

Influence of Hydrophobicity on the Chemical Treatments of Graphene

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The defect-free transfer of graphene grown by using chemical vapor deposition is essential for its applications to electronic devices. For the reduction of inevitable chemical residues, such as polar molecules and ionized impurities resulting from the transfer process, a hydrophobic polydimethylsiloxane (PDMS) film was coated on a SiO₂/Si wafer. The hydrophobic PDMS film resulted in fewer defects in graphene in comparison to a bare SiO₂/Si wafer, as measured with Raman spectroscopy. We also studied the influence of the hydrophobic PDMS film on the chemical doping of graphene. Here, nitric acid (HNO₃) was used to make *p*-type graphene. When graphene was transferred onto a SiO₂/Si wafer coated with the hydrophobic PDMS film, fewer defects, compared to those in graphene transferred onto a bare SiO₂/Si wafer, were created in graphene by HNO₃ as measured with Raman spectroscopy. The experiments suggest that when graphene is transferred onto a hydrophobic film, the number of defects created by chemical molecules can be reduced.

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I. INTRODUCTION

Graphene, a single layer of *sp*²-bonded carbon atoms, has attracted considerable interest for its extraordinary electrical, mechanical, and optical properties [1,2]. With these properties, graphene has become an ideal material for flexible electronic devices. Graphene field-effect transistors (FET) require an energy band gap to operate efficiently [3]. To create such an energy band gap, several methods have been used, such as chemical functionalization [4], applying mechanical strain [5], doping during growth [6], and applying an external electromagnetic field [7,8]. In addition, chemical functionalization has also been used to tune the Fermi energy of graphene through charge transfer [9]. Controlling the chemical functionalization is necessary to shift the Fermi energy of graphene as well as to introduce the energy band gap in a designed manner. According to reports, the rate and the yield of chemical functionalization can be altered by a supporting substrate [10], the number of graphene layers [11,12], and the presence of defects and grain boundaries [13,14]. When chemical-vapor-deposition (CVD)-grown and mechanically-exfoliated graphene is transferred onto a SiO₂/Si wafer, charge puddles are induced by charged

impurities introduced during the transfer process and by ionized impurities on the SiO₂ film [9]. Molecules left during the fabrication process of graphene field effect transistors (FETs) might also be the cause of the charged impurities resulting in the charge puddles [15–17]. In addition, chemically reactive ions, such as Na⁺, and nanoparticles make controlling the chemical functionalization difficult [9,18,19]. The impurities existing in the graphene-covered SiO₂/Si wafer strongly influence the electronic properties of graphene [15,20].

When a hydrophilic film such as silanol (SiOH) is formed on a SiO₂/Si wafer, it easily attracts polar adsorbates, such as water molecules, and causes carrier doping in graphene transferred onto a SiO₂/Si wafer [20–23]. A thin water layer was also reported to be formed when exposing hydrophilic surfaces to an ambient atmosphere, which can be captured under the impermeable graphene layer [24]. According to Lafkioti *et al.* [20], the use of hexamethyldisilazane (HMDS) for hydrophobization on a SiO₂/Si wafer can remove SiOH groups and prevent their formation. The HMDS film was also reported to screen the effects of the Coulomb interaction due to the ionized impurities on a SiO₂/Si wafer [21]. In contrast to the HMDS film, the reactivity of chemicals with graphene on a hydrophobic polydimethylsiloxane (PDMS) substrate, which is equally important, is not

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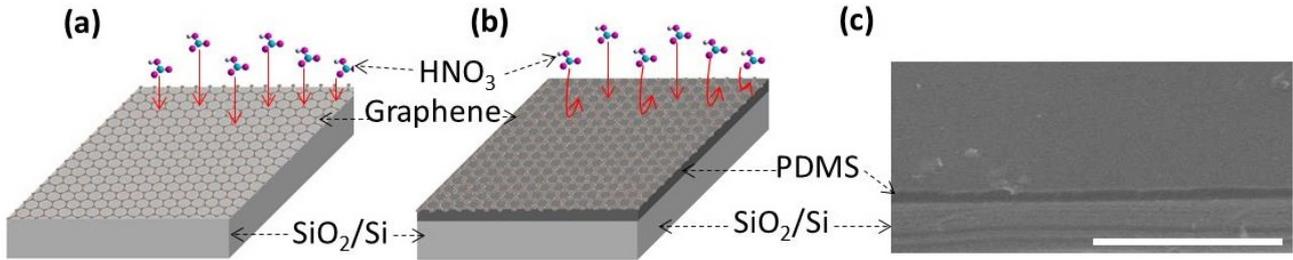


