

ZnO nano-stripes synthesized using photoelectrochemical wet etching method

L. S. Chuah^{1,*}, Asmiet Ramizy², M. A. Mahdi², Z. Hassan²

¹Physics Section, School of Distance Education, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

²School of Physics, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

Email address:

chuahleesiang@yahoo.com (L. S. Chuah)

To cite this article:

L. S. Chuah, Asmiet Ramizy, M. A. Mahdi, Z. Hassan . ZnO Nano-Stripes Synthesized using Photoelectrochemical Wet Etching Method. *International Journal of Materials Science and Applications*. Vol. 2, No. 2, 2013, pp. 74-77. doi: 10.11648/j.ijmsa.20130202.17

Abstract: To date, no approaches have been reported to fabricate the ZnO nano-stripes arrays on zinc foil substrate. In this method, zinc (Zn) foil was applied as substrates. The ZnO nano-stripes arrays on zinc foil substrate were prepared via photoelectrochemical (PEC) wet etching method without using templates and catalysts. To prepare ZnO nano-stripes structures, the samples were dipped into a mixture of HNO₃:Ethanol (1:5) with current densities of 127 mA/cm², and subjected to external illumination from a 100W lamp. The constant etch time is 30 min. After etching, the surface morphology and the nano-stripes structure of the ZnO films were characterized by scanning electron microscope (SEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). XRD pattern confirmed that the hexagonal wurtzite structure of ZnO nano-stripes were of polycrystalline structure. The optical properties of the ZnO nano-stripes arrays were characterized by Raman and photoluminescence spectroscopies at room temperature (RT). Micro-Raman results showed that A₁(LO) of hexagonal ZnO nano-stripes have been observed at 520 cm⁻¹. PL spectrum peak is obvious at 368 cm⁻¹ for ZnO film grown on zinc foil substrate. The PL spectrum peak position in ZnO nano-stripe is blue-shifted with respect to that in unstrained ZnO bulk (381nm). This can be clarified by the approximately smaller statistical area spreading of the nano-stripes. Nano-stripes ZnO can be used as a buffer or intermediate layer to lessen substrate-induced strain, similar to porous silicon.

Keywords: Nano-Stripes, ZnO, PEC, SEM, XRD, Raman, PL

1. Introduction

A typical II-VI group compound semiconductor, ZnO is an essential technological element. A various kinds of ZnO nanostructures for example nanowires, nanorings, nanobows, nanotubes, nanohelices, nanorods, nanobelts, and nanoflowers have been also described over the past few years [1-4]. Recently, one-dimensional (1-D) nanomaterials particularly oriented structures have received worldwide interests due to their outstanding properties, potential applications, and high surface area [5]. Given that ZnO possesses a wide direct band gap 3.37 eV at room temperature and large exciton binding energy of 60 meV, it has been the subject of abundance observation in reference to the utilize of nanostructures in the areas of electronics, electrode for dye-sensitized solar cells, gas sensors, biomedical science, green energy and photonics [6-10].

With lessen in size, novel electrical, chemical and optical properties are introduced, which are mainly conceived to be consequence of the surface and quantized energy (quantum

confinement) influences. In the midst of these nanostructures, the nano-stripes have extraordinary optical, electric and magnetic characteristics, and they display promising applications in photocatalytic, chemical sensor, luminescence and field emitter [11-13]. Consequently, much struggle has been produce to the synthesis and study of their characteristics.

In this paper, we report the successful fabrication of ZnO nano-stripes by a simple photoelectrochemical (PEC) method. The crystalline structure, morphologies and optical properties of the ZnO nano-stripe were investigated.

2. Experimental

To prepare nano-stripes ZnO by photoelectrochemical (PEC) wet etching approach. For the preparation of ZnO nano-stripes arrays, an ordinary simple manner was as follows: A slice of zinc foil substrate (20 x 30 x 0.25 mm³), cleaned by absolute ethanol and followed by deionized water.

The PEC etching of zinc (Zn) foil samples were carried out in a conventional electrochemical cell at room temperature using an unstirred mixture of HNO_3 :Ethanol (1:5) solution. Etching was also executed applying front-side illumination with the lamp and a standard electrochemical cell with a Pt counter electrode with external bias was applied between the sample and the cathode [14, 15]. The constant etch time is 30 min.

