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Structural and Optical Characterization of Cobalt-Doped ZnO Thin Film Deposited by Spray Pyrolysis Method

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Abstract: *In this study, undoped and Co doped ZnO thin films were deposited on glass substrates by Spray Pyrolysis method. Characterization techniques of XRD, SEM and UV-visible spectra measurements were performed to investigate the effects of Co doping on the structural and optical properties of ZnCoO thin films. The deposited films were annealed at 350^{0}C and 400^{0}C respectively for one hour and similar characterization techniques were performed. The XRD patterns of all the films showed crystalline behavior and were of hexagonal wurtzite structure. Heat treatment improved the crystallinity of the deposited films. The SEM study performed after annealing at 400^{0}C showed that incorporation of Cobalt changes the surface morphology of ZnO films from a plane smooth surface to a rough wrinkled network. The optical studies showed that, the films exhibit high transmittance and low absorbance in the visible region. But, the Co doped films had relatively lower transmittance and higher absorbance in the visible region than the undoped films. It was found that, the band gap of the films decreases with increasing doping and also with heat treatment.*

Keywords: *Spray Pyrolysis, Cobalt doping, Wurtzite Structure, Optical properties, Surface Morphology.*

Introduction

ZnO is a wide band gap (~3.37 eV) material that has potential applications in the fabrication of devices such as ultraviolet (UV) light-emitters, varistors, transparent high-power electronics, piezoelectric transducers, gas-sensors, smart windows and solar cells [1]. It is one of the materials of the II–VI family of Semiconductors which have been studied extensively for many years [2]. Its electrical and optical properties could be modified thoroughly by thermal treatment with hydrogen or by an appropriate doping process either by cationic or anionic substitution [3]. Besides, ZnO doped with transition metals has been predicted theoretically to be very good candidates for room temperature ferromagnetism [4]. As a consequence, transitional metal doped Zinc Oxide has found potential applications in spintronics [5, 6]. Several studies [7]-[13] described the growth processes of Co doped ZnO thin film and described the effect of cobalt doping on electrical, magnetic and magneto-optical properties. In recent years, Co doped ZnO thin film has been deposited by Pulsed Laser Deposition (PLD), Molecular Beam Epitaxy and Sputtering methods [14], [15]. In contrast, until now spray pyrolysis technique is rarely used as deposition technique although it represents a very simple and relatively cost-effective processing method (especially with regard to equipment costs). It offers an extremely easy technique for preparing films of any composition [16]. A few work described the deposition of Co doped ZnO thin film by this noble technique. For example, Belghazi et al [17] deposited Co doped ZnO thin film at 450^{0}C and Bhatti et al [18] at 380^{0}C temperatures respectively. However, few studies have focused on fabrication of ZnCoO thin films at relatively lower temperatures. In this study we report on the growth of Co doped ZnO thin film by spray pyrolysis technique at 230^{0}C and on the influence of Cobalt doping and heat treatment on the structural and optical properties of ZnO and ZnCoO thin films.

Experimental Details

The undoped and Co doped ZnO thin films were deposited on glass substrates by Spray Pyrolysis method at a relatively lower temperature of 230^{0}C. The precursor solution (0.1M) was prepared by dissolving Zinc Acetate compound [$Zn(CH_3COO)_2.2H_2O$] in DI water and the solution was stirred for 1 hour by a magnetic stirrer. For the purpose of Co doping, cobalt acetate [$(CH_3COO)_2.Co.4H_2O$] along with zinc acetate was used as source compound.

Before the deposition of films the glass substrates were cleaned very carefully. We kept the substrate temperature constant at 230^{0}C for the deposition of all the samples. The distance between the spray head and the substrate, liquid flow rate and air pressure were kept 20.2cm, 0.25 mL/min and 0.05 MPa respectively for all the samples. We annealed the deposited films at 350^{0}C and 400^{0}C in N_2 atmosphere for 1 hour. The structural properties of the as-deposited and annealed films were studied by the X-ray diffraction method with a Bruker's X-Ray Diffractometer with Cu-Kα radiation using the wavelength of 1.5406Å. The X-Ray Diffractometer was

operated at 40 kV and 40 mA, with the scanning angular range $20^0 \leq 2\theta \leq 65^0$ to get possible fundamental peaks for each sample. The crystallite sizes for (100) and (002) planes of the films were calculated by using the Scherrer formula,

