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Study the structural, optical and electrical properties of sprayed Zinc oxide (ZnO) thin films before and after annealing temperature

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Abstract. Zinc oxide (ZnO) thin films were deposited on glass substrates by spray pyrolysis technique by decomposition of zinc acetate dihydrate in ethanol. The ZnO thin films were deposited at 350°C and annealed at 500°C for 2 h. The substrate was R217102 glass in a size of 30 cm × 7.5 cm × 0.1 cm. The films exhibited a hexagonal wurtzite structure with a strong (002) preferred orientation. The higher value of crystallite size (20.29 nm) was attained with films annealed at 500°C, probably due to improvement of the crystallinity of the films with heating. The average transmittance of the films, by UV-Vis, was over of 95 %. The band gap energy varied from 3.279 to 3.288 eV for the non-annealed and annealed films, respectively. The electrical resistivity was measured to be 0.4 Ω.cm.

Keywords: ZnO, thin films, snnealing temperature, spray pyrolysis technique

1. Introduction

During the past few years, zinc oxide (ZnO), one of the most important binary II–VI (12–16) semiconductor compounds has attracted interest due its application in light-emitting diodes (LEDs) and laser diodes. ZnO is an important optoelectronic device material for use in the violet and blue regions because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV) [1–5]. ZnO thin films are promising candidates for applications in short-wavelength light-emitting devices, lasers, field emission devices, solar cells gas sensors, surface acoustic wave and transparent contacts [6–10]. Furthermore, very interesting characteristic, for example, fluorescence emission and laser action, have been shown by ZnO nanostructures.

ZnO thin films have been prepared using various methods such as molecular beam epitaxy (MBE) [11], chemical vapor deposition [12], electrochemical deposition [13], pulsed laser deposition (PLD) [14], sol-gel process [15], reactive evaporation [16], magnetron sputtering technique [17] and spray pyrolysis [18],

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have been reported to prepare thin films of ZnO. The spray pyrolysis technique is one of these techniques to prepare large-scale production for technological applications. It is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures. It is known that ZnO films prepared by the spray pyrolysis technique can have a wide band gap between 3 and 3.37 eV.

In present study, nanostructure ZnO based thin films can be deposited by spray pyrolysis technique on glass substrate at a substrate temperature of 350°C. The thin films were prepared with 35 ml of deposition rate, the aim of this work to study the effect of annealing temperature at 500°C of ZnO thin film on crystalline structure, optical gap energy and electrical conductivity.

2. Experimental

A ZnO precursor solution was prepared by dissolving 0.1 M $Zn(CH_3COO)_2 \cdot 2H_2O$ in water containing an equal volume of absolute methanol (99.995%) purity. A few drops of concentrated HCl were added as a stabilizer. The resulting solution was stirred at 60°C for 120 min to yield a clear, transparent solution.

The resulting solutions were sprayed onto heated glass substrates by spray pyrolysis. The substrates were heated by using the solar cells method prepared in our laboratory. The thin films were deposited at a substrate temperature of 350°C through a glass tube in the size of 30 cm × 7.5 cm×0.1 cm, which transforms the liquid to a stream formed with uniform and fine droplets of 35 μm average diameter. The resulting ZnO film was subjected to annealing treatment in air for 2 h at 500°C [19, 20].

The structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation ($\lambda = 0.15406$ nm) in the scanning range of (2θ) was between 20° and 60°. The optical transmittance of the films was measured in the range of 300–900 nm by using an ultraviolet-visible spectrophotometer (SHUMATZU 1800) and the electrical resistivity was measured in a coplanar structure obtained with evaporation of four golden stripes on the deposited film surface using the keithley Model 2400 Low Voltage Source Meter instrument.

3. Results and discussion

The effect of annealing temperature on crystal structure was demonstrated in Fig. 1; show the X-ray diffraction (XRD) spectrum of deposited ZnO thin films at 350°C with and without annealing temperature at 500°C. The obtained XRD spectra matched well with the space group P63mc (186) (No. 36-1451) [21]. As it can be seen the only diffraction peak was observed at $2\theta = 34.5°$, which is related to the plan of (0 0 2). A single (002) diffraction peak of ZnO films is detected in tow films. The spectra shows that the all films having preferential growth along c-axis or (002) plane but with the different peak intensity. The film annealed at 500°C has higher and sharper diffraction peak indicating an improvement in (0 0 2) peak intensity compared to other film. The crystalline quality of thin films enhanced with annealing temperature. Similar observations have been found by other researchers [20–22].

