Neutralization of Very-Low-Energy Ions on Pt(100)

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Charge exchange of Ar^+, N^+, and N_2^+ ions with a Pt(100) surface has been studied over incident energies ranging from 10 to 400 eV. Below 100 eV, the ion survival probably increases with decreasing energy. This increase represents the changing penetration depth of incident ions into the ion-surface interaction potential. Comparison of the result for Ar^+ incidence with that for nitrogen ions shows that resonance neutralization is of minor importance for the ion survival probability and shows the preferential neutralization of nitrogen ions at high energies.

Charge exchange between a low-energy ion and a metal surface is one of the important problems on surface dynamics extensively studied from both theoretical and experimental aspects. It is closely related to the electronic structure of the surface and especially to the surface electron density profile determined by the surface atoms. A most frequently used guideline for ion neutralization has been presented by Hagstrum concerning the Auger-type process.[1] The ion survival probability P is given by

$$P = \exp\{-v_c[(1/v_{i\perp}) + (1/v_{o\perp})]\}, \qquad (1)$$

where v_c is the characteristic velocity and $v_{i\perp}$ and $v_{o\perp}$ are the normal components of the velocity of the incoming and the outgoing ion, respectively. Usually v_c is taken to be a constant. This formula is derived for slow ions from the transition rate,[2]

$$R_t(s) = A \exp(-as), \qquad (2)$$

where s is the distance between the ion and the surface. Most of the noble-gas ion scattering experiments show the trend that P increases with increasing incident energy at energies higher than 100–200 eV. Therefore, it has been understood that P falls to zero when the incident energy goes to zero, as predicted by Eq. (1). However, very few measurements of scattered ions at very low energies ($1 \leq E_i \leq 100$ eV) have been reported, except for alkali-metal ions.[3,4]

We report in this Letter a first experimental result on the charge exchange between a metal surface and very-low-energy non-alkali-metal ions ($E_{i\,min} \simeq 10$ eV). We found that P is a monotonously decreasing function for incident energies below 100 eV. The target was Pt(100) and projectile ions were Ar^+, N^+, and N_2^+. The new finding obtained by the present experiment is useful knowledge for surface-science studies, because the high survival probability of very-low-energy ions shows the possibility of the development of a new experiment, such as ion-molecule reactions on the surface.[5] Also, we show that resonance neutralization is of minor importance, when we discuss survival ions. Our experiment demonstrates clearly the difference between noble-gas ions (Ar^+) and chemically reactive ions (N^+, N_2^+) from the viewpoint of charge exchange with the surface in the higher-energy regime ($E_i \geq 100$ eV).

The experiment was carried out with a modified apparatus described previously.[6,7] A bright Menzinger-type ion source incorporated with a mass-selecting magnet installed in a UHV chamber and an efficient deceleration-lens system produced a 10–40-nA ion current, even at very low energies ($E_i \leq 100$ eV). A Pt(100) surface was cleaned by the alternate repetition of Ar^+ sputtering, annealing in oxygen at 900 °C, and annealing in vacuum at 1200 °C. Low-energy electron diffraction showed a clear 5×20 pattern and Auger electron spectroscopy showed no detectable contamination. The scattered ions were detected with a quadrupole mass filter which is rotatable in two axis around the crystal surface, and a high transmittance in the detection system was obtained for the observation of scattered N^+ and N_2^+ ions of low survival probability at low energies.[8] The energy of the scattered ions could not be resolved. The mass filter controlled by a high-power system (Extranuclear model 011-1) allowed us to separate the mass of swift ions with a poor mass resolution ΔM of about 5. Trajectories of transmitted ions were bent by 90° with a deflector before detection with an electron multiplier in order to remove neutral species. The voltage applied to the deflector was appropriately varied according to the energy of the transmitted ions. This deflector also worked as a high-pass filter to remove most of the low-energy secondary ions. The scattered ion yield normalized with the ion current was obtained by our integrating the mass peak as a function of the incident energy.

