Laser-induced fluorescence and Langmuir probe determination of Cl_2^+ and Cl^+ absolute densities in transformer-coupled chlorine plasmas

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Laser induced fluorescence detection of Cl_2^+ has been used to track their relative concentration in a high-density inductively (transformer) coupled (TCP) 10 mTorr chlorine plasma as a function of the 13.56 MHz radio frequency (rf) power. This relative Cl_2^+ number density was compared to the total absolute positive ion density ($n_i^+ = n_{Cl}^+ + n_{Cl_2^+}$) obtained with a Langmuir probe. Both $n_{Cl_2^+}$ and n_i^+ doubled with increasing rf power from 8 to ~55 W in the capacitively coupled (dim) mode. Above the transition from a capacitively to inductively coupled (bright-mode) plasma at ~85±35 W, $n_{Cl_2^+}$ decayed with rf power while n_i^+ continued to increase. Consequently, Cl_2^+ is the dominant ion in dim-mode operation and Cl^+ is the dominant ion in bright-mode operation, at $n_i^+ \geqslant 6\times10^{10}$ cm^{-3}. With the plasma operating in the reaction ion etch (RIE) mode (the stage powered at 14.56 MHz, and no TCP power) $n_{Cl_2^+}$ tracked n_i^+ over the entire range of powers (2–150 W). Thus, Cl_2^+ is the dominant ion during capacitively coupled RIE operation. © *1999 American Institute of Physics.* [S0003-6951(99)03612-8]

Cl_2-containing plasmas are widely used to etch of silicon, aluminum and other materials used in silicon-based integrated circuits. Etch rates and the shapes of etched profiles depend on the relative fluxes of Cl_2, Cl, Cl_2^+ and Cl^+. Previously, we have reported measurements of Cl and Cl_2 number densities during slow etching [i.e., with an oxidized Si wafer, or with a Si wafer with no radio frequency (rf) bias to the stage] in a 10 mTorr chlorine, transformer-coupled plasma (TCP).[1] Under these conditions, the predominant neutral species at low TCP rf power is Cl_2, as expected. As rf power is increased, however, Cl radicals account for ~90% of all neutrals at a power density of 0.4 W/cm^3. The transition from a Cl_2 to Cl-dominated plasma is smooth, with almost no Cl_2 dissociated in the capacitive mode (up to ~80 W), and a gradual increase in percent dissociation with increasing power in the inductive mode. Similar trends were observed in other laboratory and commercial plasma reactors with sharper transitions at lower pressure.[2–4]

Fractional densities of Cl^+ and Cl_2^+ influence both plasma steady state conditions (through ion diffusion and losses) and plasma–surface interactions during etching (through ion bombardment). However, there still remains uncertainty about the relative concentrations of Cl^+ and Cl_2^+ throughout these rf power regimes.[5,6] Clarification of the relative abundance of these two ions in a 10 mTorr Cl_2 plasma as a function of rf power is the objective of this letter. Cl_2^+ ion density, $n_{Cl_2^+}$, is obtained by calibrating the measured laser-induced fluorescence (LIF) signal. n_{Cl^+} is deduced from $n_{Cl_2^+}$ and the total, absolute positive ion density $n_i^+ (= n_{Cl_2^+} + n_{Cl^+})$ is obtained *via* Langmuir probe analysis. With no rf bias power, the Si etching rate in this system is <50 Å/min, presumably due to the low (~12 V) sheath potential, and possibly suppression of etching by sputter transport of quartz from the TCP window. This slow etching rate, verified by the lack of any detectable emission from $SiCl_2$ or $SiCl_3$, corresponds to an etching product concentration of <0.1% of the 80 sccm Cl_2 flow rate. Consequently, we can safely assume that all other ions (i.e., $SiCl_x^+$) will be at much lower concentrations than either Cl^+ or Cl_2^+.

The reactor consists of a stainless steel cylindrical chamber of 36 cm inner diameter and 22 cm height. The top opening of the cylinder is covered by a 25 cm diameter quartz window. Above the window is a TCP source, consisting of a 6 in. diameter, six-loop coil antenna and matching network (LAM Research). The antenna was powered by a 3 kW Plasma-Therm generator operating at 13.56 MHz. An He-cooled chuck, equipped to hold 5 in. wafers, can be moved vertically with respect to the reactor. In these experiments, the chuck was ~12 cm from the quartz window. In the TCP mode, no rf power was applied to the stage. In the RIE mode, no power was applied to the TCP coil, and rf power was applied to the chuck at 14.56 MHz. Two quartz windows on opposite sides of the chamber allowed the laser light to pass through the plasma. For Langmuir probe measurements, one of the windows was replaced by a flange that mated to the probe.

