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Charge injection at carbon nanotube-SiO_2 interface

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Most single-wall carbon nanotube field-effect transistors show significant hysteresis in their transfer characteristics between forward and reverse gate bias sweeps. It was proposed that the hysteresis is due to a dynamic charging process at the carbon nanotube-dielectric interface. We have studied the charge injection and subsequent discharging processes at the carbon nanotube-SiO_2 interface using electrostatic force microscopy. It was observed that the water layer assists charge diffusion on the dielectric surface. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2978249]

Single-wall carbon nanotube (SWNT) based field-effect transistor (FET) has attracted much attention since it was first reported a decade ago.[1,2] Significant improvements in the performance of SWNT FET make it a possible candidate for next generation nanoelectronics. However, hysteresis usually exists in the transfer characteristics between the forward and reverse gate bias sweeps, which is problematic for logic devices. The amount of hysteresis depends on the environment and experimental parameters such as maximum gate bias, holding time, sweep rate, and temperature.[3] Early reports proposed that this hysteresis was caused by the redistribution of preexisting mobile charges in the gate dielectric in the presence of a gate bias.[4,5] Recent studies, however, suggested that charges are injected from the SWNT into the surrounding dielectric, where a thin water layer at the interface may play an important role.[6,7] Although the hysteresis can be reduced or eliminated by vacuum annealing and subsequent surface passivation or by using suspended nanotubes in vacuum,[3,4] there are serious limitations to these techniques. Furthermore, applications in areas such as gas sensing and biomolecular detection do require the device to be exposed to ambient atmosphere. It is thus important to understand the charge injection and subsequent discharging processes.

We have studied the charge injection and discharging processes at the SWNT-SiO_2 interface using electrostatic force microscopy (EFM). Asylum Research MFP-3D system and Olympus Pt coated cantilevers (OMCL-AC240TM) (spring constant ~ 2 N/m) are used for the experiments. EFM is a dual-pass noncontact imaging technique. The first scan captures the topography and the second scan is conducted at a fixed distance from the surface with a dc voltage applied to the tip [Fig. 1(a)]. The force between the tip and the sample alters the tip resonance frequency and changes the phase and amplitude signals. Attractive and repulsive forces will give rise to opposite phase shift, as shown in Fig. 1(b) for the MFP-3D system. The phase shift reveals information about the charge/potential distribution on the sample surface. Resolution of ~ 20 nm can be achieved.[8,9]

Figure 1(c) is a scanning electron microscopy (SEM) image of a typical device used in this study. The SWNTs are grown in a chemical vapor deposition system on a *p*-Si substrate with 300 nm of thermally grown silicon dioxide. 200 nm gold electrodes are sputtered through a shadow mask to form the source and drain contacts. The same device is imaged using EFM with the drain biased (V_{drain}) at 5 V, the source grounded and the gate floating [Fig. 1(d)]. A tip bias (V_{tip}) of 3 V is used during the interleave scan. The lift height is 30 nm. Strands of unconnected SWNTs that cannot be seen using SEM are clearly visible. A positive phase shift (brighter) with respect to the background SiO_2 is observed for the unconnected SWNTs, opposite to what is typically reported in the literature. This is due to the phase-force relation of the Asylum Research MFP-3D system, where attractive force results in a gain of phase, and repulsive force leads to a decrease in phase [Fig. 1(b)]. A contrast change in the SWNT channel is observed indicating that the force has changed from repulsive to attractive, which is not expected if capacitive force dominates the tip-sample interaction. The phase shift in EFM phase measurements is determined by the force gradient dF/dz between the tip and the sample. For small gradients, the changes in resonant frequency and phase are given by $\Delta\omega = -(\omega_0/2k)(dF/dz)$ and $\Delta\phi = -\arcsin[(Q/k)(dF/dz)]$, where k is the spring constant and Q is the quality factor of the cantilever.[10] The capacitive force between the tip and the sample can be represented by $F(z) = (1/2)(dC/dz)V_{dc}^2$, where V_{dc} is the potential difference between the tip and the sample. This force is always attractive and leads to positive phase shift. However, when net surface charges are present,[11]

