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Spray pyrolysis growth and material properties of In_2O_3 films

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Abstract

Indium oxide (In_2O_3) thin films have been prepared by spray pyrolysis using a very low concentration of indium precursor. The spray process parameters like the concentration of precursor in spray solution, ethanol + water, air-flow rate, substrate–nozzle distance and substrate temperature have been optimized for obtaining optically transparent, conducting and device-quality In_2O_3 films. The material properties are reported by studying the structural, electrical and optical properties of the In_2O_3 films prepared at a relatively lower temperature of 380°C. The surface morphology has been studied by scanning electron microscopy and atomic force microscopy. A possible film growth mechanism has been proposed for preparing device-quality In_2O_3 films using lower substrate temperatures. © 2002 Published by Elsevier Science B.V.

Keywords: A1. Characterization; A3. Polycrystalline deposition; B2. Semiconducting materials; B3. Solar cells

1. Introduction

Indium oxide (In_2O_3) thin film is a technologically important transparent conducting oxide (TCO) material. It is used in different fields like: photovoltaic devices, transparent windows in liquid crystal displays, sensors, antireflection coatings [1], and electrochromic devices [2]. Thin films of In_2O_3 can be prepared by a variety of techniques such as chemical vapour deposition [3], spray pyrolysis [4], evaporation of indium

followed by oxidation [5], vacuum evaporation [6], and magnetron sputtering [7]. Among these techniques, spray pyrolysis provides an easy route to fabricate thin films at low cost. It can be easily modified for mass production and device-quality oxide films can be obtained over a large area.

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.

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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 and possible growth mechanisms have been proposed.

2. Experimental procedure

Initially, two process parameters, namely the amount of hydrochloric acid in the spray solution and the solution flow rate, have been kept constant at 2 ml in 100 ml of ethanol+water mixture and 2.5 ml/min, respectively. With reference to these values, the other process parameters such as concentration of InCl_3 precursor in the solution, the volume of ethanol+water mixture taken as the spray solution, air-flow rate, substrate–nozzle distance (SND) and substrate temperature have been varied. Ethanol has been chosen [8,9] for the reasons that it is pollution-free, highly volatile and above all less expensive.

Detailed structural characterization was carried out with JEOL 803a X-ray diffractometer. Hall effect, four-probe and hot-probe measurements were carried out to study the electrical properties. Optical transmittance characteristics of the films were studied using a Hitachi 3400 UV–VIS–NIR spectrophotometer. The study of surface morphology was carried out by using a JSM 6400 JEOL scanning electron microscope and the AFM analysis was done using the Nanoscope[®] E scanning probe microscope 3138J.

3. Results and discussion

3.1. Effect of indium chloride concentration in the solution

Fig. 1 shows the XRD patterns of indium oxide films prepared at a substrate temperature of 380°C with different indium chloride concentrations ranging from 0.5 to 5.0 g in 100 ml of solution.

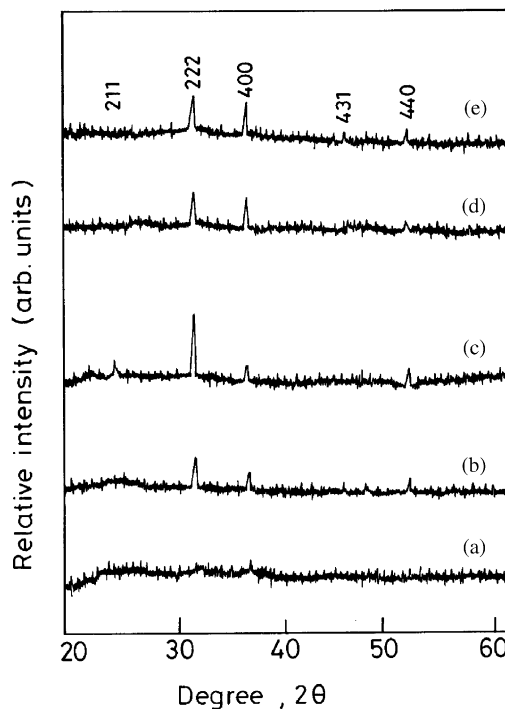


Fig. 1. X-ray diffractograms of sprayed films with different InCl_3 concentrations: (a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0 and (e) 5.0 g.

The films prepared with a low concentration of 0.5 g InCl_3 were very thin with lot of irregularities on the surface and showed mostly amorphous nature. Two peaks with less intensity corresponding to (400) and (222) planes are observed. The other films show polycrystalline nature with preferred growth along the (222) direction together with other peaks having (400), (211), (431) and (440) orientations. The films deposited with 2 g concentration show only the (222) peak with highest intensity. Above this concentration, the peak intensity along (222) is reduced and that of (400) is slightly increased. Further, the films show high resistivity values, which may be attributed to the above-mentioned structural disorder/reorientation and the observed amorphous nature.

