Conductivity engineering of graphene by defect formation

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Abstract

Transport measurements have revealed several exotic electronic properties of graphene. The possibility to influence the electronic structure and hence control the conductivity by adsorption or doping with adatoms is crucial in view of electronics applications. Here, we show that in contrast to expectation, the conductivity of graphene increases with increasing concentration of vacancy defects, by more than one order of magnitude. We obtain a pronounced enhancement of the conductivity after insertion of defects by both quantum mechanical transport calculations as well as experimental studies of carbon nano-sheets. Our finding is attributed to the defect induced mid-gap states, which create a region exhibiting metallic behaviour around the vacancy defects. The modification of the conductivity of graphene by the implementation of stable defects is crucial for the creation of electronic junctions in graphene-based electronics devices. (Some figures in this article are in colour only in the electronic version)

1. Introduction

The electronic properties of graphene have been of considerable interest lately, with several reports of unique structural and electronic properties [1–4]. In the next phase of research on graphene, it is most likely that we will witness an increased focus on the tailoring of electronic properties by means of defects, adatoms and geometrical confinement. The possibility to open band gaps, induce gap states by defects and the ability to control the conductivity by chemical and physical means is hence a crucial step in order to establish graphene as a competitive material for future electronics. It has in fact already been shown that a bandgap can be opened in graphene, and that it can be tuned as a function of carrier concentration [5]. The high sensitivity of graphene due to changes in carrier concentration is related to its low Johnson noise. This property was, e.g., used in the creation of a gas detector capable to detect the adsorption of single atom [6]. Though adsorbed gases sensibly change the bandstructure of graphene, they tend to be unstable on the graphene surface. Molecular doping of NO2 and N2O2 induces p-type behaviour in graphene [7]. The maximum resistance levels are lower for higher concentration of doping. Another road to engineer the bandstructure of graphene consists in the addition of more
stable defects using wet chemistry methods. This is attractive in view of electronics applications since such defects are physically more stable than gases attached to the graphene layer. In fact, it has been shown recently that chemically introduced vacancy defects change the electronic structure of graphene \[8\].

From the XAS analysis on a graphene layer which was chemically treated in the same manner as in this work, we have observed a spectroscopic signature that could be attributed to defect sites in the graphene planes (i.e. of \(\sigma^*\) character) \[8\]. Though the distribution of defects in graphene is certainly complex and a matter of current studies, these states of \(\sigma\) character related to a defect site could only be oriented in the graphene plane, and it has been analysed as being the result of the presence of a vacancy. Hence we start our study by considering how vacancy defects influence the electronic structure of graphene. For this reason we have considered both single vacancy and di-vacancy in the \(\pi\) bonded graphene structure through a tight-binding model with nearest neighbour interactions. In viewing the graphene as consisting of two sub-lattices, sub-lattice A and B, it is known that the effect of an impurity in the A sub-lattice is manifested in the B sub-lattice \[4\]. In particular, a vacancy in the \(\pi\)-band, i.e. the absence of \(\pi\) orbitals at the impurity site generates mid-gap states for the atoms in the B sub-lattice located in a neighbourhood around the vacancy \[9\]. These mid-gap states arise due to symmetry breaking that removes the equivalent Dirac points in the two sub-lattices.

Defects always decrease the mobility of the sample compared with its defect-free version, while they may increase the number of carriers. The latter effect is especially important here and leads to a strong conductivity rise, since for pure graphene there are no carriers at Fermi energy. We explore the relevance of defects for controlling the conducting properties, using both theoretical and experimental approach. In our theoretical study we investigate the effects on the local density of states (LDOSs) from single vacancies and di-vacancies by means of real space Green functions (GFs). In order to understand the influence of the electronic structure on the conductivity, we calculate the evolution of the LDOS as a function of distance from the defect position. From there we proceed with \textit{ab initio} density functional calculations of the electronic structure and conductivity. The experimental studies consist of point contact conductivity measurements on free-standing carbon nano-sheets (CNSs). The CNS consists of few-layer graphene with mono- or double layers at the edges (figure 1). The samples in this study were grown on a conducting substrate that serves as back contact, greatly facilitating the experimental set-up. Defects were introduced by wet chemical treatment, in accordance with previous work \[8\].

