Effect of Indium Doping on Electrical and Optical Properties of ZrO_2-SnO_2 Nanocomposite Thin Films Prepared by Sol- Gel Technique

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Abstract:- **The field of nanocomposite materials has been widely recognized as one of the most promising and rapidly emerging research areas. Improvements in the physical and chemical properties of the nanocomposites are useful in optics and electronics. It is well-known that the metal oxide composite organized by zirconium dioxide (ZrO_2) and tin dioxide (SnO_2) has been widely used as catalysts and gas sensors due to the special surface acidity of ZrO_2 and the electrical property of SnO_2. Indium(0 – 5 mol%) doped ZrO_2-SnO_2 nanocomposite thin films were prepared by sol- gel dipcoating technique on to quartz substrate. X-ray diffraction spectra of all films showed the presence of tetragonal SnO_2 along with orthorhombic $ZrSnO_4$. When indium was incorporated in the film, the crystallization decreased. This may be due to the formation of stresses by the difference in ion size between tin (0.83 Å), zirconia (0.84 Å) and indium (0.62 Å) and segregation of dopants at the grain boundaries for higher doping concentration. An average transmittance greater than 80 % was observed for all the films. The calculated band gaps of indium doped films (5.34 – 5.48 eV) were higher than that of the undoped (4.79 eV) films. Carrier concentration of the doped layer increases with increase in indium concentration. Photoluminescence spectra of the films exhibited emission bands in the visible region of the electromagnetic spectra. Such conducting indium doped ZrO_2 - SnO_2 nanocomposite thin films with diminution in the crystallite size finds application in gas sensing devices.**

Key words – Nanocomposite, Thin films, Transmittance, Conductivity, Photoluminescence

1. INTRODUCTION

ZrO_2 nanoparticles would be an ideal building block for nanocomposites since they posses several advantages such as chemical inertness, excellent thermal stability, high refractive index and high hardness. It is well-known that the metal oxide composite organized by zirconium dioxide (ZrO_2) and tin dioxide (SnO_2) has been widely used as catalysts and gas sensors due to the special surface acidity of ZrO_2 and the electrical property of SnO_2 [1]. Indium dopant can inhibit the growth of crystallite depending on the doping concentration and play an important role in the optical properties including transmittance and luminescence. Zirconia- doped indium oxide (In:ZrO) has been proposed as a candidate material with high transmittance even in a long wavelength region and with low resistivity to replace indium doped tin oxide(ITO). Since In:ZrO has high mobility and low carrier concentration, it is attracting attention since the transmittance could be maintained relatively high even in a long wavelength region. Indium has valence electron one less than tin and zirconia, so the substitutional doping of indium in SnO_2 or in ZrO_2 can act as an acceptor. The structural property such as the crystalline state influences the carrier mobility of the films. Hence to improve conductivity and the bandgap tuning, ZrO_2 - SnO_2: In films were prepared by sol- gel dip coating technique. When compared with other techniques, the sol– gel route presents some advantages such as excellent homogeneity, thickness control, possibility of depositing on complex-shaped substrates, easier control of the doping level, rather inexpensive starting materials and simple equipment [2].

In this work, we report the preparation and characterization of ZrO_2 - SnO_2: In nanocomposite thin films deposited onto quartz substrate by sol–gel dip coating technique. Structural, electrical and optical properties of these films were studied.

2. EXPERIMENTAL TECHNIQUE

ZrO_2- SnO_2:In thin films were prepared by using $ZrOCl_2$. $8H_2O$ (Sigma–Aldrich 99.5%) as the source for zirconia, $SnCl_2$. $2H_2O$ (Alfa Aesar, purity: 99 %) as the source for tin, and $InCl_3.4H_2O$ (HPLC, purity: 99.5 %) as the source for indium. Indium doped ZrO_2 - SnO_2 nanocomposite thin films were prepared by the following procedure. 2.21 g of $SnCl_2$. $2H_2O$ is dissolved in 20 ml of ethanol and stirred it for 3 h to get a transparent solution. 1.60 g of $ZrOCl_2.8H_2O$ is dissolved in 6 ml of ethanol mixed with 6 ml of 2-butanol and stirred it for half an hour. The prepared SnO_2 precursor solution is then added to ZrO_2 solution under vigorous stirring. Then, add 1.3 ml of H_2O for hydrolysis, 0.07 ml of HNO_3 for oxidation, 6 ml of ethanol and 6 ml of 2-butanol mixed with 1.25 ml of acetyl acetone(used as catalysts) under vigorous stirring in a controlled manner. The stirring was continued for another 60 min to get a clear transparent solution. Required amount (0- 5 mol %) of $InCl_3.4H_2O$ was added as dopant source and stirred the solution for another 1h. Prepared sol–gel was kept at room temperature for 3 days. The filtered

