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BLASER, Cédric, ESPOSITO, Vincent, PARUCH, Patrycja

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Understanding polarization vs. charge dynamics effects in ferroelectric-carbon nanotube devices

Cédric Blaser, Vincent Esposito, and Patrycja Paruch
DPMC–MaNEP, University of Geneva, 24 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

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To optimize the performance of multifunctional carbon nanotube-ferroelectric devices, it is necessary to understand both the polarization and charge dynamics effects on their transconductance. Directly comparing ferroelectric Pb(Zr0.2Ti0.8)O3 and dielectric SrTiO3 field effect transistors, we show that the two effects strongly compete, with transient charge dynamics initially masking up to 40% of the ferroelectric field effect. For applications, it is therefore crucial to maximize the quality of the ferroelectric film and the interface with the carbon nanotube to take full advantage of the switchable polarization. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809596]
Continuous measurements, field effect and transient auxiliary charge dynamics. In contrast, the ferroelectric polarization vs. voltage hysteresis at a cycle frequency of 500 Hz. (d) Device schema with $V_{sd}$ and $V_{gd}$ bias measured relative to the grounded drain electrode. (e) Optical microscopy image of a device, 1.5 μm nominal gap. (f) PZT coercive voltages vs. cycle frequency. Red up-triangles and blue down-triangles are from polarization vs. voltage measurements, magenta disk and green square from the transconductance measurement (Fig. 2(a)). Dashed lines are logarithmic fits of the polarization-voltage hysteresis data.

FIG. 1. Surface topography of the (a) PZT and (b) STO samples. (c) PZT polarization vs. voltage hysteresis at a cycle frequency of 500 Hz. (d) Device schema with $V_{sd}$ and $V_{gd}$ bias measured relative to the grounded drain electrode. (e) Optical microscopy image of a device, 1.5 μm nominal gap. (f) PZT coercive voltages vs. cycle frequency. Red up-triangles and blue down-triangles are from polarization vs. voltage measurements, magenta disk and green square from the transconductance measurement (Fig. 2(a)). Dashed lines are logarithmic fits of the polarization-voltage hysteresis data.

At ambient conditions, transconductance measurements clearly show the competing contributions of ferroelectric field effect and transient auxiliary charge dynamics. In continuous measurements, $V_{gd}$ is swept repeatedly back and forth, at a rate of 0.36 V/s, at a constant $V_{sd}$ bias of either 10 or 100 mV, with $I_{sd}$ recorded and averaged over several sweeps, allowing the combined effects of charge dynamics and polarization switching (when present) to be probed. In STO devices, we observe ant-clockwise, advancing hysteresis, with a wide 2.2 V window (measured at half-height), as shown in Fig. 2(b). In PZT devices, we observe clockwise, retarding hysteresis with a highly constricted shape near zero gate bias, leading to a much smaller window of only 0.2 V, as can be seen in Fig. 2(a). The two distinct polarization switching peaks at 2.6 V and $-4.0$ V are well outside this window.14

When $V_{gd}$ is swept asymmetrically, avoiding either the 2.6 V or the $-4.0$ V coercive voltage, variations of CNT conductivity in each polarization state can be accessed. As shown in the lower part of Fig. 2(a) for each branch of such asymmetric transconductance measurements, even without polarization switching there is a noticeable $I_{sd}$ increase when $V_{gd}$ is swept towards more negative values. However, when $V_{gd}$ remains below the upper coercive voltage (polarization $P_{\text{DOWN}}$), $I_{sd}$ values are 50% to 120% higher than when the polarization is $P_{\text{UP}}$. Moreover, although identical $V_{gd}$ sweep rates are used, there is negligible hysteresis. Meanwhile in STO devices, such asymmetric $V_{gd}$ sweeps result in qualitatively similar hysteresis to the full $V_{gd}$ sweeps, although with a reduced window of only 1.0 V, and offset with respect to zero gate bias, as shown in the lower part of Fig. 2(b).