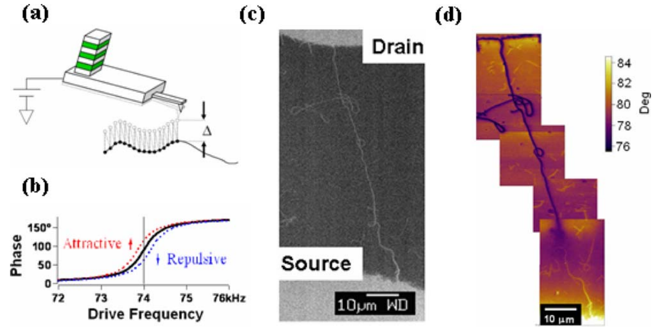

FIG. 1. (Color online) (a) Schematic illustration of the dual scan technique of EFM and (b) the corresponding phase changes with respect to the driving signal (Courtesy of Asylum Research). (c) SEM image of the SWNT FET and (d) EFM phase image of the channel while $V_{drain} = 5$ V, the source grounded and the gate floating. $V_{tip} = 3$ V during the interleave scan.

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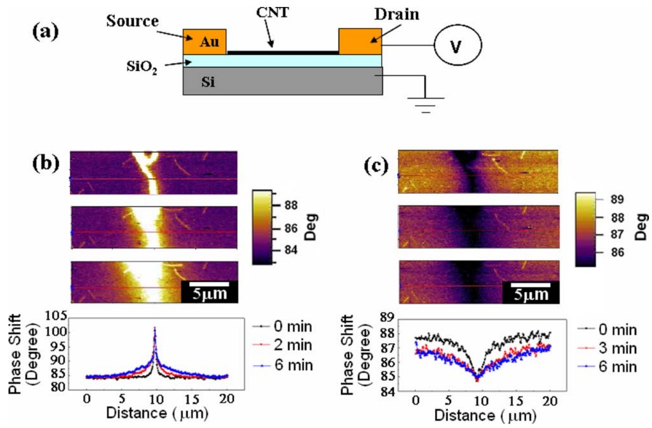

FIG. 2. (Color online) (a) Experimental setup with dc bias applied to the drain, the gate grounded and the source floating, $V_{tip}=3$ V during the interleave scan, and charging images and cross section profiles when (b) $V_{drain}=-5$ V and (c) $V_{drain}=+5$ V.

$$F(z)=\frac{1}{2}\frac{dC}{dz}V_{dc}^2+\frac{q_s q_s'}{4\pi\varepsilon_0(z+z')^2}+\frac{q_s C V_{dc}}{4\pi\varepsilon_0(z+r)^2},$$

where r is the radius of the tip. The first term on the right hand side of the equation refers to the capacitive force. The second term comes from the surface charges and their image charges located at z' in the tip. The third term comes from the interaction between the surface charges and the tip bias. It is clear that net surface charges would give rise to either attractive or repulsive forces depending on the dc bias applied to the tip. So the observed contrast change across the channel [Fig. 1(d)] is likely due to injected charges around the SWNT.

In our subsequent experiments to study the charge injection and discharging processes around the SWNT, the gate is grounded and V_{drain} of +5 or −5 V is applied during the charging step, and 0 V during the discharging process [Fig. 2(a)]. V_{tip} is kept at 3 V during the interleave scan. It was noticed that the background signal changes once V_{drain} is applied when scans are conducted near to the drain (data not shown), indicating charge injection directly from the electrode to the SiO_2 surface, consistent with the previous report.[12] Thus, an area in the middle of the channel is chosen to avoid this problem. Charging images [Fig. 2(b)] with $V_{drain}=-5$ V show bright contrast next to the SWNT, which expands over time, indicating accumulation of negative charges around the SWNT. Both the phase shift value and the width of the charged area increase as shown in the cross section line scans. Similar effects are observed when $V_{drain}=+5$ V [Fig. 2(c)] is applied, where dark contrast around the SWNT indicates accumulation of positive charges.

