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Micro-strain, Dislocation Density, Surface Morphology and Optoelectronic Properties of Indium Zinc Oxide Thin Films

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Abstract- The article reports the fabrication of Indium Zinc Oxide (IZO) thin films with different doping concentrations prepared by spray pyrolysis technique at a uniform substrate temperature of 400°C on quartz substrates. The materials fall under the category of transparent conducting oxides, hence to implant oxygen deficiency and improve crystallization the films are subjected to vacuum annealing in air ambience of 10^{-5}mbar base pressure and at 400°C for two hours. The structural profile investigated by XRD technique confirms the growth of particles in hexagonal wurtzite structure. Important structural parameter such as size of crystals, dislocations density and microstrain of thin films were calculated using Scherrer's formula and uniform deformation model (UDM) of Williamson-Hall method. SEM analysis indicated dense and uniform surface morphology for the prepared films. The films show excellent electrical property in terms of sheet resistance, moderate carrier mobility and intermediate carrier concentrations.

Keywords—TCOs, Optoelctronics, Thin films, XRD, UDM-Model, UV Vis spectroscopy

1. INTRODUCTION

Transparent conducting oxides (TCOs) are unique class of materials that conjugate transparency and conductivity in same material[1-4]. Because of its unique electrical and optical features TCOs has become an inevitable component of all the optoelectronic devices and hence this has been a thrust area of research for the last two decades[5-7]. Among metal oxides, tin doped indium oxide, ITO, is regarded as the most decisive TCO material that shows very promising electrical conductivity and very high optical transparency[7]. Zinc oxide based TCOs such as Al doped ZnO(AZO), In doped ZnO (IZO), Ga doped ZnO(GZO), Er doped ZnO and Zr doped ZnO has proved as potential candidate with TCO behavior[8-10]. Herein, we report the deposition of Indium Zinc Oxide films by spray pyrolysis technique at different atomic concentrations of indium additives in zinc oxide. Many previous reports established that the electronic properties of zinc oxide can be considerably improved when doped with Indium[11-13].Besides its excellent TCO property, IZO films are crucial materials because of the large work function, comparatively low deposition temperature and very low surface roughness. Hadri et al. reported a low resistance for Indium doped and fluorine doped ZnO samples deposited by same technique[14]. This study mainly comprises with the effect of doping and variation in doping concentrations on the structural profile of Indium zinc oxide films. We have employed XRD analysis for determination of structural characteristics and uniform deformation model for determination of micro-structural profile of prepared films. Besides, the transparent conducting property of the films was also investigated and isreported here.

2. EXPERIMENTAL

Four batches of indium zinc oxide films with 2, 4, 6 and 8at% indium doping were deposited,along with pristine ZnO thin films, on fused silica substrate by automated spray pyrolysis technique at a substrate temperature of 400^0C. Zinc acetate dihydrate and indium acetate are used as starting solutions assources for Znand In cations in IZO. 30ml of 0.2 molar zinc acetate dihydrate solution was made in a mixer of methanol, acetic acid and deionised water and is used as the host solution. Similar solutions of Indium acetate is also made in order to use as dopant. Calculated volumes ofthe indium acetate solutions is added to the parent solution and ultrasonically stirred for two hours anterior to the deposition on pre cleaned quartz plates kept at a temperature of 400^0C using Holmarc HO-TH 04 programmable spray pyrolysis system. Same program in similardeposition conditions are used for the spraying the solutions. The as deposited films were allowed to cool naturally and then the films were subjected to annealing at a temperature 200^0C for one hour for volatile contaminants on the film surface to evaporate. Later the films are annealed in vacuum at a pressure of ~ 10^{-5} mbar at 400^0C for three hours. The structural profiles of films are studied using room temperature XRD technique by RigakuMiniflex diffractometer, between the Bragg angle range of 10–90 degrees. Surface topography of the film surface were investigated with scanning electron microscope, Hitachi SU6600, Variable Pressure Scanning Electron Microscope (SEM) equipped with an energy dispersive X-ray analysis (EDAX) capability. The optical studies were carried out by taking UV-Vis transmittance spectra by a Jasco V-650 spectrometer. The electrical properties such as concentration of charge carrier, carrier mobility and resistivity of the films were measured using EcopiaHMS 3000 Hall measurement system.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis and Surface Morphology

