STRUCTURAL AND OPTICAL PROPERTIES OF UNDOPED AND Co DOPED ZnO NANOSTRUCTURED THIN FILMS

Nirmala Murugesan and Anukaliani Achuthanunni*

Received: Jul 3, 2010; Revised: Oct 12, 2010; Accepted: Nov 6, 2010

Abstract

In this study ZnO:Co nano structured thin films doped with cobalt at different concentrations were deposited on glass substrates by the sol-gel dip coating method. Characterization techniques of XRD, SEM with EDAX, and UV-Visible spectra measurements were done to investigate the effects of the Co doping concentration on the optical and structural properties of the ZnO:Co nano structured thin films. The XRD patterns of all nano structured films show the crystalline behavior and are of a hexagonal wurtzite structure. Our results reveal that, with a high percent of cobalt, not only the degree of the crystalline behavior but also a broadening of the peak occurs. The compositional analysis was carried out by energy dispersive X-ray (EDX) measurement. The optical studies show that the band gap of ZnO:Co decreases the d electron of the Co atom and band carriers of the host material. This unique property of ZnCoO films can be used to fabricate transparent electrodes in flat panel displays and metal-insulator-semiconductor diodes.

Keywords: Zinc oxide, sol-gel, dip coating, thin film

Introduction

The sol-gel process (Sagar *et al*., 2005) is simple and inexpensive in fabrication, capable of producing a large number of samples, has easier composition control and an accurately controlled mole ratio, has high solubility, better homogeneity, a lower processing temperature, and has a general advantage for large area deposition and thickness of the films. These include cobalt (Co) doped zinc oxide (ZnO) (Ivill *et al*., 2008), manganese doped ZnO (Sharma *et al*., 2003; Shinde *et al*., 2006), fluorine doped ZnO (Olvera *et al*., 2002; Guillen-Santiago *et al*., 2004), and indium doped ZnO (Lucio-Lopez *et al*., 2006) among others. On the other hand zinc oxide thin solid films have prompted as much interest as transparent conductive oxides due to their valuable properties such as high optical transparency in the visible region, low electrical resistivity, as well as high electrochemical stability, abundance in nature, and absence of toxicity (Ismail *et al*., 2001).

Co doped ZnO thin solid films have been obtained by chemical and physical

PG and Research Department of Physics, Kongunadu College of Arts and Science, Coimbatore - 641029, Tamilnadu, India. E-mail: anuplasmakasc@gmail.com

* *Corresponding author*

techniques, such as ultrasonic spray, sol–gel (Manivannan *et al*., 2001), and pulsed laser deposition (Fitzgerald *et al*., 2005). Doped with a 3d transition metal and highly transparent and conducting, ZnO is promising for the emerging field of spintronics because it can readily be deposited as a thin film. The difference in radii between divalent high-spin Co in tetrahedral coordination (0.58 Å) and divalent Zn in tetrahedral coordination (0.60 Å) are small and a Co content of more than 8 % was obtained. Some recent works (Olvera *et al*., 2002; Kim *et al*., 2002; Moreno *et al*., 2006; Pan *et al*., 2008; Song *et al*., 2007; Schmidt *et al*., 2007; Bhatti *et al*., 2008) have reported optical, morphological, and magnetic properties of Co doped ZnO thin solid films using different deposition techniques. In this paper, the structural, morphological, and optical properties of ZnCoO films were characterized in detail. The characterizations revealed an intrinsic nature between the properties and structure in Co doped ZnO films.

Experimental Method

The precursors utilized for the synthesis of ZnO:Co are: Zinc acetate dehydrate [$Zn(CH_3 COO)_2 2H_2 O$], cobalt acetate tetrahydrate [$Co(CH_3 CO)_2 4H_2 O$], 2-mithoxyethanol (DME) [$C_3 H_8 O_2$], and monoethanolamine (MEA) [$C_2 H_7 NO$] as the zinc and cobalt sources, and solvent and stabilizer respectively. All chemical materials were purchased from Merck & Co., Inc., USA, and were applied without more purification.

