Thermoelectric power of graphene as surface charge doping indicator

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We report on simultaneous thermoelectric power and four-probe resistance measurements of chemical vapor deposition grown graphene during a degas process, as well as in exposure to various gases. For all investigated samples, a dramatic change in thermoelectric power was observed and found to be sensitive to the gas molecule charge doping on the surface of graphene. The observed p-type behavior under ambient conditions supports an electrochemical charge transfer mechanism between the graphene and oxygen redox couple, while the n-type behavior under degassed conditions is ascribed to the electron doping caused by the surface states of the SiO2/Si substrate. © 2011 American Institute of Physics. [doi:10.1063/1.3609858]

Recently, graphene has emerged as a candidate material of great interest for next generation nanoelectronics. Physical properties of graphene have already been explored; fascinating electrical, thermal, optical, and mechanical characteristics have been found well integrated in this intriguing material. Compared with conventional two-dimensional semiconductor systems, such as heterostructures or quantum wells, graphene proves to be more sensitive to its environment, i.e., the supporting substrate and gases/chemicals adsorbed on the surface.1–3 Annealing graphene in high vacuum, i.e., the supporting substrate and gases/chemicals wells, graphene proves to be more sensitive to its environment and semiconductor systems, such as heterostructures or quantum materials. Compared with conventional two-dimensional electronics have been found well integrated in this intriguing characteristic temperature dependence of the TEP.10–12 At 400–500 K, however, it undergoes a drastic drop, even with a reversal of sign, and attains a negative value $\sim -50 \mu V/K$, while T is set to 500 K. When the sample is cooled back down to room temperature, S increases and eventually saturates at $\sim 32 \mu V/K$. During this annealing process, resistance ($R_{\text{starting}} \approx 3.7 \Omega$ at room temperature) first increases with T, reaches a peak value of 5.4 kΩ, and then drops to 2.3 kΩ when T is stabilized at 500 K. Upon cooling, R decreases further, saturating at 2.0 kΩ. Note that the total percentage change of S is about two times larger than that of R during annealing, indicating its high sensitivity to surface absorption of gas molecules.

The graphene specimens (monolayers) utilized in this work were synthesized by the chemical vapor deposition (CVD) method at ambient pressure on polycrystalline Cu foils and then transferred onto SiO2/Si substrates, as described in Ref. 6. Availability of large-area CVD-grown graphene2 facilitates straightforward TEP measurement by anchoring two miniature thermocouples (Chromel-Alumel, K-type) and a resistive heater on the graphene without undergoing any micro-fabrication processes.8 Use of two extra wires, as current leads, can be easily implemented to measure the four-probe resistance of the device simultaneously.9 The measured Seebeck coefficient (S) and the four-probe resistance (R) provide complementary information about CVD-grown graphene. In particular, S is very sensitive to the particle-hole asymmetry in graphene, which advances the TEP measurement as a valuable probe to investigate the adsorption mechanism of reactive gases on graphene’s surface.

Figure 1 shows the concomitant time evolution of S and R of a CVD-grown graphene device during vacuum annealing with a base pressure below $10^{-6}$ Torr. Initially, S increases gradually with temperature (T) following the characteristic temperature dependence of the TEP.10–12 At 400–500 K, however, it undergoes a drastic drop, even with a reversal of sign, and attains a negative value $\sim -50 \mu V/K$, while T is set to 500 K. When the sample is cooled back down to room temperature, S increases and eventually saturates at $\sim 32 \mu V/K$. During this annealing process, resistance ($R_{\text{starting}} \approx 3.7 \Omega$ at room temperature) first increases with T, reaches a peak value of 5.4 kΩ, and then drops to 2.3 kΩ when T is stabilized at 500 K. Upon cooling, R decreases further, saturating at 2.0 kΩ. Note that the total percentage change of S is about two times larger than that of R during annealing, indicating its high sensitivity to surface absorption of gas molecules.

Our observation unambiguously shows that under ambient conditions, the Fermi energy level ($E_F$) of graphene is located in the valence band, giving rise to p-type ($S > 0$) behavior with holes as majority carriers. During degassing, the hole carrier density of states depletes and $E_F$ starts to rise ($S$ decreases and $R$ increases), until $E_F$ crosses the charge neutrality point of graphene, where $S = 0$ and $R$ reaches the Dirac peak (shown in Fig. 1(c)). $E_F$ continues to rise after the transition of the conduction from holes to electrons, and the accumulation of electron carriers is evident from negatively increasing $S$ and decreasing $R$. For all investigated samples, graphene becomes n-type after vacuum annealing.

