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A mass spectrometric diagnostic of C_2F_6 and CHF_3 plasmas during etching of SiO_2 and Si

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Résumé. — On a effectué une analyse par spectrométrie de masse des produits neutres et des ions positifs extraits de décharges dans C_2F_6 et CHF_3 entre 0,2 et 0,8 torr (1 torr = 133 Pa) à 25 kHz. La méthode d'étalonnage de l'appareil et du calcul des pressions partielles à partir des spectres de masse à 70 eV est décrite. De nombreuses molécules ont été détectées : CF_4 , C_2F_2 , C_2F_4 , C_3F_6 , C_3F_8 , C_4F_8 , C_2HF_5 et HF, dont les réactions de formation sont discutées. On a observé que la gravure de SiO_2 et de Si induit des variations de la composition neutre de ces plasmas. Ces variations sont expliquées par la consommation des radicaux CF_n ($n = 1$ à 3) à la surface. Les ions positifs issus de ces décharges sont principalement CF_3^+ , CF^+ , CF_2^+ et CHF_2^+ . Leur formation est expliquée par l'ionisation des molécules neutres et des radicaux moléculaires.

Abstract. — A mass spectrometric analysis of the neutral products and the positive ions extracted from discharges in C_2F_6 and CHF_3 , sustained at 25 kHz with pressures between 0.2 and 0.8 torr (1 torr = 133 Pa) was performed. The apparatus calibration and the calculation of the partial pressures from mass spectra at 70 eV are described. The formation reactions of the many detected products : CF_4 , C_2F_2 , C_2F_4 , C_3F_6 , C_3F_8 , C_4F_8 , C_2HF_5 and HF are discussed. Variations in the neutral composition of these plasmas, induced by etching of SiO_2 and Si were observed. These variations are explained by the consumption of CF_n radicals ($n = 1$ to 3) at the etched surface. The main positive ions produced are CF_3^+ , CF^+ , CF_2^+ and CHF_2^+ . Their formation is explained by the ionization of neutral molecules and molecular radicals.

1. Introduction.

During the last decade, deposition and etching processes which make use of reactive low pressure plasmas have become primordial tools in the fabrication of V.L.S.I. integrated circuits and in the elaboration of unconventional thin-film materials such as hydrogenated amorphous silicon or hydrogenated amorphous silicon carbide. The study of the reaction mechanisms in these plasmas aims at the determination of the essential physicochemical parameters with a view to improve the etching or the preparation of materials [1].

Many physical methods are used for the analysis of the plasma and its interactions with surfaces : e.g. optical emission and absorption spectroscopy, mass spectrometry, laser induced fluorescence, *in situ*

ellipsometry. Among these, the mass spectrometry of reactive plasmas is a relatively simple and efficient tool for the analysis of the complex reactions produced by discharges in molecular gases [2-5].

In this paper the method used to determine the partial pressure of the neutral and stable components of C_2F_6 and CHF_3 plasmas used in SiO_2 dry etching is described. The variations in the plasma composition, caused by the etching of SiO_2 and Si have been examined. From these results, reaction mechanisms in plasma and at etched surfaces are discussed.

The paper is organized as follows : first, a description of the experimental set-up is given. Then an analysis of the gas flow in the differential pumping system is made. Follows a description of the method used for the calibration of the spectrometer, in particular when the ions produced inside by the ionization chamber differ in mass from the parent molecule and when mass interference arises. Third, the results of the calculations of the partial pressures of the C_2F_6

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and CHF_3 plasmas are given and the variations in the plasma composition during etching are studied. The evolution with time of the etching of a poly-Si- SiO_2 -mono-Si sandwich is given as an illustration. Finally the results of the mass analysis of the positive ions extracted from the discharge are given.