$$D = \frac{K\lambda}{\beta Cos\theta} \tag{1}$$

Where, 'D' is the crystallite size, 'K' is a constant known as Shape factor (k= 0.94). 'β' is the Full width at half maximum (FWHM) given in radian and 'θ' is the Bragg's angle. The interplaner spacing, 'd' was calculated by using the Bragg's relation

$$2dSin\theta = n\lambda \tag{2}$$

And, for the calculation of lattice parameter, we used the following formula

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

The Hitachi S34001N Scanning Electron Microscope was used to carry out the SEM measurement. Surface morphology of the films annealed at 400^0C was studied by SEM under 12.9mm x 5.00k magnification. The optical measurements were performed using a UV-1601, UV-visible spectrophotometer (Shimadzu Corp., Japan). This spectrophotometer was used to measure the relative transmittance and absorbance of as-deposited and annealed ZnO and Cobalt doped ZnO thin films. The absorption coefficient has been calculated from the transmission spectra by using the relation

$$\alpha = -\frac{\ln T}{t} \tag{4}$$

Where, 'T' is the normalized transmittance and t is the thickness of the film. The direct band gap have been obtained theoretically by the formula,

$$(\alpha h\nu)^2 = h\nu - E_g \tag{5}$$

The direct band gap energy have been obtained from intercept on the energy axis after extrapolation of the straight line section of $(\alpha h\nu)^2$ vs. hν curve.

Results and Discussion

A. Structural Properties

Figure 1 shows the X-ray diffraction pattern of as-deposited and annealed undoped and Co-doped ZnO thin films. The observed peaks at (100), (002), (101), (102), (110) and (103) confirmed the hexagonal wurtzite structure of the samples. 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. This indicates that Co doping did not change the crystal structure of the ZnO samples which imply that there were no secondary phases such as Co cluster or oxides. It may be due to very small amount of Co doping which was not enough for changing the crystal structure significantly. This behavior shows good agreement with the study done by Li *et al* [19]. After annealing at 350^0C and 400^0C in N_2 atmosphere for 1 hour, we observed that as the temperature increases, the intensity of the peaks increases and it becomes narrower indicating an improvement in crystallinity.

