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SOME PECULIARITIES OF THE SF_6 AND THE SF_6+O_2 DISCHARGE PLASMA[1]

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The electron distribution functions obtained as a result of the numerical solution of the Boltzmann equation are used for computing some rate coefficients and discharge characteristics in SF_6/O_2 mixtures. Attention is paid to features relevant for gaseous dielectrics and plasmochemical etching agents.

О НЕКОТОРЫХ ОСОБЕННОСТЯХ ГАЗОРАЗРЯДНЫХ ПЛАЗМ SF_6 И SF_6+O_2

Функции распределения электронов, полученные на основе численного решения уравнения Больцмана, использованы для вычисления некоторых коэффициентов и характеристик разряда в смесях SF_6+O_2. Обращено также внимание на черты, относящиеся к газообразным диэлектрикам и плазмохимическим травителям.

I. INTRODUCTION

Sulphur hexafluoride SF_6 in a pure form or in mixtures with other gases appears to be very useful for a wide variety of technological purposes. It is utilized mainly in high-power electrical engineering because of its excellent insulation property, its outstanding quenching property of the electric arc or a relatively high thermal and chemical stability. As a buffer gas SF_6 is added to n-C_3F_7I in a high-power photochemical iodine laser with long pumping time to prevent the pyrolysis inside the active medium [1].

Because of its chemical activity SF_6 discharge plasma has proved to be a suitable plasma etching agent for silicon or silicon oxide. It has been pointed out that the etch rate of SF_6 discharge was by about an order of magnitude higher than that of CF_4 [2]. The discharge plasma serves as a source of a kind of etching agent in which the fluorine atoms are supposed to be the most active. An addition of a certain amount of oxygen to SF_6 exhibits simultaneously a rise of both the production of

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F-atoms and the etch rate [2, 3]. Bruno et al. [4] considered another etching mechanism, which is based on a volume decomposition of SF_6 to the radicals SF_3 and a subsequent chain of reactions on the Si surface. Lately experimental evidence of the reaction of highly vibrationally excited molecules SF_6 with Si or SiO_2 surfaces producing SOF_2 and SiF_4 has been obtained [5, 6]. Thus, for gaining a deeper insight into the etching mechanism, a knowledge of the kind, the concentration and the energy of active particles impinging on the Si, SiO_2 surface would be very useful.

The most important processes — excitations, electron attachment, ionization or particle fragmentation, are primarily controlled by the gas particle collisions with the electrons [7]. Knowing the electron distribution function and the cross sections the collisional frequencies or other parameters of the electron gas can be calculated in dependence on the discharge conditions enabling us to draw conclusions about the mechanisms of the processes in question.

II. RESULTS AND DISCUSSION

Electron distribution functions were obtained numerically by solving the Boltzmann equation in the form reported in [8] for the electron gas in mixtures of SF_6 with different oxygen contents, changing the reduced electric field E/N from 2 to 60×10^{-16} V cm^2. Collisional cross sections for SF_6 were taken from [9], for molecular oxygen from [8, 10].

Calculations in pure SF_6 and in pure molecular oxygen render the limiting cases shown in Fig. 1 for three values of E/N. It is shown in Fig. 2 that at lower values of E/N the number of high energy electrons of the distribution decreases with increasing oxygen contents. Starting approximately from $E/N = 2 \times 10^{-15}$ V cm^2 an addition of O_2 to SF_6 enriches, on the other hand, the tail of the distribution with electrons. The effect of oxygen addition can be also demonstrated by the dependence of the mean kinetic energy of electrons $\bar{U}$ on the percentage of oxygen in SF_6, which is shown in Fig. 3. While for $E/N < 2 \times 10^{-15}$ V cm^2 $\bar{U}$ decreases moderately with the oxygen addition, for $E/N > 2 \times 10^{-15}$ V cm^2 this dependence is reversed. From the view-point of the gaseous dielectrics the addition of oxygen to SF_6 is not desirable in any case as it impairs the dielectric strength of SF_6. It is determined by the limiting value of $(E/N)^*$ at which the ionization (characterized by Townsend ionization coefficient α/N) is fully balanced by the electron attachment (dissociative attachment coefficient η/N) [9, 11]. The calculations on the basis of the distributions attained show that the dielectric strength $(E/N)^* \approx$ $\approx 3.70 \times 10^{-15}$ V cm^2 of the pure SF_6 decreases almost linearly with the growth of the oxygen contents to the value of $(E/N)^* \approx 1.10 \times 10^{-15}$ V cm^2 of the pure oxygen. There is a different situation in case of mixtures of $SF_6 + N_2$ or SF_6 + air with a suitable ratio of their components by the use of which a profitable compromise between requirements on the dielectric strength and price relations can be accomplished [12].

