

Mass spectrometric measurement of molecular dissociation in inductively coupled plasmas

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The dissociation fraction of molecules in radio frequency, planar, inductively coupled plasmas are measured for mixtures of oxygen, nitrogen, sulfur hexafluoride, and chlorine in argon. A modified gaseous electronics conference rf reference cell with an inductively coupled source is used to produce the discharges, with pressures ranging from 1.3 Pa to 5.3 Pa and applied powers from 100 W to 300 W. Neutrals are sampled from the side of the discharge, and the degree of dissociation is determined mass spectrometrically by comparison of the intensities of the parent ion peaks with the plasma power on and off. Measured dissociation levels of O₂ in Ar:O₂ mixtures ranged from 0.02 (i.e., 2% of the oxygen molecules were dissociated) to 0.08 (8%), while dissociation levels for Ar:SF₆ mixtures ranged from 0.92 to 0.98, depending upon plasma conditions. The degree of dissociation of Cl₂ in Ar:Cl₂ mixtures ranged from near 0.07 to 0.19, while dissociation levels of N₂ in Ar:N₂ mixtures were less than 2% for all plasma conditions studied. [S0021-8979(98)05202-5]

I. INTRODUCTION

Plasma enhanced etching and deposition are critical processes in the fabrication of microelectronic devices. Knowledge of the gas-phase composition of these industrial plasmas is essential in order to develop and validate the models that are being used to refine and improve these processes. One critical parameter is the degree of dissociation of the molecular gases in the feed gas caused by the discharge in the reactor. Dissociation of the gas by the plasma can significantly affect the composition of the plasma species, and thereby change critical plasma parameters, such as the electron density and energy distribution. This is especially true in high density plasmas, such as those produced in inductively coupled plasma (ICP) sources.

Many plasma models predict the degree of dissociation, or the density of radicals, that result from molecular dissociation inside the plasma. Some examples include the work of Bukowski *et al.*¹ and Wise *et al.*,² who calculated Cl densities in pure chlorine discharges in an inductively coupled gaseous electronic conference (GEC) radio-frequency (rf) reference cell. They calculated that the Cl and Cl₂ densities at the center of the plasma volume would be approximately equal, for the plasma conditions assumed by the model. Kushner and co-workers have published several works³⁻⁵ in which the degree of dissociation is calculated for molecular gases mixed with argon for several ICP-type reactors. Their calculations show that dissociation levels can vary widely, from a few percent to 99%, depending upon reactor geometry and plasma conditions.

Despite the fact that some measure of molecular dissociation is commonly calculated by plasma models, few experimental data are available to validate these calculations. Some recent measurements have been made for the dissociation levels of molecular gases in high pressure glow discharges,⁶ in helical resonator discharges,⁷ in capacitively coupled rf discharges,⁸ and in high density, inductively

coupled plasmas.⁹ Investigations of dissociation in ICP-GEC cells have been limited to pure chlorine discharges. Preliminary reports by Anderson and co-workers^{10,11} show that Cl₂ dissociation at the center of the discharge ranges from 70% to 99%, depending upon plasma conditions. Hebner¹² recently measured relative atomic chlorine densities in the center of the ICP-GEC cell, and showed that Cl densities are nearly independent of power, and increase slightly with increasing pressure. These results are in apparent contradiction with calculations performed by Deshmukh and Economou¹³ showing a significant increase in dissociation with increasing power density for a general plasma model.

In this paper we present measurements of the degree of dissociation of nitrogen, oxygen, sulfur hexafluoride, and chlorine (N₂, O₂, SF₆, and Cl₂) in mixtures with argon for plasmas generated in a GEC rf reference cell with an ICP source. We concentrate on mixtures of molecular gases with argon because of their common use in the etching of silicon-based devices. The focus of this investigation is to determine the degree of dissociation that can be obtained for these gas mixtures over a wide range of plasma conditions in order to help define the conditions under which dissociation must be seriously considered in plasma models.

