Influence of Indium doping on Zinc oxide thin film prepared by Sol-gel Dip coating technique.

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Abstract

Dip coating is a very simple technique widely used for thin film deposition. We report the conducting and transparent In doped ZnO thin films with various levels of doping (0,1,5 & 10 wt %) fabricated by sol-gel dip coating method. XRD, UV-VIS, SEM and PL are used to characterize these films. X-ray diffraction studies show that films are polycrystalline in nature and have hexagonal wurtzite structure. These films are found to show (002) preferential growth at low Indium concentrations. An increase in Indium concentration does change the crystalline quality of films but higher intensity of films are found for higher Indium concentrations. Moreover, UV-VIS spectroscopy shows the influence of Indium incorporation on the visible range absorbance of ZnO. The optical band gap depends upon Indium doping and is found to be 3.75 for pure ZnO and 3.89 for Fe doped ZnO thin film. The PL spectrum of the samples shows blue emission.

Keywords: ZnO, ZnO: Indium, XRD; SEM; UV-Vis; PL.

1. Introduction

In recent years, most researchers in material sciences have been focusing on semi-conductors, materials with a wide band gap. One of them is ZnO which is multi- functional due to its non-linear optical properties. An II –VI group semi conductors' material ZnO has wide band gap (~3.37eV) at room temperature and large exciton binding energy ~60 meV (A. Ratkovich & R. L. Penn, 2009). Due to its unique optical, electrical and semi-conducting properties ZnO thin films are extensively used in various fields. The advantages of thin films and micro and nano- structures include abundance and non-toxicity of the ZnO material, low cost and quantum size effect (S. A. Kamaruddin et al. 2010). ZnO is considered a very promising functional electronic material due to its electric, optoelectric and luminescent properties (E. Bacaksiz et al. 2008). Transition metals like Fe, Co, Ni doped ZnO have a technological advantage just for their magnetic and electric properties of spintronic materials and optoelectronic devices. Many fabrication techniques are found in literature for fabrication of ZnO thin film (M.H. Mamat et al. 2010). The methods employed for thin film deposition can be divided into thin two groups based on the method of deposition process via, physical or chemical (M. Smirnov et al. 2010).The physical methods include physical vapor deposition, laser ablation, molecular beam epitaxy and sputtering (T. Sahoo et al. 2010). The chemical methods comprise gas-phase deposition methods and solution techniques. The gas-phase methods are chemical vapor deposition (CVD) and atomic layer epitaxy (ALE) (M. Dutta et al 2008), while spray pyrolysis, sol-gel, spin coating and dip-coating is based on solution techniques. Dip-coating is a technique being considered in research to prepare thick and thin films having many advantages so simple and relatively cost-effective processing technique and is generally used for thin film preparation.

2. Experimental details

2.1 Sol-preparation

Undoped and Indium doped thin films at different dopant percentage were deposited by sol-gel Dip coating method. The technique is most suitable for the preparation of oxide films. Aqueous solution of $Zn\ (NO_{3})_{2}.6.H_2O$ (.05M) was used. Doping was achieved by addition of Indium trichloride to the precursor solution and was stirred for 10 minutes at 85^{o}C.The concentration of Indium was varied at 0,1,5 and 10% in the initial solution.

2.2 Film preparation

Here glass slides are used which are ultrasonically cleaned with alcohol and the prepared sol was dipped on to the substrates. Dip-coating process was conducted in 10 steps and the withdrawal speed was 30mm/min.At each step films were dried at hot plate at 220^{o}C for 6 min. At the end of the process the films were calcined at 700^{o}C for 1 hour. The process film deposition is shown in figure below:

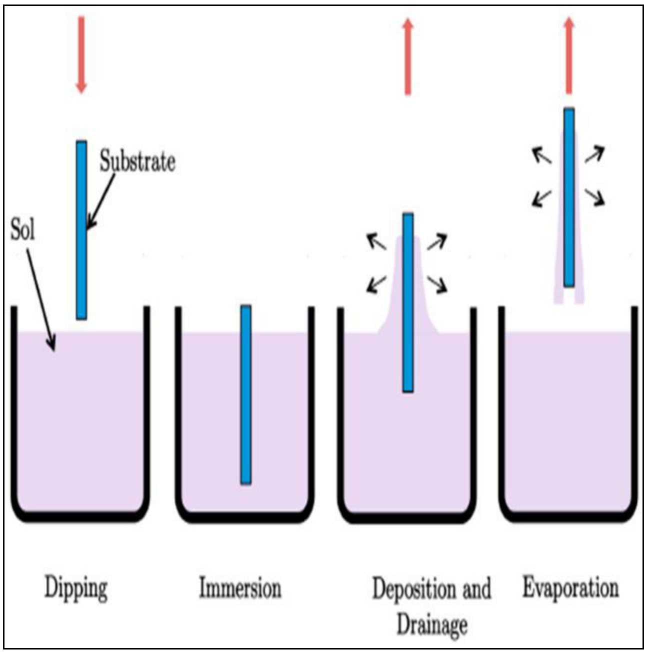

Figure1: Thin film deposition process by sol-gel dip-coating method.

