Growth of Fluorocarbon Macromolecules in a Gas Phase (I). Mass Spectrometric Investigation of Products in the Downstream Region of Ar/CF_4 Plasmas

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The growth of gaseous neutral species and positive ions was investigated in the downstream region of Ar/CF_4 plasmas by mass spectrometry. As a result, there were several series of $C_nF_{2n+1}{}^+$ ($n = 1$–7), $C_nF_{2n-1}{}^+$ ($n = 3$–8) and $C_nF_{2n-3}{}^+$ ($n = 4$–9) for the positive ions and C_nF_{2n+2} ($n = 2$–7) and C_nF_{2n} ($n = 4$–8) for the neutral species. The intensity dependence of the positive ions on the partial pressure of CF_4 was quite different from that of the neutral species, demonstrating that their growth mechanisms are independent of each other.

As demonstrated in the formation of fullerene, the growth of macromolecules in a gas phase is intriguing not only in the light of physical chemistry, as represented by the reaction rates and dynamics, but also in the light of material science. Generating plasmas of source gases is effective for the macromolecule formation, especially such as polymer formation,[1] even if spontaneous polymerization does not take place in the gases. There are, however, little investigations of the growth of gaseous macromolecules in the plasmas of the molecules containing only saturated bonding in contrast to numerous investigations of plasma polymerization on substrate surfaces. In the case of the SiH_4 plasma,[2,3] there are positive ions up to 400 amu ($Si_{12}H_x{}^+$), neutral species up to 130 amu (Si_4H_x), and negative ions up to 1200 amu ($Si_{44}H_x{}^-$). The study of the CH_4 plasma[4] shows the existence of positive ions up to 165 amu ($C_{12}H_{21}{}^+$). Compared to these cases, there are positive ions consisting of a relatively small number of atoms up to 319 amu ($C_6F_{13}{}^+$) at most in the pure CF_4 plasma.[5,6] Schwarzenbach et al.[6] have recently demonstrated that exposing a silicon surface to the pure CF_4 plasma helps the formation of high-mass positive ions up to 381 amu ($C_8F_{15}{}^+$), although this is not the case for the Al and SiO_2 surfaces.

In this letter, we show that the formation of perfluorocarbon macromolecules is promoted in the downstream region of the Ar/CF_4 plasmas without the silicon surface. The positive ions up to 393 amu ($C_9F_{15}{}^+$) and neutral species up to 400 amu (C_8F_{16}), which are the mass limit of our mass spectrometer, have been detected.

The experimental apparatus will be described in detail elsewhere. Briefly, an inductively coupled plasma was generated in a quartz tube of 50-mm diameter by supplying a radio-frequency (13.56 MHz) power of 150 W. The produced positive ions were analyzed using a quadrupole mass spectrometer contained in a "low-pressure type" Li^+ attachment mass spectrometer (ANELVA L-241G-IA), which was separated with an aperture of 0.8-mm diameter from a Li^+ attachment compartment and differentially pumped. This mass spectrometer can work as a normal mass spectrometer when the Li^+ ion is not generated. Attaching the Li^+ ion to neutral species allows the fragment-free mass analysis of the neutral species.[7,8] In ordinary ion-attachment ionization, a third body such as N_2 is additionally supplied into the ion-attachment compartment at the order of 100 Pa to stabilize the ion-attached products. In the present "low-pressure type" one, no third body is additionally supplied, allowing the mass analysis of the neutral species included in low-pressure (a few Pa) plasmas, although the probability of attaching Li^+ is very low, especially in the small species that consist of less than ten atoms. CF_4 (Carbon tetrafluoride, 99.999%, Takachiho Trading) and Ar (99.999%, Nippon Sanso) were supplied into the chamber using mass flow controllers. The operating pressure was 1.1 Pa and equal to that in the Li^+ attachment compartment. The distance between the center of the plasma and the entrance of the mass spectrometer was 90 cm.

Figure 1 shows the intensity dependence of $C_nF_{2n+1}{}^+$ ($n =$ 2–7) on the mixing ratio of CF_4 in the downstream region of the Ar/CF_4 plasmas. The total pressure was kept at 1.1 Pa in these experiments. The intensity in each ion is decreased with increasing the mixing ratio of CF_4 above a ratio of 0.3. This is the case for $CF_3{}^+$, $CF_2{}^+$ and CF^+. The F^- density is comparable to the electron density in the Ar/CF_4 plasma and increased with the mixing ratio of CF_4 in contrast to the decrease of the electron density.[9] Such a high F^- density promotes the recombination reaction with the positive ions, especially with small ions such as $CF_3{}^+$, $CF_2{}^+$ and CF^+, because the reaction is accompanied by the increase of vibrational degree of freedom in the products, stabilizing the products even under the low-pressure condition. Such stabilization cannot be expected in the recombination with the electrons. The decrease in the intensity of the small ions leads to the decrease in the intensity of the large ions shown in Figure 1 because the large ions grow from the small ions, as de-

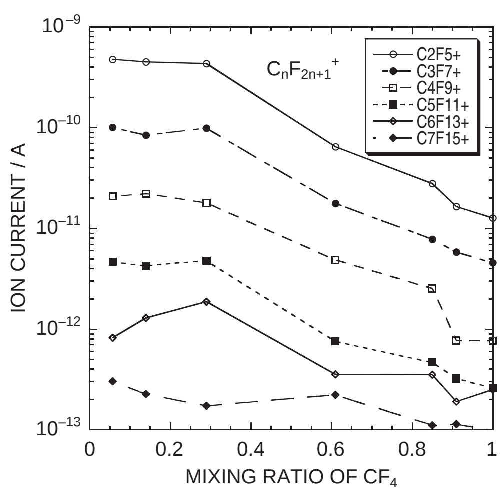

Figure 1. Intensity dependence of $C_nF_{2n+1}{}^+$ ($n = 2$–7) on the mixing ratio of CF_4. The total pressure was kept at 1.1 Pa.

