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Chlorine Radical Doping of a Few Layer Graphene with Low Damage

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We present a graphene plasma doping method using chlorine radicals generated in an inductively coupled plasma (ICP) with a double mesh grid system. Raman spectroscopy and sheet resistance measurement showed that this doping method is non-destructive and controllable approach for the p-type graphene layer doping method. And, by using a chlorine trap-doping method, the sheet resistance could be decreased to 76% at an optimized condition for the tri-layer graphene.

Graphene has gained much interest from the research community due to the tremendous potential such as high mobility of charges carriers, superior thermal and electrical conductivity properties for technological applications, etc.[1–7] Recently, large area graphene sheets were successfully synthesized through various methods, and their potential for various electronic applications was increased further.[8–15] One of the most attractive applications of large-scale graphene is flexible electronic devices.[12–14] For that application, transferred graphene should satisfy some conditions such as low sheet resistance in addition to high flexibility. In the case of chemical vapor deposition (CVD) graphene, however, serious problems such as the defects in the crystal, wrinkles and a high sheet resistance were observed.[10–14] For these reasons, many researchers have investigated various doping methods including chemical,[16–20] plasma,[21–23] and photochemical methods for large area CVD graphene.[24] However, these approaches showed severe damage to the carbon network in the graphene, and resulted in the rapid degradation on device performances.

Here, we describe a very simple technique making highly doped graphene while maintaining the nature of graphene using radicals and a trap doping method.

Experimental

Transferred single layer graphene film on a copper foil was prepared using CVD graphene grown at 1050°C by the gas flow of H_2/CH_4 (10/20 sccm). And, chlorine radical doping was conducted with the ICP system equipped with and without a double mesh grid. Figure 1a shows the trap-doping for the bi-layer graphene which contains the chlorine radical doping on the 1st layer graphene (top figure) and the 2nd graphene layer transferred on the doped 1st graphene for chlorine dopant trapping. For the doped tri-layer graphene, the 2nd graphene layer of the bi-layer graphene was again doped with chlorine radicals and followed by the 3rd graphene layer transfer on the doped 2nd graphene layer surface.

Raman spectroscopy (Renishaw, RM-1000 Invia) with excitation energy of 2.41 eV (514 nm, Ar− ion laser) was used to estimate the graphene characteristics such as defect and doping states for the graphene on SiO_2, and the sheet resistance was measured using a sheet resistance meter (Dasoleng, FPP-2400).

Results and Discussion

Figure 1b shows the ratio of the D peak intensity near 1350 cm^{-1} (defect related) over the G peak near 1600 cm^{-1} (graphite related) intensity (I_D/I_G) of the Raman spectra measured on the monolayer graphene surface before/after the chlorine radical doping with/without the double mesh grid. The rf power to the ICP source was varied from 10 to 300 W at 10 mTorr and 60 sccm of Cl_2 gas and the monolayer graphene was treated for 20s. The I_D/I_G was measured because it has been considered as a convenient way to investigate defects or disordering for the graphene layers. As shown in the figure, for the chlorine doping with the mesh grid up to 20 W of rf power, the I_D/I_G was remaining similar to that of pristine graphene. However, for the doping without the mesh grid, the I_D/I_G was increased with rf power even at 20 W of rf power and it was increased significantly as the rf power was further increased to 300 W.

Figure 2a shows the Raman spectra of the monolayer graphene for the different doping time. Generally, if the graphene structure is damaged, the peak intensity of the disorder-induced D band emerges and increases, the 2D band intensity is decreased, and the G band is also broadened. However, as shown in the figure, severe change in those peaks was not observed. The I_D/I_G ratio as a function of exposure time was measured and the results are shown in Fig. 2b. As shown,
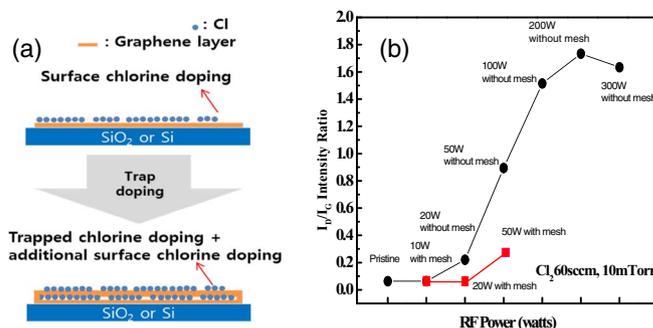

