Indium-doped Zinc Oxide Thin Films by Sol–Gel Method

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Abstract – *High quality sol-gel derived ZnO in thin films were deposited on glass substrates by spin coating at 2000 rpm. Zinc Acetate and Indium Chloride were used as precursor materials. The effect of dopant concentration and annealing in different temperature on the electrical, optical and structural properties of produced thin films were investigated. The optical transmittance spectra showed a very good transmittance of 99.5% within the wavelength of 540 nm for the film doped with 2 wt.% In . Increased dopant (more than 6 %) changed n type semiconductor to p type. Results showed that the c-axis orientation was determined by annealing temperature and that the grain size and resistance of the IZO thin films were mainly influenced by the annealing temperature.*

Keywords: *Sol-gel; thin film; annealing; grain size; transmittance; wavelength.*

I. Introduction

Transparent conducting oxides (TCO) have many applications based on their electro-optical properties. They are used in flat panel screens, laptop screens and solar cells, in electrochromic windows that respond to increasing sunlight by becoming darker, in oven windows and energy-efficient windows that keep buildings cool in the summer and trap heat inside during winter. Achieving high electrical conductivity and good optical transmission in TCO materials is crucial for most applications[1][2].

The TCOs that have already been largely investigated and used in the industry are zinc oxide (ZnO) and indium tin oxide (ITO). Zinc oxide (ZnO) is an interesting wide-band-gap semiconductor material with a direct band gap of 3.36 eV [1] at room temperature. It has crystalline structure of the wurtzite type and the unit cell with the constants a = 3.24.Å and c = 5.19 Å.

Aluminum and Indium doped ZnO [3][4] are of interest because doping improves conductivity of ZnO thin films. Various techniques have been used to deposit undoped and doped ZnO films on different substrates, including spraypyrolysis [5], organometallic chemical vapour deposition [6], pulsed laser deposition [7], sputtering [8], and sol-gel process. Among these, the sol-gel technique is credited with several advantages, such as deposition of high purity, homogeneous, cheaper, large-area films at relatively low temperatures [9]. In sol-gel, thin films are formed from cross-linked liquid chemical precursors by spin-coating, drop-coating or dip-coating the substrate followed by thermal decomposition [6].

In this paper, we concentrate on the structural, electrical and optical properties of sol-gel derived ZnO:In films deposited by spin coating. The effect of dopant concentration and annealing in different temperatures were also investigated.

II. Experimental procedure

The solutions were prepared by dissolving zinc acetate, $Zn(CH_3COO)_2 \cdot 2H_2O$ (purity 99.95%), in ethylene glycol (Merck) and mono ethanol amine, MEA(Merck). The molar ratio of mono ethanol amine to zinc acetate was maintained at 1.0 and the final molarity of zinc acetate was chosen to be 0.5 M. The solution was stirred at 50°C for 1h. The resulting clear solutions were aged at room temperature for 10 days prior to use in order to allow for formation of the sol. The dopant source was indium chloride (Merck) add in the aged solution. In order to study the effect of indium concentration and annealing temperature on the structural, electrical and optical properties of In-doped ZnO thin films, 5 values of dopant concentration (2, 4, 6, 8 and 16 wt%) and three annealing temperature were used.

The substrates were cleaned, first with acetone, and subsequently with methanol. They were further cleaned with distilled water for 20 minutes and kept in an oven at 100°C for 5 minutes. The films were deposited on glass substrates using a spin coater. The substrates were spun at 2,000 rpm while a solution was dropped from a pipette onto a substrate. Each substrate was spun for a total of 15 s. The films were then heat-treated in an oven in air at 400°C for 10 minutes in order to

decompose the precursor components and form metaloxides. This process was repeated 10 times to deposit films of desired thickness.
The grain size and the crystalline orientation of the films were determined by X-ray diffractometer (BRUKER-axs) using Cuk α radiation (λ=1.54 Å) with a ungular step of 0.01°. The surface morphology of the films was analysed by Scanning Electron Microscopy (SEM) with a LEO 145OVP . . The sheet resistance was measured by the van der Pauw [12] technique. Carrier type and concentration was measured by Hall effect measurement. Optical transmittance, band gape energy and films thickness measurements were carried out using spectrophotometer, HP-UV-Vis (Agilent 8453).

III. Results and discussion

1- Structural properties

The XRD pattern have been recorded in the 2teta range of 30-40, where the peak of hexagonal wurtzite type In-doped ZnO structure is present. This indicated that films have polycrystalline structure (Fig. 1). The XRD patterns also showed a high preferential c-axis oriented structure. Diffraction peak (002) had considerable growth, but decreased when dopant concentration increased. It was similar to other reports(30 and 40). Crystal quality of samples with lower dopant concentration was higher.
Grain size of samples were determined by means of XRD and Scherrer formula:

$$D = \frac{\kappa\lambda}{W' Cos\theta} \qquad (1)$$

$$W' = \sqrt{W^2 - \delta^2}$$

Where δ is the resolution of the spectrometer, here 0.01, λ is the wave length of X-ray related to $K_\alpha Cu$, θ is diffraction angle, *K* is a shape factor and assumes a value of 0.9 for spherical particles and *W* is half-width of maximum peak [3]. Grains size were determined 200-300 A° for all samples that was a little more than reported value. Increased dopant concentration lead to increased grain size (table 1).