With a proper sample cleaning, secondary impurity ions were not observed. After several hours, the observed secondary impurity ions were mainly (directly recoiled) H^+ ions, and thus the measurements of Ar^+, N^+, and N_2^+ ions were not affected. Ambient N_2 gas is neither molecularly nor dissociatively chemisorbed on Pt at room temperature, and Pt nitride has not been known so far. To check if N atoms exist stably on the surface
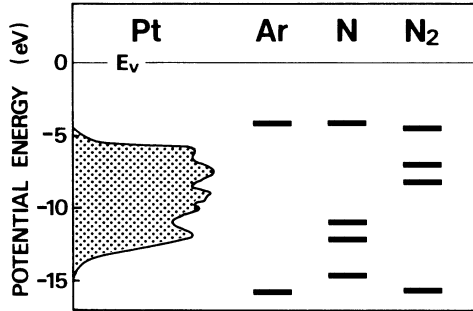
FIG. 1. Energy diagram relevant to discussion of the charge exchange between the Pt surface and Ar^+, N^+, and N_2^+ ions. The level shifting and broadening in the vicinity of the surface is ignored.

region, we have exposed the surface to sufficient amounts of N^+ and N_2^+ ion beams (5×10^{15} ions/cm^2) at several incident energies. We could not find even a trace Auger-electron spectroscopy peak originating from surface nitrogen. This fact assures us that incident N^+ and N_2^+ ions are neither absorbed into the crystal nor adsorbed on the surface, and that detected ions are not ions once chemisorbed on Pt(100).

Figure 1 shows an energy diagram relevant to the charge exchange of Ar^+, N^+, and N_2^+ ions with the Pt(100) surface.[9-11] Since the energy levels of the neutral ground states of these projectile ions lie at nearly the same position just below the bottom of the Pt valence band, the Auger transition rates to the ground states are expected to be nearly the same. The lowest excited state of neutral Ar is located above the Pt Fermi level, whereas a few excited states of N_2 and N are in resonance with the upper and the lower part of the Pt valence band, respectively.

Figures 2–4 show the scattered ion yields in the specular direction as a function of incident energy. In the case of incident N_2^+, dissociatively scattered N^+ ions were observed in addition to the survival N_2^+ ions. The N^+ signal begins to emerge from 50 eV and the N^+ yield increases linearly with increasing incident energy. The scattered ion yields show the known incident-energy dependence above the turning point of 100 eV for Ar^+ and of 120 to 140 eV for N^+ and N_2^+. Below these energies, however, they remarkably increase with decreasing energy. It appears that the yield is dependent on the energy rather than on the velocity of the ions. In a separate experiment with a two-dimensional position detector,[6] we had observed a similar increase of survival ions from a Cu(100) surface at very low energies. The angular distribution of survival ions shows that the lobe position shifts from the direction of specular reflection towards the surface ($\theta_f > \theta_i$) as incident energy decreases.

The measured yield is proportional to the product of the scattering cross section $\sigma(E_i, \theta)$ and the ion survival
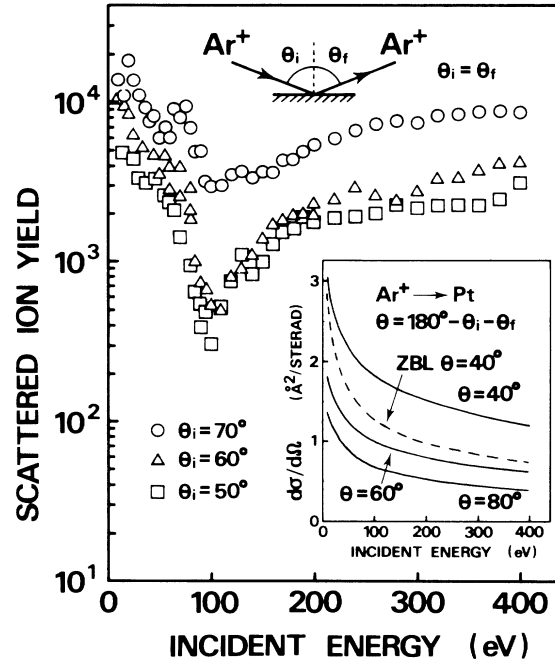

