

# Surface production of CF, CF<sub>2</sub>, and C<sub>2</sub> radicals in high-density CF<sub>4</sub>/H<sub>2</sub> plasmas

K. Sasaki,<sup>a)</sup> H. Furukawa, and K. Kadota  
*Department of Electronics, Nagoya University, Nagoya 464-8603, Japan*

C. Suzuki  
*National Institute for Fusion Science, Toki 509-5292, Japan*

(Received 24 April 2000; accepted for publication 30 August 2000)

Surface production of CF, CF<sub>2</sub>, and C<sub>2</sub> radicals in high-density CF<sub>4</sub>/H<sub>2</sub> plasmas was examined using laser-induced fluorescence spectroscopy. No significant amount of surface production was observed in pure CF<sub>4</sub> plasmas. The addition of H<sub>2</sub> into CF<sub>4</sub> plasmas enhanced the surface production of CF<sub>x</sub> and C<sub>2</sub> from fluorocarbon film deposited on the chamber wall. The characteristics of the surface production in cw discharges are reported, in comparison with surface production in pulsed discharges. In addition, it has been found that the surface production rates are determined not by the partial pressure but by the flow rate of H<sub>2</sub>, suggesting the significant consumption of feedstock H<sub>2</sub> in discharges. The surface production of CF<sub>x</sub> and C<sub>2</sub> indicates that these radicals are not the precursors for the deposition of fluorocarbon film in the CF<sub>4</sub>/H<sub>2</sub> plasma. The deposition mechanism of fluorocarbon film in the CF<sub>4</sub>/H<sub>2</sub> plasma is discussed, taking into account the surface production of CF<sub>x</sub> and C<sub>2</sub>. © 2000 American Institute of Physics. [S0021-8979(00)04723-X]

## I. INTRODUCTION

Recently, surface production of fluorocarbon radicals (CF<sub>x</sub>) has attracted special interest from the viewpoint of controlling radical densities in fluorocarbon plasmas.<sup>1-14</sup> The control of radical densities is an important issue when fluorocarbon plasmas are applied to material processing such as dry etching of SiO<sub>2</sub> and deposition of fluorinated amorphous carbon film (fluorocarbon film). The dry etching of a SiO<sub>2</sub> layer to provide contact holes is a problematic process in the fabrication of semiconductor devices. The fluorinated amorphous carbon film is a candidate for the insulation layer with a low dielectric constant in next-generation ultralarge-scale integrated circuits.

Many researchers have pointed out the importance of surface chemistry on the kinetics of gas-phase neutral radicals. Surface production of radicals is a dramatic phenomenon which significantly affects gas-phase radical densities. We have observed hollow spatial distributions (the densities near the chamber wall are higher than those in the plasma column) for the densities of CF, CF<sub>2</sub>, C<sub>2</sub>, and C<sub>3</sub> radicals in helicon-wave C<sub>4</sub>F<sub>8</sub> plasmas.<sup>1-6</sup> The hollow density distribution is direct evidence that these radicals are produced from the surface of the chamber wall. In a parallel-plate rf plasma source, Haverlag and coworkers observed that CF, CF<sub>2</sub>, and CF<sub>3</sub> radicals have maximum densities adjacent to the powered electrode,<sup>7-9</sup> indicating the production of CF<sub>x</sub> from the surface of the powered electrode. Booth and coworkers also observed surface production of CF and CF<sub>2</sub> in parallel-plate rf CF<sub>4</sub> plasmas.<sup>10-12</sup> They showed that the surface production is enhanced when the powered electrode is covered with a Si substrate. In addition, Mackie and co-workers clearly

showed the surface production of CF<sub>2</sub> by plasma beam-surface experiments.<sup>13,14</sup>

In the present work, we have investigated surface production of CF, CF<sub>2</sub>, and C<sub>2</sub> radicals in CF<sub>4</sub> plasmas with the addition of H<sub>2</sub>. In a previous letter,<sup>5</sup> we reported that surface production of CF and CF<sub>2</sub> is enhanced by the addition of H<sub>2</sub> into pulsed CF<sub>4</sub> plasma. In the present article, we report the characteristics of the surface production of CF, CF<sub>2</sub>, and C<sub>2</sub> in high-density CF<sub>4</sub>/H<sub>2</sub> plasma in detail. The surface production of CF and CF<sub>2</sub> in cw discharges is reported, in comparison with the surface production in pulsed discharge. In addition, it has been found that the important parameter that induces the surface production is not the partial pressure but the flow rate of H<sub>2</sub>.

The observation of the surface production of CF<sub>x</sub> radicals brings up a question on the deposition mechanism of fluorocarbon film. It was previously believed that the precursor for the deposition of fluorocarbon film is CF<sub>x</sub> radicals. However, according to the present experimental results, CF<sub>x</sub> radicals are not the precursor since they are produced from the surface. In the present article, a brief discussion is given on the deposition mechanism of fluorocarbon film in CF<sub>4</sub>/H<sub>2</sub> plasma.

## II. EXPERIMENT

The details of the experimental apparatus have been described in a previous paper.<sup>5</sup> Briefly, a linear machine with a uniform magnetic field of 1 kG along the cylindrical axis of the vacuum chamber was used in the experiment. The vacuum chamber was composed of a Pyrex glass tube of 9 cm diameter and two stainless-steel rectangular chambers of 20×20×10 cm. A helical antenna was wound around a quartz glass tube of 3 cm diameter, which was attached to one of the rectangular chambers. A slender plasma column of

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: sasaki@nuee.nagoya-u.ac.jp

3 cm diameter, which was confined radially by the external magnetic field, was produced by applying rf power at 13.56 MHz to the helical antenna. The electron density of the plasma column was measured using a microwave interferometer. The rf power was 300 W and 1 kW for cw and pulsed operations, respectively. In the pulsed discharge, the repetition rate and the discharge duration of plasma production were 5 Hz and 10 ms, respectively. The pressure of CF<sub>4</sub> was fixed at 5 mTorr with a flow rate of 4.4 ccm. The partial pressure of H<sub>2</sub> was varied by changing the flow rate. It is noted here that the partial pressure and the percent concentration shown below denote the amount of H<sub>2</sub> filled in the chamber before discharges. The real partial pressure of H<sub>2</sub> during discharges may be significantly different from the inputted one because of the consumption.

