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Fabrication of PZT Tubular Structures by a Template-wetting Process

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ABSTRACT

Nanotubes and microtubes of ferroelectric lead zirconate titanate (PZT) were synthesized by means of a simple and convenient process called a template-wetting process. Nanoporous alumina and macroporous Si were used as template materials to fabricate the corresponding tubes. For the improvement of the wetting properties of the wetting solution, the PZT solution was mixed with a polymer. The polymer was removed completely during annealing. The grain growth processes of the PZT nanotubes during baking and furnace annealing were examined by means of field emission electron microscope (FE-SEM) and X-ray diffractometry (XRD).

***Key words*: PZT, Nanotube, AAO template, Ferroelectric, Template-wetting**

1. Introduction

Nanotubes of conducting materials such as carbon have recently received considerable attention. However, ferroelectric nanotubes made of oxide insulators can reportedly be used in a variety of applications such as pyroelectric detectors, piezoelectric ink-jet printers, and memory capacitors.[1)]

In this work, we report on the preparation of ferroelectric lead zirconate titanate (PZT) nanotubes for the development of three dimensional (3-D) nanotube capacitors that can be used in ferroelectric random access memories (FeRAMs). PZT has been used in FeRAMs because of its promising ferroelectric properties and large capacity for data storage. However, FeRAMs with a superior charge in a limited area are more important because they can significantly reduce the size of capacitors to less than 0.1 μm^2. Within three or four years, scaling down trends will be essential for commercial FeRAMs that have a density higher than 64 Mb and technology nodes of 0.13 μm.

Currently available techniques for the deposition of PZT thin films, such as liquid-phase deposition, radio frequency magnetron sputtering, metal-organic chemical vapor deposition, as well as plasma-enhanced metal-organic chemical vapor deposition, are not stable enough for the commercialization of FeRAMs with an ultra density level. However, solutions to these technological difficulties have not yet been reported anywhere in the world.[2-4)] Hence, we used a template-directed approach, particularly template-wetting .[5-7)] On account of its simplicity, the template-wetting process in ferroelectric nanotube technology has several advantages, such as cost effectiveness and technological effectiveness.

In this study, we tried to produce both nanotubes and microtubes by using nanoporous alumina and macroporous Si as templates. Furthermore, in our systematic study, we used field emission electron microscope (FE-SEM) and X-ray diffractometry (XRD) measurements to examine the grain growth processes of PZT nanotubes during baking, rapid thermal annealing (RTA), and furnace annealing.

2. Experiments and Discussion

For the nanotubes, we used commercial nanoporous alumina from Whatman, with a pore diameter of 200 nm. In the case of microtubes, we used a macroporous Si template fabricated by means of a photoelectrochemical method. Briefly, an n-type (100) Si wafer was etched in an electrolyte solution with a concentration of 5.45 wt% of HF. The voltage was 2 V DC, and the etching current, which we controlled by changing the distance between the back of the sample and light source, was set to 7.28 mA/cm^2. We used a 100 W halogen lamp as the illumination source.

In order to prepare the PZT nanotubes and microtubes, we wet the pore walls of the porous template with a polymer containing the PZT source. A PZT sol-gel solution was mixed with polymer sources in different ratios to prepare the wetting solution. Fig. 1 shows a schematic illustration of the nanotube fabrication method. After the solution was put onto the template (Fig. 1(a)), it wet the pore walls under ambient conditions at room temperature (Fig. 2(b)) and led to a reduction of the total energy of the system.[8)] Due to the uniform wetting, the entire surface of the pore walls was completely covered. Next, the precursors in the pores were

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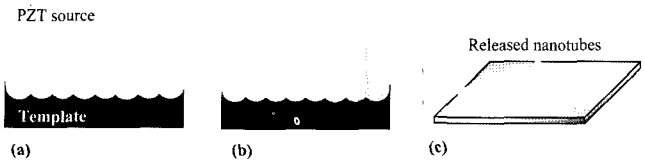

Fig. 1. Process flow for the template-wetting process. (a) Contact of the solution with template, (b) covering the pore walls, and (c) released nanotubes after etching the template.

transformed into an amorphous oxide layer when baked in an oven at 300°C for 5 min. This amorphous layer was subsequently crystallized by a thermal treatment in air for one hour at 650°C to obtain the perovskite phase, and the presence of this phase was confirmed by XRD. We deduce, therefore, that either released or free-standing ferroelectric tubes can be obtained by a controlled etching of the template.

