

Gate-Induced Modification of Water Adsorption on Dielectrics Probed by EFM and Carbon Nanotube FETs

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Humidity plays an important role in molecular electronics. It facilitates charge movement on top of dielectric layers and modifies the device transfer characteristics. Using two different methods to probe temporal charge redistribution on the surface of dielectrics, we were able to extract the surface humidity for the first time. The first method is based on the relaxation time constants of the current through carbon nanotube field-effect transistors (CNTFETs), and the second is based on electric

force microscopy (EFM) measurements. Moreover, we found that applying external gate biases modifies the surface humidity. A theoretical model based on dielectrophoretic attraction between the water molecules and the substrate is introduced to explain this observation, and the results support our hypothesis. Furthermore, it is found that upon the adsorption of two to three layers of water the surface conductivity saturates.

1. Introduction

Single-wall carbon nanotube field-effect transistors (CNTFETs) are promising candidates for future electronics due to their nanoscale dimensions, excellent performance and high sensitivity to many kinds of analytes. However, one of the major challenges regarding their operation is the noticeable gate hysteresis which is often displayed in their transfer characteristics. This phenomenon has previously been attributed to several different factors, among which mobile charges or ions within the dielectric layer,^[1] defects in the CNTs,^[2–4] chemical adsorbents on the CNTs,^[5] stationary charge traps on the dielectric,^[6–10] and CNT-bound water layers.^[11–13]

Since hysteresis involves the movement of charges, we used electrostatic force microscopy (EFM) in order to gain additional information regarding this phenomenon. In a previous study,^[14] we reported that applying gate-voltage compliance in the vicinity of grounded electrodes induces surface-charge redistribution which aims to screen the electric field that originates from the gate electrode. In a second study,^[15] we demonstrated that this electrical drift-based mobility of charge on the SiO₂ surface is the underlying mechanism for the hysteresis phenomenon in suspended CNTFETs and in on-surface CNTFETs operating at low gate voltages. Our experiments implied that the time dependence of the charge distribution process follows an exponential behavior with a single relaxation time constant, τ , which is strongly affected by 1) ambient humidity and 2) the distance from the electrodes. The first observation led us to conclude that the process is greatly assisted by water molecules, in agreement with previous studies which have investigated SiO₂ surface conductivity,^[16,17] as well as hysteresis in CNTFETs.^[11,12,18] The second observation implied that τ depends on the magnitude of the electrical fields. In a simplified model that we introduced in ref. [14] the relaxation time is described by the following relation: $\tau = \epsilon_0 \epsilon_{ox} / \sigma$, where ϵ_0 is the vacuum permittivity, and ϵ_{ox} and σ are the dielectric constant

and the conductivity of SiO₂, respectively. In this model, which assumes a linear response, σ does not depend on the external applied gate biases. Observation 2, however, raises the possibility that τ , and therefore σ as well, depend on the applied gate voltage (V_g). This gate dependence is the focus of the study herein.

In this study, we report of gate-induced modification of water adsorption on SiO₂ surfaces. Utilizing both EFM-based measurements and CNT-based measurements, we examine the effect of V_g on the time constants of the charge-redistribution process and hence on the surface conductivity. Using computational simulations, we prove that the observed effect is not related to the system's intrinsic properties, but rather results from an external factor in the device surroundings. Since ambient humidity is a reasonable possibility, we quantify its effect on the surface conductivity using CNT-based measurements. Our hypothesis, which is discussed and proved shortly, is the following: the external gate biases change the coverage of water molecules that adhere to the oxide surface, and as a result alter the conductivity and the relaxation time as well. Next, a theoretical model which details this process and is based on the dielectrophoretic (DEP) attraction between the water molecules and the substrate is presented. The results obtained from the model-based calculations are compared with the experimental ones, and the findings support our hypothesis. Furthermore, these results suggest that the surface

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conductivity saturates after the adsorption of approximately two to three layers of water which implies that CNTFETs are extremely sensitive detectors for this phenomenon.

