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THE CHARACTERIZATION OF $Zn_{1-x}Co_xO$ THIN FILMS SYNTHESIZED BY ULTRASONIC SPRAY DEPOSITION WITH CONTROLLED VISIBLE LIGHT ABSORPTION

ABSTRACT

This work examines the grown of $Zn_{1-x}Co_xO$ films at different Co concentrations at 420°C by ultrasonic spray deposition. The effect of Co concentration of $Zn_{1-x}Co_xO$ films on optical characterization, structure crystallinity and electrical conductivity was studied. Transmission spectra of $Zn_{1-x}Co_xO$ films presented three edges in the visible region, it was observed in the range of 541 and 656 nm of wavelengths, which related to the d-d transitions of Co^{2+} ion with $3d^7$ high-spin configurations in a tetrahedral crystal field formed by neighboring O^{2-}ions. The gap energy was found increases after doping by Co to maximum value of 3.373 eV at x=0.04. The Urbach energy minimum was 0.083eV, it is obtained for x=0.01. The sprayed $Zn_{1-x}Co_xO$ films exhibit a wurtzite structure with preferred orientation in the (002) direction. The maximum crystallite size of $Zn_{1-x}Co_xO$ films was 95.61 nm at x=0.06. The maximum electrical conductivity of the Co doped ZnO films was located at x=0.06.

Keywords: *$Zn_{1-x}Co_xO$, thin films; transparent conducting oxides (TCO); ultrasonic spray method*

INTRODUCTION

Zinc oxide is one of the most important semiconductor materials in the field of the environment due to optical transmission and good electrical resistivity [1]. Zinc oxide has many different applications such as sensors, fuel cell electrodes, catalysis, thermoelectric devices, field emission devices, lasers, dye solar cells (DSSCs) and electrochromic materials for displays [1- 5]. However, the latest research was based on developing new materials to use in the solar cells, ZnO thin films have a direct bandgap of 3.36 eV and has large exciton energy about 60 meV at RT [6,7]. Moreover, many experiments have been conducted to develop a new material based on zinc oxide thin films. Co doped ZnO thin films have been investigated as a new materials due to optical transmission. The cobalt concentration was playing an important parameter for obtaining the good quality such as a high thin film and optical properties. The using cobalt metal in this work can be modified the optical properties, which was played as rare earth elements in the enhancements of the electrical and optical

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properties. The aim of this work is to find a material suitable for the optometry applications with lower cost and good quality, which is prepared by a semiconductor of ZnO:Co thin films.

ZnO as thin films were obtained and prepared by various methods likely reactive evaporation, the sol-gel deposition, pulsed laser deposition (PLD) molecular beam epitaxy (MBE), magnetron sputtering technique (MSD), chemical vapor deposition (CVD), electrochemical deposition and spray pyrolysis (SPD) [5-9]. The spray ultrasonic deposition (SPD) can be used to deposition of ZnO films due to a large-scale production, it has a homogeneous composition in the deposition; it has a simple deposition on coating substrate at higher deposition temperatures with controlling the film thickness.

In the present work, we have elaborated in our laboratory the $Zn_{1-x}Co_xO$ thin films, which x varied from (x=0, 0.01, 0.02, 0.04 and 0.06). The thin films of $Zn_{1-x}Co_xO$ were deposited on a glass substrate by via ultrasonic spray deposition at a substrate temperature of 420°C. The optical characterization, structure crystallinity and electrical conductivity of final thin films have been investigated.

EXPERIMENTAL PROCEDURE

The $Zn_{1-x}Co_xO$ solutions were prepared by dissolving 0.1M zinc acetate dehydrate ($Zn(CH_3COO)_2$, $2H_2O$) and x at.% of cobalt chloride (Co_3Cl_2) with the ratio of x = 0, 0.01, 0.02, 0.04 and 0.06. The two produces were dissolved in water volume, and then have added two to three drops of HCl solution for stabilization; the $Zn_{1-x}Co_xO$ solutions were stirred at 50°C for 2 hours to transparency solution.

