

High aspect ratio lead zirconate titanate tube structures: I. Template assisted fabrication - vacuum infiltration method

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Abstract

Polycrystalline $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) microtubes are fabricated by a vacuum infiltration method. The method is based on repeated infiltration of precursor solution into macroporous silicon (Si) templates at a sub-atmospheric pressure. The pyrolyzed PZT tubes of a 2-µm outer diameter, extending to over 30 µm in length were released from the template using a selective isotropic-pulsed XeF₂ reactive ion etching of silicon. Free-standing microtubes, partially anchored at the bottom of the Si template, were then crystallized in pure oxygen atmosphere at 750 °C for 2 min using a rapid thermal annealer. The perovskite phase of the final PZT tubes was confirmed by X-ray diffraction (XRD) analysis. The XRD spectrum also revealed a small amount of the pyrochlore phase in the structure and signs of possible fluoride contamination caused most likely by the XeF₂ etching process. The surface morphology was examined using scanning electron microscopy. It was demonstrated that the whole surface of the pore walls was conformally coated during the repeated infiltration of templates, resulting in straight tubes with closed tips formed on the opposite ends as replicas of the pore bottoms. These high aspect ratio ferroelectric structures are suggested as building units for developing miniaturized electronic devices, such as memory storage (DRAM trenched) capacitors, piezoelectric scanners and actuators, and are of fundamental value for the theory of ferroelectricity in systems with low dimensionality.

Keywords: lead zirconate titanate, microtubes, template assisted method, vacuum infiltration

I. Introduction

The scaling of electronic devices down to micro- and even nanometer dimensions has stimulated great interest in developing new chemical synthesis methods and advanced fabrication techniques to produce fine structured materials of desired geometric shape with tailored physical properties. Among others, one-dimensional (1-D) ferroelectric structures with high aspect ratio such as tubes, wires and rods are reported most promising elements for future electronics applications, including miniaturized nonvolatile RAM memories, high resolution biomedical ultrasound systems, pyroelectric detectors, fluidic delivery systems or piezoelectric electromechanical systems due to their small size, increased electro-active surface area and unique properties when compared to their bulk counterparts [1–5].

Over the past decade, a variety of fabrication approaches has been employed for producing high aspect ratio 1-D like nanostructures; metal-organic vapour deposition [6], hydrothermal synthesis [7], chemical solution growth approach [8] and template-based methods [9]. Some of them have also been used successfully for fabricating more complex often three-dimensional (3-D) heterostructures that cannot be easily realized in planar device fabrication schemes. A template-assisted wetting method is referred to as most versatile and effective technique that allows the size, shape and structural properties of discrete elements as well as array pattern to be easily controlled by the template used [8,9]. The technique employs a sacrificial template consisting of pores, trenches or channels in which a sol or an precursor solution can be incorporated. In following drying and annealing steps, the solvent evaporates and the material starts to crystallize and densify, forming structures with dimensions constricted by the pore diameter and the pore length. Luo

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et al. [10] prepared an ordered array of hundreds ferroelectric nanotubes by using silicon templates with a regular periodic array of pores. In order to facilitate uniform coating the inside of the pores and increase the phase purity of the crystalline structure of the annealed material, Bharadwaja et al. [11] improved the template wetting technique for fabrication of lead zirconate titanate (PZT) microtubes by reducing the pressure above precursor solution during the wetting process and preventing the reaction between PZT and the porous Si template during annealing, respectively. More recently, a highly ordered array of ultra-thin-walled PZT nanotubes were synthesized in a porous alumina membrane through sol-gel synthesis combined with a spin-coating technique [12]. Mist-deposition template derived high aspect ratio ferroelectric structures made of PZT and SrBi₂Ta₂O₀ were also reported in the literature [13,14]. Ferroelectricity and piezoelectricity were confirmed to exist in PZT microtube structures as well as in PZT nanotubes of several tens to several hundreds nanometers wall thickness [11,13,14].

In this paper, a wafer-scale fabrication of ferroelectric microtubes using a vacuum infiltration method based on repeated immersion of a macroporous silicon template into a liquid PZT precursor under a sub-atmospheric pressure is demonstrated. The X-ray diffraction analysis and scanning electron microscopy were employed to confirm a formation of the perovskite phase at 750 °C and hollow structure of the crystallized PZT tubes with wall thickness of about 400 nm. The proposed low-cost technique provides a simple and convenient approach toward the development of functional complex oxide tube structures with high aspect ratio.

