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Effect of Annealing Temperature on the Physical Properties of the ZnO Thin Films Deposited by Ultrasonic Spray Pyrolysis

Sema KURTARAN*, Serhat ALDAĞ, Göksu ÖFÖFOĞLU

Eskişehir Osmangazi Üniversitesi, Fen-Edebiyat Fakültesi, Fizik Bölümü, Eskişehir

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Abstract: In this work optical, electrical, structural and surface properties of polycrystalline ZnO thin films grown from aqueous solutions (with pH = 5) have been reported. The films have been deposited on glass substrates by ultrasonic spray pyrolysis technique at a substrate temperature of 350 ± 5 °C. Zinc acetate dissolved in deionized water has been used as starting solution. The ZnO thin films have been annealed in air at 450 and 500 °C to improve their physical characteristics. X-ray diffraction reveals that the films are polycrystalline in nature having zincite type crystal structure. Electrical resistivity values of the films have been increased after annealing process. Films are highly transparent in the visible region. The dependence of refractive index, *n*, and extinction coefficient, *k*, on the wavelength for ZnO films has been also reported. Optical band gap values have been determined using optical method. Finally, it has been concluded that annealing temperature has an important effect on the optical, structural, surface and electrical properties of the deposited films.

Ultrasonik Kimyasal Püskürtme Yöntemiyle Elde Edilen ZnO İnce Filmlerinin Fiziksel Özellikleri Üzerine Tavlama Sıcaklığının Etkisi

Anahtar Kelimeler
İnce film
Tavlama
ZnO
X-ışını kırınımı
Yüzey özellikleri

Özet: Bu çalışmada, sulu çözeltilerden (pH = 5) elde edilen ZnO filmlerinin optik, elektriksel, yapısal ve yüzeysel özellikleri rapor edilmiştir. Filmler cam tabanlar üzerine 350 ± 5 °C taban sıcaklığında Ultrasonik Kimyasal Püskürtme tekniği ile çöktürülmüştür. Deiyonize su içerisinde çözünen Çinko asetat başlangıç püskürtme çözeltisi olarak kullanılmıştır. ZnO filmleri fiziksel özelliklerini iyileştirmek amacıyla 450 ve 500 °C sıcaklıklarda hava ortamında tavlama işlemine tabi tutulmuştur. X-ışını kırınımı analizleri, filmlerin polikristal formda ve zincite tipi kristal yapıya sahip olduğunu ortaya koymaktadır. Elektriksel özdirenç değerlerinin tavlama işlemi sonrasında arttığı belirlenmiştir. Filmler görünür bölgede yüksek geçirgenliğe sahiptirler. Ayrıca, filmler için kırılma indisi, *n*, ve sönüm katsayısının, *k*, dalgaboyuna bağlı değişimleri de rapor edilmiştir. Filmlerin optik bant aralığı değerleri optik metot yardımı ile belirlenmiştir. Sonuç olarak, tavlama sıcaklığının elde edilen filmlerin optik, yapısal, elektriksel ve yüzeysel özellikleri üzerinde önemli bir etkisi olduğu sonucuna varılmıştır.

1. Introduction

In the field of materials science, zinc oxide (ZnO) holds a very important position because of its transparency in the visible range with wide band gap [1]. The ZnO absorbs UV radiation due to band-to-band transitions, while it can be used as transparent conductive oxide (TCO) thin films, mainly for applications such as solar cells, liquid crystal displays and heat mirrors [2-5]. From all the oxide materials studied, in the last years, the ZnO has emerged as one of the most promising materials, due to its optical and electrical properties, high chemical and mechanical stability, together with its abundance in nature,

* *İlgili yazar: skurtaran@ogu.edu.tr*

which makes it a lower cost material when compared to the most currently used transparent conductive oxide materials. ZnO thin films have been prepared using various methods such as molecular beam epitaxy (MBE) [6], chemical vapor deposition [7], electrochemical deposition [8], pulsed laser deposition (PLD) [9], sol-gel process [10], reactive evaporation [11], magnetron sputtering [12] and spray pyrolysis [13-16]. Spray pyrolysis technique is preferred among these techniques because it is cheaper, simpler and more versatile than the others, which allow the possibility of obtaining films with the required properties for different applications and also when large area deposition of the films are needed. In this work optical, electrical, structural and surface properties of the ZnO thin films grown by Ultrasonic Spray Pyrolysis (USP) technique are reported.