Laser-induced fluorescence (LIF) spectroscopy was adopted for the measurements of CF, CF<sub>2</sub>, and C<sub>2</sub> radical densities.<sup>1,4</sup> The LIF signals from CF and CF<sub>2</sub> were calibrated to obtain the absolute densities.<sup>15</sup> The LIF measurement was carried out in the rectangular chamber at a distance of approximately 10 cm from the end of the helical antenna. Tunable laser pulses yielded from a dye laser or an optical parametric oscillator were launched into the plasma, and the LIF emission was detected using a monochromator and a photomultiplier tube. The spatial (radial) distributions of the radical densities along the path of the dye laser beam were obtained by changing the position of observing LIF emission. Although the wall of the rectangular chamber was located  $\pm 10$  cm from the center of the plasma column, the size of the observation port restricted the measurements to a region of  $\pm 7$  cm.

When the partial pressure of H<sub>2</sub> was changed, the CF, CF<sub>2</sub>, and C<sub>2</sub> densities varied slowly for a long time, suggesting a slow change in surface chemistry with time. The experimental data reported in the present article were obtained after sufficient seasoning discharges at each H<sub>2</sub> pressure.

### III. RESULTS AND DISCUSSION

#### A. Surface production of CF and CF<sub>2</sub> in pulsed discharges

The characteristics of surface production of CF and CF<sub>2</sub> in pulsed discharges have been reported in a previous letter.<sup>5</sup> In short, hollow spatial (radial) distributions (the radical densities in the high-density plasma column were lower than those in the outside region) were observed for the CF and CF<sub>2</sub> densities, indicating the surface production of these radicals from fluorocarbon film deposited on the chamber wall.<sup>1,2</sup> The gas-phase densities of CF and CF<sub>2</sub> were strongly dependent on the H<sub>2</sub> partial pressure. In this experiment, the electron density of the plasma column and the partial pressure of CF<sub>4</sub> remained constant when the H<sub>2</sub> partial pressure was varied; therefore the variations in the CF and CF<sub>2</sub> densities were not due to the change in the dissociation rate of feedstock CF<sub>4</sub> by electron impact. We evaluated the surface production rates of CF and CF<sub>2</sub> from their inward diffusion fluxes (toward the plasma column from the outside region), which was calculated from the gradient of the hollow-shape distributions of the radical densities using Fick's law. As a

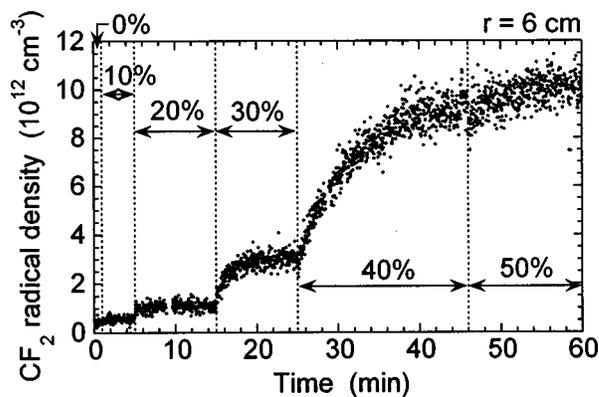


FIG. 1. Temporal variation of the CF<sub>2</sub> density at a distance of 6 cm from the center of the plasma column, when the partial percentage of H<sub>2</sub> was changed from 0% to 50%.

result, linear relationships were found between the gas-phase radical densities and their inward diffusion fluxes. This indicates that the gas-phase CF and CF<sub>2</sub> densities are determined not by the dissociation of feedstock CF<sub>4</sub> but by their surface production. Numerical comparison between the gas-phase and surface production rates of CF and CF<sub>2</sub> supports the dominance of the surface productions over the gas-phase ones due to electron impact dissociation of feedstock CF<sub>4</sub>.

#### B. Surface production of CF and CF<sub>2</sub> in cw discharge

Experiments similar to those conducted under pulsed discharge were repeated in cw discharges at an rf power of 300 W. In order to improve the signal-to-noise ratio, the rf power was terminated for a short period (50  $\mu$ s) during which the LIF measurement was carried out.<sup>1</sup> Since the repetition frequency of the measurement was 5 Hz and the time constants for diffusion and chemical reactions of CF, CF<sub>2</sub>, and C<sub>2</sub> were much longer than 50  $\mu$ s, the short-time termination of the rf power never affected the densities and the distributions of radicals.

Figure 1 shows the temporal variation of CF<sub>2</sub> density in the outside region ( $r=6$  cm) with changing partial percentage of H<sub>2</sub>. Before starting the experiment, the chamber wall was cleaned (fluorocarbon film on the chamber wall was removed) sufficiently using an oxygen discharge. In the present plasma source, the electron density was almost independent of the H<sub>2</sub> partial pressure. For an rf power of 300 W and a CF<sub>4</sub> pressure of 5 mTorr, the electron density of the plasma column, measured using a microwave interferometer, was kept at  $\sim 1 \times 10^{11}$  cm<sup>-3</sup>. As shown in Fig. 1, the addition of H<sub>2</sub> resulted in a considerable increase in the CF<sub>2</sub> density. Slow variations in the CF<sub>2</sub> density were observed immediately after the change in the partial pressure of H<sub>2</sub>.

