

Synthesis and photoluminescence properties of washboard belt-like ZnSe nanostructures*

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Washboard belt-like zinc selenide (ZnSe) nanostructures are successfully prepared by a simple chemical vapor deposition (CVD) technology without catalyst. The phase compositions, morphologies and optical properties of the nanostructures are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and photoluminescence (PL) spectroscopy, respectively. A vapor-liquid mechanism is proposed for the formation of ZnSe belt-like structures. Strong PL from the ZnSe nanostructure can be tuned from 462 nm to 440 nm with temperature varying from 1000 °C to 1200 °C, and it is demonstrated that the washboard belt-like ZnSe nanostructures have potential applications in optical and sensory nanotechnology. This method is expected to be applied to the synthesis of other II-VI groups or other group's semiconducting materials.

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Zinc selenide (ZnSe) is one of the most important II-VI group semiconductors, and is widely used in short-wavelength optoelectronics devices, high-density optical storage, full-color displays, and so on^[1-3]. Controlling the size of nanomaterials with specific microstructures may further lead to the novel properties^[4-7].

Many methods on the fabrication of ZnSe nanostructures were reported. Chen et al^[8] reported the synthesis of well-aligned ZnSe nanotube arrays based on a replacement/etching method. Jiang et al^[9] reported the synthesis of ZnSe quantum dots by injecting Se monomer at room temperature. Chen et al^[10] reported the nano-needles for application in polymer/inorganic solar cell, which was grown on catalyst-coated Si(100) substrate through pulsed-laser deposition method. However, those methods are expensive and complicated. In this paper, we report a simple catalyst-free chemical vapor deposition (CVD) technique to synthesize self-assembled ZnSe nanostructures on graphite substrate.

Source materials of high pure ZnSe (99.99%) in an alumina boat were placed in the center of heating zone of a horizontal alumina tube furnace. After being cleaned in piranha solution (30% H₂O₂/20% H₂SO₄) and rinsed with de-ionized water, the graphite wafer was placed downstream to act as the 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 gas for 1 h so as to eliminate oxygen. Then the furnace was heated

to 1000 °C, 1100 °C and 1200 °C, respectively, and those temperatures were kept for 1 h. After the systems were cooled down to 800 °C, 900 °C and 1000 °C, respectively, those temperatures were kept for 1 h again. At last, the systems were cooled down to room temperature under a constant Ar flow rate of 50 sccm. The resulted samples were obtained on the graphite wafer.

A Philips XL 30 FEG scanning electron microscope (SEM) with an energy-dispersive X-ray spectroscopy (EDS) was used to observe the morphologies and elemental compositions of the samples. An X-ray diffraction (XRD) meter (Japan Mac science) with Cu K α radiation was used to obtain phase compositions of the samples. A JEOL 2010 transmission electron microscope (TEM) was used to analyze the morphology and microstructure. The photoluminescence (PL) spectra were carried out at room temperature with a Hitachi F-7000FL spectrophotometer.

Fig.1 shows the typical SEM images of the sample 1 which was synthesized from 1000 °C to 800 °C. The low-magnification image shown in Fig.1(a) reveals that sample 1 is composed of some long washboard structures. The corresponding high-magnification image shown in Fig.1(b) shows that these products have an average width of 3–5 μ m, and are composed of two parts: one part is belt-like structure and the other is the shoulder-like structure which is symmetrically distributed on the belts. The corresponding EDS spectrum shown in the inset of Fig.1(b) demonstrates that the nanostructure is made of

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Zn and Se with a composition close to ZnSe, except for the slight excess of Se.

