

HYDROTHERMAL-ASSISTED SYNTHESIS AND PHOTOLUMINESCENCE OF ZnO MICRORODS

N. EKTHAMMATHAT^a, A. PHURUANGRAT^{b*}, S. THONGTEM^c,
T. THONGTEM^{d,e}

^a*Program of Chemistry, Faculty of Science and Technology,
Bansomdejchaopraya Rajabhat University, Bangkok 10600, Thailand*

^b*Department of Materials Science and Technology, Faculty of Science,
Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand*

^c*Department of Physics and Materials Science, Faculty of Science,
Chiang Mai University, Chiang Mai 50200, Thailand*

^d*Department of Chemistry, Faculty of Science, Chiang Mai University,
Chiang Mai 50200, Thailand*

^e*Materials Science Research Center, Faculty of Science, Chiang Mai University,
Chiang Mai 50200, Thailand*

Zinc oxide microrods were grown on Zn foils by a simple hydrothermal method. The XRD and SEM experimental results revealed the dense microrod-like wurtzite ZnO structure grown on Zn foils. The photoluminescence (PL) spectra at room temperature were measured. ZnO microrods exhibit photoluminescence broad emission at 500–650 nm using an excitation wavelength of 215 nm. By Gaussian analysis, the emission shows a maximum intensity at about 540 nm and a shoulder peak at around 570 nm which correspond to interstitial oxygen [O_i⁻] and oxygen vacancies [V_O⁺], respectively.

(Received December 9, 2015; Accepted February 7, 2015)

Keywords: ZnO; Microrods; X-ray diffraction; Photoluminescence

1. Introduction

Wurtzite ZnO with space group P6₃mc or C_{6v}⁴ is an important II–VI semiconductor material with wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1, 2]. It is an excellent electronic and photonic material due to its unique piezoelectric, pyroelectric, catalytic and photocatalytic properties. It has potential application in many fields such chemical and gas sensors, spin functional devices, UV-light emitters, light emitting diodes (LEDs), laser light source and nanosensors in harsh surroundings [1–4]. ZnO arrays or films, as an important family of ZnO nanomaterials, have been an active research field as early as the 1960s because of their applications as sensors, transducers and catalysts [1]. In the past decade, various chemical and physical techniques have been employed to synthesize ZnO nanomaterials on substrate such as hydrothermal [1, 2, 5], chemical bath deposition [6], radio frequency magnetron sputtering [7], pulsed laser deposition [8] and chemical vapor deposition (CVD) [9].

For the present research, thin film of ZnO microrods were hydrothermally grown on Zn foils in aqueous solutions of Zn(NO₃)₂·6H₂O without any template adding at the pH of 8 and 9 adjusted by NH₄OH. The morphology, crystalline structure and optical properties of the as-prepared ZnO samples were also investigated and discussed in this report.

*Corresponding authors: phuruangrat@hotmail.com

2. Experiment

All chemicals of this experiment were analytical grade and used without further purification. For the typical experimental procedure, the $15 \times 15 \times 0.25$ mm Zn foils as substrates and Zn source were carefully ultrasonically cleaned by deionized water and alcohol. Each foil was put in solutions at the pH of 8 and 9 with pH adjusted by concentrated NH_4OH solution as OH^- source. The solutions were transferred into Teflon-lined stainless steel autoclaves with 30 ml capacity. The Teflon-lined stainless steel autoclaves were tightly closed, heated at 120°C for 12 h in an electric oven and cooled to room temperature. The foils were thoroughly rinsed by deionized water several times and ethanol, and dried in an electric oven at 70°C under atmospheric environment inside for further characterization.

The products were characterized by X-ray diffraction (XRD) obtained on a Philips X'Pert MPD X-ray diffractometer with $\text{Cu-K}\alpha$ radiation. Scanning electron microscopic (SEM) analysis was conducted on a JEOL JSM 6335F scanning electron microscope operating at 35.0 kV. The photoluminescence properties were studied by a Perkin Elmer LS 50B fluorescence spectrophotometer using a Xe lamp with an excitation wavelength of 215 nm.

