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Proton sputtering from H-terminated Si(1 0 0) surfaces with slow highly charged ions

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Abstract

Proton sputtering from H-terminated Si(1 0 0) surfaces bombarded with Xe^{q+} ($q = 4$–12, $E = 2$–5 keV) were experimentally studied. Proton sputtering yields and two-dimensional (2D) distribution of protons were measured employing a time-of-flight technique with a 2D position sensitive detector. It was found that the q dependence of the proton sputtering yield from Si(1 0 0)–(2 × 1)H surface with Xe^{q+} was the same ($\sim q^5$) as that from an untreated surface, although the absolute yield was about 1/30. The yield from Si(1 0 0)–(1 × 1)H surface was about 10 times larger than that from the Si(1 0 0)–(2 × 1)H surface. The mean energy of emitted protons from Si(1 0 0)–(2 × 1)H and Si(1 0 0)–(1 × 1)H surfaces were 1.2 and 5.9 eV, respectively.

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1. Introduction

When a charged particle impacts a surface, secondary ions and neutral atoms are emitted from the surface as a result of energy deposition from the charged particle. Particle emission under singly charged ion bombardments is known to be dominated by a kinetic energy transfer, which is called a kinetic sputtering. On the other hand, highly charged ions (HCI) have large potential energy, which can make a dominant contribution to the emission of particles in the case of slow HCI. Sputtering due to the potential energy deposition rather than the kinetic energy deposition is called "potential" sputtering. Sputtering experiments with HCI had first been performed by Arifov et al. [1] and Bitenskii et al. [2] in the late 1970s. They found a strong charge (q) dependence of the secondary ion yield for nonmetals in contrast to metals. Parilis [3] proposed a Coulomb explosion model to explain these observations. In this model, a multiple electron transfer to the HCI is assumed to create a strongly charged local region. As reneutralization of the region is suppressed in insulators, ionized target atoms are ejected due to their mutual Coulomb repulsion. This model was applied to explain several experimental observations, but in these experiments, the kinetic energies

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of HCI were rather high and the contribution of kinetic sputtering was mixed up. Recently, Sporn et al. [4] measured potential sputtering yield from insulators bombarded by slow (<1 keV) Ar^{q+} ions. They found that almost all (>99%) the sputtered particles are neutral and the yields for LiF and SiO_2 are proportional to the potential energy of HCI. No sputtering enhancement for MgO was observed. To explain these findings, they proposed a sputtering model mediated by self-trapped excitons created after electronic excitation by HCI. The sputtering yield of neutral particles was found to be proportional to the potential energy of HCI or approximately proportional to q^2.

On the other hand, proton-sputtering yield with HCI shows stronger q dependence. Recently, we have found that the proton yields with various HCI are proportional to $\sim q^5$ and the energy distribution of protons normal to the target surface has a peak at ~4 eV when untreated C_{60} and CuO are bombarded by slow HCIs (Ne^{q+}, Ar^{q+}, Kr^{q+}, Xe^{q+}) with negligibly small kinetic energy (500 eV) [5,6]. The untreated C_{60} and CuO surfaces were covered with hydrocarbons. Burgdörfer and Yamazaki [7] explained this strong q dependence assuming a bond-breaking reaction of covalent C–H bonds as a result of double electron capture from the same bond based on the classical over the barrier (COB) model. Della-Negra et al. [8] reported that the proton yield from untreated CsI with 18 keV Ar^{q+} ion impact was proportional to q^3 but Cs^+ yield was not, although the kinetic energy of ions was much larger than the potential energy (~2 keV for $q = 11$). They reported similar q dependence for MeV heavy ions [9].

In order to study potential sputtering of protons under well-controlled conditions, proton-sputtering yields and kinetic energies of emitted protons were measured for well-defined H-terminated Si(1 0 0) surfaces bombarded by Xe^{q+} ($q = 4$–12, $E = 2$–5 keV).

