Advanced Materials Research Vol. 462 (2012) pp 201-205
© (2012) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.462.201

Effect of Mn Doping on Optical Properties of Nanostructured ZnO Thin Film

M. Ebrahimizadeh Abrishami[1, a], A. Kompany[2,b]

[1]Department of Physics, Neyshabur University, Iran

[2]Department of Physics, Ferdowsi University of Mashhad, Iran

[a]ebrahimizadeh@ymail.com, [b]ahmadkompany@yahoo.com

Keywords: Optical dispersion, ZnO, Thin film, Spray pyrolysis.

Abstract. Undoped and ZnO: Mn thin films with different Mn content (5, 10 and 15 mol%) were grown on glass substrates by spray pyrolysis technique. X-ray diffraction analysis showed that single phase wurtzite structure is formed in all samples. XRD results also indicated that the undoped ZnO were crystallized in c-axis oriented wurtzite structure, while the ZnO: Mn thin films were polycrystalline. The SEM results revealed that Mn presence were modified the surface morphology of the samples. The optical transmittance measurements were performed in the wavelength range from 190 to 1100 nm. The refractive index, extinction coefficient and film thickness were determined by using pointwise unconstrained minimization model. It was observed that the refractive index increased with the increase in Mn concentration. Also, the thin films exhibited the direct band gap increased from 3.20 to 3.28 eV with the increase in Mn content. The optical dispersion parameters have been calculated and analyzed by using Wemple-Di Domenico relation. The obtained values showed that dispersion energy E_d of doped samples was found to be decreasing comparing to undoped thin film.

Introduction

Zinc oxide (ZnO) thin films are widely used material for electro-optics devices such as transparent electrodes in solar cells, light emitting diodes and gas sensors due to the large band gap, transparency, high electro-chemical stability and absence of toxicity. Also, ZnO thin films with different concentration of transition metals are the topical area for fabricating magneto-optical and spintronics devices.

These thin films can be grown by several techniques including, PLD [1], sol gel [2], sputtering [3], chemical vapor deposition [4] and spray pyrolysis [5]. In the spray pyrolysis technique, the raw materials which are usually a chloride or acetates compounds are dissolved in water. Then, the droplets of the aqueous solution decomposed after falling on the hot surface and consequently formed the thin film. The spray pyrolysis has the advantages such as cheapness, safeness, simplicity and possibility to use in industry.

Optical properties of zinc oxide thin films were extensively studied because of their importance in electro-optical and magneto-optical devices. Accurate investigation of the absorption coefficient, optical band gap energy and refractive index of these films is necessary for designing and analyzing of optical devices.

In this work, ZnO and ZnO:Mn thin films have been prepared using spray pyrolysis method. We put the emphasis on Mn concentration influence on the dispersion parameters for optoelectronic application. Some important optical parameters including, refractive index n, extinction coefficient k, optical dispersion energies E_0 and E_d , optical band gap energy E_g and the ratio of charge carriers numbers to effective mass N/m^*, were evaluated.

Experimental procedures

In this work, the spray pyrolysis technique was used to grow the thin films on glass substrates. Undoped ZnO and ZnO:Mn thin films with different amounts of Mn concentration (5, 10 and 15 mol%) were prepared by depositing a 0.1 M solution obtained by dissolving zinc acetate dehydrate and manganese acetate tetrahydrate in a mixture of isopropanol and distilled water. The system adjusting was determined as follows. The glass substrates were kept at 500°C during deposition. The solution was sprayed at a flow rate about 5 CC/min using compressed air as the carrier gas. The distance of substrates to the nozzle was adjusted at 30 cm.

The crystalline phase and lattice parameters of the samples were analyzed by using X-ray diffractometer with Cu-K_α radiation. The SEM gave a visual image from the microstructure of the films. Optical transmission and absorption spectra of investigated samples were measured in the range of 190 to 1100 nm. Film thickness, refractive index and extinction coefficient were estimated using a computer program based on pointwise unconstrained minimization approach (PUM) [6].

