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Preparation and Characterization of Mn Doped Zno Nanoparticles

P. Thamaraiselvan*[1], S. Kannan[1], P. Gowthaman[2], M. Kutraleeswaran[2]
[1]Selvamm arts and Science College, Namakkal, TamilNadu, India
[2]Thin Film Centre, Department of Electronics, Erode Arts and Science College, Tamil Nadu, India

ABSTRACT

The Mn doped ZnO thin films were deposited on glass substrates by dip coating method. Characterization techniques of XRD, SEM, UV-visible spectra measurements and VSM were performed to investigate the structural, optical and magnetic properties. ZnO thin films were prepared with three different growth time of 3, 4 and 5 hours at 100°C. Manganese (Mn) was doped with the prepared ZnO thin film in three different growth layer concentrations (0.01,0.02 and 0.03mol). In Mn doped ZnO, as the concentration of manganese increases, the ferromagnetic behavior decreases.

Keywords: ZnO thin film, Dip coating, Manganese , VSM.

I. INTRODUCTION

ZnO materials have attracted a great deal of attention due to their potential applications in optoelectronics and spintronics[1-4]. ZnO has a large exciton binding energy of ~60 meV[5].which make it superior for applications in light-emitting-diodes (LED) and laser diodes (LD). ZnO has also been both theoretically predicted [6, 7] and experimentally proved [8] to be a high Curie temperature (*TC*) diluted magnetic semiconducting (DMS) material when doped with transition metals. All these fantastic properties of ZnO need to be achieved and demonstrated by *doping*, a kind of technique to "magically manipulate" the behavior of ZnO by adding a small amount of dopant atoms into ZnO. The present chapter gives detailed experimental results of the magnetic and optical properties of manganese doped ZnO nanorods, especially the temperature and magnetic field dependence of structural and morphological properties.

Recently, Zinc Oxide (ZnO) has been widely studied for its attractive applications in ultraviolet light-emitting diodes and laser diodes, because it has a direct band gap of3.37 eV at room temperature and a large exciton binding energy of 60 meV[9]. Mn doped ZnO (Mn: ZnO) is an extremely important material for its co existing magnetic, semiconducting and optical properties [10]. Mn: ZnO is regarded as promising material for spintronics applications as it shows room temperature ferromagnetism [11].

It has also been utilized as a material for the manufacture of solar cells, transparent electrodes, gas sensors, varistors of a dilute piezoelectric transducers, etc, due to its behavior of dilute magnetic semiconductor (DMS) [12]. However the micro structural effects of Mn doping in ZnO thin film are not well established.

II. EXPERIMENTAL TECHNIQUE

The Mn doped ZnO thin films were grown on ZnO seed coated glass substrates by hydrothermal technique. The magnetic property of the growth layer with Mn was further characterized by using VSM study.

A. Hydrothermal Technique

All chemicals applied were of analytical grade and supplied by Merck Co.Ltd.ZnO growth layer was prepared by adding 10 ml of de-ionized water, 0.118gms of Zinc Nitrate $Zn(NO_3)_2$and 0.560gms of hexamethylenetetramine $(CH_2)_6$ $N_4$and mixed well by magnetic stirrer for 1 hour. 0.01, 0.02 and 0.03mol of manganese (Mn) was added with 10ml of de - ionized water separately and stirred for 1 hour. The chemical composition is given in table.

Table 1. Chemical Composition Of Zno Growth Layer Solution With Mn Dopants

Chemical Name	Chemical formula	Mole required	Material taken
Zinc Nitrate	$Zn(NO_3)_2$	0.02 mol	0.118988 grams
Hexamethylenetetramine	$(CH_2)_6$ N_4	0.2 mol	0.56076 grams
De-ionized water	H_2O	---	10 ml
		0.01mol	0.010988 grams
Manganese	Mn	0.02mol	0.021976 grams
		0.03mol	0.032964 grams

ZnO growth layer solution (10 ml) was individually mixed into manganese mixture and stirred for 2 hours. In the growth process the above solution was taken in a beaker with seed coated substrates and heated in hot air oven at 100°C for three different growth periods of 3 hours, 4 hours and 5 hours. At the end of the growth period, the substrates were removed from the solution and immediately rinsed with de ionized water to remove the residuals from the surface and dried in air at room temperature. Then the above films were annealed in muffle furnace at 500°C for 1 hour. The crystal structure and morphology of Mn doped Zno nanorods were investigated by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM).

