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Nano-scale Surface Modification of Materials with Slow, Highly Charged Ion Beams

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Abstract

Some results on surface modification of Si and graphite with highly charged ions (HCIs) are presented. Modified surfaces were observed using scanning tunneling microscopy. Crater-like structure with a diameter in nm region is formed on a Si(111)-(7x7) surface by the incidence of a single HCI. The protrusion structure is formed on a highly oriented pyrolytic graphite surface on the other hand, and the structure becomes an active site for molecular adsorption. A new, intense HCI source and an experimental apparatus are under development in order to process and observe aligned nanostructures created by the impact of collimated HCI beam.

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1. Introduction

The interaction of slow, highly charged ion (HCI) with solid surfaces induces emission of X-rays, hundreds of secondary electrons and various kinds of particles, and traces of HCI impact in nanometer scale are created as a consequence of the deposition of large potential energy in HCIs. We have measured secondary ions from the surfaces of clean and hydrogen-terminated Si, and SiO_2 thin film on Si substrate, and also observed surface structure of these samples after HCI irradiation. Mass spectra of secondary ions emitted by the irradiation of HCIs exhibited unique characteristics of HCI interaction; secondary ion yield increases with the charge state approaching almost unity for highest charge states (e.g. I^{50+}), and the yield of Si and O ions as a function of the potential energy of incident HCI obeys the Coulomb explosion model [1]. The secondary electron yield associated with single HCI injection is so huge that the injection event could be recognized by monitoring the emission of secondary electrons without exception. STM observations and Raman spectroscopy in the modified structure of highly oriented pyrolytic graphite (HOPG) surfaces by the injection of HCIs have been performed [2]. We have also demonstrated the advantage of HCI over the application for single-ion implantation technique [3].

In the present paper, surface structures of Si(111)-(7x7) and HOPG irradiated with iodine HCIs were observed by a scanning tunneling microscope (STM). A newly developed experimental apparatus for nano-fabrication using HCI is also briefly described.

2. Experimental

2-1. Ion sources

Electron beam ion trap (EBIT) or electron beam ion source (EBIS) is a typical ion source for producing HCIs in very high charge states. An EBIS/EBIT comprises an electron gun that emits electron current in the order of 100mA, drift tubes for the storage of HCIs, an electron collector, and superconducting magnet that compresses electron beam at the central drift tube. Using electron beam with the acceleration voltage of 10 – 100 kV and current density of the order of 1000A/cm^2, atoms are ionized repeatedly by an electron impact inside drift tubes. Repeated electron impact also increases the kinetic energy of HCIs produced and stored inside the drift tubes, then the HCIs with excess kinetic energy surmount potential barrier and are extracted with the extraction voltage of 2-3 kV.

We have two ion sources for production of HCIs. One has an electron-beam ion trap (EBIT) arrangement[4] and installed at the University of Electro-communications (UEC). It has design parameters such as maximum electron beam energy of 300keV and electron current of 300mA. It produces 10^5 ions/s of e.g. I^{53+} or Bi^{83+}. The detail of design and performance is described elsewhere[5]. The other is an electron beam ion source (EBIS) recently developed at Kobe University, which is designed for the application of ion beam processing of materials so that it is constructed and operated easily without demanding expertise of EBIS using a separate, commercially available super-conducting (SC) magnet[6]. Maximum values of electron beam energy and electron current are 40keV and 300mA, respectively. The length of drift tube region is 20cm, which is an intermediate value between traditional EBIS (~1m) and EBIT(3cm) devices.

We note on improvements performed on the design structure shown in the earlier publications [6-8] in order to achieve target specifications. We found some errors in the calculation of magnetic field distribution, which revealed magnetic shields at electron gun and collector did not function sufficiently, then the electron gun was moved away from the SC magnet by 9cm and the magnetic shield at collector was reconstructed with thicker shield structure and stronger ceramic supports. The aperture sizes of the suppressor and extractor electrodes were choked in order to suppress the return current of electron beam toward the electron gun. Maximum electron-current increased from 20mA to 180mA by these improvements. The intensity of HCIs produced by the EBIS is in the order of 10^8 ions/s, however, the charge state distribution is peaked at lower charge states (e.g. Ar^{11+}) due to relatively high base pressure during operation in the drift tube region (~$1x10^{-7}$ Pa). We are planning to cool the drift tube electrodes by a closed-cycle refrigerator to improve the charge-state distribution.

