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Optical and Structural Properties of Electrodeposited Aluminum Oxide at Low Temperatures

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ABSTRACT

Aluminum oxide thin films, consisted of dense nanoparticles, are prepared by electrodeposition technique. DC voltage it the range 1-5 volts are used for sample preparation. Temperature of the electrodeposition bath was kept at 5°C, 10°C, 15°C and Room Temperature (RT). Nanoparticles in the range 30-100 nm are observed as a function of applied voltage. XRD results confirm the formation of alpha alumina at lower voltage of 1 V for time interval of 30 minutes, for 5, 10 and 15°C, when compared with room temperature alumina formation at 3 V. Optical properties are studied by using variable angle spectroscopic ellipsometer. Energy band gap of 4.3 eV is observed which is smaller as compared to bulk ~6 eV band gap. It is observed in this research work that continuous dense thin films of aluminum oxide can be achieved at 1 volt at lower electro bath temperatures.

1. INTRODUCTION

Among various materials of interest, Alumina (Al_2O_3, sapphire, aluminum oxide), is most widely studied and used materials in nuclear industry and microelectronic lasing industry (Izerrouken 2010). Al_2O_3 offer unique advantages as high melting and boiling points, high dielectric constant, it's chemically stability and its high strength. In addition to these properties its ability of being radiation resistive makes it an important candidate for in nuclear reactor as optic window (Izerrouken 2010). Moreover, alumina exists in seven different polymorphs (α, β, γ, θ, η, κ, χ) (Pao 2000) and it crystallizes in rhombohedral unit cell (D_{3d} space group). However the most thermodynamically stable phase is α-Al_2O_3 and all other are transitional phases obtained during calcinations of hydroxides of aluminum (Yan 2010).

Aluminum and its oxide (alumina) find a wide range of structural applications in aerospace industry because of the unique combination of ultra-lightness, high specific strength and quite good mechanical characteristics (Pao 2000, Hamidreza 2010). Whereas, low hardness, wear and corrosion resistance of aluminum and its alloys limit their applications to use directly in severe space environment. The predominant environmental factors influencing spacecrafts are to be addressed to increase their

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efficiency. The physiognomies of the radiation environment are highly reliant on the type of mission (date, duration and orbit). Radiation accelerates the aging of the electronic parts and materials thus can lead to a degradation of electrical performance and thermo-optical properties (Jibiri 2011, Kimoto 2005, Willis 1999).

By considering the above limitations, surface modification of aluminum alloys forming aluminum oxide is necessary in order to improve thermo-optical properties. Surface modification is important because world's economy bears enormous losses reaching millions dollar due to damage of surface (Konieczny 2008).Thermal control coatings having low solar absorption, high emittance values can be obtained through anodic coatings (Jibiri 2011, Willis 1999, Majid 2013).

In this research work we report the preparation of alumina thin films using electrodeposition method. The films are electrodeposited at low temperature of 5°C at a constant potential of 3 V and with variation in electrodeposition time from 30 min to 120 min with interval of 30 min.

2. EXPERIMENTAL DETAILS

Analytical grade reagents were used in this research work for electrodeposition. Microcomputer-controlled Versa stat 4 potentiostat / galvanostat was used for the deposition of alumina thin films. Aluminum alloy 7407 was used as the working electrode and is placed in vertical configuration. Electrolyte with neutral pH was used for the purpose of deposition. Electrodeposition was carried out using three electrode cells and electrolyte was de-aerated every time before the next deposition. The working electrode was vertically arranged in the electrolytic solution and the temperature of electrolyte was maintained at 5°C, 10°C and 15°C. Films are deposited at a potential of 1-3 Volts. The deposition time is varied from 30 to 120 minutes.

Before electrodeposition was carried out the aluminum alloy 7075 was polished electro-mechanically and then cleaned by using acetone and isopropyl alcohol for 15 minutes in ultrasonic bath to remove the residual organic impurities.

Aluminum oxide thin films were characterized structurally using Rigaku D/MAX-IIA X-ray Diffractometer (XRD). Copper was used as the target material with nickel filter to achieve monochromatic X-rays of λ = 1.4505 Å. The XRD is operated at a voltage of 30 kV and current of 22.5 mA. Optical properties are studied using J A Wollam M 2000 Variable Angle Spectroscopic Ellipsometer (VASE).

