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The Effect of Deposition Rate on Electrical, Optical and Structural Properties of ITO Thin Films

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Abstract: Indium tin oxide (ITO) thin films have been prepared using the reactive evaporation technique on glass substrates in an oxygen atmosphere. It is found that the deposition rate plays prominent role in controlling the electrical and optical properties of the ITO thin films. Resistivity, electrical conductivity, activation energy, optical transmission and band gap energy were investigated. A transmittance value of more than 90 % in the visible region of the spectrum and an electrical conductivity of 3×10^{-6} Ωm has been obtained with a deposition rate of 2 nm/min. XRD studies showed that the films are polycrystalline.

Key Words: Thin films, Indium tin oxide, Electronic transport, Optical properties

Introduction

Indium tin oxide (ITO) films have been widely studied over the past many years since they were found to exhibit electrically conductive and optically transparent characteristics. Therefore, ITO films are extensively used as coating electrodes in optoelectonic devices[1-3], electrolumniscent devices[4], photo voltaic cells[5], electrochromic devices[6], liquid crystal displays[7] and energy efficient windows[8]. Indium tin oxide thin films can be prepared in a variety of techniques including rf or dc sputtering[9], spray pyrolysis[10], reactive thermal evaporation[11], electron beam gun evaporation[12] and laser ablation[13]. Most of the investigations on ITO are carried out on sputter deposited films and fewer studies have been reported on thermally evaporated ITO films. The knowledge of structural and electrical as well as the optical properties is still limited and further investigations are needed to understand the physical characteristics of these films.

The opto electric properties of ITO thin films investigated in this study have been found significantly depend on the deposition parameters such as substrate temperature and deposition rate. We have found that the deposition rate is an important parameter and it seems that it has not been reached proper attention. This paper reports the studies on the electrical and optical properties of ITO thin films evaporated by thermal evaporation at different deposition rates.

Experimental

A 12-inch vacuum coating unit with an electron beam gun was used for the evaporation of indium tin oxide (ITO) thin films. Spectroscopically pure indium oxide powder (99.99%) and tin oxide powder (99.99%) taken in wt.% proportion were mixed well using a pestle and mortar. The mixture was sintered in a furnace for 6 hours at a temperature of 800 ^{0}C. The mixture was pressed into pellets, which was used as the source material for evaporation. Initially the vacuum chamber was evacuated to a base pressure of 10^{-6} mbar. Pure oxygen was admitted to the chamber with the high vacuum valve open. A steady state chamber pressure was reached by adjusting the needle valve of the bell jar of the coating unit. Glass slides were used as the substrates on which a calibrated chromal alumal thermocouple was attached. The substrates were cleaned using the standard cleaning procedure. Inside the bell jar the substrates were subjected to ionic bombardment for 5 minutes as the final cleaning before deposition. The rate of evaporation was controlled within the range 2 to 10 nm/min. The oxygen partial pressure is kept constant during the evaporation

The thickness of the film was controlled by using a crystal thickness monitor and was counter checked by using the Tolansky's multiple beam interference technique[14]. The samples were annealed in a furnace for 30 minutes at 350 ^{0}C in air. The electrical conductivity of the samples were measured by means of a conductivity cell and a Keithley programmable electrometer (model No.617). The ohmic contacts were made by pre-evaporated silver electrodes and silver paste. The conductivity measurements were carried out in a subsidiary vacuum of 10^{-3} mbar to eliminate the contamination of the film. A double beam spectrophotometer (Schimadzu 160A) was used for recording the UV/Vis spectrum. XRD spectrum of the sample was recorded by means of Schimadzu 610 A X-ray diffractometer.

Results and Discussion

Electrical Properties

Figure 1 gives the variations of the resistivity of the thermally evaporated ITO thin films deposited at different substrate temperatures ranging from 50 to 350 ^{O}C. The rate of deposition was 10 nm/min and the thickness of the film was 150nm. A sudden drop in resistivity was obtained in the temperature range between 50 and 250 ^{O} C. The lowest resistivity obtained was 4 x 10 $^{-6}$ Ωm at a substrate temperature of 300 ^{O}C. The decrease in resistivity with increase in substrate temperature could be attributed to the improved crystalline nature of the films. An increase in substrate temperature resulting in an oxygen- deficient films resulted in an increase in carrier density. Crystallinity is enhanced by heating the substrate during deposition of ITO films. The higher substrate temperature also causes an increase in grain size reducing the grain boundary scattering. The higher substrate temperature during deposition form oxygen deficient films. These oxygen vacancies are also responsible for lower resistivity in the film [15]. At the substrate temperature of 200 ^{O}C the resistivity was 9 x 10 $^{-6}$ Ωm. The results show that the optimum substrate temperature for low resistive films is 350 ^{0}C. However for the further studies, the substrate temperature was chosen as 200 ^{0}C .