The growth rate (GR) as a function of InCl_3 concentration has been studied. A linear increase in GR is observed upto a concentration of 2 g InCl_3 in solution. This type of linear GR reveals

the fact that the reaction in the present case involved is only between two species, i.e., indium-containing solution and oxygen. The film growth is assisted by a continuous adsorption of the solution on the substrate followed by the reaction between the indium-containing species and the adsorbed solvent molecules. At higher concentrations, the growth rate slows down and shows only an exponential increase. This may be due to the presence of so high an amount of indium at high solution concentrations that the available quantity of oxygen from solvent molecules is insufficient for oxide formation and to increase the GR further. It implies that the concentration of reactants on the surface of the substrate is the main factor, which reaches a saturation point after a linear growth under the chosen experimental condition. It limits the formation of the In_2O_3 layer leading to a non-linear GR at higher concentrations. The observed linear GR is limited to ≈ 600 nm/min and hence all the prepared films have thickness below this limit.

3.2. Dependence of ethanol + water mixture ratio

Spray precursor solutions were prepared using five different ethanol + water mixtures with ratios of 90:10, 80:20, 70:30, 60:40 and 50:50. InCl_3 concentration of 2 g and HCl volume of 2.0 ml were kept constant. Films were prepared at substrate temperatures ranging from 300°C to 500°C in steps of 40°C .

The films prepared with 50:50 and 60:40 ethanol + water mixture showed milky white heaps smeared over the surface. Also, the transparency and film uniformity were very poor with a lot of discontinuities and showed only amorphous structure with a high resistivity value of $> 10 \Omega\text{cm}$. The films produced with 70:30 and 80:20 ratios had very few white patches thereby showing improved transmittance and surface quality. However, only amorphous films were obtained at substrate temperatures of 300°C and 340°C , while polycrystalline In_2O_3 films were formed at 380°C and above. The resistivity values were in the range of $2\text{--}5 \Omega\text{cm}$. When the 90:10 solution was used, a uniform and well-crystallized In_2O_3 film of cubic structure with reasonably good transparency was obtained. The resistivity value was $\approx 10^{-1} \Omega\text{cm}$.

The values of percentage transmission measured at 500 nm were 72%, 55%, 49%, 31% and 28% for the films prepared using ethanol + water ratios of 90:10, 80:20, 70:30, 60:40 and 50:50, respectively.

3.3. Optimization of air-flow rate

The XRD spectra of the In_2O_3 films prepared at a substrate temperature of 380°C are shown in Fig. 2. XRD of the films prepared using 5 lpm show the sign of transformation from amorphous to crystalline nature (Fig. 2a). A somewhat improved crystallinity has been observed for the films prepared using 10 lpm flow rate (Fig. 2b). The films grown with 15 lpm show a well-crystallized phase with uniform surface as evident from the sharp peaks seen in Fig. 2c and visual observation. A possible explanation for the reactions associated with different air-flow rates can be given on the basis of the theory proposed by Siefert [10] for the preparation of oxide films by Corona spray

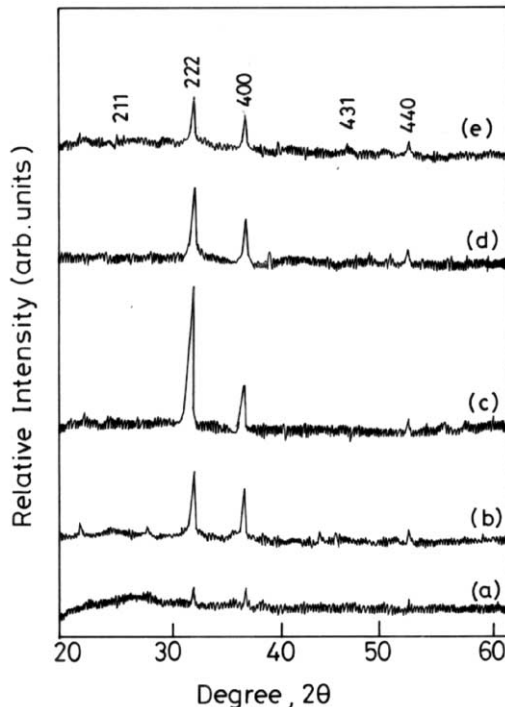


Fig. 2. X-ray diffractograms of sprayed films with different air-flow rates: (a) 5 (b) 10 (c) 15 (d) 20 and (e) 25 lpm.

pyrolysis technique. The spray process associated with 15 lpm is analogous to the chemical vapour deposition (CVD) process, which can produce films with optimum physico-chemical and optoelectronic properties at relatively lower temperatures. When the air-flow rate is very high, i.e., 20 and 25 lpm, very small droplets are formed which produce powdery particles and clusters on the substrate. Though the films show polycrystalline nature as evident from Fig. 2d and e, these type of unwanted reactions lead to the formation of irregular films with reduced transmission properties.

