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Effect of the Dip-coating Speed on the Structural and Optical Properties of ZnO Thin Films

Said Benramache[*,1], Boubaker Benhaoua[2], Foued Chabane[3], Hamza Bentrah[4], Soumia Abdessemed[5]
[1] Department of Material Sciences, Faculty of Science, University of Biskra 07000, Algeria
[2] Departments of Physics, Instuty of technology, University of El-ouad 39000, Algeria
[3] Department of mechanics, Faculty of technology, University of Biskra 07000, Algeria
[4] Department of mechanics, Engineering science, University of Batna 05000, Algeria
([1]saidzno2006@gmail.com, [2]benhaouab@yahoo.fr, [3]fouedchabane@live.fr, [3]bhamza2005@gmail.com, [4]abdessemed.soumia@yahoo.com)

Abstract-In the present paper we have study the structural and optical properties of the ZnO thin films deposited on glass substrates, we have used the dip-coating method with the Sol-Gel technique. The effect of dip-coating speeds on the transparency and structural quality of ZnO films have been studied in a crystallization temperature between 550-600 °C. We revealed that highly c-axis oriented ZnO thin films were obtained at 600 °C and immerse speed is (v = 2.17 cm/min) in this condition where the films high quality of deposition as the direction (002) peak along c-axis orientation and the grain size increases with optical gap energy increased.

Keywords- *ZnO thin films; Dip-coating method; Characteristics*

I. INTRODUCTION

ZnO is a direct wide band gap semiconductor material of 3.37 eV and a large exciton binding energy of 60 meV, at room temperature [1], which makes it transparent in visible light; operates in the UV; light emitting diodes (LEDs) and laser diodes (LDs) [2-4]. This is an attractive and promising material for many applications in surface acoustic wave device (SAW) [5, 6], transparent electrode [7], blue and ultraviolet (UV) light emitters [8], and photoanode films of solar cell [9], gas sensors [10], photovoltaic device [11], temperature room ultraviolet lasers [12]. A few reports are also showed on the study of ZnO thin films prepared by sol–gel process [13]. Sol–gel process is simple, inexpensive, and has a general advantage of large area deposition and uniformity of thickness of the films [14, 15].

ZnO is a widely used material with increasing scientific interest due to the many possibilities of modern applications. Several methods have been developed to prepare ZnO nanostructures, nanoparticles and thin films of different morphologies [16, 17]. The original method for ZnO nanoparticle synthesis that we are using was developed by Spanhel and Anderson [16].

ZnO films can be deposited by several techniques: molecular beam epitaxy (MBE) [18], magnetron sputtering technique [19], pulsed laser deposition (PLD) [20], evaporation [21], spray pyrolysis [22, 23], and sol-gel process [24].

The Sol-Gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and poly-condensation reactions [25]. The applications for sol gel-derived products are numerous such the protective coatings [26], thin films and fibers [27], Nano-scale powders [28], Opto-mechanical [29]. The Sol-Gel technique the films are produced with the application of three methods: Spain coating method, dip coating method and meniscus coating method [30]. In the presented studies dip coating method was applied.

This work was to investigated the dip-coating method and study the properties of ZnO thin films for a fundamental review of its physico-chemical parameters including crystallization material deposited, its transparency in ultraviolet dominates; the grain size; c-axis orientation and band gap energy. These parameters are studied as a function of immerse speed and annealing temperature.

II. EXPERIMENTAL DETAIL

We have Zinc acetate dihydrate ($C_4H_6O_4Zn$, $2H_2O$) as source material which was dissolved in the ethanol with 0.1 to 0.2 $mol.l^{-}$ of concentration. The mixture of zinc acetate having concentration and the ethanol was heated to 80 ° C [31] during 10 minutes; we have found that the setter transparency of the ZnO thin film is corresponding to a concentration of (0.1 M). Thus, the concentration of sol-gel is depends sensitively to the nature of the ZnO thin films transparently.

In this paper we have prepared the dip-coating method in the laboratory, the adopted. It consists to immerse the substrate in the Sol-Gel solution and withdraw it there after in stable and controlled conditions to obtain a film with uniform thickness. The speed of the dip-coating in this experiment are (V1 = 2.17 cm / min, V2 = 4.27 cm / min) and the numbers of coating substrate with drawing varied between 6 to 10 times. The film prepared on glass substrates annealing at 300 ° C in air, followed by annealing temperatures in the range of 550 -600 ° C maintaining in the four (45 min).

Crystallographic and phase structures of the thin films were determined by X-ray diffraction (XRD, Bruker AXS-8D) with CuKα radiation (λ = 0.1541 nm) in the scanning range was between 2θ = 25° and 55°. The optical properties of the deposited films were measured in the range of 300–800 nm using by an ultraviolet–visible spectrophotometer (UV, Lambda 35).

