

Graphene Treatment Using a Very Low Energy Ar⁺ Ion Beam for Residue Removal

Kyoung Seok Min¹, Ki Seok Kim², Kyoung Nam Kim²,
Anurag Mishra², and Geun Young Yeom^{2,3,*}

¹Large Scale Integration Business, Samsung Electronics, San No. 16 Banwol-Ri, Taejeon-Eup, Hwasung-City, Gyeonggi-do, 449-711, South Korea

²School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Republic of Korea

³SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Republic of Korea

The effect of Ar⁺ ion energy on the removal of the polymethyl methacrylate (PMMA) residue remaining on the chemical vapor deposited (CVD) graphene surface without damaging the graphene surface was investigated. Stable and low energy Ar⁺ ion beams having a mono-energetic energy distribution with a peak energy of 7.5 eV or 11.5 eV could be formed by using a two-grid magnetically enhanced ICP ion gun with and without the application of 25 Gauss axial magnetic field, respectively, while controlling the Ar gas flow rate. When the CVD graphene treatment was performed with the Ar⁺ ions having the ion energy peak at 7.5 eV (with the magnetic field) and 11.5 eV (without the magnetic field), the blue shift of Raman G peak from *p*-type doped to intrinsic graphene indicating the removal of residue on the graphene surface could be observed for both conditions, however, the graphene treated at 11.5 eV (without the magnetic field) showed the increase of the defect while that treated at 7.5 eV (with the magnetic field) showed no significant change of the defect. It is believed that, for the treatment of CVD graphene, possibly due to the low binding energy area such as grain boundaries and domains in the CVD graphene, low energy ions with less than the energy of 10 eV is required not to damage the graphene surface, and a magnetically enhanced ICP ion gun which can provide stable and low energy Ar⁺ ions with a mono-energetic ion energy distribution with a peak of 7.5 eV can be applicable to the residue removal on the graphene surface.

Keywords: Graphene Treatment, Ar Ion Gun, Low Energy, Magnetic Field, PMMA.

1. INTRODUCTION

According to international technology roadmap for semiconductors (ITRS), low dimensional materials such as nanotubes, nanowires, nanoparticles, graphene, etc. are potential candidates of the next generation nano device materials that may enable their use as potential solutions for future devices, interconnects, lithography, and packaging due to their unique properties.¹ Among them, graphene has been known to be one of the very promising channel materials in the fields of nano electronics because of superior electrical characteristics such as the electron mobility having $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, which is the highest ever known in pure semiconductors.²⁻⁵

To form an electronic integrated circuit using graphene, graphene layers grown by chemical vapor deposition (CVD) on the Cu substrates need to be transferred to target substrate such as silicon oxide and silicon etc. and also need to be patterned using lithographic tools to be used for electronic devices. However, during the transfer of graphene grown by CVD to the silicon oxide substrates using polymethyl methacrylate (PMMA) and during the lithography using PMMA, a thin layer of PMMA residue (1–2 nm) remains on the graphene surface and it tends to cause problems such as decreased electron mobility, *p*-doping on graphene, increased contact resistance, etc. However, removing the PMMA on the graphene surface is known to be difficult because it is not easily and completely dissolved with any solvents.⁶⁻¹⁰

*Author to whom correspondence should be addressed.

Many techniques have been investigated to remove the PMMA residue remaining on the graphene surface. To remove PMMA residue on the graphene surface, the graphene was thermally treated (150–300 °C), but due to the decomposition of PMMA during the thermal annealing, the graphene properties were affected.^{11–12} Plasma cleaning during the post-processing step was proposed as one of the low temperature treatment methods because it can remove the PMMA residue using physical and chemical reaction. In previous studies, Ar plasmas generated by inductively coupled plasma (ICP) and capacitively coupled plasma (CCP) have been investigated, and the ICP which has a lower plasma potential compared to the CCP showed less surface damage due to the lower ion energy bombardment.^{13–15} However, even for the ICP, to decrease the surface damage on the graphene surface, the plasma generated at an extremely low power of about 5 W was used, and it is not a stable plasma for ICP and may not be uniform over the graphene surface either, therefore, the plasma conditions may not be applicable in removing the residue on the graphene surface effectively.

