

Non-thermal Reversibility by Ultraviolet Irradiation of Electron Mobility in Oxidized Graphene

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Introduction

The Hummers method is widely used for oxidation of graphene, despite resulting in a surface with structural defects that degrades its characteristics, compromising its usability in high-performance devices. An alternative approach for oxidizing graphene using reactive atomic oxygen produced from oxygen molecules decomposed by a 1500°C tungsten filament in an ultrahigh vacuum (UHV) to form graphene oxide (GO) with thermal reversibility at 260°C has recently been reported.¹ However, performing annealing treatment in UHV makes this method costly.

Here, we presented a simpler and more cost-effective way to oxidize graphene layer through UV (ultraviolet)/O₃ (ozone) treatment and reduce the resulting GO through UV irradiation. Both oxidation and reduction were performed at ambient temperature in atmospheric pressure. The existence of chemical bonds between oxygen and graphene was confirmed from the XPS (X-ray photoelectron spectroscopy) spectra and directly observed by STM (scanning tunneling microscopy) topography. Moreover, changes in electrical properties of a single layer graphene-based field-effect transistor (G-FET) were also investigated. In previous works, we examined the thermal reversibility in electrical properties of a two-layer G-FET after being oxidized through UV/O₃ treatment.² A decrease in conductivity and carrier mobility was observed after oxidation, but the electrical properties recovered after subsequent H₂/Ar annealing, indicating that the oxidation with UV/O₃ treatment was thermally reversible. However, in current study we focused on the feasibility of non-thermal reduction of GO by UV irradiation which is more cost-effective than annealing in UHV.

Experimental and Results

A single layer graphene film grown on thin copper sheet (1 x 1 cm) through chemical vapor deposition method (CVD-graphene) was UV/O₃ treated for 6 min. In this treatment, oxygen gasses were channeled into a chamber, where CVD-graphene was placed inside, at a flow rate of 0.5 L/min and then ozonized using an ozone generator while simultaneously two types of ultraviolet light with wavelengths of 184.9 and 253.7 nm were produced from a low pressure mercury lamp to continuously generate reactive oxygen radicals. The STM topography of the pristine CVD-graphene and after being oxidized through UV/O₃ treatment for 6 min are shown in Fig. 1 and 2, respectively. The height difference in pristine CVD-graphene was 0.1 nm and that in GO was 1 nm, 10 times greater, indicating the presence of chemically doped oxygen atoms on the graphene layer. The GO then was irradiated by UV light several times. Each UV irradiation was performed for 6 min using the same UV light used in UV/O₃ treatment. XPS measurement was conducted to examine the concentration of doped oxygen which was calculated from the XPS peak area ratio of C–O (286.4 eV) and C–C (284.8 eV). The change in concentration of doped oxygen after each UV irradiation is shown in Fig. 3. The concentration of oxygen increased after oxidation and then decreased after UV irradiation with no C=O peak (288.9 eV) observed, indicating that the GO was reduced without introducing lattice defects.

The structure of single layer G-FET fabricated from exfoliated KISH graphite is shown in Fig. 4. The transfer characteristics of the G-FET after first and second circle of oxidation and reduction processes are plotted in Fig. 5 and 6, respectively, where the ambipolar curve of graphene can be examined. The oxidation was performed through UV/O₃ treatment for 3 min and reduction was performed through UV irradiation for 3 min. Electrical characterization of G-FET was carried out under a vacuum condition of 4.6×10^{-5} Pa using a nano-probing microscopy (Hitachi NE4000). The slope of ambipolar curve decreased after oxidation during the first redox process (Fig. 5), indicating the decreased electron mobility in graphene layer caused by the increased scattering due to the doped oxygen which obstructed the path of electron. However, a significant recovery of the ambipolar curve slope was observed after conducting UV irradiation, indicating that the GO was reduced and the electron mobility recovered. Since further recovery in the electron mobility was not observed after subsequent UV irradiation, then the second circle of redox process was undertaken. The change in behavior of ambipolar curve and electron mobility of G-FET after the second redox process (Fig. 6) was identical to the first redox process. The ambipolar curve significantly recovered to the state before oxidation after conducting UV irradiation three times. Therefore, after examining all these results, GO synthesized through UV/O₃ treatment may be reduced non-thermally by UV irradiation, which is simpler and more cost-effective than annealing in UHV, without introducing significant lattice defects.

References

- [1] Md. Zakir Hossain, et al., Nature Chemistry, **4** (2012) 305–309.
 [2] Yana Mulyana, et al., Applied Physics Letters, **103** (2013) 063107.

