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Study of Ultrasonically Sprayed ZnO Films: Thermal Annealing Effect

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ZnO thin films were deposited on microscope glass substrates by ultrasonic spray pyrolysis technique. The effects of annealing under various temperatures on the optical and structural properties of ZnO thin films were analyzed. The as-deposited and annealed ZnO thin films were investigated by UV/VIS spectrophotometer and X-ray diffractometer. Some of the optical properties of the films such as transmittance, absorbance and band gap energy were investigated by UV/VIS spectrophotometer. The crystallinity levels of the films were investigated, the structural parameters such as diffraction angle, full-width at half maximum, lattice parameters, grain size and dislocation density were calculated and structural properties were analyzed. X-ray diffraction patterns indicated that the ZnO films had a polycrystalline hexagonal wurtzite structure.

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1. Introduction

Zinc oxide (ZnO) has attracted much attention recently for potential applications because of its wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1, 2]. ZnO is one of the typical II–VI semiconductor materials having various optoelectronic device applications such as blue light-emitting diodes, electroluminescent devices, electrooptic modulators and window layers in photovoltaic cells and gas sensors [3–5].

In this work, ZnO thin films have been prepared by ultrasonic spray pyrolysis technique using zinc acetate solution as precursor. The influence of thermal annealing on the structural and optical properties of the ZnO thin films is presented.

2. Experimental

The ZnO thin films were deposited with an ultrasonic spray pyrolysis (USP) system at a substrate temperature of 375 °C. The $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.1 M) solution has been prepared and sprayed onto microscope glass substrates following conditions: 1 — the solution was sprayed through an ultrasonic nozzle with air as the carrier gas at a pressure of 1 bar; 2 — the ultrasonic frequency was 100 kHz, and the droplet size was 20 μm; 3 — the total solution (150 ml) was sprayed during 30 min, and the solution flow rate controlled by a flowmeter was kept at 5 ml min^{-1}; 4 — the distance between the nozzle and the substrate was maintained at 35 cm; 5 — the substrate temperature was controlled within ±5 °C with an iron–constantan thermocouple; 6 — after deposition process, films were annealed in air ambient at different temperatures of 200, 300 and 400 °C for 1 h.

To investigate the crystalline structure of the films, Rigaku X-ray diffractometer (XRD) using Cu K_α radiation (λ = 1.54059 Å) was employed. The accelerating voltage of 40 kV, emission current of 30 mA, and scanning speed of 2°/min were used. A range of 2θ from 20° to 80° was scanned, so that all possible diffraction peaks could be detected. The transmittance and absorbance spectra for all the films were recorded by a Shimadzu UV-2550 (double beam, 190–900 nm) spectrophotometer. The thicknesses of the films were measured by Filmetrics F20 thin film thickness measurement system and listed in Table I.

TABLE I

The thickness of the ZnO thin films as-grown and thermally annealed.

Material	Annealing temperature [°C]	Thickness [nm]
ZnO	as-grown	247
	200	331
	300	340
	400	300

3. Results and discussion

3.1. Structural analysis

Figure 1 shows the XRD spectra of ZnO thin films as-grown and annealed at different temperatures. From these spectra, it was seen that all films have a polycrystalline structure of hexagonal form, with a (002) and (101) preferred orientations and important effect of annealing temperature on the preferential orientation of the films was observed. Also, annealing temperature has a strong effect on the intensities of the diffraction peaks.

For all films, the grain size (D) was evaluated from the full width at half maximum (FWHM) for both (002) and (101) orientations by using the Scherrer equation [6], assuming a homogeneous strain across the films, and these values are given in Table II. It can be clearly seen that

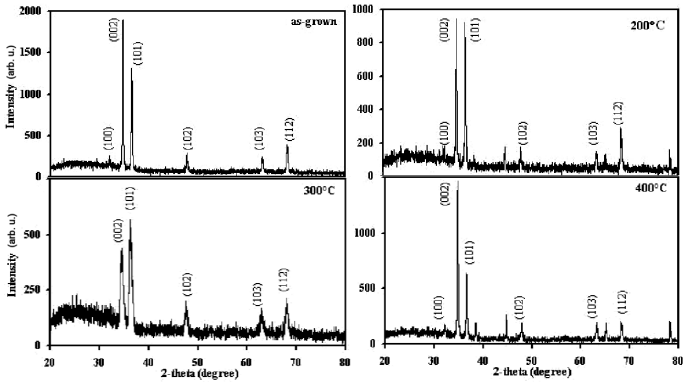

Fig. 1. XRD patterns for the ZnO thin films annealed at different temperatures.

the grain size of the as-grown ZnO films decreased from 422 to 148 Å [for (002) orientation] and 425 to 342 Å [for (101) orientation] for ZnO films annealed at 300 °C showing the deterioration in the crystallinity of the films. Similar decrease on grain size was seen for other annealed films.

Additionally, the dislocation density (δ), listed in Table II and defined as the length of dislocation lines per unit volume of the crystal, was calculated from the $\delta = 1/(D)^2$ formula [7], where D is the grain size. The crystallization levels of the films annealed at 300 °C are worse because of their high δ values which represent the amount of defects in the film. Larger D and smaller δ values indicate better crystallization of the material. This means that thermal annealing process increases the defects in the as-grown ZnO films and deteriorates crystallite quality.

TABLE II

The angle of diffraction (2θ), interplanar distance (d), the grain size (D) and the dislocation density (δ) of the ZnO thin films.

