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# The Effect of The Solution Flow Rate on The Properties of Zinc Oxide (ZnO) Thin Films Deposited by Ultrasonic Spray

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**Abstract.** In this work, we used a system based on ultrasonic spray pyrolysis technique. By witch, we have deposited thin films of zinc oxide (ZnO) with the variation of solution flow rate from 50 ml / h to 150 ml / h, and set other parameters such as the concentration of the solution, the deposition time, substrate temperature and the nozzle -substrate distance. In order to study the influence of the solution flow rate on the properties of the films produced, we have several characterization techniques such as X-ray diffraction to determine the films structure, the scanning electron microscopy SEM for the morphology of the surfaces, EDS spectroscopy for the chemical composition, UV-Visible-Nir spectroscopy for determination the optical proprieties of thin films.The experimental results show that: the films have hexagonal structure at the type (wurtzite), the average size of grains varies from 20.11 to 32.45 nm, the transmittance of the films equals 80% in visible rang and the band gap is varied between 3.274 and 3.282 eV, when the solution flow rate increases from 50 to 150 ml/h.

## INTRODUCTION

ZnO is one of the promising II-VI semiconducting materials for optoelectronics applications. It is a non-toxic, n type, direct wide band gap material (Eg = 3.3 eV at 300 K) with good electrical conductivity and high optical transparency in the visible and near-infrared region. Moreover, it offers extreme stability under harsh environmental conditions such as hydrogen plasma, high energy radiation, wet electro chemical etching and mechanical wear-tear; which makes it more suitable for space applications [1, 2].

ZnO thin films are preferred as inexpensive and stable transparent conducting oxide (TCO) and antireflection coatings in solar cells, sensor devices, liquid crystal displays, heat mirrors and surface acoustic wave devices [1,3]. Furthermore, ZnO films also find use in gas sensors [4, 5], ultraviolet laser and in optoelectronics such as light emitting diodes, photo-detectors, transparent thin film transistors, field emitters and field effect transistors [6,7].

The spray pyrolysis method is widely used for deposition of ZnO films, as 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.

## EXPERIMENTAL PROCEDURE

ZnO thin films were prepared by spraying a solution containing a 0.1M of zinc acetate dehydrate $ZnC_4H_6O_4$ $2H_2O$ in absolute volume of methanol $CH_3OH$ as a solvent on heated glass substrates using ultrasonic spray process. The glass substrates were chemically cleaned before the deposition. In all depositions the precursor solution was sprayed onto hot substrate ($T_S = 350$ °C) which was at a distance of 5 cm from the spray nozzle to the substrate in atmospheric pressure for 7 min as a time of deposition. In this study, we have prepared four samples with varying the solution flow rate from 50 ml/h to 150 ml/h. Then we will study the structural, morphological and optical proprieties of the film elaborated.

The structure and morphology of the films were analyzed by X-ray spectroscopy on a D8 ADVANCE Diffractometer using a Cu Kα radiation (λ=1.5405 A), JOEL model JSM6301F a scanning electron microscopy, respectively, the optical transmittance spectra were obtained using UV–VIS-Nir spectrophotometer, these measurements were performed using glass as reference in a wavelength range of 200–1200 nm.

## RESULTS and DISCUSSION

### 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 there is an increase in deposition rate when we increase the solution flow rate (Fig.1 (a)). This increase in deposition rate can be accounted for increase in spray volume flux over substrate surface due to rise in the solution flow rate [8].
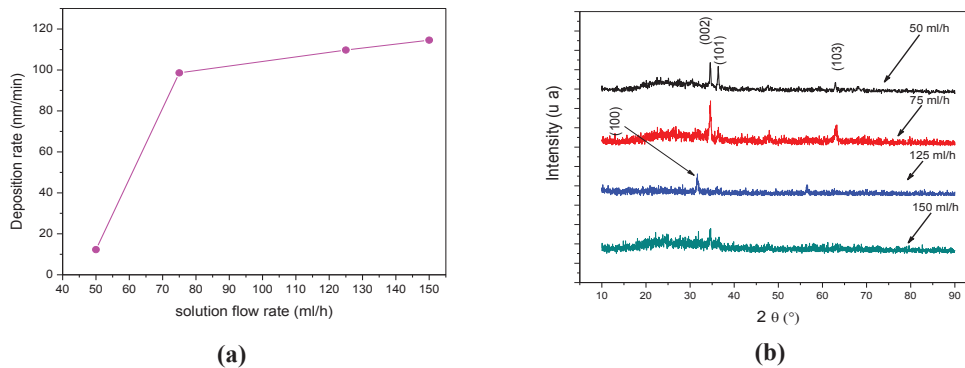


