IOP Conf. Series: Journal of Physics: Conf. Series **850** (2017) 012022 doi:10.1088/1742-6596/850/1/012022

SYNTHESIS OF ALUMINA THIN FILMS USING REACTIVE MAGNETRON SPUTTERING METHOD

G Angarita, C Palacio, M Trujillo, M Arroyave

Universidad EAFIT, Applied Electromagnetism Research Group, Cr49, No.7 sur 50, Medellin, Colombia

Email: langari3@eafit.edu.co

Abstract. Alumina (Al_2O_3) thin films were deposited on Si (100) by Magnetron Sputtering in reactive conditions between an aluminium target and oxygen 99.99% pure. The plasma was formed employing Argon with an R.F power of 100 W, the dwelling time was 3 hours. 4 samples were produced with temperatures between 350 and 400 ºC in the substrate by using an oxygen flow of 2 and 8 sccm, the remaining parameters of the process were fixed. The coatings and substrates were characterized using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Energy Dispersive Spectroscopy (EDS) in order to compare their properties before and after deposition. The films thicknesses were between 47 and 70 nm. The results show that at high oxygen flow the alumina structure prevails in the coatings while at lower oxygen flow only aluminum is deposited in the coatings. It was shown that the temperature increases grain size and roughness while decreasing the thicknesses of the coatings.

1. Introduction

Aluminum oxide or Alumina (Al_2O_3) is an outstanding ceramic material which, due to its several excellent physical and chemical properties like high electric resistivity, low thermal conductivity, high melting temperature, high hardness, refractive index of 1.7 [1], high abrasion and oxidation resistance, finds application in cutting tools, optoelectronics devices, diffusion and thermal barriers [2]. Al_2O_3 has several metastable phases structures where the most reported are: cubic γ and η phases, the monoclinic θ phase, the hexagonal χ phase, the orthorhombic κ phase and the δ phase that can be tetragonal or orthorhombic [3]. Al_2O_3 only has one stable phase (α-Al_2O_3) with a trigonal hR30 structure, melting point of 2043 ºC, and a relatively high hardness (21 GPa) [4]. The metastable phases appear when alumina is being heated in thermal processes like annealing; the ranges in which the metastable phases are formed depend upon the composition and structure of the initial material, where the stable α-Al_2O_3 is formed at about 650 ºC [4]. A large number of techniques have been reported for the deposition of amorphous and crystalline alumina in the literature, such as magnetron sputtering, ion assisted deposition, pulsed laser deposition, electron beam evaporation, chemical vapor deposition and sol-gel deposition [5]. This work focuses in the deposition of crystalline alumina from reactive magnetron sputtering technique by controlling the substrate temperature and oxygen flow.

2. Materials and Methods

Al_2O_3 films were deposited by reactive magnetron sputtering on p-type silicon (100) substrates (15 x 15 mm^2) with a native oxide layer on top of around 10 nm thick. The substrates were ultrasonically cleaned in isopropanol for 10 minutes and dried with nitrogen gas. A 99.9995 % pure Aluminum target with 50.80 mm in diameter and 6.35 mm thick was used. Prior to the deposition, the chamber was evacuated with a turbomolecular pump to a background pressure of 4.2 x 10^{-6} Torr. Ultra high purity (99.9999%) argon and oxygen gasses (Oxygen/Argon ratio of 1/5) were then introduced into the chamber using a mass flow regulator system. The desired working pressure of 6 x 10^{-3} Torr was obtained by regulating the pumping speed, which is controlled by a throttle valve in the path of high vacuum line connecting the chamber to the turbomolecular pump. Before deposition, a pre-sputtering was performed at 100 W RF power for 10 minutes in order to clean the surface of the Al target. The deposition time for all coatings was fixed at 3 hours and the influence of the substrate temperature and oxygen flow was evaluated by employing a factorial design using these two parameters at two different levels chosen according to the ranges found in the literature (2^2 factorial design) [6]. Oxygen flow varied from 2 to 8 sccm and the temperature levels were chosen at 350 and 400ºC.