Samples were chemically cleaned to clear away surface contaminants and oxides before any characterization. After etching, the samples were characterized by X-ray diffraction (XRD) measurements. The morphology and composition of the samples were examined by scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX).

All the optical measurements were studied at room temperature (RT). Raman spectroscopy was conducted with a micro-Raman/photoluminescence (Jobin Yvon HR800UV) system, for example, an integrated confocal micro-Photoluminescence spectrometer. A He-Cd laser (325 nm) was used as an excitation source for PL. Micro-Raman scattering experiments were investigated by using a Jobin Yvon HR 800 UV spectrometer system. The excitation light source was the 514.5 nm line of Argon (Ar) ion laser beam and the incident laser power of 20 mW was focused [14]. Previously the ZnO spectrum was reported, the Raman spectroscope was calibrated and checked using a silicon substrate [16].

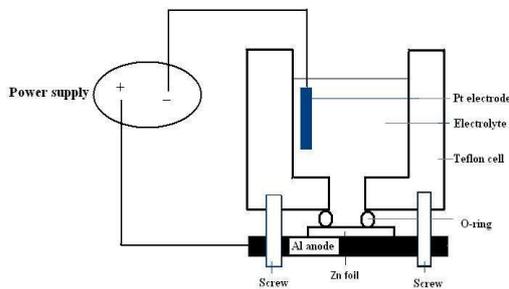


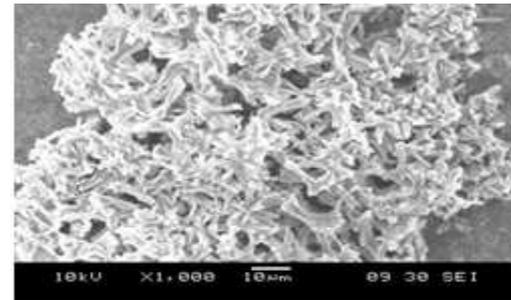
Fig. 1. The photoelectrochemical etching experimental set up used to generate ZnO nano-stripe arrays on zinc foil substrate.

In this work, micro-Raman scattering experiments were carried out in the $z(x, \text{unpolarized})\bar{z}$ scattering configuration [14]. Here, the Porto's notation is used for scattering geometries with z parallel to wurtzite c axis, and $(x, \text{unpolarized})$ refers to the polarization of the incident and scattered light [17]. Under this configuration, the allowed zone-center phonon modes that can be detected for wurtzite structure layer will be $A_1(\text{LO})$, and $E_2(\text{high})$, unless there are some disoriented microstructures [18].

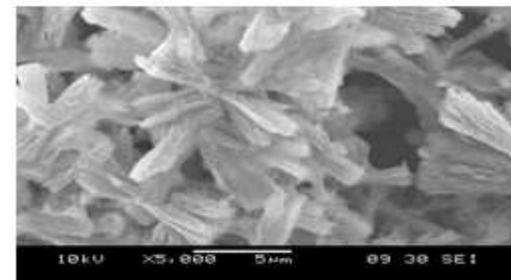
3. Results and Discussion

The morphology of a top-view ZnO nano-stripe arrays grown on a zinc foil substrate is shown in Figure 2. Fig. 2(b) shows a medium-magnification SEM image of the

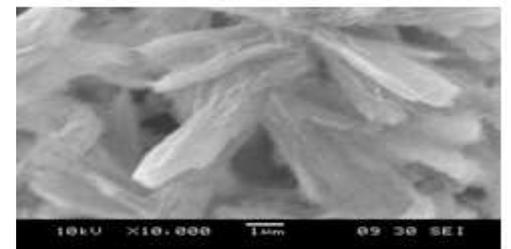
product. It can be seen from Fig. 2, that ZnO nano-stripe arrays are densely but not homogeneously distributed. The geometrical shape of the nano-stripe is clearly shown in Fig. 2(c) and (d). Figure 2c and d show the close-view SEM images of as synthesized ZnO nano-stripe structures. Figure 3 shows typical EDX results for the composition of the ZnO nano-stripe arrays grown on the zinc foil substrate. It discloses the presence of Zn and O as the only primary components, with a moderate oxygen defect (Zn/O atomic ratio = 1:1).



