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Surface property change of graphene using nitrogen ion

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Abstract

We introduced nitrogen ions to modify the graphene surface and its property changes were investigated. A graphene layer grown on 6H-SiC(0001) was irradiated with 100 eV nitrogen ions. Surface property changes were studied using photoemission spectroscopy (PES), near edge x-ray adsorption spectroscopy (NEXAFS), and atomic force microscopy (AFM). N 1s core level spectra show that three kinds of nitrogen species, nitrogen gas, graphite-like and pyridine-like nitrogen were induced on the nitrogen ion implanted graphene surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of graphene [1], it has fascinated many researchers, not only for its physical and chemical properties [2–6], but also for its industrial applications such as memory, FETs, and gas sensors [7–10]. To apply graphene to the semiconductor device, it is important to dope molecules and metals on graphene because the carrier density of the graphene layer can be controlled by doping metals and molecules [1, 11]. It is thus necessary to characterize the surface property and electronic structural changes that take place on the graphene. Because the graphene surface is very inert, however, the molecules cannot be easily adsorbed on the graphene surface. To solve this problem, there have been many efforts to functionalize the surface, including energetic particles [11, 12] such as electron beam irradiation and ion doping. In this work, we investigated the possibility of using nitrogen ions to modify the graphene surface and change its properties. Nitrogen doping has been studied by many groups, especially on carbon based materials such as carbon

nanotube and graphite. It is now known that nitrogen doping is a promising way to change the mechanical and electronic properties of these carbon based materials [13]. On the basis of these facts, we expect to bring about changes in the structure of graphene and its magnetic properties, as well as its band gap, by controlling the amount of nitrogen ion doping [14–16].

For this purpose we used low energy nitrogen (N) ions to irradiate the multi-layer graphene because the control of a N ion beam is relatively easy. The surface properties were investigated using atomic force microscopy (AFM), photoemission spectroscopy (PES), and near edge x-ray fine structure (NEXAFS).

2. Experimental details

The nitrogen-doped ($N_D \sim 9 \times 10^{17} \text{ cm}^{-3}$) Si-terminated 6H-SiC(0001) sample was purchased from Cree Research (USA). 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 at around 900 °C under a Si flux (1 \AA min^{-1}). After annealing at 1150 °C, a carbon rich ($6\sqrt{3} \times 6\sqrt{3}$)R30° electron diffraction pattern appeared. A well reconstructed surface with a graphene layer of thickness

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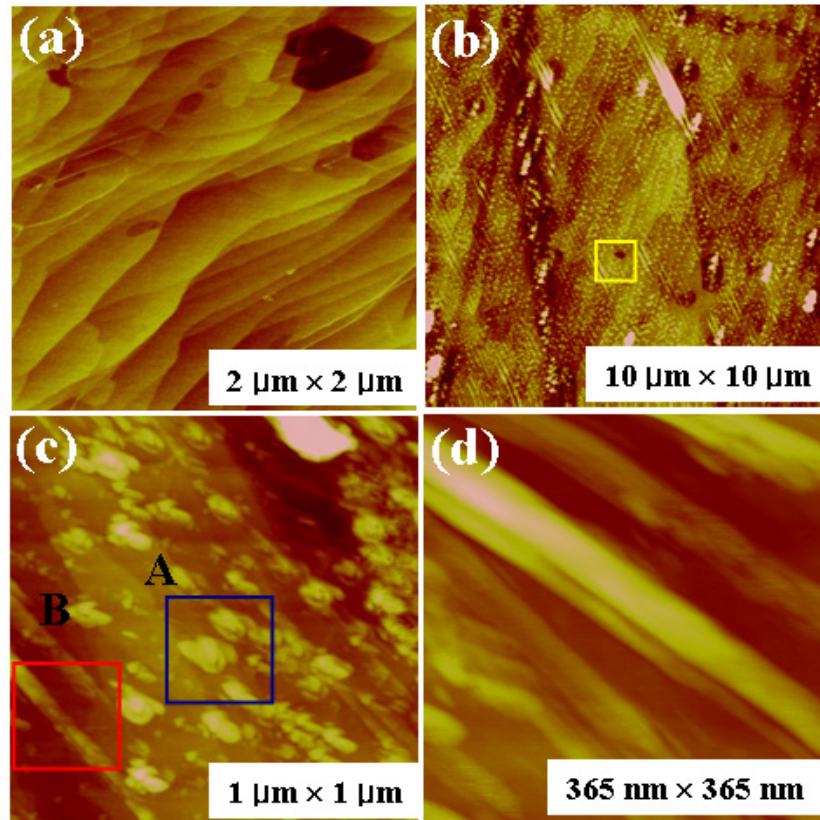


Figure 1. (a) 4-layer graphene before N ion irradiation ($2 \mu\text{m} \times 2 \mu\text{m}$). (b) 15 min N ion irradiation ($10 \mu\text{m} \times 10 \mu\text{m}$). There were two kinds of major N induced structures: (c) the popcorn-like shape ($1 \mu\text{m} \times 1 \mu\text{m}$) and (d) the bulged nano-ribbon shape ($0.36 \mu\text{m} \times 0.36 \mu\text{m}$).

