Effects of Slow Highly Charged Ion Impact Upon Highly Oriented Pyrolytic Graphite  
—Nanoscale Modification of Electronic States of Graphite Surface—

Takashi Meguro  Member

**Keywords**: graphite, diamond, highly charged ion, nanoscale modification

Nanoscale modification of electronic states induced by the impact of slow highly charged ion (HCl) onto highly oriented pyrolytic graphite (HOPG) surfaces is reviewed. The high potential energy of slow Ar$^{8+}$ induces multiple emission of electrons from the surface, providing a strong modification of the electronic states of the local area of HOPG surfaces. Size of created protrusions created by the Ar$^{8+}$-impact was about 1 nm in diameter with 400 eV of the kinetic energy, and the subsequent surface treatment by electron injection from a scanning tunneling microscope (STM) induced a localized transition from $sp^2$ to $sp^3$ hybridization at the center of the protrusion, which considered to result in the formation of nano-diamond-like structures. Figs. 1(a)-(d) summarize the variation of STM images of HOPG after the single ion impact with some optional treatment. Fig. 1(a) shows symmetric triangular features due to electronic perturbation in the case of Ar$^+$ impact, indicating multiple point which were typically seen for the single charged ion irradiation onto HOPG surfaces. On the other hand, in the case of Ar$^{8+}$ irradiation, a larger protrusion-like feature was observed due to the contribution of the Coulomb potential of ions as shown in Fig. 1(b). Similar protrusion-like features created on HOPG surface by HCI impact have been observed in the different kinetic energy region.

When electrons were injected from an STM tip into the protrusion created by the impact of Ar$^{8+}$, the center part was observed as a dark region as shown in Fig. 1(c). Here the electron injection was carried out by applying bias voltage in an STM. This transformation indicates that electronic states of the center had been modified by electron injection. The $I$-$V$ characteristics measured by scanning tunneling spectroscopy (Fig. 1(e)) represent that the dark center becomes nonconductive while the area surrounding the dark center possesses metallic nature, suggesting the formation of a large band gap via interaction with Ar$^{8+}$. Fig. 1(d) represents an STM image of the Ar$^{8+}$-impact area followed by electron injection and the additional thermal treatment in hydrogen ambient. This treatment was carried out at 600 °C for 30 min in 76 Torr of H$_2$ pressure. This structure is found to show $I$-$V$ characteristics similar to the CVD-grown poly-diamond in the field emission measurement by means of STM. The possible structure of the Ar$^{8+}$-impact site is considered to be a planar-type $sp^3$ structure with a vacancy, which is expected easily to transfer from the planar structure of $sp^2$ graphite.

Though the details of the formed structure are still being studied, HCI has potential to create novel surfaces with attractive nature completely different from the case of singly charged ion.

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**Fig. 1.** (a), (b), (c) and (d) are STM images after Ar-ion impact with certain optional treatments. (a) As Ar$^+$ irradiated, (b) as Ar$^{8+}$ irradiated, (c) after Ar$^{8+}$ irradiation followed by electron injection, and (d) after the subsequent hydrogen treatment of sample (c). (e) $I$-$V$ characteristics inside and outside of the Ar$^{8+}$ impact region measured by the scanning tunneling spectroscopy (STS). Measured positions are assigned on (c)
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Nanoscale modification of electronic states of highly oriented pyrolytic graphite (HOPG) surfaces induced by the impact of slow highly charged ion (HCl) is reviewed. The high potential energy of slow Ar$^{8+}$ induces multiple emission of electrons from the surface, which strongly modifies the electronic states of the local area of HOPG surfaces. The size of created protrusions created by the Ar$^{8+}$-impact with 400 eV of the kinetic energy was about 1 nm in diameter, and the subsequent surface treatment by electron injection from a scanning tunneling microscope (STM) induced a localized transition from $sp^2$ to $sp^3$ hybridization at the center of the protrusion, which considered to result in the formation of nano-diamond-like structures.