precursor solutions were deposited on clean quartz substrate
using a dip coating apparatus. The dip coating parameters were optimized as 10 cm/min lifting speed and 90° vertical lifting. The films were dried at room temperature and pre-fired at 250 °C for 1 h. The process of dipping and pre-firing was repeated up to 7 times, as 7 coatings were required to obtain useful data from X-ray diffraction characterization. The samples were heated up to 500 °C in air at the rate of 4 °C /min and held at this temperature for 1 h and finally cooled to room temperature with the same rate. The characterizations of these annealed films were then performed.

Crystallization phase of the films were characterized by using X-ray diffractometer (XRD) (Model XPERT-PRO) operated at a voltage of 40 KV and a current of 30 mA, using CuK_α radiation (λ=1.54 A°). The parameter setting for all XRD scans is 1.5°/min and a step size of 0.016° in a 2 h range of 20 – 70°. Optical transmittance was studied using a spectrophotometer (Model JASCO - V550) in the range of 200-900 nm. The thickness and refractive indices of the samples were calculated using Swanepoel's envelope method. Photoluminescence (PL) spectrum was recorded by using Flourolog III modular spectro- flourometer (Horiba Jobin Yvon) equipped with 450 W Xenon lamp and Hamatsu R928-28 photomultiplier. All the spectra were recorded at room temperature. Excitation wavelength used was 370 nm. The conductivity of ZrO_2 - SnO_2: In nanocomposite films was determined by four-point
probe measurements with a Keithley 6200 source meter and a cylindrical four-point probe head.

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction Studies

Fig. 1 shows the XRD pattern of ZrO_2 - SnO_2: In films for various indium doping concentrations annealed at 500 °C in air. Analysis of XRD data for 1-3 mol % of indium doped films, revealed reflections at 26.3° and 33.5° corresponding to SnO_2 (110) and (101) planes respectively [PDF No. 880287] and 51.7° corresponding to $ZrSnO_4$ (103)
[PDF No. 480889] planes, respectively. The intensity of the peak slightly decreased with increase in indium doping concentration indicating deterioration in crystal quality of ZrO_2-SnO_2: In films. In Fig. 1, neither metallic tin/zirconia nor high intensity indium characteristic peaks were observed from the XRD patterns indicating the incorporation of indium into the ZrO_2- SnO_2 lattice. The absence of ZrO_2 peaks in the XRD pattern, suggests a dispersion of ZrO_2 in SnO_2 matrix [3].

Table 1: Crystallite size, thickness and band gap of ZrO_2 - SnO_2 thin films for a) 0, b) 1, c) 3 and d) 5 mol% indium doping annealed at 500 °C.

Indium concentration (mol %)	Crystallite size (nm)		Thickness (nm)	Band gap (eV)
	SnO_2	$ZrSnO_4$		
0	6.30	7.90	226	4.79
1	4.71	6.97	339	5.34
3	4.36	6.60	317	5.37
5	3.83	4.73	222	5.48

The average crystallite size (D) of the films was calculated using Scherrer's equation [4]

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \ldots\ldots\ldots\ldots (1)$$

where K = 0.9, a correction factor, β, the full width at half maximum (FWHM) of the most intense diffraction plane, λ ,the wavelength of X-ray ($CuK\alpha$, λ = 1.5405 A°) and θ, the Bragg angle.

Table 1shows crystallite size of SnO_2 and $ZrSnO_4$ for ZrO_2 – SnO_2: In thin films. The average crystallite size of SnO_2 and $ZrSnO_4$ for ZrO_2 - SnO_2: In films (0-5 mol %) varied from 6.3 - 3.83 nm and 7.9 – 4.73 nm respectively with variation in indium concentration. The crystallite size decreased with increase in indium content, indicating deterioration in the crystal quality of the film, which may be due to the formation of stresses by the difference in ion size between tin (0.83 Å), zirconia (0.84 Å) and indium dopant (0.62 Å) and the segregation of dopants in the grain boundaries for high doping concentrations. The shift in 2θ values of (110), (101) of SnO_2 and (103) of $ZrSnO_4$ peak indicates a change in stress in ZrO_2 – SnO_2 thin films, with variation in indium concentration. These particle sizes (~ 6 nm) are used in gas sensing application.