The final $Zn_{1-x}Co_xO$ solutions were sprayed on glass substrate by ultrasonic spray on the heated glass at 420°C within 6 min deposition time.

The optical, the crystalline structure and the electrical characterizations of $Zn_{1-x}Co_xO$ thin films were investigated by a spectrophotometer (LAMBDA 25), X-ray diffraction (XRD Bruker AXS-8D) with ($\lambda = 0.15406$ nm) and tow point methods, respectively.

RESULTS AND DISCUSSIONS

Optical characteristics

The results of ultrasonically sprayed Cobalt doped ZnO thin films were investigated at different doping levels in the form of $Zn_{1-x}Co_xO$ thin films (x=0, 0.01, 0.02, 0.04 and 0.06), this is a new material can be used as optometry applications. Figure 1 presents the effect of Co doping on the transmission of $Zn_{1-x}Co_xO$ thin films at x= 0, 0.01, 0.02, 0.04 and 0.06 at the deposition temperature of 420°C. As can see from the transmission spectra of $Zn_{1-x}Co_xO$ thin films presented a three edges in the visible region were observed between 541 and 656 nm of wavelengths, which related to the d-d transitions of Co^{2+} ion with $3d^7$ high-spin configurations in a tetrahedral crystal field formed by neighboring O^{2-} ions [10,11],ascribed to the $^4A_2(F) \rightarrow {}^2E(G)$, $^4A_2(F) \rightarrow {}^4T_1(P)$, and $^4A_2(F) \rightarrow {}^2A^1(G)$ [12,13], this interpretation shows that the Co ions have substituted the Zn^{2+} ions. The absorbance spectra of $Zn_{1-x}Co_xO$ films are presented in Figure 2. It is clear that the variation in absorbance at lower photon energy was located between 1.9 and 2.3 eV present three peaks, which are confirmed to the d-d transitions of Co^{2+} ion with $3d^7$ high-spin configurations in a tetrahedral crystal field formed by neighboring O^{2-} ions.

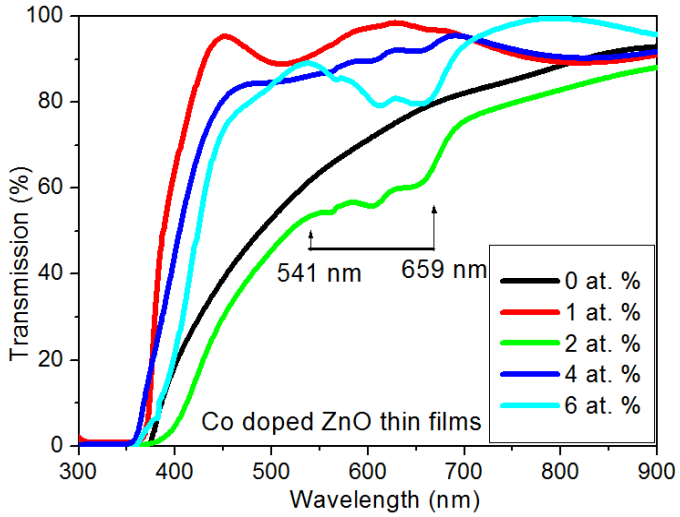


Fig. 1. Transmission spectra of Co doped ZnO thin films as a function of doping level

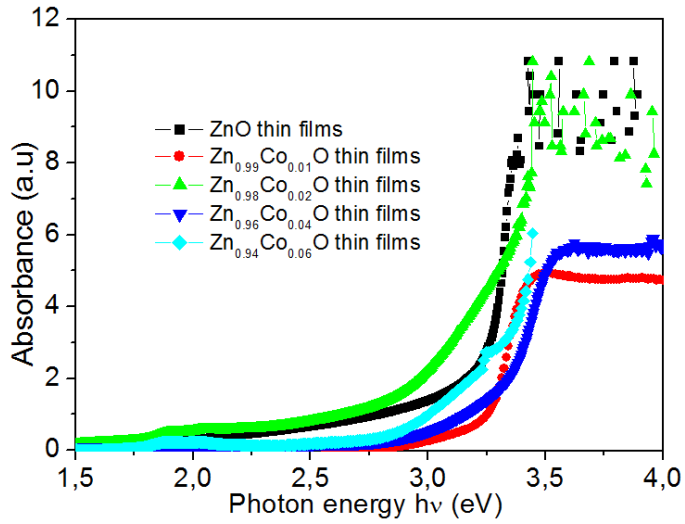


Fig. 2. Absorption spectra of Co doped ZnO thin films as a function of doping level

