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Giant tunnel-electron injection in nitrogen-doped graphene

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Scanning tunneling microscopy experiments have been performed to measure the local electron injection in nitrogen-doped graphene on SiC(0001) and were successfully compared to ab initio calculations. In graphene, a gaplike feature is measured around the Fermi level due to a phonon-mediated tunneling channel. At nitrogen sites, this feature vanishes due to an increase of the elastic channel that is allowed because of symmetry breaking induced by the nitrogen atoms. A large conductance enhancement by a factor of up to 500 was measured at the Fermi level by comparing local spectroscopy at nitrogen sites and at carbon sites. Nitrogen doping can therefore be proposed as a way to improve tunnel-electron injection in graphene.

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The exploitation of the electronic properties of graphene allows us to envision the development of new electronics based on carbon materials [1–3]. Due to the particular band structure of graphene, low-energy electronic states, driving the current in transport devices, are only available at the large parallel momentum ($k_x$) $K$ and $K'$ points in graphene. As a consequence, perpendicular tunneling of electrons into a graphene sheet is quenched at low bias voltage due to the competing large $k_x$ momentum conservation and the exponentially decaying tunneling probability with increasing $k_x$. Scanning tunneling microscopy (STM) experiments on graphene on SiO$_2$ have revealed that above 63 mV an inelastic channel corresponding to the excitation of an out-of-plane phonon is opened, which enhances substantially the tunneling current [4]. A gaplike feature in the $dI/dV$ spectroscopy is therefore observed around the Fermi level $E_F$ [4–8]. Interestingly, the same feature has been measured in spin devices using magnetic tunnel junctions [9] where magnetoconductance measurements were performed at bias voltages larger than the gap feature. Using a large bias in such devices can be a limitation as the magnetoconductance signal decreases with the bias voltage. Therefore, enhancing the electron injection at low energy in graphene turns out to be a cornerstone for improving the performances of graphene-based electronic and spintronic devices. As the quenching of electron injection is due to the momentum conservation of electrons imposed by the symmetry of the graphene sheet, breaking the symmetry of the system can lead to an enhancement of electron injection. In that respect, introducing atomic defects is a promising strategy to restore an elastic channel for vertical injection in graphene. The nitrogen doping of graphene obtained by substitution of nitrogen atoms for carbon atoms is a suitable route to achieve well-controlled and well-characterized point defects with limited atomic relaxation [6–8] while preserving the band structure of graphene. At the atomic level, nitrogen doping induces a redistribution of the electron density on one sublattice and a localized resonance at nitrogen sites [8] that have been widely studied theoretically [10]. In this paper, we perform scanning tunneling spectroscopy (STS) experiments to study the local electron injection in nitrogen-doped graphene on SiC(0001). $dI/dV$ and tunneling current decay length spectra reveal that below the out-of-plane phonon energy, elastic tunneling is allowed at nitrogen sites leading to a large enhancement of the electron injection by a factor of up to 500 close to zero bias. This interpretation is supported by first-principle calculations and well explained by a simple analytical model. Our findings allow us to propose nitrogen doping of graphene as an efficient way to improve electron injection in graphene without altering its band structure.

The graphene sample was grown by the confinement control sublimation (CCS) method on SiC(0001) [11]. It consists of about five non-Bernal stacked layers on top of SiC. The postsynthesis doping was achieved in an ultrahigh-vacuum (UHV) chamber by exposing the sample during 30 min to a nitrogen radical flux produced by a remote (~30 cm) RF plasma source (MPD21 from Oxford Applied Research [12]) fed with N$_2$ (purity 99.999%) [8]. The scanning tunneling experiments were performed with a UHV Low-Temperature (4.2 K) from Omicron GmbH using electrochemically etched tungsten tips. $dI/dV$ spectra were acquired with a lock-in detector at 710 Hz and a modulation amplitude of 24 mV. Prior to spectroscopic measurement on graphene the STM tip was calibrated on a Au(111) substrate by applying voltage pulses until the $dI/dV$ spectrum shows the onset of the Shockley surface state. This procedure is necessary to obtain reliable spectra as it was mentioned by Zhang et al. [4].
After synthesis and doping, the sample was transported in the atmosphere and outgassed in UHV at ~800°C before the STM measurements.

