Tuning the Graphene Work Function by Electric Field Effect

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ABSTRACT

We report variation of the work function for single and bilayer graphene devices measured by scanning Kelvin probe microscopy (SKPM). By use of the electric field effect, the work function of graphene can be adjusted as the gate voltage tunes the Fermi level across the charge neutrality point. Upon biasing the device, the surface potential map obtained by SKPM provides a reliable way to measure the contact resistance of individual electrodes contacting graphene.

High conductivity1,2 and low optical absorption3,4 make graphene an attractive material for use as a flexible transparent conductive electrode.5–8 This atomically thin carbon layer provides the additional benefit that its work function can be adjusted by the electric field effect (EFE). Since the band alignment of two different materials is determined by their respective work functions, control over the graphene work function is the key to reducing the contact barriers of graphene top electrode devices.9,10 Previous scanning probe based studies11–13 reveal that the work function of graphene is in a similar range to that of graphite, ~4.6 eV,14 and depends sensitively on the number of layers.15,16 However, the active controlling of the graphene work function has yet to be demonstrated.

In this study, we apply scanning Kelvin probe microscope (SKPM) techniques to back-gated graphene devices and demonstrate that the work function can be controlled over a wide range by EFE induced modulation of carrier concentration. SKPM is an atomic force microscope (AFM) based experimental technique that can map the surface potential variation of a sample surface relative to that of a metallic tip.17 The change of work function is ascribed by the Fermi level shift due to the EFE induced carrier modulation and is well quantified by the electronic band structure of graphene. On biased graphene devices, SKPM also allows us to accurately measure graphene/metal contact resistances by mapping the surface potential of a device. The wide range of control over the work function demonstrated here suggests graphene as an ideal material for applications where work function optimization is important.

Graphene samples were prepared by mechanical exfoliation18 on Si wafers covered with 300 nm thick SiO2, and then Cr/Au electrodes (5 nm/30 nm thickness) were fabricated by standard electron beam lithography. The thickness of each graphene samples was characterized by Raman spectroscopy (see Figure S1 in Supporting Information). In this work, we have studied three single layer graphene (SLG) and two bilayer graphene (BLG) transistors. Figure 1a shows a schematic diagram of the simultaneous SKPM experiments with the EFE induced carrier modulation. The SKPM measurements were performed by a commercial atomic force microscope (XE-100, Park Systems Corp.) in air and dry nitrogen environment at room temperature. During observing SKPM data, we applied an ac voltage amplitude of ~0.3–0.5 V and a frequency of 17 kHz to a Cr/Au coated probe. The SKPM images were obtained with a two-way scan method to avoid topographic artifacts. The first scan was for topography by noncontact mode with dithering resonant frequency ~120–170 kHz and the second scan was for SKPM image with 10–30 nm constant height mode.

The carrier density, and hence the Fermi energy, $E_F$, of the graphene, is controlled by the gate voltage $V_g$ applied to the degenerately doped Si substrate. Figure 1b–e shows the optical, AFM topographic, and surface potential images of one of the SLG devices used in this experiment. In general, the local surface potential $V_{CPD}$, obtained from the contact potential difference between the SKPM probe and local surface,17 is sensitively influenced by $V_g$. By comparing $V_{CPD}$
maps taken at $V_g = 0$ (Figure 1d) and 10 V (Figure 1e), we notice a much larger signal contrast at higher $V_g$. In particular, $V_{CPD}$ tends to increase to values comparable to $V_g$ on the insulating SiO$_2$ substrate. This indicates that the unscreened electric field from the back gate is the dominant source for the contrast in $V_{CPD}$ image in the bare SiO$_2$ regions. In order to minimize a direct exposure of the SKPM probe to this long-range electrostatic influence, we limit our surface potential analysis to areas within the conducting part of the device, where the subtle local surface potential variation can be readily probed.

Utilizing multiterminal device geometry, we carry out a comparison study of the surface potential (Figure 2a) and transport measurement (Figure 2b) on the same device as a function of $V_g$. In the particular device shown in this figure, we determine the charge neutral gate voltage $V_D = 48$ V.

**Figure 1.** (a) Schematic diagram for measuring the EFE modulation of the surface potential of graphene devices using the SKPM. Gate voltage $V_g$ is applied to the degenerately doped Si substrate and the electrodes of graphene device are grounded. (b–e) From top to down, optical image (b), AFM topography (c), and SKPM images of graphene device $V_g = 0$ V (d) and 10 V (e), respectively.

