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Observation of HCI-induced nanostructures with a scanning probe microscope

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Abstract. We present scanning tunneling microscope (STM) images, atomically resolved, of the nanostructures on various kinds of surfaces bombarded with highly charged ions (HCIs). In the STM image of a highly oriented pyrolytic graphite surface (Xe^{29+}-impact), a protrusion structure was observed with $\sqrt{3} \times \sqrt{3}\ R30^\circ$ surface reconstruction around the impact site. A crater-like structure was formed on a Si(111)-(7×7) surface by an I^{50+}-HCI impact. An atomic image of ∼ 0.1 nm in height was also observed around the missing topmost layers of the crater. In the case of a TiO_2(110) surface, a typical nanostructure induced by a single I^{51+}-HCI impact, relatively larger crater structure than that on the Si surface was observed; the height (∼1 nm) was higher than the atomic step of the TiO_2(110)-(1×1) surface (∼0.3 nm) and the depth reached at least 1.5 nm. This implies that the degree of the HCI-radiation effect on the TiO_2 surface is higher than that of the Si(111) case.

1. Introduction

A highly charged ion (HCI) reacts intensely with matter through deposition of its large potential energy E_p. In the collision of a HCI with a solid, such a reaction begins with transition of many electrons from a nanometer sized area of the surface to high Rydberg states of the HCI [1, 2, 3]. As a result, the interaction region is depleted and its electronic system is highly excited due to the dissipation processes of the potential energy, such as the Auger deexcitation with high energy electron emission, which induce dramatic radiation effects including nano-structure formation on surfaces [4, 5, 6], high-yield secondary electron emission [7] and cluster ion emission [8]. This effect is thought to be essentially different from that induced by irradiation of energetic neutrals and singly charged ions, where the kinetic energy of the primary particle plays a major role.

In order to understand the relaxation process of a HCI interacting with a surface, it is important to know E_p-dissipation channels. Recently we observed X-ray emission yields from I^{q+}-HCI colliding with a surface [9]. An important part of E_p is lost by X-ray emission; 30% to 40% of E_p for I^{52+} (H-like) and I^{53+} (bare ion) was measured to be dissipated mainly by K X-ray emissions. We show here results of observation of the morphological change in the surface structure due to E_p-deposition. It is expected that such a change depends strongly on the

electronic structure of the target material because electrons captured to the HCI are generally fed from the conduction and valence bands. Therefore we have obtained scanning tunneling microscope (STM) images atomically resolved of the HCI-induced nanostructures on surfaces of the following target materials with different electronic properties; highly oriented pyrolytic graphite (HOPG), Si(111) and TiO_2(110). HOPG has the layered structure with the sp^2 orbitals while Si has the diamond structure with sp^3 orbitals but they are completely covalent crystals. TiO_2 is of the rutile structure having the ionic character of about 60%.

2. Experimental

HCIs were produced in an electron beam ion trap (EBIT) at the University of Electro-Communications [10]. The HCIs having $3\times q$ keV of kinetic energy were extracted from the EBIT in leaky mode and their charge states were selected by using a sector magnet. A collision chamber (base pressure: 2×10^{-8} Pa) was connected to an observation chamber equipped with an STM apparatus [11, 12]. 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 the following procedures, and confirmed by STM. A clean surface of HOPG was prepared by cleaving with an adhesive tape in air, and the sample was installed immediately into the chamber. A Si(111)-(7×7) reconstructed surface was obtained by the normal flashing procedure in which the substrate was heated up to 1250 °C. A TiO_2(110) surface was sputtered with 2 keV Xe^+ ion beam (3 μA) for 5 minutes and then the substrate was annealed for ten minutes by radiative heating with a Ta foil whose temperature was set to 1500 °C. The cycle of sputtering and annealing procedures was repeated until an atomically flat surface was obtained.

3. Results and discussion

Figure 1 (A) shows a typical STM image of the impact site on the HOPG surface bombarded with a single Xe^{29+}-HCI. The protrusion structure is seen in the atomic image of carbons aligned regularly whose spacing is 0.25 nm. While the diameter of this structure is ∼4 nm, the height is only ∼0.3 nm which is nearly equal to the spacing of the carbon layers (0.34 nm). It was found from Raman spectroscopy and secondary ion mass spectrometry that the structure contains a lot of defects which are not only single and dimer vacancies but also cluster-size vacancies [13, 14].

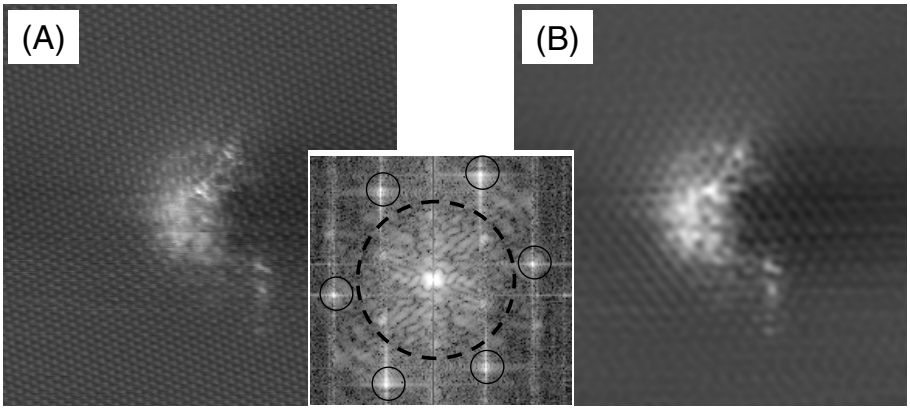

Figure 1. (A) A typical STM image of the nanostructure on the HOPG surface induced by a single Xe^{29+} impact. The inset between (A) and (B) demonstrates the result from FFT of the image (A). (B) The image was obtained by inverse FFT process of the region within the dashed circles.

