

Cross Sections for Electron-Impact Dissociation of Alternative Etching Gas, C₃HF₇O

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The search for alternative for perfluorocarbon gases from the environmental point of view has resulted in a new etching gas, C₃HF₇O (1,2,2,2-tetrafluoroethyl-trifluoromethyl ether, abbreviated as HFE-227). In this paper, the first measurement of the absolute cross sections for the dissociation of HFE-227, is reported. The neutral dissociation is measured from the threshold to 250 eV by appearance mass spectrometry in a dual electron beam device. The threshold energies for the neutral dissociation into CF, CF₂ and CF₃ are 14.7, 12.5 and 11.2 eV, respectively. The cross sections for the dissociation from HFE-227 into CF₃ and CF are larger than those from c-C₄F₈ (octafluorocyclobutane), but not for the dissociation into CF₂. Besides the neutral dissociation, the cross sections for the dissociative ionization of HFE-227 are extensively measured for the formation of twelve ionic species, i.e., CO⁺, CHO⁺, CF⁺, CHF⁺, CFO⁺, CF₂⁺, CHF₂⁺, CF₃⁺, CHF₃⁺, C₂HF₂O⁺, C₂HF₄⁺ and C₂HF₄O⁺.

KEYWORDS: 1,2,2,2-tetrafluoroethyl trifluoromethyl ether, dissociation cross section, neutral radical, electron impact, dissociative ionization cross section

1. Introduction

To date, huge amounts of perfluorocarbon (PFC) gases such as CF₄, C₂F₆ or C₄F₈ have been used for etching and cleaning in the semiconductor industry. However, strict regulations for use of PFC were introduced in 1997 in the World Environmental Congress held in Kyoto as PFC gases are thought to destroy the ozone layer. Such environmental aspects have accelerated the search for alternative gases which give high etch performance as PFCs and have a much shorter lifetime in the ozone layer. The most promising candidate so far is C₃HF₇O (1,2,2,2-tetrafluoroethyl-trifluoromethyl ether), abbreviated as HFE(hydro-fluoro-ether)-227.

Electron-impact dissociation of HFE-227 into chemically reactive species of neutral radicals and ions is the first step of chemical reactions in the plasma. However, cross section data have not been reported for either neutral dissociation or ionization cross sections. We have developed a highly-sensitive radical detection technique, i.e., appearance mass spectrometry (AMS),¹ which has successfully been applied to the cross section measurement for neutral dissociation of methane (CH₄),^{2,3} sulfur hexafluoride (SF₆),⁴ carbontetrafluoride (CF₄),⁵ octafluorocyclobutane (c-C₄F₈),⁶ trifluoromethane (CHF₃),⁵ and tetrafluorosilane (SiF₄).⁷

In this paper, we report the first measurement of partial cross sections for electron impact dissociation of HFE-227 into neutral radicals and ionic radicals.

2. Experimental

The measurement was carried out in a dual-electron-beam device combined with a quadrupole mass spectrometer (QMS), which has been used in a series of cross section studies.^{2–7} This system consists of three compartments which are differentially pumped with two turbomolecular pumps. The first compartment is a grounded dissociation cell where a primary electron beam with incident energy of $E = 5\text{--}250\text{ eV}$ and current of $I_c = 1\text{--}60\text{ }\mu\text{A}$ dissociates the HFE-227 molecule flowing at pressures of $10^{-3}\text{--}10^{-2}\text{ Pa}$. The electron beam is collected by a cylindrical cup (collector)

of 1.2 cm in diameter and 1.6 cm in length. The second compartment is a detection cell (HFE-227 pressure $10^{-5}\text{--}10^{-4}\text{ Pa}$) where a probing electron beam emitted from a rhenium filament at the energy of $E_Q = 10\text{--}25\text{ eV}$ selectively ionizes neutral radicals effusing from the dissociation cell through a 4-mm-diameter orifice into an ionization chamber. The ionized radicals are mass-separated by the QMS, and output pulses from a secondary electron multiplier in the QMS system are counted and processed by a computer. The third compartment is an electron source cell at a HFE-227 pressure of $10^{-4}\text{--}10^{-3}\text{ Pa}$ where the primary electron beam is generated from a tungsten filament biased negatively to $-V_d$. The primary beam is injected through an orifice along a magnetic field of $\sim 0.06\text{ T}$ provided by a pair of permanent magnets. Mean energies and energy spreads ($\sim 1\text{ eV}$) for both the primary and the probing electron beams are calibrated⁸) by measuring the energy dependence of Ar ionization near the threshold energy (15.75 eV).

