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An anomalous decrease in the scattered N_2^+-ion yield from Al(111)

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Abstract. The incident-energy dependence and the angular distribution of the scattered N_2^+-ion yield from an Al(111) surface were measured in the incident-energy range 10–150 eV. A sudden decrease in the incident-energy dependence of the energy dissipating N_2^+-ion yield was observed in the 45° specular scattering geometry. The observed result is closely correlated with the normal component of the kinetic energy of incident ions. We propose a possible mechanism in which the sudden decrease appears as a result of the N_2^+ dissociation induced by the translational-to-internal-energy transfer.

1. Introduction

A study of the dynamical process of atoms, molecules and ions on solid surfaces is very important for elucidating various microscopic surface phenomena. The dynamical interactions between molecules and metal surfaces occurring by means of energetic molecular ions have been intensively studied by a few groups [1–13]. One group has studied dynamical processes by projecting molecular ions in the incident energy range of a few hundreds to a few thousands of electron volts at a grazing angle below 5° onto a metal surface and has elucidated the dissociation mechanism of molecular ions [1–3]. The other group has performed experiments with 80–300 eV O_2^+ and NO^+ ions and has investigated the mechanism of the negative-ion formation which is closely correlated to a precursor state, leading to the dissociative adsorption state [4–7]. However, the very-low-energy molecular-ion beams below 100 eV have scarcely been used owing to difficulties in the beam production. The molecular ions in this energy region are very interesting from the standpoint of an investigation of chemical interactions on and with the surface. The reaction and the interaction (including the charge exchange process [8, 9]) of very-low-energy molecular ions with metal surfaces have been studied by detecting adsorbates and scattered particles [10–13]. In particular, the energy dissipation process for the surface interaction of molecular ions is considered to be important. Therefore we measured the charge neutralization by rough energy analysis of scattered ions.

Previously, we studied the surface trapping of reactive ions on Pt(001) due to the chemical interaction by means of the angular-distribution measurement of scattered ions [12]. In the present study, we have observed N_2^+ scattering on Al(111) with a rough energy analysis. Aluminium easily produces a stable nitride using energetic N_2^+ ions [14, 15]. So, the interaction potential for N_2^+ and N^+ with the Al surface

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is considered to be more attractive than that with the Pt surface. Moreover, in an impulsive collision, the translational-to-internal-energy transfer in molecular N_2^+ ions is smaller than and the translational-to-substrate-energy transfer is larger than those in the case of a Pt target, since the mass of the Al target (27) is almost the same as that of the N_2 projectile (28). Hence, in order to study the correlation between the charge exchange and energy dissipation processes, the N_2^+–Al(111) system is a good candidate. In the present study, an anomalous decrease is found in the incident-energy dependence of the ion yield of the scattered N_2^+ ions suffering energy dissipation.

2. Experiment

The experimental set-up is almost the same as that reported previously [11, 12]. The ion beam line consists of a Menzinger-type ion source, a mass-selecting magnet and a decelerating-lens system. The incident ion current was 0.1–15 nA. The scattered ions were detected with a quadrupole mass filter. The trajectories of ions passing through the mass filter were bent by 90° with a deflecting plate mounted in front of an electron multiplier, in order to prevent excited neutral species from being detected. This deflecting plate can also be used for performing a rough energy analysis of the scattered ions. In the present experiments, the scattered and the sputtered ions were energy analysed by applying a bias voltage V_b to the deflecting plate. The applied bias voltage was set to be proportional to the incident energy E_i, and then the scattered-ion yields with an energy loss proportional to the primary energy were detected as a function of the incident energy. The ion yield was obtained by integrating the mass peak and normalized with respect to the incident beam current.

An Al(111) surface was mechanically polished and cleaned by the repetition of 500 eV Ar^+ bombardment and annealing at 470–670 K. A clear 1 × 1 pattern was observed by low-energy electron diffraction and surface cleanliness was verified by secondary-ion emission measurements.

