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Synthesis and photoluminescence properties of washboard belt-like ZnSe nanostructures

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Well aligned washboard belt-like ZnSe nanostructures were prepared by atmospheric pressure thermal evaporation of ZnSe nanoparticles without the use of a catalyst. The phase structures, morphologies, and optical properties of the products were investigated by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and photoluminescence spectroscopy. The temperatures play an important role in controlling the morphologies of samples. A vapor-liquid mechanism was proposed for the formation of ZnSe washboard-like structures. The present synthetic route is expected to be applied to the synthesis of other II-VI groups or other group's semiconducting materials with controllable morphologies.

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Keyword: ZnSe, Washboard-like nanostructure, Chemical vapor deposition

1. Introduction

Low-dimensional structures of compound semiconductors, such as nanowires, nanobelts, and nanosaws, are now of significant research interest because of their potential applications in nanoscale electronics and photonics [1-3]. As one of the most important group II-VI semiconductors, zinc selenide (ZnSe) with the bulk crystal transition energy of 2.7 eV [4] at 300 K exhibits a great potential for various optoelectronic devices [5] and applications in spintronics [6], as well as for energy up-conversion and terahertz generation in a two-step optical pumping regime [7]. ZnSe has two structural polymorphs of wurtzite and zinc blende [8]. ZnSe-based nanostructures with different forms have been widely investigated recently, such as nanowires, nanobelts, nanoneedles as well as ZnSe nanorods on in situ synthesized ZnSe grains [9].

Several techniques have been developed to control the size and shape of ZnSe nanomaterial such as vapor-phase deposition (CVD), metal-organic chemical-vapor deposition (MOCVD), molecular-beam epitaxy (MBE), and thermo-chemical processes at various growth temperatures has been reported [10]. Basu et al. [11] reported the synthesis of ZnSe nanowires by a molecular-beam epitaxial (MBE) method. Jiang et al. [12] reported the synthesis of ZnSe nanoribbon and nanowires using laser ablation of ZnSe pressed powders. Zhong et al. [13] reported the synthesis of ZnSe colloidal microspheres via a hot injection route by using trioctylamine as solvent and with a relatively higher concentration of the monomer precursors.

Herein, we report a simple catalyst-free thermal evaporation technique to synthesize self-assembled ZnSe nanostructures on graphite substrate. The morphology, crystal structure and the PL spectrum of the ZnSe nanostructures are studied.

2. Experimental section

2.1. Preparation of the samples

Source materials of high pure ZnSe (99.99%) and C powders (99.99% micro-powder) with a molar ratio of 10:1 in an alumina boat were placed in the heating center of a horizontal alumina tube furnace. After three pieces of graphite wafers were cleaned in piranha solution ($30\%H_2O_2/20\%H_2SO_4$) and rinsed with de-ionized water, they were placed downstream to act as deposition substrates for materials growth. The distance between the graphite substrate and the source material is 15 cm. Prior to heating, the system was evacuated and flushed with high pure Ar for 1 h to eliminate oxygen. Then the furnace was heated to 1000 °C, 1100 °C and 1200 °C, respectively, held at those temperature for1 h, and subsequently cooled to room temperature under a constant flow rate of 50 SCCM Ar.

2.2. Characterization

A Philips XL 30 FEG scanning electron microscope (SEM) with an energy-dispersive X-ray spectroscope (EDS) was used to observe the morphologies and elemental compositions of the samples. An X-ray diffraction meter (XRD) (Japan Mac science) with Cu Kα radiation was used to obtain phase compositions of the samples. A JEOL 2010 transmission electron microscope (TEM) with selected-area electron diffraction (SAED)

was used to analyze the morphology and microstructure. A Hitachi F-7000FL spectrophotometer was used to measure the room temperature photoluminescence (PL).

3. Result and discussion

3.1. Morphology and crystal structure

Fig. 1(a) shows the SEM image of the sample 1, which was synthesized at 1000 °C. It clearly shows that the sample 1 is composed of some long washboard structures. The corresponding high-magnification images of the products are depicted in Fig. 1 (b). These products are composed of two parts: one part is belt-like structure and another part is the shoulder-like structures which are symmetrical distribution on the belts. The typical widths of the nanobelts measure from 3 μm to 5μm. EDS analysis of the washboard nanostructure shows the there are mainly Zn, and Se elements existing in the sample and the quantitative analysis demonstrates the molecular ratio of n(Zn)/n(S) is about 52:48, close to 1:1 stoichiometry of ZnSe. (Shown in Fig. 1(c)).

