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POSITIVE AND NEGATIVE CHLORINE ION KINETICS IN INDUCTIVELY- COUPLED Cl_2/BCl_3 PLASMAS

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Discharges in gas mixtures of Cl_2 , BCl_3 , Ar, and N_2 , are used by the integrated circuit industry for metal etching, and are as yet not well understood, especially in inductively-coupled plasma (ICP) sources which are rapidly becoming the industry standard for etching tools. An essential parameter that must be measured in these plasmas is the density of ions, both positive and negative, formed in the plasma. In the work presented here, LIF and laser photodetachment were used to measure relative metastable chlorine ion (Cl^{+*}) density and temperature and absolute Cl^- density as a function of gas mixture.

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INTRODUCTION

Boron trichloride (BCl_3) is commonly used in the integrated circuit (IC) industry in plasma etching processes for metal definition. Many metal-etch recipes use not only pure BCl_3 , but also combinations of BCl_3 with other gases including chlorine (Cl_2), argon and nitrogen. Few measurements have been made of the properties of BCl_3/Cl_2 plasmas or combinations of these gases with nitrogen or argon, especially in inductively coupled plasma (ICP) sources which provide the high plasma densities and low operating pressures important for sharp feature definition in etched structures.

The objective of this work was to examine the details of the positive and negative chlorine ion formation in ICP systems containing BCl_3 , Cl_2 , N_2 and Ar gas mixtures. Laser induced fluorescence (LIF) was used to measure the Cl^{+*} temperature and relative density in the center of the discharge as a function of plasma conditions. LIF is a sensitive, non-invasive, spatially localized probe of the relative number density and ion energy distribution function (EDF) (characterized by a temperature since the distribution is Gaussian) in the bulk of the plasma (1-3). Negative ion density was measured using laser photodetachment spectroscopy (4), which yielded absolute negative ion densities measured as a function of the reactor parameters.

EXPERIMENTAL CONFIGURATION

These experiments were performed in an inductively coupled Gaseous Electronics Conference (GEC) rf reference reactor. A schematic of the experimental configuration for LIF measurements is shown in Fig. 1. In this work, the reported rf power was the

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forward power minus the reflected power into the matching network. The exciting laser was focused into the chamber using a 300 mm focal length cylindrical lens oriented to produce a sheet of light parallel to the lower electrode. A cylindrical lens was used to reduce the power in the focal volume and line broadening due to saturation. LIF was collected at a right angle to the exciting beam using a 5 mm diameter 200 mm focal length lens and a prism to rotate the monochromator slits to be parallel to the exciting laser. Approximate laser probe volume was 2 mm x 2 mm x 0.5 mm high. The Cl^{+*} temperatures and relative number density were inferred by scanning the laser across the $3p^3(^4S^0)4p^5P_3 - 3p^33d^5D^0_4$ transition at 542.32 nm and monitoring the fluorescence on the $3p^3(^4S^0)4p^5P_3 - 3p^34s^5S^0_2$ transition at 479.45 nm. The resulting lineshape was then fit to a sum of two Gaussian lineshapes to account for the relative abundance of the two Cl isotopes (1).

A schematic of the experimental configuration for negative ion density measurements is shown in Fig. 2. Electron density was measured using the phase shift induced in a microwave interferometer by a plasma. The interferometer operated at 80 GHz, and microwave lenses were used to focus the microwaves through the center of the discharge (4). Microwave radiation was detected using a solid state detector, and amplified with a wideband amplifier (0.01 - 1000 MHz). Negative ion density was determined by measurement of the excess electrons produced by photodetachment of electrons from the negative ions. Since the density of photodetached electrons followed the rise time of the laser pulse and decayed over a period of a few microseconds, a transient digitizer was used to average the signal and record the time history of the photodetached electron pulse. Typically, the data presented here represent a signal averaged over 512 laser pulses. Photodetachment of electrons from Cl^- was performed with a frequency-quadrupled Nd:YAG laser (266 nm) with typical pulse energy of 15 to 20 mJ at a 20 Hz repetition rate. The laser beam was directed perpendicular to the axis of the microwave interferometer, and intersected the microwave beam at the beam waist. In some experiments, the laser was operated at the third harmonic (355 nm with 100 mJ per pulse) in order to differentiate between Cl^- and other possible negative ions in the discharge.

