Local work function and STM tip-induced distortion of graphene on Ir(111)

S J Altenburg and R Berndt
Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany
E-mail: altenburg@physik.uni-kiel.de

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Abstract
The contact conductance and the apparent barrier height $\phi$ of graphene on Ir(111) are measured with a cryogenic scanning tunneling microscope. A strong dependence of $\phi$ on the tip–sample distance is found and explained by a local lifting of the graphene film by van-der-Waals forces. Variations of $\phi$ observed within the moiré unit cell of the graphene layer are interpreted in terms of differences in the local work function and the buckling of the graphene film. Comparison to results based on density functional theory indicates that a modulation of the charge transfer between graphene and Ir(111) is the origin of the work function variations.

Keywords: graphene, work function, periodic potential, STM, Ir(111), van-der-Waals forces, contact conductance

The quasi-relativistic dispersion of the charge carriers in graphene [1] leads to a number of unique effects such as the ambipolar electric field effect [2], the anamalous quantum Hall effect [3, 4] and Klein tunneling [5, 6]. To influence the electronic properties of graphene a periodic potential may be used, which leads to anisotropic group velocities of the charge carriers [7] and the possibility to observe Hofstadter’s butterfly in the quantum hall effect [8]. A periodic potential can be introduced by a moiré effect that occurs when graphene is grown on certain transition metal surfaces such as Ru(0001) [9–11], Rh(111) [12, 13] or Ir(111) [14–16]. On the strongly coupled system graphene on Ru(0001) a periodic modulation of the work function has...
been shown by photoelectron spectroscopy of adsorbed Xe [17]. This was also found from local measurements of image potential states with scanning tunneling microscopy (STM) of graphene on Ru(0001) [18] and Rh(111) [12]. For the weakly coupled system graphene on Ir(111) a periodic potential variation in the order of 0.1–0.2 eV has been estimated from observed minigaps of the electronic dispersion measured with angle-resolved photoemission spectroscopy [15]. Recent Kelvin probe force microscopy (KPFM) experiments on this system have shown such a variation as well [19], although the absolute values are expected to underestimate variations on the nanometer scale due to averaging over a large tip diameter [20]. The STM offers the possibility to more directly investigate the local work function by measuring the distance dependence of the tunneling current. Owing to its spatial resolution and the strong localization of the tunneling current at the tip apex, lateral variations can be probed in some detail. In addition, the tunneling current decay may be used to obtain insight into the interactions between the surface and the scanning tip. Although van-der-Waals forces due to the STM tip have early been shown to induce significant relaxation effects [21], they are often neglected in analyzing scanning probe microscopy data. The observation of bistability of a graphene membrane on SiO$_2$ under the influence of a STM tip is a recent exception [22]. As to graphene on Ir(111), its geometric corrugation has intensely been investigated with atomic force microscopy [23–25] under the tacit assumption that relaxation effects may be neglected.

Here, we show that graphene on Ir(111) gets lifted significantly under the influence of the STM tip. In addition, we observe a variation of the local workfunction of graphene within the moiré unit cell of $\approx 100$ meV. The barrier is maximal in the regions where graphene is buckled away from the substrate. A comparison to density functional calculations of the moiré structure suggests a variation of the charge transfer between graphene and substrate as the origin of these workfunction differences.

Experiments were performed with a home-built STM operated at 5.2 K at a pressure below $10^{-8}$ Pa. Ir(111) surfaces were cleaned by cycles of Ar$^+$–ion bombardment and annealing at $\approx 1600$ K. Graphene islands were grown by exposing the sample to $\approx 6 \times 10^{-4}$ Pa s of ethene (C$_2$H$_4$) at room temperature and subsequent annealing at $\approx 1400$ K. Au tips were prepared by electrochemical etching, in vacuo heating and subsequent Ar$^+$–ion bombardment. Moreover, tips were prepared by gently contacting the clean Ir surface, thereby depositing gold from the tip apex onto the surface. This procedure was repeated until constant current images of graphene islands showed symmetric and steep edges in all directions. With these tips spectra of the differential conductance ($dI/dV$; $I$: current, $V$: voltage) showed only the typical features known from previous experiments [16] suggesting that the electronic density of states of the tips was featureless.

