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Optical Performance of Tin Doped Indium Oxide (ITO) Thin Films Prepared By Sol Gel Dip Coating Techniques Using Acrylamide Route

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Optical performance of Tin doped Indium Oxide (ITO) thin films prepared by sol gel dip coating techniques using Acrylamide route

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Abstract:

At present various oxide of metal semiconductors play significant role in the field of electronics device. Most of the semiconductor devices exploit the special characteristics of the junction between a p-type and n-type semiconductor, these devices can be made extremely small in size and they are incredibly fast in their response. Generally metal have good reflectivity in the electromagnetic region of infrared and visible radiation. Indium oxide material doped with tin (ITO) are recently used in the substrate material for various applications, because of it has special properties are low resistivity and high optical transmittance in the visible region. In this paper, we prepare ITO films with different tin concentration (5%, 10%, 30%, 50% and 70%) using acrylamide sol gel dip coated method and its results were reported. TCO materials have good electrical conductivity and optical transparency, and also it has n-type semiconductor with a band gap between 3.5 and 4.3 eV. An X-ray study indicates all the prepared samples were bixbyte structure. Optical behaviour of materials can be understood in the near infrared and visible spectrum. Some optical parameters refractive index, extinction coefficient and dielectric constant of ITO films are calculated from the data received from the UV transmission studies. Using W-D model the dispersion of refractive index was calculated. The optical band gap, oscillator energy, dispersion energy and optical conductivity and N/m* ratio were estimated and this material is well suitable for dye sensitized solar cell and sensor application.

Keywords: ITO, sol gel, Transmission spectra, optical behaviour

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1. Introduction:

Indium oxide doped with tin (ITO) is likely to be very good materials in the field of material science research group, in the room temperature, the material has wide band gap of 3.5 - 4.3 eV. Now-a-days ITO films used in the field of optoelectronics such as varistors, gas sensor, biosensors, transparent electrode, solar energy efficient windows, P-N junction emitting light, panel display etc. The film thickness and substrate temperature are major role to maintain the optimum condition in visible region (transparency) and near IR regions (reflectance), and also percentage of dopant, annealing temperature are optimized. Today several techniques was used to prepare ITO films including the sol gel process [1] chemical evaporation [2] pulsed laser deposition [3] and electron beam evaporation [4]. All the methods are very expensive and require for high vacuum so that we choose sol gel dip coating method. These techniques are required minimum tool cost and inexpensive method for depositing films. We know that most of the optoelectronic materials are the function of wavelength and also to predict photo electric behaviour of a device. Therefore an accurate knowledge of the structural and optical properties of ITO is important for the designing optoelectronics device. In this paper we studied some of optical behaviour such as refractive index, extinction coefficient optical band gap and complex dielectric constant and transmittance, absorbance of ITO film deposited on glass substrate.

2. Experimental procedure:

Using glass substrate the binary compound (Indium oxide) doped with tin (ITO) were deposited on one of the chemical methods such as sol gel techniques. The coating sols were prepared using 10 ml of 0.45 M solution of Indium ($InCl_3$ 4 H_2O) and tin salts ($SnCl_4$ 5H_2O) were taken in a clean glass beaker. This mixture was heated to 70 °C and we choose the pH in the range of 9 then by the addition of 0.25gm of N,N,bis methylence acrylamide, 20 minutes after we add 2 mg ammonium persulphate initiator was mixed to the solutions. After few minutes the solutions appear viscous nature. We take glass substrate in the size of breadth is 2.5 cm and 7.5 cm length and removal rate of the substrate is 1 cm/min. After the film formation the film surface was dried in microwave oven for 15 min followed by the heat treatment 350 °to 450 ° for different duration time is 15 min to 90 min. The time duration for 50 min is well optimised. Using surface profilometer to measure the films thickness its vary from 450 nm to 950nm to increase of temperature.

