STRUCTURAL AND OPTICAL STUDIES OF Mn-DOPED ZnO NANOCRYSTALLINE THIN FILMS

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Abstract

In the present work Pure and Mn-doped Zinc oxide, thin films were synthesized using the spray pyrolysis technique for pure and 5% Mn doping. All the films have been prepared on the preheated glass substrates up to 400ºC temperature. The solutions used to prepare pure and Mn-doped ZnO films contained 0.1 M of zinc acetate and 0.1M manganese acetate. The effect of Mn doping on structural properties has been investigated. The results of XRD showed all the deposited films are polycrystalline hexagonal wurtzite structure with preferred orientation of (002) direction. From the XRD results, it is observed that doping with Mn does not change the crystal structure of ZnO. Average crystalline sizes of films were found to be in the range of 35 nm to 53 nm. It means that an Increase in Mn concentration leads to an increase in the crystalline size of the films. The absorption spectra at room temperature revealed the optical properties of the films. From the spectra, it is observed that the band gap of Mn-doped ZnO thin film is greater than pure ZnO thin film.

Keywords: Mn-doped ZnO thin film, spray paralysis, X-Ray diffraction, optical properties.

1.INTRODUCTION

Zinc oxide thin films are promising materials as it is low cost, non- toxic and highly durable in nature. Zinc oxide has a large exciton Binding energy of ~60 meV [1]. Wurtzite zinc oxide (ZnO) is extremely multifunctional material with distinct properties and has a wide range of promising applications. Zinc oxide is a direct band gap (3.37eV) II-VI compound semiconductor with n-type conductivity. Due to its wide band gap and high exciton binding energy [2] it has been largely used for Lasers[3], gas sensors[4], Blue LEDs[5], thin film transistors[6], Transparent Conductors,[7], Solar cells[8], Photocatalysts [9]. Optical and electrical properties of ZnO are remarkable than other metal oxide semiconductors, due to this it has been used as an optoelectronic sensor [10-11].

Doping metal oxide semiconductors with different chemical elements have been found to influence their physical properties. Pure ZnO thin films have limitations in their applications but by varying the doping concentration one can observe drastic improvements in the structural, electrical & optical properties of thin films. Adding impurities like manganese, Iron, cobalt, nickel, Copper [12-16], etc. showed some modifications in the properties of ZnO thin films. Among these transition metals, Mn doping has an advantage because of several reasons including its high moment and small ionic radii difference between Mn^{2+} and Zn^{2+} [17], etc.

Several methods are to be adopted for the preparation of zinc oxide thin film such as chemical bath deposition [18], Spray Pyrolysis [19], sol-gel [20], sputtering [21] and SILAR [22]. Among these methods spray Pyrolysis method is used for thin film deposition because it is a low-cost method and suitable for the large production area. The present paper deals with the study and synthesis of Mn-doped ZnO thin films by using spray Pyrolysis techniques. As this technique is suitable for doping films with transition metals by simply adding it in the form of spray solution. For deposition, we are using a glass substrate as it is an inexpensive and easily available substrate. During the deposition, several parameters were adjusted such as substrate temperature, flow rate, nozzle to substrate distance, etc. Finally, structural and optical properties of the resulting films such as Crystal Structure, Crystalline Size, optical transmittance, Energy band gap, etc have been studied by X-ray diffractometer and UV-Visible spectrophotometer.

2. EXPERIMENTAL

$Zn_{1-x}Mn_xO$ films were grown on the glass substrate by spray pyrolysis technique. The solution of 0.1M Zinc acetate dehydrate [Zn $(Ch_3Coo)_2.2H_2O$] was prepared in double distilled water and manganese acetate was used as a doping agent. Manganese acetate was added in such a way to achieve an atomic concentration of 5%. Before the deposition all the glass substrates were properly cleaned by using detergent solution and then with distilled water. Along with this, the substrates were placed in warm water on a hot plate for 10 minutes and then rinsed it with acetone.

The spray pyrolysis machine initially wiped out by using acetone where the cleaned substrates had to keep. Spray machine has an output nozzle of about 1mm. the carrier gas (compressed air) was maintained at a pressure of 30psi, the distance between nozzle and substrate was about 18 cm which was kept constant throughout the deposition, the solution flow rate was about 1.5ml/min. All the films were deposited on preheated glass substrates at a temperature of 400°C. After the deposition, the films were allowed to cool at room temperature. The thickness of samples was measured by using the weighing method and noted down. Optical transmittance and absorbance were recorded using UV-VIS spectrophotometer in the wavelength range of 350nm to 1000nm. The crystallinity and phase of Mn-ZnO films were analyzed by using X-ray diffractometer.

