Studies of CF$_2$ radical and O atom in oxygen/fluorocarbon plasmas by laser-induced fluorescence

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Abstract

Laser-induced fluorescence (LIF) has been used to examine behaviors of the CF$_2$ radicals and O atoms in oxygen/fluorocarbon plasmas by utilizing a magnetic neutral loop discharge (NLD), which is characterized by the efficient plasma production around the neutral loop, ‘NL region’. It was found that, in a pure CF$_2$ plasma, the radial profile of CF$_2$ density near the NL region changes from convex to concave with increasing rf power. This implies that the NL region is a source for CF$_2$ at low rf powers and changes into a net sink at high rf powers, probably due to the excess dissociation of CF$_2$. In contrast, the O atom density in a pure O$_2$ plasma was found to be very high and increases steadily against the rf power, corresponding to the dissociation degree of more than 20%. These features, emphasized by the high dissociation efficiency of the NLD, demonstrate different behaviors of both species related with the production and loss mechanisms. In plasmas of O$_2$/CF$_2$ mixtures, it was found that the variation of O density as a function of gas composition is mostly linear, depending on the dilution factor, while that of CF$_2$ is nonlinear. This fact straightforwardly indicates that CF$_2$ is mainly lost through reaction with O$_2$ and that O is generated by the dissociation of residual O$_2$. The change in the CF$_2$ radial profile by O$_2$ addition suggested that CF$_2$ and O$_2$ react in gas-phase and that the NL region fundamentally acts as a source for CF$_2$. The results for O$_2$/CF$_2$ plasmas were also presented and understood with the same description as in O$_2$/CF$_2$ plasmas taking into account the compositional balance of C/O$_2$ and the slow surface-loss process. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

While fluorocarbon plasmas are widely used for SiO$_2$ etching in microelectronics fabrication, a full understanding of the behaviors of species in the plasma is still required to improve the etching process. Both fluorocarbon CF$_x$ ($x = 1, 2, 3$) radicals and O atoms are the most important species that correlate with polymer deposition and thus to the etch selectivity [1,2]. In particular it is deduced that the CF$_2$ radical is a precursor for the polymer and that the O atom destroys fluorocarbon species and wastes the polymer. However, their production and loss mechanisms as well as the roles in the polymer deposition have not been clearly elucidated.

Even for the most extensively studied CF$_2$ radical, a variety of possible production and loss processes have been presented to explain the complicated situation that the polymerized surface and the bulk plasma CF$_2$ density influence each other [3–10]. Spatially resolved measurements on CF$_2$ are still of major concern, and laser-induced fluorescence (LIF) [3–5,8,9] advantages this purpose. Also for the detection of the O atom, two-photon LIF [11,12] has been employed as the most reliable method. However, there have been few works on the simultaneous measurements of both species in oxygen/fluorocarbon mixtures. Most of the previous works have been performed, independently for each species, in capacitively coupled plasmas [3–6,11,13] where plasma production and plasma-surface interaction are difficult to be separated functionally, or geometrically. Concurrent measurements on advanced practical plasmas [7–9] such as inductively coupled plasmas where contributions of the gas-phase and surface processes are expected to be controlled are required.

In this work, we focus on the systematic LIF measurements of the CF$_2$ radical and O atom in the plasmas of oxygen and fluorocarbon gas mixtures employing a
magnetic neutral loop discharge (NLD) [14]. The NLD is characterized by efficient, inductively coupled plasma production in the null field. Highly dissociated oxygen (dissociation degree of >20%) and concave radial density profile of CF$_2$ radical density near the null field were characteristic to the NLD. Compositional dependence of these features in O$_2$/CF$_4$ as well as O$_2$/C$_2$F$_6$ plasmas may allow some conclusions to be drawn about the production and destruction mechanisms of both species.

2. Experimental

Experiments were performed in an NLD reactor (ULVAC), equipped with quartz windows for laser excitation and observation for the LIF measurements. The schematic of the NLD chamber (564 mm internal diameter by 150 mm high) is shown in Fig. 1(a), where a plasma emission image through the observation window is also shown. Permanent magnets were placed concentrically on the quartz plate to generate a magnetic neutral loop (NL). Plasmas were produced by introducing processing gases and applying an rf (13.56 MHz) power to the parallel loop antenna on the quartz plate. The inner side of the chamber including a grounded bottom electrode was mostly covered with alumina. Pure O$_2$, CF$_4$, C$_2$F$_6$ and their mixtures were used as the processing gas at a pressure of 30 mTorr.