3. Result and discussion:

The XRD techniques is used to determining the atomic and molecular structure of ITO films using CuKα radiation corresponding to X-ray wavelength is 0.154nm. Fig 1 shows X-ray diffraction pattern of ITO thin films (10% of tin oxide) prepared at various composition formed at different temperature. From the XRD measurements all the samples exhibit cubic bixbyite structure of Indium oxide and any other characteristic peak (Sn, SnO, and SnO_2) are absent, which indicates that the Sn atoms are probably incorporated substitutionsly into the indium oxide lattice [5-6]. Fig 2 shows the mean crystallite size of ITO films vs different tin concentration. From the graph we measure the mean crystallite size using Debye's Scherer equation from the line broadening of the (222) reflection. At low tin concentration both the microstructure and dislocation density are minimum which indicate the concentration of lattice imperfection leading to prepared orientation as shown in table 1.[2]

Fig.3 shows the Energy dispersive X-ray microanalysis it is used for the elemental analysis various composition ITO films (10%) in which the SnO_2 content (95% to 30%) was determined to be 68.0 at %, 58 at %, 47 at %, 38 at %, 29 at %, 19 at %, 14 at %, 9 at %, 5 at % respectively

Fig.4 exhibits image of scanning probe micrometer of 10% tin concentration of ITO films formed at 450°C with 10% of tin concentration. We take all the composition of tin sample we reported 10% tin concentration, from the graph we observed that the grain size decreases with increase of tin concentration. This is supported by the XRD data. And also we found the surface roughness it values in the range of 0.20 nm to 1.25 nm .

Already we find the resistivity of the films decreased from 20 ohm cm (In_2O_3 films formed at 450°C) to 0.01 ohm cm as the tin concentration increases to 10 %. Further increase of tin oxide content caused increased in resistivity. Beyond 10 % tin the resistivity increases from 0.1 ohm cm to 250 ohm cm .at 70 % tin concentration. The mobility and carrier concentration increase with increase of tin concentration up to 10 at % beyond which, they decrease. The N_d increased from 3.85 x 10^{17} cm^{-3} (In_2O_3 films formed at 450°C) to 1.25 x 10^{20} cm^{-3} up to 10 at %, beyond this value of SnO_2 content, the carrier density decreases. The value of mobility increased from 1.35×10^{-4} m^2 $V^{-1}s^{-1}$ to 49.93 $\times 10^{-4}$ m^2 $V^{-1}s^{-1}$ up to 10 at % SnO_2, beyond which the mobility decreases [7]. Fig.5 shows the variation of resistivity, mobility and carrier concentration with concentration of tin. The value of mobility and carrier concentration decreased from 49.93 $\times 10^{-4}$ m^2 $V^{-1}s^{-1}$ to 9.32×10^{-4} m^2 $V^{-1}s^{-1}$ and from 1.25 x 10^{20} cm^{-3} to 2.69 x 10^{15} cm^{-3} respectively as the tin concentration increased up to 70 %. The data are presented in table.2.

The increase in resistivity beyond 10 % Sn can be explained as follows, Most of the literature[8-9] survey describes the solubility of Sn atoms in the indium oxide lattice, the maximum solubility of tin atoms is approximately 10 at.%. In the case lower than 10 %,of tin that is Sn^{4+}ions substitute In^{3+} ions in the cation sub lattice. Due to the replacement of In^{3+} instead of Sn^{4+}, Sn atoms act as n-type donors, and the resistivity decreases with the Sn concentration. Similarly in the case higher tin content, no more Sn-atoms can be embedded in the In_2O_3-lattice, and the resistivity increases. This increase of resistivity may be due to interstitial Sn-atoms which act as charged trapping centres for the electrons [10]. Here there is no phase separation and no Bragg reflections of SnO_2 in the crystalline ITO-material does not occur in the crystalline SnO_2 material were detected for films with SnO_2 concentration up to 70 % in XRD measurements.