FIG. 2. Incident energy dependence of the scattered Ar^+-ion yield for three specular scattering geometries along the [001] azimuth. Although the intensity is given in arbitrary units, it is common to Figs. 2 to 4. Inset: The differential scattering cross sections calculated by use of the Born-Mayer potential (solid lines) and the Ziegler-Biersack-Littmark (ZBL) potential (dashed line) as a function of incident energy.

probability P. The energy dependence of σ can be roughly estimated by the differential scattering cross section assuming a binary collision event. This assumption is not valid at very low energies but we expect that it will
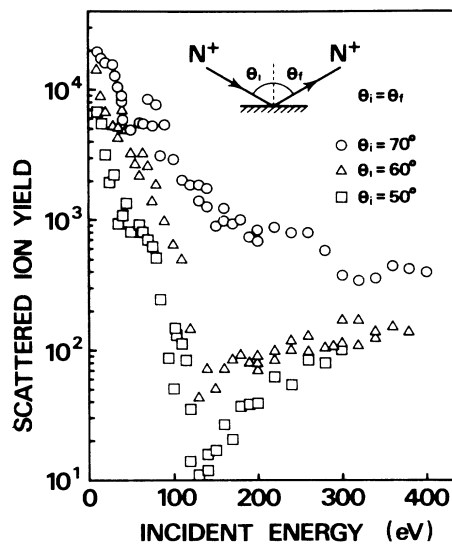

FIG. 3. Incident energy dependence of the scattered N^+-ion yield for three specular scattering geometries.
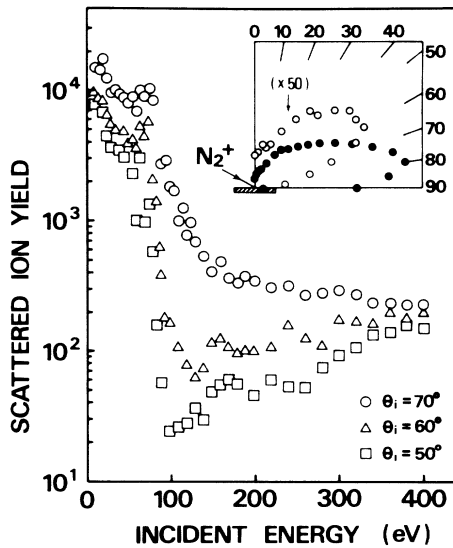
FIG. 4. Incident energy dependence of the scattered N_2^+-ion yield for three specular scattering geometries. Inset: The angular distributions of scattered N_2^+ ions at $\theta_i = 60°$ with $E_i = 200$ eV (open circles) and 50 eV (filled circles). The results for 200 eV are represented with a magnification of 50.

not lead to a serious misestimate, if only the relative value for a change of energy is discussed. The inset of Fig. 2 shows results calculated for the Ar^+-Pt case with use of the Born-Mayer potential[12] and the Ziegler-Biersack-Littmark potential.[13] In the case of the Born-Mayer potential, the relative value was found to be insensitive to the choice of parameters although the absolute value was considerably affected. It is seen that the calculated value of σ at 10 eV is 1.5 to 2.5 times as large as that at 100 eV. Since the present experimental condition is for low incident energies and large incident angles, most of the ions cannot penetrate into the crystals and are predominantly scattered out into the vacuum from the topmost layer. Therefore, the scattering cross section is expected to be even more energy independent than the calculated value shown in the inset of Fig. 2. However, the observed ion-yield increase is more than 1 order of magnitude for Ar^+ and more than 2 orders of magnitude for N^+ and N_2^+ for a corresponding change of beam energy. Angular distributions of the scattered N_2^+ ions are shown in the inset of Fig. 4. The ion yield at 50 eV is more than 10 times larger than that at 200 eV for every scattering angle. The peak position is shifted by 20° and the total ion yield changes by a factor of nearly 50. Therefore, it is clear that the experimental results show an enhancement of the ion survival probability at very low beam energies and are contradictory with the conventional understanding that the ion survival probability falls to zero when energy goes to zero.

