Effect of substrate temperature on the stability of transparent conducting cobalt doped ZnO thin films*

Said Benramache[1, †], Boubaker Benhaoua[2], and Foued Chabane[3]

[1]Material Sciences Laboratory, Faculty of Science, University of Biskra 07000, Algeria
[2]Physics Laboratory, Institute of Technology, University of El-oued 39000, Algeria
[3]Mechanics Department, Faculty of Technology, University of Biskra 07000, Algeria

Abstract: Transparent conducting Co doped ZnO thin films have been fabricated by Ultrasonic spray. The thin films were deposited at three different substrate temperatures of 300, 350 and 400 ℃. The obtained films had a hexagonal wurtzite structure with a strong (002) preferred orientation. The maximum crystallite size value of the film deposited at 350 ℃ is 55.46 nm. Spectrophotometer (UV-vis) of a Co doped ZnO film deposited at 350 ℃ shows an average transmittance of about 90%. The band gap energy increased from 3.351 to 3.362 eV when the substrate temperature increased from 300 to 350 ℃. The electrical conductivity of the films deposited at 300, 350 and 400 ℃ were 7.424, 7.547 and 6.743 $(\Omega\cdot\mathrm{cm})^{-1}$ respectively. The maximum activation energy value of the films at 350 ℃ was 1.28 eV, indicating that the films exhibit a n-type semiconducting nature.

Key words: ZnO:Co films; transparent conducting films; ultrasonic spray deposition; substrate temperature; band gap energy

DOI: 10.1088/1674-4926/33/9/093001 **EEACC:** 2110; 2550B; 2550E

1. Introduction

Zinc oxide (ZnO) is a very interesting semiconducting material with a wide and direct band gap of 3.37 eV at room temperature and a high exciton binding energy of 60 meV[1]. Transparent conducting oxides (TCO) are widely used in microelectronic devices, light emitting diodes, thin film, antireflection coatings for transparent electrodes in solar cells[2], gas sensors in surface acoustic wave devices[3], varistors, spintronic devices, and lasers[4].

ZnO thin films can be produced by several techniques such as molecular beam epitaxy (MBE), chemical vapor deposition, electrochemical deposition[3], pulsed laser deposition (PLD), sol–gel process[4], reactive evaporation, magnetron sputtering technique and spray pyrolysis[5].

Cobalt doped ZnO thin films have various applications such as transparent conductives; ferromagnetism; semiconductors; piezoelectric and solar cells, as the films have low resistivity and good optical band gap energy at low temperatures, and are transparent in the visible region[6]. A ZnO:Co film is considered to be an important material due to its high conductivity, good transparency and low cost.

In this work, we have elaborated the conductive Co doped ZnO thin films on a glass substrate using an Ultrasonic spray. The films obtained have a concentration of 2 wt%. We have studied the effect of the substrate temperatures on the crystalline structure, optical and electrical properties of the semiconductors.

2. Experimental details

The spray solution was prepared by dissolving 0.1 M ($Zn(Zn(CH_3COO)_2, 2H_2O$) in the solvent containing an equal volume of absolute ethanol solution, then a drop of NaOH solution was added as a stabilizer, after which 2% cobalt acetate tetrahydrate ($Co(CH_3COO)_2, 6H_2O$) molar ratio was added to the solution, which had been stirred and heated at 80 ℃ for 1 h to yield a clear and transparent solution. The latter was sprayed on the heated glass substrates by an ultrasonic nebulizer system (Sonics) which transformed the liquid to a stream formed with uniform and fine droplets of 30 μm average diameter (given by the manufacturer). The deposition was performed at a different substrate temperatures of 300, 350 or 400 ℃ with a 120 s deposition time[7].

The crystalline structure of the films was confirmed by X-ray diffraction (XRD) analysis using CuKα radiation with a Bruker AXS-8D diffractometer. The optical properties of the films were measured by spectrophotometer (UV, Lambda 35) in the range of 300–800 nm, and the electrical properties of the films were measured in a coplanar structure obtained with evaporation of four golden stripes on film surface. All spectra were measured at room temperature (RT).

