

Ferroelectric Lead Zirconate Titanate and Barium Titanate Nanoshell Tubes

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ABSTRACT

Wetting of the pore walls of porous templates is a simple and convenient method to prepare nanoshell tubes. Wafer-scale fabrication of ferroelectric lead zirconate titanate and barium titanate nanoshell tubes was accomplished by wetting porous silicon templates with polymeric precursors. The ferro- and piezoelectric properties of an individual ferroelectric nanoshell tube either of PZT or of BaTiO₃ 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 have also prepared highly ordered arrays of free-standing ferroelectric nanoshell tubes obtained by partial etching of the silicon template. Such materials might be used as building blocks of miniaturized devices and could have a significant impact in the field of nano-electromechanical systems.

INTRODUCTION

One-dimensional systems such as nanotubes or nanorods from various materials have attracted great interest in the last decade, because they exhibit different physical properties than their bulk counterparts. 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].

However, the preparation of functionalized nanotubes, e.g., from complex oxide ferroelectrics, still 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 materials 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 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].

Here we report on the wafer-scale fabrication of ferroelectric nanoshell tubes or ordered nanoshell tubes arrays via a simple and convenient method: wetting of porous templates. This approach allows tailoring the geometry parameters such as diameter and length of the tubes. The ferroelectric switching behaviour of an individual tube was demonstrated by atomic force microscopy.

EXPERIMENTAL DETAILS

The fabrication approach of lead zirconate titanate, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) and barium titanate (BaTiO_3) nanoshell tubes consists of wetting the pore walls of ordered porous templates, either of porous alumina [18] or macroporous silicon [19], by polymeric precursors and subsequent high temperature annealing. Polymers containing metals in the stoichiometric quantities (PZT 9906 Polymer and BATIO 9101 Polymer from *Chemat Technology, INC*) were used as precursors. After the precursors had been 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 [20]. 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 1h at 650°C for PZT and 850°C for BaTiO_3 in order to obtain the perovskite phase. The presence of this phase was confirmed by X-ray diffraction for both BaTiO_3 and PZT nanoshell tubes. By a selective etching of the template in 20-wt % KOH solution at 90°C , free ferroelectric tubes were obtained. The tubes were then washed in de-ionized water for several times to remove KOH lye and deposited on silicon or platinum-coated silicon substrates. Depending on the templates, their outer diameter ranges from 50 nm up to several microns and their length from a few microns up to more than 100 microns. Fig. 1(a) shows, for instance, ferroelectric BaTiO_3 nanoshell tubes, which are straight, smooth and have a very high aspect ratio of about 50. Note that 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. The BaTiO_3 nanoshell tubes are all capped and the caps are replicas of the pore bottoms.

A more detailed characterization of the ferroelectric nanoshell tubes can be carried out by TEM (Transmission Electron Microscopy) measurements. Fig. 1(b) shows the cross-section image of so-obtained PZT tubes in the silicon template after a single step of wetting, which yields a wall thickness of 90 nm for PZT and 100 nm for BTO nanoshell tubes. The tube walls of both BaTiO_3 and PZT nanoshell tubes consist of a crystalline layer sandwiched between two amorphous layers at the silicon-ferroelectric interface and at the internal ferroelectric surface. 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 during the TEM sample preparation, i.e. redeposition of amorphous materials during ion-milling thinning.

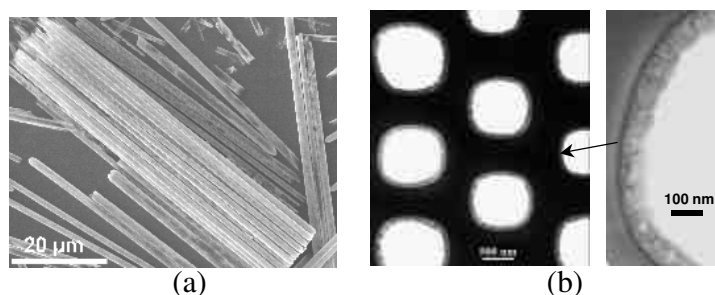


Figure 1. (a) SEM (Scanning Electron Microscopy) image of a bunch of ferroelectric nanoshell tubes consisting of barium titanate (BaTiO_3). (b) TEM cross-section of PZT nanoshell tubes in a silicon template.

