Molecular Emission of CF_4 Gas in Low-pressure Inductively Coupled Plasma

T. Y. Jung, D. H. Kim, and H. B. Lim*

*Department of Chemistry, Dankook University, Seoul 140-714, Korea. *E-mail: plasma@dankook.ac.kr*

Received October 18, 2005

CF_4 gas is one of the most common chemicals used for dry etching in semiconductor manufacturing processes. For application to the etching process and environmental control, the low-pressure inductively coupled plasma (LP-ICP) was employed to obtain the spectrum of CF_4 gas. In terms of the analysis of the spectra, trace CF radical by A-X and B-X transitions was detected. The other CF_x radicals, such as CF_2 and CF_3, were not seen in this experiment whereas strong C and C_2 emissions, dissociation products of CF_4 gas, were observed.

Key Words : Fluorinated carbon, CF radical, Low-pressure plasma, Inductively coupled plasma

Introduction

Fluorinated carbon compounds have been used for dry etching in the semiconductor manufacturing process due to their high cleaning and etching efficiencies on silicon wafers. Emission of these fluorinated carbons into the air may, however, result in severe environmental problems.

For the detection of fluorinated carbon radicals (CF_x), various diagnostic methods have been developed including optical emission spectroscopy,[1,2] laser-induced fluorescence (LIF),[3-7] UV absorption,[8,9] and mass spectrometry (MS).[10,11] Most of CF, CF_2 or CF_3 species were produced by electron impact[12,13] of CF_xX_y compounds, DC discharges[14] or rf plasma[15] in a gaseous mixture of CF_4 and Ar, and UV photodissociation of CF_xX_y.[16,17] For an example, a study for CF_x molecules using commercialized atmospheric pressure ICP-AES was reported, in which only weak F atomic emission was detected.[15]

A low-pressure ICP (LP-ICP) developed in our lab[18-20] has analytical potential for monitoring fluorinated carbons because of its relatively easy ignition, stability, high electron energy, and low-pressure emission characteristics. In this experiment, the lab-made LP-ICP optical emission system was used to obtain the emission spectrum of CF_4 gas. Identification of fluorocarbon species produced in the LP-ICP and interpretation of each spectrum are discussed.

Experimental Section

Instrumentation. The low-pressure ICP emission system used in this experiment was described elsewhere.[20,21] A schematic of the system is shown in Figure 1. A quartz viewing port was attached to the chamber to detect the emission laterally. A 27.12 MHz rf generator (Model: YSE-06F with a matching box (Model: AMN-010B), Youngsin Engineering, Republic of Korea) was used to generate the

