EFFECT OF Zn CONCENTRATION ON PHYSICAL PROPERTIES OF NANOSTRUCTURE TIN OXIDE FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

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In this study, we investigate the electrical, optical and structural properties of pure and zinc doped tin oxide thin films in details. Thin films of undoped and zinc doped tin oxide were prepared on glass substrates at 450 °C by spray pyrolysis technique. Zinc acetate dehydrate (Zn $(CH_3COO)_2.2H_2O$) was used as a source for zinc (Zn) in doped films. To obtain an optimum result, thin films were first deposited with different tin chloride concentration in start solution that was varied from 0.05M to 1M. The optimum amount of molarities was used for preparing SnO_2 thin films with different zinc doping levels. The results of X-ray diffraction show that the preferred orientation of deposited films depends on the molarities and Zn concentration in the starting solution. SEM studies show that the variation of concentration in the starting solution results in different grain sizes and shapes for different orientations. The electrical properties show that the sheet resistance of SnO_2 films increase with increasing Zn concentration. Optical transmittance measurements show that thin films are fully transparent in the visible region.

1. Introduction

Tin oxide (SnO_2) is one of the most important transparent conductive oxide materials which are attractive from scientific and technological point of view due to its interesting properties such as high electrical conductivity and high transmittance in the UV-visible region. Their property is resulted from its n-type semiconductor behavior and wide band gap. Many workers have tried to improve the physical properties of tin oxide films by doping the films with different dopants such as antimony [1], fluorine [2] and thorium [3]. There are many applications have been used for depositing these films such as gas sensors[4], transparent electrodes[5], solar cells[6] and etc. many techniques can be used to produce tin oxide films such as evaporation[7], sputtering[8], pulsed laser ablation[9] and spray pyrolysis[10]. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive for large area applications. The properties of TCO films are sensitive to the preparation conditions [10-14]. TCO films have been widely utilized as an essential part of many optoelectronic devices, such as solar cells and thin film transistors, due to their unique properties of high electrical conductivity and high optical transparency[15,16].

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2. Experimental

Undoped and zinc doped SnO_2 thin films were deposited on glass substrates at 450 °C by spray pyrolysis technique. The starting solution for SnO_2 thin films was formed by different molarities of tin chloride dehydrate ($SnCl_2.2H_2O$) diluted in 40 ml methanol. For more solubility, we added 50 drops of HCl [37 %] to the base solution. The optimum amount of molarities was used for preparing doped films. For Zn doping, an appropriate zinc acetate was dissolved in the starting solution. Zn concentration was varied from 0-25wt%. The distance between the substrates and atomizer was fixed in 25cm. Compressed air was used as the carrier gas at a flow rate of 22L/min.

3. Results and discussion

In this work, we used different tin chloride concentration in the starting solution. The molarity of the solution was varied from 0.05M to 1M. The experimental results show that the film with 0.2M concentration is optimum for obtaining high electrical conductivity and high transmission. Thus, this molarity was used for different Zn concentrations in doped films.

Fig.1 shows the XRD patterns of SnO_2 thin films prepared with different tin chloride concentrations and were recorded with a PW1840 using Cu Kα (λ = 0.154060 nm) radiation.
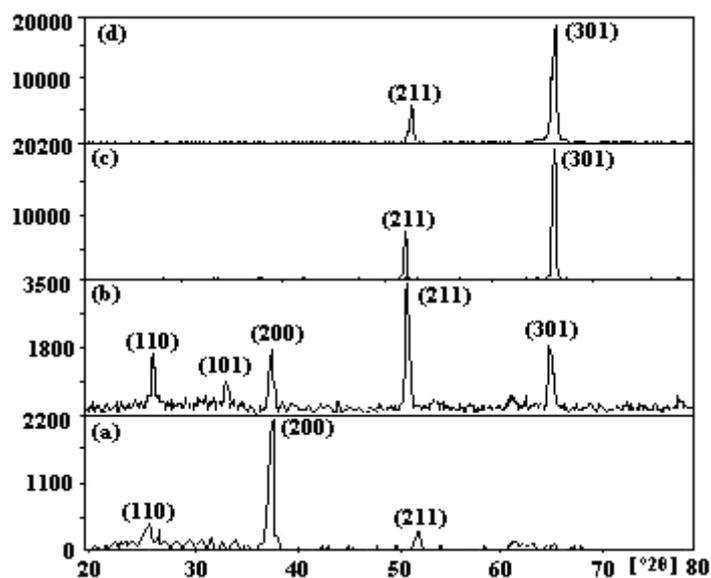

