Optical and Structural characterization of spraying ZrO₂ and doped B: ZrO₂ thin films

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Abstract. Zirconium oxide (ZrO₂) and doped with boron (B) thin films were prepared by Chemical spray pyrolysis CSP. Optical band gap energy of the films decreased from 3.83 to 3.73.55 eV via increase of doping. X-XRD patterns disclosed that films structure were polycrystalline, mixture of monoclinic and tetragonal phases. Atomic force microscopy (AFM) results assure dependence of surface morphology and roughness upon doping.

Keywords. B:ZrO₂, thin films, Optical, XRD, AFM.

1. Introduction
Zirconia (ZrO₂) is an important metal oxide [1-4]. It possesses low electrical conductivity, high thermodynamic stability, transparency in visible region, good refractive index and melting point and wide bandgap [5, 6]. Three crystal structures for ZrO₂ including, Monoclinic at room temperature, transforms to Tetragonal phase at 1170°C, and at 2370°C it transforms to cubic structure [7]. The transition of zirconia can be direct and indirect transition [8]. It possesses high resistance to corrosion, which makes it an important material [9, 10]. Zirconia was used in many applications like, optoelectronic devices [11], high power lasers [12], light emitting diodes [13], superconducting coatings [14] and gas sensors [15]. ZrO₂ thin films have been prepared by many deposition processes namely, Plasma spraying [16], laser ablation [17], chemical spraying method [18], electrochemical deposition [19], reactive direct current magnetron sputtering [20], dip coating [21], hydrothermal processing [22], liquid phase deposition method [23]. The chemical spray pyrolysis is very suitable for metal oxide thin films [24-26].

In this research pure zirconia and B doping with 1% and 3% thin films were prepared in simple and low cost CSP to study their optical, structural and Morphology.

2. Materials and Methods
Zirconium oxide thin films were prepared utilizing CSP technique. Aqueous solution containing 0.1M Zirconium oxychloride (ZrOCl₂·8H₂O) (supplied from BDH Chemicals) and oxalic acid (supplied from Merck Chemicals) disbanded in 100 mL deionized water to form the initial solution. (BCl₃) (provide by Pub Chem India) was used as a doping material, with 1 and 3%wt, drops of HCl were mixed, to get a clear solution. The glass substrate temperature was kept at 300°C cover the deposition process. After many tests, the preparation conditions were reached the followings: space between the substrate and nozzle was kept at 28 cm. Spraying time was 10s, spraying rate was 4 ml/min and time interval between two spray process were 2 min. Nitrogen was used as a carrier gas. Transmittance and absorbance spectra
were on record by double beam spectrophotometer UV–Visible in the wavelength range (300–900) nm. XRD was used to set film structure and AFM were used to obtain film morphology.

3. Results and discussion
Transmittance spectra for all samples are displayed in Figure 1 Transmittance of ZrO₂ films suffer a sharp rise in (400-600) nm and up to 600 nm arrived at 85%. Absorption coefficient (α) was specified from absorbance (A) and thickness (t) employing the relation [27]:

$$\alpha = 2.3026 \frac{A}{t}$$

Where A is the absorbance and t film thickness, Figure 2 depicts the variations of α with wavelength (λ) for ZrO₂ and different doped 1% and 1% B: ZrO₂ thin films deposited in CSP. The result disclosed that absorption coefficient has gradual increase with increase wave length (λ) for all the samples in range (400-500) nm and the photon energy increases in the same range.

![Figure 1. Transmittance spectra of deposited thin films.](image1)

![Figure 2. Variation of α with wavelength (λ).](image2)
The optical band gap ($E_g$) was specified from Tauc’s plots using the equation [28]:

$$a\nu = k(\nu - E_g)\frac{1}{2}$$

where $k$ is constant, $\nu$ is photon energy. The energy gap was set as shown in Figure 3 demonstrates of a wide bandgap semiconductor from 3.83 to 3.73 eV. These values agree with the values reported in [29]. The decrease in $E_g$ is inconsistent with structural change of ZrO$_2$ thin films. Also, the crystallinity and the grain size increases with doping.

