

Mass-resolved studies of positive ions in high density plasmas generated in CHF₃, C₂F₆ and CH₂FCF₃ and their mixtures with Ar

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ABSTRACT

We have determined the relative abundances and energy distributions of positive ions in high density plasmas generated in CHF₃, C₂F₆ and CH₂FCF₃ and their mixtures with Ar using an ion energy analyzer-mass spectrometer appended to the lower electrode of an inductively coupled GEC radio-frequency reference cell. CHF₃ and C₂F₆, which are commonly used in plasma processing, possess high global warming potentials. CH₂FCF₃, which is a popular refrigerant used in the air-conditioning industry, has a much lower global warming potential and may serve as a novel etching alternative. We find the ion composition and plasma characteristics of CH₂FCF₃ discharges to be similar to those for CHF₃.

INTRODUCTION

Low pressure radio-frequency (rf) discharges in fluorocarbon gases are commonly used for the plasma etching of semiconductor materials. Ion bombardment is a key process in plasma etching and consequently the determination of the identities, flux, and energies of the ions striking surfaces exposed to etching discharges has attracted much interest. Most investigations of positive ions in rf plasmas sustained in fluorocarbon gases have been applied to capacitively coupled reactors [1,2], and only recently have investigations been extended to inductively coupled reactors [3-6].

We report mass-analyzed ion energy distributions (IEDs), relative ion flux densities, and absolute total ion currents measured using a combined ion energy analyzer-mass spectrometer that samples ions through an orifice in the lower electrode of an inductively coupled GEC rf reference cell. Ion energies and mass-resolved ion fluxes were measured as a function of gas pressure and mixture concentration. Data are pre-

sented for discharges generated in CHF₃, C₂F₆ and CH₂FCF₃ (HFC-134a) and their mixtures with Ar.

EXPERIMENT

The discharges studied here were generated in a GEC rf reference cell reactor whose upper electrode has been replaced with a five-turn planar rf-induction coil behind a quartz window to produce inductively coupled discharges [7]. In a manner similar to that of Jayaraman *et al.* [3], a quartz annulus was mounted to the upper quartz window of the GEC cell to allow the generation of plasmas in electronegative gases over a much broader range of pressures and powers. The gas pressure is maintained by a variable gate valve between the GEC cell and the pump. Mass flow controllers regulated the gas flow, which was maintained at either 3.73 $\mu\text{mole/s}$ for pure CHF₃, C₂F₆ and HFC-134a discharges or 7.45 $\mu\text{mole/s}$ for their mixtures of with Ar.

A 13.56 MHz voltage is applied to the coil through a matching network. The rf power values presented in this article are the net power to the matching network driving the coil. The actual rf power dissipated in the plasma has been determined to be approximately 80% of the power listed. The lower electrode is grounded to the vacuum chamber.

The ion energy analyzer-mass spectrometer arrangement is identical to that used to study inductively coupled plasmas in CF₄ [5], and in Ar, N₂, O₂, Cl₂ and their mixtures [6]. Ions are sampled through a 10 μm diameter orifice in a 2.5 μm thick nickel foil spot-welded into a small counterbore located at the center of the stainless steel lower electrode. For IED measurements, the ions that pass through the orifice are mass selected by the quadrupole mass spectrometer after being energy analyzed by the 45° electrostatic

energy selector. The IEDs measured in this manner are essentially ion-flux energy distributions.

Past experience with the ion energy analyzer indicates that the ion transmission is nearly constant over the energy ranges observed here. A mass-dependent transmission correction factor which was determined by calibration with rare gas plasmas, however, was applied to the highest mass ions (mass > 40 u) in order to compensate for some decrease in the ion transmission of the quadrupole mass spectrometer with increasing mass.

For total ion current measurements, (i.e. all ion current passing through the sampling orifice), the ion optic elements at the front of the ion energy analyzer are biased such that the current passing through the sampling orifice is collected on the extractor element (the first ion optic element behind the electrode surface), and is measured using an electrometer.

RESULTS AND DISCUSSION

Figure 1 shows mass spectra of the ions produced at 1.33 Pa (10 mTorr) and 200 W in pure CHF₃, C₂F₆ and HFC-134a discharges. For C₂F₆,

the dominant ion under these conditions is CF₃⁺, which is similar to the observations of Jayaraman *et al.* [3] and Li *et al.* [4] With a measured flux equal to 30% of the total ion current, CF₃⁺ is also the principal ion fragment produced from the dissociative ionization of C₂F₆. Jayaraman *et al.* report a flux of CF₃⁺ five times higher than that of the next most abundant ion. In contrast, we observe that the intensities of CF⁺ and CF₂⁺ are nearly half that of CF₃⁺. Surprisingly, the second highest intensity in C₂F₆ is at mass 28 u, which can be attributed to the combined flux of CO⁺ and Si⁺. Both CO⁺ and Si⁺ are secondary ions (ions not produced by dissociative ionization of the parent gas) resulting from quartz etching and subsequent ion-surface and ion-molecule interactions occurring within the reactor. These secondary ions constitute the dominant mass signal for both CHF₃ and HFC-134a discharges. It is interesting to observe that the second most abundant ion in HFC-134a discharges is HF⁺, which is also a secondary ion.

