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Effect Of Temperature Deposition On The Properties Of Zno Thin Films Prepared By Low-Cost Nebulizer Spray Pyrolysis Method

Brahim Bettayeb [a], Djamal Belamri [a], Soufiane Benhamida [b], Yamina Benkrima [c], Abdelkader Benmenine[d], Amar Manseri[e]

[a] *Laboratoire de physique photonique et nanomatériaux pour usages divers, université Mohamed Khider Biskra, Algérie.*
[b] *Faculty of Mathematics and Material Sciences, Radiation and Plasma and Surface Physics Laboratory (LRPPS), University of Kasdi Merbah Ouargla, 30000, Ouargla, Algeria.*
[c] *Ecole Normale Supérieure de Ouargla, 30000, Algeria.*
[d] *Laboratoire (VPRS), Département de Chimie, Valorisation et Promotion des Ressources Sahariennes, Université Kasdi Merbah , Ouargla, Algérie.*
[e] *Centre de Recherche en Technologie des Semi-conducteurs pour Energétique, Alger, Algérie.*
Email : brahim.bettayeb@univ-biskra.dz
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Using the nebulized spray pyrolysis method, pure zinc oxide (ZnO) thin films were made on an ITO glass substrate in this study. We systematically investigate the effects of temperature deposition on the structural, morphological, optical, and electrical properties of ZnO thin films. We varied the temperature deposition from 300 to 450 C. An X-ray diffraction pattern confirmed that all the films are polycrystalline in nature and have a hexagonal wurtzite structure with a preferred orientation along the (002) plane. The Fourier transform infrared (FTIR) spectroscopy proved the formation (Zn-O) bond stretching vibration mode. The AFM result shows a change in surface morphology with an increase in temperature deposition. A maximum transmittance was observed for the sample prepared at 300 ◦C. The optical study reveals a decrease in transmittance with an increase in temperature deposition. The estimated optical gap values of the samples range from 3.19 to 3.27 eV.

Key words: Zinc oxide; thin films; Nebulizer spray pyrolysis;XRD diffraction.

1. Introduction

Zinc oxide (ZnO), a semiconductor with a wide direct band gap (3.3 eV) and a high exciton binding energy (60 meV), is getting a lot of attention from researchers because of its electrical and optical properties, which make it useful in some scientific and industrial settings [1, 2].

ZnO is a prominently researched semiconductor oxide because of its numerous adaptable and appealing qualities, such as excellent chemical and thermal stability and nontoxicity. Consequently, it possesses several potential applications in photovoltaic solar cells. Researchers are working on a number of different ways to make nanostructured ZnO right now. These include pulsed laser deposition [3], chemical bath deposition [4], thermal evaporation [5], the sol-gel technique [6], pulse laser deposition (PLD) [7], and nebulizer spray pyrolysis (NSP) [8]. One of these methods that looks promising is the nebulizer spray pyrolysis technique (NSP). It has a lot of good points, including being cheap, easy to use, putting down thin films evenly over large areas, and giving good control over composition and structure [8, 9]. Many deposition parameters, such as spray rate, substrate temperature, doping concentration, nozzle distance, and carrier gas flow rate, effectively adapt the growth of films. The present work employs the nebulizer spray pyrolysis technique to grow zinc oxide (ZnO) thin films on an ITO glass substrate. We explore the impact of temperature deposition variation on structural, optical, morphological, and electrical properties.

2. Experimental procedure

2.1. Synthesis of thin films

ZnO thin films were fabricated by using the nebulizer spray pyrolysis (NSP) process at different temperatures for deposition on an ITO glass substrate. We varied the temperature deposition range from 300, 350, 400, and 450ºC. We prepared the starting solution by dissolving 0.1 M ($Zn[OOCCH]_2HO$) in 30 ml di-ionizer water. We thoroughly stirred the solution using a magnetic stirrer for half an hour to yield a clear and transparent solution and then sprayed it on different temperature depositions. We cleaned the ITO glass substrates in acetone and distilled water, respectively, before starting the deposition. Electronic temperature controllers controlled the other preparative parameters, including the spray rate (5 ml min^{-1}), nozzle-to-substrate distance (40 cm), and temperature.

