Article

Kinetic Analysis of the Chemical Processes in the Decomposition of Gaseous Dielectrics by a Non-Equilibrium Plasma - Part 2: SF_6 and SF_6/O_2.

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Neste trabalho é realizada a simulação numérica da decomposição em fase gasosa de SF_6 e misturas de SF_6/O_2, na presença de silício. São determinadas as velocidades relativas dos processos individuais, o efeito da incerteza dos parâmetros e os coeficientes de sensibilidade. Os resultados são comparados com dados experimentais encontrados na literatura e resultados calculados previamente para a corrosão do silício, a fim de ajustar os parâmetros do modelo. À semelhança do que acontece com o CF_4, o principal agente de corrosão é o flúor atômico e a concentração das principais espécies envolvidas depende da composição da mistura. A forma das curvas de sensibilidade segue o formato geral das curvas que representam a velocidade dos processos individuais e a relação entre os coeficientes de sensibilidade calculados para as diferentes etapas de reação é uma medida da contribuição de cada uma ao processo total.

In this work, a numerical modelling analysis of the gas-phase decomposition of pure SF_6 and SF_6/O_2 mixtures, in the presence of silicon was performed. The relative rate of individual processes, the effect of the parameters uncertainties and the sensitivity coefficients were determined. The results were compared with literature experimental data for the plasma etching of silicon and with previous simulated results to adjust the model parameters. As in the CF_4 system, the main etching agent is atomic fluorine and the concentration of the major species depends on the composition of the mixture. The shape of the sensitivity curves follows the general shape of the individual rate curves and the ratio between the calculated sensitivity coefficients is closely related to the contribution of each reaction.

Keywords: sensitivity analysis, rate of production analysis, SF_6 decomposition

Introduction

In a previous paper, the plasma chemistry of pure CF_4 and CF_4/O_2 mixtures has been studied[1]. As discussed in that work, models for the plasma chemistry of SF_6/O_2 and CF_4/O_2 mixtures have been extensively investigated by different research groups[2-19]. These processes are extremely complex to be modelled and solved, considering all the homogeneous processes in the gas phase and the heterogeneous processes occurring at the gas-solid interface[20].

In this work, as explained in more detail in Reference 1, the numerical integration is used to obtain a good understanding of the main chemical processes in the gaseous phase and to estimate the relative importance of individual reactions and the sensitivity coefficients S_{ij} for the species (i) towards the model parameters (λ_j). In solving the chemical sub-model, the other processes are considered in a parameterised, simplified way. Although limited, this approach enables the analysis of the chemical system without the need of invoking the steady-state approximation and provides information about the key processes.

Formulation of the Models

The model of Ryan and Plumb[14], as well as kinetic data of Ryan[11], Kopalidis and Jorné[17] and Khairallah et al.[18], were used as a basis for the present kinetic scheme. Since the main goal of this study was the sensitivity and rate of production analysis[21], only slight modifications were made in the previous proposed models. The model was discussed by Bauerfeldt and Arbilla[19].

Experimental data from Smolinsky and Flamm[22], for CF_4/O_2 mixtures, were used to choose the boundary conditions. In that work, the total gas number density was 1.6×10^{16} cm^{-3} (0.5 Torr) and the gas mixture was excited by a 49 W,

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13.56 MHz discharge. These conditions are not exactly the same as those of the experiments of d'Agostino and Flamm[23]. In their work, the SF_6/O_2 mixtures at a total gas number density of 3.0×10^{16} cm^{-3} (1.0 Torr) in a 5 cm length aluminium tube with 27 ccSTP/min flow rate, were excited by a 45 W, 27 MHz discharge. The analysis of the stable products was performed by infrared spectroscopy/gas chromatography and gas chromatography/mass spectrometry. Oxygen and fluorine atoms were observed by emission spectroscopy. Nevertheless, the conditions of the work of Smolinsky and Flamm[22], for CF_4/O_2, were preferred in order to compare the present simulation with the results of Part 1[1].

Further details on the formulation of this sub-model can be found in our previous papers[1,19].

