International Journal of Application or Innovation in Engineering & Management (IJAIEM)
Web Site: www.ijaiem.org Email: editor@ijaiem.org, editorijaiem@gmail.com
Volume 2, Issue 7, July 2013 ISSN 2319 - 4847

Investigation the Effect of Thickness on the Structural and Optical Properties of Nano ZnO Films Prepared by d.c Magnetron Sputtering

M.F.A.Alias[1] , R.M.Aljarrah[2] , H.KH.Al-Lamy[3] and K. A.W. Adem[4]

1Physics Department. College of Science, University of Baghdad
P.O.Box. 47162,Jadiriya, Baghdad, Iraq

2Physics Department. College of Science, University of Kufa

3Physics **Department** . College of Science, University of Baghdad, Baghdad, Iraq

4Physics Department. College of Science, University of Baghdad, Baghdad, Iraq

Abstract

The objective of this research is studying the effects of film thickness on the structural and optical properties for nano ZnO films prepared by d.c magnetron sputtering technique on glass substrates. Thicknesses (t) of ZnO thin films were altered by varying the deposition time from 45 min to 90 min (t=75,150,200 and 250) nm and are determined using optical method. The X-ray diffraction spectra show that ZnO thin films are polycrystalline with the hexagonal structure and show a good c-axis orientation perpendicular to the substrate. The most preferential orientation is along the (002) direction for all sputtered deposited ZnO films, in addition another peaks appear at thickness 200 and 250 nm with orientations in (102) and (110) planes. General observations indicate that microstructure parameters, such as grain size, depend sensitively on the thickness of the film. The optical properties of nano ZnO thin films have been investigated by UV/VIS spectrometer and the band gap values are found to be with the range of 3.27 eV to 3.44eV.The ZnO film of all thickness has transmittance over 85% in the visible region, and the refractive index is about 2.1.

Keywords: Nano ZnO films, structural properties, optical properties

1. INTRODUCTION

ZnO is an II-VI transparent conducting oxide touted as a material of choice for short-wavelength optoelectronics [1][2]. This semiconductor has several favorable properties: good transparency, high electron mobility, wide and direct band gap of 3.37 eV at 300 K [3-6] , and as a consequence it absorbs UV radiation due to the band-to-band transitions, strong room temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnO as thin-film transistor and light-emitting diode, and Because of its large excitation binding energy (60 MeV) compared with other semiconductor materials [3]. ZnO has gained substantial interest in the field of semiconductor research, ZnO a high potential for room temperature light emission, and more resistant to radiation, and is multifunctional as it has piezoelectric, ferroelectric, and ferromagnetic properties. Undoped ZnO is usually n-type conductive, which is associated with the presence of native point defects (e.g., oxygen vacancies and interstitial zinc)[7][8] .The crystal structures of ZnO are wurtzit each sub lattice includes four atoms per unit cell and every atom of one kind (group-II atom) is surrounded by four atoms of the other kind (group VI), or vice versa[9]. Many techniques have been employed to produce zinc oxide such as sputtering, metal organic chemical vapor deposition, sol gel, spray pyrolysis, and pulsed laser deposition. Among these techniques, sputtering has proved to be a simple and inexpensive method [10].

Sputtering is one of the most versatile deposition techniques used for the deposition of transparent conducting oxides (TCO). When sputtering is compared to other techniques, sputtering produces layers with higher purity and better-controlled composition. It also produces films with greater adhesive strength, homogeneity and permits better control of film thickness and this technique is easy to deposit materials which could not be easily deposited using other techniques.Researchers have found that the optical properties strongly depend on the thickness of ZnO films so in this paper, we introduce the effect of thickness on the structural and optical properties of ZnO films prepared by d.c magnetron sputtering.

2. EXPERIMENTAL PROCEDURE

Typical conditions for d.c sputtering of materials are: cathode voltage of 1kV, cathode to substrate distance of 3.0 cm and a working pressure of 0.8 Torr .Substrate temperature was varied from room temperature (RT) to about 373 K .

Magnetron cathode and a sufficiently uniform magnetic field are required to confine the electrons near the target surface [9]. This mode of sputtering, known as d.c magnetron sputtering, was also employed in the present study. In general, the structural properties as well as optical properties are strongly dependent on the processing conditions.

