Growth of ZnO Nanowires Without Catalyst on Porous Silicon

H. I. Abdulgafour, Z. Hassan, F. K. Yam, and M. J. Jawad

Citation: AIP Conf. Proc. **1341**, 18 (2011); doi: 10.1063/1.3586945
View online: http://dx.doi.org/10.1063/1.3586945
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1341&Issue=1
Published by the American Institute of Physics.

Growth of ZnO Nanowires Without Catalyst on Porous Silicon

H.I. Abdulgafour, Z. Hassan, F. K. Yam, M. J. Jawad

School of Physics, Universiti Sains Malaysia, 11800-Penang, Malaysia
Email: hind_alshaikh@yahoo.com

Abstract. In this paper, porous silicon (PS) technology is used to achieve a wide range of high-quality ZnO nanowires on the porous silicon substrate (PS) with a rough morphology without any catalyst, by a simple thermal evaporation technique. The NPSi have been prepared by electrochemical etching method in the mixture of hydrofluoric acid and ethanol electrolyte using an optimized parameter by the electrochemical anodization method on n-type Si(100) substrates. The surface morphology, structural quality and optical properties of the samples were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDX), and photoluminescence (PL) measurement.

Keywords: Nanoscale materiales, nanoporous material, semiconductors, ZnO.
PACS: 81.07.-b, 78.67.Rb, 68.55.ag, 77.55.h

INTRODUCTION

TThe porous silicon (PS) surface provides a rough surface morphology to form a wetting layer by decreasing the surface energy so that ZnO nanowires can grow without any catalyst. PS has opened new possibilities for Si based integrated circuits due to its fascinating optical and electronic properties. Applications such as visible photoluminescence at room temperature, highly efficient electroluminescent devices and photodetectors have been reported previously. PS also looks promising for use in biological and chemical sensing devices [1-2]. Furthermore, PS can be easily synthesized, and the chemical etching process used would ideally be compatible with established technologies for fabricating Si-based devices.

In recent years, there is a rising interest in nanostructured porous silicon (NPSi) due to its efficient optical emission with respect to the bulk Si. The demonstration and observation by Canham on the efficient photoluminescence (PL) at room temperature make NPSi become one of the important Si based luminescence materials [3]. NPSi that has strong PL properties produces direct bandgap semiconductor typically in the range of 600-800 nm (1.5-2.0 eV) compared to bulk crystalline Si which has indirect bandgap of 1.1 eV at room temperature. Hence this unique properties results in a very efficient radioactive recombination producing light in the visible region [4].

The synthesis of one-dimensional semiconductor nanomaterials such as GaN nanowires, MgO nanowires, SnO2 nanowires, and ZnO nanowires are actively being pursued due to various remarkable physical and chemical properties distinctive from conventional bulk materials [5,6]. Because zinc oxide is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy of 60 meV, its nanomaterials have attracted extraordinary attention for their potential applications in device and interconnect integration in nanoelectronics and molecular electronics [7]. Numerous technologies have been developed to grow ZnO nanowires on different substrate materials, which include the vapor-liquid-solid (VLS) method for growth on sapphire with Au as the catalyst [8], electrodepositing for growth on anodic alumina membrane (AAM) templates [9], and the vapor-solid (VS) method without a catalyst for growth on Si (100). However, to our knowledge, few studies have been reported on the subject of catalyst-free fabrication of ZnO nanowire on a PS substrate. The rough morphology of a PS surface was proven to be advantageous for the growth of nanowires by reducing its strain and increasing the number of nuclei sites [11]. In this paper, the possible growth mechanism of the ZnO nanowires arrays is vapor–solid (VS) mechanism because no metal catalyst was used in the whole evaporation procedure. Zn vapor condenses

Enabling Science and Nanotechnology
AIP Conf. Proc. 1341, 18-20 (2011); doi: 10.1063/1.3586945

easily on the PS surface and forms a wetting layer at temperature of 850 ^{o}C without using catalyst. Apart from that, large areas well aligned ZnO nanowires, can be synthesized on nanoporous silicon using a simple single stage furnac

EXPERIMENTS

The porous silicon PS substrate was prepared by the electrochemical anodization method on n-type Si(100) substrates. In the electrochemical etching process, we used constant current density of 25 mA/cm^2 for 30 min (supplied by a Keithley 220 programmable current source) in electrolytes consisting of aqueous HF and ethanol C_2H_5OH (1:4). After etching, the samples were rinsed in deionized water, and dried in ambient air. The ZnO nanowires were fabricated on PS silicon substrates by thermal evaporation process of pure metallic Zn powder (99.9%) without the presence of a catalyst.

