

Diameter-depended thermal expansion properties of Bi nanowire arrays

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The lattice parameter of bismuth nanowires has been measured using the *in situ* high-temperature x-ray diffraction method. Single-crystalline Bi nanowire arrays with the diameters from 10 nm to 250 nm have been fabricated within the porous anodic alumina membranes by a pulsed electrodeposition technique. Different temperature dependencies of lattice parameter and thermal expansion coefficient were found for Bi nanowires with different diameters, and there is a transition from positive thermal expansion coefficient at low temperature to negative one at high temperature, and the transition temperature shifts to high temperature with the increase in the diameter of Bi nanowires. © 2005 American Institute of Physics. [DOI: 10.1063/1.2000327]

One-dimensional (1D) nanostructures, such as nanowires and nanotubes, represent the smallest dimension for efficient transport of electrons and phonons and thus are ideal building blocks for hierarchical assembly of functional nanoscale electronic and photonic structures.^{1,2} With the development of nanodevices, the study of thermal expansion properties of 1D nanomaterials have become the focus of intensive research. The thermal expansion properties of thin films and nanoparticles, such as Nb thin film,³ Se nanoparticle,⁴ Au nanoparticle,⁵ and CdSe nanoparticle,⁶ have been extensively studied, but little attention has been paid to 1D nanomaterials,^{7,8} which may be due to the difficulty in synthesizing dimension- and morphology-controlled 1D nanomaterials. Recently many attempts have been made to fabricate 1D nanomaterials, among those the porous anodic alumina membrane (AAM)-based synthesis in conjunction with electrodeposition is a relatively simple and effective route to synthesize uniformly sized nanowires,^{9,10} because the AAM has nanometer-sized channels ($\approx 20\text{--}250$ nm in diameter) with high pore density (up to 10^{10} cm⁻²) and controllable channel lengths.

Bismuth (Bi) is a semimetal with unique thermoelectric properties that result from its highly anisotropic Fermi surface, small effective electron mass, and long carrier mean-free path.^{11,12} The physical properties of Bi nanowires strongly depend on the diameters and orientations of nanowires, for example, the semimetal-semiconductor transition will happen when the diameters decrease to a certain value.^{13,14} Compared with the bulk, 1D Bi and Bi-based alloys nanowires could have a larger thermoelectric efficiencies, especially when the wire diameter is down to about 10 nm.^{15,16} Thus the study of Bi nanowires with different diameters and orientations is very important. The Bi nanowires have been prepared by different methods, such as, vacuum melting and pressure injection process,¹⁷ vapor-phase deposition technique,¹⁸ direct current and alternating current electrodeposition^{19,20} within AAM. However, the controllable fabrication of Bi nanowires with diameter down to 10 nm is still a challenge because of the decreasing filling efficiency of materials in a small pore size channel of AAM. In our previous study single-crystalline Bi nanowire arrays

with different diameters have been fabricated by the pulsed electrodeposition using a single pore size AAM, and the diameters were controlled simply by changing the pulsed deposition time.²¹

In this letter, *in situ* high-temperature x-ray diffraction is employed to study the thermal expansion behavior of Bi nanowires with different diameters within AAM.

The AAM with the ordered channel arrays was prepared from high-purity (99.999%) aluminum foil in 0.3 M oxalic acid by a two-step anodization process.¹⁹ The AAMs with the pore size of 80 nm were used to fabricate Bi nanowires with the diameters from 10 to 80, while that with pore size of 250 nm was used to fabricate 250 nm Bi nanowires. The detailed electrodeposition process can be found in our previous study.²¹

Figures 1(a) and 1(b) show two typical field emission scanning electron microscopy (FEM) (JEOL JSM-6700F) images of Bi nanowire array with the diameter of 40 nm and 60 nm. It can be seen that high filling, ordered and uniform Bi nanowire arrays were obtained. All the nanowires have the same height, implying that all the Bi ions were simultaneously deposited into the AAM in a large area. The transmission electron microscopy (TEM) (JEOL JEM-200CX) images of individual Bi nanowires with the diameters of 10 nm and 20 nm are shown in Figs. 1(c) and 1(d). One can see that the diameters of Bi nanowires are much smaller than the pore size of AAM, and the nanowires are freestanding

