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OPTICAL PROPERTIES OF UNDOPED AND INDIUM-DOPED TIN OXIDE THIN FILMS

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ABSTRACT

Thin films of Tin Oxide (SnO_2), having thickness of 200 nm, were formed on to glass substrates by thermal evaporation of high-purity SnO_2 powder in vacuum at various substrate temperatures (T_S), ranging between 25 and 200°C. SnO_2 films with varying thickness were also prepared for a fixed T_S = 100°C. Further, doping of SnO_2 films with Indium (*In*) was accomplished through solid state diffusion process by successive deposition of SnO_2 and *In* films and subsequent annealing at 200°C for 10 minutes. Both undoped and doped films were characterized optically by UV-VIS-NIR spectrophotometry in the photon wavelength ranging from 300 to 2500 nm. In the visible photon wavelength range, the average optical transmittance (T%) of the films with varying T_S was found to be 85%. The maximum value of T % was found to be 89 % around the wavelength of 700nm. The variation of absorption coefficient with photon energy in the fundamental absorption region is the steepest for T_S = 100°C. The sub-band gap (SBG) absorption is also minimum for this T_s. A fluctuating behavior of the band gap energy (E_g) with T_s is observed attaining the highest value of 3.59 eV for T_s = 100°C. The band gap energy increases with thickness but T% in the visible range decreases. The T% in the visible range varies inversely with indium doping, being highest for undoped films. The E_g increases upto 2 wt% *In* doping and gradually decreases for enhanced doping. It seems reasonable to conclude that In doping does not bring favorable optical characteristics. Undoped SnO_2 films having thickness of 200 nm and formed at substrate temperature of 100°C yield essential acceptable properties for photovoltaic applications.

Key words: Tin oxide films, Indium doping, Transmittance, Band gap energy

INTRODUCTION

Tin Oxide (SnO_2) is a wide band gap n- type semiconductor, which can be efficiently used as transparent conducting oxide. Because of its unique electrical and optical properties, SnO_2 thin films have been widely used in photocell devices, and optoelectrical displays. The films are chemically inert, mechanically hard and can resist high temperature. Indium tin oxide (ITO) thin film is a highly degenerate *n*-type semiconductor which has a low electrical resistivity of $2 - 4.3 \times 10^{-24}$ Ω-cm [Alam and Cameroon, 2000]. The low resistivity value of ITO films is due to a high carrier

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concentration because the Fermi level (E_F) is located above the conduction level (E_C). The degeneracy is caused by both oxygen vacancies and substitutional tin dopants created during film deposition. The carrier concentration of high conductivity ITO films is in the range of 10^{20}–10^{21} cm^{-3}.

Doped or undoped SnO_2 films can be prepared by many methods such as spray pyrolysis (Afify *et al*, 1996; Nunes, 2001; Elangovan and Ramamurthi, 2003), electron beam evaporation [Das and Banerjee, 1987; Mika *et al* 2004], chemical vapor deposition [Jeong-Woon Bae *et al*, 2002], magnetron sputtering [Lee *et al*], pechini method [Legnani *et al*, 2007]. Thermal evaporation is the most widely used technique. It deposits materials quickly. High quality films are produced by thermal evaporation. This method is also substrate friendly.

In the present study, pure and *In* doped SnO_2 thin films were prepared by thermal evaporation technique with different growth parameters. The effect of substrate temperature, thickness and doping percentage on the transmittance and reflectance were studied for SnO_2 films. The value of absorption coefficient and optical band gap energy were obtained from the measurement of transmittance and reflectance of the films with the variation of photon wavelength.

THEORETICAL FORMULATION

When light is incident on a crystalline solid, a part of it is reflected (R) at the surface, a part is transmitted (T) and rest is absorbed by the solid. The absorption pattern of the sample indicates the band structure of solid, energy gap between the valance band and conduction band, the nature of transition (allowed, forbidden, direct and indirect), etc.

Optical absorption is described quantitatively through the absorption co-efficient, α. The α is the fraction of incident energy intensity decreased per unit distance in an absorbing medium and it can be expressed as,

$$I = I_0 \exp(-\alpha x) \tag{1}$$

where I_0 is the intensity of incident light, x is the thickness of the material and I is the transmitted intensity.

