around 700-800 °C.[2] This has led to ongoing experimental research on doping of alumina to increase its thermal stability.

The γ-alumina structure has two main similarities with the θ phase, the FCC oxygen lattice and the mixture of octa- and tetra-hedrally coordinated aluminum ions. However, the exact structure for γ-alumina is still not well defined. It is commonly believed that the structure could be described as a defect cubic spinel with the aluminum ions randomly distributed between octa- and tetra-hedral sites. [24]

1.2 Atmospheric-Pressure Plasma (APP)

Today, low-pressure plasmas (LPPs) have already been widely investigated and found many applications in semiconductor manufacturing and processes [25]. Relatively large and uniform plasma has to be sustained and confined in a vacuum system in order to make material processing at a uniform rate across the whole chamber. The benefit of LPP is that it requires low breakdown voltage to ignite and has relatively high electron temperature and low neutral temperature. However, the major drawback of generating plasma at low pressure environment is also in the use
of a vacuum system. Vacuum systems, including the chamber, pumps and other related controlling components inside the chamber could be fairly expensive and relatively hard to adapt to changes in application requirements. Semiconductor processes, such as plasma etching and plasma deposition, can also create contamination in the vacuum chamber which will require constant cleaning, repair and maintenance. Thus, there are current researches of utilizing atmospheric pressure plasma to overcome these drawbacks in low pressure plasmas.

Atmospheric pressure plasma can be mainly categorized into several types, according to the configuration. [26] First is the corona discharge, they are usually ignited by applying a DC voltage (~10 kV) between a point electrode and a plane electrode. The distance is at the scale of several mm, and the current is usually kept low (<300 μA) to prevent arcing [27]. The second is Dielectric barrier discharges (DBDs). They are usually generated between two metal electrodes, with one or both are coated with a dielectric layer and a spacing of several mm, and could have different types of dielectric [28]. Generation of DBDs in general requires a 10~20 kV DC voltage, and the plasma can be spread relatively evenly in a large area. The last to introduce here is the atmospheric pressure plasma jet (APPJ). It consists of two concentric electrodes, where the inner one is applied with a 13.56 MHz RF power, or a 2.45 GHz microwave power. Gases with adjustable rates are introduced between the two electrodes during the discharge. The ignition condition for APPJ could be easily achievable, and the discharge of APPJ is relatively homogenous, volumetric and low in gas temperature [29].
Plasmas at atmospheric pressure has the potential advantage in both lowering the cost of manufacture and to broaden the plasma applications. In many cases the samples only require partial treatment on the surface, but on a non-planar surface. Unfortunately, sustaining a gas discharge at atmospheric pressure is proved to be much more difficult than in a vacuum chamber, since time constants for instabilities decrease with increasing pressure [31]. In a DC discharge, voltages required to ignite and sustain plasma increases as the pressure increases. As the pressure is increased further, the ignition voltage can be high enough to generate an arc between the electrodes. This is described by the Paschen’s law, and usually unfavorable in most material processing applications due to high gas temperature and small processing area which are common characteristics for arc discharges. This glow-to-arc transition sets a threshold for the discharge stability [32] and arc could usually be prevented by changing the configurations of the electrodes.

A simple approach to generate large-volume atmospheric-pressure plasmas is to create a large electric field around the cathode boundary region to supply sufficient production of electrons, which depends on the specific structure of the electrodes and different type of feed gas. [26] The comparison of breakdown voltage and electron density of different atmospheric-pressure plasmas and low-pressure plasma are listed in Table 1.3. From the table, the APPJs have similar breakdown voltage to the low pressure discharges, which can be 1-3 orders of magnitude lower than the other atmospheric-pressure discharges. At the same time, the electron densities of APPJ are also in the same range of low-pressure discharges, but lower than the rest of
atmospheric pressure discharges. [30]

Table 1.3: Breakdown voltage and electron density of plasma discharges. [30]

<table>
<thead>
<tr>
<th>Plasma Source</th>
<th>Breakdown voltage (kV)</th>
<th>Electron density (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pressure discharge</td>
<td>0.2-0.8</td>
<td>(10^8 - 10^{13})</td>
</tr>
<tr>
<td>Arc</td>
<td>10-50</td>
<td>(10^9 - 10^{15})</td>
</tr>
<tr>
<td>Corona</td>
<td>10-50</td>
<td>(10^8 - 10^{13})</td>
</tr>
<tr>
<td>DBD</td>
<td>5-25</td>
<td>(10^{12} - 10^{15})</td>
</tr>
<tr>
<td>APPJ</td>
<td>0.05-0.2</td>
<td>(10^11 - 10^{12})</td>
</tr>
</tbody>
</table>

