Graphene on a Hydrophobic Substrate: Doping Reduction and Hysteresis Suppression under Ambient Conditions

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ABSTRACT The intrinsic doping level of graphene prepared by mechanical exfoliation and standard lithography procedures on thermally oxidized silicon varies significantly and seems to depend strongly on processing details and the substrate morphology. Moreover, transport properties of such graphene devices suffer from hysteretic behavior under ambient conditions. The hysteresis presumably originates from dipolar adsorbates on the substrate or graphene surface. Here, we demonstrate that it is possible to reliably obtain low intrinsic doping levels and to strongly suppress hysteretic behavior even in ambient air by depositing graphene on top of a thin, hydrophobic self-assembled layer of hexamethyldisilazane (HMDS). The HMDS serves as a reproducible template that prevents the adsorption of dipolar substances. It may also screen the influence of substrate deficiencies.

KEYWORDS Graphene, transport properties, hydrophobic, self-assembled layer, hexamethyldisilazane, hysteresis, doping

Graphene has attracted considerable interest in recent years in view of the uncommon linear dispersion[1−3] for charge carriers and many desirable transport properties for graphene based electronics.[4,5] Among these are exceptional carrier density tunability including a reversal of the charge carrier polarity, high current densities[6,7] as well as equal or comparable mobilities for electrons and holes.[8−14] Graphene field effect transistors made by mechanically exfoliating graphene from graphite onto a thermally oxidized silicon substrate exhibit the highest quality up to this date among all explored approaches in which graphene is supported by a substrate.[15−22] Unfortunately, the characteristics of such field effect devices may vary widely. In particular, the intrinsic doping level of as prepared devices as well as the mobility exhibit a large variance. Field effect characteristics also suffer from hysteretic behavior, when measured under ambient conditions, as well as asymmetries between electron and hole transport.[23−28] Even though extensive systematic studies are still lacking and are also difficult to carry out, evidence accrues that morphology and deficiencies of the substrate, contamination during processing[29] as well as adsorbed molecules from ambient air[30] play a crucial role for these imperfections and the poor reproducibility of graphene devices. For instance very high mobilities were obtained in suspended graphene samples after current self-annealing,[31,32] which was attributed to the absence of substrate effects and the successful removal of contaminants caused by the preparation procedure by the annealing

process. Here we explore whether it is possible to also obtain reproducible characteristics for graphene supported by a substrate.

To identify a suitable approach, it is instrumental to summarize key experimental observations and theoretical considerations related to the intrinsic doping and hysteresis in graphene. The substrate surface and molecules adsorbed at this surface likely play a crucial role as they may impose their morphology on the deposited graphene.[29,33] The substrate surface quality itself depends on the morphology and the deficiencies of the SiO_2 top layer as well as on its chemical cleanliness. Various adsorbates can attach themselves to SiO_2. Hydroxyl groups ($-OH$) for instance couple to the dangling bonds of the Si on the surface and build up a layer of silanol (SiOH) groups.[34,35] This silanol layer is very hydrophilic. Dipolar molecules can easily attach to the SiOH and contribute to the charge transfer, which results in doping of the graphene flake.[36−38] Most frequently p-doping is observed, which is believed to originate from adsorbed water molecules, possibly in combination with interactions between these molecules and the substrate.[37,38] A certain amount of this doping may also result from lithography resist residues on the flake.[29]

