



A route to fabricate single crystalline bismuth nanowire arrays with different diameters

Liang Li, Yong Zhang, Guanghai Li^{*}, Lide Zhang

Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, China

Received 24 July 2003; in final form 24 July 2003

Abstract

Single crystalline bismuth nanowire arrays in anodic alumina membrane have been fabricated by pulsed electrodeposition. The nanowires of different diameters were obtained by changing the electrical parameter of the pulsed electrodeposition using anodic alumina membrane as template with the same pore size. X-ray diffraction and TEM analysis show that the bismuth nanowires are single crystalline with highly preferential orientation, and the diameter of nanowires increases with increasing the relaxation time of pulse. The growth mechanism of nanowires was discussed.

© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Bismuth, with a rhombohedral crystal lattice structure, is a semimetal with a small effective electron mass, long carrier mean free path, highly anisotropy Fermi surface and small energy overlap (about 38 meV at 77 K) between the L-point conduction band and the T-point valence band, which can lead to semimetal–semiconductor transition in bismuth nanowires with decreasing the diameter to a certain value (about 60 nm at 77 K) [1,2]. Theoretical and experimental results showed that one-dimensional bismuth nanowires could have an even larger enhancement in thermoelectric efficiency relative to the bulk and two-dimensional

systems [3–8]. Because of potential application as thermoelectric devices the fabrication of bismuth nanowire array has attracted much attention in recent years.

The template-assisted synthesis of nanowires is a conceptually simple and intuitive way to fabricate nanostructures. These templates contain very small cylindrical pores or voids within the host material, and the empty spaces are filled with the chosen material, which adopts the pore morphology, to form nanowires. Anodic alumina membrane (AAM) is frequently used for nanowire synthesis. Different filling methods have been reported for preparing nanowire array using template synthesis, including vacuum melting and pressure injection process [9], vapor-phase deposition technique [10,11] and direct current (DC) electrodeposition [12]. Recently, pulsed electrodeposition technique has become a most efficient

^{*} Corresponding author. Fax: +860-551-559434.
E-mail address: ghli@issp.ac.cn (G. Li).

method for the growth of uniform and continuous nanowires [13–18]. Sauer et al. [13] studied the fabrication of monocrystalline Ag in AAM and found that a highly conductive metal containing electrolyte, a homogeneous aluminium oxide barrier layer and pulsed electrodeposition are a prerequisite in obtaining homogeneously filled pore membranes. Guo et al. [14] have successfully fabricated highly ordered composite Ni–Cu nanowires in AAM by pulsed electrodeposition. Of which the pore size distribution, pore orientation, and surface toughness of AAM have an important effect on the properties of nanowires. The filling efficiency of material generally decreases with decreasing the diameter of nanowires, and AAM with different pore sizes is needed in order to prepare nanowires array with different diameters. In this Letter, we report the fabrication of single crystalline bismuth nanowire arrays with different diameters by pulsed electrodeposition in AAM with single pore size.

2. Experimental

The anodic alumina membrane was formed by a two-step anodization process as described previously [19–21]. First, high purity aluminum sheet (99.999%) was anodized at 40 V in 0.3 M oxalic acid electrolyte at 12 °C for 4 h. The alumina layer produced was removed by immersing it in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at 60 °C for 6 h. The second anodization process was performed under the same conditions as the first one for 12 h. After the anodization, the bottom central aluminum substrate was removed in a saturated SnCl₄ solution, then the alumina barrier layer was dissolved in 6 wt% phosphoric acid solution at 30 °C for 1.5 h to get the final AAM with the pore size of about 80 nm. A layer of Au with about 60 nm in thickness was sputtered onto the bottom side of the AAM to serve as conduction contact.