Fig.1. XRD patterns of SnO₂ with different molarities (a): 0.05M, (b):0.2M, (c): 0.8M, (d): 1M.

The figures show that all films are polycrystalline. For the films with 0.05M concentration the preferred orientation is (200). Upon increasing molarity the prominent (211) and (301) planes obtained for the films with 0.2M and 0.4M concentration. The (301) peak is also the preferred orientation for 0.6M, 0.8M and 1M, but its intensity decreases to 1M. The results of XRD also show that the full width at half maximum (FWHM) of peaks decrease with increasing molarity to 0.8M. Consequently, the grain size increases.

Fig.2 shows the XRD patterns of $Zn:SnO_2$ thin films prepared with different zinc concentrations. The top pattern corresponds to a standard SnO_2 randomly oriented polycrystalline powder pattern from the JCPDS-ICDD, 2005, with the rutile tetragonal phase [17]. Undoped SnO_2 film shows a XRD pattern similar to that of standard powder, with a slight (110), (200) preferred orientation. The figures clearly show that deposited films have preferred orientation along (211). Increasing the amount of zinc with respect to tin material changes the preferred orientation to

(101). More increasing zinc concentration to 25wt% cause the quality to be deteriorate which is clear from the decrease of peak intensity.
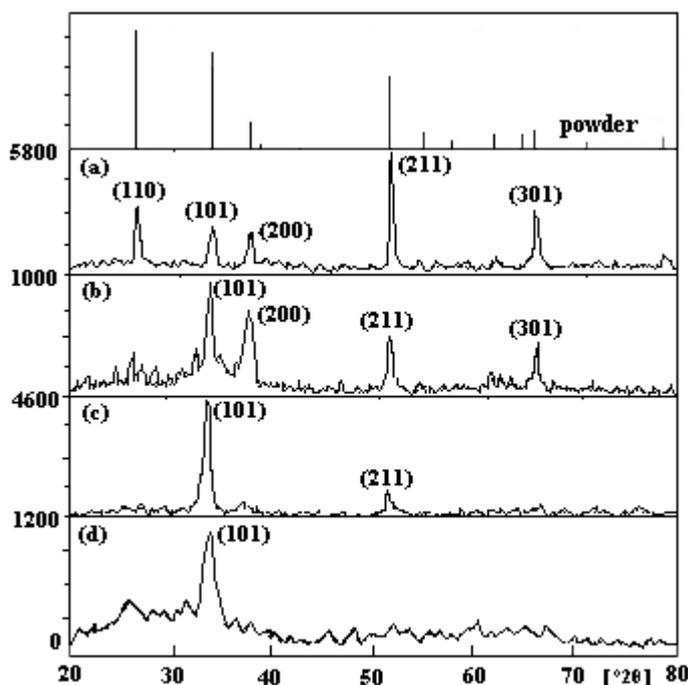

Fig.2. XRD patterns of undoped and Zn doped SnO₂ with different Zn concentration (a): undoped, (b):0.6wt%, (c): 5wt%, (d): 25wt%.