III. RESULTS AND DISCUSSION

Figure (1) show the X-ray diffraction (XRD) spectra of the ZnO thin films deposited by tow different speeds of dip-coating and crystallization temperatures at 550 and 600 °C we have observed the change of the intensity peaks with increase of the crystallization temperature has the effect of narrowing the diffraction peaks of ZnO thin films on the following directions: (100); (101); (102) and (002).The height of the peaks including that of (002) in the low speed is the crystallization along the c-axis orientation. We find that the intensity and orientation dependence of the speed of dip-coating and crystallization temperature.

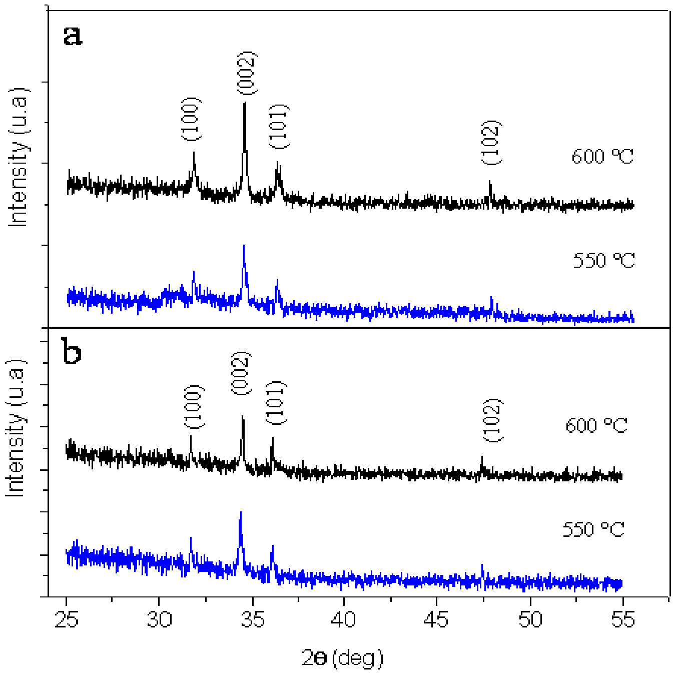

Figure 1. X-ray diffraction patterns of ZnO thin films temperature crystallization between 550 and 600 °C. v1 = 2.17 cm/min; (b) v2 = 4.27 cm/min.

The full-width at half-maximum (FWHM) value (Table 1) of the (002) peak reveals the crystallinity of the film. We can see that the quality of the films improved with the increase of the temperature and reduction of immerse speed. This is because the atoms at lower temperatures do not have enough energy to locate their right position. The critical point exists at 600 °C and low speed.

The grain size (fig.2) was calculated from the XRD patterns using Scherer's equation [32]:

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

Where G is the grain size, λ is the wavelength of X-ray (λ = 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 in degrees; this variations are shown in (Table 1).

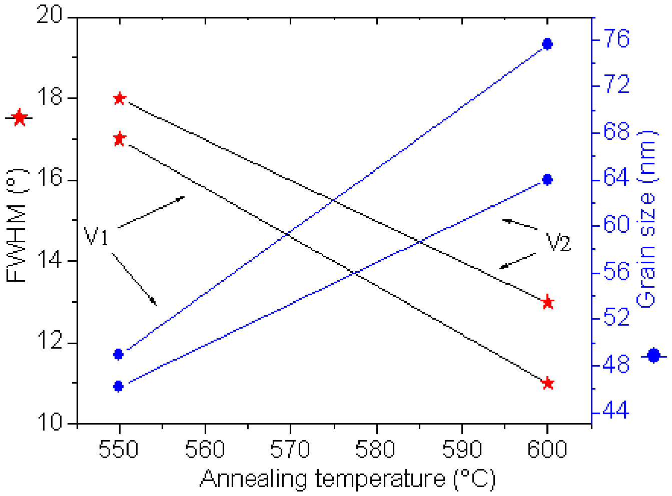

Figure 2. Characterization of the (002) peak of the ZnO thin films as a function of temperature. (a) Grain size and (b) FWHM different speeds of the dip-coating.

TABLE I. STRUCTURAL AND OPTICAL CHARACTERISTICS OF ZNO THIN FILMS OBTAINED AT DIFFERENT ANNEALING TEMPERATURE.

Coating speed Cm/min	**parameters**				
	Temperature (°C)	***Lattice parameter c***	***FWHM (°)***	***G (nm)***	***E_g (eV)***
2.17	550	5.205	13	48.91	3.287
	600	5.204	18	75.60	3.305
4.27	550	5.199	11	46.21	3.312
	600	5.197	17	63.97	3.358

Figure (2) shows the variation of full width at half maximum (FWHM) and grain size as a function of annealing temperature. The FWHM decreases with the increase in annealing temperature from 550 to 600 °C, the increase in peaks size indicating an improvement in the crystallinity of the films. Moreover, the decrease in FWHM with annealing temperature implies an increase in grain size. Crystallite size increases with increase in annealing temperature. The high qualities indicate in low speed which stabilization of atoms. The increase of annealing temperatures is in favor to the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favorable positions, resulting in the enhancement of the crystallinity and c-axis orientation of ZnO thin films.

