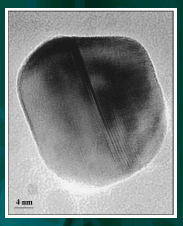
Diamond formation from graphite under highly charged ion irradiation

sp^3 formation by high dose implantation

- Transformation of sp^2 to sp^3 under high dose implantation (formation of DLC).
- High dose ion implantation induces damages into graphite.

Nanodiamond formation by swift ion bombardment into graphite



- Found in the acid residue from 350 MeV Kr ion irradiated graphite
- Room temperature
- Low yield (~ 0.01/ion)

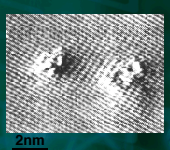
T. L. Daulton et al., Nucl. Instr. and Meth. in Phys. Res. B175-177, 12 (2001)

Unique features of HCI

- Large potential energy
- Energy transfer occurs before the direct collision
- Multiple electron emission occurs from the small area for short period.
- Local modification of surface electronic states

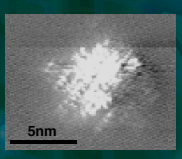
HCI irradiation on HOPG

Ar^{8+} : 4 keV



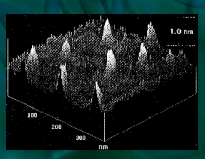
K. Mochiji *et al.* J. Appl. Phys. 82, 6037 (1997).

Xe^{44+} : 276 keV



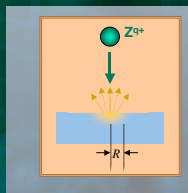
R. Minniti, *et al.* Phys. Scr., T92, 22 (2001)

U^{70+} : 2.2 keV/amu



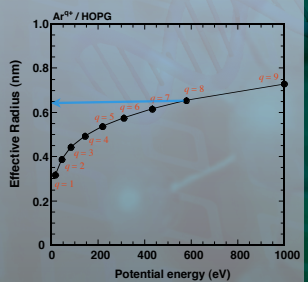
C. Uehlicke *et al.* Nucl. Instr. Meth. In Phys. Res. B90, 528 (1995)

Maximum radius of electron emission



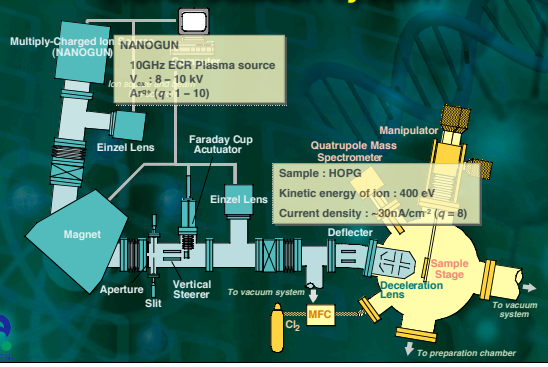
$$R = (\varepsilon W_q / 0.08 \pi n^2 e^2)^{1/5}$$

ε : the dielectrric constant of the solid
W_q : the total potential energy of a q-charge state ion
n : the atomic density of the solid
e : the electron charge



Experimental

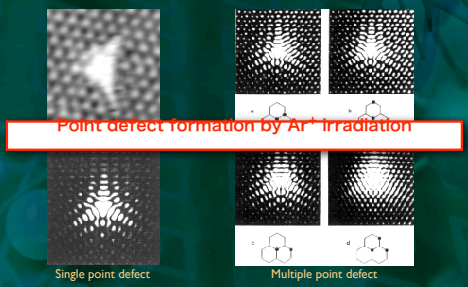
HCI irradiation system



Slow Ar^{8+} impact on HOPG

Ar^{+} impact on HOPG

(Comaprison of experiment & calculation)



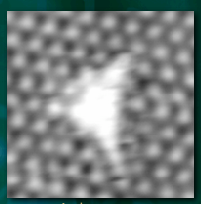
Point defect formation by Ar^{+} irradiation

Single point defect

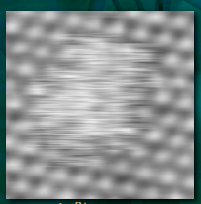
Multiple point defect

H.A. Mizes and J. S. Foster, Science, **244**, 559 (1989).

