Journal of Alloys and Compounds 504 (2010) 367–370

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Sol–Gel synthesis of $SrBi_2Ta_2O_9$ nanowires

Wen Wang*, Hua Ke, Jian-Cun Rao, Ming Feng, Yu Zhou

Institute for Advanced Ceramics, Department of Materials Science, Harbin Institute of Technology, Harbin 150001, PR China

ARTICLE INFO

Article history:
Received 2 April 2010
Received in revised form 13 May 2010
Accepted 21 May 2010
Available online 4 June 2010

Keywords:
$SrBi_2Ta_2O_9$
Sol–gel
Ferroelectric
Nanowires

ABSTRACT

We report the synthesis of perovskite ferroelectric nanowire strontium bismuth tantalate ($SrBi_2Ta_2O_9$, SBT). Sol–gel techniques have been used. The morphology and structures are analyzed via SEM, TEM and XRD. The XRD and TEM analysis show that the structure of SBT nanowires is single orthorhombic perovskite with $A2_1am$ structure space group. The obtained SBT nanowires with an average length of 35 μm and a diameter of 200 nm are c-axis preferred orientation in the templates. The formation mechanism of SBT nanowires with complex crystal structure was discussed.

1. Introduction

The synthesis of nano-sized materials has been a very active research field over the past decade years for a variety of reasons [1–3]. The process of miniaturization is important, in both microelectronics industries and microelectromechanical systems (MEMS). Ferroelectric nanostructure has stimulated extensive efforts due to their prospective applications in diverse areas including pyroelectric detectors, piezoelectric inkjet printers and memory capacitors [4,5]. Compared with the synthesis of the general nanotubes such as carbon nanotubes with simple crystal structure, the synthesis of ferroelectric compound is difficult due to the multielement and the complex crystal structures of these ferroelectrics. Fortunately, hard-template synthesis of one-dimensional ferroelectric is a versatile and inexpensive technique for producing nanostructures [6–9]. Size, shape, and structural properties of the assembly could be simply controlled by the template. Nanotubes of different ferroelectric oxides including $PbZr_{1-x}Ti_xO_3$ (PZT), $BaTiO_3$, $PbTiO_3$ and $Bi_{4-x}La_xTiO_3$ (BLT) have been synthesized by immersing a template membrane in solution [10–12]. Moreover, Morrison et al synthesized SBT nanotubes using a special equipmen in photonic Si crystals template [13], and Limmer et al. [14] synthesized a PZT nanowire using electrophoretic sol–gel method in track-etched polycarbonate (PC). Nanowires can be obtained depending on the interfacial adhesion and the solidification modes [15], in other word depending on kind and content of solvent and process of heat treatment. However, to the best of our knowledge, the SBT nanowire has been rarely seen. Herein, we report synthesis of one-dimensional SBT nanowires on anodic alumina (AAO) templates by immersing a template membrane in sol.

2. Experimental

SBT nanowires were prepared with a 0.1 M sol made by dissolving $Ta(OEt)_5$ and strontium acetate ($Sr\text{-}(OAc)_2$) in ethylene glycol (EG) at 20 °C. Solution of the bismuth subnitrate ($BiONO_3$) in EG and HAc was prepared, and was added to the Ta–Sr solution. Anodic Al_2O_3 membranes (Whatman Corporation, AAO) with a pore size of 200 nm served as template sand were dipped into the sol for 15 min, and then dried in air for 2 h. This process was repeated. The samples were calcined in air at 700 °C for 0.5 h. This process to synthesize SBT sol has been described in our previous report [16,17]. Preprocessing AAO template using HAc solvent and adjust constituents of dipping sol (HAc:EG = 7:2) can effective reduce surface tension of sol (σ_{EG} = 0.05 N/m, σ_{HAc} = 0.03 N/m).

