

Growth of ZnS Nanotowers with ZnO Core by Thermal Evaporation

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Abstract: Zinc sulfide (ZnS) of wurtzite structure nanotowers with a ZnO core has been grown using a simple catalyst-free thermal evaporation technique. The ZnS nanotowers are as long as to several tens of micrometers. The high-magnification TEM image of a single nanotower reveals clear ZnS/ZnO interface. The ZnO core is likely formed at the first stage due to the residual O₂. The PL spectrum indicates that the nanotowers have a visible emission peak centered at 409 nm.

Key words: ZnS, ZnO, thermal evaporation, crystal growth, nanostructures

INTRODUCTION

Low dimensional systems, such as quasi one-Dimensional (1D) (nanotubes, nanowires, nanobelts, ...), have been successfully synthesized and represent one of the most important frontiers in advanced materials research due to their peculiar optical, electrical, thermoelectric properties and potential application in nanodevices^[1-3]. Recently, much attention has been devoted to develop the controlled growth of 1D semiconductor with homogeneous structures and compositions. The Vapor Liquid-Solid (VLS) and the Vapor-Solid (VS) and other mechanisms for the growth of 1D nanostructures at high temperature are well recognized and have been used to synthesized various compound semiconductor nanostructures^[1]. Properties of nanostructures may depend sensitively on their structures, morphologies and sizes. Considerable efforts have been devoted to develop the controlled growth of various one-dimensional semiconductor nanostructures with homogeneous structures and compositions using laser ablation^[4] as well as template-induced^[5], solution^[6] and thermal evaporation methods^[7].

ZnS, an important II-VI semiconductor compound with direct wide band-gap energy of 3.6 eV at 300 K, has prominent application in many fields including thin film electroluminescence, phosphor in cathode-ray tube, flatpanel displays, ultraviolet light-emitting diodes, injection lasers and nonlinear optical devices^[8]. Much effort has been made to fabricate and characterize ZnS nanostructures^[9-12]. However, in comparison with ZnO, investigations on the syntheses and properties of ZnS nanostructures are quite limited. In the past few years,

ZnS nanostructures have been studied extensively and reported to have different characteristics from the bulk. ZnS has two kinds of crystal structures: Wurtzite ZnS (hexagonal phase) and zinc blende ZnS (cubic phase). In addition to nanowires^[13,14] and nanoparticles^[15], some fascinating morphologies have been reported. Ma *et al.* have synthesized wurzitestructured ZnS nanobelts and nanowindmills by thermal evaporation of ZnS powders^[7]. Zhu *et al.* have fabricated ZnS tetrapod nanocrystals by thermal evaporation of ZnS and carbon mixed powders^[16]. M.Y. Lu *et al.* have synthesized self-assembled ZnS of wurtzite structure nanocomb with ZnO sheath using thermal evaporation^[17]. In this study, we report the growth of ZnS nanotowers with ZnO core using thermal evaporation method. In the present study, ZnS tower-like with ZnO core, which were fabricated via simple thermal evaporation, are reported as a new example of 1D nanostructures. Morphology, crystal structure and luminescent properties of the nanotowers were investigated.

MATERIALS AND METHODS

ZnS tower-like with ZnO core nanostructures were synthesized in a horizontal tube furnace by a thermal evaporation method. ZnS powders mixed with graphite (1:1) were chosen as source materials. Silicon wafers were cleaned ultrasonically using hydrofluoric acid and distilled water several times and employed to collect the deposited products. The evaporation process was carried out in quartz tube, which was located in the horizontal tube furnace. A quartz boat loaded with ZnS and graphite powders, which serve as the source material, was

transferred into the center of tube furnace. The silicon wafer was located next to the center along the downstream side of the flowing gas. After being purged by high-purity argon gas 99.99%, the furnace temperature was raised to 800°C at a heating rate of 30°C per minute under a constant flow of Ar 80 standard cubic centimeters per minute (sccm). After 30 min, the temperature was raised to 1100 °C and held for 90 min. When the temperature was raised to 800 °C , hydrogen gas was introduced into the system through a mass-flow controller at rates of 16 sccm. The temperature of the substrate area was about 700-750°C due to the temperature gradient in the tube furnace. After evaporation and deposition, the flow of hydrogen turned off and the quartz tube was drawn out of the furnace when it was cooled down to 250- 300°C .

