Materials Letters 179 (2016) 198–201

Contents lists available at ScienceDirect

Materials Letters

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

Single-crystalline Bi_2Se_3 nanowires grown by catalyst-free ambient pressure chemical vapor deposition

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ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form
24 April 2016
Accepted 25 April 2016
Available online 26 April 2016

Keywords:
Bi_2Se_3
Vapor phase growth
Nanowires
Semiconductors
Nanocrystalline materials

ABSTRACT

Bi_2Se_3 nanostructures are very promising in the thermoelectrics, optics and electronics. In the letter, Bi_2Se_3 single-crystal nanowires (NWs) were successfully synthesized via catalyst-free ambient pressure chemical vapor deposition (CVD) using high purity Bi_2Se_3 powder as the source material. The morphology, microstructure and chemical compositions of the prepared Bi_2Se_3 NWs were characterized in details. The results reveal that the NWs have well-crystallized rhombohedral structure with smooth surface and their length can be up to 50 μm. The growth direction of the NWs is along [110] direction and the growth mechanism is discussed. The high-quality Bi_2Se_3 NWs have potential applications in thermoelectric, optical and electronic devices. The present method could be extended to synthesize NWs of other layer-structured materials.

1. Introduction

Thermoelectric (TE) materials are a kind of clean energy materials that can realize direct conversion between heat and electricity. Many studies have demonstrated that the improved TE performance can be achieved in low-dimensional materials due to the reduced lattice thermal conductivity via enhancing phonon scattering at boundaries [1–3].

Bi_2Se_3 is an important TE and electronic material with a narrow band-gap (Eg ~0.3 eV) [4]. Moreover, Bi_2Se_3 materials are very promising for the optical fibers due to their interesting no-linear optical effects [5]. Nowadays Bi_2Se_3 nanostructures have been synthesized by a variety of techniques. Two-dimensional nanostructures of Bi_2Se_3 have been synthesized by intercalation/exfoliation strategy [3], solvothermal technique [6] and pulsed laser deposition (PLD) [7]. One-dimensional (1D) nanostructures such as nanowires (NWs) and nanoribbons (NBs) are another low-dimensional system with great significance in science and technology. There have been some reports on vapor-growth of Bi_2Se_3 1D nanostructures. For example, Cui and co-workers [8] synthesized Bi_2Se_3 NWs and NBs by a catalyst-assisted chemical vapor deposition (CVD) method. Zou et al. [9] reported the catalyzed vapor-phase growth of Bi_2Se_3 NWs and NBs. Cha et al. [10] fabricated Bi_2Se_3 NBs using metal alloys as catalysts. Fang et al. [11] reported a catalyst-free growth of Bi_2Se_3 NBs by a long-duration low pressure (10^{-2} mTorr) vapor growth. It should be noted that the above works involved catalysts or low-pressure to achieve 1D growth of Bi_2Se_3. So the facile catalyst-free synthesis of high-quality Bi_2Se_3 NWs is still desired now.

Here we report a catalyst-free ambient pressure CVD route to single crystal Bi_2Se_3 NWs for the first time. The obtained Bi_2Se_3 NWs have high quality and the work provides an example for the facile vapor-phase growth of other V-VI compounds.

2. Experiment

Bi_2Se_3 nanowires were synthesized in a horizontal tube furnace. Graphite paper was selected as substrate to collect the grown products and no catalyst was used. In a typical run, 0.2 g of Bi_2Se_3 powder (99.99 wt%) was loaded in a ceramic boat and put in the middle zone of the tube furnace that was then sealed and evacuated by the vacuum pump, and flushed with high-purity Ar flow for three times to remove the residual oxygen. Then the furnace was heated to 700 °C within 70 min under a Ar flow of 50 sccm, and was kept for 90 min. Finally, the furnace was naturally cooled down to room temperature and the products were obtained on the downstream graphite paper at distance about 23 cm from the center.

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http://dx.doi.org/10.1016/j.matlet.2016.04.198
0167-577X/

The samples were characterized by scanning electron microscopy (SEM, Hitachi S-3400N-II), transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and energy disperse X-ray spectroscopy (EDX).

3. Results and discussion

SEM image in Fig. 1 displays an overall morphology of the sample. It can be seen that products deposited on the substrate consist of some straight 1D structures with lengths ranging from several to 50 μm. High-magnification SEM image shown in Fig. 1(b) reveals that the 1D structure is a straight NW with smooth surface. It is worth noting that the NW has well faceted lateral surfaces, implying its single-crystalline nature. Another important morphological feature of the NW is that its top is not flat and has several facets. No particle is observed on the top of all NWs grown here, suggesting no liquid-phase intermediate involved their growth.

Fig. 2(a) is a bright-field TEM image, clearly showing the smooth lateral surface of a NW. It is also found that the top of the NW consists of 2 or 3 small facets with layered steps, which is consistent with the SEM images. HRTEM image (Fig. 2(b)) depict the clear lattice fringe with lattice spacing of about 0.21 nm, which is consistent with the spacing between the (110) planes of rhombohedral phase Bi_2Se_3 (JCPDS 33-0214) and indicates its well-crystallized structure. The bright hexagonal spots can be observed in the SAED pattern taken along [001] zone axis, demonstrating that the NW is a single crystal with high-quality crystallization. The growth direction of the NW is determined to be [110] of rhombohedral Bi_2Se_3, meaning that the NW is stacked by (110) crystal planes, which is consistent with the result of previous report [7]. In addition, the angle between the top facets and the growth direction of the NW is 60°, suggesting that the NW top is covered by {100} facets.

