Ferroelectric switching of nanotubes composed of lead zirconate titanate and barium titanate


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Tubular nanostructures have attracted increasing interest as building blocks for miniaturized devices. Particularly, oxide nanotubes exhibiting ferroelectric or piezoelectric properties can serve as components for nano-electromechanical systems (NEMS). We have demonstrated wafer-scale fabrication of ferroelectric lead zirconate titanate (PZT, PbZr0.52Ti0.48O3) and barium titanate (BaTiO3) nanotubes either dispersed in a solution [1] or embedded in an ordered silicon matrix [2] using a simple and convenient fabrication method that allows full tailoring of tube dimensions as diameters, lengths and wall thicknesses. Ferroelectric switching was demonstrated via atomic force microscopy by showing a rectangular ferroelectric hysteresis loop of an individual PZT nanotube.

The fabrication procedure of BaTiO3 and PZT nanotubes consists of wetting ordered porous templates [3], such as porous alumina or macroporous silicon, by polymeric precursors containing metals in 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 because the driving force between the polymer precursor and the pore wall leads to a reduction of the surface energy of the system. The polymer precursor layer was subsequently transformed into an amorphous oxide layer by annealing in air at 300 °C and later crystallized at 650 °C for PZT under lead atmosphere and 850 °C for BTO in air for 1 h in order to obtain the perovskite phase. By selective etching of the template in 20-wt % KOH solution at 90 °C, free suspended or ordered arrays of ferroelectric nano-shell tubes embedded in silicon matrix were obtained. Figure 1a shows the resulting ferroelectric BTO nanotubes lying on a silicon substrate, which are straight, smooth, and have a very high aspect ratio of more than 50. Depending on the templates, the outer diameter ranges from 50 nm up to several μm and the length more than 100 μm. Arrays of nanotubes with one end still embedded in the silicon matrix are depicted in figure 1b.

Figure 1: Scanning electron micrograph of (a) released ferroelectric nanotubes consisting of barium titanate and (b) arrays of free-standing PZT nanotubes from silicon matrix.

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

Figure 2. TEM cross-section of PZT nanotubes in silicon template.

Ferro- and piezoelectric properties of the PZT and BaTiO$_3$ nanotubes were measured by scanning force microscopy in the so-called piezoresponse mode after they had been deposited on a Pt-coated silicon substrate. An individual ferroelectric nanotube either of PZT or of BaTiO$_3$ 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 BaTiO$_3$ 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 from a PZT nanotube with an outer diameter of 700 nm and a 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.

Figure 3. Piezoelectric hysteresis loop of an individual PZT tube measured by piezoresponse AFM (Atomic Force Microscopy).

In conclusion, we have developed a simple and inexpensive generic method to obtain ferroelectric nanotubes with sizes that can be tuned over a relatively large range. We expect that ordered arrays of free-standing ferroelectric nanotubes will be used as building blocks of miniaturized devices and have a significant impact in the field of nano-electromechanical systems. As the fabrication methods are similar to the thin-film technology, the wafer-scale integration of piezoelectric scanner arrays with silicon microelectronics is now possible. This opens up the possibility of “on-chip” massively parallel scanning probe microscopes and true random access mass storage devices [4].

References