Other aspects of SF_6 or $SF_6 + O_2$ become important if they are to serve as plasma discharge etching agents. When Si or SiO_2 are etched, an effluent product is SiF_4, e.g. in the reaction [3]:

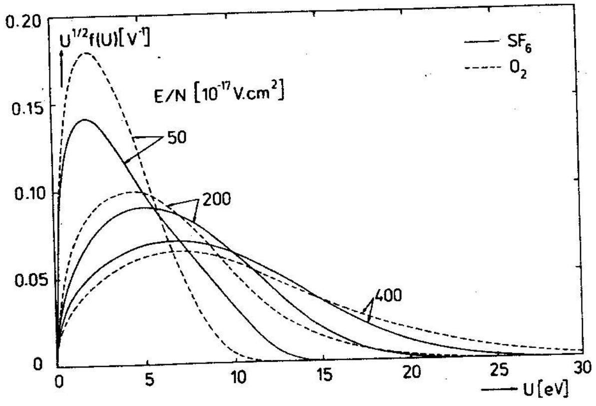

Fig. 1. Electron distribution functions in pure SF_6 (solid lines) and in pure oxygen (dashed lines) for three values of the reduced electric field E/N.

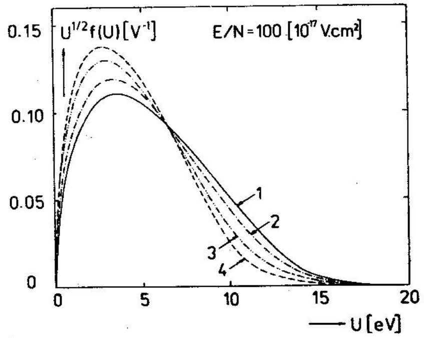

Fig. 2. Electron distribution functions in pure SF_6 (curve 1), pure O_2 (curve 4) and in their mixtures (curve 2 — ratio of SF_6 to O_2 4 : 1, curve 3 — ratio 3 : 2) for $E/N = 1 \times 10^{-15}$ V cm^2.

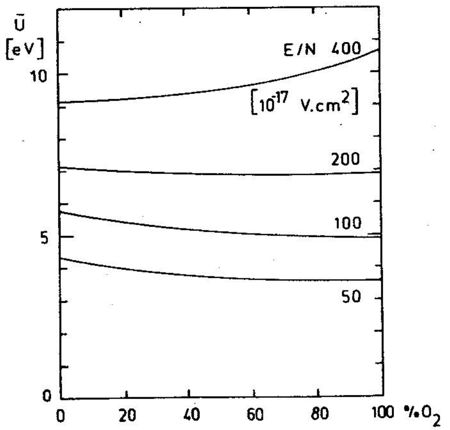

Fig. 3. Electron mean kinetic energy vs percentage of oxygen in $SF_6 + O_2$ mixture. The parameter of the curves in E/N.

$$Si + 4\,F \rightarrow SiF_4 \quad \text{or} \quad SiO_2 + 4\,F \rightarrow SiF_4 + O_2. \tag{1}$$