2. Material and Method

The ZnO thin films have been produced using an improved ultrasonic spray system. Details of the USP system is given in other report [15]. The aqueous solution of 0.1 M $Zn(CH_3CO_2)_2 \cdot 2H_2O$ has been used as spray solution. A small quantity of acetic acid has been added into the solution to ensure the pH value of 5. Spraying solution has been mixed with a magnetic mixer to prevent sedimentation. The prepared solution has been sprayed through an ultrasonic nozzle onto the glass substrates using air as carrier gas with a pressure of 1 bar. The total volume of 150 ml solution have been used and sprayed onto the substrates during 30 mins. The solution flow rate has been kept constant at 5 mlmin^{-1} and controlled by a flowmeter. The distance between the nozzle and the substrate has been maintained at 35 cm. The substrate temperature of 350 ± 5 °C has been controlled by a temperature controller. Deposited ZnO films have been annealed at two temperatures as 450 °C and 500 °C for 150 min in air. The films are labelled as Z0 (as-deposited), Z1 (annealed at 450 °C) and Z2 (annealed at 500 °C). The optical transmittance spectra of the samples have been taken by Schimadzu UV-2550 Spectrophotometer in the wavelength range of 380–900 nm at room temperature. OPT-S9000 Spectroscopic Ellipsometer has been used to determine the optical constants (refractive index and extinction coefficient) of the samples. Surface morphologies of the samples have been investigated by Park Systems XE 100 Atomic force microscope. Electrical resistivity values have been determined by a Keithley 2601 Lucas Labs. Pro 4 Four-probe system.

3. Results

3.1. Structural properties

XRD patterns of the ZnO thin films prepared by USP technique are shown in Figure 1. The presence of various diffraction peaks with different intensities indicates that the films are polycrystalline, and no amorphous phase has been detected. For all samples, suitable with other reports [2,17-21], peaks corresponding to (100), (002), (101), (102), (103) and (112) planes of the zincite ZnO crystal structure have been determined. Structural data for the ZnO films is given in Table 1. Also, XRD measurements reveal that all of the sprayed films show a preferential orientation along (002) plane, which is perpendicular to the substrate. For sample Z1, it is clear that intensity of (002) peak has been increased and full width half maximum (FWHM) value of this peak has been decreased. This shows that annealing at 450 °C caused ZnO films to have a better crystal structure. Increasing FWHM value for sample Z2 is an indication of deteriorated structure. To obtain more information about the structural properties in detail, some structural parameters such as the grain size (D), dislocation density(δ) and macrostrain <e> for (002) orientation have been calculated for all of the films using the formulas given below [22-24]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\langle e \rangle = \frac{d - d_0}{d_0} \quad (3)$$

where β is the half width of the peak with maximum intensity in radians (FWHM), D is the grain size, θ is the Bragg is angle, λ is the wavelength of light used, d is the interplanar spacing and d_0 is the interplanar spacing without deformation. The preferential orientation can be determined by using the texture coefficient $TC_{(hkl)}$ expression [25]:

$$TC_{(hkl)} = \frac{I_{(hkl)}}{I_{0(hkl)}} \left[\frac{1}{N} \sum_{i=1}^{N} \frac{I_{(hkl)}}{I_{0(hkl)}} \right]^{-1} \quad (4)$$

where I is the measured intensity, I_0 is the standard intensity (ASTM, American Society of Testing Materials) and N is the number of peaks in the pattern. Some structural parameters for the ZnO thin films are given in Table 2.

