

Indium doped Zinc oxide thin films: Effect on structural, optical and electrical characteristics.

A. Jacqueline Regina Mary¹, S.Ar umugam²

¹ Department of Physics, Jayaraj Annapackiam College for Women (Autonomous), Periyakulam, Theni Dist, Tamilnadu, India.

² Solar Energy Division, Department of Physics, The Gandhigram Rural Institute-Deemed University, Gandhigram, Dindigul Dist, Tamilnadu, India.

Abstract - The effect of Indium doping on the structural, optical and electrical properties of Zinc oxide thin films (IZO) prepared through spray pyrolysis method is reported. The dopant concentration was varied as 1, 2, 5 and 7.5 taken in mole percentage. XRD analysis show that the average grain size of IZO thin films decreases as the dopant concentration increases. When doped heavily, the optical band gap (E_g) was found to increase from 3.06 eV to 3.6 eV, which is due to Burstein-Moss effect. The optical constants such as refractive index (n) and extinction coefficient (k) are calculated from the reflectance and UV-absorbance data respectively. FTIR studies revealed the formation of Zn-O bond at 489 cm^{-1} . The overall transmittance of the IZO films are found to be above 83% in the visible and near IR region. There is a blue emission centered around 458 nm in the PL emission spectra. It is found that electrical conductivity (σ) is enhanced due to doping by observing the Four probe measurements. The optical and electrical properties of Indium doped ZnO thin films prove it to be a suitable candidate for making transparent electrodes in solar cell.

Key Words: Grain size, optical band gap, transmittance, refractive index, electrical conductivity.

1. INTRODUCTION

Zinc oxide based thin films are better choice to ITO due to their excellent electrical and optical properties in the visible region. Zinc oxide is an extensively studied material, since its electrical conductivity can be made high with high visible transmittance. It has a wide band gap of 3.37 eV and exciton binding energy of 60 meV. Transparent conductive oxide (TCO) such as ITO, ZnO thin films find applications in optoelectronic devices like solar cells, flat panel displays (eg touch panel displays), Organic light emitting diodes (OLED), and low e^- windows [1-3]. Since vacuum techniques require sophisticated instruments and maintenance, because of its simplicity, chemical methods draw attention in the synthesis of good films. But both physical and chemical deposition techniques could be employed based on the requirement to

prepare quality films. Chemical spray pyrolysis (CSP) is the method used to deposit TCO earlier; even now it continues to be the easier deposition technique for large scale production and cost effective [4-6].

Zinc oxide is highly resistive in its pure form and efforts are made by researchers to improve its electrical conductivity by intentional doping. Selection of the dopant should be based on the ionic size and electro negativity, since these two factors decide the efficiency of the dopant element. High valence group III elements are chosen to enhance the electrical properties of ZnO. Among those aluminum (AZO) and gallium (GZO) doped ZnO are studied much. There are only few reports on Indium doped ZnO (IZO). Indium doping lowers the resistivity of the films, with values ranging from 4.03×10^{-5} to $3 \times 10^{-3} \Omega\text{ cm}$ [7,8].

The present work is aimed at synthesizing good quality films for their application as transparent electrode in solar cells. The optimized zinc oxide thin films are doped with indium and its effect on the structural, optical and electrical properties of ZnO thin films are investigated.

1.1 Materials and methods

Zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and Indium chloride (InCl_3) are the precursor materials purchased from Sigma Aldrich (99%), which are dissolved in Isopropyl alcohol and de-ionized water in the ratio 3:1. The films are deposited on to pre-cleaned brosilicate glass substrate 1mm thick. Few drops of acetic acid were added to improve the solubility of Zinc acetate and Indium chloride mixture in the solvent. The resultant solution was stirred at 60°C for 1 h to yield a clear homogenous solution, which is used for coating. After coating, the In doped ZnO (IZO) films were allowed to cool to room temperature. The films were post annealed at 773K for 1 hour.