3. RESULTS AND DISCUSSIONS

Fig. 1 show XRD patterns of aluminium oxide thin film deposited at a temperature of 5°C, 10°C, 15°C and at Room temperature (RT) for 30 minutes. The presence of (110), (006) and (117) peaks confirm the formation of FCC α-Al_2O_3 at 1 volts for 5-15°C whereas, 3 volts was observed to be effective in RT deposition. No preferred orientation is observed in case of the electrodeposited alumina thin films and the films are randomly oriented. XRD patterns of films deposited at 5°C, 10°C, 15°C and at RT show similar results. In order to observe the effect of deposition temperature on

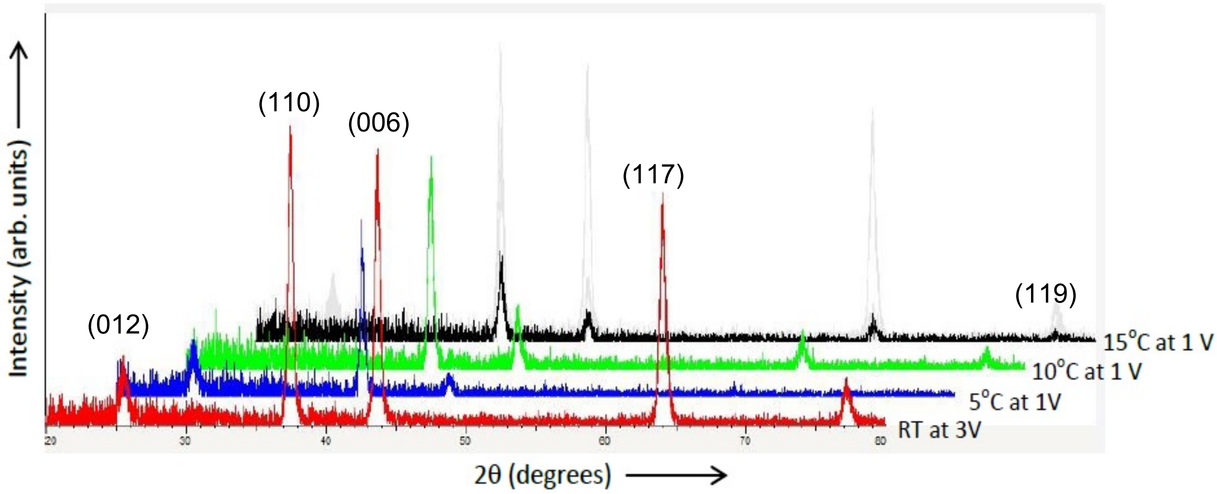


Fig. 1 XRD patterns of electrodeposited alumina thin film at varying bath temperature

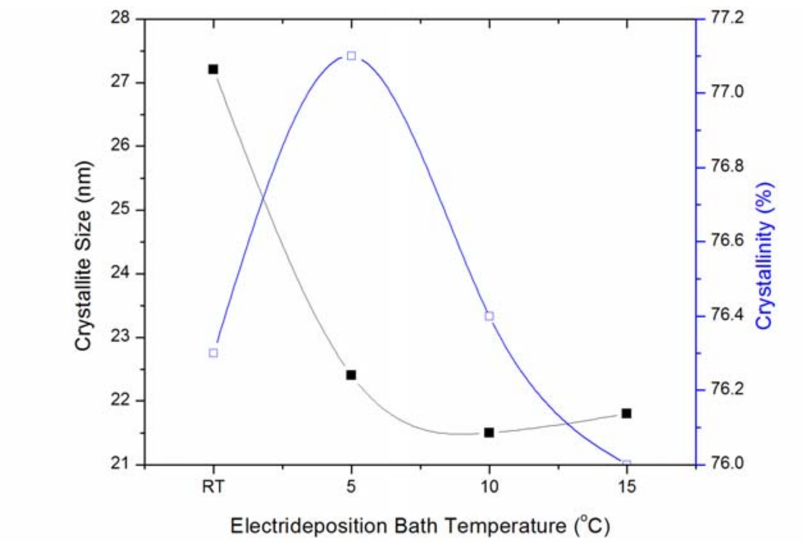


Fig. 2 variation in crystallite size and crystallinity at various electrodeposition bath temperatures

alumina thin films the films were also deposited at room temperature. Detailed results of films deposited at room temperature are reported earlier (Majid 2013).

