

Cross Section Measurements for Electron-Impact Dissociation of C_4F_8 into Neutral and Ionic Radicals

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The absolute cross sections for electron-impact dissociation of octafluorocyclobutane (C_4F_8) into the neutral radicals CF , CF_2 , CF_3 and C_3F_5 are measured from the threshold to 250 eV. This measurement was accomplished by appearance mass spectrometry in a dual electron beam device. The threshold energies for the neutral dissociation into CF , CF_2 and CF_3 are 14.5, 10.5 and 12.8 eV, respectively. The cross sections for dissociation from C_4F_8 into CF_2 and CF are much larger than those from CF_4 . Besides the neutral dissociation, the cross sections for the dissociative ionization of C_4F_8 are extensively measured for formation of CF^+ , CF_2^+ , CF_3^+ , $C_2F_3^+$, $C_2F_4^+$ and $C_3F_5^+$.

KEYWORDS: octafluorocyclobutane, dissociation cross section, neutral radical, electron impact, dissociative ionization cross section

1. Introduction

Recently, much attention has been given to octafluorocyclobutane (*c*- C_4F_8 ; hereafter abbreviated as C_4F_8) in semiconductor manufacturing with use of high-density plasmas since this etching gas enables highly selective gate-oxide etching. Neutral radical diagnostics¹⁾ revealed that the high etch selectivity correlates with a high ratio of the neutral radical CF_x ($x = 1-3$) density to the fluorine atom density in a C_4F_8 plasma. However, the measured radical composition of the plasma has not been clarified from the viewpoint of elementary processes in the gas phase. Electron-impact cross sections for dissociation into neutral and ionic radicals are crucial for understanding and modelling the C_4F_8 plasma etching.

So far, only limited data on C_4F_8 has been available. As far as the cross section for electron impact ionization is concerned, Beran and Kevan²⁾ reported that the total ionization cross section was $12.5 \times 10^{-20} m^2$ at 70 eV. However, there is no report on the energy dependence of the total ionization cross section nor the partial ionization cross sections. Furthermore, there are no data on cross sections for neutral dissociation, that is, the electron-impact dissociation of C_4F_8 into neutral radicals such as CF_3 , CF_2 , and CF . This is mainly due to the difficulties in detecting neutral radicals. Recently, we developed a high-sensitivity radical detection technique, i.e., appearance mass spectrometry³⁾ which is based on the difference between the appearance potential for ionization of the radical and that for dissociative ionization of the parent molecule. This technique has successfully been applied to the cross section measurement for neutral dissociation of methane (CH_4) into CH_3 and CH_2 radicals^{4,5)} and sulfur hexafluoride (SF_6),⁶⁾ the dissociation cross section of carbontetrafluoride (CF_4) into CF_3 , CF_2 and CF radicals⁷⁾ and CHF_3 into CF_x ($x = 1-3$) and CHF_y ($y = 1-2$) radicals,⁷⁾ as well as the cross section of tetrafluorosilane (SiF_4) into SiF_x radical ($x = 0-3$).⁸⁾

In this paper, we report the measurements of partial

cross sections for electron impact dissociation of C_4F_8 into neutral radicals and ionic radicals, based on appearance mass spectrometry.

2. Experimental

Experimental measurements were made in a dual-electron-beam device combined with a quadrupole mass spectrometer (QMS), which has been used in a series of cross section studies.⁴⁻⁸⁾ 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 incident on a sample gas at energies of $E = 5-250$ eV and currents of $I_c = 0.1-40 \mu A$ dissociates C_4F_8 flowing at a pressure of $10^{-3}-10^{-2}$ Pa, and the electron 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 (C_4F_8 pressure $10^{-5}-10^{-4}$ Pa) where a probing electron beam emitted from a rhenium filament at the energy of $E_Q = 10-25$ 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 C_4F_8 pressure of $10^{-4}-10^{-3}$ Pa where the primary electron beam is generated from a hot filament biased negatively to $-V_d$. The primary beam is injected through a 3-mm-diameter orifice along a magnetic field of ~ 0.06 T provided by a pair of permanent magnets, in order to minimize the beam energy spread and to define the beam trajectory. Mean energies and energy spreads (~ 1 eV) for both the primary and the probing electron beams are calibrated⁹⁾ by measuring the energy dependence of Ar ionization near the threshold energy (15.8 eV).

