Work function engineering of single layer graphene by irradiation-induced defects

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We report the tuning of electrical properties of single layer graphene by a-beam irradiation. As the defect density increases upon irradiation, the surface potential of the graphene changes, as determined by Kelvin probe force microscopy and Raman spectroscopy studies. X-ray photoelectron spectroscopy studies indicate that the formation of C/O bonding is promoted as the dose of irradiation increases when at atmospheric conditions. Our results show that the surface potential of the graphene can be engineered by introducing atomic-scale defects via irradiation with high-energy particles. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4826642]

Graphene is a two-dimensional carbon system with various novel properties, such as a zero-gap semi-metallic band, ballistic transport at submicron length scales, massless Dirac fermions, and an abnormal quantum Hall effect.1,2 From a practical perspective, the extraordinarily high mobility3 and thermal conductivity4 have attracted much attention and made graphene one of the most interesting and promising materials in nanotechnology. Recently, large-area graphene was successfully synthesized via vacuum graphitization of SiC or chemical vapor deposition (CVD) using a Cu or Ni substrate.5,6 Graphene grown by CVD can be transferred to a target substrate using poly-methylmethacrylate (PDMA) or poly-dimethylsiloxane (PDMS). However, there are still concerns about the possible formation of defects on the graphene surface which mainly result from: (i) the synthesis process, which is subject to the substrate state; or (ii) the transfer process, where the surface is exposed to various chemicals, electron microscopy, or the ionic fabrication process. It is, therefore, desirable to characterize and understand how defects affect graphene.7–9 On the other hand, controlling defects is a promising approach for future applications since it can engineer, or modify, the intrinsic properties of graphene.10 For example, field-effect transistors based on graphene need maneuverable p- and n-type conduction in the graphene to construct complex logic devices. As a transparent electrode, better electrical coupling (i.e., work function) between the graphene and the semiconductor, or enhanced electrical conductivity of the graphene is needed.11,12 By using chemical treatment, graphene oxide or fluorinated graphene has been developed to have an open band gap.13,14

Beam irradiation is another attractive method to generate atomic-scale defects which tend to be more stabilizing as dopants.15,16 Motivated by these requirements for possible applications, we studied how atomic-scale defects affect the properties of graphene in terms of chemical doping. In this work, we irradiated an a-beam (He2+) on CVD-grown graphene to generate controlled defects, Raman spectroscopy and Kelvin probe force microscopy (KPFM) results show that such defects have the ability to modulate the doping level of graphene, which results in a shift in the Fermi-level, EF.

The graphene was grown on a Cu substrate using the inductively coupled plasma CVD method.17,18 Three pristine samples were irradiated with a 3.04 MeV He2+ beam at doses of 1 × 1014, 5 × 1014, and 1 × 1015 cm−2. As-received pristine graphene was included as a reference for the following measurements. According to model calculations, formation of non-hexagonal rings or vacancies can take place under our irradiation conditions.19 Raman spectra were measured at ambient conditions using a LabRAM HR UV-VIS-NIR Raman microscope (Horiba Jobin Yvon). The spot size was ~1 μm2 and the power was kept at 0.5 mW to avoid local heating of the samples. Ar+ ions with an excitation energy of 2.41 eV (λD = 514.5 nm) were used as the laser source. To characterize the beam-induced effects with respect to the surface potential, we conducted KPFM using an Agilent 5500 atomic force microscope. Pt/Ir-coated conductive cantilevers were used for non-contact mode and the topography and surface potential signal were measured simultaneously with a mechanical drive frequency of 75 kHz and AC modulation of 1 V at 20 kHz. By controlling the sample bias to nullify the capacitive force caused by the contact potential difference (CPD) between the tip and the sample, the local distribution of the surface potential can be mapped out. A synchrotron radiation source (4A2 and 10D beamlines of Pohang Accelerator Laboratory) was utilized for photoemission spectroscopy (PES) analysis. Photon energies of 650 eV and 72.5 eV were used for the core level and valence band, respectively.