The IEDs of CF₃⁺ obtained in pure CHF₃, C₂F₆ and HFC-134a discharges at 200 W for pressures of 0.67 Pa, 1.33 Pa and 2.66 Pa are shown Fig. 2. For all three gases, the IEDs broaden as discharge pressure increases, exhibiting distinctly

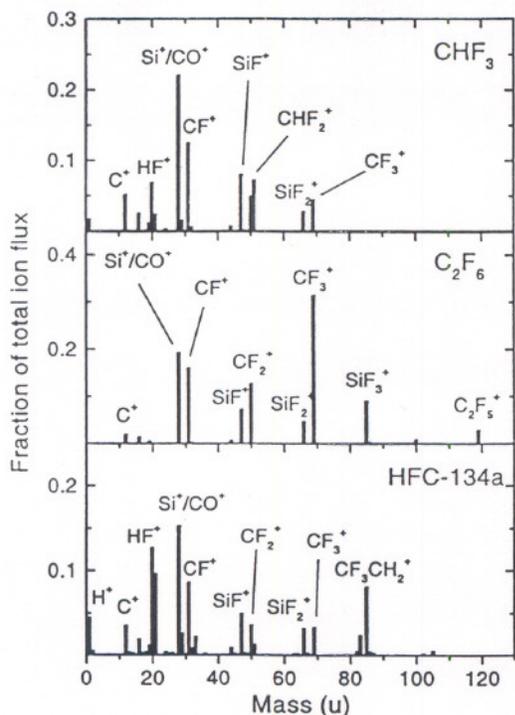


Fig. 1. Mass spectra of ions striking the lower electrode in the GEC cell from 200 W, 1.33 Pa discharges in CHF₃, C₂F₆ and HFC-134a.

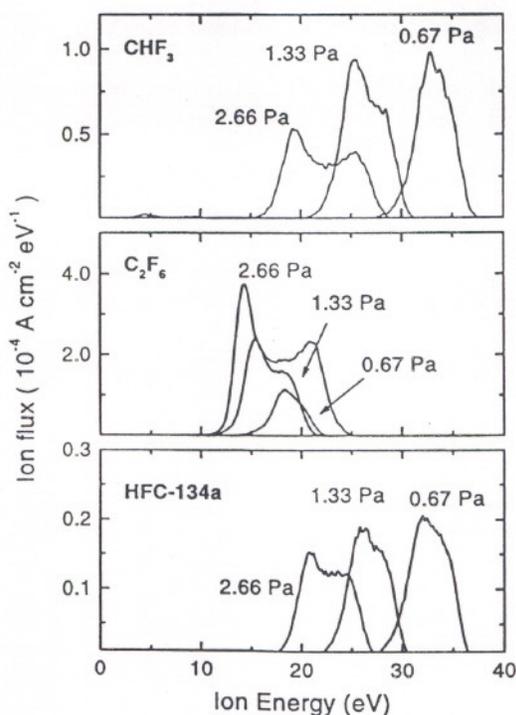


Fig. 2. IEDs of CF₃⁺ from 200 W discharges in CHF₃, C₂F₆ and HFC-134a at 0.67 Pa, 1.33 Pa, and 2.66 Pa.

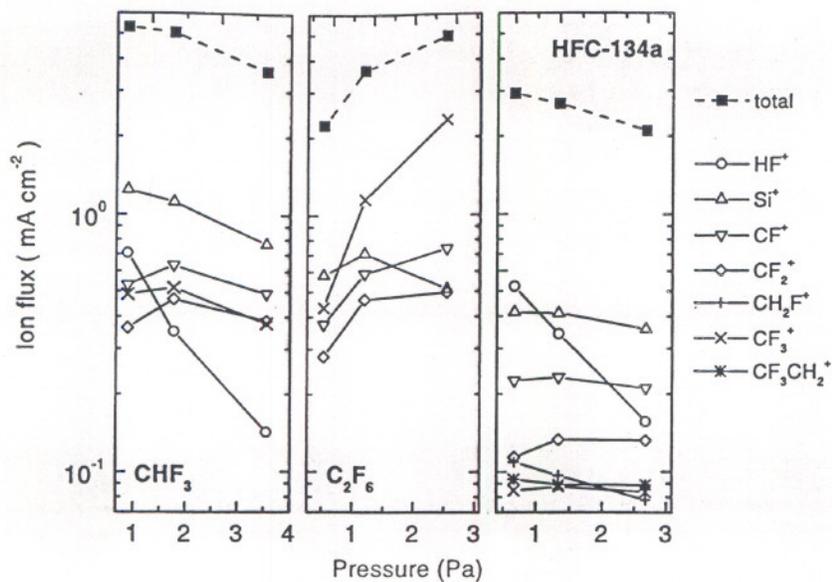


Fig. 3. Mass analyzed ion flux, as a function of pressure, obtained from 200 W discharges in CHF_3 , C_2F_6 and HFC-134a.

