One-dimensional ferroelectric monodomain formation in single crystalline BaTiO$_3$ nanowire

Zhaoyu Wang, Jie Hu, and Min-Feng Yu$^a$

Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 W. Green Street, Urbana, Illinois 61801

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The authors report the existence of one-dimensional and stable formation of ferroelectric monodomain in single crystalline BaTiO$_3$ nanowire. Piezoresponse force microscopy operated in both vertical and lateral modes showed ferroelectric polarization switching along the axial (lateral) direction of nanowire, while the polarization along the transversal (vertical) direction was strongly suppressed. Such a one-dimensional polarization formation was also found to be highly stable and nonretentive in that switched polarization spontaneously returned to its original orientation at the instant of removing the applied poling voltage. © 2006 American Institute of Physics. [DOI: 10.1063/1.2425047]

To explore the rich physics of ferroelectricity, especially at low dimensionality and at nanoscale, perfectly structured polar oxide nanomaterials are the optimal samples for study. They are also potential building blocks for the realization of nanoscale actuators, sensors, nonlinear optics, and especially high density ferroelectric nonvolatile memory devices. With the recent advance in the synthesis of particularly high density ferroelectric nonvolatile memory and the advent of nanoscale technology, it has become possible to study 1D physics of ferroelectricity using such chemically and structurally well-defined crystalline materials instead of relying only on polycrystalline thin film ceramics or molecular beam epitaxial films. A renewed theoretical interest in this context has also been initiated. For example, Fu and co-workers have applied first principles to model isolated BaTiO$_3$ and lead zirconium titanate (PZT) 1D nanostructures and revealed the existence of polarization “vortexes.” They have also shown that in 1D PZT nanowire, spontaneous formation of polarization exists, and even phase transition can occur. Geneste et al. studied size dependence of FE properties in BaTiO$_3$ nanowires from first principles and showed that stable FE polarization along the nanowire axis exists above a critical diameter of ~1.2 nm.

As one of the representative FE materials, BaTiO$_3$ has especially been the model sample for the study of ferroelectricity, especially for the exploration of superparaelectric limit in ferroelectric. Various techniques, such as contact mode piezoresponse force microscopy (PFM), electron paramagnetic resonance, x-ray diffraction (XRD), and Raman scattering, among others, have been applied to either examine the tetragonal-to-cubic phase transition or acquire the hysteresis loops in FE nanostructures for the purpose of exploring their dependence on size, temperature, and mechanical stress, thus the scale effect. However, the BaTiO$_3$ nanostructures studied thus far are mostly thin films, nanoparticles, or lithographically fabricated structures. Several studies have recently demonstrated the existence of ferroelectricity and polarization switching in chemically synthesized BaTiO$_3$ nanowires with noncontact mode electrostatic force microscopy. Here, we report the use of PFM for the direct study of FE behavior in BaTiO$_3$ nanowire. The existence of highly stable formation of 1D FE monodomain was revealed and nonremnant polarization switching along the axial direction of nanowire was realized with PFM.

PFM operated in both vertical and lateral modes was applied to study the FE behavior of individual BaTiO$_3$ nanowire. Briefly, in the vertical PFM mode, the local vertical (out-of-plane) deformation (the piezoresponse) of the sample induced by the applied ac signal is measured through the vertical deflection of the atomic force microscope (AFM) cantilever, and the out-of-plane polarization is studied; in the lateral PFM mode, the local shear (in-plane) deformation of the sample is measured through the torsional bending of the AFM cantilever, and the in-plane polarization is studied. In both PFM modes, the phase difference (0° or 180°) between the applied ac signal and the piezoresponse is determined by the orientation of the local FE polarization in sample.

The BaTiO$_3$ nanowires were made at 800 °C following a procedure similar to that reported by Mao et al. The nanowires had diameters ranging from 50 to 200 nm and lengths up to tens micrometers. The SEM micrograph in Fig. 1(a) shows a typical BaTiO$_3$ nanowire with a diameter of ~100 nm and a length of ~9 μm. Figure 1(b) is a lattice resolved high-resolution transmission electron microscopy (TEM) image, which shows that BaTiO$_3$ nanowire is single crystalline with a lattice constant of 4.02 Å and free of al-

FIG. 1. (a) SEM image of a typical BaTiO$_3$ nanowire. (b) High-resolution TEM image of a BaTiO$_3$ nanowire. Inset: the selected area electron diffraction pattern from nanowire.

$^a$Electronic mail: mfyu@uiuc.edu
most any internal defects. Selected area electron diffraction from a single nanowire, shown in the inset of Fig. 1(b), reveals that the pseudocubic BaTiO$_3$ structure has one of the three principle (100) lattice axes aligned along the wire length direction. Energy dispersive spectroscopy analysis inside TEM on different segments along a single nanowire has confirmed that the composition is identical along the nanowire and consists of Ba and Ti. XRD pattern taken from the nanowire sample was prepared by dispersing a drop of BaTiO$_3$ nanowire in absolute ethanol onto a silicon substrate coated with Au/Pd conductive layer. The PFM study was carried out at room temperature and ~10% humidity with a Nanoscope IV-Dimension 3100 AFM, equipped with a signal access module and an external lock-in amplifier (Signal Recovery model 5210). Pt/Ti coated conductive AFM probes (NSC18, MikroMasch) having a nominal force constant of 3 N/m were used. Once the nanowire was located with AFM operated in tapping mode, the probe tip was positioned to the center of the nanowire, and the AFM was switched to contact mode and engaged with zero scan size. Extreme care was taken to avoid dislocating the nanowire during the PFM measurement. The nanowire is always prepositioned so that the nanowire length direction is aligned with the fast scan direction of the lateral PFM mode.

