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Towards electron transport measurements in chemically modified graphene: effect of a solvent

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Abstract. The chemical functionalization of graphene modifies the local electron density of carbon atoms and hence electron transport. Measuring these changes allows for a closer understanding of the chemical interaction and the influence of functionalization on the graphene lattice. However, not only chemistry, in this case diazonium chemistry, has an effect on electron transport. The latter is also influenced by defects and dopants resulting from different processing steps. Here, we show that the solvents used in the chemical reaction process change the transport properties. In more detail, the investigated combination of isopropanol and heating treatment reduces the doping concentration and significantly increases the mobility of graphene. Furthermore, isopropanol treatment alone increases the concentration of dopants and introduces an asymmetry between electron and hole transport, which might be difficult to distinguish from the effect of functionalization. The results shown in this work demand a closer look at the influence of solvents used for chemical modification in order to understand their influence.

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1. Introduction

Graphene is an electronic material with high electron mobilities even at room temperature [1]. Usually, graphene is prepared by exfoliating individual layers from bulk graphite and putting them down on a substrate [2]. With such techniques it has become possible to prepare samples displaying the quantum Hall effect, testifying to the high electronic quality of such systems [3, 4]. Further improved mobilities were achieved by suspending graphene flakes [5] or, very recently, by depositing graphene on boron nitride [6]. It is generally believed that unintentional adatoms on top of the graphene flake and charge traps in the substrate limit the mobility for conventional devices [7]–[9].

Chemical modification of graphene has been achieved by a number of methods and has been investigated by Raman measurements and transport studies [10]–[13]. Applying chemistry on graphene changes the local carbon–carbon bond structure, the orbitals and hence the electronic properties of the material. At the present time, it is not clear how conventional methods used in almost any graphene sample preparation, such as baking in an inert gas atmosphere in combination with rinsing in water or organic solvents, affect the electronic quality of a graphene system. Such treatments are also standard conditions in chemical reactions and can induce a change in electron transport along with chemical functionalization itself. Therefore, solvent effects should be taken into account when analyzing the transport data of chemically derivatized graphene samples.

In the first part of this work, we present a confocal Raman spectroscopy analysis of graphene chemically modified with aromatic diazonium ions. A difference in reactivity between single layer, bi-layer and single-layer edge is observed. In the second part, we first show the influence of functionalization on the electronic transport properties of graphene, and afterwards we focus on the influence of repeated treatment with baking and rinsing in isopropanol. Here we find that treatment with only isopropanol leads to an increase in doping concentration and an asymmetry between electron and hole transport, which is partly similar to the effect of functionalization. In addition, we observe that the combined treatment with isopropanol and baking leads to higher electronic quality than just heating alone. This is further investigated at low temperatures in the last part of this paper.

2. Experimental method

Single- and bi-layer graphene flakes were exfoliated from natural graphite and deposited onto a silicon substrate covered with ≈ 285 nm thermal silicon dioxide [2] and identified using Raman spectroscopy and light microscopy [14, 15].

For the Raman spectroscopy study, chemical functionalization was carried out at room temperature by immersing the chip into a 20 mmol l^{-1} solution of water-soluble nitrobenzene diazonium salt (4-nitrobenzene diazonium tetrafluoroborate from Sigma Aldrich) [12]. After functionalization the chips were cleaned once in isopropanol (1 min), twice in water (1 min), a second time with isopropanol (1 min) and finally blown dry with nitrogen. For the electronic transport experiments, chemical functionalization was carried out at 0°C using a 4 mmol l^{-1} solution. The cleaning procedure after functionalization was the same as for the Raman spectroscopy study. It should be pointed out that because of the different reaction conditions described above, the Raman spectroscopy study and the transport study cannot be directly compared in terms of the amount of induced disorder as a function of reaction time.

During the Raman spectroscopy study, laser power was kept at 2 mW in order to avoid heating and the introduction of defects due to the laser.