In an absorbing material the α is related to the refractive index and the wavelength of the incident light. The refractive index, n, is expressed as,

$$n = n_r - ik \tag{2}$$

where, n_r is the real part of the refractive index and k is called the extinction coefficient. The α of the material at a wavelength can be related with the extinction coefficient by,

$$\alpha = \frac{4\pi k}{\lambda} \tag{3}$$

The thickness of the films was checked using an infrared interference method, which depends on the reflectance characteristics of the films. In this method the thickness of a film is given by

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2\theta}} \frac{1}{(1/\lambda_1) - (1/\lambda_2)} \tag{4}$$

where, n is the refractive index of the film, θ is the incident angle of light to the sample, λ_1 and λ_2 are the peak or valley wavelengths in the reflectance spectrum and Δm is the number of peaks or valleys between λ_1 and λ_2. The discrepancy between the values of thickness of the films measured in two methods (Edwards FTM5 Film thickness monitor and infrared interface method) was ± 10 nm.

For transmittance (T%) at normal incidence and reflectance (R%) at near-normal incidence of light on the films, expressions for the multiple reflected systems have been given by Heavens (Heavens 1959). Tomlin (1972) simplified these expressions absorbing films on non-absorbing substrates and expressed them as equations given below:

$$\frac{1+R}{T} = \frac{1}{4n_2(n_1^2 + k_1^2)} \left[\begin{array}{l} (1 + n_1^2 + k_1^2)\left\{\left(n_1^2 + n_2^2 + k_1^2\right) \cosh 2\alpha_1 + 2n_1 n_2 \sinh 2\alpha_1\right\} \\ + (1 - n_1^2 - k_1^2)\left\{\left(n_1^2 - n_2^2 + k_1^2\right) \cosh 2\gamma_1 + 2n_2 k_1 \sin 2\gamma_1\right\} \end{array} \right] \tag{5}$$

$$\frac{1-R}{T} = \frac{1}{2n_2(n_1^2 + k_1^2)} \left[\begin{array}{l} n_1\left\{\left(n_1^2 + n_2^2 + k_1^2\right) \sinh 2\alpha_1 + 2n_1 n_2 \cosh 2\alpha_1\right\} \\ + k_1\left\{\left(n_1^2 - n_2^2 + k_1^2\right) \sinh 2\gamma_1 + 2n_2 k_1 \cos 2\gamma_1\right\} \end{array} \right] \tag{6}$$

where, n_l and n_2 are the refractive indices of the film and substrate respectively, k_1 is the extinction-coefficient of the film, $n_2 = 1.45$, $\alpha_1 = \frac{2\pi k_1 d}{\lambda}$ and $\gamma_1 = \frac{2\pi n_1 d}{\lambda}$, where λ is the wavelength of light and d is the thickness of the film. Equations (5) and (6) have been solved for k_l and n_l utilizing a computerized iteration process. The absorption coefficient, α was then calculated using $\alpha = \frac{4\pi k_1}{\lambda}$. Dependence of α on photon energy has been analyzed with the existing models discussed subsequently in equation (1) to find the nature and extent of the band gap energy.

EXPERIMENTAL

Thin films of pure SnO_2 and *In* doped SnO_2 films were prepared on to chemically and ultrasonically cleaned glass substrate by thermal evaporation in vacuum (~10^{-6}Torr) using an oil diffusion evaporation unit (Edwards, E306, UK).The source material (SnO_2)

was evaporated from a molybdenum boat and the substrate was placed at a distance of 3 cm above the source. The films were deposited at various substrate temperatures from 25-200^{o}C keeping thickness constant at 200 nm. The thickness and rate of deposition of the films were measured in situ by a quartz crystal thickness monitor (FTM5, Edwards, UK).

Films of different thicknesses of 100, 150, 200, 250 and 300 nm were also grown at fixed substrate temperature of 100^{o}C.

