DECOMPOSITION AND OXYDATION OF SF_6 IN FLOW R.F. PLASMA REACTOR

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ABSTRACT

The decomposition and oxydation of SF_6 has been studied in a quartz and alumina flow reactor, capacitively coupled to a 35 MHz generator operated at 20 torr of pressure. A detailed quantitative investigation of the effluent products and of their concentration profiles *vs.* space-time and power level is presented. A mechanism is suggested for the etching process.

1. INTRODUCTION

The recent growing interest devoted to the study of SF_6 is mainly related to the investigation for the isotopic separation by means of high power laser radiation (1). Fluoride compounds, mainly CF_4, are also extensively investigated under discharge conditions as efficient source for producing active species utilized for the dry etching of semiconductor materials (2,3). Some interest has also been devoted to the behaviour of SF_6 under discharge conditions (4,5) but a detailed study was absent until recently (6,7). In this note we present the results of a systematic investigation of the decomposition and oxydation of SF_6 carried out in a quartz and alumina reactor under plasma conditions very similar to those used in our previous studies (8). In absence of external oxygen in the feeding gas mixture, the decomposition rate of SF_6 is seen to be determined by the ablation rate of the reactor quartz walls.

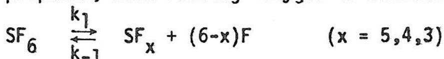
2. EXPERIMENTAL

A detailed scheme of the experimental apparatus is given in ref.(8). The reactor consists essentially of a quartz tube, 3.6 cm i.d., 1 m long, surrounded by a Pyrex water jacket and capacitively coupled to a 35 MHz, 10 kW generator by means of two external annular electrodes set at fixed separation of 18 cm. A soda-lime trap, inserted in the vacuum line at the

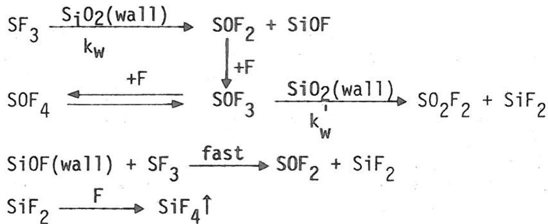
reactor end, was used to prevent the corrosive discharge products to flow in the pumps. The discharge products, sampled by means of an independent vacuum line and stored in calibrated glass bulbs equipped with teflon stop-cocks, were successively analyzed. The analysis, which has been described in details in ref.(7), has shown the presence of SF_6, F_2, SiF_4, SOF_2, SO_2F_2 and SOF_4. The presence of oxygenated compounds and of SiF_4 is due to the ablation of the reactor quartz walls by the active species produced within the discharge.
The process of SF_6 decomposition, carried on in absence or in presence of feeding oxygen, has been studied at different conditions of gas flow rates (0.1 ÷ 2 ℓ(STP)min^{-1}), and power input (2.3÷5 kW), at a constant total pressure of 20 torr.
Some runs have also been performed with an alumina tube reactor, with and without oxygen in the feeding.

3. RESULTS AND DISCUSSION

The molar fraction (x_i) of the various discharge components as a function of the power density <W> (cal cm^{-3} sec^{-1}) have been plotted in Fig.1, for three different SF_6 flow rates. In Fig.2 we have reported the SF_6 conversion degrees in each reaction product (β_i) and the total one (β_T), for three values of power density, vs. space time (V/F)(sec); V(cm^3) is the discharge geometrical volume and F (cm^3 sec^{-1}) is the volumetric flow at discharge conditions. In this plot three zones can be distinguished with peculiar product distributions:
i - at very short space times, where the main discharge product is SOF_2;
ii- at intermediate space times, where SOF_4 is the predominant component and goes through a maximum;
iii-at longer space times, where SO_2F_2, which represent the most oxygenated compounds observed, becomes the dominant specie.
It can be also observed from the total conversion curves, that the process is slightly auto-accelerated.
The etching rate (Å min^{-1}) of the quartz walls, evaluated on the basis of SiF_4 produced, has been reported in Fig.3, as a function of the space time for different power density conditions.
Runs performed with additional oxygen in the quartz reactor have shown, with increasing oxygen, that the total conversion increases, the one into SOF_2 decreases and the etching rate is almost uneffected.
No appreciable decomposition product was observed when the discharge was operated in an alumina tube. This fact points out the important role played by the recombinations of atoms and radicals into SF_6, in absence of oxygen and/or wall reactions.
If oxygen is added to the feeding SF_6, it fully reacts, at least for feeding ratios $\leq$50%, and oxygenated products are obtained, with the exception of SOF_2. The product distribution was found, in this case, to be independent on the space-time. The absence of SOF_2 under these conditions, together with point i, indicates SOF_2 as the first etching product.
On the basis of these results, the following reaction mechanism has been proposed, when feeding oxygen is absent:



$$SF_6 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SF_x + (6-x)F \qquad (x = 5,4,3)$$



