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Impact of Cobalt Doping on Structural and Optical Properties of ZnO Thin Films

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ABSTRACT

Cobalt doped zinc oxide thin films have deposited on glass substrate via spray pyrolysis techniques. The structural and optical properties of prepared thin films are characterized by Xray diffraction and UV-Vis spectrophotometer. From Xray diffraction pattern conforms single phase hexagonal wurtzite structure with c axis orientation. The average crystalline size of thin films calculated from Scherrer equation and found to be decrease with cobalt doping. The absorbances value is found to be high for cobalt doped ZnO as compared to undoped ZnO. Also, the optical characterization reveals the decrease in Energy band gap with cobalt doping.

Keywords : Semiconductor, Zinc oxide, Thin films, Xray diffraction, Absorbance.

I. INTRODUCTION

Zinc oxide is one of the efficient oxide materials among the various II-VI semiconductors. It has applications in many devices such as solar cell devices, gas sensing devices and LED [1, 2, 3]. These applications lead to the enormous increase in Zinc oxide study and its utility in different fields of science and technology. A wide band gap of 3.37eV and high exciton binding energy of 60 meV even at room temperature makes zinc oxide one of the most relevant materials in terms of research. [4 ,5] As a result of oxygen vacancies ZnO is more prominent toward n-type behavior. Standard methods of fabrication, low-cost techniques of synthesis, non-toxicity and remarkable properties make zinc oxide based thin films a topic of interest these days [6, 7, 8].

Properties of Zinc oxide may get vary with crystallite size, crystallinity, morphology, which can be varied by varying chemical composition, thermal treatment, pressure maintenance etc. [9,10,11]. All these parameters lead to improved structural, optical and morphological properties of material in most of the cases. Furthermore, properties can be enhanced by doping Zinc oxide. Dopant selection depends on ionic radii difference between and ZnO and dopant element and its electronegativity as well. As a dopant material, cobalt can enhance the optical behavior of ZnO as a result of abundant electronic state of cobalt.[12]. Such films can be obtained by means of several deposition techniques such as thermal evaporation [13] sputtering,[14], CVD [15] and spray Pyrolysis [16]. However, Spray pyrolysis is non- complicated, efficient and low-cost technique which can be implemented for large scale thin films synthesis having versatile properties.

This work deals with structural and optical study of Co doped ZnO thin films prepared by spray pyrolysis technique at constant temperature of 400°C. Deposition of thin films are performed on glass substrates due to their easy availability and low cost. This study is mainly focusing on the impact of Co as a dopant on ZnO lattice that can be responsible for improvement in its structural and optical properties. Thin film samples were prepared for pure ZnO and 10% doping of Co at ZnO lattice. X-ray diffractometer and UV-Vis spectrophotometer is opted for the characterization of both undoped and Co doped ZnO thin films.

II. METHODS AND MATERIAL

Precursor solution were prepared for both pure and cobalt doped Zinc oxide samples using zinc acetate and cobalt acetate as the starting materials. To dissolve the acetates completely, deionized water was used. Both Zinc acetate and cobalt acetate solutions were stirred continuously to get homogenous solutions. doping percentages was taken 10% to know the variation in properties of ZnO thin films as a result of addition of cobalt. The substates where the prepared solutions were to be deposited, washed and cleaned thoroughly using distilled water and acetone. Prepared solution was transferred to spray chamber where transformation of the liquid into the stream takes place in order to get a uniform and fine droplet and allowed to spray onto the preheated glass substrates. All the parameters of spray pyrolysis set-up such as Flow rate, deposition time, Nozzle to substrate distance, substrate temperature (400°C), Carrier gas pressure were adjusted and set to a desired value in order to get a good yield. Prepared solutions were transferred into the spray chamber and allowed to be sprayed onto the substrate for desired time. Structural characterization is performed using Rigaku XRD diffractometer consist of an X-ray beam of wavelength kα (Cu) = 1.5418 Å. The scanning range was maintained between 20 to 80 degrees. This study helped in determining the structure related parameters and purity of the phase.