PZT nanotubes embedded into the template were used to perform XRD analysis. To investigate the tube wall morphology by FE-SEM, we etched off the alumina template in a 30 wt% KOH solution at room temperature. In the case of the Si template, the etching process was performed at a temperature of 80°C. The Si template was then etched for 5 min to obtain vertically well-aligned PZT microtubes, which are partially attached to the template. After completion of the etching, the nanotubes were thoroughly rinsed with deionized water and, after the water had dried, they were dropped onto clean pieces of a Si wafer for the FE-SEM investigation.

2. Results and Discussion

Fig. 2(a, b, c) show FE-SEM images of the templates that were used for the nanotube preparation experiments. Fig. 2(a) shows the surface image of a commercial nanopore membrane with a pore diameter of 200 nm. Fig. 2(b, c) show surface and cross-sectional SEM images of the as-prepared microporous Si template, respectively. The average pore diameter is about 3 μm and the height is 75 μm. In addition, the as-grown pores have smooth pore walls and a relatively constant diameter along the length.

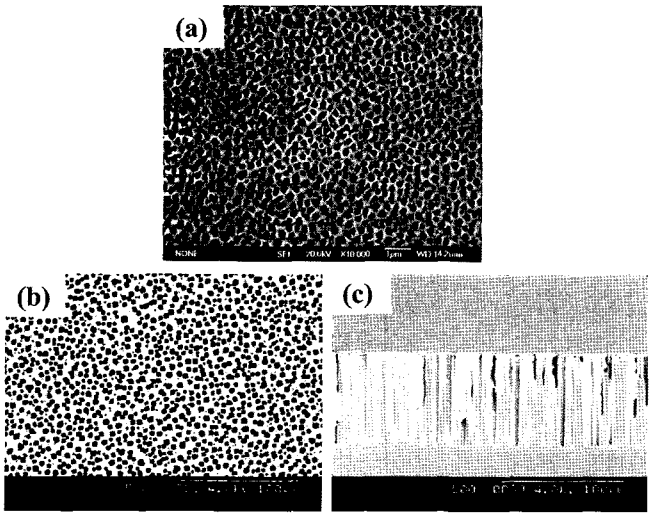

Fig. 2. Nanoporous and Microporous templates. (a) Surface image of commercial nanoporous alumina, (b) surface, and (c) cross section images of microporous Si templates obtained by a photoelectrochemical etching method.

Fig. 3(a, b) show FE-SEM images of the as-prepared PZT nanotubes that are released from the alumina template. The tubes have smooth and straight walls, and the top-view images of the nanotubes reveal that the tubes obviously have a hollow nature, which indicates that the obtained structure is tubular rather than shaped like a wire or rod. From the top-view images of Fig. 3(a), we can easily determine that the diameter of the as-prepared nanotubes is about 200 nm, which corresponds to the applied template's diameter.

As shown in Fig. 3(c, d), the PZT microtubes that we obtained by wetting the microporous Si template have an average pore diameter of 2.5 μm. To obtain these arrays of tubes, we partially etched the Si template in 30 wt% KOH at 80°C for 5 min. The microtubes attached to the bottom part of template have a 3 μm diameter, which corresponds to the diameter of the applied template. Depending on the parameters of the templates used, we can vary the diameter and length of the microtubes from a few micrometers up to more than 100 μm. In the large magnification image (Fig. 3(c)), we can clearly see the vertically standing PZT microtubes. Moreover, because the wetting is uniform in all parts of the template, we can prepare large PZT microtubes, as shown in Fig. 3(d), where the microtube arrays have an area of 500 μm × 500 μm. We can also prepare a vertically positioned microtube array in a wafer scale. In both cases, the pore walls are completely covered.

