



Available online at: www.basra-science-journal.org

ISSN -1817 -2695



Structural and Optical Characterization of ZnO Thin Films by Sol-gel Technique

Mohammad M. Ali* and Seif M. Meshari

Department of Physics, College of Science, University of Basrah, Iraq

*Email: mohammadali434@yahoo.com

Received 13-11-2013 , Accepted 11-2-2014

Abstract

The ZnO thin films have been fabricated on commercial glass substrates by sol-gel spin coating process and annealing temperatures 300°C, 400°C and 500°C. X-ray diffraction (XRD) and UV-VIS-NIR are used to characterize ZnO thin films. X-ray diffraction study show that all the films prepared in this work have hexagonal wurtzite polycrystalline structure, with lattice constants $a=b=3.260\text{\AA}$, $c=5.215\text{\AA}$. A significant increase in the XRD peak intensities for the ZnO films after annealing can be observed. Scherrer's formula was used to calculate crystallite size. The optical band gap energy of thin films is found to be direct allowed transition with average value 3.25 eV. Urbach energy is calculated. The average value of transmittance of thin films in visible range is found to be 90%-93%.

Keywords: ZnO, Sol-gel, XRD, Band gap

1.Introduction

Zinc oxide (ZnO) is an emerging material for a large number of areas. Unlike many of its competitors, ZnO is inexpensive, relatively abundant, chemically stable, easy to prepare, non-toxic and most of the doping materials that are used with it are also readily available [1]. Significant research efforts have been made in recent years for developing highly oriented and transparent ZnO thin films, because of their potential application in transparent electrode in display, window layers in solar cells, field emitters, ultraviolet laser emission, photodetectors, piezoelectricity, bio-sensors, short wavelength light emitting diode and

information technology [2-9]. Zinc oxide (II-VI) is an inexpensive n-type semiconductor having direct band gap of (~3.3 eV at room temperature) and large excitonic binding energy ~60 meV which crystallizes in hexagonal wurtzite structure ($c=5.025\text{\AA}$ and $a=3.249\text{\AA}$) [10]. Due to their unique optical, electrical and semiconducting properties, ZnO thin films are extensively used in various applications. Despite several approaches adopted for making these ZnO thin films; controlling the size, shape, crystallinity and various parameters affecting the size and shape of these materials still need to be investigated [11]. Properties of ZnO thin films show

dependence on the technique used. Apart from doping, to increase the functionality of ZnO thin film, the effect of preparation conditions on the properties have to be considered for its effective technological applications [12]. Therefore, it is essential to investigate optimum conditions for fabrication of highly oriented and transparent ZnO thin films. The main concern of researcher is to get better quality of material stoichiometry. ZnO thin films have been made by a variety of techniques, among which there can be mentioned reactive sputtering [13], spray pyrolysis [14], Zinc oxidation [15], electro deposition [16], pulsed laser deposition [17], chemical vapor deposition (CVD) [18], metalorganic CVD (MOCVD) [19], plasma enhanced CVD (PECVD) [20], low pressure sputtering [21], chemical bath deposition

(CBD) [22], and sol-gel route [23]. Sol-gel technique is widely adopted due to its comparatively simple procedure as there is no need of costly vacuum system and it has a wide-range advantage of large area deposition and uniformity of the films thickness, multi component oxide films of many compositions on various substrates at low cost [11,1]. Relatively few works have been done in this direction for ZnO film prepared by sol-gel process [24,25]. In this work, we have studied the effect of annealing the ZnO thin film at three different temperatures (300°C, 400°C and 500°C) on its structural and optical properties, x-ray diffraction (XRD) used for structural characterization. UV-VIS-NIR spectrometry used for optical characterization.