Thin films of *In* doped SnO_2 were deposited also on glass substrates. To achieve In doping, first we deposited In and then SnO_2 using two different boats. We measured the mass of both Indium and Tin Oxide according to their percentage in total mass and deposited the corresponding thickness of the materials.

The *In* doping concentration was varied from 0 to 5%, substrate temperature was kept constant at 100^{o}C and total thickness was constant at 710 nm. The above deposited films were annealed at 200°C for 10 minutes under a vacuum of 1.4×10^{-3} Pa.

The variations of transmittance and specular absolute reflectance of the films with wavelength of light incident on them were measured using a dual-beam-UV-VIS-NIR recording spectrophotometer (Shimadzu, UV-3100, Japan) in the photon wavelength range from 300 to 2500 nm. An integrating sphere detected light signals coming from the samples. The α of the films was estimated using equation 3.

To calculate the energy gap, $(\alpha h\nu)^2$ was plotted as a function of photon energy .The linear portion of the graph was then extended backward to find its intersecting point with X axis at zero α. The value of photon energy at the intersecting point is equal to the energy gap for a particular film.

RESULTS AND DISCUSSIONS

Fig. 1 shows the optical transmittance spectra of tin oxide films prepared at different substrate temperatures (as deposited, 25, 50, 100, 150, 200°C) in the photon wavelength range of 300 - 2500 nm. There are three regions in the transmission curve. In the first region (1500 nm $< \lambda \leq$ 2500 nm), the transmittance is low and almost constant. In the second region (850 nm $\leq \lambda \leq$ 1500 nm), the transmittance increases smoothly attaining maximum at 850 nm. The third region (450 nm $\leq \lambda \leq$ 550 nm) is the absorption region where the transmittance falls abruptly. The interference pattern in the transmittance manifests the homogeneity of the film.

It is observed that average transmittance in the visible region is 85% and maximum transmittance is 89% at 700 nm .It is also observed that transmittance is inversely proportional to substrate temperature in near infra red region.

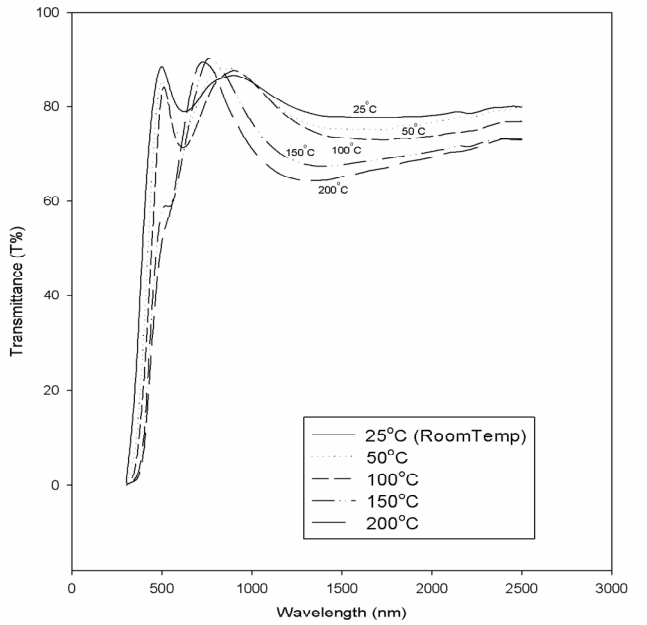

Fig. 1. Variation of optical transmittance (T%) of SnO_2 thin films deposited at various substrate temperatures with a fixed thickness of 200 nm with photon wavelength.

Fig. 2 shows the variation of absorption co-efficient,α of the films prepared at different substrate temperatures (as deposited, 25, 50, 100, 150, 200°C), with photon energy.

