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Effective doping of single-layer graphene from underlying SiO$_2$ substrates

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When a single-layer graphene (SLG) is on SiO$_2$ substrates, the charge exchange at their interface results in a dipole, which direction strongly depends on the contact potential difference between the SLG and the substrates. Due to the longer experimental charge screening length of SLG than its thickness, the charge redistribution imposes effective $p$ or $n$ doping to SLG films. The substrate-dependent doping of SLG films is further confirmed by Raman and electrical measurements. Also, the unique electronic structures of SLG films make them sensitive to the doping rather than effective gating from the SiO$_2$ substrates.

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Graphene-derived nanomaterials are promising for applications such as atomically thin transistors, sensors, and other nanoelectronic devices. Since the discovery of single-layer graphene (SLG), it has attracted intensive interest due to its two dimensionality and unique physics including quantum spin Hall effect, phase-coherent transport, bipolar supercurrent, suppression of the weak localization, and deviation from the adiabatic Born-Oppenheimer approximation. The unique structure and properties of graphene offer unprecedented opportunities and potentials in fundamental studies as well as in future nanoelectronics.

Both theoretical and experimental results have demonstrated that the Fermi energy shift of SLG can be achieved by deliberate doping from metal, gas molecules, or electrical gating. The possibility to open the energy gap in SLG films has been investigated by theoretical and experimental works, the substrate charge impurity by graphene layers has been investigated. Moreover, the effect of SiO$_2$ substrate has been ignored for a long time until a recent discovery that the surface SiO$^-$ bonds efficiently grafted the organic thin-film transistors. For the SLG films deposited on SiO$_2$ substrates, perhaps unexpected from its perfect two-dimensional structure, the carrier density inhomogeneity has been identified and attributed to either the intrinsic mechanical ripples in the SLG sheet or the charged impurities in the underlying substrates. Although the screening of the substrate charge impurity by graphene layers has been investigated by theoretical and experimental works, the impacts of the underlying SiO$_2$ substrate to graphene films are not fully elucidated. Herein, we scrutinized this issue using electrostatic force microscopy (EFM), Raman spectroscopy, and electrical characterizations. Our results suggest that the effective doping from the underlying substrate is predominant rather than the effective gating from substrates. It is concluded that the contact potential difference between SiO$_2$ substrates and SLG films controls the direction of the dipole formed at the interface. The substrate-induced electron injection (depletion) in SLG films actually imposes effective $n$-($p$-) doping to the SLG films.

SLG films were obtained using the micromechanical exfoliation technique. In brief, natural graphite flakes (from NGS) were repeatedly cleaved with adhesive tapes and then transferred to various SiO$_2$ substrates. We verified the SLG films using Raman spectroscopy and atomic force microscopy (AFM), as previously described. Raman measurements were performed at room temperature in a WITEC confocal spectrometer with a 488 nm excitation laser operated at a low power level ($\sim 1$ mW) in order to avoid any heating effect. The EFM study was performed by a dual-pass technique in tapping mode. Topography information was acquired in the first scan; the second scan was then performed while the tip was maintained at a constant distance $\sim 30$ nm above the surface based on the recorded profile. During the second scan (interleave scan), a dc voltage is applied to the tip. The long-range electrostatic force between the tip and the sample surface alters the tip resonance frequency, inducing a change in both phase and amplitude signals. Recording the phase shift reveals information about charge/potential distribution on the sample surface. An Asylum Research model MFP-3D system with Olympus (OMCL-AC240TM) Pt-coated cantilevers is used for this experiment. The tip curvature radius is $\sim 15$ nm, the quality factor is $\sim 190$, and the resonance frequency is $\sim 70$ kHz. EFM can map out the phase shift ($\Delta \phi$) of the cantilever, a lag between the drive frequency, and the cantilever oscillation. The $\Delta \phi$ is related to electrical force gradient ($dF/dz$) by the equation $\tan(\Delta \phi) \sim (k/Q)(dF/dz)$, where $Q$ and $k$ represent the quality factor and the elastic constant of the cantilever and $z$ is the distance between the tip and the sample surface. Figure 1(a) schematically shows the tip-sample system in our EFM setup. When the capacitive force dominates, the electrostatic force $F$ can be normally described as

$$F = \frac{1}{2} \frac{dC}{dz} \Delta V^2,$$

where $C$ is the capacitance of the tip-sample system and $\Delta V$ is the potential difference between the tip and the sample ($\Delta V=V_{\text{tip}}-V_0$). $V_{\text{tip}}$ is the voltage applied to the tip and $V_0$ is actually the contact potential difference between the sample and the tip. ($V_0=\Phi_{\text{sample}}-\Phi_{\text{tip}}$, where $\Phi$ represents the Fermi level of the materials.)