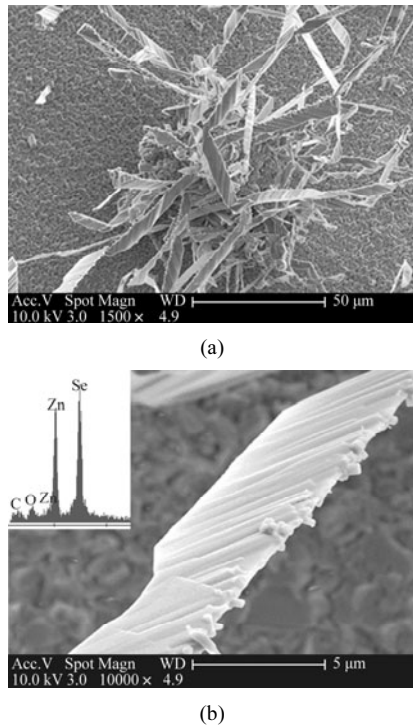
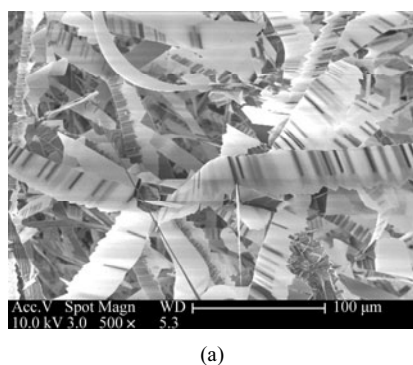
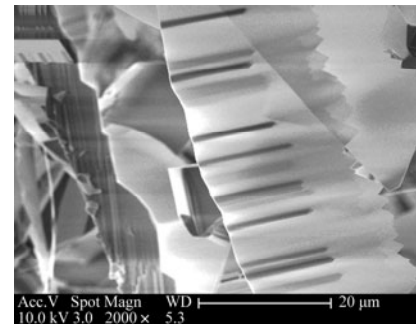


Fig.1 (a) Low-magnification SEM, (b) high-magnification SEM and EDS pattern (inset) of the sample 1

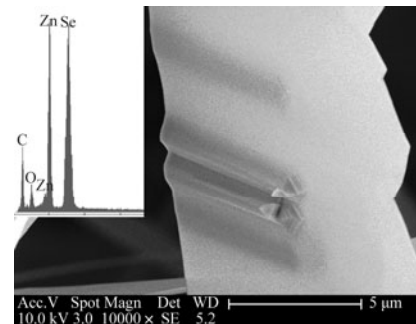
Fig.2 shows the morphologies of sample 2 obtained from 1100 °C to 900 °C. The substrate is covered with long and dense washboard belt-like products. These products are 10–15 μm in width, 100–150 nm in thickness, and over 100 μm in length. The high-magnification SEM image shows that some short nanorods grow in a symmetrical pattern parallel to the surface of nanobelt. The inset of Fig.2(c) gives an EDS pattern of sample 2. It can be seen that there are mainly Zn and Se in the product, and the quantitative analysis demonstrates that the mole ratio of $n(\text{Zn})/n(\text{Se})$ is about 51:49, which is close to 1:1, i.e., the stoichiometry of ZnSe. The XRD pattern of the sample 2 is shown in Fig.2(d). It indicates that this product consists of ZnSe with wurtzite (JCPDS No.15-0105 with $a=0.399$ nm and $c=0.655$ nm) and zinc blende (JCPDS No.65-7409 with $a=0.573$ nm) structures^[11].



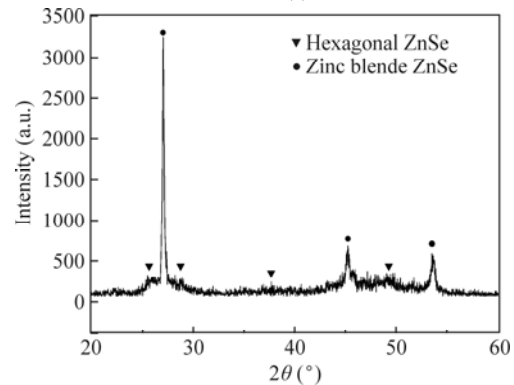
(a)



(b)



(c)



(d)

Fig.2 (a) Low-magnification SEM, (b) high-magnification SEM, (c) high-magnification SEM and EDS pattern (inset), and (d) XRD pattern of the sample 2

Fig.3 shows the typical SEM images of sample 3 obtained from 1200 °C to 1000 °C. The low-magnification images shown in Fig.3(a) and (b) indicate that the sample 3 consists of a large quantity of serration belt-like nanostructures with typical lengths of tens to several hundred micrometers and widths up to 10 μm. The high-magnification images shown in Fig.3(c) and (d) show that a small number of short nanorods are perpendicular to the growth direction of nanobelts, and the diameters of the nanorods vary in the range of several hundred nanometers. EDS spectrum shown in the inset of Fig.3(c) reveals the presences of Zn and Se with an approximate mole ratio of 6:4. Compared with Se, the boiling point of Zn is higher, so the higher the temperature is, the more the content of Zn is.

