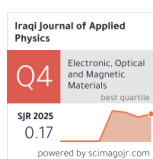


Mays W. Skakir ^{1*}
Awatif S. Jasim ²
Aidah A. Al-Door ³

Department of Physics,
College of Science,
University of Tikrit,
Tikrit, IRAQ

* Corresponding author email:
mays.w.shakir.phys503@st.tu.edu.iq



Influence of Laser Power on Crystalline Structure and Optical Characteristics of Zinc Oxide Thin Films Prepared by Pulsed-Laser Deposition

In this study, the effects of laser energy on pulsed laser-deposited zinc oxide (ZnO nano-films) with energies of 500, 700 mJ, and 400 pulses deposited on glass substrates are investigated using an Nd:YAG laser with a wavelength of 1064 nm and 6 Hz. The created films were annealed at 400°C for an hour in a special annealing furnace. Each prepared film's optical characteristics and structural XRD were then examined. The findings demonstrated that absorbance decreased with increasing laser energy, even though the energy gap for ZnO nano-films was of the direct kind for all the films and varied from 3.28 to 3.3 eV for energies of 500 and 700 mJ, respectively.

Keywords: Zinc oxide; Nanoparticles; Pulsed-laser deposition; Crystalline structure

1. Introduction

Zinc oxide (ZnO) is an intriguing inorganic substance with exceptional physical as well as chemical behavior and an important material in many scientific and technical applications. As a high-band gap semiconductor material, it possesses a band gap energy of about 3.37 eV at room temperature with a high exciton binding energy of 60 meV and hence superior optical and electronic properties [1]. ZnO exhibits high piezoelectricity, high electron mobility, and UV absorbability and is also found to be suitable in electronics, optoelectronics, sensing devices, photo catalysis, and biomedical devices [2]. Nanostructured oxide semiconductors have been gaining unprecedented interest over the past few years because of their significant importance in addressing some fundamental problems in their basic physics and their possible application as new materials [3–5].

ZnO, for instance, is an n-type wide band gap semiconductor material with energy band gap of 3.37 [1,6]. These semiconductors have been gaining considerable attention from researchers because of their immense number of applications, primarily utilized as gas-sensing devices or chemiresistors [7-9].

It must, however, be noted that ZnO is typically effective as a sensing material above 150°C [7,10,11]. Another viable alternative solution is exposure to UV light irradiation, an effective and economic means of activating and enhancing chemiresistors' sensing potential at ambient temperatures [7-9,12,13]. In addition, zinc oxide has also been described as having low toxicity, high applicability, and an environmentally friendly character, making it an ideal material to spearhead sustainable technologies to the next level.

This capability of being formed in a variety of nanostructures - nanowires, nanorods, and nanoparticles - only adds to their versatility and their potential uses in nanotechnology and material science.

2. Experimental Work

Zinc oxide (ZnO) with a nano-sized size (10-30 nm) was used in the form of high-purity powder (99.999%) manufactured by Amorphous USA. 2 gm was chosen as the mass of one sample using a sensitive balance. The powders were ground in a ceramic mortar for half an hour, and then the mixed powders were pressed with a pressure force of (5) tons in a mould made of stainless steel with a diameter of (1.5 cm) and a thickness of (0.5 cm) for (5 minutes) by a hydraulic press, forming a target with a thickness of 4 mm.

German-made microscope slides with glass bases with a size of 0.1×2.5×7.6 cm³ were used. The glass bases were cleaned to remove impurities or suspended materials because the presence of these impurities affects the properties of the prepared films. They were then ready for use before starting the sedimentation process by following the following steps:

- Washing the bases thoroughly with alcohol to remove any weather-related debris. Avoiding using detergents, as these leave chemical residues that prevent the membrane from adhering to the base. Furthermore, some detergents may scratch the base surface, affecting the membrane's consistency.
- Immersing them in distilled water and place them in an ultrasonic device for 15 minutes.
- The bases are dried using special paper and are thus ready to begin the deposition process.

