Current-induced cleaning of graphene

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A simple yet highly reproducible method to suppress contamination of graphene at low temperature inside the cryostat is presented. The method consists of applying a current of several mA through the graphene device, which is here typically a few µm wide. This ultra-high current density is shown to remove contamination adsorbed on the surface. This method is well suited for quantum electron transport studies of undoped graphene devices, and its utility is demonstrated here by measuring the anomalous quantum Hall effect.

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The discovery of graphene, a one-atom thick layer of graphite, has generated considerable interest by opening avenues in condensed matter physics [1]. Graphene is an appealing system for basic research due to its unusual electronic properties; namely, charge carriers behave like chiral massless Dirac particles [2, 3, 4, 5]. The material also holds promise for technological applications, such as in nanoelectronics [6]; in addition, graphene has been shown to be an outstanding gas sensor able to detect minute amounts of molecular dopants [2, 8]. Yet, what makes graphene an enticing material is also the source of great technological difficulties: being in essence a surface, graphene proves to be extremely sensitive to contamination.

Recently, different approaches have been put forward to address this problem. Annealing at several hundreds Celsius in ultra-high vacuum or in Ar/H2 environment has been shown to remove contamination [9, 10]. Unfortunately, however, such annealing processes are difficult to implement in a cryostat for low-temperature measurements, and transferring samples from the annealing chamber to the cryostat is not convenient, since exposure to air reintroduces contamination.

In this Letter, a simple yet highly reproducible method to suppress contamination at low temperature inside the cryostat is presented. The method is based on the application of a large current through the graphene device generating several tens of mW dissipation over a few µm2 large surface. Remarkably, graphene can sustain such extreme conditions while adsorbed contamination gets removed. We employ atomic force microscopy (AFM) to show how adsorbates, as well as intentionally deposited CdSe particles, melt away. These cleaned graphene devices allow us to measure the anomalous quantum Hall effect.

We start by briefly describing our fabrication technique. Graphene flakes are deposited by mechanical exfoliation of Kish graphite (Toshiba Ceramics) on degenerately doped silicon substrates coated with 270 nm of thermal silicon oxide. We use standard wafer protection tape as it leaves little adhesive residue on substrates. Cr/Au electrodes are fabricated on top of samples by electron beam lithography followed by lift-off in acetone and dichloroethane. Two-point dc transport measurements are conducted both at room temperature in air for AFM imaging and in a He4 cryostat.

Graphene is able to carry very high electrical currents without sustaining damage. Applying a source-drain bias V of a few Volts across the sample induces a large current flow I of a few mA, as shown in Fig. 1. Taking the sample width of 4 µm and a thickness of 0.35 nm, this translates into an extremely large current density J of a few 108 A/cm2. For comparison, J is only a few times larger in carbon nanotubes [11, 12], and for both materials J is several orders of magnitude larger than in present-day interconnects.

The effects of a large electrical current passing through a mesoscopic, conducting device include electromigration [13, 14] and Joule heating. We expect that the large power P ∼ 20 mW dissipated over a small area of a few µm2 significantly increases the sample temperature. In order to show this, we monitor the four-point resistance R of a gold strip (R ∼ 60 Ω at room T) fabricated on the substrate 30 µm away from the graphene sample. Having initially calibrated R against a commercial thermometer in thermal equilibrium, we estimate that T rises by ∼ 25 K at the gold strip when a power of 34 mW is dissipated in the graphene sample at 4.2 K. However an esti-
FIG. 2: (Color online) CdSe nanoparticles are deposited on a graphene sample, and imaged by AFM before (Fig. 2a) and after (Fig. 2b) applying a large electrical current between source and drain. Both Figs. are topographic scans. Fig. 2b indicates that most nanoparticles have vanished from the area located halfway between source and drain. Particles are not observed to cluster up nor to migrate towards the edges over the entire width of the electrodes (not shown).

