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Development and Characterization of Sol-Gel Spin Coated Zirconium Oxide Thin Films†

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Zirconia (ZrO_2) thin films have been prepared on glass substrate by the spin coating method at room temperature. The X-ray diffraction study of zirconia films confirms the tetragonal structure with preferred orientation along (111) plane. The crystallographic parameters *viz.*, lattice constant, mean grain size, micro strain, dislocation density, texture coefficient and standard deviation have been calculated and the influence of number of coatings on the properties of the film have been discussed. The maximum optical transmittances of zirconia thin film have been found to 73 % at 350 nm wavelength. FT-IR spectrum results shows existence of band stretching corresponds to Zr-O group at 420 cm^{-1}. The atomic force microscope image indicates smooth and uniform surface pattern without any pits of the pin holes.

Key Words: Zirconia thin films, Sol-gel spin coating, Grain size, Dislocation density, Band gap energy, FTIR, AFM.

INTRODUCTION

Zirconia (ZrO_2) thin films are the most promising material widely used as thermal barrier coatings on metallic alloys[1], optical wave guides[2], intermediate temperature solid oxide fuel cells (IT-SOFCs)[3], sensors[4], magnetic recording disks[5], catalytic films and in dielectrics[6]. Zirconia thin films posses good optical properties such as high refractive index[7], low optical loss, large band gap, high thermal expansion coefficients, high melting point and low thermal conductivity[8], *etc.*, There has been great technological and scientific interest in zirconia thin films due to their phase transitions. Pure zirconia exhibits three polymorphs depending on temperature: monoclinic (m) stable up to 1170 ºC, tetragonal (t) stable up to 1170-2370 ºC and above it have cubic (c) phase until it melt at 2706 ºC[9]. The properties of thin films strongly depend on the method of preparation and growth parameters. Zirconia thin films are prepared by a wide variety of deposition processes *viz.*, plasma spraying[10], sol-gel spin coating[11], electro chemical deposition[12], chemical vapour deposition[13], dip coating[14], RF sputtering, atomic layer deposition[15], atomic layer deposition[16], electron beam evaporation method[17], *etc*. Out of these, sol-gel spin coating method gives high quality oxide materials and is well adaptable for thin film preparation. The surface of films prepared by sol-gel spin coating technique is smooth which is important to achieve device quality properties. Sol-gel spin coating method is simple, feasible and size tailoring[3]. Other advantages of this method include low processing temperature, dense films, high homogeneity of material and absence of vacuum, low cost and high flexibility[18]. The present work deals with the preparation of zirconia thin films by sol-gel spin coating method using the optimized coating parameters and to investigate its structural, optical and surface properties at room temperature.

EXPERIMENTAL

The sol has been prepared by dissolving appropriate amount of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) in doubled distilled water. The stirred solution has been cooled in the ambient and then allowed for ageing in the atmospheric condition, for gelation. A cloudy sol solution was formed after 48 h of aging, which was used as the sol solution for the preparation of zirconia films. Zirconia thin films were developed by dispensing about 2 mL of the as prepared sol solution on the mineral glass substrate mounted over the turn table of the spin coating unit, which was spinned at the rate 3000 rpm for 10 s. The numbers of coatings were varied in order to get films of good thermal and optical properties. The sol-gel coated glass substrates were then baked at temperature 250 ºC for 5 min in an air furnace after coating every layer. By repeating this step for several times, pin hole free and uniform ZrO_2 films with good adherence and appreciable film thicknesses were obtained. The spin coated films were then annealed in the ambient at 350 ºC for an h. X-ray diffraction measurements of the ZrO_2

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films were recorded using Philips pananlytical diffractometer. The optical transmittance of the films was measured in the UV-visible region, using the Perkin-Elmer spectrophotometer, from which other optical constants were arrived. FTIR spectral data for the ZrO_2 films were obtained using the Shimadzu FTIR spectrophotometer in the wave number range of 2000-400 cm^{-1}. The surfaces features of the ZrO_2 films were investigated using atomic force microscope.

