Zinc Oxide Thin Films Properties Dependence on the Gas Flow Rate of Thermal Chemical Vapor Deposition

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***Abstract*— Zinc oxide (ZnO) thin films were deposited using thermal chemical vapor deposition (TCVD) method with a two furnaces system. To enhance the growth of the nanostructure, the sol-gel spin coated ZnO templates were used. To study the effect of oxygen gas flow rate on the properties of the thin films, the gas flow rate were varied from 5 to 25 standard cubic centimeter per minute (sccm). The samples were characterized using field emission scanning electron microscopy (FE-SEM), photoluminescence (PL) spectra, current-voltage (I-V) measurement, X-Ray Diffraction (XRD). The FE-SEM images showed by increasing the gas flow rate of oxygen the feet of the nano-tetrapod became longer and thinner. Additionally, I-V curve shows that resistance of the thin films increase as the deposition oxygen gas flow rate increases.**

Keywords: ZnO Nanosturctures; Thermal Chemical Vapor Deposition; ZnO template; gas flow rate

I. INTRODUCTION

Zinc Oxide (ZnO) based thin films are indeed interesting for their applications in semiconducting, photoconducting or piezoelectric and optical waveguide materials [1]. ZnO has been recognized as a promising semiconductor material owning to its wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV. ZnO also has a stable wurtzite structure with lattice spacing a = 0.325 nm and c = 0.521 nm [2]. These properties make it a potentially promising photonic material for rich optoelectronic applications, such as solar cells [3], UV photodetectors [4], blue-UV laser diodes [5], light emitting diodes [5], field emission displays [6], and so on [7]. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics [8]. Many studies had been done to produce nanostructured ZnO thin film such as nanorods, nanotubes, nanowires, nanoflowers and etc [9]. Recently, multiple synthesis techniques have been developed to fabricate ZnO nanostructure such as r. f. sputtering [10], thermal chemical vapor deposition (TCVD) [2], sol-gel spin coating [2], and plasma enhanced chemical vapor deposition (PECVD) [11]. In this research, TCVD method is used because it is more effective, low cost and as a common method compare to the others. The use of ZnO template which acts as the catalyst to the ZnO nanostructure is to strengthen the bound. There are many parameters to be studied in order to produce good quality ZnO nanostructure. One of them is to the study on the gas flow rate effect on ZnO thin film properties. In this work, ZnO thin films are deposited on quartz substrate using thermal chemical vapor deposition method [2]. In this paper, we present the growth of ZnO thin film using TCVD method and the characterization of the thin film at different oxygen gas flow rate.

II. EXPERIMENT PROCEDURE

A. Preparation of ZnO Template

ZnO templates which act as the catalyst to the ZnO nanostructure were first prepared. Based on the deposition of the ZnO template, the quartz substrate were cleaned using acetone, methanol and deionized water in ultrasonic bath for 10 minutes, in an ordered list before blown dried using nitrogen gas. To perform sol-gel method to prepare the ZnO template, the Zinc acetate dehydrate (ZnAc), Monoethanolamine and 2-Methoxyethanol were mixed altogether and being stirred using a hot plate magnetic stirrer at 80°C for 1 hour to produce a clear and homogeneous solution. After being stirred for 1 hour, the solution was then aged for a day (24 hours) to ensure that the chemical process was done and ready for deposition process. Then the substrates were placed in a spin coater rotating at 3000 rpm for 1 minute for 1 layer while the prepared solution was dropped onto the substrate in the spin coater with 15 drops for 1 layer. Next the samples were dried for 10 minutes with a temperature of 200°C and then annealed for 1 hour at a temperature of 500°C to obtain good crystallinity of the ZnO template. This process is repeated for 6 times to obtain ZnO template with 6 layers and thickness of approximately 140nm.