II. Experimental

The PZT microtubes were prepared using a templateassisted mold replication technique that integrates a solgel process with vacuum promoted wetting of the pore wall of porous templates by liquid precursor. Silicon templates' having a regular hexagonal array of two-dimensional pores with diameters 2 μ m, depth 30 μ m and



Figure 1. Schematic diagram for fabrication of PZT tube structures by the template-assisted vacuum infiltration method: a) a cleaned silicon template with an ordered array of pores, b) wetting of the pore walls by infiltration of the solution precursor at a sub-atmospheric pressure, c) a PZT layer formed on the pore walls after pyrolysis, d) XeF₂ reactive ion etching of silicon and e) an ordered array of free-standing ferroelectric tubes

an inter-pore distance 1 μ m were obtained from Nordoca Inc., Edmonton, Canada. Prior to infiltration, the templates were pre-cleaned in an oxygen plasma etcher (Plasma Technology Inc., Concord, MA). Silicon dioxide (SiO₂) appearing natively inside the pores was chemically etched out with a buffered oxide etch solution of ammonium fluoride and hydrofluoric acid in a ratio of 10 : 1 (BOE, J.T. Baker). The PZT precursor of a nominal stoichiometric composition Pb_{1.2}(Zr_{0.52}Ti_{0.48})O₃ was prepared by sol-gel method, as described elsewhere [15].

Fabrication process of the tubes is schematically shown in Fig. 1. Firstly, the cleaned and dried silicon template was immersed in an evacuated container of PZT solution for about 5 min, which makes the sol precursor infiltrate uniformly into the pores with the help of pressure balancing. Secondly, the silicon template with the precursor-layer coated pore walls was taken out and the excess sol on its surface was wiped off using a cotton swab dipped in 2-methoxyethanol. Then the template was heated from room temperature to 300-350 °C in air. The PZT layer on the sidewalls of the pore channels was transformed into an amorphous oxide layer by annealing at the above temperatures for 3 min. In order to obtain the microtubes with desired wall thickness, the "infiltration-pyrolysis-infiltration" process was repeated several times. Typically, a 400-nm-wall thickness was achieved in 20 successive infiltrations. To minimize chemical reaction between the Si template and PZT at elevated temperatures, the pyrolyzed tubes were, in the next step, released from the template along the majority of their length by selective etching of the Si. Approximately 30 µm of silicon was removed in 30 min using an isotropic-pulsed XeF, reactive ion etching tool (RIE, Xetch e'series, Xactix Inc., Pittsburgh, PA) operated at a pressure of 1 Torr with a pulse cycle of 1 min. Finally, an ordered array of free-standing PZT microtubes, anchored at the bottom of the template, was obtained by fast annealing in 99.98% oxygen at a temperature of 750 °C for 1-3 min with heating rate of 60 °C/s and cooling rate of 125 °C/s (a rapid thermal annealer, model Tsunami series RTP-600S).

The morphology of the as-synthesized microtubes and porous silicon templates was observed by scanning electron microscope (SEM, model Hitach S-3500N, Pleasanton, CA). Structural characterization on the tubes was carried out via X-ray diffraction (XRD, Scintag, Sunnyvale, CA) using CuK α radiation for 2 θ angular scans ranging from 20° to 60° with a 0.025° step size.

III. Results and discussion

Figures 2a and 2b show the SEM images of an unfilled Si template and one infiltrated with PZT. On an average, the pore diameter and the inter-pore distance are 2 µm and 1 µm, respectively; and it is notable that after 20 repeated infiltrations all the pores have sidewalls covered by a PZT layer. Figure 3 is the corresponding SEM micrograph of a regular array of free-standing PZT microtubes after a partial XeF, gas phase removal of silicon. It is apparent that the tubes are straight, nearly uniform, and completely discrete. The open ends demonstrate the hollow structure of the tubes. The wall thickness is estimated from the SEM to be about 400 nm. The inset shows a side view of the same sample, and so an efficiency of the RIE process, where the tubes, having a high aspect ratio of about 20, are anchored to the host Si matrix only at the tube base. The morphology of the crystallized (at 750 °C for 2 min) and completely released tube is shown in Fig. 4a. It is clear that during the repeated infiltration under vacuum the whole surface of the pore walls was covered resulting in the tubes with closed tips formed on the opposite ends as replicas of the pore bottoms. The rippled sidewalls located close to the open ends and irregularities in lower part of the tubes replicate the original pore profile of silicon templates fabricated by deep reactive ion etching, as shown in Fig. 4b. The PZT microtubes were further studied by XRD. After thermal annealing at 750 °C for 2 min, the X-ray diffraction analysis (Fig. 5a) revealed the polycrystalline perovskite-structure nature of the partially released tubes. In addition to perovskite phase peaks, Bragg re-



