Mechanisms of atomic and molecular ion emission during sputtering of condensed CF$_4$ molecules on Pt(111) by He$^+$ and Ar$^+$ ion bombardment

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The mechanism of secondary ion emission from a condensed CF$_4$ molecule on a Pt(111) substrate has been investigated by He$^+$ and Ar$^+$ ion irradiation. Fragments of CF$_x^+$ ($x=0-3$) ions are emitted intensively from multilayers, but are almost completely neutralized when adsorbed directly on the Pt substrate due to delocalization of the valence hole(s). The F$^+$ ion, though almost absent by Ar$^+$ bombardment, is absorbed intensively by He$^+$ bombardment. The F$^+$ ions consist of two components; one arises from a submonolayer coverage, and the other comes from multilayers. The former is mainly due to potential sputtering initiated by the F $2s$ core-hole state, while the latter is associated in part with kinetic sputtering as a consequence of F $2p$ hole creation during the He-F collision. The secondary ion emission from the surface is found to be rationalized in terms of the physisorption and chemisorption of the parent molecule, which is closely related to the localization and delocalization of the valence hole.

I. INTRODUCTION

Secondary-ion-mass spectrometry (SIMS) has been established as a powerful technique for surface compositional and structural analyses. Although its high surface sensitivity is ensured by the detection of ions which are emitted from the topmost layer of solid surfaces, the mechanism of ion emission from a surface is still not understood satisfactorily. Ions capture valence electrons on a surface via Auger and resonance neutralization processes, and their contribution is thought to be dependent on the energy position of the ionic levels relative to the valence band. If energetically possible, the most efficient process is resonance neutralization, in which the neutralization probability is determined by the nature of the valence band, especially by its width. This has been confirmed in studies of low-energy ion scattering (LEIS);[1] reactive ions such as H$^+$ undergo almost a complete neutralization on metal surfaces, but the neutralization probability is suppressed considerably on ionic-insulator surfaces with a narrow bandwidth and a large band gap. In this respect, a layer of condensed-gas molecules on a metal surface is of interest, since the surface electronic properties are changed continuously from metallic to dielectric with increasing coverage.

In sputtering, ions are formed basically during atomic collisions at a surface (kinetic sputtering), but it is also possible that the primary ions' internal potential energy plays a role in the ejection of positive ions (potential sputtering). The occurrence of potential sputtering was suspected for F$^+$ emission,[2–7] since it has the largest free-atom ionization potential, ensuring the least efficiency for collisional ionization, while the F$^+$ signal in electron-stimulated desorption (ESD) is known to be fairly large.[8–11] However, the conversion mechanism of the primary ion's potential energy into kinetic and potential energies of secondary ions is still a matter of controversy.[2–7]

In this paper, the mechanism of secondary positive ion formation is discussed by He$^+$ and Ar$^+$ bombardment of a CF$_4$ molecule adsorbed on the Pt(111) surface. So far, very few works have explored the CF$_4$ adsorbed surface, but there exist some ESD works on adsorption of F-containing molecules, such as SF$_6$ and PF$_3$, on transition-metal surfaces.[12–14] ESD of F$^+$ is believed to be initiated by the two-hole-one-electron ($2h1e$) or two-hole ($2h$) states due to the Auger decay of a deep core hole [Auger-stimulated desorption (ASD)], in which an antibonding configuration emerges if the valence holes are created in the bonding orbital, and ionic desorption occurs provided that such holes are localized for the considerably long time necessary for desorption. The same mechanism is suspected to occur in potential sputtering of F$^+$ during ion bombardment.[2–4] The localized valence holes are known to induce dissociative ionization of gas-phase molecules via the Coulomb explosion mechanism.[15] This idea was applied for physisorbed molecules on metal surfaces.[16] Thus the Coulomb explosion and its analogs seem to be accepted as a mechanism of potential sputtering of ions from surfaces. However, the valence holes are thought to be more delocalized for adsorption systems than in isolated molecules, due to interactions with the substrate valence-band states. The purpose of this paper is to discuss the lifetime of valence holes in adsorbed molecules in comparison with their desorption or dissociation time, and provides insight into the ionization and neutralization mechanisms of particles emitted from a surface through the sputtering experiment of a CF$_4$ molecule adsorbed on a Pt(111) surface.

