

# Polarization switching using single-walled carbon nanotubes grown on epitaxial ferroelectric thin films

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We have directly grown single-walled carbon nanotubes on epitaxial BaTiO<sub>3</sub> thin films, fabricating prototype carbon nanotube-ferroelectric devices. We demonstrate polarization switching using the nanotube as a local electric field source and compare the results to switching with an atomic force microscopy tip. The observed variation of domain growth rates in the two cases agrees with the changes in electric field intensity at the ferroelectric surface. © 2008 American Institute of Physics. [DOI: 10.1063/1.2985815]

The small size and exceptional electrical properties of carbon nanotubes (CNTs) have made them the subject of intense research and promising candidates for device applications such as quantum wires, and nanoelectromechanical oscillators.<sup>1,2</sup> In fundamental and applied studies, conventional field-effect architecture has been widely used to modulate CNT charge carrier density and hence control their electronic properties. In such devices, SiO<sub>2</sub> remains the most common dielectric material.

An alternative is a device combining CNT with a ferroelectric material (Fig. 1), allowing local control of domain structures in the ferroelectric film and potentially *ferroelectric* gating of the CNT. Ferroelectrics are characterized by a reversible nonvolatile electric polarization, with significant interest for memory applications. Due to their small size, CNT can act as a probe and local electric field sources,<sup>3,4</sup> allowing nanoscale studies of ferroelectric domain nucleation and growth. In parallel, the ferroelectric polarization can potentially be used to modulate charge carrier density of the CNT. Such ferroelectric field-effect doping has been demonstrated in superconducting and metallic oxides,<sup>5,6</sup> allowing local, reversible gating with a polarization of  $\sim 20\text{--}70\ \mu\text{C}/\text{cm}^2$ , depending on the ferroelectric material used, and the interface quality.

Here, we report on the fabrication and characterization of a prototype CNT–BaTiO<sub>3</sub> device with CNT grown directly on the epitaxial ferroelectric thin film. We demonstrate local control of the ferroelectric polarization using voltage pulses applied between the CNT and the conducting substrate, and compare the domain growth observed with that of atomic force microscopy (AFM)-written nanoscale domains. We find that domain growth rates agree with the electric field modeled for each case. Finally, we observe a gate-voltage-dependent “memory effect” during transport measurements, although this appears to be due to interaction with surface states rather than a ferroelectric field effect.

To fabricate the devices, CNTs were synthesized on the ferroelectric surface by chemical vapor deposition (CVD) over Fe and Mo salts on Al<sub>2</sub>O<sub>3</sub> nanoparticles,<sup>7</sup> with Ti–Pt electrodes defined by subsequent photolithographic patterning and evaporation. The ferroelectrics were all tetragonal

(001)-oriented, epitaxial thin films grown by rf-magnetron sputtering on conducting Nb:SrTiO<sub>3</sub> substrates, allowing the polarization to be switched along the *c*-axis perpendicular to the plane of the film. Different materials, including PbTiO<sub>3</sub>–SrTiO<sub>3</sub> superlattices,<sup>8</sup> PbZr<sub>0.2</sub>Ti<sub>0.8</sub>O<sub>3</sub>, PbTiO<sub>3</sub>, and BaTiO<sub>3</sub> were investigated to test their response to the high temperatures (700–1040 °C) and reducing atmosphere required for CNT growth. All Pb-containing oxides showed increased surface roughness and significant deterioration of ferroelectric properties. However, BaTiO<sub>3</sub> films subjected to 700 °C CVD with ethylene conserved a well-defined polarization, as demonstrated by subsequent macroscopic and local probe measurements of ferroelectric switching, in spite of an increase in surface roughness from  $\sim 4$  to 15 Å. In piezoforce microscopy<sup>9</sup> (PFM) images of the ferroelectric polarization in these films, we observed a strong contrast between  $P_{\text{down}}$  domains written with positive AFM tip voltage and the intrinsic polarization of the background, and weak or no contrast for  $P_{\text{up}}$  domain written with negative tip voltage, indicating that the BaTiO<sub>3</sub> films were primarily  $P_{\text{up}}$ -polarized.