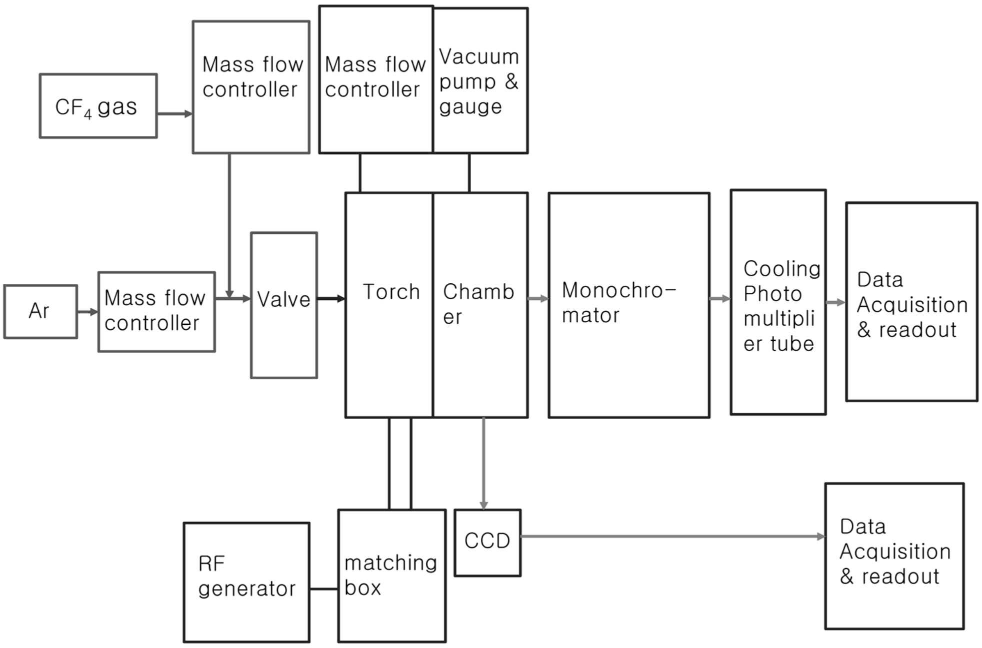

Figure 1. Schematic of LP-ICP optical emission system.

Table 1. Operating conditions of LP-ICP optical emission system

Item	Operating conditions	
ICP Generator	Frequency	27.12 MHz
	Power	250 W
Torch	Demountable type	
	Plasma gas flow	0 L/min
	Aerosol gas flow	0.5 L/min
CF_4	Gas flow	0.5 mL/min
Monochromator	Czerny-Turner mount	0.75 m focal length
	(200 nm-500 nm)	2400 grooves / mm
	(500 nm-900 nm)	1200 grooves / mm
	slit width	80 μm
Charge coupled detector (CCD)	Detection range	300-900 nm
	Well depth	160.000 photons
	Grating (10 cm focal length)	600 line/mm
	Optical fiber	100 μm diameter 5 m length
	Integration time	25 ms
	Number of averaging	3
Vacuum chamber	Pressure	~6.7 mbar

plasma. The dimensions of the torch were similar to those of a mini-torch for an atmospheric pressure ICP. There was no intermediate tube, and the flow rate of the plasma gas was controlled by a mass flow controller (MFC, model: 580E series, Brooks, Japan). For sample introduction, CF_4 gas (Seoul Special Gas Co.) (0.5 mL/min) was mixed with Ar plasma gas (0.5 L/min) using a mass flow controller (Model 580E series, Brooks, Japan) before being introduced into the torch. The operating pressure of the vacuum chamber was maintained at approximately ~6.7 mbar by a rotary pump (25.0 m^3 h^{-1}, Model: E2M18, Edwards, UK); all other dimensions and parameters were the same as those reported previously.

Emission was observed axially using a 0.75-m- focal-length monochromator (DongWoo Scientific Co, Seoul, Korea) with a grating of 2400 grooves/mm and 80 mm slit widths. The spectrum was obtained using the software provided by the manufacturer. A cone (1 mm diameter of the hole) with shielding Ar gas flow was inserted inside the vacuum chamber to prevent deposition or etching of the quartz window. For the lateral emission, a CCD detection system (K-Mac, Spectra View 2000, Daejon, Korea) with a maximum sensitivity between 400 to 800 nm was employed. The emitted light from the plasma, about 5.5 cm from the load coil, was collected and guided into the CCD by an optical fiber (K-Mac, SPF-1, Daejon, Korea). The operating conditions are summarized in Table 1.

Results and Discussion

System Stability. The lab-made low-pressure ICP ignited easily and was stable at low power condition. When 0.5 mL/min of CF_4 gas was introduced, the plasma torch gradually became foggy due to corrosion of the quartz wall by the reactive fluorine-containing species generated in the plasma. The relatively narrow inner diameter of the torch, 10 mm, and the slow plasma gas flow, 1.0 L/min, probably facilitated corrosion. The plasma torch, though corroded, was usable for about 2 weeks with daily use.

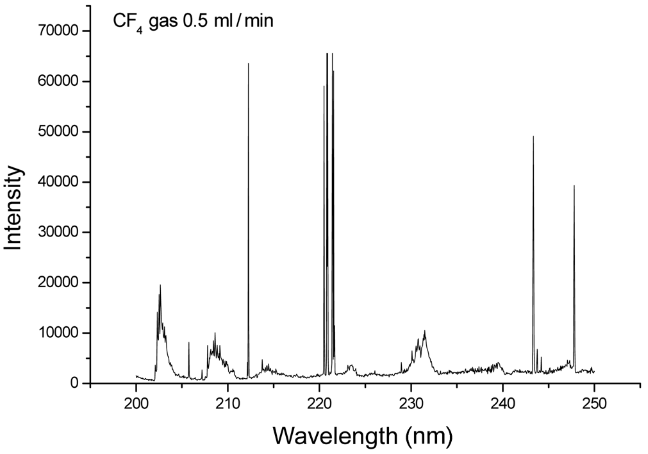

Figure 2. Emission spectrum of CF_4 gas in the range of 200-250 nm using LP-ICP.