3. Results and discussion

3.1. Structural properties

Figure 1 shows the XRD patterns of Co doped ZnO thin films with different substrate temperatures. (002) and (101) diffraction peaks were observed; the films exhibit the hexagonal wurtzite polycrystalline structure from the spectra. Many authors investigated the structure of ZnO thin films obtained by different methods and deposited onto various substrates in the literature[1, 4, 8]. Where only a (002) diffraction peak is highest one, the film forming at 350 ℃ has a higher and sharper diffraction peak indicating an improvement in (002) peak in-

† Corresponding author. Email: saidzno2006@gmail.com
Received 10 February 2012, revised manuscript received 9 May 2012

Table 1. The full width at half-maximum β, the crystallite size G, the band gap energy E_g, Urbach energy E_u, the electrical conductivity ρ and the activation energy E_a for ZnO thin films doped with cobalt measured as a function of deposition temperature.

Temperature (℃)	β (10^{-3} rad)	G (nm)	E_g (eV)	E_u (meV)	σ ($\Omega^{-1}\cdot cm^{-1}$)	E_a (eV)
300	3.14	46.22	3.351	206.34	7.424	1.19
350	2.62	55.46	3.362	108.69	7.547	1.28
400	3.67	39.61	3.348	236.88	6.743	1.07

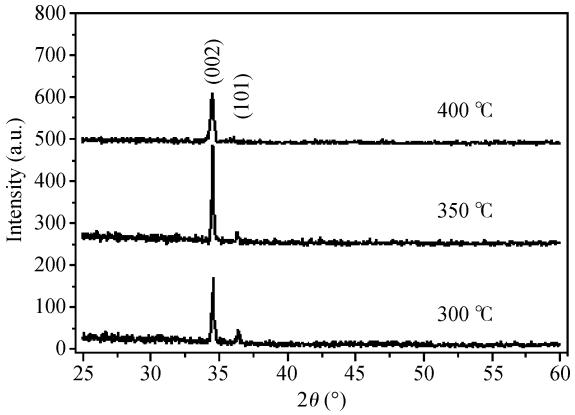

Fig. 1. X-ray diffraction patterns of ZnO thin films doped with cobalt at three different substrate temperatures.

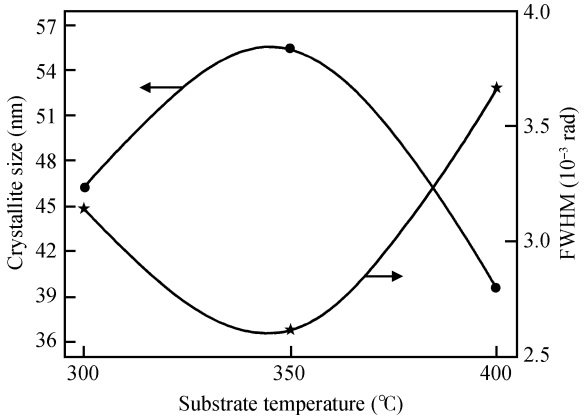

Fig. 2. Variation of the crystallite size and the FWHM of the (002) diffraction peak as a function of substrate temperature.

tensity compared to other films. This observation shows that both films have preferential c-axis orientation along the (002) plane[9], because of the high intensity, the crystalline quality of thin films enhanced at a substrate temperature of 350 ℃. The result indicates that the temperature of layers improved the structure properties.

In order to calculate the crystallite size, G (002) along the c-axis was calculated according to Scherer's equation[10]:

$$G = \frac{0.9\lambda}{\beta \cos\theta}, \tag{1}$$

where G is the crystallite size, λ is the wavelength of X-ray (λ = 1.5406 Å), β is the full width at half-maximum (FWHM), and θ is the Bragg angle of (002) peak. The values of crystallite sizes and FWHM are illustrated in Table 1.