RESULTS AND DISCUSSION

The focus of this work was studies of the effects of changes in the reactor parameters such as input power, pressure, and gas mixture on the positive and negative ion densities. Large variations were noted as functions of power and pressure; this report will focus on changes due to variations in input gas mixture. More complete results have been published elsewhere (5,6).

LIF on Boron Trichloride/Chlorine gas mixtures

Metastable chlorine ion temperature and density as a function of BCl_3/Cl_2 ratio are shown in Fig. 3. The BCl_3/Cl_2 ratio was changed by varying the mass flow of BCl_3

and Cl_2 . As the chlorine fraction in the plasma was increased from 20% to 80%, the Cl^{+*} temperature was relatively constant. This is in contrast to Ar/Cl_2 gas mixtures where the Cl^{+*} temperature increased from 1400 K to 3000 K as the chlorine fraction was increased from 10 to 100% (1). In Ar/Cl_2 plasmas, it was suggested that the increase in Cl^{+*} temperature with chlorine fraction could be due to an increased density of hot chlorine atoms (1). The energies required to dissociate Cl_2 (7) or remove a Cl from BCl_x (8) are between 2.5 and 5.5 eV. Thus the Cl^{+*} temperature could be expected to remain approximately constant with changes in the BCl_3/Cl_2 ratio. In general, the ion EDF parallel to the lower electrode measured in this work is in good agreement with values obtained by Woodworth *et al.* using a gridded ion energy analyzer placed behind a pinhole in the lower electrode surface (9).

Increasing the chlorine fraction in a BCl_3/Cl_2 plasma resulted in a factor of four increase in the metastable chlorine ion density. Increased metastable chlorine ion density with chlorine fraction could be due to a higher dissociation of Cl_2 than BCl_3 , since the dissociation energy for Cl_2 is lower than for the chlorine bonds in BCl_3 (7,8). Thus the Cl_2 may be more dissociated than the BCl_3 for a constant electron temperature. The increased Cl density due to dissociation could lead to an increased Cl^{+*} density. While recent measurements by Forrister and Anderson indicate that the Cl_2 dissociation is greater than 75 percent for these operating conditions (8), the BCl_3 dissociation is unknown for high density plasmas (10).

As shown in Fig. 4, the addition of nitrogen to a BCl_3 plasma results in a significant increase in the metastable chlorine ion density. For these measurements, the BCl_3 flow rate was 1.4 or 3.0 sccm at a pressure of 10 mTorr and input power of 400 W. At low nitrogen flow rates, the Cl^{+*} density was independent of the nitrogen flow rate. However, as the nitrogen flow rate was increased, the chlorine ion density increased by a factor of 3 to 4. Further increases in the nitrogen flow rate resulted in a decreased Cl^{+*} density. Changing the BCl_3 flow rate by a factor of two indicated that the increase in metastable chlorine ion density occurs for a relatively constant BCl_3/N_2 ratio. In both cases, the ion temperature was 2500 K, independent of nitrogen flow rate. While not shown here, the addition of nitrogen to a Cl_2 discharge resulted in a monotonic decrease in the metastable chlorine ion density.

The impact of argon addition on a BCl_3/Cl_2 plasma (2.5:7.5 sccm flow ratio) and nitrogen addition on a BCl_3/Ar plasma (3.0:2.1 sccm or 3.0:4.2 sccm flow ratios) is shown in Fig. 5. In this figure, input power was 400 W and the reactor pressure was 10 mTorr. For the case of the BCl_3/Cl_2 plasma, the addition of argon resulted in a monotonic increase in the Cl^{+*} density with no change in the Cl^{+*} temperature. A similar increase in Cl^{+*} was observed for the case of nitrogen addition to two BCl_3/Ar plasmas. For this case, the threshold for the increase in Cl^{+*} density with nitrogen addition to the BCl_3/Ar mixtures was independent of the argon partial pressure. However, the factor of two increase in Cl^{+*} was less than the factor of four increase observed for the N_2 addition to BCl_3 . These results further indicate that both nitrogen and argon increase the dissociation of BCl_3 . The gradual change in the Cl^{+*} density with argon addition appears to be consistent with the mechanisms proposed by Scheller *et al.* (11). The dramatic

increase in Cl^+ density with nitrogen addition suggests that the energy transfer from N_2 metastables to BCl_3 as proposed by Breitbarth (12), may be important in BCl_3/N_2 plasma interactions.