Comparison of STM images after irradiation of Ar^{+} and Ar^{8+}



Ar^{+} impact



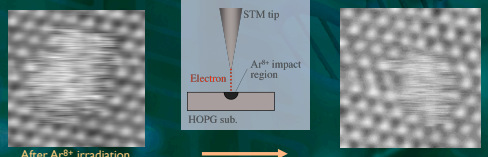
Ar^{8+} impact

Complex structure is formed by Ar^{8+} irradiation

Slow Ar^{8+} impact on HOPG

Electron injection into the Ar^{8+} impact region

Electron injection to Ar^{8+} imapct region

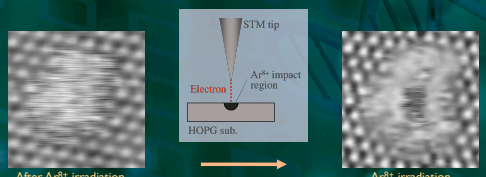


After Ar^{8+} irradiation

Electron injection from STM tip (~100 nA)

Shrinkage of the structure

Electron injection to Ar^{8+} imapct region



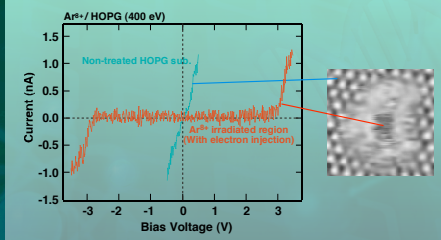
After Ar^{8+} irradiation

Electron injection from STM tip (~100 nA)

Ar^{8+} irradiation + Electron injection

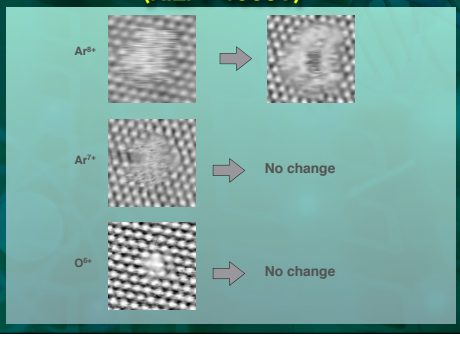
Electron injection creates "dark" region

I-V characteristic of Ar^{8+} impact area measured by STS

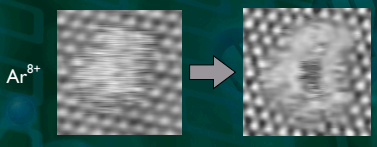


Metallic graphite changes to the non-conductive by electron injection

Comparison of STM images of HOPG surface after Ar^{8+} irradiation (K.E. = 400eV)



Transition from metallic to non-conductive



Electron injection : One-by-one process

He-Cd laser irradiation : Collective process

Slow Ar^{8+} impact on HOPG

Hydrogen treatment

Why the hydrogen treatment ?

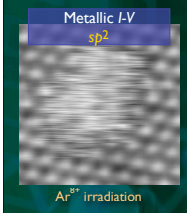
- Hydrogenated sp^3 rich amorphous carbon

  → Blue emission in PL

- Hydrogen-terminated diamond surface

  → Negative electron affinity

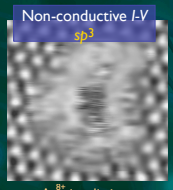
Evolution of STM images of HOPG by Ar^{8+} impact and post processes



Ar^{8+} irradiation

Evolution of STM images of HOPG by Ar^{8+} impact and post processes

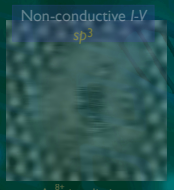
Ar^{8+} irradiation



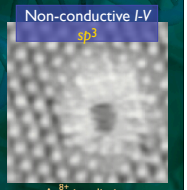
Ar^{8+} irradiation
+
Electron injection
(He-Cd laser irradiation)

Evolution of STM images of HOPG by Ar^{8+} impact and post processes

Ar^{8+} irradiation

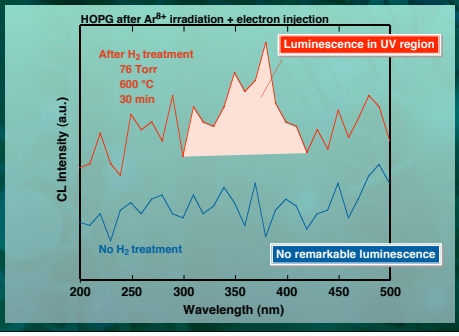


Ar^{8+} irradiation
+
Electron injection
(He-Cd laser irradiation)