All samples of ZnO:Co nano structured thin films were prepared by the sol-gel method. First, at room temperature, zinc acetate and the dopant were dissolved in a mixture of DME and MEA solution. The molar ratio of MEA to Zn^{+2} was maintained at 1. Solutions were prepared containing zinc acetate, cobalt acetate 10, 12, and 14% DME and MEA. At 70°C, solutions were vigorously stirred for 1 h by means of a magnetic stirrer to yield a clear and homogeneous solution. At room temperature, the coating solutions were aged for at least 1 day, and then deposited on glass slide substrates, which were cleaned before by dip coating. The undoped ZnO precursor was prepared in the same way. The glass slide was dipped in sol solution for 5 min, and then the film was preheated at 150°C for 15 min to evaporate the solvent and organic residuals. This procedure was repeated 5 to 8 times to reach the desired thickness. Finally the film was post-heated at 300°C for 1 h.

In this work, our intent is the investigation of the band gap in ZnO:Co nano films and so we avoided other further characterizations. The desirable characterizations are X-ray diffraction, compositional analysis, and ultraviolet-visible (UV/Vis) spectra measurements for investigating the effects of the doping concentration on the properties of Zno:Co nano structured thin films

Results and Disscussion

The X-ray diffractometer (XRD 6000, Shimadzu, Japan) with α CuK line radiation (λ = 1.5406 Å) was used for determining the crystallite phase and orientation. The crystalline size of undoped and Co-doped ZnO is calculated using Scherrer's formula,

$$D = \frac{K\lambda}{\beta \mathrm{Cos}\theta}$$

where The constant K is the shape factor = 0.94

'λ' the wavelength of X-rays (1.5406 for Cuk_{α})

θ is the Bragg's angle

β is the full width at half maximum

Figure 1(a), 1(b), 1(c), and 1(d) shows the XRD-ray patterns of all samples which were deposited on the glass substrates. The diffraction patterns reveal a good crystalline behavior without any appreciable changes from pure ZnO films and are genuinely polycrystalline with the hexagonal wurtzite structure. These results imply that there are no secondary phases such as a cobalt cluster or oxides. Wide distribution of the grain size of the samples on the film can be a possible reason resulting in the broadening of the diffraction peaks. The

result obtained is in good agreement with the work done by Li *et al*. (2007). The lattice parameters and the crystalline size of the ZnO and ZnCoO samples are shown in Table 1.

Surface morphological studies of undoped and Co doped ZnO films have been carried out using a scanning electron microscope. Figure 2(a), 2(b), 2(c), and 2(d) shows the SEM images of the undoped and Co doped ZnO films. SEM images of the ZnO resemble a granular surface. Incorporation of Co ions changed the surface morphology to a wrinkled network. Due to the enhancement of the dopant concentration more impurities were included into the ZnO crystal, resulting in more defects in the crystal so that the crystallinity of the films was affected as seen in the XRD. For the 14% Co concentration the morphology of the film changed to a network and this is in good agreement with the literature (Habibi and Sardashti, 2008; Srinivasan and Kumar, 2008).

For determining composites in different Co doping concentrations of ZnO:Co nano structured thin films, compositional analysis was performed on a Philips XL 20 SEM (Philips Electronics, NV, Netherlands) by energy dispersive X-ray (EDX) analysis. The EDX spectrum of pure and Co doped ZnO nanostructured thin film is shown in Figure 3(a), 3(b), 3(c) and 3(d). Table 2 gives the ratio of Zn:Co:O elemental composition. EDX analysis showed that the amount of Co element in the sample increased depending on the increasing Co incorporation in the solution. As a result Co incorporation has a strong effect on the optical, structural, and morphological properties of ZnO.

