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Catalytic growth and photoluminescence properties of semiconductor single-crystal ZnS nanowires

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Abstract

Semiconductor single-crystal ZnS nanowires have been successfully synthesized in bulk quantities by a new, simple and low cost process based on thermal evaporation of ZnS powders onto a silicon substrate with the presence of Au catalyst. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations show that the ZnS nanowires have diameters about 30–60 nm and lengths up to several tens micrometers. The growth of ZnS nanowires is controlled by the conventional vapor–liquid–solid (VLS) mechanism. And the photoluminescence (PL) properties of these synthesized single-crystal ZnS nanowires have been presented in this Letter. © 2002 Published by Elsevier Science B.V.

1. Introduction

Quasi one-dimensional nanostructured materials, such as nanowires and/or nanotubes have been successfully synthesized and have received much attention due to their fundamental importance, e.g., nanowires and nanotubes have great potential for testing and understanding fundamental concepts about the roles of dimensionality and size on physical properties, and they hold promise for a wide range of potential applications, including chemistry, physics, electronics, optics, materials science, biomedical science and nanodevices [1]. Considerable effort has been made on the synthesis of nanowires with different compositions and/or

nanotubes using laser ablation [2–4], template [5,6], solution [7], and other methods [8–11]. During the last decade, a considerable effort has been spent in the preparation and investigation of the group of wide-bandgap II–VI nanoscale semiconductors due to their vital optoelectronic application for laser light-emitting diodes and optical devices based on electronic and optical properties [9]. For instance, Routkevitch et al. and Xu et al. [12–15] have fabricated CdS nanowires in porous anodic aluminum membranes (AAM) by electrochemical deposition. Meanwhile, Qian's group established new chemical techniques to synthesize CdS and ZnS nanowires via solvothermal route and polymer-controlled growth [16,17]. However, it was difficult to separate CdS or ZnS nanowires from the products synthesized by the above mentioned methods, and moreover their yield is very low. Recently, laser-assisted catalytic

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growth has been developed for the synthesis of CdS, ZnS and other semiconductor nanowires [18]. Herein we report a new, simple and low cost process to prepare large-scale single crystalline ZnS nanowires based on thermal evaporation of sulfide powders under controlled conditions with the presence of Au catalyst. The nanowire growth is mediated by vapor–liquid–solid (VLS) mechanism. This method can be used to continuously synthesize and produce a large quantity of single-crystalline ZnS nanowires at relatively high purity and low cost. Photoluminescence (PL) characterization of the ZnS nanowires shows that these nanowires exhibit strong UV emissions.

2. Experimental

A silicon wafer ($0.5\text{ cm} \times 1\text{ cm}$) was used as substrate for the growth of ZnS nanowires. The substrate was cleaned by a standard treatment in piranha solution (30% H_2O_2 /20% H_2SO_4) and rinsed with de-ionized water, and then deposited with a layer of Au (about 40 nm) film using a vacuum thermal evaporator. Our synthesis is based on thermal evaporation of ZnS powders under controlled conditions with the presence of Au films used as catalyst. The ZnS powders were placed in the middle of an alumina boat, and the treated Si substrate was placed next to the ZnS and along the downstream side of the flowing argon. The alumina boat was covered with a quartz plate to maintain a higher vapor pressure and the assembly was placed at the center of the quartz tube that was inserted in a horizontal tube furnace. Prior to heating, the system was flushed with high purity Ar for 1 h to eliminate O_2 . Under a constant flow of Ar (100 sccm), the furnace was rapidly heated to $900\text{ }^\circ\text{C}$ (about 4 min) and held at this temperature for 120 min, and then cooled to room temperature. It was observed that white sponge-like products had appeared on the surface of Si substrate.

The as-deposited products were characterized using scanning electron microscopy [(SEM) JEOL JSM-6300], X-ray diffraction [(XRD) MXP18A HF], transmission electron microscopy (TEM), high-resolution transmission electron microscopy TEM [(HRTEM) JEOL-2010] and energy-dis-

persed X-ray spectrometry (EDS). For TEM and HRTEM observation, the products were ultrasonically dispersed in ethanol and a drop of the solution was then placed on a Cu grid coated with a porous carbon film. PL measurements were carried out on a HITACHI 850-type visible–ultraviolet spectrophotometer with a Xe lamp as the excitation light source at room temperature.