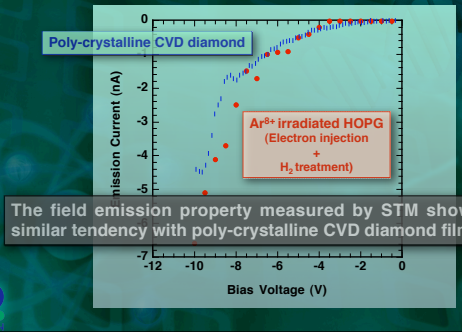


Ar^{8+} irradiation
+
Electron injection
(He-Cd laser irradiation)
+
H_2 treatment
(76Torr, 600°C, 30min)

Cathode Luminescence (@20K)



Field emission property measured by STM

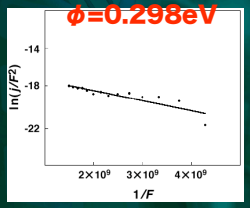


The field emission property measured by STM shows the similar tendency with poly-crystalline CVD diamond film.

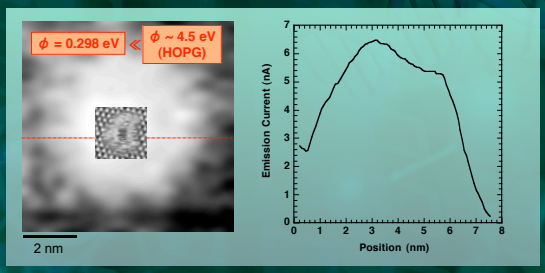
Work function of the Ar^{8+} impact region after electron injection and hydrogen treatment

$$j = \frac{e^3F^2}{8\pi h\phi t^2((e^3F)^{1/2}/\phi)} \times \exp\left[\frac{-4(2m)^{1/2}\phi^{3/2}}{3\hbar eF} v((e^3F)^{1/2}/\phi)\right] \frac{\pi kT/d}{\sin(\pi kT/d)}$$

e : the elementary electric charge
F : the electric field intensity
h : Planck's constant
φ : the work function
m : the rest electric mass
j : the current density
d : the diameter of the emission area



Field emission properties of Ar^{8+} impact region after electron injection and H_2 treatment



Effects of Ar^{8+} irradiation on graphite with post treatments

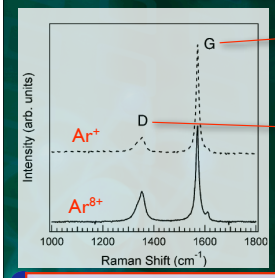
- Metallic → Non-conductive (E_g = ~6 eV)
- Field emission property similar to the CVD-diamond film (ø = 0.298 eV)

Transition from sp^2 to sp^3 occurs.

Slow Ar^{8+} impact on HOPG

Plausible formed structure

First-order Raman spectra of HOPG irradiated with Ar^+ and Ar^{8+} (@ $5x10^{13}$ ions/cm^2)

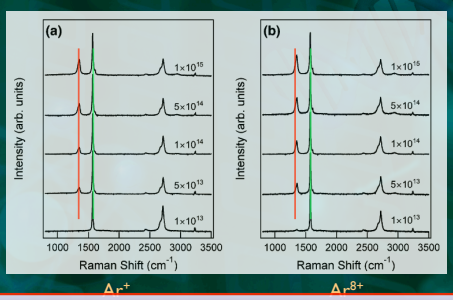


Lattice vibration in the well-crystalline graphite plane

Disorder introduced into the graphite planes via ion impacts

I(D)/I(G) for Ar^{8+} is larger than that for Ar^+ irradiation

Comparison of Raman spectra HOPG irradiated with Ar^+ and Ar^{8+}

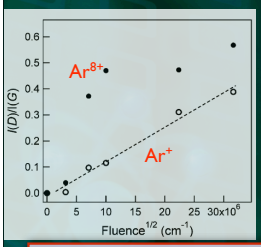


I(D)/I(G) increases with the ion fluence

Relation between G and D peaks

- I(D)/I(G) is inversely proportional to the in-plane crsytallite size *L* of graphite.
- *L* can be regarded as equal to the mean distance between vacancies introduced by the single impact of singly-charged ion.
- I(D)/I(G) is proportional to the square root of ion fluence $\phi^{1/2}$.