The tunneling current was measured with a variable-gain transimpedance amplifier to cover a typical range from 100 pA to 1 $\mu$A. To record current–distance data, the STM feedback loop was opened, the sample voltage (typically 100 mV) was kept constant, and the tip was moved towards the sample while the current was monitored. During this procedure the amplification of the transimpedance amplifier was repeatedly adjusted. Afterwards the resulting segments were shifted to obtain a continuous curve. We made sure that in spite of the unusually high currents no significant voltage drop at the input impedance of the current-to-voltage converter occurred. Maps of $dI/dz$ were measured by applying a sinusoidal modulation (typically 10 pm) to the $z$–piezoactuator and measuring the response in the tunneling current by
a lock-in amplifier. The modulation frequency ($\approx 300$ Hz) was chosen above the cut-off frequency of the feedback loop, which was reduced for these measurements, and below the cut-off of the piezo driver. The scanning velocity was chosen low enough to maintain a constant averaged current, despite the reduced speed of the feedback loop. Maps of the apparent barrier height $\phi$ were calculated from $dI/dz$ maps using

$$\phi = \frac{\hbar^2}{8m} \left( \frac{1}{I} \cdot \frac{dI}{dz} \right)^2 = \frac{\hbar^2}{8m} \left( \frac{d \ln I}{dz} \right)^2,$$

with the reduced Planck constant $\hbar$ and the electron mass $m$ [26]. The variation of $\phi$ with tip displacement was numerically calculated from smoothed current–distance curves via equation (1).

The lower left inset of figure 1(a) shows a constant current STM image of graphene on Ir(111). The so-called top regions, where the graphene hexagons are centered atop an Ir atom, appear as depressions. The areas where adjacent carbon atoms are located atop Ir atoms and in hollow sites are referred to as hollow regions. At the positions indicated in the inset, conductance-distance (CD) curves were recorded (figure 1(a)). At low conductances (see inset on the upper right showing a wider distance range) the data from hollow (red solid line) and top (blue solid line) sites are almost identical. At the elevated conductances shown in figure 1(a) clear differences between them are discernible. A gray line shows an extrapolation of the tunneling conductance of the data from the hollow region. The measured conductances of both regions lie well above this line throughout the distance range from 5 to 3.5 Å. Defining a characteristic contact conductance from the intersection of the CD curve with the extrapolated tunneling conductance, we find 0.15 $G_0$ and 0.3 $G_0$ ($G_0 = e^2/\pi \hbar$, with the elementary charge $e$) in the top and hollow regions, respectively. While there was some scatter of these values from tip to tip, the contact conductance of the top region was always lower. A similar observation was reported for graphene on Ru(0001) [11] and attributed to the larger graphene–substrate distance in the top region. Indeed, in the present case, the contact formation to the top region occurs at larger tip–sample distances (by $\approx 0.25$ Å) than in the hollow region.

To highlight the deviations of the CD curves from a purely exponential variation figure 1(b) shows the apparent barrier heights $\phi$ from the hollow and top regions (red and blue solid lines, respectively). As expected, $\phi$ is constant in the tunneling range as indicated by the gray line. At smaller distances, $\phi$ first increases, reaches a maximum close to contact and then decreases again. The maxima in the top and hollow regions are offset by $\approx 0.4$ Å.

The lateral variation of $\phi$ is obvious from maps of $\phi$ as shown in figure 2. The maps were recorded at different conductances which in turn correspond to different tip–sample

1 Depending on $I$ and $V$ the graphene sheet may also appear flat although the graphene layer is actually buckled away from the substrate in these areas [25]. At the tunneling conditions used as initial conditions for the CD curves the topograph appeared flat, insuring that the CD curves were recorded at identical heights above the Ir substrate.

2 While displacement of the STM tip in z-direction is controlled with pm precision, the absolute tip–sample distance is unknown in the experiment. To estimate this absolute distance, the measured CD curves were shifted along the abscissa (both by the same amount) to overlap with the simulation data (see below). In the simulation, the tip–sample distance is defined as the distance between the tip apex atom and the (unrelaxed) C atom representing the graphene sheet.
distances. Since the absolute tip–sample distances are unknown in the experiment, the conductance–distance relation from a simulation (see below) was used as an estimate. Figure 2(c) shows the distance dependence of the difference $\Delta \phi$ between the barrier heights in the top and hollow areas, indicating a decrease with increasing distance. From classical electrodynamics, lateral variations of a potential are expected to decay on the same length scale in the perpendicular direction. In our case the potential variation has a periodicity of approximately 2.5 nm. However, the measured decay of $\Delta \phi$ occurs on a scale of 1 Å, indicating a different origin.

