Determination of Plasma Parameters in a Dual-Frequency Capacitively Coupled CF4 Plasma Using Optical Emission Spectroscopy

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Abstract Optical emission spectroscopy measurements of dual-frequency capacitively coupled CF4 plasmas were carried out. The gas temperature ($T_g$) was acquired by fitting the optical emission spectra of a CF $B-X$ system in 201~206 nm. The atomic fluorine concentration and the electron temperature ($T_e$) were obtained by trace rare gas optical emission spectroscopy and a modified Boltzmann plot technique, respectively. It was found that the gas temperature was about 620±30 K at 50 mTorr and the atomic fluorine concentration increased while the electron temperature decreased with increasing gas pressure and power of high frequency (60 MHz). With increasing low frequency (2 MHz) power, the electron temperature also increased, but the atomic fluorine concentration was insensitive to this change. The generation and disappearance mechanisms of F atoms are discussed.

Keywords: dual-frequency capacitively coupled plasma (DF CCP), gas temperature, electron temperature, fluorine atom concentration

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1 Introduction

Dual-frequency capacitively coupled plasma (DF CCP) is widely used for the etching of thin films in semiconductor circuits manufacturing. It allows the generation and control of a medium to high plasma densities with reasonably independent control of the mean energy of positive ions striking the substrate. The plasma, which showed high etching rate and good selectivity in a wide range of processing parameters, has attracted increasing attention [1~4].

Steady progress in diagnostics for plasma characterization has allowed for considerable advances in the understanding of plasma etching and deposition processes. Many of the diagnostics, such as the Langmuir probe, are intrusive diagnostic methods, and are susceptible to contamination or hysteresis when exposed to reactive species. These problems have hampered accurate characterization of industrially relevant plasma reactors (i.e., those used in the microelectronics industry) [5,6]. Quantitative interpretation of optical emission spectra from plasmas has made it possible to measure plasma parameters such as gas temperature ($T_g$), atomic fluorine concentration, and electron temperature ($T_e$). A primary advantage of this nonintrusive technique is that it is unaffected by reactants in plasma so long as the optical access windows remain clean, and will not disturb the plasma. In this work, we use CF rotational spectroscopy [7~9] to measure $T_g$, and use trace rare gas optical emission spectroscopy (TRG-OES) [10~14] to measure the density of atomic fluorine and $T_e$ in a dual-frequency (60 MHz/2 MHz) capacitively coupled CF4/Ar plasma. The influences of discharge power and gas pressure on these plasma characteristics are discussed. Then the mechanisms of F atom production and disappearance are also analyzed.

2 Experimental setup

The experimental equipment is shown schematically in Fig. 1, details of which are given elsewhere [15,16]. Briefly, the upper electrode (210 mm in diameter) is powered with high frequency (HF, 60 MHz) and low frequency (LF, 2 MHz) sources and the lower electrode (150 mm in diameter) is grounded. The axial gap between the two parallel plates is 30 mm. The CF4 and Ar gases with purity of 99.999% flowed through a dehydration tube, which was filled with silica gel to filter the water, and the gases were then delivered into the discharge zone through gas distribution holes in the upper
electrode. The voltage on the upper electrode is measured with a high-voltage probe (PPE6KV, LeCroy).

![Fig.1 Schematic diagram of the discharge chamber and the optical measurement setup (color online)](image)

Emission spectra are collected through a viewport window with a 50 cm spectrometer (Acton SP-2500i) equipped with three gratings. The exit port of the spectrograph is coupled to a CCD camera. The plasmas were ignited in pure CF₄ or a mixture of CF₄/Ar (95/5).

### 3 Results and discussion

#### 3.1 Rotational temperature measurements of CF

The emission spectra of the CF B − X bands are shown in Fig. 2. They show two distinct peaks in the ultraviolet, due primarily to the (0,0) and (0,1) vibrational transitions of the B₂Δ − X₂Π electronic transition. The line positions and transition probabilities used in this work are compiled in the LIFBASE database/spectral simulation program [9]. This program allows simulation, with selectable line shape, of optical emission, absorption, and LIF spectra for thermal and non-thermal vibrational and rotational population distributions. We can apply LIFBASE software to fit some spectra accurately and conveniently by choosing appropriate parameters.