In this study, a stable Ar⁺ ion gun composed of an ICP ion source and two grids for ion acceleration/deceleration were used to treat the graphene surface contaminated by PMMA, and, for a lower Ar⁺ ion energy, an axial electromagnetic field from 0~50 Gauss was applied to the ICP source as a magnetically enhanced ICP source. Using the low energy Ar⁺ ion gun, the effect of low energy Ar⁺ ions on the characteristics of graphene surface has been investigated.

2. EXPERIMENTAL DETAILS

Monolayer graphene was synthesized on a Cu foil by a CVD method. 70 μm thick Cu foil was inserted to a vacuum furnace type quartz CVD chamber. For the graphene growth, the foil was annealed for 1 h at 1050 °C in H₂ 10 sccm prior to growth and the graphene was synthesized at the same temperature by a gas flow of H₂ (10 sccm)/CH₄ (20 sccm) for 30 min. After the synthesis, the Cu foil was cut into pieces, coated with PMMA, and immersed into a Cu etchant (FeCl₃) to etch away the Cu foil. When Cu was completely etched away, the graphene sheets with PMMA were rinsed in deionized water and, then, PMMA-coated graphene was transferred onto SiO₂ substrates. PMMA on graphene was removed by acetone for 30 min after the graphene was completely transferred to the SiO₂ substrates.

For further treatment of the graphene on SiO₂ obtained after the acetone cleaning of PMMA, the surface of the graphene on SiO₂ was exposed to energetic Ar⁺ ions using a 4 inch diameter two-grid ICP Ar⁺ ion gun and the effect of Ar⁺ ion gun condition on the change of the graphene surface characteristics was investigated (Fig. 1). The ICP ion gun was consisted of an ICP source operated at 13.56 MHz and two graphite grids with 5 mm holes in

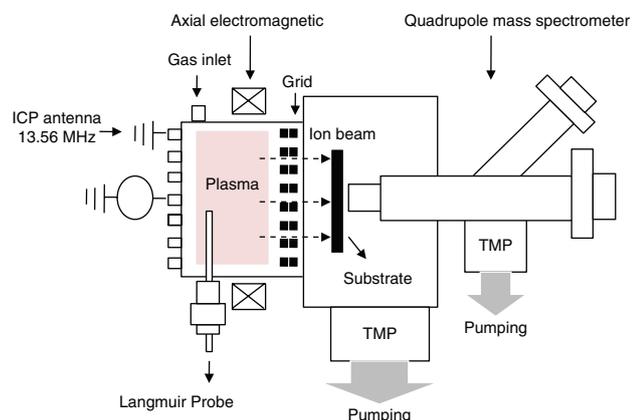


Figure 1. A schematic diagram of two-grid magnetically enhanced ICP ion gun used in this study. To measure the plasma characteristics in the ICP source, a Langmuir probe was installed in the ICP source and, to measure the Ar⁺ ion energy distribution, a quadrupole mass spectrometer with an ion energy analyzer was installed at the substrate location.

front of the ICP source to extract and control the energy of the Ar⁺ ions from the ICP source. The energy of the Ar⁺ ion was controlled by the positive voltage applied to the 1st grid near the ICP source while the 2nd grid voltage was grounded. In the ICP source, an axial electromagnet was installed, and a low axial magnetic field from 0 to 50 G was applied to an ICP ion source to change the plasma characteristics in the ICP source to operate as a magnetically enhanced ICP source. [Plasma condition: base pressure: 2.5×10^{-6} Torr, Ar gas flow rate: 50 sccm, ICP power: 250 W, 1st grid voltage: floated, 2nd grid voltage: grounded with and without the axial magnetic field].

Langmuir probe (Hiden Analytical Inc., EQP 1000) was used to measure the plasma characteristics generated by ICP source. A quadrupole mass spectrometer (QMS) (Hiden Analytical Inc., EQP 1000) was used to measure the Ar⁺ ion energy distribution incident on the graphene surface by the ion gun. Raman spectroscopy (Renishaw, RM-1000 Invia) with the excitation energy of 2.41 eV (514 nm, Ar⁺ ion laser) was used to measure the structural information of the cleaned graphene.

