Positive ion pair production by electron impact dissociative ionization of CF_4

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In electron impact dissociative ionization of CF_4, using a time-of-flight apparatus, four cation pair coincidences have been observed between F^+ ions and the fragment ions: CF_3^+, CF_2^+, CF^+, and C^+. Absolute cross sections and thresholds for cation pair production from the fragmentation of CF_4 are reported for electron impact energies from threshold to 500 eV, with the ion pair cross sections found to contribute up to 13% to the gross ionization cross section. Also, corrections are applied to recently reported partial ionization cross section data for CF_4, from which the true ion counting cross sections are computed for the first time; as well, bounds are placed on the production of neutral fluorine for electron impact energies from 20–500 eV.

1. Introduction

Recently, interest in studies on CF_4 has been heightened due to its prevalence as a feed gas for plasma etching in the microelectronics industry. With an ever increasing need to reduce feature sizes on microelectronic devices, a more detailed understanding of the fundamental atomic and molecular processes is required. In the case of plasma etching with CF_4, dissociative electron collisions ultimately determine the constituents in the fragmentation of the parent molecule, producing the neutral etch-active species fluorine, and heavier molecular fragments which may cause surface damage and contamination.

While earlier electron impact studies have determined the absolute total and partial dissociative ionization cross sections [1,2] along with total dissociation cross sections [3], and additional information has been obtained on neutral dissociation by monitoring the optical emission produced by electron impact dissociation of CF_4 [4–7], very little is known about the production of positive ion pairs. The previous studies would have counted these events in their partial ionization cross sections [1,2], thereby leading to errors in reported counting cross sections [2] (gross ionization cross sections would remain the same), and estimates on the concentration of neutrals [1].

In the current study, electron impact dissociative ionization of CF_4 is studied by coincidence techniques, enabling us to detect a pair of cations simultaneously. This technique is similar to prior photo fragmentation coincidence studies completed on CF_4 [8,9].

2. Experimental

The experimental apparatus is the same as that employed in refs. [1] and [10], and is fully described therein. Briefly, a pulsed electron beam was crossed with an effusive gas jet of CF_4 lying between two 40 mm diameter extraction grids (91.7% transmission) separated by 12 mm in an 80 V/cm electric field. The ionized products were mass-separated by a time-of-flight (TOF) mass spectrometer consisting of the extraction grids, a 150 mm long 50 mm diameter drift tube (−300 V), and were subsequently detected by a 40 mm diameter microchannel plate (MCP) detector (−2250 V). The same TOF mass spectrometer and MCP were used to measure the

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mass TOF spectrum and autocorrelation spectra. This was accomplished by utilizing three Lecroy 4208 time-to-digital converters (TDC). The TDCs can not only record negative times with respect to a common start, but were also set in cascade mode to record up to seven stop events from the MCP. The first channel recorded the TOF mass spectrum, used for setting the coincident spectra on an absolute scale based on the results in ref. [1]. The second channel recorded the autocorrelation spectrum for coincidences with F^+, while the third channel recorded coincidences with respect to one of the four carbon-containing ions CF_n^+ (n=0–3). The last channel allowed an unambiguous assignment of the ion pair partners in the F^+ autocorrelation spectrum; in addition, accidental coincidences between the carbon-containing ion pairs were used to statistically correct the F^+ autocorrelation spectrum (i.e. coincidence between CF_2^+ and CF_3^+ are not an allowed fragmentation channel for CF_4).

A typical autocorrelation spectrum for coincidences with F^+ ions is shown in fig. 1 for an electron impact energy of 150 eV. The time scale represents the time-of-flight difference between an F^+ ion and the coincident ions CF_n^+ (n=0–3); on this scale $C^+ + F^+$ coincidences will be negative in time, while all the others are positive. Four coincidence peaks