2. Experimental apparatus.

A diagram of the experimental set-up, which consists of a plasma etching reactor, an intermediate chamber and a mass spectrometer is given in figure 1. The plasma chamber is a stainless steel cylinder of 40 cm in diameter and 29 cm in height. The plasma is produced by an ENI Plasmaloc generator (0-1 000 W, 25-125 kHz) with a frequency fixed at 25 kHz and an output impedance set at 600 Ω . The two electrodes are composed of discs of 156 mm in diameter. The lower and water-cooled electrode is made of aluminium and connected to the high voltage output of the generator. The stainless steel upper electrode is connected to the ground. The sampling of neutral

molecules and positive ions is performed through a 50 μm diameter aperture drilled by electro-erosion in the grounded electrode. The interelectrode spacing is set at 10 mm. The reactor pumping is achieved by a Pfeiffer TPH 270 turbomolecular pump and an Alcatel 2030C rotary pump. The gases are injected by a circular ring on the outside of the electrodes and the flow is controlled by needle valves and measured by Brooks rotameters. The gas purity is 99.6 % for C_2F_6 and 98 % for CHF_3 . The pressure in the reactor is measured by a Vacuum General CMT 02-01 capacitance manometer and may be regulated by a Vacuum General MDV 04V automatic throttle valve. In this study the pressure varies between 0.2 and 0.8 torr. The intermediate chamber, which acts as a buffer between the pressure of the reactor and that of the analysis chamber, is pumped by a TPH 170 turbomolecular pump. The Balzers QMG 511 quadrupole mass spectrometer is placed in an analysis chamber pumped by a turbomolecular pump. A crossed beam ion source at the entry of the spectrometer produces a 1 mA electron beam which energy can be adjusted between 15 eV and 90 eV, perpendicular to the plasma

Fig. 1. — Experimental apparatus.

extracted molecular beam. For this work the electron beam energy was set at 70 eV, a value which corresponds to most of the published fragmentation spectra and thus allows the calculation of the partial pressures. After the quadrupole mass filter, the ions are deflected by 90° by an electrostatic deflector. Thus fast particles and photons are unable to reach the first conversion dynode of the secondary electron multiplier and the signal/noise ratio is improved. The intensity of the detected peak is determined by a PP 511 peak processor placed after the electrometer amplifier, and then stored and treated by a Digital MINC 23 microcomputer. A program enables the peaks of various mass and intensity to be plotted simultaneously, and their evolution with time to be followed.

3. Gas flow analysis.

The apparatus is intended for the analysis of halogenated plasmas used in etching during integrated circuit fabrication. The reaction products may, after a long time, deposit on the spectrometer and perturb its operation. In order to avoid this, the quadrupole is placed at 33 cm from the extraction aperture. Such an arrangement ensures a long apparatus lifetime.

In order to determine the partial pressures in the plasma reactor from mass spectra measurements in the analysis chamber, the gas flow conditions must be known. A scheme of the different flows and notations used is given in figure 2.

Fig. 2. — Gas flow diagram.

The following symbols are used :

- Q_M, Q_1, Q_2 flow rates (torr litre/s);
- p_r, p_c, p_s pressures (torr);
- S_0, S_1, S_2 pumping speed (or conductance) (litre/s);
- A_1, A_2 aperture areas.

For a pure gas of mass m , the pressure p_s in the analysis chamber is shown to be proportional to the pressure p_r in the reactor according to :

$$\Delta p_s = p_s - p_{so} = K(m) \cdot p_r \quad (1)$$

where p_{so} is the residual pressure in the spectrometer chamber and $K(m)$ depends on the mass of the gas and the pumping mode (0.1-1 torr for primary pumping, 5-100 mtorr for turbomolecular pumping).

For nitrogen in a primary pumping regime :

$$K(28) = 5.7 \times 10^{-8}.$$

If the aperture is assumed to be a thin wall orifice, and in the case of a molecular flow, the flow rate Q_1 at which the gas goes through the aperture A_1 may be expressed by [6, 7] :

$$Q_1 = A_1 \left(\frac{kT}{2\pi m} \right)^{1/2} (p_r - p_c). \quad (2)$$

In reality, for a pressure p_r which varies between 0.1 and 1 torr and an orifice diameter D of 50 μm , the ratio D/λ varies between 0.1 and 1 (λ is the mean free path of the gas molecules). The flow is thus that of a transition regime with :

$$Q_1 = C(p_r - p_c) \quad (3)$$

where C is the conductance of the aperture in litre/s.

If the usual expressions used for a cylindrical tube are applied to the so-called transition regime, the flow is 96-98 % molecular. In the case of nitrogen, and following the assumptions made, the conductance C of the aperture of area A_1 has the following values :

- 1.31×10^{-4} l/s for a short cylindrical tube;
- 3.05×10^{-4} l/s for a long cylindrical tube;
- 2.37×10^{-4} l/s for a thin wall orifice as given by [2].