2. Results and Discussion

The first question we addressed regarded the effect of V_g on τ . For this purpose, we directly probed the charge redistribution in between two 10 μm -gapped electrodes as a function of time, using our EFM-based method.^[14] Briefly, for each applied gate voltage, a set of consecutive force-curve measurements with different tip voltages were quickly performed. The results were fitted to a quadratic behavior in $V_g - V_{\text{tip}}$ and the parabola minimum (x_0, y_0) was extracted. The local oxide-charge density was then calculated using the equation $Q_s = -x_0 C_{\text{ox}} = -x_0 \epsilon_0 \epsilon_{\text{ox}} / t$, where t is the oxide thickness. This method overcomes the difficulty of estimating an accurate tip-charge mutual capacitance. Repeating this measurement at different times results in Q_s versus time, which fits nicely to an exponential behavior, with a time constant τ for each applied gate voltage. Figure 1 depicts $\log_{10}[Q_s(t) - Q_s(\infty)]$ versus time, where

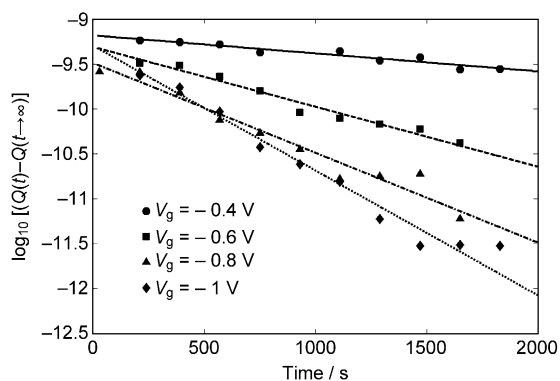


Figure 1. EFM-based measurements of $\log_{10}[Q_s(t) - Q_s(\infty)]$ versus time for different gate voltages applied at $t = 0$ s. Symbols are experimental data and lines are best fits to the exponential behavior. Error bars are smaller than the markers.

symbols are experimental data and lines are best fits to the exponential behavior. The experiment was performed for a series of gate voltages, which were each applied at $t = 0$ sec: -0.4 , -0.6 , -0.8 , -1 , -2 , and -3 V. Before applying each voltage, the system was given a sufficient recovery time, after which the surface-charge density was verified to be zero. In order to avoid changes in ambient humidity, all of the measurements were performed on the same day. The obtained results are summarized in Figure 2a. One can see that while τ does not depend on V_g for high gate voltages, a strong dependence is observed for low gate voltages ($V_g > -1$ V). Since τ and the surface conductivity are inversely proportional,^[14] this observation implies that 1) σ is indeed dependent on V_g for the low-voltage regime and 2) this dependence is non-linear.

In a former study we demonstrated that CNTs can monitor the same surface-charge-redistribution process by measuring their current as a function of time while applying a fixed value

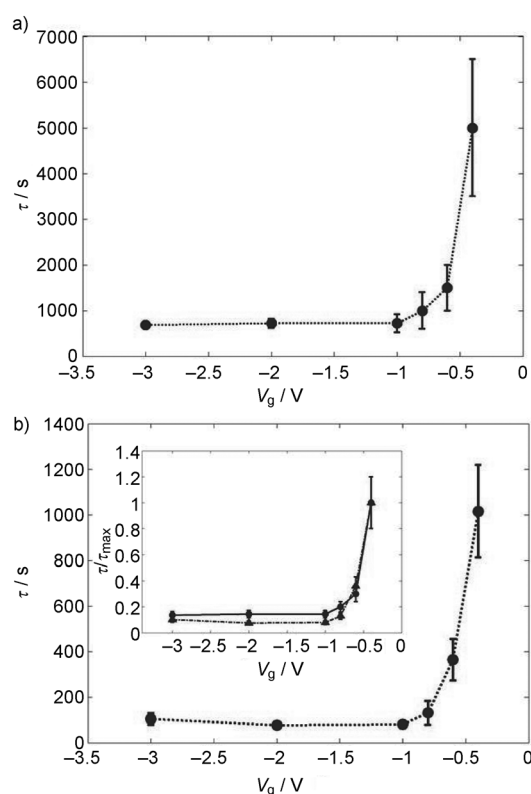


Figure 2. a) Time constants of the charge-redistribution process [$Q_s(t)$] in between two electrodes as a function of V_g , as probed by EFM technique. The gap between the electrodes was 10 μm . b) Time constants of the current decay of a CNT as a function of V_g . The CNT was suspended over a 1.8 μm gap. The experiments were conducted at 55% humidity. Inset: normalized $\tau(V_g)/\tau(V_g = -0.4 \text{ V})$ versus gate voltage for EFM-based data (circles) and CNT-based data (triangles).