**Figure 2.** (a) Top panel shows an AFM topography of the device. The surface potential map of a selected area far from the graphene edges (marked by a dotted line box) is analyzed in detail in order to minimize the effect from unscreened long ranged electrostatic force from the gate. Small spatial variations in the topographic and SKPM signals are found to be correlated on the top of the graphene surface. $V_g = 55$ V in this image. A schematic energy alignment diagram for the graphene sample and the metallic electrode is displayed where $E_{vac}$, $E_F$, and $E_D$ are representing the vacuum energy level, Fermi energy, and the charge neutrality point of graphene, respectively. (b) Transport measurement using the two outer terminals as shown in the inset. From the peak position we have $V_D = 48$ V. (c) The surface potential profile along the x-axis (averaged over the y-axis) at different gate voltages $V_g$ (at every 1 V from 39 to 60 V). (d) The CPD of graphene $V_{CPD}^r$ and electrode $V_{CPD}^e$ at different gate voltages obtained from the average surface potential in the selected gray and red shaded area in (c). The inset shows $\Delta V_{CPD} = V_{CPD}^r - V_{CPD}^e$ as a function of $V_g$. The vertical dashed line indicates $V_g = V_D$ where the corresponding $\Delta V_{CPD}$ is highlighted by the horizontal arrow.
from the gate voltage corresponding to a sharp resistance peak. In the surface potential map where $V_g$ is fixed, we observe a stepwise increase of $V_{\text{CPD}}$ at the junctions between graphene and electrodes regions, but no significant spatial variation within each region. Similar features are observed at different values of $V_g$ (Figure 2c), where the overall line profiles of $V_{\text{CPD}}$ in the two regions shift upward with a common background as $V_g$ increases. This background signal is due to the unscreened long-range electrostatic interaction between the conducting cantilever probe and the back gate and, thus, is insensitive to a small spatial position change of the SKPM tip. Since $V_g$ should not influence the local surface potential in metallic electrode, the background signal on the metal electrode surface can serve to separate the spatially constant background from the relative change in the local surface potential. In particular, the EFE induced local surface potential change in graphene, $\Delta V_{\text{CPD}}$, can be obtained by $\Delta V_{\text{CPD}} = V_{\text{CPD}}^e - V_{\text{CPD}}^g$, where $V_{\text{CPD}}^e$ and $V_{\text{CPD}}^g$ are the average $V_{\text{CPD}}$ in the electrode and the graphene, respectively (Figure 2d, inset). Interestingly, a sudden change $\Delta V_{\text{CPD}}$ is observed at the charge neutrality point ($V_g = V_D$), as indicated by the vertical dashed line. Similar features are always present at the neutrality point in other SLG samples studied in this experiment. We also perform similar measurement of $\Delta V_{\text{CPD}}$ on BLG samples. Similar to the SLG, $\Delta V_{\text{CPD}}$ of BLG can be modulated by applied gate voltage (see Figure S2 in Supporting Information). Unlike the SLG samples, however, there is no such sudden change of $\Delta V_{\text{CPD}}$ at the BLG charge neutrality point, implying the difference of the electronic structures of the samples as we will discuss later.

The relative surface contact potential difference, $\Delta V_{\text{CPD}}$, obtained above can be related to the difference in work function between two different surfaces: $\epsilon \Delta V_{\text{CPD}} = W_{\text{elec}} - W_{\text{sample}}$, where $W_{\text{elec}}$ and $W_{\text{sample}}$ are work functions of the electrode and graphene sample surfaces, respectively. Since $W_{\text{elec}}$ is insensitive to $V_g$ due to the large density of states near the Fermi level in the gold electrodes, the observed variation of $\Delta V_{\text{CPD}}(V_g)$ reflects the EFE modulation of $W_{\text{sample}}$. We note that the work function of our gold-coated tip is close to $W_{\text{elec}}$ since both the SKPM probe and the electrodes are made of gold and that they are exposed in the same experimental condition. A separately performed calibration measurement yields $W_{\text{tip}} = 4.82 \pm 0.08$ eV (see Figure S3 in Supporting Information). Using this value, we estimate $W_{\text{sample}} \approx W_{\text{tip}} - \epsilon \Delta V_{\text{CPD}}$. Figure 3a shows the resulting $W_{\text{sample}}$ as a function of $\Delta V_g = V_g - V_D$. Here we list results obtained from several SLG and BLG devices in different experimental conditions. For each data set, the transport characteristics are measured independently to obtain $V_D$. We found that $V_D$ ranges from 30 to 50 V for most devices. The positive sign of $V_D$ indicates that the samples are hole doped from the environment, suggesting a dipole layer formation on the top of graphene surface. Despite this uncontrolled environment doping, we demonstrate that the work function of sample can be tuned by EFE within the range $4.5 - 4.8$ eV for SLG and $4.65 - 4.75$ eV for BLG in ambient and dry nitrogen conditions. With further optimization using chemical functionalization, a wide range of work functions can potentially be achieved for applications which require adjustment of the work function.