Finally, by applying 0.5 s $V_{gd}$ pulses and recording the subsequent $I_{sd}$ evolution at zero gate bias, the non-volatile vs. transient nature of the ON and OFF states can be probed. In the PZT sample, in agreement with the clockwise transconductance hysteresis of Fig. 2(a), a positive $V_{gd} > 2.6$ V pulse puts the device in the almost non-conducting OFF state (0.15 nA $I_{sd}$), while a negative $V_{gd} < -4.0$ V pulse switches it ON, as shown in Fig. 2(c). The initial ON $I_{sd}$ of 1.2 nA increases gradually over ~30 s to 1.9 nA, then remains stable, showing a non-volatile effect of the two opposing polarization states at zero applied field. In the STO sample, as expected from the anti-clockwise transconductance hysteresis, positive $V_{gd}$ pulses switch ON the device, while negative $V_{gd}$ pulses switch it OFF (2.5 nA $I_{sd}$), as seen in Fig. 2(d). However, the initially high ON $I_{sd}$ of 32 nA decreases to 14 nA after 30 s, and ON and OFF states reach a common intermediate current value after ~1800 s.

The results observed in STO devices, with wide anti-clockwise hysteresis and an initially high but decaying ON $I_{sd}$ after positive $V_{gd}$ pulses, are similar to reports on Si/SiO2 field effect transistors,15 where the memory effects were attributed to charge injection into metastable states of the dielectric. In addition, surface adsorbates and in particular interfacial water molecules have been shown16 to play a crucial role in the observed dynamic processes leading to such hysteresis. However, while the hold time in the SiO2-based devices exceeded 5000 s under similar conditions, the effects in STO appear to be much more transient, possibly as a result of increased defect densities and higher electron mobility associated with the oxygen vacancies in this material.17

Comparable defect densities are expected in the PZT sample, and the effects of surface water may even be enhanced by the ferroelectric nature of the sample.18 The associated charged dynamics strongly compete with the opposing effects of the ferroelectric polarization itself. In epitaxial oxide heterostructures, where wider channel geometries avoid the field focusing and charge injection of CNT-based devices, ferroelectric field effect is characterized by a retarding transconductance hysteresis tracking the
positive and negative coercive voltages, and well-defined non-volatile conduction states at zero field, corresponding to the two opposite polarization orientations.\textsuperscript{19,20} In contrast, the present measurements show extremely constricted hysteresis, which remains retarding, but with a very narrow window well away from the actual polarization switching. Another aspect of this competition can be seen in the pulsed measurements at zero gate bias, where as much as 40\% of the final, stable ON state conduction after a negative $V_{gd}$ pulse is initially masked by transient charge dynamics effects. Likewise, in the asymmetric measurements, although it is always higher in the $P_{\text{DOWN}}$ state, significant variation of the CNT conductivity is observed during $V_{gd}$ sweeps, even though the polarization orientation is not reversed. We note that the magnitude of these variations is well beyond any effective polarization increase due to the enhanced tetragonality of the film\textsuperscript{21} as a result of its inverse piezoelectric response to the applied voltage.\textsuperscript{22}

Rather, all our measurements point to the key influence of defects, in particular during polarization switching, where the strongest transient charge dynamics effects are observed. In fact, as we have shown previously, the high defect densities present in radio-frequency sputtered ferroelectric films grown on STO substrates significantly modulate polarization switching dynamics and the growth and stability of ferroelectric domain structures.\textsuperscript{23,24} Observing ferroelectric field effect in CNT, therefore, requires high quality materials in which polarization effects will dominate. In ferroelectric BaTiO$_3$ samples with even higher defect densities (resulting from direct CNT growth in reducing conditions), charge injection and relaxation as well as adsorbate effects completely screened out the effects of the polarization, and the devices behaved as standard field effect transistors.\textsuperscript{5}

