

Kinetics of hydrogen atoms in high-density CF_4/H_2 plasmas studied by (2+1)-photon laser-induced fluorescence spectroscopy

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We measured the distribution of absolute H atom density in high-density, low-pressure CF_4 plasmas with the addition of H_2 by (2+1)-photon laser-induced fluorescence spectroscopy. The H atom density had hollow-shaped distributions, i.e., the H atom density adjacent to the chamber wall was higher than that in the plasma column. In addition, when the chamber wall was covered with hydrogenated fluorocarbon film, we detected H atoms without the addition of feedstock H_2 . These experimental results indicate surface production of H atoms from hydrogenated fluorocarbon film. The surface production rate was sensitive to the property of fluorocarbon film. When the property of fluorocarbon film was unified, the surface production rate increased linearly with the pressure of feedstock H_2 , suggesting a recycling process of H atoms between gas phase and fluorocarbon film as a mechanism of plasma-surface interaction in CF_4/H_2 plasmas. © 2003 American Institute of Physics. [DOI: 10.1063/1.1609244]

The addition of H_2 is widely used for controlling radical densities in fluorocarbon plasmas used for the dry etching of SiO_2 in the fabrication of semiconductor devices.¹ The excessive F atom density, which reduces the etching selectivity over Si, is avoided by the addition of H_2 . The reduction of the F atom density is obtained by a gas-phase reaction $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ and by the change in the surface loss rate of F atoms.² The densities of CF_x radicals also change considerably by the addition of H_2 .³ We have shown that the variations of the CF_x radical densities are attributed to the change in the surface production rates of CF_x radicals from fluorocarbon film deposited on the chamber wall.^{4,5}

As has been just described, the kinetics of CF_x radicals and F atoms in fluorocarbon plasmas with the addition of H_2 have been investigated intensively. However, no reliable diagnostics on H atoms have been reported. It is known that H atoms have a significant influence on the property of fluorocarbon film. In addition, excessive H atoms may result in the damage of Si materials. In the present work, we measured the absolute H atom density in low-pressure high-density CF_4 plasmas with the addition of H_2 by laser-induced fluorescence (LIF) spectroscopy. We employed a (2+1)-photon excitation technique which uses two wavelengths at 243 and 486 nm.⁶ The spatial distribution of the absolute H atom density was obtained by (2+1)-photon LIF.

The plasma source and the LIF system were the same as those used in a previous work.⁶ The plasma source was a linear helicon-wave machine with a uniform magnetic field of 1 kG. An rf power of 1 kW was applied to a helical antenna wound around a discharge tube of 3 cm diameter. The rf power was pulse modulated with a repetition rate of 5 Hz and a duration of 10 ms. Because of the external magnetic field and the slender discharge tube, a high-density plasma column of 3 cm diameter was localized at the center of the vacuum chamber. The pressure of feedstock CF_4 was

fixed at 5 mTorr with a flow rate of 4.4 ccm. The partial pressure of H_2 was varied by changing the flow rate. The electron density obtained at this discharge condition was roughly independent of the partial pressure of H_2 , and was $(1.2 \pm 0.2) \times 10^{12} \text{ cm}^{-3}$.⁴ Tunable laser pulses at wavelengths of 243 and 486 nm yielded from an optical parametric oscillator were launched into plasmas from the radial direction. Hydrogen atoms at the ground ($1s$) state were excited to the $2s$ state by absorbing two photons at 243 nm. The $2s$ state was excited to the $4p$ state by the third photon at 486 nm. The LIF emission at 486 nm ($4p \rightarrow 2s$) was detected using a monochromator and a photomultiplier tube. The radial distribution of the H atom density was obtained by changing the observation position of the LIF emission. The absolute H atom density was evaluated by comparing the LIF emission from H with that from Xe at a known gas pressure.⁶

The measurements of the H atom density were carried out after sufficient seasoning discharges. We employed two types of seasoning procedures.² The first was the normal seasoning procedure; sufficient seasoning discharge was applied at each H_2 partial pressure. In this letter, this seasoning procedure is referred to as "case 1." On the other hand, in the seasoning procedure of "case 2," the H atom density was measured after sufficient seasoning discharges at a H_2 percentage of 50%. This seasoning procedure made the property of fluorocarbon film on the chamber wall identical before measurements at each H_2 percentage. The measurement at each H_2 percentage was carried out rapidly to avoid the change in the property of fluorocarbon film.

