Electron temperatures of inductively coupled Cl$_2$–Ar plasmas

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Trace rare gases optical emission spectroscopy has been used to measure the electron temperature, $T_e$, in a high-density inductively coupled Cl$_2$–Ar plasma at 18 mTorr as function of the 13.56 MHz radio frequency power and Ar fraction. Only the Kr and Xe emission lines were used to determine $T_e$, because of evidence of radiation trapping when the Ar emission lines were also used for larger Ar fractions. At 600 W (10.6 W cm$^{-2}$), $T_e$ increases from $\sim$4.0±0.5 eV to $\sim$6.0±2.0 eV as the Ar fraction increases from 1% to 96%. In the H (inductive, bright) mode, $T_e$, for a “neat” chlorine plasma (including 1% of each He/Ne/Ar/Kr/Xe) increases only slightly from $\sim$3.8 to 4.0 eV as power increases from 450 to 750 W. This increase is much larger for larger Ar fractions, such as from $\sim$4.0 to 7.3 eV for 78% Ar. Most of these effects can be understood using the fundamental particle balance equation. © 2002 American Vacuum Society. [DOI: 10.1116/1.1427884]

I. INTRODUCTION

Cl$_2$–Ar plasmas are being investigated for the etching of Si and various III–V materials. We have previously reported measurements of the absolute densities of Cl$_2$, Cl, Cl$^+$, Cl$^{-}$, and Ar in inductively coupled plasmas (ICPs) containing such mixtures; such measurements should be useful to investigations of the etch mechanism, rate, selectivity, and etched profile shapes. Accurate determination of the electron temperature, $T_e$, is important for determining the rates of dissociation of Cl$_2$ and ionization of Cl$_2$, Cl, and Ar, and in assessing the mechanisms for differential charging. The electron energy distribution function (EEDF) and therefore $T_e$ can affect the undesirable etched profile anomalies, such as bowing and microtrenching, and electrical damage due to charge build-up and current flow, as have been observed in the etching of silicon device materials (e.g., Si and Al). The electron had a Langmuir probe to measure $T_e$ as a function of rf power and Ar fraction in Cl$_2$–Ar electron cyclotron resonance discharges. However, it is known that such probes are sensitive to the intermediate energy range of the EEDF and there may be a non-Maxwellian high-energy tail in these argon-containing discharges (mTorr pressure regime) to which these probes may be relatively insensitive. To this end, this paper reports measurements of $T_e$ vs rf power and Ar fraction in an ICP Cl$_2$–Ar discharge using trace rare gases optical emission spectroscopy (TRG-OES), a technique sensitive to the high-energy tail (electron energies $\geq$9.8 eV) of the EEDF.

II. EXPERIMENTAL PROCEDURE

The ICP reactor, collection and detection optics, and data acquisition system used in these experiments have been described previously. A 5% (1.2 sccm) trace rare gas equilibrium mixture of He/Ne/Ar/Kr/Xe was added to the Cl$_2$–Ar gas mixture for $T_e$ measurements at 18 mTorr. The pressure was the same with the plasma on or off. Each rare gas fraction differs marginally from the expected 1% value owing to the relative pumping speeds and transport efficiencies of each gas. These effects are taken into account in determining $T_e$. A 2-in.-diam Si(100) wafer (2–5 Ω cm, n-type, P-doped) covered with a 100-nm-thick layer of SiO$_2$ was soldered to the sample holder using In foil. Silicon dioxide etching in Cl$_2$ discharges proceeds very slowly, and without bias delivered to the sample holder etching occurs at a rate $\leq$0.5 nm/min—so the plasma remains relatively unperturbed by any etch products. All measurements are made in the ICP H-(inductive, bright) mode (13.56 MHz rf power $\geq$330 W for Cl$_2$ plasmas).

The line-integrated plasma induced emission from a region across the wafer and ~1.5 cm above it was collected through one of the UV grade quartz windows of the reactor and focused onto the entrance slit of the monochromator. It was scanned from 745 to 885 nm (for various Ar, Kr, and Xe emission lines employed in the TRG-OES model) at rates varying from 0.2 to 0.5 nm/s with a 0.175 nm bandpass to acquire the necessary emission lines. The emission intensities were corrected for the relative spectral dependencies of the monochromator and photomultiplier.