2. Experimental details

ZnO thin films were prepared by sol-gel method on commercial glass substrates. Glass substrates were cleaned with soap solution, then cleaned with acetone then washed with distilled water. As a starting material, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was first dissolved in a mixture of 2-methoxyethanol ($(\text{CH}_3)_2\text{CHOH}$) and monoethanolamine [(MEA: $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$) which was used as a stabilizer] solution with adding ethanol. The molar ratio of MEA to zinc acetate was kept to 1.5 and concentration of zinc acetate was 0.8 mol/l. The resultant solution was stirred at 75°C for 1hr to yield a clear and homogeneous solution then allowed to cool to room temperature the sol was then ready for coating. The films on glass substrates were prepared using spin-coating unit which was rotated at 3000 rpm for 30 s.

The films were preheated at temperature 200°C for 10 min in a furnace to evaporate the solvent and remove organic residuals after each coating. This procedure was repeated up to eight times to obtain the workable thickness of the film (the thickness is around 0.2 μm). The films were then post-heated (annealed) in air at 300°C, 400°C and 500°C for 1hr. The structure properties of ZnO thin films were characterized by x-ray diffraction (XRD) measurements (Panalytical X_{pert} pro, with $\text{CuK}\alpha$ radiation ($\lambda=1.5406$)). The detection angles were ranging from $2\theta=20$ to 70°. Optical transmittance was observed using UV-VIS-NIR double beam spectrophotometer in the wavelength range from 250 nm to 800 nm, and the optical band gap energy was calculated from the data of the optical transmittance and wavelength.

3. Results and discussion

3.1 Structural characterizations

The x-ray diffraction (XRD) spectrum of ZnO thin films annealed at 300°C, 400°C and 500°C fabricated by sol-gel method on glass substrates is shown in figure 1. The peaks in the XRD pattern correspond to those of ZnO patterns from JCPDS data (Powder Diffraction File, Card no: 36-1451), having hexagonal wurtzite structure with lattice constants $a=3.24982\text{\AA}$, $c=5.20661\text{\AA}$, figure 2 shows schematic diagram of hexagonal wurtzite ZnO unit cell. The XRD pattern reveals that the deposited films are polycrystalline in nature. The strong and sharp diffraction peaks indicate the formation of well crystallized sample. The lattice constant "a" and "c" of the wurtzite structure of ZnO can be calculated using the relations (1) and (2) given below [26]:

$$a = \sqrt{\frac{1}{3}} \frac{\lambda}{\sin\theta} \quad (1)$$

$$c = \frac{\lambda}{\sin\theta} \quad (2)$$

For all planes calculated average values are $a=3.260\text{\AA}$ and $c=5.215\text{\AA}$ which agrees with the JCPDS data [27]. The crystallites size (D) of the ZnO films are estimated using the Scherer formula [28]:

$$D = \frac{0.9\lambda}{\beta_{2\theta} \cos\theta} \quad (3)$$

Where λ (1.5406\AA) is the wavelength of X-Ray, D is the crystallite size, $\beta_{2\theta}$ is the broadening of diffraction line measured at half of its maximum intensity in radians and θ is the angle of diffraction. The average of grain size is found to be 40 nm. Table 1 gives the average crystallite size and lattice constants for films annealed at different annealing temperatures.

