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 a significant role in the field of electronics. 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) is recently used in the substrate material for various applications, because it has special properties of low resistivity and high optical transmittance in the visible region. In this paper, we prepare ITO films with different tin concentration (5%, 10%, 15%, 20%, 30%, 40%, 50%, 60% 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 had bixbyte structure. Optical behaviour of materials can be understood in the near infrared and visible spectrum. Some optical parameters of 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

1 Introduction
Indium oxide doped with tin (ITO) is likely to be a very good material in the field of material science research group, at 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. It is also used in Perovskite solar cells (Peng et al. 2017; Li et al. 2021; Wang et al. 2020a, b; Alam and Cameron 2001). The film thickness and substrate temperature play a major role in maintaining the optimum condition in visible region (transparency) and near IR regions (reflectance), and also percentage of dopant, annealing temperature is optimized. Today there are several techniques such as the sol gel process (Alam and Cameron 2000) chemical evaporation (Carvalho et al. 2000) pulsed laser deposition (Adurodija et al. 1999) and electron beam evaporation (Soleimanian and Ghasemi Varnamkhasti 2016). As all the methods are very expensive and require high vacuum so that we choose sol gel dip coating method. This technique is required because of minimum cost and inexpensive method for depositing films. It is understood that most of the optoelectronic devices are the function of wavelength to predict photo electric behaviour, warranting the understanding of optical and structural properties. In this paper we studied some of optical behaviour such as refractive index, extinction coefficient optical band gap and complex dielectric constant and transmittance and absorbance of ITO film deposited on glass substrate.

2 Experimental procedure

Using a 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 in a beaker were prepared using 10 ml of 0.45 M solution of Indium (InCl₃  4  H₂O) and tin salts (SnCl₄  5H₂O). This mixture was heated to 70 °C and then the pH in the range of 9 was chosen and the following were added in sequence, 0.25 g of N,N-bismethylene acrylamide and 2 mg ammonium persulphate was added after 20 min. After a few minutes the solutions appeared viscous in nature. A glass substrate in the size of breadth is 2.5 cm and 7.5 cm length is taken and the removal rate of the substrate is 1 cm/min. After the film formation, it was air dried for 15 min with final calcinations at 350–450 °C at various time intervals (15–90 min). 50 min calcinations was found to be optimum. Using surface profilometer to measure the films thickness vary from 450 to 950 nm to increase temperature.

3 Result and discussion

The XRD techniques used to determine the atomic and molecular structure of ITO films using CuKα radiation corresponding to X-ray wavelength is 0.154 nm. Figure 1A, B shows X-ray diffraction pattern of ITO thin films (5–70% 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 SnO₂) is absent, which indicates that the Sn atoms are probably incorporated substitutionally into the indium oxide lattice (Fallah et al. 2007a; George and Menon 2000). Absence of the SnO₂ and SnO peaks at 26.5° and 33.2° is an indicator of complete miscibility of In and Sn in the complete range studied (upto 70%) (Sujatha

Fig. 1 A X-ray diffraction pattern of 5%, 10%, 15%, 20%, 30% tin oxide in ITO films formed at different temperatures (a) 350 °C, (b) 400 °C and (c) 450 °C. B X-ray diffraction pattern of 40%, 50%, 60% and 70% tin oxide in ITO films formed at different temperatures (a) 350 °C, (b) 400 °C and (c) 450 °C
Optical performance of Tin doped Indium Oxide (ITO) thin films…
Devi et al. 2002). Figure 2 shows the mean crystallite size of ITO films vs different tin concentration. The (222) peak width was utilized to determine the crystallite size. The microstructure parameters are minimum for low Sn concentration (indicator of preferred orientation (Table 1) (Carvalho et al. 2000).

X-ray microanalysis (Fig. 3) 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.

Scanning probe micrometer image (Fig. 4) of 10% tin concentration of ITO films is 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 a decreasing trend for grain size with Sn increase. This is supported by the XRD data. And also we found the surface roughness it values in the range of 0.20–1.25 nm.
Increase of tin concentration up to 10% caused the resistivity to decrease from 20 to 0.01 Ω cm (Films formed at 450 °C). When the tin concentration increased further, resistivity increased (0.01–250 Ω cm). At the same time, mobility and carrier concentration increased up to 10% Sn ($N_d$ increased from $3.85 \times 10^{17}$ cm$^{-3}$ (In$_2$O$_3$ films formed at 450 °C) to $1.25 \times 10^{20}$ cm$^{-3}$, mobility increased from $1.35 \times 10^{-4}$ m$^2$ V$^{-1}$ s$^{-1}$ to $49.93 \times 10^{-4}$ m$^2$ V$^{-1}$ s$^{-1}$ up to 10 at% and decrease for further increase in Sn concentration (Ramanathan and Murali 2018) (Fig. 5A, B, C). The data of the transport parameters are indicated in Table 2. The behaviour of the films with increase of Sn concentration can be explained on the basis of the solubility of Sn atoms in the indium oxide lattice (Frank et al. 1979; Hichou et al. 2004). At Sn concentrations less than 10%, Sn$^{4+}$ ions substitute In$^{3+}$ ions (n type donors). With further increase of Sn concentration (greater than 10%), Sn solubility in the Indium oxide lattice is inhibited. The Sn impurities occupy the interstitial sites for the
higher Sn concentration (> 10%). The presence of Sn interstitials act as charged trapping centers (Hamberg and Granqvist 1986) for electrons at high Sn concentrations.