To further separate out the effects of the polarization from those of the charge injection and relaxation, the same transconductance measurements were performed at low temperature, where significant slowing of the charge dynamics is expected, and vacuum ($2 \times 10^{-7}$ mbar) also removes some of the screening effects of surface adsorbates intrinsically present at ambient conditions. On both the PZT (Fig. 3(a)) and STO samples (Fig. 3(b)), $I_{sd}$ decreases at lower temperatures, as expected for semi-conductors with progressively fewer charge carriers in the conduction band. In addition, in the PZT sample, decreasing temperature also increases the magnitude of the coercive voltages.\textsuperscript{25} Therefore, a constant $V_{gd}$ range eventually excludes one or both coercive voltage values, and the decreasing temperature can be thought of as “turning” the ferroelectric PZT device into one which behaves like a simple dielectric, with no polarization reversal. As seen in Fig. 3(a), this is exactly what happens as the lower switching peak moves from $-4.4$ V at 250 K to $-4.6$ V at 200 K and finally out of the sweep range at 150 K, whereas the upper switching peak moves from $2.4$ V to $2.7$ V at the same temperatures. For temperatures below 100 K, only anticlockwise, advancing transconductance hysteresis is observed, with no switching peaks, and the behavior resembles that of the STO-based device in Fig. 3(b). For the intermediate temperature range between 250 K and 100 K, the competition between charge dynamics and ferroelectric field effect in the PZT device actually leads to a double hysteresis in the transconductance. Whereas at room temperature the ferroelectric field effect is strong enough to just dominate, within the same $V_{gd}$ sweep range at intermediate temperature, as the coercive voltages gradually increase, the competing effects of charge dynamics become increasingly evident and dominate completely below 100 K.

At the lowest temperatures, where both PZT- and STO-based devices are functionally equivalent, charge dynamics are largely frozen out and so the defect landscape becomes more static. Under these conditions, localization effects and the electronic separation of the CNT into a series of charge puddles can strongly affect the measured transport properties.\textsuperscript{26,27} Since most of the devices contain several CNT, 10\% of which are metallic, we can also access these effects. At room temperature, the presence of any metallic CNT leads to a constant offset of the conductivity versus $V_{gd}$ bias, resulting in a non-zero $I_{sd}$ current in the OFF state (positive $V_{gd}$ bias). At low temperature, such devices have a very different behavior. Below 100 K, reproducible fluctuations, whose amplitude increases with decreasing temperature, emerge above the noise level. Their reproducibility is confirmed by multiple sweeps of the same device, including over the span of several hours, as shown in Fig. 4(a). However, every time the device is returned to ambient conditions and cooled down again, the fluctuation pattern completely changes, indicating the dynamic nature of the disorder potential landscape below the device. The fluctuation pattern is also completely different from one device to another. This phenomenon can be seen on both PZT and STO samples, confirming their functional equivalence at low temperatures.

The uniqueness of the fluctuation pattern between different thermal cycles of the same device, and its repeatability over several hours at constant low temperature are two strong indications of universal conductance fluctuations,\textsuperscript{28,29} a disorder-sensitive phenomenon which occurs in the case of phase-coherent transport by the interference of electron waves, which has also been observed in CNT.\textsuperscript{30,31} As a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Transconductance hysteresis at $2 \times 10^{-7}$ mbar on the (a) PZT and (b) STO devices. In both cases, $V_{gd}$ down sweeps are shown as solid lines, up sweeps as dashed lines, and measurements at decreasing temperatures present decreasing $I_{sd}$ values. On the PZT device, switching peaks are visible and the leftmost part of the curve shows clockwise hysteresis at 200 K and above. At 100 K and below, no switching peak is visible and the hysteresis is anticlockwise. On the STO device, all measurements show anticlockwise hysteresis, whose amplitude monotonically decreases with temperature.}
\end{figure}
response to a change in chemical potential or magnetic field, the conductance is expected to fluctuate by the universal value \( e^2/h \) as long as the phase-coherence length is at least equal to the channel length. The overall low conductance and the finite temperature of our system may explain the rather small absolute amplitude of the fluctuations observed in Fig. 4(b).

Following the theoretical work of Larkin and Khmelnitskii\(^{32}\) applied by Terrier et al.\(^{33}\) on gold nanowires, we analyze the amplitude of the conductance fluctuations \( \delta G_{\text{rms}} \) as a function of the applied \( V_{sd} \) bias, as presented in Fig. 4(c). The prediction for \( V_{sd} \gg V_c \), where \( eV_c = \hbar D/L^2 \) is the Thouless energy, \( D \) the electron diffusion constant, and \( L \) the channel length, is an increase of \( \delta G_{\text{rms}} \) with voltage \( \propto \sqrt{V_{sd}/V_c} \), followed by a decrease as a power law at higher voltages. The increase is explained by the fact that at \( V_{sd} \gg V_c \), the relevant energy range for the transport subdivides into \( N = V_{sd}/V_c \) uncorrelated energy intervals, each contributing to the fluctuations of the current by \( \approx (e^2/h)V_c \).\(^{33}\) The amplitude decreases at higher voltages as the consequence of inelastic electron-phonon scattering which suppresses interference phenomena.

