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Detection of sulfur dioxide gas with graphene field effect transistor

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Graphene grown by chemical vapor deposition on a Cu foil and transferred onto a Si wafer has been used to fabricate a field effect transistor device that was used to study the sensing of SO₂ gas. It was found by *in-situ* measurements that the SO₂ strongly p-dopes the graphene and dramatically shifts its Dirac point. This effect was used to monitor the SO₂ gas. The detector can be completely reset by thermal annealing at 100 °C in high vacuum. The response and recovery of the detector are faster at higher temperatures. Moreover, the sensitivity of the SO₂ graphene detector increases proportionally with increasing temperature. © 2012 American Institute of Physics.

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Graphene, a two-dimensional honeycomb structure of carbon atoms, possesses unusual electronic properties that make it promising for diverse electronic applications.¹ Particularly, strong alteration of electronic properties of graphene by absorption and desorption of various gas molecules allows using it as a sensing element for gas sensor applications. Schedin *et al.* reported that a gas detector based on graphene can detect the target gas molecules at very low concentrations even down to the single molecule level.² Such high sensitivity can be ascribed to graphene's extremely low-noise characteristics³ and high surface area. The mechanism of gas sensing in graphene is based on the changes of local charge carrier concentrations by adsorbed gas molecules that results in p-type or n-type doping and leads to resistance changes. Due to the high sensitivity, the electrical detection of gas molecules can be achieved even at room temperature (RT).^{2,4} This is particularly important for low-temperature gas monitoring systems, for instance, for SO₂ gas detector. Reliable detection of SO₂ gas using solid electrolytes or semiconductors can only be achieved at high temperatures (450–500 °C).⁵ However, because of the interference of air, accurate measurement of the graphene gas detector can only be carried out in an airtight chamber right now. Therefore, more research needs to be done to turn the gas detector into a real gas sensor.

Monitoring of SO₂ gas is important because it is one of the most common air pollutants from industrial complexes and vehicles and can cause acid rain that is harmful to plants, buildings, and human beings.⁶ In this study, SO₂ is mixed with inert gas and sensed with chemical vapor deposition (CVD) grown graphene configured in a field effect transistor (FET) device. It was found that the Dirac point of graphene shifts 1.09 V/ppm maximum when the graphene FET is exposed to SO₂ gas molecules in the part-per-million (ppm) range, thus demonstrating an effective way to detect SO₂ gas. The complete recovery of the detector baseline was

achieved by annealing at 100 °C in high vacuum. Because of its high response rate and simple recovery process, graphene is a promising material for the next generation of SO₂ gas sensor.

Large area graphene samples were grown on 25- μ m thick copper foils (Alfa Aesar, item No. 13382) in a cold-wall CVD furnace, as described elsewhere.^{7,8} Briefly, the copper foil (1 mm \times 10 mm) was annealed through direct current heating (over 35 A) up to 880 °C in the vacuum chamber with base pressure of 1.0×10^{-2} Torr. The foil was kept at this temperature and exposed to methane for 10 min. The CVD process results in the growth of monolayer graphene on both sides of the copper foils. A “fish out” transfer method, which we reported before, was used to transfer graphene from Cu foils onto a Si wafer (with 280 nm thick oxide layer).^{8,9} This method allows obtaining clean monolayer graphene without, e.g., PMMA residues, which is important for gas sensing applications. Micro-Raman spectroscopy (WITec Alpha 300, excitation wavelength 532 nm) was used to evaluate the quality and the number of layers of the graphene. Fig. 1 shows the optical microscope image ($\times 20$) and a typical Raman spectrum of monolayer graphene. Its sharp G band (~ 1580 cm⁻¹), high 2D band (~ 2690 cm⁻¹), a low G/2D ratio, and very low D band (~ 1350 cm⁻¹) indicate the good quality of our sample.¹⁰ The optical image shows no cracks, wrinkles, or chemical residue on the surface of the graphene.

