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Adsorption/desorption and electrically controlled flipping of ammonia molecules on graphene

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Abstract. In this paper, we evaluate the adsorption/desorption of ammonia
molecules on a graphene surface by studying the Fermi level shift. On the basis
of a physically plausible model, the adsorption and desorption rates of ammonia
molecules on graphene have been extracted from the measured Fermi level shift
as a function of exposure time. An electric-field-induced flipping behavior of
the ammonia molecules on graphene is suggested based on field effect transistor
(FET) measurements.

Contents

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1. Introduction

Electrical transport experiments on graphene have demonstrated that graphene has carrier-density-dependent conductivity [1], the quantum Hall effect [2], minimum quantum conductivity [3] and high carrier mobility [4]. Because of these characteristics, graphene is considered to be a promising new material for memory, logic, analogue, opto-electronic and sensor devices and potentially many more applications [5]–[11].

Controlling the intrinsic electrical property and being able to locally change the carrier density are important for graphene devices. It has been shown that graphene is sensitive to molecular adsorbates (e.g. NH_3, H_2O, NO_2 and CO) [12]. The Dirac cone band structure of graphene allows the control of both the carrier type and the carrier concentration induced by adsorbates owing to charge transfer from adsorbed molecules to graphene. A graphene Hall effect device is capable of sensing individual molecules of NO_2 [12]. However, the details of the strength of the adsorption and the degree of charge transfer for different adsorbates are still debated [13, 14]. In this paper, we report an experimental study of the adsorption/desorption and likely 'flipping' of ammonia molecules on synthetic, large-area graphene [15] by detecting the Fermi level shift of a graphene field effect transistor (FET).

2. Experiment

Large-area graphene films grown by chemical vapor deposition (CVD) on Cu foils of $25\,\mu$m thickness (Alfa Aesar, item no. 13382) [15] were used to study the adsorption/desorption of NH_3 molecules. The surface of the graphene-on-Cu was first coated with poly-methyl methacrylate (PMMA). After the Cu substrate was dissolved in a $Fe(NO_3)_3$ solution ($1\,M\,l^{-1}$), PMMA–graphene was removed from the solution and transferred to a SiO_2/Si substrate (p^+ doped, $\rho \sim 0.002$–$0.005\,\Omega$ cm; Addison Engineering) [11]. Finally, PMMA was removed by rinsing in acetone at room temperature. Graphene FET devices were constructed by physical vapor deposition of Au films (~ 500 nm), used as source and drain electrodes, on both sides of the graphene film. Figure 1(a) shows a schematic diagram of the graphene FET used for the transport measurement. Typically, the transport channels defined by the two electrodes deposited on graphene films were 5 mm wide and 1 mm long.

The quality and number of stacking layers of the graphene films were determined by micro-Raman spectroscopy (WITec Alpha300, 532 nm laser). Figure 1(b) shows an optical image (taken at the center of the graphene FET) of graphene on a SiO_2/Si wafer. The 300 nm SiO_2/Si wafers are almost ideal substrates for optically imaging graphene [16]. The uniformity of the color contrast in the optical image indicates uniform graphene thickness, although some small cracks were observed that were likely formed during the transfer process. The Raman spectrum (figure 1(c)) shows the following features typical of monolayer graphene: (i) a G-to-2D intensity ratio of ~ 0.5 and (ii) a symmetric two-dimensional band centered at $\sim 2680\,cm^{-1}$ with a full-width at half-maximum of $\sim 33\,cm^{-1}$ [15, 17]. The D band scattering from our sample, if present at all, was lower than the detection limit of the Raman system used.