Atmospheric pressure plasmas are highly collisional and not in equilibrium, since the electron-neutral collision frequency is much greater than the plasma frequency in atmospheric pressure. As a result, traditional characterization methods such as Langmuir probe diagnostics will not work for measuring and analyzing the electron temperature, electron density, and particle distribution of the plasma. [26]

Thus, finite element analysis simulation software (COMSOL) was used to simulate the plasma gas temperature and the gas flow in the plasma region and inside the microwave torch during operation.

1.3 Deposition of Aluminum Oxide

Currently, the most common method for depositing aluminum oxide is through chemical vapor deposition (CVD). It can be classified mainly as low pressure chemical vapor deposition (LPCVD) or atmospheric pressure chemical vapor deposition (APCVD). In LPCVD, precursor gases are introduced into the vacuum
system and the molecules of the precursor gases will be adsorbed onto the substrate surface. They then will react and the reaction will create solid product, which is the desired film coating, and other product gases. The produced gases will desorb from the substrate surface and be removed by scrubbers and pumps.

Figure 1.4: Schematic of a typical chemical vapor deposition growth mechanism. [49]

In the case of aluminum oxide, it can be done with using trimethylaluminum (TMA), aluminum chloride as the precursor in plasma enhanced CVD (PECVD) and aluminum tri-isopropoxide (ATI) with thermal CVD. [33] They can achieve a precise chemical composition, high film quality and uniformity. However, growth rate is comparatively low in CVD systems, usually on the order of 1-10nm/min, [26, 34] since only a small fraction of the incoming precursor are going to participate in the film formation, a large portion of the gas entering the chamber would just simply
pass through the chamber and removed by the pumps. Also, chlorine and hydrocarbon contaminants are commonly found in the deposited film, and high temperature corrosive gas will be commonly formed as product as well. These products may further react with the alumina film surface before being removed from the chamber and degrade the quality of the film.

![Diagram of a typical low pressure chemical vapor deposition system setup.](image)

**Figure 1.5: Schematic of a typical low pressure chemical vapor deposition system setup.** [49]

1.4 Motivation for Studies

For the first time, aluminum oxide thin films will be created by microwave plasma jet under atmospheric pressure conditions. In this study, the laser assisted plasma coating at atmospheric pressure (LAPCAP) system will be used in order to deposit aluminum oxide film on stainless steel substrates. The basic principle behind
this technique is to use the heat from the atmospheric plasma to melt and evaporate aluminum metal targets at the tip of the antenna. The vaporized aluminum atom will then be carried by the mixed helium and nitrogen gas flow in the plasma towards the substrate surface. The aluminum adhered to the surface of the stainless substrate surface will then be oxidized by the ambient oxygen in the atmosphere and forming aluminum oxide or alumina coatings.

The benefits of this concept are that no additional heat source other than the plasma will be needed and the phase of the alumina deposited could be modified as plasma condition changes. Also since it is an atmospheric process, no expensive vacuum chamber or vacuum equipment are needed, and high deposition rate are expected. Additionally it can be easily modified to deposit on non-planar surfaces by simply implementing automation between the atmospheric torch and the substrate.

This thesis is divided into chapters discussing Experimental Setup, Results and Discussion of Deposited Aluminum Oxide, and Conclusion.

Chapter 2 discusses the equipment and apparatus used for the deposition experiments. The assembly of the microwave generation and propagation system and the atmospheric-pressure plasma torch will be presented in detail in this chapter.

Chapter 3 characterizes the properties of the composition and phase of alumina deposited on stainless substrates under various deposition conditions. The results will be complemented with COMSOL simulations to allow a more through understand of the gas flow and plasma conditions inside the atmospheric torch.
during deposition.

Chapter 4 summarizes the results in this study and the future work for more detailed characterization of the plasma conditions and for improving deposited alumina film quality.
Chapter 2 : EXPERIMENTAL SETUP

2.1 Microwave Generator and Microwave Waveguides

The evaporative coating at atmospheric pressure (ECAP) experiment was powered by a 2.45 GHz microwave source. The microwave is generated by a magnetron in the generator made by Cober Electronics, Inc (Model S6F). It uses a 12kW power input and the output varies from approximately 0.5 to 6kW into a matched load with continuously adjustable power. The waveguide used to transmit microwave power from the magnetron to the atmospheric torch is the WR 284 waveguide cavities.