For fabrication of the graphene-based FET, two gold electrodes (5 \times 5 mm) were deposited on graphene-on-Si wafer by thermal evaporation of Au wire and through a metal shadow mask (channel length: 1 mm). The graphene FET was then put into the vacuum chamber^{11,12} that was connected to a 50-ppm SO₂ standard gas (volume balanced with N₂, Airgas Company). The graphene FET inside the chamber was connected to the outside measurement instruments *via* electrical feedthroughs on the vacuum chamber. In order to eliminate the initial H₂O and O₂ absorbents, the graphene SO₂ gas detector was annealed at 100 °C for 1 h and cooled down overnight to RT under high vacuum (1×10^{-9} Torr).

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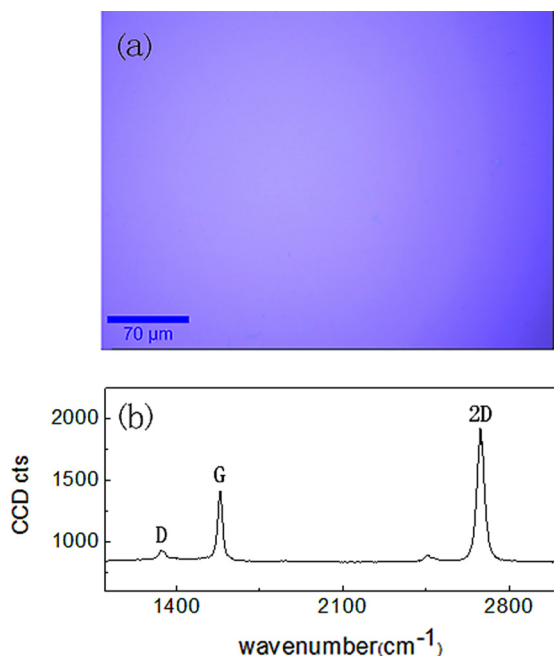


FIG. 1. (a) Optical microscope image and (b) typical Raman spectrum of the CVD grown monolayer graphene after transfer to SiO₂/Si.

Then, a predefined volume of the 50-ppm SO₂ gas was introduced through a mass flow controller and trapped in the chamber to test the response of the graphene FET as a SO₂ gas detector. Temperature dependent gas sensing measurements were carried out in the temperature range of 40 °C–100 °C. Keithley Instruments (Keithley 6514 and 6221) were controlled by a LabVIEW program to record the measurement data automatically into a computer.

Our FET device was exposed to pure N₂ after high vacuum anneal, and the result was shown in Fig. 2 (2.0 Torr). No obvious shift of the Dirac point indicated the graphene FET had no response to N₂. During the *in-situ* exposure to SO₂, the FET curves were recorded to map the evolution of the position of the Dirac point. In Fig. 3(a), the black curve was obtained at room temperature (after annealing the sample at 100 °C for 1 h and then cooling it down to RT overnight in the vacuum chamber). The Dirac point located around zero gate bias indicates that almost all of the initial doping introduced by absorbents such as O₂ and H₂O, and other residual molecules had been removed. This clean gra-

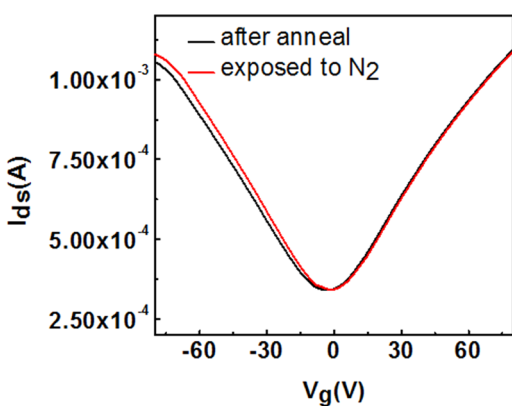


FIG. 2. The response of the graphene FET to pure N₂ gas. The drain-source voltage is 2.53 V.

