Regular Paper

Fabrication of a Graphene Nanoribbon with Electron Beam Lithography Using a XR-1541/PMMA Lift-Off Process

Sang-Chul Jeon[†] and Young-Su Kim
Department of Nano Patterning Process, National NanoFab Center , Daejeon 305-806, Korea

Dong-Kyu Lee
Department of Industrial Engineering Chemistry, Chungbuk National University, Cheongju 361-763, Korea

This report covers an effective fabrication method of graphene nanoribbon for top-gated field effect transistors (FETs) utilizing electron beam lithography with a bi-layer resists (XR-1541/poly methtyl methacrylate) process. To improve the variation of the gating properties of FETs, the residues of an e beam resist on the graphene channel are successfully taken off through the combination of reactive ion etching and a lift-off process for the XR-1541 bi-layer. In order to identify the presence of graphene structures, atomic force microscopy measurement and Raman spectrum analysis are performed. We believe that the lift-off process with bi-layer resists could be a good solution to increase gate dielectric properties toward the high quality of graphene FETs.

Keywords: Graphene nanoribbon, XR-1541/PMMA, Electron beam lithography

1. INTRODUCTION

Graphene, which is a single sheet of carbon atoms in honeycomb lattice, is an emerging material to enable continuation of the scaling down of silicon based CMOS technology due to its special electrical properties [1-3], and the many efforts are being maded to realize graphene field effect transistors (FETs) with high performance. Since graphene is a zero band gap material with a linear energy-momentum dispersion relation, accordingly graphene FETs show a low ON-OFF current ratio of ~10 and a high OFF state current [4-7]. It is, therefore, required to open a band gap and lower the conductivity in order to achieve semiconducting properties. One way is to pattern the graphene into a narrow ribbon, which confines the carriers to a quasi one-dimension. The energy band gap of graphene nanoribbon (GNR) depends on the width and orientation of the ribbon similarly to what happens with carbon nanotubes and a width of less than 10 nm can offer a sufficient energy bandgap to achieve the operation of a grapheme structure as an FET with a high ON-OFF current ratio [8,9]. In order to fabricate the fine GNR, top down lithography with an electron beam is carried out, and for pattern transfer, XR-1541 (hydrogen silsesquioxane) films, as a negative tone high-resolution electron beam lithography (EBL) resist, are used. Due to a high resistance tendency in the etching process, XR-1541 resists are difficult to remove after reactive ion etching (RIE). Also, XR-1541 films are known that have doping properties accompanying complementary n- and p-type doping when exposed by an electron beam. For these reasons, the existence of resist residues on the surface of graphene causes variations in the gating properties such as the shift of the Dirac point [10]. In this study, GNR is fabricated by EBL with XR-1541/poly methtyl methacrylate (PMMA) bi-layer resists and resist residues on the surface of GNR are successfully removed by way of a combination of the RIE process to cast away remaining PMMA/graphene films and the lift-off process to eliminate the XR-1541 resists. We developed a new process method which can increase the top-gated dielectric properties with the removal of impurities on the

[†] Author to whom all correspondence should be addressed:
E-mail: jsc0515@nnfc.re.kr

Trans. Electr. Electron. Mater. 11(4) 190 (2010): S.-C. Jeon *et al.*
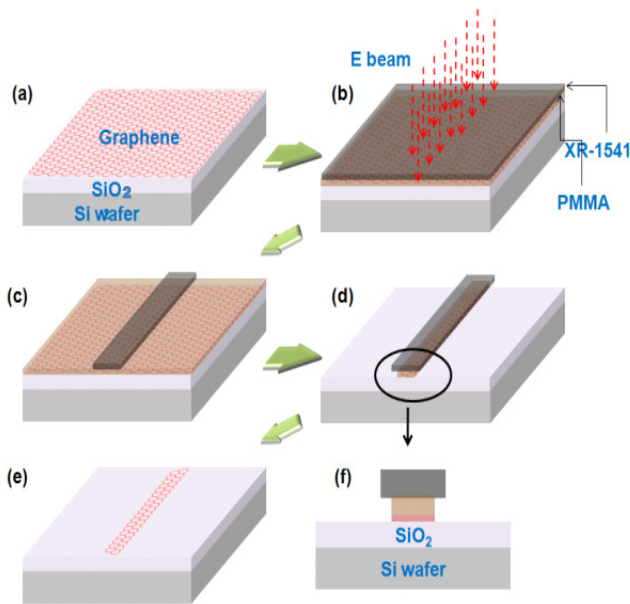
191