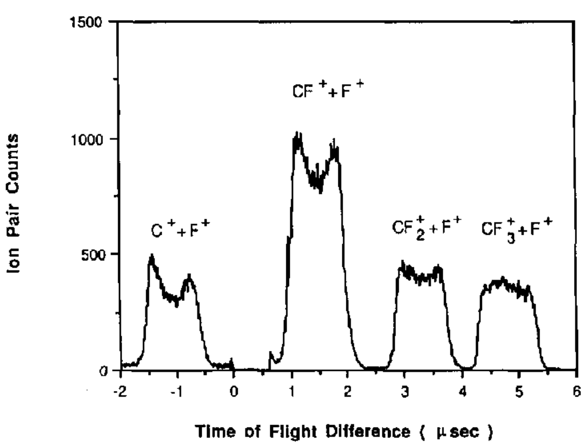

Fig. 1. Time-of-flight autocorrelation spectrum for coincidences between F^+ ions and other fragment ions following the electron impact dissociative ionization of CF_4 at 150 eV. The horizontal axis indicates the time-of-flight difference with respect to F^+. Four coincidences are observed as indicated in the figure (the F^+ self-coincidence pulse has been deleted).

are clearly visible representing coincidences between F^+ and CF_n^+ (n=0–3). The largest peak is the $F^+ + CF^+$ coincidence with over 100000 integrated counts, representing approximately 15 h of data collection at an experimental repetition rate of 20 kHz. The other coincident peaks are typically smaller, with 35000 to 40000 integrated counts in their peaks. The statistical background was generally under 1000 counts with the exception of the $F^+ + CF_3^+$ coincidence which typically had 5000 to 7000 background counts in the peaks. This is due to the large mass signal of CF_3^+, which typically accounts for 60–70% of the total ion counts in a TOF spectrum (see ref. [1]). The statistical background was kept to a minimum by reducing the electron beam current to under 0.1 pA (dc equivalent at 20 kHz, or ≈30 electrons/pulse) such that the total count rates were typically under 1% of the duty cycle, hence the accidental coincident rate cannot be greater than 0.01^2 or 0.01%.

3. Results and discussion

Cross sections. A summary of positive ion pair production cross sections for electron impact dissociative ionization of CF_4 is given in table 1 from threshold to 500 eV with 20% uncertainties in the cross sections. Also, the coincident cross sections for all the ion pairs are shown in fig. 2. As can be seen from table 1 and fig. 2, the maximal cross sectional values for the coincident cross sections ranged from 0.04 Å^2 for $CF_3^+ + F^+$ to 0.14 Å^2 for the $CF^+ + F^+$ pair, with all the ion pair cross sections comparable to or larger than the doubly ionized cross sections observed in ref. [1] (also shown in table 1). Furthermore, there is a weak correlation between the size of the cross section for a given ion pair, and its possible precursor doubly charged ion. That is CF_2^{2+} and the $CF^+ + F^+$ pair both have larger cross sections than CF_3^{2+} and the $CF_2^+ + F^+$ pair, with the ion pair cross sections generally twice as large as the respective doubly charged ion.

Since the coincident contributions were collaterally counted in previously measured electron impact partial-ionization cross sections (PICS) for CF_4 [1,2], amendments have been applied to our earlier results in ref. [1] by subtracting out the coincident contribution to each PICS. The *corrected* absolute

Table 1
Absolute positive ion pair production cross sections (Å^2) for electron impact dissociative ionization of CF_4. Also included are corrected electron impact partial ionization cross sections (Å^2) for CF_4 taken from Ma et al. [16]