Fig. 3(a) shows a scanning TEM image with a rectangular zone on which the EDX element mappings were taken. Element mappings for Bi and Se (Fig. 3(b) and (c)) demonstrate that the elements uniformly distribute in the nanowire. Fig. 3(d) is the EDX spectrum showing signal of Bi and Se. The quantitative element analysis indicates that Bi and Se are ca. 45.65 at% and 54.35 at%, respectively, indicating the Se deficiency in the NW.

Here the growth and characterization data of Bi_2Se_3 nanowires can be reproducible through the fine control of the experimental conditions. In general, the formation of plate-like nanostructures of Bi_2Se_3 is more favorable without the assistant of catalyst due to its layered structure. It is known that Bi_2Se_3 is constructed by covalently bonded quintuple atomic layers (QLs) in the sequence of -Se-Bi-Se-Bi-Se- and the QLs are connected through the weak van der Waals force [12]. So Bi and Se atoms prefer to arrange in the layer by layer manner, resulting in the plate-like morphology of the products [13].

In our work, it is found that some NWs grow from the edges of the nanoplates, as shown in Fig. 4(a) and (b), which is similar with the observation in the literatures [13,14]. In our case, the nucleation and formation of the plate-like structure of Bi_2Se_3 should be a spontaneous layered growth process that has been evidenced by the SEM observations. Fig. 4(c) and (d) display the chemical compositions at the top of nanoplate and the head of the NW. The Se/Bi atomic ratio of nanoplate at the top (1.59) is lower than that at the head (1.72) of the

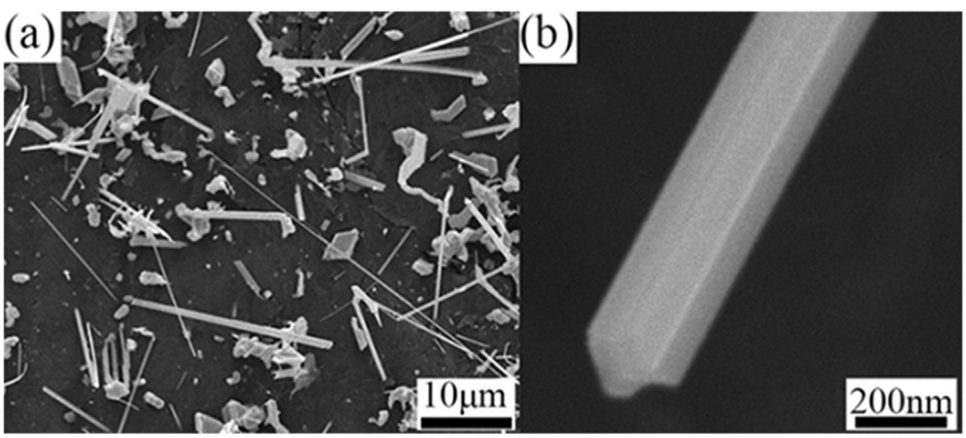

Fig. 1. A low magnification SEM image of Bi_2Se_3 nanowires grown on graphite paper b a high magnification SEM image of individual Bi_2Se_3 nanowire.

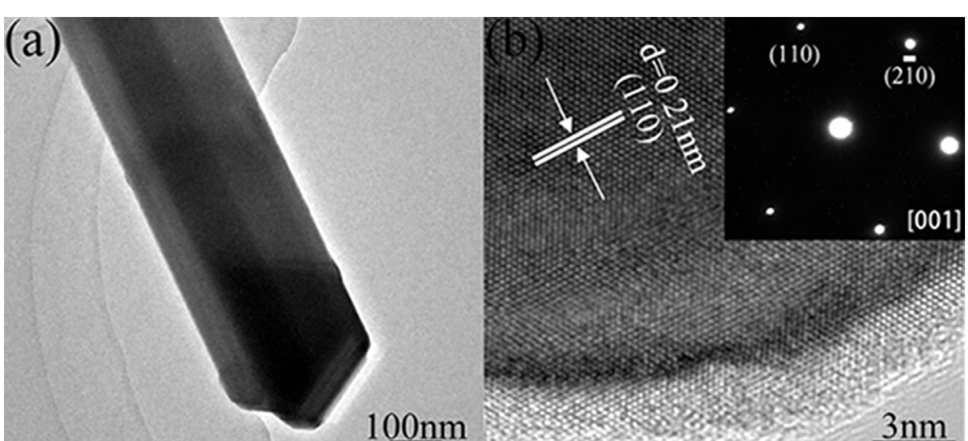

Fig. 2. (a) TEM image of an individual Bi_2Se_3 nanowire. (b) HRTEM image of a nanowire. The inset is the corresponding SAED pattern.