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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.13, pp 5342-5346, November 2014

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Optical parameter determination of ZrO_2 thin films prepared by sol gel dip coating

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Abstract : Zirconium Oxide (ZrO_2) thin films were prepared on glass substrates by sol-gel dip coating method using Zirconium Oxychloride Octahydrate, Isopropanol and Acetyl acetone as precursor, solvent and stabilizer respectively. In the present work, the optical properties of the Zirconia thin films have been studied. Samples with different number of layers were prepared by repeating the dipping and drying processes. Then, the sol gel derived films were annealed at 500°C. The crystalline structure of the ZrO_2 film was determined using X-ray diffraction. The films found to show tetragonal phases at the annealing temperature of 500°C. The UV-Visible transmission and reflectance spectra were used to observe the optical properties of the thin films. The average refractive index of the thin films was found to be 1.9, calculated using reflectance and transmission spectra. The measured band gap values of the ZrO_2 thin films were nearly 4.8 eV. SEM analysis showed that the films have cracked plane morphology, as a result of their contraction during heat treatment.
Keywords - Zirconium Oxide; sol-gel; dip coating; XRD; reflectance; refractive index.

Introduction

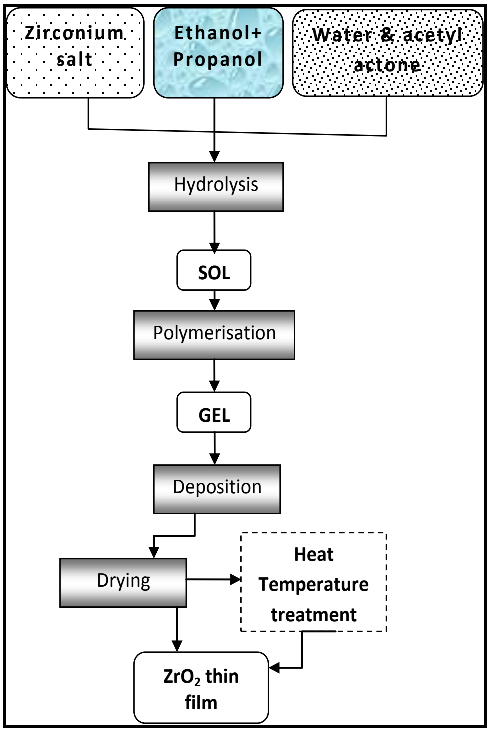
Zirconia (ZrO2) thin films have potential applications in optics such as protective barriers, interference filters, anti-reflection, selective reflection coatings, photochromism, high power laser mirrors and passive and active waveguides and in functional applications such as oxygen sensors or buffer layers in micro- electronic devices. All of these applications are based on the interesting combination of mechanical, chemical, and physical properties exhibited by these ceramics. There are different techniques to obtain thin films (physical vapour deposition, sputtering, electron beam evaporation, sol–gel, etc.). Among them the sol– gel route provides some advantages such as simplicity and low cost, capability of coating large surface areas, low processing temperatures, high optical quality of films, etc. In addition, this method is suitable to obtain almost any single- or multi-component oxide coating (ZrO2, Al2O3, SiO2, TiO2, etc.). These films can be deposited by spin and dip coating technique.

The parameters, refractive index and the thickness of the film, play an important role in optical applications. The thickness can be controlled by the deposition process and the refractive index can be tuned by the temperature treatment[1]. There are different techniques to characterize the thickness and refractive index, such as by measuring the transmittance[2], by ellipsometry[2] and by the Brewster angle technique[1]. The aim of this work is to present the results of the refractive index and extinction coefficient for the ZrO2 films prepared by dipping technique in a sol–gel solution.

Experimental Details

A. Synthesis of Zirconium oxide thin films

In the present study, nanocrystalline Zirconia thin films were fabricated using inorganic precursor. The starting material used was Zirconium Oxychloride Octahydrate salt. It was dissolved in the Isopropanol and ethanol mixture (in the ratio 1:1). The water for hydrolysis and nitric acid for oxidation were then added to the salt-alcohol solution. Acetyl acetone was used as a stabilizer to the solution and stirred vigorously for few hours at room temperature. The experimental flow chart was shown in figure below.