3.4. Influence of SND

The SND was varied between 20 and 40 cm keeping other parameters constant and the substrate temperature fixed at 380°C. Fig. 3 shows the variation of resistivity (ρ), carrier density (n) and mobility (μ) values with different SND values. It is observed from the figure that the values of μ and n reach a maximum for the SND of 25 cm and then decrease. The resistivity value shows a minimum at 25 cm. Fig. 4 shows the variation of thickness (t), optical transmittance ($T\%$) at 500 nm and refractive index ' n_f ' for the In_2O_3 films prepared at various substrate to nozzle distances. It is interesting to note that the thickness, transmittance and refractive index values are maximum for the films prepared at the SND of 25 cm which is in coincidence with the optimum electrical properties seen in Fig. 3 for the same SND. The possible explanation is that the thermal energy gained by a droplet is sufficient enough to effect complete vaporization of the solvent, i.e., the heterogeneous reaction takes place just at the substrate surface.

The observed deteriorated properties of the films prepared at distances above and below SND=25 cm may be explained based on the nature of the reaction and the oxidation process at the substrate [11,12]. When SND=20 cm, the optical and electrical values are lower than the optimum values. At a shorter distance, heat absorbed by the solvent molecules in the droplet is not enough to vaporize them completely. Since the droplet has some residual solvent, it gets coated over the substrate as a very thin layer, which reduces the substrate temperature drastically. It

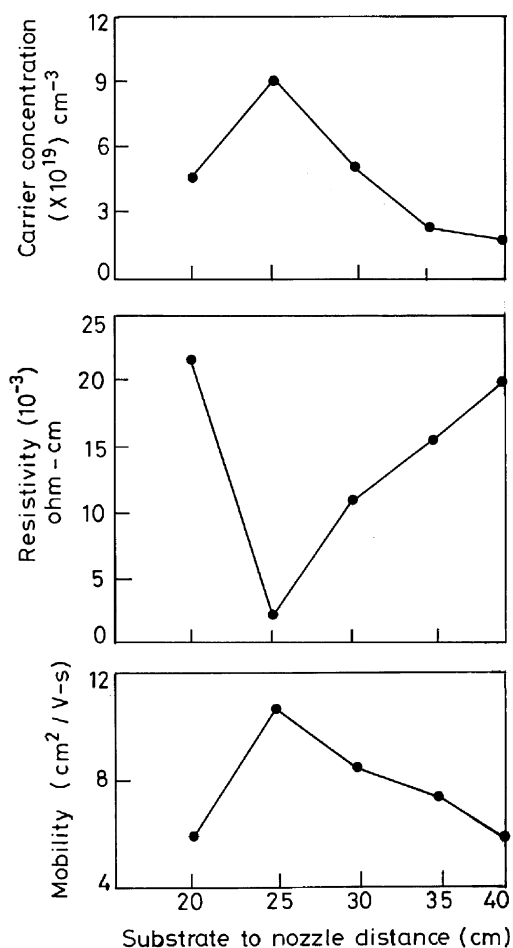


Fig. 3. Variation of carrier concentration (n), resistivity (ρ) and carrier mobility (μ) of In_2O_3 films with different SND.

leads to a homogeneous reaction resulting in very thin In_2O_3 films with white foggy nature.

When the SND is > 25 cm, the accumulation of thermal energy by each droplet is so high that it evaporates most of the solvent molecules well above the substrate surface. The droplet disintegrates into smaller particles near the substrate leading to homogeneous reaction and powdery formation. This kind of reaction leads to the deposition of a very thin film first, over which powder coating is observed which can be wiped off. This limits the In_2O_3 film growth, giving rise to a very thin film of high resistivity with powdery nature.