Figure 2 shows the CF and CF<sub>2</sub> radical densities at the center of the plasma column as a function of the H<sub>2</sub> percentage. The increases in the CF and CF<sub>2</sub> densities were marked for H<sub>2</sub> percentages of 30%–40%, and were saturated at an H<sub>2</sub> percentage of 50%. In the experiment, the partial pressure of CF<sub>4</sub> was fixed at 5 mTorr and the electron density remained almost constant when the H<sub>2</sub> partial pressure was

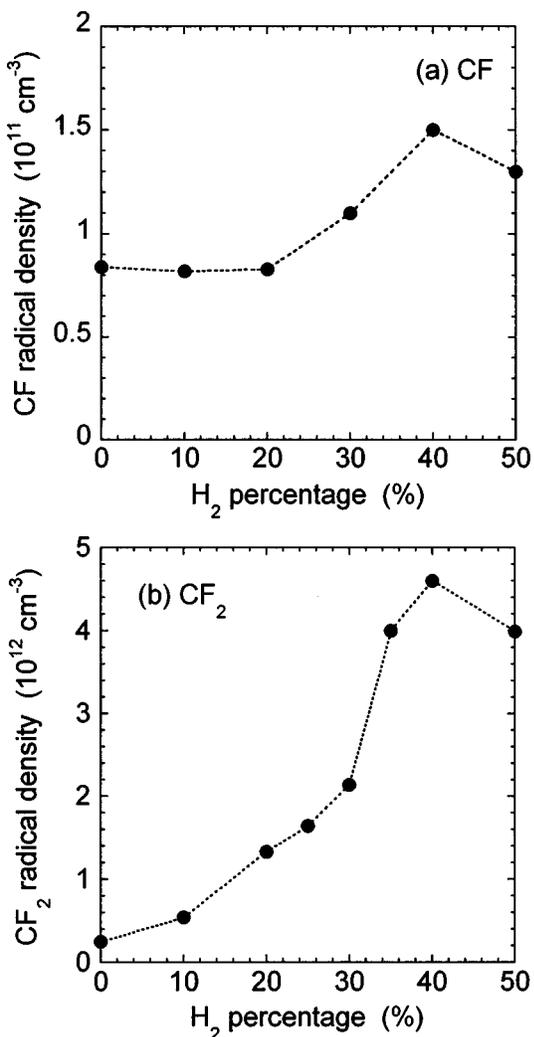


FIG. 2. Densities of: (a) CF and (b)  $\text{CF}_2$  at the center of the plasma column as a function of the partial percentage of  $\text{H}_2$ .

varied. Therefore, the variations of the CF and  $\text{CF}_2$  densities shown in Fig. 2 are not due to the change in the dissociation rate of feedstock  $\text{CF}_4$  by electron impact.

The spatial (radial) distributions of the CF and  $\text{CF}_2$  densities are shown in Fig. 3 for  $\text{H}_2$  percentages of 10%, 30%, and 50%. The plasma column was localized within  $-1.5 \leq r \leq 1.5$  cm by the external magnetic field, and the wall of the rectangular chamber was located at  $r = \pm 10$  cm. As shown in Fig. 3(a), the CF density had hill-type radial distributions for  $\text{H}_2$  percentages lower than 30%. The hill-type density distribution indicates the following production and loss mechanism of CF radicals. CF radicals are produced in the plasma column by electron impact dissociation. They diffuse toward the outside region and adsorb on the surface of the chamber wall. In other words, for low  $\text{H}_2$  partial percentages, the source and the sink of CF are the plasma column and the chamber wall, respectively. The peaked distribution shown in Fig. 3(a) suggests that the surface loss probability  $\alpha$  of CF radicals is large, roughly on the order of  $10^{-1}$ . This surface loss probability is evaluated from the density distribution using an equation  $1/\lambda = v\alpha/2D(2-\alpha)$ ,<sup>16</sup> where  $\lambda$  is the linear extrapolation length (the CF density extrapolates to

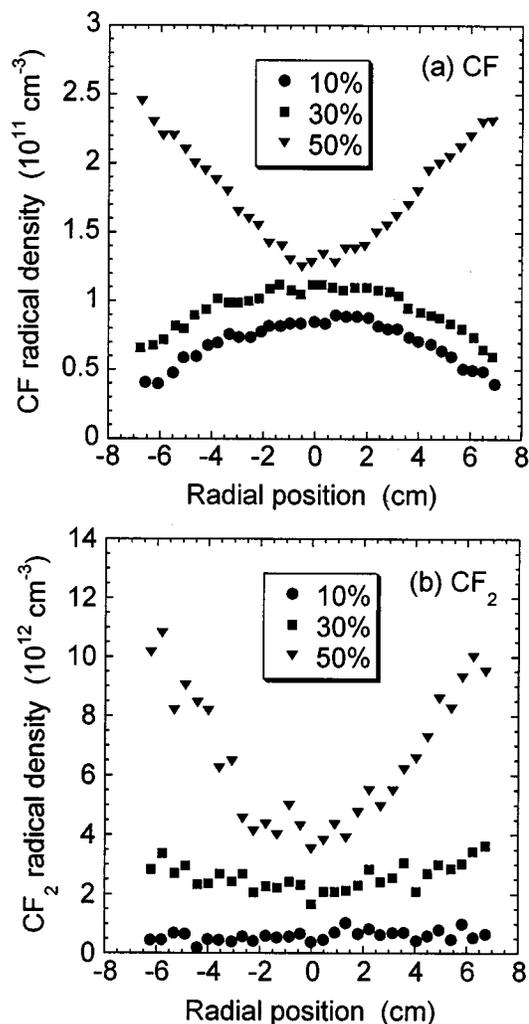


FIG. 3. Radial distributions of the: (a) CF and (b)  $\text{CF}_2$  densities at  $\text{H}_2$  percentages of 10%, 30%, and 50%.