Fig. 1. Schematics of fabrication for graphene channel: (a) The transferred graphene films, (b) e beam irradiation on the bi-layer resists, (c) pattern transfer to poly methtyl methacrylate (PMMA) resists with XR-1541 barriers, (d) reactive ion etching (RIE), (e) lift-off process, and (f) cross-sectional view after RIE.

GNR and expect to obtain many benefits in the production of integrated FET devices.

2. EXPERIMENTS

We prepared a silicon wafer with graphene films grown by the chemical vapor deposition method and transferred on SiO_2 films with a thickness of 3,000 Å. The substrate was then spin-coated with PMMA electron beam resists with a thickness of 1,000 Å as a bottom layer and a XR-1541 negative resists of 500 Å thickness as a top layer. Nanoribbon patterns were fabricated by the XR-1541 resist with EBL writing (100 eKV; ELIONIX, ELS7000, Japan), and transferred to the bottom layer of the PMMA after development by the use of DPD-200D (DONG-JIN, Korea) and de-ionized water in a 3:1 ratio for 100 seconds. According to the etching barrier of the XR-1541 resist pattern, subsequent PMMA resists and graphene films are eliminated by the use of RIE (ICP380; Oxford, UK) with oxygen gas. In order to remove XR-1541/PMMA resists on the surface of the graphene channel, the specimen was dipped into dichloromethane, and then the lift-off process was carried out. Atomic force microscopy (AFM) and Raman spectra were measured and analyzed to identify the graphene structures.

3. RESULTS AND DISCUSSION

Figure 1 shows the schematics of fabrication for the graphene channel with EBL, using XR-1541/PMMA bi-layer resists. PMMA is coated on the graphene films, and XR-1541 is coated above in sequence. In terms of the XR-1541 resolution by bi-layer coating, it is proved that PMMA does not affect the contrast and the sensitivity of XR-1541 resists [11]. In a traditional single layer process with XR-1541, the fabrication of GNR for FET structures is not an appropriate process due to the following issues:

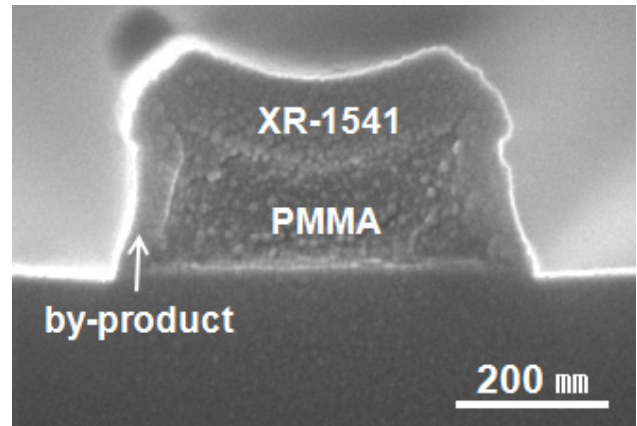1) During RIE by oxygen etchant, both XR-1541 resists and gra-