B. Characterization of the thin films

XRD pattern of the films was obtained using the X'PERT PRO X – ray diffractometer, which was operated at 40 KV and 30 mA with CuKα1 radiation of wavelength 1.5407Å. Optical transmittance and reflectance were measured covering the spectral regions from 300 nm to 800 nm with a standard UV–vis spectrophotometer (Schimadzu 1800).

Results and Discussion

A. XRD Analysis

Figure 1 shows the XRD patterns of sol gel derived ZrO_2 thin films on glass substrates annealed at 500°C. The XRD patterns reveal that all the samples have both tetragonal and monoclinic phases. The films showed tetragonal peaks, such as (101), (200), (211) orientations[3], at about 2θ = 30.2°, 50.3° and 60° and a monoclinic (111) peak reflection at 35.7°.

The average crystallites size (D) was calculated from the XRD pattern of the films using Debye–Scherrer formula as follows:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where β is the full-width at half maximum of the peak measured on a 2θ scale, λ is the X-ray wavelength (CuK_{α} radiation λ=1.5405 Å), θ is the Bragg diffraction angle of the XRD peak. The average crystallite size is found to be nearly 2.25 nm for all the samples.

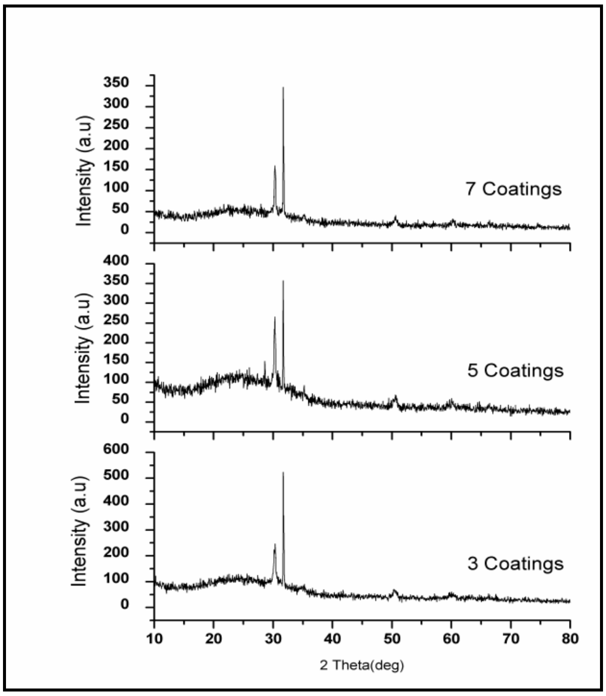


Figure 1 X-ray diffraction pattern of ZrO_2 thin films annealed at 500°C.

B. UV – Vis Spectroscopy Analysis

The optical properties of ZrO_2 thin films are highly influenced by the chemical formulation, fabrication method[4] and processing parameters. Figure 2 shows the transmittance and reflectance spectra of the ZrO_2 thin films on glass substrate annealed at 500 °C. Measurements of transmittance and reflectance at normal incidence of the films deposited on glass substrate were carried out in the wavelength range 300–800 nm. For all the samples, higher transmittance is observed in the UV region and the absorption edge is near to 295 nm, which may allow it using as UV-filters. No interference effect was observed in the transmission curves and this smoothness may be due to the non-uniformity or slight tapered thickness of the samples. The average reflectivity of the sample is equal to 12.5% in the range from 300 to 800 nm and with a minimum value of 11.4% at $\lambda = 415.7$ nm.