The primary electron beam collides with the HFE-227 molecules and creates various neutral radicals and ionic species. First, ions are eliminated by the positive bias ($\sim 50\text{ eV}$) of the ionization chamber and the QMS with respect to the dissociation cell. Neutral radicals are detected using the AMS technique.^{1–7}

Figure 1 shows the semilogarithmic plot of the QMS output for $m/z = 69$ (CF₃⁺) as a function of the energy E_Q of the probing electron beam. When the primary beam is turned off, the CF₃⁺ signal is detected as a result of the dissociative ionization, $\text{HFE-227} \rightarrow \text{CF}_3^+ + (\text{other fragments})$, above the threshold energy of 15.5 eV. In Fig. 1, the difference of signal intensity between beam-on (filled circles) and beam-off (open circles) conditions is attributed to the ionization of CF₃ radicals effusing from the dissociation cell. The threshold energy for the CF₃ ionization was found to be 10.4 eV as mentioned below (§3.1) and hence the probing electron energy E_Q is fixed at 10.8 eV for CF₃ detection. In a similar manner, the value of E_Q for CF and CF₂ detection was determined to be 12.3 eV and 12.8 eV, respectively.

Radical signal S , which is obtained as the difference in the time-integrated QMS output between the case of the primary beam turned on and that of the beam turned off, linearly increases with the integration time t . As electron-impact disso-

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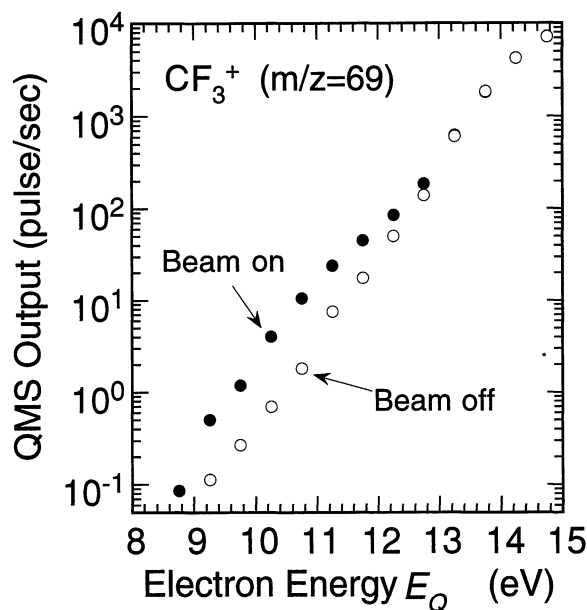


Fig. 1. Quadrupole mass spectrometer output for $m/z = 69$ (CF_3^+) as a function of probing beam energy E_Q with the primary beam turned on (filled circles) and the primary beam turned off (open circles). The primary beam energy is 100 eV.

ciation occurs between an HFE-227 molecule and an electron, the slope dS/dt which is experimentally determined by the least-squares method must be proportional to the dissociation cross section $\sigma(E)$ as

$$\frac{dS}{dt} = \eta I_c p \sigma(E), \quad (1)$$

where η is the proportional constant which will be clarified later, I_c and E are the current and energy of the primary beam, respectively, and p is the HFE-227 pressure in the dissociation cell. The dependence of the CF_3 signal (dS/dt) on the primary beam current I_c and the HFE-227 pressure is shown in Figs. 2(a) and 2(b), respectively. These figures show linear increase of the radical signal with respect to the primary beam current and the HFE-227 pressure. Accordingly, it can be assessed that multiple processes such as (i) electron scattering to induce the increased path length and the decreased energy, or (ii) secondary reactions between dissociated intermediate species to produce CF_3 radicals, are negligible. The linear dependence on the electron current and the pressure was also confirmed for the CF_2 and CF species.

3. Results and Discussion

3.1 Cross sections for ionization

In order to determine the threshold energy for ionization, the data shown on a logarithmic scale in Fig. 1 were replotted on a linear scale in Fig. 3. The threshold energy corresponds to the point crossed by the straight line indicated in Fig. 3 and the small tail deviating from the straight line is caused by an energy spread of the probing beam. Thus, the threshold energies for the dissociative ionization of HFE-227 were obtained as shown in the bottom line in Tables I and II.

