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Research Article

PREPARATION OF ALUMINA (Al_2O_3) THIN FILMS BY SOL-GEL DIP COATING AND CHARACTERIZATION

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ABSTRACT

Aluminium oxide (Al_2O_3) thin films are an outstanding ceramic material due to its excellent properties. Al_2O_3 thin films are deposited on Si (100) and quartz substrates using sol-gel dip coating technique. The films are deposited with 15 dips and the films are annealed at different temperatures such as 100°C, 200°C, 400°C and 600^{0}C. The films are analysed using X-ray diffractometer (XRD) and double beam UV-Visible spectrophotometer to study the structural and optical properties. The XRD studies of the films deposited on Si (100) substrates annealed at 200°C, 400°C and 600°C showed the sharp peaks indicating the polycrystalline θ-Al_2O_3 of cubic structure, whereas the films deposited on quartz substrates indicated the formation of polycrystalline γ-Al_2O_3 of cubic structure with less intensity. The optical studies of the films on quartz substrates showed the absorbance ~ 265-205 nm wavelength indicating the bandgap of ~ 4.68 eV, 4.82 eV, 5.37 eV and 6.1 eV in the annealed temperature of 100°C, 200°C, 400°C and 600°C respectively. The transmittance of the films is ~90-95% depending on the annealed temperature. The effect of annealed temperature on the structural and optical properties of the Al_2O_3 films is investigated.

INTRODUCTION

Aluminium oxide or Alumina (Al_2O_3) is a polymorphic material exists in several crystalline phases such as γ, η, θ, δ, k and α phases at different ambient conditions. The formation of Al_2O_3 phases is dependent on the deposition technique and the processing parameters such as pressure and temperature [1-3]. Normally, amorphous phase forms at low temperatures; γ-Al_2O_3 phase is dominant at intermediate temperatures and α-Al_2O_3 phases tend to grow at high temperatures. Al_2O_3 is an important ceramics offering excellent physical and chemical properties such as high melting temperature, high hardness, high transparency, medium refractive index, wide bandgap, abrasion and oxidation resistance and good thermal properties. Al_2O_3 ceramics are widely used by the electric and electronic industries [4-6].

Thin films of Al_2O_3 have received attention due to their applications in optical coatings, opto-electronics, oxygen permeation barrier coatings, dielectric layers, wear-resistant coatings, refractory coatings, anti-reflection coatings, anticorrosive coatings, microelectronic devices and sensors. It's wide transparency, good thermal and chemical stability, superior electrical and mechanical properties make it suitable for wide range of applications. Due to its high electrical resistivity, Al_2O_3 coatings are also of interest in microelectronics industry [7-10]. These applications area make synthesis and characterization of Al_2O_3 thin films attractive. The problems associated with thin film synthesis of Al_2O_3, are due to the existence of different crystalline phases. Controlling the formation of the desired phase is often difficult. The most stable is α-phase, also known as corundum with hexagonal structure at elevated temperatures [11,12].

Various techniques such as chemical methods, magnetron sputtering, plasma-enhanced vapour deposition, spray pyrolysis, vacuum arc technology are being used to prepare Al_2O_3 thin films [4-6,9,10]. Among them, chemical method (sol-gel dip coating process) is used to form metal oxide thin films. The sol-gel process is a wet-chemical technique used for the fabrication of metal oxides, starting from a chemical solution containing colloidal precursors (sol). Typical precursors are metal alkoxides, metal chlorides, metal nitrates, and metal sulphates, undergo hydrolysis and poly condensation reactions to form a sol-gel can be deposited on a substrate to form a thin film by dip-coating technique. The

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sol-gel technique is cheap, high quality, large surface area and a low-temperature synthesize technique allows the fine control on the chemical composition. Dip coating is a simple, economic and effective method to produce high quality films [13].

In the present work, Al_2O_3 thin films are deposited on quartz substrates by sol- gel dip coating technique and the films are characterized by X-ray diffraction (XRD) and UV-Visible spectroscopy to investigate the structural and optical properties at different annealed temperatures.

Expertimental Details

Preparation of Al_2O_3 precursor sol

The sol-gel process is a wet-chemical technique for the preparation of metal oxides, starting from a chemical solution containing colloidal precursors (solution). Aluminium nitrate is dissolved in 2-methoxyethanol and stirred continuously to form a solution, which undergo the hydrolysis and poly condensation reactions. This solution is maintained at 70°C and stirred at 1000 rpm for 30 min using magnetic stirrer. After 30 min, mono ethanolamine is added drop wise and mixed at 1000 rpm for 2 hr using magnetic stirrer to obtain the gelly nature of the solution.

