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Featured Letter

Sol-gel template synthesis of $BaTiO_3$ films with nano-periodic structures

Go Kawamura [a,b,*], Kazuhiro Ohara [a], Wai Kian Tan [c], Hiroyuki Muto [c], Kazuhiro Yamaguchi [d], Aldo R. Boccaccini [b], Atsunori Matsuda [a]

[a] Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan
[b] Institute of Biomaterials, University of Erlangen-Nuremberg, Cauerstraße 6, 91058 Erlangen, Germany
[c] Institute of Liberal Arts and Science, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan
[d] Electrical and Electronic Engineering Course, National Institute of Technology, Ibaraki College, Hitachinaka, Ibaraki 312-8508, Japan

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ABSTRACT

$BaTiO_3$ films with novel nano-periodic structures were prepared by a sol-gel template synthesis. A through-hole type anodic aluminum oxide film was used as a template. The nano-periodic structure was drastically modified by applying a spray cleaning process during spin-coating of the template with a $BaTiO_3$ sol. The formation mechanism was discussed from the viewpoint of liquid bridge force and surface tension applied during the drying process. The novel structures are promising for various functional devices, in which the nano-periodicity improves their performance.

1. Introduction

Materials with piezoelectricity have been attractive since its discovery in 1879 [1]. Nowadays, a variety of applications are proposed, such as sensors [2], microelectromechanical systems [3,4], energy harvesting [5], and multiferroic devices [6]. For each application, the giant piezoelectric effect is desired. In this regard, porous piezoelectric materials have been synthesized because the piezoelectric constant of materials could be increased by incorporating appropriate porous structures [7]. This is mainly because the piezoelectric responses are influenced by the weight of the material itself, i.e., lower-density piezoelectric materials are required. Moreover, the porous structure of piezoelectric materials is also very important for some applications. For example, the pore size and orientation of piezoelectric materials have been optimized for hydrophone application [8]. Biomedical applications of porous piezoelectric materials have been investigated in terms of regenerative medicine [9]. Furthermore, piezoelectric composites are generally more susceptible, for example, multiferroic nanocomposite with ferrimagnetic nanopillars embedded in a piezoelectric matrix showed that electric polarization could be tuned by appling magnetic fields via off-diagonal magnetostrictive-piezoelectric coupling [10].

The fabrication of isolated piezoelectric $BaTiO_3$ (BTO) nanotubes has been reported, where a liquid phase deposition of BTO on a typical anodic aluminum oxide (AAO) template was employed [11]. On the contrary, BTO films with nano-periodic porous structures were synthesized by a sol-gel method using a through-hole open-ended AAO template at both sides in this work. The nano-periodic porous structures were altered by incorporating a spray cleaning process during sol-gel spin-coating of the AAO template with a BTO sol.

2. Experimental

A commercial through-hole AAO membrane (ultrathin type; horizontal size:15 × 15 mm, thickness: 270–320 nm, pore size: 500 nm, pore-pore distance: 450 nm; TopMembranes Technology, China) was used as a template. The as-received AAO membrane was placed on a poly(methyl methacrylate) (PMMA) substrate, thus the AAO membrane was first transferred to a SiO_2 substrate by dissolving PMMA with acetone for the following process including heat treatment at high temperatures.

To prepare a BTO sol, 2.55 g of $Ba(CH_3COO)_2$ (99.0%; Wako, Japan) and 5 ml of acetic acid (99.9%; Wako, Japan) were mixed and stirred at 60 °C. Separately, 2.97 ml of $Ti(OC_3H_7)_4$ (95.0%; Wako, Japan) was mixed with 2.97 ml of acetylacetone (99.0%;

* Corresponding author at: Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441-8580, Japan.
E-mail address: gokawamura@ee.tut.ac.jp (G. Kawamura).

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Wako, Japan). Then the sols were mixed and added to a mixture of 37.06 ml of 2-methoxyethanol (99.0%; Wako, Japan) and water to obtain 0.2 M BTO sol.

The BTO sol was dropped manually onto the AAO template, then it was spun at 5000 rpm for 30 s. During spinning, 0.3 ml of 2-methoxyethanol was sprayed on some of the samples to remove the BTO sol from the top surface of the AAO template. The spraying was carried out directly from above with the distance of 10 cm between the spray and the sample. After drying it on a hot plate set at 100 °C for 10 mins, the substrate was pre-annealed at 150 °C for 30 mins. This BTO coating process was repeated 3 times to increase the amount of BTO in the tubular pores of the AAO template. The BTO-coated AAO substrate was annealed at 800 °C for 1 hr. Finally, the AAO template was completely dissolved by immersing the sample into a 0.03 wt% NaOH solution for 24 hrs.

The samples were observed with a scanning electron microscope (SEM, Hitachi S-4800, Japan, Acc. Vol.: 40 kV). Elemental analyses were carried out using an energy dispersive X-ray spectroscope (HORIBA, EX-X50, Japan) attached to the SEM. An X-ray diffractometer (XRD, Rigaku Ultima IV, Japan, Cu-Kα, range: 20–60°, step: 0.02°) was used to analyze the crystal structure of the samples.

