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Influence of In/Sn ratio on nanocrystalline indium tin oxide thin films by spray pyrolysis method

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ABSTRACT

Nanocrystalline Indium Tin Oxide thin films were prepared by spin cum spray pyrolysis technique with varying wt % of indium and tin. The polycrystalline nature of the films observed from XRD pattern with cubic structure. The various structural parameters were calculated and reported in this paper. Increasing the indium wt % helps to improve the structural optical and electrical properties of the films. The absorption edge towards blue wavelength indicates the presence of nano particles. The films prepared with high indium wt % have the good optical band gap of 3.7 eV. The electrical conductivity of the films increases with increasing the indium wt % on the formation of ITO thin films.

Keywords: ITO thin films, Spray pyrolysis, XRD, UV.

INTRODUCTION

In view of the technological importance, a great deal of basic research and development has been carried out on the electrical and optical properties of indium oxide based materials. Rupprecht [3] carried out one of the first investigations on the indium oxide (In_2O_3). Since then different techniques have been used for the preparation of these oxide films [4-6]. The conductivity of these films can be increased by introducing various type of dopants such as tin, cadmium, antimony and fluorine. Considerable attention has been given to the study of tin doped indium oxide (ITO) films, because of their enhanced electrical and optical quality, compared to other transparent conductors. ITO is an In_2O_3 based material that has been doped with Sn to improve the electrical conductivity. Here tin acts as a cationic dopant in the In_2O_3 lattice and substitute on the indium sites to bind with the interstitial oxygen. The ITO films, with a band gap greater than 3 eV is highly transmitting in the visible region and hence is preferred in most of the applications. In the present paper we report on the doping ratio dependence of structural and optical properties of ITO films, prepared by economical spin cum spray pyrolysis technique

MATERIALS AND METHODS

The Indium Tin Oxide (ITO) thin films were prepared on to the glass substrates (2.5 x 6.5 cm) which are chemically and ultrasonically cleaned. Indium (III) chloride and tin (II) chloride is taken as a precursor. Indium (III) chloride and Tin (II) chloride of calculated amount was dissolved in 10 ml isopropyl alcohol with various indium and tin wt ratio say 80:20, 20:80,60:40, 40:60 and 50:50 for 0.5 M concentration. The mixed solution was stirred at room temperature for 45 minutes using magnetic stirrer.

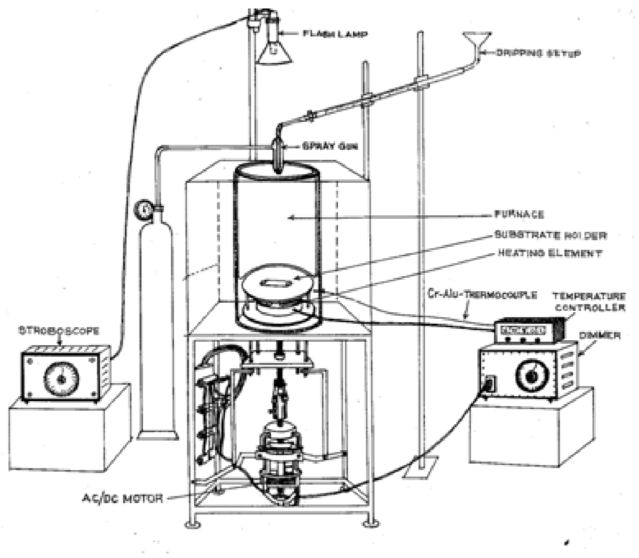

Fig. 1. Schematic Diagram of Spin cum spray Coating system

The experimental setup consists of stainless steel substrate holder attached to a universal motor. A 2Kw heater coil is used to heat the substrate holder and the set up is isolated from the surrounding with a chamber made up of heat insulator fiberglass. This is again surrounded by glass wool insulation. The spinning rate of the substrate is monitored by a stroboscope arrangement, which enables to optimize the system for uniform thickness and repeatability and the thickness of the films .The solution has been taken in the burette at the level of 10 ml height, by which the solution drip rate is maintained. The cleaned glass substrate has been kept on the stainless steel base of the furnace and the furnace is switched ON to obtain the equilibrium set temperature. After reaching the steady set-temperature in the controller, the substrate has been given rotation by motor arrangement. The stroboscope flash lamp is used to set the RPM of the substrate as shown in fig [1]. After reaching a steady set-RPM, the stopper in the burette tube is opened for dripping the solution onto the substrate.

