Materials Science-Poland, *Vol. 27*, *No. 1*, *2009*

The growth morphology of ZnO hexangular tubes synthesized by the solvothermal method

Y. LI*, X. LIU, Y. ZOU, Y. GUO

College of Science, Civil Aviation University of China, Tianjin, 300300, P.R. China

A novel hexangular tube structure of ZnO has been successfully synthesized via the solvo-thermal method, using $Zn(NO_3)_2 \cdot 6H_2O$ and NaOH as starting materials. The results showed that the supersaturation near the surface of ZnO crystal is higher than that inside the crystal, which leads to a preferential growth along *c*-axis of the side surface. The strain between the surface and the bulk of ZnO rods drives ZnO rods into tubular structure. The spectroscopic results show that ZnO tubes possess the wurtzite structure. Three emission peaks have been detected, a violet peak at about 399.9 nm, a blue emission at about 448.5 nm and a green emission at about 549.8 nm.

Key words: *zinc oxide; solvo-thermal method; electron microscopy; X-ray diffraction; photoluminescence*

1. Introduction

Zinc oxide, a wide-gap II–VI semiconductor with a direct band gap of about 3.37 eV at room temperature, is a well known material suitable for generating ultraviolet (UV) light [1]. Furthermore, a large exciton binding energy of about 60 meV in ZnO, significantly larger than the thermal energy at room temperature (26 meV), can ensure an efficient exciton emission at room temperature under low excitation energy [2, 3]. Because of these properties, zinc oxide is widely used in various applications such as photonic devices, transparent conductors, solar cell windows, surface acoustic devices and gas sensors [4, 5]. The optical, electrical and magnetic properties of zinc oxide are affected by its particle size, morphology, purity and chemical composition [6–9]. Thus, necessary efforts should be made to synthesize zinc oxide and undertake morphological studies. Various morphological crystallites of zinc oxide such as nanorods and microflowers have been synthesized by various methods [10–12]. Nanotubes of ZnO are expected to improve the luminescence efficiency of electro-optic devices and the sensitivity of chemical sensors. Wang et al. [13] prepared ZnO nanotubes by

*Corresponding author, e-mail: liyan01898@163.com

the sol-gel method within the pores of an anodic aluminum oxide template. Kong et al. [14] have prepared single-crystal nanorings by a solid-vapour process. Yan et al. [15] have synthesized aligned ZnO taper-tubes under hydrothermal conditions, using a zinc foil as a deposition substrate of ZnO. However, complex procedures, sophisticated equipment, rigid experimental conditions or a low yield are involved in these methods. Large-scale use will require the development of simple, low-cost approaches to the synthesis of inorganic, functional nanomaterials. ZnO nanotube bundles were successfully synthesized by Yu et al. [16] using a single solution method, but ZnO tubes in clusters were obtained, not in dispersive conditions. To our knowledge, solvohydrothermal synthesis of ZnO nanotubes has been rarely reported. In this work, hexangular ZnO tubes have been successfully synthesized by a simple and effective solvothermal method, without any catalysts, templates or substrates. The morphologies, structure and the photoluminescence properties of zinc oxide tubes were characterized by scanning electron microscopy (SEM), fluorescence spectrophotometry (FR) and X-ray diffraction (XRD).

2. Experimental

All analytical grade reagents: zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), sodium hydroxide (NaOH), absolute alcohol (C_2H_5OH) and sodium chloride (NaCl) were purchased from the commercial market without further purification.

