Pure & Appl. Chem., Vol. 68, No. 5, pp. 1059–1063, 1996.
Printed in Great Britain.

Measurements of CF_x and SiH_x radicals in ECR and RF plasmas used for material processing

T. Goto

Department of Quantum Engineering, Nagoya University, Nagoya 464-01, Japan

Abstract: In material processing using plasmas, although radicals such as SiH_3, SiH_2, and CF_3 are very important as precursors of thin film in CVD and protection film on the side wall in etching, their measurements in plasmas have never been made for the lack of measurement methods. We developed new laser spectroscopic techniques such as infrared diode laser absorption spectroscopy and modified laser induced fluorescence spectroscopy, and succeeded in making in-situ measurements of densities of CF_x and SiH_x radicals in plasmas used for etching and deposition for the first time. Those results are described in this review.

Introduction

In etching processing using ECR and RF fluorocarbon plasmas, CF_x (x=1-3) radicals play important roles as precursors of protection thin film on the side wall. In CVD processing using ECR and RF silane plasmas, SiH_x (x=1-3) radicals are important as precursors for the formation of hydrogenated amorphous silicon thin film. Among them, SiH_3, SiH_2, and CF_3 radicals are particularly important, but their measurements in plasmas have never been made for the lack of measurement methods.

We developed new laser spectroscopic techniques such as infrared diode laser absorption spectroscopy (1,2), modified laser induced fluorescence spectroscopy and ring dye laser absorption spectroscopy, and succeeded in making in-situ measurements of densities of CF_x and SiH_x radicals and clarifying their behaviors in plasmas used for etching and deposition processing for the first time.

In this review, our main measurement results on the CF_x and SiH_x radicals in on-off modulated ECR and RF plasmas are described.

Outlines of measured radicals and measurement methods

Table 1 shows the CF_x and SiH_x radicals the behaviors of which we measured in on-off modulated ECR and RF plasmas, together with transitions used for the radical measurements and measurement methods.

All radicals other than SiH_2 and Si were measured using infrared diode laser absorption spectroscopy (IRLAS). Thus, by using IRLAS, many kinds of radicals could be measured and many data about important radicals have been accumulated for last few years. This IRLAS is only one in-situ measurement method of CF_3 and SiH_3 radicals in plasmas at moment.

The SiH_2 and Si radicals in silane plasmas were measured using modified laser induced fluorescence spectroscopy (MLIF) and ring dye laser absorption spectroscopy (RLAS), respectively.

Measurement method and experimental apparatus

Figure 1 shows the block diagram of the experimental arrangement for radical measurements in plasmas using IRLAS. The measurements were made for RF and ECR plasmas. In the case of RF plasma, the RF chamber of 40 cm diameter was used. It had circular plane parallel electrodes of 20 cm diameter and 3 cm separation, and the on-off modulated RF power (13.56MHz) was fed to the electrodes. The chamber could be moved vertically so that the spatial distribution of the radical density between the electrode could be measured. This discharge modulation technique enabled us to obtain absorption signals with a good S/N ratio. In the case of ECR excitation, the same chamber was used and only the RF head was replaced by the ECR head.

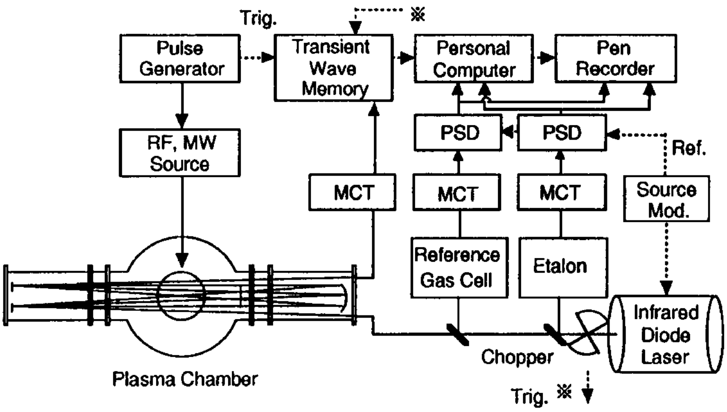

Fig.1 Block diagram of the experimental arrangement for radical measurements using IRLAS. PSD represents the phase sensitive detection.