![Fig.2 Emission spectra of the CF B−X bands (pure CF₄, P=50 mTorr, P₁=300 W and P₂=50 W)](image)

Fig. 3 shows the experimental and simulated optical emission spectra of the CF B − X system in 201.5 ~ 204 nm. The rotational temperature inferred from the simulated spectrum is near 620 K for the CF₄ plasma at 300/50 W (high/low frequency powers) and 50 mTorr. The rotational temperature showed by CRUDEN [8] is ~800 K in a dual-frequency (2 MHz, 27 MHz) capacitively coupled commercial etching system. These temperatures reflect the fact that the population distributions result more directly from the B₂Δ state production mechanism because the B₂Δ state radiative lifetime of 20 ns allows very few thermalizing collisions to occur [9]. Fitting the vibrational temperature by the CF should assume its excited electronic state being equilibrated with the vibrational mode. However, the lifetime of the CF excited state is shorter than the reciprocal of the collision frequency, and there are not enough collisions to equilibrate the vibrational temperature. Therefore vibrational temperature is not reported here as it is not believed to be physically meaningful [7,8]. As there are enough collisions during the lifetime of the CF, rotational temperature in the ground state is much closer to the gas translational temperature [9]. The rotational temperature of the excited CF state should be above that of the CF ground state.

![Fig.3 Comparison of experimental with simulated spectra for CF B−X bands in CF₄ plasma. P=50 mTorr, P₁=50 W and P₂=300 W](image)

#### 3.2Atomic fluorine concentration measurements

Absolute atomic fluorine concentration is determined by using trace rare gas optical emission spectroscopy (TRG-OES) [10~13]. In this case, argon was introduced as the probe gas. By comparing the intensity of fluorine at 703.7 nm with that of the actinometer Ar at 750.4 nm, it is possible to determine the absolute concentration of fluorine by using:

\[
N_F = K N_{Ar} \frac{I_F}{I_{Ar}},
\]

where the \(N_F\) and \(N_{Ar}\) denote the relative concentrations of F and Ar, respectively. And \(I_F\) and \(I_{Ar}\) represent the line intensities of the F (703.7 nm) and Ar
(750.4 nm), respectively. $K$ is given by \[ K = \frac{\int_0^\infty \sigma_{A\ell}(\varepsilon)\sqrt{f}(\varepsilon)d\varepsilon}{\int_0^\infty \sigma_{P}(\varepsilon)\sqrt{f}(\varepsilon)d\varepsilon} \] \tag{2}

where $\sigma_{A\ell}(\varepsilon)$ and $\sigma_{P}(\varepsilon)$ are the excitation cross sections of Ar and F atoms due to electron impact to their ground state at energy $\varepsilon$, and $f(\varepsilon)$ is the electron distribution function.

Eq. (1) assumes that the population of the excited state for each species is well characterized by unique excitation mechanisms, and that the ratio of the electron impact cross sections is independent of electron temperature. The threshold energy of line F located at 703.7 nm is about 14.5 eV, which is close to 13.5 eV of the Ar at 750.4 nm, and they also have similar cross sections. Therefore, as shown in Eq. (2), $K$ is mainly dependent on the electron distribution function. The proportional constant, $K$, is 4.3, as measured by Kawai et al. \cite{14} in a CF$_4$ helicon plasma operated at low power. Cunge et al. \cite{13} also investigated the proportional constant in capacitively coupled discharge under similar conditions, it is in good agreement with the result of Kawai et al. In addition, he believed that the power variation between 30 W and 150 W was smaller to keep roughly the same electron energy distribution function (EEDF) shape. EEDF measurements in an argon low-pressure capacitively coupled RF discharge have been reported by Godyak et al. \cite{17}. The EEDF shape does not vary significantly with gas pressure between 10 mTorr and 90 mTorr. The validity of Eq. (1) has also been proved by titration experiments on CF$_4$/O$_2$/Ar plasma \cite{10}. In our experiment, conditions are very similar to that set by Cunge et al, thus $K=4.3$ was used and the absolute concentration of atomic fluorine was measured as a function of pressure (Fig. 4), which is close to that presented in Ref. \cite{18} for an RF capacitively coupled plasma discharge at frequency of 81 MHz in Ar/CF$_4$.

3.3 Electron temperature measurements

In order to measure the $T_e$ (electron temperature) by using spectroscopic methods, the plasma is generally assumed to be in steady state, and excited-state populations also follow the Boltzmann law, simultaneously. The assumption is based on a local thermodynamic equilibrium, which ignores the actual details of the excitation and radiation processes.