12 \AA was found after further annealing at 1400°C [12]. This is almost equivalent to 4-layered graphene, which will hereafter be referred to as multi-layer graphene. The graphene/SiC was irradiated with nitrogen ions of energy 100 eV at room temperature in the UHV chamber. The nitrogen ions were generated using an ion gun (PHP 3000), and the measured sample current was $0.4 \mu\text{A cm}^{-2}$ during ion beam irradiation.

The effects of the nitrogen ion irradiation on the graphene/SiC were investigated using AFM, NEXAFS, and PES. Before and after nitrogen ion irradiation, the C $1s$ (N $1s$) core level spectra was measured using a photon energy of 320 eV (500 eV) with a total resolution of 200 meV (200 meV) at the 8A2 HR-PES beamline in the Pohang accelerator laboratory (PAL). The binding energy and the spectral resolution of C $1s$, N $1s$ and Si $2p$ were calibrated by measuring the Au $4f_{7/2}$ core level and the Au Fermi edge. The NEXAFS spectra of the C K-edge (N K-edge) were measured at the 2B1(8A1) 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 .

3. Data and results

Figure 1 shows the changes on the surface morphology obtained from AFM before and after nitrogen ion irradiation. As shown in figure 1(a), we found the distinctively layered structure photographed before N ion irradiation. After

confirming the graphene layers, we performed N ion irradiation for 15 min, as shown in figure 1(b). As can be seen in this image, we observed that the few top layers were destroyed whereas the bottom layer remained unchanged. This result accords well with the NEXAFS result, which indicates that some layered structure is in existence (see in figure 3). Magnifying this image (marked as the yellow box), we found two kinds of destructive patterns; one is a popcorn shaped major destructive species marked as A, and the other is a bulged ribbon shape in the region B, as shown in figure 1(c). Moreover, a much more enlarged image of the bulged ribbon shape emerged, as shown in figure 1(d).

To track the variations of the electronic structure, we measured C and N $1s$ core level photoemission spectra (CLPES) as a function of the N ion irradiation time. As shown in figure 2(a), we found that, on the multi-layer graphene, the C $1s$ spectrum in figure 2(a) consists of two peaks before N ion irradiation. One originated from the single layer-like graphene (marked as S), and the other is induced by the multi-layer graphene (marked as G), which is similar to graphite.

When they were irradiated with N ions for 5 min, two new peaks, with the binding energy (BE) of 286.2 eV (C2) and 283.8 eV (C1) appeared in figure 2(b). Increasing the amount of N ion irradiation to 10 min (figure 2(c)) and 15 min (figure 2(d)), the intensity of these two peaks also increased. The chemical shift of these two peaks informs us that they are incorporated with N atoms, and C1 originates from the $-C-N$

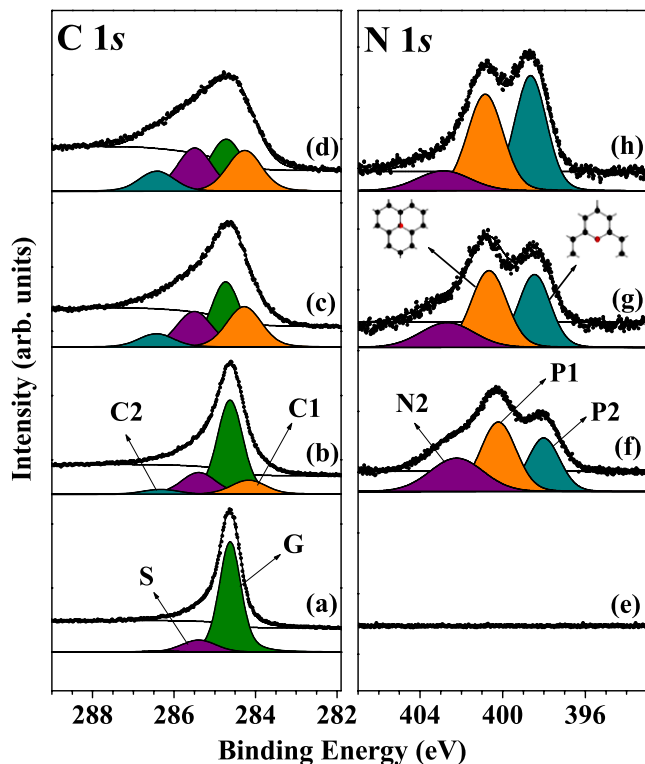


Figure 2. PES spectra of C 1s measured at a photon energy of 330 eV upon nitrogen ion irradiation of (a) 0 min, (b) 5 min, (c) 10 min, and (d) 15 min. PES spectra of N 1s obtained at a photon energy of 650 eV upon nitrogen ion irradiation of (e) 0 min, (f) 5 min, (g) 10 min, and (h) 15 min. Carbon is the black circle and nitrogen is the red circle in the model structure of the graphite-like (P2) and the pyridine-like (P1) structure induced by N ion doping