of voltage to the gate.^[15] Thus, in order to verify our above-mentioned observation, we conducted another experiment which was designed to examine the effect of V_g on the time constants of the current of the CNT. In this measurement, we used a CNT which was suspended over a 1.8 μm gap, and measured its current as a function of time while applying the same series of gate voltages as before: -0.4 , -0.6 , -0.8 , -1 , -2 , and -3 V. Before applying each value, the gate voltage was fixed at 0 V until no current changes were observed in order to reset the charge drifting on the surface of the device. The time constants of the exponential fits to the current decay of the CNT for each value of V_g are summarized in Figure 2b. The inset of Figure 2b depicts the normalized $\tau(V_g)/\tau(V_g = -0.4 \text{ V})$ for the two sets of measurements (EFM-based in circles and CNT-based in triangles), and one can see that the obtained patterns are very similar. The same behavior was found for four other tubes as well, supporting our conclusion regarding the dependence of the surface conductivity on V_g . Notice that the values of τ in Figure 2b are approximately five times smaller than the values in Figure 2a. As we have already demonstrated, τ is strongly affected by the distance from the electrodes.^[14] Therefore, this difference can be explained by the fact that the gap in the CNT-based measurement is roughly five times smaller than the gap in the EFM-based experiment.

In order to verify that the discovered dependence of the surface conductance is not related to the geometry of the system, we used a finite element analysis software (COMSOL Multiphysics 4.2a) to perform physical simulations of our system.^[14] As opposed to the experimental data, the extracted τ of the temporal charge distribution process is constant according to the simulation at all V_g regimes, and for varying gap sizes. The fact that the source of the experimentally observed dependence is not accounted for in the computational simulation implies that it is not related to the intrinsic properties of the system. Instead, this observation probably derives from the device surroundings. Such an external component which has a well-known effect on SiO₂ surface conductivity is ambient humidity.^[16,17] It is therefore appealing to suggest a hypothesis regarding the influence of V_g on the amount of water which is adsorbed on the surface of the device. In order to verify this hypothesis, however, it is first necessary to quantify the effect of ambient humidity on the SiO₂ conductivity.

In a former study using EFM-based measurements of the surface-charge redistribution, we reported that ambient humidity greatly affects the SiO₂ surface conductivity.^[14] In order to quantify this effect, we used CNT-based measurements, and monitored the current of the CNT as a function of time upon applying $V_g = -0.8$ V at $t = 0$ s and keeping the voltage constant. This process was repeated several times, and under different ambient humidity [%h] conditions. The normalized time constants [$\tau(\%h)/\tau(\%h=45\%)$] of the exponential fits to the current decay of the CNT for each humidity percentage are summarized in Figure 3. As expected, τ exhibits a strong dependence on ambient humidity, and the saturation range is around 60% humidity and above. The same behavior was observed for other CNTs as well.

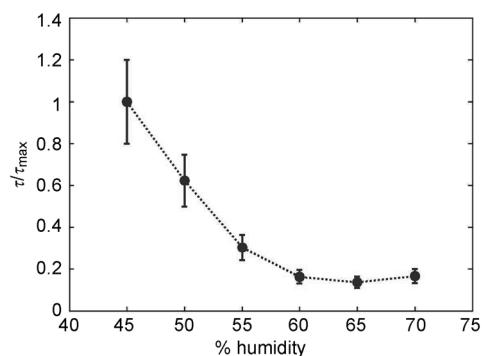


Figure 3. Normalized time constants, $\tau(\%h)/\tau(\%h=45\%)$, of the current decay of the CNT upon applying $V_g = -0.8$ V at $t = 0$ s as a function of humidity.

