Structural, optical and electrical properties of zinc oxide (ZnO) thin films deposited by a spray pyrolysis technique

Yacine Aoun[1, †], Boubaker Benhaoua[2], Brahim Gasmi[3], and Said Benramache[3, 4, †]

[1]Mechanical Department, Faculty of Technology, University of Biskra, Biskra 07000, Algeria
[2]VTRS Laboratory, Institute of Technology, University of El-Oued, El-Oued 39000, Algeria
[3]Laboratoire de Physique des Couches Minces et Application, University of Biskra, Biskra 07000, Algeria
[4]Material Sciences Department, Faculty of Science, University of Biskra, Biskra 07000, Algeria

Abstract: Zinc oxide (ZnO) thin films were deposited on glass substrates by spray pyrolysis technique decomposition of zinc acetate dihydrate in an ethanol solution with 30 mL of deposition rate, the ZnO thin films were deposited at two different temperatures: 300 and 350 ℃. The substrates were heated using the solar cells method. The substrate was R217102 glass, whose size was $30 \times 17.5 \times 1$ mm^3. The films exhibit a hexagonal wurtzite structure with a strong (002) preferred orientation. The higher value of crystallite size is attained for sprayed films at 350 ℃, which is probably due to an improvement of the crystallinity of the films at this point.The average trans mittance of obtain films is about 90%–95%, as measured by a UV–vis analyzer. The band gap energy varies from 3.265 to 3.294 eV for the deposited ZnO thin film at 300 and 350 ℃, respectively. The electrical resistivity measured of our films in the order 0.36 Ω·cm.

Key words: ZnO; thin films; substrate temperature; spray pyrolysis technique
DOI: 10.1088/1674-4926/36/1/01xxx **EEACC:** 2570

1. Introduction

Zinc oxide (ZnO), a II–IV semiconductor, has a wide direct gap of 3.37 eV at room temperature and large exciton binding energy of 60 meV[1], which has attracted much attention because of its wide prospects in optoelectronic devices, such as solar cells, light emitting diodes (LED), laser diodes and acoustic–optical devices[2−5]. In solar cells, ZnO thin films are used as an anti-reflective coating (ARC) and transparent conductive oxide (TCO) due to their high optical transmittance in the visible light region, high band gap energy ($E_g \approx 3.3$ eV), optimum refractive index ($n \sim 2.0$), and natural n-type electrical conductivity[6, 7]. ZnO can be used as a heat mirrors, piezoelectric devices[8], thin films[9], and for chemical and gas sensing[10].

ZnO thin films have been prepared using various methods, such as molecular beam epitaxy (MBE)[11], chemical vapor deposition[12], electrochemical deposition[13], pulsed laser deposition (PLD)[14], sol–gel process[15], reactive evaporation[16], magnetron sputtering technique[17], and spray pyrolysis[18], which have been reported to prepare thin films of ZnO. The spray pyrolysis technique is one of these techniques to prepare large-scale production for technological applications. It is possible to alter the mechanical, electrical, optical, and magnetic properties of ZnO nanostructures.

In the present study, nanostructure ZnO based thin films can be deposited by spray pyrolysis technique on glass substrateat two substrate temperatures of 300 ℃ and 350 ℃. The thin films were prepared with 30 mL of deposition rate, the aim of this work is to study the effect of substrate temperature on crystalline structure, optical gap energy, and electrical resistivity.

2. Experimental

In this study, the organic solar cells were fabricated through this process. We fabricated the organic solar cells, which consisted of a mirror layer inside (ITO glass) and a substrate holder. We established the substrate layer to maintain the substrate temperature using the mirror layer. The organic solar cells use solar energy to heat a substrate glass with deposition of ZnO solution on substrate (see Figure 1). The reflective layer is designed to reflect the maximum amount of solar energy incident upon it back through the glass substrate. The structure of the spray deposition system and fabricated organic solar cells are shown in Figure 1. The substrate was heated by absorber plate and we maintained a temperature of 300 ℃ and 350 ℃ when the active solution was sprayed onto the substrate glass.