The Numerical Method

The differential equations were solved using the Runge-Kutta-4-Semi-Implicit Method[24] as implemented in the kinetic program KINAL[25]. The kinetic results were analysed by comparing the relative importance of each reaction, in other words, by calculating the contribution of each step to the total rate of concentration change for each specie. The sensitivity coefficients[26] were calculated by the Direct Decomposed Method[27] in order to estimate the effect of parameters' uncertainties on the predicted concentrations. Since some of the parameters and coefficients, such as electron number density, branching ratios and heterogeneous reaction rate constants, are very difficult to evaluate, an additional test was done by changing some of the parameters within their range of uncertainty.

Results and Discussion

Pure SF_6

The chemical model for the SF_6 and SF_6/O_2 plasmas used in the etching of silicon was studied previously in our laboratory[19]. This model consists of a set of dissociation, gas phase recombination, and solid phase association (surface adsorption, reaction and further desorption) reactions. The complete reaction set and boundary conditions may be found in our earlier paper[19], as well as the results for the kinetic simulation. An initial relevance analysis was also performed in that work. Initial conditions for the simulation are listed in Table 1 and are the same as used in reference 19.
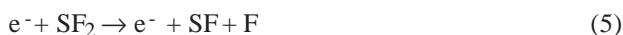
As in our previous work on CF_4 and CF_4/O_2 systems[1] and, also, as considered by other authors[14], we assumed that a negligible loss of free radicals occurs at the walls. The reaction set model and the general approach were very similar to that of pure CF_4 system[1].

Table 1. Numerical simulations initial conditions.

Temperature	313K
Total pressure	0.5 Torr
Flow	24.37 cm^3 STP/min
Plasma length	5.0 cm
Initial Concentrations (molecules cm^{-3})	
Total [M]	1.54×10^{16}
[F]	1.00×10^{10}
[Si]	1.00×10^{14}

The experimental results of d'Agostino and Flamm[23] were used for comparison. Evidences from other experimental works[7,11,17,18] were taken into account.

The SF_6 dissociation may be assumed to occur by the following set of reactions:

$$e^- + SF_6 \rightarrow e^- + SF_5 + F \tag{1}$$

$$e^- + SF_5 \rightarrow e^- + SF_4 + F \tag{2}$$

$$e^- + SF_4 \rightarrow e^- + SF_3 + F \tag{3}$$

$$e^- + SF_3 \rightarrow e^- + SF_2 + F \tag{4}$$

$$e^- + SF_2 \rightarrow e^- + SF + F \tag{5}$$

$$e^- + SF \rightarrow e^- + S + F \tag{6}$$

The experimental evidence of several publications[28,29] suggests that SF_6 breaks down to SF_2 very fast, on a time scale that is short with respect to that required for further reaction of the dissociation fragments. So, Ryan and Plumb[14] considered the production of SF_2 as a "direct" process, within the framework of their model:

$$e^- + SF_6 \rightarrow e^- + SF_2 + 4F \tag{7}$$

The rate for reaction 7 was calculated by scaling the experimental value of Phelps and Van Brunt[30], to fit the data of d'Agostino and Flamm[23]. The other possibility is to consider, in an explicit way, each of the dissociation steps (reactions 1 to 4)[17]. A good description of the system is obtained using the dissociation rate of reference 30, for reaction 1 in combination with the estimated electron density for the experiments of reference 23, and considering reactions 2 to 4 to be fast enough so that the primary process (reaction 1) becomes the determinant step.

Both possibilities were considered in these simulations. In a first approach, k_7, was set as 28 s^{-1} and k_1 was set as zero, k_j being the rate constant for reaction j. In a second approach k_1 was set as 56 s^{-1}, k_7 was set as zero and k_2 to k_6 were set an order of magnitude higher than k_1. The integration of the rate equations shows that the results for F atom in the plasma region differ in about 7% and the values for the SF_6 loss differ in less than 3%. So, the comparison of modelling results with experimental data of etching rate and of SF_6 conversion would

not give insight to this point. The main differences are obtained for the SF_2 and SF_5 concentrations. Considering that the primary dissociation occurs by reaction 1, the SF_5 concentration is 1.8 times higher and the SF_2 concentration is one order of magnitude lower. We interpret these results as an indication of the need to determine the intermediates concentration in the experimental system, in order to choose between one of the previous reaction sequences.