In the usual treatment of charge exchange, the interaction region is divided into three parts, i.e., incoming path, collisional region, and outgoing path. The contribution from the collisional part is expected to be small at very low energies, since this process occurs when the projectile approaches a target atom close enough to cause the overlapping of wave functions and to form a quasi-molecule. Therefore, for the result at very low energies it is relevant to discuss the resonance (RN) and Auger neutralization (AN) processes in the incoming and outgoing paths. There exist controversies in theoretical studies[14,15] as to whether the transition rate of RN is by far higher than that of AN or Auger deexcitation.

To see the contribution of resonance neutralization, we compare the yields of Ar^+ with that of N^+ and N_2^+ in the very-low-energy regime, where RN is thought to contribute for only the latter two species. A comparison among Figs. 2 to 4 shows that the yields for these three projectile ions are nearly identical at the same incident angles and energies ($E_i \leq 100$ eV). This indicates that resonance neutralization is of minor importance, as pointed out by O'Connor et al.,[16] when we discuss the survival probability of scattered ions. The real transition rate of RN may be much lower than that of AN. Another possibility is that reionization from electronically excited states (resonance ionization or autoionization) is possible with considerable probability and that the apparent ion survival probability is determined by the deexcitation rate of the Auger processes.

The only way to explain the steep decrease of the scattered ion yield with increasing energy is to assume that it reflects the steep increase of the transition rate of RN, AN, and collisional neutralization at close encounter. That is to say, at very low energies, the value of P is determined by the closest approach distance between the ion and the surface atom, $s_0(E_i)$, rather than the residence time in the vicinity of the surface. Suggestive phenomena are seen in ion neutralization spectroscopy for excited $He^+(2s)$ ions incident on Ni.[1] The Auger electron peak around 35 eV disappears as the energy of the ions is raised from 5 to 80 eV.

If we assume that the Auger process determines the incident-energy dependence of the ion survival probability at very low energies, it can modeled phenomenologically as follows. We account for the energy dependence of the characteristic velocity v_c implicitly through the closest approach distance s_0 via

$$v_c = (A/a)\exp(-as_0). \tag{3}$$

In specular reflection, the parallel component of velocity is nearly conserved and we assume that the ion-surface interaction is expressed by a repulsive potential of the form, $V(s) = B\exp(-bs)$. Equating the perpendicular energy to $V(s)$,[17] we obtain

$$v_c \propto v_i^{(2a/b)}. \tag{4}$$

From Eqs. (1) and (4), it is evident that P is a decreasing function of v_i if $2a/b > 1$. It is reasonable to assume

that $a \simeq b$ at very low energies, since the repulsive interaction and the Auger transition depend on overlapping of the same wave functions.[18] According to the universal behavior of the v_i dependence of v_c suggested by O'Connor et $al.$,[16] a relation $v_c \propto v_i^2$ is satisfied, when v_i is small. Therefore, the energy dependence of the ion survival probability can be explained qualitatively within Hagstrum's approach if we limit ourselves to the very-low-energy regime. However, the observed V-like shape of the ion yield cannot be reproduced by any choice of the parameters of a or b. This indicates that the real charge exchange is complicated by other processes, and the present experimental result is clearly inconsistent with the simple model.

Next, we turn to the energy regime above 100 eV. The yield of Ar^+ begins to increase while those of N^+ and N_2^+ continue to decrease. Above 200 eV the yield Ar^+ is about 10 times as large as those of N^+ and N_2^+, for comparable incident angles and energies, whereas the yields of N^+ and N_2^+ are nearly the same. The results manifest the different surface interaction between a nonreactive noble-gas ion and reactive nitrogen ions. At the close projectile–target-atom encounter, wave functions overlap and a quasimolecule is formed. Charge exchange happens by the diabatic crossing of energy levels. Since Ar^+ has only one hole in the $3p$ level, but N^+ (N_2^+) has 4 (5) holes in the $2p$ and the valence state, respectively, the probability that an electron fills a hole is much higher for N^+ (N_2^+). This hypothesis is the most probable interpretation for the preferential neutralization of reactive species, and was used by Kasi et $al.$ in regard to neutralization of C^+, O^+, and Ne^+ on Ni(111).[19] Another possible effect which complicates the charge exchange is reionization. This will easily take place as well as the collisional neutralization at the close encounter. The scattered ions at high energies will be a mixture of reionized ions and the survival ions which suffered no neutralization.

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