Absolute density measurement of cyanogen fluoride in CHF_3/N_2 electron cyclotron resonance plasma using infrared diode laser absorption spectroscopy

Koji Miyata, Hiroyoshi Arai, Masaru Hori,[a] and Toshio Goto
Department of Quantum Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

(Received 20 May 1997; accepted for publication 6 August 1997)

The absolute density of the cyanogen fluoride (FCN) molecule has been measured in a CHF_3/N_2 electron-cyclotron-resonance (ECR) plasma using infrared diode laser absorption spectroscopy. The $R(22)$ rotational-vibrational line at 1060.340 cm^{-1} in the ν_1 fundamental of $^{19}F^{12}C^{14}N$ was used for the spectroscopy. The extinction process of FCN in the afterglow was discussed on the basis of the decay rate after discharge termination. Moreover, the absolute FCN density in a CHF_3 ECR plasma during etching of silicon nitride has been calculated on the basis of the data shown in our previous study [K. Miyata *et al.*, J. Vac. Sci. Technol. A **15**, 568 (1997)]. It was found that approximately 10% of nitrogen atoms coming from silicon nitride formed FCN. © *1997 American Institute of Physics.* [S0021-8979(97)03622-0]

I. INTRODUCTION

Infrared diode laser absorption spectroscopy (IRLAS) has been developed as a technique for measuring molecules and radicals in process plasmas used for electronic device fabrication. Molecules and radicals in process plasmas are of crucial importance because the processes progress as they react on wafers. The IRLAS measurement of CF_x ($X=1-3$) radicals and CHF_3 and CF_4 molecules in fluorocarbon plasmas,[1–3] SiH and SiH_3 radicals and SiH_4 molecules in silane plasmas,[4,5] and CH_3 radicals in methane and methanol plasmas[6] have been reported previously.

Si_3N_4 has been used as a passivation layer, a masking layer for the local oxidation of silicon, and an *etch stop layer* for the self-aligned contact structure. In these processes, plasma-based etching using fluorocarbon gases has been commonly employed to achieve anisotropic etching. Recently, high-density plasmas have attracted much attention because they allow higher anisotropy than conventional plasmas do. However, high-density plasmas have a problem of low selectivity. A high selectivity of Si_3N_4 to Si is required for the local oxidation of silicon. On the other hand, a high selectivity of SiO_2 to Si and Si_3N_4 is required for the self-aligned contact process. Though etching of Si_3N_4 has been studied intensively, the mechanisms of Si_3N_4 etching have not been clarified sufficiently.

Knowledge of etch products is very helpful to clarify the mechanism of the plasma-based etching. Quadrupole mass spectrometry and optical spectroscopy have been applied to the measurement of the products of Si_3N_4 etching in fluorocarbon-based plasmas.[7–9] It was reported that N_2, NF_x, and CN are produced as a result of Si_3N_4 etching. In our previous study, it was reported that cyanogen fluoride (FCN) is the major etch product of Si_3N_4 in a CHF_3 electron-cyclotron-resonance (ECR) plasma, and the FCN density during the etching of Si_3N_4 has been estimated to be of the order of $10^{11}-10^{12}$ cm^{-3}.[10] However, the accuracy of the estimate was insufficient for discussing the importance of FCN.

In this study, the absolute FCN density was measured in a CHF_3/N_2 ECR plasma with a greater accuracy than that in the previous study. The extinction of FCN in the afterglow was discussed on the basis of the decay rate after discharge termination. In addition, the importance of FCN as the etch product of Si_3N_4 was also evaluated.

II. EXPERIMENT

Our experimental apparatus has been described previously,[10] and it is described briefly here. The reactor is 40 cm in diameter and 40 cm in height. A stainless substrate plate is 9 cm in diameter. Two magnet coils were arranged symmetrically and they provided a divergent magnetic field. The ECR region of 875 G was at 15 cm above the substrate plate. Continuous 2.45 GHz microwave power was introduced into the reactor from its top. In this study, no substrate was loaded in the plasma and no bias voltage was applied to the substrate plate (which was grounded); polymerization occurred on the substrate plate during the plasma discharges.