3. RESULT AND DISCUSSION

3.1. Structural characterization:

Fig.1. shows a X-ray diffraction pattern for the pure and Mn-doped ZnO thin film. The diffraction peaks intensities correspond to the planes such as, [100], [002], [101], [110], [102], [103] and [112] were observed which indicates that all the deposited film exhibits hexagonal wurtzite crystal structure. No any extra peaks related to crystal phases of Mn metal were observed which indicates all the films are single phase. The lattice parameter of 'a' & 'c' of the deposited film was calculated by using,

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

Where, $d_{h,k,l}$ is an Interplanar spacing distance, h, k, l are Miller indices, a and c are Lattice parameters

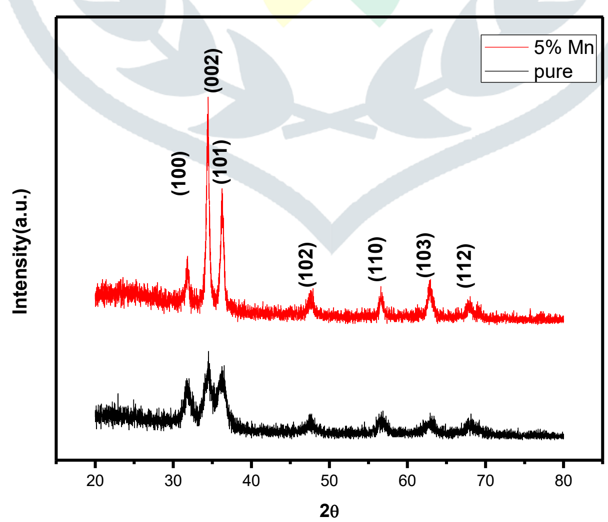

Figure 1: **XRD graph for Mn doped ZnO thin films**

The values of the calculated lattice parameters are listed in the table (1). The lattice parameter goes on increasing with increasing Mn concentration. Since Mn^{+2} ions have a higher ionic radius as compared to the Zn^{+2} ions. The change in lattice parameter is related to strain present in Mn–ZnO thin films. From the lattice parameter, we have calculated the strain present in the ZnO thin films using formula,

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad \text{.......................} \quad (2)$$

Where, β is the full-width half maxima.

The strain present in the ZnO and 5% Mn-doped ZnO were tabulated in a table (1). As Mn is doped in ZnO, the strain decreases, it indicates that Mn is properly incorporated in ZnO. The average crystallite size of pure and Mn-doped ZnO films was calculated by using Scherrer formula as,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{.......................} \quad (3)$$

Where, D is the Crystalline size, K is the Shape factor (0.94), λ is the wavelength of Cukα radiation, β is Full-width half maxima, θ is an angle of diffraction. The average crystalline size found in the range of 35nm to 53nm. Distortion parameter, the volume of a unit cell of the pure and Mn-doped ZnO calculated from the XRD data, it is observed that all the parameters increase with doping of Mn in ZnO.

Table 1: Structural Parameters of pure and Mn doped ZnO thin films

Samples	a (Å)	c (Å)	u parameter	$V(Å)^3$	ε	D (nm)
Pure	3.2448	5.2045	0.3795	47.4553	0.003621	34.9664
5%	3.2476	5.2090	0.3798	47.5784	0.002410	52.4602

Table: 1 XRD analysis.

3.2. Optical Properties:

Figure (2) shows optical transmittance spectra for the pure and doped Mn films deposited onto the glass substrate. From the graph it is observed that, in the visible region pure ZnO has optical transmittances greater than 55% and by introducing manganese the transmittance as increased above 60%.

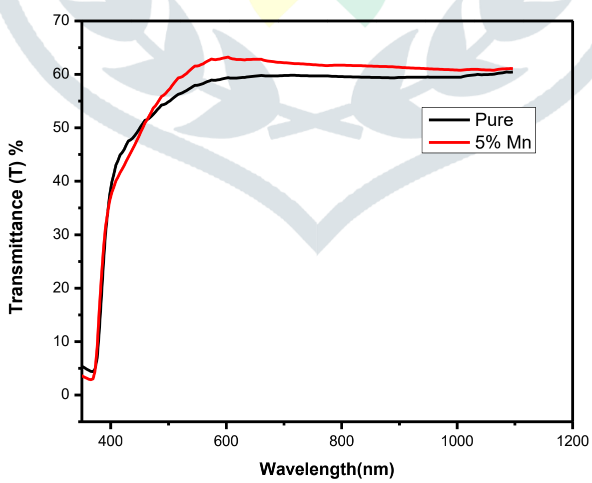

Figure 2: Optical Transmittance spectra of pure and Mn doped ZnO thin films

In addition, Optical properties of pure and Mn-doped ZnO film can be studied by using UV- visible spectrophotometer. The optical absorbance spectra of pure and Mn-doped ZnO film were recorded in the range 350nm to 900nm. The curve of absorbance versus wavelength is plotted in figure 3, shows an absorbance edge shift towards lower wavelength as Mn-doped with ZnO.