The lattice constant c and diffraction peak angles of ZnO thin films (see Table 1) are calculated using the following equation [23]:

$$d_{h\,k\,l} = \left(\frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}\right)^{-\frac{1}{2}} \quad (1)$$

where a, c are the lattice parameters, $(h,\ k,\ l)$ is the Miller indices of the planes and d_{hkl} is the interplanar spacing.

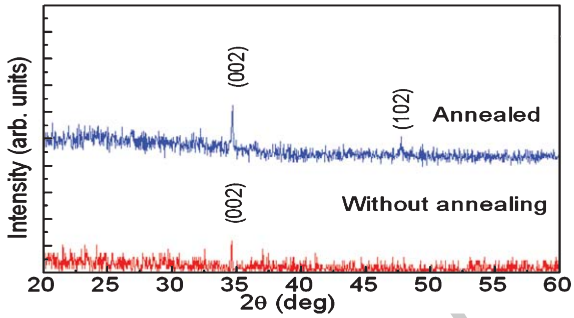

Fig. 1. X-ray diffraction spectra of ZnO thin films with and without annealing temperature at 500°C.

Table 1

Recapitulating measured values of Bragg angle (2θ), the inter planar spacing (d), the full width at half-maximum (FWHM), the crystallite size (G), the lattice parameters (c and a) and the main strain (ε) of deposited ZnO thin films at 350°C with and without annealing temperature at 500°C

T_S (°C)	hkl (deg)	(A°)	FWHM (deg)	(nm)	(A°)	(A°)	(A°)	(%)
Without 35	002	34.27	2.61452	0.52	16.01	5.229035	3.268147	0.443
Annealed 35	002	34.63	2.58815	0.41	20.29	5.176316	3.235197	−0.5702

The strain ε values in our films were estimated from the observed shift, in the (0 0 2) diffraction peak between their positions in the XRD spectra via the formula [23]:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100\% \tag{2}$$

where ε is the mean strain in ZnO thin films (Table 1), c the lattice constant of ZnO thin films and c_0 the lattice constant of bulk (standard $c_0 = 0, 5206$ nm).

The crystallite size of ZnO thin films which are estimated using the well-known Debye-Scherrer formula [21]:

$$G = \frac{0.9\lambda}{\beta \cos\theta} \tag{3}$$

where G is the crystallite size, λ is the wavelength of X-ray ($\lambda = 1.5406$ A°), β is the full width at half-maximum (FWHM), and θ is the half diffraction angle of the centroid of the peak. Table 1 presents the some information's on the structure properties of ZnO thin films of (0 0 2) diffraction peak were measured as a function: with and without annealing temperature at 500°C. It can be seen from Table 1 that the good crystallinty are achieved in the films annealed at 500°C, where also obtained by [20].

Figure 2 shows the optical transmission spectra of ZnO thin films with and without annealing temperature at 500°C. As it can be seen, a height transparent spectra $T(\lambda)$ of the thin films in visible region, the average transmission is over 95%. The region of the absorption edge in the all layers due to the transition between the valence band and the conduction band is located between 360–390 nm, in this region the transmission decreased because of the onset fundamental absorption.

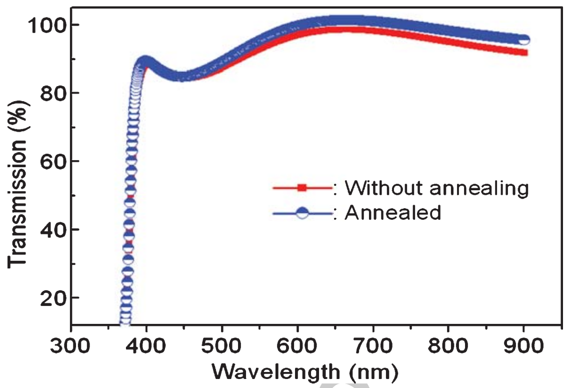

Fig. 2. Transmission spectra T(λ) of ZnO thin films sprayed with and without annealing temperature at 500°C.

