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J.-H. Park,[1] W. Jung,[1] D. Cho,[2,3] J.-T. Seo,[1] Y. Moon,[1] S. H. Woo,[4] C. Lee,[2,3] C.-Y. Park,[1] and J. R. Ahn[1,3,5,a)]

[1]Department of Physics, Sungkyunkwan University, Suwon 440-746, South Korea
[2]Department of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, South Korea
[3]Integrated Nanostructure Physics (CINAP), Institute for Basic Science (IBS), Sungkyunkwan University, Suwon 440-746, South Korea
[4]College of Pharmacy, Chungnam National University, Daejeon 305-764, South Korea
[5]SAINT, Sungkyunkwan University, Suwon 440-746, South Korea

The clean removal of a poly(methyl methacrylate) (PMMA) film on graphene has been an essential part of the process of transferring chemical vapor deposited graphene to a specific substrate, influencing the quality of the transferred graphene. Here we demonstrate that the clean removal of PMMA can be achieved by a single heat-treatment process without the chemical treatment that was adopted in other methods of PMMA removal. The cleanness of the transferred graphene was confirmed by four-point probe measurements, synchrotron radiation x-ray photoemission spectroscopy, optical images, and Raman spectroscopy. © 2013 AIP Publishing LLC.
[http://dx.doi.org/10.1063/1.4824877]

Graphene, which has extraordinary physical properties, has been produced by various methods such as mechanical exfoliation,[1] epitaxial growth,[2,3] chemical vapor deposition (CVD),[4,5] chemical synthesis,[6,7] and reduction of graphene oxides.[8,9] In particular, CVD graphene has widened the potential applications of graphene.[10–12] Because graphene produced by CVD is generally grown on metal foils such as nickel or copper, the graphene must be transferred to other substrates in order to be used in certain applications, for example, as an insulator.[13,14] The typical transfer process of CVD graphene includes spin coating with poly(methyl methacrylate) (PMMA), chemical etching of the metal foil, transfer to a specific substrate, and removal of the PMMA film by chemical treatment.[5,15] The high quality of the CVD graphene is often degraded through the transfer process, mostly because of PMMA residuals and defects that are produced during chemical treatment.[16–18] The residuals originate from chemical fragments of PMMA for the most part and are very strongly adhered to defective regions of graphene.[19,20] Residuals and defects lower the overall performance of graphene devices and make it difficult to effectively analyze the intrinsic physical properties of CVD graphene. Recent research on the transfer of CVD graphene has focused on clean removal of the PMMA residuals. Heat treatment[21,22] and electron irradiation[19] after treatments with chemicals, such as acetone, were reported to be effective for clean removal of PMMA. However, clean removal of PMMA is still problematic because the complicated methods involved are fundamentally based on chemical treatments that are not environmentally friendly and result in PMMA residuals and defects in the graphene.

Here we show that clean removal of a PMMA film on CVD graphene can be achieved using a single heat-treatment process without chemical treatment. Other methods have focused on the removal of PMMA residuals, which are produced after chemical treatment. In this work, the PMMA film on CVD graphene was thermally heated at a temperature of $400\,^{\circ}C$ under a pressure of $5 \times 10^{-4}\,Torr$ without chemical treatment. The heat treatment cleaned the CVD graphene more effectively than chemical treatment or combined chemical and heat treatment. These results suggest that heat treatment without chemical treatment results in fewer chemical fragments of PMMA and defects when compared to chemical treatment processes. The cleanness of the CVD graphene was further confirmed by lower sheet resistance (measured with a four-point probe), lower intensities of the PMMA-originated components in C $1s$ core-level spectra, higher transparency in an optical image, and lower intensity of the so-called D peak in Raman spectra, which is generally activated by defects in graphene. This conceptual shift in research on the clean removal of PMMA will simplify the process, make it greener, and will guarantee better performance of graphene devices.