Figure 1. (a) Schematic drawing for bi-layer trap-doping: For bi- and tri-layer doped graphenes, after adsorption of Cl radical, one mono-layer graphene was transferred onto the doped graphene surface (b) Ratio of the D peak intensity over the G peak intensity (I_D/I_G) of the Raman spectra measured on the graphene surface as a function of rf power with/without the mesh grid during the Cl radical doping.
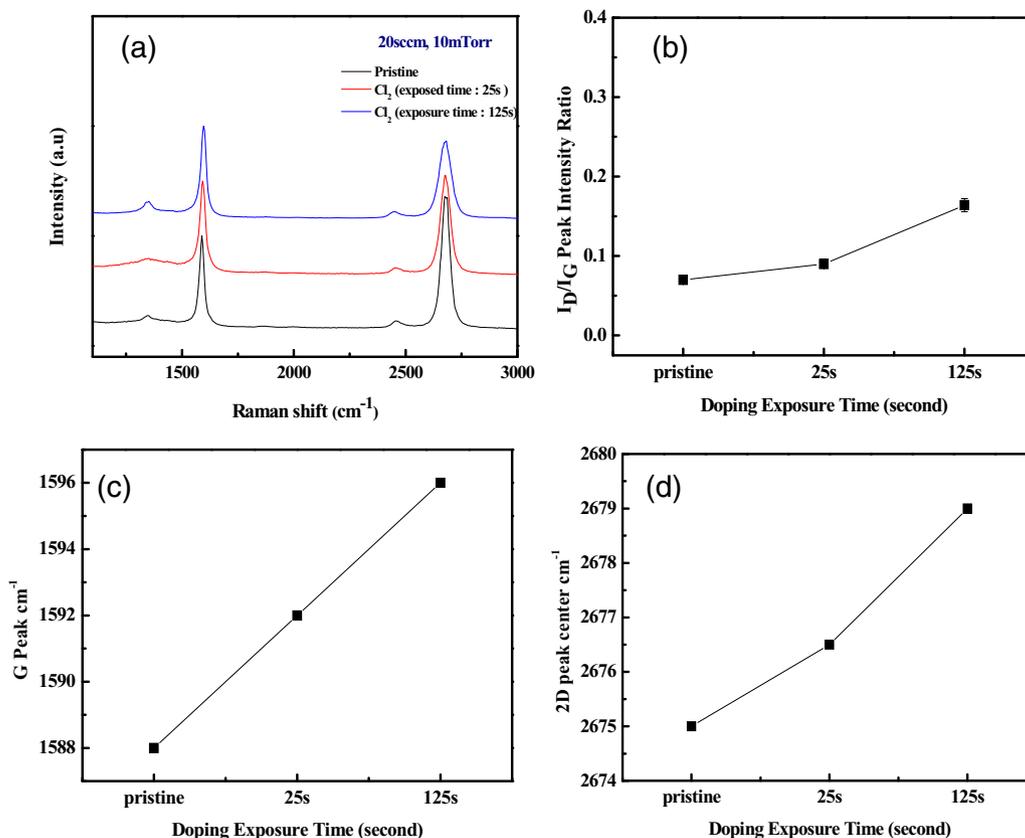
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Figure 2. (a) Raman spectra of the graphene before and after the chlorine radical doping with the double mesh grid for different exposure time. (b) The I_D/I_G measured as a function of exposure doping time for (a). The shift of (c) G peak position and (d) 2D peak position as a function of exposure time.

the I_D/I_G ratio was slightly increased from 0.07 to 0.09 after 25s of exposure time, and but it was tripled after 125s of exposure time. The determination of the doping polarity can be made by correlating the peak positions of the G and 2D bands. Fig. 2c and 2d are the changes of G and 2D peak center obtained from Figure 2a, respectively. As shown in the figures, as the doping exposure time is increased, the G and 2D peaks were blue-shifted and, as the exposure time is increased

to 125s, the G and 2D peak centers were blue-shifted by 8 cm^{-1} and 4 cm^{-1}, respectively. From these results, it can be found that p-doping was obtained on the graphene surface while minimizing the graphene damage.

Figure 3 shows the sheet resistance measured for mono-, bi-, tri-layer graphenes fabricated with/without the chlorine radical. As shown in the figure, for the undoped graphene, the sheet resistance was decreased from 600 ohm/sq. for the monolayer graphene to 434 ohm/sq. for the bi-layer graphene and to 287 ohm/sq. for the tri-layer graphene. However, by the chlorine radical doping, the sheet resistance of the mono, bi-, and tri-layer graphene could be further decreased by showing 307 ohm/sq. for monolayer graphene (50% decrease), 113 ohm/sq. for the doped bi-layer graphene (74% decrease), and 70 ohm/sq. for the doped tri-layer graphene (76% decrease). Therefore, significant decrease in the sheet resistance could be obtained even for a few layer graphene using the chlorine radical doping method.

Conclusions

In this study, by radical doping, physical damage to the graphene surface could be effectively prevented by showing no significant increase of I_D/I_G during the chlorine plasma doping while showing blue shifts of G peak and 2D peak indicating p-type doping to the graphene. By using the trap doping method, the decrease of the sheet resistance of about 76% by showing 70 ohm/sq. could be obtained for the tri-layer graphene.
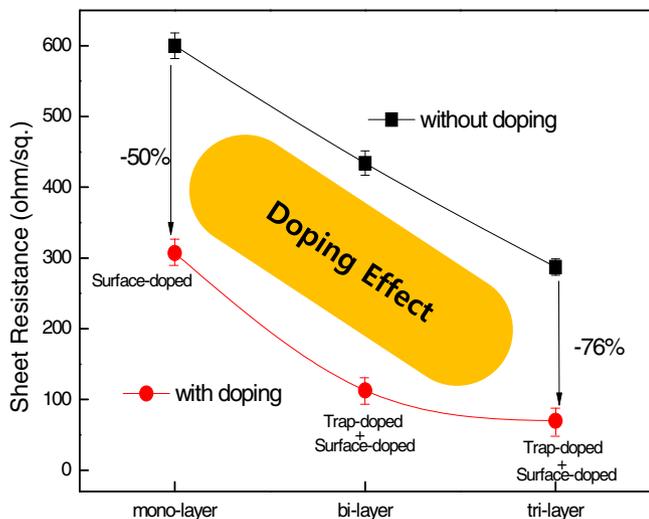

Figure 3. Change of sheet resistance with/without the chlorine radical doping for mono-, bi-, and tri-layer graphene. For bi- and tri-layer graphene doping, the trap-doping method was used. Chlorine doping on the graphene surfaces was performed using the ICP source with the double mesh grid at 20 W of rf power with 10 mTorr Cl$_2$ for 20s.

Acknowledgments

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