Phase shift as a function of time at different distances from the SWNT is shown in Fig. 3(a) for $V_{drain}=-5$ V. For areas near to the SWNT, injected charges accumulate to a saturation value within seconds. Since each image takes 8 s to collect, the actual charging time should be shorter. Typical FET transfer characteristics study requires much longer time, which implies that it is unlikely that we can eliminate the hysteresis simply by decreasing the gate bias sweeping time. Figure 3(b) shows the phase shift as a function of distance away from the SWNT at different times. The inset of Fig. 3(b) shows the width increase in the charged area during the charging process, which is an indication of how fast the injected charges move under electric field. However, extraction of charge drifting rate is difficult because the electric field around the SWNT is highly nonuniform. The charging range is likely restricted by the field distribution around the SWNT.

It is believed that the injected charges at the SWNT-dielectric interface screen the gate bias and generate hysteresis behavior. The charge dissipation process is thus important for better understanding of the transfer characteristics of a SWNT FET. After charging at $V_{drain}=-5$ V for 10 min, we ground the drain and scan the same area. It is observed in Figs. 4(a) and 4(b) that charges next to the SWNT diffuse back to the SWNT immediately after the drain is grounded. A peak of surface charge density is thus formed. This peak gradually moves away from the SWNT as more charges diffuse back to the SWNT. The surface property of the SiO_2 is expected to affect the diffusion process greatly. The thermally grown SiO_2 surface consists of Si–OH silanol groups, and is typically hydrated by water molecules when stored in ambient.[13] Whether the water layer or the silanol groups traps charges has been under debate. We have studied the position of the peak as a function of time at temperatures ranging from 30 to 180 °C. At every temperature (30 min is given for the temperature to stabilize), $V_{drain}=-5$ V is applied (the gate grounded) for 10 min before the discharging images are collected. It is observed that the speed at which the peak moves away from the SWNT decreases initially as temperature increases from 30 to 60 °C [inset of Fig. 4(c)]. After which, the speed starts to increase as shown in Fig. 4(c). We suggest that the water layer plays an important role

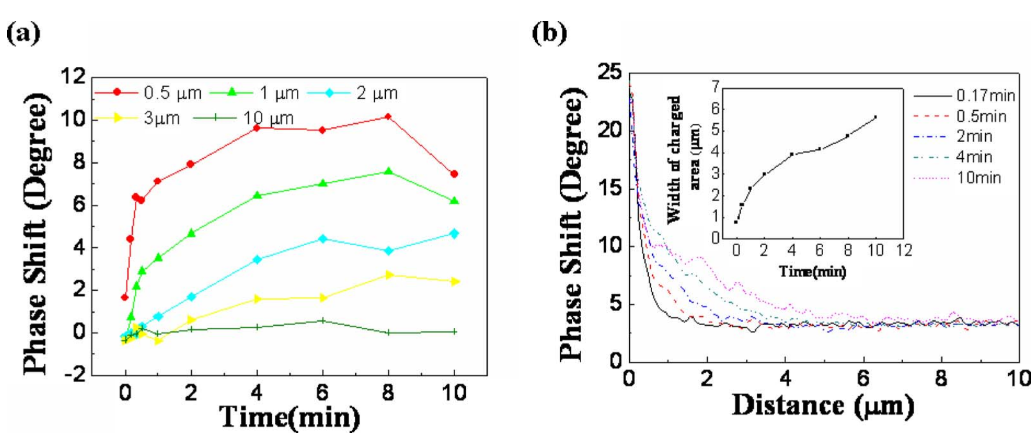

FIG. 3. (Color online) (a) Phase shift as a function of time at different distances away from the SWNT for $V_{drain}=-5$ V, showing the accumulation of charges over time. (b) Phase shift as a function of distance from the SWNT. Inset of (b) shows the extension of the charged area as a function of time.

