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Reduction of metal contact resistance of graphene devices via CO₂ cluster cleaning

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We report on a cleaning technique using CO₂ clusters for large-scale mono-layer graphene fabricated via chemical vapor deposition (CVD) and its application to reduce contact resistance of the CVD graphene device. We found that polymeric residues, i.e., polymethyl methacrylate and photoresist which are generated during transfer and patterning of graphene, can be effectively removed via rapid shrinkage, induced by thermal energy transfer to low temperature CO₂ clusters. By applying the CO₂ clusters to the cleaning of the interface between metal and graphene, the metal contact resistance of the fabricated graphene field effect transistor was lowered to 26.6% of pristine graphene. The contact resistance shows the best result at an optimized CO₂ cluster cleaning condition with a flow rate of 201/min, and the resistance was further lowered to 270 Ω μ m when a gate bias of -40 V was applied. We expect that the proposed CO₂ cluster cleaning to be a very promising technique for future device application using 2-dimensional materials, as it can enable low-energy, large-area, high-throughput, and mass-production-compatible process. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4881635]

Graphene, which has the honeycomb structure of carbon, is a typical 2-dimensional material. Since its study in 2004,¹ many researchers in various fields have shown its interesting properties.^{2,3} However, we face a serious limitation in the fabrication of high performance graphene devices, e.g., significant contact resistance at graphene-metal interfaces. According to the previous work on simulations of the contact resistance, the electrical properties of graphene-field effect transistors (FETs) deteriorate with increasing contact resistance,⁴ and reduction of the contact resistance is found to be essential to fabricate high-performance graphene-based devices.

The reasons for which contact resistance of graphene devices is induced have been studied by other research groups.^{5–7} First, graphene is known to have very small density of states around the charge neutral point due to its intrinsic linear dispersion relation.⁵ Second, under equilibrium, some portion of the charge transfers from graphene to metal (or metal to graphene) via a potential step inducing a dipole layer at the interface, which becomes an obstacle to charge transfer.^{6,7} To reduce contact resistance, various studies have been conducted, e.g., inducing edge-contact,⁸⁻¹⁰ applying back gate bias,^{11,12} using metals that have a high bonding energy with graphene,^{7–9} operating devices at low temperatures,¹³ using low power O_2 plasma,¹⁴ and performing plasma treatment to improve contact with metal via changing surface property from hydrophobic to hydrophilic.¹⁵ However, it is also thought that polymer residues cause an increase in the contact resistance. When devices are fabricated using chemical vapor deposition (CVD)-graphene, two types of polymeric materials are usually employed: polymethyl methacrylate (PMMA) to transfer the graphene onto the SiO₂/Si wafer and photoresist to generate the electrode pattern. Both polymers cannot be perfectly removed with acetone and thus have significantly deleterious effects on the electrical properties of the graphene devices,¹⁶ so cleaning graphene has become an important issue for graphene research. Recently, various cleaning methods have been introduced, e.g., annealing,^{16,17} plasma treatment,¹⁸ current-induced cleaning,¹⁹ electrostatic force cleaning,²⁰ the low-molecular-weight-PMMA method,²¹ wet chemical treatment,²² and mechanical force cleaning via AFM.²³ But, no methods have proven to be effective for cleaning large scale CVD graphene.

In this work, we demonstrate a technique for reducing contact resistance by using a CO₂ cluster cleaning. The processing steps for graphene device fabrication are shown in Figure 1(a). Negative photoresist was coated on the graphene sample. After development, the negative photoresist left fewer residues behind than did the positive photoresist. By using photo-lithography, we exposed the sample to ultra-violet light and developed the exposed part to form an electrode pattern. The mask that we used for photo-lithography contained transmission line method (TLM) patterns which can be used to measure contact resistance. Since our purpose in this experiment was to investigate the change in contact resistance, we conducted CO₂ cluster cleaning confined only under the electrode area. To study the dependence of flow rate and the number of scans of the CO₂ cluster, four different conditions were tested: 151/min, 4 times; 151/min, 6 times; 201/min, 4 times;

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FIG. 1. (a) Process to fabricate the graphene device with CO_2 cluster cleaning. The TLM electrode pattern was generated using photo-lithography. The CO_2 cluster cleaning was applied to specific area which contacts the bottom of the electrode after device fabrication, (b) principle of gas cluster formation at the converging-diverging nozzle, and (c) schematic description of the removal mechanism of polymeric residues by low temperature CO_2 clusters.