For the electronic transport experiments, Ohmic contacts were defined on the graphene flakes using standard electron beam lithography techniques followed by the evaporation of Cr/Au (2/40 nm). The highly doped silicon substrate is used as a global gate to tune the overall Fermi energy of the device. The Hall bar used to investigate the influence of isopropanol and heating treatment on the transport properties of graphene is patterned in a second electron beam lithography step followed by reactive ion etching.

3. Results and discussion

3.1. Raman spectroscopy of chemically functionalized graphene

Raman spectroscopy is a powerful tool both for identifying the number of graphene layers [14, 15] and for monitoring the doping [16, 17], defects [18] and chemical functionalization [12, 13] of graphene. The most prominent features in the Raman spectra of graphene are the G band (about 1580 cm^{-1}) and the two-dimensional (2D) band (about 2700 cm^{-1}). In addition, in the presence of defects or at the edge of graphene, the disorder-induced D-line located at about 1350 cm^{-1} can be observed [19]. Here we functionalize graphene using diazonium chemistry and monitor the introduction of defects in the graphene lattice by measuring the intensity of the D-line of the Raman spectra.

Diazonium chemistry has previously been used to functionalize a variety of carbon forms [20]–[24], and it was recently shown that graphene can also be functionalized in a similar manner as the other carbon forms using the same chemistry [12, 13]. In this experiment, a flake is used that has both single- and bi-layer domains, allowing the direct identification of differences in the chemical reactivity towards the diazonium reagent. In figure 1(a), the 2D map of the integrated D-peak intensity is shown after 20 min immersion in the reaction medium. Bright areas correspond to high intensity and dark areas to low intensity. Three distinct domains with different intensities are visible, which can be attributed to bi-layer, single layer or single-layer edge of the graphene flake, respectively. This is further shown in figure 1(b), where the intensity of the D-peak along the white line in figure 1(a) is plotted.

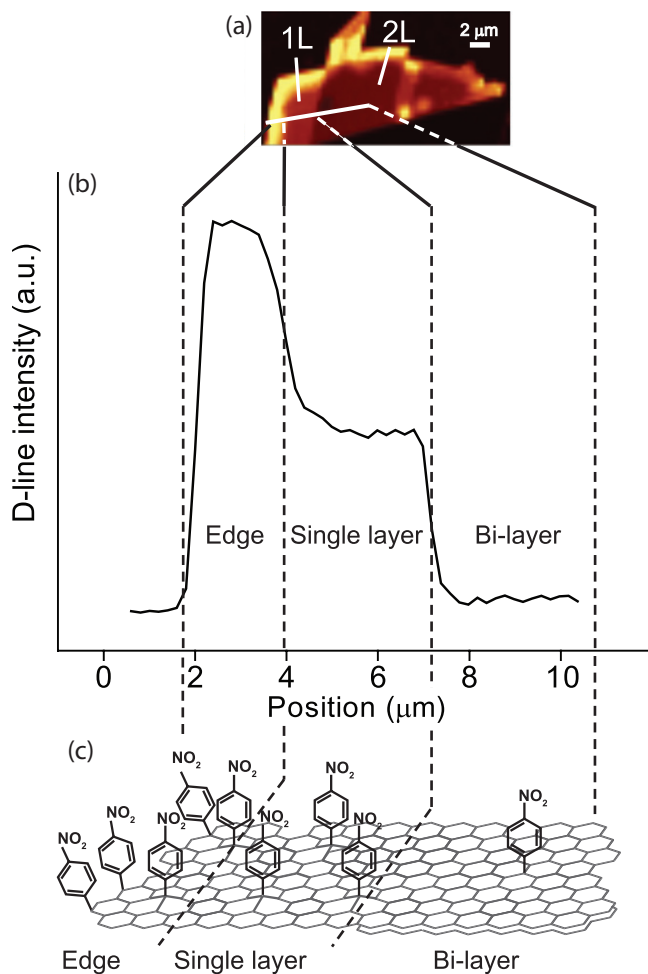


Figure 1. (a) Raman 2D map of the D-line intensity of the investigated graphene flake. (b) D-line intensity along the white line in (a). (c) Schematic representation of the difference in reactivity between the edge area, the single-layer area and the bi-layer area.