The SEM micrographs of pure SnO_2 thin films with different molarities shown in Fig.3. The SEM pictures clearly demonstrate that all of SnO_2 thin films are almost uniform. Upon increasing tin chloride concentration in the starting solution the surface morphology of the films changes and the grains size increase. Thus SEM studies corroborate the XRD findings. The difference in grain shapes, as observed in SEM studies, was reflected in XRD analyses as they lead to different orientations. The films with the morphology of characteristic needle shaped grains showed the preferred orientation along (200) plane, whereas the rectangular and cuboidal shaped grains were oriented along the planes of (301) and (211), respectively [18].
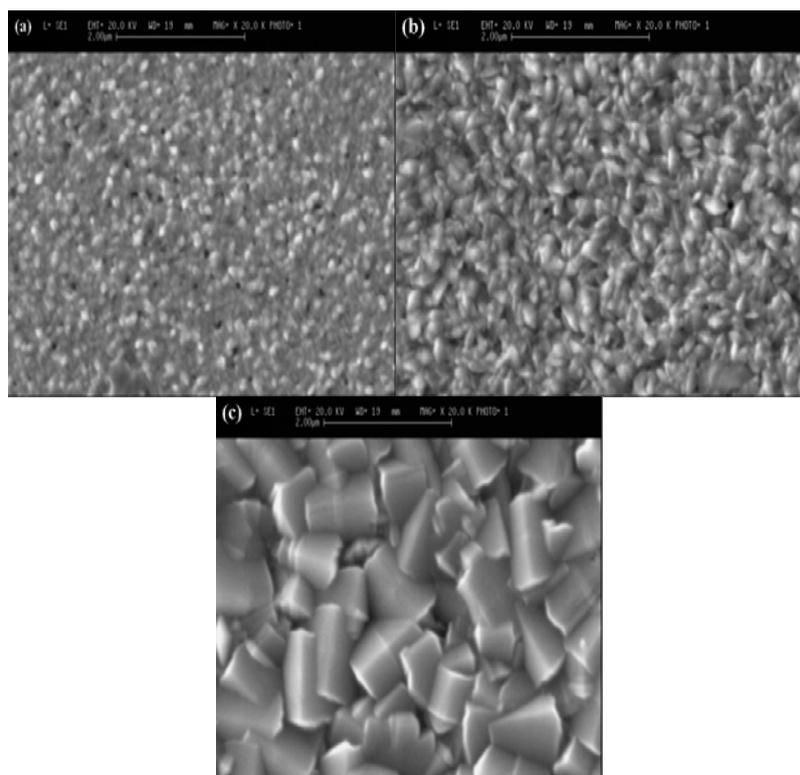
Fig. 3. SEM micrograph of SnO$_2$ thin films with different molarities (a): 0.05M, (b): 0.2M, (c): 0.8M.

Fig.4 shows the SEM micrographs of pure and Zn doped SnO$_2$ thin films. It is clear that upon increasing the Zn concentration in the starting solution, the surface morphology of the films change and the grain sizes decrease. In this state the crystalline structure deteriorates. Thus, SEM studies confirm the XRD findings for obtaining the amorphous structure in high Zn concentrations.
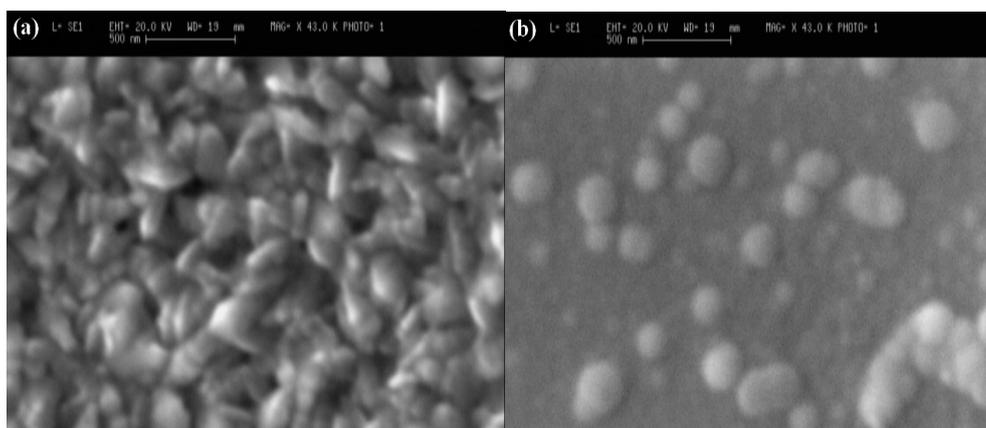