The morphological properties and deposition rate of the films were evaluated using Atomic Force Microscopy (AFM) with a NANOSURF EasyScan 2 device using a CT170 tip in noncontact mode. The deposition rate of the coatings was measured by marking a line on the substrates with an alcohol soluble marker in order to create step heights that were then measured by AFM. The roughness measurements were made over an area of 50 x 50 μm^2 and the grain size measurements were made over 5 x 5 μm^2. Meanwhile, Scanning Electron Microscopy (SEM) was used to evaluate the morphology of the coatings, and Energy Disperse Spectroscopy X-Ray (EDS) was used to qualitatively observe the different elements in the deposited coatings, these two techniques were accomplished by using a JEOL JSM-6701F Field Emission Scanning Electron Microscope (FESEM). X-Ray Diffraction (XRD) was used to study the crystalline phases of the coatings with a PANalytical Diffractometer Empyrean device using a copper anode ($K\alpha$ = 1.5405 Å and $K\beta$ = 1.5444 Å).

3. Results and discussion

3.1. Scanning Electron microscopy

Figure 1. shows a micrograph taken by FE-SEM at 270,000 magnifications of the deposited films, where a granular structure can be seen, this structure is typical of coatings deposited by sputtering.

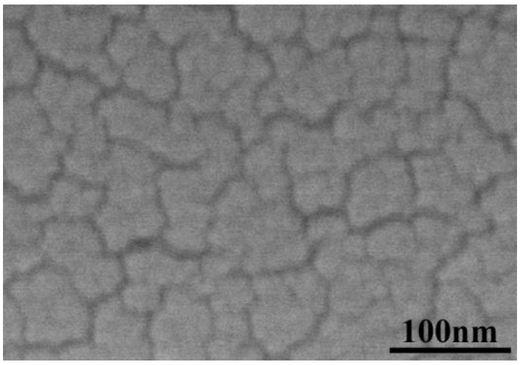

Figure 1. FE-SEM micrograph of a coating deposited at 350ºC and 8sccm.

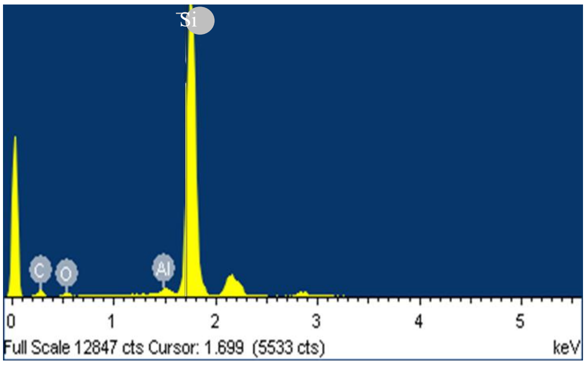

Figure 2. EDS analysis of a coating deposited at 350ºC and 8sccm.

EDS graph (Figure 2) shows the presence of aluminum, oxygen, silicon and carbon in the samples, which proves that aluminum in presence of oxygen was deposited; the silicon is attributed to the substrate and carbon to the impurities of the environment.

3.2. Atomic force microscopy
The measured thickness and calculated deposition rate of the films can be observed in Figure 3, which reveals that the higher the temperature, the more material is deposited, this can be attributed to a greater affinity of the aluminum and oxygen adatoms [7] to the substrate surface at high temperatures.

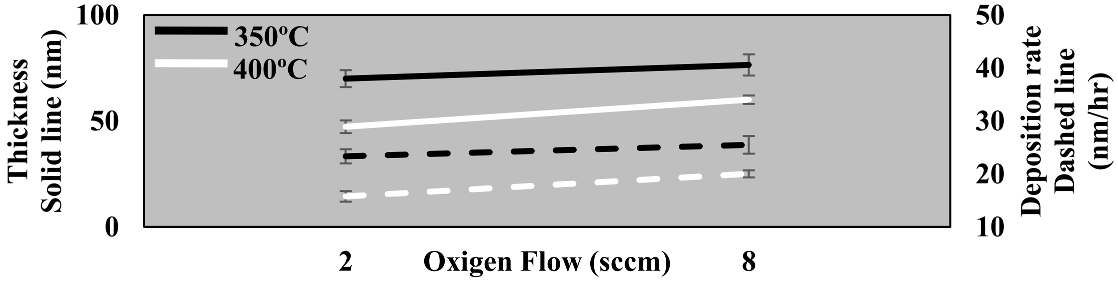

Figure 3. Oxygen and temperature influence in the thicknesses (solid lines) and sputtering rates (dashed lines) of the coatings.

