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Synthesis and characterization of amorphous aluminum oxide thin films prepared by spray pyrolysis: Effects of substrate temperature

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ABSTRACT

Amorphous and non-crystalline aluminum oxide thin films have been deposited on glass substrate by spray pyrolysis method. The structural, morphological and optical properties were investigated using X-Ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV-visible spectrophotometry. For two specific molarities (0.15 M and 0.25 M), substrate temperature was varied between 250 °C, 350 °C, 500 °C, and 550 °C. The XRD results exhibited dominant amorphous nature for all samples as expected, whereas SEM and AFM showed the presence of substrate temperature effects on alumina thin film properties. Enhancement of optical transmittance with temperature increase was observed. Using the transmittance data other optical quantities namely absorption coefficient, optical band gap, refractive index and extinction coefficient, dielectric constants, volume and surface energy loss functions and optical conductivity were determined. It was also observed that the volume energy loss (VELF) increases more than the surface energy loss (SELF).

1. Introduction

Aluminum oxide, or in the more famous name alumina, as an important member of the family of the ceramics has a wide range of applications such as microelectronic and nanoelectronic devices [1] and its different categories like metal-oxide semiconductor, based structures as gate oxides [2], metal–nitride–oxide–semiconductor, complementary metal–oxide–semiconductor devices [3], VLSI applications, alternating-current thin-film electroluminescent (ACTFEL) [4] and various coatings such as refractory coatings, antireflection coatings, anticorrosive coatings [5], water-repellent coatings [6], and sporadic application such as humidity sensors [7], ceramic–metal composites [8], bioceramic materials in bioengineering [9], organic light emitting devices, solar selective coatings [10], bar code readers, optical lenses and windows [11].

To achieve such capabilities, alumina should have unique properties [12], such as high thermal conductivity, high hardness, high radiation resistance [13], high refractive index [2], high dielectric constant [14,15], high chemical and thermal stability [16,17] and high transparency [1].

Different and sometimes contradictory properties of alumina make it versatile and according to our tendency, we can use it; for example for optoelectronic applications, good homogeneity with both good density and dielectric characteristics as well as a low surface roughness [2] is preferred whereas in solar selective coatings and humidity measurements high porosity is required [1,18].

Amorphous alumina thin films can be deposited by several techniques such as solution-chemistry [19], chemical vapor deposition [20], metal-organic chemical vapor deposition [21], spray pyrolysis [22,1,16], thermal evaporation [23],electron beam evaporation [1,24], magnetron sputtering [25,26], off plane filtered arc method [27], anodization [28,29], plasma enhanced chemical vapor deposition [30], filtered vacuum arc [31], plasma-enhanced chemical vapor deposition [32], sol–gel [4,33], electrophoretic deposition at low temperatures [34], pulsed laser deposition [35], aerosol-jet deposition [36,11], and atomic layer deposition [37,38].

Within this approach, spray pyrolysis is suitable for the preparation of efficient, time-resistant and inexpensive alumina thin films [12],since it is very simple, low cost and does not require vacuum or exotic gas [1,39]. In this method, the film formation takes place by the condensation of atoms or molecules onto a heated substrate. Thus, the substrate temperature, carrier gas flow, substrate rotating speed, number of spraying sequences, spraying distance, solution flow rate and molarity play an important role in forming the structure of the films ranging from amorphous to crystalline.

As many researchers investigated the various aspects of alumina either bulk or thin film, amorphous or crystalline structure, but their most efforts concentrated on limited physical properties of alumina such as electrical properties and its application as a humidity sensor [1,7], morphological and structural properties and its application as a solar thermal absorber [12,16], different preparation conditions and doping material for optimized layer [19,40], electronic structure and

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electron energy loss function of alumina [41–43], corrosion behavior of alumina based ceramics [5,44] and different theoretical evaluations of alumina properties [45]. Although there are several reports with notable and useful results especially by sol–gel [17] and spray pyrolysis [2,15,46] methods, but among the broad scope of the subject, we have strived to cover more physical properties of alumina thin films than their works.

In this report we have prepared alumina thin films at different substrate temperatures in two specific molarities onto glass substrate by SP and investigated their structural, morphological and optical properties such as refractive index, absorption coefficient, extinction coefficient, band gap, dielectric constants, surface and volume energy loss, and optical conductivity.

2. Experimental details

Our SP device is an experimental apparatus (SCS 86, made by Modern Technology Development Co., Iran), and has the following typical features: spraying unit including a swivel stainless steel (ss) plate over the heater for rotation and heat treatment of substrate, a moving (up and down and rotational) nozzle unit with its controlling tools (e.g. velocity, distance, pressure, aperture diameter,…), solution time controller and compressor.

Our optimized values are as follow: The nozzle-substrate distance (H = 27 cm) and the carrier gas pressure (air, p = 1.5 bars), these conditions as well as substrate rotational speed, nozzle aperture diameter and time of solution spraying are fixed and substrate temperature is varied between 250 °C, 350 °C, 500 °C, and 550 °C while the molarity was in two fixed values 0.15 M and 0.25 M.

