Sputtering of C_{60} Fullerenes Physisorbed on Ar, Xe, H_2O, O_2, and C_8F_{18} Matrix Films Studied with Time-of-Flight Secondary Ion Mass Spectrometry

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The ionization and fragmentation of C_{60} fullerenes were investigated using matrix films covered with C_{60} molecules and bombarded with 1.5-KeV He^+ ions. C^+, $C_{60}{}^+$, and $C_{60}{}^{++}$ ions were sputtered from the C_{60} molecules that were physisorbed on Ar and Xe matrix films, whereas the sputtering of C_{60} on the O_2 and C_8F_{18} matrix films induced an additional emission of ion adducts, such as $(OC_{60})^+$ and $(FC_{60})^+$, as well as the fragment ions, $C_{(60-2n)}{}^+$ ($n = 1-10$). Very few ions were sputtered from the C_{60} molecules that were adsorbed on the H_2O matrix film and the Ni(111) substrate. The ions are thought to be created at the surface when C (C_{60}) collides with the Ar, Xe, O, and F species via the electron-promotion mechanism, and the formation of quasi-molecules is manifested from the emission of the ion adducts. The fragmentation occurs during the interaction with the reactive species at the surface, and the delayed ionization/fragmentation of the internally excited C_{60} molecules in the gas phase has negligible contribution in the present experiment. The matrix effect arises from the suppressed neutralization of the $C_{60}{}^+$ ion because of the localization of a valence hole. The $C_{60}{}^+$ ion undergoes neutralization on the H_2O film because the hydrogen bond has some covalent character.

1. Introduction

Fullerenes are highly stable molecules with respect to impact-induced fragmentation. The excitation of gas-phase fullerene molecules has been studied extensively using various methods, such as single[1] and multiple[2] photon absorption, electron impact,[3−5] and collisions with protons,[6] helium ions,[7] heavier ions,[8] and highly charged ions.[9] The internal energy of excited fullerenes is dissipated via the emission of electrons (thermionization), the release of neutral or charged particles (fragmentation), and radiative cooling. The excited fullerenes create similar fragment ions irrespective of the methods of initial excitation. The fragmentation pattern of $C_{60}{}^+$ is characterized by large fragment ions separated by C_2 units. The sequential C_2 loss is thought to be a dominant process for the formation of smaller fragments.[10−12] However, there exist conflicting experimental and theoretical studies that make us believe the ejection of large neutral fragments is important.[2,13,14]

The C_{60} scattering[15−17] and sputtering[18,19] experiments from solid surfaces give additional insights into the neutralization, fragmentation, and ionization of fullerenes. It was revealed that the primary $C_{60}{}^+$ ions were neutralized almost completely on the graphite surface and that the excited neutrals scattered off the surface were reionized in the gas phase because of delayed thermionic emission on a microsecond time scale.[17] Since the ionization potential of the C_{60} molecule (7.6 eV)[17] is higher than the work function of typical metals and semiconductors (∼5.0 eV), the $C_{60}{}^+$ ion undergoes efficient resonance neutralization during both scattering and sputtering processes at the surface. When no electronically excited C_{60} species are emitted from the surface, it is predicted that the ions must be formed in the gas phase because of delayed thermionic emission from the vibrationally excited C_{60} molecules. Therefore, the ionization and fragmentation of fullerenes on solid surfaces are still open to question. The $C_{60}{}^+$ ion may be extracted directly from the surface if the resonance neutralization is quenched. In this respect, it was demonstrated that positive ions are sputtered efficiently by the electron bombardment of physisorbed nanoclusters on solid argon film, which is due to a Coulomb explosion.[20−22] Solid argon has also been used as a matrix of the "low-temperature matrix isolation technique" for the study of reactive intermediates and free radicals that are formed in the gas phase.[23−25] These experimental results suggest that the isolation of C_{60} molecules using appropriate matrixes induces ion sputtering from the surface. In the present paper, we explore the possibility of $C_{60}{}^+$ sputtering using time-of-flight secondary ion mass spectrometry (TOF−SIMS). The ionization of the C_{60} molecules, physisorbed on thin Ar, Xe, H_2O, O_2, and C_8F_{18} films, is investigated by bombarding the C_{60} molecules with He^+ ions. The mechanisms of ionization and fragmentation of C_{60} molecules at the surface are discussed in comparison with the gas-phase experiments that have been previously reported.