Figure 2 shows the variation of the resistivity of ITO thin films evaporated at 200 ^{O}C as a function of deposition rate. It is shown that the resistivity reveals strong dependence on the deposition rate. The film of thickness 150 nm exhibits a linear increase in the resistivity of more than 200% from an initial value of 3 x 10 $^{-6}$ Ωm to 7 x 10 $^{-6}$ Ωm for a range of deposition rate from 2 to 10 nm/min. Similarly an increase in resistivity is obtained with rise in deposition rate for a film deposited at 150 ^{0}C. These results show that the substrate temperature can be significantly lowered by choosing a lower rate of evaporation without compromising the film properties.

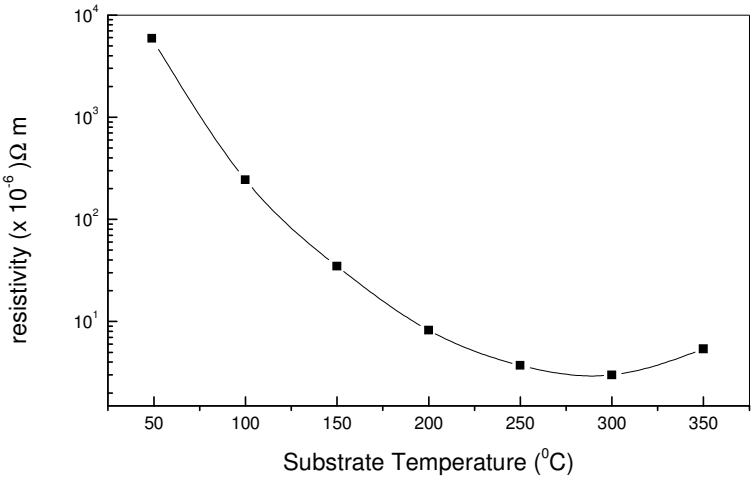

Figure 1. Resistivity as a function of substrate temperature**.**

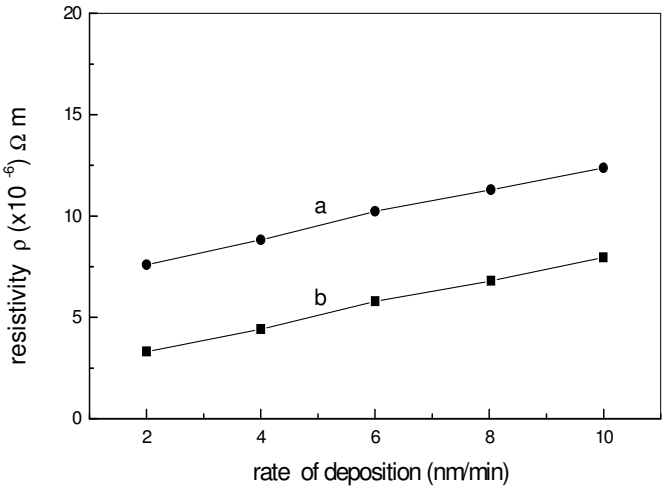

Figure 2. Change of resistivity of ITO thin films as a function of deposition rate for substrate temperature a) 150 ^{0}C b) 200^{0}C

The electrical conductivity studies have been carried out in the temperature region of 30 to 300 ^{0}C. The electrical conductivity as a function of inverse of temperature is given in **Figure 3**. The activation energy is obtained using the relation.

$$\sigma = \sigma_0 \exp(-\delta E/kT)$$

where σ is the electrical conductivity, δE is the activation energy, σ_0 is a constant, k is the Boltzmann constant and T is the temperature in absolute scale. The conductivity studies on films deposited at a

substrate temperature of 200 ^{0}C and was deposited at a rate of 10 nm/min showed that two activation energies existed at different temperature regions. The activation energy in the lower temperature region (30-130 ^{0}C) for a film of thickness of 150 nm was 0 .042 eV and in the higher temperature region (130-220 ^{0}C) it was 0.451 eV. The activation energies obtained for different films deposited at various deposition rates is as shown in **Table 1**. The results indicated the presence of two donor levels, one deep and one shallow, near the bottom of the conduction band. Hoffman et. al have reported the activation energies as 0.035 and 0.045 in the corresponding regions respectively [16] . Both levels depended on the deposition rate and were found to decrease with decreased deposition rate. The results show that the film tends to complete degeneracy state as the deposition rate is decreased.