Fig. 2 shows variation of crystallite size and crystallinity at various deposition bath temperatures. The crystallite size decreases as the electrodeposition temperature is increased where as the crystallinity of the electrodeposited films increases as the electrodeposition temperature is decreased from Room Temperature (RT) to 5°C where as for 10°C and 15°C the crystallinity decreases as compared to the film deposited at 5°C.

Optical properties of electrodeposited alumina (Al_2O_3) films were studied using Variable Angle Spectroscopic Ellipsometry operated at an angle of incidence of 65° within the wavelength range of 200-1700 nm. Not only the effect of increase in the deposition time is studied but also the effect of variation in thickness is also taken into consideration. Optical properties of films electrodeposited at room temperature have been reported earlier (Majid 2013, Riaz 2008).

Figs. 3 and 4 show the refractive index and extinction coefficient of electrodeposited alumina thin films prepared at room temperature as well as at low electrodeposition bath temperature at 1-3 Volts. Deposition was carried out for 30 min. Both refractive index and extinction coefficient decreases with increase in wavelength showing normal dispersion behavior. At a wavelength of 300 nm the refractive index and extinction coefficient is 1.65 and 0.0836, respectively. As the electrodeposition temperature was lowered from room temperature to 5°C the refractive index increases from 1.6 to 1.8 eV (at λ = 300 nm). The value of bulk refractive index is reported in literature to be around