Nitrogen atoms substituted to carbon atoms (graphitic nitrogen) in graphene on SiC(0001) appear in the STM images as bright spots with a triangular shape [bottom right inset in Fig. 1(a)]. This can be attributed to a combination of charge transfer between the nitrogen and the three neighboring carbon atoms [8] and the opening of the elastic channel as shown in the following. The $dI/dV$ spectrum this inelastic excitation appears as two onsets symmetric with respect to the Fermi level $EF$ [4]. Indeed, momentum conservation in the tunneling process imposes a large in-plane momentum $k_{\parallel}$ for electrons tunneling to graphene where the only available states are at the $K$ points. However, above a threshold voltage corresponding to the energy of an out-of-plane graphene phonon, an inelastic tunneling channel is opened, which leads to a large increase of the tunneling current. In the $dI/dV$ spectrum this inelastic excitation appears as two onsets symmetric with respect to $EF$ at the energy of the phonon. The spectrum measured above a nitrogen atom is totally different [Fig. 1(a)]. The inelastic signal almost disappears, only fainted onsets can be seen [top inset in Fig. 1(a)]. This is indicative of a strong decrease of the inelastic/elastic transmission ratio. A quantitative comparison of the conductance at nitrogen and carbon sites cannot be obtained from the curve in Fig. 1(a) as these spectra were measured with a constant current condition before measurement ($U = 1\,V, I = 500\,pA$). Indeed the nitrogen atoms lie in the graphene plane as it was suggested by voltage-dependent STM measurements [8] and confirmed by $ab\ initio$ calculations on monolayer [13] and bilayer [14,15] graphene. Electronic effects lead to an apparent height of about 1 Å, the tip-sample distance is larger above the nitrogen atom than above graphene. In order to quantitatively compare the conductance at carbon and nitrogen sites, spectra have to be measured with the same tip-sample distance (constant height mode). Such data are displayed in Fig. 1(b). The measurements obtained with the same tip-sample separation reveal a huge increase of $dI/dV$ above nitrogen. At $EF$ the conductance at the Fermi level above a nitrogen atom is 70 times larger than on the graphene sheet revealing a very large enhancement of electron injection at nitrogen sites.

The increase of conductance above nitrogen atoms was systematically observed as shown in Fig. 2. Figure 2(a) displays the current image measured in constant height mode on an area with two nitrogen atoms. Figure 2(b) shows the evolution of the spectra along a line crossing a nitrogen atom [cf. dotted line of Fig. 2(a)] revealing the increase of the $dI/dV$ signal above nitrogen over a distance characterized by a full width at half maximum of 5 Å. This extent corresponds to the typical size of the triangular pattern associated with a nitrogen atom in the STM images. Such a spatial extension also corresponds to the variation of the potential around a nitrogen atom [10]. The ratio between the conductance at the Fermi level above graphene (0.017 nS) and above nitrogen (9.15 nS) in Fig. 2 is about 500, which is larger than the above-mentioned measure (ratio of 70). As will be discussed below, we attribute this difference to the tip-sample distance that is larger in the second case, which increases the ratio of conductance between nitrogen and graphene. In Fig. 2(c) we show a conductance map measured in constant current mode at 2.5 mV. Although this mode reduces the contrast, it allows us to obtain more details along the whole image. This image shows again that the conductance is stronger above the nitrogen atoms confirming that the phonon gap feature vanishes above nitrogen as previously observed in the spectrum of Fig. 1(a). Interestingly, on a nitrogen pair identified as two nitrogen...
atoms in second neighbor positions, a strong contrast with atomic resolution is clearly observed in the $dI/dV$ map. The spectra in Fig. 2(d) measured on the nitrogen atoms and between the nitrogen atoms of this pair clearly reveal that although the inelastic feature is almost suppressed above the nitrogen atoms, it is unaffected at the central position between the N atoms. This is in line with previously reported data showing that the inelastic feature is observed at the center of a nitrogen pair [7].

Details on the tunneling mechanism at nitrogen sites can be obtained by measuring the voltage-dependent current decay length $\lambda$ measured on a reference Au(111) sample (black), N-doped graphene carbon area (blue) and above a graphitic nitrogen atom in graphene (red). (b) $\lambda$ mapping at 20 mV extracted from spectra measured at each point of the topographic image shown in the inset (10 $\times$ 10 nm$^2$, $U = 0.1$ V, $I = 500$ pA).

FIG. 3. (Color online) (a) Voltage dependent current decay length $\lambda$ measured on a reference Au(111) sample (black), N-doped graphene carbon area (blue) and above a graphitic nitrogen atom in graphene (red). (b) $\lambda$ mapping at 20 mV extracted from spectra measured at each point of the topographic image shown in the inset (10 $\times$ 10 nm$^2$, $U = 0.1$ V, $I = 500$ pA).