Dip coating

The substrate is attached with the dipping probe of the dip coating apparatus and the dipping velocity is set at 0.5 mm/s (30 mm/min) with a dipping delay of 30 sec. With these setting, the substrate is dipped in the as prepared Al_2O_3 precursor solution repeatedly for 15 times at a constant pulling rate of 0.5 mm/s. The thin layer deposits itself on the substrate, while it is dipped in the solution. The withdrawing is carried out at a constant speed to avoid any jitters. The speed determines the thickness of the coating. Excess liquid will drain from the surface and solvent evaporates from the liquid, forming the thin layer. It is air-dried and then annealed at different temperatures such as 200°C, 400°C and 600°C for 30 minutes to obtain a uniform, dense film and good adhesion with the substrate. X-ray Diffractometer (Bruker D8 with 40 kV and 30 mA) with theta/theta mode is used for the structural analysis of the Al_2O_3 thin film samples. The UV-Visible double beam spectrophotometer (Shimadzu, UV-1800) is used to study the optical properties of the films in the wavelength range 190 nm-1100 nm.

RESULTS AND DISCUSSIONS

Structural studies - X-Ray Diffraction

Al_2O_3 thin films are characterized by X-ray diffraction technique to study the structural properties. The intensity versus 2θ values is obtained from computer aided data acquisition system. The diffraction pattern obtained is compared with the standard JCPDS pattern and XRD pattern are indexed. Fig. 2 shows the XRD pattern of the Al_2O_3 films on Si (100) annealed at 200°C substrates showed the strong reflections appeared ~ 32.6° and 62.3° corresponding to θ-Al_2O_3 phase [JCPDS #23-1009]. The very strong peak is from the silicon substrate. The other two reflections are from the θ-Al_2O_3 phase. The Al_2O_3 films annealed at 400°C (Fig.3) also showed two strong peaks corresponding to θ-Al_2O_3. The peak intensities of the films increased with increasing annealing temperature. The phase formation depends on the preparation method and process parameters.

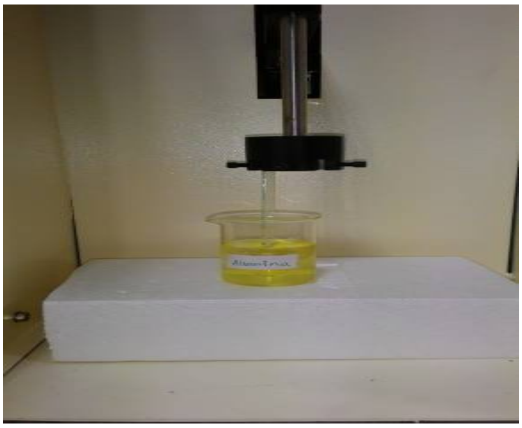

Fig 1 Deposition of Al_2O_3 thin films on Quartz substrates by Dip coating

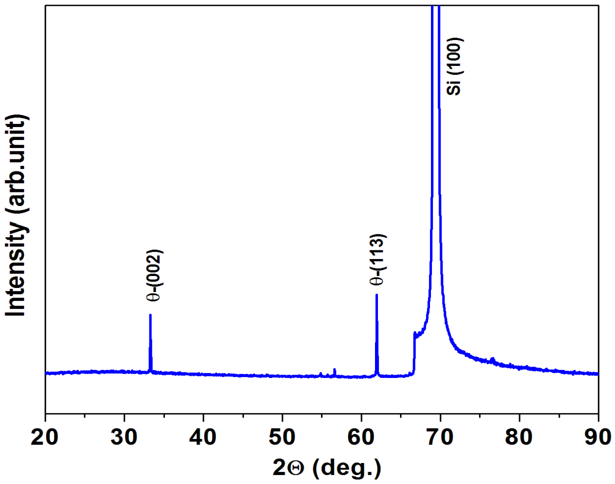

Fig 2 XRD pattern of the Alumina thin film deposited on Si (100) substrate and annealed at 200 °C.

