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Effect of cobalt doping on the structural and optical properties of sprayed Zno thin films

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ABSTRACT

In this paper, we report the deposition of the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films on glass substrates by using the chemical spray pyrolysis technique and subsequently the effect of Co on the structural and optical properties of the deposited ZnO thin films were characterized. X-ray diffraction (XRD) measurement shows that all the deposited films have preferential orientation along the c-axis with a strong (002) peak observed at 2θ H” 34°. Scanning electron microscopy (SEM) results show that the surface morphology of the films is strongly depends on the concentration of Co. Spectrophotometry measurements reveal that transmission values of the of 4% and 8% Co are higher than that for pure ZnO and the absorbance increases with increasing Co doping concentration, the optical energy band gap of the deposited pure ZnO thin films was equal to 3.37 eV while it was found to be 3.12 and 3.108 eV for the doped ZnO with Co.

KEYWORDS

Transparent conductive oxides;
Structural properties;
Optical properties.

INTRODUCTION

Recently there has been a considerable attention on the transparent conducting oxides like ZnO[1-5], its unique characteristics such as wide band gap which is about 3.37eV. The large exciton binding energy of 60meV, abundance in natural which make it a low material, low resistivity, nontoxic, high optical gain at room temperature, high chemical and mechanical stability[6-9] make a ZnO thin film a distinctive candidate to use in several applications such as, gas sensing[10], light emitting diodes[11], surface acoustic wave[12], transparent electrodes[13], photovoltaic devices[14], Varistors[15], solar cells[16], and UV photodetectors[17].

Several deposition methods have been used to preparing ZnO thin films; including electrochemical deposition[18], atmospheric pressure chemical vapor deposition[19], metal organic chemical vapor deposition (MOCVD)[20], atomic layer deposition[21], pulsed laser deposition (PLD)[22], sol-gel dip coating[23], reactive RF magnetron sputtering[24], DC sputtering evaporation[25], and spray pyrolysis[26].

In this work, we report the deposition of the pure ZnO and doped ZnO:Co with 4% and 8% concentration thin films on glass substrates by using the chemical spray pyrolysis technique, and subsequently the effect of Co on the structural and optical properties of the deposited ZnO thin films were characterized by various tools. The structural and optical proprieties of the sample were characterized by XRD, SEM and transmission and absorption spectra.

EXPERIMENTAL WORK

The pure ZnO and Co doped ZnO thin films were synthesized on glass substrates by using the chemical spray pyrolysis technique. The precursor solution for spray pyrolysis was prepared by dissolving 0.1 M of zinc acetate dehydrate ($Zn(CH_3Coo)_2.2H_2O$) supplied from [Merck chemicals Germany] in the mixture of re-distilled water and a few drops of Acetic acid to prevent the formation of hydroxides and cobalt chloride (0.1 $CoCl_2$ Sigma-Aldrich) as a source of dopant. The concentration of Co was used to be 4% and 8%. Prior to the deposition, the glass substrates were cleaned with acetone and re- distilled water using an ultrasonic bath. After many deposition trials, we got the following preparative conditions including; the substrate temperature was kept at 450 ^{O}C during the experimental work, gas carrier (10^5 pascal), spray rate (5ml/min), nozzle to substrate distance (30 cm), and the spray time was 7 Sec lasted for two minutes to avoid excessive cooling. The film thickness was measured by gravimetric method and were found to be approximately 300± 30 nm.

The crystalline quality was investigated by XRD (Philips PW 1840) with CuK_α radiation having a wavelength of 1.541Å over the diffraction angle ($2\theta = 20^o$-70^o). The morphology of the film surface was imaged by SEM using scanning electron microscope model SM-6460 LV, while the absorption and transmission spectra of the sample were measured using a double beam spectrophotometer (Shimdzu 1650 U- probe) in the wavelength range (380- 900 nm).

RESULTS AND DISCUSSION

Figure 1 depicts the XRD diffraction patterns for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films. The figure shows that all the films are polycrystalline with hexagonal wurtzite structure with a strong and dominating nature of the peak corresponding to (002) reflection; which indicates the preferential C- axis orientation of crystalline. The intensity of this peak reduces as the Co content increase.