The energy dependence of the partial ionization cross section was obtained for twelve ionic species by measuring the QMS output current of each species: CO^+ ($m/z = 28$), CHO^+ (29), CF^+ (31), CHF^+ (32), CFO^+ (47), CF_2^+ (50), CHF_2^+ (51), CF_3^+ (69), CHF_3^+ (70), $\text{C}_2\text{HF}_2\text{O}^+$ (79), C_2HF_4^+

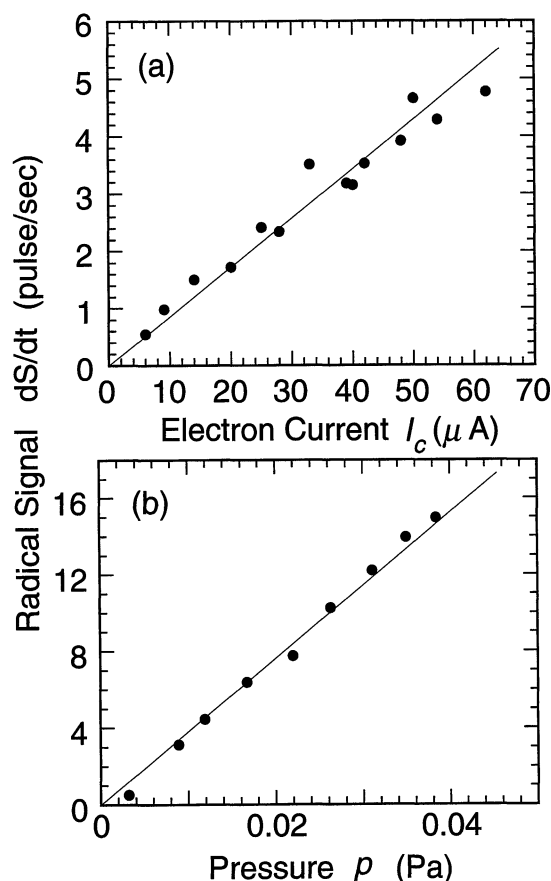


Fig. 2. (a) CF_3 signal vs electron current I_c at $p = 9.1 \times 10^{-3}$ Pa; (b) CF_3 signal vs pressure p at $I_c = 40 \mu\text{A}$.

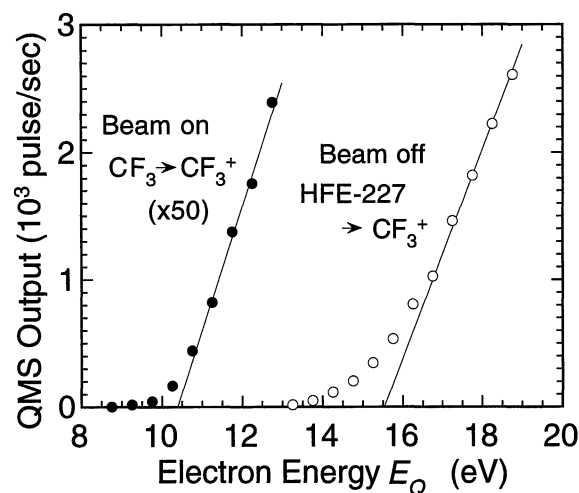


Fig. 3. Quadrupole mass spectrometer output for CF_3^+ as a function of probing beam energy E_Q with the 100 eV primary beam turned on (filled circles) and off (open circles).

(101) and $\text{C}_2\text{HF}_4\text{O}^+$ (117). Here the QMS current was measured as a function of the probing beam energy with the primary beam turned off. Signals from other ionic species were extremely small and masked by a background noise. As reported in previous papers,²⁻⁷⁾ the mass discrimination effects of the QMS were taken into account to determine the absolute values of the cross sections. To cover a mass range from $m/e = 28$ to 117, CF_4 and SF_6 were chosen as ref-

Table I. Partial cross sections for dissociative ionization of HFE-227 into CO^+ , CHO^+ , CF^+ , CHF^+ , CFO^+ and CF_2^+ in units of 10^{-20} m^2 , together with the threshold energies.