B. Deposition of ZnO Nanostructure

ZnO nanostructure were deposited using TCVD technique having two furnace system as shown in Figure 1, with the main parameter being varied was the oxygen gas flow rate. The deposition process was completed with the zinc nanopowder placed in alumina boat as precursor in furnace 1, while the ZnO template was placed horizontally in furnace 2. The temperature was set to 700°C in furnace 1 so that the zinc nanopowder will evaporated, while the temperature of furnace 2 was set to 500°C. There are two inlet gasses which are oxygen and argon where the gas flow rate of oxygen was varied during the deposition process. The deposition time was

30 minutes with argon gas flow at 100 sccm which acts as the carrier gas while oxygen was varied from 5, 10, 15, 20 to 25 sccm for the deposition of nanostructures. The samples were then cooled down until both of the furnaces reaches the temperature below 100°C before it can be extract from the furnace. During the cooling process the argon gas flow was maintained. The nanostructure ZnO thin films were characterized using field emission scanning electron microscopy (FE-SEM) for surface morphology, X-Ray Diffraction (XRD, Broker AXS D8 Advance) for physical properties, two point probes (Solar Simulator) for electrical properties, and photoluminescence (PL, FlouroMax 3 Horiba Jobin Vyon) for optical properties. The overall process is shown in Figure 2.

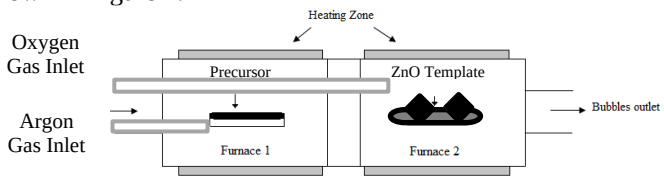


Figure 1 : Schematic diagram of two-furnace TCVD system setup

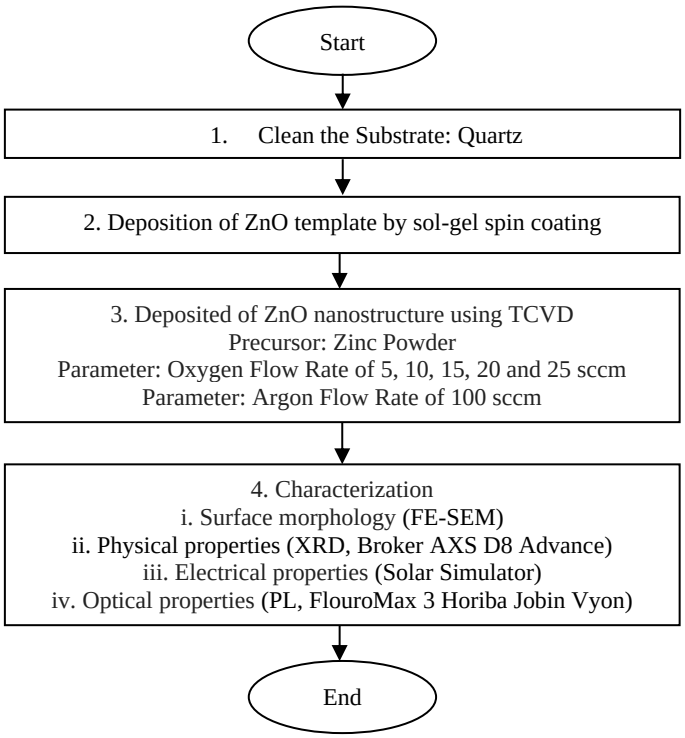
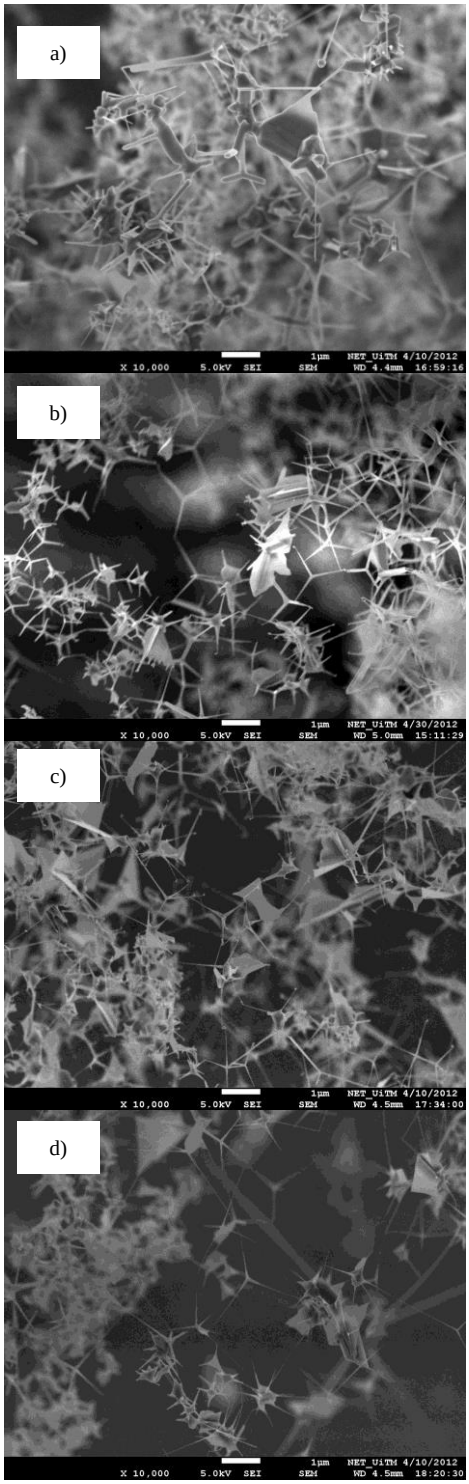