Figures

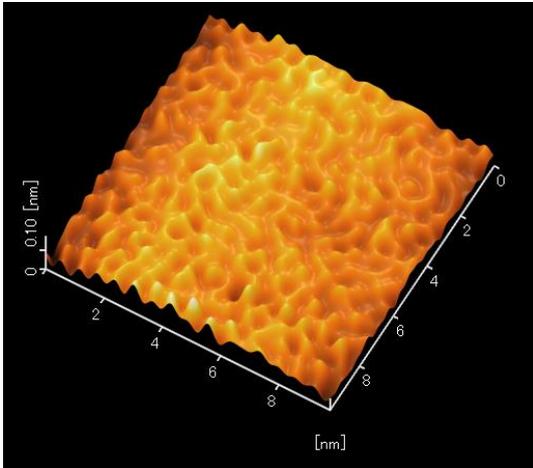


Fig. 1 STM topography of pristine CVD-graphene (height difference: 0.1 nm)

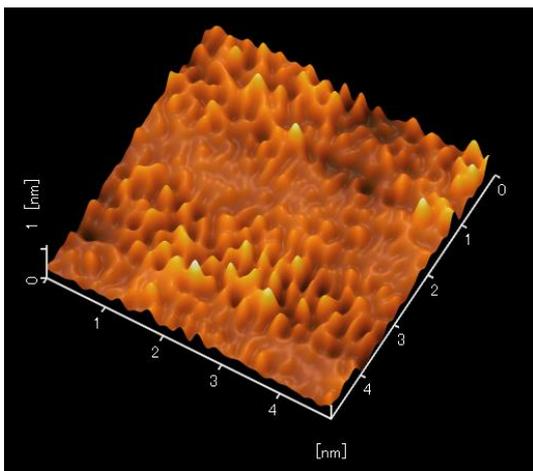


Fig. 2 STM topography of oxidized CVD-graphene by UV/O₃ treatment (height difference: 1 nm)

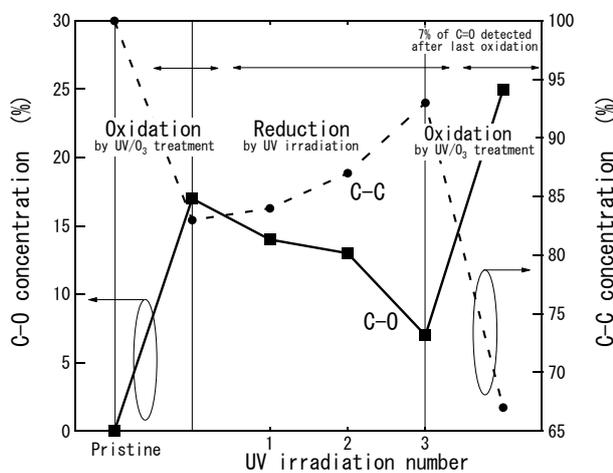


Fig. 3 Quantity of doped oxygen on CVD-graphene after UV/O₃ treatment and UV irradiation

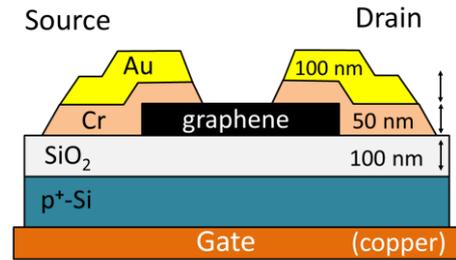


Fig. 4 Structure of fabricated graphene-FET

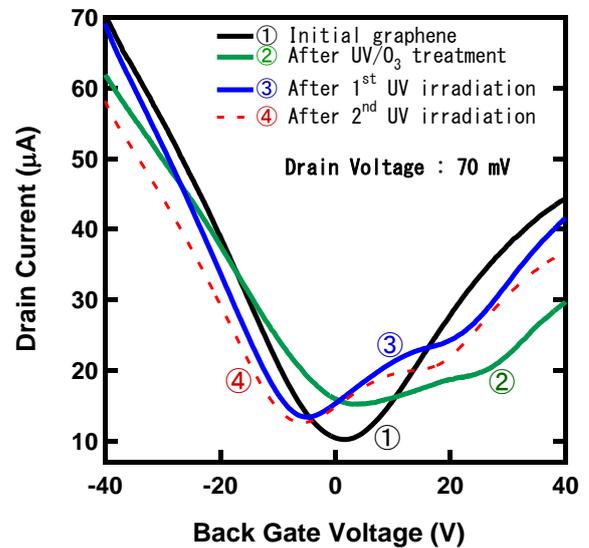


Fig. 5 Graphene-FET's transfer characteristics after first circle of redox process

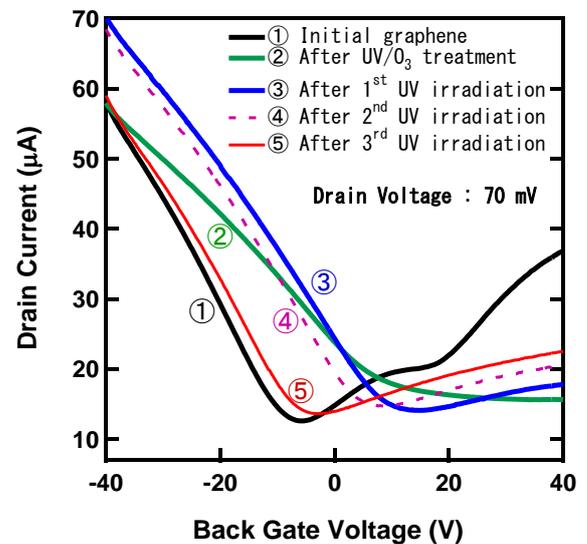


Fig. 6 Graphene-FET's transfer characteristics after second circle of redox process