II. EXPERIMENT

The discharges investigated in this work were generated in a GEC rf reference cell,^{14,15} modified for use with an inductively coupled plasma source. The basic inductively coupled source has been described in detail elsewhere.¹⁶ Briefly, the inductively-coupled source replaces the upper parallel-plate electrode with a 1 cm thick quartz window as a vacuum interface, and a 5-turn planar coil powered by a 13.56 MHz power supply. This design has been modified to include an electrostatic shield and a 3 mm thick quartz insulator between the coil and the 1-cm quartz window¹⁷ (except for the Ar:Cl₂ discharges, as discussed in Sec. III D). The

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electrostatic shield significantly reduces capacitive coupling to the plasma which helps maintain a predominately inductive discharge. For all the measurements presented here, the lower electrode, which consists of a 16.2 cm diam stainless steel plate, is maintained at ground potential, and the power reported is the forward power applied to the induction coil minus the reflected power to the matching network. Due to the power dissipated in the induction coil and the surrounding hardware, the rf power dissipated in the plasma has been shown to be approximately 60% of these values when the electrostatic shield is in place,¹⁷ and 80% when the shield is removed.¹²

The gas enters the cell through one of the 2.75 in. side ports, and the flow and ratios of the gas mixture were maintained by flow controllers. The total flow rate for all of the experiments presented here was 3.7 $\mu\text{mol/s}$ (5 sccm), and the gas pressure in the reactor was maintained by regulating the speed of the turbopump.

The mass spectrometer used here is the same device used previously to measure ion-energy distributions from argon plasmas in a capacitively coupled GEC cell.¹⁸ The device was mounted on the 6 in. flange opposite the turbo pump port, and for most of the measurements presented here, the tip of the sampling cone was positioned approximately 1 cm from the outer edge of the lower electrode plate (i.e., 9.2 cm from the cell axis), and 1 cm above the surface of the lower electrode plate. Gas was sampled through a 0.2 mm diam hole in the end of a stainless steel sampling cone. The position of the sampling cone could be moved horizontally over a range of 10 cm to determine the degrees of dissociation as a function of distance from the edge of the lower electrode plate.

For the present measurements the ion-energy analyzer was not used, and the mass spectrometer was operated in "residual gas analyzer" mode. Electron-impact (70 eV) mass spectra were obtained with the plasma off and with the plasma on. In each case, between 10 and 40 spectra were obtained and averaged. The degree of dissociation, D , was then calculated using the equation

$$D = 1 - \left(\frac{I_{\text{on}}}{A_{\text{on}}} \right) \left(\frac{A_{\text{off}}}{I_{\text{off}}} \right), \quad (1)$$

where I_{on} and I_{off} are the intensity of the parent ion peak with the plasma on and off, respectively, and A_{on} and A_{off} are the intensity of the Ar^+ peak (mass 40 u) with the plasma on and off, respectively. The intensities of the peaks of interest were determined from the area of each mass peak, which was obtained by integrating the signal across the peak. This proved to be a more reproducible measure of the peak intensity than the peak heights. The parent ion peaks for the gases used were O_2^+ (mass 32 u) for oxygen, N_2^+ (mass 28 u) for nitrogen, and Cl_2^+ (mass 70 u) for chlorine. The ion SF_6^+ is not produced by electron impact, so SF_5^+ (mass 127 u) is the parent ion for sulfur hexafluoride.

