Secondary-Ion Emission in Grazing Collisions between Highly Charged Ions and Surfaces

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Abstract. In order to study the potential sputtering processes in collisions between highly charged ions and surfaces, we conducted secondary-ion mass spectroscopy, measured simultaneously with the scattered atoms at grazing incidence angles. Efficient proton emission was observed in both metal (Al) and wide-gap semiconductor (GaN) surfaces. We conclude that the electron capture by highly charged ions above the surface caused the efficient proton emission. The three-dimensional momentum of protons emitted from the surface was successfully visualized, and the anisotropic angular distribution of the momentum was observed. Contrary to the adsorbed atoms or molecules, no efficient emission of the substrate atoms was observed in the metal (Al) surface.

1. Introduction

Many interesting phenomena concerning the interaction between highly charged ions (HCIs) and solid surfaces have been reported during the past decade. Typical examples are large sputtering yields of secondary particles [1–9] and nanostructure formation with high efficiency [10–16]. It has been reported that secondary electrons and ions, as well as atoms, molecules and clusters, are emitted from various solid surfaces with large probabilities, which rapidly increase with an increase in the charge state of the HCIs [1, 5, 8, 9, 17]. It has also been reported that nanostructures are efficiently formed with a probability of ~1 per incident ion, and their size or volume increases with an increase in the charge state of the incident ion [11, 12, 15, 16]. Potential energy transfer from HCIs to the solid surfaces may largely contribute to this phenomenon.

The secondary-particle emission induced by the potential energy transfer from ion to surface is called potential sputtering (PS). PS is a very important process since it is considered as an initial process in the nanostructure formation on the surface [18]. However, no direct evidence on PS has been observed, although there have been some affirmative results by comparison with the theoretical models [5, 7] and several indirect evidences extrapolated from the zero-collision-energy limit [4, 17]. The lack of direct evidence may be due to the difficulty of separating PS from kinetic sputtering (KS).

Stökel et al. have already been successful in the direct observation of potential emission (PE) of secondary electrons by measuring the electron yields as a function of the energy loss of projectile ions [19]. We tried to selectively observe PS by means of grazing incidence collision and the coincidence detection of secondary ions and scattered projectile atoms. The aim of this study is to elucidate PS
using some coincidence-detection techniques between secondary ions and the scattered ions characterized by their energy loss.

2. Experimental

The experimental apparatus and procedures have been described in detail elsewhere [9, 20, 21]. Briefly, highly charged Ar ions, extracted from a compact electron beam ions source (EBIS) [22], were introduced into a ultra high vacuum (UHV) chamber \((1.0 \times 10^{-7} \text{ Pa})\). The beam energy of the \(\text{Ar}^{q+}\) ions \((q = 3, 8, 9, 11 \text{ and } 14)\) was \(2.5 \times q \text{ keV}\). Secondary ions emitted from solid surfaces were detected by a time resolved two-dimensional position sensitive anode simultaneously with the scattered Ar atoms. The surfaces were cleaned by bombardment with \(\text{Ar}^+\) (2.3 keV and 0.3 \(\mu\)A) extracted from a duoplasmatron ion source. The surface cleanliness was checked \textit{in situ} by observing the light emission of excited neutral atoms sputtered from the surfaces. Even if a clean surface was prepared just after the \(\text{Ar}^+\) irradiation, the surface will be covered with impurities because of the low flux \((\sim 1 \times 10^6 \text{ ions cm}^{-2}\text{s}^{-1})\) of HCIs. We considered the surfaces to be covered by a monolayer of hydrocarbon molecules in a steady state [21].

The incidence angle of HCIs was kept about 0.5° to the direction parallel to the surface. The grazing angle collisions were achieved by applying electric bias to a pair of deflectors set before and after the target. Initial kinetic energies of \(\text{Ar}^{q+}\) \((q = 3, 8, 11 \text{ and } 14)\) along the surface normal direction, i.e. \(E_\perp = E_0 \sin^2 \theta_s\), were small enough (0.6, 1.5, 2.1 and 2.7 eV, respectively) to contribute to KS of secondary ions. The acceleration of projectile ions due to image charge, however, should contribute to the process.