ZnO solution were prepared by dissolving 0.1 M ($Zn(CH_3COO)_2$, $2H_2O$) in asolvent containing equal volume absolute methanol solution (CH_3OH) (99.995%) purity. We then added a few drops of concentrated HCl solution as a stabilizer, and the mixture solution was stirred at 60 ℃ for 120 min to yield a clear and transparent solution. The reaction can be represented as:

$$Zn(CH_3COO)_2 \cdot 2H_2O + 2R - OH \rightarrow$$
$$Zn(CH_3COO)_2 + 2R - OH + 2H_2O. \quad (1)$$

The chemical reaction may take place on the heated substrate to produce ZnO thin film as follows: when a droplet of the solution reaches the heated substrate, a chemical reaction of the zinc acetate with water solution takes place under the stimulated temperature, which provides the formation of ZnO thin films[2].

† Corresponding author. Email: aounyacine07@gmail.com; saidzno2006@gmail.com
Received 3 April 2014, revised manuscript received 19 August 2014

Figure 1. A photograph of the experimental setup.

$$\mathrm{Zn(CH_3COO)_2 \cdot 2H_2O} \frac{300\ ^\circ\mathrm{Cor350\ ^\circ C}}{\text{depositedas}} \rightarrow \mathrm{ZnO + CO_2 + CH_4 + steam.} \quad (2)$$

The resulting solutions were sprayed on the heated glass substrates by a spray pyrolysis technique, the substrates were heated by using the solar cells method, and this was prepared in our laboratory. The thin films were deposited at two substrate temperatures of 300 ℃ and 350 ℃, onto glass whose size was $30 \times 17.5 \times 1$ mm^3, which transforms the liquid to a stream formed with uniform and fine droplets of 35 μm average diameters.

The structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation ($\lambda = 0.15406$ nm), the scanning range of (2θ) was between 20° and 60°. The optical transmittance of the films was measured in the range of 300–900 nm by using an ultraviolet–visible spectrophotometer (SHUMATZU 1800) and the electrical resistivity was measured in a coplanar structure obtained with evaporation of four golden stripes on the deposited film surface using the Keithley Model 2400 low voltage source meter instrument.

3. Results and discussion

The XRD spectrum of the ZnO thin films grown at 300 ℃ and 350 ℃ are shown in Figure 2. The obtained XRD spectra matched well with the space group P63mc (186) (No. 36-1451)[19]. As can be seen, the only diffraction peak was observed at $2\theta = 35.29°$ and 34.5° for sprayed films at 300 ℃ and 350 ℃, respectively, which is related to the plan of (002). Zaier *et al.*[20] found that for sprayed ZnO thin films at a substrate temperature ranging between 250 ℃ and 450 ℃, a single (002) diffraction peak of ZnO films is detected in all films. The spectra shows that all of the films have a preferential growth along c-axis or (002) plane but with different peak intensity. The film deposited at 350 ℃ has a higher and sharper diffraction peak, indicating an improvement in (002) peak intensity compared to the other films.The crystalline quality of thin films

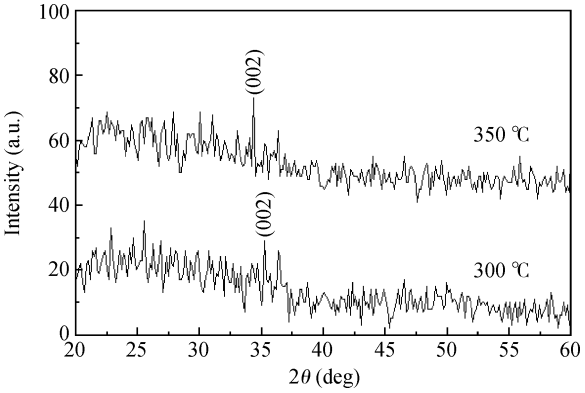

Figure 2. X-ray diffraction spectra of ZnO thin films sprayed at 300 ℃ and 350 ℃.

was enhanced at 350 ℃. Similar observations have been found by other researchers[21, 22].

The lattice constant c and diffraction peak angles of ZnO thin films (see Table 1) are calculated using the following equation[21]:

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

where a, c are the lattice parameters, (h, k, l) is the Miller indices of the planes, and d_{hkl} is the interplanar spacing.

The strain ε values in our films were estimated from the observed shift in the (002) diffraction peak between their positions in the XRD spectra via the formula[21]:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100\%, \quad (4)$$

where ε is the mean strain in ZnO thin films (Table 1), c the lattice constant of ZnO thin films, and c_0 the lattice constant of bulk (standard $c_0 = 0.5206$ nm).