and 201/min, 6 times. These were optimized through trial and error, and we controlled the number of scans rather than the treatment time. This is because the equipment was designed for a large wafer size (diameter = 300 mm). A schematic diagram of the gas cluster cleaning apparatus is shown in Figure $S1.^{32}$ We used ultrapure CO₂ as a carrier gas and also as a cluster source. The pressure and gas flow rate (Q = 10-20 l/min) were controlled by a valve and a mass flow controller. The cooled gas is condensed as a group $(T_{Nozzle} = -50 \,^{\circ}\text{C})$ and is spread out after passing through the vacuum chamber and the nozzle ($P_{vac} = 0.3 - 0.5$ Torr), while spraying with a sudden pressure drop during cooling due to expansion. The size distribution of the clusters formed by the cluster generation can be dependent on CO₂ flow rate (Q), nozzle temperature (T_{Nozzle}), vacuum chamber pressure (P_{vac}), nozzle angle ($\theta_{Nozzle} = 15^{\circ}$), spray distance (d = 50 mm), and the processing time $(t_{op} = 4-6 \text{ s})$. However, T_{Nozzle} , θ_{Nozzle} , and d are used as fixed variables. Even though the stage rotates with a fixed angular velocity, we cannot be fully convinced that the CO_2 clusters from jet nozzle were uniformly released onto the sample, and therefore we observe a normalized effect by controlling the number of scans (each scan takes approximately 1 s). The last step is the electrode deposition and lift off. Using an electron beam evaporator, we deposited Cr/Au (5 nm/50 nm) electrode. We used Cr as a buffer layer because the dipole layer between Cr and graphene is narrower than that of other metals. Thus, we can achieve relatively low contact resistance.⁹

This cleaning method uses a gas cluster as a physical removal medium of contaminants for cleaning CVD graphene. The process is capable of removing undesirable contaminants, such as film-typed and particle-typed residues, generated during the device manufacturing process (see Figure 1(a)). Gas cluster cleaning uses clusters which are formed with few to thousands of molecules. Since the freezing temperature of CO₂ is relatively high at 194.5 K, compared to other gases, e.g., 87.1 K for Ar and 77.2 K for N₂, CO₂ clusters can be formed very effectively by adiabatic expansion through converging-diverging nozzle in a short time, as shown in Figure 1(b). Here, very low energy can be supplied to the atoms in substrate by the cluster as the kinetic energy of an atom in a cluster is equal to the total energy of the cluster divided by the cluster size.²⁴ However, it is obvious that cleaning efficiency and surface morphology of the substrate depend on cluster size and velocity.

In this work, the gas clusters are introduced to the surface of the contaminated graphene sample, cooling and removing the contaminants without leaving secondary contaminants behind. It is understood that when CO₂ gas cluster collides with the contaminated surface, it cools or freezes polymeric residues and causes a difference in the thermal expansion coefficients between the contaminant and the substrate. Rapid volume shrinkage of the residues induces the contaminants to easily detach from the substrate.²⁶ See Figure 1(c) as a schematic model for the removal processes of the residues on graphene using CO₂ gas clusters. Here, low energy CO2 gas cluster can clean the contaminants, while leaving graphene unharmed. Note that this method can be applied to treat large-scale graphene in a mass-production-compatible way, similar to plasma treatment, and it is more economical in terms of cost and time, compared to mechanical cleaning and inducement of edge-contact. Also note that this method is relatively safe for devices and is also environmentally friendly, in contrast to wet chemical cleaning, which can be corrosive to fine features such as metal lines.27,28

Figure 2(a) shows the optical images showing the change of the graphene surfaces for CO₂ cluster cleaning and Figure 2(b) is schematic of the energy band diagram of the graphene-metal contact. From a sheet of graphene, we fabricated electrode-patterned samples via photo-lithography, treated them under the different conditions, and took pictures before depositing the metal to compare the differences in the surface images. We can observe that the CO₂ cluster-treated graphene sample is cleaner than the pristine graphene. We can observe a significant amount of the remaining photoresist residue around the channel area on the left of Figure 2(a)(pristine state) because the channel area is relatively narrow when compared to other parts, while the pattern of the treated sample is very clean. For the cleaned area, graphene makes direct contact with the metal. In contrast, for the contaminated area, even though remaining PMMA residues are very thin, they can act as a barrier between the graphene and metal, as shown in the band diagram of Figure 2(b). The charge transfer will therefore be obstructed by the barrier,



FIG. 2. (a) Optical images before and after CO_2 cluster cleaning and (b) energy band diagram of the graphene device for contaminated area (W: work function, E_{gP} : band gap of PMMA,³⁰ X: electron affinity of PMMA³⁰). We treated patterned-sample before metal deposition.

leading to an increased contact resistance. Therefore, contact resistance can be reduced by eliminating polymeric residues through low-power O_2 plasma treatment, annealing, or the Al_2O_3 encapsulation method.^{14,29} However, these methods are found to deteriorate the electrical properties of CVD graphene devices, e.g., lowering carrier mobility and inducing undesirable shift of charge neutral point.