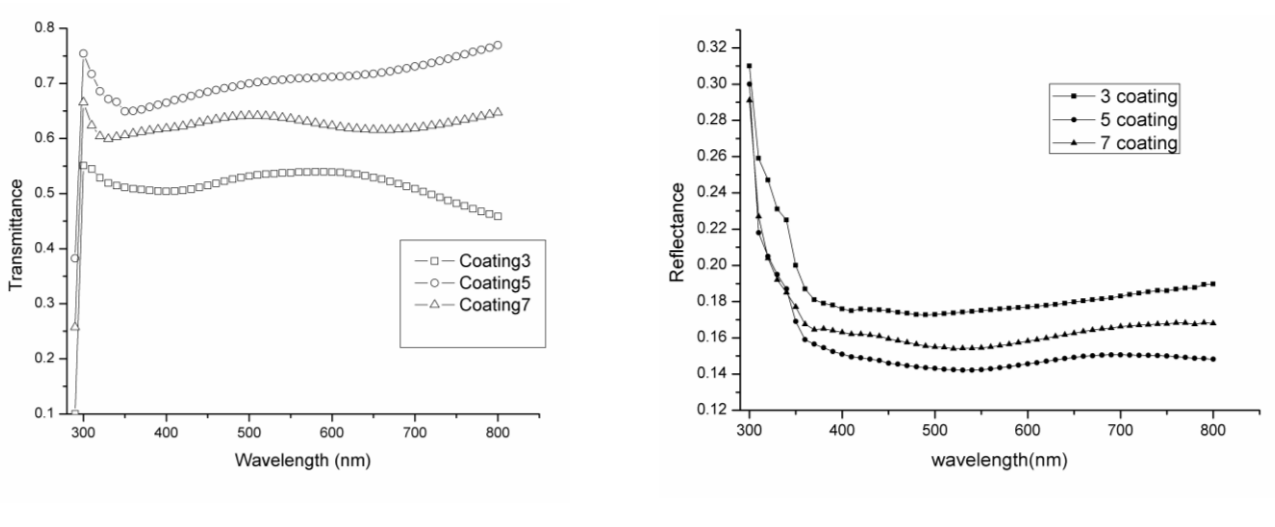


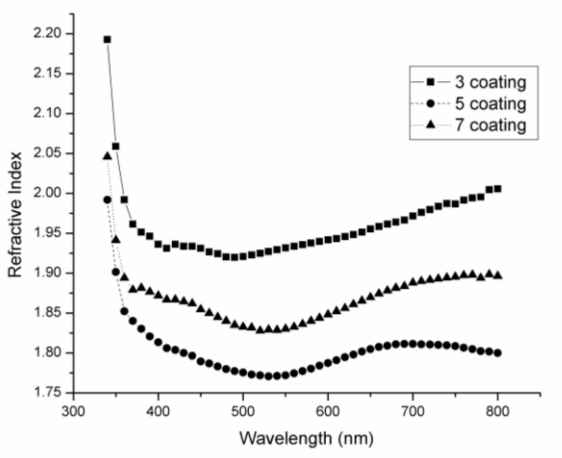
Figure 2 Transmittance and reflectance of the annealed zirconia thin films

Refractive index

The refractive index of a material is the most important property of any optical system that uses refraction. It influences the optical characteristics of the film, such as transmission spectrum, reflection spectrum etc. If a sample is transparent or semi-transparent in a certain spectral region, it is possible to calculate real and imaginary part of complex refractive index (m = n + ik) from its reflectance and transmittance at any arbitrary wavelength. The refractive index can be calculated from the from transmission & reflectance spectrum using the Fresnel equation[2],

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

where k is known as the extinction coefficient and is calculated using formula $k = \alpha\lambda/4\pi$. The values of n and k are calculated and are plotted in Figure 3.



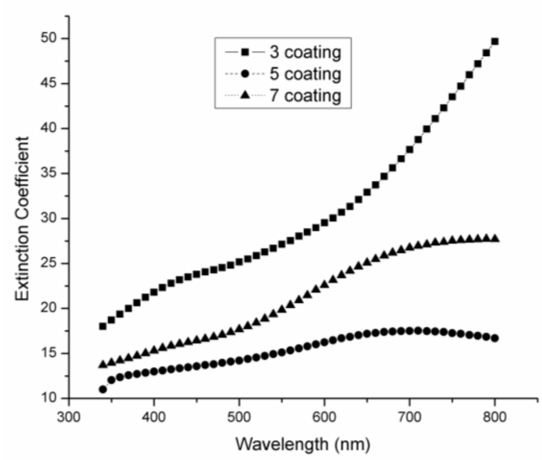


Figure 3 Refractive index and extinction coefficient vs wavelength

Optical band

The energy band gap of the films was found by Tauc method. The Figure 4 shows the plot of $(\alpha h\upsilon)^2$ as a function of hυ of the incident light. The band gap energies can be calculated by extrapolating the linear portion of the curve to the energy axis. The band-gap energies of the deposited ZrO_2 thin films that were obtained by extrapolation of the curve ranged from 4.16 to 4.19 eV. The band-gap energies of the all the ZrO_2 thin films are nearly the same.

