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Ion-surface charge exchange during sputtering and low-energy H^+ scattering from Ar, Kr, and Xe layers formed on metal surfaces

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Low-energy H^+ scattering from condensed Ar, Kr, and Xe layers formed on Au has been investigated in comparison with the sputtering of secondary ions in order to establish a comprehensive picture of ion emission from surfaces. The hole created in the Ar $3p$ orbital is localized at any coverage, as evidenced by the emission of sputtered Ar^+ and scattered H^+ ions, whereas the Xe $5p$ hole is rather delocalized, especially in the low-coverage regime, so that almost complete neutralization of Xe^+ and H^+ occurs. The nature of the localization/delocalization of ionic holes in thick rare-gas layers is also examined.

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Particle-surface interactions have attracted considerable attention from both the fundamental and practical points of view. However, one of the most fundamental problems, i.e., the mechanism of charge exchange, is still poorly understood. An electron capture (or loss) can trigger an internal evolution in the surface species and thus lead to a variety of processes, such as the fragmentation of a molecule, reaction at the surface, stimulated desorption, vibrational excitation, and so forth. This subject provides a basis for the study of various surface analysis techniques using ions, such as low-energy ion scattering (LEIS), secondary-ion mass spectroscopy (SIMS) and electron- and photon-stimulated desorption. Thus far, a variety of mechanisms regarding the formation of ions and their subsequent emission from surfaces have been proposed.[1–3] If energetically possible, the most probable and efficient charge-transfer mechanism in the case of a metal surface is resonant charge transfer.[2,4] Reactive ions such as H^+ undergo efficient resonance neutralization on metal surfaces, whereas the neutralization probability is suppressed on highly ionic compound surfaces due to the localization of the H $1s$ hole.[5] The noble-gas ions survive neutralization considerably even at metal surfaces because they are neutralized mainly via the two-electron Auger process. The presence of a large band gap and the high binding energy of insulating materials play a decisive role not only in the neutralization but also in nonadiabatic electronic transitions. In this context, thin layers of physisorbed atoms or molecules on a metal surface are of interest. With increasing coverage, the surface electronic properties can be continuously changed from metallic to insulating. To date, a large number of SIMS studies have been done,[6,7] but very little attention has been paid to this point. To the best of my knowledge, moreover, no LEIS studies of physisorbed systems have been performed. Sputtered neutral yields are known to be very high for physisorbed systems, and electronic sputtering has been proposed for the erosion process of thick films.[8,9]

In the present work, the results of a study of the sputtering of and H^+ scattering from Ar, Kr, and Xe layers formed on a Au substrate are presented. It is shown that the charge-transfer process on Xe changes markedly between submonolayer adsorption and multilayer formation but that no significant change occurs on an Ar layer, indicating that the Xe $5p$ hole is delocalized due to resonant tunneling to the valence band of Au, especially in the submonolayer-coverage regime, whereas the Ar $3p$ hole tends to be localized at any coverage. The neutralization of H^+ on a thick Xe layer is also different from that on Kr and Ar layers due to hybridization between the Xe $5p$ orbitals or the effects of the valence band. These findings lead to the conclusion that simple physisorption can be realized for Ar adsorption, but that some chemical interaction is involved in the adsorption of Xe.