III. RESULTS

Figure 1 shows a part of the spectrum of Ar, Kr, and Xe emission lines at $\sim$760 W for a 1% Ar Cl$_2$–Ar plasma. These
and other Kr and Xe emission lines are used in the TRG-OES model\textsuperscript{13} to determine $T_e$ as a function of rf power and Ar fraction. The model assumes a Maxwellian EEDF for electronic energies, $\varepsilon$, mainly in the range 9.8 to $\sim$15 eV given by

$$\frac{dn_e}{d\varepsilon} = \frac{2n_e}{\sqrt{\pi}} \left( \frac{kT_e}{\varepsilon} \right)^{3/2} \exp \left( -\frac{\varepsilon}{kT_e} \right)$$

(1)

to determine the best match between the observed and computed emission intensities of the rare gases, with $T_e$ as the only adjustable parameter.

All previously reported measurements of $T_e$ by the TRG-OES technique (in chlorine and oxygen-containing plasmas) have used Ar, Kr, and Xe lines.\textsuperscript{13,18,19} When $n_g(T_e) = n_g(T_e)^{1/2}$ ($n_g$ is the gas density, $r$ the optical path length $\sim$reactor radius, and $T_g$ the gas temperature) exceeds $\sim 5 \times 10^{13}$ cm$^{-3}$ K$^{-1}$\textsuperscript{20} as it does in this study for Ar fractions exceeding 1%, Ar emission in the $<$200 nm wavelength range is reabsorbed by the Ar atoms. This radiation trapping causes repeated excitation of energy levels above the excited states ($2p_x$ Paschen levels, $x = 1-10$) that eventually decay to the $2p$ levels, with emission occurring at each of the Ar wavelengths (750.4, 751.5 nm, etc.), resulting in enhanced emission intensities. One can either correct for this effect,\textsuperscript{20} or not use Ar emission and determine $T_e$ over the narrower range of energies sensed by Kr and Xe emission, resulting in a somewhat degraded accuracy.

Figure 2 plots $T_e$ vs Ar fraction at a fixed power of 600 W (areal power density of 10.6 W cm$^{-2}$, volume power density of 0.7 W cm$^{-3}$), with $T_e$ determined by either the Kr and Xe lines only or the Kr, Xe, and Ar lines (corrected for radiation trapping of Ar emission, as described elsewhere\textsuperscript{20}). (The error bars for each datum point are from uncertainties in the parameters in the model.) For a “neat” Cl$_2$ plasma with the 5% TRG mixture added (only $\sim$1% Ar) both techniques should be accurate, and they both yield an electron temperature of $\sim$4.7$\pm$0.7 eV. Given the excellent agreement, it seems reasonable to use only the Kr and Xe lines to determine $T_e$ as a function of rf power and Ar fraction.

For higher Ar fractions, where radiation trapping becomes significant, Fig. 2 shows that using the Ar, Kr, and Xe lines consistently determines an electron temperature $\sim$1 eV higher than that computed using only the Kr and Xe lines. This could be real—an indication of an increase in “temperature” of electrons with energies $\sim$13 eV and a few eV higher at high Ar fractions, or it could be due to an underestimate of the radiation trapping effect. Refinements in the TRG-OES model would be needed to resolve this minor issue. Hereafter, all $T_e$ are determined without using Ar emission lines.

Figure 2 shows that $T_e$ increases from $\sim$4.0$\pm$0.5 eV for a “neat” Cl$_2$ plasma (1% Ar) to $\sim$6.0$\pm$2.0 eV for a “neat” Ar plasma (96% Ar), with the biggest changes occurring for Ar fractions exceeding 40%. This factor of $\sim$1.6 increase in $T_e$ can be understood by examining the fundamental particle balance equation for an electropositive plasma (Ar, or a highly dissociated Cl$_2$ plasma)\textsuperscript{21}

$$T_e = \frac{E_{act}}{\ln \left( \frac{A_0 n_g d_{eff}}{\nu_B(T_e)} \right)}$$

(2)

