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Secondary ion emission from a water and fluorine adsorbed Si(1 0 0) surface irradiated with electrons and highly charged ions

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Abstract

Secondary ion emission phenomena from a water and fluorine adsorbed Si(1 0 0) surface irradiated with electrons and highly charged ions (HCIs) were studied. In the case of HCI impact ($400 \text{ eV}/q \text{ Ar}^{q+}$, $4 \leq q \leq 8$), H^+ and F^+ ions were detected in addition to $\text{Si}(\text{H})^+$ and SiOH^+ ions resulted from a kinetic energy transfer. The yields of H^+ and F^+ , which were also observed in the case of electron impact, increased with q like q^γ ($\gamma \sim 3$). This is the first paper reporting a strong charge state dependence of heavy adsorbate yields when slow HCIs bombard a well-defined surface covered with adsorbate.

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1. Introduction

Emission phenomena of secondary ions induced with singly charged ions and electrons are widely applied in the field of surface analysis, e.g. elemental and structural analyses of adsorbed surfaces. In the case of singly charged ion irradiation, secondary ions consisting of substrate and adsorbate are sputtered as a result of kinetic energy

transfer. On the other hand, in the case of electron stimulated desorption (ESD), secondary ions are desorbed via electronic transition. In such a case, ionized atoms originated from adsorbate are effectively emitted compared to substrate materials, i.e. ESD is effective to the elemental analysis of the adsorbates. Furthermore observation of angular distribution of desorbing ions is known to give information on the structure of adsorbed state [1].

Highly charged ions (HCIs) with low kinetic energy could evoke secondary ion emission resulted from potential energy transfer, which was expected to make slow HCIs a new tool of high-sensitivity elemental analysis and surface modification [2]. These expectations have promoted studies of HCI induced secondary particle emission

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from surface adsorbates [3–8] and from substrate materials [2,9–13].

In the case of HCl impact on an untreated CuO target containing hydrogen as an impurity, it was found that (1) the H^+ yields were proportional to q^γ ($\gamma \sim 5$) and (2) H^+ exhibited narrow kinetic energy distribution peaking at a few eV [3]. The observation was explained by a formation of two-hole state of a hydrogen-contained chemical bond produced by resonant electron transfers to HClIs [14] and the subsequent H^+ emission due to Coulomb repulsion (pair-wise bond-breaking model) [4]. The pair-wise bond-breaking model is in some sense analogous to Auger stimulated desorption (ASD) process [15] in the case of ESD, in which the ionization of core level followed by Auger transitions creates a two-hole final state leading to ion desorption. H^+ yield from a well-defined hydrogen terminated Si(100) surface has recently been reported [5,6], in which strong q dependence was again observed and explained with the pair-wise bond-breaking model. It is noted that analogy of sputtering mechanism between HCl impact and electron impact was also reported on a LiF target [11].

These experimental and theoretical works left interesting questions [6], e.g. whether angular distributions of desorbing ions in HCl- and electron-impacts are similar or not, and whether yields of well-defined heavier adsorbates than hydrogen display strong charge dependence. For these purposes, it is important to observe secondary ions from the same surface irradiated with HClIs and electrons. In the present report, we briefly describe the experimental setup and discuss similarities and differences between HCl- and electron-induced ion desorptions.

2. Experiment

The sample holder and the secondary ion detector are schematically drawn in Fig. 1. Slow HClIs were prepared by an electron beam ion source (EBIS) cooled with liquid nitrogen, which was kept at around 2×10^{-10} Torr during operation [16]. HClIs extracted from the EBIS were charge-state and mass-selected with a Wien-filter, periodically swept with a deflector to form a pulse

train of 50 ns width, and finally guided into the measurement chamber [5].

The sample holder was mounted on a rotational and linear feed-through at the center of the measurement chamber. In order to extract positively charged secondary ions effectively, the sample was biased positively and the mesh (2 mesh/mm) positioned 10 mm from the sample was grounded. The sample was held in a molybdenum plate of 0.5 mm thick with a rectangular window and sandwiched between a ceramic heater and a molybdenum thin plate of 0.2 mm thick with a rectangular window. At 140 mm from the sample, a two-dimensional position sensitive detector (2D-PSD) was mounted on a turntable, which could be rotated with the same axis as the sample holder. The 2D-PSD (active diameter of 42 mm- ϕ) consisted of a flat mesh shielding the electric field, a triple stage microchannel plate and a wedge-meander-strip inductive electrode with a germanium layer, which provides two-dimensional position (X and Y) and arrival time (t) of emitted ions. The initial energy and angle of emission were evaluated with these three quantities. As shown in Fig. 1, the impact angle θ was defined with respect to the surface normal at the moment of impact. The intensity of the HCl beam was monitored time to time by reflecting the ions to the 2D-PSD by applying a high voltage on the sample. The total dose of HClIs during measurements was less than $10^9/\text{cm}^2$, i.e. the beam induced surface modification is expected to be negligibly small. The measurement chamber was also equipped with an electron gun, with which ESD experiments could also be made. The typical pulse width was 20 ns.

