Mass Spectrometric Analysis of Chemical Species in the Downstream Region of Ar/CF_4/H_2 Plasmas

Yuji TAMAI, Hiroshi OKUMURA, Kenji FURUYA and Akira HARATA

Department of Molecular and Material Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

(Received: 7 September 2008 / Accepted: 27 November 2008)

The mass analysis of positive ions and neutral species was conducted in a downstream region of Ar/CF_4/H_2 plasmas. The neutral species were ionized by the attachment of the Li^+ ion before mass-analyzing. As a result, C_nF_{2n-2} (n = 3–8), C_nF_{2n-4} (n = 3–9) and $C_nF_{2n-5}^+$ (n = 5–10) appeared additionally in the Ar/CF_4/H_2 plasmas, compared to the Ar/CF_4 plasma, where C_nF_{2n+2} (n = 1–7), C_nF_{2n} (n = 4–8), $C_nF_{2n+1}^+$ (n = 1–7), $C_nF_{2n-1}^+$ (n = 3–7) and $C_nF_{2n-3}^+$ (n = 3–9) appeared. In addition, several fluorocarbons containing hydrogen atom(s) appeared. The production of highly unsaturated neutral species is derived through the abstraction reactions of the F atom from C_mF_n by the H atom with the HF production, whereas that of highly unsaturated $C_mF_n^+$ is due to different reaction mechanisms.

Keywords: plasma, CF_4, H_2, ion attachment, mass spectrometry, high-mass species

1. Introduction

Anisotropic etching of the Si wafer by mixed-gas plasmas using CF_4 and H_2 is promoted. It is believed that the film deposited on the etching wall prevents side-wall etching [1]. Controlling the kind and concentration of chemical species in the plasmas is significant for optimizing the character of the film. However, little has been known about the growth mechanisms and source species of the film. One reason is difficulty in the identification of chemical species in the plasmas, especially of high-mass neutral species.

Mass spectrometry is an appropriate method to identify chemical species included in the plasmas. It needs an ionization process. However, most of the conventional ionization methods cause fragmentation, resulting in the difficulty in their identification.

Li^+ ion attachment mass spectrometry (IAMS) allows fragment-free detection of neutral species [2-6]. We have recently found that various high-mass positive ions and neutral molecules with a mass number up to 400 amu are present in the downstream region of Ar/CF_4 plasmas [7]. In addition, we have clarified the growth mechanisms of the high-mass positive ions [8]. In this report, we show experimental results of the mass analysis of high-mass neutral species using IAMS in the downstream region of Ar/CF_4/H_2 plasmas, as well as positive ions. The formation mechanisms of their chemical species observed are discussed based on the enthalpy changes of the reactions.

2. Experimental Procedure

A schematic view of the experimental setup is depicted in Fig. 1. The chamber was pumped by a 550 $l \cdot s^{-1}$ turbomolecular pump. An inductively coupled plasma was generated in a quartz tube with a 50 mm inside diameter by supplying a radio-frequency (RF,

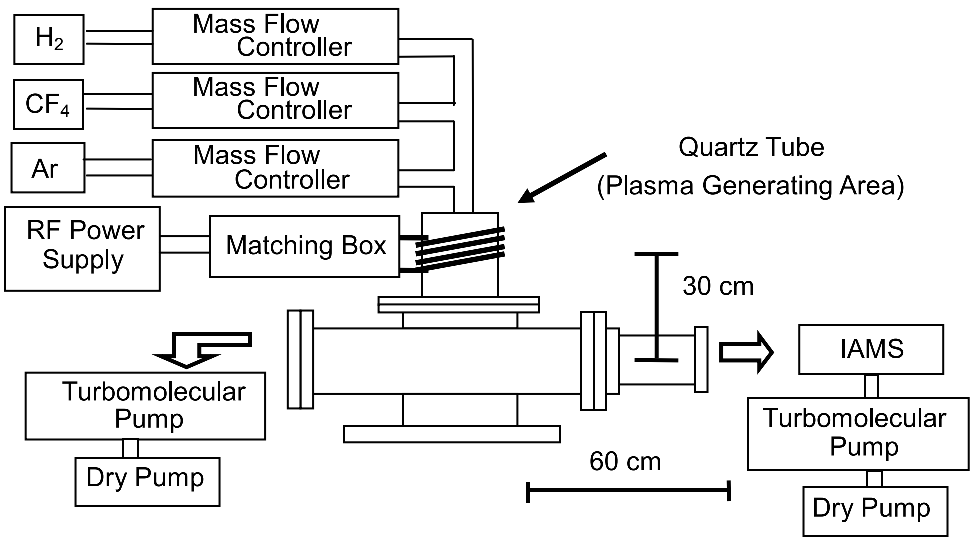

Fig. 1. Schematic view of the experimental setup.