Under proper environment conditions, the optical properties of Sn-doped In_2O_3 films at various compositions were analysed. The Oxygen defect play very important role in the prepared samples. The loss of transmission is responsible for the grain boundaries with an increase in Sn dopant content. Thus a decrease in grain size with increase Sn concentration resulted in an increase in grain boundaries in In_2O_3 films. In this sol gel techniques we have to use glass substrate prepared films behaves as transparent material in the wavelength range of 450 and 1100 nm , because the transmittance values are high at these wavelengths. The transmittance values slightly increases so increase in highly transmitting properties of ITO. The transmittance spectrum gives the information of surface Plasmon's resonance indicating the crystallite size in the nanometre range. Transmittance spectra give the information of transmittance of ITO film deposited on glass substrate and also we found that transmittance value increases from 50% to 80%. The transmittance of the films exhibited ripples pattern due to interference of light which may due to the characteristic of interference between light and nanostructured materials [11]. The transmission was found to be maximum for low SnO_2 concentration of In_2O_3 and decreased with an increase in SnO_2 concentration. The two factors such as oxygen vacancies and scattering at grain boundaries are important role in the decrease of optical transmission.

N-type of Sn-doped In_2O_3 materials has indirect band gaps and its optical property such as absorption well suitable for photovoltaic applications. From the optical absorption data we determined the optical absorption measurements. The value of absorption coefficient calculated from the following equation

$$\alpha = \frac{1}{t}\,\mathrm{In}\left(\frac{A}{T}\right)\text{---------------------------------}(1)$$

where α is the absorption coefficient in cm-1. T is the thickness of the films. A is absorbance and T is transmittance. The nature of transition is determined using the following equation

$\alpha h\gamma = A (h\gamma - E)^n$------------------------(2)

where hγ is photon energy Eg is an energy gap. A is energy dependent constant and n is an integer. The optical band gap value measured all the composition of Sn doped Indium oxide thin films. They are obtained by extrapolating the linear portions to the energy axis as shown in fig 6. From the graph we observed that ITO thin films exhibit indirect transition, its band gap value in between 3.85 to 4.02 eV. The band gap value increases with increase in tin concentrations in the indium oxide lattice. In the earlier report [6,12,21] the allowed direct transitions of different ITO thin films and their optical band gap is 3.5 to 4.5 eV. Using the observed reading from the optical transmittance spectra to calculate the refractive index and the extinction coefficient using the following equation

$N = [N_1 + (N_1^2 - s^2)^{1/2}]^{1/2}$ ------------------(3)

$N1 = 2s \frac{TM - Tm}{T_M T_m} + \frac{s^2+1}{2}$----------------(4)

T_M and T_m are the values of maximum and minimum transmission values at a particular wavelength s is the refractive index of the substrate. Refractive index can be estimated by extrapolating envelops corresponding to T_M and T_m. Extinction coefficient (k) of the ITO films are estimated using the following equation

$K = \frac{\alpha\lambda}{4\pi}$--------------------(5)

Fig.6 shows the plot of refractive index as a function of wavelength λ for different percentages of SnO_2 in ITO films. The refractive index (n) was evaluated from the measured transmittance versus wavelength graph [13]. The refractive index was found to decrease with wavelength. It was observed that the refractive indices of the Sn-doped In_2O_3 thin films were smaller than for the pure In_2O_3 film in the measured wavelength range [14]. The decrease in refractive index was attributed to the lowering in the value of grain size and increase in the porosity of the ITO film with the increase in Sn concentration

Various compositions of tin doped indium oxide thin films and its dielectric behaviour as shown in fig.7. Using the following formula the real ($\in_r$) and imaginary ($\in_i$) parts of the dielectric constant were determined.

$\in = \in_r + \in_i = (n + iK)^2$---------- (6)

$\in_r = n^2 - k^2$ --------------- (7)

And $\in_i$= 2nk ----------- (8)

The dielectric constant is one of the well known properties of materials. The dielectric constants (real part) provide the speed of light slowing down in the material. From the graph we observed that the higher refractive index value of the glass substrate of prepared films has maximum value of real part of the dielectric constant. Similarly the imaginary part of the dielectric constant value has minimum value because prepared films have low extinction coefficient value. The dispersion and dissipative rate of the wave in the medium is calculated by the real and imaginary part of the dielectric constant. Using the following equation the optical conductivity was studied.

