CF₄ Decomposition Using Low-Pressure Pulse-Modulated Radio Frequency Plasma*

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CF₄ is one of the most stable gases among perfluorocompounds (PFCs) whose decomposition is extremely difficult. In this study, CF₄ decomposition was investigated using a pulse-modulated radio frequency (RF) plasma of 2 MHz, which is applicable to plasma etching and novel functional material manufacturing processes. When the absolute pressure and 100% CF₄ and 99.5% O₂ flow rates were set at 80 Pa and 0.1 and 0.2 NL/min, respectively, almost complete CF₄ decomposition was achieved at the pulse modulation frequency range of 25 kHz to 99 kHz. The analysis of the by-product of CF₄ decomposition was carried out using a CO₂ gas analyzer and a Fourier transform infrared spectrophotometer (FTIR) with a pulse modulation frequency of 75 kHz. It was known that 10%, 50% and 24% of CF₄ are converted to CO, CO₂ and COF₂, respectively. It was considered that the remaining 16% of carbon is converted to carbon particles or other organic substances.

Key Words: Plasma, Chemical Reaction, Pollutant, Perfluorocompounds, CF₄, Decomposition, Inductively Coupled Plasma, Pulsed Radio Frequency Plasma

1. Introduction

Perfluorocompounds (PFCs) are used as etching gases and also as cleaning gases for the plasma chemical vapor deposition (CVD) equipment in a semiconductor manufacturing process. PFCs, such as CF₄, C₂F₆, C₃F₈, SF₆ and NF₃, have extremely large global warming potentials (GWPs) and long lifetimes in stratosphere. For example, the GWP of CF₄ is 6500 times larger than that of carbon dioxide (CO₂)^{(1),(2)}. Therefore, the emission of these gases has to be reduced worldwide.

As abatement methods for PFCs, the chemical adsorption, catalyst and combustion methods have been used. However, these methods have problems associated with a low decomposition efficiency, a high operation cost and large equipment. As a new method, the plasma method^{(1),(3)} has been attracting attention, because it is very compact and easily adaptable to the existing equipment with a low operation cost. Recently, the applications of a nonthermal corona discharge plasma to the

decomposition of hazardous pollutants such as NO_x and VOC⁽⁴⁾⁻⁽¹¹⁾ have been significant. Some researchers attempted to apply the nonthermal plasma for a PFC abatement system⁽¹²⁾⁻⁽¹⁸⁾. However, it was difficult to decompose CF₄ with the nonthermal plasma, because the electron energy is too low to dissolve the C-F bonds in CF₄.

As a PFC abatement system using an atmospheric-pressure high-temperature thermal plasma, Itatani et al.⁽¹⁹⁾ investigated the CF₄ removal using the combined system of the atmospheric pressure discharge arc plasma and water wall as an absorber of HF. As a result, more than 98% of CF₄ removal was achieved. Mizuno et al.⁽²⁰⁾ investigated chlorofluorocarbon (CFC) decomposition that causes ozone layer destruction using an atmospheric-pressure inductively coupled radio frequency (RF) plasma with a pilot scale plant. Because this abatement system is typically located downstream of a dry vacuum pump and operated at an atmospheric pressure, the exhaust gas is diluted hundredfold using the N₂ purge gas of the dry vacuum pump. As a result, the volume of the exhaust gas increases and the concentration of PFC decreases. Therefore, the decomposition efficiency typically decreases. Moreover, thermal NO_x is produced when the plasma temperature exceeds 800°C.

As an abatement method for PFCs using a low-

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Fig. 1 Inductively coupled pulse-modulated RF plasma system for CF_4 decomposition

pressure inductively coupled plasma, Tonnis et al.⁽²¹⁾ proposed a reduction system for PFC emissions from dielectric etching tools. Vartanian et al.⁽²²⁾ also carried out a long-term evaluation of this system. Using this type of plasma abatement system driven at a low pressure, it is possible to decompose directly the exhaust gas from the process chamber without the N_2 dilution of the dry vacuum pump. As a result, the decomposition efficiency increases and NO_x generation is avoided. In our previous study⁽²³⁾, using a double-coil-type inductively coupled plasma reactor with a 2 MHz power supply, which is a similar system to that reported by Tonnis et al.⁽²¹⁾, CF_4 was successfully decomposed. Furthermore, a performance evaluation based on the CF_4 decomposition efficiency using 2 MHz and 4 MHz power supplies was carried out as a function of power, pressure, flow rate and quantity of O_2 added⁽²⁴⁾.

