



## Structure and optical properties of ZnS/SiO<sub>2</sub> nanocables

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### ABSTRACT

The nanocables with a single crystal ZnS core and a thin amorphous SiO<sub>2</sub> shell were successfully synthesized by a simple thermal evaporation method with the mechanism of Vapor–Solid growth. Its morphology and microstructure were determined by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and photoluminescence spectroscopy (PL). The ZnS/SiO<sub>2</sub> nanocables have diameters in the range of 20 nm–250 nm, lengths of several tens of micrometers. The core of the nanocable has a cubic sphalerite structure with the coexistence of periodically alternating twins along the [111] growth direction and stacking fault. The nanocables show strong room-temperature photoluminescence with four emission bands centering at 548 nm, 614 nm, 649 nm and 670 nm that may originate to the impurity of ZnS, existence of Si and oxide-related defects.

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### 1. Introduction

As an important II–VI semiconductor, ZnS has wide bandgap energy of 3.66 eV. It is used as a key material for ultraviolet light-emitting diodes, injection lasers, as phosphors in cathode-ray tube, thin film electroluminescence, flat-panel display and IR windows [1–3]. It has been reported that ZnS nanowires could be easily damaged by electron beam irradiation [4]. So it was assumed that wrapping these semiconductor materials with a dense and stable shell, for example Si or SiO<sub>2</sub> nanotubes. This core-shell structure can prevent oxidation and damage of the semiconductor in the core. The great refractive index of semiconducting nanowires wrapped with insulating thin shell can constitute a natural optical waveguide nanocable [5].

The ZnS/SiO<sub>2</sub> core-shell structure has been reported before [4,5–8], and the ZnS core all show the hexagonal wurtzite structure. Here, we present a general method to synthesize the ZnS/SiO<sub>2</sub> nanocables. In our work, the ZnS nanowires exhibit typical cubic sphalerite structure with periodically alternating twins along the [111] growth direction that have not been reported in the ZnS/SiO<sub>2</sub> core-shell structure.

### 2. Experimental method

The ZnS/SiO<sub>2</sub> nanocables were synthesized by simple thermal evaporation method in a horizontal tube furnace at 1100 °C. A schematic drawing of the experimental setup is shown in Fig. 1. The

source material was the mixture of high purity ZnS and SiO<sub>2</sub> powders (99.999%) with the molar ratio 1:1. Prior to heating, the reaction chamber was pumped to a vacuum of 0.1 Pa. The carrier gas (Ar+5% H<sub>2</sub>) was introduced through the tube at a flow rate of 50 standard cubic centimeters per minute (sccm). The source material was rapidly heated to 1100 °C from room temperature within 10 min and was kept at 1100 °C for 60 min. A piece of Si (111) wafer was used as substrate, which was located at downstream position of source material. The distance between the source material and substrate was 10 cm and the deposition temperature is about 750 °C. Subsequently, the furnace was cooled down to room temperature. The chamber pressure was kept at about 4×10<sup>−4</sup> Pa in the entire process. The collected product was characterized by field emission scanning electron microscopy (FE-SEM) (JEOL, JSM-6700F) and transmission electron microscopy (TEM) (JEOL-2010) equipped with an X-ray energy-dispersive spectroscopy. The photoluminescence (PL) at room temperature was measured by He–Cd laser with a wavelength of 260 nm, a power of 5–15 mW as the excitation source (see Fig. 1).

### 3. Results and discussion

A low-magnification FE-SEM image of the product was displayed in Fig. 2(a). It reveals that the product consists of large quality of nanowires and they are interlaced. The high-magnification FE-SEM image depicted in Fig. 2(b) shows that these nanowires are not totally straight; some of them have many knots. The diameters of these nanowires are not uniform yet, about 20–250 nm.