Although the stable aluminium nitride formation was observed by irradiating energetic nitrogen ions [14, 15], we consider that the present results were not affected by the nitride formation, because the experimental beam current was made as low as possible and the observed results were always reproducible under various conditions of changing beam current, beam-impinging position and scanning speed.

3. Results and discussion

Figures 1 and 2 show scattered-N_2^+-ion and sputtered-Al^+-ion yields as a function of the incident energy in specular scattering geometries at $\theta_i = 60°$ and 45°, respectively, where θ_i is the angle of incidence measured from the surface normal. In figure 1, the scattered N_2^+-ion yield shown by the full triangles corresponds to a deflector bias voltage where the highest-energy component of the scattered N_2^+ ions could be properly detected (case A). The previous experiments for the Pt(001) target were carried out in this experimental condition [9, 12, 13]. The bias voltage V_b applied to the deflecting plate was given by the ratio $b = V_b\,(\mathrm{V})/E_i\,(\mathrm{eV}) = 10$. The scattered N_2^+-ion yield decreases steeply and increases slightly through the minimum point with increasing incident energy, as seen in figure 1. The incident-energy dependence for $b = 10$ is similar to that of the N_2^+-ion yield scattered from the Pt(001) surface. In the present studies, two other ratios $b = 2.9$ (case B) and $b = 1.4$ (case C) were used. These two b-values were appropriately selected as the detected N_2^+-ion yield took the maximum values at an incident energy of 70 eV in the 60° specular scattering geometry. In cases B and C at 60° specular scattering, the scattered-N_2^+-ion yields are higher than that in case A in the energy range above 30 eV. The N_2^+ ions in cases B and C are scattered through inelastic processes which may include the re-ionization of neutralized molecules, because the kinetic energy of the detected ions in cases B and C is smaller than that in case A and sputtered Al^+ ions appear in this energy region.

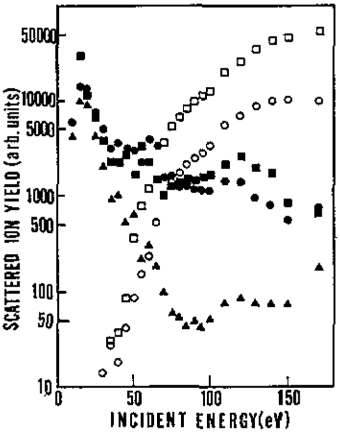

Figure 1. *Scattered-ion yields as a function of incident energy for* N_2^+ (●, ■, ▲) and Al^+ (○, □) in the N_2^+ incidence at $\theta_i = 60°$. Specularly scattered ions along the [11$\bar{2}$] azimuth were detected. The yield is given in arbitrary units. The intensity is common to figures 1, 2, 3 and 5. The ratio b of deflector bias voltage (in volts) to incident energy (in electron volts) is 10 for triangles, 2.9 for circles and 1.4 for squares.

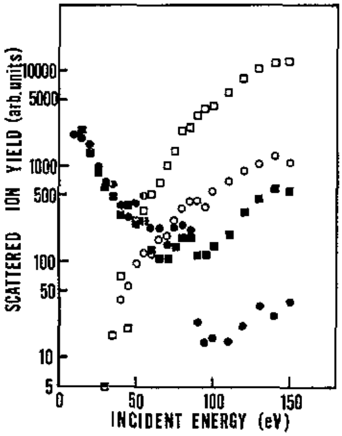

Figure 2. *Scattered-ion yields at* $\theta_i = 45°$. See figure 1.

In the 45° specular scattering shown in figure 2, the scattered-N_2^+-ion yields of cases B and C are nearly equal in the incident-energy range below 80 eV and show the same tendency as those observed in the 60° specular scattering geometry. However, the scattered-N_2^+-ion yield for case B suddenly decreases by one order of magnitude at an incident energy of 80–90 eV, while the yield for case C changes gradually and increases through a shallow minimum point. It is seen in the sputtered-Al^+-ion yield in figures 1 and 2 that scattered and sputtered ions are effectively energy analysed by changing the b-value of case B to that of case C.