3. Results and Discussion

3.1 Structural properties

3.1.1 X-Ray diffraction analysis

Figure(2) shows XRD analysis of pure ZnO and Indium doped ZnO (1, 5 and 10 at %) thin films grown on glass substrate at room temperature(RT).The main peaks of ZnO (100), (002) and (101) have a hexagonal wurtzite polycrystalline structure can be seen in all patterns. For all the samples (012), (110) and (013) peaks are also found. Strong preferential growth occurs along(100) for pure ZnO thin film On doping with Indium, it occurs at (002) for 1% and 5% Fe doped ZnO thin films. However, it occurs at (101) for 10% Indium doped ZnO. According to XRD analysis higher intensity of peaks are found as Indium concentration increased. To calculate average grain size we use shearer's relationship (A. Ratkovich & R. L. Penn, 2009).

$$Dav = K\,\lambda / \beta\cos\theta \qquad (1)$$

Where, λ is the wavelength of X-ray, β is the full width at half the maximum intensity (FWHM) of the peak, θ is the Bragg angle and K is the shape factor of the average crystallite which equal to 0.9.

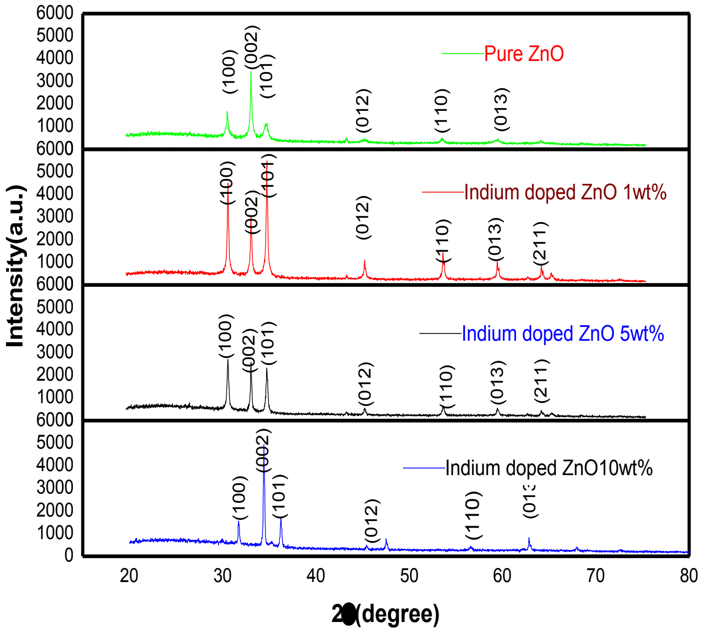

Figure 1: XRD analysis of pure ZnO and (1,5and10wt %) Indium doped ZnO thin films at room temperature.

Table1: Crystalline size of pure and Indium doped ZnO.

Indium concentration[%]	Crystalline siz[nm]	Lattice parameter=b [Å]	Lattice parameter c [Å]	Unit cell volume
0	23.04	3.2490	5.2078	47.70
1	21.37	3.2481	5.2074	47.66
5	20.41	3.2478	5.2070	47.62
10	19.59	3.2474	5.2068	47.58

3.1.2 Micro structural Analysis

The morphology of Indium doped ZnO thin films were observed by SEM.Figure shows SEM micrographs of pure and Indium doped ZnO thin films. Figure2 (a) shows Hexagonal structure with hexagons all over the plane surface. Figure 2(b). also shows hexagonal geometry with larger hexagonsFig2(c) shows spherical morphology with some rod-like structures.Fig2(d) shows distinguished spherical morphology with small spheres which are closely dense and packed. It is also noticed that grain size decreases on Indium doping.