Table 1 Activation energies of various films

Rate of deposition (nm)	Activation energy ΔE_1	ΔE_2
2	0.020	0.350
4	0.025	0.380
6	0.032	0.402
8	0.038	0.424
10	0.042	0.451

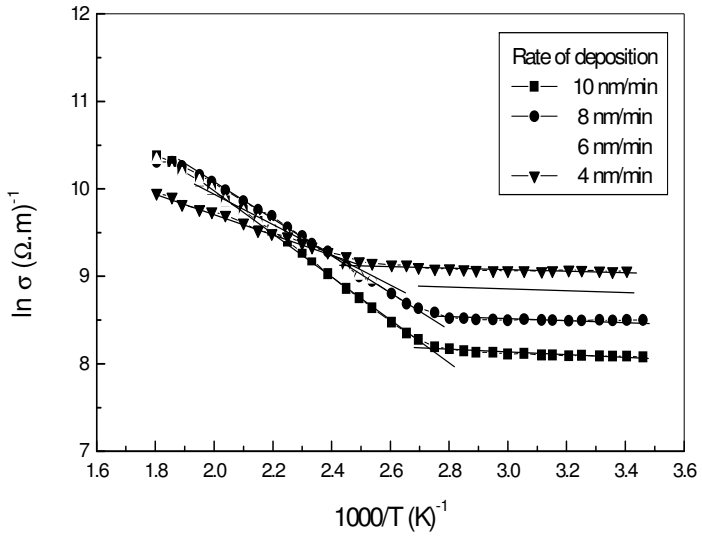

Figure 3. Plot of ln σ Vs 1000/T for ITO thin films prepared at various deposition rates.

Optical Properties

The optical transmission spectra corrected for the attenuation of the glass substrate from 300-800 nm for indium tin oxide film deposited at different deposition rates is shown in **Figure 4** . The results reveal that the deposition rate plays an important role in film properties. From the spectra it can be seen that with decrease in deposition rate the transmission percent increases. The low transparency at higher deposition rate is most probably attributed to the small grain size and amorphous nature, which is revealed in the XRD patterns. The sharp decrease in the transmittance at the lower wavelength region is due to the fundamental absorption and the average transmission in the visible region goes up

to 90 % for a film of thickness150 nm and prepared at a deposition rate of 2 nm/min. There was a shift in the absorption edge to shorter wavelength with the decreased deposition rate. The direct band gap was calculated from the transmission data in the lower wavelength region using the assumption that the transmission probability becomes constant near the absorption edge and the absorption coefficient for the direct allowed transition can be described as a function of photon energy.

$$\alpha \propto (h\nu\text{-}Eg)^{1/2}$$

where α is the absorption coefficient, Eg is the energy gap and $h\nu$ the photon energy. The plots of α^2 vs. $h\nu$ had a linear region and extrapolation of the straight line to zero absorption gave the energy gap for different films of various deposition rates which are listed in **Table 2**. The energy gap values obtained are in good agreement with the other reported values[17-19].

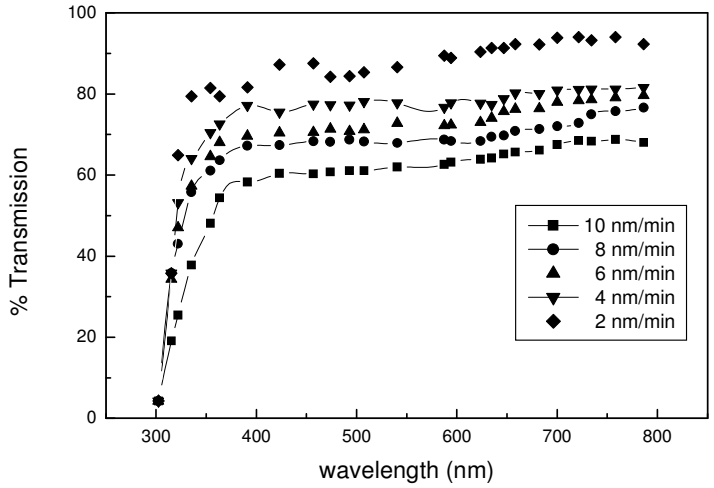

Figure 4. Optical transmission spectra for ITO films prepared at various deposition rates.

Table 2. Band gap energy of various films.