Graphene FET devices on SiO_2/Si substrates were clamped on a ceramic heater, which was then placed in a high-vacuum chamber equipped with electrical and gas feed-throughs. The vacuum chamber can be evacuated to a pressure of 5×10^{-8} torr using a turbo pump (Turbo-V 81-M, Varian). Vacuum-annealing of the samples was performed *in situ* by heating the graphene on SiO_2/Si samples at $150\,°$C for 2 h at 5×10^{-8} torr in order to eliminate

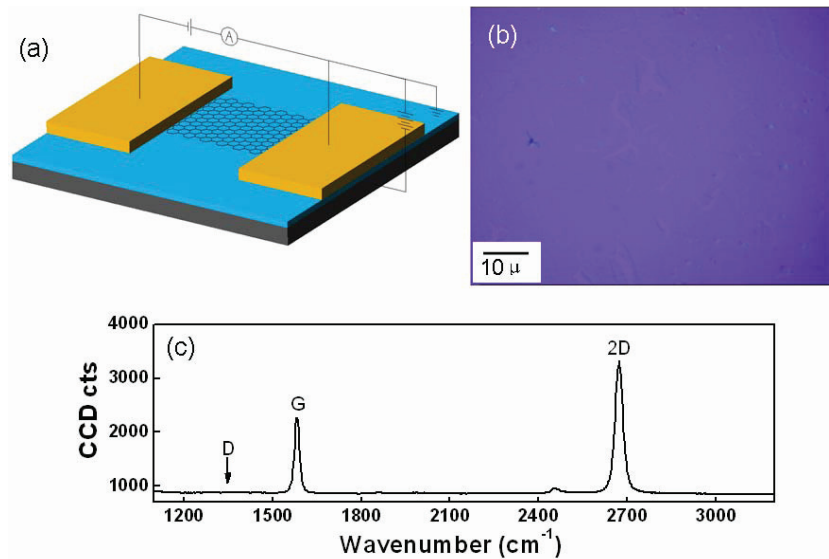**IOP** Institute of Physics **Φ** DEUTSCHE PHYSIKALISCHE GESELLSCHAFT

Figure 1. (a) Schematic diagram of a large-area graphene FET supported on a 300 nm thick SiO_2-on-Si substrate. Two Au films were deposited as electrodes for the source and the drain. The size of the graphene in (a) is about 5×5 mm^2. The typical distance between the source and the drain is 1 mm. (b, c) Optical image (b) and Raman spectrum (c) of the large-area graphene taken from the center of (b).

pre-existing adsorbates (i.e. H_2O, O_2 molecules). After this vacuum-annealing, the samples were then exposed to NH_3 gas (99.99%; Airgas) for known exposure times. FET measurements were made by a programmable voltage source (2611A, Keithley) and a digital voltmeter/ammeter (6221 and 6514, Keithley). A back-gate bias (V_{gs}) ranging from -100 to $+100$ V was applied on the Si side of the SiO_2/Si substrate. To improve the signal-to-noise ratio, a relatively high source–drain voltage (V_{ds}) of 1.5 V was applied to the device, while the source–drain current (I_{ds}) was monitored as a function of the applied back-gate bias.