ZnO crystalline powder was prepared according to the following procedure. Aqueous solutions of zinc nitrate hydrate (0.01–0.1 M) and sodium hydroxide (0.02–0.2 M) were prepared using deionized water. NaOH solution was added drop-by-drop into $Zn(NO_3)_2$ solution at room temperature under vigorous stirring which resulted in the formation of a white suspension. The suspension was separated with a centrifuge, thrice washed with distilled water, and finally washed with absolute alcohol. The separated powder was dried at 60 °C for 24 h in an oven to obtain the precursor. Subsequently, 3 g of the precursor material and 0.15 g NaCl were added into 30 ml of absolute alcohol, the mixture was mixed, and then sealed in a Teflon-lined autoclave with an interior volume filled in 35%. The autoclave was treated solvothermally at 180 °C for 72 h. Afterwards, the resulting white precipitate was washed with distilled water and alcohol for several times to obtain ZnO crystallites.

The morphology of ZnO particles was examined by 1530VP model field emission scanning electron microscopy (SEM) in the China National Academy of Nanotechnology Engineering. X-ray diffraction (XRD) with CuK_α radiation (λ = 0.1542 nm) on a DX-2000 X-ray diffractometer was used for checking the formation and identification of compounds in the obtained particles. Photoluminescence (PL) spectra of ZnO nanocrystals were recorded with a WGY-10 fluorescence spectrophotometer equipped with a Xe lamp (150 mW). The excitation wavelength was fixed at 325 nm. The emission spectrum of solid zinc oxide powder samples at room temperature was observed in the wavelength range of 300–600 nm by using a monochromator and a photomultiplier.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-obtained ZnO crystallites synthesized solvothermally at 180 °C for 72 h. The obtained ZnO crystals possess a wurtzite structure. The diffraction peaks can be well indexed to hexagonal ZnO with lattice parameters of a = 0.324982 nm and c = 0.520661 nm (JCPDS Card No. 36-1451). All diffraction peaks with high intensity imply that ZnO crystals can grow very well in a solvent of alcohol containing little water.

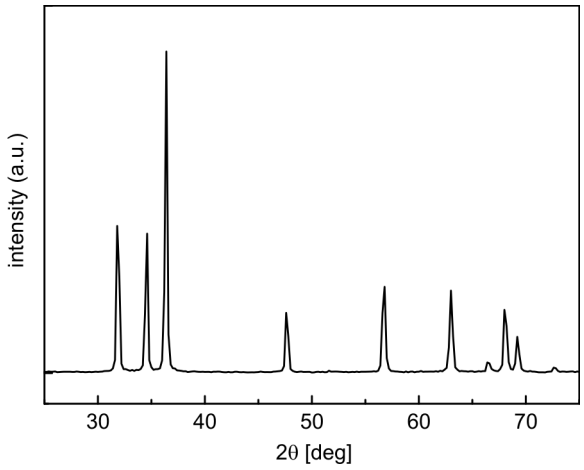

Fig. 1. XRD pattern of the synthesized ZnO tubes

The SEM images in Fig. 2 give a general overview of the synthesized products, which are hexangular pillars, hexangular tapers, or a combination of the both, with holes on their surface and an empty interior. The dimensions of the ZnO hexangular tubes are 1–2 μm in length, 400–600 nm in external diameter and 100–300 nm in inner diameter. The local wall thickness of the tube is ca. 100–150 nm. The top (0001) and bottom $(000\bar{1})$ surfaces are partly or completely open and the side faces can also have some holes, as shown in Fig. 2a, b and d. It implies that the bottom face breaks earlier, and more easily than the side faces during the growth. Interestingly, for some tubes, it can be clearly seen that the cracks in the bottom face are ready to collapse downward (Fig. 2f), and a special structure of a thick tube holding a thin tube or a hexangular pillar in its cavity was observed in some tubes (Fig. 2d, e). We also found that the surface layer density and the firmness of the synthesized ZnO tubes are higher than those of the bulk due to the faster growth and higher supersaturation along *C*-axis in the side surface, leading to a preferential nucleation and growth at 180 °C, a relative high temperature. It is understood that the strain, coming of the inner shrink of ZnO rods during its overgrowth for a long time (72 h) causes a collapse or crack between the surface layer and the inner of ZnO rods, which prompts the ZnO rods to be tubes. Meanwhile sodium chloride crystallites, not dissolving in alcohol, play an