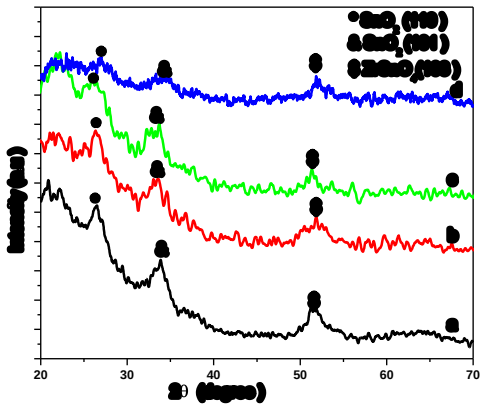

Fig.1 XRD pattern of ZrO_2-SnO_2 nanocomposite doped with a) 0, b) 1, c) 3 and d) 5 mol % Indium annealed at 500°C

3.2 Optical studies Optical transmittance spectra of ZrO_2 - SnO_2: In films were recorded in the wavelength region 200 - 900 nm are shown in fig. 2. It was very clear from the transmittance spectra that the ZrO_2 - SnO_2 :In films had better transparency than pure ZrO_2 - SnO_2 films (80 % at 525 nm for undoped ZrO_2 - SnO_2 and 96 % at 525 nm for ZrO_2 - SnO_2 doped with 1 mol % indium), except at high doping levels. The shift in the absorption edge may be attributed to carrier concentrations, carrier distributions and defects presented in the film. When the doping concentration increased, the amplitude of the fringe pattern became smaller. The slight decrease of transmittance at

higher doping concentrations may be due to the scattering of photons by crystal defects created by doping.

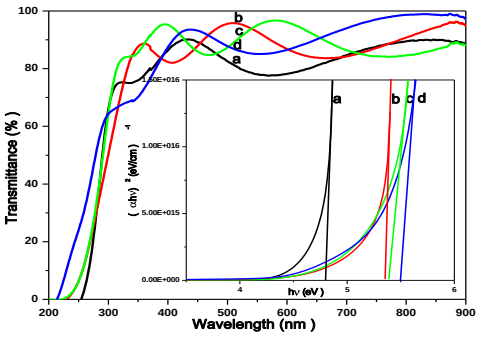

Fig.2 Transmission spectra of ZrO_2–SnO_2 nanocom- posite thin films for a) 0 b) 1 c) 3 and d) 5 mol % indium doping annealed at 500 ºC. (Inset shows plot of $(\alpha h\nu)^2$ versus hν curve)

The optical band gap can be deduced from the transmittance using Tauc's relation [5]

$$\alpha h\nu = \left(h\nu - E_g\right)^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Where hν is the photon energy, α, the absorption coefficient corresponding to frequency ν, E_g, the band gap energy. Assuming a direct transition between valence and conduction bands, the energy band gap (E_g) was determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. (Inset Fig.2: $(\alpha h\nu)^2$ versus hν plot). Calculated values of E_g are given in Table 1. The band gap of the films varied from 4.79 to 5.48 eV with variation in indium content. The band gap of indium doped films was higher than that of the undoped samples (4.79 eV) and E_g increased with the increase in the doping concentrations. It is supposed that the contribution from In^{3+} ions on substitutional sites of Zr^{4+}/sn^{4+} ions and In-interstitial atoms determine the widening of the band gap caused by increase in carrier concentration. Also the widening might be due to low crystallinity.

The carrier concentration of the doped layer can be calculated from the band gap by using the following equation

$$N^{2/3} = \frac{\Delta E_g}{2.77*10^{-16}} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

where ΔE_g[eV], widening of the gap to the Burstein – Moss effect, N(cm^{-3}), carrier concentration. Calculated values of carrier concentration are given in table 2. In fact increasing the carriers cause to increasing the scattering and then decreasing the transmission.

Table 2: Carrier concentration of ZrO_2 - SnO_2 thin films for a) 1, b) 3 and c) 5 mol % indium doping annealed at 500 ºC.

