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Effects of 1 MeV Electron Beam Irradiation on Multilayer Graphene Grown on 6H-SiC(0001)

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Graphene layers grown on 6H-SiC(0001) were irradiated with 1 MeV electron beam to functionalize its surface. A surface analysis using atomic force microscopy, the near edge X-ray adsorption fine structure spectra of C K-edge, and photoemission spectroscopy suggests that the electron beam irradiation in ambient condition can induce oxidation of the graphene layer.

Since Geim and his co-workers¹ extracted individual ultrathin sheets of carbon atoms (graphene) using graphite crystals, graphene has been attracting much interest because of its scientific and technological importance.^{2,3} It has been suggested that, by controlling the carrier density using metal or molecules in the graphene layer, it may be possible to manipulate the occupation of electron states near Fermi level and the magnitude of the gap between the valence band and the conduction band.⁴ In addition, to functionalize their surfaces using a direct chemical grafting process⁵ is also an important means to further expand their potential.

However, the graphene surface is electronically so stable that molecules such as NH₃ and pyridine are difficult to chemisorb on the graphene surface at room temperature. So, we introduced an electron beam intentionally to modify the surface structure of graphene. Previous studies, have shown carbon nanostructures to be quite sensitive to particle irradiation, leading to the formation of unexpected and exciting structures.^{6–9} Although the existence of artifacts associated with electron beams in the analysis of carbon materials has been known, detailed investigation of these phenomena is still lacking. In this paper, we introduce an electron beam to functionalize the graphene surface. Changes in the basic properties of graphene layers on 6H-SiC(0001) are investigated by using AFM, PES, and NEXAFS after 1 MeV electron beam irradiation.

The nitrogen-doped ($N_D \sim 9 \times 10^{17} \text{ cm}^{-3}$) Si-terminated 6H-SiC(0001) sample was purchased from Cree Research (U.S.A.). The annealing temperature was monitored with an infrared pyrometer by assuming an emissivity of 0.90. After sample outgassing to 900 °C, we annealed it around 900 °C under a Si flux (1 Å/min). After annealing at 1150 °C, a carbon

rich ($6\sqrt{3} \times 6\sqrt{3}$)R30° electron diffraction pattern appeared. A well reconstructed 1×1 surface with a 12 Å thick graphene layer was found after further annealing at 1400 °C.¹⁰ This is almost equivalent to 4-layered graphene, which will hereafter be referred to as multilayer graphene. The graphene/SiC was irradiated with a 1 MeV electron beam (e-beam) at room temperature in ambient conditions. By using the electron beam accelerator at Korea Atomic Energy Research Institutes (KAERI)¹¹ for the 1 MeV e-beam irradiation, the graphene layer was irradiated with a total fluence of 0, 50, and 100 kGy at room temperature in ambient conditions. E-beam was irradiated on the sample with the normal incidence angle. Because the e-beam dosage is related to the energy, time, and the electron beam flux, we changed the expose time to control the e-beam dosage, and we calibrated the dosage based on the measured value using a dosimeter (B3WINdows, GEX, U.S.A.).

The effects of irradiation on the graphene/SiC was investigated using AFM, NEXAFS, and PES. Before and after e-beam irradiation, C 1s, O 1s, and Si 2p core level spectra were measured using the photon energy of 635 eV with a total resolution of 250 meV at 8A2 HR-PES beamline in the Pohang accelerator laboratory (PAL). The binding energy and the spectral resolution of C 1s, O 1s, and Si 2p were calibrated by measuring the Au 4f_{7/2} core level and the Au Fermi edge. The NEXAFS spectra were measured at 2B1 PES beamline in the partial electron yield (PEY) detection mode with a retarding voltage of –210 V and an accelerating voltage of 1.6 kV.¹² Molecular bonding information for the top few layers of the multilayer films was obtained from the PEY mode NEXAFS spectra by considering probing depths of less than 10 Å.¹³ The photons had a degree of polarization of about 85%, with an incident photon energy resolution of 350 meV near the carbon K-edge region.