II. EXPERIMENT

Experiments were made 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. The surfaces were irradiated with He$^+$ and Ar$^+$ ions with an incidence angle of 20°, and the ions emitted normal to the surface were detected using a hemispherical
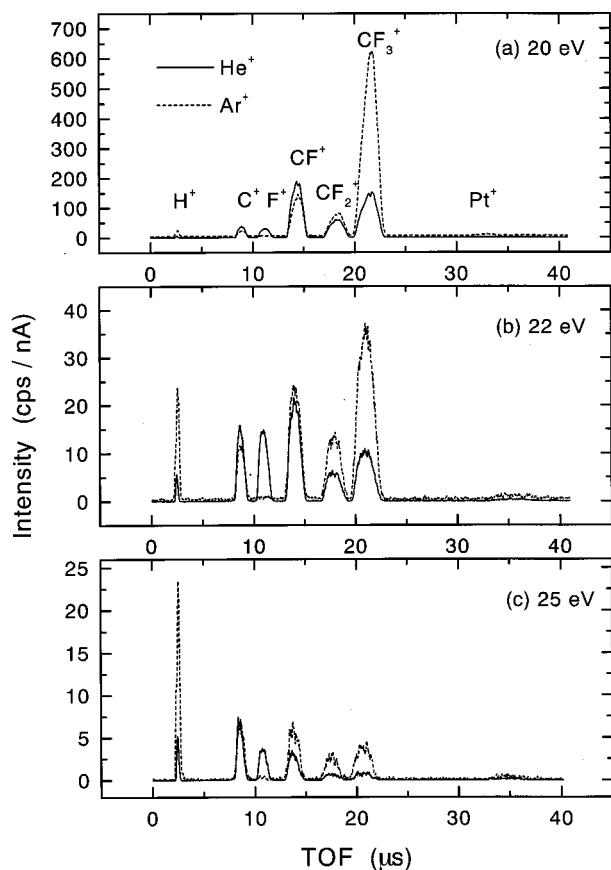
FIG. 1. TOF ion mass spectra of positive ions ejected from the CF_4 molecule (15 L) adsorbed on Pt(111), obtained by 2-keV He^+ (solid lines) and Ar^+ (dotted lines) bombardment. Measurements were made at kinetic energies of 20, 22, and 25 eV by applying a bias voltage (20 V) to the surface.

FIG. 2. Energy distributions of secondary ions ejected from the CF_4 (15 L) adsorbed Pt(111) surface by irradiation of $E_0 = 2$ keV He^+. The sample was biased with 20 V to gain a better ion mass resolution.

electrostatic energy analyzer (ESA) operating with a constant energy resolution of 0.5 eV. The ion beam was chopped by an electrostatic deflector into pulses with a width of 100 ns and a frequency of 40 kHz, so that the emitted ions were detected by the time-of-flight (TOF) technique using the same ESA (a mean radius of 50 mm). To avoid sample damage, the ion-beam current was reduced to below 5 nA/cm^2, and each measurement was finished within 10 s. The coverage of the CF_4 layer was estimated from the decay curve of the Pt surface-peak intensity in LEIS using a $E_0 = 100$ eV He^+ beam as a function of the exposure time. The Pt(111) substrate was mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The clean surface was obtained by Ar^+ sputtering and heating in oxygen. The cleanliness of the surface was confirmed from the spectra of TOF-SIMS and He^+LEIS.