X ray diffraction pattern of the films are presented in figure 1, showing XRD of both undoped and doped ZnO thin films. The patterns wascompaed with ICDD card 36-1451, and formation of ZnO wurtzite stuctue was confirmed[15]. No second phase ha been detected in any of the films. This confirmed doping f indium in the crytal of ZnO.Doping imparted notable variation in XRD pattern of ZnO thin films. Undoped ZnO film is highly textured in a c-axis orientation (002) conjointly; the set of films doped with 2% In shows similar orientation along (002) direction. However variations in positions of peaks and number of reflections were observed as a result of variation in concentrations of indium in wurtzite ZnO.This is attributed to the effect that no indium oxide phase is formed along the preferential (002) direction. In ZnO, one Zn and one O are the nearest-neighbors with Zn–O bond length along the *c* axis and the direction of same orientation is the clear evidence that no indium atoms occupy these sites. This situation is modified in 4% and 6% concentrations of indium. At octahedral sites the geometrical constraints are comparatively weak and Zn_i are more stable octahedrons, but higher impurity level modified the defect structure of ZnO[16]. Variations in structural features are resulted from the replacement of Zn^{2+} and occupation of In^{3+} ions at the interstitial site in the hexagonal lattice structure.

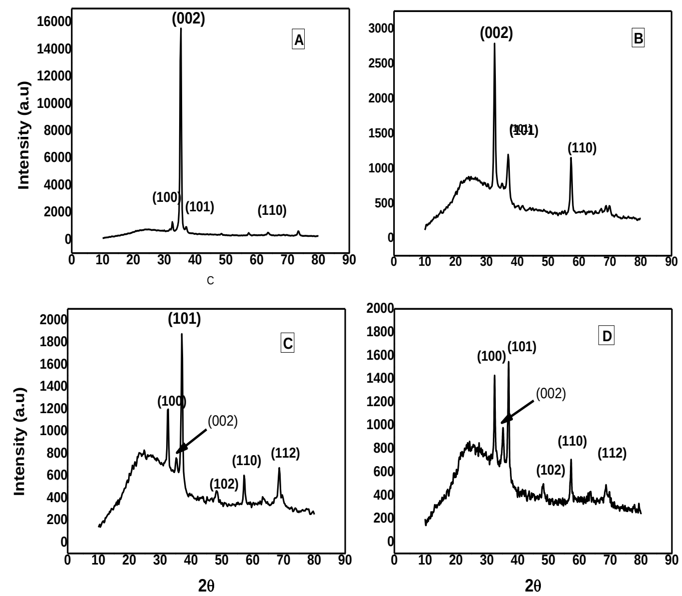

Figure.1. XRD pattern of the thin films deposited by spray pyrolysis technique (a)undoped ZnO (b) 2% Indium doped ZnO (c) 4% Indium doped ZnO (d) 6% Indium doped ZnO.

The sizes of crystallites on film surface are calculated using Debye-Scherrer's formula[16]. The micro-strain, one of the important factor in lattice dynamics, was calculated from uniform deformation model (UDM) of Williamson-Hall (W-H) plot[17]. UDM adduce the strain on lattice is assumed to be uniform along all crystallographic directions and therefore all the material properties are independent of the direction along which they are measured. The W-H equation is given by

$$\beta \cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin\theta \quad (1)$$

Where D is the crystallite size, ε is lattice micro-strain, and β is FWHM. The y- intercept value of the W-H plot represents the average crystallite size and the slope represents micro-strain in the lattices [Table I]. From the Williamson and Smallman's formula, δ = 1/D2, the dislocation density is determined and tabulated [Table I]. As deduced from Table I, the crystallite size on the film surface were found decreasing as the concentration of Indium increases. The results of micro strain and dislocation density on films surface found increased as intensification in the doping concentration.

