EXCITATION AND ION BOMBARDMENT IN CHLORINE PLASMAS AT HIGH AND LOW FREQUENCY

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Introduction

Chlorine-containing plasmas are used in the semiconductor industry for etching materials such as silicon, chromium, aluminum and III-V compound semiconductors (see for examples review articles [1-4]). Previously we reported the concentration of Cl$_2^+$ in a parallel plate discharge as a function of the applied frequency$^5$. We have now studied and analyzed the etching characteristics, time-dependent and average optical emission from various species, and the energy of Cl$_2^-$ and Cl$^+$ ions incident on the electrodes.

Experiments were carried out in chlorine plasmas at 0.3 torr using two large parallel plate reactors$^6$ (reactor I: 7.5 cm. dia. lower electrode, reactor II: 19.8 cm. electrodes, 3.0 cm interelectrode spacing) and one small system$^5$ (reactor III: 3.18 cm. dia., 1 cm. interelectrode spacing). As shown in fig. 1, instantaneous power to reactor III was measured using a wide band multiplying oscilloscope and average power was derived from the high frequency product output. Instantaneous and time-average emission from excited states of Cl ($^S^0\rightarrow ^P$ at 725.6 nm), Cl$^+$ ($^3D^0\rightarrow ^9P$ at 386.1nm), Cl$_2^+$ (A$^2Π_u\rightarrow X^2Π_g$ at 455nm) and Ar (4p$^1[1/2]\rightarrow 4s^1[1/2]$) at 750nm were measured as a function of position between the electrodes.

Emission waveforms were generated and measured at low frequency using a boxcar averager and scanning a variable delay, narrow bandwidth gate across several cycles of the applied RF voltage. At high frequency, pulse counting was employed. The difference in phase between the voltage and optical channels was small at 220 KHz (44_nsec, or 3.5 $^\circ$).

At 13.2 MHz the lag time was computed to be 59 ns. Direct measurement, using a fast GaAs light emitting diode (LED) mounted in the optical field in front of the reactor gave an experimental delay of 67 ns. Operating a chlorine discharge at 0.3 torr, total current through the reactor led voltage by 57 $^\circ$ and the peak in Cl emission from the sheath near an electrode occurred when the electrode was momentarily positive. That is, Cl light emission from the each sheath at high frequency is in phase with applied voltage at the adjacent electrode.

Between 5 and 0.5 MHz, the peak applied voltage at constant power exhibits a large increase with decreasing frequency (fig. 2). Both the increase and transition frequencies correlate closely with an increase in Si etch rate, emission from (and concentration of) Cl$^+$, and Cl$^+$ ion current and energy at the electrode (see below).

Ion composition measured with a mass spectrometer shows a Cl$^+$ signal which increases by a factor of 50 as frequency is lowered from 27 MHz to 100 KHz, while Cl$^+$ displays essentially no variation$^6$. Ion energies are much greater at 100 KHz than at 13 MHz and at both frequencies the Cl$^+$ ion concentration is greater than Cl$_2^+$ at high energy, with the converse being true at low energy. The ratio of peak ion energies to peak applied RF potential are $\approx 0.33$ in the high frequency region (above the voltage transition) but $\approx 1$ in the low frequency regime.

Relative emission intensities from Cl$_2^+$, Cl$^+$, Ar and He as a function of frequency and power are shown in figures 2 and 3. Observed emission wavelengths, transitions and excited state energies are listed in Table I. The Cl$_2^+$ emission (fig. 2) is most intense at high frequency, displays a slight minimum at $\sim 5$ MHz, goes through a broad maximum between 500 KHz and 100 KHz and then drops slightly at 10 KHz. This nearly frequency independent behavior agrees
well with mass spectrometric Cl₂⁺ density data and also with the time-averaged ground state
Cl₂⁺ concentration measured by laser induced fluorescence⁵ (also shown in figure 2). Unlike
Cl₂⁺, emission from Cl⁺ exhibits a ~30-fold intensity increase as frequency is lowered which
correlates with the increase in applied voltage and mass spectrometric Cl⁺ density.

To relate optical emissions to number density, small amounts of Ar and He were added as an
actinometer⁷ to sense the relative electron energy-density distribution. Argon emissions at
several levels close in energy to those of the Cl emitting states (see Table I) also show a decrease
in intensity with decreasing frequency. This reflects a decrease in the time-averaged excitation
by electrons (i.e. electron density) in this energy range with decreasing frequency, and is at least
partly explainable in terms of the time-dependent behavior of the discharge.