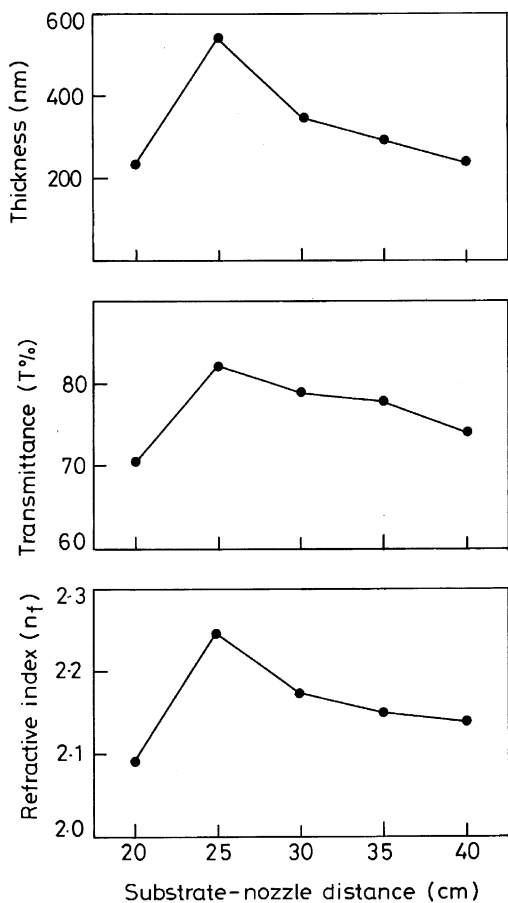


Fig. 4. Variation of thickness (t), % transmittance (% T) and refractive index (n_f) with SND.

3.5. Influence of substrate temperature

The composition and crystalline properties of the In_2O_3 films at substrate temperatures varying from 300°C to 500°C were studied using the X-ray diffraction analysis. Body-centred cubic (BCC) structure with the (222) predominant plane of crystallization has been identified for all the films deposited at substrate temperatures at and above 340°C as shown in Fig. 5. The film deposited at 300°C shows an amorphous nature which is evident from the broad feature observed in the region $2\theta = 15\text{--}30^\circ$ along with the (222) and (400) peaks of very low intensity just appearing. The film prepared at 380°C shows well-developed peaks corresponding to (222), (400), (440) and

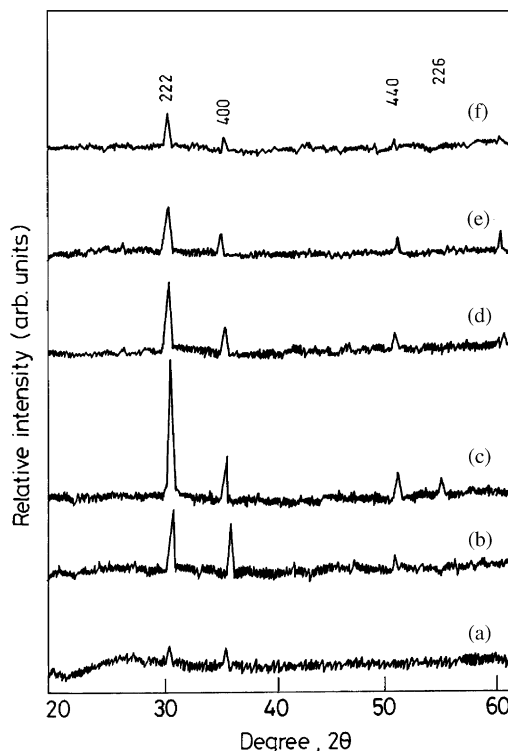


Fig. 5. XRD patterns of In_2O_3 films deposited at different substrate temperatures: (a) 300°C (b) 340°C (c) 380°C (d) 420°C (e) 460°C and (f) 500°C.

(622) planes. When the temperature is increased above 420°C up to 500°C, the intensities decrease for all the peaks. Kosltin et al. [13] report a change in preferred orientation between (400) and (222) in In_2O_3 films prepared using InCl_3 as the starting material in spray pyrolysis technique. But in the present study, the films are found to be (222) oriented and the resistivity value is very low of $\approx 1.5 \times 10^{-3} \Omega \text{cm}$ at 380°C. This may be attributed to the presence of interstitial indium and the close packing of indium and oxygen ions for the (222) orientation as reported by Nagatoma et al. [14]. It is interesting to note that no other peaks corresponding to face-centered cubic (FCC) or hexagonal structure are observed.

The dependence of the In_2O_3 film growth mechanism on substrate temperature can be explained on the basis of the reactions associated with the low-temperature chemical vapour

deposition (LTCVD) process [15,16]. Four possible film growth mechanisms, as a function of substrate temperature, explain the growth of In_2O_3 films with different properties in the present work. In the first case, the sprayed droplets impinge on the substrate kept at a low temperature of 300°C , which is not sufficient to initiate reaction in the droplet. Films with foggy nature are formed. In the second stage, 340°C is enough to make precipitates in the droplets and the solvent is evaporated just prior to touching the heated substrate, which initiates the decomposition of the oxide.