Figure 1 shows the history of the H atom density observed during the seasoning procedure of case 1. Before starting the experiment, fluorocarbon film on the chamber wall was removed sufficiently by using an O_2 discharge. With the cleaned chamber wall and no feedstock H_2 , we observed no H atoms in the plasma. As shown in Fig. 1, after changing the percentage of H_2 to 10% and 20%, the H atom density reached the steady-state value rapidly. In these con-

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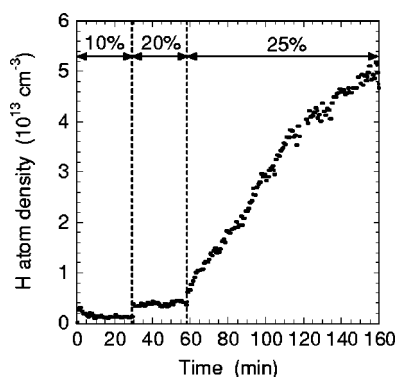


FIG. 1. Temporal variation of the H atom density during the seasoning procedure of case 1. The partial percentage of H_2 is indicated.

ditions, the deposition rate of fluorocarbon film on the chamber wall was negligibly slow. When the H_2 percentage was changed to 25%, we observed a slow increase in the H atom density for 100 min as shown in Fig. 1. During the seasoning discharge at 25%, we observed the growth of fluorocarbon film on the chamber wall.

The steady-state H atom density after the seasoning procedure of case 1 is shown in Fig. 2 as a function of the partial pressure of H_2 . The H atom density was measured at the center of the plasma column and at a distance of 8 cm from the center of the plasma column (outside of the plasma column). At H_2 percentages of 10% and 20%, the H atom densities at $r=0$ cm and $r=-8$ cm were the same, indicating that the radial distribution of the H atom density was uniform. The increase in the H atom density at H_2 percentages lower than 20% was proportional to the H_2 partial pressure (the dotted line in Fig. 2). On the other hand, the H atom densities at H_2 percentages of 25% and 50% were higher than the aforementioned trend, and the H atom densities in the outside area were higher than those at the center of the plasma column.

In the seasoning procedure of case 2, the H atom densities were different from those observed in the seasoning procedure of case 1. Figure 3 is a similar plot to Fig. 2 for the case of the seasoning procedure of case 2. The H atom density increased linearly with the partial pressure of H_2 . However, the slope of the linear relationship in Fig. 3 was larger than that in Fig. 2. (The proportional relationship in Fig. 2 is represented in Fig. 3 by the dotted line.) It should be empha-

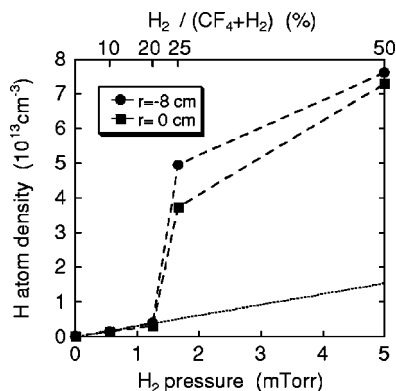


FIG. 2. Relation between the H atom density and the partial pressure of H_2 observed in the seasoning procedure of case 1.

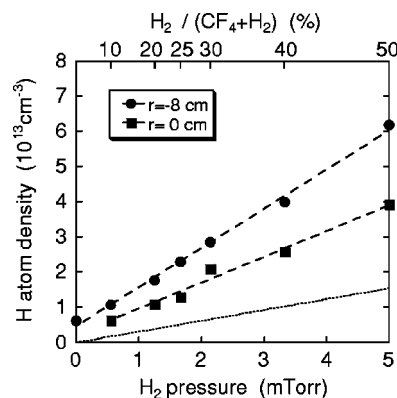


FIG. 3. Relation between the H atom density and the partial pressure of H_2 observed in the seasoning procedure of case 2.

sized that we detected H atoms with no feedstock H_2 in the seasoning procedure of case 2.

