Solid State Science and Technology, Vol. 18, No 1 (2010) 343-348
ISSN 0128-7389

STUDY ON THE STRUCTURAL AND OPTICAL PROPERTIES ON THE EFFECT OF DEPOSITION TIME ON THE ZnO NANORODS GROWN ON POROUS SILICON SUBSTRATE

S. Amizam[1,3], H.A. Rafaie[1,3], M.H. Mamat [2,3], Z. Khusaimi[1,3], M.Z. Sahdan[2,3], S. Abdullah[1,3] and M. Rusop[2,3]

[1]*Faculty of Applied Sciences,*
University Technology MARA, 40450 Shah Alam, Malaysia

[2]*Faculty of Electrical Engineering,*
University Technology MARA, 40450 Shah Alam, Malaysia

[3] *NANO-SciTech Centre, Institute of Science,*
University Technology MARA, 40450 Shah Alam, Malaysia

ABSTRACT

In this study, we investigated the structural and optical properties of ZnO Oxide (ZnO) Nanorods grown on Porous Silicon (PSi) substrate at different deposition time. By using sol-gel immersed method that contained zinc nitrate hexahydrate ($Zn(NO_3)_2.6h_2O$) and hexamethenamine ($C_6H_{12}N_4$) the ZnO Nanorods on PSi was synthesized. A homogenous and stable solution was prepared by dissolving the $Zn(NO_3)_2.6h_2O$ in a solution of DI water and hexamethenamine. The molar ratio of nitrate solution and hexamethenamine is 1:1. The structural properties of the samples were characterized using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) and photoluminescence (PL) for optical properties. The SEM images showed that the nanorods with different aspect ratio were formed through tuning the deposition time when the molar concentration was 0.01 M. From the XRD measurement result, it can be seen that the growth orientation of ZnO Nanorods was [100] and [101]. Photoluminescence (PL) spectra show that the ZnO Nanorods exhibit a strong-violet (UV) emission of 398 nm and several weak emissions in the blue and green bands.

INTRODUCTION

For the several years, ZnO has attracted great attention of researcher due to its unique physical properties. ZnO is an II-VI semiconductor with a wide and direct band-gap of 3.37 eV at room temperature [1]. Growing attention in one dimensional (1D) oxide materials especially ZnO nanorods is being displayed due to their novel properties and potential applications in nano-devices and optoelectronics [2]. ZnO nanorods have been prepared by various methods such as chemical vapor deposition (CVD) [3-10] metal organic chemical vapor deposition (MOCVD) [11-13] hydrothermal [14] and sol-gel method [15]. Among these methods, sol-gel has distinct potential advantages due to its simplicity, safety, low cost of the apparatus and raw materials, lower crystallization temperatures, ability to tune microstructure via sol-gel chemistry, compositional control

Corresponding Author: suhaidah_amizam@yahoo.com

and large surface area coating capability [16]. The immersion technique on the growing ZnO nanorods has attracted considerable attention because of its unique advantages such as it is a simple, low temperature (60-100°C), high yield and more controllable process [16]. In this study, we will focus on the preparation of ZnO nanorods at different deposition time grown on PSiNs substrate using sol-gel method.

EXPERIMENTAL

In this study, the ZnO nanorods were synthesized on PSi substrate by using immersed sol-gel method at different deposition time. In a typical procedure, 0.01 M zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] was mixed with hexamethylenetetramine (HMT) [$C_6H_{12}N_4$] solution. In this process, the ratio of $Zn(NO_3)_2 \cdot 6H_2O$ and HMT is 1:1. The solution was slowly stirring at 60°C for 2 hours and aging 24 hours at room temperature until complete dissolution.