In addition, transmission electron microscopy (TEM) images of individual ZnSe washboard belt-like structure provide further insight into the structure of these materi-

als. Fig.4(a) shows the TEM of a single nanobelt with a width of 800 nm. Fig.4(b) shows the high resolution TEM (HRTEM) image of the ZnSe nanobelt. The lattice fringes between the adjacent planes are 0.325 nm and 0.304 nm, which correspond to the (002) crystal fringe of wurtzite structure and (101) crystal fringe of zinc blende structure, respectively.

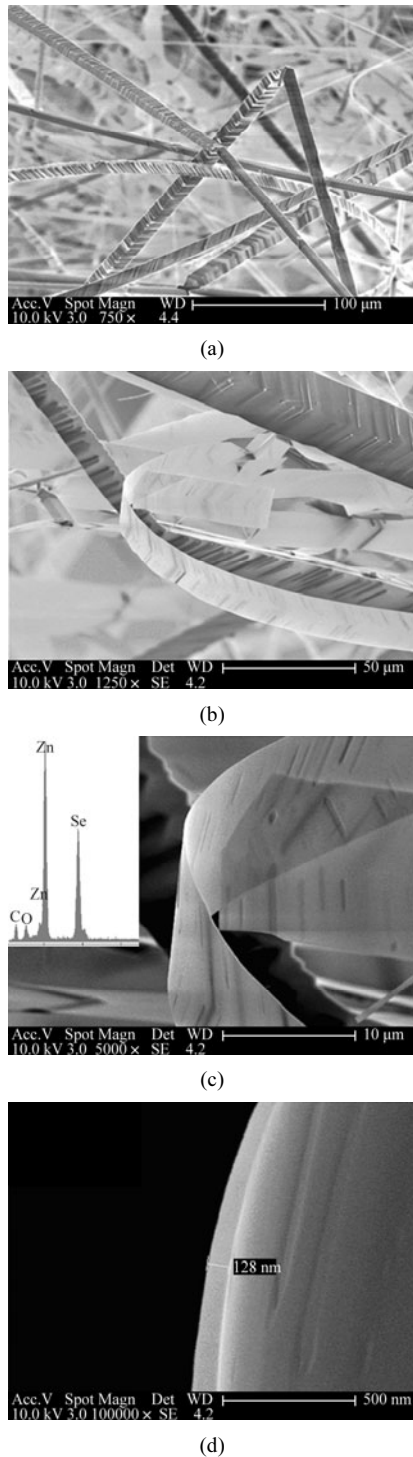


Fig.3 (a,b) Low-magnification SEM, (c) high-magnification SEM and EDS pattern, (d) high-magnification SEM of the sample 3

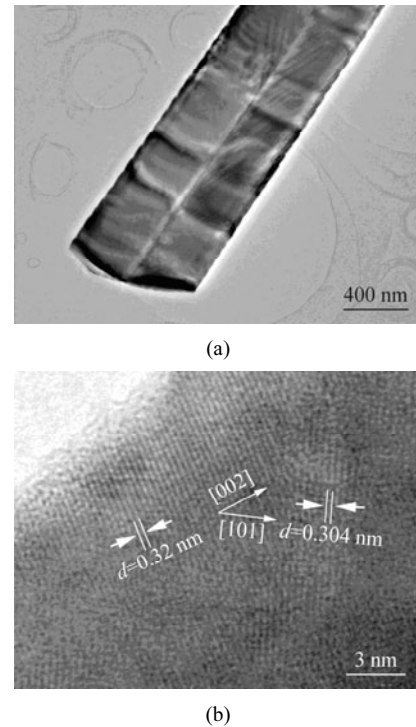
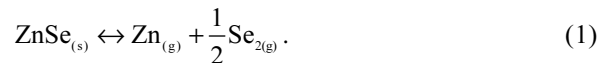


