Journal of Fluorine Chemistry, 16 (1980) 209–227

Received: February 7, 1980

THE ABLATION OF QUARTZ WALL BY SF_6 UNDER RADIOFREQUENCY DISCHARGE.

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SUMMARY

The behaviour of SF_6 in quartz and alumina tubes of a flow reactor capacitively coupled to a 35 MHz radiofrequency generator has been investigated at pressure of 20 torr, with power levels of $3.5 \div 5.5$ cal cm^{-3} sec^{-1} and gas flow rates ranging between 0.1 and 2 l(STP) min^{-1}. A combination of gaschromatographic, mass spectrometric and infrared spectrophotometric techniques has shown the presence of SO_2F_2, SOF_4, SOF_2, SiF_4, F_2, O_2 together with unreacted SF_6 in the discharge products.

A detailed quantitative investigation of the effluent products and of their concentration profiles versus space time and power is presented and a general mechanism for the ablation process of the quartz wall is suggested.

INTRODUCTION

The recent attention devoted to the study of SF_6 is mainly related to the investigations for the isotopic separation induced by high power laser radiation [1]. The molecule of SF_6 is known to present several vibrational levels, which are resonant with some emission lines of CO_2 laser; this has allowed the carrying out of many studies of the laser radiation effect on the decomposition process.

The chemical behaviour of SF_6 under microwave discharge conditions has been investigated by Emeléus and Tittle [2], and Brunner et al.[3] have utilized SF_6 discharge as a source of fluorine atoms for HF chemical lasers. Only recently fluoride compounds, mainly CF_4, have become the subject of extensive investigation for the dry etching of semiconductor materials [4, 5, 6, 7]. The results of a detailed investigation of the decomposition and oxidation of SF_6 carried out in quartz or alumina reactor tube under plasma conditions will be presented in this note.

The ablation process of the quartz walls has been studied in absence and in presence of added oxygen in the feed gas and it has been found that the decomposition rate of SF_6 is determined by the ablation process of quartz walls in absence of oxygen.

EXPERIMENTAL

The experimental apparatus is shown schematically in Fig.1. The reactor consists essentially of a quartz tube, (3.6 cm. internal diameter, 1 m long) surrounded by a Pyrex jacket through which refrigerating water is pumped at constant and metered rates (1 - 4 l min^{-1}). This also allows the calorimetric measurements of the total power transferred from the generator to the plasma. The reactor is capacitively coupled to a 35 MHz, 10 kW

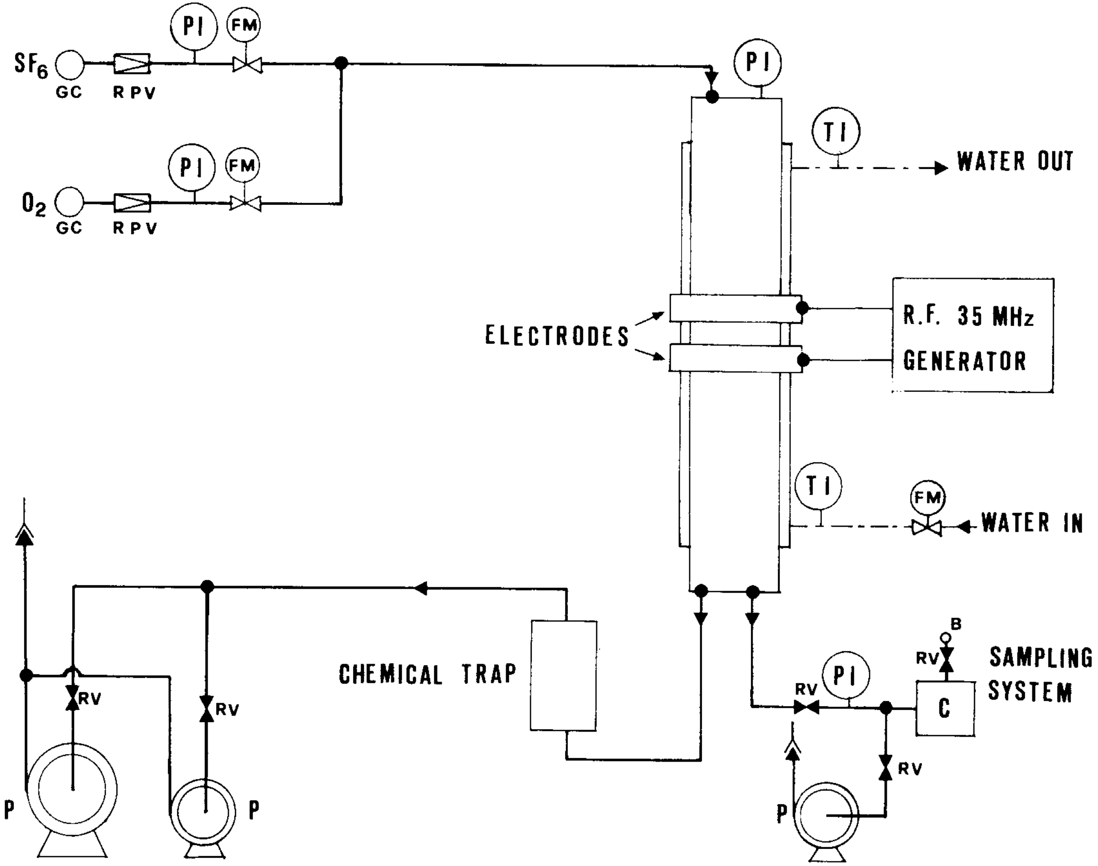

Fig. 1. Scheme of the experimental apparatus.