Bismuth nanowires array was deposited from a plating solution consisted of BiCl₃ 40 g/l, tartaric acid 50 g/l, glycerol 100 g/l, NaCl 70 g/l and HCl 1 mol/l. The pH value of the electrolyte was adjusted to about 0.9 by adding appropriate amounts

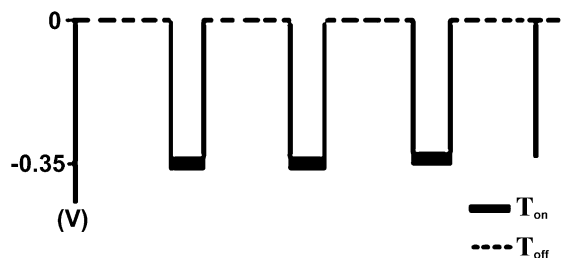


Fig. 1. Schematic of the pulse cycle for the pulsed electrodeposition. T_{on} and T_{off} represent the deposition time and relaxation time of each pulse cycle, respectively.

of aqueous ammonia 5 mol/l in order to avoid corrosive attack of the AAM.

The pulsed electrodeposition was carried out at -0.35 V applied between graphite anode and AAM cathode in a common two-electrode glass plating cell at 10 °C with different pulse cycles, as shown schematically in Fig. 1. The relaxing time (T_{off}) between two successive pulsed cycles was varied to study the influence of the pulsed time on the structure of bismuth nanowires. The duty cycle (pulsed deposition time T_{on}) was kept as constant, 10 ms.

Dissolving AAM in an aqueous solution of 5 wt% NaOH, and immersing them in an ultrasonic bath for 10 min obtained the nanowires for TEM observation. A drop of solution was placed on a carbon grid and allowed to dry prior to electron microscopy analysis. TEM analysis was performed using a JEOL JEM-200CX transmission electronic microscope and a JEOL 2010 high resolution transmission electron microscope. X-ray diffraction spectra were obtained on a rotating anode X-ray diffractometer (D/MAX-rA) with Cu K α radiation ($\lambda = 1.542 \text{ \AA}$).

3. Results and discussion

Fig. 2 shows XRD patterns of bismuth nanowire arrays fabricated with different relaxation time together with the standard diffraction peaks of bismuth (JCPDS No.5-0519). From the patterns, we can see that there is a very strong diffraction peak at $2\theta = 48.90^\circ$ corresponding to (0 2 2) plane of bismuth for samples fabricated with the relaxation

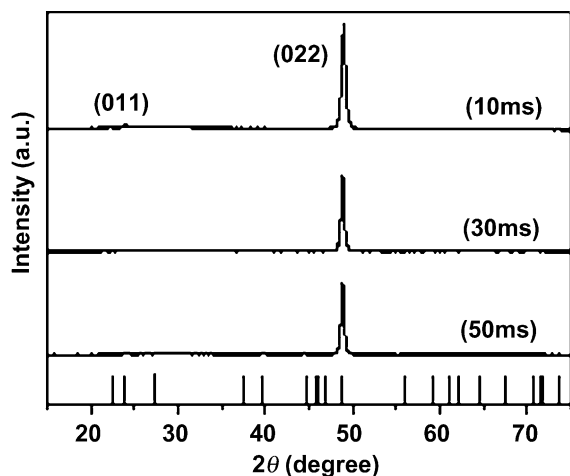


Fig. 2. XRD patterns of bismuth nanowire arrays with different relaxation time.

time 30 and 50 ms. In addition, two peaks (0 1 1) and (0 2 2), the ratio of which is integral, are found for nanowire arrays fabricated with the relaxation time 10 ms. At the same time, all other peaks are very weak. The nanowires are a rhombohedral lattice structure as comparing with the standard diffraction of bulk bismuth. It is worthy to note that the orientation of all the samples are the same in spite of the different relaxation time. This result indicates that bismuth nanowires grow preferentially along [0 2 2] direction.