![Figure 1](image-url)
2. Modelling of defects and prediction of properties

2.1. Modified LDOSs

The LDOSs of a single graphene sheet, both acid treated and untreated, are modelled in real space by the dressed graphene GF, \( G'(r, r'; \omega) = G_0'(r - r'; \omega) + G_0(r - r_0; \omega)T(\omega)G_0'(r_0 - r; \omega) \). Here we discuss the results for an impurity located at the position \( r_0 = \{r_1, r_2\} \). The dressed GF is thus given in terms of the homogeneous GF \( G_0'(r - r'; \omega) \) with the diagonal and off-diagonal elements given around the Fermi level \( E_F = 0 \) by \( g_{A}^{r}(r - r'; \omega) \approx g_{A}^{r}(k_F|\mathbf{r} - \mathbf{r}'|) [2\omega \log(D/|\omega|) + i\pi] / (4\pi \rho \omega^2) \) and \( g_{B}^{r}(r - r'; \omega) \approx -J_0(k_F|\mathbf{r} - \mathbf{r}'|) (2D + i\pi|\omega|) / (4\pi \rho \omega^2) \), respectively, whereas the \( T \)-matrix is given by

\[
T(\omega) = [1 - \hat{U} G_0'(0, \omega)]^{-1} \hat{U}.
\]

where \( \hat{U} = (U_A, U_B) \) is the impurity potential matrix, where \( U_A \) (\( U_B \)) is the scattering potentials at \( r_A (r_B) \), whereas \( j_0(x) \) is a Bessel function of the first kind, \( \nu_F \) is the Fermi speed, \( k_F \) is the Fermi wave vector and \( \rho \) is the graphene planar density and is related to the energy cut-off \( D = 5-10 \text{ eV} \) through \( 4\pi \rho \omega^2 D^2 \). Although this approximation does not describe the modified LDOS quantitatively correct, it gives a sufficient qualitative account. First we consider a single impurity located at \( r_A \). As we are considering a vacancy, we let \( U_A \rightarrow \infty \). The perturbation to the LDOS to the A sub-lattice then becomes \( \delta N_A(r, \omega) = -3\delta G_0'(r, r; \omega) / \pi \approx \omega \omega_i \sqrt{(k_F|\mathbf{r} - \mathbf{r}_A|)} / (4\pi \rho \omega^2) \), showing that the Dirac points remain in the A sub-lattice. The perturbed LDOS in the B sub-lattice, on the other hand, becomes

\[
\delta N_B(r, \omega) \approx \frac{1}{4\pi \rho \omega_i^2} \left( \frac{2D + i\pi}{\omega} \right)^2 \left[ \frac{(k_F|\mathbf{r} - \mathbf{r}_A|)}{\omega_i} \right] (\omega_i \omega_i' + i\pi) \] (2)

which is clearly diverging at the Fermi level, i.e. as \( \omega \rightarrow 0 \). This divergence signifies the existence of mid-gap states for the carbon atoms in the B sub-lattice. Using more sophisticated approximations, which removes the unphysical singularity, show that the mid-gap states are indeed present in the B sub-lattice [4, 9].

2.2. Calculations of electronic structure and resistivity

We performed \textit{ab initio} density functional calculations of the graphene electronic structure in the presence of single vacancies and di-vacancies. The calculations employed the projector augmented wave method, and the plane wave cut-off energy was set to 750 eV. The generalized gradient approximation (GGA) was used for the treatment of exchange-correlation functional and a lateral \( 8 \times 8 \times 1 \) supercell of graphene with a di-vacancy was considered for the calculations. This yields an effective vacancy concentration of 0.0156. The geometry of the supercell in the presence of the defect was optimized using Hellmann–Feynman forces with a tolerance of 0.01 eV Å\(^{-1}\). A \( \Gamma \)-centred \( 3 \times 3 \times 1 \) set of \( k \)-points was used in the Monkhorst–Pack scheme with a Gaussian broadening of 0.2 eV.

