Ion compositions and energies in inductively coupled plasmas containing SF_6

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(Received 8 September 2000; accepted 9 October 2000)

Inductively coupled plasmas were generated in pure SF_6 and in Ar/SF_6 and O_2/SF_6 mixtures in a Gaseous Electronics Conference rf reference cell. Absolute total ion current densities, relative ion intensities, and ion energy distributions at the grounded electrode were measured and the influences of pressure, power, and mixture concentration on these quantities examined. In addition to ions derived directly or indirectly from SF_6, ions resulting from quartz etching and sulfur oxidation contribute moderately to the total ion flux. The dominant sulfur-containing ion observed under most conditions is S^+, indicating a large degree of SF_6 dissociation. [DOI: 10.1116/1.1330261]

I. INTRODUCTION

High density plasmas generated in mixtures of SF_6 with rare or simple diatomic gases are involved in many dry etching processes (see, for example, Refs. 1–3). Ion bombardment is a key component of these processes and consequently the determination of the identities, flux, and energies of the ions striking surfaces exposed to etching discharges is necessary in order to understand, accurately model, and ultimately refine the plasma etching process.

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 Gaseous Electronics Conference (GEC) rf reference cell. Data are presented for discharges generated in SF_6 and in mixtures of SF_6 with argon and with oxygen.

II. EXPERIMENT

The discharges studied 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.[4] The design of the GEC rf reference cell is described in detail elsewhere.[5,6] A quartz annulus developed[7] to allow the generation of plasmas in electronegative gases over a much broader range of pressures and powers was mounted on the upper quartz window of the cell. Mass flow controllers regulated the flow, which was maintained at 3.73 μmol/s (5 sccm) for pure SF_6 discharges and 7.45 μmol/s (10 sccm) for mixtures of SF_6 with Ar or with O_2.

The ion sampling arrangement is identical to that used to study inductively coupled plasmas in several fluorocarbon gases.[7–10] 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.[11]

Past experience with the ion energy analyzer indicates that the ion transmission is nearly constant over the energy ranges observed here.[11] A mass-dependent transmission correction factor, 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. These factors were determined by calibration with rare gas plasmas[12] and approach a factor of 22 for the largest mass ion observed, SF_5^+ at 127 u.

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. Total ion current measurements exhibit a reproducibility of ±15%. The total ion current is partitioned into mass channels according to the mass spectrum of ions. The absolute intensities of the measured IEDs are then determined by scaling the measured values of the ion current for the appropriate mass channel to the total ion current. The ion flux densities presented here are derived by dividing the total measured ion current by the area of the 10 μm diameter sampling hole.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the mass spectrum of ions extracted from a 0.67 Pa (5 mTorr), 200 W inductively coupled plasma (ICP) generated in pure SF_6. Stable discharges in pure SF_6 could be sustained at 200 W for only a narrow range of pressures around 0.67 Pa (5 mTorr). The ion spectrum contains several ions of similar intensity. These are ions derived directly or indirectly from SF_6 as well as secondary ions resulting from plasma–surface interactions as well as ion–molecule reactions. The predominant ion is S^+ at mass 32 u. The relative ion intensities at masses 32 and 34 u are consis-

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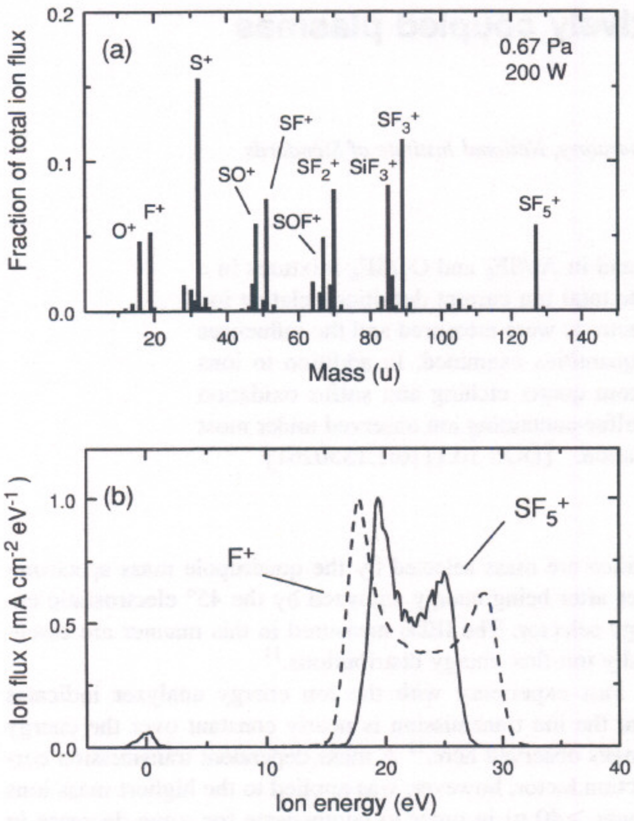

FIG. 1. (a) Mass spectrum of ions striking the grounded electrode in an inductively coupled SF_6 discharge sustained at 0.67 Pa (5 mTorr) and 200 W. (b) Normalized energy distributions of SF_5^+ (solid lines) and F^+ (dashed lines) ions under these conditions.