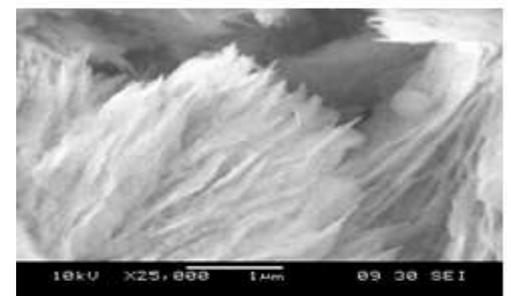
(a)



(b)



(c)



(d)

Fig. 2. SEM images of ZnO nano-stripe arrays on zinc foil substrate with different magnification views: (a) 1,000, (b) 5,000, (c) 10,000, and (d) 25,000.

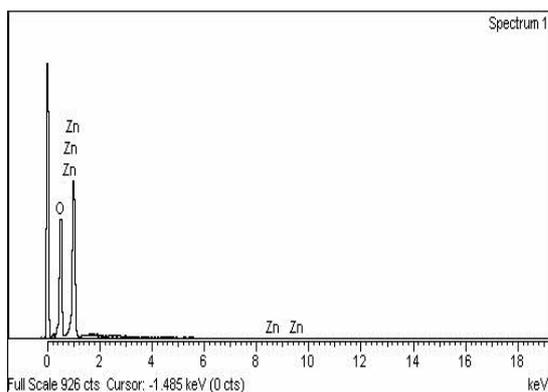


Fig. 3. The corresponding EDX pattern of the ZnO nano-stripe arrays on zinc foil substrate.

Figure 4 shows an XRD pattern of the as-synthesized samples. The diffraction peaks can be recorded to wurtzite ZnO, exclude for those distinguished as Zn coming from the zinc (Zn) foil substrate. Prominently, when compared with the common diffraction form, the (002) diffraction peaks are improved and much stronger than the other peaks, symbolizing the highly preferential growth of the ZnO nano-stripes along their c-axis, perpendicular to the Zn foil substrate surface.

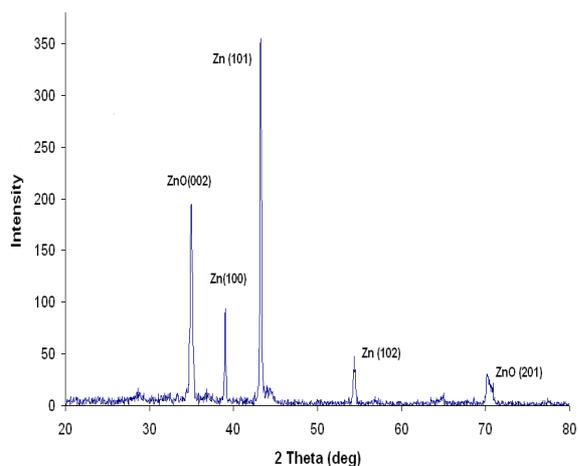


Fig. 4. X-ray diffraction pattern of the ZnO nano-stripes on Zn foil.

Figure 5 shows the Raman scattering spectrum of the ZnO nano-stripes. A strong peak appears at 438 cm^{-1} which corresponds to the E₂(H) mode of wurtzite phase of ZnO, which is the intrinsic characteristic of the Raman-active mode of wurtzite hexagonal ZnO [19], while the 530 - 620 cm^{-1} peak is attributed to the presence of Zn interstitials [20]. The A₁(LO) Raman line-shape is very sensitive to lattice disorder in ZnO crystals, because the non-stoichiometric defects will disrupt the long range ionic ordering [21]. The disorder will induce the phonon modes near the A₁(LO) on the phonon dispersion curve to be Raman active [22]. For ZnO nano-stripes, only the allowed Raman phonon modes of A₁(LO) are clearly visible at 530 cm^{-1} for growth on Zn foil.