3. RESULTS AND DISCUSSION

For the treatment of the graphene surface, a very low energy Ar⁺ ion beam is required. Therefore, to generate a low energy Ar⁺ ion beam using the two grid ion beam source, the 1st grid of the ion beam was left floated while the 2nd grid was grounded (G). While the 1st grid is floated and the 2nd grid was grounded, the plasma characteristics of the ICP ion source were investigated as a function of Ar gas flow rate using a Langmuir probe inserted in the ICP ion gun as shown in Figure 1. As shown in Figure 1, in addition to the Ar gas flow rate, axial magnetic field was applied to the ICP source to change the

plasma characteristics in the ICP source during the operation of the Ar plasma. Figure 2 shows the effect of Ar gas flow rate and axial magnetic field of 25 Gauss on the (a) plasma density and (b) plasma potential of the ICP source of the Ar⁺ ion gun measured using a Langmuir probe. As the rf power to the ICP source, 250 Watts was used while the Ar gas flow rate to the source was varied from 25 to 125 sccm. As shown in Figure 2(a), the increase of Ar gas flow rate in the source from 25 to 125 sccm increased the plasma density in the ICP chamber from 5×10^{11} to about $1.25 \times 10^{12}/\text{cm}^3$ possibly due to the increase of Ar gas pressure in the ICP chamber. The addition of the axial magnetic field of 25 Gauss also increased the plasma density at the same Ar gas flow rate, therefore, at the 25 sccm of Ar gas flow rate, the plasma density was increased from 5×10^{11} to $7.5 \times 10^{11}/\text{cm}^3$ and, at the 125 sccm of Ar gas flow rate it increased from 1.25×10^{12} to $1.5 \times 10^{12}/\text{cm}^3$. In the case of plasma potential, as shown in Figure 2(b), the increase of Ar gas flow rate from 25 to 125 sccm without the axial magnetic field decreased the plasma potential of the ICP source from about 15 to 7.5 V and, by the addition of the 25 Gauss of axial magnetic field, the plasma potential was further decreased by showing the decrease

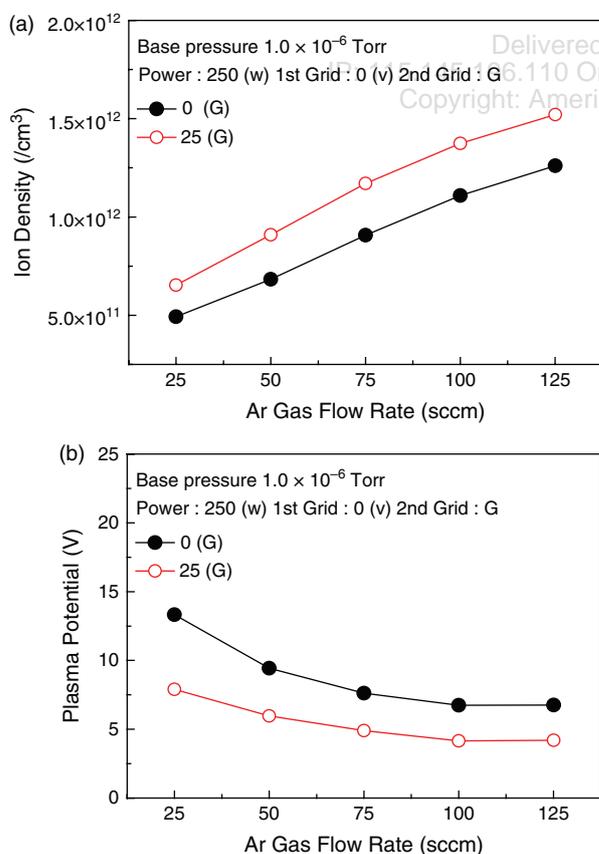


Figure 2. (a) Plasma density and (b) plasma potential of the ICP source of the Ar⁺ ion gun with/without a low axial magnetic field of 25 Gauss measured with a Langmuir probe.

of the plasma potential from 7.5 to 5 V when the Ar gas flow rate was increased from 25 to 125 sccm.

