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The impact of outgassing of molding compound on graphene for gas sensing

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***Abstract*—Packaging is an indispensable part in microelectronics manufacturing industry, where transfer molding as an essential step is typically included for encapsulation. Recently, with the fruitful achievements of research on graphene in gas sensing, there is also urgent need for study on how the packaging process will affect the graphene, to develop compatible manufacture protocol for practical graphene-based gas sensor. In this work, we carried out experiments on how molding compound outgassing affects graphene for gas sensing. Our results show that although there is some impact on the electrical properties of the graphene, there is no change in the microstructure, and only a slight and manageable change in gas sensing abilities. This work suggests that graphene could maintain performances after epoxy molding packaging processes.**

Keywords—graphene; molding compound outgassing; packaging; gas sensing.

I. INTRODUCTION

Microelectromechanical-system (MEMS)-based gas sensor research has drawn tremendous attention in recent years, focusing on features such as miniaturisation, lowering cost, bio-compatibility, practical implementation and commercialisation. Gas sensors have a wide range of potential application areas, such as environmental hazard monitoring, precision agriculture, and artificial olfaction (electronic noses) for point of care, etc [1-4]. Numerous materials have been developed and studied for gas sensing, among which graphene remains as one of the most promising candidates. Graphene is an intriguing two-dimensional (2D) carbon-based nanomaterial comprised of an atomically thin layer of sp^2-bonded carbon atoms in a hexagonal honeycomb arrangement. The vast surface area of 2D graphene is advantageous for contact with guest molecules, with other merits including high electrical conductivity and mobility, low noise level of current, and high mechanical strength and chemical stability. Besides, as a unique 2D material, the band structure of graphene has a Dirac cone with zero bandgap, where its Fermi level can be tuned by doping through various methods [5]. Scalable graphene production has already been feasible in commercial products. Those advantages and properties render it with huge potential for gas sensing, and several gas sensing systems have already been established according to literature, such as wafer-scale microsensor arrays and high-sensitivity graphene sensors with surface modifications [6-10].

Nevertheless, despite the inspiring achievements of graphene-based gas sensors in research, the progress in moving the technology outside the lab is deficient. To implement a sensor system for practical use, extra standard manufacturing procedures in factories are needed to make a sensory core into a real device. One of the main procedures is the packaging process. Here, transfer molding is an essential step in low-cost encapsulation of the device, which includes heating the molding compound. During the process, high temperature and outgassing from the molding compound adsorbed on graphene surface may affect the sensing material and cause changes in surface properties or doping effect [11,12]. This could be detrimental to the performance of graphene-based gas sensors. To this end, we carried out a study about how the heating and molding compound outgassing impacts the electrical properties of graphene and its gas-sensing performances.

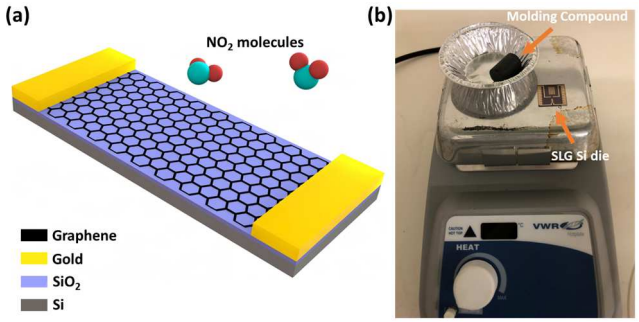

Fig. 1. (a) Schematic illustration of single-layer graphene (SLG) connected with gold electrodes on SiO_2/Si substrate for gas (NO_2) sensing; (b) Photograph of the experiment set up for exposing the graphene chip samples heated under molding compound outgassing. The whole setup is covered with a quartz dome (not shown here).