The p-type behavior (at ambient) of carbon nanostructures, including single(multi)-walled nanotubes (SWNTs and MWNTs) and activated carbon fibers, has been a topic of

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debate due to various interpretations. In the present work, it can be explained as the consequence of electrochemically mediated charge transfer from graphene to the oxygen redox couple in the adsorbed water layer. Recently, a similar charge transfer mechanism has been employed to interpret the $E_F$ pinning in hydrogen-terminated diamond and in graphene, affirming that it is a general phenomenon which may influence the properties of semiconductors when the band lineup between the ambient and electronic states in the semiconductor is appropriate. Specifically, as shown in Fig. 2(a), the redox potential of oxygen lies between $-5.66$ and $-4.83$ eV with respect to the vacuum level, depending on the pH value of the solution (0 to 14, respectively). This energy range is markedly below the charge neutrality point of graphene, given that its work function is $-4.6$ eV. Therefore, spontaneous electron transfer would occur from the graphene to the mildly acidic oxygen/water layer at ambient, mediated by the redox reaction, $O_2 + 4H^+ + 4e^- = 2H_2O$, resulting in the observed p-type behavior. On the other hand, the n-type behavior of CVD-grown graphene after vacuum annealing is consistent with previous observations on mechanically exfoliated graphene and can be attributed to electron doping caused by the surface states of its SiO$_2$/Si substrate. As illustrated in Fig. 2(b), the work function of SiO$_2$ is $-3.03$ eV, thus the $E_F$ of vacuum-annealed graphene is expected to be pinned in the conduction band.

The difference in $E_F$ between the graphene at ambient and degassed conditions leads to distinct temperature dependence of $S$ and $R$ before and after vacuum annealing. For oxygen loaded p-type graphene, both $S$ and $R$ increase quadratically during heating (as shown in Fig. 3), suggesting that screened Coulomb scattering by charged impurities may be the dominating scattering mechanism. For annealed samples, in which charged impurities due to gaseous species are largely reduced, linear temperature dependence is evident in $S$ and $R$, and Mott’s relation is recovered. Specifically, Mott’s formula for TEP states that,

$$S(T) = \frac{k_B}{e} \frac{\partial}{\partial E} \left( \frac{e}{E} \right) \left|_{E=E_F} \right.$$  

where $e$ is the electron charge, $k_B$ is Boltzmann’s constant, and $\sigma$ is the conductivity. For the
The high sensitivity of the TEP of graphene to surface charge doping is further demonstrated in Fig. 4, where the device is exposed to N$_2$O and NH$_3$. In this study, we start with a fully degassed graphene sample, i.e., initially n-type (S = −32 μV/K). Upon exposure, it becomes either p-doped (for air and N$_2$O) or further n-doped (for NH$_3$), depending on the properties of the gaseous species. For example, the exposure to N$_2$O converts graphene to p-type, evidenced by the change in the sign of S (Fig. 4(a)) and the appearance of a maximum in R (Fig. 4(b)), but with a slower rate compared to exposure to the ambient air. N$_2$O acts as an electron acceptor for graphene, while NH$_3$ acts as a weak electron donor, consistent to previous studies on SWNTs. Recently, the absorption of N$_2$O and NH$_3$ on graphene has been calculated numerically, and the strength of the charge transfer from/to graphene is found to be −0.099e and 0.027e, respectively, in qualitative agreement with the magnitude change in TEP in our experiment. Note that the change in S is monotonic during the exposure, but non-monotonic for R (increase or decrease in resistance depending on the type of the dominating carriers), and therefore S is a better choice of a charge doping indicator. Finally, we stress that the initial degassed state can be recovered after gas exposure by repeating the vacuum annealing process described above to 500 K. Repetitive exposure–annealing cycles have shown no “poisoning” effects of the introduced gases to the graphene devices.

In conclusion, we show that the TEP of CVD-grown graphene is a sensitive probe to the surface charge doping from the environment. Compared with conventional conductometric methods, the thermoelectric sensing paradigm demonstrated herein has the following unique advantages, in addition to its high performance: (1) powered by heat, free energy in electronic systems; (2) associated with intrinsic material properties instead of contact-related properties due to the absence of excitation current; and (3) provides easy means of multiplexed sensing by eliminating multiple current sources and detection interferences. This device concept might be of practical importance in gas/chemical sensing.

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9See supplementary material at http://dx.doi.org/10.1063/1.3609858 for measurement details.