Energy (eV)	CO^+	CHO^+	CF^+	CHF^+	CFO^+	CF_2^+
12.3		0.01				
12.8		0.03		0.003		
13.3		0.14		0.005		
13.8		0.32		0.007		
14.3	0.003	0.52		0.009		
14.8	0.005	0.80		0.011		
15.8	0.029	1.60	0.002	0.017	0.002	
16.8	0.065	2.39	0.004	0.022	0.006	0.001
17.8	0.104	3.34	0.007	0.032	0.012	0.001
18.8	0.152	4.18	0.011	0.039	0.018	0.002
20.8	0.257	6.25	0.021	0.058	0.032	0.004
22.8	0.349	8.19	0.038	0.076	0.049	0.006
24.8	0.443	9.98	0.068	0.096	0.068	0.010
28.8	0.607	13.17	0.165	0.164	0.104	0.025
30.8	0.711	14.74	0.237	0.218	0.121	0.037
32.8	0.781	16.00	0.323	0.280	0.142	0.051
34.8	0.853	17.25	0.463	0.346	0.164	0.067
36.8	0.926	18.35	0.648	0.426	0.189	0.084
38.8	0.997	19.38	0.877	0.486	0.211	0.102
40.8	1.043	20.14	1.133	0.557	0.236	0.119
43.8	1.116	21.39	1.527	0.676	0.271	0.148
48.8	1.223	22.78	2.071	0.837	0.320	0.192
53.8	1.308	24.11	2.510	0.953	0.362	0.226
58.8	1.376	24.84	2.848	1.041	0.392	0.252
63.8	1.443	25.29	3.157	1.105	0.415	0.272
68.8	1.500	25.76	3.410	1.160	0.439	0.293
73.8	1.533	25.96	3.622	1.208	0.457	0.305
78.8	1.569	26.17	3.803	1.245	0.473	0.319
83.8	1.587	26.24	3.962	1.263	0.485	0.329
88.8	1.600	26.28	4.053	1.286	0.495	0.337
93.8	1.620	26.34	4.161	1.291	0.498	0.341
98.8	1.634	26.22	4.220	1.298	0.507	0.347
103.8	1.642	26.21	4.278	1.312	0.518	0.351
108.8	1.660	26.16	4.327	1.301	0.517	0.354
113.8	1.658	26.10	4.338	1.303	0.518	0.355
118.8	1.657	26.02	4.355	1.300	0.523	0.354
123.8	1.634	25.81	4.340	1.284	0.523	0.350
Threshold energy	15.2 eV	14.0 eV	16.5 eV	15.0 eV	16.5 eV	17.0 eV

erence gases and the fragment ions CF_x^+ ($x = 1-3$) and SF_y^+ ($y = 2-5$) were measured. These data were compared with the known partial ionization cross sections of CF_4 ⁹⁾ and SF_6 ,¹⁰⁾ which gives the mass sensitivity of the QMS.

In this way, the absolute cross sections for dissociative ionization of HFE-227 were obtained, and the results are shown in Fig. 4, Table I and Table II.

3.2 Cross sections for neutral dissociation

To our knowledge, the threshold energy for the appearance of neutral radicals as a result of the dissociation of HFE-227 has never been measured. To measure the threshold energies, the dependence of the neutral radical signal on the primary beam energy E was measured, especially for low energies. The result in the case of CF_3 radical is shown in Fig. 5. Similar measurements have been carried out for CF and CF_2 radicals. The obtained threshold energies for the neutral dissociation are listed on the bottom line in Table IV.

The absolute value of cross sections was determined using the same method as described previously.²⁻⁷⁾ Following is an example of the calibration process for CF_3 radical. Taking into account surface loss in the dissociation cell, vacuum conductance and mass discrimination factor of QMS, we obtain the expression³⁾ for the cross section

$$\sigma = \frac{\mu\gamma}{\beta} \frac{k + C_a + C_b}{\sigma^*[\text{HFE-227}]C_a} \frac{dS}{dt}, \quad (2)$$

where γ is the constant independent of radical species and μ is the constant expressing the mass discrimination effect of QMS. σ^* denotes the ionization cross section for $\text{CF}_3 \rightarrow \text{CF}_3^+$, $[\text{HFE-227}]$ is the number density of the HFE-227 molecule in the dissociation cell, and $\beta = l'l'I_c/e^2$ for the electron path length l , l' and the current I_c , I' in the dissociation cell and the detection cell, respectively. The proportional constant $\mu\gamma/\beta$ is obtained by measuring the neutral dissociation cross section of CF_x ($x = 1-3$) from CF_4 and comparing

Table II. Partial cross sections for dissociative ionization of HFE-227 into CHF_2^+ , CF_3^+ , CHF_3^+ , $\text{C}_2\text{HF}_2\text{O}^+$, C_2HF_4^+ and $\text{C}_2\text{HF}_4\text{O}^+$ in units of 10^{-20} m^2 , together with the threshold energies.

