

Effects of Cobalt Doping on Optical Properties of ZnO Thin Films Deposited by Sol–Gel Spin Coating Technique

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Abstract: Cobalt (Co) doped Zinc Oxide (ZnO) thin films, containing different amount of Cobalt nanoparticles as the Co doping source, deposited by the sol–gel spin coating method onto glass via annealing temperature at 400°C, have been investigated by optical characterization method. The effect of Co incorporation on the surface morphology was clearly observed from scanning electron microscopy (SEM) images. Optical conductivity and optical constants such as absorption coefficient, reflectivity, extinction coefficient, and refractive index as a function of photon energy were calculated, and it was found that the doping with Co led to decrease absorption coefficient, extinction coefficient, refractive index and bandgap energy, while the optical conductivity increased at higher photon energies. The optical band gap depends on the Co doping level and on the particle size and crystallinity of the films and is in the range of 3.05–3.17 eV. The optical band gap widening is proportional to the one-third power of the carrier concentration.

Key words: Cobalt doped ZnO thin film, Optical properties, Sol-gel

1. INTRODUCTION

ZnO thin films are a novel direct broad band gap II-VI compound semiconductors. At room temperature, the bandwidth reached 3.37 eV, and the exciton's binding energy also reached 60 meV [1]. Common the ZnO structure is a hexagonal wurtzite crystal structure. ZnO has a material rich source, easy mining, low cost, non-toxic environment-friendly, chemical high stability, easy to achieve doping, easy to control the growth process, etc [2].

Zinc oxide (ZnO) is one of transparent conducting oxide (TCO) materials whose thin films attract much interest because of typical properties such as high chemical and mechanical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region, low cost and non-toxicity [1, 3]. At present, the method of preparing ZnO thin films is more, mainly

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magnetron sputtering, pulse laser deposition (PLD), chemical vapor deposition (CVD), Spray Pyrolysis, molecular beam epitaxy (MBE) and sol-gel method [3-8]. Its, the sol-gel method does not require a vacuum device and is thus significantly reduced production costs, simplification of the process, and easy to control the film composition, generated. The adhesion of the film to the substrate is strong. In the lower temperature directly under the system into the coating, annealing to obtain polycrystalline structure is a new technology.

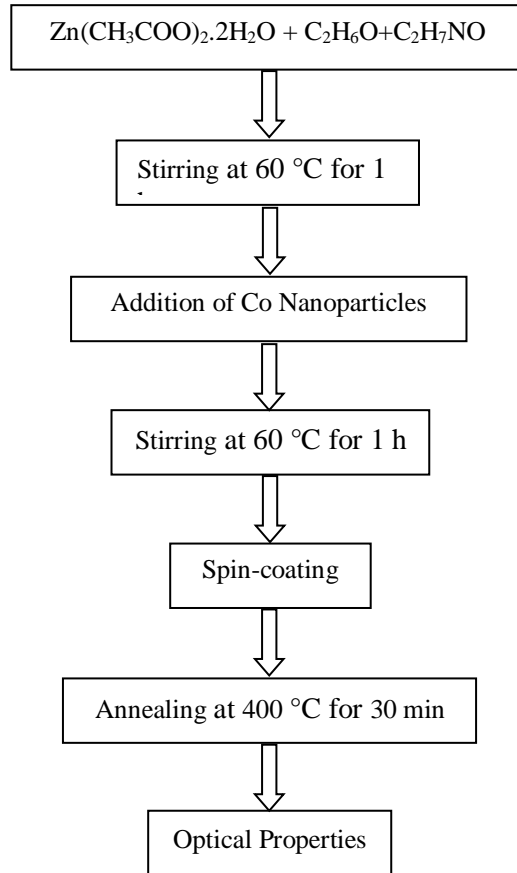
Its synthetic temperature is low (about 300 °C), material uniformity is good, and CVD and sputtering method, it is expected to improve production efficiency, has been electricity sub-material industry attaches great importance.

In addition, the doping of the ZnO thin film can be effectively improved crystal structure and performance. For example, the Al dopant can be prepared good performance of ZnO transparent conductive film. Doped Mg can be effective adjust the band gap of ZnO thin films, improve its optical properties. Nano-ZnO doped with Pd or Ag elements can greatly improve its photocatalytic activity of ZnO. Co, Ni, Mn and other elements can be a good performance of the magnetic material [6, 9-13]. But at present, the preparation of the sol-gel method Co-doped ZnO transparent conductive thin films were prepared by spin coating method. The effect of doping concentration on the optical constants such as absorption coefficient, reflectivity, extinction coefficient, refractive index, and optical conductivity of Co-ZnO thin films was investigated.