Spin deposition has been carried out on glass substrates at 400°C substrate temperature for achieving oxidation. Uniform spreading of the alcoholic metal solution is achieved by spinning the substrate. After sprayed, the coated substrate was allowed to naturally cool down to room temperature before being taken out from the substrate holder. The characterization of such as structural, optical and electrical on as deposited films carried out using X-ray Diffractometer (Shimadzu XRD-6000) , UV-Vis (Jasco-570 UV/VIS/ NIR) spectrometer and Vander-paw apparatus respectively and reported in this paper.

RESULT AND DISCUSSION

Structural Studies on Indium Tin Oxide films

The X-ray diffractogram of as prepared Indium Tin Oxide with various ratios (at wt %) are shown in figure 2. All the films have polycrystalline in nature with cubic structure evident from X-ray diffraction. Several peaks are observed in the pattern at 2θ=30, 35, 51 and 60 assigned to the (2 2 2), (4 0 0), (4 4 0) and (6 2 2) crystals plane respectively for the ITO films.

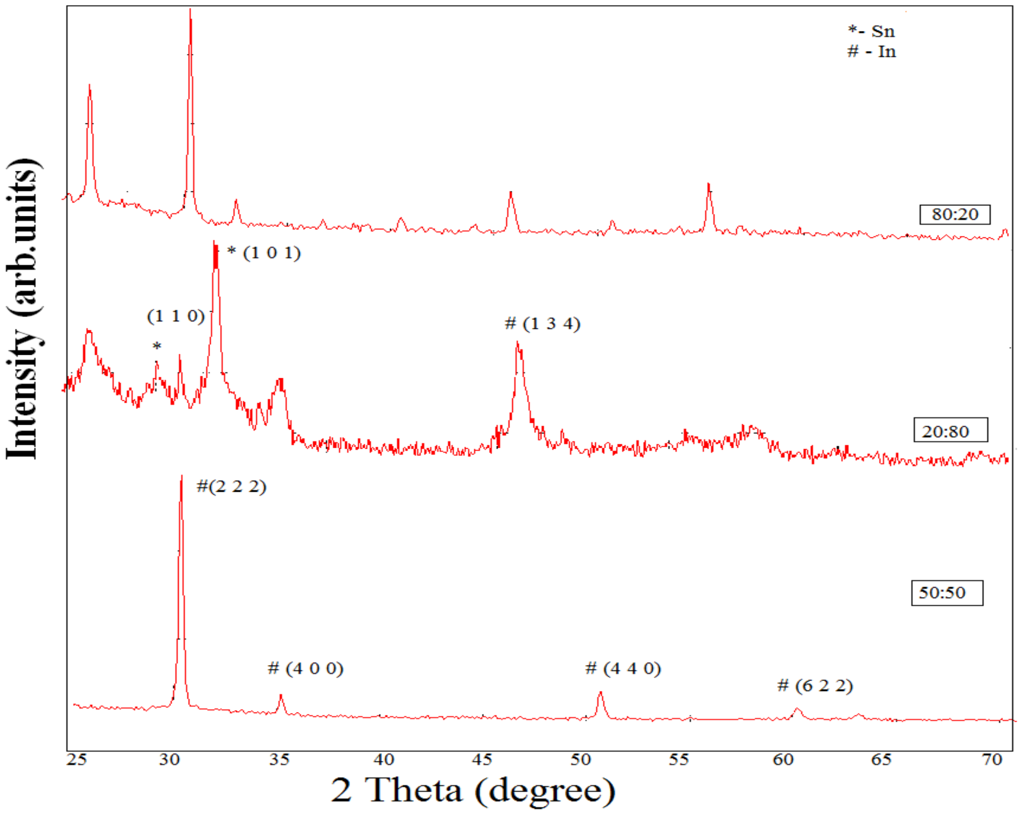

Fig.2. XRD pattern of ITO with various wt % ratios (In: Sn)

Table.2. Structural parameters of Spray coated ITO films for [2 2 2] plane

Ratio (In:Sn)	d (A°)	2θ (θ)	FWHM (β)	D (A°)	a (A°)	$\rho\ (10^{15})$ lines/m^2	$\varepsilon\ (10^{-3})$
80:20	2.73908	30.4093	0.29680	277	0.79	4.7	0.70
20:80	2.95695	30.2000	0.90000	91	0.85	4.0	0.21