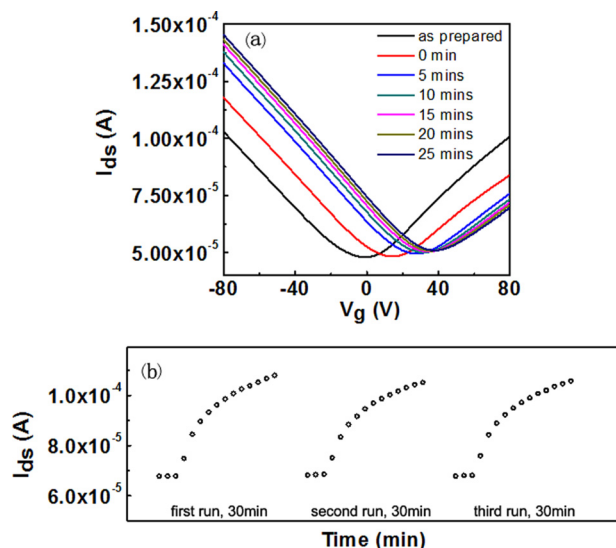


FIG. 3. The response of the graphene FET to SO₂ gas at RT. (a) Time dependence of drain-source current (I_{ds}) versus gate bias (V_g) at a drain-source bias of 2.53 V. (b) Reproducibility of the graphene FET as a SO₂ gas detector at RT for exposure to 50-ppm SO₂ for a drain-source voltage of 2.53 V and gate voltage of -50 V. The measurement time of each sample run was 30 min.

phene in the FET was then exposed to SO₂ gas *via* a mass flow-controller (Sierra, smart-Trak) with a 10-sccm flow for 2 min to introduce the standard 50-ppm SO₂ gas into the vacuum chamber. This process was controlled by a LabVIEW program to make sure that at every batch exactly the same volume of SO₂ gas was introduced into the chamber resulting in a pressure change from 1.0×10^{-9} Torr to 2.0 Torr. The electrical response was immediately recorded after trapping the SO₂ gas in the chamber and repeated every 2.5 min for a total time of 30 min. Fig. 3(a) shows that as SO₂ gas adsorbs on the graphene surface, it induces a shift of the curve (drain and source current (I_{ds}) versus gate bias (V_g)) to the positive side. Initially, the Dirac point is at zero gate bias (before introducing the SO₂ gas), and after 10 min exposure to the SO₂ gas, it is at about +30 V and then gradually shifts to its final position of about +35 V. First-principles calculations showed that dipolar molecules can act as donors or acceptors of electrons, respectively.¹³ In our case, SO₂ acts as an acceptor and induces heavy p-doping of the graphene. The carrier density ρ introduced by the SO₂ gas deposited on the graphene sensor can be estimated by the equation $\rho = CV_D/eS = \epsilon_0\epsilon_r V_D/ed$, where V_D is the shift of Dirac point, e is the electron charge, ϵ_r is the dielectric constant of SiO₂, and d is the thickness of the SiO₂ layer. Using this equation for $V_D = 33.9$ V from Fig. 3(a), the carrier density of 2.63×10^{12} cm⁻² corresponding to the final state for 50-ppm SO₂ at RT was obtained.

Reproducibility is one of the most important features of gas sensors. It was reported graphene detectors can completely recover by heating them at 150 °C in vacuum, and repetitive exposure to certain gases showed no poisoning effects.² We find that annealing at 100 °C in high vacuum (1.0×10^{-9} Torr) for 1 h can remove almost all the doping of the graphene. Fig. 3(b) shows the I_{ds} response as a function of time for three sample runs at the gate bias of -50 V (drain voltage: 2.53 V). After each run, the graphene detector was

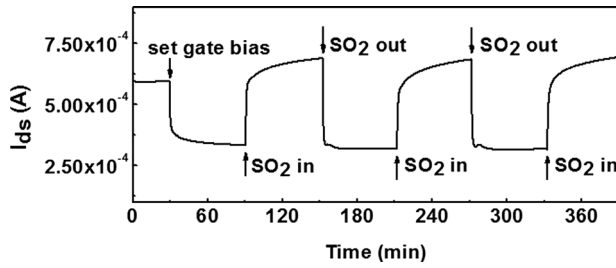


FIG. 4. The response of the graphene FET to SO₂ gas (50-ppm) at 100 °C. The drain-source voltage is 2.53 V and the gate voltage is -50 V.