At the substrate temperature 380°C (third stage), a sustained thermal reaction is taking place in which the film formation mechanism is associated with the volatilization of the precipitated indium salt and diffusion of the resulting vapour to the heated substrate, followed by its decomposition to the In_2O_3 film. No residues or powdery formation is observed. This type of film growth is similar to the mechanism associated with LTCVD by which uniform films are deposited. The fourth stage process is associated with substrate temperatures $> 420^\circ\text{C}$. It leads to a homogeneous nucleation of the vapour phase forming oxide particles and clusters of particles on the substrate giving rise to films with non-uniform surface.

3.6. Structural properties of In_2O_3 films

The XRD data are given in Table 1 for the In_2O_3 films deposited at substrate temperatures

340°C , 380°C , 420°C , 460°C and 500°C . The calculated value of cubic lattice constant $a = 10.11 \text{ \AA}$ is in good agreement with the value of $a = 10.12 \text{ \AA}$ reported in the literature [17].

The grain size calculations are made using the Scherrer–Bragg equation

$$l = \frac{0.9\lambda}{B \cos \theta} \text{ nm}, \quad (1)$$

where B is the full-width at half-maximum (FWHM) of the diffraction peak, λ is the X-ray wavelength (nm) and ‘ θ ’ is the diffracting angle. The grain size is found to be increasing from 19.0 to 21.6 nm with increasing substrate temperatures. The very small grain size values are attributed to the broader XRD peaks observed in Fig. 5.

3.7. Electrical properties of In_2O_3 films

The electrical properties are studied for these films prepared at different substrate temperatures and are shown in Fig. 6. The hot probe and the Hall effect measurements have confirmed n-type semiconducting nature for all the In_2O_3 films. A high carrier concentration of $1.5 \times 10^{20} \text{ cm}^{-3}$ with a low resistivity of $1.28 \times 10^{-3} \Omega \text{ cm}$ has been observed for the indium oxide films prepared after optimizing all the deposition conditions as explained in the previous sections. It shows that these films are highly degenerate. This is in accordance with the observation for indium oxide single crystals in which the onset of degeneracy

Table 1
XRD data of In_2O_3 films spray deposited at different substrate temperatures

hkl	Standard relative intensity	d -value (nm)	Observed d -values at ($^\circ\text{C}$) (relative intensities in parenthesis)				
			340	380	420	460	500
211	13	4.130	—	—	4.149(17)	4.187(12)	—
222	100	2.921	2.938(100)	2.938(100)	2.928(100)	2.947(81)	2.936(100)
400	33	2.529	2.540(82)	2.540(72)	2.534(63)	2.547(55)	2.545(45)
411	8	2.385	—	—	—	—	—
332	6	2.157	—	—	—	—	—
431	10	1.984	—	—	—	—	—
440	36	1.788	1.792(40)	1.792(45)	1.792(40)	1.792(35)	—
611	6	1.641	—	—	—	—	—
541	4	1.561	—	—	—	—	—
622	24	1.525	1.529(34)	1.529(40)	1.529(30)	1.529(30)	—

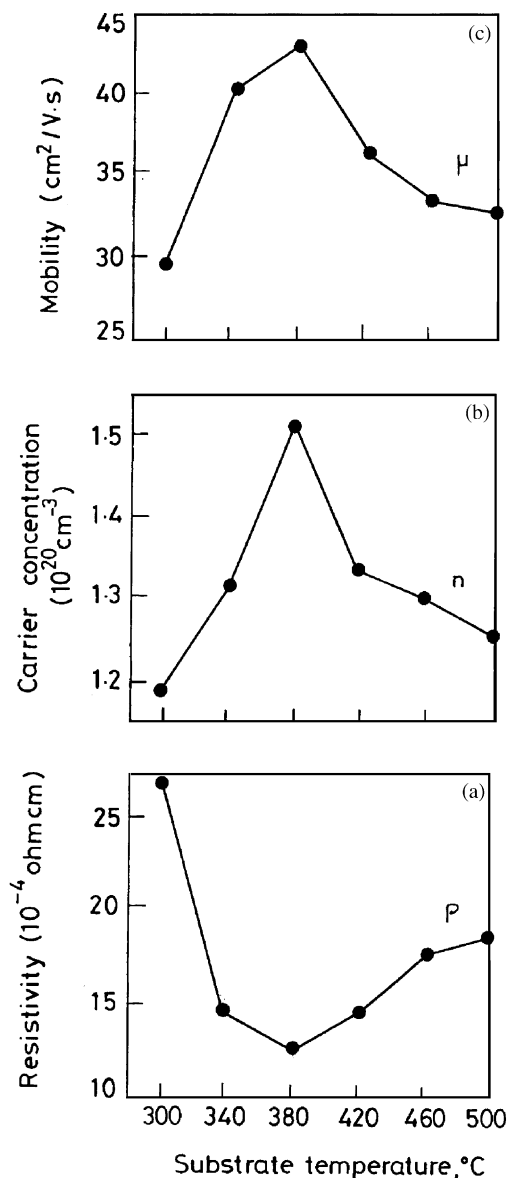


Fig. 6. Variation of: (a) resistivity (ρ) (b) carrier concentration (n) and (c) mobility (μ) of In_2O_3 films with different substrate temperatures.

starts even at a carrier density value of $1.48 \times 10^{18} \text{ cm}^{-3}$ [18].