A White-type multiple reflection cell was installed in the reactor. An infrared diode laser beam was introduced into the cell and passed 40 times through the plasma. The beam was located 1.5 cm above the substrate plate. The laser frequency was scanned and the absorption signal due to FCN was detected by a mercury–cadmium–telluride infrared detector. An infrared region from 1060.16 to 1060.38 cm^{-1} was surveyed in this study. The laser beam was modulated at 400 Hz with a mechanical light chopper and detected with a lock-in amplifier. To estimate the FCN density, the spatial distribution of the FCN molecule was assumed to be uniform in the White-type multiple reflection cell.

III. DESCRIPTION OF FCN MEASUREMENT

Figure 1 shows the infrared absorption spectrum for the CHF_3/N_2 ECR plasma in a wave-number range from 1060.16 to 1060.38 cm^{-1}. This measurement was carried out

[a]Electronic mail: hori@nuee.nagoya-u.ac.jp

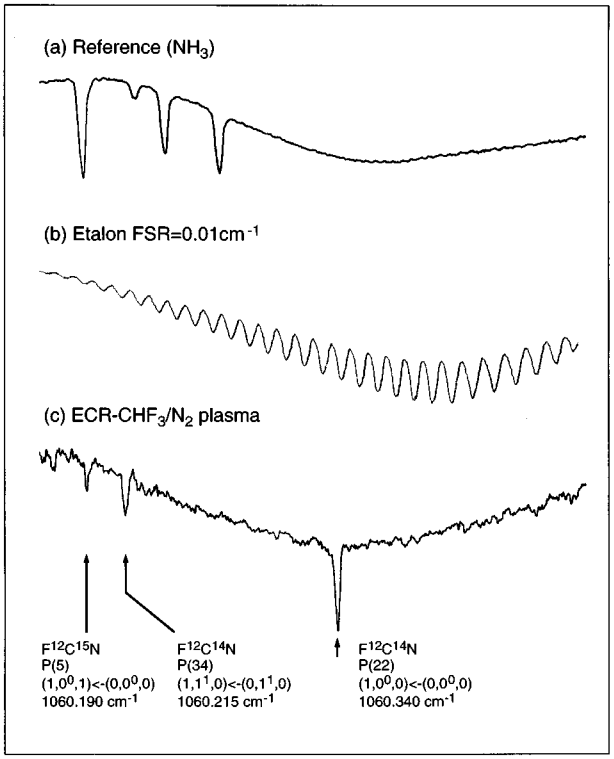

FIG. 1. Spectrum between 1060.16 and 1060.38 cm^{-1}. (a) NH_3 reference, (b) 30-cm vacuum-spaced etalon, (c) CHF_3/N_2 ECR plasma. The condition was a pressure of 0.4 Pa, a microwave power of 800 W, a flow rate of CHF_3/N_2 of 46/10 sccm.

at a total gas pressure 0.4 Pa, a microwave power 800 W, and a CHF_3/N_2 flow rate 46/10 sccm. The absorption spectrum of NH_3 and the fringes of a 30-cm vacuum-spaced etalon, shown respectively in Figs. 1(a) and 1(b), were used to determine the wave number of the FCN absorption spectrum. Several absorption lines attributed to FCN molecules were found, and the strongest was the P(22) at 1060.340 cm^{-1} in the ν_1 fundamental vibration of $^{19}F^{12}C^{14}N$.[11] For the other absorption lines shown in the figure, the intensities were smaller than that of P(22) and they were attributed to a hot-band line and an isotope line. In this study, the P(22) line in the ν_1 fundamental of $^{19}F^{12}C^{14}N$ was used to achieve a high sensitivity.

