Vacuum 86 (2012) 871–875

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Effect of heat treatment on characteristics of nanocrystalline ZnO films by electron beam evaporation

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ARTICLE INFO

Article history:
Received 8 August 2010
Received in revised form
13 February 2011
Accepted 15 March 2011

Keywords:
ZnO films
X-ray diffraction
Annealing temperature
Optical transmission
SEM images

ABSTRACT

Zinc oxide thin films have been grown on glass substrate at room temperature by electron beam evaporation and then were annealed in annealing pressure 600 mbar at different temperatures ranging from 250 to 550 °C for 30 min. Electrical, optical and structural properties of thin films such as electrical resistivity, optical transmittance, band gap and grain size have been obtained as a function of annealing temperature. X-ray diffraction has shown that the maximum intensity peak corresponds to the (002) predominant orientation for ZnO films annealed at various temperatures. The full width at half maximum, decreases after annealing treatment which proves the crystal quality improvement. Scanning electron microscopy images show that the grain size becomes larger by increasing annealing temperature and this result agrees with the X-ray diffraction analysis.

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1. Introduction

Transparent conductive oxide (TCO) films are used in variety of applications because of their special physical properties such as large band gaps, typically larger than 3 eV, and consequently high optical transparency in visible spectral region. Also these films have low resistivities ($\rho < 10^{-4}$ Ω cm) [1]. Among them, Zinc oxide has been paid attention because it has a direct wide band gap, a large optical absorption coefficient, a very large exciton binding energy (60 meV), high chemical and thermal stability, good piezoelectric properties and lower cost than another TCO films [2–4]. Various deposition techniques have been employed to produce ZnO films such as pulsed laser deposition, RF or DC sputtering, chemical vapor deposition, sol gel process, plasma-assisted molecular beam epitaxy (MBE) and electron beam evaporation [5–7]. New applications require ZnO films with lower resistivity and higher optical transmission over the visible wavelength region. Thin films of ZnO are widely used in optoelectronic devices, transparent electrodes, light emitting diodes, laser diodes, gas sensors and so on [8,9]. In our opinion, among these different deposition methods, the electron beam technique is a promising method for producing ZnO films with low resistivity and high transparency. The properties of ZnO films depend on various parameters such as deposition rate, substrate temperature, pressure, annealing temperature and so on. In order to produce and to be able to reproduce, exact optimization of deposition parameters is necessary. Among these parameters, annealing temperature is one of the important factors influencing electrical resistivity, optical and structural characteristics of ZnO thin films. The annealing can be done during evaporation by heating up the substrate [10,11] and/or under certain oxygen pressure during the evaporation [12]. In this work we performed the annealing treatment in air at 600 mbar after the deposition of the films. In this way, optical, electrical and structural properties are investigated before and after the annealing treatment by analyzing X-ray diffraction (XRD), optical transmittance, electrical resistivity and morphology.

2. Experimental procedure

ZnO films were deposited on glass substrate by e-beam evaporation. The chamber pressure was kept below3 $\times 10^{-5}$ mbar. The distance between the substrate and target was 10 cm and substrate temperature was kept at room temperature. High purity (99.99%) polycrystalline ZnO was used as source evaporation in our method. Glass substrates were first rinsed in acetone and ethanol, with ultrasonic vibration for 5 min, respectively. The substrates were then rinsed thoroughly in deionized water and

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0042-207X/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.vacuum.2011.03.017

dried in a high purity N_2 gas stream just before they were loaded into the system for film deposition. Deposition rate ranged from 0.1 to 0.15 nm s^{-1}. The thickness of deposited films was controlled using a quartz crystal thickness monitor to have a film thickness of 100 nm. The deposited films then have been annealed in air at pressure 600 mbar for 30 min at each temperature in the temperature range 250–550 °C in furnace to investigate the influence of annealing on electrical, optical and structural properties. The sheet resistance of thin films was measured by a four point probe device. The structure of the films was determined by X-ray diffraction measurements with 10 kV, 35 mA, Cu Kα radiation with wavelength of 1.548 Å (D8 Advance Bruker), in the scan range of 2θ between 30° and 70° with a step size of 0.04 (2θ/s). The surface morphology of the ZnO films was investigated by scanning electron microscopy (SEM). The transmittance of the ZnO films was measured using a double-beam spectrophotometer (Shimadzu UV 3100).