The absorbance spectra have been recorded using a spectrophotometer JASCO V-570. The magnetic properties were studied using VSM.

III. CHARACTERIZATION OF ZNO NANORODS WITH MN

The Surface morphology and Optical characterization of the thin films were carried out by scanning electron microscope with EDX, UV–Vis spectrophotometer and magnetic properties of the Mn doped ZnO thin films were measured using Vibrating Sample Magnetometer (VSM).

IV. RESULTS AND DISCUSSION: STRUCTURAL PROPERTIES

A. XRD Analysis

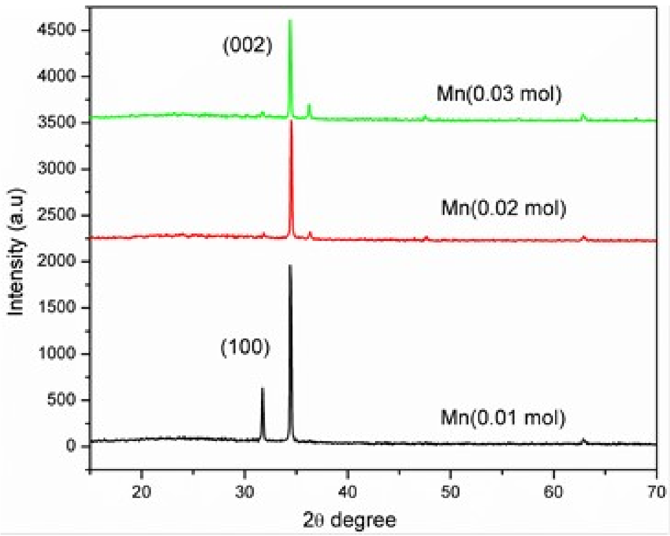

Figure 1. XRD patterns of Mn doped ZnO thin films

Figure 1 shows the XRD patterns of Manganese doped ZnO thin films in three different molar concentrations of 0.01mol, 0.02 mol and 0.03mol. From the XRD patterns it is clearly seen that, as the concentration of manganese increases from

0.01to0.03mol the strength of the (002) diffraction peak is decreased. In 0.01mol manganese concentration, very low (100) peak and very strong (002) peak is observed. As concentration increases from 0.01to 0.02mol, (100) peak is not seen and (002) peak is suppressed. As again manganese concentration increased to 0.03mol, the (002) peak is still suppressed. Hexagonal wurtzite structure was observed in the annealed films. Since wurtzite structure is non-Centro symmetric, it is more favorable for inducing and studying magnetism in any material [13].

V. MORPHOLOGICAL STUDIES

B. Scanning Electron Microscopy (SEM)

The SEM images of the ZnO doped with different concentration (0.01, 0.02 and 0.03)mol of Mn were given in Figure 2(a), Figure 2(b) and Figure 2(c).Many rod-like hexagonal structures can be clearly seen.

The SEM images of the manganese doped ZnO were given in Figure 2 with different concentrations of 0.01, 0.02 and 0.03 mol. In the SEM image of 0.01 mol manganese concentration, the hexagonal structured nano rods were seen clearly. As the manganese concentration increased from 0.01 mol to 0.02 mol, the width of the nanorods was decreased. As the manganese concentration again increased from 0.02 to0.03mol, the width of the nanorods was further deceased and number of rods was increased. Figures show the SEM images of a Mn doped ZnO film. The SEM images of ZnO resemble a granular surface. The incorporation of Mn ions changed surface morphology to a wrinkle network. The crystalline nature of films was affected due to the enhancement of dopant concentration by which more impurities were included in the ZnO crystal [14,15].This SEM images were in accordance with the XRD results which indicates that, as c-axis orientation decreased the size of the nanorods were decreased