The energetic e-beam irradiation in ambient condition can modify not only the surface geometrical structure but also the surface chemical structure.¹⁴ Figure 1 shows a series of AFM

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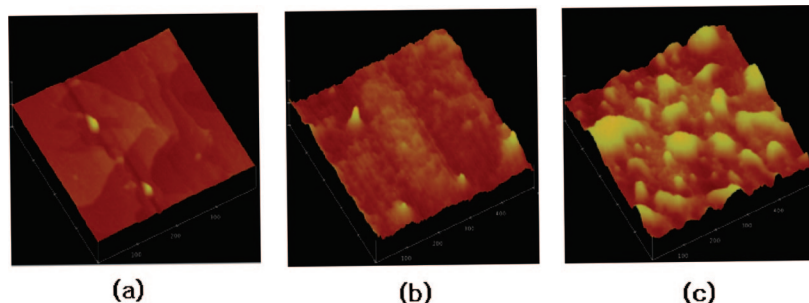


Figure 1. AFM image of a multilayer graphene upon 1 MeV electron beam irradiation with a flux of 0 (a), 50 (b), and 100 kGy (c), 500 nm \times 500 nm. Layered structure was broken after e-beam irradiation.

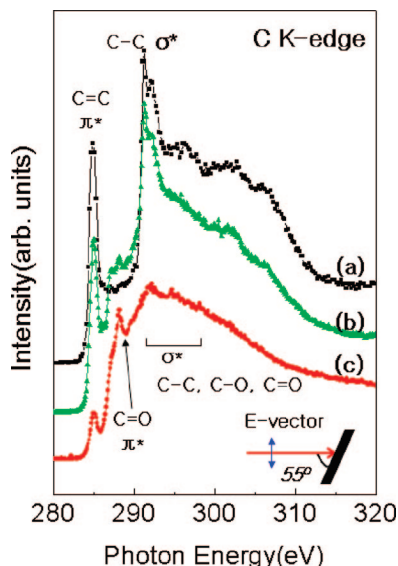


Figure 2. NEXAFS C K-edge spectra of (a) 0, (b) 50, and (c) 100 kGy measured at the magic angle (55°). C=C π^* was decreased and oxygen related bonds were increased after 1 MeV electron beam irradiation on a multilayer graphene.

image before and after e-beam irradiation on the multilayer graphene. Here, changes in the surface morphology are seen clearly.

The layered structure before e-beam irradiation can be seen in Figure 1a. After the 50 kGy e-beam irradiation (Figure 1b), the layered structure was destroyed, many small flakes were formed, and a hillock appeared. As the e-beam dose increased to 100 kGy (Figure 1c), the number of hillocks increased and the height was enhanced. Furthermore, the surface roughness increased as the electron beam irradiation proceeded. The root-mean-square (rms) roughness was 3.7, 7.9, and 25.6 Å after e-beam irradiation of 0, 50, and 100 kGy, respectively.

We introduced NEXAFS and PES to clarify the nature of the changes in the chemical structure during and after the e-beam irradiation. Figure 2 shows a set of C K-edge NEXAFS spectra. The spectra were measured at 55° . It is known that NEXAFS spectra do not depend on the molecular orientation at the magic angle. Before e-beam irradiation, C=C π^* (285 eV) and C-C σ^* (291.3 and 292.1 eV) were shown. After 50 kGy e-beam irradiation, C=C π^* decreased and the new features at 287 and 288.2 eV appeared. This change is attributed to hydrogenated carbon and C=O π^* states.¹⁵ The C=C π^* decreased almost 21%. As the beam fluencies were increased to 100 kGy, 80% of C=C π^* was decreased and the C=O and C-O related bonding states were enhanced. At the same time, C-C, C-O, and C=O located between 291 and 296 eV were also increased. These results indicate that e-beam irradiation induces oxidation by breaking the C=C π^* bond.

