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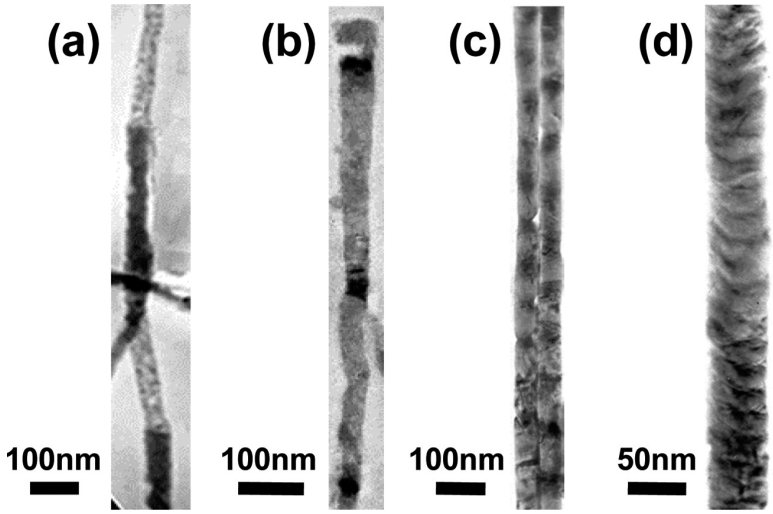

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Direct Electrodeposition of Highly Dense Bi/Sb Superlattice Nanowire Arrays

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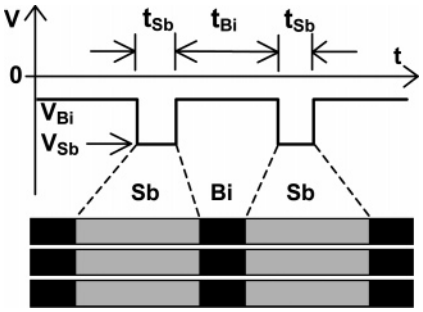
Heterostructure formation in one-dimensional nanostructures is equally important for their unique physics properties and has produced much interesting research.[1−3] Recently Yang et al.[4] developed a hybrid pulsed laser ablation/chemical vapor deposition (PLA-CVD) process for the synthesis of Si/SiGe nanowires with longitudinally ordered heterostructures. Almost at the same time, Charles M. Lieber et al.[5] demonstrate the synthesis of GaAs/GaP superlattices by laser-assisted catalytic growth using GaAs and GaP targets.

Theoretical study indicated that superlattice nanowires are promising systems for the thermoelectric applications, because this structure is believed to be better in reducing phonon transport and keeping high electron mobility.[6,7] Starting from Martin's pioneer work about template-based methods for the preparation of nanomaterials,[8] many important thermoelectric materials such as one-dimensional (1D) Bi,Sb nanowires have been synthesized,[9] especially in recent years. $Bi_{1-x}Sb_x$, $Bi_{2-x}Sb_xTe_3$, $Bi_2Te_{3-y}Se_y$, and Bi_2Te_3 nanowires have been synthesized by Stacy et al and Penner et al;[10−13] however, the report on superlattice formation in 1D nanostructure arrays of these thermoelectric materials is still lacking. Based on Searson, Mallouk, and Bai's method of preparing "striped" nanowires,[14] here in this paper, we developed the method to synthesize 1D Bi/Sb superlattice nanowires in anodic alumina membranes (AAM) by means of a pulsed electrodeposition technique in a single ethanol bath.

A two-step anodization was used to fabricate the AAM template as described previously.[15] First high-purity aluminum foils were anodized in a 0.3 M oxalic acid solution for 5 h to prepare preliminary alumina layer at a constant voltage of 40 V at 15 °C. After removal of the alumina layer in a mixture of 6 wt % H_3PO_4 and 1.5 wt % $H_2Cr_2O_4$, the aluminum foils were oxidized again for 12 h at the same conditions mentioned above. The thought-hole AAM was obtained after chemically removing the remaining aluminum and the alumina barrier layer. The pore diameter of AAM can be enlarged by immersing AAM into 5 wt % H_3PO_4 solutions, and the pores sizes can be adjusted by controlling the etching time. The pore diameter of the AAM used here is about 50 nm, the thickness of the AAM is about 75 μm, and the pore density is about 2.31×10^{10} cm^{-2}.