3. Results and discussion

3.1. Electrical properties

Fig. 1 exhibits the influence of annealing temperature on resistivity of ZnO thin films. It was observed that the resistivity was increased monotically with annealing temperature from 4×10^{-4} to 18×10^{-4} Ω cm with an increase in annealing temperature from 200 to 350 °C. While further temperatures increase up to 550 °C, lead to significant increase of resistivity. This behavior is in good agreement with reported behavior in literature [13]. But the resistivity values obtained were lower than those reported by other authors [14]. As a result, higher annealing temperature was led to the formation of higher resistance films. This is basically due to the decrease of carrier concentrations and/or decrease of carrier mobility at higher annealing temperature [15]. It seems that the increase in resistivity at annealing temperatures between 200 and 350 °C is due to the scattering of free carriers by ionized impurities [16]. In high annealing temperatures (550 °C), scattering of free carriers by acoustic and optical phonons is also important. Also, optical phonon contribution dominates at higher temperatures. The piezoelectric scattering by acoustic phonons results in a temperature dependence of the mobility of the form $\mu_L \propto 1/T$ [17]. In fact high annealing temperatures lead to the decrease of mobility of charge carriers in ZnO films. Thus, in higher temperature, decrease of carrier concentration and carrier mobility was led to increase of resistivity.

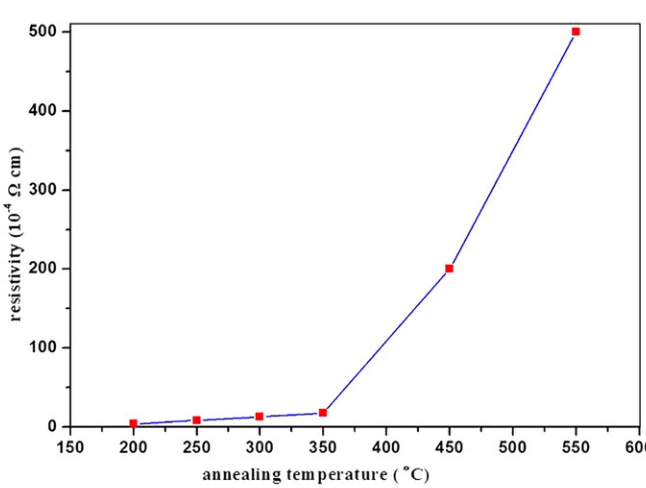

Fig. 1. Resistivity of the ZnO thin films as a function of annealing temperature.

3.2. Structural properties

Fig. 2 shows the high angle XRD pattern of the prepared ZnO thin films. The X-ray diffraction measurements for 2θ scans between 300 and 700 have been obtained from ZnO films annealed at different temperatures. It can be found that before heat treatment, the films are amorphous. The diffraction peaks (100), (002), (101), (110) and (103) of standard ZnO powder were observed for all the annealed samples, indicating that the samples were polycrystalline hexagonal wurtzite structure. The peak intensities are increased by increasing annealing temperature. The maximum intensity peak corresponds to the (002) predominant orientation. Also the influence of annealing temperature on grain size of ZnO thin films is investigated. The crystalline size of ZnO in the films was calculated by Scherrer's formula [18]

$$D = 0.9\lambda/\beta \cos\theta \tag{1}$$

Where D is the grain size, λ (1.548 Å) is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle of the XRD peak. The average grain sizes in the films annealed at various temperatures were calculated and are shown in Table 1. It can be seen that the particle size increases with increasing the annealing temperature and the c-axis orientation improves. The increase in grain size with higher annealing temperature has also been observed by other investigators [19–21].