2-2. Experimental apparatus using HCI beams

The experimental results shown in the present paper are obtained using the EBIT at the UEC. The HCIs of iodine were extracted with the leaky mode operation from the EBIT and their charge states were selected by using a sector magnet. The kinetic energy of HCIs (I^{q+}) is 3 x q keV for the present experiments. A collision chamber with base pressure of $2x10^{-8}$ Pa was connected to an observation chamber equipped with an STM apparatus [9,10]. The sample irradiated with HCIs was transported between the chambers in the vacuum. Before HCI-bombardments, the well-defined surfaces of the samples were prepared with standard cleaning procedures, and confirmed by the STM images. For HOPG surfaces after irradiation, dye molecules (Bis- MSB) were deposited using a Knudsen-Cell. The average thickness of deposited layers was 1nm as monitored with a quartz microbalance. The sample was annealed at 100^oC after the deposition. All of the STM images were observed at room temperature.

Formation of periodic structure created by the irradiation of single HCI would be intelligible demonstration in order to display the characteristics of HCI on the application for nano-processes. We have developed an apparatus to process a sample with periodically arranged traces of HCI irradiation at Kobe University. The periodic structure will be formed using a mask with small holes (the diameter is less than 100nm) made of a thin film of SiO_2. The apparatus comprises an electrostatic deceleration lens system, a sample preparation chamber and a UHV-STM. The preparation chamber has LEED optics, a sputter ion gun and a 7-axes goniometer, as shown in Fig.1, with which the position of the base plate that supports the mask and sample is adjustable with respect to the incident HCI beam with degrees of freedom of XYZ translation and rotation around Z-axis. The goniometer also equips an XY stage driven by piezoelectric motors (Nanomotion Ltd.) for precise translation of the mask against the sample with the resolution of 50-100nm. The sample is also vertically transferable over 20cm between the LEED observation level and HCI beam level.

3. Results and Discussion

Figure 2 shows a STM image and depth profile of the crater-like structure created by the impact of a single I^{50+} HCI on the Si(111)-(7x7) surface. The dark domain indicates the removal of topmost layers, and it has an area of $5.5nm^2$ and the maximum depth is ~0.35nm. Similar measurements of removed volume for different charge states ($30 \leq q \leq 50$) resulted in the outstanding q-dependence; the volume sharply increases with the charge of incident ion. In other words, the size of crater is controllable with the incident charge q. The mechanism of sputtering of Si atoms could be discussed by an analysis on ion charge dependence of sputtered volume and quantity of emitted secondary ions. The detailed description of the discussion will appear in a separate publication [11].

An example for selective adsorption of molecules at the impact sites is exhibited in Fig. 3. Figure 3(A) is a STM image of HOPG surface after the irradiation of I^{30+} HCIs showing many dots with protruding structure randomly sprinkled over the surface. The size of dots is few nm. A STM image after the deposition of Bis-MSB molecules over the HCI-irradiated surface is shown in Fig.3(B). The size of sprinkled islands is increased to ~10nm compared to Fig. 3(A), that means the Bis-MSB molecules condense at the traces of HCI injection, since a Bis-MSB molecule has elongated structure with the length of ~2 nm. The present results mean that the irradiation of HCI creates active nano-spots on an inert substrate, that is, HCI is utilized for the production of functional material with nanometer size. The irradiation of singly charged ions may be able to form active spots, however, production efficiency estimated from Raman peak intensity for certain fluence is much smaller than those of HCI impact [2], and we cannot definitely monitor the incidence of singly charged ion by detecting secondary electrons. The advantage of HCI is that the incidence is recognized certainly due to the large secondary electron yield [3].

Acknowledgments

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Figure captions

Fig.1 A 7-axes goniometer for positioning a screening mask of incident ions and a sample holder independently with respect to the incident HCI beam. (The mask is not mounted in the picture.) The base stage supporting the mask and sample is movable for XYZ directions and rotatable around Z-axis. The XY stage mounted on the base stage enables translation of the mask.

