

AN IMPROVED METHOD FOR TRANSFERRING GRAPHENE GROWN BY CHEMICAL VAPOR DEPOSITION

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In this paper, we report an improved transfer of graphene by directly picking up the graphene with target substrates and the comparison of such transferred graphene samples with other graphene samples transferred by the commonly used “PMMA-based transfer” method. Raman spectroscopy studies show that this “direct transfer method” does not degrade the graphene structure and field effect transistor measurements show that it does not introduce any extra doping in graphene; in contrast, PMMA-based transfer samples have strong *n*-type doping.

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We also find that graphene samples achieved by this direct transfer method show higher mobility than graphene obtained from the PMMA-based transfer method.

Keywords: Graphene; transfer; FET measurement; Dirac point; mobility.

1. Introduction

Graphene, experimentally studied since the 1960's,^{1,2} has attracted more recent interest for its interesting electronic,^{3,4} and other properties. The properties of graphene such as extremely high carrier mobility,⁵ high thermal conductivity,^{6–8} low resistivity,⁹ large specific surface area and high mechanical strength^{10,11} make it a promising material for future devices and materials.^{2,12,13} Future applications of graphene will require large scale growth and transfer from growth substrates such as Cu.^{14–17} Currently, the most commonly used transfer method involves application of a layer of PMMA to support the graphene film after etching the growth substrate.^{16,18} However, graphene samples that were transferred by PMMA showed strong *n*-type doping (after annealing in high vacuum) even after the PMMA was “removed”, as observed by us and other groups,¹⁹ which is due to a small amount of residual PMMA remaining on the graphene, and perhaps other residues from the processing such as from the solvent(s) used that are meant to remove the PMMA. When residual PMMA is left on graphene, charge transfer

evidently occurs at the interface between graphene and PMMA.

Based on a “direct transfer method” that we have previously reported,^{14,17} in this work we have further improved the transfer process with easier operation and higher yield. FET measurements show that this direct transfer method yields higher carrier mobilities for the graphene, eliminates the doping caused by PMMA, and thus provides an option for obtaining CVD graphene from growth substrates, and allowing transfer to arbitrary substrates.

2. Experiment

The graphene samples were grown on 25- μm thick copper foils (Alfa Aesar, item No. 13382) with a CVD process.^{20,21} A cold-wall chamber was used to synthesize graphene with methane and hydrogen gas as precursors. The quality and number of layers of the as-grown graphene were evaluated by Micro-Raman spectroscopy (WITec Alpha300, excitation wavelength 532 nm).^{14,22} Figure 3 shows the typical Raman spectra of monolayer graphene with sharp

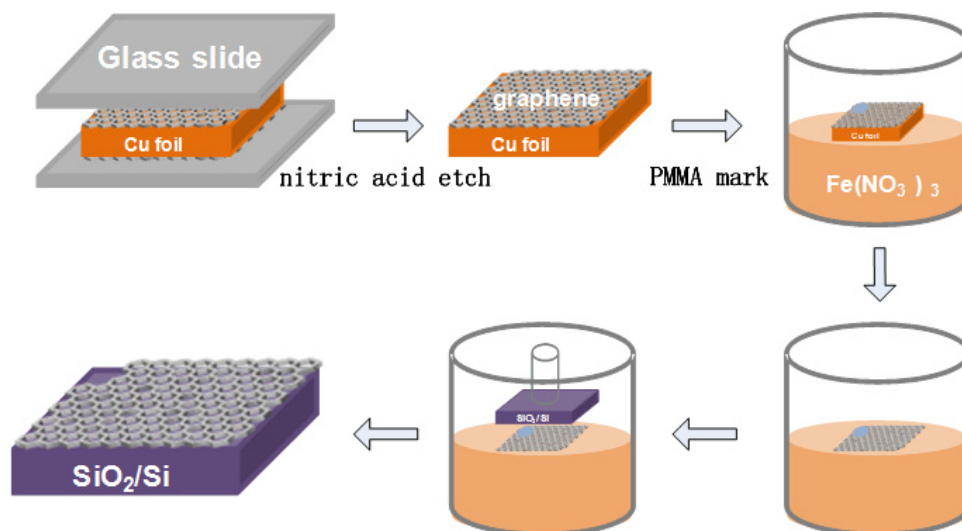


Fig. 1. Schematic illustrates of the “direct transfer” method. The graphene/copper foil is first flattened between two glass slides so that it will better float on the solution surface. After “pick up” such as with a Si wafer piece, de-ionized water and hydrochloric acid are used to clean the graphene.

