Synthesis of ZnS Nanobelts with Multi Photoluminescence Peaks

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Abstract: Single-crystalline wurtzite ZnS nanobelts were synthesized using Chemical Vapor Deposition (CVD) method without any catalyst. The selected-area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) indicate that the nanobelt is pure single crystal ZnS. The room temperature photoluminescence (PL) spectrum of the products shows that there are three broad emission peaks at 510, 410 and 340 nm, respectively. The broad emission peak at 340 nm is divided into two narrow peaks with full width at half maximum (FWHM) of about 1 nm.

Key words: ZnS, nanobelts, photoluminescence, synthesis

INTRODUCTION

Zinc sulfide, an important semiconductor compound of the II-VI groups, has a wide band-gap energy of 3.7 eV (Sockal et al., 1996) at 300 K. ZnS is a luminescent material well known for its photoluminescence, (Falck et al., 1992) electroluminescence, (Tang and Cameron, 1996) etc., which enable wide applications in the fields of displays (Bredol and Merikhi, 1998) sensors and lasers (Falck et al., 1992; Prevenink, 2000). Moreover, zinc sulfide is also widely used in photocatalysis (Wada et al., 1998; Fujimaru et al., 1998). In recent years, nanocrystalline ZnS attracted much attention because properties in nanofluids differ significantly from those of their bulk counterparts (Das et al., 1999). Therefore, much effort has been made to control the size, morphology and crystallinity of the ZnS nanocrystals with a view to tune their physical properties. The recent trend in nanomaterials research is toward one-dimensional nanostructured materials because of their wide range of potential applications in nanoscale devices (Frank et al., 1998; Heath et al., 1998; Hu et al., 1999; Xu et al., 1999). One-dimensional ZnS nanostructures such as nanorods, (Chen et al., 2003) nanowires, (Wang et al., 2002a; Meng et al., 2003) nanobelts, (Li and Wang, 2003; Zhu et al., 2003; Jiang et al., 2005) and nanotubes (Wang et al., 2002b) have been produced by different synthesis techniques such as the solvothermal process, (Chen et al., 2003) thermal evaporation of ZnS powder, (Wang et al., 2002; Meng et al., 2003; Li and Wang, 2003; Zhu et al., 2003; Jiang et al., 2003) liquid crystal template method (Jiang et al., 2001) etc. Li and Wang (2003) have reported wurtzite ZnS nanobelts synthesized by thermal evaporation of ZnS powder at 1200°C for 2 h. Two groups have reported hydrogen-assisted growth of ZnS nanostructures (Zhu et al., 2003; Jiang et al., 2003) by thermal evaporation of ZnS powder at temperature over 1100°C for a period of 1.5-4 h. All of the above fabrication processes of the ZnS nanobelts were time-catalyst-consuming.

In this study, we report Synthesis of ZnS nanobelts with multi Photoluminescence peaks without any catalyst by thermal evaporation of ZnS powder. The room temperature photoluminescence (PL) spectrum of the products shows that there are three broad emission peaks at 340, 410 and 510 nm respectively. The broad emission peak at 340 nm is divided into two narrow emission peaks.

MATERIALS AND METHODS

In a typical process, ZnS powders were loaded in an alumina boat. And then the boat transferred to the center of a long quartz tube inserted into a horizontal tube furnace. Another empty alumina boat, which existed in the down stream of the furnace, employed as a collector. The furnace temperature was raised to 800°C at a heating rate of 30°C per minute under a constant flow of 95% Ar and 5% H₂. After 30 min the temperature was raised to 1100°C and held for 2½ h. After the reaction completed, the furnace was allowed to cool down. The deposit cotton like material on the empty boat collected and investigated by X-ray diffraction (Cu Ka radiation), Scanning Electron Microscopy (JSM JEO 6700F), Transmission Electron Microscopy (JEM JBSOL 1010) and energy dispersive X-ray spectroscopy (EDS). The Photoluminescence (PL) spectrum (Confocal Laser MicroRaman Spectrometer, He- Cd laser, excitation wavelength 325 nm) was obtained at room temperature.

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RESULTS AND DISCUSSION

The morphology of the as-synthesized collected product ZnS nanobelts at temperature about 750-800°C grown with evaporated ZnS without any catalyst was firstly examined by SEM. Figure 1a presents a typical SEM image of the cotton-like product. Randomly distributed one-dimensional nanostructures with typical lengths in the range of several tens to several hundreds of micrometers can be observed in the image. Some of them even have lengths on the order of millimeters. The enlarged image Fig. 1b reveals these nanostructures have belt-like shape. The bending and swirling morphologies clearly indicate the typical morphological features of nanobelts. The widths of the belts are in the range of 1.5-2 µm with average thickness of the nanobelts is about 70 nm. The width-to-thickness ratio of the nanobelts is about 5-20 and the widths of the nanobelts were uniform along their entire length. Figure 1c shows the EDS analysis of the nanobelts. The result shows that the atomic ratio of S to Zn is less than 1:1 which demonstrates that in the products there are some vacancies of S.

The X-ray diffraction (XRD) pattern Fig. 2 of the as-prepared samples shows that the samples are well crystallized. All the peaks can be indexed as (100), (002), (101), (110), (103) and (112) crystal planes, which suggests that the samples are pure, wurtzite-phase structured ZnS with lattice parameters a = 3.820 Å and c = 6.257 Å.

We now determine if the nanobelts are of the same crystal structure. This analysis relies on Selected-area Electron Diffraction (SAED). For the nanobelts, Fig. 3b is the SAED pattern from a fine nanobelt shown at the center of Fig. 3a. The diffraction pattern revealed that the ZnS nanobelt had a single crystalline hexagonal structure. The nanobelt growth occurred along the (001) direction. We have examined several nanobelts and the same results were obtained in our experiment.

The PL spectrum at room temperature was examined using a Confocal Laser MicroRaman Spectrometer, He-Cd laser, excitation wavelength 325 nm. The PL spectrum of the ZnS nanobelts at room temperature shows in Fig. 4. The spectrum reveals that there are three broad emission peaks at 340, 410, 510 nm, respectively. The 340 nm emission peak is attributed to the spontaneous emission originating from band-to-band transition (Ding et al., 2004). The broad emission peak at 410 nm should be originated from the surface states (Yang et al., 2001). The third broad emission peak is at 510 nm is mainly attributed to the S vacancies in the single crystal ZnS nanobelts.
CONCLUSIONS

Single-crystalline wurtzite ZnS nanobelts were synthesized using CVD process without any catalyst. The widths of the nanobelts are in the range of 1.5-2 μm, the thickness is about 70 nm and the lengths from several tons to several hundreds of μm. The room temperature PL spectrum of the products shows that there are three broad emission peaks at 340, 410 and 510 nm, respectively. The broad emission peak at 340 nm is divided into two narrow peaks with full width at half maximum (FWHM) of about 1 nm.

REFERENCES