III. EXPERIMENTAL RESULTS

Figure 1 shows typical TOF-SIMS spectra obtained by He^+ and Ar^+ irradiation ($E_0 = 2$ keV). The Pt(111) surface was exposed to a CF_4 gas of 15 L (1 L$=1.3\times10^{-4}$ Pa s). The measurements were made by applying a bias voltage ($+20$ V) to the sample in order to gain a better ion-mass resolu-
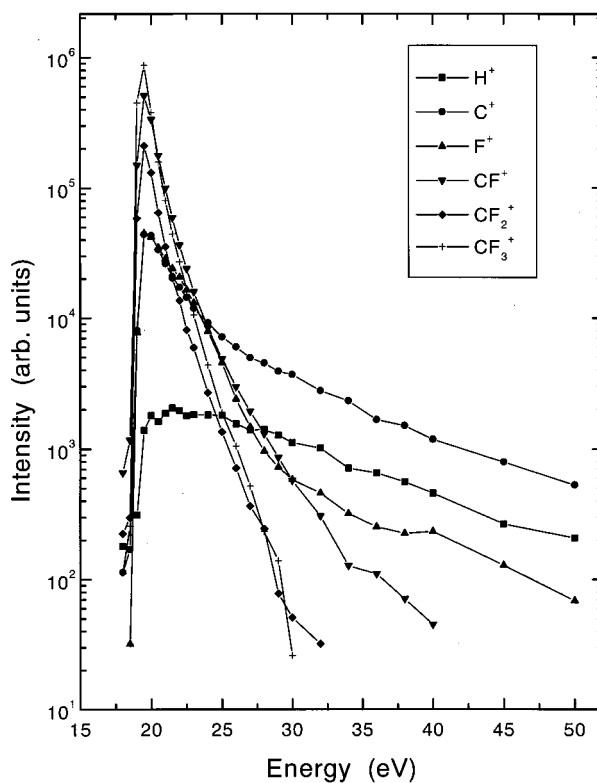
tion, and the ions emitted perpendicular to the surface with kinetic energies of 20, 22, and 25 eV were detected. Some fragment ions such as CF_3^+, CF_2^+, CF^+, and C^+ [denoted hereafter as CF_x^+ ($x=0-3$) ions] are visible, together with the contaminant H^+ ions, for both He^+ and Ar^+ irradiation. The sputtered CF_4^+ ion is unstable and readily dissociated into the CF_x^+ ions. It should be noted that the F^+ ion is sputtered intensively by He^+ irradiation but it is almost absent by Ar^+ irradiation, suggesting that the origin of the F^+ ion is completely different from that of the CF_x^+ ions. A larger potential energy of He^+ (24.6 eV) than that of Ar^+ (15.6 eV) may be responsible for F^+ emission. That the heavier-mass CF_x^+ ions are sputtered more efficiently by Ar^+ than by He^+ implies that the CF_x^+ ions are caused by kinetic sputtering during atomic collisions at the surface.