In order to analyze the graphene surface more closely, we conducted transmission electron microscopy (TEM). Figures S2(a)–S2(d) are the TEM images taken from different sample conditions. From the TEM figures, we can notice that the graphene sheets have many wrinkles, some residues, and hole-type defects. According to the images, the number of hole-type defects increases with the CO₂ cluster treatment. These hole-type defects may induce an edge contact between graphene and metal, so we can anticipate that contact resistance decreases^{9,10} with the CO₂ cluster cleaning.

When graphene makes contact with metal, various factors affect charge transfer and thereby contact resistance, e.g., energy barrier arising from remaining residues and nonuniform Fermi level at the interface. Here, we investigated the effect of the graphene cleaning by CO₂ clusters on contact resistance. We coat PMMA on the graphene sheet to support it and use photoresist to make an electrode pattern. These polymeric residues cannot be removed thoroughly with acetone. Conventional cleaning methods, as introduced earlier, focus on removing residues on the channel area, whereas we focus on the contact area to observe a change in the contact resistance. Through CO_2 cluster cleaning, we attained significantly lowered contact resistance and doubled mobility. Figure 3(a)is the graph showing the change in contact resistance for various CO₂ cluster conditions, and the detailed data are shown in Table S1. According to the data, pristine graphene shows the largest contact resistance of $6.35 \text{ k}\Omega \mu \text{m}$ with a large standard deviation because of non-uniformly distributed residues. On the other hand, all the CO₂ cluster-treated samples have lower contact resistance and lower standard deviation than the pristine sample. In particular, the lowest average contact resistance, $1.69 \text{ k}\Omega \mu \text{m}$, was obtained from the 201/min, 4-times-treated device. This value is 73.3% lower than that of the pristine graphene. Moreover, hole mobility also improved for all the treated devices and was even twice higher for the 201/min, 4-times-treated device (Figure S3). We think that the primary reason for the improvement of the electrical properties is the cleaning effect. The reduction of polymeric residues by CO₂ cluster cleaning brought about a free charge transfer between graphene and metal so as to reduce contact resistance. It is interesting to observe hole-type defects generated after the CO₂ cluster cleaning, as we inspected graphene via TEM in Figure S2. We suppose that these holes might induce nano-scale edge contact to the metal. However, the 201/min, 6-times-treated device showed no further improvement in contact resistance, as shown in Figure 3(a). We assume that excessively intensive treatment can generate redundant defects on graphene, and therefore charge scattering increases drastically³¹ and so does contact resistance.

A cleaning technique using CO_2 clusters was demonstrated to clean large scale CVD graphene and therefore to lower metal contact resistance of the CVD graphene FET devices. It was found that low energy CO_2 clusters are very



FIG. 3. Electrical performances of CVD graphene devices before and after CO_2 cluster cleaning. (a) Contact resistance, (b) change in contact resistance by gate modulation for different CO_2 cluster cleaning conditions, pristine and CO_2 cluster 20 l/min, 4-times-treated device. Other data are shown in Figure S4. Values represent contact resistances (k $\Omega \mu m$).

effective in removing PMMA and photo-resist residues generated during the fabrication of graphene FET, by detaching them through volume shrinkage at lowered temperature. It is expected the CO₂ cluster cleaning to be a very promising technique for future device applications using 2D materials, as it presents surface residues removal selectivity and mass-production compatibility as a low-energy, large-area, and high-throughput process.

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- ¹K. 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).
- ²K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer, Solid State Commun. 146, 351 (2008).
- ³J. H. Seol, I. Jo, A. L. Moore, L. Lindsay, Z. H. Aitken, M. T. Pettes, X. Li, Z. Yao, R. Huang, D. Broido, N. Mingo, R. S. Ruoff, and L. Shi, Science 328, 213 (2010).
- ⁴K. N. Parrish and D. Akinwande, Appl. Phys. Lett. **98**, 183505 (2011).
- ⁵K. Nagashio and A. Toriumi, Jpn. J. Appl. Phys., Part 1 50, 070108 (2011).
- ⁶E. J. H. Lee, K. Balasubramanian, R. T. Weitz, M. Burghard, and K. Kern, Nat. Nanotechnol. 3, 486 (2008).
- ⁷G. Giovannetti, P. A. Khomyakov, G. Brocks, V. M. Karpan, J. Van den Brink, and P. J. Kelly, Phys. Rev. Lett. 101, 026803 (2008).
- ⁸Y. Matsuda, W.-Q. Deng, and W. A. Goddard III, J. Phys. Chem. C 114, 17845 (2010).
- ⁹L. Wang, I. Meric, P. Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L. M. Campos, D. A. Muller, J. Guo, P. Kim, J. Hone, K. L. Shepard, and C. R. Dean, Science 342, 614 (2013).
- ¹⁰J. T. Smith, A. D. Franklin, D. B. Farmer, and C. D. Dimitrakopoulos, ACS Nano 7, 3661 (2013).

