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Ferroelectric Properties of Individual Barium Titanate Nanowires Investigated by Scanned Probe Microscopy

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ABSTRACT

We report scanned probe investigations on the ferroelectric properties of individual single-crystalline barium titanate nanowires. We show that nonvolatile electric polarization can be reproducibly induced and manipulated on these nanowires, thereby demonstrating that nanowires as small as 10 nm in diameter retain ferroelectricity. The coercive field for polarization reversal is determined to be ∼7 kV/cm, and the retention time for the induced polarization exceeds 5 days. These nanowires should provide promising materials for fundamental investigations on nanoscale ferroelectricity, and they may also be useful in nanoscale nonvolatile memory applications.

Ferroelectric oxides, which exhibit a spontaneous electric polarization that can be reoriented with an external field, have received considerable attention because of their utilization in nonvolatile memory devices.[1−5] These oxides also exhibit other related properties, including piezoelectricity, pyroelectricity, and large dielectric constants, and they have been used in fabricating microactuators, sensors, and capacitors.[1−3] With the miniaturization trend in device size, the size-dependent evolution of ferroelectricity in nanocrystalline and thin-film samples has been the focus of many research efforts,[3,6−12] and nanoscale oxides have been shown to exhibit many unique properties, such as size-induced depression of the phase transition temperature[3,6,8,9] and the emergence of ferroelectricity in thin antiferroelectric films.[10] Despite intense experimental efforts, however, a clear fundamental understanding of nanoscale ferroelectricity has yet to emerge.[3]

Here, we report the scanned probe characterization of individual single-crystalline barium titanate ($BaTiO_3$) nanowires synthesized by a solution based method.[13] Scanned probe microscopy investigations show that nonvolatile electric polarization can be reproducibly induced and manipulated on these nanowires by an external electric field, demonstrating that they remain ferroelectric despite their small radial dimension. The coercive field for polarization reversal is determined to be ∼7 kV/cm, and the retention time for the induced polarization exceeds 5 days. Nonvolatile polarization domains as small as 100 nm^2 in size can be induced on these nanowires, suggesting that ferroelectric nanowires may be used to fabricate nonvolatile memory devices with an integration density approaching 1 terabit/cm^2.

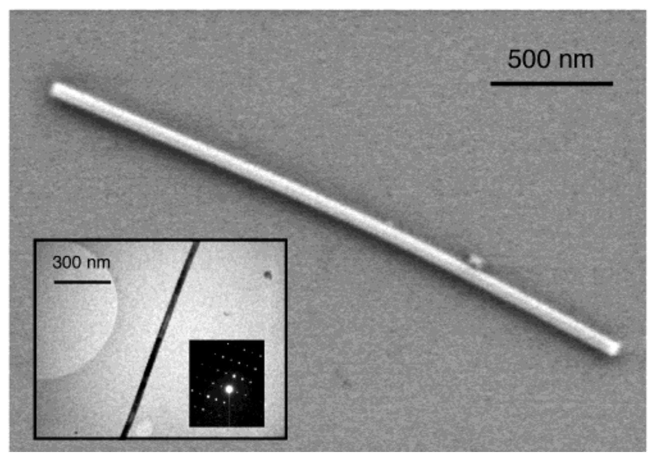

Figure 1. Scanning electron microscopy (SEM) image of an isolated $BaTiO_3$ nanowire. Inset: transmission electron microscopy image of an isolated $BaTiO_3$ nanowire with a convergent beam electron diffraction (CBED) pattern obtained from the same wire.

The barium titanate nanowires investigated here were synthesized by solution-phase decomposition of barium titanium isopropoxide ($BaTi[OCH(CH_3)_2]_6$),[14] as reported previously.[13] This synthesis yields well-isolated $BaTiO_3$ nanowires with diameters ranging from 5 to 60 nm and lengths reaching up to >10 μm.[13] Figure 1 shows a scanning electron microscope (SEM) image of a representative nanowire, with convergent beam electron diffraction (CBED) data shown in the inset. The CBED pattern in Figure 1