I(D)/I(G) vs $\phi^{1/2}$ for the irradiation of Ar^{+} and Ar^{8+}

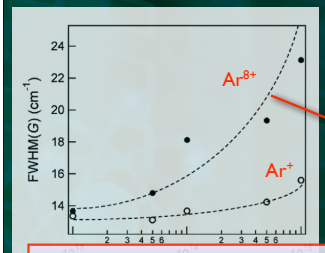


For Ar^{+} irradiation, *I(D)/(G)* increases linearly with the increasing of $\phi^{1/2}$.

Ar^{+} irradiation induces the vacancy formation.

The defects introduced by Ar^{8+} irradiation are NOT simple vacancies BUT some defect complex.

FWHM(G) vs ion flucence



FWHM(G) increases when the clustering of vacancies starts in graphite.

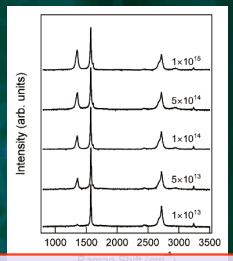
FWHM(G) increases rapidly for Ar^{8+} irradiation.

The irradiation-induced defects for Ar^{8+} must be vacancy clusters.

Formation of vacancy clusters (singly charged ion)

- In case of Ar^{+} irradiation, the formation of the vacancy clusters is followed by the amorphization of graphite, because the clustering occurs as a result of the overlap of the cascades for the direction parallel to the surface.

Formation of vacancy clusters (Highly charged ion)



Enough intensity

Sharp peak

Amorphization does not occur for Ar^{8+} irradiation

Summary of Raman spctroscopic measurements

- The defects introduced by Ar^{8+} impacts is NOT simple vacancies as is the case of Ar^{+} impacts but vacancy clusters.
- Second-order Raman features retained enough intensity and sharpness against Ar^{8+} irradiation in spite of the formation of vacancy clusters which leads to the amorphization for Ar^{+} irradiation.

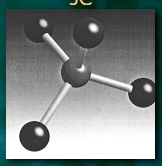
Summary of Raman spctroscopic measurements

- The defects introduced by Ar^{8+} impacts is NOT simple vacancies as is the case of Ar^{+} impacts but vacancy clusters.
- Second-order Raman features retained enough intensity and sharpness against Ar^{8+} irradiation in spite of the formation of vacancy clusters which leads to the amorphization for Ar^{+} irradiation.

