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Relating hysteresis and electrochemistry in graphene field effect transistors

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Hysteresis and commonly observed p-doping of graphene based field effect transistors (FETs) have been discussed in reports over the last few years. However, the interpretation of experimental works differs; and the mechanism behind the appearance of the hysteresis and the role of charge transfer between graphene and its environment is not clarified yet. We analyze the relation between electrochemical and electronic properties of graphene FETs in a moist environment extracted from the standard back gate dependence of the graphene resistance. We argue that graphene based FETs on a regular SiO_2 substrate exhibit behavior that corresponds to electrochemically induced hysteresis in ambient conditions, and can be caused by a charge trapping mechanism associated with sensitivity of graphene to the local pH. © *2011 American Institute of Physics*. [doi:10.1063/1.3665196]

I. INTRODUCTION

Graphene, as a single atom thick layer of carbon atoms, has already showed potential for application in electronics and biosensing.[1] However, graphene as a truly 2D system is ultrasensitive[2] to the underlying substrate and surface chemistry, which alters the charge transport properties of pristine graphene. One of the main issues in graphene devices is a hysteretic behavior of its resistance observed in ambient conditions, when a gate voltage is swept back and forth. The presence of hysteresis and commonly observed p-doping of graphene based field effect transistors (FETs) was already discussed in recent reports.[3–6] The interpretation of experimental works differs; and the mechanism behind the appearance of hysteresis and the role of charge transfer between graphene and its environment are not clarified yet.

In an ideal case of grounded graphene its charge neutrality point (CNP) is located at zero back gate voltage. However, in ambient conditions most of the graphene based FETs show initial p-doping (CNP is positioned at positive Vg) and hysteresis. We point out that these two effects can be related but do not necessarily have the same nature. The doping of graphene can be caused either by the adsorbates on top or underneath the graphene surface[2–4] or by the electrochemical processes involving graphene.[5–7] Depending on the nature of the dopant or the electrochemical environment, the initial doping can be either p or n, which introduces a shift of the graphene CNP to positive or negative gate voltages, respectively. One should keep in mind that even in the absence of a net doping the dynamic response of the graphene resistance, namely hysteresis, can be different.

There are two types of directions defined for hysteresis; positive and negative.[4] The positive direction of hysteresis corresponds to the CNP shifting toward negative voltages while the gate voltage is swept further into the negative regime. In case of negative hysteresis the shift of the resistance with respect to the gate voltage is in the opposite direction: The CNP shifts toward more positive values while sweeping the gate into the negative regime. Wang *et al*.[4] proposed that negative and positive hysteresis directions can be attributed to two competing mechanisms: capacitive coupling and charge trapping from/to graphene, respectively.

Capacitive coupling enhances the local electrical field near graphene, inducing more charge carriers and causing a negative direction of hysteresis. An example of a mechanism for capacitive coupling is a dipole layer placed in between graphene and the back gate. In moist air and without additional treatment of the silicon oxide substrate (a common insulator for a graphene based FET) this dipole layer exists as adsorbed water molecules at room temperature[3,8] or ordered ice at low temperature.[4,9] The capacitive coupling mechanism is also dominant in electrolyte-gating devices, via ions in the electrical double layer.[4] The positive direction of hysteresis is caused by a charge trapping mechanism. Accumulated charge in trap centers will start screening the electric field of the back gate. One example of trap centers is the surface states in between SiO_2 and graphene.[4,10–12] In the case of graphene based FETs, traps in bulk SiO_2 or the SiO_2/Si interface were excluded in a recent report by Lee *et al*.,[13] who measured time scales that were too fast for these types of trapped centers.

A separate charge transfer mechanism observed for the hydrogenated surface of diamond,[14] carbon nanotubes,[15] and graphene based FETs,[5–7] is the dissociation of adsorbed water and oxygen on the carbon surface. Because water in equilibrium with air is slightly acidic (pH = 6), the electrochemical potential of the carbon surface is higher than that of the solution, resulting in electron transfer from graphene. Therefore, a graphene FET possesses a net p-doping in moist air. The electron transfer is mediated by oxygen solvated in water and can occur in the opposite direction with increasing pH. This redox can therefore influence the dynamic response

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of graphene devices under an applied back gate and cause a positive hysteresis.