The investigate of the effect of Co concentration on the optical property of $Zn_{1-x}Co_xO$ thin films, the optical bandgap energy E_g of $Zn_{1-x}Co_xO$ thin films was determined from transmission spectra by the following relations [14]:

$$A = \alpha\, d = -\ln T \tag{1}$$

$$(\alpha h\upsilon)^2 = B(h\upsilon - E_g) \tag{2}$$

where A, d, T, α; B, $h\nu$ and E_g are the absorbance, the film thickness, the transmittance, the absorption coefficient, a constant, the photon energy and the optical gap, respectively. These variations of the optical property of the $Zn_{1-x}Co_xO$ are shown in (Figure 3a) typical variation of $(\alpha h\nu)^2$ with photon energy $(\alpha h\nu)^2$ used for determination of the optical gap, it

is found by extrapolation of the linear region to $(\alpha h\nu)^2 = 0$ [15]. However, The disorder of $Zn_{1-x}Co_xO$ thin films also was determined by the following equation [16]:

$$\alpha = \alpha_0 \left(\frac{h\nu}{E_u} \right) \tag{3}$$

where α_0 and E_u are a constant and the Urbach energy, respectively.

In Figure 3a shows a plot of $(\alpha h\nu)^2$ vs. photon energy $h\nu$ of $Zn_{1-x}Co_xO$ thin films, it is used to determine the optical energy by extrapolation of $(\alpha h\nu)^2 = 0$ in the linear region [15]. On the other hand, to determine the Urbach energy of $Zn_{1-x}Co_xO$ thin films we use the variation of $Ln\alpha$ as a function of $h\nu$ (see Figure 3b), which is calculated by $E_u = \frac{\Delta h\nu}{\Delta Ln\alpha}$ with the leaner variation of $Ln\alpha$ as a function of $h\nu$.

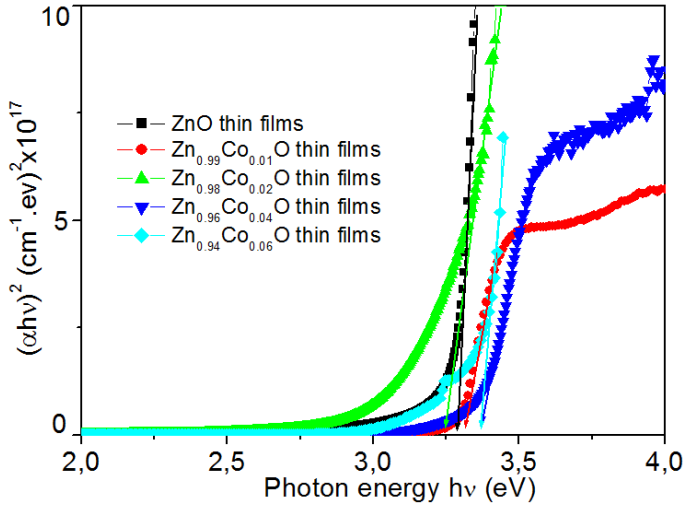


Fig. 3a. The typical variation of $(\alpha h\nu)^2$ vs. photon energy $h\nu$ for Co doped ZnO thin films