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Optimized deposition parameters

| | |
|--------------------------------------|------------------------|
| Zinc acetate solution concentration: | 0.2M |
| Substrate temperature | : 673±5 K |
| Substrate to Nozzle distance | : 25cm |
| Volume of the solvent | : 25ml |
| Spray rate | : 4ml/ minute |
| Dopant concentration (In): | 1, 2, 5 & 7.5 (mole %) |

1.2 Characterization technique

The crystallographic orientation of the IZO samples was studied by XPERT-PRO X-ray diffractometer and micro structural analysis was done with TESCAN VEGA3 scanning Electron microscope. The optical absorption-transmission studies were carried out using UV-Vis spectrophotometer (Shimadzu, model UV-1800, Japan) in the wavelength range 190-1100nm. FTIR Spectra are recorded by Perkin Elmer BX II spectrometer between the wave number region 4000cm⁻¹ to 400cm⁻¹. The d.c electrical resistivity was measured by Four probe method.

2. Results and Discussion

In this section, the structural and morphological changes with the increase in the Indium (dopant) concentration are analyzed. Optical properties through band gap (E_g), refractive index (n) and electrical properties through resistivity (ρ) are investigated. Device performance is calculated from figure of merit (φ).

2.1 Scanning Electron Microscopy

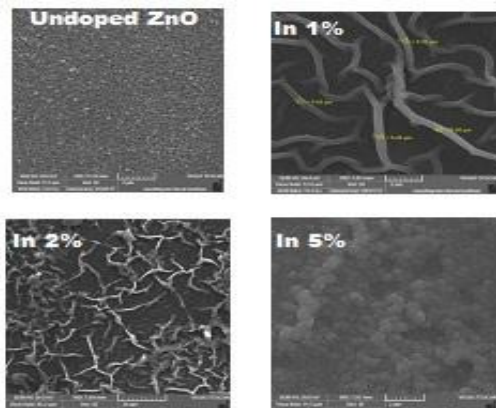


Fig. 1 SEM images of ZnO thin films doped with different In concentration (mole %).

Figure 1 shows the SEM micrograph of both undoped and doped IZO films with 11.0kx magnification. Undoped films have smooth, closely packed grains which are uniformly distributed. When Indium (1%) was incorporated, the morphology changes to well defined nano fibers forming chain throughout the surface. The average width of the nano fibre was measured as 440nm. As the concentration of the dopant increases the surface becomes broken chain like nano structure. When the In concentration reaches 5% the morphology modified to spherical shaped particles spread throughout the surface.

2.2 Structural properties

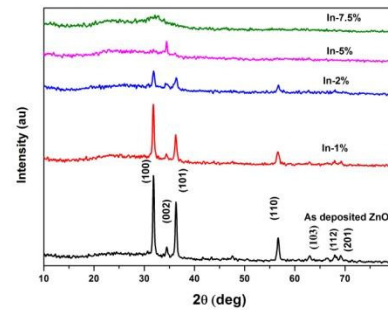


Fig. 2(a) XRD pattern of undoped and In doped ZnO thin films

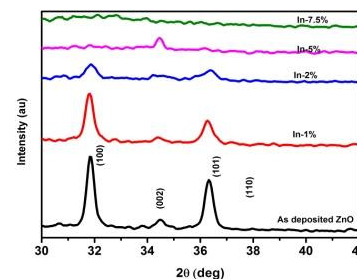


Fig. 2(b) XRD pattern of undoped and In doped ZnO thin films (scan angle 2θ from 30° to 42°)

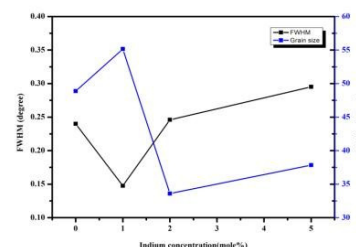


Fig. 2(c) Variation of FWHM and grain size with different Indium %.

