Vol 14 No 8, August 2005
1009-1963/2005/14(08)/1608-05

Chinese Physics

© 2005 Chin. Phys. Soc.
and IOP Publishing Ltd

Study of effect of H_2 addition on the production of fluorocarbon radicals in H_2/C_4F_8 inductively coupled plasma via optical emission spectroscopy actinometry*

Huang Song(黄 松)†, Xin Yu(辛 煜), and Ning Zhao-Yuan(宁兆元)

Department of Physics, Suzhou University, Suzhou 215006, China

(Received 16 September 2004; revised manuscript received 23 November 2004)

C_4F_8 plasma with the addition of H_2 is generated by the inductively coupled plasma (ICP) method. The relative densities of CF, CF_2, H and F radicals are determined by actinometric optical emission spectroscopy (AOES) as a function of the gas flow rate ratio R=H_2/(H_2+C_4F_8) at a pressure of 0.8 Pa and an input r.f. power of 400W, while that of HF is measured by quadrupole mass spectrometry (QMS). The results show that plasma activity increases firstly and then decreases with increasing R. As the gas flow rate ratio R changes from 0 to 0.625, relative densities of both CF and CF_2 decrease, and the relative [CF] has a similar tendency as the calculated [CF], indicating that CF radicals are generated mainly by the electron impact dissociation of CF_2 radicals. Production of HF is also discussed.

Keywords: optical emission spectroscopy, fluorocarbon radicals, C_4F_8 ICP plasma
PACC: 5270, 5275

1.Introduction

Fluorocarbon (CF_4, C_4F_8, CHF_3, etc.) gas plasmas are commonly used in dry etching of silicon dioxide (SiO_2), silicon (Si) and other materials for the fabrication of ultralarge-scale integrated circuits.[1−6] To date, there have been many studies focused on the dissociation mechanisms of source gases because their products (radicals) are different and play important roles in etching process.[4,7−9] Takahashi*et al*[8] have measured the densities of CF_x, H, F radicals and CHF_3 molecule in CHF_3 electron cyclotron resonance (ECR) plasma and found that CF_3 and CF_2 radicals are formed mainly through electron impact dissociation of the CHF_3 molecules, and CF radicals and F are formed mainly through electron impact dissociation of the CF_2 radicals. Den *et al*[9] also elucidated the dissociation mechanism of CF_4 and C_4F_8 in ECR plasma. In CF_4 ECR plasma the CF and CF_2 radicals are produced by direct electron dissociation of the parent gas, while in the case of C_4F_8 ECR plasma CF radicals are found to be generated from electron dissociation of CF_2 radicals. To obtain a high etching selectivity, H_2 is usually added to fluorocarbon plasmas.[6] Generally, the addition of H_2 results in a decrease in the F density and an increase in the CF_x densities in a certain range.[10] F etches both Si and SiO_2, while CF_x, serving as precursors for polymerization, decrease the etching rate of Si. Hence a high etching selectivity is obtained. There are also studies on the dissociation mechanism of C_4F_8, C_2F_6, CF_4 and CHF_3 with the addition of H_2 in ECR plasma.[4]

However, there are few such studies in an inductively coupled plasma though many investigations on etching mechanism or the dependence of etching rate on the precursor radicals have been conducted in inductively coupled plasma (ICP),[11−13] Recently, ICP has been the subject of many experimental and theoretical investigations owing to the fact that a high density plasma with good uniformity is easily obtained by ICP discharge under low pressure without an external magnetic field. Moreover, the ICP reactor can be easily scaled up to accommodate a large wafer size, compared with other facilities, such as Helicon

*Project supported by the Foundation of Key Laboratory of Thin Films, Jiangsu province, China, and the National Natural Science Foundation of China (Grant No 10305008).

†E-mail: vipsonghuang@yahoo.com.cn

wave plasma, electron cyclotron resonance plasma, etc.[14,15]

In this paper, we measure the relative densities of the radicals (CF, CF_2, H, F, HF) in H_2/C_4F_8 ICP plasma as a function of the gas flow rate ratio R=$H_2/(H_2+C_4F_8)$ via optical emission spectroscopy and quadrupole mass spectrometry. The effect of H_2 addition on the production of fluorocarbon radicals in H_2/C_4F_8 ICP plasma is investigated.