The morphology and composition of the product were examined using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDXA) X-Ray Diffraction (XRD) patterns measured with Cu K á radiation and High-Resolution Transmission Electron Microscopy (HRTEM).

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the product. All the peaks could be attributed to ZnS (wurtzite ZnS: $a = 0.382098$ nm, $c = 0.62573$ nm) and ZnO (wurtzite ZnO: $a = 0.324982$ nm, $c = 0.520661$ nm). Figure 2 a and b show the low magnification and high magnification SEM images of the tower-like nanostructures. From these images, the length of the ZnS tower-like with ZnO core is about several tens of micrometers. Figure 3a shows the corresponding bright-field TEM image of a single nanotower. The diameter of the nanotower varied from the base to the head. Figure 3b is the bright and dark TEM images of the nanotowers taken with the ZnS and ZnO diffraction spots. The bright and dark diffraction contrast images correspond to the ZnS shell and ZnO core, respectively. This high-magnification TEM image of a single nanotower reveals clear ZnS/ZnO interface. Analysis of spectra obtained by EDS indicated that regions A and B in Fig. 3b are composed mainly of Zn/S and Zn/O, respectively. The EDS spectra are shown in Fig. 3c and d. The Selected Area Electron Diffraction pattern (SAED) taken from the area including both regions A and B is shown in Fig. 3e indicating that the diffraction spots, corresponding to ZnS and ZnO. The HRTEM images of the regions A and B representing ZnS shell and ZnO core are shown in Fig. 3f. That growth direction of

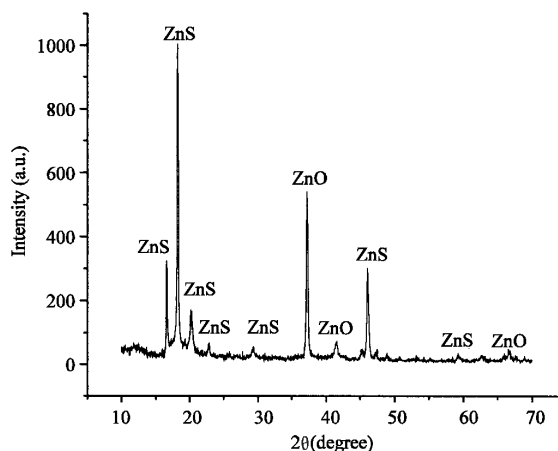
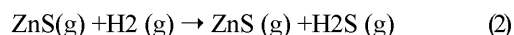
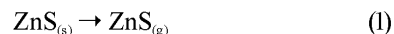


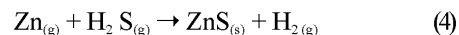
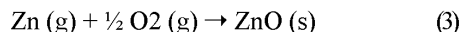
Fig. 1: XRD pattern of the as-synthesized ZnS tower-like with ZnO core

ZnS shell with ZnO core nanotower was analyzed to be along [0 0 0 1]. The result is in agreement with those reported previously^[18,19].

The thermal evaporation of ZnS powders in the ambient including H₂ at high temperature can be expressed in the following chemical reaction equations:



The ZnS (g), Zn (g) and H₂S (g) were then transported to the substrate at 700-750°C to form the nanostructures. The residual O₂ (g) in the furnace may react with Zn to form ZnO:



The Gibbs free energy (ΔG) for Eq. 3 and 4 at 700-750°C are positive and negative, respectively^[17]. Therefore reaction of Eq. 4 can proceed. Only when the temperature is lowered to about 600-800°C before H₂ gas is introduced in the system, the reaction of Eq. 3 can be effective. Then, the residual O₂ (g) is expected to react with Zn (g) to form ZnO core. It is therefore considered that ZnO core was formed early during the first stage. Then covered with ZnS as a shell, to form finally ZnS tower-like with ZnO core.