Figure 3 shows the scattered-ion yields in case B for three kinds of specular scattering geometry: $\theta_i = 40°$, 45° and 60°. The above-mentioned sudden decrease which was observed at $\theta_i = 45°$ was also observed at $\theta_i = 40°$. The incident energies at the onset of the sudden decrease are 85 eV and 70 eV for 45° and 40° incidences, respectively. Then, the normal components of the incident energy, $E_i \cos^2 \theta_i$, at the onset of the sudden decrease are 43 eV and 41 eV for the 45° and the 40° incidences, respectively. Since these normal components of the incident kinetic energy are nearly equal, the normal energy is confirmed as contributing to the sudden decrease. In the 60° specular scattering geometry, a gradual decrease in the ion yield was observed at an incident energy of 120 eV and is considered to correspond to the sudden decrease observed at the 45° incidence. For the 60° incidence, the normal incident energy at the onset of the decrease is 30 eV which is smaller than those for the 45° and 40° incidences. This difference is caused by a larger surface-parallel-to-normal energy transfer in the scattering process for the 60° incidence, because the parallel incident energy is higher than in the other two cases.

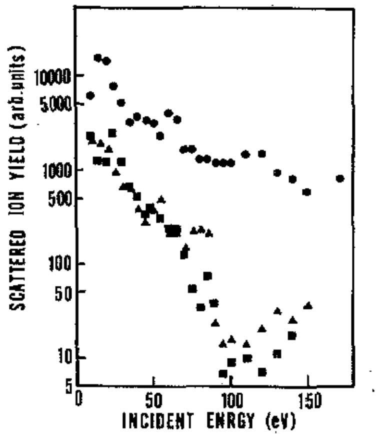

Figure 3. Scattered-ion yields for N_2^+ in the N_2^+ incidence. The ratio b is 2.9. The incidence angle measured from the surface normal θ_i was 40° for squares, 45° for triangles and 60° for circles. The specularly scattered ions along the [11$\bar{2}$] azimuth were detected.

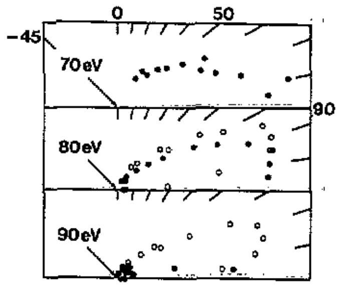

Figure 4. Angular distributions of scattered N_2^+ ions at $\theta_i = 45°$ with $E_i = 70$, 80 and 90 eV. The scale is arbitrary for each diagram. The ratio b was 2.9 for full circles and 1.4 for open circles.

The angular distribution of scattered N_2^+ ions at the incidence angle $\theta_i = 45°$ is shown in figure 4. From a comparison of the situations below and above the appearance energy of the sudden decrease in case B, the lobe position for the 90 eV incidence is found to shift much closer to the surface parallel than that for the 80 eV incidence; from $\Psi_e = 15°$ to $\Psi_e = 5°$ (where Ψ_e is the exit angle from the surface parallel), the lobe width for the 90 eV incidence is much narrower than that for the 80 eV incidence. Therefore, the ion yield of N_2^+ ions scattered to large scattering angles is strongly reduced for the 90 eV incidence in comparison with that for the 80 eV incidence. This result shows that the impulsive collision with a small impact parameter contributes dominantly to the sudden decrease in the scattered-N_2^+-ion yield. Moreover, the N_2^+ ions scattered along the surface parallel observed for 80 and 90 eV incidences are considered to be scattered through a soft collision where the orientation of the incident N_2^+ ions is surface parallel.

The peak position for 80 and 90 eV in case C is located at $\Psi_e = 15$–$25°$, which is larger than that in case B. So, the N_2^+ ions detected in case C are considered to be scattered through an impulsive collision and produced by the re-ionization process in the collisional region.