E (eV)	$C^+ + F^+$	$CF^+ + F^+$	$CF_2^+ + F^+$	$CF_3^+ + F^+$	CF_3^+	CF_2^+	CF^+	C^+	F^+	CF_2^{2+}	CF_3^{2+}
40				0.001	2.262	0.171	0.107	0.034	0.019		
45			0.001	0.003	2.501	0.197	0.171	0.087	0.053	0.002	0.002
50		0.001	0.004	0.006	2.689	0.219	0.201	0.124	0.088	0.006	0.004
55		0.004	0.009	0.010	2.830	0.233	0.215	0.140	0.106	0.011	0.006
60		0.009	0.013	0.014	2.933	0.250	0.255	0.181	0.176	0.022	0.011
65	0.001	0.018	0.018	0.018	3.009	0.262	0.285	0.216	0.235	0.034	0.017
70	0.002	0.027	0.023	0.022	3.067	0.270	0.296	0.231	0.256	0.040	0.020
75	0.006	0.037	0.027	0.025	3.109	0.275	0.294	0.232	0.256	0.043	0.022
80	0.009	0.048	0.033	0.029	3.138	0.276	0.286	0.232	0.247	0.046	0.023
85	0.012	0.055	0.035	0.031	3.159	0.279	0.286	0.236	0.254	0.048	0.025
90	0.015	0.065	0.038	0.033	3.173	0.280	0.285	0.244	0.263	0.052	0.026
95	0.019	0.075	0.042	0.036	3.179	0.278	0.285	0.250	0.273	0.056	0.027
100	0.024	0.082	0.045	0.037	3.183	0.277	0.288	0.254	0.283	0.059	0.028
110	0.031	0.099	0.050	0.040	3.178	0.274	0.282	0.249	0.282	0.061	0.028
120	0.037	0.108	0.051	0.041	3.165	0.272	0.276	0.240	0.279	0.063	0.029
130	0.044	0.116	0.053	0.041	3.146	0.269	0.264	0.237	0.282	0.064	0.030
140	0.047	0.121	0.052	0.041	3.122	0.268	0.253	0.242	0.295	0.065	0.032
150	0.050	0.127	0.054	0.043	3.094	0.264	0.241	0.245	0.297	0.066	0.033
160	0.054	0.132	0.055	0.043	3.067	0.263	0.235	0.241	0.292	0.066	0.033
170	0.056	0.133	0.055	0.043	3.039	0.262	0.233	0.235	0.286	0.065	0.032
180	0.063	0.138	0.055	0.042	3.011	0.259	0.225	0.224	0.271	0.064	0.032
190	0.062	0.136	0.053	0.041	2.983	0.255	0.220	0.222	0.269	0.063	0.032
200	0.060	0.135	0.054	0.044	2.952	0.248	0.215	0.222	0.264	0.062	0.033
250	0.057	0.122	0.048	0.039	2.823	0.237	0.201	0.204	0.254	0.058	0.030
300	0.066	0.129	0.049	0.037	2.710	0.223	0.174	0.180	0.204	0.053	0.025
350	0.062	0.123	0.046	0.032	2.617	0.213	0.157	0.167	0.186	0.049	0.022
400	0.048	0.106	0.041	0.032	2.532	0.207	0.157	0.166	0.191	0.045	0.020
450	0.045	0.100	0.039	0.030	2.461	0.201	0.146	0.159	0.181	0.042	0.019
500	0.042	0.092	0.035	0.027	2.400	0.199	0.141	0.152	0.176	0.039	0.018

electron impact PICS (the doubly charged cross sections have no correction) for CF_4, based on the results in ref. [1], have been included in table 1. The uncertainties in the absolute PICS are ±15%, as determined from the error analysis in ref. [1]. With the aid of table 1 and ref. [1], it can be seen that the downward corrections are smallest for CF_3^+ (by far the largest ion signal in the mass spectra [1,2]), generally under 1.5%, while the amendments are much larger for the other single PICS: maximum corrections are 18% for CF_2^+, 27% for C^+, 42% for CF^+ ($CF^+ + F^+$ is the largest coincident signal in fig. 1), with the largest correction for F^+ (58%) which has contributions from all four coincidence pairs.

As a consequence of the amended PICS and the coincident pair cross sections in table 1, it is possible for the first time to make an accurate determination of the true counting cross section for the ionization of CF_4; however note, the gross ionization cross sections will remain the same as they are invariant to how the coincidence pairs are counted (separately or in the PICS). Thus, using the data from table 1, the revised ion counting cross sections, $\sigma_{\text{ion count}}$, are summarized in table 2, along with the gross ionization cross sections, $\sigma_{\text{ion gross}}$, and the counting total of the cation pair production cross sections, $\sigma_{\text{coinc. total}}$. The cross sections are computed as:

$$\sigma_{\text{coinc. total}}(E) = \sum_{n=0}^{3} [\sigma_{CF_n^+ + F^+}(E)], \tag{1}$$

$$\sigma_{\text{ion count}}(E) = \sum_{i}^{\text{all}} [\sigma_i^{\text{PICS}}(E)] + \sigma_{\text{coinc. total}}(E), \tag{2}$$