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1. Introduction

In the case of singly charged ion irradiation upon graphite, high-dose-ion irradiation is necessary to induce the transformation of $sp^2$ to $sp^3$ in combination with some structural reconstruction(18,22). This transformation does not occur by the single impact of singly charged ion. It is well-known that the impact of slow highly charged ions (HCl) onto solid surfaces provides multiple electron emission, and that the emission process strongly modifies the local electronic states of target surfaces and several applications of HCl in nanotechnology have been reported in materials processing(3)-(10). The author and coworkers have firstly demonstrated that the single impact of slow HCl (Ar$^{8+}$; kinetic energy = 400 eV) on highly oriented pyrolytic graphite (HOPG) surfaces with the subsequent electron injection upon the impact region induces the transition of $sp^2$ to $sp^3$ hybridization(11)-(16), and review the results here.

2. Experiment

Fig. 1 shows a schematic illustration of experimental setup used in this study. The system consists of five columns; i) ion source, ii) the beam line which consists of Einzel lenses, a magnet, a steerer, a Faraday cup current monitor, a deflector and a deceleration system for charge selection, collimation, acceleration, and deceleration, iii) ion irradiation chamber, iv) the multiple sample stocker, and v) the introduction chamber. A 10 GHz electron cyclotron resonance plasma source (Nanogun(17), Pantechnik) generated Ar$^{q+}$ ($q = 1 – 10$) ions with 10 kV of extraction voltage. The extracted Ar$^{q+}$ was focused in the Einzel lens system and the charge state of Ar$^{q+}$ was selected by a magnetic field. The kinetic energy was controlled by deceleration lenses placed before the sample stage, and was fixed at 400 eV here. The ion current in the beam line was measured by the Faraday cup between the magnet and the second Einzel lens. To eliminate the contribution from neutral species, which is involved in the ion beam, the ion beam was bent 7° using a deflector. The beam size at the sample surface was about 10 mm.

Samples used were high-grade HOPG substrates in this experiment. Except the stripping of surface layers by a Scotch tape, no other surface treatment was done prior to the experiment. After HCl irradiation, surfaces were evaluated by scanning tunneling microscopy (STM) and Raman Spectroscopy in ex-situ condition. All experiments were done at room temperature.

3. Results and Discussion

3.1 Structural and Electrical Discussion on The Ar$^{8+}$-Impact Site

Figs. 2(a)-(d) summarize the variation of STM images of HOPG after the single ion impact with some optional treatment. Fig. 2(a) shows symmetric triangular features due to electronic perturbation in the case of Ar$^{8+}$ impact, indicating multiple point defects which were typically seen for the singly charged ion irradiation onto HOPG surfaces(19). On the other hand, in the case of Ar$^{8+}$ irradiation, a larger protrusion-like feature was observed due to the contribution of the Coulomb
potential of ions as shown in Fig. 2(b). Similar protrusion-like features created on HOPG surface by HCl impact have been observed in the different kinetic energy region (19)-(24). Fig. 3 shows typical size of protrusion as a function of potential energy (total ionization energy) of incident ion. Open and solid circles indicate size of protrusion created by Ar and Xe HCl impact, respectively. The size of protrusion increases with potential energy. It has been reported that the height of protrusion is constant at ~1nm and is independent of potential energy (24). The inserted figure in Fig. 3 summarize the kinetic energy dependence of size of protrusion in the case of Ar\textsuperscript{8+} impact. Here the size of protrusion seems to increase also with the kinetic energy. However, this tendency is seen only at the low kinetic energy region. At a higher kinetic energy region, the size of protrusion does not depend on the kinetic energy (24). It is also of interest that the height of protrusions is reported to be independent of the potential energy (24).

When electrons were injected from an STM tip into the protrusion created by the impact of Ar\textsuperscript{8+}, the center part was observed as a dark region as shown in Fig. 2(c). Here the electron injection was carried out by applying bias voltage in an STM. This transformation indicates that electronic states of the center had been modified by electron injection. The I-V characteristics measured by scanning tunneling spectroscopy (Fig. 2(e)) represent that the dark center becomes nonconductive while the area surrounding the dark center possesses metallic nature, suggesting the formation of a large band gap via interaction with Ar\textsuperscript{8+}.