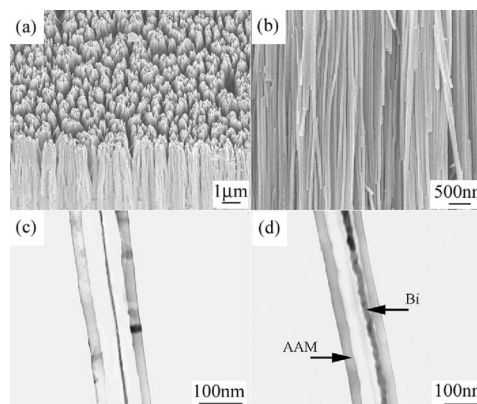


FIG. 1. FEM images of Bi nanowire array: (a) 40 nm and (b) 60 nm; TEM images of a single Bi nanowire within AAM: (c) 10 nm and (d) 20 nm.

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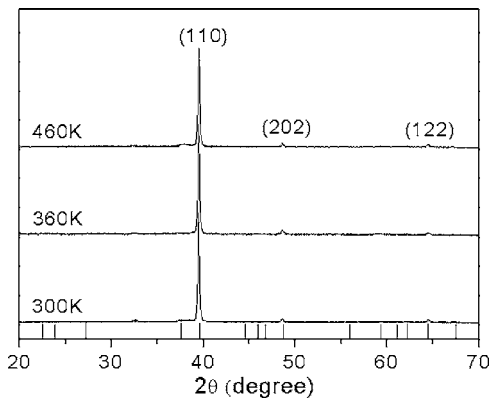


FIG. 2. XRD patterns of Bi nanowire arrays with the diameter of 10 nm at different temperatures.

inside the pore of the AAM. In fact, changing the pulsed deposition time can modulate the diameters of Bi nanowires. In this paper when the pulsed deposition time changes from 10 ms to 25, 30, 35, and 50 ms, keeping the delayed time at 60 ms, the diameter of Bi nanowires increases from 10 nm to 20, 40, 60, and 80 nm.

To investigate thermal expansion behavior of the Bi nanowire arrays with different diameters, *in situ* high-temperature x-ray diffraction (XRD) (Philips PW 1700X) was performed in the temperature range from 300 to 500 K under high vacuum atmosphere. Temperatures were kept constant at each point for 20 min before measurement, and scans were carried out for $20^\circ < 2\theta < 80^\circ$. Figure 2 shows XRD patterns of the Bi nanowire array with the diameter of 10 nm at different temperatures together with the standard powder diffraction pattern of bismuth (JCPDS No. 85-1331), which shows that the Bi nanowires preserve a rhombohedral lattice structure as comparing with the standard diffraction of bulk bismuth, and no structure change has happened in the entire measuring temperature range. The Bi (110) peak is the dominant peak, and its intensity is much higher than all other peaks, revealing high (110) growth orientation of the Bi nanowires. Bi nanowires with (110) and other growth orientations have also been fabricated in the previous reports.^{13,19,22}

From the x-ray diffraction pattern and Bragg equation, $2d \sin \theta = \lambda$ (d , θ , and λ are the interplanar spacing, diffraction angle, and x-ray incidence wavelength, respectively), the lattice parameter d can be calculated. The lattice parameters of (110) plane of Bi nanowires with different diameters (10, 20, 40, 60, 80, and 250 nm) were studied, and the results are shown in Fig. 3. One can see that the lattice parameter firstly increases with increasing temperature and then decreases at certain temperature for Bi nanowires with the diameter in the range 20–60 nm, and there is a critical transition temperature, T_c , at which the temperature coefficient of lattice parameter changes from positive to negative [see Figs. 3(a)–3(c)]. The T_c shifts to high temperature with the increase of the diameter from 20 nm to 60 nm. The lattice parameter of Bi nanowires with a diameter of 10 nm always decreases with increasing temperature and there is not a transition temperature, while that with a diameter of 80 and 250 nm always increases. These results indicate that Bi nanowires with a very small diameter might possess a negative thermal expansion behavior even at room temperature region. It is also worthy to note that: (1) the lattice parameter

