Fabrication of Antimony Junction Nanowires in Anodic Alumina Membranes

Liang Li,* Yanhe Xiao, Youwen Yang, Guanghai Li, Yan Li, and Lide Zhang
Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructure, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, P. R. China

(Received June 27, 2005; CL-050824)

Antimony junction nanowire arrays were fabricated in the anodic alumina membranes using the pulsed electrodeposition technique for the first time. The etching period in phosphoric acid controls the diameter and the length of each segment of nanowires. The repeating times of etching and electrodeposition control the number of junction.

In the past few years, one-dimensional (1D) nanostructured materials have attracted great interest because of their unique properties and potential technological applications.[1,2] Many methods, such as laser ablation, CVD, and hydrothermal method, have been developed to fabricate nanowires and other nanostructured materials.[3–5] Among them the anodic alumina membrane (AAM)-based synthetic methods have been proved to be very effective routes to fabricate 1D metal and semiconductor nanowires and nanotubes.[6–8] It is worthy to note that nanowires with different morphologies were also fabricated by designing the special pore morphology of the AAM. Lee et al. have fabricated linearly joined carbon nanotubes longer than 60 nm and smaller than 30 nm in diameters in AAM.[9] Gao et al. and Li et al. have fabricated *Y*-junction Cu nanowires and carbon nanotubes in AAM.[10,11] Recently, Li et al. has successfully fabricated tapering Bi nanowires in AAM by simply changing the pulsed parameters.[12]

Antimony (Sb) is an important element in both fundamental research and practical application. For example, Sb is an important component in forming III-V Sb-based semiconductor materials which are valuable in electronics and optoelectronics as well as in forming thermoelectric materials.[13] Amorphous and polycrystalline Sb nanowires have been prepared in AAMs using the vapor-phase deposition technique and their transport properties have been also studied.[14,15] Single-crystalline Sb nanowire arrays have been prepared by pulsed electrodeposition in AAMs in our group.[16] In this letter, we present a versatile method to fabricate Sb junction nanowires by pulsed electrodeposition in the AAM for the first time.

The ordered porous AAM with the pore size of 60 nm was prepared using a two-step anodic anodization process as described previously.[17] A layer of Au film was sputtered onto one side of the AAM to serve as the cathode electrode. The pulsed electrochemical deposition was carried out at −1.1 V in a common two-electrode plating cell with a graphite rod as the counter electrode. The pulse time was 400 μs and the delayed time between the two pulse times was 800 μs. During the negative pulse time, the Sb was electrodeposited into the nanopores of AAM. Detailed process of pulsed electrodeposition is shown in Ref. 16.

Figure 1 schematically illustrates the procedure for the fabrication of Sb junction nanowire array in AAM. Firstly, Sb nanowires with the diameter corresponding to the pore size of the AAM were electrodeposited into the nanopores of the AAM with

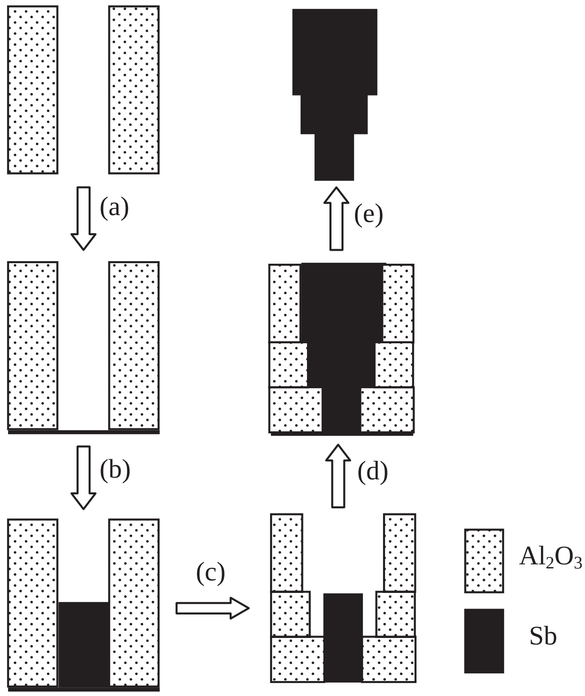

Figure 1. Schematic diagram of fabrication of Sb junction nanowire array in the anodic alumina membrane (AAM). (a) Sputtering deposition of Au film on the bottom of AAM, (b) electrodeposition of Sb into the nanopores of the AAM, (c) floating the AAM on the top of the H_3PO_4 solution to etch the nanopores, (d) electrodeposition of Sb into the etched nanopores, and (e) removal of the AAM to obtain free-standing nanowires.

proper depositing time. Secondly, the AAM was floated on the top of H_3PO_4 (5 wt %) solution with the top surface of the AAM facing the solution (30 °C, 30 min). Finally, the AAM was carefully rinsed with deionized water for several times and then electrodeposited to obtain the final Sb junction nanowires.

Figure 2 shows the X-ray diffraction (XRD, Philips PW 1700x) pattern of Sb junction nanowire arrays. From the pattern, one can see that there is only one diffraction peak, corresponding to (110) plane of bulk hexagonal Sb, indicating that the Sb junction nanowire arrays are highly oriented along the $[11\bar{2}0]$ crystal direction.