Indium concentration (mol %)	Carrier concentration ($x10^{22}$ cm^{-3})
1	8.37
3	11.30
5	12.43

3.3Photoluminescence

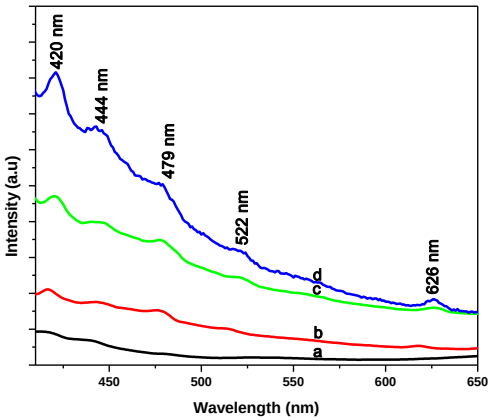

Fig. 3 Photoluminescence spectra ZrO_2–SnO_2 nanocomposite thin films for a) 0 b) 1 c) 3 and d) 5 mol % indium doping annealed at 500ºC.

Fig.3 depicts the photoluminescence spectra of pure and indium doped ZrO_2–SnO_2 nanocomposite thin films at an excitation wavelength of 370 nm [6,7]. The emission spectra of pure ZrO_2 - SnO_2 thin films annealed at 500ºC consists of emission peaks at 415, 434, 479 and 535 nm. The emission spectra of ZrO_2-SnO_2: In thin films consists of emission peaks at 417, 444,477,515 and 617 nm, 419,444,478,521 and 626 nm, 420,444,479,522 and 626 nm respectively for 1, 3 and 5 mol% indium doping. The emission peak at 420 nm may be due to oxygen vacancies in $ZrSnO_4$ which interact with interstitial atoms of zirconium and tin and lead to the formation of trapped states within the band gap giving rise to PL [6]. The peak at 444 nm is due to midgap trap states of SnO_2. The peak at 479 nm is due to singly charged oxygen vacancies in SnO_2 film. The green emission at 522 nm is associated with the presence of more defect levels (oxygen vacancies) in thin film and radiative recombination of a hole in the valence band with an electron occupying the deep oxygen vacancy energy band. The emission at 617 nm is related to surface defect states. The blue shift may be attributed to the reduction of size and grain boundaries. Higher relative PL intensity of doped ZrO_2-SnO_2 film can elucidate that rich oxygen deficiency, such as oxygen vacancy and oxygen-indium vacancy, is useful for improving the film conductivity.

3.4 Conductivity

Fig. 4 shows the variation in conductivity of ZrO_2-SnO_2: In thin films for various indium doping concentrations. Electrical conductivity measurements of doped samples were found to be increasing with indium concentration. It is very clear from the figure that ZrO_2 – SnO_2 with 5 mol % indium doping had practically lowest resistivity. The decrease in resistivity might be naturally due to the acceptor action of indium. On doping, zirconia/ tin at lattice sites might be progressively replaced by indium atom and/or indium could occupy interstitial position, promoting the conductivity. Indium at interstitials might be acting as scattering centers and this may also support the enhancement of conductivity. The electrical

conductivity is related to the number and mobility of carriers. Initially doped indium ions (In^{3+}) might have substituted Zr^{4+}/Sn^{4+} sites or gone to the interstitial positions leading to the release of free carriers. H.-G. Kang et al. has reported that decrease in the hole concentration and the increase in the resistivity with the dopant concentration indicate that dopant is not incorporated well into the desired substitutional sites. The highest hole concentration achieved in this study was $12.43x10^{22}$ cm^{-3} for the film with In/Sn ratio≤ 0.2.

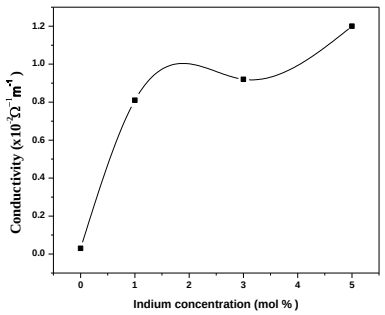

Fig.4 Variation of conductivity with different indium concentration in indium doped ZrO_2 - SnO_2 films

CONCLUSION

Undoped and indium doped ZrO_2 – SnO_2 nanocomposite thin films were deposited onto quartz substrate and annealed at 500°C by sol – gel dip coating technique. XRD pattern of these films showed variation in crystallite size. Crystallite size of SnO_2 and $ZrSnO_4$ decreased with increase in indium concentration. An average transmittance greater than 80 % was observed for all the films. The optical band gap values, relative PL emission intensity and conductivity of these films increased with increase in indium concentration. Such films with high value of conductivity and having transmittance greater than 80 % may be preferred in optoelectronic applications.

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