Finally, the photoluminescence (PL) spectra of the sample were measured at room temperature using a He-Cd laser with an excitation wavelength of 325 nm. The PL peak for the ZnS tower-like with ZnO core synthesized in

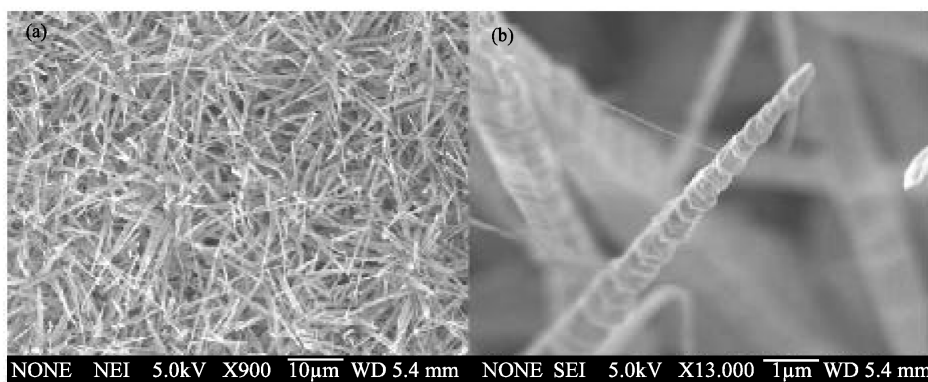


Fig. 2: SEM images of the as-synthesized ZnS tower-like with ZnO core structure (a) shows the general SEM image of the tower-like structure, (b) SEM image of the single tower-like structure