The value given by relationship (2) which falls between the two others is retained. Furthermore, as $p_c \ll p_r$, there is a very good approximation :

$$Q_1 = A_1 \left(\frac{kT}{2\pi m} \right)^{1/2} p_r.$$

Orifice n° 2 of area A_2 has a diameter of 4 mm and is 1 mm long. It may be treated as a hole in a thin wall. The pressure p_c varies between 2×10^{-6} and 2×10^{-7} torr. The flow is thus always molecular with a flow rate :

$$Q_2 = A_2 \left(\frac{kT}{2\pi m} \right)^{1/2} (p_c - p_s) = \Delta p_s \cdot S_2.$$

By posing $\Delta p_c = p_c - p_{co}$ and noting that the residual pressures are such that $p_{co} = p_{so}$, it follows that :

$$\Delta p_s = \frac{A_2}{S_2} \left(\frac{kT}{2\pi m} \right)^{1/2} (\Delta p_c - \Delta p_s). \quad (4)$$

On the other hand, $\Delta p_c = \frac{Q_1 - Q_2}{S_1}$.

The experimental equation (1) may thus be expressed theoretically by :

$$K(m) = \frac{A_1 \cdot A_2}{S_1 \cdot S_2} \left(\frac{kT}{2\pi m} \right) \times \left[1 + A_2 \left(\frac{1}{S_1} + \frac{1}{S_2} \right) \left(\frac{kT}{2\pi m} \right)^{1/2} \right]^{-1}. \quad (5)$$

The numerical calculation of this equation shows that the term in square brackets is approximately equal to 1, with an accuracy better than 2 % for $m \geq 20$ a.m.u. Thus $K(m)$ may be determined from (5) when the conductance of the tubes and values is known. For nitrogen, $S_1 = 123$ l/s and $S_2 = 50$ l/s give $K(28) = 5.5 \times 10^{-8}$, a result which is in good agreement with the experimental value.

In a mixture of gases containing several sorts of molecules of different masses, the relationship (1) is assumed to be valid for the partial pressure of each component.

4. Calculation of partial pressures from the mass spectrometric measurements.

If $i(m_j)$, expressed in amperes, is the intensity of a peak of mass m_j coming from the fragmentation in the ion source of the molecule of mass m , there exists a proportional relationship between $i(m_j)$ and $\Delta p_s = p_s - p_{so}$:

$$i(m_j) = \sigma(m_j) \cdot F(m_j) \cdot (p_s - p_{so}) \quad (6)$$

where $\sigma(m_j)$ (in cm^2) is the partial ionization cross-section of the molecule of mass m for the ion of mass m_j , and $F(m_j)$ is the transmission coefficient of the mass spectrometer between the ion source and the secondary electron multiplier for the ion of mass m_j ($F(m_j)$ in $\text{A}/\text{cm}^2 \cdot \text{torr}$). The product $\sigma(m_j) \cdot F(m_j)$ is the spectrometer sensitivity in (A/torr).

Taking into account the equation (1) :

$$i(m_j) = \sigma(m_j) \cdot F(m_j) \cdot K(m) \cdot p_r \quad (7)$$

In the simple case where the ion and the molecule have the same mass ($m = m_j$) the global transmission coefficient of the apparatus may be determined experimentally :

$$T(m_j) = K(m_j) \cdot F(m_j) \quad (8)$$

The coefficient $T(m_j)$ was determined using a standard gas mixture which composition is as follows :

Gas	Relative molecular concentration
Helium	10.3 % (± 0.3 %)
Xenon	10.0 %
Krypton	9.8 %
Nitrogen	9.9 %
Argon	60.0 %

The variation of $T(m_j)$ as given by equation (7) for a standard-gas pressure p_r between 0.1 and 1 torr is illustrated by the figure 3. The partial ionization cross-sections $\sigma(m_j)$ at 70 eV are those given by Rapp and Englander-Golden [8].

The partial pressure p_r of a gas of mass m may be determined from the intensity $i(m_j)$ of an ion of mass m_j by the proportional relationship :

$$i(m_j) = \sigma(m_j) \cdot \frac{K(m)}{K(m_j)} \cdot T(m_j) \cdot p_r \quad (9)$$

Fig. 3. — Transmission coefficient $T(m_j)$.