**FIGURE 1.** (a) Deposition rate as function of solution flow rate. (b) XRD patterns of ZnO thin films prepared at various solution flow rate.

# 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(b).The XRD patterns of the films indicate the existence of a ZnO single phase with a hexagonal wurtzite structure corresponding to the JCPDS data card (36-1451) [9]. For the solution flow rate was more than 50 ml/h the films are polycrystalline and the crystallites have oriented preferentially along to the plane (002) perpendicular to the substrate. But, when the solution flow rate equals 125 ml/h the preferential orientation of the crystallites changed from the conventional c-axis (002) orientation to the (100) orientation. The reason as to why the change of the preferred orientation took place could be explained by the oxygen content in the film [10].The mean average grain size (D) of the ZnO films was calculated using the classical Scherrer formula given by [11]:

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

Where the constant k is the shape factor (usually equal to 0.9), $\lambda$ is the wavelength of X–ray, $\theta$ is the Bragg's angle and $\beta$ is the full width of the half maxima (FWHM). It is well known that the mean grain 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 [12]. There is a decrease of average grain size from 32.45 nm to 20.11 nm with increasing of solution flow rate (Fig.2).This decreases could be explained by increases the number of solution droplets which leads to increase the random deposition.
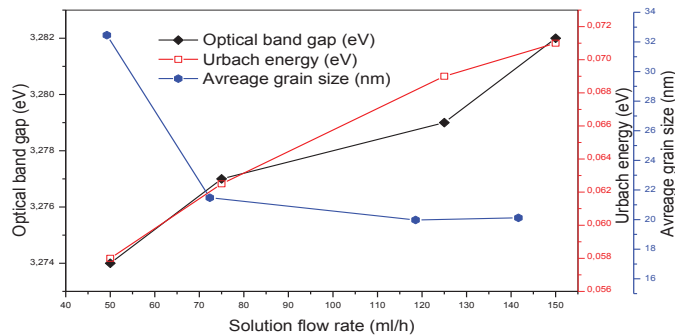


**FIGURE 2.** Variation of average grains size, optical band gap and the urbach energy with solution flow rate.

## Surface Morphology

The SEM analysis of the ZnO film synthesized was done to study surface morphology. The SEM images of ZnO thin film synthesized at $Ts = 350\ °C$ and for the solution flow rate equals to 50 ml/h, 75 ml/h, 125ml/h, 150 ml/h respectively (Fig. 3). The SEM images show that our samples of ZnO thin films have a smooth, non-porous and granular surface. The thickness of our thin films increases with the increasing the solution flow rate.
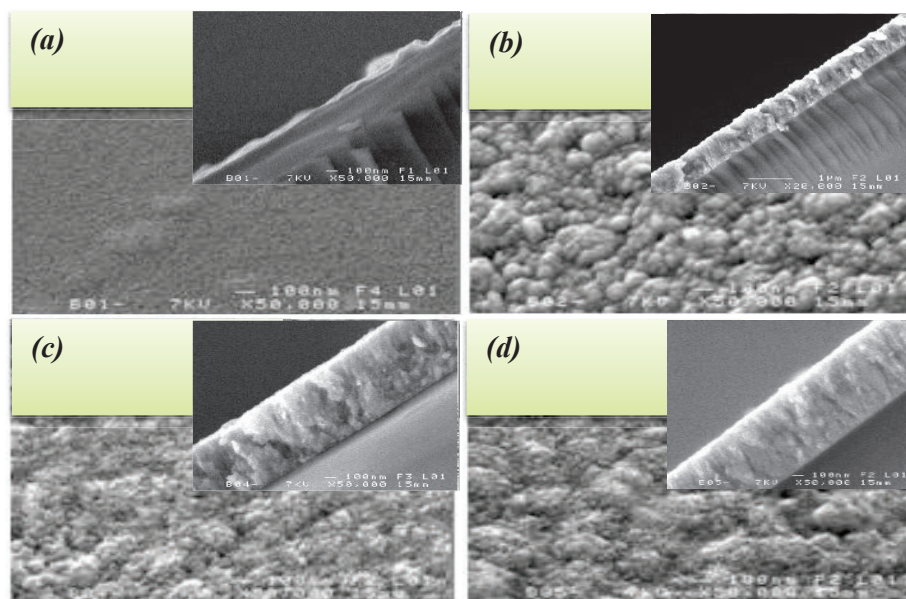


