

# Effect of laser irradiation on structural and optical Properties of ZnO thin films prepared by sol-gel method

Ausama I. Khudiar

Center of Applied Physics Research, Directorate of Materials Research,  
Ministry of Higher Education and Scientific Research, Baghdad - Iraq.

\*corresponding author, E-mail: [ausamaikhudiar@yahoo.com](mailto:ausamaikhudiar@yahoo.com)

## Abstract

Zinc oxide thin films were prepared by sol-gel process. The sol was prepared from zinc acetate dehydrate. Methoxyethanol and monoethanolamine were used as solvent and stabilizer, respectively. Structural investigation including microstructure was carried out by X-ray diffraction (XRD) analysis. The films give a hexagonal wurtzite structure with diffraction peaks at (100), (002) and (101). It is found that the particle size of the films change after N<sub>2</sub> laser irradiation. Optical properties of the thin films were determined by using UV-VIS-NIR spectrometer. It was found that the band gap of the thin films decreased from 3.16 eV to 2.6 eV after N<sub>2</sub> laser irradiation. Such films can be applied on silicon solar cells as the changes in the band gap are acceptable as a requirement for good anti-reflecting coating element.

**Keyword:** ZnO thin films, Laser Irradiation, Structural and Optical properties.

## 1. Introduction

Laser crystallization of thin films on glass is widely used to improve the electronic transport. In the production of flat panel displays, laser crystallization increases the carrier mobility in thin film transistors. Suitable laser intensity profiles in combination with multiple scanning sequences have been used to reduce the number of grain boundaries [1, 2]. Among the semiconductors of the group II–VI, chalcogenide semiconductors have received much interest as they find applications in optoelectronic devices. Such semiconductors have band gaps between 1 and 3 eV in the visible region. Zinc oxide is an inexpensive n-type semiconductor having direct band gap of 3.3 eV which crystallizes in hexagonal Wurtzite structure ( $c = 5.025$  and  $a = 3.249$ ) [3]. Due to large exciton binding energy of 60 meV, they have potential applications in Optoelectronic devices such as in solar cells, Optical wave guide, Light emitting diodes (LED). Various gas, chemical and biological sensors were based on ZnO thin film. Thin films of Zinc oxide can be prepared by various techniques; among them are Sputtering, Chemical Vapor Deposition (CVD), Laser ablation, Sol-gel methods [4-6]. 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. In the present work we have used sol-gel methods to prepare ZnO liquid and spin coating process for film preparation. Zinc acetate dihydrate was used as the precursor material. The Sol-gel process has the advantages of controllability of compositions, simplicity in processing and is cost effective [7]. We have studied the effect of N<sub>2</sub> laser irradiation on the structural and optical properties of ZnO thin films. X-ray diffraction (XRD) was used for structural characterization. UV-Vis spectrometry was used for optical characterization.

## 2. Experimental details

Zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was dissolved in a solution of isopropanol and monoethanolamine. The molar ratio of MEA to zinc acetate was 1.0 and the concentration of zinc acetate

was 0.7 mol/l. The resultant solution was stirred at 50 °C for 1 h to yield a clear and homogeneous solution. The solution was finally aged at room temperature for 24 h. ZnO films were prepared on glass substrate by repeated coating. Spin coating was performed at room temperature, with a rate of 3000 rpm for 30 s. After depositing each times, the films were preheated in air at 275 °C for 10 min. After repeating the coating procedure five times for the final film thickness of approximately 200 nm, the films were finally postheated at 500 °C for 1 h in air using an electronic furnace. The thin films were irradiated with a pulsed TEA N<sub>2</sub> laser of wavelength 337.1 nm and energy of 200μJ and time of irradiation was 5 min. For measuring the optical absorption of thin films, a double beam UV/VIS/NIR Spectrophotometer (Camspec-M550) was used. The XRD measurements were carried out using an X-Ray Diffractometer PW 1830 PANalytical which has tube anode; copper using the wavelength 1.54056Å.