zero at a distance  $\lambda$  beyond the chamber wall),  $v$  is the average speed of CF radicals, and  $D$  is the diffusion coefficient of CF radicals.<sup>17</sup> The surface loss probability on the order of  $10^{-1}$  is consistent with values reported in the literature.<sup>18-20</sup>

On the other hand, at an  $\text{H}_2$  percentage of 40%, a dramatic change was observed in the radial distribution of the CF density. For  $\text{H}_2$  percentages higher than 40%, the radial distributions had hollow shapes, namely, the CF densities in the outside region were higher than those in the plasma column. According to the hollow distribution, the production and loss mechanisms of CF radicals for  $\text{H}_2$  percentages higher than 40% are diametrically opposite to those for  $\text{H}_2$  percentages lower than 30%. For  $\text{H}_2$  percentages higher than 40%, the plasma column is the sink of CF radicals, and the source of CF is located in the outside region (CF radicals are mainly produced in the outside region). CF radicals produced in the outside region are transported toward the plasma column by diffusion. Electron impact processes play the role of the sink of CF in the plasma column, while the source of CF in the outside region is considered to be the surface of the chamber wall covered with fluorocarbon film.<sup>1,2</sup> Accord-

ingly, the hollow distribution of CF is direct evidence of the surface production of CF.

The radial distribution of the CF<sub>2</sub> radical density was nearly uniform for H<sub>2</sub> percentages lower than 10%, as shown in Fig. 3(b). The uniform distribution indicates that the production and loss rates of CF<sub>2</sub> on the chamber wall are negligible. At an H<sub>2</sub> percentage of 30%, the radial distribution of the CF<sub>2</sub> density was slightly hollow. When the H<sub>2</sub> percentage was higher than 40%, hollow radial distributions with high aspect ratios were observed. Therefore, for H<sub>2</sub> percentages higher than 40%, the production and loss mechanisms of CF<sub>2</sub> are similar to those of CF, namely, CF<sub>2</sub> radicals are mainly produced from the fluorocarbon film on the chamber wall and are transported toward the plasma column by diffusion. CF<sub>2</sub> radicals are lost in the plasma column due to electron impact processes. In other words, the source and the sink of CF<sub>2</sub> are the fluorocarbon film on the chamber wall and the plasma column, respectively, when the H<sub>2</sub> percentage is higher than 40%.

The importance of electron impact processes for the loss of CF<sub>x</sub> in the plasma column is understood by considering reaction rate coefficients. The rate coefficients for electron impact ionization of CF and CF<sub>2</sub> are on the order of 10<sup>-9</sup> cm<sup>3</sup>/s for an electron temperature of 6 eV,<sup>21</sup> which corresponds to the loss frequency on the order of 10<sup>2</sup> s<sup>-1</sup> for an electron density of 1 × 10<sup>11</sup> cm<sup>-3</sup>. The frequency of electron impact dissociation is expected to be on similar order. Although the rate coefficients for dissociative electron attachment to CF and CF<sub>2</sub> are unknown to date, there is a possibility that they are much larger than the rate coefficient for dissociative electron attachment to CF<sub>4</sub> (on the order of 10<sup>-11</sup> cm<sup>3</sup>/s for an electron temperature of 6 eV).<sup>22</sup> On the other hand, polymerization reaction among CF<sub>x</sub> radicals, which is another possibility for the loss of CF<sub>x</sub>, has a rate coefficient less than 1 × 10<sup>-12</sup> cm<sup>3</sup>/s,<sup>23-25</sup> corresponding to the loss frequency of ~10<sup>0</sup> s<sup>-1</sup> for a CF<sub>x</sub> density of 5 × 10<sup>12</sup> cm<sup>-3</sup>. The pumping loss of CF<sub>x</sub> is negligible in the present experiment since the residence time of neutral species is on the order of 10<sup>0</sup> s. Accordingly, as described in previous papers,<sup>1,2,5</sup> the density of CF<sub>x</sub> at the center of the plasma column is determined by a balance equation

$$\frac{\partial n_{\text{CF}_x}}{\partial t} = k_p^x n_{\text{CF}_4} n_e - \nabla \cdot \Gamma_{\text{CF}_x} - k_L^x n_{\text{CF}_x} n_e = 0, \quad (1)$$

or

$$n_{\text{CF}_x} = - \frac{\nabla \cdot \Gamma_{\text{CF}_x}}{k_L^x n_e} + \frac{k_p^x}{k_L^x} n_{\text{CF}_4}, \quad (2)$$

where  $n_{\text{CF}_x}$  and  $n_{\text{CF}_4}$  denote the densities of CF<sub>x</sub> ( $x=1,2$ ) and CF<sub>4</sub>, respectively,  $n_e$  is the electron density,  $k_p^x$  is the reaction rate coefficient for the production of CF<sub>x</sub> from CF<sub>4</sub> by electron impact,  $k_L^x$  is the reaction rate coefficient for the loss of CF<sub>x</sub> due to electron impact processes, and  $\Gamma_{\text{CF}_x}$  denotes the diffusion flux of CF<sub>x</sub> radicals. The terms  $k_p^x n_{\text{CF}_4} n_e$  and  $k_L^x n_{\text{CF}_x} n_e$  represent the production and loss rates of CF<sub>x</sub> in the gas phase, respectively, while the term  $\nabla \cdot \Gamma_{\text{CF}_x}$  repre-

