

Preparation and characterisation of single-crystalline structure Sb/Bi₂Te₃ superlattice nanowires

Junli Fu¹ ✉, Jinbo Shen², Honglong Shi¹, Yujie Liang¹, Zhen Qu¹, Wenzhong Wang¹

¹School of Science, Minzu University of China, Beijing 100081, People's Republic of China

²School of Electronic Engineering, Beijing University of Posts and Telecommunications, Beijing 100876, People's Republic of China

✉ E-mail: fujl08@muc.edu.cn

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High figures of merit is important and necessary for thermoelectric materials in a particular engineering application of thermoelectric generation. Crystalline is an important factor for the high figures of merit of thermoelectric materials. Single-crystalline structure Sb/Bi₂Te₃ superlattice nanowires (SLNWs) were synthesised in large quantity by pulsed electrodeposition technology using porous anodic alumina oxide as a template. The X-ray diffraction result indicates that the as-prepared compound consists of rhombohedral phase Bi₂Te₃ and monoclinic phase Sb. Transmission electron microscope images demonstrate that the segments of SLNWs are built by Bi₂Te₃ and Sb alternately and exhibit the distinguished interface between two segments. The average diameter and length of each segment are about 80 and 90 nm, respectively. The composition of neighbouring segments was investigated by selected area electron diffraction (SAED), further verifying that the neighbouring segments of SLNWs are comprised of Bi₂Te₃ and Sb. Meanwhile, the spot pattern of SAED indicates these segments are crystallised well.

1. Introduction: There is a renewed interest for searching and fabricating the high figures of merit (ZT) thermoelectric materials in the engineering application because of the increasing urgency in the world's supply of energy [1, 2]. High ZT of thermoelectric materials can be achieved in nanostructured materials such as nanowires, nanorods, nanobelts, superlattice thin films and multilayered systems [3–5]. Venkatasubramanian *et al.* [6] reported the highest ZT of 2.4 in Bi₂Te₃/Sb₂Te₃ superlattice film. Several other multilayered systems also show the improved thermoelectric properties over their homogeneous counterparts [7].

Superlattice nanowires (SLNWs) are advantaged systems in improving the ZT of thermoelectric materials, because they can reduce the phonon transport and keep high electron mobility [8]. It is well known that Bi₂Te₃ and its compounds are the most important thermoelectric materials around room temperature. Recently, preparation of the BiTe and its alloys SLNWs has been attracting more and more attention. Bi/Sb, Ag/Bi₂Te₃, Bi/BiSb and BiTe/BiSbTe thermoelectric SLNWs have been prepared by pulsed electrodeposition method [9–11]. Wang *et al.* [12] prepared the Bi₂Te₃/Te SLNWs by using the precipitation reaction method under a nanoconfined system of the supersaturated Bi_{0.26}Te_{0.74} alloy. Chen and co-workers [13] fabricated novel T-shaped Bi₂Te₃-Te hetero nanojunctions by a simple and facile solvothermal method. In addition, antimony can optimise the thermoelectric properties in a large number of thermoelectric systems. Compared with the PbTe_{1-x}Se_x solid solution alloys, the ZT of Pb_{9.6}Sb_{0.2}Te_{10-x}Se_x has a significantly enhanced. For Pb_{9.6}Sb_{0.2}Te₃Se₇ system, a maximum ZT of 1.2 was obtained at 650 K [14]. In the system of AgPbmSbTe_{2+m}, the ZT of 2.2 at 800 K can be achieved [15]. Sb/Bi₂Te₃ SLNWs which has to be both advantages of SLNW and antimony into one is promising in increasing the ZT of thermoelectric materials, so it is valuable for us to prepare and study the thermoelectric properties of Sb/Bi₂Te₃ SLNWs.