The D-peak intensity of the bi-layer region is hard to identify, as the signal overlaps with adsorbed species [12]. It has previously been shown by Strano and co-workers [13] that long reaction times and an extensive washing procedure are necessary to identify a small D-peak on bi-layer graphene after functionalization with diazonium ions. On single-layer graphene, the D-line integral is significantly higher than on bi-layer. The higher reactivity towards diazonium chemistry for the single layer than for the bi-layer has been attributed to fewer ripples on the bi-layer surface [12] and to screening of electron-hole puddles in the bi-layer [13]. Furthermore, the single-layer part can be divided into two regions of distinct intensities: a bulk single layer with a lower D-peak intensity and an edge single layer with a higher intensity. This increased edge intensity has also been shown earlier and is attributed to a higher reactivity of the reagents towards the edge, due to a higher degree of flexibility, which is necessary to change the local geometry from planar sp^2 to tetrahedral sp^3 . In addition, it was recently shown that these edge regions grow over the whole single-layer area with prolonged reaction time [12]. This is an

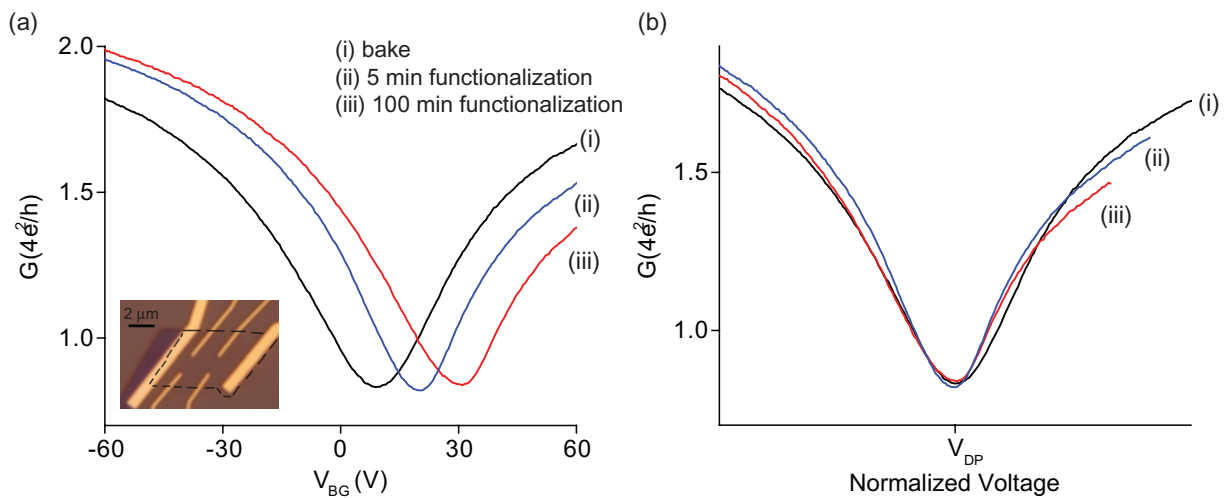


Figure 2. (a) Room temperature measurement of two-terminal conductance as a function of backgate voltage (i) after baking the sample, (ii) after 5 min functionalization and (iii) after 100 min functionalization. (b) The curves in (a) laterally shifted and normalized with respect to the Dirac point (V_{DP}). The inset in (a) shows a light microscope image of the investigated sample, where the dotted line indicates the contour of the graphene flake.

indication that near defects or functional groups on the surface, carbon atoms react more easily with the diazonium reagents. In figure 1(c), the difference in reactivity between the different parts of the flake is schematically illustrated. For a detailed investigation of the dependence of disorder as a function of exposure time to the reaction medium, see Koehler *et al* [12].

3.2. Room temperature transport measurements

The possibility of controlled doping and, as investigated above, selective functionalization of graphene edges makes the chemical modification of graphene interesting for electronic transport experiments.

