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Influence of the solution flow rate on the properties of zinc oxide (ZnO) nano-crystalline films synthesized by ultrasonic spray process

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ABSTRACT

In this paper, ZnO nano-crystalline films were synthesized onto hot glass substrates by ultrasonic spray pyrolysis technique. The solution contains zinc acetate dihydrate ($ZnC_4H_6O_4{\cdot}2H_2O$) mixed with methanol. The influence of the solution flow rate on the properties of ZnO was investigated. All films deposited were characterized by various techniques such as X-ray diffraction to determine the films structure, the scanning electron microscopy (SEM) for the morphology of the surfaces and UV–visible spectroscopy to determine the optical proprieties. The results show that ZnO nano-crystalline films have a hexagonal structure at type wurtzite. The crystallite size was varied between 36.79 and 20.11 nm, the optical transmission around 80% in visible rang and the optical band gap is varied from 3.274 to 3.282 eV.

1. Introduction

ZnO is one of the promising II–VI semiconducting materials for optoelectronics and photovoltaic applications. It is a non-toxic, n type and direct wide band gap material (E_g = 3.3 eV at 300 K) with good electrical conductivity and high optical transparency in the visible and near infrared region. [1,2]. ZnO thin films are preferred as inexpensive and stable transparent conducting oxide materiel (TCO) in solar cells as anti-reflection coatings, liquid crystal displays, surface acoustic wave devices [1,3], gas sensors [4,5],and field effect transistors [6,7]. The spray pyrolysis method is one of the many techniques, which is widely used for the deposition of ZnO thin films, it is simple, flexible, low cost and applicable for large-scale production in short time. This technique can offer expertise solution to the surface engineering research and industrial applications. It is well known, that the growth steps of film such as nucleation, condensation and subsequent growth are strongly related and largely influenced by used technique and deposition parameters. In the case of spray pyrolysis, the two major parameters which are widely influenced on film growth steps are substrate temperature which controls the particles energy and motion onto substrate and the spray's volume flux arriving to the substrate surface which is controlled by a parameter namely solution flow rate.

In present work, ZnO nano-crystalline films have been deposited by ultrasonic spray pyrolysis. Solution flow rate effect on structural, morphological, optical and electrical properties of ZnO films have been investigated.

2. Experimental details

ZnO thin films were prepared by spraying a solution containing a 0.1 M of zinc acetate dihydrate $ZnC_4H_6O_4{\cdot}2H_2O$ in absolute volume of methanol CH_3OH as a solvent on heated glass substrates using ultrasonic spray process. The substrates were chemically cleaned before the deposition. In all depositions the substrates were heated at temperature equals to 350 °C. The distance from the spray nozzle and substrate was fixed at 5 cm. The films were prepared in atmospheric pressure for 7 min as a time of deposition. The elaborated films were characterized in order to study their structural, morphological and optical properties. The structure of the films was analyzed by X-ray diffraction using D8 ADVANCE diffractometer with a Cu K-α radiation (λ = 0.15405 nm). The surface morphology was analyzed by a scanning electron microscopy (JSM6301F). The optical transmittance spectra were obtained using UV–visible spectrophotometer by using glass as reference in a wavelength range of 200–1200 nm.

3. Results and discussion

3.1. Structural properties

To investigate the crystalline quality of the ZnO thin films with various values of solution flow rate, XRD analysis is carried out and the results are shown in Fig. 1. The XRD patterns of the films

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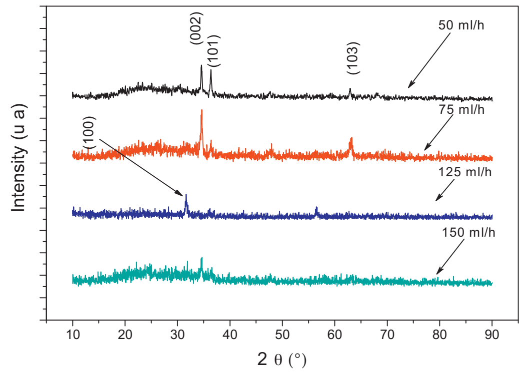