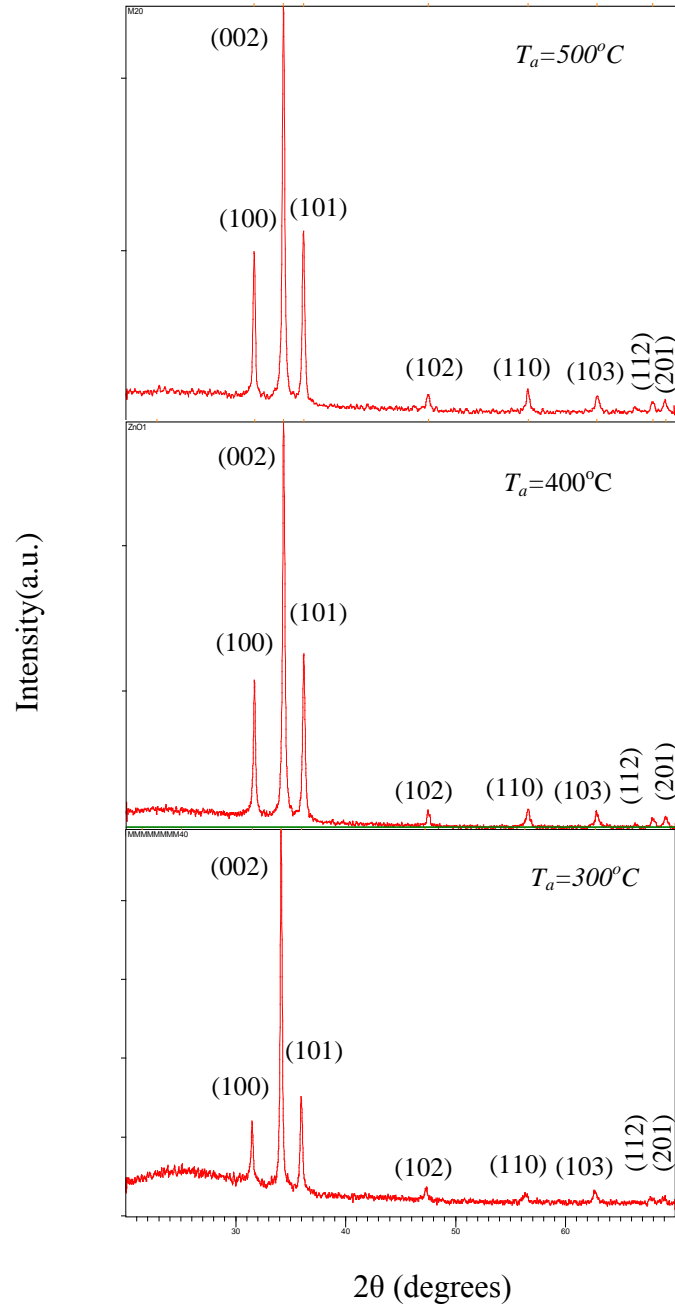


Figure 1. XRD spectrum of ZnO thin films annealed at 300°C, 400°C and 500°C

Table 1. Average crystallite size and lattice constant for ZnO films annealed at 300°C, 400°C and 500°C

Annealing Temperature (°C)	Crystallite Size D (nm)	Lattice Constants	
		a (Å)	c (Å)
300	35	3.259	5.214
400	50	3.261	5.217
500	35	3.260	5.214

From the table we observe that the average crystallite size suddenly increases at 400°C and again is reduced to the same value with the increase in annealing temperature. This may be due to the fact that on heat treatment, the flow of fluid near

the substrate interface coagulates, to reorganize the grain size to increase. The coagulation process discontinues on further increasing the heat treatment temperature with threshold around 400°C [29].