$\sigma = \alpha nc$ ---------(9)

Using W.D model, some of the optical properties such as dispersion and spectral dependence of the refractive index of many semiconductors are calculated from the following equations.

$n^2 = 1 + \left(\frac{E_0 E_d}{E_{2o-(h\gamma)2}}\right)$ ----------(10)

Where n is the refractive index, E_o is the average excitation energy known as the oscillator energy. E_d is the dispersion energy called the oscillator strength and hγ is the incident photon energy. The detailed procedure of dispersion parameter such as average excitation energy and dispersion energy were estimated [15]. When a graph is plotted between $(n^2-1)^{-1}$ versus $(h\gamma)^2$ for ITO thin films, which yields a straight line for normal behaviour having the slope $(E_0E_d)^{-1}$ and the intercept with the vertical axis equal to E_o/E_d. The values of the parameter E_0 and E_d

can be estimated from the positive curvature deviation from linearity at longer wavelength is usually observed due to the negative contribution of lattice vibrations on the refractive index. The value of optical constant reported in the table. Then carrier concentration has been calculated from the plasma frequency whose expression is given below

$\in = \in_{\alpha} - (\in_{\alpha}\ w_p 2)/w^2$ --------(11)

In a semiconductor the carrier concentration denoted as (N) and also it varies according to the square of plasma frequency w_p as [16-17]

$W_p^2 = (4\pi Ne2)\ (me * \ \epsilon \propto)$ --------(12)

Using equation 12 we calculate carrier concentration and plasma frequency [18 -20] If the carrier concentration is known the effective mass of the charge carrier could be found out from the plasma frequency. The band gap energies increase due to the decrease in crystallite size.

4. Conclusion:

Using sol gel dip coating method the various concentration of tin doped with indium oxide powder was coated in the clean glass substrate. Structural property and its micro behaviour of prepared films were analysed by XRD techniques which indicate bixbyte structure corresponding (222) peak. From the XRD measurement data we found some microstructure property. The Grain size increases with decrease of tin concentration (5%). Energy dispersive spectra confirm the presence of tin, indium and oxide are presented in our samples. Surface roughness observed in the atomic force microscopy. Tin concentration increases to 10% the resistivity of the films decreased from 20 ohm cm (Indium oxide at 450 ̊C) to 0.01 ohm cm .Beyond 10% tin the resistivity increases from 0.1 ohm cm to 250 ohm am at 70% tin concentration. The value of mobility and carrier concentration increases up to 10% tin concentration beyond this value of Tin oxide the carrier density decreases. Finally we have to calculate the single oscillator and dispersion energy were calculated from the data of optical transmission measurements in the ITO thin films. This material well suitable for solar cell application, sensors behaviour and also photo activity degradation of dye and other organic pollutants.