Fig. 1. The XRD pattern of ZnO thin films.

indicate that the ZnO thin films have a hexagonal structure type wurtzite corresponding to the JCPDS data card (36–1451) [8] with cell parameters $a = 0.324$ nm and $c = 0.518$ nm. It can be seen at 125 ml/h flow rate the preferential orientation of the crystallites changed from the conventional c-axis (0 0 2) orientation to the (1 0 0) orientation. The reason as to why the change of the preferred orientation took place could be explained by the oxygen content in the film [9]. When the solution flow rate equal to 150 ml/h, the intensity of (0 0 2) peak is lower than other samples. It can be explained by presence an amorphous phase in film network due to the increasing of droplets number with high velocity. In this case, the films have low cristallinity.

The crystallite size (D) of the ZnO films was calculated using the classical Scherrer formula given by [10]:

$$D = \frac{k\lambda}{\beta \cos\ \theta} \tag{1}$$

where, the constant k is the shape factor (usually equal to 0.9), λ is the wavelength of X-ray, θ is the Bragg's angle and β is the full width of the half maxima (FWHM). It is well known that the crystallite size measured by this method is usually less than the actual value. This is the consequence of internal stress and defects in deposited thin films [11]. The variation of average grain size with solution flow rate is illustrated in Fig. 2. The lattice stress in the ZnO thin films is calculated from the following relation:

$$\sigma = \left[\frac{2c_{13}^2 - (c_{11} + c_{12})c_{33}}{c_{13}}\right]\left(\frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}}\right) \tag{2}$$

Where, c_{bulk} is the unstrained lattice parameter of ZnO equals to 0.5206 nm, c_{film} is the lattice parameter of the strained films calculated from X-ray diffraction data and $C_{11} = 209.7$ GPa,

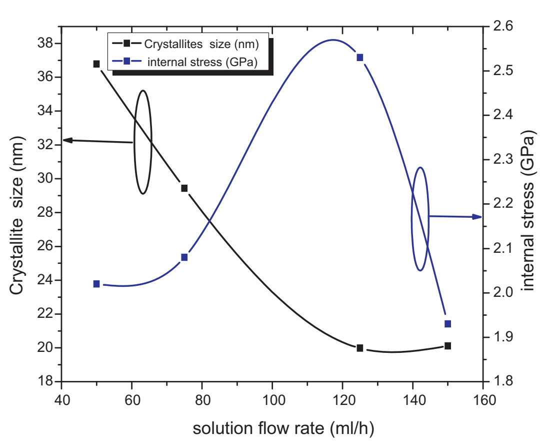

Fig. 2. Crystallite size and internal stress as function of solution flow rate.

$C_{12} = 121.1$ GPa, $C_{13} = 105.1$ GPa and $C_{33} = 210.9$ GPa are the stiffness constants of bulk ZnO. The estimated values of stress σ in the films grown at different solution flow rate are shown in Fig. 2. The positive values of estimated stress for the films indicate that the lattice constant c is lower than the unstressed bulk sample. The positive sign indicates that the films are in a state of tensile stress. It is well known that the tensile stress is likely responsible of resulting from the oxygen vacancies which exist in ZnO thin films. However, the compressive stress may be due to zinc interstitials [12]. The obtained films have a polycrystalline nanostructure; the obtained crystallite size is ranged from 36.79 to 20.11 nm. As seen that the average grain size is reduced with increasing of solution flow rate. It could be explained by increasing of stress due to the rise of internal strain in the formed crystallites. The increase of the stress can be accounted by increasing of solution particles number, which creates defects in the film network. Above 125 ml/h flow rate, we noticed a decrease of stress and an increase in the crystallite size; this can be due to the change in growth direction at this flow rate.