The generation of stress and strain is due to the difference in ionic radii of zinc and Indium ions. The ionic radii of In3+ ions are higher than Zn2+ and the incorporation of Indium ions in the Zinc site of the lattice induce more strain on crystal lattice.

Figure 2. Shows the SEM micrographs of indium doped ZnO thin films. 2at% indium dope films show a surface morphology with uneven, non-dense and random distribution of rice like particles. No pores or cracks are observed. Particle size appears in the range 400 to 700nm. A dense and uniform distribution of rice like particles are observed on the surface of 4at% indium doped ZnO films. The increased presence of dopant atoms resulted in an increase in the density of particles. The surface appears to be uniform and continuous with no pores. No noticeable change in particle shape or size is observed, when compared to 2at% indium doped films.

Table.1.Micro stain, dislocation density and grain size calculated from different methods

sample	**Grain Size (nm)**		**Dislocation density Δ x10^{15} m^{-2}**		**Micro-strain W-H plot (ε)x 10^{-3}**
	Scherer's formula(nm)	W-H Plot (nm)	Scherer's formula	W-H Plot	
ZnO	34.45	37.76	8.43	7.01	1.36
IZO (2%)	28.12	25.82	12.65	15.00	2.05
IZO (4%)	21.45	23.57	21.73	18.00	3.45
IZO (6%)	11.34	10.28	77.76	94.63	5.57

The surface morphology showed considerable variation on further increase in dopant concentration. The thick packing of rice like particle disappears. Instead the surface appears to be consisting of large rice like particles lay on a matrix of shapeless smaller particles. The particle size varies from 300 to 500nm. A drastic change in the surface morphology observed when the doping concentration is increased to 6 at%. A switching from rice like particle to quasi spherical morphology occurred on increasing the dopant concentration at 6at%. The surface became smoother and more uniform. Particle size appeared to be around 300 to 500nm. Compositions of the In doped ZnO thin films deposited onto quartz substrates were measured by EDS analysis not displayed in article as figure.

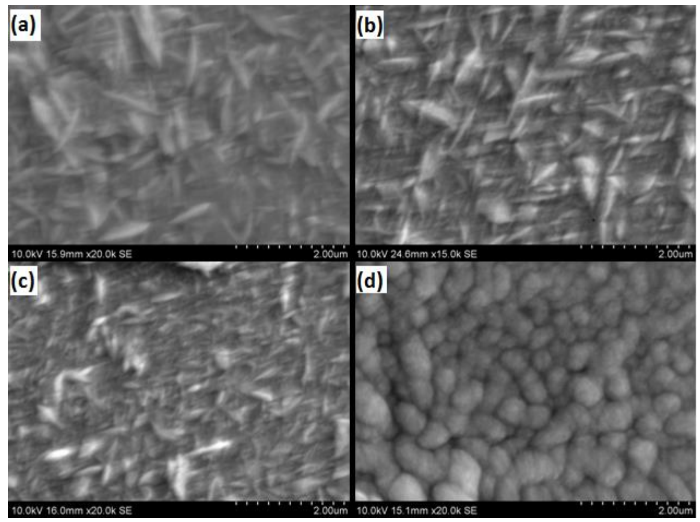

Figure.2. Scanning Electron Micrographs of (a) undoped ZnO (b) 2% Indium doped ZnO (c) 4% Indium doped ZnO (d) 6% Indium doped ZnO**.**

3.2. *Optoelectronic Properties*

The UV-Vis optical transmittance spectra of IZO films at different doping concentrations are displayed in figure.3. From the analysis transmittance spectra of indium Zinc Oxide films, it is seen that indium at moderate level of doping concentrations enhances the transparency of the films meanwhile at high concentration 6% of In occupancy the transparency is dropped steeply to lower percentages. This may be due to the restructuring of the electronic level of the materials. The optical band gaps of the films were also measured from the absorption onset of the transmittance spectra. Both the percentage of transmittance and optical band gap of the materials ate plotted and displayed in figure 4.