Generally, the increase of gas temperature results in the production of vibrationally excited molecules, which might affect the cross section. The gas temperature in the dissociation cell is estimated to be $\sim 100^\circ C$ from the wall temperature of dissociation cell which is heated by

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Table I. Threshold energies (eV) for the appearance of ions from neutral species.

Neutral parent	CF_3^+	CF_2^+	CF^+	Remarks
C_4F_8	18.1	20.3	19.2	Measured
CF_3	8.5	17.1	21.4	
CF_2		11.4	14.6	Refs. 9 and 10
CF			9.1	

the hot filament. In the present data analysis, however, it is assumed that the C_4F_8 molecule is in its vibrational ground state, because there is no report on the effect of vibrationally excited states of C_4F_8 on the cross section into neutral and ionic radicals.

The primary electron beam collides with the C_4F_8 molecules and creates various neutral radicals and ionic species. First, ions are eliminated by the positive bias (~ 10 eV) of the ionization chamber and the QMS with respect to the dissociation cell. Neutral radicals are detected using threshold ionization techniques,³⁻⁸⁾ which are based on approximately 5 eV difference in the ionization thresholds for the parent molecule dissociative ionization and the radical ionization. In advance, the threshold energies for the ionization of C_4F_8 and CF_x radicals are summarized in Table I. The top line indicates the thresholds for dissociative ionization of C_4F_8 which were measured in the present experiment (see §3.1). The thresholds for radical ionization were reported by Tarnovsky and co-workers.^{10,11)}

Figure 1 shows examples of the semilogarithmic plot of the QMS output for $m/e = 50$ (CF_2^+) as a function of the energy E_Q of the probing electron beam. The energy scale of E_Q was calibrated with the measurement of the known ionization threshold (15.75 eV) of argon. When the primary beam is turned off, the CF_2^+ signal is detected as a result of the dissociative ionization, $\text{C}_4\text{F}_8 \rightarrow \text{CF}_2^+ + (\text{other fragments})$, above the threshold energy of 20.3 eV. In Fig. 1, the output signal of CF_2^+ with the primary beam of 100 eV turned on (filled circle) is larger than the signal with the beam off (open circle) in a region of energies lower than 19 eV. The difference between them is attributed to the electron impact ionization of CF_2 radicals effusing from the dissociation cell. The threshold energy for the CF_2 ionization was found to be 11.4 eV as mentioned below (§3.1) and hence the probing electron energy E_Q is fixed at 13.0 eV for CF_2^+ detection. In a similar manner, the value of E_Q for CF and CF_3 detection was determined to be 12.5 eV.

Let the radical signal S be the difference in the time-integrated QMS output between the case of the primary beam turned on and that of the beam turned off. Then, the value of S can be expressed in terms of the partial dissociation cross section $\sigma(E)$ as

$$S = \eta I_c \sigma(E) p t, \quad (1)$$

where η is the proportional constant which contains the mass dependence of the QMS sensitivity, I_c and E are the current and energy of the primary beam, respectively, p is the C_4F_8 pressure in the dissociation cell, and t is the integration time for pulse counting. The energy E

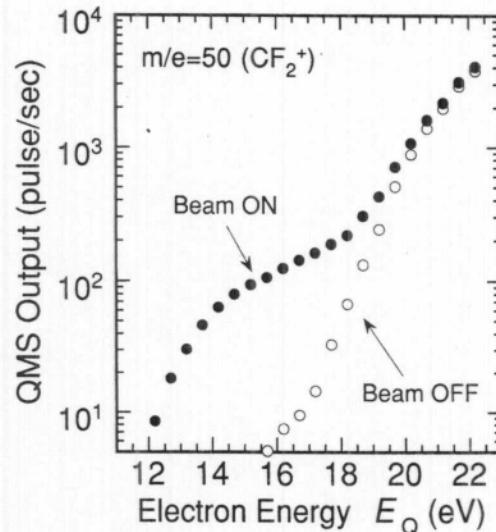


Fig. 1. Quadrupole mass spectrometer output for $m/e = 50$ (CF_2^+) as a function of probing beam energy E_Q with the primary beam turned on (filled circles) and the primary beam turned off (open circles). The primary beam energy is 100 eV.

