VNU Journal of Science: Mathematics – Physics, Vol. 33, No. 2 (2017) 29-33

A Simple, One-step, Seedless Hydrothermal Growth of ZnO Nanorods on Printed Circuit Board Substrate

Mai Hong Hanh*, Nguyen Viet Tuyen, Pham Van Thanh, Hoang Chi Hieu

Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Hanoi, Vietnam

Received 20 March 2017
Revised 25 April 2017; Accepted 25 May 2017

Abstract: High quality, high density, and well-aligned zinc oxide (ZnO) nanorods have been synthesized on cost-effective printed circuit board (PCB) substrates via a simple, seedless, one-step, low-temperature hydrothermal method based galvanic cell structure. It was found that the outer diameters of the ZnO nanorods range from 50 nm to 400 nm. The as-grown ZnO nanorods prefer to grow along the c axis. The morphologies of the ZnO nanorods were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). The crystallinity properties were characterized by Raman spectroscopy and photoluminescence (PL) spectroscopy.

Keywords: ZnO nanorods, printed circuit boards (PCB), hydrothermal method.

1. Introduction

ZnO, a direct wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV) is considered to be one of the most important semiconductor materials due to its excellent electrical and optical properties and wide applications in ultraviolet lasers, photodetectors, solar cells, chemical and bio sensors [1-6]. For these applications, it is essential to have one-dimensional (1D) ZnO nanocrystals such as nanorods, nanowires, nanotubes with good alignment, high crystallinity, and high density. Recently, well-aligned ZnO nanorods have been successfully grown on different kinds of substrates by using a simple, low-temperature, hydrothermal technique [7-8]. To produce well-aligned ZnO nanorods, researchers have used both expensive substrates, such as GaN, Si, or sapphire, and low-cost substrates, such as ITO or FTO, which usually require the additional assistance of a gold catalyst or ZnO seed layer [6, 9, 10]. However, the poor conductivity of these substrates (e.g. GaN, Si) might limit their applications in some electronics and optoelectronics. The pre-deposition of a ZnO seed layer normally requires high temperature, and extra experimental steps. It also introduces impurities, and influences the adhesion of ZnO nanostructures to the underlying substrates [11]. Furthermore, expensive substrates and multi-step syntheses for vertical growth, among others, have also limited the use of ZnO nanocrystals in electrical and optical applications.

Among metal substrates for growing ZnO nanocrystals, printed circuit board (PCB) containing a thin cooper layer on top of insulating fiber glass is an ideal metal substrate for electrical and thermal

*Corresponding author. Tel.: 84-967292460.
Email: hanhhongmai@hus.edu.vn

https://doi.org/10.25073/2588-1124/vnumap.4200

conductance due to its good conductive and cost-effective properties. These properties are particularly important for the use of ZnO nanocrystals in both medical, industrial and optoelectronics applications. However, the fabrication of high density, high quality and well aligned 1D ZnO nanorods on PCB substrate sill remains a complex task. It is because of a big lattice mismatch between the substrate and ZnO material which leads to non-aligned growth of ZnO nanorods. Since PCB substrates can only withstand rather low temperatures, implementing a seed layer, whose annealing would be required high temperatures, is also a challenge for synthesizing high density, high quality, well – aligned ZnO nanorods. In fact, Chew et al. developed a method to grown ZnO nanowires on a PBC using hydrothermal method in which a seed layer was deposited on the substrate by using Joule heating method [12, 13]. The localized ZnO nanowires with high density were successfully grown for memory resistor application. However, the method requires a complex, multi-step synthesis which required an assistant of an external current applied on the copper thin layer during the synthesizing process.

In this paper, we report a convenient approach for the vertical and large area growth of ZnO nanorods on PCB substrates. Herein, by applying a simple, one-step, seedless hydrothermal method based on galvanic cell structure [14], ZnO nanorods with high density, high crystallinity, and good alignment were grown directly on the PCB substrate. The crystallinity and surface morphologies of the as-grown ZnO nanorods will also be discussed.

2. Experiment

Seedless growth of ZnO nanorods

ZnO nanorods were grown on PCB substrates by a hydrothermal growth technique, which is based on galvanic cell structures. The substrates was polished with SiC sandpaper and then ultrasonically cleaned with acetone, ethanol, and deionized (DI) water sequentially. After being cleaned, the surface oxide was removed by dipping the substrates in low concentration HCl, followed by an ultrasonic rinse in DI water. In order to create a galvanic cell structure, Al foil was used to cover the edge of the substrates. The uncovered area is where ZnO nanorods would be grown (Figure 1).