Figure 2. Scanning electron microscope (SEM) images of silicon templates with a regular hexagonal array of macropores: a) as-received, unfilled and b) infiltrated with PZT



Figure 3. SEM photograph of an ordered array of PZT microtubes (the inset shows a side-view micrograph of free-standing tubes attached partially to the host silicon matrix)

flections of a pyrochlore phase are noticed in the XRD pattern. As has largely been reported for synthesis of lead-based ferroelectric films, on heat treatment, formation of an intermediate pyrochlore and fluorite phase may be kinetically favoured over the perovskite phase. Rørvik et al. [9] demonstrated that the metastable fluorite phase formed during high temperature annealing can be transformed into the perovskite phase afterwards by an extension of annealing time. The concept is based on the fact that once the fluorite phase is formed from the amorphous precursor the further transformation into the perovskite phase is slow because the driving force associated with the nucleation of the perovskite phase is reduced. At higher temperatures, the perovskite phase is the preferred phase because heterogeneous nucleation of metastable phases is less likely. To study whether the PZT microtubes could be obtained without the unwanted non-ferroelectric phase, several different thermal budgets were employed in our annealing experiments. It was demonstrated that any change in heat treatment procedures used for finalizing high aspect ratio tube structures, such as annealing at higher temperatures or prolonged heating, resulted in an irreversible damage of the tubes. Figures 6a and 6b illustrate representative micrographs of broken PZT microtubes after annealing at a temperature of 800 °C for 1 min and the tubes annealed at 750 °C for 10 min, respectively. As can be seen from the figure, annealing at elevated temperatures caused buckling and melting of tubes, whereas during the prolonged annealing the microtubes become typically squeezed and bundled together in the middle.



Figure 4. SEM image of: a) the released tube and b) a pore profile - a cross-sectional image



Figure 5. X-ray diffraction pattern of: a) PZT tubes with a wall-thickness of about 400 nm and b) the 400-nm-thick PZT film [16]

Comparing the XRD patterns obtained for the 400nm-thick PZT film [16] and as-synthesized PZT microtubes with wall thickness of about 400 nm (Figs. 5a and 5b), it is apparent that the perovskite phase with a small amount of the pyrochlore phase is formed in both structures, while as an additional Bragg peak at about 36° dominates the lower part of the diffractogram of the released tubes. Bharadwaja *et al.* [11] matched that peak with the oxyfluorides of Zr/Ti cations forming in the structure due to XeF₂ gas phase etch step for silicon template removal process. They further reported that the fluoride contamination can be minimized by mild boric acid treatment.

The results show that the vacuum infiltration technique is a simple and convenient template-based fabrication method for producing the high aspect ratio ferroelectric microtube structures with tailored dimensions. Successive infiltrations of macroporous Si templates under sub-atmospheric pressure facilitate uniform, thickness-tunable, coating the inside of the Si template pores. On partial removal of the Si template by the XeF₂ treatment, it is possible to produce an ordered array of ceramic microtubes in which each tube is completely discrete. However, control of the phase composition and morphology of PZT microtubes in terms of the possible contamination upon a removal process of the Si template and quality of pore channels in templates, respectively, remains a challenge for the potential use of the tubes. Moreover, the processing conditions related to thermal budget and oxygen flow in a RTA furnace need to be further optimized.

IV. Conclusions

In summary, ferroelectric PZT microtubes with the diameter of 2 μ m, the length of about 30 μ m and the wall thickness of ~400 nm were successfully prepared using a modified template-assisted method. A conformal coating of the pore walls of macroporous Si templates was achieved by the repeated infiltration of a PZT solution into pore channels under sub-atmospheric pressure. On partial removal of the Si template, it was possible to produce a periodic array of free-standing ferroelectric tubes as mold replicas of a regular array of 2-D pores. Rapid thermal annealing at 750 °C for



Figure 6. SEM images of damaged tubes: a) annealed at an elevated temperature of 800 °C for 1 min, b) crystallized at 750 °C with an extension of annealing time to 10 min.

2 min was shown to be sufficient to obtain well-crystallized microtubes. The tubular morphology and perovskite phase of PZT tubes were confirmed with SEM and XRD. The as-prepared microtubes can be readily manipulated and so would facilitate the fabrication of more complicated architectures for use in miniaturized electronic devices.

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