The origin of the secondary ions has been investigated from their energy distributions, because kinetically sputtered ions have much broader energy distributions than ions caused by potential sputtering.[7] The energy distributions of sputtered secondary ions by He^+ and Ar^+ irradiation, respectively, are shown in Figs. 2 and 3. The energy distributions of the CF_x^+ ions are rather narrow for both He^+ and Ar^+ irradiation. The higher-energy tail, characteristic of kinetic sputtering, is conspicuous for the element ions such as C^+ and F^+. The contaminant H^+ ions are caused by kinetic sputtering. The energy distribution of F^+ observed in the ESD experiment is usually as narrow as around 2 eV at full width at half maximum.[17] The broader energy distribution of F^+ in
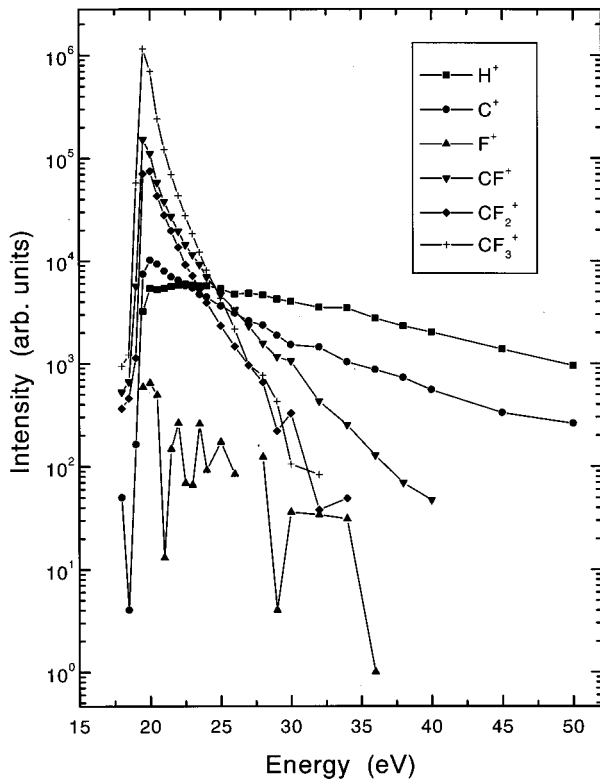
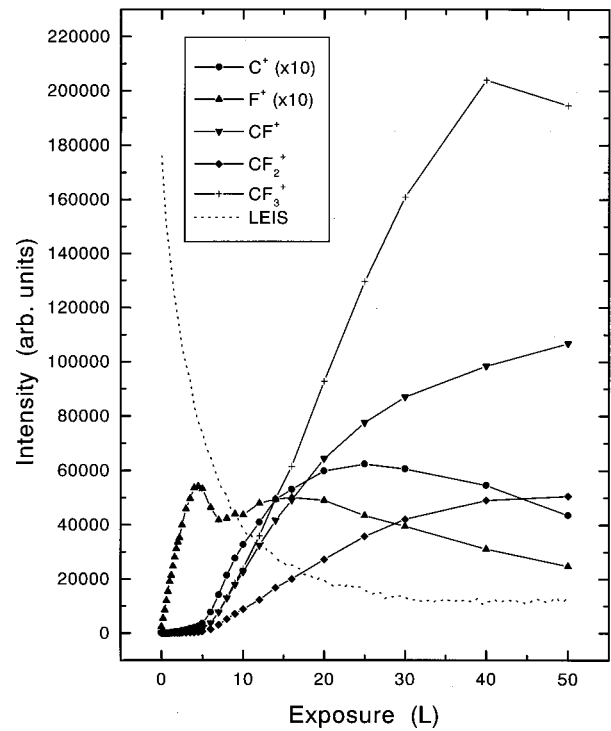FIG. 3. Same as in Fig. 2, but for an irradiation of $E_0 = 2$ keV Ar$^+$.

FIG. 4. Evolution of the secondary ions from CF$_4$ adsorbed on the Pt(111) surface as a function of the exposure. The intensity of the Pt surface peak in He$^+$ LEIS ($E_0 = 100$ eV) is shown by a dotted line.

Fig. 2 strongly suggests that both kinetic and potential sputterings contribute to the F$^+$ desorption.