2. EXPERIMENTAL DETAILS

In this experimental procedures, the raw materials pure zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), anhydrous ethanol ($\text{C}_2\text{H}_6\text{O}$), ethanolamine ($\text{C}_2\text{H}_7\text{NO}$) and analytically pure cobalt nanoparticles (Co) were used for the synthesis of Co-ZnO via precipitation process as shown in Scheme 1. First 10 g of zinc acetate dissolved in 30 ml of absolute ethanol. The quality of 2.7 g of ethanolamine was added as a stabilizer and then stirred at the reflux temperature of 60 °C for 1 h. Then add the quality of 0.4 g of pure cobalt powder, followed by stirring at 60 °C for 1 h.

ZnO and Co-ZnO thin films were deposited using the spin coating technique on quartz glass substrate. The glass substrates were cleaned in acetone, rinsed with distilled water, and subsequently dried before deposition. The substrate is then placed on the hot plate which heated before progressively until the deposition temperature is reached. All films were annealed at 400 °C during 30 min. The optical and surface morphology measurements were performed using Shimadzu UV-VIS double beam spectrophotometer in the wavelength range 350-850 nm and scanning electron microscope (SEM, VEGA3, TESCAN, Czech).



Scheme 1. Flow chart of preparation of Co-ZnO nanoparticles sol-gel

3. RESULTS AND DISCUSSION

In order to further study the Co doping concentration on the surface morphology of the ZnO thin film was analyzed, as shown in Fig. 1(a)-(e) for the sample doping concentration of 0%, 1%, 2%, 4% and 8% SEM images.