G band ($\sim 1580\text{ cm}^{-1}$), 2D band ($\sim 2690\text{ cm}^{-1}$) and a low G/2D ratio. The small D peak indicates that the graphene has low defect density.²³

A schematic of the transfer process is shown in Fig. 1. The graphene-Cu-graphene sample was first flattened between two glass slides and then floated on 10% nitric acid to “gently” remove graphene on one side for 2 min. After that, the exposed Cu foil was dissolved in an aqueous etchant (3 g/ml $\text{Fe}(\text{NO}_3)_3$) for several hours. A small drop of PMMA is placed on one corner of the floating sample as a marker because monolayer graphene is nearly transparent²⁴ and can be hard to find after the copper substrate is etched away. After the copper was completely removed, the graphene sample is then ready for pick up by a target substrate. A Si wafer piece with a 285 nm thick thermal oxide layer was used. After cleaning in acetone in an ultrasonic bath for 10 min, the Si wafer piece was brought into contact with the graphene from the top (see Fig. 1). The sample was then rinsed in 10% HCl (60°C) for half an hour in an attempt to remove residual Fe^{3+} ions.

3. Results and Discussion

In order to evaluate this direct transfer approach, graphene transferred by the PMMA-based method was prepared as a control. Two graphene on Cu samples (S1 and S2) were prepared with each one cut into two pieces and then transferred by direct (S1-D, S2-D) and PMMA-based (S1-PMMA, S2-PMMA) methods. Figure 2 shows the optical images of samples S1-PMMA (a) and S1-D (b). Significant PMMA residue is left on the graphene

surface after PMMA-based transfer; in contrast in terms of optical images, the direct transfer method yields “clean” graphene. Although cracks are hard to avoid during the direct transfer process, millimeter scale areas with continuous graphene can be easily found throughout the sample. In Fig. 2(b), one continuous area is more than 50 mm^2 . This is a size scale that means that the direct transfer method can be used for the fabrication of various devices, such as chips, sensors, FETs, and so on.

Figure 3 shows the Raman spectra (WITec Alpha300, 532 nm laser) of samples S1-D (b) and S1-PMMA (a). The increase of the 2D/G ratio for S1-D indicates a cleaner surface.²⁵ Following Raman spectroscopy of the samples, Au electrodes were evaporated and field effect transistor (FET) measurements were made to test electrical properties. The FET devices were fabricated as reported in our previous work.^{26,27} Both annealing and FET measurements were performed in the same high vacuum chamber. The gate bias (V_g) as a function of drain source current (I_{ds}) could be obtained via the measurement.

FET measurement of ideal (perfectly pristine) graphene is expected to have the linear dispersion “V” shape response of I_{ds} versus V_g , with the charge neutral point at zero gate bias.^{28,29} Figure 4 shows I_{ds} versus V_g of the four samples after annealing at 120°C for 1 h at a pressure of 1.0×10^{-8} Torr. The difference of the zero point currents for each FET measurement could be attributed to the difference in the defect density or impurity level of each graphene film while the shift in the Dirac point is due to the initial doping.

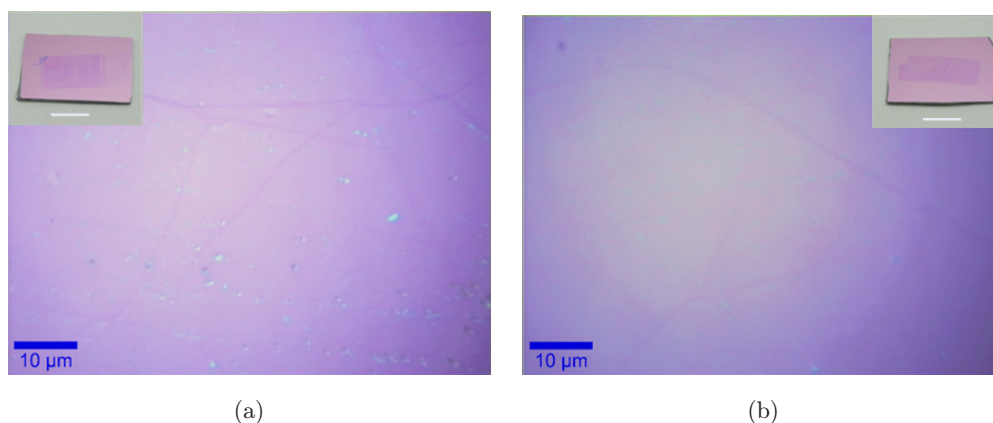


Fig. 2. Optical photograph of graphene transferred onto a SiO_2 -on-Si substrate: (a) By the standard PMMA-based method and (b) by the “direct transfer” method. The scale bars in the insets are 5 mm.