3. Results and discussion

All graphene FETs were measured at room temperature. Figure 2 shows the typical response of the I_{ds} to the gate bias for the as-prepared graphene FET under ambient conditions. A linear I_{ds}–V_{gs} curve is observed across the gate bias range used for the as-prepared graphene FET samples. With the gate bias ramped from -80 to 80 V, the I_{ds} decreased from 2.0 to 0.8 mA, indicating that the as-prepared graphene was heavily p-typed; this may be due to the adsorption of water molecules from air or PMMA residue from the transfer process [18] or both. Thus, the Dirac point was outside the range of the gate biases that were studied. To minimize the presence of other adsorbates prior to exposure to NH_3, the samples were heated at 150 °C for 2 h under vacuum at 5×10^{-8} torr. After annealing, a V-shaped gate response of the I_{ds} is observed from the graphene FET, as shown in figure 2. The *in situ* annealing thus yielded a Dirac point that is closer to zero gate bias, demonstrating the removal of (at least some) adsorbates and the recovery of the intrinsic bias dependence of graphene.
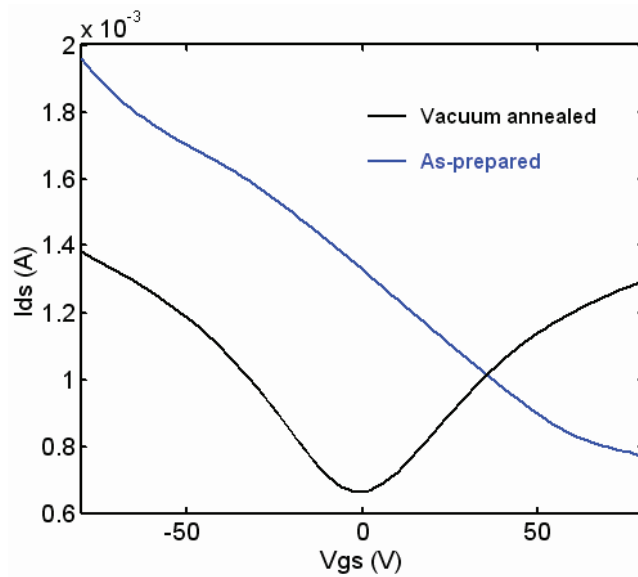
Figure 2. The drain–source current variation of as-prepared (blue) and vacuum-annealed (black) graphene FET as a function of the Si back-gate bias.
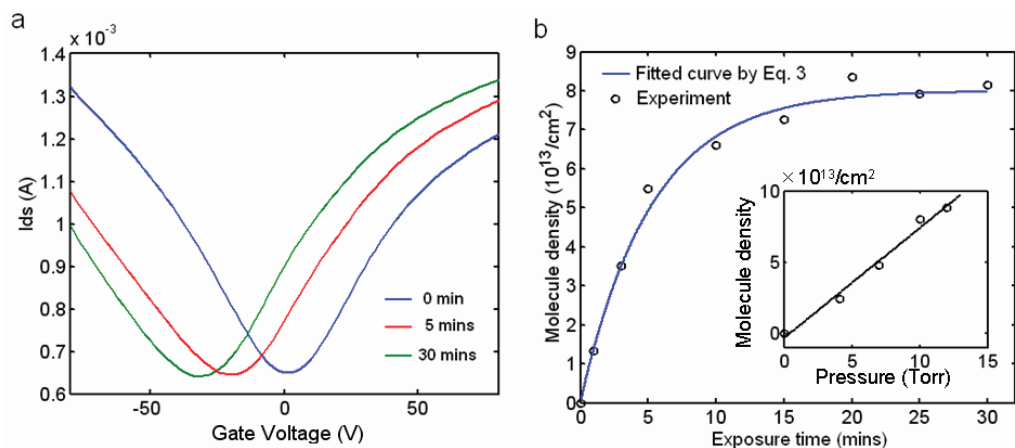

Figure 3. (a) The drain–source current variation of as-prepared graphene FET immediately after exposures to NH_3 gas for 0, 5 and 30 min. (b) Time evolution of the NH_3 molecule density on the graphene surface, obtained from the measurement of V_D. The inset of (b) shows the saturated molecule density as a function of the NH_3 gas pressure.

To study the effect of adsorption of NH_3 on the electrical response of graphene, the FET devices were exposed to $NH_3(g)$ after vacuum-annealing. The vacuum-annealed graphene FET was exposed to 10 torr of NH_3 gas for a total time of 30 min. Figure 3(a) shows the time evolution of the I_{ds} versus V_{gs} during this exposure to NH_3 gas. Initially, the Dirac point is close to +3 V back-gate bias; after 5 min of exposure, the Dirac point appears at -18 V and then gradually shifts to its final position at about -30 V. These results suggest that ammonia molecules are adsorbed on the graphene surface and cause a shift in the Fermi level in graphene from the Dirac point to the conduction band.