generator by means of two external annular electrodes set at a fixed separation of 18 cm. The gas flow rates are regulated by means of needle valves and metered on calibrated flow meters. A 0.45 m^3 min^{-1} rotary pump provided the required pressure in the discharge tube. A soda-lime chemical trap prevents the corrosive gases from flowing into the pump. The discharge products are sampled at the bottom of the reactor through an independent pumping system and collected in calibrated glass bulbs equipped with Teflon stop-cocks. The qualitative analysis of the collected samples, performed by means of gc-ms and IR spectrometry, has shown the presence of SF_6, O_2, F_2, SiF_4, SO_2F_2, SOF_4, SOF_2. The presence of SiF_4 and oxygenated compounds, even in absence of external oxygen in the gas feed , is due to the ablation process of the reactor quartz walls by the active species produced within the discharge. The quantitative analysis of the reacted gases has been carried out by titrating fluorine as fluoride after reaction with mercury and analyzing the fluorine free gases by means of a gas chromatograph (6.5 ft. x 1/8" in. column, filled with Porapak QS, carrier gas He at 20 cc/min, T = 60°C, TC detector). Details of the analytical procedure can be found in ref. [8]. It is worth to mention that all precautions have been taken to avoid hydrolysis in the sampling procedures.The sampling bulbs were heated under vacuum, overnight, prior to use and filled and evacuated with the discharge mixture two or three times before the final sampling. The mercury, kept under vacuum after heating and stirring, was poured into the sampling bulbs under vacuum conditions. The absence of HF in the sampling mixture is, however, a strong evidence of the absence of any hydrolysis reaction. The flow rate of SF_6 has been varied between 0.1 and 2 l(STP) min^{-1} at constant pressure of 20 torr. For the SF_6/O_2 system, the oxygen has been added up to 45%. The power input ranged form 2.5 to 5 kW. Similar experimental conditions have been used for the runs performed with the alumina tube.

RESULTS

a) SF_6 in a quartz reactor.

The quantitative investigation on the discharge products (SF_6, SO_2F_2, SOF_4, SOF_2, SiF_4, F_2 and O_2) has been carried out as a function of the specific power input <W> ($cal.cm^{-3}\ sec^{-1}$), (obtained from the ratio of the total power to the reactor volume, $V(cm^3)$), and space time V/F (sec) with F = gas flow rate at discharge conditions ($cm^3\ sec^{-1}$). The molar fractions of the discharge products have been plotted in Fig.2 as a function of the specific power, for three different gas flow rates. In Fig.3 the molar fractions have been plotted versus the space time, for three values of power input. The conversion of SF_6 in each discharge product (β_{SOF_2}, $\beta_{SO_2F_2}$, β_{SOF_4}) and the total conversion (β_T) can be derived from these plots. The results are shown in Fig.4, where the conversions have been plotted versus the space time, for three values of power input. It can be observed that, an increase in power input or in space time leads to an increase of β_T and of SiF_4 formation. In Figs.3 and 4 three regions can be distinguished at different space times. In the first one, at very low times, where the total conversion of SF_6 is relatively low, the main reaction product is SOF_2; in the second one, at intermediate values of times, where very high values of β_T are observed, the most abundant reaction product is SOF_4, which rises to a maximum; the third one starts from the maximum value of SOF_4. In this zone the profile of β_T has almost reached the constant value of 1, the formation of SiF_4 still increases whereas SOF_4 decreases in favour of the more oxygenated