The synthesis of ZnO nanowires was carried out in a quartz tube. The substrate was placed at the top of an alumina boat with the polished faces toward the Zn powder. The boat was then inserted to the center of a quartz tube furnace. The furnace was slowly heated from 450^{o}C to 850^{o}C under a continuous flow of highly pure argon and wet oxygen gases. A constant flow-rate of 300 sccm was maintained for 1h. After the evaporation, the alumina boat was slowly drawn out from the furnace and cooled down to room temperature. A white-colored layer was formed on the polished face of PS substrates.

The surface morphology, structural quality and optical properties of the samples were examined by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), energy dispersive spectroscopy (EDX), and photoluminescence (PL) measurement.

RESULTS AND DISCUSSIONS

In our previous work, Fig. 1 shows the top-view SEM image of PS sample prepared at 30 minutes of etching time. For this sample, an uniform distribution of pores around 250 to 300 nm has been observed for PS sample prepared at optimized condition.

The entangled and uniform ZnO nanowires were formed on the PS substrate by simple oxidation of Zn powders, as revealed by FESEM image. The lengths of the entire nanowires were few microns long with diameter of about 80 to 115 nm. However, a wetting layer was formed under these nanowires, and the direction of the nanowires was dependent on the morphology of this wetting layer, as shown in the highly magnified image in Figs. 2(a) and (b).

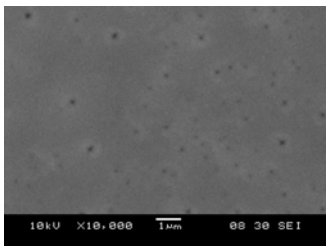

FIGURE 1. SEM image of PS sample prepared on 30 minutes of etching time.

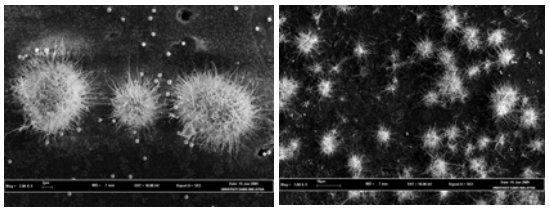

FIGURE 2. T(a) Low: (b) high magnification of FESEM images of ZnO nanowires on PS.

The composition of the ZnO nanowire grown on PS at 850ºC as examined by the energy dispersive X-ray (EDX) analysis indicates that the synthesized ZnO nanowires consist of zinc and oxygen without other contaminant elements and the result is presented in Fig. 3.

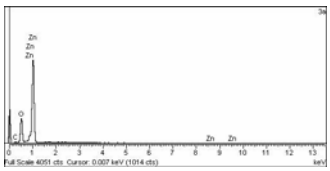

FIGURE 3. EDX images of ZnO nanowires grown on PS at 850ºC

For further understanding of the influence of the morphology, XRD is used to study the crystalline structure and the crystalline alignment. Fig. 4 shows the XRD pattern of the product, the wetting layer and the nanowires on PS substrate. All intense peaks are assigned to the wurtizite phase of ZnO- hexagonal structure nanowires with a unit-cell constant a of 3.248 Å and c of 5.206 Å, it was in good agreement with standard values (JCPDS card No. 01-089- 7102: a_o=3.2495 Å and c_o= 5.2069 Å) . This indicates that good crystallinity of the ZnO samples have been grown by VS method. The XRD pattern was used to calculate the crystallite size of ZnO nanoparticles with increase in temperature using Scherrer's formula from Cullity [8].