The effect of the electron number density on the modelling results was also investigated: a factor of two in this parameter changes the fluorine atom concentration by a factor of about 1.3. The results shown in this work were obtained with an electron number density of 1.0×10^{10} cm^{-3} and considering reaction 7 as the main path of SF_6 decomposition.

For the simulation conditions, a residence time of 1.0×10^{-3} s is equivalent to a linear distance of 0.22 cm (origin of the plasma region) and a residence time of 2.25×10^{-2} s is equivalent to 4.98 cm (end of the plasma region). The space beyond 5.0 cm, equivalent to a linear time greater than 2.26×10^{-2} s, is the "afterglow" region, where the reactive species continue reacting towards equilibrium. Using this time scale, the comparative rates of individual processes for the main gaseous species are displayed in Table 2. As shown by these results, the species SF_x recombine rapidly with F atoms. In fact, in pure SF_6, the main reactions of F atoms are with SF_x radicals:
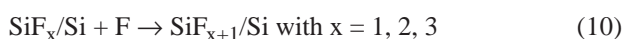
$$SF_x + F + M \rightarrow SF_{x+1} + M \text{ with x = 1, 2, 3, 4, 5} \qquad (8)$$

The symbol M is used for a non reacting molecule, as usual. The main reactions are with SF_2, SF_4 and SF_5, which take account for 80%-90% of fluorine consumption, depending on the distance of the discharge origin. The recombination reaction to give gaseous F_2 represents about 10% in the origin of the plasma region and less than 8% in the middle of the reactor.

Surface reactions are artificially more important in the origin of the plasma region as a consequence of the boundary and initial conditions used in the computer simulation. For the selected residence times and initial values of $[Si]_{initial}$ and $[SF_6]_{initial,}$ the number of Si atoms in the surface decreases rapidly. If the number of active sites had been considered constant during the whole process, the rate of attack to the surface would be proportional to the fluorine atoms concentration, since the solid phase association reaction:

$$Si + F \rightarrow SiF/Si \qquad (9)$$

was considered as the rate determining step.

For pure SF_6, the main stable gaseous products are SiF_4 and F_2. These products are formed by the set of reactions:

$$SiF_x/Si + F \rightarrow SiF_{x+1}/Si \text{ with x = 1, 2, 3} \qquad (10)$$

$$SiF_4/Si \rightarrow SiF_4 \qquad (11)$$

and

$$2F + M \rightarrow F_2 + M \qquad (12)$$

$$2F(s) \rightarrow F_2(s) \qquad (13)$$

$$F_2(s) \rightarrow F_2 \qquad (14)$$

Table 2. Contribution of individual reactions to kinetic processes in the plasma region.