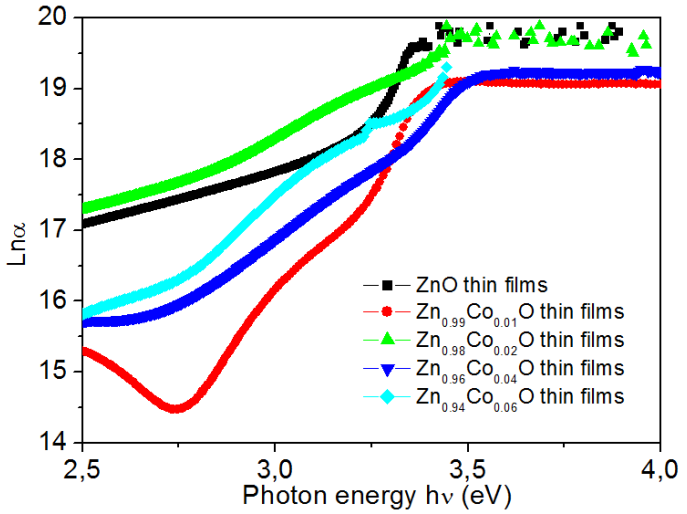


Fig. 3b. The drawn of $\ln\alpha$ as a function of photon energy ($h\nu$) for deduce the Urbach energy for Co doped ZnO thin films

The variation of optical bandgap energy and Urbach energy of the transparent $Zn_{1-x}Co_xO$ thin films are shown in Figure 4. Firstly we have observed that the variations of optical gap energy are reversed with the values of Urbach energy due to the transition tail width. The increase in optical gap from x=0 to 0.01 and x=0.02 to 0.06 can be related to the active transitions involving 3d levels in Co^{+2} ions and strong sp-d exchange interaction between itinerant sp ZnO orbits and the localized d of the dopant which result in narrowing the valence band EV and the conduction band EC due to the motion of EC upwards and EV downwards hence doping by Co causes the band gap broadening. However, From Figure 4 one can be observed that the minimum Urbach energy was obtained with x=0.01 and x=0.04 of $Zn_{1-x}Co_xO$ thin films due to the narrow in the transition tail width and shift effect as expressed as [17,18].

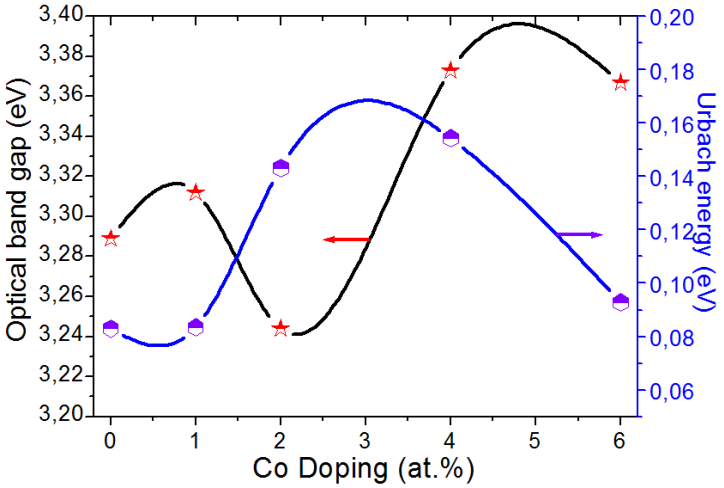


Fig. 4. The variation of optical band gap and Urbach energy of Co doped ZnO thin films as a function of doping level

Crystalline structure

The XRD patterns spectra of sprayed $Zn_{1-x}Co_xO$ thin films are presented in Figure 5, it is showing that all samples having a hexagonal structure (wurtzite) with (101), (002) and (102) diffraction peaks are observed. The (002) peak is the highest one indicating that the preferred orientation along the c-axis with (002) plane, because of the high intensity and different degrees of substitution of Zn^{2+} ions with Co^{2+} ions. These results indicated that the Co doping can be improved the structure properties. However, the structure information about these thin films such as the lattice parameters a and c, mean strain ε and grain size D were calculated from X-ray diffraction patterns using the following equations [19]:

$$d_{hkl} = \left(\frac{4}{3}\frac{h^2+hk+k^2}{a^2} + \frac{l^2}{c^2}\right)^{-\frac{1}{2}} \tag{4}$$

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{5}$$

where $(h,k,l), d_{hkl}, \lambda$, β and θ are the Miller indices, the interplanar spacing, the X-ray wavelength, the FWHM, and the Bragg angle, respectively.

