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Structural and optical properties of undoped zinc oxide thin films deposited by pneumatic spray pyrolysis technique

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Abstract

ZnO thin films have been prepared on glass substrates at various temperatures 150, 250, 350 and 450°C, using pneumatic spray pyrolysis technique in order to investigate the structural and optical properties of the films. The analysis of DRX diagrams shows that the deposits have a polycrystalline structure with (100), (101) and (002) textured orientation. Electro-optical properties depend on process parameters such as solution concentration and substrate temperature. The UV-Visible spectrophotometer of films confirmed that it is possible to obtain transparent ZnO thin films in the visible region with optical gap energy of approximately 3.2 eV.

Keywords: ZnO thin film, pneumatic spray pyrolysis, XRD diagrams, transmission spectra, band gap energy.

1. Introduction

Zinc oxide (ZnO), a II-VI compound semiconductor with a direct gap (E_g = 3.37 eV at room temperature), has received great interest as a promising candidate for the fabrication of ultraviolet (UV) light-emitting devices [1,2], electro and photoluminescent devices [3-5], also it can be used as transparent electrode in solar cells [6].

ZnO thin films have been deposited by a variety of methods such as r.f. sputtering [6-8], reactive thermal evaporation [9], chemical vapor deposition [10,11], pulsed laser deposition (PLD) [12-14], plasma enhanced CVD [15] and spray pyrolysis [16-18].

The spray pyrolysis technique (SPT) has some advantages compared to other methods. It is quite simple and the required setup is less expensive and more flexible for process modification. Due to the use of less expensive chemicals at air pressure conditions it is attractive from an economical point of view as well [4,17]. Additionally, by using this technique one can produce large area films without the need of vacuum and the produced films can be controlled step by step [19].

In this paper, we describe the effect of deposition parameters on the structural and optical properties of undoped ZnO thin films prepared by spray pyrolysis technique.

2. Experimental details

Spray pyrolysis is basically a chemical process which consists in spraying a solution onto a heated substrate. The controlled temperature of the substrate allows the activation of the chemical reaction between the compounds leading to the formation of the desired thin films. The performances of the deposited material depend on certain number of physical and chemical properties resulting from the conditions of preparation.

Our ZnO films have been deposited onto glass substrates kept at a distance of 25 cm from the spray gun nozzle. These films have been prepared by spraying a 0.025, 0.05 and 0.1 $mol.l^{-1}$ solution of zinc acetate dihydrate mixed with bistilled water. Films with various substrate temperatures situated between 150 and 450°C were obtained; the substrate temperature was cotrolled using a chrome-allumel thermocpouple placed above the substrate.

The optical spectra were recorded by a Shimadzu 3101 PC spectrophotometer. The optical transmittance of the films was measured for wave lengths spanning from 300 to 900 nm. The optical gap was calculated using Tauc's relation. X-ray diffractometer was used to determine the crystallographic structure using the 1.5406 Å wavelength CuK_α ray. The grain size was estimated using Sherrer's formula.

3. Results and discussion

3.1. Structural properties

3.1.a/ Refractive index and porosity

For our ZnO thin films deposited on silicium (111) substrate, we determined refractive index ‘n’ values through the ellipsometry measurements, the porosity ‘P’ of this films is obtained by using Lorentz Lorentz formula [19]

$$P=1-[(n_{film}^2-1)(n_{bulk}^2+2)/(n_{film}^2+2)(n_{bulk}^2-1)] \qquad (1)$$

n_{bulk}: refractive index of ZnO skeleton accepted as 2.008 [20]
n_{film}: refractive index of ZnO films

Figures 1 and 2 represents ‘n’ and ‘P’ values for templates deposited at various temperature substrate with different molarities. It can be seen that the value of the refractive index of our ZnO films deposited using the SPT are in the reasonable range of 1,75 – 2 , which corresponds to that of ZnO bulk. In figure 2, the results can be related to the quality of films, it can be shown that the films deposited at low substrate temperature (below 205 °C) are less dense and have a more porous structure than the films prepared at higher temperature.