where $n_g$ is the gas density, $d_{eff}$ an effective ion diffusion length\textsuperscript{21} (4.2 and 4.3 cm for Cl$^+$ and Ar$^+$, with ion mean free paths $\lambda_i$ of 1.8 and 1.7 cm, respectively), $\nu_B(=\sqrt{eT_e/M_i})$ the speed of positive ions as they enter the plasma sheath, and $M_i$ the ion mass. $E_{act}$ and $A_0$ are the activation energy and preexponential factor, respectively, in the Arrhenius expression for the ionization rate constant of the neutrals. It has been shown that, $n_g \gg n_{Cl_2}$ at 600 W for all Ar fractions,\textsuperscript{1} so Cl and Ar are the dominant neutrals in the plasma determining $T_e$.\textsuperscript{171}}
The ionization rate constants for Cl\textsuperscript{19,22} and Ar\textsuperscript{23} are

\[ k_{i;e}(\text{Cl}) = 7.56 \times 10^{-8} \exp\left(-\frac{13.74}{T_e}\right) \text{cm}^3 \text{s}^{-1}, \]  

\[ k_{i;e}(\text{Ar}) = 7.93 \times 10^{-8} \exp\left(-\frac{19.20}{T_e}\right) \text{cm}^3 \text{s}^{-1}. \]  

The small difference in \( A_0, M_i, \lambda_i, \) between Cl\textsuperscript{+} and Ar\textsuperscript{+} implies that differences in these parameters contribute negligibly to any change in \( T_e \) when the mixture is changed. By the same token, the gas density, \( n_g \), is probably similar in Cl\textsubscript{2} and Ar plasmas. (The temperature of a comparable Cl\textsubscript{2} plasma was found to be about twice that of an Ar plasma at the same power,\textsuperscript{24} halving the number density. This is roughly canceled by a doubling of the number density in the highly dissociated Cl\textsubscript{2} plasma). On the other hand, \( E_{\text{act}} \) is 19.20 eV for Ar, compared to 13.74 eV for Cl. This 5.46 eV increase in \( E_{\text{act}} \) ought to increase \( T_e \) by a factor of \( \sim 1.4 \), in good agreement with the measured factor \( \sim 1.6 \pm 0.2 \) increase in \( T_e \) as the plasma changes from being Cl dominant (1% Ar) to Ar dominant (96% Ar). The absolute \( T_e \) computed from Eq. (2) is 4.0 eV for an Ar plasma. This value is low, but nearly within the uncertainty of the measurement.

Figure 3 shows \( T_e \) as a function of rf power for different Ar fractions. \( T_e \) increases with rf power for all Ar fractions. From 350 to 750 W it increases relatively little for chlorine-rich plasmas, from \( \sim 3.8 \) to 4.0 eV for 1% Ar and from \( \sim 4.5 \) to 4.6 eV for 13% Ar, and by much larger factors (\( \sim 1.75 \)) for bigger Ar fractions, from \( \sim 3.5 \) to 5.0 eV for 40% Ar and \( \sim 4.0 \) to 7.3 eV for 78% Ar.

The increase in \( T_e \) with rf power has been observed previously\textsuperscript{22} and can be compared with the predicted behavior using Eq. (2). For the 95% Cl\textsubscript{2} discharge (1% Ar), we have shown that percent dissociation of Cl\textsubscript{2} increases from \( \sim 60 \) to 86% from 350 to 750 W, thereby increasing \( n_g \) by a factor of \( \sim 1.45 \) (from \( \sim 6.6 \) to \( \sim 9.6 \times 10^{14} \text{cm}^{-3} \), including estimates of the effect of gas heating\textsuperscript{22}). This increase in \( n_g \) would decrease \( T_e \) by a factor of \( \sim 1.2 \). However, this is balanced by other effects of the dissociation of Cl\textsubscript{2} in generating species of higher ionization activation energy \( E_{\text{act}} \) (13.74 eV for Cl\textsuperscript{19,22} vs 13.34 eV for Cl\textsubscript{1}—Refs. 19 and 26) and smaller ionization preexponential factor \( A_0 \) (7.56 \( \times 10^{-8} \text{cm}^3 \text{s}^{-1} \) for Cl\textsuperscript{19,22} vs 1.18 \( \times 10^{-7} \text{cm}^3 \text{s}^{-1} \) for Cl\textsubscript{1}—Refs. 19 and 26). Together, these last two differences would increase \( T_e \) by a factor of \( \sim 1.26 \). The net effect is a negligible increase in \( T_e \) by a factor of \( \sim 1.05 \) over this power range for both the 1% and 13% Ar fractions, consistent with the experimental findings.