When m and $m_j \geq 20$ the approximation (cf. Eq. (5)) $\frac{K(m)}{K(m_j)} = \frac{m_j}{m}$ is adopted. The partial ionization cross-sections $\sigma(m_j)$ used in (9) are taken from the literature [8-10]. For molecules where $\sigma(m_j)$ is unknown, either the factor S (Ref. [11]) or the factor B (Ref. [11]) are used, with :

$$S(m_j) = \frac{\sigma(m_j)}{\sigma(28, N_2)} \quad (\text{Ref. [11]})$$

$$B(m_j) = \frac{\sigma(m_j)}{\sigma(43, n C_4 H_{10})} \quad (\text{Ref. [12]})$$

In the case of pure gases (e.g. CHF_3 , C_2F_6 , CF_4) the term $\left[\sigma(m_j) \cdot \frac{K(m)}{K(m_j)} \cdot T(m_j) \right]$ is determined experimentally.

By comparison with the known standard-gas cross-section, the apparatus allows the evaluation of the partial ionization cross-sections [13].

5. Neutral composition of the C_2F_6 and CHF_3 plasmas.

The experimental conditions are the following :

- total pressure $p_r = 0.2$ to 0.8 torr;
- gas flow rate $Q_M = 40$ sccm;
- power = 250 W;
- frequency = 25 kHz.

5.1 THE NEUTRAL COMPOSITION OF THE C_2F_6 PLASMA.

— The main peaks and their assignment recorded for the C_2F_6 plasma are given in table I. Each mole-

Table I. — Assignments of peaks detected in the C₂F₆ plasma.

m/e (a.m.u.)	ion	parent molecules
62	C ₂ F ₂ ⁺	C ₂ F ₂
69	CF ₃ ⁺	CF ₄ , C ₂ F ₄ , C ₂ F ₆ , C ₃ F ₆ , C ₃ F ₈ , C ₄ F ₈ , C ₄ F ₁₀
81	C ₂ F ₃ ⁺	C ₂ F ₄
93	C ₃ F ₃ ⁺	C ₄ F ₆ , C ₄ F ₈
100	C ₂ F ₄ ⁺	C ₂ F ₄ , C ₂ F ₆ , C ₃ F ₆ , C ₃ F ₈ , C ₄ F ₈ , C ₄ F ₁₀
119	C ₂ F ₅ ⁺	C ₂ F ₆ , C ₃ F ₈ , C ₄ F ₁₀
131	C ₃ F ₅ ⁺	C ₃ F ₆ , C ₄ F ₈ , C ₄ F ₁₀
143	C ₄ F ₅ ⁺	C ₄ F ₆ , C ₅ F ₈
150	C ₃ F ₆ ⁺	C ₃ F ₆
169	C ₃ F ₇ ⁺	C ₃ F ₈
181	C ₄ F ₇ ⁺	C ₄ F ₈

cular ion can originate from several parent molecules. When only one molecule contributes to the detected peak of intensity $i(m_j)$ (e.g. $m/e = 81$ for C₂F₄), the partial pressure is given by the relationship :

$$p(m) = \frac{i(m_j)}{T(m_j) \sigma_{it} \sum \alpha} \cdot \frac{m}{m_j} \quad (10)$$

where σ_{it} is the total ionization cross-section and α the relative abundance of the peak of mass m_j in comparison with the main peak of the parent molecule [11, 12, 14]. More generally, in the case where the ion of mass m_j may have for origin several different molecules (e.g. $m/e = 69$ for CF₃⁺) the mass interference is taken into account by using the expression :

$$p(m) = \left[\frac{i(m_j)}{T(m_j) \cdot m_j} - \sum_{m'} p(m') \frac{\sigma(m_j, m')}{m'} \right] \cdot \frac{m}{\sigma(m_j, m)} \quad (11)$$

where $p(m')$ is the partial pressure of the parent molecules of mass m' which contribute to the intensity of the ion m_j and $\sigma(m_j, m)$ is the ionization cross-section for the ion m_j of the molecule of mass m .

The molecules for which the partial pressure $p(m)$ was calculated from the corresponding intensity $i(m_j)$ by means of equation (11) are listed in table I. The neutral composition of plasmas can thus be obtained by resolving the system of linear equations (11). A program allows the microcomputer to calculate the partial pressures $p(m)$.