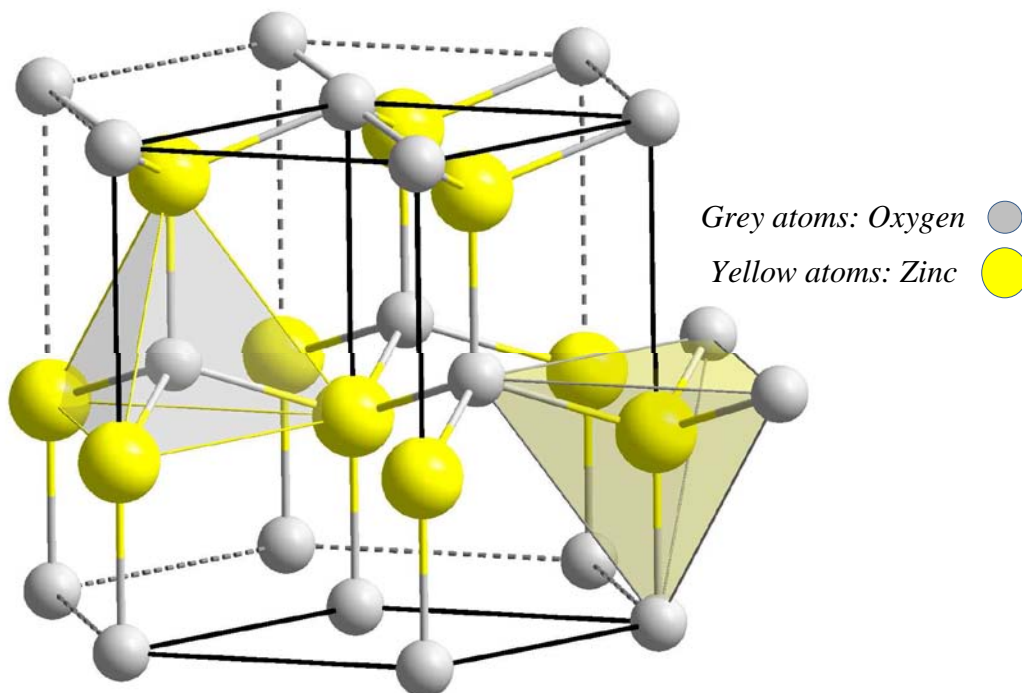


Figure 2. Schematic diagram of the hexagonal wurtzite ZnO unit cell.

3.2 Optical characterizations

The optical transmission spectrum of the ZnO thin films deposited at different annealing temperatures on glass substrates is shown in figure 3. The average value of transmittance of thin films in the visible range is found to be 90% - 93%. The spectra show interference fringes which has its origin in the interference of light reflected between air-film and film-substrate interface. The appearance of interference fringes indicates smooth reflecting surface of the film and low scattering loss at the surface [12]. The optical absorption coefficient α was

calculated for each film using the equation [28]:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \quad (4)$$

where t is the film thickness and T is the transmittance.

The value of band gap is estimated from fundamental absorption edge of the films. For the direct transitions, the absorption coefficient is expressed by [30]:

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (5)$$

where A is the constant, E_g is the energy gap, ν is the frequency of the incident radiation and h is Planck's constant.

Figure 4 shows the plot $(\alpha hv)^2$ vs. hv . The energy gap E_g of the samples was evaluated from the intercept of the linear portion of each curve for different annealing temperature with the hv in X-axis. The presence of a single slope in the plot suggests that the films have direct and

allowed transition. Table 2 gives values of E_g of the films deposited at different annealing temperatures, we can show from the table 2 the value of band gap as calculated above agrees nearly with band gap of bulk ZnO (~3.37 eV).

Table 2. Band gap E_g for ZnO thin films at different annealing temperatures as estimated from Fig.4

Annealing Temperature (°C)	Band gap E_g (eV)
300	3.25
400	3.24
500	3.25

Figure 5 shows that the absorption coefficient $\alpha(v)$ of ZnO thin films is plotted as a function of the photon energy (hv). The absorption coefficient of ZnO thin films is found to be zero in forbidden energy region and it is found to increase rapidly with the decrease in wavelength beyond energy band gap. Zero absorption coefficients of ZnO thin films in visible range of spectrum make these thin films suitable as window layer in Solar Cells. It is assumed that the absorption coefficient α near the band edge shows an exponential dependence on photon energy for many materials. This dependence is given by [31]:

$$\alpha = \alpha_o \exp \left[\frac{hv}{E_u} \right] \quad (6)$$

Where α_o is a constant and E_u is Urbach energy which is the width of the tails of the localized state associated with the amorphous state in the forbidden band. The logarithm of the absorption coefficient $\alpha(v)$ of ZnO thin films annealed at 300°C, 400°C and 500°C is plotted as a function of the photon energy (hv) in figure 6. The values of Urbach's energy (E_u) are calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves and the values of Urbach's energy for films annealed at different temperatures is shown in table 3. From the table, the increase in Urbach energy between 400°C and 500°C may be attributed to the increase thermal induced structural disorder of the film within this temperature range [32].