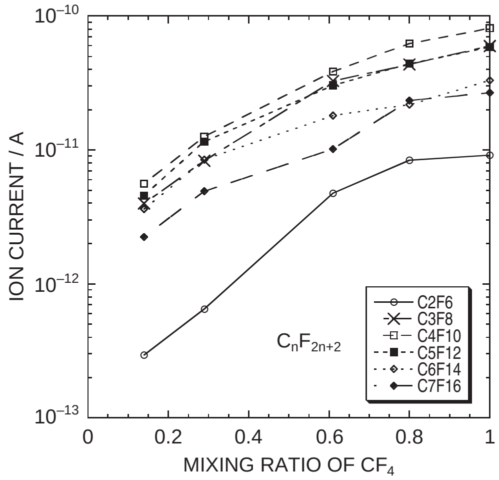

Figure 2. Intensity dependence of C_nF_{2n+2} ($n = 2$–7) on the mixing ratio of CF_4. The total pressure was kept at 1.1 Pa.

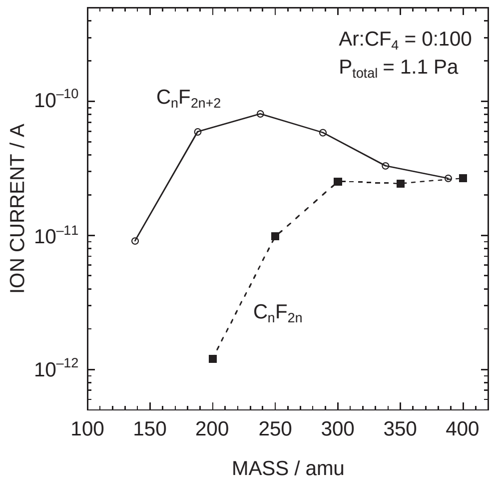

Figure 3. Plots of the intensity in C_nF_{2n+2} ($n = 2$–7) and C_nF_{2n} ($n = 4$–8) observed in the downstream region of the pure CF_4 plasma as a function of the mass number.

scribed later. Detailed experiments on the mixing ratio resulted in the remarkable increase in the intensity of the all ions up to a ratio of 0.05.[10]

The intensity dependence of C_nF_{2n+2} ($n = 2$–7) on the mixing ratio of CF_4 in the downstream region of the Ar/CF_4 plasmas is shown in Figure 2. The weak intensity of C_2F_6 and C_3F_8 in the figure is due to the relatively low probability of attaching Li^+ to them. Schwarzenbach et al.[6] have proposed on the basis of their mass spectrometric investigation in the pure CF_4 plasma that the large positive ions are formed by the ionization of the large neutral species since the average residence time of the positive ions in the plasma is short because of the ambipolar electric field that drives them to the sheath. All the neutral species shown in Figure 2 are, however, increased in their intensity with the mixing ratio of CF_4 in contrast to the $C_nF_{2n+1}{}^+$ case. This finding demonstrates that the large positive ions observed are produced not by the ionization of the large neutral species in the downstream region of the plasmas but through the addition reaction of relatively smaller ions with the neutral species that exist with relatively high density in the plasmas, such as CF_3, CF_2 and CF_4.

There were $C_nF_{2n-1}{}^+$ ($n = 3$–8) and $C_nF_{2n-3}{}^+$ ($n = 4$–9) for the positive ions and C_nF_{2n} ($n = 4$–8) for the neutral species in the observed mass spectra, as well as $C_nF_{2n+1}{}^+$ and C_nF_{2n+2} shown in Figures 1 and 2. The background signal level was less than 1×10^{-13} A in the present mass spectrometer. The plots of the intensity in C_nF_{2n+2} ($n = 2$–7) and C_nF_{2n} ($n = 4$–8) observed in the downstream region of the pure CF_4 plasma as a function of the mass number are shown in Figure 3 without any correction for the probability of attaching Li^+. The probability of attaching Li^+ to relatively large molecules that consist of more than ten atoms is thought to be roughly constant because there are many vibrational degrees of freedom enough for the immediate intramolecular relaxation of the collision energy in the addition reaction, allowing the comparison of the intensity among C_nF_{2n+2} with the different n value ($n > 3$) and also in the case of C_nF_{2n}. These plots in Figure 3 strongly suggest the existence of macromolecules with much more than 400 amu in the downstream region of the plasma.

In conclusion, we have demonstrated by mass spectrometry that there are large positive ions and neutral species such as $C_9F_{15}{}^+$ and C_8F_{16} in the downstream region of the Ar/CF_4 plasmas. In addition, the experimental results of the intensity dependence of their species on the Ar/CF_4 mixing ratio have indicated that the growth mechanism of the positive ions is independent of that of the neutral species. The growth of perfluorocarbon macromolecules in a gas phase would be applicable to the development of materials such as thin films.

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