II. EXPERIMENTAL

We used a commercial grade epoxy molding compound, provided by the company BESI as the equipment supplier in the project. BESI also provided typical settings for high volume manufacturing, i.e. 175 °C and an extended cure time of 20 min to ensure complete outgassing. Meanwhile, commercial monolayer graphene (SLG) samples were obtained from Graphenea, where the SLG with different sizes and shapes were transferred to an oxidized Si wafer, where gold electrodes were also deposited for connection (illustrated in Fig. 1a). The molding compound outgassing tests were carried out by placing the molding compound and SLG chip side by side on a heater with additional quartz cover as shown in photograph in Fig. 1b. The set-up was cooled down to room temperature naturally after heating. Here, we also added the sole heating of graphene without molding compound as a control experiment.

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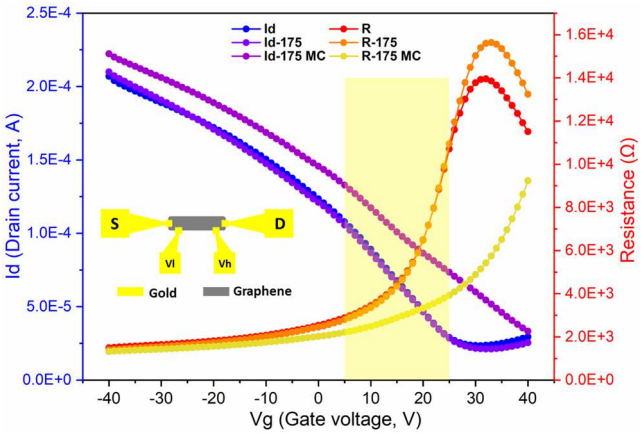

Fig. 2. Comparison of the I-V (drain current - gate voltage) curves and corresponding resistance of single layer graphene (SLG) under original, heated and heated with molding compound states. Yellow highlighted areas are used to calculate the field-effect mobility.

III. Results and Discussion

A. Electrical characterisation

Electrical tests were directly conducted on a probe station connected to a semiconductor parameter analyser, with a 4-probe configuration (illustrated in Fig. 2 inset), to record the drain current-gate voltage characteristics (I_d-V_g curves) as well as the corresponding resistance of rectangular-shaped graphene. The Si substrate acts as the gate of the device. The drain-source voltage was set as 0.5 V, and the gate voltage changed from -40 to 40 V at a sweep speed of 1 V/s. As shown in Fig. 2, the original graphene sample's Dirac (charge neutrality) point can be located at around 27 V. The reason that the Dirac point is not at close to zero position, we speculate, is due to some doping effect and residue contamination during manufacturing or from the environment during transporting and storing in ambient for some time.

The field-effect mobility from the linear part (yellow-highlighted) is calculated based on the following equations:

$$\mu_{ef} = \frac{dI_d}{dV_g} \times \frac{L}{WV_{DS}C_{EDL}} \qquad (1)$$

$$C_{EDL} = \varepsilon_{SiO_2}\varepsilon_0/d_{thickness} \qquad (2)$$

where L and W are the length and width of graphene samples, I_d, V_g and V_{DS} are drain current, gate voltage and drain-source voltage, respectively. C_{EDL} is electrical double-layer capacitance [13]. The rectangular-shaped graphene (80×20 μm) delivered a mobility of 851.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$, as well as a resistance of 2531.6 Ω at a gate voltage of 0 V. Here, the mobility is lower than graphene's theoretically high mobility but comparable to other CVD graphene in previous literatures from few hundreds to more than one thousand [14]. Again, we believe this is due to manufacture, transporting and storing processes. In addition, the SiO_2 substrates with some impurities may also trap charges which could impact the graphene mobility [15].

As can be seen, after heating the graphene sample solely under ambient conditions, there is no significant change in I-V curve or shifting of the Dirac point. The calculated mobility in the yellow-highlighted range after heating treatment slightly decreases to 825.9 $cm^2 \cdot V^{-1} \cdot s^{-1}$. Besides, compared to original graphene, the resistance of heating-treated samples remains almost the same at 0 V, but shows some increase when the gate voltage is swept to higher values. When it comes to samples with heating treatment with molding compound, the outgassing clearly shows some impact on the electrical properties of graphene. The Dirac point shifts to a higher gate voltage compared to original or heated samples, while the resistance also decreases at 0 V. Based on the calculation, the mobility decreases to 629.9 $cm^2 \cdot V^{-1} \cdot s^{-1}$. Here, from the electrical property aspect, we can say that the molding compound outgassing during the packaging process resulted in additional p-type doping impact on the graphene.

