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Nanoshell tubes of ferroelectric lead zirconate titanate and barium titanate

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Wafer-scale fabrication of ferroelectric oxide nanoshell tubes as well as ordered nanotube arrays have been accomplished using a simple and convenient fabrication method that allows full tailoring of tube dimensions as well as array pattern and size. Using different silicon and alumina templates, barium titanate and lead zirconate titanate tubes with diameters ranging from 50 nm up to several micrometers meter and lengths of more 100 μm have been fabricated. Ferroelectric switching of submicrometer tubes has been shown using piezoresponse scanning probe microscopy. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1592013]

One-dimensional systems, such as nanotubes or nanorods of many materials, have attracted great interest in the last decade, because they exhibit different physical properties than their bulk counterparts. The preparation of carbon nanotubes by a simple method[1] along with their particular effects (e.g., the transistor effect[2]) has generated a revolutionary research field. In the last years, research on inorganic nanotubes has been rapidly increasing. Nanotubes made of materials such as metals, semiconductors, or oxides were obtained by the roll-up of thin films deposited onto a sacrificial layer,[3] self-assembly,[4–8] or template-mediated fabrication.[9–15] However, the preparation of functionalized nanotubes, for example, complex oxide ferroelectrics, remains a challenge in materials science.

The broad range of properties of ferroelectric oxides, such as spontaneous polarization, high dielectric permittivity as well as piezo- and pyroelectricity, make ferroelectric nanotubes an extremely interesting material class for research as well as for applications. Recently, ferroelectric nanorods with diameters as small as 5 to 60 nm and with lengths of more than 10 μm were obtained by a solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands.[16] By means of electrostatic force microscopy, ferroelectric switching was shown in a 12-nm-diameter rod.[17]

In this letter, we demonstrate wafer-scale fabrication of ferroelectric nanotubes and ordered nanotubes arrays using a simple and convenient fabrication method that allows full tailoring of tube dimensions (diameter, length, and wall thickness) as well as array pattern and size. Ferroelectric switching of an individual tube was also demonstrated by atomic force microscopy. We have used a simple and convenient method to prepare mesoscopic ferroelectric oxide tubes with piezoelectric properties. This approach consists of wetting of the pore wall of porous templates, either porous alumina or macroporous silicon,[18] by polymeric precursors. The driving force of the process leads to reduction of the surface energy of the system.[19] Lead zirconate titanate ($PbZr_{0.52}Ti_{0.48}O_3$, PZT) and barium titanate ($BaTiO_3$, BTO) nanotubes were fabricated by using precursors containing the metals in the stoichiometric quantities (PZT 9906 Polymer and BATIO 9101 Polymer from *Chemat Technology*). After the precursor had been brought into contact with the template, it formed a layer on the pore walls. This wetting occurred under ambient conditions at room temperature. The polymer precursor layer was subsequently transformed into an amorphous oxide layer by annealing in air at 300 °C and later crystallized in air at 650 °C for PZT and 850 °C for BTO for 1 h in order to get the perovskite phase. The presence of this phase was confirmed by x-ray diffraction for both BTO and PZT tubes. By selective etching of the template in 20-wt % KOH solution at 90 °C, free ferroelectric tubes were obtained. The tubes were then washed in deionized water several times and deposited on silicon or platinum-coated silicon substrates. Figure 1 shows an example of the resulting ferroelectric BTO nanotubes, which are straight, smooth, and have a very high aspect ratio of 50 or more. The outer diameter can be easily tuned by using different templates. The hollow nature is obvious from the

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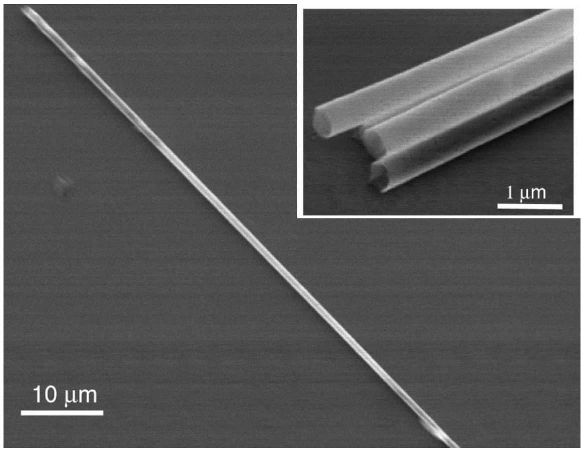

FIG. 1. Scanning electron microscopy (SEM) image of single nanoshell BTO tube on silicon substrate. The inset shows an SEM image of the free open ends of PZT tubes.

inset of Fig. 1, in which the open ends of individual nanotubes are depicted. The wetting process was so uniform that a complete covering of the whole surface of the pore walls occurred. All pores of the processed templates were blind holes. Figure 2 shows capped BTO nanotubes whereas the caps are replicas of the pore bottoms. In Fig. 3, a transmission electron microscope (TEM) image shows the cross section of PZT tubes in a silicon template after a single step of infiltration, which yields a wall thickness of 90 nm for PZT and 100 nm for BTO nanotubes. The tube wall of both BTO and PZT consists of a polycrystalline layer sandwiched between two amorphous layers at the silicon–ferroelectric interface and at the internal surface.