Table 3. Urbach energy for ZnO thin films annealed at different temperatures

Annealing Temperature (°C)	Urbach energy E_u (meV)
300	51
400	102
500	61

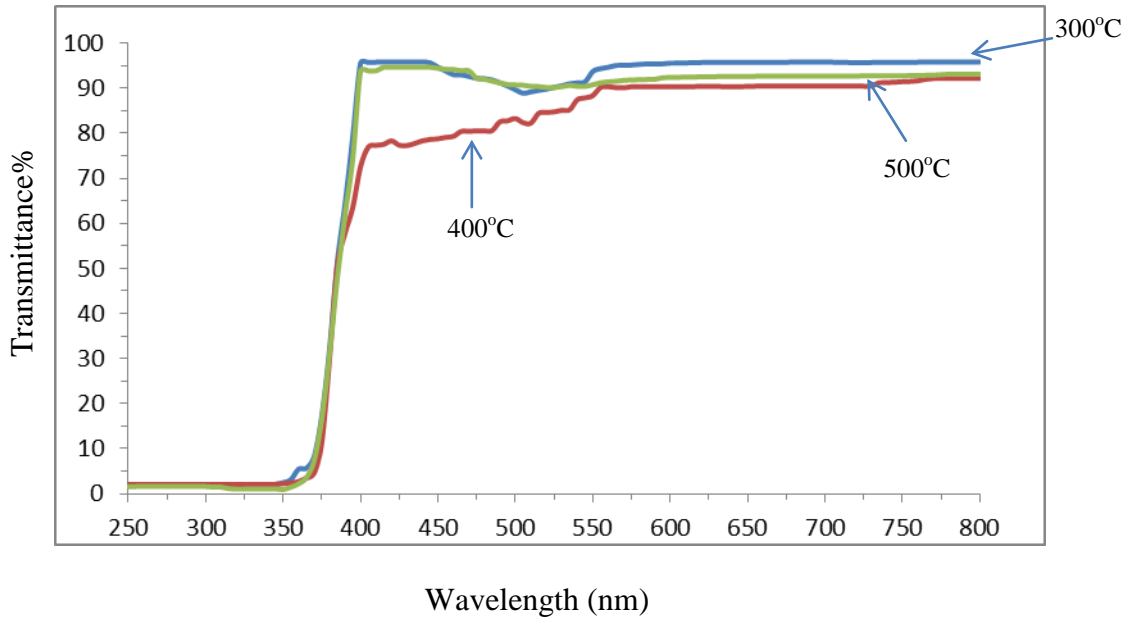


Figure 3. Transmission spectra of ZnO thin film annealed at 300°C, 400°C and 500°C

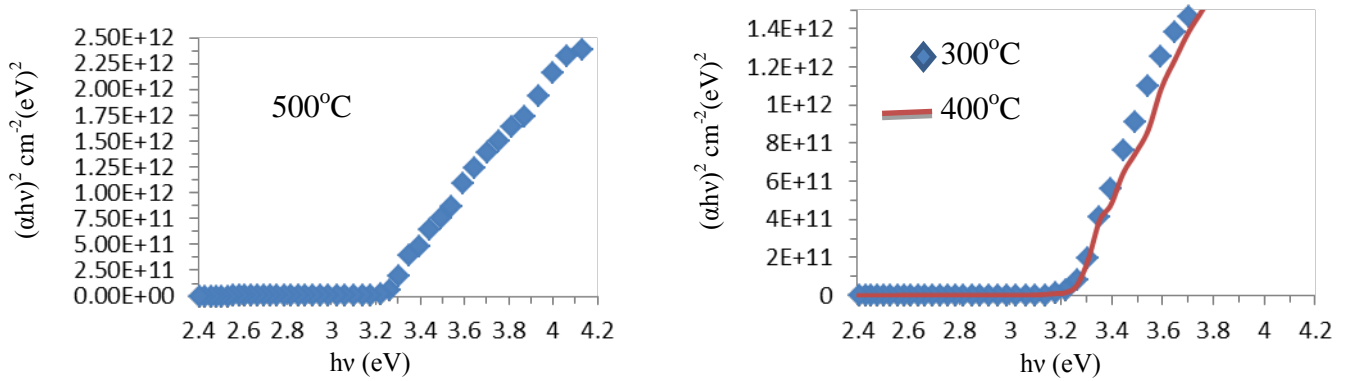


Figure 4. The plots $(\alpha hv)^2$ vs. photon energy $h\nu$ for ZnO films at different annealing temperatures