A recent report by Fu *et al.*[16] opened the discussion of whether graphene pH sensitivity is caused by charge transfer directly between graphene and the solution[17–19] or if the sensitivity is mediated by a layer on top of or next to graphene (either oxide or polymer residue). This layer can provide terminal hydroxyl groups that can be protonized or deprotonized depending on the proton concentration in the solution (pH), yielding a bound surface charge layer, which can electrostatically induce carriers in graphene. Recently it was reported that application of a gate potential can lead to a local change of pH in a thin water film next to an oxide substrate.[20] We argue that a combination of these two effects can result in a positive hysteresis in graphene, where the residues act as mediators for charge trapping actuated by pH changes induced via gate electrical field. We emphasize that both cases, independent of whether the charge trapping is direct or mediated by residues, would lead to the same direction in hysteresis and will be undistinguishable in transport experiments. Although replacement of the silicon oxide with either a hydrophobic[3,12] or an oxygen free[5] substrate did show suppression of both initial p-doping and hysteretic behavior, none of the reports link the chemical redox to the direction of hysteresis.

In this work we analyze the relation between electrochemical and electronic properties of graphene FETs in a moist environment. We argue that graphene based FETs on a regular SiO_2 substrate exhibit behavior that corresponds to electrochemically induced hysteresis in ambient conditions, caused by charge trapping mechanisms associated with the sensitivity of graphene to the local pH.

II. METHODS

Samples were obtained by mechanical exfoliation of graphite (highly ordered pyrolytic graphite or Kish) on an oxidized n^+-doped silicon substrate (300 or 500 nm thick oxide layer), which functions as a back gate. The SiO_2 wafers are commercially available from Silicon Quest International, where the oxide is prepared by dry oxidation. Single layer graphene flakes were chosen based on their optical contrast and thickness measured by atomic force microscopy. A small number of samples were inspected with Raman spectroscopy to verify the number of layers. Ti/Au (5/40 nm thick) electrodes were prepared using standard electron beam lithography and lift off techniques. For electrical measurements samples were placed in a vacuum can with base pressure of 5×10^{-6} mbar, using a standard low frequency ac lock-in technique with an excitation current of 100 nA. The carrier density in graphene is varied by applying dc voltage (Vg) between the back gate electrode and the graphene flake, as depicted in Fig. 1(a). The charge carrier mobilities (μ) ranged from 2500 up to 5000 cm^2/Vs^{-1} at a charge carrier density of $n = 2 \times 10^{11}$ cm^{-2}.

The sensor properties of the devices were studied in the following way. First, we pumped down the sample can (95 cm^3 in volume) to the base pressure. Then a valve connecting the can to a volume containing liquid water and filled

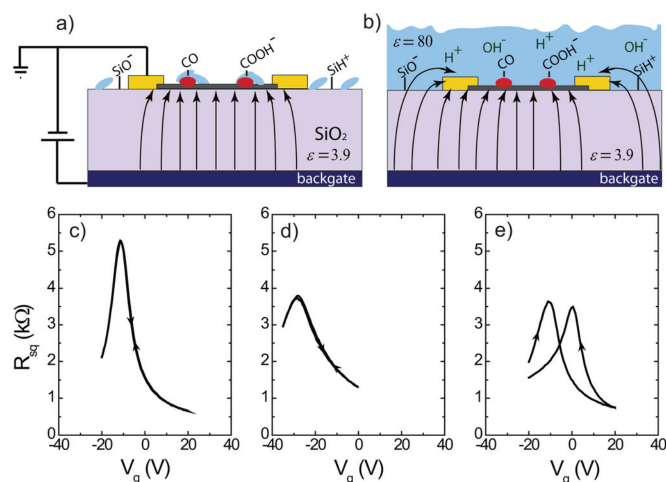

FIG. 1. (Color online) (a) Scheme of a graphene based device with a discontinuous layer of adsorbed water in the case of a short exposure to H_2O vapor. Dangling bonds in SiO_2, lithographic polymer remains (red ovals) on the graphene surface, and electric field lines between graphene and the back gate are schematically drawn. (b) A continuous thin layer of water on the graphene surface in the case of flooding the sample with water vapor. (c) Graphene resistance vs gate voltage after annealing (initial state), (d) after a short exposure to water vapor, and (e) positive hysteresis developed after further flooding with water vapor.