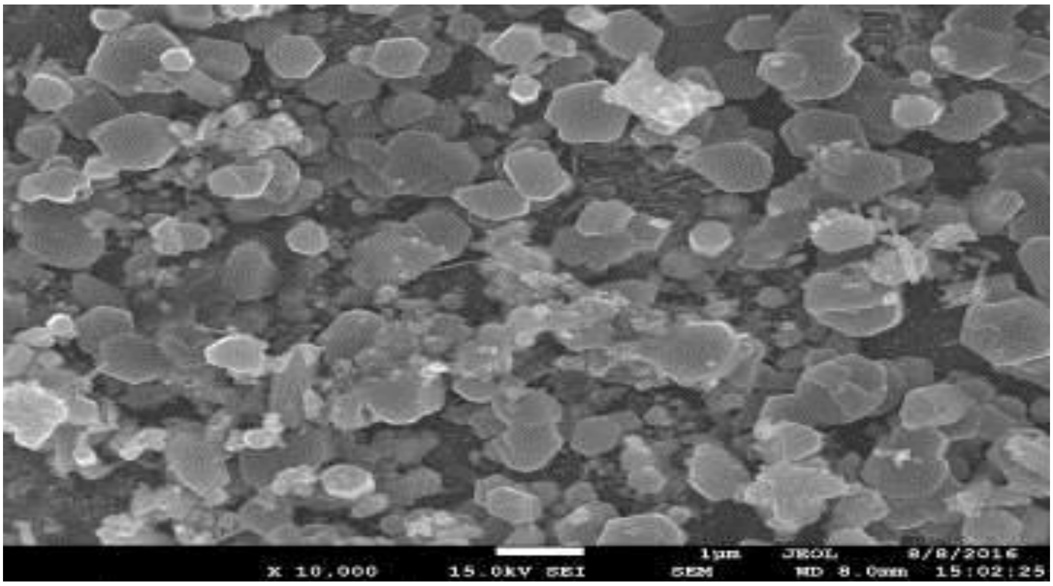

Fig. 3 (a) Pure ZnO

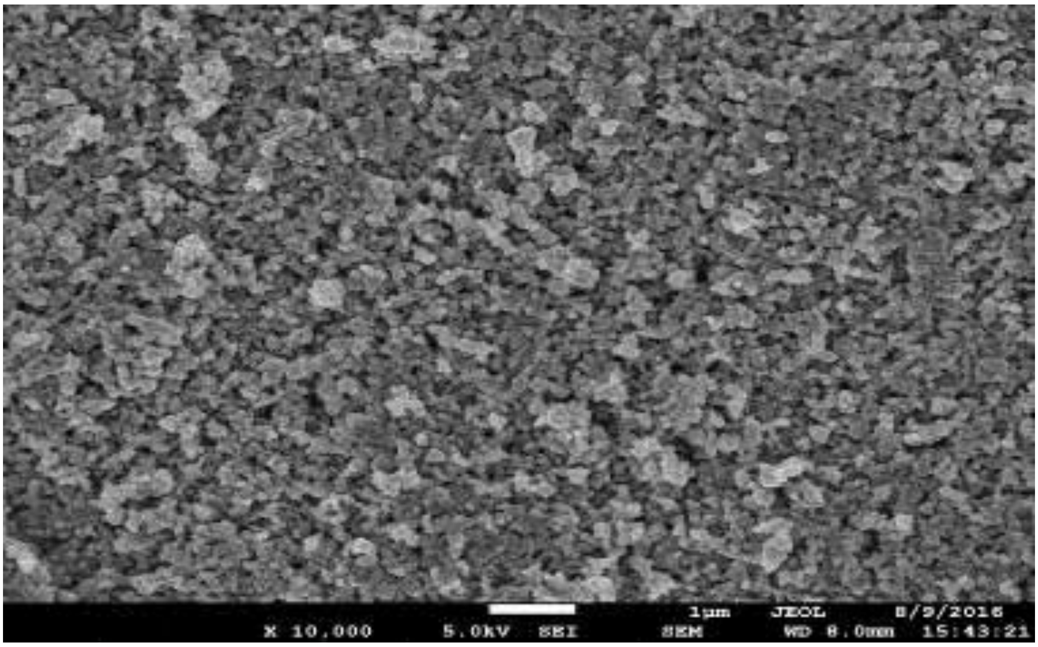

Fig. 3 (b) Indium doped ZnO 1 wt%

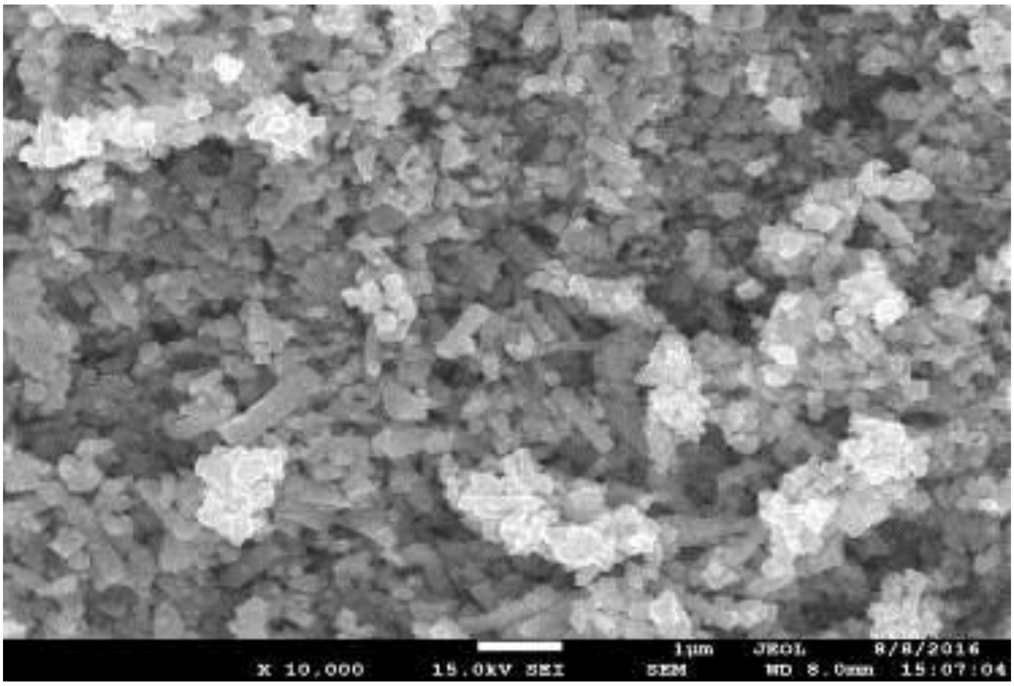

