

Hydrothermal synthesis and photoluminescent properties of ZnO nanorods

Libo Fan, Hongwei Song*, Te Li, Lixin Yu, Zhongxin Liu, Guohui Pan, Yanqiang Lei, Xue Bai, Tie Wang, Zhuhong Zheng, Xianggui Kong

Key Laboratory of Excited State Physics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 Eastern Nan-Hu Road, Changchun 130033, PR China

Available online 15 March 2006

Abstract

ZnO nanorods with hexagonal structures were synthesized by the hydrothermal method at different conditions. Their room-temperature emission spectra and fluorescent dynamics were studied. The ultraviolet emissions of excitons (3.2 eV) and visible emissions (2.0 eV) from deep levels (DLs) of defects were observed. The results demonstrate that preparation condition pH influences the intensity ratio of the exciton emissions and DLs, as well as the decay time constant of DLs emissions.

© 2006 Published by Elsevier B.V.

Keywords: ZnO nanorods; Hydrothermal synthesis; Photoluminescent properties

1. Introduction

One-dimensional (1D) structures, such as nanowires, nanorods and nanotubes have aroused remarkable attention due to a great deal of potential applications in data storage, advanced catalyst, photoelectronic devices, etc. [1,2]. Moreover, in comparison with zero-dimensional (0D) structures, the space anisotropy of 1D structures provides a better model system to study the dependence of electronic transport, optical and mechanical properties on size confinement and dimensionality [3,4]. As an important photoelectronic material, 1D ZnO nanomaterials also attracted extensive interest in the past decade. Especially, UV-nanowire laser under optical excitation in ZnO was realized at room temperature by Yang et al. in 2001 [3].

Recently, we synthesized ZnO nanorods by a hydrothermal method, which was originally reported by Wang et al [5]. It is conceived that preparation of 1D ZnO nanostructures via wet chemical routes without involving catalysts or templates provides a promising option for large-scale production of well-dispersed materials [6–9]. The photoluminescent properties of semiconductors, such

as the luminescence of excitons or deep levels (DLs), depend upon the preparation techniques strongly [10].

2. Experiments

All chemicals were analytic grade reagents without further purification. In a typical synthesis, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ were dissolved in deionized water to form 1.0 M of $\text{Zn}(\text{NO}_3)_2$ solution and 1.0 M $(\text{NH}_4)_2\text{CO}_3$ solution, respectively. 10 mL of 1.0 M $\text{Zn}(\text{NO}_3)_2$ solution was dropped slowly into 20 mL of 1.0 M of $(\text{NH}_4)_2\text{CO}_3$ solution and stirred vigorously to obtain a precipitate. The precipitate was filtered and repeatedly rinsed with deionized water to remove the residual reactants. Then, it was dispersed in ~70 mL deionized water by stirring for 30 min. Subsequently, 1.0 M of NaOH solution was dropped slowly into the above solution stirred at the same time to adjust the pH to 8. After stirring for another 10 min, the obtained suspension was transferred averagely into four Teflon-lined 25 mL capacity autoclaves. The hydrothermal synthesis was conducted at 180 °C for 20 h. After the reaction was completed, the white powder product was collected by centrifugation and dried at 80–90 °C for 12 h in a vacuum condition. Finally, the ZnO rods (a) were obtained by calcining at 400 °C for 30 min. As comparison,

*Corresponding author. Fax: +86 431 6176320.

E-mail address: hwsong2005@yahoo.com.cn (H. Song).

another similar experiment has also been performed, only by changing the pH of the precursor solution to 13. (ZnO nanorods, **b**)

Two samples were characterized by XRD using a rotating anode X-ray diffractometer with CuK α radiation ($\lambda = 1.5405 \text{ \AA}$). Photoluminescent spectra were measured by a LabRam Raman Spectrometer (Jobin–Yvon Company, France) and excited by a 325 nm He–Cd laser source. Fluorescent dynamics were measured on an FL920-Fluorescence Lifetime Spectrometer (Edinburgh Instruments) with MCP-PMT. The excitation source was an optical parametric amplifier (OPA) pumped by a Ti/sapphire regeneration amplifier (Spectra Physics Co. Ltd.), which provided a 130 fs full width at half maximum (FWHM) pulse (wavelength: 345 nm, repetition rate: 1 kHz).