13.56MHz) power of 150 W (ARIOS, ERFS-511). The produced positive ions were analyzed using a quadrupole mass spectrometer contained in a low-pressure Li^+ attachment mass spectrometer (CANON ANELVA, L-241G-IA), which was separated by an aperture with 0.8 mm in diameter from a Li^+ attachment compartment and was differentially pumped with a 220 $l{\cdot}s^{-1}$ turbomolecular pump. 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. The natural abundance of $^6Li^+$ is 7.6%, and then would disturb the assignment of mass peaks observed through the Li^+ ion attachment. This spectrometer contains a simple magnetic mass filter for selecting $^7Li^+$, reducing the $^6Li^+/^7Li^+$ ratio to 3.3%.

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-attachment 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), Ar (99.999%, NIPPON SANSO) and H_2 (99.999%, NIPPON SANSO) were supplied into the chamber using mass flow controllers (KOFLOC, 360). The pressure was measured with a ceramic capacitance gauge (PFEIFFER, CCR364) and a cold cathode gauge (BALZERS, KR260) in the chamber, and with an ionization gauge (ANELVA, MG-2F) in the mass spectrometer. The base pressure was 6×10^{-5} Pa in the chamber and 1×10^{-7} Pa in the mass spectrometer. The operating pressure was 1.0 Pa and equal to that in the Li^+ attachment compartment. The distance between the center of the plasma source and entrance of the mass spectrometer was 90 cm. Three grids were used only while observing neutral species by IAMS. These grids prevent excessive electrons and positive ions produced in the plasma from flowing into the Li^+ ion attachment mass spectrometer. The DC voltages of 0, −71 and +79 V were applied to each of three grids in order of those close to the plasma, respectively.

We estimated reaction enthalpies by conducting the geometry optimization and frequency calculations under the B3LYP/6-31+G(d) level followed further by the same calculations under the B3LYP/6-311+G(3*df*) level with the GAUSSIAN03 program package [9] using a high performance server (IBM, eServer p5 model 595) set up in the Computing and Communication Center of Kyushu University.

3. Results and discussion

3.1 Mass spectra

Typical mass spectra of neutral species and positive ions observed in the downstream region of the $Ar/CF_4/H_2$ plasma are shown in Fig. 2. Neutral species were observed as their Li^+ ion adducts. The plasma was generated under conditions of an RF power of 150 W, a pressure of 1.0 Pa, flow rates of 102 sccm for Ar, 31.5 sccm for CF_4 and 10 sccm for H_2. The abbreviation M_N means $C_MF_NLi^+$ in Fig. 2a and $C_MF_N{}^+$ in Fig. 2b. The superscript "O" and "H" means the presence of the O or H atom(s) in the species, for example, $2_4{}^{H2} = C_2F_4H_2Li^+$ in Fig. 2a and $4_7{}^{O} = C_4F_7O^+$ in Fig. 2b. We observed