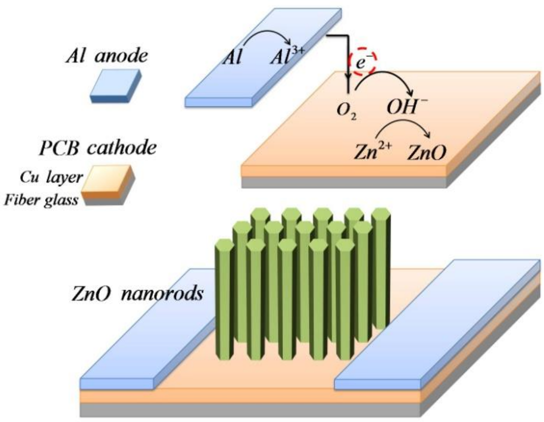

Figure 1. Schematic illustration of the galvanic cell-based fabrication process of ZnO nanorod arrays. Al is used as the sacrificing anode and ZnO growth occurs on the PCB cathode substrate.

Afterwards, the as-prepared substrates were dipped into a mixture of 80 mM zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$), which was placed in a sealed vitreous bottle isolated by an oil bath. The substrates were suspended facing downwards in the solution for 5 h with the temperature of the oil bath maintained at 90^{o}C. The Al layer was then removed and the substrates were again rinsed with DI water to remove residual salts from the surface before being air-dried.

Characterization

The crystal structure of the ZnO nanorods was characterized by X-ray diffraction (X-ray Powder Diffraction System D5000 Siemens) and Raman spectroscopy (Labram Hr800, Horiba). The morphology of the sample surface was examined by scanning electron microscopy (SEM) (Nova NanoSEM 450). Photoluminescence (PL) measurements were performed using a continuous wave He-Cd laser operated at 325 nm as an excitation light source.

3. Results and discussion

As shown in Figure 2, well-aligned ZnO nanorods are observed to stand vertically on PCB substrates at a high density. The nanorods' diameter ranges from 50 to 400 nm. The X-ray diffraction pattern, as seen in Figure 3, indicates the preferential growth of ZnO nanorods in the (002) direction. The as-grown ZnO nanorods have hexagonal wurtzite structure with lattice parameters $a = 3.24$ and $c = 5.2$ which is well suited with the previous studies [15, 16].

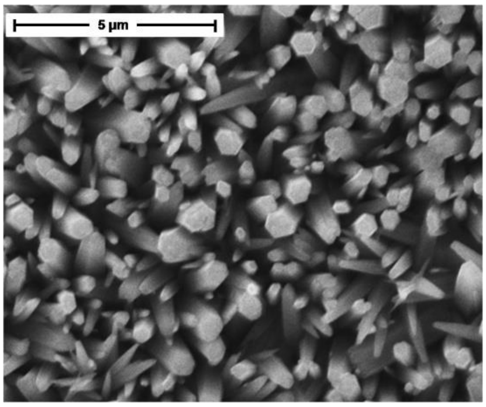

Figure 2. SEM images of ZnO nanorods on PCB, concentration 0.08M, hydrothermal time 5 hours.

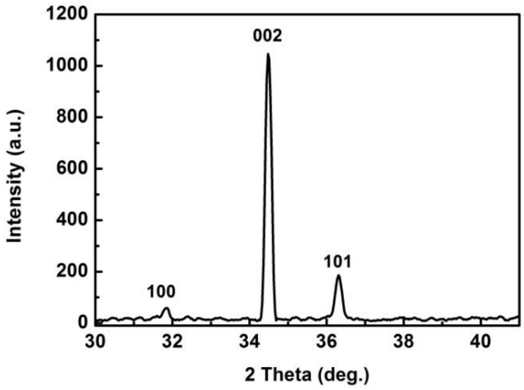

Figure 3. XRD pattern of ZnO nanorods grown on PCB substrate with Al on the edge.