In the calculations of the graphene conductivity we used an all-electron scalar-relativistic version of the tight-binding linear muffin-tin orbital (TB-LMTO) method [10] within the local spin-density approximation [11] (LSDA) to the density functional theory [12]. The valence basis consisted of s-, p- and d-orbitals. The atomic sphere approximation (ASA) was employed here, which required an additional empty sphere to be present in the graphene layer per two carbon atoms and other empty spheres between graphene layers with a spatial distribution similar to the one already used successfully for graphite [13]. The integrations over the 2D BZ were performed on a uniform mesh of about 5000 \( k \) points. Such high density of \( k \)-mesh is crucial for the accurate description of states near the Dirac point.

The random distribution of defects in the system is described by means of the coherent potential approximation (CPA) [14, 15]. This single-site approximation has been shown to be successful in predicting properties of systems with random disorder, thus averaged over all possible combinations of impurity distributions. The CPA can deal with systems with arbitrary low concentration of impurities while its numerical requirements remain modest compared with the supercell method for disordered systems. The CPA has been used in other studies of graphene, where it was argued that CPA gives very good results for the description of the physical properties of graphene [16, 17]. The question concerning applicability of the CPA near Dirac point was studied by Skrypnyk and Loktev [18]. They have noted that only renormalized approaches as CPA can be efficiently close to the van Hove singularities in the spectrum. Furthermore, it was found that in the vicinity of the Dirac point a correction to the CPA self-energy is needed. In order to assess the accuracy of the CPA method we calculated the total density of states (DOS) at the Dirac point. We subtracted the DOS curve of the impurity calculation from the DOS of ideal graphene, and in this way we obtained the induced features of the DOS. We performed this calculation using CPA as well as a supercell approach using a defect concentration of 1%. Both the supercell calculation and the CPA calculation yield as the main effect of the impurities, a mid-gap state, located in energy at the Dirac point (data not shown). The intensity and width of the mid-gap state are quite similar from the two calculations, where the main difference is that the CPA method results, as is often the case, in a somewhat broaden mid-gap state, compared with the supercell results. For the interpretation of the experimental data presented here, the difference between the two methods is sufficiently small for us to reliably make use of the CPA results. The conductance was calculated from the Kubo linear response theory, a standard approach for theoretical calculations of transport properties of materials.

3. Experimental verification

3.1. Graphene model system

The results from theory are predictions for an idealized material which is not in contact with any surroundings. In order to experimentally verify the predictions, we have used well-characterized CNSs (figures 1(a) and (b)). These CNSs were grown by plasma-assisted chemical vapour deposition
(CVD) on a conducting substrate as a model system for graphene [19]. The CNS consists of 1 µm graphene sheets protruding from a 20 nm layer of graphite. The estimated thickness is 2–3 graphene layers at the top and about seven monolayers in the vicinity of the substrate. The thus supported CNS is allowing both wet chemical treatment [8] and point contact measurements without the adverse effects associated with removal of the CNS from the growth substrate and the deposition and contacting required for the conductivity study (schematics is shown in figure 1(e)) [20]. Compared with graphene adhered and contacted, i.e. on top of SiO2, this set-up is likely to reduce the influence of substrate charges and impurities from graphene processing which might shade the effect of defects on the conductivity.

3.2. Sample preparation

The defects were introduced in the CNS by a treatment with concentrated aqueous HCl as described [8], the CNSs were exposed to 35% concentrated aqueous HCl at 90 °C for 3 h. The HCl was removed from the flasks using a pipette and the samples were treated with deionized water for 10 h at 90 °C, followed by a thorough rinse with RT deionized water and drying in air at 150 °C for 3 min. In order to assess the effect of this acid treatment, a reference sample was prepared using deionized water instead of the aqueous HCl then followed by the same wash–rinse–dry protocol. Water, in contrast to aqueous HCl, cannot induce permanent defects. The samples are in the following referred to as ‘acid treated’ and ‘reference’, respectively. All samples, including the as-deposited, were handled in air.

3.3. DC measurement set-up

The CNS samples were electrically contacted with an Omniprobe nano-manipulator inside a FEI Strata DB235 focused ion beam/scanning electron microscope (FIB/SEM). The current–voltage (I–V) measurements of the CNS were performed by using a Keithley 6430 source meter. The tungsten tip of the manipulator is in situ ion polished in the FIB providing a better definition of the tip/graphene contact area as well as a reduction of the oxygen on the W surface.