RESULTS AND DISCUSSION

Structural properties: X-ray diffraction (XRD) profile of the ZrO_2 thin films spin coated at different number of coatings shows tetragonal phase (t) of zirconia with preferred orientations along (111) plane with highest peak intensity $2\theta = 30.48°$, is shown in Fig. 1. The other orientations observed correspond to the plane (200), (220) and (311).The lattice constants evaluated from the XRD data are a = 5.04 Å and c = 5.15 Å and these values are well in agreement with the standard values of JCPCDS PDF data file number 02-0733. The average grain size of ZrO_2 films were calculated from the full width half maximum of the diffraction peak using the Scherrer equation. The average grain size of 10th number of coating was 60 nm. From the plot it is evident that the peak intensity and sharpness of all the planes increases as the number of coatings increases which may be due to more number of particles will be stacked in the layer. Further for lower number of coatings the peak intensity is very low, on other hand, when the numbers of coatings are increased, the intensity count and peak sharpness of all planes increases and this may attributed to increase in film thickness and presence of small-sized grains. The full width half maximum decreases as number of coating increases, which may be due to the excessive accumulation of the ZrO_2 particulates on the substrate surface[9]. Thin films having 10 number of coating have the stable tetragonal phase structure which may be due to the reduction of the surface energy caused by small grains[20]. After that as the number of coating increases (on 12th and 14th) the monoclinic phase exists which is due to the increase in thickness cause a reduction in the closed packing of the crystallites over the substrate surface. The existence of monoclinic phase may be due to increase in thickness, large grain size and OH^- anionic impurities due to the solvent water[9,20]. The dislocation density was calculated using the relation $\delta = 1/D^2$ (Table-1). The texture coefficient of the film defined by Barret and Massalcki can be used to describe preferred orientation of the film and is given by:

$$T.C_{hkl} = \frac{I_{(hkl)}/I_{0(hkl)}}{1/N\Sigma I_{(hkl)}/I_{0(hkl)}}$$

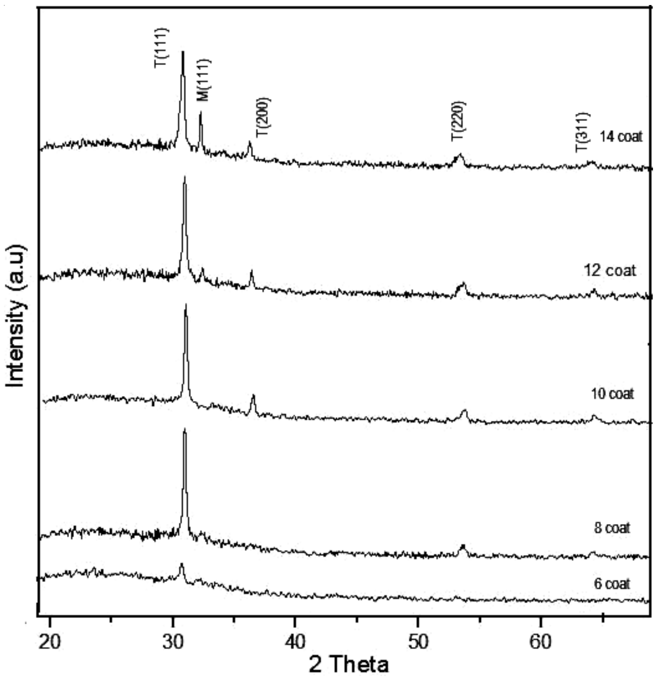

Fig. 1. XRD pattern of spin coated zirconia thin film

From the Table-1, it is evident that the particle size increases from lower value to the higher value which indicates an increase in grain growth as number of coating increases. The decrease in grain growth after 10th coating may be attributed to the deterioration effect of the crystallites. The texture coefficient has been found to be high for 10th number of coating which may be due to the preferred orientation and stabilization of tetragonal phase. The standard deviation (σ) and number of reflection per unit area (N) have been found to increase with the increase in the number of coating which indicates the excessive crystallite growth.

Optical characterization: The optical transmission spectra of the zirconia thin films with 6, 8, 10, 12, 14th number of coatings are shown in Fig. 2. The figure illustrates, for the zirconia thin film, a steep raise in the optical transmittance in the wavelength region 300-375 nm and it remains constant in the wavelength zone 375-800 nm. Optical transmittance is found to be maximum with the value 60-73 % at the wavelength 350 nm, for the zirconia films deposited with 6, 8, 10, 12, 14th numbers of coatings. As number of coating increases the optical transmission spectra decreases and this may be due to the presence of fine grains and scattering of light due to defects. These results are well agreed with Subramanian *et al.*[9] investigated CSZ thin films annealed at varying temperature. The variation of absorption coefficient with photon energy is shown in Fig. 3. The extension coefficient k_f is obtained from the

TABLE-1
CRYSTALLOGRAPHIC PARAMETERS OF THE ZrO_2 THIN FILMS

Number of coating	Average particle size (nm)	Dislocation density (× 10^{14})	Micro strain (× 10^{-3})	Texture coefficient	Standard deviation (σ)	Number of reflections (× 10^{14})
6	49	4.02	0.726	0.9990	0.42750	2.3
8	59	2.86	1.017	0.9990	0.47580	2.9
10	60	2.71	7.030	1.0056	0.47880	4.3
12	57	2.97	7.050	0.9990	0.51187	8.3
14	45	4.88	9.340	0.9990	0.52230	20.0