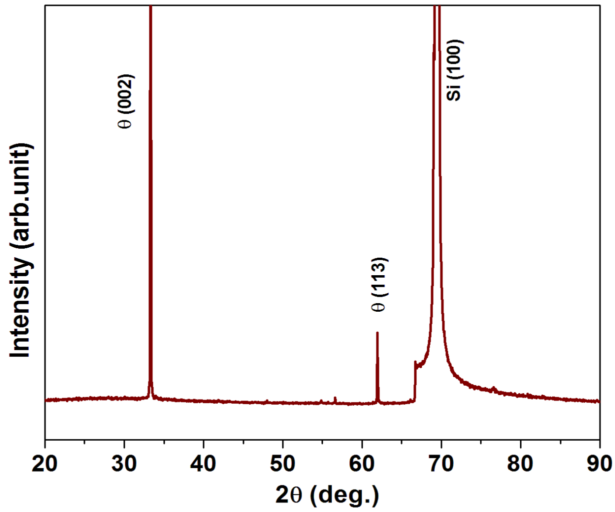

Fig 3 XRD pattern of the Alumina thin film deposited on Si (100) substrate and annealed at 400 °C.

Figure 4 shows the XRD pattern of the Al_2O_3 film deposited on quartz substrate and annealed at 200°C and revealed that the reflections are corresponding to polycrystalline γ-Al_2O_3 of fcc structure. It shows the reflections ~46° and 65.8° are from the γ-Al_2O_3 [5,7]. The films annealed at 600°C also showed two small peaks indicating the γ-Al_2O_3 of face centred cubic structure (Fig.5). These peaks matched with the standard JCPDS No. 50-741.

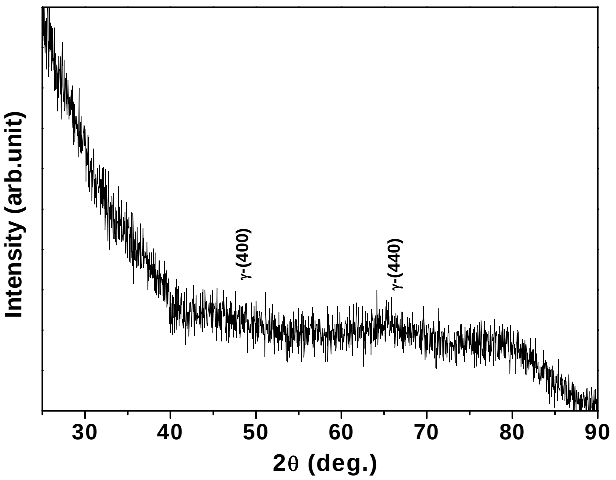

Fig 4 XRD pattern of the Al_2O_3 thin film on quartz substrate and annealed at 200 °C.

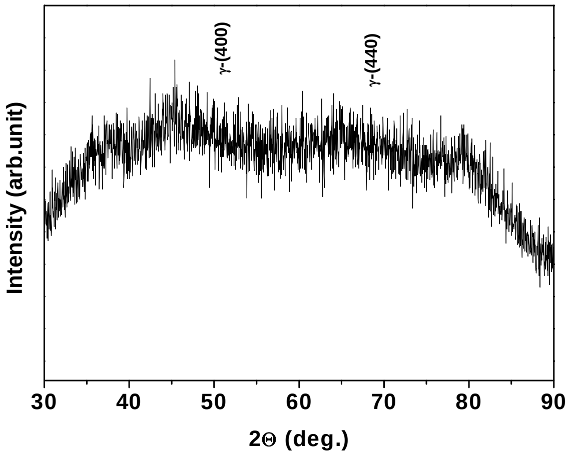

Fig 5 XRD pattern of the Al_2O_3 thin film on quartz substrate and annealed at 600 °C.

The peak intensities of the films increased with increasing annealing temperature. In general, phase formation of Al_2O_3 depends strongly on the substrate temperature and the nature of the substrate. The silicon substrate is crystalline in nature and hence it favours for the formation of high temperature phase (θ- Al_2O_3) due to is lower surface energy. Balakrishnan *et al.* studied the phase transition and thermal expansion studies of alumina thin films using high temperature X-ray diffraction [3]. The studies revealed the cubic γ- Al_2O_3 phase in the temperature range 300–973 K. At temperatures ≥1073 K, the δ and θ phases of Al_2O_3 were observed.

Optical Properties - UV-Visible Spectroscopy

UV-Visible double beam spectrophotometer is used to measure the absorbance and transmittance of the films. The absorption coefficient α (λ) can be calculated from the following equation;

$$\alpha(\lambda) = 2.303\left(\frac{A}{t}\right)$$

where *t* is the thickness of the film and *A* is the absorbance of the film. The frequency dependent absorption coefficient can be written as

$\alpha h\nu = A\,(h\nu - E_{opt})^n$

where *A* is the constant depends on the properties of the material, hν is the incident photon energy, the exponent *n* can have values of 1/2, 3/2, 1, 2 and 3, depending on the nature of electronic transition and E_{opt} is the optical band gap. Values of 2 and 1/2 for *n* are used for the indirect and direct electronic transitions, respectively [5,7]. Figure 6 shows the optical absorption behaviour of Al_2O_3 films annealed at different temperatures. The absorption occurred ~250 nm wavelength indicating the transition from valence band to conduction band. The sharp absorptions denote the direct band gap of the material.