Figure 2(a) shows a three-dimensional representation of a BaTiO$_3$ nanowire acquired with tapping mode AFM. The diameter of the nanowire is 95 nm. PFM measurements were performed with positive contact force at the same chosen spot on this nanowire. Figures 2(b)–2(e) show the in-field hysteresis phase loops and piezoresponse amplitude loops acquired from the nanowire with the lateral and vertical PFM modes, respectively. The loops were acquired by scanning a dc bias (additionally applied between the AFM tip and the sample) from −15 to 15 V in 200 steps, with the duration of each step being 0.5 s. At the end 0.1 s of each step, the piezoresponse amplitude and the phase difference between the applied ac testing signal and the piezoresponse were measured. The applied ac signal has amplitude of 1 V (peak-to-peak) and frequency of 5 kHz. The hysteresis phase loop acquired with the lateral PFM mode [Fig. 2(b)] shows a well-defined, symmetric “square” loop, and the amplitude loop [Fig. 2(c)] shows a “butterfly shape,” resembling the classic $P$–$E$ hysteresis loop and the amplitude loop of bulk crystaline BaTiO$_3$. Similar loops were also obtained from other nanowires having smaller diameters down to ~50 nm. Such loops, combined with additional studies shown later, strongly imply the existence of in-plane, switchable FE polarization and strong shear response (the $d_{15}$ response) in the nanowire. In contrast, the phase and amplitude loops [Fig. 2(d)] acquired with the vertical PFM mode show very small PFM response (more than 50 times smaller) and no obvious hysteresis.

Such an existence of strong in-plane polarization was further corroborated with our sampling study. In the sampling study, PFM phase values were measured with lateral PFM mode at 20 spots distributed across the whole length of a pristine nanowire having a length of 6 μm and a diameter of 70 nm under zero dc bias. The stable phase value, as shown in Fig. 3(a), indicated the existence of a singular polarization direction (a monodomain) along the whole nanowire length. A lateral PFM phase image [Fig. 3(c)] was also acquired from a nanowire of 80 nm in diameter [Fig. 3(b)] and showed an obvious contrast between the nanowire and the substrate and a uniform FE phase along the nanowire, again demonstrating the existence of a monodomain along the length of the nanowire. A 0.15 N/m cantilever was used to avoid displacing the nanowire. For lateral PFM the effect...
of electrostatic interaction between the sample and the cantilever was found being negligible, as the signal was detected through the twisting of AFM cantilever.) Interestingly, we have also rotated a nanowire (thus the polarization) azimuthally by 180° on surface as shown in the insets of Figs. 3(d) and 3(e), and acquired the hysteresis phase loops before [Fig. 3(d)] and after the rotation [Fig. 3(e)]. The hysteresis loop reversed its orientation, indicating the apparent geometric reversal of the polarization direction, as expected.

Further dynamic domain switching studies revealed that the native polarization existed in BaTiO$_3$ nanowire was highly stable. Electric poling of the nanowire intended to permanently reverse the polarization was performed locally by an AFM tip. Negative dc pulses with amplitude up to $-25$ V were applied locally on the nanowire. As expected, the local polarization of the nanowire was switched (by the lateral electric field component under the sharp AFM tip) when the bias is on, but the switched polarization instantly reversed back to its original polarization direction once the dc bias was removed, as shown in Fig. 4.

We now discuss the experimental results. In the lateral PFM mode, the observed polarization switching in the hysteresis loop [shown in Fig. 2(b)] corresponds to a 180° switching along the $c$ polar axis, induced by the lateral electric field component in the inhomogeneous electric field underneath the AFM tip.$^{21}$ However, in the vertical PFM mode, in order to observe apparent domain switching, the existence of an out-of-plane polarization would be necessary, which would require a 90° domain switching from the axial polarization. However, a 90° domain switching is associated with the formation of highly stressed lattice structure and high surface energy domain boundaries; it would thus be energetically unfavorable and suppressed. The observed phase shift and the small amplitude response in the vertical PFM mode in Fig. 2 reflect simply the behavior of a pure piezoelectric or a dielectric polarized by the applied dc bias. The existence of 1D monodomain formation (as revealed in Fig. 3) in such a BaTiO$_3$ nanowire can be understood from an energetic point of view. The simple formation of head-to-head oriented domains along the nanowire axis is simply energetically unfavorable, and is forbidden. The allowed domain walls for tetragonal BaTiO$_3$ crystal are 180° and 90° domain walls. It explains also why the BaTiO$_3$ nanowires in our study had highly stable ferroelectric polarization and resisted the permanent (remnant) switching from their original polarization, as shown in Fig. 4. During the polarization switching measurement, it is expected that the induced switching is confined within the small nanowire segment underneath the tip, and is thus local. The nanowire outside this segment still possesses the original polarization orientation. Such a locally switched segment with reversed polarization, as argued above, would become energetically highly unfavorable for existence once the electric bias is removed; as a result, it spontaneously switches back to the original orientation.

The question, which is of both scientific and practical importance, remains on whether the FE polarization formation and the FE switching behavior would be different for nanowires having even smaller diameters. An early study$^{10}$ has shown the solution phase synthesis of BaTiO$_3$ nanowires having diameters down to 10 nm, though the synthesis procedure is found to be extremely delicate. We instead are exploring the chemical etching approach for getting smaller diameter nanowires for further studies.

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