2. Experiment

The experiments were conducted in an ultrahigh-vacuum (UHV) chamber (base pressure: below 1×10^{-9} Pa) that was equipped with facilities for standard surface characterization. The TOF−SIMS experiment was performed in such a manner that the sample, floated with a bias voltage of +500 V, was irradiated with a 2-keV He^+ beam through a grounded stainless-steel mesh (the ion impact energy was 1.5 keV). The mesh was placed 4 mm above the sample surface, and the positive ions passed through the mesh into the field-free region of a linear TOF tube (67-cm long). The ions were detected with a channel electron multiplier. A pulsed He^+ beam (∼50 ns, 30 kHz) with a low ion flux (∼10 pA/cm^2) was used for TOF−SIMS to minimize charging and damaging the surface. The substrate was a Ni(111) surface. Ni(111) was mounted on a sample holder and was cooled to 13 K using a closed-cycle helium refrigerator.

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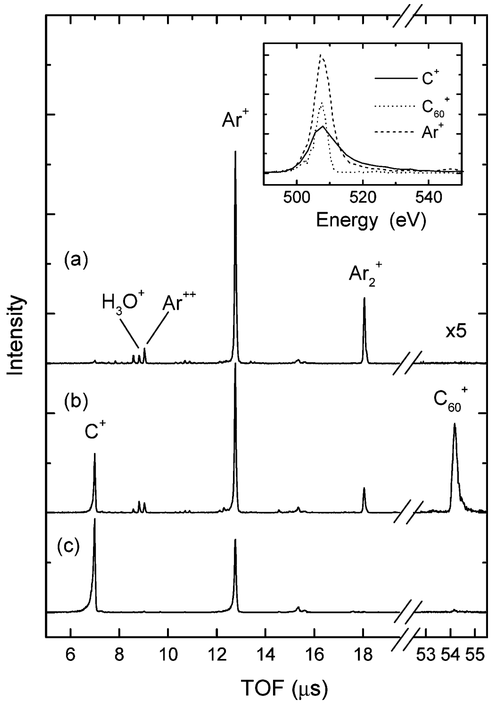

Figure 1. TOF−SIMS spectra from the 50-ML Ar film (a) and the C_{60} adsorbed Ar films with the C_{60} coverage of 0.6 ML (b) and 2.5 ML (c). Inset: the energy spectra of the C^+, C_{60}^+, and Ar^+ ions converted from the TOF−SIMS spectrum (b).

The surface was heated for cleaning up to 1200 K by electron bombardment from behind. The matrix Ar, Xe, H_2O, C_8F_{18}, and O_2 films were deposited on the Ni(111) surface at 13 K by backfilling the UHV chamber. The C_{60} molecule was deposited on the matrix surface by thermal evaporation from a source that was placed just in front of the surface. The coverage of the matrix films (the C_{60} molecule) was determined from the evolution curves of sputtered ion intensities from both adsorbate and substrate as a function of exposure (evaporation time). This can be done because the films grow without agglomeration at low temperatures and the secondary ions are most likely sputtered from the topmost surface layer.

3. Experimental Results

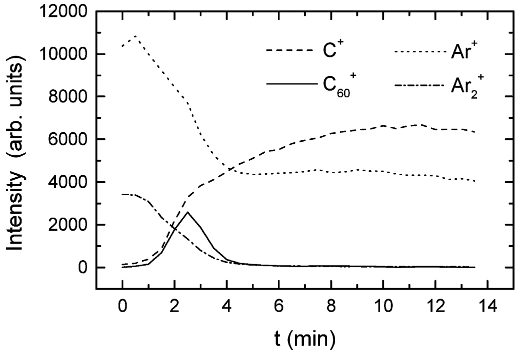

Figure 2. Evolutions of the typical secondary-ion intensities as a function of the evaporation time of the C_{60} molecules on the 50-ML Ar matrix film.