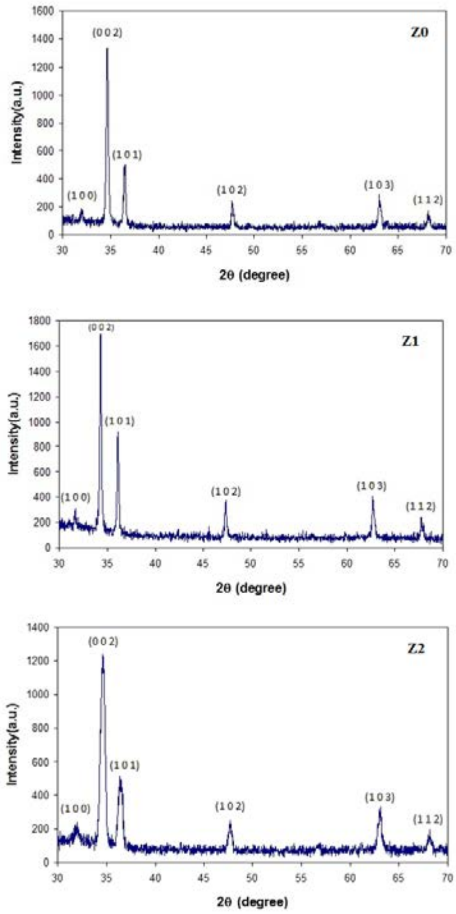

Figure 1. XRD patterns of the ZnO thin films.

Table 1. Structural data for the ZnO thin films. Diffraction angle (2θ), interplanar spacing (d), intensity ratio (I/I_0), Miller indices (hkl) and crystal systems.

Material	2θ (°)	d (Å)	I/I_0	(hkl)	Crystal system
Z0	32.04	2.792	7.9	(100)	Zincite
	34.64	2.587	100	(002)	Zincite
	36.46	2.462	35.8	(101)	Zincite
	47.74	1.904	16.7	(102)	Zincite
	56.84	1.619	4.1	(110)	Zincite
	63.02	1.474	20.8	(103)	Zincite
	68.12	1.375	10.2	(112)	Zincite
Z1	31.70	2.820	8.0	(100)	Zincite
	34.28	2.614	100	(002)	Zincite
	36.08	2.487	53.7	(101)	Zincite
	47.40	1.916	20.2	(102)	Zincite
	62.68	1.481	25.5	(103)	Zincite
	67.80	1.381	13.1	(112)	Zincite
Z2	31.88	2.805	8.5	(100)	Zincite
	34.60	2.590	100	(002)	Zincite
	36.42	2.495	37.4	(101)	Zincite
	47.70	1.905	14.9	(102)	Zincite
	56.72	1.622	4.8	(110)	Zincite
	62.98	1.475	22.5	(103)	Zincite
	68.08	1.376	9.2	(112)	Zincite

Table 2. Some structural parameters for the ZnO thin films. Texture coefficient (TC), FWHM (β), grain size (D), dislocation density (δ) and macrostrain ($<e>$).

Material	Z0	Z1	Z2
TC	2.93	2.58	2.98
β×10^{-3} (rad)	4.62	3.98	9.08
D(nm)	31	36	16
δ(line/nm^2)x10^{-3}	1.04	0.77	3.91
$<e>$×10^{-3}	-1.35	2.86	-2.19

3.2. Electrical properties

The electrical resistivity values of the ZnO thin films have been determined using a four-probe set-up. It has been seen that annealing caused a dramatic increase in the resistivity values of ZnO films. The resistivity values of the Z0, Z1 and Z2 films have been determined as 3.47×10^1 Ωcm, 8.16×10^4 Ωcm and 7.65×10^5 Ω cm, respectively. The minimum resistivity value (3.47×10^1 Ωcm) is obtained for the as-deposited Z0 film. Despite the improved crystal structure of sample Z1, it has a higher resistivity value than sample Z0. We think that annealing in air atmosphere caused some oxygen atoms to join structure creating an acceptor effect. This will cause a decrease in the carrier concentration and increase the resistivity values.