The crystallite size of ZnO thin films are estimated using the well-known Debye-Scherrer formula[23]:

Table 1. Recapitulating measured values of Bragg angle (2θ), the inter planar spacing (d), the full width at half-maximum (FWHM), the crystallite size (G) and lattice parameters (cand a) for ZnO thin films deposited at 300 ℃ and 350 ℃.

T_S (℃)	hkl	2θ (deg)	d (Å)	FWHM (deg)	G (Å)	c (Å)	a (Å)	ε (%)
300	002	35.29	2.54125	0.51	16.35	5.082502	5.189391	−2, 3722
350	002	34.54	2.59469	0.38	21.91	3.176564	3.243369	−0.3191

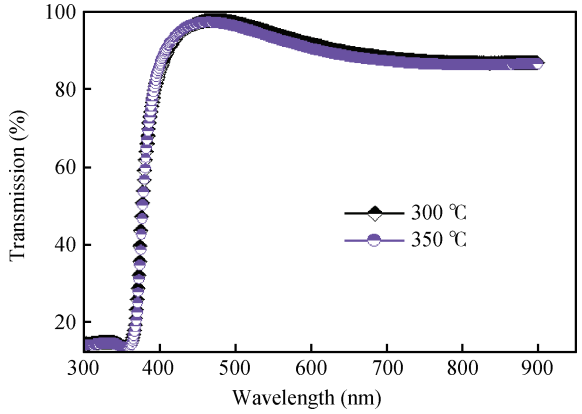

Figure 3. Transmission spectra $T(\lambda)$ of ZnO thin films sprayed at 300 ℃ and 350 ℃.

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

where G is the crystallite size, λ is the wavelength of X-ray ($\lambda = 1.5406$ Å), β is the full width at half-maximum (FWHM), and θ is the half diffraction angle of the centroid of the peak. Table 1 presents the structure properties of ZnO films whichmeasured the (002) diffraction peak at 300 ℃ and 350 ℃. It can be seen from Table 1 that good crystallinity isachieved in the films sprayed at 350 ℃, which wasalso obtained by Ref. [22].

Figure 3 shows the optical transmission spectra of ZnO thin films with substrate temperature. As can be seen, there is a height transparent spectra $T(\lambda)$ of the thin films in the visible region, and the average transmission is over 90%. The region of the absorption edge in the all layers due to the transition between the valence band and the conduction band is located between 360–390 nm. In this region, the transmission decreased because of the onset fundamental absorption.

The optical band gap energy E_g was measured from the transmission spectra using the following relations[24]:

$$(Ah\nu)^2 = C(h\nu - E_g), \tag{6}$$

where A is the absorbance, d is the film thickness; T is the transmission spectra of thin films; α is the absorption coefficient values; C is a constant, $h\nu$ is the photon energy ($h\nu = \frac{1240}{\lambda(\text{nm})}$ (eV)); and, E_g is the band gap energy of the semiconductor. As was shown in (Figure 3), a typical variation of $(Ah\nu)^2$ as a function of photon energy ($h\nu$) used for deducing optical band gap E_g is determined by extrapolation of the straight line portion to zero absorption ($A = 0$)[11], the values of E_g are listed in Table 2. In addition, we have used the Urbach tail energy (E_u), which is related to the disorder in the film network,

Table 2. Recapitulating measured values of band gap energy (E_g), Urbach energy (E_u), and electrical resistivity (ρ) for ZnO thin films deposited at 300 ℃ and 350 ℃.

T_S (℃)	E_g^a (eV)	E_u (meV)	ρ (Ω·cm)
300	3.294	089.8	0.359
350	3.265	083.4	0.373

which is expressed as[21, 23]:

$$A = A_0 \exp\frac{h\nu}{E_u}, \tag{7}$$

where A_0 is a constant, $h\nu$ is the photon energy, and E_u is the Urbach energy. The Urbach tail energy E_u is calculated from the slope of $h\nu$ versus photon energy ($h\nu$) plot and the obtained values are shown in Table 2.

As is clearly seen in Figure 4, the optical gap energy of ZnO thin films arechanged from 3.265 to 3.294 eV with the increase of substrate temperature from 300 ℃ and 350 ℃, respectively. This indicates a narrowing of the optical band gap. The decrease in optical energy gap might be interpreted as a Moss-Burstein shift, which was ascribed to an increase of free carrier concentration, this leads to a downward shift of the Fermi level to below the band edge[25]. The same phenomena are carried out by Ali *et al.*[26], who reported similar results in ZnO thin films prepared by the radio frequency technique. However, in Figure 5 we obtained the inverse result for the Urbach energy: the Urbach energy E_u decreases from 89.8 meV to 83.4 meV as substrate temperature increases from 300 and 350 ℃, indicating the reduction of structural disorder and defects in the ZnO thin films. This is related to an improvement in the crystalline structure, as indicated by XRD spectra.