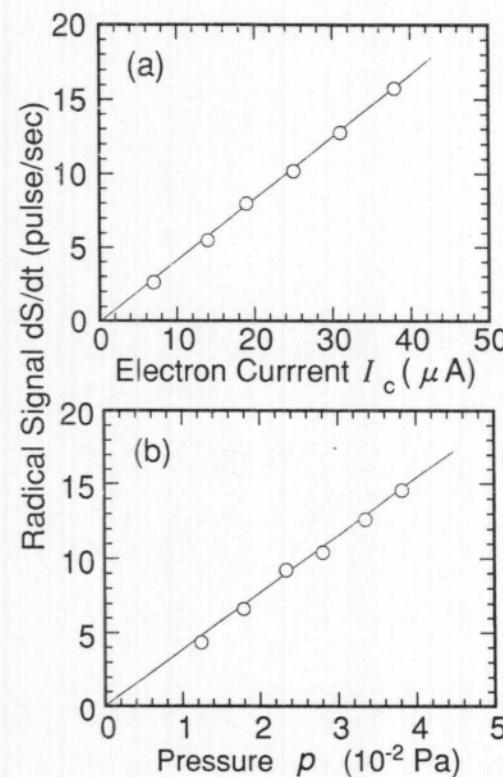


Fig. 2. (a) CF_2 signal vs electron current I_c at $p = 3.4 \times 10^{-2}$ Pa;
(b) CF_2 signal vs pressure p at $I_c = 31 \mu\text{A}$.

of the primary electron beam is given by $(eV_D - e\Delta V)$, where ΔV corresponds to the voltage drop along the hot filament. The radical signal S linearly increases with the integration time t , and the slope dS/dt of the line determined by the least-squares method is proportional to the dissociation cross section.

The dependence of the CF_2 signal (dS/dt) on the primary beam current I_c was measured, with the results shown in Fig. 2(a). These data show that the radical signal is a linear function of the electron current. Lin-

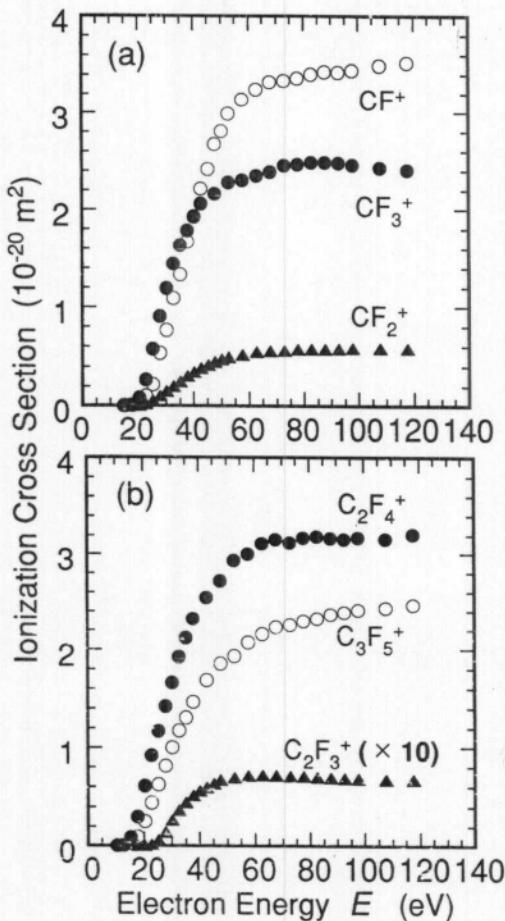


Fig. 4. Partial cross sections for ionization (a) $\text{C}_4\text{F}_8 \rightarrow \text{CF}_3^+$, CF_2^+ and CF^+ , and (b) $\text{C}_4\text{F}_8 \rightarrow \text{C}_2\text{F}_3^+$, C_2F_4^+ and C_3F_5^+ .