The absorption onset of the transmittance of the indium doped ZnO thin films are affected greatly with the variations in In concentrations. The fundamental absorption onset of the metal oxide thin films corresponds to electron transitions from valence band to conduction band and this edge indicate the point of transition and is regarded as optical band gap of materials. Band gap increased from 3.23eV for undoped ZnO films to 3.26eV for 2 at% In doped films. The increase in band gap is due to the increase in carrier concentration due to indium doping. The variation of band gap and carrier concentration of ZnO films with indium doping concentration is presented in figure.5.

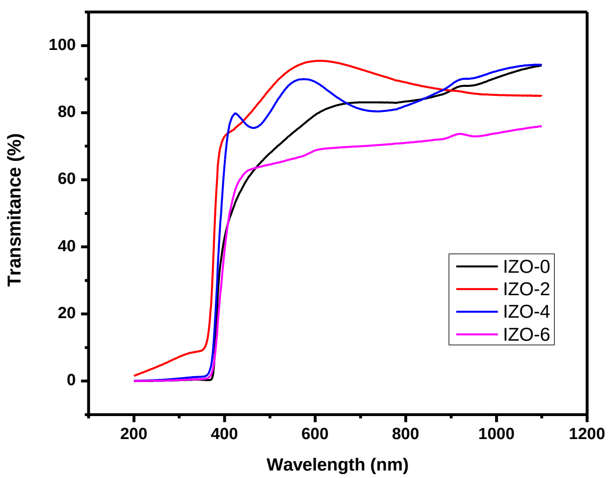

Figure.3. Optical transmittance spectra of undoped and In doped ZnO films

Figure.5.shows that the variations in band gap of indium doped ZnO films are due tovariations in the carrier concentration in the films. The carriersgenerated by the indium donors give rise to Burstein Moss effect which resulted in widening of band gap. This widening of optical band gap resulted in the high optical transparency of 2% In doped ZnO films, however both the transparency and E_g found decreased for 4at% In and 6 at% In doped films.

Formulation of different proportions of IZO influenced the electrical properties of the films and the measured features are exhibited in table.2. Van der Pauw Hall measurement performed on the samples exhibited negative Hall coefficient and hence films are n-type TCOs. Sheet resistance, carrier concentration and carrier mobility were obtained from Hall measurement. The sheetresistance value decreased to 5.58X10^{-3}Ω- cm for 4at% In doped films with moderate carrier mobility and free carrier concentration.