3. Results and Discussion

The X-ray diffraction (XRD) patterns of all produced samples shown in Figs. (1) and (2) are initially orientated across the c-axis vertical to the substrate surface and exhibit a hexagonal wurtzite structure, which is in agreement with the findings of other studies [14,15]. The increase in pulses altered the direction of the film and affected the Miller indices at (100), (002), and (101), the selected direction. When compared to a conventional bulk spectrum, there was a slight change in the peak positions and peaks with larger FWHM because more stoichiometric ZnO films were formed. Diffraction peaks are widened by the tiny particle size of ZnO nano films. As the Energy increased, the crystal size of the films shrank [16,17].

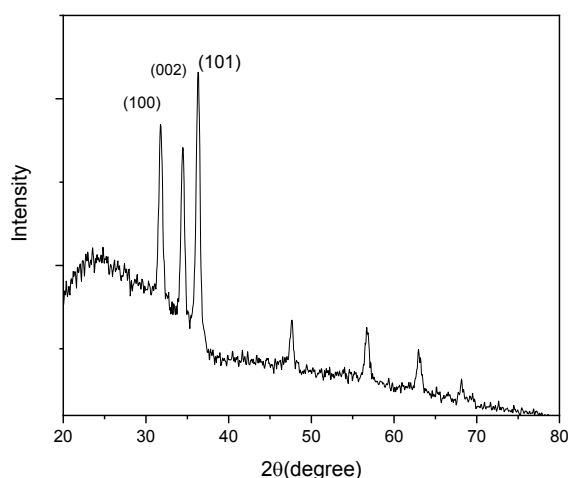


Fig. (1) XRD pattern of ZnO film on quartz with diverse annealing temperatures at energy of 700 eV

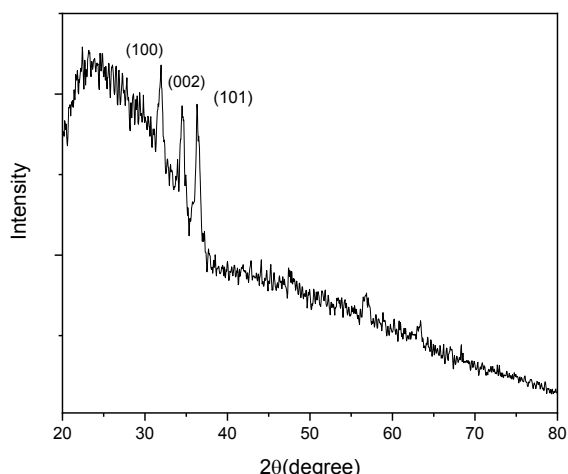


Fig. (2) XRD pattern of ZnO film on quartz with diverse annealing temperature at energy of 500 eV

In the visible spectrum, where absorption spectra were displayed in Figs. (3), (4) and (5), the prepared ZnO films have shown a poor optical absorbance and hence good transmittance (over 80%). With increasing energy of laser, the absorption edge has been found to gradually transfer to a larger wavelength range [18,19].

Increased absorbance at short wavelengths in the visible spectrum is a characteristic of the films. This trait allows us to employ them in gas sensor applications.