2.2 Thin films characterization

The elaborated films were characterized using X-ray diffraction (BRUKER - AXS type D8) equipped with X'Pert High Score under Cu Kα (λ = 1.5406Å) radiation. The scanning range of (2θ) was taken between 25˚ and 70˚ in order to investigate the structural properties. We employed a Fourier transformed infrared (FTIR) Cary 600 Series FTIR spectrometer to detect the chemical and vibrational bonds of the prepared samples, performing scan measurements in the range of 400–4000 cm^{-1} range. Atomic force microscopy in contact mode using an MFP-3D Stand Alone AFM (Asylum Research) achieved the surface morphologies of the films. We used the Cray 100 Agilent Technologies to measure the optical transmittance spectra of all prepared films in the spectral range of 300–800 nm. To measure the electrical resistivity, Keithley source meter model 2400 is equipped with a four-point DC probe setup. All measurements were carried out at room temperature (RT).

3. Result and discussions

3.1 Structural properties

X-ray diffraction patterns (XRD) of ZnO thin films deposited on ITO substrate for different temperature deposition were recorded in the range 25 to 70° and are shown in Fig. 1. One can observe that the XRD patterns exhibit peaks indexed in the (100), (002), (101), (102), (110), (103) and (200) planes, which are assigned to the hexagonal wurtzite of the ZnO structure and match well with the standard spectrum (JCPDS, No. 36-1451) [10]. No other crystalline impurities are detected in the XRD patterns, confirming the high purity of the synthesized ZnO films. As shown in Fig. 1, the intensity of the (002) peak increases as the temperature of deposition increases, indicating the preferred orientation and confirming that the growth is enhanced along the c axis [11]. It is evident from Fig. 1 that the structural properties of the ZnO films strongly depend on deposition temperature. The films deposited at 400 oC exhibit highly oriented films as compared to the other deposited temperatures. Furthermore, XRD patterns display very fine peaks indicating good crystallinity of thin films; a similar observation was also reported in litherator [2].

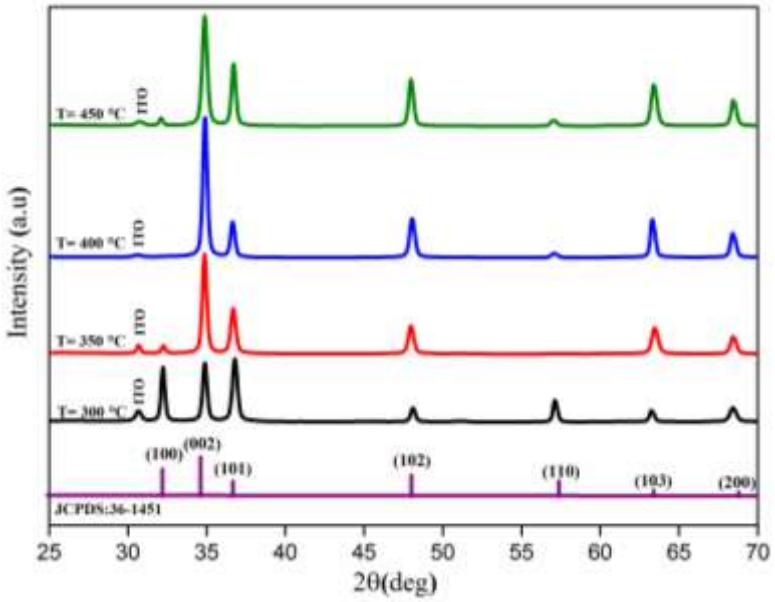

Fig. 1: XRD patterns for ZnO thin films prepared at different temperature deposition

Lattice parameter a of the deposited films has been calculated from the values of 2θ and inter-planar spacing relation for the cubic structure, as given bellow [12]:

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

Where d_{hkl} is inter-planar spacing, (hkl) are the Miller indices of the planes linked to the (002) .

