Research Paper

Surface and Electrical Characterization of Electrochemically Oxidized Graphene

Young-Jun Yu*

Department of Physics, Chungnam National University, Daejeon 34134, Republic of Korea

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Abstract

After the oxidation process of graphene was shown to lead to zero conductance ($\sim 0 \mu\text{S}$) based on the electrochemistry, the natural reduction in the graphene oxide behavior resulting in a recovery of the conductance ($\sim 200 \mu\text{S}$) was observed under exposure to ambient conditions during a 24 h period. Furthermore, damage to the graphene oxide surface during the repeated atomic force microscopy scanning process owing to the weakening of the van der Waals force between the oxidized graphene and SiO_2 substrate was characterized. These results provide significant information regarding the remaining time of electrochemical oxidation and the mechanical properties of graphene.

Keywords: Graphene, Reduction, Oxidation, Graphene oxide, Electrochemistry

I. Introduction

An electrochemical redox of carbon networks leads to a tuning conductivity from the disruption of an sp^2 carbon network when sp^3 -conjugated carbon is applied in a nanometer-sized point detector, and the source of oxidation in the carbon network is elucidated as a defect in the carbon bonding [1-14]. The oxidation of graphene, which has a two-dimensional carbon bonding structure, is also a significant subject for various applications such as sensors and dielectric layers [1-14]. Although graphene oxide (GO) can be obtained through various avenues, electrochemistry processes using an electrolyte are promising for the fabrication of GO [1,9]. In particular, when employing a negative to positive electrolyte gating voltage potential, we can realize the oxidation and reduction of graphene [1,8,9]. Although many studies have been conducted on the electrical properties in the redox of graphene through electrochemistry [1-14], the electrical and surface characterization of fully oxidized graphene is still required.

In this study, the natural reduction process of graphene oxidized using an electrolyte was considered. In particular, it was observed that the naturally reduced behavior of graphene oxide leads to a recovery of the conductance under exposure to ambient conditions during

a 24 h period. Furthermore, the damage to the graphene oxide surface when applying an atomic force microscopy (AFM) scanning process was investigated.

II. Experimental details

The graphene field-effect transistor (FET) applied in this study was prepared using mechanically exfoliated graphene on a 280-nm-thick SiO_2 substrate [see Fig. 1(a)] [8,9,15,16]. Upon employing e-beam lithography, Cr/Au (5/50 nm thickness) metal electrodes were placed in contact with the graphene/ SiO_2 [see Fig. 1(b)]. To avoid a chemical reaction between the Cr/Au metal electrodes and sulfuric acid (H_2SO_4 , 1 M) electrolyte during the electrochemistry process, a poly methyl methacrylate (PMMA) passivation layer was utilized on a graphene FET. After coating of the PMMA, a window for viewing only the electrochemistry reaction between graphene and electrolyte in the graphene channel area was fabricated using e-beam lithography [see Figs. 1(c) and 1(d)].

Figure 2(a) shows a schematic diagram of the conductance variation of the PMMA window on a graphene FET under application of either an electrolyte (V_{EG}) or a back-gate voltage (V_{BG}). Here, a measurement of the conductance variation was utilized using standard lock-in techniques. The initially hole-doped condition of the graphene was observed based on the accumulated

*Corresponding author
E-mail: yjyu@cnu.ac.kr

Figure 1. (Color online) Schematic diagram of (a) mechanically exfoliated graphene on SiO₂/Si substrate, (b) metal in contact with graphene, (c) fabrication of PMMA window on graphene FET for electrochemistry study, and (d) optical image of graphene FET under PMMA window.

Figure 2. (Color online) (a) Schematic diagram of conductance measurement of graphene FET under PMMA window by applying either a back gate (V_{BG}) or an electrolyte gate (V_{EG}). Conductance variation as a function of (b) V_{BG} and (c) V_{EG} .

carrier density $n = (C_{BG}/e) \cdot V_{CNP-BG} \approx 1 \times 10^{12} \text{ cm}^{-2}$, where $C_{BG} = 12 \text{ nF/cm}^2$, e , and $V_{CNP-BG} = 14.30 \text{ V}$ are the capacitance for 280-nm-thick SiO₂ [9], the electron charge, and charge-neutral position for applying V_{BG} in Fig. 2(b), respectively. By contrast, the electrolyte gating (V_{EG}) on the same graphene FET allows the charge-neutral position $V_{CNP-EG} = 0.48 \text{ V}$ in Fig. 2(c). Because the initially accumulated charge carrier density in Fig. 2(b) is commensurate with that in Fig. 2(c) as $n = (C_{BG}/e) \cdot V_{CNP-BG} = (C_{EG}/e) \cdot V_{CNP-EG}$, the capacitance (C_{EG}) of a H₂SO₄ (1 M) electrolyte can be assumed as $C_{EG} = 357 \text{ nF/cm}^2$, which is comparable to a previous report [9].

To inspect the surface properties of graphene, AFM, and electric force microscopy (EFM) measurements were

Figure 3. (Color online) Conductance variation (red line) of graphene as a function of time when applying V_{EG} (black line). Here, (A) and (B) indicate the initial and oxidized conditions.

employed using a commercial AFM system (XE-100, Park Systems Co.), as described in Figs. 4 and 5. The topography measurement applied a noncontact mode by oscillating a cantilever at $\sim 170 \text{ kHz}$. The EFM measurement was utilized by applying an AC voltage of 0.5 V, an amplitude of 17 kHz, and a DC voltage of 1.0 V to the conductive probe [15,16].