B. Microstructre analysis

We also carried out Raman and SEM (scanning electron microscopy) characterisation to check for any microstructural changes of the graphene. The Raman spectra were collected by a Renishaw inVia Raman microscope with 633 nm laser, as shown in Fig. 3a. All three samples show clear typical graphene peaks (D, G and 2D band) as labelled. For original single-layer graphene, the D, G and 2D band peaks are located at around 1325, 1591 and 2647 cm^{-1}, respectively [16]. After heating the samples, we observed a slight blue shift of the peaks compared to original one. For example, the G band peak position of solely heated graphene is at 1598 cm^{-1} while heated with

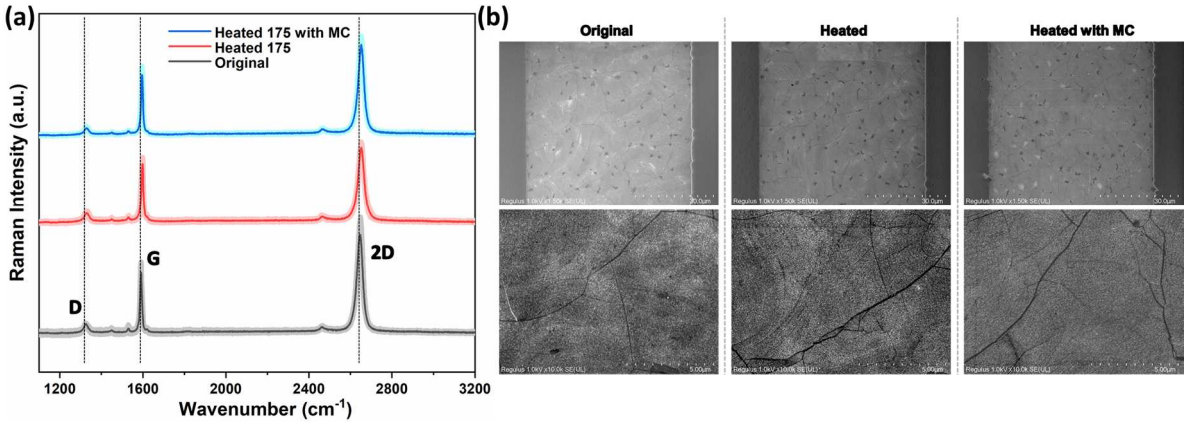

Fig. 3. Structure characterisation: (a) Raman spectra (shaded areas represent plus or minus one standard deviation from the mean) and (b) SEM images of different SLG graphene samples (original, heated and heated with molding compound).