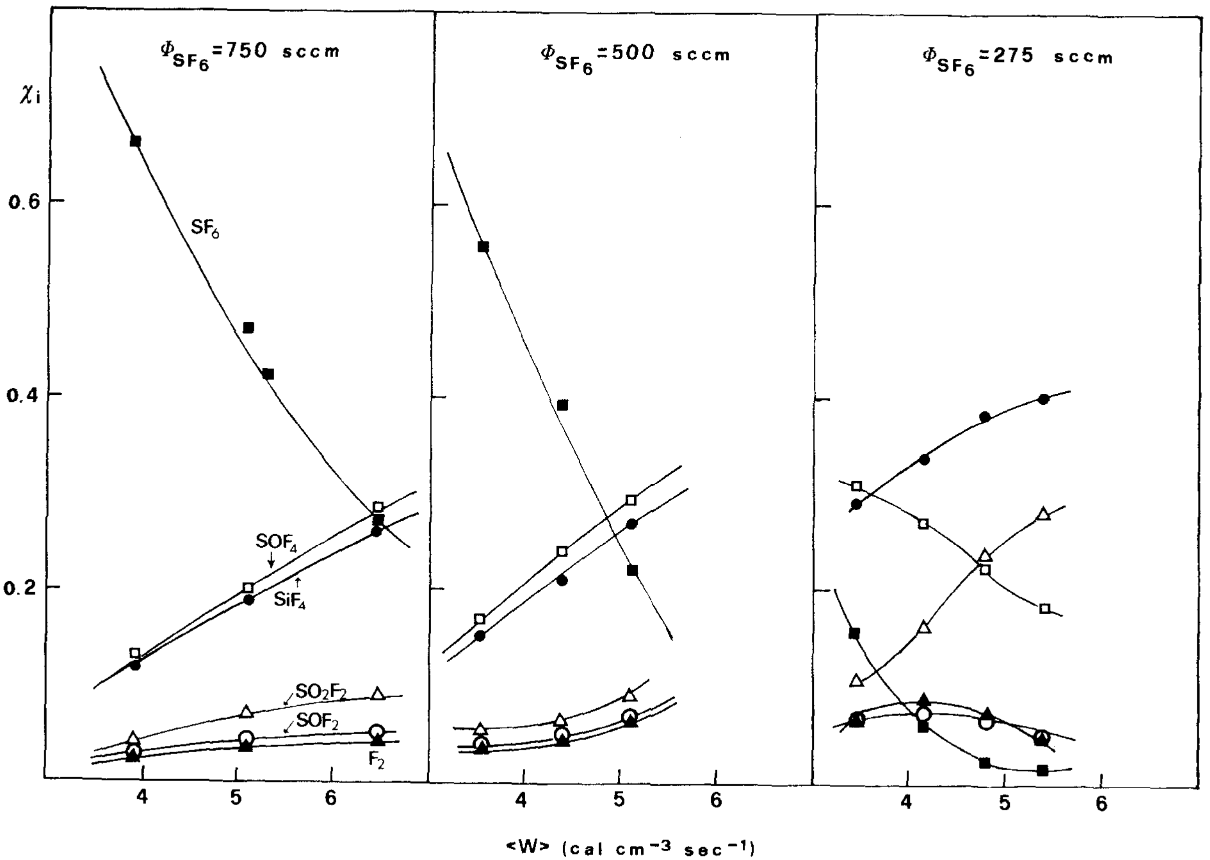

Fig.2. Molar fractions (χ_i) of the discharged gases versus power density (<W>) for three values of gas flow rate.(■ SF_6; □ SOF_4; △ SO_2F_2; ○ SOF_2; ● SIF_4; ▲ F_2)