important role as initial growth nuclei of ZnO rods, and a pipeline was left behind rinsing during the next procedure. Figure 2 shows two stages in the mechanism of a single tube growth on the surface of sodium chloride crystallite. In the first stage, an initially grown sheet along the surface of sodium chloride crystal turns into a roll or a hexangular pillar. In the second stage, a hexangular pillar or a roll transforms into a hexangular tube with a simultaneous collapse or a shrink inside ZnO rods. We may suggest that these are nanotubular type rods with polycrystalline walls consisting of wurtzite-type ZnO nanograins, rather than the well known nanotubes of the multisheet carbon nanotube type.

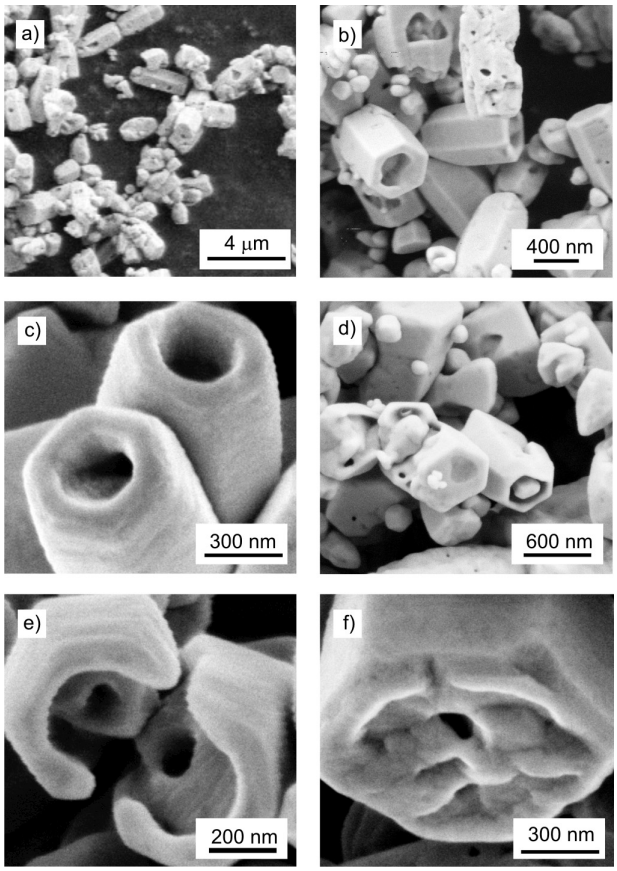

Fig. 2. SEM images of the synthesized ZnO tubes

The room temperature photoluminescence spectra of the as-prepared ZnO crystallites fabricated for 72 h at 180 °C were recorded, as shown in Fig. 3. A weak violet peak at about 399.9 nm was observed exhibiting a red shift compared to that of the reported 380 nm [17]. In addition, a broad blue emission at about 448.5 nm and a green emission centred at about 549.8 nm are also observed for these samples.

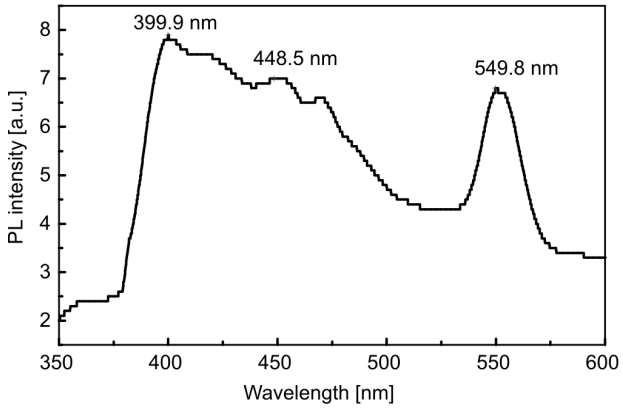

Fig. 3. Photoluminescence spectrum of the synthesized ZnO tubes

It is commonly accepted that the violet emission originates from the contribution of the near-band-edge emission of wide band gap ZnO, while the green peaks result from the recombination of electrons in single oxygen vacancies with photoexcited holes in the valence band. The stronger intensity of the green luminescence indicates a higher defect density due to oxygen vacancies in this material.

