Desorption and Sputtering on Solid Surfaces by Low-Energy Multicharged Ions

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Abstract. Desorption and sputtering on solid surfaces interacting with slow multicharged ions were studied by two different experimental methods: time-of-flight secondary ion mass spectrometry (TOF–SIMS) coupled with low-energy ion scattering spectroscopy (LEIS), and optical emission spectroscopy (OES) of secondary particles. Spectra reveal the anisotropic angular dependence of proton emission on an Al surface interacting with Ar\(^{q+}\) (\(q = 8\) and 14) ions at the incidence angle of \(~0.5^\circ\) (tangential angle to the surface). Simultaneous spectra of a GaN surface, scattering Ar\(^+\) ions and scattering protons reveal the kinetic energy distribution of Ar\(^{5+}\) (15 keV, \(~10^\circ\)) and the dependence of the protons on the kinetic energy of Ar\(^+\). Spectra of secondary particles, conducted on a Ti surface irradiated with Ar\(^{3+}\) ions (30 keV) at normal-incidence angle, reveal the mean velocity \(<v_\perp>\) of sputtered Ti substrate atoms perpendicular to the surface, measured by analyzing intensity decay as a function of distance from the surface.

1. Introduction
Sputtering and desorption on solid surfaces by low-energy multicharged ions are attracting attention because of their potential for many applications and their interesting fundamental aspects. High sputtering yields and strong charge–state dependence have been reported for various materials [1–12]. Efficient secondary-particle emission induces some nanostructure formation and deformation on the surface [13–19]. The weak dependence of yield on kinetic energy indicates that not kinetic but rather electronic processes play a key role in sputtering.

The Coulomb explosion model [20, 21] has been examined to explain charge–state dependence. The model generally accurately describes collisions with highly charged ions (charge state \(q > ~20\)) and the charge–state dependence of sputtering yield and nanostructure size. However, it does not accurately describe sputtering due to multicharged ions with low or medium charge state and very low kinetic energy. One reason for this is that the kinematics of collision processes are not yet well understood. Studies on the kinetic energy or emission angle of secondary particles are scarce [22–25] compared with those on sputtering yields or nanostructure size. Studies on neutral species that might play a role in nanostructure formation as major secondary particles are also scarce [26, 27].

This review paper focuses on two subjects: the kinematics of secondary ions and scattered ions detected at glancing-incidence or off-normal-incidence angles, and the mean velocity of sputtered neutral atoms detected at normal–incidence angles. Kinematics studies were achieved by coincidence measurements on scattered atoms/ions and secondary ions with an originally developed time-of-flight secondary ion mass spectrometry (TOF–SIMS) analyzer. Velocity studies were achieved by optical
emission spectroscopy (OES). Experimental methods and results of the two different studies are described separately below.

2. Experimental methods

Mass or momentum spectroscopic studies of secondary ions were conducted with an originally developed device based on a TOF–SIMS analyzer. Three-dimensional (3D) momentum vectors of secondary ions were successfully measured with this device, and the angular dependence of emitted ions was reconstructed directly from the momentum distribution. A novel TOF–SIMS analyzer combined with a low-energy ion scattering spectrometer (LEIS), very recently developed, was used to measure the TOF of secondary ions in coincidence with the kinetic energy of scattered ions. The mean velocity of sputtered and excited atoms was measured by optical spectroscopy.

2.1. TOF measurements of secondary ions

Details of the experimental setups and procedures are described elsewhere [22, 25, 26, 28, 29]; only a brief description is presented here.

Figure 1a shows the experimental setup for 3D-momentum spectroscopy of secondary ions. Ar\(^{q+}\) ions (charge state \(q\), \(2.5 \times q\) keV) are introduced into a collision chamber evacuated by a turbo molecular pump. An ion beam passes through an aperture (A; diameter 2 mm), is deflected by a couple of parallel deflection plates (D), and collides with a target surface (T) of polycrystalline Al or single-crystalline GaN(0001) at glancing-incidence angle \(\sim 0.5^\circ\). Scattering Ar atoms or ions capture some electrons at the target surface, to become Ar\(^{(q-n)+}\) ions, where \(n\) is the number of electrons (0 \(\leq n < q\)) captured. The ions are deflected by a parallel plate analyzer (P). Neutral Ar atoms give a signal pulse at the channel-electron neutral detector (ND). Secondary ions emitted from the target surface are extracted with the ion focusing lenses (IFL), weakly biased negative to the target surface. They work as a focusing lens for velocity-map imaging or momentum imaging [22, 25], so TOF analysis with 2D-position sensitive detection of secondary ions enables measurement of 3D momentum. The waveforms of the three different signals from the 2D-position detector are recorded with a digital oscilloscope (DO), event by event, when an Ar atom hits the neutral detector (ND). The secondary-ion momentum
vector is reconstructed from time and position information by a computer (PC).