The intensities of these peaks were normalized to the intensity of the Ar^+ peak, as in Eq. (1), in order to account for any changes in plasma temperature when the plasma power was turned on and off. This is a critical aspect of the measurement technique since previous measurements^{19,20}

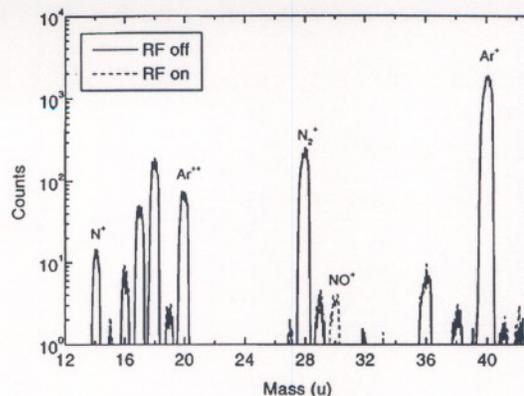


FIG. 1. Mass spectra of an Ar:N₂ (80:20) Ar mixture with the plasma off (—) and on (---). The total gas pressure was 2.7 Pa, and the applied rf power was 350 W.

have shown that neutral temperatures can increase by several hundred degrees in discharges generated in argon or chlorine in ICP-GEC cells. These temperature increases can have a significant influence on the local density (or pressure) inside the plasma. Normalizing the parent ion intensity to the Ar^+ peak also compensates for any other changes in experimental conditions, including drift in detector efficiency, variations in pumping speed, and small fluctuations in pressure.

The uncertainty of the measured values of D for the Ar:N₂, Ar:O₂, and Ar:SF₆ mixtures is ± 0.01 (1 σ), based upon the reproducibility of the measurements of D on different days. Relative uncertainties between measurements made during a single experimental run, i.e., measurements of D as a function of pressure or applied power, are less than ± 0.01 . For the Ar:Cl₂ mixtures the uncertainty is ± 0.02 because of the effects of changing surface conditions as discussed in Sec. III D. All systematic errors should be removed by the procedure (discussed above) of normalizing all intensities to the Ar^+ peak. The lower detection limit of D for this experiment is 0.02 (2% dissociation), while the upper detection limits are determined by the absolute uncertainty of the measurement.

III. RESULTS AND DISCUSSION

A. Argon–nitrogen (Ar:N₂) mixtures

Figure 1 shows a representative mass spectrum from a 350 W plasma in an Ar:N₂ (80:20) mixture at 2.7 Pa (20 mTorr) overlaid on a mass spectrum of the same gas mixture with the plasma turned off. With the exception of the formation of some NO^+ with the plasma on, the mass spectra are nearly indistinguishable. This is true for a wide range of plasma conditions, including nitrogen concentrations from 1% to 50%, pressures from 1.3 Pa to 5.3 Pa, and applied powers from 100 W to 350 W. Thus, for all these conditions, the degree of dissociation of nitrogen is determined to be less than 0.02, the experimental detection limit of this apparatus.

B. Argon–oxygen (Ar:O₂) mixtures

By contrast, one can clearly observe in Fig. 2 an example of how the intensity of the O_2^+ peak decreases in an

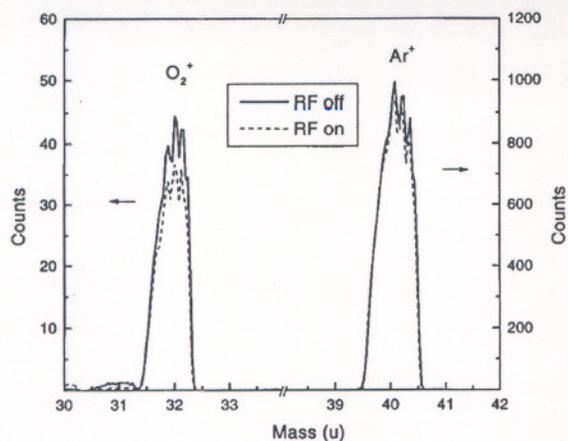


FIG. 2. Mass peaks for O_2^+ and Ar^+ for an Ar: O_2 (90:10) mixture with the plasma off (—) and on (---). The total gas pressure was 1.3 Pa, and the applied rf power was 300 W.

Ar: O_2 mixture when the discharge is ignited. For the 10% oxygen mixture shown in Fig. 2, the calculated degree of dissociation is 0.09 for a plasma at a pressure of 1.3 Pa and 300 W applied power.

