

Review on Synthesis of ZnO Doped with Metal Composites and Its Structural Properties by Sol-gel Technique

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ABSTRACT

ZnO is a material having unique structural, optical and electrical properties doping level, The c-axis lattice parameter shifts towards higher values with increase of manganese content in the film. The first part of this paper represents the synthesis of ZnO thin film by sol-gel technique and study of its structural properties by XRD. The next part of this review presents the influence of Mn, In doping on structural properties of ZnO by XRD studies. XRD study shows that all film prepared in this work have wurtzite structure with lattice constants $a=b=3.260\text{\AA}$ $c=5.214\text{\AA}$. The doped films are found to show (002) preferential growth at low Indium concentrations. An increase in Indium concentration causes a decrease in crystalline quality of films as confirmed by XRD technique. The XRD spectra of Mn doped ZnO also show that all samples have hexagonal wurtzite structures. The doping favours c-axis orientation along (002) planes upto 5% of Mn.

Keywords: ZnO, Mn, In, XRD

1. INTRODUCTION

A thin film is a layer of material ranging from fractions of nanometer to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefitting from thin film formations [1]. One of the most wideband gap semi-conductors that draw worldwide attention of researchers is ZnO [2]. The unintentional n-type compared with hexagonal wurtzite structure possesses unique properties such as high electrochemical stability, resistivity control transparency in the visible range with a wide bandgap and high quantum yield. These appealing properties are utilized in a wide range of applications including stimulated emissions with high optical gain and loss [3]. There are many reports in literature describing the preparation of ZnO thin films by variety of techniques including PLD, RF magnetron sputtering, chemical vapour deposition

(CVD), spray pyrolysis [4,5]. Metal doped ZnO has the potential to be multifunctional material with coexisting optical, semi-conducting and magnetic properties. The interest in doping ZnO is to explore the possibility of improving these characteristics. Doping of metal into ZnO allows the creation of sub-energy levels in the bandgap to make use of it as UV detectors and light emitters. ZnO was doped with Mn, In, Al, Ca, Fe etc. for electrical and optical applications. In the present paper we present the effect of Mn and In doping on ZnO thin film.

The effect of In concentration on the structural, morphological, electrical and optical properties have also been studied. These films are found to show preferential growth at low Indium concentrations. An increase in Indium concentrations causes a decrease in crystalline quality of films as confirmed by XRD technique which leads to an introduction of defects in ZnO.

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For low concentration Mn doping, the reduction in bandgap has theoretically explained as the consequence of exchange interaction between the d-electrons of transition metal ion (Mn) and s and p electrons of the host band. For higher concentration (>3mol%) Mn doping, the augmentation is due to large bandgap of Mn (4.2eV)[6]. Similarly the effect of other metal on ZnO have been studied and results are obtained for their structural properties by XRD technique.

2. BRIEF DESCRIPTION FOR SYNTHESIS OF ZNO THIN FILM BY SOL-GEL TECHNIQUE

2.1 Experimental Details

All the reagents used in the present work for the chemical synthesis were of analytical grade. Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was first dissolved in a 2-methoxyethanol ($(\text{CH}_3)_2\text{CHOH}$) with mono ethanolamine (MEA: $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) which was used as a stabiliser. The molar ratio of MEA to zinc acetate was kept to 1.0 and concentration of zinc acetate was 0.80 mol/l. The resultant solution was stirred at 60°C for 1 h to yield a clear and homogeneous solution ready for coating. The coating was performed with freshly prepared solution. The films on ultrasonically cleaned quartz substrates were prepared using spin-coating unit which was rotated at 3000 rpm for 30 s. The films were preheated (baked) at temperature 250°C for 5 min in a furnace to evaporate the solvent and remove organic residuals. The spincoating to preheating procedure was repeated ten times. The films were then post-heated (annealed) in air at 400°C for three hour. The phases of ZnO thin film were determined by X-ray diffraction, using Panalytical Diffractometer type PW3710 with Cu Ka radiation ($\lambda = 0.154 \text{ nm}$).

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Analysis

The XRD pattern of ZnO thin film fabricated by sol-gel method on quartz substrates is shown in Figure 1. All the peaks of the ZnO thin films correspond to the peaks of standard ZnO (JCPDS S6-314). For all the samples, (100), (101) and (002) diffraction peaks are observed in the XRD pattern, showing the growth of ZnO crystallites along different directions. Strong preferential growth is observed along (002) plane indicating that the films are oriented along c-axis [7]. The typical hexagonal wurtzite structure of thin films is inferred from the XRD pattern. The crystallites sizes (D) of the films are estimated using the Scherer formula [8] $D = K\lambda / \cos\theta$, Where K constant is wave length of X-Ray λ is FWHM.