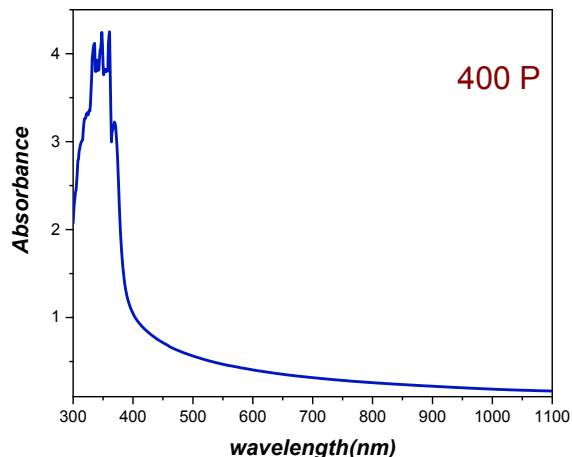


Fig. (3) Absorption spectrum of ZnO film on quartz at an energy of 700 eV

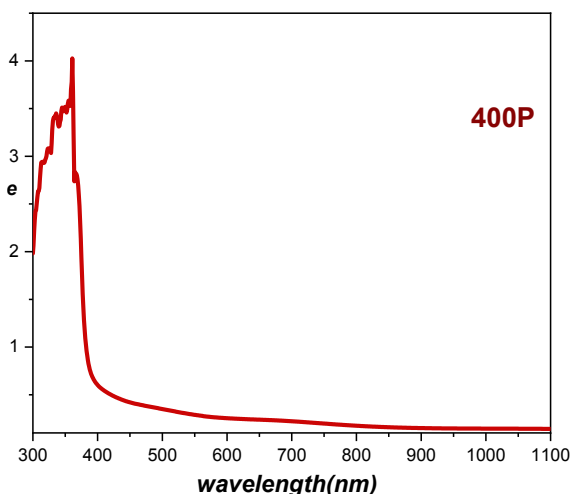


Fig. (4) Absorption spectrum of ZnO film on quartz at an energy of 500 eV

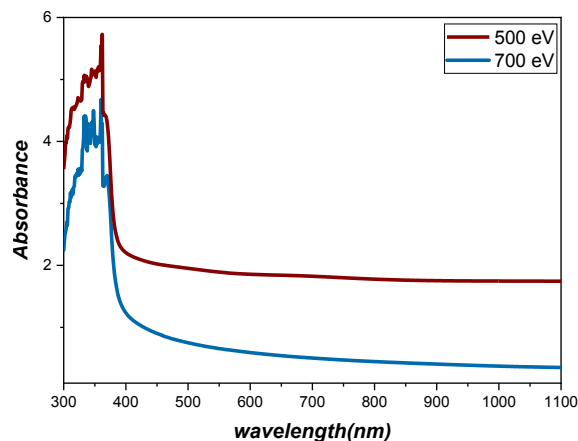


Fig. (5) Absorption spectrum of ZnO film on quartz at energies 500 eV and 700 eV

According to the study, this explains why the absorbance is at its lowest at long wavelengths as the incident photon's energy is lower than the semiconductor's energy gap value [20]. This shows the increase in the energy gap with growth in the thickness of films. The process used to determine the absorption coefficient (α) is as follows [21]:

$$\alpha = 2.303 A/t \quad (1)$$

where (A) is the absorbance and (t) is the thin film's thickness in nanometers (nm). This description is used when there is a substantial likelihood of the permitted direct transition. Tauc's equation was used to compute the optical band gap energy [22]:

$$ah\nu = (h\nu - E_g)^n \quad (2)$$

where $n=1/2$ denotes a direct transition, B is a constant, $h\nu$ is the incident photon energy (eV), and E_g is the optical band gap (eV). The values of the optical energy band gaps have been obtained by extrapolating the linear part of the curves of $(ah\nu)^2$ vs. $h\nu$, as shown in Figs. (6), (7), and (8), and 3.28 and 3.3 eV are the measured energy band gap values [23].

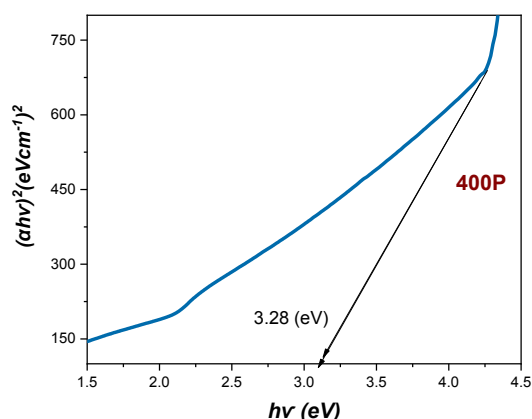


Fig. (6) Determination of the energy gap of ZnO film on quartz at an energy of 700 eV