To summarize the data so far, using EFM-based measurements as well as CNT-based measurements we found that both the applied gate voltage and ambient humidity have a strong influence on the time constants of the charge-redistribution process, and hence on the SiO₂ surface conductivity. The significant effect of surface water on the conductivity has already been mentioned in previous reports.^[16,17] It is assumed that water molecules facilitate the drift-based movement of

charge on the SiO₂ surface. The influence of the gate voltage, however, is less straightforward. By using computational simulations we found that the effect of V_g is not related to the geometry of the system or to any other intrinsic property. In light of this, we propose the following hypothesis: the amount of water molecules on the SiO₂ surface, which usually depends on ambient humidity alone (for a given temperature), is increased upon applying V_g , and as a result, the surface conductivity is increased as well.

One possible reason why water molecules from the surrounding environment may be attracted and adsorbed onto the dielectric surface is their high dipole moment, $p = 6.2 \times 10^{-30}$ C m. When such a polarized object is found in a nonuniform electric field (such as the one induced upon applying voltage to the gate at $t = 0$ s), a force which is known as DEP acts upon it. This force is given by Equation (1):

$$\vec{F} = (\vec{p} \cdot \nabla) \vec{E} \quad (1)$$

where \vec{p} is the dipole of the particle and \vec{E} is the electric field. This DEP force can change the partial pressure of water molecules on SiO₂ relative to their partial pressure high above the surface, according to the fluid statics Equation (2):

$$\frac{dP}{dz} = \rho \cdot \vec{a} \quad (2)$$

where $\frac{dP}{dz}$ is the water partial-pressure gradient in the z direction (perpendicular to the sample surface), ρ is the density of the water molecules, and \vec{a} is the DEP force-induced acceleration on a single water molecule. Using the ideal gas equation one finds Equation (3):

$$\frac{dP}{dz} = \frac{P}{RT} \cdot N_A \cdot 10^3 \cdot (\vec{p} \cdot \nabla) \vec{E} \quad (3)$$

where R is the gas constant, T is the temperature and N_A is the Avogadro number. This first-order differential equation has the following solution [Eq. (4)]:

$$P_0 = P_\infty \cdot e^{\frac{N_A \cdot 10^3 \cdot p \cdot (E_0 - E_\infty)}{RT}} \quad (4)$$

where P_0 and E_0 are the water partial pressure and the electrical field on top of the SiO₂ surface, and P_∞ and E_∞ are the water partial pressure and the electrical field high above the device. Finally, it is possible to obtain the number of water layers on the SiO₂ surface as a function of the temperature and the water partial pressures on the surface and far above it according to the Brunauer–Emmett–Teller isotherm [Eq. (5)]:^[19]

$$\begin{aligned} X &= \frac{P_0}{P_s} \\ C &= e^{\frac{(H_1 - H_s)}{RT}} \\ \theta &= \frac{CX}{(1 - X)(1 + (C - 1)X)} \end{aligned} \quad (5)$$

where P_s is the saturation partial pressure of water high above the surface at a given temperature, H_i is the adsorption enthalpy of water on SiO_2 ($H_i \approx 42 \text{ kJ mol}^{-1}$ [20]), H_L is the liquidation enthalpy of water ($H_L = 40.65 \text{ kJ mol}^{-1}$ [21]), and θ is the number of water layers on the surface.

In order to examine the agreement between this model and our experimental data, we used computational simulations again to extract E_0 and E_∞ for different values of V_g . Next, we calculated the amount of water layers on the SiO_2 surface under different gate and humidity conditions according to Equations (4) and (5). Figure 4a shows the calculated number of water layers as a function of V_g at 55% humidity. One can observe, in agreement with our hypothesis, that the amount of water layers is indeed modified by the applied gate voltage. According to our experimental findings which probed the charge-redistribution process at $\sim 55\%$ humidity (Figure 2a and b), for $V_g \leq -1 \text{ V}$ the surface conductivity is no longer dependent on V_g . In Figure 4a one can see that at 55% humidity, there are 2.5 layers of water or more on the SiO_2 surface for $V_g \leq -1 \text{ V}$. Figure 4b depicts the calculated number of water layers as a function of humidity upon applying $V_g = -0.8 \text{ V}$. Notice that when the humidity is 60% and above, there are again 2.5 layers of water or more on the SiO_2 surface. This result is in agreement with our experimental findings, which show that for applying $V_g = -0.8 \text{ V}$ the dependence of the surface conductivity on ambient humidity indeed saturates at approximately 60% humidity (Figure 3).