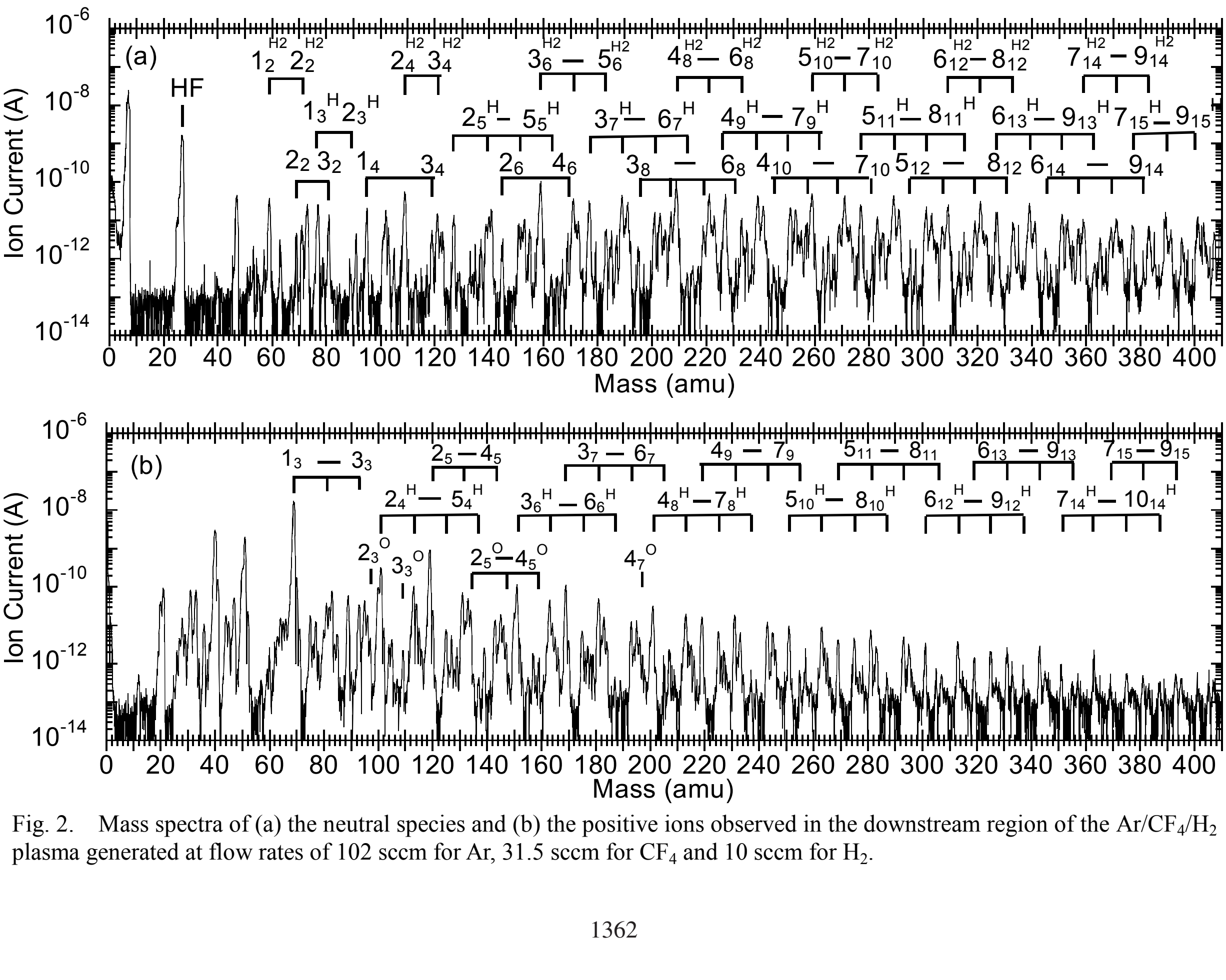

Fig. 2. Mass spectra of (a) the neutral species and (b) the positive ions observed in the downstream region of the $Ar/CF_4/H_2$ plasma generated at flow rates of 102 sccm for Ar, 31.5 sccm for CF_4 and 10 sccm for H_2.

neutral species containing up to 9 carbon atoms and positive ions up to 10 carbon atoms. Compared to the Ar/CF_4 plasmas, various unsaturated neutral species and positive ions appeared additionally in the $Ar/CF_4/H_2$ plasma.

3.2 Neutral species

All the observed neutral species are summarized in Table 1. We have previously found only C_nF_{2n+2} (n = 1–7) and C_nF_{2n} (n = 4–8) in the Ar/CF_4 plasmas [7]. In the $Ar/CF_4/H_2$ plasmas, a variety of species with more unsaturated chemical bonds, such as C_nF_{2n-2} and C_nF_{2n-4}, appeared. The H atom produced through the decomposition of the H_2 gas injected in the plasma would lead to the formation of C_nF_{2n-2} and C_nF_{2n-4} through the abstraction reaction of the F atom from C_MF_N. Hikosaka et al. [11] have reported that the CF_2 density were increased two orders of magnitude after the hydrogen injection, whereas the CF_3 density increased twice due to the abstraction reaction by the H atom from CF_3, $CF_3 + H \rightarrow CF_2 + HF$, in the CF_4/H_2 plasma, in which the RF power was 50 W and the partial pressures of CF_4 and H_2 were 18.8 and 0.75 Pa, respectively. This result suggests the efficient F abstraction from relatively high-mass species. In addition, the concentration of the F atom in the plasma was reduced through the HF production, disturbing the formation of species with relatively high F/C ratios.