Shown in Fig. 4 is the evolution of the sputtered secondary ion intensities (at $E = 20$ eV, with a sample bias of $+20$ V) as a function of exposure obtained by $E_0 = 2$ keV He$^+$ irradiation. The amount of the adsorbed CF$_4$ molecules can be estimated from the decay curve of the Pt surface peak intensity in He$^+$ LEIS ($E_0 = 100$ eV), as shown by the dotted line. This method is useful for determining the 1 ML coverage if the multilayer starts to grow after the completion of the first monolayer. This is in fact the case for SF$_6$, CO, Ar, Kr, and Xe adsorption on Pt(111),[18] where the appearance of the secondary ions and the disappearance of the Pt surface peak intensity occur at the same exposure, corresponding to the completion of the first monolayer or the beginning of the multilayer formation. In the present case, the Pt peak intensity decreases rapidly in the low-coverage regime, but does not go to zero even for prolonged exposure. On the other hand, the evolution curves of the CF$_x^+$ ions exhibit a threshold exposure at around 5 L. These results show that the three-dimensional island of the CF$_4$ molecules starts to grow at around 5 L before completion of the first monolayer. The absence of the fragment CF$_x^+$ ions from the two-dimensional layer is due to the occurrence of efficient neutralization of the sputtered ions. In this context, the F$^+$ ion is rather exceptional, as it increases steeply in intensity at the initial adsorption stage, forms a peak, and then exhibits a second onset at around the same coverage as for the emergence of the CF$_x^+$ ions. Almost the same evolution curves of the CF$_x^+$ intensities are observed by Ar$^+$ bombardment as
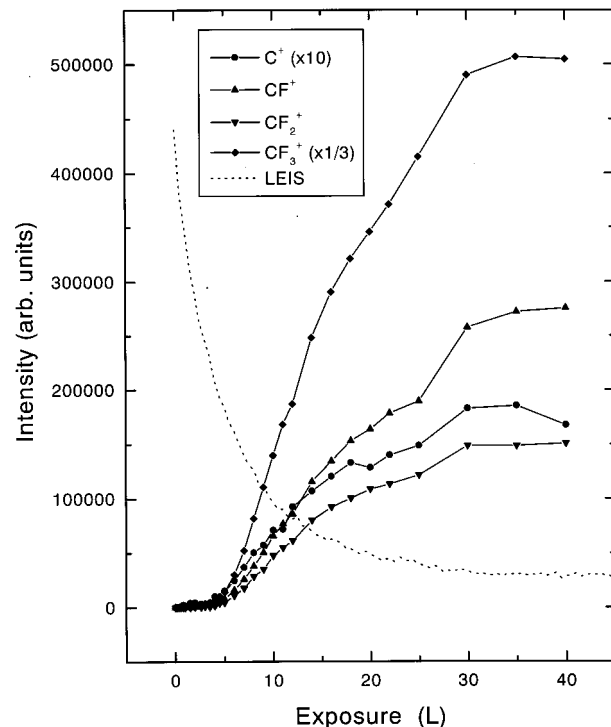

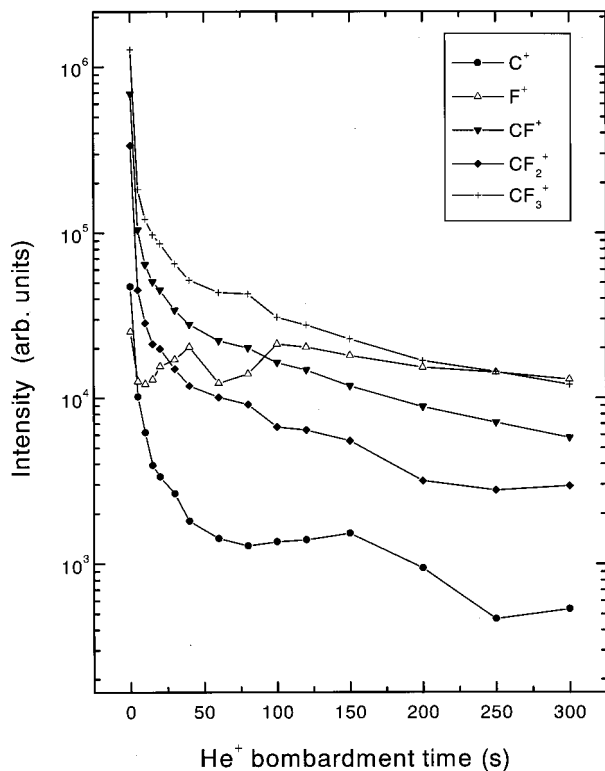FIG. 5. Same as in Fig. 4, but for irradiation of $E_0 = 2$ keV Ar$^+$.

FIG. 6. Effects of the prolonged He$^+$ (2 keV) ion irradiation on the yields of sputtered secondary ions from the CF$_4$ (50 L) adsorbed Pt(111) surface. The experiments were made by a sequence of intense He$^+$ irradiations ($E_0 = 2$ keV, 10 μA/cm^2) followed by a TOF-SIMS measurement ($E_0 = 2$ keV, 5 nA/cm^2) for 10 s.

shown in Fig. 5, where the F$^+$ intensity was too small to be plotted.