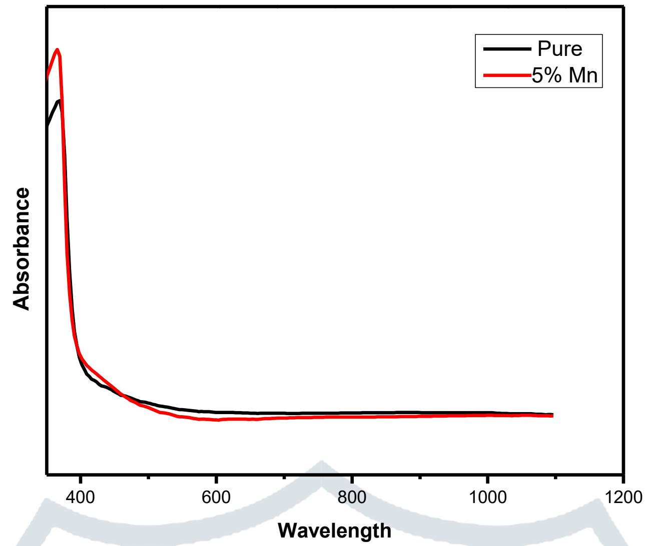

Figure 3: Optical absorbance spectra for the undoped and Mn doped ZnO thin films

Doping of Mn influencedthe band gap of ZnO, The optical band gap energies of the deposited film determined by the graph of $(\alpha h\nu)^2$ against photon energy using the following relation,

$$\alpha h\nu = A\,(h\nu - E_g)^{n/2} \quad \ldots\ldots\ldots\ldots (4)$$

Where, α is an absorption coefficient, A is Constant, Eg is the band gap of the material. For the direct band gap material n = ½. The optical band gaps of the material were determined by intercept of this plot on the energy axis. The values of optical band gaps are3.2227eV for pure ZnO and for 5% Mn it is 3.2940eV which indicates that the band gap of Mn doped ZnO increases. The band gap values of Mn-doped ZnO films increased due to the Burstein–moss effect. Figure 4, shows an optical band gaps of pure and Mn doped ZnO thin films. The variation in the band gaps reveal that the optoelectronics properties of materials can be changed by doping with Mn in ZnO.

The R.I of deposit film were calculated by using the relation,

$$\frac{n^2-1}{n^2+1} = 1-\sqrt{\frac{E_g}{20}} \quad \ldots\ldots\ldots\ldots (5)$$

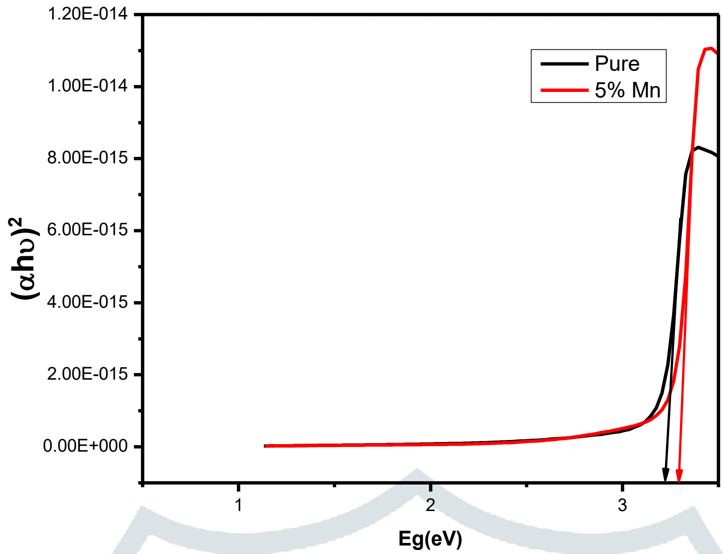

Figure 4: Relation between $(\alpha h\upsilon)^2$and (Eg) for pure and Mn doped ZnO thin films

Table 2: Energy bad gap and Refractive index of pure and Mn doped ZnO

Samples	Refractive index	Bandgap (eV)
Pure	2.00259	3.2227
5%	2.01317	3.2940

4. CONCLUSION

Pure and Mn-doped ZnO films were deposited onto a glass substrate with temperature 400°C using spray pyrolysis technique. The pure and Mn-doped ZnO thin films are polycrystalline hexagonal wurtzite structure with preferential growth in the (002) plane. It is observed that crystalline size, volume, and lattice parameters are increased as the Mn dopant is introduced in the ZnO lattice. Also, the strain is decreased with Mn introduction. Optical transmittance is found to be greater than 60% for 5% Mn doping concentration and it is in the visible range and it is found to increase with the addition of Mn dopant as compare to undoped ZnO. The optical energy band gap of ZnO thin films increased from 3.2227eV to 3.2940eV for 0% and 5% Mn doping respectively. In addition, the refractive index is found to increase with Mn doping. All these conditions make these thin films promising to be used for solar cell and gas sensing applications.

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