1. Introduction

Graphene has attracted attention in various areas of device applications because of its superior electrical properties [1, 2]. Exfoliated graphene cleaved from highly oriented pyrolytic graphite is often used in attempts to secure these properties, but the process is limited in size to micrometre scales. To overcome this weakness, a chemical synthesis technique, referred to as chemical vapour deposition (CVD), has been adapted and used successfully to make a large graphene sheet [3]. Nevertheless, the CVD approach still has some challenges, such as synthesizing graphene with large grains [4, 5] or cleanly handling graphene in a field-effect transistor (FET) fabrication process [6]. With respect to fabrication, the use of organic materials, such as poly (methyl methacrylate) (PMMA) or a photoresist (PR), for transfer or lithography on a SiO₂ substrate is the most serious obstacle when it comes to developing high-quality graphene devices using a wet process [7]. This induces the unwanted doping of graphene, resulting in an absence of a charge neutrality point (CNP) [8] with a high gate voltage up to 100 V. The carrier mobility is also degraded by these charged impurities [9].

Several approaches, including annealing [7, 10, 11], chemical treatment [12, 13], doping control [14], interface engineering [15], and metal mask-based photolithography techniques [6] have been used to solve the low carrier mobility problem. Additionally, suspending graphene that avoids the charge scattering shows a high carrier mobility of 100 000 cm² V⁻¹ s⁻¹ [16, 17], and placing graphene on a substitute substrate, such as hexagonal boron nitride, shows a highly improved carrier mobility of 37 000 cm² V⁻¹ s⁻¹ [18]. Furthermore, screening effects in graphene that reduce the long-range scattering of charged impurities have recently been reported [9, 19, 20]. Among these, there are interesting papers regarding graphene field effect transistor (G-FET) transport properties that are affected by water. Chen et al describe that ionic screening in G-FETs caused by the deionized water exposure (18 MΩ cm) resulted in CNP restoration.
with a carrier mobility of $\sim 1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [21]; and dielectric screening by a similar mechanism also resulted in CNP restoration with a carrier mobility of 70000 cm$^2$ V$^{-1}$ s$^{-1}$ [22]. Unlike their explanation, in contrast, we found that the electrical property restoration by water did not take place immediately but took some time. It seems that the restoration is not only because of the screening effects by water but also de-doping of graphene by Joule heating with water concluded based on our experimental results.

In this paper, the electrical property change of G-FETs (G1 to G8) in a thermo-humidistat chamber by Joule heating either with or without water is studied. Based on the analysis of Raman spectroscopy and $I_d-V_g$ ($I_d$: drain current, $V_g$: gate voltage) measurement for all of the samples, the significant parameters that affect this restoration phenomenon are discussed.

2. Experimental

2.1. Device sample preparation

CVD-grown graphene (Graphene Square Co.) was transferred by a well-known wet transfer technique by using PMMA [3] on a 300nm thick SiO$_2$/Si substrate, and the G-FET structures with 10μm length and 2 μm width were fabricated. The source and drain metal pads (Cr/Au, 30/50 nm) were then directly evaporated on the graphene using photolithography with a PR (AZ GXR 601, AZ Electronic Materials) and a developer (AZ 300 MIF, AZ Electronic Materials). Afterwards, the PR was again coated and patterned as a line-shaped mask on the graphene across three pads in the middle. The area of graphene that was not protected by the PR mask was etched out by reactive ion etching as shown in figure 1(a). Lastly, the samples were dipped in acetone for about 20h.

2.2. Measurement

The Keithley 2400 that applies voltage while simultaneously measuring current was connected to the drain–source channel, and the Keithley 187 was used to set the gate voltage relative to the Si under the SiO$_2$ substrate layer (see figure 1(a)). The $I_d-V_g$ characteristics of device G1 before dipping it into acetone are depicted in figure 1(b). However, in this measurement, we were not able to measure the CNP of this PR-coated (~20 nm) device while the drain–source and gate-Si voltages were swept from 0.5 V to 1.0 V and from 0 V to 100 V, respectively.
3. Results and discussion

3.1. CNP restoration and high mobility characterization of G-FETs

To figure out the change in the electrical property of G-FET when water is on the graphene, device G2 was first investigated by measuring the current in real time with a fixed drain-source voltage (0.1 V) across the channel and a fixed gate-Si voltage (0 V). While measuring the current change, there are four moments that we swept the gate voltage from −10 to +30 V which are described as the peak-like signals with numbers on the top in figure 1(c). These signals consist of $I_d-V_g$ characteristics; the detail of the fourth one is enlarged in the inset, and all of these four characteristics are plotted in figure 1(d).