The increase of plasma density and the decrease of the plasma potential by the increase of Ar gas flow rate is believed to be related to the change of plasma operation mode of the ICP source from capacitively coupled plasma (CCP) mode to ICP mode with the increase of Ar gas flow rate by the increased ionization in the ICP source. The addition of a small axial magnetic field of 25 Gauss to the plasma increases the helical motion of the electrons in the plasma and decreases the loss of electrons in the plasma to the wall, therefore, the increase of plasma density with 25 Gauss of axial magnetic field is related to the increased ionization of the Ar gas in the ICP source by the helical motion of the electrons in the ICP source. The decrease of plasma potential with the application of the 25 Gauss of magnetic field is believed to be related to the decrease of the ICP antenna voltage, which is related to the plasma potential by the increased conductance with the increase of plasma density in the ICP source. Therefore, by increasing the Ar gas flow rate and by the application of a small axial magnetic field, Ar⁺ ions with a lower plasma potential with a higher plasma density could be obtained in the two-grid type Ar⁺ ion source.

Using the QMS located on the substrate location, the energy of the Ar⁺ ions incident on the substrate was measured for a fixed 50 sccm of Ar gas flow with and without 25 Gauss of axial magnetic field while applying 250 Watts of rf power to the ICP source and the results are shown in Figure 3. As shown in the figure, the energy of the Ar⁺ ions incident on the substrate showed a Gaussian shaped energy distribution peaked at about 11.5 eV and about 7.5 eV for without and with the magnetic field. In the case of the flux to the substrate, the ion flux without the magnetic field was higher than that with the magnetic field. When the results in Figure 3 are compared with the plasma

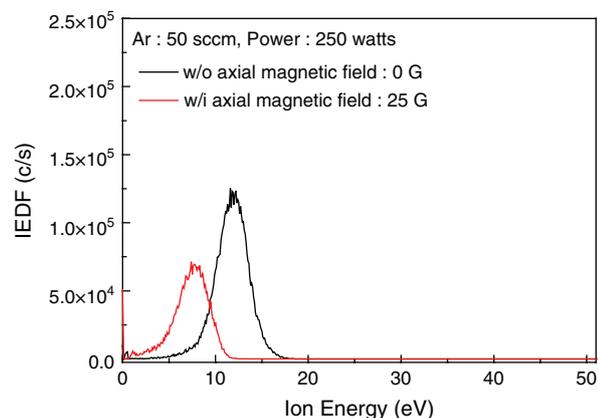


Figure 3. Ar⁺ ion energy distribution measured at the substrate location for the ICP ion gun with/without a low axial magnetic field of 25 Gauss measured using a quadrupole mass spectrometer with an ion energy analyzer.

characteristics of the ICP source in Figure 2, it can be seen that the ion energy distribution of the extracted ion beam on the substrate is related to the sheath potential at the 1st grid, therefore, is related to the plasma potential of the ICP source. However, even though the ion flux extracted to the 1st grid should be higher with the magnetic field than that without the magnetic field due to the higher plasma density in the ICP source for the condition with the magnetic field, the lower ion flux obtained on the substrate with the magnetic field is believed to be related to the increased scattering loss of the ions extracted on the 1st grid to the 2nd grid. It is due to the formation of a thinner sheath between the plasma and the 1st grid caused by the higher plasma density and lower sheath potential, and which decreased the directionality of the extracted ions and decreased the ions extracting through the 2nd grid. Even though the ion flux on the substrate was decreased with the addition of a small axial magnetic field, by using the axial magnetic field to a two-grid ICP ion source, a stable and very low mono energetic Ar⁺ ion beam could be obtained.

Using the low energy Ar⁺ ions extracted with the conditions in Figure 3, the monolayer pristine graphenes transferred on the SiO₂ substrates as mentioned in the experimental section were treated for 5 minutes for the removal of the PMMA residue remaining on the monolayer graphene. Figure 4 shows the Raman spectra of the graphenes before and after the treatment using the conditions in Figure 3. The Raman spectrum is able to indicate the presence of monolayer graphene and the status of graphene.¹⁶⁻¹⁷ Figures 4(a) and (b) show the spectra before and after the treatment without the magnetic field and Figures 4(c) and (d) show those before and after the treatment with the 25 Gauss of axial magnetic field. As shown in the figures, the peaks at about 1580 cm⁻¹ and 2680 cm⁻¹ related to the G peak and 2D peak of crystalline graphene, respectively, were observed. In addition, a peak near 1340 cm⁻¹ (D peak) related to the defect of the graphene was also observed. Figures 4(b) and (d) are the narrow scan data of the G peaks in Figures 4(a) and (c), respectively. As shown in the figures, in the case of pristine