Agostino et al. listed possible sequences of the collisional processes for releasing free fluorine in the SF_6 discharge for both with and without oxygen in [2]. As the main decomposition processes yielding the fluorine species they quote the dissociative attachments:

$$e + SF_x \rightarrow SF_{x-1} + F^- \qquad (x = 4-6) \tag{2}$$

$$e + SF_x \rightarrow SF_{x-1}^- + F. \tag{3}$$

The detachment processes and the dissociation may also contribute to the rise of the atomic fluorine:

$$e + F^- \rightarrow F + 2e \tag{4}$$

$$e + SF_x \rightarrow SF_{x-1} + F + e \tag{5}$$

$$e + F_2 \rightarrow F + F + e. \tag{6}$$

If oxygen is added to SF_6, F-atoms are released likewise by oxidation of the radicals SF_x:

$$O + SF_5 \rightarrow SOF_4 + F \tag{7}$$

$$O + SF_3 \rightarrow SOF_2 + F. \tag{8}$$

By the present calculations we obtain the dependences of the rate constants on the amounts of oxygen in SF_6 multiplied by the relative concentration of the pertinent component of the $SF_6 + O_2$ mixture; they are plotted in Fig. 4 for $E/N = 100 \times 10^{-17}$ V cm². It can be seen that among the most abundant sources of the fluorine species mainly reaction (3) must be considered. Unfortunately, owing to the lack of a detailed knowledge of the dissociation and excitation cross sections the curve E in Fig. 4 represents the summary excitation rate coefficient. In any case, if compared with the curves SF_5^- and F^- it indicates that the dissociation can contribute through reaction (5) to the F-atom production as well. The curves representing the main production of fluorine and oxygen atoms cross each other within the interval from 20 to 40 percent of O_2 in which Agostino et al. [2] found the maximum of the etch rate.

Even if the production of the vibrationally excited molecules appears to be the highest in Fig. 4 the maximum of the etch rate in the $SF_6 + O_2$ discharge cannot be explained by the mechanism suggested in [5]. An addition of the oxygen should rather decrease the population of the vibration states of the SF_6 molecule owing to the vibrational-translational transitions. The present calculations support the etching mechanism discussed in [2, 3]. However, a possible source of the fluorine atoms as the most active particles need not be the dissociative attachment processes only but the direct disssociation as well. The particle balance equations should be solved to obtain a deeper insight.

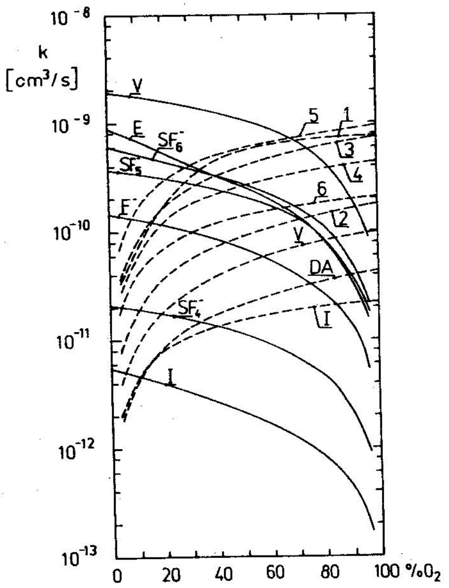

Fig. 4. Production rates as a function of the oxygen contents of the $SF_6 + O_2$ mixture for $E/N = 1 \times 10^{-15}$ V cm². Full lines are related to the species of the SF_6 components: V — vibrationally excited, E — electronically excited, SF_6^-, SF_5^-, SF_4^-, F^- — negative ions, I — positive ions. Dashed lines mark the rates of the oxygen species: V — vibrationally excited, DA, I — negative and positive ions, 1—6 electronically excited molecules with the excitation thresholds 0.98, 1.63, 4.50, 5.16, 7.20, 9.70 eV, respectively.

III. CONCLUSION

Two distinct features of the dependence of the electron distribution in $SF_6 + O_2$ on the electric field strength can be distinguished. At lower values of E/N the maximum of the distribution shifts to the origin of the energy scale and the tail is reduced with the growth of the portion of oxygen contents, at a high E/N the trends are opposite. The calculations reveal a roughly linear decrease of the dielectric strength $(E/N)^*$ of the $SF_6 + O_2$ mixture with the growth of the oxygen contents. Under the discharge conditions the calculations show that the fluorine and the oxygen atoms are produced with high rates; this supports their significant role in the etching mechanism. In view of the high production of the vibrationally excited molecules of SF_6 by the electrons their share in the etching mechanism cannot be ignored especially if they are generated exclusively by a laser radiation in which case an etching of the glass materials has been proved [5].

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