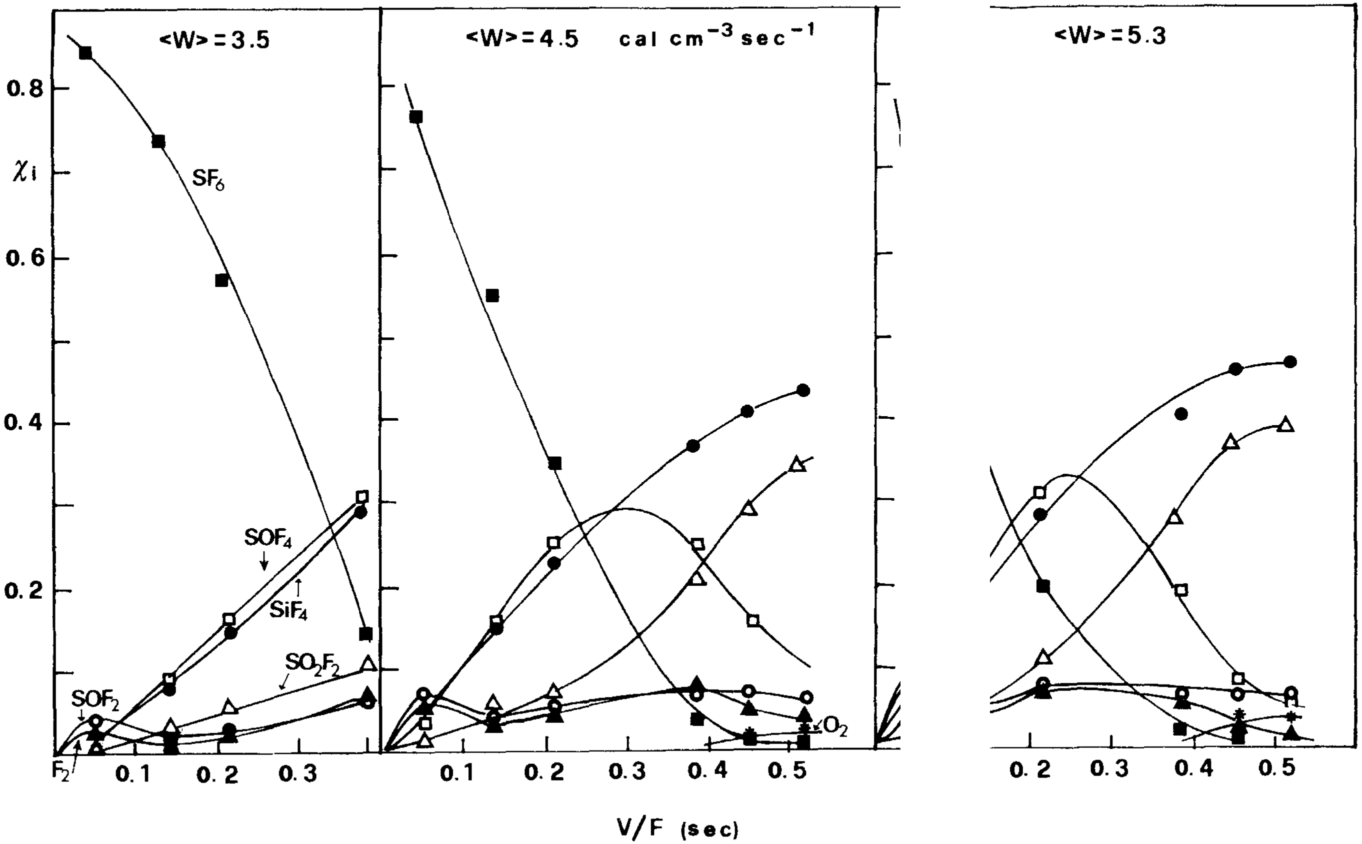

Fig.3. Molar fractions (χ_i) of the discharged gases versus spa e (V/F) for three values of the power density.(■ SF_6; □ SOF_4; △ SO_2F_2; ○ SOF_2; ● SIF_4; . ✱ O_2)

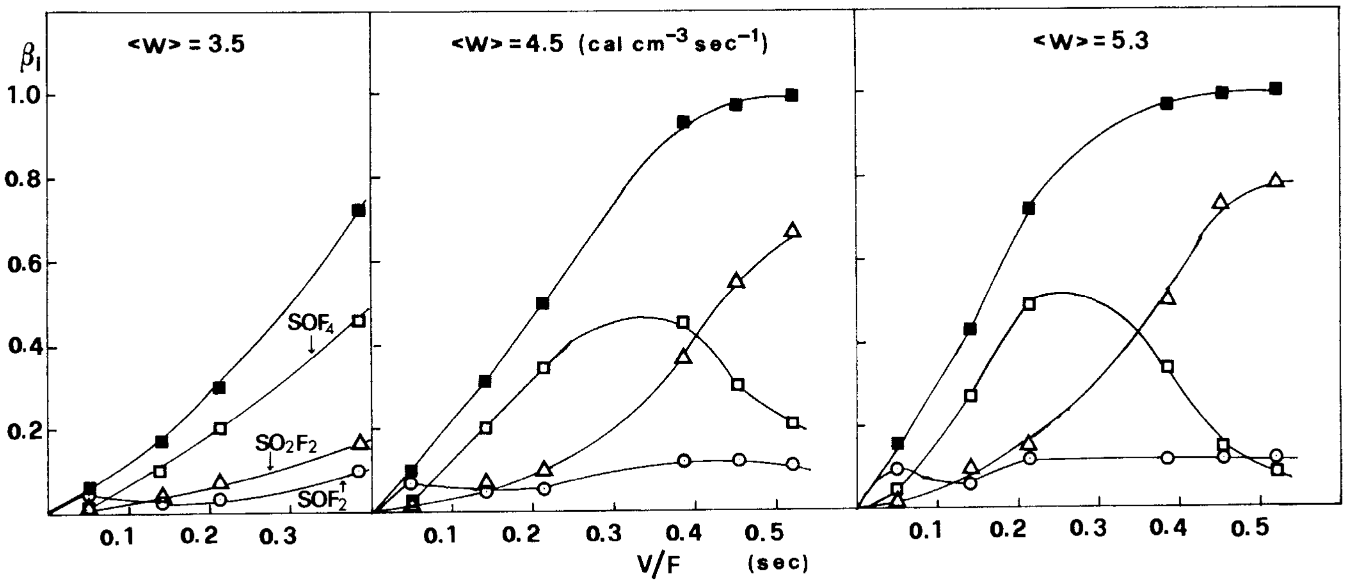

Fig. 4. Degree of conversion (β_i) of SF_6 into SOF_4 (□), SO_2F_2 (△), SOF_2 (○) and the total conversion (■) versus space time (V/F) for three values of power density.

product SO_2F_2. The presence of free oxygen has been observed only at very high values of space time. The profile of F_2 is practically coincident to that of SOF_2 for the whole time interval examined. It can also be observed, from Fig.4, that the β_T profile is typical of autoaccelerated processes.

On the basis of SiF_4 formation, the etching rate, E (in Å min^{-1}), can be derived [9] and the result is shown in Fig.5 versus the space time, for three values of power density.

