In situ synthesis of Bi/Bi$_2$S$_3$ heteronanowires with nonlinear electrical transport

Xiaohu Huang$^{a,*}$, Youwen Yang$^b$, Xincun Dou$^a$, Yonggang Zhu$^a$, Guanghai Li$^a$

$^a$ Key Laboratory of Material Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China
$^b$ College of Material Science and Engineering, Hefei University of Technology, Hefei 230009, PR China

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Abstract

Bi/Bi$_2$S$_3$ heteronanowires were in situ synthesized via an electrochemical synthesis. Pure Bi nanowires were first formed in the pores of AAM by electrodeposition. With increasing the reaction temperature, Bi$_2$S$_3$ were formed through reaction between Bi and S. The synthesized Bi$_2$S$_3$ microhedgehogs composed of nanoneedles were found standing on the surface of AAM after overgrowth. The possible growth process was proposed briefly. Nonlinear electrical transport was observed in the Bi/Bi$_2$S$_3$ system. The obtained Bi/Bi$_2$S$_3$ heterostructure may find applications in optical, electrical and gas sensor devices.

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1. Introduction

Micro- and nano-materials which assembled from nanoscale structures have attracted great interest in the past years, not only due to their novel properties, but also to their potential application in practical devices [1–7]. Heterojunctions are the basis of microelectronics, and heterostructured micro- or nano-materials could be applied in novel sensor nanodevices [8,9]. The semimetal bismuth (Bi) is a valuable material with many particular properties, such as high anisotropic Fermi surface, small energy overlap (about 38 meV at 77 K) between the L-point conduction band and the T-point valence band [10]. Alloys containing Bi are very important in many fields [11]. Among them, bismuth sulfide (Bi$_2$S$_3$) is a direct band gap semiconductor with an $E_g$ of 1.30 eV that is useful in photovoltaic materials and photodiode arrays; it also belongs to a family of solid-state materials with applications in thermoelectric-cooling technologies based on the Peltier effect [12,13]. Recently, many methods, including the mechanical milling [14], CVD [15], soft membrane [16], microwave irradiation [17], solvothermal reaction [18], have been developed for the synthesis of various Bi$_2$S$_3$ micro- and nano-structures. It could be expected that combining these two materials together may show some interesting and novel properties. Herein, we fabricated Bi/Bi$_2$S$_3$ heterostructure through an in situ electrochemical route. Nonlinear electrical transport was measured.

2. Experimental

In a typical synthesis, anodic alumina membrane (AAM) was prepared by a two-step anodization process as described in previous work [19]. The deposition solution is a nonaqueous solution by dissolving BiCl$_3$ and abundant S powder in dimethyl sulfoxide (DMSO). Electrodeposition was performed at potential of $-1.2$ V applied between graphite anode and AAM cathode in a sealed two-electrode glass cell. The deposition temperature was tuned from room temperature to 130 °C before the nanowires overgrow the pores of AAM. The crystal phase of our specimen was determined by X-ray diffraction (XRD) spectra on a Philips X’Pert power X-ray diffractometer using Cu K$_\alpha$ ($\lambda=1.542$ Å) radiation. Field emission scanning electron microscopy (FE-SEM, FEI Sirion 200), energy-dispersive X-ray (EDX, Inca Oxford), transmission electron microscopy (TEM, H-800) and selected area electron diffraction (SAED) techniques were used to study the morphology, composition and crystalline structure. Transport measurement was performed on Keithley 4200 SCS Semiconductor Characteri-
3. Results and discussion

Fig. 1(a) and Fig. 1(b) are the XRD spectra obtained from the top and back surface of the sample, respectively. It can be seen that the crystal phase of our specimen from the top side is pure orthorhombic Bi₂S₃ (JCPDS No. 84-0279), and the intensity of (2 0 0) peak is the strongest among all the peaks. The peak labeled by letter “S” is from the residual sulfur (JCPDS No. 89-6764), similar phenomena was also observed on CVD-grown Bi₂S₃ nanowires [20]. In Fig. 1(b), we can see that, except the (2 0 0) peak of orthorhombic Bi₂S₃ and the residual sulfur, other peaks belongs to rhombohedral Bi, which is denoted by “Bi”. The standard diffraction peaks of Bi (JCPDS No. 85-1330) are listed as lines in Fig. 1(b). The XRD spectra from both surfaces suggest the existence of Bi/Bi₂S₃ heterostructure.

