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RESEARCH ARTICLE

ENHANCEMENT OF OPTICAL AND ELECTRICAL PROPERTIES OF ZNO THIN FILMS USING INDIUM DOPING

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ABSTRACT

Pristine and indium doped ZnO thin films were prepared on fused silica substrate using chemical spray pyrolysis technique. All films were vacuum annealed at 400^0C for three hours at a vacuum of 10^{-5}mbar. The XRD analysis revealed a shift of preferred orientation from (002) to (101) direction at higher indium doping concentration. A minimum sheet resistance of 1.986 $X10^{-2}$ Ωcm and a maximum transmittance of 93% were achieved for 2 at% indium doped ZnO films. The band gap of ZnO films showed an increase with doping concentration, majorly due to Burstein Moss effect.

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INTRODUCTION

The unique physical and chemical properties including wide direct band gap and large excitation binding energy make ZnO an attractive material for a number of applications including light emitting diodes[1,2], transistors[3,4], gas sensors[5,6] and photovoltaics[7,8]. Many methods can be employed to produce the ZnO thin films such as CVD[9], sputtering[10], sol gel[5], hydrothermal[11], spray pyrolysis[12] etc. Among these spray pyrolysis is a low cost method and is suitable for large area production. ZnO has hexagonal close packed structure with empty octahedral sites. These empty sites make ZnO suitable for doping as dopant atoms can easily occupy these sites[13]. Indium is a group III element with an oxidation state of +3. When substituted on the Zn site of ZnO, In^{3+} acts as a shallow donor. The loosely bound extra electron of indium occupies the conduction band and act as a carrier in ZnO matrix. This work discusses the effect of indium doping concentration on the structural, electrical and optical properties of spray deposited ZnO thin films.

MATERIALS AND METHODS

Pristine and indium doped zinc oxide thin films were prepared on fused silica substrates at 400^0C using spray pyrolysis technique.

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A 0.2 molar solution of zinc acetate ($Zn(CH_3COO)_2.2H_2O$) was made in a solvent containing methanol, water and acetic acid in a ratio 65:25:10. Same solvent was used to prepare 0.2 molar indium acetate solution. The indium acetate solution was added to zinc acetate solution in calculated amount to achieve indium doping and the solution was stirred well ultrasonically before deposition. Five batches of solutions were made with various indium content (0,2,4,6 and 8 at%). The solutions were sprayed to cleaned fused silica substrate at 400^0C with air as carrier gas using Holmarc HO-TH-04 automated spray pyrolysis equipment. Optimized spray parameters such as spray nozzle- substrate distance (15cm) and solution flow rate (4ml/minute) were kept constant for all samples. The spray nozzle was symmetrically moved parallel to the substrate surface throughout the deposition process to achieve uniform deposition. The films were allowed to cool after deposition and were then annealed at 400^0C in a high vacuum of 10^{-5} mbar for two hours. ZnO films with five different indium doping levels namely 0, 2,4,6,8 at% were prepared and were named IZO-0, IZO-2, IZO-4, IZO-6 and IZO-8 respectively. The thicknesses of the films were measured using spectroscopic ellipsometric technique with Angstrom Sun Technologies Inc. SR-200. The X ray diffraction profiles of the samples were recorded using Rigaku-Miniflex X-ray diffractometer (Cu-$K\alpha$-radiation – $1.54A^0$). The electrical properties of the films were studied using Van der Pauw four probe method (ECOPIA HMS 3000 Hall measurement system). UV- Visible spectroscopy was employed to study the optical transparency of the films (Perkin Elmer Lambda 35). The data from transparency measurement

was used to calculate the band gap of the films by constructing the Tauc plot.

RESULTS AND DISCUSSION

The prepared films are of uniform thickness with thickness equal to 300±10nm. Any variation in the property of the films due to the effect of thickness can be neglected.

Structural properties

The XRD profiles show the polycrystalline nature of the films. The peak positions are compared with ICDD card number 36-1451 and formation of ZnO wurtzite structure is confirmed. The polycrystalline nature is attributed to the low kinetic energy of the sprayed atoms, which limits the movement of zinc atoms to growth locations with minimum surface energy on the substrate surface. For ZnO wurtzite structure (002) direction is the preferred growth orientation as it helps the reduction of surface free energy[14]. The IZO-0 and IZO-2 samples showed growth along the (002) direction, which is perpendicular to the substrate surface[15].