PSi was used as a substrate. The p-type Si(100) wafer were used for the PSi formation. The preparing parameters for the PSi are as follows: The electrolyte contains HF and ethanol with volume mixing ratio of 1:1. The current density is 20 mA/ cm^{-2} and etching time is 20 min. Subsequently, the fresh PSi was rinsed with deionized water to avoid the existence of electrolyte. The volume of the solution was 50 ml and the PSi substrates were put into a vessel containing the nitrate solution mention above. The temperature of the vessel was kept at 95ºC for 1, 2, 5, 15, 24 and 48 hours. Subsequently, the samples were taken out and put into a furnace. The temperature of the furnace was ramped to 150ºC and kept constant for 1 hour, and then the samples were annealed at 600ºC for 1 hour. The structural properties of the ZnO nanorods were observed using SEM (JSM-6360LA) and XRD (D-5000 SIEMENS). The optical properties of the ZnO nanorods were characterized using photoluminescence spectrometer (FluoroMax3) at room temperature.

RESULTS AND DISCUSSIONS

The SEM image of the ZnO nanorods grown on PSi substrate prepared under different deposition time at 95°C are shown in figure 1 (a-f). Using the simple and low-temperature method from aqueous solution, ZnO nanorods were successfully obtained. From the figure below, it can be seen that the morphologies of ZnO nanorods are significantly different. The average diameter of the ZnO nanorods is ~ 2000 nm, ~830 nm, ~500 nm, ~166 nm, ~498 nm and ~1000 nm for samples (a), (b), (c), (d), (e) and (f) respectively. The average length of the samples is ~1.52 µm, ~1.86 µm, ~2.68 µm, ~3.56 µm, ~2.46 µm and ~3.15 µm respectively. It was found that the length/diameter aspect ratios of the ZnO nanorods increases and the diameters decreases as the deposition time prolong. However, when the deposition time reached 24 h, the diameter of nanorods become bigger and when the deposition time at 48 h in figure 1(f), it show that the nanorods were grown at the end of microrods. Based on the above discussion, the optimized reaction time for the formation of the nanorods is 15 h.

