VOL. 20, NO. 3, 2021, 32-36
www.elektrika.utm.my
ISSN 0128-4428

ELEKTRIKA
Journal of Electrical Engineering

Morphology and I-V Characteristics of Electrochemically Deposited Zinc Oxide on Silicon

Ahmad Bukhairi Md Rashid, **Mastura Shafinaz Zainal Abidin***, **Shaharin Fadzli Abd Rahman,** and **Amirjan Nawabjan**

School of Electrical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.

*Corresponding author: m-shafinaz@utm.my

Abstract: This paper reported on the electrochemical deposition of zinc oxide (ZnO) on (100) p-silicon (p-Si) substrate using different volume ratio electrolyte mixture. The deposition process was done in room temperature with a current density of 10 mA/cm^2 for 30 minutes. Prior to the experiment, all samples were treated by RCA cleaning steps. The 0.1 M of zinc chloride ($ZnCl_2$) and potassium chloride (KCl) electrolyte mixture were used at a 1:1, 3:1 and 5:1, namely Sample A, B and C. All samples were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). The results show that all samples have the same morphology of a flake-like structure with different Zn:O ratio between 2 to 3 for all samples. The current-voltage (I-V) characteristic graph was obtained by dark current measurement using Keithley SMU 2400 and the threshold voltage (V_{th}) values were determined at 2.21 V, 0.85 V and 1.22 V for sample A, B and C respectively which correlates with Zn:O ratio. The highest value of Zn:O ratio can be found in sample A while the lowest from sample B. Based on these results, it shows that electrochemical deposition technique is capable of being used to deposit the flake-like structure ZnO on semiconductor material to form the p-n junction which behaves like a diode. The value of V_{th} seems to be Zn:O ratio dependent. Higher ratio of Zn and O will cause the higher value of intrinsic carrier concentration and built-in potential which will increase the V_{th} value.

Keywords: electrochemical deposition, ZnO, structural, electrical

Article History: received 22 September 2021; accepted 16 December 2021; published 27 December 2021.

1. INTRODUCTION

Semiconductor is a material that has a conductivity level somewhere between insulator and conductor such as silicon (Si) and germanium (Ge) [1]. These types of materials are unique as they will conduct electricity when a certain voltage or current is achieved. However, current flow depends on the junction created between two different layers that built from p-doped material and n-doped material [2] which apply the concept of combination and recombination of electron and hole. P-doped layer will have hole as the majority carrier and n-doped layer will have electron as the majority carrier. When these two layers were brought together, it will form a p-n junction and the electron from n-doped layer can diffuse to p-doped layer to combine with hole thus will conduct electricity. Usually, the junction is created by doping one side of Si with boron to form a p-type layer and another side with phosphorus to form a n-type layer [2]. Alternatively, the p-n junction can be formed by depositing a layer of p-type material on n-type Si substrate or vice versa to form a p-n junction [3].

Zinc oxide (ZnO), is an inorganic compound with wide bandgap (3.4 eV) and large excitation binding energy [4]. By nature, ZnO is n-type material which is suitable to be deposited on a p-type substrate to form a p-n junction. An application such as solar cell is expected to have better performance with the presence of ZnO as it has wider bandgap compared to Si. Typically, the p-n junction created by doping Si with boron and phosphorus lacks in harvesting photon with higher energy as it will be converted into heat. This will lower the efficiency of the junction created. Better performance with high energy photon would be achieve when ZnO is deposited onto Si substrate.

Various deposition processes had been reported to deposit ZnO on Si substrates, such as arc discharge [5, 6], pulse laser deposition (PLD) [7, 8], pyrolysis [9, 10] and also electrochemical deposition [11-13]. The electrochemical deposition is a process where a film of conducting material is deposited from a solution containing ions onto an electrically conducting surface. This process is acceptably cost-effective, has high deposition rate, simple and quick. The process to deposit can be done by altering several parameters such as current density [14-16], temperature [17], electrolyte concentration [18], deposition time [19], pH [20] and agitation [19, 21]. The electrochemical deposition is mostly attempted for depositing conducting material onto conductor substrate. There only few had reported about deposition onto a semiconductor substrate due to constraints of thermodynamic and kinetics of the deposition process involved [22]. Therefore, this work had explored the feasibility of electrochemical deposition of ZnO on p-Si to further understand on mechanism involved and characteristics of deposited samples. Different volume ratio of electrolyte samples was used to observe any changes on structural properties of deposited ZnO. Particularly, initial studies on morphology and current-voltage (I-V) characteristics of ZnO/Si samples were observed as both are basic parameters that leads towards overall electrical performance and application.