Figure 3 shows the typical transmission electron microscopy (TEM, JEOL JEM-210CX) image of individual Sb nanowire after complete etching of the AAM in NaOH solution. It can be seen that the Sb nanowire consists of three segments with different diameters: (1) nanowire with the diameter corresponding to the pore size (60 nm) of AAM, (2) nanowire with relative large diameter of 75 nm, and (3) nanowire with the maximum

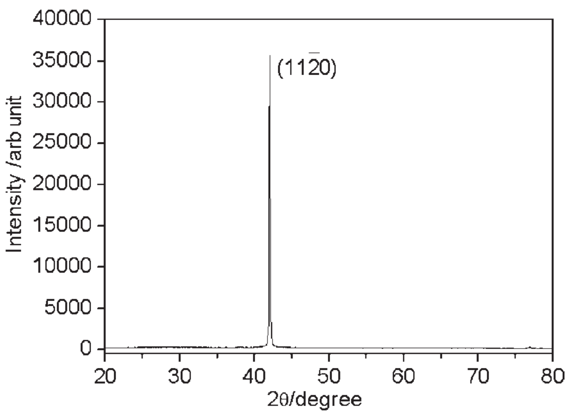

Figure 2. XRD pattern of the Sb junction nanowire array.

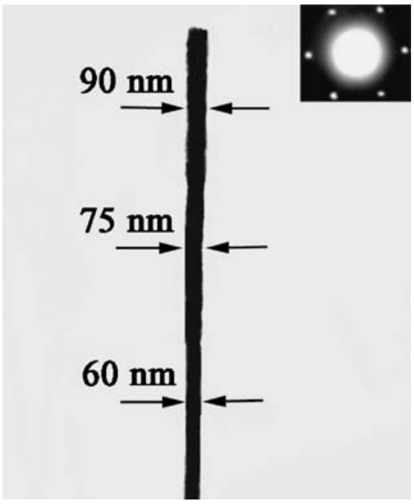

Figure 3. TEM image and the corresponding SAED pattern of individual Sb junction nanowire.

diameter of 90 nm. The corresponding selected area electron diffraction (SAED) patterns show that the nanowire is single-crystalline.

From the fabrication process of Sb junction nanowires, one can see that the etching period and the repeating etching times are two key factors. As shown in Figure 1c, after the AAM with Sb nanowires was floated on the top of H_3PO_4 solution, the upper pore (empty nanopores) of the AAM was quickly etched and enlarged. The bottom part (filled nanowires) of the AAM was slowly etched due to the relative close interface between the Sb nanowire and the pore wall of AAM, and the etching depth increased with increasing the etching period. When the etched AAM was electrodeposited again, the Sb three-junction nanowires were fabricated (Figure 1d). Therefore, from the technical viewpoint, we can obtain junction nanowires by circular etching and electrodepositing in AAM. In addition, it is easy to understand that the etching period controlled the diameter and length of each segment of nanowires, namely, the length and diameter of each segment increases with increasing the corresponding etching time.

In conclusion, we have successfully fabricated Sb junction nanowire arrays in AAM by simply etching AAM in phosphoric acid solution using pulsed electrodeposition technique. We expect that this method can be used to fabricate other metal junction nanowire arrays in AAM and applied to circuits in the future nanodevices.

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

References

1 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, E. Kim, and H. Yan, *Adv. Mater.*, **15**, 353 (2003).
2 J. W. Wang and Y. D. Li, *Adv. Mater.*, **15**, 445 (2003).
3 N. Fukata, T. Oshima, K. Murakami, T. Kizuka, T. Tsurui, and S. Ito, *Appl. Phys. Lett.*, **86**, 213112 (2005).
4 C. H. Liang, Y. Shimizu, T. Sasaki, H. Umehara, and N. Koshizaki, *J. Phys. Chem. B*, **108**, 9728 (2004).
5 Y. Liu, Y. G. Zhang, Y. H. Hu, and Y. T. Qian, *Chem. Lett.*, **34**, 146 (2005).
6 K. H. A. Lau, L. S. Tan, K. Tamada, M. S. Sander, and W. Knoll, *J. Phys. Chem. B*, **108**, 10812 (2004).
7 X. P. Shen, M. Han, J. M. Hong, Z. L. Xue, and Z. Xu, *Chem. Vap. Deposition*, **11**, 250 (2005).
8 C. J. Li, Y. G. Guo, B. S. Li, C. R. Wang, L. J. Wan, and C. L. Bai, *Adv. Mater.*, **17**, 71 (2005).
9 J. S. Lee, G. H. Gu, H. Kim, K. S. Jeong, J. Bae, and J. S. Suh, *Chem. Mater.*, **13**, 2387 (2001).
10 T. Gao, G. W. Meng, J. Zhang, S. H. Sun, and L. D. Zhang, *Appl. Phys. A*, **74**, 403 (2002).
11 J. Li, C. Papadopoulos, and J. Xu, *Natur*e, **402**, 253 (1999).
12 L. Li, Y. Zhang, G. H. Li, W. H. Song, and L. D. Zhang, *Appl. Phys. A*, **80**, 1053 (2005).
13 A. L. Prieto, M. Martin-Gonzalez, J. Keyani, R. Gronsky, T. Sands, and A. M. Stacy, *J. Am. Chem. Soc.*, **15**, 2388 (2003).
14 J. Heremans, C. M. Thrush, Y. M. Lin, S. B. Cronin, and M. S. Dresselhaus, *Phys. Rev. B*, **63**, 85406 (2001).
15 M. Barati, J. C. L. Chow, P. K. Ummat, and W. R. Datars, *J. Phys: Condens. Matter*, **13**, 2955 (2001).
16 Y. Zhang, G. H. Li, Y. C. Wu, B. Zhang, W. H. Song, and L. D. Zhang, *Adv. Mater.*, **14**, 1227 (2002).
17 H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).

Published on the web (Advance View) August 13, 2005; DOI 10.1246/cl.2005.1274