Table 1. calculated value of grain size for In(various wt.%) ZnO samples

Dopant concentration (wt%)	2	4	6	8
Grain size (A°)	229.8	245.4	265	284.1

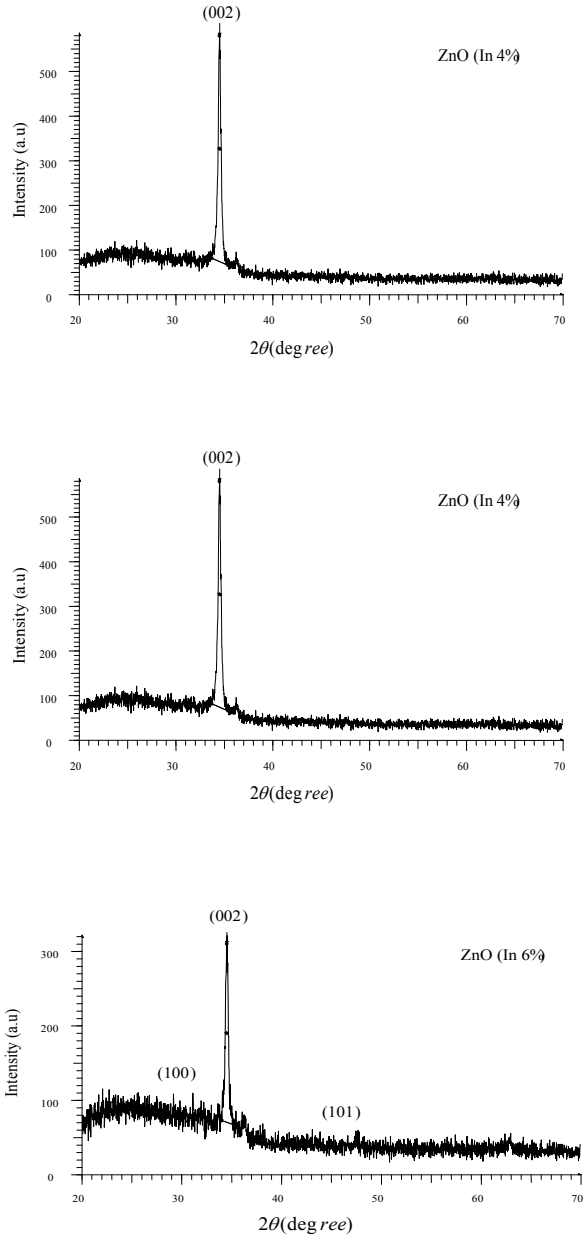

Fig. 1. XRD pattern of Indium (various wt.%) ZnO thin films

2- Optical properties

Some samples showed transmittance of 99.5% (In ,2 wt.% and ZnO in 540nm). There is no report for such a transmittance of ZnO films. High percentage of visual spectrum pass through films. The highest transmittance related to In (4 wt.%) ZnO sample.

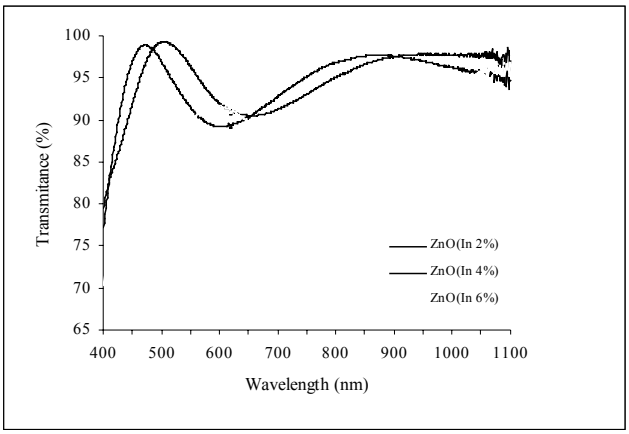

Fig. 2. Visual transmittance spectra for Indium ZnO thin film.

Increased dopant concentration reduces transmittance of samples. The reasons for reduced transmittance of visual spectra are incident diffraction caused by Indium atoms surrounded by ZnO (Indium atom a little larger than Zn) and crystal imperfection. film thickness was calculated by following equation (visual spectra between 400-1200 nm)

$$d = \lambda_1\lambda_2 / 2n(\lambda_1 - \lambda_2) \qquad (2)$$

where λ_1 and λ_2 are maximum and minimum wave lengths of transmittance spectra. Increased Indium percentage of solution leads to increased thickness deposited on sample (Table 2).