The diffusion constant \( D \) is not a well-defined quantity, but reported values for CNT range from 50 \( \text{Ref. 30} \) to 900 \( \text{cm}^2/\text{s} \).\(^{34}\) Even with the highest value, our \( V_c \) is below 0.03 mV and thus, the whole curve of Fig. 4(c) in the regime \( V_{sd} \gg V_c \). Following Ref. 33, we fit our data with

\[
\delta G_{\text{rms}} = C \frac{e^2}{h} \sqrt{\frac{V_{sd}}{V_c}} \left( \frac{L_p(V_{sd})}{L} \right)^2.
\]

Because of the device specific constant \( C \), only the relative phase-coherence length \( L_p \) can be extracted. In regime I (increasing \( \delta G_{\text{rms}} \)), \( L_p \propto V_{sd}^p \), where \( p = 0.09 \pm 0.04 \). In regime II (decreasing \( \delta G_{\text{rms}} \)), \( L_p \propto V_{sd}^p \), where \( p = 0.77 \pm 0.02 \). Inserting these values into Eq. (1) results in the dashed and solid lines in Fig. 4(c). The transition between the two regimes is around 200 mV, which corresponds to the energy for optical phonon emission in single-walled CNT\(^{35}\) and confirms the role of electron-phonon scattering in the amplitude decrease of the fluctuations. Whereas Ref. 36 predicts a \( 1/\sqrt{V_{sd}} \) decay, we observe \( \delta G_{\text{rms}} \propto V_{sd}^{\gamma} \) with \( \gamma = 1.04 \pm 0.04 \).

In conclusion, we show that the transport properties of semi-conducting CNT on ferroelectric materials are affected by two competing influences: the polarization and the charge dynamics at the film surface. To integrate CNT-ferroelectric devices in applications, it is therefore necessary to optimize the quality of the ferroelectric film and its interface with the CNT to the highest possible level. Realistically, the former is a more accessible goal since, while surfactant and organic adsorbates may be avoidable, under ambient conditions, interfacial water is always present. Since the charge dynamics are transient, these results point to the potentially greater usefulness of such devices for non-volatile zero gate bias applications, once the conductance state is fully stabilized. At lower temperatures, the effects of the strongly varying disorder landscape become even more significant, especially given the increasing coercive voltages for a fixed \( V_{sd} \) range. Eventually, the variations of the disorder landscape dominate completely, leading to characteristic conductance fluctuations in metallic CNT, highlighting the role of electron-phonon scattering at higher \( V_{sd} \) bias.

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\(^12\)G. L. Yuan, L. W. Martin, R. Ramesh, and A. Uedono, Appl. Phys. Lett. 95, 012904 (2009).

See supplementary material at http://dx.doi.org/10.1063/1.4809596 for additional transconductance measurements. For the 53 devices measured, the behavior at 0.36 V/s \( V_{gd} \) sweep rate varies from the very narrow window shown to partial or even complete dominance by the transient effects. However, as sweep rates were decreased to minimize the influence of transient effects, the hysteretic window widened, highlighting the increasing dominance of the ferroelectric field effect.


For PZT, the \( d_{33} \) piezoelectric constant is \( \sim 50 \text{ pm/V} \) and the polarization \( \sim 75 \mu \text{C/cm}^2 \) for a tetragonality of 1.0475 and in-plane lattice constant of 4.148 Å, out-of-plane lattice constant of 3.96 Å. For the asymmetric 7 V voltage sweep between approximately \(-3 \text{ and } 3.96 \text{ Å} \), a piezoelectric deformation of 350 pm would therefore be expected. The resulting change in tetragonality of \( \sim 0.2\% \) should not significantly affect the effective polarization.