After about 40 min had elapsed, a water droplet was dropped on the device G2 (see the arrow in figure 1(c)). At this moment the third gate sweeping was being carried out, and the current exhibited slight vacillations, as described by the green dotted curve of figure 1(d). From the fourth gate sweeping on, the CNP returned back close to a zero gate voltage, and its carrier mobility became as extraordinarily large as 101 300 and 100 900 cm$^2$ V$^{-1}$ s$^{-1}$ for holes and electrons, respectively, near the CNP. The mobility was calculated by the following equation [23–25]:

$$\mu_{\text{FE}} = \left( L_{\text{ch}}g_m/(W_{\text{ch}}C_G V_{\text{DS}}) \right),$$

where $\mu_{\text{FE}}$ is the field-effect mobility, $L_{\text{ch}}$ is the channel length, $W_{\text{ch}}$ is the channel width, $V_{\text{DS}}$ is the fixed drain voltage (0.1 V), $C_G$ is the gate capacitance (11 nF cm$^{-2}$) [26], and $g_m$ is the transconductance ($dI_d/dV_g$).

Considering the above results, the mobility of about 10 000 000 cm$^2$ V$^{-1}$ s$^{-1}$ is extraordinarily large compared to the previous results in CVD grown graphene devices. The CNP restoration with a high mobility was not, however, only a one time occurrence but it happened many times, even in different samples at different experiments. So the mobility of our CVD graphene instantaneously became as large as the exfoliated ones at the moment it encountered a wet environment condition in the chamber, but it went down as low as 1000 cm$^2$ V$^{-1}$ s$^{-1}$ in ambient condition for the electron mobility afterwards. This might be because of the ionic screening effect but it is true that more research is needed to reveal this unknown mechanism; more experimental data and another measurement method for the device mobility with other samples in similar situations will be helpful to verify the clarity of the experimental results.

3.2. Investigation of the parameters for the electrical property restoration

3.2.1. Decoupling existence of water and current flow. The result described above claims that the restoration of the electrical property is not only because of the water effect but also other buried reasons such as the existence of current flow, which is accompanied by Joule heating. In order to decouple these parameters a thermo-humidistat chamber was used.

Table 1. Devices from G1 to G5 with different parameters for the experiment. All of the devices were identical and the real time current flow measurement was carried out in ambient conditions for the devices G1 and G2 while it was done in a thermo-humidistat chamber for the devices G3, G4 and G5. The restoration was observed only when parameters of water and current flow simultaneously existed.

| Parameter          | G1   | G2   | G3   | G4   | G5   |
|--------------------|------|------|------|------|------|
| Water              | O    | O    | O    | O    | X    |
| Current flow       | O    | O    | O    | O    | X    |
| Joule heating      | O    | O    | O    | O    | O    |
| Restoration        | X    | O    | X    | O    | O    |

In this experiment, it was able to form (or deform) a thin layer of water on the device surface which is due to the temperature difference between the sample surface and the air in the chamber, as discussed in section 3.4, which gives us a capability to separate the parameters as tabulated in table 1, and we confirmed that there was not the restoration in the devices G3 but in G4 and G5.

Device G3 was placed in the chamber with set temperature and relative humidity conditions of 50 °C and 70%, respectively. These conditions were maintained while we measured the current in real time with fixed drain (0.1 V) and gate (0 V) voltages. Meanwhile, the gate voltage was swept seven times from −10 to +15 V, and the details of this experiment are shown in figure 2(a). The blue and green curves indicate the temperature and relative humidity changes reaching to each set point. The red curve corresponds to the measured current in real time. The seven $I_d-V_g$ characteristics which are depicted as the peak-like signals in the red curve are extracted and plotted in figure 2(b).