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure of 1×10^{-10} mbar) equipped with facilities for standard surface characterization. The ion beams were extracted from a discharge and were mass analyzed using a Wien filter. In the LEIS experiment, the surface was bombarded by He^+ and H^+ ions with an incidence angle of 20° and the positive ions emitted normal to the surface were detected by means of a hemispherical electrostatic energy analyzer (ESA) operating with a constant energy resolution of 2 eV. The ion beam could be chopped by an electrostatic deflector into pulses with width of 100 ns and frequency of 40 kHz. Thus, the emitted ions were detected by the time-of-flight (TOF) technique. The TOF-SIMS measurements were made in such a manner that the sample, floated with a bias voltage of +500 eV, was irradiated by a primary He^+ or Ar^+ beam (2 keV) through a grounded stainless-steel mesh placed 4 mm above the sample, and the positive ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. The energy distribution of the sputtered ions could be measured using the ESA in the TOF mode. To avoid sample damage, the ion beam current was reduced to below 5 nA/cm^2 and each measurement was completed within 10 s. A polycrystalline Au foil with a thickness of 200 μm was mounted on a sample holder which was cooled to 10 K by means of a closed-cycle He refrigerator. The surface was cleaned by Ar^+ sputtering at room temperature. The cleanliness of the surface was confirmed from the TOF-SIMS spectra as well as the LEIS spectra (using $E_0=1$ keV He^+), which revealed no peak other than Au. The one monolayer (1 ML) coverage of the Ar, Kr, and Xe layers was determined from the decay

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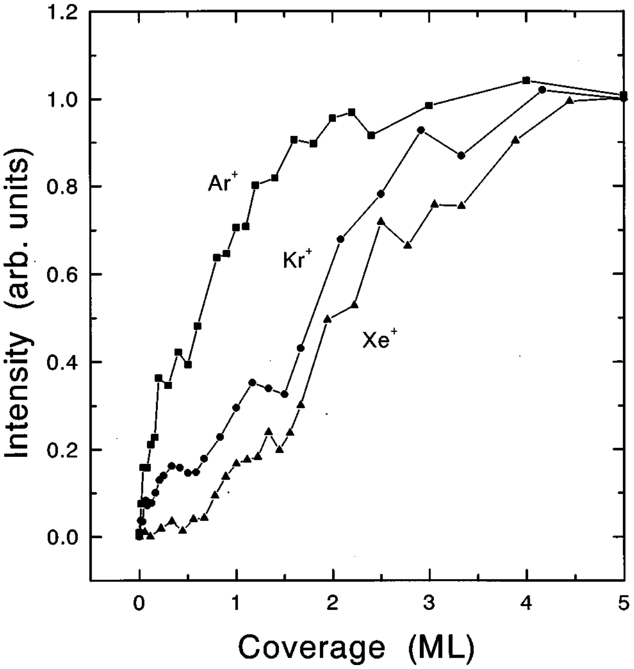

FIG. 1. The intensities of sputtered secondary ions as a function of coverage. Ar, Kr, and Xe layers formed on a polycrystalline Au surface were bombarded with $E_0 = 2$ keV Ar^+ ions and the secondary ions emitted normal to the surface were detected. The intensities at the 5 ML coverage are normalized by multiplying by a factor of 1.5 and 3.2 for Kr^+ and Xr^+, respectively.