In figure 2(a), room temperature measurements of the conductance (G) as a function of backgate voltage (V_{BG}) are shown (i) for an unfunctionalized sample (only heated to remove dopants from the surface), (ii) after 5 min of functionalization and (iii) after 100 min of functionalization. These are two-terminal measurements on an unpatterned graphene flake (see the light microscope image of the measured device in the inset of figure 2). From figure 2(a), it can clearly be seen how functionalization leads to increased p-doping of the graphene flake. Before functionalization the point of minimum conductance (the Dirac point, V_{DP}) is located at +9 V in the backgate. After 5 min of functionalization the Dirac point is shifted to +21 V and after 100 min of functionalization the Dirac point is at +31 V. In figure 2(b), where backgate traces are normalized with respect to V_{DP} , it can be seen that functionalization introduces a small asymmetry between electron and hole transport. This asymmetry is much weaker than observed previously by Farmer *et al* [10]. In addition, it can be seen from figure 2(b) that the mobility (slope of G versus voltage) of the graphene flake is not significantly changed after functionalization. Both observations can be explained by a lower amount of functionalization due to the low temperature (0 °C) used in this work.

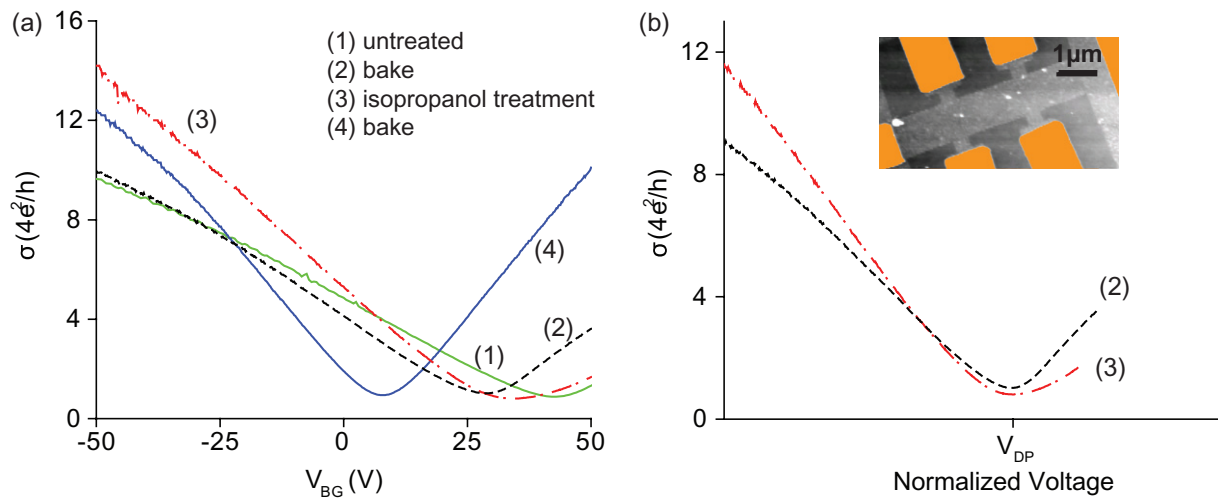


Figure 3. (a) Room temperature measurement of four-terminal conductivity as a function of backgate voltage (1) for an untreated Hall bar, (2) after heating, (3) after isopropanol treatment and (4) after a second heating. (b) The curves after (2) baking and (3) isopropanol treatment from (a) normalized with respect to the Dirac point (V_{DP}). The inset shows a scanning force micrograph (SFM) image of the measured Hall bar where the contacts are highlighted in orange for clarity.

In the functionalization process described above, the graphene flake is first immersed in water containing reactive diazonium ions and afterwards in isopropanol to remove unreacted species and improve the drying step. In order to analyze the influence of only chemical functionalization on the electronic transport properties of graphene, it is crucial to know the effect of the involved solvents. In the following, we will therefore investigate the influence of isopropanol and baking on the transport properties of graphene, which are part of the chemical and physical treatments involved in the reaction and measurement process.