The morphologies and structures of the SBT nanowires were determined by the field – emission scanning electron microscope (SEM, Hitachi S–4700), X-ray diffractometer (XRD, Rigaku D/max-rB), transmission electron microscope (TEM, Philips CM-12). For SEM and TEM observations, the AAO template embedded with SBT nanowires were soaked in a 4 M NaOH solution to remove the alumina completely, and then the resulting product was washed in the deionized water for several times. For TEM investigation, the SBT nanowires were put in the deionized water and subjected to the ultrasonic treatment for several minutes, and then a drop of suspension was placed on the carbon-coated copper grid to carry out TEM studies. To measure the P–E hysteresis loops of the SBT nanwire arrays, both surfaces of the arrays with the template were firstly polished carefully with sand papers until SBT nanowires were emerged, and then a layer of Au with a thickness of 100 nm was sputtered on both sides of the template as electrode. The measurement was performed at a Radiant Technologies Precision Workstation ferroelectric test system.

3. Results and discussion

Scanning electron microscopy (SEM) images of the as-prepared products were shown in Fig. 1. SBT nanowires had a length of 35 μm

* Corresponding author at: Institute for Advanced Ceramics, Department of Materials Science, Harbin Institute of Technology, No. 92, West Da-Zhi Street, Harbin, Heilongjiang 150001, PR China. Tel.: +86 451 86402040; fax: +86 451 86414291.
E-mail addresses: wangwen@hit.edu.cn (W. Wang), hua_ke@hit.edu.cn (H. Ke).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.05.118

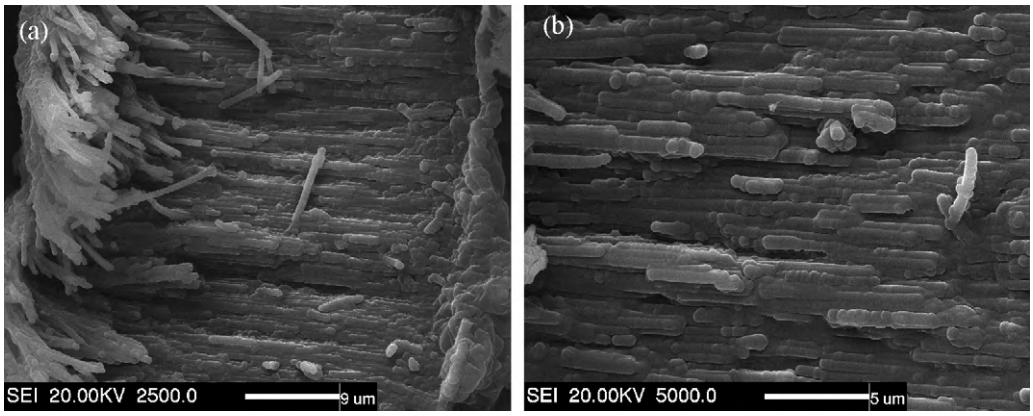

Fig. 1. SEM micrographs of SBT nanowires.

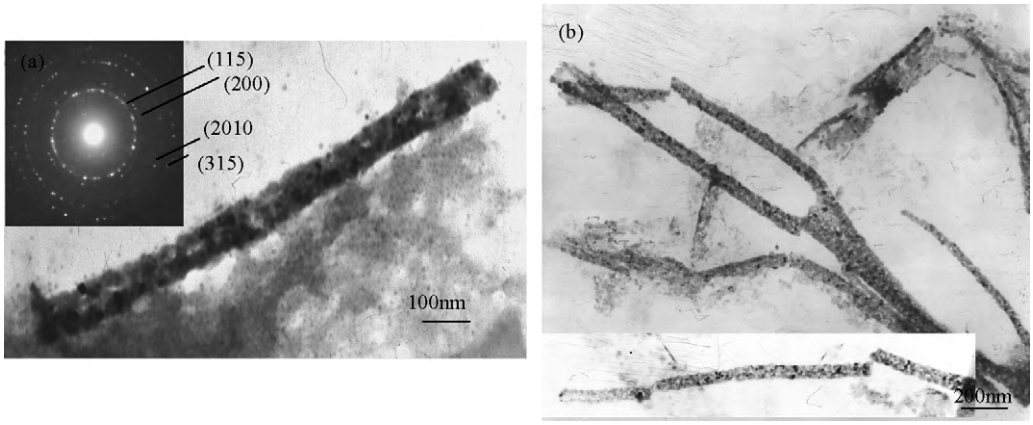

Fig. 2. TEM of the as-synthesized SBT nanowires (a) micrograph and diffraction patterns and (b) nanowires suffered damage.

and a diameter of 200 nm and are considered to be throughout the entire length of the template channel. The sol–gel process was so uniform that a complete covering of the pore occurred.

