KINETIC AND SPECTROSCOPIC ANALYSIS OF SF_6-O_2 MIXTURES IN ELECTRICAL DISCHARGES

R. d'Agostino, V. Colaprico and F. Cramarossa
Centro di Studio per la Chimica dei Plasmi del C.N.R.- Istituto di Chimica Generale ed Inorganica, Università di Bari- Via Amendola 173, 70126 Bari (Italy).

ABSTRACT

The decomposition processes of SF_6-O_2 mixtures under radiofrequency discharge has been studied in a flow reactor as a function of the residence time and the feed composition at the constant pressure of 1 torr. Analysis of the discharge products and the emission intensities of electronically excited F- and O-atoms have been utilized for suggesting a kinetic reaction mechanism.

1. INTRODUCTION

SF_6 and SF_6-O_2 mixtures have recently been used /1/ among the various perfluorurated gases for the "dry etching" of silicon integrated circuits with the aim of finding new reagents and for a better understanding of the role played by some active species in the plasma-surface processes. A good knowledge of the chemistry and kinetics of the decomposition process of these mixtures in electrical discharges is essential in designing and operating large scale reactors.

The present study deals with SF_6-O_2 gas mixtures under R.F. flow discharge conditions operated in alumina tubular reactor at 1 torr. We have studied the progress of the decomposition process by analyzing the dicharge stable products as a function of the space-time and by measuring the emission intensities of F- and O-atoms. Profiles of F-atom densities have been determined with recently suggested spectroscopic technique /2, 3/. Direct titration of F-atoms with chlorine has confirmed the spectroscopic analysis. The conversions data of SF_6 and O_2 into stable products have been fitted by an over-all bimolecular process which can find its interpretation in a simplified kinetic mechanism.

2. EXPERIMENTAL

Details of the experimental apparatus can be found elsewhere /1d/. The analysis has been carried out at 1 torr, with power input of 45 watts, feed composition $|O_2|/(|O_2|+|SF_6|)$ ranging between 0 and 0.8 and residence time between 8 and 70 m sec.

The analysis of the stable products was performed by means of various techniques, as detailed in ref.4. SF_6, F_2, SOF_4, SO_2F_2, and O_2 were found to be the main discharge products.

SF_4 and SOF_2 were found only as trace species when oxygen is present in the feed.

The axial radiation from the discharge tube was sampled through a sapphire window and focused on the plane slit of a 1 m Jarrel-Ash monochromator, equipped with a 1180 grooves/mm grating and an EMI QB photomultiplier. 1% of Ar or N_2 were added as "actinometer" gases to the discharge mixtures and their emissions measured as a function of the feed composition in order to determine the excitation efficiency of the discharge electrons. Chlorine for F-atom titration was fed at 90° in the afterglow stream by means of specially designed teflon system, which allows to monitor the chemiluminescent recombination $Cl + Cl + M = Cl_2 + M + h\nu$, which follows the rapid reaction $Cl_2 + F = ClF + Cl$.

3. RESULTS AND DISCUSSION

In figure 1 the molar fractions of the main stable discharge species are reported as a function of the space-time V/F (m sec) (with V = discharge volume and F = total gas flow rate at the temperature and pressure of the reactor) for a 20% feed composition. One can observe that the molar fractions of both SF_6 and O_2 decrease with increasing the time and that the main reaction products are SO_2F_2 , SOF_4 and F_2. The eventual introduction into the discharge zone of silicon substrates in such a small amount to avoid any loading effects, leads to a remarkable variation of the product distribution, with the appearence of SiF_4 and SOF_2, and a significative lowering of fluorine concentration. The presence of silicon substrates does not, however, alter the overall SF_6 decomposition process.

The study of the decomposition processes in the discharge and the design of rectors for dry etching require the knowledge of the densities of the main unstable species; among those F- and O-atoms are of particular interest because both are reported /1d/ to interact with silicon during etching processes.

In figure 2 the molar fractions of F-atoms and the relative O-atom emission intensities (7775 A) are reported as a function of the space time. The molar fractions of O_2 and F_2 have also been included in the figure for comparison. It can be observed that the atom profiles closely follow those of the parent molecules. The F-atom molar fractions have been evaluated on the basis of the titration data and of the determination of the excitation efficiency of the discharge electrons responsible of the excitation of the emitting states; this has been done by means of the addition of the "actinometer" foreign gases /3/. The close relationship between F-atom emission and their concentration should apply also for O-atoms, although a direct titration of O-atoms has not been performed.