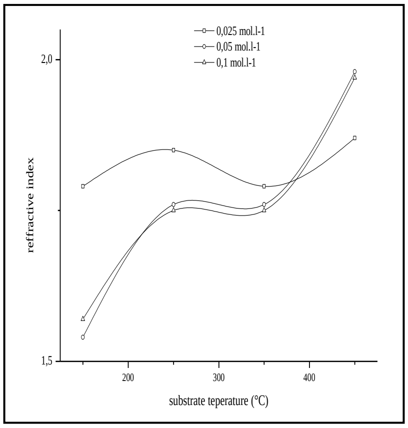


Figure 1: refractive index values of ZnO thin films deposited at various substrate temperature and molarities

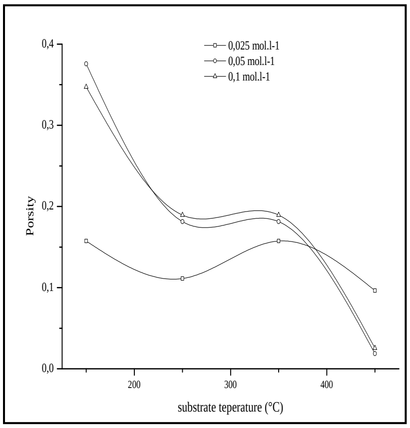


Figure 1: Porosity of ZnO thin films deposited at various substrate temperature and molarities

3.2.b/ X-ray diffraction (XRD)

X-ray diagrams obtained for 2θ scans between 20˚ and 70˚ indicated that all deposited films on the glass substrates were polycrystalline and retained a hexagonal würtzite structure with (100), (101) and (002) textured orientation. As shown in figure 3, when the growth temperature increases, the peaks become more intense indicating an increase in the crystallite size.

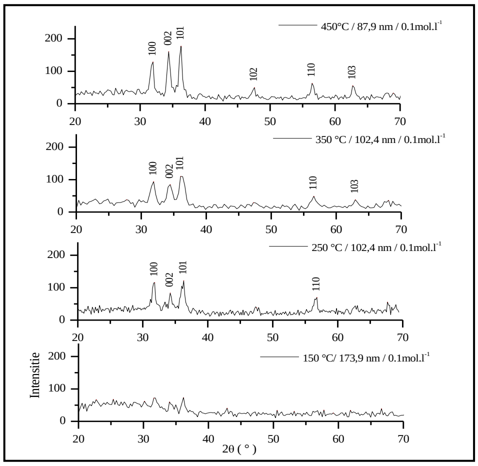


Figure 3: X-ray 2θ scans of ZnO grown on glass substrate at various temperatures with 0.1mol.l^{-1}.

Figure 4 shows that at 350°C, ZnO peaks appear for all solution concentrations from 0.1 to 0.025 mol.l^{-1}.

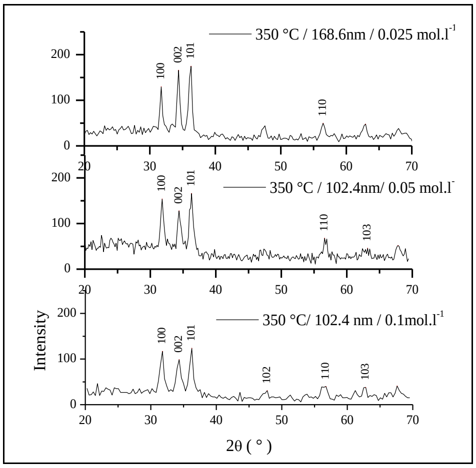


Figure 4: X-ray 2θ scans of ZnO grown on glass substrate at at 350°C with various molarities.

Through these results we can say that, we obtained an amorphous ZnO films at low temperature (150 °C) have a less pure ZnO, more defects and impurities, with the increase of the substrate temperature the quality of our deposits be better when we obtained more pure ZnO thin films due to the high level of thermal decomposition of the compounds spraying.

For each deposits, the mean crystallite size ‘D’ has been calculated from the (002) diffraction peak width using Sherrer’s formula [16,20,21]:

$$D = 0.94\lambda/(\beta_{hkl} \cos\theta_{hkl}) \qquad (2)$$

λ: X- ray wavelength (λCuK_{α} =1.5406 Å);

θ_{hkl}: Bragg diffraction angle;

β_{hkl}: line width at half-maximum.

From figure 5, we can see the dependence of deposition parameters on the crystallite size. These values presented by previous figure are comparable to literature [22].