The asymmetry in the conductivity and the hysteresis in the field effect may also originate from adsorbates,[23,24,27,39] but both are still not fully understood. For example, in the case of water, the most abundant dipolar adsorbate under ambient conditions, the doping and hysteresis mechanism are still controversially debated. Wehling et al. argued that only highly ordered H_2O clusters[37] are able to act as dopants, or doping from H_2O molecules has to be mediated by defects in the SiO_2 substrate.[38] Such H_2O molecules connect to the silanol groups on the surface. Lee et al.[40] concluded that the
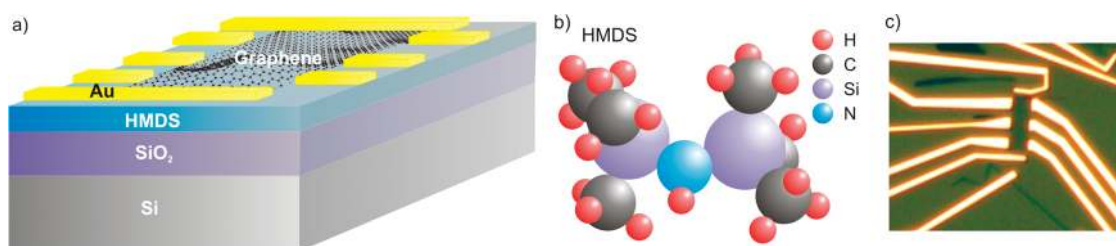

FIGURE 1. (a) Schematic of the contacted graphene sample on top of an HMDS self-assembled layer. (b) Three-dimensional structure of the HMDS molecule. (c) Optical image of the contacted graphene flake.

silanol groups themselves cause the hysteresis effect and adsorbates may just amplify it under ambient conditions. Leenaerts et al.[36] introduced the orientation of the water molecules as an important parameter controlling the doping effect of water. This work was based on DFT-calculations and did not require the presence of the substrate as a clustering template. The hysteresis in the field effect was also studied on carbon nanotubes.[41−44] Kim et al. for instance asserted that expanded clusters of water, which couple to the silanol groups of the substrate, surround the nanotube and cause the hysteretic behavior. McGill et al.[43] have shown a reduction of hysteresis on SWNTs on a hydrophobic layer of octadecyltrichlorosilane (OTS).

According to our experience, the intrinsic doping level drops and hysteresis is suppressed or vanishes when placing graphene in vacuum and pumping for an extended time. Heating the sample in vacuum to above 140 °C is very beneficial, but even without heating the hysteresis and doping level are reduced. This suggests that loosely bound species, like water attached to the silanol groups of the surface, are the main culprits for hysteresis.[23] Strongly bound silanol groups or charge traps in the oxide would be stable even at elevated temperatures. An important observation is that most samples return to their initial state in terms of doping and hysteresis (within a tolerance of a few percent only) after a short time (<1 min) when exposing the flake back to air. This reversibility suggests that doping adsorbates preferentially attach to particular locations determined by the substrate specifics. A similar argument was invoked previously in refs 23, 45, and 46 where also the effect of dipolar water molecules on top of the flake was discussed. On the basis of this information, we conclude that chemical hydrophobization of the substrate to remove and prevent the formation of silanol groups and thus the coupling of adsorbates should provide a good solution to the venture of obtaining reproducible characteristics such as low-intrinsic doping and weak hysteresis for graphene supported by a substrate. Here we show that a thin, hydrophobic self-assembled organic layer on top of the SiO$_2$ fulfils these requirements.

The substrates, which consist of an n+-Si wafer with a 300 nm thick thermal oxide, were prepared by the following procedure: The SiO$_2$ layer was successively cleaned in N-methyl-pyrrolidone, acetone, and 2-propanol at 55 °C.

