



Two-step synthesis of Bi_2Te_3 -Te nanoarrays with sheet-rod multiple heterostructure

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ARTICLE INFO

Article history:

Received 11 May 2010

Received in revised form

17 August 2010

Accepted 12 September 2010

Available online 17 September 2010

Keywords:

Array

Thermoelectric materials

Solvothermal

ABSTRACT

Bi_2Te_3 -Te arrays with sheet-rod multiple heterostructure were obtained in large scale, using Te nanorod arrays as the in-situ templates under solvothermal process. The array is formed by the ordered Bi_2Te_3 -Te rods where Bi_2Te_3 sheets distribute from the top face to the bottom face along the Te rod vertically. The microstructure of the heterostructure was studied through X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The electrical conductivity and Seebeck coefficient of the arrays were also studied. The course of reaction was monitored so as to propose a possible growth mechanism of such novel heterostructure. The key for the preparation of such heterostructure is to balance the velocity between the dissolution of Te rods and the formation of Bi_2Te_3 sheets. This synthetic approach could be promising to prepare self-assembled low-dimensional nanoarrays of metals and semiconductors with high yield.

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1. Introduction

Low-dimensional nanostructured materials such as nanowires, nanorods, nanobelts and nanotubes are especially attractive for nanoscience studies as well as for nanotechnology applications because of their superiority in mesoscopic physics and fabrication of nanoscale devices which are different from those bulky or nanoparticle materials [1,2]. Among all the challenges in well-defined low-dimensional nanomaterials, the most fundamental one should be how to control the growth of nanostructures.

The synthesis of the bismuth-telluride has attracted much interest because of its high thermoelectric figure of merit ZT at room temperature. Low-dimension materials have been proved to be an effective approach to greatly enhance the ZT value [3,4]. The reduction of dimension can result in the increase of density of states (DOS) around Fermi level and the enhancement of phonon scattering, which can heighten the Seebeck coefficient and reduce the thermal conductivity, respectively. Thus, the incorporation of low-dimensional nanostructures into bulk TE materials could effectively enhance TE performance. Pure Bi_2Te_3 materials with different structures have been extensively developed by hard templates approach, kinetic control solution growth, ball milling, melt spinning technique and self-assembly process [5–16]. Some possible mechanisms to explain the formation of Bi_2Te_3

nanocrystals, such as “mono-atom model” and “continuous nucleation model” have subsequently been proposed [17,18]. The nanostructure-contained Bi_2Te_3 based materials exhibit good TE performance due to structural modification induced by low-dimensional nanostructures [11–14]. Besides, Te/Bi and Bi_2Te_3 core/shell heterostructure nanowires have been found with enhanced thermoelectric properties [14]. Among various structures, heterostructure nanowires are predicted to exhibit better thermoelectric performance than conventional nanowires or superlattice films [19]. Thus, the synthesis of Bi_2Te_3 with heterostructure is of much interest for both chemists and materialists.

In our previous work, dispersed Bi_2Te_3 -Te sheet-rods were synthesized successfully by a mild and convenient technique [20]. While, from practical application point of view, devices should consist arrays of parallel nanowires in large scale to effectively transfer thermal energy, since a single nanowire is not able to transport enough current to make a device working. It is still a challenge to find a simple and universal strategy with a high degree of control for fabricating the thermoelectric nanowire arrays. Here, we report a simple route for large-scale growth of Bi_2Te_3 -Te sheet-rod arrays by using Te nanorod arrays as the in-situ templates through organic-assisted solvothermal method. The advantage of the procedure reported here is the first step to grow Te nanorods on a substrate continuously, compactly and orderly on large scale by physical deposition, instead of individual and discrete Te nanostructures synthesized previously reported by a chemical solvothermal method. This kind of low-dimensional heterostructure could be potential thermoelectric material with