Typical TEM images of SBT nanowires were presented in Fig. 2, in which the inside solid region was clearly identified. In Fig. 2b, nanowires have suffered damage during handling sample. Electron diffraction patterns were presented in the inset of in Fig. 2a. The different rings in Fig. 2a indicate that the nanowires are composed of small polycrystalline grains. Further analysis on the electron diffraction patterns revealed that nanowire had a perovskite structure, which matched well with the values from XRD results (in Fig. 3).

Fig. 3 shows the XRD pattern of the nanowires. As it indicated, SBT crystallized in the orthohombic (ferroelectric perovskite, JCPDS 490609) phase at 700 °C. SBT nanowires are almost grown in *c*-axis, as shown in Fig. 3. If the surface and interior of a finite-diameter 1D nano-object is rigidly occupied by atoms, it is often called a nanowire or nanorod. Ordered nanowires fall into several structural classes according to Allen [18]. The basic idea is to (1) choose a maximally linear, charge-neutral, and (if possible) dipole-free atomic cluster containing a single formula unit, and (2) use (if possible) the symmetry axis of this linear cluster as the growth axis and distribute by translations and screw rotations the atomic cluster to give a stoichiometric nanowire with some symmetry around the growth axis and minimal surface polarity. For SBT, the crystal structure still remains orthorhombic phase above T_c (608 K) and changes to tetragonal phase above 900 K [19]. The displacive ferroelectric $SrBi_2Ta_2O_9$ is described at room temperature in space group $A2_1am$ as a commensurate modulation of an idealized *Fmmm* parent structure [20]. Since this *Fmmm* structure may itself be described as a derivative of a structure of *I4/mmm* symmetry, it has been customary to define *c*-axis as the long axis and to select *a*-axis as the polar axis direction for ferroelectricity.

The crystal structure of $SrBi_2Ta_2O_9$ consists of Bi_2O_2 layers and perovskite-type $SrTa_2O_7$ units with double TaO_6 octahedral layers. And it was studied by neutron and electron diffraction, which revealed orthorhombic distortion with space group $A2_1am$. The structural distortion with this noncentrosymmetric space group is responsible for the displacive-type ferroelectric behavior of the compound, that is, atomic displacements along the *a*-axis form cor-

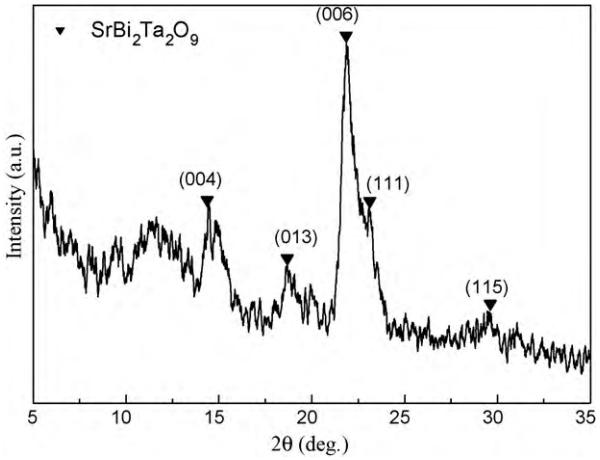

Fig. 3. XRD pattern of the as-synthesized nanowires with AAO membrane.