The as-synthesized samples were studied by FE-SEM, as shown in Fig. 2. A mass of deposits located on the top surface of the AAM (Fig. 2(a)) are in the form of spheres with size of around 40 μm (Fig. 2(b)). It is clear that the spheres are in the shape of hedgehog, consisting of large numbers of nanoneedles (see Fig. 2(c)). The diameter of the nanoneedles is in the range of tens of nanometers to hundreds of nanometers (Fig. 2(d)).

The Bi/Bi₂S₃ heterostructure can be clearly seen from Fig. 3(a), the inset is a magnified image of the nanowires in the pores of AAM, and the diameter of the nanowires is around 72 nm. The EDX analysis is used to determine the composition of the nanowires and the nanoneedles, as shown in Fig. 3(b) and (c). When EDX spectrum collected from the underneath nanowires in the pores of AAM, only signals of Bi were detected. While signals of both Bi and S were detected when EDX spectrum collected from the microhedgehog composed of nanoneedles, and the atomic ratio of Bi versus S is ca. 19.8:29.8, which is very close to 2:3. The EDX spectra further confirm that the nanowires in the pores of AAM is Bi, while the microhedgehogs composed of nanoneedles is Bi₂S₃. These results are consistent with the XRD characterization.

Fig. 4 shows the typical TEM images of the Bi nanowire and Bi₂S₃ nanoneedle and the corresponding SAED patterns. From Fig. 4(a), we can see that the diameter of the Bi nanowire is consistent with the FE-SEM result, and the corresponding SAED pattern (inset of Fig. 4(a)) indicates the nanowire is polycrystalline Bi with rhombohedral crystal structure. As the insets of Fig. 4(b) shows, SAED patterns taken from the randomly selected regions marked by two black circles along the nanoneedle clearly indicate that the nanoneedle is single crystalline Bi₂S₃ with orthorhombic crystal structure, and the growth direction is along [1 0 0], which is consistent with the XRD results.

The growth process of Bi/Bi₂S₃ heterostructure can be briefly described as below. First pure Bi nanowires were deposited in the pores of AAM at room temperature. Before the Bi nanowires overgrow the pores of AAM, the temperature was increased around 110 °C, Bi and S then can efficiently react to form Bi₂S₃. According to the report of ZnS nanowires synthesized by similar method [21], the formation of Bi₂S₃ in the DMSO solution containing BiCl₃ and elemental S may be through the following reaction process:

\[2\text{Bi}^{3+} + 3\text{S} + 6\text{e} = \text{Bi}_2\text{S}_3\]

The temperature plays a vital role in the formation of the Bi/Bi₂S₃ heterostructure. If the temperature was below 100 °C, only separate phases of Bi and S were obtained. The sulfur source was abundant in the solution, and the experiments in the same solution were repeated with similar results. The formation of Bi₂S₃ nanoneedles is attributed to the concentration gradient of the reactant rather than the decreasing of the Bi salt. The dissolution of Bi sources into the solution gives a concentration gradient of BiCl₃ in the region closest to the AAM. As a result, the growth of Bi₂S₃ along Bi₂S₃ [1 0 0] direction decreases gradually from the nanocrystal roots to the tips, and finally needle-like shape was formed. This is similar to the case of ZnO nanoneedles [22]. In previous reports, the hollow spherical Bi₂S₃ composed of nanorods and Bi₂S₃ flowers composed of nanoneedles were synthesized through membranes-directing method [16]. In our case, no soft membrane was used. Although the exact mechanism is not clear, it was thought that the AAM embedded with
Fig. 2. FE-SEM top images of Bi/Bi$_2$S$_3$ heterostructure with different magnified magnitude.

