A Facile Route to Fabricate Single-crystalline Antimony Nanotube Arrays

Liang Li,* Yanhe Xiao, Youwen Yang, Xiaohu Huang, Guanghai Li, and Lide Zhang
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Science, Hefei 230031, P. R. China

(Received March 22, 2005; CL-050381)

Single-crystalline antimony nanotube arrays are fabricated in the anodic alumina membranes using the pulsed electrodeposition technique for the first time. The thickness of Au layer sputtered on the anodic alumina membrane and the pulsed electrodeposition technique are two key factors to produce single-crystalline nanotubes.

Since the discovery of carbon nanotubes, much attention has been focused on nanotube materials because of their novel properties and potential applications in nanodevices.[1,2] In the recent years, many methods have been developed to prepare different types of nanotubes. Among these, the anodic alumina membrane (AAM)-assisted preparation has been widely used to obtain the desired nanotubular materials owing to their controllable sizes and lengths of nanochannels in the AAM. However, all current methods used the so-called "molecular anchor" to pretreat the nanochannels, and the as-prepared samples were amorphous or polycrystalline.[3–5] Therefore, it is still a challenge to develop a method to fabricate single-crystalline nanotube arrays in the AAM by a simple route. As in bismuth, antimony (Sb) is a semimetal with an energy overlap (180 meV) between the conduction and valence bands at 4.2 K, and electronic transport phenomena occur via both electrons and holes, thus unusual transport properties can be expected in one-dimensional nanostructures of antimony. Sb is also a promising thermoelectric material in the future nanodevices.[6] Amorphous and polycrystalline Sb nanowires were prepared in AAM using the vapor-phase deposition technique.[6,7] Recently, our group has successfully fabricated single-crystalline Sb nanowire arrays in AAM using pulsed electrodeposition technique.[8] However, there are few reports on the Sb nanotubes[9,10] and still no report on the fabrication of single-crystalline Sb nanotube arrays in AAM. In this letter, we present the fabrication of single-crystalline Sb nanotube arrays in AAM using a pulsed electrodeposition technique for the first time.

The ordered porous AAM was prepared using a two-step anodic anodization process.[11] A layer of Au was sputtered onto one side of the AAM to serve as a cathode electrode. The pulsed electrochemical deposition was carried out at -1.3 V in a common two-electrode plating cell with a graphite rod as the counter electrode. The pulse time was 1 ms and the delayed time between the two pulses was 2 ms. During the negative pulse time, the Sb was electrodeposited into the pores of AAM. The electrodeposition process paused during the delayed time. The electrolyte contained 0.01 M $SbCl_3$, 0.06 M $C_6H_8O_7 \cdot H_2O$, and 0.03 M $Na_3C_6H_5O_7 \cdot H_2O$. The pH of the solution was adjusted to 2 by adding 1 M H_2SO_4. A schematic representation of forming Sb nanotube arrays is shown in Figure 1.

Figure 2 shows the X-ray diffraction (XRD, Philips PW 1700x) pattern of Sb nanotube arrays. From the pattern, we can see that there is almost one diffraction peak of (110) plane,

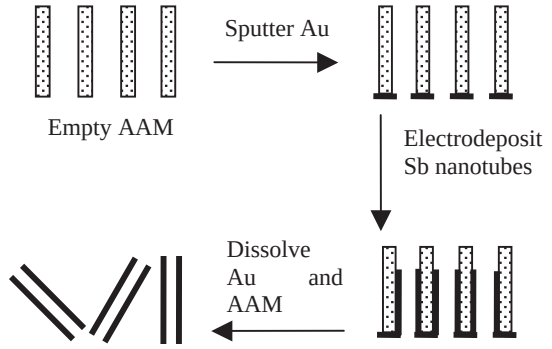

Figure 1. Schematic representation of the fabrication of Sb nanotube array in AAM.

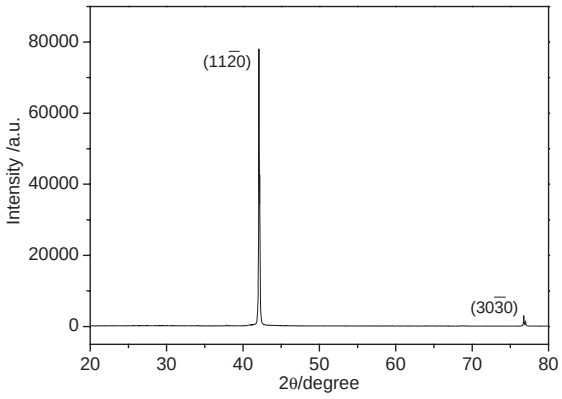

Figure 2. XRD pattern of the Sb nanotube arrays.

whose intensity is much higher than all other peaks, indicating that the Sb nanotube arrays are highly oriented along the [11$\bar{2}$0] crystal direction.

