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Temporal phenomena in inductively coupled chlorine and argon–chlorine discharges

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Reproducible modulations in low-pressure, inductively coupled discharges operating in chlorine and argon–chlorine mixtures have been observed and studied. Changes in the light output, floating potential, negative ion fraction, and charged particle densities were observed. Here we report two types of unstable operational modes in an inductively coupled discharge. On the one hand, when the discharge was matched, to minimize reflected power, instabilities were observed in argon–chlorine plasmas over limited operating conditions of input power and gas pressure. The instability window decreased with increasing chlorine content and was observed for chlorine concentrations between 30% and 60% only. However, when operating at pressures below 5 mTorr and the discharge circuit detuned to increase the reflected power, modulations were observed in a pure chlorine discharge. These modulations varied in nature from a series of sharp bursts to a very periodic behavior and can be controlled, by variation of the matching conditions, to produce an apparent pulsed plasma environment. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1897060]

Negative ion-related "instabilities" or modulations[1–9] in inductively coupled discharges have generated much interest as these discharges are widely used for industrial materials processing such as etching and deposition. These instability oscillations have previously been related to the capacitive (E) to inductive (H) transition[4] and have generally been observed in a region where the discharge is not matched resulting in a high reflected power.[2,3,7] Others have reported instabilities in O_2 and Ar/SF_6 discharges[1,3,4] while we have previously reported the study of reproducible instabilities in a low-pressure 13.56 MHz inductively coupled Gaseous Electronics Conference (GEC) cell operating in oxygen when the discharge was optimally matched to the resolution of our measurement system (±10 W).[5] In this case the instabilities were observed in the form of periodic modulations in the light output, floating potential, electron and positive and negative ion densities. In the present report we continue the study of diatomic electronegative gases in inductively coupled discharges by considering chlorine and argon-chlorine mixtures. In particular we demonstrate that reproducible, periodic modulations can be produced and controlled by slight variation of the matching conditions, some producing essentially a pulsed plasma environment.

The inductively coupled plasma (ICP)system used here is different from that used in our previous measurements.[5] The present system has a planar 6-turn water-cooled coil that couples power to the plasma through a 21 mm thick, 200 mm diameter quartz window. The lower, 200 mm diameter, stainless steel electrode and the stainless steel vacuum vessel were grounded. The gap between the quartz window and the bottom stainless steel electrode is 85±5 mm. The central connection of the upper planar coil is powered at a driving frequency of 13.56 MHz through a matching unit formed by a series variable capacitor and a variable capacitor shunted across the coil. At no time during measurements was an external pulsing unit used. The plasma chamber was evacuated to a base pressure of $\sim 2\times 10^{-6}$ Torr. The flow rates of argon and chlorine into the chamber were fixed in the appropriate ratios and the pumping rate adjusted to obtain the required pressure. In this ICP system we do not observe the sudden "jump" in the light emission and the electron density nor the hysteresis effect often associated with the capacitive to the inductive mode transition.[5]

The plasma was characterized 4 cm above the lower electrode using several diagnostics described previously.[5] The total light emission, from 450 nm to 1064 nm, was monitored using a fast photodiode. An unbiased Langmuir probe provided measurements of the floating potential. The probe-based laser photodetachment technique[5,10,11] was used to measure the chlorine negative ion fraction (n_-/n_e). The experimental arrangement consisted of a 5 mm diameter cylindrical beam, from a frequency quadrupled Nd:YAG laser (266 nm), aligned to be collinear with an uncompensated 0.5 mm diameter platinum wire probe positively biased to detect electrons detached from the negative ions. The necessary conditions[10,11] for probe voltage and laser beam energy were determined to ensure that the negative ion fractions were measured correctly. The laser photon energy (4.65 eV) was sufficient to photodetach Cl^- which is the dominant negative ion and has an electron affinity of 3.6 eV.[12,13] The negative ion fraction was determined from measurements of the dc electron current (I_{dc}) in the absence of the laser pulse and the increase in the current (ΔI^-) immediately after the pulse using the appropriate relationship. Here the photodetachment current, ΔI^-, will be presented as this gives a direct representation of the negative ion behavior in the discharge. Time-resolved measurements were made through the instability cycle by triggering measurements at a specific phase of the instability observed on the output of the photodiode. A delay generator allowed measurements to be made at regular intervals throughout the instability.