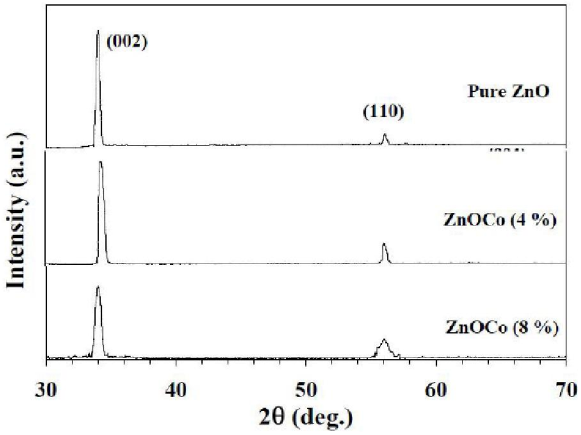


Figure 1: X-ray diffraction patterns for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films

The (110) peak was also observed at 2θ H”56^o, but this peak is of much lower intensity than the (002) peak. The figure does not show any peaks correspond to Co; this result is in a good agreement with the results reported by Benzarouk et al[27] and Rao and Kumar[28].

The crystallite size (D) of (002) peaks has been calculated from the full width half maximum (FWHM) of the XRD spectrum using the Scherer formula[29]:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (1)$$

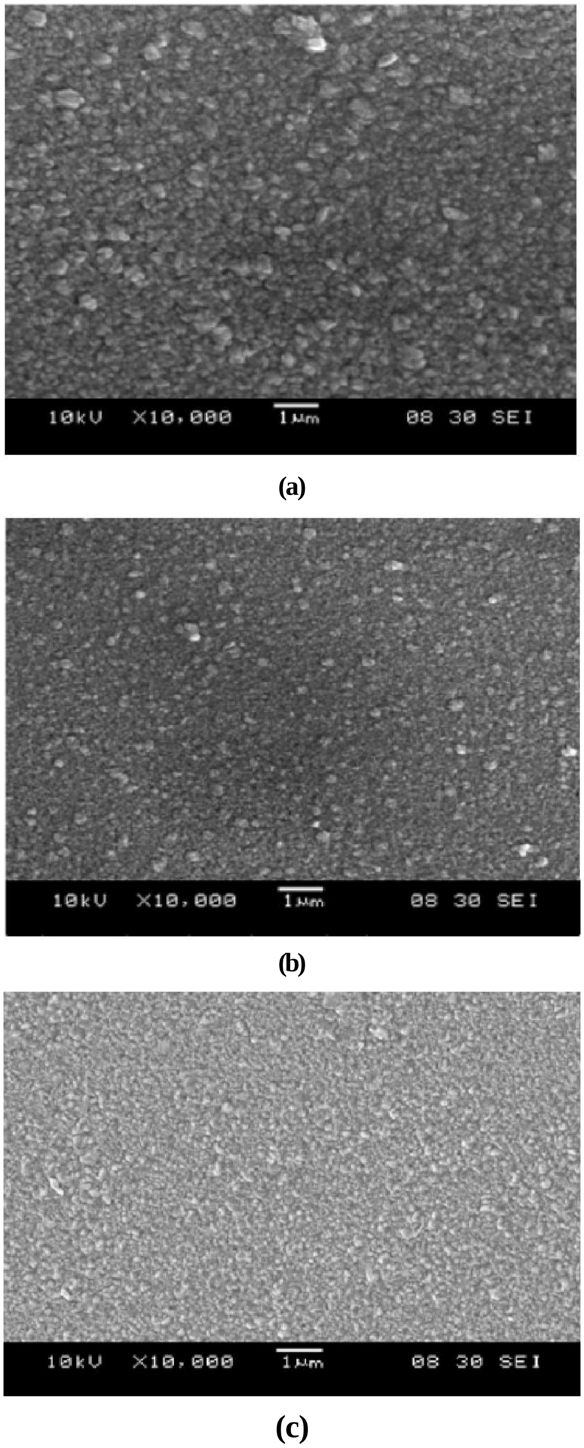
Where λ is the wavelength of XRD, θ is the Bragg angle and β is the FWHM and it was equal to 41.147nm, 33.149 nm and 35.625 nm for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films. It has been found that the crystallite size decrease with the increase in Co concentration. TABLE 1 shows X-ray diffraction data summary of three deposited thin films. This behavior could be related to the difference between the ionic radius namely 0.074, 0.0745 nm for Zn^{+2} and Co^{+2} respectively.