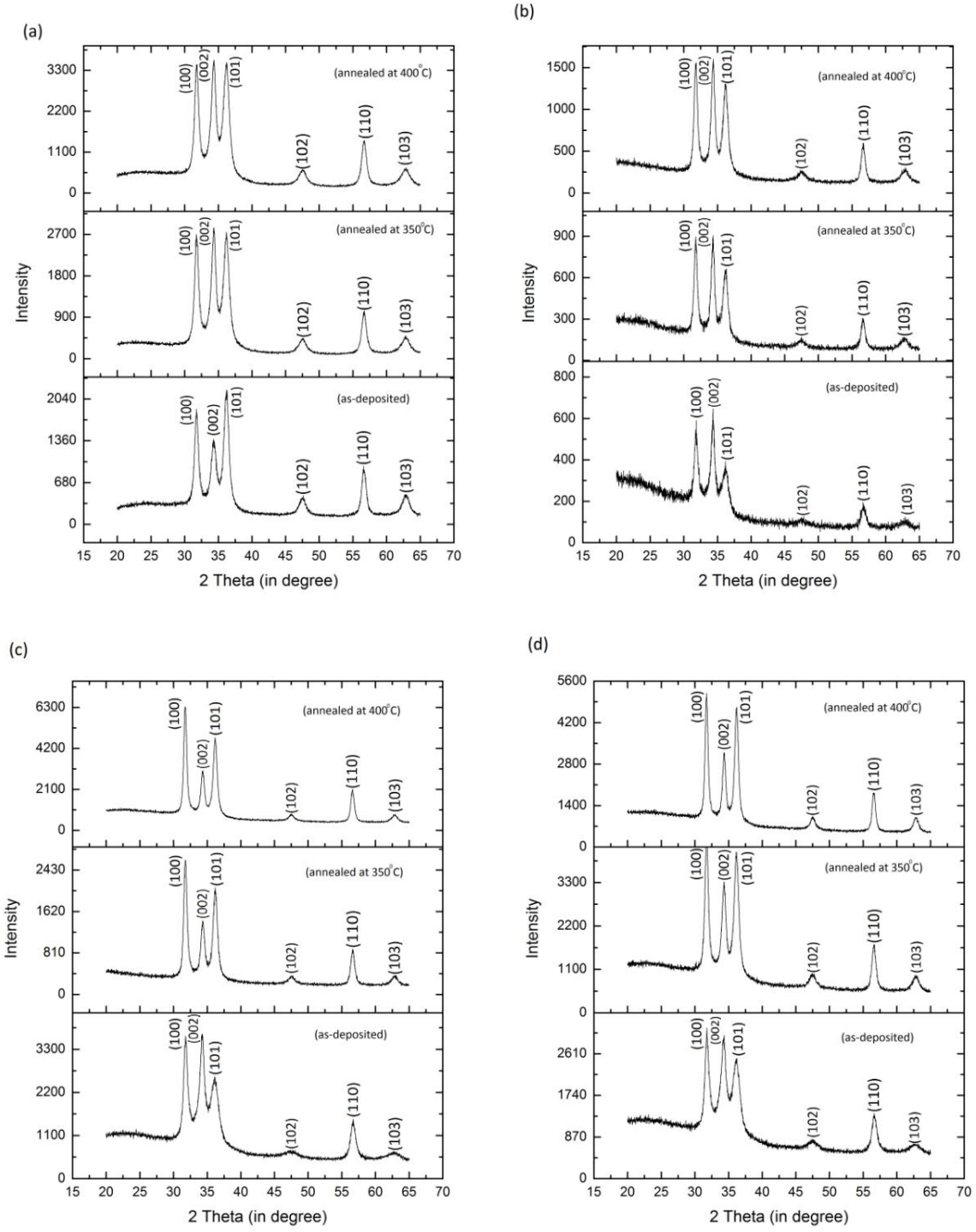

Figure 1. XRD spectra of (a) ZnO thin film, (b) 3% doped ZnO thin film, (c) 5% doped ZnO thin film and (d) 7% doped ZnO thin film.

The interplaner spacing and the lattice parameter for the (100) and (002) peaks of the ZnO and ZnCoO samples are shown in table 1, table 2 and table 3 respectively. In this study, crystallite sizes have been calculated by the Scherrer formula and are represented in Figure 2. It can be observed that crystallite size varies with the variation of dopant concentration. The presence of Co dopant not only inhibited the growth of oxide but also limited the crystal growth, as suggested by the observed difference in crystallite size with respect to as-deposited ZnO. The increase of crystallite size with annealing temperature could be due to the fact that the annealing process decreases the crystal strain and increase the dislocation density in the crystal. It is to note that, the values of crystallite sizes that are found in this study are less than the values found by Bhatti et al [18]. It is observed that the values given in Table 1, Table 2 and Table 3 almost agree with those obtained from the ASTM card for polycrystalline ZnO powder of hexagonal structure [20].

Table 1. XRD data chart for the as-deposited undoped and doped ZnO films.

Dopant Concentration	**Crystallite Size (nm)**		**Interplaner Spacing 'd' (Å)**		**Lattice Parameter (Å)**		**ASTM standard**	
	For (100) peak	**For (002) peak**	**For (100) peak**	**For (002) peak**	**a = b**	**c**	**a = b (Å)**	**c (Å)**
0%	9.1823	6.0409	2.8141	2.6130	3.2494	5.226		
3%	7.7438	8.1921	2.8099	2.6091	3.2446	5.2182	3.250	5.207
5%	6.4870	5.7547	2.8118	2.6144	3.2468	5.2288		
7%	6.0345	3.9336	2.8133	2.6137	3.2485	5.2274		

Table 2. XRD data chart for the undoped and doped ZnO films annealed at 350^0C**.**

Dopant Concentration	**Crystallite Size (nm)**		**Interplaner Spacing 'd' (Å)**		**Lattice Parameter (Å)**		**ASTM standard**	
	For (100) peak	**For (002) peak**	**For (100) peak**	**For (002) peak**	**a = b**	**c**	**a = b (Å)**	**c (Å)**
0%	9.7780	7.9926	2.8143	2.61052	3.2497	5.2210		
3%	11.0840	8.7765	2.8147	2.60933	3.2512	5.2186		
5%	12.6822	10.4341	2.8156	2.6095	3.2511	5.2190	3.250	5.207
7%	10.2974	7.3184	2.8168	2.6103	3.2526	5.2206		

Table 3. XRD data chart for the undoped and doped ZnO films annealed at 400^0C.