CF$_2$ radical and O atom were measured using the same LIF measurement system (LaVision) with different setup, as shown in Fig. 1(b) and (c). The excitation laser beam was passed through the chamber center, aligned parallel and 50 mm below the alumina top plate. The CF$_2$ radical was detected using an intensifier-gated charge coupled device (CCD) camera through a bandpass filter (250–400 nm) with an excitation wavelength of 234.3 nm (X1A1(0,0,0) → A1B1(0,11,1)). The CF$_2$ density N(CF$_2$) was relatively measured as a function of the radial distance $r$ from LIF images of the CCD camera by subtracting the plasma emission signal and by normalizing with a Rayleigh signal. For the O atom detection, the 226 nm laser beam was focused into the chamber with a quartz lens (focal length 750 mm) so as to excite the 2p$^4$(^3P) → 2p$^3$3p(^3P) two-photon transition. The resultant LIF emission was observed with the CCD camera through a narrow band interference filter (845 nm). The O density N(O) was absolutely obtained through a calibration procedure using a photolysis of O$_2$ whose details are described in the literature [11,12].

Decay characteristics of both species in the afterglow plasmas were investigated by synchronous time-resolved measurements providing square-wave pulses (on/off time = 4.0/0.2 s) to the rf power supply and the LIF measurement system. Life time, or decay time constant $\tau$ for the CF$_2$ radical and O atom was evaluated from fundamental exponential parts of the decay curves, and were related to the diffusion constant $D$ and the reflection coefficient $R$ using the theoretical solution for surface loss process [15] given by

$$\tau = \frac{A_0^2}{D} + \frac{2l_0}{\bar{v}} 1 + R \left( 1 - \frac{1}{R} \right)\ldotp$$

Here $A_0$ is the geometrical diffusion length given by $A_0^2 = \left( \frac{1}{\pi h_0^2} + 2.405\sqrt{r_0^3} \right)^{-1}$ where $h_0$ and $r_0$ are the effective chamber height and radius, respectively, $l_0$ is the ratio of chamber volume to surface area given by $2l_0 = \left( h_0^{-1} + r_0^{-1} \right)^{-1}$, $\bar{v}$ is the mean velocity given by $\bar{v} = (8kT/mn)^{1/2}$ where $T$ is the temperature, $m$ the mass and $k$ is the Boltzmann constant, and $R = 1 - \alpha$ is the reflection coefficient where $\alpha$ is the sticking coefficient.

3. Results and discussion

3.1. Pure CF$_4$ plasma

The NLD plasma is characterized by the efficient plasma production in the null field, as demonstrated by the plasma emission image in Fig. 1(a). The plasma production region, which will be referred to as ‘NL region’ hereafter, seems to be centered somewhat inward against the NL position located at around $r \sim 140$ and 60 mm below the alumina plate. It was also confirmed by a parallel electron density
measurement and was interpreted as a result of the balance between plasma production and wall loss.

Fig. 2(a) shows the radial profiles of CF$_2$ radical density in a pure CF$_4$ plasma at various rf powers. The CF$_2$ density (at $r = 0$ mm) as a function of rf power is replotted in Fig. 2(b). Note that the profile near the NL region changes from convex to concave with increasing the rf power. This fact indicates that the NL region is a source for CF$_2$ at low rf powers and changes into a net sink at high rf powers. As for the loss mechanism at high rf powers, the destruction (excess dissociation) of CF$_2$ is deduced, emphasized by the high dissociation efficiency of the NLD. In this situation, it is deduced that the NL region is a source for CF$_2$ and the CF$_2$ density outside the NL region is brought about by the diffusion of CF$_2$, being saved from the destruction in the NL region and from the surface-loss on the chamber wall.

It is expected that the CF$_2$ density distribution in the axial direction is also concave, dominated by the NL region, as well as in the radial direction. Originating from the steady-state distribution, complicated features are observed in the temporal variation of the radial CF$_2$ density profile in the afterglow, as shown in Fig. 3(a). Replotted decay curves at chamber center ($r = 0$ mm) and near edge ($r = 240$ mm) in Fig. 3(b) suggest diffusion-induced phenomena accompanying high-order modes; they are intuitively interpreted as axial and radial redistributions, converging to a fundamental surface-loss process. Representative decay time constants $\tau$ at various pressures $p$ were evaluated from exponential parts of the fundamental mode, and were analyzed with Eq. (1).

The results are summarized in Table 1, including the results obtained below. The estimated diffusion constant $D$ is consistent with the literature [3] probably due to the inner chamber material (alumina), while the sticking coefficient $\alpha$ is somewhat small.

