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ANNEALING EFFECT ON STRUCTURAL AND OPTICAL PROPERTIES OF ZnO FILMS PREPARED BY ULTRASONIC SPRAY PYROLYSIS

Seniye KARAKAYA*

Physics Department, Science&Art Faculty, Eskişehir Osmangazi University, Eskisehir,Turkey

ABSTRACT

Zinc Oxide (ZnO) thin films were deposited on glass substrates via the ultrasonic spray pyrolysis technique. The films were subsequently annealed in ambient air from 350°C to 550°C for 3h. The morphology and structural properties of the thin films were studied by atomic force microscopy (AFM) and X-ray diffractometry (XRD) techniques. The X-ray diffraction studies revealed that the films are polycrystalline with the hexagonal structure and a preferred orientation along (002) directions. The optical properties of the films were characterized by UV-vis spectroscopy. The transmission values of the annealed ZnO films were average 80% within the visible range (400–700 nm). The optical band gap values of the films are between 3.27 and 3.23 eV. Electrical resistivity of the films was measured using four-probe measurement system. The electrical resistivity of the films decreased with the increasing annealing temperature. According to our investigation results, it can be seen that annealing treatment plays an important role on the some physical properties of ZnO films.

Keywords: ZnO, Ultrasonic Spray Pyrolysis Technique, XRD, AFM

1. INTRODUCTION

Zinc oxide (ZnO) is an II–VI group compound semiconductor having high electrical conductivity and high optical transmittance (>80%) in the visible and infrared region [1-2]. It exhibits n-type conductivity and possesses wurtzite hexagonal structure as well as it is a low cost, nontoxic, high stable and abundance in nature.

ZnO thin films can be deposited by several techniques, such as molecular beam epitaxy (MBE) [3-4], chemical vapor deposition [5], electrochemical deposition [6], pulsed laser deposition (PLD) [7], sol–gel technique [8], magnetron sputtering technique [9] and spray pyrolysis [10]. Compared with other techniques, the spray pyrolysis technique is one of these techniques to prepare large-scale production for technological applications.

In this study, the effect of different annealing temperature conditions on the optical and structural properties of ZnO thin films were investigated. Annealing is an important method for enhancing the quality of films [11]. In general, the properties of the film changes with annealing at high temperatures and different atmospheres. Generally, crystallinity degree increases with thermal annealing [12]. Accordingly, in this study crystallinity of ZnO thin films increases with thermal annealing.

2. EXPERIMENTAL

The ZnO thin films have been produced using an ultrasonic spray system. The aqueous solution of 0.2 M $Zn(CH_3CO_2)_2 . 2H_2O$ has been used as spray solution. A small quantity of acetic acid has been added into the solution. 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 100 ml solution have been used and sprayed onto the substrates during 20 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

*Corresponding Author: seniyek@ogu.edu.tr

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 three temperatures as 350 °C, 450 °C and 550 °C for 3 hours in air. The optical transmittance spectra of the samples have been taken by Schimadzu UV-2550 Spectrophotometer in the wavelength range of 300–900 nm at room temperature. Surface morphologies of the samples have been investigated by Park Systems XE 100 Atomic force microscope. The images were obtained using Atomic Force Microscope by non-contact mode with scanning area of 2.5 μm x 2.5 μm. Electrical resistivity values have been determined by a Keithley 2601 Lucas Labs. Pro 4 Four-probe system.

3. RESULTS AND DISCUSSION

The XRD pattern (20°≤2θ≤80°) of ZnO film is given in Figure 1. All the films have typical hexagonal wurtzite structure and prefer to (002) orientation. After annealing the films, the intensity of the (0 0 2) peak increases. The average grain size (*D*) of the films was calculated using the full width at half maximum (FWHM) of (002) peak from the Scherer's equation [13]:

$$D = \frac{K\lambda}{\beta\ Cos\theta} \tag{1}$$

where K=0.9 is the shape factor, λ is the wavelength of incident X-ray, β is the FWHM measured in radians and θ is the diffraction angle. The dislocation density (δ) of the films is given by the Williamson and Smallman's relation:

$$\delta = 1\ /\ D^2 \tag{2}$$

The crystallinity degree of the films can be good because of their small δ values which represent the amount of defects in the film. The values of FWHM, grain size (D) and δ of the ZnO films calculated for (002) planes are given in Table 1. Also, the variation of grain size of as-grown and annealed ZnO films are presented in Figure 2. It is seen that with increase in annealing temperature grain size also increased. The obtained results of grain size are in good agreement with earlier reported work of Shivaraj et al. [14].The increase of the crystallinity degree and the crystallite size increase with annealing temperature can be explained by the atoms have enough energy to diffuse towards normal sites, the (0 0 2) direction for the hexagonal ZnO structure is the most favorable growth plan because it requires the lowest surface energy [11, 15, 16].