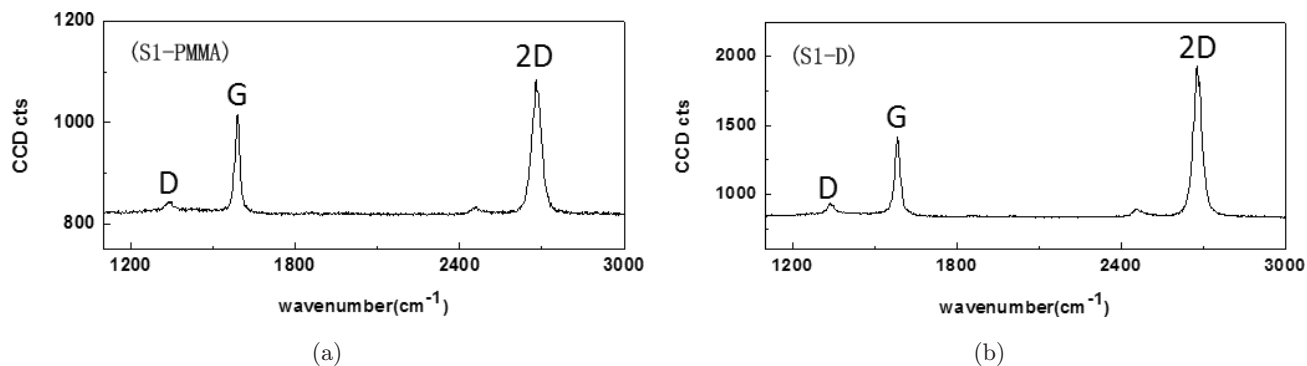


Fig. 3. Raman spectra (532 nm laser excitation wavelength) for graphene transferred onto the SiO₂-on-Si substrate. (a) Raman spectra obtained from a sample obtained by the standard PMMA-based method. FWHM (Lorentz fit) of 2D band is ~ 40 cm⁻¹. (b) Raman spectra obtained from a sample obtained by the direct transfer method. FWHM (Lorentz fit) of 2D band is ~ 38 cm⁻¹.

Samples S1-PMMA and S2-PMMA have the Dirac point at a negative gate bias side showing strong *n*-doping of the samples; while the curves for the direct transfer samples (S1-D and S2-D) each have the Dirac point very close to zero gate bias, indicating a very low doping level.

A previous paper claimed that water and air doping can be removed by gently heating,¹² which can also be demonstrated by our direct transfer method. Before annealing, the samples show strong *p*-doping likely due to doping by O₂ and/or H₂O,^{12,30,31} but after annealing they show nearly no