- ¹¹A. Venugopal, L. Colombo, and E. M. Vogel, Appl. Phys. Lett. 96, 013512 (2010).
- ¹²P. Blake, R. Yang, S. V. Morozov, F. Schedin, L. A. Ponomarenko, A. A. Zhukov, R. R. Nair, I. V. Grigorieva, K. S. Novoselov, and A. K. Geim, Solid State Commun. 149, 1068 (2009).
- ¹³F. Xia, V. Perebeinos, Y.-M. Lin, Y. Wu, and P. Avouris, Nat. Nanotechnol. 6, 179 (2011).
- ¹⁴J. A. Robinson, M. LaBella, M. Zhu, M. Hollander, R. Kasarda, Z. Hughes, K. Trumbull, R. Cavalero, and D. Snyder, Appl. Phys. Lett. 98, 053103 (2011).
- ¹⁵M. S. Choi, S. H. Lee, and W. J. Yoo, J. Appl. Phys. **110**, 073305 (2011).
- ¹⁶A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff, and R. M. Wallace, Appl. Phys. Lett. 99, 122108 (2011).
- ¹⁷Y.-C. Lin, C.-C. Lu, C.-H. Yeh, C. Jin, K. Suenaga, and P.-W. Chiu, Nano Lett. 12, 414 (2012).
- ¹⁸Y. D. Lim, D. Y. Lee, T. Z. Shen, C. H. Ra, J. Y. Choi, and W. J. Yoo, ACS Nano 6, 4410 (2012).
- ¹⁹J. Moser, A. Barreiro, and A. Bachtold, Appl. Phys. Lett. 91, 163513 (2007).
- ²⁰W. J. Choi, Y. J. Chung, S. Park, C.-S. Yang, Y. K. Lee, K.-S. An, Y.-S. Lee, and J.-O. Lee, Adv. Mater. 26, 637 (2014).
- ²¹J. W. Suk, W. H. Lee, J. Lee, H. Chou, R. D. Piner, Y. Hao, D. Akinwande, and R. S. Ruoff, Nano Lett. 13, 1462 (2013).
- ²²Z. Cheng, Q. Zhou, C. Wang, Q. Li, C. Wang, and Y. Fang, Nano Lett. 11, 767 (2011).
- ²³A. M. Goossens, V. E. Calado, A. Barreiro, K. Watanabe, T. Taniguchi, and L. M. K. Vandersypen, Appl. Phys. Lett. 100, 073110 (2012).
- ²⁴N. Toyoda and I. Yamada, IEEE Trans. Plasma Sci. **36**, 1471 (2008).
- ²⁵H. Choi, H. Kim, D. Yoon, J. W. Lee, B.-K. Kang, M.-S. Kim, J.-G. Park, S.-B. Kwon, and T. Kim, Microelectron. Eng. 102, 87 (2013).
- ²⁶C. W. Bowers, U.S. patent 5,853,962 (1998). ²⁷N. Narayanswami, J. Electrochem. Soc. **146**, 767 (1999).
- ²⁸N. Narayanswami, J. Heitzinger, J. Patrin, D. Rader, T. O'Hern, and J. Torczynski, Particles on Surfaces 5&6: Detection, Adhesion and Removal (28th Annual Meeting of the Fine Particle Society, 1999), p. 251.
- ²⁹A. Hsu, H. Wang, K. K. Kim, J. Kong, and T. Palacios, IEEE Electron Device Lett. 32, 1008 (2011).
- ³⁰S. M. Sayyah, A. B. Khaliel, and H. Moustafa, Int. J. Polym. Mater. 54, 505 (2005).
- ³¹J.-H. Chen, W. G. Cullen, C. Jang, M. S. Fuhrer, and E. D. Williams, Phys. Rev. Lett. 102, 236805 (2009).
- ³²See supplementary material at http://dx.doi.org/10.1063/1.4881635 for additional information and experimental results.