FABRICATION AND CHARACTERISATION OF ZnO THIN FILM BY SOL–GEL TECHNIQUE

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Article Info	Abstract
<p><i>Received: 17.12.2019</i> <i>Accepted: 08.01.2020</i></p> <p>Keywords: ZnO; Thin film; Sol–Gel technique</p>	<p>We investigated the structural and optical properties of zinc oxide (ZnO) thin film as the n-type semiconductor. In this work, the sol–gel method used to fabricate ZnO thin film on glass substrate with 0.5 mol/l of zinc acetate dehydrates. The crystals quality of the thin film analyzed by X-ray diffraction and the optical transmittance was carried out by an ultraviolet-visible spectrophotometer. The DRX analyses indicated that ZnO film have polycrystalline nature and hexagonal wurtzite structure with (002) preferential orientation and the measured average crystallite size of ZnO of 207.9 nm. The thin film exhibit average optical transparency about 90 %, in the visible region, found that optical band gap energy was 3.282 eV, the Urbach energy also was calculated from optical transmittance to optimal value is 196.7 meV.</p>

1. Introduction

ZnO is a very most important semiconductor material due to its applications [1]. It has a direct and wide band gap of 3.3eV in the near–UV spectral region [2], and a large exciton binding energy (60meV) at room temperature [3]. It consider that the ZnO is an n-type semiconducting with high density and good crystalline quality [4], but the use of ZnO as a semiconductor in electronic devices due to the high transmittance and good electrical conductivity [5]. Therefore, ZnO thin films are promising candidates for applications in short–wavelength light–emitting devices, lasers, field emission devices, solar cells and sensors [1–6]. Nanocrystalline ZnO thin films can be produced by several techniques such as reactive evaporation [7], molecular beam epitaxy (MBE), magnetron sputtering technique [8], pulsed laser deposition (PLD) [9], spray pyrolysis [10], sol–gel process [11], chemical vapor deposition, and electrochemical deposition [12].

In this work, ZnO thin film was deposited on glass substrate by (spin coating) sol–gel method, ZnO solution was prepared using a zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) with precursor molarity of 0.5 mol.l⁻¹.

2. Materials and methods

ZnO thin film was deposited on glass substrate using a spin coating method, ZnO solution was prepared by dissolving 0.5 mol.l^{-1} of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in the solvent of absolute methanol solution (CH_3OH) (99.995%) purity, then have added drops of monoethanolamine solution as a stabilized, the mixture solution was stirred and heated at 50°C for 6 h to yield a clear and transparency solution.

The solution was then spin coated onto the glass substrate, which was rotated at 4000 r/min for 50 s. The films were dried in air at 200°C for 30 min on a hot plate. The procedure from coating to drying was repeated 6 times, the final ZnO thin film as annealed in air at 600° for 2 hours.

Crystallographic and phase structure of the thin film was determined by X-ray diffraction (XRD, Bruker AXS-8D) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) in the scanning range of (2θ) was between 20° and 55° . The optical transmittance of the deposited film was measured in the range of 300–900 nm by using ultraviolet–visible spectrophotometer (LAMBDA 25).

3. Results and Discussions

The crystal structure of the deposited ZnO film was studied using X-ray diffraction (XRD). XRD spectra of ZnO films were showed in Fig. 1. As can be seen, the diffraction peaks were observed at $2\theta = 31.30^\circ$, 34.50° , 36.24° and 47.30° which are related to the following plans (100), (002), (101) and (102) respectively (JCPDS File NO.75–0576 from ASTM) [13]. These peaks confirmed that the films are polycrystalline in nature.

Fig. 1. XRD spectrum of ZnO thin films prepared using spin coating method.

The variation of the crystallite size of the ZnO thin films with substrate temperature was calculated from the four diffraction peaks, using the full width at half maximum (FWHM) in conjunction with the Debye–Scherer formula [3]:

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

where G is the crystallite size, λ is the X-ray wavelength ($\lambda = 1.5406 \text{ \AA}$), β the full width at half-maximum (FWHM), and θ is Bragg angle of the diffraction peaks.

The grain size of ZnO on glass was 207.9 nm, it shows that the grain becomes more uniform and bigger in size on our sample.

According to the hexagonal symmetry, the lattice constant can be calculated by the following formula [14]:

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

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

The lattice parameters are substrate dependent. This gives rise to a mismatch between the substrate and the deposited thin films. The latter is responsible for the resulting strains and stresses. We estimated the strain ε values in each thin film deposition via the formula [15]:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100 \% \quad (3)$$

where ε is the mean strain in ZnO thin films, c the lattice constant of ZnO thin films is 0.51952 nm, and c_0 the lattice constant of bulk (standard $c_0 = 0.5206 \text{ nm}$) [13].

The strain was equal to -0.21% for the ZnO thin film deposited on glass substrate. The negative value of the strain in the film means that the sample is in a tensile condition.

Fig. 2, shows the optical transmissions spectra of ZnO thin film, as it can be seen, a height transparent spectra $T(\lambda)$ with exhibited average optical transparency over 90 %, in the visible range. The region of the absorption edge 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 of fundamental absorption. As it was shown in the inset of

Fig. 2, shows a typical variation of (LA) vs. photon energy of ZnO thin film for deducing the Urbach energy, which is related to the disorder in the film network, is expressed as [15]:

Fig. 2. Transmission spectra $T(\lambda)$ of ZnO thin films, the inset of Fig. 2, shows a typical variation of $(\text{Ln}A)$ vs.

$$A = A_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (4)$$

where A_0 is a constant and E_u is the Urbach energy was 196.7 meV. The optical band gap energy E_g was measured from the transmission spectra using the following relations [14]:

$$(Ah\nu)^2 = C(h\nu - E_g) \quad (5)$$

where A is the absorbance, C is a constant, $h\nu$ is the photon energy ($h\nu = \frac{1240}{\lambda(\text{nm})}(\text{eV})$) 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 ($A=0$) [3] the value of E_g was 3.282 eV.

Fig. 3. The typical variation of $(Ah\nu)^2$ vs. photon energy of deposited ZnO thin film.

In this work, Table 1 presents the comparative results of our work with other researches; we have compared the structural, optical and electrical properties of the ZnO thin films.

Table 1. The comparative study of the structural, optical and electrical properties of ZnO thin films at different conditions.

Annealing temperature (°C)	Deposition method	Phase	Crystallite size G (nm)	Average transmission (%)	Optical energy E_g (eV)	Electrical conductivity σ ($\Omega \cdot \text{cm}$) ⁻¹	Rf.
550	Sol—gel Spin Coating	ZnO	7.01	80	3.21	$3.5 \cdot 10^2$	[16]
550	Sol—gel Spin Coating	ZnO+5%Cu	3.21	80	3.20	$2.75 \cdot 10^2$	[16]
as-deposited	electron beam evaporation	HoF3-doped ZnO	50	85	3.26	1000	[17]
400	electron beam evaporation	HoF3-doped ZnO	50	85	3.32	45	[17]
400	RF magnetron sputtering	ZnO	57	85	3.25	-	[18]
600	Sol—gel Spin Coating	ZnO	207.9	90	3.282	-	This work

4. Conclusions

In summary, the high quality ZnO film on glass substrate was fabricated. The DRX analyses indicated that ZnO film has polycrystalline nature and hexagonal wurtzite structure with (002) preferential orientation with a high average crystallite size of 207.9 nm. The thin film exhibit average optical transparency about 90 %, in the visible region, ZnO film has optical gap energy of 3.282 eV and the Urbach energy value is 196.7 meV.

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