

Diagnostics of inductively coupled chlorine plasmas: Measurement of Cl_2^+ and Cl^+ densities

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The absolute densities of positive ions (Cl_2^+ and Cl^+) are obtained over a 2–20 mTorr pressure range and 5–1000 W input radio-frequency rf power range in a transformer-coupled Cl_2 plasma. The relative number density of Cl_2^+ is measured by laser-induced fluorescence. These laser-induced fluorescence data are calibrated by Langmuir-probe measurements of total positive-ion density at low powers to yield absolute values for $n_{\text{Cl}_2^+}$ and are corrected for changes in rotational temperature with rf power. In turn, the $n_{\text{Cl}_2^+}$ data are used to determine the effective-mass correction for refined Langmuir-probe measurements of the total positive-ion density. The density of Cl^+ is then the difference between the total positive-ion and Cl_2^+ densities. For all the pressures, Cl_2^+ is found to be the dominant ion in the capacitively coupled regime (input powers below 100 W), while Cl^+ is the dominant ion at higher powers (>300 W) of the inductively coupled regime. Experimental results are compared to those from a simple global model. This work is a continuation of a study that provides a complete set of experimentally measured plasma parameters over a broad range of conditions in a chlorine plasma, produced with a commercial, inductively coupled rf source.

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I. INTRODUCTION

Anisotropic etching of fine patterns into integrated circuits is made possible by the directional positive-ion bombardment that can be obtained when wafers are immersed in low-pressure plasmas. One of the most important gases used in the plasma etching of silicon and aluminum is Cl_2 . The dominant ion in predominantly Cl_2 -containing discharges can be either Cl_2^+ or Cl^+ . The etching yield (Si-per-incident ion) and etch profile shapes are no doubt different for Cl_2^+ and Cl^+ . Measuring the relative ion fluxes is, therefore, important for understanding and simulating etch profile evolution.

As part of our study to provide a complete set of plasma parameters for a Cl_2 plasma produced with a commercial plasma source,¹ we presented electron temperatures (T_e) and electron energy distribution functions in an inductively coupled chlorine plasma over a 1–20 mTorr pressure range and a 1–1000 W power range,¹ obtained by Langmuir probe and trace rare gases optical emission spectroscopy.^{2,3} We computed T_e from a simple zero-dimensional model. We also have reported measurements of neutral (Cl and Cl_2) number densities by actinometry,⁴ electron and total positive-ion densities by Langmuir probe and microwave interferometry methods,⁵ and gas temperatures by optical emission spectroscopy with trace amounts of nitrogen.⁶ All

of these data were obtained in the same reactor for the same range of conditions.

Several studies have been reported in which total positive-ion and/or electron densities were measured in an inductively coupled, high-density chlorine plasma.^{7–9} It is important, however, to know not only the total ion density, but also the individual densities of each ion. In addition to the more practical reasons given above, knowledge of the Cl_2^+ and Cl^+ densities ($n_{\text{Cl}_2^+}$ and n_{Cl^+}) is important because these ions diffuse and recombine differently, thus influencing the plasma particle balance. Modeling studies generally suggest that Cl_2^+ dominates at low power, but considerable disagreement exists as to whether Cl^+ or Cl_2^+ become dominant at high power.^{10–13} Two recent experimental studies indicate that Cl^+ can become the major positive ion at high powers.^{14,15}

Previously, we reported measurements of Cl_2^+ densities that were obtained by laser-induced fluorescence in a 10 mTorr chlorine plasma.¹⁵ The fluorescence signal from Cl_2^+ was then normalized to the total positive-ion density at low power, measured with a Langmuir probe, to obtain the absolute density of Cl_2^+ . Here, we extend this study over the pressure range of 2–20 mTorr and also introduce a temperature correction that compensates for the wider rotational energy partitioning in converting the laser-induced fluorescence signals into Cl_2^+ number densities at the higher gas temperatures and powers. The total positive-ion densities (n_i^+) were initially obtained by Langmuir-probe analysis with an assumed effective ion mass of 48. In this study we