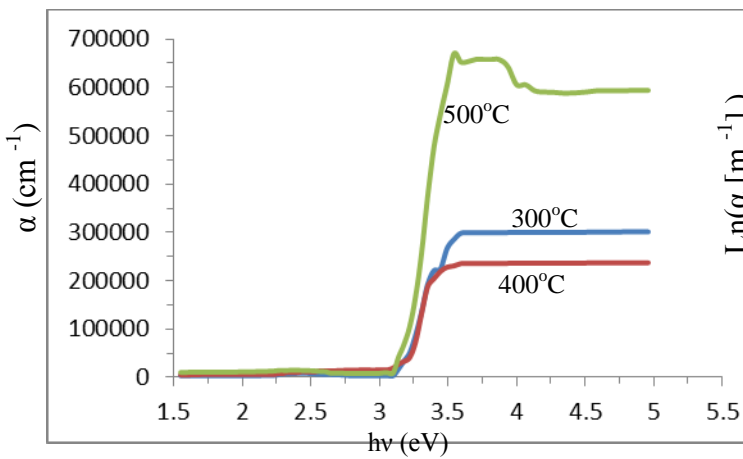


Figure 5. The plots α vs. $h\nu$ of ZnO thin films at different annealing temperatures

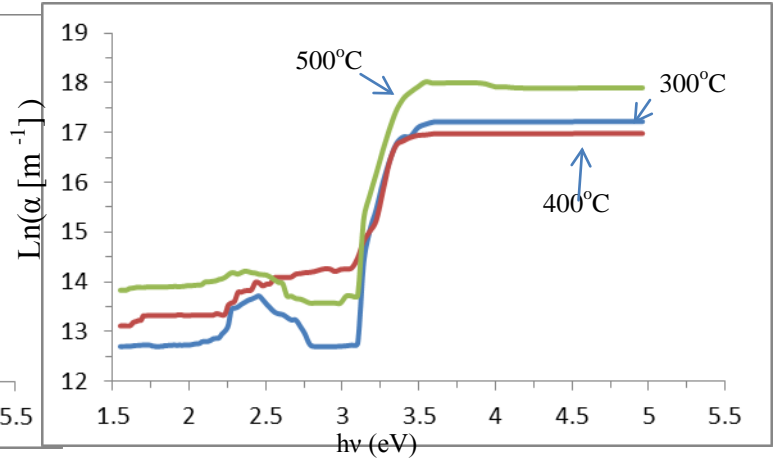


Figure 6. The plots $\ln(\alpha)$ vs. $h\nu$ of ZnO thin films at different annealing temperatures

4. Conclusions

ZnO thin films prepared on commercial glass substrates by sol-gel spin coating technique with 0.8 M zinc acetate solutions, with post annealing temperatures at 300°C, 400°C and 500°C. Films have been characterized using optical and structural measurements. The structural characterization of the film was done by X-Ray Diffraction (XRD). The x-ray diffraction analysis revealed that all samples have hexagonal wurtzite structure. The lattice constants were calculated, which agreed with that of bulk ZnO. The crystallites sizes as measured are found to

be in the range of 35-50 nm. The transmission spectrums of the films were recorded by UV-VIS-NIR spectrophotometer. All the films exhibit high transmittance (90%-93%) in the range of 250 nm to 800 nm, thus making the films suitable for optoelectronic devices, for instance as window layers in solar cells. The optical energy band gaps gave value of 3.25 eV, which agrees approximately with that of bulk ZnO. The Urbach energies of the ZnO films are found to be in the range of 51-102 meV.