Figure 1b shows the experimental setup for a novel, recently developed combination TOF–SIMS/LEIS analyzer [29, 30]. This setup permits simultaneous detection of secondary ions, scattered atoms/ions and secondary electrons. The TOF–SIMS analyzer is basically as described in Fig. 1a except that it has a longer flight tube and a position-insensitive detector. Secondary electrons emitted from the target surface are extracted by a couple of specially designed electrodes that coaxially surround the target holder [29]. Ions reflect on the target surface, scatter, are dispersed along the z axis by a Wien filter (or an $E \times B$ analyzer) and a charge state analyzer (or a parallel plate), then are detected by a 2D position sensitive detector (PSD). The Wien filter works as a velocity-dispersion filter; i.e. exit slits extend in the z direction, permitting analysis of the velocity and charge-state distribution of the scattered $\text{Ar}^{(q-n)+}$ ions from the z-displacement of the sensed position relative to that of the neutral atoms. The difference in TOF between secondary-ion $T_1$ and scattered-atom/ion $T_2$, or $t_{12} = T_1 - T_2$, was also recorded with the DSO event by event.

Figure 2 shows projectile-beam profiles converted from the 2D position images taken with the PSD detector. The peak position of the 15.20-keV beam is shifted 0.9 mm in the +z direction compared to that of the 15.00-keV beam, but both spectra maintain their widths of ~2.5 mm (FWHM). The relationship between energy and displacement, i.e. the $E-z$ calibration factor of the Wien filter, was found to be 220 eV/mm [30]. The energy resolution (550 eV) is not good because of the wide (1 mm) entrance slit. A few structures observed in both spectra may be due to non-uniformity of the trap potential of ions in the electron beam ion source (EBIS) [30, 31] used here. Preliminary energy analysis of the primary ion beam is required for high-resolution measurements.

2.2. Optical emission measurements of secondary neutral atoms
Details of the experimental setup appeared in a previous study [27]. Multicharged Ar ions extracted from a 10-GHz electron cyclotron resonance ion source [32] are focused with an electrostatic lens, and their mass-to-charge ratios are analysed by 90° sector magnets. The ion beam passes through a hole (inner diameter 10 mm), then irradiates a polycrystalline Ti target surface at a normal- incidence angle. We could move the surface linearly along the beam axis with a motion feedthrough. Light emitted from the surface is focused by an optical lens that is set on the optical axis perpendicular to the beam axis, dispersed with a visible monochromator, and detected with a photomultiplier tube. The hole is negatively biased (~ –100V) to repel secondary electrons. The current of the ion beam (~2 µA) is measured with a current–voltage conversion amplifier (1 V/µA). The background pressure, $1 \times 10^{-6}$ Pa,
is monitored with a cold cathode ion gauge. To eliminate any pre-existing oxidized layer and other impurities, the target surface is cleaned by irradiation with an Ar\(^+\) (10 keV) beam for an hour.

3. Results and discussion

3.1. Angular distribution of protons emitted from a polycrystalline Al surface

The angular distribution of protons emitted from a polycrystalline Al surface was measured by 3D-momentum analyzer (Fig. 1a). Figure 3 shows a 2D plot of the number of protons as functions of emission angle \(\alpha\) \((-\pi/2 \leq \alpha \leq \pi/2\) given by Eq. 1 and of kinetic energy \(E_k\) given by Eq. 2:

\[
\alpha = \tan^{-1}\left(\frac{P_y}{P_z}\right)
\]

\[
E_k = \left(\frac{P_x^2 + P_y^2 + P_z^2}{2m}\right)
\]

where \(P_x, P_y\) and \(P_z\) are the \(x, y\) and \(z\) components, respectively, of the momentum vector of a proton and \(m\) is its mass. The upper limit of the detectable angle of protons, or ‘acceptance angle’ shown by white curves in Fig. 3, decreases monotonically with an increase in \(E_k\). It is important to note that the momentum analyzer can detect all protons having kinetic energy less than 2 eV.