**FIGURE 3.** The SEM images for our samples of ZnO thin films prepared at different values of solution flow rate: (a) 50 ml/h, (b) 75 ml/h, (c) 125 ml/h and (d) 150 ml/h.

## Optical Proprieties

UV-VISBLE-Nir spectroscopy analysis show that the transmittance values of our thin films equal to 80% in visible rang (Fig.4 (a)). The optical band gap was calculated by the following expression:

$$(\alpha h\nu)^2 = A(h\nu - Eg)^{\frac{1}{2}} \tag{2}$$

Where α is absorption coefficient, A is the constant independent of photon energy (hυ), h is the Planck constant and Eg is the energy band gap of the semi-conductor was estimated by assuming a direct transition between valence and conduction bands; by extrapolation of the linear region to $(\alpha h\upsilon)^2 = 0$ [13]. The optical band gap energy was found to increase due to increase in solution flow rate (Fig.2). This increases due by decreases of the average grains size [14, 15] and increases of film thickness [16].The urbach energy were estimated using the following relation:

$$\alpha = \alpha_0 + \exp\left(\frac{h\nu}{E_U}\right) \tag{3}$$

Where, $\alpha_0$ is a constant and $E_U$ is the urbach energy, the urbach energy $E_U$ is calculated from the slope of Ln$\alpha$ versus photon energy (h$\upsilon$). The urbach energy increased with increasing the solution flow rate (Fig.2). This increase could be explained by decrease the average grain size which indicates that the structural disorder and the number of defects in the ZnO thin films increased with increasing the solution flow rate. The refractive index n of our ZnO thin films was calculated using the Ravindra et al relation [17, 18] given by:

$$n = 4.08 - 0.62E_g \tag{4}$$

The values of refractive index of our samples decrease when the solution flow rate increases (Fig.4(b)). This decrease could be explained by decreasing in the average grain size [19].
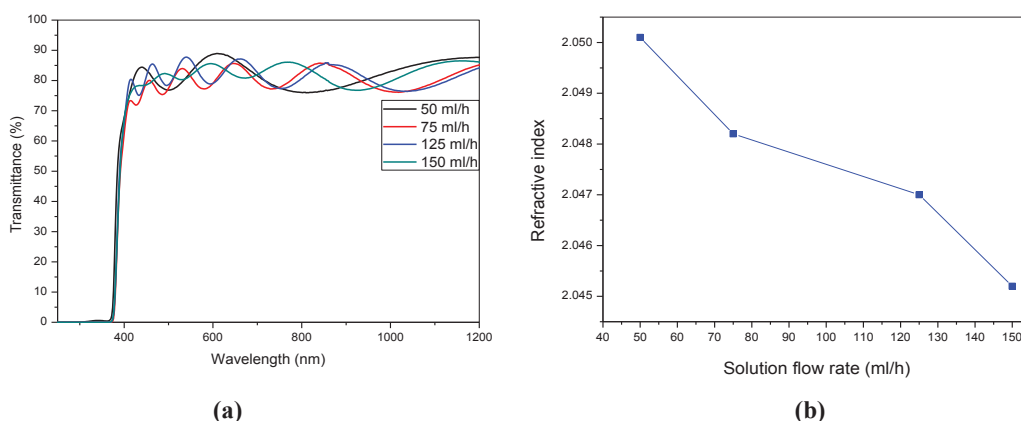