2. Experiment

2.1. ICP plasma apparatus

The experiments are performed in an inductively coupled plasma apparatus with a vacuum chamber of 0.3 m in diameter as shown in Fig.1. R.f. input power with frequency 13.56 MHz is supplied through an external excitation coil. An r.f. magnetic flux is produced following Ampere's law, which passes through the dielectric window into the plasma chamber. The time-varying r.f. magnetic flux density induces an r.f. electric field according to Faraday's law. This electric field accelerates plasma electrons and sustains the plasma. A water-cooled substrate holder is located 0.2 m below the dielectric window and its surface is maintained at a constant temperature of 20°C during the ICP discharge.

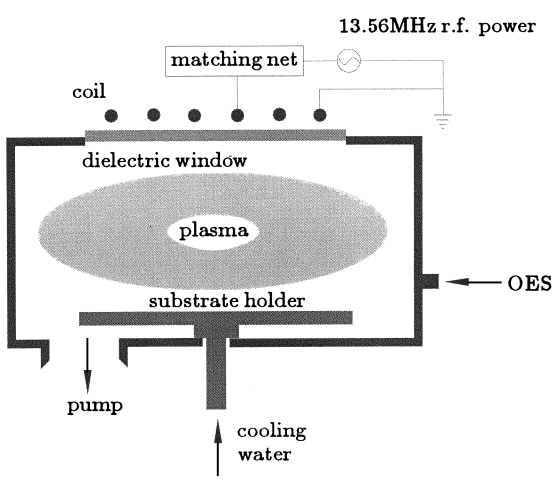


Fig.1. Schematic diagram of the ICP plasma apparatus.

2.2. Actinometry

The actinometrical technique, which uses the emission from an inert probe gas to obtain relative densities of radicals of interest in the plasma, was well developed by Coburn and Chen.[16] In the actinometrical method, the density of any radical of interest $[X]$ is related to the density of the actinometer $[A]$ by the equation

$$[X]/[A] \propto I_X/I_A, \tag{1}$$

where I_X and I_A are the optical emission intensities from radicals X and A, respectively. It should be remembered, however, that the applicability of Eq.(1) is limited to radicals for which the following conditions hold:[17,18] 1) direct electron-impact excitation is by far the most important excitation process from the ground state to the emission state; 2) the excited states decay primarily by photo-emission; 3) the electron impact excitation cross sections for radicals must have a similar threshold and shape as a function of electron energy. It is well known that the first two conditions are often met in practice. However, the third condition of similar threshold energies is rarely met because the choice of actinometer is limited to a few gases (He, Ar and N_2). Despite this difficulty, Eq.(1) is very often successfully employed, providing information on the general trend of the change of densities of the radicals with the variation of a system parameter.[18,19] Actinometrical optical emission spectroscopy (AOES) has been extensively applied to the study of CF, CF_2, H and F in C_2H_2/SF_6 plasmas,[17] and CF, CF_2 and F in H_2/CF_4, CF_4/C_2F_4, H_2/C_2F_6, and H_2/C_3H_8 plasmas.[20] Helium may be used, but it has a threshold energy of 23.73 eV (at 447.1 nm), which is far greater than the threshold energies of most of the radicals of interest. Argon is typically a better option with its threshold energy of 13.47 eV (at 750.3 nm). Nitrogen is sometimes used as an actinometer, but this gas cannot be considered inert because it is also incorporated into the growing film. For these reasons, to obtain relative densities of radicals of interest (such as CF, CF_2, H and F) in our experiment, Ar is used preferably because its threshold energy is much closer to that of CF (~6 eV at 202.4 nm), CF_2(~4.5 eV at 251.9 nm), H (12.09 eV at 656.3 nm) and F (14.74 eV at 703.5 nm) than that of He.