Fig.4 . SEM micrograph of (a): SnO$_2$ and (b): 25%- Zn:SnO$_2$ thin films.

Fig.5 shows the sheet resistance of SnO$_2$ films as a function of tin chloride concentration in the starting solution. The sheet resistance was measured by using the 2-probe method. It can be seen that sheet resistance (R$_{sh}$) decreases with increasing molarity in solution. The decrease of sheet resistance may be related to decrease of the grain boundaries and scattering of carrier concentration in grain boundaries. We can also see an increasing in sheet resistance in 1M due to decreasing (301) peak intensity and increasing the full width at half maximum.
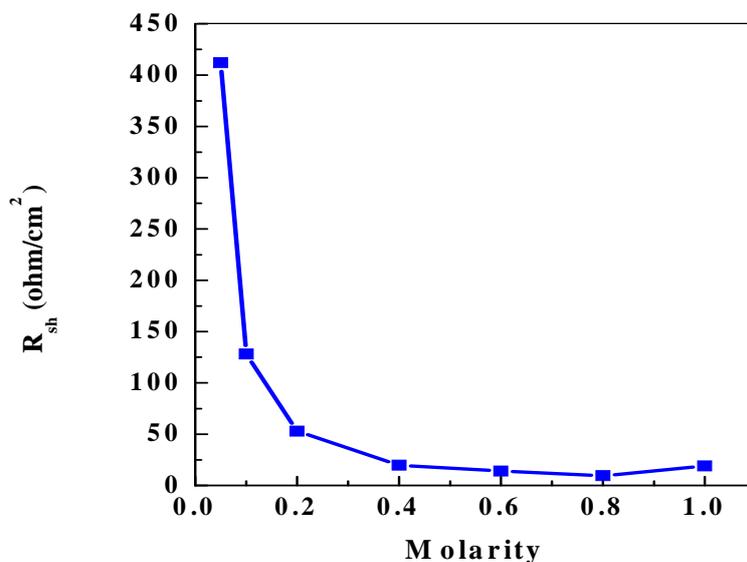
Fig.5. Variation of sheet resistance as a function of tin chloride concentration in the starting solution

The electrical properties of Zn doped SnO_2 thin films with different Zn concentration were showed in Fig.6. The result shows that sheet resistance increases with increasing Zn concentration to special weigh percent and then decreases. The increase in electrical properties of SnO_2 films with increasing Zn concentration can be explained through two cases. 1) The concentration of free charge carriers in SnO_2 decreases by the Zn concentration, because Zn has two valance electrons less than Sn. Zn^{2+} can be substituted the Sn atom or occupies the interstitial sites in crystalline lattice. Therefore, the number of free electrons decrease and sheet resistance increases. 2) This increase in the sheet resistance is attributed to the decrease in the grain size of the films as evidenced by the SEM and XRD results. The variation of grain size calculated from XRD results is shown in Table 1.
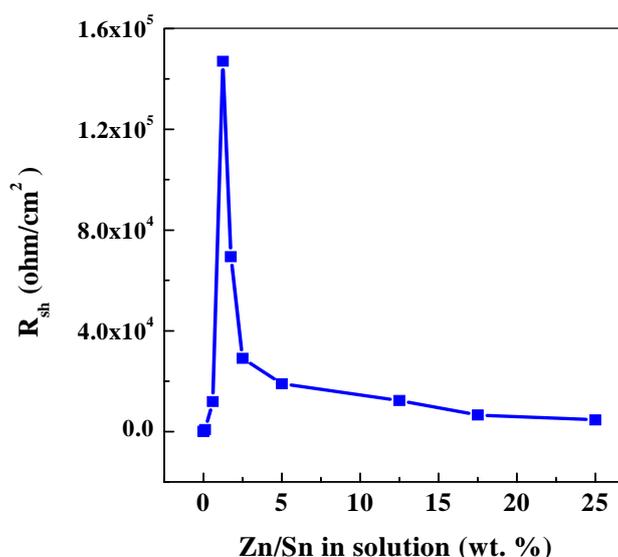