The average grain size was calculated from Debye-Scherrer formula [13]:

$$G = \frac{0.9\lambda}{\beta \cos\theta} \qquad (2)$$

Where G is the grain size, β is the full width at half-maximum (FWHM) of the most intense diffraction peak, λ is the X-ray wavelength (1.54056 Å) and θ is the Bragg angle at the (002) peak. All calculated parameters are tabulated in Table 1, and we can find that the estimated crystalite size, determined from the (002) peak, has a nano. It is observed that the values of crystallite size are stable from 34.25 nm at deposition temperatures of 300 and 350 °C; after that, they slowly increase at 400 °C from 34.26 nm. This behavior can signify a lesser structural deformation [14]. However, at 450 °C, the crystalite size decreases around 29 nm. This result can be explained by the decrease of defects and strain in the ZnO lattice structure.

Table 1: Values of Bragg angle 2θ, lattice constants $c_{(002)}$, grain size G, thikness of films t and optical band gap energy E_g of ZnO thin films prepared at different temperature deposition.

T (˚C)	2θ (deg)	$c_{(002)}$ (Å)	G (nm)	t (nm)	Eg (eV)	σ $(\Omega.cm)^{-1}$
300	34,8632	5.119	34.25	300.297	3.27	34,57
350	34,8429	5.472	34.25	219.399	3.25	49,88
400	34,8714	4.989	34.26	209.784	3.21	41,05
450	34,8542	5.269	29.36	144.430	3.19	27,66

3. 2 Fourier Transform Infrared (FT-IR) analysis

FT-IR is known as one of the very suitable techniques used for the identification of the chemical bonding vibration modes properties of synthesized material. Fig. 3 shows the FT-IR spectra of the ZnO thin layer for different temperature depositions. The FT-IR transmission spectrum was recorded in the range from 400 to 4000 cm^{-1}. The spectrum shows absorption bands at wavenumbers located at 412, 433, 472, 493, 543, 759, and 908 cm^{-1}. These absorption peaks can be assigned to the metal-oxygen (Zn-O) bond stretching vibration mode, as reported by other researchers [2, 9]. The absence of zinc acetate or other oxide from FT-IR spectra confirms the formation of zinc oxide nanoparticles.

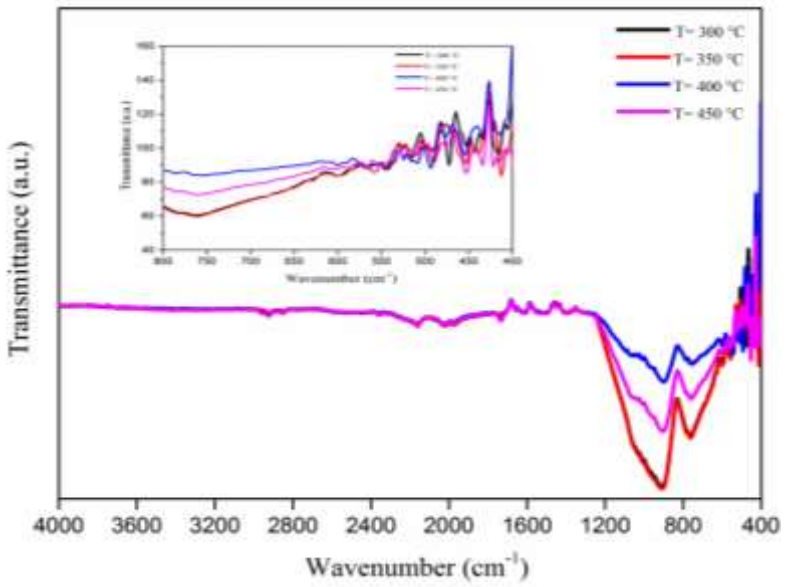

Fig. 3: FTIR spectra for ZnO thin films prepared at different temperature deposition

3.3 Atomic Force Micrograph (AFM) Study

Fig. 4 illustrates the 2D surface topography of pure ZnO thin films synthesized using the NSP technique on an ITO substrate, with deposition temperatures ranging from 300 to 450 °C. The images clearly show uniformly dispersed spherical grains of varying sizes covering all sample surfaces. We can also observe that the morphology of all samples roughens as the deposition temperature increases. The evidence clearly demonstrates that the diameter of the spherical grains gradually increases as the deposition temperature rises. This behavior leads to an increase in the roughness of large crystals, which suggests a high level of crystallinity in the film, as confirmed by XRD analysis.