3. Results and discussion

Phase and structure of the as-prepared samples have been investigated by X-ray diffraction as shown in Fig. 1. XRD patterns show the peaks at diffraction angle of $2\theta = 31.77, 34.45, 36.30, 39.03, 43.26, 47.53, 54.33$ and 56.60 deg in the 2θ range of 20 – 60 deg. They can be indexed to the (100), (002), (101), (102) and (110) planes at $2\theta = 31.77, 34.45, 36.30, 47.53$ and 56.60 deg of wurtzite hexagonal chinese white ZnO structure comparing with the database of JCPDS No. 36-1451 [10]. Other diffraction peaks can be indexed to the (100) (101) and (102) planes at $2\theta = 39.03, 43.26$ and 54.33 deg of hexagonal Zn structure comparing to the database of JCPDS No. 04-0831 [10]. There was no detection of other characteristic peaks of impurities in the XRD patterns. All diffraction peaks of the chinese white ZnO samples are strong and narrow which indicate the presence of well-defined crystalline of the as-prepared ZnO samples. The (002) strong diffraction peak is higher than that of the JCPDS database, suggesting the main preferred growth orientation of the chinese white ZnO rods along the [001] direction or c axis [11, 12].

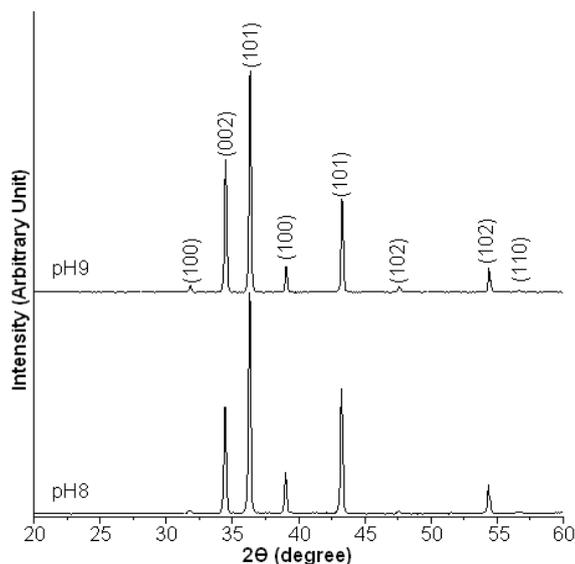


Fig. 1 XRD patterns of ZnO hydrothermally prepared in the solutions with the pH of 8 and 9.

The morphologies and microstructures of the as-grown samples were characterized by FE-SEM. The morphologies of ZnO grown on Zn foils in the solutions with two different pH values by the hydrothermal method are shown in Fig. 2. They are clearly seen that hexagonal ZnO microrods were prepared in the solutions with the pH of 8 and 9. They always grow along the c axis which has the lowest energy of hexagonal crystalline structure [13]. The direct observation on the evolution of morphologies and microstructures are in agreement with the above analysis based on the XRD patterns. Clearly, these ZnO microrods are 500 nm long with the diameters in the range of 50–140 nm.

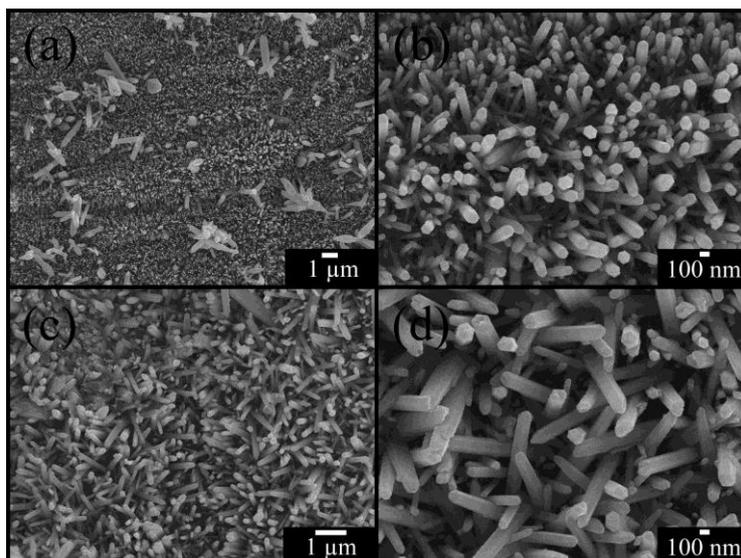


Fig. 2 SEM images of ZnO hydrothermally prepared in the solutions with the pH of (a, b) 8 and (c, d) 9 at two magnifications