The thickness of the films (t) was determined using the optical method:

$t = \lambda\Delta x/2x$ …… (1)

where x is the fringes width, Δx is the fringes shift, and λ is laser wavelength.
The structures of the films were characterized by X-ray diffraction (XRD) with Cu K_α radiation λ = 0.15406 nm. From the peaks position and the integral width at half maximum of the respective peak, the grain sizes of prepared ZnO films were calculated; the average grain size in the c-axis orientation estimated using the Debye-Scherrer relation [10]:

$D_{XRD} = 0.9\lambda / B \cos\theta$…… (2)

where D_{XRD} is the mean particle size, θ is the Bragg diffraction angle and B is the full width at half maximum (FWHM) of the diffraction peak. Distance (d) calculated for all set of films using the Bragg equation [11]:

$d = n\lambda/2\sin\theta$ …….. (3)

Optical absorption data on the deposited films was measured using Shimadzu UV1650PC spectrophotometer to determine the optical absorbance of the films as a function of wavelength at room temperature. A correction for substrate absorption was made by placing an identical uncoated glass substrate in the reference beam.
The optical energy gap (E_g) determined by using Tauc equation [12]:

$(\alpha h\upsilon) = B (h\upsilon - E_g)^r$…… (4)

where B is Tauc constant and hυ is the photon energy, α is the absorption coefficient. For r=1/2 yields linear dependence, which describes the allowed direct transition. The optical energy gap of the film can be obtained by plotting $(\alpha h\nu)^2 \sim h\nu$ and extrapolating the straight line portion of this plot to the energy axis.

The optical behavior of a material is generally utilized to determine its optical constant [refractive index (n), extinction coefficient (k), real and imaginary parts of dielectric constant ($\varepsilon_1$and ε_2)].
The extinction coefficient characterizes absorption of the electromagnetic wave energy in the process of propagation of a wave through a material. The wave intensity (I) after it passes a distance *x* in an isotropic medium is equal to[12]:

$I = I_0 \exp(-\alpha x)$ …… (5)

where I_0 is the intensity at $x = 0$. For many applications, the extinction coefficient k is equal to[12]:

$$k = \frac{\alpha\lambda}{4\pi}$$ …… (6)

where *λ,* is the wavelength. The normal-incidence reflectivity *R* can also be given by[13]:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$ …… (7)

Then the refraction index value can be calculated from the formula [13]:

$$n = \sqrt{\frac{4R}{(R-1)^2} - k^2} - \left[\frac{(R+1)}{(R-1)}\right]$$ …… (8)

The complex index of refraction (n_c) is defined as [12]:

$n_c = n + ik = \varepsilon^{1/2} = [\varepsilon_1 + i\varepsilon_2]^{1/2}$…….. (9)

where *n* is the real refractive index. The optical constants, *n* and *k*, are real, and can be determined from optical measurements. From Equation (10), it follows that [12]:

$\varepsilon_2 = n^2 - k^2$ ..... (10)
$\varepsilon_1 = 2nk$ ……. (11)

3. RESULTS AND DISCUSSION

Fig. (1) shows the XRD for ZnO thin films deposited on glass substrates at different thicknesses (75, 150, 200 and 250 nm). The patterns show that all the films have a peak located at $2\theta \approx 34.4^o$ with hkl (002). In addition another peaks appear at thickness (200 and 250) nm located at $2\theta = 47.4^o$ and 56.58^o with hkl{(102) and (110)} respectively. All set of

films reveal only an intense diffraction peak around 34.4º, which corresponds to (002) of the wurtzite phase of ZnO. This indicates that the growth of all films is highly oriented along c-axis. Table (1) shows all the peaks observed in all films and the standard peaks from JSPDS and its intensities [14].
Our result declared a good coincidence with the reference data and declared that the films have a good crystalline with hexagonal structure and the degree of crystalline increases with increasing the thickness.

The grain size was calculated by Scherer's formula. The values of grain size show in Table (1). This table shows that the grain size of the prepared films at (002) plane films increase from 9.462 nm to 11.8522 nm when the film thickness increased from 50 to 200 nm. Therefore, it is observed that the increased thickness provides a better crystallization for the films.

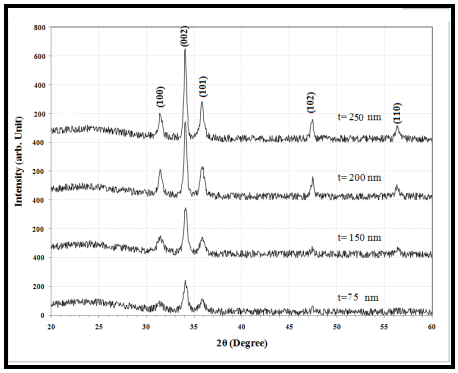


Fig (1). XRD for ZnO thin films deposited on glass substrates at different thicknesses.