Fig. 3 (c) Indium doped ZnO 5 wt%

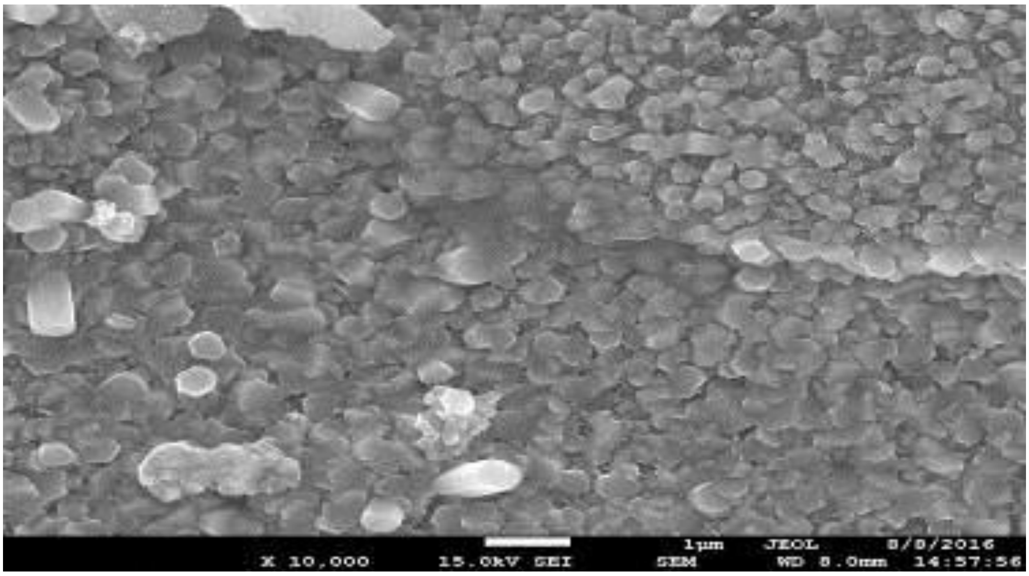

Fig. 3 (d) Indium doped ZnO 10wt%

Figure -3(a, b, c and d) shows SEM micrograph.

