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Research Article

Effect of Substrate Temperature on the Microstructural, Morphological, and Optical Properties of Electrosprayed ZnO Thin Films

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Polycrystalline ZnO thin films were prepared on silicon substrates using electrospray method with vertical setup. Water and ethanol were used as solvents for zinc acetate dehydrate and no postdeposition annealing was required for formation of ZnO. The influence of substrate temperature in the range of 150–250°C on surface morphology and roughness was studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and optical profilometry. An improvement of surface quality and smoothing of the films with temperature were obtained. X-ray diffraction measurements revealed that, at all investigated substrate temperatures, the films were polycrystalline with crystallites' sizes decreasing with temperature. Besides, the preferred crystal orientation varies with the substrate temperature. The analysis of surface chemical composition and oxidation state was performed with X-ray photoelectron spectroscopy (XPS). It was shown that, at substrate temperature of 200°C, the deposited ZnO films were closest to the stoichiometric ones. In general, the films at 150°C were oxygen-deficient, while at other studied temperatures, the films had excess of oxygen more pronouncedly at 200°C. Spectral ellipsometric measurements confirmed that the structural disorder is the highest at 150°C and improves with temperature. Refractive indexes for films at 200°C and 250°C are almost the same, 1.97 and 1.93, respectively, at wavelength of 600 nm, while for the sample deposited at 150°C, the refractive index is substantially lower, 1.67. The optical band gap is slightly influenced by the substrate temperature: 3.27 eV at 150°C and 3.32 eV at 200°C.

1. Introduction

Due to its remarkable properties such as transparency in VIS and NIR spectral regions, low resistivity, biocompatibility, and long-term stability, ZnO gains increasing scientific interest. Additionally, ZnO is inexpensive and nontoxic and finds diverse applications in the fields of optoelectronics [1], bio and gas sensing [2–4], and integrated optical devices [5] and for optically transparent electrodes in flat panel displays [6] or solar cells [7] for self-cleaning coatings [8].

Thin ZnO films have been deposited using different vacuum-based techniques like RF sputtering [9], atomic layer deposition [10], plasma-enhanced chemical vapor deposition [11], pulsed laser deposition [4], and molecular beam epitaxy [12]. However, these deposition methods require expensive facilities and precursors and sometimes impose restrictions on operation conditions (limiting coating area for instance). Sol-gel process [13], spray pyrolysis [14], dip coating [15], and electrostatic spray deposition (also referred to as electrospraying) [16, 17] are regarded as a cost-effective alternative for preparation of ZnO films. Among them, electrospraying is particularly attractive, because it requires relatively simple setup and offers easy control of morphology and stoichiometry. Besides, it produces fine droplets with submicron sizes that do not agglomerate. These droplets are highly wettable and have strong adhesive properties, thus enabling uniform coating of the substrate.

Electrostatic setups with horizontal [17] and vertical configurations [18] have already been used and amorphous or crystalline films with diverse properties have been deposited

using different deposition parameters. The effects of experimental parameters on jet characteristics and electrosprayed patterns and some properties of ZnO films are studied [19–21]. Typically zinc acetate and zinc nitrate are used as organic sols, and water, ethanol, isopropanol, 2-methoxy ethanol, and propylene glycol are used as solvents. An addition of acetic acid, nitric acid, hydrochloric acid, and 2-aminoethanol has been reported.

One of the crucial factors in electrospraying is the temperature of the substrate during the deposition because it controls the interplay between the precursor decomposition and the rate of solvent evaporation. According to our knowledge, a detailed investigation of the impact of substrate temperature on overall properties of ZnO does not exist. Mahmood et al. [22] have studied the effect of substrate temperature in the range of 100–170°C on morphological properties of deposited ZnO films and observed little influence. This could be expected because the decomposition temperature of Zn acetate is higher than 200°C [16].

