

Influence of Zn doping on electrical and optical properties of multilayered tin oxide thin films

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Abstract. In this study, the electrical and optical properties of Zn doped tin oxide films prepared using sol–gel spin coating process have been investigated. The SnO₂:Zn multi-coating films were deposited at optimum deposition conditions using a hydroalcoholic solution consisting of stannous chloride and zinc chloride. Films with Zn doping levels from 0–10 wt% in solution are developed. The results of electrical measurements indicate that the sheet resistance of the deposited films increases with increasing Zn doping concentration and several superimposed coatings are necessary to reach expected low sheet resistance. Films with three coatings show minimum sheet resistance of 1.479 kΩ/ in the case of undoped SnO₂ and 77 kΩ/ for 5 wt% Zn doped SnO₂ when coated on glass substrate. In the case of single layer SnO₂ film, absorption edge is 3.57 eV and when doped with Zn absorption edge shifts towards lower energies (longer wavelengths). The absorption edge lies in the range of 3.489–3.557 eV depending upon the Zn doping concentration. The direct and indirect transitions and their dependence on dopant concentration and number of coatings are presented.

Keywords. Transparent conducting oxides; electrical and optical properties; tin oxide films; zinc doping; spin coating.

1. Introduction

Non-stoichiometric and doped films of metal oxides such as tin, cadmium, indium, zinc and their various alloys, deposited by various techniques exhibit high transmittance in the visible region and nearly metallic conductivity. In the last few decades, numerous transparent and electrically conductive metal oxide thin films have been extensively investigated (Chitra and Shailaja 1995; Shanti *et al* 1999). These transparent conductors have found major applications in a variety of active and passive electronic and opto-electronic devices (Chopra *et al* 1983) ranging from aircraft window heaters to charge coupled imaging devices. Heterojunction of transparent conductive oxides on bulk semiconductors (Vishwakarma *et al* 1992; Luo and Thomas 1993; Van Den Meerakker *et al* 1993) shows considerable promise for use in inexpensive solar cells. Of these, tin oxide and doped tin oxides are well known for their transparency when made into thin films and are expected to find wide use as transparent electrodes in many devices such as liquid crystal displays, heat shields (Granquist 1990), solar cells (Lampert 1981) and gas sensing devices (Nanto *et al* 1986). The performances of these devices are greatly dependent on the electrical and optical properties of the transparent electrodes. It must also be noted that, for applications in electronics or optics,

a very high quality film surface is required, in contrast to the case of sensor applications where a large developed surface is needed (Chatelon *et al* 1999).

The methods that are used more often for depositing undoped and doped SnO₂ films are rf sputtering (Kulkarni and Knickerbocker 1992; Karasawa and Miyata 1993), chemical vapour deposition (Park *et al* 1995), spray pyrolysis (Tarey and Raju 1985; Lane *et al* 1992), sol–gel dip coating (Chatelon *et al* 1994) and spin coating (Sunita *et al* 2002). In fact, the electrical and optical behaviours of these films greatly depend upon the deposition technique (Chopra *et al* 1983). In this work we have chosen the sol–gel spin-coating method. The most important qualities of sol–gel process are its potential to introduce a wide spectrum of dopants and modifiers into the films and ease to control the morphology. Among the different sol–gel coating techniques available, the spin coating method seems to be simple, low cost process and requires less complicated equipment compared to other methods.

2. Experimental

2.1 Film deposition

For the deposition of undoped SnO₂ thin films, the following precursor was prepared (Sunita *et al* 2002). Starting from stannous chloride (SnCl₂·2H₂O), the sol was prepared by mixing it with water, propanol (C₃H₇OH) and

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isopropanol (2-C₃H₇OH) in the following molar ratio: SnCl₂·2H₂O : H₂O : C₃H₇OH : 2-C₃H₇OH :: 1 : 9 : 9 : 6. We have extended this hydro-alcoholic solution method for the preparation of Zn-doped tin-oxide thin films. Hydro-alcoholic zinc solution was simultaneously prepared by dissolving certain amount (5, 8 and 10 molar wt% in solution) of zinc chloride (ZnCl₂) in proportionate amount of propanol and *iso*-propanol taken in a separate vessel. This solution was stirred at room temperature for 1 h and added to the SnO₂ solution. The doped mixture was finally stirred for about 2 h in order to get initial clarity.