Fig.4 (a) TEM image and (b) HRTEM image of sample 3

Vapor-solid (VS) and vapor-liquid-solid (VLS) mechanisms have been widely used to explain the formation of one-dimensional structures^[12,13]. In this paper, we consider that the formation of ZnSe multiple-based structures can be enucleated by the VS mechanism. Therefore, the chemical reaction employed in the synthesis of washboard belt-like ZnSe nanostructures can be described as



Here we propose a growth mechanism for the washboard belt-like ZnSe nanostructures, where the growth process can be separated into four stages as shown in Fig.5. Firstly, the hot ZnSe gases will decompose to generate Zn gas and Se₂ vapor at high temperature, and then they flow to the low temperature region (step A) with the Ar carrier gas and react with each other to form zinc blende-structured ZnSe belt structures (step B). Then, with the decrease of concentration and temperature of vapor, ZnSe particle seeds are formed over the surface of the nanobelt structures. In the third step, Zn gas and Se₂ vapor dissolve in ZnSe seeds continually, and small ZnSe nanobelts precipitate out and grow (Step C) through the “weed growth” model^[14]. The structure of ZnSe crystal is determined by the reaction temperature. For sample 1, the temperature is low, so the products are zinc blende structure. With the increase of temperature, a little wurtzite ZnSe is formed on the surface of nanobelts. For sample 3, the high-density wurtzite ZnSe is formed on the surface of nanobelts due to the highest temperature (Step D).

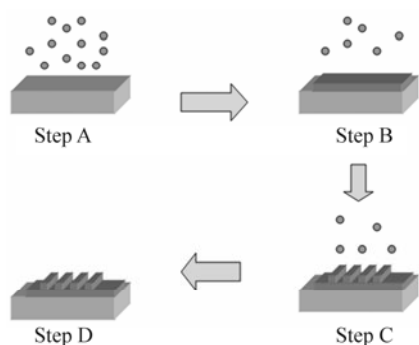


Fig.5 Schematic diagram of the formation process of the washboard belt-like ZnSe nanostructures

The PL property of ZnSe materials is intricate because it is sensitive to the synthetic conditions, crystal size and shape. Fig.6 shows the PL spectra of sample 1, sample 2 and sample 3 at room temperature, which were investigated by using He-Cd laser at 325 nm as the excitation source. For sample 1, the intense peak at 466 nm is due to the near-band-edge emission of cubic zinc blende-structured ZnSe, which is in accordance with the previous reports^[15]. A weak broad emission peak at 545 nm can be detected, which is often connected with the doped ion or defect state emission^[16,17]. For sample 2, the emission of the ZnSe nanostructures has a large blue shift from the bandgap emission of the bulk materials (2.7 eV), and the origin of this blue-shifted emission peak is usually attributed to the bound exciton emissions of some hexagonal wurtzite-structured ZnSe (with a band gap of 2.874 eV)^[18,19]. The PL emission intensity mainly results from the recombination of excited electrons and holes^[20], and the recombination rate is determined by the reaction temperature. The higher the reaction temperature is, the lower the PL intensity is^[21]. For sample 3, the reaction temperature is higher, so the lower PL intensity is observed.

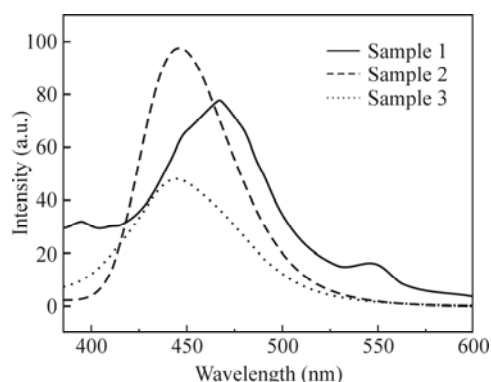


Fig.6 PL spectra of the samples 1, 2 and 3

In summary, washboard belt-like ZnSe nanostructures are successfully synthesized using a simple CVD method. The studies show that the morphologies of the products can be well controlled by adjusting the reaction tem-

perature. VS growth mechanism is proposed for the formation of the washboard belt-like ZnSe nanostructures. These washboard belt-like ZnSe nanomaterials exhibit strong visible PL from 440 nm to 462 nm, and can serve as important integrated nanoscale optoelectronic devices. The method described here is of interest to commercial production and can be used to synthesize other II-VI or other group's semiconductor micro/nanostructures.

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