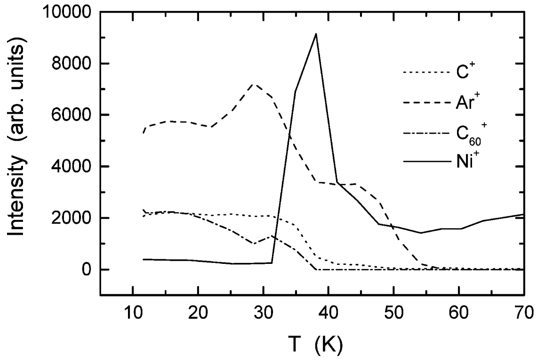

Figure 3. Temperature-programmed TOF−SIMS intensities of typical secondary ions from the 50-ML Ar matrix film on which 0.6 ML of the C_{60} molecules was deposited at 13 K. The temperature was increased at a rate of 5.0 K/min.

Figure 1 shows the typical TOF−SIMS spectra of positive ions: (a) the pure Ar film that was deposited on the Ni(111) substrate, with a thickness of 50 monolayers (ML), is compared with the Ar films covered with C_{60} molecules that were evaporated for (b) 2.5 min and (c) 10 min. The measurements were made at 13 K. The Ar^+, Ar_2^+, and Ar^{++} ions are the main ion species sputtered from the Ar film that is not covered with C_{60}. However, upon the adsorption of the C_{60} molecules, the C^+ and C_{60}^+ ions are sputtered together with the C_{60}^{++} ions (not shown). The C_{60}^+ and C_{60}^{++} ions decrease in intensity when the coverage of C_{60} is increased, whereas the C^+ intensity is not significantly changed. In Figure 2, the intensities of typical secondary ions are shown as a function of the evaporation time of the C_{60} molecules. The yields of the Ar^+ and Ar_2^+ ions decay almost linearly between 0.5 and 4 min because of the growth of the C_{60} film and then become almost constant. The coverage of the C_{60} molecules is estimated from these decay curves and 1 ML is assigned to 4-min deposition time. The C_{60}^+ ion exhibits a peak in intensity at 0.6 ML (2.5 min), but very few ions are emitted after the multilayer is formed. In contrast, the C^+ ion increases monotonically in intensity with the increasing coverage of C_{60} molecules. There are no C^+ and C_{60}^+ ions sputtered from the pure C_{60} film when it is deposited directly on the Ni(111) substrate. The Ar^+ ion is sputtered considerably even after the C_{60} multilayers are formed. These experimental results show that the Ar atoms tend to segregate to the surface of the C_{60} film in the multilayer coverage regime. The absence of the Ar_2^+ ion suggests that the coverage of Ar is submonolayer without the formation of agglomerates. It is likely that a 2D gaslike phase is formed.

The C^+ and Ar^+ peaks in Figure 1 are asymmetric, with a tail toward the shorter TOF side. This tail comes from the release of swift ions. In contrast, the C_{60}^+ peak has a tail toward the longer TOF side because of the contribution of slow ions. The slow ions may be formed in the gas phase as a consequence of delayed electron emission from the excited neutrals in the ion extraction region (4 mm from the surface). To clarify the origins of these slower secondary ions, the TOF−SIMS spectrum in Figure 1b is converted to the energy spectrum and the result is shown in the inset of Figure 1. Energy resolutions depend on the ion species, and they are approximately 4.5, 2.5, and 0.5 eV for C^+, Ar^+, and C_{60}^+ ions, respectively. For all of the ions examined here, their peaks show approximately the same kinetic energy. Furthermore, the low-energy cutoffs of the energy spectra (500 eV) confer with the acceleration voltage applied to the sample (+500 V). This result indicates that all the ions are formed at the surface, and the ions that are formed in the gas phase, via delayed ionization, contribute negligible results in the present experiment.