The films were deposited on a glass substrate with an area, 22 × 22 mm, by spin coating. The glass substrate was cleaned using organic solvents and deionized water in ultrasonic cleaner, and dried at 80°C for about 20 min. The films were deposited while the substrate was spinning at 2300 rpm and spin time of 25 s. The films were dried at 100°C for about 15 min and fired at 480°C in air for about 15 min. Multi-coating films were prepared by repeating the coating–drying–annealing cycle. Preparation of sol and deposition of film were carried out under approximately similar laboratory conditions.

2.2 Characterization measurements

Thickness of the deposited film was estimated by gravimetric method using a microbalance with sensitivity, 1 µg. The thickness, t , of the film is given by

$$t = \frac{(m_1 - m_0)}{a \times r}, \quad (1)$$

where m_0 is the mass of the substrate before deposition of the film, m_1 the mass of the deposited substrate, a the surface area of the substrate and r the bulk density of SnO₂.

2.2a Sheet resistance and resistivity measurements: For the measurement of sheet resistance of the deposited films two wires were soldered with indium contacts at the ends of the sample. I – V characteristics were recorded using Keithley 236 I – V source measure unit and METRICES-ICS software. The films were taken in the resistor mode and current was measured with voltage sweep of 20 V in steps of 0.5 V. Then by using I – V data, sheet resistance (R_s) of the samples was calculated using the relation

$$R_s = \frac{p}{\ln 2} \times \frac{V}{I}, \quad (2)$$

where V is the applied potential and I the measured current.

The resistivity, r , of the deposited film was determined by using the relation

$$r = R_s \times t. \quad (3)$$

Table 1 shows the variation of sheet resistance and resistivity with increasing acceptor dopant concentration (wt% in solution) in the case of single and multi-layer films. Figure 1 shows the variation of sheet resistance with dopant concentration and number of coatings. The sheet resistance of SnO₂ film increases with increasing dopant concentration. The sheet resistance of the films decreases with increase in the number of coatings.

2.2b Optical absorption measurements: Optical absorption studies were carried out using SECOMAM UV-vis spectrophotometer in the wavelength range 200–1100 nm using Dathelit software. Neglecting the reflectance, the absolute absorption coefficient, a , was determined directly from the spectrometer readings, by using the relation

$$a = \frac{2.303}{t} \times OD, \quad (4)$$

Table 1. Values of film thickness (t), sheet resistance (R_s) and resistivity (r) of SnO₂:Zn films with different doping concentrations and number of coatings.

Zn doping concentration in solution	Number of coatings	Thickness of the deposited film (nm)	Sheet resistance (R_s) (kΩ/)	Resistivity, r (Ω-cm)
0 wt%	1	103.79	13.057	1.355×10^{-1}
	2	162.92	4.757	7.750×10^{-2}
	3	211.63	1.479	3.130×10^{-2}
5 wt%	1	99.85	3112.85	3.108×10^1
	2	155.38	139.28	1.391×10^0
	3	199.25	77.20	7.711×10^{-1}
8 wt%	1	94.38	4055.42	6.301×10^1
	2	150.52	766.32	1.192×10^1
	3	194.35	170.75	2.653×10^0
10 wt%	1	90.45	4961.360	4.512×10^1
	2	143.74	862.172	1.239×10^1
	3	191.46	227.121	4.348×10^0

where OD is the optical density or absorbance and t the thickness of the film. The plot of a vs photon energy was used to determine the absorption edge. The absorption edge of the deposited films can be determined by extrapolating the linear portion of the curve to zero absorption. Variation of absorption coefficient, a , with photon energy of undoped and Zn doped films are shown in figures 2–4. Figure 2 indicates the shift in the absorption edge with increase in number of coatings in the case of undoped SnO_2 films. Figure 3 shows the variation of absorption edge with increase in the dopant concentration, and figure 4 indicates the shift due to number of coatings in 5 wt% Zn doped SnO_2 film.