Process	Rate (particles cm^{-3} s^{-1})		
	Pure SF_6	25% O_2 / 75% SF_6	80% O_2 / 20% SF_6
Main reactions for SF_2 radicals			
$e + SF_6 \rightarrow e + SF_2 + 4F$	$4.013 \times 10^{+17}$	$2.749 \times 10^{+17}$	$3.832 \times 10^{+16}$
$SF_3 + SF_3 \rightarrow SF_2 + SF_5$	$2.816 \times 10^{+17}$	$7.604 \times 10^{+16}$	$1.654 \times 10^{+8}$
$SF_2 + O(^3P) \rightarrow SOF + F$	zero	$-6.168 \times 10^{+16}$	$-3.807 \times 10^{+16}$
$SF_2 + F + M \rightarrow SF_3 + M$	$-6.821 \times 10^{+17}$	$-2.908 \times 10^{+17}$	$-2.505 \times 10^{+14}$
$SF_2(s) \rightarrow SF_2$	$3.499 \times 10^{+15}$	$7.535 \times 10^{+14}$	$7.250 \times 10^{+11}$
Main reactions for SF_5 radicals			
$e + SF_6 \rightarrow SF_5 + F + e$	$4.013 \times 10^{+17}$	$2.749 \times 10^{+17}$	$3.832 \times 10^{+16}$
$SF_5 + SF_5 \rightarrow SF_6 + SF_4$	$-3.415 \times 10^{+17}$	$-4.573 \times 10^{+16}$	$-3.097 \times 10^{+12}$
$SF_5 + F + M \rightarrow SF_6 + M$	$-6.297 \times 10^{+17}$	$-4.561 \times 10^{+17}$	$-4.753 \times 10^{+15}$
$SF_4 + F + M \rightarrow SF_5 + M$	$5.720 \times 10^{+17}$	$2.316 \times 10^{+17}$	$1.949 \times 10^{+13}$
Main reactions for F atoms			
$e + SF_6 \rightarrow e + SF_5 + F$	$4.013 \times 10^{+17}$	$2.749 \times 10^{+17}$	$3.832 \times 10^{+16}$
$e + SF_6 \rightarrow SF_2 + 4F + e$	$1.605 \times 10^{+18}$	$1.100 \times 10^{+18}$	$1.533 \times 10^{+17}$
$2F + M \rightarrow F_2 + M$	$-1.891 \times 10^{+17}$	$-7.411 \times 10^{+17}$	$-5.942 \times 10^{+17}$
$e + F_2 \rightarrow e + 2F$	$2.165 \times 10^{+17}$	$6.347 \times 10^{+17}$	$4.970 \times 10^{+17}$
$SF_2 + O(^3P) \rightarrow SOF + F$	zero	$6.168 \times 10^{+16}$	$3.807 \times 10^{+16}$
$SOF + O(^3P) \rightarrow SO_2 + F$	zero	$5.444 \times 10^{+16}$	$3.843 \times 10^{+16}$
$SF_4 + F + M \rightarrow SF_5 + M$	$-5.720 \times 10^{+17}$	$-2.316 \times 10^{+17}$	$-1.949 \times 10^{+13}$
$SF_3 + F + M \rightarrow SF_4 + M$	$-1.284 \times 10^{+17}$	$-1.321 \times 10^{+17}$	$-1.555 \times 10^{+14}$
$SF_2 + F + M \rightarrow SF_3 + M$	$-6.821 \times 10^{+17}$	$-2.908 \times 10^{+17}$	$-2.505 \times 10^{+14}$
$SO_2F + F + M \rightarrow SO_2F_2 + M$	zero	$-5.732 \times 10^{+16}$	$-5.191 \times 10^{+16}$
$F \rightarrow F(s)$	$-4.511 \times 10^{+16}$	$-8.930 \times 10^{+16}$	$-7.996 \times 10^{+16}$

The symbols SiF_{n+1}/Si, F(s) and F_2(s) indicate adsorbed species on the surface.

As previously discussed, the recombination reactions of fluorine atoms with the SF_x radicals, dominate the chemistry in the gaseous phase, limiting the conversion of SF_6.
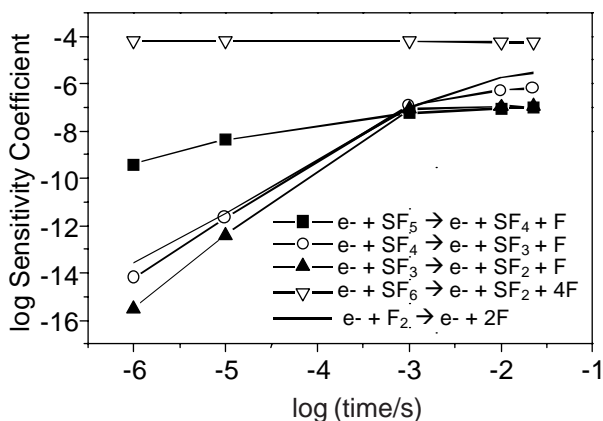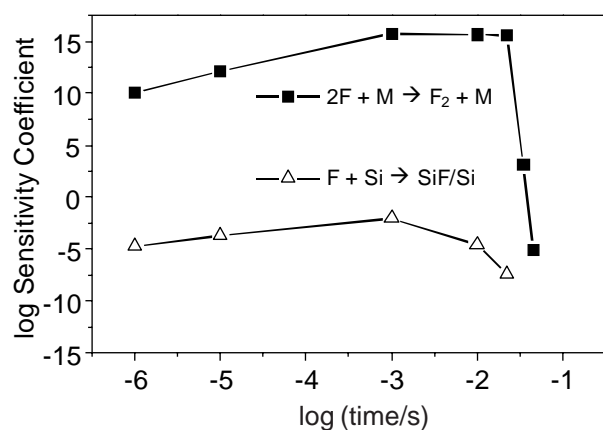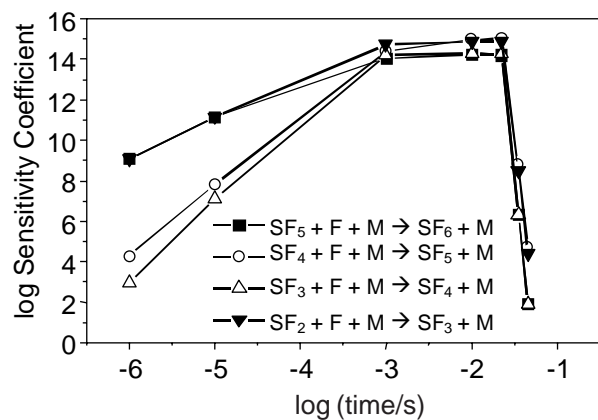

