Effect of substrate temperature on structural and optical properties of sprayed indium oxide thin films

R. SATHYAPRIYA, P. KATHIRVEL[a*], J. CHANDRASEKARAN[b]
Department of Physics, SNS College of Technology, Coimbatore 641 035, Tamilnadu, India
[a]Department of Physics, United Institute of Technology ,Coimbatore-641 020, Tamilnadu, India
[b]Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-641 020, Tamilnadu, India

Conducting and transparent indium oxide thin films are prepared by chemical spray deposition of aqueous solution of indium chloride. X–ray diffraction and optical transmission are used to characterize these films. X-ray diffraction study reveals that all the films are highly crystalline and oriented along <222> direction and the film crystallinity increases with increase in film thickness. Band gap energy of the films depends on thickness and varies from 3.53 eV to 3.5 eV. It is observed that resistivity of the films decreases with thickness, while mobility increases.

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1. Introduction

Indium oxide (In_2O_3) is a transparent conducting oxide with high electrical conductivity and high optical transmittance in the visible region which makes it useful as transparent electrode for display systems [1], solar energy heat mirrors [2], window layers in heterojunction solar cells [3,4] etc . TCOs have high transmittance in the visible region and reflectance in the IR region. Because a TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between these properties is required. In general most of the known TCOs are n-type materials such as SnO_2, $In2O_3$, CdO, ZnO, Cd_2SnO_4, $ZnSnO_4$, $MgIn_2O_4$, and $Zn_2In_2O_5$. Spray pyrolysis involves optimization of many process parameters. Definite control on the optoelectronic properties and growth mechanism of the films can be realized only if one investigates thoroughly the influence of every process parameter on the film properties. This procedure helps in preparing high-quality conducting oxide films, which are useful for the development of photovoltaic solar cells and TCO films. [3-10].

The aim of the present work is to prepare highly conducting In_2O_3 films using very low concentration of the indium precursor solution so that the production cost will be low. Detailed investigations have been carried out to study the influence of the spray pyrolysis process parameters on the film deposition and properties of the In_2O_3 films.

2. Experimental procedure

Indium oxide thin films were deposited on heated glass substrates by spraying an alcoholic solution, containing indium chloride hydrate InCl3·4H2O (Fulka 99.9%), using the ultrasonic spraying system presented in [2]. Indium oxide films were deposited on heated glass substrates by spraying 0.1 M precursor solution. Generally in spray pyrolysis technique, indium oxide on hot surface/atmosphere is formed in principle on reversible endothermic reaction as

$$2InCl_3 + 3H_2O \ (\text{----}\rightarrow) \ In_2O3 + 6HCl$$

If this reaction were completed, the resulting indium oxide film would become highly stoichiometric. Since the films obtained by pyrolytic decomposition are conducting, the expected reactions are

$$In_2O_3(s) \ \text{--}\rightarrow \ In_2O(g) + O_2(g)$$

$$In_2O(g) + 2O^{2-} \ \text{----}\rightarrow \ In_2O_3(s) + 4e$$

The precursor solution was prepared by dissolving $Incl_3$ (99%), in double distilled deionized water. The solution was sprayed onto heated glass substrates held in the temperature range 350°C to 550°C in terms of 50ºC with an accuracy of ± 5°C.

3. Results and discussion

3.1 Structural properties of indium oxide films

The composition and crystalline properties of the In_2O_3 films at substrate temperatures varying from 3001C to 5001C were studied using the X-ray diffraction analysis. Body-centered cubic (BCC) structure with the (2 2 2) predominant plane of crystallization has been identified for all the films deposited at substrate temperatures at and above 350ºC as shown in Fig. 1. The film deposited at 350ºC shows an amorphous nature which is evident from the broad feature observed in the region 2θ 15-23 along with the (2 2 2) and (4 0 0) peaks of very low intensity just appearing. The film prepared at 450ºC shows well-developed peaks corresponding to (2 2 2) and (4 0 0) . When the temperature is increased above 450ºC up to 550ºC, the intensities decrease for all the peaks. Kosltin et al. [11] report a change in preferred orientation between (4 0 0) and (2 2 2) in In_2O_3 films prepared using $InCl_3$ as the starting material in spray pyrolysis technique.

The crystallite size (D) was calculated using the Scherer's formula [79] from the Full Width at Half Maximum (FWHM),

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

when β is the full-width at half maximum (FWHM) of the diffraction peak, λ is the wavelength source and θ is the diffraction angle.

The dislocation density (δ) can be evaluated from the crystallite size (D) by the following relation [2]

$$\delta = \frac{1}{D^2} \quad (2)$$

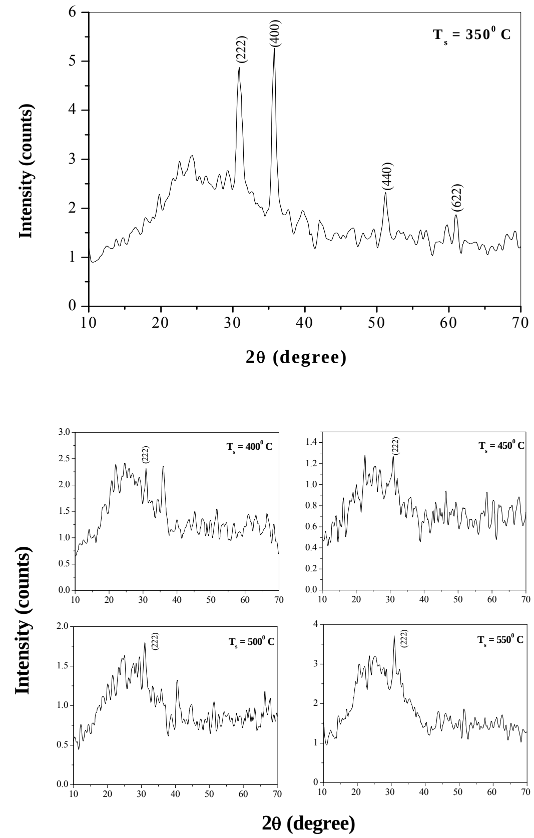

Fig.1. XRD - patterns of In_2O_3 films at different substrate temperatures.