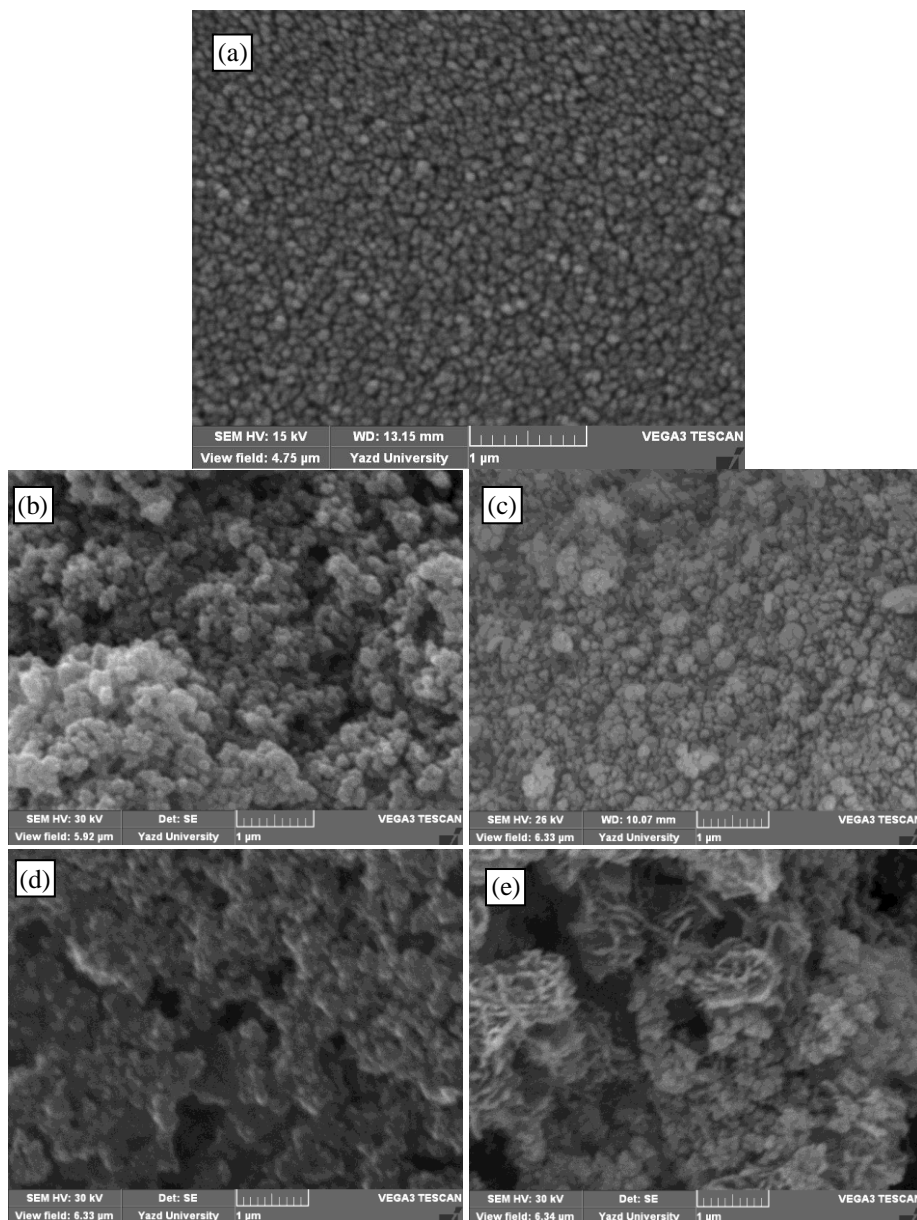


Fig. 1. The SEM images of Co-ZnO thin film with the concentrations of (a) 0%, (b) 1%, (c) 2%, (d) 4% and (e) 8% of Co.

The undoped film, Fig. 1a can be described as a structure of very fine particles, with a mean diameter around 30 nm, For the 1 at.% Co-doped sample,

Figure 1b, the surface structure is not completely flat and looks wrinkled, with a mean diameter around 60 nm. Finally, the 2 at.% Al-doped sample, Figure 1c, clearly show a bimodal structure with large particles in the 50–150 nm range around which and on which much finer nanoparticles can be observed, with a mean diameter around 70 nm. The particle sizes observed by SEM are in good agreement with the calculated sizes determined by the Williamson-Hall method [14].

From the figure can be seen, into the proper Co^{2+} doping can effectively improve the surface texture of the film, when the doping concentration is 2%, the grain size is the most uniform and the film density is best, the grain size is about 70 nm.

The Uv-vis reflectance spectra of Co-ZnO thin films are shown in Fig. 2. It is found that the reflection rate of the undoped ZnO begins to decrease at 380 nm, while the band edge of the Co-doped ZnO sample shifted to longer wavelengths with the increase of the Co doping concentration. In addition, the reflection rate of the Co-doped ZnO decreases with the increase of the Co doping concentration. When the doping concentration reaches 4%, the reflection rate in visible light range decreases up to 40% between 600 and 700 nm, which has very important signification in making full use of solar cells.

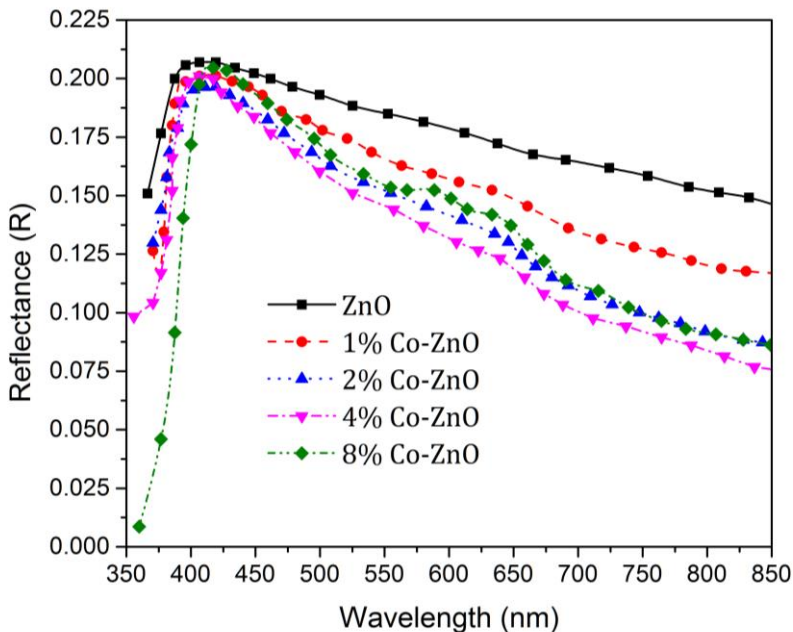


Fig. 2. The reflectance spectra of ZnO and Co-ZnO thin films.