2. METHODOLOGY

In this work, ZnO was deposited on the p-Si (100) substrate with the resistivity of 0.008-0.018 Ωcm by the electrochemical deposition method. Zinc (Zn) plate was used as the anode while p-Si (100) substrate as the cathode. All samples were treated by RCA cleaning steps prior to the experiment.

The details of the sample preparation and pre-treatment had been reported in [23]. Deposition of ZnO on Si substrates was done at room temperature using different electrolyte composition between zinc chloride ($ZnCl_2$) and potassium chloride (KCl) with the volume ratio of 1:1, 3:1 and 5:1 named as sample A, B, and C respectively. The applied current density was set to 10 mA/cm^2 for 30 minutes. The setup used in this study is shown in Figure 1.

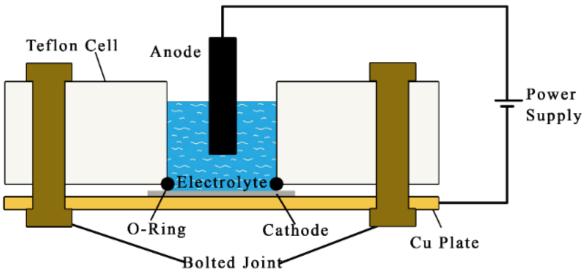


Figure 1. Experiment setup

Based on the setup, the Zn plate that was used as the anode is expected to play an important role in the deposition process. Based on chemical reaction shown in equation 1 below, the oxidation process will occur at the anode where the Zn plate will be oxidized to become Zn^{2+} ion and dissolved in the electrolyte. These Zn^{2+} ions that comes from Zn plate will be used to maintain the concentration of Zn^{2+} ion in the electrolyte as Zn^{2+} ion is being used to be deposited on the cathode surface. Then, Zn^{2+} ion will react with hydroxide ion in the electrolyte to form zinc hydroxide ($Zn(OH)_2$). Finally, $Zn(OH)_2$ would be transformed into ZnO via reduction process which would be deposited onto Si substrate at the cathode as represented by equation 3.

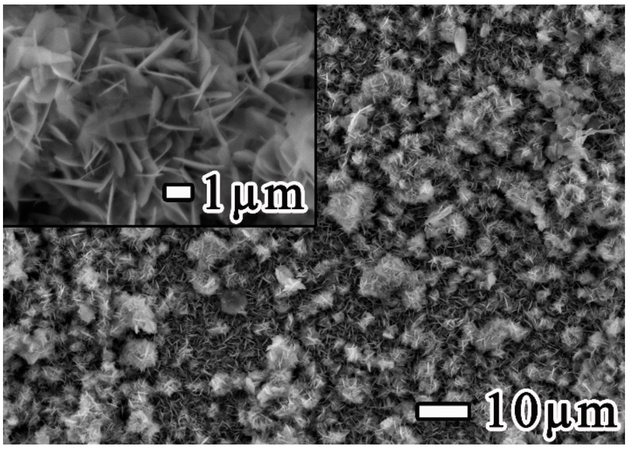
$$Zn \rightarrow Zn^{2+} + 2e \quad (1)$$
$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2 \quad (2)$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

Next, the samples were characterized using scanning electron microscopy (SEM) (JEOL JEM-ARM 200F) with energy-dispersive X-ray (EDX) spectroscopy module to observe their morphology and composition details. The samples also being characterized by using Keithley SMU 2400 to determine the I-V characteristic of the junction created between ZnO and Si. Copper tape has been used as the contact for both back and top of surface substrates. From the I-V characteristic, the threshold voltage (V_{th}) was determined to identify the suitable operating condition of the junction such that conducting path between p-layer and n-layer would be created [24].