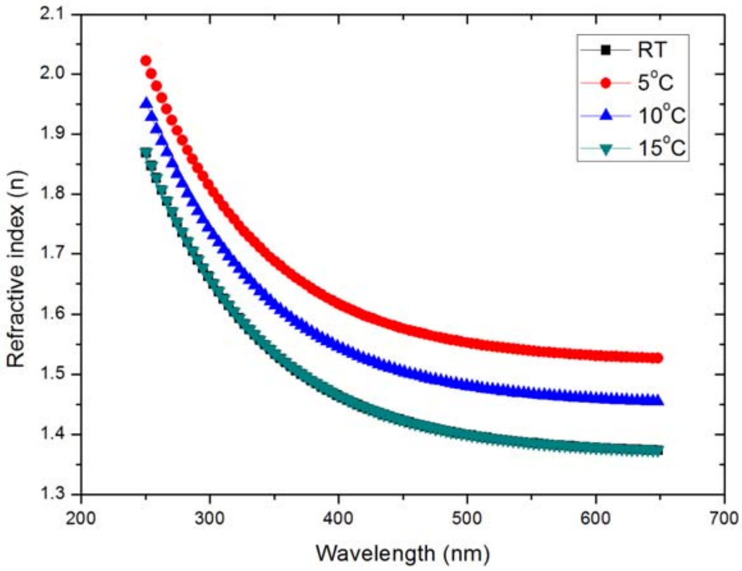


Fig. 3 Effect of electrodeposition bath temperature on refractive index

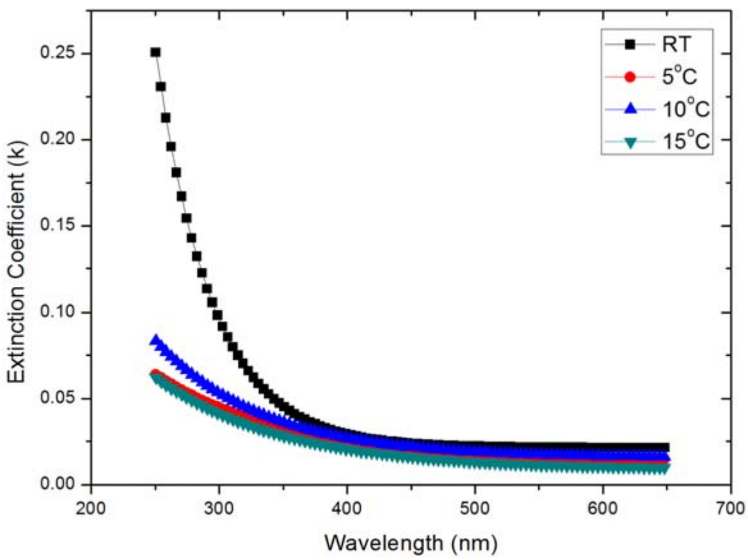


Fig. 4 Effect of electrodeposition bath temperature on Extinction Coefficient

1.82 (at λ = 300 nm) and our values of refractive index close to bulk refractive index indicate that the films are dense with very little pores present in it.

Refractive index can be used to calculate the porosity of films also. These porosity calculations require standard data. The standard data required in these studies is taken from material based models present in Variable Angle Spectroscopic Ellipsomtery (VASE). The porosity values for the samples are found to be in the range of 0.5-5%.

VASE was also used to measure the thickness and surface roughness of the electrodeposited thin films. Thickness of the films increases from 1 μm to 1.6 μm with increase in deposition time form 30 min to 120 min and the surface roughness is in the range of 5.9 nm to 15.395 nm. The low values of surface roughness indicate that these films are well suited for its application as barrier coatings.

Another optical constant of interest is absorption coefficient (α). It is measure of the ability of the material to absorb photons. Absorption coefficient is determined using Eq. (1).

$$\alpha = \frac{4\pi k}{\lambda} \tag{1}$$

The absorption coefficient is related to Exciton energy (hv) and band energy as in Eq. (2).

$$(\alpha h v)^{1/n} = A\left(hv - E_g\right) \tag{2}$$

Where, h is the Planck's constant, v the frequency of incident radiation and A is the constant. The factor n can be 1/2, 2 and 3/2 for direct and indirect allowed and direct forbidden transitions depending on the type of transition taking place in k-space. The α^2 vs. E curve in Fig. 3 show direct transition in radiated Al_2O_3 thin films electrodeposited at 3 V for 30 min deposited at different electrodeposition temperatures. At room temperature the band gap of the films is found to be 4.3 eV where as for 5°C, 10°C and

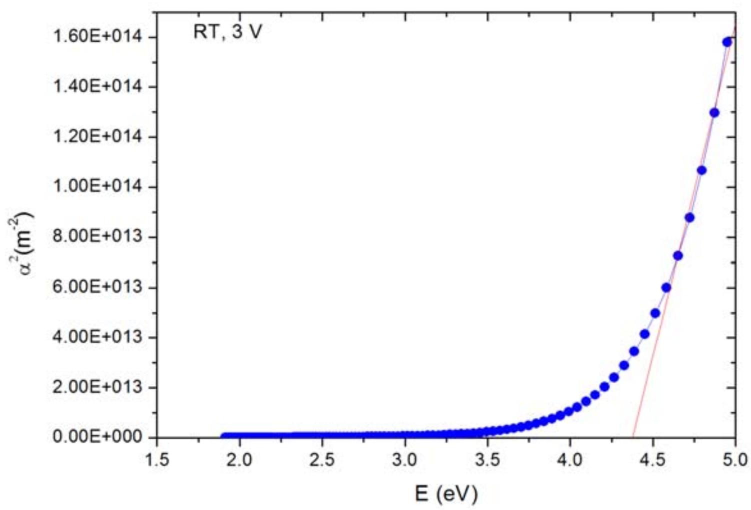
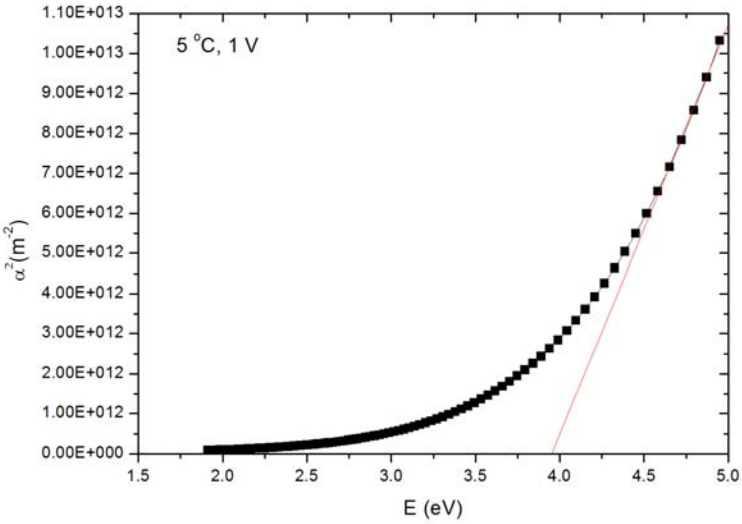
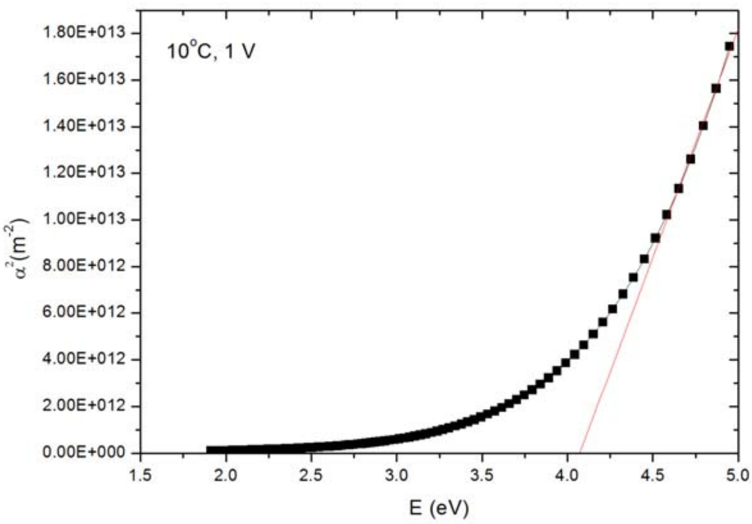