**FIGURE 4.** (a)The transmittance of ZnO thin films with different values of solution flow rate as function of wavelength. (b) Refractive index of ZnO thin films as a function of solution flow rate.

## CONCLUSION

In summary, we have grown ZnO thin films using ultrasonic spray at different values of solution flow rate. We found that the structural, optical and morphological proprieties of our samples depend of 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.

# REFERENCES

1. F. D. Paraguay., W. L. Estrada, D. R. Acosta, E. Andrade, M. M. Yoshida, *Thin Solid Films* **350,** 192-202 (1999).
2.  S. O. Kucheyev, J. S. Williams, C. Jagadish, J. Zou, C. Evans, A. J. Nelson, A. V. Hamza, *Phys. Rev*. **B 67,**  094115 (2003).
3. B. Y. Oh, M. C. Jeong, T. H. Moon, W. Lee, J. M. Myoung, J. Y. Hwang, D. S. Seo, *Jour.Appl. Phys*.  **99,** 124505 (2006).
4. H. T. Wang, B. S. Kang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S. J.  Pearton, *Appl. Phys Lett*. **86**, 243503 (2005).
5. V. R. Shinde, T. P. Gujar, C. D. Lokhande, *Sens. Actuators* **B 120,** 551-559 (2007).
6. Y. C. Kong, D. P. Yu, B. Zhang, S. Q. Feng, *Appl. Phys. Lett*. **78**,  407 (2001).
7. S. E. Demian, *J. Mater. Sci. Mater. Electron*. **5** 360-363 (1994).
8. C. M. Mahajan, M. G. Takwale. *Journal of Alloys and Compounds* **584** 128–135 (2014).
9. Joint, Committee on Powder Diffraction Standards, "Powder Diffraction File", *International Center for Diffraction Data, Swarthmore* **PA**,  card 36–1451, (1988).
10. R.  Jayakrishnan,  K.  Mohanachandran,  R.  Sreekumar,  C.  Sudha,  K .P.  Vijayakumar. *MaterialsScience in Semiconductor Processing* **16** 326–331 (2013).
11. K. Venkateswarlu, A. Chandra, N. Rameshbabu, "X-ray peak broadening studies of nanocrystalline hydroxyapatite by Williamson–Hall analysis", Physica B 405*,* 2010, pp.4256–4261.
12. A. Ashour, M. A. Kaid, N.Z. El-Sayed, A. A. Ibrahim, *Appl. Surf. Sci*. **252**, 7844–7848 (2006).
13. A. Bouraiou, M. S. Aida, O. Meglali, N. Attaf, *Curr.  Appl.  Phys*. **11** 1173–1178 (2011).
14. A. Mosbah, S. Abed, N. Bouhssira, M. S. Aida, E. Tomasella, *Materials Science and  Engineering* **B 129,** 144–149 (2006).
15. M. Caglar, S. Ilican , Y. Caglar, F. Yakuphanoglu , *Applied    Surface   Science* **255** 4491–4496 (2009).
16. T. Prasada, M. C. Santhoshkumar, *Applied  Surface Science*  **255**, 4579–4584 (2009).
17. N. M. Ravindra, V. K. Srivastava*, Infrared Phys*. **19** 603 (1979).
18. M. Mekhnache, L Saad Hamideche, H. Benzarouk, A. Amara , L. Cattin, J. C. Bernède, M. Guerioune, *Superlattices  and  Microstructures* **49**, 510–518 (2011).
19. M. Mazilu, N. Tigau, V. Musat, *Optical Materials*  **34,** 1833–1838 (2012).