Applied Surface Science 332 (2015) 76–79

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surfactant-assisted solvothermal synthesis of single-crystal zinc antimonide nanorods

Mianzeng Zhong [a], Xiuqing Meng [a], Jingbo Li [a,b,*]

[a] Zhejiang Provincial Key Laboratory of Solid State Optoelectronic Devices, Zhejiang Normal University, Jinhua 321004, China
[b] State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, China

ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form
21 December 2014
Accepted 8 January 2015
Available online 24 January 2015

Keywords:
ZnSb
Nanocrystalline materials
Nanorods
Crystal growth

ABSTRACT

One-dimensional ZnSb nanorods with the diameter of 20 nm have been synthesized by one-step surfactant-assisted solvothermal method. The ZnSb nanorods have single-crystalline structure with a growth direction of [0 0 1]. The experimental results indicate that the final morphologies of ZnSb nanostructures can be controlled by the surfactant.

1. Introduction

In recent years, the synthesis and applications of nanostructured materials have been extensively studied due to their special properties related to their special nanostructures and their numerous applications in nanodevices. In particular, semiconductor nanorods as a kind of one-dimensional nanostructured materials have attracted increasing attentions owing to the large surface-to-volume ratio and quantum-mechanical confinement effects (QCE) which are considered to be crucial for the function and application of nanodevices [1–4]. Large number of semiconductor nanorods, such as ZnO [3], ZnS [5], TiO_2 [6], Bi_2Te_3 [7], and Sb_2Te_3 [8], have been synthesized by various methods. Very recently, ZnSb nanostructures have been prepared by electrochemical deposition method [9,10]. However, a simple, quick, and cheap fabrication method of ZnSb nanorods or nanowires is urgently needed.

Zinc antimonide (ZnSb) is one of most promising thermoelectric material with the high figure of merit (ZT) in the intermediate temperature range (450–700 K) [11,12]. Previous studies are mainly on the bulk materials of zinc antimonide. For thermoelectric materials, the figure of merit ZT is theoretically defined as $ZT = \sigma S^2 T/K$, where σ is the electrical conductivity, K is the thermal conductivity, T is the absolute temperature, and S is the Seebeck coefficient. In order to achieve the high ZT value, it is necessary to reduce the thermal conductivity and enhance the Seebeck coefficient and electrical conductivity. Nanostructured thermoelectric materials have the potential to improve the ZT value due to quantum size and surface effects of the charge and heat carriers [7,13]. Quantum confinement of the charge carriers enhances the Seebeck coefficient and electrical conductivity owing to the increase of density of states at the Fermi level [7,14]. Meanwhile, intense boundary and interface scattering of heat carriers decreases thermal conductivity in nanosystems [8,15]. However, there are rare studies on the nanostructures, especially one-dimensional nanostructures, of zinc antimonide, although their preparation is strongly desired. Recently, various techniques have been applied to prepare one-dimensional nanorods and among them, surfactant-assisted solvothermal synthesis is verified an effective fabrication method [7,16]. In this letter, we present a surfactant-assisted solvothermal route for the preparation of anisotropic hexagonal ZnSb nanorods with cetyl-trimethyl ammonium bromide as the structure-controlling agent, antimony(III) chloride and zinc chloride as the reactants, and N,N-dimethylformamide as the solvent at 180 °C.

2. Experimental

In a typical synthesis process, 1 mmol of zinc chloride ($ZnCl_2$) and 2 mmol cetyl-trimethyl ammonium bromide (CTAB) were

* Corresponding author at: Zhejiang Provincial Key Laboratory of Solid State Optoelectronic Devices, Zhejiang Normal University, Jinhua 321004, China.
E-mail address: jbli@semi.ac.cn (J. Li).

http://dx.doi.org/10.1016/j.apsusc.2015.01.125
0169-4332/

added to a 100 mL three-neck round-bottom flask. 20 mL solution including 15 mL N,N-dimethylformamide (DMF) and 5 mL ammonium hydroxide ($NH_3{\cdot}H_2O$) was added to the above flask under constant magnetic stirring, meanwhile, the flask was purged with Ar flow thoroughly. After the two precursors were completely dissolved, 1 mmol of antimony(III) chloride ($SbCl_3$) was added to the above solution. 2 mmol sodium borohydride was added to another 20 mL N,N-dimethylformamide (DMF) under magnetic stirring. After several minutes, all sodium borohydride dissolved. Then this 20 mL N,N-dimethylformamide contained 2 mmol sodium borohydride was injected into the above flask dropwise. The resulting homogeneous solution was transferred into a teflon-lined stainless-steel autoclave with a capacity of 50 mL, which was sealed and kept at 180 °C for 24 h and then cooled to room temperature under ambient conditions. After the autoclave was cooled down to room temperature, the black products were washed several times with ethanol and distilled water, followed by drying at 80 °C for 10 h under vacuum.

