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Doping graphene with metal contacts

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Making devices with graphene necessarily involves making contacts with metals. We use density functional theory to study how graphene is doped by adsorption on metal substrates and find that weak bonding on Al, Ag, Cu, Au and Pt, while preserving its unique electronic structure, can still shift the Fermi level with respect to the conical point by $\sim 0.5$ eV. At equilibrium separations, the crossover from $p$-type to $n$-type doping occurs for a metal work function of $\sim 5.4$ eV, a value much larger than the graphene work function of 4.5 eV. The numerical results for the Fermi level shift in graphene are described very well by a simple analytical model which characterizes the metal solely in terms of its work function, greatly extending their applicability.

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Recent progress in depositing a single graphene sheet on an insulating substrate by micromechanical cleavage enables electron transport experiments on this two-dimensional system\textsuperscript{11,12}. Such experiments demonstrate an exceptionally high electron mobility in graphene, quantitization of the conductivity, and a zero-energy anomaly in the quantum Hall effect, in agreement with theoretical predictions\textsuperscript{3,4,5,6,7}. The spectacular effects arise from graphene’s unique electronic structure. Although it has a zero band gap and a vanishing density of states at the Fermi energy, graphene exhibits metallic behavior due to topological singularities at the $K$-points in the Brillouin zone\textsuperscript{3,4} where the conduction and valence bands touch in conical (Dirac) points and the dispersion is essentially linear within $\pm 1$ eV of the Fermi energy.

In a free-standing graphene layer the Fermi energy coincides with the conical points but adsorption on metallic (or insulating) substrates can alter its electronic properties significantly\textsuperscript{8,9,10,11,12,13,14,15}. Since electronic transport measurements through a graphene sheet require contacts to metal electrodes\textsuperscript{2,12,16,17} it is essential to have a full understanding of the physics of metal-graphene interfaces. In this paper we use first-principles calculations at the level of density functional theory (DFT) to study the adsorption of graphene on a series of metal substrates. The (111) surfaces of Al, Co, Ni, Cu, Pd, Ag, Pt and Au, covering a wide range of work functions and chemical bonding, form a suitable system for a systematic study.

Our results show that these substrates can be divided into two classes. The characteristic electronic structure of graphene is significantly altered by chemisorption on Co, Ni and Pd but is preserved by weak adsorption on Al, Cu, Ag, Au and Pt. Even when the bonding is weak, however, the metal substrates cause the Fermi level to move away from the conical points in graphene, resulting in doping with either electrons or holes. The sign and amount of doping can be deduced from the difference of the metal and graphene work functions only when they are so far apart that there is no wave function overlap. At the equilibrium separation, the doping level is strongly affected by an interface potential step arising from the direct metal-graphene interaction.

Based upon the DFT results, we develop a phenomenological model to describe the doping of graphene, taking into account the metal-graphene interaction. The model uses only the work functions of graphene and of the clean metal surfaces as input. For a given metal substrate, it allows us to predict the Fermi level shift in graphene with respect to the conical points \textit{i.e.}, both the type and concentration of the charge carriers. The model also predicts how metal work functions are modified by adsorption of graphene.

Some details of how DFT ground state energies and op-
timized geometries are calculated for graphene on metal (111) surfaces are given in Ref. [18]. We fix the in-
plane lattice constant of graphene to its optimized value
a = 2.445 Å and adapt the lattice constants of the met-
als accordingly. The graphene honeycomb lattice then
matches the triangular lattice of the metal (111) sur-
faces in the unit cells shown in Fig. 1. The approxi-
mation made by this procedure is reasonable, since the
mismatch with the optimized metal lattice parameters
is only 0.8-3.8%. We have verified explicitly that the
structures shown in Fig. 1 represent the most stable con-
figurations of graphene on the metal substrates studied.
The equilibrium separations, binding energies and work
functions are listed in Table I.

<table>
<thead>
<tr>
<th>Metal</th>
<th>d_{eq} (Å)</th>
<th>∆E (meV)</th>
<th>W_M (eV)</th>
<th>W (eV)</th>
<th>W_{exp} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gr</td>
<td>2.05</td>
<td>125</td>
<td>5.47</td>
<td>4.48</td>
<td>4.6^a</td>
</tr>
<tr>
<td>Ni</td>
<td>2.05</td>
<td>160</td>
<td>5.44</td>
<td>3.66</td>
<td>3.9^a</td>
</tr>
<tr>
<td>Co</td>
<td>2.30</td>
<td>84</td>
<td>5.67</td>
<td>4.03</td>
<td>4.3^a</td>
</tr>
<tr>
<td>Pd</td>
<td>3.41</td>
<td>27</td>
<td>4.22</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>3.33</td>
<td>43</td>
<td>4.92</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>3.26</td>
<td>33</td>
<td>5.22</td>
<td>4.40</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>3.31</td>
<td>30</td>
<td>5.54</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>3.30</td>
<td>38</td>
<td>6.13</td>
<td>4.87</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>3.3^a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aRef. [8]

The results immediately show that the metals can be
divided into two classes. Graphene is chemisorbed on Co,
Ni and Pd(111), leading to binding energies ∆E ∼ 0.1
eV/carbon atom and equilibrium separations d_{eq} ≲ 2.3
Å. In contrast, adsorption on Al, Cu, Ag, Au and Pt(111)
leads to a weaker bonding, ∆E ≲ 0.04 eV/carbon atom,
and larger equilibrium separations, d_{eq} ∼ 3.3 Å. These
results are in agreement with previous calculations and
experimental data [5, 10, 12, 21, 22].