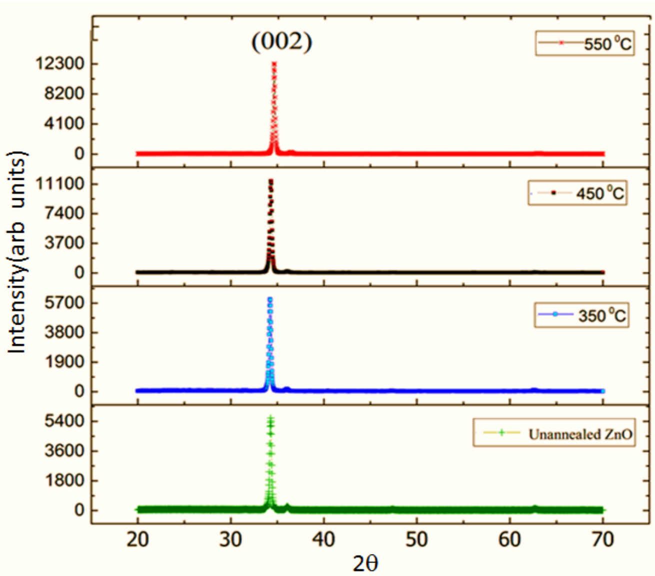

Figure 1. XRD patterns of ZnO thin films as-deposited and annealed at different annealing temperatures

Table 1. Some structural parameters for the ZnO thin films. FWHM (β), grain size (*D*), dislocation density (δ)

Film	$\beta x10^3$(rad)	D (nm)	δ x10^{-4} (line/nm^2)
Zn0 (Unannealed)	7,05	21	22,6
350 ^{0}C	4,38	32	9,76
450 ^{0}C	4,55	33	9,18
550 ^{0}C	4,73	35	8,16

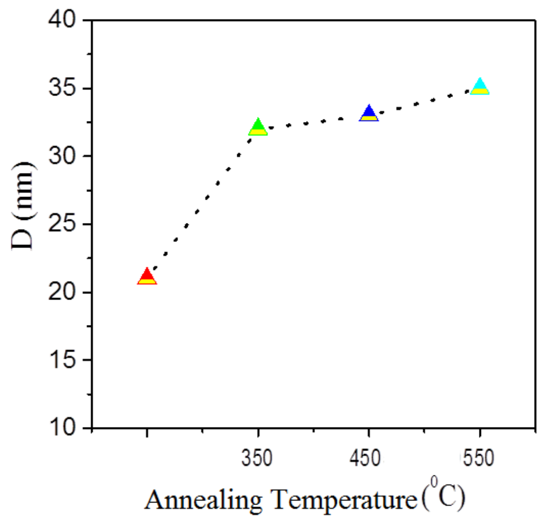

Figure 2. The variation in grain size of ZnO thin films as-deposited and annealed at different annealing temperatures.

The optical transmittance spectra of ZnO thin films (Figure 3) show that the transmittance is decreased with annealing. The optical absorption edge was determined by the optical absorption, a simple method that provides explanation for the features concerning the band structure of the film. The optical absorption edge was analyzed by the following relationship [17].

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \qquad (4)$$

where *A* is a constant which depends on refractive index of the material, $h\nu$ is the photon energy, E_g is the optical band gap and *n* is an exponent index determining the type of transition in the band gap. The value of n = 1/2 and 2 corresponds to the existence of direct and indirect band gap, respectively. The optical band gap is evaluated through the $(\alpha h\upsilon)^2$ vs (hν) relation by extrapolating the linear region of the curves on the energy axis ($(\alpha h\upsilon)^2=0$). Figure 4 shows the plots of $(\alpha h\nu)^2$ vs. (hν). The optical band gap is varied from 3.27 eV to 3.23 eV and found to decrease with annealing.

Figure 5 shows a three dimensional surface morphology image of the ZnO films prepared by USP. There are regions with different heights for each sample. ZnO films annealed at 350°C has a smoother surface texture when compared to others, showing a island-growth mechanism. For samples annealed at 450°C and 550°C a needle-like texture and layer-by layer mechanism is dominant. Also, rms (R_q) and average (R_a) roughness values of the films have been given in Table 2.

The electrical resistivity values of the ZnO thin films have been determined using a four-probe set-up. The resistivity of the films is found to decrease with annealing temperature (see Table 2). The electrical resistivity of pure ZnO films depends on the oxygen deficiencies or the presence of interstitial Zn in the ZnO lattice. The oxygen deficiencies or Zn interstitials in the ZnO lattice are increased with annealing temperature and may be attributed to the increase in free electrons [18,19].