Under proper environment conditions, the optical properties of Sn-doped In$_2$O$_3$ films at various compositions were analysed. The Oxygen defect plays a very important role in the prepared samples. The loss of transmission is due to the scattering of light at the grain boundaries formed by the small grains with increase of Sn concentration in Indium oxide films. In sol gel techniques we have to use glass substrate prepared films is used which behaves as transparent material in the wavelength range of 450 and 1100 nm, because the transmittance values are high at these wavelengths. As the transmittance values slightly increases so there is an increase in highly transmitting properties of ITO. The transmittance spectrum (Fig. 6A–C) gives the information of surface Plasmon’s resonance indicating the crystallite size in the nanometre range. The transmittance of the films exhibited ripples pattern due to interference of light in nanostructured materials (Fallah et al. 2007b). Maximum transmission is observed for low Sn concentration (< 10%). The transmission decreased for Sn concentration > 10%. Oxygen vacancies and scattering at grain boundaries play an important role in the decrease of optical transmission.

Transmittance spectra (Fig. 6A) give the information of transmittance of ITO film deposited on glass substrate. The decrease in optical transmission with increase of Sn content is also due to the scattering of light at grain boundaraiyes and oxygen vacancies as explained earlier.

Table 2 Electrical behaviour of ITO films at various concentrations

| S. no | Concentration of SnO$_2$ (%) | Resistivity (ohm cm) | Mobility × 10$^{-4}$ (m$^2$ V$^{-1}$ s$^{-1}$) | Carrier concentration (cm$^{-3}$) |
|-------|-------------------------------|----------------------|-----------------------------------------|----------------------------------|
| 1     | 5                             | 0.01                 | 38.75                                   | 1.61 × 10$^{18}$                |
| 2     | 10                            | 0.10                 | 49.93                                   | 1.25 × 10$^{20}$                |
| 3     | 15                            | 0.65                 | 29.65                                   | 3.20 × 10$^{17}$                |
| 4     | 20                            | 2.61                 | 26.57                                   | 8.89 × 10$^{16}$                |
| 5     | 30                            | 17.45                | 19.85                                   | 5.81 × 10$^{16}$                |
| 6     | 40                            | 56.89                | 10.34                                   | 1.06 × 10$^{15}$                |
| 7     | 50                            | 72.97                | 8.65                                    | 9.88 × 10$^{15}$                |
| 8     | 60                            | 176.20               | 4.13                                    | 8.57 × 10$^{15}$                |
| 9     | 70                            | 250                  | 3.73                                    | 6.69 × 10$^{15}$                |

Fig. 5 A to C variation of room temperature resistivity, mobility and carrier concentration of ITO films with different concentration of tin oxide
N-type of Sn-doped In$_2$O$_3$ materials has indirect band gaps and its optical property such as absorption render them appropriate candidates for photovoltaics. The computation of absorption coefficient was done from the following equation

\[ \alpha = \frac{1}{t} \ln \left( \frac{A}{T} \right) \]  

(1)

(\(\alpha\)—absorption coefficient in cm$^{-1}$, T—film thickness, A—absorbance and T—transmittance). The Tauc’s relation below was used to determine nature of transition.

\[ \alpha h\gamma = A(h\gamma - E)^n \]  

(2)

where \(h\gamma\) is photon energy \(E_g\) 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 (linear portion extrapolated to energy axis shown in Fig. 6B). From the graph we observed that ITO thin films exhibit indirect transition and 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 (George and Menon 2000; Smith et al. 1984; Dhanasekaran et al. 2012) the allowed direct transitions of different ITO thin films and their optical band gap is 3.5–4.5 eV. Using the observed readings from the optical transmittance spectra, refractive index and extinction coefficient were computed as follows (Swanepoel 1984),

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

(3)

\[ N_1 = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \]  

(4)

The different parameters in the above equations have the usual meaning. Extinction coefficient (k) of the ITO films are estimated using the following equation

\[ K = \frac{\alpha \lambda}{4\pi} \]  

(5)

Figure 6C shows the plot of refractive index as a function of wavelength \(\lambda\) for different percentages of Sn in ITO films. The behaviour of refractive index with increase in
wavelength is a decreasing trend. Sn doped films exhibit lower refractive index values compared to undoped indium oxide (Senthilkumar et al. 2010). The above behaviour can be attributed to the small grain size observed with increase of Sn concentration in the Indium oxide lattice as well as the increase in porosity with increase of Sn concentration. The lower value of refractive index can also be related to the packing density of grains in the films. Increase in the porosity of films may result in low packing of the grains and hence there a reduction of the refractive index. Similar behaviour has been reported for TiO$_2$ films (Mechiakh and Bensaha 2006). The decreasing trend of refractive index with increase of Sn concentration can be explained in terms of the decrease of grain size and increased porosity.