4. Conclusion

Hexangular tube structure of ZnO can be successfully synthesized by a solvohydrothermal treatment. SEM photos reveal that dimensions of the hexangular tubes of ZnO are 1–2 μm in length, 400–600 nm in the external diameter and 100–300 nm in the inner diameter. The local wall thickness of a tube is about 100 nm to 150 nm. The supersaturation near the side surface of the growing ZnO crystal is higher than that at its centre, leading to a preferential nucleation and growth along *c*-axis direction of the side surface than the inside. The strain between the surface and the inside of ZnO rods could drive the ZnO rods to be tubes. The XRD and PL results show that the ZnO tube crystallites possess a wurtzite structure, and a weak violet emission at about 399.9 nm, a broad blue emission at around 448.5 nm and a green emission centred at about 549.8 nm are observed for these samples. The ZnO tube structure may be promising in developing novel devices.

Acknowledgements

This project is supported by the Natural Science Foundation of Tianjin, China, No. 043602911, 05yfJMTC 12900.

References

[1] KIM D.K., MANZOOR U., Scr. Med., 54 (2006), 807.
[2] CHEN Z., GAO Q.M., RUAN M., SHI J.L., Appl. Phys. Lett., 87 (2005), 93113-1-3.

[3] VOROBEV V.A., J. Optic. Tech., 7 (2005), 690-247-9.
[4] UMAR A., RAHMAN M.M., KIM S.H., HAHN Y.B., Chem. Commun., 2 (2007), 166.
[5] WAMA R., UTIYAMA M., PLASHNITSA V.V., MIURA N., Electrochem. Commun., 9 (2007), 2774.
[6] WANG Q.X., YOU L.P., ZHANG X.Z., WANG R.M., LV Y.Z., GUO L., Rare Metals, 25 (2006), 193.
[7] POKROPIVNY V.V., KASUMOV M.M., Tech. Phys. Lett., 33 (2007), 44.
[8] XIE X.H., LI X.J., YAN H.H., Mater. Lett., 60 (2006), 3149.
[9] LAZARECK A.D., CLOUTIER S.G., KUO T.F., TAFT B.J., KELLEY S.O., XU J.M., Nanotechn., 17 (2006), 2661.
[10] SINGH J., TIWARI R.S., SRIVASTAVA O.N., Nanosci. Nanotechnol., 7 (2007), 1783.
[11] XU F.S., LIU X.F., TSE S.D., COSANDEY F., KEAR B.H., Chem. Phys. Lett., 449 (2007), 175.
[12] SHANG T.M., SUN J.H., ZHOU Q.F., GUAN M.Y., Cryst. Res. Technol., 42 (2007), 1002.
[13] WANG Z., LI H.L., Appl. Phys. A, 74 (2002), 201.
[14] KONG X.Y., DING Y., YANG R., WANG ZH.L., Science, 303 (2004),1348.
[15] YAN CH.L., XUE D.F., Electrochem. Comm., 9 (2007), 1247.
[16] YU Q.J., FU W.Y., YU C.L., YANG H.B., WEI R.H., LI M.H., LIU SH.K., SUI Y.M., LIU ZH.L., YUAN M.X., ZOU G.T., WANG G.R., SHAO CH.L., LIU Y.CH., J. Phys. Chem. C, 111 (2007),17521.
[17] KAUR M., BHATTACHARYA S., ROY M., DESHPANDE S.K., SHARMA P., GUPTA S.K., YAKHMI J.V., Appl. Phys A-Mater., 87 (2007), 91.

Received 31 January 2008
Revised 19 December 2008