The optical absorption coefficient (α) was evaluated using the following equation [15]:

$$\alpha(\nu) = 2.303 \frac{A}{t} \quad (1)$$

which, A is absorbance and, t is film thickness. As seen in Fig. 3, the absorption coefficient (α) decrease with increasing of wavelength and the doping with Co led to decreasing the absorption coefficient at visible region.

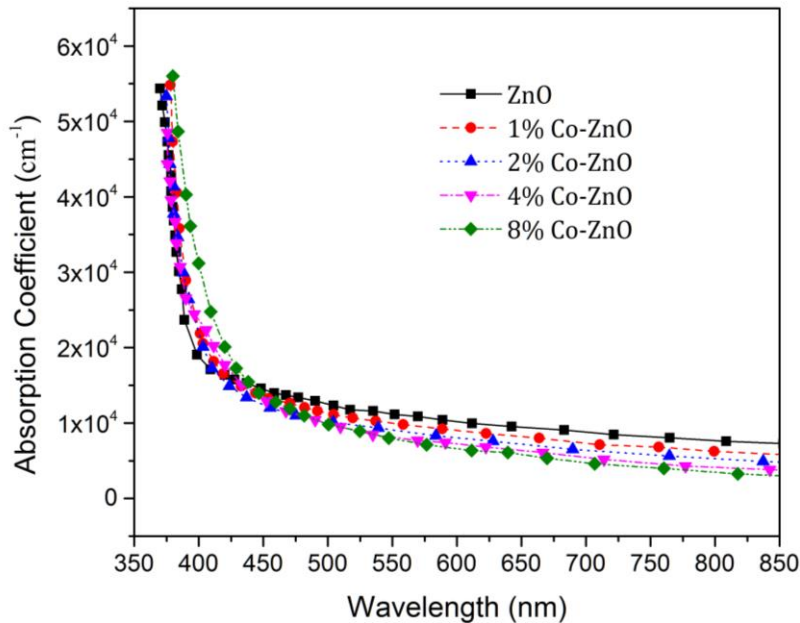


Fig. 3. The absorption coefficient (α) of ZnO and Co-ZnO thin films.

The variation of the extinction coefficient with photon energy shown in Fig. 4, for ZnO and Co-ZnO thin films. It clearly notes the likely behaviors with the absorption coefficient (α) variation. This conforms to the relation [13]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (2)$$

where k is the extinction coefficient, and (λ) is the wavelength.

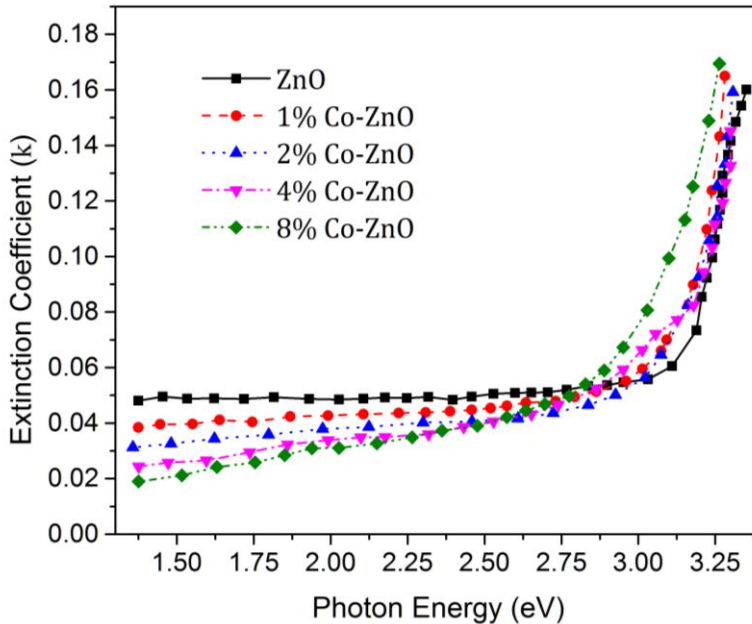


Fig. 4. The extinction coefficient (k) of ZnO and Co-ZnO thin films.