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Figure 2(a) and 2(b) shows the XRD pattern of IZO thin films deposited for various In dopant concentrations. The films are polycrystalline with hexagonal structure with preferred orientation along (100) plane up to In 2%. Further increase in In content (In 5%), intensity of (100) peak weakens and (002) crystal plane starts to grow leading to reorientation of the crystal [5]. When the concentration reaches 7.5% there is a hump at 31° and no peaks are observed indicating the amorphous nature of the films. At higher doping level insoluble In atoms segregate at the grain boundaries inhibit the growth of ZnO: In crystals [5]. The overall picture depicts the deterioration of crystallinity of the films, as the concentration grows. Variation of FWHM, grain size with different Indium content is shown in Figure 2(c). The grain size varies from 46nm to 55nm for undoped and In doped films.

2.3 Optical properties

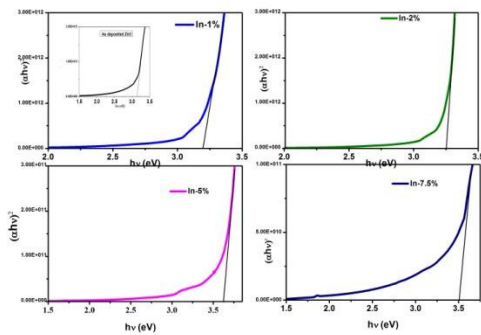


Fig. 3 $(ahv)^2$ vs $h\nu$ plot for as deposited (inset) and IZO thin films for different In dopant (mole %).

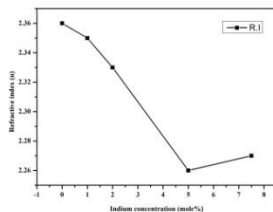


Fig. 4 Variation of Refractive index for various In dopant (mole %)

The optical absorption studies show that maximum absorbance of all the films are less than 1.4 and found to decrease in the UV in the region. The absorption edges are blue shifted from 410nm to 407nm. Thereafter the absorption is constant in the visible and near IR region. The optical band gap calculated using Tauc's relation is given by,

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

for direct allowed transition. This variation of $(\alpha h\nu)^2$ with photon energy ($h\nu$) were plotted and it is shown in figure (3) with the undoped curve shown as the inset. The extrapolation of the linear portion of the curves to $\alpha = 0$, gives the optical band gap energies. The optical band gap energies (E_g) for undoped to In doped ZnO films were found to vary between 3.06eV to 3.6eV, According to Burstein - Moss effect, the optical band gap (E_g) should increase due to the incorporation of In ions. Which is due to the shifting of Fermi level into the conduction band due to doping, in degenerate semiconductors [8]. The variation of refractive indices (n) with Indium concentration is shown in Figure (4). The index of refraction was calculated from reflectance data and found to vary between 2.36 to 2.24 and In 5% posses he minimum value.

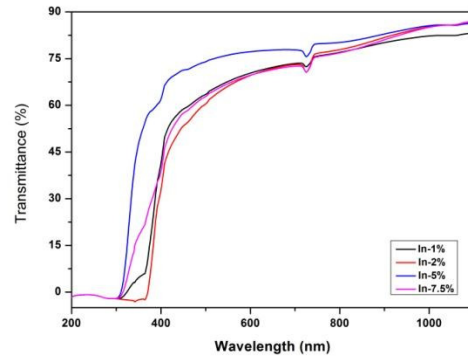


Fig. 5 The optical transmission spectra of IZO for different In dopant (mole %).

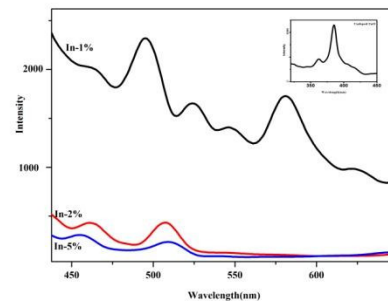


Fig. 6 Photoluminescence Spectra thin films as deposited (inset) and IZO films for different In dopant (mole %)

It could be seen from figure 5, that the average transmittance of the films are 80% in the visible region and it is 83% in the near IR region. Apart from a small dip in the

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transmission, the films are found to be highly transparent with maximum transparency obtained for In 5%. The PL emission spectra of IZO films are shown in figure 6. The NBE emission peaks for In-1% are more intense than 2% and 5% in the PL spectra. The blue emission at 462nm for In-1% is shifted to 456nm and the green emission at 506 nm shifted to 508 nm for higher Indium concentrations. A broad peak at 580 nm is absent for In-2% and In-5%.