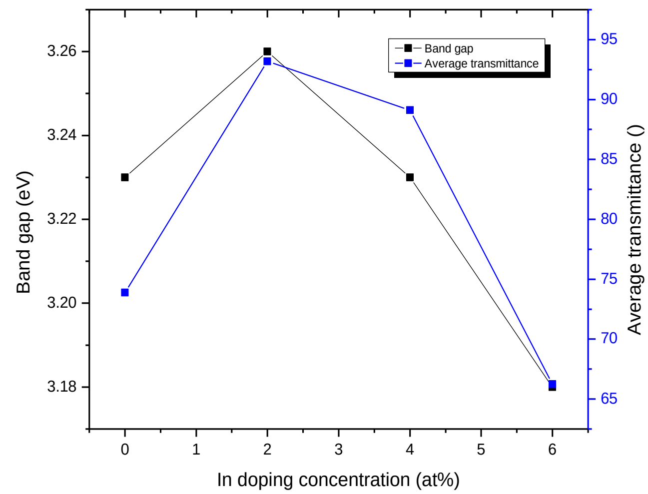

Figure.4. Variation of transmittance and band gap with In doping concentration

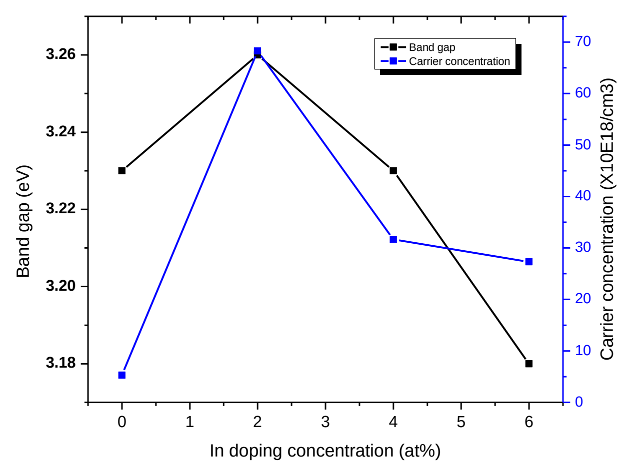

Figure.5. Variation of band gap and carrier concentration with In dopingconcentration

Table.2. Electrical properties of the thin films of ZnO doped with In at different concentrations

Sample	**Resistivity (Ω- cm)**	**Carrier Concentration (cm^{-3})**	**Carrier Mobility (cm^2/Vs)**
ZnO	2.20X10^{-2}	3.16 X10^{19}	9.930
IZO (2%)	1.19X10^{-2}	2.72X10^{19}	19.24

IZO (4%)	5.58X10^{-3}	6.82 X10^{19}	16.36
IZO (6%)	1.05 X10^{-2}	1.92 X10^{19}	31.12

The reduction in the resistivity is due to an increase in the free-electron concentration with indium incorporation in the ZnO films. 2% In doped samples show prominent electrical features in terms of carrier concentration and resistivity, meanwhile the moderate mobility is a limiting factor.Sample doped with 6% of Indium show resistivity 1.05 X10^{-2} Ω- cm with excellent carrier mobility. Despite the higher level of doping, the carrier concentration is less in this sample. XRD results showed a probability of indium atoms occupying interstitial positions of ZnO matrix. These interstitial atoms do not contribute to carrier concentration. This might have limited the carrier concentration in 6 at% In doped films. The high carrier mobility explains the improvement in resistivity of the films. SEM micrographs of the film show a switching of particle shape from rice like to more uniform quasi spherical for 6 at% In doped films. This could result in reduction of scattering of carriers at grain boundaries. This will increase in the mean free path of carriers thereby increasing the carrier mobility.·All the films possessed excellent electrical features compared to the undoped films.

4. CONCLUSION

ZnO and Zr doped ZnO thin films were grown on fused silica substrates at 400^{0}C using automated chemical spray pyrolysis technique. The doping concentration of Indium was selected as 0,2,4 and 6 at% of Zinc.The films were then subjected to vacuum annealing at 10^{-5} mbar at 400^{0}C for three hours. The structural profile investigated by XRD technique revealed growth of ZnO wurtzite structure with preferred orientation along (002) direction. A shift in preferred growth orientation was found for higher order doping which was attributed to thepresence of Indium ions. A rice like surface morphology was observed for pristine and moderately doped ZnO films. But for 6at% Indium doped film, a quasi-spherical surface morphology was observed. Optical transmittance measurement done by UV-Vis spectroscopy revealed an improvement in transparency with Indium doping. Highest transparency was obtained for 2 at% Indium doped film and transparency decreased with further doping. This increased transparency was due to widening of band gap in 2at% Indium doped film caused by Burstein Moss effect. The resistivity was minimum for 4 at% Indium doped films which had highest value for carrier concentration and moderate value for carrier mobility.

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