In our nano-manipulation experiment, the CNSs are contacted with a sharp tip at room temperature. The probe needle is manoeuvred in the x, y and z-directions until it contacts a CNS. All movements are carefully monitored in real time by continuously scanning the electron beam in the FIB/SEM. The tip/CNS contact in figure 1(d) is established in the upper part of the CNS (for schematic representation of tip and CNSs, see figure 1(c)). The tip/CNS contact can be precisely observed through a slight bending of the CNS in the realtime scanning electron microscope (SEM) images. The voltage was scanned from −1 to 1 V in 30–40 s with no applied gate voltage. A reference SEM image was recorded before and after each measurement. When the tip/CNS contact is not sufficiently strong, occasional drift and tip vibrations led to a (I–V) temporary detachment of the tip seen as a current drop in the curves. Such I–V curves were not considered in the further evaluation. In this measurement geometry CNSs are available in abundance with a surface density of 10⁶ cm⁻². Therefore, the conductivity of a large quantity (>400) of CNS could be assessed and consequently, the data can be extracted with a high statistical precision. Three to five measurements are taken at the same location. The magnetic field inside the FIB/SEM chamber is found to be approximately 66 mT in ultra high resolution mode.

4. Result and discussion

4.1. Influence of vacancy defect on DOSs

In our first approach to understand the electronic structure in functionalized graphene, the LDOS of a single graphene sheet, both defect free and defect containing, is modelled by means of real space GFs. Consider a single impurity located at (rF), which signifies the existence of a metallic component extends over several lattice sites around the impurity. In order to substantiate the model considerations above we have performed density functional calculations using the Vienna Ab-initio Simulation Package for a graphene sheet with a di-vacancy [21, 22]. The value of the DOS at the Fermi level (EF), which signifies the existence of a metallic conducting component, is shown in figure 3. A relatively large peak arising from the pz orbital develops at the Fermi level for an edge atom around the di-vacancy. If one moves away from the defect site, the DOS at EF decreases, but the metallic component extends over several lattice sites around
the defect centre. Our inset of figure 3, we show the DOS at the Fermi level for both sub-lattices, suggesting an oscillating behaviour. A closer inspection (main body of figure 3) reveals that this is simply due to the fact that the two different sub-lattices in the graphene sheet show different decay rates away from the defect centre. Our \textit{ab initio} calculations are in agreement with the model calculations discussed above, that is vacancies introduce a metallic component in the electronic structure, and this metallicity, extending to several lattice constants, should be sufficient to enhance the conductivity of the graphene.

4.2. Influence of vacancy defect on resistivity

The central aspect of this paper is the conductance of graphene as a function of vacancy defects, which we describe in the following \textit{ab initio} calculations. For simplicity we only considered single C vacancies in these calculations, but in light of the discussion above, we expect the results to hold also for other vacancy geometries. The results of our calculations are shown in figure 4. It is obvious that as the concentration of vacancies grows, the 0 K temperature resistivity decreases with at least one order of magnitude compared with the material containing no vacancies. In the concentration regime of $x \leq 0.005$ it is seen from figure 4 that the conductivity depends exponentially with respect to defect concentration. This is actually a normal result for regular semiconductors [23], and can be explained from a Fermi–Dirac distribution of electron states. For a larger concentration of vacancies ($x > 0.005$) it is found that the resistivity slightly increases (figure 4), and appears to saturate close to a constant level for a defect concentration of 3–5%. These results verify our conclusions drawn from the character of the electronic structure in the presence of vacancies. The results in figure 4 should therefore be seen as a transition from a semi-metallic regime (or rather a regime where the effects of Zitterbewegung dominate) with limited conductivity [2, 24], to a regime of highly conducting graphene. This transition is driven by defects via the creation of mid-gap states, which produce an extended regime of metallic character together with a small shift of the Fermi level away from the Dirac point. Once this regime has been fully established, the addition of more defects produces scattering centres which reduce the conductivity, resulting in a more conventional behaviour. The connection between defects and resistivity in graphene is very intricate. Similar changes in the DOSs were observed in graphene nanoribbons, where states in the mid-gap appear at interfaces [25].