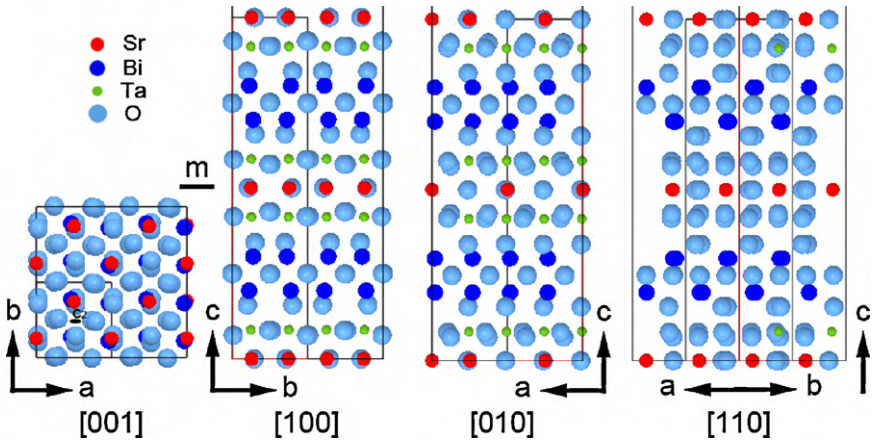

Fig. 4. The projection of atoms position of $SrBi_2Ta_2O_9$ unit cell with space group of A21*am* in different directions. [0 0 1] direction shows 2×2 unit cells, others 2×1. The original unit cell was framed out. Please note the C2 screw axis in [0 0 1] projection and the mirror planes in other projections.

responding positions in the parent tetragonal (*I4/mmm*) structure cause spontaneous ferroelectric polarization [9]. In Fig. 4 shows the projection of atoms position in different directions. The original unit cell was framed out with [0 0 1] direction showing 2×2 unit cells, others 2×1. There is a mirror plane just at the middle of and perpendicular to *c*-axis. There is also a C_2 screw axis. Both are also indicated in Fig. 4. A simple way to make a charge-neutral nanowire with nonpolar surfaces is by choosing the *c*-axis as the growth axis, and thinking of the nanowire as being built from *c*-axis-oriented Bi_2O_2 and $SrTa_2O_7$ pairs. Thus *c*-axis- oriented $SrBi_2Ta_2O_9$ nanowires (Fig. 3) are an obvious choice of structure, and are very favorable for theoretical modeling due to the symmetry. The terminal surfaces are nonpolar layers either of Sr–O, Ta–O, Bi or O with the dangling bonds compensated by adsorbed species like H^+ or OH^- [21]. Thus the whole nanowire has no net dipole with charge-neutral state. As considering other planes, for example (1 0 0), (0 1 0) or (1 1 0) planes, the difficulty is that these planes are dipolar. So the exposed surface cannot be terminated by these planes. This means that it is impossible for the nanowires to grow along [1 0 0], [0 1 0], [1 1 0] or other directions.

For ferroelectric property measurement, Au top dots of 100 μm diameter had been deposited on test SBT nanowires with the Au bottom continuous electrodes. Ferroelectric switching of the sample were typically measured from hysteresis loops as shown in Fig. 5. The low charges may be due to the property of the samples, which were fabricated from the loose combination of clusters nanowire. Then, it is reasonable to expect that individual nanowire of such material with a much more highly ordered structure will show a higher charge. As displayed by the loops, the charges decreased after reaching the max polarization, which should be attributed to the leakage current caused by the adsorbed moisture and interspaces between nanowires. The hysteresis loop was not saturated, which could be solved by making smaller electrode consisting fewer nanowires.

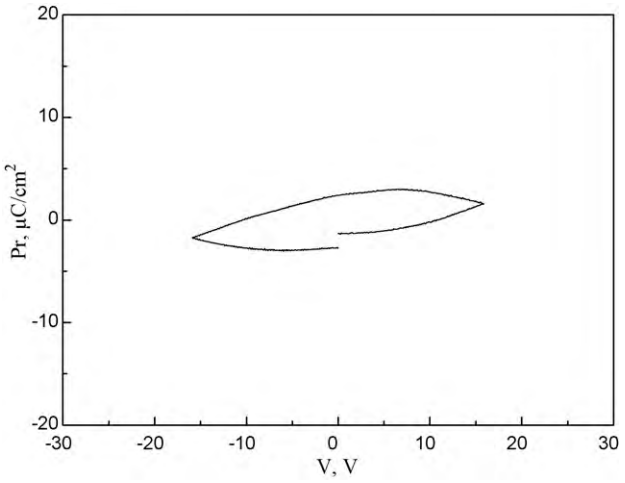

Fig. 5. Hysteresis loop of SBT nanowires with AAO membrane.