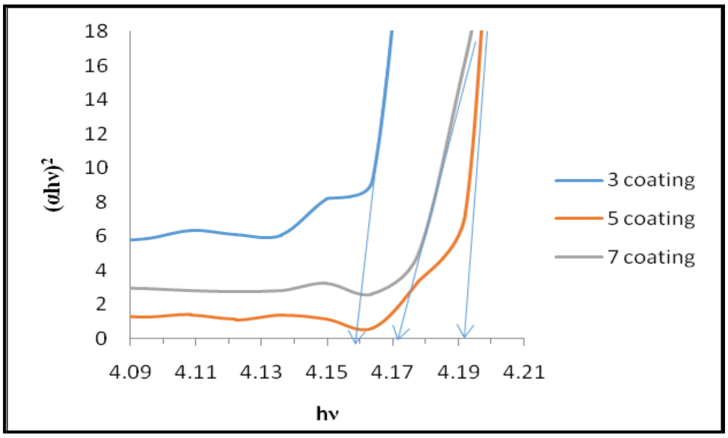


Figure 4 Energy Bandgap Plot for the prepared thin films

C. Surface morphology studies

The Scanning Electron Microscopic (SEM) images of the ZrO_2 coatings with different number of layers are presented in Figure 5.The films show a very cracked morphology with several mud-flat cracks. This may be due to the effect of the removal of water and alcohols from the film[3].

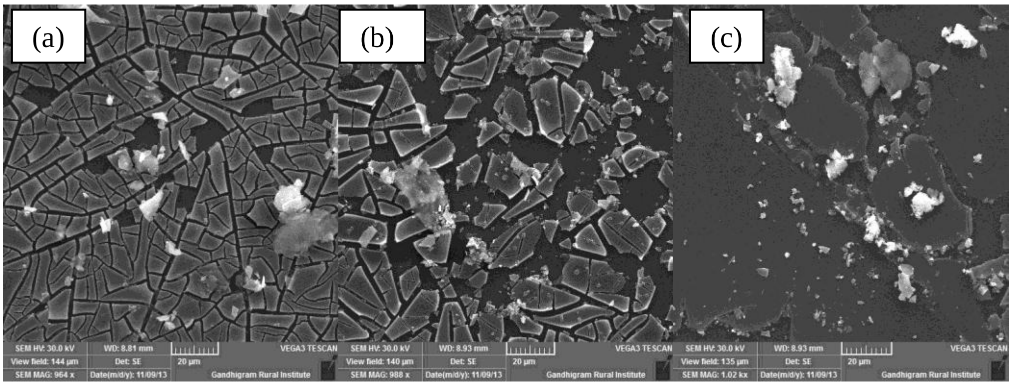


Figure 5 SEM images of ZrO_2 thin films a) 3 coating b) 5 coating c) 7 coating

Conclusion

Zirconium Oxide thin films have been prepared by sol gel dip coating method on glass substrates using Zirconium Oxychloride Octahydrate (ZOO) as inorganic precursor. The sol gel derived films were annealed at 500°C. Crystal structure and surface morphology of these layers were studied by XRD, SEM techniques, when the surface bonding properties were investigated by FTIR. XRD data showed the mixed structure of monoclinic and tetragonal with crystallite size of 2.25 nm. The PL emission peak at 426 nm indicates the presence of oxygen vacancies which interact with interfacial atoms of zirconium giving rise to photoluminescence.

Acknowledgement

The first author is grateful to the DST, New Delhi for extending financial support to carry out this work under INSPIRE Fellowship [IF.No.120274/2012].

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