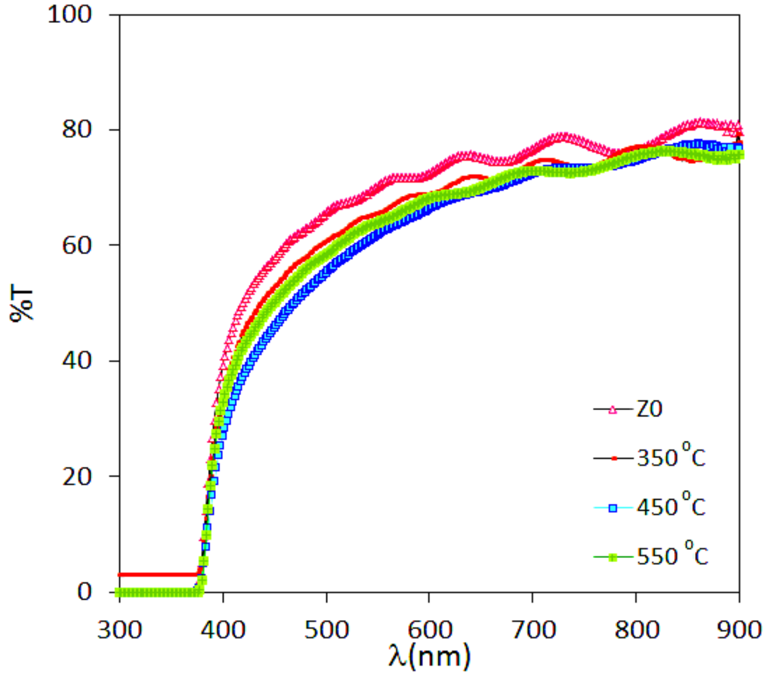

Figure 3. Optical transmission spectrum of ZnO thin films as-deposited and annealed at different annealing temperatures

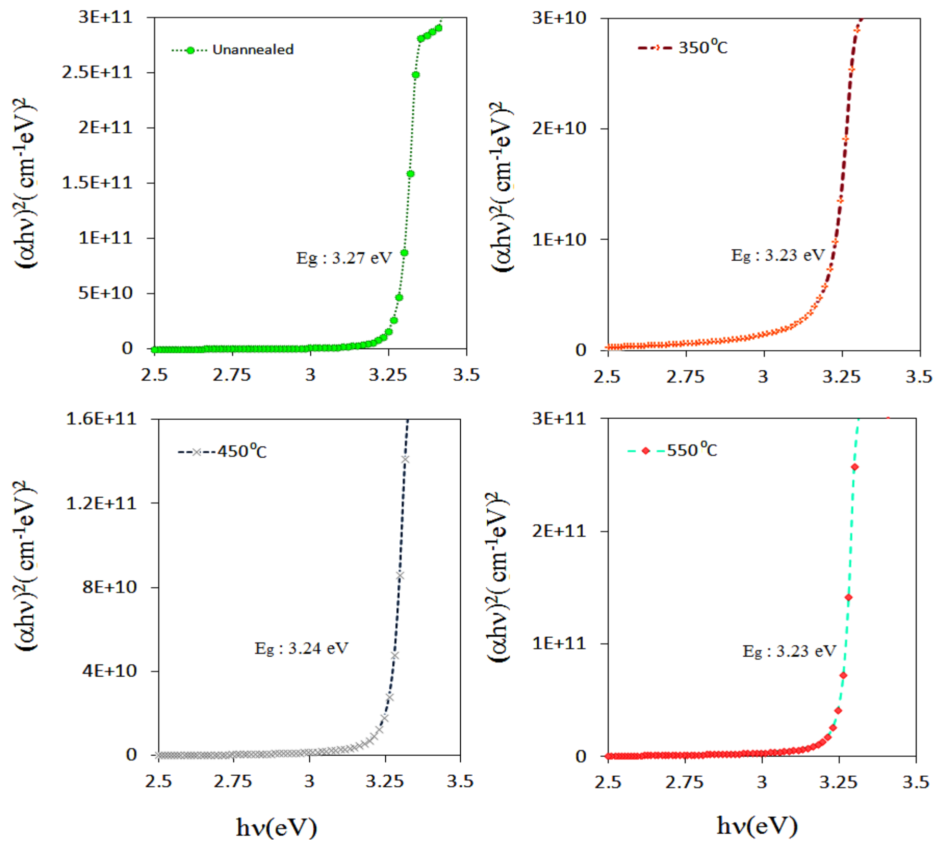

Figure 4. $(\alpha h\nu)^2$ v/s hν plot of ZnO films as-deposited and annealed at different annealing temperatures