The SEM micrographs for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films on glass substrates are shown in Figure 2; it can be seen that the surface morphology of the films is strongly

TABLE 1: X-ray diffraction data summary of pure ZnO and Co with 4% and 8% concentration doped ZnO thin films.

Reference	2θ (°)	FWHM (°)	Crystallite size (nm)
Pure ZnO	34.200	0.200	41.147
ZnOCo (4%)	34.150	0.231	35.625
ZnOCo (8%)	34.046	0.248	33.149

depends on the concentration of Co, while Figure 3 shows the elemental analysis of the Co with 4% and 8% concentration doped ZnO thin films on glass substrates.



(a)

(b)

(c)

Figure 2 : SEM micrographs for (a) the pure ZnO, (b) Co with 4% and (c) 8% concentration doped ZnO thin films on glass substrates

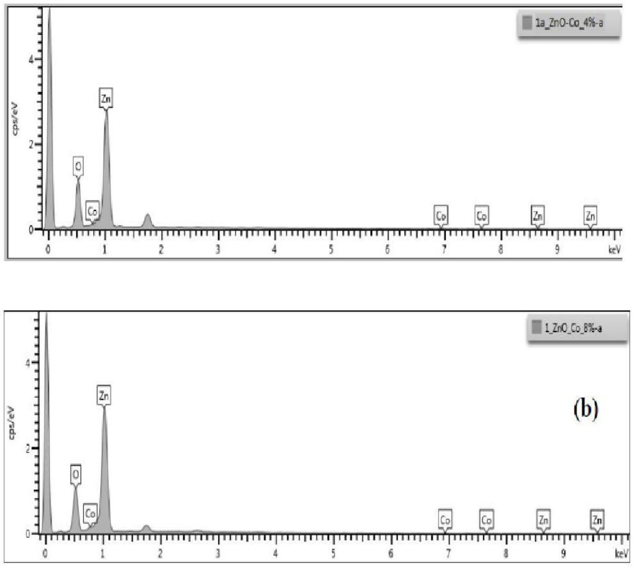
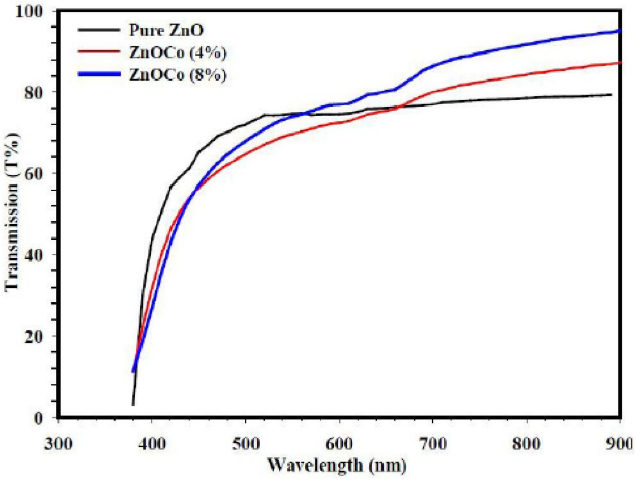


Figure 3 : The elemental analysis of the Co with (a) 4% and (b) 8% concentration doped ZnO thin films on glass substrates.

The optical transmission spectra of the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films on glass substrates is shown in Figure 4; the figure shows that the transmittance of 4% and 8% Co is higher than that for pure ZnO. The increase in transmittance with cobalt content may be due to the decrease in scattering of photons by crystal defects created by doping. It is well known that the free carrier absorption by the photons may also affect the value of the optical transmittance[30,31].