It consists of mainly five sections:

1. An aluminum 90° E-bend or H-bend, depending on the experimental requirements. They change the direction of the microwave propagation from vertical to parallel.

2. A two-port circulator with an embedded water load. It ensures that the reflected microwave is absorbed in the water load instead of travelling back to the magnetron.

3. A dual directional coupler, which has a 60 dB power attenuation at both ports for detecting forward and reflected microwave power respectively.

4. A 3-stub or 4-stub tuning system, which can continuously adjust the reflected microwave power by inserting or extracting one or more of the tuning stubs in order to change the impedance matching. The reflected power is tuned so that it is less than 5% of the output power in all experiments.
5. A WR 284 to 7/16 coaxial adapter, which couples the microwave from WR 284 cavity into the antenna of the plasma torch.

The aluminum E-Band, H-Bend, two-port circulator, dual directional coupler, 4-stub tuning system are all made by CoberMuegge LLC, USA, while the 3-stub tuning system and the WR284 to 7/16 adapter are custom made in the University of Illinois Urbana-Champaign.

Fig 2.1: Setup of the evaporative coating at atmospheric pressure (ECAP) experiment.
Fig 2.2: Schematic of microwave generation and propagation waveguides in the ECAP system. [26]

2.2 Atmospheric Pressure Plasma Torch (APPT)

The atmospheric pressure plasma torch (APPT) used for the ECAP experiment was designed and fabricated at the University of Illinois Urbana Champaign. It is a three coaxial cylinder design with decreasing diameter closer to the top of the torch. The cylinders were made with copper. The antenna was made with tungsten and connected to the coaxial adapter by a receptacle jack made by HUBER & SUHNER Group, USA and a 7/16 DIN adapter by RF Parts Company, USA. The diameter of the tungsten antenna was ¼” in diameter and 6 ¼” in length. The quartz discharge tube had an outer diameter of 16.2 mm and an inner diameter of 13mm, made by the Technical Glass Products, Inc., USA. It was fixed in the inside of the torch by two Teflon rings between the discharge tube and the copper cylinders. The inlet gas is fed
into the APPT from the bottom of the outermost copper cylinder, and a Teflon pad was placed at the bottom of the outermost cylinder wall in order to prevent arcing between the antenna and the copper cylinder as well.

All the processing gases (helium, argon, nitrogen, oxygen, hydrogen, etc) are controlled through various RMA-Master flowmeters made by Dwyze Instruments, Inc., USA. They can be individually controlled in order to generate different types of plasma with different gas mixtures. In the EVAP study helium and nitrogen are mainly used to create the plasma profile and gas temperature required for the alumina deposition. A schematic of the APPT is shown in fig. 2.3 and an actual view is shown in fig. 2.4.

Fig 2.3: Schematic of the atmospheric pressure plasma torch (APPT). Dimensions shown are in inches. [26]
Fig 2.4: Actual view of the atmospheric pressure plasma torch (APPT).

The APPT used in the EVAP study could generate APP with a plasma gas temperature raging from room temperature to a maximum of 3000 °C, depending on the applied power, gas flow rate and the type of processing gases introduced. In helium plasma, the APPT plasma could usually self-ignite to generate APP with a helium flow between 10-30 liters per minute, but an igniter could also be used. It can be placed on the tip of the antenna to help plasma ignition when needed. The igniter is made of a sharp metal wire (usually tungsten or copper) with a ceramic insulator break to stop microwave transmission to the user for safety considerations. Pure argon, nitrogen or air APP can be also is obtained by first igniting the helium plasma, then mixing each of them into the helium and then slowly turning the helium off. The
view of APPT in operation is shown in fig. 2.5.

Fig 2.5: Atmospheric-pressure plasma torch (APPT) in operation with aluminum target in place. Processing gas used is 20% nitrogen in helium, with a total gas flow of 18 Lpm. Forward power is around 1500W.