Defects formation by Ar^{8+}

Energy gap vs number of carbon atoms

5C

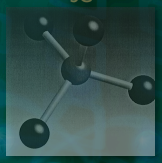


HOMO = −4.284 eV
LUMO = 9.407 eV

Eg = 13.691 eV

Energy gap vs number of carbon atoms

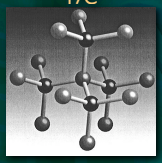
5C



HOMO = −4.284 eV
LUMO = 9.407 eV

Eg = 13.691 eV

17C

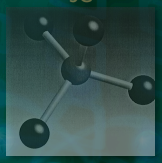


HOMO = −1.568 eV
LUMO = 6.558 eV

Eg = 8.126 eV

Energy gap vs number of carbon atoms

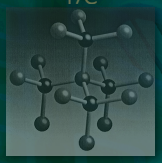
5C



HOMO = −4.284 eV
LUMO = 9.407 eV

Eg = 13.691 eV

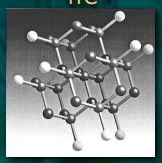
17C



HOMO = −1.568 eV
LUMO = 6.558 eV

Eg = 8.126 eV

41C

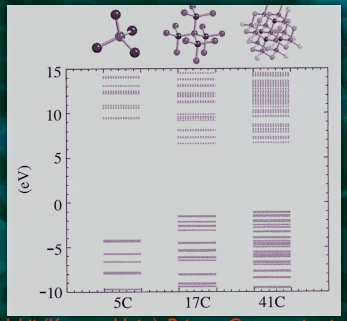


HOMO = −1.166 eV
LUMO = 6.597 eV

Eg = 7.763 eV

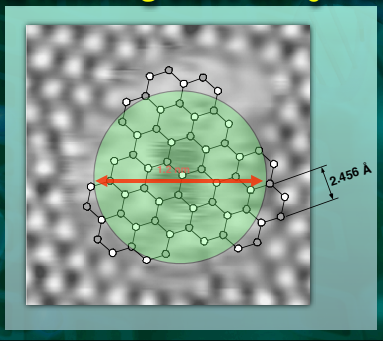
Symmetric diamond structures show LARGE energy gap

Energy gap vs number of carbon atoms

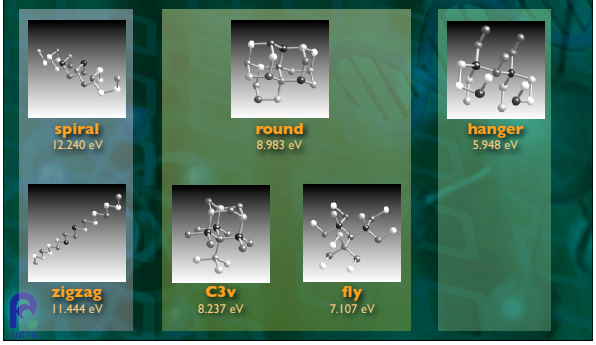


T. Ishii (Kagawa Univ.), Private Communication.

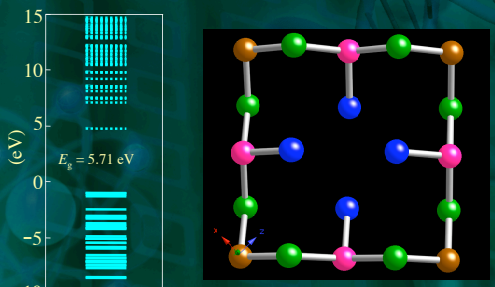
Complex structure formed by Ar^{8+} impact and the following electron injection



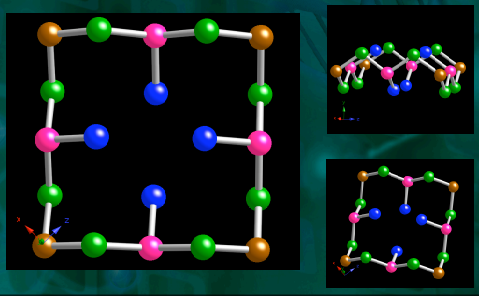
sp^3 cluster models with 20 carbon atoms



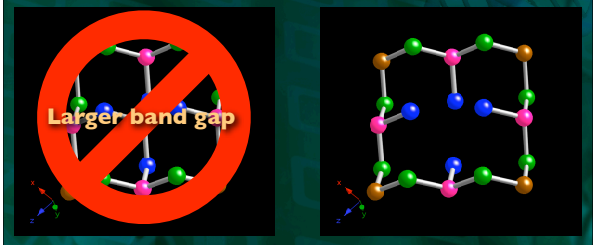
Band gap of S4 cluster



C_{20} cluster (S4)

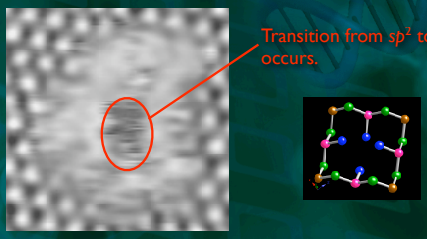


S4 cluster



Defects formation by Ar^{8+}

Structure of HCl impact region

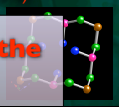


Plausible structure of the impact region

Structure of HCI impact region

Vacancy clusters are formed at the impact region

Transition from sp^2 to sp^3 occurs. (Defective structure)



Vacancy formation is the key process

Why the transition from sp^2 to sp^3 occurs?

From graphite to diamond ?

- From an *ab-initio* calculation for the core-excited states in diamond and graphite, the transition barrier from graphite to diamond becomes zero with core excitation or doping of multiple holes in graphite.

Univ. of Tokyo/Prof. Watanabe,
Osaka Univ./Prof. Yoshida

Multiple holes generated by HCI induces the transition from graphite to diamond?