As shown in Fig. 3, in the seasoning procedure of case 2, the H atom densities in the outside area were higher than those in the plasma column at all the H_2 percentages. The radial distributions of the H atom density observed in the seasoning procedure of case 2 are shown in Fig. 4. The region corresponding to the high-density plasma column is shown by the shaded area in Fig. 4, and the chamber wall is located at a distance of 10 cm from the center of the plasma column. As has been reported previously,^{4,5,7} such hollow-shaped distributions are maintained stationarily by the production in the outside area and the loss in the plasma column. Because of the separation between the production and loss areas, there is diffusion flux of H atoms from the outside toward the plasma column. Considering the fact that we detected H atoms with no feedstock H_2 , the source of H atoms in the outside area is reasonably considered to be hydrogenated fluorocarbon film on the chamber wall.

According to these experimental results, it is known that H atoms are produced by both gas-phase and surface processes. The dominant gas-phase production process is electron impact dissociation $H_2 + e \rightarrow H + H + e$. Since the electron density is independent of the H_2 partial pressure, the rate of this reaction is proportional to the density of feedstock H_2 , provided that the reduction of the H_2 density due to dissociation is negligible. The proportional relationship be-

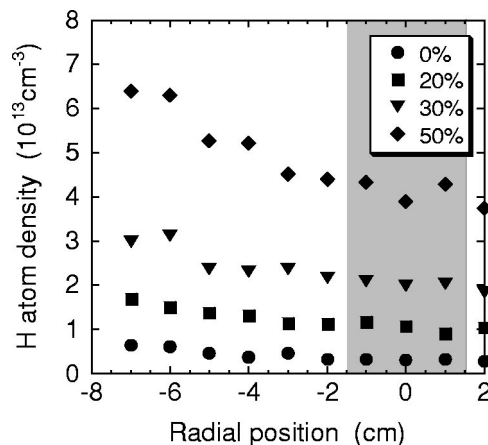


FIG. 4. Radial distribution of the H atom density observed at various H_2 percentages. The seasoning procedure was case 2.

tween the H atom density and the partial pressure of H₂ at H₂ percentages of 10% and 20% shown in Fig. 2 is explained by an assumption that electron impact dissociation of H₂ is the dominant production process of H atoms. Negligible surface production of H atoms is supported by the uniform distribution of the H atom density. Considering the rate coefficient of 1.5×10^{-9} cm³/s for the aforementioned reaction,⁸ the slope of the proportional relationship corresponds to a lifetime of approximately 25 μs for H atoms.

The significant increase in the H atom density at an H₂ percentage of 25% in the seasoning procedure of case 1 is attributed to the enhancement of surface production from hydrogenated fluorocarbon film on the chamber wall. When both the gas-phase and surface productions are present, the H atom density n_H is determined by a simple balance equation;

$$2k_P n_{H_2} n_e - k_L n_H n_e + Q_S = 0, \quad (1)$$

where n_{H_2} and n_e are the densities of H₂ and electron, respectively, k_P is the rate coefficient for $H_2 + e \rightarrow H + H + e$, k_L is the rate coefficient for the loss of H by electron impact processes in the plasma column, and Q_S represents the surface production rate. It is noted that the diffusion loss (surface loss) is neglected in Eq. (1), since the diffusion direction of H is inward when the distribution of the H atom density is hollow. The slow increase during the seasoning procedure of case 1 at an H₂ percentage of 25% reflects the increase in Q_S due to the change in the property of fluorocarbon film. Accordingly, the value of Q_S is sensitive to the property of fluorocarbon film. When the property of fluorocarbon film was unified by the seasoning procedure of case 2, the H atom

density increased linearly with the H₂ pressure. This experimental result suggests that the surface production rate has a form;

$$Q_S = Q_{S0} + k_S n_{H_2}, \quad (2)$$

where Q_{S0} and k_S are constants. From Eq. (2), a recycling process of H atoms is supposed as a mechanism of plasma-surface interaction in the CF₄/H₂ plasma.

Finally, it is noted that the absolute H atom densities observed at high ($\geq 25\%$) H₂ percentages are higher than CF_x and F atom densities in the same plasmas.^{4,5} It has been shown by the present work that H atoms are major species in fluorocarbon plasmas with the addition of H₂.

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