### 3.2. Pure O$_2$ plasma

Behaviors of the O atom in a pure O$_2$ plasma are shown in Fig. 4(a)–(c). Note that, in Fig. 4(a), the absolute value at 400 W corresponds to the high dissociation degree of 20% and steadily increases against the rf power, in contrast to the rf power dependence of the CF$_2$ radical shown in Fig. 2(b). This fact demonstrates the high dissociation efficiency of the NLD and indicates that the above-mentioned destruction process for CF$_2$ radical does not exist in the O atom reasonably. The radial distribution of O atom density shown in Fig. 4(b), obtained by shifting the lens and the CCD camera, is relatively uniform, and its decay curve in the afterglow shown in Fig. 4(c) exhibits a simple exponential decay. These features illustrate that the diffusion of O atom in a pure O$_2$ plasma is faster than that of CF$_2$ radical in a pure CF$_4$ plasma. Similar to the case of CF$_2$ radical, decay time constants $\tau$ at various pressures $p$ were evaluated and analyzed with Eq. (1). The results are listed in Table 1.
Table 1  
Summary of decay characteristics for CF₂ radical and O atom in the afterglow plasma

| Species | Thermal velocity $\bar{v}$ (cm/s) | Atmosphere gas | Diffusion constant $D_P$ (Torr cm²/s⁻¹) | Sticking coefficient $\alpha$ | Chamber radius $r_0$ (cm) | Geometry height $h_0$ (cm) | Pressure $p$ (mTorr) | Decay time constant $\tau$ (ms) | Source |
|---------|----------------------------------|----------------|----------------------------------------|-----------------------------|---------------------------|--------------------------|------------------|------------------------|--------|
| CF₂     | $3.6 \times 10^4$                | CF₄            | 50                                     | 0.02                        | 15                        | 28                       | 30               | 36                     | This work |
| CF₂/O₂  | 85/15                            | 56             | 0.03                                   |                              | 1                         | 1                       | 1                | 28                     |        |
| CF₃     | 3.5                              | 6.8            | 0.03                                   |                              | 1                         | 1                       | 1                | 222                    | Ref. [3] |
| CF₃/O₂  | 50/50                            | 60             | 0.06                                   |                              | 5.5                       | 14                       | 50               | 6                      |        |
| Ar      | 90                               | 40             | 0.02                                   |                              | 20                        | 1.5                      | 400              | 1                      | Ref. [20] |
| O₂      | 150                              | 1              | 20                                     | 1.5                        | 400                       | 1                        | 400              | 1                      | Ref. [16] |

The estimated diffusion constant $D$ is apparently larger than that of CF₂ radical. Compared with the literature [16], however, the estimated $D$ and sticking coefficient $\alpha$ is somewhat small, probably due to the differences in the evaluation method and the inner chamber material.

3.3. O₂/CF₄ Plasma

Behaviors of the CF₂ radical and O atom in O₂/CF₄ plasmas are summarized in Fig. 5. Density $N$ and decay time constant $\tau$ (in the afterglow) of CF₂ and O are indicated as a function of gas composition in O₂/CF₄ mixtures. On adding O₂ to pure CF₄, the CF₂ density $N$(CF₂) decreases nonlinearly and more drastically than expected from the dilution factor. The results simply mean that CF₂ is lost through some reaction with O₂ or O. However, from the results of similar experiments, Booth et al. [13] have speculated that the dominant reactive channel is

$$O + CF₂ \rightarrow FCO + F,$$

and that reaction with molecular oxygen

$$O₂ + CF₂ \rightarrow CO₂ + 2F$$

is very slow, referring to the estimation of bimolecular rate constants by Plumb and Ryan [17].

On the other hand, the O density $N$(O) on adding CF₄ to a pure O₂ initially increases and reaches a maximum at 15% CF₄ addition. This initial increase upon CF₄ addition is consistent with previous works [11,16] where coverage of the reactor walls with F atom (leading to elongation of O atom lifetime) and change in physical properties of plasma have been speculated. The present increase in the O atom by CF₄ addition is, however, somewhat small, compared with those reported [11,16]. This may be attributed to the reduced sticking coefficient $\alpha \sim 0.02$ in a pure O₂ plasma (associated with the inner chamber material) which would not be reduced so much even in the presence of F atom.