The inset between Figs. (A) and (B) shows the result from fast Fourier transform (FFT) of the image (A). It is found that, in addition to the diffraction spots from the undisordered lattice as shown by six solid circles, the diffraction spots with long range order appear in the dashed circle. The image (B) was reproduced by inverse FFT of the region enclosed with the dashed circle. It is to be noted that the long range structure appears only around the impact site, which corresponds to $\sqrt{3} \times \sqrt{3}\ R30^\circ$ surface reconstruction.

Figure 2 (A) shows an STM image of the Si(111)-(7×7) surface bombarded with an I^{50+}-HCI. "Corner holes" and "adatoms" of the DAS (Dimer-Adatom-Stacking fault) structure [15] are visible as regularly aligned black- and bright-spots, respectively. An HCI-impact site is seen as the deep crater structures at the center of the image, in addition to several native defects due to missing adatoms or adsorption spots of residual gas molecules in the chamber which is seen as darker sites than the adatom spots. The area of the missing adatoms is approximately 6 nm^2 which implies that about 10 adatoms were removed in this case. Although a measured depth-profile cannot be determined precisely, because it depends on the tip shape, we observed that the depth of this crater is at least 0.35 nm, nearly the same as the height of one step of the DAS structure. The crater has the brighter edges around the missing topmost layer. The height of the site is measured to be ∼0.1 nm, which would have been caused by adsorption of Si atoms that were not sputtered away but moved from initial lattice positions.

Figure 2 (B) shows an STM image of the TiO_2 surface bombarded with an I^{51+}-HCI. The inset represents the close-up image of the unbombarded portion in which we can see the atomic structure of TiO_2(110)-(1×1) surface as bright and dark rows being parallel to the [001] direction [16]. The spacing of the rows is about 0.6 nm. A typical impact site on this surface shows the "caldera" structure having the relatively high outer rim of the crater. The maximum height reaches ∼1 nm which is higher than that single atomic step of this surface (=∼0.3 nm) and the depth is measured to be 1.5 nm at least. This result implies that the degree of the HCI-radiation effect on the TiO_2 surface would be higher than that of the Si(111) case.

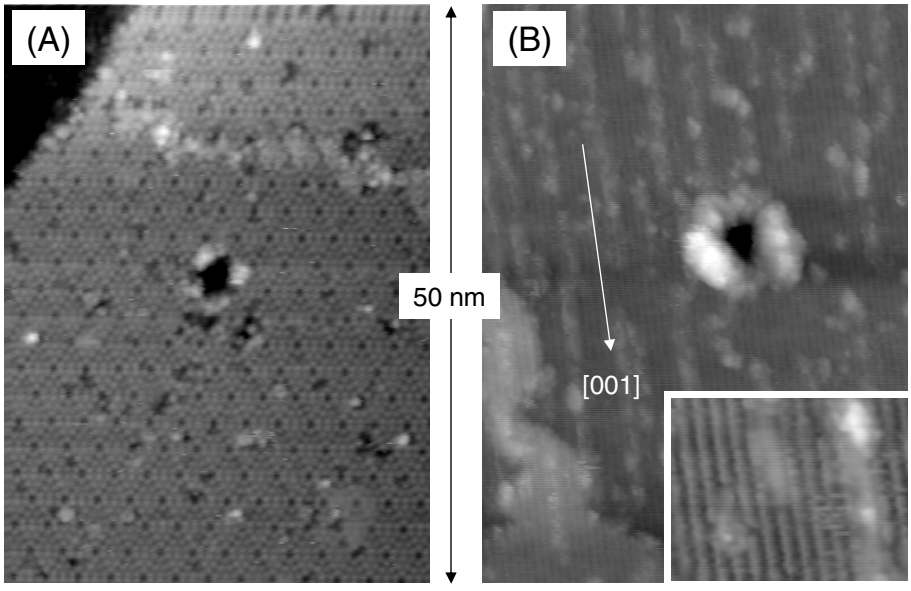

Figure 2. (A) A typical STM image of the crater structure on the Si(111)-(7×7) surface bombarded with an I^{50+} HCI. (B) An STM image of the TiO_2 surface bombarded with an I^{51+}-HCI. The inset shows the close-up image of the unirradiated portion in which the atomic structure can be seen as bright and dark rows.

It should be noted that the STM image does not show the topography directly but shows the electron density of state on the surface. This leads often to a misunderstanding of the fine surface structure although relatively large surface structures such as a step can be correctly observed. Indeed, it is considered that although the oxide row of the TiO_2(110)-(1×1) surface, so called the "bridging oxide", is the topmost atoms, its STM image is seen as the darker line than that of the Ti row (see the inset of Fig. 2 (B)) [16]. An atomic force microscope (AFM) is suitable for observing topographic structures although it is difficult to obtain high resolution images with the AFM technique as compared with the STM method. Terada *et al*. [17] reported that the STM images of Xe^{46+}-impact sites on an HOPG surface show sizes similar to those obtained with the AFM method where the step edge of graphite observed with the STM is much sharper than that with the AFM. In order to confirm whether the STM images of the impact sites reflect the surface topography, we observed the I^{51+}-bombarded TiO_2 surface by using an AFM. In the preliminary observation, an AFM image of the impact site showed the hillock-type structure. We consider that the AFM image might have been convoluted with the AFM tip shape structure having a ∼20 nm curvature and, as a result, the "caldera" structure would be shown as the hillock. By using a well advanced AFM technique, we are going to observe the fine surface structure of HCI-impact sites on not only TiO_2 but also completely ionic materials such as LiF.

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