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Graphene/mica based ammonia gas sensors

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In this paper, graphene/mica and graphene/SiO₂ based ammonia gas sensors are compared. It is found that adsorbed NH₃ molecules result in up-shifting of the Fermi level in graphene, leading to a significant increase in graphene resistance. In comparison with SiO₂ supporting substrate, the mica supporting substrate is found to induce more p-doping in graphene, in favour of NH₃ molecule adsorption, yielding a high sensitivity. These findings suggest that the substrate plays an important role in mediating the interaction between graphene and NH₃ molecules and that mica can be an excellent underlying substrate for graphene for ammonia gas detection. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905039>]

Graphene is a single atomic layer of carbon atoms, bound in a honeycomb lattice. Due to its excellent electrical properties, graphene has been the research focus of many researchers in the past 10 years for several electronic applications including sensors, high frequency electronics, energy storage devices, etc. Thanks to its unique quantum conductivity and electronic states^{1,2} and high surface to volume ratio,³ graphene is considered as an excellent sensing element for sensing applications. Geim and his team were the first to prove graphene is capable of detecting individual gas molecules based on the Hall Effect measurements.⁴ Then, several structures of graphene sensors have been employed to detect a variety of gases and vapors.^{5–7} Till now, many types of graphene based gas sensors have been demonstrated to have high sensitivities. Indeed, it was revealed that chemical vapor deposited (CVD) pristine graphene can detect an extremely low concentration of NH₃ gas with a detection limit as low as sub ppm using UV light illumination.⁸ Other different forms of graphene such as graphene foam⁹ and graphene oxide^{10,11} were as well used to detect ammonia gas. Functionalization is also considered as an efficient way to improve graphene sensitivity to ammonia gas.¹² However, the gas detection mechanism is still under debate.^{13–18} Since charge transfer is critical for graphene sensitivity to gas molecules, the interactions between graphene and different absorbed gases and vapors have been investigated. It has been confirmed that gas molecules with different compositions and structures interact with graphene in different ways.¹⁶ For example, open shell impurities like NO₂, etc., interact directly with graphene while inert impurities like H₂O and NH₃ are usually physisorbed, and they may not act as direct dopants for graphene, i.e., they may not cause doping to perfect free-standing graphene.¹³ Hence, for NH₃ molecules, the graphene underlying substrate can play a fundamental role in mediating their interactions with graphene.

In this paper, we report on the experimental studies of the interaction of NH₃ molecules with graphene supported by two different substrates, i.e., mica and silicon oxide, in

order to provide further insight into the impact of supporting substrates on ammonia molecule-graphene interaction.

Muscovite mica is the most commonly used mica group whose formula is KAl₂(Si₃AlO₁₀)(F,OH)₂. It is a well-known natural insulating material and it is widely used in electrical devices, say, transformers, capacitors, etc., thanks to its high dielectric strength and high chemical and thermal stability. Recently, mica has attracted a lot of attention as an atomically flat substrate for electronic devices. It was reported also that when graphene is attached onto mica, a strong p doping is induced in graphene.^{19–21} In this work, muscovite mica films were obtained using the conventional micro-mechanical exfoliation technique. In other words, various thicknesses of mica were obtained through repeatedly cleaving a piece of crystalline mica with an adhesive tape.

Single layer graphene was transferred onto SiO₂/Si substrates and freshly cleaved mica with a thickness of about 100 μm to make the two terminal devices. Monolayer CVD graphene on copper foil was used here. First, the large sheet of graphene on copper was cut carefully in small pieces. Then, the graphene was transferred on the mica and SiO₂ substrates by Poly(methyl methacrylate) (PMMA) assisted transfer technique. First, PMMA was spin coated on graphene/Cu foil pieces, and then the samples were baked at 105 °C for 5 min to remove remaining solvents. The copper was etched using ammonium persulfate solution. PMMA supported graphene floated on the solution after removal of Cu. These films were rinsed with deionized water to remove ammonium persulfate and then transferred onto mica or SiO₂/silicon substrates. The samples were baked at 180 °C for 1 h to enhance the adhesion of transferred graphene to the substrates. Finally, the PMMA was removed by immersing the samples in acetone solution for more than 12 h.