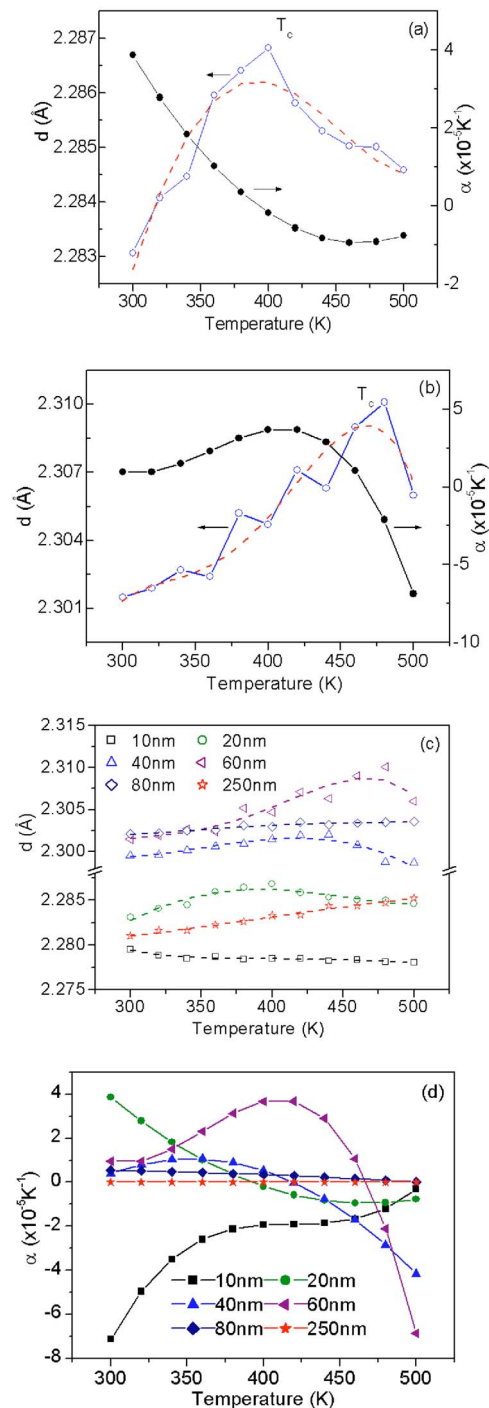


FIG. 3. (Color online) Temperature dependences of lattice parameter, d (open symbols), and thermal expansion coefficient, α (close symbols), of Bi nanowires with different diameters (the dashed line is the fourth-order polynomial fitting). (a) 20 nm, (b) 40 nm, (c) and (d) 10–250 nm.

of the (110) plane of the Bi nanowire is larger than that of Bi bulk material (2.2730 Å). Compared with the bulk, the decreased or increased lattice constants were observed in different nanomaterials. The intrinsic reasons are different depending on the processing histories and surface structure of the nanomaterials.^{5,23} (2) The lattice parameters of the Bi nanowires with a very large diameter (for 250 nm, the lattice parameter is 2.281 Å) have a tendency to be close to that of the bulk, because large nanowires should have a similar behavior to that of the bulk.

