Orientation-dependent work function of graphene on Pd(111)

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Selected-area diffraction establishes that at least six different in-plane orientations of monolayer graphene on Pd(111) can form during graphene growth. From the intensities of low-energy electron microscopy images as a function of incident electron energy, we find that the work functions of the different rotational domains vary by up to 0.15 eV. Density functional theory calculations show that these significant variations result from orientation-dependent charge transfer from Pd to graphene. These findings suggest that graphene electronics will require precise control over the relative orientation of the graphene and metal contacts. © 2010 American Institute of Physics. [doi:10.1063/1.3495784]

Graphene, a two-dimensional crystalline sheet of carbon,1 has generated considerable attention owing to its ultrathin geometry, high carrier mobility,2 and tunable band gap,3 with potential applications in high-performance low-power electronics4 and as transparent electrodes.5 Since graphene-based devices require metal (or metallic) contacts, knowledge of the electronic properties, for example, nature of the contact (Ohmic or Schottky) and electron transport at the metal–graphene interfaces is essential. Previous theoretical studies of graphene-metal contacts indicated that their electronic properties depend on the graphene–metal interaction energies.6 For example, strongly interacting metals can induce a charge transfer from or to graphene, resulting in p- or n-type doping, respectively.6 Here, using Pd(111) as a model substrate, we focus on understanding the influence of metal substrate and the in-plane orientation of graphene on its work function. Using a combination of in situ low-energy electron microscopy (LEEM) (Ref. 8) and density functional theory (DFT) calculations we show that monolayer graphene on Pd(111) exhibits a work function that varies significantly with domain orientation, a result of spatial variations in charge transfer at the graphene–Pd interface. Our results suggest that a precise control over graphene orientation with respect to the metal contacts is essential for the realization of large-scale graphene electronics.

In our experiments, the Pd(111) single-crystal substrate was first saturated with carbon by annealing at ∼900 °C overnight in a tube furnace in a flow of 90% Ar–10% CH4 at 760 Torr. Sample temperature in the LEEM was measured using a type-C thermocouple spot-welded to a washer in intimate thermal contact with the crystal. The surface was cleaned by cycles of sputtering using 1.5 keV Ar+ and annealing at ∼900 °C. Monolayer graphene was grown by cooling from ∼900 to 790 °C at the rate of ∼1 K/s, a well-established process used to segregate C from the bulk to the surface.9–11 The sample was then quenched to room temperature for analysis. To determine graphene layer thickness and work function,12,13 LEEM image intensities I versus electron energy E data were acquired at 0.1 eV intervals between E=−5 and 30 eV and 0.01 eV intervals between E=0 and 2.5 eV.

Figure 1(a) is a representative LEEM image from Pd(111) covered with monolayer graphene. The spatial variations in image contrast, as we show below, result from different rotational domains of graphene, each with its own characteristic electron reflectivity. Selected-area low-energy electron diffraction (LEED) (Ref. 14) measurements yielded at least six distinct patterns [see Fig. 2(a)], indicative of a polycrystalline film. In Fig. 2(a), the sixfold symmetric spots highlighted by two arrows correspond to Pd(111)-1×1 and graphene-1×1 lattices, respectively. In all patterns, the graphene is rotated with respect to the substrate. The angles of rotation θ are −2°, −5°, −10°, +17°, +22°, and +26° with a measurement uncertainty of ±1°. θ is the angle between Pd[110] and graphene [1120] with the positive (negative) sign denoting in-plane clockwise (counterclockwise) rotation. Figure 1(b) shows the six domains color-coded, with the 22°-rotated domain being the most abundant. The inner sets of sixfold symmetric spots in Fig. 2 indicate ordered superstructures whose periodicities are larger than the graphene and Pd lattice constants. These structures are moiré patterns resulting from superposing the graphene and Pd(111) lattices. Similar patterns occur for graphene on other

FIG. 1. (Color online) (a) LEEM image of monolayer graphene on Pd(111). Field of view is 14.5 µm and E=17.7 eV. (b) Graphene domains color-coded using the color scheme of Fig. 2.