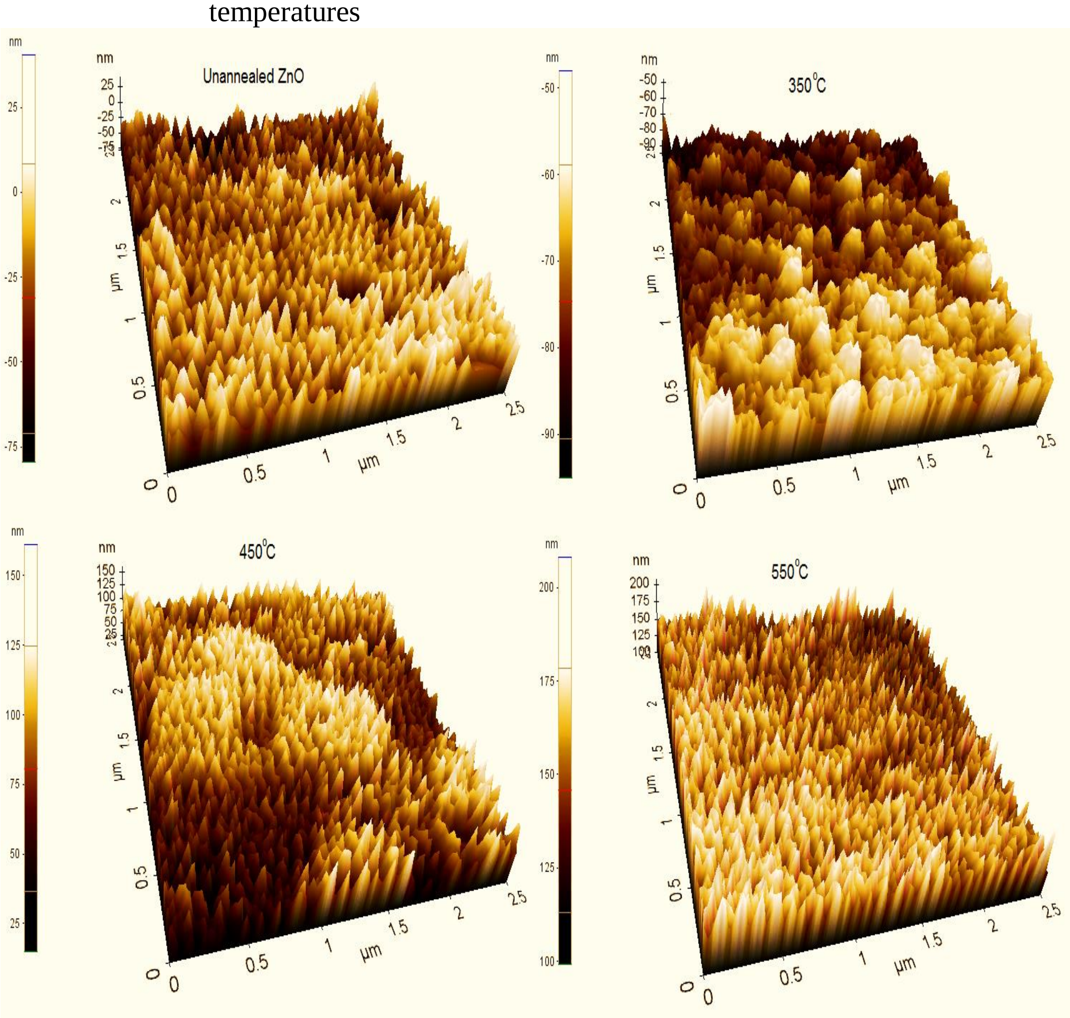

Figure 5. AFM images of ZnO films as-deposited and annealed at different annealing temperatures.

Table 2. Roughness and electrical resistivity values of ZnO films as-deposited and annealed at different annealing temperatures.

Film	R_q(nm)	R_a(nm)	ρ (Ω.cm)
Unannealed ZnO	12	9	8.64×10^{-1}
350°C	14	10	4.52×10^{-2}
450°C	19	15	2.35×10^{-2}
550°C	29	22	1.92×10^{-2}

4. CONCLUSION

ZnO films can be deposited by USP method on glass substrates. The structural and morphological properties of the ZnO films were influenced by annealing temperature. XRD pattern of ZnO films showed polycrystalline wurtzite with a preferential (0 0 2) orientation. It is observed that the grain size in the ZnO films increases along the (0 0 2) direction with the annealing temperature. As a result larger grain size was obtained which improves the crystal quality because of thermal energy in the grains and also fewer defects in grain boundaries. The lowest resistivity of 1.92×10^{-2} Ωcm was obtained at an annealing temperature of 550 °C. The results show that the resistivity decreases as the annealing temperature increases.

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