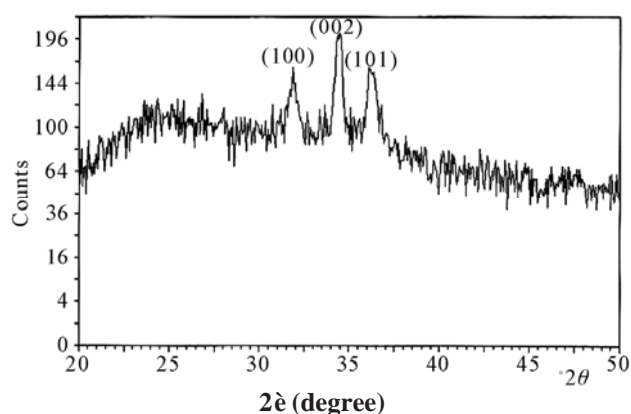


Fig.1. XRD pattern of ZnO Thin Film

3.2 Effect of Indium and Mn Doping on Structural Property of ZnO by XRD:

The XRD pattern has been recorded in the 2θ range of 30-40, where the peak of hexagonal wurtzite type Indoped 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; we analyzed the structure of the samples basing on XRD. Figure 2 shows their XRD patterns.

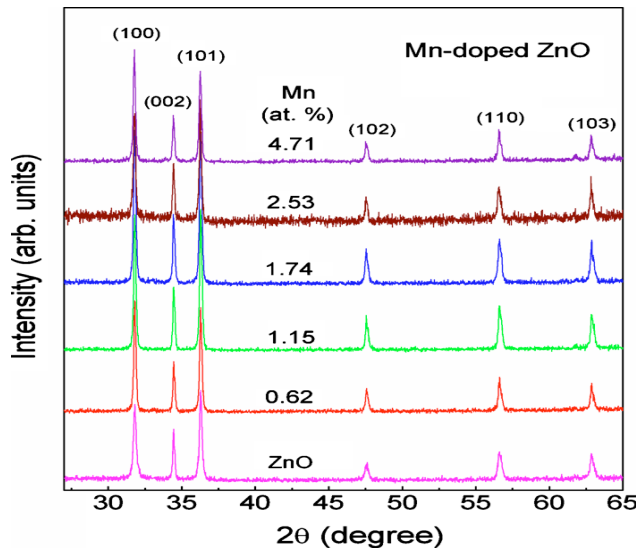


Fig.2. Color online_ XRD patterns of the Mn-doped ZnO

All the samples are single phase in the ZnO wurtzite structure and the presence of Mn did not lead to the formation of manganese-related secondary phases. This result was also confirmed by selected-area electron diffraction patterns where no extra diffraction spots beyond those of the ZnO structure from secondary phases were found. Having paid attention to the position of XRD peaks, we observed their slight shift toward smaller diffraction angles. Here, the slight shift in XRD peaks could be explained as follows: the Mn concentration decreases along the depth of the diffused samples, and decreases from the surface to the core region of one single nano rod, as mentioned above. The regions with low Mn concentrations would not cause a remarkable shift in XRD peaks. Only regions with high Mn concentrations cause this shift. It is assigned to the substitution of Mn^{2+} for Zn^{2+} in the ZnO lattice because the ionic radius of Mn^{2+} 0.80

Å is greater than that of Zn^{2+} 0.74 Å. The lattice parameters a and c obtained for the pure ZnO sample are about 3.246 Å and 5.212 Å, respectively, while those for the 4.71 at. % Mn-doped sample are about 3.253 Å and 5.238 Å, respectively. This small difference in lattice parameters proves one part of Mn dopants located at interstitial sites, which act as extrinsic defects and contribute to the broadening of the XRD peaks. The XRD line width of the 4.71 at. % Mn-doped sample obtained is about 18.7% greater than that of the pure ZnO sample.

4. CONCLUSION

We have grown ZnO thin film on quartz substrate by sol-gel technique with 0.8M Zinc acetate by solutions. Film has been characterized using structural measurement. The XRD analysis revealed that all samples have wurtzite hexagonal structure. The crystallites sizes as measured using XRD are found to be the range of 18-24 nm.

In doped ZnO samples are (002). The preferentially oriented although orientations become lower as the In concentration increased implying that doping with In lead to an introduction of defects in ZnO Crystals.

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