Scanning electron microscopy (SEM) was used for the study of surface morphological changes of ZnO films annealed at different temperatures. Fig. 3a–e exhibits the SEM images of the films annealed at 250, 350, 450, 550 °C and as-deposited respectively. It can be seen that the grain size becomes larger by increasing annealing temperature and this result agrees with the XRD analysis.

3.3. Optical transmittance

Information concerning optical transmittance is important in evaluating the optical performance of conductive oxide films. Transmittance spectra in the UV and visible wavelength regions of the ZnO films, annealed at different temperatures, are shown in Fig. 4. As can be observed, the optical transmission of the ZnO films, in the visible wavelength region, improves with increasing the annealing temperature. Moreover the ZnO film transmission changed from 10% (for the as-deposited) to 95% (for annealed at

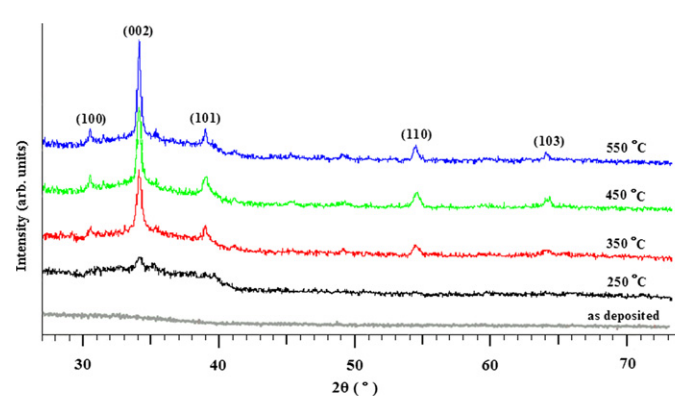

Fig. 2. XRD patterns of ZnO films annealed at various temperatures.

Table 1
Electrical, structural and optical properties of the different temperature annealed ZnO thin films. (Films thickness and annealing pressure are 100 nm and 600 mbar respectively).

Deposition temperature (°C)	Resistivity (Ω cm)	2θ(°)	β(°)	Particle size (nm)	Band gap (eV)
250	8.5×10^{-4}	34.08	0.37	22.5	3.29 ± 0.02
350	18×10^{-4}	34.22	0.35	23.8	3.28 ± 0.02
450	200×10^{-4}	34.34	0.33	25.3	3.27 ± 0.02
550	500×10^{-4}	34.44	0.32	26.1	3.26 ± 0.02

550 °C) at 700 nm. The increase in optical transmittance with temperature can be attributed to the increase of structural homogeneity and crystallinity [22].

3.4. Estimation of the band gap

Ignoring the reflectivity which is expected to be low, the absorption coefficient (α) may be determined from the film transmission, T, as fallows

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{d} \quad (2)$$

Where d is the thickness of the film. The relation between absorption coefficient (α) and photon energy for direct transitions can be written as [23].

$$\alpha h\upsilon = A\left(h\upsilon - E_g\right)^{1/2} \quad (3)$$

Where A is an energy-independent constant and E_g is the optical band gap. The Plots of $(\alpha h\nu)^2$ versus $h\nu$ will have a linear region and extrapolation of the straight line to zero absorption gives the energy gap for different annealing temperature, which are shown in Fig. 5. The energy gap values obtained are in good agreement with other reported values [24]. Fig. 5 shows that the band gaps energy are 3.29 ± 0.02, 3.28 ± 0.02, 3.27 ± 0.02 and 3.26 ± 0.02