4. Conclusions

Finely arrayed $SrBi_2Ta_2O_9$ nanowires can be prepared by immersing a template membrane in sol with reducing surface tension. To minimize surface polarity, SBT nanowires oriented preferentially along the growing axis (*c*-axis) by translation and rotation of atomic clusters of SBT. There is a need to deposit ferroelectric nanowire on the inside of trenches for Tera bits random-access memories (RAMs), both dynamic DRAMs and non-volatile ferroelectric FRAMs.

Acknowledgments

The authors would like to thank the financial support from National Natural Science Foundation of China with the Project Nos. 50502013 and 50872024, NSFC-RFBR joint Project No. 51011120099, and the Project (HIT. NSRIF. 2009031) of Natural Scientific Research Innovation Foundation in Harbin Institute of Technology.

References

[1] S.R. Kulkarni, A. Wu, J. Alloys Compd. 490 (2010) 155.
[2] F. Zhang, S.G. Chen, Y.S. Yin, J. Alloys Compd. 490 (2010) 247.
[3] M. Rlgout, H. Niu, C. Qin, L. Zhang, C. Li, X. Bai, N. Fan, Nanotechnology 19 (2008) 245303.
[4] J.E. Spanier, A.M. Kolpak, J.J. Urban, L. Grinberg, L. Ouyang, W.S. Yun, A.M. Rappe, H. Park, Nano Lett. 6 (2006) 735.
[5] J.J. Urban, J.E. Spanier, L. Ouyang, W.S. Yun, H. Park, Adv. Mater. 15 (2003) 423.
[6] X.Y. Zhang, X. Zhao, C.W. Lai, J. Wang, X.G. Tang, J.Y. Dai, Appl. Phys. Lett. 85 (2004) 4190.
[7] J.F. Scott, C.A. Paz de Araujo, Science 246 (1989) 1400.
[8] T. Mihara, H. Yoshimori, H. Watanade, C.A. Araujo, J. Appl. Phys. 34 (1995) 5233.
[9] Y. Shimakawa, Y. Kubo, Y. Nakagawa, S. Goto, T. Kamiyama, H. Asano, F. Izumi, Phys. Rev. B 61 (2000) 6559.
[10] Y. Luo, I. Szafraniak, N.D. Zakharov, Appl. Phys. Lett. 21 (2003) 440.
[11] B.A. Hernandez, K.S. Chang, E.R. Fisher, P.K. Dorhout, Chem. Mater. 14 (2002) 480.

[12] B.I. Seo, U.A. Shaislamov, S.W. Kim, H.K. Kim, B. Yang, S.K. Hong, Physica E 37 (2007) 274.
[13] F.D. Morrison, Y. Luo, I. Szafraniak, V. Nagarajan, R.B. Wehrspohn, M. Steinhart, J.H. Wendorff, N.D. Zakharov, E.D. Mishina, K.A. Worotilov, A.S. Sigov, S. Nakabayashi, M. Alexe, R. Ramesh, J.F. Scott, Rev. Adv. Sci. 4 (2003) 114.
[14] S.J. Limmer, T.L. Hubler, G. Cao, J. Sol-Gel Sci. Technol. 26 (2003) 577.
[15] G. Cao, D. Liu, Adv. Colloid Interface 136 (2008) 45.
[16] Y. Zhou, W. Wang, D.C. Jia, F. Ye, Mater. Chem. Phys. 77 (2002) 60.
[17] M. Feng, W. Wang, Y. Zhou, J. Sol-Gel Sci. Technol. 52 (2009) 120.
[18] P.B. Allen, Nano Lett. 7 (2007) 6.
[19] E.C. Subbarao, J. Phys. Chem. Solids 23 (1962) 665.
[20] A.D. Rae, J.G. Thompson, R.L. Withers, Acta Cryst. B 48 (1992) 418.
[21] J.E. Spanier, A.M. Kolpak, J.J. Urban, I. Grinberg, Q.Y. Lian, W.S. Yun, A.M. Rappe, H. Park, Nano Lett. 6 (2006) 735.