III. RESULTS AND DISCUSSION

The XRD pattern for pure ZnO and 10% cobalt doped ZnO is shown in figure (1). Both the samples are observed to be single phased with hexagonal crystal structure having space group P63mc. Indicating clearly that cobalt has been successfully incorporated into the ZnO lattice as substitutional atom. No other extra peak can be observed corresponding to any other foreign impurity. The XRD pattern consist of peaks due to (100), (002), (101), (102), (110), (103), (112) planes. The position at 34.50O position the sharp and highest intense peak in obtained which corresponds to (002) plane. The peak intensity of (002) is higher than other peaks indicating that prepared films are nanocrystalline in nature and has c-axis preferred orientation perpendicular to the substrate. Peak intensity is found to be decreased with Co doping in ZnO which may be due to degradation of crystalline quality after the introduction of Co+2 in ZnO lattice [17]. Average crystallite size was evaluated for (002) plane using XRD results of samples. With the help of Full width and half maxima (FWHM) values, Grain sizes were calculated using Debye Scherrer formula. [18]

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

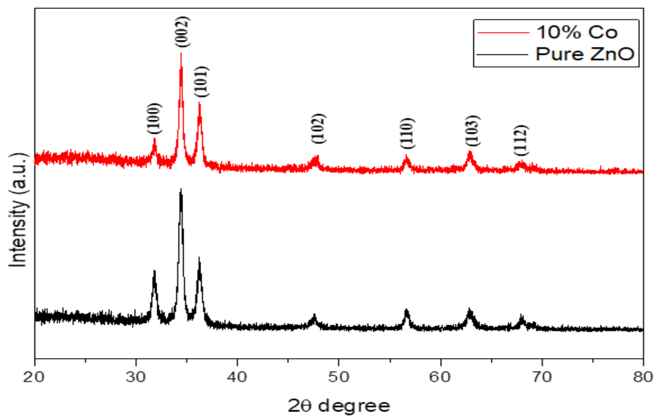

FIG (1): XRD PATTERNS OF PURE AND CO-DOPED ZNO THIN FILMS

Here, D stands for average crystallite size, β stands for full width half maxima, $\lambda = 1.54A^0$ corresponds to wavelength of X-ray, K is constant (~ 0.9), θ is Bragg's angle. The corresponding Grain sizes values are reported in Table 1. The estimated values of the crystallite size confirm that Both the samples are of nanosized in nature. With addition of Co concentration there is decrease in Grain size observed with increase in strain, which may attribute to increase in grain boundaries [19]. Lattice parameters and strain values were also estimated using XRD analysis and tabulated in the Table (1). Lattice constants have found to be decreased with addition of Co content.

The lattice parameter values 'a' & 'c' of the prepared thin films were calculated using the formula,

$$\frac{1}{d_{h,k,l}^2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} \quad (2)$$

Where, $d_{h,k,l}$ - Interplaner spacing distance, h, k, l – Miller indices, a and c – Lattice parameters

Doping	a	c	c/a	D(nm)	Strain
Pure ZnO	3.248856	5.21088	1.603912	22.32566	0.004383
10% Co	3.246281	5.20740	1.604113	20.52485	0.004606

TABLE 1: STRUCTURAL PROPERTIES OF PURE AND CO-DOPED ZNO SAMPLES

Optical studies were performed using UV-Vis spectrophotometer using which optical absorption spectra of Pure and Co doped films is graphically elaborated in figure (2). Sharp and sudden change in absorption can be observed with cobalt doping as compared to pure ZnO in visible region of spectrum. This observation of increase in optical absorbance may imply the existence of direct transitions.