Corresponding Author: suhaidah_amizam@yahoo.com

Solid State Science and Technology, Vol. 18, No 1 (2010) 343-348
ISSN 0128-7389

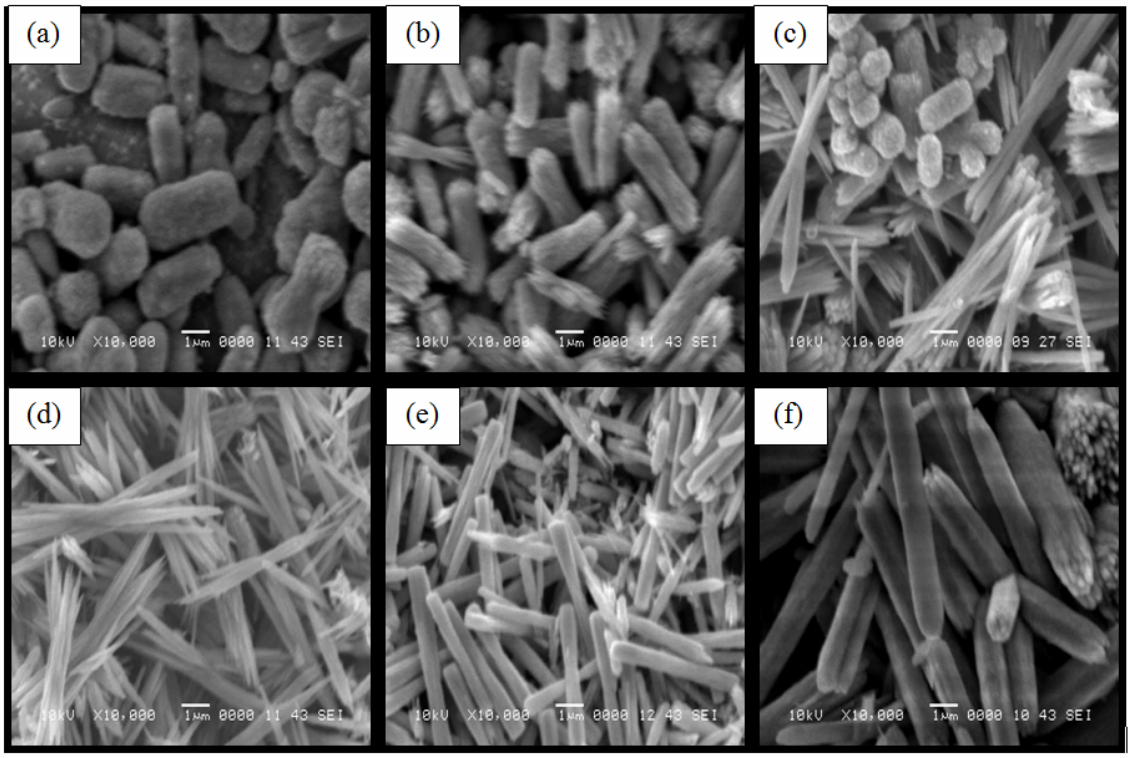

Figure 1: SEM images of ZnO randomly oriented nanorods on PSiNs at different deposition time: (a) 1 h; (b) 2 h; (c) 5 h; (d) 15 h; (e) 24 h and (f) 48 h.

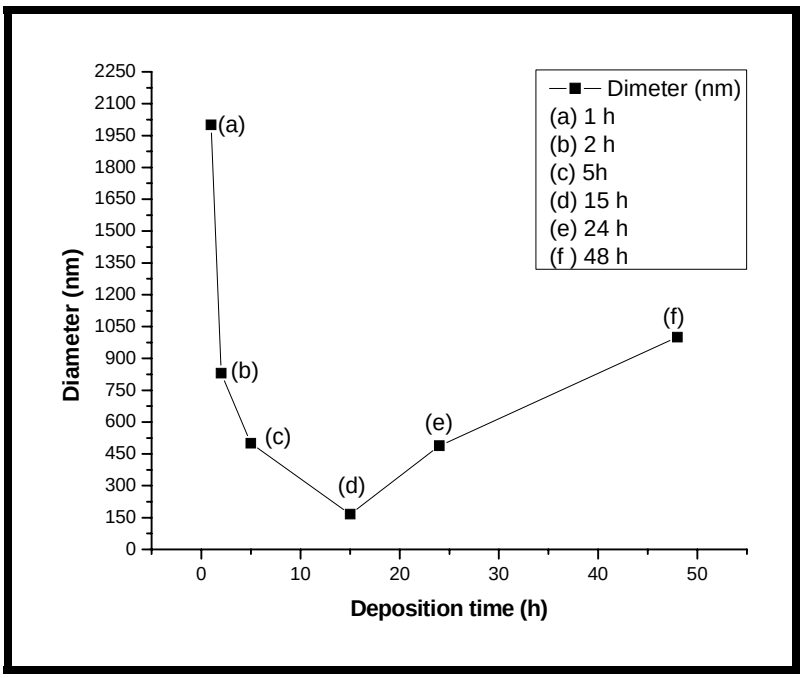

Figure 2: The dependence of average diameter of ZnO nanorods on deposition time.