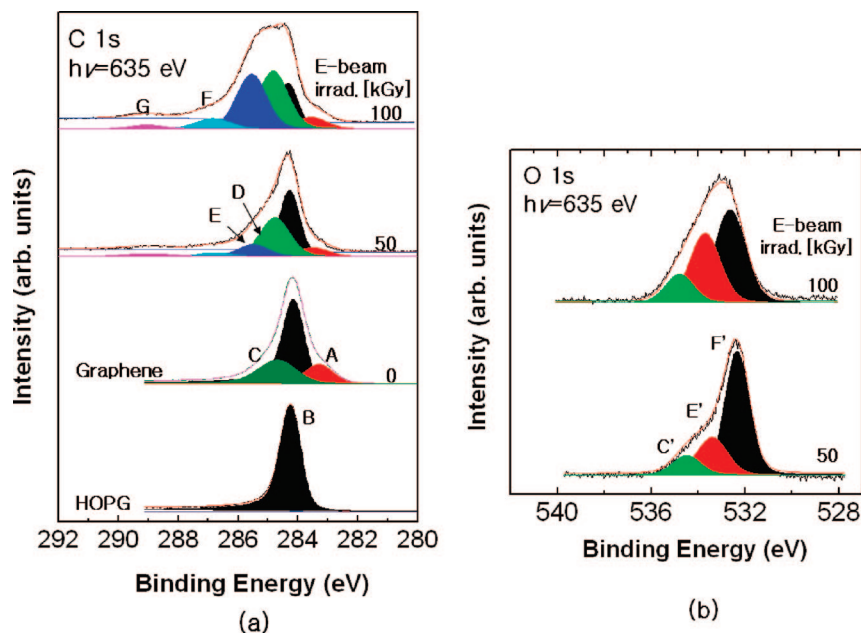


Figure 3. PES spectra. (a) C 1s core-level spectra recorded from HOPG and graphene before and after e-beam irradiation. (b) O 1s core-level spectra from graphene layer after 50 and 100 kGy e-beam irradiation.

PES spectra explained more detailed chemical structures. Figure 3 show a set of C 1s(a) and O 1s(b) spectra. For qualitative analysis, each spectrum was normalized to the highest intensity, decomposed the spectra using a fitting procedure. There is no oxygen related component in the multilayer graphene before electron beam irradiation.¹⁶ After 50 kGy e-beam irradiation, oxygen related components appeared and a high energy shoulder was increased depending on the dosing. C 1s also increased the high energy components. In the Si 2p (not shown here) spectra, the small high energy shoulders originated from Si oxycarbide were enhanced, but they show negligible e-beam irradiation dependencies. This means that the oxidation process induced by e-beam occurs only on the surface range.

In Figure 3a, four kinds of C 1s core levels are shown. The bottommost one is taken from the highly oriented pyrolytic graphite(HOPG). We can see that a single peak B originated from six-membered hexagonal rings with carbon atoms(C—C=C) at the binding energy of 284.2 eV. On the multilayer graphene (the second spectrum), there are three components, one is B and two peaks, A and C, come from the interface states. After 50 kGy e-beam irradiation, the spectrum was deconvoluted into four new components corresponding to carbon atoms in different oxygen-containing functional groups: the epoxide carbon, where a single oxygen atom bonded to two adjacent carbon atoms at 284.8 eV, the pyridine-like carbon E in C—O—C at 285.6 eV, the carbonyl carbon F(C=O) at 286.8 eV and the carboxylate carbon G(O—C=O) at 289 eV. Also the O 1s spectra in Figure 3b shows three oxygen components related with the carboxylate oxygen at 532.63 eV (G') and 533.65 eV (E') and the epoxy bridged oxygen 534.83 eV (D'). These components match well with carbon features.

He et al.¹⁷ have reported that the graphite oxide forms a complex structure during oxidation and contains two kinds of regions: the aromatic region with unoxidized benzene rings and the region with aliphatic six-membered rings using solid-state ¹³C NMR spectra of graphite oxide. Je-Luen et al.¹⁸ have also shown the details of how oxygen attacks carbon bonds to break up the atomic structure of graphite based on the density functional theory. It has been shown that the epoxy bridges are energetically favored and they tend to line on the graphite surfaces. As a result, they induced tension in the underlying lattice to break the carbon bonds. Our results agreed well with the previously reported results. The AFM result in Figure 1 shows that the graphene layer was broken to small graphene flakes after 50 kGy e-beam irradiation. And, as continuing the e-beam irradiation, the surface roughness increased and some hillocks were enhanced. In addition, NEXAFS results in Figure 2 and PES results in Figure 3 well support the fact that the e-beam irradiation induces oxidation.

In conclusion, we studied the effects of electron beam irradiation on the graphene layers grown on 6H-SiC(0001). After

1 MeV electron beam irradiated on the graphene surface, the layered feature was destroyed and small hillocks appeared. As the e-beam irradiation increased, the size of the hillocks was enhanced. The major chemical composition of the hillocks was graphite oxide derivatives. Thus, the electron beam irradiation in ambient environments induced oxidation of the graphene layer.

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