- Generation of multiple holes at the graphite surface by approach of HCI
- Multiple hole generation reduces the transition barrier from graphite to diamond
- Transition from sp^2 to sp^3 occurs

When the slow HCI approaches to the graphite surface,

Large Coulomb potential of HCI induces ...

... the generation of multiple holes,
Reduction of the transition barrier from graphite to diamond.

... and, the formation of vacancy (cluster).
Generation of the low band gap structure.

Why the electron injection process is necessary to form nanodiamond ?

- Direct collision of ion affects the nano-diamond structure ?

New approach

Suppress the effect of direct collision.

(Low K.E. condition)

↓

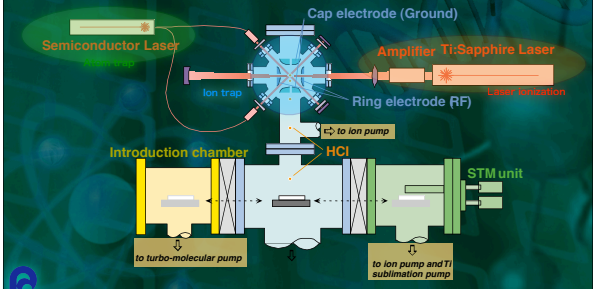
Extremely slow HCI

Generation of extremely slow HCI

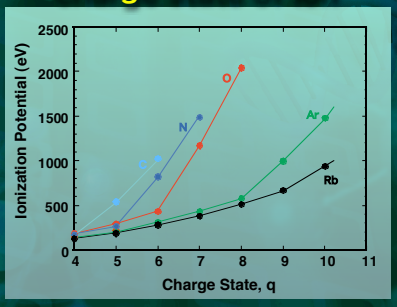
(collaboration with Prof. Kumagai & Dr. Matsuo)

Atom cooling by MO trap
+
Laser ionization by high power laser
+
Ion capture by RF trap
+
In situ STM observation

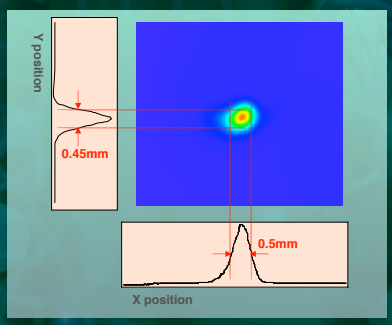
Extremely slow HCI generation using multi-trap system



Ionization potential vs charge state of ion

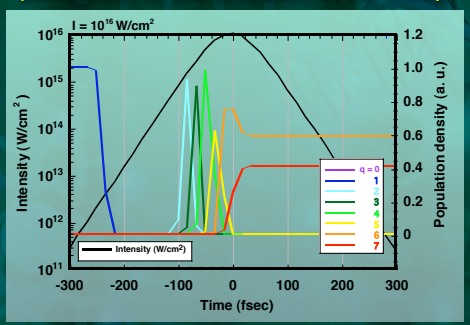


Rb atoms in the MO trap system

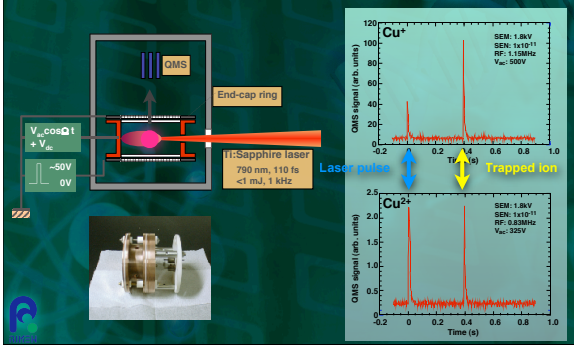


Laser ionization

(Simulation of the ionization of Rb atom)



Ion capture by RF trap system



Summary

- Ar^{8+} impact and the electron injection creates non-conductive sp^3 region on graphite.
- After the hydrogen treatment, the impact region shows the field emission tendency similar to the CVD diamond film.
- Band gap of S4 cluster shows a good agreement with the experimental results.
- From the Raman spectroscopy, vacancy clusters are formed by the Ar^{8+} impact.

Collaboration

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Great Thanks

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