To identify the changes in the graphene electronic
structure induced by adsorption, we calculate the band
structures as illustrated in Fig. 2 for some typical exam-
ple cases. When graphene is chemisorbed (on Co, Ni,
and Pd) the graphene bands are strongly perturbed and acquire a mixed graphene-metal character. In particular,
the characteristic conical points at K are destroyed, see
the bottom panels of Fig. 2. When the interaction is
weaker (Al, Cu, Ag, Au, Pt), the graphene bands, includ-
ing their conical points at K, can still be clearly identi-
fied; see the upper panels of Fig. 2. However, whereas
in free-standing graphene the Fermi level coincides with
the conical point, adsorption generally shifts the Fermi
level. A shift upwards (downwards) means that electrons
(holes) are donated by the metal substrate to graphene
which becomes n-type (p-type) doped.

For metal-graphene equilibrium separations, graphene
is doped n-type on Al, Ag and Cu, and p-type on Au
and Pt; the corresponding Fermi level shifts are plotted
in Fig. 3. Because the work functions of graphene, W_G,
and of most metal surfaces, W_M, differ, as soon as graphene
interacts with a metal, electrons are transferred from one
This electron transfer results in the formation of an interface dipole layer and an accompanying potential step formation at the graphene-metal interface. Right: plane-averaged difference electron density $\Delta n(z) = n_{M|G}(z) - n_M(z) - n_G(z)$ showing the charge displacement upon formation of the graphene-Pt(111) interface.

FIG. 4: (Color online) Left: schematic illustration of the parameters used in modeling the interface dipole and potential step formation at the graphene-metal interface. Right: plane-averaged difference electron density $\Delta n(z) = n_{M|G}(z) - n_M(z) - n_G(z)$ showing the charge displacement upon formation of the graphene-Pt(111) interface.

to the other to equilibrate the Fermi levels. A schematic representation is shown in Fig. 1 for the case of electron transfer from graphene to the metal. To a good approximation, the graphene density of states (DOS) is described by $D(E) = D_0|E|$, with $D_0 = 0.09/(eV^2$ unit cell) for $E$ within 1 eV of the conical points. Since this DOS is much lower than that of the metal, equilibrium is effectively achieved by moving the Fermi level in graphene and even a small electron transfer will shift the Fermi level significantly. A transfer of 0.01 electrons would lower the Fermi level by 0.47 eV.

This electron transfer results in the formation of an interface dipole layer and an accompanying potential step $\Delta V$. We can use the plane-averaged electron densities $n(z)$ to visualize the electron redistribution $\Delta n(z) = n_{M|G}(z) - n_M(z) - n_G(z)$ upon formation of the interface. As shown in Fig. 4, $\Delta n(z)$ is localized at the interface. The sign and size of the interface dipole are consistent with the changes of the metal work function upon adsorption of graphene, see Table I.

Naively one would assume that graphene is doped with electrons if $W_G > W_M$ and doped with holes if $W_G < W_M$. The crossover point from $n$- to $p$-type doping would then be at $W_M = W_G$. The results obtained at the equilibrium separations of the graphene sheet and the metal surfaces ($d \sim 3.3$ Å; see Fig. 3) show that this is clearly not the case. Instead, the crossover point lies at $W_M - W_G = 0.9$ eV. Only when the graphene-metal separation is increased significantly does the crossover point decrease to its expected value, as illustrated by the upper curve for $d = 5.0$ Å in Fig. 3. This clearly demonstrates that the charge redistribution at the graphene-metal interface is not only the result of an electron transfer between the metal and the graphene levels. There is also a contribution from a metal-graphene chemical interaction. Such an interaction, which has a significant repulsive contribution, has been found to play an important role in describing dipole formation when closed shell atoms and molecules are adsorbed on metal surfaces [23, 24].

The dependence of this interaction on the metal-graphene separation $d$ is mapped out in Fig. 6 in terms of the dependence of the Fermi level shift $\Delta E_F$ on $d$. We use the parameters shown in Fig. 4 to construct a simple and general model with which to understand these results. The work function of the graphene-covered metal is given by $W(d) = W_M - \Delta V(d)$ where $\Delta V$ is the potential change generated by the metal-graphene interaction. The Fermi level shift in graphene is modeled as $\Delta E_F(d) = W(d) - W_G$. The key element is modeling the potential step $\Delta V = \Delta V_{tr}(d) + \Delta V_c(d)$ in terms of a “non-interacting” charge transfer contribution $\Delta V_{tr}$ driven by the difference in work functions and a contribution $\Delta V_c$ resulting from the metal-graphene chemical interaction.