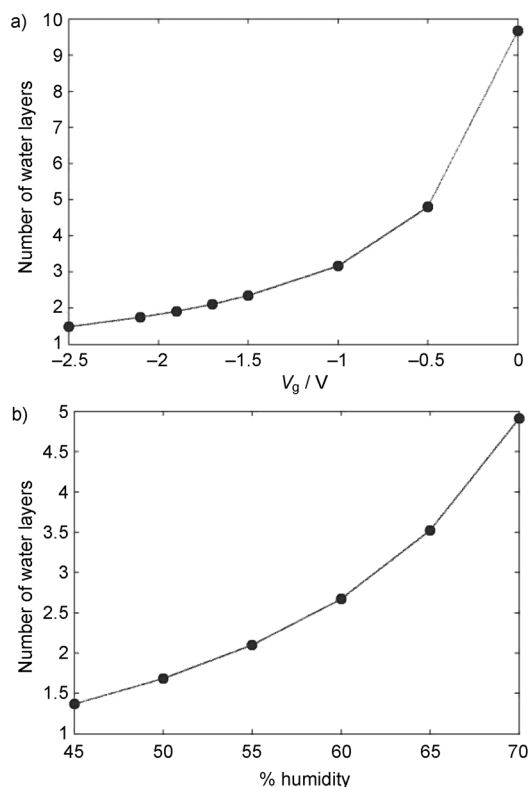


Figure 4. a) Number of water layers as a function of V_g for 55% humidity. b) Number of water layers as a function of humidity for $V_g = -0.8 \text{ V}$. $E_0 - E_\infty$ values were extracted from the computational simulation. Error bars are smaller than the markers.

To clarify these results further we use the data in Figure 4 to convert the CNT-based τ vs. V_g data (Figure 2b) and τ vs. humidity data (Figure 3) into τ vs. number of water layers, as depicted in Figure 5. One can observe that the two data sets are in good agreement with each other, and furthermore, the dependence of τ on the number of water layers saturates upon adsorption of approximately 2.5 layers for both data sets, as discussed before.

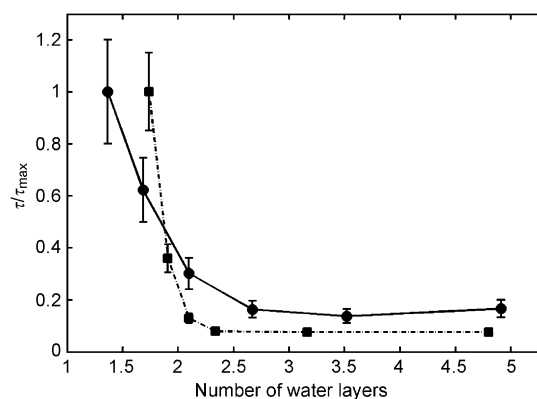


Figure 5. τ versus number of water layers, as calculated from the CNT-based τ versus V_g data (Figure 2b, squares) and τ versus humidity data (Figure 3, circles), using the data of Figure 4.

The experimental data and the theoretical model support our hypothesis, according to which external gate biases modify the surface humidity, which can be very different from the average humidity in the lab. Moreover, these results imply that surface conductivity depends on the number of water layers adsorbed on it up to approximately 2.5 layers. Above that, the conductance saturates and the dependence becomes much weaker if any.