bond (283.8 eV), and C2 is originates from the $-\text{C}=\text{N}$ bond (286.2 eV) [17, 18].

To clarify the role of N ion irradiation, we measured N 1s core level spectra. After confirming the cleanliness of graphene, shown in figure 2(e), we irradiated with the N ion beam for 5 min. As shown in figure 2(f), we found that the N 1s spectra consist of three peaks marked as N2, P1, and P2, indicating binding energies of 402.6, 400.6, and 398.4 eV, respectively. Moreover, as we increased the N ion irradiation time from 10 min (figure 2(g)) to 15 min (figure 2(h)), the intensity of the N 1s peak increased. However, the relative intensity of N2, P1, and P2 was changed. That is, the relative intensity of N2 and P1 decreased and the intensity of P2 increased, and became the major component after 15 min of N ion irradiation. Through a spectral analysis, we defined the origins of N2, P1 and P2 to be molecular nitrogen gas, the graphite-like structure, and the pyridine-like structure, respectively. As the number of N ions was increased, the pyridine-like structure became the major feature by bond breaking of $\text{C}=\text{C}$. This result matched well with those of C 1s spectra, indicating that the intensity of $\text{C}=\text{N}$ has gradually increased.

NEXAFS C and N K-edge spectra in figure 3 show the types of molecular bonds taking place on the modified surface after N ion irradiation. In figure 3(a), the intense $\text{C}=\text{C}\pi^*$ feature at a photon energy of 285 eV (A) was shown before N

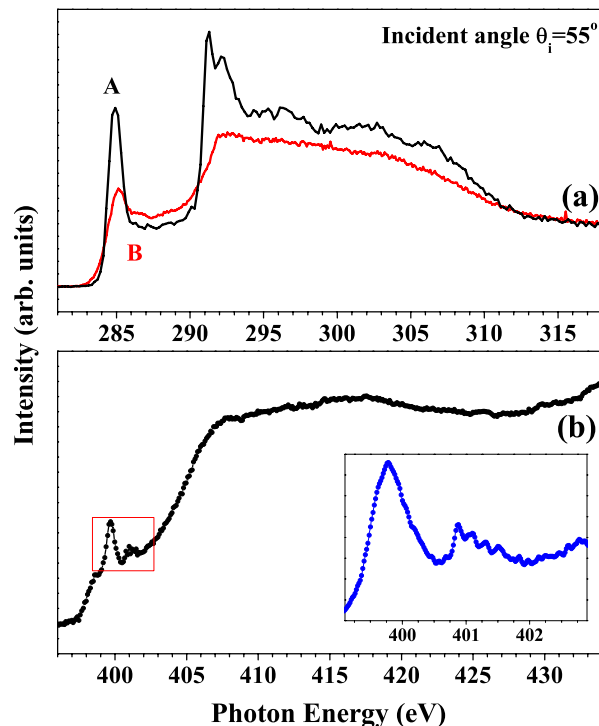


Figure 3. NEXAFS spectra of the C K-edge (a) were measured at the photon incident angle (θ_i) of 55° (magic angle) before (black line) and after (red line) 15 min N ion irradiation. NEXAFS spectra of the N K-edge (b) were measured at the photon incident angle (θ_i) of 55° (magic angle) before (black line) and after (red line) 15 min N ion irradiation. The inset in (b) shows well resolved N2 molecular vibration structures.

ion irradiation. However, the intensity of the $\text{C}=\text{C}\pi^*$ feature (marked as A) decreased to 54.5%, and $-\text{C}=\text{N}$ and $-\text{C}-\text{N}$ related features increased at a photon energy of 286.4 eV (B) after 15 min of N ion irradiation. Interestingly, the $\text{C}=\text{C}\pi^*$ feature (A) is still the major feature and has a good angle dependence (not shown here). This strongly supports that carbon–nitrogen bonds were induced by breaking $\text{C}=\text{C}\pi^*$ states, and that the graphene structure partially remained. Moreover, when we measured the N K-edge, shown in figure 3(b), we confirmed three distinctive features at around 400 eV. Each feature was centered at photon energies of 398.6 eV, 399.6 eV, and 401 eV, which are related with the pyridine-like bond, graphite-like bond, and molecular nitrogen bond, respectively. Moreover, we could find clear evidence of the existence of N2 in the enlarged spectra of figure 3(b). The peaks between 400 and 402 eV are the N 1s $\rightarrow \pi^*$ excitation and its side band. The vibrational fine structure of π^* was given by the N_2 molecules and previously Chen *et al* [19] also reported the resonance spectra with synchrotron radiation.