After fitting the experimental data with the fourth-order polynomial, $a = \sum_{n=0}^4 a_n T^n$, as shown in Fig. 3(c) (dashed lines), the obtained coefficients a_n can be used to calculate the thermal expansion coefficient. The thermal expansion coefficient is defined by²⁴

$$\alpha = \frac{1}{a_0} \frac{\partial a}{\partial T} = \frac{1}{a_0} (a_1 + 2a_2 T + 3a_3 T^2 + 4a_4 T^3). \quad (1)$$

The $\alpha(T)$ curves of the Bi nanowires with different diameters are also plotted in Fig. 3(d). It can be clearly seen that the Bi nanowires have either positive or negative thermal expansion coefficient depending on the temperatures and the diameters of Bi nanowires, and the transition temperature of the thermal expansion coefficient from positive to negative is consistent with that obtained from the lattice parameter. It is noteworthy that the thermal expansion coefficient of Bi nanowires with a diameter of 10 nm is always negative, that with a diameter of 20 nm always decreases, that with a diameter of 40 nm and 60 nm first increases and then decreases, and that with a diameter of 80 and 250 nm is always positive.

The positive thermal expansion is commonly observed in most bulk material, which can be understood by accounting for the effects of the anharmonic lattice potential on the equilibrium lattice separations and characterized by the Gruneisen parameter.²⁵ In most cases, negative thermal expansion, mainly originating from a structural related phase transition, have been observed among anisotropic systems in only a narrow temperature range. A negative thermal expansion coefficient has been observed in AgI nanowires, when the structure changes from hexagonal close packed to body centered cubic due to the restriction of the AAM wall to the nanowires claimed by the authors.⁸ Theoretical calculation based on Gruneisen's Law with certain simple assumptions indicated that highly anisotropic bulk material Bi has either positive or negative thermal expansion behavior depending on crystallographic directions.²⁶ In the present study a transition of the thermal expansion coefficient from positive at low temperatures to negative at high temperatures has been observed in free-standing rhombohedral (110) Bi nanowires (20–60 nm) within AAM and without structural change over the whole temperature range studied. It is noticed that Bi nanowires with different orientations might have different behaviors, and further work concerning the behavior of Bi nanowires with orientations other than (110) will be essential. Our results proved, for the first time from experiment, that the lattice thermal contraction is an intrinsic property of Bi nanowires. The similar phenomenon was also observed in nanoparticles, in which the effect of the valence electron energy on the equilibrium lattice positions was introduced. In terms of the minimum energy principle, a transition of thermal expansion coefficient from positive to negative was anticipated at certain temperature T_c , which varied with the diameters of nanoparticles.⁵ As to nanowires, where discrete levels are separated by only a few meV, the electronic effects become significant even at ordinary temperatures, and the influence of the valence electron potential on the equilibrium lattice separation in nanowires thus should be taken into consideration. Lattice shrinking results in an increase in the level separation at elevated temperature, which, on the one hand, reduces the number of electrons occupying the excited states as dictated by the Fermi-Dirac factor and, on the other hand,

raises the thermal energy of individual electrons in the excited states. These two factors compete delicately to achieve a lower electronic potential energy that results in the transition from thermal expansion to thermal contraction. Other factors, such as defects, surface stress, and finite-size modified lattice potential, might be significant in determining the thermal behaviors of nanowires.

In conclusion, single-crystalline Bi nanowire arrays with diameter ranging from 10 nm to 250 nm oriented along the [110] direction have been fabricated by pulsed electrodeposition. It was found that there is a transition of the thermal expansion coefficient from positive to negative at a critical temperature T_c , and the T_c shifts to high temperature with increasing diameter, which might be attributed to the effect of the valence electron potential on the equilibrium lattice separation in the low-dimensional system having discrete electronic energy levels. Our results show a promise in studying the nature of the thermal expansion properties of nanowires.

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¹C. M. Lieber, *Sci. Am.* **285**, 58 (2001).

²Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, E. Kim, and H. Yan, *Adv. Mater. (Weinheim, Ger.)* **15**, 353 (2003).

³R. Banerjee, E. A. Sperling, G. B. Thompson, H. L. Fraser, S. Bose, and P. Ayyub, *Appl. Phys. Lett.* **82**, 4250 (2003).

