Adsorption Distance Effects on Gas Adsorption Induced Scattering in Graphene Gas Sensors

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Abstract

Monitoring graphene's electronic response to adsorbates is widely used in graphene chemical sensors. Although the electrical modulation of graphene-adsorbate doping response is well studied, a detailed understanding of the associated scattering response is still lacking. In this work, the scattering response of pristine graphene to tuning voltage (TV) modulation of the graphene-CO₂ van der Waals (vdW) complex formed by CO₂ adsorption on graphene is investigated and shown to depend on the adsorption distance of the CO₂ scattering centers (carbon and oxygen atoms of CO₂) from graphene. The gas adsorption induced reduction in field-effect mobility is in the order 0 V < -40 V < 40 V while doping is in the order -40 V < 0 V <40 V suggesting that carrier scattering is not influenced by only doping concentration as the -40 V tuned complexes showed higher carrier scattering despite having a lower doping concentration. The scattering trend is consistent with **Density Functional Theory** (DFT) simulations which show that at TV = 0 the adsorption distance is maximum but decreases with TV application with a minimum at +TV consequently the scattering potential is maximum at +TV and minimal at TV = 0 V.

1. Introduction

Graphene's low noise, high mobility, 2D nature, and atomic layer thickness, makes it a very sensitive gas sensor with single molecule sensitivity.^{1),2)} Additionally, the electrical tuning of the van der Waals (vdW) complexes formed by the adsorbed gas molecules on graphene result in changes in its density of states, doping characteristics, molecular re-orientation adsorption and distance.3) Nevertheless, while the effect of such electrical modulation of the graphene-molecule adsorption distance on the doping characteristics is well studied,³⁾ its associated effect on the gas adsorption induced scattering is lacking. In this work, the scattering response of pristine graphene to electrically induced molecular re-orientation of adsorbed CO_2 molecules is studied. Using experimental measurements and Density Functional Theory (DFT) simulations the adsorbed molecules vdW bonding retention after the electric field is turned off is demonstrated for different tuning voltages (TV). Thereafter, the TV induced gas adsorption induced scattering is investigated and shown to be dependent on the graphene- CO_2 adsorption distance.

2. Experimental Section

The 2 µm by 1 µm pristine graphene device was obtained by mechanical exfoliation of highly ordered pyrolytic graphite (HOPG) to SiO₂/Si substrate and electrodes were defined using standard procedure involving electron beam lithography, plasma etching, metal evaporation and Ar/H2 cleaning as described elsewhere.³⁾ The gas sensing experiment involved monitoring the conductivity response of the graphene sensor to 100 % CO2 at TV = -40 V, 0 V and +40 V separately with interruptions at 12 minutes, 27 minutes, (chamber full), 33 minutes, 37 minutes, 47 minutes and 56 minutes to measure the transfer characteristics. After 56 minutes, TV application was stopped and only the transfer characteristics were measured periodically in intervals of 30 minutes until 206 minutes. The schematics for the experimental procedure and device are shown in Fig. 1a.

3. Results and Discussion

The doping concentration (n_d) due to adsorbed CO₂ was obtained from the shift in the charge neutrality point of graphene with respect to vacuum (ΔV_{CNP}) using the formula:

$n_d = (C_g/e)\Delta V_{CNP} \qquad (1)$

where C_g (gate capacitance) is given by $\varepsilon_0 \varepsilon_r / t_{ox}$ and e, ε_0 , ε_r , t_{ox} are the electronic charge, permittivity of vacuum, relative permittivity of SiO₂, and SiO₂ thickness respectively. The doping concentration (Fig. 1b) increased with TV in the



Fig.1 (a) Experimental and device schematics (right). (b) Doping concentration vs time. (c) Change in mobility vs time. (d) Number of adsorbed molecules obtained from the doping concentration. Blue background represents region with TV off (i.e. 'vdW bonding memory' region) and white background represents region with TV on.

order -40 V < 0 V < 40 V. This agrees with previous reports³⁾ in which CO₂ acted as an acceptor at TV = 0 V and +TV and a weak donor at –TV. Hours after the TV experiment was stopped, the graphene-CO₂ vdW complexes exhibited doping characteristics unique to each TV suggesting that they possess a 'vdW bonding memory' which enables their properties to be studied even after the TV is turned off.⁴⁾ Fig. 1c shows the change in mobility ($\Delta\mu$) obtained from the relationship

$$\Delta \mu = \mu_{\max(vac)} - \mu_{\max(gas)}$$
(2)

where $\mu_{\max(vac)}$ and $\mu_{\max(gas)}$ are the maximum field-effect mobilities in vacuum and the gas environment respectively. The gas adsorption induced scattering increased in the order 0V < -40 V< 40 V which agrees with DFT simulations of the TV-induced gas adsorption distance modulation due to re-orientation of adsorbed gas molecules on the graphene surface. The carbon of CO_2 distance (Å) from graphene was 3.0207, 3.0517, 3.0126 for -40 V, 0 V and 40 V respectively while the graphene sheet distance (Å) from the two oxygen atoms of CO_2 was (3.0207, 3.0264), (3.0598, 3.0652), (3.0311, 3.0321) for -40 V, 0 V and 40 V respectively. Since these atoms act as scattering centers, the closer they are to the graphene surface the stronger the scattering potential that will be experienced by carriers in graphene suggesting that scattering increases in the order 0 V < -40 V < 40 V which is consistent with experimental measurements. Additionally, the number of adsorbed molecules per minute obtained

from Fig. 1d were of similar order of magnitude (256, 188, 171 for -40 V, 0 V and 40 V respectively) demonstrating that the observed scattering trend is due to differences in the gas adsorption distance and not just the number of adsorbed molecules or doping concentration.

4. Conclusion

Using experiments and DFT simulations, the gas adsorption induced scattering is shown to have a strong contribution from electrical modulation of the graphene-gas molecule adsorption distance such that the TV-induced complexes show higher carrier scattering with increasing TV with a maximum at +TV and minimum at TV = 0 due to the higher gas adsorption distance in the latter.

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References

- S. Rumyantsev, G. Liu, M. S. Shur, R. A. Potyrailo and A. A. Balandin, Nano Lett. 12 [5], 2294 (2012).
- J. Sun, M. Muruganathan and H. Mizuta, Sci. Adv. 2 [4], e1501518 (2016).
- M. Muruganathan, J. Sun, T. Imamura and H. Mizuta, Nano Lett. 15 [12], 8176 (2015).
- O. G. Agbonlahor, M. Muruganathan, T. Imamura and H. Mizuta, ACS Sensors acssensors.0c00403 (2020).