On the other hand, a pulse-modulated inductively coupled RF plasma has been investigated by the recent development of controlling and switching semiconductor elements. Tanaka and Sakuta⁽²⁵⁾ and Samukawa⁽²⁶⁾ showed that plasma parameters, such as the electron and gas temperatures, can be controlled by changing the modulation frequency of an RF plasma⁽²⁷⁾ and demonstrated the possibility of the valuable applications of a pulse-modulated inductively coupled RF plasma to plasma material processing. If a pulse-modulated RF plasma is used for a PFC abatement system, more effective low energy PFC reduction may be possible, because the gas temperature decreases, keeping the electron temperature high.

In the present study, CF_4 decomposition was first performed using a pulse-modulated low-pressure inductively coupled RF plasma. When the RF current was modulated in the pulse frequency range of 25 to 99 kHz and in the duty ratio range of 50 to 99%, the CF_4 decomposition efficiency was obtained as a function of effective power. Moreover, by-products, such as CO , CO_2 and COF_2 , were analyzed using a CO_2 gas analyzer and a Fourier transform infrared spectrophotometer (FTIR).

Fig. 2 Schematic diagram of experimental setup

2. Experiments

2.1 Inductively coupled plasma reactor

The inductively coupled pulse-modulated RF plasma system for CF_4 decomposition is shown in Fig. 1. This system is manufactured by Pearl Kogyo Co., Ltd. The specifications are as follows: RF frequency = 2 MHz, maximum power = 2.0 kW, rising and falling time < 10 μs , pulse frequency = 100 Hz–99 kHz, and duty ratio (the ratio of power on period to power off period) = 5–99%. An RF signal is generated by a signal generator. Pulse modulation is performed using a switching circuit and a pulse generator. The RF signal is amplified by a power amplifier. Two variable capacitors (VC1: 100–2 000 pF and VC2: 8–1 400 pF) and a 2 500 pF capacitor are used for manual impedance matching in the circuit. An alumina tube of 330 mm length, 60 mm outer diameter, and 49 mm inner diameter is used in the plasma reactor. A 5-mm-diameter copper tube coil is wound around the alumina tube for 17 turns. The length of the reactor is 150 mm. The cooling water flows in the copper tube. The induction coil is covered by a silicone layer in order to cool the alumina tube uniformly with the cooling water.

2.2 Experimental setup and methods

A schematic diagram of the experimental setup is shown in Fig. 2. The 100% CF_4 and 99.5% O_2 gases are prepared, and the desired flow rate and concentration are

obtained by a set of mass flow controllers. Note that the CF_4 flow rate in this experiment is nearly the same as that in commercial semiconductor manufacturing equipment. In this paper, the flow rate is expressed as “NL/min” (N: normal) at 20°C and one atmosphere. The reactor is pumped down by the dry vacuum pump (Ebara Co., A30 W). The pressure in the plasma reactor is regulated by needle valves. A digital Pirani vacuum gauge (UL-VAC, Inc., GP-1 000 H) is used for pressure measurement. After the gas is diluted by N_2 purging in the dry vacuum pump, a gas sample is obtained with diaphragm pumps, and the CF_4 and CO_2 concentrations are determined by a gas chromatograph (GC) with a thermal conductivity detector (TCD) (Shimadzu Co., GC-8AI) and a CO_2 gas analyzer (Horiba, Ltd., VIA-510), respectively. The toxic

gases, such as F_2 , CO and COF_2 , produced by CF_4 decomposition are removed using an absorber prior to their exhaustion.

The power is calculated by subtracting the reflected power from the input power to the circuit displayed in the active power meter of the power supply, and the effective power is calculated by multiplying the power by the duty ratio. The applied voltage and current waveforms are measured by an oscilloscope (Tektronix Japan, Ltd., TDS210) through a voltage divider (Tektronix Japan, Ltd., P6015A) and a current probe (Tektronix Japan, Ltd., P6021). Figures 3 (a)–(c) and 4 (a)–(c) show the voltage and current waveforms of the duty ratios of 50%, 75% and 99% for a pulse frequency of 25 kHz. It is shown in Figs. 3 and 4 that

Fig. 3 Current waveform of pulse-modulated RF plasma (pulse frequency = 25 kHz; (a) duty ratio = 50%, (b) 75%, and (c) 99%)

Fig. 4 Voltage waveform of pulse-modulated RF plasma (pulse frequency = 25 kHz; (a) duty ratio = 50%, (b) 75%, and (c) 99%)

Fig. 5 Measurement procedure of reaction by-product analysis using FTIR

there are two maximum peaks in the current and voltage waveforms. This phenomenon occurs because the sampling rate is very low. The RF waveform is displayed by increasing the sampling rate. However, the sampling rate is greatly reduced by all means on the time scale to display the pulse waveform. When the duty ratios are 50%, 75% and 99%, the plasma is generated in the power off period as well, because the power off period is short (less than 30 μ s).

