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Influence of Annealing on the Optical Properties of Zirconium Oxide Thin Films Prepared by Sol Gel Method

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***Abstract*—Zirconium Oxide is an attractive material which can act as an antireflection coating for Solar Cells (SCs) based on Silicon and InGaAsP heterostructures, thermal barrier coatings and oxygen sensor. This article describes the preparation and characterization of Nanocrystalline ZrO_2 thin films deposited on glass substrates by dip coating method. The ZrO_2 thin films were synthesized by sol gel method using Zirconium Oxychloride Octahydrate as a precursor material. The optical, structural and surface bonding properties of the thin films prepared with and without post annealing were examined by optical spectroscopy, X-ray diffraction and FTIR spectroscopy, respectively. The XRD results showed tetragonal structure for films annealed at 550 ºC and amorphous structure was observed for the sample without annealing. XRD result also showed that annealing temperature increases crystalline nature. It was found that optical reflectance and transmittance of thin ZrO_2 films decrease with the annealing temperature in the spectral range 300– 800 nm. FTIR spectra revealed the formation of Zr-O bond.**

Keywords—Zirconium Oxide; sol gel; XRD; FTIR; UV visible spectroscopy

I. INTRODUCTION

Zirconium oxide (Zirconia, ZrO_2) is one of the most well studied transition-metal oxides in optical fields. Because of the excellent optical properties of ZrO_2 films such as high refractive index, large optical band gap, low optical loss and high transparency in the visible and near-infrared region, they are widely used in the optical fields including high-reflectivity mirrors, broadband interference filters, antireflection coatings and active electro-optical devices [1–3]. Moreover, Zirconia based thin films have good adhesion to substrates such as glass, ceramics, silicon, sapphire etc., and also high corrosive resistance. These thin films have a high mechanical stability and serve to improve the properties (especially the scratch resistance) of varnishes and coatings applied as top coats to automobiles.

For optical applications, transparency and homogeneity of thin films on the substrate are very important. Many techniques such as sol–gel process, plasma spray, electron beam evaporation, sputtering and pulse laser deposition (PLD) can be employed to deposit zirconium coatings. Among these methods, sol–gel derived dip and spin coating are simpler and more convenient film-growing methods that produce materials with desirable properties for specific applications. Because the sol–gel technique is a room temperature process of low cost, with inexpensive equipment.

In this paper, some results concerning the optical and structural properties of thin ZrO_2 layers with and without annealing have been reported. For this purpose, ZrO_2 thin films synthesized by sol gel method using the dip coating technique.

II. EXPERIMENTAL DETAILS

A. Material Synthesis

The coating solution for thin films was prepared by dissolving Zirconium Oxychloride Octahydrate (ZOO) in 2-propanol and ethanol mixture (in the ratio 1:1). The solution was stirred at room temperature for 45 minutes using a magnetic stirrer. The water for hydrolysis and nitric acid for oxidation were then added to the salt-alcohol solution. Acetyl acetone was added to the solution as a chelating agent and stirring was continued for a further 45 minutes [4]. The resulting solution was coated on cleaned glass substrates by dip coating technique. A cleaned glass plate has also been taken for reference, was named as G. The coating process was carried out at room temperature under air. The processes of coating and drying were repeated for 5 times. This sample was named as Z1. Another film of same procedure was annealed in a muffle furnace at 550°C. It was named as Z2. The prepared films were studied for their structural and optical properties.

B. Characterization Details

XRD patterns of the films were obtained using X – ray diffractometer, X’PERT PRO, which was operated at 40 KV and 30 mA with CuKα1 radiation of wavelength 1.5407 Å. The Fourier Transform Infra Red (FTIR) spectra of the samples were recorded using the Shimadzu IR affinity - 1 spectrophotometer in the range of 400–4000 cm^{-1}. Optical transmittance and reflectance were measured covering the spectral region from 200 nm to 800 nm with a standard UV–vis spectrophotometer (Schimadzu 1800).

III. RESULTS AND DISCUSSION

A. XRD - Structural Study

XRD pattern of ZrO_2 thin films was presented in Fig. 1. It reveals that no peak is observed for the film without annealing (Z1), whereas a small peak with low intensity appeared in the annealed film (Z2). The small diffraction peak around 30.27° belongs to tetragonal ZrO_2, which is well-matched with the JCPDS card for tetragonal ZrO_2 (Card no: 80-2155) [4].

