Secondary-ion emission from GaN(0001) and dodecanethiol/Au(111) surfaces irradiated with Ar$q^+$ ($q = 4–8$)

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Abstract. Secondary-ion mass spectroscopic (SIMS) studies have been performed to investigate desorption or sputtering processes of various solid surfaces interacting with highly charged ions (HCIs). We have recently developed an HCI-SIMS apparatus capable of detecting secondary ions, secondary electrons and scattered atoms/ions simultaneously. This apparatus allows us to analyze solid surfaces in four different operation modes: 1) low-energy ion scattering spectroscopy (LEIS), 2) SIMS in coincidence with LEIS, 3) SIMS triggered by scattered neutral atoms and 4) SIMS triggered by secondary electrons. The coincidence experiments with two different operation modes 2) and 4) were conducted with a GaN(0001) and a dodecanethiol/Au(111) self-assembled monolayer surface, respectively, in collisions with Ar$q^+$ ($q = 4–8$) (2.5$q$ keV). It was successful to measure two different SIMS spectra which were taken by triggering with the scattered Ar$^+$ ions and the secondary electrons in Ar$^{6+}$ collisions.

1. Introduction

The electron capture cross section increases almost linearly with an increase in the charge state of the incident ion [1]. In the classical over-the-barrier (COB) model, the critical distance between ion and target material, where the electron capture occurs, increases linearly with the square root of the charge state [2, 3]. The probability of electron capture is distributed within a limited collision energy range around the most probable populated level [4]. The width of the reaction window is proportional to the collision velocity under the assumption of uncertainty between the interaction time and the barrier height formed by HCI and the target matter. Therefore, the electron capture processes by highly charged ions have an important characteristic of state-selective reactions with large cross sections.

Fragmentation of molecules and desorption of surface atoms are often induced after electron capture, because the valence electrons corresponding to chemical bonds are preferentially captured by HCI [5, 6]. The electronic transitions may play key roles in the fragmentation or desorption processes. However, the details of the processes has not been cleared yet especially in desorption or sputtering on the surfaces. To clear the mechanisms of their processes, qualitative or spectroscopic studies as well as quantitative studies are necessary. The velocity, momentum and kinetic energy as well as the emission yields of product particles are very important. We have developed a novel surface analyzer which can detect scattered atoms/ions, secondary ions, and secondary electrons [7] to investigate the details of fragmentation and desorption processes induced by slow highly charged ions. The main objective of this study is to evaluate performance of this apparatus by two prepared surfaces of GaN and dodecanethiol/Au(111) self-assembled monolayer surfaces.
2. Experimental
The schematic illustration of our experimental setup is shown in figure 1. The mass-to-charge \((m/q)\) ratio of Ar\(^{q+}\) \((q = 4–8)\) ions extracted from a compact electron beam ion source (EBIS) [8] was selected with an analyzer magnet. After adjusting their focus and trajectory with an electrostatic lens (L\(_2\)) and four parallel plates (P\(_{10}\), P\(_8\), P\(_2\) and P\(_{10}\)), the ions collide with the target surface at an angle, \(\theta \approx 10–15^\circ\) tangential to the surface. The velocity and charge state of the scattered ions or atoms of Ar\(^{q'q}\) \((1 \leq q' \leq q)\) that capture \(q'\) electrons from the surface were analyzed with the Wien filter (WF) and the charge separator (CS), respectively [7]. When each scattered ion or atom hits the detector, three signal waveforms from the position-sensitive anode (D\(_3\)) were recorded with a digital storage oscilloscope (DSO). One can analyse the position \((x, y)\) (see the coordinates in figure 1) by a simple arithmetic operation on the pulse heights of the waveforms [5, 6]. The Wien filter works as a velocity-dispersion filter; i.e. the spacing of exit slits extends along the \(y\) direction [8]. Therefore, displacement along the \(y\)-axis of the sensed position of a scattered ion with respect to that of a neutral atom reflects its charge state and velocity. The charge state and velocity of the scattered ion can be analyzed from its displacement.

Secondary ions and electrons emitted from the surface were detected with two different multichannel plates (MCP) D\(_1\) and D\(_2\). The secondary ions were extracted with an electrostatic lens biased \(-30\) V with respect to the surface potential, whereas the secondary electrons were extracted with a pair of rings biased +30 and +80 V. Since the surface of the MCP detector D\(_2\) is biased about +390 V, the electrons with kinetic energy larger than 2 eV arrive at the detector after passing through two rings. The \(m/q\) ratios of the secondary ions were analysed with a time-of-flight mass spectrometer.

