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 $\sim 4.0 \pm 0.5$ eV to $\sim 6.0 \pm 2.0$ 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 ~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 ~4.0 to 7.3 eV for 78% Ar. Most of these effects can be understood using the fundamental particle balance equation. [DOI: 10.1116/1.1427884]

I. INTRODUCTION

Cl_2–Ar plasmas are being investigated for the etching of Si and various III–V materials.[1–7] We have previously reported measurements of the absolute densities of Cl_2, Cl, Cl_2^+, 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.[1] 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).[8–10]

Eddy *et al.* have used a Langmuir probe to measure T_e as a function of rf power and Ar fraction in Cl_2–Ar electron cyclotron resonance discharges.[2] 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[11,12] 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 $\geqslant$9.8 eV) of the EEDF.[13]

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II. EXPERIMENTAL PROCEDURE

The ICP reactor, collection and detection optics, and data acquisition system used in these experiments have been described previously.[1,14] A 5% (1.2 sccm) trace rare gas equimixture 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.[15–17] 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[13] 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 $\leqslant$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 >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 ~760 W for a 1% Ar Cl_2–Ar plasma. These

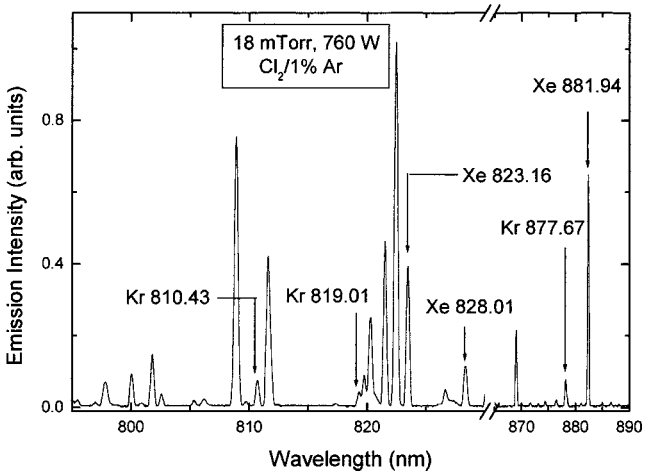

FIG. 1. Optical emission spectrum of an 18 mTorr Cl_2-Ar (1% Ar) ICP plasma at 760 W rf power with 5% of the trace rare gas mixture, from 795 to 830 nm and from 865 to 890 nm. The labeled rare gas emission lines are: Kr (810.43, 819.01, and 877.67 nm) and Xe (823.16, 828.01, and 881.94 nm).

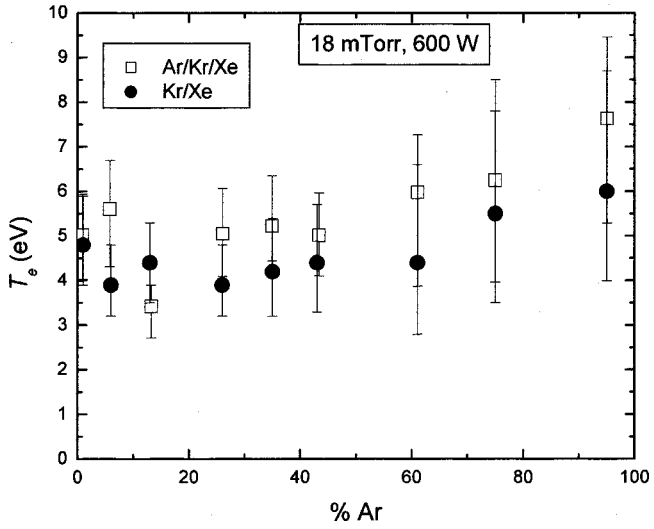

FIG. 2. Electron temperature (T_e) vs Ar fraction at 600 W rf power in an 18 mTorr Cl_2-Ar ICP plasma with 5% of the trace rare gas mixture. The electron temperature is computed using either the Kr and Xe lines only or the Ar, Kr, and Xe lines.

and other Kr and Xe emission lines are used in the TRG-OES model[13] to determine T_e as a function of rf power and Ar fraction. The model assumes a Maxwellian EEDF for electronic energies, ε, mainly in the range 9.8 to ~15 eV given by

$$\frac{dn}{d\varepsilon}=\frac{2n_e}{\sqrt{\pi}}\frac{1}{(kT_e)^{3/2}}\sqrt{\varepsilon}\exp\left(\frac{-\varepsilon}{kT_e}\right) \tag{1}$$

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.[13,18,19] When $n_g(T_g)r/T_g^{1/2}$ (n_g is the gas density, r the optical path length~reactor radius, and T_g the gas temperature) exceeds $\sim 5\times 10^{11}\,\mathrm{cm^{-2}\,K^{-1}}$,[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,[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 $\mathrm{W\,cm^{-2}}$, volume power density of 0.7 $\mathrm{W\,cm^{-3}}$), with T_e determined by using either the Kr and Xe lines only or the Kr, Xe, and Ar lines (corrected for radiation trapping of Ar emission, as described elsewhere[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 ~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 ~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 ~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 ~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)[21]

$$T_e=\frac{E_{\mathrm{act}}}{\ln\left(\dfrac{A_0 n_g d_{\mathrm{eff}}}{\nu_B(T_e)}\right)}, \tag{2}$$

where n_g is the gas density, d_{eff} an effective ion diffusion length[21] (4.2 and 4.3 cm for Cl^+ and Ar^+, with ion mean free paths λ_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, $n_{\mathrm{Cl}}\gg n_{\mathrm{Cl_2}}$ at 600 W for all Ar fractions,[1] so Cl and Ar are the dominant neutrals in the plasma determining T_e.