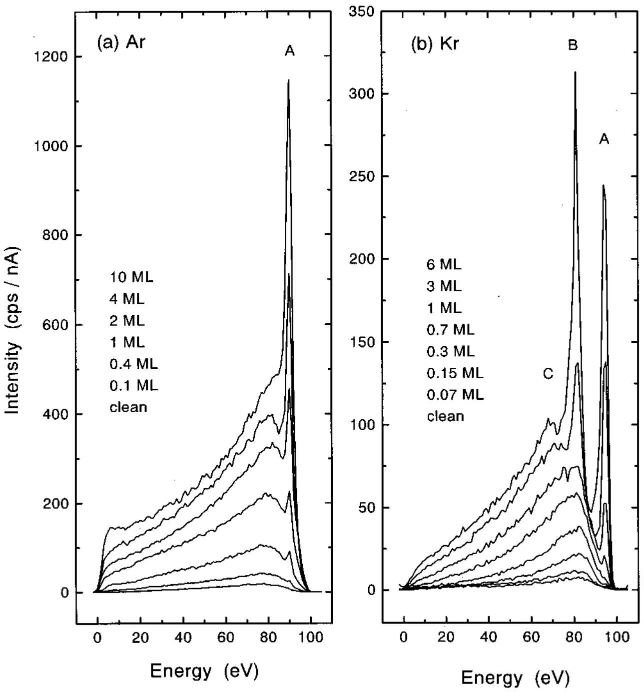

FIG. 2. Energy spectra of H^+ scattered from (a) Ar and (b) Kr adsorbed on a Au substrate as a function of coverage. The surfaces were irradiated with an $E_0 = 100$ eV H^+ beam at the incidence angle of 20° and the ions scattered normal to the surface were analyzed. The intensities are normalized through the ion beam current. cps indicates counts per second.

curve of the Au surface-peak intensity in LEIS (using an $E_0 = 100$ eV He^+ beam to minimize the sputtering effect) as a function of exposure time, and the film thickness was estimated on the basis of this value.

Figure 1 shows the intensities of sputtered secondary ions as a function of coverage obtained by bombardment with primary Ar^+ ions ($E_0 = 2$ keV). The intensities are normalized to 5 ML coverage. The sputtered Ar^+ intensity increases steeply from the initial stage of adsorption and tends to become saturated in the higher-coverage regime. On the other hand, very few Xe^+ ions are emitted at the initial stage and then the emission increases gradually in intensity after the first monolayer is formed. The results for Kr^+ lie between these two cases. The low Xe^+ ion emission for submonolayer coverage is caused by the preferential neutralization of Xe^+ directly adsorbed on the Au substrate. It might be presumed that a contribution in the Ar^+ yield, especially at the earlier stage of adsorption, comes from a double excitation of Ar^{**} in a close encounter, followed by autoionization far from the surface. The doubly charged ions emerge in the multilayer regime but their intensities are much smaller than those of the singly charged ions.[7] This double excitation is more efficient in symmetric collision systems[10] and, hence, a primary Ar^+ ion might lead to a high Ar^+ yield. However, almost the same evolution curves are obtained for Ar^+, Kr^+, and Xe^+ using primary He^+ ions, indicating that the doubly excited species make very little contribution to the sputtered ion yields.

Figure 2 shows the energy spectra of H^+ ions ($E_0 = 100$ eV) scattered from the Ar and Kr layers formed on Au as a function of coverage. The intensities are normalized through the ion beam current. The clean Au surface exhibits a broadly humped background, which is caused by the reionization of H^0.[5] With increasing coverage, the surface peak of H^+ scattered from the adsorbate becomes pronounced relative to the background. The surface peak consists of the elastic peak *A* and two energy-loss peaks, *B* and *C*. The loss peaks are remarkable for Kr but almost negligible for Ar. This kind of energy loss is caused by the electron-hole pair excitation of the surface or the reionization of H^0.[5] The intensities of both the background and the surface peak are higher at the Ar surface than at the Kr surface. Note that the surface peak of H^+ appears even with a very low coverage of Ar. The energy spectra of H^+ scattered from the Xe layer are shown in Fig. 3. The H^+ intensity is considerably smaller than that from the Ar and Kr surfaces. The surface peaks are absent in the submonolayer-coverage regime, and no marked increase of the H^+ intensity occurs for a multilayer of Xe.

To date, a large number of studies of rare-gas adsorption on metal substrates have been done.[11–21] It is expected that the adsorption of rare-gas atoms is much simpler than that of other chemically reactive species because of the weak interaction between the adatom and the metal surface. This weak physical interaction is reflected in the small adsorption energy. However, the adsorption energy of Xe on transition-metal surfaces is quite high, suggesting the existence of interactions other than the van der Waals force. Moreover, the work-function decrease (0.4–1.4 eV) upon adsorption of rare-gas atoms[12–14] implies the existence of some charge-