Figure 1. (a) Current–distance (CD) curves recorded at different positions of the moiré unit cell (see inset lower left) at $V = 100$ mV, averaged over 10 measurements and smoothed. Lower left inset: constant-current STM image of graphene on Ir(111), $V = 100$ mV, recorded at a large current of $I = 1 \mu$A, where clear structure is discernible in the unit cell. Upper right inset: CD data shown over a wider range of distances. Results of simulations (see text) are shown by dotted lines. As the absolute tip–sample distance is unknown in the experiment, the measured CD curves were shifted along the abscissa (both by the same amount) to overlap with the simulation data. The gray line indicates the extrapolated tunneling conductance for the hollow region. Only at small distances the simulated curves deviate from the measured data. (b) Experimental (solid lines) and simulated (dotted lines) barrier height $\phi$ calculated from CD data shown in (a) Experimental and simulated data match, except for very low distances (see text).
Close to contact an increase of the measured barrier height has been reported for $C_{60}$ on Cu(111) [27]. In that case the modification of $\phi$ was attributed to a relaxation of the tip and the sample, which effectively reduces the tunneling gap. For $C_{60}$, being rigid and strongly bonded to the substrate, these relaxation effects are limited to a distance range of $\approx 0.5$ Å from contact, where strong short-range forces occur. Graphene on the other hand is only weakly coupled to the Ir(111) substrate. Therefore the weaker long-range forces may be expected to induce significant relaxation, which in turn may be the origin of the observed increase of $\phi$. In this scenario, assuming similar coupling to the tip and the substrate within the moiré unit cell, the maximum of $\phi$ should be located at similar graphene–tip distances. Indeed, the observed offset of $\approx 0.4$ Å matches the buckling of the graphene layer of 0.35 Å [28].

To verify that a relaxation can indeed modulate $\phi$ to the extent observed in the experiments, we use the following model. The graphene–Ir interaction is approximated by a harmonic potential with a spring constant $\alpha$. The tip is modeled as a paraboloid of Au atoms in an fcc arrangement (see figure 3(c)). The interaction between the tip and graphene is obtained by adding pairwise Lennard–Jones potentials $\Phi_{LJ}$ for all Au atoms:

![Figure 2](image-url)
$\Phi_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],$

$r$ denotes the distance between the atoms. Values of the well depth $\epsilon$ and the zero-crossing $\sigma$ are available for the interaction between identical atoms. Here, we use the Lorentz–Berthelot combination rules [29] to estimate effective values $\epsilon_{\text{Au,C}}$ and $\sigma_{\text{Au,C}}$ as

$$
\epsilon_{\text{Au,C}} = (\epsilon_{\text{Au}} \cdot \epsilon_{\text{C}})^{1/2},
\sigma_{\text{Au,C}} = (\sigma_{\text{Au}} + \sigma_{\text{C}})/2,
$$

with $\epsilon_{\text{Au}} = 440$ meV, $\sigma_{\text{Au}} = 2.637 \text{ Å}$ [30], $\epsilon_{\text{C}} = 2.4$ meV and $\sigma_{\text{C}} = 3.04 \text{ Å}$ [31].

To compare with the experiments, the conductance $G(d)$ was calculated as

$$
G(d) = G_i \cdot \exp \left[ -2 \left( \frac{m}{\hbar^2} \overline{\varphi} \right)^{1/2} (d - \Delta d) \right].
$$

$\Delta d$ is the displacement of the C atom that results from the interaction with the tip, while $d$ is the distance between the tip apex atom and the (unrelaxed) C atom. The initial conductance $G_i$ was chosen to fit the experimental results. The average work function $\overline{\varphi} = (\varphi_{\text{tip}} + \varphi_{\text{sample}})/2$ of tip and sample was adjusted according to the slope of experimental CD curves in the tunneling
\( \phi \) was calculated from the CD curves via equation (1). To account for the geometric height variation in the moiré unit cell, the tip was placed 0.4 Å closer to graphene for the top region while keeping the conductance at the same value, as observed in the experiments.\(^4\)

Dashed lines in figures 1 and 2 show results of the simulations. Despite the simplicity of the model the agreement with the measurements is remarkable. Deviations only occur at very small tip–sample distances, where additional factors such as tunneling to neighboring C atoms are expected to play a role. While the precise values of the adjustable parameters may be of minor importance, we find that reasonable values lead to good agreement with the experimental data. This suggests that the observed intriguing behavior of \( \phi \) is largely due to relaxations of the atoms forming the tunneling contact.