It should be noted that, with further CF₄ addition beyond this maximal point, the $N$(O) decreases mostly linear. This variation of the O density seems to be dependent on the dilution factor rather than the reaction with CF₂ expressed in Eq. (2). Thus, from the compositional dependence of both $N$(CF₂) and $N$(O), it is concluded that CF₂ is mainly lost through the reaction with molecular O₂ expressed in Eq. (3) and that O atom is generated by the dissociation of residual O₂.

The variations of the decay time constants $\tau$ as a function of gas composition show no sign of the gas-phase reaction between O and CF₂ in the afterglow and rather should be understood as a result of the partial pressure dependence of

![Fig. 4](image-url)  
(a) O atom density vs. RF power ($r = 0$ mm), (b) O atom density as a function of radial position (rf power = 400 W) and (c) decay curve of O atom density in the afterglow ($r = 0$ mm, rf power = 1800 W), in a pure O₂ plasma.
the diffusion constant in a mixture of gases [18], expressed by

\[
P_{AB} = P_A \frac{D_A}{D} + P_B \frac{D_B}{D}
\]

where \( D_X \) (\( X = A, B \)) are a diffusion constant in and a partial pressure of gas \( X \), and \( D_{AB} \) and \( P_{AB} \) are a diffusion constant in the mixture and a total pressure. For example, diffusion constants \( D \) and sticking coefficients \( \alpha \) for \( CF_2 \) and \( O \) at \( CF_2/O_2 = 85/15 \) plasma are presented in Table 1, assuming that \( \alpha \) of \( O \) atom is the same to that in a pure \( O_2 \) and that \( D \) of \( CF_2 \) in a pure \( O_2 \) is as in Ref. [18].

Effects of \( O_2 \) addition on the \( CF_2 \) density profiles were also investigated. The results are shown in Figs. 6(a) and (b), to be compared with Fig. 2. Fig. 6(a) shows that, in spite of the significant decrease in the magnitude with \( O_2 \) addition of 15\%, the overall profiles (the polarities of the curvature) do not change so much, compared with Fig. 2(a). Thus, it is deduced that \( CF_2 \) is lost in gas-phase uniformly, or near the NL region which dominates the profiles. Further \( O_2 \) addition, as shown in Fig. 6(b), changes the profile near the NL region from concave to convex, suggesting that the NL region changes from a net sink for \( CF_2 \) to a source. The rapid gas-phase reaction with \( O_2 \) may prevent \( CF_2 \) from diffusion and subsequent processes (reflection on the wall, destruction in the NL region) and thereby reveal that the NL region fundamentally acts as a source for \( CF_2 \).

3.4. \( O_2/CF_8 \) plasma

Experiments were also carried out in \( O_2/CF_8 \) plasmas in order to find common and chemistry dependent behaviors of \( CF_2 \) and \( O \) as to \( O_2/CF_4 \) plasmas. The radial profiles of \( CF_2 \) density in a pure \( CF_8 \) plasma and the effects of \( O_2 \) addition are shown in Figs. 7(a) and (c). Compared with a pure \( CF_4 \) plasma shown in Fig. 2(a), the radial profiles of \( CF_2 \) as a function of \( rf \) power in a pure \( CF_8 \) plasma shown in Fig. 7(a) exhibit almost the same trend that the profile near the NL region changes from convex to concave with increasing the \( rf \) power although differing in the magnitude. This means that the NL region is a source for \( CF_2 \) at low \( rf \) power and changes into a net sink at high \( rf \) power, commonly to both the \( CF_4 \) and \( CF_8 \) systems. As for the difference in the magnitude by about one order, responsible are the larger cross-section \( \sigma \) for electron-impact dissociation of \( CF_8 \) into \( CF_2 \) [19] and the slow surface loss process described below. Temporal variations of \( CF_2 \) in the afterglow of a pure \( CF_8 \) plasma were also found to be similar to those of a pure \( CF_3 \) plasma shown in Fig. 3 although the time scale was the longer. Measurements on decay time constant \( \tau \) at various pressures in a pure \( CF_8 \) plasma indicated the smaller values for diffusion constant \( D \) and sticking coefficient \( \alpha \) than in a pure \( CF_4 \) plasma, as listed in Table 1. The smaller \( D \) for \( CF_2 \) in the \( CF_8 \) system has not been reported while diffusion constants dependent on the atmosphere have been reported by several authors [18,20]. The smaller \( \alpha \) is due to the fluorocarbon film deposition on the reactor wall, as reported by many authors, and is responsible for the slow surface-loss process together with the smaller \( D \).

