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Growth and molarity effects on properties of alumina thin films obtained by spray pyrolysis

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A B S T R A C T

Various and versatile applications of alumina in materials science and engineering specially in semiconductor and energy conversion technology encouraged us to prepare and investigate its physical properties as much as possible. Hence, after depositing of alumina thin films on glass substrates by a spray pyrolysis technique, structural, morphological, and optical properties of the films were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and UV–visible spectrophotometry. Different optical quantities, such as optical band gap, refractive index and extinction coefficient, were determined in this article for different molarities (from 0.10 M to 0.25 M) at two specific substrate temperatures (250 °C and 500 °C). XRD results showed the prevailing amorphous phase in all samples as expected, whereas SEM, XPS, and FTIR presented the presence of molarity effects on alumina properties. Decrease of optical transmittance with molarity increase was notable. Using the transmittance data other optical quantities were obtained by a numerical approximation method.

1. Introduction

Alumina is the most cost effective and widely used material in the family of engineering ceramics. Aluminum oxide, commonly referred to as alumina, possesses strong ionic interatomic bonding giving rise to its desirable material characteristics. Alumina thin films are considered materials of interest because of their excellent properties [1,2], such as high thermal conductivity, low permeability of alkali ions, high hardness [3], high chemical and thermal stability [4], and high radiation resistance [3]. These films also possess a high refractive index [5], high dielectric constant [6,7], durability against hostile environments and high transparency [8].

Due to these properties, alumina thin films have a wide range of applications: metal-oxide semiconductors (MOS) [9], SONOS (metal-nitride-oxide-semiconductor) and CMOS (complementary metal-oxide-semiconductor) devices [10] based structures as gate oxides [11], thin-film transistors (TFTs) [12], surface passivation of silicon solar cells [13], refractory coatings, antireflection coatings, anticorrosive coatings [9], microelectronic devices, capacitance humidity sensors, heat sinks in ICs and passivation of metal surfaces, VLSI applications [6], water-repellent coatings [8], waveguide lasers, buffer layers for superconductors [2], organic light emitting devices (OLED), solar selective coatings, bar code readers, optical lenses, and windows [14].

Most of the optoelectronic applications require films with good homogeneity, both good density and dielectric characteristics as well as a low surface roughness [11]. Although in solar selective coatings and special applications (e.g. humidity measurements [6]) we face different situations, the surface morphology (high porosity) plays a key role in the device efficiency [15].

Alumina thin films can be deposited by several techniques such as solution-chemistry [4,16], chemical vapor deposition (CVD) [17], metal–organic chemical vapor deposition (MOVCD) [3], spray pyrolysis [5,12,18], electron

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beam deposition [19], magnetron sputtering [20,21], off plane filtered arc method [22], anodization [23], filtered vacuum arc [24], plasma-enhanced chemical vapor deposition (PECVD) [25], sol–gel [26,27], electrophoretic deposition at low temperatures [28], pulsed laser deposition [29,30], aerosol-jet deposition (AJD) [31,14], and atomic layer deposition (ALD) [32–34].

On one hand, wide range application areas make synthesis and characterization of aluminum oxide films attractive, and on the other hand, there are few reports of fabrication of transparent alumina thin films [14], especially by a spray pyrolysis technique. Spray pyrolysis is suitable for the preparation of efficient, time-resistant and inexpensive alumina thin films. They can be easily prepared using spray pyrolysis since it is a very simple, low cost method over large area [6], and does not require vacuum or exotic gas. In this method, the deposition process needs fine droplets to react on the heated substrate, owing to the pyrolytic decomposition of the solution. The hot substrate provides thermal energy for thermal decomposition and subsequent recombination of the constituent species. The phenomenon for the preparation of a metal oxide thin film depends on surface hydrolysis of metal salt on a heated substrate surface [35]. 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 mentioned before, there are not many reports about preparation and complete characterization of alumina thin films. Many researchers are interested in certain aspects of alumina. Shamala et al. have performed an admirable work on investigating its characteristics but focused on electrical properties and its application as a humidity sensor [6,9]. Duta et al. have also characterized morphological and structural aspects of these films as a solar thermal absorber [2,15].

There are numerous reports about depositing alumina thin films using aluminum(III) acetylacetonate dissolved in different solvents [5,6,9,11,12], but we have examined aluminum(III) chloride as a precursor according to Duta et al. [2,15,18] methods in different molarities at two specific substrate temperatures onto glass substrate by spray pyrolysis (SP) to compare them in different situations, and investigated their structural, morphological and optical properties such as refractive index, extinction coefficient, and band gap.

2. Experimental details

Our SP device is an experimental apparatus named 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 a 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, etc.), solution time controller, and compressor.

Our optimized values are as follows: the nozzle–substrate distance ($H=27$ cm) and the carrier gas pressure (air) $p=1.5$ bar. These conditions as well as substrate rotation speed and nozzle aperture diameter are fixed. The substrate temperatures are adjusted at two specific values (250 °C and 500 °C). An electronically controlled resistive heater was used to achieve such desired substrate temperatures. Since we sprayed all contents of solutions, different durations and thicknesses are obtained in each case.

50 mL aqueous alcoholic solutions of $AlCl_3$ (98%, Merck) 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 (water:ethanol = 1:1, in volumes). The precursor solutions with different molarities, namely 0.10 mol/L, 0.15 mol/L, 0.20 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 two fixed substrate temperatures. These substrate temperatures were 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 higher substrate temperatures (250–500 °C) evaporation and precipitate sublimation occur in succession and vapors diffuse towards the substrate, where they react chemically in heterogeneous gas–solid form to give the final film. At very high substrate temperatures chemical reaction takes place before the vapor reaches the substrate and gives powdery coating [6].

The films structure and composition were investigated using an X-ray diffractometer (PW 1840-Diffractometer, Philips) with Cu Kα (15 kV, 30 mA) radiation. The surface morphology was observed using a scanning electron microscope (SEM) HITACHI S4160. Surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, Twin Anode XR3E2, X-ray Source Systems). Infrared spectrum of samples was recorded using a Fourier transformed infrared (FTIR) spectrophotometer (Perkin-Elmer spectrum 65). Thickness measurement of the films was done by a Dektak system. Optical transmission for samples was measured with a Varian Cary100 UV/visible spectrophotometer. The optical constants of the films were calculated using a point-wise unconstrained minimization approach [36,37].

For easier reference to the samples, they are named as shown in Table 1.

3. Results and discussion

The XRD patterns of alumina thin films deposited at different molarities and substrate temperatures are presented in Fig. 1. Apparently, no significant differences can be observed between them. All the films contain dominant amorphous phases especially at 500 °C. Although it is possible to form some by-products such as AlOOH and

Table 1
Sample labels.

	0.10 M	0.15 M	0.20 M	0.25 M
250 °C	A1	B1	C1	D1
500 °C	A2	B2	C2	D2