Fig. 2 A STM image (A) and depth profile (B) of crater-like structure created by the impact of a single I^{50+} HCI on the Si(111)-(7x7) surface.

Fig. 3 (A) A STM image of HOPG after the irradiation of I^{30+} HCIs. (B) A STM image after vapor deposition of Bis-MSB molecules over the surface HOPG after the irradiation of HCIs.

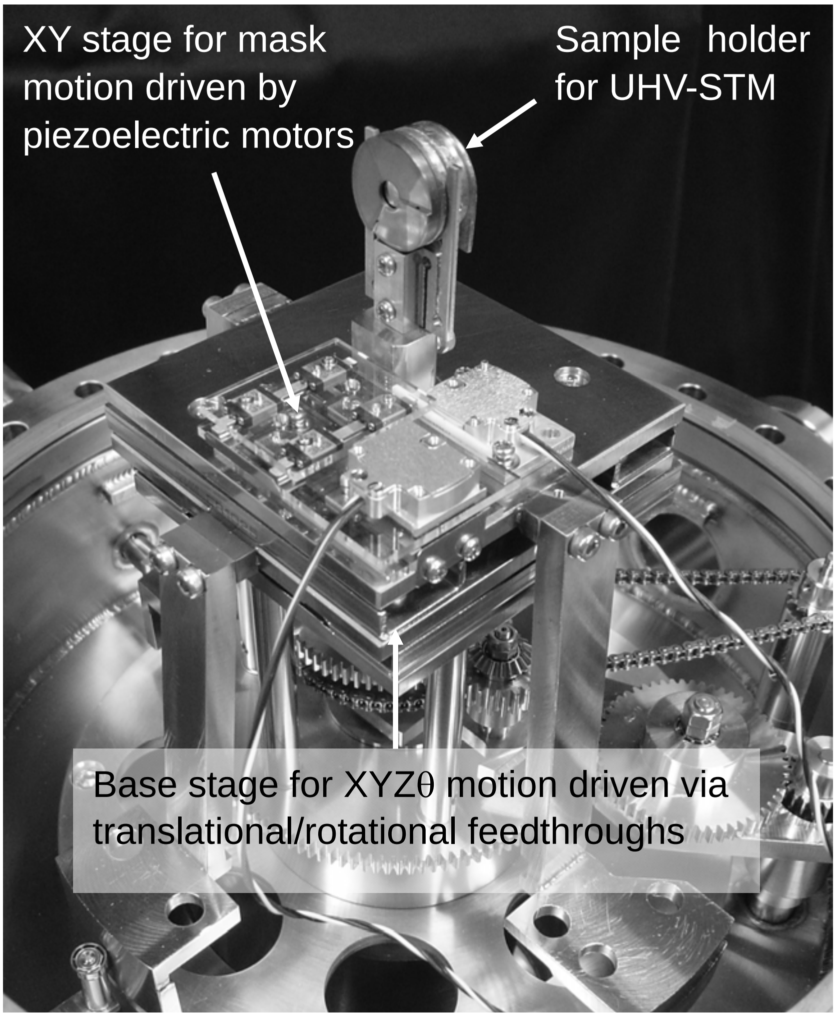

Fig. 1 Sakurai *et al*.