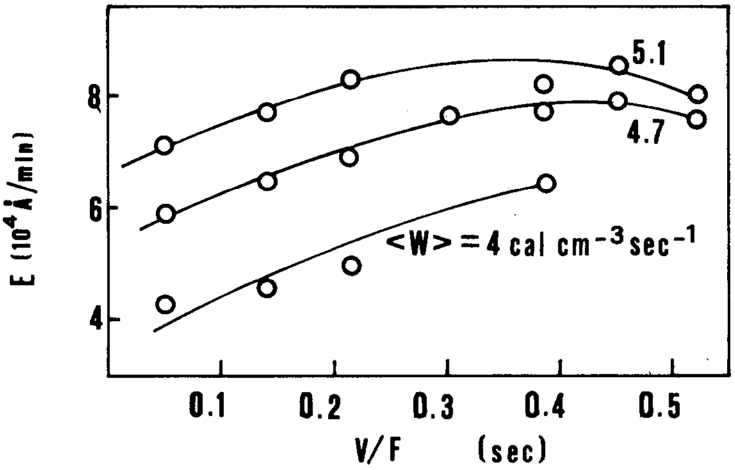

Fig. 5. Ablation (E) versus space time (V/F) for three values of power density.

b) SF_6/O_2 in quartz reactor.

The molar fractions of the discharge products and the degrees of conversion have been plotted in Figs.6 and 7, respectively, as a function of the percentage of the external oxygen, for two values of total gas flow rate. It can be observed that, while the SF_6 molar fraction decreases with increasing the percentage of added oxygen, that of SiF_4 remains practically unchanged. Free oxygen is present among the discharge products only at feeding compositions higher than 20%, while for lower values it is completely utilized to give oxyfluride compounds. The appearance of free oxygen in the discharge mixture coincides with the disappearance of SOF_2 in favour of the more oxygenated SO_2F_2. The SOF_4 profile presents a well pronounced maximum, in correspondence of which the SO_2F_2 molar fraction starts a very rapid increase. The F_2 profile no longer coincides with that of SOF_2, as observed with pure SF_6, and it

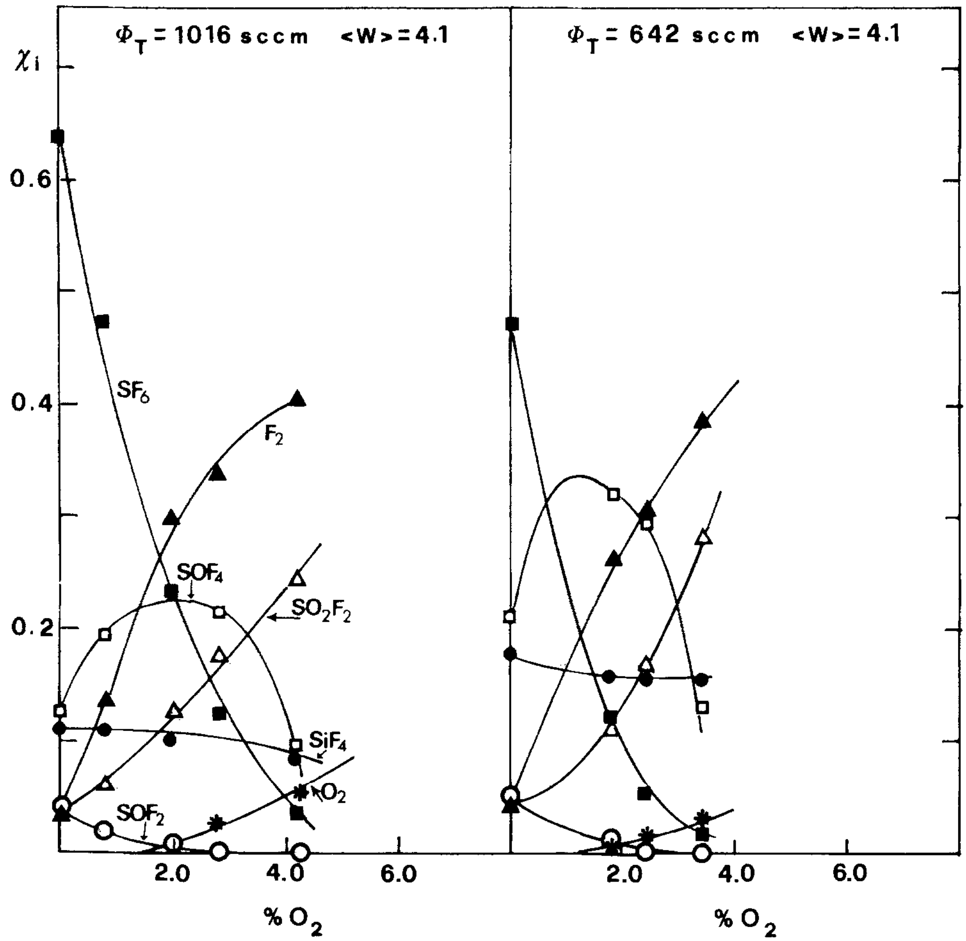

Fig. 6. Molar fractions (χ_i) of the discharged gases versus the percentage of added oxygen for two values of total flow rate. (■ SF_6; ☐ SOF_4; △ SO_2F_2; ○ SOF_2; ● SIF_4; ▲ F_2; ✱ O_2)