2. Experiment

A schematic diagram of the experimental setup is shown in Fig. 1. Low energy HCI are produced by the electron beam ion source (EBIS) cooled with liquid nitrogen [10], which was operated at around 4×10^{-10} Torr. HCIs extracted from the EBIS were charge-state and mass-selected with the EXB (Wien) filter and were swept by the deflector in front of the aperture into the UHV chamber to form short pulses (40 ns–2 μs, 50 kHz). A target holder was mounted on a rotation and linear feedthrough at the center of the UHV chamber. A ceramic heater was on the holder to heat a target sample up to 1500 K. In order to accelerate and accumulate the secondary ions, a gold plated W-mesh (30 μm-∅, 30-mesh/inch) was placed in front of the target, parallel to its surface. The target was biased positively and the mesh was grounded, which accelerates the secondary ions. A 2D position-sensitive detector (2DPSD) was mounted on a turntable. The 2DPSD consists of a triple-staged 48 mm-∅ micro-channel plate and wedge-meander-strip inductive electrodes with a Ge layer anode. The distance between the 2DPSD and the target was 140 mm. Fig. 2 shows a schematic diagram of the measurement system. The time-of-flight (TOF) of the secondary ions was determined using the pulse from the pulse generator as a start signal and a fast timing pulse from the Ge layer of the 2DPSD as a stop signal. Analog signals from the wedge-meander-strip electrodes and from the TAC were digitized by a PC-controlled analog-to-digital converter (ADC). The 2D position of the secondary ions is calculated from wedge-meander-strip's digital data on the PC. Because this system accumulated and detected 100% of the emitted protons, only a small number of incident ions were necessary and the beam induced modification of the sample surfaces was

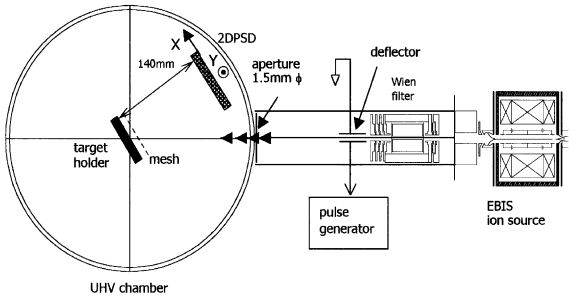


Fig. 1. A schematic diagram of the experimental setup.

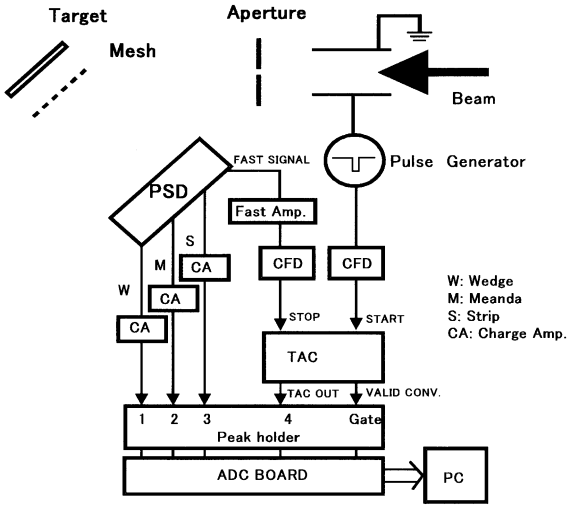


Fig. 2. A schematic diagram of the measurement system.

negligibly small because the bombarded ion numbers were very small compared with the number of the surface Si atoms (6.78×10^{14} cm^{-2}), in the order of 10^7 for proton yield measurements and below 10^9 for 2D distribution measurements. The beam size on the target was about 2×5 mm^2. The projectile ion beam intensity was monitored with this system time to time by reflecting the ions to the 2DPSD by applying a high voltage on the target. The beam intensity was controlled so that the average number of ions in each chopped ion train was much smaller than unity. When we measure the direct beam intensity, if the chopped ion train has two ions, the system counts them as one ion because the system can handle only one particle in the process time. This system process time is limited by 4-channel ADC data acquisition time (20 μs), which is much longer than chopped ions pulse width (<2 μs).

