

Photoluminescence studies from ZnO nanorod arrays synthesized by hydrothermal method with polyvinyl alcohol as surfactant

Zeyan Wang, Baibiao Huang^{*}, Xiaojing Liu, Xiaoyan Qin, Xiaoyang Zhang, Jiyong Wei, Peng Wang, Shushan Yao, Qi Zhang, Xiangyang Jing

State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

Received 12 December 2007; accepted 3 January 2008

Available online 16 January 2008

Abstract

Well-aligned ZnO nanorod arrays have been synthesized by a simple hydrothermal method with polyvinyl alcohol as surfactant on F:SnO₂ conductive glasses substrates. Visible violet photoluminescence has been observed at room temperature. A series of annealing treatments in different environments have been made in order to investigate the nature of these emissions. The violet emission shows no change after annealing in air, while shifts to the ultra-violet region after annealing in H₂. It is concluded that the violet emission is due to V_{Zn} defect formed at the surface of the ZnO nanorods.

© 2008 Elsevier B.V. All rights reserved.

Keywords: ZnO nanorods; Photoluminescence; Polyvinyl alcohol

1. Introduction

ZnO is a superior II–VI semiconductor with a wide-direct bandgap of 3.37 eV, and an exciton-binding-energy of about 60 meV. These properties make it a potential candidate for fabricating blue and ultra-violet (UV) optical devices, such as field effect transistors (FETs), light-emitting diodes (LEDs) and laser diodes (LDs) [1–3]. Other applications such as vatistors, solar cell windows, sensors and catalysts [4–7] were also widely used because of its superior properties.

One-dimensional (1D) ZnO nanostructures now have attracted increasing attention owing to their promising applications in nano scale optoelectronic devices. Various methods have been reported for synthesizing 1D ZnO nanomaterials such as electrochemical deposition (ED) [8], chemical vapor deposition (CVD) [9], pulsed laser deposition (PLD) [10] and hydrothermal methods [11], etc. Photoluminescence (PL) properties have been widely investigated. UV, green and orange emissions have been observed. And

their origins have been studied [12,13]. However, visible violet (VV) emission has rarely been reported. In this letter, we report that VV as well as UV, green or orange emission is also possible to observe from the 1D ZnO nanorods array grown by hydrothermal method with polyvinyl alcohol (PVA) as surfactant.

2. Experimental

ZnO nanorod arrays were synthesized from zinc nitrate in a neutral aqueous solution by hydrothermal method. The procedure consists of two steps: (1) modification of FTO substrates with a thin layer of ZnO nanoparticles by spin coating, and (2) hydrothermal growth of ZnO nanorods in aqueous solution. The colloid solution was yielded by dissolving zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 0.75 M) in the mixed solution of ethanolamine ($NH_2CH_2CH_2OH$, 0.75 M) and 2-methoxyethanol ($CH_3OCH_2CH_2OH$). The solution was dropped onto FTO substrates for spin coating, and then the substrates were annealed at 300 °C for 10 min. Three cycles were needed to form a dense and uniform dispersed ZnO nanoparticle layer on the substrates. The subsequent hydrothermal growth was carried out at 95 °C for 8 h in a stainless steel autoclave by immersing the modified substrates in the aqueous solution containing zinc nitrate

^{*} Corresponding author. Tel.: +86 531 8836 6324; fax: +86 531 8836 5969.

E-mail addresses: wangzeyan@mail.sdu.edu.cn (Z. Wang), bbhuang@sdu.edu.cn (B. Huang).

hexahydrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, 5\text{mM}]$, methenamine $[(\text{CH}_2)_6\text{N}_4, 5\text{mM}]$ and polyvinyl alcohol (PVA). Subsequently, the product were thoroughly washed by deionized water to eliminate residual salts, and dried by N_2 flows before characterization.

The morphology of the nanorods was characterized using JEOL JSM-6700F field emission scanning electron microscopy (FE-SEM). X-ray diffraction (XRD) analysis was performed with a Rigaku D/Max- γ A diffractometer with $\text{CuK}\alpha$ radiation. The photoluminescence (PL) measurements were carried out on an Edinbergh FLS920 fluorescence spectrophotometer with a 450 W Xe lamp as the excitation light source at room temperature.

3. Results and discussion

Fig. 1 shows us the SEM images of the ZnO nanorods grown on the substrates with PVA as surfactant. From the top view and the cross-sectional view images, it can be clearly seen that, the as grown nanorods are well-aligned, oriented in a perpendicular fashion and arranged in a very large uniform arrays on FTO substrates. The diameter of the as grown nanorods is ranging between 20 and 40 nm, and its length is about 400–500 nm. Comparing to the nanorods grown under the same conditions without PVA, our nanorods are thinner. We implied that this is caused by the addition of PVA, which will be