Room temperature optical transmittance was measured by a Varian Cary 100 UV/Vis spectrophotometer (Varian, Inc., USA). Figure 4 shows the optical transmittance spectra of the films in the wavelength region range from 500 to 2500 nm. It is evident that the optical

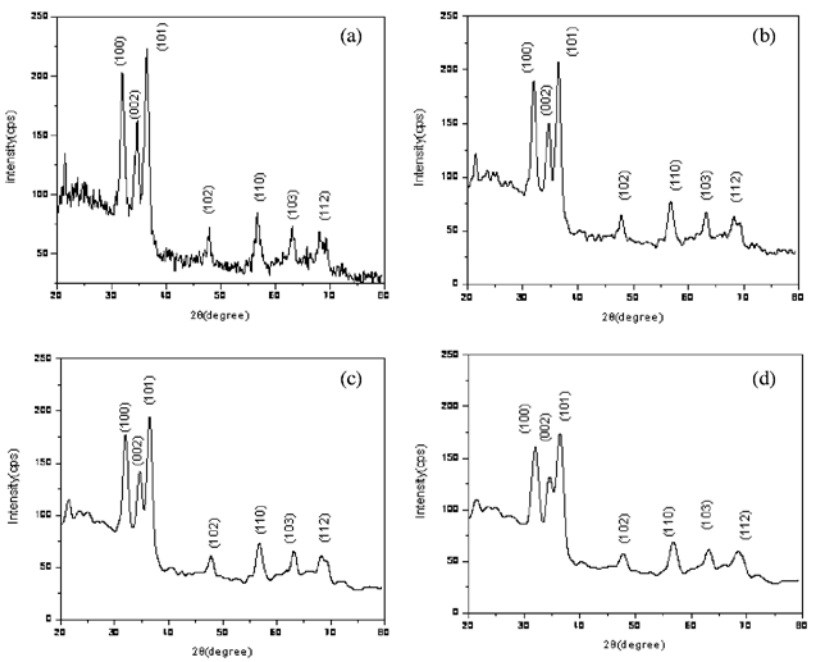

Figure 1. (a) XRD pattern of ZnO
(b) XRD pattern of $ZnCo_{0.10}O$
(c) XRD pattern of $ZnCo_{0.12}O$
(d) XRD pattern of $ZnCo_{0.14}O$

Table 1. XRD parameters

Dopant concentration	hkl	2θ (Degree)		Interplanar distance (d) (Å)		Crystallite size (nm)
		Observed	JCPDS	Observed	JCPDS	
0.00%	100	31.85	31.77	2.80	2.81	45.88
	002	34.63	34.42	2.58	2.60	36.94
	101	36.35	36.25	2.47	2.48	37.17
5.00%	100	31.79	31.77	2.81	2.81	40.71
	002	34.61	34.42	2.59	2.60	30.42
	101	36.31	36.25	2.47	2.48	34.35
10.00%	100	31.77	31.77	2.81	2.81	37.76
	002	34.25	34.42	2.61	2.60	35.41
	101	36.15	36.25	2.48	2.48	28.78
14.00%	100	31.71	31.77	2.82	2.81	26.82
	002	34.18	34.42	2.62	2.60	29.62
	101	36.01	36.25	2.49	2.48	27.31