The optical band gap energy E_g was measured from the transmission spectra using the following relations [11]:

$$(Ah\upsilon)^2 = C(h\upsilon - E_g) \tag{4}$$

where A is the absorbance, d is the film thickness; T is the transmission spectra of thin films; α is the absorption coefficient values; C is a constant, $h\nu$ is the photon energy ($h\nu = \frac{1240}{\lambda(nm)}(eV)$) and E_g the band gap energy of the semiconductor. As it was shown in (Fig. 3) a typical variation of $(Ah\nu)^2$ as a function of photon energy ($h\nu$) used for deducing optical band gap E_g, it is determined by extrapolation of the straight line portion to zero absorption ($A = 0$) [18] the values of E_g are listed in Table 2. Besides, we have used the Urbach tail energy (E_u), which is related to the disorder in the film network, as it is expressed follow [23]:

$$A = A_0 \exp\left(\frac{h\upsilon}{E_u}\right) \tag{5}$$

where A_0 is a constant $h\nu$ is the photon energy and E_u is the Urbach energy, the latter decreased with increasing the band gap is indicating the decrease of defects as it was illustrated in (Table 2).

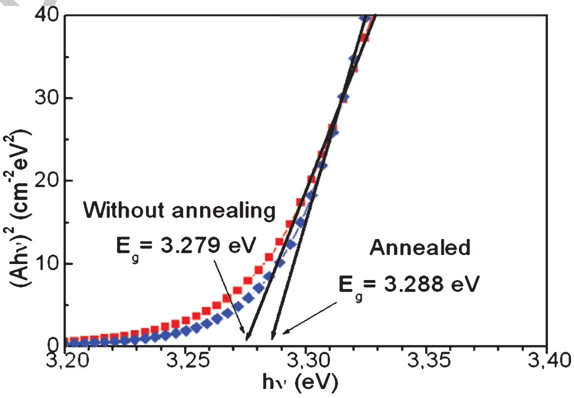

Fig. 3. The typical variation of $(Ah\nu)^2$ vs. photon energy of deposited ZnO thin film at 300 and 350°C.

Table 2
Recapitulating measured values of band gap energy (E_g), Urbach energy (E_u), and electrical resistivity (ρ) of deposited ZnO thin films at 350°C with and without annealing temperature at 500°C

T_S (°C)	$E_g{}^a$(eV)	E_u(meV)	ρ (Ω.cm)
Without	3.279	056.1	0.509
Annealed	3.288	048.7	0.421

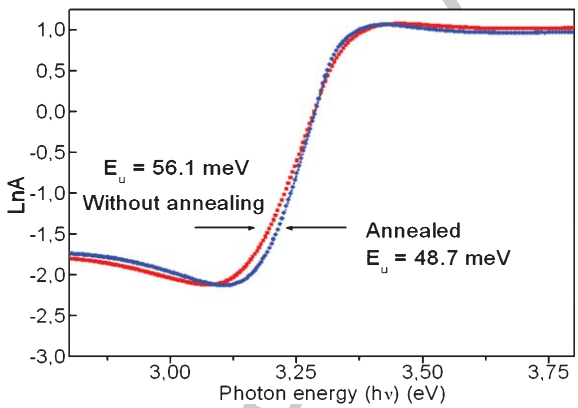

Fig. 4. The typical variation of LA vs. photon energy of deposited ZnO thin film at 300 and 350°C.

As clearly seen in the Fig. 3, the optical gap energy of ZnO thin films are changed from 3.279 to 3.288 eV of sprayed films with and without annealing temperature at 500°C, respectively. However, in Fig. 4 obtained inversely for the Urbach energy, which the minimum value was reached with ZnO thin film annealed at 500°C (see Table 2). Table 2 shows that the electrical resistivities of our films are in qualitative agreements with the band gap energy (see Table 2), the decrease in the electrical resistivity can be explained by increasing of the potential barriers, because the introduced atoms are segregated into the grain boundaries, this interpretation is consistent with the authors [20, 23–26]. This can be explained by decreasing of the crystallite size (see Table 1). One can note that the annealing temperature effect is clearly observed in the layer quality.

4. Conclusions

In conclusion, highly transparent conductive ZnO thin films were deposited on glass substrate by spray pyrolysis technique. The ZnO thin films were deposited at a temperature of 350°C and annealed at a 500°C, the substrates were heated using the solar cells method. The influence of annealing temperature on structural, optical and electrical properties was investigated. The films exhibit a hexagonal wurtzite structure with a strong (002) preferred orientation. The average transmittance of obtain films is over of 95 % measured by UV-vis analyzer. The band gap energy varies from 3.279 to 3.288 eV for the without to annealed ZnO thin film at 500°C, respectively. The electrical resistivity measured of our films in the order 0.4 (Ω.cm).

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