The discrimination between direct and indirect transition is possible on the basis of the dependence of absorption

coefficient on photon energy. The direct transitions can be expressed as

$$a \approx (E_{pt} - E_g)^{1/2}, \tag{5}$$

with E_g being the vertical separation between the valence and conduction bands and E_{pt} the photon energy (Bube 1960). The plot of a^2 vs photon energy is used to determine the direct transition gap.

For indirect transitions

$$a \approx (E_{pt} - E_G + E_{ph})^2, \tag{6}$$

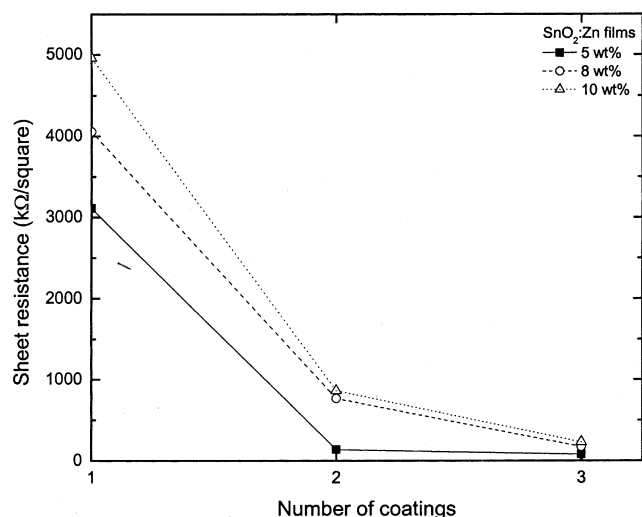


Figure 1. Variation of sheet resistance (R_s) with number of coatings for different Zn doping concentrations.

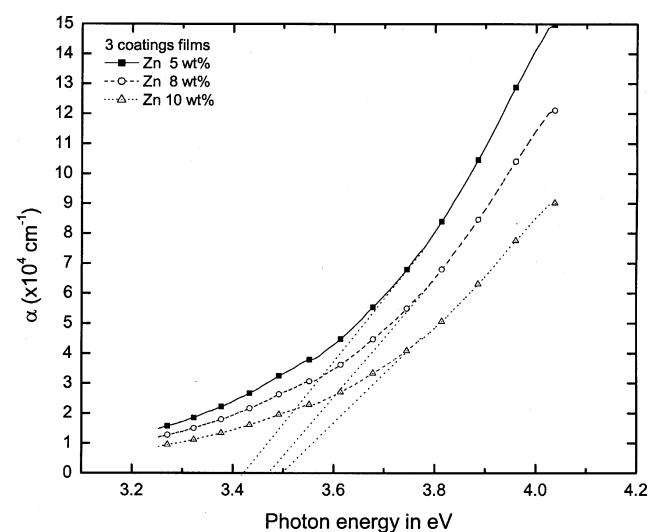


Figure 3. Absorption coefficient (a) as a function of photon energy for different Zn doping concentrations.

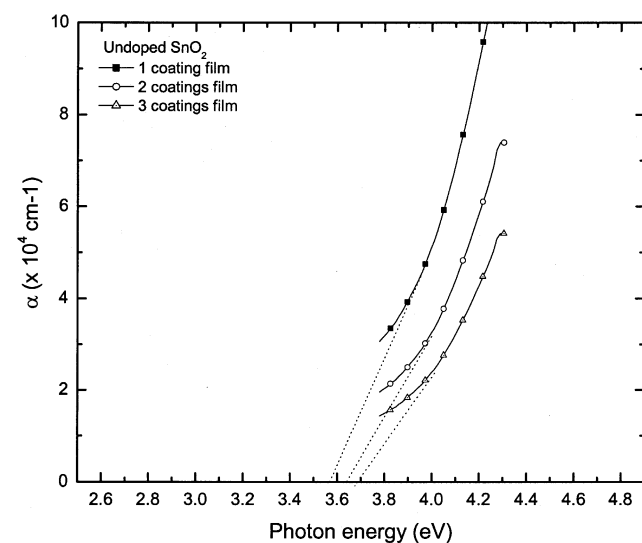


Figure 2. Variation of absorption coefficient (a) with number of photon energy for different coatings of undoped SnO_2 films.