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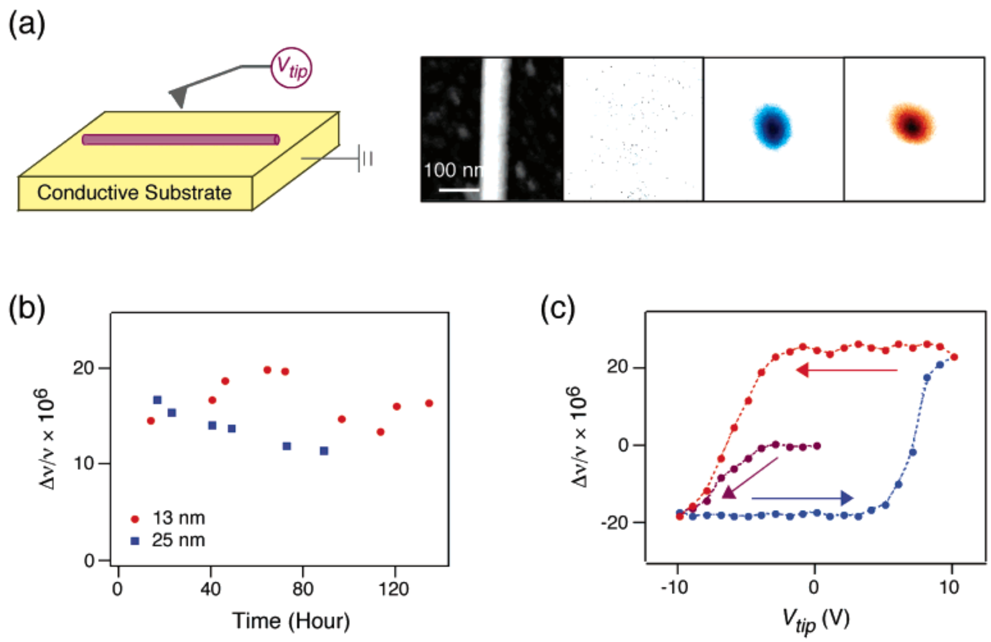

Figure 2. (a) Schematic diagram illustrating the experimental geometry. The panels on the right show a topographic image of an 18-nm diameter $BaTiO_3$ nanowire (first) and electrostatic force microscope (EFM) images obtained from the same wire. The second panel shows an EFM image of the as-deposited nanowire, and the third and fourth panels show EFM images obtained after the writing procedure with $V_{tip} = -10$ V and $V_{tip} = +10$ V, respectively. Red, white, and blue in EFM images correspond to the resonance frequency shifts of −10, 0, and 10 Hz, respectively. (b) Plot of the fractional shifts in the cantilever resonance frequency ($\Delta\nu/\nu = (\nu_0 - \nu)/\nu_0$) as a function of time measured from two different nanowires of diameters 13 nm (circles) and 25 nm (squares). The writing was performed with $V_{tip} = +10$ V for 3 min, while the reading was performed at $V_{tip} = -2$ V at each time point. (c) Plot of $\Delta\nu/\nu$ as a function of the writing voltage (V_{tip}) obtained from a $BaTiO_3$ nanowire with 15 nm diameter. Each data point in the plot was obtained by applying the writing voltage for 3 min and subsequently measuring the shift in the cantilever resonance frequency at $V_{tip} = -2$ V. The V_{tip} scan sequence was from 0 to −10 V (magenta), −10 V to +10 V (blue), and +10 V to −10 V (red). In (a)−(c), the distance between the tip and the top surface of the nanowire was 10 nm during the writing procedure and 35 nm during the reading procedure.

reveals that $BaTiO_3$ nanowires have a roughly cubic perovskite structure consistent with bulk $BaTiO_3$ and that one of the principal axes is aligned along the wire axis. At room temperature, the bulk $BaTiO_3$ unit cell exhibits tetragonal symmetry with a slight elongation along the c axis (c/a = 4.038 Å/3.994 Å=1.011).[1] Unfortunately, due to the broadening of the diffraction spots that obscures the small tetragonal distortion of the unit cell, the data in Figure 1 alone do not establish which principal axis lies along the wire axis.