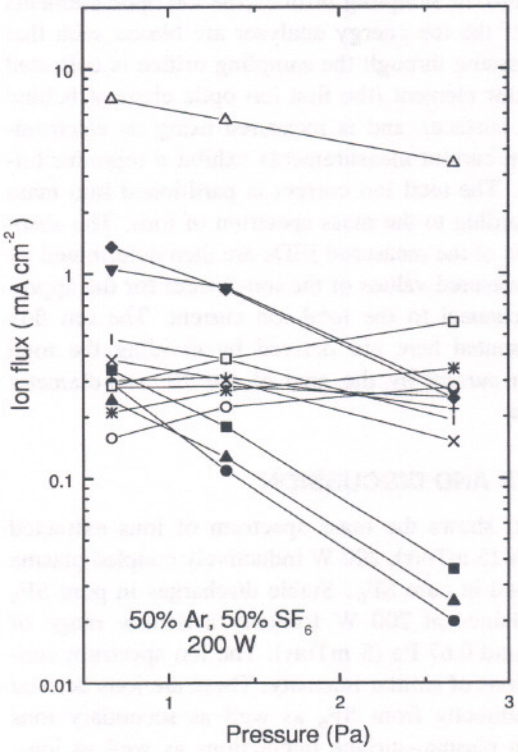

FIG. 2. Mass-resolved ion fluxes from 50% SF_6/50% Ar discharges at various pressures. All discharges were sustained at 200 W.

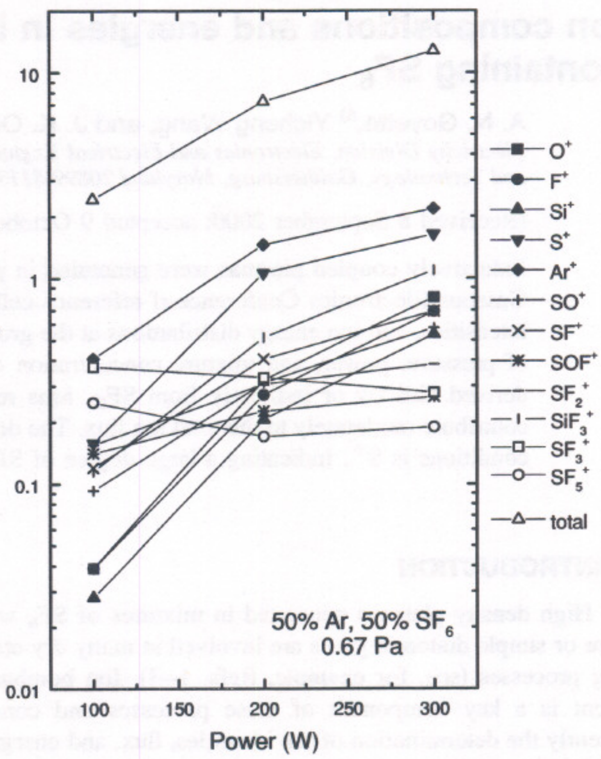

FIG. 3. Mass-resolved ion fluxes from 50% SF_6/50% Ar discharges at various powers. All discharges were sustained at 0.67 Pa (5 mTorr).

tent with the isotopic abundances of sulfur, indicating that O_2^+ does not contribute significantly to the detected flux of 32 u ions. The predominance of S^+ in the ion spectrum suggests a high degree of SF_6 dissociation in the plasma since S^+ is a minor product of dissociative ionization of SF_6 by electron impact.[13] Molecular dissociation fractions in Ar/SF_6 ICPs generated in the same GEC cell were previously measured by Wang *et al.*[14] Although no data for pure SF_6 ICPs were reported, dissociation fractions in Ar/SF_6 ICPs exceeding 0.90 were reported for pressures ranging from 1.3 Pa (10 mTorr) to 6.7 Pa (50 mTorr) and for powers from 100 to 300 W. It is likely that similarly large SF_6 dissociation fractions exist under our conditions as well.