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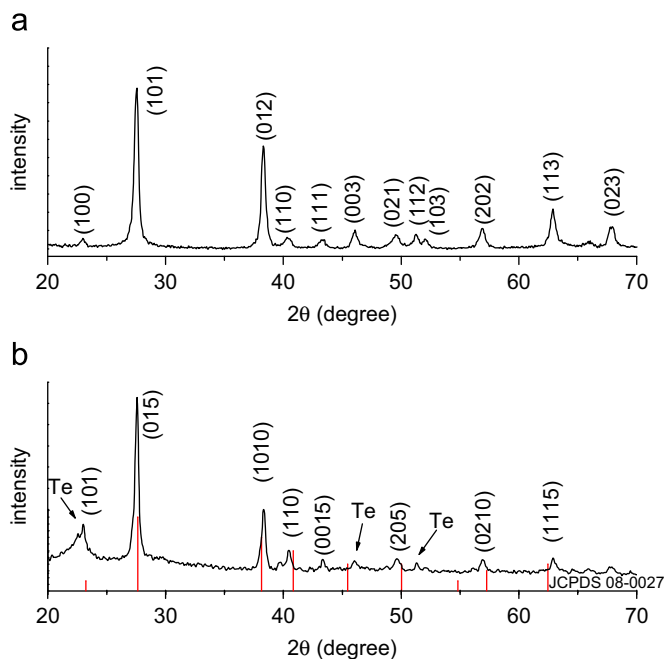


Fig. 1. (a) XRD patterns of Te nanorods. (b) XRD patterns of Bi₂Te₃-Te nanocomposite.

enhanced ZT value considering that it could offer increased phonon scattering to reduce the lattice thermal conductivity while keeping the conduction of carriers.

2. Material and methods

Tellurium (99.99%), KOH (82.0%), BiCl₃ (98.0%), EDTA-2Na (99.0%) and *N,N*-dimethylformamide (DMF, 99.5%) (all chemicals were from Beijing Chemical Co. Limited) were used directly for synthesis without further purification. First, telluride films in the form of nanorod arrays were prepared (26 mm × 70 mm) in a simple physical vapor deposition (PVD) system as follows: tellurium powders were mounted on the evaporating dish which is connected to the alternating current (AC) power supplies. Common glass substrates (26 mm × 70 mm) were cleaned thoroughly by diluted nitric acid and acetone, and dried under the nitrogen airflow. After loading the substrate onto the substrate holder (parallel to the dish), N₂ gas was introduced into the chamber and vacuumized three times to remove oxygen. All the working pressure was maintained at 2×10^{-6} Torr in the deposition process. Then Bi₂Te₃-Te sheet-rod arrays were fabricated by employing the as-deposited Te nanowire arrays as in-situ templates through the organic-assisted solvothermal method. The procedure is as follows: 0.1 mmol (0.060 g) BiCl₃, 0.2 mmol (0.140 g) EDTA-2Na, 6 mmol (0.333 g) KOH and 30 ml