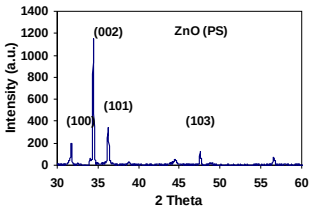

FIGURE 4. X-ray diffraction spectrum of ZnO nanowires grown on PS at 850ºC

The overwhelming (0 0 2) peak at 34.42^{o} indicates that the preferred orientation of ZnO product is much higher than the other peaks, which means the nanostructures are preferentially aligned in the c-axis direction. Fig. 5(a) shows the PL spectrum of the ZnO nanowires grown at 850 ^{o}C on NPSi substrate. The PL spectrum of the ZnO nanostructures was measured using He–Cd laser with an excitation wavelength of 325 nm at room temperature. A strong ultraviolet (UV) emission with a characteristic narrow band at approximately 385 nm, a very weak green band (510–580 nm) and an almost negligible blue band (440–480 nm) were observed. The full width at half maximum (FWHM) of the UV peak is 14 nm. The UV region and the green emission generally correspond to the direct recombination excitons through an exciton-exciton collision process, where one of the excitons radiactively recombines to generate photon. The band at the longer wavelength could be attributed to the radial recombination of photo-generated holes with electrons belonging to the singly ionized oxygen vacancy in ZnO.

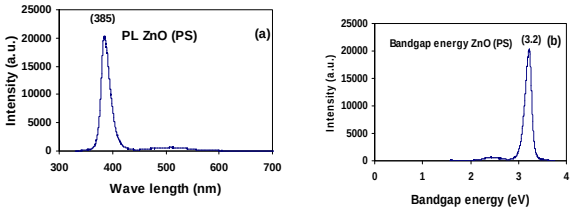

FIGURE 5. X(a) PL spectrum and (b) bandgap energy of ZnO nanowires on PS substrate at 850 ^{o}C

Estimation of bandgap energy is also obtained from PL measurements. In this study, bandgap energy of ZnO nanowires sample is focused at UV near band edge area. Fig. 5 (b) shows the PL photon energy of ZnO nanowires grown on PS substrate at deposition temperature of 850 ºC. The estimated bandgap energy was calculated using E= hc/λ equation [12]. The bandgap energy value of ZnO samples grown on PS was determined to be 3.2 eV. Meanwhile, the strong UV emission in the PL spectrum indicates that the ZnO nanowires have good crystal quality with few oxygen vacancies. The absence of deep-level emission indicates low impurity concentration and high crystalline quality in ZnO nanowires.The large area of growth and high quality of prepared ZnO nanowires make it a potentially good material for applications in optoelectronic devices.

CONCLUSION

In summary, we have synthesized large-scale ZnO nanowires on PS without using catalyst at 850 ^{0}C by simple oxidation of Zn powders. The high quality ZnO nanowires morphology of the as-grown nanostructures is readily adjustable by controlling the growth temperature and gas flow rate. This no-catalyst growth technique on rough surfaces may have a potential application for fabricating nanoelectronic and nanooptical devices.

ACKNOWLEDGMENTS

This work was financially supported by the RU grant Postgraduate Research Grant from Universiti Sains Malaysia.

REFERENCES

1. L T Canham. (1990), . Appl Phys Lett, 57, 1046-1048.
2. Zhe Chuan Feng and Raphael Tsu. Porous Silicon. World Scientific, 35.
3. K.A. Sekak and S. Abdullah. (2006). International Journal of Solid State Science and Technology, Vol. **17**, No 2 (2009) 116-122 ISSN 0128-7389.
4. Y. H. Yang, B. Wang, and G. W. Yang, Nanotechnol. **17**(2006)5556.
5. T. R. Zhang, W. J. Dong, M. K.-Brewer, S. Konar, R. N. Njabon, and Z. R. Tian, J.Am. Chem. Soc. **128**(2006)10960.
6. V. V. Ursaki, E. V. Rusu, A. Sarua, M. Kuball, G. I. Stratan, A. Burlacu, and I. M. Tiginyanu, Nanotechnol. **18**(2007)215705.
7. T. M. Shang, J. H. Sun, Q. F. Zhou, and M. Y. Guan, Cryst. Res. Technol. **42**(2007) 1002.
8. C. Klingshirn, Chemphyschem. **8**(2007)782.
9. N. Al-Hardan, M.J. Abdullah, A. Abdul Aziz, Appl. Surf. Sci. **255** (2009) 7794.
10. B.D. Cullity, in: Elements of X-ray Diffractions,Addison-Wesley, USA, 1978 102
11. M. Rajalakshmim, A.K. Arora, B.S. Bendre, S. Mahamuni, J. Appl. Phys. **87** (2000) 2445.
12. Y.F. Chen, K.M. Bagnall, H.J. Ko, K.T. Park, Z. Zhu, T. Yao, J. Appl. Phys. **84** (1998) 3912.