The sample was cut from a B-doped Cz-grown Si(100) wafer (orientation accuracy $\pm 0.5^\circ$) with a resistivity of $18 \Omega\text{cm}$ and its size was $24 \times 14 \times 0.5 \text{ mm}^3$. Before insertion into the measurement chamber, the sample was chemically treated to protect the Si surface with a thin oxide layer [17]. The thin oxide layer was removed by heating the sample at 1170 K for 3 min by several times, which yielded a well-defined Si(100)-(2 \times 1) surface [17]. The temperature of the sample was monitored using an optical pyrometer. The measurement chamber was evacuated by a series of 500 and 70 l/s turbo molecular pumps and the base pressure

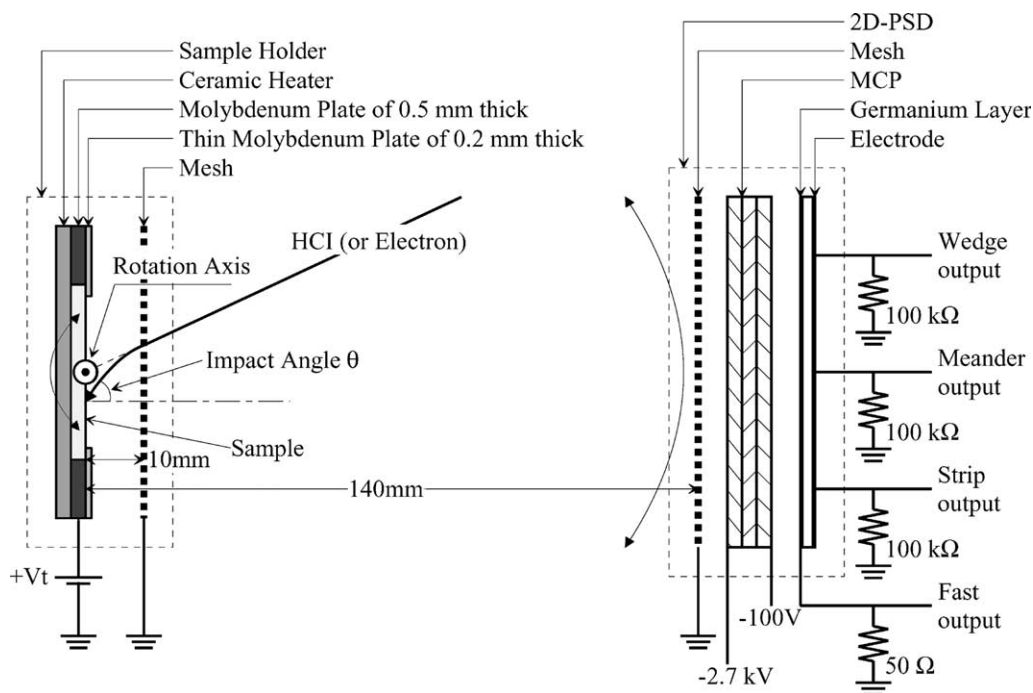


Fig. 1. A schematic drawing of the sample holder and the secondary ion detector. The sample holder and 2D-PSD could be independently rotated around the same rotation axis at the center of the measurement chamber.

was $\sim 1 \times 10^{-10}$ Torr after 72 h bake-out. A liquid-nitrogen-cooled shroud was used during the sample heating, which helped to keep the pressure better than 3×10^{-9} Torr. Major degassing components during the sample heating were H_2 and CO with a small amount of H_2O ($\sim 2 \times 10^{-10}$ Torr). The present study was carried out on the sample left in the background ambience after the above-mentioned treatment, i.e. no intentional introduction of adsorbate was made. Details of the data acquisition system are given elsewhere [5].

3. Results and discussion

3.1. Electron impact

A time of flight (TOF) spectrum of secondary particles emitted from the Si(100) surface irradiated with 450 eV pulsed electrons is shown in Fig. 2 (impact angle $\theta = 28^\circ$, target bias = 150 V). The position of the peak (a) was found to be inde-

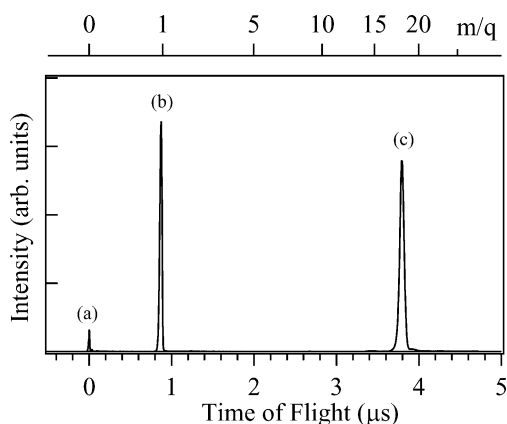


Fig. 2. A TOF spectrum of secondary particles emitted from the Si(100) surface irradiated with 450 eV electrons. Peaks (a), (b) and (c) correspond to photon, H^+ and F^+ ions, respectively.

pendent of the sample bias and accordingly is attributed to photons emitted when the pulsed electron hit the sample. Actually the width of the peak (a) is the same as the pulse width of the

electron beam. At the top of the figure, the axis of mass to charge ratio is given, which was derived assuming the initial velocity of secondary ions to be zero. It is seen that the peaks (b) and (c) were identified as H^+ and F^+ ions, respectively.

