

## Characterization of ZnO Thin-Films Structure Using X-Ray Powder Diffraction Measurements for Solar Cells Fabrication

Nagla El Badri Mohammed Saeed El Badri<sup>1\*</sup>, Mubark Dirar Abd Alla<sup>2</sup>, Abd Elazeem Mohalimed Ali<sup>3</sup><sup>1</sup>Physics Department, College of Applied and Industrial Sciences, University of Bahri, Khartoum North, Sudan<sup>2</sup>Physics Department, Faculty of Science, Sudan University of Sciences and Technology, Khartoum, Sudan<sup>3</sup>Physics Department, Faculty of Education, AL- Zaiem Al-Azhari University, Khartoum, SudanDOI: [10.36347/sjpm.2020.v07i05.001](https://doi.org/10.36347/sjpm.2020.v07i05.001)

| Received: 17.03.2020 | Accepted: 25.03.2020 | Published: 12.05.2020

\*Corresponding author: Nagla El Badri Mohammed Saeed El Badri

### Abstract

### Original Research Article

Thin-films of semiconductors are widely used as an anti-reflection layer in solar cell fabrication. Zinc oxide attracts a great concern today as semiconductors and alternative material due to its electrical, optical and photonic properties in solar cell fabrication. Thus the aim of this work is to investigate the crystal structure composition and grain size of ZnO thin-films (amorphous structure) obtained from annealed Zn, ZnS, and ZnSO<sub>4</sub> at 1000°C for 3, 6 and 9 by using X-ray diffractometry while commercial ZnO used as a control sample. Results revealed that the XRD pattern for ZnO thin-film obtained from Zn annealed at 1000°C for 3, 6 and 9 hours was found to be at 002, 003, 101 respectively while for ZnO samples obtained from ZnS treated under the same condition recorded at 201, 202 and 114. Moreover, findings showed that the XRD spectra for ZnO samples obtained from ZnSO<sub>4</sub> treated under the same conditions was 118, 009, and 220 respectively while for the commercial sample found to be at 403. The pattern for commercial sample exhibited the highest value of intensity and ZnO thin-film crystal morphology was a cubic shape centered with a density of 4.0963 kg or g/cm<sup>3</sup>. Generally, the nano size of the prepared ZnO thin-films of different samples decreased as the annealing time increased in the range of 30.60- 41.70 nm for 9 and 3 hours at 1000°C respectively. These findings indicated that high annealing temperature for a long time improves the structure of ZnO thin-films samples and control their structure at the nano size level where it promotes and enhances their electrical, optical, photonic properties to be used in new generation of solar cells.

**Keywords:** Intensity, nano-size, Semiconductors, Thin-films, ZnO, XRD spectra.**Copyright © 2020:** This is an open-access article distributed under the terms of the Creative Commons Attribution license which permits unrestricted use, distribution, and reproduction in any medium for non-commercial use (NonCommercial, or CC-BY-NC) provided the original author and source are credited.

## INTRODUCTION

Zinc oxide (ZnO) is well known for its properties where it exhibits semiconducting, piezoelectric or pyroelectric and photonic properties among many others. Thus, it is not surprising to find ZnO in many devices, optoelectronics, sensors, biomedical, electrochemical, solar cells, photovoltaic..... etc [1, 2]. The control of its structure at nano size level provides novel and enhanced electrical, mechanical, chemical and optical properties that help to understand many processes occurring in new generation of solar cell [3-5]. Generally, it has strong luminescence properties in the green-white region of the spectrum; therefore it can be used as suitable material for phosphor application. However, its emission spectrum has a peak at 495nm and a very broad half-width of 0.4eV. Moreover, it is friendly semiconductor material and an inexpensive luminescent compound. It has an antimicrobial effect on harmful

bacteria [6] and protects skin and eyes from UV radiation without causing irradiation [3]. There is no any evidence that ZnO is carcinogenic or genotoxic or produce toxins in humans [7]. Moreover, ZnO has much higher electron diffusivity than TiO<sub>2</sub>, high electron mobility, large excitation binding energy, available at low-cost, and stable against photo-corrosion [8]. ZnO is a well-known II-VI semiconductor having a direct band gap in the ultraviolet range (3.37 eV) and a large exciton binding energy (60 meV), which makes it very prospective due to its extensive physical properties. ZnO films are a promising material for optoelectronics; spintronics and sensor technology [9]. Therefore it is considered as a promising and alternative substance in the future to be used in many fields. The control of its structure at nano size level provides and enhances the electrical, mechanical, chemical and optical properties. Thus the aim of this work is to investigate the crystal structure, composition and grain size of ZnO thin-films (amorphous structure) obtained from annealed Zn, ZnS,

and ZnSO<sub>4</sub> using X-ray diffractometry. Zinc oxide (ZnO) is used as a semiconductor in this research because of its wurtzite structure with a wide-band gap and a large exciton binding energy.