Various compositions of tin doped indium oxide thin films and its dielectric behaviour is shown in Fig. 7. Using the following formula the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant were determined.

\[ \varepsilon = \varepsilon_r + \varepsilon_i = (n + iK)^2 \]  \hspace{1cm} (6)

\[ \varepsilon_r = n^2 - k^2 \]  \hspace{1cm} (7)

And

\[ \varepsilon_i = 2nk \]  \hspace{1cm} (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.

It is observed from the graph, that a higher real part of dielectric constant is observed for low Sn content. The refractive index for these films is high hence, the dielectric constant is high. The real part of dielectric constant is high for low Sn concentrations ITO films, the real part of dielectric constant computed using the relation $\varepsilon_r = n^2 - k^2$, hence, high values of refractive index results in high $\varepsilon_r$.

From the graph (Fig. 7A, B) it is observed that the films with high refractive index values have maximum value for the real part of the refractive index. A minimum value is observed.

Fig. 7  A & B variation of real part of dielectric and imaginary part of dielectric as a function of wavelength
for imaginary part of dielectric constant due to the low extinction co-efficient values for these films (Fig. 8A, B).

By measuring the dielectric constant (real and imaginary part) it is possible to understand the dispersion and dissipative rate of the wave in the medium. Using the following equation the optical conductivity was studied.

$$\sigma = \alpha n c$$  \hspace{1cm} (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.

$$n^2 = 1 + \left( \frac{E_0E_d}{E_{2\omega-(h\gamma)^2}} \right)$$  \hspace{1cm} (10)

The parameters in the above equation have the usual meaning. The detailed procedure of dispersion parameter such as average excitation energy and dispersion energy were estimated (Osuwa et al. 2009). When a graph (Fig. 9A, B) is plotted between $(n^2 - 1)^{-1}$ versus $(h\gamma)^2$ for ITO thin films, slope $(E_0E_d)^{-1}$ and intercept with y-axis gives $E_d/E_0$.

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 3. Then carrier concentration has been calculated from the plasma frequency whose expression is given below

$$\varepsilon = \varepsilon_e - (e_a w_p^2) / w^2$$  \hspace{1cm} (11)

Carrier concentration (N) of a semiconductor is related to plasma frequency $\omega_p$ as follows (Dhanasekaran and Mahalingam 2012; Manifacier et al. 1976).

$$W_p^2 = (4\pi Ne2)(me^s \varepsilon \propto)$$  \hspace{1cm} (12)

Using Eq. 12 we calculate carrier concentration and plasma frequency (Zeng et al. 2002; Swanepoel 1986; Dhanasekaran et al. 2012; Ramanathan and Murali 2013) If the
carrier concentration is known the effective mass of the charge carrier could be found out from the plasma frequency.

4 Conclusion

The results of this investigation clearly point to the possibility of preparing ITO films with different Sn concentrations (5–70%) by the simple and economical polyacrylamide sol gel dip coating technique. The structural, optical and electrical properties of ITO films with different Sn concentration were studied. As evidenced from the X-ray diffraction analysis, the crystallite size was found to decrease with Sn doping, which agree with earlier studies. The small grain size observed in the present study further paves the way for using photocatalytic environmental remediation, wherein, it is possible to adsorb more dye molecules in the industrial waste water (more surface area) and help in removal of the dye contamination. The sensitivity of the gas sensor also will be improved because of the small grain size. The transmission properties decrease with higher Sn concentration. The dependence of the optical parameters (refractive index, band gap, extinction co-efficient, optical conductivity, 

Table 3

| S. no | Concentration of SnO₂ (%) | R.I (n) | E₀ | Eₐ | E₉ | E | ωₑ×10¹⁵/s | m* | N/m* |
|-------|--------------------------|--------|----|----|----|---|-------------|----|------|
| 1     | 5                        | 2.10   | 7.71| 14.65| 3.85| 4.41| 3.31| 0.87| 1.43×10²⁰|
| 2     | 10                       | 2.00   | 7.75| 14.81| 3.88| 3.80| 3.53| 0.90| 2.88×10¹⁷|
| 3     | 30                       | 1.88   | 7.78| 14.93| 3.89| 3.53| 3.81| 0.91| 6.38×10¹⁶|
| 4     | 50                       | 1.82   | 7.92| 14.97| 3.96| 3.31| 3.92| 0.92| 1.07×10¹⁶|
| 5     | 70                       | 1.80   | 8.04| 15.03| 4.02| 3.24| 4.12| 0.93| 7.19×10¹⁵|

Fig. 9 Shows variation of \((n^2 - 1)^{-1}\) as a function of \(E^2\) for 5% and 50% tin concentration for Indium oxide thin films
dielectric constant, dispersion energy and oscillator) depend on the Sn concentration in the ITO films.

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Conflict of interest The authors have not disclosed any competing interests.

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