Corresponding Author: suhaidah_amizam@yahoo.com

Solid State Science and Technology, Vol. 18, No 1 (2010) 343-348
ISSN 0128-7389

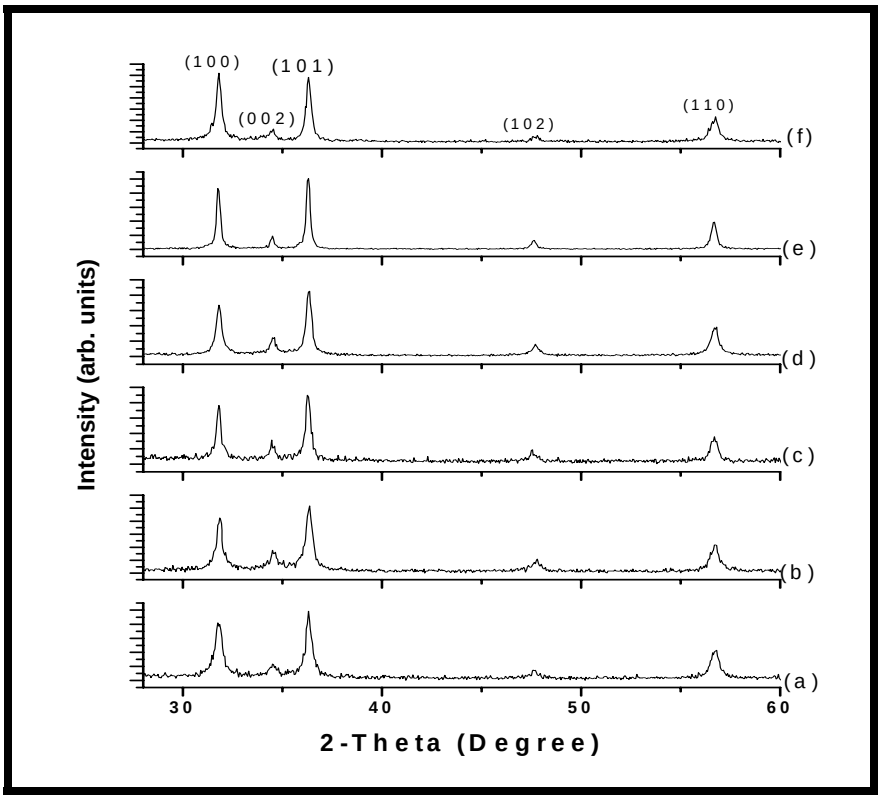

Figure 3: XRD patterns of ZnO Nanorods

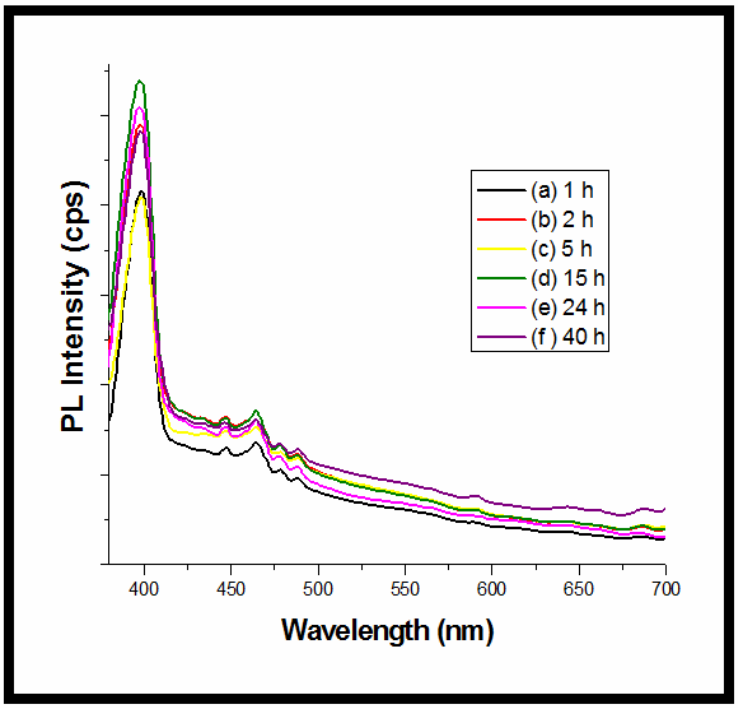

Figure 4: PL spectra of the ZnO nanorods grown on PSiNs at different immersion time at different deposition time.

Corresponding Author: suhaidah_amizam@yahoo.com

Figure 3 display a typical XRD pattern for the ZnO nanorods. All the peaks of the nanorods prepared under different deposition time can be well indexed to hexagonal wurtize ZnO (JCPDS card, No. 079-2205). From the XRD analysis, the strongest peak obtained from all samples corresponds to the (101) plane at $2\theta = 36.25°$.

The PL spectra of the ZnO nanorods grown on PSiNs substrate at different immersion time are shown in figure 4. From the graph, it can be observed that each spectrum consists of a strong band ultraviolet (UV) PL band located at 398 nm and the weak blue emission band centered at 465 nm. Generally, there are three PL bands in UV, green and yellow emissions observed in ZnO. The UV emission of ZnO was attributed to direct recombination of excitons through an exciton-exciton collision process, where one of the excitons radiatively recombines to generate a photon called the exciton emission process [17] and the green-yellow emissions are identified as being from the radiative recombination of the electrons from shallow donors with the trapped holes from singly ionized oxygen vacancies and interstitial oxygen [18]. In our results, there are no green emission band are observed. However, a broad blue emission band appears in the graph.