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No

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Figures

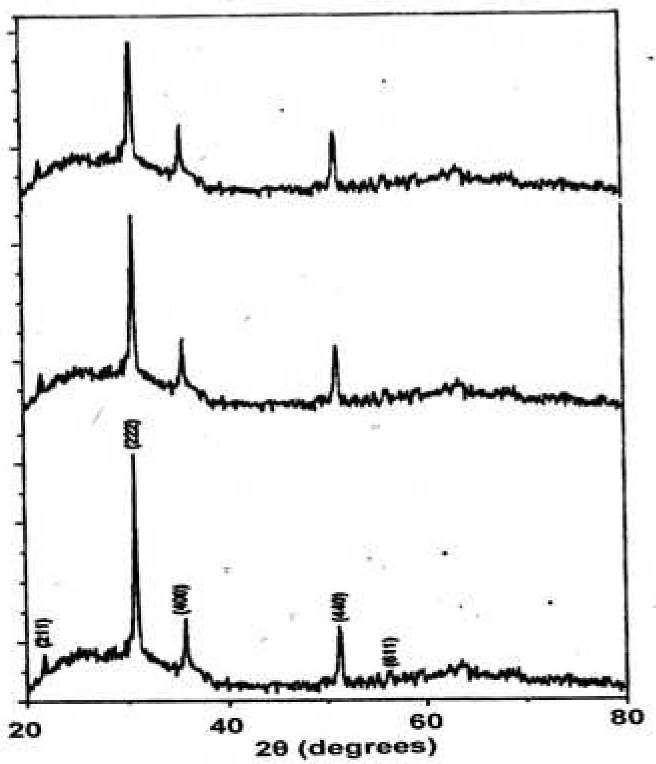

Figure 1

X-Ray diffraction pattern of 10% tin oxide in ITO films formed at different temperatures (a) 350° C (b) 400 °C (c) 450 °C

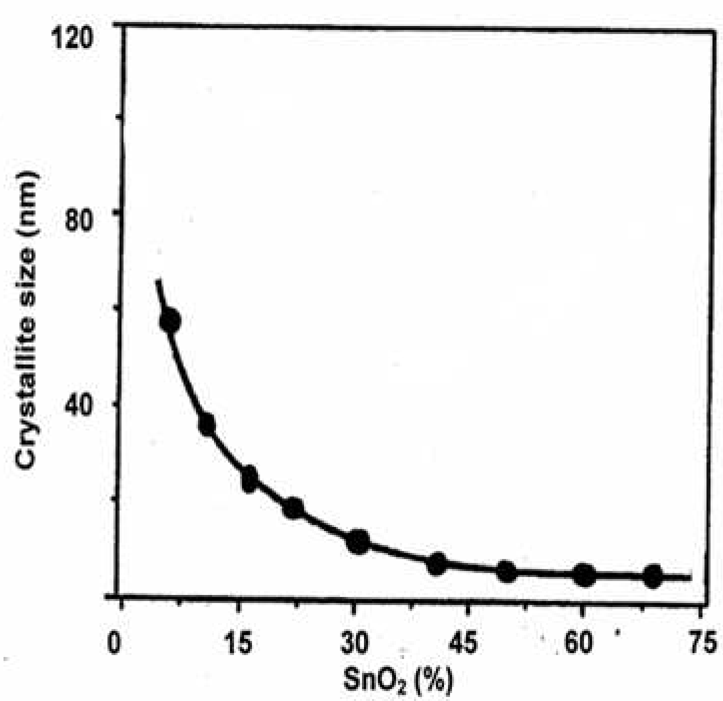

Figure 2

Mean crystallite size with increase of tin concentration.

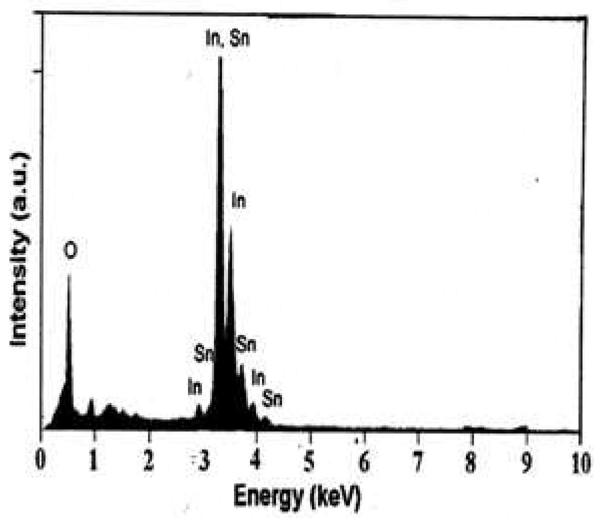

Figure 3

shows EDXA spectrum of ITO films (90% Indium oxide-10% tin oxide)