An Au layer serving as a working electrode was evaporated on one side of the AAM. Then the pulsed electrodeposition was carried out under modulated voltage control in a common two-electrode electrochemical cell at 16 °C. The single ethanol electrolyte consisted of 0.01 M $BiCl_3$, 0.08 M $SbCl_3$, 0.2 M H_3BO_3, 0.01 M $C_4H_6O_6$, and 0.1 g of $CH_3(CH_2)_{11}SO_3Na$; the initial pH value was adjusted to 2 by adding appropriate amounts of HCl. Scheme 1 illustrates the synthesis process of superlattice nanowire arrays using the pulsed electrodeposition technique, and two alternative potentials were employed to prepare the Bi/Sb superlattice nanowires within the AAM. The noble element Bi is kept in dilute concentration to limit the amount of Bi co-deposited with the Sb since the Bi deposition potential is much less negative than that of Sb. An

Scheme 1. Superlattice Nanowire Arrays Preparation



average potential V_{Bi} of −0.60 V was applied between cathode and anode for t_{Bi} of 40 s to prepare the Bi segment, followed with an average potential V_{Sb} of −1.40 V for t_{Sb} of 15 s to prepare the Sb segment. The deposition current density of Bi and Sb segments are about 0.8 mA/cm^2 and 4 mA/cm^2, respectively. The segments we obtained at −0.60 V consisted of almost pure Bi, while the segments obtained at −1.40 V consisted predominantly of Sb with a little trace of Bi. The electrodeposition process is controlled by a computer during the whole deposition so that such a procedure can give uniform segment lengths all along the nanowires. The electrodeposition process is stopped when the wires emerge from the AAM surface (as evidenced by a sudden increase of the plating current).

A FE-SEM image of the Bi/Sb nanowire arrays is shown in Figure 1a, it is obvious that the nanowires grow well in AAM, and the diameter of the nanowire is just the same as the pore diameter of AAM. Figure 1b shows the TEM image of the single superlattice nanowire; it can be found that nanowires are formed segment by segment. The physical basis of the image contrast in the TEM images is the difference in atomic weights, which results in the electron-dispersing ability of Bi being stronger than that of Sb, so the darker sections correspond to Bi segments and the brighter sections correspond to Sb segments. The diameter of the nanowire is about 50 nm, and the lengths of the Bi and Sb segments are respectively about 60 and 100 nm, corresponding to a deposition rate of 1.5 and 6.7 nm s^{-1}, respectively. The corresponding diffraction pattern of the nanowire is shown in Figure 1c, two sets of diffraction patterns can be clearly seen, which correspond to the monoclinic Bi($\bar{2}21$), (201), and (022) and hexagonal Sb(1 $1\bar{2}$ 0), (1 $0\bar{1}$ 10), and (2 $1\bar{3}$ 10) lattice planes, respectively.

Figure 2a is a HRTEM image of a typical interface of Bi/Sb superlattice nanowire, a clear interface of Bi and Sb segment can be seen; the sketch map shown in Figure 2b describes the interface between the Bi and Sb segments.