with saturated vapor (H_2O or D_2O at 32 mbar saturation pressure) at 25 °C, was kept open for 1 s (short exposure to the vapor). After measurement, the valve to the sample was fully opened, connecting the sample volume to the water container (flooding with water vapor). In the case of ethanol vapor exposure the procedure was kept the same, but the partial pressure of ethanol in the liquid cavity was 78 mbar. The purity of heavy water and ethanol was 99.9%. A graphene based FET on a hydrophobic substrate was also prepared by exposure of SiO_2 to hexamethyldisilazane (HMDS) vapor prior to graphene deposition. HMDS forms a self-assembled monolayer that protects graphene from the influence of dangling bonds in silicon dioxide and prevents adsorbtion of water molecules in the vicinity of graphene.

III. RESULTS AND DISCUSSION

In ambient conditions the devices appear to be p-doped, with a pronounced positive hysteresis in the dependence of resistivity versus gate voltage (not shown). To remove adsorbates from the graphene surface we performed global annealing of the device in vacuum at 130 °C for 1.5 h. After annealing, the gate dependence does not show hysteresis and becomes symmetric around the CNP (Fig. 1(c)), which is located at a negative gate voltage (−11 V), indicating electron doping. Similar shifts toward negative gate voltages were observed by Romero *et al.*[10] and associated with SiO_2 surface states. We will call this position of the charge neutrality point the initial position (after annealing). Short exposure to water does not cause hysteresis, but reduces μ by 25% compared with the initial state and can be attributed to the increase of a number of the scatter centers for charge carriers (Fig. 1(d)).[2] Because graphene is hydrophobic, we assume that during the short exposure adsorbates only occasionally agglomerate on the graphene surface in the vicinity

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of polymer leftovers, which are unavoidably present after the lithography step (Fig. 1(a)).

Flooding the sample chamber with H_2O vapor assures full coverage of the previously annealed SiO_2 and graphene surface with a thin film of water (3 nm thick),[21] similar to ambient conditions. After flooding we observe both electron-hole asymmetry and a highly hysteretic behavior of the graphene device, where the CNP for trace and retrace are situated at Vg of opposite signs (Fig. 1(e)). Moreover, a decrease of the scanning rate in gate voltage sweeps (V/s) leads to more pronounced hysteresis with the spacing between trace and retrace maxima increasing from 6.5 V at 1 V/s up to 23.5 V for 0.1 V/s. The cycle of annealing and water exposure was repeated a few times, showing reproducible results. The positive direction of hysteresis indicates a charge trapping mechanism, while electron-hole asymmetry can be explained in two ways: real asymmetry due to doping of graphene under the contacts[22] or an artifact of charging and discharging graphene due to the hysteresis. Because we do not observe asymmetry in the initial curve, the latter situation will be assumed in further discussions.

Next, we present a novel analysis of hysteretic back gate voltage sweeps from the point of view of time-dependent shifts in CNP. These shifts represent a change in carrier density within a certain time, equivalent to a current. We estimate this current corresponding either to the charge flow in or out of graphene, or induced charge, in the following way. Charge current is extracted by comparing the non hysteretic Dirac curve of graphene, which is briefly exposed to water vapor, to the curves after the sample is flooded, measured at different scan rates: 0.5; 0.25, and 0.1 V/s. The exact procedure is shown in Figs. 2(a) and 2(b). For each scan rate the gate voltage axis was divided into fixed regions ΔV_{fixed}. A change in voltage ΔV_{fixed} induced a change in the carrier density and resistance ΔR accordingly. As a result of the charge trapping mechanism induced by water, the same ΔR will require a different value of gate voltage ΔV_i in the case of the non-hysteretic curve. The difference between ΔV_{fixed} and ΔV_i will be proportional to the amount of additionally induced or transferred charge in graphene. The charge current ($A/\mu m^2$) in graphene can then be calculated as:

$$I_i = \frac{e\alpha(\Delta V_i - \Delta V_{fixed})}{\Delta V_{fixed}/\beta} \tag{1}$$

where e is the elementary charge, $\alpha = 2 \times 10^{14}$ m^{-2}V^{-1} with $e \times \alpha$ the charge capacitance per unit area for 500 nm SiO_2, and β is the scan rate of the gate sweep (V/s).

