CHARACTERIZATION OF AN RF DISCHARGE IN CHLORINE

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ABSTRACT

A combined theoretical-experimental study of the bulk plasma characteristics of a 13.56 MHz parallel-plate discharge in chlorine at pressures of about 1 Torr has been carried out. From the measured current waveform a model generates the local electric field waveform, the time-varying electron density, and the power density in the central portion of the bulk plasma. The calculated average power input per unit discharge length is compared with experiment.

1. INTRODUCTION

RF discharges in chlorine are often used for etching semiconductors. The etching process is controlled in part by the formation of reactive species in the bulk plasma. Reactive chlorine atoms are produced efficiently by processes such as dissociative electronic excitation while positive ions are produced by electron-impact ionization. Compared with Freon discharges, which create many radical and molecular fragments and ions, the chlorine discharge is chemically simple and more amenable to study.

Experimentally, the bulk plasma properties were distinguished from the sheath properties by making measurements at different electrode spacings with the assumption that for constant peak current the sheath conditions do not vary with spacing. The central discharge region is modeled simply as a spatially-uniform volume-controlled plasma with the electron balance dominated by single-step electron-impact ionization and attachment and with the electron energy distribution in equilibrium with the local instantaneous electric field. Required relationships between the ionization frequency, the attachment frequency, the electron drift velocity, and electric field are provided by solutions of the time-independent Boltzmann equation for mixtures of Cl₂ and Cl which result from Cl₂ dissociation.

2. THEORETICAL MODEL

Various possible electron production and loss processes were considered for the discharge model. These included production by one-step electron-impact ionization, two-step ionization, electron detachment from negative ions, Penning ionization, and collisions of excited particles, and loss by ambipolar diffusion, attachment, and recombination. The dominant processes were estimated to be single-step electron-impact ionization and attachment. Thus the central portion of the discharge is modeled simply as a spatially-uniform volume-controlled plasma with the electron density...
\( n_e(t) \) given by the continuity equation

\[
\frac{dn_e}{dt} = [v_i(t) - v_a(t)]n_e(t),
\]

(1)

where \( v_i(t) \) is the ionization frequency and \( v_a(t) \) is the attachment frequency. The contributions of the positive and negative ions to the current were estimated to be small compared with the electron contribution because the ions are too massive to respond to the high frequency field. Thus the conduction current is taken to be solely electron current and the total current is written

\[
I(t) = eA n_e(t) v_d(t) + I_d(t),
\]

(2)

where \( e \) is the electronic charge, \( A \) is the cross-sectional area of the discharge, \( v_d(t) \) is the electron drift velocity, and \( I_d \) is the displacement current in the discharge, the latter being proportional to the time derivative of the local electric field \( E(t) \). For steady state we require that the time-average ionization rate equal the time-average attachment rate, or

\[
\tau \int_0^\infty \frac{dn_e}{dt} dt = 0,
\]

(3)

where \( \tau \) is the period of the rf cycle. Although the electron density varies in time, its variation is periodic. For the gas pressures and frequencies in this study it appears that the electron energy distribution can be taken to be in equilibrium with the local instantaneous electric field in the discharge. (This approximation is supported by observations of strongly modulated light output by ourselves and others.) Thus the ionization frequency, attachment frequency, and drift velocity vary with time through their dependence on \( E/N \), where \( N \) is the total gas number density.

Although the externally measured voltage does not necessarily reflect the behavior of the local field at the center of the discharge, the externally measured current does correspond to the internal current. Consequently we use an externally measured current waveform to calculate the electric field waveform. To obtain \( E(t) \) for a given current waveform an iterative procedure is used, with \( v_d \) and \( I_d \) in Eq. (2) depending on time through their dependence on \( E \). The calculated time-dependent electric field is multiplied by the current to predict a time-dependent power input per unit discharge length at its center, \( P_1(t) \), and that power input -- or its time-averaged value, \( \langle P_1(t) \rangle \) -- is compared with experimentally measured values. To determine the contribution of the central discharge region to the total discharge power, power input measurements are made at different electrode spacings.

In addition to providing values of power input per unit length for comparison with the experimental measurements, the model also provides the time-varying electron density, ionization frequency, attachment frequency, and electron drift velocity. The dependence of the latter three quantities on the field is obtained from Boltzmann calculations.
3. BOLTZMANN CODE

To evaluate the ionization frequency, attachment frequency, and drift velocity, a steady-state Boltzmann code [2] was used to calculate the electron energy distribution function as a function of Cl/Cl composition and E/N. For this calculation a fairly complete set of cross sections describing the various electron-molecule and electron-atom interactions is required. However, only the cross sections for attachment and ionization in molecular chlorine have been measured directly [3]. To determine a more complete set of cross sections for molecular chlorine, an iterative approach was employed using experimental drift velocity and characteristic energy data from Bailey and Healey [4] and ionization and attachment coefficient measurements from Bozin and Goodyear [5]. Rather than using the results from Bailey and Healey for pure chlorine, derived from mixture data, we compared their actual mixture data for a 20% Cl/80% He mixture with the Boltzmann calculations. For those calculations we used helium cross sections from Kieffer [6]. The set of molecular chlorine cross sections used in this work describes ionization, attachment, momentum transfer, and excitation to one vibrational state and three electronic states. Chlorine atom cross sections were estimated for momentum transfer, excitation to the first electronic level, and ionization. Boltzmann calculations were made for fractional Cl₂ concentrations from 0.4 to 0.6.