The evolution of the molar fractions $\frac{p(m)}{p_r}$ of the main neutral molecules detected as a function of the total pressure is given in figure 4. The principal mole-

Fig. 4. — Molar fractions in the C₂F₆ plasma.

cules present are C₂F₆ and CF₄, which is in agreement with the work of Truesdale and Smolinsky [15]. The species C₂F₂, C₂F₄, C₃F₆, C₃F₈ and C₄F₈ were also detected. The partial pressure of C₂F₂ was not calculated, as its ionization cross-section was unknown. The authors quoted above did not observe the presence of C₂F₂, C₃F₆ and C₄F₈.

The existence of C₂F₂ in the discharge indicates the presence of CF radicals which recombine according to the reaction :

The formation of other molecules C₂F₄, C₃F₆, C₃F₈ and C₄F₈ is attributed to the recombination reactions between the CF, CF₂, CF₃ and C₂F₅ radicals which are produced from electron impact dissociation of C₂F₆ [1, 16].

The decrease in molar fraction of C₂F₆ with increasing pressure is due to the increase in the molecule residence time t_R in the plasma

$$t_R = \frac{N_{\text{Mo}} V}{Q_M} \quad (13)$$

where

$$N_{\text{Mo}} (\text{cm}^{-3}) = 3.5 \times 10^{16} p_r (\text{torr});$$

$$V = \text{reactor volume (cm}^3\text{)};$$

$$Q_M = \text{flow rate of C}_2\text{F}_6 \text{ molecules (molecules/s)}.$$

In fact, the kinetic balance for C_2F_6 can be expressed by [17] :

$$\frac{Q_M}{V} - \frac{N_M}{t_R} = k_1 N_M \quad (14)$$

where N_M is the concentration of C_2F_6 in the plasma and k_1 is the electron impact dissociation rate constant (s^{-1}). The molar fraction of C_2F_6 is thus given by

$$\frac{N_M}{N_{M_0}} = [1 + k_1 t_R]^{-1}. \quad (15)$$

This relationship explains the results shown in figure 4.

5.2 THE NEUTRAL COMPOSITION OF THE CHF_3 PLASMA.

— The peaks recorded for CHF_3 and their assignment are given in the table II. As in the case of the C_2F_6 plasma discussed above, the underlined molecules are those for which the partial pressure was calculated from the intensity of the corresponding molecular ion. The calculation method used to determine the partial pressures is identical to that given for the C_2F_6 plasma, although certain problems specific to the CHF_3 plasma were encountered. The CHF_3 plasma produces a « teflon » type polymer CF_xH_y [15, 18] which coats the electrodes and reactor walls. The extraction orifice thus tends to be reduced in diameter with time. This obstruction was shown to be a linear function of time : the transmission coefficient $T(m_j)$ value can thus be corrected. Regular cleaning of the reactor by a C_2F_6 - O_2 plasma is needed to restore the extraction hole to its initial size. On the other hand the intensity of different peaks as a function of run time (Fig. 5) reaches a

Table II. — Assignments of peaks detected in the CHF_3 plasma.

m/e a.m.u.	ion	parent molecules
20	HF^+	<u>HF</u>
51	CHF_2^+	<u>CHF_3</u> , C_2HF_5
62	$C_2F_2^+$	<u>C_2F_2</u>
69	CF_3^+	<u>CF_4</u> , CHF_3 , C_2F_4 , C_2HF_5 , C_2F_6 , C_3F_6 C_3F_8 , C_4F_8 , C_4F_{10}
81	$C_2F_3^+$	<u>C_2F_4</u>
93	$C_3F_3^+$	<u>C_4F_6</u> , C_4F_8
100	$C_2F_4^+$	<u>C_2F_4</u> , C_3F_6 , C_3F_8 , C_4F_8 , <u>C_4F_{10}</u>
101	$C_2HF_4^+$	<u>C_2HF_5</u>
119	$C_2F_5^+$	<u>C_2F_6</u> , C_3F_8 , C_4F_{10}
131	$C_3F_5^+$	<u>C_2F_6</u> , <u>C_4F_8</u> , C_4F_{10}
150	$C_3F_6^+$	<u>C_3F_6</u>
169	$C_3F_7^+$	<u>C_3F_8</u>
181	$C_4F_7^+$	<u>C_4F_8</u>

a)

b)

Fig. 5a, b. — Evolution of the peaks 51 (CHF_2^+) and 20 (HF^+) with time in the CHF_3 plasma.

stationary state only after 2.5 min at 0.5 torr. This long establishment time constitutes the response time of the pumping system to any pressure variation caused by the plasma decomposition, and is of the same order of magnitude as the residence time t_R . The figure 6 shows that the establishment time depends on the pressure p_r and the decomposition degree which is greater in CHF_3 than in C_2F_6 .