As a further check of the model figure 3(a) shows the force on the central C atom, the total force on a graphene patch (illustrated in (d)) and the total force including the Ir substrate\(^5\) versus the tip–sample distance. We find a maximum attractive force of \( \approx 1.15 \) nN. DFT calculations for a more reactive W tip interacting with the graphene–Ir system \[25\] lead to a comparable value of \( \approx 1.7 \) nN. In a related case, a Cu tip contacting \( C_{60} \), maximal attractive forces were in a similar range (1.5 to 2.2 nN) \[27\]. Figure 3(b) shows the lifting of the contacted C atom during the tip approach. The contacted C atom is lifted by up to 12 pm. Owing to the fairly long range of the attractive van-der-Waals force the nearest-neighbor C atoms are lifted by similar amounts, as illustrated in the side and top view in figure 3(d). Therefore the neglect of C–C interactions in the model is justified.

The variations of the workfunction within the moiré unit cell may be explained by comparison to the results of DFT calculations. According to \[28\] a charge transfer from graphene towards the sample takes place in the hollow regions. This localized charge transfer induces a dipole moment pointing out of the surface plane, effectively reducing the surface dipole moment \[32\]. This translates to a local reduction of the workfunction in the hollow regions, as experimentally observed.

\(^3\) \( \phi_{\text{top}} = 4.1 \) eV and \( \phi_{\text{hollow}} = 4.05 \) eV for figure 1 and \( \phi_{\text{top}} = 3.5 \) eV and \( \phi_{\text{hollow}} = 3.45 \) eV for figure 2. The different values in figures 1 and 2 are most likely due to different tip apices in the experiments. A difference of \( \Delta \phi \approx 50 \) meV between top and hollow regions yielded a good fit between simulation and experiment for all measurements. For \( \Delta d = 0 \), i.e. without relaxation effects as for large tip–sample distances, equation (1) and equation (2) yield that \( \phi = \phi_{\text{tip}} \). Since \( \phi_{\text{tip}} \) is constant, the variation of the local work function of the sample \( \Delta \phi_{\text{sample}} = 2 \Delta \phi \) for large tip–sample distances or \( \Delta \phi_{\text{sample}} = 2 \Delta \phi \) from the simulation fits. Thus \( \Delta \phi_{\text{sample}} \approx 100 \) meV.

A lower value of 35 meV has been reported from KPFM data \[19\]. However, this technique is expected to underestimate potential variations on the nanometer scale \[20\]. The observation of minigaps in the electronic dispersion relation measured by angle–resolved photoemission spectroscopy led to an estimate for the potential variation of between 100 meV and 200 meV \[15\].

\(^4\) To account for the increased reactivity of the hollow region towards metal atoms \[33\] \( e_c \) was increased by a factor of 1.1 compared to the value used for the top region. The spring constants were \( \alpha_{\text{top}} = 4.5 \) N m\(^{-1}\) and \( \alpha_{\text{hollow}} = 4.8 \) N m\(^{-1}\) to account for the distance dependence of the graphene substrate coupling \[34\]. These values are somewhat larger than an estimate obtained from electron energy loss spectroscopy data for the out-of-plane acoustic phonon branch (ZA), \( \alpha_{\text{ZA}} = 3.3 \) N m\(^{-1}\) \[35\].

\(^5\) The force between tip and substrate was calculated by adding up the attractive van-der-Waals forces for an atom in front of a surface \[36\] for all tip atoms. \( \epsilon_v = 682 \) meV, \( \sigma_v = 2.542 \) Å (values for Pt \[30\]).
In conclusion, we have shown that the local workfunction of graphene on Ir(111) varies within the moiré unit cell by $\approx 100$ meV, showing maximum values in the top regions. The contact conductance is well below $G_0$ and higher in the hollow regions than in the top regions. For tip–sample separations below $\approx 5$ Å the graphene sheet gets lifted significantly by van-der-Waals forces between graphene and STM tip. This lifting leads to an increase of the measured apparent barrier height $\phi$ at small tip–sample distances. Similar issues may arise in other weakly coupled systems such as layered crystals.

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