The charge transfer contribution is modeled by a plane capacitor model as indicated in Fig. 4 $\Delta V_{tr}(d) = \alpha N(d)z_d$ where $\alpha = e^2/\varepsilon_0A = 34.93$ eV/Å with $A = 5.18$ Å$^2$ the area of the graphene unit cell and $N(d)$ is the number of electrons (per unit cell) transferred from graphene to the metal (becoming negative if electrons are transferred from the metal to graphene). $z_d$ is the effective distance between the charge sheets on graphene and the metal. $z_d < d$ as most of the charge is located between the graphene layer and the metal surface as illustrated in Fig. 4. We model it as $z_d = d - d_0$ with $d_0$ a constant.

Integrating the (linear) density of states of graphene yields a simple relation between $N(d)$ and $\Delta E_F(d)$: $N = \pm D_0\Delta E_F^2/2$. Using the relations introduced in the previous two paragraphs we can then express $\Delta E_F(d)$ as

$$\Delta E_F(d) = \pm \sqrt{1 + 2\alpha D_0(d - d_0)|W_M - W_G - \Delta V_c(d)| - 1} / \alpha D_0(d - d_0)$$

(1)

where the sign of $\Delta E_F$ is given by the sign of $W_M - W_G$.
The critical metal work function \( W_M = W_0 \) where the Fermi level is at the conical points of graphene, can be obtained from Eq. (1) for \( \Delta E_F(d) = 0 \). It gives \( W_0(d) = W_G + \Delta_c(d) \). The contribution of the chemical interaction term \( \Delta_c \) depends strongly on the distance \( d \) between graphene and the metal surface. At a large distance \( d \gtrsim 4.2 \text{ Å} \), \( \Delta_c \ll 1 \text{ eV} \) and \( W_0(d) \approx W_G = 4.5 \text{ eV} \), whereas at the equilibrium separation \( d_{eq} = 3.3 \text{ Å} \), \( \Delta_c \approx 0.9 \text{ eV} \) and \( W_0(d) \approx 5.4 \text{ eV} \). This agrees with the DFT results shown in Fig. 3. The chemical interaction thus leads to a sizeable potential step at the equilibrium separation, which is downwards from metal to graphene, and one can immediately obtain the work function \( W \) by Eq. (1) is demonstrated in Figs. 3 and 5. From \( \Delta E \) the Fermi level is at the conical points of graphene, can stand the graphene, Fermi level shifts in graphene for all metal substrates. If we fit these \( \Delta_c(d) \) should vanish. Therefore, parametrizing \( \Delta_c(d) = e^{-\kappa d}(a_0+a_1 d+a_2 d^2) \) gives \( \kappa = 1.6443 \text{ Å}^{-1} \), \( a_0 = -2048.56 \text{ eV} \), \( a_1 = 1363.87 \text{ eV/Å} \), \( a_2 = -205.737 \text{ eV/Å}^2 \), where \( d \gtrsim 3.0 \text{ Å} \). The general applicability of this equation to all metal substrates can be explained from the weak metal-graphene interaction. The charge redistribution is then dominated by exchange repulsion and is almost independent of the metal species [26].

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[18] We use a plane wave basis set with a kinetic energy cutoff of 400 eV in the PAW formalism, at the level of the local spin density approximation, as implemented in VASP [19]. The supercell contains a slab of six layers of metal atoms with a graphene sheet adsorbed on one side and a vacuum region of \( \sim 12 \text{ Å} \). A dipole correction is used [20]. We apply 36 \times 36 and 24 \times 24 k-point grids to sample the Brillouin Zone (BZ) of the small and large cells in Fig. 1, respectively, and use the tetrahedron method for BZ integrations that include the \( \Gamma \), \( K \) and \( M \) special points. Total energies are converged to \( 10^{-5} \text{ eV} \).
[25] We obtain \( \Delta_c(d) \) by least-squares fitting Eq. (1) to the DFT results for \( \Delta E_F(d) \) for Cu (111) with \( d_{0} = 2.4 \text{ Å} \). This value of \( d_{0} \) provides the best fit of \( \Delta E_F(d) \) for other metal surfaces. At large \( d \) the chemical interaction term \( \Delta_c(d) \) should vanish. Therefore, parametrizing \( \Delta_c(d) = e^{-\kappa d}(a_0+a_1 d+a_2 d^2) \) gives \( \kappa = 1.6443 \text{ Å}^{-1} \), \( a_0 = -2048.56 \text{ eV} \), \( a_1 = 1363.87 \text{ eV/Å} \), \( a_2 = -205.737 \text{ eV/Å}^2 \), where \( d \gtrsim 3.0 \text{ Å} \). The general applicability of this equation to all metal substrates can be explained from the weak metal-graphene interaction. The charge redistribution is then dominated by exchange repulsion and is almost independent of the metal species [21].