Fig. 2. Scanning electron microscopy image: poly methtyl methacrylate (PMMA) resists are re-deposited with SiC compounds on both sidewalls.
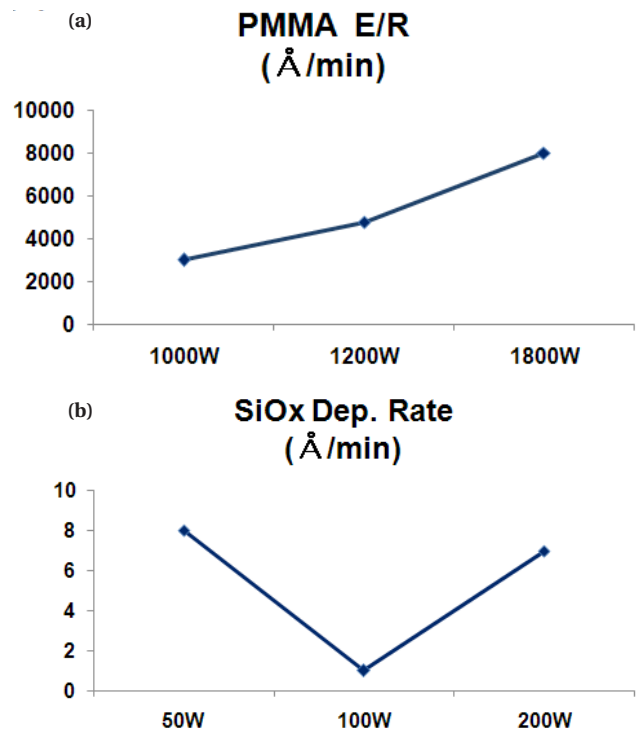

Fig. 3. (a) Poly methtyl methacrylate (PMMA) etching rate comparison with variation of ICP power and (b) SiO_x deposition rate with bios power.

phene films are reacted and removed simultaneously. Moreover, SiO_2 film used as an inter layer dielectric is etched by oxygen also.

2) Since XR-1541 resists contain an oxide group, H_2SO_4/H_2O_2 or HF-based chemicals are recommended for their removal. However, In this case, because graphene structures with carbon covalent bonding are also removed simultaneously by such chemicals, wet etching is not available in this process.

In order to deal with these problems, we tried out a lift-off process with bi-layer resists on the fabrication process of graphene FETs. PMMA, a conventional positive tone resist for the lift-off process and XR-1541 resists for pattern transfer are selected. At an initial attempt on the lift-off process after RIE, the XR-1541 re-
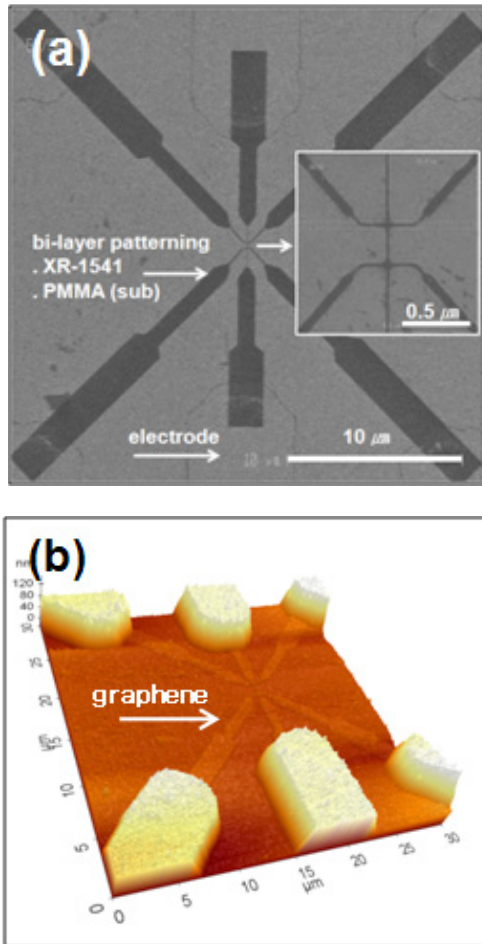
Fig. 4. Scanning electron microscopy image with graphene nano ribbon: (a) e beam lithography with bi-layer resists on the graphene films (Insert is sub 50 nm of graphene nanoribbon), and (b) atomic force microscopy image after formation of metal electrodes and lift-off process.