It will be a real advantage if high-performance ZnO films could be prepared at moderate temperatures without commonly applied postdeposition annealing at high temperature. Therefore, it is worthwhile to determine the lowest substrate temperature at which the formation of ZnO will take place and to fully characterize ZnO films deposited at this temperature. Thus, the application of ZnO films in organic electronics will be substantially enhanced because films would be easily deposited on thermosensitive substrates by one-step procedure using cost-effective method of electrospraying.

In this paper, we study ZnO thin films prepared by electrospray method using zinc acetate dehydrate as precursor and water and ethanol as solvents. In order to check the possibility for preparation of high-performance ZnO thin films at the lowest substrate temperature, no postdeposition annealing at high temperature is applied. The influence of substrate temperature in the range of 150–250°C on surface morphology and roughness was studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and optical profilometry. The crystal structure is confirmed by X-ray diffraction. The analysis of surface chemical composition and oxidation state is performed with X-ray photoelectron spectroscopy (XPS), while the optical behaviour is followed through spectral ellipsometry. The tuning of films' properties simply by changing the substrate temperature is demonstrated and discussed.

2. Experimental Part

The initial solution for the electrospraying was prepared by dissolving of 0.400 g of zinc acetate dehydrate in 1.8 ml deionized H_2O, subsequent dilution with 12 ml ethanol, and adding of few drops of acetic acid for clearing the solution. The solution was stirred for 2 hours and aged for 24 h at room temperature. All chemicals (Sigma-Aldrich) were of analytical reagent grades and were used without further purification.

Thin ZnO films with thickness around 200 nm were deposited using an electrostatic setup with vertical configuration, presented in Figure 1. The emitter was a 5 ml syringe

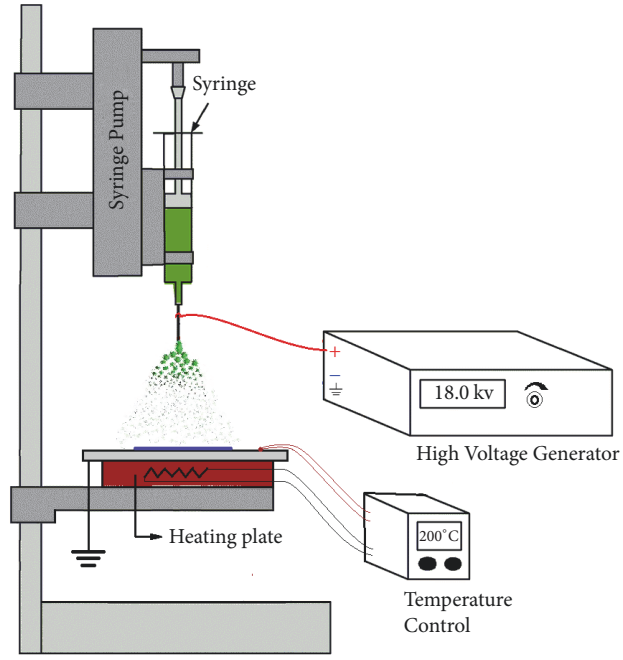


Figure 1: Experimental setup for deposition of ZnO thin films by the method of electrospraying.

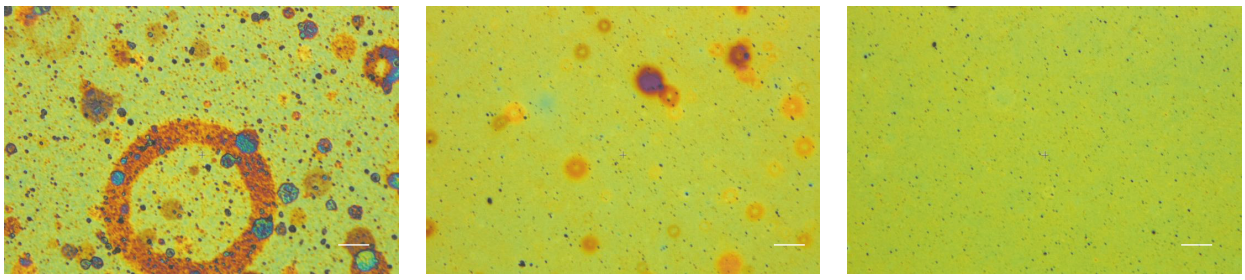
with stainless steel needle of outer to inner diameter of 508 to 241 microns and the collector is a stainless steel-duralumin plate grounded in a safe way and heated at temperatures of 150, 200, and 250°C by the heater with thermocontroller. The distance between the emitter and collector was kept at 6 cm and a high voltage of 18 kV with positive polarity was applied via a DC power supply (Applied Kilovolts, UK).