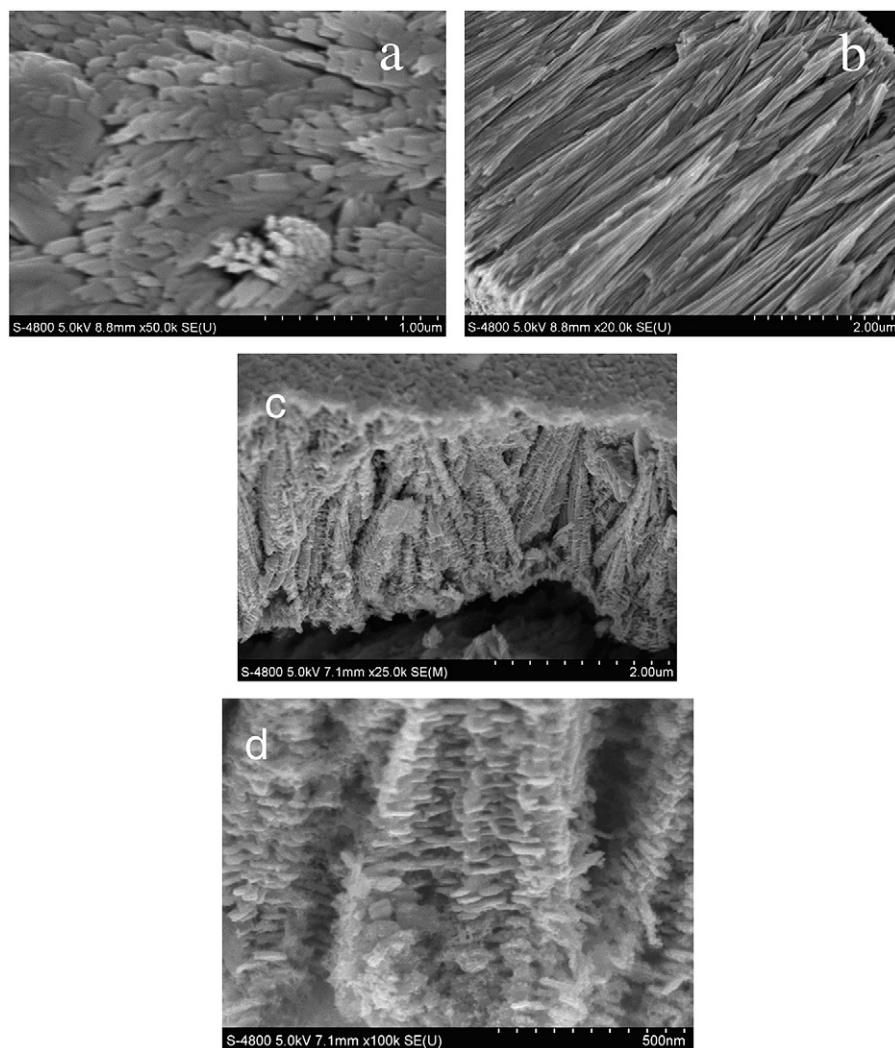


Fig. 2. FE-SEM images of (a) as-deposited Te nanorod arrays, (b) Bi₂Te₃-Te heterostructure array and (c,d) magnified image from (b).

DMF were added into a 50 ml autoclave and stirred for 0.5 h, then the Te nanowire thin films were added, and the mixture was kept at 180° for 36 h. Finally Bi₂Te₃-Te arrays in sheet-rod shape were obtained. The product was washed several times by deionized water and dried before further characterization.

The phase and the crystallographic structure of the products were determined by the X-ray diffraction (XRD, Rigaku D/max-γ) with graphite monochromatized CuKα radiation ($\lambda = 1.54178 \text{ \AA}$). The morphology and microstructure of the nanowire arrays were observed by field emission scanning electronic microscopy (FE-SEM, HITACHI S-4800), and transmission electron microscopy (TEM, HITACHI H-8100). Further structural and elemental analysis were performed by high resolution TEM (HRTEM, FEI Tecnai F20), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDS). Electric conductivity was characterized by four-probe method by a PZ158 instrument. A similar measurement method with Purkayastha et al. [21] was introduced to obtain Seebeck coefficient (*S*). The *S* value was determined from the slope of the measured Seebeck voltage versus the temperature difference across the specimen. Temperature gradient was established by a WY-99 double-door (A and B) temperature-control device, in which branch range A was performed as the heater and B as a heat sink. Electrodes monitoring the Seebeck voltage drop between the two thermocouples were adhered to the substrate before the deposition process, which can minimize the contact resistance.