2.3. Experimental details

Total flow rate of reactive gases, $H_2+C_4F_8$, is kept at 40 sccm. The actinometer gas Ar flow rate is set to 2 sccm during the whole OES experiment. The emission intensities of various radicals CF, CF_2, H, F and Ar are determined respectively in the H_2/C_4F_8 plasma by measuring their characteristic emission lines with a S-2000 spectrometer. The emission wavelength for each radical of interest is listed in Table 1[21,22] The

relative densities of all these radicals [CF], [CF_2], [H], [F] are obtained by AOES.

Table 1. Spectral data of radicals of interest.

Radicals	Wavelength λ/nm	System
CF	202.4	$B^2\Delta - X^2\Pi$
CF_2	25.9	$A^1B_1 - X^1A_1$
H_α	656.3	$2p^2P^0_{3/2}$–$3d^2D_{3/2}$
F	703.5	$3s^2P_{3/2}$–$3pP^0_{3/2}$
Ar	750.3	$4s^1[1/2]$–$4p^1[1/2]$

Quadrupole mass spectrometry (QMS) is used to study the relative density of HF radicals formed in ICP since HF emission cannot be observed via optical emission spectroscopy. For the mass analysis, it should be noted that the signal of fluorocarbon radicals from the mass spectrum such as CF, CF_2 and F will come from not only the original fluorocarbon present in plasma but also the component of C_4F_8 that might segment or break into CF, CF_2 and F in the ionizer. The analysis of fluorocarbon radicals such as CF, CF_2 and F, hence, cannot represent the amount of these radicals that are produced in the plasma. However, the signal of HF is obtained only from the component present in plasma and, therefore, can be used to estimate the behaviour of it as a function of R in the H_2/C_4F_8 plasma.

3. Results and discussion

3.1. Optical emission spectrum in H_2/C_4F_8 ICP plasma

A sample optical emission spectrum of H_2/C_4F_8 ICP plasma is shown in Fig.2 with the flow ratio R of 0.05, a pressure of 0.8 Pa and an input r.f. power of 400 W. The radicals, such as CF (202.4 nm), CF_2 (251.9 nm), CH (431.4 nm), C_2 (471.5 nm, 516.5 nm, 563.5 nm), H (486.1 nm, 656.3 nm) and F (703.5 nm), can be observed easily. It is worth noting that C_2 radicals, which have a strong emission intensity among these radicals, are believed to be formed via gas-phase collision reaction between carbon-containing radicals.[10] A peak of C_3 at 404.4 nm can also be observed.

3.2. Plasma activity for H_2/C_4F_8 ICP plasma

The emission line intensity of Ar (750.3 nm) as a function of R is shown in Fig.3, which is normalized to unity at its maximum. It can be found that the addition of H_2 has a strong influence on the Ar emission: that is, H_2 affects the plasma activity. Concept of the plasma activity "K" was suggested by Durrent *et al.*[23] Reaction caused by the electron impact is one of the dominating processes in the low temperature plasma and parameter $K = \overline{\rho} \times \overline{E}$ is used to give a rough indication of the activity of the plasma, where $\overline{\rho}$ is the mean electron density and $\overline{E}$ is the mean electron energy. Thus, by referring to the parameter K it is possible to avoid constant reference to an increase in the electron density or the electron mean energy (or both). At a constant actinometer density, trends of the change of the emission are usually related to the electron density or electron mean energy (or both). Thus, the emission line intensity of Ar (I_{Ar}) can be used to denote "K". In Fig.3, I_{Ar} increases rapidly with increasing R up to 0.25 and then decreases gradually. This indicates an initial increase and then a decrease of plasma activity K, and also an implication of variation for plasma reaction when adding H_2 into the C_4F_8 plasma.