3.3. Spectroscopic ellipsometry and optical constants

Spectroscopic Ellipsometer (SE) has been used to determine the refractive indices (n), extinction coefficient (k) and thicknesses (d) of the films. Cauchy-Urbach dispersion model has been used to fit the experimental data. In this dispersion model, the refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ as a function of the wavelength are given by;

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \qquad (5)$$

$$k(\lambda) = A_k\, e^{B_k(E-E_b)} \tag{6}$$

where A_n, B_n, C_n, A_k and B_k are Cauchy-Urbach parameters[26]. For the samples having depolarization effect, the incident angle should be appropriately determined. So, different incident angles were tried in order to take the measurements. The optimum angle was determined to be 70˚ using experimental delta spectra. Delta spectra of the ZnO thin films are shown in Figure 2. A good fit has been found between the experimental and theoretical data. However, there are some deviations for the data. This is probably due to the depolarizing effect of roughness, grain boundaries and morphologies of the films which affect the experimental data. Also, backside reflection of glass substrates may also cause deviations on fitted values. Data has been fitted according to Cauchy-Urbach model, which works well for nearly transparent materials. Thicknesses and model parameters are given in Table 3.

Refractive index (n) spectra of the films are shown in Figure 3. Extinction coefficient (k) spectra of the films are shown in Figure 4. Annealing in air atmosphere caused ZnO films to have higher refractive index values. This is probably a result of better packing of particles which in turn affects the density of the structure after annealing. Figure 4 show that all samples have small extinction coefficient values. This is an expected result as our films have high transmittance.

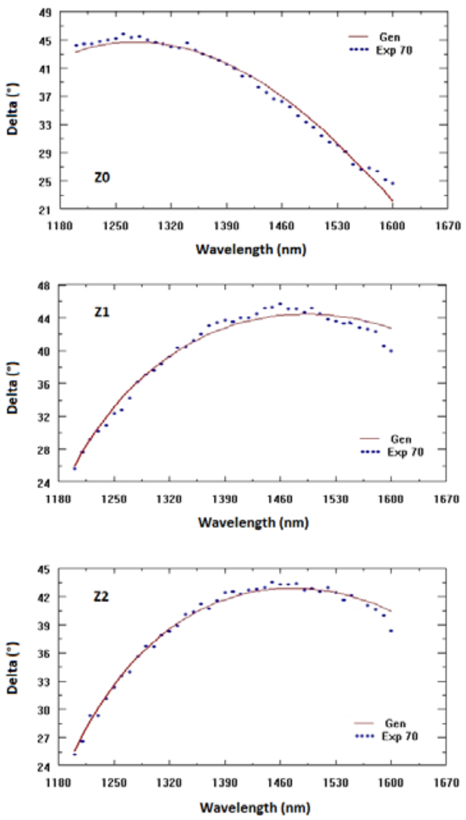

Figure 2. Delta spectra of the ZnO thin films.

Table 3. Thickness (t) and model parameters of the ZnO thin films.

Material	Z0	Z1	Z2
t(nm)	256	297	299
A_n	1.84	1.89	1.87
B_n (nm)^2	0.12	0.07	0.08
C_n (nm)^4	0.13	0.17	0.07
A_k	0.7	0.89	0.86
B_k (eV)$^{-1}$	1.23	1.51	1.52
MSE	0.75	0.84	0.31