From Fig. 6a, it is observed that the resistivity value of the In_2O_3 films goes on decreasing up to 380°C and, after reaching a minimum, then increases when the substrate temperature is

increased further whereas, the carrier concentration (n) increases, as seen in Fig. 6b, with increasing substrate temperature up to 380°C and then shows a decreasing trend up to 500°C . This can be related to the observed improvement in crystallinity of the In_2O_3 films which become fully crystallized at 380°C without any residual amorphous content. Beyond 380°C , the film crystallinity is reduced.

The carrier mobility value is found increasing up to a maximum value of about $42.6 \text{ cm}^2/\text{V.s}$ and then decreasing as seen in Fig. 6c. The overall observed mobility values are higher compared to the value of $7.81 \text{ cm}^2/\text{V.s}$ for the In_2O_3 films prepared by the reactive thermal deposition technique [19]. It is comparable to the value of $30 \text{ cm}^2/\text{V.s}$ reported for DC-sputtered ITO [20]. This may be attributed to the fact that the In_2O_3 films prepared in the present work are preferentially oriented along the (222) direction, where the number of carrier scattering centers are minimum and are of device-quality nature [9].

The mean free path of the free carriers for these films was calculated using Eq. (4) [21]

$$l = \frac{h}{2e} \left[\frac{3n}{\pi} \right]^{1/3} \mu_{\text{H}}, \quad (2)$$

where n is the carrier concentration and μ_{H} is the Hall mobility. The values are in the range of 8.5–10.2 nm, which are very low compared to the grain size values of ≈ 19.0 – 21.6 nm observed by XRD studies. It predicts that the carrier-scattering mechanism due to grain boundaries is greatly reduced for the In_2O_3 films prepared in the present study thereby increasing the conductivity of the films. Though the grain size is found to be increasing from 19 to 21.6 nm when the temperature is increased from 340°C to 500°C , the variation is not a significant one for the In_2O_3 films prepared in the present work. Because of this fact, the observed carrier concentration value is also nearly constant and varies between 1.2×10^{20} and $1.5 \times 10^{20} \text{ cm}^{-3}$ only. Further, the resistivity values do not change much and are observed in the range of 1.28 – $2.7 \times 10^{-3} \Omega \text{ cm}$. These results show that electrical properties of the In_2O_3 films are varied by the grain size. It means that when the

preparation conditions are optimal, grain size does not vary much with processing parameters.

3.8. Optical properties of In_2O_3 films

Fig. 7 shows the optical transmittance spectra of the In_2O_3 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 380°C and comparatively lower transmission values are recorded for other films prepared at temperatures below and above the optimum 380°C. The % T values at 500 nm are 68, 79, 88, 67, 66 and 65 for the substrate temperatures 300°C, 340°C, 380°C, 420°C, 460°C and 500°C, respectively (Table 2). The increase in % T is attributed to the well adherent and crystallized nature of the film throughout the coated area, which is obtained due to uniform oxidation and improvement in lattice arrangement. The reduced % T behavior at higher temperatures may be due to impaired crystallinity of the films as evident from the XRD results (Fig. 5), which showed peaks with reduced intensity.

The optical band gap of polycrystalline In_2O_3 films was calculated from the optical absorption and transmission studies. The optical absorption α is related to the band gap of a semiconductor film, which satisfies the equation

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2}, \quad (3)$$

where A is a constant, E_g is the optical band gap and $h\nu$ is the incident photon energy. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ showing straight line fits indicate that the In_2O_3 films prepared in the present work are direct band gap semiconductors. The linear intercept at the $h\nu$ -axis gives direct band gap values of 3.60, 3.64, 3.71, 3.70, 3.72 and 3.72 eV for the films prepared at 300°C, 340°C, 380°C, 420°C, 460°C and 500°C, respectively. 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. Further, the In_2O_3 films prepared at 380°C have a band gap value of 3.71 eV with preferred orientation along the (222) plane. This is in agreement with the observation that higher band gap values of the order of 3.75–3.81 eV are associated with (222) orientation for the In_2O_3 films prepared by the reactive thermal evaporation