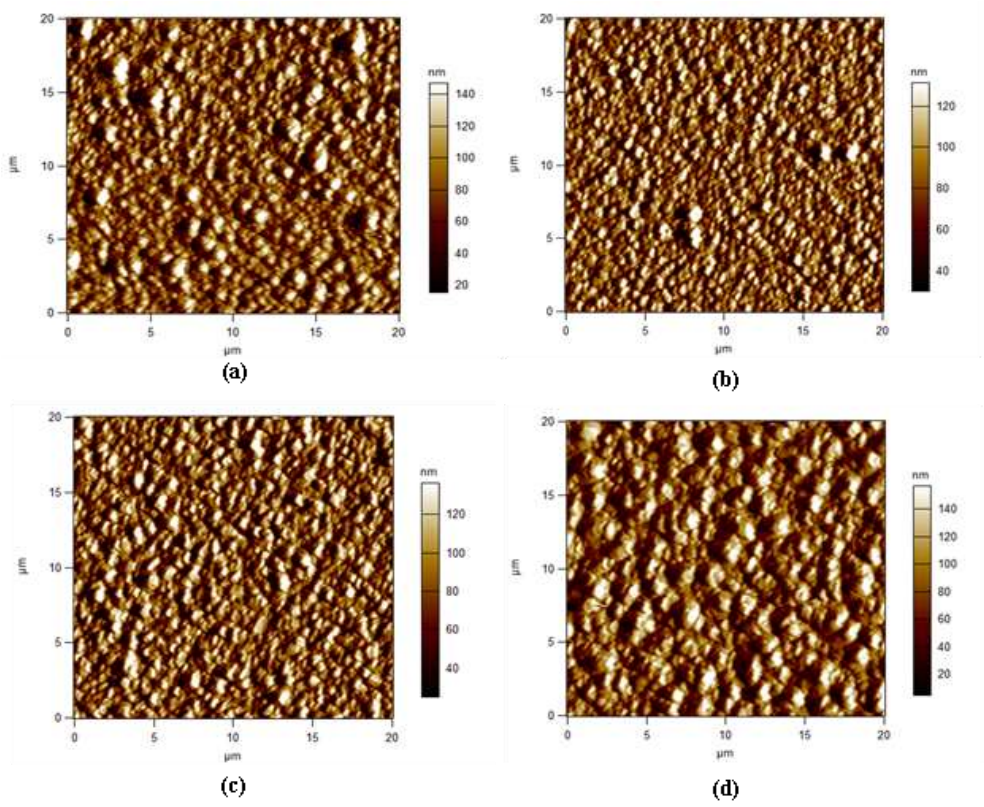

Fig. 4: AFM micrograph for ZnO thin films prepared with different temperature deposition; (a) T= 300°C, **(b) T= 350**°C, **(c) T= 400**°C, **(d) T= 450**°C.

3.4 Optical properties

The transmittance spectra of the ZnO thin layer recorded at a wavelength ranged from 300 to 800 nm at different deposition temperatures grown on ITO substrates are presented in Fig. 5. It is clear that the optical transmittance of the deposited thin layer is gradually decreasing from 80% to 14% in the visible region as the temperature of deposition increases. Meanwhile, the sample prepared at 300 °C exhibits high visible average transmission at about 80%. It was observed from all spectra that the deposited film reveals lower transmittance in the UV region; this behavior is due to the region of the fundamental absorption edge in the layers [2].