3. Results and discussion

The XRD pattern of the Te nanorod arrays obtained by PVD is shown in Fig. 1a, which can be indexed as pure Te phase (JCPDS 86-2269). The SEM image of the Te nanorod arrays is shown in Fig. 2a and b, which displays well-controlled orientated-grown nanorods with 30–50 nm in diameter and above 3–4 μm in length. After organic-assisted solvothermal reaction with Bi source, the composition of the formed sheet-rod nanoarrays could be identified from XRD data (shown in Fig. 1b). Compared from pure Te nanorods, the intensity and the FWHM of diffraction peak at around $2\theta = 23.02^\circ$ changed dramatically, together with the EDS spectrum (as shown in Fig. 3b and discussed subsequently), suggesting the Bi₂Te₃ phase was formed, thus a mixture of Bi₂Te₃ and Te was obtained. The SEM images of the Bi₂Te₃-Te arrays were shown in Fig. 2c and d. Large scale Bi₂Te₃-Te arrays aligned one by one in sheet-rod heterostructure with rod length up to 2 μm were observed. The finally obtained Bi₂Te₃-Te nanorods (~2 μm) become shorter than the original Te nanorods (~3–4 μm) template, which is due to the partial dissolution of the Te nanorods during the reaction between Te and Bi. Shown from a closer view of the nanorods (see Fig. 2d), the sheets have grown on the surface of the Te nanorods with the plane perpendicular to the axial direction of the wires, and some sheets from different wires join with each other.

It has been reported formerly that hexagonal Bi₂Te₃ nanoplates could be epitaxially grown on surface of Te rods to form strings of

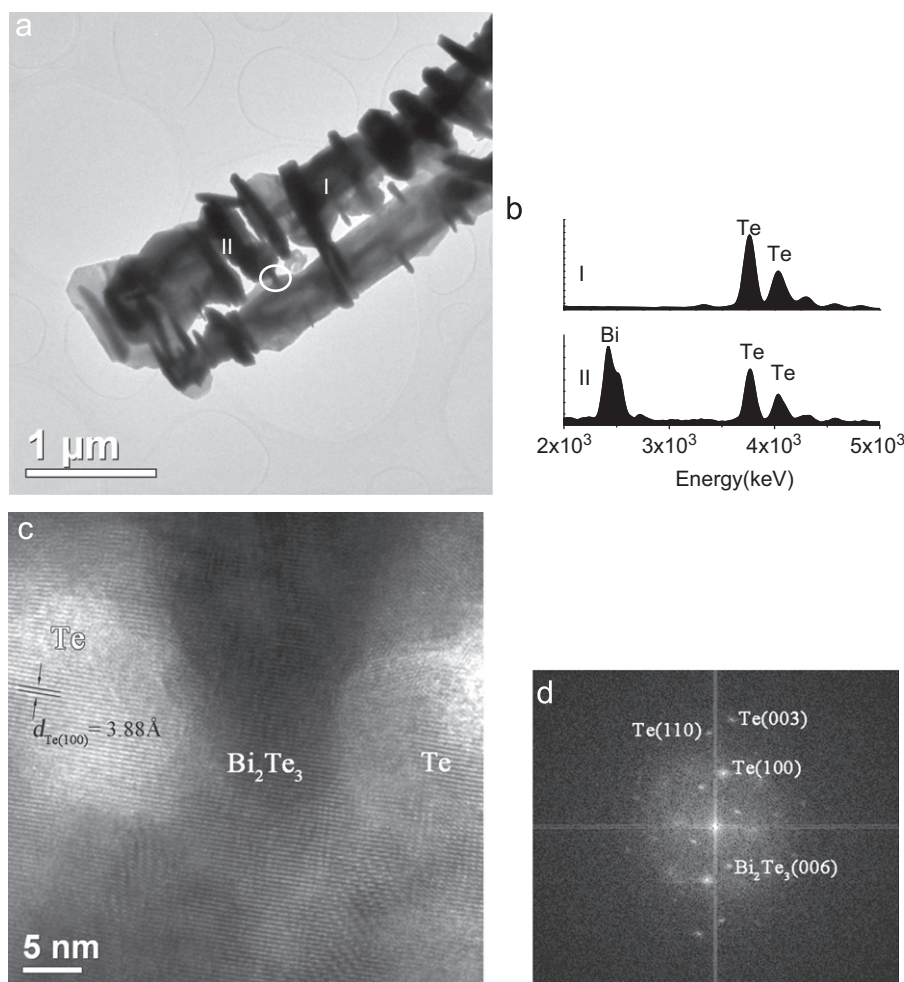


Fig. 3. (a) TEM images of the Bi₂Te₃-Te nano sheet-rod. (b) EDX patterns taken from different regions indicated as I and II in (a). (c) HRTEM image taken from the circled area in (a) and (d) corresponding FFT patterns from (c).