For each device, noncontact topographic AFM scans were used to determine the position of the CNT. The CNTs were presumed to be single walled due to their small diameters (0.8–2.2 nm as determined from their height profile). To investigate CNT-controlled polarization switching in the BaTiO<sub>3</sub> film, we held the CNT (and its electrodes) at ground

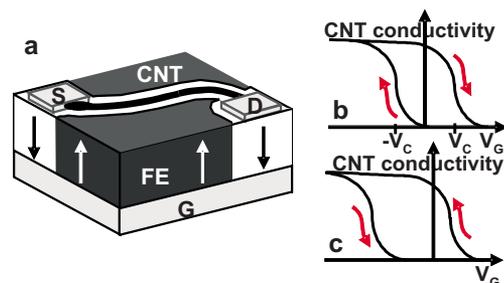


FIG. 1. (Color online) (a) Schematic representation of a CNT-ferroelectric device. Voltage applied across the ferroelectric can reverse the polarization. (b) For a *p*-type channel, remanent polarization maintains an effective field as  $V_G$  is swept through zero: a clockwise hysteresis in the conductivity with a threshold voltage shift correlated with the coercive field of the material would be expected. (c) In conventional field effect devices, counterclockwise hysteresis in the conductivity would be expected.

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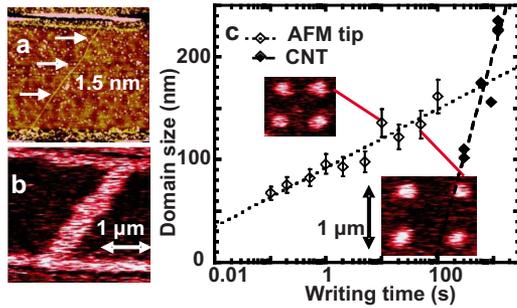


FIG. 2. (Color online) (a) AFM topography showing CNT position and diameter (indicated). (b)  $P_{\text{down}}$  domain formed by  $-10$  V, 20 min pulse applied to the conducting substrate in the device. (c) The half width of CNT-written domains and the radius of circular nanoscale domains (insets) written with 12 V pulses applied to the AFM tip show different domain growth rates as a function of writing time.

potential, while applying  $\pm 10$  V pulses to the conducting substrate, imaging the resulting ferroelectric domain structure by PFM. As shown in Fig. 2(b), we could switch the polarization direction using negative voltage applied to the Nb:SrTiO<sub>3</sub> substrate, resulting in the formation of a  $P_{\text{down}}$ -polarized (bright) domain which clearly follows the CNT position, determined from the surface topography [Fig. 2(a)]. Positive voltage applied to the substrate produced no observable change in PFM contrast compared to the already  $P_{\text{up}}$ -polarized (dark) background.

We note that PFM requires AFM tip-surface contact for good electromechanical coupling. In our case, contact scanning significantly damaged, and often completely destroyed the CNT, making sequential images of opposite polarity switching in the *same* CNT unfeasible. Therefore, using a different device for each measurement, we applied sequences of opposite polarity voltage pulses to the substrate, then imaged the resulting polarization state. Pulses of positive then negative voltage produced a  $P_{\text{down}}$  domain underneath the CNT. Pulses of negative then positive voltage gave uniform  $P_{\text{up}}$  polarization in the entire device. These data suggest that  $P_{\text{down}}$  domains formed during negative voltage application were reversed by applying positive voltage, although the resulting  $P_{\text{up}}$  polarization cannot be distinguished from the intrinsic polarization of the sample. All written domains remained stable over the 1–2 day duration of the experiment, even once the CNT itself had been completely removed from the surface by repeated PFM imaging.

To extract a quantitative characterization of domain growth under the CNT, we compared the size of the resulting domains with that of AFM-written domains [Fig. 2(c)], following Ref. 10. The AFM-written domains show a logarithmic dependence of radius on the duration of the applied voltage pulse (writing time). The half width of the CNT-written domains increased much more steeply over the range of available data. In fact, although domains  $\sim 50$ – $100$  nm wide appear to grow faster under the AFM tip, the data can be extrapolated to show a crossover at  $\sim 170$  nm, at which point domain growth is more rapid under the CNT.<sup>11</sup>

To analyze these different domain growth rates, we considered the electric field produced by an AFM tip at 12 V or a CNT at 10 V, each in contact with a 200 nm thick BaTiO<sub>3</sub> film [dielectric constant 2000 Ref. 12] over a metallic substrate. The AFM tip was modeled as a charged sphere of radius  $\alpha=20$  nm, and the CNT as an infinite wire of radius

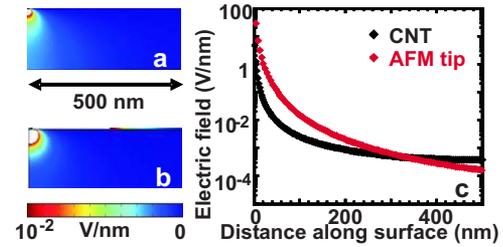


FIG. 3. (Color online) (a) Electric field component  $E_z$  generated by the CNT and (b) AFM tip in the ferroelectric film. (c)  $E_z$  at the ferroelectric surface shows a crossover in field intensity in agreement with domain growth rate data.