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lattice-mismatched substrates. From LEED, we measure \( \lambda = 22 \pm 17 \pm 12 \pm 5 \pm 3 \pm 1 \) Å, with accuracies of \( \pm 0.1 \) Å, respectively, for different graphene orientations. We find agreement between the calculated and experimental \( \lambda \) values for \( \theta = 2.1^\circ, 5.7^\circ, 11^\circ, 14^\circ, 19^\circ, \) and \( 26^\circ \), respectively. Furthermore, we determine the electron work function of the electron gun filament \( \Phi_{\text{fil}} \) and the sample work function \( \Phi_S \) of each orientation \( \theta \) from 0° to 60°. We obtain good agreement between the calculated and experimental \( \lambda \) values for \( \theta = 2.1^\circ, 5.7^\circ, 11^\circ, 14^\circ, 19^\circ, \) and \( 26^\circ \), which yield \( \lambda = 21.8 \pm 17.2 \pm 12.6 \pm 9.9 \pm 7.3 \pm 19.2 \) Å, respectively. Figure 2(b) shows the atomic models, whose surface unit cells are \((3 \times 7 \times 3)\)-R19°, \((39 \times 39)\)-R16°, \((21 \times 21)\)-R11°, \((13 \times 13)\)-R14°, \((7 \times 7)\)-R19°, and \((7 \times 7)\). We now focus on how in-plane orientation affects electronic structure. In LEEM, all electrons are specularly reflected from the sample for sufficiently low incident electron energies \( E \). When \( E \) exceeds the difference between the work functions of the electron gun filament \( \Phi_{\text{fil}} \) and the sample surface \( \Phi_{\text{surface}} \), the reflected intensity \( I \) decreases due to electron-surface interactions. Hence, we used \( I \) versus \( E \) data to determine \( \Phi_{\text{surface}} \) (Ref. 12) for the different graphene orientations. Figure 3(a) plots \( I \) normalized to the intensity \( I_0 \) at \( E = 0 \) eV, with the solid and dashed curves denoting monolayer graphene domains and clean Pd(111), respectively. The ratio \( I/I_0 \) decreases from unity to 0.9 at an energy \( \varphi \), the electron injection threshold energy, that is characteristic of the work function. For all the six graphene domains, \( \varphi \) is \( \approx 1.3 \) eV lower than the value corresponding to clean Pd(111), showing that graphene substantially decreases the work function. The high-resolution plot in Fig. 3(b) reveals that the work functions \( \Phi_G \) of the different domains are not the same. In fact, they differ by up to 0.15 eV.

To compare with absolute work functions in the literature, we calibrate following the procedure described in Ref. 17 and references therein. For clean Pd(111), we measure \( \varphi = 2.2 \pm 0.1 \) eV. The literature value of \( \Phi_{\text{Pd}} = 5.3 - 5.6 \) eV. Then, \( \Phi_{\text{Pd}} = (\Phi_{\text{Pd}} - \varphi) = 3.1 - 3.4 \) eV. Similarly, we determine \( \Phi_G \) for each domain from the solid curves in Fig. 3. Our knowledge of \( \Phi_{\text{Pd}} \) limits the accuracies of \( \Phi_G \) to \( \pm 0.15 \) eV. However, the work function differences are precise to \( \pm 0.02 \) eV. Choosing \( \Phi_{\text{Pd}} = 5.6 \) eV and \( \Phi_{\text{fil}} = 3.4 \) eV yields \( \Phi_G \) values between 4.25 and 4.42 eV for the different graphene domains. The orientation-averaged value \( \langle \Phi_G \rangle \) is \( 4.3 \pm 0.1 \) eV, in good agreement with previous results. In comparison, \( \Phi = 4.5 \) eV for free-standing graphene.