Fig. 3 shows TEM images of Bi nanowires fabricated with the relaxation time of 10 ms. A bundle of nanowires removed from the AAM can be clearly seen in Fig. 3a, and the average diameter of the nanowires is about 20 nm, which is much smaller than the pore size of the template with the diameter of 80 nm, as clearly shown in Fig. 3b, in which the nanowires are still within the pores of the AAM. A single nanowire and the corresponding SAED are shown in Fig. 3c. One can see that the nanowire is relative uniform. The SAED shows that the nanowires are single crystals with a rhombohedral lattice structure, which further confirms the XRD results. Figs. 4 and 5 show TEM images of Bi nanowires fabricated with the relaxation time of 30 and 50 ms, respectively. The average diameter of Bi nanowires fabricated with the relaxation time of 30 ms is about 33 nm, and

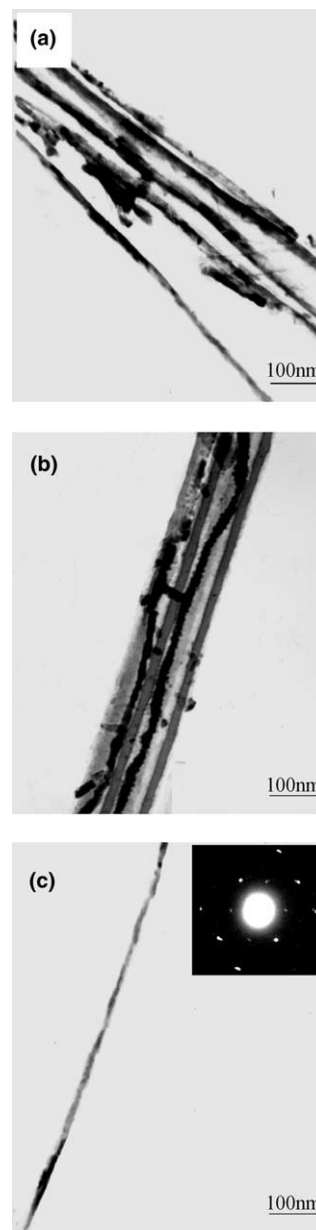


Fig. 3. TEM images of bismuth nanowires fabricated using the relaxation time 10 ms with the diameter of 20 nm, (a) free standing, (b) inside the template and (c) a single.

that of 50 ms is about 80 nm. The corresponding SAED patterns of a single nanowire also indicate the nanowire is a single crystal. These results indicate that the diameters of Bi nanowires can be modulated by changing the relaxation time of

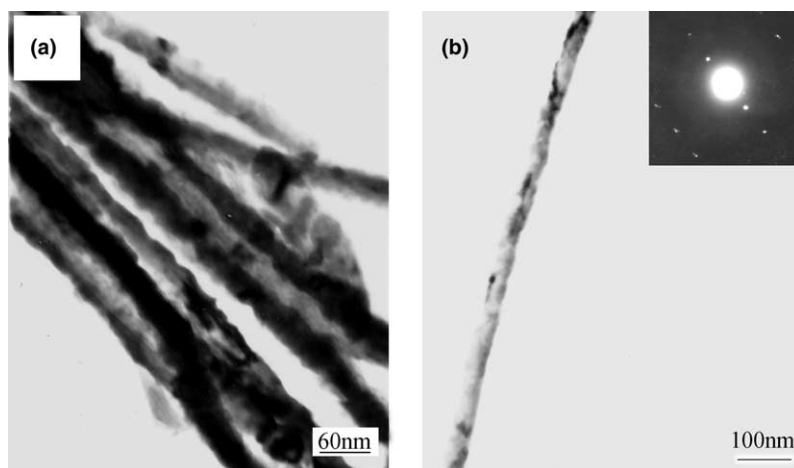


Fig. 4. TEM images of bismuth nanowires fabricated using the relaxation time 30 ms with the diameter of 33 nm, (a) free standing and (b) a single.