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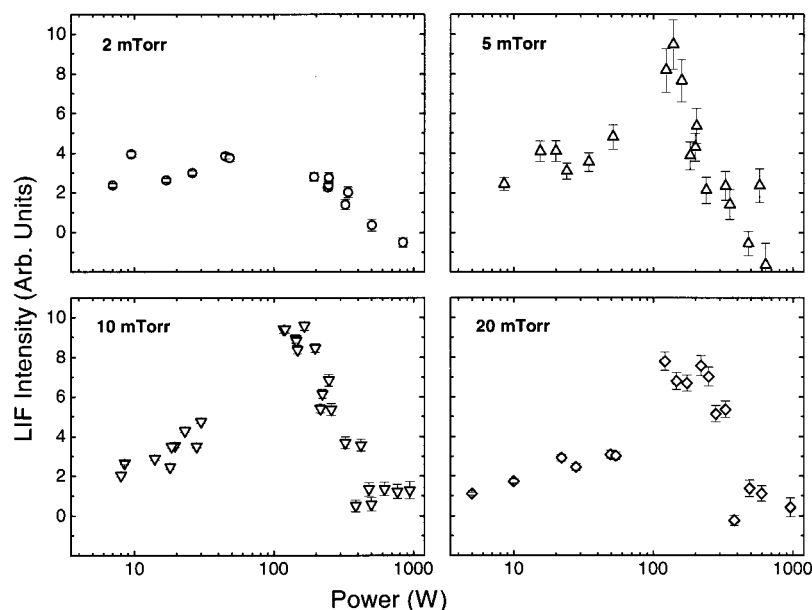


FIG. 1. Laser-induced fluorescence signal intensity of Cl_2^+ at 3960 Å induced by 3876.4 Å laser radiation as a function of rf power at 2, 5, 10, and 20 mTorr Cl_2 .

obtained more reliable n_i^+ values by using a realistic ion mass by varying between $M_i \approx 70$ amu (Cl_2^+) at the lowest power and $M_i \approx 35$ amu (Cl^+) at the highest power. The assumption that Cl_2^+ is the dominant positive ion at low power is supported by modeling, and is discussed below. As described previously,¹⁵ the density of Cl^+ is obtained from the difference between the absolute values of n_i^+ and $n_{\text{Cl}_2^+}$. Cl^+ is shown to be the dominate positive ion at high power.

II. EXPERIMENTAL PROCEDURE

The transformer-coupled plasma (TCP) reactor used here has been described in detail previously,¹ as were the Langmuir-probe setup and the procedure for determination of total positive-ion density.

The relative concentration of Cl_2^+ was determined by the laser-induced fluorescence (LIF) method that was described in previous experiments with a 10 mTorr plasma.¹⁵ In that experiment, the plasma was operated in an inductively coupled mode (with a transformer-coupled plasma antenna) and in a capacitively coupled mode (applying power to the chuck only).¹⁵ In the present experiment, no power is applied to the chuck. The LIF apparatus consisted of an excimer-pumped dye laser and an optical emission spectrometer. A Lambda Physik model EMG 201 XeCl excimer laser (10 Hz repetition rate, 3080 Å, 20 ns pulse length, 150 mJ pulse energy) pumped a Lambda Physik model FL2002 dye laser (nominal output of 3.5 mJ/pulse at 3876 Å, with BiBuQ dye, dissolved in cyclohexane). The laser beam was parallel to the wafer surface at a distance of ~ 3 cm. The LIF signal was collected from a ~ 1 -cm-long region over the center of the 12.5-cm-diam wafer. LIF and plasma-induced emission (PIE) signals were observed through a UV-grade quartz window, normal to the laser beam, and were imaged with a fused-silica lens onto the entrance slit of a 0.25 m focal length monochromator (MacPherson model 218).

The monochromator was set to pass the 3960 Å signal to a GaAs photomultiplier tube (PMT). The signal bandwidth

was 10 Å (full width at half maximum), determined by the 400- μm -wide entrance and exit slits. The PMT output was directed to a two-channel boxcar integrator (model SR 280). One channel monitored the transient LIF signal plus the plasma-induced emission background emission. The second channel monitored the PIE signal delayed by 10 μs , allowing the <1 μs LIF signal (mostly determined by the RC time constant of the detection system) to decay to a negligible level. Experiments were done by varying input rf power (5–1000 W) and discharge pressure (2–20 mTorr Cl_2). LIF signals were normalized for drifts in laser intensity, following the procedure given in Ref. 15.