Defects cause not only impurity states, but also accept or donate charge, thus causing a shift of the Fermi energy in the studied system. We have compared the Fermi levels for different impurity concentrations in order to quantify the influence of the Fermi level shift on conductivity. In order to distinguish between the contributions from the Fermi level shift and impurity scattering on the conductivity, we have considered a model system as follows. The GF of the model system is identical to that of a graphene with a very low concentration of defects (0.1%), but the Fermi level corresponding to a much larger concentration of defects (metallic regime, i.e. 1% defect) was used in the spirit of the rigid band approximation. The system will further be denoted as graphene II. Therefore, the difference between the graphene II system and the original graphene consists only in a change in the Fermi energy. The calculated resistivity of graphene II is shown as a (red) diamond (near the origin) in figure 4. Clearly the conductivity of graphene II is greatly enhanced compared with the original graphene with an impurity concentration of 0.1%, although their only difference is 0.016 Ry change in the Fermi energy.

In a metallic regime the residual resistivity originates from impurity scattering and it is thus expected to be proportional to the impurity concentration. Graphene with $x = 1\%$ and the graphene II with $x = 0.1\%$ (figure 4) should differ mainly by the amount of impurity scattering as compared with the different conductivity regimes of graphene with $x = 0.1\%$. When the ratio of the resistivities between the two systems with the same Fermi energy and different impurity concentrations i.e. graphene at $x = 1\%$ and the graphene II at $x = 0.1\%$, is...
evaluated, it indeed approximates the expected proportionality for metals. Therefore the initial decrease in the resistivity curve in figure 4 is due to an increased metallic component of the electronic structure, with negligible influence from impurity scattering. At higher defect concentrations (0.5% and above) the effect of the impurity scattering becomes important, and the balance between these two effects causes the resistivity to grow with large defect concentrations.

In the experimental situation, the dangling bonds around the defects in graphene are most likely to be saturated with hydrogen, oxygen or hydroxide groups. In order to account for this, we have carried out density functional theory calculations saturating the dangling bonds around di-vacancies with H and/or O atoms. The LDOS of the carbon atoms around the defect at the Fermi level reaches, as in the calculations of vacancies with dangling bonds, finite values suggesting that metallicity persists upon addition of H and/or O to the carbon atoms in the neighbourhood of the vacancies.

4.3. IV characterization of CNSs

The presence of oxygen and the absence of chlorine was verified by x-ray photoelectron spectroscopy in model CNS system. In our XAS measurements, we observe in-plane, $\sigma^*$-type orbitals appearing after the acid treatment which indicates the presence of vacancies. In order to confirm this result reported in [8], we carried out IR spectroscopy that could give information on the identity of polar functional groups. Unfortunately the proportion of polar bonds to bulk non-polar carbon was too low for any safe conclusions to be drawn. In fact, when graphene is damaged, for example, by electron irradiation, both, single and di-vacancies were found [26, 27]. But as shown above, the appearance of mid-gap states is valid for both single and di-vacancies and therefore, at this stage, our transport experiment is only sensitive to the presence of defects, but not to their detailed character. Figure 5 shows three $I–V$ measurements performed on the reference sample and figure 6 shows three $I–V$ curves of acid treated (defect induced) sample, demonstrates that the $I–V$ curves on individual CNS are reproducible. The $I–V$ curves of figures 5 and 6 are symmetric and non-linear, where the reference sample shows currents in the range 0.1–10 $\mu$A and the acid treated sample in the range 0.01–1 mA at 1 V. The currents in the as-deposited sample are about two times lower than in the reference sample. In order to evaluate the curves quantitatively, we have measured the resistance at bias voltages from $-0.6$ to $0.6$ V. Every recorded $I–V$ curve results in a number of resistance values taken at different bias voltages $V_b$. Both negative and positive voltages are considered for the evaluation since no systematic asymmetry was seen in the $I–V$ curves for opposite bias. The resistances are plotted in histograms for each voltage value (figure 7). The scatter of the resistance data between the different CNSs on the same sample is due to changes in size of the CNS and of the contact point of the needle.