FIG. 2. (Color online) (a) LEED patterns of the six graphene domains with rotational angles \( \theta = -2^\circ, -5^\circ, -10^\circ, +17^\circ, +22^\circ, +26^\circ \). Dashed and solid arrows show Pd[110] and graphene [1120] directions, respectively. (b) Atomic models of Pd(111) (darker contrast spheres) and graphene layers (lighter contrast spheres) rotated by \( \theta_c = -2.1^\circ, -5.7^\circ, -11^\circ, +14^\circ, +19^\circ, +26^\circ \). Rhombi highlight the unit cells of each moiré pattern. The arrow is Pd[110].

FIG. 3. (Color online) (a) Normalized image intensity \( I/I_0 \) vs \( E \) for graphene domains with \( \theta = 2^\circ, 5^\circ, 10^\circ, 17^\circ, 22^\circ, 26^\circ \). Dashed curve is clean Pd(111). (b) Magnified view of rectangle in (a), with the x-axis shifted by the work function of the electron gun filament \( \Phi_{\text{fil}} = 3.4 \) eV. The vertical dotted lines show the range of \( \Phi \). (c) Computed planar average of electron transfer density \( \Delta n \) vs normal coordinate \( z \) for \( \theta = 19^\circ \). The dashed line within the graphene–Pd interface shows the integration limit for the effective transferred charge \( q \). (d) Contour plots of \( \Delta n \) in the plane half-way between graphene and the top Pd layer for \( \theta = 19^\circ \) and 30°.
potential through a supercell of six Pd(111) layers and 12 Å vacuum, we find $\Phi_{Pd}=5.59$ eV, consistent with previous calculations. DFT simulations with periodic boundary conditions require the graphene layer to be commensurate with Pd(111), so we keep graphene at its equilibrium lattice constant (2.445 Å) and strain the substrate accordingly. Since the strain value is specific to each orientation $\theta$, the effects of strain and $\theta$ on $\Phi_G$ cannot be separated. Thus, we focus on the domain with the lowest strain, $\theta=19^\circ$. We calculate $\Phi_G = 4.14$ eV for this orientation, which is smaller than that of free-standing graphene, consistent with our experiments. We attribute this work function decrease to the formation of an effective dipole layer oriented away from the substrate. This dipole results from the transferred electron density around the surface, which has an oscillatory character and integrates to a positive charge $Q$ toward vacuum and $-Q$ toward the substrate [Fig. 3(c)]. We also calculated $\Phi_G$ for $\theta =5.7^\circ$ and $10.9^\circ$, finding values lower than free-standing graphene despite large substrate strains ($\sim 1\%–5\%$). These results are consistent with recent calculations for $\theta=30^\circ$ showing similar surface dipoles.

We gain insight into the physical origin of the orientation-dependence of the work function from the contour plots in Fig. 3(d), which compare the electronic transfer in the plane midway between graphene and the first Pd layer for $\theta=19^\circ$ and $30^\circ$. For the latter orientation, which has sixfold in-plane symmetry, the integrated transferred charge $q = 0.0092$ e/C atom. This value is different from that of the $19^\circ$ orientation, $0.0105$ e/C atom. Clearly, the oscillatory behavior of the transferred charge is sensitive to changes in bonding at the graphene–Pd interface and varies with in-plane orientation of graphene. As a result, the strength of the effective dipole layer, and hence the work function varies with domain orientation.

In conclusion, we observed six rotational domains of monolayer graphene on Pd(111), whose work functions are all different and lower than that of free-standing graphene. Our calculations suggest that this orientation dependence arises from spatial variations in charge transfer at the graphene–Pd interface. We expect similar phenomenon for graphene on other metals, although the magnitude of work function variation may depend on the strength of the graphene–metal interactions. Therefore, a precise control over the relative orientation between graphene and metal contacts is desirable for the large-scale fabrication of graphene devices.

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