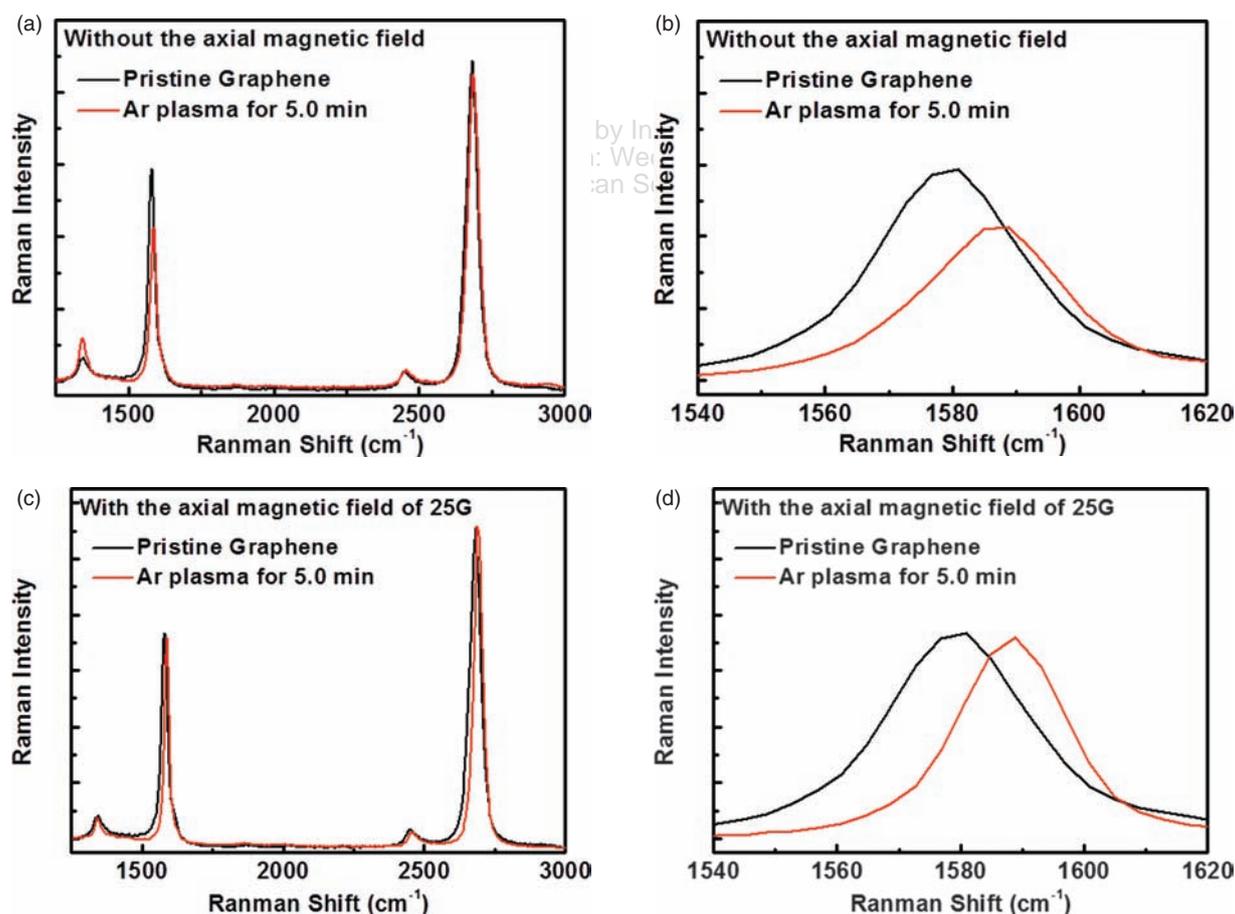


Figure 4. Raman spectra of the graphene before (pristine CVD graphene transferred to SiO₂ substrate) and after the treatment with the two-grid ICP Ar⁺ ion gun (a) without the magnetic field (mono energetic distribution with a peak energy of 11.5 eV) and (b) with the magnetic field (mono energetic distribution with a peak energy of 7.5 eV). Narrow scan Raman 2D peaks in (a) and (c) are shown in (b) and (d), respectively. The graphene was treated for 5 minutes.

