

Chemically Homogeneous and Thermally Reversible Oxidation of Epitaxial Graphene: A Step Towards Better Performance Graphene-Based Electronics

Graphene, a one-atom thick, honeycomb-shaped lattice of carbon atoms with exceptional physical and electronic properties, is promising for next-generation electronics applications. Many researchers and engineers consider that graphene could be a rival to silicon in creating faster, thinner and flexible electronic devices. However, a major challenge in realizing graphene-based electronics is to make the electronic properties of graphene tunable. Unlike semiconductors such as silicon, pure graphene is a zero band-gap material, making it difficult to electrically "turn-off" the flow of current through it. Therefore, pristine graphene is not suitable for the digital circuitry that comprises the vast majority of integrated circuits.

In an attempt to control its properties and make graphene more functional, many researchers have been investigating methods for chemically altering graphene. The most widely used strategy is "Hummer's method" which oxidizes graphene [1]. However, the chemical inhomogeneity and irreversibility of the resulting graphene oxide surface arise because of the use of aggressive oxidizing agents [2, 3]. Collaborative work between US and Japanese researchers of different institutes including Northwestern University, Gunma University, The University of Tokyo, and RIKEN has recently led to the development of a new method to oxidize graphene that overcomes the collateral damage encountered in Hummer's method.

Chemical modification of graphene is very difficult because of the bonding nature of the carbon atoms forming hexagonal networks. Typically, researchers employ strong acidic conditions, such as those used in Hummer's method [1], but these damage the honeycomb-shaped lattice and result in a material that is difficult to control. Here, we present an alternative approach for oxidizing epitaxial graphene using atomic oxygen in ultrahigh vacuum. In our method, we introduced oxygen gas (O_2) into an ultra-high vacuum chamber, which housed a hot tungsten filament ($\sim 1500^\circ\text{C}$) that caused the oxygen molecules to dissociate into atomic oxygen.

The highly reactive oxygen atoms then uniformly bonded to the graphene lattice.

The graphene oxide thus formed in ultra-high vacuum is chemically homogeneous and thermally reversible, which can lead to well-controlled properties and can be exploited in high-performance electronics. The chemical homogeneity and reversibility of the oxidized graphene were characterized by various surface probe techniques including scanning tunneling microscopy (STM) and high-resolution X-ray photoelectron spectroscopy (HR-XPS) [4]. HR-XPS measurements were performed using a Scienta SES-200 at the Photon Factory BL-13A (KEK-PF PAC 2009S2 007), Japan. The incident and emission angles with respect to the surface normal for the photon and photoelectron beams were 65° and 0° , respectively. The total energy resolution was ~ 70 meV.

Typical STM images of pristine and oxidized graphene on the SiC(0001) substrate are shown in Fig. 1. Careful inspection reveals that each oxygen feature has a uniform appearance in STM images, which suggests a chemically uniform binding state for atomic oxygen on epitaxial graphene. Chemical homogeneity is further confirmed by HR-XPS. Although the chemisorbed oxygen is stable at room temperature, it can be reversibly removed by annealing the oxidized surface at 260°C .

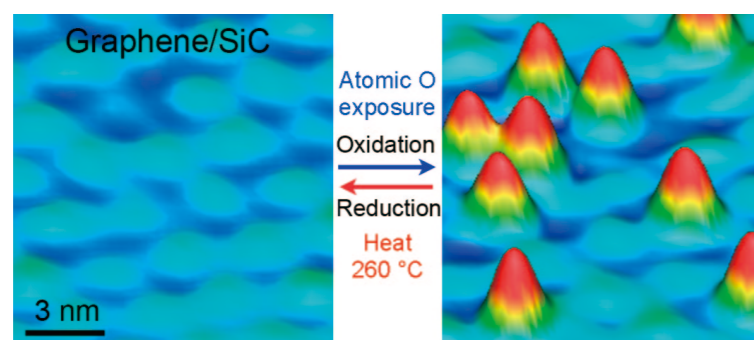


Figure 1 Scanning tunneling microscope (STM) images of before (left) and after (right) oxidation of graphene on a silicon carbide (SiC) substrate. Pyramidal-shaped protrusions in the right image are the individual oxygen atoms bonded to the graphene lattice. STM images were acquired at a sample bias of +2.4 V and a tunneling current of 50 pA.

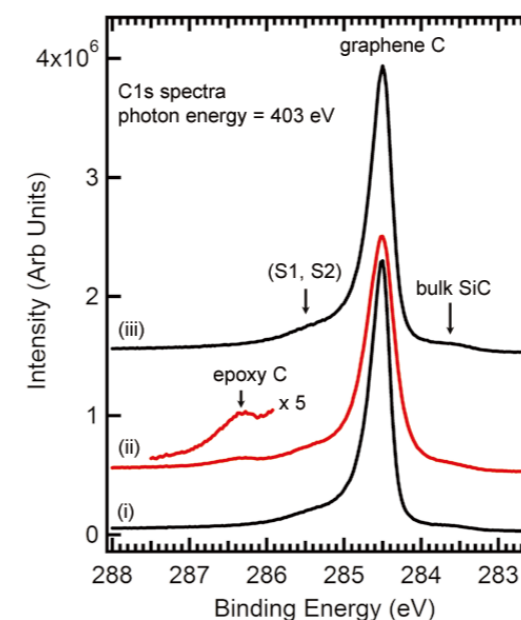


Figure 2. C1s X-ray photoelectron spectra measured at KEK-PF BL13A (PF-PAC: 2009S2 007). (i) Pristine epitaxial graphene on an SiC substrate. (ii) Oxidized graphene using atomic oxygen in UHV (red). (iii) The clean graphene was recovered after heating at 260°C . S1 and S2 peaks are ascribed to the buffer layer C atoms. $h\nu = 403$ eV.

Figure 2 shows a series of C 1s XPS spectra of (i) pristine graphene on an SiC substrate, (ii) graphene oxidized by atomic oxygen in UHV and (iii) annealed graphene at 260°C . In the HR-XPS spectrum of Fig. 2(ii), the C1s peak at 286.3 eV, which is located at 1.8 eV higher binding energy than the sp^2 C1s peak of graphene, is ascribed to the epoxy species on the epitaxial graphene surface [5]. Note that S1 is ascribed to the carbon atoms in the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ structure bound

to one Si atom of the SiC(0001) surface and to three C atoms in the sp^2 -bonded layer, and S2 is the component emitted from the remaining sp^2 -bonded carbon atoms in the buffer layer. After annealing at 260°C , the C1s peak corresponding to the epoxy species completely disappears, and the spectrum of pristine epitaxial graphene is reestablished [Fig. 2 (iii)].

These results clearly indicate that the original pristine epitaxial graphene surface can be recovered by thermal reduction of the oxidized surface; the UHV oxidation–reduction process is fully reversible, in stark contrast to the highly defective and partially oxidized surface that results from the reduction of Hummer's method graphene oxide. We think that this is an important step towards realizing new classes of two-dimensional nanomaterials by chemical modification of graphene.

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