Subsequently, the substrate was treated in an O$_2$-plasma to remove organic residues. To hydrophobize the SiO$_2$ surface, the substrate was left in a partially covered beaker in HMDS[47] (hexamethyldisilazane/acetone 1:1) solution for 15−20 h (The solution is left under a fume hood). The HMDS molecules (Figure 1b) form an ordered self-assembled layer on the substrate. The long duration of exposure to HMDS was found to be crucial. Graphene is then deposited on the HMDS layer by micromechanical cleavage from HOPG[8] and identified by means of optical microscopy and Raman spectroscopy. The observed contrast and color of the graphene flakes found on HMDS do not differ much from the ones on bare SiO$_2$. To obtain a well-defined geometry out of the graphene flakes, a Hall bar shape was patterned by using a PMMA mask defined by electron-beam lithography and an O$_2$ plasma etch. In a second e-beam lithography step, contacts were written and fabricated by evaporation of 3 nm Cr and 30 nm Au (Figure 1a,c). To characterize the sample doping, we studied the field effect at room temperature without and with annealing of the samples at ∼140 °C for a time period of 1−2 h. In addition, quantum Hall effect (QHE) measurements were carried out at 1.6 K to assess the transport quality. For the sake of comparison, reference samples were prepared in the same fashion except that no HMDS layer was deposited prior to graphene exfoliation.

In Figure 2a the mobility extracted from the slope of the line through the coordinate origin and the field effect data at a fixed hole density of 1.25×10^{12} cm^{-2} and the intrinsic doping level are plotted for the reference graphene flakes prepared on bare SiO$_2$ with and without pumping and heat treatment (red circles and discs). As one approaches the Dirac point, the mobility increases rapidly. This complicates a comparison with reported mobility data in the literature. Here we have chosen a high density for a meaningful comparison among different samples. The graphene samples deposited on a bare SiO$_2$ substrate exhibited charge neutrality at back-gate voltages between +50 and +60 V, which corresponds in our geometry (0.7×10^{11} cm^{-2}/V) to a high p-doping level between 3.5 and 4.2×10^{12} cm^{-2}. Previous experience has shown however that this voltage varies strongly from flake to flake and seems to depend on processing details. The field effect curves for up and down sweeps of the back-gate voltage are depicted in Figure 2b
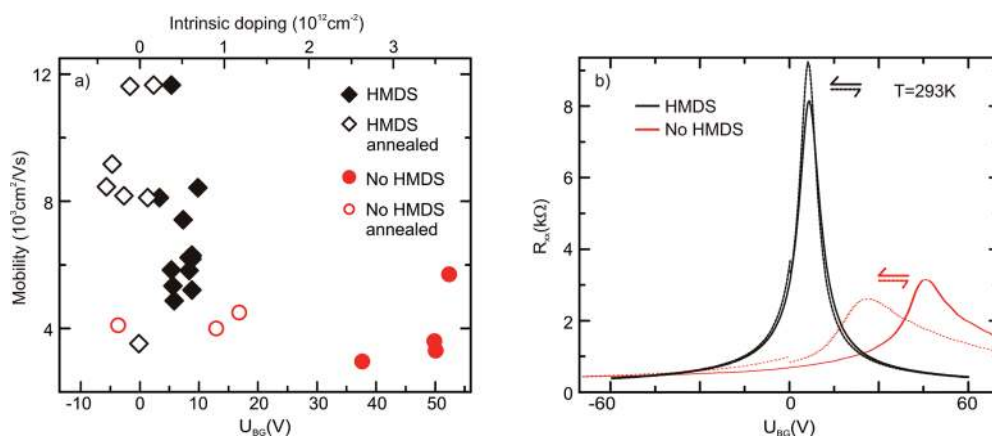
FIGURE 2. (a) Mobility versus charge neutrality point of graphene deposited on bare SiO_2 (red circles and discs) and on HMDS (black full and empty diamonds), without (filled signs), and with (empty signs) annealing in vacuum ($p \sim 10^{-6}$ mbar) at $T = 140$ °C for 1 h. The mobility is determined at a hole density of $n = 1.25 \times 10^{12}$ cm^{-2}. The charge neutrality point for not annealed samples on bare SiO_2 is determined by the mean value of the charge neutrality points of both sweep directions as the exact doping cannot be measured due to the hysteresis. (b) Field effect measurement at $T = 293$ K for graphene on HMDS (black curve) and for graphene on bare SiO_2 (red curve).