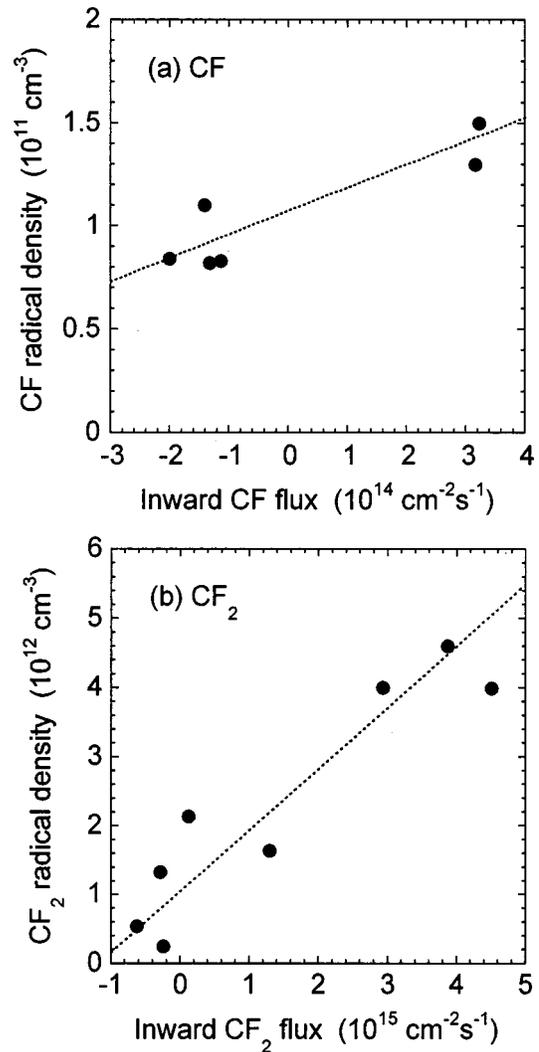


FIG. 4. Relationships between the: (a) CF and (b) CF<sub>2</sub> densities at the center of the plasma column and their inward diffusion fluxes.

sents the diffusion of CF<sub>x</sub>. The diffusion flux  $\Gamma_{\text{CF}_x}$  can be evaluated from the slope of the density distribution using Fick's law

$$\Gamma_{\text{CF}_x} = -D_{\text{CF}_x} \nabla n_{\text{CF}_x}, \quad (3)$$

where  $D_{\text{CF}_x}$  is the diffusion coefficient for CF<sub>x</sub>. In the evaluation, the diffusion coefficients determined by Horikoshi *et al.* [ $D_{\text{CF}} \cdot P = 85$  cm<sup>2</sup> Torr/s ( $P$  is the gas pressure)]<sup>17</sup> and Suzuki *et al.* ( $D_{\text{CF}_2} \cdot P = 30$  cm<sup>2</sup> Torr/s)<sup>19</sup> were employed, and the density gradient at  $r = \pm(2-4)$  cm was used for  $\nabla n_{\text{CF}_x}$ . When CF<sub>x</sub> has a hollow density distribution, the direction of  $\Gamma_{\text{CF}_x}$  is inward (toward the plasma column from the outside region).

When a cylinder of infinite length is assumed,  $\nabla \cdot \Gamma_{\text{CF}_x} \approx \Gamma_{\text{CF}_x} \cdot (S/V) \approx \Gamma_{\text{CF}_x} \cdot (2/a)$  with  $S$ ,  $V$ , and  $a$  being the surface area, volume, and radius of the plasma column, respectively. Therefore, according to Eq. (2), a linear relationship should be found between  $n_{\text{CF}_x}$  and  $\Gamma_{\text{CF}_x}$  since  $n_e$  and  $n_{\text{CF}_4}$  are constant in the present experiment. Figure 4 shows the experimental relationships between  $n_{\text{CF}_x}$  and  $\Gamma_{\text{CF}_x}$ . The nega-

tive  $\Gamma_{CF_x}$  indicates that the diffusion flux is outward from the plasma column. Since a jump from a hill-type distribution to a hollow one was observed for the CF density at an  $H_2$  percentage of 40%, the data points in Fig. 4(a) are separated into two localized regions. However, linear relationships are found experimentally between the densities of CF and  $CF_2$  and their diffusion fluxes. This result supports the validity of the reaction and transport mechanisms of  $CF_x$  radicals represented by Eq. (1).

The properties of the surface production of CF and  $CF_2$  in cw discharges are essentially similar to those in pulsed discharges reported previously.<sup>5</sup> In both cw and pulsed discharges, the surface production of CF and  $CF_2$  is enhanced by the addition of a large amount of  $H_2$  into  $CF_4$  plasmas. Although the overall characteristics are essentially similar, we can find two differences in the experimental results observed in cw and pulse discharges. One is the lower CF radical density in cw discharges, and the other difference is that hill-type density distributions are never observed in pulsed discharges. These differences are probably attributed to the following reasons. One reason is the difference in the electron density. The cw and pulsed discharges are operated at rf powers of 0.3 and 1 kW, respectively, resulting in the lower electron density in cw discharges. In addition to the difference in the electron density, the enhancement of the surface production due to time-modulation effect in pulsed discharges is responsible to the difference in the experimental results observed in cw and pulsed discharges. As reported in a previous article,<sup>1</sup> in the afterglow phase of pulsed discharges, the surface production of CF and  $CF_2$  stops and radicals are lost due to diffusion (adsorption) to the chamber wall. The adsorbed radicals return to the gas phase during the discharge phase, which is the mechanism of the enhancement of the surface production in the discharge phase of pulsed discharges.<sup>1</sup> In cw discharges, the enhancement of the surface production due to the time-modulation effect disappears, resulting in the lower CF density and the hill-type density distributions observed at low  $H_2$  partial pressures. In other words, the enhancement of the surface production observed in cw discharges is due purely to a chemical effect.

### C. Surface production of $C_2$ radicals

Figure 5 shows the  $C_2$  density at the center of the plasma column as a function of the  $H_2$  partial percentage. The data were obtained in pulsed  $CF_4/H_2$  plasmas with a rf power of 1 kW (the condition employed in the experiment reported in a previous letter<sup>5</sup>). The  $C_2$  density was strongly dependent on the  $H_2$  percentage, and high  $C_2$  densities were observed for  $H_2$  percentages of 25%–30%.

