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POSITIVE AND NEGATIVE IONS IN SF₆ PLASMA USED FOR ETCHING.

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ABSTRACT

The positive and negative ions issued from a radiofrequency discharge in SF₆ have been identified by mass spectrometry. The major positive ions are SF₃⁺ and SF₅⁺, the negative ions are SF₃⁻, SF₅⁻, F⁻ and S₂F⁻. The electron and ion density measurements, obtained from Langmuir probe, give evidence of electron attachment.

\( n_e \sim 10^8 - 10^9 \text{ cm}^{-3}, n_+ = n_- \approx 10^{10} \text{ cm}^{-3} \). A kinetic scheme is proposed.

1. INTRODUCTION

The chemical reactivity of SF₆ plasma with regards to silicon and other materials concerned with integrated circuits (refractory metals, silicides, polyimides) is recent use of SF₆ gas.

Opposite to freons SF₆ does not deposit polymer films on the surface in contact with the plasma. However, concerning the plasma itself, the use of SF₆ greatly complicates the reactionnal medium. There are two reasons for that : firstly a great number of secondary products are formed, especially when a SF₆ – O₂ mixture is used (1) (2) (3) and secondly the SF₆ molecule has a high electron attachment (4).

The aim of this paper is to present the experimental results obtained from the mass spectrometry and the Langmuir probe analysis of SF₆ r.f plasma. The composition of the SF₆ plasma was determined : the neutral molecule concentration, the identification of the positive and the negative ions, the determination of the ion and the electron densities and the electron temperature. The influence of the etching reactor parameters was investigated : pressure (20 - 200 mtorr), silicon area to be etched (0 - 40 cm²), flow rate (8 - 40 sccm), r.f. power (10 - 70W).

From these results, the main reactions involved in the SF₆ plasma will be discussed and a reaction scheme for the generation of atomic fluorine proposed.

2. EXPERIMENTAL APPARATUS

The apparatus used has already been described (3). The main features will be briefly given here. The particles are extracted from the r.f. plasma through a sampling orifice of 200 µm in diameter and 200 µm in length drilled in a Macor ceramic probe disposed at the wall of the alumina tube. A differential pumping system assures the secondary vacuum behind the probe. The quadrupole mass filter (m/e = 1 - 300) is placed in view of the sampling orifice. For the detection of positive or negative ions, a cylindrical electrostatic lens placed behind the probe is biased in order to optimize the intensity of the ion beam.
The Langmuir probe consists of a tungsten wire of 0.46 mm in diameter and 6 mm in length. A r.f. choke is placed in the electrical circuit used to measure the probe characteristic: \( i = f(V) \).

The purity of \( \text{SF}_6 \) gas is better than 99.85 % (\( \text{O}_2 \) < 500 ppm, \( \text{N}_2 \) < 500 ppm, \( \text{H}_2\text{O} \) < 15 ppm, \( \text{CF}_4 \) < 15 ppm).

### 3. ANALYSIS BY MASS SPECTROMETRY.

#### 3.1. Positive ion detection

Figure 1 shows the evolution of the positive ion currents \( i(\text{SF}_6^+) \) (\( n = 1-5 \)) and \( i(\text{SOF}_3^+) \), as a function of the pressure. A 20 cm\(^2\) silicon area considerably modifies the ion current intensities. An increase in \( i(\text{SF}_3^+) \) and especially in \( i(\text{SF}_2^+) \) is observed. \( \text{S}_2\text{F}_7^+ \), \( \text{S}_2\text{F}_5^+ \) and \( \text{SiF}_3^+ \) are detected. At the same time the concentration of \( \text{SF}_4 \) in the discharge is increased. This brings evidence that \( \text{SF}_3^+ \) and \( \text{SF}_2^+ \) are in part due to \( \text{SF}_6 \) ionization.

The increase in \( i(\text{S}_2\text{F}_7^+) \) and \( i(\text{S}_2\text{F}_6^+) \) in presence of a silicon sample is in agreement with the formation reaction:

\[
\begin{align*}
[1] \quad & \text{SF}_3^+ + \text{SF}_6 \rightarrow \text{S}_2\text{F}_7^+ + \text{F}_2 .
\end{align*}
\]

#### 3.2. Negative ion detection

The negative ions are extracted from the \( \text{SF}_6 \) plasma by means of a positive bias of the electrostatic lens placed behind the sampling probe. The results obtained as a function of the power are given in Figure 2. Four negative ions were detected: \( \text{SF}_3^- , \text{SF}_5^- , \text{F}^- \) and \( \text{S}_2\text{F}_7^- \).