The phase shift can then be derived as

$$\Delta \phi = -\arcsin \left[ \frac{Q d^2 C}{2k dz^2} (\Delta V)^2 \right].$$

As seen from Eq. (2), the minimum phase shift occurs when $V_{\text{tip}}=V_0$. Therefore, $V_0$ is obtained by fitting the phase-
shift data at different $V_{\text{tip}}$ to the following equation: 
\[ \Delta \phi = -\arcsin[S(V_{\text{tip}} - V_0)^2] + T, \] 
where $S$ is related to the parameter $(Q/2k)(d^2C/dz^2)$ and $T$ is the offset in experimental measurements. The value of $V_0$ can be determined from the valley point of the fitted curve. The SiO$_2$ substrates [300 nm thermal oxide on As-doped Si (0.001–0.005 Ω cm)] with various values of $V_0$ (0.86, 0.50, 0.19, and 0.10 V) were selected. It is noted that the values vary with the method of growing SiO$_2$ and the cleaning process of SiO$_2$ surface. It is believed that the impurities or surface chemical bonds may cause the difference in $V_0$. We have also intentionally modified the surface of SiO$_2$ substrates with $m$-aminophenyl trimethoxysilane, where the $V_0$ for the modified substrates can be extended to $-0.12$ V.

SLG films obtained from mechanical exfoliation sometimes are in junction with the few-layer-graphene (FLG) films. We first show that the $V_0$ of the isolated SLG is different from that of the SLG connected to FLG films. Figure 1(b) demonstrates the typical EFM images (left: $V_{\text{tip}} = -1.5$ V and right: $V_{\text{tip}} = +1.5$ V) for the graphene films on a SiO$_2$ substrate, where A and B represents the SLG connected to FLG films and the isolated SLG. Figure 2(c) shows that the SLG films A and B are with the same thickness $0.9$ nm. It is worthy pointing out that this measured thickness falls into the range of reported SLG thickness which varies from 0.4 to 1.2 nm. The variation has been attributed to the AFM instrumental offset. The isolated graphene B gives a brighter contrast than A at negative tip voltage, while a darker contrast is obtained if the tip voltage is positive. The nice fitting of the EFM results to Eq. (3) indicates that the capacitive force dominates under our EFM measurement conditions [Fig. 1(d)]. It allows us to extract the $V_0$ for both samples. The $V_0$ of the isolated graphene B is $\sim 0.74$ V, which is higher than that of SLG A (0.65 V). Since both A and B are on the same substrates (with a $V_0$ of 0.89 V), the observed lower $V_0$ of SLG A must be attributed to the influence from the jointed FLG films which exchange carriers with the SLG A. Datta et al. showed that the $V_0$ of FLG films increases with film thickness, approaching a bulk value for many-layer graphenes. Their results suggested that the SLG was not able to completely screen off the substrate $V_0$, likely owing to its intrinsically low carrier concentration. Similarly, our experiment demonstrates that the isolated SLG B can only partially screen off the substrate $V_0$ (0.89 V), giving a measured $V_0$ of 0.74 V. The better screening observed for SLG A (0.65 V) therefore suggests that the connected FLG films can provide carriers to the SLG for enhancing the screening effect.

