Characterization of Zirconium Oxide Thin Films Prepared by Sol - Gel Method

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Abstract: Zirconium Oxide (ZrO$_2$) is an interesting material in optical filters, gas sensors and protective coatings owing to their outstanding optical, chemical, thermal and mechanical properties. Zirconium Oxide thin films were deposited on glass substrates by sol gel dip coating method, using alcoholic solutions. The dipping solution was prepared from Zirconium Oxychloride Octahydrate and Isopropanol with Acetyl acetone. In order to find the influence of the number of layers on the properties of ZrO$_2$ thin films, samples with different number of layers were prepared by repeating the dipping and drying processes. After coating, the sol gel derived films were heated at 500°C, to complete the dehydration of the ZrO$_2$ precursors. Various characterization techniques were used to evaluate the crystalline structure and grain size (XRD), the morphology (SEM), surface bonding properties (FTIR) and luminescence properties (PL) of ZrO$_2$ films. XRD data exhibited that at 500°C temperature nanosized ZrO$_2$ films with tetragonal and monoclinic phases have been formed. FTIR spectra revealed the formation of Zr-O bond. Photoluminescence studies displayed a strong emission peak at 426 nm and relatively weak emission peak at 488 nm.

Keywords:- Zirconium Oxide; sol-gel; dip coating; XRD; SEM; FTIR and Photoluminescence.

Introduction and Experimental:

Crystalline ceramics are widely studied for optical applications owing to their high refractive index and transparency in the near UV-visible region. These materials are chemically and photo chemically stable and their excellent optical, mechanical, thermal and electrical properties make them ideal media for applications in Photonics.

Zirconia (ZrO$_2$) is a polymorphic material; it has several crystal structures at different temperatures. By controlling the temperature, one can tune the properties of Zirconia for particular applications. Among various fabrication techniques, the sol gel process is the widely used method of preparing ceramic oxide thin films. The main advantage of the sol gel process is it has the ability to form inorganic structures at relatively low temperature.

The aim of this investigation is to find, the influence of the number of layers on the structure, surface bonding and luminescence properties of ZrO$_2$ thin films.
In the present study, inorganic precursor route was chosen for the fabrication of Nano crystalline Zirconia thin films [1]. First, Zirconium Oxchloride Octahydrate was diluted in the 2-Propanol and Ethanol mixture (in the ratio 1:1). The solution was stirred 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 as a chelating agent to the solution and stirring was continued for a further 45 minutes.

The ZrO$_2$ films were prepared by dipping the glass substrates into the prepared sol gel solution. After dipping, the film layer was dried in air for a few minutes. The processes of coating and drying were repeated for 7 times. Finally, the films were annealed at 500°C. The annealed films were studied for their morphology, structural, surface bonding and photoluminescence properties.

**Results and Discussion:**

**X-ray diffraction studies**

The X-ray diffraction spectra of sol gel derived ZrO$_2$ thin films on glass substrates annealed at 500°C are shown in Figure 1. The XRD patterns reveal that all the samples are polycrystalline with characteristic peaks of ZrO$_2$ at 30.2°, 50.3° and 60° which are assigned to the (101), (200), (211) tetragonal planes respectively [2] and a monoclinic peak at 35.7° with (111) orientation.

![XRD patterns of ZrO$_2$ thin films](image)

Figure. 1. XRD patterns of ZrO$_2$ thin films

The grain size of the nanocrystalline film was calculated from the FWHM of the dominant diffraction peak (111) using Debye Scherer equation,

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

where D is the grain size, K=0.9 is a correction factor, $\beta$ is the full width at half maximum (FWHM) of the most intense diffraction plane, $\lambda$ is the wavelength of X-ray (CuK$_\alpha$ radiation $\lambda$=1.5405 Å) and $\theta$ is the Bragg angle. The crystallite size from the dominant peak is found to be nearly 2.25 nm for all the samples.

**Surface morphology studies**

Figure 2 shows the Scanning Electron Microscopic images of the surface of prepared ZrO$_2$ thin film samples.

![SEM images of ZrO$_2$ thin films](image)

Figure. 2. SEM images of ZrO$_2$ thin films a) 3 coating b) 5 coating c) 7 coating
The SEM images of the samples reveal that these solids are mainly constituted by large polyhedral structures or irregular laminar structures with a remarkable trend to fracture as suggested by the occurrence of a number of fissures. This fact is attributable to the effect of the removal of water and alcohols of different molecular size. The ZrO$_2$ films present plane cracked morphology, as product of their contraction during heat treatment.

**FT-IR spectral studies**

Figure.3. FT-IR spectra of ZrO$_2$ thin films

Figure. 4. PL spectra of ZrO$_2$Films

Figure 3 shows the Fourier Transform Infrared Spectroscopy of the ZrO$_2$ films. It can be seen that the samples exhibited absorption peaks located near 416 and 420 cm$^{-1}$ which give an indication of presence Zr-O stretching bond. The bands observed at 1456-1578 cm$^{-1}$ are characteristic of Zr-O-C species. The absorptions at 2926 cm$^{-1}$, 3535 cm$^{-1}$, 3508 cm$^{-1}$ correspond to the vibration of stretching and deformation of the O-H bond due to the absorption of water and co-ordination of water. The peak that observed at about 2347 cm$^{-1}$ is ascribed to the occurrence of C-H bond.

**Photoluminescence studies**

The room temperature photoluminescence spectra of ZrO$_2$ thin films observed at excitation wavelength 295 nm are shown in Figure 4. It is seen that the PL peaks of ZrO$_2$ samples are almost in the same wavelength position, but having varying intensities for different number of layers. These results indicate that the number of coatings does not alter the luminescence mechanism of ZrO$_2$ films. The PL intensity of 7 coating ZrO$_2$ is higher than that of the sample with lesser number of coatings. The spectra show an intense emission peak at 426 nm (blue) and a weak emission peak at 488 nm (blue-green). This may due to oxygen vacancies in ZrO$_2$ [3]. It was seen that the PL intensity of ZrO$_2$ thin films increases with an increase in the number of layers. This increase is due to improvement in crystalline quality and an increase in oxygen vacancies.

**References:**


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