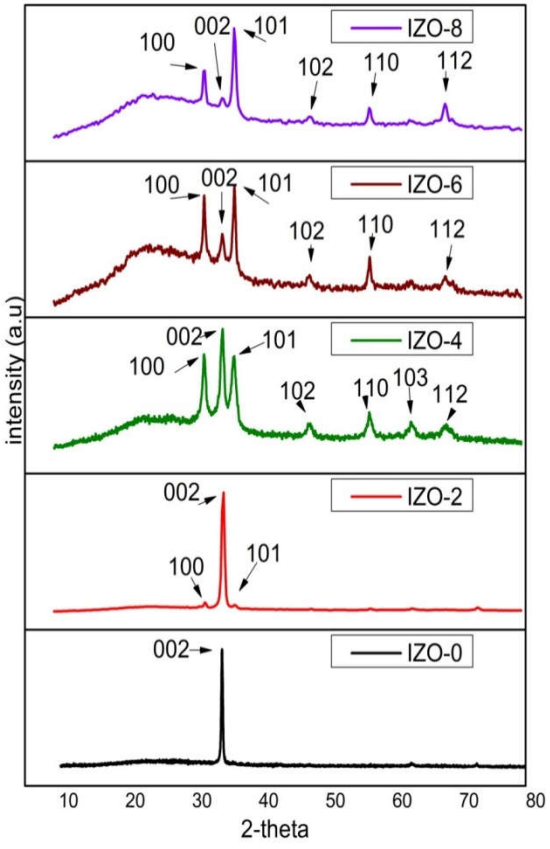

Figure 1. XRD profiles of pristine and In doped ZnO films

The XRD profiles show that the crystalline quality of the ZnO films have deteriorated with indium doping. As the concentration of indium increases the intensity of 002 peak decreases and growth appeared in 100 and 101 directions. Beyond indium doping level of 4 at% the preferred orientation of the films switched from 002 to 101 direction. Similar behavior of crystalline nature on extrinsic doping has been reported earlier[16,17,18]. During the film growth the presence of dopant atoms will induce a difference in reactions occurring on the substrate surface. This brings changes in the surface free energy and the direction of film growth[19]. For further understanding of the effect of indium doping on the crystalline nature of the prepared films the lattice parameters, microstrain, crystallite size and dislocation density of films are calculated from the XRD profiles. The lattice constants of the hexagonal structure are calculated using the relation.

$$\frac{1}{d^2}=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2} \quad \ldots(1)$$

Where d is the interplanar spacing in the direction (hkl) given by the equation

$$n\lambda = 2d\sin\theta \quad \ldots(2)$$

The crystallite size of the films are found using Sherrer formula

$$D=\frac{0.9\lambda}{\beta\cos\theta} \quad \ldots(3)$$

Where β is the FWHM for the prominent XRD peak at 2θ The lattice strain perpendicular to the substrate surface is estimated as[20]

$$\varepsilon=\frac{c-c_0}{c_0}X100 \quad \ldots(4)$$

where ε is the mean strain in the thin films with lattice constant c and c_0 the lattice constant of bulk (standard c_0 = 0.5206nm). The dislocation density, which is a measure of the number of dislocations in unit volume of a crystal is calculated using[21]

$$\delta=\frac{1}{D^2} \quad \ldots(5)$$

where D is the crystallite size

Table 1. Structural details of pristine and indium doped ZnO films

Sample Name	''c' value Å	Lattice Strain (%)	Crystallite size (nm)	Dislocation density
IZO-0	5.198	-1.53×10^{-1}	45.12	4.93×10^{14}
IZO-2	5.202	-7.68×10^{-2}	37.76	7.01×10^{14}
IZO-4	5.205	-1.95×10^{-4}	25.82	15×10^{14}
IZO-6	5.213	1.34×10^{-3}	23.57	18×10^{14}
IZO-8	5.235	5.57×10^{-3}	10.28	94.63×10^{14}

