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Deposition of aluminum oxide by evaporative coating at atmospheric pressure (ECAP)

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ABSTRACT

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. Following the similar concept as the laser-assisted plasma coating at atmospheric pressure (LAPCAP) [1], 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. By using the thermal energy from the microwave plasma, solid 99.99% + purity aluminum were evaporated and then produce a PVD-like alumina coating on a work piece. The aluminum target was inserted in the center of the microwave torch feeding a melt pool and evaporated into the surrounding plasma plume. A bottle neck was made in the antenna and could reduce the heat loss by 84%, thus allowing higher temperatures to exist in the sample-holder antenna tip. Gas shielding was used to keep the work gas pure. The film was deposited as Al_2O_3 using oxygen from the environment. Deposition rate was around 2 μm/min. Gas flow rate around the antenna tip was about 0.9 m/s, and the temperature of the plasma was about 1400 °C at 1350 W input power from simulations. Alpha and other metastable phases of aluminum oxide were found on the deposited films.

1. Introduction

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 and chemically stable, and these properties make it suitable for many different applications [6,10–12]. Alumina could be found in a number of crystalline phases or polymorphs (α, γ, η, δ, κ, χ, etc.), the α phase is thermodynamically stable at any temperatures up to its melting temperature at 2051 °C, but the other metastable phases like γ or θ also appears frequently in alumina growth studies as well [2]. 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 [3].

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 the 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 [2,3,6,10–12]. Fig. 1 illustrates some phase transition relations for the common metastable alumina phases [4,5]. The transformations to the phase from other metastable phases typically take place at above 1000 °C and are all irreversible [3,6].

Currently, the most common method for depositing aluminum oxide is though 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. In the case of aluminum oxide, it can be done by using trimethylaluminum (TMA), aluminum chloride as the precursor in plasma enhanced CVD (PECVD) and aluminum tri-isopropoxide (ATI) with thermal CVD [7]. 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 1–10 nm/min [8,9], 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 [13]. 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 [13].

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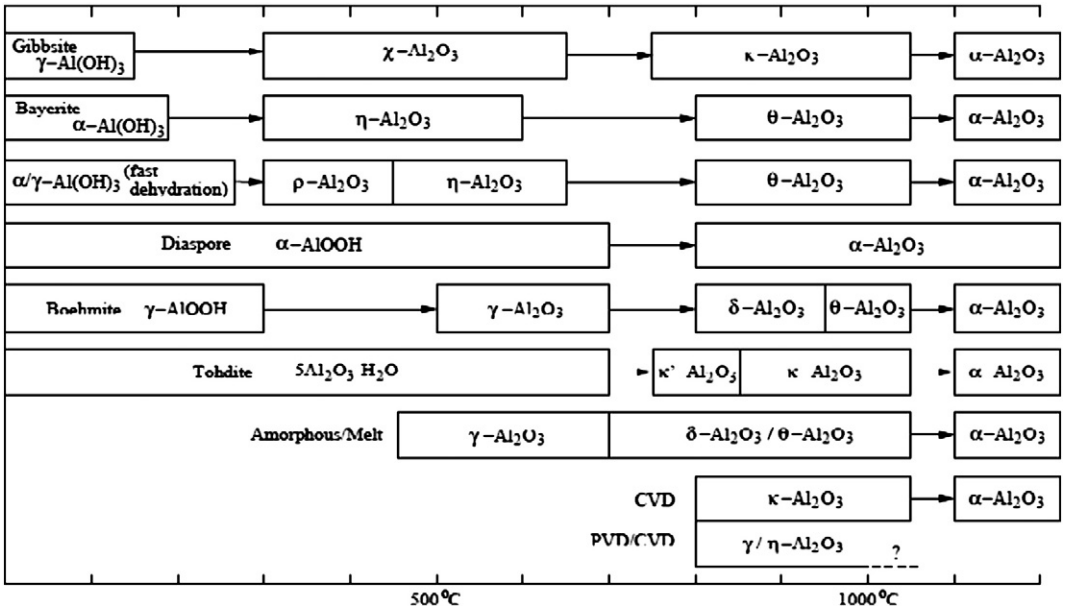

Fig. 1. Commonly accepted transition sequences of the alumina from the hydroxides to corundum (α-Al_2O_3) during thermal treatment [4,5].

For the first time, aluminum oxide thin films will be created by microwave plasma jet under atmospheric pressure conditions. 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. Compared with other common low pressure process such as RF sputtering or DC reactive sputtering, the ECAP concept can achieve deposition rate of one to two orders of magnitude higher while achieving similar film morphologies and properties [21,22]. Also since it is an atmospheric process, no expensive vacuum chamber or vacuum equipment are needed. Unlike other plasma torch spray processes, the ECAP system does not require an external source of aluminum oxide powder to be brought into the plasma spray to coat the substrate; rather, it uses the aluminum from its antenna and converts it into the aluminum oxide film desired with the microwave power and surrounding oxygen while it reaches the substrate surface. Additionally, it can be easily modified to deposit with different materials or on non-planar surfaces by simply using a gas shield around the torch or implementing automation between the atmospheric torch and the substrate.

2. Experimental

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 12-kW power input, and the output varies from approximately 0.5 to 6 kW 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. The aluminum E-Band, H-Bend, two-port circulator, dual directional coupler and 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.

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 (11 mm) DIN adapter by RF Parts Company, USA. The diameter of the tungsten antenna was ¼" (6.35 mm) in diameter and 6 ¼" (158.75 mm) in length. The quartz discharge tube had an outer diameter of 16.2 mm and an inner diameter of 13 mm, 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 flow meters made by Dwyze Instruments, Inc., USA. They can be individually controlled in order to generate different types of plasma with different gas mixtures.

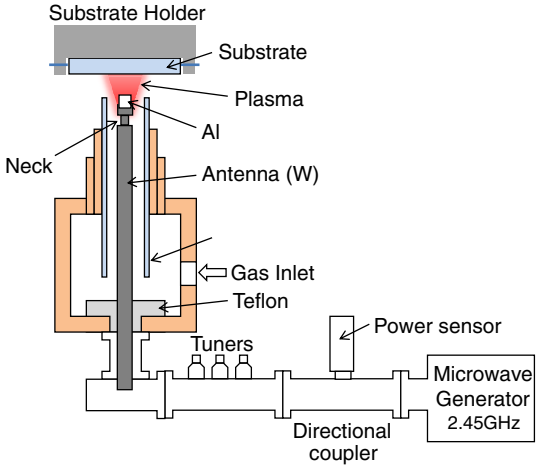

Fig. 2. Schematic figure of the atmospheric pressure plasma torch (APPT) [8].