Fig.6. Variation of sheet resistance respect to Zn concentration in solution

Table 1. The variation of sheet resistance and grain size for SnO₂ films with different Zn concentration

Zn/Sn in solution (wt. %)	R_{sh} (kΩ/)	Average grain size calculated from XRD (nm)
0	0.07	32.7
0.6	11.9	-
1.75	69.4	15.39
5	19	18.45
17.5	6.5	-
25	4.6	17.74

Fig.7 shows the optical transmittance spectra of SnO₂ films prepared with different molarities of SnCl₂.2H₂O material. It is clear that the transparency of SnO₂ films decrease with increasing molarity of the starting solution. The transmittance value of 83% for 0.05M SnO₂ thin films decreases to 7% for 1M SnO₂ thin films in the visible region (550nm).
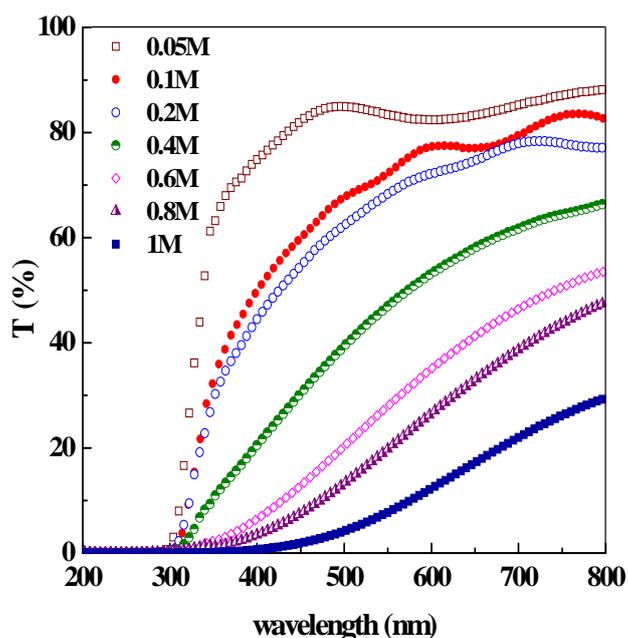