Dopant Concentration	**Crystallite Size (nm)**		**Interplaner Spacing 'd' (Å)**		**Lattice Parameter (Å)**		**ASTM standard**	
	For (100) peak	**For (002) peak**	**For (100) peak**	**For (002) peak**	**a = b**	**c**	**a = b (Å)**	**c (Å)**
0%	10.3218	9.0110	2.8136	2.6101	3.2489	5.2202		
3%	11.4281	9.3600	2.8132	2.6084	3.2485	5.2168		
5%	14.2087	10.7777	2.8171	2.6098	3.2529	5.2196	3.250	5.207
7%	13.2557	9.7988	2.8182	2.6085	3.2541	5.2170		

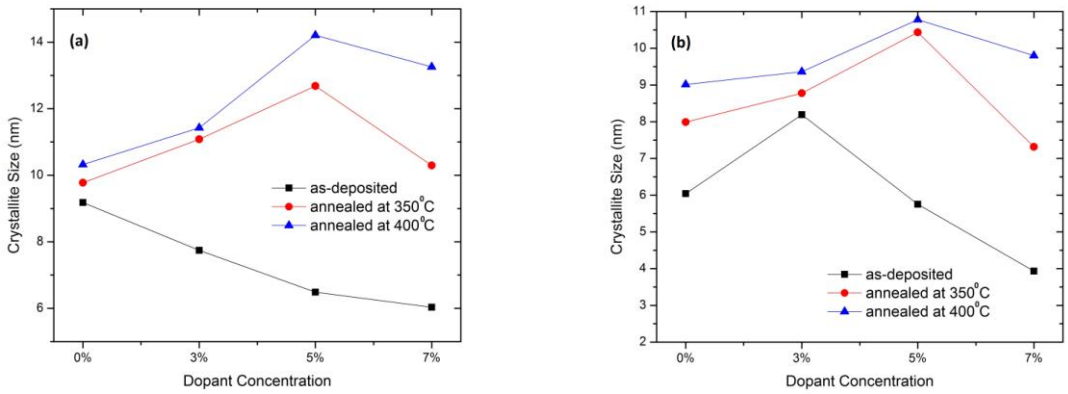

Figure 2: Variation of Crystallite size with Co dopant concentration (a) for (100) peak and (b) for (002) peak.

B. Surface Morphological Characteristics

Figure 3 shows the SEM micrographs of undoped, 3% doped and 7% doped ZnO thin films respectively. From these figures it is apparent that incorporation of Co dopants in ZnO thin film changed the surface morphology.