(dotted and solid red line, respectively). A strong hysteresis is observed. It is attributed to dipolar adsorbates,[23,44,46] the configuration of which changes upon sweeping. The different configurations produce an electric field that influences the charge carrier density in the sample. Under ambient conditions, the most probable candidate is water from the atmosphere. It has been demonstrated previously that vacuum annealing of the graphene samples (150 °C, 1 h) can help to remove adsorbates such as H_2O, NO_x, CO_2 and reduce both hysteresis[23] and the intrinsic doping level.[30] However, when exposing the sample back to air, approximately the same doping level is recovered and the hysteresis returns. This memory effect has been observed in several samples during our work and indicates that adsorbates responsible for doping return to the same amount on the coupling sites of the graphene flake. Moser et al.[45] have argued in a similar fashion as described in the introduction. Presumably defects such as edges, wrinkles, etc. serve as fixed docking sites on the graphene flake, which are not healed by heat treatment in vacuum.

Figure 2a also contains data points from a total of 13 graphene flakes without annealing and from 7 samples after annealing, all deposited on top of an HMDS self-assembled layer (black diamonds). Charge neutrality was reproducibly obtained at low back-gate voltages (<10 V) even without annealing. Field effect curves recorded during up and down sweeps of the back-gate voltage of a graphene flake on an HMDS treated substrate are plotted in Figure 2b (dotted and solid black lines, respectively). Hysteresis has vanished nearly entirely, even under ambient conditions. The plotted curve is symmetric for electrons and holes which can be due to the inhibition of doping as doping induced asymmetries were already shown in literature.[23,27] The scattering potential of dopants suppresses conductance on one side of the charge neutrality point depending on the p- or n-type doping character of the adsorbates. Here, the hydrophobic layer inhibits the adsorption of for instance dipolar molecules that

may act as dopants. As a result the asymmetry has largely vanished. Although significant scatter in the mobility remains, these HMDS treated samples on average exhibited higher charge carrier mobility. We note that in literature different procedures have been used to extract the mobility (Hall mobility, field effect data with or without local derivative) and that frequently mobility values close to the Dirac point where the mobility rises rapidly have been quoted. This makes a meaningful comparison with reported values in the literature difficult. For the processing procedures described above and the HOPG starting material employed here, samples on bare SiO_2 typically had a mobility of ~4000 cm^2/(V s). Graphene prepared on HMDS-treated SiO_2 showed varying mobilities but values up to ~12.000 cm^2/(V s) were reached. Magnetotransport data recorded on a graphene sample deposited on top of a hydrophobic HMDS layer are plotted in Figure 3.

