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Influence of metal work function on the position of the Dirac point of graphene field-effect transistors

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We studied the effect of metal contact on the position of the Dirac point by means of transport measurements. To determine the sole effect of metal contact, we prepared more than 100 graphene devices following the same fabrication procedure and with a device layout that differed only in the type of metal electrode used. By measuring the peak position of the resistance, the Dirac points (V_g^{Dirac}) were recorded in the gate response. The work function of metal-graphene complex was found to be a fair phenomenological indicator of the location of V_g^{Dirac} in the transfer response. © 2009 American Institute of Physics. [doi:10.1063/1.3274039]

Electron transport through graphene has been extensively studied both theoretically and experimentally, in part due to the potential applications of graphene in nanoelectronics, but also because of scientific interest in the peculiar electronic structure of these materials. Perfect, infinite graphene is a zero-gap semiconductor, as its conically shaped valence and conduction bands touch each other at the Fermi level.¹ This feature provides a sound mapping of the energy dispersion of the massless Dirac fermions in free space, thereby delighting physicists in various fields.² The vanishing carrier density and linear dispersion relation near the Fermi level, combined with the geometrical peculiarity of graphene whereby every atom is on the surface, make the electronic structure highly tunable by external sources. Control of the Dirac point is not only of scientific interest but may also be exploited in graphene-based electronic devices. Previous studies have demonstrated modulation of the Dirac point along with changes in the concentration of external dopants or variations in the electrostatic bias.^{3,4} The ionic concentration and pH have also been shown to affect the position of the Dirac point. It has been suggested that charged ions present in the solution may screen impurity charges that have been unintentionally embedded in graphene devices.⁵⁻⁷

In transport experiments, however, the position of the Dirac point has been rather arbitrary and ambiguous. The effects of metal contact, edge shape, defects, and adsorbed species are intertwined and difficult to parameterize separately.⁸⁻¹¹ The effect of the metal contact is particularly intriguing because all transport measurements inevitably involve a metal-graphene interface.¹²⁻¹⁴ In the present work, we measure the position of the Dirac charge neutrality point, V_g^{Dirac} , in the gate transfer curve, which is obtained by averaging the values from four to six devices with the same type of metal electrode. We trace the role of the metal work function in determining the position of V_g^{Dirac} . Our findings indicate that the value of V_g^{Dirac} in the gate response scales with the work function of the metal-graphene complex. On the basis of the response, the metal-graphene interfaces can be

broadly categorized as either physically adsorbed or chemically bonded. In our experiments, graphene sheets were micromechanically cleaved from highly oriented pyrolytic graphite. Graphene devices were prepared over a heavily doped Si substrate with a 300 nm thick thermally grown SiO₂ layer. Once a suitable graphene sheet had been selected using optical microscopy and atomic force microscopy (AFM), deep UV lithography and electron-beam lithography were applied to generate electrode patterns onto the selected graphene sheet. To form the source and drain electrodes, various metals with different work functions were deposited by sputtering (for Co, Ni, Ti, Cr, Pd, and Au) or electron beam evaporation (for Pt, Au, Ti, Pd, and Al). The film-deposition technique had only a minor effect on the position of the Dirac point. To discriminate the effect of the metal work function, the fabrication parameters were kept constant as much as possible. We fabricated more than 100 graphene devices with different metal electrodes following the same fabrication process and using the same device layout. To determine the effect of the metal-graphene interface, we performed first-principles density functional theory calculations¹⁵ using the Vienna *Ab Initio* Simulation Package (VASP) and the provided pseudopotentials.^{16,17} The generalized gradient approximation was used in the description of the exchange correlation potential.¹⁸ The plane-wave basis set was employed with an energy cutoff of 400 eV.¹⁹

The main objective of our work was to elucidate the correlation between the type of metal electrode and the position of the Dirac point. With this motivation, we measured the gate-dependent resistance of graphene devices fabricated with various metal electrodes, as shown in Fig. 1(a). The inset of Fig. 1(b) shows an AFM image of a typical graphene transistor. We applied the same fabrication procedure for all devices, only changing the type of metal electrode used; the channel length of the devices was maintained at approximately 2 μm . The peak resistance corresponds to the position of the Dirac point of the graphene channel, V_g^{Dirac} , which varies depending on the type of metal electrode, as shown in Figs. 1(a) and 1(b). The width of the transfer curve also changes depending on the type of electrode. Nevertheless, in

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FIG. 1. (Color online) (a) Two-probe gate-transfer characteristics measured from graphene transistors with various metal contacts. (b) Measured Dirac points plotted as a function of the work function of the metal electrode (averaged values from four to six devices). The inset of (b) shows an AFM image of a graphene field-effect transistor.

this work, we concentrate on the position of the Dirac point rather than the variation in the width of the transfer curve. Various device parameters are likely to affect the width of the resistance curve, including the metal work function, the interface dipole, and the sample quality.²⁰ We note that shifts in the Dirac point can be easily utilized in sensor applications, whereas the width of the transfer curve is a much more complicated parameter that must be analyzed in terms of several device parameters. In Fig. 1(b), V_g^{Dirac} (V) appears to be correlated with the magnitude of the metal work function. Since the metal contact, as an electron reservoir, adjusts the Fermi level of the graphene, the position of the Dirac point should have some relation with the metal work function. However, the Fermi level alignment between a metal contact and graphene can be additionally affected by the interface dipole, as well as by the metal-graphene interface geometry. In this regard, we need to classify the metals into two groups: (1) metals that physisorb onto graphene (namely, Al, Au, and Pt) and (2) metals that chemisorb onto graphene (i.e., Ti, Ni, Co, and Pd). The relations between V_g^{Dirac} and metal work function for each group are plotted in Figs. 2(a) and 2(b), respectively. In addition to the work functions of the bare metal surfaces (as obtained from the literature²¹), the work functions of the metal-graphene complexes are also included for comparison. The presented work functions for the metal-graphene complexes were calculated from the geometry of a metal surface with a graphene over-layer, as reported previously.¹⁴ In actual devices, the interface geometry between the metal electrode and graphene is likely to vary significantly, and a generic model for the interface is