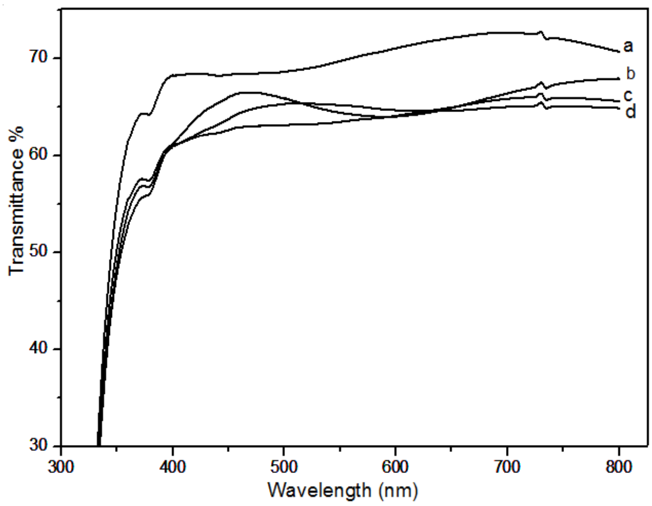

Fig. 2. Variation transmittance with wavelength with (a) 8th coating (b) 10th coating (c) 12th coating (d) 14th coating

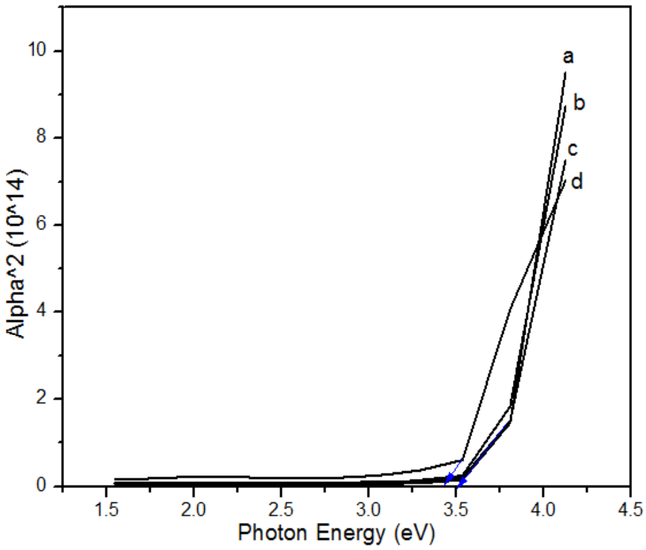

Fig. 3. Variation of absorption coefficient with photon energy; (a) 8th coating (b) 10th coating (c) 12th coating (d) 14th coating

transmission spectra and the absorption coefficient α can be obtained from the relation, $\alpha = 4\pi k_f/\lambda$ and the band gap energy (E_g) proportional to absorption coefficient can be obtained from the following relation $(\alpha h\nu)^2 = k\,(h\nu - E_g)$; k is a constant. The direct band gap can be calculated from the graph between α^2 *versus* photon energy where the tangent intercepting the energy axis is the band gap value. The band gap energy of the zirconia film is found to be 3.5 eV for 6, 8 and 10th coating and slightly decrease to 3.4 eV as number of coating increases to 12th and 14th coating which may be due to the packing density decreases as number of coating increases. The low value of band gap be may due to the nonstoichiometric nature of the films. These results well agreed with the value repoted by Ramamurthy *et al.*[21]. The study reveals that the zirconium oxide thin films prepared by optimized spin coating method offers good optical properties useful for wide band gap applications. The FTIR transmission spectra of the ZrO_2 thin films are shown in Fig. 4 and the peaks are attributed to Zr-O stretching in tetragonal ZrO_2. The Zr-O stretching band was observed at 420 cm^{-1} for lesser number of coatings

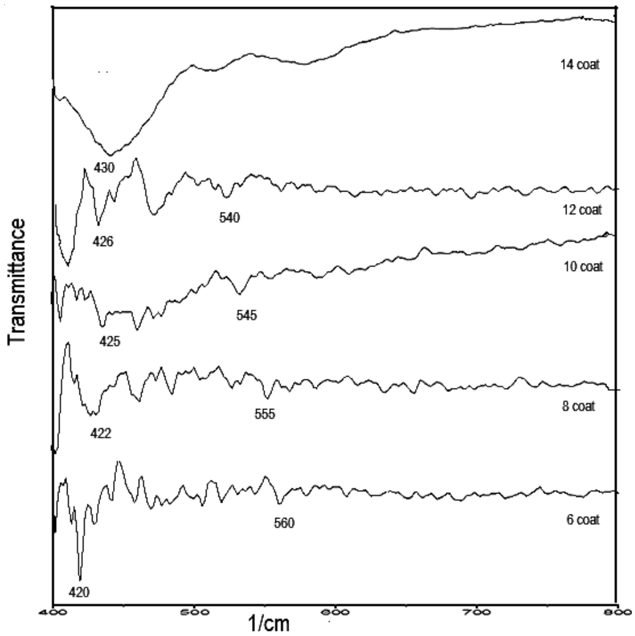

Fig. 4. FTIR spectra of zirconia thin films spin coated with different number of coatings; a) 8th coating b) 10th coating c) 12th