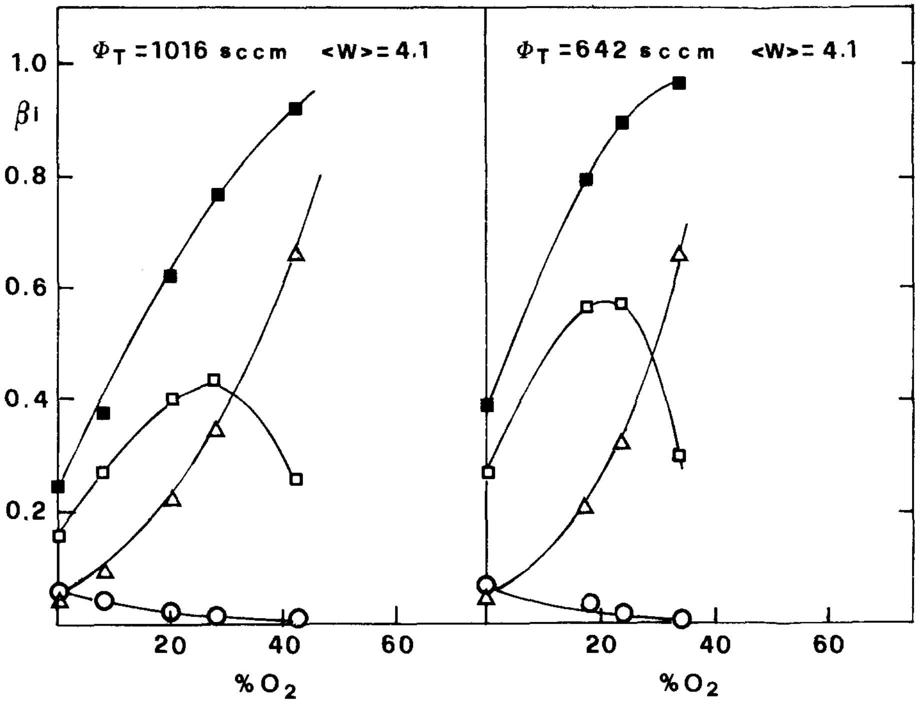

Fig. 7. Degree of conversion (β_i) of SF_6 into each reaction product and the total conversion versus the percentage of added oxygen for two values of total flow rate. (Symbols as in Fig. 6).

reaches very high values, while the ablation product, SiF_4, does not vary appreciably.

c) <u>SF_6 and SF_6/O_2 in alumina reactor</u>.

The runs performed with pure SF_6 have shown that the discharge-decomposition products recombine totally to SF_6 outside the discharge region. Any attempt to reveal the presence of products such as SF_4, S_2F_{10} or F_2 failed, at least within the detection limits of the analytical techniques used. The addition of external oxygen leads to the formation of SO_2F_2, SOF_4 and F_2 (Fig. 8). SOF_2 is completely absent, even at very low values of oxygen addition. The influence of the power input is almost negligible.

DISCUSSION

A detailed analysis of the kinetic mechanism for the decomposition and oxidation of SF_6 under our experimental conditions is extremely complex because of the presence of both homogeneous and heterogeneous processes. In addition, the effective discharge region is limited to only a small central fraction of approximately 1/4 of the reactor diameter, with large effects of mass transfer and recombination processes within the relatively cold external region.

In Table 1 we have collected the most relevant reactions which can occur in the three main regions into which the reactor can ideally be subdivided. Below the discharge zone, atoms and radicals recombine to give the stable species which have been detected in the reacted mixtures. In the plasma region we have both decomposition processes involving electrons and homogeneous recombination reactions. The dissociation mechanism can occur by direct electron impact or through processes involving vibro-rotationally excited molecules. The formation of SF_3, which is reported as the main radical in the decomposition process of SF_6 [10], does not occur by a single step process.

It is known that the first step of the direct electron impact on SF_6 in the formation of SF_5 and/or SF_5^- [11], which rapidly decompo to the more stable SF_3. The diffusion region plays a very important role under our experimental conditions of relatively high pressure.

Two main processes are operative in this region: a) the homogeneous recombination reactions; b) the mass transfer of the active species from the plasma to the reactor walls, and of the species originating in the ablation process, from the walls to the plasma core.

The reactions which occur at the wall surface are mainly heterogeneous recombinations and etching reactions. The etching product SiOF(s) reported in Table 1 should be considered as an intermediate species towards the formation of SiF_4.

Fluorine atoms have not been included in Table 1 as active species for the SiO_2 surface etching: their contribution is still an open question also for etching system fed with freons and contradictory findings and results are present in the literature. This problem, however, has been extensively discussed in ref. [6]. We do not have definite evidence to exclude the contribution of fluorine atoms in the SiO_2 etching process under SF_6 discharges; the inclusion of their contribution, however, does not alter the general picture of the ablation process.