The measured data collected in resistance histograms were fitted with a log–normal distribution, which is used to determine the average resistance as well as the standard error of the resistance at each voltage. These resistance values and their associated errors are shown in figure 8, as a function of bias voltage. The average resistance of the reference sample is about 50 times higher than the resistance of the acid treated sample. This change in resistance is much larger than the standard error of our measurement (figure 8), and we can safely conclude that our described method of chemical treatment can be used to tune the conductance of CNS with more than one order of magnitude. Furthermore, from the experimental curves (figure 8) we observe for both reference and acid treated samples a decrease in the resistance with increasing voltage. This could be either an intrinsic effect of the electronic structure of the CNS or could be related to local structural modifications of the nano-sheets appearing at higher bias voltages. In fact, when we increase the voltage to about 4 V, we observe an increase in current by one order of magnitude followed by a drop in current close to the leakage current level of the set-up which is about 50 pA. A subsequent SEM observation demonstrates that in this case, several 10 nm large holes were created in the CNS. When the measurement was carried out between $-1$ and $1$ V, no visual changes could be noted on the CNS structures in the SEM images and, as shown above, subsequent measurements on the same CNS show a reproducible resistivity. Therefore, the non-linearity of the $I–V$ curves should be an intrinsic property of the CNS.

From the SEM images, we measured the average surface area of the CNS in this study (figures 1(a) and (b)). We obtain the resistivity to be 150 $\mu\Omega$ m in the reference sample and 3.5 $\mu\Omega$ m in the acid treated sample at 0.3 V. From a
comparison with resistivity values reported in the literature, the resistivity of the reference sample corresponds well to the value found for nanocrystalline graphite with a crystallite size of 2–5 nm [28]. In fact, the CNSs studied in this work consist of structurally coherent domains or grains with a diameter between 2 and 5 nm in very good correspondence to the above value [20]. This similarity points to the CNS behaving as graphite concerning their resistivity. Deviations from a crystalline arrangement at C atoms in the grain boundaries in the as-grown CNS will lead to an increase in the resistivity as observed here. The agreement between our measurements and resistivities measured on nanocrystalline graphite underlines that the obtained resistivity values are CNS resistivities, with only a minor influence of the contact resistance. Thus, the decrease in resistivity can only be related to a decrease in the CNS resistivity. Furthermore, we have carried out control experiments where we have positioned the manipulator tip on top of the 20 nm thick graphite film on top of the substrate. Since this graphite material is grown by the same growth procedure, the contact resistance in this measurement is very similar to the one in the CNS measurements. We obtained resistances as low as 10–100 $\Omega/m$ which is small compared with the resistances measured on the CNS. When a graphene sheet is exfoliated from a graphite crystal, the resistivity of this sheet when positioned onto a Si substrate will be five times lower, in the non-gated state, than in graphite [2]. Some consequences of the acid treatment on the CNS structure can be estimated from our observations. Structural changes with a size of several 10 nm appear in the CNS after the acid treatment as observed in high resolution SEM images. Our conductivity measurements show that the acid treatment has modified the CNS structure. Such structural modification could be nucleated at step edges present in high density (the CNS thickness changes between 2–7 monolayers) and at the grain boundaries. One may speculate that a part of the about 50 times decrease of the resistivity upon acid treatment could be attributed to a thinning mechanism of the CNS, leaving on average more sheets exhibiting a graphene-like behaviour.

With this in mind, the decrease in the average resistivity from 150 to 3.5 $\mu\Omega/m$ measured here is by one order of magnitude higher than what would be expected from just a thinning of the CNS layers and moving from a graphite character to a graphene-like conductivity. It should also be noted that the absolute value of the non-gated average resistivity is about 3.5 $\mu\Omega/m$, which is as low as in measurements on low defect graphene [2]. Still, the acid treated CNS will keep a similar grain size and grain boundary.
defects as the reference sample since the acid treatment is not likely to cure such defects. Therefore, we conclude that the huge change in resistivity upon acid treatment is largely driven by the creation of defects, and this experimental result is consistent with the theoretical results reported here. The presence of vacancy defects is further stressed by our x-ray spectroscopic measurements which also show a very good agreement with the DOS calculated for vacancy defects in graphene [8].

5. Conclusion

In conclusion we have demonstrated an increase in the conductivity of CNSs and graphene by more than one order of magnitude by means of engineered introduction of defects. This behaviour is drastically different from the conductivity of defectuous carbon nano-tubes [29]. The method to create the defects demonstrated in this paper is very simple and widely available, hence opening up a huge possibility of similar investigations on graphene in various geometries, on different substrates and in combination with other defects like adsorbed atomic or molecular species.

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