3. Results and discussion

SEM observation (Fig. 1a) reveals that the synthesized products consist of a large quantity of nanowires with typical lengths in the range of several to several tens of micrometers. XRD measurement (Fig. 1b) shows that the products are

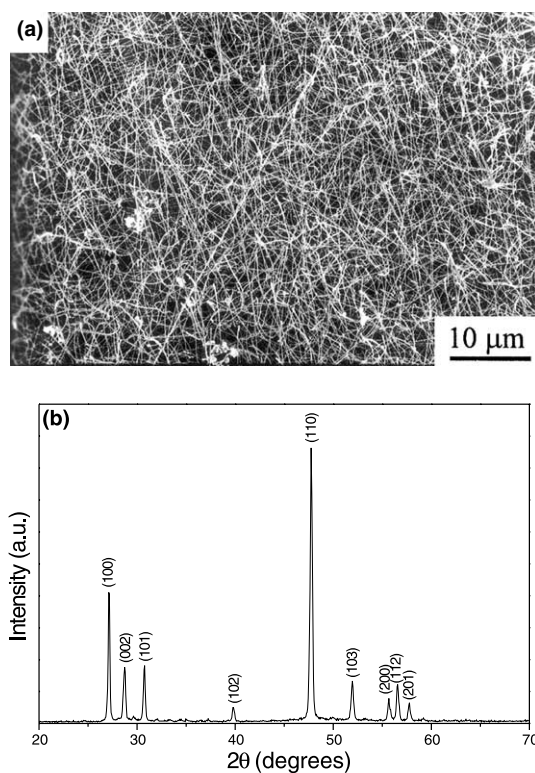


Fig. 1. The structure and morphology of ZnS nanowires (with wurtzite crystal structure). (a) Typical SEM image of the as-synthesized ZnS nanowires obtained from thermal evaporation of ZnS powders containing Au film as catalyst at $900\text{ }^\circ\text{C}$. (b) XRD pattern recorded from the ZnS nanowires.

wurtzite (hexagonal) structured ZnS with lattice constants of $a = 0.3825$ nm and $c = 0.6270$ nm, consistent with the standard values for bulk ZnS [19]. The morphology, structure and composition of the ZnS nanowires have been characterized in detail using TEM, HRTEM, selected area electron diffraction (SAED) and EDS. TEM studies show that the nanowires are linear with uniform diameters, and typically terminated with a nanoparticle at one end. Fig. 2a reveals a typical image of single crystalline ZnS nanowires with diameter about 30–60 nm. The nanowires have high aspect ratio, and their lengths are about several to several tens

micrometers, however, several hundred micrometers nanowires can also be observed on the SEM image. EDS analysis demonstrates that a 1:1 Zn:S composition within experimental error and are consistent with stoichiometric ZnS (shown in Fig. 3b). TEM observation also reveals that most of the ZnS nanowires terminate in a nanoparticle at one end is shown in Fig. 2b. The nanoparticle at the tip of the nanowire generally appear dark and have high contrast compared with the nanowire. EDS measurements made on the nanoparticle and ~ 30 nm away on the nanowire indicate that the nanoparticle is composed of Au, Zn and S (shown in

