Ferroelectric Lead Zirconate Titanate and Barium Titanate Nanotubes

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Wetting of the pore walls of porous templates is a simple and convenient method to prepare nanotubes. Ferroelectric lead zirconate titanate and barium titanate nanotubes were fabricated by wetting of porous silicon templates of polymeric precursors. The ferro- and piezoelectric properties of an individual ferroelectric either of a PZT or a BaTiO3 nanotube were electrically characterized by measuring the local piezoelectric hysteresis. A sharp switching at the coercive voltage of about 2 V was shown from the hysteresis loop. The corresponding effective remnant piezoelectric coefficient is about 90 pm/V. We also expect that free-standing ferroelectric nanotubes obtained by partial etching of the silicon template will be used as building blocks of miniaturized devices and can have a significant impact in the field of nano-electromechanical systems.

INTRODUCTION

One-dimensional structures such as nanotubes or nanorods from many materials have attracted great interest in the last decade, because they exhibit different physical properties than their bulk counterparts. For example, the successful preparation of carbon nanotubes by a simple method [1] along with their bouquet of new effects (e.g. the transistor effect [2]) has generated a completely new research field. Various nanotubes made of such materials as metals or semiconductors were also obtained by methods such as the roll-up of thin films deposited onto a sacrificial layer [3], self-assembly [4–8] or template-mediated fabrication [9–15].

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However, the preparation of functionalized nanotubes, e.g., from complex oxide ferroelectrics, still remains a challenge in material science. Ferroelectric oxides are an important class of functional materials for research and for applications since they exhibit interesting properties such as spontaneous polarization, high dielectric permittivity as well as piezo- and pyroelectric effects. Recently, ferroelectric nanorods with diameters as small as 5 to 60 nm and with lengths of more than 10 \( \mu \)m 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]. We point out that, for practical applications, especially with diameters in the mesoscale range, ferroelectric oxide tubes are the counterparts for the simple rods.

Here we report on the fabrication of ferroelectric nanotubes by wetting of porous templates. This approach allows tailoring the geometry parameters such as diameter and length of the nanotubes. The ferroelectric switching behaviour of an individual tube was also demonstrated by atomic force microscopy.

**EXPERIMENTAL PROCEDURE**

The fabrication approach of lead zirconate titanate, \( \text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3 \) (PZT) and barium titanate (\( \text{BaTiO}_3 \)) nanotubes consists of wetting the pore walls of porous templates, such as macroporous silicon [18], by polymeric precursors and subsequent high temperature annealing. Polymers containing metals in the stoichiometric quantities (PZT 9906 Polymer and \( \text{BaTiO}_3 \) 9101 Polymer from Chemat Technology, INC) were used as precursors. After the precursors were brought into contact with the template, they wetted the pore walls under ambient conditions at room temperature and led to a reduction of the whole energy of the system [19]. Then, the polymeric precursors in the pores were transformed into an amorphous oxide layer by annealing in air at 300°C. This amorphous layer was subsequently crystallized by a thermal treatment in air for one hour at 650°C for PZT and 850°C for \( \text{BaTiO}_3 \) to obtain the perovskite phase. The presence of this phase was confirmed by X-ray diffraction for both \( \text{BaTiO}_3 \) and PZT nanotubes. Free ferroelectric tubes were obtained by a selective etching of the template in 20 wt% KOH solution at 90°C. They were then washed in de-ionized water for several times to remove the KOH solution and deposited on silicon or platinum-coated silicon substrates. Figure 1 shows the resulting ferroelectric \( \text{BaTiO}_3 \) nanotubes, which are
FIGURE 1 SEM (Scanning Electron Microscopy) image (c) of a bunch of ferroelectric nanotubes consisting barium titanate. (a) the open ends, (b) the middle part, and (d) the capped tips of nanotubes.

straight, smooth and have a very high aspect ratio of about 50. Depending on the templates, their outer diameter ranges from 50 nm up to several micrometers and their length from a few micrometers up to more than 100 µm. The hollow nature is obvious from Fig. 1(a), in which the open end of nanotube is depicted. Note that the wetting process was so uniform that a complete covering of the whole surface of the pore walls occurred. The length of the nanotubes can be seen from Fig. 1(c), which is around 100 µm. All pores of the processed templates were blind holes. Figure 1(d) shows capped BaTiO₃ nanotubes whereas the caps are replicas of the pore bottoms. A single step of infiltration yields a wall thickness of around 100 nm for both PZT and BaTiO₃ nanotubes.