The environment change, however, was not enough to form a water layer on the graphene channel and the electrical properties remained unrestored as described in figure 2(b), even though there was an electric current flowing through the channel. This expresses that the existence of water is necessary in this experiment. Therefore, as shown in figure 2(c), we conducted an experiment on device G4 using a different temperature (60 °C) and relative humidity (90%) to ensure that a water layer formed on the device, and it was found that the current change behaved unstably when the relative humidity changed abruptly and a water layer might be formed as indicated by the purple arrow in figure 2(c). After this strange behaviour, the CNP gradually returned close to the zero gate voltage regime; the resulting carrier mobility again instantaneously became 16 000 and 17 400 cm$^2$ V$^{-1}$ s$^{-1}$ for holes and electrons, respectively (see the 7th curve in figure 2(d)). This suggests that the presence of water and current flow are simultaneously required to restore the electrical properties of graphene.

To guarantee reproducibility, the same experiment was performed with device G5, as shown in figure 3(a). Again, the CNP was restored following a rapid change in relative humidity (see the online supporting materials (stacks.iop.org/JPhysD/48/455102/mmedia)), and the carrier mobility...
rose back up to 55,200 and 36,800 cm² V⁻¹ s⁻¹ for holes and electrons, respectively. Meanwhile, it was found that, from the third gate voltage sweeping, the electron mobility was degraded asymmetrically based on an observation of a reduced carrier mobility of ~10,200 and 670 cm² V⁻¹ s⁻¹ for holes and electrons, respectively. This mobility asymmetry between the holes and electrons has been reported occasionally [27] using various techniques, including (1) channel doping [28], (2) pinning of the charge [29], and (3) installing a p–n junction under the metal pads [30].

Following this experiment, we lowered the set points (temperature and relative humidity to 20 °C and 40%, respectively) to remove the water layer on device G5 (see the online supporting materials (stacks.iop.org/JPhysD/48/455102/mmedia)) and found that the shapes of the $I_d-V_g$ curves were maintained and that the CNP hardly moved over the course
of an hour (figure 3(b)) even without a water layer; however, the carrier mobility dropped to 2,000 and 540 cm$^2$ V$^{-1}$ s$^{-1}$ for holes and electrons, respectively. This suggests that, after the device was cleaned, the water layer on the device is primarily responsible for producing the high levels of mobility which supports the idea of screening effects.

### 3.2.2. Decoupling all parameters; existence of water, current flow and Joule heating.

Interestingly, after conducting the measurement on device G5, the CNP of device G6 also came back close to the zero gate voltage as shown by the blue curve in figure 4(a), which was carried out in an ambient condition. The carrier mobility levels for device G6 became 870 and 230 cm$^2$ V$^{-1}$ s$^{-1}$ for holes and electrons, respectively, which are as high as those for device G5 indicated in figure 3(b). This result was due to the structure of our specific G-FET, in which every second graphene channel (right part of the G-FET in figure 1(a)) was electrically and thermally connected to the first one (left part of the G-FET in figure 1(a)), and device G6 was connected to device G5 as a second one. Based on this fact, we could decouple the current flow and Joule heating effects as tabulated in table 2 because device G6 only experienced the annealing of diffused Joule heating from device G5 with water on it. There were two more devices; G7, which experienced the same as device G3, and G8, which none of the parameters affected in an ambient condition.

Based on these samples, we came to the conclusion that Joule heating combined with water causes polymer residue removal and thus contributes to the de-doping of graphene, which is then accompanied by CNP restoration. It was reported that the thermal annealing gave rise to the dehydrogenation of the polymer, and it could be etched using oxidative gas such as CO$_2$ [31]. We infer that the Joule heating of

| Table 2. Devices from G3 to G8 with different parameters for the experiment. All of the devices were identical and the real time current flow measurement was carried out in a thermo-humidistat chamber for the devices G3 and G3 while it was done in an ambient condition for the devices G6, G6 and G8. The restoration was observed only when parameters of water and current flow simultaneously existed. |
|---|---|---|---|---|---|
| In thermo-humidistat chamber | In ambient condition |
| | G3 | G5 | G6 | G7 | G8 |
| Water | O | O | O | O | O |
| Current flow | O | O | O | O | O |
| Joule heating | O | O | O | O | O |
| Restoration | X | X | O | O | X |
the graphene led to the dehydrogenation of the polymer residue and the water vapour generated might act as the oxidative gas, since the bond energy of O–H in water is similar to that of O = O in O₂ (~497 kJ mol⁻¹) [32], and then might attack carbon bonding to decompose the polymer residue. However, the exact mechanism behind this inference should be further investigated in detail.