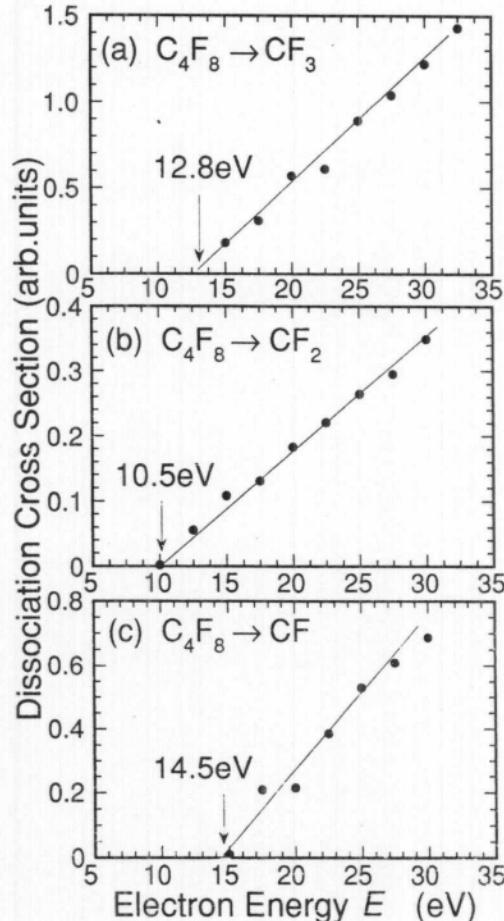


Fig. 5. Relative cross sections near the threshold for neutral dissociation of C_4F_8 into (a) CF_3 , (b) CF_2 and (c) CF .

C_3F_5^+ (131) were measured as a function of the probing beam energy with the primary beam turned off. Signals from other ion species were also investigated, but they were much lower than the ions described above. As reported in previous papers,⁴⁻⁸⁾ we have to take into account the mass discrimination effects of the QMS to determine the absolute values of the cross sections. To cover a mass range from $m/e = 31$ to 131, CF_4 and SF_6 were chosen as reference 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 ¹²⁾ and SF_6 ,¹³⁾ which gives the mass sensitivity of the QMS.

In this way, the absolute cross sections for dissociative ionization of C_4F_8 were obtained, and the results are shown in Fig. 4 and Table II. The sum of the measured partial cross sections at energy $E = 67.8$ eV and 72.8 eV gives the total ionization cross section of $(11.7-11.8) \times 10^{-10} \text{ m}^2$ which is in good agreement with the existing datum of $12.5 \times 10^{-20} \text{ m}^2$ at $E = 70$ eV²⁾ within an error of 10%.

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 C_4F_8 has never been measured. Estimation of the threshold energies is very difficult, even from simple enthalpy calculations, because C_4F_8 has a complicated molecular

structure compared to CF_4 and other molecules with a tetrahedral structure. There is only one *ab-initio* molecular orbital calculation of the threshold energies for C_4F_8 neutral dissociation into F , C_2F_4 and so on.¹⁴⁾ To measure the threshold energies, the dependence of the neutral radical signal on the primary beam energy E was measured, especially for low energies, with the results shown in Fig. 5. According to these measurements, the threshold energies for the neutral dissociation were obtained and listed on the bottom line in Table IV.

The absolute value of cross sections was determined using the same method as described previously.⁴⁻⁸⁾ Let us take an example of the CF_2 radical and summarize the calibration process briefly. The partial cross section σ for the dissociation from C_4F_8 to CF_2 can be expressed as

$$\sigma = \frac{\alpha}{\beta \sigma^* [\text{C}_4\text{F}_8]} \frac{dS}{dt}, \quad (2)$$

where σ^* denotes the ionization cross section for $\text{CF}_2 \rightarrow \text{CF}_2^+$, $[\text{C}_4\text{F}_8]$ is the number density of the C_4F_8 molecule in the dissociation cell, and $\beta = \ell \ell' I_c I' / e^2$ 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 α depends on the vacuum conductances, C_a and C_b , of two orifices through which the radical effuses out of the dissociation cell. The value of α also depends on the surface loss rate k . Taking these

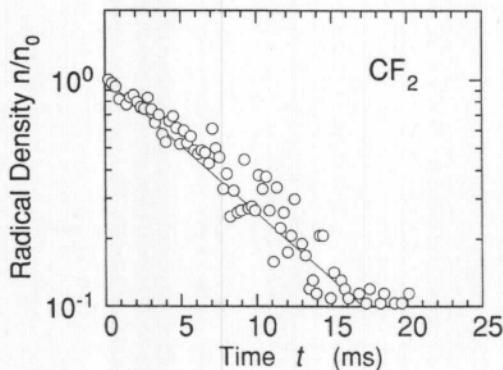


Fig. 6. Density decay after turning off the primary electron beam for CF_2 radical.

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 (ℓs^{-1})	C_b (ℓs^{-1})	k (ℓs^{-1})
CF_3	8.69	0.46	0.62	0.65
CF_2	7.38	0.54	0.73	0.76
CF	5.21	0.69	0.92	1.27

factors into account, we find the final expression⁵⁾ for the cross section

$$\sigma = \frac{\mu\gamma}{\beta} \frac{k + C_a + C_b}{\sigma^* [C_4F_8] C_a} \frac{dS}{dt}, \quad (3)$$

where γ is the constant independent of radical species and μ is the constant expressing the mass discrimination effect of QMS. The vacuum conductances for CF_2 are found to be $C_a = 0.54 \ell \text{s}^{-1}$ and $C_b = 0.73 \ell \text{s}^{-1}$.