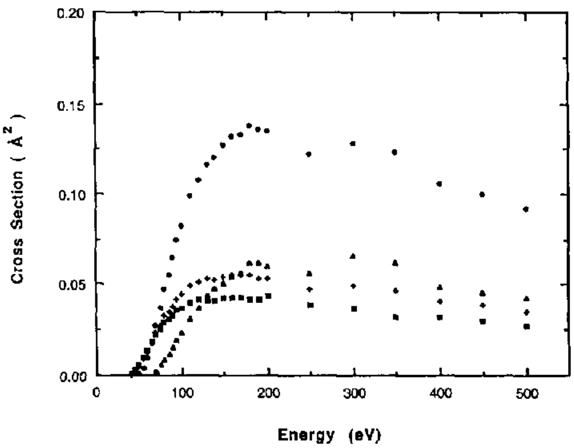

Fig. 2. A plot of the absolute positive ion pair production cross sections (coincident cross sections) versus electron impact energy for the electron impact dissociative ionization of CF_4. Squares: $CF_3^+ + F^+$; crosses: $CF_2^+ + F^+$; dots: $CF^+ + F^+$; triangles: $C^+ + F^+$.

$$\sigma_{\text{ion gross}}(E)=\sum_{i}^{\text{all}}[q_i\sigma_i^{\text{PICS}}(E)]+2\sigma_{\text{coinc. total}}(E)\,, \qquad (3)$$

where $\sigma_{CF_n^+ + F^+}(E)$ represents the four coincident pair cross sections shown in table 1 as a function of impact energy E, $\sigma_i^{\text{PICS}}(E)$ is an absolute *amended* PICS and q_i is the number of charges on the corresponding ion fragment ($q_i = 1$ for cations and 2 for dications) with the sum over i being over all amended PICS shown in table 1. As can be seen in table 2, $\sigma_{\text{coinc. total}}$ contributes up to 6% to the ion counting cross sections, and as much as 13% to the gross ionization cross sections (summarized as "%gross" in table 2) – the contribution to the gross ionization cross section is essentially twice as large as the counting cross section due to the fact that the cation pair cross sections, contained in $\sigma_{\text{coinc. total}}$, are counted twice in the gross cross section (see eq. (3)).

The neutral dissociation cross sections first computed in ref. [1] have also been revised based on the results in this work. Using the fact that

$$\sigma_{\text{neutral dissoc.}}=\sigma_{\text{total dissoc.}}-\sigma_{\text{ion count}}\,, \qquad (4)$$

where $\sigma_{\text{total dissoc.}}$ is the total electron impact dissociation cross section (counting) for CF_4 taken from ref. [3], and noting that $\sigma_{\text{neutral dissoc.}}$ is a counting cross section, the revised values for $\sigma_{\text{neutral dissoc.}}$ are summarized in table 2 [#1]. For impact energies above the cation pair formation thresholds (36 eV), the current results lead to an upward revision of our previously estimated neutral dissociation cross sections [1] by as much as a factor of two; however, it should be noted that the uncertainties remain the same as before [1]: 50–100%. Also, it is not clear at this time why the revised results for $\sigma_{\text{neutral dissoc.}}$ remain so constant from 50–250 eV (~ 1 Å^2).

With the results at hand it is now possible to appraise the production of neutral fluorine following electron impact dissociation of CF_4. Upper and lower bound estimates for the gross cross sections for neutral fluorine production can be determined by using the following rules:

(i) For the lower bound we count only contributions we are certain about (i.e. $e^- + CF_4 \rightarrow CF_3^+ + F + 2e^-$), and for channels with unknown fragments, we preferentially choose the channel which minimizes the fluorine production (i.e., $e^- + CF_4 \rightarrow CF_2^+ + F_2 + 2e^-$). The lower bound cross section is equated as:

$$\sigma_F^{\text{lower}}=\sigma_{CF_3^+}+\sigma_{CF^+}+\sigma_{CF_3^{2+}}+\sigma_{CF_2^+ + F^+} + \sigma_{C^+ + F^+}\,. \qquad (5)$$