In Fig. 6 we show the effects of prolonged ion-beam irradiation on the yields of the secondary ions from the CF$_4$ (50 L) adsorbed Pt(111) surface. The experiments were made by the sequence of He$^+$ irradiation (10 μA/cm^2) followed by measurements of the TOF-SIMS spectra (5 nA/cm^2) for 10 s. All of the ions except for F$^+$ decay in intensity by almost two orders of magnitude upon He$^+$ bombardment for 300 s, whereas the F$^+$ yield is relatively unchanged for this sputtering time. The He$^+$ irradiation causes not only dissociation but also desorption of the adsorbed CF$_4$ molecule and its fragments. The decay of the CF$_x^+$ ions by He$^+$ irradiation indicates that they originate due to the molecularly adsorbed CF$_4$. On the other hand, a F$^+$ ion can be emitted efficiently even from the fragment species.

IV. DISCUSSION

Secondary ion emission occurs provided that the valence holes are localized for the time necessary for desorption (10^{-13}–10^{-14} s). The absence of CF$_x^+$ ions from the first monolayer indicates that the valence holes tend to delocalize on the Pt(111) surface. It is known that the dissociation probability of physisorbed molecules is closely related to the lifetime of the valence holes: Klekamp and Umbach[19] showed that a SF$_6$ molecule on the Ni(111) surface is readily disso-

ciated in thick layers by irradiation of the He I UV light, whereas SF$_6$ is hardly dissociated in the first monolayer if it is adsorbed directly on the metal substrate. They suggested that the excitation of the nonbonding $1_{tu}/5t_{1u}$ orbital electron to the unoccupied $2t_{2g}$ orbital is responsible for the molecular dissociation. The breakdown of the molecular dissociation in the lower coverage regime was ascribed to the delocalization of such an excitation.

The interaction of molecules with a metal surface was addressed in terms of chemisorption and physisorption. The covalency in bonding, realized for chemisorption systems, is defined as a quantum-mechanical sharing of valence electrons as a consequence of the overlap of wave functions. The resonance neutralization is correlated to chemisorption of ions and, therefore, its probability should be a good measure of covalency in bonding. In LEIS, in fact, the ion neutralization event was elucidated successfully according to this scheme:[1,20] Reactive ions such as H$^+$, N$^+$, and O$^+$, with open-shell valence orbitals undergo resonance neutralization during transient chemisorption and, hence, the ions are neutralized almost completely on a metal surface due to a delocalization of the ionic hole. On the other hand, noble-gas ions can survive neutralization even on metal surfaces because the ionic hole tends to be localized during transient physisorption. Similarly, the neutralization of sputtered secondary ions in SIMS should be related to the nature of the bonding of parent adsorbates. In fact, physisorbed noble-gas atoms such as Ar can be sputtered as ions from a very low-coverage regime, even when it is in direct contact with Pt.[18] It should be noted that valence orbitals of the CF$_4$ molecule are located as deep as 16.2–25.1 eV below the vacuum level,[21] which are deeper than the binding energy of the Ar 3p state (15.8 eV). Despite this fact, an almost complete neutralization of the sputtered CF$_x^+$ ions occurs in the submonolayer coverage regime. This is probably because some chemical interactions, such as donation and backdonation of valence electrons, exist between CF$_4$ and the Pt substrate, by which the valence holes created in the molecule can diffuse into the band. In the multilayer regime, ion neutralization is suppressed due to localization of the valence hole in the physisorbed CF$_4$ molecule. In this context, the behavior of the F$^+$ ion is significantly unusual. A F$^+$ ion can be created kinetically during He-F collision via the electron promotion mechanism.[7] The second onset of F$^+$ in Fig. 4 (7 L), corresponding well to the onset of the CF$_x^+$ ions, can be explained in terms of kinetic sputtering as a consequence of the creation of a F 2p valence hole during the He-F collision. The decrease in the F$^+$ yield with a further increase in the coverage may be caused by the blocking effect of the overlayer on the energetic He^0 atoms backscattered from the Pt substrate.