3.2. Morphological properties

The SEM analysis of the ZnO thin films was done to study surface morphology. The SEM images of ZnO thin film synthesized at substrate temperature equal to 350 °C with solution flow rate of 50 ml/h, 75 ml/h, 125 ml/h and 150 ml/h (Fig. 4). The SEM images show that ZnO thin films synthesized for a solution flow rate equals 50 ml/h exhibit a smooth and uniform surface (Fig. 4(a)). From the crystallite size curve, this sample has a larger grains than other samples because a few numbers of droplets with low velocity fall onto substrate surface which permit to growth the film with better way. When, we increase the solution flow rate more than 50 ml/h the film surface changed to the granular surface and the grain size decreases due to the increasing of the velocity and numbers of droplets (Fig. 4(b) – (d)). In this case, the nucleation step was fast in the film which done a film with low crystallinity.

The cross sectional images show that the film with a solution flow rate equals 50 ml/h grow parallel to the substrate surface. When, we increase the solution flow rate more than 50 ml/h, the growth has been changed from parallel to perpendicular shape due by the increasing of droplets velocity. Furthermore, the thickness of ZnO thin films increases with increasing the solution flow rate.

3.3. The deposition rate

The deposition rate of our samples was calculated by division the film thickness on the time of deposition. The experimental results show that deposition rate increases with increasing the solution flow rate (Fig. 3). This increase of deposition rate could be accounted by increasing of the solution volume sprayed onto substrate surface due to rise in the solution flow rate [13].

3.4. Optical properties

The transmittance spectra of ZnO thin films elaborated at 350 °C have shown in Fig. 5. The optical transparency equal to 80% in visible rang.

The optical band gap of ZnO thin films was calculated by the following expression:

$$(\alpha h\upsilon)^2 = A\left(h\upsilon - E_g\right)^{\frac{1}{2}} \tag{3}$$

where, α is absorption coefficient, A is the constant independent of photon energy ($h\upsilon$), h is the Planck constant and E_g is the energy band gap of the semi- conductor equals the energy which provide an electron; in order to do a direct transition between valence and

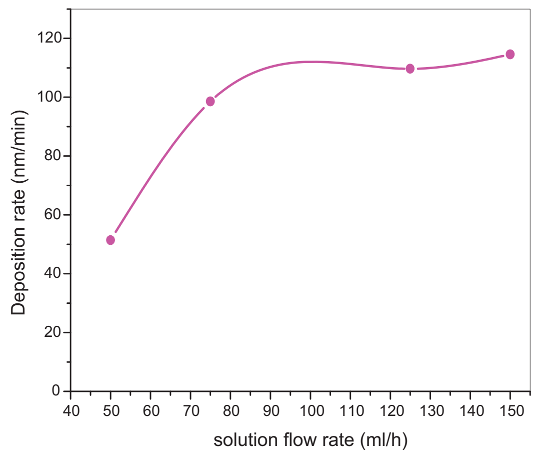

Fig. 3. Deposition rate as function of solution flow rate.

