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Characteristics of a Single-Layer Graphene Field Effect Transistor with UV/Ozone Treatment

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The performance of a single-layer graphene field effect transistor treated with UV/ozone at various temperatures is studied. It is observed that the number of the defects in graphene sheet increases with the UV/ozone treatment time, evidenced by Raman spectra. Moreover, the UV/ozone treatment dopes graphene into p-type as the time increases, which is consistent with the electric transfer measurements. With the increase in the UV/ozone treatment time, the mobility of graphene transistor degrades, and the degradation accelerates with the increase in temperature. We further verified by XPS measurement that the oxygen related carbon group O=C-O formation is the main cause for the mobility degradation.

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Graphene, a two-dimension single-layer of carbon atoms with honeycomb structure, where carbon-carbon bonds in plane are sp^2 hybridized, has been widely investigated owing to its unique and attractive electrical, physical and chemical properties.¹⁻⁹ Graphene is an energy gapless material, in which the conduction and valence bands meet at Dirac point.¹ It exhibits ballistic transport on a submicron meter scale, very high mobility for both hole and electron,^{1,2} and high current carrying capability,⁵ leading to a promising material for potential applications for high frequency device,⁷ gas sensor,^{10,11} flexible electronics,^{12,13} and photonics,^{14,15} etc.

Previously, the Ultraviolet/ozone (UVO) treatment is applied to reduce the concentration of oxygen vacancies in high-k gate stack, suppress the gate leakage current and improve the properties of conventional silicon based MOSFETs.^{16,17} For graphene, the oxygen molecule is known to adsorb on graphene surface and induce chemical hole doping.^{18,19} It has also been recently reported that the oxygen content in graphite oxides affects the electronic structure. The transmittance and energy bandgap of graphite oxide film can be tuned by the oxidation time. For example, the energy bandgap can be tuned from 1.7 to 2.4 eV by varying the oxidation time.²⁰ The ab initio density functional theory method has been performed to study the adsorption of ozone molecules on graphene basal plane.²¹ It is reported that the orbital rehybridization induced by epoxide groups trigger a strong intervalley scattering and changes dramatically the conduction properties of graphene.²¹ Very recently, the large chemical enhancement in surface-enhanced Raman scattering (SERS) has been reported, where the UVO treated graphene grown by chemical vapor deposition (CVD) method significantly improves the reproducible SERS signals over a centimeter-scale graphene surface.²² However, the UVO impact on a single-layer graphene (SLG) field effect transistor at various temperatures has not been addressed so far.

Raman spectroscopy has been widely applied in the study of graphite by providing useful information on the disorder or defects induced D band, in-plane vibration of sp^2 carbon atoms and the stacking orders related G and 2D bands.²³ The full width at half maximum (FWHM) of 30 cm^{-1} at 2D band can be considered as a detector for a single-layer graphene.²⁴ The electron or hole doping may be reflected in the stiffening and sharpening of the G band.²⁵ In this report, we have examined the characteristic of SLG by UVO treatment at various temperatures via Raman spectra and electrical characterizations.

Experimental

Graphene sheets were acquired via a mechanical exfoliation from bulky graphite using an adhesive Scotch tape (3M company, USA)

method. Subsequently, graphene is transferred onto degenerated silicon substrate with a thermally grown 90 nm SiO_2 , serving as a conventional back-gate dielectric. Before graphene transfer, SiO_2 surface is cleaned with acetone, isopropyl alcohol (IPA), and piranha solutions for each 10 minutes. The optical images of graphene are acquired by an Olympus (BX51M) microscopy, and the UVO treatment is done in a Samco UV-1 at various temperatures. The SLG is identified by the optical contrast through an optical microscopy, further verified by Raman spectra, as described in introduction part. The Raman measurements with the excitation laser lines of 532 nm (2.33 eV) were performed using a WITEC alpha 300 R Confocal Raman system in air ambient environment. The Raman emission was collected by an Olympus 100 $\times$ objective (N.A. = 0.8) and the excitation laser was set low power to prevent potential structure damages to graphene during measurement. The Ti(5 nm)/Au(50 nm) electrodes, patterned by conventional optical lithography, were formed by electron beam evaporation, followed by an acetone liftoff process. The I - V characteristics of graphene field effect transistors were carried out by a Keithley 4200-SCS semiconductor parameter analyzer in ambient air with a shield chuck.