3.3. Atomic force microscopy and Raman spectroscopy analysis

Atomic force microscopy was employed (figures S2(a) and (b)) (stacks.iop.org/JPhysD/48/455102/mmedia) and the Raman spectroscopy results were analyzed (figures 4(b) and (c)) to confirm whether or not the polymer residue was removed. Regardless of the amount of polymer residue remaining, the slope of the Raman spectrum for polymer residue remained constant, leading to the baseline Raman spectrum for graphene, but the main Raman signals for graphene (2D and G) became noticeable as the polymer residue was removed [33]. To clarify, the details shown in figures 4(b) and (c), five Raman spectra for devices from G3 to G8 were analyzed in terms of the peak positions, peak ratios, and full-width at half-maximum (FWHM) of the 2D peak. These samples were made from the same sheet of CVD-grown graphene, so the signals should be similar to one another. However, obvious differences between them were visible, which can be accounted for by de-doping. Firstly, as shown in figure 4(b), the G positions for all of the signals were the same, but there were considerable differences in the 2D peak positions. This is in accordance with the amount of de-doping [34, 35] taking place. Generally, as graphene is p-doped, the 2D peak is blue-shifted and the CNP gate voltage becomes located on the positive side. From this perspective, the above results also agree with the CNP gate voltages, which were larger than 15 V for device G3, around 5 V for device G5, and almost 0 V for device G6. Moreover, as shown in the left of figure 4(c), the 2D/G ratio value for device G6 was larger than for the others, which also reflects the highest amount of de-doping that occurred since the 2D/G ratio value increases as the amount of doping decreases [34, 35]. The D/G values for all the samples were consistently in the range of 0.32 to 0.4, reflecting the fact that the qualities of the samples are all the same, and the differences in electrical performance between samples only came from the amount of doping. Lastly, as shown in the right of figure 4(c), the FWHM values of the 2D positions for device G8 were the greatest because these values also depend on the amount of de-doping taking place [34, 35].

3.4. The mechanism for water layer formation

We observed that there was a certain amount of humidity change necessary to form a water layer, but it is not appropriate to only consider the humidity change alone because the relative humidity also depends on temperature. Therefore, we calculated the current vapour pressure of water to exclude the correlation with temperature change. It was apparent that some reaction took place when the humidity rapidly changed; we expect that it occurred when a water layer formed suddenly. The vapour pressure gradient when the event occurred (indicated by the purple arrow in figure 2(c)) was 50.46 hPa min⁻¹, which was deduced from the Goñi–Gratch equation (see figure S3(b)) (stacks.iop.org/JPhysD/48/455102/mmedia). The values corresponding to figures 2(a) and 3(a) were 45.88 and 67.21 hPa/min, respectively (see figures S3(a) and (c)) (stacks.iop.org/JPhysD/48/455102/mmedia). To demonstrate that a slow change in humidity cannot form a water layer (figure S4) (stacks.iop.org/JPhysD/48/455102/mmedia), we slowly increased the relative humidity while maintaining the temperature at 60 °C using the G7 sample; the current flow was definitely affected by the humidity change, but the CNP was not restored. This proves that a thin water layer was hardly formed by a slow increase in humidity. From these experiments, we determined that a minimum water vapour pressure gradient of around 50 hPa min⁻¹ is required to form a water layer and induce CNP restoration for graphene.

4. Conclusion

We demonstrated the electrical property restoration of p-doped G-FETs when their channels were covered by water while electric current flowed through them. As a result, the CNP was returned close to the zero gate voltage and the carrier mobility showed up to about 100000 cm² V⁻¹ s⁻¹ with the water screening and stabilized at around 1000 cm² V⁻¹ s⁻¹ after the water removal. The mechanisms behind this phenomenon observed in the experiments carried out in the thermo-humidistat suggest that the current flow which induces annealing of the graphene leads to the removal of the polymer residue and CNP restoration when combined with water. This approach is very useful to restore the CNP and enhance the graphene mobility.

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