3. Conclusions

In conclusion, using both EFM-based measurements and CNT-based measurements we have demonstrated that for low gate potentials, there is a strong dependence between V_g and the surface conductivity. In order to verify that this dependence is not related to intrinsic properties of the system, we used computational simulations, and concluded that the observed effect results from an external factor in the device surroundings. Since humidity is such an external factor which is known to influence the surface conductivity, we suggested that V_g changes the amount of water on the dielectric, and thus, indirectly, changes its conductivity as well. In order to examine this hypothesis, we first measured and quantified the influence of ambient humidity on the SiO_2 conductivity. Next, we introduced a theoretical model which details the mechanism through which the gate potential increases the number of water layers on the surface, and the model-based calculated results were compared with the experimental ones. The findings supported our hypothesis, and furthermore, suggested that upon the adsorption of two to three layers of water the surface conductivity saturates.

These findings are of great importance, first by establishing that the surface humidity can be much higher than the average environmental humidity, and second by observing that it can be modified by external gate voltages. This information is very relevant to CNTFETs as well as to other nano-scale devices whose operation is very sensitive to the actual surface humidity. In addition, several interesting applications for such an ability can be imagined. For example, it is known that the rate constant of several chemical reactions can be controlled by the amount of surrounding water layers. It should be possible, then, to covalently attach the relevant molecules to the surface of the device, and obtain a gate-controlled chemical reaction—a long desired “bridge” between electronics and surface chemistry.

Experimental Section

For the CNT-based charge-redistribution measurements, suspended CNTFETs were fabricated using a growth-at-the-end method.^[22,23] The processing was performed on 500 nm SiO₂ thermally grown on highly *p*-doped silicon substrate, using photolithography techniques. First, source and drain electrodes were patterned from 5 nm chrome covered with 40 nm platinum, with gaps of 1.8 μm between source and drain. Next, the devices were submerged in 1:6 buffer oxide etch (BOE) for two minutes in order to etch trenches of about 200 nm deep between each electrode pair. Finally, iron nanoparticles were deposited at specific places on top of the electrodes, and the CNTs were grown by chemical vapor deposition (CVD) with a methane/hydrogen gas mixture at 900 °C. This technique yields extremely clean devices, since the CNT growth is performed at the last step of the process, and all resist residues are burned and disposed of in the CVD process. All experiments were performed at 300 K. Experiments which required control of ambient humidity were performed inside a humidity chamber. A schematic representation of the CNT-based measurements experimental setup is depicted in Figure 6a.

The samples that were used for EFM-based charge-redistribution measurements were fabricated in the described-above manner,

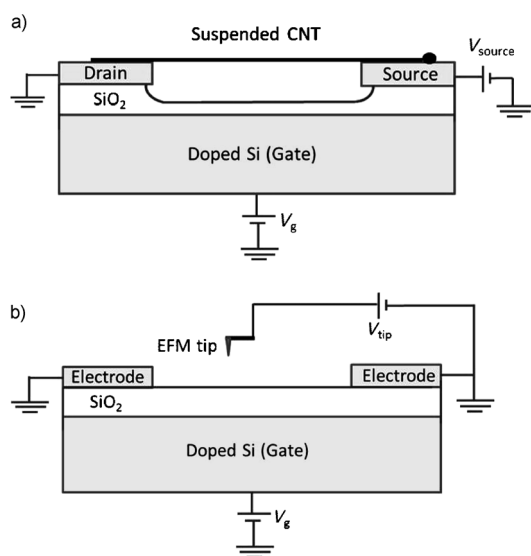


Figure 6. a) Experimental setup for the CNT-based measurements. b) Experimental setup for the EFM-based measurements.

with 10 μm gaps between source and drain and with no trench. Experiments were performed on a commercial AFM Nanoscope V Dimension 3100 from Veeco Instruments. The cantilevers used were manufactured by MikroMasch, with triangular shape, 200 μm in length and 40 μm in width. The nominal spring constant was 3 N m⁻¹ and the resonant frequency ranged from 45 to 75 kHz. The quality factor *Q* was approximately 250. The tips were made of Si coated with Cr-Au to ensure a metallic behavior, and their nominal radius of curvature was less than 50 nm. All experiments were performed in ambient conditions. A schematic representation of the EFM-based measurements experimental setup is depicted in Figure 6b.

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