3. Results and discussion

The synthesized products were examined by X-ray diffraction (XRD) technique with Cu Kα irradiation (λ = 1.5418 Å), and the XRD patterns of samples are shown in Fig. 1. All the observed diffraction peaks in the pattern are well indexed to the hexagonal ZnSb (JCPDS-18-0140; $a = b = 4.304$ Å, $c = 11.07$ Å), and no secondary phases are found. The morphology and size of the as-synthesized products were investigated using field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Minato-ku, Tokyo, Japan). Fig. 2 shows the field-emission scanning electron microscope (FESEM) images of the as-prepared products obtained on different concentration of cationic surfactant CTAB. Fig. 2a is a low magnifications FESEM image of the as-prepared products with adding 2 mmol cationic surfactant CTAB, which shows that the typical products consist of a large number of nanorods. Fig. 2b is a typical SEM image of a single nanorod, which shows that the diameter of this nanorod is about 108 nm and the length is about 1.2 μm. However,

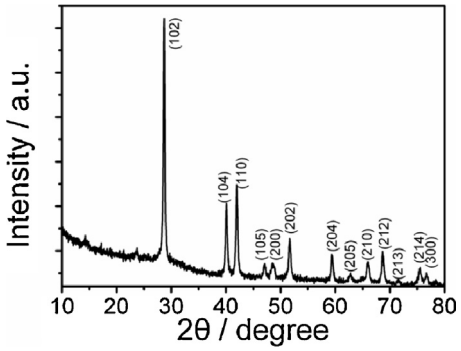

Fig. 1. X-ray diffraction pattern of the prepared product.

when the cationic surfactant CTAB added to 4 mmol, the diameter of nanorods become small. Fig. 2c reveals that a large number of nanorods are randomly dispersed on the surface of the substrate. The high-magnification FESEM image (Fig. 2d) shows that the diameter of nanorods is about 20 nm. The chemical composition of as-prepared nanorods was determined by energy-dispersive X-ray spectrometer (EDS). Fig. S3 is the EDS spectrum of nanorods, it can be seen that besides the elements Cu and C from the substrate of carbon-coated copper grid, only peaks of the elements Zn and Sb are detected in the EDS pattern. The atom ratio of Zn and Sb in the nanorod in about 1:1, which further confirms that the nanorods are ZnSb.

The structure details of the nanorods were examined by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEOL, JEM 2100F). Fig. 3a is a typical TEM image taken from a single nanorod. The selected-area electron diffraction (SAED) (Fig. 3c) taken from this single nanorod shows a spot pattern that is consistent with a high quality single crystal with hexagonal structure recorded from the [0 1 0] zone axis. The HRTEM image of ZnSb nanorod is shown in Fig. 3b. The clear lattice fringes show that the ZnSb nanorod have a well-defined crystal structure. Meanwhile, the lattice spacing

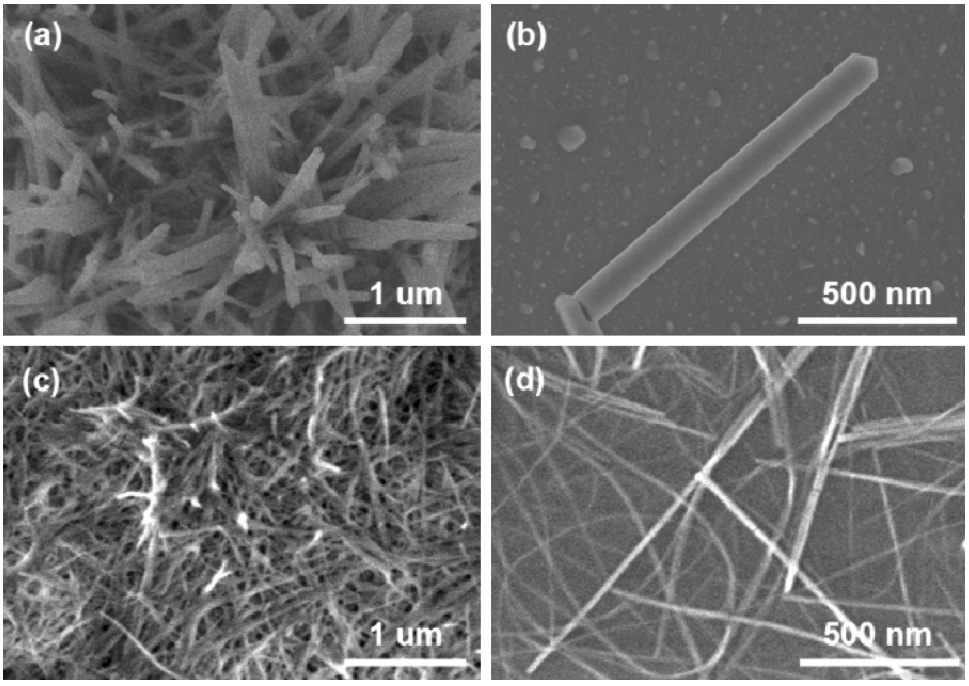

Fig. 2. (a and b) FESEM images of the as-prepared ZnSb nanorods with adding 2 mmol CTAB at low and high magnifications, respectively. (c and d) FESEM images of the as-prepared ZnSb nanorods with adding 4 mmol CTAB at low and high magnifications, respectively.