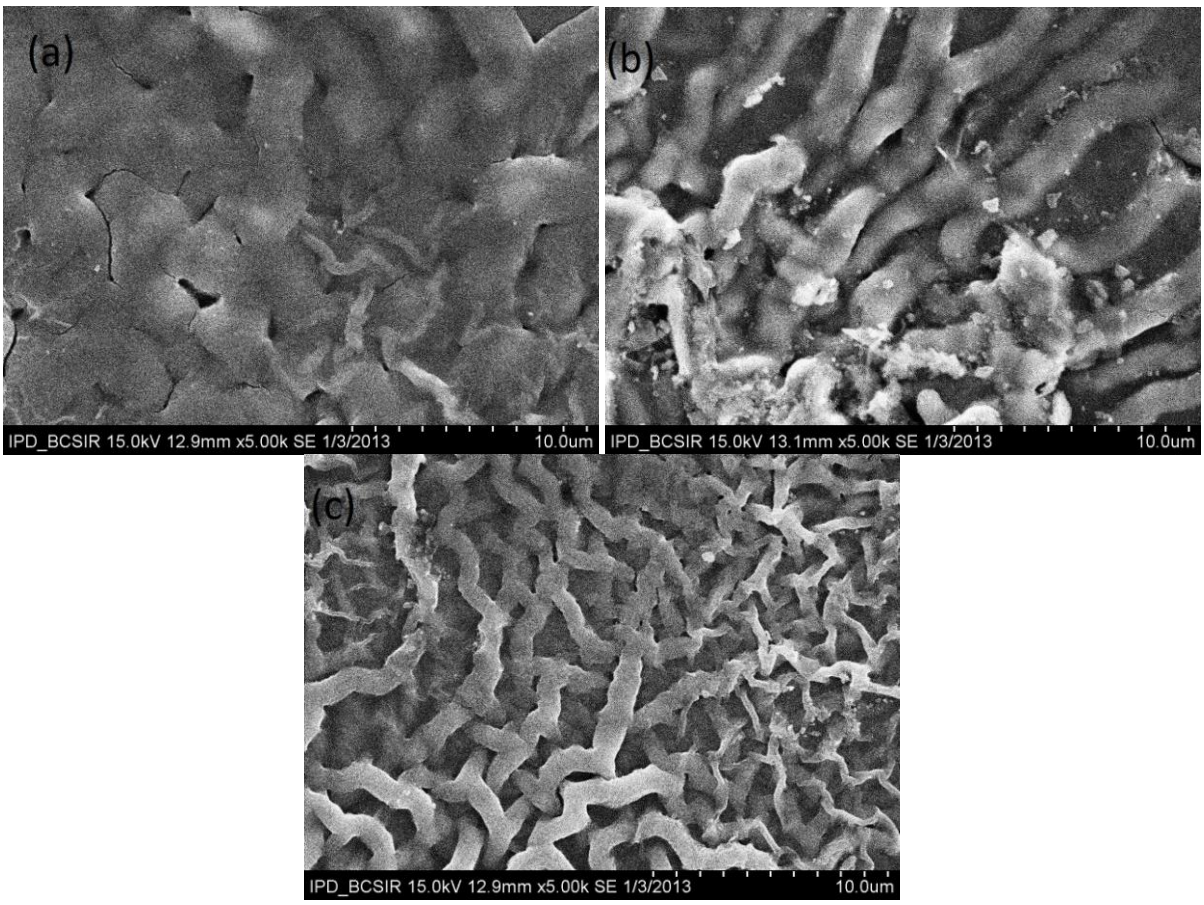

Figure 3. SEM micrograph of (a)undoped ZnO thin film, (b) 3% doped ZnO thin film and (c) 7% doped ZnO thin film annealed at 400^0C.

From figure 3, it can be observed that, SEM image of ZnO resembles a plane surface; but, with the incorporation of doping, Co^{2+} changed the surface morphology to a wrinkled network and this is in good agreement with the literature [21]. This may be due to the cause that Co^{2+} increased the roughness of the film surface.

C. Optical Properties

Figure 4 represents the variation of transmittance T (%) with wavelength of undoped, 3% doped, 5% doped and 7% Co doped ZnO thin films. Transmittance is obtained in the wavelength range 400-1100 nm. It is evident that the optical transmittance increases in the visible region and decreases in the ultraviolet region for all the samples. But in the visible region with the increase of (0-7%) Co^{2+} concentration, there is a gradual decrease in the transmittance spectra of the samples. After heat treatment, there are slight changes in the transmittance spectra of all the films (figure 4). But the overall trend is similar to that of as-deposited films.