The knowledge of absolute FCN density is essential for a quantitative examination of the influence of FCN molecules. In this study, the FCN density was calculated on the basis of the following equation:

$$N=(1/S)\int I_A(\nu)d\nu. \tag{1}$$

Here, N is the density of FCN, S is the line strength, and $I_A(\nu)$ is the absorption coefficient obtained from the absorption intensity. To evaluate the integration, $I_A(\nu)$ was assumed to have a Doppler broadened line shape at a temperature of 300 K, which corresponded to the reactor wall temperature. The line strength is given by

$$S=S_b\times gA\ \exp(-FhC/\kappa_B T)/Q, \tag{2}$$

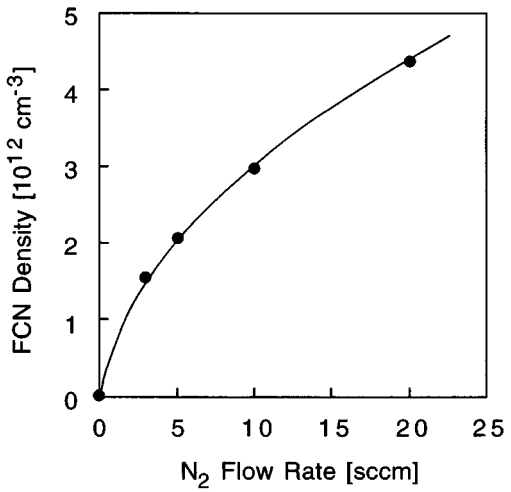

FIG. 2. FCN molecular density as a function of N_2 flow rate. CHF_3 flow rate, pressure, and microwave power were 46 sccm, 0.4 Pa and 800 W, respectively.

where S_b is the band strength, g is the statical weight, A is the Hönl–London factor, F is the term value, T is the temperature of the FCN molecule, and Q is the partition function. The band strength for the ν_1 transition of FCN has been reported to be 60 km/mol.[12] This value agrees well with the value of 63 km/mol for the C–F stretching transition of the CF radical.[13] We used $S_b=60$ km/mol, $A=0.5$, $g=2J+1=45$, $T=300$ K, and $Q=\kappa_B T/hCB$, where B is the rotational constant for the transition.[11] The FCN density was calculated to be 3×10^{12} cm^{-3} at a pressure of 0.4 Pa, a microwave power of 800 W, and a CHF_3/N_2 flow rate of 46/10 sccm. The sensitivity for the measurement is estimated to be better than 2×10^{10} cm^{-3}, which corresponds to 1% absorption in our experimental system.

IV. RESULTS AND DISCUSSION

A. Characterization of FCN molecules in CHF_3/N_2 ECR plasma

Figure 2 shows the FCN density as a function of the N_2 flow rate at a pressure of 0.4 Pa, a microwave power of 800 W, and a CHF_3 flow rate of 46 sccm. The FCN density increased and was saturated slightly with increasing N_2 flow rate. The result shows that the production of FCN was limited by the N_2 supply in the present condition. The FCN molecule is considered to be produced through electron-impact dissociation of CHF_3 and N_2 molecules and reactions between radicals such as CF and N. It is noted that with no flow of N_2 FCN was still proved to exist in the plasma. The FCN density with no flow of N_2 was estimated to be of the order of 10^{10} cm^{-3} and seemed unstable although this measurement might not be sufficiently accurate because the FCN density was close to the detection limit. This observation indicates that N_2 was supplied to the plasma through small air leak and/or desorption from the reactor walls to produce FCN in the plasma.

To evaluate extinction processes of the FCN molecules in the afterglow, the decay rate of the FCN density after the discharge termination was measured at two pressures of 0.4

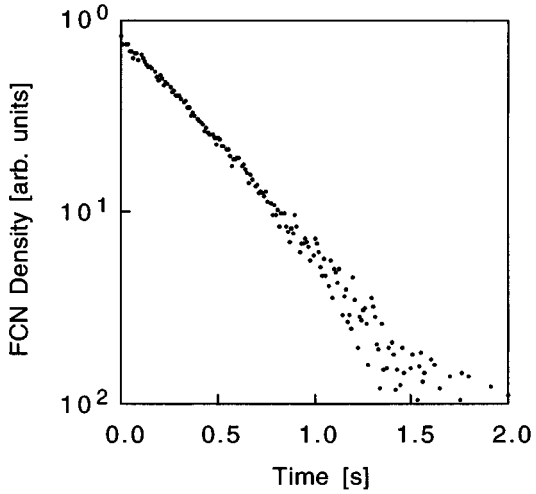

FIG. 3. Logarithm plot of the decay of FCN density in arbitrary unit. The condition was a pressure of 0.4 Pa, microwave power of 800 W, flow rate of CHF_3/N_2 of 46/10 sccm.