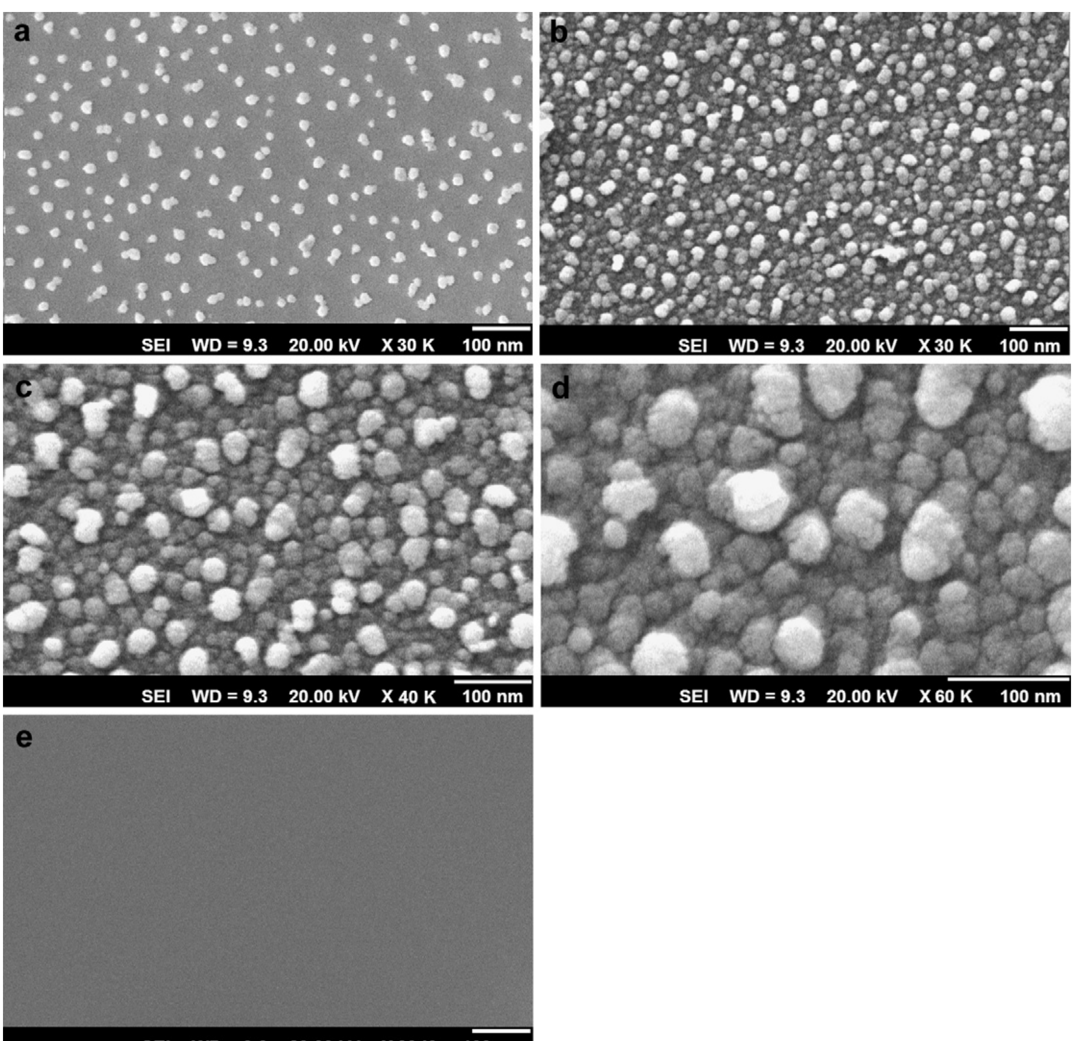

Fig. 3. SEM images of the as-deposited (curve e) and annealed (a: 250 °C, b: 350 °C, c: 450 °C, d: 550 °C) ZnO thin films.