The chamber was equipped with the White-type multi-reflection system. It consisted of three mirrors of 200 cm curvature radius and 200 cm interval to obtain an absorption signal with a good S/N ratio by increasing the optical path length. The laser beam was passed few tens times through the plasma. The IR diode laser was cooled down with a He compressor and its frequency was coarsely selected by varying the temperature and tuned minutely by changing the laser current. The laser power was of the order of 0.1 mW and the laser linewidth was around 10 MHz. For SiH_3, acetylene was used as a reference gas to determine the absolute value of the wavenumber of each rovibrational line accurately. For CF_x, N_2O was used. A confocal etalon was used to provide the relative scale of the wavenumber (one fringe = 0.01 cm^{-1}). The reference spectrum and interference fringe signals were detected with lock-in-amplifiers. The radical absorption spectrum was measured with a transient wave memory.

Main measurement results

One example of the observed absorption spectrum for R branch lines of the CF_3 ν_3 band and the transient absorption intensity of the R (18) line are shown in Fig.2. As the derivation method

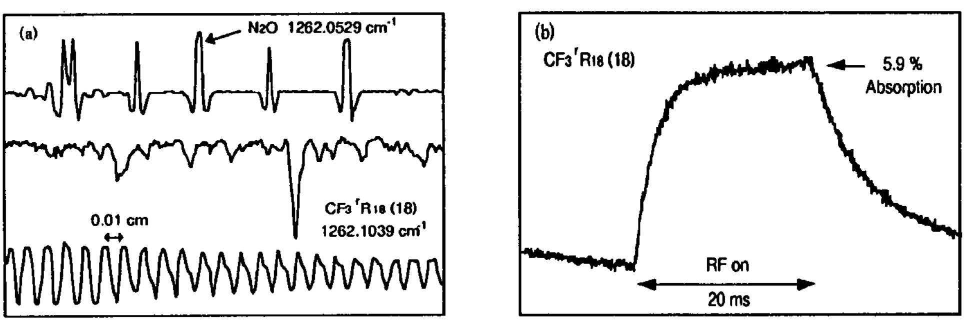

Fig.2 Observed absorption spectrum of the CF_3 ν_3 band and transient absorption intensity of the R (18) line in the RF CHF_3 plasma.

Table 1 CFx and SiHx radicals measured in on-off modulated ECR and RF plasmas.

Molecule	Radical	Band (μm)	Plasma	Method	Reference
SiH_4	SiH_3	ν_2 (15)	RF, ECR	IRLAS	3, 4, 5, 6
	SiH_2	A-X (0.6)	RF	MLIF	7
	SiH	v=0-1 (5)	RF, ECR	IRLAS	8, 6
	Si	4s-3p^2 (0.29)	RF, ECR	RLAS	9, 6
CF_4	CF_2	ν_3 (9)	RF	IRLAS	
	CF	v=0-1 (8)	RF	IRLAS	10
CHF_3	CF_3	ν_3 (8)	RF, ECR	IRLAS	11, 12, 13-16
	CF_2	ν_1 (9)	RF, ECR	IRLAS	11, 12, 13-16
	CF	v=0-1 (8)	RF, ECR	IRLAS	11, 12, 13-16
C_4F_8	CF_3	ν_3 (8)	ECR	IRLAS	17
	CF_2	ν_1 (9)	ECR	IRLAS	17
	CF	v=0-1 (8)	ECR	IRLAS	17

IRLAS : Infrared diode laser absorption spectroscopy
MLIF : Modified laser induced fluorescence spectroscopy
RLAS : Ring dye laser absorption spectroscopy

of the radical density from the absorption data shown in Fig.2 was described before (1) , it is abbreviated here. As shown in Fig.2, the CF_3 radical density decayed during few tens milli – seconds because the filling pressure was high in the RF plasma. On the other hand, in the ECR plasma, the CF_x radical had long life time because the filling pressure was low and their densities decayed during few seconds.