Fig. 5. Raman spectrum measurement: the two peaks of around 1,600 cm^{-1} and 2,700 cm^{-1} represent the single layer of graphene.

sists were not lifted off well. In order to investigate the improper lift-off phenomenon, a specimen after RIE and the lift-off process is prepared and analyzed by scanning electron microscopy (SEM).

As shown in Fig. 2, the PMMA underneath the XR-1541 is not removed by the reaction with lift-off solvent. With additional etching for complete removal of graphene films after RIE, it is observed that the PMMA has reacted with SiO_2 and re-deposited on the sidewalls of the PMMA. During PMMA/graphene etching, oxygen is used as a plasma gas. At this point, the major chemical component of the PMMA/graphene is carbon. So PMMA/graphene resists are etched by oxygen and by-products as CO_2 gas are vaporized and pumped out. However, in the SiO_x layer which appeared after graphene etching, the inclination of the deposition is a more dominant effect than the etching because SiO_x bonding is easily broken due to the low ion bombardment of oxygen and recombination with Si and oxygen by means of an imperfect chemical reaction. The deposited thickness before-and-after etching is measured by an ellipsometer. The deposited thickness of SiO_x is 7 Å/min. At this rate, SiO_x polymer is re-deposited on the sidewalls of the PMMA, and acts as an obstacle to the regular lift-off process. We optimized the etching parameters related bias and inductively couple plasma (ICP) so as to minimize the re-deposition rate of the SiO_x which was added during
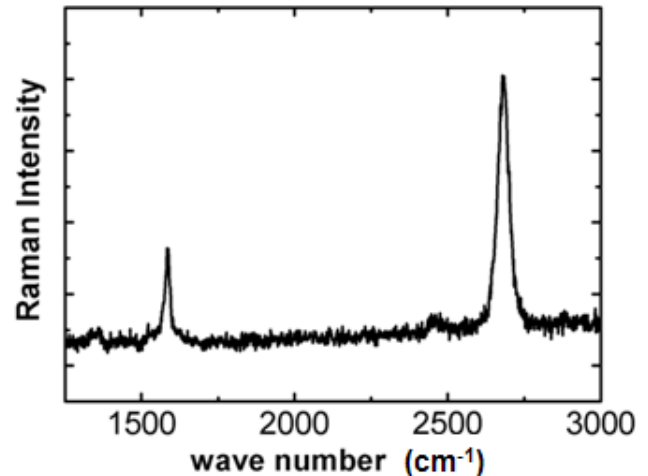
additional over etching. Fluorine etchant gas can prevent the re-deposition of SiO_x. However, at this point, the use of fluorine etchant is not effective on account of the decrease of the etching selectivity of the XR -1541 resists and the increase of the rate of SiO_x loss. ICP Power is set at 1,800 W at the primary stage to minimize the degree of over etching, and then reduced to 1,200 W and 1,000 W in sequence. We fixed the ICP power as 1,000 W, the lowest power at which the plasma is stable at a pressure of 20 mT and measured the oxide deposition rate by changing the bias power from 200 W, 100 W, and to 50 W. The etching rate of the PMMA by ICP top power and SiO_x deposition rate by bios power are shown in Fig. 3.

The measured oxide deposition rates are 7 Å/min at 200 W, 1 Å/min at 100 W, and 8 Å/min at 50 W, respectively. The lowest deposition rate is optimized under the condition of 100 W of ICP power. The final parameter conditions of RIE for PMMA/graphene are a pressure of 20 mT, oxygen flow rate of 30 sccm, 1,000 W of ICP top power, and 100 W of bottom power at 40°C for 60 seconds. The SEM image after the EBL process and the AFM image of the GNR after the lift-off process are shown in Fig. 4.