Fig. 3(a) is the TEM image of a single wire. It can be observed that the 1D nanostructure consists of core-sheath nanocable structure. The core is about 18 nm in diameter and the sheath is about 3 nm in thickness. The contrast between the core and the shell is obvious. EDS

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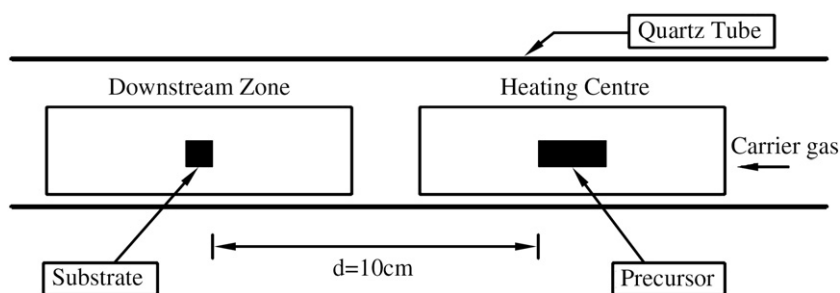


Fig. 1. The experimental setup.

measurement shown in Fig. 3(b) indicates that the nanocables consist of the element Zn, Si, O and S, and the atomic ratios of Zn to S, Si to O are 1:1 and 1:2, respectively. It can be well proved that our product is nanocables with a single crystal ZnS core and a thin amorphous SiO<sub>2</sub> shell. A typical high-resolution TEM (HR-TEM) image of the nanocable and the SAED pattern taken from the corresponding core are shown in Fig. 3(c) and (d), which exhibit that the core can be indexed as a cubic sphalerite phase. The HR-TEM image reveals the coexistence of periodically alternating twins along the [111] growth direction and stacking fault. The zigzag angles are 141° (70.5°+70.5°), in accordance

with the relative rotational angle of (111) twin crystal in face-centered cubic (fcc) structure. Twin crystals along {111} faces in fcc structure are observed occasionally due to their crystallographic characteristic [9,10]. This structure is also obviously reflected in the SAED pattern, in which a series of small diffraction spots occur between two adjacent main spots. These main spots correspond to the ZnS cubic sphalerite structure and the small spots are caused by the twins and stacking fault.

No nanoparticles observed at any tips of the nanostructures. So the growth of ZnS/SiO<sub>2</sub> core-shell nanocables in our product can be controlled by the conventional VS mechanism. The formation of ZnS/SiO<sub>2</sub> core-shell nanocables are proposed as follows. With the increase of the reaction temperature, ZnS powder evaporate first at a relatively high temperature. Then the ZnS gas was transported and deposited on the silicon substrate in the low-temperature region to form nucleus. ZnS molecules increase gradually to form ZnS nanowires. With further increase of processing temperature, evaporation of SiO powders led to the formation of SiO<sub>x</sub> vapors [11]. The SiO<sub>x</sub> vapors were transported by the carrier gas to the low-temperature region and then react with the remnant oxygen in the tube to form SiO<sub>2</sub>. The ZnS nanowires can be used as templates for the deposition of SiO<sub>2</sub>, resulting in the formation of amorphous SiO<sub>2</sub> cylindrical shape layers [12]. Finally the ZnS/SiO<sub>2</sub> core/shell nanostructures were formed. The whole growth process of the nanostructures is based on the vapor-solid growth mechanism.