Figure 2 : The flow chart of experiment

III. RESULTS & DISCUSSIONS

A. Surface Morphology

Figures 3 (a) to (e) show the top view of FE-SEM images of the ZnO nanostructure thin films deposited by TCVD at oxygen flow rate of 5, 10, 15, 20 and 25 sccm, respectively. From Figure 3, we can see that the nano-tetrapod like shape of ZnO nanostructures is formed. The formation of nano-tetrapod was controlled by the interaction of Zn powder vapor, Ar and O_2 gas. The ZnO tetrapod of different sizes was obtained in range of oxygen gas pressure. From the FE-SEM images the feet of the nano-tetrapod became longer and thinner as the oxygen flow rate increases. The nano-tetrapod growth start from oxygen flow rate of 5 sccm to the highest flow rate of 25 sccm. The dimension of the nano-tetrapod was affected by the synthesis parameters [12].



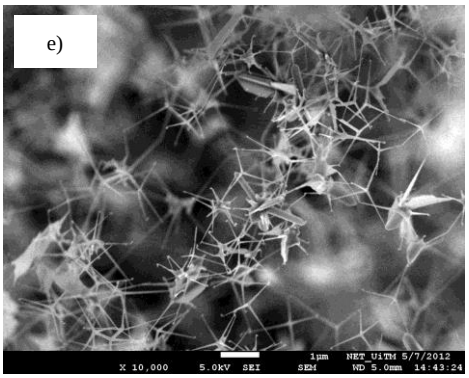


Figure 3 : FE-SEM images for ZnO thin films with oxygen flow rate at (a) 5sccm, (b) 10sccm, (c) 15sccm, (d) 20sccm, and (e) 25sccm

TABLE I. AVERAGE LEG SIZES OF ZNO NANOSTRUCTURES

Gas flow rate (sccm)	Average leg sizes of ZnO Nanostructures (nm)
5	90.2
10	83.8
15	65.6
20	49.1
25	42.6

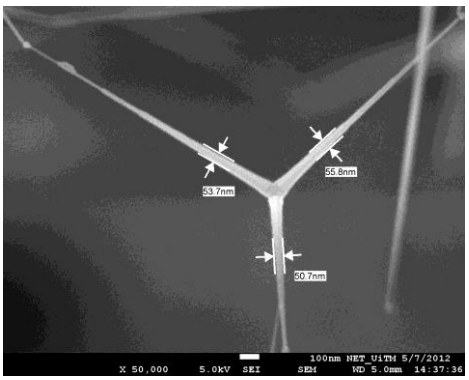


Figure 4 : FE-SEM images for ZnO thin films with enlarged ZnO tetrapod

The size of the tetrapod legs was measured (Figure 4) and the average is shown in Table 1. It can be seen that the size decrease with the increasing gas flow rate.