2.3 Aluminum Target, Tungsten Antenna and Stainless Steel Substrate

The aluminum target used is a 99.99%+ pure aluminum obtained from Kurt J. Lesker. It is in the form of cylinder pellets, with $\frac{1}{8}$ inch diameter x $\frac{1}{8}$ inch in height. Aluminum pellets with high purity will be required, since the deposition rate of aluminum oxide decreases as impurity within the target increases. 1000 series aluminum alloy (99% pure aluminum) samples were tested and the deposition rates were close to negligible.
Fig 2.6: High purity aluminum pellets used for the APPT target in EVAP experiments.

The antenna used for the EVAP study is 99.95% pure tungsten with a diameter of ¼ inch, and around 6.5 inch total in length. A cup of 0.08 inch in depth and 0.2 inch in diameter was made for the placement of the aluminum target. The diameter of the cup was made slightly larger than the size of the aluminum target to accommodate molten aluminum and aluminum oxide during and after the experiment so that aluminum overflows at the antenna tip could be avoided.

A bottleneck was also created about 1/8 inch below the tip of the tungsten antenna. The diameter of the antenna is reduced from the normal ¼ inch to around 0.1 inch, and the height of this bottleneck is around 0.1 inch as well. The purpose of this bottleneck is to reduce the thermal conductivity and thus the heat transfer from
the tip to the bottom of the antenna, as the APP plasma are generated at the tip and it would be the hotter than the bottom end where no plasma is formed.

From Fourier’s law:

\[ \frac{dQ}{dt} = -UA\Delta T \]

where \( \frac{dQ}{dt} \) is the amount of heat transferred per unit time in W, \( U \) is the conductance in W/m\(^2\)K, \( A \) is the cross sectional area in meter squares and \( \Delta T \) is the temperature difference between the two ends in Kelvins. By reducing the diameter of the antenna from 0.25 inch to 0.1 inch at the neck, the heat lost through the antenna is reduced by 84% \( (1-(0.1/0.25)^2) \). This design could effectively increase the aluminum target temperature with the same input power, or in other words achieve the same temperature with a lower input power, which makes the process more efficient and reduce microwave leakage as well. Zirconium oxide could also be placed in between the aluminum target and the antenna to further insulate the target and reduce heat lost to the antenna, but machining zirconium oxide to fit between the target and the antenna may be costly and time consuming due to its extremely high hardness and toughness properties.
Fig 2.7: Tungsten Antenna used for the APPT in EVAP experiments. A cup was made on the top to accommodate the aluminum target and a neck was cut to decrease the rate of thermal conductivity from the cup to the bottom of the antenna.

Fig 2.8: Schematic of the tungsten antenna used for the APPT in EVAP experiments. A cup was made on the top to accommodate the aluminum target and a neck was cut to decrease the rate of thermal conductivity from the cup to the bottom of the antenna.
The substrates used are 304 stainless steel as they are readily available and could remain chemically inert while sustaining the high gas temperature of the APP. They are machined to 1 inch diameter discs and are mounted onto a homemade stainless steel substrate mount. The sample is then put on top of the APP for about 30 sec to obtain alumina coating. The size for the substrate is chosen to be 1 inch diameter so that it could have a large surface area for collecting aluminum vapors yet easily fit into various stage holders for tools used in thin film characterization such as SEM, XRD, and XPS etc.

![Stainless substrate mounted on the substrate holder before (left) and after (right) deposition for the APPT in EVAP experiments.](image)

**Fig 2.9:** Stainless substrate mounted on the substrate holder before (left) and after (right) deposition for the APPT in EVAP experiments.
Chapter 3 : RESULTS AND DISCUSSION

3.1 Film Characterization and Phase Determination

3.1.1 X-ray Photoelectron Spectroscopy (XPS)

The first step to characterize the film deposited in the ECAP study is to determine the elemental composition of the surface of the sample to ensure aluminum oxide was indeed deposited on the stainless substrate. This can be done using X-ray photoelectron spectroscopy. An XPS system (Physical Electronics PHI 5400) has an X-ray source to produce radiation under ultra-high vacuum and when they are absorbed by different elements, each of them will produce a set of XPS peaks at their characteristic binding energy. These peaks could then be used to identify the present of different elements and the amount of element present in the area irradiated, since the number of electrons detected is directly related to the amount of the element present on the surface. A typical XPS spectrum for the aluminum oxide film deposited using the ECAP system is shown in fig. 3.1.
Fig 3.1: XPS spectrum for alumina coating on stainless steel substrate via ECAP. Input microwave power setting for this sample was 1500W.