Results and Discussion

Fig. 1a–1c show the Raman spectra of UV/ozone treated SLG for different time at 25°C, 50°C and 100°C, respectively. All the Raman spectra shown in this paper are calibrated using silicon peak at 520 cm^{-1} . Since our graphene sheet is prepared by mechanical exfoliation from bulky graphite, therefore there is no D band in Raman spectra of graphene with a pristine structure. It only has two main characteristic peaks of G and 2D bands before UVO treatment, where the peak position for G and 2D bands are around 1580 and 2670 cm^{-1} , respectively. The presence of D band is caused by the disordered or defected structure of graphene.^{22–25} The number of defects is almost negligible, even after UVO treatment for 1 minute at 25°C. The intensity ratio of D band to G band (I_D/I_G) is often used to estimate the amount of defects in carbon materials.^{25,26} However, once the temperature is elevated, there is a noticeable D band and I_D/I_G is 0.29 and 0.78 at 50°C and 100°C, respectively for the 1-minute UVO treated samples, shown in Fig. 1b and 1c. As the UVO treatment time extends, the D band occurs, the FWHM of D band also expands, shown in Fig. 1a–1c. The I_D/I_G increases to ~ 1.3 after 4 minutes UV/ozone treatment. The 2D band is a second-order two-phonon process and exhibits a strong frequency dependence on the excitation laser energy.²⁷ According to Raman spectra in Fig. 1a–1c, it can be seen that the symmetric and sharp 2D band, where its FWHM is $\sim 30 \text{ cm}^{-1}$, is the best indicator for a single-layer graphene. It is also reported that the intensity ratio

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Figure 1. Raman measurements of UV/ozone treated SLG for different time at (a) 25°C, (b) 50°C, (c) 100°C. (d) Intensity of I_D/I_G (empty symbols) and I_{2D}/I_G (solid symbols).

of 2D to G band, I_{2D}/I_G, is dependent on the number of graphene layers, and a high I_{2D}/I_G (>1), narrow 2D peak of the Lorentzian shape is considered a fingerprint of single-layer graphene.²⁸ From Fig. 1a, it is observed that the I_{2D}/I_G after 0, 1, 2, 4 minutes UVO treatment is respectively 2.05, 1.83, 1.61, and 0.11 at 25°C. The temperature dependence of I_D/I_G and I_{2D}/I_G are summarized in Fig. 1d. Compared to the I_D/I_G at room temperature, the I_D/I_G at high temperature has a remarkable increase with the UVO treatment time. In the meanwhile, the I_{2D}/I_G decreases significantly at high temperature. It was observed that after 2-minute UVO treatment the I_{2D}/I_G at 50°C decreases to 0.26, which is ~7 times smaller than that at 25°C. It is also shown that the D+D' band occurs in Raman spectra after 4-, 2-, 1-minute UVO treatment at 25°C, 50°C, and 100°C, respectively, shown in Fig. 1a–1c.

The continuous enhancement in I_D/I_G with the increase of the UVO treatment time and temperature, shown in Fig. 1d, indicates that UVO treatment induces disorders or defects in graphene sheet. As D band presents the defects density in graphene sheets, the strong D peak at high temperature corresponds to very high defects density. The reduction of I_{2D}/I_G is accelerated by the temperature, showing that the ozone is more prone to react with the carbon atoms in graphene sheet at high temperatures. It is similar to the graphene treated by sputtered metal or irradiation ions with large kinetic energy, resulting in the removal of carbon atoms from graphene lattice and creating disorders or defects.²⁶ The decrease of I_{2D}/I_G also indicates a stronger doping since the graphene is exposed to the UVO treatment.