As already described, the potential energy of the primary ion plays a role in F$^+$ emission. In fact, unique behaviors of the F$^+$ emission, such as the emergence of the low-coverage peak (Fig. 4) and the very small change in intensity by He$^+$ bombardment (Fig. 6), may be explained in terms of the potential sputtering. It might be presumed that the Coulomb explosion, resulting from two valence holes due to the Auger decay of the He$^+$ 1s hole or a deeper core hole, might be

responsible for the F^+ ion emission. In this case, however, strong localization of the valence holes in a CF_4 molecule is required so that the F^+ ion should be emitted efficiently from the thick, physisorbed CF_4 layer rather than from the first monolayer which is chemisorbed directly on the Pt substrate. The decay of the F^+ yield with increasing coverage is not explainable by this picture.

For a better understanding of the neutralization mechanism of the CF_x^+ ions, it might be interesting to make contact with the experimental results of CF_3^+ scattering at metal and perfluoro-polyether (PFPE) surfaces since the PFPE might act like a frozen CF_4 gas.[22] Recently, Kleyn and co-workers revealed that essentially all CF_3^+ ions are neutralized on the Ag(111) surface, whereas the neutralization is suppressed on the PFPE surface.[23,24] The results are similar to the present sputtering experiment. However, some fragment ions such as CF^+ and C^+ are ejected without neutralization during the CF_3^+ scattering from the Ag(111) surface. Probably, this is due to the higher kinetic energy in the scattering experiment (100–500 eV) than the energy of the sputtered ions (<10 eV). It should be noted that no fragment of F^+ ions is observed either for the Ag(111) surface nor the PFPE surface during scattering of the primary CF^+, CF_2^+, and CF_3^+ ions. This result may suggest that holes in the primary ions (ionization potential of 8.9, 11.4, and 9.11 eV for CF_3, CF_2, and CF) are hardly accommodated in F (17.4 eV) after dissociation. It is possible that the F^+ ion, if created, is neutralized completely as it moves away from the surface. This fact also suggests that the creation of a shallow valence hole in CF_4 may not lead to kinetic sputtering of F^+, which is consistent with a sputtering experiment using the primary Ar^+ ion. The sputtering of F^+ may require the creation of a deeper hole associated with the potential energy of the primary He^+ ion (24.6 eV).

To gain insight into the mechanism of the potential sputtering, a survey of the related phenomena in ESD and PSD is instructive. Recently, Madey and co-workers[13,14] performed a number of experiments in the ESD of F^+ ions from metal surfaces covered with ultrathin films of condensed gases, and discussed the charge exchange of desorbing ions through the thin film. It was reported that the ESDIAD (ESD ion angular distribution) pattern of F^+ from the SF_6 adsorbed W(110) surface at 80 K showed a single spot normal to the surface, and that no pattern with the threefold symmetry expected from the molecularly adsorbed SF_6 species was obtained.[12] Moreover, the F^+ signal persists without significant change until a higher surface temperature (>1600 K) is attained. In more recent ESDIAD studies of the PF_3 adsorbed Ru(0001) surface,[13,14] a large enhancement of the F^+ yield was observed if the surface was damaged by the electron beam. These results are consistent with the behavior of F^+ emission seen in Fig. 6. Moreover, it is known that the F^+ ion is ejected from the chemisorbed F adatom on the metallic TiC(111) surface by excitation of a 2-keV He^+ ion due to potential sputtering.[25]

As already described, the potential sputtering of F^+ from strongly chemisorbed F adatoms or dissociatively chemisorbed species on the metal surfaces should not be initiated by the valence holes. The valence holes created in the F $2p$ resonance state due to the Auger decay of a deep-core hole (which is assumed in the ASD mechanism) are so short lived (10^{-15} s), in comparison with the time necessary for molecular dissociation or desorption from the surface ($10^{-14} – 10^{-13}$ s), that no F^+ ion emission occurs (the band effect). Judging from the lifetime, the desorption of a $2s$ core-excited F^* atom is more likely to initiate the event. The F $2s$ hole can be created due to the nonadiabatic hole exchange with the primary He^+ ion.[7,25]