Figure 3. Band gap values of deposited films.

Figure 2.a shows the XRD patterns, reveal that the deposited films are polycrystalline and mixture of monoclinic and tetragonal phases with preferred grain orientations along (111), (020), (201), (212), (113) and (231). The planes (111), (020), (201) and (113) of monoclinic zirconia (m-ZrO$_2$) [JCPDS card no. 13-307] and (212) and (231) planes of tetragonal zirconia (t-ZrO$_2$) [JCPDS card no.17-923].

Crystallite size of ZrO$_2$ thin films was calculated using Debye Scherer’s formula given in Eq. (3) [30, 31].

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

Where, $\beta$ is FWHM in radian, $\lambda$ is X-ray wavelength and $\theta$ is Bragg angle. $D$ was calculated from the plane (020) for monoclinic phase, note that the intensity of reflection is slightly enhanced as it seen from Figure 3. Defects such as strain and dislocation density have the minimum value, which may be due to the improvement in crystallinity achieved by using boron as a dopant material.

Table1. Shown the dislocation density ($\delta$) by equation (4) [32] and the microstrain ($\varepsilon$) could be calculated by equation (25) [32].

$$\delta = \frac{1}{D^2}$$

$$\varepsilon = \frac{\beta \cos \theta}{4}$$
Table 1. Structural parameters of deposited films.

| Samples wt % | (hkl) Plane | 2θ(ᵒ) | FWHM (°) | (D) (nm) | Microstrain (Line².m⁻¹) x10² | (6) (Line. m⁻²) x10¹⁵ |  d (Å) | Standard | Calculated |
|---------------|-------------|-------|----------|----------|-----------------------------|------------------------|--------|----------|------------|
| 0             | (020)       | 34.37 | 0.45     | 18.37    | 0.195                       | 2.963                  | 0.285  | 0.285    |            |
| 1             | (020)       | 34.37 | 0.38     | 21.75    | 0.164                       | 2.113                  | 0.290  | 0.290    |            |
| 3             | (020)       | 34.37 | 0.23     | 35.94    | 0.99                        | 0.774                  | 0.296  | 0.296    |            |

Figure 4. XRD patterns of the deposited films (a) D (b) ε (c) δ(d).
Surface morphology and roughness of the prepared films were examined by AFM. The two and three dimensional AFM images are shown in Figs 5.a,b,c. The AFM images demonstrate that, before doping, the grown grains have a smoother surface (Figure 5a). It is evident from (Figure 5.b,c) AFM images that average crystallite size of B:ZrO$_2$ films increases with increase of dopant. The morphology changes are due to the different crystallization of ZrO$_2$ and densification of the films. The root mean square roughness ($R_{rms}$) and average roughness ($R_a$) of prepared films are shown in Table 2.

As can be seen the $R_{rms}$ and $R_a$ follow the dopant. The $R_a$ value of 0.68 nm for pure thin films increased to 0.86 nm and 8nm by increasing doping to 2% and 4% min in respectively. The AFM assure the dependence of topography parameters upon doping.

Figure 5. a. AFM 2D and 3D image of pure ZrO$_2$ thin films, b. and c. AFM images of the doped B:ZrO$_2$ 1% and 3%.
Table 2. Topography parameters of the deposited films.

| Samples wt% | Average Particle size nm | $R_a$ nm | RMS |
|-------------|--------------------------|----------|-----|
| 0           | 80                       | 0.68     | 0.796 |
| 2           | 90                       | 0.86     | 0.994 |
| 4           | 95                       | 8.00     | 9.16  |

4. Conclusions
The optical, structural and morphological properties of pure and B:ZrO$_2$ thin films on glass substrate by simple and low cost CSP technique were investigated. The films demonstrate a wide bandgap in the range from 3.73 to 3.83 eV. XRD of ZrO$_2$ and doped thin films show a polycrystalline with a mixture of monoclinic and tetragonal phases. The average dislocation density values were found to decrease with doping of B. The small value of dislocation density confirms that the films are good quality polycrystalline ZrO$_2$ thin films. Topographical parameters of prepared films are increased with increasing doping.

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