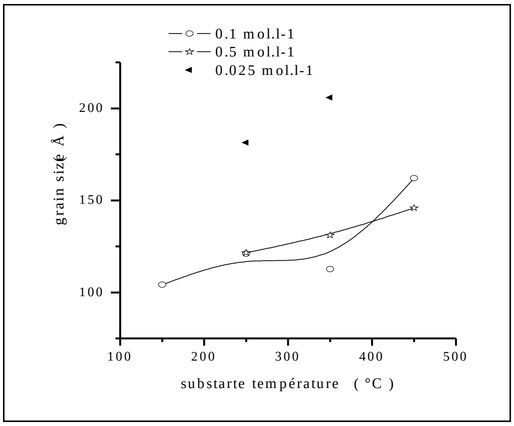
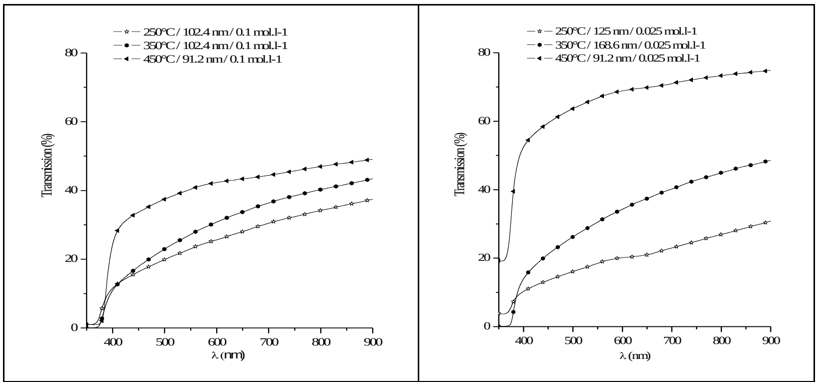


Figure 5: Grain size values of ZnO thin films deposited at various substrate temperatures with deferent molarities.

4. Optical properties

The optical transmission spectra of ZnO thin films are obtained by using a UV-Vis-NIR spectrophotometer. Figure 6 shows that the transmittance of deposits depends on growth conditions. We can see that the transmittance of films increases with the deposition temperature, and at high temperature, it decreases with the molarity.



(a)	(b)

Figure 6. Transmission spectra of ZnO thin films deposited at various substrate temperatures ((a) 350°C,(b) 450°C)

As seen, transmission up to 70% confirms that our films deposited at high temperature have a good quality. The most important feature in the transmission spectra is also the absence of interference fringes in the spectrum of all our films deposited by spray pyrolysis. The sharp fall observed in transmission below 400 nm due to band gap absorption. The band gap 'E_g' for each film is determined by means of graphical method and the absorption coefficient is derived from the transmittance data. We can determine the absorption coefficient as follows [16,17,21]:

$$\alpha(\lambda)=(1/d)\ln(1/T) \tag{3}$$

α: absorption coefficient;
λ : wavelength;
d: film thickness;
T: transmittance of thin film.

For a direct gap such as for ZnO, Tauc's formula can be given by the following expression [16,17,22]:

$$Ah\nu = A(h\nu-E_g)^{1/2} \tag{4}$$

A: constant of proportionality;
hν: energy of the incident photon.
E_g: gap energy of ZnO thin films.

Figure 7 presents the variation of $(\alpha h\upsilon)^2$ according to the incident energy of a ZnO thin film deposited on glass substrate at 450°C with different molarities, measurements give a value of approximately 3.2 eV.

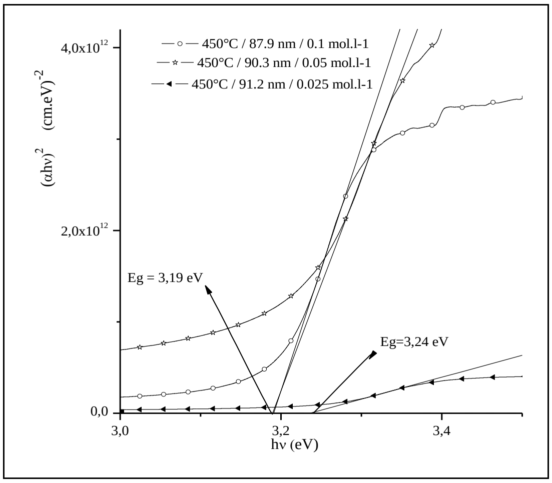


Figure 7. Variation of $(\alpha h\upsilon)^2$ with (hυ) for ZnO thin film deposited at 450°C .

In addition, figure 8 represents the different Eg values of all our ZnO thin films; they found mean value of 3.2 eV is in agreement with results reported by others [17,19].

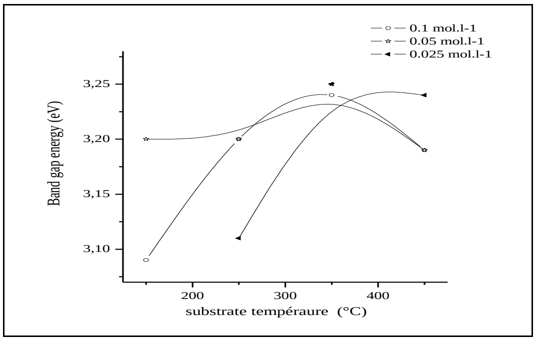


Figure 8. Band gap energy values for ZnO thin films deposited at different substrate temperature.