The behavior of EFE tuned $W_{\text{sample}}$ can be explained by the change of $E_F$ in graphene devices. From the schematic diagram in Figure 3b, we note $W_{\text{sample}} = \Delta W_a + W_{0g} - E_F$, where $\Delta W_a$ is the offset of work function due to the adsorbate dipole layer formation and $W_{0g}$ is the intrinsic work function of undoped graphene. In order to estimate $W_{0g}$ from the measured $W_{\text{sample}}$, an independent estimation of $\Delta W_a$ is necessary. In the experiments performed in air and dry nitrogen atmosphere, we estimated $|\Delta W_a| < 50$ meV for both SLG and BLG (see Figure S4 in Supporting Information). This upper bound of $|\Delta W_a|$ allows us to estimate the work functions of undoped SLG and BLG from the measured
Figure 4. (a) Current ($I$) and bias voltage ($V_{SD}$) characteristic of a SLG device. The slope of the curves indicates the two terminal resistance of device (3.44 kΩ). Upper inset shows the optical microscope image of the device. Lower inset shows the resistance as a function of $V_g$. The vertical arrow indicates the gate voltages and dotted line, $V_g$. (b) Topographic AFM image (top) and surface potential images of the area marked by the red rectangular box in (a). The drain electrode is grounded while the source electrode is biased by $W_{sd}$ between electrodes and graphene. The proportion of the source and drain contact resistances and the channel resistance are marked by $r_s$, $r_d$, and $r_c$, respectively.

Finally, we discuss the simultaneous SKPM surface potential mapping on graphene devices with a finite bias voltage $V_{SD}$ applied between two electrodes. Figure 4a shows the current ($I$) versus $V_{SD}$ characteristics at a fixed gate voltage. The slope of $I$–$V_{SD}$ yields a resistance of 3.44 kΩ which includes the contributions of contact resistances between each electrode and the graphene channel. The simultaneous SKPM surface potential mapping provides a way to estimate these contributions independently. Figure 4b displays topographic and surface potential mapping of the same device with increasing $V_{SD}$ from 0 to 2 V. The surface potential of the grounded source electrode remains close to 0 V, while the surface potential of the biased drain electrode shifts upward as $V_{SD}$ increases. From the horizontal profile of these images (Figure 4c), we clearly observe linearly increasing $V_{CPD}$ in the channel and kinks in $V_{CPD}$ at the junctions. We attribute these sudden potential drops to the contact resistance between the electrodes and graphene. By taking the grounded drain electrode as the reference point ($V_{CPD} (V_{SD} = 0)$) and normalizing the $V_{CPD}$ by $V_{SD}$, all the surface potential profiles at different $V_{SD}$ collapse into one universal curve ($V_{CPD} (V_{SD}) - V_{CPD} (V_{SD} = 0)) / V_{SD}$ (Figure 4d). The vertical ratios between the kinks and the slope correspond to the source and drain contact resistances ($r_s$ and $r_d$) and graphene channel resistance ($r_c$). Considering that the total two terminal resistance of this device is 3.44
kΩ, we obtain $r_s: r_c: r_s = 0.5: 1.7: 1.24$ kΩ for this particular device.

In conclusion, by employing a gate modulated SKPM measurement, we have demonstrated that the work function of graphene can be substantially adjusted by EFE. This widely tunable work function makes graphene an attractive material for low contact barrier electrodes. The simultaneous SKPM surface potential imaging allows us to evaluate the contacts of graphene devices.

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Supporting Information Available: Optical images and Raman spectroscopy of single-layer graphene (SLG) and bilayer graphene (BLG) for confirming thickness, the surface potential modulation of a BLG device by the change of gate voltage, the calibration of the work function of SKPM probes, and work function offset of SLG and BLG. This material is available free of charge via the Internet at http://pubs.acs.org.

References