The crystalline structure was examined by X-Ray Diffraction. XRD patterns for the samples are shown in Figure 5. All samples exhibit peaks at 32°, 34.5° and 36.5° which corresponds to ZnO having 001, 002 and 101 structures [13]. From these results, we can say that the deposited nanostructures belong to hexagonal wurtzite structure. Comparing all samples it can be seen that the film deposited with 20 sccm gives the peak with the highest intensity. As the results consist of multiple peaks we can call this as poly-crystalline structure.

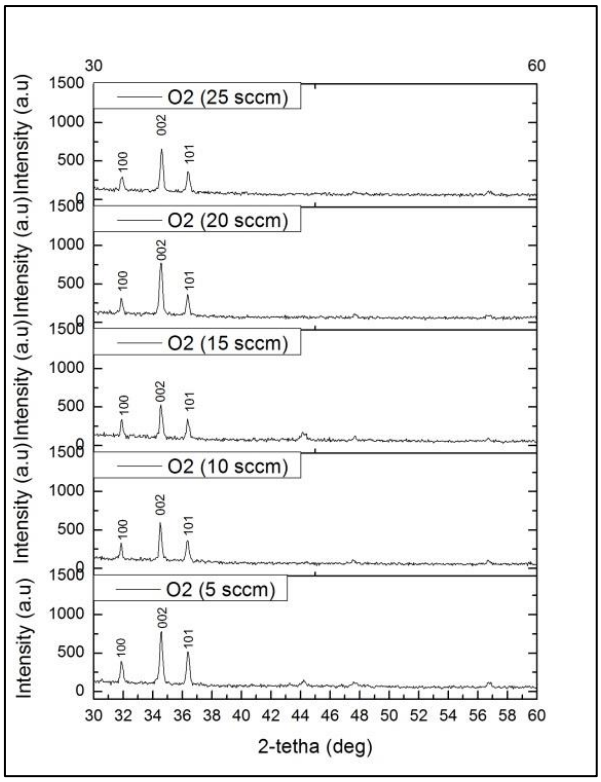


Figure 5 : Show is XRD pattern of template

B. Electrical Properties

Electrical properties of the ZnO thin films were characterized using two point probe. Gold were first deposited onto the samples contact using sputter coater which act as the metal contact before the measurement is done. The current-voltage (I-V) curve is shown in Figure 6. I-V curve shows that resistance of the thin films increase as the deposition oxygen gas flow rate increases.

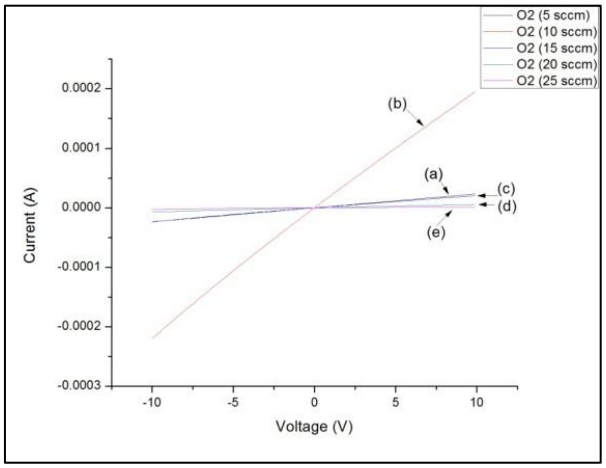


Figure 6 : IV curve for ZnO thin films with oxygen flow rate at (a) 5sccm, (b) 10sccm, (c) 15sccm, (d) 20sccm, and (e) 25sccm

The resistivity was obtained from these characteristics by using the formula shown below:

$$\rho = R\frac{wt}{l}$$

Where ρ is the resistivity, t is the thin film thickness; and R is the resistances which are obtained from the graph. Thicknesses of the thin films were obtained using surface profiler. Resistivity of each of the thin film is plotted in Figure 7. From Figure 7, we can see that the when the oxygen gas flow rate is increase the resistivity will also increase.