⁴H. Y. Zhang and B. S. Mitchell, *Mater. Sci. Eng., A* **270**, 237 (1999).

⁵W. H. Li, S. Y. Wu, C. C. Yang, S. K. Lai, K. C. Lee, H. L. Huang, and H. D. Yang, *Phys. Rev. Lett.* **89**, 135504 (2002).

⁶J. Y. Zhang, X. Y. Wang, M. Xiao, L. Qu, and X. Peng, *Appl. Phys. Lett.* **81**, 2076 (2002).

⁷Y. Maniwa, R. Fujiwara, H. Kira, H. Tou, H. Kataura, S. Suzuki, and Y. Achiba, *Phys. Rev. B* **64**, 241402 (2001).

⁸Y. H. Wang, C. H. Ye, G. Z. Wang, L. D. Zhang, Y. M. Liu, and Z. Y. Zhao, *Appl. Phys. Lett.* **82**, 4253 (2003).

⁹Y. Zhang, G. H. Li, Y. C. Wu, B. Zhang, W. H. Song, and L. D. Zhang, *Adv. Mater. (Weinheim, Ger.)* **14**, 1227 (2002).

¹⁰M. J. Zheng, L. D. Zhang, G. H. Li, X. Y. Zhang, and X. F. Wang, *Appl. Phys. Lett.* **79**, 839 (2001).

¹¹F. Y. Yang, K. Liu, K. Hong, D. H. Reich, P. C. Searson, and C. L. Chien, *Science* **284**, 1335 (1999).

¹²L. D. Hicks, T. C. Harman, and M. S. Dresselhaus, *Appl. Phys. Lett.* **63**, 3230 (1993).

¹³Y. M. Lin, S. B. Cronin, J. Y. Ying, M. S. Dresselhaus, and J. P. Heremans, *Appl. Phys. Lett.* **76**, 3944 (2000).

¹⁴Y. M. Lin, X. Z. Sun, and M. S. Dresselhaus, *Phys. Rev. B* **62**, 4610 (2000).

¹⁵J. Heremans and C. M. Thrush, *Phys. Rev. B* **59**, 12579 (1999).

¹⁶Y. M. Lin, O. Rabin, S. B. Cronin, J. Y. Ying, and M. S. Dresselhaus, *Appl. Phys. Lett.* **81**, 2403 (2002).

¹⁷T. E. Huber and K. Celestine, *J. Appl. Phys.* **64**, 6588 (1988).

¹⁸J. Heremans, C. M. Thrush, Y. M. Lin, Z. Zhang, M. S. Dresselhaus, and J. F. Mansfield, *Phys. Rev. B* **61**, 2921 (2000).

¹⁹X. F. Wang, J. Zhang, H. Z. Shi, Y. W. Wang, G. W. Meng, X. S. Peng, and L. D. Zhang, *J. Appl. Phys.* **89**, 3847 (2001).

²⁰Y. Peng, D. H. Qin, R. J. Zhou, and H. L. Li, *Mater. Sci. Eng., B* **77**, 246 (2000).

²¹L. Li, Y. Zhang, G. H. Li, and L. D. Zhang, *Chem. Phys. Lett.* **378**, 244 (2003).

²²Z. B. Zhang, X. Z. Sun, M. S. Dresselhaus, J. Y. Ying, and J. P. Heremans, *Appl. Phys. Lett.* **73**, 1589 (1998).

²³W. Qin, Z. H. Chen, P. Y. Huang, and Y. H. Zhuang, *J. Alloys Compd.* **44**, 1915 (2001).

²⁴T. Saotome, K. Ohashi, T. Sato, H. Maeta, K. Haruma, and F. Ono, *J. Phys.: Condens. Matter* **10**, 1267 (1998).

²⁵N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976), Chap. 25.

²⁶B. G. Childs, *Rev. Mod. Phys.* **25**, 665 (1953).