Table 2 shows that the electrical resistivities of our films are in qualitative agreement with the band gap energy (see Table 2). The increase in the electrical resistivity can be explained by the increase ofthe potential barriers because the introduced atoms are segregated into the grain boundaries, this interpretation is consistent with the authors[18, 19, 21–24]. This can be explained by decreasing of the crystallite size (see Table 1). One can note that the substrate temperature effect is clearly observed in the layer quality.

4. Conclusions

In conclusion, highly transparent conductive ZnO thin films were deposited on glass substrate by the spray pyrolysis technique. The ZnO thin films were deposited at two different temperatures (300 ℃ and 350 ℃), the substrates were heated using the solar cell method. The influence of deposition temperature on structural, optical and electrical properties was investigated. The films exhibit a hexagonal wurtzite structure with a strong (002) preferred orientation. The average trans-

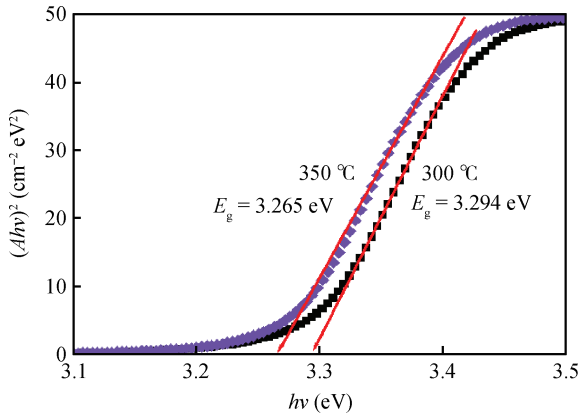

Figure 4. The typical variation of $(Ahv)^2$ versus photon energy of deposited ZnO thin film at 300 and 350 ℃.

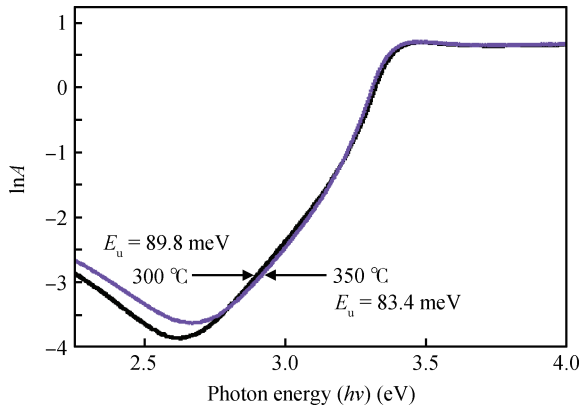

Figure 5. The typical variation of LA versus photon energy of deposited ZnO thin film at 300 ℃ and 350 ℃.

mittance of obtain films is about 90%–95%, which was measured by a UV–vis analyzer. The band gap energy varies from 3.265 to 3.294 eV for the deposited ZnO thin film at 300 ℃ and 350 ℃, respectively. The electrical resistivity measured of our films is in the order of 0.36 Ω·cm.

Acknowledgments

This work was supported in part by the National Project Research (PNR) and VTRS laboratory of El–Oued University, X–ray diffraction data in this work were acquired with an instrument supported by the University of Biskra. We thank Prof. A. Chala and B. Gasmi (Biskra University) for the assistance in XRD data acquisition.

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] Zuo C, Wen J, Zhong C. First-principles study of the electronic structures and optical properties of C–F–Be doped wurtzite ZnO. Journal of Semiconductors, 2012, 33(7): 072001

[4] Zhu X, Wu H, Wang S, et al. Optical and electrical properties of N-doped ZnO and fabrication of thin-film transistors. Journal of Semiconductors, 2009, 30(3): 033001

[5] Xiong C, Yao R H, Wan W J, et al. Fabrication and electrical characterization of ZnO rodarrays/CuSCN heterojunctions. Optik, 2014, 125(1): 785

[6] Pakhuruddin M Z, Yusof Y, Ibrahim K, et al. Fabrication and characterization of zinc oxide anti-reflective coating on flexiblethin film microcrystalline silicon solar cell. Optik, 2013, 124(24): 5397