III. RESULTS AND DISCUSSION

A. LIF data

Cl_2^+ ions are excited from the $v''=0$ vibrational level of the $X^2\Pi_i$ ground electronic state to the $n'=10$ “vibrational level” of the $A^2\Pi_i$ excited state by laser radiation in the range of 3860–3890 Å.^{15,16} The excited ions fluoresce, decaying to v'' levels of the ground state. The maximum amount of fluorescence signal at 3960 Å (transition to the $v''=1$ state, to avoid intense scatter laser light) was obtained with the excitation wavelength at 3876.4 Å, corresponding to excitation to one of the rotational levels within the vibronic band (see Fig. 1 in Ref. 15).

The intensity of the LIF signal as a function of rf power measured at 2, 5, 10, and 20 mTorr is shown in Fig. 1. At all pressures the LIF intensity increases with TCP power in the capacitively coupled (<100 W, “dim-mode”) regime, jumps to a higher value as the plasma makes a transition to the inductively coupled (>100 W, “bright-mode”) regime, and then continuously decreases with increasing power in the inductively coupled regime. While the LIF signals plotted in Fig. 1 are proportional to the population of the rovibrational level probed by the laser, they are not necessarily proportional to the relative density of the ground state of Cl_2^+

(the sum of all rotational and vibrational levels populated at steady state). One has to correct for the changes of the population of the chosen rotational and vibrational levels with rf power to convert the LIF signals into relative densities of Cl_2^+ , since the rotational and vibrational temperatures of Cl_2^+ change with power. Here, we apply the correction for changes in population of the ground-state rotational level explicitly, and estimate and include in the error bars a possible change in population of the ground-state vibrational level.

B. Population of the rotational level

The population of the ground electronic state rotational level, $J''=29$, the average of the two levels monitored (28.5 and 29.5), is proportional to

$$N_{J''} \propto (2J''+1)(B''/kT) \exp[-B''J''(J''+1)/kT], \quad (1)$$

where B'' is the ground-state rotational constant (0.2686 cm^{-1}).¹⁷ We assume that the Cl_2^+ rotational temperature is equilibrated with the translational gas temperature and will use the gas temperature measured under the same conditions, and reported elsewhere,⁶ to compute the relative decrease in $N_{J''}$ with increasing power and gas temperature. Therefore, ignoring vibrational effects for the moment, the LIF signal intensity divided by $N_{J''=29}$ is proportional to the total population of Cl_2^+ .

C. Population of the vibrational level

The vibrational-level populations of Cl_2^+ , however, are not necessarily in thermal equilibrium with other degrees of freedom of Cl_2^+ or the neutral gas. The vibrational population distribution of the ground electronic state of Cl_2^+ immediately after formation is determined by the Franck–Condon factors for electron-impact ionization from each v'' level of the ground state of Cl_2 . This population distribution could be quite hot or possibly inverted, even if Cl_2 is vibrationally very cold. Once formed, Cl_2^+ can thermalize with the neutral gas. Although nonresonant vibrational–vibrational (V – V) energy transfer is slow for neutral–neutral collisions, it has been shown to be fast for collisions between diatomic ions and neutrals such as N_2^+ and N_2 .¹⁸ This is due to long-range polarization effects that cause N_2^+ to lose vibrational energy at the gas-kinetic collision rate, often with charge exchange, and sometimes with multiple quanta being lost in a single collision. If we assume that a similarly fast process occurs with Cl_2^+ and Cl_2 , then at low power, the vibrational temperature of Cl_2^+ will equilibrate with that of Cl_2 (assumed to be close to the wall temperature at low power). This is true even at the lowest pressure (2 mTorr), since the gas-kinetic collision rate ($\sim 1 \times 10^4 \text{ s}^{-1}$ at 2 mTorr and 300 K) is fast compared to the ion loss rate due to diffusion ($\sim 3 \times 10^3 \text{ s}^{-1}$).

At high power, the situation is more complicated. At high pressure (20 mTorr), the percent dissociation of Cl_2 in the plasma is about 85% at 1000 W and the gas temperature is $\sim 1000 \text{ K}$. Consequently, a gas-kinetic collision rate of vibrational equilibration of Cl_2^+ with Cl_2 ($\sim 1 \times 10^4 \text{ s}^{-1}$) is larger than the rate at which the ions diffuse to the walls

($\sim 2 \times 10^3 \text{ s}^{-1}$), hence, its vibrational temperature would still be about the same as that of Cl_2 . Fortunately, the vibrational constant of Cl_2^+ is large enough (640 cm^{-1}) that the population of its $v''=0$ only changes from 95% at 300 K to 60% if its vibrational temperature reaches the highest gas temperature recorded (1000 K). Thus, if the vibrational temperature were to increase from 300 K at low power to 1000 K at 1000 W, then the fraction of Cl_2^+ in $v''=0$ would decrease by only $\sim 37\%$, and the raw LIF data in Fig. 1 would have to be increased by this amount at the highest power to correct for the effect.

