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Observation of the *memory steps* in graphene at elevated temperatures

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We found that the current-voltage characteristics of graphene transistors exhibit an intriguing feature—an abrupt change in the current near zero gate bias at temperatures above 500 K. The strength of this effect, which we refer to as the *memory step* by analogy with the *memory dips*—known phenomenon in electron glasses, depends on the rate of the gate voltage sweep. The slower the sweep, the more pronounced is the step in the current. Despite differences in examined graphene transistors, the memory step always appears at $V_g \approx 0$ V. The observed memory steps are likely related to the slow relaxation processes in graphene. This new phenomenon in graphene can be used for applications in sensors and switches. © *2011 American Institute of Physics*. [doi:10.1063/1.3596441]

Unique properties of graphene, such as extremely high carrier mobility[1,2] and intrinsic thermal conductivity,[3,4] chemical inertness and mechanical stiffness[5] have attracted enormous attention. Many unique features of this material have already been understood. Practical applications of graphene in transparent electrically conductive electrodes and thermal management seem to be rather realistic. Far less clear is how to capitalize on graphene's electronic properties. Here, we report a new electronic effect in graphene, which we observed at elevated temperatures $T > 500$ K. This effect can be a signature of slow relaxation processes or phase transitions in the graphene electronic system. In the vicinity of this transition, graphene is extremely sensitive to external perturbations, and therefore can be used for electronic high temperature sensing applications.

Graphene samples were produced by mechanical exfoliation from bulk highly oriented pyrolytic graphite. Graphene flakes, placed on standard Si/SiO$_2$ substrates, were identified using micro-Raman spectroscopy. We have reported details of our Raman inspection elsewhere.[6,7] The 8 nm Ti/80 nm Au metal layers were sequentially deposited on graphene by the electron-beam evaporation to produce the drain and source contacts.[8,9] The degenerately doped Si substrate acted as a back gate. The current-voltage (I-V) characteristics (drain current versus gate voltage) were measured using a semiconductor parameter analyzer (Agilent 4156B). The characteristics were determined at temperatures from 300 to 540 K for several single layer graphene transistors. The measurement protocol was as follows: at the drain voltage $V_d = 100$ mV, the gate voltage $V_g = -40$ V was applied and kept constant for 2 s. Then the gate voltage was swept from -40 to 80 V and back to -40 V. In some cases, the single sweep from -40 to 20 V was used.

Figure 1(a) shows a scanning electron microscopy (SEM) image of a typical devices used for the study while Figs. 1(b)–1(d) present three examples of the input I-V characteristics of graphene transistors at different T. For all examined transistors, the charge neutrality point at room temperature (RT) ranged from 10 to 40 V. All the samples demonstrated a hysteresis for the direct and reverse gate voltage sweeps. The inset shows the effective mobility in graphene as a function of temperature. The effective mobility at $V_g = -40$ V as a function of temperature was calculated as

$$\mu_{\text{eff}} = \frac{L_g}{R_{Ch} C_g (V_{GS} - V_D) W}, \tag{1}$$

where V_{GS} is the intrinsic gate-to-source voltage, V_D is the gate voltage corresponding to the minimum of current at the charge neutrality point, L_g is the transistor gate length, C_g is the gate capacitance per unit area, W is the gate width, and R_{Ch} is the channel resistance (see Ref. 9 for the calculation details). With an increase in T, the hysteresis became more pronounced, and the difference between the gate voltages corresponded to the current minimum increased.

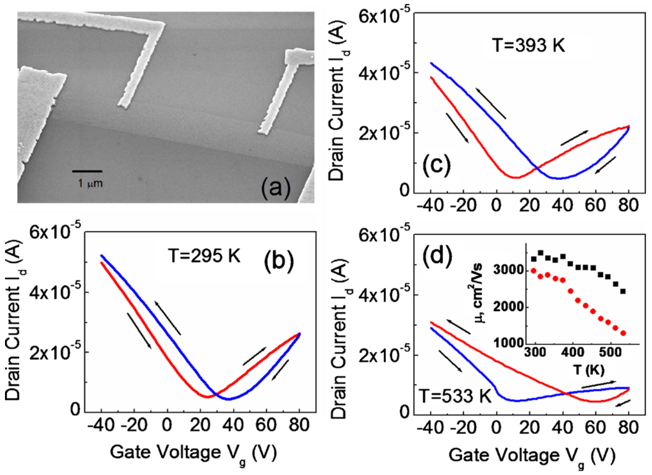

FIG. 1. (Color online) (a) SEM image of a representative four-terminal graphene device. [(b)–(d)] Current-voltage characteristics of a graphene back-gate transistor at different T. The inset shows the temperature dependence of the mobility in graphene at $V_g = -40$ V for the direct (filled symbols) and reverse (open) sweeps, respectively.