Table 1. Neutral species observed in the $Ar/CF_4/H_2$ plasma.

species	range of n
C_nF_{2n+2}	1–7
C_nF_{2n}	4–8
C_nF_{2n-2}	3–8
C_nF_{2n-4}	3–9
$C_nF_{2n+1}H$	1–7
$C_nF_{2n-1}H$	2–8
$C_nF_{2n-3}H$	4–9
$C_nF_{2n-5}H$	5–9
$C_nF_{2n}H_2$	1–7
$C_nF_{2n-2}H_2$	2–8
$C_nF_{2n-4}H_2$	3–9

The reaction enthalpies summarized in Table 2 indicate that the abstraction reactions of the F atom from C_mF_n by the H atom are exothermic in the case of the number of carbon atoms being 3 and 4 and that the reactions can take place.

The formation of chemical species containing the hydrogen atom(s) would be due to the reactions, $C_mF_n + H \rightarrow C_{m-1}F_{n-2} + CF_2H$, as the first step. The growth of CF_2H would lead to the various H-containing species. In addition, the abstraction of H from the H-containing species by the F atom would inhibit the formation of H-containing species with three or more H atoms.

Table 2. Enthalpy changes ($\Delta_r H^o$) in some HF formation reactions estimated through the B3LYP/6-311+G(3*df*) level calculations.

Reactions	$\Delta_r H^o$ (kcal·mol^{-1})
$C_3F_8 + H \rightarrow CF_3CF_2CF_2 + HF$	−54.5
$C_3F_8 + H \rightarrow CF_3CFCF_3 + HF$	−83.9
$CF_3CF_2CF_2 + H \rightarrow CF_2CFCF_3 + HF$	−308.8
$CF_3CFCF_3 + H \rightarrow CF_2CFCF_3 + HF$	−279.4
$CF_2CFCF_3 + H \rightarrow CFCFCF_3 + HF$	−62.1
$CF_2CFCF_3 + H \rightarrow CF_2CFCF_2 + HF$	−83.0
$CFCFCF_3 + H \rightarrow CFCFCF_2 + HF$	−126.7
$CF_2CFCF_2 + H \rightarrow CF_2CCF_2 + HF$	−283.2
$CFCFCF_2 + H \rightarrow CFCFCF + HF$	−32.5
$CF_2CCF_2 + H \rightarrow CFCCF_2 + HF$	−68.3
$CFCFCF + H \rightarrow CFCCF + HF$	−299.5
$CFCCF_2 + H \rightarrow CFCCF + HF$	−86.3
$C_4F_{10} + H \rightarrow CF_3CF_2CF_2CF_2 + HF$	−59.5
$C_4F_{10} + H \rightarrow CF_3CF_2CFCF_3 + HF$	−95.8
$CF_3CF_2CF_2CF_2 + H \rightarrow CF_3CF_2CFCF_2 + HF$	−315.1
$CF_3CF_2CFCF_3 + H \rightarrow CF_3CFCFCF_3 + HF$	−301.1
$CF_3CF_2CFCF_2 + H \rightarrow CF_2CF_2CFCF_2 + HF$	−46.8
$CF_3CFCFCF_3 + H \rightarrow CF_3CFCFCF_2 + HF$	−106.9
$CF_3CFCFCF_2 + H \rightarrow CF_3CFCCF_2 + HF$	−272.7
$CF_2CF_2CFCF_2 + H \rightarrow CF_2CFCFCF_2 + HF$	−329.1
$CF_3CFCCF_2 + H \rightarrow CF_2CFCCF_2 + HF$	−93.7
$CF_2CFCFCF_2 + H \rightarrow CF_2CFCCF_2 + HF$	−119.9
$CF_2CFCCF_2 + H \rightarrow CFCFCCF_2 + HF$	−70.2

Fig. 3a shows the intensity dependence of C_nF_{2n+2} (n = 2 and 4) and C_nF_{2n} (n = 4 and 6) on the flow rate of H_2 in the $Ar/CF_4/H_2$ plasmas. The pressure of Ar and CF_4 were 0.7 Pa and 0.3 Pa in these experiments, respectively. The intensity of C_nF_{2n+2} (n = 1 and 2) and C_nF_{2n} (n = 4 and 5) were increased with the flow rate of H_2. In contrast, the intensity of C_nF_{2n+2} (n > 2) and C_nF_{2n} (n > 5) were decreased or almost constant with increasing the flow rate of H_2.