Figure 3 shows the TOF−SIMS intensities of positive ions from the C_{60} (0.6 ML) adsorbed Ar film as a function of temperature. The Ar film evaporates at 38 K, as revealed by the decrease in the C^+, C_{60}^+, and Ar^+ intensities, whereas the Ni^+ ion peaks in intensity at this temperature. There are no Ni^+

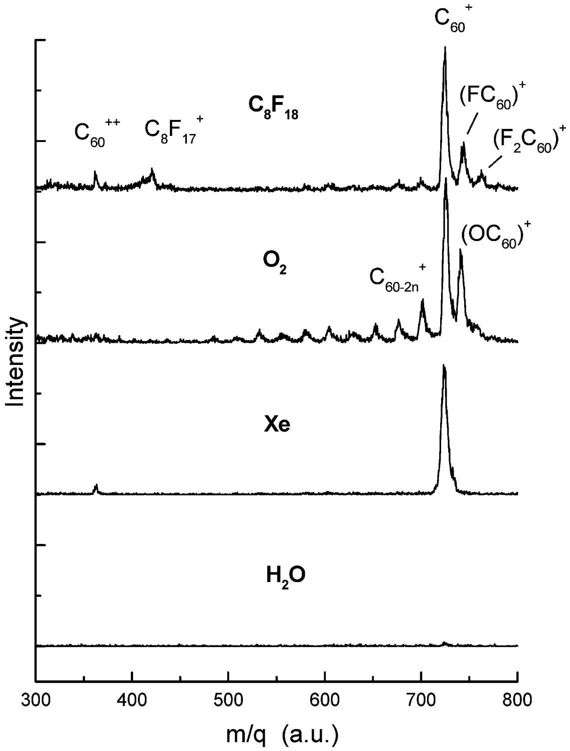

Figure 4. Mass spectra of $C_{60}{}^{r+}$ and its fragment/complex ions from the 0.6 ML of the C_{60} molecules adsorbed on the matrix films of H_2O, Xe, O_2, and C_8F_{18} with the thickness of 50 ML.

ions sputtered from the clean Ni(111) substrate, which indicates that the Ar monolayer enhances the ionization probability of the sputtered Ni^0 atom. The same phenomenon has been observed for the water-adsorbed Ni(111) surface.[26] The long tail of the Ni^+ intensity toward the higher temperature indicates the presence of some contaminants on the film surface (which is mainly water). After evaporation of the multilayer, a small amount of Ar remains on the surface up to 55 K. These Ar atoms induce the ionization of C^0 to some extent, though the $C_{60}{}^{+}$ ions are not formed in the absence of the thick Ar film. The Ar^+ ($C_{60}{}^{+}$) intensity exhibits a peak (dip) at 28 K, where the $C_{60}{}^{+}$ ion decreases in intensity because the isolated C_{60} molecules tend to agglomerate or diffuse into the Ar film. In contrast, the C^+ intensity is unchanged up to the evaporation temperature of the Ar film.