In Fig. 2 we have reported the variation of the crystallite size and FWHM. Since the crystallite size is inversely proportional to the FWHM, we found that the crystallite size increased at first as the FWHM decreased. Zhang[11] observed that the intensities of the (002) peaks of ZnO films on the seed layer increase as their FWHM values decrease, indicating an improvement in the crystallinity of the films. The increase of the crystallite size has been indicated by the enhancement of the crystallinity and c-axis orientation of Co doped ZnO thin films.

3.2. Optical characteristics

Figure 3 shows the optical transmission spectra of Co doped ZnO thin films with a substrate temperature; it was also measured for comparison. As can be seen, a region of strong transparency is located between 400–800 nm. All films exhibit an average optical transparency over 62%–90% in the visible range. The range between 365–385 nm is the region of the absorption in the layers due to the transition between the valence

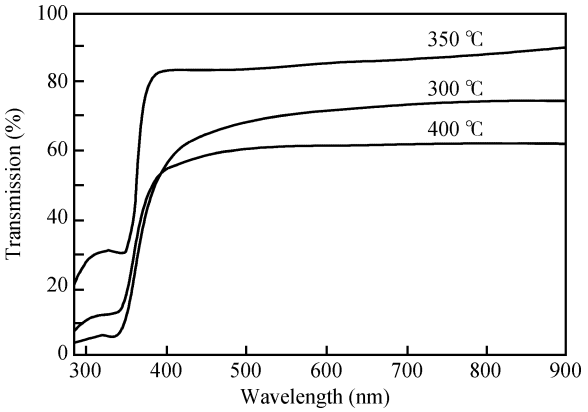

Fig. 3. Optical transmission spectra of Co doped ZnO thin films at different substrate temperatures.

band and the conduction band (inter-band transition)[11, 12], in this region the transmittance decreased because of the onset fundamental absorption edge. We note that the substrate temperature effect is clearly observed in the layer quality.

The optical band gap energy E_g was measured from the transmission spectra using the following relationship[13]:

$$A = \alpha d = -\ln T, \tag{2}$$

$$(Ah\nu)^2 = C(h\nu - E_g)/A = \alpha d, \tag{3}$$

where A is the absorbance, d is the film thickness; T is the transmittance spectra of thin films; α is the absorption coefficient values; C is a constant, $h\nu$ is the photon energy and E_g is the energy band gap of the semiconductor, determined by extrapolation of the linear region to $(\alpha h\nu)^2 = 0$[14]. The Urbach energy, which is related to the disorder in the film network, is

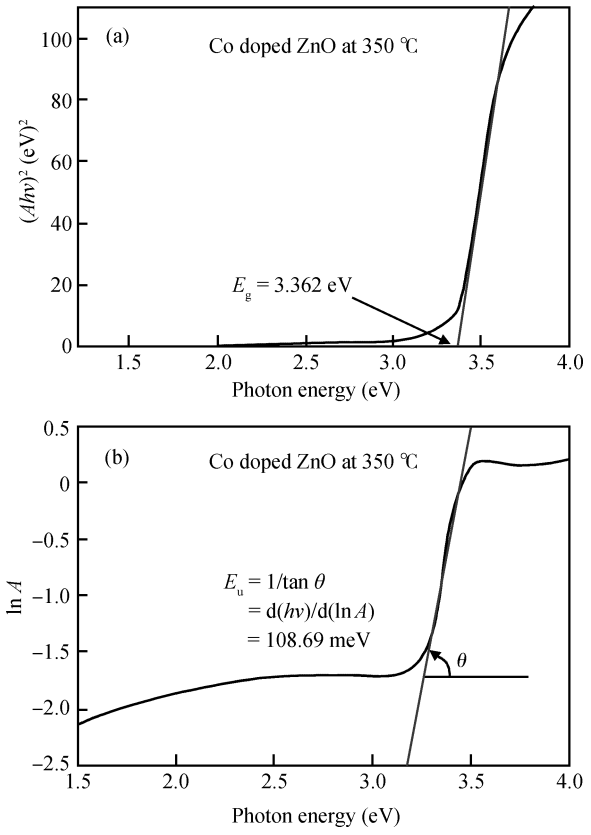

Fig. 4. Typical variation of $(Ahv)^2$ and $\ln A$ drawn as a function of photon energy hv used respectively for (a) extrapolation of the band gap energy and (b) Urbach energy determination.

