Influence of Sol Concentration on the Properties of Spin Coated Zirconia Thin Films

A Kavitha 1, N Sankara Subaramanian 2 and S Vadivel 3

1, 2 Thinfilm Research Laboratory, Department of Physics, Thiagarajar college of Engineering, Madurai – 625 015, Tamil Nadu State, India.
3 Department of Physics, Paavai Engineering College, Paavai Nagar, Pachal - 637 018 Namakkal District, Tamilnadu State, India.

1 kavitha_26sep@yahoo.com , 2 shankersathiya@yahoo.com , 3vadivel.physics@gmail.com

Abstract. Present work involves with the preparation of Zirconia thin films on glass substrate by the cost effective spin coating method at different sol concentration and investigation of its structural, optical and surface properties. XRD profile of Zirconia thin films prepared at different concentration conforms tetragonal phase with preferred orientation along the (111) plane. The average particle size evaluated from the XRD data for solute concentration 0.3 mole is 61 nm. The optical transmittance of the Zirconia thin films have been measured in the visible and NIR region. The band gap energy lies in the range of 3.6 - 3.8 eV for thin films prepared at different concentrations. FTIR analysis shows the peaks 472 and 485cm⁻¹ are attributed to Zr-O stretching in tetragonal ZrO₂. The surface morofological features of the Zirconia thin films have been investigated from the 2D and 3D AFM images, which indicates smooth and uniform surface pattern without any pits of the pin holes.

1. Introduction
Ceramic coatings has been applied to high energy applications due to its low thermal conductivity, high band gap, high thermal expansion coefficients and high wear resistance [1-3]. Ceramic material particularly Zirconia thin films are used in thermal barrier coatings, optical coatings, buffer layers oxygen sensors, heat resistant coatings, ion conductors and optical storage elements etc [4-6]. There has been great scientific concentration in Zirconia thin films due to their phase transitions. Pure Zirconia exhibits three polymorphs depending on temperature: monoclinic (m) stable up to1170°C, tetragonal (t) stable up to 1170-2370°C, and above it have cubic (c) phase until it melt at 2706°C [7]. The property of thin films strongly lies on the method of preparation and growth parameters. Zirconia thin films has been prepared by a wide variety of deposition processes Viz., Plasma spraying [8], sol-gel spin coating [9], chemical spraying method [10], electro chemical deposition [11], ion assisted deposition [12], dip coating [13], hydrothermal processing [14], electron beam evaporation method [15] etc.. Out of these, sol-gel spin coating method gives us high superiority oxide materials and is well adaptable for thin film preparation. The surface of films prepared by sol-gel spin coating technique is very smooth which is very important to achieve desire properties for many applications. Other advantages of this method include high purity of precursor, high homogeneity of material, low processing temperature, absence of vacuum, low cost and high flexibility. The grain size and thickness generally inclined by the number of coatings and concentration of the sol. The sol concentration affects the thickness via the viscous drag on the substrate by the moving liquid [16, 17]. The present
work deals with the influence of sol concentration on the preparation of Zirconia thin films and to investigate its structural, optical and surface properties.

2. Experimental:
Aqueous solutions of ZrO$_2$ with concentrations of 0.1, 0.2, 0.3 and 0.4 mol dm$^{-3}$ were prepared using Zirconium Oxychloride Octahydrate (ZrOCl$_2$.8H$_2$O) as starting material. In order to adsorb and remove the acids produced the salt was mixed with 100 ml doubled distilled water. The solution was stirred well in magnetic stirrer for about an hour at a temperature of 85˚ C. The solution was air cooled in the ambient and then aged in open beakers at room temperature for gelation. After a period of aging, the solution becomes gel. ZrO$_2$ thin films were developed by dispensing about 2 ml of the as prepared gel on the glass substrate mounted over the turn table. Zirconia thin films have been deposited on glass substrates using the following optimum coating parameters: 1) coating period of the sol - 2-5 day 2) spin rate – 3000 rpm 3) spin time – 15sec 4) baking temperature - 400˚C 5) baking duration -7 minutes. The sol-gel coated substrates were baked at a temperature of 400˚ C for 7 minutes in air after each spin coating. By repeating this step for several times, pin hole free and uniform ZrO$_2$ films were obtained. The coated films were then annealed at temperature of 600˚ C for one hour duration each.