The extinction coefficient of the ZnO film slowly increases with Co doping in the visible photon energy region. The increase of film thickness with increasing Co content will increase surface optical scattering and optical loss, which induces the increase of extinction coefficient.

The refractive index (n) of the Co-ZnO thin films was calculated by the following relation [15]:

$$R = (n - 1)^2 / (n + 1)^2 \quad (3)$$

where R is the normal reflectance.

As seen from Fig.5, the average refractive index of the undoped ZnO film in the visible region was found to be 2.46. With 8% Co content it reaches to 2.15. The decrease in the refractive index may be due to the increase of Co content attributed to the decreasing in the crystallite size with Co content. The increase of refractive index with Co content can be explained on the basis of the contribution from both lattice distortion and the disorder of the films.

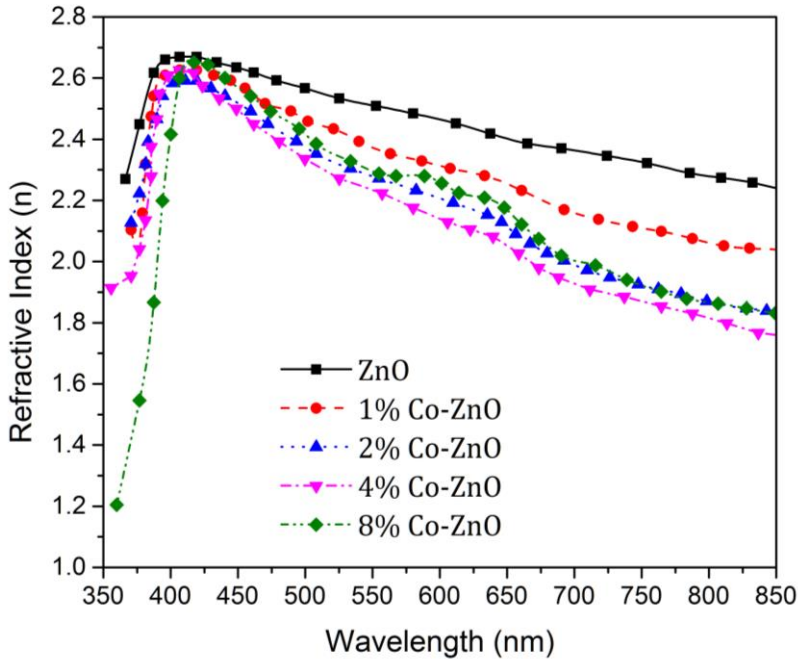


Fig. 5. The refractive index (n) of ZnO and Co-ZnO thin films.

By the relationship between the absorption coefficient (α) and photon energy ($h\nu$) to obtain an optical band gap (E_g) using [14]:

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (4)$$

where B is a constant. The linear extension of $(\alpha h\nu)^2$ - $h\nu$ curve is obtained an optical bandgap E_g .

It can be seen from Fig. 6 that the optical bandgap of ZnS thin films with Co doping concentration of 0%, 1%, 2%, 4%, and 8% were 3.17, 3.15, 3.13, 3.11 and 3.05 eV respectively. The results show that with the doping concentration, the optical bandgap of the film gradually decreases. This might be, on the one hand, the transition metal ion Co^{2+} is substituted for substitution, the Fermi level moves up to the conduction band, and the Co^{2+} ion is not filled on the d orbit. The electrons and ZnO conduction bands and valence bands occur in the electrons occurring in s - d and p - d orbital hybridization produces degenerate energy levels, causing optical bandgap narrowing; On the one hand it may be Co^{2+} as the donor ion, with the doping concentration increase, the defect concentration also increases, the bottom of the conduction band and the value of the top of the extended Urbach ends formation [16]. This makes the optical band gap narrow. The narrower optical band causes the valence band electrons

are excited to jump to the energy absorbed by the conduction band. The less obvious the absorption of the red-shift is, the more obvious by other researchers [17, 18].