Owing to the low pressure and temperature, dual-frequency capacitively coupled CF$_4$/Ar plasma is difficult to satisfy the conditions of local thermodynamic equilibrium (LTE), most probably, the population density of the excited states is not in Boltzmann equilibrium. In our experiment, electron densities are between $10^9$ cm$^{-3}$ and $10^{11}$ cm$^{-3}$ according to LI et al. \cite{19} under similar conditions, which are consistent with nonequilibrium plasmas in corona balance. So a modified Boltzmann plot technique \cite{20} is used in our study, which considers that the upper energy levels of the argon atoms used for the plasma diagnosis are close to a corona balance \cite{18}, that is, the population and depopulation mechanisms of the argon energy levels studied are mainly collisional (electron collisions with ground Ar atoms) and radiative (spontaneous radiative decay), respectively. Gordillo-Vazquez et al. \cite{20} have investigated the corona model and obtained a modified Boltzmann formula as follows \cite{21}:

$$\ln \frac{I_{ij}\lambda_{ij} \sum_{i>j} A_{ij}}{A_{ij}a_{i1}} = \frac{E_{1i}}{KT_e} + D,$$ \tag{3}

where $I_{ij}$ and $\lambda_{ij}$ are the intensity and wavelength of the spectral lines, respectively. $D$ is a constant, $A_{ij}$ is the Einstein coefficient, $E_{1i}$ is the excitation energy of level $i$, $a_{i1}$ is the coefficient in an exponential approximation of the electron impact excitation rate coefficient from ground state to level $i$. The parameters for fitting $T_e$ using Eq. (3) are given in Ref. \cite{22}.

3.4 Effects of pressure on $T_e$ and F atom concentration

Electron temperature ($T_e$) calculated by the modified Boltzmann formula at different pressures for a given power of HF ($P_h=50$ W) and LF ($P_l=50$ W) sources in DF CCP is presented in Fig. 4. The experimental results show that the electron temperature gradually decreases with increasing pressure. That is because the average kinetic energy decreases with reducing mean free path and there are more frequent collisions between electrons due to increased pressures. As a tendency of average kinetic energy, $T_e$ also decreases with increasing discharge pressure from 15 mTorr to 90 mTorr in a mixture of Ar/CF$_4$ (5/95) plasma.

The fluorine atom concentration was measured to be $(5.6$ to $7.2) \times 10^{12}$ cm$^{-3}$ for discharge pressures from 15 mTorr to 90 mTorr and fixed powers ($P_h=50$ W and $P_l=50$ W), as shown in Fig. 4. Above 30 mTorr, with the increase of pressure, the fluorine atom concentration shows a trend of monotonic increase in DF CCP. The increased pressure can result in higher plasma concentration. It is not surprising to observe that the fluorine atom concentration increases with increasing pressure.
This is due to higher collision probability, shorter mean free path, and smaller electron temperature at higher pressure.

### 3.5 Effects of HF/LF power on $T_e$ and F atom concentration

Fig. 5 shows the fluorine atom concentration and $T_e$ as a function of HF power at fixed pressure (50 mTorr) and LF power (50 W). The phenomenon is almost the same as that shown in Fig. 4 at different pressures. This can be attributed to the increase of plasma density with increasing HF power. Higher electron density, more ion-molecule collisions, and a shorter mean free path will be conducive to the generation of higher fluorine atom concentration and smaller electron temperature ($T_e$) with increasing HF power.

![Fig. 5 Atomic fluorine concentration and electron temperature as a function of high frequency power in Ar/CF$_4$ plasma ($P$=50 mTorr, $P_h$=50 W)](image)

The electron temperature increases obviously with the increase of LF power, which was proved by computer simulations [23] using the particle-in-cell method. As the sheath width increases linearly with increasing low frequency power, the width of the bulk plasma is reduced considerably. The electron temperature is determined for a given gas by the product of dimensions of bulk plasma and operating pressure only [24]. Thus the decrease in the dimensions of the bulk plasma results in the increased electron temperature at a fixed pressure in DF CCP.

### 3.6 The production and loss mechanisms of F atom

In order to explain the behaviors of the F atom with HF and LF power and feed gas pressure, we should consider the production and loss processes of the F atom firstly. In low pressure and cold plasma, the F atom is mainly generated by electron impact dissociation in the gas phase. As shown in Table 1, these reactions may be considered as possible dissociation and ionic channels of F atom production.