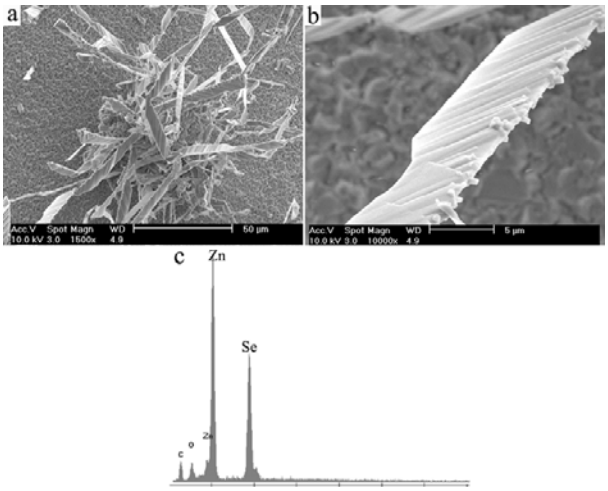

Fig. 1. Low-magnification (a), high-magnification(b) SEM images and EDS patterns of the sample 1.

Fig. 2(a) and 2(b) show the SEM images of sample 2 obtained at 1100 °C mainly consists of large-scale long washboard beltlike structures. The nanobelts have thickness of 100-150 nm, width of 10-15 μm, and extend to over 100 μm in length. Fig. 2(c) and 2(d) show the magnified SEM images. Some short nanorods grow in a symmetrical pattern parallel with the surface of nanobelt.

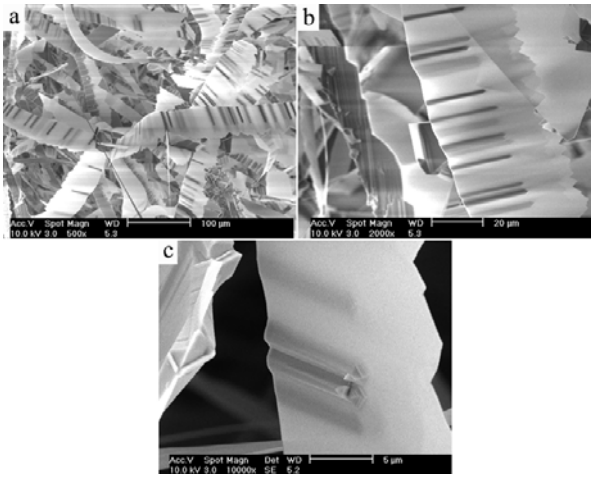

Fig. 2. Low-magnification (a), high-magnification (b,c) SEM images of the sample 2.

A change of morphology was observed by changing the temperature. Fig. 3 shows typical SEM image of sample 3 obtained at 1200 °C. Compared with sample 1 and 2, the sample 3 is of quite different structures. Fig. 3(a) indicates that the sample 3 consist of a large quantity of serration beltlike nanostructures with typical lengths of tens to several hundred micrometers and widths up to 10 μm. Fig. 3(b) and 3(c) show the magnified SEM images of the sample 3. It can be clearly observed that a small number of short nanorods were perpendicular to the growth direction of nanobelts. The diameter of these nanorods varies in the range of several hundreds nanometers.

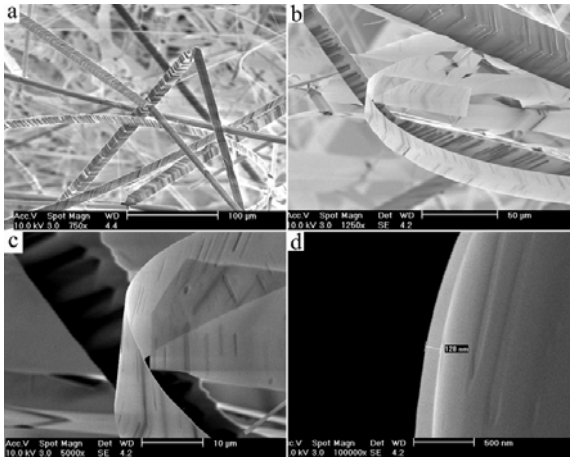

Fig. 3. Low-magnification (a, b) and high-magnification (c, d) SEM images of the sample 3.