(ii) For the upper bound, among the uncertain channels, those which maximize the fluorine production are chosen (i.e. $e^- + CF_4 \rightarrow CF_2^+ + 2F + 2e^-$) in addition to the definite channels. The upper bound cross section is then computed as:

$$\sigma_F^{\text{upper}}=\sigma_{CF_3^+}+2\sigma_{CF_2^+}+3\sigma_{CF^+}+4\sigma_{C^+} + 3\sigma_{F^+}+\sigma_{CF_3^{2+}}+2\sigma_{CF_2^{2+}}+\sigma_{CF_2^+ + F^+} + 2\sigma_{CF^+ + F^+}+3\sigma_{C^+ + F^+}+4\sigma_{\text{neutral dissoc.}}\,. \qquad (6)$$

The averages between eqs. (5) and (6) are listed in table 2, where the numbers in parenthesis indicate half the deviation between the upper and lower bound cross sections. From table 2, it is seen that the neutral fluorine cross sections, σ_F, are comparatively large, surpassing even the gross ionization cross sections also shown in table 2 – but this should not be surprising when one considers that almost every co-

[#1] Since the parent ion CF_4^+ has never been observed, we can equate $\sigma_{\text{ion count}}$ as a purely dissociative ion counting cross section.

Table 2
Summary table of conglomerate cross sections from the electron impact dissociation of CF_4, cross sections defined as follows: $\sigma_{coinc.\,total}$: counting total of cation pair production cross sections from table 1; $\sigma_{ion\,count}$: ionization counting cross section from table 1; $\sigma_{ion\,gross}$: gross ionization cross section from table 1; $\sigma_{neutral\,dissoc.}$: neutral dissociation cross section (counting); σ_F: average gross cross section for production of neutral fluorine. All units for cross sections are in Å^2. Other symbols defined as: %gross: percent contribution of cation pair production to the gross ionization cross section; E: electron impact energy.

E (eV)	$\sigma_{coinc.\,total}$	%gross [a]	$\sigma_{ion\,count}$	$\sigma_{ion\,gross}$	$\sigma_{neutral\,dissoc.}$ [b]	σ_F [c]
20			0.365	0.365	0.449	1.263 (0.898)
25			0.917	0.917	0.769	2.455 (1.571)
30			1.585	1.585	0.915	3.421 (1.947)
35			2.149	2.149	0.924	4.044 (2.059)
40	0.001	0.05	2.594	2.595	0.906	4.527 (2.157)
45	0.004	0.25	3.017	3.025	0.899	5.017 (2.341)
50	0.012	0.69	3.342	3.364	0.958	5.488 (2.590)
55	0.022	1.23	3.564	3.603	1.044	5.892 (2.832)
60	0.036	1.83	3.864	3.933	0.979	6.068 (2.856)
65	0.054	2.57	4.112	4.217	0.908	6.176 (2.847)
70	0.074	3.39	4.254	4.388	0.900	6.306 (2.898)
75	0.095	4.23	4.326	4.486	0.936	6.449 (2.991)
80	0.118	5.19	4.367	4.554	0.983	6.585 (3.096)
85	0.133	5.74	4.420	4.626	1.001	6.671 (3.154)
90	0.152	6.46	4.474	4.704	1.003	6.727 (3.190)
95	0.172	7.20	4.520	4.775	0.999	6.763 (3.211)
100	0.188	7.77	4.560	4.835	0.990	6.785 (3.219)
110	0.219	8.99	4.574	4.882	1.011	6.837 (3.269)
120	0.237	9.70	4.561	4.890	1.030	6.854 (3.296)
130	0.254	10.38	4.546	4.894	1.028	6.824 (3.287)
140	0.261	10.67	4.538	4.896	1.008	6.761 (3.254)
150	0.275	11.24	4.514	4.888	0.996	6.701 (3.229)
160	0.284	11.68	4.481	4.864	0.994	6.665 (3.219)
170	0.287	11.90	4.439	4.823	1.002	6.638 (3.223)
180	0.297	12.42	4.384	4.777	1.021	6.625 (3.239)
190	0.293	12.42	4.336	4.725	1.026	6.583 (3.232)
200	0.292	12.50	4.289	4.676	1.031	6.541 (3.227)
250	0.266	12.00	4.073	4.427	0.947	6.135 (2.977)
300	0.281	13.35	3.850	4.209	0.870	5.770 (2.744)
350	0.262	13.10	3.674	4.007	0.776	5.395 (2.491)
400	0.227	11.83	3.545	3.837	0.655	5.003 (2.205)
450	0.214	11.59	3.423	3.698	0.557	4.677 (1.966)
500	0.197	11.02	3.321	3.575	0.459	4.371 (1.734)