Scanning Electron Microscope (Philips 515, 30 kV accelerating voltage), Atomic Force Microscope (MFP-3D, Asylum Research, Oxford Instruments), and optical profiler (Zeta-20, Zeta Instruments) were used for characterization of the surface morphology and roughness of the films, while the crystal status of the films and the surface chemical composition and oxidation state were inspected by X-ray diffraction measurements (Philips 1710) and through X-ray Photoelectron Spectroscopy (AXIS Supra electron spectrometer, Kratos Analitycal Ltd.), respectively.

Refractive index, extinction coefficient, and thickness of the films were determined from spectroscopic ellipsometry measurements (UVISEL 2, HORIBA Jobin Yvon). The measurements were performed at 70° incident angle in the spectral range from 250 nm to 820 nm and 2 nm increment step.

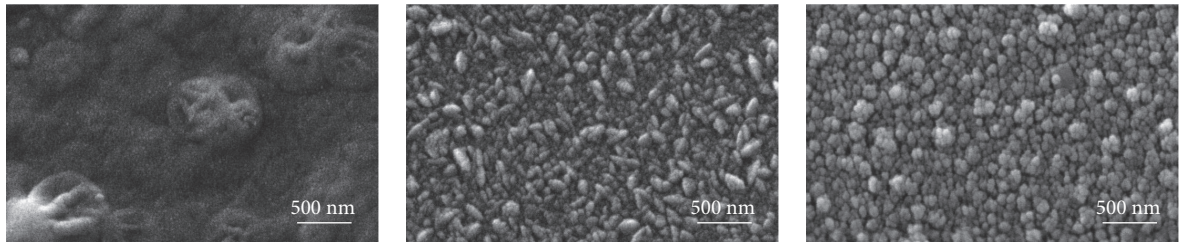
3. Results and Discussions

The comparison of films surface quality is presented in Figure 2, where optical microscope images of ZnO films deposited at different temperatures are shown. The improvement of surface quality and smoothing of the films with temperature are well seen. The rms roughness is 52 nm for the films deposited at 150°C and 22 nm for those deposited



(a) (b) (c)

Figure 2: Optical microscope images of the surface of ZnO thin films obtained by electrospray at 18 kV and substrate temperature of 150°C (a), 200°C (b), and 250°C (c). The bar is 15 μm.



(a) (b) (c)

Figure 3: SEM pictures of 200 nm thick ZnO thin film deposited at 18 keV and distance of 6 cm at substrate temperature of 150°C (a), 200°C (b), and 250°C (c).

at 200 and 250°C. Besides, the number and diameter of the prints of the droplets observed at low substrate temperature significantly decrease with temperature and almost completely disappear at 250°C. At low substrate temperature, the mobility of the species across the substrate's surface is restricted to some extent and it is possible for them to "freeze" immediately after landing, thus limiting the chance to get together with other droplets and to produce a continuous film. With increasing the temperature, the mobility of the droplets across the substrate enhances significantly, enabling in this way the formation of high-quality surface without the prints of the droplets.

Another possible reason for different surface state may be the uncomplete decomposition of zinc acetate at temperature of 150°C, leading to deterioration of films' optical quality. Using thermogravimetric analysis of Zn precursors, Jayaraman et al. [23] have shown that the decomposition of zinc acetate starts at around 150°C and completely finishes at 300°C. It should be noted that the results in [23] are obtained for solid powder samples, while in our case the zinc acetate is delivered at very small amounts and some difference in decomposition temperature is very likely to exist. Whatever the difference, we could expect the amount of zinc acetate in ZnO films to decrease with temperature.