The LIF apparatus consisted of an excimer laser-pumped dye laser and 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

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Physik model FL2002 dye laser (nominal output of 3.5 mJ/pulse at 3876 Å, using BiBuO dye, dissolved in cyclohexane) tuned to excite fluorescence in Cl_2^+. LIF and plasma-induced emission (PIE) were observed through quartz window, normal to the laser beam, and were imaged with a lens onto the entrance slit of a 0.25 m focal length monochromator (MacPherson model 218) equipped with a GaAs photomultiplier tube (PMT). The monochromator was set to pass 3960 Å fluorescence with a band width of 10 Å set by the 400 μm wide slits. The PMT output was directed to a two-channel boxcar integrator (model SR 280). One channel monitored the transient LIF signal plus the PIE background at 3960 Å. The second channel monitored the PIE signal delayed by 10 μs, allowing the <1 μs LIF signal [mostly determined by the resistance-capacitance (RC) time constant of the detection system] to decay to a negligible level. The LIF intensity was measured as a function of rf power for a 10 mTorr Cl_2 plasma, and additionally as a function of laser pulse energy (0.38–1.28 mJ) to assess the effect of drift in laser power during the rf power dependence measurements. The transmitted laser pulse energy was varied within the above range by placing a combination of quartz flats in front of the beam.

Positive ion density was measured by a Scientific Systems Langmuir probe. Values were obtained from a fit of the ion current part of current–voltage characteristics by the Laframboise model.[7] The effective ion mass was initially assumed to be 48 amu (corresponding to the 50/50 fraction of Cl^+ and Cl_2^+ ions),[7] and was then corrected using the LIF data to obtain self-consistent results. The effective ion mass is 70 amu for lower power (for ~100% Cl_2^+) and 35 amu for high power(for ~100% Cl^+), with intermediate values consistent with the $[Cl^+]/[Cl_2^+]$ ratio.

Laser radiation in the range of 3860–3890 Å excites Cl_2^+ ions from the $v''=0$ vibrational level of the $X\,^2\Pi_i$ ground electronic state to the $n'=10$ ''vibrational level''[8] of the $A\,^2\Pi_i$ excited state.[9,10] Excited ions fluoresce at wavelengths longer than or equal to the laser wavelength, corresponding to transitions from $n'=10$ to v'' levels of the ground state. To determine the most suitable laser wavelength for excitation, a fluorescence excitation spectrum was obtained by scanning the laser wavelength from 3860 to 3890 Å, with the bandpass of the monochromator at 3960 Å to capture the $n'=10\rightarrow v''=1$ emission. This redshifted vibronic band was chosen to avoid scatter light from the laser. This spectrum is shown in Fig. 1 for the 10 mTorr Cl_2 plasma at 165 W TCP power. Figure 1 reveals that an excitation wavelength of 3876.4 Å produces roughly a maximal LIF signal at 3960 Å. This corresponds to excitation to the $J'=30.5$ (R branch) and 27.5 (P branch) rotational levels, within an uncertainty of ± 1. The laser and monochromator wavelengths were fixed at these values in the experiments described below.

Three sets of LIF measurements were made as a function of TCP power. During each set, the laser power started at ~1.5–3 mJ and decayed by ~40% by the end of the run. Measurements were done in random order of TCP power to eliminate any systematic error. Nonetheless, a dependence of the LIF signal on laser pulse energy (Fig. 2) at constant TCP power (200 W) was performed to assess the validity of ignoring the degradation in laser pulse energy. The LIF intensity showed a moderately saturated, linear dependence on the laser pulse energy, over a range of pulse energies wider and somewhat lower than that encountered in each set of experiments. Even higher laser energies would result in a greater degree of saturation. Consequently, ignoring the decay in laser power introduced a negligible ($\pm 7\%$) scatter in the LIF signal versus TCP power. The three sets of measurements were normalized at a common TCP power to account for long term drifts in optical alignment, laser wavelength, and detector sensitivity.