The ferroelectric properties of individual $BaTiO_3$ nanowires were investigated using an ultrahigh vacuum scanned probe microscope (SPM) with a conductive tip operating in a noncontact mode, a strategy that has been successfully applied to study ferroelectric properties of thin film samples.[15−21] A schematic diagram illustrating the experimental geometry is presented in Figure 2. To induce or "write" local electric polarization perpendicular to the nanowire axis, a voltage (V_{tip}) was applied to the conductive tip while holding the tip at a fixed distance above a nanowire that lies on a gold substrate. The written polarization was then probed or "read" using electrostatic force microscopy (EFM) by measuring the shift in the resonance frequency ($\Delta\nu = \nu_0 - \nu$) of a SPM cantilever while scanning it with a small V_{tip}. This shift $\Delta\nu$ is directly proportional to the electrostatic force felt by the tip and thus the magnitude of the electric polarization on the nanowire.[15−22] A plot of $\Delta\nu$ as a function of tip position provides a spatial map of electric polarization directions on the nanowire.

The panels in Figure 2a show representative EFM images obtained from an 18-nm diameter nanowire along with a topographic image. These EFM images are obtained by subtracting an image at $V_{tip} = +2$ V from that at $V_{tip} = -2$ V to eliminate the capacitive contribution between the tip and the nanowire, and hence they exhibit only the contribution from the local ferroelectric polarization. The leftmost EFM image obtained from the as-deposited nanowire shows no discernible EFM contrast, indicating that pristine nanowires do not exhibit polarization perpendicular to the wire axis. The EFM images obtained after the writing procedure with $V_{tip} = -10$ V and $V_{tip} = +10$ V clearly show, on the other hand, that a local electric polarization perpendicular to the wire axis can be induced by an external electric field.

Comparison of the two EFM images in Figure 2a further shows that the shift in the cantilever resonance frequency changes sign after changing the writing procedure from $V_{tip} = +10$ V to $V_{tip} = -10$ V, thus indicating a reversal of the polarization direction. The EFM images obtained as a function of the duration of V_{tip} show that the original induction and reversal of polarization can be performed on the time scale of seconds, which is the time resolution of the current experiment. Moreover, investigations on many nanowires with different diameters show that a local polarization can be induced and reversed repeatedly on a