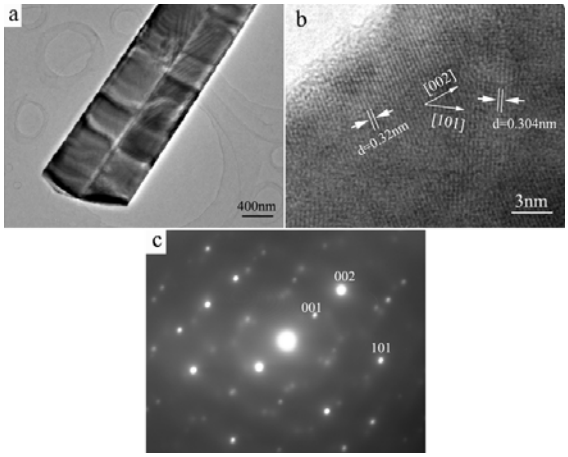

Fig. 4. TEM image of an individual ZnSe nanobelts(a), HRTEM image(b) and SAED pattern(c).

In addition, transmission electron microscopy (TEM) images of individual ZnSe washboard belt-like structure provide further insight into the structure of these materials. Fig. 4(a) shows the TEM of a single nanobelt with a width of 800nm. The corresponding SAED pattern shown in Fig. 4(c) shows the single-crystal nature of the nanobelt. Fig. 5(b) corresponds to the HRTEM image of the ZnSe nanobelt. The lattice fringes between the adjacent planes are 0.32 nm and 0.304 nm, which correspond to the (002) and (101) crystal fringes, respectively.

3.2. The growth mechanism

Vapor-solid (VS) and vapor-liquid-solid (VLS) mechanisms have been widely used to explain the formation of one-dimensional structures [14, 15]. In our work, we considered that the formation of ZnSe multipod-based structures could be enucleated by the VS mechanism. Therefore, the chemical reactions we employed in the synthesis of washboard belt-like ZnSe nanostructures could be described as follows:

$$ZnTe_{(s)} \leftrightarrow Zn_{(g)} + \frac{1}{2}Te_{2(g)} \qquad (1)$$

The temperature plays an important role in synthesizing washboard belt-like ZnSe nanostructures. For the sample 1, the temperature is low, so the "weed growth" model dominated the synthesis process [16]. With the increasing temperature, the ZnSe vapor pressure and concentration increase rapidly so much ZnSe washboard beltlike structures form in sample 2, where the ZnSe concentration is high enough for the formation of high density of nanobelts. For the sample 3, the ZnSe vapor pressure and concentration are very high, the "weed growth" model was repressed, only some ZnSe serration beltlike nanostructures formed.

3.3. Photoluminescence spectra

Room-temperature PL properties of the washboard belt-like ZnSe nanostructures were also investigated using a He–Cd laser line at 325 nm as the excitation source. Fig. 5 is the room-temperature PL spectra of sample 2. The intense peak at 466 nm is due to the near-band-edge emission of ZnSe, in accordance with the previous reports [17]. A weak broad emission peak at 545 nm can be detected, which is often connected with the doped ion or defects state emission [18, 19].

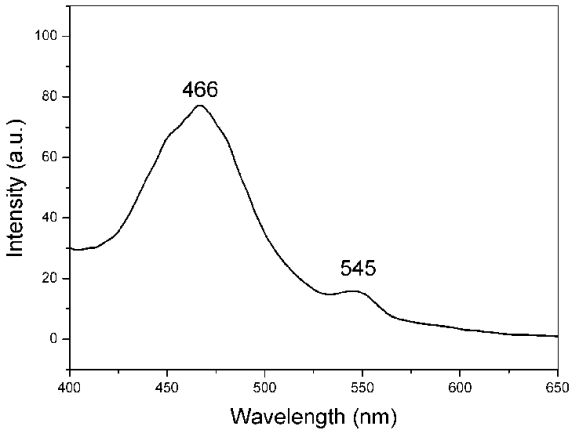

Fig. 5. PL spectrum of the sample 2.

4. Conclusions

In summary, washboard belt-like ZnSe nanostructures were successfully synthesized using a simple chemical vapor deposition method. Studies found that the morphologies of the products could be well controlled by adjusting the reaction temperature. Vapor-solid growth mechanism is proposed for the formation of washboard belt-like ZnSe nanostructures. Considering the simplicity of the procedure, the easily morphology controlled and high yield of products, the method described here is likely to be of interest to commercial production and to synthesize other II-VI or other group's semiconductor micro-/nanostructures with controllable morphology.

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