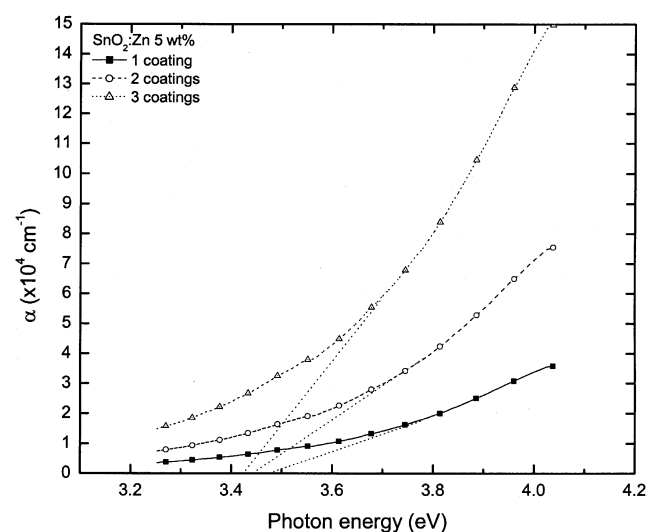


Figure 4. Plot of absorption coefficient (a) vs photon energy ($h\nu$) for SnO_2 :Zn (5 wt%) films of different number of coatings.

where E_{ph} is the photon energy and E_G the minimum separation between the valence and conduction bands. Figure 5 shows the shift in the absorption edge with increase in number of coatings in the case of undoped SnO_2 films. The shift in the direct transition edge with increase in the dopant concentration is shown in figure 6. Figure 7 indicates the variation of absorption coefficient with increase in the number of coatings in 5 wt% Zn doped SnO_2 film.

For a single photon frequency, the plot of $\alpha^{1/2}$ vs photon energy should show two linear regions (Shanti *et al* 1999). Figure 8 shows the variation of indirect transition with the number of coatings in the case of undoped SnO_2 films. Figure 9 shows the shift in the indirect transition with increase in the dopant concentration. Figure 10 shows

the indirect transition shift due to increase in the number of coatings in 5 wt% Zn doped SnO_2 film. Table 2 shows the absorption edge, direct transition and indirect transition values of the SnO_2 films doped with 0–10 wt% of Zn.

3. Results and discussion

3.1 Electrical properties

Tin oxide films close to stoichiometry condition exhibit very high sheet resistance and resistivity, whereas non-stoichiometric films have low sheet resistance. Decrease in the sheet resistance in the case of non-stoichiometric films has been attributed to oxygen vacancies created in

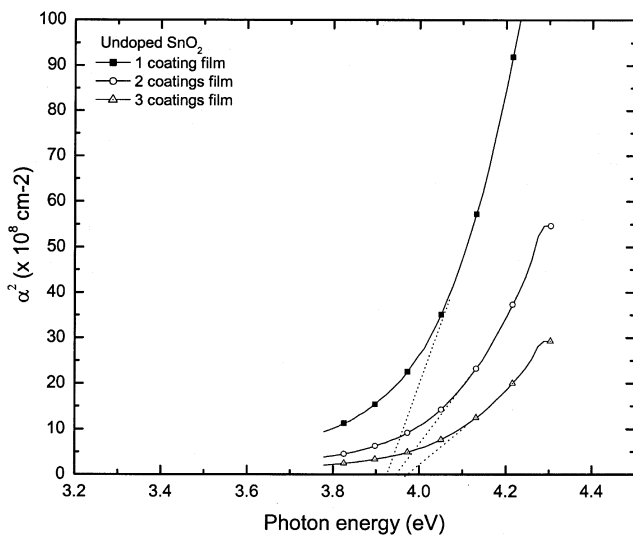


Figure 5. Variation of α^2 as a function of photon energy for different coatings of undoped SnO_2 films.