Despite its high formation cross-section the \( \text{SF}_6^- \) ion was not detected. In similar conditions, Lergon et al. (4) did not observe this ion either, but evidence of its existence was given during experiments on electron beam – \( \text{SF}_6 \) interaction (5). Its absence in the discharge is attributed to the auto-detachment reaction and to the ion-molecule reaction:

\[
\begin{align*}
[2] \quad & \text{SF}_6^- + \text{SF}_6 \rightarrow \text{SF}_5^- + \text{F} + \text{SF}_6
\end{align*}
\]

The formation of the detected negative ions (especially \( \text{SF}_3^- \) and \( \text{SF}_5^- \)) is attributed to the dissociative attachment reactions:

\[
\begin{align*}
[3] \quad & \text{e}^- + \text{SF}_6 \rightarrow \text{SF}_5^- + \text{F}
\end{align*}
\]

The ion-molecule reaction [2] may also contribute to \( \text{SF}_5^- \) formation.

In the \( \text{SF}_6-\text{O}_2 \) plasma many other kinds of negative species were observed such as: \( \text{O}_2^- , \text{SOF}_3^- , \text{SOF}^- , \text{SO}_2\text{F}^- , \text{SOF}_2^- \).

### 4. LANGMUIR PROBE DIAGNOSTIC

In the \( \text{SF}_6 \) electronegative discharge one defines \( n_e \) electron density, \( n_- \) negative ion density, \( n_+ \) positive ion density, \( T_e \) electron temperature.

Setting \( \beta = n_0^- / n_- \) and thus \( n_0^- / n_- = 1 - \beta \). The probe characteristics \( i = f(V) \) obtained in the Ar-\( \text{SF}_6 \) plasma shows that a progressive addition of \( \text{SF}_6 \) leads to a decrease in the current intensity of the negative branch \( I_- \). This result brings evidence of the electronegative character of the \( \text{SF}_6 \) plasma.
The method of analysis of the $i = f(V)$ probe characteristic is that of Doucet (6). In a pure SF$_6$ plasma the following values have been obtained: $n_e = n_- = 10^{10}$ cm$^{-3}$, $v_e = 10^8$ to $10^9$ cm$^{-3}$, $kT_e = 4 - 10$ eV, depending on the conditions of pressure, power and gas mixture. An increase in $kT_e$ is observed when $n_e$ decreases. This is attributed to the fact that electron attachment consumes the low energy electrons and thus shifts the mean energy of the resulting electron distribution towards higher energies (Fig. 3).

It is observed that either in SF$_6$, or in SF$_6$–Ar mixtures where [SF$_6$] > 10%, the mean plasma potential $V_g$ is negative (-20 to -40 V) compared to the grounded electrode. This result, in agreement with other authors (7) (8), indicates that the electrodes are bombarded by negative ions during some part of the period.

5. REACTION SCHEME IN AN SF$_6$ DISCHARGE

By the use of the inelastic collision cross-sections $e^- -$ SF$_6$, $e^- -$ SF$_6$ and $e^- -$ F$_2$ (9) (10) the rate constants of different processes have been calculated for a Maxwellian electron distribution. Then by using the values for the concentrations of the species measured either by mass spectrometry or Langmuir probe, the production rates for the main reactions have been estimated. The reaction scheme thus obtained is represented in Figure 4.

This kinetic scheme gives rise to the following remarks. The dissociative ionization reactions producing SF$_n^+$ and the dissociative attachment reactions producing SF$_n^+$ are two important sources of atomic fluorine.

The rate constant $k_x$ obtained for electronic excitation of SF$_6$ is too low (<10$^{-13}$ cm$^3$ sec$^{-1}$) to explain the SF$_4$ concentration. The existence of a SF$_6$ fragmentation mechanism by electron impact which produces neutral radicals SF$_n^-$ ($n < 5$) and for which the rate constant $k_d$ is two or three times greater than $k_x$ (i.e., 10$^{-11}$ - 10$^{-10}$ cm$^3$ sec$^{-1}$) must be assumed.

The production rates of atomic fluorine given by the scheme of Figure 4 show that three reaction types (ionization, attachment, dissociation) must be considered.

6. CONCLUSION

The analysis of a SF$_6$ r.f. discharge by means of mass spectrometry and Langmuir probe was performed.

Three groups of electron – SF$_6$ reactions are involved in the decomposition of the molecule: electron dissociative attachment, shown by electron and ion density measurements and by the detection of three main negative ions i.e. SF$_6^-$, SF$_5^-$ and F$^-$; SF$_6$ and SF$_4$ dissociative ionization which leads mainly to SF$_3^+$ and SF$_3^+$; electron impact dissociation which explains the SF$_4$ formation. All these kinds of reactions contribute to the production of the atomic fluorine which etches the silicon.

A critical examination of the influence of discharge parameters upon both the positive and negative ion intensities and neutral molecules enables a reaction scheme of the discharge to be proposed.

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Fig. 1. Positive ion intensities as a function of pressure (50 W, 10 sccm, A(Si) = 0).
Fig. 2. Negative ion intensities in $\text{SF}_6$ plasma as a function of power (0.13 torr, 20 sccm).

Fig. 3. $n_+$, $n_-$, and $n_e$, $T_e$ in $\text{SF}_6$ plasma as a function of pressure (25 W).
Fig. 4. Elementary processes in a SF₆ rf discharge for F atom generation. (200 mtorr, 50 W).

production rates $r \times 10^{13}$ cm⁻³ sec⁻¹ indicates the detected species.