The films were prepared with various ratio (In: Sn) say 80:20, 20:80 and 50:50 at 400° C as substrate temperature shown in fig.2. The intensity and the structural properties improve when the Indium wt % is equal with Sn (50:50) or more (80:20) is clearly observed from the XRD pattern. When the wt % of the Indium is less (20:80) than Sn, some of the tin oxide peaks observed and indicated in star symbol. The lattice parameter (a) are calculated in this case by means of the plane-spacing equation for cubic crystal, which is give by,

$$a = d/\sqrt{(h^2 + k^2 + l^2)} \qquad (1)$$

Where'd' is the interplanar distance and (h k l) are the Miller indices. The average crystalline size is calculated by using the Scherer's formula given by,

$$D = \frac{K\ \lambda}{\beta\ cos\theta} \qquad (2)$$

Where, k is taken as 0.9, λ is wavelength of X-Ray used, β is the full width half maximum (FWHM) of the prominent peaks and θ is the glancing angle. The origin of the strain is also related to the lattice misfit, which in turn depend upon the deposition conditions. The micro strain (ε) developed in the ITO films is calculated using the formula,

$$\varepsilon = \frac{\beta\ cos\theta}{4} \qquad (3)$$

The dislocation density is estimated from Williamson and Smallmax method using the relation (De and Mishra 1997),

$$\rho = \frac{15\ \varepsilon}{a\ D} \qquad (4)$$

Where ε is the micro strain and 'a' and 'D' are the lattice constant and crystalline size respectively. The calculated value such as lattice constant (a), crystalline size (D), micro strain (ε) and dislocation density (ρ) are tabulated in table 2 for (2 2 2) plane. From the table it is observed that the wt % of Indium plays an important role on the formation of ITO films. The wt % of indium is equal or more than tin wt % have the crystalline size of 27 nm where as the film prepared with 20 % as indium shows 12 nm as particle size in which some tin oxide peaks were observed evident (* symbol) from X-ray diffractogram.

Optical studies on ITO films

The analysis of optical absorption Spectra is one of the most productive tools for understanding and developing the band structure and energy band gap, E_g. The absorption and optical band gap (E_g) of as grown ITO films are shown in figure (3 and 4). The absorption shift towards blue region clearly indicates the presence of Nanocrystals on the ITO films. The films prepared at 60:40 wt % have the highest absorption percentage (5%) than other cases are evident from fig.3. The high transparent nature of the films (90 %) obtained at 80:20 and 50:50 wt % ratio and other films also have well transparency.

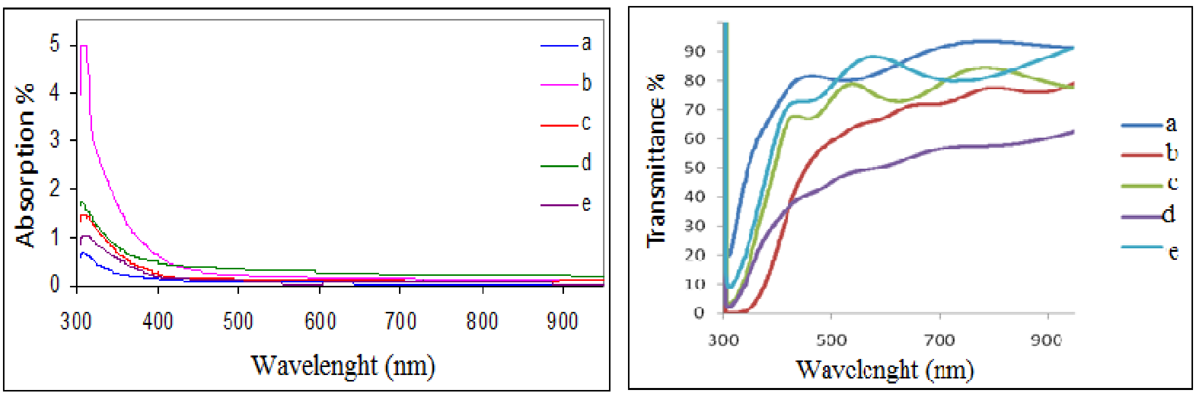

Fig.3. Absorption and transmittance spectra of ITO films with various wt % of In: Sn: 80:20 (a), 60:40 (b), 40:60 (c), 20:80 (d) and 50:50 (e)