These surface processes are selectively observed in the grazing incidence collisions, since kinetic energy transfer into atoms sited below the surface is very small. The perfect neutralization due to electron capture is also selectively observed when neutral atoms are detected. However, if coincidence is not detected, the possibility of KS cannot be excluded because incident Ar ions prefer to enter the bulk because of their heavy mass. Therefore, coincidence detection of the scattered neutral atoms with secondary ions makes it possible to observe PS above the surface followed by complete neutralization induced by multi-electron capture of HCIs.

The flight time and pulse height of secondary ions were recorded by a digital oscilloscope at the same time as scattered Ar atoms were detected by a channel electron multiplier. The three dimensional momentum of each secondary ion emitted from the surface was obtained from their signals [9, 21, 23, 24].

3. Results and discussion

The time-of-flight secondary-ion mass spectroscopy (TOF-SIMS) was conducted in a polycrystalline Al and single-crystalline GaN(0001) and (000\(\overline{1}\)) surfaces interacting with HCIs.

3.1. \textit{TOF-SIMS spectra.} The TOF-SIMS spectra of Al and GaN surfaces interacting with \(\text{Ar}^{8+}\) are shown in Fig. 1. The position of each broken line indicates the flight time of the ion with zero kinetic energy. The vertical axes of Fig. 1(b) and (c) are the intensities normalized by the total number of Ar atoms. Therefore, one can compare the intensity of each spectrum between (b) and (c). Almost all peaks were assigned to ionic fragments of hydrogen and hydrocarbon molecules adsorbed on the surface; in particular, the proton peak was very intense. This result indicates that adsorbates are preferentially emitted from the surfaces with the incidence of slow HCI at the grazing angle. No ionic species of aluminium and aluminium compounds were observed. It is interesting to note that Ga\(^+\) ions were emitted from only the GaN(0001) surface, whereas N\(^+\) ions were emitted more intensely from the \((000\overline{1})\) surface than the \((0001)\) surface. We conclude that this discrepancy is due to the lattice polarity of the wurtzite GaN crystal [20]. Wurtzite GaN has two lattice polarities, e.g. the \((0001)\) surface terminated with gallium atoms and the \((000\overline{1})\) surface terminated with nitrogen atoms [25]. The TOF-SIMS spectra of Fig. 1(b) and (c) indicate that the topmost atoms are preferentially desorbed as
ions from the solid surfaces interacting with HClIs at the grazing incidence angle. The lattice polarity of the compound semiconductor surface in the macroscopic scale is one of the most important factors for the thin film depositions in the formation of heterostructures and multi-quantum well structures. However, there are some serious problems in the usual coaxial impact collision ion scattering spectroscopy (CAICISS), which has often been used as a surface-polarity analysis [26], mainly being 1) difficulty of in-situ measurement and 2) serious damage to the surface and bulk. The present TOF-SIMS method using HClIs makes in situ monitoring of the lattice polarity of the compound semiconductor surfaces possible with less damage since, compared with experimental results, no sample rotation mechanism and model calculation are required but only a very low dose of ions ($\leq 1 \times 10^{10}$ ions/cm$^2$) with low kinetic energy in the direction parallel to the surface normal [20].

3.2. Charge state dependence of proton emission intensity. Fig. 2 shows the emission intensity of protons as a function of the charge state of incident ions. The charge state dependence of the proton emission intensity for the GaN(0001) surface was $q^4$ [9], whereas that for the Al surface was not $q^n$ but was saturated above $q \geq 10$ [21]. The saturation was also less significant in the case of non-grazing incidence angles [1] than that of grazing incidence angles as shown in Fig. 2. The $q^n$-dependences of proton emission intensity (yields) without saturation have also been reported elsewhere in the case of non-grazing incidence angles to various surfaces [8, 27].