Energy (eV)	CHF_2^+	CF_3^+	CHF_3^+	$\text{C}_2\text{HF}_2\text{O}^+$	C_2HF_4^+	$\text{C}_2\text{HF}_4\text{O}^+$
12.3						0.001
12.8						0.002
13.3		0.01				0.006
13.8		0.02				0.009
14.3		0.05	0.001			0.014
14.8		0.08	0.001	0.001	0.003	0.018
15.8	0.002	0.20	0.003	0.004	0.023	0.028
16.8	0.010	0.39	0.005	0.012	0.071	0.039
17.8	0.034	0.69	0.009	0.023	0.166	0.049
18.8	0.074	0.99	0.013	0.034	0.270	0.061
20.8	0.221	1.69	0.022	0.058	0.473	0.086
22.8	0.433	2.58	0.034	0.081	0.738	0.109
24.8	0.656	3.49	0.046	0.101	0.996	0.131
26.8	0.926	4.36	0.055	0.123	1.229	0.151
28.8	1.186	5.30	0.065	0.146	1.442	0.172
30.8	1.409	6.06	0.075	0.167	1.657	0.189
32.8	1.607	6.78	0.081	0.186	1.841	0.206
34.8	1.764	7.45	0.090	0.201	2.029	0.219
36.8	1.956	8.09	0.097	0.218	2.184	0.234
38.8	2.086	8.72	0.102	0.232	2.355	0.248
40.8	2.257	9.20	0.107	0.243	2.473	0.257
43.8	2.406	9.84	0.114	0.261	2.668	0.272
48.8	2.687	10.67	0.122	0.281	2.873	0.288
53.8	2.888	11.49	0.131	0.300	3.072	0.302
58.8	3.062	11.99	0.135	0.315	3.225	0.314
63.8	3.143	12.34	0.141	0.325	3.346	0.322
68.8	3.230	12.52	0.142	0.330	3.418	0.326
73.8	3.282	12.73	0.145	0.338	3.508	0.331
78.8	3.337	12.81	0.145	0.342	3.559	0.335
83.8	3.357	12.93	0.149	0.348	3.625	0.338
88.8	3.372	12.95	0.148	0.348	3.647	0.340
93.8	3.386	12.91	0.149	0.355	3.691	0.343
98.8	3.394	12.93	0.147	0.354	3.690	0.341
103.8	3.400	13.05	0.149	0.354	3.726	0.346
108.8	3.402	12.95	0.148	0.356	3.757	0.345
113.8	3.394	12.96	0.147	0.358	3.743	0.344
118.8	3.373	12.90	0.145	0.361	3.763	0.346
123.8	3.341	12.81	0.145	0.360	3.753	0.343
Threshold energy	18.5 eV	15.5 eV	17.2 eV	15.6 eV	16.0 eV	12.8 eV

the obtained signal intensity with the reported cross section data.⁵⁾ C_a and C_b denote the vacuum conductances of two orifices through which the radical effuses out of the dissociation cell. k is the surface loss rate.

To obtain vacuum conductances C_a and C_b for CF_3 radical, vacuum conductances for five different gases (N_2 , Ar, CF_4 , SF_6 , HFE-227) are carefully measured and plotted as a function of $m^{-1/2}$, where m denotes the mass number. The result showed linear dependence of C_a and C_b on $m^{-1/2}$ as expected from vacuum conductance analysis in molecular flow regime, and the interpolated values for CF_3 conductances are found to be $C_a = 0.60 \text{ l s}^{-1}$ and $C_b = 0.31 \text{ l s}^{-1}$.

The surface loss rate k can be obtained by measuring the time decay of the radical density after turning off the primary electron beam. The radical density exponentially decreases with the time constant $\tau = V/(k + C_a + C_b)$ for the volume V of the dissociation cell. The result of the observed density

decay for CF_3 is shown in Fig. 6, which gives $\tau = 15.0 \text{ ms}$ and $k = 0.17 \text{ l s}^{-1}$. In the same manner, the parameters for CF and CF_2 are measured and summarized in Table III.