4. Conclusion:

The results reported in the present paper show that ZnO thin films obtained by spraying an aqueous solution of zinc acetate dehydrate onto glass substrate at different substrate temperatures are polycrystalline with (100), (101) and (002) textured orientations, the (002) peak intensity increases with the temperature of deposition. The transmission spectra confirmed that high transparency, good and dense structure can be obtained using high substrate temperature and lower molarities. The ZnO thin films obtained have band gap energy of 3.2 eV.

References

[1] Mingsong Wang, Sung Hong Hahn, Eui Jung Kim, Jae Seong Kim, Sunwook Kim. Thin Solid Films 516 (2008) 8599-8603.
[2] A. Van Djiken, E. A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink. Journal of Luminescence 87-89 (2000) 454-456
[3] S.A. Studenikin, Nickolay Golego and Michael Cocivera. JOURNAL OF APPLIED PHYSICS, VOLUME 84, NUMBER 4.15 AUGUST 1998.
[4] A. Ortíz, C. Falcony, J. Hernández A, M. Garcia, J. C. Alonso. Thin Solid Films 293 (1997) 103-107.
[5] Takashi SEKIGUCHI, Naoki OHASHI and Yoshihiro TERDA. Jpn. J. Appl. P
[6] Z. Zhao, M. Vinson, T. Neumuller, J. E. McEntyre, F. Fortunato and A. T. Hunt, G. Ganguly. Pre print of Poster 4P2. 11 to be presented at 29 th IEEE PVSC New Orleans 20-24th May 2002.
[7] S. H. Jeong, J. W. Lee, S. B. Lee, J. H. Boo. Thin Solid Films 435 (2003) 78-82.
[8] A. Mosbah, A. Moustaghfir, S. Abed, N. Bouhssira, M. S. Aida, E. Tomasella, M. Jacquet. Surface & Coatings Technology 200 (2005) 293-296.
[9] B. D. Yao, Y. F. Chan, and N. Wang. APPLIED PHYSICS LETTERS. VOLUME 81. NUMBER 4. 22 JULY 2002.
[10] A. Umar, S. Lee, Y H Im and B Hahn. INSTITUTE OF PHYSICS PUNLISHING. Nonotechnology 16 (2005) 2462-2468.
[11] Xiang Liu, Xiahua Wu, Hui Cao, and R. P. H. Chang. JOURNAL OF APPLIED PHYSICS, VOLUME 95, NUMBER 6. 15 MARCH 2004.
[12] V. Srikant and D. R. Clarke. J. Appl. Phys. 81 (9), 1 May 1997.
[13] B. J. Jin, H. S. Woo, S. Im, S. H. Bae, S. Y. Lee. Applied Surface Science 169-170 (2001) 521-524.
[14] X. W. Sun, H. S. Kwok. JOURNAL OF APPLIED PHYSICS, VOLUME 86, NUMBER 1. 1 JULY 1999.
[15] Z. Y. Xiao, Y. C. Liu, D. X. Zhao, J. Y. Zhang, Y. M. Lu, D. Z. Shen, X. W. Fan. Science Direct. Journal of Luminescence 122-123 (2007) 822-824.
[16] S.A. Studenikin, Nickolay Golego and Michael Cocivera. JOURNAL OF APPLIED PHYSICS, VOLUME 83, NUMBER 4. 15 FEBRUARY 1998.
[17] D. Zaouk, Y. Zaatar, R. Asmar, J. Jabbour. MICOELECTRONICS JOURNAL 37 (2006) 1276-1279
[18] C. Messaoudi1, S. Abd-lefdil, D. Sayah, et M. Cadene. EUR. PHYS. J. AP 1, 181{184 (1998).
[19] B. J. Lokhande, M. D. Uplane. APPLIED SURFACE SCIENCE 164 (2000) 243-246.
[20] Khedija Bouzid, Abdelkader Djelloul, Noureddine Bouzid, and Jamal Bougdira. PHYS. STATUS SOLIDI A 206, No. 1, 106-115 (2009).
[21] L.Hadjeris, L.Herissi, M.B.Assouar, T.Easwarakhanthan, N.Attaf, J.Bougdira and M.S.Aida. Semicond. Sci. Technol. 24 (2009) 035006 (6pp).
[22] A. Mosbah; S. Abed, N. Bouhssira, M. S. Aida, E. Tomasella. Materials Science and Engineering B 129 (2006) 144-149.