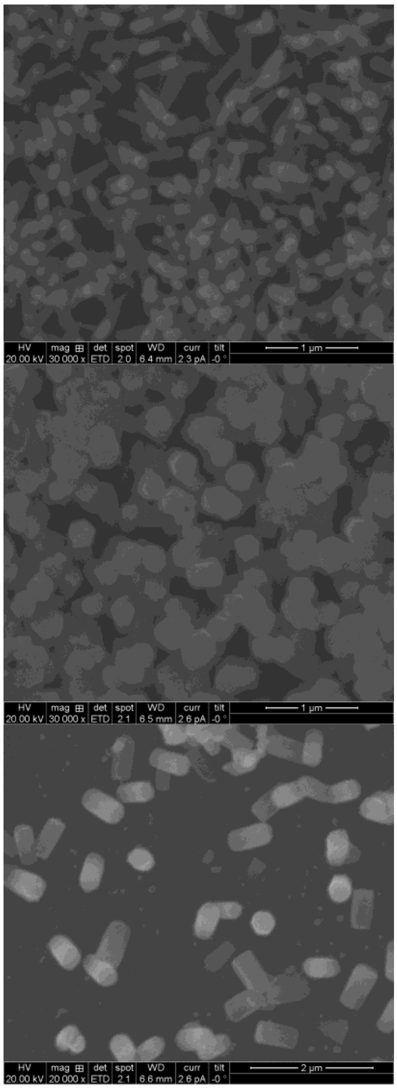

Figure 2. (a) 0.01 mol Mn (b) 0.02 mol Mn and (c) 0.03 mol Mn SEM spectrum of manganese doped ZnO

C. Energy Dispersive Analysis of X-rays (EDX)

The EDX spectroscopy was used to know the percentage of the element present in the sample. The ZnO thin films were prepared using three (0.01, 0.02 and 0.03mol) different concentration of Mn. From the obtained data of EDX 0.01mn shown that the Zn, O and Mn were present in the thin film were 89:7.5:3.5 percentages respectively. The EDX results of 0.02 Co shows that the ZnO and Mn present in the thin film were of 90:6.0:4.0 percentages respectively and the EDX results of 0.03Mn shows that the Zn, O and Mn were present in the thin film were of 62:27:11 percentages respectively. EDX figures are shown in fig. 3

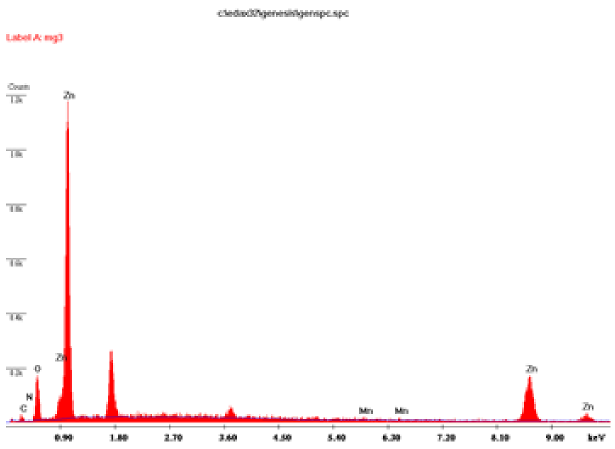

Figure 3. EDX spectrum of (0.03 mol) manganese doped ZnO

Table 2. Data Of Edx Spectrum Of 0.03 Mol Manganese Doped Zno

Elem	Wt %	At %	K-Ratio	Z	A	F
C K	8.88	21.56	0.0185	1.1389	0.1829	1.0004
N K	0.57	1.19	0.0015	1.1273	0.2400	1.0011
O K	26.67	48.60	0.1158	1.1168	0.3883	1.0013
MnK	1.92	1.02	0.0188	0.9212	0.9963	1.0668
ZnK	61.96	27.63	0.5610	0.9033	1.0024	1.0000
Total	100.00	100.00				

VI. OPTICAL PROPERTIES

D. UV –VIS Absorbance and Transmittance

Figure 4. shows the absorption spectra of manganese doped Zno nanorods. The optical absorption edge has a tendency to shift to an upper wavelength with increase in manganese concentration. The intensity of the optical absorption edge is low when manganese concentration is at 0.01 mol. When the concentration is increased to 0.02 mol, the intensity of the absorption has-been increased to a very large extent. Again when the concentration of the manganese is increased to 0.03 mol, again the intensity gets increased. From the results, as manganese concentration is increased the intensity of the absorption also gets increased.