To obtain the proportional constant γ in eq. (2), electron impact dissociations of CF_4 into CF_3 , CF_2 and CF were measured in the present experiment and compared with the previously reported cross sections.⁵⁾ This calibration procedure³⁾ automatically includes the determination of the proportional constant μ , i.e., the mass discrimination effect of QMS for CF_3 , CF_2 and CF. Finally, the radical ionization cross section σ^* in eq. (2) was determined for CF_x ($x = 1-3$) from the recent data.¹¹⁾

Generally, fragment species produced by the electron impact dissociation of molecules have certain kinetic energies with angular velocity anisotropy. These make the calibration of the cross section more complex. However, in the present experiment, most of the neutral radicals produced in the dis-

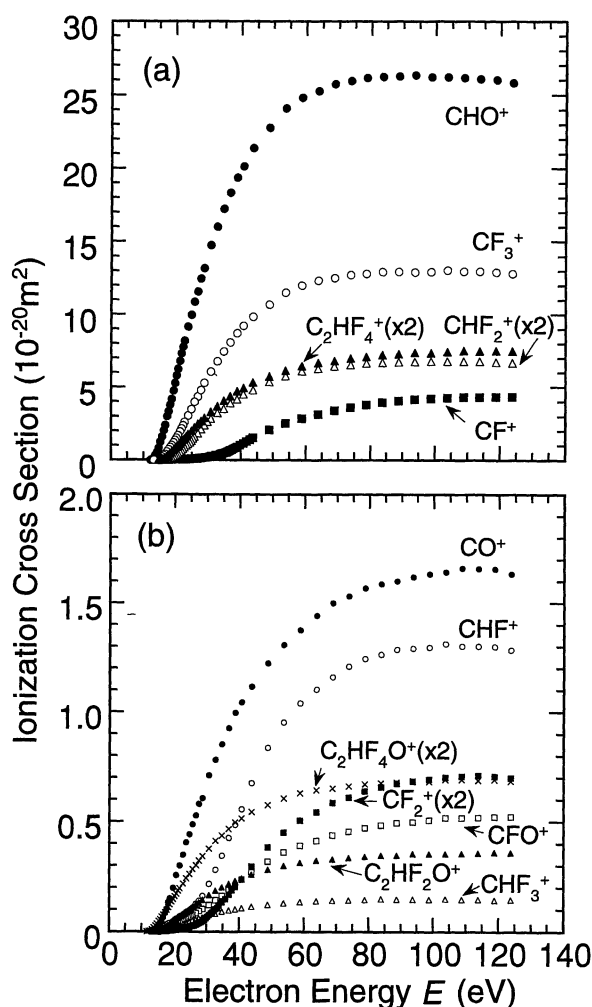


Fig. 4. Partial cross sections for ionization (a) $\text{HFE-227} \rightarrow \text{CHO}^+, \text{CF}_3^+, \text{CF}^+, \text{C}_2\text{HF}_4^+$ and CHF_2^+ , and (b) $\text{HFE-227} \rightarrow \text{CO}^+, \text{CHF}^+, \text{CFO}^+, \text{C}_2\text{HF}_2\text{O}^+, \text{C}_2\text{HF}_4\text{O}^+, \text{CF}_2^+$ and CHF_3^+ .

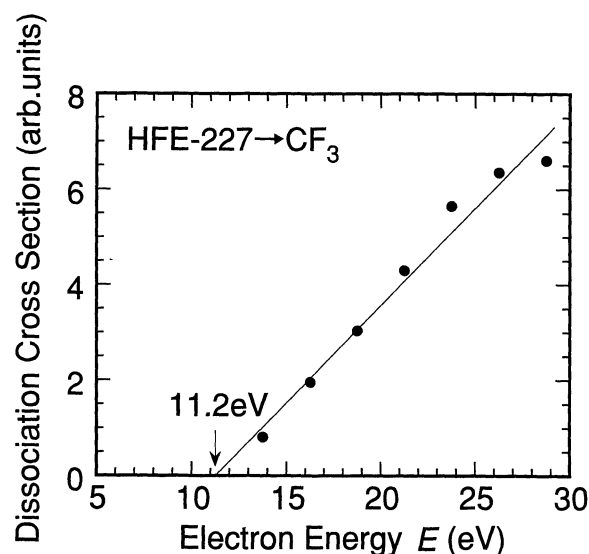


Fig. 5. Relative cross section near the threshold for neutral dissociation of HFE-227 into CF_3 .

Table III. Decay time constant τ , vacuum conductances C_a and C_b and surface loss rate for dissociation products, CF_3 , CF_2 , and CF .

Product	τ (ms)	C_a (l s^{-1})	C_b (l s^{-1})	k (l s^{-1})
CF_3	15.0	0.60	0.31	0.17
CF_2	22.7	0.49	0.26	$< 10^{-2}$
CF	18.2	0.42	0.22	0.25

sociation cell effuse into the detection chamber after many collisions with the wall surfaces, as is inferred from the long decay time constant (see Table III). Accordingly, the initial kinetic energy and angular anisotropy are negligible in the data analysis.