$SiOF(wall) + SF_3 \xrightarrow{fast} SOF_2 + SiF_2$

$SiF_2 \xrightarrow{F} SiF_4\uparrow$

In this mechanism it is assumed that a discharge equilibrium is established between SF_6 and SF_x and that SF_3 and SOF_3 are the primary and secondary main active species for the etching process, while fluorine atoms are not considered active species for the etching (9). The presence of secondary active species can account for the observed auto-accelerated etching rates, if the heterogeneous processes are not limiting steps with respect to diffusion, under our conditions of relatively high pressure and temperature. The rate of decomposition of SF_6, as well as the intermediate role played by SOF_2 and SOF_4, is also accounted for by the proposed mechanism.

According to this mechanism the rate of SiF_4 appearance in the gas phase $r(SiF_4)$ [mole cm^{-3} min^{-1}] is given by:

$$r(SiF_4) = k_w[SF_3] + k_w'[SOF_3] \quad (1)$$

If we assume a steady-state condition for SF_3, the rate of SF_6 disappearance is given by:

$$-r(SF_6) = 2r(SiF_4) - k_w'[SOF_3] \quad (2)$$

On the other hand the appearance rate of a component i can be expressed by:

$$r_i = \frac{d(\chi_i/\Sigma_i \nu_{is} \chi_i)}{d(V/F^o)}$$

where χ_i is the molar fraction, ν_{is} gives the sulphur atoms contained in the i-th component, F° (mole min^{-1}) is the molar flow rate of SF_6 in the feeding gas.

The SF_6 disappearance and SiF_4 appearance rates, full and dashed lines, respectively, have been plotted in Fig.4 as a function of the parameter V/F°, for two values of power density. These rates have been obtained by differentiating cubic equations which have been found to best fit to the experimental data.

It can be seen from the figure that $-r(SF_6) = 2r(SiF_4)$ for $V/F^\circ \to 0$, while for longer times and higher power density $-r(SF_6)$ becomes even smaller than $r(SiF_4)$. This result is in accordance with eq. (2) if one considers that at very short space time $[SOF_3]$ is negligible, but it increases with time. From eq.(2) it is also expected that the term $[2r(SiF_4)+ r(SF_6)]$ should depend linearly on the concentration of SOF_3 and consequently of SOF_4. This behaviour is confirmed by the results shown in Fig. 5, where the term $[2r(SiF_4) + r(SF_6)]$ has been plotted *vs*. the molar fraction of SOF_4, at two values of power density.

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REFERENCES

(1) F. Brunner, T.C. Cotter, K.L. Kompa and D. Proch, J. Chem. Phys. 67, 1547 (1977).
(2) C.J. Mogab, A.C. Adams and D.L. Flamm, J. Appl. Phys. 49, 3796 (1978).
(3) H.F. Winters, J.W. Coburn and E. Kay, J. Appl. Phys. 48, 4973 (1977).
(4) H.J. Emeleus and B. Tittle, J. Chem. Soc., S1644 (1963).
(5) L. Bertrand, M.J. Gagné, R.G. Bosisio and M. Moisan, IEEE J. Quantum Electronics, 14, 8 (1978).
(6) G. Bruno, P. Capezzuto, F. Cramarossa and G. Latrofa, XI Congresso Nazionale di Chimica Inorganica - Cosenza, Sett. 1978 - IG
(7) G. Bruno, P. Capezzuto and F. Cramarossa, J. Fluorine Chem. 14, n.2 (1979).
(8) P. Capezzuto, F. Cramarossa, R. d'Agostino and E. Molinari, Combust. Flame 33, 251 (1978).
(9) Heinecke, Solid State Electronics 18 1146 (1975).

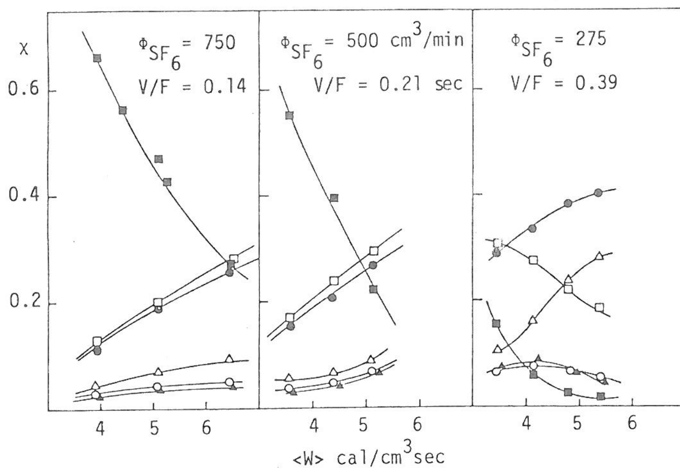

Fig. 1- Molar fractions of discharged gases *vs.* power density.
(■ SF_6; □ SOF_4; ● SiF_4; △ SO_2F_2; ○ SOF_2; ▲ F_2)