3.3. The solid curve in Fig. 2(a) is the $q$-dependence of proton yields $Y(H^+)$ calculated with a model that was a modification of the model proposed by Burgdörfer and Yamazaki [1]. In the model [1], proton sputtering yields can be calculated by integrating the time-dependent ionization probabilities of proton and carbon atoms over the interaction time $t_i$ for the multielectron capture by HClIs as follows:

$$Y(H^+) = \frac{N_H K}{r} \int_0^{t_i} dt \cdot p(H^+,t) \cdot p(C^+,t) \exp\left[-r(H^+,t) + r(C^+,t)\right],$$  \hspace{1cm} (1)
Fig. 2. The $q$-dependence of proton emission intensity or sputtering yields for (a) polycrystalline Al and (b) single crystalline GaN(0001) surfaces interacting with Ar$^{q+}$ ($q = 3, 8, 9, 11$ and $14$) at grazing angle. □ and △, the present results [9, 21]; + and ×, Burgdörfer and Yamazaki [1]; solid curve, model calculation with image acceleration [21]; broken curve, model calculation without image acceleration [1]; dash-dotted curve, $q^{4.0}$.

Fig. 3. 3D-momentum images of protons emitted from the GaN(0001) surface interacting with Ar$^{8+}$ [9]. The momentum distributions projected to the (a) $P_x$-$P_y$, (b) $P_x$-$P_z$ (c) and $P_y$-$P_z$ planes are shown. The $x$- and $z$-axes are parallel to the beam axis and the TOF axis, respectively.
where \( N_{H} \) is the number of hydrogen atoms per unit area, \( K \) is a constant related to the geometrical factor between incident ions and hydrogen atoms, \( \tau \) is a characteristic correlation time where \( C^{+} \) and \( H^{+} \) maintain their ionic charge state, \( p(X^{+}, t) \) (\( X = H \) or \( C \)) is the ionization probability of hydrogen or carbon and \( r(X^{+}, t) \) (\( X = H \) or \( C \)) is the reneutralization rate of hydrogen or carbon ions due to charge transfer from neighbouring atoms or ions. We calculated the time-dependent distance between the projectile ion and surface \( z(t) \) by solving the following motion equation with image force, which is used to evaluate the interaction time \( t_{I} \) above the surface [21].

\[
m \frac{d^{2}z(t)}{dt^{2}} = -\left( \frac{q_{eff}(t)}{4|z(t)|^{2}} \right)
\]  

(2)

Here, \( z(t) \) is the distance of the projectile ion measured from the surface, \( m \) is the projectile mass and \( q_{eff}(t) \) is the effective charge, which is obtained from the classical over-the-barrier model (COB) [28]

\[
q_{eff}(t) = \frac{1}{2} |W z(t)|^{2},
\]  

(3)

where \( W \) is the work function of the surface. A solution of eq. (2), which is substituted into eq. (3), is given by an analytical equation with variable separation form [21]

\[
v_{z}(t) = v_{0} + \frac{W}{24m} [z_{c}^{4} - z^{4}(t)]^{3/2} \sin^{2} \theta ,
\]  

(4)

where \( z_{c} \) is the critical distance, \( v_{0} \) is the initial velocity of the incident ion and \( \theta \) is the incidence angle to the direction parallel to the surface. Then, \( t_{I} \) is given as the root of \( z(t_{I}) = 0 \) with the initial condition of \( z(0) = z_{C} \). This calculation reproduced the saturation behaviour better than the original one without the image acceleration effect as seen in Fig. 2. It should be noted that the saturation behaviour is largely influenced by \( t_{I} \) rather than \( N_{H} \), since the absolute value of sputtering yields is sensitive to \( N_{H} \). Therefore, we conclude that the saturation behaviour observed in the grazing incidence collisions with a metal surface is due to shortening of the interaction time for multi-electron capture by image acceleration of incident ions.