To investigate the influence of isopropanol and heating, we use the Hall bar shown in the inset of figure 3(a). The width of the Hall bar is $\approx 1 \mu\text{m}$ and the length between two voltage probes is $\approx 2 \mu\text{m}$. All the following measurements are four-terminal measurements. For the isopropanol treatment, the chip with the Hall bar is immersed in isopropanol for 5 min and afterwards blown dry with nitrogen gas. The heating of the sample is carried out in the sample holder while the vacuum is constantly pumped. In order to monitor changes in the conductivity of the sample during the heating, a constant current of 10 nA is applied to the Hall bar and the four-terminal resistance is measured at $V_{BG} = 0 \text{ V}$. The sample is always heated at $150 \text{ }^\circ\text{C}$ until the measured resistance is stable. This may take many hours.

In figure 3(a), the conductivity (σ) of the Hall bar as a function of applied V_{BG} (1) for the untreated sample, (2) after heating the sample, (3) after treating the sample with isopropanol and (4) after heating the sample again is plotted. It can be seen that both the mobility and the position of the Dirac point change significantly after the different treatments.

For the untreated sample, the Dirac point is located at +43 V. The extensive doping of the pristine sample is probably due to resist residues and other dopants accumulated during the processing steps. In order to remove these dopants, we always bake our samples before starting the measurements (as we also did before functionalization). Here it can be seen that after the

initial baking of the sample, the Dirac point has moved to +26 V. The corresponding change in mobility will be discussed below. As a next step, we treat the sample with isopropanol. Figure 3 shows that the Dirac point is shifted from +29 to +34 V in the backgate after the isopropanol treatment, which means that isopropanol significantly p-dopes graphene. From figure 3(b), where traces before and after isopropanol treatment from figure 3(a) are normalized with respect to V_{DP} , it can, in addition, be seen that isopropanol introduces a strong asymmetry between the electron and hole conductivities. It has been shown above that in the absence of significant sp^3 hybridization of the graphene surface, functionalization with diazonium salt does not lead to a suppression of conductance, but only a shift of the Dirac point to more positive backgate voltages. The observed asymmetry after isopropanol treatment is larger than that observed after functionalization (figure 2(b)). However, it is similar to the asymmetry found by Farmer *et al* after functionalization [10]. The qualitative similarities between the changes in the conductivity of graphene after isopropanol treatment and the changes observed after functionalization suggest that with the functionalization procedure described above it might be difficult to separate the effects of the diazonium salt and the effects of isopropanol.

In the final step we heat the sample a second time in order to see if we can remove the dopants introduced by the isopropanol treatment. Surprisingly, the Dirac point not only shifts back to +29 V, where it was located before the isopropanol treatment, it shifts much further to +8 V. Together with the corresponding increase in mobility, this suggests that the electronic quality of graphene can be improved by repeated isopropanol treatments followed by heating. In the case of measurements (1) and (3), it is difficult to extract the electron mobilities and thus only the hole mobilities will be compared in the following. For the untreated graphene flake (1), we obtain a hole mobility of $2100 \text{ cm}^2 \text{ V s}^{-1}$. After the first heating step (2), the mobility has increased to $2700 \text{ cm}^2 \text{ V s}^{-1}$. The following isopropanol treatment (3) increases the mobility further to $3600 \text{ cm}^2 \text{ V s}^{-1}$ and after the last heating (4) the mobility reaches $4700 \text{ cm}^2 \text{ V s}^{-1}$. Generally, we expect the introduction/removal of dopants to decrease/increase the mobility. Here, after the isopropanol treatment, an increase in hole mobility is observed together with an increased doping. This might be due to the removal of some dopants and the introduction of a different kind of dopant.

The fact that annealing the sample removes dopants and improves the mobility is generally accepted. Therefore, baking is normally a part of standard processing procedures for graphene. However, that a subsequent treatment with isopropanol followed by annealing is removing even more dopants has to our knowledge not been noted so far. We observe here that repeated treatment with isopropanol followed by heating improves the quality of the sample far beyond the improvement due to the first heating.