Thereafter, four interdigitated Au/Ti (with thickness of 100 nm/10 nm) electrodes were deposited onto the transferred graphene through a shadow mask. The thin Ti layer was deposited first to enhance the adhesion of Au. Optical lithography processes were not applied to avoid any possible

FIG. 1. Raman spectra of graphene/mica (red) and graphene/SiO₂ (black).

photoresist residues on graphene. The typical spacing between the two electrodes was 1 mm.

After being transferred onto the substrates, the transferred graphene was characterized first using an optical microscope. The graphene was found to be quite uniform except for some cracks and ripples that were formed during the transfer process. It has been reported that the possible PMMA residues from the transfer process and adsorbates from the environment could cause p doping to graphene.^{22,23} Furthermore, Raman spectroscopy (exciting wavelength at 532 nm) was carried to examine the quality of graphene, as shown in Figure 1. The spectra show sharp and symmetric 2D bands, which are a clear evidence of single layer graphene. The weak D bands indicate that the graphene was of high quality of crystalline structure. It is also interesting to note the presence of a sharp peak at $\sim 3600\text{ cm}^{-1}$ for graphene/mica, which can be attributed to OH groups on mica substrate.²¹

The intensity of the 2D peak, known to be sensitive to charge doping,²⁴ decreased in graphene/mica sample in comparison with graphene/SiO₂ sample, suggesting the occurrence of doping in graphene associated with the mica substrate. In addition, the 2D and G peak frequencies are found to shift, respectively, about 8 cm^{-1} and 4 cm^{-1} upward in comparison with the graphene/SiO₂ sample. These are other indicators of doping occurred in graphene/mica sample.²⁵

To examine electrically mica induced doping effect on graphene, two sets of CVD single layer graphene field effect transistors (GFET) were made. One set was based on

graphene/SiO₂/Si and the other was made from graphene/mica/SiO₂/Si where the mica flake thickness was about 70 nm. The both GFETs had their channel width of $4\text{ }\mu\text{m}$. Figures 2(a) and 2(b) show the 3D structure and the optical image of the mica based GFET on SiO₂/Si substrate, respectively. In Figure 2(b), the graphene ribbon with a size of $75\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ appears as a darker stripe located on the top of mica flake (green-blue color).

The GFETs transfer characteristics are shown in Figure 3. Since the minimum channel conductance of GFETs is observed for positive threshold voltage (V_{th}) in both GFETs, this implies that their Fermi levels were below the Dirac point, in other words, both graphene channels were p-doped. We can also see that for the sample of graphene/mica V_{th} is further up-shifted (positive shift), indicating that the mica could induce more hole doping to graphene than the SiO₂ substrate.

The carrier mobility of GFETs²⁶ was calculated by

$$\mu = \frac{L V_{ds}}{W C} \times |g_m| = \frac{L t V_{ds}}{W \epsilon \epsilon_0} \times \frac{\Delta I_{ds}}{\Delta V_{gs}}, \quad (1)$$

where ϵ is the dielectric constant ($\epsilon_{mica} \approx 8.1$, $\epsilon_{SiO_2} \approx 3.9$), L is the length of graphene channel ($4\text{ }\mu\text{m}$), W is the width of graphene channel ($4\text{ }\mu\text{m}$), V_{ds} is the source drain voltage (0.02 V), and t is the thickness of the gate dielectric ($t_{mica} = 70\text{ nm}$ and $t_{SiO_2} = 285\text{ nm}$). The maximum transconductance, g_m , can be obtained by differentiating the transfer curves in Figure 3. The corresponding effective mobility (μ_{eff}) is $2588\text{ cm}^2/\text{V s}$ and $1321\text{ cm}^2/\text{V s}$ for the GFET with graphene on mica and graphene on SiO₂, respectively. It is obviously seen that the mobility of graphene/mica based FET is significantly higher than that of the graphene/SiO₂ based FET. This finding is consistent with what we observed before.²⁷ The increase in the mobility of the GFETs can be attributed to the smooth mica surface that leads to less carrier scattering in graphene on mica than on SiO₂.

Our two terminal devices were tested using a gas chamber with nitrogen as the background gas. 1000 ppm ammonia gas in synthetic air (oxygen/nitrogen $\sim 1/4$) was fed into the chamber with a total flow rate of 500 sccm. NH₃ gas concentration could be tuned from 10 to 500 ppm. The sensing temperature was set through a temperature controller with a thermocouple near the sample surface. The applied voltage between the electrodes was 100 mV.