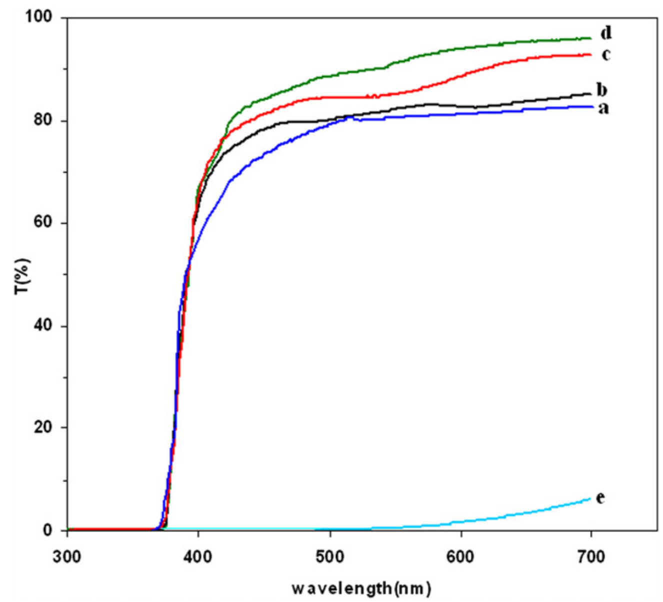

Fig. 4. Optical transmission spectra of ZnO thin films at various annealing temperature (a: 250 °C, b: 350 °C, c: 450 °C, d: 550 °C and e: as-deposited).

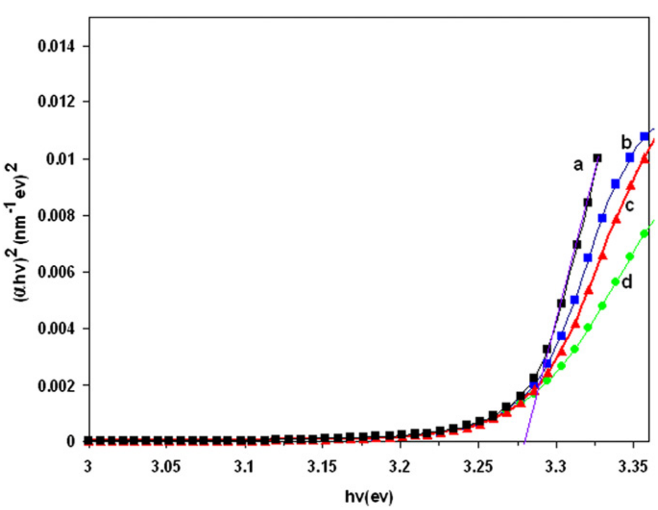

Fig. 5. Plots of $(\alpha h\nu)^2$ versus hν for ZnO thin films annealed at various temperatures (a: 250 °C, b: 350 °C, c: 450 °C and d: 550 °C).

for 250, 350, 450 and 550 °C respectively. Thus the band gap energy decreases with increasing annealing temperature. This may be due to the decrease of defects, which could be the number of oxygen vacancies and/or grain boundaries. Increasing annealing temperature will result in decreasing oxygen vacancies which lead to a decrease the carrier concentration in the conduction band [25]. On the other hand, annealing process improve crystallinity and increase average grain size that result in decreasing defects, therefore band gap energy decreased [26]. Decrease in band gap energy can be correlated with the XRD results.

4. Conclusion

Zinc oxide films were deposited on glass substrates by e-beam evaporation technique. The samples have been annealed in air with annealing pressure 600 mbar at various temperatures to investigate the effect of annealing treatment on the structural, electrical and optical properties. Electrical conductivity of samples decreases with increasing annealing temperature up to 550 °C. Optical transmittance increase by heat treatment and at 550 °C, reach to %95. XRD patterns show that ZnO thin films crystallization improved as a result of the annealing treatment and change in properties of samples due to change in annealing temperature and structure of layers. Direct gap energy of ZnO was calculated in different annealing temperatures that have been found similar to other reports. The optical band gaps in ZnO films by various annealing temperatures are from 3.26 eV to 3.29 eV. SEM images show that the grain size becomes larger by increasing annealing temperature and this result agrees with the XRD analysis. Finally, annealing temperature has an important role in controlling electrical resistivity, optical and structural properties.

Acknowledgment

The authors wish to thank the Isfahan University for their support.

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