A Cu foil with a thickness of $25\,\mu m$ (Alfa Aesar) was placed at the center of a quartz tube and annealed for 2 h at a temperature of $1000\,^{\circ}C$ with H_2 gas flow of 100 sccm. Subsequently, the Cu foil was further annealed for 30 min with CH_4 gas flow of 20 sccm and H_2 gas flow of 100 sccm at the same temperature. After rapidly cooling to room temperature, graphene grown on the Cu foil was coated with PMMA. The Cu foil was removed by an etchant (CE-100, Transene Company) and subsequently washed with de-ionized (DI) water. The sample was immersed in a HNO_3 solution for 10 min and subsequently washed with DI water to eliminate remaining Cu residuals. A resulting PMMA/graphene sheet was transferred onto a SiO_2/Si substrate. The same transfer process described above was used before the removal of the PMMA film on the graphene transferred to a SiO_2/Si substrate. Heat treatment with (or without) acetone treatment was performed at the center of a quartz tube in a vacuum of $2 \times 10^{-3}\,Torr$ for 30 min.
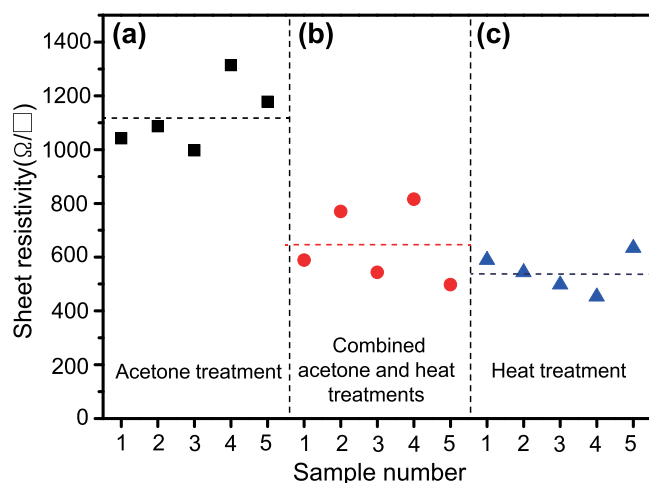
a)Electronic mail: jrahn@skku.edu

FIG. 1. Sheet resistivity of CVD graphene transferred to a SiO$_2$/Si substrate. The PMMA film on the CVD graphene was removed using different methods: (a) acetone treatment without heat treatment (sold black rectangles), (b) combined acetone and heat treatments (solid red circles), and (c) heat treatment without chemical treatment (solid blue triangles). Dotted lines denote average values.

Figure 1 shows the sheet resistivity, which was measured using a four-point probe, of the transferred graphene after removal of the PMMA film by different methods. When the PMMA film was removed with acetone [Fig. 1(a)], the average sheet resistivity was approximately 1110 $\Omega/\square$. When the PMMA residuals were further removed by heat treatment (400 °C at a pressure of 5×10^{-4} Torr) after the acetone treatment [Fig. 1(b)], the average sheet resistivity was reduced to approximately 630 $\Omega/\square$. In comparison to PMMA-removal processes based on acetone treatment, when heat treatment without chemical treatment was adopted to remove the PMMA film [Fig. 1(c)], the average sheet resistivity of 520 $\Omega/\square$ was lower than those produced by acetone treatment alone and by combined acetone and heat treatment. The lower sheet resistance suggests that the single heat-treatment process is simpler, more effective, and greener than the complicated processes based on chemical treatment for removal of the PMMA film. Specifically, sheet resistivity is related to the amount of PMMA residuals present, defects in the graphene, and doping in the graphene. Chemical and defect analysis of the removal of the PMMA film were further performed as follows. For chemical analysis of the remaining residuals after removal of the PMMA film, synchrotron radiation x-ray photoemission spectroscopy experiments were performed. Figure 2 shows C 1*s* core-level spectra of the transferred CVD graphene, which were measured at a photon energy of 340 eV after removal of the PMMA film. The C 1*s* spectra were fitted using the Doniach-Sunjic line shape.[19,20,23] The C 1*s* spectra are composed of five components: the C$_1$ component originates from the sp_2 C—C bond of graphene, the C$_2$ component originates from the sp_3 C—C bond near defects of graphene, the C$_3$ component originates from the polymer backbone (C—C bond) of PMMA, the C$_4$ component originates from the methoxy functional group (C-O bond) of PMMA, and the C$_5$ component originates from the carboxyl functional group (O-C=O bond) of PMMA.[19,20,23] Figure 2(a) shows the C 1*s* spectrum of transferred graphene after acetone treatment. The distinctive existence of the PMMA-originated components