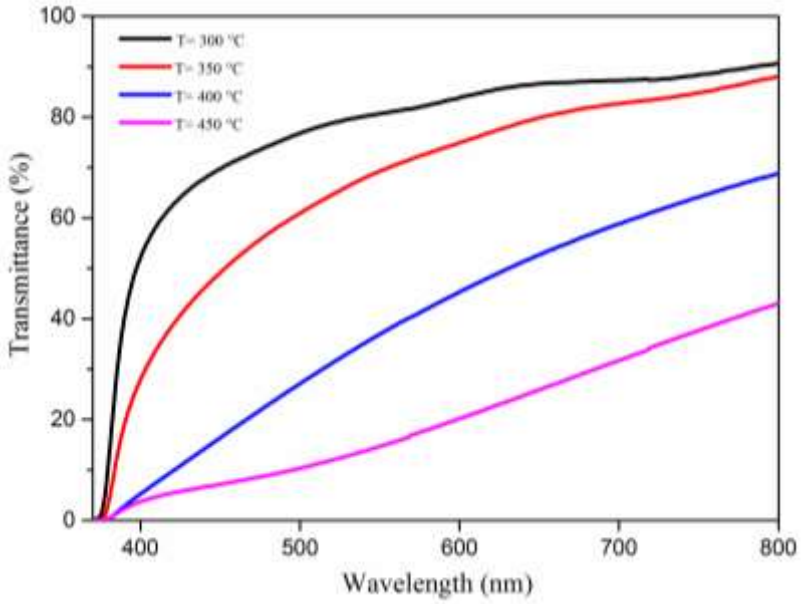

Fig. 5: Spectral transmittance plots of ZnO thin films prepared at different temperature deposition

The absorption coefficient has been calculated from Lambert's formula [16]:

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \tag{3}$$

where T and t are the transmittance and thickness of the films respectively.
The Optical energy gap E_g and absorption coefficient α are related from the Tauc's relation [17]:

$$(\alpha h\nu)^n = B\left(h\nu - E_g\right) \tag{4}$$

where α is the absorption coefficient, (hν) is the photon energy, and B is a constant. The E_g values were evaluated by plotting $(\alpha h\nu)^2$ against (hν) and extrapolating the linear portion of the curve to the energy axis at α = 0. Fig. 6 shows the plot of $(\alpha h\nu)^2$ vs. (hν); the corresponding E_g values are tabulated in Table 1. It is found that the E_g shifted from 3.27 eV to 3.19 eV as the temperature deposition increased from 300 °C to 450 °C. These observed values of the optical band gap are in good agreement with the reported value [18].

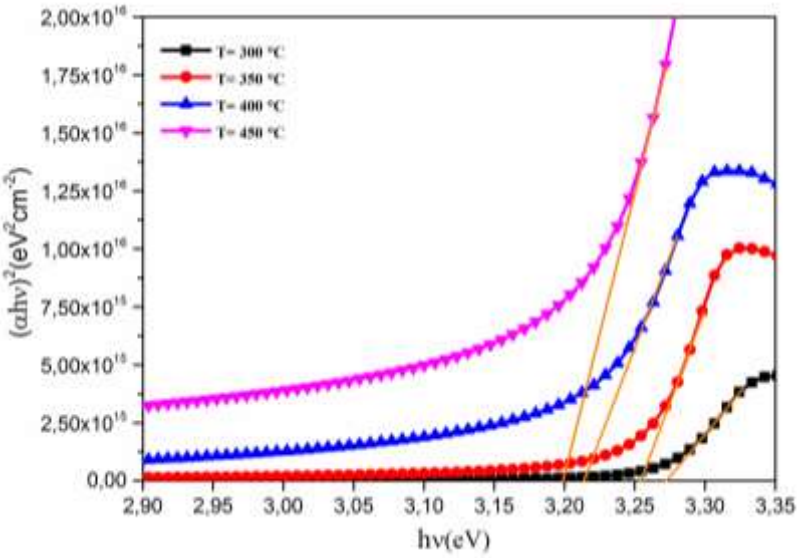

Fig.6: Estimation of band gap energy (Eg) from Tauc's relation of ZnO thin films prepared at different temperature deposition