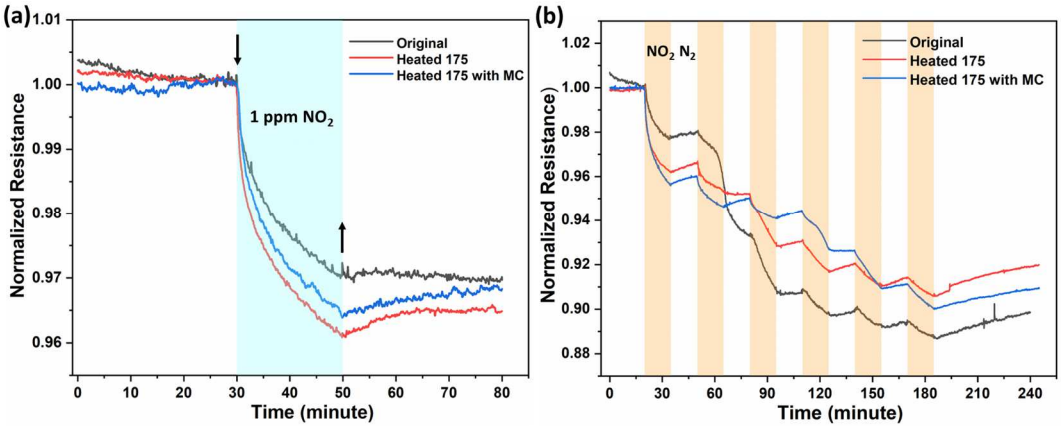

Fig. 4. Gas sensing performances of graphene samples (original, heated and heated with molding compound). Real time response to (a) one single cycle of exposure to 1 ppm of NO_2 for 20 minutes (blue highlighted); (b) repeated cycles of exposure to sequential 1 ppm of NO_2 pulses (15 minutes each, orange highlighted).

molding compound is 1596 cm^{-1}. Similar trend could also be seen in D and 2D band. We believe that this due to some compressed stress formed on the surface of graphene as well as the doping effect during the heating process [17]. Besides, all three samples exhibit low average I(D)/I(G) ratio (0.141, 0.147 and 0.106 for original, heated and heated with molding compound samples) as well as higher than 1 of I(2D)/I(G) value, indicating that the three samples are all single layer graphene with relatively low defects [18].

When it comes to SEM (Hitachi Regulus 8230) shown in Fig. 3b, all three samples deliver similar smooth surface morphology with grain-like structures, while under higher magnification, we can observe uniform distribution of dots on the surface. As reported in literatures, we believe these phenomena are from the preparation process of CVD growth of graphene using Cu catalyst on SiO_2 substrates [19,20]. Nevertheless, there is no distinguishable difference between the three samples in SEM images, implying that heating or molding compound outgassing do not obviously impact the graphene morphology at microstructure level.

C. Gas sensor evaluation

Finally, we evaluated the gas-sensing performances of all graphene samples. The testing was conducted in a typical controlled gas sensing set up including V-OVG (Owlstone Inc Vapour Generator), MFCs (mass flow controllers), stainless steel chamber connecting to source meter. The gas total flow was kept at 500 sccm. In the single-cycle test, the three samples were stabilised in N_2 and then exposed to NO_2 for 20 minutes. As we can see from Fig. 4a, in the stabilisation stage, the resistance of the original graphene keeps decreasing while the heated sample resistances remain slightly more stable. When exposed to NO_2 gas, the original graphene has a response of about 3.0% resistance change, while the heated samples have a higher response, with 3.8% for heated and 3.4% for heated with molding compound. The slightly stronger resistance response of heated samples compared to the original is likely due to the heating process, which can facilitate the desorption/decomposition of impurities or other species adsorbed on the graphene surface, as well as help the sample to reduce the shifting during stabilisation.

We also performed repeated gas sensing testing, as shown in Fig. 4b. The samples were exposed to NO_2 and N_2 in turns repeatedly. At the beginning of the stabilisation stage, we can also observe a similar decreasing shifting of resistance in the original graphene sample, which is in accordance with single-cycle testing. Again, in the first cycle, the heated samples have a higher response than the original one. However, in the next few cycles, the response of the original graphene becomes stronger, and there is response variation in other samples. Until the 5th and 6th cycle, the response to NO_2 gas of all three samples gradually becomes stable and almost parallel, indicating that all samples begin to show similar performances. This could be ascribed to the fact that all unreversible binding sites have been mostly taken over, and reversible binding sites function as sensing elements.

IV. Conclusion

In summary, to study how molding compound outgassing under high-temperature impacts graphene-based gas sensors during the packaging process, we carried out control heating experiments, structure characterisation and performance evaluation. It can be concluded that heating, as well as molding compound outgassing, may shift the Dirac point of graphene regarding electrical properties but no observable influence on the microstructure. As for gas sensing performances, the responsiveness of samples only shows differences in the stabilisation stage and the few initial sensing cycles, and then gradually tends to be similar afterwards. Our results suggest that the outgassing of molding compound under heating conditions does have some impact on the graphene samples, but in a manageable manner which will not significantly alter the sensing ability of graphene, so that the related factories/companies are encouraged to continue procedures for packaging graphene sensing cores into practical devices.

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