The Shubnikov de Haas (SdH) oscillations[9,10,13,14] exhibit good quality. They start at approximately 820 mT (inset to Figure 3b). The longitudinal resistance is symmetric for both field directions and oscillation minima are observed up to a filling factor of 62. The extracted scattering time from the onset of the SdH oscillations was approximately 0.16 ps.[32] For a sample on untreated SiO_2 the scattering time was shorter by a factor of 2 or more. For the calculations of this value a simple model was used taking the onset of the SdH oscillations as the first magnetic field strong enough to allow a charge carrier to carry out a full cyclotron orbit without scattering ($\omega_c \tau \approx 1$).[32] Despite this apparent improvement of the transport properties, the mobility values achieved are not able to compete with the mobilities reported on current annealed freestanding flakes.[31,32] This could be due to remaining effects of the template, resulting, for example, from defects in the deposited HMDS layer as well as residues (e.g., PMMA) from the processing. Indeed we anneal our samples just up to 150 °C in high vacuum (10^{-6} mbar). According to Ishigami et al.,[29] the removal of PMMA residues
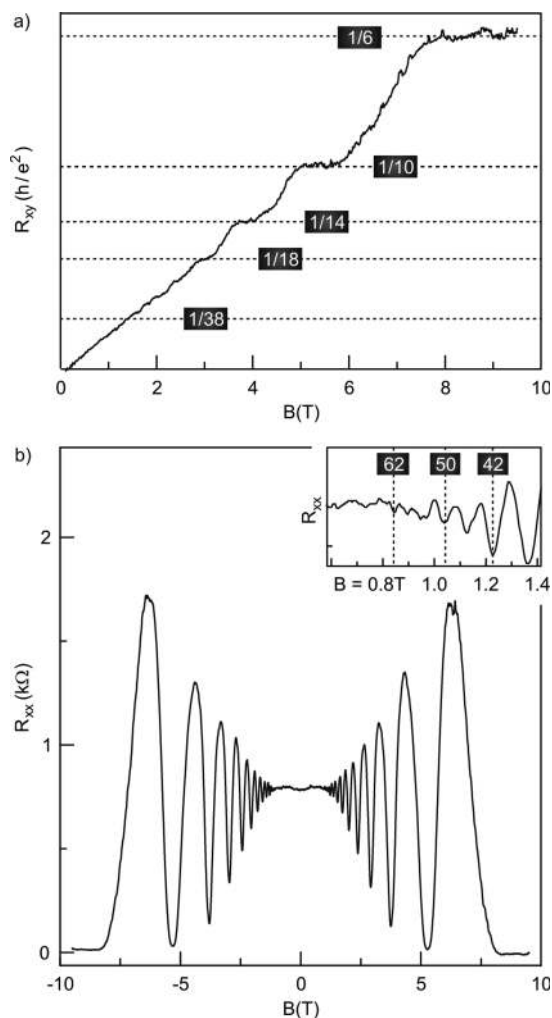
FIGURE 3. Hall effect measurement at $T = 1.6$ K on a graphene flake on HMDS ($n = 1.25 \times 10^{12}$ cm^{-2}). (a) R_{xy} versus magnetic field, (b) R_{xx} versus magnetic field. Inset: magnification of the low field part of the positive field R_{xx} measurement.

requires annealing temperatures as high as 400 °C. At present, insufficient statistics is available to conclude whether quantum Hall data is generally of higher quality in HMDS treated samples. We were however able to unequivocally establish that the main advantages of preparing graphene on HMDS are the reproducibly low intrinsic doping and the absence of hysteresis even under ambient conditions.

The drastic drop in the intrinsic doping level for graphene deposited on the HMDS self-assembled layer is attributed to its hydrophobic nature. The observed contact angle of water on the wafer serves as a measure of the hydrophobicity. For the HMDS layer we measured a contact angle of ∼94°. A test measurement on a flake deposited on a self-assembled monolayer (SAM) of OTS with a smaller contact angle of ∼73° resulted in comparable intrinsic doping (∼0.5 × 10^{12} cm^{-2}) compared to HMDS priming and reduced hysteresis.

Bare SiO$_2$ on the other hand exhibits a very small, with our setup not measurable, contact angle. It is hydrophilic since, without treatment, it is OH-terminated. Water mol-

ecules attach easily to the hydrogen of these silanol groups on the SiO$_2$ to form a thin water film. The dipolar nature of water dopes the graphene layer.[46] HMDS apparently screens the flake from such influences. It likely displaces water molecules during its deposition as it can replace the OH groups on the substrate. Water molecules cannot attach or reorganize on the HMDS layer. The deposited graphene flake lies on a Si−C−H carpet, which forms a chemically well-defined substrate with methyl groups that appear inert for the graphene flake. Loosely speaking, the HMDS layer may act as a kind of liquid surface on which the flake is floating.

In summary, a Si/SiO$_2$ substrate modified with a thin, hydrophobic organic template forms an excellent surface for the deposition of graphene. It inhibits polar adsorbates providing a chemically well-defined and hydrophobic surface. The main merits are a reproducibly low intrinsic doping level largely independent from ambient conditions and processing details and a suppression of hysteretic behavior in the field effect even under ambient conditions.

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