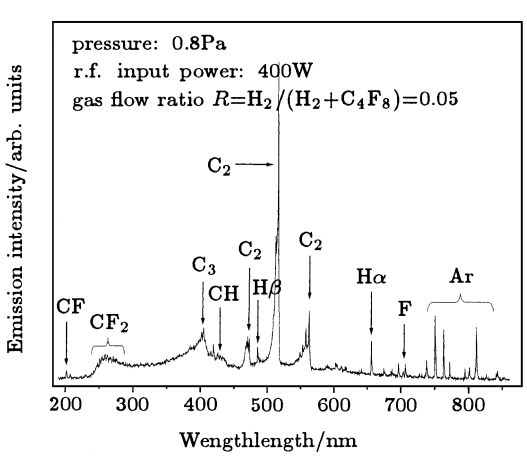


Fig.2. A sample optical emission spectrum in H_2/C_4F_8 ICP plasma.

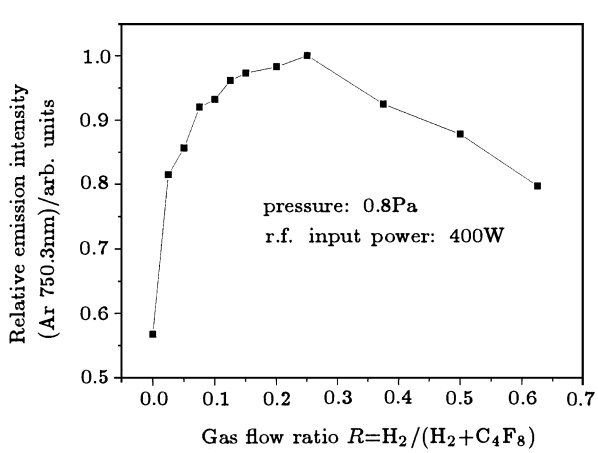


Fig.3. Relative emission intensity of Ar as a function of gas flow ratio R=$H_2/(H_2+C_4F_8)$.

3.3. Production of CF radicals in H_2/C_4F_8 ICP plasma

Relative CF and CF_2 densities [CF] and [CF_2] vs R from 0 to 0.625 are plotted in Fig.4 and each curve is normalized to unity at its maximum. It can be expected that [CF] and [CF_2] decrease with increasing R due to the decreasing flow rate of C_4F_8.

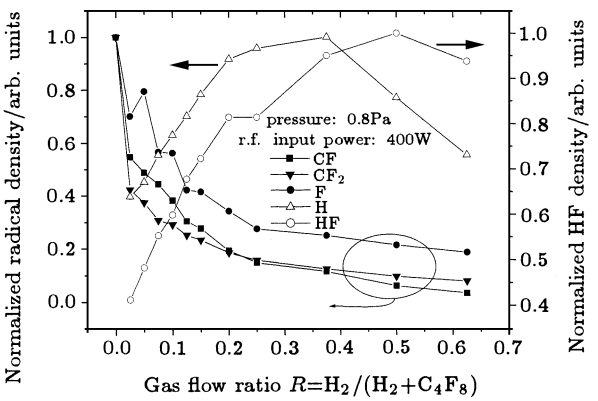


Fig.4. Relative densities of CF, CF_2, H, F and HF as functions of R.

In order to understand the behaviour of CF radicals shown in Fig.4, we examine the assumption that the CF radicals are formed through electron impact dissociation of the CF_2 radicals. If it is assumed that the main loss mechanism is recombination at the chamber wall, we can apply the equation[8]

$$CF_2 + e \rightarrow CF + F, \tag{2}$$

and

$$\kappa n_e [CF_2] = [CF] / \tau, \tag{3}$$

where κ is the rate coefficient for the reaction, n_e is electron density and τ is the lifetime of CF radicals. Assuming that τ is a constant independent of the variation of R, a qualitative estimation of κn_e can be obtained by measuring the optical emission intensity of an Ar radical line I_{Ar} as shown in Fig.2. Then Eq.(3) can be written as

$$I_{Ar} [CF_2] \propto [CF]. \tag{4}$$

This method of qualitative analysis has been used in analysis of CHF_3 plasma discharge and is described in detail by Takahashi *et al.*[8] They reported that CF radicals are generated mainly by the electron impact dissociation of CF_2 radicals in the ECR CHF_3 plasma. Den *et al*[9] have also used this method and showed that the CF and CF_2 radicals are produced in CF_4 ECR plasma by direct electron dissociation of the parent gas, while in the case of C_4F_8 ECR plasma CF radicals are found to be generated from electron dissociation of CF_2 radicals. In our work the relative [CF] and calculated [CF] ($\propto I_{Ar} [CF_2]$) are plotted in Fig.5, both of which are normalized to unity at their maximum values obtained at R equal to 0. It can be seen that the dependence of the relative [CF] and the calculated values on R are very similar, suggesting that direct dissociation of the CF_2 radicals contributes to the production of CF radicals.