Figure 1. Sensitivity coefficients for atomic fluorine, relative to its production by SF_x and F_2 dissociation reactions, for the plasma etching of silicon in pure SF_6 as a function of time.
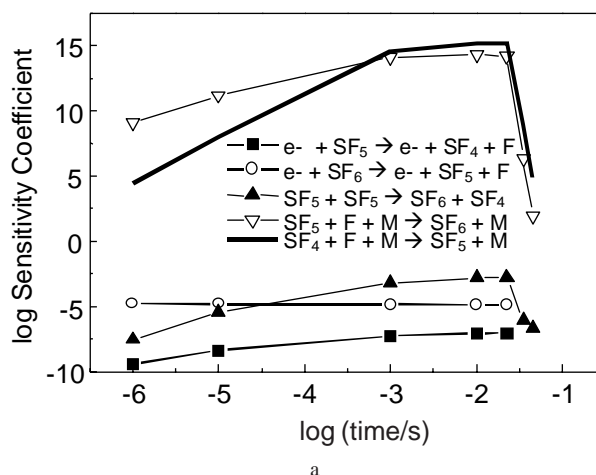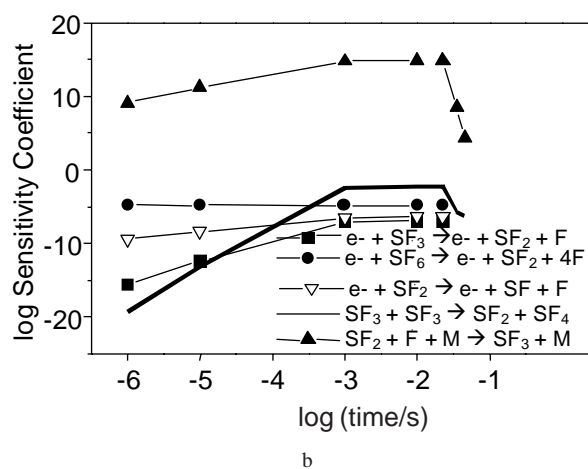

Figure 2. Comparison of sensitivity coefficients for atomic fluorine relative to consumption reactions : production of F_2 and SiF(Si) (2a) and gas phase recombination reactions of SF_x radicals (2b), for the plasma etching of silicon in pure SF_6 .

Figure 3. Sensitivity coefficients relative to the most relevant production and consumption reactions for SF_5 (3a) and for SF_2 (3b) for the plasma etching of silicon in pure SF_6 as a function of time.

For the SF_5 radical the rate of recombination with fluorine atoms is about twice the rate of the self-reaction to give SF_6 and SF_4 radicals. A similar relation is observed for SF_2 radicals.

In Figures 1 - 3, the sensitivity coefficients S_{ij} for the main species towards the parameters of the model are shown. As for the CF_4 plasma, the results stress the conclusions taken up to now: the shape of the sensitivity curves follows the general shape of the individual rate curves and the ratio between the S_{ij} values is closely related to the contribution of each reaction.

When comparing the $S_{F, j}$ coefficients for the electron impact reactions (Figure 1), it is clear that, in these simulations conditions, the degree of products dissociation by electron impact is negligible, that is, the SF_x radicals react rapidly with neutral species rather than dissociating to a SF_{x-1} species plus F atom. Both Table 2 and Figure 2 show that the main sink of atomic fluorine is the molecular gas phase recombination.