3. Results and discussion

The XRD patterns of different ZnO samples were shown in Fig. 1. As seen, two samples were well crystallized. All diffraction peaks in the XRD patterns of two ZnO samples can be indexed as the pure hexagonal structure, which are consistent with the results in the standard card (JCPDS 05-0664). In the standard bulk ZnO powders, lattice constants a and c are 3.249 and 5.205 \AA , respectively. Obviously, all diffraction peaks were broader in **a** than those in **b**, which indicates that the average crystallite size of the nanorods was smaller in **a** than that in **b**.

Fig. 2 shows the TEM images of two samples. It can be seen that rod-like ZnO powders formed in the two samples. The aspect ratios (the ratio of the length to the diameter) of the nanorods varied with different preparation conditions. As pH was 8, the average diameter of the rods was 30 nm and length was 300 nm. As pH value was 13, the diameter varied little but the length decreased significantly. Therefore, the aspect ratio of the nanorods was larger in **a** than that in **b**. The selected-area electron diffraction (SAED)

pattern (inset in Figs. 2(a) and (b)) further proved that the nanorods had better crystal in **a** than that in **b**.

Fig. 3 shows the photoluminescent spectra for different ZnO powders at room temperature under a 325 nm excitation. It can be seen that both samples have two emission peaks, a narrower peak at $\sim 3.2 \text{ eV}$ and a broader peak at $\sim 2.0 \text{ eV}$. The near-UV peak at 3.2 eV ($\sim 380 \text{ nm}$) originates from the recombination of excitons [11], while the peak at 2.0 eV ($\sim 600 \text{ nm}$) from the recombination emission between the conduction band or shallow donors and interstitial oxygen (O_i), which acts as DL O_i center [12,13]. The ratios of integral intensity of the visible to the UV emission were 3.09 and 2.10 for **a** and **b**, respectively. This suggests that, there were much DL defects in two samples, which leads to the quenching of the exciton emission and the enhancement of the emission originated from the recombination of the oxygen defects [10]. This conclusion was also proved further by the following dynamics of fluorescence.

Figs. 4(a) and (b) show the fluorescent dynamics of the exciton and the defect emission, respectively. The

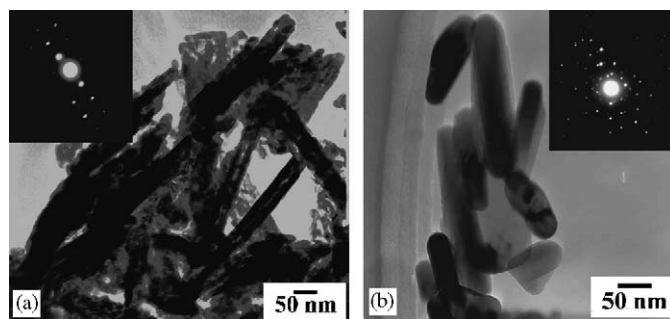


Fig. 2. TEM images of different ZnO rods. The insets are SAED patterns of corresponding ZnO nanorods.