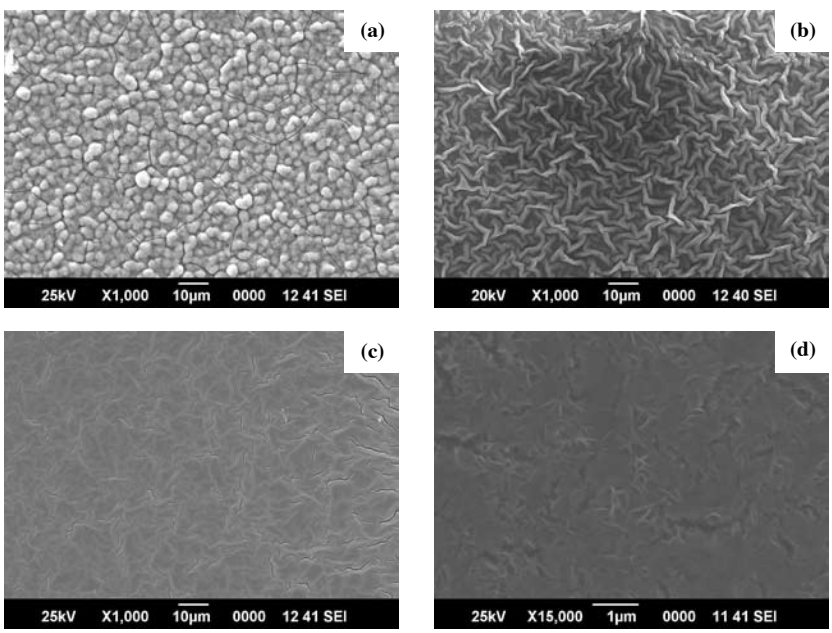

Figure 2. (a) SEM Image of ZnO
(b) SEM Images of $ZnCo_{0.10}O$
(c) SEM Images of $ZnCo_{0.12}O$
(d) SEM Images of $ZnCo_{0.14}O$

transmittance increases in the visible region and decreases in the UV region for a sample. With the increase of 0, 10, 12, and 14% Co concentration, the optical transmittance spectra of the samples gradually decreased in the visible region. Transmittance in the undoped film is almost 90-95% for the visible region. The optical band gap of the Co doped ZnO nano films was estimated by extrapolation of the linear relationship

$$(\alpha h\nu)^2 = h\nu - E_g ,$$

where α is the absorption coefficient,

$h\nu$ is the photon energy, and

E_g is the optical band gap of nano films.

It is determined by theory of the direct optical absorption. Figure 5 shows the $(\alpha h\nu)^2$ vs. photon energy curves of ZnO nano films with varying doping concentrations and the band gap values are shown in Table 3. The

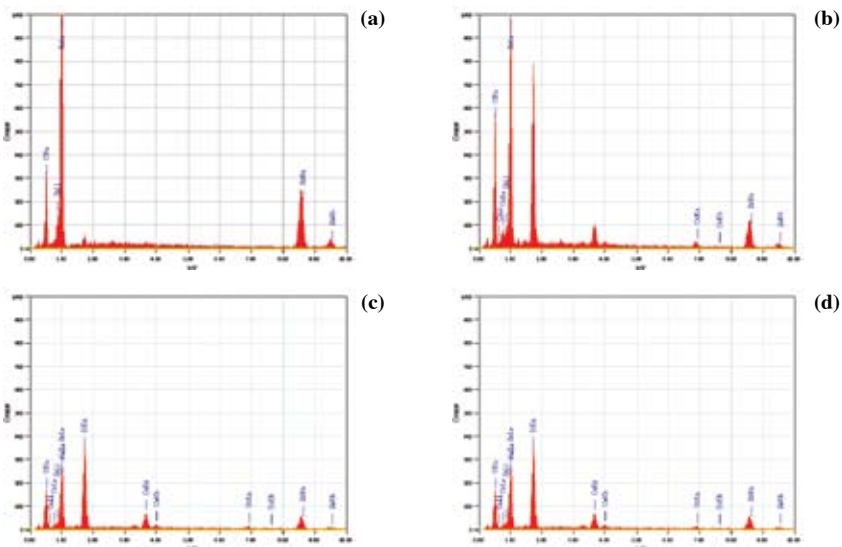

Figure 3. (a) EDX Spectrum ZnO
(b) EDX Spectrum of $ZnCo_{0.10}O$
(c) EDX Spectrum of $ZnCo_{0.12}O$
(d) EDX Spectrum of $ZnCo_{0.14}O$