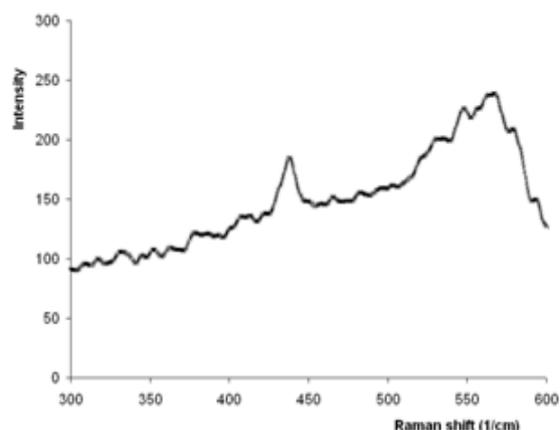


Fig. 5. Room temperature micro-Raman spectrum of ZnO nanostructures.

Photoluminescence (PL) spectroscopy is an efficient method for evaluating the optical properties of semiconductor materials. Figure 6 shows a typical room-temperature PL spectrum of the ZnO nano-stripes arrays, with a dominant emission peak centered at 368 nm, which corresponds to the ultraviolet (UV) emission of ZnO with a band gap of 3.39 eV. Many researchers have reported the optical properties of ZnO nanostructures. Generally, the UV emission peak of ZnO is attributed to the near-band-edge (NBE) emission of wide-band-gap ZnO.

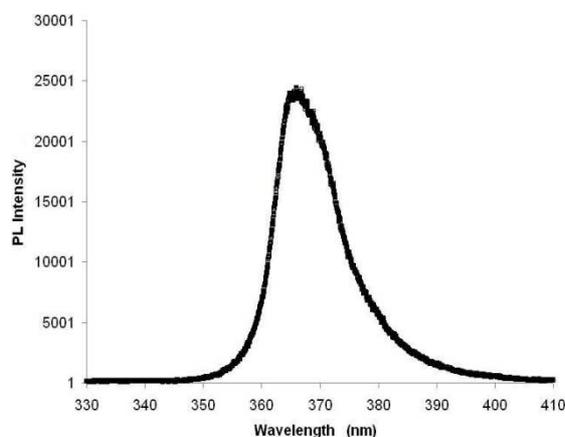


Fig. 6. The PL spectra obtained from the surfaces of the ZnO nano-stripes.

4. Conclusion

Large-scale ZnO nano-stripe arrays have been successfully synthesized on zinc foil by a simple and low-cost method. We synthesized the ZnO nano-stripes without any catalysts or templates. PL and Raman spectra show that these ZnO nano-stripes arrays have good optical properties. Room-temperature photoluminescence (PL) spectrum of nano-stripe arrays shows a strong emission band at about 368 nm. Furthermore, the novel ZnO nano-stripes reported here may have potential applications as functional blocks in

fabrication of optoelectronic nanodevices.

Acknowledgements

Financial support from FRGS grant and Universiti Sains Malaysia are gratefully acknowledged.