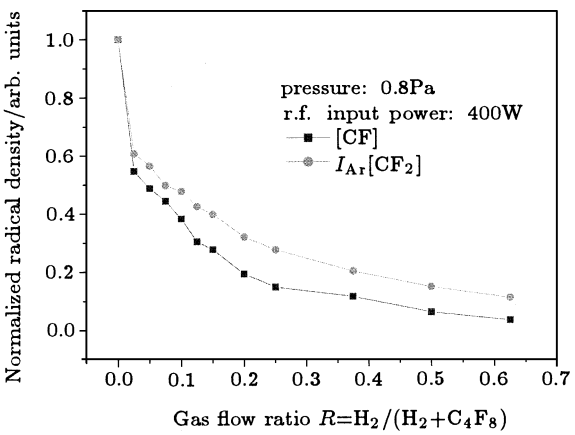


Fig.5. Relative [CF] and calculated [CF] (I_{Ar} [CF_2]) as functions of R.

The results shown in Fig.5 can be explained in terms of dissociation kinetics in H_2/C_4F_8 ICP discharge.

The structure of C_4F_8 is the cyclocombination of $(\text{-}CF_2\text{-})_4$. C-C and C-F bond energy is 3.0 and 4.8 eV, respectively. Hence, the CF_2 radicals are easily produced because C–C bond energy is much lower than C–F bond energy. And then CF radicals are produced due to the electron impact dissociation of the CF_2 radicals. The process can be expressed by the following reactions:

$$C_4F_8 + e \rightarrow CF_2 + e, \tag{5}$$

and

$$CF_2 + e \rightarrow CF + F. \tag{6}$$

3.4. Production of H, F and HF radicals in H_2/C_4F_8 ICP plasma

Relative densities [H], [F] and [HF] vs R from 0 to 0.625 are also plotted in Fig.4. It is clearly seen that [F] decreases with increasing R mainly due to the following two reasons: 1) the gas flow rate of the parent gas C_4F_8 content decreases with R; 2) the reactions of F with H and H_2 are:

$$H + F \rightarrow HF, \tag{7}$$

$$H_2 + F \rightarrow HF + H. \quad (8)$$

Both of them have been suggested as important mechanisms for the decrease in F density by other authors.[6,24]

For [H], its behaviour shows a inverted "U" shape. As expected, [H] increases firstly with increasing R due to the reaction

$$H_2 + e \rightarrow 2H \quad (9)$$

and the reaction (8). As R increases further, a gradual decrease in [H] can be understood from the following three aspects: 1) the reaction of F with H will consume H, leading to a decrease in [H]; 2) the F abstraction reaction

$$C_xF_y + H \rightarrow C_xF_{y-1} + HF \quad (10)$$

can also cause a decrease in [H] and an increase in [HF]; 3) reaction (8) may be restrained with increasing R due to less and less feed of C_4F_8.

All the above reactions do lead to a decrease in [H]. However, it should be noted that reaction (9) would produce more H with increasing R, which disagrees with our experimental observation of a decrease in [H] as R becomes large than 0.375. It is worth noticing that the variation of the plasma activity K with R shown in Fig.3 has a similarity with that of [H] in Fig.4. As we know, plasma activity is a measure of plasma chemical reaction. Clearly, plasma activity, $K = \overline{\rho} \times \overline{E}$, eventually determines the reactions among the parent gases, radicals, electrons, etc. So, the decrease in [H] with large R results from the decrease of plasma activity, considering reaction (9) is performed via the electron impact dissociation.

