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Improvement of structural and optical properties of ZnO thin films by thermal annealing

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Undoped ZnO thin films were prepared by sol gel method and deposited on ITO substrate using dip-coating technique. The effects of annealing treatment on structural and optical properties were investigated. The starting material was zinc acetate dihydrate, 2-methoxyethanol was used as solvent and monoethanolamine (MEA) as stabilizer. Structural and optical measurements show an important effect of annealing treatment on texture, grain sizes, strains, band gap and refractive index. Annealing at 600°C gives the best structural and optical properties of ZnO thin films.

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1. Introduction

Among the well know semiconducting materials employed in new technologies, zinc oxide held a unique position, not only in chemical industry or in medicine, but also in space engineering and in a variety of functional devices. A renewed interest is especially devoted to zinc oxide in the form of thin film due to its properties such as the large band gap of 3.37 eV, the large exciton binding energy of 60 meV, the low resistivity and the high transparency in the visible range. ZnO thin films found applications in a lot of field such as in solar cells [1-3], surface acoustic wave devices, gas sensors [4], light emission diodes (LEDs) [5, 6] and it is also suitable compound for optoelectronics devices [7, 8]. Such applications require good textured films; these characteristics depend on the deposition method. ZnO films have been deposited by several methods like spray pyrolysis [9], molecular beam epitaxy [10], chemical vapour deposition [11], RF magnetron sputtering [12] and sol gel [13-15]. The sol-gel is very interesting because of its low coast, good film's quality and height surface morphology with an excellent control of depositing parameters and of molecular level composition. It has also the advantage of lower crystallising temperature and gives the greatest possibility to prepare thin films for technological applications. Moreover, the dip coating technique is interesting because the film thickness and quality can be controlled easily.

Refractive index is one of the fundamental properties for an optical material, because it is closely related to the electronic polarization of ions and the local field inside materials. The evaluation of refractive indices of optical materials is considerably important for the applications in integrated optic devices, such as switches, filters and modulators ...etc. Where, refractive indices are the key constants for device design [12].

It is possible to determine optical constants, such as refractive index, absorption coefficient, and dielectric constant by analyzing transmittance spectrum [16–18]. Senadım et al. [19] investigated the annealing effects on the properties of ZnO films prepared by pulsed filtered cathodic vacuum arc deposition. They found that the refractive index of ZnO films increases with increasing annealing temperature from 200 to 600 ◦C. However, few works were reported on the effects of annealing temperature above 600 ◦C on the optical constants of ZnO film.

In the present work we, have investigated the influence of thermal treatment on structural and optical properties of ZnO thin films pre-heated at low temperature. The films were then deposited on highly cleaned ITO substrates by dip coating technique. The effects of temperature on film orientation and crystallite sizes are investigated. The evolution of strains, lattice parameters, band gap and refractive index were also studied.

2. Experimental

Zinc acetate dihydrate was mixed with 2-methoxyethanol at room temperature, when the solution turned milky an equimolar amount of MEA was added drop by drop to obtain a clear and transparent solution after stirring at 60 °C for 2h, the final solution concentration was 0.34 M. The films were deposited on ITO substrates which were cleaned in distilled water and boiling acetone. The films were then deposited by dip coating technique with a speed level of 4.6 cm/min. The obtained films were preheated at 250 °C for 15min, the stage of depositing and preheating was repeated 10 times to reach a thickness of 230 nm. The films were heated at 450-550 and 600 °C for 1h.

Films structure was analyzed with X-ray diffraction by a Bruker D8 Advance diffractometer (λ= 1.502 Å). The thickness of the films was measured using profilometer. Optical properties were analyzed using UV-Visible spectrophotometer (Shimadzu, UV-3101) and Jobbin Yvon Horriba ellipsometer.

3. Results and discussion

3.1 Structural properties

Fig. 1 shows X-ray diffraction diagram of ZnO films annealed at 450-550 and 600 °C. All films reveal three peaks corresponding to (100), (101) and (002) plans of hexagonal ZnO wurtzite according to JCPDS file (36-1451). As can be seen in this figure, the film annealed at 450 °C shows very weak peaks with no preferred orientation.

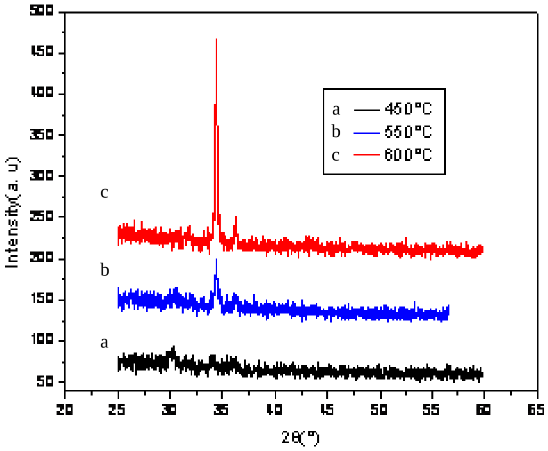

Fig. 1. XRD diagram of ZnO thin films annealed at 450, 550 and 600 °C.

