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Synthesis, Structural and Optical Properties of $Zn_{1-x}Co_xO$ of Thin Films by Spray Pyrolysis Method

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Abstract: *We report on the structural and optical properties of Co-doped ZnO thin film by spray pyrolysis method. The thin films were characterized by X-ray diffraction and UV spectroscopy techniques. X-ray diffraction result confirms developed thin film have hexagonal crystal structure without any extra impurities. Doping ZnO with Co content increases the values of lattice constants changes. The u parameter value varying with increasing Co doping; it confirms Co substituting in ZnO crystals. The average crystalline size was determined by Scherrer's formula and in the range of 20-23 nm. The optical properties of these thin films show the optical band gap Co-doped ZnO thin films have smaller than that of pure ZnO thin film. This study undertakes the effect of the Co structural and optical properties of ZnO thin films. The results are quality and quantitatively*

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

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I. Introduction

In recent years, the use of thin films due to their outstanding optical and electrical properties compared to thick films was intensively increased. Zinc oxide is an inorganic compound with n-type conductivity and found to adopt a hexagonal crystal structure. Due to its versatility, zinc oxide thin films have great applications in products like gas sensors[1], self-cleaning[2], solar cells[3]and LED[4] etc…., As zinc oxide is abundant in nature, less costly and non-toxic. Many researchers prefer this material than other oxides. ZnO thin films can be synthesized by many techniques like CBD[5], pulse laser deposition[6], spin-coating[7], magnetron sputtering[8] and spray pyrolysis[9] etc. Among these, spray pyrolysis technique (SPT) is better than other deposition technique as it is less expensive, easy to operate and less time-consuming. In recent years transition metal ions such as $Fe2^+$, CO^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} etc., are excellent dopants in ZnO semiconductor Materials [10-13]. These metals as a dopant in host material have the ability to modify not only the band gap energy, but also the electronic structures due to electronic interaction between electrons of transition metal ions with s-p electrons of the host band. G. K. Mani et.al. observed that the value of energy band gap of the ZnO films decreased from 3.26 to 3.22eV after Co doping [14]. Co is a member of group VII of the P.T.it is similar to iron & nickel in its physical properties. Cobalt as metal has excellent properties like resistance to corrosion & resistance to oxidation. Cobalt, when alloyed with other metals, is found to show unusual magnetic strength with many important uses.

In this paper, we mainly deal with the various changes that can be observed in ZnO after Cobalt doping.Y. Febrianti & his coworkers studied synthesis & characterization of Cobalt Doped ZnO Nanorods by hydrothermal method and observed that with increase in doping concentration absorbance at UV & visible range increases up to 3%; then again decreases above 3% [15]. A. R. Khantoul reported on structural and optical properties of Co-doped ZnO thin films that optical band gap of the ZnO sample decreased with an increase in Co concentration [16]. Due to all these versatile change properties after cobalt doping in this work, we are reporting on an investigation of structural & optical properties of ZnO particles doped with Cobalt ions prepared by the spray pyrolysis technique. The structural & optical properties of ZnO were studied using X-ray diffraction (XRD) with CuKa radiation & UV-Visible spectroscopy respectively.

Experimental

A thin film of ZnO and cobalt doped ZnO were deposited using advance spray pyrolysis techniques. Before the deposition, all the glass substrates were cleaned with detergent solution and distilled water. This was followed by treatment like boiling in chromic acid, clean with distilled water. A solution of 0.1M Zinc acetate dehydrate [Zn (CH3Coo) 2 2H2O] was prepared in double distilled water cobalt acetate was added to staring solution to achieve the desired percentage of cobalt doping. The air was used as a carrier gas pressure at 30 psi.

The nozzle to substrate distance was 18 cm kept constant during the deposition solution flow rate was held kept constant at 1.5ml /min. The optimized substrate temperature was 400^{O}C kept constant for deposition of ZnO and Co-ZnO thin film. After deposition, the film was allowed to cool at room temperature

The phase and crystalline of ZnO and Co-ZnO film sample was analyzed by X-ray diffractometer. For the study of optical properties, UV-visible spectrophotometer in the wavelength range 200 nm-1100 nm was used. The thickness of the film was measured by weight by difference method using a sensitive semi microbalance.