X-ray diffraction measurements of the ZrO$_2$ films were recorded using Philips pananalytical diffractometer. The optical transmittance of the films has been measured in the UV- Visible region, using the Perkin and Elmer spectrophotometer, from which other optical constants were arrived. FTIR spectral data for the ZrO$_2$ films were obtained using the SHIMADZU FTIR spectrometer in the wave number range of 2000-400 cm$^{-1}$. The surfaces feature of the ZrO$_2$ films has been investigated using Atomic Force Microscope (AFM).

3. Result and Discussion
3.1 Micro Structural properties
XRD analyses of spin coated ZrO$_2$ thin films were prepared at different solute concentrations are shown in Figure 1. The films prepared at different solute concentrations confirms metastable tetragonal phase of Zirconia thin films with preferred orientation along (111) plane. The other orientation observed with relatively lower intensities are (200), (220) and (311). For lower solute concentration the peak intensity is very low, on other hand, when the concentrations are increased, the intensity count and peak sharpness of all planes abruptly increases and this may attributed to increases oriented over growth and presence of large-sized grains. As solute concentration increases the tetragonal phase changes to monoclinic phase and have a sharp peak at 31°. The grain size of ZrO$_2$ films were calculated from the full width half maximum using the Scherrer equation and tabulated in table 1.

$$D = \frac{0.94\lambda}{\beta \cos \theta},$$

where D is the grain size, $\beta$ is the full width half maximum of the most intense plane, $\lambda$ is the wavelength of X-ray (CuK$\alpha$ radiation $\lambda=1.5406\AA$, $\theta$ is the Bragg angle. As the solute concentration increases the grains size also increases which may be due to the solute particles becomes larger thereby increasing the chance of more solute to be gathered together forming a grain. The FWHM value decreases linearly as the concentration increases indicating a better crystallinity of the films with higher solute concentration [16,17].The dislocation intensity and micro strain were calculated using the relation $\delta = 1/D^2$ and $\varepsilon = \beta \cos \theta / 4$. The dislocation density and micro strain tend to decreases as solute concentration increases which may be due to crystalline structure of the Zirconia thin films. At higher solute concentration dislocation density and strain increases due to the change in the preferred orientation of the films [18]. The texture coefficient of the film defined by Barret and Massalcki [19] can be used to describe preferred orientation of the film is given by

$$T.C_{hkl} = \frac{I_{(hkl)} / I_0_{(hkl)}}{1/N \sum I_{hkl} / I_{0hkl}}$$
Where $T.C_{(hkl)}$ is the texture coefficient of the (hkl) plane, $I_{i(hkl)}$ is the measured intensity, $I_{o(hkl)}$ is the standard intensity of JCPDS power diffraction pattern of the corresponding peak and $N$ is the number of reflection considered for the analysis. From the tabular column the value $T.C_{(hkl)} = 1$, for 0.3 mole concentration represents films with randomly oriented crystallites, while lower values indicate the abundance of grains oriented in a given (hkl) direction. The evaluated value of $T.C$ equals to unity implies that randomly oriented crystallites and chemically stable due to its closely packed surface. Standard deviation $\sigma$ from the powder diffraction condition was calculated by the following expression and tabulated for different solute concentration.

$$\sigma = \sqrt{\frac{\sum I^2_{hkl} - \left(\frac{\sum (I_{hkl})^2}{N}\right)}{N}}$$

The standard deviation $\sigma$ is less for 0.3 mole solute concentration compare to another solute concentration which indicates the crystalline structure of thin films.