Both aluminum and oxygen peaks are observed in the spectrum and their atomic percentage (32.10% for Al and 18.26% for O in the spectrum). The small carbon peak was from organic contaminants in the air after the deposition, and its well-known binding energy of 285eV was used for calibrating the spectrum for other elements. The nitrogen and oxygen peaks were from the outgassing from the film surface, as they are the processing gases in the deposition process. Outgassing occurs
since the morphology of the film was porous, as shown in fig 3.4 later in this chapter. Aluminum nitride AlN could not form on the substrate surface in this sample since AlN will start decompose at temperature above 1370°C and bulk oxidization will occur, turning it into aluminum oxide. The substrate surface temperature was found to be above 1400°C, as shown in fig 3.12 later. From the XPS spectrums it can be concluded that aluminum oxide is being deposited onto the stainless substrate with EVAP using APPJ.

3.1.2 Characterization of Film Morphology Using Scanning Electron Microscope (SEM)

To determine film morphology, scanning electron microscope (SEM) could be used to obtain the necessary information. SEM’s is one type of electron microscope that uses electron beam to illuminate specimens and then produce an image, usually magnified from about 10x to 10kx. The electrons emitted from the SEM electron source will interact with the specimen and producing different signals to be detected in various detectors. Secondary electrons, back-scattered electrons, characteristic X-rays and cathodoluminescence are the four most typical signals produced by an SEM machine. For our application secondary electron signals alone are sufficient for the morphology determination. The SEM used for this morphology study is Hitachi S-4700 High Resolution SEM and it can resolve features down to 1.5mm at 15kV electron beam energy. Pictures of the 800W aluminum oxide film samples under SEM are shown in fig 3.2 and optical image for the 1500W sample shown in fig 3.3.
Fig 3.2: SEM images for alumina coating on stainless steel substrate via ECAP. Top: Low magnification (30x). Bottom: High magnification (5000x). Microwave power input was 800W.
Under SEM images, the deposited alumina film showed microscopic crack across the film surface, and some local delamination seems to occur as well. This is probably due to the dramatic change of substrate temperature at the end of the alumina film deposition. The APPJ plasma with 80% helium and 20% nitrogen will produce a gas temperature around 1000-1500°C with 800W input power, and it will be rapidly cooled to room temperature after deposition. This thermal shock and the difference in thermal expansion coefficient between 304 stainless steel and alumina would thus cause the film to crack and delaminate from the surface. At higher magnification, the film morphology looks porous and small spheres seems to be forming clusters on the film surface as well. It was unclear whether the same structure would still exist below the film surface or a completely different
morphology would be found beneath the surface. Thus a focus ion beam (FIB) analysis was performed and will be described in the following section.

3.1.3 Focused Ion Beam (FIB)

The working principle for a FIB machine is similar to that of a SEM, but use a focused beam of ions instead of electrons to image the sample in the chamber. Metal sources (usually gallium) are heated to wet a tungsten needle tip, and the electric field applied at this tiny tip causes the liquid metal to ionized and eject ions through field emission. These emitted ions are then focused and used for imaging. Elemental gold can also be deposited on top of the film sample surfaces to protect the film surface during this imaging process, as the high mass of the gallium ion can sputter the film surface off from the sample as well. When the desired area is located, a high current of focused gallium ion will be directed to remove material by sputtering.

From this a cross section of the film sample can be obtained and the whole structure or morphology of the film would be revealed. The FIB used in this study was FEI Dual Beam 235 FIB and has resolution up to 2.5nm for accelerating voltage between 0.2 to 30 keV. The aluminum oxide film sample was first deposited with a thin layer of gold on top of the film surface to prevent sputtering of the film from the ion gun during sputtering area selection and imaging. Pictures of the FIB for the alumina film is shown in fig 3.4 and a close up image for the film morphology is shown in fig 3.5.
Fig 3.4: FIB image showing the cross section of alumina EVAP coating on stainless steel substrate. Microwave input power was 800W.
Fig 3.5: A close up FIB image showing the porous structure of the alumina coating at 800W power on stainless steel substrate.

The morphology of the alumina sample deposited with 800W input microwave power was found to be completely porous, all the way through from the surface of the film to the film-substrate interface.