The absolute values of partial cross sections for the dissociation of HFE-227 into CF_3 , CF_2 and CF radicals are shown in Fig. 7 and Table IV. We estimate the error of CF , CF_2 and CF_3 cross sections to be $\pm 27\%$, $\pm 9\%$ and $\pm 17\%$, respectively,³⁾ which mainly originates from the signal intensity under cross section measurements. The error bars for each radical species at an energy of 100 eV are shown in Fig. 7.

It is notable in the present experiment that CHF_2 and C_2HF_4 were also detected by AMS. The signal intensity of such large fragment radicals was almost comparable to those of CF_x radical signals. Because of a lack of the radical ionization cross sections, the absolute cross section for these dissociations was not determined but might be comparable with that of CF_x radicals ($x = 1-3$).

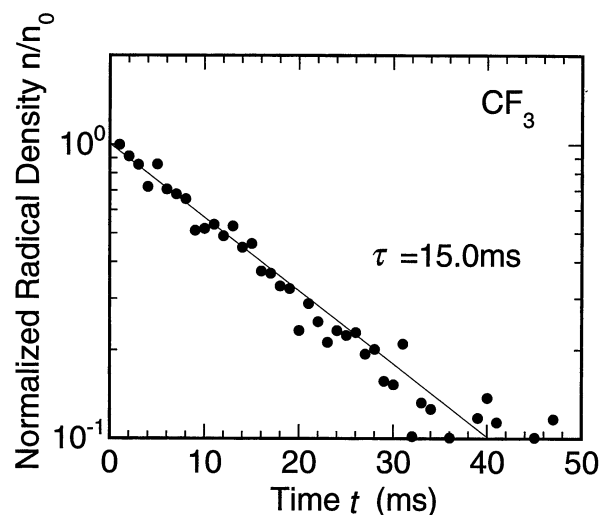
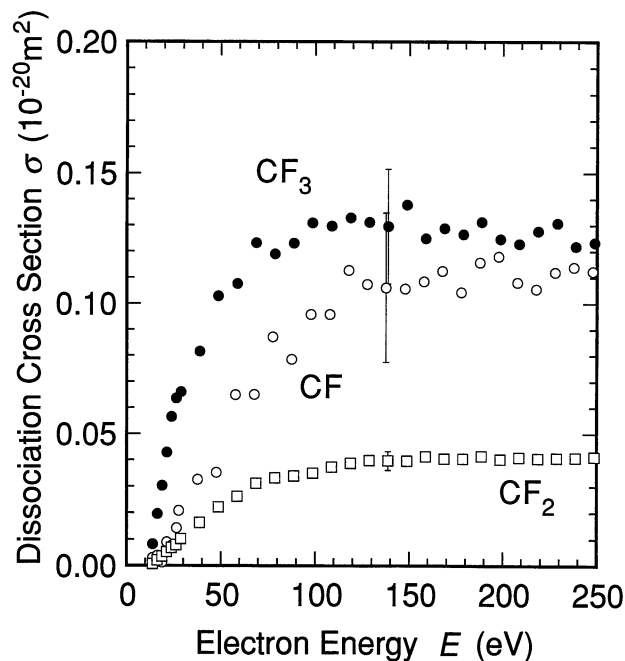
Dissociation cross sections of HFE-227 into neutral and ionic species are compared with that of typical perfluorocarbon etching gas $\text{c-C}_4\text{F}_8$. The total ionization cross section of HFE-227, i.e., summation of the measured partial ionization cross sections is $5.5 \times 10^{-19} \text{ m}^2$ at an energy of 100 eV, which is almost 5 times larger than the total ionization cross section of $\text{c-C}_4\text{F}_8$ ⁶⁾ obtained in the same way, which suggests that HFE-227 can produce more plasma than $\text{c-C}_4\text{F}_8$. As for the sum of the cross sections for neutral dissociation into CF , CF_2 and CF_3 radicals, HFE-227 has a cross section ($2.6 \times 10^{-21} \text{ m}^2$) almost 1.5 times larger than that of $\text{c-C}_4\text{F}_8$ at an energy of 100 eV. These results suggest that HFE-227 has a larger total dissociation cross section than $\text{c-C}_4\text{F}_8$, although neutral dissociation into other radical species is not measured.