The data in Figs. 2 and 3 show that the degree of dissociation of O_2 in an Ar: O_2 mixture ranges from 0.02 to 0.09 over a wide range of plasma conditions. While this degree of dissociation is moderate, Fig. 3 shows clear trends in the measured values of D as the plasma conditions are changed. Figure 3(a) shows a significant decrease in the degree of dissociation as the pressure is increased in the plasma from 1.3 Pa to 5.3 Pa, with the power and oxygen mixture fraction held constant at 300 W and 20%, respectively. This may be attributed to the increased probability of recombination of the fragment atoms, either in the gas phase or at the surfaces, as the pressure increases. Another possible cause of this trend is a reduction in plasma electron density as the oxygen concentration increases due to dissociative electron attachment to oxygen.

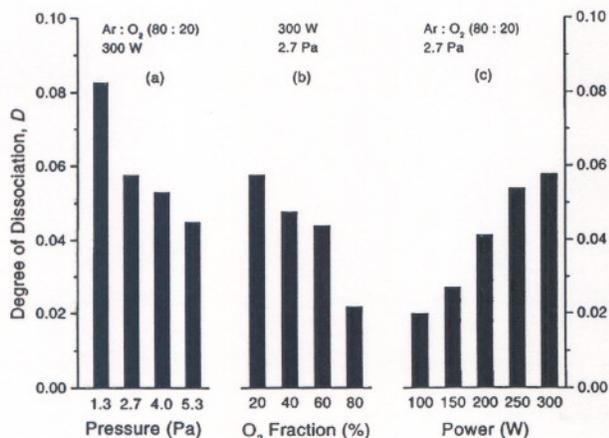


FIG. 3. Dependence of the degree of dissociation for Ar: O_2 mixtures as a function of (a) pressure, (b) O_2 concentration, and (c) power.

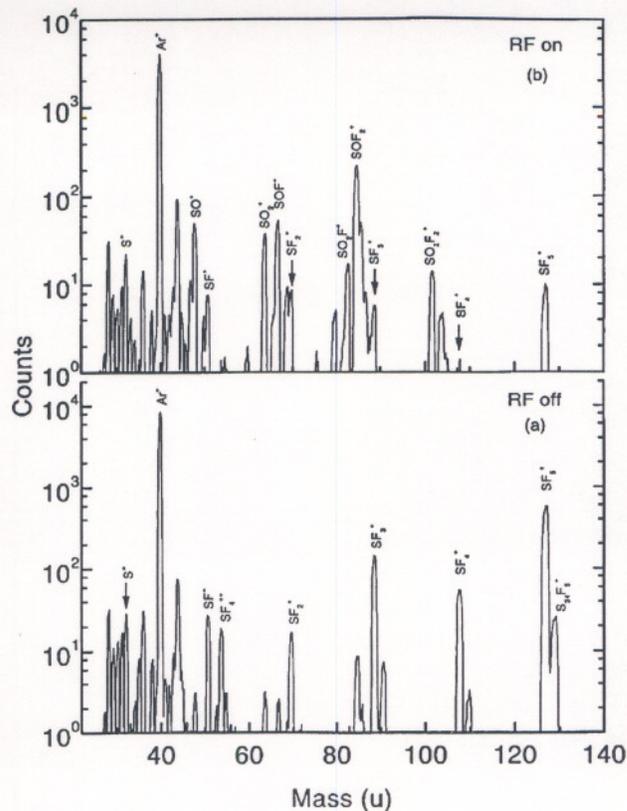


FIG. 4. Mass spectra of an Ar: SF_6 (95:5) mixture with the plasma (a) off and (b) on. The total pressure was 4.0 Pa, and the applied rf power with the plasma on was 200 W.

A similar trend in dissociation is apparent in Fig. 3(b) where D decreases with increasing concentration of O_2 . Finally, Fig. 3(c) shows a trend of increasing dissociation with increasing rf power, ranging from near the detection limit of 0.02 at 100 W to nearly 0.06 at 300 W, for a 20% O_2 mixture at 2.7 Pa.