The c value of pristine ZnO film is less than that of unstrained ZnO lattice. This might be due to the strain developed in the films due to the effect of deposition parameters[22]. The c value increased with indium doping. The ionic radius of In^{3+} (81pm) is greater than that of Zn^{2+} (74pm). When the larger In^{3+} ion substitutes a Zn^{2+} ion in a ZnO lattice there will be corresponding increase in lattice parameters. In other words, the increase in c value is a proof of incorporation of indium ions in the zinc sites of ZnO lattice. The crystallite size reduces from 45.12nm for undoped ZnO film to 10.28nm for IZO-8. Clearly, higher level indium doping deteriorated the crystalline quality of ZnO thin films. During the spray deposition process, the increased presence of In^3 ions in the spray solution will

result in an increase in the number of nucleating centers. These impurity based nucleation centers will exert drag forces on boundary motion of constituent atoms. This will affect the crystal growth and results in a reduction of crystallite size[23]. The negative values of micro strain imply compressive strain in films IZO-0, IZO-2 and IZO-4, whereas tensile strain is observed for IZO-6 and IZO-8. The reasons for the observed strain might be the grain boundaries and intrinsic defects formed during the film growth[24].

Electrical properties

Indium atoms are n type dopant for ZnO films and are presumed to replace Zn atoms in the ZnO film, thereby increasing the carrier concentration. The sheet resistance of thin films is given by the equation

$$R_s = \frac{1}{N\mu e} \quad \ldots(6)$$

Where N is the carrier concentration, μ is the mobility and e is electronic charge. The result from Hall measurement of the prepared films is tabulated in table 2. Indium doping has improved the conductivity of the ZnO film by up to two orders. The improvement in conductivity can be attributed to the additional free carriers generated by doping. 2 at% indium doped films show minimum resistance of 1.986 $X10^{-2}\Omega$cm. The variation of sheet resistance, carrier mobility and carrier concentration with indium doping is graphically presented in Figure 2.Despite the increase in carrier concentration the sheet resistance increased for IZO-4, with respect to IZO-2, owing to the low free carrier mobility in IZO-4. The carrier concentration reduces with further Increase in the indium doping concentration. Similar effect has been reported for zirconium doped zinc oxide[25]. At high level doping the dopant atoms form some kind of neutral defects which do not contribute to carrier concentration. Instead they agglomerate at grain boundaries and suppress the grain growth and result in smaller grains[26].

Table 2. Results from Hall effect measurement

Sample Name	Sheet resistance (Ωcm)	Carrier Concentration (cm^{-3})	Carrier Mobility (cm^2/Vs)
IZO-0	2.026 $X10^{0}$	5.271 $X10^{17}$	5.840
IZO-2	1.986 $X10^{-2}$	6.025 $X10^{19}$	5.216
IZO-4	5.584 $X10^{-2}$	6.829 $X10^{19}$	1.636
IZO-6	1.670 $X10^{-1}$	2.729 $X10^{19}$	1.369
IZO-8	1.041 $X10^{-1}$	1.927 $X10^{19}$	3.112

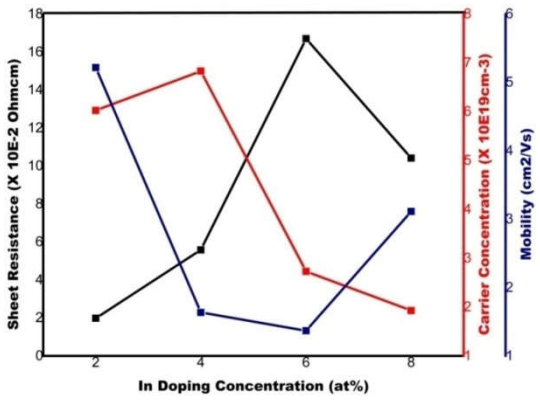

Figure 2. Variation of sheet resistance, carrier concentration and carrier mobility with doping concentration

Optical properties

The optical transparencies of the films are studied using UV-visible spectroscopy. The optical transmittance spectra of the films are shown in figure 3**.** All the deposited films are transparent with average transmittance (at 550nm) ranging from 56 to 93%. We observed that indium doping at 2 and 4 at% drastically enhanced the transparency of the ZnO films. At higher level doping the transparency decreases as low as to 56% for 8 at% In doping.