and 1.3 Pa and three N_2 flow rates of 5, 10, and 20 sccm. The input flow rate of CHF_3 gas and microwave power were fixed at 46 sccm and 800 W, respectively. Figure 3 shows a logarithmic plot of the decay of FCN density at a pressure 0.4 Pa and a N_2 flow rate 20 sccm. The decay was almost linear in the logarithmic plot. In the present condition, the decay rate was $2.8\ s^{-1}$, which corresponded to the pumping rate. Several measurements of the decay rate were carried out and the results are summarized in Table I.

Even after the plasma termination, many particles have possibilities to react with the FCN molecules because FCN is known to be chemically unstable at room temperature. In evaluation of the decay rates, therefore, removal processes due to pumping and reactions should be taken into consideration. The net decay rate r_N is given by

$$r_N = r_P + r_R, \tag{3}$$

where r_P and r_R are the pumping rate and the reaction rate, respectively. From Table I, r_R was less than $0.1\ s^{-1}$ at 0.4 Pa. In this case, the FCN molecules are considered to be removed only by pumping. On the other hand, r_R was in the range between 0.17 and $0.5\ s^{-1}$ at 1.3 Pa, indicating that the extinction reaction other than pumping occurred. It is noted that the extinction mainly occurs on the reactor walls at such low pressures. There are many possible reactions of FCN molecules, for example,

$$FCN + CF_2 \rightarrow CF_3CN, \tag{4}$$

$$FCN + CHF_3 \rightarrow CF_3CN + HF, \tag{5}$$

where reaction (4) is a termolecular reaction. It is noted that CF_2 radicals in reaction (4) are produced in the plasma and survive after the plasma termination due to its long lifetime.[14] The CF_2 radical density has been reported to be of the order of $10^{12}\ cm^{-3}$ in CHF_3 ECR plasmas.[10] The FCN removal reactions are enhanced with increasing pressure, that is, increasing concentration of particles, such as CF_2 and CHF_3. As shown in Table I. r_R depended on the N_2 flow rates even at a constant pressure of 1.3 Pa since chemistry changed with varying N_2 flow rate. It has been reported that FCN is hazardous, especially explosive in air mixture,[15] and probably noxious as other cyanides are. Under such low pressure conditions, FCN is pumped out from the apparatus as shown here. Therefore, all experiments where FCN is generated should be carried out with cautions.

TABLE I. Decay rate of the FCN density after the plasma termination. The pumping decay rate was calculated from the reactor geometry, flow rate, and pressure. The reaction rate was calculated using Eq. (3).

Condition		Decay rate		
Flow rate (CHF_3/N_2 sccm)	Pressure (Pa)	Net r_N (s^{-1})	Pumping r_P (s^{-1})	Reaction r_R (s^{-1})
46/20	0.4	2.8	2.8	≤0.1
46/10	0.4	2.4	2.4	≤0.1
46/5	0.4	2.2	2.2	≤0.1
46/20	1.3	1.4	0.86	0.5
46/10	1.3	1.1	0.73	0.4
46/5	1.3	0.83	0.66	0.17

B. Evaluation of FCN as etch products of Si_3N_4

The FCN measurement in a CHF_3 ECR plasma has been carried out during the etching of Si_3N_4 in our previous study.[10] It has been reported that the FCN density during the Si_3N_4 etching was of the order of $10^{11}-10^{12}\ cm^{-3}$ under the condition where Si_3N_4 with an area of $25\ cm^2$ were etched at a rate of 4.8 nm/s. However, the precise value of the FCN density during the etching of Si_3N_4 has not been reported yet. For the condition presented in the previous study, the FCN density was derived to be $4\times10^{11}\ cm^{-3}$.

