Surface Processes of Highly Charged Ions

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Abstract. Striking features of radiation effects by a highly charged ion (HCI) impact onto a surface are shown. The HCI-impact effects depend strongly on the electronic property of the target material and are restricted within the nanometer-sized area on the surface. Further, a challenging experiment for application of HCI-based nano-processing is presented. One of the examples for the processing can be seen in the interaction of a HCI with a hydrogen-terminated Si surface. We try to produce a SiO nano-structure on the Si surface with a chemical reaction of oxygen molecules to the active region induced by individual HCI impacts.

1. Introduction
A highly charged ion (HCI) is one of the most active particles reacting violently with the matter, e.g., electron, atom, molecule, cluster and solid surface. An electron beam ion trap (EBIT) is a useful device for investigating these reactions. An EBIT can not only trap efficiently HCIs with very high charge state but also extract the slow HCI-beam with low emittance. By using the Tokyo-EBIT facility [1] at the university of Electro-Communications, two kinds of research projects are going on, one is for atomic physics and the other is for surface science and technology. Representative research subjects in atomic physics are to reveal the Quantum electrodynamic (QED) and the relativistic effects, observed in resonant interaction between electrons and HCIs of heavy elements having few electrons [2, 3]. For the surface experiments, on the other hand, the mechanism of the interaction of slow HCIs with a surface is investigated by measuring secondary emission yields of various kinds, such as X-rays [4, 5, 6], visible photons [7] and ions [8], and by observing surface modification induced by individual HCI impacts [9, 10, 11].

In this article, we show a few limited results in the recent surface experiments. HCI-surface reaction is triggered by multiple electron transfer from the surface to the approaching HCI. The slow incident ion has sufficient time for capturing many electrons before arriving at the surface. The electronic system of the surface is, in turn, excited through this process. Consequently, dramatic radiation effects such as secondary ion and neutral emission, excitation of plasmons and excitons, and dislocation of surface atoms are induced. Since the charge transfer cross-section increases rapidly with incident ion charge q, these effects would be enhanced in a higher-q HCI impact. The mechanism of these phenomena is considered to be essentially different from that induced by energetic neutrals and singly charged ions where the kinetic energy of the primary particles plays a major role.

It is considered that the radiation effects are induced in close relation to the electronic property of a target material because of the strong coupling of the incident HCI with target...
electrons. The surface density of active electrons is thought to be one of the most important parameters for governing the degree of the effects. Accordingly, we investigate the HCI-induced surface modification for various kinds of target materials: gold (metal), silicon (semiconductor) and TiO\(_2\) (oxide), using a scanning tunneling microscope (STM). The observation reveals that the HCI-surface reaction is restricted within the nanometer-sized area on the surface. This result suggests that the individual HCI impacts could be applied to nano-processing. Here, the preliminary result of the processing to produce a SiO nano-structure on a hydrogen-terminated silicon surface is presented.

2. Experimental

Iodine HCIs, I\(^{q+}\), having \(3 \times q\) keV of kinetic energy were extracted from the Tokyo-EBIT and their charge states were selected by using a sector magnet. A collision chamber (base pressure: \(2 \times 10^{-8}\) Pa) was connected to an observation chamber equipped with a STM apparatus [12, 13]. The sample irradiated with HCIs was transported between the chambers in the vacuum. Before HCI irradiation, clean, well-defined surfaces were prepared by the ordinary methods: a repetition of annealing and ion-sputtering procedures was employed for Au(111) and TiO\(_2\)(110) surfaces, and a repetition of flashing procedures was for clean Si(111)-(7\(\times\)7) and Si(100)-(2\(\times\)1) surfaces. A hydrogen-terminated Si(100) -(2\(\times\)1) surface was obtained with exposure of atomic hydrogen to a clean Si (100) surface.