Although the details of the formed structure are still being studied, a possible scenario for the creation of non-conductive region is as follows. When slow Ar\textsuperscript{8+} approaches the HOPG surface, the electrons are depleted at the surface below Ar\textsuperscript{8+} due to the strong Coulomb potential of Ar\textsuperscript{8+} to extract electrons from graphite surface. During the subsequent reconstruction of bonds, the nanoscale sp\textsuperscript{3} region with a wide energy gap is created by the single impact of Ar\textsuperscript{8+}. Ab initio calculation of core excitation of graphite predicts that the graphite structure becomes unstable with the valence hole, and that the transformation into diamond from graphite can be induced at room temperature by doped holes (27). The similar theoretical prediction have also been reported by Watanabe et al. (28). Therefore it is considered that the conversion from sp\textsuperscript{2} to sp\textsuperscript{3} hybridization occurred after the Ar\textsuperscript{8+} impact with successive electron injection.

Recently, an influence of slow Ar\textsuperscript{8+} impact on the HOPG layers...
has been discussed by means of the time-dependent density functional theory (TDDFT) and molecular dynamics simulation done with use of the Earth Simulator. This calculation has not been completed yet, but it is found at the present stage that fast but incomplete charge transfer from graphite to Ar ion and formation of sp²-like bond network in graphene layers occur.

### 3.2 Effects of Thermal Treatment in Hydrogen Ambient

It is well-known that the H-terminated p-type diamond surfaces exhibit negative electron affinity (NEA) to show high electron field emission property. Fig. 2(d) represents an STM image of the Ar³⁺-impact area followed by electron injection and the additional thermal treatment in hydrogen ambient. This treatment was carried out at 600 °C for 30 min in 76 Torr of H₂ pressure. Electronic states of the impact region seem to be more stable after the treatment. It is clear that a certain structure appeared at the surrounding defective region, however the structure is different from the original graphite. This is due to the recrystallization by the annealing effect at high temperature.

Figs. 4(a) and 4(b) show the field emission characteristics of the treated structure measured by STM. In these measurements, the tip of STM was fixed at 15 nm above the center of the Ar³⁺-impact region. Fig. 4(a) shows a raw data of I-V curve at the Ar³⁺-impact with the thermal treatment in hydrogen. This curve shows the similar tendency with CVD-grown poly-diamond film. From the observation of field emission image taken by STM and the line profile of emission current, it is confirmed that electron emission occurs from inside the Ar³⁺-impact site. Since the position of the STM tip is fixed at 15 nm from the surface, size of the emission area is larger than the original structure. In the case of Ar³⁺-impact region on HOPG without thermal treatment in hydrogen, the structure was unstable under high electric field, and no electron emission was observed.

Fig. 4(b) shows a Fowler-Nordheim (F-N) plot estimated from (a) using the equation shown above figures. The calculated work function φ from the equation was estimated to be 0.298 eV. As compared with the work function of non-treated HOPG (φ ~ 4.5 eV), the obtained value of φ is low, showing that electron emission occurs easily on the Ar³⁺-irradiated HOPG with the thermal treatment. Work functions of hydrogen-terminated polycrystalline diamond and hydrogen-terminated diamond-like carbon (DLC) are reported as 3–5 and 0.2–0.3 eV, respectively, suggesting that the created structure by a Ar³⁺-impact of sample surface in this experiment is similar to the DLC.

### 3.3 Raman Analysis of The Ion-Impact HOPG Surfaces

Raman spectroscopy is very sensitive to the defect structure in HOPG. Figs. 5(a) and 5(b) show comparison of Raman spectroscopic analysis of HOPG after Ar⁺ and Ar³⁺ irradiation. Fig. 5(a) represents the intensity ratio of the D peak to the G peak, I(D)/I(G), as a function of a square root of incident ion fluence, √. In the case of Ar⁺-impact, I(D)/I(G) linearly increases with the increase of √, while I(D)/I(G) shows a considerable saturation in high √ region for Ar³⁺ incidence. It has been reported that this tendency was explained by the formation of vacancy clusters due to the overlap of the irradiation-induced cascades, suggesting that the defects introduced by Ar³⁺ impact are some defect complex such as vacancy clusters. This consideration is supported also by the ion fluence, dependence of the full width half maximum of G peak, FWHM(G) of Ar³⁺-irradiated HOPG (Fig. 5(b)), which shows that FWHM(G) drastically increases in the range of high √ region, while FWHM(G) of Ar⁺-irradiated HOPG is almost constant. Niwase has discussed the disordering of graphite induced by SCI irradiation using Raman spectroscopy and transmission electron microscopy and revealed that FWHM(G) increases drastically when the clustering of vacancies starts, showing a good agreement with the present results. In the case of Ar⁺-irradiation, the vacancy cluster formation is followed by the amorphization of HOPG due to the overlap of collision cascades for the direction parallel to the surface. The onset of amorphization is reported to be identical to the disappearance of the second-order Raman features. In this study, for Ar³⁺ irradiation, second-order peaks retain enough intensity and sharpness.
indicating that the amorphization does not occur though the vacancy clusters are formed. The mechanism of the cluster formation under Ar$^+$ irradiation is essentially different, suggesting that the individual Ar$^+$ creates vacancy clusters directly at the impact sites.