Radial distributions of the  $C_2$  density are shown in Fig. 6 for  $H_2$  percentages of 10%, 28%, and 40%. For  $H_2$  percentages lower than 25%, radial distributions of the  $C_2$  density were roughly uniform, while for  $H_2$  percentages higher than 25%, hollow radial distributions were observed. It is obvious that  $C_2$  is not produced from  $CF_4$  by electron impact processes. Therefore, the hollow distributions shown in Fig. 6 indicate that not only CF and  $CF_2$  but also  $C_2$  radicals are produced from fluorocarbon film deposited on the chamber

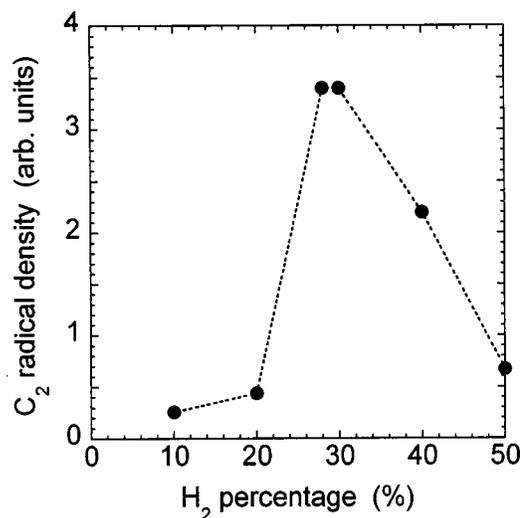


FIG. 5. Density of  $C_2$  at the center of the plasma column as a function of the partial percentage of  $H_2$ .

wall. We observed that the  $C_2$  density had peaks at around  $r = \pm 5$  cm, suggesting that the principal source of  $C_2$  was the surface of the Pyrex glass tube.

The inward diffusion flux of  $C_2$  was evaluated from the slope of the density distribution using Fick's law. Figure 7 shows the relationship between the  $C_2$  density at the center and the inward diffusion flux. As shown in the figure, a proportional relationship is found between the density and the inward flux of  $C_2$ . The curve passes through the origin of the figure, indicating that the production of  $C_2$  in the gas phase [corresponding to the second term on the right-hand side of Eq. (2)] is negligible.

The characteristics of the surface production of  $C_2$  in  $CF_4$  plasmas with the addition of a large amount of  $H_2$  were similar to those in  $C_4F_8$  plasmas reported in a previous article.<sup>4</sup> The  $C_2$  density was higher for a higher plasma density, suggesting the importance of ion bombardment in the surface production of  $C_2$ . Since the plasma density in the cw

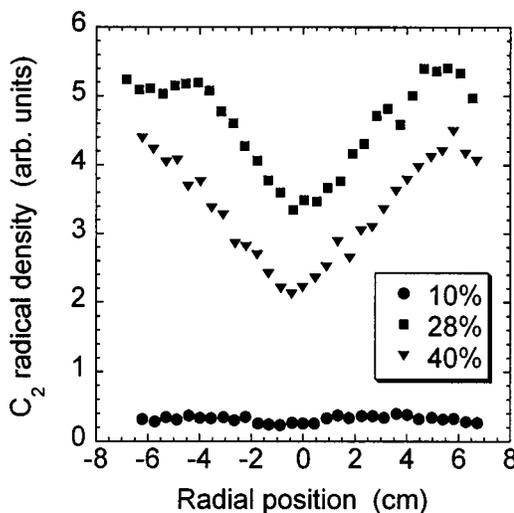


FIG. 6. Radial distribution of the  $C_2$  density at  $H_2$  percentages of 10%, 28%, and 40%.

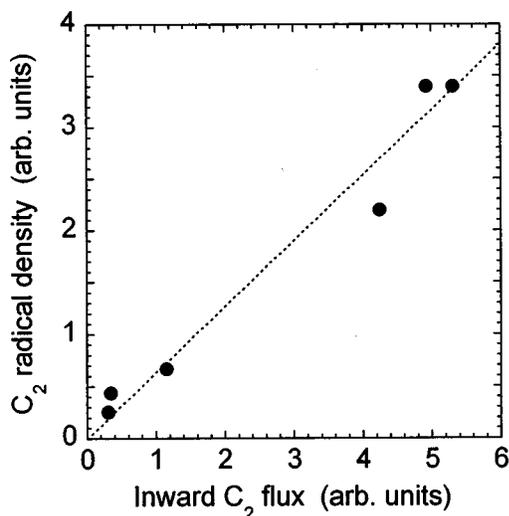


FIG. 7. Relationship between the  $C_2$  density at the center of the plasma column and its inward diffusion flux.

discharge at an rf power of 300 W was much lower than that in the pulsed discharge at an rf power of 1 kW, the  $C_2$  density in the cw discharge reported in the previous section was negligible.

#### D. Effect of the flow rate of $H_2$

The experimental results described above are summarized as a function of the partial pressure of  $H_2$  admixed into  $CF_4$  plasmas. However, we have found that it is not the partial pressure but the flow rate of  $H_2$  that is the important parameter for the enhancement of the surface production of CF,  $CF_2$ , and  $C_2$ .

The pumping system used in the present experiment was composed of a turbomolecular pump and an oil rotary pump. In this system, the overall pumping speed for  $H_2$  was strongly dependent on the pumping speed of the oil rotary pump, while the pumping speed for  $CF_4$  was determined only by the conductance at a gate valve installed in front of the turbomolecular pump. Hence, we were able to change the pumping speed of  $H_2$  by using three different oil rotary pumps having various pumping speeds, while keeping the pumping speed of  $CF_4$  at a fixed value.