In the following we demonstrate how this effect can be harnessed to remove contaminants from graphene samples. AFM imaging reveals the influence of the large electrical current on the morphology of the sample surface. Figs. 3a-b display AFM scans for the signal amplitude at various stages of the cleaning process. Typically, freshly deposited graphene sheets have an average roughness $R_a \simeq 0.1$ nm. Right after fabrication (Fig. 3a) $R_a \simeq 0.4$ nm is measured, suggesting the presence of contamination on top of graphene. Fig. 3b captures an intermediate state obtained by ramping $V$ to 3 V. Contaminants migrate and cluster up. As $V$ is further increased, the sample area halfway between source and drain becomes almost as smooth as the substrate (Fig. 3c, for $V = 4.6$ V) and the roughness is down to $R_a \simeq 0.1$ nm, as before fabrication. Fig. 3c also shows that some contamination has accumulated at the corner of the device (such a migration is not observed with CdSe particles).

This contamination removal has drastic effects on the sample doping. Electric field effect can be used to dope graphene either with electrons or holes, resulting in a minimum conductivity at the charge neutrality point. The black curve in Fig. 3d represents the low-bias conductance $G$ as a function of a back gate bias $V_{bg}$ applied to the silicon substrate, for the same sample as in Fig. 1 but prior to any large current flow. Measurements are performed under helium atmosphere at $T = 76$ K in a cryostat. $G$ decreases continuously as a function of $V_{bg}$, which indicates that the conductance minimum is beyond the voltage range and that doping is important. After high-bias treatment we observe a well-defined conductance minimum $G_{\text{min}}$ close to zero $V_{bg}$ that denotes the reduction of doping.

The strong shift of $G_{\text{min}}$ to zero $V_{bg}$, along with the recovered smoothness of the sample, indicates that unavoidable fabrication residues act as dopants that are re-
moved upon passing a large electrical current through the sample. These residues may consist in part of non-dissolved PMMA [9]. Note that in air, this cleaning process tends to be counterbalanced by the doping effect of other molecular adsorbates (e.g., oxygen), as a result of which $G_{min}$ is found to slowly drift in time back to large, positive $V_{bg}$ values.

Special care has to be taken to preserve the integrity of the device upon applying large source-drain biases; we proceed as follows. Setting $V_{bg} = 0$ we slowly raise $V$. We regularly hold $V$ constant to monitor the time-dependence of the current $I$. If $I$ stays constant, we keep increasing $V$. This is repeated until $I$ continuously decreases as a function of time and saturates (see Fig. 3e for a fixed $V = 5$ V, sample of Fig. 1 and Fig. 3d.) The continuous decay of $I$ at fixed $V$ and $V_{bg} = 0$ signals a smooth shift of $G_{min}$ to zero $V_{bg}$. Note that an acceleration of the current decay usually precedes the rupture of graphene.

Remarkably, this simple cleaning technique allows us to observe the anomalous, half-integer quantum Hall effect (QHE) \[2\, 3\] that is the signature of a clean, single graphene layer. In graphene, the $n^{th}$ Landau level (LL) energy reads $E_n = \text{sgn}(n)\nu_F \sqrt{2e\hbar|n|B}$, where $n$ is the electron or hole LL index and $\nu_F \approx 10^6 \text{ m s}^{-1}$ is the Fermi velocity. Edge channels have a degeneracy $g = 4$ that accounts for both spin and sub-lattice degeneracies. The presence of electron and hole edge channels at the neutrality point (LL index $n = 0$) reduces the number of current-carrying modes by half, yielding $g = 2$ (see schematic of Fig. 4.) The two-point Landauer conductance reads $G = \sum g \cdot e^2/h$, where the sum is carried over all the levels, and is therefore quantized in $4e^2/h \cdot (n+1/2)$ as $V_{bg}$ is swept \[17\]. Fig. 4 shows a clear quantization at $1/2 \cdot 4e^2/h$ whereas the other plateaus are not as well defined (the same is observed for 5 other samples). The robustness of the first plateau is explained by the large energy gaps $|E_{\pm 1} - E_0| \approx 1200$ K at $B = 9$ T. Importantly, the plateau is visible only after the current-induced cleaning process. This indicates that our process enhances the mobility of the sample and/or improves the homogeneity of the doping over the device area.

To conclude, we have demonstrated a simple, yet highly reproducible technique to obtain clean graphene devices out of initially highly contaminated samples. Our method takes advantage of the large electrical current density that graphene can sustain to remove contaminants from the sample surface. Compared to other methods, the reported technique has the advantage to be operative at low $T$ inside a cryostat, without having to cycle the cryostat to room $T$. In addition, we avoid contamination in air that would naturally occur upon transferring the device from the annealing chamber to the cryostat.

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