[7] Kang D W, Kuk S H, Ji K S, et al. Effects of ITO precursor thicknesson transparent conductive Al doped ZnO film for solar cell applications. Solar Energy Materials and Solar Cells, 2011, 95(1): 138

[8] Mariappan R, Ponnuswamy V, Chandra B A, et al. Structural, optical and electrical characterizationof nebulizer-sprayed ZnO nano-rods. Superlattices and Microstructures, 2014, 65(1): 184

[9] Castaneda L, Moreno-Valenzuela J, Torres-Torres C. Chemisorptive detection by electrical and nonlinear optical absorption properties of a nanostructured ruthenium-doped zinc oxide film. Optik, 2013, 124(24): 5209

[10] Yua H, Fan H, Wang X, et al. Synthesis and characterization of ZnO microstructures viamicrowave-assisted hydrothermal synthesis process. Optik, 2014, 125(3): 1461

[11] Gahtar A, Benramache S, Benhaoua B, et al. Preparation of transparent conducting ZnO:Al films on glass substrates by ultrasonic spray technique. Journal of Semiconductors, 2013, 34(7): 033001

[12] Amoupour E, Ziabari AA, Andarva H, et al.Influence of air/N_2 treatment on the structural,morphological and optoelectronic traitsof nanostructured ZnO:Mn thin films. Superlattices and Microstructures, 2014, 65(1): 332

[13] Karak N, Samanta P K, Kundu T K.Green photoluminescence from highly oriented ZnO thin film for photovoltaicapplication. Optik, 2013, 124(24): 6227

[14] Keskenler E F, Turgut G, Dogãn S. Investigation of structural and optical properties of ZnO films co-doped with fluorine and indium. Superlattices and Microstructures, 2012, 52(1): 107

[15] Ramesh J, Pasupathi G, Mariappan R, et al. Structural and optical properties of Ni doped ZnO thin films using sol–gel dip coating technique. Optik, 2013, 124(3): 2023

[16] Acharya A D, Sarwan B, Panda R, et al. Tuning of TCO properties of ZnO by silver addition. Superlattices and Microstructures, 2014, 67(1): 97

[17] Zhang H, Yang S, Liu H, et al. Preparation and characterization of transparent conducting ZnO:W films by DC magnetron sputtering. Journal of Semiconductors, 2011, 32(4): 043002

[18] Benramache S, Belahssen O, Arif A, et al. Correlation between crystallite size-optical gap energy and precursor molarities of ZnO thin films. Journal of Semiconductors, 2014, 35(4): 041001

[19] Benramache S, Chabane F, Benhaoua B, et al. Influence of growth time on crystalline structure, conductivity and optical properties of ZnO thin films. Journal of Semiconductors, 2013, 34(2): 023001

[20] Zaier A, Oum Elaz F, Lakfif F, et al. Effects of the substrate temperature and solution molarity on the structural opto-electric properties of ZnO thin films deposited by spray pyrolysis. Mater Sci Semicond Processing, 2009, 12: 207

[21] Benramache S, Benhaoua B. Influence of substrate temperature and Cobalt concentration on structural and optical properties of ZnO thin films prepared by ultrasonic spray technique. Superlattices and Microstructures, 2012, 52(4): 807

[22] Benramache S, Benhaoua B, Chabane F. Effect of substrate temperature on the stability of transparent conducting cobalt doped ZnO thin films. Journal of Semiconductors, 2012, 33(9): 093001

[23] Benramache S, Belahssen O, Guettaf A, et al. Correlation between electrical conductivity–optical band gap energy and precursor molarities ultrasonic spray deposition of ZnO thin films. Journal of Semiconductors, 2013, 34(11): 113001

[24] Benramache S, Benhaoua B. Influence of annealing temperature on structural and optical properties of ZnO:In thin films prepared by ultrasonic spray technique. Superlattices and Microstructures, 2012, 52(6): 1062

[25] Lina J C, Peng K C, Yehc T Y, et al. On the structure and characterization of Al, Sc-co-doped ZnO-films varying with 0–2.37 wt.% Sc contents. Thin Solid Films, 2009, 517: 4715

[26] Ali A I, Ammar A H, Abdel Moez A. Influence of substrate temperature on structural, optical properties and dielectric results of nano-ZnO thin films prepared by radio frequency technique. Superlattices and Microstructures, 2014, 65: 285