Figure 5 shows the optical absorbance spectra for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films. The maximum absorption for all

Figure 4 : The optical transmission spectra of the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films on glass substrates



the deposited films occurs at 395nm and decay exponentially after 400 nm. The figure also shows that as the Co content increases, the absorption edge moves to word longer wavelength (red shift) and the absorbance increases with increasing Co doping concentration. The increasing in absorbance with Co doping may be due to the increase morphological changes due to Co content[32].

To determine the optical energy band gap for the three deposited thin films, we have to use Tauc Model[33] assuming a direct transition between valence and conduction bend from the expression:

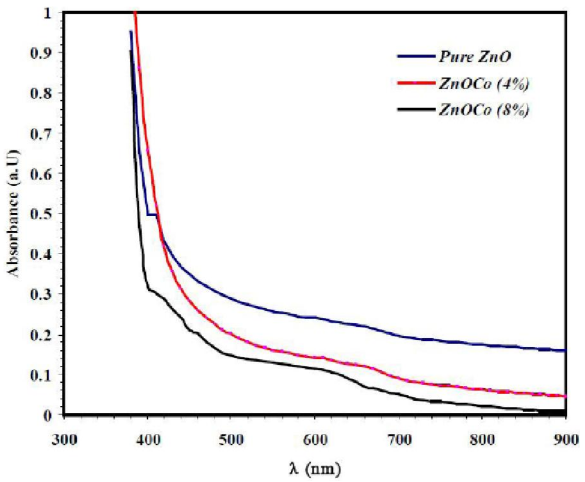


Figure 5: The optical absorbance spectra for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films.

$$\alpha h\upsilon = B(h\upsilon - E_g)^{1/2} \qquad (2)$$

Where B is constant, E_g is the optical band gap, α is the absorption coefficient and $h\nu$ is the incident photon energy.

Figure 6 shows the Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$. Band gap could be derived by extrapolating the linear portion of the graphs to the $h\nu$ axis. From the plot the Eg was determined to be 3.38eV for the pure ZnO and this value is quite similar to the theoretical ZnO E_g and also in a good agreement with the reported value by Jandow et al[34]. while it was found to be 3.12 and 3.108 eV for the doped ZnO with Co; the results show that Eg decreases as the Co concentration increases. The decrease in E_g result could be attributed to the decrease in the order of crystallanity.

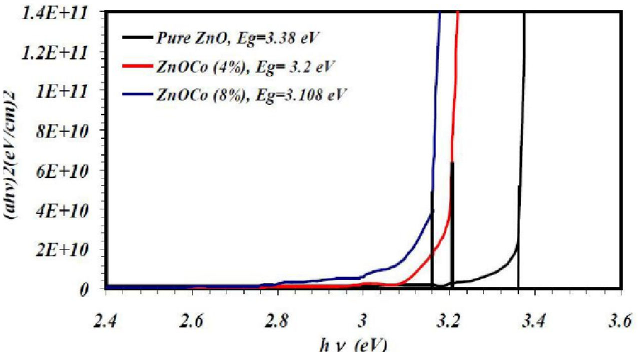


Figure 6: Band gap dereviation by Tauc Model for the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films.

CONCLUSION

In summary, the effect of Co on the structural and optical properties of the deposited ZnO thin films have been investigated. The structural characterizations showed that the pure ZnO and Co with 4% and 8% concentration doped ZnO thin films has preferential orientation along the c-axis with dominant (002) peak observed at 2θ H” 34^{o}, SEM results show that the surface morphology of the films is strongly depends on the concentration of Co. Spectrophotometry measurements reveal that transmission and absorption value increases with increasing Co doping concentration, the optical energy band gap of the deposited pure ZnO thin films was equal to 3.37 eV while it was found to be 3.12 and 3.108 eV for the doped ZnO with Co. The decrease in E_g result could be attributed to the decrease in the order of crystallanity

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