OPTICAL SPECTROSCOPY AND MASS SPECTROMETRY STUDIES OF SF$_6$ AND CF$_4$ HOLLOW CATHODE RIE PLASMAS

L. L. Tezani$^1$, R. S. Pessoa$^{1,2}$, G. Petraconi$^1$ and H. S. Maciel$^1$

$^1$Laboratório de Plasmas e Processos, Departamento de Física, Instituto Tecnológico de Aeronáutica, 12228-900, S. J. dos Campos, SP, Brazil.

$^2$IP&D, Universidade do Vale do Paraíba, 12244-000, S. J. dos Campos, SP, Brazil.

Abstract: In this work the optical emission spectroscopy and neutral mass spectrometry techniques are used to monitor pure SF$_6$ and CF$_4$ plasmas and/or its mixture or mixed with O$_2$. These plasmas were generated in a radiofrequency Hollow Cathode Reactive Ion Etching reactor at the following constant experimental condition: gas pressure at 26 mTorr, flow at 20 sccm and discharge power at 150W. Through the mass spectra was observed a high concentration of gas source species SF$_5^+$, SF$_4^+$, CF$_3^+$ and CF$_2^+$ in the plasma. The presence of other species such as SF$_4^+$, SF$_2^+$, SF$^+$ and CF$^+$ was observed in lower quantity (< 1% in total gas pressure). The atomic fluorine was not observed in all experiments, for this reason we used also the actinometry method in order to monitor its density during plasma. High density order of (0-13)×10$^{17}$ m$^{-3}$ of atomic fluorine was observed in all experiment, being the highest obtained with the addition of low flow of O$_2$ in SF$_6$ and CF$_4$ plasma mixture.

Keywords: Hollow Cathode Reactive Ion Etching; Sulphur hexafluoride; Carbon tetrafluoride; Optical spectroscopy; Mass spectrometry.

1. Introduction

The chemistry study of radiofrequency (RF) sulphur hexafluoride (SF$_6$) and carbon tetrafluoride (CF$_4$) plasma, either pure or mixed with other gases such as oxygen (O$_2$), is growing every day due different applications in semiconductor industry [1]. Currently, in the field of microelectronics, SF$_6$ and/or CF$_4$ plasma etching of materials such as silicon (Si), silicon dioxide (SiO$_2$), silicon carbide (SiC) and others, is used in micro-scale for making microelectromechanical systems (MEMS), trenches crossroads, for formation of isolation channels, etc [2]. However, in this field of application, not all processes involved in the formation of plasma and interaction between the plasma particles and etched surface are fully understood, so the study of SF$_6$ and CF$_4$ plasma chemistry is essential to better control the generation of reactive species in plasma and consequently the process outcome.

Several steps are usually involved in the process of fluorinated plasma etching. Initially reactive particles are generated in plasma by dissociation of neutral gas molecules by electron impact, and then these particles are directed to the material surface by diffusion where they are adsorbed. Subsequently, volatiles products are formed through chemical reactions that are desorbed from the surface being removed by vacuum system (if the reaction product is not volatile is formed a passivated film) [3]. In the case of SF$_6$ and CF$_4$ molecules, these are dissociated (SF$_6$+e→S$_x$F$_y$ or (S$_x$F$_y$)+n$_e$+e, where x = 1-2, y = 1-5 and n = 1-5 and 2CF$_4$+e→CF$_3$+CF$_2$+3F+e) to generate atomic fluorine (F) which is the main agent in the silicon etching due to its high affinity. With the addition of O$_2$ can be observed a higher production of F through the chemical reaction O+SOF$_x$→ SF$_x$+F for low concentrations of oxygen in SF$_6$ plasmas and O+COF$_y$→CF$_y$+F to CF$_4$ plasmas [4]. Being the monitoring of the species generated in plasma important for efficient control of the etching process.

In this work the optical emission spectroscopy and neutral mass spectrometry techniques are used to monitor pure SF$_6$ and CF$_4$ plasmas and/or its mixture or mixed with O$_2$. These plasmas were generated in a radiofrequency (RF) Hollow Cathode Reactive Ion Etching (HCRIE) reactor. Moreover, through the use of actinometry method the concentration of atomic fluorine was determined.