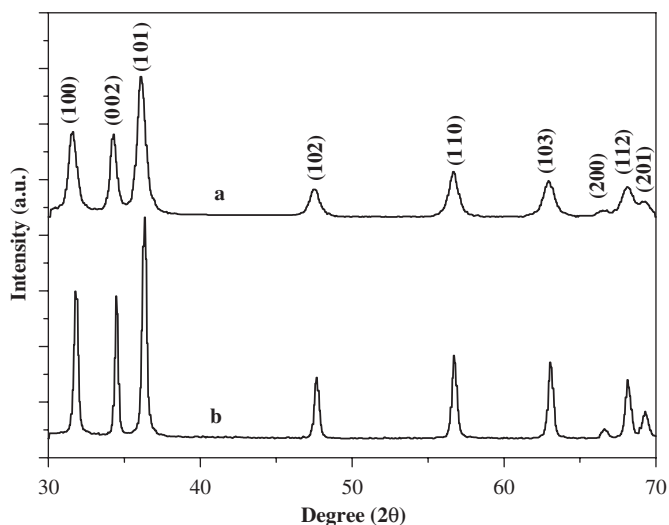


Fig. 1. XRD patterns of different ZnO rods.

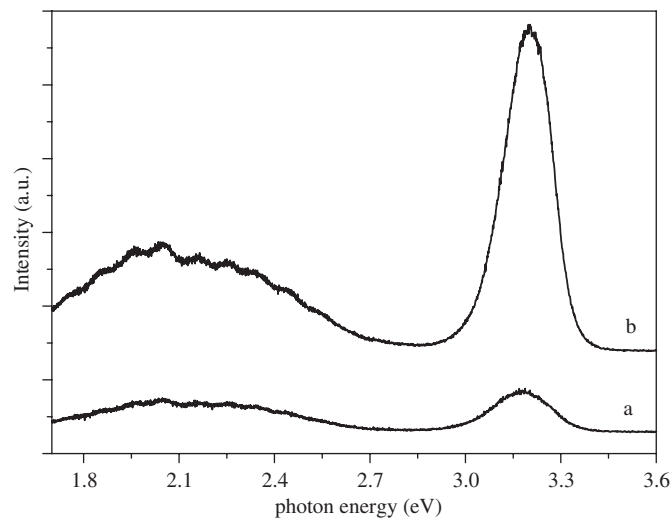


Fig. 3. Photoluminescent spectra of different ZnO rods excited by a 325-nm laser at room temperature.

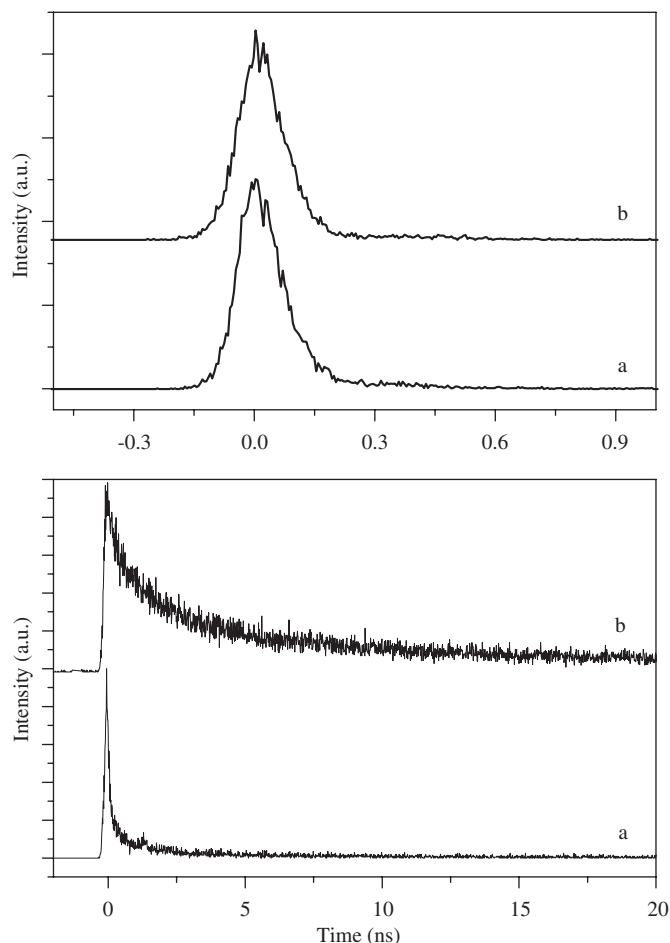


Fig. 4. Fluorescent decay curves of (a) exciton emission at 392 nm and (b) defect emission at 600 nm.