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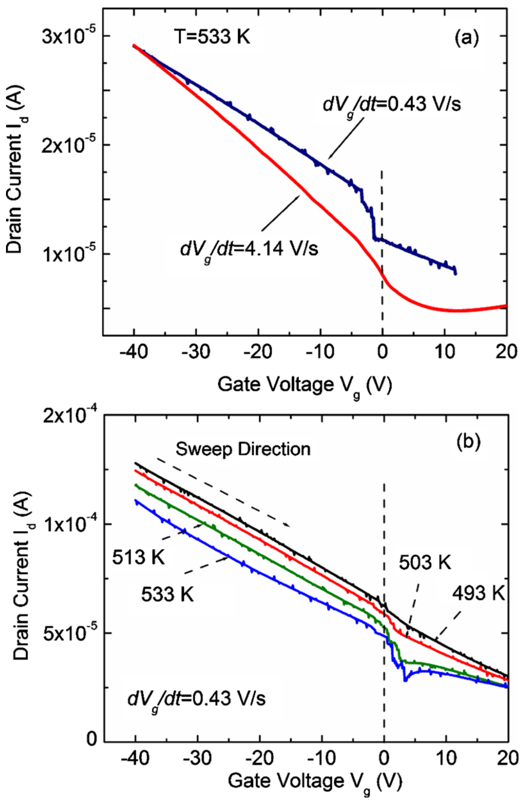

FIG. 2. (Color online) (a) Current-voltage characteristics of a graphene back-gate transistor at $T=533$ K measured at two different voltage sweep dV_g/dt rates. (b) I-V characteristics of a graphene back-gate transistor at different temperatures.

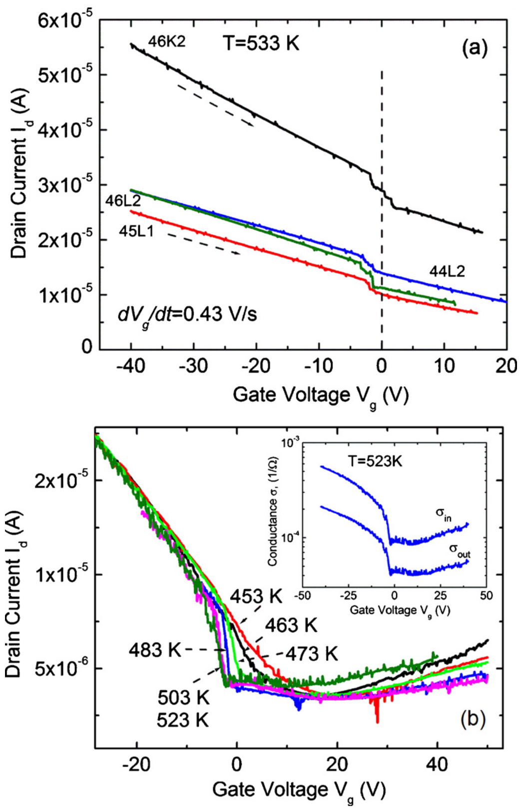

FIG. 3. (Color online) (a) Memory steps at $T=533$ K ($T=260$ °C) observed in several different graphene transistors. Note that the step occurs near $V_g \approx 0$ V despite the fact that graphene transistors had different shapes, charge neutrality points, and electrical conductivities. (b) I-V characteristics measured in the four-probe configuration for the back-gate transistor at different elevated T. The memory step was again observed near $V_g=0$ V. The inset shows the conductance between the outer and inner contacts in the four-probe measurements.

The hysteresis of I-V characteristics in graphene has been studied previously.[10–15] It is linked to the slow carrier relaxation processes in graphene. These processes depend on temperature and can be affected by contamination from ambient air and the substrate. Such slow relaxations occur in many materials owing to various mechanisms, such as trapping and detrapping of carriers by deep levels with small capture cross sections σ_C, slow change in the scattering cross-section, and the electron glass behavior.[16–19] As seen in Fig. 1, despite strong changes in I-V characteristics with T, the current at the charge neutrality point depends on T only weakly. For the majority of the tested devices, the minimum conductivity remained within the range $(5.4-6.4)e^2/h\ \Omega$.

At temperatures above 500 K (or 220 °C), we found a new feature in I-V characteristics at $V_g \approx 0$. At the fast gate voltage sweep, it looks like a very small change in the slope of the drain-current versus the gate-voltage. At the slow gate-voltage sweep, a clear step forms in I-V characteristic. Figure 2(a) shows I-V characteristics measured with $dV_g/dt = 4.15$ V/s and $dV_g/dt=0.43$ V/s sweep rates for one of the transistors. As one can see, the shape of I-V curves strongly depends on dV_g/dt. The slower is the scan, the more pronounced is the step. We refer to this feature as the "step" using an analogy with similar features—*memory dips*—in electronic glasses. Cooling the transistor and heating it again reproduced the I-V dependence including the step. Figure 2(b) shows the evolution of the characteristics with temperature for $dV_g/dt=0.43$ V/s.