$\gamma=1$  nm. Using numerical simulations (COMSOL MULTIPHYSICS) we mapped out the strength of the electric field component  $E_z$  along the polarization axis, which drives domain nucleation and growth [Figs. 3(a) and 3(b)]. Comparing  $E_z$  at the surface of the ferroelectric film in Fig. 3(c), we find a crossover in the respective field intensities at  $\sim 330$  nm, which agrees qualitatively with the extrapolated crossover in the domain growth data at 170 nm.

To investigate the effect of the ferroelectric polarization on the CNT we also measured device transport. We applied a small voltage ( $V_{\text{SD}}=10$ – $50$  mV) across the CNT while the substrate voltage  $V_G$  was either swept continuously, or applied as pulses  $V_P$  of different magnitude and duration. All the devices contained a single, semiconducting  $p$ -type CNT 1.5– $4$   $\mu\text{m}$  long, with  $\sim 100$ – $200$   $k\Omega$  resistance in the fully conductive state. Most devices showed a pronounced counterclockwise hysteresis for continuous  $V_G$  sweeps, with a threshold voltage shift of  $\sim 6$  V [Fig. 4(a)]. During voltage pulse application, CNT conduction increased for negative  $V_P$  and decreased for positive  $V_P$ . However, an opposite response was observed once the substrate was regrounded: positive  $V_P$  resulted in increased conduction, while negative  $V_P$  led to a nonconducting state. The persistence of this response was relatively short (a few seconds) at ambient conditions, but increased to over 500 s in vacuum at 200 K [Fig. 4(b)]. This memory effect depended on  $V_P$  duration, with a diminished response for  $\pm 3$  V pulses shorter than  $\sim 1$ – $10$  ms. Higher voltages ( $\pm 25$  V) produced a response down to pulses of  $\sim 100$  ns. We note here that Sakurai *et al.*<sup>13</sup> reported measurements on CNT deposited on polycrystalline PbZr<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> suggesting ferroelectric field effect during gate voltage sweeps; no pulsed measurements were reported.

Taken together, these transport data suggest that although we observe a potentially useful memory effect in our devices, ferroelectric field effect is not the dominant mechanism. The counterclockwise hysteresis for continuous  $V_G$

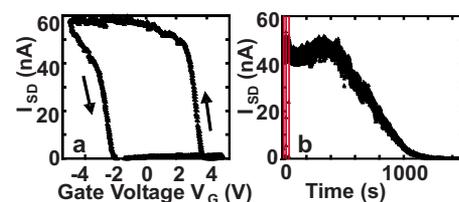


FIG. 4. (Color online) (a) Counterclockwise hysteresis observed in CNT conduction ( $V_{\text{SD}}=100$  mV) as a function of continuously swept  $V_G$  at ambient conditions. (b) Positive  $V_P$  (applied at times indicated by red lines) results in CNT conduction which persists for over 500 s at 200 K.

sweeps, and the direction of the response measured after  $V_p$  pulses are quite clearly opposite to what would be expected for a ferroelectric field-effect modulation of a  $p$ -type semi-conducting channel. In fact, this behavior is very similar to that reported by Fuhrer *et al.* on  $\text{SiO}_2/\text{Si}$ , where charge injection into the oxide surface states was suggested as the mechanism for the observed memory effect.<sup>14</sup> In the  $\text{BaTiO}_3$  films such states are eminently plausible, especially given the surface deterioration during CNT growth. The high field intensities around the CNT (see Fig. 2) during  $V_p$  application could promote charge injection and trapping at the surface of the ferroelectric film. The devices appear highly sensitive to the surface chemistry, with a much longer persistence of the memory effect observed at low temperatures in vacuum. Such sensitivity could prove useful to probe the role of surface interactions and defects during polarization switching, a subject attracting much recent interest.<sup>15–17</sup> As for a ferroelectric field-effect-CNT device, fabrication using deposition of CNT on as-grown monocrystalline ferroelectric films could be a promising pathway. Alternatively, conformal coating of CNT with a ferroelectric oxide material, as proposed by Kawasaki *et al.*<sup>18</sup> could be implemented.

In conclusion, we have shown that CNTs can be directly grown on perovskite oxides. Using prototype CNT– $\text{BaTiO}_3$  devices we demonstrated switching of the ferroelectric polarization due to the local electric field applied with the CNT. Finally, although we observed a modulation of CNT electronic state, this effect appears to be due to interaction with neighboring surface states rather than the ferroelectric polarization.

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