A more detailed characterization of the ferroelectric nanotubes can be carried out by TEM (Transmission Electron Microscopy) measurement. Figure 2 shows the cross-section image of so-obtained PZT tubes in the silicon template. The tube walls of both BaTiO₃ and PZT nanotubes consist of a crystalline layer sandwiched between two amorphous layers at the
FIGURE 2 TEM cross-section of PZT nanotubes in silicon template.

silicon-ferroelectric interface and at the internal ferroelectric surface. While the amorphous layer at the silicon-ferroelectric interface is the result of a reaction between the oxide and silicon due to the high crystallization temperature. The inner amorphous layer might be an artefact of the TEM sample preparation, i.e. redeposition of amorphous materials during ion-milling thinning.

Ferro- and piezoelectric properties of the PZT and BaTiO₃ nanotubes were measured by scanning force microscopy in the so-called piezoresponse mode [20, 21] after they had been deposited on a Pt-coated silicon substrate. An individual ferroelectric nanotube either of PZT or of BaTiO₃ was probed by a conductive tip or electrically characterized by measuring the local piezoelectric hysteresis. The as-prepared nanotubes showed only weak ferroelectric properties. In order to improve their properties, the ferroelectric nanotubes were annealed again at 700°C for one hour in an oxygen atmosphere for BaTiO₃ nanotubes and in a lead oxide atmosphere for PZT nanotubes. This high temperature treatment allows to remove defects and to convert the amorphous layers into the ferroelectric perovskite phase. Figure 3 shows the piezoelectric hysteresis loop obtained on a PZT tube with an outer diameter of 700 nm and wall thickness of 90 nm. The loop is rectangular and shows a switching at the coercive voltage of about 2 V. The effective remnant piezoelectric coefficient is about 90 pm/V.
**DISCUSSION**

Ferroelectric nanotubes are attractive due to their remarkable electrical and mechanical properties. Individual free standing tubes and ordered arrays of tubes embedded in silicon have an outstanding potential as building blocks of miniaturised devices in the field of nano-electromechanical systems (NEMS). The highly ordered arrays of ferroelectric nanotubes can be obtained on a large scale by selective etching of the silicon templates. Figure 4 shows an array of free standing ferroelectric nanotubes on a silicon wafer.

Several applications based on piezoelectric nanotubes have been proposed [23]. First of all, a new type of cantilever can be fabricated from a single piezoelectric nanotube (Fig. 5(a)). Inner and outer electrodes in the
FIGURE 5 Potential piezoelectric devices: (a) schematic of sub-micron piezoelectric scanners and active cantilevers (1. piezoelectric tube, 2. electrodes, 3. substrate, 4. tip), (b) mass storage devices, and (c) tunable photonic crystals.

same configuration as the classical piezoelectric scanner used in nowadays scanning probe microscopes will allow a 3D movement of the free end of the tube. As the tube walls are very thin, the deflection of the nanotube can be controlled precisely by small voltages applied to the electrodes. Moreover, such a cantilever can also act as a detector due to the interaction between itself and the sample surface. This ferroelectric nanotube cantilever could serve as both cantilever and scanner in atomic force and scanning tunnelling microscopy.

Ordered arrays of ferroelectric nanotubes also have large application potential in the field like mass storage devices (Fig. 5(b)) similar to IBM millipede storage devices [22]. In such devices, all the micro-cantilevers (piezoelectric tubes) scan independently their individual area and write/read data in an associated section of the storage medium, which is called a bit array of a storage field. Compared to the conventional mass storage devices the ferroelectric probe arrays permit a fully random read/write with an increased access speed since the individual storage field is not read out in series, but in parallel. The speed of the proposed device could potentially exceed the present access time limit, which is in the 10 ms range.

Photonic bandgap (PBG) materials may also be formed by highly ordered two-dimensional arrays of ferroelectric nanotubes. By applying an external electric field, each nanotube can be deflected in several ways, thus lead to periodicity and/or symmetry changes or introduction of well-defined defects
in the arrays. All these shifts allow the tuning of both the photonic bandgap position and width.

CONCLUSION

We have developed a very simple and inexpensive generic method to obtain ferroelectric nanotubes with sizes tunable over a relatively large mesoscopic range. As examples we prepared lead zirconate titanate and barium titanate nanotubes with good piezoelectric and ferroelectric properties. These ferroelectric nanotubes with diameters of several hundred nanometers and with wall thicknesses of a few tens of nanometers will be ideal candidates for electromechanical system such as mesoscopic actuators similar to current piezoelectric scanners, mass storage devices as well as tunable photonic crystals.

REFERENCES

An atomic force microscope provided with a conductive tip and a lock-in detection system is used to measure the piezoelectric vibrations generated by the sample via converse piezoelectric effect when an ac voltage is applied across the sample. The existence of a hysteresis in the piezoresponse signal is directly associated with the polarization switching in the sample region underneath the tip.


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