Aqueous alcoholic solutions of $AlCl_3$ (98%, Merck), with a volume of 50 ml, were used as precursors for the alumina films preparation. Deionized water (W) and absolute ethanol (C_2H_5OH, 99.9%, Merck) were used as solvents (with an equal volume percent). The precursor solutions with different molarities — namely 0.15 mol/L, and 0.25 mol/L concentrations, were sprayed perpendicularly onto preheated glass substrates (previously immersed in HNO_3 10% solution for 24 h and then cleaned with acetone and dry air) at various substrate temperatures. This range was chosen intentionally since slow reaction at lower temperatures (<250 °C) would yield foggy films due to insufficient time for the spreading of the droplets. At high substrate temperatures (>550 °C) chemical reaction takes place before the vapor reaches the substrate and gives powdery coating [6]. Moreover, at higher temperature the glass substrate will deteriorate, and a diffusion of substrate elements to main layer is possible [39].

To achieve higher substrate temperature, other substrates should be used like as silicon, quartz or metallic ones. Fig. 1 shows a flowchart of the procedure that was used for depositing the alumina thin films using spray pyrolysis route.

The films structure and composition were investigated using an X-ray diffractometer (PW 1840-Diffractometer, Philips) with CuKα(40 KV, 30 mA) radiation. The surface morphology was observed using a Scanning Electron Microscope (SEM) HITACHI S4160. Surface measurement was done with an atomic force microscopy (AFM) by Veeco CP Research instrument using Si cantilever. The thickness were measured by Dektak Profilometer. Optical transmission for samples measured with a Varian Cary100 UV/Visible spectrophotometer. The optical constants of the films were calculated using pointwise unconstrained minimization approach (PUMA) [47].

For easier refer to the samples, they are named as follow:

3. Results and discussion

The XRD patterns of alumina thin films deposited at different molarities and substrate temperatures are presented in Fig. 2. Apparently, no significant differences can be observed between them, all the films containing a dominant amorphous phases especially at higher

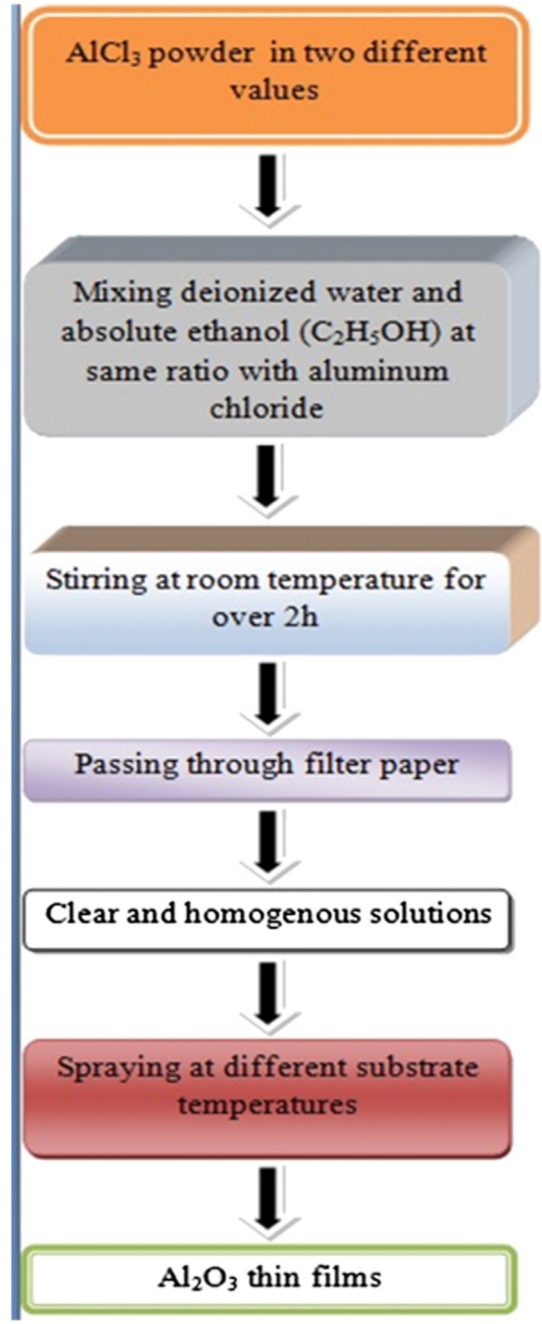

Fig. 1. The flowchart of the procedure of preparing alumina thin films.

temperature, it is accepted that alumina in the temperature range below 600 °C has an amorphous structure regardless of the deposition methods [1,7,37] even with some doping material [40].

The SEM micrographs of alumina thin films at different substrate temperatures in two specific molarities are shown in Fig. 3. From the micrographs, one can see that in each molarity, the samples initially consisted of nanosized grains that gradually start to interconnect with each other by increasing the substrate temperature, until an incorporated Coalescence of the grains is formed, of course some pores also start growing with temperature increment over the surface and it seems a spongy structure is formed. This may be attributed to vacancies due to volatile molecules that have left the samples surface by heat treatment. The radius of these pores is increased with addition of substrate temperature.

Such structure is suitable for special applications such as solar spectral selectivity (trapping of solar light or infiltration of metal