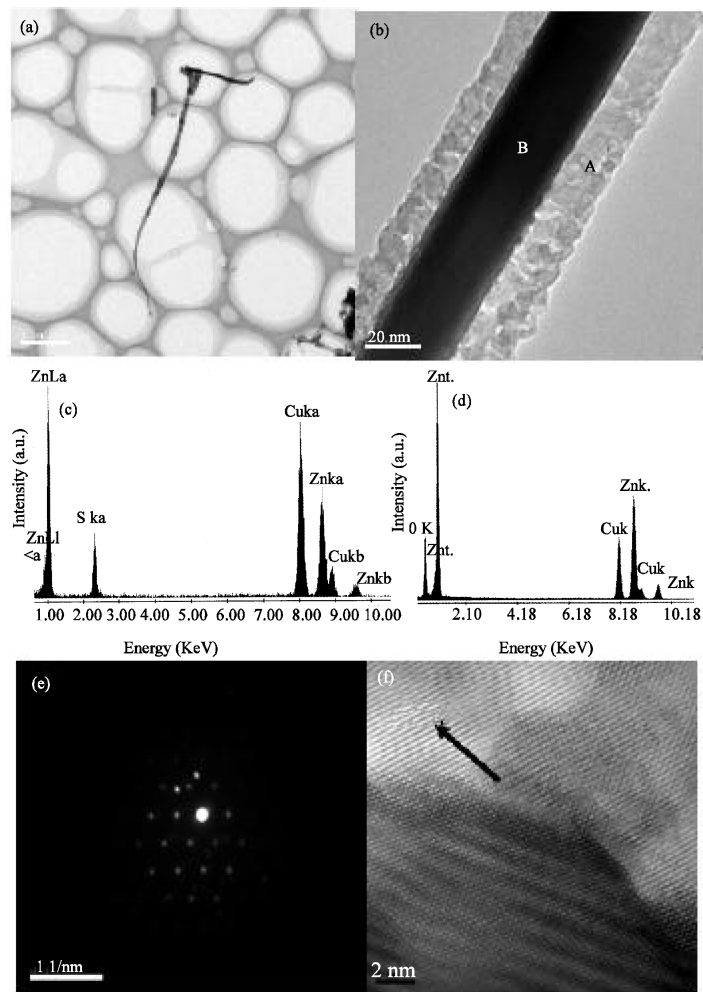


Fig. 3: TEM images of the as-synthesized ZnS tower-like with ZnO core structure (a) Shows the corresponding bright-field TEM image of a single nanotower, (b) The bright and dark diffraction contrast images correspond to the ZnS shell and ZnO core, (c) and (d) The EDS spectra of the ZnS shell and ZnO core, (e) SAED taken from the area including both regions A and B, (f) The HRTEM images of the regions A and B representing ZnS shell and ZnO core

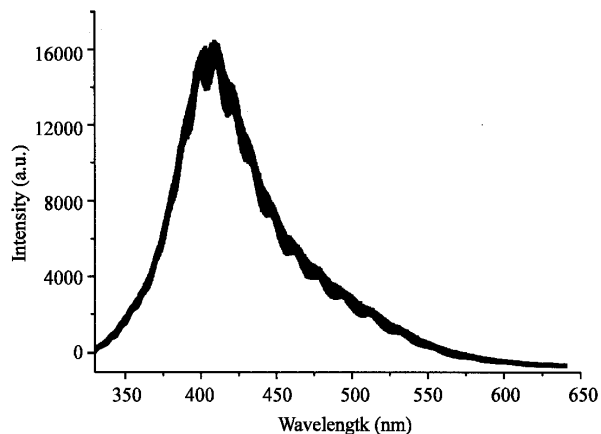


Fig. 4: Room-temperature PL spectrum of the as-synthesized ZnS tower-like with ZnO core structure

the temperature range of 700-750°C shows visible emission. As shown in Fig. 4, The spectra exhibit a strong emission centered at 409 nm. This visible emission may originate from some self-activated centers, vacancy states, element sulfur species on the surface, or interstitial states associated with the peculiar nanostructures as in previous reports^[8,20-22]. The new ZnS-ZnO composite nanostructures may have useful applications for advanced luminescence materials.

CONCLUSION

Zinc Sulfide (ZnS) of wurtzite structure nanotowers with a ZnO core has been grown using a thermal evaporation and catalyst-free condensation method. The as synthesized nanotowers were found to grow along [0001] direction. During the first stage of growth, Zn vapor react with residual O₂ to form ZnO core. The growth of a ZnS (shell)/ZnO (core) structure was never reported previously. The PL spectra indicate that the nanotowers have a visible emission peak centered at 409 nm.

REFERENCES

1. Xia, Y., P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, 2003. One-Dimensional nanostructures: Synthesis, Characterization and applications. *Adv. Mater.*, 15: 353-389.
2. Ding, Y., X.D. Wang and Zh. L. Wang, 2004. Phase controlled synthesis of ZnS nanobelts: Zinc blende vs wurtzite. *Chem. Phys. Lett.*, pp: 398-32.