Table (1). The experimental and standard values of peaks, intensity and grain size for prepared ZnO thin film at different thickness.

Thick. (nm)	2θ (Degree)	d_{hkl} (Exp.) (Å)	d_{hkl} (Std.) (Å)	hkl	Int (Exp. (a.u.)	Int (Std.)%	FWHM (Deg.)	G.S (nm)
75	31.46	2.841	2.814	(100)	40	57	0.70	11.1
	34.12	2.626	2.603	(002)	200	44	0.48	16.3
	35.86	2.502	2.476	(101)	80	100	0.55	14.3
150	31.46	2.841	2.814	(100)	105	57	0.70	13.1
	34.12	2.626	2.603	(002)	308	44	0.42	18.6
	35.86	2.502	2.476	(101)	110	100	0.55	14.3
200	31.48	2.840	2.814	(100)	151	57	0.47	16.5
	34.1	2.627	2.603	(002)	509	44	0.33	23.7
	35.88	2.501	2.476	(101)	205	100	0.5	15.7
	47.47	1.914	1.911	(102)	130	23	0.31	26.3
	56.35	1.631	1.625	(110)	65	32	0.42	20.2
250	31.47	2.840	2.814	(100)	165	57	0.4	19.4
	34.08	2.629	2.603	(002)	609	44	0.3	26.0
	35.85	2.503	2.476	(101)	235	100	0.47	16.7
	47.42	1.916	1.911	(102)	135	23	0.3	27.2
	56.34	1.632	1.625	(110)	80	32	0.4	21.2

Optical study of ZnO films was carried out in the wavelength range 300–1100 nm at room temperature for the film deposited on glass substrate. Figure (2) shows the transmittance spectra of ZnO thin films with different thickness. It is noticed that all obtained films exhibit a high transmittance over (80%) in the visible region with sharp absorption edge nearly at 360 nm.
The transmittance spectra of the films decrease as film thickness increases, which subsequently increase absorption. The onset of absorption edge for films became less sharp which is due to the fact that bigger crystalline sizes are

deposited; and because in the case of more atoms are present in the film so more states will be available for the photons to be absorbed.

The linear dependence of $(\alpha h\nu)^2$ with hν indicates that ZnO films are direct transition type semiconductors at all thickness. The photon energy at the point where $(\alpha h\nu)^2$ is zero is E_g. The value of optical energy gap decreases with increasing of thickness for all samples as shown in Fig. (3) and Table (2). This is due to the increase in localized density of states near the band edges and in turn decreases the value of Eg with thickness. Also the decrease of direct band gap with the increase of thickness can be attributed to an increase of particle size, decrease of strain and increase of lattice constant [15].

This means that the thickness also effects on the band gap of the film. These results show a good agreement with the research [16].

Fig. (4) shows the variation of extinction coefficient (k) with wavelength at different thicknesses. We know that the extinction coefficient depends mainly on absorption coefficient according to the relation (6) for this reason; we notice the increasing of extinction coefficient with increasing photon energy because the absorption coefficient is increased. It is observed from these figures that the k decreases with the increase film thickness. This is due to decrease the grain boundaries of the film structure. This means that direct electronic transition happens. Variation of the refractive index versus wavelength, for different ZnO film thicknesses is shown in Fig. (5). We can notice from this figure that the refractive index, in general increases with increasing of thickness and it is increase from 1.82 to 2.19 with increasing thickness from 75nm to 250 nm at wavelength equal to 365 nm as shown in figure (5). This behavior may be due to the change in the bond length due to the decrease in the packing density because of increases in degree of crystallite of films. . Our results appear good agreement with other researches [17][18]. The variation of the ε_r and ε_i versus wavelength for ZnO films deposited at RT with different thickness shown in Figs. (6) and (7). The behavior of ε_r is similar to that of the n because of the smaller value of k^2 compared with n^2. While ε_i is mainly depends on the k values. Our results are listed in Table (2).

Table (2) The dependence of the band gap, extinction coefficient, refractive Index, the real and imaginary parts of dielectric constant on the thickness for ZnO films.