Figure 8 shows the  $C_2$  radical density observed in pulsed discharges as a function of the partial pressure of  $H_2$ . The partial pressure of  $CF_4$  and the rf power were fixed at 5 mTorr and 1 kW, respectively. Different pumping speeds of 7.8, 17, and 42 l/s for  $H_2$  were obtained by changing oil rotary pumps. The experimental results described in the above sections were obtained at a pumping speed of 17 l/s. As seen in Fig. 8, the  $C_2$  density was not determined by the partial pressure of  $H_2$ . The enhancement of the surface production of  $C_2$  was achieved at a lower  $H_2$  partial pressure when a faster pumping speed for  $H_2$  was employed.

The same experimental result is plotted in Fig. 9 as a function of the flow rate of  $H_2$ . It is clear that the enhancement of the surface production of  $C_2$  was achieved at an  $H_2$  flow rate of  $\sim 3$  ccm for all pumping speeds. This result indicates that not the partial pressure of  $H_2$  before discharge

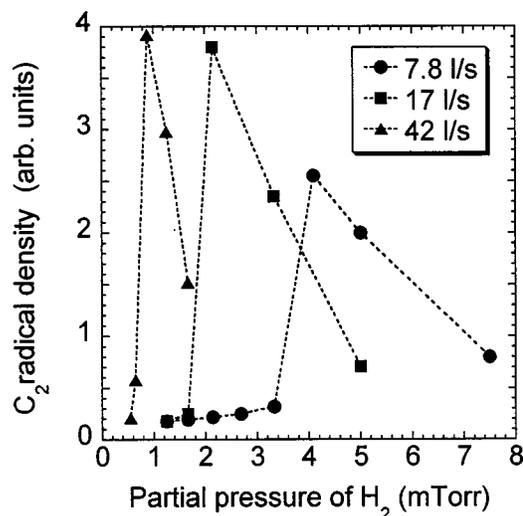


FIG. 8.  $C_2$  density observed at three different pumping speeds for  $H_2$ , as a function of the partial pressure of  $H_2$ .

but the flow rate of  $H_2$  during discharge is the important parameter in the enhancement of the surface production. Although further investigation is necessary to understand the mechanism of this experimental result, it is concluded from the experimental result that feedstock  $H_2$  is significantly consumed in discharges.

#### E. Deposition mechanism of fluorocarbon film

The present experimental results showing the surface production of CF,  $CF_2$ , and  $C_2$  bring up a question on the deposition mechanism of fluorocarbon film in  $CF_4/H_2$  plasmas. Conventionally, it is believed that the precursor for the deposition of fluorocarbon film is  $CF_x$  radicals. However, according to the present experimental results, when a large amount of  $H_2$  is admixed into  $CF_4$  plasmas, CF and  $CF_2$  are not the precursors for deposition since they are produced

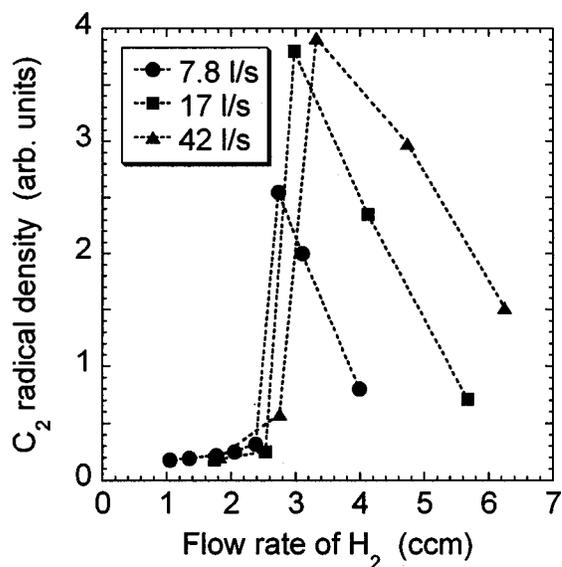


FIG. 9.  $C_2$  density observed at three different pumping speeds for  $H_2$ , as a function of the flow rate of  $H_2$ .

from the surface. Unfortunately we have no diagnostics for  $\text{CF}_3$ . However, considering experimental results reported by Haverlag and co-workers,<sup>7-9</sup> it may be reasonable to assume that  $\text{CF}_3$  radicals are also produced from the surface when the surface production of CF and  $\text{CF}_2$  is observed. Therefore, unknown species other than  $\text{CF}_x$  should contribute to the deposition of fluorocarbon film, when a large amount of  $\text{H}_2$  is admixed into  $\text{CF}_4$  plasmas.

Booth *et al.*, Stoffels *et al.*, and our group have proposed higher-order radicals  $\text{C}_x\text{F}_y$ , which contain multiple carbon atoms in a molecule, as the precursor for the deposition of fluorocarbon film.<sup>2,11,26</sup> Stoffels *et al.*<sup>26</sup> and Schwarzenbach *et al.*<sup>27</sup> have observed various polymerized molecules in  $\text{CF}_4$  plasmas by mass spectrometry. We have recently shown a good correlation between the deposition rate of fluorocarbon film and the densities of higher-order molecules in  $\text{C}_4\text{F}_8$  plasmas.<sup>28</sup> Cunge and Booth have suggested that a fluorine-poor condition in the gas phase triggers the polymerization of  $\text{CF}_x$  (the production of  $\text{C}_x\text{F}_y$ ).<sup>11</sup> The fluorine-poor condition is realized in the present  $\text{CF}_4/\text{H}_2$  plasma when a large amount of  $\text{H}_2$  is added.<sup>29</sup> However, the gas pressure in the present experiment ( $\leq 10$  mTorr) is much lower than that in the experiment carried out by Cunge and Booth. The efficiency of gas-phase polymerization may be significantly lower in low-pressure plasmas since polymerization reactions are three-body reactions in nature. Accordingly, the deposition mechanism of fluorocarbon film under the present experimental conditions is not fully understood. Further investigation is necessary to understand the gas-phase polymerization and the plasma-surface interaction in fluorocarbon plasmas.