Basing on the above discussion, the growth of ZnO structure can be proposed as follows:



The formation of $\text{Zn}(\text{OH})_4^{2-}$ ions from Zn^{2+} and OH^- ions under hydrothermal reaction is a key role in the formation of hexagonal wurtzite ZnO microrods in the same way as the previous reports. The primary ZnO molecules begin to nucleate on Zn foils because the dissolution of Zn atoms into the solutions can cause a concentration gradient of Zn^{2+} ions normal to the Zn foils. The intrinsic electric field of the polar ZnO lattice is responsible for further growth of the ZnO crystals. The ZnO crystal lattice can be described as alternating planes, composed of Zn^{2+} and O^{2-} which are stacked along the c-axis. The oppositely charged ions produced positively charged surface on the (0001) plane and negatively charged surface on the other, resulting in polarization along the c-axis. The preferred c-axis orientation of ZnO microstructure is driven by electrostatic interaction between the polar charge to minimize surface energy. Finally, the ZnO microrods were grown on Zn substrates [14–16].

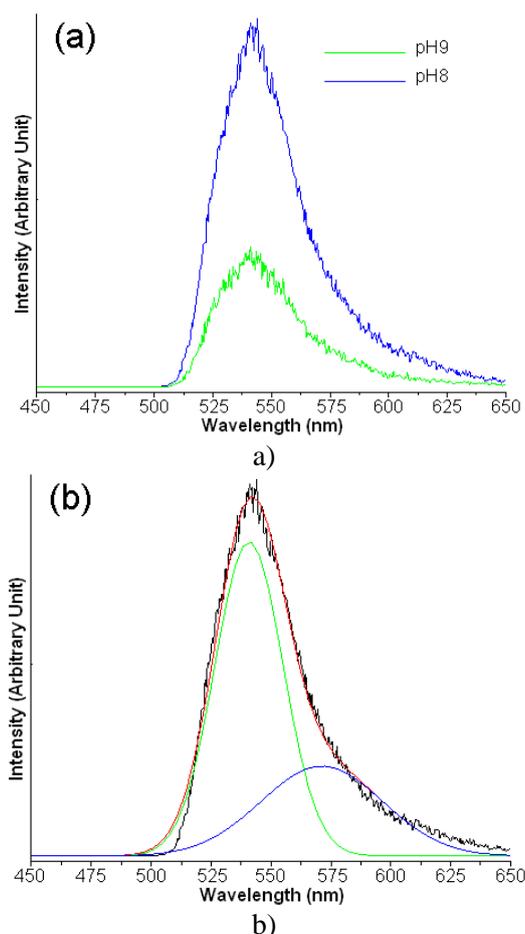


Fig. 3 PL spectra of (a) ZnO prepared by the 120 °C and 12 h hydrothermal reaction in the solutions with the pH of 8 and 9 and (b) Gaussian analysis of ZnO hydrothermally prepared in the solution with the pH of 8

The room-temperature photoluminescence spectra of the as-prepared ZnO samples are shown in Fig. 3. They were obtained by using an excitation wavelength of 215 nm. The samples exhibit very broad emission bands extending approximately from 500 to 650 nm. According to the Gaussian analysis, they present two green emission peaks at maximum intensity of about 540 nm (2.30 eV) and a shoulder peak at around 570 nm (2.18 eV). A number of different hypotheses have been proposed for green emission, such as singly ionized oxygen vacancy, doubly charged oxygen vacancy, oxygen antisite and surface defects. Green emission is commonly attributed to the singly ionized oxygen vacancy and is easily influenced by surface modification [13]. The green band at 540 nm and 570 nm are related to interstitial oxygen [O_i^-] and oxygen vacancies [V_O^+], respectively [17, 18].