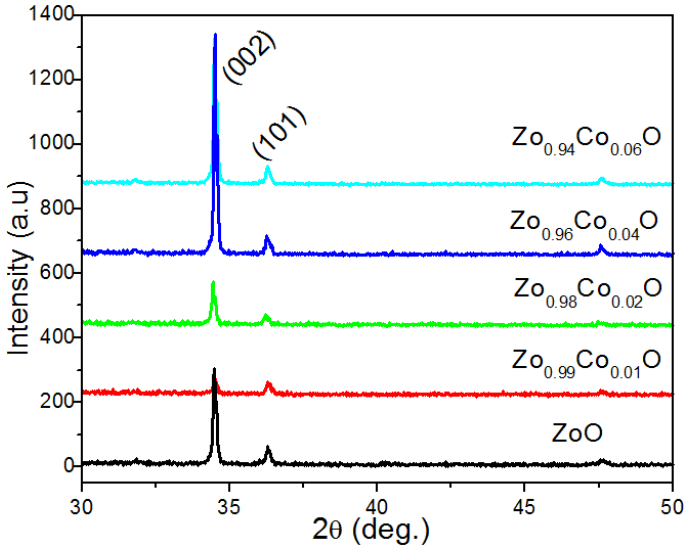


Fig. 5. X-ray diffraction spectra of Co doped ZnO thin films with various cobalt concentrations

Figure 6, presented the variation of c_0- c of (002) peak in $Zn_{1-x}Co_xO$ thin films as a function of Co concentration. As shown in Figure 6 that the variation I c_0- c of (002) peak is 1 of 1000 times, it is approach to zero, the increase of c_0- c with Co concentration can be indicated by the increase in the defects, which was found to improve the electrical property of $Zn_{1-x}Co_xO$ thin films.

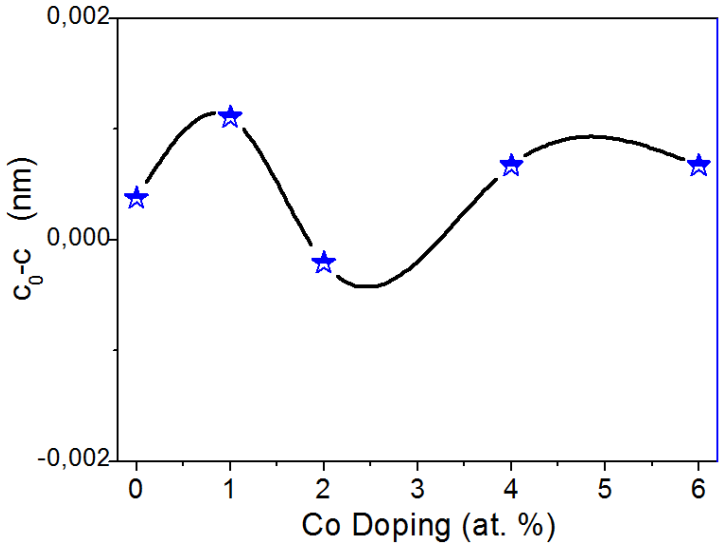


Fig. 6. The Variation of c0-c of (002) peak in Co doped ZnO thin films as a function of doping level

Figure 7 also presents the variation of crystallite size as a function of Co concentration. As can be seen, the variation of crystallite size increased with increasing x=0 to x=0.06 up a maximum value of 95.61 nm. This is can be indicated by the enhancement of the structure crystallinity and the c-axis orientation of $Zn_{1-x}Co_xO$ thin films as expressed as [20].