20 mV measured simultaneously with the image shown in the inset. This mapping shows a uniform value of $\lambda$ on the carbon areas of around -0.2 Å and a clear larger value on nitrogen atoms of ~0.4 Å. A consequence of the different decreasing lengths at nitrogen and carbon sites is that the conductance ratio between these sites is expected to be distance dependent. Indeed this ratio is expected to increase with the tip-sample distance $z$ according to the quantity $\exp[z(1/\lambda_C - 1/\lambda_N)]$ where $\lambda_C$ and $\lambda_N$ are the decreasing lengths at $E_F$ above carbon and nitrogen sites respectively. This allows us to understand the different $dI/dV$ ratios measured to be 70 in Fig. 1(b) and 500 in Fig. 2(b). In these measurements, the current above the graphene area at a reference bias of 100 mV is $I_1 = 110$ pA in the Fig. 1(b) and $I_2 = 12$ pA in the Fig. 2(b). This means that the tip-sample distance in the two measurements varies by $\Delta z = 0.45$ Å for $V = 100$ mV. The ratios of conductance are therefore expected to vary by a factor of 5.7 (with $\lambda_C = 0.18$ Å and $\lambda_N = 0.42$ Å at the Fermi level), which is close to the ratio 500/70.

Using the DFT-NEGF method and setup described in Ref. [16], $dI/dV$ spectra including vibrational effects were calculated directly above a nitrogen dopant in graphene and above pristine graphene. For all calculations shown we use a tip-to-sample distance of $d = 5$ Å since tunneling at larger

1We use a split DZP basis set, a mesh cutoff of 200 Ry, a Monkhorst-Pack $k$-point mesh of $1 \times 2 \times 1$ and the Ceperley-Alder LDA functional [22] to calculate the electronic structure. Supercell dimension and $k$$_i$ of $27 \times 12.8$ Å(101)/27 $\times 17$ Å(81) is used to calculate inelastic transport for pristine/nitrogen doped graphene.
The Dirac point is seen at the expected bias value. As in the measurements reproduced, and the dip caused by inelastic tunneling into the $V_b$ with the constant height measurement of Fig. 1(b), both the $dI/dV$ features. As discussed previously [16] the 130 meV gap is graphene close to the intensity of the signal above nitrogen. For imaging condition brings the intensity of the signal above nitrogen pairs (8.5˚A away from either site) and seen to graphene has been enhanced to allow a better comparison with $\Gamma - \pi$ matrix element $\langle \pi,0|V|\pi,0\rangle$. In $k$ space the potential obviously couples all states. In this very localized limit, the main matrix element $\langle \pi,0|V|\pi,0\rangle$ has been estimated to be about 10 eV [10]. Because of the different extensions of the orbitals the other matrix element should be much weaker, allowing us to keep just one off-diagonal term $v = \langle \pi,0|V|\pi,0\rangle$. We can now directly adapt the calculation by Wehling et al. [21] and calculate the self-energy and the local Green’s function corresponding to the new $\Gamma$ elastic channel. Finally, in a second-order perturbation theory, the local density of states on the nitrogen site is $n_i(E) \approx v^2 n_{\pi}(E)/(E - E_s)^2$ where $n_{\pi}(E)$ is the corresponding density of states of the $\pi$ states in the presence of the nitrogen impurities [10] and $E_s$ is the energy of the free-electron-like state [21].

Close to the Dirac point $E \approx 0$ and the intensity of the new channel is a fraction ($\lambda_{el}/\lambda_{ph}$)² of the inelastic channel, where $\lambda_{el-\pi}$ is the electron phonon coupling strength. Assuming $v$ to be at least equal to $\lambda_{el-\pi}$ (about 0.5 eV [21]) we see that the elastic channel can be at least as efficient as the inelastic channel in agreement with the experiments and the above \textit{ab initio} calculations.

In conclusion, using STM/STS we measured an increase of differential conductance leading to a vanishing of the phonon gaplike feature at nitrogen sites. This leads to a two orders of magnitude increase in electron injection into graphene. First-principles calculations reveal that although the inelastic excitation of graphene phonon still occurs at nitrogen sites, an elastic channel opens that substantially increase the conductance. Therefore we expect that nitrogen doping of graphene can be used to improve tunnel electron injection in graphene-based devices.

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[15] Luc Henrard (private communication).