heated to 100 °C in high vacuum (1.0×10^{-9} Torr) for 1 h and cooled down overnight to RT. The three curves in Fig. 3(b) show that all the adsorbed SO₂ gas molecules can be eliminated by such a treatment, and the doping is reproducible upon re-exposure to the SO₂ gas. For the SO₂ gas with same volume and concentration, the graphene detector had the same response rate and final state, thus showing good reproducibility.

For testing the detector performance at higher temperatures, the graphene FET was maintained at 100 °C and exposed to the standard 50-ppm SO₂ gas. The response of the detector was tested for three sample runs. Fig. 4 shows the time evolution of I_{ds} (drain-source current) of the detector exposed to SO₂ gas at -50 V gate bias (before setting the gate bias, its value is zero). It is clear that with the constant 2.53 V drain voltage, the I_{ds} increased rapidly as soon as the graphene FET detector was exposed to the SO₂ gas at 100 °C. The I_{ds} increased 76% in the first 2 min and then gradually approaches its final state (100%) within 30 min. The reset process is significantly faster than the response process. Within only 2 min, after the vacuum level in the chamber returned to 1.0×10^{-9} Torr, I_{ds} returns to about 98% of its initial value. With continuous pumping for 10 min (vacuum level: 1.0×10^{-9} Torr), the initial state of the graphene FET maintained at 100 °C is completely restored, and the prior exposure restore has no effect on the following measurement cycles. Fig. 4 shows how reproducibility of the graphene SO₂ detector is at 100 °C. The response and reset rate, the top and initial value of I_{ds} , are reproduced under the same conditions. Comparing Figs. 4 and 3(b), one sees that the graphene FET is more sensitive at 100 °C with faster response rate and higher response value compared to the RT measurements. In addition, the recovery of the detectors at 100 °C (10 min) is faster than at room temperature (overnight).

The graphene-FET SO₂ detector was tested to obtain the time evolution curves of I_{ds} versus V_g at different temperatures: RT, 40 °C, 60 °C, 80 °C, and 100 °C. After each measurement, the detector was reset by annealing at 100 °C (1.0×10^{-9} Torr) to eliminate the existing doping before it was used for the next measurements at another temperature. The detector was heated to the designated temperature and exposed to 50-ppm SO₂ gas, and the FET curves were recorded every 2.5 min. Experimental results shown by dots in Fig. 5(a) indicate the evolution of the Dirac point position. We now present a physical model, denoting the density of SO₂ gas molecules on the graphene surface as n and the density of SO₂ gas molecules in the gas phase as n_g , with the