The degree of dissociation of O_2 in Ar: O_2 mixtures showed no detectable dependence upon the horizontal position of the sample probe tip relative to the lower electrode plate, i.e., how far the probe was positioned from the outer edge of the lower electrode plate. This suggests that these levels of dissociation may be similar to those in the center of the discharge. A direct measurement of the dissociation in the center of the discharge was not possible due to the relative size of the sampling cone and the spacing between the lower electrode plate and the window in the ICP source.

C. Argon-sulfur hexafluoride (Ar: SF_6) mixtures

For Ar: SF_6 mixtures the degree of dissociation is significantly greater than observed for either Ar: N_2 or Ar: O_2 mixtures. This is clear from the mass spectra shown in Fig. 4 for an Ar: SF_6 mixture (95:5). Figure 4(a) shows a portion of the mass spectrum (from mass 25 u to 140 u) with the plasma off. As one would expect, this mass spectrum is similar to the standard electron-impact mass spectrum for sulfur hexafluoride²¹ except for the presence of argon. The cluster of mass peaks below 40 u is primarily due to background signal from residual pump oil and air in the system.

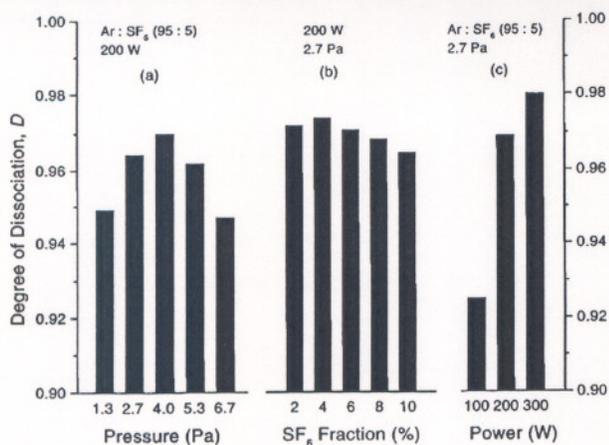


FIG. 5. Dependence of the degree of dissociation for Ar:SF₆ mixtures as a function of (a) pressure, (b) SF₆ concentration, and (c) power.

The mass spectrum shown in Fig. 4(b) was taken with the rf plasma on, and shows a significant reduction in the intensity of the SF₅⁺ peak at mass 127 u. This reduction in intensity corresponds to a degree of dissociation of 0.97. Additionally, all peaks associated with the mass spectrum of SF₆, with the exception of the S⁺ peak, also exhibit a significant reduction in intensity with the discharge on. This is indicative of the dissociation products from the SF₆ reacting with impurities in the plasma system, such as water and O₂. Reactions of this sort have been observed in high pressure glow discharges containing SF₆, and result in the formation of sulfur oxyfluorides,²² such as SOF₂, SO₂, and SO₂F₂. Mass peaks indicative of these compounds are evident in Fig. 4(b).

The trends in dissociation of SF₆ with changing plasma conditions are interesting because they are not monotonic, unlike those observed for oxygen (Fig. 3). The expected trend of increasing dissociation with increasing power is clearly evident in Fig. 5(c), where *D* increases from 0.92 to 0.98 as the applied power increases from 100 W to 300 W for an Ar:SF₆ mixture (95:5) at 2.7 Pa. However, peaks are observed in the measured trends of the degrees of dissociation with increasing pressure and SF₆ concentration, as shown in Figs. 5(a) and 5(b).

Figure 5(a) shows the degree of dissociation for a 5% SF₆ mixture at 200 W as the pressure is increased from 1.3 Pa to 6.7 Pa. The degree of dissociation exhibits a maximum of 0.97 at a total pressure of 4 Pa, dropping down to 0.95 at both 1.3 and 6.7 Pa. Figure 5(b) shows a much smaller variation in *D* as the concentration of SF₆ is increased from 2% to 10%.