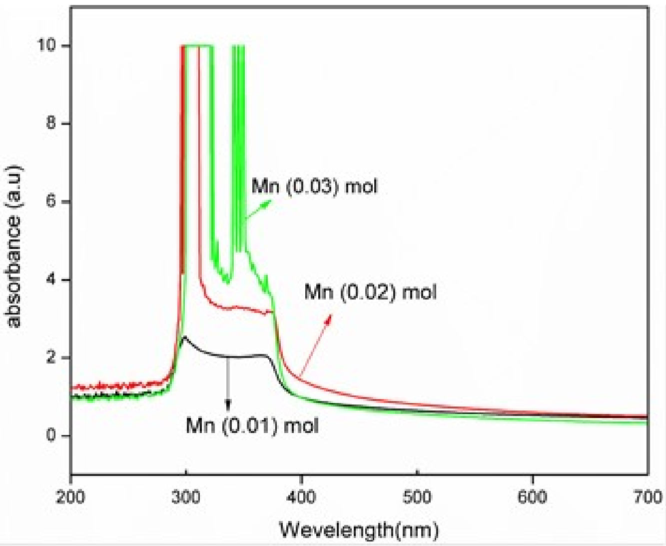

Figure 4. UV-Vis absorption spectra of Manganese doped ZnO

Figure 5 shows the optical transmittance spectra of samples with three different growth molar of manganese doped ZnO with 0.01 mol, 0.02 mol and0.03 mol, annealed at a constant temperature of 500℃ for 1 hour. The effect of change in the manganese concentration on the optical transmittance was investigated. A slight decrease in average transmission was observed with the increase of manganese molar concentration and was attributed to the increase of surface roughness. The optical transmittance of Mn doped ZnO film was found to decrease from 70%, 60%, to 45% with the increase of manganese concentration. From the above figure, it is clear that all the samples have sharp absorption edges in the wavelength on between 360 and 400nm.These absorption edges shifted to shorter wavelengths (blue shifted) when Mn was incorporated into the ZnO films, these blue shifts may have been caused by doping-induced film degradation [16].

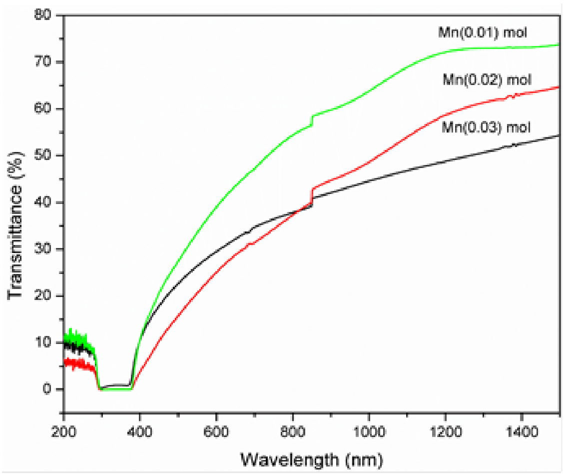

Figure 5.UV-Vis Transmittance spectra of Manganese doped ZnO with different mol

VII. MAGNETIC PROPERTIES

E. Vibrating Sample Magnetometer (VSM)

The magnetic properties of Mn doped ZnO were estimated by VSM measurements. The temperature of 100°C 5 hours shows an M-H hysteresis loop, MZO thin films were studied and shown in Fig. 6. It is observed from VSM data that the film exhibited ferromagnetic behavior for all the concentrations (0.01, 0.02 and 0.03mol of Mn) of dependent.

The temperature 100°C hysteresis loops showed the presence of ferromagnetism in Mn doped films. The undoped films showed no evidence of ferromagnetism at this temperature has been reported by Garcia et al. for ZnO nano structures Garcia [17]. The mechanism of formation of ferromagnetic films by doping with a small concentration of magnetic ions may not be associated with super exchange or double exchange interaction. It may be associated with modification of defects in the vicinity of magnetic ions [18]. Sundaresam et al. [19] have accounted that the ferromagnetic behavior can be associated with oxygen defects in such low dimensional systems.