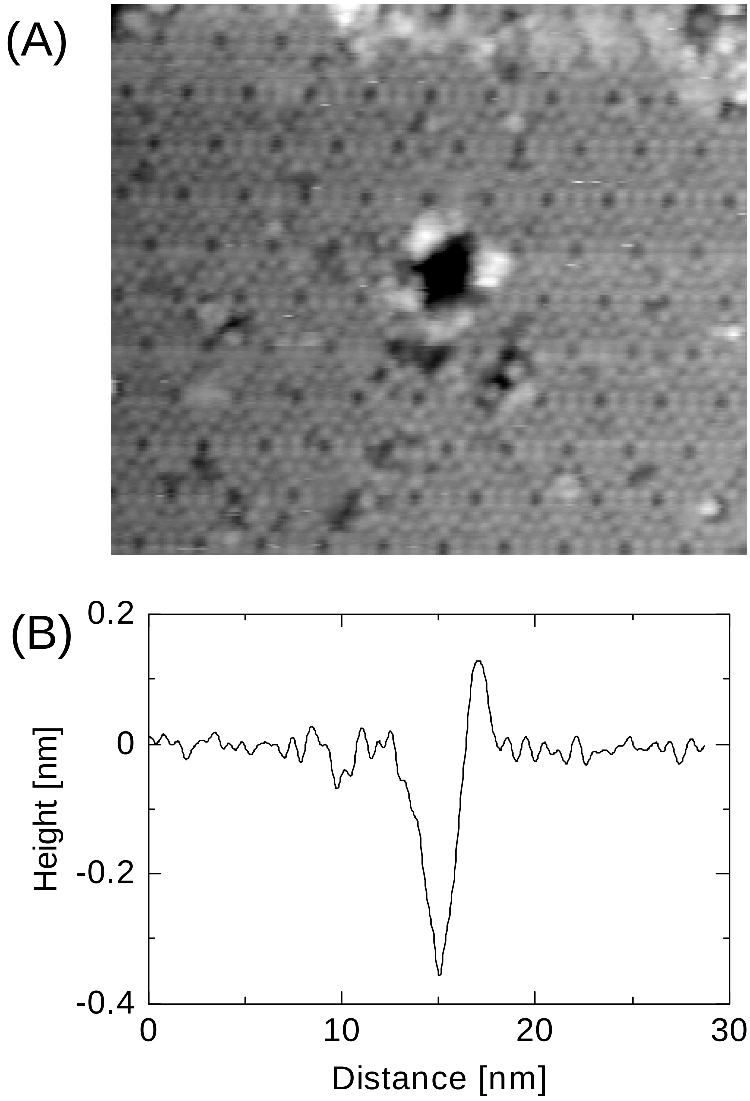

Fig. 2 Sakurai *et al.*

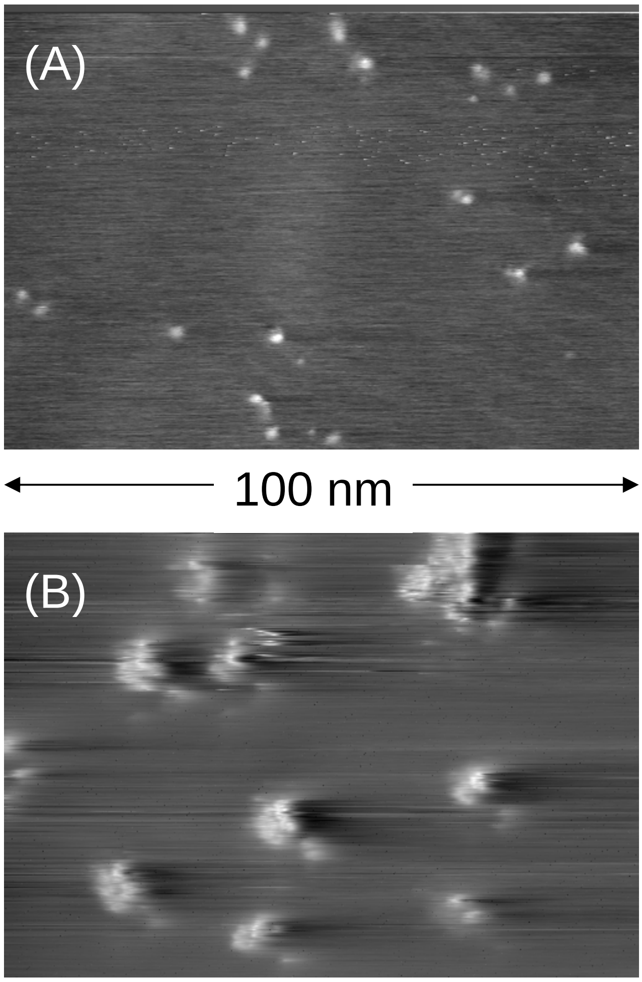

Fig. 3 Sakurai *et al*.