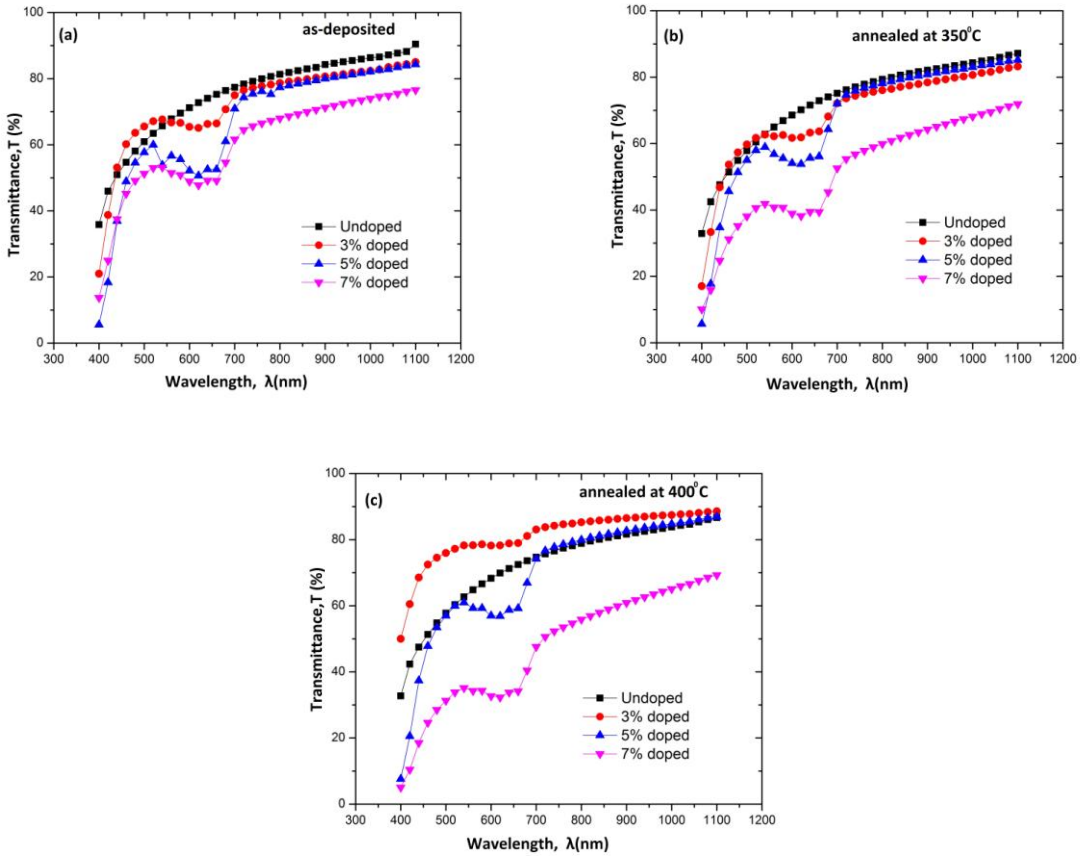

Figure 4.Variation of Transmittance (T%) with wavelength λ (nm) for ZnO and Cobalt-doped ZnO thin films (a) as-deposited, (b) annealed at 350^0C and (c) annealed at 400^0C.

Figure 5 represents the variation of absorbance with wavelength of undoped, and Co doped ZnO thin films. It is evident that absorbance decreases in the visible region and increases in the ultraviolet region for all samples. But in the visible region the doped films show three absorption peaks and with the increase of (0-7%) Co concentration, there is a slight increase in the absorption peaks which may be due to absorption by Co^{2+} present in the doped films. After heat treatment, there are slight changes in the absorbance spectra of all the films (figure 5). But the overall trend is similar to that of as-deposited films.