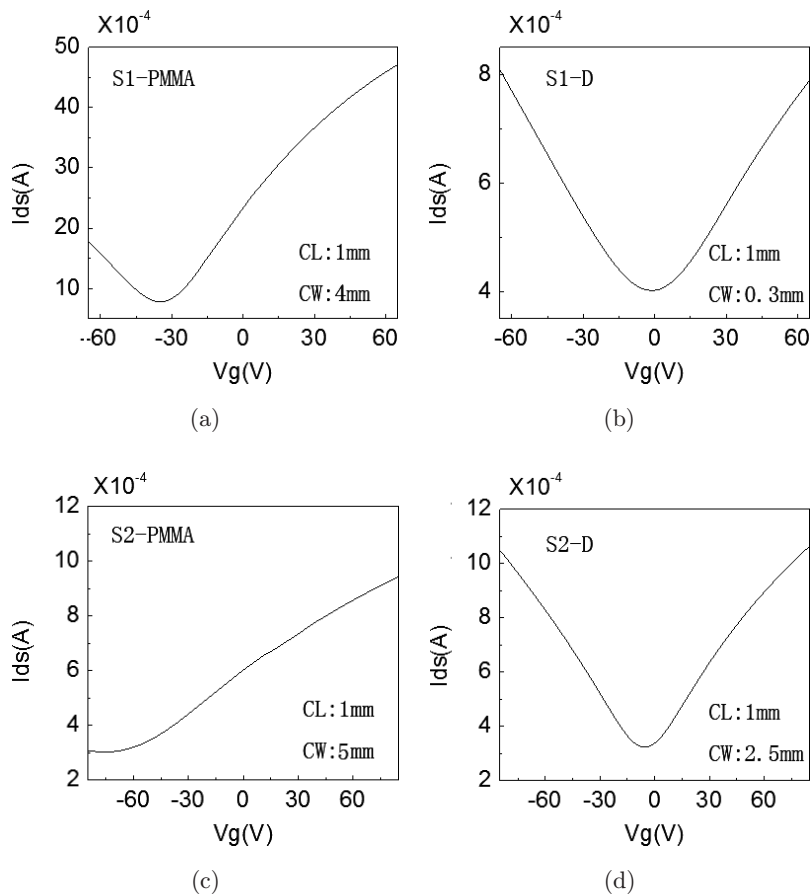


Fig. 4. FET measurements of (a) Sample S1-PMMA, (b) Sample S1-D, (c) Sample S2-PMMA and (d) Sample S2-D. CL means channel length; CW means channel width.

Table 1. Mobility values as a function of transfer method.

	PMMA-based transfer	Direct transfer
Hole mobility	$\sim 700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$\sim 1580 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Electron mobility	$\sim 800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$\sim 1480 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

doping. The strong n -doping of the samples transferred with PMMA is due to residual PMMA that is not removed by acetone. A FET device from the direct transfer sample was soaked in acetone for 1 h before a second FET measurement was made and there was little change in the location of the Dirac point, which shows that long time exposure to acetone has almost no doping affect on the graphene film and a small effect can be eliminated by annealing. As shown in the optical microscopy image [Fig. 2(a)], some “dots” remain on the PMMA-transferred graphene, which was also observed by other group, were PMMA residue.¹⁸ For S1-PMMA, we exposed to fresh acetone multiple times during removal of the PMMA layer but for S2-PMMA, the acetone was changed just once. As shown in Fig. 4(c), S2-PMMA was more heavily doped.

The electron and hole mobilities of S1-D and S1-PMMA were also obtained from Fig. 4 using the equation $\mu = (L/WC_{\text{OX}}V_d)(\Delta I_d/\Delta V_g)$ (see Ref. 32) and were listed in Table 1. S1-D has values for each that are about twice those of S1-PMMA, suggesting that the PMMA transfer process might adversely influence carrier mobility. Figure 5 shows Dirac point positions for ten different samples for each transfer method. For the direct transfer samples, all

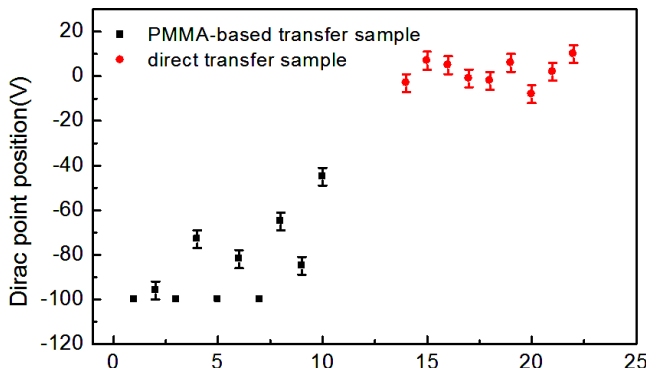


Fig. 5. Statistical results of the Dirac point position. Note that, the positions beyond -100 V are out of measurement range and are all marked as -100 V .

the Dirac points are located around zero bias, indicating a low doping level.

4. Summary and Conclusion

In conclusion, graphene samples were transferred with two different methods, one with a PMMA supporting layer and one with direct lift. From the optical image, it is obvious that the direct transfer samples are cleaner than PMMA-based transfer samples. In addition, millimeter scale coherent areas are easily found within the direct transfer sample, which is an adequate size for most micro-scale device applications. The Raman spectra for the two samples show no obvious differences, which proves that direct transfer method has no effect to the graphene’s quality. The FET measurements demonstrate that the direct transfer sample has a very low doping level since its Dirac point is located around the zero gate bias. Furthermore, the calculated carrier mobilities of the device from the direct transfer method are much higher than PMMA-based transfer method.