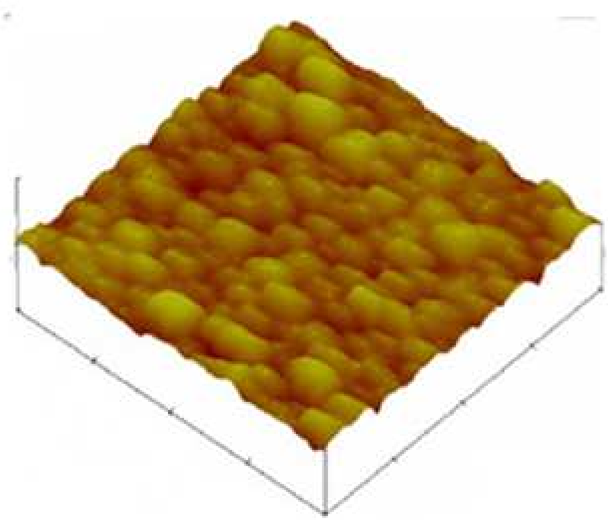

Figure 4

shows AFM of ITO films formed at 450 °C

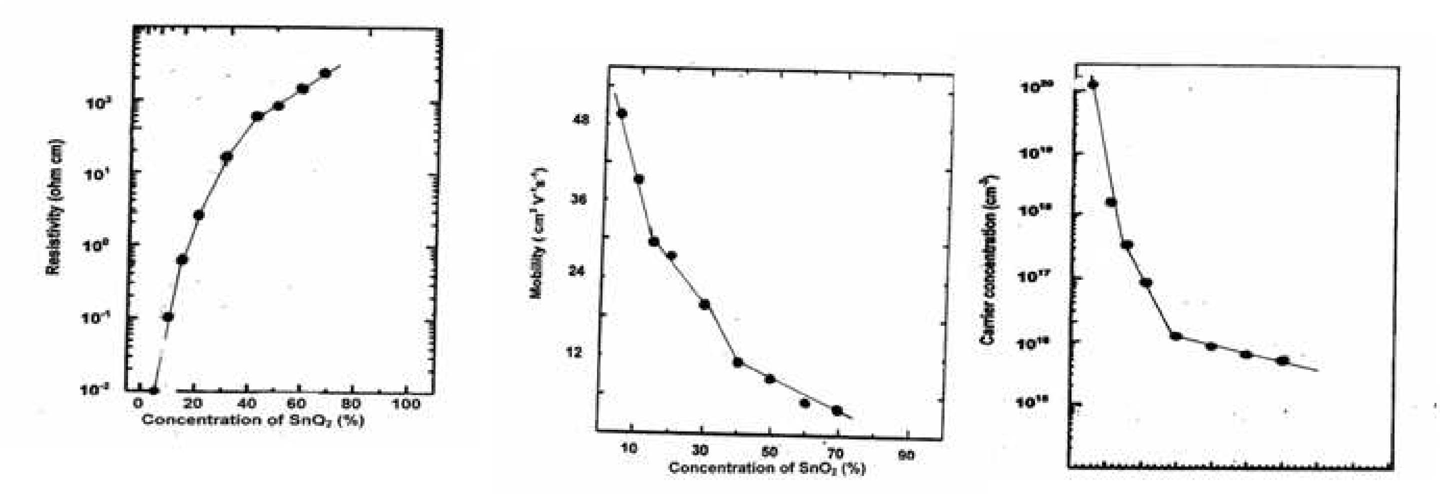

Figure 5

shows the variation of room temperature resistivity, mobility and carrier concentration of ITO films with different concentration of tin oxide