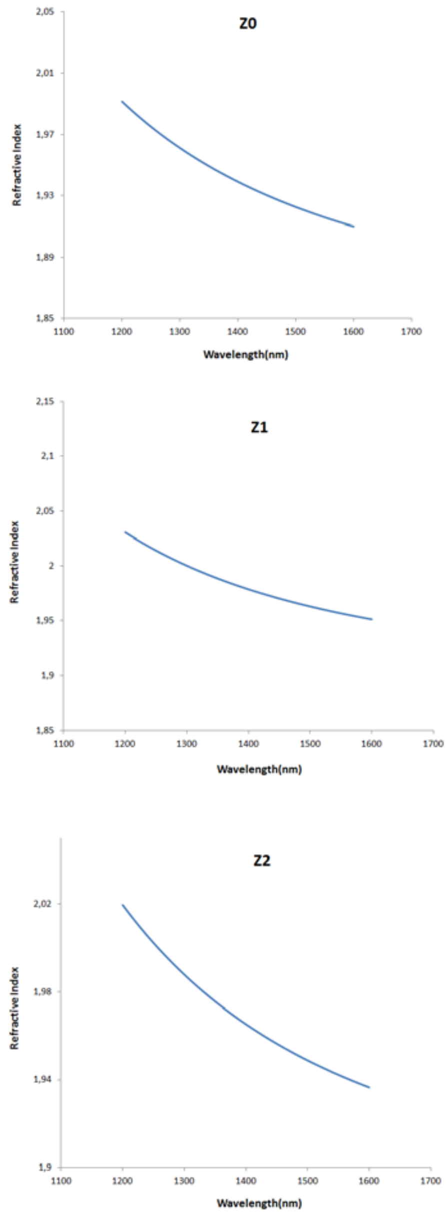

Figure 3. Refractive index (n) spectra of the ZnO films.

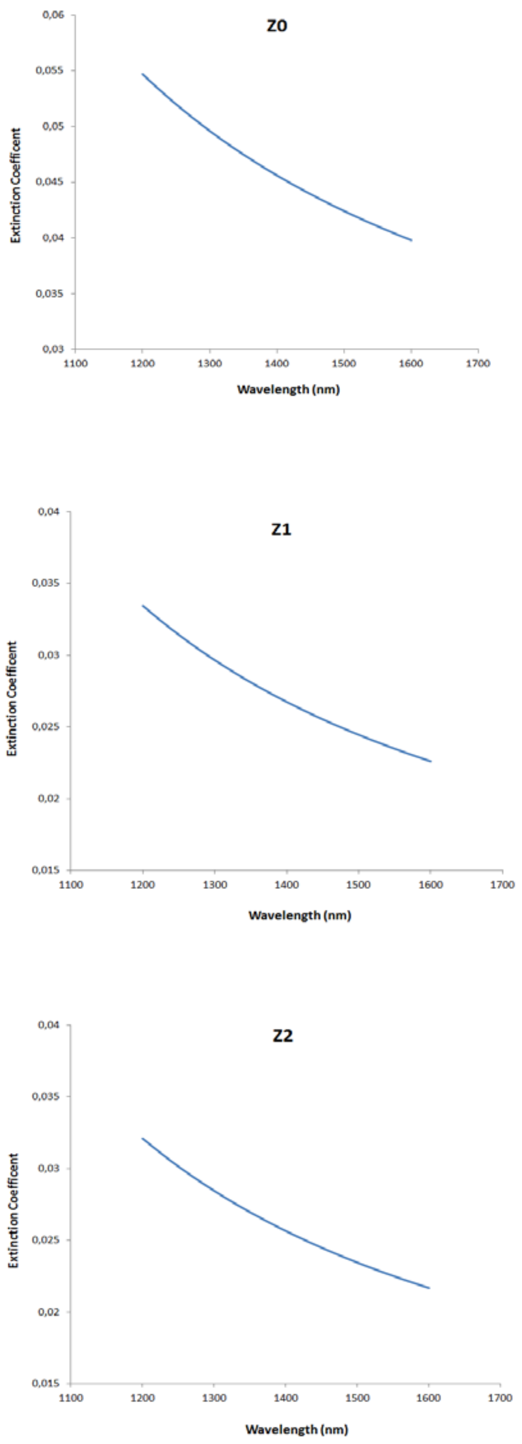

Figure 4. Extinction coefficient (k) spectra of the ZnO films.

3.4. Optical properties

The transmittance spectra of the ZnO thin films are shown in Figure 5. All films behaved as opaque materials because of their high absorbing properties at short wavelengths and as transparent materials at long wavelengths. At about 370 - 390 nm wavelength range, the transmittance values increased remarkably as the wavelength increased and this range refers to the fundamental absorption region. Despite its higher thickness when compared to as-deposited sample (Z0), annealing in air, at 450 °C, caused sample Z1 to have higher transmittance value than sample Z0. This may be related to the decreasing roughness and smooth surface morphology of this sample obtained after annealing.