N-type Si(1 0 0) samples were chemically cleaned by repeated NH_4:H_2O_2:H_2O (1:1:5) and HF:H_2O (1:20) treatments and after the last HF:H_2O treatment, the Si samples were set in the UHV chamber within 20 min. The base pressure of the UHV chamber was 3×10^{-10} Torr after 450 K baking for 48 h. The samples were kept at 1200 K for 2 min in the UHV, and then reconstructed Si(1 0 0)-(2×1) clean surfaces were obtained. H-terminated Si(1 0 0) surfaces were prepared in the UHV chamber by exposing the Si(1 0 0)-(2×1) reconstructed clean surfaces to atomic hydrogen. The coverage of H was measured by thermal desorption spectra (TDS). Two types of H-terminated surface were prepared. A Si(1 0 0)–(2×1)H surface was obtained by exposing the Si(1 0 0)-(2×1) clean surface to atomic hydrogen keeping the substrate temperature at 600 K. A Si(1 0 0)–(1×1)H surface was obtained by exposing the Si(1 0 0)–(2×1)H surface at room temperature to atomic hydrogen until the coverage saturated. The Si(1 0 0)–(2×1)H surface is known to be atomically flat through a scanning tunneling microscopy (STM) study [11]. On the other hand the Si(1 0 0)–(1×1)H surface is not atomically flat despite the surface shows (1×1) LEED pattern, because a bond-breaking H-termination (H–Si═Si–H → H–Si–H, H–Si–H) and an etching reaction (H–Si–H + 2H → SiH_4) occur during the atomic hydrogen exposure at room temperature [11]. These surfaces are easily converted to the reconstructed Si(1 0 0)-(2×1) clean surface by heating at 1200 K in UHV.

3. Results and discussions

Proton yields from a Si(1 0 0)–(2×1)H surface bombarded with Xe^{q+} ($q = 4$–12, $E = 2$–5 keV) are shown in Fig. 3 together with those from an untreated CuO bombarded with Xe^{q+} ($q = 7$–22, $E = 500$ eV) [8]. The solid line is the results of simulation for hydrocarbons [9]. The dashed line shows q^5 dependence. The q dependence of the proton sputtering yield was found to be the same ($\sim q^5$) as that from the untreated surface, although the yield was about ~3% of the untreated surface. This indicates that the primary process of the proton sputtering from the Si(1 0 0)–(2×1)H surface can be explained by the COB model although the total yield is governed by the reneutralization efficiency.

The proton yields from Si(1 0 0)–(2×1)H and Si(1 0 0)–(1×1)H surfaces bombarded with Xe^{8+} (3 keV) were 1.2×10^{-4}/ion and 1.3×10^{-3}/ion, respectively. The saturation coverage of Si(1 0 0)–(2×1)H surface is 1.0 monolayer and that of Si(1 0 0)–(1×1)H surface is about 2 monolayer

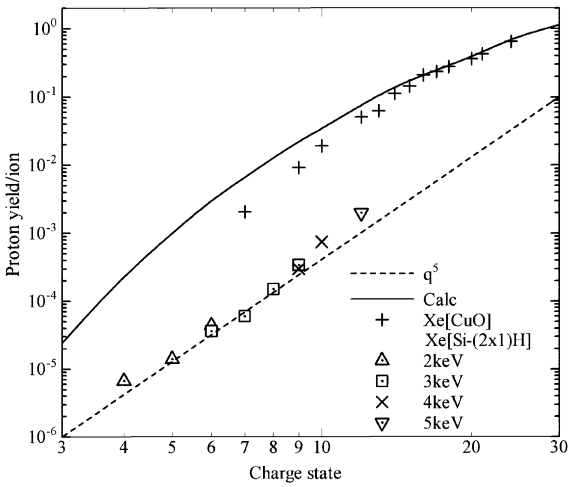
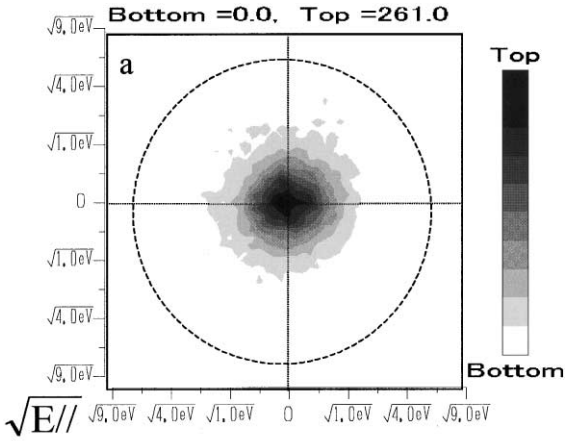


Fig. 3. Proton yields from a Si(1 0 0)–(2 × 1)H surface and from a CuO surface covered by hydrocarbons. The solid line is a calculation for hydrocarbons on the CuO surface [9] and the dashed line represents q^5 dependence.

