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Chemical environment dominated Fermi level pinning of a graphene gas sensor



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ABSTRACT

The time evolution of the Fermi level of the graphene channel during a gas sensing process is systematically investigated. A Fermi level converging behavior at negative back-gate voltage and a Fermi level pinning behavior at positive back-gate voltage are observed during NH₃ gas sensing process for an originally p-type doped graphene channel. The experimental results confirm that the original p-type doping level has a significant effect on the energy level where the Fermi level converges (CFL). An empirical model is proposed for the Fermi level converging and pinning behavior: the up-shift of Fermi level suppresses the electron injection from NH₃ to graphene while it enhances the electron extraction from graphene to the original p-type doping agent such as H₂O. At positive back-gate voltage, the significantly suppressed electron injection from the freshly absorbed NH₃ is complemented by the electron extraction from graphene to the original p-type doping agent. That is why a graphene channel shows no response to NH₃ when the Fermi level is pushed above CFL even though it is still significantly below the donor level of NH₃. The results in this report reveal a general interplay behavior between the freshly introduced testing gas and the original dopant of the graphene.

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1. Introduction

Graphene has been intensively studied as a promising gas sensing material due to its ultra-high surface-volume ratio, roomtemperature stability and low electric noise [1-5]. The fundamental mechanism of graphene gas sensing is the charge transfer between the adsorbed molecule and graphene. The charge transfer is determined by the Fermi level of graphene [6-8]. However, the interesting thing is that the graphene Fermi level can be easily changed by chemical or electrical doping due to the low density of states (DOS) [9–11]. So, the gas sensing performance can be tuned by both chemical and electrical doping [6-8,12]. Because of this unique feature, the saturation of gas sensing response is not only determined by the equilibrium between adsorption and desorption, but also affected by the Fermi level shift. When different molecular are absorbed by graphene, they will all affect the graphene Fermi level through charge transfer. This process results in a universal cross sensitivity in graphene gas sensing. It is widely reported that H₂O and O₂ in air significantly changes the graphene

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http://dx.doi.org/10.1016/j.carbon.2017.08.026 0008-6223/© 2017 Elsevier Ltd. All rights reserved. Fermi level [6,13]. Thus, the cross sensitivity between testing gas and H_2O or O_2 through their effect on the Fermi level is of particular importance. Quantitative and qualitative study of this cross sensitivity is a very important step towards calibration of the graphene gas sensor against the environment introduced zero drift. A general understanding of the cross sensitivity between two gas species through combined effect on graphene Fermi level is even more important.

Besides the interaction between different gases molecular in doping effect, electrical doping also has great effect on the molecule doping [12,14]. The interplay between the electrical doping and chemical doping is of fundamental and practical interest. Because electrical doping can be precisely controlled by bias voltage, it provides an effective way of studying the doping of a molecule under different graphene Fermi level. Recently, the electrically tunable molecular doping of graphene has received increasing attentions [15–17]. M. Muruganathan et al. have reported that the van der Waals interaction between the graphene and molecule could be tuned by back-gate bias voltage [16]. Their theoretical and experimental results also show that the charge transfer depends on the electric field on the graphene surface. Most recently, Pablo Solís-Fernandez et al. have demonstrated an electrically tunable







doping effect of piperidine on graphene [17]. A. K. Singh et al. have reported that a negative back gate voltage reduces the p-type doping of NO₂ while enhances the n-type doping of NH₃ for graphene [15]. Their results suggest a fixed converging Fermi level at the final equilibrium state for a gas at a given concentrations regardless of the gate bias conditions. But their result suggests a Fermi level ~185 meV below the Dirac point (the intersection point of valence and conductive energy band of graphene) for NH₃, which is in contrast to early reports of NH₃ donor level expected to be above the Dirac point [15,18–20]. The mechanism behind this large deviation between the experimental result and theoretical prediction is still not very clear.

To address this issue, the correlation between gas sensing performance and graphene Fermi level is investigated by monitoring the time evolution of the Fermi level during the gas sensing process under a large range of bias voltages in this work. The charge transfer between graphene and the dopants (the testing gas molecular, originally adsorbed molecular such as H_2O or O_2) could be effectively tuned by back-gate bias. The interplay between the freshly introduced testing gas and the original dopant of graphene is depicted by the time evolution of the Fermi level under different bias conditions. The chemical environment related Fermi level converging and pinning behavior strongly suggest a complementary effect of the original p-type dopant against freshly introduced NH₃. The results in this work reveal a general interplay between different adsorbed molecule dopants through their effects on the graphene Fermi level. This interplay is very important for gas sensor calibration and developing an electrically tunable gas sensor, which is highly desired for improving the sensitivity and selectivity [14,15].

