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Template-based synthesis and piezoelectric properties of $BiScO_3$–$PbTiO_3$ nanotube arrays

Caifu Zhong [a], Zhenya Lu [a, *], Xiaohui Wang [b], Longtu Li [b]

[a] College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China
[b] State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

Template-based electrophoretic deposition of $BiScO_3$–$PbTiO_3$ (BSPT) nanotubes (NTs) were achieved using anodic alumina oxide (AAO) membranes and sol–gel method. The effect of the electrophoretic current and deposition time on the morphology of the BSPT tubes was investigated. Crystal structure and micrograph of the NT arrays were characterized by X-ray diffraction, transmission electron microscopy, and field-emission scanning electron microscopy. It was shown that as-prepared NTs were polycrystalline with a perovskite structure. Good piezoelectricity was observed in these ferroelectric BSPT NTs, the average value of local effective piezoelectric coefficient d_{33}^* was 60 pm/V for the NTs with wall thickness of 30 nm.

1. Introduction

Ferroelectric thin films with a perovskite structure are very important for use in nonvolatile memories, microelectromechanical systems and high-frequency electrical components due to their extremely high ferroelectric and piezoelectric activity [1–3]. As proved by many studies, $BiScO_3$–$PbTiO_3$ (BSPT) exhibited a high Tc and comparable ferroelectric and piezoelectric properties with those traditional perovskite system at the morphotropic phase boundary (MPB) [4]. Developing high quality, low cost and low loss BSPT materials for high frequency applications is a challenging aspect for investigation. It is known that ferroelectric and piezoelectric properties of perovskite are sensitive to their composition and microstructure. Many sub-micron or nanocrystalline BSPT powders and thin films have been investigated in recent years by classic hydrothermal method [5], sol–gel process [6] or other wet chemical technique. However, the particle growth and interparticle aggregation are inevitable in these processes, which might induce instability to their applications. Exploring perovskite BSPT with one-dimensional (1D) nanostructures (such as nanowire (NW), nanotube (NT) etc.) is an available way to avoid these defects and facilities their potential applications in high-density memory system and nano-devices.

Although several examples of solution-based syntheses of perovskite NTs/NWs have been reported recently [7–10], limited information is available regarding the BSPT with 1D structure. Among the fabricating methods of ferroelectric NTs, the anodic alumina oxide (AAO) membrane-based electrodeposition is a relatively simple and effective route, because of its simplicity, cost-effectiveness, and precise control over length, diameter, and composition of NTs [11,12]. In this paper, direct current (DC) electrodeposition was employed to prepare BSPT NTs arrays in the pores of AAO membranes via an aqueous sol–gel process. Structural modification of the samples was carried out by adjusting the deposition parameters. The influence of morphologies on the piezoelectric properties of the NTs was discussed.

2. Experiment

In a typical procedure, highly ordered AAO membranes were prepared by a two-step anodization from the 99.9% aluminum foil as described elsewhere in detail [12]. The templates had a thickness about 20 μm and a diameter around 200 nm. A thin layer of Au with thickness of about 10 nm was sputtering deposited onto one side of the templates serving as the working electrode. The precursor electrolytes for the deposition of BSPT NTs contained a MPB composition of $0.36BiScO_3$–$0.64PbTiO_3$ (5 mol% Pb excess) via an aqueous sol–gel method [13]. Electrodeposition process was

* Corresponding author.
E-mail address: zhylu@scut.edu.cn (Z. Lu).

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carried out at room temperature using a two-electrode system with a platinum foil as anode for 2 h. Concentration of the electrolyte and deposition current density was adjusted during the process, and each condition was repeated over three times to ensure the reliability of the results. Then the samples were cleaned in ethanol and DI water, and annealed at 750 °C for 2 h in atmosphere.

Crystal structures of the specimens were determined by x-ray diffraction (XRD 2500, Rigaku, Tokyo, Japan). Microstructures of the NTs were observed by a field emission scanning electron microscope (FE-SEM, LEO-1530, LEO, Oberkochen, Germany) and a transmission electron microscope (TEM, JEOL-2010, Japan). For FE-SEM and TEM observations, the AAO membrane was partly dissolved with 0.5 M NaOH solution, and then rinsed out with deionized water for several times. The effective piezoelectric coefficients d^*_{33} was measured by a scanning probe microscopy system (SPM, SPI4000&SPA300HV, Seiko, Tokyo, Japan), with a conductive Rh-coated Si cantilever.

3. Results and discussion

Fig. 1 shows the FE-SEM images of the as-prepared BSPT NT arrays deposited under different current densities and concentrations (0.24 M–0.1 mA/cm^2, 0.4 M–0.1 mA/cm^2, 0.4 M–1 mA/cm^2, respectively) for 2 h. The outer diameters (about 200 nm) of the samples are nearly the same corresponding to the diameter of nano-pores in the AAO templates. It demonstrates that the cations in the solution are inclined to concentrate on the pore wall of AAO membranes by the driving electric field during the deposition process. When applying a relative low current density ~0.1 mA/cm^2, the successive NTs with smooth and straight walls were obtained at the deposition concentration higher than 0.24 M (Fig. 1a, b). The thickness of the tubular wall had an evident increase with deposition concentration from 0.24 M (Fig. 1a) to 0.4 M (Fig. 1b). Adjusting the current density to 1 mA/cm^2 for the electrolyte with 0.4 M concentration, the wall of the BSPT NTs (Fig. 1c) became thicker and rough attributing to the bigger nanoparticles comprised in the NTs[10], and no evident difference of the morphology was found for the nanotubes with the current density higher than 1 mA/cm^2. Besides, the effect of deposition time on the morphology of the NTs was also investigated. Prolonging the deposition time from 1 h to 2 h, the length of the NTs increased evidently and the wall thickness changed indistinctively. All the samples reached a length of 20 μm (thickness of the AAO membranes) after depositing for 2 h at different current densities. Consequently, all the specimens for further characterizations were prepared by a deposition time of 2 h.