Similar measurements were made for the other matrix films. Figure 4 shows the mass spectra of positive ions obtained from the 0.6-ML C_{60} molecules physisorbed on the H_2O, Xe, O_2, and C_8F_{18} films with a thickness of 50 ML. The mass spectrum of C_{60} adsorbed on the Xe film is essentially identical to the results found for the Ar film, not only in terms of the ion species, but also in terms of their intensities. In addition to the $C_{60}{}^{+}$ ion, a small peak of the $C_{60}{}^{++}$ ion was clearly identified. Very few ions are sputtered from C_{60} adsorbed on the H_2O film: the $C_{60}{}^{+}$ intensity was at most 2% of that found for the Ar and Xe films. The remarkable matrix effect that was observed is evidence that the $C_{60}{}^{+}$ ions are created at the surface during the sputtering process. Not only were the fragment ions, $C_{(60-2n)}{}^{+}$ ($n = 1-10$), sputtered, but the complex ions were also sputtered when O_2 and C_8F_{18} were used as matrix films. A comparison of the results between the reactive (O_2, C_8F_{18}) and nonreactive (Ar, Xe) matrixes clearly shows that fragmentation of the C_{60} molecules is induced chemically by their interaction with the reactive species. In fact, the coexistence of the complex ions for the O_2 and C_8F_{18} matrix films strongly suggests that the C atoms are abstracted by the transiently chemisorbed O and F atoms on the C_{60} surface. The chemical sputtering results show a similar fragmentation pattern of the $C_{60}{}^{+}$ ions to that observed in the gas-phase experiments.[7] However, this behavior cannot be explained by the sequential evaporation of the C_2 molecules because the sputtering occurs at the surface within a time scale of subpicoseconds.

4. Discussion

The mechanism of secondary-ion emission is complicated. It is still an open question as to how the kinetic energy and charge of the primary ion lead to the ionization of the neutral species at the surface. Another important aspect of secondary-ion emission is ion neutralization as the ions move away from the surface. Matrix films are relevant to both ionization and neutralization processes. The matrix effect on the neutralization of $C_{60}{}^{+}$ will be discussed first and then the ionization mechanisms of C_{60} are discussed in terms of the kinetic and potential (or electronic) sputtering.

The matrix effect that was observed involves the isolation of the $C_{60}{}^{+}$ ion not just from the Ni(111) substrate but also from the other C_{60} molecules. The overlapping of the π orbitals results in the conduction of the C_{60} film, so the isolation of the individual C_{60} molecules is important for the $C_{60}{}^{+}$ ion to survive resonance neutralization. It is for this reason why the $C_{60}{}^{+}$ ion is sputtered only in the submonolayer coverage of C_{60} (see Figure 2). The isolation effect of the H_2O film is very weak relative to the other matrix films. This phenomenon can be explained by the delocalization of a valence hole in the H_2O film. In this respect, we have investigated low-energy H^+ scattering from molecular-solid films.[27] It was revealed that the yield of the H^+ ions scattered from a H_2O film is about 1/60 of that scattered from an O_2 film. This result has been explained by the presence of the hydrogen bonds having some covalent character: the H^+ ion transiently forms a H_3O^+ ion, and a hole delocalizes in the overlapped valence orbitals of water (especially concerning the $3a_1$ orbital, which is broadened considerably because of the formation of hydrogen bonds). In the present case, the ionization potential of C_{60} (7.6 eV) is smaller than that of water ($\sim$10 eV).[27] However, the molecular orbitals (MOs) of the $C_{60}{}^{+}$ ion satisfy the quasi-resonance condition ($\pm$5 eV) with the $3a_1$ and $1b_1$ MOs of the hydrogen-bonded H_2O molecules. Therefore, the valence hole in the $C_{60}{}^{+}$ ion tends to diffuse into the valence orbitals of the H_2O matrix during the sputtering time, which results in a very small sputtering yield of the $C_{60}{}^{+}$ ion. The quasi-resonance condition is energetically satisfied between the MOs of $C_{60}{}^{+}$ and the $1\pi_u$, $1\pi_g$ orbitals of the O_2 molecules as well. However, in this case, the hole tends to localize in the MOs of the $(C_{60}-O_2)^+$ complex without diffusion into the bulk, hence, the $C_{60}{}^{+}$ ion survives neutralization considerably. The strong isolation effect is expected only for the species condensed with weak van der Waals interactions.