3.3 Momentum image of secondary ions. Fig. 3 shows the 3D-momentum images of protons emitted from the GaN(0001) surface interacting with Ar\(^{8+} \) [9]. Note that the x- or z-axis is parallel to the beam axis or the TOF axis, respectively. The momentum was significant in the z-direction despite the beam direction being almost parallel to the x-axis. This fact indicates that PS plays a key role in the sputtering processes of protons. Fig. 4 shows the angle dependence of the momentum distribution of protons emitted from a polycrystalline Al surface interacting with Ar\(^{q+} \) (\( q = 6, 8 \) and 14) [21]. Here, \( \alpha \) is defined as \( \tan^{-1}(P_{y}/P_{x}) \), that is, the angle between the momentum vector \( P \) and the z-axis in the \( Y-Z \) plane. Note that the angle dependences in Fig. 4 were plotted for all protons having a kinetic energy of less than 2 eV [21], since the acceptance angle of the TOF analyzer covers 180° for protons with such low kinetic energies. The experimental data have large fluctuations, but the distributions have a tendency to become flat as the incident charge state becomes high. This means that a population with a large \( \alpha \)
in an increase in incident charge state. In fact, the populations with $|\alpha| > 60^\circ$ were 2.0% for Ar$^6+$, 3.5% for Ar$^8+$ and 5.9% for Ar$^{14+}$. Another interesting feature is that each distribution has a dent around $\alpha \sim 0^\circ$. This fact shows that protons prefer not to eject in the direction normal to the surface but to eject in the direction parallel to the surface. The anisotropic angular distribution of protons from the contaminated surface interacting with HCIs was predicted by Burgdörfer [29].

Fig. 5 shows the classical trajectories of protons emitted at angle $\alpha$ at the origin of the coordinate system with the kinetic energy of 2 eV [21]. It was assumed that the proton moves in a Coulomb field induced by Ar$^{14+}$, and is travelling along the straight line with the constant velocity $V_x (=4.1 \times 10^5$ m/s) at $Y = 0$ and $Z = R_C (=33.6$ au). We also assumed that the Ar$^{14+}$ captured an electron at the position of ($-R_C/2$, 0, $R_C$). The figure shows the trajectories projected to the $Y$–$Z$ plane perpendicular to the beam. Although the discrepancy from linear trajectories is not so large, because the incident ion will rapidly move away from the proton, it is clear that the protons emitted in directions with large $\alpha$ angles are repelled by the surface or the $X$–$Y$ plane. This calculated result indicates that the experimental results shown in Fig. 4 were caused by the Coulomb repulsion between projectile ions and protons after electron capture. This is a kind of post-collision interaction. Therefore, we conclude that the anisotropic angular distribution in the momentum is due to Coulomb repulsion between protons and projectile ions, which has been known as a kind of ‘post-collision interaction’ [21].

4. Summary and future prospects

We investigated the mechanisms of secondary-ion emission from metal and semiconductor surfaces interacting with HCIs at grazing incidence angles. In order to selectively observe PS induced by electron capture of the HCIs, we adopted the coincidence detection technique with scattered atoms. Efficient emission of protons, as well as hydrocarbon ions, was observed in both metal and semiconductor surfaces, whereas no significant emission of substrate atoms as ions was observed in the Al surface. In contrast, Ga$^+$ was only observed in the GaN(0001) surface, which was terminated with Ga atoms, the so-called Ga-polarity surface. These results show that adsorbates, or the substrate atoms in the topmost layer, are preferentially desorbed as secondary ions in the grazing collisions between HCIs and the surfaces.

The emission intensity of protons increases rapidly with an increase in the charge state $q$ of the HCIs. The $q$-dependence of the proton emission intensity in a metal (Al) surface is saturated more significantly than that in a semiconductor (GaN) surface or that in a contaminated surface with non-grazing incidence collisions. These results suggest that shortening of interaction time due to image acceleration of the incident ions enhances the saturation in grazing incidence collisions with metal surfaces.

The momentum distribution of protons emitted from the surfaces interacting with HCIs was successfully visualized in three dimensions. This was the first 3D-visualization of the PS process. We observed the anisotropic angular distribution of the momentum, and conclude that the anisotropy is due to a kind of post-collision interaction between protons and the scattered incident ions just after the electron capture.

Fig. 5. Calculated classical trajectories of protons that are emitted toward angle $\alpha$ at the origin of the coordinate with the kinetic energy of 2 eV [21]. The proton moves in a Coulomb field induced by Ar$^{14+}$ that is travelling along the straight line with the constant velocity $V_x (=4.1 \times 10^5$ m/s) at $Y = 0$ and $Z = R_C (=33.6$ au).
We have just started some experiments using a new instrument, which allows us to measure energy loss of the scattered ions simultaneously with secondary ions and electrons [30]. It is expected that PS can be made clear using this experimental setup.

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