3. Results and discussion

Figure 1 shows typical STM images of Au(111), Si(111), Si(100) and TiO\(_2\)(110) surfaces irradiated with I\(^{50+}\). Each observation is performed in the high resolution so that the atomic surface structure can be seen. For the gold surface (metal target), no impact site is found although the irradiated area is carefully observed. Further, in a secondary ion mass spectrometry (SIMS) measurement for the surface, the yield of sputtered Au\(^+\) is so weak that no clear peak of Au\(^+\) appears in the SIMS spectrum. In a recent report for observation of dislocations on a gold surface bombarded with Xe\(^q+\) (\(q < 45\)) [14], it was concluded that nanometer sized...
structures were created by the nuclear stopping power of the primary ions rather than by the multiple electron transfer, that is, no $q$-dependence was observed. These results suggest that the radiation effect by individual HCl impacts is very week for the gold surface in which conduction electrons can rapidly compensate a depletion site created by the multiple electron transfer.

For the Si surfaces (semiconductor target), an HCl-impact site is seen as the deep crater structure at the center of each image, in addition to several small native defects due to missing surface atoms or adsorption spots of residual gas molecules in the chamber. The crater sizes are nearly the same for the both surfaces: the area of crater is approximately 6 nm$^2$ and the depth is at least 0.3 nm. In our previous work [10], it was revealed that the HCl-radiation effects were enhanced with $q$ on a Si(111)-(7×7) surface by individual HCl impacts ($P^+$, $q \geq 30$). For the TiO$_2$ surface (oxide target), a typical impact site shows the “caldera” structure having the relatively high outer rim of the crater. The maximum height reaches $\sim$1 nm which is higher than that single atomic step of this surface ($=\sim0.3$ nm) and the depth is measured to be 1.5 nm at least. The STM observation shows the created impact site on the TiO$_2$ surface is much larger than that on the Si surface. Further, it was found from previous SIMS measurements for these surfaces [10, 11] that the secondary ion emission yield from TiO$_2$ is also larger than that from Si. From these results we could conclude that the degree of the HCl-radiation effect on the TiO$_2$ surface is higher than that of the Si surfaces.

As seen Fig. 1, nano-structures on the Si surfaces are created following that large amount of surface atoms are sputtered by individual HCl impacts. This result is very important for application of the HCl-beam to the nano-processing. One of the examples of the processing can be seen in the interaction of a HCl with a hydrogen-terminated Si (Si-H) surface. The Si-H surface is chemically stable because dangling bonds of Si atoms are fully terminated by hydrogen atoms. The nanometer sized crater structure might become an active region by removal of many hydrogen adsorbates and appearance of open valence bonds on the impact site. This implies that Si-O nano-structure can be created through selective reactions of oxygen gas with this active region.

![Figure 1. Nano-structure on a Si(100)-(2×1)-H surface by the I$^{44+}$ bombardment. The HCl irradiation was performed with O$_2$ gas exposure.](image)

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Figure 2 shows a nano-structure on a Si(100)-(2×1)-H surface by the I^{44+} bombardment. HCI irradiation was performed under the condition that partial pressure of O_2 gas was 2×10^{-6} Pa and irradiation time was 4 hours. The surface atomic structure of dimer lines can be seen in this image, which is kept although O_2 gas was exposed more than several hundreds Langmuir to the surface. On the other hand, this structure cannot be seen on the H-removal region at the impact site, which is instantly contaminated by O_2 gas with a high sticking probability [15]. The impact site with several nanometers in diameter would contain Si-O_x bondings formed by the surface chemical reaction. The same nano-structure can be produce by using STM where a pulse current is injected from the STM tip into a nano-portion to sputter hydrogens [16].

The HCI-processing has an advantage that the nano-structure can be efficiently produced on the semiconductor substrate with high density (>10^{11} structures/cm^2). Physical and chemical properties of this nano-structure are being investigated with electron energy loss spectroscopy, FTIR spectroscopy and scanning tunneling spectroscopy.

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