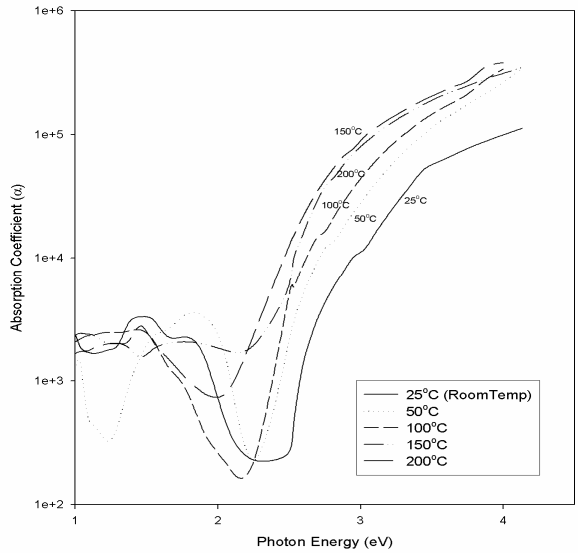

Fig. 2. Variation of absorption coefficient (α) of SnO_2 thin films deposited at various substrate temperatures with a fixed thickness of 200 nm with photon energy.

The rise of absorption co-efficient with photon energy at the fundamental absorption region is the steepest in case of the film deposited at the substrate temperature 100°C. Sub band gap absorption is also minimum for this film. Near infrared absorption indicates the sub band gap (SBG) levels in the sample. The lesser the SBG, the better is the sample. From these observations we can conclude that the film which was deposited at the substrate temperature of 100°C is superior to all other films from the view point of optical absorption.

Fig. 3 shows the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) to find the value of band gap energy of the films prepared at different substrate temperatures. The extrapolation of the straight-line portion of the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) to zero absorption gives the direct band gap of the films. The band gap energies of the sample prepared at the substrate temperatures 25, 50, 100, 150 and 200°C are 3.42, 3.56, 3.59, 3.38 and 3.48 eV, respectively as shown in Fig. 3. It is observed that the band gap energy adheres to literature value for the sample which was prepared at substrate temperature of 100°C.

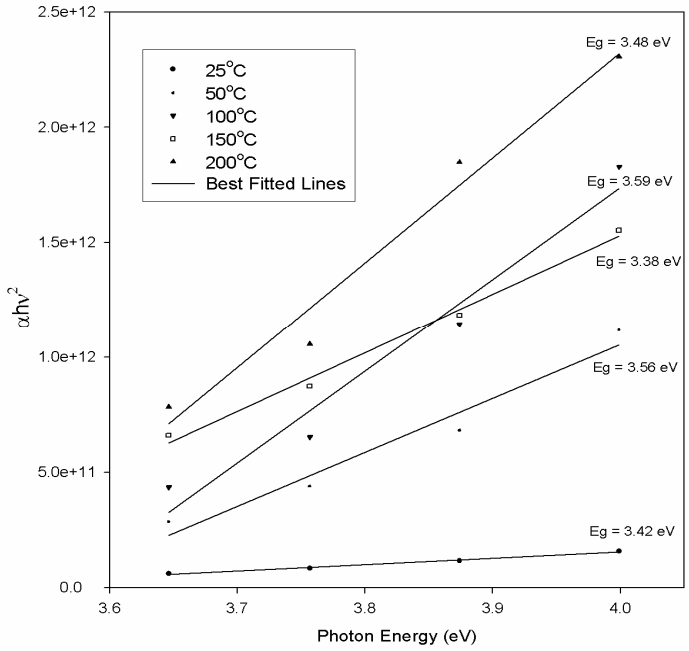

Fig. 3. Variation of $(\alpha h\nu)^2$ at various substrate temperatures with a fixed thickness of 200 nm with photon energy.

The variation of energy gap with substrate temperature is depicted in fig 4.It is observed that the band gap energy increases with substrate temperature. It is also observed that band gap energy decreases if the substrate temperature is greater than 100°C, but it again increases when substrate temperature is greater than 150°C.