Probe measurements in reactive plasmas are sometimes thought to be unreliable due to contamination of the probe

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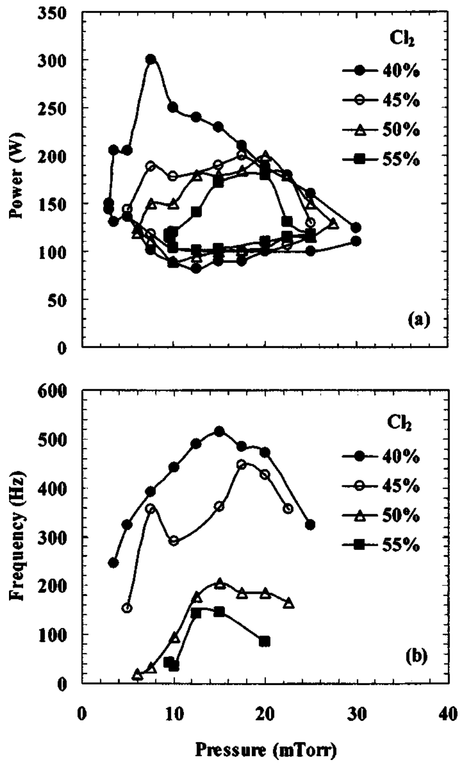

FIG. 1. (a) The input power and gas pressure window for the instability for different chlorine concentrations (measured reflected power ~0 W). (b) The dependence of the instability frequency on pressure at different chlorine fractions.

tip by coatings which will change the probe to plasma potential and reduce the measured collected current. To ensure accurate measurements were made, after each individual measurement (e.g., between changing the time delay, or changing plasma operating conditions), a pure argon discharge was run to clean the probe tip by drawing electron current sufficient to have it glow bright red. In any given data set (one plot) taken at different times (>1 month apart) the maximum relative fractional variation was less than 20%.

Two types of phenomena are discussed below: an instability that occurs in argon–chlorine mixtures in a fully matched system and regular fluctuations, bursts and modulations that are dependent on the matching conditions. When the discharge was optimally matched in argon–chlorine mixtures, i.e., the matching adjusted to produce zero measured reflected power, regular periodic fluctuations similar to those reported in oxygen[5] were observed on the output of the fast photodiode and the uncompensated Langmuir probe over limited operating conditions of input power, gas pressure and chlorine concentrations [Fig. 1(a)]. Starting with a pure argon discharge, the input power, gas pressure and chlorine fraction were varied and a systematic search for oscillations in the optical emission from the plasma was performed over the frequency range 1 Hz to 1 MHz to detect unstable behavior. The system was matched for all operating conditions. The instability was first evident at about 30% chlorine concentration ($n_-/n_e \sim 1.5$), disappearing at about 60% chlorine concentration ($n_-/n_e \sim 1.7$) [Fig. 1(a)]. This figure also illustrates that the power and pressure window of the instability varies with chlorine concentration with the largest window occurring with 40%. This is significantly different to previous observations in Ar/SF_6 plasmas where the power and pressure window of the instability increased with increasing

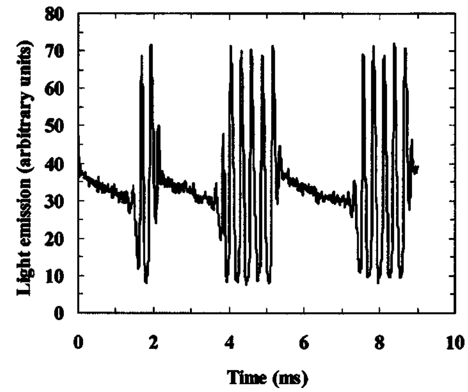

FIG. 2. The time-varying optical emission for a pure chlorine plasma operating at 4.4 mTorr with 361 W input power.

electronegativity[3] i.e., increasing SF_6 content. We do not yet have an explanation for this behavior, although it should be noted that the electrical circuits and plasma chemistries are very different for the two experiments. Where observed, the frequency increases with increasing total pressure with a maximum at approximately 15 mTorr and decreases with increasing chlorine content [Fig. 1(b)]. It was typically a few hundred Hz for 40% chlorine content and between 30 Hz and 130 Hz for 55% chlorine content. The fluctuations in the argon–chlorine discharge were similar to those reported in oxygen[5] but had lower frequencies (O_2: 3 kHz $< f <$ 21 kHz). The frequency generally decreased with increasing input power. Time-resolved measurements through one period of the instability were made where the oscillations were most pronounced i.e., at 50% chlorine concentration. These show that the time-varying electron, positive ion and negative ion densities, and optical emission are in phase and modulated by about 30%.