The PL is used to further investigate the optical properties of the as-synthesized ZnS/SiO<sub>2</sub> nanocables. The room temperature PL spectrum is shown in Fig. 4, using a He-Cd laser at 273 nm as the excitation source and a 370 nm filter wavelength. As shown in Fig. 4, peak deconvolution by Gaussian fit (shown by the symbol line) gives four Gaussian bands centering at about 548 nm, 614 nm, 649 nm and 670 nm, respectively (the lower bands shown in Fig. 4). The Gaussian curve fits well with the experiment one. It has been reported that the dopants of Cu, Mn or Cd can shift the luminescence position of ZnS nanocrystals [13–18]. Therefore, the emission peak at about 548 nm should be assigned to the impurities or defect centres in the ZnS nanowires, which has been reported by some literature [19–23]. The emission band centering at 614 nm is exactly accordant with the Si nanotubes which exhibited visible-light emission centering at 615 nm. In the article about SiO<sub>x</sub>, F. Yun et al. [24] reported that a broad peak was found at 1.67 eV (743 nm) and 1.83 eV (678 nm), corresponding to  $x=1.19$  and 1.35, respectively. With increasing oxygen, the peak position will shift blue. Our experiment was processed in the air of deoxidization and it can cause the oxygen deficiency of the SiO<sub>x</sub> sample. So we speculate that 649 nm and 670 nm can be attributed to oxide-related defects in the SiO<sub>2</sub> shell (see Fig. 4).