Figure (3) shows the optical transmission spectra of ZnO thin films as a function with dip-coating speeds at 600 °C. As can be seen, a region of strong transparency is located between 400-800 nm. The value of the transmission is about 60-80 %, and 380-400 nm is the region of the absorption edges in the layers due to the transition between the valence band and the conduction band (Inter-band transition). We are noting that the speed effect is clearly observed in the layer quality.

The absorption coefficient α of ZnO thin films was determined from Transmittance measurements by the following equation [33]:

$$A = \alpha\, d = -\ln T \qquad (2)$$

Where T is the normalized transmittance and d is the film thickness. These absorption coefficient values were used to determine photon energy (optical energy gap). The photon energy (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression [34]:

$$(\alpha h\upsilon)^2 = B(h\upsilon - E_g) \qquad (3)$$

Where B is a constant, E_g is the energy band gap (Table 1) of the semiconductor; is determined by extrapolating the straight line portion of the spectrum to

$$(\alpha h\upsilon)^2 = 0$$

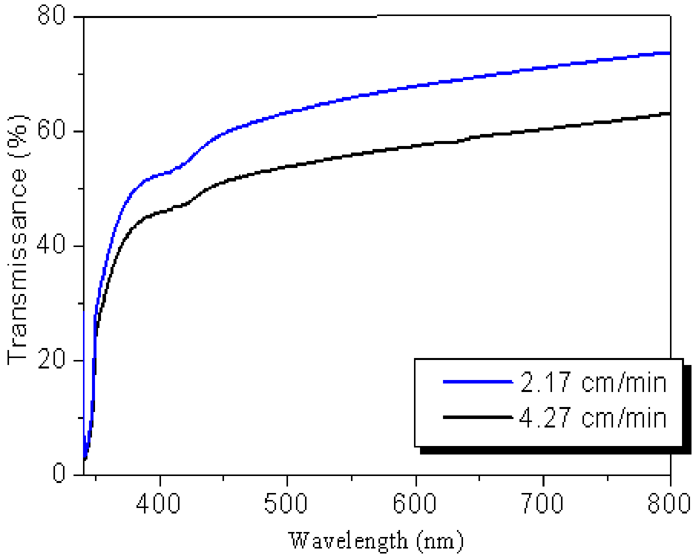

Figure 3. transmission spectra of ZnO thin films at 600 °C.

Figure (4) shows the typical variation of the Band gap energy E_g as a function of speed is demenstrated in (Table 1). We have obtained increases of the optical gap energy with increasing the speed, which may be attributed to the similar ionic radius between O^{2-} and Zn^{2+}. We find that the optical gap and transparency dependence of the speed of dip-coating and crystallization temperature.

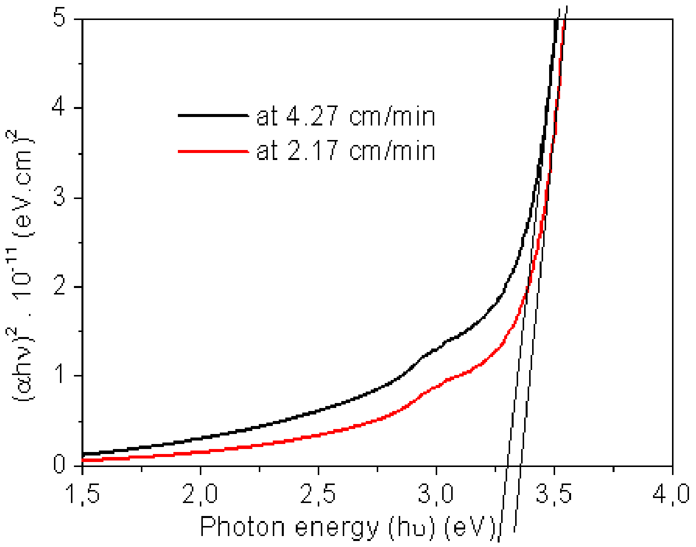

Figure 4. variation optical gap energy at 600 °C.

IV. CONCLUSIONS

In conclusion, highly transparent ZnO thin films have been fabricated on glass substrate by dip-coating were formed at 600 °C. The structural and optical properties were investigated, all the films are nanocrystalline structure wurtzite and (002) oriented. The grain size increased from 64 to 75 nm. The average transmittance is about 70-80 %, in the visible region, and the band gap energy increased from 3.305 to 3.358 eV, which may be attributed to the similar ionic radius between O^{2-} and Zn^{2+}. The decreases of the lattice parameter c are attributed to the decrease of the defects. In this study the ZnO thin films are annealed at 600 °C and deposited in low speed.

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Said Benramache was born in Algeria in 1981. He obtained his Engineer and his Magister degrees in materials science in 2005 and 2008 respectively. He works now towards PhD degree in physic. His research interests are on cell solar and photovoltaic. He is currently an assistant Lecturer, in Materials Science Department, Biskra University, Algeria.
e-mail: saidzno@yahoo.fr