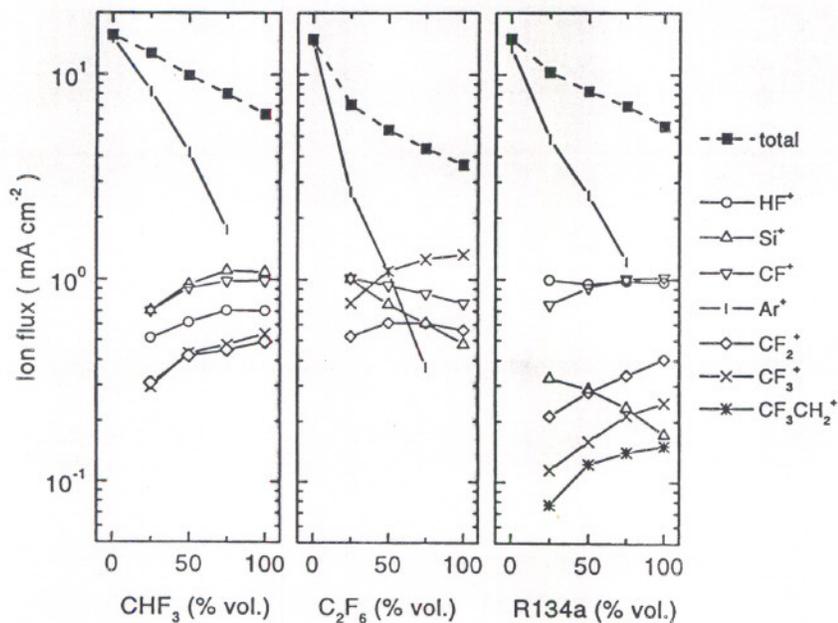


Fig. 4. Mass analyzed ion flux, as a function of gas composition, obtained from 200 W, 1.33 Pa discharges in argon mixtures with CHF_3 , C_2F_6 and HFC-134a.

bimodal structures at 2.66 Pa. The bimodal energy distributions are caused by rf modulation of ionic motion through the ground sheath. The increase of rf modulation with pressure can be attributed to the decrease of the ground sheath capacitance resulting from a more confined plasma as the pressure increases. The mean ion energy observed in C_2F_6 changes little with pressure. However, it clearly decreases with pressure in CHF_3 and HFC-134a discharges, indicating that the electron temperature decreases significantly with increasing pressure.

The relative ion compositions as a function of pressure in pure CHF_3 , C_2F_6 and HFC-134a discharges are shown in Fig. 3. In C_2F_6 , the magnitude of the total ion flux more than doubles from 0.67 Pa to 2.66 Pa, and is largely attributable to a dramatic increase of CF_3^+ . The fact that the CF_3^+ flux is such a strongly increasing function of gas pressure suggests that in addition to electron-impact ionization of C_2F_6 , reactions between ions and either C_2F_6 or its dissociation fragments may be important mechanisms contributing to CF_3^+ production in these discharges. Little is known about such ion-molecule reactions, however. For both CHF_3 and HFC-134a, the total ion fluxes decrease with increasing pressure. In particular, the HF^+ fluxes decrease rapidly with pressure, indicating collisional destruction of this species.

The mass analyzed ion fluxes from discharges containing varying proportions of CHF_3 , C_2F_6 and HFC-134a with Ar are shown in Fig. 4. Although the Ar^+ intensity sharply decreases with the reduction of Ar supplied to the plasma, the relative fluxes of all other significant ions in these discharges change much less than the corresponding increase in the concentration of fluorocarbon gas in the feed mixture. The decrease in the total ion current in these discharges with increasing fluorocarbon concentration may be partly due to reduced plasma densities resulting from increasing electron attachment to the fluorocarbon gases and their dissociation products.

SUMMARY

Several ionic species with significant intensities were observed in discharges containing CHF_3 , C_2F_6 and HFC-134a. The dominant ion is not

always the principal ion resulting from electron-impact ionization of the feed gas. Ions resulting from erosion of the quartz coupling window constitute significant fractions of the reactive ion composition for these plasmas, under some conditions comprising nearly 25% of the measured ion current. The CF_3^+ flux rises dramatically as a function of pressure in pure C_2F_6 discharges, contributing to an overall increase in ion current under these circumstances. For all other discharges studied, the CF_3^+ flux displays a much weaker dependence on discharge pressure, and the total ion flux decreases at elevated pressures as might be expected from a reduction of electron temperature at higher collisional frequencies. Although the Ar^+ intensity sharply decreases with the reduction of Ar supplied to the plasma, the relative fluxes of all other significant ions in these discharges change much less than the corresponding increase in the concentration of fluorocarbon gas in the feed mixture. Depending on the discharge conditions, the ion energy distributions vary from fairly narrow and single-peaked to very broad and bimodally structured, the latter being indicative of parasitic capacitive coupling modulating the ions' energy as they traverse the plasma sheath. The dependence of the IEDs on discharge conditions illustrates the importance of measuring IEDs in determining relative ion flux intensities, since the relative ion flux intensities will depend on the energy of the ions sampled.

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