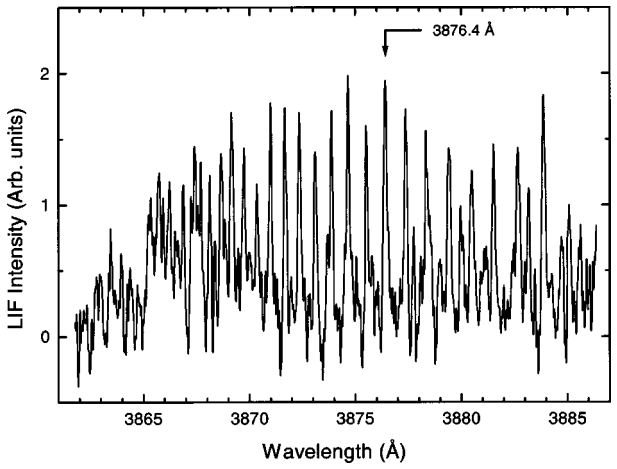

FIG. 1. Fluorescence excitation spectrum of Cl_2^+ in a 10 mTorr Cl_2 plasma at 165 W TCP power. The peak labeled 3876.4 Å is the transition corresponding to excitation to $J'=30.5\pm 1$ (R branch) and 27.5 ± 1 (P branch).

n_{Cl^+} and $n_{Cl_2^+}$ are shown in Fig. 3 as a function of power for (a) TCP and (b) RIE plasmas with 10 mTorr Cl_2. At low TCP powers (8–40 W) in the dim, capacitive mode, $n_{Cl_2^+}$ follows n_i^+. This suggests that $n_{Cl_2^+}$ is the dominant ion at lower power (see below), consistent with the fact that the gas phase is overwhelmingly Cl_2.[1] We therefore calibrated the LIF measurements by normalizing $n_{Cl_2^+}$ to n_i^+ from 8 to 40 W. Above ~100 W, the TCP plasma enters the inductive mode, and n_i^+ increases more strongly with power, as expected. In contrast, $n_{Cl_2^+}$ decreases by a factor of ~10 as TCP

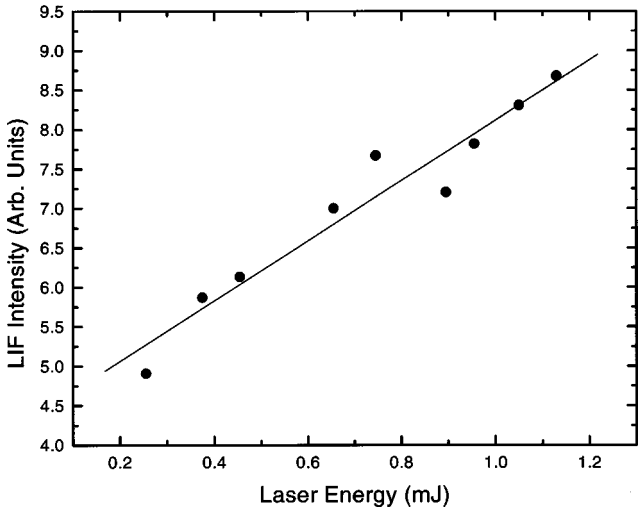

FIG. 2. LIF intensity of Cl_2^+ vs laser pulse energy in a 10 mTorr Cl_2 TCP plasma at 200 W.

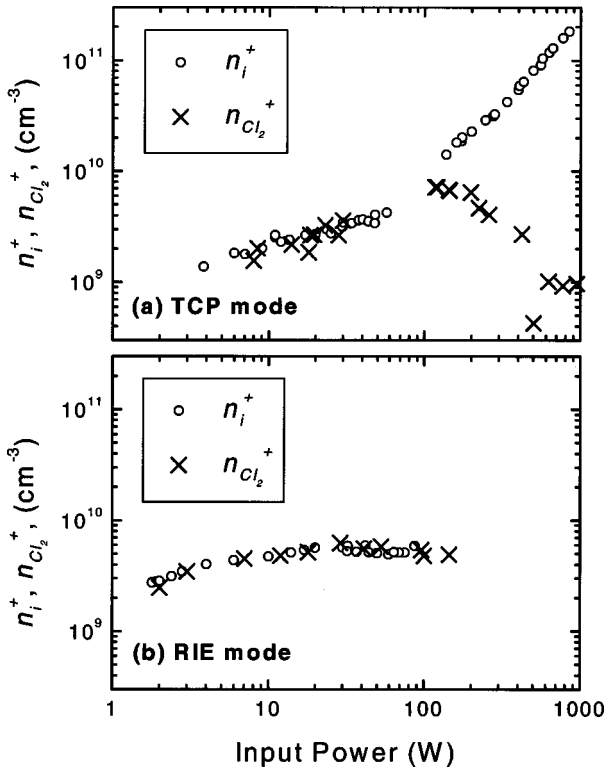

FIG. 3. $n_{Cl_2^+}$ (measured by LIF) and n_i^+ (measured with a Langmuir probe) vs power in 10 mTorr Cl_2 plasmas: (a) TCP and (b) RIE.

power increases from ~150 to 1000 W. At 300 W, n_i^+ ($=n_{Cl^+}+n_{Cl_2^+}$) is an order of magnitude larger than $n_{Cl_2^+}$, so $n_{Cl^+}/n_{Cl_2^+}\approx 10$; at this same power $n_{Cl}/n_{Cl_2}\sim 1$.[1] At 1000 W, $n_{Cl^+}/n_{Cl_2^+}\approx 200$, while $n_{Cl}/n_{Cl_2}\approx 20$.