The exprimental results obtained with both quartz and alumina reactors, with and without the addition of external oxygen, can be reasonably interpreted, at least qualitatively, on the basis of the general scheme reported in Table 1.

Table 1 Relevant reactions within the reactor

	Plasma region (r ≃ 0.5 cm)	Diffusion region (r ≃ 1.3 cm)	Wall surface
Discharge region	$SF_6 \overset{+e}{\rightleftarrows} SF_3 + 3F$	$SF_3 + 3F \longrightarrow SF_6$	$SF_3 + 3F \longrightarrow SF_6$
	$F_2 \overset{+e}{\rightleftarrows} 2F$	$2F \longrightarrow F_2$	$2F \longrightarrow F_2$
			$SF_3 + SiO_2(s) \longrightarrow SOF_2 + SiOF(s)$
	$SO_2F_2 \left\{ \begin{array}{l} \overset{+e}{\rightleftarrows} SO_2F + F \\ \overset{+e}{\rightleftarrows} SOF_2 + O \end{array} \right.$	$\longleftarrow SO_2F_2$	$SOF_3 + SiO_2(s) \longrightarrow SO_2F_2 + SiOF(s)$
			$SiOF(s) + SF_3 \longrightarrow SOF_2 + SiF_2$
			$SiOF(s) + SOF_3 \longrightarrow SO_2F_2 + SiF_2$
		$SOF_3 \longleftarrow SOF_2 + F$	$SOF_2 + F \longrightarrow SOF_3$
	$SOF_4 \overset{+e}{\rightleftarrows} SOF_3 + F$	$SOF_4 \longleftarrow SOF_3 + F$	$SOF_3 + F \longrightarrow SOF_4$
	$SiF_4 \overset{+e}{\rightleftarrows} SiF_2 + 2F$	$SiF_4 \longleftarrow SiF_2 + 2F$	$SiF_2 + 2F \longrightarrow SiF_4$
	$SF_3 + O \longrightarrow SOF_3$		
	$SF_3 + O_2 \longrightarrow SO_2F_2 + F$		
	$SOF_3 + O \longrightarrow SO_2F_2 + F$		
	$O_2 \overset{+e}{\rightleftarrows} 2O$	$2O \longrightarrow O_2$	$2O \longrightarrow O_2$
Out of discharge recombination region	Atoms and radicals recombine to stable species : SF_6, SiF_4, SO_2F_2, SOF_4, SOF_2, F_2, O_2		

When using SF_6 in an alumina reactor without oxygen in the feed, the reaction scheme reduces itself only to the decomposition and recombination processes of sulphur-fluorine species, without any reactive process with the reactor walls [4]. The species detected outside the discharge region is only SF_6.

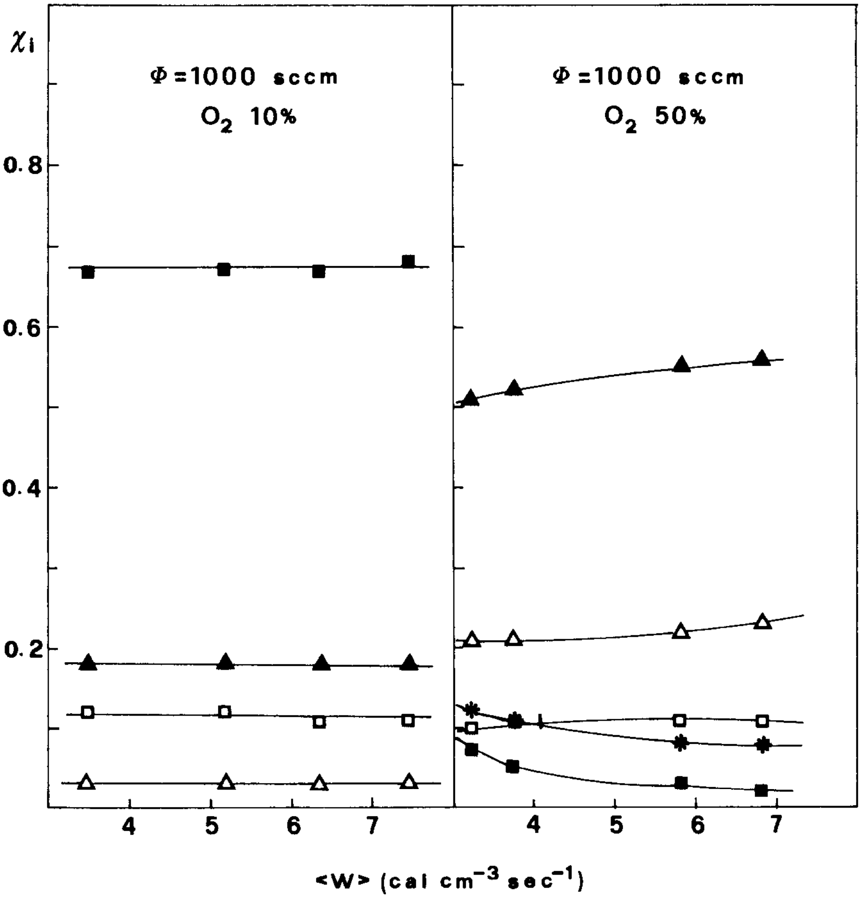

Fig.8. Molar fractions (χ_i) of the discharged gases in the alumina reactor versus power density (<W>) for two values of added oxygen percentage (■ SF_6; □ SOF_4; △ SO_2F_2; ▲ F_2; ✱ O_2).