Figures 3a and 3b show the sensitivity coefficients for the main SF_5 and SF_2 reactions.

By comparing the $S_{SF5,j}$ values (Figure 3a) it is shown that, at the origin of the plasma region the main source of SF$_5$ radicals is the dissociation of SF$_6$, reaction 1. At the end of the plasma region, recombination reactions become more relevant, mainly the SF$_4$ + F recombination:

$$SF_4 + F + M \rightarrow SF_5 + M \qquad (15)$$

A similar situation arises for SF$_2$ (Figure 3b). The $S_{SF2,j}$ coefficients for the SF$_6$ dissociation, reaction 7, and for reaction 4, clearly reflects the larger contribution of the former to the formation of SF$_2$ (Figure 3b). Both $S_{SF5, e-+SF6\rightarrow e-+SF5+F}$ and $S_{SF2,e-+SF6\rightarrow e-+SF2+4F}$ coefficients do not depend on the distance from the origin, due to the low conversion of SF$_6$. Again, at the origin of the plasma region, SF$_2$ radicals are mainly formed by electron impact dissociation reactions. Nevertheless, for larger concentrations of intermediate products, the recombination reactions of the other radicals become a rather important source of SF$_2$.

The S_{SF2} and the S_{SF5} coefficients for the gas phase recombination reactions :

$$SF_2 + F + M \rightarrow SF_3 + M \qquad (16)$$

and

$$SF_5 + F + M \rightarrow SF_6 + M \qquad (17)$$

are very similar since the rates for both processes are also very similar and are higher than the coefficients for further electron impact dissociation of SF$_2$ and SF$_5$.

SF$_6$ / O$_2$ Mixtures

The experimental evidences[23] show that SO$_2$F$_2$, SOF$_4$ and SO$_2$ appear as the main new products. Also, as O$_2$ concentration increases relatively to SF$_6$ concentration, the amount of SO$_2$F$_2$ increases relatively to SOF$_4$. These results were also observed in our previous simulation[19].

In the presence of O$_2$, oxygen atoms compete with F atoms for the SOF$_x$ and SF$_x$ species. The result is that, in the presence of O$_2$, the fluorine atom concentration increases up to a maximum value. The further decrease in F concentration with added oxygen is due to dilution and to the decrease of electron energy (the latter causes the SF$_6$ electron dissociation rate to decrease).

Figure 4a shows the sensitivity coefficients for the main atomic fluorine formation reactions. At the origin of the plasma region, dissociation of SF$_6$ is clearly the most relevant process. As the atomic oxygen concentration increases, their reactions with SF$_5$ and SF$_2$ to form SOF$_4$ + F and SOF + F, respectively, become competitive with electron impact dissociation and other SF$_x$ reactions.

As in the pure SF$_6$ system, both the individual rates and the sensitivity coefficients S_F are quite similar for the

SF$_x$ + F recombination reactions, being the largest sensitivity coefficient found for the gas phase recombination of atomic fluorine with SF$_5$ (Figure 3a), followed by the coefficients for the recombination reactions with SF$_2$, SF$_4$ and SF$_3$ (Figure 4b). Since oxygen atoms compete with fluorine atoms for these radicals, the relative importance of F$_2$ gas phase formation:

$$2F + M \rightarrow F_2 + M \qquad (18)$$

becomes larger (see Figure 4b and Table 2), being about 40% in the plasma region.

Figures 5a and 5b show the SO$_2$F$_2$ and SOF$_4$ sensitivity coefficients, calculated for the main parameters. The sensitivity coefficients confirm that the main path of formation of SO$_2$F$_2$ is the reaction with O(^{3}P) atoms:

$$SOF_2 + O \rightarrow SO_2F_2 \qquad (19)$$

which is faster than SO$_2$F reaction with F atoms:

$$SO_2F + F + M \rightarrow SO_2F_2 + M \qquad (20)$$
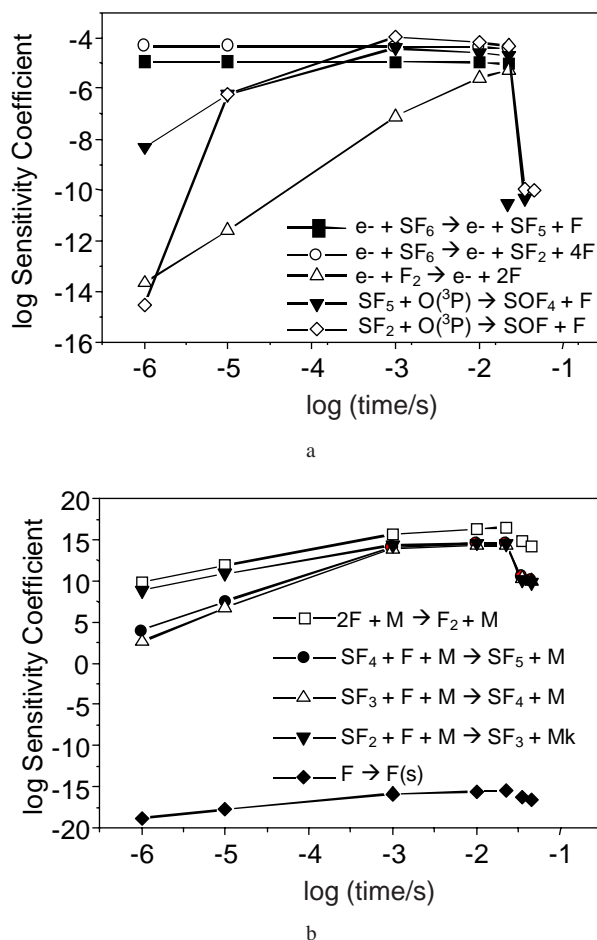

a

b

Figure 4. Sensitivity coefficients for atomic fluorine relative to the most relevant production reactions (4a) and consumption reactions (4b) for the plasma etching of silicon in a mixture 75% SF$_6$ and 25% O$_2$ as a function of time.
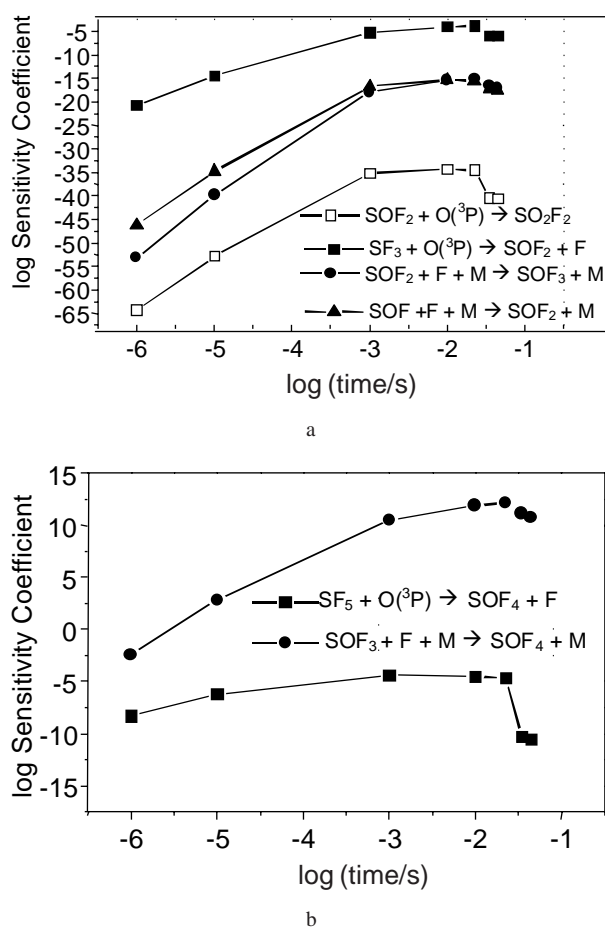
a

b

Figure 5. Sensitivity coefficients relative to the most relevant reactions the production and consumption of SO_2F_2 (5a) and SOF_4 (5b) for the plasma etching of silicon in a mixture 75% SF_6 and 25% O_2 as a function of time.