The capacitively coupled RIE plasma behaves similarly to the TCP, dim-mode plasma. $n_{Cl_2^+}$ (normalized to n_i^+ at ~3 W) tracks n_i^+ to the highest attainable power (130 W). Note that the LIF and the Langmuir probe data were both collected from the same region, close (~1 cm) to the chuck and far (~12 cm) from the TCP coil. This could explain the fact that at low powers the plasma density in the RIE mode is higher than that for the TCP mode, which is also capacitively coupled in this low power regime.

As noted above, we assume that there are relatively few Cl^+ ions at low TCP powers in the capacitive mode. In this regime, dissociation of Cl_2 is typically a few percent for a 10 mTorr Cl_2 plasma.[1–4] Ions are produced by the ionization of neutral according to reactions (1)–(3):

$$Cl+e\rightarrow Cl^+ +2e, \tag{1}$$

$$Cl_2+e\rightarrow Cl_2^+ +2e, \tag{2}$$

$$Cl_2+e\rightarrow Cl+Cl^+ +2e. \tag{3}$$

The rate of reaction (3) is much less than the comparable rates of reactions (1) and (2),[11] while the loss rates of Cl^+ and Cl_2^+ (mainly to the walls) are about equal. Therefore, because $n_{Cl}/n_{Cl_2}\ll 1$ at TCP powers of <40 W, the dominant ion should be Cl_2^+, and our procedure for the calibration of the LIF signal to derive absolute $n_{Cl_2^+}$ densities is justified.

In the RIE case, the close match of the two curves indicates that the dominant positive ion remains Cl_2^+ even at the highest powers. The plasma volume in this case is small, and the dissociation of Cl_2 is inefficient at such a low plasma density. Therefore, we expect the gas phase to be mostly Cl_2 and the dominant ion to be Cl_2^+ [according to reaction rates (1)–(3)], as for the TCP in the dim mode.

The normalized LIF signals plotted in Fig. 3 are actually proportional to the population of the rovibrational level probed by the laser, not the sum of all populated rotational and vibrational levels. The Cl_2^+ number densities in Fig. 3 are thus uncorrected for changes in the population of the rotational and vibrational levels probed by the laser. The population of rotation level $J''=29$ (the average of the two levels monitored: 28.5 and 29.5) is proportional to $(2J''+1)\times(B''/kT)\exp[-B''J''(J''+1)/kT]$, where B'' is the ground state rotational constant (0.2686 cm^{-1}).[9] If the gas temperature T (assumed to be equilibrated with the Cl_2^+ rotational temperature) were to increase from 330 to 1000 K (likely an overestimate) over the power range from 40 to 1000 W in Fig. 3(a), then the relative population of $J''=29$ would fall from 1.0 at 330 K to 0.65 at 1000 K, from rotational heating alone. Similarly, vibrational heating due to the same increase in gas temperature would cause the relative population of the $v''=0$ level probed by the laser to drop from 1.0 to 0.67.[7] Consequently, no more than a factor of ~2.3 of the tenfold decrease in $n_{Cl_2^+}$ from 150 to 1000 W TCP power can be attributed to rotational and vibrational heating of Cl_2^+.

In conclusion, we have shown that the dominant positive ion in a 10 mTorr Cl_2 TCP plasma is Cl_2^+ in dim-mode operation (rf power $<85\pm35$ W) and Cl^+ in bright-mode operation ($\geqslant$100 W). At the highest TCP powers investigated, $n_{Cl^+}/n_{Cl_2^+}=200$ if the effects of heating on the LIF signal are ignored and ~90 if the upper limits of such effects are included. For an RIE Cl_2 plasma, Cl_2^+ is always dominant, up to the highest power investigated (150 W). Measurements at other pressures (1–20 mTorr Cl_2) in the TCP reactor suggest that the relative densities of Cl^+ and Cl_2^+ are fairly pressure independent, with power dependencies similar to that reported here for 10 mTorr.

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