Figures 3 and 4 illustrate the effect of substrate temperature on the surface morphology of electrosprayed ZnO films. It is seen that films deposited at 150°C differ significantly from the other two: they consist of circular formations with microns and submicron sizes and worm-like interior, while the films at higher substrate temperature consist of small grains with sizes in the range of 70–170 nm. With increasing the substrate temperature from 200°C to 250°C, the shape of the grains slightly changes from elongated to oval shape, which is seen from Figures 3 and 4. The approximate height of the surface grains can be determined from the surface profiles shown in Figure 4(d). For substrate temperature of 200 and 250°C, the heights are in the range of 20–50 nm, while for the films deposited at 150°C they are between 10 and 30 nm.

It is interesting to check how the crystalline status of the films changes with temperature of deposition. Figure 5 presents XRD spectra of the films deposited at 18 kV onto substrates heated at 150, 200, and 250°C. At all studied temperatures, the films are polycrystalline and exhibit hexagonal wurtzite structure [24]. XRD spectra of the films show three prominent peaks at 31.8°, 34.43°, and 36.3° and also few peaks with low intensities (not shown in the figure).

It is seen from Figure 5 that the preferred crystal growth varies with the substrate temperature: at 150°C it is in (002) plane, while for higher temperature it is in (100) plane. The crystallite size (D) has been calculated from the peak with (100) orientation using Debye-Scherrer's formula [24]:

$$D = \frac{0.9\lambda}{\Delta\Theta\cos(\theta)}, \quad (1)$$

where θ is the Bragg diffraction angle, $\Delta\Theta$ is the full width at a half maximum in radians, and λ (= 0.15406 nm) is the wavelength of incident X-ray radiation. It was found that the crystallites sizes decrease with temperature from 27.4 nm for 150°C to 23.4 nm and 21.5 nm when the substrate is heated at 200 and 250°C, respectively.