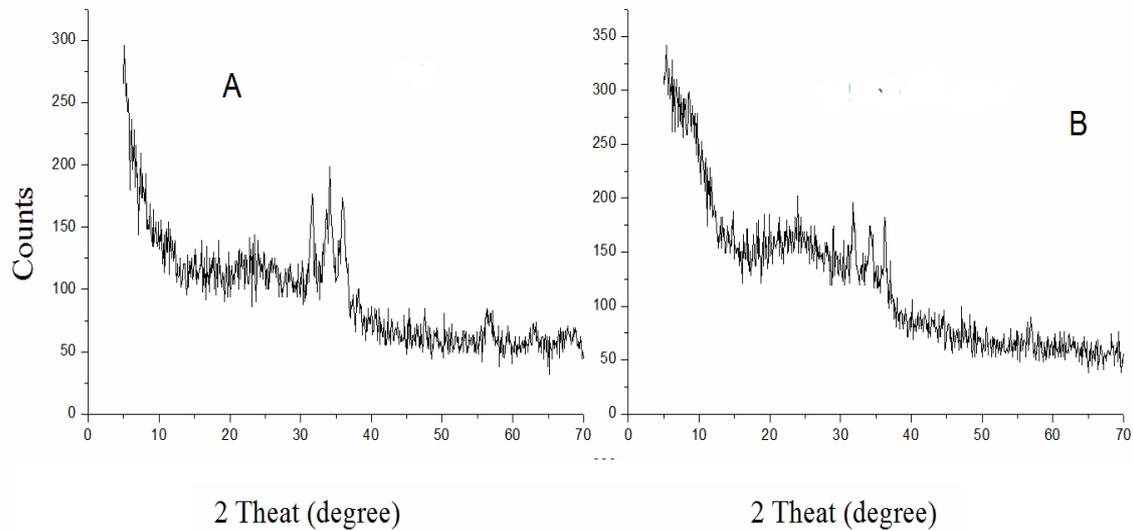
### 3. Results and Discussion

#### 3.1. Structural Properties

The structure of ZnO thin films were studied using high resolution X-ray diffraction (XRD). XRD spectra of the thin films were showed in Fig. 1. The XRD peaks of 31.48°, 35.26° and 37.17° were correspond to ZnO (100), (002) and (101) respectively in Fig. 1 A. Theses peaks confirmed that the film was polycrystalline in nature and the type of structural was a hexagonal wurzite[5]. The crystalline size (D) of the crystallites can be determined using the Scherrer's formula from the full width at half maximum (FWHM)  $\beta$  [8, 9];

$$D = 0.94\lambda/\beta\cos\theta \quad (1)$$

where  $\lambda$  is the wavelength of the X-ray used,  $\beta$  is the FWHM and  $\theta$  is the angle between the incident and scattered X-ray. The crystalline size of ZnO was 32.01 nm. Fig. 1 B show XRD of ZnO in film after laser irradiation. The structural of ZnO thin film was a hexagonal wurzite. The full width at half maximum (FWHM) of the thin films increased after laser irradiation. The crystalline size of ZnO thin films was 13.65 nm.



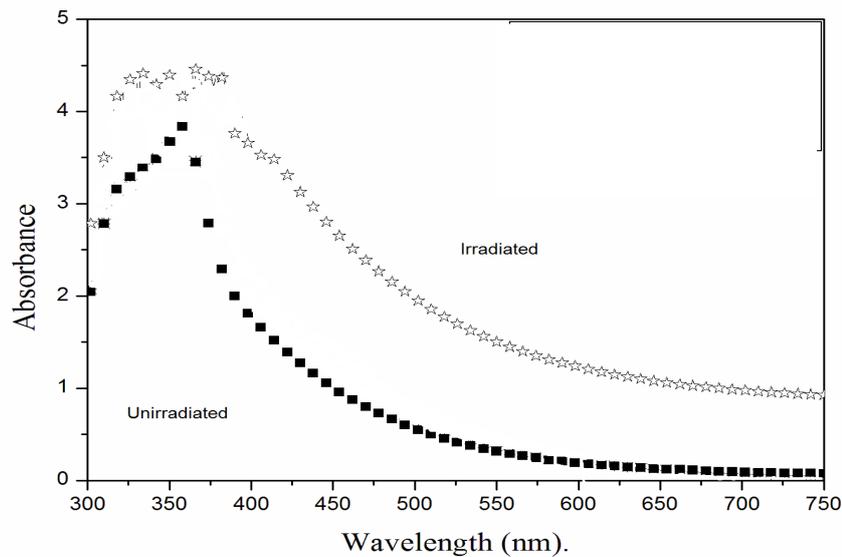
**Figure 1:** XRD of ZnO thin films before and after laser irradiation.

### 3.2: Optical properties

The optical absorption spectra of ZnO films deposited onto a glass substrate were measured at room temperature in the spectral range 300– 750 nm. Figure 2 shows the variation of absorption coefficient ( $\alpha$ ) with wavelength ( $\lambda$ ). The absorption coefficient is found to increase after laser irradiation of the thin film. This is possibly due to the decrease in crystalline size and the increase in the number of defects [10]. It is clearly seen from the optical spectra that the absorption edge shifts towards longer wavelength for irradiated films. This shift indicates a change of the optical band gap.