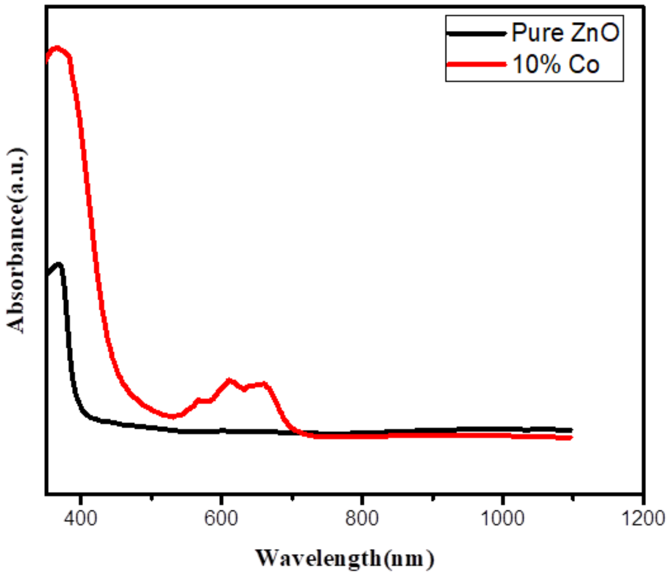

FIG (2): ABSORPTION SPECTRA OF PURE AND CO-DOPED ZNO THIN FILMS

The optical band gap of E_g is calculated using the following Equation,

$$\alpha = \frac{A(h\nu - Eg)^n}{h\nu} \quad (2)$$

Where, 'A' and 'n' are constants, value of 'n' equal to 1/2 for the direct band gap semiconductor. The plot of $(\alpha h\nu)^2$ verses Photon energy for both the samples is shown in figure (3).

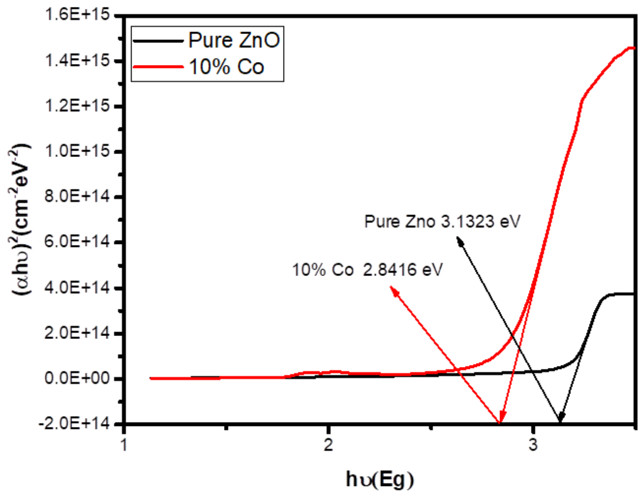

FIG (3): BANDGAP OF PURE AND 10% CO-ZNO THIN FILMS

Table (2) shows the band gap results of both pure ZnO and Co-doped ZnO samples. Evidently, the band gap of Co-doped ZnO decreased gradually from 3.13 eV to 2.84 eV with respect to Co doping. This result may be associated sp-d hybridization that creates a shallow impurity level of dopant atom [20].

Doping	Bandgap (eV)
Pure ZnO	3.1323
10%Co	2.8416

Table 2: Band gap of Pure and Co-doped ZnO thin films

IV. CONCLUSION

In this work, we have prepared Pure and Co-doped ZnO Thin films by chemical spray pyrolysis method on glass substrate. The films observed to be polycrystalline in nature with orientation along c-axis and most intense peak along (002) plane. As a result of cobalt incorporation into ZnO lattice the hexagonal wurtzite nature remains same. As an impact of Co doping grain size decreases consequently crystalline quality decreases. Local strain values have found to be increased with doping may imposing large distortion in the lattice as a result of which reduction in crystallinity observed. Optical analysis indicates doped sample have high absorbance in range of 350nm to 450nm. This increase in absorption due to doping may imply the incorporation of Co^{+2} ions which is substituting the Zn^{+2} ions at the host lattice. This replacement is producing stress in the films thereby forming the structural deformation and resulting in higher absorbance. Optical band gap values are changing from 3.13eV to 2.84 eV for pure and Co-doped ZnO respectively due to exchange interactions.

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