At low pressure (2 mTorr) and high power (1000 W), Cl_2 is more than 90% dissociated⁴ and Cl_2^+ will retain more of its initial population because of the low Cl_2 number density and the inefficient vibrational energy transfer with Cl . Judging from potential curves for Cl_2 and Cl_2^+ ,¹⁹ ionization of Cl_2 $v''=0$ will excite more Cl_2^+ $v''=1$ than $v''=0$ in a vertical transition. If a substantial population of Cl_2 $v''=1$ is present, however, it will more likely result in population of Cl_2^+ $v''=0$ and Cl_2^+ $v''=2,3$ in vertical transitions from the inner and outer walls of the Cl_2 potential curve. Consequently, the relative population of Cl_2^+ $v''=0$ might actually increase if a substantial fraction of Cl_2 $v''=1$ is formed at higher power. If the vibrational population of Cl_2^+ is dictated by these Franck–Condon effects, then the LIF data at high power and low pressure would have to be decreased to convert the signals into relative Cl_2^+ number densities, due to a five-fold increase in Cl_2 $v''=1$ at 1000 K (assuming the Cl_2 vibrational temperature is equilibrated with the gas temperature). A full treatment of this issue is beyond the scope of this article. Given reasonable estimates for the vibrational overlap integrals of the Cl_2 and Cl_2^+ vibrational levels, it seems unlikely that this downward correction would exceed a factor of 2.

D. Ion densities

Raw LIF data (open triangles) from a 10 mTorr Cl_2 plasma as well as the data corrected for the depopulation of the rotational level due to the increase of gas ($=\text{Cl}_2^+$ rotational) temperature with increasing input rf power are shown in Fig. 2. (Ref. 6 showed that this temperature increases sublinearly with power from 300 to 1000 K over the 5–1000 W rf power range.) The error bars represent both the statistical uncertainties in measured LIF signals and the possible correction due to change in the population of the vibrational level (i.e., the data points are not corrected for changes in the vibrational populations). The same procedure was applied for the 2, 5, and 20 mTorr data, though not shown. These corrected values correspond to the relative number density of Cl_2^+ .

Both the relative density of Cl_2^+ and the total positive-ion density measured with a Langmuir probe (see Ref. 5 and below) increase in the capacitively coupled mode. In the inductively coupled mode, n_i^+ increases at a faster rate as rf power increases while the relative density of Cl_2^+ rapidly decays. Since the gas phase in the capacitively coupled dim mode consists overwhelmingly of Cl_2 , the rate of creation of Cl_2^+ is much faster than that of Cl^+ in the electron-impact

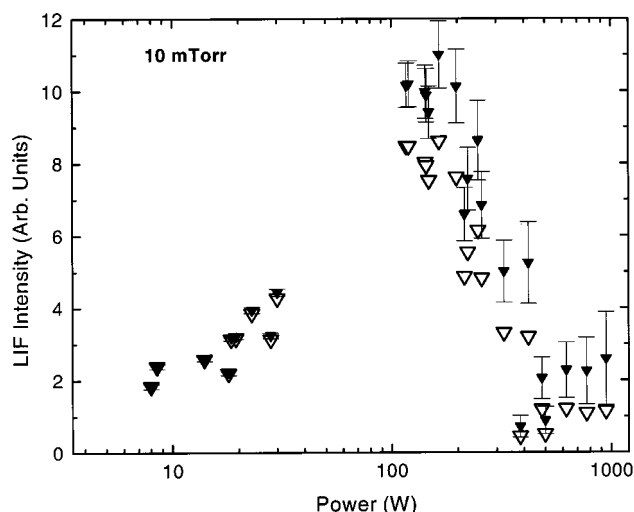


FIG. 2. LIF signal (open triangles) and relative density of Cl_2^+ (closed triangles) as a function of rf power for a 10 mTorr Cl_2 plasma.

ionization of Cl_2 , and the destruction rates of both ions are relatively similar, we assumed that the dominant ion in the dim mode is Cl_2^+ . We, therefore, obtained absolute densities of Cl_2^+ by normalizing the relative $n_{\text{Cl}_2^+}$ to n_i^+ over the capacitively coupled regime of operation.