[a] %gross $= (2\sigma_{coinc.\,total}/\sigma_{ion\,gross}) \times 100\%$.

[b] $\sigma_{neutral\,dissoc.} = \sigma_{total\,dissoc.} - \sigma_{ion\,count}$, where $\sigma_{total\,dissoc.}$ is the total electron impact dissociation cross section (counting) for CF_4 taken from Winters and Inokuti [3].

[c] The average between the upper and lower bound cross sections for neutral fluorine production. The numbers in parentheses are the deviation of this average, see text for further discussion.

incidence cross section and PICS in table 1 (excepting only $\sigma_{CF_3^+ + F^+}$) can contribute at least one fluorine atom to the dissociation reaction, thereby adding at least one unit of their respective partial cross section to σ_F. Also, for impact energies above 40 eV, it appears that most of the neutral fluorine production is formed in association with ionization; the pure neutral contribution is apparently less then ≈20% from 50 eV on up (generally decreasing with higher energies).

Appearance potentials. Table 3 lists the electron impact energy at which the ion pairs are first observed (experimental threshold) – based on 1 eV increments in electron impact energy. In general, the

Table 3
Appearance potentials (AP) for cation pair formation from the electron impact ionization of CF_4. Also listed are the expected zero translational thresholds (ZT) and the appearance potentials from Codling et al. [8] based on photofragmentation of CF_4. All units are in eV

	A.P. (this work)	ZT	A.P. (Codling)
$C^+ + F^+$	63	47.2	62.0
$CF^+ + F^+$	42	39.3	47.5
$CF_2^+ + F^+$	40	38.1	42.4
$CF_3^+ + F^+$	36	32.4	37.6

ion pair thresholds appear in the same order as the computed zero translational kinetic energy thresholds (shown in parenthesis in table 3), with the experimental thresholds typically 2–4 eV above the zero translational thresholds. The notable exception is the $C^+ + F^+$ coincidences, whose experimental threshold is 16 eV above its zero translational threshold; however, this is not unreasonably high when one considers that the dissociative kinetic energy must be divided among up to five fragmentary atoms (i.e. ≈ 3 eV kinetic energy per atom). It should be noted that these thresholds are very close to those measured by Codling et al. [8], also listed in table 3, obtained from photofragmentation coincidence studies on CF_4 using synchrotron radiation.

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References

[1] C. Ma, M.R. Bruce and R.A. Bonham, Phys. Rev. A 44 (1991) 2921.
[2] K. Stephan, H. Deutsch and T.D. Märk, J. Chem. Phys. 83 (1985) 5712.
[3] H.F. Winters and M. Inokuti, Phys. Rev. A 25 (1982) 1420.
[4] K.A. Blanks, A.E. Tabor and K. Becker, J. Chem. Phys. 86 (1987) 4871.
[5] K.A. Blanks and K. Becker, J. Phys. B 20 (1987) 6157.
[6] S. Wang, J.L. Forand and J.W. McConkey, Can. J. Phys. 67 (1989) 699.
[7] P.J.M. van der Burgt and J.W. McConkey, J. Phys. B, to be published.
[8] K. Codling, L.J. Frasinski, P.A. Hatherly, M. Stankiewicz and F.P. Larkins, J. Phys. B 24 (1991) 951.
[9] D.M. Curtis and J.H.D. Eland, Intern. J. Mass Spectrom. Ion Phys. 63 (1985) 241.
[10] C. Ma, C.R. Sporleder and R.A. Bonham, Rev. Sci. Instr. 62 (1991) 909.