Figure 3 shows the field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) image of the Sb nanotube array after the AAM was partly etched in 1 M NaOH solution for 15 min, which indicates that large-area and ordered nanotube array was formed in the AAM. From the top image of the nanotubes, one can see that the diameter of the nanotubes is about 60 nm, corresponding to the pore size of the AAM used. Figure 4 shows the typical high-resolution transmission electron microscopy (HRTEM) image of the nanotubes and corresponding electron diffraction (ED) pattern (HRTEM, JEOL-2010), which indicates that the nanotube is uniform in diameter, and the wall thickness is about 13 nm, which is in the size range calculated from the full width at half-maximum of the XRD peaks (10–15 nm). The HRTEM lattice fringes are perpendicular to the axis of the nanotubes and show an interplanar spacing of about 0.213 nm, which corresponds to the (11$\bar{2}$0) plane of the bulk hex-

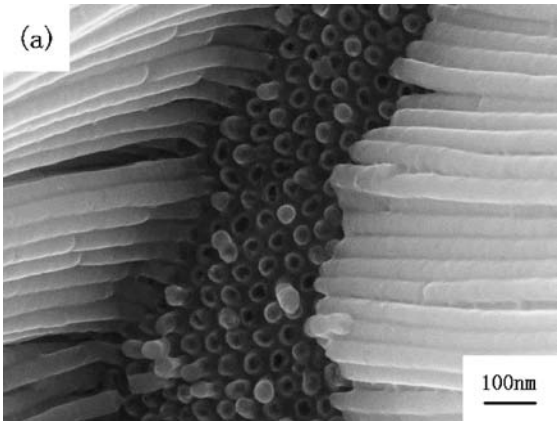

Figure 3. SEM top-view image of Sb nanotube arrays.

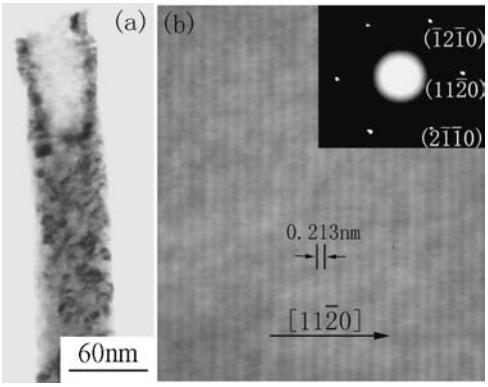

Figure 4. HRTEM image and SAED pattern of the Sb nanotubes.

agonal Sb. It indicates that the growth direction is along the [11$\bar{2}$0] direction, which is in agreement with the XRD result. The ED and HRTEM results demonstrate that the Sb nanotubes are single crystals. One can see that the hollow space of the tube is not very obvious, which may be due to the thick wall thickness or the nature of the metal Sb. The same phenomenon was also observed in the previous report.[12]

To fabricate single crystalline Sb nanotube arrays, two key factors must be well controlled. One is that the thickness of Au layer sputtered on the AAM should be thin enough not completely covering the pores of AAM, as shown in Figure 1. The Sb is preferentially deposited on the Au, and then grows along the axis direction of the nanochannels of AAM to form nanotubes. The other factor is the pulsed electrodeposition technique. During the pulse time (from 500 μs to 1 ms), which is so short that only a small number of Sb is consumed and no large concentration gradient is formed, the Sb is electrodeposited into the pores. The delayed time (from 1 ms to 2 ms), which is long enough, provides enough time for the Sb concentration to recover. Therefore the pulse time controls the atom-by-atom growth of nanotubes, which favors the perfect crystallinity and preferential orientation of nanotubes.

In conclusion, we have successfully fabricated single crystalline Sb nanotube arrays in AAM using pulsed electrodeposition technique. The diameter of nanotubes is about 60 nm and depends on the pore size of AAM used. The Sb nanotubes are single crystals and highly oriented along the [11$\bar{2}$0] crystal direction. We expect that this method can be used to fabricate other single crystalline metal nanotube arrays.

This work was supported by the National Natural Science Foundation of China (No. 10474098).

References

1 S. Iijima, *Nature*, **354**, 56 (1991).
2 J. W. Wang and Y. D. Li, *Adv. Mater.*, **15**, 445 (2003).
3 B. B. Lakshmi, P. K. Dorhout, and C. R. Martin, *Chem. Mater.*, **9**, 857 (1997).
4 J. C. Bao, C. Y. Tie, Z. Xu, Q. F. Zhou, D. Shen, and Q. Ma, *Adv. Mater.*, **13**, 1631 (2001).
5 M. S. Sander, M. J. Côté, W. Gu, B. M. Kile, and C. P. Trilpp, *Adv. Mater.*, **16**, 2052 (2004).
6 J. Heremans, C. M. Thrush, Y. M. Lin, S. B. Cronin, and M. S. Dresselhaus, *Phys. Rev. B*, **63**, 85406 (2001).
7 M. Barati, J. C. L. Chow, P. K. Ummat, and W. R. Datars, *J. Phys.: Condens. Matter*, **13**, 2955 (2001).
8 Y. Zhang, G. H. Li, Y. C. Wu, B. Zhang, W. H. Song, and L. D. Zhang, *Adv. Mater.*, **14**, 1227 (2002).
9 H. M. Hu, M. S. Mo, B. J. Yang, M. W. Shao, S. Y. Zhang, Q. W. Li, and Y. T. Qian, *New J. Chem.*, **27**, 1161 (2003).
10 D. B. Wang, D. B. Yu, Y. Y. Peng, Z. Y. Meng, S. Y. Zhang, and Y. T. Qian, *Nanotechnology*, **14**, 748 (2003).
11 L. Li, Y. Zhang, G. H. Li, and L. D. Zhang, *Chem. Phys. Lett.*, **378**, 244 (2003).
12 H. M. Hu, M. S. Mo, B. J. Yang, M. W. Shao, S. Y. Zhang, Q. W. Li, and Y. T. Qian, *New J. Chem.*, **27**, 1161 (2003).

Published on the web (Advance View) June 4, 2005; DOI 10.1246/cl.2005.930