Studies of individual semiconducting carbon nanotube (CNT) sensors have been perfomed based on resistivity changes attributed to molecular adsorption on CNTs and partial electron transfer to the CNTs [19]. A recent first-principles calculation on graphene predicts that dipolar molecules can act as donors or acceptors with a small charge transfer χ (e.g. 0.027e for NH_3) [13]. This is consistent with calculations on defect-free CNTs [19]. Based on this calculated charge transfer of electrons from ammonia to graphene, the number density of the ammonia molecules, n, on the graphene surface can be estimated as

$$n\chi = \frac{C V_D}{eS} = \frac{\varepsilon_0 \varepsilon_r V_D}{ed}, \tag{1}$$

where C is the capacitance of the graphene FET, V_D is the back-gate voltage shift of the Dirac point relative to that of vacuum-annealed graphene, S is the surface area, e is the electron charge, ε_r is the dielectric constant of SiO_2 and d is the thickness of SiO_2. The values of n have been plotted as a function of exposure time in figure 3(b). The inset of figure 3(b) shows the saturated molecular density, with this assumed charge transfer, as a function of the NH_3 gas pressure.

The adsorption/desorption of the molecules can be understood based on a 'physically plausible' model. Denoting the number density of the molecules in the gas phase as n_0 (a constant in our experiments) and the number density on the graphene surface as $n(t)$, the dynamics of the adsorption can be expressed as a rate equation,

$$\frac{dn(t)}{dt} \equiv \frac{dn(t)_{ad}}{dt} - \frac{dn(t)_{de}}{dt} = n_0 p_0 - np, \tag{2}$$

where t is the duration of exposure of graphene to NH_3 gas, p_0 is the adsorption rate and p is the desorption rate. In this model, the number of molecules that are adsorbed on $(dn(t)_{ad}/dt)$ and desorbed from $(dn(t)_{de}/dt)$ the surface per unit time is assumed to be proportional to the concentration of gas-phase (n_0) and surface (n) molecules, respectively. The adsorption/desorption rates are assumed to be dependent only on the temperature. We also assume that the density of molecules on the surface $n(t) = 0$ at $t = 0$, meaning that vacuum-annealing removes all adsorbates. By solving equation (2), the density of the molecules on the surface as a function of exposure time is obtained as

$$n(t) = \frac{n_0 p_0}{p}(1 - e^{-pt}). \tag{3}$$

A curve fitted to the $n(t)$ data using equation (3) is shown in figure 3 as well. The extracted values of p and $n_0 p_0$ are 0.0027 and $2.1 \times 10^{10}\,cm^{-2}$, respectively, and hence with the assumptions mentioned above, at a NH_3 gas pressure of 10 torr, about $2.1 \times 10^{10}\,NH_3$ molecules are adsorbed on $1\,cm^2$ of graphene and 0.27% molecules desorb in 1 s. It is worth noting that the values of p suggest a sensing response time $(t_0 = 1/p)$ if graphene FET is considered as an $NH_3(g)$ sensor.

Many studies as well as theoretical works [13, 20] have reported that graphene has to be functionalized to achieve its impressive gas-sensing performance. *Ab initio* studies of the gas adsorption on graphene corroborate the role of impurities or vacancies, thus demonstrating a stronger gas adsorption at sites of atomic substitutions or defects [20]. The high sensitivity obtained on reduced graphene oxide gas sensors also supports the importance of functionalization [21]. Recently, experiments compared the electrical gas-sensing performance
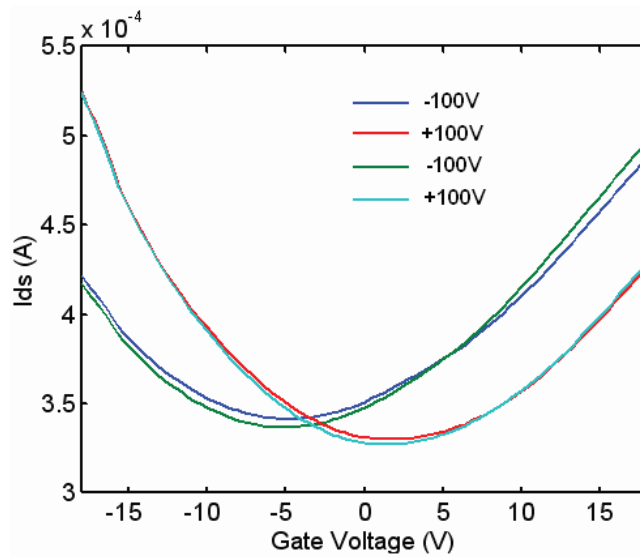
Figure 4. The FET measurement of graphene with ammonia molecules in a low back-gate bias range of $\pm 20\,\mathrm{V}$ following a high back-gate bias pulse. The sequence of 5 s pulses is -100, $+100$, -100 and $+100\,\mathrm{V}$. Four curves are obtained after each pulse, respectively.