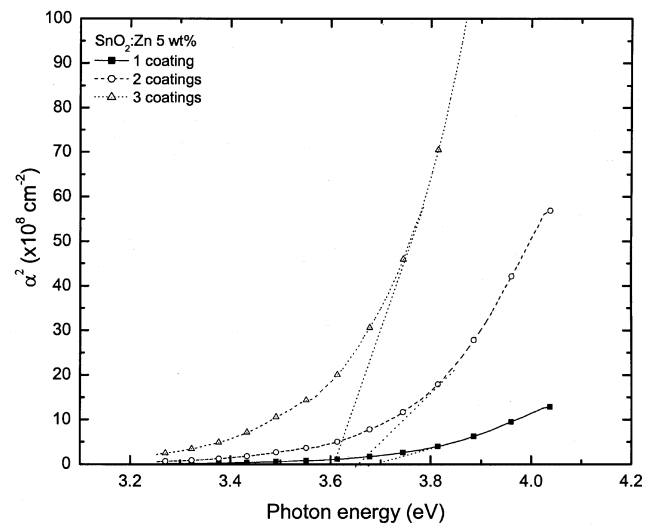


Figure 7. Plot of α^2 vs photon energy for $\text{SnO}_2:\text{Zn}$ (5 wt%) films with different number of coatings.

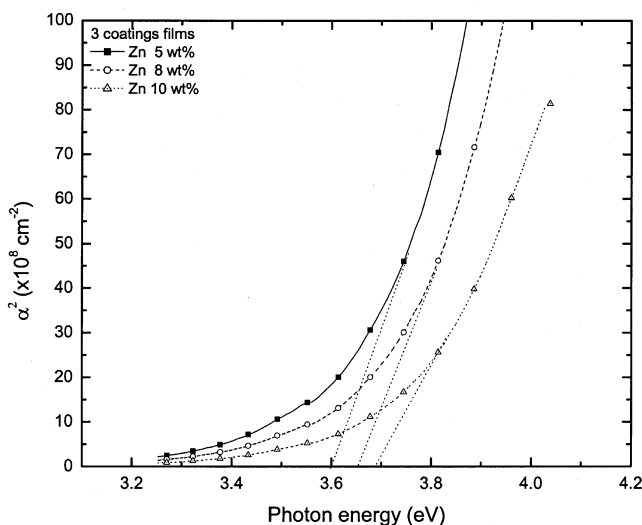


Figure 6. Plot of α^2 vs photon energy for three coatings of $\text{SnO}_2:\text{Zn}$ films with different Zn doping concentrations.

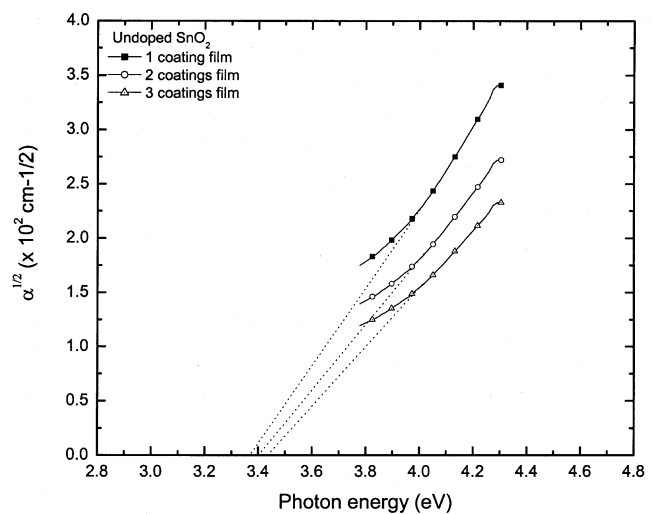


Figure 8. Plot of $\alpha^{1/2}$ vs photon energy for different coating films of undoped SnO_2 .

the structure. Then the formula for the tin oxide thin film is SnO_{2-x} , where x is the deviation from the stoichiometry (Chopra *et al* 1983). It is possible to decrease sheet resistance and increase the n -type conductivity of SnO_{2-x} , like other TCOs, by doping with donor impurities. Two important donors are antimony and fluorine, which increase the n -type electrical conductivity to several orders. F^{1-} substitutes O^{2-} and Sb^{3+} substitutes Sn^{4+} so that an extra electron enters the lattice (Freeman *et al* 2000). However, a lower valency cation as acceptor impurity such as Al^{3+} in SnO_2 produces a hole and decreases the n -type conductivity (Chopra *et al* 1983; Freeman *et al* 2000; Kawazoe *et al* 2000). With the exception of some limited applications, most of the investigations have been focused on increasing the n -type electrical conductivity of TCOs with