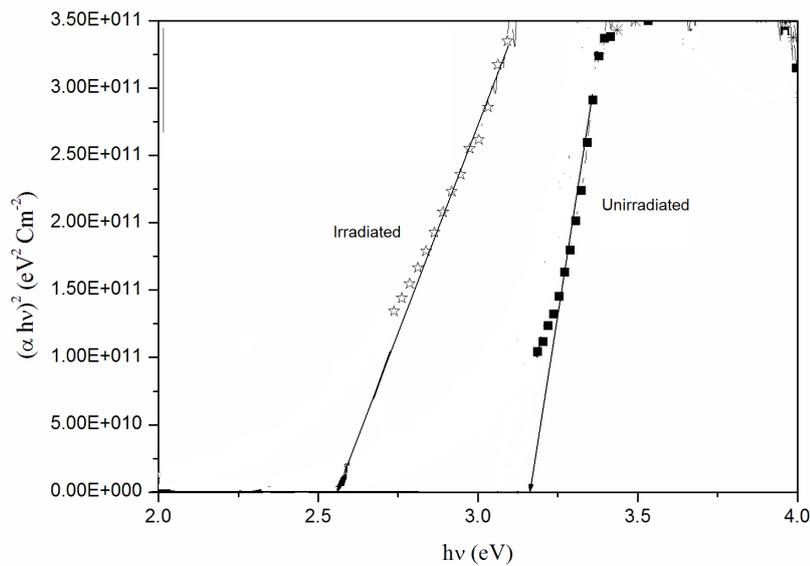
The value of optical band gap ' $E_g$ ' is calculated using the following relation [11, 12];

$$\alpha = A (h\nu - E_g)^n/h\nu \quad (2)$$



**Figure 2:** Absorption coefficients ( $\alpha$ ) versus wavelength ( $\lambda$ ) plot for ZnO film before and after irradiation with pulsed N<sub>2</sub> laser having energy 200 $\mu$ J.

where  $A$  is a constant and  $n$  is equal to  $1/2$  for direct band gap semiconductors. The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  are shown in Fig. 3 for ZnO system films. We find the optical band gap decreased with laser irradiation. The decrease in the optical band gap of ZnO system films may be explained on the basis of the model of density of states in amorphous semiconductor proposed by Mott and Davis [13]. According to this model, the width of localized states near the mobility edges depends on the degree of disorder and defects presented in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds [14] are produced as a result of insufficient number of atoms deposited in the amorphous films [15]. The unsaturated bonds are responsible for the formation of some defects in the films. Such defects produce localized states in the amorphous solids.



**Figure 3:** Optical band gap of ZnO: Cd thin films.

#### 4. Conclusion

We have instigated the optical and structure properties of the ZnO thin films. In spite of the insignificant change in the structure with the laser irradiation that the crystalline size decreased for thin films, it is found that the optical band gap decrease with laser irradiation also, a result has been attributed to the increase in the localized tail states.

#### References

- [1] Khan, S.A.; Zulfequar, M.; Husain, M. *Vacuum* 2004, 72, 291–296.
- [2] Bahishti, A.A.; Majeed Khan, M.A.; Kumar, S.; Husain, M.; Zulfequar, M. *Chalcogen. Lett.* 2007, 4 (12), 155–160.
- [3] K.J. Chen, T.H. Fang, F.Y. Hung, L.W. Ji, S.J. Chang, S.J. Young, Y.J. Hsiao, *Applied Surface Science* 254: 5791–5795, 2008.

- [4] J.H. Park, S.J. Jang, S.S. Kim, B.T. Lee, *Appl. Phys.Lett.* 89: 121108, 2006.
- [5] J.J. Chen, M.H. Yu, W.L. Zhou, K. Sun, L.M. Wang, *Appl. Phys. Lett.* 87: 173119, 2005.
- [6] S.Y. Kuo, W.C. Chen, Cheng F C.P., *SuperlatticesMicrostruct.* 39: 162–170, 2006.
- [7] Canyon Zhang, *Journal of Physics and Chemistry of Solids* 71: 364–369, 2010.
- [8] Ausama I. Khudiar, M. Zulfequar, Zahid H. Khan, *Journal of Non-Crystalline Solids* 357: 1264–1269, 2011.
- [9] Young-Sung Kim, Weon-Pil Tai, *Applied Surface Science* 253: 4911–4916, 2007.
- [10] Kale, R.B.; Lokhande, C.D. *Semicond. Sci. Technol.* 2005, 20, 1–9.
- [11] Chien-Yie Tsay, Min-ChiWang, *Ceramics International* 39: 469–474, 2013.
- [12] Nanda Shakti, P.S.Gupta, *Applied Physics Research* 2: 91, 2010
- [13] N. F. Mott, E. A. Davis, *Electronic Processes in Non-Cryst. Mater.* pp. 382 & 428 Clarendon, Oxford 1979.
- [14] S. R. Ovshinsky, D. Adler *Contemp. Phys.* 19: 109,1978.
- [15] M. L. Theye, *Proceeding of the Fifth International Conference on Amorphous and Liquid Semiconductors* 1: 479, 1973.