![Fig. 6 Atomic fluorine concentration and electron temperature as a function of low frequency power in Ar/CF$_4$ plasma ($P$=50 mTorr, $P_h$=50 W)](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficients (cm$^3$/s)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_4$ + e → CF$_3$ + F + e</td>
<td>$k_1=1.38\times10^{-8}\exp(-16.0/T_e)$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>2</td>
<td>CF$_4$ + e → CF$_2$ + 2F + e</td>
<td>$k_2=2.22\times10^{-8}T_e^{0.99}\exp(-14.77/T_e)$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>3</td>
<td>CF$_4$ + e → CF + 3F + e</td>
<td>$k_3=7.29\times10^{-9}T_e^{1.16}\exp(-28.26/T_e)$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>4</td>
<td>CF$_3$ + e → CF$_2$ + F + e</td>
<td>$k_4=6.48\times10^{-8}T_e^{-0.96}\exp(-11.25/T_e)$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>5</td>
<td>CF$_2$ + e → CF + F + e</td>
<td>$k_5=1.16\times10^{-8}T_e^{0.38}\exp(-14.35/T_e)$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>6</td>
<td>CF$_3$ + e → CF$_2$ + 2F + 2e</td>
<td>$k_6=9.36\times10^{-8}\exp(-20.4/T_e)$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>7</td>
<td>CF$_4$ + e → CF$_3$ + 2F + 2e</td>
<td>$k_7=1.27\times10^{-8}\exp(-29.0/T_e)$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>8</td>
<td>CF$_4$ + e → CF$^+$ + 3F + 2e</td>
<td>$k_8=1.04\times10^{-8}\exp(-33.3/T_e)$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>9</td>
<td>CF$_3$ + e → CF$^+$ + F + 2e</td>
<td>$k_9=2.20\times10^{-8}\exp(-18.6/T_e)$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>10</td>
<td>CF$_2$ + e → CF$^+$ + F + 2e</td>
<td>$k_{10}=2.33\times10^{-8}\exp(-17.0/T_e)$</td>
<td>Dissociative ionization</td>
</tr>
<tr>
<td>11</td>
<td>F$_2$ + e → F$^-$ + F</td>
<td>$k_{11}=4.5\times10^{-8}T_e^{-1.35}\exp(-0.15/T_e)$</td>
<td>Dissociative attachment</td>
</tr>
<tr>
<td>12</td>
<td>F$^+$ + e → F$^-$ + F + e</td>
<td>$k_{12}=1.18\times10^{-8}\exp(-5.77/T_e)$</td>
<td>Dissociation</td>
</tr>
<tr>
<td>13</td>
<td>F$^+$ + CF$_3$ → CF$_3^+$ + F</td>
<td>$k_{13}=1\times10^{-9}$</td>
<td>Nonresonant charge transfer</td>
</tr>
<tr>
<td>14</td>
<td>X$^+$ + F$^-$ → X + F</td>
<td>$k_{14}=4\times10^{-7}$</td>
<td>Ion recombination</td>
</tr>
</tbody>
</table>
Table 2. The reactions of fluorine atoms with other radicals in the gas phase

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficients (cm$^3$/s)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_3$+F→CF$_4$</td>
<td>$K_1 = 2.3 \times 10^{-13} \times P$ (mTorr)</td>
<td>Recombination</td>
</tr>
<tr>
<td>2</td>
<td>CF$_2$+F→CF$_3$</td>
<td>$K_2 = 9 \times 10^{-16} \times P$ (mTorr)</td>
<td>Recombination</td>
</tr>
<tr>
<td>3</td>
<td>CF+F→CF$_2$</td>
<td>$K_3 = 9.6 \times 10^{-18} \times P$ (mTorr)</td>
<td>Recombination</td>
</tr>
<tr>
<td>4</td>
<td>F+e→F$^+$(+2e)</td>
<td>$K_4 = 1.3 \times 10^{-8} \exp(-16.5/T_\gamma)$</td>
<td>Ionization</td>
</tr>
<tr>
<td>5</td>
<td>F+CF→F$_2$</td>
<td>$K_5 = 6.77 \times 10^{-34}$</td>
<td>Recombination</td>
</tr>
</tbody>
</table>

Under the present conditions, due to the lower dissociation degree of CF$_4$, the density of CF$_4$ is higher than those of other species. F atoms are predominantly produced in reactions (1) and (6), and that could be confirmed by the higher density of CF$_4$ and CF$^+_4$ in CF$_4$ discharge [26], while the other reactions can be ignored due to their smaller rate coefficients or lower concentration of reactants.

The main loss mechanisms of F atoms consist of three possible paths: loss by pumping, loss by reacting with other radicals in the gas phase, and loss by diffusing and sticking on the chamber wall and electrode [27]. In our experiment, the flow rate of the parent gas is 30 sccm and the pressure is 50 mTorr. So the rate of pumping is about 0.6 s$^{-1}$ only, and the loss by pumping can thus be neglected.

As shown in Table 2, these reactions are the main causes of fluorine atom loss in the gas phase. Rate constants of the reactions are quoted from Refs. [25,28].