Negative Ion Formation

The identity of the negative ions detected in these experiments was verified by using two different wavelengths of the Nd:YAG laser. The energy required to photodetach an electron from Cl^- is 3.6 eV (341 nm) (13). The energy of the photon at 266 nm is 4.7 eV, well above the energy required for photodetachment of Cl^- . Since the energy required to photodetach an electron from Cl_2^- is 2.5 eV (13) a lower photon energy was used to detect Cl_2^- ions. To differentiate between Cl^- and Cl_2^- , the third harmonic of the Nd:YAG laser (355 nm, 3.5 eV) was used. For the 266 nm radiation, a large signal was observed corresponding to the detachment of electrons from Cl^- . This photodetachment signal was characterized by a very sharp rise time, corresponding to the rise time of the laser pulse. The signal for 355 nm radiation was much smaller despite the five times larger pulse energy, and didn't have a rise time characteristic of a photodetachment process, but rather was more characteristic of an optogalvanic signal. From this we conclude that the density of Cl_2^- in this discharge was very small compared to the density of Cl^- . An estimate of the upper bound for Cl_2^- density in this discharge assuming that the photodetachment cross section for Cl_2^- is the same as that for Cl^- , is $1.3 \times 10^8 \text{ cm}^{-3}$, approximately three orders of magnitude smaller than the Cl^- density measured. Thus, we conclude that compared to Cl^- , Cl_2^- is not an important species in ICP discharges through Cl_2 .

Similarly, for BCl_3 discharges, copious photodetached electrons were detected at 266 nm, but again no significant signals were observed at 355 nm. Photodetachment thresholds for BCl_x^- should be at very low energies (0.33 eV) (14), well below the photon energy at 355 nm, so the presence of these negative ions should be detectable with 355 nm radiation. As was the case in Cl_2 discharges, the absence of significant signal at 355 nm indicates that very little BCl_x^- is being formed in BCl_3 ICP discharges, and the only negative ion formed in significant quantities is Cl^- . Based on the sensitivity of our measurement, the highest density of BCl_x^- that might be in the discharge is the same as mentioned above for Cl_2^- ($1.3 \times 10^8 \text{ cm}^{-3}$), again assuming that the unknown BCl_x^- photodetachment cross section is the same as that for Cl^- .

Chlorine negative ion density and electron density were measured as a function of gas mixture for several commercially relevant gas mixtures. Figure 6 shows the Cl^- and electron densities as functions of the chlorine fraction in a Cl_2/Ar gas mixture. It would be expected that in the absence of interactions with Ar metastables, as the Cl_2 fraction is decreased and the gas mixture approaches 100% Ar, the Cl^- density should approach zero approximately linearly (the solid line on the graph). But if Ar metastables were responsible for depleting the Cl_2 density, the Cl^- density should fall off more rapidly (as indicated by the dashed line, for example) since Cl_2 is a precursor for Cl^- formation. This is not the trend seen in Fig. 6: for Cl_2 fractions below 20%, the negative ion density is

above the linear extrapolation. The interpretation of this is made more difficult by the measurements of electron density also shown in Fig. 6: electron density greatly increases as the Cl_2 fraction goes below 20%, which should increase Ar metastable density, or increase the dissociation of Cl_2 , both of which should decrease the Cl^- density measured. To fully understand this requires measurements of the electron temperature for varying chlorine/argon ratios.