Fig. 6. — Establishment times in the CHF_3 and C_2F_6 plasmas.

The figure 7 shows the evolution of the molar fractions of the different molecules detected in the CHF_3 plasma as a function of the pressure p_r . As

Fig. 7. — Molar fractions in the CHF₃ plasma.

in the case of C₂F₆, the variation in the concentration of CHF₃ with p_r is explained by the increase in t_R (see Eqs. (13) and (15)).

The results obtained are in agreement with those of Truesdale and Smolinsky [19] for the most abundant molecules, which are CHF₃, HF, CF₄, C₂F₆, C₂F₄. However, in addition, the species C₂HF₅, C₃F₆, C₃F₈, C₄F₆ and C₄F₈ were detected, whereas the species C₂H₂ and C₂HF cited by the above authors were not observed.

The existence of the C₂HF₅ molecule indicates the presence of the CHF₂ radical in the CHF₃ plasma.

The following recombination reaction can be proposed :

The radical CF₂ is also produced by the electron impact fragmentation of CHF₃ [1, 19]. The following reaction may thus also be proposed :

5.3 VARIATIONS INDUCED BY ETCHING OF Si AND SiO₂.

5.3.1 C₂F₆ plasma. — The table III gives the gaseous effluents detected by mass spectrometry in the presence of a 100 mm diameter wafer of Si or SiO₂.

The PF₃ and PF₅ species result from the etching of the doped C.V.D. oxide which contains 8 to 9 wt. % phosphorus. An increase in the partial pressures of C₂F₂, C₂F₄ and C₃F₆ is observed during the etching of Si (Table IV), whereas during the etching of SiO₂

Table III. — Gaseous effluents resulting from etching of SiO₂ and Si.

m/e a.m.u.	ion	molecules	
		SiO ₂ etching	Si etching
44	CO ₂ ⁺	CO ₂	
47	COF ⁺ , SiF ⁺	SiF ₄ , COF ₂	SiF ₄
66	SiF ₂ ⁺ , COF ₂ ⁺	SiF ₄ , COF ₂	SiF ₄
87	SiF ₃ ⁺	SiF ₄	SiF ₄
88	PF ₃ ⁺	PF ₃	
107	PF ₄ ⁺	PF ₅	

Table IV. — Composition variations induced by etching of SiO₂ and Si (in % of molar fractions).

C ₂ F ₆ plasma			
		with SiO ₂	with Si
69*	CF ₄	- 9 (± 2)	- 2 (± 0.4)
62	C ₂ F ₂	- 16 (± 3)	+ 2.4 (± 0.5)
81	C ₂ F ₄	- 35 (± 8)	+ 40 (± 10)
150	C ₃ F ₆	- 20 (± 5)	+ 14 (± 1)
169	C ₃ F ₈	- 10 (± 2)	+ 1 (± 1)

CHF ₃ plasma			
		with SiO ₂	with Si
20	HF	+ 20 (± 5)	+ 11 (± 2)
51	CHF ₃	- 19 (± 5)	- 19 (± 2)
69*	CF ₄	- 4 (± 1)	- 0.8 (± 0.2)
81	C ₂ F ₄	+ 4 (± 1)	+ 85 (± 20)
119	C ₂ F ₆	- 19 (± 4)	- 7 (± 2)
150	C ₃ F ₆	- 40 (± 8)	- 15 (± 3)
169	C ₃ F ₈	- 27 (± 6)	- 7.5 (± 1.5)

(*) after mass interference corrections.

the partial pressures of CF₄, C₂F₂, C₂F₄, C₃F₆ and C₃F₈ decrease. These species arise from the recombination of the CF, CF₂ and CF₃ radicals [15, 18]. The variations in plasma composition during SiO₂ etching are thus an indirect experimental proof of the consumption of CF_n ($n = 1 - 3$) radicals in the surface reaction. The etching reaction of SiO₂ thus limits the recombinations such as (12) and :

Plasma etching of Si consumes essentially atomic fluorine; the CF_n radicals are thus free to recombine

among themselves, explaining the increase in the partial pressures of the C_nF_m molecules (except CF_4 and C_2F_6) during etching of Si.