![Figure 1 XRD spectra of Zirconium Oxide thin films prepared at different concentration (a) 0.1mole (b) 0.2mole (c) 0.3mole and (d) 0.4mole.](image)

**Table 1** Crystallographic parameters of the Zirconium Oxide thin films coated at different concentrations.

| Concentration in mole dm$^{-3}$ | Particle size in nm | Texture coefficient | Standard deviation $\sigma$ | Dislocation density $\delta * 10^{15}$ line/meter$^2$ | Micro Strain $\varepsilon * 10^{-5}$ line$^2$/m$^4$ |
|---------------------------------|---------------------|---------------------|-----------------------------|---------------------------------|------------------|
| 0.1                             | 51                  | 0.999               | 0.4358                      | 37                              | 76               |
| 0.2                             | 59                  | 0.999               | 0.4758                      | 28                              | 70               |
| 0.3                             | 61                  | 1.0056              | 0.408                       | 27                              | 69               |
| 0.4                             | 57                  | 0.999               | 0.51187                     | 29                              | 71               |

The 2D and 3D AFM image of the zirconia thin films spin coated with solute concentration 0.3 mole is shown in the Figure 2 (a, b). The AFM micrograph illustrates smooth 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.
3.2 Optical characterization

Transmission spectra of the ZrO$_2$ thin films prepared at different solute concentrations are shown in Figure 3. From the figure it is evident that for all the films, the transmittance spectra lie in the UV-Visible region. The transmittance is found to be 65-75% at the wavelength 400 nm for the Zirconia thin films prepared at different solute concentrations. Further, the figure shows that the transmittance increases with the increase in scattering due to large grain size and crystal aggregate, caused by the increase in film thickness with concentration [16]. The extinction coefficient k$_f$ is obtained from the transmission spectra using the relation,

$$ Kf = \frac{2.303 \log (1/T) \lambda}{4\pi t} $$

where T is the transmittance, $\lambda$ is the wavelength of light and t is the thickness of the corresponding film. The absorption coefficient $\alpha$ can be obtained from the relation $\alpha = \frac{(4\pi k_f)}{\lambda}$ 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.

Figure 3(a) Transmittance spectra of Zirconia thin films and Figure 3(b) Variation of $\alpha^2$ with photon energy prepared at different solute concentration (a) 0.1 (b) 0.2 (c) 0.3 and (d) 0.4 mole.
The variation of square of the absorption coefficient with photon energy of zirconia thin films prepared at different solute concentration is shown in Figure 3(b). The band gap energy value is found to be 3.6 - 3.8 eV. These values are coincides with the values reported by Ramamurty et al [20]. The low value of band gap may due to the non stoichiometric nature of the films. Moreover the band gap energy has been found to increase with the increase in concentration, which may be attributed to the increases in carrier density with increase in solute concentration [7].

### 3.3 FT-IR spectroscopy

![FTIR spectra of zirconia thin films](image)

Figure 4 FTIR spectra of Zirconia thin films spin coated with (a) 0.1 (b) 0.2 (c) 0.3 and (d) 0.4 moles.

Figure 4 shows the FT-IR spectra of the Zirconia thin films, prepared at different solute concentrations. The FT-IR spectrum, of the thin films prepared at 0.1- 0.3 mole concentration shows absorption band at 472 cm$^{-1}$. This band was shifted to 485 cm$^{-1}$ on increasing the solute concentration at 0.4 moles. The peaks 472 and 485 cm$^{-1}$ are attributed to Zr-O stretching in tetragonal ZrO$_2$. This shift in the absorption band at lower to higher frequency, with increase in solute concentration may be attributed to an increases of the Zr-O bond strength. The band observed around 2500cm$^{-1}$ is characteristic of Zr-O species. The bands at 3500cm$^{-1}$ are characteristic of OH groups [21].

### 4. Conclusion

Zirconia thin films were developed by cost effective spin coating method with different solute concentrations. The ZrO$_2$ thin films prepared with different solute concentrations indicates tetragonal phase with preferred orientation along the (111) plane. The tetragonal phase stabilization in the Zirconia thin films arises due to the presence of large-sized grains. The increase in optical transmittance with increase in solute concentration may be attributed to the reduced gain boundary scattering due to the enhanced crystallinity. The evaluated band gap energy lies between 3.6 - 3.8 eV. FTIR analysis shows the peaks 472 and 485cm$^{-1}$ are attributed to Zr-O stretching in tetragonal ZrO$_2$. The AFM image further shows accumulation of large number of fine grains associated with hump like oriented growth of the crystallites.
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