Fig. 3. (a) FE-SEM image of the Bi/Bi$_2$S$_3$ heterostructure, the inset is the magnified image of the Bi nanowires with diameter of about 72 nm. (b) EDX spectrum from the nanowires, as marked in the inset of it. (c) EDX spectrum from the microhedgehog composed by nanoneedles, as marked in the inset of it. (d) process of the formation of the microhedgehogs.
Bi nanowires induces a special local electric field, the outspread and aggregation of the Bi$_2$S$_3$ nanoneedles under this electric field lead to form the microhedgehogs, and this process is shown with typical images of Fig. 3(d). Compared with the Sb/Bi and Ag/Ag$_2$S heteronanowires, which were conducted in two kinds of solution one after the other [8,9], the fabrication of Bi/Bi$_2$S$_3$ heterostructure was just conducted in one solution, and the Bi deposits were sulfided in situ by adjusting the deposition temperature.

Transport measurement was conducted by dc two-electrode method at room temperature. The schematic configuration is illustrated in Fig. 5(a). Fig. 5(b) shows the $I$–$V$ curves of the Bi/Bi$_2$S$_3$ heterostructure. Current and resistance were recorded at room temperature during sweeping the voltage from $-2$ to $2$ V (the solid line) and from $2$ to $-2$ V (the dotted line). Obvious nonlinear $I$–$V$ curve was observed. The inset of Fig. 5(b) is the corresponding $R$–$V$ curves, the resistance decreases with increasing the bias voltage. To check the electrical contact behavior and the influence of Bi nanowires, the $I$–$V$ feature of pure Bi nanowire array with the diameter of about 72 nm was measured, as shown in the right corner inset of Fig. 5(b), nearly linear $I$–$V$ curve can be seen, and the resistance is about 15 $\Omega$, indicating the nanowires are metallic. Previous calculation revealed that the semimetal–semiconductor transition will occur when the diameter of Bi nanowires decreases to below 65 nm [23], and experimental results indicated that Bi nanowires with diameters larger than 70 nm are metallic, and that with diameters of about 50 nm or smaller are semiconductor [24]. Our result is consistent with these results, and the measured results are also sound compared to the results of “Y” shaped Bi nanowire array [25]. Bi$_2$S$_3$ is a semiconductor with band gap of 1.3 eV [12]. Nonlinear transport property was reported for both single Bi$_2$S$_3$ nanowire [18] and Bi$_2$S$_3$ nanowire bundle [26]. The Bi/Bi$_2$S$_3$ heterostructure forms metal–semiconductor (M–S) junction, which could be act as Schottky diodes, and rectification behavior would be expected [27]. However, as shown in Fig. 5(a), considering the metal electrode on Bi$_2$S$_3$ side, the sample measured is more like M–S–M junction. So nonlinear and almost symmetric $I$–$V$ curves were observed, as shown in Fig. 5(b), which was frequently observed on M–S–M junctions in nanoscale [18,26,28]. Further work is necessary to elucidate the electrical properties of the Bi/Bi$_2$S$_3$ heterostructure and explore other properties of such system.

4. Conclusion

In summary, we have in situ synthesized Bi/Bi$_2$S$_3$ heterostructure including Bi nanowires and Bi$_2$S$_3$ nanoneedles by adjusting the deposition temperature. The Bi$_2$S$_3$ nanoneedles were assembled to form microhedgehogs. The Bi/Bi$_2$S$_3$ heterostructure shows nonlinear $I$–$V$ property at room temperature, which may be used in switching device. We believe that this novel in situ electrochemical route can be extended to synthesize other heterostructured materials.
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