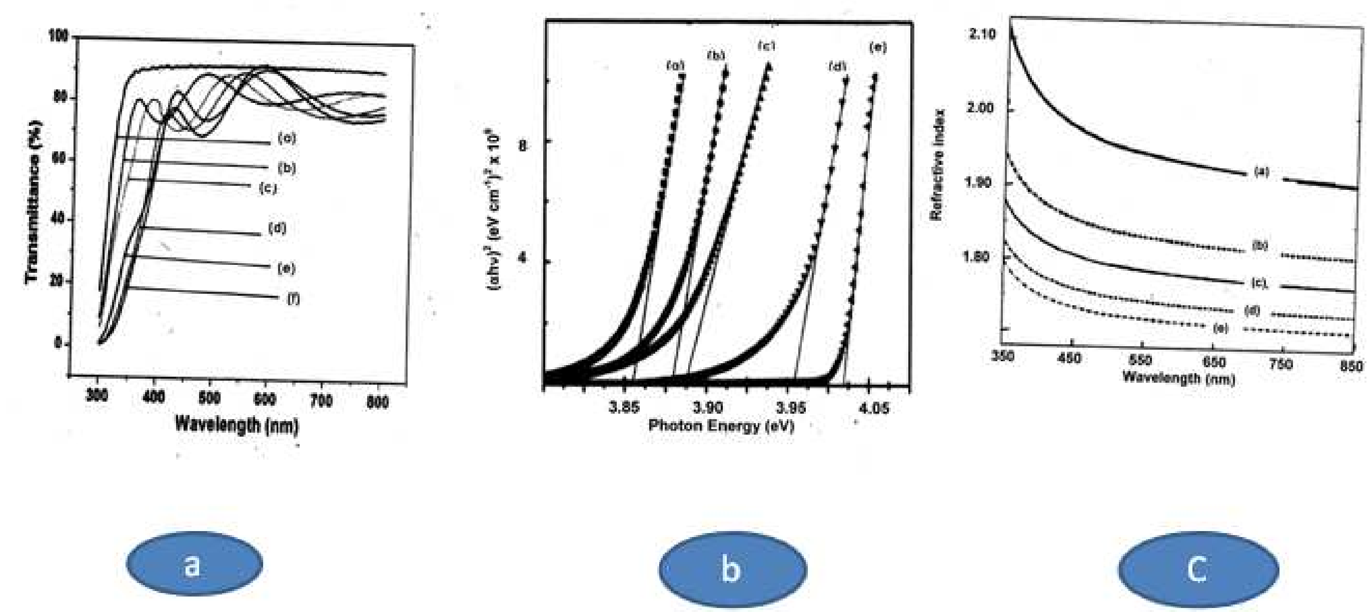

Figure 6

shows the (a) Transmission spectra (b) Tauc's plot (C) Refractive index with wavelength of ITO films with different concentrations of tin oxide (a) glass (b) 70% (c) 50% (d) 30% (e)15% (f) 5%