Fluorine and oxygen atoms compete for SOF_2, the second reaction giving SO_2F_2, being clearly more important in determining SO_2F_2 concentration. Reaction with atomic fluorine:

$$SOF_2 + F + M \rightarrow SOF_3 + M \qquad (21)$$

forms SOF_3, which further reacts to give SOF_4. The main paths forming SOF_4 are:

$$SF_5 + O(^3P) \rightarrow SOF_4 + F \qquad (22)$$

$$SOF_3 + F + M \rightarrow SOF_4 + M \qquad (23)$$

The relative contributions of reaction 23, in comparison with reaction 22, increases as SOF_3 concentration grows up in the reactor. For the 25% O_2 mixture, the $S_{SOF4,SOF3+F \rightarrow SOF4}/M$ coefficient is higher than the $S_{SOF4,SF5+O(3P) \rightarrow SOF4+F}$, confirming that the main path of formation of SOF_4 is through the $SOF_3 + F$ reaction.

In Figure 6 the rate of formation of gaseous SiF_4 as function of the distance from the discharge origin and the mole percent of O_2 in the feed is displayed. A minimum is
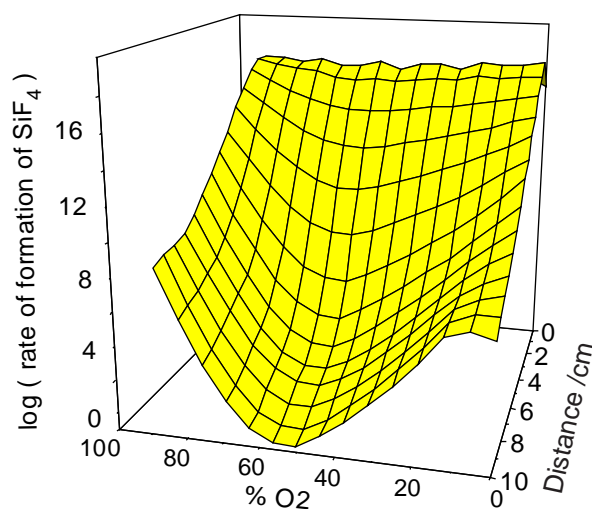

Figure 6. Rate of formation of gaseous SiF_4 as a function of the distance from the discharge origin and the mole percent of O_2 in the feed.

observed in this surface, which corresponds to nearly 50% of O_2 in the afterglow region. From the simulated data, the atomic fluorine concentration is maximum for 50% of oxygen, so that the rate of etching is also maximum and SiF_4 is almost totally formed in the first centimetres of the reactor. In other conditions, the etching rate is slower and the SiF_4 formation is observed through the total length of the reactor. So, the atomic fluorine is considered the active etching agent in this modelling, while the primary etching reaction is rate controlling.

As expected, the concentration of atomic fluorine and the rate of formation of SiF_4, in the plasma region, are higher for the SF_6 and SF_6/O_2 systems than for the CF_4 and CF_4/O_2 systems[1b]. However, in the afterglow region, the inverse is observed, mainly because the recombination of F atoms with the SF_x radicals is faster than the reactions with CF_3 and CF_2. For the boundary conditions of these simulations, the final concentrations of SiF_4 are equal because it is limited by the total number of silicon atoms used in the simulation.

Conclusions

The numerical integration of rate equations has been applied to the study of the gas-phase decomposition of pure SF_6 and SF_6/O_2 mixtures in the presence of silicon.

As expected, the results of this computer simulation are in good agreement with previous results from literature and provide complementary information about these systems. The rate of production and the sensitivity analysis, as well as the computed concentrations, show that the major features of plasma etching of silicon are explained in terms of the gas-phase reactions.

As for the CF_4 and CF_4/O_2 systems, the model was proposed to reproduce the experimental conclusion that atomic fluorine is the active etching agent. The primary etching reaction appears to be the most significant process and the sequential fluorination reactions have no significant sensitivities since their rates were purposely chosen not to be rate controlling.

The kinetic analysis shows that many key processes are poorly known and need a better determination. The major uncertainties in the gas phase chemistry are the branching ratios for the primary dissociation processes, the cross sections for electron impact dissociations and the electron number densities.

A more complete model should include a detailed description of the surface chemistry and the transport of radicals and ions, which were crudely parameterised in this work. Also, the formulation of such a model must involve the consideration of the energy distribution of particles and temperature gradients, reactions of electronically and vibrationally excited species, positive and negative ions chemistry and polimerization reactions.

Acknowledgements

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