References

- [1] Znaidi L., Touam T., Vrel D., Souded N., Ben Yahia S., Brinza O., Fischer A. and Boudrioua A., *Acta Physica Polonica A*, **121**, 1, 165-168 (2012).
- [2] Tang Z. K., Wong G. K. L., Yu P., Kawasaki M., Ohtomo A., Koinuma H. and Segawa Y., *Applied Physics Letters*, **72**, 25, pp. 3270-3272, June (1998), [doi:10.1063/1.121620](https://doi.org/10.1063/1.121620)
- [3] Li Y. B., Bando Y. and Golberg D., *Applied Physics Letters*, **84**, 18, pp. 3603-3605, May (2004), [doi:10.1063/1.1738174](https://doi.org/10.1063/1.1738174)
- [4] Tsukazaki A., Ohtomo A., Onuma T., Ohtani M., Mankino T., Sumiya M., Ohtani K., Chichibu S. F., Fuke S., Segawa Y., Koinuma H. and Kawasaki M., *Nature Materials*, **4**, 1, pp. 42-46, January (2005), [doi:10.1038/nmat1284](https://doi.org/10.1038/nmat1284)
- [5] Lee S. H., Lee S. S., Choi J. J., Jeon J. U. and Ro K., *Microsystem Technologies*, **11**, 6, pp. 416-423, June (2005), [doi:10.1007/s00542-004-0494-0](https://doi.org/10.1007/s00542-004-0494-0)

- [6] Salaoru I., Buffat P. A., Laub D., Amariei A., Apetroaei N. and Rusu M., *Journal of Optoelectronics and Advanced Materials*, **8**, 3, pp. 936-940, June (2006).
- [7] Xu J. Q., Pan Q. Y., Shun Y. A. and Tian Z. Z., *Sensors and Actuators B: Chemical*, **66**, 1-3, pp. 277-279, July (2007).
- [8] Chen K. J., Hung F. Y., Chang S. J. and Young S. J., *Journal of Alloys and Compounds*, **479**, 1-2, pp. 674-677, June (2009), [doi:10.1016/j.jallcom.2009.01.026](https://doi.org/10.1016/j.jallcom.2009.01.026)
- [9] Majumdar S. and Bnerji P., *Journal of Applied Physics*, **107**, 6, pp.063702-063702-4, May (2010), [doi:10.1063/1.3353862](https://doi.org/10.1063/1.3353862)
- [10] Chennupati Jagadish and Stephen J. Pearton, China: Elsevier (2007).
- [11] Ziaul Raza Khan, Mohd Shoeb Khan, Mohammad Zulfequar and Mohd Shahid Khan, *Materials Sciences and Applications*, **2**, pp.340-345, May (2011), [doi:10.4236/msa.2011.25044](https://doi.org/10.4236/msa.2011.25044)
- [12] Nada Shakti and Gupta P. S., *Applied Physics Research*, **2**, 1, pp. 19-28, May (2010).
- [13] Li Z. and Gao W., *Mater. Lett.* **58**, 1363(2004).
- [14] Lee J. H., Yeo B. W. and Park B. O., *Thin Solid Films*, **457**, 333(2004).
- [15] Kashani H., *J. Electron. Mater.* **27**, 876 (1998).
- [16] Souletie P., Bethke S., Wessels B. W. and Pan H., *J. Cryst. Growth* **86**, 248 (1988).
- [17] Petrov G. I., Shcheslavskiy V., Yakovlev V. V., Ozerov I., Chelnokov E. and Marine W., *Appl. Phys. Lett.* **83**, 3993 (2003).
- [18] Zhang X. T., Liu Y. C., Zhang J. Y., Lu Y. M., Shen D. Z., Fan X. W. and Kong X. G., *J. Cryst. Growth* **254** 80 (2003).
- [19] Sang B., Nagoya Y., Kushiya K. and Yamase O., *Sol. Energy Matter. Sol. Cells* **75**, 179 (2003).
- [20] Li B. S., Liu Y. C., Zhi Z. Z., Shen D. Z., Lu Y. M., Zhang J. Y., Kong X. G. and Fan X. W., *Thin Solid Films* **414**, 170 (2002).
- [21] Chen Y., Bagnall D. M., Koh H., Park K., Hiraga K., Zhu Z. and Yao T., *J. Appl. Phys.* **84**, 3912 (1998).
- [22] Ortega-Lopez M., Avila-Garcia A., Albor-Aguilera M. L. and Sanchez Resendiz V. M., *Mater. Res. Bull.* **38**, 1241 (2003).
- [23] Znaidi L., *Mater. Sci. Eng.* **B174**, 18 (2010).
- [24] Sagar Pramod, Shishodia P.K., Mehra R. M., Okada H., Wakahara Akihiro and Yoshida Akira, *Journal of Luminescence* **126**, 800-806 (2007).
- [25] Bahadur Harish, Samanta S. B., Srivastava A. K., Sood K. N., Kishore R., Sharma R. K., Basu A., Kar Rashmi M., Pal Prem, Bhatt Vivekanad and Chandra Sudhir, *Material Science* **41**, 7562 (2006).
- [26] Suryanarayana C. and Grant. Norton M., *X-Ray Diffraction A practical approach*, New York: plenum press (1998).
- [27] Joint Committee on Powder Diffraction Standards, *Powder Diffraction File*, Card no: 36-1451.
- [28] Sumangala D., Devi Amma, Vaidyan V. K. and Manoj P.K., *Material Chemistry and Phys.* **93**, 194 (2005).
- [29] Ghosh T., Bandopadhyay S., Roy K. K., Maiti A. K. and Goswami K., *Crystal Research and Technology*, **44**, 879-882 (2009).
- [30] Caglar M., Ilıcan S. and Caglar Y., *Thin Solid Films*, **517**, 17, pp. 5023-5028, July (2009).
- [31] Urbach F., *Physical Review*, **92**, 1324-1324 (1953).
- [32] Xue S. W., Zu X. T., Zhou W. L., Deng H. X., Xiang X., Zhang L. and Deng H., *Journal of Alloys and Compounds*, **448**, 21-26 (2008).