3.5 Electrcal properties

In order to investigate the electrical properties of the prepared ZnO thin films, Hall effect measurements were performed. The measured values of conductivity are shown in Table 1. Fig. 7 represents the plot of conductivity as a function of temperature of depositions of all samples. One can see from Fig. 7 that the conductivity increases from 34.57 $(\Omega.cm)^{-1}$ to reach the maximum value of 49.88 $(\Omega.cm)^{-1}$ from the sample prepared at temperature 350 ˚C. This result can be attributed to the presence of defects such as interstitial zinc atoms and oxygen vacancies; the same behavior was observed in the study of Garnier et al. [19]. From temperatures of deposition greater than 350 ˚C, the conductivity of ZnO films decreases to the minimum value of 27.66 $(\Omega.cm)^{-1}$ from samples deposited at 450 ˚C. Generally, undoped ZnO films exhibit n-type conductivity due to their native defects like oxygen vacancies (Vo) and the interstitial of zinc (Zni) in the ZnO lattice [20].

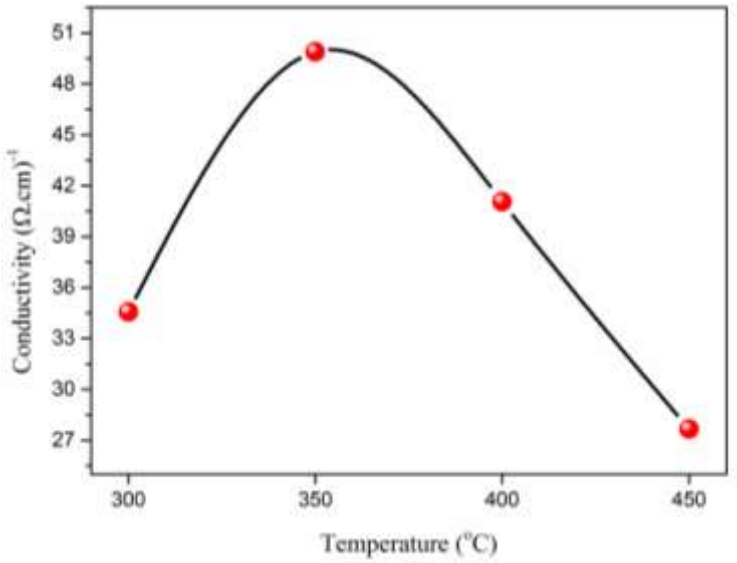

Fig.7: Eectrical conductivity for ZnO thin films prepared at different temperature deposition

4. Conclusion

In the current research, pure ZnO thin films have been successfully synthesized from zinc acetate as a source of Zn by the nebulized spray pyrolysis (NSP) technique on an ITO glass substrate. The effect of temperature deposition, which ranged from 300 to 450 ˚C, on the structural, morphological, optical, and electrical properties of ZnO thin films was investigated. XRD spectra revealed that all films are crystalline with hexagonal wurtzite ZnO structures. XRD data confirmed that the ZnO thin films were highly oriented along the (002) direction. We found that the average crystallite size of the thin films ranges from 29.36 nm to 34.25 nm. FTIR spectroscopy of all ZnO samples showed stretching vibrations linked to the standard functional groups of the ZnO crystal. AFM investigations revealed that all films displayed a granular, polycrystalline morphology, and grain size increased as the temperature deposition increased. The optical measurements show that transmittance decreases with an increase in temperature deposition. The optical gap energy values of the thin films are found to be in the range of 3.27 to 3.19 eV for temperatures changed from 300 to 450 °C, respectively, and the electrical vonductivity is found between 27.66 and 34.57 $(\Omega.cm)^{-1}$. Consequently, high-quality ZnO thin films have been fabricated utilizing an economical nebulized spray pyrolysis process, and the resulting quality indicates their potential uses in optoelectronic devices.

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