Fig.7. Optical transmittance of SnO₂ thin films with different molarity

Optical transmittance measurements of Zn:SnO₂ films with different Zn concentrations are shown in Fig.8. The pictures show that prepared films are fully transparent in the visible region. The average transmittance for doped films is higher than 71%. The picture also shows that the edge absorption of the films increase with increasing Zn concentration in solution
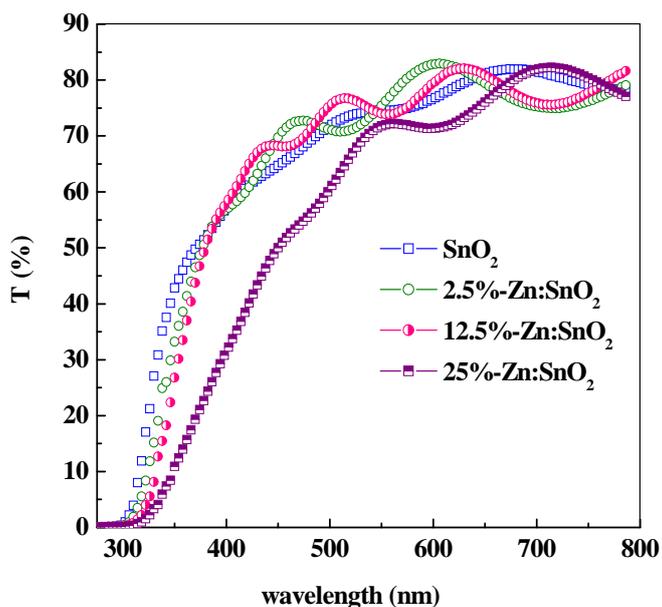
Fig.8. Optical transmittance of Zn:SnO₂ thin films with different Zn concentration
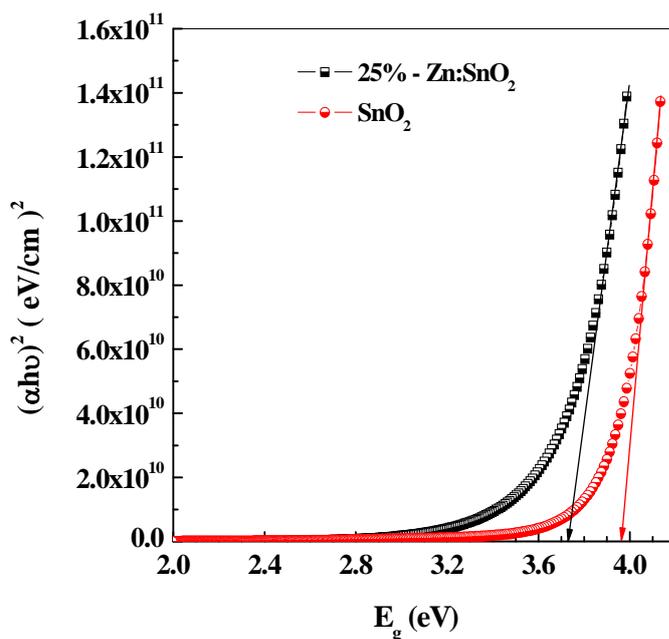

Fig.9. Variation of band gap for SnO₂ thin films doped with Zn.

The fundamental absorption refers to the optical transition of electrons from the valence band to conduction band and can be used to determine the nature and values of optical band gap of the films [19].

The absorption coefficient (α) value as a function of photon energy for direct transition from valence band to conduction band can be calculated by following equation:

$$\alpha = A\left(h\upsilon - E_g\right)^n$$

where E_g is the band gap energy, $h\upsilon$ is the photon energy and A is the fixed parameter. The exponent n is ½ for direct transitions and 2 for indirect transitions. Many workers reported that

SnO_2 has a direct band gap [20]. Fig.9 shows a plot of $(\alpha h \upsilon)^2$ as a function of E_g for $Zn:SnO_2$ films. It is clear that pure SnO_2 films have a band gap about 3.95 eV. Upon increasing Zn concentration the band gap decreases to $\sim$ 3.75 eV.

4. Conclusion

In this work, thin films of tin oxide with different $SnCl_2.2H_2O$ concentration were prepared on glass substrates at 450 °C by spray pyrolysis technique. The physical properties of SnO_2 thin films were characterized by different methods. The results of characterization show that the grains size of SnO_2 films increase with increasing molarity of the starting solution and thereby sheet resistance and transparency decrease. The optimum molarity was used for preparing SnO_2 thin films with different zinc doping levels. The results of XRD show that the preferred orientation of the films changes from (211) to (101) with increasing Zn concentration in solution. From SEM, we can find that crystalline structure was deteriorating with increasing Zn concentration. The band gap of the films also decreases from 3.95 eV to 3.7 eV with increasing Zn concentration.

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