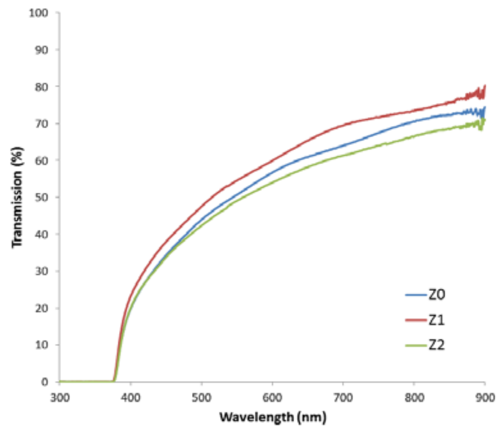

Figure 5. The transmittance spectra of the ZnO thin films.

The optical band gap values of the ZnO thin films have been determined using the optical method. In this method, the band gap values are obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ to $(\alpha h\nu)^2 = 0$. The plots are given in Figure 6. It has been determined that all films have direct band gaps. The optical band gap values of Z0, Z1 and Z2 films have been calculated as 3.20 eV, 3.20 eV and 3.19 eV, respectively.

3.5. Surface properties

Three-dimensional AFM images of the films are shown in Figure 7. AFM images show that sample Z0 consists of particles with different size collapsed to form agglomerates. After annealing at 450 °C, the surface of the sample Z1 has been taken a shape including homogeneous particles which are distinguishable. For sample Z2, which is annealed at 500°C, surface consisted of smaller particles with respect to other samples. However, the particles have different dimensions which are distributed randomly on the surface. Roughness values of Z0, Z1 and Z2 films have been determined as 54 nm, 36 nm and 57 nm, respectively. As a result, sample Z1 takes attention as having the most homogeneous morphology and lowest roughness value.