In these experiments, several samples made in the same conditions were measured in order to check the repeatability

FIG. 2. (a) Schematic of the 3D structure. (b) Optical microscope image of mica based GFET fabricated on SiO₂/Si substrate. The width of the graphene ribbon and the channel length are mentioned in black and red, respectively.

FIG. 3. The transfer curves under $V_d = 20$ mV for GFETs with graphene/mica (red) and graphene/SiO₂ (black).

of the devices. Once graphene based sensors were exposed to NH₃ gas, the resistance increased quickly and significantly. However, the recovery (desorption) occurred slowly as illustrated in Figure 4. NH₃ molecules are well known reducers with a strong electron donating capability, and they thus donate electrons to the graphene surface where they adsorb. Thus, upon introduction of NH₃ molecules to the sensors, NH₃ molecules increase electron concentration, leading to an upward shift of the Fermi level toward the Dirac point. Note that as the graphene was initially p doped, the upward shift of the Fermi level would cause the Fermi level to shift toward the Dirac point, leading to an observed increase in the resistance upon exposure to NH₃ gas.

From Figure 4, one can note that graphene/mica sensor showed faster and more significant increase in the resistance (19%) in comparison of graphene/SiO₂ sensor (11%) within 30 min of exposure to NH₃ gas at room temperature (RT). The recovery of graphene/SiO₂ is much slower than that of graphene/mica, suggesting that the desorption of adsorbed NH₃ molecules is faster on graphene/mica surface. To accelerate the recovery process, the sensors were annealed at 150 °C for 1 h. This anneal treatment was found to be sufficient to remove remaining adsorbates and set the resistance back to its initial value before NH₃ gas was loaded.

From Figures 5(a) and 5(b), the devices showed good responses to different concentrations of NH₃ at RT. Graphene/mica showed a resistance increase of ~4% within just 1 min of exposure to 50 ppm NH₃ and ~1% of resistance increase for 1 min exposure to 20 ppm NH₃. It is clearly seen

FIG. 4. Real-time detection at RT of 500 ppm NH₃ using mica (red) and SiO₂ (black) as substrates.

that graphene/mica sensor has higher sensitivity and reversibility than graphene/SiO₂ sensor.

This could be explained in terms of the substrate-dependent doping and hydrophilicity of the mica. In fact, p doping induced by mica leads to a downward shift of the graphene Fermi level, creating additional states around the Fermi level. Hence, the highest occupied molecular orbital (HOMO) of NH₃ can have a significant overlap with graphene orbitals and cause large charge transfer.

The faster recovery of graphene/mica can be explained in two processes, i.e., fast process which could be dominated by the outer surface of graphene and slow process which arise from the inner surface that is in contact with the substrates.¹⁷ The slow desorption process is related to gas diffusion through the slit pores at the interface between graphene and its supporting substrate. The properties of this interface are strongly dependant on the adhesion of graphene to it. As mica surface is much smoother and more hydrophilic than silicon oxide surface, one can claim that more water molecules can diffuse at the interface between graphene and mica creating slit pores that could facilitate the diffusion of NH₃ molecules.

The above results remain also consistent at 100 °C as shown in Figures 6(a) and 6(b). At this temperature, the desorption is improved whereas the adsorption is decreased. This can be explained based on the fact that high temperatures cause thermal fluctuations of ammonia gas molecules so that they easily detach from graphene surface.

In summary, we have compared the performances of graphene/mica and graphene/SiO₂ based ammonia gas

FIG. 5. Response to: (a) 50 ppm and (b) various concentrations (20 ppm, 50 ppm, and 100 ppm, respectively) of NH₃ at RT for graphene on mica (red) and graphene on SiO₂ (black).

FIG. 6. Response to: (a) 50 ppm and (b) various concentrations (20 ppm, 50 ppm, and 100 ppm, respectively) of NH_3 at 100 °C for graphene on mica (red) and graphene on SiO_2 (black).

sensors at room temperature and 100 °C. We clearly show experimentally the impact of the substrate mediated doping on ammonia gas detection based on the facts that mica substrate induces more significant p-doping in graphene/mica than graphene/ SiO_2 substrate and that graphene/mica sensor shows clearly a higher sensitivity than the graphene/ SiO_2 sensor. These interesting results can play an important role in selection of the supporting substrates for graphene based sensing applications.

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