platelet structures due to a minimum mismatch crystal structure, i.e., $(0001)_{\text{Te}} \parallel (0001)_{\text{Bi}_2\text{Te}_3}$ and $[2\bar{1}\bar{1}0]_{\text{Te}} \parallel [2\bar{1}\bar{1}0]_{\text{Bi}_2\text{Te}_3}$, and relatively high surface energy on the top-bottom facets of nanoplates [7,9]. In order to understand the formation mechanism of the Bi_2Te_3 -Te sheet-rod heterostructure, we further studied the composition and crystallographic orientation relationship by TEM and HRTEM. As presented in Fig. 3a the morphology of single Bi_2Te_3 -Te sheet-rod heterostructure, the sheets were grown out of a rod and were separated from each other from the top to the bottom face with sheets thicknesses range from 20 to 30 nm. The local chemical compositions were analyzed by EDS. As shown in Fig. 3b, the atomic composition ratio of Bi/Te in the sheets (indicated as region II) is about 2.02:3.10, which is in good agreement with that of the stoichiometric composition of Bi_2Te_3 . While in the rod (indicated as region I), the major composition is Te with little trace of Bi, indicating that nanostructures are composed of Te rod and Bi_2Te_3 sheets.

HRTEM was employed to further study the crystal structure of the Bi_2Te_3 -Te heterostructure. As seen from Fig. 3c, a representative HRTEM image of Bi_2Te_3 -Te sheet-rod arrays, was acquired from the circled area in Fig. 3a. According to the standard ICDD PDF card (No. 08-0027), rhombohedral Bi_2Te_3 crystal (space group $R\bar{3}m$) (1 6 6) with hexagonal cells $a=4.43$ and $c=29.91$ Å, while

tellurium has hexagonal structure [space group $P3_121$ (1 5 2) (No. 86-2269)] with $a=4.454$ and $c=5.924$ Å. Due to the small lattice mismatch between two crystals' (100) planes $((a_{\text{Te}}-a_{\text{Bi}_2\text{Te}_3})/a_{\text{Te}} \sim 0.54\%)$, it is more easier for Bi_2Te_3 sheet to grow out from the Te along its [0001] orientation. Fast Fourier transformation (FFT) (Fig. 3d) from the HRTEM figure (Fig. 3c) was used to further study the phase orientation relationship between the Te rods and Bi_2Te_3 sheets during the crystal growth. If Bi_2Te_3 sheets grew out from Te rods epitaxially, Te (100) and Bi_2Te_3 (101) planes which have similar interplanar spacing at around