To probe the doping effect in graphene, we fabricated SLG field effect transistors and examined their transfer characteristics. The optical image of fabricated SLG FETs is shown in the inset of Fig. 2a. In Fig. 2a, the I_{ds}-V_{bg} curve is observed to shift toward positive voltage with the increase of the UVO treatment time. A p-type doping can induce a positive V_{Dirac} shift in graphene, where V_{Dirac} is the voltage at Dirac point. Accordingly, the doped carrier concentration in graphene

can be approximately estimated using the following equation,^{29–31}

$$n = C_{gs} \Delta V_{Dirac} / q \quad [1]$$

where C_{gs} is the capacitance between channel and back gate per unit area, and q is the unit charge. For 90 nm SiO₂, $C_{gs} = 38.3$ nF/cm². Fig. 2a shows the V_{Dirac} right shifts after the UVO treatment on graphene at room temperature, and the ΔV_{Dirac} is 12 V subjected to the UVO treatment for 1 minute. Based on the above equation, the hole doping concentration in graphene sheet introduced by the UVO treatment is around 2.8×10^{12} cm⁻². While for the UVO treatment at 100°C for 1 minute, the ΔV_{Dirac} is 22 V, the corresponding hole doping concentration is around 5.3×10^{12} cm⁻². Note that the behavior of I_{ds}-V_{bg} shift is quite different from those induced by the voltage stressing, in which there are almost parallel I_{ds}-V_{bg} shifts, indicating the degradation of carrier mobility may be negligible in graphene sheet.³² The carrier mobility can be deduced by the following expression,^{8,32}

$$\mu = dI_{ds} / dV_{bg} \times [L / (WC_{gs} V_{ds})] \quad [2]$$

where L and W is channel length and width, respectively. It is observed that both hole and electron mobility of SLG FETs degrade after UVO treatment. From Fig. 2, it can be seen that the hole mobility of SLG FETs reduces to 23% and 10% of the initial value without the UVO treatment, for the 1-minute UVO treatment at 25°C and 100°C, respectively. Fig. 3 shows the X-ray photoelectron spectroscopy (XPS) of graphene films treated with and w/o the UVO at 25°C and 100°C. The XPS measurement was performed by using a monochromated Al K α (1486.7 eV) X-ray source at power of 150 W (15 kV $\times$ 10 mA). The spectra presented here were corrected by referencing the binding energy to the C1s peak at 284.6 eV. The results show the main C1s peak, which is related to the sp^2 hybridized carbon-carbon bonds, was slightly broadened by hole doping after UVO treatment. There is a clear band at around 288.9 eV, which is related to the carboxylic group O-C=O originated from the oxygenated carbon atoms.²²

Figure 2. (a) Transfer characteristics of SLG FET as a function of the UVO treatment at 25°C. (b) The I_{ds} - V_{gs} measurements of SLG FET as a function of the UVO treatment at 100°C. The V_{Dirac} presents the minimum conductance in transfer characteristics. Inset in (a) shows the optical image of a measured SLG field effect transistor (FET).

Moreover, it is worth mentioning that the band intensity of O-C=O bonds increases with temperature. This can be understood that with the increase in temperature, it is easier for the graphene film to be oxidized in UVO; the bonding of C with O becomes more favorable in higher temperature to form the defects. Hence, the O-C=O bond is the main cause for the performance degradation of graphene devices treated by UVO. It is consistent with the observations in the transfer process of CVD grown graphene treated by H_2 or Ar ambient anneal-

Figure 3. XPS spectra of the graphene before and after UVO treatment at various temperatures.

ing, after which, the field effect mobility increases due to removal of the O-C=O bonds in graphene sheet.³³

Based on the aforementioned, the UVO treatment dopes the graphene sheet into p-type, which is evidenced by the Raman and electric transfer characteristics. On the other hand, the UVO treatment damages the symmetric honeycomb structure of graphene sheet and the defects create in the pristine graphene sheet, resulting the degradation of carrier mobility. When UVO treatment time and temperature increases, more defects are generated and also the mobility significantly decreases. It is caused by the formation of the O-C=O bonds, which is verified by XPS measurement.

Conclusions

In summary, the performance of a single-layer graphene field effect transistor treated with UVO at various temperatures is studied. The UVO treatment has a p-type doping effect in graphene sheet, evidenced by Raman and electric transfer measurements. After the UVO treatment, the pristine structure of graphene sheet is destroyed and the defects are generated, resulting in the degradation of the mobility. The degradation is accelerated at high temperature and the O-C=O bonds are the main cause for the mobility degradation, verified by XPS measurement.

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