Material	2θ		d [Å]		D [Å]		δ [Å]$^{-2} \times 10^{-6}$	
	(002)	(101)	(002)	(101)	(002)	(101)	(002)	(101)
ZnO (as-grown)	34.64	36.44	2.587	2.464	422	425	5.62	5.54
ZnO (annealed at 200 °C)	34.84	36.60	2.573	2.453	371	381	7.27	6.89
ZnO (annealed at 300 °C)	34.80	36.54	2.576	2.457	148	342	45.7	8.55
ZnO (annealed at 400 °C)	34.82	36.62	2.575	2.452	368	371	7.38	7.27

TABLE III

The volume of the unit cell (V) and the lattice parameters (a, b, and c) of the ZnO thin films.

Material	Calculated			ASTM card [9]		
	V [Å]^3	$a = b$ [Å]	c [Å]	V [Å]^3	$a = b$ [Å]	c [Å]
ZnO (as-grown)	46.89	3.2347	5.1748	47.6	3.250	5.207
ZnO (annealed at 200 °C)	46.27	3.2221	5.1460			
ZnO (annealed at 300 °C)	46.49	3.2282	5.1516			
ZnO (annealed at 400 °C)	46.23	3.2197	5.1490			

In order to investigate variation of lattice parameters of the ZnO films with thermal annealing temperature, the volume of the unit cell (V) and the lattice parameters (a, b, and c) of the hexagonal ZnO were calculated according to the relations [8]:

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad \text{and} \quad V = \frac{\sqrt{3}}{2}a^2 c\,. \tag{1}$$

It is concluded that these values given in Table III almost agree with those obtained from the ASTM card for polycrystalline ZnO powder of hexagonal structure [9]. As seen from Table IV, the lattice constant (c) value of the ZnO films slightly decreases with the annealing temperature.

TABLE IV

Band gap energies (E_g) and Urbach parameters (E_0) for ZnO thin films.

Material	E_g [eV]	E_0 [meV]
ZnO (as-grown)	3.24	103
ZnO (annealed at 200 °C)	3.26	84
ZnO (annealed at 300 °C)	3.27	81
ZnO (annealed at 400 °C)	3.25	98

3.2. Optical analysis

The optical absorbance and transmittance spectra of all films are presented in Fig. 2. The average optical transmittance in the wavelength region (from 500 to 900 nm) of ZnO thin films before thermal annealing is 43.8%, while after annealed at 200 °C, 300 °C and 400 °C, the transmittance is 53.2%, 64.4%, and 45.8%, respectively. The transmittance is obviously increased with the thermal annealing, especially for films annealed at temperatures of 200 °C and 300 °C.

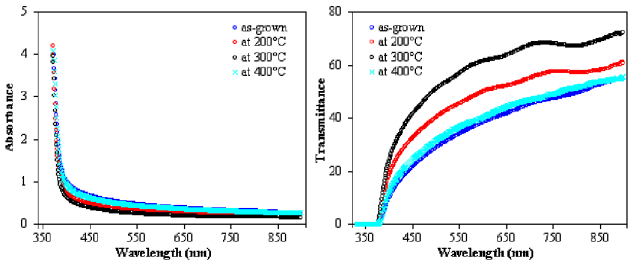

Fig. 2. Absorbance and transmittance spectra for the ZnO thin films.

In order to determine the band gap energy E_g, the absorption coefficient data were analyzed. The relationship between the absorption coefficient α and the photon energy $h\nu$ for direct transition is given by [10]:

$$\alpha h\nu \sim (h\nu - E_g)^{1/2}. \tag{2}$$

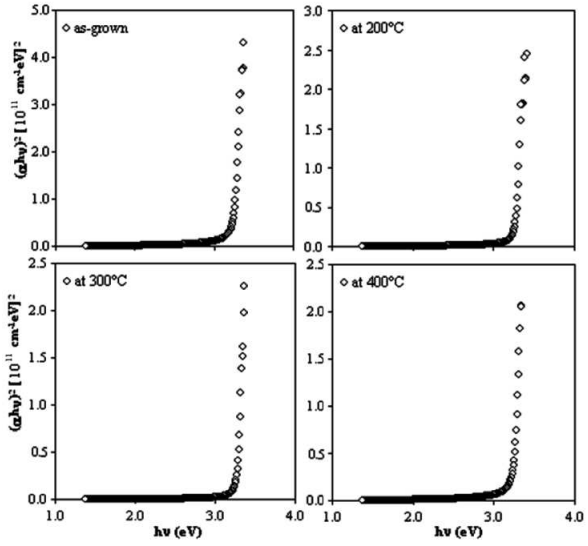

Fig. 3. The $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ for the ZnO thin films.

The plots of $(\alpha h\nu)^2$ as a function of the photon energy $h\nu$ for all films are shown in Fig. 3. The optical band gap energy E_g could be obtained through extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$. The estimated band gap energy values are listed in Table IV. The optical band gap of the as-grown ZnO films slightly increases with the thermal annealing, but this increase is not considered as important. It is known that band gap energy of ZnO is sensitive to small changes in structural effects such as grain boundary configuration and film stress.

Generally, the absorption coefficient $\alpha(h\nu)$ in the low energy range follows the well-known exponential law, which is given by the Pankove expression [11]:

$$\alpha(h\nu) = \alpha_0 \exp(h\nu/E_0) \quad \text{for} \quad h\nu < E_g\,, \tag{3}$$

where α_0 is a constant, and E_0 is an Urbach parameter, having dimensions of energy and describing the width of the localized states in the band gap. From the slopes of the linear relationship between $\ln\alpha$ and $h\nu$ in the tail region, the Urbach parameters E_0 for the all films were estimated, and these results are given in Table IV.

Acknowledgments

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