![Figure 1. The schematic illustration of experimental setup](image)

EBIS, Electron Beam Ion Source; L\(_1\) and L\(_2\), Einzel lenses; MS, \(m/q\) selector; P\(_{10}\), P\(_8\), P\(_2\) and P\(_{10}\); Parallel plate deflectors; D\(_1\) and D\(_2\), MCP detectors of secondary ions and electrons; TOF-MS, Time-of-flight mass spectrometer; WF, Wien filter; CS, Charge separator; D\(_3\), Position-sensitive MCP detector of the scattered ions and atoms; DSO, Digital storage oscilloscope; LAN, Local area network; PC, Personal computer
This apparatus allows us to analyze solid surfaces in four different operation modes: 1) low-energy ion-scattering spectroscopy (LEIS), 2) SIMS in coincidence with LEIS, 3) SIMS triggered by scattered neutral atoms and 4) SIMS triggered by secondary electrons. The operation mode 1) needs only D₃ signals of scattered ions. The mode 2) needs the coincidence detection of secondary ions and scattered ions. The surface can be analyzed by mode 4) if TOF-MS is measured with the start signals of secondary electrons. The results of surface analyses by modes 2) and 4) will be presented in this paper.

The background pressure of the collision chamber was maintained below 6 × 10⁻⁷ Pa. The kinetic energy of Ar⁺ was 2.5 × q keV. The scattering angle was about 20° with respect to the direction of incident Ar⁺ ions. The flight length and acceleration voltage of secondary ions were 728 mm and 120 V, respectively, in the TOF-MS.

3. Results and discussion

Figure 2 shows the 2D-distributions of scattered Ar atoms and Ar⁺ ions detected with D₃ in collisions of Ar⁶⁺ ions with a GaN(0001) surface. The y positions of Ar atoms stayed constant at 23 mm as shown with a white broken line, whereas those of Ar⁺ ions decreased linearly with an increase in the electric field of the charge separator E₉S, as shown by a red solid line. These figures clearly demonstrate that the scattered atoms and ions were completely separated by the parallel plate CS.

Figure 3 shows the correlation map of the time difference between T₁ (flight time of secondary ion in the TOF-MS) and T₂ (flight time of scattered ion from surface to D₃), and the displacement y of the scattered Ar⁺ ion at the D₃ detector (data taken under E₉S = 267 V/cm). In the case of Ar²⁺ incidence, T₁ (≥4.5 µs) was much longer than T₂ (≈ 1.9 µs). An intense proton spectrum was clearly observed in figure 3(a) and in the TOF spectrum, as shown in figure 3(b). The velocity dispersed pattern corresponding to LEIS spectrum is shown in figure 3(c), although we have not yet converted the displacement y into the kinetic energy. The pass energy of the Wien filter was estimated to be 15.0 ± 0.6 keV. Three components of the velocity peaks, indicated by arrows, are seen in the figure. The three peaks were mainly due to the components of the proton spectrum. This suggests that proton emission from the GaN(0001) surface correlates with three different energy losses of scattered Ar⁺ ions.

Figure 4 shows the TOF spectra of secondary ions emitted from a dodecanethiol/Au(111) surface [9] interacting with Ar⁷⁺ (q = 4, 6 and 8). These data were taken with the start signals of secondary electrons (operation mode 4). The other experimental conditions were the same as those in the case of GaN(0001). The surface is a self-assembled monolayer (SAM) comprising the ligand group (sulphur),
the alkane chain ((CH₂)₁₁) and the terminal functional group (CH₃). Protons as well as molecular ions, such as H₂⁺, C₂Hₙ⁺ (n = 2–6), and C₃Hₘ⁺ (m = 4–8) coming from the chain and the terminal group, were observed in the spectra. These secondary ions were also observed in collisions between Arᵢ⁺ (q = 5–9) and alkanethiol-SAMs at θ = 60° [9]. The relative yield of a specific ion with respect to the total number of detected ions is charge state dependent. For example, the relative yield of protons increased with an increase of q, whereas relative yields of molecular ions decreased. This tendency, i.e. the different q-dependence between protons and other ions with heavier mass, was also observed in GaN and SiC surfaces partially covered with hydrocarbon molecules [10].

The SIMS in coincidence with scattered ions which were dispersed with their kinetic energies was successful in the present study. However their absolute energies have not been determined yet. We are preparing to achieve the LEIS measurements by calibrating the Wien filter. Triple coincidence detection among the scattered ions, secondary electrons, and the secondary ions is expected in the next stage.

4. Conclusions
A novel SIMS apparatus that allows us to perform coincidence detection between secondary ions and scattered atoms/ions or secondary electrons has been developed. A SIMS measurement by coincidence detection with scattered ions was performed in collisions between Arᵢ⁺ ions and a GaN(0001) surface at θ ~ 12°. We recognized three velocity components of Ar⁺ ions detected in coincidence with secondary ions. The secondary ions, such as protons and molecular fragments were observed in the collisions of Arᵢ⁺ (q = 4–8) with a dodecanethiol/Au(111) surface.

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