Figure 4 shows the angular distributions of secondary protons having kinetic energy less than 2 eV. The statistical results are not good because of the small amount of data; however, deviation from isotropic cosine distribution is clearly demonstrated for Ar\(^{14+}\) and Ar\(^{8+}\). Distributions tend to flatten as the incident charge state increases, indicating that a population with a large \(\alpha\) increases with an increase in the incident charge state. In fact, the populations of \(|\alpha| > 60°\) are 
(2.0 ± 0.6) \%, (3.5 ± 1.1) \% and (5.9 ± 1.9) \% for Ar\(^{6+}\), Ar\(^{8+}\) and Ar\(^{14+}\), respectively. This is the first experimental demonstration of the anisotropic angular distribution of secondary ions produced in collisions between multicharged ions and surfaces. The physics of the anisotropy has not yet been clarified, but we previously proposed a classical model wherein the multicharged ion captures some electrons above the target surface and repels a proton back to the surface [22]. Such anisotropic angular distribution of protons from a contaminated surface was predicted at first by Burgdörfer [34]. He considered that the phenomena occur due to Coulomb repulsion between proton and projectile ions, which is a

![Figure 4. Angular distributions of secondary protons for which \(E_k < 2\) eV: (a) Ar\(^{14+}\); (b) Ar\(^{8+}\); (c) Ar\(^{6+}\). (Reprinted from [22])](image)

![Figure 5. 2D position image of Ar\(^+\) scattered on a GaN(0001) surface in off-normal incidence of Ar\(^{6+}\) (15 keV) [30].](image)
3.2. Kinematics of proton emission induced by electron capture of multicharged ions

To investigate proton desorption or sputtering due to electron capture by multicharged ions in detail, we tried to measure the kinetic energy of scattered ions and the TOF of secondary protons simultaneously with the TOF–SIMS/LEIS analyzer (shown in Fig. 1b and described in Section 2.1).

Figure 5 shows a 2D position image of Ar⁺ scattered on the GaN(0001) surface in off-normal incidence (~10° tangential to the surface) of Ar⁶⁺ (15 keV) ions. The vertical axis \( z \) can be converted to the kinetic energy of Ar⁺ from the \( E–z \) calibration factor described in Section 2.1. The horizontal axis \( y \) relates to the longitudinal scattering angle \( \phi \) of Ar⁺. However, it is impossible to determine the relationship at present since calibration measurements between \( y \) and \( \phi \) have not yet been successful. Note that this 2D image does not correspond to the characteristic banana-shaped angular scattering distribution that indicates surface channelling [35], although the images resemble one another.

Figure 6 shows the LEIS spectrum for the kinetic energy distribution of Ar⁺, converted from Fig. 5. The width (FWHM) of the Ar⁺ spectrum is ~2.6 times that of the primary Ar⁶⁺ spectrum, indicating significant energy loss up to ~2.0 keV. The peak of the Ar⁺ spectrum is around 14.4 keV. This kinetic energy distribution suggests that elastic binary collisions between Ar ions and surface atoms play an important role in the scattering process. Kinetic energies of Ar ions scattered on gallium and nitrogen atoms are calculated to be 14.4 and 13.6 keV, respectively, from the simple classical equation [36]

\[
\frac{E}{E_0} = \left( A \cos \theta + \sqrt{1 - A^2 \sin^2 \theta} \right)^2, \quad A = \frac{M_1}{M_2}
\]  

or the well-known \( k \) factor, taking into account the scattering angle \( \theta = 15° \). In Eq. 3, \( E_0 \) and \( E \) are the energies of the primary and scattered ions, respectively, and \( M_1 \) and \( M_2 \) are the masses of the primary ion and target atom, respectively. It is thus natural to consider that binary collisions of Ar ions with the topmost Ga atoms and the second topmost N atoms play key roles.

Figure 7a shows the 2D correlation plot of \( t_{12} \) (difference in TOF between secondary-ion \( T_1 \) measured by TOF–SIMS and scattered ion \( T_2 \) measured by LEIS) and displacement \( z \) measured by 2D PSD. Figures 7b and c show the integrated intensities along the vertical and horizontal axes. Figure 7b is almost the same as the usual SIMS spectrum, because \( T_1 >> T_2 \). Very efficient proton emission was observed. Efficient proton emission is the most important feature of desorption and ionization due to electron capture by highly charged ions on various solid surfaces, i.e. ‘potential sputtering’ [1, 6, 7, 22, 25, 28–30, 34, 37]. Weak N⁺, Ga⁺ and GaN⁺ peaks originating from substrate atoms are also observed, together with some hydrocarbon-ion peaks originating from contaminants. Figure 7c corresponds to the charge-state distribution of scattered atoms/ions Ar⁺ \( (q' = 0–2) \) measured by the usual LEIS. The charge fractions of the spectra with \( q' = 0, 1, \) and 2 are 66%, 23% and ≤ 11%, respectively. Figure 7d shows the 2D correlation plot between the time difference \( t_{12} \) of protons and the kinetic energy \( E \) of scattered Ar⁺. The vertical axis of this figure is calculated from the displacement \( z \) of Fig. 7a. The scale of the horizontal axis is limited to the time range corresponding to the proton peaks of Fig. 7a or...
7b. The $E-t_{12}$ distribution slightly but clearly leans, as shown by the red line, confirming that $t_{12}$ of protons changes with the kinetic energy of Ar +, simply because $T_2$ depends on the kinetic energy.