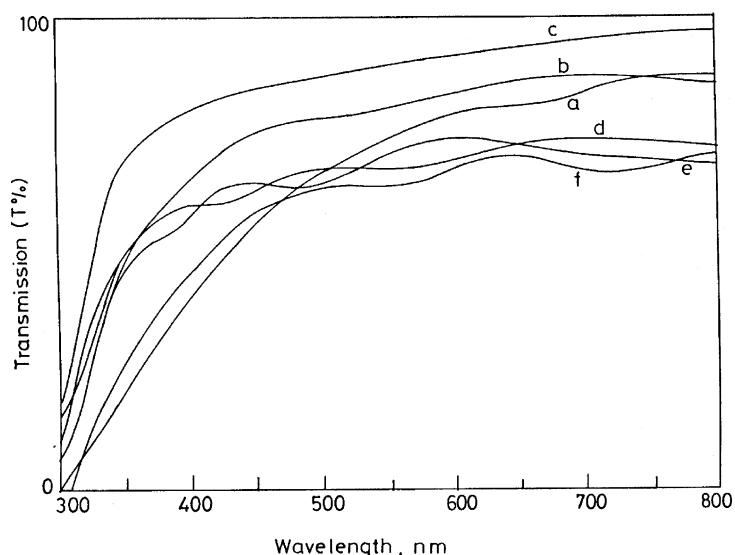


Fig. 7. Optical transmission spectra of In_2O_3 films prepared at different substrate temperatures: (a) 300°C (b) 340°C (c) 380°C (d) 420°C (e) 460°C and (f) 500°C.

Table 2

Optical transmittance and band gap values of In_2O_3 films prepared at different temperatures

Substrate temperature ($^{\circ}\text{C}$)	Transmission at 500 nm (% T)	Band gap (eV)
300	68.4	3.60
340	78.5	3.64
380	87.7	3.71
420	67.0	3.70
460	65.6	3.72
500	65.0	3.72

technique [22]. However, Vasu et al. [23] have reported that the preferred orientation for their spray pyrolyzed In_2O_3 films is along the (400) plane when the films were prepared using a mixture of indium chloride and tin chloride.

The refractive index ' n_f ' values were calculated in the wave length range of 400–800 nm for the In_2O_3 film prepared in the optimum process conditions keeping the substrate temperature constant at 380°C . A continuous decrease in n_f values with increase in wave length was observed. The n_f value at 500 nm is ≈ 2.1 , which is very close to the reported value of 2.0 [24]. Further, the refractive index values are found to be lower for the films prepared at temperatures below and above 380°C .

3.9. Surface morphology of the films

An analysis of the SEM pictures of In_2O_3 films prepared at the substrate temperatures 340°C , 380°C , 420°C and 460°C has been made. It is clearly seen from the pictures that the surface smoothness, uniformity and grain size increase with increase in substrate temperature up to 380°C and then deteriorates. Fig. 8 shows the SEM picture of In_2O_3 film prepared at 380°C . The surface is covered with grains of uniform size and the grain size is found to be the maximum of about $0.1\ \mu\text{m}$. A study of the surface morphology by AFM gives a three dimensional presentation of the grain arrangement. Fig. 9 shows the AFM picture of the In_2O_3 film prepared under the optimized conditions at 380°C . The average grain size calculated using the standard statistical averaging

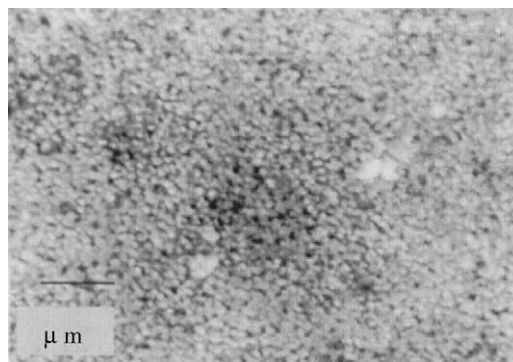


Fig. 8. Scanning electron microscopy (SEM) picture of In_2O_3 film deposited at 380°C .

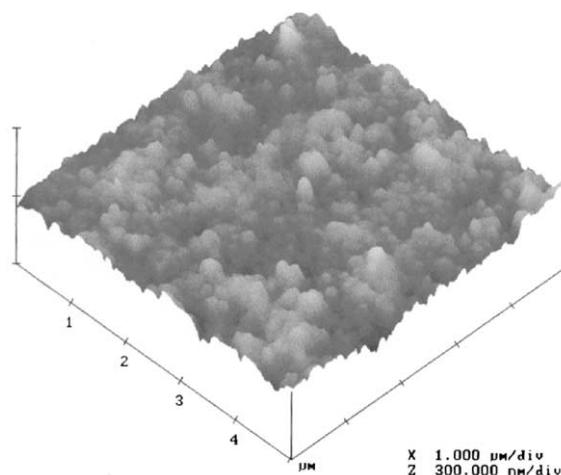


Fig. 9. AFM picture of In_2O_3 film deposited at 380°C .

technique is $\approx 0.15\ \mu\text{m}$, which is in close agreement with SEM observation. A smooth and uniform surface morphology is evident from the AFM picture, which also supports the observations made from the SEM pictures.