Figures 3–6 present $n_{\text{Cl}_2^+}$ and n_i^+ as functions of rf power (closed and open symbols, respectively), as well as densities of Cl_2^+ and Cl^+ computed from a global model (solid and dashed lines, respectively), for pressures ranging from 2 to 10 mTorr. The details of the model were presented previously¹ and the input parameters in the present case are pressure and total positive-ion density. Positive-ion density is used instead of power to simplify the calculation, and presumably make it more reliable. The input positive-ion density is taken from the Langmuir-probe measurements in Figs. 3–6. This choice of input parameters circumvents the difficulties in solving the energy balance equation, and assures that the sum of the computed $n_{\text{Cl}_2^+}$ (solid line) and n_{Cl^+}

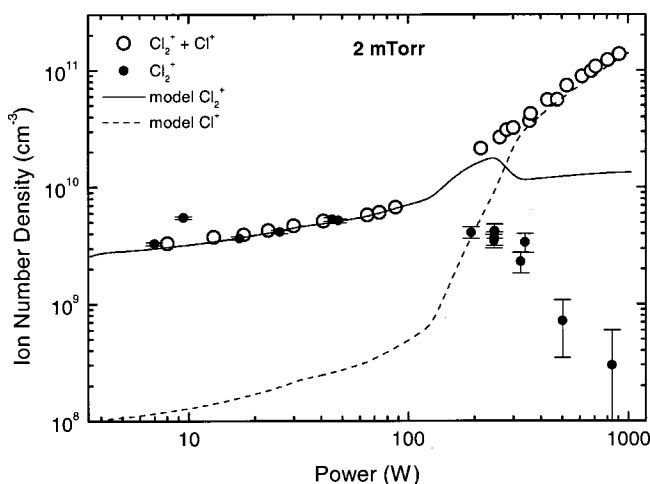


FIG. 3. Total positive-ion density, density of Cl_2^+ , and modeled densities of Cl_2^+ and Cl^+ as functions of rf power for a Cl_2 plasma at 2 mTorr.

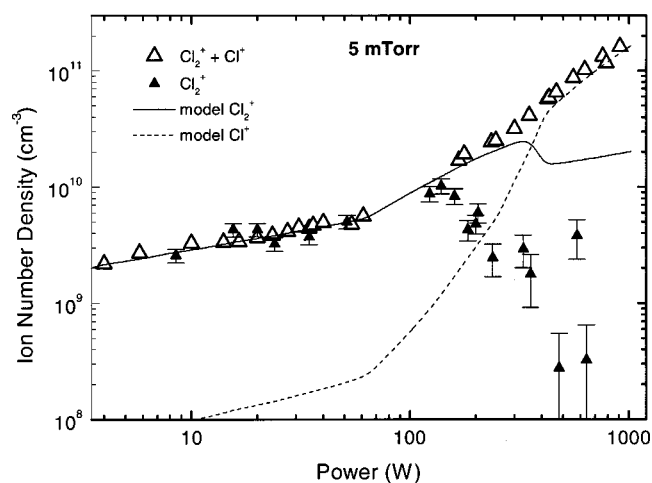


FIG. 4. Total positive-ion density, density of Cl_2^+ , and modeled densities of Cl_2^+ and Cl^+ as functions of rf power for a Cl_2 plasma at 5 mTorr.

(dashed line) is exactly equal to the measured total positive-ion density (open symbols). The results of the model, though overestimating $n_{\text{Cl}_2^+}$ at higher powers, undoubtedly support the experimental observation that Cl_2^+ is the dominant ion in the dim mode, thereby validating our normalization procedure.

The data in Figs. 3–6 show that the densities of both ions are fairly independent of pressure from 2 to 20 mTorr. The correction for temperature leads to somewhat higher densities of Cl_2^+ at the higher rf powers studied than those presented in Ref. 7 at 10 mTorr, but they are still much smaller than the corresponding densities of Cl^+ .