In pure argon or pure chlorine discharges no instabilities were observed when the matching conditions were optimized to minimize the reflected power. However in pure chlorine, when the discharge was detuned to increase the reflected power, a variety of modulations, with different light emission temporal characteristics, were observed at very low pressures (<5 mTorr). These varied from a modulated series of sharp bursts (Fig. 2) to a very periodic behavior [Fig. 3(a)]. Recent detailed electrical measurements[14] suggest that these modulations are not the *E* to *H* mode transitions discussed previously but rather fluctuations within the *H* mode. Chabert *et al.*[3] report that a pure inductive instability can also be produced in their global model, depending on the matching conditions of the system. The modulations described below may well be related to this prediction of the model.

The highly modulated behavior, of the type shown in Fig. 3(a), particularly attracted our attention since it appeared to have the characteristics of a pulsed plasma. Time-resolved measurements of the electron saturation current and the photodetachment current signal (ΔI^-) confirmed this behavior [Fig. 3(b)]. The sudden increase of negative ions in the "off" period is the behavior often associated with the afterglow of a pulsed plasma when dissociative attachment to form negative ions becomes a dominant process.[15,16] Here negative ions were only detected when the electron density began to decay at $t \sim 0.8$ ms. This negative ion behavior is similar to previous reports in actively pulsed plasmas[17–19] and is consistent with a calculated electron attachment rate ($\sim n_g K_{att}$) of

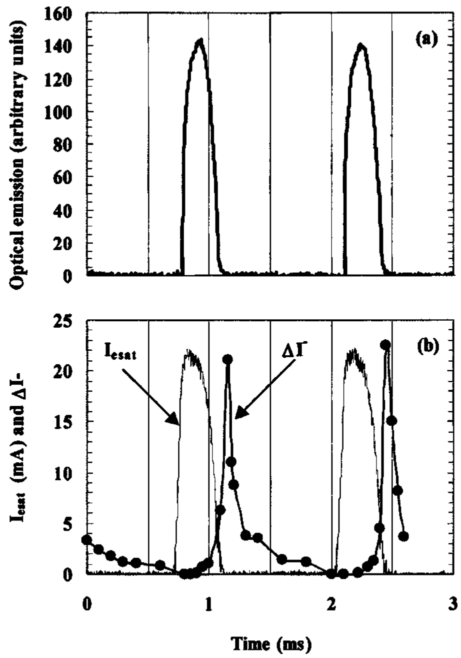

FIG. 3. The time-varying (a) optical emission and (b) the photodetachment current signal ($\Delta\Gamma$) (black line and solid circles) and electron saturation current (grey line) for an instability in pure chlorine at a gas pressure of 2.8 mTorr with 363 W input power.

29 μs for a gas pressure of 4 mTorr, assuming an electron temperature of 5 eV in the early afterglow. The increase in negative ions can be explained by an increase in the electron attachment rate caused by both an increase in the fraction of low energy electrons and a decrease in the electron dissociation rate, leaving more Cl_2 to participate in the electron attachment process. By the end of the afterglow, the negative ions have been lost through nearly field-free diffusion and recombination with positive ions. At the beginning of the "on" period, gas breakdown is rapid with an ionization rate of $\sim n_g K_{iz}$ giving a risetime of ~ 1 μs. During the "on" period negative ions are not observed due to the high dissociation of Cl_2 molecules ($e + Cl_2 \rightarrow 2Cl + e$, ~ 3.2 eV). The calculated rates are in good agreement with our experimental observations. Hence with this self-modulation there is a regular transition between an electron–ion plasma in the "on" period and an ion–ion plasma in the "off" period. It was possible to change the frequency of this "pulsing" instability from tens of hertz to kilohertz by slight variations of the forward power to reflected power ratio or the gas pressure. Recent detailed electrical measurements[14] indicate that this pulsing behavior is a form of relaxation modulation created when the system causes the rf generator protection circuit to be activated, followed by attempts to achieve the set point.[9] It is important to note that when operating in a pure argon discharge, no instabilities were observed even when there was a substantial reflected power. Therefore negative ions are crucial for this instability to occur and it is not solely caused by the matching conditions.

In conclusion we have shown that the temporal behavior observed in low pressure plasmas are very dependent on the electronegative gas used and on the electrical operating conditions of the system. We find evidence of two distinct phenomena in our inductively coupled system. Matched argon–chlorine plasmas exhibit instabilities similar to those reported previously and attributed to the E to H mode transitions. In pure chlorine slight mismatching produces a variety of regular fluctuations, bursts and modulations. In particular a reproducible, controllable "pulsed plasma" mode, with potential advantageous for industrial applications such as etching in order to reduce charging effects and perhaps even for optical switches, can be established.

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