These observations reveal that ZnO nanorods can be grown directly on PCB substrates by the one-step growth technique based on galvanic cell structure with high density without using a seed layer. As demonstrated in Figure 1, the mechanism of the growth was described by Zheng et al. [14]. Accordingly, the equimolar aqueous solution mixture of $Zn(NO_3)_2 \cdot 6H_2O$ and $C_6H_{12}N_4$ was the nuclei source for the growth of ZnO, of which $Zn(NO_3)_2$ provided Zn^{2+} while $C_6H_{12}N_4$ hydrolyzed the water solution to produce OH^-. Due to the more negative reduction potential of Al in comparison with Cu, the Al layer acted as the sacrificing anode while the PCB substrates acted as the cathode. As a result, by covering the edge of the PCB substrate with Al foil, the contact potential between the PCB conductive substrate and the Al layer created a bias. The bias drove the chemical reactions, which in their turn induced the growth of ZnO on the exposed substrate area. In due process, Al lost electrons to develop positive charges Al^{3+} whereas the lost electrons moved to the PCB substrate cathode.

Subsequently, reduction reactions of dissolved oxygen ($O_2 + 2H_2O + 4\ e^- \longrightarrow 4OH^-$) occurred on the cathode that were followed by the formation of $Zn(OH)_2$, of which the dehydration formed ZnO on the exposed PCB area. In fact, this ZnO growth mechanism is similar to that of the electrochemical deposition which also does not require the pre-deposition of a ZnO seed layer. However, in this case, instead of using an external power source, a galvanic cell was employed directly in the equimolar aqueous solution. In comparison with previous reports on synthesizing well-aligned ZnO nanorods, it is thus easier to implement this seedless method.

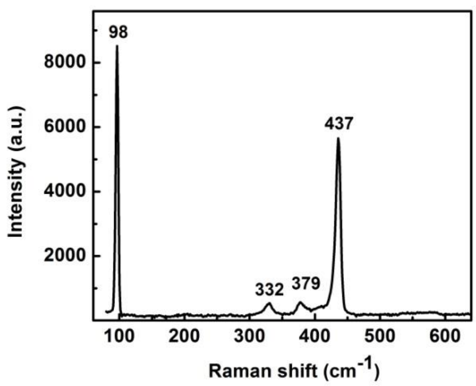

Figure 4. Raman spectrum of the as-grown ZnO nanorods.

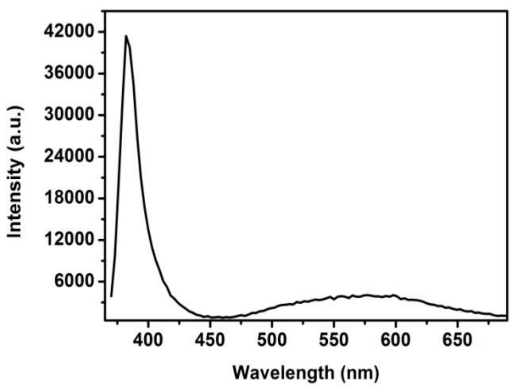

Figure 5. Photoluminescent spectrum of the as-grown ZnO nanorods taken at room temperature.

Figure 4 shows the Raman spectra of the ZnO nanorods samples, which exhibit main peaks at 98 cm^{-1} and 437 cm^{-1}, corresponding to the optical phonon E_2 (low) and E_2 (high) of the ZnO, respectively. These strong and sharp peaks indicate the high crystallinity of the grown ZnO nanorods [17].

Figure 5 shows the room temperature PL spectrum of the ZnO nanorods, which contains a narrow UV emission peak and a weak broad green emission band. Centering at 384 nm (~ 3.3 eV), the UV emission peak corresponds to the near-band-edge emission and free exciton peak of ZnO. On the other hand, the broad green emission band of the visible region is located at ∼570 nm (~ 2.18 eV) and can be attributed to the intrinsic defects or oxygen vacancies in the ZnO, such as the single and double ionized oxygen vacancies [17]. Also, the high intensity ratio between the UV emission and green emission band indicates that high crystallinity ZnO nanorods were seedless synthesized from the method.

4. Conclusion

In conclusion, we have presented a simple, one-step, seedless hydrothermal method to synthesize of ZnO nanorods. The method is taking advantage of galvanic cell structure, and has been demonstrated on a PCB substrate. SEM images and X-ray diffraction patterns demonstrate that the well-aligned ZnO nanorods could be synthesized on a PCB substrate without the assistance of a seed layer. Room temperature PL spectrum exhibits strong ultraviolet emission, Raman spectrum presents strong and sharp intensity peaks at 98 cm^{-1} and 437 cm^{-1} indicative of high crystal quality of the as-grown ZnO nanorods. We believe that the high quality ZnO nanorods grown on cost-effective PCB substrates presented in this work can be a potential candidate for the future electronic and sensory applications.