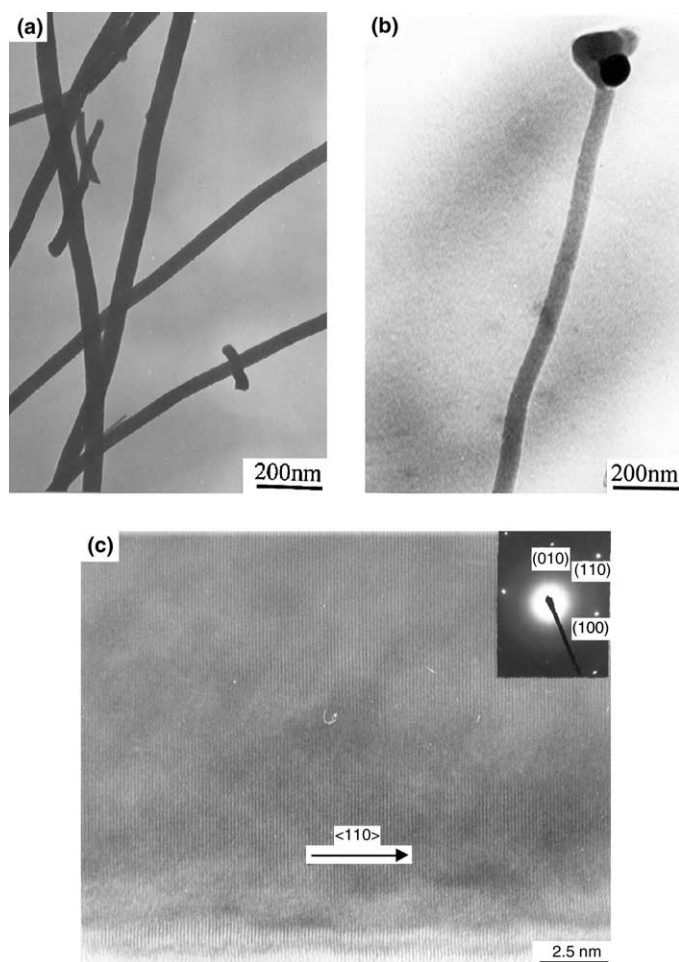


Fig. 2. (a) TEM image ZnS nanowires. (b) TEM image of the end of a nanowire. The dark flattened sphere at the nanowire end is the catalyst nanoparticle. (c) HRTEM image of a ~ 40 nm diameter nanowire. The (1 1 0) lattice places (separation = 0.1921 nm) are clearly visible and perpendicular to the wire axis.

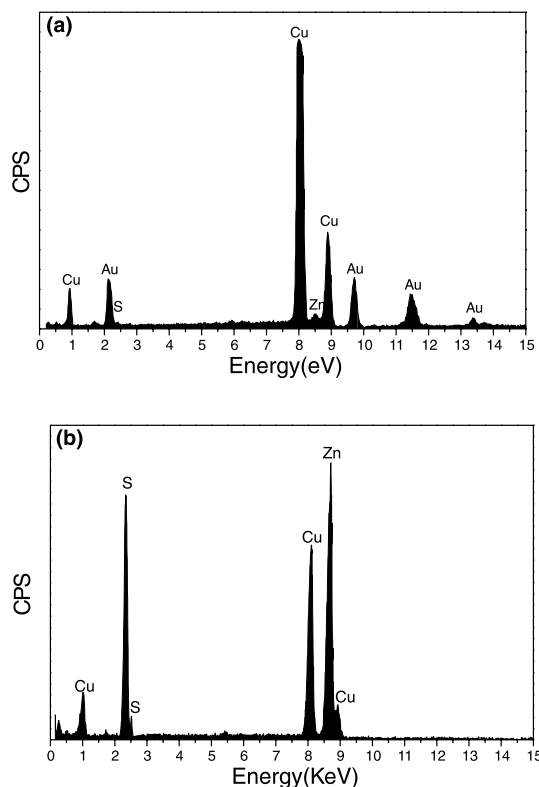


Fig. 3. EDS spectra of the nanoparticle and nanowire in Fig. 2c: (a) corresponds to the nanoparticle at the end of the nanowire, and (b) to the nanowire.

Fig. 3a). The Cu peaks are generated by the copper grid. The SAED pattern and HRTEM image (Fig. 2c) reveal that the ZnS nanowires are structurally uniform and single crystalline. The SAED pattern (Fig. 2c, inset) recorded perpendicular to the nanowire long axis could be indexed for the $[00-1]$ zone axis of single crystalline ZnS and suggests that the nanowire growth occurs along the $\langle 110 \rangle$ direction. In addition, the lattice-resolved image of a ZnS nanowire with diameter about 40 nm clearly reveals the (110) atomic planes with separation of 0.1921 nm.