According to Suwanboon [20] when the pre-heating temperature is lower than 300 °C the film had a random preferential growth because the complete vaporization of solvents and thermal decomposition of precursor did not occur at pre-heating stage but at post-heating one. So it may be assumed that at such annealing temperature the thermal energy is not enough for the structural relaxation and texture of the film.

On the contrary, when the temperature exceeds 450 °C, the films exhibit preferred orientation along c axis according to (002) plane, this one grows rapidly when annealing at 600 °C. This result can also be explained by considering the minimization of the surface free energy of each crystal plane. In this case the thermal energy necessary for relaxation and crystallization is reached and the films have highly preferred orientation along c-axis perpendicular to substrate surface.

The crystallite sizes of ZnO films were estimated using Scherer's formula (1) [21]:

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

Where: D is the crystallite diameter,

λ is the wavelength,

θ is the Bragg's angle,

B is the width at half maximum (FWMH)

Table 1 presents the average crystallite sizes of the films annealed at 450-550 and 600 °C. We note that the grain sizes increase with increasing annealing treatment indicating a better films cristallinity.

Table 1. Crystallite sizes calculated from XRD measurements for ZnO thin films

Temp. (°C)	2θ(°)	width	hight	D (nm)	**D**$_{moy}$ (nm)
450	30.125	0.38916	10.152	21.145	33.914
	34.038	0.69286	12.942	11.994	
	36.062	0.12181	5.7862	68.604	
550	30.420	0.54755	9.7082	15.039	21.466
	34.382	0.33506	37.760	24.824	
	36.166	0.34068	13.128	24.536	
600	31.744	0.19385	13.017	42.616	38.006
	34.396	0.20091	221.86	41.402	
	36.219	0.27866	20.790	30.002	

According to the values of lattice parameters given in the JCPDS file 36-1451 (a_0=3.24982, c_0=5.20661) we have calculated the cell parameters of the films using XRD spectra and the following relation:

Table 2 summarizes the calculated lattice parameters and strain using the following relation:

Where:

$$e_{zz} = \frac{c_0 - c}{c_0} \qquad (2)$$

and

Cij are the elastic constants of zincite.

C_0 the strains free lattice parameter (JCPDS file 36-1451).

Table 2. Lattice parameters and strain values for ZnO thin films

Temp. (°C)	a	c	ζzz	C33 (couche)	σ
450	3.421	5.262	1.06	126	-394.58
550	3.389	5.211	0.08	29.66	-91.34
600	3.250	5.209	0.04	25.10	-77.004

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + k^2 + hk) + l^2 \frac{a^2}{c^2}}} \qquad (3)$$

According to the estimation of extensive strains given in table 2, we can see that the greatest value belongs to the film annealed at 450 °C. This result is due to the stress induced by the random crystallization which is in agreement with the XRD spectrum. On the other hand, the film annealed at 600 °C exhibits the lowest strain value indicating a good crystallinity.

3.2. Optical properties

Fig. 2 shows the transmittance spectra of the films annealed at 450-550 and 600 °C. The films present high transmittance in the visible region of 90%.

$$C_{33}^{film} = \frac{0.99 C_{33}^{cristal}}{(1 - e_{zz})^4}$$

$$\sigma = \left[2C_{13} - \frac{(C_{11} + C_{12}) C_{33}^{film}}{C_{13}} \right] e_{zz} \qquad (4)$$

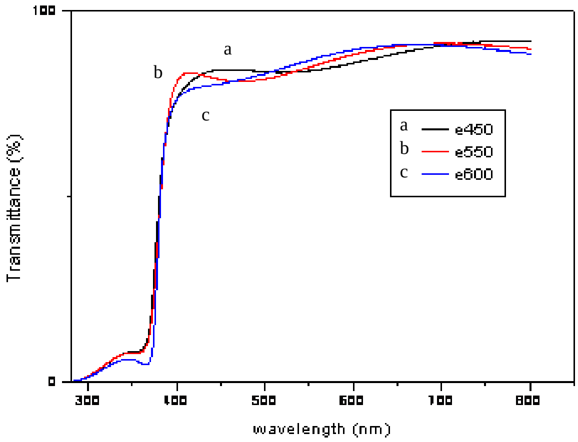

Fig. 2. Transmittance spectra of ZnO films annealed at 450, 550 and 600 °C.