Fig. 1. (Color online) (a) HNO₃ doping on a graphene/SiO₂/Si wafer. (b) HNO₃ doping on a graphene/PDMS/SiO₂/Si wafer. (c) An SEM image of the cross section of a PDMS-coated SiO₂/Si wafer (scale bar : 200 μm).

yet understood, where the PDMS film has been used as a substrate for flexible electronics [25]. In this research, we have studied the influence of the hydrophobicity of PDMS, confined between CVD-grown graphene and a SiO₂/Si wafer, on the chemical treatments of graphene.

II. EXPERIMENTS AND DISCUSSION

Compared with other techniques, CVD is one of the most promising techniques proposed to synthesize large-area high-quality graphene, which is not possible using the conventional method of mechanical exfoliation of graphite. Monolayer graphene was synthesized on a copper foil (with a thickness of 25 μm) in a CVD chamber by using a gas mixture of methane, hydrogen, and argon at flow rates of 21, 99, and 99 sccm, respectively and at a pressure of 9.7 Torr at 1020 °C for 15 min. The copper foil was etched using ferric chloride (FeCl₃), followed by rinsing with poly(methyl methacrylate) (PMMA)/graphene in deionized (DI) water more than five times (for approximately 30 min each). The PMMA/graphene samples were transferred onto a bare SiO₂/Si wafer with a 300-nm-thick SiO₂ film and onto a PDMS-coated SiO₂/Si wafer. The PMMA film was then removed by immersing the samples in acetone for 30 min. To hydrophobize a SiO₂/Si wafer, we added PDMS as a thin film over the SiO₂/Si wafer by submerging it in a PDMS solution (Sylgard 184A : Sylgard 184B = 10 : 1) for 72 h.

For chemical doping, we dipped the graphene/SiO₂/Si and graphene/PDMS/SiO₂/Si wafers in 35% concentrated nitric acid (HNO₃) because it is stable at this percentage value [26]. This 35% concentrated solution of HNO₃ was prepared using DI water. The samples were doped with HNO₃ for 15 min and then rinsed for a few seconds with DI water. Finally, Raman spectra were acquired using an InVivo Raman system with an 1800-line/mm grating and a 532-nm excitation laser.

We investigated the influence of the hydrophobicity of PDMS on the chemical doping of CVD-grown graphene by using Raman spectroscopy. Figures 1(a) and 1(b) show schematic of HNO₃ doping on a graphene/SiO₂/Si wafer and HNO₃ doping on a graphene/PDMS/SiO₂/Si

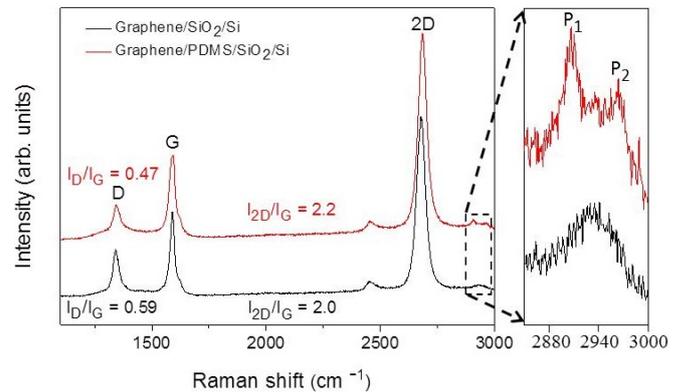


Fig. 2. (Color online) Representative Raman spectra of graphene on bare SiO₂/Si (black line) and PDMS-coated SiO₂/Si (red line) wafers, where the Raman spectra were enlarged to clarify the positions of the Raman peaks (P₁ and P₂) originating from PDMS.

wafer respectively. As described in Fig. 1(b), the HNO₃ doping was partially limited by the hydrophobic PDMS film. Figure 1(c) shows a scanning electron microscopy (SEM) image of a cross section of a PDMS-coated SiO₂/Si wafer.