Figure 4 shows the morphology of the coating, were a granular structure with some cluster type grain agglomerations can be seen, this structure is typical of coatings deposited by sputtering where the films growth is of columnar nature.

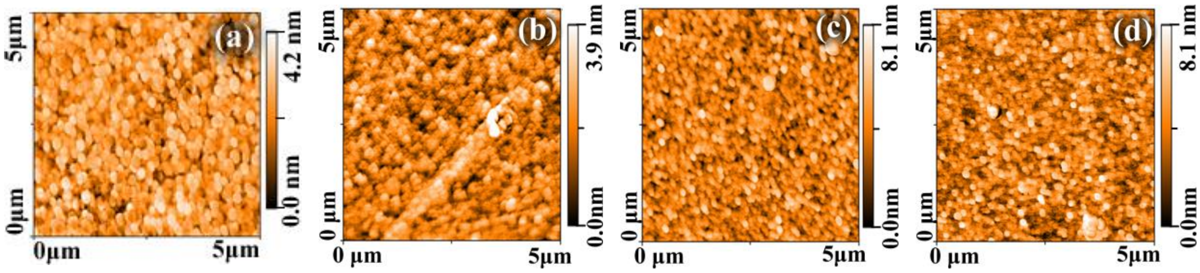

Figure 4. AFM micrographs of deposited coatings at: (a) 350ºC and 2 sccm, (b) 350ºC and 8 sccm, (c) 400ºC and 2 sccm and (d) 400ºC and 8 sccm.

Figure 5 shows the grain sizes and roughness of the coatings. It can be seen that the grain size and roughness decreases when the temperature increases, this behaviour can be explained by the increase of the nucleation sites due to a larger travel time of the adatoms in the substrate surface which in turn produces higher quantity of grains with small grain sizes in the film [7].

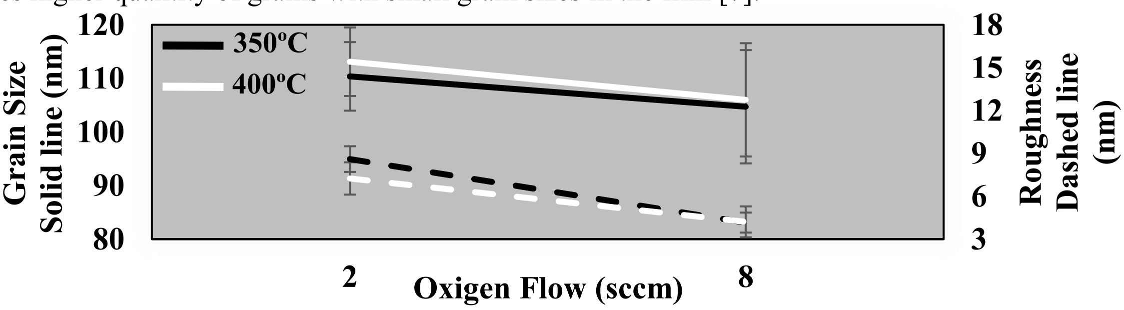

Figure 5. Oxygen flow and substrate temperature influence in the grain size (solid line) and roughness (dashed line) of the deposited films.

3.3. X-Ray diffraction
The normalized XRD spectra of the films is shown in Figure 6. The patterns used for the identification of the XRD peaks belong to the ICCD and COD databases and have the following reference codes: 00-026-0031 (Al_2O_3) [8], 96-901-2003 (Al) [9] and 96-901-2602 (SiO_2) [10].