Thickness (nm)	E_g (eV)	n	k	ε_r	ε_i
75	3.41	1.80	2.55	4.1	1.1
150	3.35	1.95	2.42	4.5	1.05
200	3.32	2.10	2.21	4.8	1.0
250	3.27	2.20	1.81	5.2	0.8

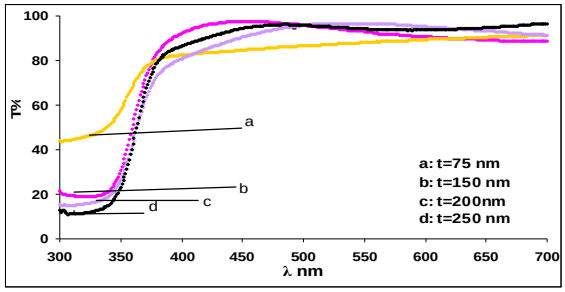


Fig.(2) Transmittance versus wavelength for ZnO films at different thicknesses.

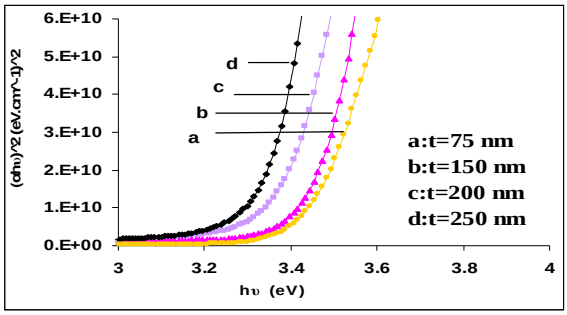
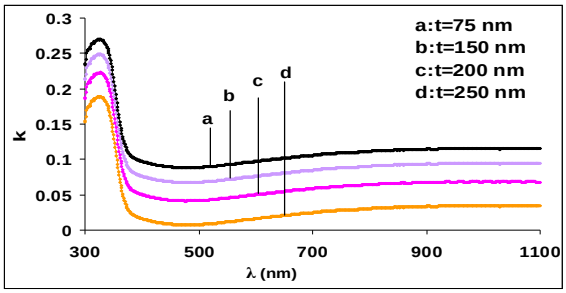
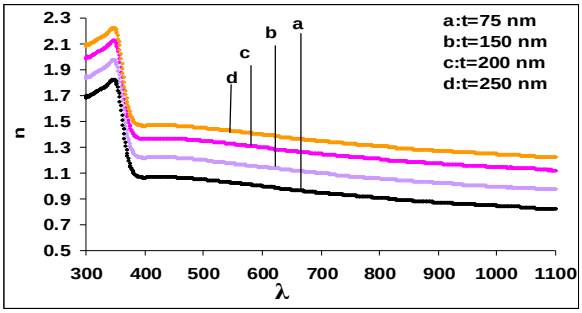


Fig (3) Variation of $(\alpha h\upsilon)^2$ versus hυ for ZnO films at different thickness.



Fig(4) Variation of k versus wavelength for ZnO films at different thickness.



Fig(5) . Variation of n versus wavelength for ZnO films at different thickness.

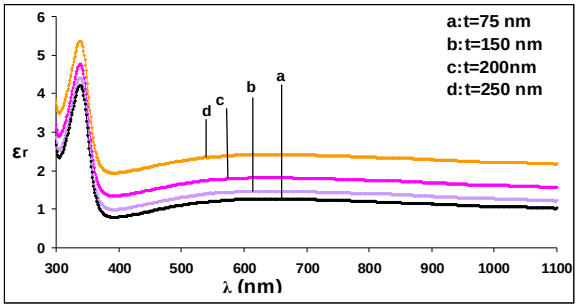


Fig.(6) Variation of ε_r as a function of wavelength for ZnO films at different thickness

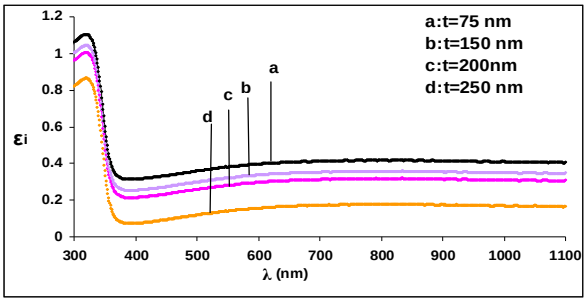


Fig. (7) Variation of ε_i as a function of wavelength for ZnO films at different thickness.

4. CONCLUSION

Conductive and transparent ZnO thin films were deposited by dc magnetron sputtering from Zinc target, and the corresponding structural and optical characteristics of theprepared films as a function of thickness are reported.
.

1- The XRD pattern is clearly shown demonstrated three important planes of hexagonal structure (100,002 and 101) for various thicknesses.