The oxygen addition leads to the formation of oxygenated compounds, whose distribution is almost independed of power, and space-time as shown in Fig. 8. In this case oxygen molecules and atoms rapidly react with radicals, blocking their recombination to SF_6, and a discharge equilibrium distribution of products is established.

It should be noticed, however, that SOF_2 is not obtained in the alumina reactor, even at low oxygen content in the feed. On the other hand the results obtained in the quartz reactor without oxygen in the feed, plotted in Figs. 3 and 4, show that SOF_2 is the main oxygenated product at short space-times. When oxygen is added to the feed, the molar fraction of SOF_2 decreases with increasing the oxygen addition and vanishes at ~ 30% of O_2, as can be seen in Fig.6

This evidence indicates that SOF_2 is a primary species of the etching process and an intermediate compound for the formation of other oxy-fluorinated products, and that the SF_3 radical is one of the probable etchants through the surface reactions reported in Table 1.

From inspection of Fig. 6 it can also be observed that the addition of oxygen causes an increase of fluorine in the reaction products by a factor as large as 8, while the rate of production of SiF_4 is almost unaffected ($E = 6.0 \pm 0.5X10^4$ Å min^{-1} at $<W> = 4.0$ $cal\ cm^{-3}\ sec^{-1}$). This fact suggests a relatively small contribution of fluorine atoms to SiO_2 etching under our experimental conditions

The results for the quartz reactor without oxygen in the feed, reported in Fig. 5, shows an increase of the etching rate with the space-time, and those of Fig. 3 indicate that, even when the molar fraction of SF_6 is reduced almost to zero, the SiF_4 molar fraction continues to increase while SOF_4 reaches a maximum and then decreases. It can be therefore concluded that SOF_4 is an intermediate towards the formation of SO_2F_2, probable according the reaction

$$SOF_3 + SiO_2(s) \longrightarrow SO_2F_2 + SiOF(s)$$

An indication that SOF_x radicals, other than SF_3, can act as etching species, has been obtained with a discharge in pure SO_2F_2 at low pressure [12]. We have observed etching of quartz with a rate of about 1/3 as compared with pure SF_6 under the same discharge conditions. A possible route for the formation of SOF_3 from SO_2F_2 is reported in Table 1.

On the basis of the arguments above, a simplified mechanism [13] for the decomposition of SF_6 and the ablation of the quartz walls has been proposed, in the absence of oxygen. It is assumed that a discharge equilibrium is established between SF_6 and SF_3 radicals and that the disappearance of SF_6 is caused by the depletion of SF_3 and SOF_3, which are responsible for the quartz ablation:

$$SF_6 \rightleftharpoons SF_3 + 3F$$

$$\begin{tikzcd}
SF_3 + SiO_2(s) \arrow[r, "kw"] & SOF_2 + SiOF(s) \arrow[d, "+F"] & \\
 & SOF_3 + SiO_2(s) \arrow[r, "k'w"] & SO_2F_2 + SiOF(s)
\end{tikzcd}$$

This mechanism can account for the observed autoacceleration of both SF_6 decomposition and quartz ablation processes, if one considers that the secondary etchant SOF_3 is produced near to the walls with which it can react before diffusing away. In this case the rate of SiF_4 appearance in the gas phase, r_{SiF_4} (mole cm^{-3} sec^{-1}), can be expressed as

$$r_{SiF_4} = k_w[SF_3] + k'_w[SOF_3]$$

The observed near independence of the etching rate on the proportion of the added oxygen, should be explained by the fact that the presence of oxygen, while increasing the SF_6 conversion through the reaction $O(O_2)+SF_3 \longrightarrow SOF_3$ and consequently decreasing $[SF_3]$, also increases proportionally the formation of SOF_4 and, presumably, of SOF_3 radicals.

CONCLUSION

It can be concluded that, although the kinetic mechanism for the decomposition and oxidation of SF_6 under our experimental condition is extremely complex, a general picture of the ablation process of the quartz walls can reasonably be obtained on the basis of processes which involve sulphur-fluorine and sulphur-oxygen-fluorine radicals. The contribution of fluorine atoms to the process cannot be excluded on the basis of our results, but further investigation is required for a better understanding of the etching processes in vie of the potential use of SF_6 for the dry etching of semiconductors materials.

ACKNOWLEDGMENT

The authors wish to thank Mr. G. Latrofa and Mr. V. Colaprico for technical assistance.

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