المميزات التركيبية والضوئية للأغشية الرقيقة للمركب ZnO المحضرة بتقنية Sol-gel

محمد محسن علي و سيف محمد مشاري
قسم الفيزياء، كلية العلوم، جامعة البصرة، العراق

الخلاصة

حضرت الأغشية الرقيقة لـ ZnO على قواعد من الزجاج بطريقة (sol-gel spin coating) بدرجة حرارة تحضير للمحلول 75°C لمدة ساعة واحدة ثم بردت الى درجة حرارة الغرفة بشكل تدريجي للحصول على محلول (Sol). رسب المحلول على القواعد الزجاجية بطريقة (spin coating) لمدة 30 s بعدها تم دراسة تأثير المعاملة الحرارية (التلدين) بدرجات حرارية مختلفة 300°C و 400°C و 500°C على الخواص التركيبية والضوئية. عملية تحليل التركيب البلوري تمت باستخدام حيود الاشعة السينية (XRD) للأغشية المحضرة وظهرت نتائج التحليل ان جميع الاغشية المحضرة تمتلك تركيباً بلورياً متعدد التبلور نوع hexagonal wurtzite حيث تبقى الاغشية محافظة على هذا التركيب البلوري على مدى جميع درجات حرارة التلدين المستخدمة. الاغشية المحضرة والملدنة لها ثوابت شبيكية مقارنة جداً للثوابت الشبيكية الموجودة في البطاقات القياسية المعروفة عالمياً في هذا المجال وهي ($a=b=3.260\text{\AA}$, $c=5.215\text{\AA}$). تم استخدام علاقة شيرار لحساب الحجم الحبيبي لتلك الاغشية. تم قياس فجوة الطاقة الضوئية ونفاذية الاغشية للضوء باستعمال مطياف UV-VIS-NIR بمدى الاطوال الموجية 250 nm-800 nm وكانت الاغشية لها خاصية الانتقال المباشر المسموح بمعدل فجوة طاقة 3.25eV وكذلك تم حساب طاقة Urbach (وهي طاقة الربط المستتارة: والتي تعتبر عرض الذبول للحالة المتمركزة والمرافقة لحالة اللاتبلور في الحزمة الممنوعة). كان معدل نفاذية الاغشية للضوء المرئي بحدود 90%-93%.