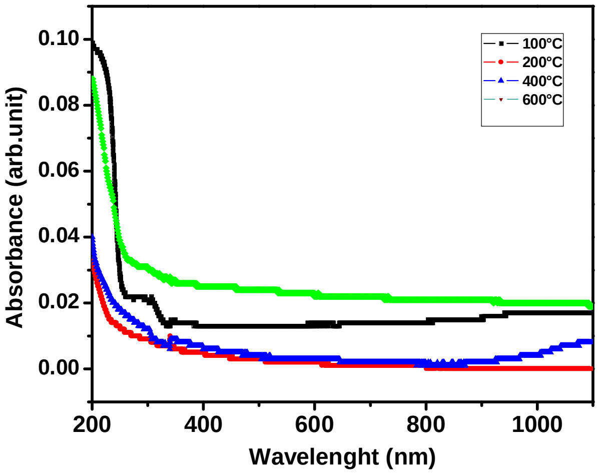

Fig 6 Absorbance spectra versus wavelength of the Al_2O_3 films on quartz substrates and annealed at different temperatures.

The absorption edge is different for the films annealed at different temperatures. It is observed that the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ are linear over a range of photon energies indicating the direct transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis (X-axis) give the energy band gaps. From these intercepts, the band gaps are deduced for the films and are found to be 4.68 eV, 4.82 eV, 5.37 eV and 6.1 eV in the annealed temperature range of 100°C-600°C. The typical plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for the Al_2O_3 film annealed at 200°C is shown in figure 7. The band gap energy increased with the increase of annealing temperature due to the increased crystallinity [14].

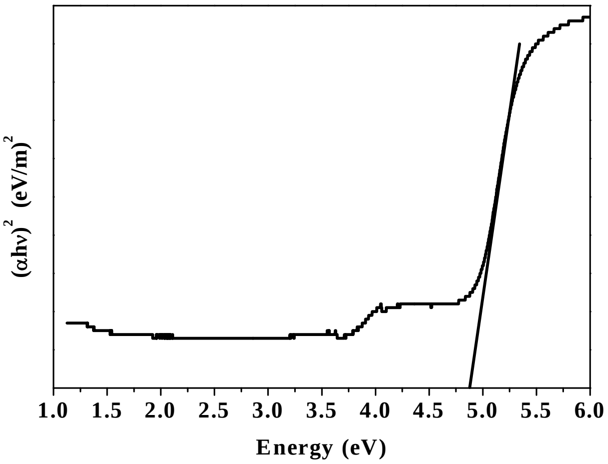

Fig 7 $(\alpha h\upsilon)^2$ versus $h\upsilon$ plot of the Al_2O_3 film annealed at 200°C

The transmittance spectra of Al_2O_3 films are measured in the wavelength range 190-1100 nm using UV-Visible spectrophotometer. Figure 8 shows the transmittance spectra of Al_2O_3 films deposited on quartz substrates and annealed at different temperatures. Figure shows the transmittance of ~ 90-95 % depends on the annealed temperatures. The transmittance increased with the increase of substrate temperature until 400°C. At 600° C, the transmittance decreased slightly. Murali *et al.* [4] deposited alumina films and the XRD studies indicated the amorphous nature of the films annealed up to 300°C and above this temperature, γ-Al_2O_3 is observed. Films with transmission in the range of 90% with a band gap of 5.75 eV was obtained.

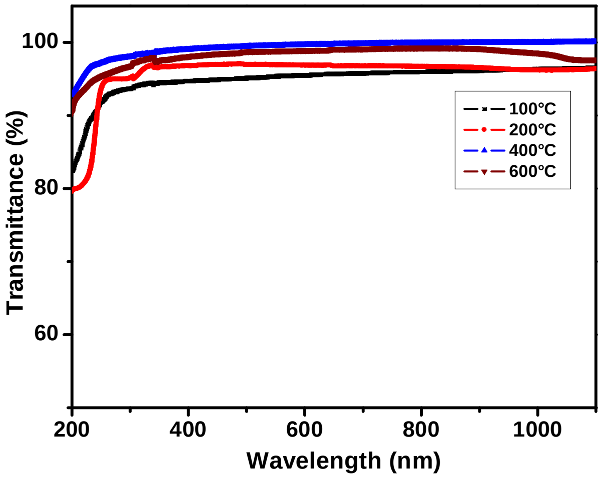

Fig 8 Transmittance spectra versus Wavelength of the alumina films on quartz substrates and annealed at different temperatures