In addition to the observed increase in sample quality after the combination of isopropanol treatment and heating, the effect of isopropanol treatment alone should also be pointed out. Isopropanol treatment alone leads to increased p-doping and electron–hole asymmetry. These two effects are partly seen after chemical functionalization as well, and therefore it is important to be very careful when assigning shifts of the Dirac point and changes in electron–hole symmetry solely to the introduction of modifying species.

To evaluate the connection between functional groups and transport experiments, an estimate of the mean distance between the defects induced by the functional groups is necessary. This may be possible by evaluating the Raman data as shown by Lucchese *et al* [25]. However, our Raman data and transport data are from two different measurement cycles on different samples. Simulations showing the connection of defect spacing and transport in graphene

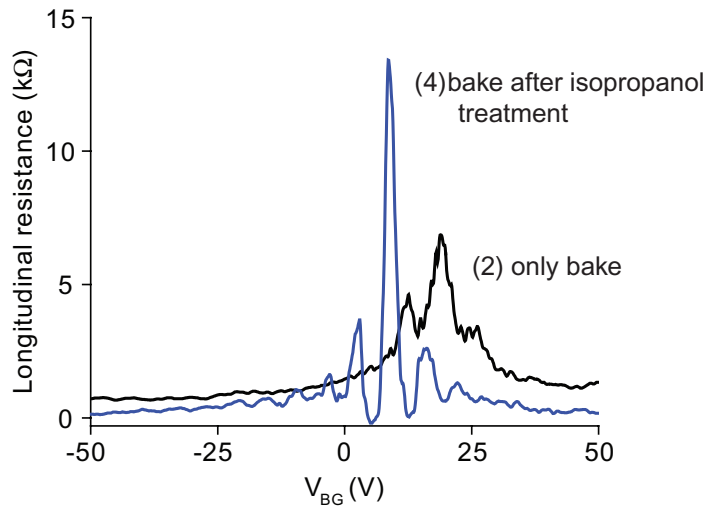


Figure 4. Longitudinal resistance as a function of backgate voltage at 4 K after (2) heating and (4) isopropanol treatment and heating measured at a magnetic field $B = 5$ T.

nanoribbons have been shown by Lopez-Bezanilla *et al* [26]. For further investigation of functionalized graphene and the influence of different solvents, it would therefore be favorable to perform Raman spectroscopy studies parallel with transport studies in order to make a more quantitative study of defect density.

3.3. Low-temperature transport measurements

The quantum Hall effect and the corresponding magneto-oscillations of longitudinal resistance are found in 2D systems of high quality and at low temperatures. The quality of the quantum Hall effect is a direct measure of the quality of the electronic system. Therefore, to further investigate the influence of isopropanol treatment and confirm the improvement of the electronic quality of graphene, we perform transport measurements in a magnetic field at $T = 4$ K.

Figure 4 shows the four-point longitudinal resistance (R_{xx}) of the flake as a function of V_{BG} at fixed magnetic field $B = 5$ T after the first heating (2) and after isopropanol treatment and the second heating (4). (Equations (2) and (4) correspond to figure 3.) Before isopropanol treatment, R_{xx} does not go to zero and only a weak splitting of the main resistance peak is observed. In contrast, after isopropanol treatment and heating, R_{xx} is clearly zero for filling factor $\nu = 2$ and, in addition, several more oscillations in R_{xx} are visible.

These measurements show that the electronic quality of the graphene flake is indeed improved after treating it with isopropanol and heating it.

4. Conclusions

In conclusion, we have presented confocal Raman spectroscopy studies of chemically functionalized single- and bi-layer graphene and have shown that the reactivities of the edges and the single-layer parts are larger than those of the bi-layer parts. Furthermore, we have performed a transport study of chemically modified graphene and found that the influence of

isopropanol treatment is comparable to the influence of functionalization itself. It is shown that isopropanol leads to p-doping similar to that observed after functionalization. In addition, it is observed that isopropanol treatment followed by heating significantly improves the electronic quality of graphene beyond the improvement due to heating alone.

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