There are a lot of methods to prepare SLNWs. In comparison to other methods, the template-based electrochemical deposition method has advantage in tailoring the composition and length of individual segment of nanowires, which is important for improving the ZT of thermoelectric materials. Li and co-workers [16] fabricated the polycrystalline structure Sb/Bi₂Te₃ SLNWs by pulsed

electrochemical deposition process, but the crystalline is not well. Crystalline is an important factor for the high figures of merit of thermoelectric materials. In this Letter, we electrodeposited single-crystalline structure Sb/Bi₂Te₃ SLNWs by using the porous anodic alumina oxide (AAO) as template, and discussed the phase structure, morphology and crystalline of the as-grown Sb/Bi₂Te₃ SLNWs.

2. Experiment section: The Sb/Bi₂Te₃ SLNWs were pulsed electrodeposited into AAO templates. A two-step anodising process was used to fabricate the AAO membranes. The electrolyte solution consisted of SbCl₃ (0.04 M), Bi(NO₃)₃•5H₂O (0.004 M), HTeO²⁺ (0.006 M), C₆H₈O₆ (0.52 M) and HNO₃ (1 M). Sb/Bi₂Te₃ SLNWs was fabricated on a CHI 760C electrochemical workstation at room temperature. Platinum plate, saturated calomel electrode (SCE), and the AAO template of three-electrode electrochemical cell were used as counter, reference and working electrodes, respectively. It is well-known that the crystalline of material can be influenced by the concentration of electrolyte solution and the electrodeposition potential [16]. The results of cyclic voltammograms and morphologies of the as-prepared SLNWs show that the pulse potential waveforms between -0.1 and -0.9 V (against SCE) is the well potential for the growth of single-crystalline structure Sb/Bi₂Te₃.

The scanning electron microscope (SEM, HitachiS-4800) and transmission electron microscope (TEM, JEM2010) were used to evaluate the morphology, size and microstructure of the nanowire arrays. The phase structure of the products was obtained by selected area electron diffraction (SAED) and X-ray diffraction (XRD, XD-3 diffractometer with Cu K α).

3. Results and discussion: Fig. 1 shows the XRD pattern of AAO templates filled with the as-prepared SLNWs. The five peaks marked with filled star can be indexed to (0 1 5), (1 0 10), (0 0 15), (0 0 21) and (0 1 23) planes of the Bi₂Te₃ with rhombohedral lattice phase according to the standard power diffraction file (JCPDS Card No. 15-0863). Meanwhile, the other two peaks marked with black down-pointing triangle shown in

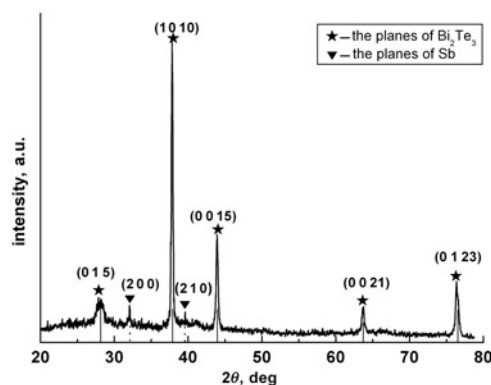


Fig. 1 XRD pattern of AAO templates filled with SLNW arrays

Fig. 1, are indexed to (2 0 0) and (2 1 0) planes of the Sb with monoclinic lattice phase (JCPDS Card No. 26-0101). The result of the XRD pattern shows that the prepared compound is composed of rhombohedral lattice phase Bi_2Te_3 and monoclinic lattice phase Sb.

The SEM images of the SLNWs after the templates were partially removed are shown in Fig. 2a and b. The diameter of the nanowires is uniformly about 80 nm, and the aspect ratio is about 100. The large-scale nanowire arrays are obtained as shown in Fig. 2a and b, which indicates that the prepare efficiency is very high via the present method of electrodeposition. Furthermore, the alternately ordered segments can be easily distinguished. To get a better view of the morphology of the nanowires, Fig. 2c and d show the TEM images of the SLNWs. Fig. 2d shows the enlarged TEM image of the SLNWs as shown in Fig. 2c. From the TEM image, it can be seen that the segments of SLNWs are alternately ordered and the interface between two segments is clearly distinguished. The diameter of each segment is about 80 nm, and the length is the same as about 90 nm for each segment, which is in agreement with the result of SEM image.