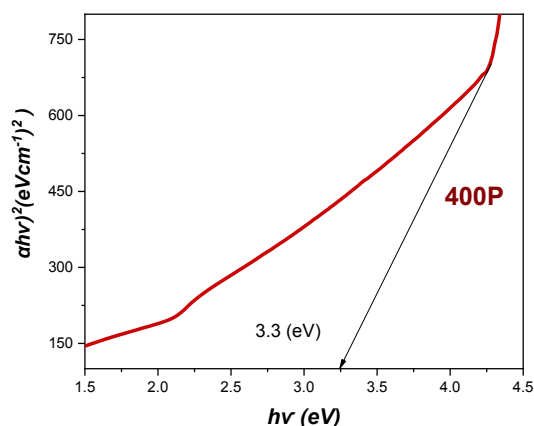


Fig. (7) Determination of the energy gap of ZnO film on quartz at an energy of 500 eV

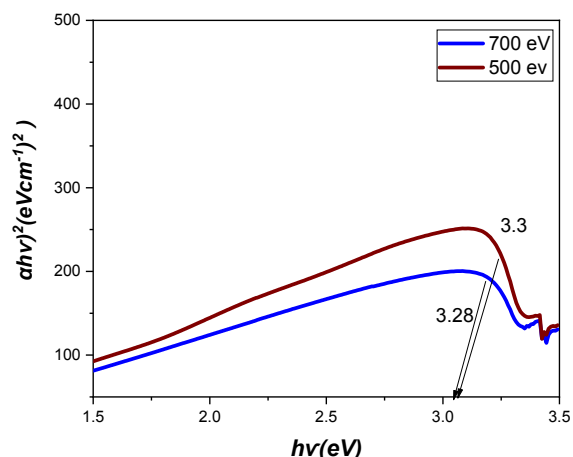


Fig. (8) Determination of the energy gap of ZnO film on quartz at two energies energy of 500 eV and 700 eV

These findings are highly consistent with our earlier theoretical work, where we demonstrated that quantum confinement causes the energy band gap values to decrease with increasing particle size [24]. It was discovered that band gap diameters increased as the thin film's thickness increased [25,26]; the increase has been due to a reduction in the particle size; hence, the energies of the optical band gaps are directly dependent on the level of crystallinity of the thin film [27].

4. Conclusions

Zinc oxide (ZnO) films were prepared by PLD on glass substrates, and X-ray diffraction results revealed a hexagonal, polycrystalline wurtzite ZnO structure. Optical properties revealed that increasing the energy led to a shrinkage in the crystal sizes of the films, resulting in the smallest grain size at 400 pulses. This result is important for the manufacture of gas sensors. The measured energy band gap values are 3.28 and 3.3 eV, which are similar to the theoretical values.

References

- [1] Ü. Özgür et al., "A comprehensive review of ZnO materials and devices", *J. Appl. Phys.*, 98(4) (2005).
- [2] S. Mollazadeh, M. Mackiewicz and M. Yazdimamaghani, "Recent advances in the redox-responsive drug delivery nanoplateforms: A chemical structure and physical property perspective", *Mater. Sci. Eng. C*, 118 (2021) 111536.
- [3] A. Tricoli, M. Righettoni and A. Teleki, "Semiconductor gas sensors: dry synthesis and application", *Angewandte Chemie Int. Ed.*, 49(42) (2010) 7632-7659.
- [4] D.R. Miller, S.A. Akbar and P.A. Morris, "Nanoscale metal oxide-based heterojunctions for gas sensing: A review", *Sens. Actuat. B: Chem.*, 204 (2014) 250-272.