2- The grain size increased with increasing the film thickness.

3-The linear dependence of $(\alpha h\nu)^2$ to $h\nu$ indicates that ZnO films at all different thickness are direct transition type semiconductors.

4- The optical band gap of the films decreases with increasing thickness.
5- The refractive index is about 2.1.

References

[1.] Yu-lin Wang, "Fabrication and Characterization of Zinc Oxide Light Emitting Diodes", Ph.D. Thesis, University of Florida, 2009.
[2.] H. Kumar Y.Dav, K. Sreenivas, and V. Guptaa.," Influence of Post Deposition ,Annealing on the Structural and Optical Properties of Mn doped ZnO Thin Films", Journal of Applied Physics, 99, pp.083507 ,2006.
[3.] B. Kumar, T. Rao" Effect of Substrate Temperature on Structural Properties of Nanostructur Zinc Oxide Thin Films Prepared by Reactive DC Magnetron Sputtering", Digest Journal of Nanomaterials and Biostructures , 6(3), pp. 1281-1287 ,2011.
[4.] M. Kang,S. Kim, Y.Kim and J. Ryu." Dependence of the Optical Anisotropy of ZnO Thin Films on the Structural Properties ", Journal of the Korean Physical Society, 57, (2), pp. 389_394, 2010.
[5.] Y.Choi, J.Kang, D. Hwang, and S.Park"Recent Advances in ZnO-Based Light-Emitting Diodes], IEEE Transactions on Electron Devices, 57(1),, 2010.
[6.] R. Romero, M.C. López, D. Leinen, F. Mart´ın, J.R. Ramos Barrado "Electrical Properties of the n-ZnO/c-Si Heterojunction Prepared by Chemical Spray Pyrolysis", Materials Science and Engineering B ,110,pp 87–93,2004.
[7.] T.Yanga, B.Yaoa, T.T. Zhaoa, G.Z.Xinga,c, H. Wanga, H.L.Pana,R.Denga,Y.R. Suia, L.L. Gaoa .H.Z. Wanga, T. Wuc, D.Z. Shenb," Sb Doping Behavior and its Effect on Crystal Structure, Conductivity and Photoluminescence of ZnO Film in Depositing and Annealing Processes", Journal of Alloys and Compounds 509 ,pp:5426–5430,2011.
[8.] P. Wang, N. Chen, Z. Yin, F.Yang, Ch. Peng, R. Dai, and Y. Bai."As-doped p-type ZnO Films by Sputtering and Thermal Diffusion Process ", Journal of Applied Physics 100, pp: 043704, 2006.
[9.] L.P Schuler," Properties and Characterization of Sputtered ZnO", Ph.D. Thesis,University of Canterbury Christchurch, New Zealand, 2008.
[10.]B. Ray, "II-VI Compounds", Pergamum Press, 1st edition printed in Great Britain by Neil and Co. Ltd. of Edinburgh, p.p:162, (1969).
[11.]C. Kittle, "Introduction to Solid State Physics" Thomsen Press New Delhi, 8th Edition 2005.
[12.]J.Tauc," Amorphous and Liquid Semiconductor", Plenums Press, New York and London, 1974.
[13.]J. Pankove," Optical Process in Semiconductor",Prentice Hall Inc1975.
[14.]N 1997 JCPDS-International Centre for Diffraction Data. All rights resaved PCPDFWIN ,1.30, Card no. 36-1451.
[15.]S. Aksoy, Y. Cagalar, S. Ilican, M. Caglar ." Effect of Sn Dopants on the Optical and Electrical Properties of ZnO Films", Optica Applicata, XL (1) ,p.p:7-14,2010.
[16.]A. A. Alnajjar. "ZnO:Al Grown by Sputtering from Two Different Target Sources: A Comparison Study ",Advances in Condensed Matter Physics. (2012), Article ID 682125, 8 pages doi:10.1155/2012/682125
[17.]M. Caglar, Y. Caglar, S. Ilicani. "The Determination of the Thickness and Optical Constants of the ZnO Crystalline Thin Film by using Envelope Method", Journal of Optoelectronics and Advanced Materials, 8 (4), pp.1410 – 1413,2006.
[18.]W.X.Cheng, A. L.Ding, X. S. Zheng, P. S. Qiu and X. Y. He. "Optical and Electrical Properties of ZnO Nanocrystalline Textured Films Prepared by DC Reactive Magnetron Sputtering]",Journal of Physics: Conference Series 152 (2009) 012036 doi: 10.1088/ 1742-6596/152/1/012036.