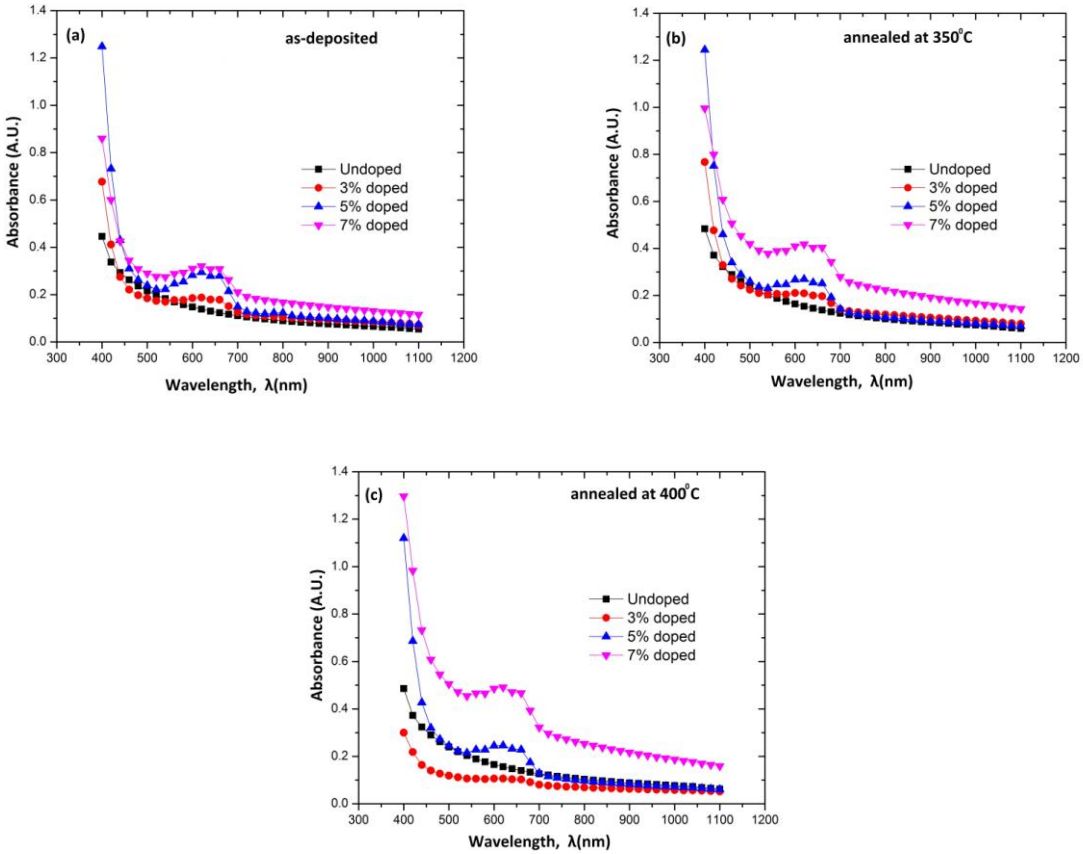

Figure 5. Variation of absorbance (A.U) with wavelength λ (nm) for undoped and doped ZnO thin films (a) as-deposited (b) annealed at 350^0C and (c) annealed at 400^0C.

Variation of absorption Coefficient (α) with photon energy (hν) for undoped and Co doped ZnO thin films are shown in the figure 6. It can be observed from the figure that the absorption coefficient gradually increases with photon energy. But in the energy range 2.75eV~3.65eV there is sharp rise in the value of absorption coefficient indicating some absorption peaks in this energy range.

These absorption bands $^4A_2(F) \rightarrow {}^2E(G)$, $^4A_2(F) \rightarrow {}^4T_1(P)$ and $^4A_2(F) \rightarrow {}^2A_1(G)$, are due to the crystal field transition in the high spin state of Co^{2+} ($3d^7$) in the tetrahedral coordination [22]. Zn^{2+} in the ZnO is situated in the tetrahedral coordinate sites; these observations clearly indicate that Co is substituted for Zn^{2+} in ZnO and that the oxidation state of the Co ions in the polycrystalline Co doped ZnO. The optical energy gaps of the Co-doped ZnO samples are considerably smaller, showing thereby that the band gap of ZnO can be tuned by Co-doping. All co-doped samples gave UV as well as blue-green emissions, somewhat weaker than in undoped ZnO. It is evident that, after heat treatment, the figure resembles the same pattern.