The origin of H is tentatively attributed to water molecules in the residual gas because of the following two reasons: (1) the angular distribution of H^+ was qualitatively the same as those reported previously from H_2O adsorbed Si(100) surface [18,19] and (2) H_2O is the only residual gas reactive on Si(100) surface. It is noted that (1) H_2O is dissociatively adsorbed on a Si(100) surface at the room temperature to form Si–H and Si–OH and (2) H^+ ions are dominantly emitted from the OH bond, which was confirmed by comparing H^+ emission from H_2O adsorbed Si(100) surfaces with monohydride Si(100) surfaces [18,19].

On the other hand, the origin of F^+ is not known. It has been reported that even when the amounts of fluorine was less than the detection limit of Auger electron spectroscopy, F^+ was detected in the ESD study [20,21]. An early theoretical work showed that $0.4e^-$ is transferred to the F atom from the Si atom in the same bond [22], i.e. Si–F covalent bond has a highly ionic character. In the case of ionic targets, ASD process [15] is known to play an important role: the ionization of core level, e.g. F 2s, followed by intra-atomic Auger transitions creates a two-hole state of fluorine.

The angular distribution of F^+ was also measured, showing that four peaks appeared along the crystallographic direction of the Si(100) surface, i.e. $[0\ 1\ 1]$ and $[0\ \bar{1}\ 1]$, which is consistent with previous ESD works on fluorine adsorbed Si(100) surfaces [20,21,23]. The surface condition was checked with this ESD experiment before and after the HCl irradiation, where the relative intensity of H^+ and F^+ ions to the photon signal as well as the angular distributions were confirmed to be unchanged.

3.2. HCl impact

Fig. 3(A) shows a TOF spectrum of secondary ions emitted from the Si(100) surface irradiated with $400\text{ eV}/q\text{ Ar}^{4+}$ (impact angle $\theta = 45^\circ$, target

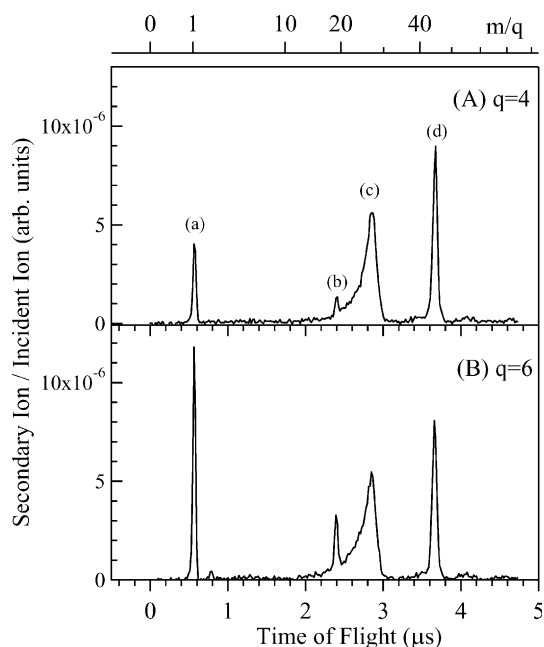


Fig. 3. TOF spectra of secondary ions emitted from the same Si(100) surface as used in Fig. 2 irradiated with (A) 1.6 keV Ar^{4+} ions and (B) 2.4 keV Ar^{6+} ions. Peaks (a), (b), (c) and (d) correspond to H^+ , F^+ , $Si(H)^+$ and $SiOH^+$ ions, respectively. Secondary ion yields were normalized to the number of incident HCIs.

bias = 400 V). It is seen that the photon peak detected during the ESD measurement was not observed. Then in order to determine the time zero, TOF spectra for more than three different sample biases were taken. At the top of the figure, the axis of mass to charge ratio thus determined is shown. In addition to the H^+ (peak (a)) and F^+ (peak (b)) ions which were observed also for electron impact, $Si(H)^+$ and $SiOH^+$ ions (corresponding to the peaks (c) and (d), respectively) were detected. The $Si(H)^+$ peak skewed to shorter TOF side, which corresponds to energetic emission induced by kinetic energy transfer.

Fig. 3(B) shows a TOF spectrum of secondary ions for $400\text{ eV}/q\text{ Ar}^{6+}$ ions. It is seen that the yields of $Si(H)^+$ and $SiOH^+$ ions did not depend on the charge state, which is qualitatively the same as those observed for monohydride Si(100) surface [6]. On the other hand, the H^+ and F^+ yields were about three times larger than those for Ar^{4+} . Similar experiments were performed for Ar^{q+} ions

as high as $q = 8$, and found that not only H^+ yields but also F^+ yields were proportional to q^γ ($\gamma \sim 3$). This is the first paper reporting a strong charge state dependence of heavy adsorbate yields when slow HCIs bombard a well-defined surface covered with adsorbate. Mechanism of the H^+ and F^+ desorption for the system presented here will be discussed elsewhere together with the angular distribution.

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