The potential energy of the primary He^+ ion may induce sputtering of the $C_{60}{}^{+}$ and fragment ions. As a consequence of Auger neutralization of the He^+ ion, multiple valence holes can be created in the C_{60} molecules. It is known that if multiple valence holes are localized in a nanometer-sized domain the positive ions can be emitted electronically because of Coulomb repulsion. This phenomenon has been studied extensively in the electron-stimulated desorption (ESD) of cations from water,[20] Na,[22] and NaCl[21] nanoclusters physisorbed on Ar matrix film. To affirm this phenomenon, an ESD experiment with C_{60} molecules physisorbed on Ar film was performed (the result is not shown explicitly). There were no ions relevant to the C_{60}

molecules emitted. This result is consistent with the results from the gas-phase experiments, in which no direct evidence of the Coulomb explosion of C_{60} was obtained,[28] although counterclaims suggest that the multiply charged fullerenes undergo asymmetric fission[29] and multifragmentation.[30] The C_{60}^+ ions should not be emitted from the dimers of multiply charged C_{60} molecules via an intermolecular Coulombic repulsion, because the positive charges are separated with more distance. It is thus concluded that the C_{60}^+ ion and its fragments are emitted via the kinetic sputtering process during collisions with the matrix species.

The matrix films also play a role in emission of the C^+ ion because it is not sputtered when the C_{60} molecule is adsorbed directly on the Ni(111) substrate and the H_2O film. There were no C^+ ions emitted from the clean graphite surface either, but the adsorption of a monolayer of Ar on graphite increases the C^+ yield largely. These results suggest that the C^+ ions are formed during collisions between the sputtered C^0 atoms and the physisorbed Ar atoms as they move away from the surface.

In the kinetic sputtering process, the electron-promotion mechanism is thought to be responsible for ionization.[31] Quasi-molecules (C−X) are formed between one of the C atoms of C_{60} and one of the elements (X = Ar, Xe, F, and O) of the matrix films; the electrons are excited along the highly promoted antibonding molecular orbital. Since the ionization potentials of all these matrix species are higher than those of C and C_{60}, the C 2s and 2p orbital characters should dominate the antibonding orbital. Therefore, the promotion of the antibonding σ orbital results in an excitation of one or two electrons from the C_{60} molecule. The electrons move into the conduction band of the matrix films or above the vacuum level, which results in the formation of C_{60}^+ and C_{60}^{++} ions. The C^+ ion can be formed via the electron-promotion mechanism in the presence of the matrix film. The C_{60} molecules are so stable that they are thought to be ionized without fragmentation during collisions with the Ar and Xe atoms. On the other hand, the F and O atoms are trapped partly by C_{60} molecules during the formation of quasi-molecules, thereby resulting in the emission of a considerable amount of complex ions such as $(FC_{60})^+$ and $(OC_{60})^+$ from the C_8F_{18} and O_2 matrix films. The C_{60}^+ ion and complex ions can be created transiently on the H_2O matrix film as well, but they undergo efficient neutralization before leaving the surface because of delocalization of the valence hole.

The matrix species can also be excited via the electron-promotion mechanism during symmetric collisions in the film,[32] and the C_{60} molecules are ionized as a consequence of the deexcitation of the species. In this respect, the results from the gas-phase Penning ionization of C_{60} are instructive.[33] The internal energies for all of the metastable rare-gas atoms are sufficient for ionization of C_{60}, and the only ion produced from the interaction with the excited rare-gas species is C_{60}^+. The cross section for Penning ionization of C_{60} by a Xe* atom is approximately 1 order of magnitude smaller than that of an Ar* atom because of the small ionization potential of Xe (12.1 eV) relative to Ar (15.8 eV).[33] This result is inconsistent with the nearly equal yield of the C_{60}^+ ions between the Xe and Ar matrixes. In this respect, the effect of the primary He^+ ion on the ionization of the C_{60} molecules should be noted. The comparable C_{60}^+ yields for all matrixes except for water appears to be explained if the C_{60} molecule is ionized by the primary He^+ ion. However, the shortcoming of this mechanism is that the kinetic energy that is necessary for desorption of the C_{60}^+ ion is not provided directly by the He^+ ion; the C_{60}^+ ion must survive until the collision cascade evolves from the bulk for the sputtering to occur. The role of the primary ion's charge in the sputtering of C_{60}^+ can be checked by comparison with the results using a primary neutral beam.