The exact explanation for these trends is difficult to assess, although it is reasonable to conclude that the variations in *D* for the SF₆ mixtures result from the complex chemical reactions between the SF₆ fragments and the impurities in the reactor. The results presented here were reproducible within the stated uncertainties, but the actual values of *D* may vary considerably from reactor to reactor due to differences in O₂ and H₂O concentrations. However, it is important to note that while these trends in the dissociation of SF₆ may depend

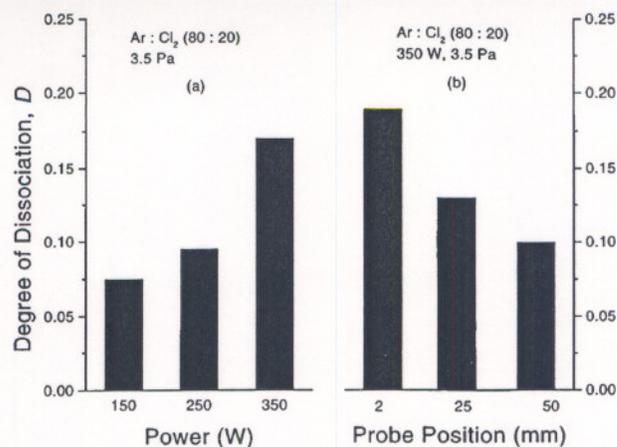


FIG. 6. Dependence of the degree of dissociation for a Ar:Cl₂ (80:20) mixture at 3.5 Pa as a function of (a) power and (b) probe position (distance from the edge of the lower electrode plate).

upon the presence of unknown amounts of impurities, the degree of dissociation for SF₆ was measured to be large (above 0.90) for all conditions investigated here, thus indicating the importance of dissociation in SF₆ containing plasmas.

D. Argon-chlorine (Ar:Cl) mixtures

Dissociation data for Ar:Cl₂ mixtures were measured without the electrostatic shield described in Sec. II, because a discharge could not be maintained with the shield in place for chlorine concentration levels above a few percent. Thus for the chlorine-containing mixtures, the GEC cell used here was configured nearly identically to those in which other studies of chlorine discharges were performed.^{10,11,19,20,23}

The data in Fig. 6 show that the dissociation levels of Cl₂ in an Ar:Cl₂ mixture fall between those of Ar:O₂ and Ar:SF₆ mixtures, ranging from 0.07 to 0.19 for the range of conditions presented here. These values are of similar magnitude as those calculated by Hoekstra and Kushner⁵ for an Ar:Cl₂ (70:30) discharge in an industrial ICP reactor. Unfortunately, a quantitative comparison between the experimental data and the theoretical calculations is not possible due to significant differences in the size of the reactor, the flow rates, and the power levels used in each study. It is interesting to note that the measured degrees of dissociation presented here for the chlorine mixture are much lower than the large degrees of dissociation (70%–99%) measured^{10,11} and calculated^{1,2} for pure chlorine discharges in other GEC cells. This possible discrepancy may be attributed to the spatial dependence of the dissociation observed in chlorine-containing discharges, which is discussed below.

The dependence on applied power shown in Fig. 6(a) is similar to that observed for Ar:O₂ and Ar:SF₆ mixtures, with *D* increasing significantly with increasing power. Dissociation levels were observed to be independent of Cl₂ concentration over a range of Cl₂ levels from 10% to 20%. The pressure dependence could not be measured at this time due to limitations in the pumping system used for corrosive gases.