The calculated charge current curves (Fig. 2(c)) resemble the electrovoltaic characteristics of graphene based electrochemical cells with controlled pH.[17] A graphene based device on a SiO_2 substrate can act as a working electrode in the thin layer of water covering the hydrophilic oxide surface. Thus we can consider graphene based devices as electrochemical cells. Moreover, the height of the observed peaks scales linearly with the scan rate of the applied gate voltage (Fig. 2(d)) which, for an electrochemical cell, suggests that these peaks originate from a non-Faradaic or non-diffusion limited process involving the adsorbed ions on the graphene surface.[17] We performed the same sequence of experiments with graphene devices on HMDS primed SiO_2. In contrast to graphene on hydrophilic SiO_2 we observe neither hysteresis nor any changes in the graphene resistance under water vapor exposure (not shown).

From the fact that the initial curve (after annealing) has no hysteresis we can exclude charge trapping in the surface states of SiO_2. Comparing with a local current annealing procedure,[4] here we globally annealed the sample, which assures desorption of H_2O molecules from the whole SiO_2 surface and prohibits their diffusion back to the graphene surface. The hysteresis appears only when the amount of water in the system is high enough to form a continuous layer. The linear scaling of extracted height of current peaks with scan rate indicates the reversible charging of an ionic layer at the graphene surface (electrode) by an applied gate voltage. The absence of hysteresis of the graphene resistance when HMDS is used supports the idea that the trapping mechanism happens by the presence of a water layer on the SiO_2 surface. The dielectric constant of water is $\varepsilon_{H2O} = 80$, much higher than $\varepsilon_{oxide} = 3.9$. Therefore the electrical field lines in the device deviate from plane capacitor and can be present in the water layer (Fig. 1(b)). The strong electrical field across the water layer can either cause dissociation of water molecules[23] or proton release/uptake by terminal OH^- groups at the oxide surface, as previously described.[16,20] Both these mechanisms lead to a local pH change in the graphene vicinity. Depending on the pH, the dangling bonds of the oxide or polymer remains on the graphene will change their charge state, inducing an opposite charge in graphene.[16,23] At the present time we cannot pinpoint the exact identity of the ionic species causing the change of environment around the

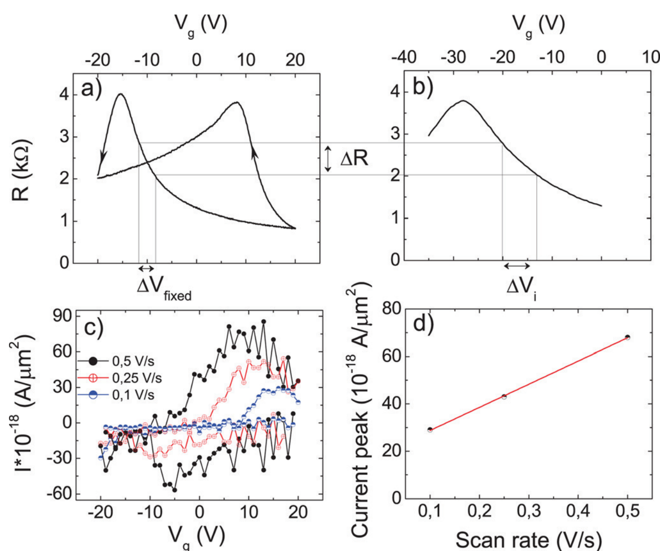

FIG. 2. (Color online) Calculation of the charge current in graphene. (a) Gate voltage dependence of graphene resistance "flooded" with water vapor and measured at a rate of 0.1 V/s. The curve is divided into parts with a fixed step in gate voltage ΔV_{fixed}, corresponding to the change in resistance ΔR. (b) Gate dependence of graphene resistance briefly exposed to H_2O vapor. As a result of the charge transfer now the same ΔR requires a different value of applied voltage ΔV_i. (c) Calculated charge current vs gate voltage for three different scan rates: 0.5; 0.25, and 0.1 V/s. (d) Linear scaling of the peak, at positive gate voltage shown in (c), with the scan rate.