[C$_3$ (binding energy = 285.7 eV), C$_4$ (286.2 eV), and C$_5$ (289.0 eV)] clearly shows that there is a considerable amount of PMMA residuals on the transferred graphene. In comparison to the acetone treatment, the heat treatment did not leave the PMMA-originated components (C$_3$, C$_4$, and C$_5$) in the C 1*s* spectrum, as shown in Figs. 2(b) and 2(c). The lower intensity of the C$_2$ component for the heat-treatment method, compared to that of the acetone treatment, reflects the fact that less residuals were created through heat treatment than through acetone treatment. When heat treatment without acetone treatment was adopted [Fig. 2(c)], the C$_1$ and C$_2$ components shifted toward a lower binding energy by 0.3 eV. The binding energy shift is likely a result of doping in the graphene due to the heat treatment,[21,24] which suggests the heat treatment without chemical treatment makes graphene more adhesive to the substrate. The results of the C 1*s* spectra lead us to the conclusion that the PMMA film can be removed more effectively by a single-process heat treatment without chemical treatment.
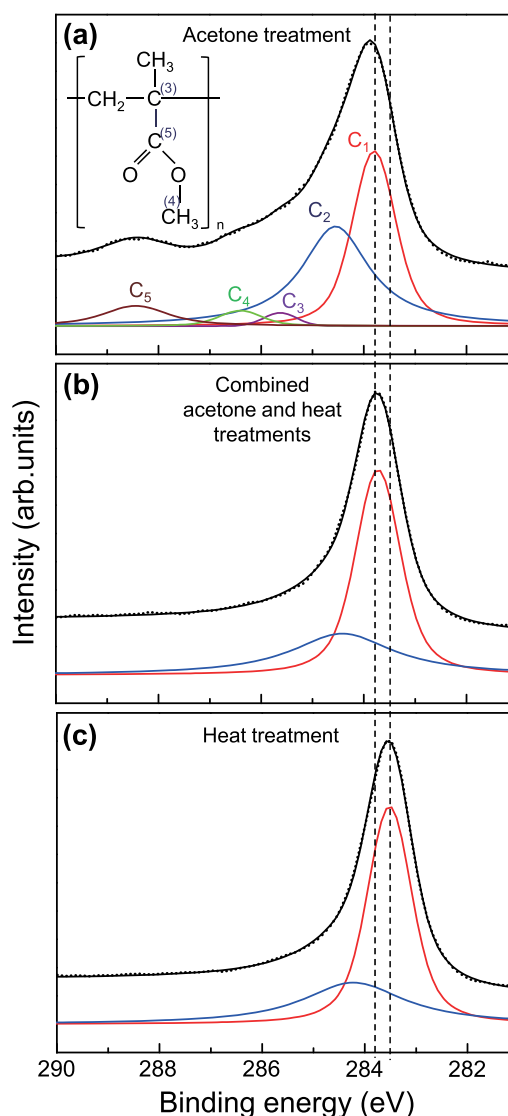

FIG. 2. C 1*s* core-level spectra of CVD graphene transferred to a SiO$_2$/Si substrate. The PMMA film on the CVD graphene was removed using different methods: (a) acetone treatment without heat treatment, (b) combined acetone and heat treatments, and (c) heat treatment without chemical treatment.
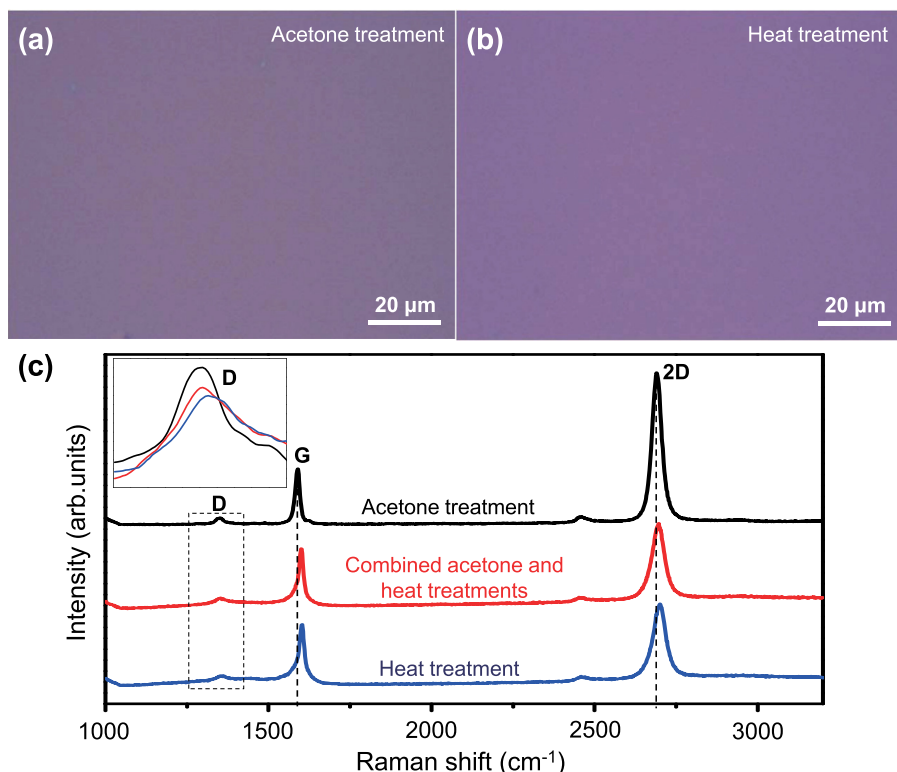
FIG. 3. (a) and (b) Optical images and (c) Raman spectra of CVD graphene transferred to a SiO$_2$/Si substrate. The PMMA film on the CVD graphene was removed using different methods: (a) acetone treatment without heat treatment and (b) heat treatment without chemical treatment. In (c), the D peaks are magnified in the inset.

