Supplementary information for:

Fully-inverted Single-Digit Nanometer Domains in Ferroelectric Films

Noureddine Tayebi,[1,2] Yoshie Narui,[3] Nathan Franklin,[1] C.Patrick Collier,[3,4] Konstantinos P. Giapis,[3] Yoshio Nishi,[2] and Yuegang Zhang[1,5,*]

[1] Intel Corporation, 2200 Mission College Boulevard, Santa Clara, California 95054, USA.

[2] Department of Electrical Engineering, Stanford University, 420 Via Palou Mall, Stanford, California 94305, USA.

[3] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA.

[4] Oak Ridge National Laboratory, Center for Nanophase Materials Sciences, Oak Ridge, TN 37831, USA.

[5] The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

* Corresponding author, e-mail: yzhang5@lbl.gov

Effect of electrode size increase by gold nanoparticle reduction

Figure S1 shows other nanopencils with individual SWNT electrodes (2–3 nm in diameter), which were exposed using a nanosecond pulse etching technique (see subsequent sections for procedure). Using these nanopencils, no inverted domains were observed on the 50 nm thick PZT film even when 10 V pulses were applied for 100 μs. Instead of decreasing the film thickness, an experiment was tried where the electrode size was increased by electrochemically forming a gold nanoparticle at the exposed tip (see subsequent sections for procedure). Figures S1b,c show TEM images of the same probe with a 3nm SWNT electrode before and after gold nanoparticle formation, respectively. The size of the electrode was thus increased from 3 nm to about 250 nm. Note that gold reduction occurred only at the exposed end of the SWNT electrode, which confirms that the SWNT electrodes were electrically insulated by the SiO_x sheath except at the exposed end. This excludes current leakage through the sheath during the writing process using individual SWNT electrodes that might have been at the origin of the non-inverted domains on this film. The electrode with the gold nanoparticle was used to apply 10 V pulses on the 50 nm PZT film. This time inverted domains of 82.5 nm were observed [Fig. S1d]. The noisy nature of the inverted domains is due to the rough surface of the reduced gold nanoparticles, which affects the contact between the probe and PZT film. The observation of domain inversion with the larger electrode reaffirms the dependence of domain stability on the ratio of electrode size to the ferroelectric film thickness.
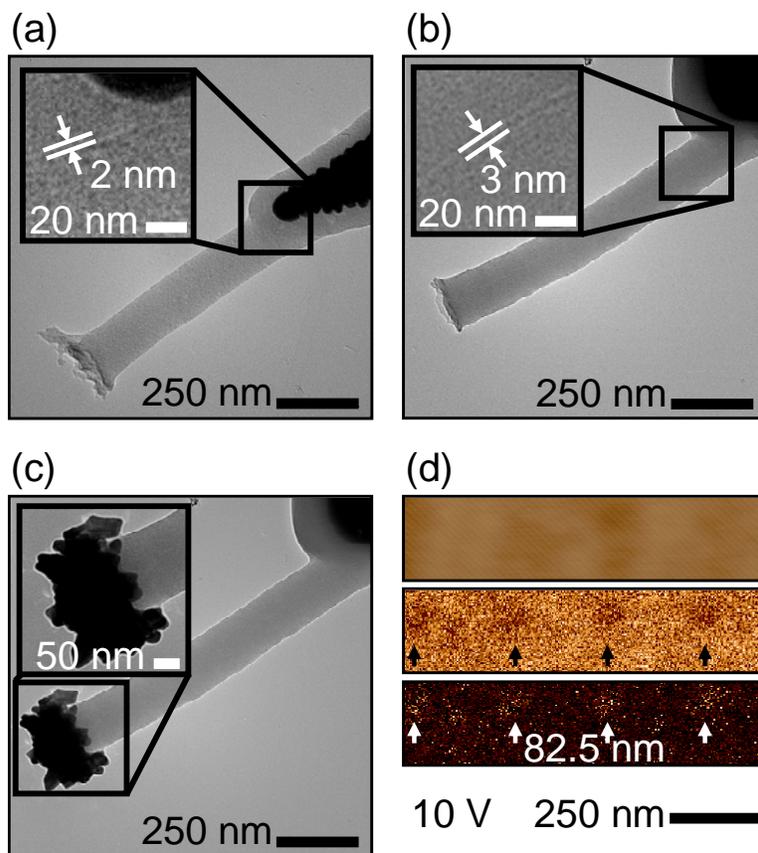
Figure S1. Effect of electrode size increase on domain inversion of 50 nm thick PZT film. (a) TEM image of a nanopencil probe with a 2 nm SWNT electrode exposed using the pulse etching process (see Methods). No inverted domains were observed on the 50 nm PZT film using this probe at a 10 V pulse. (b) TEM image of a nanopencil probe with 3 nm SWNT electrode. (c) TEM image of the nanopencil probe shown in **b** after electrochemical reduction of gold nanoparticles onto the exposed SWNT (see Methods). The electrode size increased from 3 nm to 250 nm. (d) PFM height (top), amplitude (middle) and phase (bottom) images of a 50nm-thick PZT-film surface with 82.5 nm ferroelectric inverted domains formed by applying 10 V pulses to the film through the nanopencil shown in (c).