Fig. 5 Band gap of alumina thin film electrodeposited at RT, 5°C, 10°C and 15°C





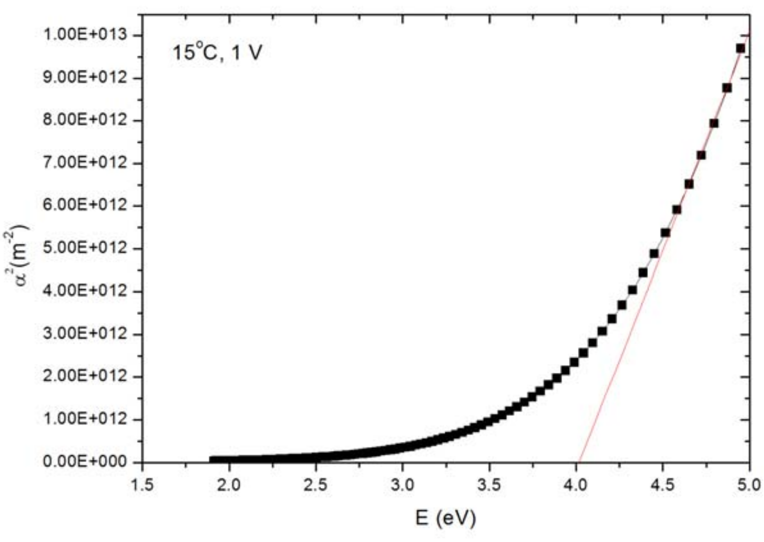


Fig. 5 Continued

4. CONCLUSIONS

Aluminum oxide thin films are electrodeposited at 5°C, 10°C, 15°V and at RT. 1-3 volts were used for depositing films for 30 min, 60 min, 90 min and 120 min. XRD results confirmed the formation of stable aluminum oxide phases at 1 volt for electro bath temperature of 5-15°C. Whereas, formation of α-Al_2O_3 was observed at 3 volts for RT deposition. Variable Angle Spectroscopic Ellipsometry results showed that with increase in deposition temperature the refractive index increases because of the increase in film thickness i.e., the films become denser. The refractive index values are in the range of 1.62 to 1.8. The band gap decreases from 4.4 eV to 3.89 eV with decrease in electrodeposition bath temperature to 5°C.

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