#### IV. CONCLUSIONS

We have examined the characteristics of surface production of CF,  $\text{CF}_2$ , and  $\text{C}_2$  radicals in high-density  $\text{CF}_4/\text{H}_2$  plasmas. As a result, it has been shown that the addition of  $\text{H}_2$  enhances the surface production from the fluorocarbon film deposited on the chamber wall. The gas-phase radical densities have been explained in terms of a simple reaction-transport model. It has also been shown that the important parameter that induces the surface production is not the partial pressure of  $\text{H}_2$  before discharge but the flow rate of  $\text{H}_2$  during discharge, suggesting the significant consumption of feedstock  $\text{H}_2$ . The observation of the surface production of  $\text{CF}_x$  radicals raises a question as to the deposition mechanism of fluorocarbon film in  $\text{CF}_4/\text{H}_2$  plasmas; further investigation is necessary to understand the gas-phase polymerization and the plasma-surface interaction in fluorocarbon plasmas.

- <sup>1</sup>C. Suzuki, K. Sasaki, and K. Kadota, *J. Appl. Phys.* **82**, 5321 (1997).
- <sup>2</sup>C. Suzuki, K. Sasaki, and K. Kadota, *J. Vac. Sci. Technol. A* **16**, 2222 (1998).
- <sup>3</sup>C. Suzuki, K. Sasaki, and K. Kadota, *Jpn. J. Appl. Phys., Part 1* **37**, 5763 (1998).
- <sup>4</sup>C. Suzuki, K. Sasaki, and K. Kadota, *Jpn. J. Appl. Phys., Part 1* **38**, 6896 (1999).
- <sup>5</sup>K. Sasaki, H. Furukawa, C. Suzuki, and K. Kadota, *Jpn. J. Appl. Phys., Part 2* **38**, L954 (1999).
- <sup>6</sup>K. Takizawa, K. Sasaki, and K. Kadota, *Proceedings of the 17th Symposium on Plasma Processing*, edited by H. Sugai (The Japan Society of Applied Physics, Nagasaki, Japan, 2000), p. 491.
- <sup>7</sup>M. Haverlag, E. Stoffels, W. W. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *J. Vac. Sci. Technol. A* **12**, 3102 (1994).
- <sup>8</sup>M. Haverlag, W. W. Stoffels, E. Stoffels, J. H. W. G. den Boer, G. M. W. Kroesen, and F. J. de Hoog, *Plasma Sources Sci. Technol.* **4**, 260 (1995).
- <sup>9</sup>M. Haverlag, E. Stoffels, W. W. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *J. Vac. Sci. Technol. A* **14**, 384 (1996).
- <sup>10</sup>J. P. Booth, G. Cunge, P. Chabert, and N. Sadeghi, *J. Appl. Phys.* **85**, 3097 (1999).
- <sup>11</sup>G. Cunge and J. P. Booth, *J. Appl. Phys.* **85**, 3952 (1999).
- <sup>12</sup>J. P. Booth, *Plasma Sources Sci. Technol.* **8**, 249 (1999).
- <sup>13</sup>N. E. Capps, N. M. Mackie, and E. R. Fisher, *J. Appl. Phys.* **84**, 4736 (1998).
- <sup>14</sup>N. M. Mackie, V. A. Ventruro, and E. R. Fisher, *J. Phys. Chem. B* **101**, 9425 (1997).
- <sup>15</sup>C. Suzuki, K. Sasaki, and K. Kadota, *Proceedings of the 15th Symposium on Plasma Processing*, edited by S. Miyake (The Japan Society of Applied Physics, Hamamatsu, Japan, 1998), p. 330.
- <sup>16</sup>P. J. Chantry, *J. Appl. Phys.* **62**, 1141 (1987).
- <sup>17</sup>K. Horikoshi, M. Murakami, S. Mashino, M. Goto, and T. Arai, *Proceedings of the 3rd Asia-Pacific Conference Plasma Science & Technology* (Japan Society for the Promotion of Science, Tokyo, Japan, 1996), p. 201.
- <sup>18</sup>J. P. Booth, G. Hancock, N. D. Perry, and M. J. Toogood, *J. Appl. Phys.* **66**, 5251 (1989).
- <sup>19</sup>C. Suzuki, K. Sasaki, and K. Kadota, *Jpn. J. Appl. Phys., Part 2* **36**, L824 (1997).
- <sup>20</sup>T. Arai, M. Goto, K. Horikoshi, S. Mashino, and S. Aikyo, *Jpn. J. Appl. Phys., Part 1* **38**, 4377 (1999).
- <sup>21</sup>R. A. Bonham, *Jpn. J. Appl. Phys., Part 1* **33**, 4157 (1994).
- <sup>22</sup>D. Hayashi, M. Nakamoto, N. Takada, K. Sasaki, and K. Kadota, *Jpn. J. Appl. Phys., Part 1* **38**, 6084 (1999).
- <sup>23</sup>F. B. Leclerc, A. P. Smith, G. D. Hayman, and T. P. Murrells, *J. Chem. Soc., Faraday Trans.* **92**, 3305 (1996).
- <sup>24</sup>C. Suzuki, K. Sasaki, and K. Kadota, *Plasma Chem. Plasma Process* (to be published).
- <sup>25</sup>I. C. Plumb and K. R. Ryan, *Plasma Chem. Plasma Process.* **6**, 205 (1986).
- <sup>26</sup>W. W. Stoffels, E. Stoffels, and K. Tachibana, *J. Vac. Sci. Technol. A* **16**, 87 (1998).
- <sup>27</sup>W. Schwarzenbach, G. Cunge, and J. P. Booth, *J. Appl. Phys.* **85**, 7562 (1999).
- <sup>28</sup>K. Sasaki, K. Takizawa, N. Takada, and K. Kadota, *Thin Solid Film* (to be published).
- <sup>29</sup>K. Usui, K. Sasaki, C. Suzuki, and K. Kadota, *Jpn. J. Appl. Phys., Part 1* **38**, 4373 (1999).