4. Conclusions

The dense prism ZnO microrods were prepared on Zn foils by the hydrothermal method in the solutions with the pH of 8 and 9, adjusted by NH_4OH . XRD patterns and SEM images revealed the presence of wurtzite hexagonal prism ZnO microrods grown along the [001] direction. Room temperature PL spectra using excitation at 215 nm shows a maximum intensity at about 540 nm (2.30 eV) and a shoulder peak at around 570 nm (2.18 eV). The green band at 540 nm and 570 nm were caused by the interstitial oxygen [O_i^-] and oxygen vacancies [V_O^+], respectively.

Acknowledgement

We wish to thank the Thailand's Office of the Higher Education Commission for providing financial support through the National Research University (NRU) Project for Chiang Mai University (CMU).

References

- [1] C. Yan, D. Xue, *J. Cryst. Growth* **310**, 1836 (2008).
- [2] J.H. Yang, J.H. Zheng, H.J. Zhai, L.L. Yang, J.H. Lang, M. Gao, *J. Alloy. Compd.* **481**, 628 (2009).
- [3] R. Yi, N. Zhang, H. Zhou, R. Shi, G. Qiu, X. Liu, *Mater. Sci. Eng. B* **153**, 25 (2008).
- [4] O. Lupan, L. Chow, L.K. Ono, B.R. Cuenya, G. Chai, H. Khallaf, S. Park, A. Schulte, *J. Phys. Chem. C* **114**, 12401 (2010).
- [5] D. Wang, C. Song, Z. Hu, W. Chen, X. Fu, *Mater. Lett.* **61**, 205 (2007).
- [6] X. Hou, L. Wang, B. Yu, F. Zhou, W. Liu, *Particuology* **8**, 458 (2010).
- [7] P. Prepelita, R. Medianu, B. Sbarcea, F. Garoi, M. Filipescu, *Appl. Surf. Sci.* **256**, 1807 (2010).
- [8] F.K. Shan, B.C. Shin, S.W. Jang, Y.S. Yu, *J. Eur. Ceram. Soc.* **24**, 1015 (2004).
- [9] X.H. Wang, R.B. Li, D.H. Fan, *Appl. Surf. Sci.* **257**, 2960 (2011).
- [10] Powder Diffract. File, JCPDS Internat. Centre Diffract. Data, PA 19073–3273, U.S.A.(2001).
- [11] L.Z. Pei, H.S. Zhao, W. Tan, H.Y. Yu, Y.W. Chen, Q.F. Zhang, *Mater. Charact.* **60**, 1063 (2009).
- [12] Y.C. Chen, H.Y. Cheng, C.F. Yang, Y.T. Hsieh, *J. Nanomater.* **2014**, 1 (2014) Article ID 430164.
- [13] J.Y. Kim, H. Jeong, D.J. Jang, *J. Nanopart. Res.* **13**, 6699 (2011).
- [14] S.F. Wei, Q. Jiang, J.S. Lian, *Trans. Nonferrous. Met. Soc. China* **18**, 1089 (2008).
- [15] C. Jia, X. Zhang, Y. Chen, Y. Su, Q. Zhou, M. Xin, Y. Lv, W. Kong, *Appl. Surf. Sci.* **254**, 2331 (2008).
- [16] L. Jiang, G. Li, Q. Ji, H. Peng, *Mater. Lett.* **61**, 1964 (2007).
- [17] F. Güell, J.O. Ossó, A.R. Goñi, A. Cornet, J.R. Morante, *Superlattice. Microst.* **45**, 271 (2009).
- [18] Y.F. Mei, G.G. Siu, Ricky K.Y. Fu, Paul K. Chu, Z.M. Li, Z.K. Tang, *Appl. Surf. Sci.* **252**, 2973 (2006).