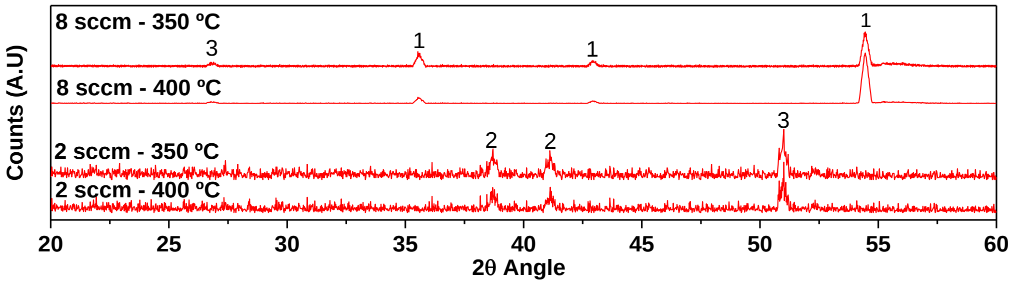

Figure 6. XRD spectra of the synthetized coatings, 1) κ-Al_2O_3 [8], 2) Al [9], 3) SiO_2 [10].

Figure 6 shows that under high oxygen flow (8 sccm) orthorhombic alumina (κ-Al_2O_3) was formed in the films. At low oxygen flow (2 sccm) only aluminum and a greater noise in the XRD can be observed, this is attributed to the low content of oxygen in the chamber, which is not enough to form a stoichiometric alumina structure in the entire film. The high noise can be attributed to a film rich in aluminum with a somewhat amorphous structure from the little reaction between aluminum and oxygen. In the other hand, the temperature at which the experiments were carried out was not enough to make an important change in the XRD spectra of the coatings.

4. Conclusions

Orthorhombic alumina (κ-Al_2O_3) films were produced by reactive RF magnetron sputtering with grain sizes ranging from 100 and 115 nm. The oxygen flow plays a crucial role in synthesizing alumina; it was found that at 2 sccm only Aluminium was deposited whereas at 8 sccm the quantity of oxygen was enough to form Al_2O_3. In addition, it was found that at higher oxygen flow rates, the coatings had an increase in their grain size and roughness.

It was found that the substrate temperature was not sufficient to cause changes in the crystalline structure of the material; however, there were found significant decreases in the thickness of the coatings at higher temperatures as well as increases in their roughness and grain size.

References

[1] Wypych G 2010 Physical and Chemical Properties *Handbook of Fillers (3rd Edition).*

[2] Khanna A and Bhat D G 2006 Nanocrystalline gamma alumina coatings by inverted cylindrical magnetron sputtering *Surf. Coatings Technol.* **201** 168–73.

[3] Levin I and Brandon D 1998 Metastable Alumina Polymorphs: Crystal Structures and Transition Sequences *J. Am. Ceram. Soc.* **81** 1995–2012.

[4] Zhang S and Ali N 2007 The Physical, Mechanical, and Thermal Properties of Hard Materials *Nanocomposite thin films and coatings : processing, properties and performance* (Imperial College Press) p 615.

[5] Zhang X, Zhu J, Zhang L, Kishimoto K, Du S and Yin X 2013 Crystallization of alumina films deposited by reactive magnetron sputtering with resputtering technique at low temperature *Surf. Coatings Technol.* **228** S393–6.

[6] Box G E P, Hunter J S and Hunter W G 2005 *Statistics for Experilllenters: Design, Innovation, and Discovery* (New Jersey: Wiley-Interscience).

[7] Mattox D M 1998 *HANDBOOK OF PHYSICAL VAPOR DEPOSITION (PVD): Film Formation, Adhesion , Surface preparation and contamination control* (Noyes Publications).

[8] Okumiya M and Yamaguchi G 1971 The Crystal Structure of κ′-Al 2 O 3 , the New Intermediate Phase *Bull. Chem. Soc. Jpn.* **44** 1567–70.

[9] Fortes A D, Wood I G, Vočadlo L, Knight K S, Marshall W G, Tucker M G and Fernandez -Alonso F 2009 Phase behaviour and thermoelastic properties of perdeuterated ammonia hydrate and ice polymorphs from 0 to 2GPa *J. Appl. Crystallogr.* **42** 846–66.

[10] Hazen R M, Finger L W, Hemley R J and Mao H K 1989 High-pressure crystal chemistry and amorphization of quartz *Solid State Commun.* **72** 507–11.