It is important to emphasize that all graphene samples demonstrated this kind of the step at V_g close to but not exactly equal to zero despite having different shapes of the graphene flakes, conductivities, and the charge neutrality points. Figure 3(a) shows I-V characteristics for several samples. The voltage corresponding to the step varies slightly from sample to sample remaining close to $V_g=0$. In order to verify how robust and reproducible this feature in I-V characteristic of graphene at elevated T, we kept the transistors at ambient environment for two weeks. As a result of aging, the conductivity dropped but the steps at $T > 493-503$ K were still clearly observed for all graphene devices. To further test reproducibility, we prepared another batch of back-gated graphene transistors, which had four in-plain contacts and different I-V characteristics. These transistors had much smaller hysteresis at RT and the Dirac voltage was within a few volts from $V_g=0$ V. The transistors have shown stable characteristics over sufficiently long time (about one month). The *memory step* was observed again although at slightly lower T and of slightly different shape. The striking feature was that the memory step appeared at $V_g=0$ V again [Fig. 3(b)]. By measuring the conductance between the outer, σ_{out}, and inner, σ_{in}, contacts in the four-probe configuration, we were able to prove that the observed memory step is not related to the metal contacts. The σ_{out} and σ_{in} depend identically on V_g (see inset). We monitored the leakage current to exclude it as a possible mechanism of the memory step.

The exact origin of the memory step in graphene with different charge neutrality points and the reasons for its intriguing appearance near $V_g=0$ are not clear. However, one notices a similarity between the observed feature in graphene and those studied in electron glasses.[16–19] The electron glasses demonstrated memory effects including the so-called memory dips in the current versus gate-voltage dependence. Several mechanisms responsible for the memory dip have been discussed.[16–18] In both systems, graphene and electron glass, this irregularity is found at $V_g=0$ and its amplitude is very sensitive to temperature.[19] However in contrast to our experiments, the memory dips in electron glasses are observed at cryogenic temperatures and the amplitude of the dip increases with the increase of the gate voltage scan speed.

According to the theories that describe memory dips in electron glasses, many processes in solid-state systems involve slow conductance G changes, which suggest nonequilibrium phenomena.[16] In degenerate Fermi systems, e.g., metals and heavily doped semiconductors, the fluctuations in the conductance reflect the temporal changes in the potential experienced by the charge carriers.[20,21] Such potential fluctuations may be structural, involving slow dynamics of atoms which, in turn, may be triggered by a modified state of local charge distribution. A slow release or trapping of carriers, likewise, manifest itself in the slow conductance fluctuations.[16] Either mechanism may lead to the conductance fluctuations that extend to very low frequencies and reveal themselves in the low-frequency spectrum dominated by $1/f$ and generation-recombination (G-R) noise (f is the frequency). There are other mechanisms, which may lead to G changing slowly with time. This may occur, for example, due to annealing of defects, diffusion of injected dopants, light exposure, irradiation, and other instances involving changes in the potential landscape, or the density of carriers in the conducting system.

We have previously observed the signatures of slow trapping-emission processes in the low-frequency noise data from graphene transistors.[9,22] Specifically, from G-R peaks at very low f, we extracted time constants $\tau > 1$ second.[9] Other relaxation processes in graphene may take hours or even weeks. For example, we observed a slow recovery of electronic properties, e.g., mobility, of the electron-beam irradiated graphene when the samples were annealed or left for a long time in vacuum or ambient conditions.[23–25] Here, we found the memory steps at elevated T, which is high enough to trigger annealing processes, and slow relaxation resulting in G change. Other graphene-specific slow relaxation processes can be related to the topological corrugations, which have been proved to exist in graphene and might be responsible for its stability.[5] The topological corrugations on the nanometer and micrometer scale can change slowly, particularly as T changes from RT to above 500 K.

The memory dips in G in electronic glasses were also associated with the hopping type of electron conductivity.[18] This mechanism can have its analog in graphene. It is known that in graphene, there exist simultaneously electron and hole puddles.[26,27] They are the result of the inevitable presence of disorder, which leads to emergence of the electron-rich and hole-rich regions. The puddles are considered to be among factors limiting graphene mobility.[27] One can envision that electron and hole hopping among the puddles and slow evolution of the puddles themselves lead to the slow G changes on the time-scale required for the observation of the memory steps.

The discovered abrupt change in current due to the memory step can be used for low-voltage memory applications. Further studies are needed to understand the memory step dependence on ambience since a very large transconductance associated with the memory step might be promising for applications in the low-voltage low-power sensors.

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