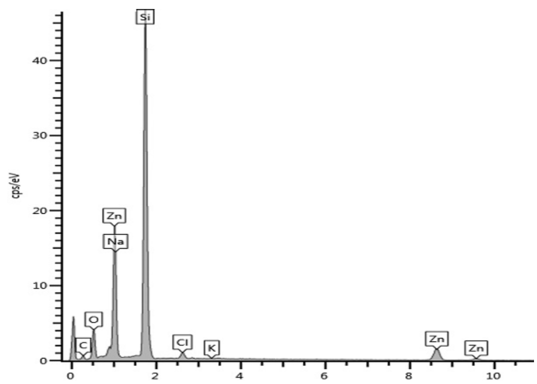
3. RESULTS AND DISCUSSION

Figures 2, 3 and 4 show the SEM images and EDX spectra for sample A, B, and C. From SEM images, all samples indicated that flake-like structure ZnO was formed on Si substrate, similar as reported by [25]. Based on our previous work in [23], the thickness of ZnO layer produced in these samples were estimated to be in 20 to 50 µm. Besides, length of the ZnO flakes were around 1 to 3 µm, with crossing-randomly distributed on the substrates. As reported by [26], ZnO nanoflake may exhibits strong photoluminescence peak which indicates the relationship between the applications in solar cell.

In general, the growth mechanism of ZnO on the Si substrate will follow the Volmer-Weber growth mechanism, that also known as 3D island formation [22]. The process starts with the nucleation process on the Si surface. Then, the nucleation site allows the formation of nuclei (island) that will evolve to form grain. Further formation of nuclei will occur on the existing island and finally, the stack of nuclei will form a ZnO layer on the Si substrate.

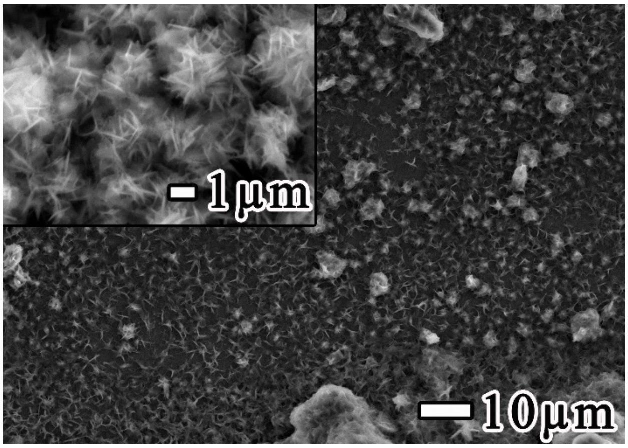


(a)

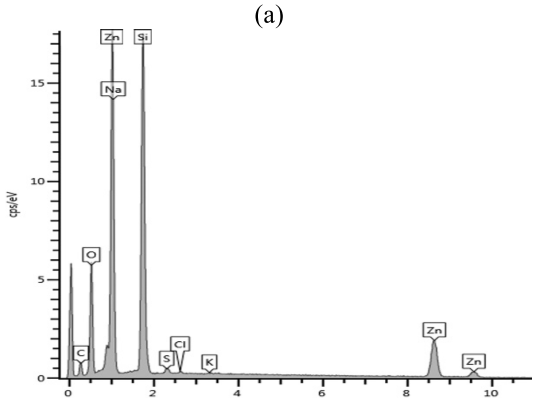


(b)

Figure 2. Sample A (a) Top surface morphology, and (b) EDX spectra

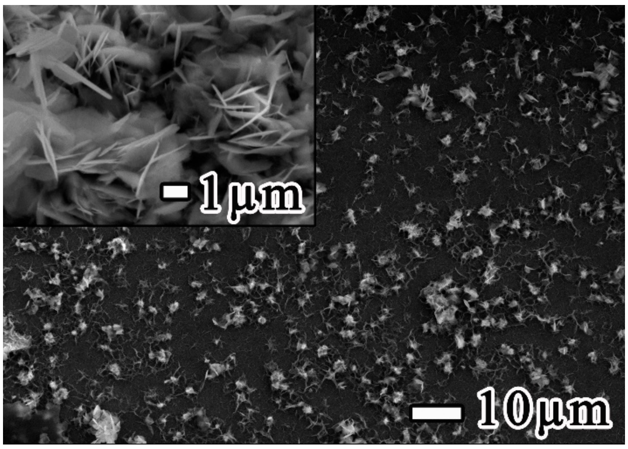


(a)