In contrast, for the larger Ar fractions (40% and 78%), the gas dissociation is nearly complete (\( \sim 90\% \)) for rf powers >450 W,\textsuperscript{1} presumably because of the increase in \( T_e \) with Ar fraction (Fig. 2). While the change in \( n_g \) with power due to dissociation is not important in determining \( T_e \), the change in \( n_g \) with power due to gas heating still is. For the 78% Ar Cl\textsubscript{2}–Ar discharge, we have shown\textsuperscript{1} that \( n_{\text{Cl}} + n_{\text{C}} \) decreases by only \( \sim 1.1 \) from 3.1 to 2.8 \( \times 10^{11} \text{cm}^{-3} \) over the rf power range investigated, while the Ar density decreases by a factor of \( \sim 2.4 \) from 4.5 to 1.9 \( \times 10^{14} \text{cm}^{-3} \), based on an assumed linear rise in \( T_g \) from 300 K (350 W) to \( \sim 1000–1200 \text{ K} \) (800 W).\textsuperscript{22} Using Eq. (2), the decrease in the net gas density, \( n_g = n_{\text{Cl}} + n_{\text{C}} + n_{\text{Ar}} \), ought to increase \( T_e \) by a factor of \( \sim 1.30 \), which is somewhat less than the factor of \( \sim 1.75 \) increase observed under these conditions. The Cl\textsubscript{2}-containing plasmas are largely heated by the kinetic energy released into Cl-atoms following the dissociation of Cl\textsubscript{2}. Consequently, the \( \sim 40\% \) increase in \( T_e \) with increasing power in 96% Ar plasmas is even harder to explain, given the smaller temperature rise expected under these conditions. Perhaps \( T_e \) is even higher, \( \sim 2000–2500 \text{ K} \), at higher rf powers (\( \sim 750 \text{ W} \)) than the assumed values from a larger ICP system studied previously.\textsuperscript{24} Equivalent rf powers coupled into this larger ICP system\textsuperscript{24} and the system used in this study corresponds to a factor of \( \sim 3 \) larger power density for the reactor used in this study versus that of the larger ICP system in Ref. 24 and a probable factor of \( \sim 1.7 \) increase in the above assumed values of \( T_g \) in the ICP used in this study.\textsuperscript{24}

IV. CONCLUSIONS

Electron temperatures representative of the high-energy tail (\( \geq 9.8 \text{ eV} \)) of the EEDF were measured in Cl\textsubscript{2}–Ar ICPs by TRG-OES. Only the Kr and Xe emission lines were used to determine \( T_e \), because of radiation trapping when the Ar emission lines were also used for larger Ar fractions. At 600 W, \( T_e \) increases with Ar fraction from \( \sim 4.0 \pm 0.5 \text{ eV} \) for a "neat" (1% Ar) Cl\textsubscript{2} discharge to \( \sim 6.0 \pm 2.0 \text{ eV} \) for a "neat" (96% Ar) Ar discharge, due to the larger ionization activation energy of Ar (19.20 eV) versus that of Cl (13.74 eV). \( T_e \) is \( \sim 4.0 \text{ eV} \) and relatively independent of rf power (\( \sim 350 \) to 750 W) for the lower Ar fractions (1% and 13%) and is strongly dependent on power for larger Ar fractions, increasing from 3.5 to 5.0 eV (40% Ar) and 5.0 to 7.3 eV (96% Ar) over the same power range. Most of this can be explained by
the reduction in number density due to gas heating, combined with the change in composition of chlorine-containing plasmas ($\text{Cl}_2$ dissociation into $2\text{Cl}$) with increasing power.

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15. It is not surprising that the pressure in these Cl$_2$–Ar discharges is the same for the plasma on and off, since the mean free path for neutrals ($\sim 0.3 \text{ cm}$) is much less than the diameter ($\sim 10.7 \text{ cm}$) of the adjoining tube between the reactor and the pumping system (Refs. 16 and 17).
27. Reference 21 determined a square root dependence of gas temperature with rf power but since this dependence may be very reactor specific and the power density in this reactor is $\sim 3 \times$ that in Ref. 21, a linear dependence was assumed here.