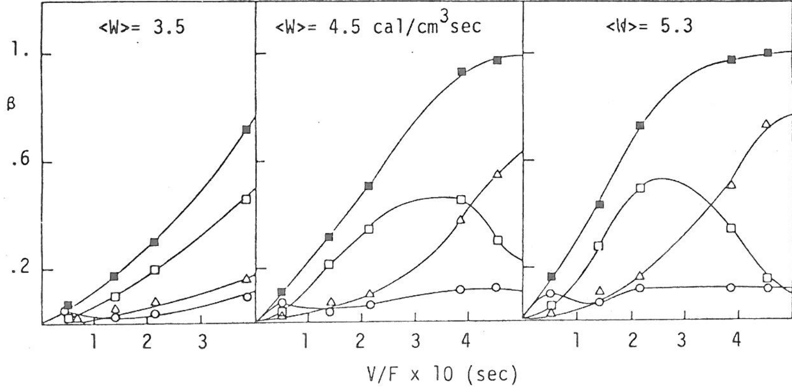

Fig. 2 - Degrees of conversion *vs.* space time. (symbols as in Fig.1).

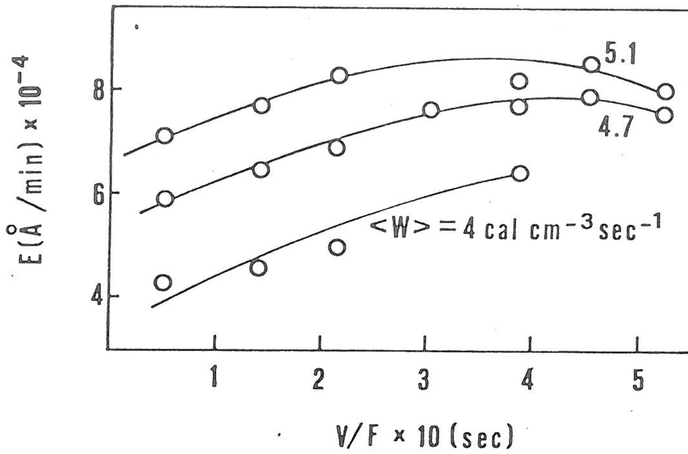

Fig. 3 - Etching rates *vs.* space-time.

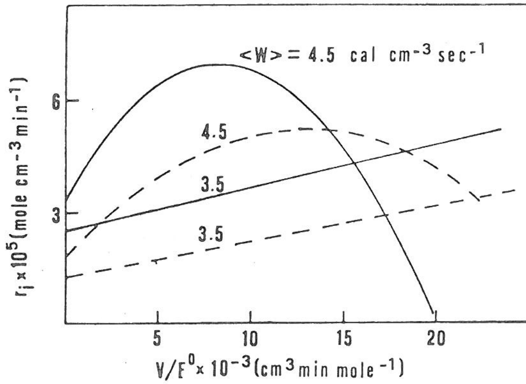

Fig. 4 - SiF_4 appearance (dashed lines) and SF_6 disappearance (full lines) *vs.* V/F°.

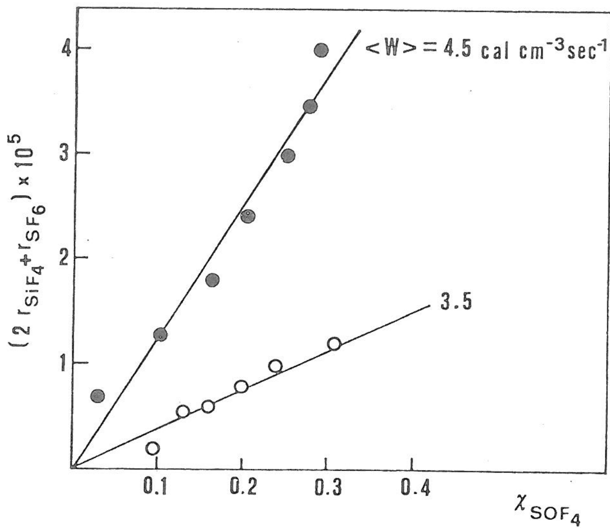

Fig. 5 - $(2r_{SiF_4} + r_{SF_6})$ *vs.* SOF_4 molar fractions (see text).