fluorescent lifetimes for excitons and DLs were obtained by fitting. It can be seen from Fig. 4(a) that the exciton-emission decays deviated from exponential rule. The exciton lifetimes was 70 ps for **a**, and 65 ps for **b**, which agreed with the reported results (50–300 ps) of bound-exciton lifetime in bulk ZnO [14]. The fluorescence decay is dominated by radiative decay of the excitons and various nonradiative processes such as captured by DL traps, low-lying surface states, and multiphonon scattering [15]. According to the emission spectra in Fig. 3, some defect states were involved in the two samples. This will lead the nonradiative relaxation to increase. In Fig. 4(b), there were two decay components for the defects emission, a faster one and a slower one. The fast one was 0.12 ns for **a** and 1.47 ns for **b**, while the slow one was 2.8 ns for **a** and 16.6 ns

for **b**. The relative proportion of the fast process was 12% in **a** and 29% in **b**. The existence of two decay components suggests that two kinds of defect states may be involved. The long-lived defect states in **b** decreased more greatly than those in **a**.

4. Conclusions

In summary, ZnO nanorods with hexagonal structure were synthesized by the hydrothermal method. As pH was 8, the obtained ZnO rods had a larger aspect ratio than those obtained as the pH was 13. And more, much defect states were involved, which influenced the photoluminescent properties of ZnO rods significantly. The UV emission from the excitons (3.2 eV) and visible emission (2.0 eV) from the DLs were observed in the two samples. The lifetime of the excitons was ~ 70 ps at room temperature. Two decay components were observed for the fluorescent dynamics of DLs.

Acknowledgments

The authors gratefully thank the financial supports of Nation Natural Science Foundation of China (Grant no. 10374086) and Talent Youth Foundation of Jilin Province (Grant no. 20040105).

References

- [1] S. Lijima, *Nature (London)* 354 (1991) 56.
- [2] X.F. Daun, Y. Huang, Y. Cui, J.F. Wang, C.M. Lieber, *Nature (London)* 409 (2001) 66.
- [3] M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* 292 (2001) 1897.
- [4] Y. Xia, P. Yang, *Adv. Mater.* 15 (2003) 351.
- [5] J. Wang, L. Gao, *J. Mater. Chem.* 13 (2003) 2551.
- [6] X.Y. Zhang, J.Y. Dai, H.C. Ong, N. Wang, H.L.W. Chan, C.L. Choy, *Chem. Phys. Lett.* 393 (2004) 17.
- [7] J. Wang, L. Gao, *Solid State Communications* 132 (2004) 269.
- [8] X. Wang, Y.D. Li, *J. Am. Chem. Soc.* 41 (2002) 2446.
- [9] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Nihara, *Adv. Mater.* 11 (1999) 1307.
- [10] Z. Qiu, K.S. Wong, *Appl. Phys. Lett.* 84 (2004) 2739.
- [11] T.W. Kim, T. Kawazoe, S. Yamazaki, M. Ohtsu, T. Sekiguchi, *Appl. Phys. Lett.* 84 (2004) 3358.
- [12] A.B. Djuricic, Y.H. Leung, W.C.H. Choy, K.W. Cheah, W.K. Chah, *Appl. Phys. Lett.* 84 (2004) 2635.
- [13] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, *Appl. Phys. Lett.* 78 (2001) 2285.
- [14] J. Wilkinson, K.B. Ucer, R.T. Williams, *Radiat. Meas.* 38 (2004) 501.
- [15] S. Hong, T. Joo, W. II Park, Y.H. Jun, G.C. Yi, *Appl. Phys. Lett.* 83 (2003) 4157.