Results and discussion

Characterization. Fig.1 shows the XRD patterns of the undoped and ZnO thin films with 5, 10 and 15 mol% of manganese concentration grown at 500°C on glass substrates. The major peaks in these patterns are in close agreement with JCPDS data file for ZnO powder corresponding to the reflection peaks of the wurtzite structure which are indexed in this figure. All four films exhibit random orientations, because glass substrates allowed the films to crystallize randomly. But, It is observed that the undoped ZnO crystallites preferably crystallize in [002] orientation. While, decreasing [002] peak intensity with the presence of Mn atoms in structure is evident. The preferential c-axis orientation has been also observed in undoped ZnO thin films grown by other deposition techniques. In this case, Mn ions prevent the crystallization from orienting [002] reflection plane. We have obtained $i_{[002]}$ which is described as the ratio of [002] peak intensity to the sum of three main peaks ([100], [101] and [002]). As noted in Table 1, the calculated value $i_{[002]}$ for ZnO film is close to unity which means a quite [002] oriented thin film and decreases with the increase in Mn concentration which means the polycrystalline nature of samples. The lattice constants determined from XRD data, the average crystalline size calculated from Scherrer's formula are summarized in Table 1.

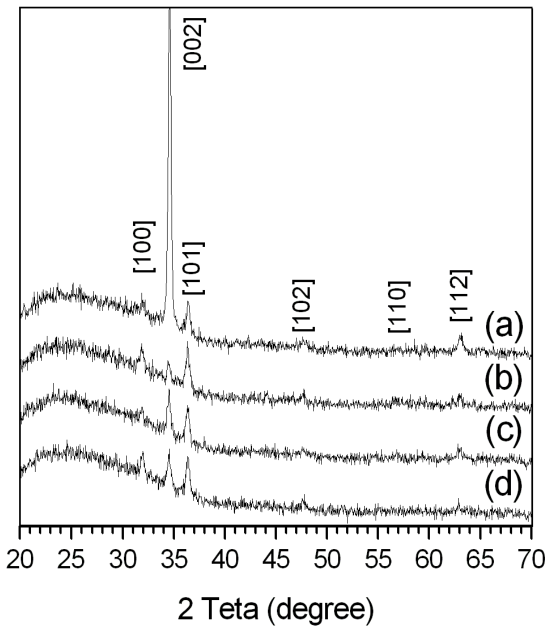

Fig. 1. XRD patterns of the thin films of ZnO with different Mn concentration: (a) 0.0 mol%, (b) 5.0 mol%, (c) 10.0 mol% and (d) 15.0 mol%.

Fig.2 shows the typical SEM images of of the undoped and ZnO thin films with 5 mol% of manganese concentration grown at 500°C on glass substrates. The SEM images of ZnO:Mn films show that the grain boundaries are well defined and the grains distribution over the surface is more uniform comparing to the undoped ZnO film.

Table 1. Structural studies investigated by using XRD analysis.

Mn content (mol%)	0.0	5.0	10.0	15.0
[002] peak position (°)	34.64	34.4	34.52	34.48
$i_{[002]}$ (%)	88	46	39	32
Lattice const. a (Å)	3.2400	3.2425	3.2420	3.2390
Lattice const. c (Å)	5.1750	5.1768	5.1760	5.1765
Crystalline size (nm)	29.25	24.07	24.72	25.36

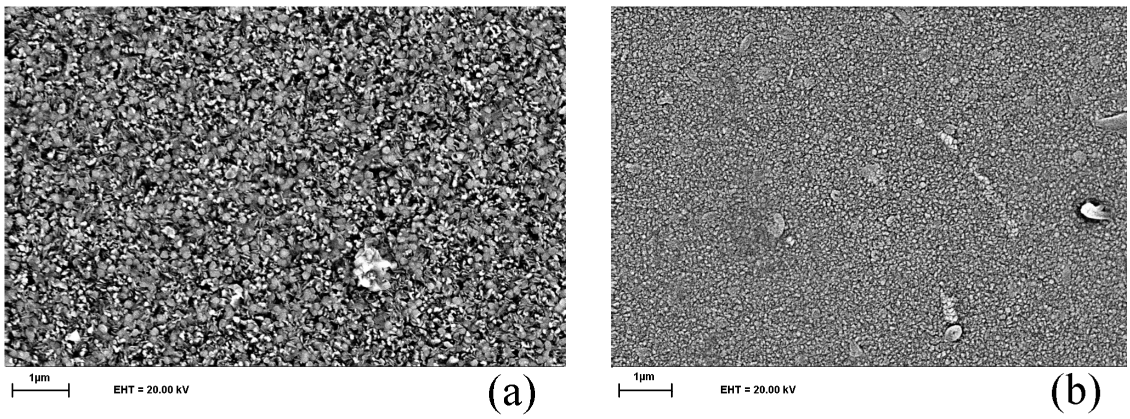

Fig.2. SEM images of ZnO thin films with (a) 0.0 mol%, (b) 5.0 mol% Mn concentration.