Elastic scattering of Ar ions with hydrogen atoms at $\theta = 15^\circ$ is impossible because the mass ratio is too large, so direct recoil of hydrogen atoms by primary ions is excluded. Therefore it is considered that, after pure potential sputtering of hydrogen atoms adsorbed on the topmost Ga or N atoms in the second layer, incident ions scatter on their surface atoms.

3.3. Sputtering of substrate atoms in collisions of multicharged ions

We did not observe efficient emission of substrate atoms in our previous work on glancing-incidence collisions with Al [22], GaN [25, 28–30], SiC [25] and Cu surfaces. However, we did observe excited neutrals of substrate atoms (Al+) in normal incidence of low-energy multicharged ions in our earlier study [26]. We measured the mean velocity parallel to the Al surface, or $<v_\parallel>$, by optical emission spectroscopy measurement of Doppler broadening. We recently conducted an optical measurement of the mean normal velocity $<v_\perp>$ of Ti+ atoms sputtered from a polycrystalline Ti surface irradiated with Ar$^{3+}$ (30 keV).

Figure 8 shows the normalized intensity of Ti I: 670 nm (second-order wavelength of Ti I: 335 nm (3d$^2$4s4p $\rightarrow$ 3d$^2$4s$^3$)) as a function of distance between observation point and surface. The distance $Z$ was changed by adjusting the surface with linear motion feedthrough as described in Section 2.2. $I_0$ is the intensity at $Z = 0$ mm. The experimental curve at $Z > 0$ (a) Linear plot; (b) Semi-logarithmic plot for $Z \geq 0$. The broken curve is the slit function; the solid, dashed-dotted and dashed-double-dotted curves are fitted curves.
deconvolutes with the slit function (Gaussian curve), determined from the curve at \( Z < 0 \) corresponding to the decay curve of emission intensity given by

\[
I = \sum_k I_0 k \exp \left( -\frac{Z}{\tau_k \cdot \langle v_\perp \rangle} \right),
\]

where \( \tau_k \) and \( I_0 k \) are the lifetime and spontaneous emission intensities, respectively, at \( Z = 0 \) of the \( k \)-th excited state of the atom [38]. The terms for which \( k > 1 \) define the cascade components. One can obtain the \( \langle v_\perp \rangle \) value by fitting Eq. 4 with known lifetimes into the decay curve in Fig. 8. The slow dashed-dotted decay curve in Fig. 8b is considered to be a cascade component with a long lifetime (> 10 ns). The dashed-double-dotted curve was drawn by assuming \( \tau_k \) of Ti\(^+\) (3d\(^2\)4s\(^4\)p \( x^3G \)) to be 10.6 ns [39]. As a result, \( \langle v_\perp \rangle \) = \((7 \pm 3) \times 10^4 \) m/s was obtained for the Ti\(^+\) atoms. The \( \langle v_\perp \rangle \) obtained in the present study is significantly larger than the \( \langle v_\parallel \rangle \) of Al\(^+\) atoms emitted from Al and Al\(_2\)O\(_3\) surfaces interacting with Ar\(^q+\) (\( q = 1–9 \)) [26]. Generally speaking, a \( \langle v_\perp \rangle \) value depends on not only the actual velocity of the sputtered atoms but also the escape probability of the corresponding electrons.

4. Conclusions

We conducted TOF–SIMS coincidence measurements on scattered atoms/ions and secondary ions, and OES measurements of sputtered neutral atoms, to investigate the dynamics of desorption and sputtering due to electron capture by slow multicharged ions. We successfully obtained simultaneous TOF–SIMS and LEIS measurements by means an original experimental setup. We also measured the mean velocity, perpendicular to the surface, of sputtered substrate atoms by OES. We observed anisotropic distributions in the proton emissions for glancing-incidence collisions, and found that potential sputtering of protons induced by electron capture is followed by elastic scattering between projectile ions and surface atoms in the first or second layers.

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