donors (Lewis and Paine 2000) but there are few reports available on carrier type conversion by high acceptor doping such as Al^{3+} and Zn^{2+} . In this work, Zn^{2+} ions have been selected to study the effect of acceptor doping on the electrical conductivity of SnO_2 thin films. The selection is based on ionic radius of Sn^{4+} ($r = 0.71 \text{ \AA}$) and Zn^{2+} ($r = 0.74 \text{ \AA}$), which are close to each other (Minami 2000; Mohammad-Mehdi *et al* 2003). With the substitution of Sn^{4+} ions with Zn^{2+} , one broken bond (hole) is produced, which acts as acceptor energy level near the valence band. These levels accept electrons from the valence band and thus increase the hole concentration or p type conductivity. The effect is similar to bulk crystalline semiconductors in which doping with acceptors changes from an n -type semiconductor to a p -type one (Phillips *et al* 1994).

Considering sheet resistance (R_s) and resistivity (ρ) measurement results, it is seen that, sheet resistance (R_s) of film was less at 5 wt% of acceptor dopant and increases with increasing acceptor dopant concentration (figure 1). This may be attributed to the reduction in the n -type conductivity in SnO_2 film. Further, it can also be observed that the sheet resistance of the doped SnO_2 film decreases with increasing number of layers. In the present study, we find that the film with 5 wt% acceptor dopant and 3 coatings shows optimum sheet resistance value of about $77 \text{ k}\Omega/$. The sheet resistance of pure SnO_2 film with 3 coatings was found to be $1.479 \text{ k}\Omega/$. It can also be observed that sheet resistance and resistivity of the films decreases with increasing number of coatings. Minimum sheet resistance and resistivity were observed in the case of films with three coatings (table 1).

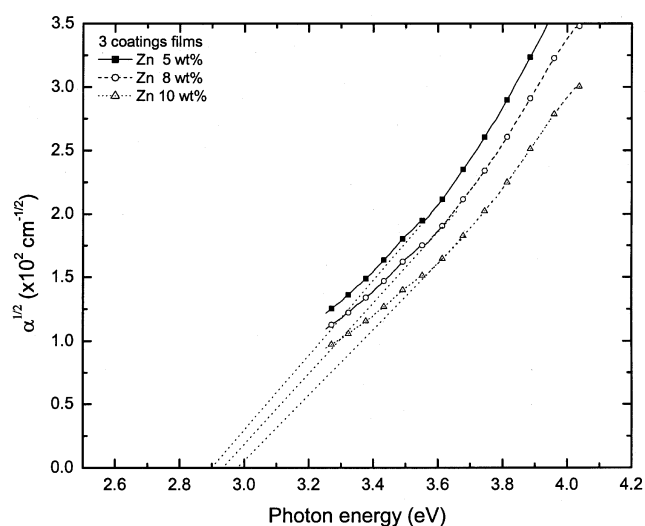


Figure 9. Variation of $\alpha^{1/2}$ as a function of photon energy ($h\nu$) for $\text{SnO}_2:\text{Zn}$ films of various Zn concentrations.

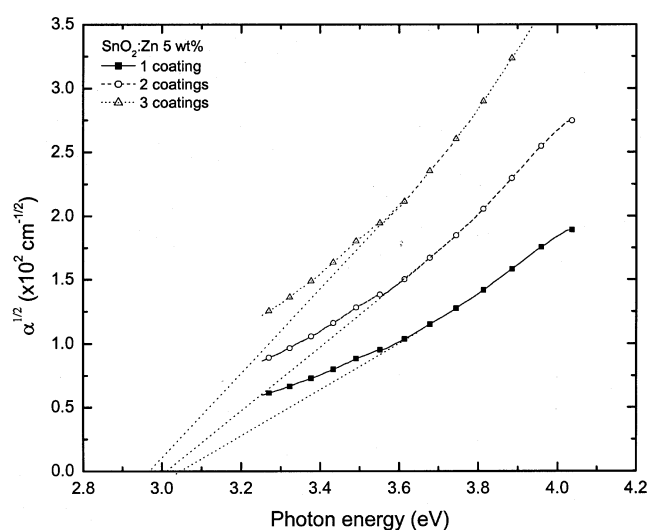


Figure 10. Plot of $\alpha^{1/2}$ versus photon energy for $\text{SnO}_2:\text{Zn}$ films with different number of coatings.