In order to calculate the optical band gap, the dependence of $(\alpha h\nu)^{1/2}$ versus photon energy was plot and shown in Fig. 3. Optical band gap was obtained by extrapolation. The different results are given in table 3.

Table 3. Optical band gap and refractive index of ZnO thin films

Temperature (°C)	450	550	600
Gap (eV)	3.376	3.366	3.346
Refractive index	1.842	1.942	2.049

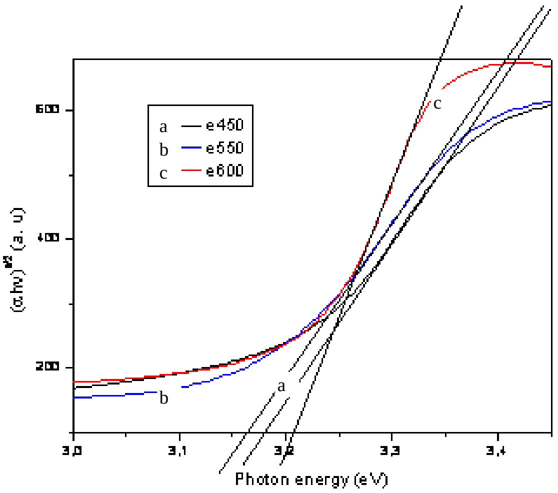

Fig. 3. plot of $(\alpha h\nu)^{1/2}$ versus photon energy of ZnO thin films annealed at 450, 550 and 600 °C.

We notice that the gap exhibits slight blue shift with increasing annealing temperature; this shift is probably due to the changes of ZnO film quality with increasing temperature. The film annealed at 600 °C presents the smallest gap and it is expected to have the best quality with the lest defects.

Table 3 gives also the values of refractive index of the films. It is worth noting that the refractive index increases with increasing heating temperature from 450°C to 600°C. This result can be explained by the increase of films densification with increasing temperature.

Fig. 4 represents the absorption coefficient curve determined from the following relation:

$$T = \exp[-\alpha(\lambda) d] \qquad (5)$$

where T is the transmittance, d the thickness and α is the absorption coefficient of the ZnO thin film.

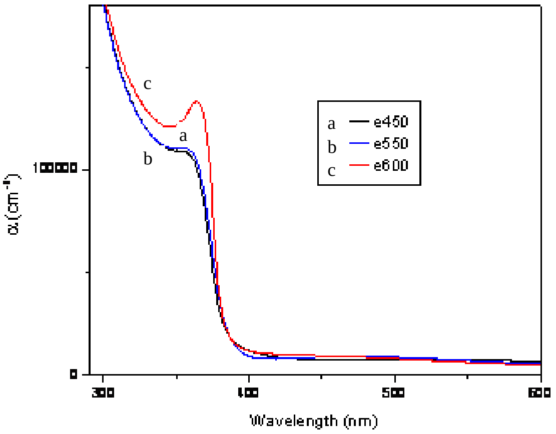

Fig. 4. Absorption spectra of ZnO films annealed at 450, 550 and 600 °C.

We note that the films are transparent in the visible region and have a strong absorption in the near ultra-violet with the emergence of an exitonic absorption band.

Fig. 5 shows the Urbach plots of the ZnO thin films, it is the plot of In [α (λ)] versus photon energy and it represents the width of the band tail. We remark that Urbach curve increases with increasing temperature.

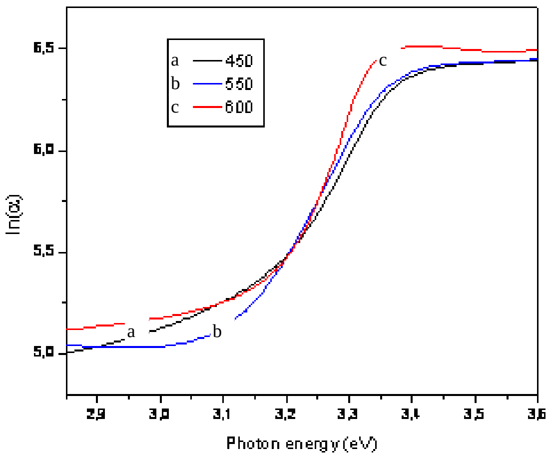

Fig. 5 Urbach plot of ZnO thin films annealed at 450, 550 and 600 °C.

The extinction coefficient shown in Fig. 6 was calculated from the following formula:

$$K(\lambda) = \frac{\alpha(\lambda)\lambda}{4\pi} \quad (6)$$

Where K(λ) is the extinction coefficient.