Moreover, in order to analyze the by-products of CF_4 decomposition, the FTIR with a mercury cadmium telluride detector (Biorad Co. FTS3000) is used. The procedure for the analysis is shown in Fig. 5. A gas sample is obtained downstream of the dry vacuum pump using a syringe. In the dilution process, after N_2 of $Q_1 = 1$ L/min is poured into the gas-sampling bag until the volume reaches 0.5 L, 16 mL gas sample is injected into the bag and diluted to 1/32.3. In the analysis process, the diluted sample flows through the gas cell (volume = 0.12 L) of the FTIR at a rate of 5 L/min. The FTIR spectrum is analyzed by a personal computer with an attached software. As a result, the peaks of the by-products of CF_4 decomposition are identified and their concentrations are measured.

3. Results and Discussion

3.1 CF_4 decomposition using pulse-modulated RF plasma

Figure 6 shows the CF_4 decomposition efficiency as a function of the effective power for a pulse frequency of 25 kHz. The pressure and CF_4 and O_2 flow rates are 80 Pa and 0.1 and 0.2 NL/min, respectively. Since 100% CF_4 is mixed with O_2 , the CF_4 concentration at the inlet of the reactor is 33%. This figure indicates that changing the duty ratio slightly affects the CF_4 decomposition efficiency and complete CF_4 decomposition is achieved with an effective power of more than 1 500 W.

Figure 7 shows the CF_4 decomposition efficiency as a function of effective power for a pulse frequency of 50 kHz. When the duty ratio is 50%, the CF_4 decompo-

Fig. 6 Effective power vs CF_4 decomposition efficiency (pulse frequency = 25 kHz)

Fig. 7 Effective power vs CF_4 decomposition efficiency (pulse frequency = 50 kHz)

sition efficiency is approximately 5% lower than that with nonpulsed modulation. When the duty ratio is 75%, the CF_4 decomposition efficiency is almost the same as that with nonpulsed modulation in the range of 0 to 1 000 W. However, a stable plasma is not generated, because it is difficult to perform plasma matching with a matching box in the range of more than 1 000 W. When the duty ratio is 99%, the CF_4 decomposition efficiency is almost the same as that with nonpulsed modulation, and complete CF_4 decomposition is achieved with an effective power of more than 1 500 W.

Figure 8 shows the CF_4 decomposition efficiency as a function of effective power for a pulse frequency of 75 kHz. It is clear that changing the duty ratio slightly affects the CF_4 decomposition efficiency. Complete CF_4 decomposition is achieved with an effective power of more than 1 500 W.

Figure 9 shows the CF_4 decomposition efficiency as a function of effective power for a pulse frequency of 99 kHz. Similar to Fig. 8, it is indicated that changing the duty ratio slightly affects the CF_4 decomposition efficiency. Complete CF_4 decomposition is achieved with an effective power of more than 1 500 W.

From these results, it is known that the pulse duty ra-

Fig. 8 Effective power vs CF₄ decomposition efficiency (pulse frequency = 75 kHz)

Fig. 9 Effective power vs CF₄ decomposition efficiency (pulse frequency = 99 kHz)

tio and frequency slightly affect the CF₄ decomposition efficiency. This is probably due to the relatively large rising time of the pulse (around 10 μs), induced by pulse modulation being performed before power amplification. CF₄ decomposition can be initiated by the cleavage of the C-F bond upon electron impact. The collision frequency and electron temperature increase by electron acceleration, resulting in an enhanced CF₄ decomposition. Since the pulse rise time is in the order of 10 μs, the electron acceleration rate is not sufficiently high for CF₄ decomposition. The pulse rise time of less than 1.0 μs is essential for effective CF₄ decomposition. It is assumed that pulse modulation performed after power amplification with a small rising time increases the CF₄ decomposition efficiency.

3.2 Analysis of by-products of CF₄ decomposition

It is considered that CF₄ decomposition proceeds according to the following reactions upon electron (e) impact^{(2), (28), (29)} induced by the plasma.

The CF₃ and CF₂ generated by the decomposition of CF₄ are converted to CO, CO₂ and COF₂ by the following

Fig. 10 Effective power vs CF₄ and CO₂ concentrations (pulse frequency = 25 kHz, duty ratio = 75%)

chemical reactions^{(18), (30)}.

In these reactions, CF₂, CF₃ and COF are unstable intermediate products and typically not detected. CO, CO₂ and COF₂ are stable by-products. Because the GWPs of these by-products are much lower (~ 1) than that of CF₄ (~ 6500), the induction of chemical reactions (1)–(9) is effective in reducing the large global warming effect of CF₄.