Al_2O_3 films are deposited on stainless steel and quartz substrates by the sol gel process. Films with 1000 nm thickness are prepared by spin coating method. XRD of the film annealed at 400°C showed the amorphous nature of the film. The refractive index and extinction coefficient are found to be 1.56 and 0.003 at 600 nm, respectively [15]. Al_2O_3 films deposited on Si (111) substrates by metal organic chemical vapor deposition (MOCVD) using aluminum–acetyl acetonate as precursor. At low temperatures (350-550° C) amorphous films are obtained. As the temperature increased > 550°C, presence of crystalline Al_2O_3 is obtained [16]. α-Al_2O_3 films are deposited using reactive magnetron sputtering above 700°C in a PVD system. Si wafers and CrN-coated cemented carbides are used as substrates. The XRD studies indicated the γ-Al_2O_3 films on the Si substrate and Al_2O_3 film with α-phase is obtained on the CrN underlayer at 700°C and pure α-Al_2O_3 film is deposited at 750° C [12]. Optical and structural properties of alumina thin films are deposited using filtered cathodic vacuum arc and annealed in the temperature range 200-900°C. The films annealed at low temperatures (200°C-600°C) revealed amorphous structure with smooth surface [17]. Reactive electron beam evaporation technique is used to deposit Al_2O_3 thin films on Si substrates and the samples are prepared at different oxygen flow rates. Films are characterized by spectroscopic ellipsometry, atomic force microscopy and Grazing Incidence X-ray reflectivity measurements [18]. The Al_2O_3 films are deposited on Si (100) and quartz substrates in the substrate temperature range 27°C-700° C by PLD. The XRD studies indicated the amorphous nature of the films at low substrate temperatures (27°C-400°C) and cubic γ-Al_2O_3 phase at temperatures ≥ 500°C. The ellipsometry and UV–Visible spectroscopy analysis revealed that the refractive index increased from 1.698 to1.749 and 1.65 to1.80 (at 632.8 nm), respectively as the temperature increased from 27°C to 700 °C. The variation in the structural and optical properties is correlated as a function of substrate temperature [7]. A sol-gel technique is applied to prepare Al_2O_3 films using $AlCl_3$-$6H_2O$ as starting material and acetylacetone as additive. The as-prepared films are amorphous. At the temperature 600°C, γ-Al_2O_3 is formed and transformed to α-Al_2O_3 at temperatures over 1200°C [19]. Ultra-fast anodization method was developed for obtaining ordered nano-pores on aluminium (Al) foil. First anodization was carried out for 10 min, followed by 3 min of second anodization at high voltage (150 V). The anodized samples were analysed by field emission scanning electron microscope. The alumina (Al_2O_3) peaks were identified by XRD technique [20]. Al_2O_3 thin films are prepared on glass substrates by the sol-gel dip-coating technique. Structural and optical properties of the films are studied as a function of annealing temperature (100-500°C). The refractive index of the films increased from 1.56 to 1.66 (at 550 nm), while optical band gap decrease from 4.15 eV to 4.11 eV with the increase of annealing temperature from 100°C to 500°C [14]. All these studies indicated the phase formation and hence the properties depend on the preparation method and process parameters. In the present work, the polycrystalline, γ-Al_2O_3 film is obtained with high purity at a very low temperature of 200°C and its bandgap was 4.68 eV - 6.1 eV in the temperature range of 100-500°C.

CONCLUSIONS

Al_2O_3 thin films are deposited on quartz substrates using sol-gel dip coating method. The stable solution is obtained using 2-methoxyethanol and the prepared Al_2O_3 thin films, are good adherent and crack free. The samples are annealed at different temperatures range 100°C - 600°C. The XRD pattern revealed that the films deposited on Si (100) substrates annealed at different temperatures showed the sharp peaks indicating the polycrystalline θ-Al_2O_3 phase, whereas the films deposited on quartz substrates indicated the formation of polycrystalline γ-Al_2O_3 of cubic structure with reduced intensity. XRD studies of the films indicated the formation of θ-Al_2O_3 and γ-Al_2O_3 phases at ≥ 200°C on silicon and quartz substrates respectively. The optical studies shows bandgap in the range of 4.68 eV-6.1 eV in the temperature range 100°C-600°C and hence the bandgap increased with increase of annealing temperature. The present studies investigated that the simple cost effective sol-gel method can be used for the formation of polycrystalline γ-Al_2O_3 films at a very low temperature of 200°C.

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