The uniformity and spatially resolved defect density of the transferred CVD graphene were further analyzed using optical images and confocal Raman spectroscopy. As shown in the optical images in Figs. 3(a) and 3(b), the transferred graphene after PMMA removal by heat treatment without a chemical treatment was more transparent than that after the acetone treatment. The optical images also suggest that the single heat-treatment process results in more uniform graphene than the acetone treatment. Figure 3(c) shows Raman spectra of the transferred graphene after removal of the PMMA film. The Raman spectra are composed of three typical peaks called D, G, and 2D.[25,26] The D, G, and 2D peaks originate from the TO phonon at the $\bar{K}$ point of the Brillouin zone (BZ) of graphene, the breathing modes of sp_2 carbon atoms, and two phonons with opposite momentum in the highest optical branch near the $\bar{K}$ point, respectively.[25,26] Because the D peak is generally activated by defects in the graphene, the intensity ratio of the D and G peaks reflects the

uniformity of graphene.[25,26] As shown in Fig. 3(d), the intensity of the D peak measured after heat treatment without acetone treatment was lower than the intensities measured after acetone treatments with or without a further heat treatment. The blue shifts of the G and 2D peaks after the heat treatment originates from doping in the graphene,[27] which is consistent with the shifts of the C$_1$ and C$_2$ components in the C 1s spectrum. Figure 4 shows Raman maps of the intensity ratio of the D and G peaks. The Raman maps demonstrate that the defect density was lower when heat treatment was performed without chemical treatment.

In conclusion, the PMMA film on CVD graphene that was transferred to a SiO$_2$/Si substrate was cleanly removed by a single heat-treatment process without chemical treatment. The heat treatment was performed at a temperature of 400 °C under a pressure of 5×10^{-4} Torr. The heat treatment without chemical treatment left fewer PMMA residuals and defects on the graphene when compared to chemical treatment processes, such as acetone, with or without a further heat treatment. Higher uniformity of the graphene was confirmed by lower sheet resistivity, lower intensities of the PMMA-originated components in C 1s core-level spectra, higher transparency, and lower intensity ratios of the D and G peaks in Raman spectra. This method of PMMA removal is thus simpler, greener, and more effective than other methods based on chemical treatment.
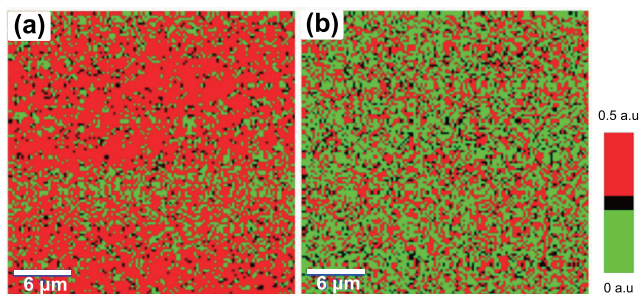

FIG. 4. Raman maps of the intensity ratios of the D and G peaks of CVD graphene transferred to a SiO$_2$/Si substrate. The PMMA film on the CVD graphene was removed using different methods: (a) acetone treatment without heat treatment and (b) heat treatment without chemical treatment.

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