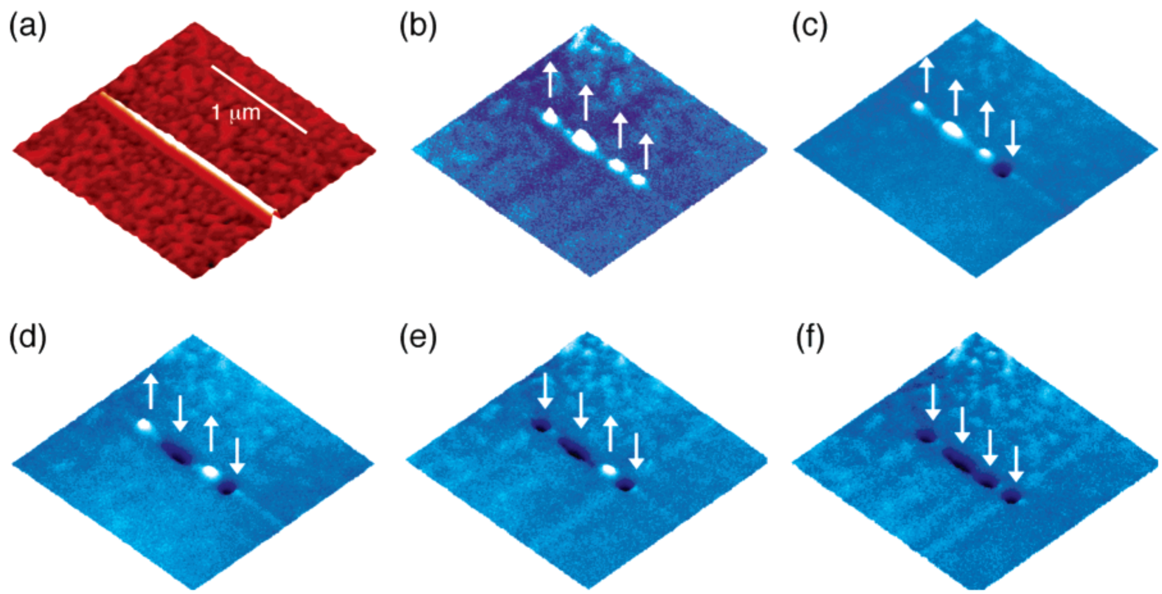

Figure 3. (a) Three-dimensional topographic image of a 12-nm diameter $BaTiO_3$ nanowire. (b)−(f) Successive three-dimensional EFM images showing that four distinct polarization domains can be independently manipulated by an external electric field. In these EFM images, the bright and dark colors correspond to a resonance frequency shift of +10 Hz and −10 Hz, respectively, and the white arrows indicate the polarization directions. The upward and downward polarization spots were written with $V_{tip} = -10$ V and $V_{tip} = +10$ V, respectively. The distance between the tip and the top surface of the nanowire was 10 nm during the writing procedure and 35 nm during the reading procedure.

nanowire as small as 10 nm in diameter. Finally, the measurement of the retention time presented in Figure 2b demonstrates that the electric polarizations induced on nanowires do not decay significantly over a period exceeding 5 days in an ultrahigh vacuum environment, illustrating their nonvolatile nature.

Two characteristic features of ferroelectric materials are that their electric polarization can be reoriented by an external electric field greater than the coercive field, E_c, and that the reversal of this polarization exhibits hysteresis.[1−3] The measurement of local polarization reversal on a representative $BaTiO_3$ nanowire with 15 nm diameter is presented in Figure 2c, and it shows that the polarization reversal indeed exhibits a clear memory effect with a remanence-to-saturation ratio close to 1. Based on the known experimental geometry and by assuming the relative dielectric constant of a $BaTiO_3$ nanowire to be ~1200 as in bulk crystals,[23] E_c can be calculated directly from the value of V_{tip} at which the polarization signal goes through 0. Measurements on different nanowires with diameters ranging from 10 to 50 nm show that $E_c \sim 7$ kV/cm irrespective of nanowire diameter. This value of E_c compares favorably to $E_c \sim 10$ kV/cm measured from a bulk $BaTiO_3$ single crystal,[24] but it is smaller than typical $E_c \sim 30$ kV/cm for polycrystalline samples.[23] Since the E_c values are known to be sensitive to the presence of domain walls and defects,[23,25,26] the observed $E_c \sim 7$ kV/cm demonstrates that $BaTiO_3$ nanowires are nearly free of defects.

Parts b−f of Figure 3 show successive EFM images of four distinct polarization domains written on a 12-nm diameter nanowire, and they illustrate that multiple nanoscale polarization domains can be induced and independently manipulated on a single $BaTiO_3$ nanowire. Here, the second polarization domain was intentionally written over a 200-nm long wire segment, whereas the remaining three domains were written with the tip position fixed over a particular spot. The EFM images in Figure 3b−f clearly show that the second polarization domain appears approximately 4 times larger than the other circular spots, demonstrating that the EFM technique can distinguish among polarization domains of different lengths along the nanowire.

Close inspection of Figures 2 and 3 provides information about the smallest possible size of a polarization domain on a nanowire. Specifically, Figures 2 and 3 show that an EFM spot induced by a tip fixed at a particular position is roughly circular in shape and that its size is ~30 nm, as determined by the half-width at half-maximum. This size is roughly the same as the tip−nanowire distance during the reading procedure, and it shows that the size of the smallest EFM feature is limited by the tip−sample distance due to the long-ranged nature of electrostatic interactions. Considering that the size of a polarization domain perpendicular to the wire axis is limited by the nanowire diameter, the circular shape of the EFM spots suggests that the spatial extent of the polarization is comparable to the nanowire diameter and hence polarization domains as small as 100 nm^2 in size can be induced on a nanowire. This spatial dimension is an order of magnitude smaller than the smallest size of polarization domains reported from previous studies of ferroelectric thin films.[19,21]

The present study shows that nanoscale nonvolatile polarization can be reproducibly induced and independently manipulated on ferroelectric nanowires composed of single-crystalline $BaTiO_3$. As demonstrated by the hysteresis measurements on individual nanowires, these ferroelectric nanowires are ideally suited for fundamental studies of nanoscale ferroelectricity and piezoelectricity. The observation that polarization domains as small as 100 nm^2 can be reproducibly manipulated with a well-defined coercive field suggests that these nanowires may be well suited for the realization of nanoscale nonvolatile memory devices based on nanowire crossbar arrays.[27]

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