원자힘 현미경의 습도 조절에 의한 그래핀 국소 산화

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Humidity dependent size control of local anodic oxidation on graphene using Atomic Force Microscope

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Abstract

We demonstrate nanoscale local anodic oxidation (LAO) patterning on few layer graphene using atomic force microscope (AFM) at room temperature and normal atmosphere. We focus on the humidity dependency in nanoscale oxidation of graphene. The relationship between the oxidation size and the AFM setting values, such as set point, tip speed, and humidity are observed. By changing these values, proper parameters were found to produce features on demand size. This technique provides an easy way to form graphene oxide lithography without any chemical resists. We have obtained oxidation size down to 50-nm with 6-nm-height oxide barrier line with 0.1μ m/s tip scanning speed and micrometer size symbols on a graphene flake. We attribute the bumps to local anodic oxidation on graphene surface and combination of oxygen ions into the graphene lattice.

Recently graphene has received huge spotlight due to its extraordinary electronic behaviors and its transport properties [1-6]. The most commonly used method to fabricate graphene-based devices has been using conventional semiconductor fabrication process, such as e-beam lithography and subsequent photolithography patterning followed by plasma etching. But the chemical resists used in these processes have an effect on graphene pristine electronic properties. To overcome this problem, the alternative lithography techniques, scanning probe microscopy, have shown great potential for patterning with mechanical cutting or oxidation on various materials. Local anodic oxidation (LAO) with conductive AFM tips has been used to fabricate nanoscale structures on metallic or semiconductor surfaces [7-14]. Forthermore LAO lithography on graphene have been tried to fabrication GO in the nanometer-scale [15-17]. LAO lithography can be achieved in the ambient condition without using any chemical resist, PMMA or photoresist, which produces unwanted contamination on material surfaces in conventional lithography [17-19]. From LAO, bumps of graphene oxide (GO) can be generated by covalently functionalized graphene with oxygen functional groups and it has been researched as a applicable modification of graphene lattice for electronic and optoelectronic areas. A cluster of sp2-hybridized carbons forming a GO in graphene can be used to manipulate electronic and optical gaps using relative portion of sp2 in sp3 bonded carbons with various size, shape [15]. By merging with graphene, GO is expected to be a promising candidate material for next generation thin film electronic devices. In this letter we report local anodic oxidation (LAO) with conductive AFM tips on graphene flakes in various humidity. We also report that depending on the ambient conditions bumps of oxidized graphene can be formed on the surface. This result suggests that total amount of oxidation can be decided by water molecules in surrounding atmosphere.

We have experimented local anodic oxidation (LAO) patterning on few layer graphene flakes using Park Systems XE-100 AFM system with vibration isolation system and acoustic enclosure. Homemade humidity controller is used to make an adequate atmosphere. For both imaging and lithography, a conductive platinum tip was used in a non-contact tapping mode. As shown in Fig. 1, negatively biased voltage is applied on the tip and ground is connected to the backside of n-doped silicon substrate. As we apply negative bias to the tip, vapored water molecules in air are condensed between tip and graphene surface to form water meniscus [19]. Decomposed water is react with graphene to form graphene oxide by electric field induced energy. In this way, the electrochemical oxidation in small area can be achieved continuously as tip moves according to CAD design. An electric field (E > 10^7V/m) generated between AFM tip and grounded graphene can decompose

water molecules and dissociated positive hydrogen ions (H+) can be adsorbed on graphene into ions (e.g., H+, OH−, and O^2−). Oxygen containing negatively charged ions (e.g., OH− and O2−) are gathered around the anode and contribute to the formation of oxides on graphene, which acts as a cathode [21].

We have conducted LAO lithography on graphene to engrave a micrometer size alphabet that represents the university−abbreviated name by dot patterning mode as shown in Fig. 6. In this experiment, the AFM tip does not continuously tapping according to the drawing line direction but the tip moves a hole CAD image from left to right end repeatedly until scanning whole image area. And the bias voltage is only applied at which a colored pixel position where the LAO ocurrs on graphene. Even if height of LAO lines are not uniformly produced due to dot patterning direction but oxidized areas are clearly recognized. The evidence of dot pattering mode is the existance of squashed area on graphene along side of LAO area. The height of upper and lower part of alphabet is slightly higher than dotted area.