4. 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 optimized process

parameter for the preparation of device-quality In_2O_3 films are: concentration of InCl_3 is 2 g/100 ml, ethanol + water mixture is 90:10, air-flow rate is 15 lpm, substrate–nozzle distance is 25 cm and the substrate temperature is 380°C .

The best In_2O_3 film prepared in this set of optimized conditions has a resistivity of $1.28 \times 10^{-3} \Omega\text{cm}$ and a band gap value of 3.71 eV with a transmission of $\approx 88\%$. The XRD results show the cubic structure with (2 2 2) preferred orientation together with a less prominent (4 0 0) plane. At temperatures $> 380^\circ\text{C}$, the peak intensities are found to be decreasing which may be due to the less uniform surfaces (as evident from the SEM and AFM pictures) which might have been caused by the deteriorated crystalline nature of the films.

The values of percentage transmission at 500 nm, band gap, carrier density, and Hall mobility are found to increase when the substrate temperature is increased from 300°C to 380°C and then decreased. The reasonably higher mobility values in the range of $30.0\text{--}42.6 \text{ cm}^2/\text{Vs}$ may be due to the very low mean free path values compared to the grain size value of $\approx 22 \text{ nm}$. This has reduced the influence of grain boundary scattering to a greater extent.

References

- [1] K.L. Chopra, S. Major, D.K. Pandya, *Thin Solid Films* 102 (1983) 1.
- [2] C.G. Granquist, *Sol. Energy Mater. Sol. Cells* 60 (2000) 2301.
- [3] J. Kane, H.P. Schweizer, *Thin Solid Films* 29 (1975) 155.
- [4] J.C. Manificier, L. Szepessy, J.F. Bresse, M. Peroten, R. Stuck, *Mater. Res. Bull.* 14 (1979) 109.
- [5] S. Naguchi, H. Sakai, *J. Phys. D.* 13 (1980) 1129.
- [6] K.R. Murali, V. Sambasivam, M. Jayachandran, M.J. Chockalingam, N. Rangarajan, V.K. Venkatesan, *Surf. Coat. Technol.* 35 (1988) 297.
- [7] W.G. Haines, R.H. Bube, *J. Appl. Phys.* 49 (1978) 304.
- [8] O.P. Agnihotri, M.T. Mohammed, A.K. Abbas, K.I. Arshak, *Solid State Commun.* 47 (1983) 195.
- [9] M.G. Takawale Chitra Agashe, V.G. Bhide, *J. Appl. Phys.* 70 (1991) 7382.
- [10] W. Siefert, *Thin Solid Films* 120 (1984) 275.
- [11] W.A. Byrant, *J. Mater. Sci.* 12 (1977) 1285.
- [12] W. Siefert, *Thin Solid Films* 120 (1984) 267.
- [13] H. Kostlin, R. Jost, W. Lems, *Phys. Stat. Sol. A* 29 (1975) 87.
- [14] T. Nagatoma, Y. Maruta, O. Omoto, *Thin Solid Films* 192 (1990) 17.
- [15] W. Desisto, M. Sosnowski, F. Smith, J. Deluca, R. Kershan, K. Dwight, A. World, *Mater. Res. Bull.* 24 (1989) 753.
- [16] J.C. Viquie, J. Spitz, *J. Electrochem. Soc.* 122 (1975) 585.
- [17] Ph. Parent, H. Dexpert, G. Tourillon, J.M. Grimal, *J. Electrochem. Soc.* 139 (1992) 276.
- [18] R.L. Weiher, R.P. Lay, *J. Appl. Phys.* 33 (1962) 2834.
- [19] P. Thilakan, J. Kumar, *Thin Solid Films* 292 (1997) 50.
- [20] J. Touskova, J. Kovanda, L. Dobiasova, V. Parizek, P. Kielar, *Sol. Energy Mater. Sol. Cells* 37 (1995) 357.
- [21] G. Sanan, R. Rup, A. Mansingh, *Thin Solid Films* 190 (1990) 287.
- [22] P. Thilakan, J. Kumar, *Vacuum* 48 (1997) 463.
- [23] V. Vasu, A. Subrahmanyam, *Thin Solid Films* 193/194 (1994) 696.
- [24] W.W. Mobzen, *J. Vac. Sci. Technol.* 12 (1975) 99.