2. Experimental

Fig. 1(a) shows the schematic of a graphene FET. The device was fabricated on a highly p doped silicon substrate with 300 nm SiO₂. The highly p-doped silicon substrate served as a back gate. The graphene used in our device was prepared by typical chemical vapor deposition (CVD) method on copper substrate [21–23]. Then the graphene was transferred to the substrate by wet transfer method with PMMA vehicle [24,25]. 0.3 mol/L (NH₄)₂S₂O₈ was used as copper etching agent. Graphene was patterned into ribbon by photolithography with O₂ plasma etching. The ribbon width (W) is 20 µm. 10 nmthick Ti and 100 nm-thick Au were deposited on graphene ribbon as source-drain contact electrodes through e-beam evaporation. After fabrication, the device was annealed at 300 °C in a mixed gas ambient of Ar/H₂ (97 sccm/3 sccm) at the pressure of 50 Pa for 1 h to remove the residues and improve the quality of the graphene-metal contact [26]. The optical image of the device is shown in Fig. 1(b), where the graphene channel length (L) is 128 µm. From the Raman Spectrum (Fig. 1(c)) obtained on the graphene channel, the sharp G band (1580 cm⁻¹), 2D band (2670 cm⁻¹) with high ratios I_{2D}/I_G ~2 and low D (1350 cm⁻¹) band confirm the high quality of the monolayer graphene [27,28].

The transfer characteristic curve of the graphene FET at atmosphere condition is presented in Fig. 1(d). The voltage of charge neutral point (V_{CNP}) in the transfer curve is over 100 V, which is beyond the bias voltage scanning range in our test. It indicates that the prepared graphene channel is originally heavily p doped. It is attributed to the adsorption of water molecules, oxygen molecules and the other possible organic residues during the fabrication process [8,29–31]. The mobility of holes is estimated by $\mu = L/(WC_{ox}V_{DS})\partial I_{DS}/\partial V_{BG}$, where C_{ox} is the back-gate capacity of the SiO₂ insulator layer with a typical value 11.5 nF/cm². The carrier mobility of the graphene channel in our device is approximately 1200 cm²V⁻¹s⁻¹. The linear curve of I_{DS} versus V_{DS} in Fig. 1(d) inset

confirms an Ohmic contact between the graphene and metal electrodes.

Ammonia, which is a typical n-type dopant for graphene, was chosen as the test gas in this work. It was introduced into a vacuum chamber with mass flow control system. The volume of the vacuum chamber is 10 L. The flow of dry NH_3 was controlled by a mass flow gauge. To explore the effect of the original chemical status of graphene on the gas sensing behavior, the tests were carried out under three different balance gas conditions: (I) dry N_2 (99.999% purity) as balance gas; (II) dry air as balance gas and (III) vacuum without balance gas. Device baking under vacuum is also adapted to reduce the originally adsorbed O_2 and H_2O . The details of the calculation methods for the ammonia concentration and the tests under these three background conditions are demonstrated in supplementary information.

All of the tests were carried out at 300 K. The absorption of NH_3 on graphene at different back-gate bias conditions were investigated by measuring the change of the drain-source current (I_{DS}) with Agilent 4155C semiconductor parameter analyzer. The fast transfer characteristic sweeping bias voltage was from -25 to 25 V programmed by Keysight B2901A.

3. Results and discussions

The fast transfer characteristic scanning has been adopted in this work to capture the dynamic process of the gas sensing. Fig. 2(a) exhibits the programmed V_{BG} for fast transfer characteristic scanning with a holding-back-gate voltage (V_{BGH}) at -25 V. The V_{BG} holds at -25 V for most of the time except a fast scanning from -25 V to 25 V within 10 s after each 3 min. A series of transfer characteristic curves can be obtained during exposure to NH₃ at -25 V V_{BGH} (Fig. 2(b)). By this method, the contribution of mobility and doping concentration to the response could be clearly identified.

The response of the device to 1000 mg/m³ NH₃ under background with N_2 as balance gas (condition I) is illustrated in Fig. 2(c). As the back gate voltage V_{BGH} increases from -50 to 50 V, the relative change of the conductivity $(|\sigma - \sigma_0|/\sigma_0)$ of the gas sensor decreases from 26% to 10%, where σ_0 is the initial conductance of device at different V_{BGH}. This result indicates that a negative gate voltage improves the amplitude of response, which is consistent with A. K. Singh et al.'s experiment [15]. Moreover, combining with the extracted mobility μ (shown as Fig. S1 in supplementary information) from those transfer characteristic curves at various V_{BGH} , the testing ammonia gas introduced electron injection (n_d) can be calculated from the reduction of hole concentration $(n_d = p_0 \text{-} p_{carrier}, where p_0 \text{ and } p_{carrier}$ are the initial and current hole concentration, respectively). The hole concentration is obtained by $p = I_{DS}L/(q\mu WV_{DS})$. The time evolutions of the n_d are plotted in Fig. 2(d). As the device has been exposed to the testing gas NH_3 , n_d increases and eventually saturates. Importantly, the amplitude of the saturated nd significantly decreases as V_{BGH} increases. It indicates that a positive V_{BGH} suppresses the absorption of NH₃ molecule on graphene or the charge transfer from NH₃ to graphene or both.

The Fermi level is a convenient measure of material's capability of gaining and providing charges. The Fermi level (related to Dirac point: $E_f - E_{f0}$) of the graphene channel is calculated by $E_f - E_{f0} = -\hbar v_f \sqrt{\pi p_{carrier}}$, where E_{f0} is the Dirac point energy of graphene, \hbar is reduced Plank constant, and v_f is Fermi velocity of carriers (10⁶ m/s).

The time evolutions of Fermi level $(E_f - E_{f0})$ at various V_{BGH} at different gas sensing test conditions are plotted in Fig. 3. When N₂ is used as balance gas, the time evolution of $E_f - E_{f0}$ of the device without baking is presented in Fig. 3(a). When dry NH₃ is

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