References

- [1] Z. W. Pan, Z. R. Dai, Z. L. Wang, Nanobelts of Semiconducting Oxides. *Science*, 291 (2001) 1947–1949.
- [2] Z.L. Wang, J. H. Song, Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays. *Science*, 312, (2006) 242–246.
- [3] S.H. Lee, H. J. Lee, D. Oh, S. W. Lee, H. Goto, R. Buckmaster, T. Yasukawa, T. Matsue, S. K. Hong, M. W. Cho, T. Yao, Control of the ZnO Nanowires Nucleation Site Using Microfluidic Channels. *J. Phys. Chem. B* 110, (2006) 3856 – 3859.
- [4] Y. Li, F. Qian, J. Xiang, C. M. Lieber, Nanowire Electronic and Optoelectronic Devices. *Mater. Today*, 9, (2006) 18–25.
- [5] J. M. Bao, M. A. Zimmler, F. Capasso, Broadband ZnO Single-Nanowire Light-Emitting Diode. *Nano Lett.* 6 (2006) 1719–1722.
- [6] J. T. Hu, T. W. Odom, C.M. Lieber, Chemistry and Physics in One Dimension: Synthesis and Properties of Nanowires and Nanotube. *Acc. Chem. Res.* 32, (1999) 435–445.
- [7] H. J. Fan, P. Werner, M. Zacharias, Semiconductor Nanowires: From Self-Organization to Patterned Growth. *Small*, 2, (2006) 700–717.
- [8] W. W. Wang, Y. J. Zhu, L.X. Yang, ZnO-SnO₂ Hollow Spheres and Hierarchical Nanosheets: Hydrothermal Preparation, Formation Mechanism, and Photocatalytic Properties. *Adv. Funct. Mater.* 17, (2007) 59–64.
- [9] C. W. Cheng, G. Y. Xu, H. Q. Zhang, Y. Luo, Fabricating ZnO Nanorods Sensor for Chemical Gas Detection at Room Temperature. *J. Nanosci. Nanotechnol.* 7, (2007) 4439–4442.
- [10] J.H. Y. Yang, S.P. Lau, S. F. Yu, A. P. Abiyasa, M. Tanemura, T. Okita, H. Hatano, High-Temperature Random Lasing in ZnO Nanoneedles. *Appl. Phys. Lett.* 89, (2006) 011103.
- [11] L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai, P. D. Yang, General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds. *Nano Lett.* 5, (2005) 1231–1236.
- [12] L. Vayssieres, Growth of Arrayed Nanorods and Nanowires of ZnO from Aqueous Solution. *Adv. Mater.*, 15, (2003) 464–466.
- [13] H. J. Fan, M. Zacharias, Manipulation of Crawling Growth for the Formation of Sub-Millimeter Long ZnO Nanowalls. *J. Mater. Sci. Technol.* 24, (2008) 589–593.
- [14] L.S. Chuah, Z. Hassan, S.S. Ng, H. Abu Hassan, Porous Si(111) and Si(100) as an intermediate buffer layer for nanocrystalline InN films, *Journal of Alloys and Compounds* 479, (2009) L54-L58.
- [15] L.S. Chuah, Z. Hassan, H. Abu Hassan, Nanoporous InN films synthesized using photoelectrochemical wet etching, *IEEE International Conference on Semiconductor Electronics Proceedings (ICSE)*, (2006) 618-621.
- [16] Y. X. Wang, X. Y. Li, G. Lu, X. Quan, G. H. Chen, Highly oriented 1-D nanorod arrays on zinc foil: direct growth from substrate, optical properties and photocatalytic activities, *J. Phys. Chem. C*, 112 (2008) 7332-7336.
- [17] L.S. Chuah, Z. Hassan, H. Abu Hassan, Optical characterization of nanoporous GaN through electroless wet chemical etching, *Materials Science-Poland*, Vol. 26, No. 3, (2008) 609-615.
- [18] L.S. Chuah, Z. Hassan, H. Abu Hassan, Optical characterization of GaN thin film grown on Si(111) by radio-frequency plasma-assisted molecular beam epitaxy, *Malaysia-Japan International Symposium on Advanced Technology (MJISAT)*, 1-6 (2007) - on CD.
- [19] J. H. Yang, J. H. Zheng, H. J. Zhai, L. L. Yang, Low temperature hydrothermal growth and optical properties of ZnO nanorods, *Cryst. Res. Technol.* 44, (2009) 87-91.
- [20] P.S. Xu, Y. M. Sun, C. S. Shi, F. Q. Xu, H. B. Pan, Native point defect states in ZnO, *Chinese Physics Letters*, 18 (2001) 1252-1253.
- [21] L.S. Chuah, M. A. Ahmad, Z. Hassan, Nanocrystalline ZnO film grown on porous SnO₂/Si(111) substrates, *Composit Interfaces*, 18 (2011) 627-632.
- [22] L.S. Chuah, Z. Hassan, S.K. Mohd Bakhori, Optical analysis of nanocrystalline ZnO films coated on porous silicon by Radio Frequency (RF) Magnetron Sputtering, *Composite Interfaces*, 18 (2011) 441-448.
- [23] L.S. Chuah, Z. Hassan, S. S. Tneh, Single crystalline ZnO nanowires by oxidizing granular zinc film, *Journal of Dispersion Science and Technology*, 32 (2011) 677-679.