Deconvolution and Filtering

Several periods of each digitized waveform record were transformed into Fourier series with
harmonic multiples of the applied RF frequency and filtered by Fourier series truncation.

Emission from the discharge [Iₖ(t)] is the net result of excitation to the emitting state (i),
ξ(t), the total quenching (nᵢ/tᵢ) and the transition from the upper (i) to lower (j) optical states
(nᵢ/tᵢ):

\[
Iₖ(t) = I₀ \frac{nᵢ}{tᵢ} \frac{d nᵢ}{dt} = \xiᵢ - \frac{nᵢ}{tᵢ}
\]

where I₀ is a constant and nᵢ is the number density of species in the emitting state. Combining
(1) and (2):

\[
\xiᵢ = \frac{tᵢ}{I₀} \left[ Iₖ(t) + \frac{d Iₖ}{dt} \right]
\]

and if Iₖ(t) is expressed as a Fourier series:

\[
Iₖ(t) = \frac{1}{2} b₀ + \sum_{k=1}^{∞} \left\{ a_k \sin kωt + b_k \cos kωt \right\}
\]

then eq. 3 may be written as

\[
\xiᵢ(t) = \frac{tᵢ}{I₀} \left\{ \frac{1}{2} b₀ + \sum_{k=1}^{∞} \left[ (b_k - a_k kωt) \sin kωt + (a_k + b_k kωt) \cos kωt \right] \right\}
\]

which is used to compute the rate of excitation, ξᵢ(t), from measured intensity and the
quenching rates (tᵢ).

RESULTS AND DISCUSSION

The spatial dependence of time average emission from Cl (4p⁴S⁰→4s⁴P [726nm]), Cl₂⁺
(A₂Πₚ→X²Π₂ [455nm]), Cl⁺ (4d⁴S⁰→4s⁴P [386nm]) and argon
(4p¹S⁰[1/2]→4s⁵P⁰[1/2] [751nm], added only at low frequency) are shown in fig. 4. At high
frequency Cl⁺ intensity was too small to be measured. Assuming that emission arises from
direct excitation of ground state species, these spatial profiles will reflect the convolution of
excitation (by energetic electrons) with species concentration.

The previous Cl₂⁺ concentration profiles we measured by laser fluorescence⁵ agree well with
the emission from the central part of the plasma (fig 4), while the position of the emission peak
at high frequency agrees with the sheath boundaries from laser fluorescence.

The time-resolved emissions from excited Cl (fig. 5) and Cl₂⁺ at high frequency displayed
markedly different phases and extents of modulation. In the central region of a 13 MHz
discharge, charge and neutral species densities should remain relatively constant over a period
of the applied field. At this frequency the mean electron energy and rate of excited state population will oscillate because the energy relaxation time is an appreciable fraction of a quarter period. The frequency of energy oscillation should be twice the RF frequency\(^{10}\), which is confirmed by the dominant second harmonic in fig. 5. If the average electron mobility and effective characteristic electron energy loss frequency, \(\kappa\nu\), are taken to be independent of electron energy, the ratio of peak electron energy (sum of average plus the 2nd harmonic) to the average value (dc component) is given by\(^{10}\):

\[
\frac{\epsilon_p}{\epsilon} = 1 + \frac{\frac{\kappa\nu}{2\omega}}{\left[1 + \left(\frac{\kappa\nu}{2\omega}\right)^2\right]^{1/4}}
\]

\(\kappa\nu\) was estimated using eqn. 6 with the additional assumption \(\xi_i \sim \epsilon_{av}\) at all time, which requires the assumption that the total number of electrons stay relatively constant with time. Regardless, \(\kappa\nu\) computed from eq. 6 would still represent the effective reciprocal lifetime for electrons in the energy range that populates the emitting state.

Attachment will be the fastest loss process for electrons under these conditions. Data and computations\(^{11}\) show that for average electron energies above 1 eV, the attachment rate constant will be \(\leq 5 \times 10^{-10}\) cm\(^{-3}\). Hence if the competing process, electron impact detachment, were neglected, the number density would only decay by about 9% in 1/4 cycle at 13.3 MHz (gas assumed near ambient temperature, 0.3 Torr: \(\sim 10^{-16}\) cm\(^{-3}\)). On the other hand at low frequency when \(\kappa\nu/2\omega\) is large enough to thermalize electron energy near the field zero crossing, there will be almost complete attachment.

The excitation waveform in figure 5 close to the center of the discharge has a dominant second harmonic relative to the other components. To extrapolate to the center symmetry point and evaluate \(\kappa\nu\), we retained only this second harmonic which gives \(\frac{\epsilon_p}{\epsilon} = 0.392\) or \(\kappa\nu = 65.0\) MHz.