Detection of CF_x species. When CF_4 gas is introduced into the plasma, various species containing F can be produced by dissociation. The most common species that have been studied previously are CF, CF_2, and CF_3 radicals, which have bands at 220-320 nm and near 600 nm at the pressure of 1-100 mtorr. In case of CF radicals, weak A-X and B-X emission systems were observed and investigated in the UV, 220 to 300 nm region.[22,23] In those cases pure CF_x gases were introduced for qualitative study and no report has been released for quantitative work.

In this experiment, the spectrum obtained with about 0.1% (v/v) CF_4 in Ar using the monochromator with the axial-viewing mode is shown in Figure 2, which is magnified for the detection of CF_x radicals. As shown in the figure, weak violet-degraded bands were observed at 247.6 nm and 240.0 nm, which matched with the most prominent band center of A-X system of CF (0-2) and (0-1), respectively. The other A-X bands were not seen in this observation. Presumably the intensities were too weak to be observed or overlapped with other strong Si peaks due to poor resolution. A series of bands appeared at 202.5, 209.7, 210 and 213 nm, which matched with the B-X transition. These A-X and B-X transition bands were not seen when no CF_4 gas was introduced. Therefore, the observation of this series of weak bands provides the strong evidences of the presence of CF radicals in this low pressure plasma. In this axial-viewing mode, series of all violet degraded NO bands, such as 205.59, 214.81, 226.18, 236.32, 247.01, and 258.63 nm, were too weak to be observed. OH and NH bands were also too weak to be observed with this axial-viewing (Data was not shown.). However, the strong OH bands (~306 nm) and NH band (~336 nm) with Ar(I) lines (> 700 nm) were observed with lateral-viewing of the plasma using the CCD, as shown in Figure 3. These OH and NH bands presumably resulted from the entrainment of residual gas in the chamber.

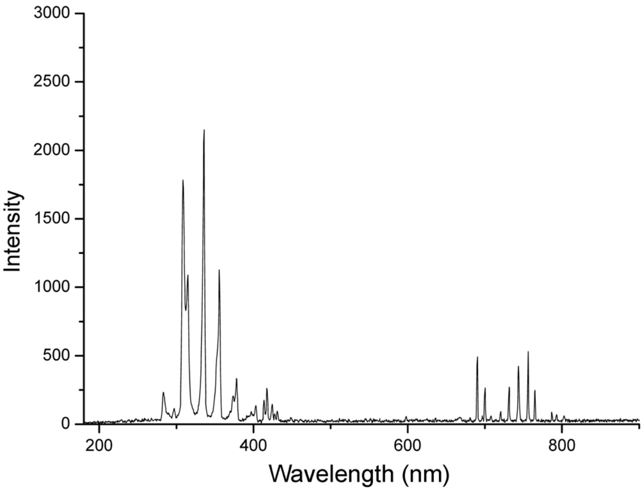

Figure 3. Emission spectrum of CF_4 gas using CCD with side-viewing mode.

Since the CF_2 radical is known to be remarkably stable and fairly non-reactive, the emission band for CF_2 might be seen in the spectrum more easily than the others, if present. The emission bands of the CF_2 system in the UV region (250-350 nm) are well-known[12] and most of the bands have been analyzed by the ν_2 regression.[17] However, the band system ($^1B_1$–$^1A_1$) in this UV range didn't appear in this observation. The visible emission of the CF_2 ($^3B_1$-$^1A_1$) system had also been reported at wavelengths between 470-720 nm,[24,25] showing a very sharp band structure (non-continuum). This emission was not observed in this experiment, either. For the CF_3 radical, the UV band emission should be observed between 230-300 nm with the most intense peaks between 255-275 nm.[16] In addition, the visible emission of CF_3 always appeared along with the UV emission.[17] The visible continuum emission bands of CF_2 and CF_3 usually showed red-shifts. However, these bands were not observed in this experiment. As a result, emission bands of the CF_2 and CF_3 system (UV and Visible) were not found in the UV and Visible emission spectra observed in this study. Only weak bands from CF radicals were observed in this low-pressure plasma at ~6.7 mbar.