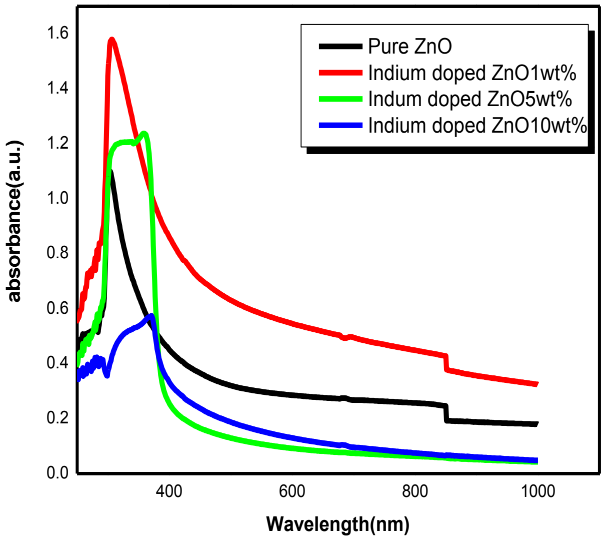

Figure-4: Absorption spectra of ZnO and Indium doped ZnO thin film.

4. Optical properties

4.1. UV-Vis Spectra

The UV-vis spectra of undoped and Indium doped ZnO thin films are shown in figure 4.The first one has peaked absorbance at 304 nm which can be attributed to the transition of electrons from the valence band to the conduction band of ZnO ($O_{2p} \longrightarrow Zn_{3d}$) (C.Gumus et al 2006). The addition of Indium ions shifted this peak to 306 nm for 1%, to 318nm for 5% and 330nm for 10% Indium. This red shift observed at the edge of the absorption spectrum is a clear indication of the Indium incorporation into the ZnO matrix (S. Fujita and K. Kaneko, 2014). The red shift may occur due to the strain caused by Indium doping and the change in the band structure of ZnO. The optical band gap is found to be 3.75 for pure ZnO and 3.89 eV for 10% Indium doped ZnO.

4.2. Photoluminescence study

Photolumniscence spectra of pure ZnO and Indium doped ZnO thin films have been shown in figure: 5. In PL spectrum a strong UV peak occurs at 394nm due to free exciton transition with two visible peaks at 454nm and 487nm for pure ZnO. On Indium doping at 1% four peaks is observed, two UV emission peaks at 394nm and 422nm and two blue emission peaks with larger intensity. Also on increasing the doping concentration UV emission peak and blue emission peaks are observed .However intensity varies for 5% and 10% Indium doped ZnO. The best result is obtained for 10% indium doped ZnO thin film.

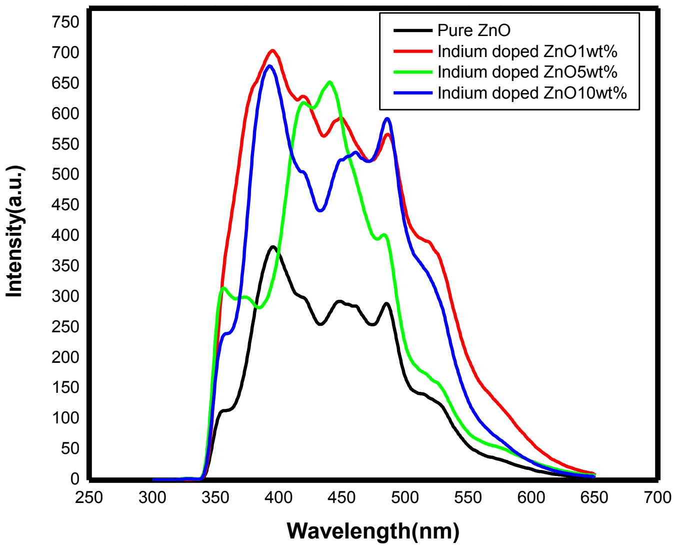

Figure-5: Photolumniscence study of pure and Indium doped ZnO.

5. Conclusion

In this work, structural and optical properties of Indium-doped ZnO thin films prepared by sol-gel dip coating method have been investigated .Based on the research results of Indium doped ZnO thin films reported by us and other groups ,it is considered that valence state of indium plays a great role in the variation of properties of ZnO thin films. The XRD analysis results of our experiments shows that all films have hexagonal wurtzite structure. UV-Vis spectra of ZnO thin films shows that 1 at %. Incorporation can improve the crystalline quality and ultraviolet emission of ZnO thin film i.e., More Indium incorporation Detroiters the crystalline quality.

Considering the structural and optical properties, the fabricated Indium doped ZnO thin film prepared by cost effective method, dip- coating can be used as a suitable material for optoelectronic applications.

6. Acknowledgement

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