Table .1. X-Ray diffraction data.

S. No	2θ in degrees		'a' in Å		'd' spacings (10^{-10} m)		hkl
	Observed	Standard	Observed	Standard	Observed	Standard	
1	30.915	30.576	10.12	10.12	2.89010	2.89010	222
2	35.863	35.451	8.667	10.12	2.60178	2.60178	400
3	31.049	30.576	9.969	10.12	2.87793	2.87793	222
4	31.188	30.576	9.9265	10.12	2.86542	2.86542	222
5	30.953	30.576	9.9998	10.12	2.88663	2.88663	222

Table. 2. Micro structural parameters of In_2O_3 films.

Thickness in Å	D (nm)	$\delta x 10^{15}$ lines/m^2
2400	40	10.9
1900	35	10.2
1670	30	5.8
1500	28	18.3
1230	26	13.8

4. Optical properties of In_2O_3 films

Fig. 2 shows the optical transmittance spectra of the In2O3 films prepared at different substrate temperatures. The percentage transmission (%T) value in the visible region is found to increase with increase in substrate temperature. A maximum transmission behavior is observed for the In_2O_3 films prepared at 350ºC and comparatively lower transmission values are recorded for other films prepared at temperatures below and above the optimum 400ºC. The %T values at 700nm are 71, 89, 94.42, 94.70, and 96.8 for the substrate temperatures 300ºC, 400ºC, 450ºC, 500ºC and 550ºC, respectively (Table 3).

$$K_f = \frac{\alpha\lambda}{4\pi} \tag{4}$$

where 'α' is the absorption coefficient and 'λ' is the space period defining the distance traversed by the wave on a periodic time.

The optical band gap of crystalline In_2O_3 films was calculated using the formula,

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{5}$$

where A is a constant, E_g is the optical band gap and hν is the incident photon energy.

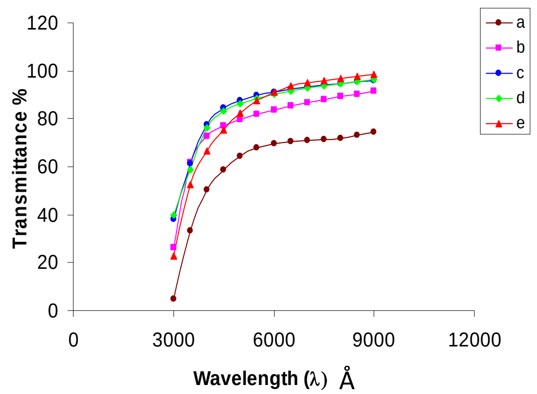

Fig. 2. The variation of transmittance of In_2O_3 films with substrate temperatures: (a) 350°C (b) 400°C (b) 450°C (d) 500°C (e) 550°C.

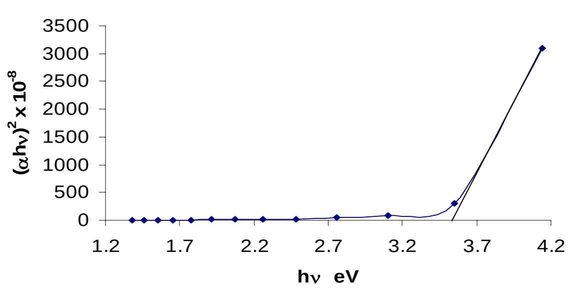

Fig. 3. Band gap energy determination of In_2O_3 film at 350°C.

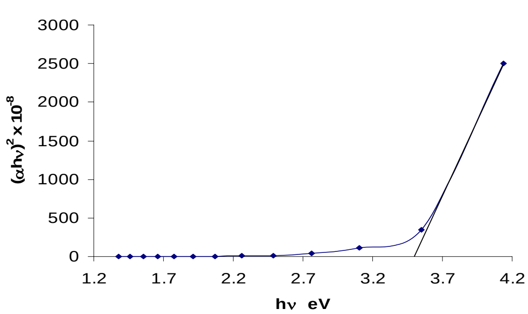

Fig. 4. Band gap energy determination of In_2O_3 film at 550°C.

Table. 3. Optical parameters of indium oxide thin films.

S. No	Substrate temperature (°C)	Thickness in A°	Transmission at 7000 A°
1	350	2240	71.730
2	400	1900	89.152
3	450	1670	94.628
4	500	1500	94.703
5	550	1230	96.892

As the substrate temperature increases, the percentage of transmittance increases. Absorption is minimum at low energy and increases with optical energy. Extinction coefficient is in the order of 10^{-2} [4]. Band gap energy is not significant varying from 3.53 to 3.51 eV [5]. This high value of band gap confirms the surface smoothness and uniformity of the In_2O_3 films prepared under the optimized spray pyrolysis conditions in the present work.

5. Conclusions

Indium oxide films have been successfully prepared using the spray pyrolysis technique. The influence of various process parameters on the film properties has been carried out and the spray pyrolysis parameters have been optimized to give good quality films. The texture of the film changing from < 222 > to < 400 >as substrate temperature and thickness of the film increases. The values of percentage transmission at 700 nm, band gap are found to increase when the substrate temperature is increased from 350ºC to 450ºC and then decreased. This may be reduced the influence of grain boundary scattering to a greater extent.

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*Corresponding author: pk_ponn@yahoo.co.in