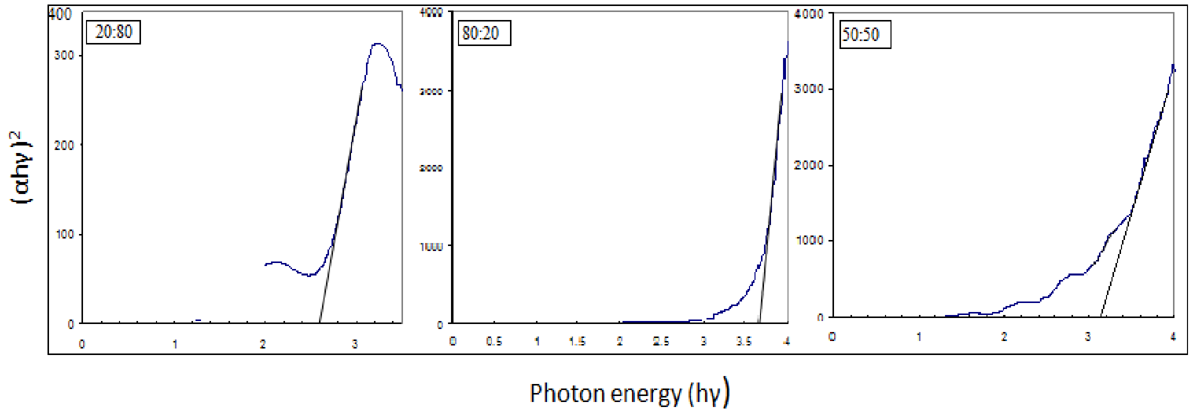

Fig.4. Optical band gap of ITO films with the ratio of In: Sn

To find the suitability of the device formation with silicon substrate was studied by calculating its band gap of ITO at various ratios. The band gap value could be obtained from the optical absorption spectra by using Tauc's relation,

$$\alpha = \frac{A}{h\vartheta}(h\vartheta - E_g)^n \qquad (5)$$

Where α is the absorption coefficient, $(h\vartheta)$ is the photon energy and A is a constant. The direct band gap of the semiconductor obtained from the relation,

$$\alpha h\vartheta = A(h\vartheta - E_g)^{1/2} \qquad (6)$$

Fig.3. shows the variation of $(\alpha h\vartheta)^2$ versus $(h\vartheta)$ for the ITO films. The straight nature line nature of the films over the wide range of photon energy indicates the direct type of transitions. The optical band gap has then been determined by extrapolation of the linear region on the energy axis. The optical band gap of 2.6 eV was observed in the 20:80 ration ITO films. When increasing the indium wt %, the band gap increases with 3.2 eV (50:50) and 3.7 eV (80:20) shown in fig.4.

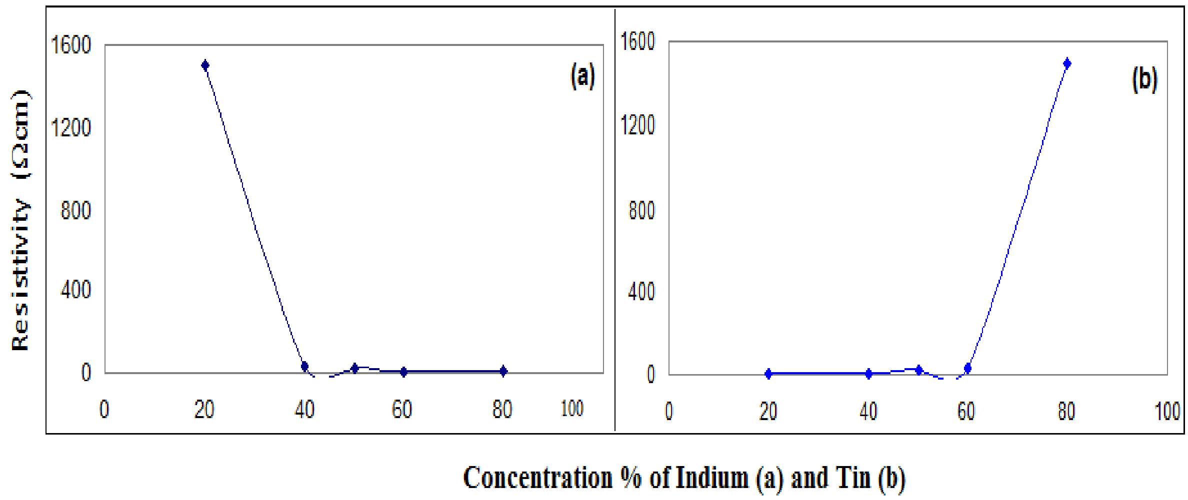

Fig.5. Electrical resistivity variation on ITO films at wt % of In and Sn.