graphene, the G peak was observed near 1580 cm⁻¹ indicating *p*-type doped state possibly due to the remaining PMMA residue on the transferred graphene surface in addition to a small defect peak possibly due to the damage on the surface during the transfer of graphene on SiO₂ substrates. As shown in Figures 4(a) and (b), after the treatment of the graphene using the low energy Ar⁺ ions for 5 minutes without the magnetic field (mono ion energy distribution with a peak of about 11.5 eV), the blue shift of G peak from 1580 cm⁻¹ to 1588 cm⁻¹ close to that of the intrinsic graphene indicating the removal of the PMMA by the Ar⁺ ion treatment was observed. However, the D peak related to the defect on the graphene surface was increased indicating the damage on the surface after the treatment of graphene with the Ar⁺ ions obtained without the magnetic field. However, when the pristine graphene surface was cleaned with the condition obtained with the magnetic field (mono ion energy distribution with a peak energy of about 7.5 eV) as shown in Figures 4(c) and (d), the similar blue shift of G peak indicating the removal of PMMA residue was observed without increasing the D peak intensity possibly indicating no noticeably significant damage after the treatment with the Ar⁺ ions obtained with the magnetic field.

In fact, during the surface treatment with and without the magnetic field, even though the treatment time was the same for both, the Ar⁺ ion doses on the graphene surface during the treatment are not same because the Ar⁺ ion flux is lower for the case with the magnetic field as can be seen in Figure 3. The area of the Ar⁺ ion energy distribution in Figure 3 is related to the Ar⁺ ion flux to the substrate and the ion flux without the magnetic field is ~1.73 times larger. Therefore, to investigate the effect of Ar⁺ ion dose on the damage on the graphene surface, the ratio of the D peak intensity over the G peak intensity (I_D/I_G) of the Raman spectra was measured as a function

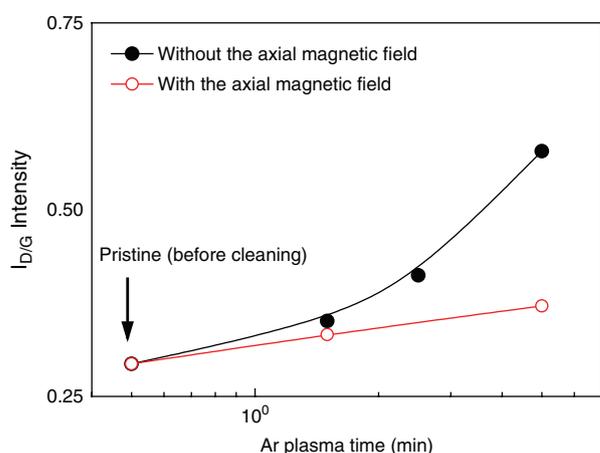


Figure 5. The ratio of the D peak intensity over the G peak intensity (I_D/I_G) of the Raman spectra measured on the graphene surface as a function of graphene treatment time for the conditions of with (7.5 eV) and without (11.5 eV) the magnetic field.

of graphene treatment time for the conditions with and without the magnetic field in Figure 3 and the results are shown in Figure 5. As shown in the figure, for the treatment without the magnetic field, the I_D/I_G was increased significantly with increasing the Ar⁺ ion treatment time while, for the condition with the magnetic field, the I_D/I_G was not increased significantly with increasing the treatment time. Therefore, the graphene surface appears to be more damaged by the energy of the Ar⁺ ions than the dose of the Ar⁺ ions and, for the graphene treatment with a plasma, to remove the residue on the surface without damaging the graphene, the ion energy lower than 10 eV appears to be required.