Figure 7 shows the electron density and Cl^- density as the BCl_3 to Cl_2 ratio is changed. Although the electron density doesn't change as the gas ratio is varied, the Cl^- density shows a strong dependence on the gas mixture. The straight line in the figure indicates the expected Cl^- dependence if the processes leading to Cl^- formation from Cl_2 and BCl_3 are independent of each other; *i.e.*, if the processes were independent, then the Cl^- density should change linearly from the value for pure Cl_2 to that for pure BCl_3 . This line can also be thought of as the sum of the Cl^- production contribution from dissociation of each species. For gas mixtures containing a substantial amount of both gases (for example, the 50/50 mixture), the Cl^- density is significantly below this line. The reason for this low Cl^- density is unknown, but is possibly caused by increased Cl^- losses due to volumetric ion-ion recombination with Cl_x^+ or BCl_x^+ , which would tend to lower the Cl^- density, especially when substantial amounts of BCl_x were present. The low Cl^- density may also be caused by variations in electron temperature with Cl_2/BCl_3 ratio.

The only case in which N_2 addition had a significant effect was in pure BCl_3 , shown in Fig. 8. Although the electron density didn't change as nitrogen was added to the discharge, the Cl^- density nearly doubled as the N_2 flow was increased. The N_2 flow rate at which this change occurred corresponded to a similar increase in the Cl^+ density reported above. This behavior was possibly due to energy transfer from N_2 metastables which are known to promote dissociation of BCl_x species (12,15). The Cl formed in these reactions could recycle into Cl_2 at the substrate leading to formation of Cl^- causing an increased Cl^- density with increasing N_2 flow.

SUMMARY

LIF has been used to measure the temperature and relative density of metastable chlorine ions, and the density of negative ions in inductively coupled discharges containing BCl_3 , Cl_2 , N_2 and/or Ar. In the center of the plasma, the Cl^{+*} temperature varied between 2000 and 3000 K for most conditions investigated, significantly hotter than the temperatures of argon neutrals and ions in this discharge geometry. It was proposed that hot neutrals, neutrals that carry a little of the energy of dissociation with them into subsequent ionization, are primarily responsible for the elevated Cl^{+*} temperatures. The addition of BCl_3 to a Cl_2 plasma significantly decreased the density of metastable chlorine ions without changing their temperature. Addition of nitrogen to a BCl_3 plasma resulted in a maximum of a factor of four increase in the Cl^{+*} density while the addition of argon resulted in a monotonic increase in the Cl^{+*} density. These results suggest that energy transfer from long lived nitrogen states and argon metastable states can enhance the decomposition of BCl_3 .

Measurements of chlorine negative ion densities have also been performed: for all gas mixtures, Cl^- densities were in the low 10^{11} cm^{-3} range; no evidence of significant densities of other negative ion species was found. The Cl^- density was up to a factor of three smaller than the electron density. Interactions of Ar metastables with Cl_2 were evident, leading to anomalous behavior of the Cl^- density with discharge parameters in Ar/ Cl_2 mixtures. Addition of BCl_3 to Cl_2 discharges also caused anomalous changes in the Cl^- density. In BCl_3/N_2 mixtures, the Cl^- density changed by a factor of two as the nitrogen flow rate increased; this supports previous studies which indicated that energy transfer from N_2 metastables can enhance the dissociation of BCl_3 , leading to the enhanced Cl^- formation observed in our experiments.

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Fig. 1. Schematic of the experimental setup for LIF measurements.

Fig. 2 Schematic diagram of experimental setup used for measurement of Cl^- density.

Fig. 3. Metastable chlorine ion temperature (a) and relative density (b) in the center of the plasma as functions of Cl_2 .

Fig. 4. Relative metastable chlorine ion density in the center of the plasma as a function of additional nitrogen flow rate to a BCl_3 plasma.

Fig. 5. Relative metastable chlorine ion density in the center of the plasma as a function of either additional nitrogen or argon flow rate.

Fig. 6 Cl⁻ density and electron density as functions of Cl₂/Ar ratio.

Fig. 7 Electron density and Cl⁻ density as functions of Cl₂/BCl₃ ratio. Input power was 300 W with a total flow rate of 10 sccm at 20 mTorr.

Fig. 8 Cl⁻ and electron densities as functions of N₂ flow rate for pure BCl₃ discharges.