of 'dirty' and intrinsic graphene devices [14]. It has been reported that the responses of intrinsic graphene devices are surprisingly small even upon exposure to a strong analyte such as ammonia vapor. The unintentionally 'functionalized' residual polymer layer from the lithographic resist served to help concentrate the gas molecules or possibly enhance charge transfer. In our studies, a certain degree of Fermi level shift due to ammonia molecules was detected on performing an FET measurement at room temperature. These results may be due to the PMMA residue from the transfer process [11] and defects in the graphene grain boundary. Our previous works demonstrate that the typical grain size of CVD-grown graphene is $\sim 10\,\mu\mathrm{m}$, which is two orders lower than the length of graphene devices [22].

Another main point of interest is that the value of the charge transfer rate χ between dipolar molecular adsorbates and graphene may depend strongly on molecular orientation with respect to the graphene surface [13]. The NH_3 molecule could, among other possibilities, orient with the N end of the molecule closest to the surface and the C_{3v} axis essentially perpendicular to the surface ('**u**' for 'up') or, alternatively, with the H atoms adjacent to the surface and the C_{3v} axis again perpendicular to the surface ('**d**' for 'down'). To determine whether there could be an effect from molecular orientation of adsorbed NH_3 molecules, a scan at low gate bias from -20 to $+20\,\mathrm{V}$ was carried out immediately after applying a high-gate-bias pulse ($+100$ or $-100\,\mathrm{V}$) for 5 s to the graphene FET devices. Figure 4 shows four sequential I_{ds}–V_{gs} measurements in each with the application of one pulse before the scan. The four pulses were applied in the sequence of -100, $+100$, -100 and $+100\,\mathrm{V}$. Due to the interaction between the electric field and the molecular dipoles, we suggest that the high-positive-gate-bias pulse aligns NH_3 molecules along the **d** orientation and that the high-negative-bias pulse flips NH_3 molecules to the **u** orientation. The low-gate-bias scan is assumed to have a smaller effect on the orientation of the molecules. The measured curves clearly show that back-gate voltages of the Dirac point are (repeatably)

-6 V (for -100 V pulses) and $+3$ V (for $+100$ V pulses). Compared with the vacuum-annealed result, V_D for the **u** orientation is about -9 V, while a negligible shift occurs for the **d** orientation. This result indicates that almost all the NH_3 molecules flip from the **u** orientation to the **d** orientation when a $+100$ V pulse is applied, and the **u** orientation has a relatively large charge transfer ratio, which is consistent with a prediction based on the asymmetry of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ammonia molecule [13]. The **u** orientation is energetically favored [13] and this explains the donor character observed at zero bias in our experiment. The flipping of some molecular dipoles on graphene could be the reason for the hysteretic behavior reported in other electric field effect measurements [18].

4. Summary and conclusions

In this paper, we have reported our study of the adsorption/desorption and flipping behavior of NH_3 molecules on a graphene surface through observation of the Fermi level shift, inferred to be from a partial charge transfer from the NH_3 molecules to graphene. A simple model has been used to evaluate the rates of adsorption and desorption of NH_3 molecules on graphene from the measured shift of the Fermi level as a function of exposure time. An electric-field-induced flip of the molecular dipoles (i.e. NH_3 molecules) is suggested from measured back-gate voltage shifts in the Dirac point after electric field pulses were applied via the gate bias.

Acknowledgments

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