Ferro- and piezoelectric properties of the PZT and BTO nanotubes were measured by scanning force microscopy in the so-called piezoresponse mode[20,21] after they had been deposited on Pt-coated silicon substrate. Individual ferroelectric tubes of PZT and BTO were probed by a conductive tip and electrically characterized by measuring the local piezoelectric hysteresis. The as-prepared nanotubes showed only weak ferroelectric properties. To improve the ferroelectric properties, we introduced an additional thermal treatment for the free tubes at 700 °C for 1 h in oxygen for BTO nanotubes and in lead oxide atmosphere for PZT nanotubes. SEM investigations (not shown here) confirmed that the shape and morphology of the tube is not changed by this high-temperature annealing. This treatment allows conversion of the amorphous layer into the perovskite ferroelectric phase and removal of the defects resulted after etching process. Figure 4 shows the piezoelectric hysteresis loop finally obtained on a PZT tube with an outer diameter of 700 nm and wall thickness of 90 nm. The piezoelectric signal is an unambiguous proof of the piezoelectricity of the tubes. The hysteresis in the piezoresponse signal is directly associated with the polarization switching and ferroelectric properties of the sample. Moreover, the rectangular shape of the hysteresis loop showing a sharp ferroelectric switching at a coercive voltage of about 2 V is connected with a high quality of ferroelectric material. The effective remanent piezoelectric coefficient is of about 90 pm/V and is comparable with usual values obtained on PZT thin films. Here, we point out that it is difficult to compare these values to the piezoelectric coefficients of bulk material since the measurement was performed on a tube geometry that has a relatively intricate field distribution and vibrational modes.

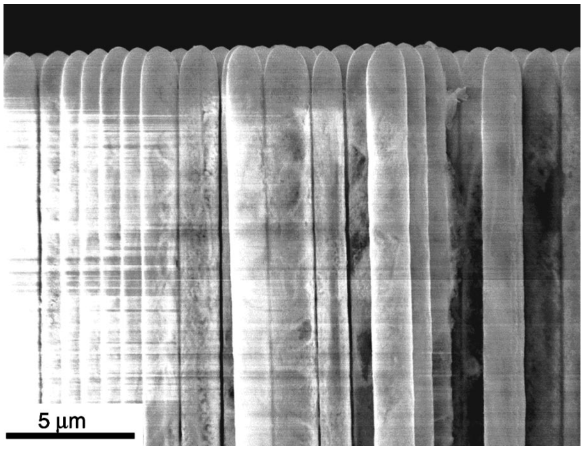

FIG. 2. SEM image of the closed tip of the piezoelectric tube array showing uniform coating of the whole surface of the pore walls up the close end.

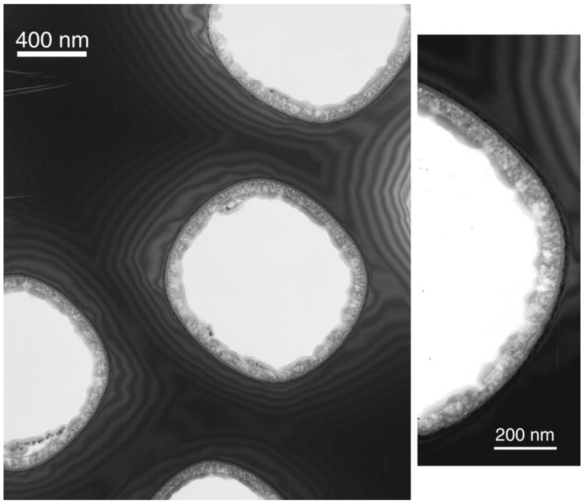

FIG. 3. Cross-section TEM images of PZT nanotubes embedded in a silicon template. The right inset shows the image of a tube wall at higher magnification confirming the polycrystalline nature of PZT.

In conclusion, we have developed a very simple and inexpensive generic method to obtain ferroelectric nanotubes with sizes that can be tuned over a relatively large mesos-

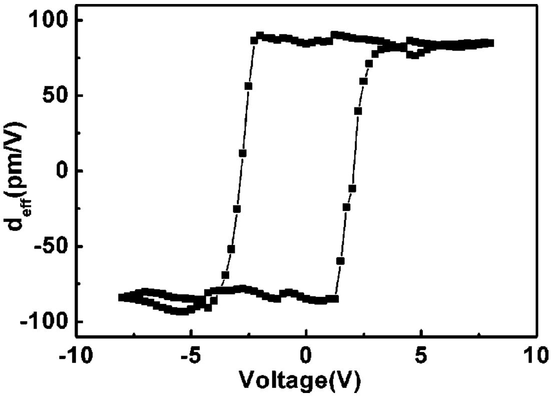

FIG. 4. Effective piezoelectric coefficient as a function of the applied voltage measured on a PZT nanoshell tube. The characteristic hysteresis loop is directly associated with the ferroelectric switching.

copic range. As examples, we prepared lead zirconate titanate and barium titanate nanotubes exhibiting piezoelectric hysteresis and ferroelectric properties. For practical applications, ferroelectric oxide tubes are more desirable than simple rods, especially with diameters in the mesoscale range. We expect that free-standing ferroelectric tubes obtained by partial etching of the silicon template would be used as building block of miniaturized devices and will have a significant impact in the field of nano-electromechanical systems. Piezoelectric tubes with diameters in the micron range and a higher aspect ratio than the bulk counterpart will enable extreme miniaturization of scanners. As the fabrication methods are similar to the thin-film technology, the wafer-scale integration of the piezoelectric scanner and scanner arrays with silicon microelectronics is now possible. This opens up the possibility of ‘‘on-chip’’ scanning probe microscopes and free moving part, true random access mass storage devices,[22] similar to the millipede concept.[23]

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