The energy distributions of SF_5^+ and F^+ ions shown in Fig. 1(b) exhibit a distinctly bimodal structure indicative of rf modulation of the ions' energy as they traverse the plasma sheath, with the lightest ions experiencing the greatest modulation.[15] The center of the distribution, which corresponds to the average plasma potential, lies near 22 eV and is comparable to that observed for C_2F_6 and c-C_4F_8.[9]

In order to extend the range of pressures and powers over which discharges could be operated, 50% Ar/50% SF_6 mixtures were used to investigate the trends in relative ion intensities with pressure and power. The results are shown in Figs. 2 and 3, respectively. The fluxes of Ar^+ and other atomic ions display the greatest sensitivity to changing pressure. In addition, the absolute and relative intensities of SF_3^+, SF_5^+ and SOF^+ rise significantly with pressure. The dominant ion shifts from Ar^+ at 0.67 Pa (5 mTorr) to SF_3^+ at 2.67 Pa (20 mTorr). This trend may be attributable to rela-

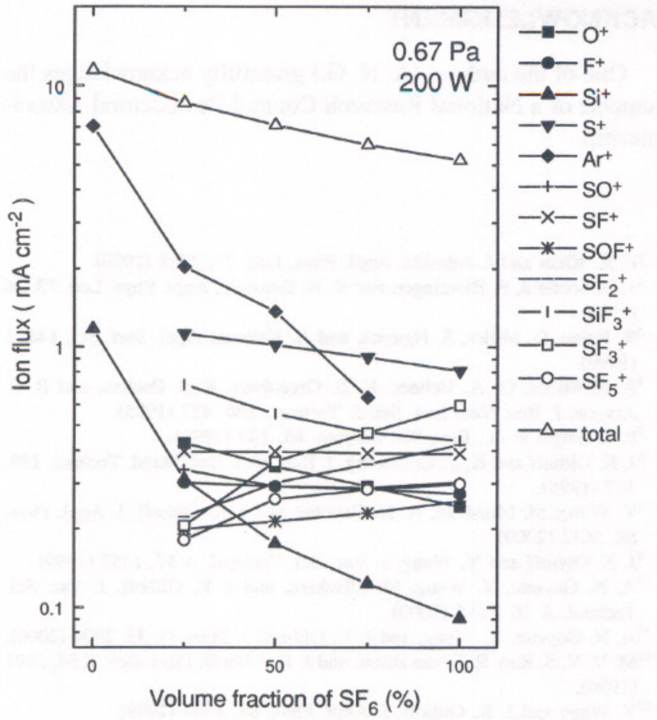

FIG. 4. Mass-analyzed ion fluxes in discharges containing SF_6 for various mixtures with Ar. All discharges operated at 0.67 Pa (5 mTorr) and 200 W.

tively less dissociation of the SF_6 feed gas with increasing pressure, and to a potentially increasing role of gas–phase ion–molecule reactions in the plasma. The significant fluxes of ions which contain either Si or O also illustrate the significance of plasma–surface and ion–molecule interactions to ion generation in these plasmas. Important ion–molecule processes which can significantly affect the contributions to the total ion flux of ions generated by plasma-surface and ion-molecule interactions, such as

$$Ar^{+}+SF_6 \rightarrow SF_5^{+}+F+Ar, \tag{1}$$

and interactions with fragment ions, such as

$$SF_5^{+}+SF_6 \rightarrow SF_3^{+}+SF_6+F_2, \tag{2}$$

have been investigated by others.[16,17] Ion conversion resulting from ion–molecule interactions and interactions with decomposition products are likely to be more significant at higher pressures.

Figure 3 shows the influence of discharge power on relative ion intensities. The total ion flux increases a little more than a factor of 5 from 100 W to 300 W, with Ar^{+} consistently having the highest intensity. Nearly all the fluxes of significant ions increase monotonically with power. The intensities of SF_3^{+} and SF_5^{+}, however, decrease slightly in this range. A shift in the ion composition towards higher fluxes of lighter ions such as we observe in Ar/SF_6 ICPs could be explained by enhanced SF_6 dissociation and decomposition at higher discharge powers.

The mass-resolved flux of positive ions extracted from discharges generated in different mixtures of SF_6 and Ar at 0.67 Pa (5 mTorr) is shown in Fig. 4. As might be expected, the Ar^{+} flux decreases as the SF_6 concentration is raised, while the fluxes of heavier SF_x^{+} ions correspondingly increase. S^{+} remains the dominant SF_x^{+} ion in all mixtures which contain SF_6. In addition, the intensity of Si^{+} flux decreases substantially and that of SiF_3^{+} decreases to a lesser extent as a function of SF_6 concentration. The relative fluxes of Si^{+} and SiF_3^{+} are small for the discharges investigated here as compared to that observed for discharges generated in fluorocarbons.[7,9]