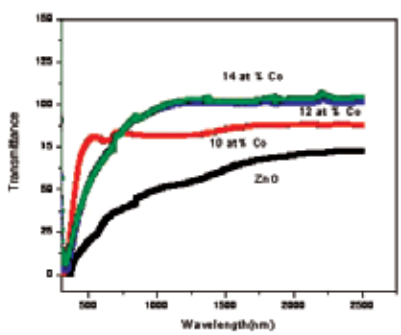

Figure 4. Transmittance spectra of ZnCoO

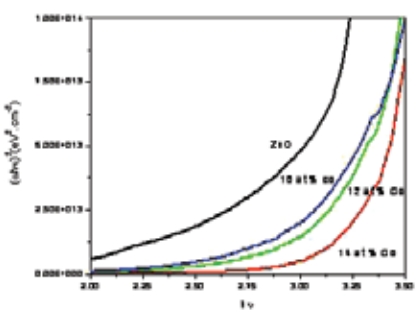

Figure 5. Optical Band gap of ZnCoO

Table 2. Compositional analysis of ZnCoO

Dopant concentration	Experimental Results (Atomic %)		
	Zn	Co	O
0.00%	29.62	-	70.38
10.00%	3.11	0.65	70.50
12.00%	6.80	1.12	66.51
14.00%	13.31	1.17	85.52

Table 3. Band gap energy

Dopant concentration in ZnO	Band gap energy (E_g) eV
0.00%	3.20
10.00%	3.19
12.00%	3.15
14.00%	3.00

band gap value decreases with the increasing Co doping concentration. This may due to the sp-d exchange interactions (Singh *et al.*, 2009).

Conclusions

Co doped ZnO nano films were prepared with different values of Co content by the sol-gel dip-coating method. The diffraction patterns reveal a good crystalline behavior with the hexagonal wurtzite structure. The EDX of the samples were prepared with different values of the Co/Zn atomic ratio. Room temperature optical transmittance spectra of samples were performed and showed that the visible transmission of films generally decreases with the increase of the Co content and is high (> 90%). Due to the exchange interaction between the localized d shell electrons of the magnetic ions and the delocalized band states, the optical band gap E_g decreases from 3.20 to 3.0 eV for the increasing doping concentration. This unique property of ZnCoO films can be used to fabricate transparent electrodes in flat panel displays and metal-insulator-semiconductor diodes, which could replace p-n junctions to exploit electroluminescence of ZnO, instead of the difficulty of creating consistent, reliable p-type ZnO

References

Bhatti, K.P., Malik, V.K., and Chaudhary, S. (2008). Cobalt substituted ZnO thin films: a potential candidate for spintronics. J. Mater. Sci.: Mater. Electron., 19(8-9): 849-854.

Fitzgerald, C.B., Venkatesan, M., Lunney, J.G., Dorneles, L.S., and Coey, J.M.D. (2005). Cobalt-doped ZnO - a room temperature dilute magnetic semiconductor. Appl. Surf. Sci., 247(1-4):493-496.

Guillen-Santiago, A., Olvera, M. de la L., Maldonado, A., Asomoza, R., and Acosta, D.R. (2004). Electrical, structural

and morphological properties of chemically sprayed F-doped ZnO films: effect of the aging-time of the starting solution, solvent and substrate temperature. Phys. Stat. Sol., (a), 201(5):952-959.

Habibi, M.H. and Sardashti, M.K. (2008). Structure and morphology of nanostructured zinc oxide thin films prepared by dip vs spin-coating methods. J. Iran. Chem. Soc., 5(4):603-609.

Ismail, B., Abaab, M., and Rezig, B. (2001). Structural and electrical properties of ZnO films prepared by screen printing technique. Thin Solid Films, 383(1): 92-94.

Ivill, M., Pearton, S.J., Rawal, S., Leu, L., Sadik, P., Das, R., Hebard, A.F., Chisholm, M., Budai, J.D., and Norton, D.P. (2008). Structure and magnetism of cobalt-doped ZnO thin films. New J. Phys., 10:065002.