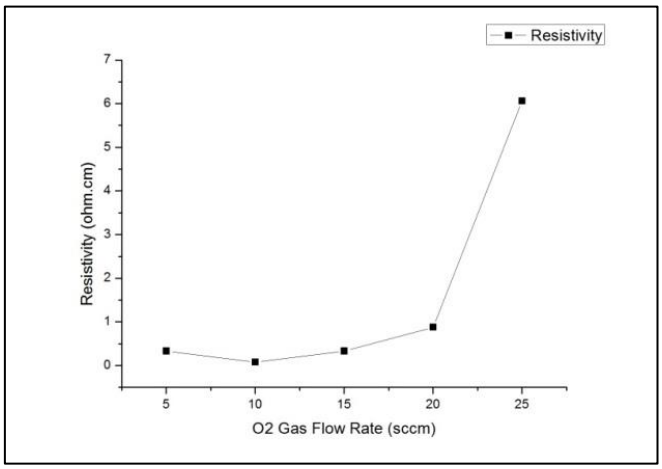


Figure 7 : Resistivity of ZnO thin films with increment of oxygen gas flow rate

A. Optical Properties

Room temperature PL measurements of the ZnO nanoparticles were obtained under excitation of He-Cd laser (325 nm) to study the light emitting properties of the samples. PL spectra obtained from the samples deposited at different gas flow rate are shown in Figure 8. From the spectra, a strong PL emission at 380 nm for all samples which is a near-band edge UV emission is observed. This is due to the electronic transition from near conduction band to valence bands [2]. From the spectra, when the oxygen flow rate is high, the visible emission is low. The great amount of oxygen vacancies do contribute to the visible emission, but the surface state may play a more important role in the visible emission, because the thinner part has a larger surface to volume ratio [14].

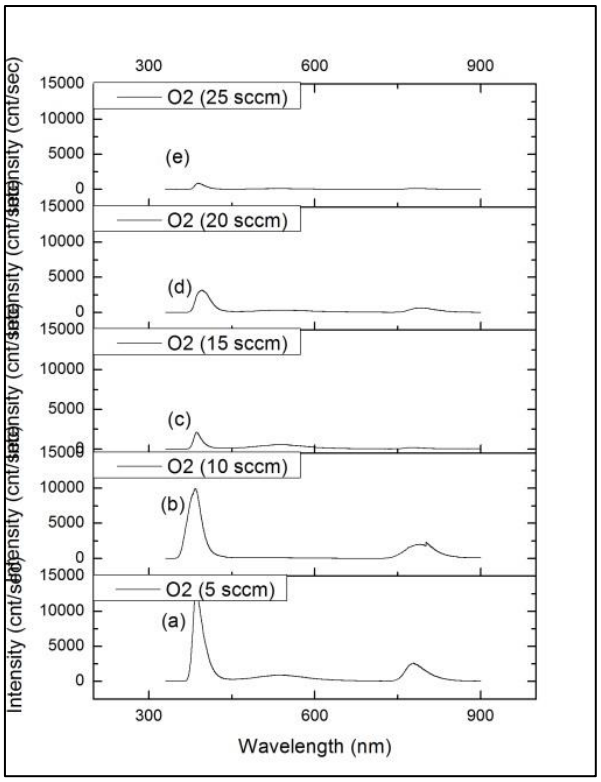


Figure 8 : Photoluminescence Spectra of ZnO thin films for oxygen in (a) 5sccm, (b) 10sccm, (c) 15sccm, (d) 20sccm and (e) 25sccm

IV. Conclusion

ZnO thin films having nanostructures (tetrapod) were deposited by using TCVD method at gas flow rate of oxygen varied from 5, 10, 15, 20, 25 sccm. The FE-SEM images showed by increasing the gas flow rate of oxygen the feet of the nano-tetrapod became longer and thinner. Additionally, I-V curve shows that resistance of the thin films increase as the deposition oxygen gas flow rate increases. From PL spectra, it can be seen that the visible emission is lowered as the O_2 flow rate increased. These results conclude that the oxygen flow rate has some effect on the growth of ZnO nanostructures and their characteristics. For future recommendation, in order to further investigate the effect of gas flow rate on the nanostructure growth, the study on gas flow rate with increasing temperature can be considered.

