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Effect of deposition rate on the structural, optical and electrical properties of Zinc oxide (ZnO) thin films prepared by spray pyrolysis technique

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ABSTRACT

Zinc oxide (ZnO) thin films were deposited on glass substrates by spray pyrolysis technique decomposition of Zinc acetate dihydrate in an ethanol solution with various deposition rates, the ZnO thin films were deposited at 350 °C, the substrates were heated by using the solar cells method. The substrate was R217102 glass in a size of 30 cm × 7.5 cm × 0.1 cm. Nanocrystalline films with a hexagonal wurtzite structure with a strong (0 0 2) preferred orientation were observed at all sprayed films. The maximum value of grain size (21.91 nm) is attained of sprayed films with 30 ml. The decrease of the strain of ZnO films is probably due to an improvement of the crystallinity of the films. The average transmittance of all films is about 90 – 95% measured by UV – vis analyzer. The band gap energy varies from 3.265 to 3.286 eV was affected by deposition rates lying between 10 and 35 ml. The electrical resistivity of the films decreased from 0.394 to 0.266 (Ω cm). The best results are achieved in sprayed films between 25 and 30 ml.

1. Introduction

Zinc oxide (ZnO), an II – IV semiconductor, has a wide direct gap of 3.37 eV at room temperature and large exciton binding energy of 60 meV [1–3], which has attracted much attention for its wide prospects optoelectronic devices such as solar cells, light emitting diodes (LED), laser diodes and acoustic – optical devices [4–8]. In solar cells, ZnO thin films are used as an anti-reflective coating (ARC) and transparent conductive oxide (TCO) due to its high optical transmittance in the visible light region, high band gap energy (e.g., ∼3.3 eV), optimum refractive index ($n \sim 2.0$) and natural n-type electrical conductivity [9–11]. ZnO can be used as a heat mirrors, piezoelectric devices [12], thin films [13] and chemical and gas sensing [14].

ZnO thin films have been prepared using various methods such as molecular beam epitaxy (MBE) [15], chemical vapor deposition [16], electrochemical deposition [17], pulsed laser deposition (PLD) [18], sol-gel process [19], reactive evaporation [20], magnetron sputtering technique [21] and spray pyrolysis [22], 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.

Many researchers have studied the effects of microstructure and processing on electrical conduction in ZnO nanostructures [23–26]. It is known that ZnO films prepared by the spray pyrolysis technique can have a wide band gap between 3 and 3.37 eV, El Sayed et al. [27] had controlled the effect of cadmium content on the film structure and optical absorption for this ZnO microstructured.

In present study, nanostructure ZnO based thin films can be deposited by spray pyrolysis technique on glass substrate where substrate temperatures are maintained at 350 °C for all experimentation. The thin films were deposited at different rates, the aim of this work to study the effect of deposition rate on crystalline structure, optical gap energy and electrical conductivity.

2. Experimental

ZnO solution were prepared by dissolving 0.1 M ($Zn(CH_3COO)_2$, $2H_2O$) in the solvent containing equal volume absolute methanol solution (99.995%) purity, then we have added a few drops of concentrated HCl solution as a stabilizer, the mixture solution

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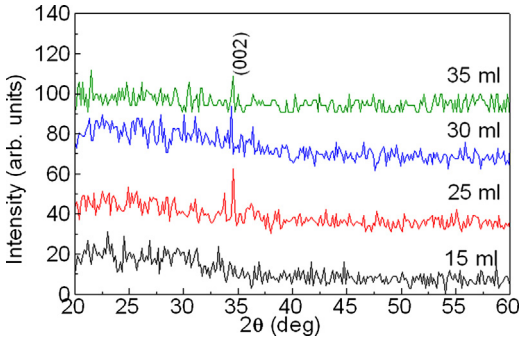

Fig. 1. X-ray diffraction spectra of ZnO thin films at different deposition rates.

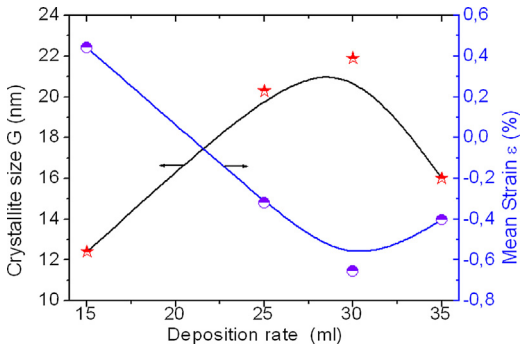

Fig. 2. The variation of crystallite size and lattice parameter *c* as a function of deposition rate in ZnO thin films.

was stirred at 60 °C for 120 min to yield a clear and transparent solution. The substrate was R217102 glass in a size of 30 cm × 7.5 cm × 0.1 cm, prior to pumping, the substrate (R217102 glass) were cleaned with alcohol in an ultrasonic bath and blow-dried with dry nitrogen gas.