When sample deposited with 1500W input microwave power was put under the FIB imaging system, no image could be obtained due to severe surface charging. Since alumina is a ceramic material and an insulator, electrons or ions from the FIB source will slowly charge up on the surface and image contrast would be lost. This surface charging phenomena was not observed in the porous alumina film deposited with 800W microwave power, however. This raised suspicion that the morphology of
the film made with 1500W microwave power may be of a different phase or a structure that is denser than the one found in 800W, which would have more surface coverage and caused surface charging on the FIB system. Therefore, in order to resolve this alumina phase problem, an X-ray diffraction run was performed to find out whether the alumina coating obtained in ECAP are amorphous or crystalline, and whether the phase of the alumina would be different at different microwave power levels.

3.1.4 X-ray Diffraction Measurements (XRD)

X-ray diffraction is a method for determining the atomic or molecular structure of the sample. From Bragg’s law, atoms with a regular spacing (crystals) can produce a diffraction pattern as the X-ray scattering off different atoms and a constructive interference will occur when the path length difference equals to an integer multiple of the wavelength. This diffraction pattern is unique to crystal structures and thus could be used to determine phases for a material. X-ray is used to produce the diffraction pattern since their wavelengths are in the same order of magnitude as the crystal plane spacing of atoms (in the order of 1-100 Å), and thus diffraction can be maximized. A Philips X’Pert MRD system was used to perform the analysis. It uses the X-ray from the copper K-alpha line at 0.15148nm and is optimized for thin film material applications. The XRD spectrums obtained for the 800W and 1500W samples are as shown in fig 3.6 and 3.7.
Fig 3.6: XRD spectrum for the 800W alumina sample. The closest match for this spectrum is alumina in δ phase.

Fig 3.7: XRD spectrum for the 1500W alumina sample. The closest match for this spectrum is alumina in β phase.
The XRD spectrum for the 800W samples matches the spectrum of the $\delta$ phase alumina the closest, and the spectrum of the $\beta$ phase turns out to be the closest match for the 1500W sample. However, none of the alumina phases in the XRD library matches the spectrum perfectly. The spectrum of AlN and AlON were also compared to check for the possibility of nitride formation and they did not match the sample spectrum either. Thus, the only remaining logical explanation for these imperfect match sample XRD spectrums could be that these deposited alumina films actually consisted of a mix of alumina phases, and the most predominant phase in the film will show up as the closest match to the sample. Transmission electron microscope is thus used to determine whether the above assumption was true and there indeed more than one phase coexisted on the alumina film samples.

3.1.5 Transmission Electron Microscope (TEM)

Unlike SEM, the beam of electrons in a TEM transmits through the sample instead of scattering on surface of the sample. TEM has the benefit of achieving an order of magnitude higher resolution than typical SEM because the electron beam itself carries the image. It allows the user to examine the finest detail on the sample since the resolution of TEM can be as small as a single column of atoms. The TEM used for the EVAP alumina sample phase determination was the JEOL 2100 Cryo TEM. It operates at 200kV and the point resolution limit as low as 0.27nm could be achieved.

Since TEM requires a thin sample for analysis, the alumina samples deposited by ECAP were first submerged in an ethanol beaker in an ultrasonic bath for about
10 minutes. This removes the alumina coating from the stainless steel substrate and put the alumina particles in a liquid suspension. Then a micropipette was used to transfer the suspension to a holy carbon grid, the alumina particles would then adhere onto the grad after all ethanol had been evaporated, and that completes the TEM sample preparation. TEM images of the alumina sample are shown below in fig 3.8 and 3.9.

Fig 3.8: TEM image for the 800W alumina sample. Mix of amorphous and crystalline structure was observed in the image.
Fig 3.9: TEM image for the 1500W alumina sample. Crystalline structure was observed in the center part of the image.

To determine the phase from these TEM images, first the d-spacing of all different types of aluminum oxide is obtained from the XRD library. Since the image from the TEM is a two dimensional image, only crystal plane that is parallel to the z-axis are considered (i.e. l=0). The atomic spacing that is measured from the image is related to the d spacing used in crystallography through a simple equation:

\[ a = d \sqrt{(h^2 + k^2 + l^2)} \]

where \( a \) is the atomic spacing, \( d \) is the d-spacing and \( h \), \( k \), \( l \) and the Miller indexes. Fortunately, all phases except beta and gamma has a different
atomic spacing so comparing one to two spacing in the image are generally sufficient to determine the phase of alumina in the image. The d-spacing for various alumina phase and Miller indexes are listed in table 3.1.