The nitrogen atoms were estimated to be fed at a rate of 7×10^{17} atoms/s from Si_3N_4 into the plasma via the etching reaction. With the residence time of 0.5 s and the reactor volume of $1\times10^5\ cm^3$, the nitrogen atom density in the plasma is estimated to be $4\times10^{12}\ cm^{-3}$. This estimation leads to the conclusion that approximately 10% of the nitrogen atoms formed FCN molecules. It is evident that the FCN molecule is one of the major products of etch reactions of Si_3N_4.

V. CONCLUSIONS

Measurement of the FCN density in a CHF_3/N_2 plasma has been carried out by means of IRLAS. The absolute density of FCN was calculated to be $3\times10^{12}\ cm^{-3}$ in the CHF_3/N_2 ECR plasma at a pressure of 0.4 Pa, a microwave power of 800 W, and a CHF_3/N_2 flow rate of 46/10 sccm. From the study of the FCN decay rate, it was found that the FCN molecules were extinguished only by pumping at a low pressure of 0.4 Pa while they were also extinguished by gas-phase reactions under a high pressure of 1.3 Pa. The FCN density during the etching of Si_3N_4 in the CHF_3 ECR plasma was calculated to be $4\times10^{11}\ cm^{-3}$. Since the FCN density during the etching of Si_3N_4 is very large, FCN is expected to be an major etch product of Si_3N_4. It has been shown that IRLAS can be used for *in situ* monitoring of the absolute

FCN density in the Si_3N_4 etching process. IRLAS has the potential ability to detect various etch products. Therefore, we expect that the IRLAS measurement is applicable to *in situ* monitoring of etching processes for various materials as well as Si_3N_4.

ACKNOWLEDGMENTS

The authors would like to thank Professor Akihiro Kono for a review of this manuscript and Tatsushi Kuno for his experimental assistance.

[1] M. Magane, N. Itabashi, N. Nishiwaki, T. Goto, C. Yamada, and E. Hirota, Jpn. J. Appl. Phys., Part 2 **29**, L829 (1990).
[2] K. Maruyama, K. Ohkouchi, Y. Ohtsu, and T. Goto, Jpn. J. Appl. Phys., Part 1 **33**, 4298 (1994).
[3] K. Maruyama, A. Sakai, and T. Goto, J. Phys. D **26**, 199 (1993).
[4] Y. Yamamoto, H. Nomura, T. Tanaka, M. Hiramatsu, M. Hori, and T. Goto, Jpn. J. Appl. Phys., Part 1 **33**, 4320 (1994).
[5] N. Itabashi, N. Nishiwaki, M. Magane, S. Naito, T. Goto, A. Matsuda, C. Yamada, and E. Hirota, Jpn. J. Appl. Phys., Part 2 **29**, L505 (1990).
[6] S. Naito, N. Ito, T. Hattori, and T. Goto, Jpn. J. Appl. Phys., Part 1 **32**, 5721 (1993).
[7] J. Dulak, B. J. Howard, and Ch. Steinbrüchel, J. Vac. Sci. Technol. A **9**, 775 (1991).
[8] P. E. Clarke, D. Field, A. J. Hydes, D. F. Klemperer, and M. J. Seakins, J. Vac. Sci. Technol. B **3**, 1614 (1985).
[9] D. Field, D. F. Klemperer, and I. T. Wade, J. Vac. Sci. Technol. B **6**, 1614 (1988).
[10] K. Miyata, M. Hori, and T. Goto, J. Vac. Sci. Technol. A **15**, 568 (1997).
[11] H. Jones and J. Lindenmayer, J. Mol. Spectrosc. **113**, 339 (1985).
[12] T. J. Lee and S. C. Racine, Mol. Phys. **84**, 717 (1995).
[13] T. Nakanaga, F. Ito, and H. Takeo, J. Mol. Spectrosc. **165**, 88 (1994).
[14] K. Takahashi, M. Hori, and T. Goto, Jpn. J. Appl. Phys. Part 1 **33**, 4745 (1994).
[15] F. S. Fawcett and R. D. Lipscomb, J. Am. Chem. Soc. **86**, 2876 (1964).