The dissociation data in Fig. 6(b) indicate that for the Ar:Cl₂ mixture *D* exhibits a significant dependence upon the position of the sampling probe, with the largest values of *D* measured near the edge of the lower electrode (probe position=0). This suggests that for Ar:Cl₂ mixtures the degree of dissociation at the center of the discharge may be significantly greater than in the region outside of the radius of the lower electrode. This would be consistent with the results of model calculations for Ar:Cl₂ discharges in ICP reactors which exhibit dissociation levels nearly a factor of 2 higher in the center of the discharge compared to the levels near the edge of the electrodes.⁵ Even greater spatial variations in dissociation are predicted by calculations modeling pure chlorine discharges in ICP-GEC cells.¹

During the course of running the Ar:Cl₂ discharges, the surfaces of the stainless steel vacuum chamber, electrodes, and sampling probe were modified by the deposition of a brownish substance. The production of this substance has been reported previously in other GEC cells used with chlorine-containing plasmas.²³ Analytical analysis indicates that the substance deposited on the lower electrode is copper chloride, produced by the reaction of the chlorine-containing plasma with the copper gaskets in the GEC cell. As reported previously,²³ the presence of this deposited substance can affect both the discharge and the performance of various diagnostics. We observed that while an Ar:Cl₂ plasma was run for several minutes in our GEC cell, whose interior surfaces were coated with this substance from previous chlorine plasmas, the mass 70 u mass signal, indicative of Cl₂ concentration, decreased with time until it disappeared, while the Ar⁺ signal remained essentially unchanged. Surprisingly, the Cl₂⁺ signal remained undetectable even when the discharge was turned off. This suggests that over time the plasma affects the surface conditions within the cell in such a way that chlorine molecules are removed from the gas, presumably at the surfaces, even without the presence of a plasma. This condition eventually reverses itself (by allowing the cell to sit with the plasma off), and the original chlorine-to-argon signal ratio is recovered, indicating a return to the "original" surface conditions.

For the dissociation data presented here, this time-dependent effect was minimized by taking dissociation data for short periods of time after the plasma was struck, and then checking to make sure the initial ratio of the ion signals was reproducible immediately after the plasma was turned off. This effect implies, however, that care must be taken, at least in GEC cells, to assess if the initial gas concentrations determined by the flow controllers reflect the actual gas concentrations inside the discharge. The use of nickel-plated copper gaskets may eliminate the formation of this deposited material, but nickel-plated gaskets are presently not included in the "standard" GEC cell configuration.

IV. CONCLUSIONS

For the range of plasma conditions investigated here, the degree of dissociation of N₂ in Ar:N₂ mixtures was less than the limit of detection (0.02) of this experimental arrangement. For Ar:O₂ mixtures, the observed degree of dissociation

for the oxygen molecules was moderate, ranging from 0.02 to 0.09, with the highest dissociation levels occurring at the highest powers, lowest pressures, and lowest O₂ concentrations. The dissociation levels for SF₆ in Ar:SF₆ mixtures were greater than 0.90 for all plasma conditions studied here, ranging from 0.92 for applied powers of 100 W to 0.98 for an applied power level of 300 W. The degree of dissociation for SF₆ exhibited little dependence upon total pressure or concentration of SF₆. For the Ar:Cl₂ mixture studied, the degree of dissociation of Cl₂ varied from near 0.07 to near 0.20, depending upon the plasma power and probe position.

As one might expect, the degree of dissociation for the diatomic gases exhibits a correlation with the strength of the molecular bond that is broken during each dissociation process. Thus nitrogen, with a N–N bond strength of 9.76 eV, exhibits little or no dissociation, while oxygen (with an O–O bond strength of 5.08 eV) and chlorine (with a Cl–Cl bond strength of 2.48 eV) each exhibit progressively more dissociation.²⁴ This suggests that the dominant process for dissociation is due to electron impact.

Interestingly, SF₆, with an S–F bond strength²⁵ (3.4 eV) between that of oxygen and chlorine exhibits the highest degree of dissociation of all the molecules studied here, indicating that other factors play a role in determining the dissociation level of more complex molecules. The most likely cause of the enhanced dissociation for SF₆ is the large cross section for dissociative electron attachment exhibited by this molecule.²⁶

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