Through PES and NEXAFS, it was possible to clearly distinguish three kinds of nitrogen related species; a pyridine-like bond, a graphite-like bond, and a molecular nitrogen bond, respectively. The AFM image in figure 1 offers an explanation that some of the $\text{C}=\text{C}$ bonds might have been broken and the pyridine-like species were formed by substitution of nitrogen atoms in the hexagonal structure, which is in accord with the theoretical result [20].

Moreover, we can speculate that the edge of the popcorn shape in figure 1(c) was terminated with the pyridine-like structure after breaking the C=C bond. The bulged ribbon shaped structure in figure 1(d) originated from the graphite-like structure by substitution of N atoms [21, 22]. As a result, we infer that the bulged ribbon shaped structure is the only place on the surface structure where gaseous N₂ molecules can be.

4. Conclusion

In conclusion, through PES and NEXAFS we found three kinds of N incorporated structures, molecular nitrogen gas (N₂), graphite-like nitrogen, and pyridine-like nitrogen, after the low energy N ion irradiation. An AFM analysis revealed two surface morphological changes: a popcorn-like structure and a bulged ribbon shaped structure.

Acknowledgments

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References

- [1] Geim A K and Novoselov K S 2007 *Nat. Mater.* **6** 183
- [2] Song B Z, Li X, Wu X, Brown N, Naud C, Mayou D, Li T, Hass J, Marchenkov N, Conrad E H, First Ph N and de Heer W A 2006 *Science* **312** 1191
- [3] Zhang Y B, Tan Y-W, Stormer H L and Kim Ph 2005 *Nature* **438** 201
- [4] Ohta T, Bostwick A, Seyller T, Horn K and Rotenberg E 2006 *Science* **313** 951
- [5] Kim K-J, Lee H, Choi J-H, Lee H-K, Kang T-H, Kim B and Kim S 2008 *J. Phys.: Condens. Matter* **20** 225017
- [6] Zhou S Y, Gweon G-H, Fedorov A V, First Ph N, de Heer W A, Lee D-H, Guinea F, Neto A H C and Lanzara A 2007 *Nat. Mater.* **6** 770
- [7] Stankovich S, Dikin G H, Dommett B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 *Nature* **442** 282
- [8] Li X, Wang X, Zhang L, Lee S and Dai H 2008 *Science* **319** 1229
- [9] Sutter P W, Flege J-I and Sutter E A 2008 *Nat. Mater.* **7** 406
- [10] Li Y, Sinitskii A and Tour J M 2008 *Nat. Mater.* **7** 966
- [11] Krasheninnikov A V and Banhart F 2007 *Nat. Mater.* **6** 723
- [12] Kim K-J, Choi J-H, Lee H, Lee H-K, Kang T-H, Han Y-H, Lee B-C, Kim S and Kim B 2008 *J. Phys. Chem. C* **112** 13062
- [13] Stafström S 2000 *Appl. Phys. Lett.* **77** 3941
- [14] Ma Y, Foster A S, Krasheninnikov A V and Nieminen R M 2005 *Phys. Rev. B* **72** 205416
- [15] Hagiri I, Takahashi N and Takeda K 1994 *J. Phys. Chem. A* **108** 2290
- [16] Yazyev O V and Katsnelson M I 2008 *Phys. Rev. Lett.* **100** 047209
- [17] Chan L H, Hong K H, Xiao D Q, Lin T C, Lai S H, Hsieh W J and Shih H C 2004 *Phys. Rev. B* **70** 125408
- [18] Lim S H, Elim H I, Gao X Y, Wee A T S, Ji W, Lee J Y and Lin J 2006 *Phys. Rev. B* **73** 045402
- [19] Chen C T, Ma Y and Sette F 1989 *Phys. Rev. A* **40** 6737
- [20] Kotakoski J, Krasheninnikov A V, Ma Y, Foster A S, Nordlund K and Nieminen R M 2005 *Phys. Rev. B* **71** 205408
- [21] Wu Y P, Jiang C Y, Wan C R, Fang S B and Jiang Y Y 2000 *J. Appl. Polym. Sci.* **77** 1735
- [22] Deng Z W and Souda R 2002 *Thin Solid Films* **406** 46