SWNT pick up and dielectric coating

As grown SWNTs are attached to commercially available metal-coated conductive atomic force microscope (AFM) probe-tips (Nanosensors Inc.) using the pick-up technique developed by Lieber and co-workers (ref. S1). Briefly, isolated and vertically aligned SWNTs are grown on an oxidized silicon substrate by chemical vapor deposition. Silicon substrates are spin coated with several drops of iron catalyst solution at 3000 rpm until dry. The substrates are then placed into a tube furnace at 900º C purged with 500 standard cubic centimeters (sccm) of argon and annealed for 10 min under a flow of 500 sccm argon and 100 sccm hydrogen. Methane is added at 1000 sccm for 7 min followed by a return to annealing conditions for 10 min. Then, the metal-coated tips are used to image the vertically grown SWNTs using a Digital Instruments multimode AFM with a Nanoscope IV controller. During scanning, the probe-tips pick up individual SWNTs (or a bundle of SWNTs), which attach to the probe-tips by van der Waals forces and thus create SWNT-based probes.

Subsequently, the SWNT probe-tips are placed on a grounded electrode in a low-pressure glass reactor. An argon gas flow at 7.5 sccm is introduced to the reactor through a bubbler containing tetraethyl orthosilicate (TEOS) liquid kept at 20^oC. The reactor pressure is controlled at 95 mTorr. An inductively coupled plasma is then struck upstream of the electrode at a power of 100 Watts and a frequency of 13.56 MHz. The SiO_x deposition continues for two minutes. Successful nanopencil fabrication is verified using a Phillips EM420 transmission electron microscope (TEM) operating at 120 kV.

SWNT electrode exposure using the sharpening process

The SWNT electrode exposure, or nanopencil "sharpening", was performed using an Asylum Research MFP-3D scanning probe microscope. This is achieved by repetitively scanning a 20×20 μm area of a conductive diamond film with a root mean squared roughness of 9 nm (a part of the base of a conductive diamond AFM tip from Nanosensors inc.). The scanning was performed under contact mode at a speed of 100 μm/s while applying a 0.5 V bias between the nanopencil and the diamond surface. The height and current signals were simultaneously monitored and recorded [Fig. 2 in manuscript] using the conductive AFM module. A force of 5 nN was used for all the SWNT electrode exposures. Scanning is stopped once the current starts to flow indicating that the SWNT electrode is exposed. A smaller (1×1 μm area) scan was then performed at a 2.5 μm/s speed and I–V curves were taken at highly conductive spots identified in the current distribution scan to confirm the nanopencil conductivity. Successful electrode exposures were further verified using a Phillips EM420 TEM operating at 120 kV.

PZT ferroelectric film growth

Atomically smooth (RMS = 0.17-0.2 nm), single crystal PZT films are deposited on a 50 nm single crystal $SrRuO_3$ (SRO) film deposited on $SrTiO_3$(100) using metal-organic chemical vapor deposition (MOCVD) at a 605 ^{o}C temperature under a 5 torr pressure with Ti, Zr, Pt precursor fluxes of 0.07 ml/min, 0.025 ml/min and 0.165 ml/min, respectively (ref. 14 in manuscript).

Data write and read

The write/read experiments were performed using an Asylum Research MFP-3D scanning probe microscope. The nanopencils are used as conducting probes to write inverted domain dots on the

PZT films following the same method described in ref. 7 in manuscript. The ferroelectric PZT films are initially polarized in an upward direction and placed on a grounded electrode. A nanopencil probe is first brought into contact with the film surface. Positive electrical pulses (varying from 3 to 10 V) with a pulse width of at most 100 μs are then applied to the PZT surface through the conductive nanopencil core. The ferroelectric domains are imaged using the same nanopencil probes under the piezoresponse-force microscopy (PFM) mode where domain walls show dark contrast in amplitude images and the inverted domains show 180° phase shift to the background film.

Electrical characterization of PZT films

25 nm thick platinum pads (20×20 μm^2 or 25×25 μm^2 in size) are deposited on the PZT films to serve as a top electrode. The SRO substrate is used as a bottom electrode. The capacitance vs bias measurements of the metal-PZT-metal capacitor are carried out using an Agilent Technology LCR-meter at a 1 MHz frequency with a 50 mV ac bias. The polarization vs bias measurements are carried out using a Radiant Technology system at a 10 KHz frequency.

Modeling of electric field mapping within the PZT film

The modeling of the electric field component along the polarization axis was modeled using the COMSOL-MULTTIPHYSICS package. The SWNT electrode of various sizes is modeled as a metallic wire sheathed with a 65 nm thick SiO$_x$ film in contact with the PZT film on a grounded metallic electrode. The properties of the PZT films determined experimentally are used in the simulations. The bias is applied to the electrode and fixed charge and fixed field assumptions are adopted. Axial symmetry is assumed in the model.

SWNT electrode exposure using the high voltage (HV) pulse etching process

A nanosecond HV-pulse etching method was also used to remove the SiO_x located at the apex of a fully insulated SWNT probe [Figs. 3a,b in manuscript]. The probe is brought within a few nanometers of a grounded platinum surface and a pulse of at least 20 V is then applied. The probes are mounted into an electrostatic force microscopy (EFM) tip holder, which allows for the direct probe biasing. The separation distance between the tip and the surface (z-position) is controlled by a feedback loop in force calibration mode. Using a signal access module (break-out box), the low voltage z-position signal is monitored with an SR 830 lock-in amplifier, which triggers an Agilent waveform generator. When the nanotube is within a few nanometers of the platinum surface, the waveform generator triggers an Agilent 8114A pulse generator to apply a 100 ns pulse to the tip. The applied potential is varied until a significant change in the z-position is observed.

Gold nanoparticle reduction at the exposed end of the SWNT electrode

Gold nanoparticles are electrochemically reduced at the exposed end of the SWNT electrode using a similar technique to the one described in ref. S1. The exposed nanopencil probes are immersed in aqueous solution of $AuCl_4^-$ held at – 200 mV. Gold nanoparticles are electrodeposited potentiostatically by applying a ~ 40 V pulse. No particle formation was observed on the SiO_x-coated nanotube sidewalls or AFM tip support.

References

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