From Fig. 4(a), one can see that the GNR is oriented on the metal electrodes after applying the mix-and-match technique with EBL and an optical aligner. The resist pattern of XR-1541 performs the role of an etching barrier to plasma RIE. Under optimal RIE conditions, it can be seen that the lift-off process is accomplished and GNR remains well underneath the electrodes as shown in Fig. 4(b).

In order to identify the presence and electronic structure of graphene films, The Raman spectrum [12] is measured as shown in Fig. 5. From the Raman spectrum on the graphene channel obtained after RIE and the lift-off process, the two most intense features of the G and 2D peaks are shown at 1,583 cm^{-1} and 2,678 cm^{-1}, respectively. This suggests that graphene has mono layer characteristics, which is verified by the fact that the ratio of I_{2D}/I_G is approximately 3 and the 2D peak has a symmetric shape. Also because no 2D peak is appeared at about 1,350 cm^{-1} it seems that the quality of graphene has been maintained without damage.

4. CONCLUSIONS

For fabrication of useful graphene electronic devices, further development of the fabrication process as well as synthesis

Trans. Electr. Electron. Mater. 11(4) 190 (2010): S.-C. Jeon *et al*.

193

techniques of high quality graphene are required. As a part of this process of improvement, we used top down lithography by utilizing EBL for the purpose of controlling the graphene band structure. To remove all resist residues which lie on the graphene channel, RIE and lift-off techniques with XR- 1541/PMMA bilayer resists were applied. Through the RIE and bi-layer process, GNRs were successfully finalized and demonstrated to have no damage. From these developments, we expect that the study of graphene- based FETs will become more accelerated.

REFERENCES

[1]   K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature **438**, 197 (2005) [DOI: 10.1038/nature04233].

[2]   Y. Zhang, Y. W. Tan, H. L. Stormer, and P.   Kim, Nature **438**, 201 (2005) [DOI: 10.1038/nature04235].

[3]   F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, Nature Mater. **6**, 652 (2007) [DOI: 10.1038/nmat1967].

[4]   M. C. Lemme, T. J. Echtermeyer, M. Baus, and H. Kurz, IEEE Electron Device Lett. **28**, 282 (2007) [DOI: 10.1109/LED.2007.891668].

[5]   I. Meric, M. Y. Han, A. F. Young, B. Ozyilmaz, P. Kim, and K. L. Shepard, Nature Nanotech. **3**, 654 (2008) [DOI: 10.1038/nnano.2008.268].

[6]   S. Kim, J. Na, I. Jo, D. Shahrjerdi, L. Colombo, Z. Yao, E. Tutuc, and S. K. Banerjee, Appl. Phys. Lett. **94**, 062107 (2009) [DOI: 10.1063/1.3077021].

[7]   F. Xia, D. B. Farmer, Y. M. Lin, and P. Avouris, Nano Lett. **10**, 715 (2010) [DOI: 10.1021/nl9039636].

[8]   M. Y. Han, B. Ozyilmaz, Y. Zhang, and P. Kim, Phys. Rev. Lett. **98**, 206805 (2007) [DOI: 10.1103/PhysRevLett.98.206805].

[9]   X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, Science **319**, 1229 (2008) [DOI: 10.1126/science.1150878].

[10]   K. Brenner and R. Murali, Appl. Phys. Lett. **96**, 063104 (2010) [DOI: 10.1063/1.3308482].

[11]   H. Yang, A. Jin, Q. Luo, J. Li, C. Gu, and Z. Cui, Microelec. Eng. **85**, 814 (2008) [DOI: 10.1016/j.mee.2008.01.006].

[12]   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. Gaim, Phys. Rev. Lett. **97**, 187401 (2006) [DOI: 10.1103/PhysRevLett.97.187401].