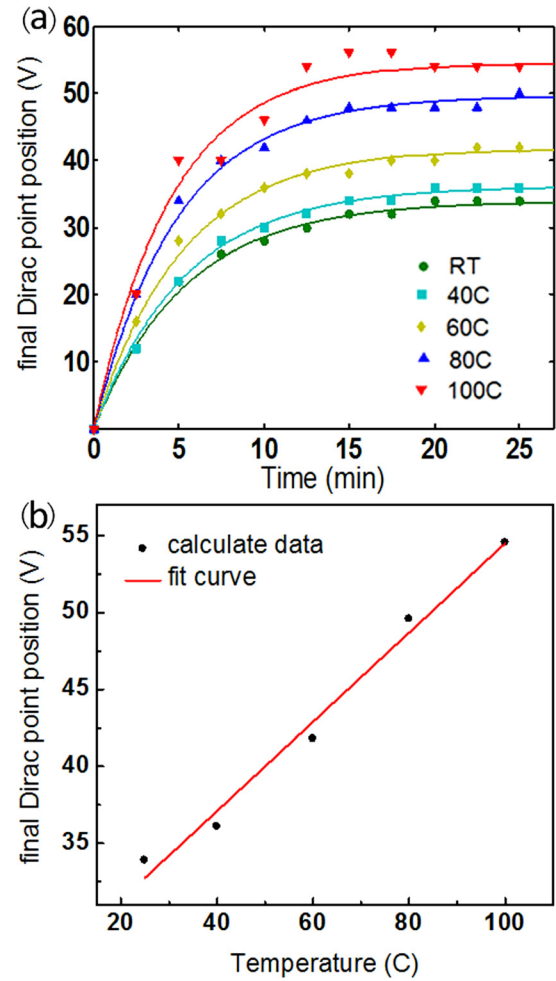


FIG. 5. (a) The shift of the graphene Dirac point at different temperatures. (b) The final Dirac point position as a function of temperature. 50-ppm SO₂ gas was used in all the experiments.

assumption that n_g in these experiments is constant. The dynamics of the adsorption/desorption rate can be expressed by the following equation:¹²

$$\frac{dn(t)}{dt} \equiv \frac{dn_{ad}}{dt} - \frac{dn_{de}}{dt} = n_g p_g - np, \quad (1)$$

where t is the exposure time of graphene to the SO₂ gas, and p_g and p are the adsorption and desorption rates, respectively. It is also assumed that the adsorption and desorption rates depend only on the temperature, and the initial state has no adsorbates ($n(t) = 0$ at $t = 0$). The density of the SO₂ molecules on the graphene surface as a function of exposure time can be obtained by solving Eq. (1),

$$n(t) = \frac{n_g p_g}{p} (1 - e^{-pt}). \quad (2)$$

Denoting the charge transfer from SO₂ to graphene as ω , the Dirac point position shift V_D as a function of exposure time t can be expressed as

$$V_D = \frac{e d \omega}{\epsilon_0 \epsilon_r} \cdot \frac{n_g p_g}{p} (1 - e^{-pt}) = \frac{k}{p} (1 - e^{-pt}), \quad (3)$$

where $k = \frac{e d \omega}{\epsilon_0 \epsilon_r} \cdot n_g p_g$. Five curves fitted to the V_D using Eq. (3) are shown in Fig. 5(a). The extracted Dirac point

position shift V_D at RT, 40 °C, 60 °C, 80 °C, and 100 °C from the fits are 33.9 V, 36.09 V, 41.8 V, 49.6 V, and 54.5 V, respectively. It is also clear from Eq. (3) that V_D depends linearly on the concentration of SO₂ adsorbed on graphene, so the “shifting rate” of the Dirac point of graphene to the SO₂ concentration at RT, 40 °C, 60 °C, 80 °C, and 100 °C are 0.678 V/ppm, 0.721 V/ppm, 0.836 V/ppm, 0.992 V/ppm, and 1.09 V/ppm, respectively. Such large rates demonstrate the high sensitivity of the graphene detector to the SO₂ gas. Additionally, the final Dirac point positions depend linearly on temperature, Fig. 5(b), and the sensitivity of this detector increases as temperature increases from RT to 100 °C.

A graphene FET was fabricated and tested as a SO₂ gas detector at different temperatures by *in-situ* FET measurements in a high vacuum chamber. Adsorbed SO₂ molecules heavily p-dope graphene and thus shift its Dirac point position dramatically demonstrating that graphene FETs are viable SO₂ gas detectors. At room temperature, the Dirac point shifted 0.678 V/ppm to the positive side, and the resistance decreased about 60% at a SO₂ concentration of 50-ppm. At 100 °C, the Dirac point shifts 1.09 V/ppm to the positive side, and resistance decreased over 100% at a SO₂ concentration of 50-ppm. The detector reset time is quite long at lower temperatures, but it significantly decreases with increasing temperature (only 10 min at 100 °C). The sensitivity of the SO₂ graphene detector increased linearly between RT and 100 °C.

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