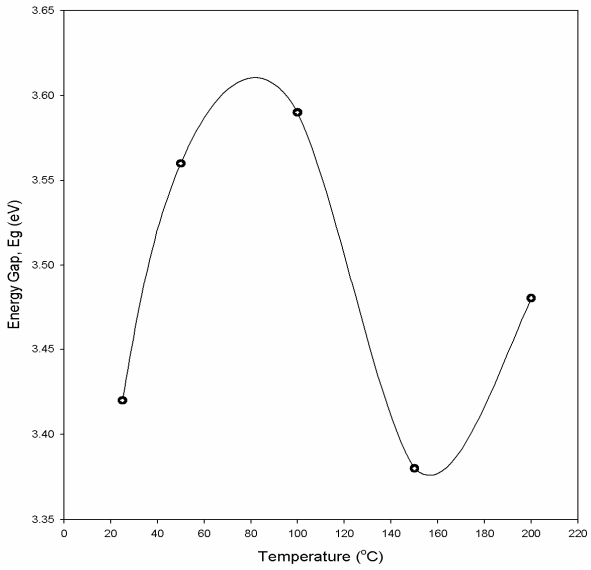

Fig. 4. Variation of energy gap (E_g) of SnO_2 thin films of thickness 200 nm with varying substrate temperature.

The results are in accordance with the findings of Shamala *et al*. 2004. The increment of band gap energy with substrate temperature may be attributed to the partial filling of the conduction band of tin oxide, resulting in a blocking of the lowest states. This widening of the optical band gap is termed as Burstein-Moss shift (Raghupathi *et al*. 2005). The shift is given by the relation.

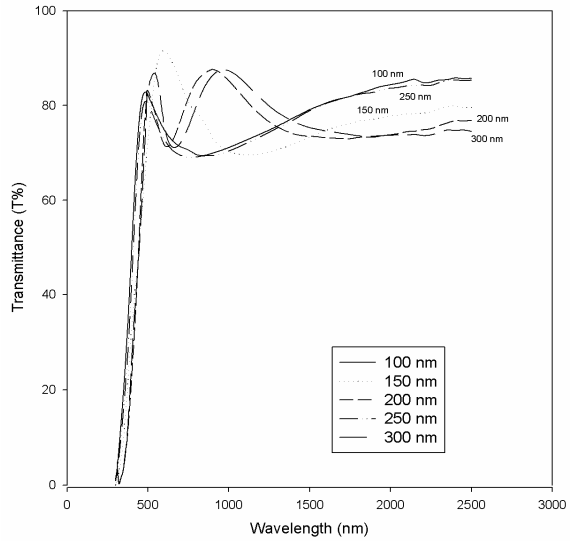

Fig. 5. Variation of optical transmittance (T%) of SnO_2 thin films of various thickness deposited at a substrate temperature of 100°C with photon wavelength.

$$E_g = E_{go} + \Delta E_g^{BM}$$

where, E_{go} is the intrinsic band gap and ΔE_g^{BM} is the Burstein-Moss shift.

Fig. 5 shows the variation of transmittance with photon wavelength of tin oxide thin films of different thickness such as 100, 150, 200, 250, and 300 nm prepared at a constant substrate temperature of 100°C. It is observed that maximum transmittance at visible range is obtained for the thickness 100 nm (92%). But the film of thickness 200nm shows good interference pattern which indicates better homogeneity and good quality. The maximum T% in case of the film having a thickness of 200 nm is slightly less than the film with thickness 100 nm. But considering the homogeneity of the film, the film prepared at T_s = 200°C is considered to be better.

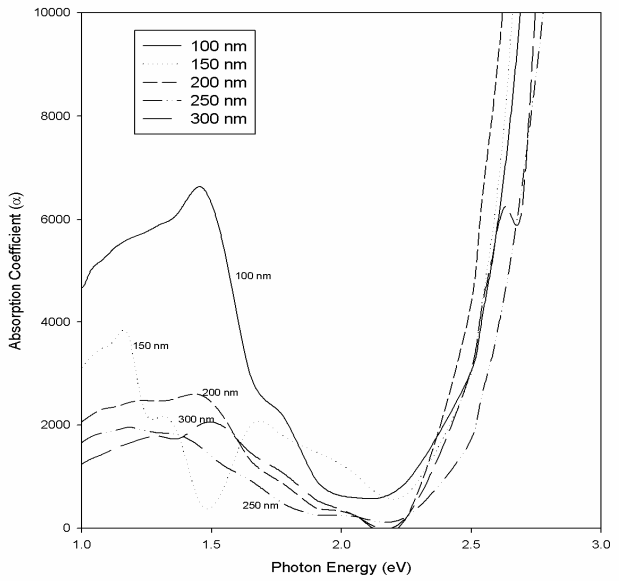

Fig. 6. Variation of absorption coefficient (α) of SnO_2 thin films of various thickness deposited at a substrate temperature of 100°C with photon energy.