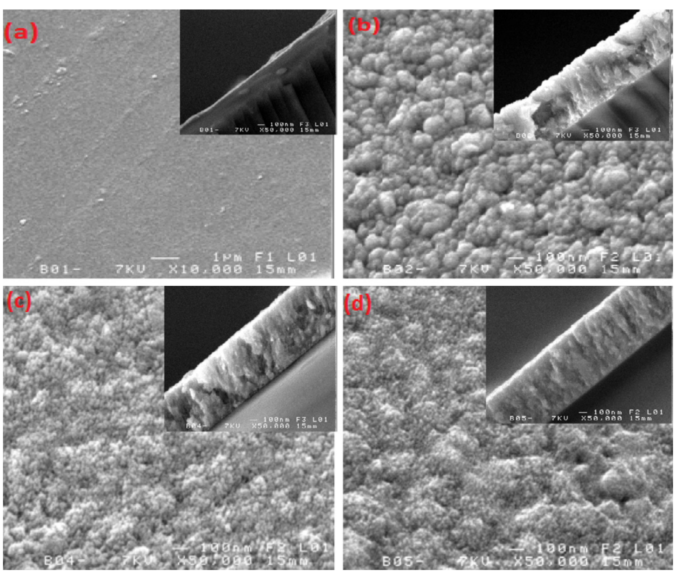

Fig. 4. The SEM images for our samples of ZnO thin films prepared at different values of solution flow rate: (a) 50 ml/h, (b) 75 ml/h, (c) 125 ml/h and (d) 150 ml/h.

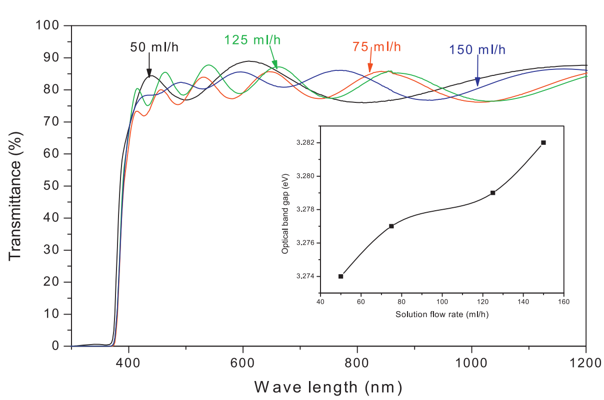

Fig. 5. Transmittance spectra and optical band gap of ZnO thin films as function of solution flow rate.

conduction bands. The value of optical band gap can be found by extrapolation of the linear region to $(\alpha h\upsilon)^2 = 0$ [14].

The optical band gap energy increases with increasing the solution flow rate (Fig. 5). It could be explained by decreases of the crystallite size [15,16] and increases of film thickness [17].

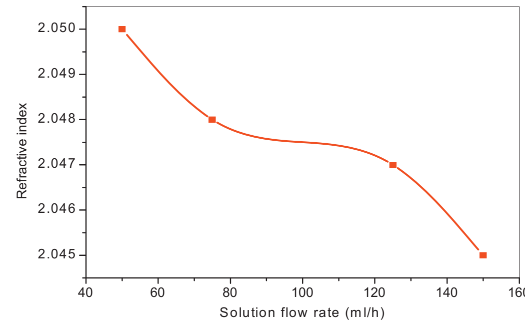

Fig. 6. Refractive index of ZnO thin films as a function of solution flow rate.

Table 1
The resistivity of ZnO thin films at different solution flow rate.

Solution flow rate (ml/h)	Crystallite size D (nm)	Resistivity ρ (Ω cm)
50	36.79	1.59×10^{-2}
75	29.44	2.6×10^{1}
125	19.97	2.7×10^{1}
150	20.11	4.3×10^{1}

The refractive index of ZnO thin films elaborated at different solution flow rate is calculated using Ravindra relation [18,19] given by:

$$n = 4.08 - 0.62 \times E_g \quad (4)$$

The values of refractive index of our samples decrease when the solution flow rate increases (Fig. 6). This decrease is attributed to increase of grains boundaries due to the decrease of the crystallite size [20].

3.5. Electrical properties

The electrical resistivity of ZnO thin films elaborated at different values of solution flow rate is illustrated in Table 1. As seen the resistivity increases with increasing the solution flow rate. This increase in electrical resistivity could be explained by reduction of crystallite size which increases the probability of grain boundary scattering [21].

4. Conclusion

In summary, we have grown ZnO thin films using ultrasonic spray at different values of solution flow rate. We found that the films are polycrystalline. The crystallite size decreases with increasing the solution flow rate. The optical transparency of our films in visible rang depending on solution flow rate.

The optical band gap increases with the solution flow rate. Finally, we conclude that the solution flow rate is the interesting factor for control the quality of the thin films deposited by ultrasonic spray.

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