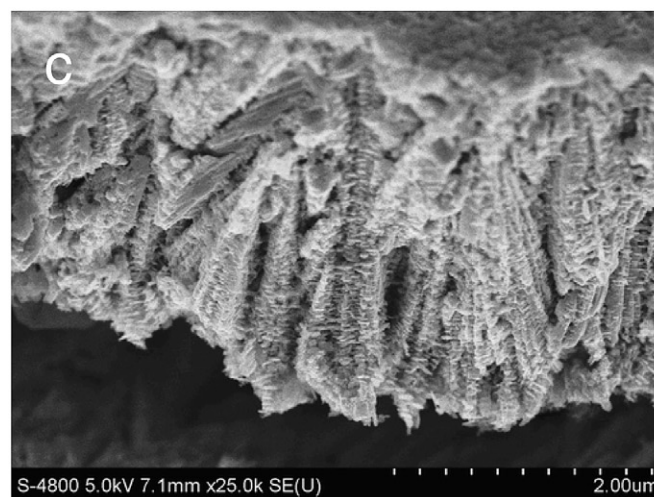
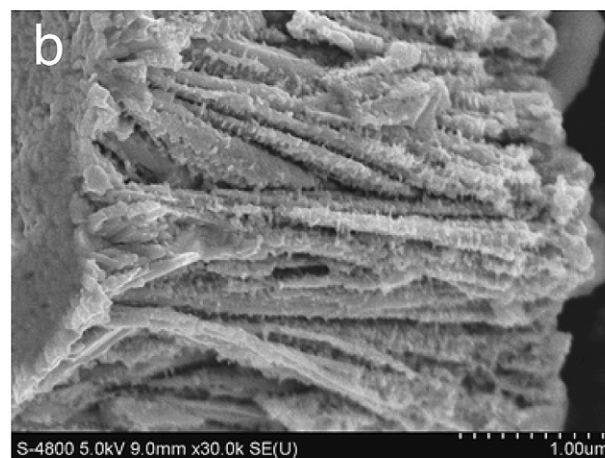


Fig. 5. The FE-SEM images of the products with different reaction time (a) 12 h; (b) 24 h and (c) 36 h.

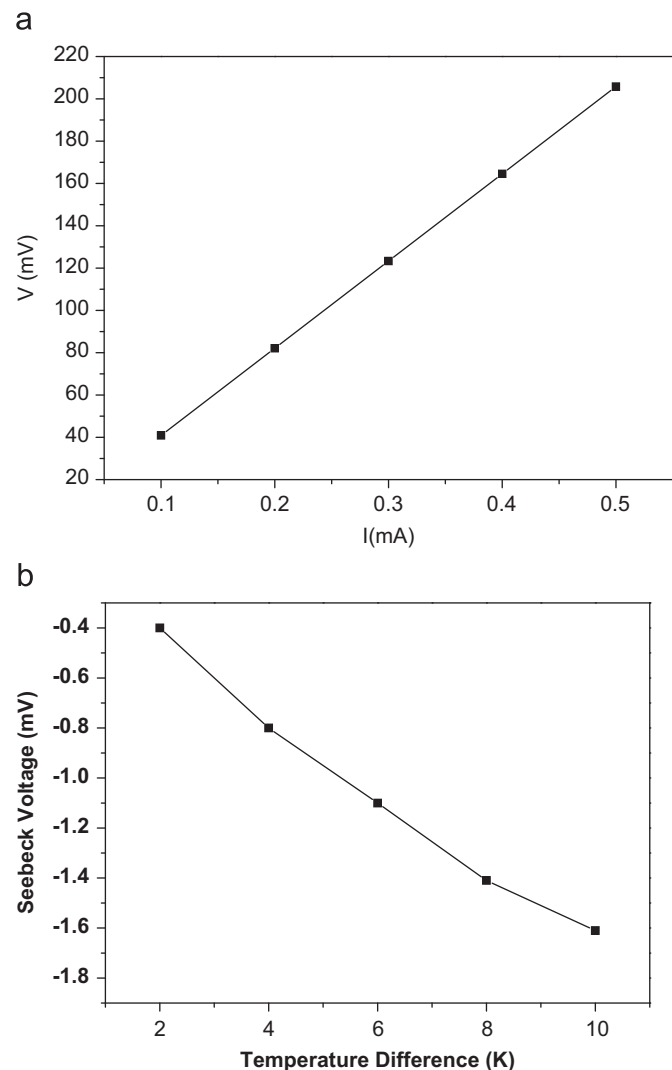


Fig. 4. (a) I - V characteristics of the film of arrays and (b) dependence of the Seebeck voltage as a function of temperature difference along the thermoelectric film.