Fig. 6 shows the variation of absorption co-efficient with photon energy of SnO_2 thin films of different thickness such as 100, 150, 200, 250, 300 nm prepared at constant substrate temperature 100°C. It is observed that absorption coefficient variation is the steepest in case of thickness 200 nm. SBG absorption is also a minimum for thickness of 200 nm. Therefore, from these results the film of thickness 200 nm is considered to be better.

In Fig. 7, $(\alpha h\nu)^2$ is plotted against photon energy ($h\nu$) to find the value of band gap energy of the thin films of different thickness such as 100, 150, 200, 250, 300 nm at constant substrate temperature 100°C. The band gap energies of the samples of different thickness 100, 150, 200, 250 and 300 nm are 3.5, 3.54, 3.58, 3.6 and 3.6 eV, respectively.

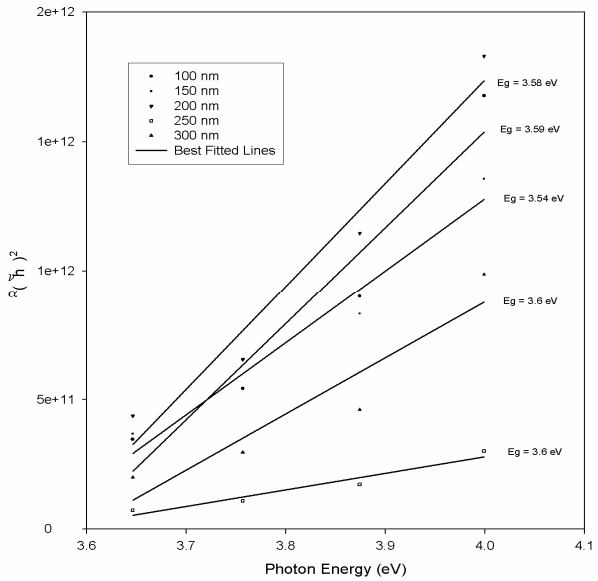

Fig. 7. Variation of $(\alpha h\nu)^2$ at various thicknesses for a fixed substrate temperature of 100°C with photon energy.

In Fig. 8 the energy gap variations are shown with different thickness of thin films of SnO_2. It is observed that from thickness 100 to 150 nm the band gap energy decreases when the film thickness is increasing.

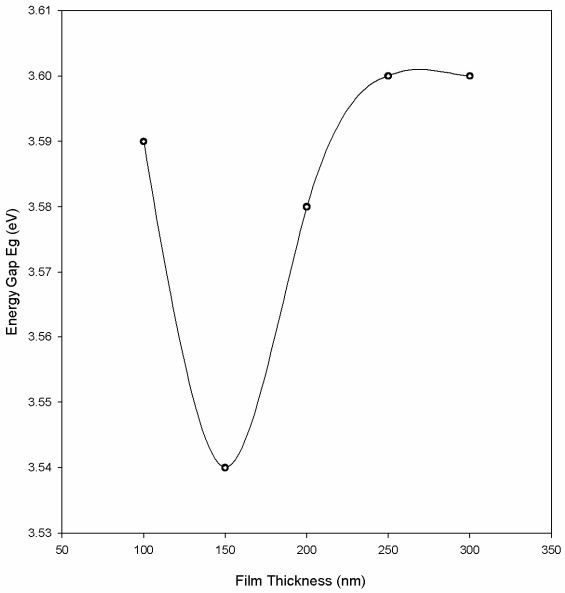

Fig. 8. Variation of energy gap (E_g) of SnO_2 thin films deposited at substrate temperature of 100°C with varying film thickness.

But when the thickness is more than 150 nm the band gap energy increases with the thickness and it remains almost constant for thickness 250 and 350 nm.