In figure 3 the total conversions of SF_6 and of O_2 along with the conversions of SF_6 into SO_2F_2 and SOF_4 have been plotted as a function of the space-time. The experimental data have been fitted assuming a "plug-flow" reactor and an overall bimolecular process, with a reaction rate $r = k |O_2| |SF_6|$. Best fit curves have been obtained with $k = 5.3\ 10^9\ cm^3\ mole\ \ sec^{-1}$. This kinetic behaviour can be rationalized by the simplified reaction sequence reported below:

$$SF_x = SF_{x-1} + F \qquad (x = 3\text{-}6) \tag{1}$$

$$SF_x + O,\ O_2 \longrightarrow \left| \begin{array}{l} SOF_2 \\ SOF_4 \\ SO_2F_2 \end{array} \right. \qquad (x = 3\text{-}5) \tag{2}$$

$$SOF_2 + F,\ F_2 \longrightarrow SOF_3,\ SOF_4 \tag{3}$$

in which the sequence of rapid reactions between SF_x radicals and F-atoms leads to a discharge equilibrium among the SF_x species. Reactions (2), which represent the oxidation processes and likely involve atomic more than molecular oxygen, are the rate determining step for the over-all conversion process of SF_6 into products. This should explain the observed dependence of both SF_6 and O_2 concentration, in fact the concentration of SF_x radicals is directly related to $|SF_6|$ and that of O-atoms to $|O_2|$ (see figure 2).

The absence of SOF_2 in appreciable amounts at any times should be considered an indication that reaction (3) is very rapid in presence of high values of F-atom concentrations; in fact a drastic lowering of $|F|$, observed when Si samples are introduced in the discharge stream, leads to the appearence of SOF_2 among the discharge products and to a decrease of SOF_4. It can also be observed from the inspection of figure 3 that the conversion into SO_2F_2 closely parallels that into SOF_4. This should exclude any direct significant transformations between the two oxyfluorides under the present conditions.

REFERENCES

(1) a) R. Heinecke, Standard Telecomunications Laboratory CVD, Project RP7-78 Annual Report, 1972 (unpublished); b) J. J. Wagner and W. W. Brand, in "Proceedings of the Fourth International Symposium on Plasma Chemistry", Zürich, 1979; c) T. S. Chuang, J. Chem. Phys., 74, 1453 (1981); d) R. d'Agostino and D. L. Flamm, J. Appl. Phys., 52, 162 (1981).

(2) J. W. Coburn and M. Chen, J. Appl. Phys., 51, 3134 (1980).

(3) R. d'Agostino, F. Cramarossa, S. De Benedictis, G. Ferraro, J. Appl. Phys., (to be published).

(4) G. Bruno, P. Capezzuto, F. Cramarossa, J. Fluorine Chemistry, 14, 115 (1979).

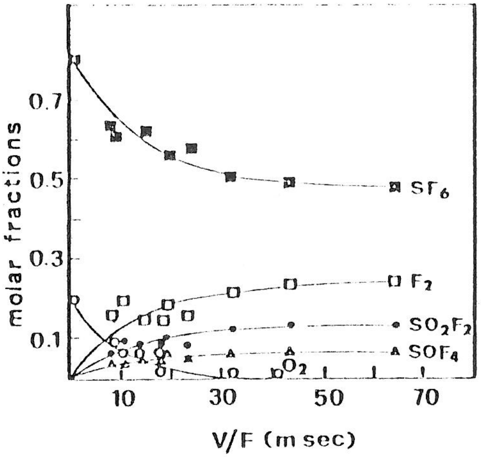

Fig. 1 - Molar fractions of main stable products vs. space-time at 20% O_2 in feed.

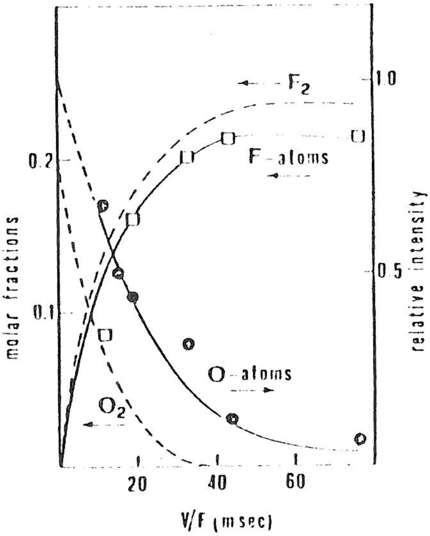

Fig. 2 - F, F_2, O_2 molar fractions and O-atom relative emission intensities vs. space-time.

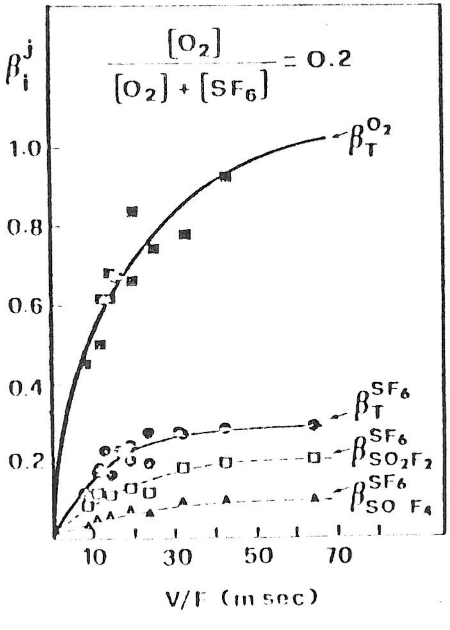

Fig. 3 - O_2 and SF_6 total conversions and SF_6 partial ones vs. space-time. Full curves are calculated (see text).