[12]. The proton yield from Si(1 0 0)–(1 × 1)H surface was about 10 times larger than that from Si(1 0 0)–(2 × 1)H surface, although the number of H-atom on the surface was only twice. This can be attributed to atomic level roughness of the Si(1 0 0)–(1 × 1)H surfaces. In electron impact experiments, the desorption cross-sections of protons from surfaces are known to be several orders of magnitude smaller than the production cross-sections of protons from gas phase targets. These data are explained as due to proton neutralization by surface electrons. The density of surface electrons decreases rapidly with increasing distance from the surface. Because the hydrogen atoms on Si(1 0 0)–(1 × 1)H rough surfaces have on the average larger distance from the surface compared with that of Si(1 0 0)–(2 × 1)H flat surfaces, and are expected to have lower probability to be reneutralized, which is consistent with the observation.

Fig. 4(a) and (b) shows 2D distributions of protons when 3 keV Xe^{8+} ions bombarded Si(1 0 0)–(2 × 1)H and Si(1 0 0)–(1 × 1)H surfaces, respectively. The protons from the Si(1 0 0)–(2 × 1)H surface show very sharp 2D distribution compared with that of the Si(1 0 0)–(1 × 1)H surface. Assuming that the protons observed at the center of



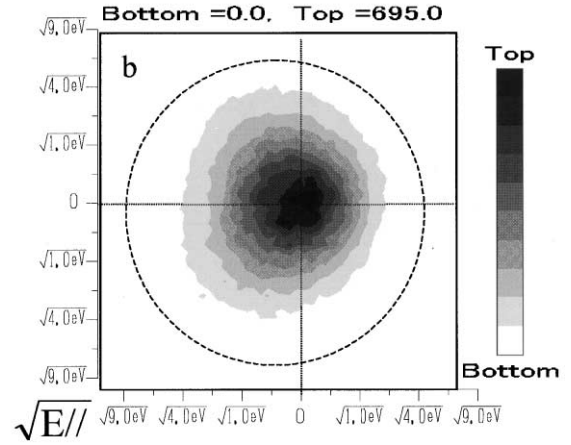


Fig. 4. 2D $E_{\|}$ distributions of sputtered protons from (a) Si(1 0 0)–(2 × 1)H and (b) Si(1 0 0)–(1 × 1)H surfaces (3 keV X^{8+} bombardment, target-bias = 325 V).

the 2D distribution have no kinetic energy parallel to the surface ($E_{\|}$), the distance from the center of the distribution corresponds to the square root of the $E_{\|}$.

The figure indicates that the protons from the Si(1 0 0)–(2 × 1)H surface have smaller $E_{\|}$ than those from the Si(1 0 0)–(1 × 1)H surface. The mean values of $E_{\|}$ were 1.2 eV for the Si(1 0 0)–(1 × 1)H surface and 0.6 eV for the Si(1 0 0)–(2 × 1)H surface. We estimated the kinetic energy normal to the surface ($E_{\perp}$) of an emitted proton from its TOF. The mean values of $E_{\perp}$ were estimated to be 0.6 and 4.7 eV for the Si(1 0 0)–(2 × 1)H and the

Si(1 0 0)–(1 × 1)H surfaces, respectively. The mean total energies of emitted protons were 1.2 eV for the Si(1 0 0)–(2 × 1)H surface and 5.9 eV for the Si(1 0 0)–(1 × 1)H surface. If we assume that the protons get its kinetic energy from Si^+–H^+ Coulomb potential energy, the neutralization time of the Si^+ ion on the Si surface can be estimated from the emitted proton energy [7]. The estimated lifetimes were 2.7 fs for the Si(1 0 0)–(2 × 1)H surface and 11 fs for the Si(1 0 0)–(1 × 1)H surface. The Si^+ lifetime for the Si(1 0 0)–(1 × 1)H surface seems to be about four times longer than that for the Si(1 0 0)–(2 × 1)H surface, which is at least qualitatively consistent with the difference of the surface roughness.

4. Summary

Proton sputtering yields from the well-defined Si(1 0 0)–(2 × 1)H surface with HCI showed the same q dependence (q^5) as that from the hydrocarbons on the untreated surface despite the yield was decreased to about ~3%. Proton sputtering yield was increased 10 times when H-terminated Si(1 0 0)–(2 × 1)H surface was replaced by atomically rough Si(1 0 0)–(1 × 1)H surface. The neutralization time of the Si^+ ion of Si(1 0 0)–(2 × 1)H surface was estimated to be four times shorter than that for the Si(1 0 0)–(1 × 1)H.

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