Once the absolute density of Cl_2^+ and, therefore, that of Cl^+ , have been obtained, the total positive-ion density can be corrected, using the appropriate ion mass. Initially, n_i^+ was determined from the ion saturation part of a $I-V$ curve using a model that utilizes a Laframboise numerical solution based on orbital-motion-limited theory^{5,20} and assuming an effective ion mass equal to 48 amu, which corresponds to equal amounts of Cl_2^+ and Cl^+ . The effective ion mass is

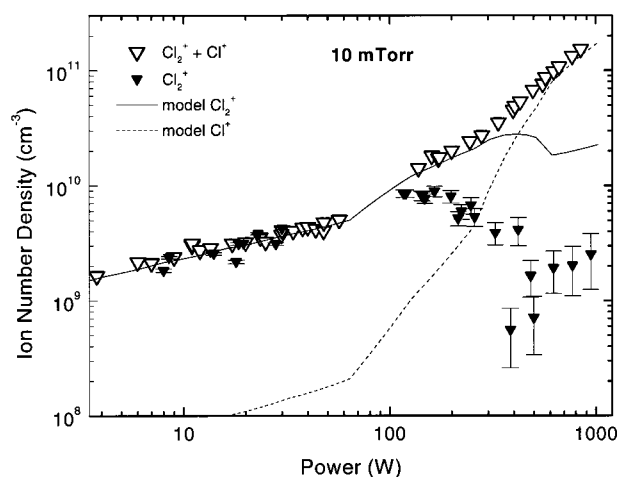


FIG. 5. Total positive-ion density, density of Cl_2^+ , and modeled densities of Cl_2^+ and Cl^+ as functions of rf power for a Cl_2 plasma at 10 mTorr.

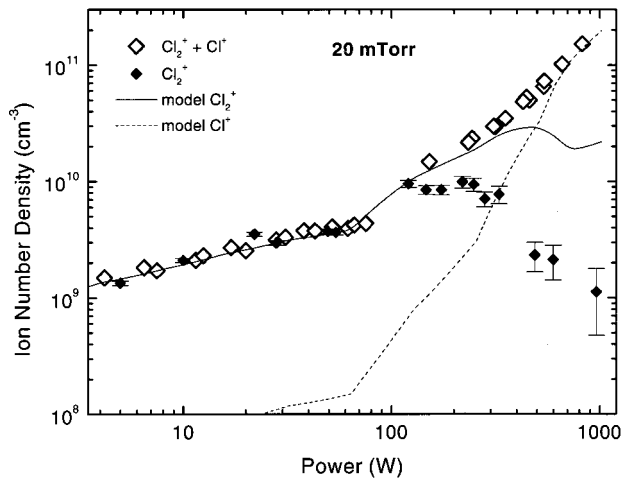


FIG. 6. Total positive-ion density, density of Cl_2^+ , and modeled densities of Cl_2^+ and Cl^+ as functions of rf power for a Cl_2 plasma at 20 mTorr.

$$M_{\text{eff}} = \left(\frac{f_{\text{Cl}_2^+}}{M_{\text{Cl}_2^+}^2} + \frac{1-f_{\text{Cl}_2^+}}{M_{\text{Cl}^+}^2} \right)^{1/2}, \quad (2)$$

where $f_{\text{Cl}_2^+} = n_{\text{Cl}_2^+}/n_i^+$. This correction increases n_i^+ at low power, when Cl_2^+ is the dominant ion ($M_{\text{eff}} \approx 70$) and decreases it at high power, when Cl^+ is the dominant ion ($M_{\text{eff}} \approx 35$). The procedure must be iterative, since the correction to n_i^+ changes $n_{\text{Cl}_2^+}$, but it converges very rapidly. The original ($M_{\text{eff}}=48$, closed triangles) and corrected data for 10 mTorr (open triangles) are shown in Fig. 7. The total ion density values presented in Figs. 3–6 are the corrected measurements, obtained from this procedure.

Comparison of $n_{\text{Cl}_2^+}$ and n_i^+ shows that at all pressures the discharge has practically no Cl^+ when it is operated in the capacitively coupled mode. When an increase in power causes the plasma to switch into an inductively coupled