Figure 10 shows the CF₄ and CO₂ concentrations as a function of effective power with pulse modulation. The pulse frequency and duty ratio are set at 25 kHz and 75%, respectively. The gas is diluted approximately 55-fold by N₂ purging downstream of the dry vacuum pump. Therefore, 33% of CF₄ is diluted to around 6000 ppm without the plasma (effective power of 0 W). Since the flow rate after CF₄ decomposition is uncertain because of the variation in the mole number due to CF₄ decomposition, the concentrations of by-products upstream of the dry vacuum pump are not calculated. Therefore, the by-product concentrations are shown as the concentrations downstream of the dry vacuum pump. When complete CF₄ decomposition is achieved, around 50% of CF₄ is converted to CO₂.

Figure 11 shows the CF₄ and CO₂ concentrations as a function of effective power without pulse modulation. When complete CF₄ decomposition is achieved, 50% of CF₄ is converted to CO₂. It is known from Figs. 10 and 11 that the conversion ratio of CF₄ to CO₂ is not affected by pulse modulation.

Figure 12 shows the FTIR spectrum for the case of complete CF₄ decomposition with pulse modulation for the pulse frequency and duty ratio of 25 kHz and 75%, respectively. The pressure, effective power, and CF₄ and O₂ flow rates are 80 Pa, 1500 W, and 0.1 and 0.2 NL/min, re-

Fig. 11 Effective power vs CF_4 and CO_2 concentrations (without pulse modulation)

Fig. 12 FTIR spectrum for CF_4 decomposition using pulse-modulated RF plasma (pulse frequency = 25 kHz, duty ratio = 75%, and effective power = 1 500 W)

Fig. 13 FTIR spectrum for CF_4 decomposition using RF plasma (without pulse modulation, effective power = 1 500 W)

spectively. In Fig. 12, the peaks of CO , CO_2 , COF_2 and H_2O are identified. The H_2O peaks are produced by H_2O entering through the syringe or the gas-sampling bag during the sampling process. The by-product concentrations are analyzed using the spectral library of the attached software to FTIR; the concentrations of CO and COF_2 are identified as 610 ppm and 1 450 ppm downstream of the dry vacuum pump, respectively. The reaction by-product ratios for CF_4 decomposition, namely, the CO , CO_2 and COF_2 ratios, are 10, 50 and 24%, respectively.

Figure 13 shows the FTIR spectrum for the case of

complete CF_4 decomposition without pulse modulation. The pressure, effective power, and CF_4 and O_2 flow rates are 80 Pa, 1 500 W, and 0.1 and 0.2 NL/min, respectively. From these results, the concentrations of CO and COF_2 are calculated as 610 and 1 250 ppm, respectively. The reaction by-product ratios for CF_4 decomposition, namely, the CO , CO_2 and COF_2 ratios, are 11, 50 and 22%, respectively.

It was shown from the results of Figs. 12 and 13 that the COF_2 ratio increases and the CO ratio decreases using the pulse-modulated RF plasma. The conversion of CF_4 to COF_2 may be more desirable than that to CO because COF_2 is easily removed using a chemical scrubber with liquid calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution.

The final product CaF_2 is nontoxic and can be recycled as a material for fluorine. Because $\text{Ca}(\text{OH})_2$ is easily available and inexpensive, the removal of COF_2 can be inexpensive.

4. Conclusions

CF_4 decomposition and reaction by-product analysis were carried out using the pulse-modulated RF plasma and the following conclusions were obtained.

(1) When the pulse frequency was set at 25, 75 and 99 kHz, complete CF_4 decomposition was achieved with an effective power more than 1 500 W irrespective of the duty ratio.

(2) When the pulse frequency was set at 50 kHz with a duty ratio of 50%, the CF_4 decomposition efficiency was approximately 5% lower than that without pulse modulation. However, when the duty ratio was set at 75% and 99%, the CF_4 decomposition efficiency was almost the same as that without pulsed modulation.

(3) When the pulse frequency and duty ratio were 50 kHz and 75%, a stable plasma was not generated because impedance matching was difficult when the effective power was larger than 1 000 W.

(4) As the by-products of CF_4 decomposition, CO , CO_2 and COF_2 were identified and their concentrations were measured using the FTIR.

(5) As the reaction by-product ratios for CF_4 decomposition using the pulse-modulated RF plasma, the CO , CO_2 and COF_2 ratios were 10, 50 and 24%, respectively.

(6) It was shown that the COF_2 ratio increases by 2% and the CO ratio decreases by 1% using the pulse-modulated RF plasma. This is a desirable tendency because COF_2 is easily removed using a chemical scrubber with liquid $\text{Ca}(\text{OH})_2$ solution.

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