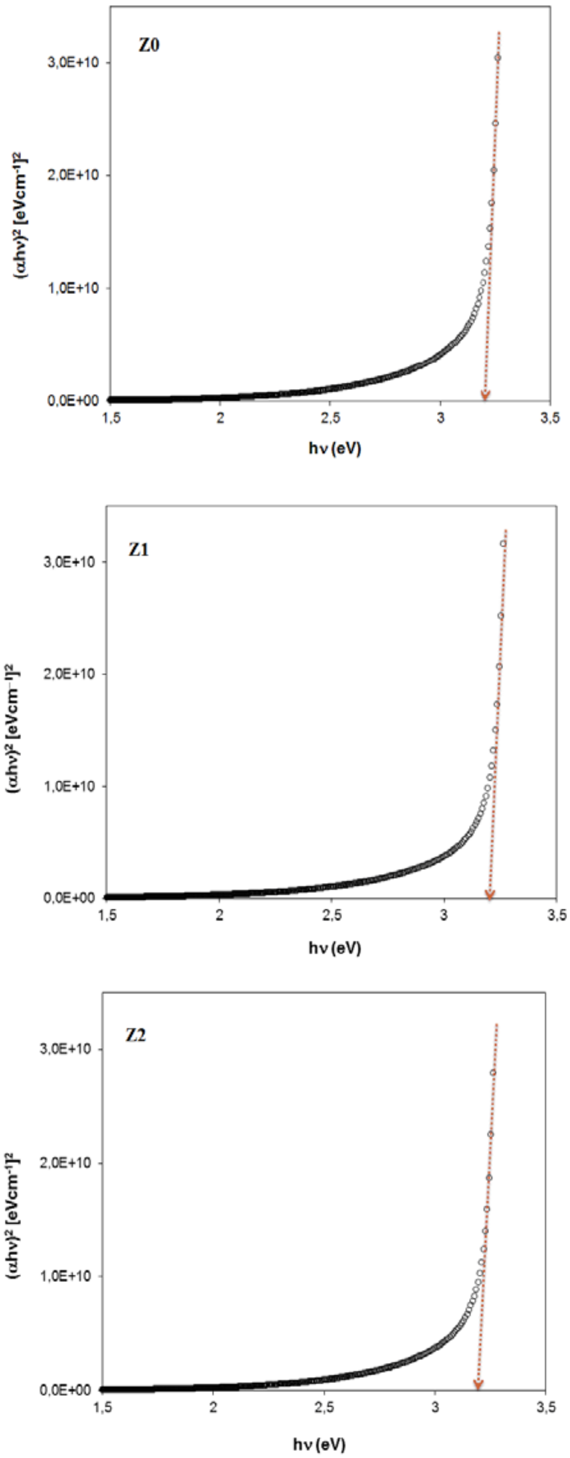

Figure 6. $(\alpha h\nu)^2 \sim (h\nu)$ plots of the ZnO thin films.

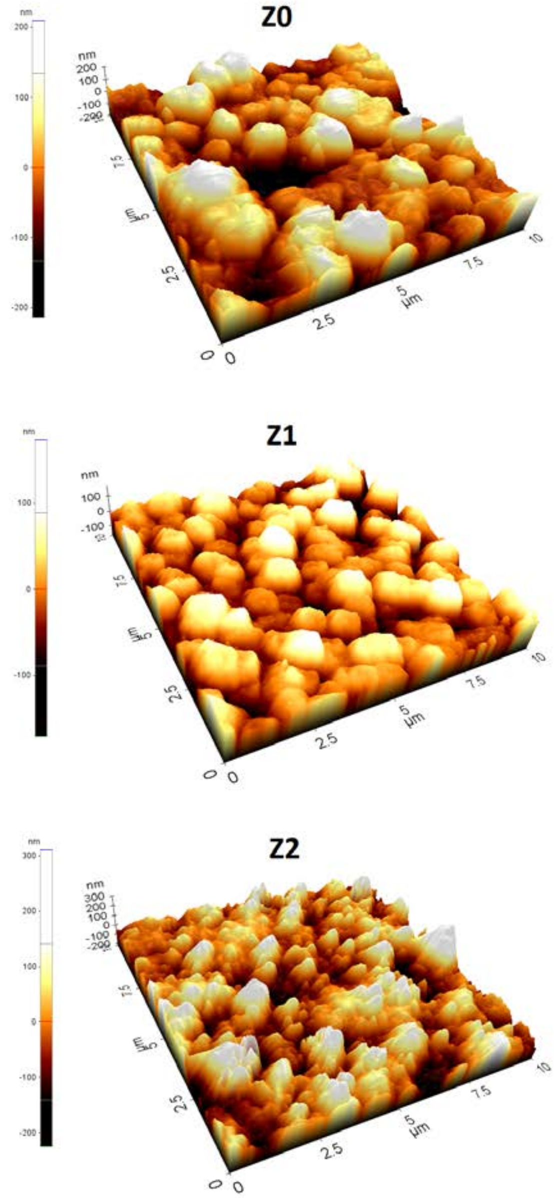

Figure 7. AFM images of the ZnO thin films.

4. Discussion and Conclusion

In this work, ZnO thin films have been obtained by a simple and economic technique, namely Ultrasonic Spray Pyrolysis. The effect of annealing temperature on the optical, structural, electrical and surface properties of the ZnO thin films has been investigated. Transmittance spectra of the films have been obtained by UV-VIS Spectrophotometer and optical method has been used to determine the band gap values. It has been seen that annealing does not caused an important change in optical band gap values. However, sample Z1 has the highest transmittance among others. There has been a dramatic change on the electrical resistively values of the films after annealing process. We think that this is probably related to the decrease of carrier concentration by oxygen adsorption, during annealing. Annealing also caused ZnO films to have high refractive index values which is a result of better packing of the particles. Sample Z1 has been determined to have the most homogeneous morphology and lowest roughness value. Generally, annealing at 450 °C resulted in better results. In our future works, we will try to perform this annealing for various durations.

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Symbols

µm	micrometer
ml	Milliliter
M	Molar
nm	nanometer
ºC	centigrade degrees
%	Percent