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would be advantageous in representing variations in the density of states (DOS) while suppressing interference between the initial and final states of the emitted electrons. Also, such high excitation energy can give the valence band DOS over a wider range, stretching to the C$_{2s}$ states. As shown in Fig. 4(a), both samples show a five-band feature, which are assigned to C$_{2p_x}$ (0 $\pm$ 4 eV), the overlap of C$_{2p_y}$ and C$_{2p_z}$ ($\sim$6 eV), C$_{2p_y}$ ($\sim$8 eV), s-p mixed hybridized state ($\sim$11 eV), and C$_{2s}$ ($\sim$8 eV). With He$^{2+}$ treatment, the C$_{2p}$ peak was clearly developed, which is associated with deformation of the carbon network (sp$^2$) or formation of dangling bonds. The whole spectrum was observed to shift towards the Fermi level after the He$^{2+}$-treatment, indicating depletion of electrons, which is consistent with the KPFM results.

Next, we focused on the origin of the doping effect by irradiation using PES about the core levels. Since the graphene is only 0.3 nm thick, surface sensitive methods, such as PES, provide valuable information about the nature of the bonding before and after irradiation. The PES survey scan spectra for the core level were acquired by using a photon energy of 650 eV. In Fig. 4(b), the PES results for Cls of both pristine (top) and 1 $\times$ 10$^{15}$ cm$^{-2}$ He$^{2+}$-treated graphene (bottom) are given to identify C/O groups occurring on the surface. Both spectra are referenced to Cls at 284.7 eV and a simple Shirley-type correction is introduced to remove the background noise caused by inelastic electron scattering. Both spectra feature a strong peak at the higher binding energy and relatively broad FWHM of $\sim$2.1 eV due to superposition of the C/O functional groups. To establish the various existing C/O groups, the Cls peaks are divided into four symmetric Gaussian curves at 284.8 eV, 285.6 eV, 287.0 eV, and 288.7 eV, which are assigned to C-C, C-O, C=O, and C=O, respectively. As shown in Fig. 4(b), the existence of C-O (peak area ratio of 22%) and C=O (4%) can be confirmed in the Cls for the pristine graphene, but C=O is not detectable before irradiation. However, for the He$^{2+}$-treated graphene, the formation of C=O becomes observable (5%) and the C=O also increases slightly up to 6%, while C-C is reduced from 74 to 68%. Therefore, it is evident that the carbon bonds broken by the He$^{2+}$ beam are spontaneously reconstructed toward either C=O or C=O-O, where the formation of an oxygen anion requires hole doping of the graphene, implying that the hole doping effect is closely associated with this bond reconstruction. Consistent with these results, Shin et al. demonstrated that highly resistive graphene oxide can be obtained by removing the C-O using a N$_2$H$_4$ solution and claimed that C-O and C=O play a major role in hole doping in graphene oxide and that N groups compensate for the hole carriers by effectively removing C=O. We attribute the hole doping effect to the charge transfer taking place during bond reconstruction between the irradiation-induced broken C bonds and O$_2$ molecules. The three ex situ measurements of KPFM, PES, and Raman spectroscopy were conducted and showed the same doping effect. Exposure to air does not influence the types of doping. Therefore, we supposed this result indicates that the p-doping of graphene induced by He$^{2+}$ irradiation is rather robust. For understanding the more intrinsic transport properties, such as hole or electron conduction, measurement of the conductance–gate voltage plot might be ideal. An intriguing approach is to carry out scanning gate microscopy where the source–drain current can be governed by the bias voltage of the AFM tip.

In conclusion, our results show that He$^{2+}$ irradiation results in the p-doping effect that could be directly determined by KPFM. The effect is attributed to the charge transfer (interaction) between broken C bonds and ambient O$_2$ molecules, which results in C=O or C–OO bonds. Surface-sensitive PES measurements confirm that the C=O and C–OO bond density increases after He$^{2+}$ beam irradiation. Overall, hole doping leads an increase in the work function by as much as 400 mV, where this increase shows a logarithmic behavior with respect to the irradiation dose. The generation of defects using inert gas ions has the advantage of being a simple process with precise tuning of the work function of graphene.

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