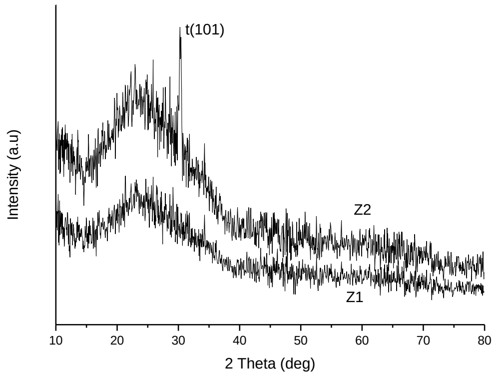

Fig 1. XRD pattern for the prepared ZrO_2 films

The fullwidth at half maximum of the (101) tetragonal phase was used for the estimation of the crystallite sizes using Scherrer's equation;

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

where D is the crystallite size, λ is wavelength of the radiation, θ is the Bragg's angle and β is the full width at half maximum. Crystallite diameter was computed as 27 nm for the 550°C annealed ZrO_2 thin film sample.

B. *FTIR spectroscopy*

Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflectance mode (ATR) was used to characterise ZrO_2 thin films deposited on glass substrates.

The results of FT-IR analysis performed to characterize the chemical structure of the thin films prepared was illustrated in Fig. 2. The peaks observed around 3500 cm^{-1} correspond to the stretching and deformation of the O-H bond due to the absorption of water and co-ordination of water. Signals ranging from 2920 and 2850 cm^{-1} belong to aliphatic C–H stretching. The broad band ranging from 1200–2200 cm^{-1} was made up of α,β- unsaturated ester bands. In the FTIR spectrum, the annealed film shows more intensity than the other film.

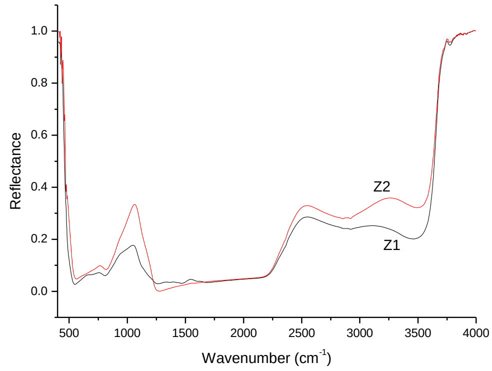

Fig 2. FTIR spectra of the prepared ZrO_2 films

The peak at 870 cm^{-1} was made up of contributions from Zr–O stretching vibrations. The band at 670 cm^{-1} produced by a Zr–O bending vibration appears in the spectra of thin films. Peaks occurred below 610 cm^{-1} belong to Zr–O bond vibrations. It can be seen that the samples exhibited absorption peaks located near 418 and 426 cm^{-1} which give an indication of presence Zr-O stretching bond [5].

C. *Optical reflectance*

Fig 3 shows the reflectance spectra of the prepared ZrO_2 thin film samples.

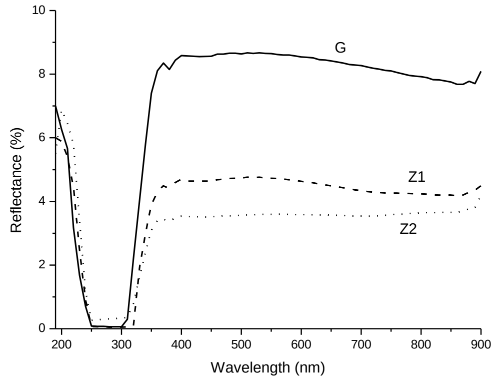

Fig 3. Reflectance for the prepared ZrO_2 films

The spectra illustrate a deep and broad minimum of reflectance in the UV domain and a maximum in the visible and infrared domains. The annealing process decreases the reflectance in the visible and IR region.

D. *Optical Transmittance*

The variation of transmittance of ZrO_2 thin films with and without annealing is shown in Fig 4.

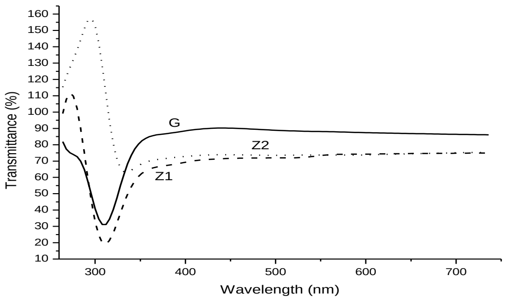

Fig 4. Transmittance for the prepared ZrO_2 films

It is evident from the spectra that in the ultra-violet region the transmittance is lower than that in the visible region. The decrease in transparency is due to the presence of tetragonal ZrO_2 in the film [6]. The maximum transmittance is probably due to the existence of an interfacial layer with low refractive index between ZrO_2 and glass substrates.

IV. CONCLUSION

Nanocrystalline Zirconium Oxide thin films were prepared by sol gel dip coating method. For the obtained ZrO_2 films, the structural and optical properties were investigated by XRD, FTIR and UV Visible spectroscopies. The XRD analysis revealed that the film exhibited tetragonal structure with dominat (101) orientation. The reflectance and transmittance of ZrO_2 films were maximum at visible and IR region. With the annealing, the reflectance gets decreased which is suitable for antireflection applications.

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