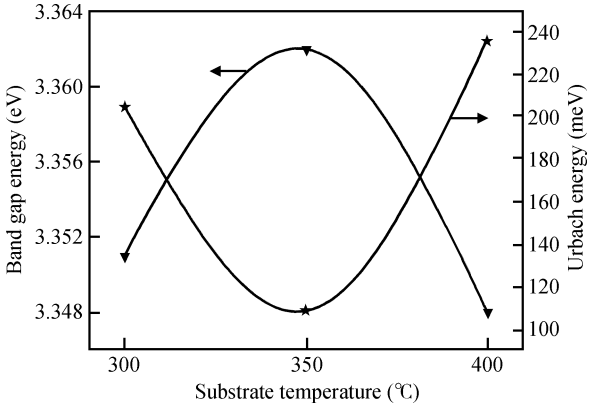

Fig. 5. Variation of band gap energy and Urbach energy of Co doped ZnO films as a function of deposition temperature.

expressed as[15]:

$$A = A_0 \exp \frac{h\upsilon}{E_u}, \tag{4}$$

where A_0 is a constant and E_u is the Urbach energy, the variations of the band gap energy and the Urbache energy are shown in Table 1.

Figures 4(a) and 4(b) show a typical variation of $(Ahv)^2$ and $\ln A$ drawn as a function of photon energy (hv). Figure 4(a) is used to extrapolate the band gap energy, while Figure 4(b) is used to deduce the Urbach energy.

Figure 5 shows the variation of the band gap energy E_g with the Urbach energy as a function of the substrate temperature. We have obtained an increase in the optical gap as the substrate temperature increased from 300 to 350 ℃, which may be attributed to the similar ionic radius between Co and Zn[16]. The band gap is broad due to the increase in the transition tail width and shift effect, as reported in the literature[12, 17]. We found that the optical gap and transparency were affected by the deposition temperature. These observations are applied also to the Urbach energy, which is related to the disorder in the film network, where the decrease in Urbach energy is attributed to the decrease of the defects, as expressed in the literature[15, 18].

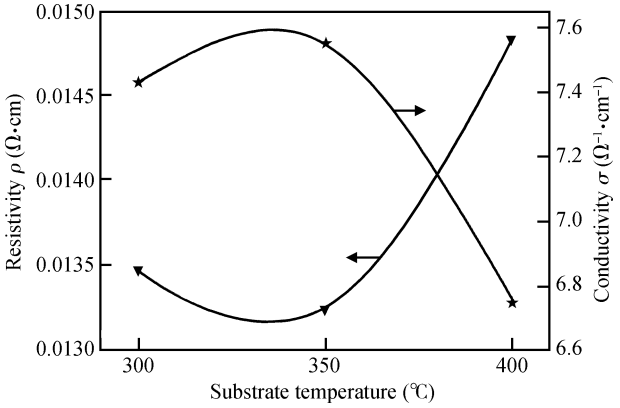

Fig. 6. Variation of electrical resistivity and conductivity of Co doped ZnO thin films at different substrate temperatures.

3.3. Electrical properties

Figure 6 shows the variation of the electrical resistivity ρ and the conductivity σ of Co doped ZnO films as a function of substrate temperature. As can be seen, the resistivity is inverse to the conductivity, the electrical resistivity decreases with the increase of conductivity. The maximum conductivity value of the film is 7.547 $(\Omega\cdot\text{cm})^{-1}$, this was obtained at 350 ℃, at this temperature the resistivity value of the film is 0.1325 Ω·cm, and the higher preferential was along the c-axis orientation. The increase in the conductivity of the film has been explained by the displacement of the electrons, the latter come from the Co^{2+} donor ions in the substitutional sites of Zn^{2+}[19], and formation of the molecular ZnCoO existed on the surface, The increase of the electrical resistivity with the deposition temperature is explained by the increase of the potential barriers, because the introduced atoms are segregated into the grain boundaries[18].