Observation of F and C atom. The F atom emission in other plasmas has been observed previously at longer wavelengths, 683.4, 685.6, 690.2, 690.9, and 703.7 nm.[12,15] A highly excited state of the F atom (~14.7 eV) usually makes it difficult to observe the atomic lines in the Ar ICP. In spite of its inherently weak line intensity, the F atom is known to be the most reactive species for plasma etching among the fluorinated carbon radicals in terms of mass spectrometric study.[10,11] In this experiment it was unclear to say the observation of F atom in the plasma because the weak peaks at 683.4 and 685.6 nm were not consistently observed and the peaks just above 690 nm were not observed.

Evidently, the expected Si (I) peaks were observed with strong intensities in 212.412 nm, 220.798 nm, 221.089 nm, 221.667 nm, 243.515 nm, etc. (Fig. 2), which were not seen in the background spectrum without the CF_4 gas. These Si atomic peaks definitely came from the corrosion of the quartz torch by the reaction with fluorine species generated from the plasma with CF_4 gas. The most prominent line of Si (I) in atmospheric pressure ICP was 251.611 nm. Other Si (I) lines were observed at 250.690, 251.432, 251.920, and 390.552 nm. From Figure 4, the Ar (I, 383.468 nm) line and the Si (I, 390.552 nm) line were observed. However, Ar (I, 394.898 nm) that was supposed to have a stronger intensity than Ar (I, 383.468 nm) in atmospheric pressure ICP was not observed in this plasma with or without CF_4 gas.

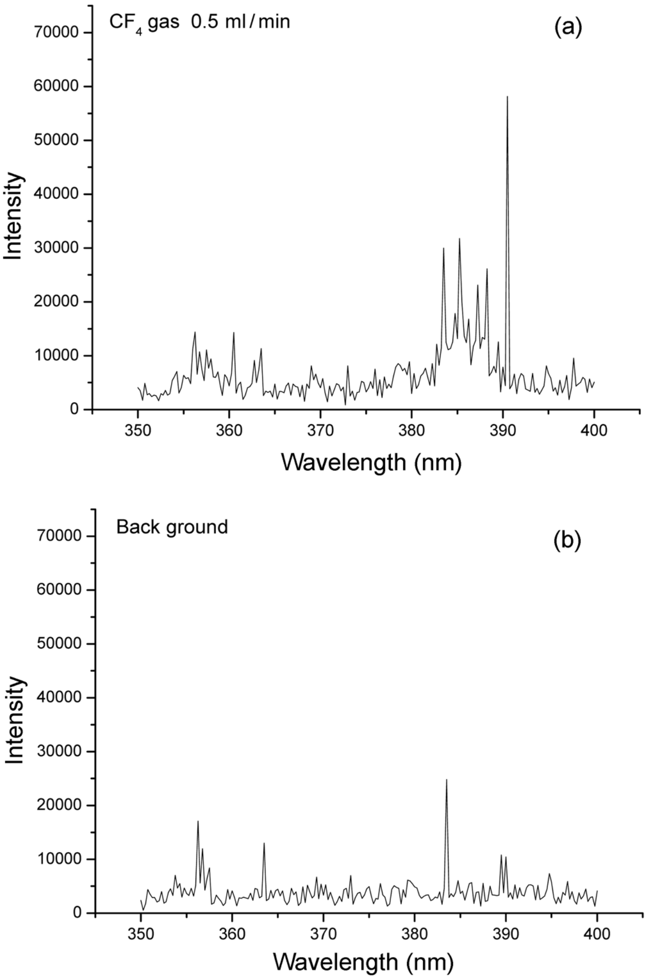

Figure 4. Emission spectrum (axial-viewing) of LP-ICP in the range of 350-400 nm: a) with CF_4 gas, b) with Ar gas only.