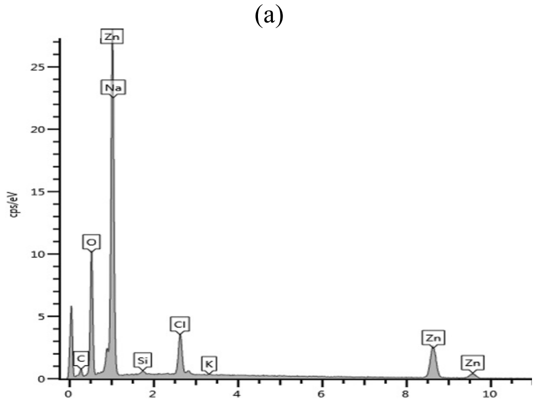


(b)

Figure 3. Sample B (a) Top surface morphology, and (b) EDX spectra



(a)



(b)

Figure 4. Sample C (a) Top surface morphology, and (b) EDX spectra

As the $ZnCl_2$ volume ratio increased from sample A to sample C, the uniformity of the deposited ZnO distribution on the Si substrate surface increased. The EDX spectra also shows that the amount of Si element detected was significantly varied, where sample A had 50.5%, sample B had 28.7%, and sample C had 0.4%. This trend suggested that more Si surface had been covered by Zn and O deposits for Sample C, compared to Sample A. Moreover, the amount of Zn and O detected are reversely proportional to the amount of Si detected, as shown in Figure 5. This further confirmed that more Zn and O were deposited on sample C. Therefore, more percentage of Zn and O can be expected to be deposited on the substrate when higher ratio of $ZnCl_2$ over KCl is used. This could be due to a large amount of Zn^{2+} presence in the electrolyte during the process. As reported by [27], the balance stoichiometry for ZnO was Zn:O (1:1). Yet, the EDX result of this study shows that the ratio between Zn to O for sample A, B and C was obtained at 2.81, 2.35 and 2.49 respectively. This ratio implies that there are numbers of Zn atom that are still free and did not bonding with O atom to fully form ZnO [15] .

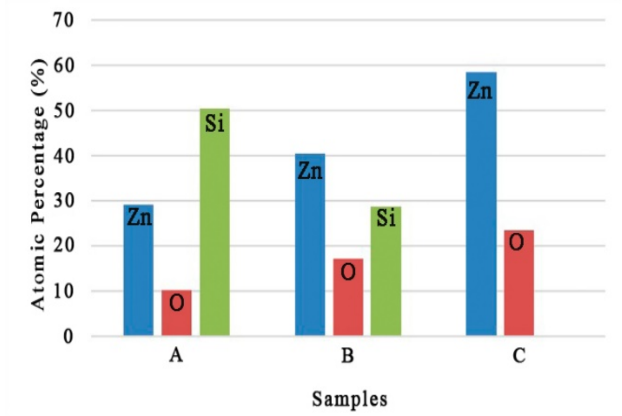


Figure 5. Atomic percentage of Zn, O, and Si for samples A, B, and C

From the I-V curve in Figure 6, the V_{th} values were determined as 2.21 V, 0.85 V and 1.22 V for sample A, B and C respectively. The V_{th} seems to associate with the ratio of Zn:O of the samples. Sample B which has the lowest ratio of Zn:O gave the lowest V_{th} reading, while the highest V_{th} was obtained by sample A that had the highest Zn:O ratio in this work. As reported by [28], as the ratio of Zn:O increases, the value of intrinsic carrier concentration will also increase. Thus, the value of built-in potential will increase which causes V_{th} value also increases which comply with the following equations:

$$V_{bi} = \emptyset_{BO} - \emptyset_n \tag{4}$$

where,

$$\emptyset_{BO} = \emptyset_m - \chi$$

$$\emptyset_n = \frac{kT}{q}\ln\left(\frac{N_C}{N_D}\right)$$

V_{bi} = Built in potential

N_D = Donor atom concentration

N_C = effective density of states in conduction band

$\emptyset_{BO}$= ideal Schottky barrier height

$\emptyset_m$= work function

χ= electron affinity

$\frac{kT}{q}$ = Thermal voltage

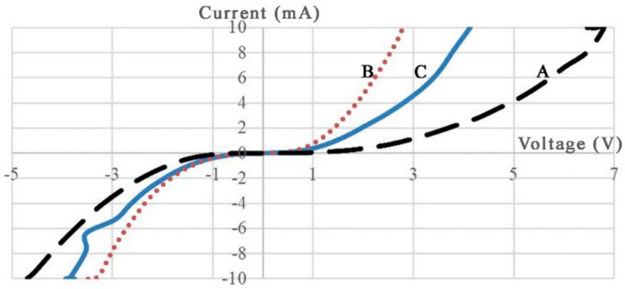


Figure 6. I-V characteristic for sample A, B, and C

In this work, the ZnO/Si samples were heterojunction structure. It is found that the obtained reverse current is considerably too high for solar cell application. Normally, the current flow in the p-n junction under the dark is based on reverse saturation current typically very small as it used to overcome the barrier between p-n junction. It is speculated that this high current indicates that low junction, thus electron can freely move between the junction although in reverse saturation current condition. More analysis data such as ideality factor, reverse saturation current, parallel resistance and series resistance value would be needed to further verify the properties of the junction created, towards solar cell application.

4. CONCLUSION

This work had shown that ZnO layer can be deposited on semiconductor material (p-Si substrate) although the thermodynamic and kinetics of the process are reported to be quite complex. The SEM results have shown that ZnO with flake-like structure is obtained for all samples which have a possible application in solar cell and photoluminescent devices. By increasing the volume ratio of $ZnCl_2$ presence in the electrolyte mixture, the amount of Zn and O deposited on the Si substrate will also increase. The balance stoichiometry of ZnO which is Zn:O (1:1) might be achieved by further optimization works. The V_{th} value shows a relationship with the ratio of ZnO. The lower value of V_{th} might be useful towards low power consumption for device applications.

ACKNOWLEDGMENT

This work has been supported by Universiti Teknologi Malaysia and the Ministry of Higher Education through FRGS/1/2020/TK0/UTM/02/43 grant.

REFERENCES

[1] A. Shaheen, W. Zia, and M. S. Anwar, "Band structure and electrical conductivity in semiconductors," *LUMS School of Science and Engineering, Lahore, Pakistan*, 2011.

[2] A. Sproul, "Understanding the pn Junction," *Solar Cells: Resource for the Secondary Science Teacher*, 2003.

[3] R. K. Gupta, K. Ghosh, and P. K. Kahol, "Fabrication and characterization of NiO/ZnO p–n junctions by pulsed laser deposition," *Physica E: Low-dimensional Systems and Nanostructures,* vol. 41, no. 4, pp. 617-620, 2009.

[4] J. Lee, and Y. Tak, "Electrodeposition of ZnO on ITO electrode by potential modulation method," *Electrochemical and Solid State Letters,* vol. 4, no. 9, pp. C63, 2001.

[5] E. G. Gamaly, and T. W. Ebbesen, "Mechanism of carbon nanotube formation in the arc discharge," *Physical Review B,* vol. 52, no. 3, pp. 2083, 1995.

[6] F. Fang, J. Kennedy, J. Futter, and J. Leveneur, "ZnO nanostructures synthesized by arc discharge for optical coating and sensor applications." pp. 869-873.

[7] J. A. De Mesa, A. M. Amo, J. J. C. Miranda, H. O. Salazar, R. V. Sarmago, and W. O. Garcia, "Effects of Deposition Pressure and Target-Substrate Distance on Growth of ZnO by Femtosecond Pulsed Laser Deposition," *Journal of Laser Micro/Nanoengineering,* vol. 11, no. 1, 2016.

[8] M. Tsoutsouva, C. Panagopoulos, D. Papadimitriou, I. Fasaki, and M. Kompitsas, "ZnO thin films prepared by pulsed laser deposition," *Materials Science and Engineering: B,* vol. 176, no. 6, pp. 480-483, 2011.

[9] G. Kenanakis, and N. Katsarakis, "Ultrasonic spray pyrolysis growth of ZnO and ZnO: Al nanostructured films: application to photocatalysis," *Materials Research Bulletin,* vol. 60, pp. 752-759, 2014.

[10] J.-L. Zhao, X.-M. Li, S. Zhang, C. Yang, X.-D. Gao, and W.-D. Yu, "Highly (002)-oriented ZnO film grown by ultrasonic spray pyrolysis on ZnO-seeded Si (100) substrate," *Journal of materials research,* vol. 21, no. 9, pp. 2185-2190, 2006.