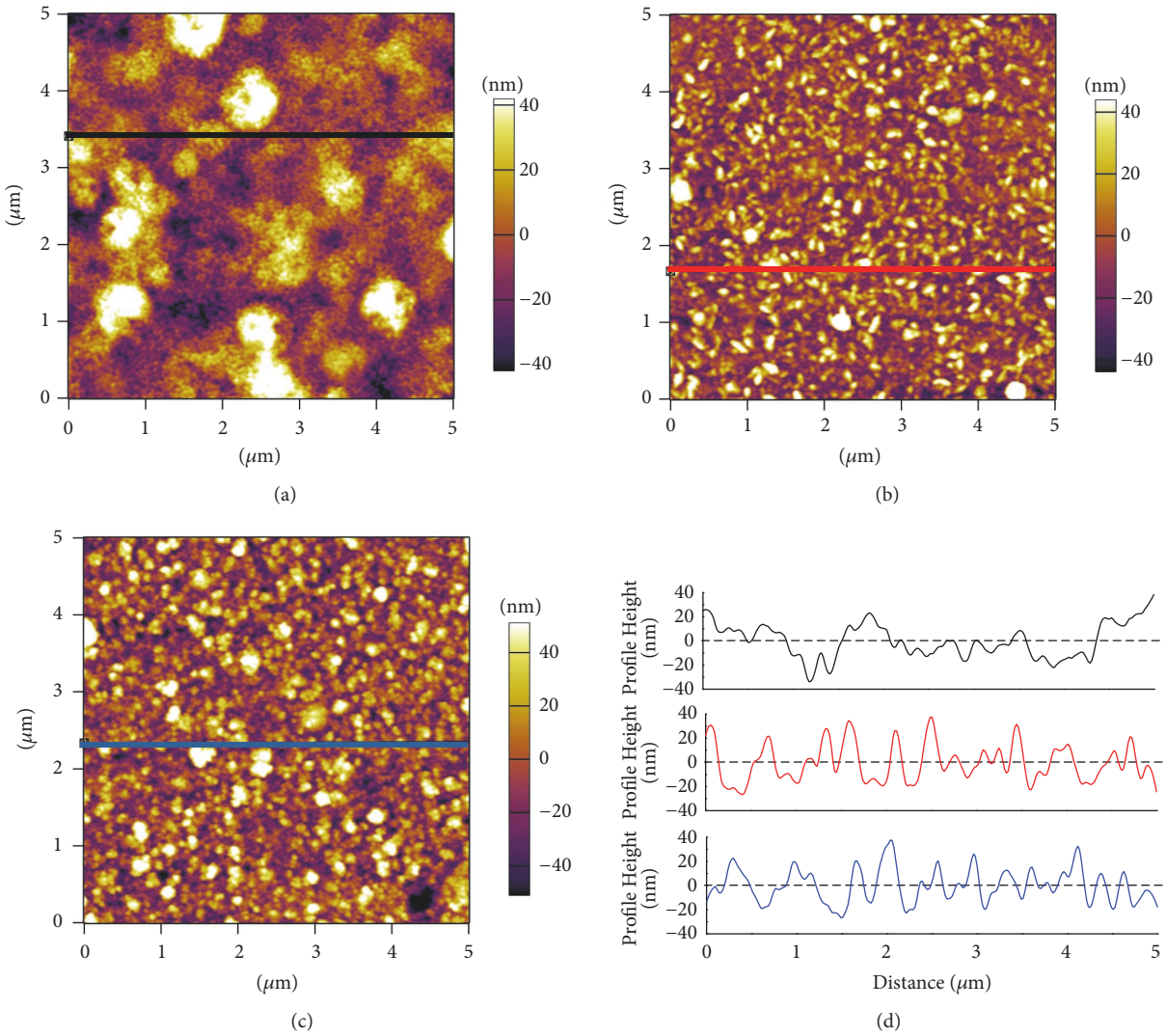


FIGURE 4: AFM pictures of ZnO films with thicknesses of 200 nm deposited at substrate temperatures of 150°C (a), 200°C (b), and 250°C (c) along with the surface profiles taken at denoted lines.

The analysis of surface composition as a function of substrate temperature was performed by X-ray photoelectron spectroscopy (XPS). Figure 6 presents Zn 2p and O1s XPS spectra of ZnO films deposited at substrate temperatures of 150, 200, and 250°C. The XPS peak positions of Zn 2p3/2 and 2p1/2 are located at 1021.4 eV and 1044.4 eV, respectively, and there is no change in the binding energy with temperature.

The O1s peaks as a function of substrate temperature are shown in Figure 6(b). For all temperatures, the peaks are wide and asymmetrical and could be deconvoluted to two peaks using Gaussian peak function. The two peaks are located at 529.9 eV and 531.2 eV. The O1 peak located at lower binding energy indicates the amount of oxygen atoms in a fully oxidized, stoichiometric environment. It can be attributed to O^{2-} ions in the wurtzite structure of the hexagonal Zn^{2+} ion array, which are surrounded by zinc atoms that are fully complemented by the nearest-neighbour O^{2-} ions [25]. Therefore, the peak at binding energy of 529.9 eV can be attributed to Zn–O bonds. The O1 peak located at higher binding energy is ascribed to oxygen bonded in OH^{-} and CO_x groups or interstitial oxygen [26, 27]. The relative area of the lower energy O1 peak varies from 44% at 150°C to 48% at 200°C and to 31% at 250°C. Considering the fact that the higher the integrated intensity, the higher is the amount of oxygen that is bonded to Zn atoms, we could conclude that, at a substrate temperature of 200°C, the deposited ZnO films are closest to the stoichiometric ones. The atomic percentage ratios of O to Zn are 0.97, 1.06, and 1.01 for the films deposited at substrate temperatures of 150, 200, and 250°C, respectively.