The increase in the electrical conductivity indicates that the film is a semiconductor; the measurement activation energy of the samples can be the doping quality for both films. The activation energy of the film can be calculated by the following relationship[20]:

$$\sigma = \sigma_0 \exp \frac{E_a}{KT}, \tag{5}$$

where σ is the electrical conductivity; σ_0 is the pre-exponential factor; K is the Boltzmann constant; T is the temperature of the sample and E_a is the activation energy for the conductivity, shown in Fig. 7.

The refractive index n is calculated using the Herve–Vandamme model. In a semiconductor, n de-

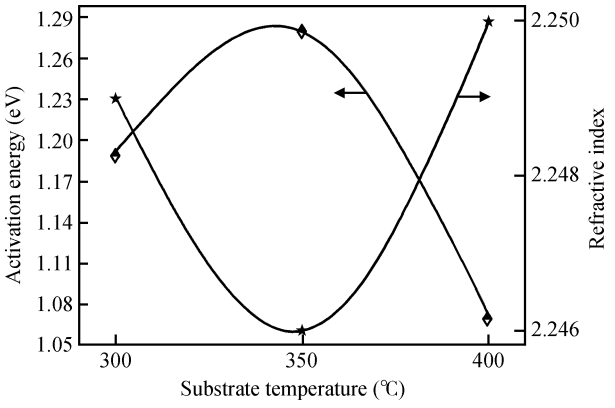

Fig. 7. Variation of the activation energy and the refractive index of Co doped ZnO thin films as a function of deposition temperature.

creases when the band gap energy E_g is increased. The Herve–Vandamme relationship[21] is:

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2, \quad (6)$$

where A and B are constants as $A \approx 13.6$ eV and $B \approx 3.4$ eV; E_g is the band gap energy and n is the refractive index of the films.

Figure 7 shows the variation of the activation energy E_a and the refractive index n as a function of the deposition temperature. The refractive index variation is in good agreement with the variation of the films disorder (Fig. 5), since it is well known that the refractive index is reduced in highly disordered films and reached its minimum value of 2.24 at the substrate temperature, however at this temperature the maximum value of the activation energy E_a was 1.28 eV, indicating that the transparent conducting ZnCoO exhibits an n-type semiconducting nature, where applied the relationship: $E_a < \frac{E_g}{2}$.

4. Conclusions

In conclusion, highly transparent conducting Co doped ZnO thin films have been fabricated on a glass substrate using an Ultrasonic spray. The structural, optical and electrical properties were investigated. All the films are polycrystalline structure wurtzite and (002) oriented. The average transmittance is about 62%–90%, in the visible region, and the band gap increased from 3.351 to 3.362 eV, which may be attributed to a similar ionic radius between Co^{2+} and Zn^{2+}. The decrease in Urbach energy is attributed to the decrease of defects. The increase in the conductivity of the samples has been explained by displacement of the electrons. From the measurement of the activation energy and optical gap, the samples are shown to be n-type in nature and exhibit semiconducting behavior in the ZnO thin films deposited at 350 ℃.

Acknowledgments

The authors would like to thank Prf. A. Attaf, Prf. A. Chala, Dr. H. Ben Temam, Mr. B. Gasmi, Dr. H. Ghodbane, Mr. C. Mahboub for helpful discussion.