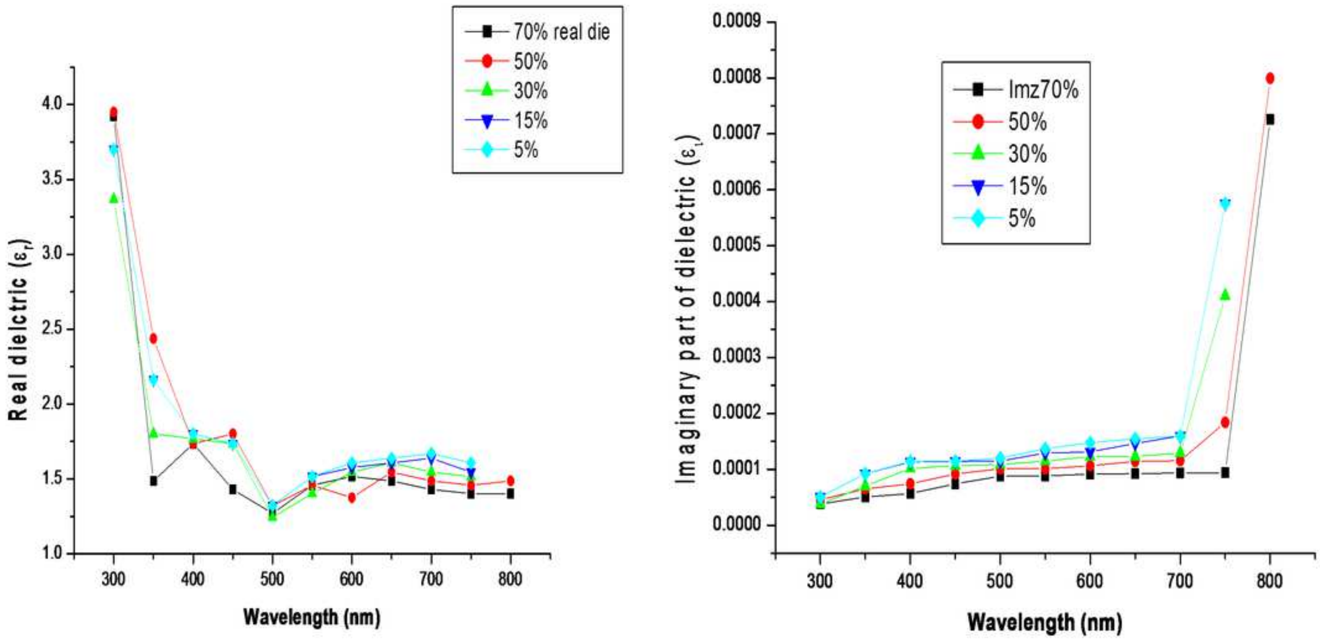

Figure 7

shows the variation of real part of dielectric and imaginary part of dielectric as a function of wavelength

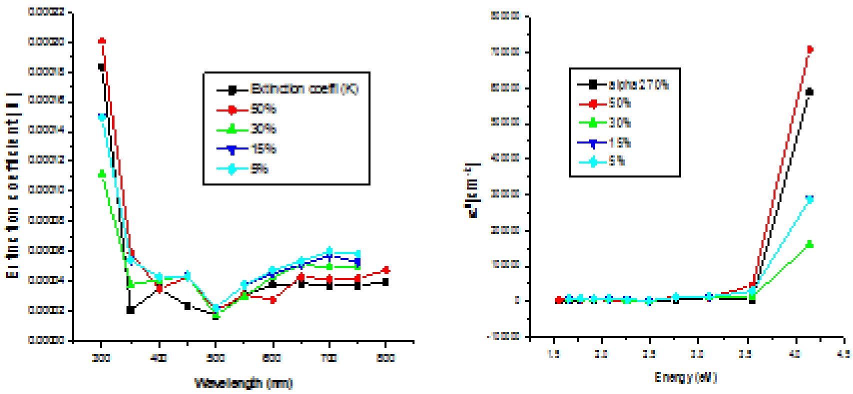

Figure 8

shows variation of extinction coefficient of ITO thin films at various compositions.

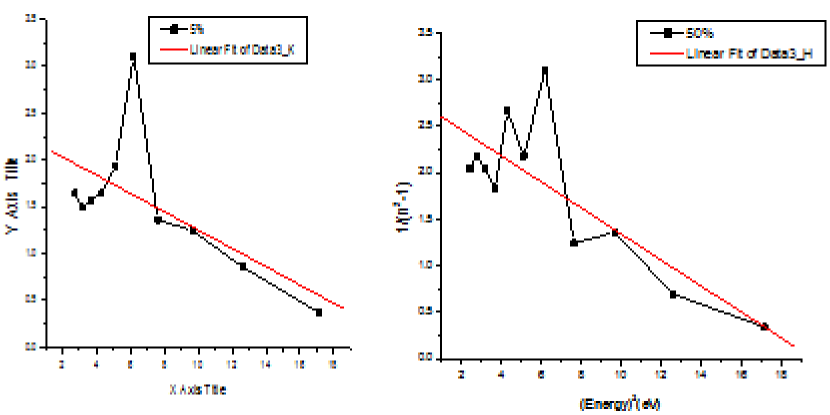

Figure 9

shows variation of (n2-1)-1 as a function of E2 for 5% and 50% tin concentration for Indium oxide thin films.