Raman spectroscopy is a powerful tool for detecting the electronic properties of graphene and for distinguishing between single-layer, bilayer, and multilayer graphene [27]. In addition, it is sensitive to the carrier doping level [28], defects [29,30], and strains [31–33]. Figure 2 shows the Raman spectra of monolayer graphene on bare SiO₂/Si and PDMS-coated SiO₂/Si wafers. The positions of the G and the 2D peaks of graphene on the bare SiO₂/Si were 1591 and 2678 cm⁻¹, respectively, where the G peak (E_{2g} mode) corresponds to the in-plane stretching of the C–C bonds of the graphitic sp² crystalline carbon atoms and the 2D peak (G' mode) is an indicator of graphene that originates from the second-order double-resonance process related to a phonon near the K point in graphene. The positions of the G and the 2D peaks of graphene on the PDMS-coated SiO₂/Si wafer were 1592 and 2685 cm⁻¹, respectively. The P₁ (2907 cm⁻¹) and the P₂ (2964 cm⁻¹) peaks in the enlarged spectra originate from PDMS [34].

The Raman spectra of graphene on the bare SiO₂/Si

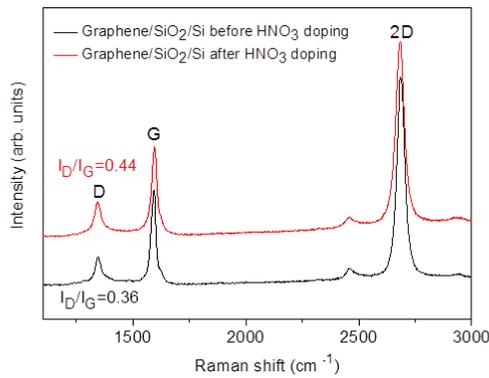


Fig. 3. (Color online) Representative Raman spectra of graphene on a bare SiO₂/Si wafer before (black line) and after (red line) the chemical treatment with HNO₃.

and the PDMS-coated SiO₂/Si wafers are different. First, the positions of the *G* and the 2D peaks of graphene on the PDMS-coated SiO₂/Si wafer exhibit blue shifts compared to those of graphene on the bare SiO₂/Si wafer. The blue shifts could be attributed to the compression strain of graphene due to the PDMS film [35]. Second, the intensity of the 2D peak of graphene on the PDMS-coated SiO₂/Si wafer is higher than that of graphene on the bare SiO₂/Si wafer, but both have nearly the same intensity of the *G* peak. Thus, the intensity ratio I_{2D}/I_G of graphene on the PDMS-coated SiO₂/Si wafer is greater than that of graphene on the bare SiO₂/Si wafer. This increased the I_{2D}/I_G ratio of graphene on the PDMS-coated SiO₂/Si wafer indicates a reduction in impurities, as observed in the case of HMDS [28].

The Raman peaks of graphene on the bare SiO₂/Si wafer at 1342 cm⁻¹ and of graphene on the PDMS-coated SiO₂/Si wafer at 1343 cm⁻¹, known as the *D* peak, arise from the breathing of the hexagonal carbon ring due to the presence of defects [36, 37]. The *D* peak originates from the transverse optical phonon due to the intervalley double-resonance process at the Brillouin zone corner [36, 37]. Of note is that a substantial change in the intensity of the *D* peak was observed after the PDMS treatment. The I_D/I_G ratio of graphene on the PDMS-coated SiO₂/Si wafer is 0.47 where the average value of the I_D/I_G ratios obtained from different graphene samples is 0.43 ± 0.04 , which is smaller than the I_D/I_G ratio of 0.59 for graphene on the bare SiO₂/Si wafer, where the average value of the I_D/I_G ratios obtained from different graphene samples is 0.53 ± 0.07 . The decrease in the I_D/I_G ratio also suggests that, compared to the bare SiO₂/Si wafer, the impurities are reduced when graphene is transferred onto the PDMS-coated SiO₂/Si wafer. The increase in the I_{2D}/I_G ratio and the decrease in the I_D/I_G ratio demonstrate that carrier-doping sources, such as polar molecules, can be effectively prevented by hydrophobization. The Raman results are consistent with the enhanced performance of