The next step of our investigation concerns the influence of substrate temperature on the optical properties of ZnO films. Refractive index (n) and extinction coefficient (k) (the so-called optical constants) along with film thickness (d) of ZnO thin films were determined through ellipsometric measurements and consequent modelling using DeltaPsi2 commercial software (HORIBA Jobin Yvon). The measured

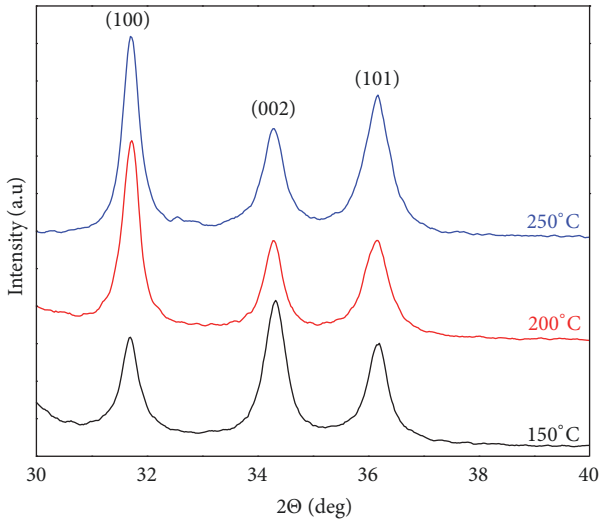


FIGURE 5: XRD pattern of 200 nm thick ZnO thin film deposited at 18 keV and distance of 6 cm at denoted substrate temperatures.

parameters are the ellipsometric angles Ψ and Δ that are defined as

$$\tan(\Psi) = \frac{|r_p|}{|r_s|}, \quad 0^\circ \le \Psi \le 90^\circ$$
$$\Delta = \delta_p - \delta_s, \quad 0^\circ \le \Delta \le 360^\circ, \tag{2}$$

where r_p and r_s and δ_p and δ_s are the amplitude and phases of reflection coefficient for p- and s-polarized light, respectively. To extract the parameters of interest (n, k, and d), a physical model of the studied film has to be set up, which allows a theoretical calculation of Ψ and Δ. The unknown parameters are derived by nonlinear minimization of the difference between the measured and calculated ellipsometric functions. In our studies, we use three-layered model that comprises thin (3 nm) native oxide on the silicon substrate, ZnO film, and top layer consisting of 50% voids. The unknown parameters are the thicknesses of the film and the top layer, as well as all parameters in the dispersion model describing the optical constants. For modelling n and k as a function of wavelength, we use Forouhi-Bloomer dispersion equations described in detail elsewhere [28].

The calculated dispersion curves of n and k as a function of the substrate temperature are shown in Figure 7. For wavelength higher than 400 nm, the films deposited at 200 and 250°C are transparent ($k = 0$), while films at lower substrate temperature have some absorption. At higher energies, the absorption of the film substantially increases and is more pronounced for films deposited at higher temperatures. Refractive indexes for films at 200°C and 250°C are almost the same: n at 600 nm is 1.97 and 1.93, respectively (Table 1). The small difference may be due to a slightly different stoichiometry, revealed by XPS measurements. It is seen form Figure 7 that the refractive index of ZnO films deposited at 150°C is significantly lower as compared to other samples: n at 600 nm is 1.67. This confirms the presence of organic residues

TABLE 1: Refractive index (n) and extinction coefficient (k) at wavelength of 600 nm, optical band gap energy ($E_{g,dir}$) in eV, and Urbach energy (E_U) in meV.

T_{sub} (deg)	n at 600 nm	k at 600 nm	$E_{g,dir}$ (eV)	E_U (meV)
150	1.67	0.045	3.27	221
200	1.97	0	3.32	35
250	1.93	0	3.31	69

that are not completely removed from the film due to the lower temperature that is insufficient for their decomposition. Further, the optical band gap for allowed direct transitions ($E_{g,dir}$) is calculated using the so-called Tauc's plot, where $(\alpha E)^2$ is plotted versus E and from the linear part of the curve, $E_{g,dir}$ is calculated at $(\alpha E)^2 = 0$ [29] (α is the absorption coefficient in cm^{-1} calculated from extinction coefficient using relation $\alpha = 4\pi k/\lambda$ and E is the light energy in eV).