CONCLUSIONS

In this work, a simple and low temperature method was developed to synthesis ZnO nanorods. By adjusting deposition time, different sizes of nanorods were obtained without any catalyst on PSi substrate. The ratio of length/diameter of ZnO increased with the increasing deposition time. Photoluminescence measurement showed the highest intensity of UV emission at 15 h deposition time. It can be concluded that sol-gel immersion method has a great potential in large-scale and low-cost preparation of ZnO nanorods.

ACKNOWLEDGEMENTS

This study is supported by the Ministry of Science and Technology (MOSTI) and the author would like to thank Nano-SciTech Centre members and Microwave Technology Centre (MTC), Universiti Teknologi MARA (UiTM) Malaysia for materials and characterization equipment.

REFERENCES

[1]. C.J Lee, T.J. Lee, S.C. Yu, Y. Zhang, H. Ruh and H.J. Lee: Appl. Phys. Lett., 2002, 81, 3648-3650.
[2]. X. Tian, Fang Pei, Jinbo Fei, Chao Yang, Hongyu Luo, Dongyue Luo and Zhenbang Pi: Physica E, 2006, 31, 213-217.
[3]. H.Y. Lu, S.Y. Chu and S.H. Cheng: J. Cryst. Growth, 2005, **274**, 506-511.
[4]. P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham,

Corresponding Author: suhaidah_amizam@yahoo.com

R. He and H.J. Choi: Adv. Funct. Mater., 2002, **12**, 323–331.
[5]. Y.C. Kong, D.P. Yu, B. Zhang, W. Fang and S.Q. Feng: Appl. Phys. Lett. 2001, **78,** 407-409.
[6]. T.Y. Kim, J.Y. Kim, S.H. Lee, H.W. Shim, S.H. Lee, E.K. Suh and K.S. Nahm: Synth. Met., 2004, **144,** 61-68.
[7]. J.S. Lee, M.I. Kang, S. Kim, M.S. Lee and Y.K. Lee: J. Cryst. Growth, 2003, **249**, 201-207.
[8]. C.L. Xu, D.H. Qin, H. Li, Y. Guo, T. Xu and H.L. Li: Mater. Lett., 2004, **58** 3976–3979.
[9]. H. Ham, G.Z. Shen, J.H. Cho, T.J. Lee, S.H. Seo and C.J. Lee: Chem. Phys. Lett. ,2005, **404**, 69–73.
[10]. J.B. Baxter and E.S. Aydil: J. Cryst. Growth, 2005, **274**, 407–411.
[11]. M.C. Jeong, B.Y. Oh, W. Lee and J.M. Myoung: J. Cryst. Growth, 2004, **268,** 49– 154.
[12]. C. Shaoqiang, Z. Jian, F. Xiao, W. Xiaohua, L. Laiqiang, S. Yannling, X. Qingsong, W. Chang, Z. Jianzhong and Z. Ziqiang: Appl. Surface Science, 2005, **241,** 384-391.
[13]. L. Tang, X.B. Bao, H. Zhou and A.H. Yuan: Physica E, 2008, **40**, 924–928.
[14]. Q. Ahsanulhaq, A. Umar, and Y.B. Hahn: Nanotechnology, 2007, **18** 115603 (7pp).
[15]. C. Shaoqiang, Z. Ziqiang, Z. Jianzhong, J. Zhang, S. Yanling, K. Yu,W. Wang, X. Wang, F. Xiao, L. Laiqiang and L. Shao: Appl. Surf. Sci., 2004, **230**, 418–420.
[16]. L. Vayssieres, K. Keis, S. Lindquist, A. Hagfeldt, J. Phys. Chem. B 105
[17]. D.M. Bengal, Y.F. Chen, Z. Zhu and T. Yao, Appl. Phys. Lett **70**,2230(1997)
[18]. Wu X L, Siu G G, Fu C L and Ong H C 2001 *Appl. Phys. Lett.* **78** 2285

Corresponding Author: suhaidah_amizam@yahoo.com