4. CONCLUSIONS

In this article, the surface of the monolayer CVD graphene which has PMMA residue on the graphene surface after the transfer from Cu to SiO₂ substrate using PMMA followed by the removal of PMMA using acetone has been treated using low energy Ar⁺ ions obtained by a two-grid ICP ion gun installed with/without an axial magnetic field. And, the effect of the energy and dose of Ar⁺ ions during the treatment for the removal of the PMMA residue and the formation of the damage on the graphene surface was investigated. Mono energetic low energy Ar⁺ ions with a peak at 11.5 eV could be obtained in a two-grid ICP ion gun by controlling the ICP source condition while floating the 1st grid voltage and grounding the 2nd grid voltage. Especially, by using an axial magnetic field of 25 Gauss in the ICP source, a lower Ar⁺ ion energy distribution with a peak at 7.5 eV could be obtained. When the treatment of the graphene surface with the Ar⁺ ions with/without the magnetic field having the ion energy peak at 7.5 eV/11.5 eV was performed, the blue shift of Raman G peak from *p*-type doped to intrinsic indicating the cleaning of graphene could be observed for both conditions having the peak energy of 11.5 eV and 7.5 eV, however, the graphene treated at 11.5 eV (without the magnetic field) showed the increase of Raman peak related to the defect while that treated at 7.5 eV (with the magnetic field) showed no significant change of the peak related to the defect. The defect on the graphene layer was more sensitive to the Ar⁺ ion energy than the Ar⁺ ion dose. It can be concluded that a low energy Ar⁺ ion source installed with an axial magnetic field is a promising candidate for plasma treatment of the 2 dimensional materials. This low ion energy technique can be extended to etching and doping of graphene further.

Acknowledgments: This research was supported by Nano Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012M3A7B4035323) and was also supported by the Industrial Strategic technology development program

(10041926, Development of high density plasma technologies for thin film deposition of nanoscale semiconductor and flexible display processing) funded by the Ministry of Knowledge Economy (MKE, Korea).

References and Notes

1. <http://www.itrs.net/Links/2007ITRS/>
2. K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, *Nature* 490, 192 (2012).
3. F. Schwierz, *Nature Nanotechnol.* 5, 487 (2010).
4. A. K. Geim and K. S. Novoselov, *Nature Mater.* 6, 183 (2007).
5. S. V. Morozov, K. S. Novoselov, M. I. Katsnelson, F. Schedin, D. C. Elias, J. A. Jaszczak, and A. K. Geim, *Phys. Rev. Lett.* 100, 016602 (2008).
6. M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, *Nano Lett.* 7, 1643 (2007).
7. Y. C. Lin, C. Jin, J. C. Lee, S. F. Jen, K. Suenaga, and P. W. Chiu, *ACS Nano.* 5, 2362 (2011).
8. E. H. Hwang, S. Adam, and S. Das Sarma, *Phys. Rev. B* 76, 195421 (2007).
9. Y. Niimi, T. Matsui, H. Kambara, K. Tagami, M. Tsukada, and H. Fukuyama, *Phys. Rev. B* 73, 085421 (2006).
10. A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colomobo, E. M. Volgel, R. S. Ruoff, and R. M. Wallace, *Appl. Phys. Lett.* 99, 122108 (2011).
11. Y. C. Lin, C. C. Lu, C. H. Yeh, C. Jin, K. Suenaga, and P. W. Chiu, *Nano Lett.* 12, 414 (2012).
12. J. Moser, A. Barreiro, and A. Bachtold *Appl. Phys. Lett.* 91, 163513 (2007).
13. Y. D. Lim, D. Y. Lee, T. Z. Shen, C. H. Ra, J. Y. Choi, and W. J. Yoo, *ACS Nano.* 6, 4410 (2012).
14. N. Peltekis, S. Kumar, N. McEvoy, K. Lee, A. Weidlich, and G. S. Duesberg, *Carbon* 50, 395 (2012).
15. N. McEvoy, H. Nolana, Nanjundan Ashok Kumara, T. Hallama, and G. S. Duesberg, *Carbon* 54, 283 (2013).
16. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, *Phys Rev Lett.* 97, 187401 (2006).
17. L. M. Malard, J. Nilsson, D. C. Elias, J. C. Brant, F. Plentz, E. S. Alves, A. H. C. Neto, and M. A. Pimenta, *Phys Rev B* 76, 201401 (2007).

Received: 1 February 2014. Accepted: 24 April 2014.

Delivered by Ingenta to :
IP: 115.145.196.110 On: Wed, 13 Dec 2017 00:31:56
Copyright: American Scientific Publishers