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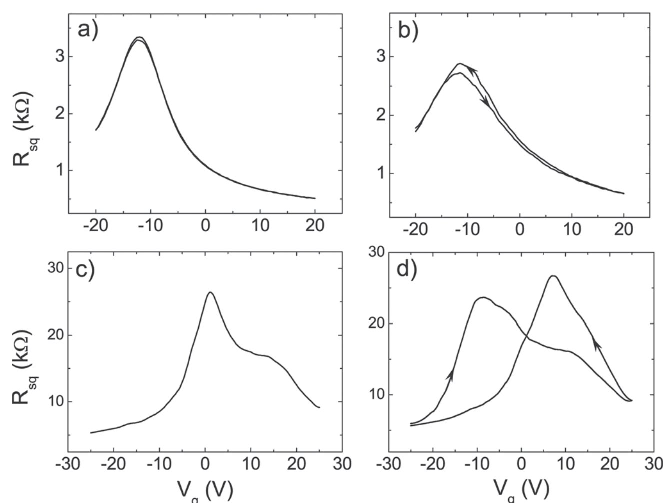

FIG. 3. Changes in graphene resistance vs gate voltage under exposure to ethanol and D_2O vapors. (a) the initial state; (b) after further flooding with ethanol vapor; (c) the initial state (for another sample); and (d) previously mentioned [(c)] sample after further flooding with D_2O vapor.

graphene. A possible electrochemical reaction on the unprotected Au electrodes is not relevant, as this was ruled out by Wang *et al.*,[4] where both samples with protected and unprotected gold contacts showed the same type of hysteresis.

Because the dipole nature of water molecules is often discussed in relation to the hysteresis observed in graphene devices,[3,4,9] we decided to study the response of graphene resistance to ethanol vapors. A pure neutral ethanol solution has at least 100 times less concentration of H^+ and OH^- ions than pure water.[24] However the dipole moment of an ethanol molecule $\vec{p}_e = 1.68D$ is comparable to that of water $\vec{p}_w = 1.85D$,[24] which makes it possible to separate the electrochemical from electrostatic influences on the charge carrier density in graphene. In Figs. 3(a) and 3(b) the changes in graphene resistivity under ethanol vapor exposure are presented. Except for the reduction of charge carrier mobility by 25% (comparable to water exposure), neither considerable hysteresis nor doping were observed.

We also performed similar experiments using D_2O vapor with another set of samples. Chemically, D_2O molecules behave similarly to H_2O. However, D^+ ions are two times heavier than H^+, whereas the relative increase in mass of OD^- ions compared to OH^- is negligible. If the electrochemical process on the graphene surface is proton diffusion limited, one expects to observe a different behavior of the hysteresis at various scan rates. Experimentally we do not observe any significant difference in graphene responses between H_2O and D_2O. Heavy water exposure causes doping and direction of the hysteresis comparable to normal water values (Figs. 3(c) and 3(d)).

Our experiment with ethanol vapor supports the idea that the polarity of molecules adsorbed in the graphene vicinity does not influence the dynamic response of graphene resistance to a gate voltage. We suggest that the main reason of the observed hysteresis in ambient conditions is the electrochemical activity of water molecules in the graphene environment.

IV. CONCLUSIONS

We have shown that the commonly observed positive hysteresis in graphene FETs can be derived from the electrochemical activity of water adsorbates on the SiO_2 substrate. In a moist environment a standard graphene FET can act as an effective electrochemical cell, with graphene being an electrode in the thin layer of water. Therefore the application of the back gate voltage may lead to local changes of pH, which, in turn, affect the carrier density in graphene. From this point of view we suggest that, next to the contact doping effect, the observed electron-hole asymmetry in graphene resistance appears as an artifact of the hysteresis caused by charge trapping. Conducted experiments with ethanol vapor and heavy water did not show a relation between the hysteresis and either dipole moment or mass of adsorbed molecules, supporting the idea of electrochemical activity of water as a key element in the dynamic response to gate voltage sweeping. These findings give a further insight to graphene-related electrochemistry outside an ideal electrochemical cell and open perspectives for the application of a graphene FET as a memory element.

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