A strong carbon atomic peak, C (I) 247.856 nm was seen due to the dissociation of CF_4 gas in the plasma, as shown in Figure 2. Another carbon atomic peak was also observed at 579.351 nm (Spectrum was not shown), but no carbon ionic peaks were seen in this plasma. Instead, Swan bands of C_2 emission, the first positive band of carbon, were observed, as shown in Figure 5. Among the three strong band systems attributed to this molecule, the Swan band was of very frequent occurrence in sources containing carbon.[26] The most intense peak, the 0-0 transition, was observed at 516.52 nm but is obscured by many Ar (I) peaks (Spectrum was not shown). In this Figure 5, a series of the second strongest peaks were seen at 473.71 nm (1-0), 471.52 nm (2-1),

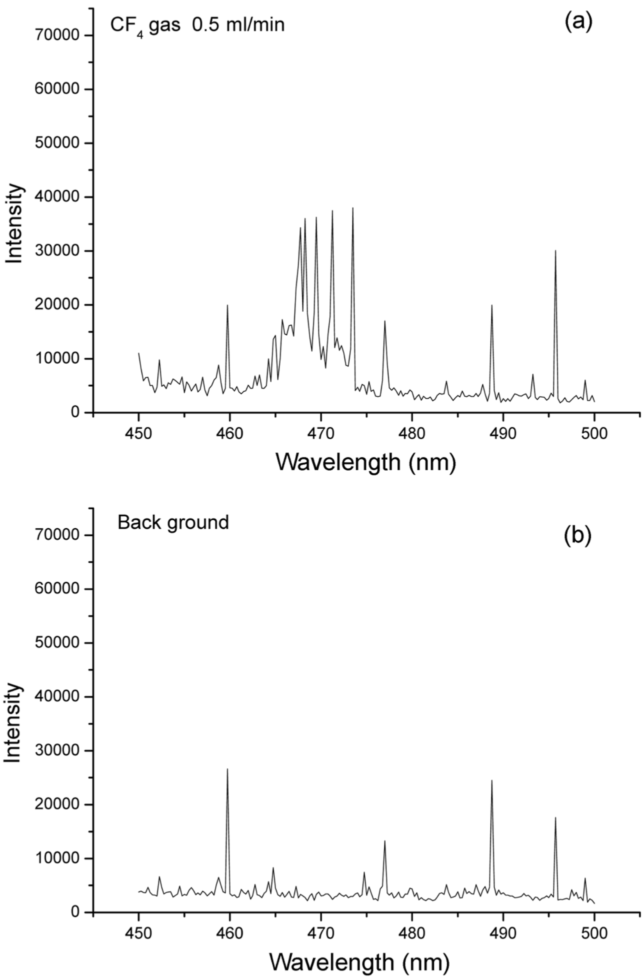

Figure 5. Emission spectrum (axial viewing) of LP-ICP in the range of 450-500 nm: (a) with CF_4 gas, (b) without CF_4 gas.

469.76 nm (3-2), 468.48 nm (4-3), 467.86 nm (5-4), and 466.87 nm (6-5). The 3-1 and 4-2 transitions were also observed at 437.14 nm and 436.52 nm (Spectrum was not shown). These C_2 swan bands were not observed without CF_4 gas. Therefore, strong evidence suggesting the presence of the C_2 molecule in this plasma with CF_4 gas was proof that most C-F molecules were dissociated in this low-pressure plasma and produced C, C_2, and small amount of F and CF.

In conclusion, when 0.1% (v/v) CF_4 gas was introduced into the LP-ICP, the emission of the trace CF radical was observed at 202.5, 209.7, 210, and 213 nm for B-X transition and 247.6 and 240 nm for A-X transition. The other CF_x radicals, such as CF_2 and CF_3, were not seen in this experiment, which suggests that they were dissociated in this plasma. Strong C and C_2 emissions, dissociation products of CF_4 gas, were observed in this plasma.

Acknowledgement. This work was supported by Internal Research Fund of Dankook University, 2005.

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