It is seen from Table 1 that the optical bang gaps of the three films are almost the same, although a slight decrease in $E_{g,dir}$ is observed for the film deposited at the lowest temperature. Further, the Urbach energy, which is a measure of the structural disorder, is calculated from the spectral region, where α obeys an exponential decay, using the linear fit of the plot $\ln(\alpha)$ versus E. The structural disorder is the highest at 150°C and improves with temperature. The Urbach energy is the smallest for the film deposited at 200°C.

In the present study, the thickness of the films is 200 nm. Our additional experiments on films with different thicknesses show that the surface morphology is slightly influenced by the film thickness. Besides, films have similar optical constants. This gives us the confidence that the drawn conclusions are generally valid.

4. Conclusions

The preparation of polycrystalline ZnO thin films with tunable properties and chemical composition using electrospray method with vertical setup is demonstrated. Instead of the generally implemented postdeposition annealing for formation of ZnO, heating of substrate to moderate temperature (200°C) during deposition is applied in order for high-performance ZnO to be obtained. Thus deposition of ZnO thin films on thermosensitive substrates will be enabled, benefiting in this way the application of ZnO thin films in electronics. An improvement of surface quality and smoothing of the films with temperature are obtained. At substrate temperature of 150°C, rms roughness is 52 nm and it decreases to 22 nm when the temperature rises to 200°C and 250°C. Interestingly, even at 150°C, films are polycrystalline with crystallites sizes slightly decreasing with temperature: from 27 nm to 21 nm. It is revealed that the preferred crystal growth depends on temperature: it is in (002) plane at 150°C and in (100) plane for higher temperatures. The XPS analysis shows that the films deposited at 150°C are oxygen-deficient, while at other studied temperatures, the films have excess of oxygen more pronouncedly at 200°C: the atomic percentage ratios of O to Zn are 0.97, 1.06, and 1.01 for the