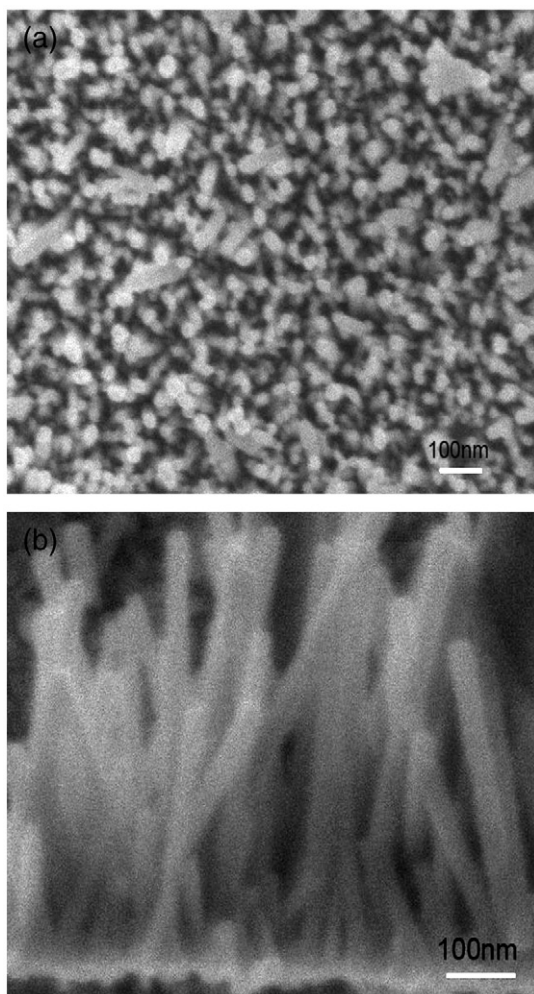


Fig. 1. (a) Top view and (b) cross-section view SEM image of the as grown ZnO nanorods.

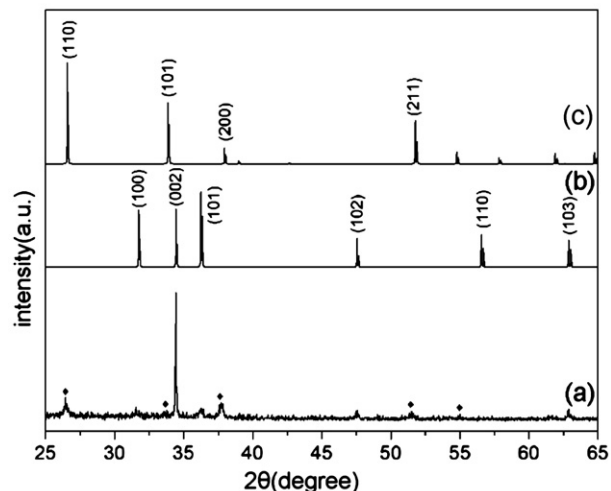


Fig. 2. XRD patterns of (a) as grown ZnO nanorods on F:SnO₂ glass substrate (u), (b) and (c) standard XRD pattern of ZnO and SnO₂.

discussed in details elsewhere. According to the X-ray diffraction pattern in Fig. 2, zincite (wurtzite ZnO) is the only crystallographic phase detected. The strongest reflection was (002) compared to (101) and (100) for more isotropic and randomly oriented samples, which suggested that (002) is the preferred orientation.

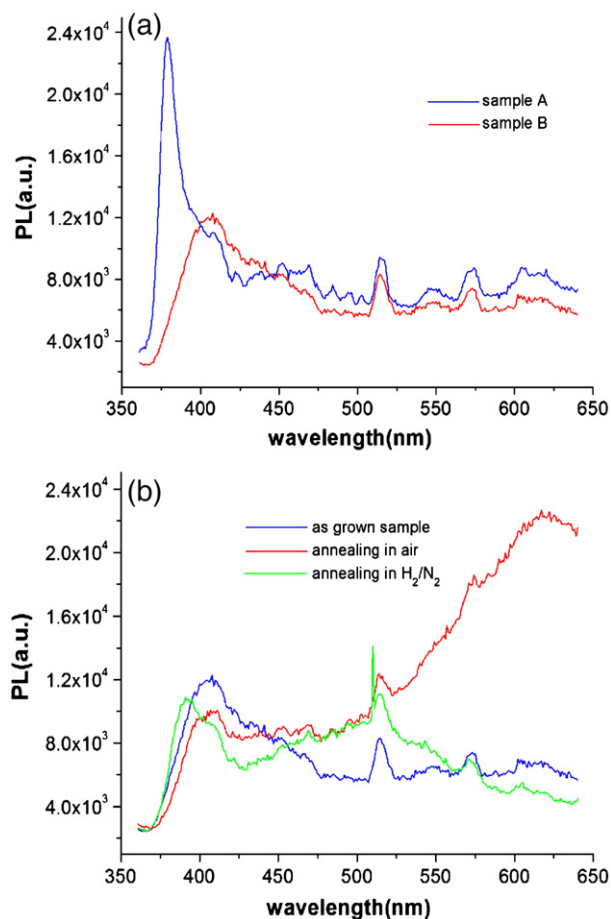


Fig. 3. Photoluminescence spectra of as grown ZnO nanorods without (sample A) and with (sample B) PVA (a), annealed samples in different gas environments (b).