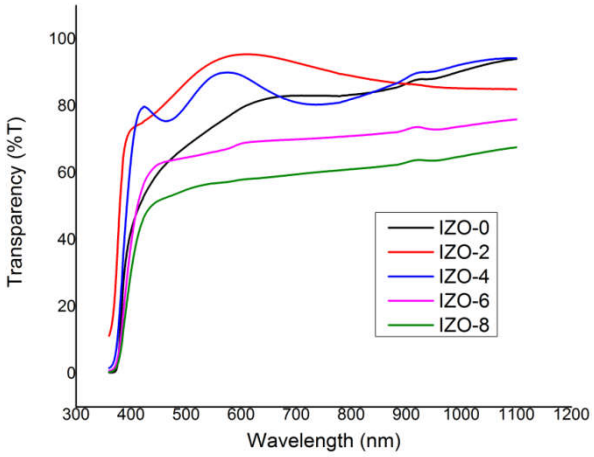

Figure 3. Transmittance spectra of pristine and In doped ZnO films

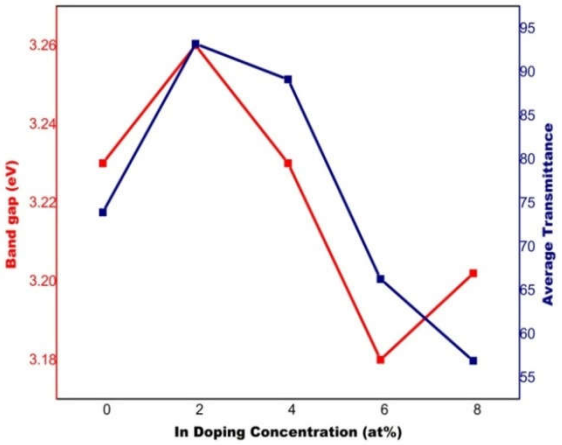

Figure 4. Variation of band gap and average transmittance with In doping

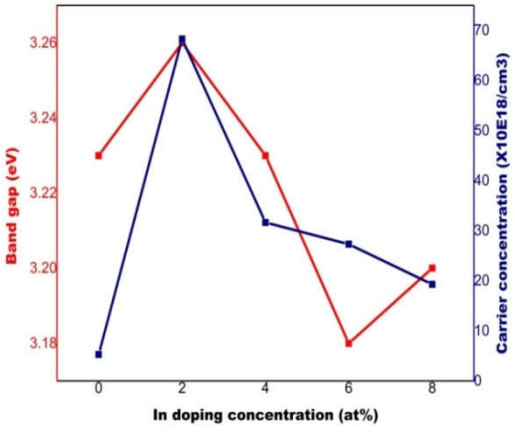

Figure 5. Variation of band gap and carrier concentration with In doping

The band gaps of the films are found by constructing the Tauc plot for each film. The variation of band gap and average transmittance with indium doping concentration plotted in figure 4. The plot reveals the dependence of transparency on the band gap of the films for IZO-0, IZO-2, IZO-4 and IZO-6. The decrease in transmittance for IZO-8 must be due to the poor crystallanity of the[27]. The small crystallite size would result in an increase in the scattering of light at the boundaries and corresponding reduction in transmittance.To study the dependence of band gap on indium doping, a graph is plotted connecting the variations of band gap and carrier concentration with indium doping (Figure 5). The graph reveals that the band gaps of the films are majorly determined by the carrier concentration in the films. This might be attributed to Burstein Moss effect in which the additional carriers generated by indium doping populate states within the conduction band pushing the Fermi level to higher energy resulting in an increase in band gap. The slight increase in the band gap for IZO-8 might be due to the poor crystallanity of the film. The small crystallite size and high dislocation density will give rise to a quantum confinement effect which results in an increase in band gap[27].

Conclusion

Indium doped ZnO thin films are prepared using spray pyrolysis technique. The effect of indium doping concentration on the structural, electrical and optical properties of ZnO thin films is studied. The preferred orientation showed a shift from 002 to 101 on high level indium doping. The conductivity and transparency of ZnO films considerably increased on indium doping. The band gap variation with indium doping was attributed to Burstein Moss effect. With a sheet resistance of 1.986 $X10^{-2}$ Ωcm and an average transparency of 93%, 2 at% indium doped ZnO films are found to be an excellent candidate for transparent conducting oxide applications.

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