Table 3.1: The d-spacing for various alumina phases. [33-39]

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For the 800W sample, the atom spacing was measured to be around 3.960Å between the adjacent atoms, this matches the (110) plane for the beta and gamma phase. The next closest atom was then measured to differentiate between beta and gamma, and it was measured to be 4.13Å and matches the (210) plane for the beta phase, thus the crystal in the sample was beta alumina. Similarly for the 1500W sample, the distance between adjacent atoms were measured to be 3.365 Å and that matches with the (110) plane of the alpha alumina, and thus the crystal in that sample was in alpha phase. In both cases the crystal is in a difference phase than the XRD predicted. Thus the TEM analysis confirmed there were more than one crystal phase present in both alumina thin film samples made by ECAP.
Fig 3.10: Zoom in TEM images for determining the phase of ECAP deposited alumina. Top: 800W and bottom: 1500W samples, with crystal plane direction indicated on the image.

3.2 COMSOL Computer Simulation

As the plasma in APPJ was operating in atmospheric pressure, the plasma formed was highly collisional and away from equilibrium. Also, the electron-neutral collision frequency was much greater than the plasma frequency in atmospheric pressure. Therefore, traditional characterization methods such as Langmuir probe
diagnostics would not work for measuring electron temperature, electron density, or particle distribution of the plasma. Thus, to better understand the plasma and gas condition in the APPJ during operation, COMSOL, a finite element analysis simulation software, was used to simulate the plasma gas temperature and the gas flow in the plasma region and inside the microwave torch during operation. It could give an estimate of the time average of both the gas flow profile inside the quartz tube in the APPJ and the gas temperature of the plasma formed at the tip of the tungsten antenna. The Reynolds number was calculated to be around 3000, which put it in the transition region between laminar and turbulent flow.

The standard turbulent flow kappa-epsilon model was thus used to determine the gas flow inside the APP torch. It first calculates the turbulent kinetic energy $\kappa$ and dissipation energy $\varepsilon$ in the fluid transport equation. Then the turbulent velocity $\mu$ can be calculated, since $\mu=\rho C \kappa^2/\varepsilon$, where $\rho$ is the fluid density and $C$ is an empirical determined constant around 0.09. The input flow was set to be $1.2 \times 10^{-4}$ kg/s for helium and $6.36 \times 10^{-5}$ kg/s for nitrogen, corresponding to 15 Lpm and 3 Lpm air equivalent flows respectively. The COMSOL simulation estimated the gas velocity in the APPJ quartz tube to be around 0.7m/s throughout most part of the tube, and there is an increase in velocity around the tip of the antenna up to around 0.9m/s, due to the change of shape at the tip of the antenna. Predicted flow velocities at the antenna tip for various input flow rate are shown in fig 3.12.
Fig 3.11: COMSOL simulation image for gas flow profile inside the APPJ. The highest rate of flow was located at the area outside the tip of the antenna at around 0.9 m/s.

![Gas Flow velocity at antenna tip](image)

Fig 3.12: Predicted gas flow velocity at the antenna tip by COMSOL simulation. Condition of flow in fig 3.10 is shown by the dotted lines.
By coupling the previous turbulent flow model and the RF microwave heating module, which solves for the electric field distribution and dielectric heating inside the APPJ, the plasma gas temperature was also simulated for the 800W and 1500W microwave input power case. To account for the reflected power, a USB microwave power sensor (Mini-Circuits, Model PWR-SEN-6G+, USA) was used to monitor the reflected power in the waveguide. In both cases the reflected power was measured to be around 10% of the input power and thus the net input power used for the simulation were 720 and 1350W for 800W and 1500W case respectively. The temperature of the 800W case was simulated to be around 1700°C and 1000°C at the top of the target and the location of the substrate (solid black line near the top of fig 3.13 and fig 3.14), respectively. For the 1500W case, the temperature was simulated to be around 2900°C and 1400°C respectively. Predicted temperature at the substrate center and maximum plasma temperature for various microwave power input are shown in fig 3.15.

The temperatures obtained from the COMSOL simulation seems to be physical since in both cases they are close or above the boiling point of aluminum and allow evaporation to occur. The temperature at the substrates also stays below the melting point of the 304 stainless steel. This agrees with the experimental observations since no substrate melting was observed in the ECAP experiment.