FIG. 2. (Color online) Position of the Dirac point in the gate response in relation to the work function of the metal electrode. The open squares represent the work functions of the metal surfaces (Ref. 21), and the solid triangles indicate the work functions of the metal-graphene complexes, as published previously (Ref. 14). The work function of the Ti-graphene complex, denoted by a solid star, was calculated using first-principles methods, as described in the text. The class of metals that physisorb onto the graphene surface are shown in (a) and those that chemisorb are represented in (b).

FIG. 3. (Color online) Geometries employed to calculate the work function of the Ti-graphene complex. (a) A Ti_{55} metal nanoparticle adsorbed onto graphene. (b) A Ti_{55} metal nanoparticle sandwiched between two graphene monolayers. (c) Four layers of Ti slab with graphene layers on both surfaces. The local potentials calculated along the arrows are plotted in the bottom panels. The energies in the vertical axes are with respect to the Fermi level.

difficult to identify. This feature will be discussed below.

It is noteworthy that V_g^{Dirac} (V) scales almost linearly with the work function of the metal-graphene complex [Fig. 2(a)]. Whereas, the relation between the V_g^{Dirac} (V) and the bare metal work function has a slight deviation, which may be ascribed to the presence of the dipole at the metal-graphene interface.¹⁴ In the case of chemisorbed metals [Fig. 2(b)], the correlation between the Dirac point and the metal work function becomes much less clear. We attribute this behavior to changes in the interface dipole arising from strong hybridization of the local charge associated with the metal-carbon chemical bonds. These findings indicate that, for the chemisorbed metals, the work function of the bare metal surface cannot be used as a relevant parameter for V_g^{Dirac} (V) of the graphene channel. However, the work function of the metal-graphene complex could be a salient parameter for V_g^{Dirac} (V), irrespective of whether the metal binds with graphene chemically or physically. These results thus indicate that the metal-graphene complex acts as a whole to adjust the Fermi level of the graphene channel.

Note that the work functions of the metal-graphene complexes, as shown by the solid triangles in Figs. 2(a) and 2(b), were obtained using a system comprised of a metal surface in contact with a graphene layer. In a realistic contact, however, the interface may not be a perfect two-dimensional interface between a well-defined metal surface and an infinite graphene layer. Instead, the metal surface may have islands and voids, such that the carbon atoms in the graphene layer may form chemical bonds with the metal islands. In this respect, it is pertinent to calculate the work function of the metal-graphene complex using various interface geometries. As a representative system, we calculated the work function of three different interface geometries of a Ti-graphene complex (Fig. 3). The optimized geometries for an icosahedral Ti_{55} nanoparticle on graphene, a Ti_{55} nanoparticle sandwiched between two graphene monolayers, and four layers of infinite Ti slab with graphene over-layers on both sides are shown in Figs. 3(a)–3(c), respectively. The graphene and metal layers were placed in the xy plane, and a vacuum region longer than 10 Å was included along the z direction (indicated by arrows in Fig. 3) in the supercell. We plotted the local potential along the z direction to calculate the work function of each interfacial geometry, as shown in the bottom panels of Fig. 3. The flat region of the local potential corre-

sponds to the vacuum level, which is emphasized by horizontal dotted lines.

The geometries in Figs. 3(a)–3(c) have work functions of 3.45, 3.99, and 3.83 eV, respectively. Comparison of Figs. 3(b) and 3(c) discloses that differences in the local interface shape of a metal-graphene complex can result in variations in the work function on the order of a few tenths of electron volts. A somewhat larger difference in work function is observed between the metal-exposed [Fig. 3(a)] and graphene-exposed [Figs. 3(b) and 3(c)] systems. Note that in a previous work it was assumed that the graphene overlayer was only on one side of the slab,¹⁴ whereas we used a symmetric slab geometry in order to directly determine the vacuum level in the plot of the local potential. Thus, an averaged value between the cases of the metal-exposed and graphene-exposed slabs can provide a better comparison with previous results. This indicates that despite the uncertainty in the interface geometry, the work function of the metal-graphene complex can be a good phenomenological indicator of the position of the Dirac point of the graphene channel. In the case of a physisorbed metal, it is thought that the effect of the interface geometry is less significant. Variation in the interfacial geometry gives rise to different amount of dipole effect. Nevertheless, as we observe in Fig. 2(a), V_g^{Dirac} is likely to be limited in the monotonic linear relation with the work function of the metal-graphene interface.

In summary, we have investigated the effect of the metal electrode characteristics on the position of the Dirac point of a graphene electron channel. To determine the position of the Dirac point, the peak of the resistance in the gate response was recorded. We compared the measured shifts of the Dirac point with the work function of various metal electrodes, and found that the different types of electrodes should be categorized as physisorbed or chemisorbed, and that the work function of the metal-graphene complex is a reasonable phenomenological indicator of the location of the Dirac point.

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