The cross section data obtained in the present study allow a qualitative comparison of the neutral radical production rate between conventional perfluorocarbon plasmas and the HFE-227 plasma. For example, CF_2 radical production from electron impact dissociation of HFE-227 has a 2.0 eV higher threshold energy and $\sim 50\%$ less cross section (electron energy $\leq 250 \text{ eV}$) than $\text{c-C}_4\text{F}_8$ ⁶⁾ which is used for highly selective etching of SiO_2/Si . As for CF and CF_3 radicals, however, the HFE-227 has larger cross sections with almost the same thresholds in comparison to $\text{c-C}_4\text{F}_8$. These results suggest that HFE-227 has a tendency to produce more CF and CF_3 radicals than $\text{c-C}_4\text{F}_8$, while $\text{c-C}_4\text{F}_8$ provides more CF_2 radicals than HFE-227. The difference in radical composition due to feeding gases, i.e., $\text{c-C}_4\text{F}_8/\text{Ar}$ and HFE-227 has been compared in an inductively coupled plasma, and the result indicates that dominant radical species is CF_2 in both cases. The reason why CF_2 radical density is high even though the production rate of CF_3 is high in HFE-227 plasma is presumably

Table IV. Partial cross sections for dissociation of HFE-227 into neutral fragments in units of 10^{-20} m^2 , together with the threshold energies.

Energy (eV)	CF	CF ₂	CF ₃
13.7		0.0007	0.008
16.2	0.0039	0.0020	0.020
18.7		0.0036	0.030
21.2	0.0090	0.0051	0.043
23.7		0.0067	0.057
26.2	0.0143	0.0079	0.064
27.7	0.0209		
28.7		0.0102	0.066
37.7	0.0326		
38.7		0.0162	0.082
47.7	0.0353		
48.7		0.0222	0.103
57.7	0.0650		
58.7		0.0263	0.108
67.7	0.0651		
68.7		0.0312	0.123
77.7	0.0872		
78.7		0.0333	0.119
87.7	0.0786		
88.7		0.0340	0.123
97.7	0.0959		
98.7		0.0351	0.131
107.7	0.0959		
108.8		0.0374	0.130
117.7	0.1128		
118.7		0.0389	0.133
127.7	0.1075		
128.7		0.0400	0.131
137.7	0.1061		
138.7		0.0398	0.130
147.7	0.1057		
148.7		0.0397	0.138
157.6	0.1085		
158.7		0.0414	0.125
167.6	0.1125		
168.7		0.0406	0.129
177.7	0.1044		
178.7		0.0405	0.127
187.7	0.1158		
188.7		0.0416	0.131
197.7	0.1181		
198.7		0.0404	0.125
207.7	0.1082		
208.7		0.0411	0.123
217.7	0.1055		
218.7		0.0407	0.128
227.7	0.1120		
228.7		0.0408	0.131
237.7	0.1140		
238.7		0.0409	0.122
247.7	0.1125		
248.7		0.0413	0.123
Threshold energy	$14.7 \pm 2.5 \text{ eV}$	$12.5 \pm 0.3 \text{ eV}$	$11.2 \pm 0.7 \text{ eV}$

due to secondary reaction of neutral radical species produced by electron impact dissociation of the parent gas. It should be noted that a HFE-227 molecule has an oxygen atom in it. In the present work, we did not measure oxygen-related rad-

Fig. 6. Density decay after turning off the primary electron beam for CF₃ radical.Fig. 7. Absolute cross sections for neutral dissociation of HFE-227 into CF₃ (filled circles), CF₂ (open squares) and CF (open circles).

ical species, but it can be presumed that there is some effect of oxygen to react with fluorocarbon deposit on the etching surfaces.

4. Conclusions

In conclusion, extensive measurements of the cross sections were reported for (1) the dissociative ionization from C₃HF₇O (HFE-227) into twelve ionic species, i.e., CF_x⁺, CHF_x⁺ ($x = 1-3$), CO⁺, CHO⁺, CFO⁺, C₂HF₄⁺ and C₂HF_yO⁺ ($y = 2, 4$) and (2) the neutral dissociation from HFE-227 into CF_x ($x = 1-3$), as a function of electron energy. The measured threshold energies for neutral dissociation into CF₃, CF₂ and CF were 11.2 eV, 12.5 eV and 14.7 eV, respectively. As for dissociation into CF and CF₃, the cross

sections of HFE-227 were larger than those of $c\text{-C}_4\text{F}_8$. However, it was found that CF_2 radicals can be more easily produced by $c\text{-C}_4\text{F}_8$ because of its larger cross section and lower threshold energy compared with HFE-227. In addition, other radical species such as C_2HF_4 and CHF_2 are found to exist as products of electron impact dissociation of HFE-227, although absolute cross sections could not be determined.

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