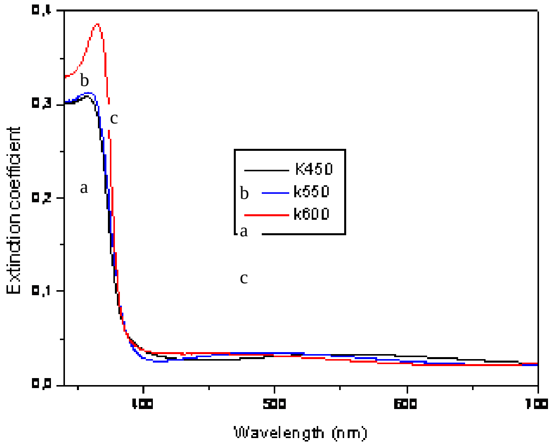

Fig. 6. Extinction coefficient of ZnO films annealed at 450, 550 and 600 °C.

Note that the spectra obtained indicate that the extinction coefficient increases with increasing annealing in the ultraviolet region especially for the film annealed at 600 °C.

4. Conclusion

ZnO thin films were prepared by sol gel method and deposited by dip coating technique on ITO substrates. Structural characterization by XRD shows the formation of ZnO wurtzite structure and proves that highly orientation is achieved under annealing at 600 °C. Optical absorption, crystallite sizes, refractive index and optical band gap of the samples were found to be influenced by thermal treatment since increasing annealing results on good crystallinity by reducing the stress and giving great refractive index making these films suitable to be used optoelectronics.

References

[1] A. Y. Lare, B. A. Godoy, Cattin C. L, A. K Jondo, D. T. Abachi, E. F. R. Diaz, F. M. Morsli, A. K. Napo, E. M. A. Del Valle, F. J. C. Berne`de Applied Surface Science. **255**, 6615 (2009).

[2] S. J. Tarka, M. G. Kanga, S. Parka, J. H. Jangb, J. C. Leeb, W. M. Kimc, J. S. Leea, D. Kima, Current Applied Physics. **9**, 1318 (2009).

[3] O. Lupan, S. Shishiyanu, V. Ursaki, H. Khalla, L. Chow, T. Shishiyanu, V. Sonte, E. Monaico, S. Raileane **93**, 1417 (2009).

[4] P. P. Sahay Journal of Materials Science. **40**, 4383 (2005).

[5] P. Görrn, F. Ghaffari, T. Riedl, W. Kowalsky Solid-State Electronics. **53**, 329 (2009).

[6] D. C. Kim, W. S. Han, B. H. Kong, H. K. Cho C. H. Hong, Physica B: Condensed Matter. **401**, 386 (2007).

[7] Z. Sofiani. B. Sahraoui, M. Addou, R. Adhiri, M. Alaoui, B. Derkowska, W Bala Journal of Applied Physics. **101**(6), 063104(1-5), (2007).

[8] M. Alaoui Lamrani, M Addou, Z. Sofiani, B Sahraoui, J. Ebothe, A. El Hichou, N. Fellahi, J. C. Bernede, R, Dounia, Optics Communications, **277**(1), 196 (2007).

[9] J. Benny, K. G. Gopchandran, P. K. Manoj, P. Koshy V. K. Vaidyan, Bulletin of Material Science. **22**, 921 (1999).

[10] Y. Feng, Y. Zhou, Y. Liu, G. Zhang, X. Zhang Journal of Luminescence. **120**, 233 (2006).

[11] H. Funakubo, N. Mizutani, M. Yonetsu, A. Saiki, K. Shinozaki Journal of Electroceramics. **4**, 25 (1999).

[12] W. Lail, C T. Lee, Materials Chemistry and Physics. **110**, 393 (2008).

[13] G. T. Delgado, C. I. Z. Romero, S.A. M Hernandez, R. C Perez, O. Z. Angel, Solar Energy Materials & Solar Cells. **93**, 55 (2009).

[14] K. R. Murali, Journal of Physics and Chemistry of Solids. **68**, 2293 (2007).

[15] T. Ratana, P. Amornpitoksuk, T. Ratana, S. Suwaboon, Journal of Alloys and Compounds. **470**, 408 (2009).

[16] T. Gungor, B. Saka Thin Solid Films. **467**, 319 (2004).

[17] D. A. Minkov, Journal of physics D: Applied Physics. **22**, 1157 (1989).

[18] S.W. Xue, X.T. Zu, W. G. Zheng, et al. Physica B. **381**, 209 (2006).

[19] E. Senadım, H. Kavak, R. Esen, Journal of physics, Condensed Matter. **18**, 6391 (2006).

[20] S. Suwanboon, Naresuan University Journal. **16**, 173-80 (2008).

[21] A A. Davydov, A. A. Glebkin, Izv Akad Nauk SSSR, Neorg Mater. **8**, 883 (1972).

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