In the case of etching of Si in a CF_4 plasma, a kinetic model based on balance equations such as (14) has allowed a quantitative interpretation of these variations [17]. Two other attempts to elaborate a detailed kinetic modelling of CF_4-O_2 , CF_4-H_2 and CF_4 plasma have been published recently [20, 21]. These studies show that several reaction rate constants are unknown and are only estimated. To achieve more complete models, one needs measurements of the concentrations of all species involved in the etching process. Improvements will be obtained by using laser diagnostics [22]. But such measurements have not yet been published.

The results reported here have been obtained in a relatively simple experimental apparatus and bring informations on the chemical-physics of the plasma. Moreover the variations of the chemical composition of the ionized gas which have been observed during the etching of Si and SiO_2 can be used to control the etching process itself. This has been verified on a sandwich of poly-Si/ SiO_2 /mono-Si : during the plasma etching the variations in gas composition caused by the etching of the different layers are clearly seen (Fig. 8). The etching of SiO_2 is shown by the peak 47 (COF^+) and the peaks 62 ($C_2F_2^+$), 81 ($C_2F_3^+$) and 150 ($C_3F_6^+$) are seen to decrease as predicted by the observations made above (Table IV).

5.3.2 CHF_3 plasma. — The variations in composition of the CHF_3 plasma during etching are given in table IV and show :

- (i) an increase in the decomposition of CHF_3 and thus an increase in HF concentration during etching of Si and SiO_2 ;
- (ii) an increase in the partial pressure of C_2F_4 during etching of Si;
- (iii) a decrease in the partial pressures of C_2F_6 , C_3F_6 and C_3F_8 during etching of SiO_2 .

Moreover, the C_2HF_5 pressure, not given in table IV, falls below the detection limit.

The results are consistent with the interpretation given above for the C_2F_6 plasma. The radical recombination reactions such as

and the reactions (16)-(18) are limited by the more rapid consumption of CF_n radicals in the etching reaction.

5.3.3 C_2F_6 - CHF_3 plasma. — The gas mixture C_2F_6 - CHF_3 is industrially used in M.O.S. technology to obtain selective etching of SiO_2 over Si. The mass spectrometric analysis shows the same peaks in the C_2F_6 - CHF_3 plasma as observed in the CHF_3 plasma, although the masses 64, 82 and 113 are also detected. These peaks are assigned to the $C_3H_2F_6$, C_2HF_3 and C_3HF_5 molecules respectively (Table V). Other

Fig. 8a-e. — Evolution the neutral composition of the C_2F_6 plasma during etching of Si- SiO_2 -Si sandwich.

Table V. — Additional molecules formed in the C₂F₆-CHF₃ plasma.

m/e	ion	parent molecules
64	C ₂ H ₂ F ₂ ⁺	C ₃ H ₂ F ₆
82	C ₂ HF ₃ ⁺	C ₂ HF ₃
113	C ₃ HF ₄ ⁺	C ₃ HF ₅

possible assignments were rejected because of the high proportion of hydrogen required for their synthesis [23].

A typical molar fraction of these new species lie between 0.1 and 0.3 %.

The polymers deposited on the reactor electrodes participate in the physical and chemical processes of the CHF₃-C₂F₆ discharge. It has been observed that, depending on the starting gas used, C₂F₆ or CHF₃ slight variations (~ 1 %) in the composition were observed. Thus C₂HF₅ and HF were detected in the C₂F₆ plasma after discharges in CHF₃, and similarly after having used a reactor which produces a C₂F₆ plasma, C₄F₆ and C₄F₈ species were detected in a CHF₃ plasma. We believe that the polymer film is attacked by ion bombardment and liberates the CF₂, CHF, CF and CH radicals which then participate in the plasma physico-chemistry. The nature and the concentration of these radicals depends on the « history » of the reactor, that is to say, on the state of the surface of the electrodes [24, 25].

Likewise, ions such as C₃F₃⁺, C₃F₅⁺ and C₄F₇⁺ appear in the presence of a C₂F₆-He plasma. These ions, undetected in a C₂F₆ plasma are attributed to the sputtering of the polymer film on the electrodes [23].

6. Mass analysis of positive ions extracted from the plasma.

The positive ions, impinging on the upper electrode are sampled through the 50 μm orifice without any bias system. The quadrupole filter analyses the ions by mass. No corrections of the measured ionic intensities have been effected.