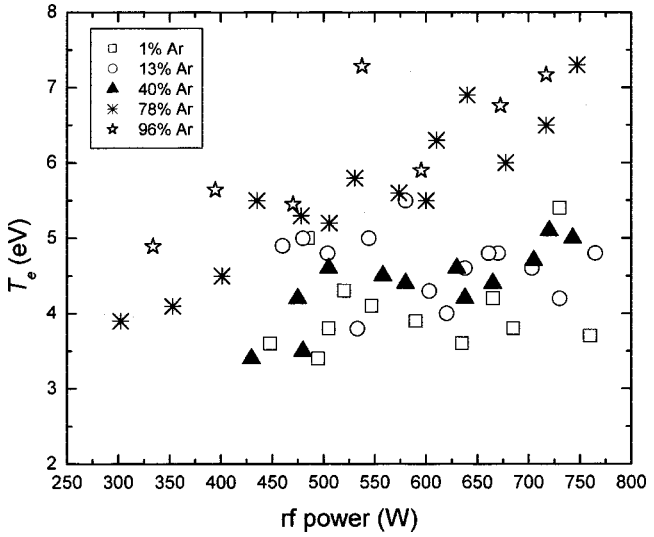

FIG. 3. Electron temperature (T_e) vs rf power and Ar fraction (1%, 13%, 40%, 78%, and 96%) in an 18 mTorr Cl_2–Ar ICP plasma with 5% of the trace rare gas mixture.

The ionization rate constants for Cl[19,22] and Ar[23] are

$$k_{iz}(\mathrm{Cl}) = 7.56\times10^{-8}\exp\left(\frac{-13.74}{T_e}\right)\mathrm{cm^3\,s^{-1}}, \quad (3)$$

$$k_{iz}(\mathrm{Ar}) = 7.93\times10^{-8}\exp\left(\frac{-19.20}{T_e}\right)\mathrm{cm^3\,s^{-1}}. \quad (4)$$

The small difference in A_0, M_i (35.5 vs 40.0 amu) and λ_i between Cl^+ and Ar^+ 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_2 and Ar plasmas. (The temperature of a comparable Cl_2 plasma was found to be about twice that of an Ar plasma at the same power,[24] halving the number density. This is roughly canceled by a doubling of the number density in the highly dissociated Cl_2 plasma). On the other hand, E_{act} is 19.20 eV for Ar, compared to 13.74 eV for Cl. This 5.46 eV increase in E_{act} ought to increase T_e by a factor of ~1.4, in good agreement with the measured factor $\sim1.6\pm0.2\times$ 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 ~3.8 to 4.0 eV for 1% Ar and from ~4.5 to 4.6 eV for 13% Ar, and by much larger factors (~1.75) for bigger Ar fractions, from ~3.5 to 5.0 eV for 40% Ar and ~4.0 to 7.3 eV for 78% Ar.

The increase in T_e with rf power has been observed previously[25] and can be compared with the predicted behavior using Eq. (2). For the 95% Cl_2 discharge (1% Ar), we have shown[1] that percent dissociation of Cl_2 increases from ~60 to 86% from 350 to 750 W, thereby increasing n_g by a factor of ~1.45 (from ~6.6 to $\sim9.6\times10^{14}\,\mathrm{cm^{-3}}$, including estimates of the effect of gas heating[24]). This increase in n_g would decrease T_e by a factor of ~1.2. However, this is balanced by other effects of the dissociation of Cl_2 in generating species of higher ionization activation energy E_{act} (13.74 eV for Cl[19,22] vs 13.34 eV for Cl_2—Refs. 19 and 26) and smaller ionization preexponential factor A_0 ($7.56\times10^{-8}\,\mathrm{cm^3\,s^{-1}}$ for Cl[19,22] vs $1.18\times10^{-7}\,\mathrm{cm^3\,s^{-1}}$ for Cl_2—Refs. 19 and 26). Together, these last two differences would increase T_e by a factor of ~1.26. The net effect is a negligible increase in T_e by a factor of ~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 (~90%) for rf powers >450 W,[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_2–Ar discharge, we have shown[1] that $n_{Cl_2}+n_{Cl}$ decreases by only ~1.1 from 3.1 to $2.8\times10^{14}\,\mathrm{cm^{-3}}$ over the rf power range investigated, while the Ar density decreases by a factor of ~2.4 from 4.5 to $1.9\times10^{14}\,\mathrm{cm^{-3}}$, based on an assumed linear rise in T_g from 300 K (350 W) to ~1000–1200 K (800 W).[24,27] Using Eq. (2), the decrease in the net gas density, $n_g(\approx n_{Cl_2}+n_{Cl}+n_{Ar})$, ought to increase T_e by a factor of ~1.30, which is somewhat less than the factor of ~1.75 increase observed under these conditions. The Cl_2-containing plasmas are largely heated by the kinetic energy released into Cl-atoms following the dissociation of Cl_2. Consequently, the ~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_g is even higher, ~2000–2500 K, at higher rf powers (~750 W) than the assumed values from a larger ICP system studied previously.[24] Equivalent rf powers coupled into this larger ICP system[24] and the system used in this study corresponds to a factor of ~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 ~1.7 increase in the above assumed values of T_g in the ICP used in this study.[24]

IV. CONCLUSIONS

Electron temperatures representative of the high-energy tail (≥9.8 eV) of the EEDF were measured in Cl_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 $\sim4.0\pm0.5$ eV for a "neat" (1% Ar) Cl_2 discharge to $\sim6.0\pm2.0$ 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 ~4.0 eV and relatively independent of rf power (~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 (Cl_2 dissociation into 2Cl) with increasing power.

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