Figure 3 shows the CF_3, CF_2 and CF radical densities as a function of H_2 partial pressure in on-off modulated RF CHF_3 (6.7 Pa) /H_2 plasma. It has been found that the CF_3 radical density decreases more rapidly with the increase in H_2 pressure than the CF_2 and CF radical densities do. Figure 4 shows the CF_3, CF_2 and CF radical densities as a function of on-off period of the ECR CHF_3 plasma. Here the dissociation degree of CHF_3 molecule measured with IRLAS was 80 % or even higher.

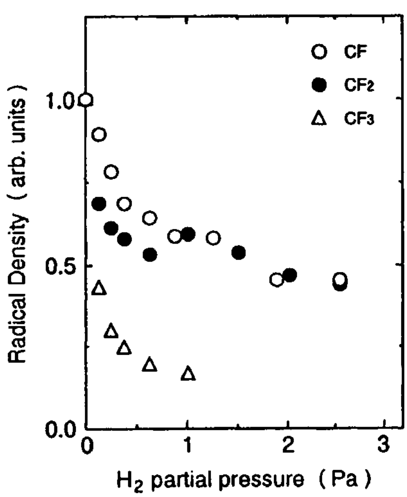

Fig.3 CF_3, CF_2 and CF radical densities as a function of H_2 partial pressure in RF CHF_3 (6.7 Pa) /H_2 plasma. The RF power was 145 W and the flow rate 45 sccm.

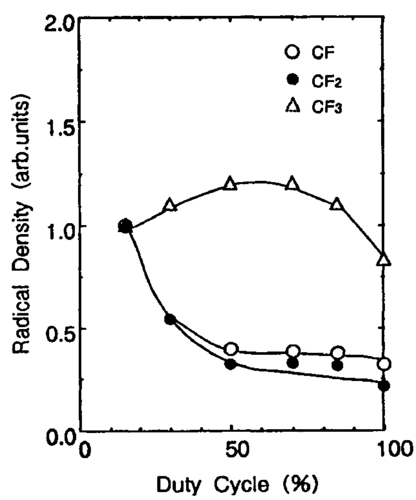

Fig.4 CF_3, CF_2 and CF radical densities as a function of on-off period of the ECR CHF_3 (0.4 Pa) plasma. The MW power was 300 W and the flow rate 5 sccm.

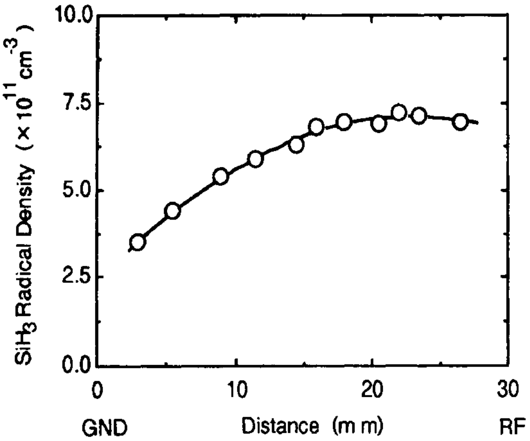

Fig.5 Spatial distribution of the SiH_3 radical density in the RF SiH_4/H_2 (6.7 Pa/4 Pa) plasma. The RF-on- period power was 125 W and the flow rate was 16 sccm.