Reactions (7), (8) and (10) may contribute to the production of HF in H_2/C_4F_8 plasma. Besides the above reactions, it is necessary to note that HF may also be produced by the surface reaction at the chamber wall, that is, the adsorbed H reacts with fluorocarbon polymer to form HF, which is subsequently desorbed back into the plasma. Thus [HF] reaches a maximum value at R=0.5 as shown in Fig.4.

4. Conclusion

H_2/C_4F_8 plasma has been generated by inductively coupled plasma method. Optical emission spectroscopy and quadrupole mass spectrometry have been used to investigate the effect of addition of H_2 on the production of fluorocarbon radicals. The results have shown that addition of small amount of H_2 can enhance the plasma activity while it can be restrained for large gas flow rate of H_2. H_2 addition has an important role in the production of fluorocarbon radicals. Relative densities of both CF and CF_2 radicals decrease with gas flow rate ratio R, while the relative [H] has a similar tendency as that of plasma activity. The results also show that the source of CF comes from the electron impact dissociation of CF_2 radicals in the H_2/C_4F_8 plasma, and the generation of HF in the plasma is mainly due to the gas phase and surface reactions.

References

[1] Vasenkov A V, Li X, Oehrlein G S and Kushner M J 2004 *J. Vac. Sci. Technol.* A **22** 511

[2] Li X *et al* 2004 *J. Vac. Sci. Technol.* A **22** 500

[3] Min J H, Lee G R, Lee J K, Moon S H and Kim C K 2004 *J. Vac. Sci. Technol.* B **22** 893

[4] Miyata K, Hori M and Goto T 1996 *J. Vac. Sci. Technol.* A **14** 2343

[5] Kushner M J 1982 *J. Appl. Phys.* **53** 2923

[6] Ho H, Kin J H, Whang K W and Lee S H 1996 *J. Vac. Sci. Technol.* A **14** 1088

[7] Kazumi H, Hamasaki R and Tago K 1996 *Plasma Source Sci. Technol.* **5** 200

[8] Takahashi K, Hori M and Goto T 1994 *Jpn. J. Appl. Phys.* **33** 4745

[9] Den S *et al.* 1996 *Jpn. J. Appl. Phys.* **35** 6528

[10] Huang S, Xin Y and Ning Z Y 2005 *Acta Phys. Sin.* **54** 1653 (in Chinese)

[11] Rueger N R, Beulens J J, Schaepkens M, Doemling M F, Mirza J M, Standaert T E F M and Oehrlein G S 1997 *J. Vac. Sci. Technol.* A **15** 1881

[12] Standaert T E F M, Schaepkens M, Rueger N R, Sebel P G M and Oehrlein G S 1997 *J. Vac. Sci. Technol.* A **16** 239

[13] Li X, Li L, Hua X F, Oehrlein G S, Barela M and Anderson H M 2002 *J. Vac. Sci. Technol. A* **20** 2052

[14] Yoon N S, You K I and Hwang S M 1999 *Surf. Coat. Technol.* **112** 34

[15] Yoon N S, Hwang S M and Choi D I 1997 *Phys. Rev.* E **55** 7536

[16] Coburn J W and Chen M 1980 *J. Appl. Phys.* **51** 3134

[17] Durrant S F, Mota R P and Moraes M A 1992 *J. Appl. Phys.* **71** 448

[18] Walkup R E *et al* 1986 *J. Chem. Phys.* **84** 2668

[19] Durrant S F and Moraes M A 1998 *J. Vac. Sci. Technol.* A **16** 509

[20] d'Agostino R *et al* 1983 *J. Appl. Phys.* **54** 1284

[21] Kiss L D B *et al* 1992 *J. Appl. Phys.* **71** 3186

[22] d'Agostino R *et al* 1987 *J. Appl. Phys.* **61** 2754

[23] Durrant S F *et al* 1992 *Thin Solid Films* **220** 295

[24] Usui K *et al* 1999 *Jpn. J. Appl. Phys.* **38** 4373