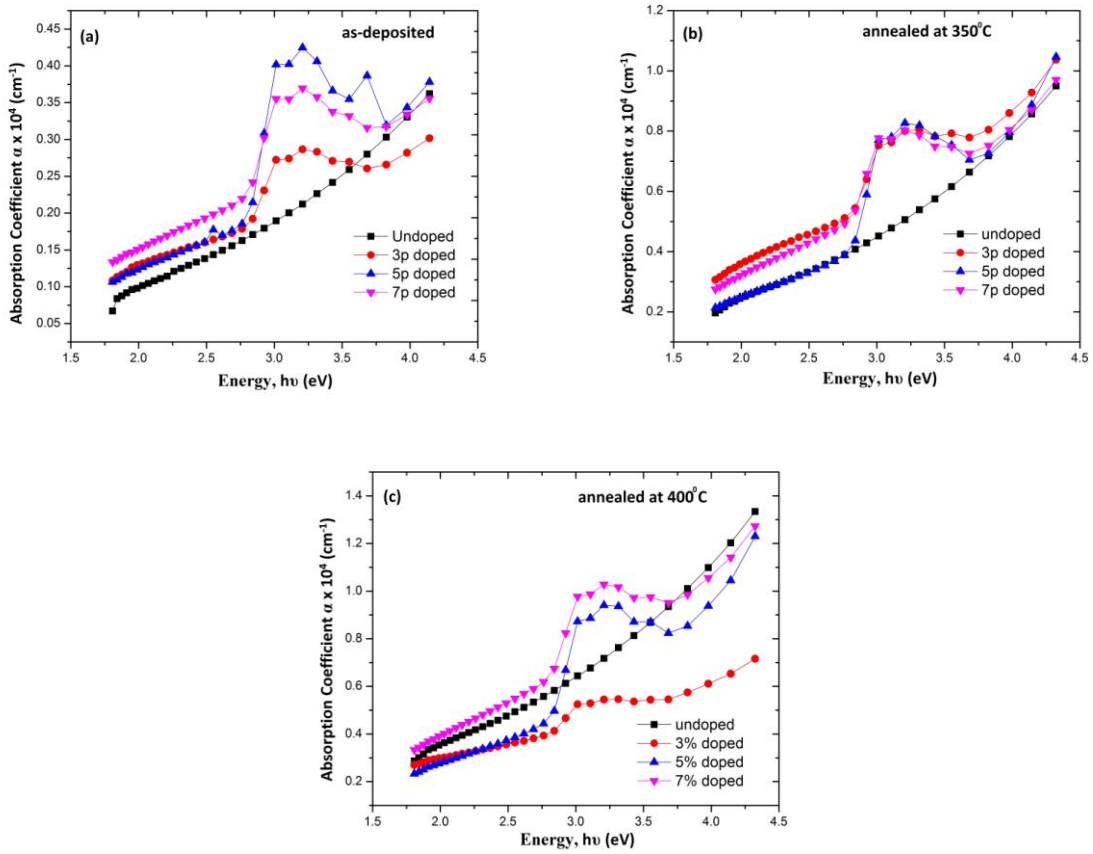

Figure 6. Variation of absorption Coefficient with photon energy for undoped and Co doped ZnO films (a) as-deposited (b) annealed at 350^0C and (c) annealed at 400^0C.

The optical band gap (E_g) has been determined from the plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for undoped and doped ZnO thin films. The direct band gap energy of the films have been obtained from intercept on the energy axis after extrapolation of the straight line section of $(\alpha h\nu)^2$ vs. $h\nu$ curve. The band gap values are shown in the figure 7. It has been found that, the values of band gap decreases with increasing Co^{2+} concentration. This may be due to the sp-d exchange interactions [23].

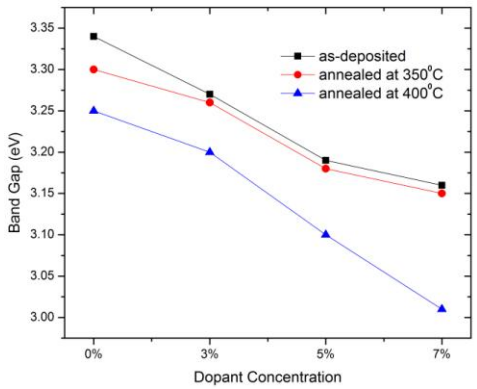

Figure 7. Variation of direct band gap with dopant concentration for undoped and Co doped ZnO thin films.

It is evident that band gap also decreases with temperature as seen for the films after post-deposition heat treatment. This may be due to the fact that, when temperature increases, the amplitude of atomic vibrations increases resulting into a decrease in band gap.

Conclusions

ZnO and Cobalt-doped ZnO thin films have been deposited onto glass substrates by using low-cost spray pyrolysis deposition. In this study we have shown that, Co doped ZnO thin films can be fabricated by Spray Pyrolysis method at relatively lower temperature of 230^0C. The diffraction patterns reveal a good crystalline behavior with the hexagonal wurtzite structure. The post-deposition heat treatment improves the crystallinity of the film. SEM micrographs show that incorporation of Co dopants changes the surface morphology of ZnO thin film from a plane smooth surface to a rough wrinkled network. Optical transmittance Spectra of samples shows that the visible transmission of the films generally decreases with the increase of the Cobalt content. Cobalt doping introduces some absorption peaks in the visible region of the transmission spectra. Absorbance spectra shows that absorbance decreases in the visible region and increases in the ultraviolet region for all samples. The value of absorption coefficient also increases significantly in the visible range to ultraviolet range. 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. Band gap of the undoped and doped samples also decreases with temperature. These properties indicates that, the ZnCoO thin films can be used to fabricate dilute magnetic semiconductors (DMS) for spin based light emitting diodes and transistors.

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