It is very difficult to check the concentration on the so-short Bi,Sb segments in the Bi/Sb superlattice nanowires by an energy-dispersive X-ray microanalysis (EDX); thus, we fabricated two kinds of samples in the same electrolyte as described previously. An average potential V_{Bi} of −0.60 V was used to prepare the

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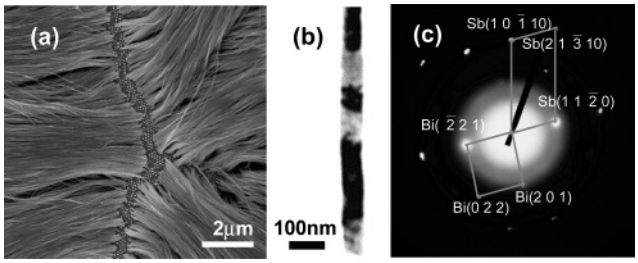

Figure 1. (a) FE-SEM image of the Bi/Sb nanowire arrays. (b) TEM image of a single superlattice nanowire. (c) Its diffraction patterns belong to hexagonal Sb and monoclinic Bi, respectively.

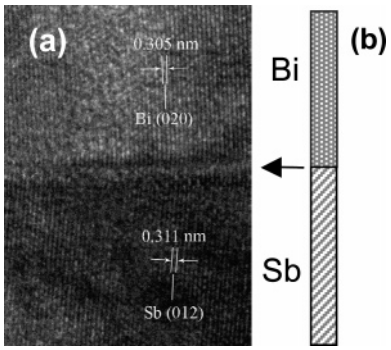

Figure 2. (a) HR-TEM image of a typical interface and (b) schematical map of nanowire.

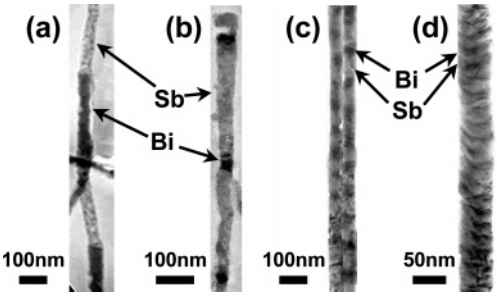

Figure 3. TEM images of Bi/Sb superlattice nanowires.

nanowire whose component is the same as Bi segment in the Bi/Sb superlattice nanowires, and EDX analysis indicates that the components of the nanowires consist of Bi and Sb, and the Sb element is no more than 5%. Also the other sample we obtained under the average potential V_{Sb} of -1.40 V revealed that the Bi element in the Sb segment is no more than 15%.

To prepare the Bi/Sb superlattice nanowires using the pulsed electrodeposition technique, the lengths of Bi and Sb segments in superlattice nanowire arrays can be respectively modulated by changing the deposition time t_{Sb} and t_{Bi}, deposition potential V_{Bi} and V_{Sb}, and the concentrations of Bi^{3+} and Sb^{3+} ions in electrolyte. Here, four kinds of samples with different period structures are shown in Figure 3. The diameters of the nanowires are about 50 ± 7 nm, and the lengths of Bi and Sb segments are in the ranges of 13−350 and 13−325 nm, respectively.

Since the diameter of nanowires satisfactorily corresponds to the pore diameter of the membrane, we can get sizes and density controllable superlattice arrays through adjusting hole size, period, and shape of the AAM template;[16,17] the diameter of the superlattice nanowire can be controlled in a wide range from 8 to 200 nm, and the density from 9.10×10^{10}cm^{-2} to 1.44×10^{9}cm^{-2}.

Furthermore, the method we report here is a quite suitable for preparing other system such as single-domain magnetic superlattices, etc. Moreover, the binary phase nanowires that are quite difficult to make or to control the components in the normal way can be prepared with a sequence process such as heat treatment. In addition, this method can even be used to fabricate nanorods or nanodots by releasing the nanowire from the membrane and dissolving one kind of material of the superlattice nanowires.

In summary, we report a method for preparing superlattice nanowire arrays in a single ethanol bath by using a pulsed electrodeposition technique; here Bi/Sb superlattice nanowire arrays have been fabricated by using this method, and also four kinds of modulated structures of Bi/Sb superlattice nanowires with different periods have been synthesized. This simple and efficient method can be expected to be used in other systems which can be electrodeposited.

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Supporting Information Available: The detailed preparation procedure of the AAM and Bi/Sb superlattice nanowires, sample preparation for observation, EDX results, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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