#### 4. Conclusion

ZnS/SiO<sub>2</sub> core/shell nanocables were successfully synthesized by a simple thermal evaporation method. The ZnS core has a cubic sphalerite structure with the coexistence of periodically alternating twins along the [111] growth direction and stacking fault. The

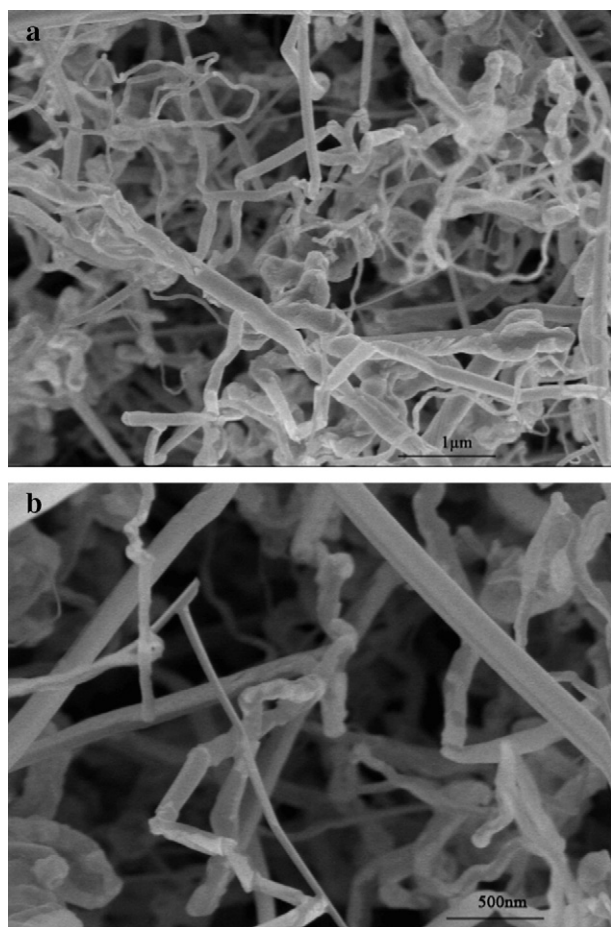
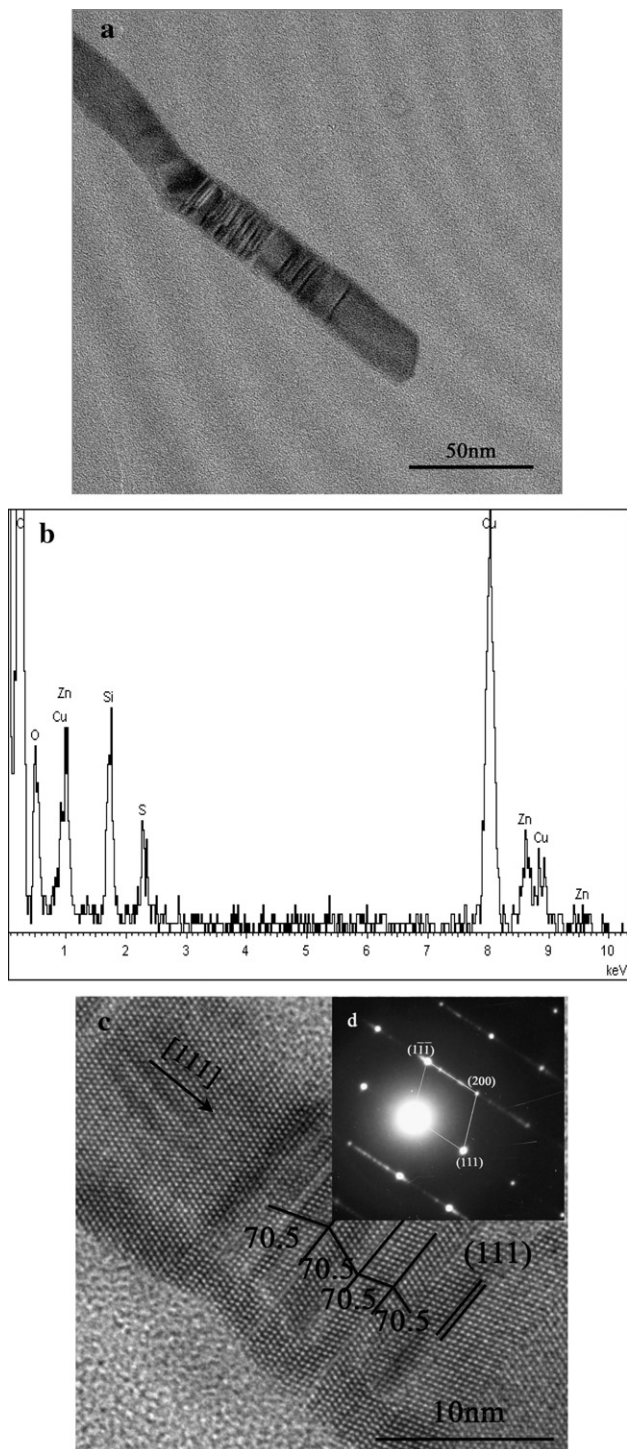
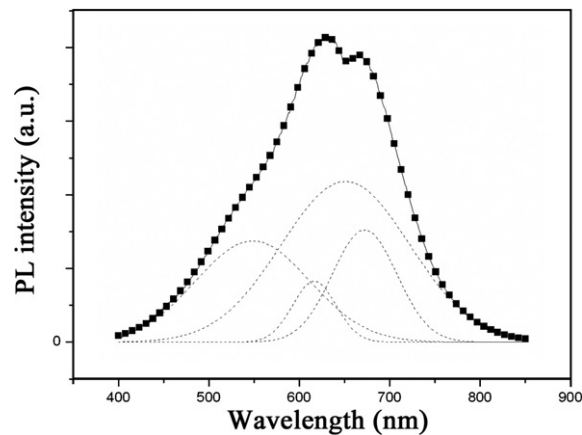


Fig. 2. FE-SEM image of as-synthesized ZnS/SiO<sub>2</sub> nanocables: (a) a typical image of ZnS/SiO<sub>2</sub> nanocables at a low magnification. (b) A high-magnification FE-SEM image of the ZnS/SiO<sub>2</sub> nanocables.

growth mechanism of the product follows a VS process. The diameters of the nanostructures were about 20–250 nm. The room-temperature PL spectrum of our product show four emission bands centering at about 548 nm, 614 nm, 649 nm and 670 nm, respectively, which may originate to the impure ZnS, existence of Si and oxide-related defects.



**Fig. 3.** (a) Image of a single ZnS/SiO<sub>2</sub> nanocable. (b) The EDS spectra of as-synthesized ZnS/SiO<sub>2</sub> nanocable. (c) An HRTEM image of the corresponding nanocable. (d) The image of SAED pattern taking from the corresponding core.



**Fig. 4.** PL spectra of ZnS/SiO<sub>2</sub> nanocables at room temperature. The lower curves indicate peak deconvolution by Gaussian fit.

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