3. Results and discussion

The fabrication process of BTO film with a nano-periodic structure is summarized in Fig. 1. First, the AAO template was fully filled with the BTO sol by the spin-coating process (A). It is worth mentioning here that a BTO layer was formed on the bottom of the AAO membrane as well as on the top because there was a narrow gap between AAO membrane and the surface of the SiO_2 substrate. During the drying and pre-annealing processes, as the volume of BTO decreased, the pillars of BTO became thin (B). After the NaOH treatment (C), it was clearly found that the pillars had thick top and bottom parts and thin middle part, which is a typical liquid bridge shape. This shape formed presumably because the pillars were touched and sandwiched in the top and bottom BTO layers, thus the liquid bridge force (indicated by red arrows in the third illustration of Fig. 1) was applied to the BTO pillars during the drying process. A complete removal of the AAO template was confirmed by energy dispersive X-ray spectroscopy.

By spray cleaning with 2-methoxyethanol during spin-coating of AAO with BTO, the nano-periodic structure was drastically changed, as shown in Fig. 2. The spray cleaning completely removed BTO from the top surface of the AAO template (A). Thus, the liquid bridge force was not applied to the pillars of BTO during the drying process, resulting in the thin coating of the inner wall of the AAO template with BTO (B). This also indicated that the surface tension of the AAO template was sufficiently larger than that of BTO, hence the surface of the AAO template was fully wetted by BTO. Otherwise, sparse or no deposition of BTO on the inner wall of the AAO template would have occurred. After NaOH treatment (C), BTO nanotube arrays were obtained. In order to further confirm the formation of nanotube array structure of BTO, a tilted image was also taken and is shown in Fig. 3. The high magnification image of highlighted square region on the left of Fig. 3 was used for BTO thickness estimation, which was around 15–20 nm.

The crystallization behavior of the BTO film obtained in this work was investigated. Fig. 4 shows the XRD patterns of BTO nanotube array films heated at 700 and 800 °C for 1 hr. The XRD pattern of a BTO flat film (thickness: 70 nm) which was prepared by the same process without using the AAO template is also shown as a reference. As seen in the pattern of the flat BTO film, peaks

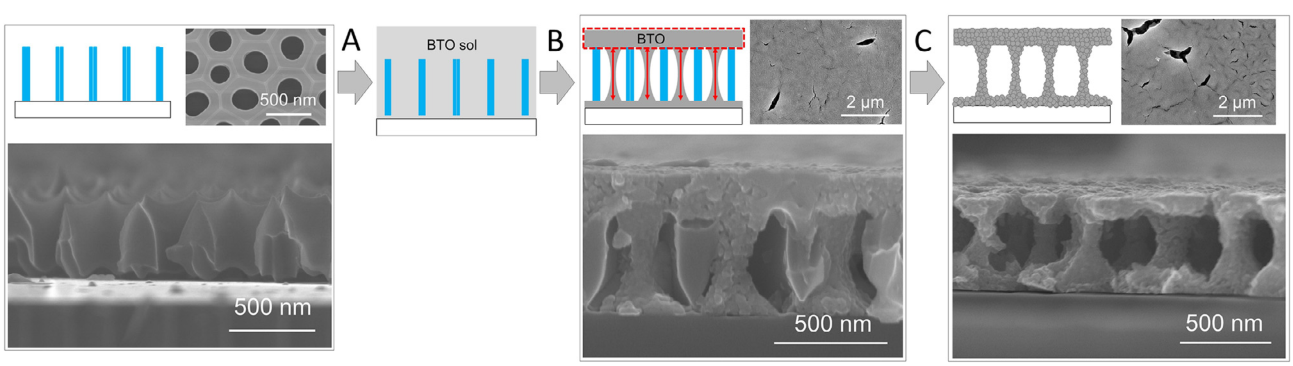

Fig. 1. Schematic of the fabrication process for the BTO film with a liquid bridge structure. From left to right: AAO on SiO_2; BTO coated AAO (only illustration); heat treated BTO coated AAO; AAO removed BTO with a liquid bridge structure.

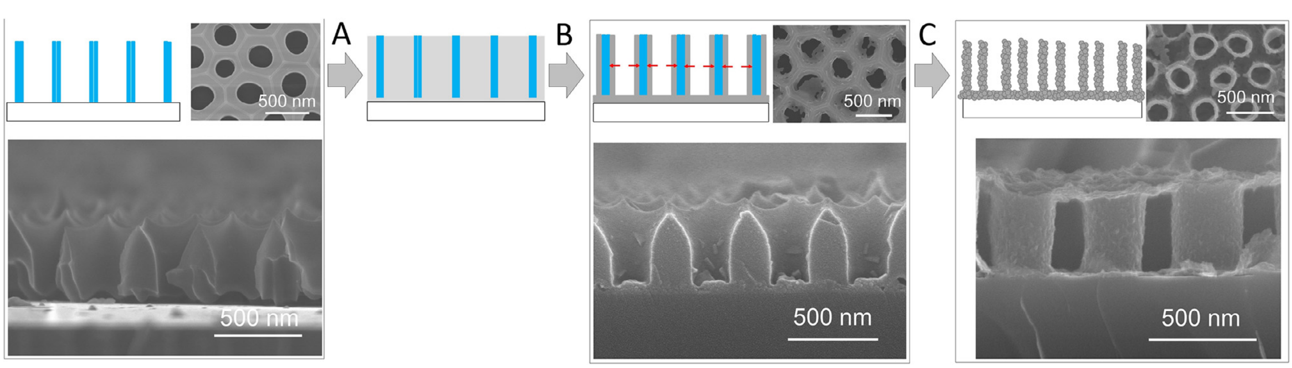

Fig. 2. Schematic of the fabrication process for the BTO film with a nanotube structure. From left to right: AAO on SiO_2; BTO coated AAO (after spray cleaning, only illustration); heat treated BTO coated AAO; AAO removed BTO with a nanotube structure.