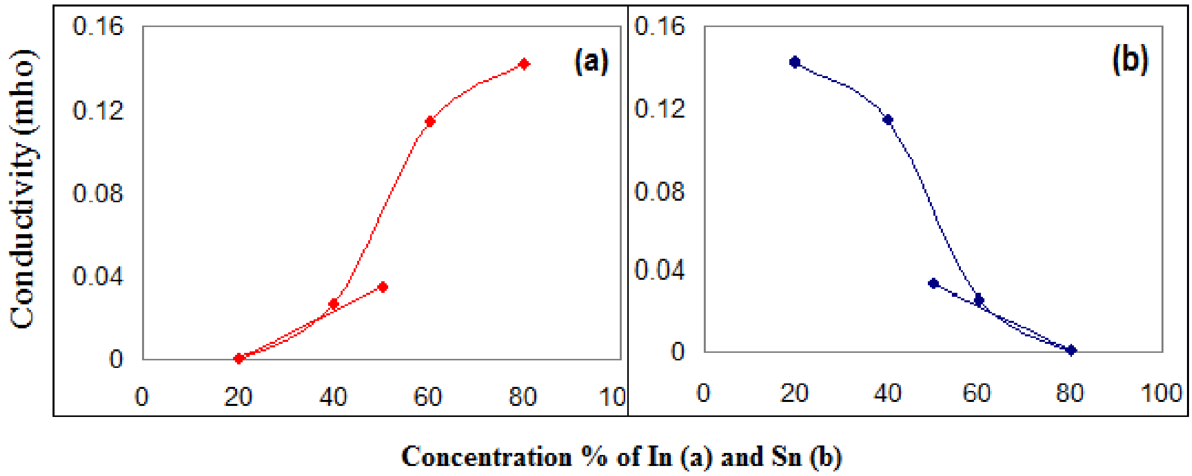

Fig. 6. Electrical conductivity variation of ITO films at wt % of In (a) and Sn (a)

Electrical resistivity studies on ITO films

The electrical resistivity and conductivity studies on as prepared ITO films are shown in figure (5 and 6). It is clearly observed from the graph that the resistivity increase with decreasing indium wt %. Further increasing the wt % of indium the resistivity decreases in ITO films. Increasing the tin wt % on the formation of ITO films shows the high resistivity shown in fig.5 (b). Fig.6 shows the electrical conductivity of the films with various wt % of tin and indium. It is observed that the conductivity increases (fig.6a) with increasing the Indium wt % on ITO nanocrystalline thin films. On the other hand, the conductivity increase with decreasing the concentration of tin wt % showed in fig.6 (b).

CONCLUSION

ITO thin films were prepared by economical spray pyrolysis method with various wt % of indium and tin. The structural properties improves with increasing Indium wt % is evident from XRD pattern. There are some more peaks observed corresponding to (101) and (110) plane when decreasing indium wt % which is due to formation of Tin oxide. The average particle size of 27 nm observed with more indium percentage. The absorption shift toward blue indicates the presence of nano particle on ITO films. Increasing the wt % of indium leads to increase the optical band gap (3.2-3.7 eV) of ITO films. The electrical resistivity analysis shows that the conductivity of the films increases with increasing indium wt % which provides information on future potential applications.

REFERENCES

[1]. M.D. Benoy et al, *Brazilian journal of Physics*, vol. 39, no. 4, **(2009)**
[2]. Yoshitaka Aoki et al, *Journal of Materials Chemistry*, 16, 292–297, **(2006)**
[3]. Rupprecht G Z. Phys. 139 504**(1954)**
[4] Cruz L R O and Santos O J, Materials Letters 12 72**(1991)**
[5] Hongbin Ma et al, Surf. And Coatings Tech. 153 131**(2002)**
[6]. Giovanni Neri et al, *Sensors and Actuators B*, 30, 222-230, **(2008).**
[7]. Gurlo.Aet al, *Sensors and Actuators B*, 44, 327-333 ,**(1997).**
[8]. Jiaqiang Xu et al, *Sensors and Actuators B*, 115, 642-646, **(2006).**
[9]. Jiaxiang Liu et al, *Journal of Material Processing Technology*, 209, 3943-3948 **(2009).**
[10]. Makhija.K.et al, *Bulletin Material Science*, 28, 9-17,**(2005).**
[11]. Mark Nocun and Zuzanna Pajak , *Optical Applications*, 18, 181-187 **(2008).**

[12]. Neri.G et al, *Sensors and Actuators B*, 132, 224-233 **(2008).**
[13]. Steffes.H et al, *Sensors and Actuators B*, 68, 249-253 **(2000).**
[14]. Stoica.T.F et al, *J. of Optoelectronics and Advanced Materials*, 7, 2353-2358 **(2005).**
[15]. Zheng Jiao et al, *Sensors and Actuators B*, 94, 216-221 **(2003).**
[16]. L. Kerkache et al, *Int. Conference on Renewable Energies and Power Quality*,**(2010)**
[17]. Deshpande.S, et al, *Journal of Nanoscience and Nanotechnology*, 7,1-4.**(2007)**
[18]. Dewei Chu, et al, *Sensors and Actuators B*, 137 630-636, **(2009).**