[11] W. Schwarzacher, "Electrodeposition: a technology for the future," *Electrochemical Society Interface,* vol. 15, no. 1, pp. 32-33, 2006.

[12] M. R. Tolosa, J. Orozco-Messana, A. Lima, R. Camaratta, M. Pascual, and M. Hernandez-Fenollosa, "Electrochemical deposition mechanism for ZnO nanorods: diffusion coefficient and growth models," *Journal of The Electrochemical Society,* vol. 158, no. 11, pp. E107, 2011.

[13] S. Lee, *Encyclopedia of chemical processing*: Taylor & Francis US, 2006.

[14] M. Khelladi, L. Mentar, A. Beniaiche, L. Makhloufi, and A. Azizi, "A study on electrodeposited zinc oxide nanostructures," *Journal of Materials Science: Materials in Electronics,* vol. 24, no. 1, pp. 153-159, 2013.

[15] H.-S. Chin, and L.-S. Chao, "The effect of thermal annealing processes on structural and photoluminescence of zinc oxide thin film," *Journal of Nanomaterials,* vol. 2013, 2013.

[16] A. K. Yıldırım, and B. Altıokka, "Effect of Potential on Structural, Morphological and Optical Properties of ZnO Thin Films Obtained by Electrodeposition," *J. Mater. Sci. Eng. B,* vol. 5, no. 3-4, pp. 107-112, 2015.

[17] S. Hori, T. Suzuki, T. Suzuki, S. Miura, and S. Nonomura, "Effects of deposition temperature on the electrochemical deposition of zinc oxide thin films from a chloride solution," *Materials Transactions,* vol. 55, no. 4, pp. 728-734, 2014.

[18] J. Yu, H. Sun, L. Zhao, Y. Wang, M. Yu, H. Luo, Z. Xu, and K. Matsugi, "Effects of electrolyte concentration and current density on the properties of electro-deposited NiFeW alloy coatings," *Bulletin of Materials Science,* vol. 40, no. 3, pp. 577-582, 2017.

[19] T. Tuaweri, E. Adigio, and P. Jombo, “A study of process parameters for zinc electrodeposition from a sulphate bath,” *International Journal of Engineering Science Invention,* vol. 2, no. 8, pp. 17-24, 2013.

[20] P. U. Londhe, and N. Chaure, "Effect of pH on electrodeposited ZnO thin films." pp. 671-672.

[21] N. Whitehead, R. Ditchburn, W. McCabe, and R. Van Der Raaij, “Factors affecting the electrodeposition of ^{226}Ra,” *Journal of radioanalytical and nuclear chemistry,* vol. 160, no. 2, pp. 477-485, 1992.

[22] G. Oskam, J. Long, A. Natarajan, and P. Searson, “Electrochemical deposition of metals onto silicon,” *Journal of Physics D: Applied Physics,* vol. 31, no. 16, pp. 1927, 1998.

[23] A. B. M. Rashid, M. S. Z. Abidin, S. F. Abd Rahman, and A. Nawabjan, “Influence of electrochemical deposition parameters on morphological properties of ZnO on Si (100),” *Materials Research Express,* vol. 6, no. 2, pp. 026414, 2018.

[24] P. Hazra, S. Singh, and S. Jit, “Studies on ZnO/Si Heterojunction Diode Grown by Atomic Layer Deposition Technique,” *Journal of nanoelectronics and optoelectronics,* vol. 8, no. 4, pp. 378-382, 2013.

[25] C. Liu, Y. Chen, H. Cui, B. Marí, and R. Wang, "The aggregation structure of flat pentagonal flake ZnO films by electrodeposition method." pp. 1583-1586.

[26] P. K. Samanta, and A. Saha, “Wet chemical synthesis of ZnO nanoflakes and photoluminescence,” *Optik,* vol. 126, no. 23, pp. 3786-3788, 2015.

[27] S. Lindroos, and M. Leskelä, “Growth of zinc peroxide (ZnO2) and zinc oxide (ZnO) thin films by the successive ionic layer adsorption and reaction–SILAR–technique,” *International Journal of Inorganic Materials,* vol. 2, no. 2-3, pp. 197-201, 2000.

[28] Z. Pan, X. Cheng, B. Mar, and H. Cui, “The aggregation structure of flat and curve pentagonal flake of ZnO films by electrodeposition method,” 2016.