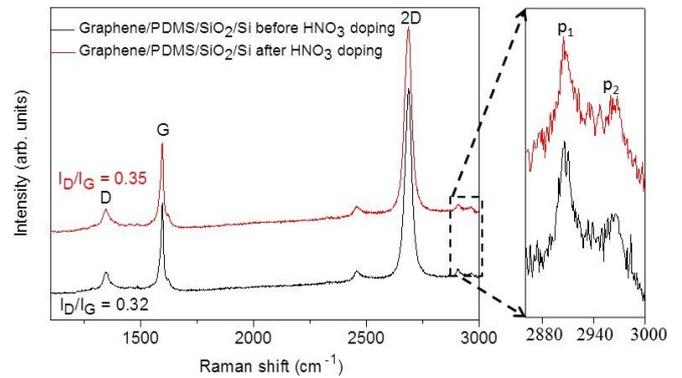


Fig. 4. (Color online) Representative Raman spectra of graphene on a PDMS-coated SiO₂/Si wafer before (black line) and after (red line) the chemical treatment with HNO₃, where the Raman spectra were enlarged to clarify the positions of the Raman peaks (*P*₁ and *P*₂) originating from PDMS.

graphene FETs after hydrophobization of a substrate [20]. On the other hand, the existence of the typical Raman peaks of PDMS at 2907 and 2964 cm⁻¹, as shown in the enlarged Raman spectra in Fig. 2, indicates that the PDMS film still underlies graphene after the transfer process.

We further studied the influence of the hydrophobic PDMS film on the chemical doping of graphene using HNO₃, and the results are shown in Figs. 3 and 4. When graphene is chemically functionalized using HNO₃, the intensity of the *D* peak related to defects of graphene was reported to increase [38]. HNO₃ was also reported to act as a *p*-type dopant in graphene [26]. We confirmed that the I_D/I_G ratio was enhanced after graphene on a bare SiO₂/Si wafer was doped with HNO₃, as shown in Fig. 3. The I_D/I_G ratios of graphene on a bare SiO₂/Si wafer before and after the chemical doping with HNO₃ were 0.36 and 0.44 respectively where the average values of the I_D/I_G ratios obtained from different graphene samples were 0.36 ± 0.03 and 0.41 ± 0.04 , respectively. As a comparative experiment, the Raman spectra of graphene on a PDMS-coated SiO₂/Si wafer before and after the same chemical doping with HNO₃ were measured, and the results are shown in Fig. 4. Before the chemical doping with HNO₃, the I_D/I_G ratio was 0.32, where the average value of the I_D/I_G ratios obtained from different graphene samples was 0.32 ± 0.01 . After the chemical doping, the I_D/I_G slightly increased by smaller increments (*i.e.*, 0.03), where the average value of the I_D/I_G ratios obtained from different graphene samples was 0.35 ± 0.01 . When a bare SiO₂/Si wafer was used, as described above, the I_D/I_G ratio increased from 0.36 to 0.44 after the chemical doping with HNO₃, and the difference between these values was very large (*i.e.*, 0.12). The changes in the I_D/I_G ratios suggest that when a PDMS film is used, fewer defects are created after the chemical doping with HNO₃.

III. CONCLUSION

We have studied the influence of a hydrophobic film on the chemical treatment of graphene. As a hydrophobic film, PDMS was used and coated on a SiO₂/Si wafer. CVD-grown graphene was transferred onto the PDMS-coated SiO₂/Si wafer, which was compared to graphene on a bare SiO₂/Si wafer. The number of defects in graphene was measured from the I_D/I_G intensity ratio of the Raman spectrum. During the transfer process of graphene, defects on graphene can be created by chemical residues. We also used chemical doping with HNO₃ to create defects in graphene. In both cases, when the hydrophobic film underlies graphene, fewer defects are created in graphene after the chemical treatments.

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