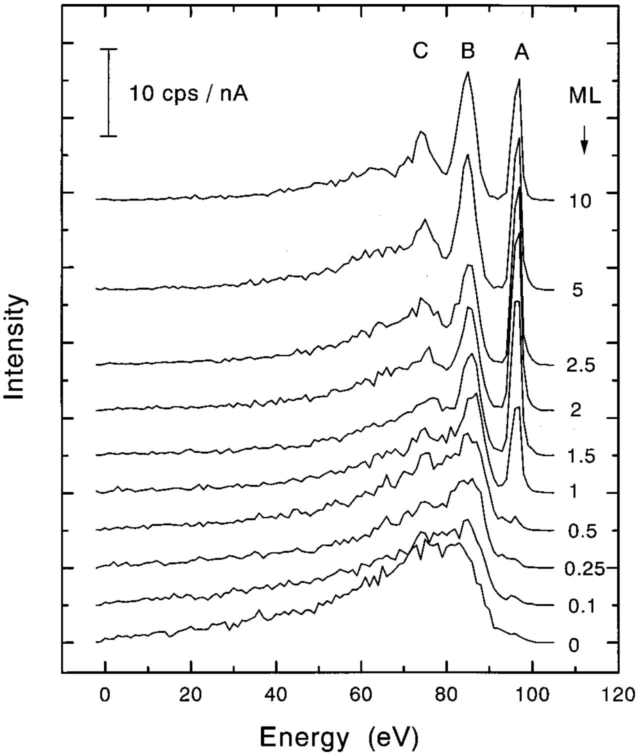

FIG. 3. Energy spectra of H^+ scattered from Xe adsorbed on a Au substrate as a function of coverage. The measurements were made under the same conditions as those in Fig. 2. The intensities are normalized through the ion beam current. cps indicates counts per second.

transfer interactions in bonding. The nature of the bonding of rare-gas adatoms on metal surfaces has been discussed extensively in order to elucidate these experimental results,[15–20] but some controversies still exist.

Ultraviolet photoelectron spectroscopy (UPS) from Xe adatoms has been utilized as a powerful probe for investigating variations in the surface electrostatic potential.[21] The major hypotheses in this approach are that adsorbed Xe resides outside the surface dipole layer and that the Xe levels are pinned to the vacuum level. Therefore, the binding energy of the Xe $5p$ level is directly related to the local work function near the adsorption site. The binding-energy shift observed in UPS should be rationalized in terms of not only the initial-state effect mentioned above but also a final-state effect arising from the relaxation process. It should be noted that the np^5 hole state created in rare-gas atoms during sputtering and scattering of H^+ ions is essentially the same as the final state observed in UPS. Therefore, some insight into the final-state electronic configuration or the nature of the bonding of rare-gas atoms on a surface should be obtained from the neutralization of the sputtered rare-gas ions and scattered H^+ ions.

On metal surfaces like Au, the H $1s$ orbital merges into the valence band and forms a resonance state. The lifetime of the valence hole originating from the H $1s$ hole, as estimated from $\tau = \hbar / W$ where W represents the bandwidth, is quite small relative to the ion-surface interaction time (5×10^{-15} s), so that complete neutralization of H^+ occurs (the band effect).[22] The hole survives for a much longer time on the surface of molecular solids and, hence, a marked surface peak of H^+ due to survival of the resonance neutralization is observed. The surface peak has so far been observed only for ionic compounds with highly ionic bonds, such as alkali-metal halides and alkaline-earth halides, whereas no appreciable surface peak appears for metals and covalent materials. The H^+ ion probes the local electronic configuration around target atoms and H^+ scattering has been successfully applied to the analysis of the nature of bonding of alkali-metal adatoms on the basis of ion neutralization.[23] The underlying concept of this approach is that the neutralization probability of the H^+ ions, or delocalization of the valence hole, should be related to covalency in bonding, which is defined as the quantum-mechanical sharing of valence electrons (holes). The highly localized nature of the rare-gas *np* hole in the thick physisorbed layer clearly shows that the existence of electronic levels at the same energy position is not sufficient for the occurrence of a resonant electronic transition and the formation of covalentlike orbital hybridization is necessary. The occurrence of complete neutralization of sputtered Xe^+ and scattered H^+ shows that the Xe $5p$ orbital is not isolated but has some covalent hybridization with the valence-band orbitals of the Au surface. On the other hand, a typical physisorption state is realized for Ar on Au, as evidenced by the highly localized nature of the Ar $3p$ hole in the submonolayer-coverage regime. The holes in physisorbed species decay via the Auger process during a lifetime ($>10^{-14}$ s) that is much longer than that of resonance neutralization ($<10^{-15}$ s).