4. EXPERIMENT

The discharge operated between identical 3.8 cm diameter, water-cooled, anodized Al electrodes with the electrode spacing varied from 1 to 2.5 cm. Chlorine flow, regulated by a mass flow controller at a rate of 10 sccm, was perpendicular to the discharge axis; the gas residence time in the discharge region was estimated to be somewhat greater than 0.3 sec. The pressure was set from 1.0 to 1.5 Torr, measured with a capacitance manometer, and adjusted with a throttling valve between the reactor and the Roots blower and roughing pump. Two quartz windows, 5.6 cm apart, were epoxied to the 3-dimensional Pyrex cross container for viewing the discharge and for molecular chlorine absorption measurements. A cold trap was located between the reactor and throttling valve.

Power from a 13.56 MHz generator was coupled into the discharge through a matching network. RF voltage was monitored at the top electrode and current was monitored inductively between the lower electrode and ground. Instantaneous power was calculated from digitized current and voltage waveforms with the current waveform corrected for stray capacitance and for the time delay due to the current probe. With the peak-to-peak current held fixed at 300, 400, and 500 mA, the average power per unit length of discharge plasma was determined by varying the electrode spacing.

The fractional Cl₂ dissociation in the discharge was measured by a 9-pass absorption measurement with 357 nm radiation from an excimer-pumped dye laser. The laser beams passed through the quartz windows in a plane extending through the discharge axis and normal to the flow direction. The incident and transmitted laser energy was monitored with pyroelectric detectors, and measurements were made with the discharge off and under vacuum to account for window and mirror losses and for calibration. Although the region between the discharge and the windows contained excess molecular chlorine, the chlorine density was taken to be uniform for the absorption measurements since diffusion between the active discharge and the surrounding region was estimated to be rapid.

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5. RESULTS

For the parameter ranges used in this study the discharge appeared stable with its visible emission originating from a cylinder defined by the parallel plate electrodes. Bright regions (=1 mm thick) were observed close to the electrodes. Their thickness was independent of gap spacing at constant peak-to-peak current. The more diffuse luminous region of interest in this study extended between those bright zones.

In the absorption measurements the folded laser beam extended over a 1 cm region centrally located between the electrodes. The molecular chlorine density was determined to be axially uniform in this region from measurements made with the laser beam folded in a plane perpendicular to the discharge axis. The measured fractional Cl\textsubscript{2} density in the discharge varied between 0.6 and 0.4, decreasing with increasing pressure and current. To determine the atomic chlorine density for the Boltzmann code, we assumed that the gas pressure in the discharge did not change with dissociation.

With the digitized current waveform as input, the computer code generated \( E(t) \), \( P_1(t) \), and \( n_e(t) \). Figure 1 shows one rf cycle of the conduction current waveform for a 1.0 Torr discharge with a peak-to-peak current of 300 mA and a gap spacing of 2 cm; also shown is the corresponding calculated time-dependent electric field. The electric field waveform is narrower than the approximately sinusoidal current waveform, although the two are virtually in phase. The displacement current never exceeds about 17% of the total current. During the RF cycle \( n_e(t) \) is modulated by about 5%, reaching a maximum during each half cycle approximately 30° after the current and electric field have peaked. The calculated time-averaged electron density ranged from about \( 4 \times 10^9 \text{ cm}^{-3} \) at the lowest pressure and current to about \( 7 \times 10^9 \text{ cm}^{-3} \) at the highest current and pressure.

The time-averaged power input per unit length, \( \langle P_1(t) \rangle \), was determined experimentally from the slope of plots of input power vs gap spacing as shown in Fig. 2. Straight-line plots were obtained for gaps from 1.0 to 2.5 cm for all operating conditions. In Fig. 3, values of \( \langle P_1(t) \rangle \) derived from electrical measurements are compared with the values calculated from our theoretical model with the current waveform and fractional Cl\textsubscript{2} dissociation as experimental input parameters. All the electrical measurements agree with the model results to within 15%, with most of the results agreeing to within 10%. The degree of uncertainty in the measured results is suggested by the two sets of data points for 300 mA and 1.0 Torr, which were obtained from two different experiments. Thus, although there is some uncertainty in the results, the agreement between the measured and predicted values and trends suggests that the model provides a realistic description of the bulk plasma.

REFERENCES


Fig. 1. One rf cycle of the conduction current and the E/N (1 Td = \(1 \times 10^{-17} \text{V cm}^2\)) obtained from the model. E/N is small but finite near the zero crossing.

Fig. 2. Input power vs gap spacing. The slope is equal to \(<P_1(t)>\).
Fig. 3. Measured and predicted values of $<p_1(t)>$. In the left two graphs $<p_1(t)>$ is plotted vs current at constant pressure and in the right two graphs vs pressure at constant current.