Optical properties. The Characteristics of light propagating through the ZnO and ZnO:Mn films depends on the optical properties of thin films. The most important optical properties are refractive index, extinction coefficient and their dependence to the wavelength which can be determined by studying the transmission spectra. Fig.3(a) shows the optical transmittance spectra (in the wavelength range from 300 to 1100 nm) of undoped ZnO and ZnO thin films with 5, 10 and 15 mol% of manganese concentration. The films are highly transparent in the visible region even the values of transmittance increase up to 96% at some wavelengths.

Determination of the refractive index. There are different approaches to calculate the refractive index *n* using the recorded values of transmittance in terms of wavelength. In order to calculate the *n* and *k*, we have followed an analysis described by a numerical method (pointwise unconstrained minimization). In this model, the thicknesses and the optical constants of films can be determined from the transmittance spectra which are not including interference fringe patterns. Chambouleyron *et al.* [6] extended the applicability of this method to the retrieval of the optical constants of semiconductor films. The variations of refractive index versus wavelength calculated for the all samples are shown in Fig. 3(b). As shown in this figure, the refractive index increases with the increase Mn concentration. The thicknesses of the samples calculated by this model are summarized in Table 2.

Determination of dielectric constant. The interactions between incident photons and electrons dominate on these observed changes in refractive index. The refractive index has been applied to describe the contribution of free carriers. The relation between the dielectric constant ε_∞ wavelength λ and refractive index is given by the equation [7]

$$n^2 = \varepsilon_\infty - \left(\frac{e^2}{4\pi c^2 \varepsilon_0}\right)\left(\frac{N}{m^*}\right)\lambda^2 \quad (1)$$

where N is the free carrier concentration and m^* is the effective mass of carriers. The ratio N/m^* and the high frequency dielectric constant ε_∞ were calculated from the Eq. (1) for different Mn concentration (Table 2). The behavior of obtained values of N/m^* are decreasing with the Mn concentration increasing. The reason of this relation originates in tendency of Mn atoms to accumulate in the grain boundaries and play a significant role in grain boundaries oxidation, decreasing the oxygen deficiencies and hence carrier density in specimens.

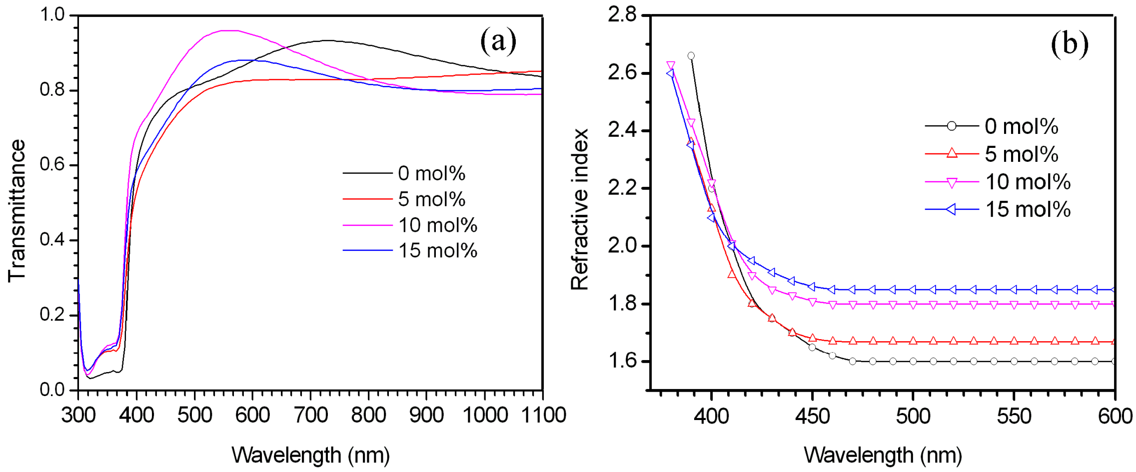

Fig.3. (a) Transmittance spectra and (b) refractive indices of undoped ZnO and ZnO thin films with different Mn concentration.