In this work the absolute density of CF$_2$ is measured by the UVLED brand band absorption, which is in the range of 10$^3$ cm$^{-3}$. When the gas pressure ranges from 10 mTorr to 90 mTorr, the loss rate of CF$_2$+F→CF$_3$ is estimated to be below 10$^{12}$ cm$^{-3}$·s$^{-1}$. We did not measure the densities of CF and CF$_3$ in our experiment, but SINGH et al. [26] and RAKHIMOVA et al. [18] found that these densities are below 4×10$^{13}$ cm$^{-3}$ under similar conditions. Both the density and the rate coefficient of CF are lower than those of CF$_2$, thus the loss of the F atom by recombinating with CF is negligible. However, the density of CF$_3$ is higher than that of CF$_2$, the loss rate of CF$_3$+F→CF$_4$ is estimated to be more than 10$^{14}$ cm$^{-3}$·s$^{-1}$. As the high electronegativity in the CF$_4$ plasma, the density of electron is about 10$^{10}$ cm$^{-3}$, reaction (4) is less important. The recombination of F atoms could also be ignored due to the extremely small rate coefficient for F+F→F$_2$. In conclusion, the recombination of F and CF$_3$ might be responsible for the main loss of the F atom in the gas phase.

In the cylindrical or plane-parallel discharge, radicals lost by diffusing and sticking on the chamber wall and electrodes are very important. The loss rate with probability is given by [24,29,30]

$$K_D = \frac{D_F}{\Lambda_0^2},$$

$$K_w = \frac{\gamma}{2(2-\gamma)} \frac{S}{V} \left( \frac{8K_BT_\gamma}{\pi M_R} \right)^{1/2},$$

where $D_F$ is the diffusion coefficient of a F atom in plasma, $D_F/\Lambda_0^2$ is related to the diffusion loss rate, and Eq. (5) is related to the loss rate at the chamber wall and electrodes, $\gamma$ is the sticking coefficient on the wall, $S$ and $V$ represent the surface area of the electrode and volume of the plasma discharge, $K_B$ is the Boltzmann coefficient, $T_\gamma$ is the temperature of gas, and $M_R$ is the reduced mass of the F atom and the CF$_4$ molecule. $\Lambda_0$ is the effective diffusion length, which could be calculated by [27,30]

$$\frac{1}{\Lambda_0} = \left( \frac{\pi}{d} \right)^2 + \left( \frac{2405}{r} \right)^2,$$

where $d$ is the electrode spacing (3 cm) and $r$ is the radius of powered electrode (10.5 cm).

In our oblate cylindrical reactor, due to the small electrode spacing, the axial diffusion to the electrode surfaces is more significant than the radial diffusion. When the gas pressure is 50 mTorr and gas temperature fitted by LIFBASE is about 600 K, $D_P$ is calculated to be about 4.0×10$^3$ cm$^2$·s$^{-1}$. $\gamma$ is reported about 0.02 [25], $K_D \approx 4000$ s$^{-1}$ and $K_w \approx 500$ s$^{-1}$. Due to the faster diffusion, the wall loss is considered to be the rate limiting step, $K_{loss} \approx K_w$ [24]. In that case, the loss rate is more than 10$^{15}$ cm$^{-3}$·s$^{-1}$, which is even higher than that of the recombination of F and CF$_3$. Thus the loss of the F atom by diffusion on the wall is possibly more significant than that in the gas phase. However, when the electrodes are covered by a thick polymer film, the sticking coefficient becomes increasingly smaller, and then the loss rate of radial diffusion and reaction with other radicals in the gas phase are of the same order of magnitude. In that case the F atom loss in the gas phase is becoming increasingly important.

4 Summary and conclusion

In summary, the gas temperature, electron temperature, and fluorine atom concentration in argon/fluorocarbon plasmas have been investigated with dual-frequency sources using optical emission spectroscopy. The experimental and simulated optical emission spectra of the CF $B-X$ system are used to determine the rotational temperature, which is near 620 K using LIFBASE software for CF$_4$ plasma at 50 mTorr in
dual-frequency ($P_1=50$ W and $P_2=300$ W) capacitively coupled plasma. The electron temperature and fluorine atom concentration can be controlled by varying the discharge pressure and powers of dual-frequency CCP sources. As the pressure increases, the mean free path is shortened, and the diffusion coefficient is decreased with increasing feeding gas, the collision is enhanced, which help to increase the density of F atom. At higher HF power, the electron density is higher, hence, the production of F atoms is enhanced. In general, the electron density is independent of the LF power, thus the density of F remains nearly unchanged when the power of LF increases from 0 W to 90 W.

References


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