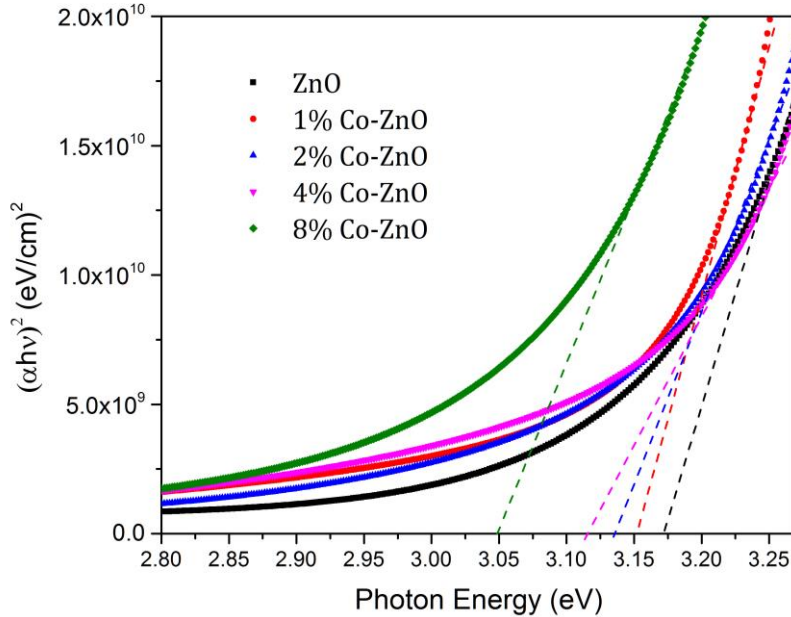


Fig.6. Transmission spectra of ZnO thin films with different Co doping concentrations

The optical conductivity (σ) was calculated by the following relation [14]:

$$\sigma = \alpha n c / 4\pi \quad (5)$$

where c is light velocity. Fig. 7 shows the variation of optical conductivity for different Co content versus incident photon energy. As shown in Fig.7, the optical conductivity increase with increasing of photon energy, and the Co dopant led to increasing its values at higher photon energies after (2.9 eV), while before that optical conductivity continues increasing but with values little few than that of undoped ZnO films.

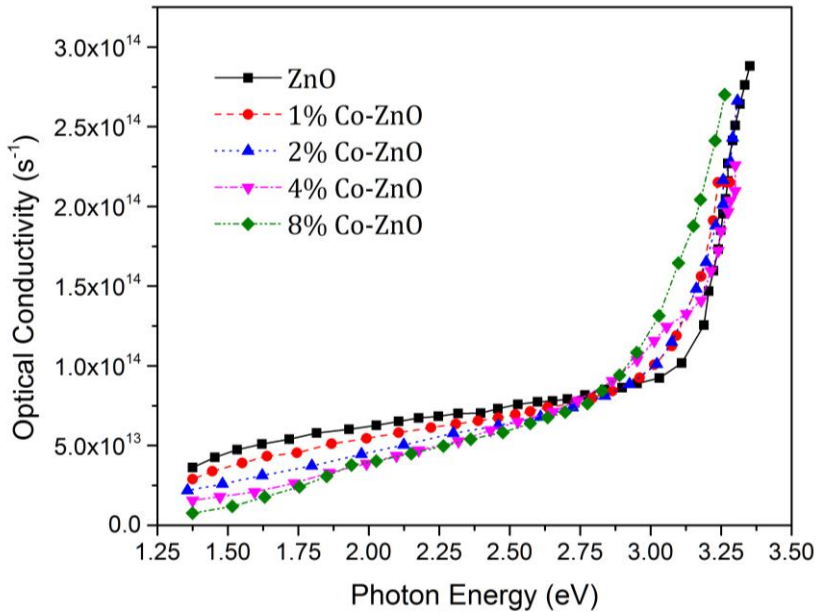


Fig. 7. The optical conductivity (σ) of ZnO and Co-ZnO thin films.

4. CONCLUSION

The optical properties of undoped and Co-doped ZnO films were thin films deposited by the sol-gel spin coating technique onto glass substrates at (400°C) have been investigated. According to SEM results, improve the surface texture of the film depending on the cobalt content was clearly observed. Co dopant led to increasing the absorption coefficient and optical conductivity at higher photon energies after (2.9 eV), which refers to the Co-ZnO films importance in photovoltaic and optoelectronic devices. The results show that proper doping can improve the optical performance when the Co doping amount is within 2%, the film has good compact surface, light and band gap width. The values of the optical band gap E_g decreased with increasing Co concentration. Both the refractive index and extinction coefficient were affected by Co incorporation. The variation of refractive index with doping also provides the possibility to set the refractive index to any desired value required for use in filters.

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