To investigate the formation of the PZT crystallinity, we

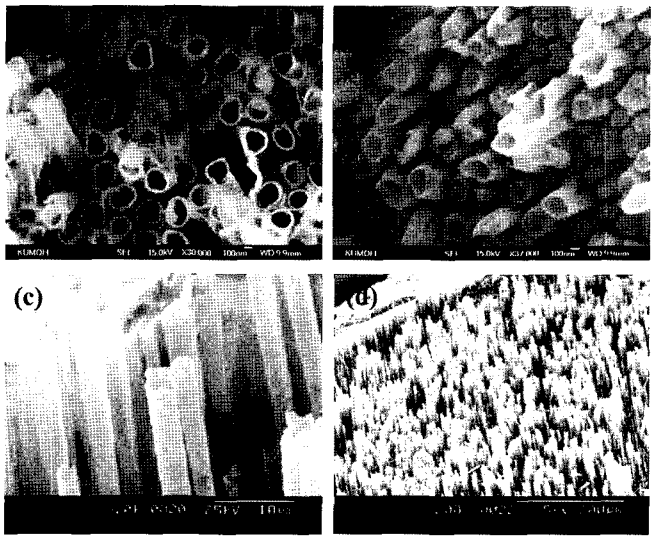

Fig. 3. FE-SEM SEM images of PZT nano (a and b) and microtubes (c and d), respectively. The vertically aligned PZT microtubes were obtained by using microporous Si templates, which were baked at 300°C and annealed at 600°C, respectively.

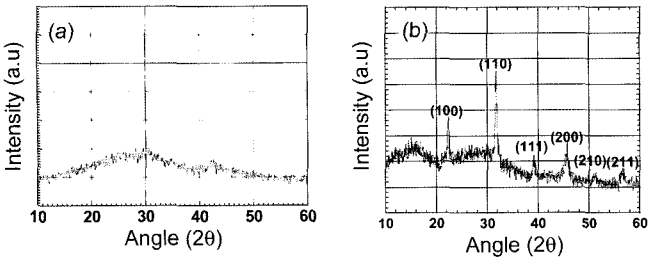

Fig. 4. XRD patterns of the PZT nanotubes. (a) after annealing at 500°C, (b) after annealing at 650°C, respectively.

took XRD measurements in steps of 0.05°, at a speed of 1° / min, and a range 10° to 80°. The PZT nanotubes located within the anodic aluminum oxide (AAO) template were used for the XRD measurement.

Fig. 4(a, b) show XRD patterns of PZT nanotubes annealed at different temperatures. This process was performed in order to analyze the crystallization temperature of the PZT. In Fig. 4(a, b), the XRD results are compared for the samples annealed at 600°C and 650°C, respectively. The annealing temperature greatly influences the crystallization of the PZT. We found that strong reflections of (100), (101), (110) and (201) of the tetragonal PZT occurred at $2\theta = 220$, 30.90, 31.40 and 50.40, respectively, in the sample that was annealed at 650°C (Fig. 4(b)), whereas no peaks were obtained after annealing at 600°C (Fig. 4(a)).

4. Conclusion

We successfully prepared PZT nanotubes within the nanopores of porous alumina membrane templates by using a template-wetting method. The FE-SEM images show that the produced PZT nanotubes are vertically well-aligned in the templates. In addition, the diameters of the as-prepared nanotubes are around 200 nm and 3 μm, which coincide with the pore diameters of the template we used. The XRD results show that the as-prepared nanotubes have a polycrystalline structure. In summary, the obtained PZT nanotubes are very promising candidates for use in nanotube capacitors.

Acknowledgments

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