Several origins can be considered for the sudden decrease in the N_2^+-ion yield. The most probable mechanism is the dissociation of N_2^+ ions. The translational-to-internal-energy transfer leads to the dissociation of the molecule. In the O_2/Ag(111) system, a calculation based on *ab-initio* pair potentials shows that the dissociated fraction becomes larger with increasing surface corrugation and depends on the normal incident energy [6]. Moreover, the dissociated fraction increases abruptly in the narrow range of normal incident energies on scattering from the corrugated surface. These results agree with our observation, although the angle of incidence and the interaction potentials differ from those in the present case. In the present case, the sudden decrease was observed prominently at 45° incidence, where the large surface corrugation is felt by an incident molecule compared with at 60° incidence, and the onset of the sudden decrease depends on the normal component of the incident energy.

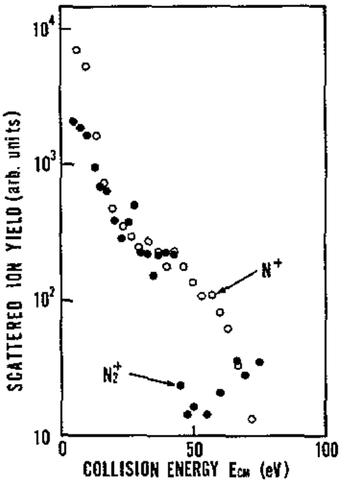

Figure 5. Scattered-ion yields for N_2^+ (●) and N^+ (○) in the N_2^+ and N^+ incidences, respectively. The incident energy was scaled by impact energy in the centre-of-mass system. The incidence angle measured from the surface normal θ_i was 45°. The specularly scattered ions along the [11$\bar{2}$] azimuth were detected.

Figure 5 shows the incident-energy dependence of the scattered N_2^+- and N^+-ion yields in the 45° specular scattering geometry. The incident energy was scaled by the impact energy in the centre-of-mass system based on a binary collision, because the ion survival probability is determined by the ion penetration depth (i.e. the normal component of the incident energy) in the very-low-energy region [16], and the impact energy in the centre-of-mass system plays an important role in an inelastic process such as the translational-to-internal-energy transfer. The N_2^+-ion yield agrees marvellously with the N^+-ion yield in the region below about 40 eV. This result means that the ion penetration depth is nearly equal in the two cases. The sudden decrease was observed only in the N_2^+ incidence and is a characteristic property of the molecular ion. So, the dissociation, which is probably resonant, by translational-to-internal-energy transfer is considered to be the most probable origin of the sudden decrease. In the present experiment, however, we could not detect dissociated N_{dis}^+ ions. This result is different from that in the Pt(001) target system [13] and the difference is considered to be caused by high reactivity of the N atom with the Al surface. The dissociated N^+ ion is trapped on the surface and neutralized.

Another probable mechanism for the sudden decrease is the enhancement of the neutralization probability through an impulsive collision. However, the degree of Auger neutralization and quasi-resonant neutralization of the N_2^+ ion is considered to be equal to that of the N^+ ion because the energy level of the ground state of N_2 is nearly equal to that of N. Moreover, the degree of the neutralization induced by the diabatic crossing between the Al L and M shells and the N–L shell [17, 18] in the N_2^+ case is considered to be also equal to that in N^+ cases. So, the sudden decrease is not considered to be caused by the abrupt change in the neutralization probability. At this stage, we cannot discuss the matter further nor clearly explain why the sudden decrease is observed only in case B. A detailed energy analysis will be carried out by the use of a hemispherical energy analyser in a future study.

In summary, we have measured the incident-energy dependence and the angular distribution of the scattered-N_2^+-ion yield in the 10–150 eV energy range. The sudden decrease in the incident-energy dependence of the scattered-N_2^+-ion yield was observed in case B for the 45° specular scattering geometry. This phenomenon is closely correlated to the normal component of kinetic energy of incident ions. We propose one possible process: the dissociation induced by the translational-to-internal-energy transfer causes the sudden decrease in the N_2^+-ion yield.

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