## MATERIALS AND METHODS

### Samples Collection and Preparation

Zinc metal (65.38), compounds of zinc sulphide (ZnS), zinc sulphate (ZnSO<sub>4</sub>) and commercial zinc oxide (M.W. 81.38) in a powder form (British Drug Houses LTD) collected from University of Khartoum and Sudan for Science and Technology. Three grams of each collected sample put in a crucible and oxidized in a furnace (England, Maximum Temperature 1200°C) at 1000°C for 3, 6, 9 hours respectively while the commercial ZnO was not subjected to the oxidation process and used as a control sample.

### Preparation of ZnO thin-films from prepared ZnO samples

ZnO thin-films prepared on the indium titanium oxide (ITO) glass slides of dimension 2.5x 2.5cm<sup>2</sup> by coating method on the conducting side of the ITO glass. ITO slides purchased from US. Firstly ITO slides cleaned using absolute alcohol (ethanol) and then fixed on a wood plate using scotch tape on the conducting side of the ITO glass. One ml of the absolute ethanol added to one gram of each ZnO sample and then mixed well for 30 min to obtain homogenized paste (sol-gel technique). Then the prepared paste of each ZnO samples coated, spread and flattened with a razor blade on the same side of ITO slide to obtain ZnO thin-films [10]. All thin-films left to dry on the air for three days. It is known as ZnO thin-film electrode.

### Characterization of ZnO thin-films structure with X-ray Powder Diffraction (XRD) Measurements

The crystal structure or composition of ZnO thin-films (amorphous structure) identified by XRD method with X-ray diffractometry (D8 Advance Bruker X-ray) at room temperature with Monochromated CuK $\alpha$  ( $\lambda = 1.54\text{\AA}$  and  $1.5444\text{\AA}$ ), in the scan range of  $25^\circ < 2\theta < 70^\circ$  with scan rate of  $(2\theta/s) 0.08$  [11]. Particles nano- size of prepared ZnO samples calculated by using Scherrer equation [12], the size of the ZnO thin films calculated with the full-width at half maximum value of the ZnO peaks. The Scherrer equation used as shown below:

$$D = K\lambda / \beta \cos\theta \dots\dots\dots (1)$$

Where,  $\beta$  is the width of the observed diffraction line at its half intensity maximum, K is the shape factor set to 0.9 and  $\lambda$  is the wavelength of Cu K $\alpha$ .

## RESULTS AND DISCUSSION

### X-Ray Diffraction (XRD) pattern of ZnO thin-films

Results shown in Fig-1 and Table-1 represents XRD pattern of ZnO thin-films prepared from different compounds. The XRD pattern for ZnO obtained from Zn annealed at 1000°C for 3, 6 and 9 hours showed that

the crystal position found to be at 002, 003, 101 respectively. With regards to the ZnO samples obtained from ZnS annealed at the same temperature for the same time, results revealed that the XRD spectra found at 201, 202 and 114, while for ZnO samples obtained from ZnSO<sub>4</sub> the spectra was at 118, 009, 220 and for the commercial sample was at 403. The pattern for commercial sample exhibited the highest value of intensity. Similar study conducted by [13] who found that all ZnO films grown by dual ion beam sputtering using different annealing temperature have preferred orientation at 002. Also they found that the full-width at half-maximum (FWHM) of XRD from the (002) crystal plane observed to reach to a minimum value of  $0.139^\circ$  from ZnO film, annealed at 600°C.

Results claimed that the XRD pattern of ZnO thin-films fabricated from different samples in this work exhibited peaks at  $(2\theta)$  values of  $23.81^\circ$ ,  $31.992^\circ$ ,  $34.67^\circ$  respectively. Similar results reported by [13] who found that the position of (002) peak was observed to decrease consistently from  $34.630^\circ$  to  $34.552^\circ$  for the films annealed at 400°C and 700°C then somewhat increased to  $34.554^\circ$  for the film annealed at 800°C. As reported by [14], the angular peak position of ZnO powder is usually located at  $34.42^\circ$ . Generally, the shift in cross-ponding peak position of the investigated samples in this study might be due to the stress changing due to high temperature for a long time [13]. They explained that high annealing temperature enhanced the angular peak position.