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 results of the observed density decay of CF_2 are shown in Fig. 6, which gives $\tau = 7.38 \text{ ms}$ and $k = 0.76 \ell \text{s}^{-1}$. In the same manner, the parameters for CF and CF_3 are measured and shown in Table III.

The proportional constant γ in eq. (3) can be obtained, just as in the previous study on methane.⁵⁾ In the present experiment, electron impact dissociation of CF_4 into CF_3 , CF_2 and CF were measured and compared with the previously reported cross sections.⁷⁾ This calibration procedure automatically includes the determination of the proportional constant μ , i.e., the mass discrimination effect of QMS for CF_3 , CF_2 and CF but not for C_3F_5 . Finally, the radical ionization cross section σ^* in eq. (3) was determined for CF_x ($x = 1-3$) from the recent data.¹⁰⁾ However, such data are not available for C_3F_5 , hence only the relative cross sections were obtained for this radical.

Generally, fragment species produced by the electron impact dissociation of molecules have certain kinetic energies with angular anisotropy. These phenomena make the calibration of the cross section more complex. How-

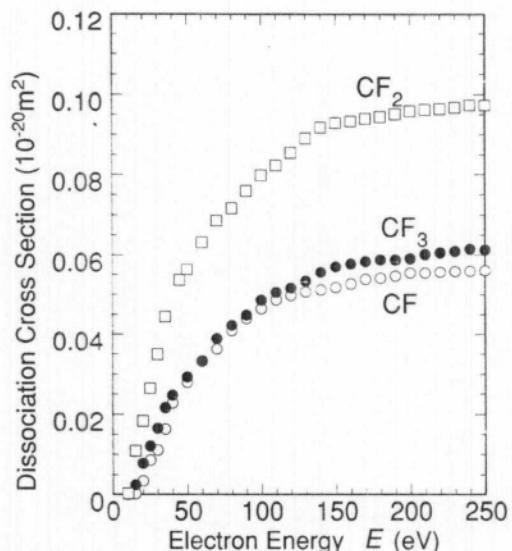


Fig. 7. Absolute cross sections for neutral dissociation of C_4F_8 into CF_3 (filled circles), CF_2 (open squares) and CF (open circles).

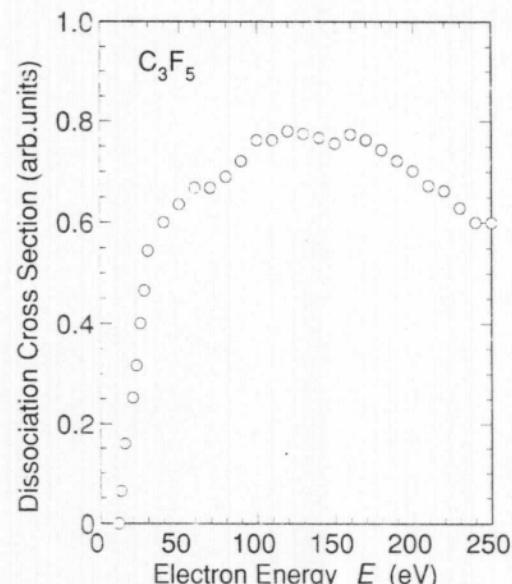


Fig. 8. Relative cross sections for dissociation of C_4F_8 into the neutral radical C_3F_5 .

ever, in the present experiment, neutral radicals produced in the dissociation cell effuse into the detection chamber after collisions with the wall surfaces of the dissociation cell, as is inferred from the very slow decrease in radical signal after turning off the primary electron beam (Fig. 6). Accordingly, the initial kinetic energy and angular anisotropy are assumed to be negligible in the data analysis.

The absolute values of partial cross sections for the dissociation of C_4F_8 into CF_3 , CF_2 and CF radicals are shown in Fig. 7 and Table IV. The relative cross sections of the dissociation into C_3F_5 are shown in Fig. 8. We estimate that the absolute uncertainty of the cross section is $\pm 100\%$ and the relative uncertainty is $\pm 20\%$, as discussed previously.⁵⁾

The cross section data obtained in the present study allow qualitative discussions on the neutral radical com-