III. Results and discussion

Based on the electrolyte gating, the conductance of the graphene FET was modulated, as shown in Fig. 3. By applying $V_{EG} = 0.0$ to -1.0 V , the conductance of the graphene FET was tuned from 450 to 0 μS. This behavior has been reported as the formation of an sp^3 (C-O or C=O) bond on the graphene surface through a chemical reaction with the H₂SO₄ electrolyte [1-14]. The oxidation of graphene was exactly started under $V_{EG} = -1.0 \text{ V}$ (marked by blue dashed line) and during applying the electrolyte gating in Fig. 3, the V_{EG} was also tuned from -1.0 to 0.23 V (marked by blue arrow in Fig. 3) for guaranteeing that the conductance variation of graphene depends on V_{EG} , exactly. As a result, the sp^3 bonds block the carrier transport on the graphene channel, leading to zero conductance, and this suppressed conductance (0 μS) of the graphene FET cannot be recovered by applying $V_{EG} = +0.75 \text{ V}$ (see Fig. 3). This indicates that the graphene channel surface is dominantly oxidized, nearly leading to a degradation of the conductance. Note that, although there was no variation of conductance for applying $V_{EG} = +0.75 \text{ V}$ during 15 s, the time enough to release sp^3 leads to reduction behavior as shown in Fig. 5.

Figure 4. (Color online) Topography images of graphene under (a) initial (A) and (b) oxidized (B) conditions of graphene shown in Fig. 3. EFM images of graphene under (c) initial (A) and (d) oxidized (B) conditions of graphene shown in Fig. 3.

Figure 5. (Color online) (a) Conductance as a function of DC-bias voltage (V_{DS}) for graphene FET after 24 h from condition B shown in Fig. 3. Here, the black and red lines are I - V_{DS} curves measured after the (b) first, (c) second and (d) third, (e) fourth AFM scanning processes, respectively. (b) First and (c) second scanned topography images of graphene channel after 24 h from condition B shown in Fig. 3. (d) Third and (e) fourth scanned topography images of graphene channel leading to an electric characterization of red I - V_{DS} curve in (a). Here, the arrows in (d) and (e) indicate the damage to the graphene surface during the AFM scanning process.

Figure 4 shows the AFM and EFM images for the opened graphene channel area using the PMMA window before (A) and after (B) oxidation, as indicated in Fig. 3. Before oxidation (A) in Fig. 3, a clean topography of the graphene surface was exhibited, as shown in Fig. 4(a). However, a defective topography of the graphene surface after oxidation was observed, as indicated in Fig. 4(b). This means that applying an electrolyte gate of $V_{EG} = -1.0$ V leads to the oxidation of most of the graphene surface with the formation of undesired defects. Furthermore, the electrical condition of the graphene surface before and after oxidation is as shown in Figs. 4(c) and 4(d). The EFM images of the

graphene surface in (A) and (B) of Fig. 3 show a distribution with a potential of $V_{EFM} = \sim 5$ and ~ 1.2 V, as indicated in Figs. 4(c) and 4(d), respectively. This shows that the dominant sp^3 bonds on the graphene surface suppress the conductance.

By contrast, as revealed in Fig. 5(a), a slight recovery in the conductance (black I - V_{DS} curve of ~ 200 μ S) of the graphene FET occurs owing to a reduction of the weak sp^3 bonds on the graphene oxide exposed to ambient conditions for a 24 h period. Here, the I - V_{DS} curve, shown in Fig. 5, was measured by applying a DC-bias voltage between two-terminal metal contacts. For the first and second scanned topographic images taken after the 24 h period, as shown in Figs. 5(b) and 5(c), respectively, although topographical defects compatible with those shown in the AFM image before the 24 h period (Fig. 4 (b)) remain, a recovery in the conductance from 0 to 200 μ S can be seen as shown in Fig. 5(a). However, during the continuous AFM measurements for the third and fourth scanning processes, the conductance of the graphene FET is degraded again to zero (red I - V_{DS} curve), as shown in Fig. 5(a). As previously reported [17,18], this indicates that a van der Waals force in GO/SiO₂ weaker than that in the graphene/SiO₂ allows the GO surface to be easily damaged (marked with arrows) by the AFM tip, as indicated in Figs. 5(d) and 5(e). Although the noncontact mode of the AFM system applied in this study was utilized for measuring the topography, the damaging behaviors (marked with arrows) shown in Figs. 5(d) and 5(e) lead to a failure (red I - V_{DS} curve) of the graphene FET, as indicated in Fig. 5(a). Note that, because of wearing residues out on PMMA mask during AFM scanning, the topography shows a little noisy and the scale bar is difference for each topography images. However, the exactly damaged area between first, second and third, fourth scanned topography images are exhibited as marked with arrows in Figs. 5 (d) and 5(e). Thus, we should employ a fine-tuned atomic force between the AFM tip and GO surface to avoid damage to the GO during the scanning process.

IV. Conclusions

In this study, the oxidation of graphene was achieved using electrochemistry. Furthermore, evidence of the reduction behavior exhibiting a recovery in conductance from oxidized graphene with zero conductance was

observed. Because this result can be investigated only under exposure to ambient conditions, it indicates that the weak sp^3 bonds can be reduced again to an sp^2 bonding condition. Thus, this result allows us to provide significant information indicating that electrochemical oxidation on the graphene surface is not permanent and that the GO surface can be damaged using an AFM tip.

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