0.388 nm should appear simultaneously at the diffraction figure, however, we could not distinguish Te (1 0 0) and Bi_2Te_3 (1 0 1) diffraction spots clearly from Fig. 3d. This is due to Te nanorods are polycrystalline growing along particular orientation, i.e., perpendicular to the substrate. Bi_2Te_3 sheets choose to grow in the direction with minimum energy, not epitaxially along the lattice match plane.

The Bi_2Te_3 -Te sheet-rod arrays exhibit a linear current-voltage (I - V) curve (see Fig. 4a), indicating that the contacts are ohmic. The slope yields a resistance of $\sim 410 \Omega$. According to one-dimensional (1D) electrical transport model, we obtained an electrical conductivity $\sigma \sim 180 \text{ S/m}$, indicating a good electrical transport. The lower electrical conductivity of arrays is probably due to numerous interspaces between the sheet-rod arrays in the film. Fig. 4b shows that the Seebeck voltage varies nearly linearly as a function of the corresponding temperature difference. The Seebeck voltage is measured between different points on the film surface. Then Seebeck coefficient (S) is calculated to be about $-170 \mu\text{V K}^{-1}$ from the slope, which means that the Bi_2Te_3 film is an n-type semiconductor. An even higher S value of the films in the cross-sectional direction is expected due to the microstructure of nanowire arrays. Then those films are promising material applied for cooler device.

In order to study the formation mechanism of Bi_2Te_3 sheet-rod nano-arrays, time-dependent experiments were carried out. Fig. 5a-c shows the SEM images of samples at different reaction times: 12, 24 and 36 h. In the first step we obtained the 3–4 μm Te nanorods arrays with smooth surface (Fig. 2a), after 12 h reaction in the second step, the surface of the Te nanowires becomes rough with many dots appearing (Fig. 5a). And, the Te nanowires were partly dissolved in the solution processing at this stage, which is necessary in the growth of Bi_2Te_3 sheets. When reaction time was extended to 24 h, plenty of Bi_2Te_3 nucleations were formed along the nanorods and the length of the rods were shortened to 2–3 μm (Fig. 5b). As the reaction continued to 36 h, well-proportioned Bi_2Te_3 -Te sheet-rod arrays were obtained, where Bi_2Te_3 sheets distribute from the top face to the bottom face along the Te rod vertically (Fig. 5c).

Based on the experimental results, a possible formation mechanism of the Bi_2Te_3 -Te sheet-rod arrays can be expressed as follows: in the first step, Te nanorods arrays were formed during physical deposition. During the next solvothermal treatment with Bi^{3+} salt and EDTA-2Na, the defects on crystalline Te rods caused by KOH simultaneously are easy to undergo a reaction with $[\text{Bi}(\text{EDTA})]^+$ to form Bi_2Te_3 seeds on Te rods, as described in Fig. 4a. The orientation relationship of the growth direction between Bi_2Te_3 and Te is chosen in minimum energy way, which has been discussed above. Then, the newly nucleated Bi_2Te_3 seeds tend to grow into Bi_2Te_3 sheets under the influence of EDTA. [9] Further epitaxial growth of the Bi_2Te_3 seeds perpendicular to the axial direction of the Te rods results in the

structure of Bi_2Te_3 sheets from the top to the bottom face. Finally, Bi_2Te_3 -Te sheet-rod arrays are fabricated successfully.

4. Conclusions

In summary, semiconductor materials Bi_2Te_3 -Te array in multiple heterostructure that we call “sheet-rod” can be grown using Te nanorods as the in-situ templates under the solvothermal process. The possible mechanism is an in-situ growth of Bi_2Te_3 nanosheets on Te nanorods. This method is simple and easy to control. This synthetic protocol could be extended for the synthesis of nanowire arrays of other metal chalcogenides. The films of nanowire arrays also exhibit attractive thermoelectric properties, leading to novel thermoelectric materials and devices for applications.

Acknowledgments

The work was supported by the National Natural Science Foundation of China under Grant no. 50772005, the National High Technology Research and Development Program of China under Grant no. 2009AA03Z322 and Beijing Technology Topic Program under Grant no. Z08000303220808.

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