Deposition rate (nm/min)	Band Gap (eV)
2	3.60
4	3.53
6	3.42
8	3.31
10	3.20

XRD spectrum of the indium tin oxide film deposited at various deposition rates shows a polycrystalline nature of the film. The main peaks are identified by the ASTM powder data and were analyzed. **Figure 5** corresponds to the films deposited using various deposition rates at a substrate

temperature of 200 ^{O}C. The films show maximum intensity peak corresponding to (321) predominant orientation. The other peaks observed are (211), (222), (400),(420), (431) and (440). It is seen in the figures that the peaks are suppressed for a film deposited at a higher deposition rate. An improvement of crystallinity was observed for films deposited at a lower deposition rate. The preferred orientation depends on the film thickness[20] and deposition conditions [21].

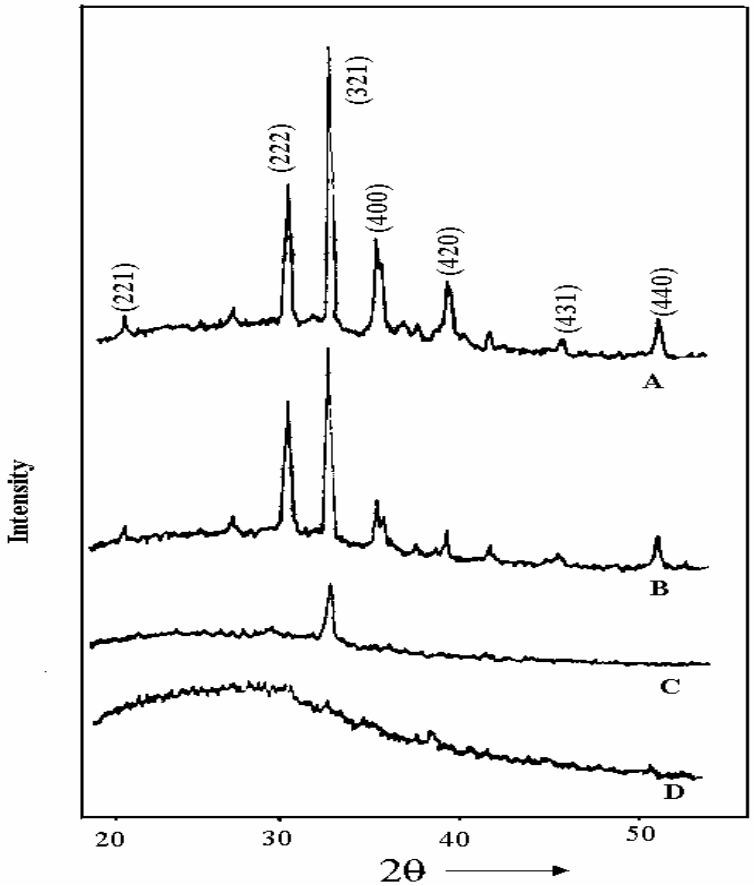

Figure 5. XRD pattern of the samples deposited at various deposition rates.
(A) 2 nm/min, (B) 4 nm/min, (C) 6nm/min, (D) 10 nm/min.

The grain size is also obtained from he full width half maximum (FWHM) of the X-ray peak using the Scherrer's formula $D = \left(\frac{0.9\,\lambda}{\beta_{\frac{1}{2}}}\right)\mathrm{Cos}\,\theta$

Where λ =0.1541 nm, $\beta_{\frac{1}{2}}$ = B-b where B is the observed width of the peak at an angle 2θ and half maximum intensity and b is the effect of the instrument determined from the broadening of the monocrystalline silicon diffraction line. The estimated grain size for the films deposited at different deposition rates are shown in **Table 3.** This indicates that the ITO thin films deposited at low deposition rate promote the formation of crystalline phase. Higher deposition rate causes lower grain size together with amorphous structure implied by XRD studies. In addition high deposition rate may also change the ITO composition. [22]

Table 3. Grain size of various films deposited at various rates.

Rate of deposition (nm)	grain size (nm)
2	57.2
4	48.4
6	35.3
8	28.3

Conclusions

ITO thin films of high conductivity and high visible transmittance were obtained by varying the deposition rate. High quality films with resistivity as low as 3 x 10^{-6} Ωm and transmittance over 90 % were obtained by controlling the deposition parameters. The activation energies were calculated to be 0.032 eV and 0.402 eV for a film of thickness 150 nm and deposited at a rate of 6 nm/min. The optical band gap was found to vary from 3.60 eV to 3.20 eV with decrease in the deposition rate. The crystallinity was found to be increased by decreasing the deposition rate. The film exhibits the reflection from the (321) planes as the most predominant peak in X ray diffraction pattern. The grain size was found to increase with decreased deposition rate.

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