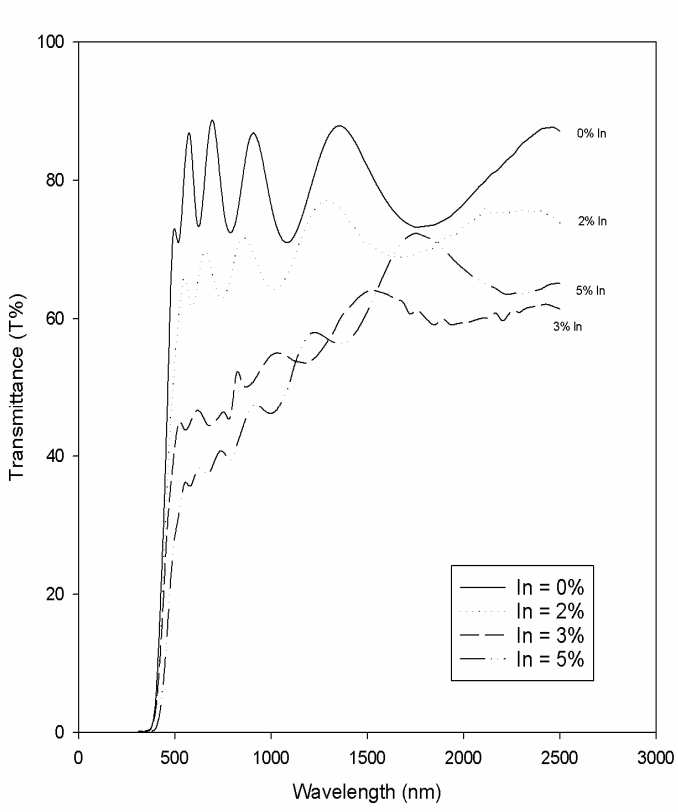

Fig. 9. Variation of optical transmittance (T%) of indium doped SnO_2 thin films at varying wt% of indium with photon wavelength.

Fig. 9 shows the variance of transmittance with photon wavelength of *In* doped SnO_2 thin films where the percentage (wt%) of *In* are 0, 2 and 3%, and thickness is constant (710 nm). The above deposited films were annealed at 200°C for 10 minutes. It is observed that the transmittance of the undoped film is highest (88% in the visible region). Up to 2% doping, it is good (about 72% in the visible region). But when it is more than 2% the transmittance in the visible region decreases to 40% to 50% .The decrease of transmittance at higher doping concentrations may be due to the increased scattering of photons by crystal defects created by doping, which is in accordance with the findings of other workers (Manoj *et al.* 2007).

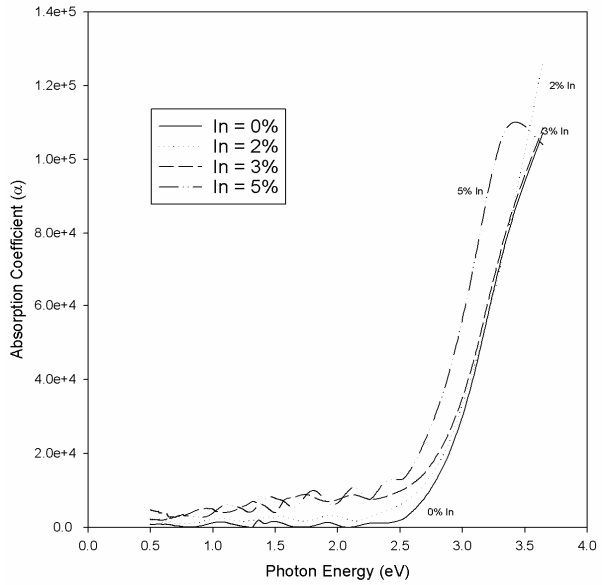

Fig. 10. Variation of absorption coefficient (α) of indium doped SnO_2 thin films at varying wt% of indium with photon energy.

Fig. 10 shows the variation of absorption coefficient with photon energy of *In* doped SnO_2 thin films (percentage of *In* 0, 2, 3 and 5%, respectively). Their thickness was kept constant (710 nm).