The tendency of the plots shown in Fig. 3a can be reasonably explained by taking into account the F abstraction from C_nF_{2n+2} and C_nF_{2n} by the H radical as follows: The existence of various C_nF_{2n+2} and C_nF_{2n} in the Ar/CF_4 plasma [7] indicates that CF_x (x = 1–3) produced by the decomposition of CF_4 react to produce these high-mass species. Hikosaka et al. [12] have reported that the densities of CF_x increased by supplying H_2 in the Ar/CF_4 plasmas. Then, if there were no loss processes of C_nF_{2n+2} and C_nF_{2n} caused by the H_2 supply, the density of each C_nF_{2n+2} and C_nF_{2n} in the plasma should be increased with the H_2 flow rate. Actually, the F abstraction from C_nF_{2n+2} and C_nF_{2n} by the H radical can take place as their loss processes. The rate of the F abstraction would be increased with the number of the F atoms contained in the reactants, C_nF_{2n+2} and C_nF_{2n}. Therefore, it is expected that the densities of C_nF_{2n+2} and C_nF_{2n} would be increased with the H_2 flow rate in the case of relatively small n because the formation of C_nF_{2n+2} and C_nF_{2n} would be prior to their loss. On the contrary, their loss processes would be prior to their formation in the case of relatively large n. In addition, the loss of C_nF_{2n} by the F abstraction would be reduced by the formation of C_nF_{2n} through the F abstraction from C_nF_{2n+2}.

The intensity dependence of C_4F_4 and C_4F_6 on the flow rate of H_2 is shown in Fig. 3b. The intensity of highly unsaturated species was increased with the flow rate of H_2 above a flow rate of 5 sccm. This finding strongly suggests that highly unsaturated species are produced by stepwise abstraction reactions of the F atoms from C_nF_{2n+2} and C_nF_{2n}.

3.3 Positive ions

All the observed positive ions are summarized in Table 3. We have previously found only $C_nF_{2n+1}^+$ (n = 1–7), $C_nF_{2n-1}^+$ (n = 3–7), and $C_nF_{2n-3}^+$ (n = 3–9) in the Ar/CF_4 plasmas. In the $Ar/CF_4/H_2$ plasmas, $C_nF_{2n-5}^+$ (n = 5–10) appeared additionally. Furthermore, various positive ions containing the H atom appeared.

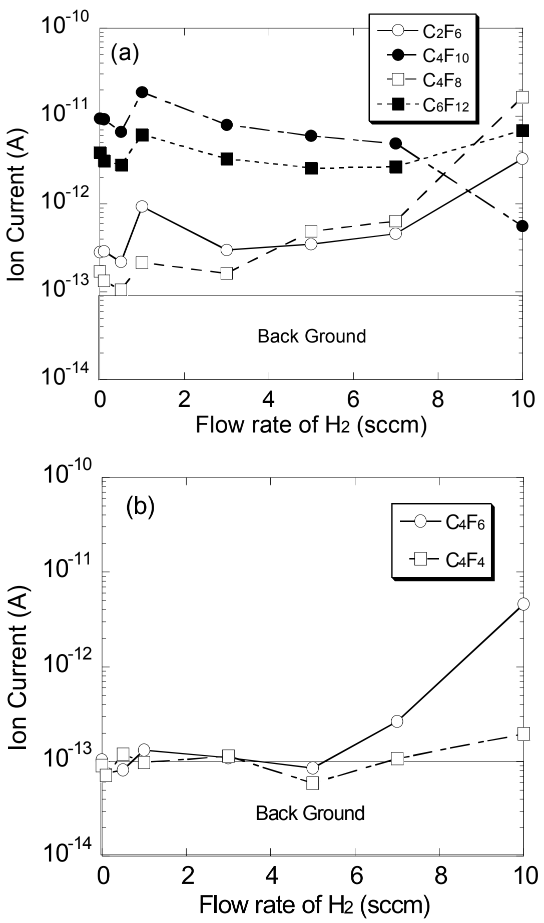

Fig. 3. Intensity dependence of the neutral species on the flow rate of H_2: (a) C_nF_{2n+2} (n = 2 and 4) and C_nF_{2n} (n = 4 and 6) and (b) C_4F_4 and C_4F_6.