There are two possible models for the growth of conventional crystal whiskers or nanowires namely the screw dislocation and VLS models. It is well known that the presence of a liquid drop is essential for the effective operation of the VLS mechanism. Solidified spherical droplets at the tips of the nanowires are commonly considered to be

the evidence for the operation of the VLS mechanism, which is in agreement with our experimental conditions and the observed results (Fig. 2b). The EDS analysis also shows that these nanoparticles only contain Au, Zn and S and the data presented suggests that these nanowires were grown through the well-known VLS process with Au film as the catalysts [20–22]. Although the detailed mechanism on ternary phase diagrams of Au–ZnS is still not fully understood, we think that very small miscible droplets of Au–ZnS may be generated rapidly during the heating process of the reaction and hence act as nucleation sites in the VLS growth of ZnS nanowires [23]. In our experiment process, the ZnS vapor is rapidly generated at relatively high temperature for the fast heating speed by vaporizing the ZnS powders, transported to and reacted with the Au liquid to form alloy droplets. As ZnS in the droplets become supersaturated, ZnS nanowires will be formed.

The room temperature PL of the ZnS nanowires was examined and shown in Fig. 4. The excited wavelength was 335 nm and a 430 nm filter was used. Two emission bands have been observed in the PL spectrum of ZnS nanowires. One is at 450 nm while the other is at about 520 nm. Usually, two emissions are observed from semiconductor nanoparticles – excitonic and trapped luminescence [24,25]. The excitonic emission is sharp and is located near the absorption edge of the particles, while the trapped emission is broad and Stokes-shifted. Only the trapped luminescence arising from the surface states is observed in the pure ZnS

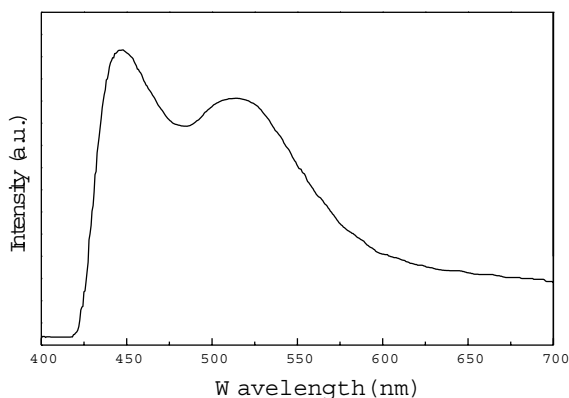


Fig. 4. PL spectrum of the ZnS nanowires.

nanoparticles [24,25]. Yang et al. [26] has also reported that pure ZnS nanoparticles show the only luminescent peak at 450 nm. It was therefore reasonable to believe that the blue light emission from the ZnS nanowires in our work could be attributed to the above-mentioned surface states. However, another broad and weak luminescent peak (about 520 nm) of ZnS nanowires has also been observed in our work. PL experiments show that strong visible-light emits from co-doped ZnS nanoparticles at room temperature and their luminescent peaks are about 530 nm [26]. In our experiment, Au film is served as catalyst and reacted with ZnS vapor to form Au–Zn–S alloy. When Au ions are doped in ZnS nanowires, the luminescence centers are formed. Because luminescence center may be trapped electrons and holes, the luminescence peaks are at long wavelength and broad. Therefore, we can say that the green light emission from the ZnS nanowires in our work could be attributed to the presence of Au ions.

4. Conclusion

In conclusion, ZnS single-crystal nanowires have been synthesized in bulk quantities by a simple and high-yield method. SEM, TEM and HRTEM observations show that the ZnS nanowires have diameters of about 30–60 nm and lengths up to several tens of micrometers. Their growth should be explained by the VLS wirelike growth mechanism. PL measurements taken on the bulk nanowires show blue and green light emissions, which were attributed to the surface states of ZnS nanowires and the presence of Au ions. Considering the simplicity of the procedure and the high-yield of ZnS nanowire single-crystals, the method described here is likely to be of interest to commercial production and to synthesize other II–VI group semiconductor nanowires.

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