2. Experimental

This work was carried out using a HCRIE reactor. This reactor differs from conventional parallel plate RIE reactor due adaptation of a cylinder electrode on self-bias electrode as can be seen in Fig. 1. For more details about the reactor geometry and physics see ref. [2].
The vacuum system consists of two pumps that are combined to achieve a working pressure about \(10^{-2}\) Torr. The first is a mechanical pump (E2M-80 - Edwards) and the second a roots-type pump (EH500 - Edwards), thus providing an effective pumping speed of 110 L/s. The fluorinated gases used in this study were SF₆ (purity = 99.99\%) and CF₄ (purity = 99.99\%), such gases were mixed together or with O₂ (99.99\%), keeping the total flow constant in 20 sccm and a pressure of 26 mTorr. For the generation of the plasma a 13.56 MHz RF power source was used (ATX600 - Advanced Energy) which allows for rf powers in the range of 100-600 W. In this work the RF power was fixed at 150W.

**Figure 1.** Schematic diagram of the hollow cathode RIE reactor with the plasma diagnostic tools. Distance values are in cm.

### 2.1 Optical emission spectroscopy and actinometry method

The optical characterization of plasma was performed by analysis of spectra obtained by optical emission spectrometer UV-VIS brand Ocean Optics USB4000 model with resolution of 1.5 nm, operating in the ultraviolet and visible range (200-850 nm). The optical fiber (1 mm in diameter) was placed in front of the optical quartz window to avoid disturbing the plasma (Fig. 1). It was used the program OOIBase32 for the acquisition of optical spectra. Several peaks were observed in all spectra, but in this work only the peaks (F = 703.7 nm, O = 845.0 nm and Ar = 750.4 nm) were focused.

Here, the method of actinometry was used to determine the relative density of the F atom and O present in plasma etching environment. For this, Ar gas was used as actinometer and this was fixed at 1 sccm (approx. 5\% of the total gas concentration). The density of \(n_F\) and \(n_O\) are given by the following relationships [5]:

\[
 n_F = K_F n_{Ar} \left( \frac{I_F}{I_{Ar}} \right) 
\]

(1)

\[
 n_O = K_O n_{Ar} \left( \frac{I_O}{I_{Ar}} \right) 
\]

(2)

where \(n_{Ar}\) is the Ar density, \(K_F\) and \(K_O\) are constants related to the ratio of the cross sections of electronic excitation of the species. This constant depends on the conditions of discharge, since the cross sections are connected to the energy of particles, which is related to the discharge pressure. Several studies indicates that the value of \(K_F\) for fluorinated gases such as SF₆ and CF₄ are between 0.56 - 4.0 and \(K_O\) is equal 1 to O₂. In this work, the used value of \(K_F\) is based on the lowest published value, ie, 0.56 [2].

### 2.2 In situ plasma etching environment analysis: the mass spectrometry technique

The analysis of the relative concentration of species extracted from the plasma was performed by using a Vacuum Process Gas Analyser, Hiden HPR-30, which allows to analyze mass up to 300 atomic mass unit (amu) with a resolution 1 amu, adapted to the vacuum chamber through a drifting tube. The residual species were sampled through a micro orifice located at the mass spectrometer’s entrance, undergoing subsequent electron impact ionization at constant electron energy of 70 eV. This energy is sufficient to ionize the neutral gas species that enter through the quadrupole RF mass filter that thus, is detected and classified as a function of their mass-to-charge ratio. The typical operation pressure within the mass spectrometer was \(1 \times 10^{-7}\) Torr.

### 3. Results and Discussions

#### 3.1 Mass Spectrometry

In this work was used the mass spectra analyze in order to verify the main neutral species formed during SF₆ and CF₄ plasmas and their mixtures with O₂.