References

[1] Zhang Y, Wu C, Zheng Y, et al. Synthesis and efficient field emission characteristics of patterned ZnO nanowires. Journal of Semiconductors, 2012, 33(2): 023001
[2] Zhang H, Liu H, Lei C, et al. Low-temperature deposition of transparent conducting Mn–W co-doped ZnO thin films. Journal of Semiconductors, 2010, 31(8): 083005
[3] Vernardou D, Kenanakis G, Couris S, et al. The effect of growth time on the morphology of ZnO structures deposited on Si (100) by the aqueous chemical growth technique. J Cryst Growth, 2007, 308(1): 105
[4] Prepelita P, Medianu R, Sbarcea B, et al. The influence of using different substrates on the structural and optical characteristics of ZnO thin films. Appl Surf Sci, 2010, 256(8): 1807
[5] Bahs Z B, Oral A Y. Effects of Mn and Cu doping on the microstructures and optical properties of sol–gel derived ZnO thin films. Opt Mater, 2007, 29(3): 672
[6] Van L H, Hong M H, Ding J. Structural and magnetic property of Co doped ZnO thin films prepared by pulsed laser deposition. Journal of Alloys and Compounds, 2008, 449(1): 207
[7] Vimalkumar T V, Poornima N, Jinesh B K, et al. On single doping and doping of spray pyrolysed ZnO films, structural and electrical optical characterization. Appl Surf Sci, 2011, 257(20): 8334
[8] Kavak H, Tuzemen E S, Ozbayraktar L N, et al. Optical and photoconductivity properties of ZnO thin films grown by pulsed filtered cathodic vacuum arc deposition. Vacuum, 2009, 83(3): 540
[9] Kalaivanan A, Perumal S, Pillai N N, et al. Characteristics of GZO thin films deposited by sol–gel dip coating. Materials Science in Semiconductor Processing, 2011, 14(1): 94
[10] Rani S, Suri P, Shishodia P K, et al. Synthesis of nanocrystalline ZnO powder via sol–gel route for dye-sensitized solar cells. Solar Energy Materials and Solar Cells, 2008, 92(7): 1639
[11] Zhang C. High-quality oriented ZnO films grown by sol–gel process assisted with ZnO. Journal of Physics and Chemistry of Solids, 2010, 71(2): 364
[12] Li Y, Gong J, McCune M, et al. I–V characteristics of the p–n junction between vertically aligned ZnO nanorodsand polyaniline thin film. Synthetic Metals, 2010, 160(3): 499
[13] Ayadi Z B, Mir L E, Djessas K, et al. Effect of the annealing temperature on transparency and conductivity of ZnO:Al thin films. Thin Solid Films, 2009, 517(22): 6305
[14] Abdullah H, Norazia M N, Shaari S, et al. Influence of post-annealing temperature on the properties exhibited by nanostructured In doped ZnO thin films. Thin Solid Films, 2010, 518(1): 174
[15] Daranfed W, Aida M S, Hafdallah A, et al. Substrate temperature influence on ZnS thin films prepared by ultrasonic spray. Thin Solid Films, 2009, 518(3): 1082
[16] Subramanian M, Tanemura M, Hihara T, et al. Magnetic anisotropy in nanocrystalline Co-doped ZnO thin films. Chem Phys Lett, 2010, 487(1): 97
[17] Jain A, Sagar P, Mehra R M. Band gap widening and narrowing in moderately and heavily doped n-ZnO films. Solid-State Electron, 2006, 50(2): 1420
[18] Hafdallah A, Yanineb F, Aida M S, et al. In doped ZnO thin films. Journal of Alloys and Compounds, 2011, 509(18): 7267
[19] Zhang D H, Yang T L, Ma J, et al. Preparation of transparent conducting ZnO:Al films on polymersubstrates by r. f. magnetron sputtering. Appl Surf Sci, 2000, 158(1): 43
[20] Wu S P, Zhao Q Y, Zheng L Q, et al. Behaviors of ZnO-doped silver thick film and silver grain growth mechanism. Solid State Sciences, 2011, 13(3): 548
[21] Mekhnache M, Drici A, Hamideche L S, et al. Properties of ZnO thin films deposited on (glass, ITO and ZnO:Al) substrates. Superlattices and Microstructures, 2011, 49(3): 510