220KHz time-resolved emission waveforms from Cl, \(\text{Cl}^+\), \(\text{Cl}_2^+\) and Ar all are virtually identical in the center of the discharge at 220KHz. This is true despite the fact that there are substantial differences between the energy onset and shape of the excitation cross sections. In the sheath regions at low frequency there is qualitatively similar behavior. Emission near an electrode peaks sharply at \(\sim 70\) ns (\(\sim 6^\dagger\)) before the voltage reaches its positive peak, then falls to near zero at the voltage zero-crossing, and finally rises to a second maximum which lags the peak negative applied potential by \(\sim 300\) ns. The peak during the positive part of the cycle is caused by electron impact excitation reactions (7-12):

\[
\begin{align*}
\text{Cl}_2 + e & \rightarrow \text{Cl}^+_2 (A^2\Pi_d) + 2e & (E_{th} = 14\text{ eV}) \\
& \rightarrow \text{Cl}^+_2 (D^2\Pi_0) + \text{Cl} + 2e & (E_{th} = 35\text{ eV}) \\
& \rightarrow \text{Cl} + (S^2\Pi) + \text{Cl} & (E_{th} = 13.2\text{ eV}) \\
\text{Cl} + e & \rightarrow \text{Cl}^+_2 (D^2\Pi_0) + e & (E_{th} = 32\text{ eV}) \\
& \rightarrow \text{Cl} + (S^2\Pi) + e & (E_{th} = 10.7\text{ eV}) \\
\text{Ar} + e & \rightarrow \text{Ar}(4p^3[1/2]) + e & (E_{th} = 13.5\text{ eV})
\end{align*}
\]

Owing to the high mobility of electrons relative to ions, the peak flux of electrons \(E > E_{th}\) occurs near the peak positive voltage.

The 300ns lag in emission relative to the peak negative applied voltage is roughly the time required at the voltage maximum for an ion to accelerate across a 0.4 cm sheath under free-fall. Thus we identify the lag in emission with the time for ions to cross the sheath at low frequency (below the lower ion transit frequency or LITF\(^6\)), when the field is near its maximum value. Evidence favors the ejection of secondary electrons from ion bombardment of the surface which induce electron impact excitation as they are accelerated away from the electrode as the dominant way emission is induced in the momentary negative sheath. That is:
followed by reactions 9-12. Previous studies of emission linewidths at low frequency\textsuperscript{14} indicate that Cl ($^4S^o$) in the sheath is formed solely by (11) when the electrode is positive, but that (9) is dominant when the electrode is negative.

Emission from the high frequency sheath is strikingly different in that emission is observed predominantly during the positive part of the cycle. This difference in emission from the negative sheath can be understood in terms of the lower characteristic potentials and ion bombardment energy (only $V_p/\pi, \sim 25$ eV) above the upper ion transit frequency (UITF) in this discharge\textsuperscript{6}. There are relatively low yields of secondary electrons and greatly reduced rates of excitation and ionization at the momentary high frequency cathode.

The low frequency current-voltage-power waveforms show that plasma admittance dominates the susceptance: that the voltage and current are nearly in phase so that there is very little negative input power over a cycle. At high frequency the phase shift was about 50° for this reactor, but we believe most of this shift is attributable to fringing capacitance since the voltage and current were nearly in phase for the large diameter (19.8 cm) reactor under similar conditions\textsuperscript{6}.

Acknowledgment

Bruce Duncan and Richard Bruce contributed to this work.

References

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IP: CI = 13.07 eV; CI₂ = 11.5 eV, E' is the energy of the emitting state relative to the ground state.

1. Apparatus used to obtain time and spatially-resolved plasma induced emission.
2. Mass spectrometric (MS) determination of ion compositions effusing through the pinholes in the electrode of reactor I (0.3 torr, 0.6 W/cm²). Optical emission (OE) from Cl₂⁺ (A²Π_u) and Cl⁺ 4d⁷D⁰ (see Table I), and peak-to-peak voltage in reactor II (0.3 Torr, 0.33 W/cm²). Laser induced fluorescence (LIF) measurement of Cl₂⁺ in the center of reactor III (0.30 torr, 0.44 W/cm²).

3. Cl, Ar and He optical emission intensities vs. frequency recorded in reactor II. (0.3 torr, 0.33 W/cm²).
4. Time average emission profiles at high and low frequency (reactor III).

5. Time dependent excitation of Cl atoms in a chlorine discharge as a function of position at 13.2 MHz (reactor III).