- [5] S.M. Sze, Y. Li and K.K. Ng, **“Physics of Semiconductor Devices”**, John Wiley & Sons (2021).
- [6] H. Wang and A.L. Rogach, “Hierarchical SnO₂ nanostructures: recent advances in design, synthesis, and applications”, *Chem. Mater.*, 26(1) (2014) 123-133.
- [7] A.C. Catto et al., “An easy method of preparing ozone gas sensors based on ZnO nanorods”, *RSC Adv.*, 5(25) (2015) 19528-19533.
- [8] S.W. Fan, A.K. Srivastava and V.P. Dravid, “UV-activated room-temperature gas sensing mechanism of polycrystalline ZnO”, *Appl. Phys. Lett.*, 95(14) (2009).
- [9] G. Korotcenkov and B.K. Cho, “Ozone measuring: What can limit application of SnO₂-based conductometric gas sensors?”, *Sens. Actuat. B: Chem.*, 161(1) (2012) 28-44.
- [10] K. Aguir, C. Lemire and D.B.B. Lollman, “Electrical properties of reactively sputtered WO₃ thin films as ozone gas sensor”, *Sens. Actuat. B: Chem.*, 84(1) (2002) 1-5.
- [11] X. Zhou et al., “Recent progress on the development of chemosensors for gases”, *Chem. Rev.*, 115(15) (2015) 7944-8000.
- [12] S. Park et al., “UV-enhanced NO₂ gas sensing properties of SnO₂-core/ZnO-shell nanowires at room temperature”, *ACS Appl. Mater. Interfaces*, 5(10) (2013) 4285-4292.
- [13] Z.R. Tian et al., “Complex and oriented ZnO nanostructures”, *Nature Mater.*, 2(12) (2003) 821-826.
- [14] A.B. Yadav et al., “Hydrogen gas sensing properties of Pd/ZnO thin films grown on n-Si<100> substrates at room-temperature by thermal evaporation and sol-gel techniques: A comparative study”, *Indian J. Pure Appl. Phys.*, 51(11) (2013) 792-799.
- [15] S.A. Maki, A.A. Shehaband and E.Y. Abed, “A Study of Structure and Optical Properties of ZnO Thin Films Deposited by Using Thermal Evaporation Technique under Different Flow Rate of Oxygen O₂”, *Ibn AL-Haitham J. Pure Appl. Sci.*, 26(1) (2017) 137-143.
- [16] B.L. Zhu et al., “Effect of thickness on the structure and properties of ZnO thin films prepared by pulsed laser deposition”, *Japan. J. Appl. Phys.*, 45(10R) (2006) 7860.
- [17] M.S. Al-Assiri et al., “Optical Properties of Annealed ZnO Thin Films Fabricated by Pulsed Laser Deposition”, *Silicon*, 7 (2015).
- [18] N. Shakti and P.S. Gupta, “Structural and optical properties of sol-gel prepared ZnO thin film”, *Appl. Phys. Res.*, 2(1) (2010) 19.
- [19] M. Rusop et al., “Properties of zinc oxide thin films prepared on silicon (100) and glass substrates by pulsed laser deposition technique with different oxygen gas pressures”, *Surf. Eng.*, 23(1) (2007) 68-72.
- [20] D. Lin-Vien et al., **“The handbook of infrared and Raman characteristic frequencies of organic molecules”**, Elsevier (1991).
- [21] S. Bhatia, N. Verma and M. Aggarwal, “Thermal, optical and gas sensing properties of ZnO films prepared by different techniques”, *The Euro. Phys. J. Appl. Phys.*, 81(1) (2018) 10101.
- [22] M.A. Salim, “Effect of thickness on the optical properties of ZnO thin films prepared by pulsed laser deposition technique (PLD)”, *Iraqi J. Phys.*, 15(32) (2017) 114-121.
- [23] M. Sowjanya et al., “Structural and Optical Properties of Pure Wurtzite ZnO under Uniaxial Strain Based on First-Principles Study”, *Acta Physica Polonica A*, 137(3) (2020).
- [24] F.A. Hasan and M.T. Hussein, “Study of some electronic and spectroscopic properties of ZnO nanostructures by density functional theory”, *Mater. Today: Proceed.*, 42 (2021) 2638-2644.
- [25] N. Nithya, “Effect of thickness on the properties ZnO thin films”, *Adv. Appl. Sci. Res.*, 3(6) (2012) 4041-4047.
- [26] V. Kumar et al., “Role of film thickness on the properties of ZnO thin films grown by sol-gel method”, *Thin Solid Films*, 539 (2013) 161-165.
- [27] Y.C. Lin et al., “Effect of process conditions on the optoelectronic characteristics of ZnO:Mo thin films prepared by pulsed direct current magnetron sputtering”, *Thin Solid Films*, 518(17) (2010) 4928-4934.