To summarize, we have demonstrated AFM local anodic oxidation and the size of oxidized graphene can be affected by surrounding atmosphere condition, especially humidity. The bumps are supposed to consist of non-volatile graphene oxide that have larger thickness than graphene layer. And the dependency of humidity in production of graphene oxide refers that reaction of oxygen ions with graphene occurs in between tip and graphene. We have patterned several LAO lines on graphene and the formation of oxide was confirmed with adequate lithography condition.

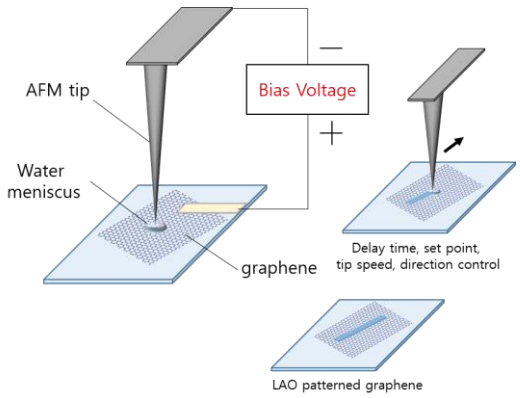

FIG. 1. Schematic diagram of the AFM LAO lithography setup. An external voltage source is used to apply negative bias to the AFM tip and ground the graphene. Naturally assembled water meniscus, which facilitates local anodic oxidation, is formed between AFM tip and graphene. Non−volatile graphene oxide is formed after biased AFM tip moves above the targeted graphene and constantly tapping on designated area.

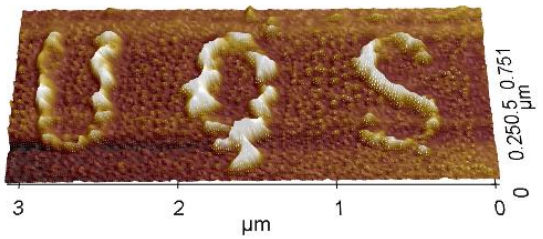

FIG. 2. At −10V biased voltage and 30% humidity, results shows non−continuous oxidation of symbol in micrometer size feature.

REREFENCES

[1] 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).

[2] Y. Zhang, Y.−W. Tan, H. L. Stormer, and P. Kim, Nature 438, 201 (2005).

[3] 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).

[4] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science 312, 1191 (2006).

[5] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, and A. K. Geim, Science 315, 1379 (2007).

[6] A. K. Geim and K. S. Novoselov, Nature Materials 6, 183 (2007).

[7] S. C. Minne, P. Flueckiger, H. T. Soh, and C. F. Quate, Journal of Vacuum Science & Technology B 13, 1380 (1995).

[8] B. Irmer, M. Kehrle, H. Lorenz, and J. P. Kotthaus, Appl. Phys. Lett. 71, 1733 (1997).

[9] S. Myhra, Nanobiotechnol 3, 212 (2007).

[10] R. Garcia, R. V. Martinez, and J. Martinez, Chem. Soc. Rev. 35, 29 (2006).

[11] S. B. A. C. H. A. M.−S. K. A. C. C. C. A. H. Lee, Nanotechnology 16, 2082 (2005).

[12] R. Held, T. Heinzel, P. Studerus, and K. Ensslin, Physica E: Low−Dimensional Systems and Nanostructures 2, 748 (n.d.).

[13] P. Avouris, R. Martel, T. Hertel, and R. Sandstrom, Appl Phys A 66, S659 (1998).

[14] M. Tello and R. Garcı ´a, Appl. Phys. Lett. 79, 424 (2001).

[15] S. Masubuchi, M. Arai, and T. Machida, Nano Lett. 11, 4542 (2011).

[16] S. Masubuchi, M. Ono, K. Yoshida, K. Hirakawa, and T. Machida, Appl. Phys. Lett. 94, 082107 (2009).

[17] L. Weng, L. Zhang, Y. P. Chen, Rokhinson, L. P., Appl. Phys. Lett. 93, (2008).

[18] K. Kumar, O. Sul, S. Strauf, D. S. Choi, F. Fisher, M. G. Prasad, and E. Yang, Nanotechnology, IEEE Transactions on 10, 849 (2011).

[19] I.−S. Byun, D. Yoon, J. S. Choi, I. Hwang, D. H. Lee, M. J. Lee, T. Kawai, Y.−W. Son, Q. Jia, and H. Cheong, ACS Nano 5, 6417 (2011).

[20] 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, (2006).

[21] J. Č ervenka, R. Kalousek, M. Bartoš ík, D. Š koda, O. Tomanec, and T. Š ikola, Applied Surface Science 253, 2373 (2006).