Kim, J.H., Kim, H., Kim, D., Ihm, Y.E., and Choo, W.K. (2002). Magnetic properties of epitaxially grown semi-conducting Zn1–xCoxO thin films by pulsed laser deposition. J. Appl. Phys., 92(2):6066-6071.

Li, J.H., Shen, D.Z., Zhang, J.Y., Zhao, D.X., Li, B.S., Lu, Y.M., Liu, Y.C., and Fan, X.W. (2007). The effect of Mn^{2+} doping on structure and photoluminescence of ZnO nanofilms synthesized by sol gel method. J. Lumin., 122-123:352-354.

Liu, X.J., Song, C., Zeng, F., and Pan, F. (2008). Donor defects enhanced ferromagnetism in Co:ZnO films. Thin Solid Films, 516(23):8757-8761.

Lucio-Lopez, M.A., Maldonado, A., Castanedo-Perez, R., Torres-Delgado, G., and Olvera, M. de la L. (2006). Thickness dependence of ZnO: In thin films doped with different indium compounds and deposited by chemical spray. Sol. Energ. Mater. Sol. C., 90(15):2362-2376.

Manivannan, A., Dutta, P., Glaspell, G., and Seehra, M.S. (2006). Nature of magnetism in Co- and Mn-doped ZnO prepared by sol-gel technique. J. Appl. Phys., 99(8): 08M110-3.

Moreno, M.S., Kasama, T., Dunin-Borkowski, R.E., Cooper, D., Midgley, P.A., Steren, L.B., Duhalde, S., and Vignolo, M.F. (2006). Local study of the magnetism of Co-doped ZnO thin films. J. Phys. D: Appl. Phys., 39(9):1739-1742.

Olvera, M. de la L., Maldonado, A., and Asomoza, R. (2002). ZnO:F thin films deposited by chemical spray: effect of the fluorine concentration in the starting solution. Sol. Energ. Mater. Sol. C., 73(4):425-433.

Pan, F., Song, C., Liu, X.J., Yang, Y.C., and Zeng, F. (2008). Ferromagnetism and possible application in spintronics of transition-metal-doped ZnO films Mater. Sci. Eng., R., 62(1):1-35.

Sagar, P., Kumar, M., and Mehra, R.M. (2005). Influence of hydrogen incorporation in sol-gel derived aluminum doped ZnO thin films. Thin Solid Films, 489(1-2): 94-98.

Schmidt, H., Diaconu, M., Hochmuth, H., Benndorf, G., Von Wenckstern, H., Biehn, G., Lorenz, M., and Grundmann, M. (2007). Electrical and optical spectroscopy on ZnO:Co films. Appl. Phys. A., 88(1):157-160.

Sharma, P., Gupta, A., Rao, K.V., Owens, F.J., Sharma, R., Ahuja, R., Guillen, J.M.O., Johansson, B., and Gehring, G.A. (2003). Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO. Nat. Mater., 2(10):673-677.

Shinde, V.R., Gujar, T.P., Lokhande, C.D., Mane, R.S., and Han, S.-H. (2006). Mn doped and undoped ZnO films: A comparative structural, optical and electrical properties study. Mater. Chem. Phys., 96(2-3):326-330.

Singh, P., Kaushal, A., and Kaur, D. (2009). Mn-doped ZnO nanocrystalline thin films prepared by ultrasonic spray pyrolysis. J. Alloy. Compd., 471(1-2): 11-15.

Song, C., Pan, S.N., Liu, X.J., Li, X.W., Zeng,

F., Yan, W.S., He, B., and Pan, F. (2007). Evidence of structural defect enhanced room-temperature ferromagnetism in Co-doped ZnO. J. Phys.: Condens. Matter, 19(17):176229.

Srinivasan, G. and Kumar, J. (2008). Effect of Mn doping on the microstructures and optical properties of sol-gel derived ZnO thin films. J. Cryst. Growth, 310(7-9): 1841-1846.