3.4 Possible Structure of HOPG at The Ar$^+$ Impact Site

In order to discuss the structure of sp$^3$ region created by the HCI sp impact, the electronic level structures have been estimated by DV-Xα molecular orbital calculations$^{[37][38]}$. Assuming that the spherically symmetric sp$^3$ structures similar to the bulk diamond is formed at the impact site, more than 80 carbon atoms are necessary to explain a low HOMO-LUMO energy gap about ~6 eV, of which value is observed in the STM experiments. However, it is clear that approximately 20 carbon atoms are contained in the sp$^3$-converted region at most from the STM observation, and that the symmetric sp$^3$ carbon models are not suitable. It is revealed that the most probable carbon model named “S4” can be expected as a candidate structure of the HOPG surface induced by the Ar$^{8+}$ ions, that has the smallest energy gap, i.e. 5.71 eV.$^{[37][38]}$

The “S4” model consists of 20 carbon atoms and its form is a planar-type sp$^3$ structure with a vacancy, which is expected easily to transfer from the planar structure of sp$^2$ graphite. As mentioned in Section 3.3 defects and disordering are induced in sp$^2$ region, and it is acceptable that sp the sp$^2$ region contains some defects similar to the sp$^2$ region. The “S4” model has vacancy at center, which is identical to this consideration. If no vacancy is introduced in “S4” model, the HOMO-LUMO energy gap becomes larger, and does not consistent with experimental results. Existence of vacancy in “S4” model is the key to build most probable defective structure with sp$^3$ carbons created by Ar$^+$ impact and the subsequent electron injection.

4. Summary

Nanoscale modification of electronic states of HOPG surface induced by a slow Ar$^{8+}$ impact is reviewed. Ar$^{8+}$ irradiation modifies HOPG containing local sp$^2$ structures to nanodiamonds possessing sp$^3$ structures. This conversion process is significantly different from the conventional process, which requires a high dose of ion beam irradiation. The high potential energy of slow Ar$^{8+}$, which induces multiple emission of electrons from the surface, induces a strong modification of the electronic states of the local area of surfaces. The subsequent surface treatment by electron injection from an STM tip provide a localized transition from sp$^2$ to sp$^3$ hybridization in HOPG. It is of interest from Raman measurements that the vacancies are introduced by Ar$^{8+}$ impact in sp$^2$ region, and that the DV-Xα calculation reveals the presumable structural model of sp$^3$ region which is identical to the defective and more planar sp$^3$ structure.

The HCI impact would also be expected to offer attractive surface modification techniques which are completely different from those obtained by singly charged ion impact. For example, expanded polytetrafluoroethylene (ePTFE) used as an artificial bio-material is frequently associated with postoperative leakage of the cerebrospinal fluid due to its low adhesiveness with fibrin glue and the surrounding tissue. However the ion-irradiated ePTFE surfaces show the superior adhesive property with the tissue$^{[39][40]}$. In general, the ion irradiation onto soft materials such as polymers can strongly modify the surface nature, and we believe that HCI has potential to create novel surfaces with attractive nature completely different from the case of singly charged ion.

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Takashi Meguro
(Member) was born in Tokyo, Japan, on August 21, 1956. He received a Ph. D. degree in electronic material engineering from Waseda University in 1988, and is presently a Team leader at Beam Application Team, RIKEN. He has worked on beam assisted material engineering employing ion, electron or laser beam. Japan Applied Physics Society member.