Currently, the reactive collisions of C_{60}^+ and C_{70}^+ ions with SF_6 and O_2 target molecules have been investigated only in gas-phase experiments.[34,35] There were no complex ions observed except for C_nF^+ ($n = 1-11$) in the $C_{60}^+ + SF_6$ collision at the center of mass collision energy between 25 and 300 eV.[35] This provides a sharp contrast to the present study. The emission of the $(FC_{60})^+$ and $(OC_{60})^+$ ions is characteristic of the chemical sputtering from a solid surface, and it is relevant to the formation of the quasi-molecules associated with the ionization of C_{60}. In the gas-phase experiment, it is suggested that the fragmentation cross section of C_{70} molecules in collision with oxygen increases, especially at low energies because of the contribution of exothermic reactions, such as $C_{70}^+ + O_2 \rightarrow C_{68}^+ + 2CO$.[34] Moreover, the strong decrease in the fragmentation of the C_{60}^+ ion is observed with increasing velocity of the primary ion during the He^+-C_{60} collisions.[7] This phenomenon has been attributed to the transition from vibrational to electronic excitation with an increase in the velocity of He^+. The collision with the slow He^+ ion induces the vibrational excitation of the C_{60}^+ ions, leading to the sequential evaporation of the C_2 units, whereas electronic excitation is induced by the fast He^+ ions, which is responsible for the multifragmentation of smaller C_n^+ ions ($n < 15$). There are no C_n^+ ions observed in the present study because both the ionization and fragmentation of the C_{60} molecules are caused by slow collisions with the matrix elements rather than with the primary He^+ ion. The sequential loss of the C_2 molecules is the mechanism of fragmentation of the isolated C_{60}^+ ion in the gas phase. In the present experiment, no fragment C_{60-2n}^+ ions were observed for the Ar and Xe matrixes. This, however, does not necessarily exclude the possibility that the C_{60}^+ ions are fragmented in the gas phase during or after their passage through the ion acceleration region (which is 4 mm from the surface). The C_{59}^+ ion has previously been observed with low abundance during $C_{60}^- -$He collisions,[36] and this phenomenon can be explained as a single knockout process from C_{60}^-, which has a lower internal energy than C_{60}^+. The odd number of C atoms can be abstracted during the chemical sputtering of C_{60} in the O_2 and C_8F_{18} matrix films, but no $C_{(60-2n+1)}^+$ ions were observed in the present experiment. This is most likely because the $C_{(60-2n+1)}^+$ ions are unstable species that decay into C_{60-2n}^+ and C immediately at the surface.

5. Summary

It was found for the first time that the C_{60}^+ ions are sputtered efficiently when they are isolated on or in the thin-matrix films composed of rare-gas atoms and some molecules. Fragmentation of C_{60}^+ ions does not occur when they are sputtered from the Ar and Xe matrixes, whereas the O_2 and C_8F_{18} matrixes induce chemical sputtering of the C_{60} molecules. This results in the emission of fragment ions as well as in the complex ions such as $(OC_{60})^+$ and $(FC_{60})^+$. The yields of the C_{60}^+ ions are almost comparable for the Ar, Xe, O_2, and C_8F_{18} matrix films, but very few ions were sputtered from C_{60} adsorbed on the H_2O film. The C_{60}^+ ions are thought to be created during the collision of the C_{60} molecules with the Ar, Xe, O, and F species via the electron-promotion mechanism. The formation of the quasi-molecules appears to be related to the emission of the ion adducts. The charge of the primary He^+ ion may make a small contribution to the sputtering of C_{60}^+ and C_{60}^{++}, which can be checked by comparison with the results using a primary He^0 beam. The small C_{60}^+ yield from the H_2O film is attributed to the delocalization of the valence hole because of the hydrogen bonds, which have some covalent character. Thus, the suppression of the ion neutralization probability in the weakly bound matrix films is responsible for the efficient sputtering of the C_{60}^+ ions.

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