However, results in this study reported that ZnO thin-film crystal morphology was cubic shape centered with density of  $4.0963\text{ kg or g/cm}^3$  or  $\text{m}^3$ . As reported by [15], all the peaks of ZnO dye-sensitized solar cells that observed at (100), (002) and (101) had hexagonal shape. Also [16-18] found that the shape of ZnO thin-film was hexagonal ZnO wurtzite structure. The hexagonal shape of ZnO thin films indicated their purity and well crystalline formation [19]. Those authors reported that the diffraction peaks match the standard phase (JCPDS # 01-079-0207) which was (100), (002) and (101). The cubic shape of the studied samples showed that there were still some impurities in the prepared ZnO samples which required high temperature for a long period of time that essential for annealing process. These findings claimed that as the annealing time increased the peak intensity of different samples increased. The increase of intensity peak in this study may be attributed to the gradual change of polycrystalline structure to single-crystalline structure due to the increase of annealing time [20]. The high intensity of commercial ZnO may be referred to nano-crystals grow in a preferential or along the c-axis to the surface of the substrate, in this case FTO [16]. Moreover, high temperature of annealing may improve the crystallinity formation of ZnO samples. According to [21] who found that the crystallization of ZnO thin-

films improved by an adequate support of thermal energy.

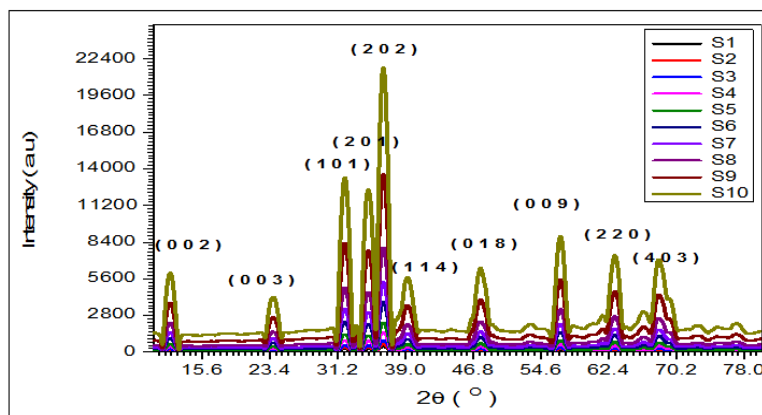


Fig-1: X-Ray Diffraction (XRD) pattern of different ZnO thin-film samples.

**LEGEND**

**S1:** ZnO thin film prepared from ZnS annealed at 1000°C for 3 hours. **S6:**ZnO thin film prepared from ZnSO<sub>4</sub> annealed at 1000°C for 6 hours.  
**S2:** ZnO thin film prepared from Zn annealed at 1000°C for 3 hours.**S7:**ZnO thin film prepared from ZnS annealed at 1000°C for 9 hours.  
**S3:** ZnO thin film prepared from ZnSO<sub>4</sub> annealed at 1000°C for 3 hours.**S8:**ZnO thin

film prepared from Zn annealed at 1000°C for 9 hours.  
**S4:** ZnO thin film prepared from ZnS annealed at 1000°C for 6 hours.**S9:**ZnO thin film prepared from ZnSO<sub>4</sub> annealed at 1000°C for 9 hours  
**S5:** ZnO thin film prepared from Zn annealed at 1000°C for 6 hours.**S10:**ZnO thin film prepared from commercial ZnO. Control sample.