Since sputtered rare-gas ions have much heavier mass and smaller kinetic energy ($E = 0-5$ eV) than scattered H^+, their emission from the surface provides us with information about the behavior of ionic holes over a longer time scale ($10^{-14}-10^{-13}$ s). The ion yield, particularly that of Xe^+, increases gradually after the completion of the first monolayer, which can be ascribed to the ion neutralization effect, suggesting that the Xe $5p$ hole is not perfectly localized even for multilayers on this time scale, as a consequence of the hybridization between the Xe $5p$ orbitals or the band effect from the substrate.

As shown in Fig. 2, the intensity of the H^+ ions scattered from Ar and Kr increases in the multilayer regime. This finding indicates that H^+ ions scattered from deeper layers can survive neutralization and contribute to the surface peak. On the other hand, no evolution of the H^+ intensity occurs for a multilayer of Xe because the H^+ ions scattered from the deeper layer are preferentially neutralized. The significant difference in the intensity of H^+ among the multilayers of Ar, Kr, and Xe cannot be explained simply in terms of quasiresonant neutralization (QRN) because the requirement for the occurrence[4] of QRN (within ±5 eV of the H $1s$ level, 13.6 eV) is satisfied for all target species examined here (Ar $3p$, 15.8 eV; Kr $4p$, 14.0 eV; Xe $5p$, 12.1 eV). Moreover, the charge-exchange probability of H^+ in gas-phase collisions is comparable for these target species.[24] The expected neutralization probability according to QRN is around 0.5 as far as the localized core levels are concerned.[22,25] Therefore, the very highly efficient neutralization of H^+ on the Xe multilayer relative to the thick Ar and Kr layers implies that the hole is still delocalized to some extent due to the hybridization between the Xe $5p$ orbitals.

The energy-loss peak is caused by the electron promotion mechanism via a transient quasimolecular state during collision.[26,27] Electron excitation occurs along the highly promoted antibonding orbital, which is formed due to hybridization between the H $1s$ and rare-gas np orbitals.[23] Peak B (peak C) is caused by one-electron excitation (simultaneous two-electron excitation). In a gas-phase experiment, the probability of target excitation (*e-h* pair excitation) increases in the order Ar, Kr, and Xe.[28] The present experimental result might be explicable along these lines. However, the reionization of neutralized H^0 is known to contribute significantly to the inelastic surface scattering.[5,23] Despite this fact, peak B from the thick Ar layer is very small, indicating that H^+ is hardly neutralized on the incoming trajectory even if it penetrates into the thick Ar layer (even in this case, H^+ should be neutralized during the violent collision via the QRN process). The peak-B intensity from Kr grows only in the multilayer-coverage regime. This fact indicates that a longer travel distance (or a longer interaction time) is required for H^+ to capture the electron in the Kr layer and peak B comes from reionization rather than the *e-h* pair excitation. In this context, the presence of peak B due to surface scattering on Xe implies that H^+ captures the Xe $5p$ electron efficiently. The neutrals backscattered from the solid can be partly reionized during collision with surface atoms, resulting in the broadly tailed background in the H^+ spectra.[5,22] Such reionized H^0 atoms undergo resonance neutralization during the outgoing trajectory from the surface and, hence, the intensity of the background should also be related to the extent of hybridization between the rare-gas np orbitals.

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