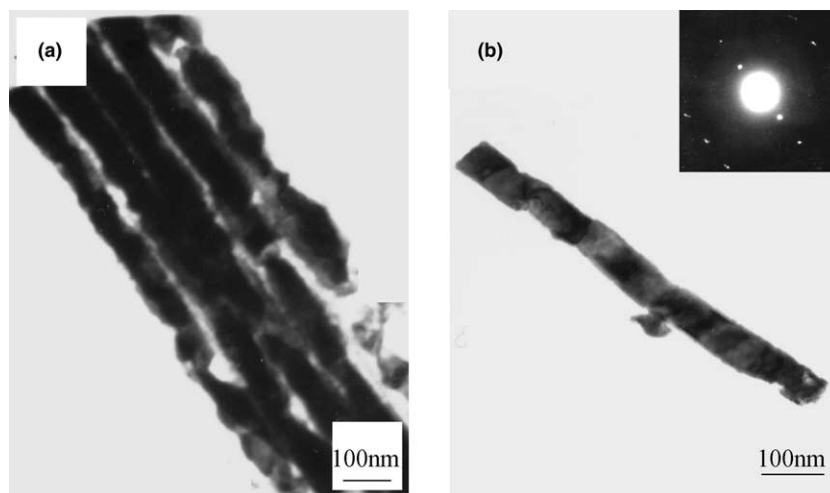


Fig. 5. TEM images of bismuth nanowires fabricated using the relaxation time 50 ms with the diameter of 80 nm, (a) free standing and (b) a single.

pulsed electrodeposition. The length of the nanowires depends only on the thickness of AAM. From TEM images, one also can see that most nanowires are cylindrical in shape and identical in diameter, but there are some twist or rupture in the nanowires, which might result from the mechanical force during the ultrasonication treatment of the TEM samples.

Above results indicate that the diameters of Bi nanowires can be controlled from 20 to 80 nm (the pore size of the empty AAM) through modulating

the relaxation time of pulse from 10 to 50 ms with the constant pulsed deposition time of 10 ms. It was also found that when the relaxation time was shorter than 10 ms, the crystallinity of nanowires gradually decreases, and in some cases even no nanowires can be fabricated. The selection of the optimal relaxation time is very important in the growth of single crystalline Bi nanowires.

Previous studies have shown that the degree of preferred orientation of Bi nanowire is imperfect and the peak positions changed randomly when

the diameters of nanowires changed from 23 to 95 nm [22,23]. Comparatively, the XRD analysis in the present study reveals that the preferential orientation of Bi nanowires with different diameters is the same and along [0 2 2] direction.

Zhang et al. [24] have discussed the mechanism of pulsed electrodeposition and pointed out that the pulsed time in each pulse cycle was so short, compared to the relaxation time, that only a small number of metal ions were reduced during one pulse, and the metal ion concentration gradient at the reaction interface produced can be recovered during the relaxation time. Thus the pulsed time controls the atom-by-atom growth of Bi nanowires, which favored the preferentially oriented growth of the nanowires. During the pulsed deposition time, the metal ions at the reaction interface are consumed, but can be recovered during the relaxation time, and the recover degree becomes better and better gradually with increasing relaxation time. When the relaxation time is much long, enough metal Bi ions can be provided for electrodeposition, and Bi ions have adequate time to diffuse along the direction vertical to axes of the pores of template, which provide initial atom by atom growth on all area of the bottom of pores, in which a continuous growth along the direction of pores takes place. But under a relative short relaxation time the number of metal Bi ions provided and recovered is not enough, resulting in an initial growth only on part area of the bottom of the pores, which leads to a thin nanowires.

With this technique it is possible to fabricate nanowire heterostructure since we can grow bismuth nanowire in a template with different diameters (and different characters), i.e., nanowires with either semiconductor and/or semiconductor/semimetal. The transport and thermoelectric properties of nanowire array depend on the orientation of nanowires, and thus the fabrication of nanowires array with different preferential orientation is very important, further work is under way.

4. Conclusion

We have successfully fabricated single crystalline Bi nanowire arrays by pulsed electrodeposition. A

very easy route to prepare Bi nanowire arrays with different diameters using AAM with a single pore size was proposed. The Bi nanowires are highly oriented along [0 2 2] direction. It was found that the diameter of Bi nanowires can be modulated by changing the relaxation time of pulsed electrodeposition, and when the relaxation time changed from 10 to 50 ms and keep constant pulse deposition time at 10 ms, the average diameter of Bi nanowires increases from 20 to 80 nm. The selection of the optimal relaxation time is very important in the growth of single crystalline Bi nanowires.