3. Bellucci, S., 2005. Carbon nanotubes: Physics and Applications. *Phys. Stat. Sol. (c)* 2: 1-34.
4. Zhang, Y.F., Y.H. Tang, N. Wang, D.P. Yu, C.S. Lee, I. Bello and S.T. Lee, 1998. Silicon nanowires prepared by laser ablation at high temperature. *Appl. Phys. Lett.*, pp: 72-1835.
5. Zhu, J. and S. Fan, 1999. Nanostructure of GaN and SiC nanowires based on carbon nanotubes. *J. Mater. Res.*, pp: 14-1175.
6. Holmes, J.D., K.P. Johnston, R.C. Doty and B.A. Korgel, 2000. Control of Thickness and Orientation of Solution-Grown Silicon Nanowires. *Sci.*, pp: 287-1471.
7. Ma, C., D. Moore, J. Li and Zh. L. Wang, 2003. Nanobelts, Nanocombs and Nanowindmills of Wurtzite ZnS. *Adv. Mater.*, 15: 228-231.
8. Gong, J., S.G. Yang, J. Duan, R. Zhang and Y.W. Du, 2005. Rapid synthesis and visible photoluminescence of ZnS nanobelts. *Chem. Commun. (Cambridge)*, pp: 351.
9. Lin, M., T. Sudhiranjan, Ch. Boothroyd and K.P. Loh, 2004. Influence of Au catalyst on the growth of ZnS nanowires. *Chem. Phys. Lett.*, pp: 400-175.
10. Fang, X.S., C.H. Ye, L.D. Zhang, Y.H. Wang and Y.C. Wu, 2005. Temperature-controlled catalytic growth of ZnS nanostructures by the evaporation of ZnS nanopowders. *Adv. Func. Mater.*, 15: 63-68.
11. Wang, Y., L. Zhang, Ch. Liang, G. Wang and X. Peng, 2002. Catalytic growth and photoluminescence properties of semiconductor single-crystal ZnS nanowires. *Chem. Phys. Lett.*, pp: 357-314.
12. Xiong, Q., G. Chen, J.D. Acord, X. Liu, J.J. Zengel, H.R. Gutierrez, J.M. Redwing, L.C. Lew Yan Voon, B. Lassen and P.C. Eklund, 2004. Optical properties of rectangular cross-sectional ZnS nanowires. *Nano letters*, 4: 9-1663.
13. Meng, X.M., J. Liu, Y. Jiang, W.W. Chen, C.S. Lee, I. Bello and S.T. Lee, 2003. Structure-and size-controlled ultrafine ZnS nanowires. *Chem. Phys. Lett.*, pp: 382-434.
14. Jiang, Y., X.M. Meng, J. Liu, Z.R. Hong, C.S. Lee and S.T. Lee, 2003. ZnS Nanowires with Wurtzite Polytype Modulated Structure. *Adv. Mater.*, 15: 1195-1198.
15. Kumbhojkar, N., V.V. Nikesh and A. Kshirsagar, 2000. Photophysical properties of ZnS nanoclusters. *J. Appl. Phys.*, pp: 88-6260.
16. Zhu, Y.C., Y. Bando, D.F. Xue, D. Golberg and J. Am, 2003. Nanocable-Aligned ZnS nanocrystals. *Chem. Soc.*, pp: 125-16196.

17. Lu, M.Y., P.Y. Su, Y.L. Chueh, L.J. Chen and L.J. Chou, 2005. Growth of ZnS nanocombs with ZnO sheath by thermal evaporation. *Appl. Surface Sci.*, pp: 244-96.
18. Wang, Z.L., X.Y. Kong and J.M. Zuo, 2003. Induced growth of asymmetric nanocantilever arrays on polar surfaces. *Phys. Rev. Lett.*, pp: 91-185502.
19. Moore, D., C. Ronning, C. Ma and Zh. L. Wang, 2004. Wurtzite ZnS nanosaws produced by polar surfaces. *Chem. Phys. Lett.*, pp: 385-8.
20. Yin, L.W., Y. Bando, J.H. Zhan, M.S. Li and D. Golberg, 2005. Self-Assembled highly faceted wurtzite-type ZnS single-crystalline nanotubes with hexagonal cross-sections. *Adv. Matter.*, (Weinheim, Ger.), 17: 1972-1977.
21. Ye, C.H., X.S. Fang, G.H. Li and L.D. Zhang, 2004. Origin of the green photoluminescence from zinc sulfide nanobelts. *Appl. phys. lett.*, pp: 85-3035.
22. Hu, J., Y. Bando, J. Zhan and D. Golberg, 2005. Growth of Wurtzite ZnS Micrometer-Sized Diskettes and Nanoribbon Arrays with Improved Luminescence. *Adv. Funct. Mater.*, 15: 757-762.