Table 3. Positive ions observed in the $Ar/CF_4/H$ plasma. ($N_M^H = C_MF_NH^+$)

species	range of n
$C_nF_{2n+1}^+$	1–7
$C_nF_{2n-1}^+$	3–8
$C_nF_{2n-3}^+$	3–9
$C_nF_{2n-5}^+$	5–10
$C_nF_{2n}H^+$	1–7
$C_nF_{2n-2}H^+$	2–8
$C_nF_{2n-4}H^+$	3–9
$C_nF_{2n--6}H^+$	5–10

The intensity plots of the observed positive ions with respect to the mass number at 10 sccm H_2 flow rate are shown in Fig. 4. In the case of the Ar/CF_4 plasma, $C_6F_9^+$ was maximal in intensity in the $C_nF_{2n-3}^+$ series and the intensity was 1×10^{-12} A. The $C_nF_{2n-3}^+$ series remarkably increased the intensity in the $Ar/CF_4/H_2$ plasma, as shown in Fig. 4, although the intensity of the $C_nF_{2n+1}^+$ and $C_nF_{2n-1}^+$ series was similar to that in the Ar/CF_4 plasma. In particular, $C_nF_{2n-3}^+$ (n = 3–5) were stronger than $C_6F_9^+$. These findings suggest that the enhanced formation of relatively small $C_nF_{2n-3}^+$ leads to the $C_nF_{2n-5}^+$ formation.

We could not detect high-mass $C_mF_n^+$ positive ions having even-numbered F atoms. This finding indicates that the stepwise F abstraction reactions from the $C_nF_{2n+1}^+$ and $C_nF_{2n-1}^+$ series by the H atom are negligible for the formation of $C_nF_{2n-3}^+$ and $C_nF_{2n-5}^+$.

There was an intensity alternation with carbon number in the $C_nF_{2n-5}^+$ series, as shown in Fig. 4. This finding suggests that the formation of larger $C_nF_{2n-5}^+$ is not due to the growth of smaller $C_nF_{2n-5}^+$ but due to the reactions of reactants belonging to different series and that the reactivity of the reactants depends significantly on the parity of the number of carbon atoms contained in the reactants.

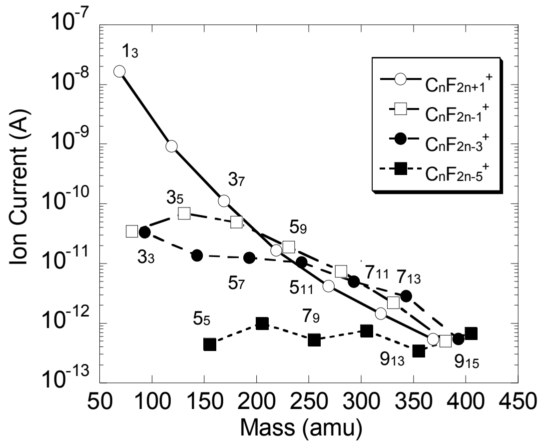

Fig. 4. Intensity plots of the positive ions observed in the downstream region of the $Ar/CF_4/H_2$ plasma with respect to mass number. The abbreviation M_N represents $C_MF_N^+$.

Acknowledgements

This work is partly supported by a Grant-in-Aid for Scientific Research C (No. 17540471) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. One of the authors (Y. T.) acknowledges the Computing and Communications Center of Kyushu University for the free use of a high performance server.

[1] M. Sekine, J. Plasma Fusion Res. **83**, 319 (2007).
[2] T.Fujii, Chem. Phys. Lett. **191**, 162 (1992).
[3] T. Fujii and K. Syouji, J. Appl. Phys. **74**, 3009 (1993).
[4] T. Fujii, J. Appl. Phys. **82**, 2056 (1997).
[5] Y. Shikowa, M. Nakamura, H. Maruyama, Y. Hirano, Y. Taneda, M. Inoue and T. Fujii, BUNSEKI KAGAKU **53**, 475 (2004) [in Japanese].
[6] M. Sablier, K. Iwase, G. Sato and T. Fujii, Chem. Phys. Lett. **409**, 342 (2005).
[7] K. Furuya, S. Yukita, H. Okumura and A. Harata, Chem. Lett. **34**, 224 (2005).
[8] K. Furuya, S. Yukita and A. Harata, Jpn. J. Appl. Phys. **45**, 5219 (2006).
[9] M.J. Frisch *et al.*, GAUSSIAN 03, Revision D.01, Gaussian, Inc., Wallingford CT, 2004.
[10] M. Nakamura, Y. Hirano, Y. Shiokawa, M. Takayanagi and M. Nakata, J. Appl. Phys. **74**, 3009 (2006).
[11] Y. Hikosaka, H. Toyoda and H. sugai, Jpn. J. Appl. Phys. **32**, L690 (1993).
[12] Y. Hikosaka, M. Nakamura and H. Sugai, Jpn. J. Appl. Phys. **33**, 2157 (1994)