II. Result and Discussion

Structural characterization:

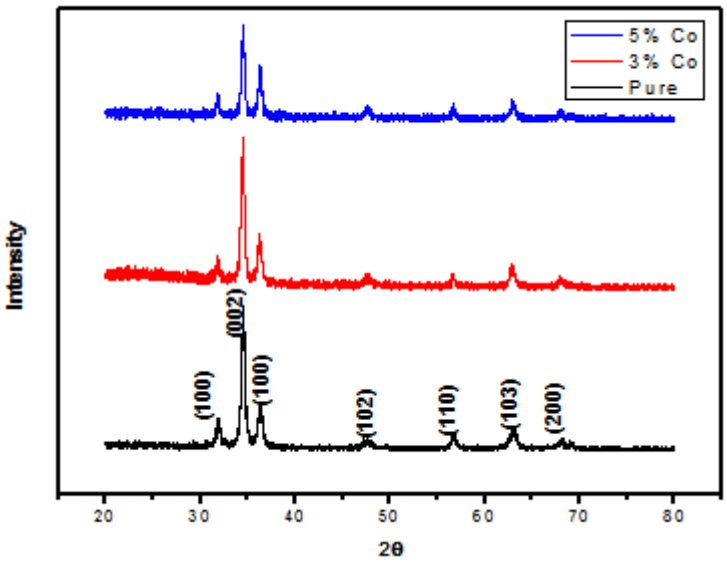

Figure: 1 XRD graph for Co doped ZnO thin films

Fig.1 shows the X-ray diffraction pattern of $Zn_{1-x}Co_xO$ and thin film deposited on a glass substrate at temp 400^0C. All the films were polycrystalline with a structure that belongs to the ZnO hexagonal wurtizite. The intensive peaks corresponds (100), (002), (101), (110), (102), (200) and (103) planes for pure zinc oxide sample. As shown in fig. 1 no extra impurity phases were observed. As cobalt doping increase the intensive peak (002) of intensity changes. From this result confirms that cobalt doping upto 5% there is no change of crystal structure. The lattice parameters were calculated using following formula.

$$\text{Sin}^2\theta=\frac{\lambda^2}{4a^2}\left[\frac{4}{3}(h^2+hk+k^2)+\frac{l^2a^2}{c^2}\right] \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Where 'a' &'c' are lattice parameters, θ-Bragg's angle of peaks, hkl-miller indices, λ -wavelength of X-ray diffraction. The lattice parameter 'a' &'c' were determined the (100) and (002) planes respectively as follows,

$$a=\frac{\lambda}{\sqrt{3}sin\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$c=\frac{\lambda}{2sin\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Calculated lattice parameter values as shown in table 1.The volume (v), distortion parameter (u) and bond length (L) of deposit sample were calculated from XRD data.

The average crystalline size of the film was calculated from X-ray line broadening of a diffraction peak using Scherrer's formula,

$$D=\frac{0.9\lambda}{\beta cos\,\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where, D- Average crystalline size of the particle,
β- Full Width Half Maxima (FWHM),
λ −Wavelength of CuKa X-ray radiation ($1.54A^0$),
θ - Angle of diffraction.

The lattice strain (ε) is determined using the tangent formula,

$$\varepsilon=\frac{\beta}{4tan\,\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The volume (v) of the crystalline structure can be determined by,

$$v = \frac{\sqrt{3}}{2} a^2 c \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where, a and c are the lattice parameters.

The value of lattice parameters of the film is given in table 1.It is observed that the value of lattice parameter 'a' of undoped ZnO film was small as compared to the Co doped ZnO thin films. As doping Co content, the value of lattice parameter 'c' increases, it means that prepared films orientation along the c axis. In addition the c/a ratio and volume of unit cell increase with increasing Co doping. The value of u parameter in the range of 0.3781 to 0.3783 of pure and cobalt doped thin films .Based on this structural study it confirms that cobalt surely substituted in ZnO host matrix. The change in structural parameter with cobalt doping it may be due to larger ionic radius of Co^{2+} is (88.5pm) as compared to the Zn^{2+}(74 pm).

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

Samples (%)	a (nm)	C (nm)	c/a	D (nm)	Strain	Volume $(nm)^3$	u
Pure	0.324439	0.51956	1.601409	20.50534	0.001051	0.046757	0.378319
3	0.324155	0.52028	1.605021	21.25508	0.000923	0.046871	0.378101
5	0.324279	0.52064	1.605529	22.10103	0.000957	0.046837	0.378239

Optical Characterization:

The optical study of the deposited films was carried out by using UV-Visible spectrophotometer. The optical absorption spectra of pure and Co-doped ZnO film were taken in the range of 350 to 800 nm Fig. (2) Shows absorption spectra of pure and doped thin film. From fig (2). It is observed that the absorption edge shift towards higher wavelength as the concentration of cobalt increased in ZnO. The direct band gap energy of deposited films was determined using Tauc and Devi's Mott Eq.

$$(\alpha h\nu)^n = K(h\nu - E_g) \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where, hν- Incident photon energy, α- absorption coefficient, E_g- energy band gap of material.
The exact value of band gap was determined by extrapolating the straight line portion of $(\alpha h\nu)^2$verses hν.