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References

1. D. R. Dreyer, R. S. Ruoff and C. W. Bielawski, *Angew. Chem. Int. Ed. Engl.* **49**, 9336 (2010).
2. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.* **22**, 3906 (2010).
3. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science* **306**, 666 (2004).
4. C. Berger *et al.*, *J. Phys. Chem. B* **108**, 19912 (2004).
5. X. Du, I. Skachko, A. Barker and E. Y. Andrei, *Nat. Nanotechnol.* **3**, 491 (2008).
6. W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi and R. S. Ruoff, *Nano Lett.* **10**, 1645 (2010).
7. A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, *Nano Lett.* **8**, 902 (2008).
8. S. Chen *et al.*, *ACS Nano* **5**, 321 (2011).
9. J.-H. Chen, C. Jang, S. Xiao, M. Ishigami and M. S. Fuhrer, *Nat. Nanotechnol.* **3**, 206 (2008).

10. C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science* **321**, 385 (2008).
11. I. W. Frank, D. M. Tanenbaum, A. M. van der Zande and P. L. McEuen, *J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.* **25**, 2558 (2007).
12. F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov, *Nat. Mater.* **6**, 652 (2007).
13. W. W. Cai, Y. W. Zhu, X. S. Li, R. D. Piner and R. S. Ruoff, *Appl. Phys. Lett.* **95**, 123115 (2009).
14. X. Li et al., *Science* **324**, 1312 (2009).
15. X. Li, W. Cai, L. Colombo and R. S. Ruoff, *Nano Lett.* **9**, 4268 (2009).
16. X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo and R. S. Ruoff, *Nano Lett.* **9**, 4359 (2009).
17. X. Li, W. Cai, I. H. Jung, J. H. An, D. Yang, A. Velamakanni, R. Piner, L. Colombo and R. S. Ruoff, *ECS Trans.* **19**, 41 (2009).
18. A. Reina, H. Son, L. Jiao, B. Fan, M. S. Dresselhaus, Z. Liu and J. Kong, *J. Phys. Chem. C* **112**, 17741 (2008).
19. V. Geringer, D. Subramaniam, A. K. Michel, B. Szafranek, D. Schall, A. Georgi, T. Mashoff, D. Neumaier, M. Liebmann and M. Morgenstern, *Appl. Phys. Lett.* **96**, 082114 (2010).
20. W. Cai et al., *Science* **321**, 1815 (2008).
21. W. W. Cai, R. D. Piner, Y. W. Zhu, X. S. Li, Z. B. Tan, H. C. Floresca, C. L. Yang, L. Lu, M. J. Kim and R. S. Ruoff, *Nano Res.* **2**, 851 (2009).
22. A. C. Ferrari et al., *Phys. Rev. Lett.* **97**, 187401 (2006).
23. Y. Hao, Y. Wang, L. Wang, Z. Ni, Z. Wang, R. Wang, C. K. Koo, Z. Shen and J. T. L. Thong, *Small* **6**, 195 (2010).
24. R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres and A. K. Geim, *Science* **320**, 1308 (2008).
25. C. Casiraghi, S. Pisana, K. S. Novoselov, A. K. Geim and A. C. Ferrari, *Appl. Phys. Lett.* **91**, 233108 (2007).
26. S. Chen, W. Cai, D. Chen, Y. Ren, X. Li, Y. Zhu and R. S. Ruoff, *New J. Phys.* **12**, 125011 (2010).
27. Y. Ren, S. Chen, W. Cai, Y. Zhu, C. Zhu and R. S. Ruoff, *Appl. Phys. Lett.* **97**, 053107 (2010).
28. G. W. Semenoff, *Phys. Rev. Lett.* **53**, 2449 (1984).
29. P. Avouris, Z. Chen and V. Perebeinos, *Nat. Nanotechnol.* **2**, 605 (2007).
30. O. Leenaerts, B. Partoens and F. M. Peeters, *Phys. Rev. B* **77**, 125416 (2008).
31. T. O. Wehling, A. I. Lichtenstein and M. I. Katsnelson, *Appl. Phys. Lett.* **93**, 202110 (2008).
32. C.-Y. Su, Y. Xu, W. Zhang, J. Zhao, A. Liu, X. Tang, C.-H. Tsai, Y. Huang and L.-J. Li, *ACS Nanotechnol.* **4**, 5285 (2010).