In all mass spectra were observed the formation of HF⁺ (20 uma), since F has a high reactivity with the H (1 uma) atom. The H appears from contamination of the reactor by H₂O molecules. The formation of HF in plasma is a limiting factor in the formation of F atom, thus...
decreasing the density of F in plasma. Other particles that appear as contaminants is the CO$_2^+$ and CO$^+$. Fig. 2 illustrates the main peaks in the mass spectra obtained for SF$_6$/CF$_4$ plasma as a function of CF$_4$ flow. From mass spectra of SF$_6$/CF$_4$ plasma, it was observed the generation of various species, some found in large quantities (Fig. 2), such as: SF$_3^+$, SF$_4^+$, CF$_3^+$, and CF$_4^+$. Other species were also observed but in low quantities (<1% in total gas pressure) such as SF$_4^+$, SF$_5^+$, SF$^+$ and CF$^+$. Atomic species such as F$^+$, C$^+$, and S$^+$ were not detected. With increasing of CF$_4$ flow, a decrease in the percentage of SF$_3^+$ in plasma and an increase of CF$_3^+$ was observed, as expected.

Through the Fig. 3 can observe the evolution of species of higher intensity as a function of O$_2$ flow in SF$_6$ plasma. Initially there is a small increase in the intensity of SF$_5^+$, but with the increase of O$_2$ (>5 sccm) occurs a rapidly decrease in its intensity. With the addition of O$_2$ in CF$_4$ plasmas, occurs the formation of several species, such as CF$_5^+$, CF$_2^+$, O$_2^+$ and CO$_2^+$ at a higher intensity compared with other particles (CF$^+$, C$^+$, and CO$^+$). As in the cases of SF$_6$/CF$_4$ and SF$_6$/O$_2$ was not detected the F atom in any spectra analyzed in CF$_4$/O$_2$ plasma. In Fig. 4 can observe the evolution of species with greater intensity in the plasma as a function of O$_2$ flow.

Through the study of mass spectrometry was detected mainly the presence of molecular species in plasma, in all cases were not detected F atoms. For this reason we used also the optical emission spectroscopy technique with the actinometry method to monitor the density of F present in the discharge.

### 3.2 Actinometry method

With the analysis of optical spectra it was possible to determine the relative density of F and O in the plasma, through the use of relationships (1) and (2).

The mixture of CF$_4$ in SF$_6$ plasma provides a high density of F in low concentration of CF$_4$. The value of F density was varied between (0.6-0.1)×10$^{17}$ m$^{-3}$. 

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**Figure 2.** Evolution of particles with greater intensity created in SF$_6$/CF$_4$ plasmas (SF$_5^+$, SF$_4^+$, SF$_3^+$, and CF$_4^+$) as a function of the CF$_4$ flow.

**Figure 3.** Evolution of particles with greater intensity created in SF$_6$/O$_2$ plasmas as a function of O$_2$ flow.

**Figure 4.** Evolution of particles with greater intensity created in CF$_4$/O$_2$ plasmas (CF$_5^+$, CF$_4^+$, O$_2^+$, and CO$_2^+$) as a function of the O$_2$ flow.
The use of the actinometry method in SF₆/CF₄ plasmas produce lower densities F compared to the results obtained through the SF₆/O₂ and CF₄/O₂, this fact occurs because the addition of O₂ promote a way to more in the dissociation of fluorinated molecules as mentioned previously.

This study indicates that high rates of etching Si can be achieved with the use of plasmas of SF₆ and CF₄ with low flows of O₂ (< 40%) in the HCRIE reactor.

4. Conclusion

In this article, molecular species and atomic F was monitored through the mass spectroscopy and actinometry method. The mixture of SF₆/CF₄ allow the formation of various species SF₅⁺, SF₃⁺, SF₃⁺ and CF₂⁺ and the density of F ranged between (0.6-0.1)×10¹⁷ m⁻³. The addition of O₂ gas in SF₆ and CF₄ plasma allowed the formation of SF₅⁺, SF₄⁺, SF₃⁺ and O₂⁺ to SF₆/O₂ plasma and CF₅⁺, CF₄⁺, CF₂⁺ and CO₂⁺ to CF₄/O₂ plasma, being the SF₆/O₂ plasma and the density range between (0.6-0.1)×10¹⁷ m⁻³ and (0.9-9)×10¹⁷ m⁻³, respectively. This study indicates that high rates of etching Si can be achieved with the use of plasmas of SF₆ and CF₄ with low flows of O₂ (< 40%) in the HCRIE reactor.

Acknowledgements

The financial support of Brazilian agencies programs PNPD-CAPES (process number 02765/09-8) and PNM-CNPq is strongly acknowledged.

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