and this band is shifted to 430-422 cm^{-1} with increase in number of coatings, which is attributed to an increase in the Zr-O band strength. Likewise the bond metal-oxygen-metal has been observed with low intensity at 560 cm^{-1} has been shifted to 540 cm^{-1}. This can also be correlated to the increase in crystallization with increase in number of coatings as is evident in the XRD spectra. The band from 3443 cm^{-1} is characteristic of OH stretching vibrations. These results are well in agreement with the reports presented by Joy *et al.*[14].The 2D and 3D AFM image of the zirconia thin films spin coated with 10 numbers of coatings is shown in the Figs. 5 and 6. The AFM micrograph illustrates smooth and uniform surface pattern without any dark pits, pin holes and cracks. The AFM image further shows accumulation of large number of fine grains associated with hump like oriented growth of the crystallites.

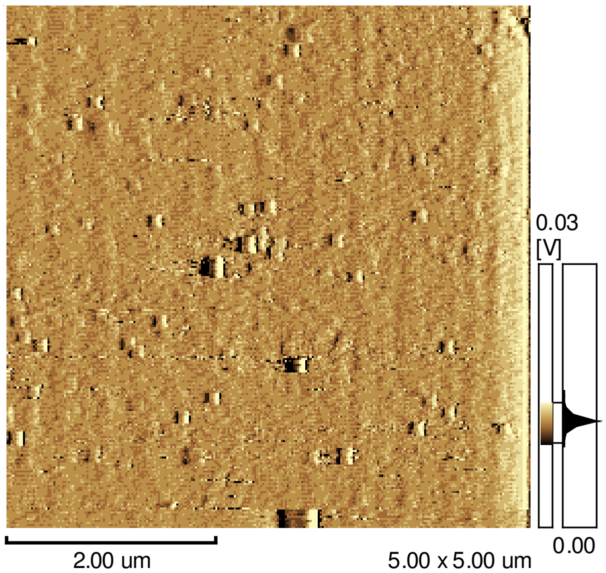

Fig. 5. 2D AFM image of the zirconia thin film spin coated with 10th number of coating

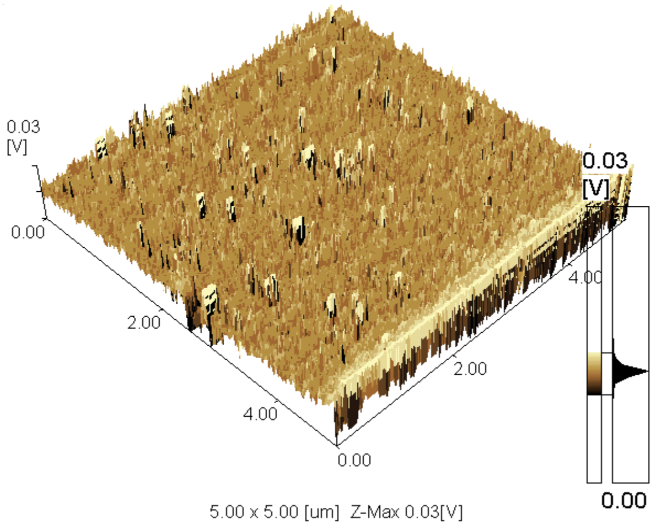

Fig. 6. 3D AFM image of the zirconia thin film spin coated with 10th number of coating

Conclusion

ZrO_2 thin films were prepared by conventional spin coating method with different number of coatings. The tetragonal phases of zirconium oxide thin films were prepared at room temperature with the particle size of 60 nm. The decrease in grain size with the increase in number of coatings may be attributed to the oriented over growth as a result of preferred nucleation. Optical transmittance of the zirconia films decreases with the increase in number of coatings, which may be attributed to the decrease in grain boundary scattering effect due to the enhanced crystallinity with the increase in number of coatings. The extinction coefficient decreases with the increase in the number coatings, which may be due to the homogenity of the films. The band gap decreases with the increase in the number of coatings and this may be attributed to the increase in carrier density. The FTIR studies reveal that absorption band observed at 420 cm^{-1} confirms that Zr-O stretching. The 2D and 3D AFM image of the zirconia films spin coated with 10 numbers of coatings illustrates smooth and uniform surface pattern without any pits of the pin holes.

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