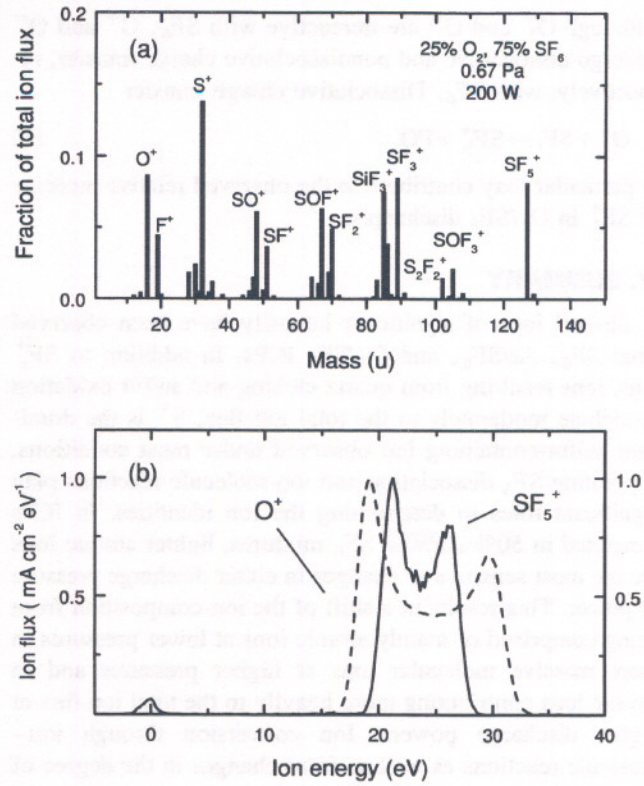

FIG. 5. (a) Mass spectrum of ions striking the grounded electrode in 75% SF_6/25% O_2 discharge sustained at 0.67 Pa (5 mTorr) and 200 W. (b) Normalized energy distributions of SF_5^{+} (solid lines) and O^{+} (dashed lines) ions under these conditions.

Figure 5(a) shows the mass-resolved flux of positive ions extracted from a discharge generated in a 75% SF_6/25% O_2 discharge at 0.67 Pa (5 mTorr) and 200 W. Corresponding energy distributions of SF_5^{+} and of O^{+} for these operating conditions are shown in Fig. 5(b). Stable discharges could not be maintained with higher fractions of O_2. The ion spectrum and energy distributions shown in Fig. 5(b) closely resemble those observed in the pure SF_6 discharge operated under identical conditions shown in Fig. 1(a). Not surprisingly, the intensities of O^{+} and sulfur oxyfluoride ions (SOF_x^{+}) are higher in the mixture than they are in pure SF_6. The relative intensities of the lighter sulfur fluoride ions are diminished while that of SF_5^{+} increases slightly, although S^{+} remains the dominant ion. Similar analysis of the fluxes of 32 and 34 u ions indicates roughly 20% of the flux of 32 u ions is due to O_2^{+}.

The pathways and rates of reaction between SF_6 and oxygen cations and anions have been studied by Morris *et al.*[18]

Although O_2^+ and O^- are unreactive with SF_6, O^+ and O_2^- undergo dissociative and nondissociative charge transfer, respectively, with SF_6. Dissociative charge transfer

$$O^+ + SF_6 \rightarrow SF_5^+ + FO, \tag{3}$$

in particular may contribute to the observed relative increase of SF_5^+ in O_2/SF_6 discharges.

IV. SUMMARY

Several ions of significant intensity have been observed from SF_6, Ar/SF_6, and O_2/SF_6 ICPs. In addition to SF_x^+ ions, ions resulting from quartz etching and sulfur oxidation contribute moderately to the total ion flux. S^+ is the dominant sulfur-containing ion observed under most conditions, suggesting SF_6 dissociation and ion-molecule reactions play significant roles in determining the ion identities. In ICPs generated in 50% Ar/50% SF_6 mixtures, lighter atomic ions are the most sensitive to changes in either discharge pressure or power. This results in a shift of the ion-composition from being comprised of mainly atomic ions at lower pressures to more massive molecular ions at higher pressures and to atomic ions contributing more heavily to the total ion flux at higher discharge powers. Ion conversion through ion–molecule reactions as well as from changes in the degree of SF_6 dissociation very likely contributes to these observed trends. The trends with SF_6 concentration are complex, although the intensities of nearly all SF_x^+ ions rise with SF_6 concentration. Addition of 25% O_2 to a 0.67 Pa (5 mTorr), 200 W SF_6 discharge resulted in higher fluxes of O^+ and SF_5^+, but produced little change in ion energies with respect to pure SF_6 discharges.

ACKNOWLEDGMENT

One of the authors (A. N. G.) gratefully acknowledges the support of a National Research Council Postdoctoral Associateship.

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