Acknowledgements

This work is supported by the National Key Project of Fundamental Research for Nanomaterials and Nanostructures.

References

- [1] Z.B. Zhang, X.Z. Sun, M.S. Dresselhaus, J.Y. Ying, *Appl. Phys. Lett.* 73 (1998) 1589.
- [2] Z.B. Zhang, J.Y. Ying, M.S. Dresselhaus, *J. Mater. Res.* 13 (1998) 1745.
- [3] L.D. Hicks, M.S. Dresselhaus, *Phys. Rev. B* 47 (1993) 16631.
- [4] Y.M. Lin, O. Rabin, S.B. Cronin, J.Y. Ying, *Appl. Phys. Lett.* 81 (2002) 2403.
- [5] L.D. Hicks, M.S. Dresselhaus, *Phys. Rev. B* 47 (1993) 12727.
- [6] J.P. Heremans, C.M. Thrush, D.T. Morelli, M.C. Wu, *Phys. Rev. Lett.* 88 (2002) 216801.
- [7] Y.M. Lin, X.Z. Sun, M.S. Dresselhaus, *Phys. Rev. B* 62 (2000) 4610.
- [8] A.L. Prieto, M.M. Gonzalez, J. Keyani, R. Gronsky, T. Sands, A.M. Stacy, *J. Am. Chem. Soc.* 125 (2003) 2388.
- [9] Z.B. Zhang, D. Gekhtman, M.S. Dresselhaus, J.Y. Ying, *Chem. Mater.* 1 (1999) 1659.
- [10] J. Heremans, C.M. Thrush, Y.M. Lin, Z. Zhang, M.S. Dresselhaus, J.F. Mansfield, *Phys. Rev. B* 61 (2000) 2921.
- [11] J. Heremans, C.M. Thrush, Z. Zhang, X. Sun, M.S. Dresselhaus, J.Y. Ying, D.T. Morelli, *Phys. Rev. B* 58 (1998) R10091.
- [12] K. Liu, C.L. Chien, P.C. Searson, K.Y. Zhang, *Appl. Phys. Lett.* 73 (1998) 1436.
- [13] G. Sauer, G. Brehm, S. Schneider, K. Nielsch, R.B. Wehrspohn, J. Choi, H. Hofmeister, U. Gösele, *J. Appl. Phys.* 91 (2002) 3243.
- [14] Y.G. Guo, L.J. Wan, C.F. Zhu, D.L. Yang, D.M. Chen, C.L. Bai, *Chem. Mater.* 15 (2003) 664.

- [15] K. Niensch, F. Müller, A.P. Li, U. Gösele, *Adv. Mater.* 12 (2000) 582.
- [16] D. Dobrev, J. Vetter, N. Angert, R. Neumann, *Appl. Phys. A* 69 (1999) 233.
- [17] K.H. Choi, H.S. Kim, T.H. Lee, *J. Power Sources* 75 (1998) 230.
- [18] M. Sun, G. Zangari, M. Shamsuzzoha, R.M. Metzger, *Appl. Phys. Lett.* 78 (2001) 2964.
- [19] K. Niensch, F. Muller, A.P. Li, U. Gosele, *Adv. Mater.* 12 (2000) 582.
- [20] H. Masuda, H. Yamada, M. Satoh, H. Asoh, M. Nakao, T. Tamamura, *Appl. Phys. Lett.* 71 (1997) 2770.
- [21] H. Masuda, K. Fukuda, *Science* 268 (1995) 1466.
- [22] Y. Peng, D.H. Qin, R.J. Zhou, H.L. Li, *Mater. Sci. Eng. B* 77 (2000) 246.
- [23] X.F. Wang, J. Zhang, H.Z. Shi, Y.W. Wang, G.W. Meng, X.S. Peng, L.D. Zhang, *J. Appl. Phys.* 89 (2001) 3847.
- [24] Y. Zhang, G.H. Li, Y.C. Wu, B. Zhang, W.H. Song, L.D. Zhang, *Adv. Mater.* 14 (2002) 1227.