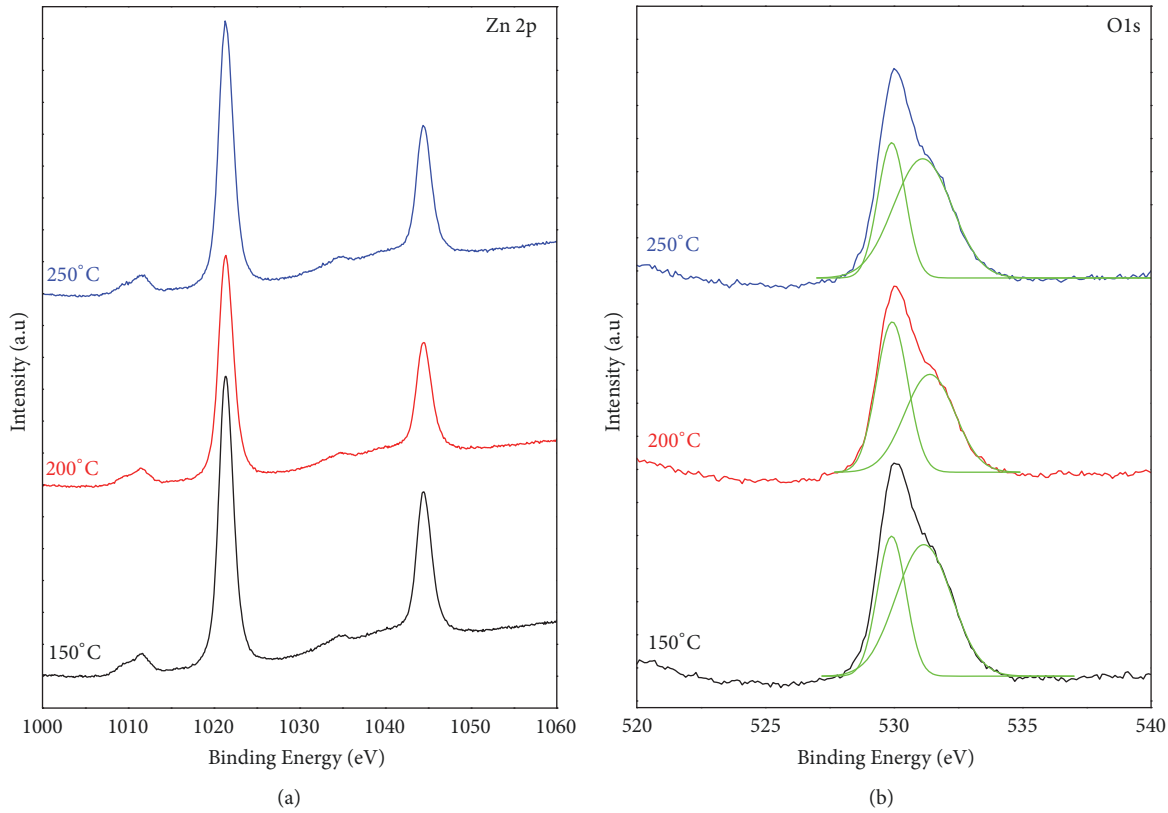


Figure 6: XPS spectra of Zn 2p (a) and O1s (b) peaks for 200 nm thick ZnO thin films deposited at 18 keV and distance of 6 cm at denoted substrate temperatures.

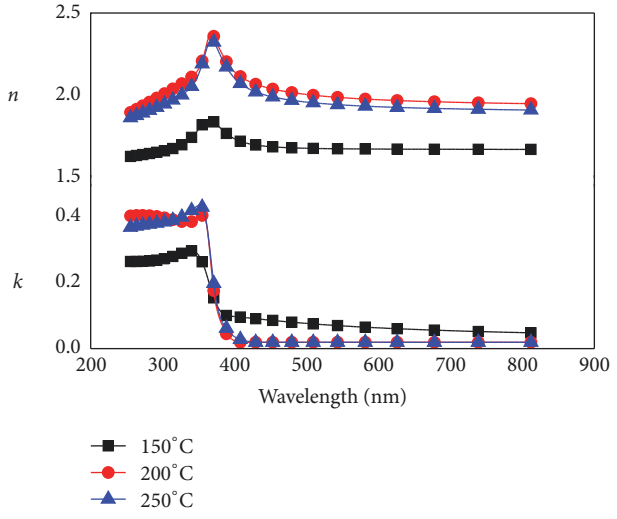


Figure 7: Dispersion curves of refractive index (n) and extinction coefficient (k) of ZnO thin films with thickness of 200 nm deposited at different substrate temperature denoted on the figure.

films deposited at substrate temperatures of 150°C, 200°C, and 250°C, respectively. Although the O/Zn ratio is approximately 1 for films at 250°C, the amount of oxygen that is bonded to Zn atoms is the highest at a substrate temperature of 200°C; that is, the last are closest to the stoichiometric ones, while the others have structural defects. The possible reason could be the presence of some strains in the crystal grating which increase with temperature. The values of Urbach energies for the films, calculated from ellipsometric measurements, vary from 221 meV through 35 meV to 69 meV for substrate temperature of 150°C, 200°C, and 250°C, respectively, thus indicating that the structural disorder is the smallest at 200°C. Refractive indexes for films at 200°C and 250°C are almost the same, 1.97 and 1.93, respectively, at wavelength of 600 nm, while for the sample deposited at 150°C, refractive index is substantially lower, 1.67, thus confirming the presence of some organic residues. The optical band gap is slightly influenced by the substrate temperature: 3.27 eV at 150°C and 3.32 eV at 200°C and 250°C.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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