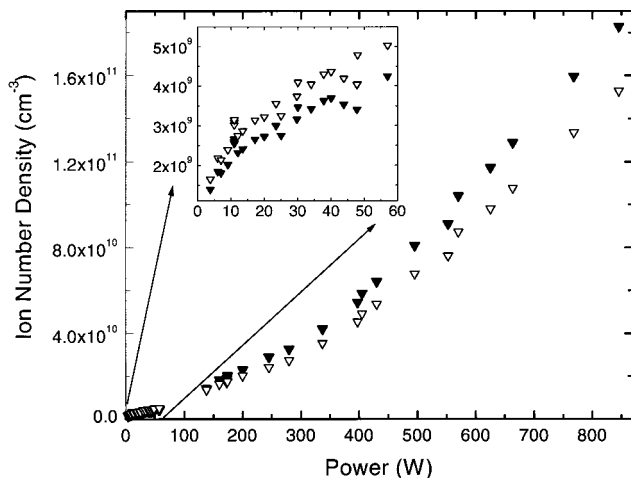


FIG. 7. Correction of total positive-ion density for the change in the effective ion mass for the data from a Cl_2 plasma at 10 mTorr. n_i^+ was determined from both the Langmuir-probe data with the assumption that $M_{\text{eff}}=48$ amu (closed triangles), the actual M_{eff} (open triangles), obtained using the LIF results.

mode, $n_{\text{Cl}_2^+}$ reaches a maximum of $\sim 1 \times 10^{10} \text{ cm}^{-3}$, and further increases in rf power lead to a decrease in $n_{\text{Cl}_2^+}$. At the higher powers of the inductively coupled regime, the discharge is dominated by Cl^+ . At 2 mTorr, $n_{\text{Cl}_2^+}$ appears to peak just before reaching the inductive mode at a somewhat lower number density ($\sim 7 \times 10^9 \text{ cm}^{-3}$). This relative dominance of Cl_2^+ vs. Cl^+ is qualitatively similar to that between Cl_2 and Cl , although it is much less dependent on pressure. The transition from predominantly Cl_2^+ to predominantly Cl^+ is much sharper than the transition from Cl_2 to Cl ,⁴ and occurs at about 100 W at all pressures. In contrast, the transition from Cl_2 to Cl -dominated conditions occurs at ~ 100 W at 5 mTorr and below, but at 200 W for 10 mTorr, and 400 W for 20 mTorr.⁴ Another difference between the trends of the neutrals and ions is that at the higher rf powers $n_{\text{Cl}^+}/n_{\text{Cl}_2^+} \sim 100\text{--}1000$, while $n_{\text{Cl}}/n_{\text{Cl}_2} \sim 10\text{--}30$.⁴

The simple, zero-dimensional model qualitatively describes the behavior of $n_{\text{Cl}_2^+}$ in Figs. 3–6, although it overestimates its density at the highest rf powers at all pressures by about an order of magnitude. Our computed $n_{\text{Cl}^+}/n_{\text{Cl}_2^+}$ values are similar to the ratios of $\sim 5\text{--}10$ computed by Wise Lymberopoulos, and Economu at high inductive powers.¹² These values are somewhat larger than the high-power values of ~ 2 computed by Meeks and Shon,¹⁰ and much higher than the modeling results of Ventzek, Grapperhaus, and Kushner¹¹ ($n_{\text{Cl}^+}/n_{\text{Cl}_2^+} \sim 0.4$). Finally, the relative independence of the total ion density with pressure is in agreement with other experimental studies^{8,9} and at least one modeling study.¹²

IV. CONCLUSIONS

We have probed Cl_2^+ by laser-induced fluorescence in a chlorine discharge over a pressure range of 2–20 mTorr at rf powers between 5 and 1000 W. The LIF signal from Cl_2^+ was corrected for changes in gas temperature to obtain the relative density of Cl_2^+ . The relative values of $n_{\text{Cl}_2^+}$ were then normalized at low power to n_i^+ from Langmuir-probe measurements to obtain absolute values of $n_{\text{Cl}_2^+}$.

At all pressures, Cl_2^+ is shown to be the dominant ion in the capacitively coupled regime of operation (<100 W), while Cl^+ is dominant at higher, inductively coupled powers (>300 W). For pressures from 5 to 20 mTorr, $n_{\text{Cl}_2^+}$ reaches a maximum of $\sim 1 \times 10^{10} \text{ cm}^{-3}$ at ~ 130 W. At 2 mTorr, $n_{\text{Cl}_2^+}$ peaks while still in the capacitive mode at $\sim 7 \times 10^9 \text{ cm}^{-3}$. The trend of Cl_2^+ being dominant in the capacitively coupled mode and Cl^+ in the inductively coupled mode qualitatively follows the relative dominance of the corresponding neutral Cl_2 and Cl , although the rf power at which the transition where one species dominates the other depends on pressure much more for the neutrals.

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