6.1 POSITIVE IONS IN A C₂F₆ PLASMA. — The evolution of the relative ionic intensities as a function of the pressure is given in figure 9. The most abundant ion is always CF₃⁺. In order to determine the possible origin of these different ions, the partial ionization cross-sections σ_{ij} of CF₄, C₂F₆ and CHF₃ were measured according to the same method we used for SiH₄ [13]. The partial ionization constants k_{ij} were calculated for a Maxwellian distribution function f(ε) of the electron energy according to the relation :

$$k_{ij} = \int_{eV_{aj}}^{\infty} \left(\frac{2\varepsilon}{m_e} \right)^{1/2} \sigma_{ij}(\varepsilon) \cdot f(\varepsilon) \cdot d\varepsilon \quad (20)$$

Fig. 9. — Relative ionic intensities in the C₂F₆ plasma.

where V_{aj} is the appearance potential for the ion of mass m_j and m_e is the mass of the electron.

The evolution of the relative values of k_{ij}/∑_j k_{ij} thus obtained for the different molecular ions of

Fig. 10. — Partial ionization constants for C₂F₆.

C_2F_6 as a function of the mean electron energy is given in figure 10. Comparison with figure 9 shows that the electron impact ionization reactions of C_2F_6 are not sufficient to explain the experimental results. In fact the two main reactions are [1] :

Other ionization sources must also be taken into account : first the ionization of other neutral molecules formed in the plasma, in particular CF_4 :

Second, the ionization of molecular radicals [26] :

When a wafer with SiO_2 or poly-Si film is put on the lower electrode no changes are observed in the relative abundances of the positive ions which reach the upper electrode. However all the absolute ionic intensities are seen to be divided by a factor of 1.7 ± 0.3 . This is explained by the difference in the secondary electron emission coefficients of aluminium and silicon.

6.2 POSITIVE IONS IN A CHF_3 PLASMA. — The variation in relative abundance of the ionic intensities for a CHF_3 plasma as a function of the reactor pressure is given in figure 11. The comparison with the ionization constants given in figure 12 shows that at low pressure the relative intensity of CHF_2^+ cannot be simply explained by the direct ionization of CHF_3 [1] :

Fig. 11. — Relative ionic intensities in the CHF_3 plasma.

Fig. 12. — Partial ionization constants for CHF_3 .

There may be two causes of the high abundance of CHF₂⁺. First, the ionization of the CHF₂ radical produced during CHF₃ dissociation :

Second, the ion-molecule reactions observed by Pabst *et al.* [27] :

At a higher pressure the relative abundance of CHF₂⁺ falls off rapidly whereas the relations (26) suggest the opposite. However, as shown in figure 7, the large decomposition of CHF₃ limits the yields of the reactions (26). Moreover, the formation of C₂F₆ and CF₄ gives rise, by ionization, mainly to CF₃⁺ as shown in figure 11.

In the presence of SiO₂ or Si, the ion intensity in CHF₃ plasma varies only within the limits of the reproducibility of the measurements.

To summarize, the ionic abundances measured in the C₂F₆ and CHF₃ plasmas are notably different from those which result from direct electron impact on the injected molecules. Other ionization sources exist : dissociative ionization of the synthesized molecules, ionization of molecular radicals. For the CHF₃ plasma the high proportion of CHF₂⁺ at low pressure is explained by ion-molecule reactions and the ionization of the CHF₂ radical.

Etching of SiO₂ and Si does not perceptibly modify the relative ionic intensities. In the case of the C₂F₆ plasma a decrease in the absolute intensity of the extracted ions is observed.

7. Conclusion.

The calibration of a quadrupole mass spectrometer used for the analysis of the composition of C₂F₆ and CHF₃ plasmas has been described. The partial

pressures of the molecules synthesized in these plasmas (CF₄, C₂F₆, C₂HF₅, C₃F₆, C₃F₈, C₄F₆, C₄F₈, C₅F₈, HF) have been determined from the mass spectra at 70 eV. The reactions leading to the formation of these molecules have been examined. Modifications in the neutral composition of these plasmas during etching of SiO₂ and Si were observed, and are clearly shown to arise from the role of the CF_n radicals during etching of SiO₂ and atomic fluorine during etching of Si. The relative abundance of the positive ions coming from the discharges of C₂F₆ and CHF₃ were measured, and are seen to differ from those obtained by electron impact of the injected molecules. These results are explained by radical ionization reactions and ion-molecule reactions.

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