Fig. 2 show the TEM images of the BSPT NTs at different deposition conditions, revealing that the average wall thickness of the NTs increased as the deposition concentration increased, approximately from 5 to 20 nm with deposition concentration from 0.24 M (Fig. 2a) to 0.4 M (Fig. 2b) at 0.1 mA/cm^2. Limited to the concentration of the electrolyte at room temperature, it is difficult to get BSPT NT arrays with much thicker walls by increasing the concentration larger than 0.4 M. Thus by setting the deposition concentration value at 0.4 M, the thickness dependence with the current density was explored for the BSPT NTs, as shown in Fig. 2c, d. The average thickness of the NTs firstly increased linearly from about 5 nm to 20 nm with the current density from 0.05 mA/cm^2 to 0.1 mA/cm^2. When the current density continued to increase to 1 mA/cm^2, the thickness of the NTs only slightly increased to about 30 nm (Fig. 2c), and no significant change would be observe with the current density higher than 1 mA/cm^2. SAED pattern of the isolated NT with wall thickness of 20 nm is inserted in Fig. 2b. The weak diffuse rings doped with bright spots suggest that these BSPT NTs are polycrystalline.

For further characterizing the structure of the BSPT NTs, XRD patterns of the as-prepared samples obtained under different concentration (0.24, 0.4 M) and current densities (0.1, 1 mA/cm^2) are revealed in Fig. 3. Excluding some weak peaks according to rutile TiO_2 (marked with rotundities, the AAO membranes were adhered on Ti substrates during the annealing and XRD characterization), all the position of other peaks agrees well with those of standard perovskite phases of BSPT, suggesting a solid-solution phase is formed at the composition range. Moreover, the X-ray patterns are broadened as observed in the spectrums, which could also be expected for the nanocrystalline structure in the films. Additionally, the intensity of the peaks increases with the wall thickness of the NTs which may be attribute to the bigger nanoparticles consisted in the thicker walls as shown in Fig. 2.

To check the piezoelectric property of the BSPT NTs, AFM was used to measure the local effective piezoelectric coefficients, as shown in Fig. 4. The measurement was achieved by fixing the SPM tip above the samples and applying a DC voltage from −10 V to 10 V while recording the deformation displacement signal. Dozens of the "displacements–voltage" curves were obtained by locating the tip above different areas of each sample, and Fig 4 shows the typical loops for the samples. For the blank AAO template, the displacement signal was very small, most likely from the noise of the testing system. However, typical well-shaped "butterfly" loops are observed with a maximum displacement of 0.4 nm, 0.3 nm and 0.22 nm for the prepared BSPT NTs with wall thickness of 30 nm, 25 nm and 20 nm respectively, indicating well ferroelectricity for the materials. Besides, the effective piezoelectric coefficient d^*_{33} calculated from all the measured curves was about 50–70 pm/V, 30–50 pm/V, and 20–35 pm/V for the NTs with wall thickness of about 30 nm, 25 nm and 20 nm respectively. For the NTs samples with smaller wall thickness (about 5 nm and 15 nm), the displacement signal was relative small, and was difficult to be distinguished from the noise signals. It was obvious that the piezoelectric coefficient for the NTs with thicker wall was much larger than that of NTs with thinner wall, which may also be

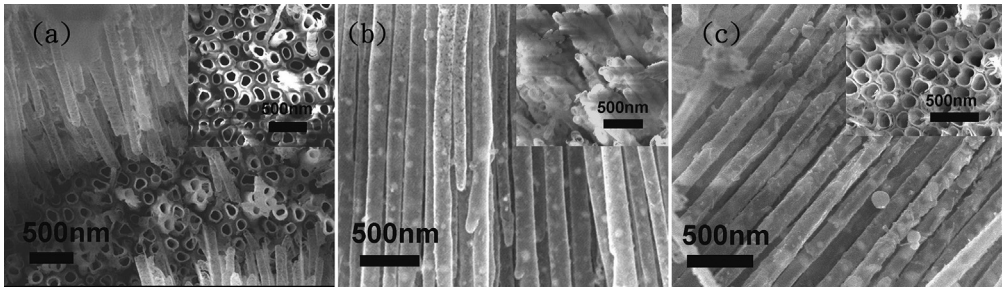

Fig. 1. FE-SEM images of the as-prepared BSPT NT arrays obtained under different current densities and concentrations: (a) 0.24 M–0.1 mA/cm^2, (b) 0.4 M–0.1 mA/cm^2, (c) 0.4 M–1 mA/cm^2.