Acknowledgements

This work was supported by the National Foundation for Science and Technology Development of Vietnam (NAFOSTED) through Grant No. 103.03-2015.27.

References

[1] J.-H. Choy, E.-S. Jang, J.-H. Won, J.-H. Chung, D.-J. Jang, and Y.-W. Kim, "Soft Solution Route to Directionally Grown ZnO Nanorod Arrays on Si Wafer; Room-Temperature Ultraviolet Laser," Adv. Mater., vol. 15, no. 22, pp. 1911–1914, 2003.

[2] C. Soci et al., "ZnO Nanowire UV Photodetectors with High Internal Gain," Nano Lett., vol. 7, no. 4, pp. 1003–1009, 2007.

[3] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, and P. Yang, "Nanowire dye-sensitized solar cells," Nat Mater, vol. 4, no. 6, pp. 455–459, Jun. 2005.

[4] J. A. Anta, E. Guillén, and R. Tena-Zaera, "ZnO-Based Dye-Sensitized Solar Cells," J. Phys. Chem. C, vol. 116, no. 21, pp. 11413–11425, 2012.

[5] T.-J. Hsueh, C.-L. Hsu, S.-J. Chang, and I.-C. Chen, "Laterally grown ZnO nanowire ethanol gas sensors," Sensors Actuators B Chem., vol. 126, no. 2, pp. 473–477, 2007.

[6] S. N. Sarangi, S. Nozaki, and S. N. Sahu, "ZnO nanorod-based non-enzymatic optical glucose biosensor," J. Biomed. Nanotechnol., vol. 11, no. 6, pp. 988–996, 2015.

[7] S. S. Low, M. T. T. Tan, H.-S. Loh, P. S. Khiew, and W. S. Chiu, "Facile hydrothermal growth graphene/ZnO nanocomposite for development of enhanced biosensor," Anal. Chim. Acta, vol. 903, pp. 131–141, 2016.

[8] S. Nozaki, S. N. Sarangi, K. Uchida, and S. N. Sahu, "Hydrothermal Growth of Zinc Oxide Nanorods and Glucose-Sensor Application," Soft Nanosci. Lett., vol. 3, no. November, pp. 23–26, 2013.

[9] Song, WangWang, E. Riedo, and Z. L. Wang, "Systematic Study on Experimental Conditions for Large-Scale Growth of Aligned ZnO Nanwires on Nitrides," J. Phys. Chem. B, vol. 109, no. 20, pp. 9869–9872, 2005.

[10] Q. Zhao et al., "Morphological effects on the field emission of ZnO nanorod arrays," Appl. Phys. Lett., vol. 86, no. 20, p. 203115, 2005.

[11] K. Huo et al., "Direct and Large-Area Growth of One-Dimensional ZnO Nanostructures from and on a Brass Substrate," J. Phys. Chem. C, vol. 111, no. 16, pp. 5876–5881, 2007.

[12] Z. J. Chew and L. Li, "Localised zinc oxide nanowires growth on printed circuit board by in-situ joule heating," Mater. Lett., vol. 76, pp. 226–228, 2012.

[13] Z. J. Chew and L. Li, "A discrete memristor made of ZnO nanowires synthesized on printed circuit board," Mater. Lett., vol. 91, pp. 298–300, 2013.

[14] Z. Zheng, Z. S. Lim, Y. Peng, L. You, L. Chen, and J. Wang, "General route to ZnO nanorod arrays on conducting substrates via galvanic-cell-based approach.," Sci. Rep., vol. 3, no. AUGUST, p. 2434, 2013.

[15] O. Madelung, U. Rössler, and M. Schulz, Eds., "Zinc oxide (ZnO) crystal structure, lattice parameters," in II-VI and I-VII Compounds; Semimagnetic Compounds, Berlin, Heidelberg: Springer Berlin Heidelberg, 1999, pp. 1–5.

[16] Z. L. Wang, "Zinc oxide nanostructures: growth, properties and applications," J. Phys. Condens. Matter, vol. 16, no. 25, p. R829, 2004.

[17] R. Zhang, P.-G. Yin, N. Wang, and L. Guo, "Photoluminescence and Raman scattering of ZnO nanorods," Solid State Sci., vol. 11, no. 4, pp. 865–869, 2009.