Determination of Optical band gap. There are different approaches to calculate the optical band gap energy E_g by using above spectral data. The band gap values of the films was evaluated by exploitation of the linear portion of the $(\alpha h\upsilon)^2$ versus $h\upsilon$ plot obtained from Tauc`s relation

$$\alpha E^2 = C(E - E_g)^{1/2} \tag{2}$$

where α is the absorption coefficient and $h\upsilon$ is the photon energy. The absorption coefficient is calculated from the transmittance and the film thickness calculated in foregoing section. The extinction coefficient k was used to determine absorption coefficient using the formula $\alpha = 4\pi k/\lambda$. As seen in Table 2, E_g increases with the increase in Mn concentration. The results indicate that the band gap blueshifts with the increase in Mn content which has been also reported by Fukumura *et al.* [8] in epitaxial Mn-doped ZnO films. This blueshift can be related to higher bond energy of Mn-O than Zn-O.

Dispersion energy parameters of the thin films. Refractive index data below the interband absorption edge can be analyzed using single effective oscillator model of Wemple–Di Domenico [9] defined by the following relation

$$n^2(E) = 1 + \frac{E_d E_0}{E_0^2 - E^2} \tag{3}$$

where E, E_0 and E_d are photon energy, effective dispersion oscillator energy and dispersion energy, respectively. The average strength of interband optical transitions is described by dispersion energy, E_d. Both of E_0 and E_d were obtained by plotting $(n^2\text{-}1)^{-1}$ versus E^2 and determining the slope and intercept of line to vertical axis. The values calculated from this model are summarized in the Table 2. The parameters E_0 for all samples approximately satisfy the relationship of $E_0 \approx 2E_g$.

The parameter E_d for ZnO wurtzite crystal structure is 18.1 eV and it is clearly observed that dispersion energy E_d sensibly decreases with progressive growth in Mn concentration. This can be easily understood by taking account of interband transitions in magnetic atoms [10].

Table 2. Dispersion parameters of sprayed undoped ZnO and ZnO thin films with different Mn content.

Mn content (mol%)	0.0	5.0	10.0	15.0
Film tickness (nm)	400	360	330	330
ε_∞	2.56	2.79	3.24	3.42
$N/m^* \times 10^{46}$ ($cm^{-3}.g^{-1}$)	6.8	2.4	1.9	1.5
E_g (eV)	3.20	3.23	3.26	3.28
$E_0 \approx 2E_g$ (eV)	6.28	6.34	6.58	6.77
E_d (eV)	18.1	13.8	13.2	13.0

Summary

In the present work, undoped and ZnO:Mn thin films with different Mn content (5, 10 and 15 mol%) were successfully prepared on glass substrates by using spray pyrolysis technique. The XRD revealed that despite the wurtzite single phase structure, Mn ions prevent the crystallization from c-orienting. The refractive index, extinction coefficient and film thickness were determined by using pointwise unconstrained minimization model. The effects of Mn content on dispersion properties of deposited thin films were studied. The values of E_g are increasing when Mn content increases. Also, E_d is decreasing with the increase in Mn content which relates to Mn influences on optical transition bands.

References

[1] K.H. Park, Y.Y. Song, E.K. Lee, L.S. Son, S.K. Oh, S.C. Yu and H.K. Kang: Korean Chem. Soc. Vol. 55 (2009), p. 2685

[2] C.-Y. Tsay, K.-S. Fan, S.-H. Chen and C.-H. Tsai: J. Alloys. Compd. Vol. 495 (2010), p. 126

[3] S.J. Lim, S. Kwon and H. Kim: Thin Solid Films, Vol. 516 (2008), p. 1523

[4] D. Kim, I. Yun and H. Kim: Curr. Appl. Phys. Vol. 10 (2010), p. 459

[5] P. Singh, A. Kaushal and D. Kaur: J. Alloys. Compd. Vol. 471 (2009), p. 11

[6] I. Chambouleyron, S.D. Ventura, E.G. Birgin and J.M. Martinez: J. Appl. Phys. Vol. 92 (2002), p. 3093

[7] T.S. Moss, in: Optical Properties of Semiconductor, Butter Worths Scientific Publication Ltd., London (1959).

[8] T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma and M. Kawasaki: Appl. Phys. Lett. Vol. 75 (1999), p. 3366

[9] S.H. Wemple and M. Di Domenico: Phys. Rev. B. Vol. 3 (1971), p. 1338

[10] S.H. Wemple: Phys. Rev. B. Vol. 7 (1973), p. 3767