Effects of \( O_2 \) addition on the radial profiles of \( CF_2 \) density in \( O_2/CF_8 \) plasmas were almost the same to those in \( O_2/CF_4 \) plasmas as follows. As shown in Fig. 7(b), the overall profiles do not change with \( O_2 \) addition of 50\% in spite of the significant decrease in the magnitude, compared with Fig. 7(a). As shown in Fig. 7(c), further \( O_2 \) addition changes the profile near the NL region from concave to convex.
suggesting that the NL region changes from a net sink for CF₂ to a source. Thus, it is also deduced that CF₂ is lost in gas-phase uniformly, or near the NL region and that the NL region fundamentally acts as a source for CF₂. The results obtained in this experiment suggest that the production and destruction mechanisms of CF₂ radical are common to CF₄ and C₄F₈ systems except for the quantitative differences in the parameters (σ, D, τ) mentioned above although different surface production mechanisms have been proposed recently [4,5].

Density \( N \) and decay time constant \( τ \) (in the afterglow) of CF₂ radical and O atom as a function of gas composition in O₂/CF₄ plasmas are summarized in Fig. 8. The variations of \( τ \) of CF₂ and O as a function of gas composition should be understood as the partial pressure dependence of the diffusion constant \( D \) expressed in Eq. (4), similar to the case of O₂/CF₄ plasmas. Compared with O₂/CF₂ plasmas, the larger τs of CF₂ and O in O₂/CF₄ plasmas are attributed to smaller \( D \) in the C₄F₈ system, as presented for C₄F₈ = 50/50 plasma in Table 1. Slight deviation form this observation in τ(O) for 70–80% O₂ may be due to a drastic change in the gas composition.

As for the CF₂ density \( N(CF₂) \) in O₂/CF₄ plasmas, the nonlinear dependence of \( N(CF₂) \) also suggests that CF₂ is lost through some reaction with O₂, while its magnitude and variation as a function of gas composition are largely different from those of O₂/CF₄ plasmas. On the other hand, the O density \( N(O) \) on adding C₄F₈ to a pure O₂, initially increases, reaches a maximum at 5% C₄F₈ addition and then decreases nonlinearly. This nonlinear dependence of \( N(O) \), differently from O₂/CF₂ plasmas, appears to indicate that O atom is lost through some reaction, however, it may be corrected assuming the full dissociation of C₄F₈ and taking into account the compositional balance of C/O₂.

Fig. 9 shows the CF₂ radical and O atom density as a function of C and O₂ in O₂/CF₄ and O₂/CF₈ plasmas, replotted from Figs. 5 and 8. It is shown that, although the magnitude of CF₂ density differs by about one order between O₂/CF₄ and O₂/CF₈ plasmas, variations of CF₂ and O as a function of C and O₂ are very similar. This similarity evidences the description where CF₂ is mainly lost through reaction with O₂ and O is generated by the dissociation of residual O₂, in both the O₂/CF₄ and O₂/CF₈ plasmas. Thus, the behaviors of CF₂ and O in O₂/CF₄ plasmas are understood with the same description as in O₂/CF₄ plasmas taking into account the compositional balance of C/O₂ and the slow surface loss process.

4. Summary

The application of spatially and temporally resolved LIF technique to the oxygen/fluorocarbon plasmas utilizing the
NLD can provide valuable insight into the production and loss mechanisms of CF$_2$ radical and O atom. The major points of this study can be listed as follows:

1. The radial profiles of CF$_2$ radical density near the NL region changes from convex to concave with increasing the rf power. This means the NL region is a source for CF$_2$ at low rf power and changes into a net sink at high rf power, probably due to the excess dissociation of CF$_2$.

2. The O atom density at 400 W corresponds to the high dissociation degree of 20% and steadily increases against the rf power, demonstrating the high dissociation efficiency of the NLD.

3. In O$_2$/CF$_4$ plasmas, the variation of O density as a function of the partial pressure is mostly linear while that of CF$_2$ is nonlinear. This means that CF$_2$ is lost through some reaction with O$_2$ and that O is generated by the dissociation of residual O$_2$.

4. The variation of decay time constants shows no sign of gas-phase reaction between O and CF$_2$, and can be explained by the partial pressure dependence of the diffusion constant.

5. The overall CF$_2$ density profiles do not change so much with O$_2$ addition of 15%. It is deduced that CF$_2$ is lost in gas-phase uniformly, or near the NL region which dominates the profiles. Further O$_2$ addition reveals that the NL region fundamentally acts as a source for CF$_2$.

6. The results for O$_2$/CF$_4$ plasmas are also understood with the same description taking into account the compositional balance of C/O$_2$ and the slow surface-loss process.

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