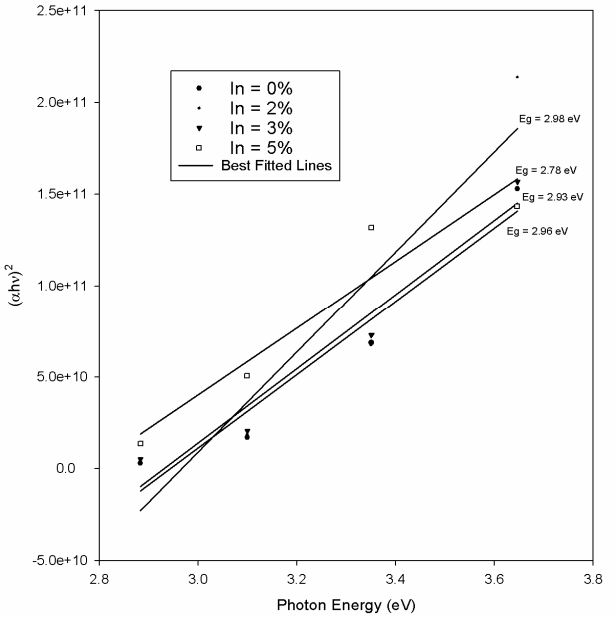

Fig. 11. Variation of $(\alpha hv)^2$ of indium doped SnO_2 thin films at varying wt% of indium with photon energy.

The above deposited films were annealed at 200°C for 10 minutes. The rise of absorption co-efficient with photon energy at the fundamental absorption region is the steepest in case of 2% *In* but SBG absorption is minimum for 0% *In*.

Fig. 11 shows the plot of $(\alpha h\nu)^2$ versus photon energy($h\nu$) to find the band gap energy of the *In* doped SnO_2 thin films. The band gap energy for different percentage of *In* such as 0, 2, 3 and 5% are 2.96, 2.98, 2.93 and 2.77 eV, respectively.

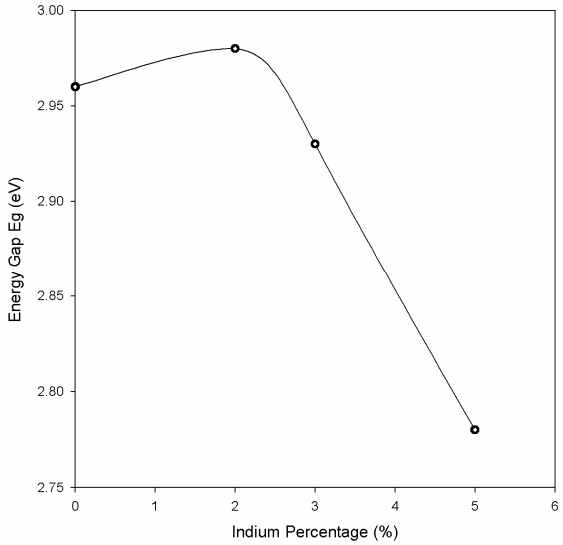

Fig. 12. Variation of energy gap (E_g) of *In* doped SnO_2 thin films with varying wt% of *In*.

Fig. 12 shows the band gap energy of the *In* doped SnO_2 thin films with different percentage of *In*. It is observed that the band gap energy increases with *In* percentage up to 2% then it decreases when *In* percentage is more than 2% which is in accordance with the findings of previous workers (Matthews, 1965).

CONCLUSIONS

Pure SnO_2 thin films deposited by thermal evaporation technique exhibit an average 85% transparency in the visible region. Optical study of the films deposited at different substrate temperatures (25, 50, 100, 150, 200ºC) with a constant thickness of 200 nm shows that the film which is deposited at 100ºC is superior in quality than the others.

It is found that the film of 200 nm deposit at 200°C gives minimum SBG absorption and good interference pattern.

The optical measurement of *In* doped SnO_2 thin films where the wt% of *In* are 0, 2, 3 and 5% show that transmittance decreases with increasing *In* content. The band gap energy increases up to 2 wt% of *In* but decreases for the wt% of *In* more than 2.

From the above investigations, it may be concluded that undoped film having thickness of 200 nm prepared at substrate temperature 100ºC yield essential acceptable properties for photovoltaic application.

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