The resulting solutions were sprayed on the heated glass substrates by spray pyrolysis technique, the substrates were heated by using the solar cells method, and this letter was prepared in our laboratory. The thin films were deposited at different rates varies from 10 to 35 ml started by 5 ml at 350 °C (3 min of deposition time), which transforms the liquid to a stream formed with uniform and fine droplets of 35 μm average diameter (given by the manufacturer).

Crystallographic and phase structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation (λ ≡ 0.15406 nm) in the scanning range of (2θ) was between 20° and 60°. The optical transmittance of the deposited films was measured in the range of 300 – 900 nm by using an ultraviolet-visible spectrophotometer (SHUMATZU 1800), whereas the electrical conductivity σ of the films and Urbach energy (E_u), which is related to the disorder in the film network, the electrical resistivity ρ was measured in a coplanar structure obtained with evaporation of four golden stripes on the deposited film surface; the measurements were performed with keithley Model 2400 Low Voltage Source Meter instrument. All X-ray diffraction, transmittance spectra *T(λ)* and electrical measurements are carry out at room temperature (RT).

3. Results and discussion

3.1. The crystalline structure of ZnO thin films

The X-ray diffraction (XRD) spectrum of the ZnO thin films is shown in Fig. 1. The obtained XRD spectra matched well with the space group P63mc (186) (No. 36-1451) [28]. As it can be seen the only diffraction peak was observed at 2θ ≡ 34.5°, which is related to the plan of (0 0 2). The peak at position 34.5° corresponding to the (0 0 2) plans is very sharp, the film obtained with 30 ml has higher and sharper diffraction peak indicating an improvement in (0 0 2) peak intensity compared to other films, revealing that the films are nanocrystalline and a preferred orientation with the *c*-axis perpendicular to substrate. The crystalline quality of thin films enhanced at a deposition rate of 30 ml. Similar observations have been found by other researchers [29–31].

The lattice constant *c* and diffraction peak angles of ZnO thin films (see Table 1) are calculated using the following equation [22]:

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

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

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 [29]:

$$\varepsilon = \frac{c - c_0}{c_0} 100\% \quad (2)$$

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 $c_0 \equiv 0,5206$ nm).

Table 1 presents the crystallite size of ZnO thin films which are estimated using the well-known Debye-Scherrer formula [32]:

$$G = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

where *G* is the crystallite size, λ is the wavelength of X-ray (λ ≡ 1.5406 Å), β is the full width at half-maximum (FWHM), and θ is the half diffraction angle of the centroid of the peak.

Fig. 2 shows the variation of the crystallite size and mean strain of (0 0 2) diffraction peak as a function of deposition rate. It can be seen from Fig. 2 that the crystallite sizes increased with 30 ml and then decreased within increasing deposition rate of 30 – 35 ml (see Table 1). The increase of the crystallite size could be explained by an improvement in the crystallinity of the films. Moreover, the decrease of the crystallite size, this confirms the deterioration in the crystallinity of the films. As can be seen, an increase in the film deposition rate 15 – 30 ml the mean strain decreases from 0.443 to−0.654%. Swapna et al. [33], they observed that the reduction of mean strain with increase in crystallite can be explained by the existence of sufficiently thicker films in less strained (or more relaxed) state. This result in reduction of mean strain with increase

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*) and lattice parameters (*c* and *a*) for ZnO thin films as a function of deposition rate.

Deposition rate (ml)	*hkl*	2θ (deg)	*d* (Å)	FWHM (deg)	*G* (nm)	*c* (Å)	*a* (Å)
15	0 0 2	34.57	2.59251	0.67	12.41	5.185024	3.240640
25	0 0 2	34.66	2.58599	0.41	20.29	5.171972	3.232482
30	0 0 2	34.54	2.59469	0.38	21.91	5.189391	3.243369
35	0 0 2	34.27	2.61452	0.52	16.01	5.229035	3.268147