Since there is no experimental evidence for dissociative adsorption of CF_4 on the Pt(111) surface, F^+ desorption is thought to occur from the chemisorbed CF_4 molecule. For a gas-phase CF_4 molecule, the mechanism of CF_x^+ ion creation is studied from the measurement of the appearance potential in photofragmentation;[26] the CF_3^+ ion is produced from the excitation of the $1t_1$ (binding energy 16.2 eV), $4t_2$ (17.4 eV), and $1e$ (18.5 eV) orbitals; the CF_2^+ ion from the $3t_2$ (22.1 eV) orbital; the CF^+ ion from the $4\alpha_1$ (25.1 eV) orbital; and the F^+ and C^+ ions from the $2t_2$ (40.3 eV) and $3\alpha_1$ (43.3 eV) orbitals. The $2t_2$ and $3\alpha_1$ orbitals, respectively, have F $2s$ orbital characters of 82% and 69%.[27] Thus the creation of the F $2s$-related core hole is responsible for F^+ desorption from the CF_4 molecule as well. The branching ratio of the F^+ and C^+ ions is almost comparable in the photofragmentation.[26] The same tendency is observed when the CF_4 molecule is excited by a 900-eV He^+ ion in the gas phase;[28] the product distribution is 54% CF_3^+, 24% CF_2^+, 10% CF^+, 5% F^+, and 4% C^+. The C^+ emission is hindered for CF_4 on the Pt(111) surface in the submonolayer coverage, suggesting that the dissociation pathway is different between F^+ and C^+. The absence of the C^+ ions implies that they are neutralized efficiently on the Pt(111) surface. The same should occur for the F^+ ion if it is ejected after the Auger decay of the $2t_2$ or $3\alpha_1$ hole in the chemisorbed CF_4 molecule. F^+ emission is more likely to result if the $2s$-core-excited F^* atom is initially ejected and intra-atomic Auger decay follows. The creation of the F $2s$ hole may not be sufficient to induce the C-F bond breakage, and a subsequent rearrangement of the valence orbitals into the antibonding configuration may be required. Such a rearrangement of the valence electrons, caused by a screening of the core hole, is more likely to take place on a metal surface than on a physisorbed molecular surface, thereby leading to the preferential F^+ emission in the submonolayer coverage regime, as seen in Fig. 4. A similar dissociation channel is shown to occur in gaseous molecules using synchrotron radiation;[29–31] the resonant excitation of a core-level electron to the antibonding σ^* orbitals of HBr, HCl, and CF_4 molecules induces bond cleavage prior to the Auger decay of the core hole.

V. CONCLUSION

The mechanism of the secondary ion emission has been investigated in sputtering of a CF_4-adsorbed Pt(111) surface during He^+ and Ar^+ bombardment. Secondary ions except for F^+ undergo efficient neutralization in the first monolayer,

but their yields increase rapidly in the multilayer regime. The covalency of CF_4 in bonding with the Pt(111) substrate is responsible for the delocalization of the valence hole. The valence hole tends to be localized in physisorbed multilayers from which the CF_x^+ ions are emitted considerably. The F^+ ion is sputtered efficiently even in the submonolayer coverage regime, and can be emitted not only from the CF_4 molecule but also from F adatoms or the chemisorbed fragment species on the surface. Photofragmentation or ion-induced fragmentation experiments with a gaseous CF_4 molecule showed that F^+ and C^+ emission occurs from a F $2s$ hole state, but the emission of a C^+ ion is hindered for CF_4 chemisorbed on a Pt(111) surface due to resonance neutralization. Thus the F^+ emission is thought to be initiated by the core-hole state rather than by the valence-hole state. A core hole in a chemisorbed CF_4 molecule may induce a rearrangement of the valence electrons into an antibonding state, thereby leading to emission of a core-excited F* atom. The ionization occurs via intra-atomic Auger decay after breakage of the chemisorptive bond and, hence, the resulting F^+ ions can survive resonance neutralization even on a metal surface.

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