To investigate the structure and composition, Fig. 3 shows the TEM image and the corresponding SAED of SLNWs. Fig. 3a shows the TEM image of SLNWs selected from sample randomly, in which the neighbouring segments are marked as A and C, respectively. The interface between segments A and C is marked as B. Compared with segments A and C, the colour of interface B is brighter and the length is shorter. Fig. 3b shows the SAED

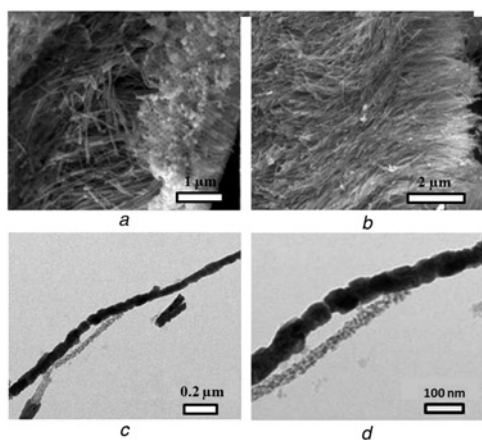


Fig. 2 Morphologies of the as-prepared SLNWs
a SEM image of AAO templates and SLNWs
b SEM image of SLNWs
c TEM image of SLNWs
d Enlarged image of the SLNWs in Fig. 2c

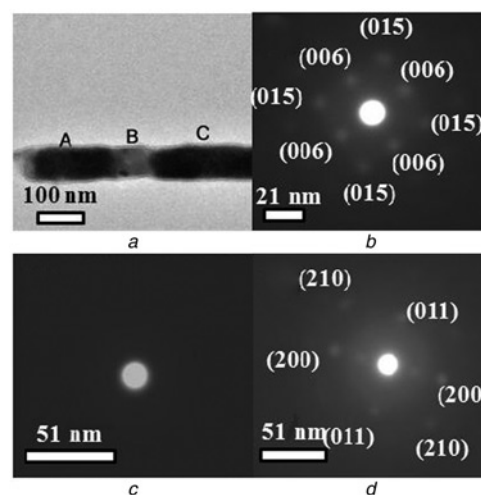


Fig. 3 TEM image of SLNW and the corresponding SAED patterns
a TEM image of SLNW
b SAED of segment A
c SAED of segment B
d SAED of segment C

of segment A. The spot pattern of SAED shown in Fig. 3b indicates that segment A is single-crystalline structure, and can be indexed as rhombohedral Bi_2Te_3 phase (JCPDS Card No. 15-0863) with (0 1 5) and (0 0 6) planes. The SAED pattern of interface B shown in Fig. 3c indicates that the interface B is not crystallised. The SAED pattern of segment C is shown in Fig. 3d, which also exhibits spot pattern, indicating the crystalline nature of segment C. The SAED pattern of segment C can be indexed as (0 1 1), (2 0 0) and (2 1 0) planes of monoclinic lattice phase of Sb (JCPDS Card No. 26-0101). The TEM image and the corresponding SAED shown in Fig. 3 indicate that the SLNWs of $\text{Sb}/\text{Bi}_2\text{Te}_3$ with obvious segment have been prepared successfully in this Letter.

4. Conclusion: In this Letter, we prepared the $\text{Sb}/\text{Bi}_2\text{Te}_3$ SLNWs by pulse electrodeposition combined with AAO template route. The result of XRD pattern shows that the fabricated compound consists of Bi_2Te_3 with rhombohedral lattice phase and Sb with monoclinic lattice phase. Bi_2Te_3 segment alternates orderly with Sb segment, and the length and diameter of each segment are about 90 and 80 nm, respectively, which can be shown by the SEM and TEM images. The spot pattern of SAED for Bi_2Te_3 segments and Sb segments indicates that $\text{Sb}/\text{Bi}_2\text{Te}_3$ SLNWs prepared successfully in this work is single-crystalline structure.

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6 References

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