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REFERENCES

[1] L. Znaidi, G.J.A.A. Soler Illiab, S. Benyahiaa, C. Sanchezb, A.V. Kanaeva "Oriented ZnO thin films synthesis by sol–gel process for laser application," *Thin Solid Films*, Vol. 428, pp. 257-262, 2003.

[2] S. S. Shariffudin, N. Z. Zakaria, S. H. Herman and M. Rusop "Effect of Deposition Temperature on the Characteristics of Zinc Oxide Nanoparticles This Films Deposited by Thermal Chemical Vapour Deposition," 2011. ICEDSA 2011. *International Conference on Electronic Devices, Systems and Applications* on, pp. 272-275, 2011,

[3] W. J. Jeong, S. K. Kim, and G. C. Park, "Preparation and characteristic of ZnO thin film with high and low resistivity for an application of solar cell," *Thin Solid Films*, Vol. 506-507, pp. 180-183, 2006.

[4] Liqiao Qin, Christopher Shing, Student Member, IEEE, and Shayla Sawyer, Member, IEEE "Metal–Semiconductor–Metal Ultraviolet Photodetectors Based on Zinc-Oxide Colloidal Nanoparticles," *IEEE Electron Device Letters*, Vol. 32, No. 1, pp. 51-53, 2011.

[5] Yong-Seok Choi, Jang-Won Kang, Dae-Kue Hwang, and Seong-Ju Park, "Recent Advances in ZnO-Based Light-Emitting Diodes," *IEEE Transactions on Electron Devices*, Vol. 57, 2010.

[6] Zhixian Lin, Yun Ye, Lian Ma and Tailiang Guo "The Study of a Tetrapod-like Nanostructure ZnO Field Emission Display," *Materials and Devices Conference* on 2009, pp. 80-83, 2009.

[7] Cha-Hsin Chao, Jing-Shun Huang, and Ching-Fuh Lin "Low-Temperature Growth of Surface-Architecture-Controlled ZnO Nanorods on Si Substrates," *J. Phys. Chem. C*, Vol. 113, pp. 512-517, 2009.

[8] Zhiyong Fan and Jia G. Lu "Zinc Oxide Nanostructures: Synthesis and Properties", *University of California, Irvine, USA*, pp. 1-25, 2005.

[9] S.S. Shariffudin, M.Z. Musa, M.H. Mamat and M. Rusop, "Effect of Gold Catalyst Thickness on Zinc Oxide Thin Films", *ICSE Proc.*, pp. 72-75, 2010.

[10] Ping-Feng Yang, Hua-Chiang Wen, Sheng-Rui Jian, Yi-Shao Lai, Sean Wu, Rong-Sheng Chen, "Characterizations of ZnO Thin Films Deposited onto Langasite Substrates by r.f. Magnetron Sputtering," pp. 1-5, 2007

[11] Dalong Zhao, Devin A. Mourey, and Thomas N. Jackson "Low-Temperature Pulsed-PECVD Zno Thin-Film Transistors," *Journal of Electronic Materials*, Vol. 39, no. 5, pp. 554-558, 2010.

[12] Run Wu, Changsheng Xie "Formation of tetrapod ZnO nanowhiskers and its optical properties," *Materials Research Bulletin*, Vol. 39, pp. 637-645, 2004.

[13] J. Wei, C.Yang, B.Y.Man, M.Liu, C.S.Chen, A.H.Liu, L.B.Feng "Characterization and optical properties of ZnO tetrapod nanorods synthesized by two-step method," *Physica B*, Vol. 405, pp. 1976-1979, 2010.

[14] Hua Zhang, Li Shen, and Shouwu Guo, "Insight into the Structures and Properties of Morphology-Controlled Legs of Tetrapod-Like ZnO Nanostructures," *J. Phys. Chem. C*, Vol. 111, pp. 12939-12943, 2007.

[15] Hisashi Yamamoto, Yoshio Otani, Takafumi Seto, Pat Nartpochananon, Tawatchai Charinpanitkul, "Generation of uniform tetrapod-shaped zincoxide nanoparticles by gas-phase reaction with using flow restrictor," *Advanced Powder Technology*, Vol. 23, pp.71-79, 2012.