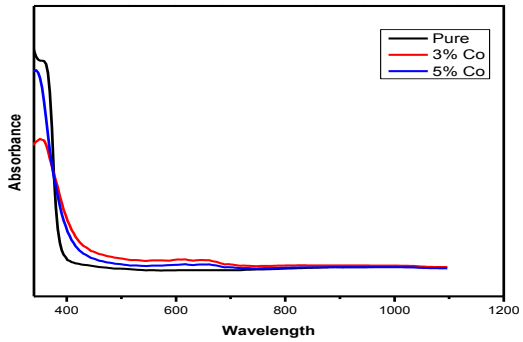

Figure: 2 Absorbance verses wavelength for Co doped ZnO thin films

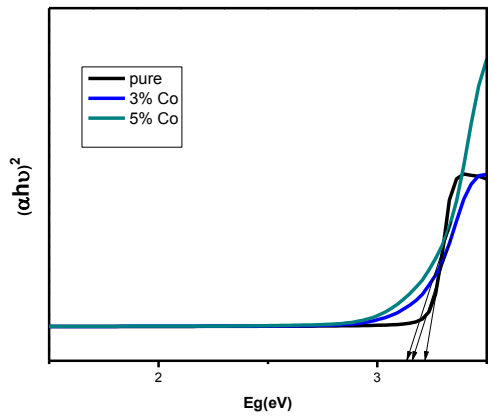

Figure:3 The relation between $(\alpha h\upsilon)^2$ and (hυ) for Co doped ZnO thin films.

The band gap energies were tabulated in table (2). It is observed that the band gap energy, decreased from 3.2231 eV to 3.1387 eV with increased cobalt doping concentration. Decreased in band gap is also a reason, mainly due to the sp-d exchange interaction between the localized 'd' electron and band electron of cobalt ions which is incorporated in ZnO lattice.

Table 2: Energy bad gap of

Doping concentration (%)	Band gap (Eg)
0	**3.2231**
3	**3.1640**
5	**3.1387**

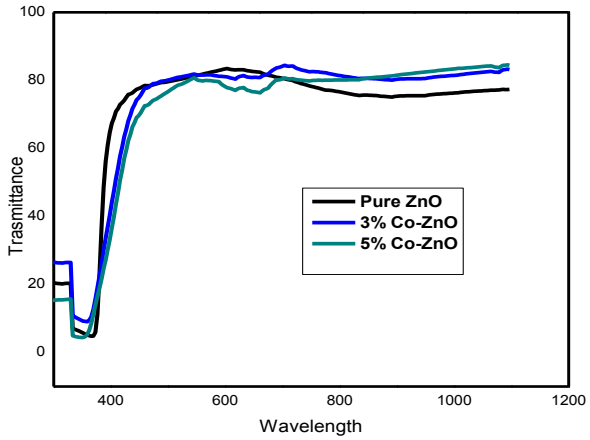

Figure:3 Transmission verses wavelength for Co doped ZnO thin films

To study optical properties of pure and cobalt doped ZnO thin films. The transmittance spectra of the films were studied in the wavelength range 300nm to 1100nm using UV-Visible spectrophotometer. A transmittance spectrum of the film is shown in fig… It is observed that the value of transmittance is high in the visible range and it is minimum in the wavelength range of 350nm to 390 nm. It is seen that the transmittance value of all the samples is 70% to 80%. Below 450nm there is a sudden fall in transmittance which is due to strong absorbance of the films. The transmittance of pure ZnO is found to be maximum in the visible region. It is observed that transmittance decreases with increase in dopant concentration which may be due to decrease in crystallanity. Decrease in transmittance may also be due to the roughness of the film.

III. Conclusion

Pure and cobalt doped ZnO thin films were successfully deposited on glass substrate with 400 ^{0}C substrate temperature by spray pyrolysis method. The systematic investigation of structural and optical properties of pure and Co doped ZnO thin films were carried out. From structural study, all prepared thin films have hexagonal (wurtizite) crystal structure and average crystal size was found to be in the range of 20 nm to 23 nm. The lattice parameter a changes with increasing cobalt doping concentration. The lattice parameters, c/a ratio and volume of unit cell varing with increasing cobalt content. The absolute strength of these absorption bands increases almost linearly with the increase in Co concentration in ZnO. With increasing Co concentration band gap of the material affected and it is decreases with increasing Co doping concentration. From structural and optical study prepared thin film can be suitable for solar cell and gas sensing application.

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