Table 2. calculated value of thickness for Indium (various wt.%) ZnO samples

Dopant concentration (wt%)	2	4	6
Grain size (A°)	272.9	329.7	721.6

Absorbance percentage was very high in UV region, in contrast to visual region. UV absorbance increased as increasing in sample thickness and Indium concentration.
The band gap value was estimated by extrapolation of the linear portion of $(\alpha h\upsilon)^2$ as a function of $h\upsilon$ ($h\upsilon = \frac{hc}{\lambda}$) using the relation $\alpha = 2.303\ \frac{A}{d}$, where α is absorption coefficient, A is absorption percentage (A= -Ln T) and d is thickness (Fig. 3 and Fig. 4).

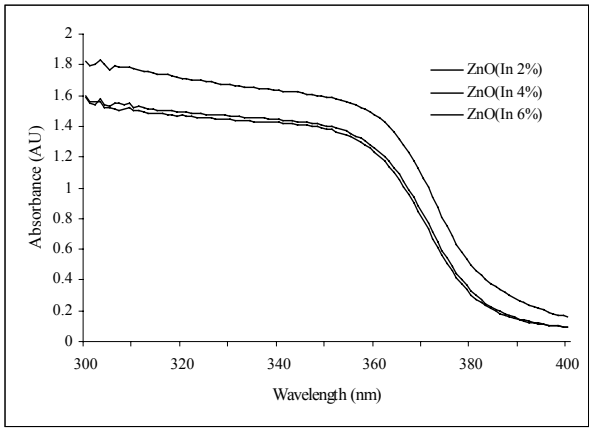

Fig. 3. UV absorbance spectra for Indium (various wt%) ZnO thin film

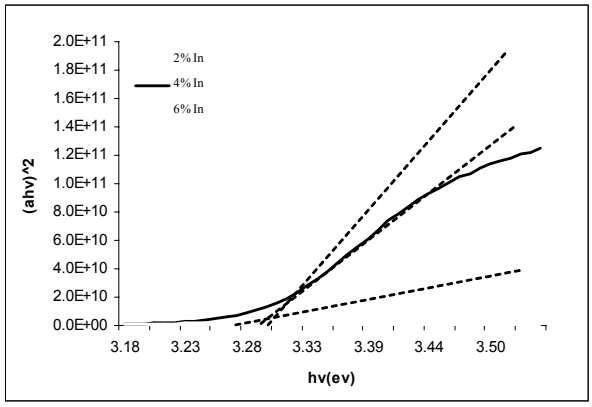

Fig. 4. Variation of $(\alpha h\upsilon)^2$ as a function of $h\upsilon$ for band gap calculating of Indium (various wt%)

The band gap value was found 3.2 eV. This value was similar to other reports [10]. It can be observed from Fig. 4 that band gap decreased with increasing dopant (Table 3).

Table 3. Band gap value for Indium (various wt.%) ZnO samples

Dopant concentration (wt%)	2	4	6
Band gap (eV)	272.9	329.7	721.6

3- Electrical properties

Pure ZnO is a well-known n-type transparent semiconductor and has a high resistivity. Adding

Indium impurity to semiconductor, it substituted by Zn (because of their similarity of ionic radius). Since Indium has one more electron than Zn, acts as donor impurity and creates an n-type semiconductor. Hall effect measurements certify this issue. This substitution lead to an increase of electron concentration and a very high decrease of electrical resistivity. So we have a semiconductor of high conductivity. Values in table 4 shows how surface resistivity decreases (less than half) with increasing of impurity percentage.
Increasing impurity (higher than 6%) lead to change n-type semiconductor to p-type. This phenomenon has not been reported so far. The reason of this changing might be a decrease in donor property of Indium following an increase of impurity. So Indium acts as acceptor impurity and substituted for Oxygen. Indium has 3 electron less than Oxygen and could absorb radical electron that lead to increased pores. Therefore, changing in carriers type resulted in changing of n-type semiconductor to p-type.
At the initiation of changing, decreased carriers lead to decreased resistivity, because the number of pores was few. But increase of impurity lead to increased carriers concentration, so that the least resistivity was observed at impurity of 32%.

Table 4. Calculated value for resistivity, carriers concentration and mobility for Indium (various wt.%) ZnO samples.

Dopant concent ratio	Surface resistivity	Special resistivity	Carriers concentratin	Mobility
0	5763.97	-	-	-
2	400.64	1.09E-2	-1.15E19	49
4	406.69	1.34E-2	-9.55E18	48
6	422.51	3.05E-2	-8.72E17	234
8	2175.81	-	-	-
16	1086.66	-	-	-
32	222.39	-	-	-

IV. Conclusion

Structural properties of IZO films shows a good growth at (002) peak in comparable with other peaks. Decreased half width of the (002) peak with increasing dopant concentration revealed that x-ray diffraction from grain boundary increased , that was aroused from increased grain size. Sample with lower amounts of impurity showed better Crystalline structure quality. High transparency (99.5%) was observed for samples with 2% dopant at 540 nm. Mean transparency of sample was higher than 90%. Non of samples showed transparency lower than 70%.
Considerable point in this research is that of converting n-type to p-type semiconductor with increasing impurity (higher than 6%).
Conductivity initially decreases as converting semiconductor and decreasing carrier concentration. But following the increasing impurity, the carrier concentration increases so that the lowest resistivity was observed with impurity of 32%.

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