3.2 Optical properties

The classical Drude free-electron theory can be used to explain the optical phenomenon near the infrared region. Despite the fact that classical Drude free electron theory having been superseded by quantum theory many years ago, it works quite well for TCOs (Coutts *et al* 2000). An important optical characteristic of TCOs is that they are transparent in the wavelength region 400–1500 nm. At wavelengths shorter than 400 nm, absorption occurs due to the fundamental band gap, and thus light cannot be transmitted due to quantum phenomenon. It is known that the band structure is dependent on the nature and quantity of dopant present and heavy doping of semiconductor leads to band structure distortion (Fistul 1969). The large change in the effective mass indicates nonparabolicity of the conduction band and hence the analysis of the band diagram is difficult.

The spectral dependence of the absorption coefficient has been computed using Moss–Burstein shift from the transmission and reflection data for the determination of the fundamental absorption edge, which lies in the UV

Table 2. Values of absorption edge, direct transition gap and indirect transition gap in SnO₂:Zn films with various Zn concentrations and number of coatings.

Zn doping concentration in solution	Number of coatings	Absorption edge (eV)	Direct transition (eV)	Indirect transition (eV)
0 wt%	1	3.570	3.924	3.368
	2	3.635	3.941	3.399
	3	3.681	3.970	3.443
5 wt%	1	3.489	3.689	3.064
	2	3.451	3.650	3.022
	3	3.420	3.606	2.969
8 wt%	1	3.522	3.713	3.090
	2	3.481	3.674	3.084
	3	3.468	3.652	2.934
10 wt%	1	3.557	3.743	3.147
	2	3.519	3.719	3.117
	3	3.501	3.689	2.982

region and it is shown in figures 3–5 for undoped and Zn doped SnO₂ films. We find that in single coating films the absorption edge lies at 3.570 eV for SnO₂ film whereas for the zinc doped films, the absorption edge shifts towards lower energies region and lies in the range 3.489–3.557 eV depending upon dopant concentration. It is also observed that absorption edge shifts towards lower energies (higher wavelengths) with increase in the number of coatings. The maximum shift is observed for the dopant concentration of 5 wt% and of three coating films. Similar shift in the absorption edge in the single coating films was first observed by Moss (1954) and Burstein (1954) in In:Sb films and Shanti *et al* (1999) in SnO₂:Sb films. Figures 5–7 indicate that the direct transition of single coating films for undoped tin oxide films occurs at 3.924 eV whereas for Zn doped films, it lies in the range of 3.689–3.743 eV depending upon the doping concentration. Shift in the direct transition as a function of number of coatings reveals that the direct transition edge shifts towards lower energy region with increase in the number of coatings.

The indirect transition energies are obtained from the plot of $\alpha^{1/2}$ vs photon energy. From figures 9–10, it can be seen that for the undoped tin oxide film the indirect transition occurs at 3.368 eV whereas for the SnO₂:Zn films, it lies in the range 3.064–3.147 eV. Values of all optical measurements are tabulated in table 2.

4. Conclusions

Transparent Zn doped tin oxide thin films have been prepared by sol-gel spin coating technique. The Zn doped SnO₂ films were deposited with dopant concentration ranging from 0–10 wt% in solution. For each concentration, films with various numbers of (up to three) coatings were prepared. In the SnO₂ films, Zn²⁺ acts as an acceptor, so that with increasing Zn doping, up to 10 wt%, sheet

resistance of the film increases. Single coating films have shown high sheet resistance of the order of a few M Ω / and it decreases to a few k Ω / in multi-coating films. Investigation on the optical properties of doped SnO₂ film reveals that the absorption edge, direct transition and indirect transition shifts towards lower energies (higher wavelength) region due to Zn doping. The study of these parameters as a function of dopant concentration and number of coatings indicate that optical absorption edge shifts towards higher energy region with increase in dopant concentration and towards lower energy region due to increase in the number of coatings.

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