**Table-1: Sample sources, annealing time, produced compounds, the miller indices (khi) and diffraction angle of ZnO samples (Crystal morphology using Millar coefficient).**

Serial No.	ZnO sample sources	Annealing time at 1000°C in hours	Compounds	peak (h k l)	2θ
1	Zn (S1) annealed for 3 hrs	3	(NH <sub>4</sub> ) <sub>3</sub> SiF <sub>6</sub> NO <sub>3</sub>	002	11.970°
2	Zn (S2) annealed for 6 hrs	6	Zn <sub>0.64</sub> Al <sub>0.36</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.18</sub> H <sub>2</sub> O	003	23.81°
3	Zn (S3) annealed for 9 hrs	9	Zn <sub>6</sub> Al <sub>2</sub> O <sub>9</sub>	101	31.992°
4	ZnS(S4) annealed for 3 hrs	3	Zn <sub>6</sub> Al <sub>2</sub> O <sub>9</sub>	201	34.67°
5	ZnS(S5) annealed for 6 hrs	6	Zn <sub>6</sub> Al <sub>2</sub> O <sub>9</sub>	202	36.59°
6	ZnS(S6) annealed for 9hrs	9	(NH <sub>4</sub> ) <sub>3</sub> SiF <sub>6</sub> NO <sub>3</sub>	114	39.157°
7	ZnSO <sub>4</sub> (S7) annealed for 3 hrs	3	Zn <sub>0.64</sub> Al <sub>0.36</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.18</sub> H <sub>2</sub> O	018	47.165°
8	ZnSO <sub>4</sub> (S8)annealed for 6 hrs	6	Zn <sub>6</sub> Al <sub>12</sub> O <sub>9</sub>	009	56.749°
9	ZnSO <sub>4</sub> (S9)annealed for 9 hrs	9	(NH <sub>4</sub> ) <sub>3</sub> SiF <sub>6</sub> NO <sub>3</sub>	220	63.18°
10	Commercial ZnO (S10)	Not treated	Zn	403	68.189°

**Table-2: Nano size of ZnO thin-films obtained from different Zn compounds.**

Serial No.	Zn compounds in powder form	Annealing time in hours at 1000°C	Grain Size of ZnO thin films ( nm)
1	Zn metal	3	41.7
2	ZnS	3	34.95
3	ZnSO <sub>4</sub>	3	36.175
4	Zn metal	6	32.68
5	ZnS	6	34.54
6	ZnSO <sub>4</sub>	6	34.48
7	Zn metal	9	32.68
8	ZnS	9	33.37
9	ZnSO <sub>4</sub>	9	32.6
10	Commercial ZnO	Not treated	30.48

The structural properties obtained by XRD and SEM showed that the crystal qualities of the ZnO thin-films significantly improved as the annealing temperature increased [20]. The crystallization of ZnO is essential because this compound can be used in various application and different devices.

### Nano size of ZnO thin-films obtained from different Zn compounds

Nano sizes of ZnO thin-films obtained from different sources calculated using Scherre equation. Generally, the nano size of prepared ZnO thin-films decreased as the annealing time increased (Table-2). As it can be seen from the results, nano size of ZnO thin-films obtained from Zn metal was 41.7 nm after annealing at 1000°C for 3 and 32.68 nm after annealing at the same temperature for 6 and 9 hours while for ZnO thin films obtained from ZnS under the same conditions were 34.95, 34.54 and 33.37 nm respectively. Also findings exhibited that the nano size of ZnO thin-films obtained from ZnSO<sub>4</sub> that treated under the same conditions was 36.175, 34.48 and 32.6 nm respectively while for ZnO thin-film prepared from commercial ZnO was 30.48 nm. These findings were similar to those obtained by [22] who reported that as the annealing temperature increased the grain size decreased. Results revealed that these values were higher than that obtained by [23] who found that the crystal size of ZnO thin-film was 1.5 nm when it annealed at 500°C. Khan *et al.*, [24] characterized the multilayer ZnO thin films deposited by sol gel spin coating method. They found that the crystal size of single layer of ZnO at 2θ 33.504 was 7.96 nm while for 3 layers was 11.15, 18.9 nm at 2θ 33.498 and 56.15 respectively. Also they found that the crystal size for 5 layers of ZnO thin-film was 17.7, 16.5, 19.4 and 20.8 nm at 2θ 33.509, 38.875, 56.149 and 66.99.4 respectively. Another study conducted by [25], who synthesized ZnFe<sub>1.96</sub>La<sub>0.04</sub>O<sub>4</sub> nano-particles after subjection to the annealing temperature of 900°C for 2 h, 6 h, 12 h, 24 h and 48 h. They found that ZnFe<sub>1.96</sub>La<sub>0.04</sub>O<sub>4</sub> nano-particles decreased with the increase of annealing time.

### CONCLUSION

Results in this work revealed that high annealing temperature for a long time improves the structure of ZnO thin-films samples and control their structure at the nano size level where it promotes and enhances their electrical, optical, photonic properties to be used in new generation of solar cells.

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