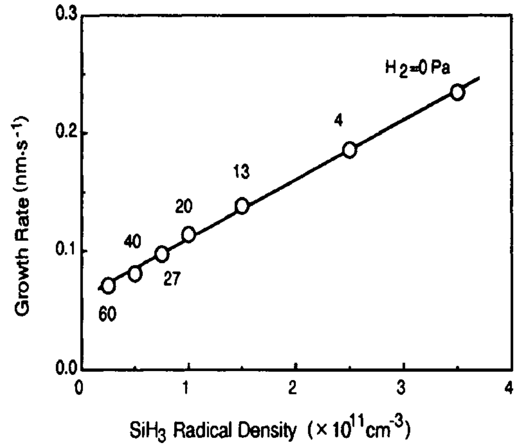

Fig.6 Correlation of the SiH_3 radical density and the growth rate of the a-Si : H thin film measured changing the H_2 pressure in the RF SiH_4/H_2 plasma. The SiH_4 pressure was 6.6 Pa, the flow rate was 10 sccm and the RF on-power was 125 W.

It has been found for the first time that the CF_3 radical density changes slightly but the CF_2 and CF radicals decrease fairly with the duty cycle. Namely the ratio of those radical densities changes considerably with the duty cycle. This result shows that the ratio of the radical densities can be controlled with a simple on-off plasma modulation.

Figure 5 shows the spatial distribution of the SiH_3 radical density between two electrodes observed in the SiH_4/H_2 (6.5 Pa/4 Pa) gas mixture and the RF power of 125 W. The absolute SiH_3 radical density is of the order of 10^{11} to 10^{12} cm^{-3}. It increases gradually with the distance from the grounded electrode, becomes flat and decreases gradually. Using this result, the flux density of SiH_3 incident to the substrate was obtained, from which the growth rate of a-Si : H through SiH_3 was estimated. The calculated growth rate from SiH_3 amounted to a significant fraction of the measured value.

Figure 6 shows the correlation of the SiH_3 radical density and the growth rate of a-Si : H thin film measured when changing the H_2 pressure. It shows a linear relationship between the two quantities and therefore that the SiH_3 radical contributes considerably to the a-Si : H thin film formation.

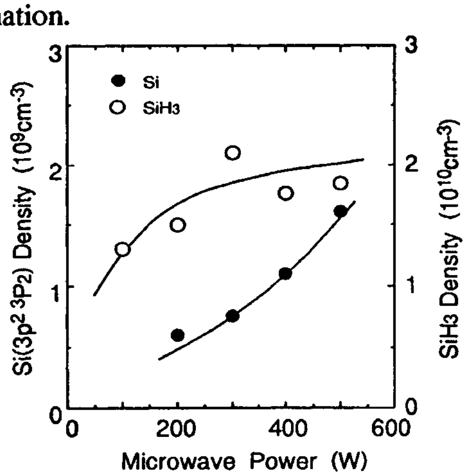

Fig.7 SiH_3 and Si radical densities as a function of microwave power in the on- off modulated ECR SiH_4 (50%) /H_2 plasma. The total pressure was 1.3 Pa.

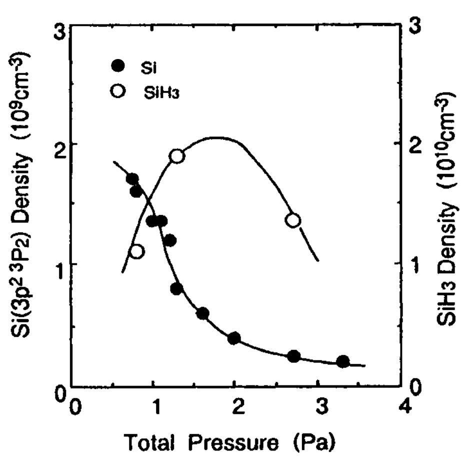

Fig.8 SiH_3 and Si radical densities as a function of total pressure in the on-off modulated ECR SiH_4 (50%) /H_2 plasma. The microwave power was 400 W.