Photoluminescence (PL) spectra obtained from the sample without (sample A) and with PVA (sample B) are shown in Fig. 3(a). Sample A exhibits a sharp peak at 379 nm (UV), while sample B shows a broad and relatively weak peak at 408 nm (VV) instead. And three weak peaks at 514 nm, 574 nm, 607 nm were observed in both samples. In order to investigate the nature of the VV emission, a series of annealing treatments had been made in different environments. Two samples were collected in the same growth condition, then annealed in one of the two environments; either 500 °C in 5% H₂/95% N₂ for 2 h, or 500 °C in air for 2 h. One sample was left untreated as a control. Room temperature PL spectra of these samples after annealing treatments are shown in Fig. 3(b). The 500 °C O₂ treatment caused a great increase on orange emission and a slightly decrease on violet emission. But the band-edge emission was still absent. The green emission was slightly increased as a shoulder of the broad orange emission. However, The 500 °C H₂ treatment caused a nearly complete quenching of the orange emission and the violet emission peak shifts to UV region with a peak centered at 390 nm. And the green emission increased a little with appearance of a sharp peak at 510 nm. According to Vanheusden's theory, the green emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy. When annealing the sample in reductive atmosphere, a stronger green emission was found with the increase of oxygen vacancies. While annealing the sample in oxidative atmosphere, the number of oxygen vacancies decreased. And interstitial oxygen ions were generated at the same time which would finally cause a strong orange emission and a relatively low green emission. Our results were in good accordance with the above theory and we implied the green and orange emissions were attributed to V_{O}^+ and O_i^- respectively. On the point of VV emission, Cordaro et al. [14] indicated there was an electron trap associated with ionized oxygen vacancy V_{O}^+ with a level about 0.33 eV below the conduction band. According to our results, the VV emission lied with a peak at 408 nm (3.039 eV) which is exactly consistent with Cordaro's theory. But we did not agree with the origin of this luminescence, because of the blue shift during annealing in H₂/N₂. We implied that VV emission might be associated with the V_{Zn}^- defect in the depletion layer formed by the interaction between PVA and Zn(OH)²⁺ units. This kind of defect disappeared during the annealing treatment in reductive environment and the transition between the conduction band and defect level turn back to the near band-edge emission again.

4. Conclusions

With PVA as surfactant, well-aligned ZnO nanorod arrays had been fabricated by hydrothermal method on FTO substrates.

The as-prepared nanorods were single crystals with a preferred orientation along (001). The PL spectra showed a VV emission instead of the near band-edge emission. Orange and green emissions were increased in oxidative and reductive annealing environments respectively. The VV emission shifted back to UV emission again after the reductive annealing. And we implied the VV emission might be associated to the V_{Zn}^- defect in the depletion layer formed during the growth process with PVA. Further investment is under process on the exact nature of this emission.

Acknowledgment

This work was financially supported by a research grant from the National Basic Research Program of China (No. 2007CB613302) and the National Natural Science Foundation of China (Nos. 51721002 and 10774091).

References

- [1] H.T. Ng, J. Han, T. Yamada, P. Nguyen, Y.P. Chen, M. Meyyappan, *Nano Lett.* 4 (2004) 1247.
- [2] R.F. Service, *Science* 276 (1997) 895.
- [3] E.M. Wong, P.C. Searson, *Appl. Phys. Lett.* 74 (1999) 2939.
- [4] M.S. Ramachalam, A. Rohatgi, W.B. Carter, J.P. Shaffer, T.K. Gupta, *J. Electron. Mater.* 24 (1995) 413.
- [5] J. Zhong, A.H. Kitai, P. Mascher, W. Puff, *J. Electrochem. Soc.* 140 (1993) 3644.
- [6] K.S. Weissenrieder, J. Muller, *Thin Solid Films* 300 (1997) 30.
- [7] J. Rodriguez, T. Jirsak, J. Dvorak, S. Sambasivan, D.J. Fischer, *J. Phys. Chem., B* 104 (2000) 319.
- [8] R. Liu, A.A. Vertegel, E.W. Bohannon, T.A. Sorenson, J.A. Switzer, *Chem. Mater.* 13 (2001) 508.
- [9] J.J. Wu, S.C. Liu, *Adv. Mater.* 14 (2002) 215.
- [10] B.J. Jin, S. Im, S.Y. Lee, *Thin Solid Films* 366 (2000) 107.
- [11] L. Vayssieres, *Adv. Mater.* 15 (2003) 464.
- [12] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, *Appl. Phys. Lett.* 78 (2001) 2285.
- [13] B. Lin, Z. Fu, Y. Jia, *Appl. Phys. Lett.* 79 (2001) 943.
- [14] J.F. Cordaro, Y. Shim, J.E. May, *J. Appl. Phys.* 60 (1986) 4186.