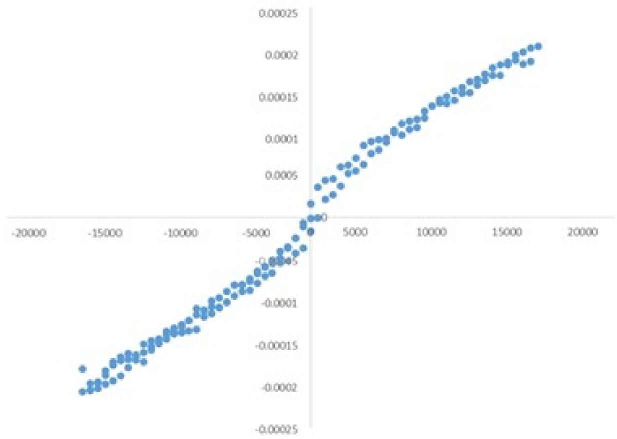

Figure 6. VSM profile of magnetic moment (emu) versus applied field (G) curve of0.01 mol Manganese-doped ZnO.

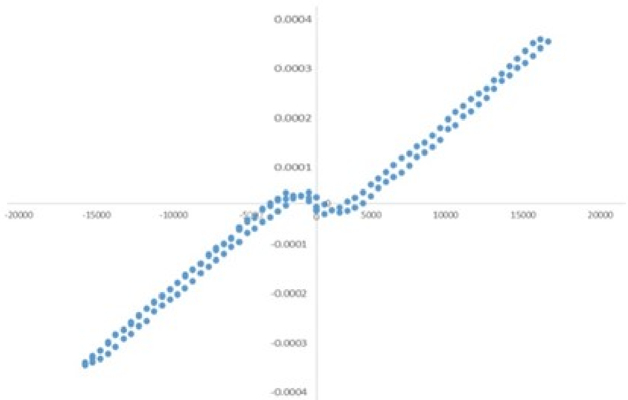

Figure 7. VSM profile of magnetic moment (emu) versus applied field (G) curve of 0.02mol Manganese-doped ZnO

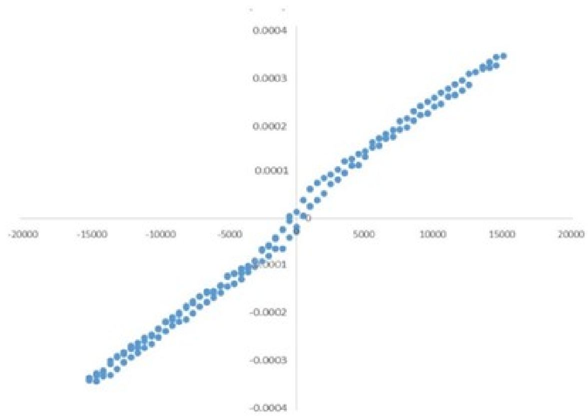

Figure 8. VSM profile of magnetic moment (emu) versus applied field (G) curve of 0.03mol Manganese-doped ZnO

We observed that there is a proportional change in the shape of the hysteresis between the retentivity and the opposite retentivity. At 0.01mol retentivity and in magnetic forces there are no changes. In0.02 mol there is a moderate change between retentivity and in magnetic forces and in 0.03 mol there is no modulation in it.

In Mn doped ZnO, as the concentration of manganese increases, the ferromagnetic behavior decreases. The decrease in ferromagnetic behavior is due to the presence of amount of oxygen interstitials in the ZnO host matrix increase the distance between magnetic ions and reduce the coupling and also the ferromagnetism. The native point defects such as oxygen vacancies are very common in ZnO nano particles giving rise to ferromagnetic behavior [20]. The slightly higher magnetization observed in co-doped ZnO samples as compared to Mn doped ZnO may be due to the presence of higher concentration of defects [21].

VIII. CONCLUSION

ZnO nano rods had been successfully synthesized in a dip coating method at low growth temperature of 90°C for different growth periods and annealed at 500°C.The UV-Vis optical absorption edge has a tendency to shift to an upper wavelength with increase in manganese concentration. The optical transmittance of Mn doped ZnO film was found to decrease from 70%, 60%, to 45% with the increase of manganese concentration. In Mn doped ZnO, as the concentration of manganese increases, the ferromagnetic behavior decreases. The native point defects such as oxygen vacancies are very common in ZnO nanoparticles giving rise to ferromagnetic behavior

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