Ferro- and piezoelectric properties of the PZT and BaTiO₃ nanoshell tubes were measured by scanning force microscopy in the so-called piezoresponse mode [21,22] after they had been deposited on a Pt-coated silicon substrate. An individual ferroelectric nanoshell tube either of PZT or of BaTiO₃ was probed by a conductive tip or electrically characterized by measuring the local piezoelectric hysteresis. The as-prepared nanoshell tubes showed only weak ferroelectric properties. To improve their properties, we introduced an additional thermal treatment for the free tubes at 700 °C for one hour in an oxygen atmosphere for BaTiO₃ nanoshell tubes and in a lead oxide atmosphere for PZT nanoshell tubes. SEM investigations (not shown here) confirmed that the shape and morphology of the tube are not changed by this high-temperature annealing. This treatment allows conversion of the amorphous layer into perovskite ferroelectric phase and removal of the defects resulting from the etching process. Fig. 2 shows the piezoelectric hysteresis loop finally obtained on a PZT tube with an outer diameter of 700 nm and wall thickness of 90 nm. This 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 remnant piezoelectric coefficient is 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.

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 porous templates. Fig. 3 shows an array of free standing ferroelectric nanoshell tubes on a silicon wafer.

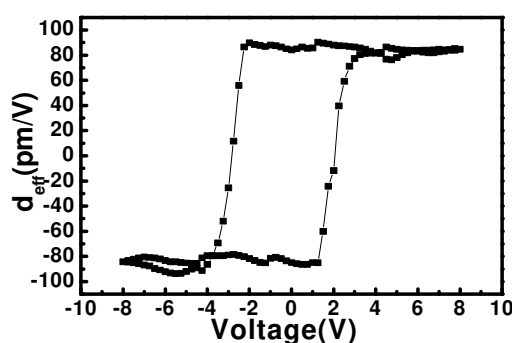


Figure 2. Piezoelectric hysteresis loop of an individual PZT tube measured by piezoresponse AFM (Atomic Force Microscopy).

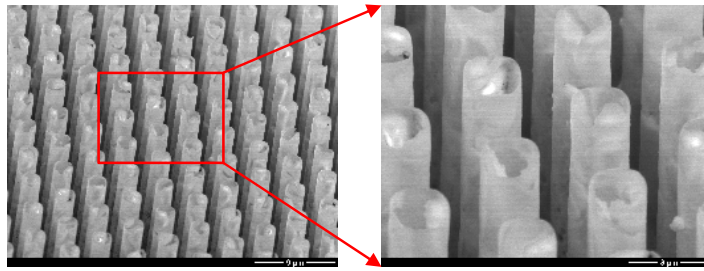


Figure 3. Array of free-standing PZT nanoshell tubes obtained by selective, partial etching of a Si template in aqueous KOH at 90°C for 16 minutes.

Several applications based on piezoelectric nanoshell tubes have been proposed [23]. First of all, a new type of cantilever can be fabricated from a single piezoelectric nanoshell tube (Fig. 4(a)). Inner and outer electrodes in the same configuration as the classical piezoelectric scanner used in state-of-the-art 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 nanoshell tube can be controlled precisely by small voltages applied to the electrodes. Moreover, such a cantilever can also act as a detector due to its interaction with the sample surface. This ferroelectric nanoshell tube cantilever could serve as both cantilever and scanner in atomic force and scanning tunnelling microscopy.

Ordered arrays of ferroelectric nanoshell tubes also have a large application potential, e.g., as mass storage devices (Fig. 4(b)) similar to IBM millipede storage devices [23]. In such devices, all the micro-cantilevers (piezoelectric tubes) independently scan 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 fully random read/write processes, 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 nanoshell tubes (Fig. 4(c)). By applying an external electric field, each nanoshell tube can be deflected in several ways, thus leading to periodicity and/or symmetry changes or the introduction of well-defined defects in the arrays. All these shifts allow the tuning of both the photonic bandgap position and width.

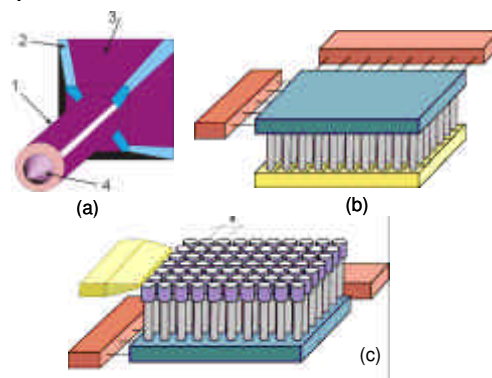


Figure 4. Potential piezoelectric devices. (a) Schematic of sub-micron piezoelectric scanners and active cantilevers: 1. piezoelectric tube; 2. electrodes; 3. substrate; 4. tip. (b) Mass storage devices. (c) Tunable photonic crystals.

CONCLUSION

We have developed a very simple and inexpensive generic method to obtain ferroelectric nanoshell tubes with sizes that can be tuned over a relatively large mesoscopic range. As examples we have prepared lead zirconate titanate and barium titanate nanoshell tubes with good piezoelectric and ferroelectric properties. For practical applications, ferroelectric oxide tubes are more desirable than simple rods, especially in the mesoscale range. We expect that free-standing ferroelectric tubes obtained by partial etching of the porous template may be used as building blocks 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 [24].

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