Figure 7 shows SiH_3 and Si radical densities as a function of microwave power in the on-off modulated ECR SiH_4 (50%) /H_2 plasma. The SiH_3 radical density is of the order of 10^{10} cm^{-3} and the Si radical density is of 10^9 cm^{-3}. On the other hand, in the RF SiH_4/H_2 plasma, the SiH_3 radical density was very high ($\sim 10^{12}$ cm^{-3}) and the Si radical density was very low (10^8 cm^{-3} or lower) . Thus, it has been shown that the behaviors of radicals are rather different in the ECR and RF plasmas.

Figure 8 shows SiH_3 and Si radical densities as a function of total pressure in the on-off modulated ECR SiH_4 (50%) /H_2 plasma. In the low total pressure region, particularly the Si radical density becomes higher.

From the results shown in Figs.7 and 8, it is presumed that the contribution of Si radical to a-Si : H thin film in the ECR SiH_4/H_2 plasma is rather larger than that in the RF SiH_4/H_2 plasma.

Conclusions

By using the developed IRLAS and some other laser spectroscopic techniques, we have made the in-situ measurements of the CF_x and SiH_x radical densities and clarified the behaviors of those radicals in the ECR and RF plasmas for thin film processing for the first time. These results will be very useful results for the development of material processing.

References

1. N. Itabashi, K. Kato, N. Nishiwaki, T. Goto, C. Yamada and E. Hirota, Jpn. J. Appl.Phys. 27, L1565 (1988) .
2. N. Itabashi, K. Kato, N. Nishiwaki, T. Goto, C. Yamada and E. Hirota, Jpn. J. Appl.Phys. 28, L325 (1989) .
3. N. Itabashi, N. Nishiwaki, M. Magane, T. Goto, A.Matsuda, C. Yamada and E. Hirota : Jpn. J. Appl. Phys. 29, 585 (1990) .
4. N. Itabashi, N. Nishiwaki, M. Magane, S. Naito, T. Goto, A. Matsuda, C. Yamada and E. Hirota, Jpn. J. Appl. Phys. 29, L505 (1990) .
5. H. Nomura, A. Kono and T. Goto, Jpn. J. Appl. Phys. 33, 4165 (1994) .
6. Y. Yamamoto, H. Nomura, T. Tanaka, M. Hiramatsu, M. Hori and T. Goto, Jpn. J. Appl. Phys. 33, 4320 (1994) .
7. A. Kono, N. Koike, K. Okuda and T. Goto, Jpn. J. Appl. Phys. 32, L534 (1993) .
8. T. Goto, Mat. Res. Soc. Symp. Proc. 297, 3 (1993) .
9. M. Hiramatsu, M. Sakakibara, M. Mushiga and T. Goto, Meas. Sci. & Technol. 2, 1017 (1991) .
10. M. Magane, N. Itabashi, N. Nishiwaki, T. Goto, C. Yamada and E. Hirota, Jpn. J. Appl. Phys. 29, L829 (1990) .
11. K. Maruyama, A. Sakai and T. Goto, J. Phys. D 26, 199 (1993) .
12. K. Maruyama, K. Ohkouchi, Y. Ohtsu and T. Goto, Jpn. J. Appl. Phys. 33, 4298 (1994) .
13. K. Takahashi, M. Hori, K. Maruyama, S. Kishimoto and T. Goto, Jpn. J. Appl. Phys. 32, L694 (1993) .
14. K. Takahashi, M. Hori and T. Goto, Jpn. J. Appl. Phys. 32, L1088 (1993) .
15. K. Takahashi, M. Hori, S. Kishimoto and T. Goto, Jpn. J. Appl. Phys. 33, 4181 (1994) .
16. K. Takahashi, M. Hori and T. Goto, Jpn. J. Appl. Phys. 33, 4745 (1994) .
17. K. Miyata, M. Hori and T. Goto, Jpn. J. Appl. Phys. 34, L444 (1995) .