The APPJ temperature simulation results could also explain the different phases observed in the coatings made with different microwave power settings. The temperatures at the substrate were 1000°C for the 800W sample and 1400°C for the
1500W one. With reference to the transition sequence as described in figure 1.1, $\delta$ phase could be formed in temperature between 700°C to 1050°C and $\alpha$ phase would be observed in temperature above 1100°C. Both $\delta$ and $\alpha$ phase were observed in previous characterization results in the 800W sample and 1500W sample respectively, and the simulated temperature were in good agreement with the alumina phases obtained in the experiment.

Fig 3.13: COMSOL simulation image for plasma temperature profile of APPJ at 800W input power.
Fig 3.14: COMSOL simulation image for plasma temperature profile of APPJ at 1500W input power.

Fig 3.15: Predicted temperature at the substrate center and maximum plasma temperature by COMSOL simulation. Temperature profile in fig 3.11 and 3.12 are shown by the dotted lines.
4.1 Conclusions

Aluminum targets have been evaporated using microwave APPJ in the ECAP experiment. It was demonstrated that aluminum oxide could be successfully coated onto 304 stainless steel substrates using ECAP with helium and nitrogen gas mix and APP microwave plasma. Only high purity aluminum target could produce aluminum oxide coating at an observable rate, and using aluminum chloride as the target would result in chloride contamination of the film. Many techniques such as XPS, SEM, FIB, XRD and TEM were used to characterize the alumina film formed using this deposition method. The film was confirmed to be aluminum oxide from the elemental composition. The film morphology was found to be porous under low power deposition but denser under high power deposition conditions. Nitrogen and helium was also found on the film surface as they were outgassing from the porous film during XPS measurements. $\delta$ phase and $\beta$ phase alumina was found in the 800W sample and $\beta$ phase and $\alpha$ phase alumina was found in the 1500W sample. The phase of the deposited alumina film was determined to vary according to changes in input microwave power, and more than one phase of alumina could simultaneously form in the alumina film, in the form of nano crystal, and could be seen under TEM images. Different phases of alumina nano crystal could be identified by measuring the $d$-spacing on the TEM images and comparing them to the known data spacing values of various phases.
The plasma gas and temperature profile of the microwave APPJ was simulated using finite element analysis simulation software COMSOL. The Reynolds number was calculated to be around 3000 and the flow inside the APPJ was in turbulent regime. The standard turbulent flow kappa epsilon model was used to model this turbulent flow inside the APPJ. The flow profile was found to peak around the antenna tip. By coupling the turbulent flow model and the RF microwave heating model, the dielectric heating inside the APPJ and thus the temperature profile was simulated. The temperature profile was found to be close to the boiling point of the alumina at the target surface and below melting point of the 304 stainless steel at the substrate surface. The temperature profile also correctly predicted the different phases obtained for samples prepared with different input microwave power.

4.2 Future Work

Different type of substrate could be used in addition to stainless steel substrates. Alumina is a good protection barrier to reactive metals such as copper, but it has a much lower melting point and so the substrate distance and microwave power may have to be recalibrated to avoid substrate damage in copper or other material with lower melting points.

For the phase control of the alumina film obtained in this study, a higher power of microwave input could be used to increase plasma temperature or to anneal the substrate after deposition if the alpha phase is the desired phase for the application. However this would probably require remote and automated control of the system as
microwave leakage would increase and safety to the operating personal would have to be considered. Also, oxygen could be used in the gas mix as an additional source of oxygen in addition to the ambient oxygen. The temperature profile of the plasma could also be changed by varying the amount of oxygen added into the APPJ. Currently the temperature profile would be too low for deposition when oxygen is introduced into the APPJ, so this may have to be done simultaneously with the increase in power and automation so that a reasonable deposition rate could be observed.

In order to have a more detail understanding of the mechanism involved in the alumina film formation and the aluminum target consumption, plasma modeling, target modeling and the modeling of the interaction between plasma and target may be studied. For the plasma modeling, all the interaction cross sections for the four components in the current plasma (helium and nitrogen from gas feed, oxygen and water vapor from ambient air) must be considered for an accurate estimate of all the plasma parameters for the APPJ during operation. The aluminum target also requires a molecular dynamic modeling to model the shape changes and gas absorption of the processing gases in the molten phase of the target during deposition. Finally the interaction between the atmospheric plasma and the aluminum target have to be modeled for the energy transfer from the ions and neutrals of the plasma to the aluminum target while moving across its surface.
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