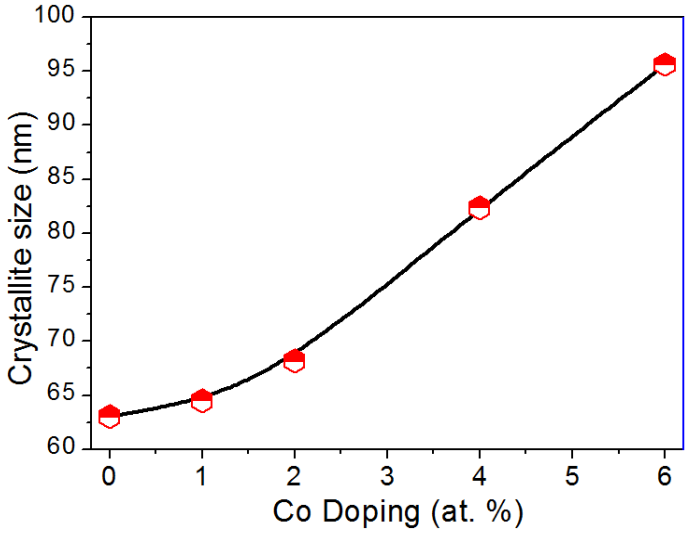


Fig. 7. The variation of crystallite size of Co doped ZnO thin films with various cobalt concentrations

Electrical conductivity

Figure 8 shows the variation of electrical conductivity σ of $Zn_{1-x}Co_xO$ thin films as a function of Co concentration. As clearly seen, the conductivity increased markedly from σ = 11.24 to 19.57 $(\Omega.cm)^{-1}$ with the Co concentration increase from x=0 to 0.06 at %. The increase in the conductivity of $Zn_{1-x}Co_xO$ thin films can be explained by electrons displacement, which is related to the ions Co^{2+} donors in the substitutional sites of Zn^{2+}, this is affected by an increased carrier density.

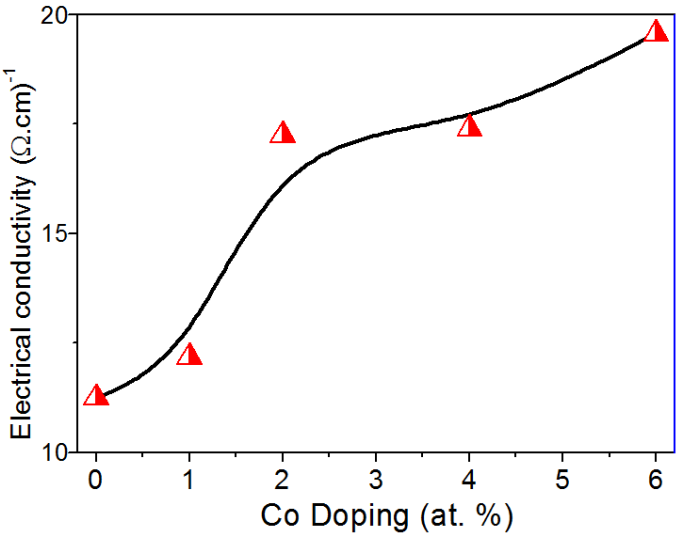


Fig. 8. The Electrical conductivity of Co doped ZnO thin films as a function of doping level

CONCLUSIONS

High-quality $Zn_{1-x}Co_xO$ thin films (x=0, 0.01, 0.02, 0.04 and 0.06) were synthesis on glass substrate at 420 °C by ultrasonic spray deposition. Optical characterization, crystallinity and electrical conductivity have been investigated and drastically improved by this method.

Transmission spectra $Zn_{1-x}Co_xO$ thin films presented three edges in the visible region were observed between 541 and 656 nm of wavelengths, which related to the d-d transitions of Co^{2+} ion with $3d^7$ high-spin configurations in a tetrahedral crystal field formed by neighboring O^{2-} ions. The band gap energy was increased after doping by Co and reaching a maximum value of 3.373 eV at x=0.04. The minimum value of Urbach energy was 0.083 eV, it is obtained at x=0.01 of Co doping. The sprayed $Zn_{1-x}Co_xO$ thin films exhibit a wurtzite structure with preferred orientation in the (002) direction, and no peaks referred to cubic CoO are observed. The maximum crystallite size of $Zn_{1-x}Co_xO$ thin films was 95.61 nm at x=0.06. The maximum electrical conductivity of the Co doped ZnO thin films was located at x=0.06.

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