It is likely that the screening effect is originated from the charge exchange (as a result of dipole formation) between the graphene and the substrates. In principle, it is possible to control the polarity of the dipole—hence the type of the charge added into the graphene layers—by selecting the substrates with suitable $V_0$. To demonstrate the possibility, we examined the effect of various SiO$_2$ substrates on the $V_0$ of SLG and FLG. Figure 2(a) shows that the measured $V_0$ either increases or decreases with the sample thickness, depending on the initial $V_0$ of bare substrates (shown as the points at 0 V).
Interestingly, when the substrate has a small size of FLG films to reduce the unwanted doping effect from these processes may give uncertain doping effects. Figure 3 shows the transfer characteristics (drain current vs gate voltage) for three transistor devices based on the selected SLG films on various substrates (with $V_{G0} = 0.86$, 0.50, and −0.12 V, respectively). The shape and the size of mechanically exfoliated graphene films are difficult to control. Consequently, the quantitative comparison between devices cannot be based on obtained absolute conductance. Fortunately, the gate voltage corresponding to the valley point in the transfer curves, which indicates the transition point between electron and hole conductions, allows us to characterize the relative Fermi level (or doping behaviors). The transistors based on SLG or FLG films and therefore no significant charge exchange occurs between the graphene layers and the substrates. These results clearly suggest that the contact potential difference between the substrate and graphene layers drives the carrier redistribution at the substrate-graphene interface.

If a SLG or a thin FLG is used, the direct consequence of the incomplete potential screening (or charge exchange) is the electron injection or depletion in graphene. In a general sense, electron injection (depletion) is referred to the effective $n$-($p$-) doping from substrates to FLG or SLG films. Figure 2(b) plots the change in the sample $V_{G0}$ after SLG screening vs the initial substrate $V_{G0}$, showing the substrate-dependent doping effect to SLG films. The positive value of $[V_{G0}(SLG)−V_{G0}(sub)]$ indicates that the electron concentration in SLG is increased and the negative one represents the decrease in electron concentration. The effect of substrates demonstrated in Fig. 2(b) only refers to the change in carrier concentration (or shift of Fermi energy); for example, $n$ doping occurs when $V_{G0}(SLG)−V_{G0}(sub)$ is $>0$. The eventual doping state of the SLG, however, also depends on its initial carrier concentration (contributed from the possible $p$ doping in ambient). Nevertheless, the results postulate the possibility of tuning electronic property of graphene devices by substrates.

To examine the doping from substrates electrically, we prepared graphene field-effect transistors by evaporating source and drain electrodes (Au with a channel length $\sim 15 \mu m$) directly on top of the graphene films without using any photolithography process. The photoresist or other chemicals involved in photolithography or impurities resulting from these processes may give uncertain doping effects.
results suggest that the effective gating from the substrates is not as pronounced as the direct doping. This could be attributed to the unique semimetallic characteristics of SLG films which make them less sensitive to the effective gating attributed to the unique semimetallic characteristics of SLG is not as pronounced as the direct doping. This could be

Raman spectroscopy is a powerful tool to reveal intrinsic optical properties and structures of various carbon materials. Figure 4(a) shows typical Raman spectra for a SLG obtained at room temperature with 488 nm laser excitation. The characteristic G (~1582 cm\(^{-1}\)) and 2D (~2690 cm\(^{-1}\)) Raman bands are sensitive to the presence of doping.\(^{10,29}\) Electron and hole dopings not only impose shifts of the ambipolar character for SLG films but also have distinct effects on the Raman modes for SLG films. It has been reported that p doping caused upshifting for both G and 2D Raman frequencies, while n doping resulted in opposite shifting in G and 2D frequencies.\(^{10,29}\) Based on these observations, the Raman 2D vs G frequency map has been used to distinguish the n or p doping to SLG films.\(^{29}\) Figures 4(b)–4(d) map the 2D- and G-band frequencies measured at different locations of the SLG film on three substrates with \(V_0=0.86, 0.50, \) and ~0.12 V, respectively. The data points in each graph can be fitted by a downward (or upward) line, showing that variation in 2D frequency inversely (or proportionally) correlates with variation in G frequency, where the downward (upward) line indicates that the SLG is n-(p-)doped. The Raman results for these SLG films are consistent with the electrical characterizations, confirming that n or p doping can be controlled by the substrates with various values of \(V_0.\)

In summary, we studied the \(V_0\) of SLG on insulating substrates using EFM. It was found that graphene layers tend to screen off the potential of the underlying substrates as a result of the charge exchange (dipole formation) at their interface. The charge exchange leads to the doping in graphene films, which, in turn, modulates the electronic properties of the SLG films. The doping effect (p or n doping) is controlled by the contact potential difference between substrates and graphene. Such substrate-dependent doping was confirmed by electrical measurements for the graphene transistors made on various substrates.

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