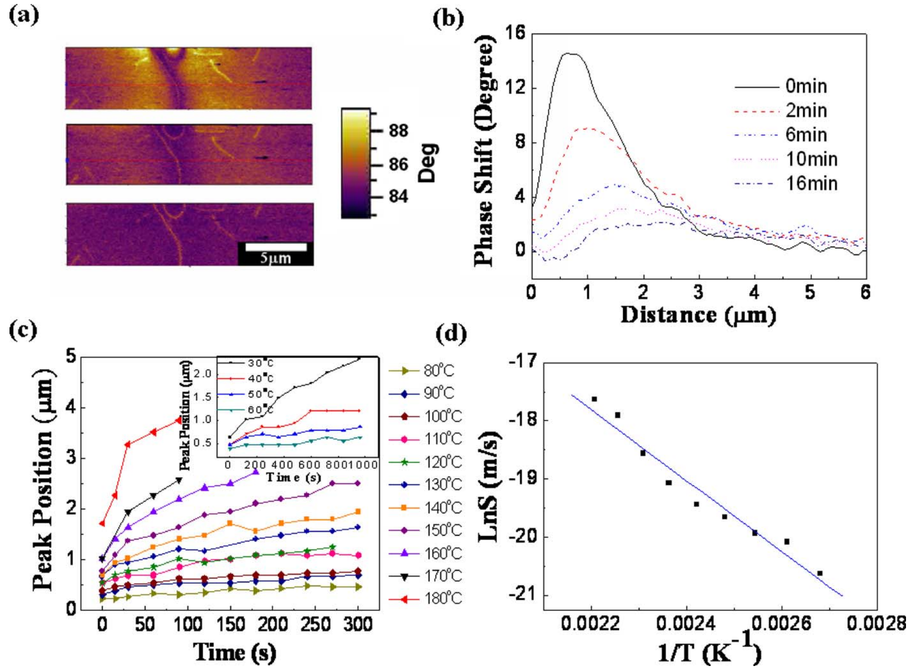

FIG. 4. (Color online) (a) Room temperature discharging images taken at 0, 3, and 6 min after V_{drain} (−5 V for 10 min) is turned off to show the diffusion of injected charges. (b) Cross section profiles show the movement of surface charge density peak. (c) The peak position as a function of time at different temperatures ranging from 80 to 180 °C. Inset shows the opposite trend from 30 to 60 °C. (d) Plot of ln S, S being the speed of the peak movement, as a function of $1/T$ reveals an activation energy of ~0.53 eV.

in the trapping and diffusion of the charges at low temperature. As temperature increases, water gradually evaporates and the silanol groups on the SiO_2 surface, acting as electron trapping sites, start to dominate. In an attempt to analyze the trap depth, we take linear fits of the curves in Fig. 4(c) and obtain the speed (S) at which the peaks move away from the SWNT. Since S is related to charge diffusion, which is proportional to $\exp(-E_0/k_BT)$, where E_0 is the trap depth, k_B is the Boltzmann constant and T is the temperature, then by plotting ln S as a function of $1/T$ between 100 and 180 °C [Fig. 4(d)], we can obtain the activation energy. We notice that this is a very crude simplification since the curves in Fig. 4(c) are not exactly linear, especially during the initial stage. However, a rather good linear fit is obtained, which gives an activation energy of ~0.53 eV. This value is similar to what is reported for bottom gate organic transistors with a SiO_2 dielectric.[14] We are working on a more comprehensive model to extract the diffusion coefficients at different temperatures, which should be a better approach to calculate the activation energy. We have also carried out similar discharging experiments with $V_{drain}=+5$ V and gate grounded. The results are rather different and intriguing (see supplementary material). The charge diffusion is normal at the beginning of the process. However, at a later stage, an inverse signal is observed around the SWNT. Further investigation is needed to understand this observation.

In conclusion, we have studied the charge injection and discharging processes at the SWNT-SiO_2 interface. Accumulation of charges around the SWNT under bias is observed. Dissipation of the injected charges at different temperatures suggests the important role of water layer in mediating the charge diffusion.

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