2.3 Electrical properties

The electrical properties of semiconducting oxide films depend on doping effect and also its deviation from the stoichiometry [1]. The electrical properties of IZO thin films are summarized in table 1. The resistivity ρ is calculated by $\rho = R_s d$ where R_s is the sheet resistance and d is the thickness of the film. The ZnO thin film doped with In 1% has minimum resistivity compared with other IZO films. Conductivity could not be measured for IZO 7.5%. This may be due heavy doping, where there is an enhancement of grain boundary scattering resulting from ZnO lattice disorder [3].

Table -1: The electrical properties of Indium doped Zinc oxide thin films

| In Concentration (mole %) | Sheet resistance $10^3 (\Omega \square^{-1})$ | Figure of merit $(\phi) 10^{-2}$ | Resistivity $\rho (\Omega \text{ cm})$ | Thickness (μm) | Conductivity (Scm^{-1}) |
|---------------------------|-----------------------------------------------|----------------------------------|----------------------------------------|---------------------------|----------------------------------|
| 0 | 22.65 | 0.30 | 45.07 | 1.99 | 0.22 |
| 1 | 8.87 | 0.76 | 10.12 $\times 10^{-2}$ | 1.15 | 0.99 |
| 2 | 7.02 | 1.10 | 13.05 $\times 10^{-2}$ | 1.86 | 0.76 |
| 5 | 7.61 | 0.88 | 21.84 $\times 10^{-2}$ | 2.87 | 0.48 |

For optoelectronic device applications, the figure of merit (ϕ) of the films plays an important role. The device performance is determined from ϕ and is calculated by using the formula

$$\phi = \frac{T^{10}}{R_s}$$

Where T^{10} is the transmittance at 550 nm and R_s is the sheet resistance. The figure of merit for the IZO films deposited for various concentrations are listed in Table 1. The figure of merit (ϕ) increases with doping and then it falls for heavy doping. The highest value of figure of merit

$1.10 \times 10^{-2} \square \Omega^{-1}$ is obtained for In2% films which is higher than value reported ($1.5 \times 10^{-4} \square \Omega^{-1}$) for Indium doped films. [5]. Doping reduces the resistivity of the films from 45.07 $\Omega \text{ cm}$ (undoped ZnO) to a minimum of 0.10 $\Omega \text{ cm}$ (In doped ZnO), which may be due to the replacement of Zn^{2+} ions by In^{3+} ions in the Zn lattice. This provides extra electrons for conduction thereby increasing the conductivity of the IZO thin films. As reported by Hadri et.al it is shown that Indium content is a factor that affects the electrical properties.[8]

3. CONCLUSIONS

The effect of Indium dopant on structural, optical and electrical properties of ZnO thin films was investigated. The IZO films are polycrystalline and doping reorients the crystal plane from (100) to (002) plane. SEM micrographs reveal the nano fibrous structure with a average width of the nano fibre as 440nm. The optical band gap varies from 3.06eV to 3.6eV due to doping. The average transmittance of the films are 80% in the visible region. The highest value of figure of merit $1.10 \times 10^{-2} \square \Omega^{-1}$ was obtained for 2% IZO films. The resistivity of the films decreases from 45.07 $\Omega \text{ cm}$ for the undoped to a minimum of 0.10 $\Omega \text{ cm}$ (In 1%) for the doped samples. These IZO films synthesized by spray pyrolysis can be good contenders for the application as the transparent electrode in solar cell.

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BIOGRAPHIES



Mrs.A.Jacquiline Regina Mary, Associate Professor of Physics has 27 years of teaching experience in Jayaraj Annapackiam college for women, Periyakulam. Area of specialization is thin film solar cell .



Dr.S.Arumugam, Professor of Physics has 30 years of teaching experience in Gandhigram university, Dindigul. Area of specialization includes solar energy, thin film solar cell, Nanoscience.