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Article

A Study on Greenhouse Gas(PFCs) Reduction in Plasma Scrubbers to Realize Carbon Neutrality of Semiconductors and Displays

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Abstract: Perfluorinated compounds (PFCs) are used in the manufacturing process of the semiconductor and display industries, and the need for emission reduction is growing as a greenhouse gas with a very large global warming potential. The decomposition characteristics of etch type and water film (WF) type plasma-wet scrubbers were investigated. The PFCs used in the study were CF_4, SF_6, NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8, and the destruction removal efficiency (DRE) and by-product gas generation rate according to the changes in the parameters (total flow rate and power) of the plasma-wet scrubber were confirmed. When the total flow rate was 100 L/min and the measured maximum power (11 kW), the reduction efficiency of CF_4 in the etch type was 95.60 % and the DRE of other PFCs was 99.99 %. And, in the WF type, the DRE of CF_4 was 90.06 %, that of SF_6 was 96.44 %, and that of other PFCs was 99.99 %. When the total flow rate was 300 L/min and 11 kW, the DRE of SF_6 in the etch type was 99 %, and the DRE of NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 were 99.80 %, 95.34 %, 85.38 %, 88.49 %, and 98.22 %, respectively. And, in the WF type, the DRE of SF_6 was 94.39 %, and the DRE of NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 were 99.80 %, 95.34 %, 85.38 %, 88.49 %, and 98.22 %, respectively. The by-product gas generation rate was significantly lower in the WF type.

Keywords: PFCs; Plasma-wet Scrubber; DRE; By-product

1. Introduction

Mixed gases of various compositions are used in the semiconductor and display industries, and CO_2, CF_4, SF_6, and N_2O are mainly emitted as waste gases. Perfluorocarbons (PFCs) such as CF_4, SF_6, CHF_3, and C_3F_8 are widely used in etching, deposition, and cleaning processes in semiconductor and display industries.[1-3] PFCs have a great impact on global warming because their global warming potential (GWP) and lifetime are very high compared to CO_2 and CH_4. Table 1 shows the GWP and lifetime of greenhouse gases. PFCs were designated as one of the six major greenhouse gases in the 1997 Kyoto Protocol and regulated internationally for their emissions. [4,5] Emissions of PFCs are increasing with the growth of the semiconductor and display industries. As international interest in carbon reduction increases, reduction of PFCs is necessary.[6,7]

As a way to reduce PFCs emissions, process optimization, recycling/recovery, and reduction technologies are proposed. Among gases with low GWP, there is no gas that can replace PFC, and it takes a long time to develop alternative gases. In addition, semiconductor and display manufacturing processes are complex, making it difficult to optimize processes for reduction or implement recycling and recovery facilities.[8-11] Scrubbers used in the semiconductor and display industries were initially developed to remove air pollutants. As interest in greenhouse gas emissions increased, scrubbers were developed and improved to handle greenhouse gases as well.[12]

There are various types of scrubbers such as burn, heat, and plasma, and the treatment efficiency is high in the order of heat, burn, and plasma.[13] In order to increase PFCs treatment, wet treatment facilities are combined at the rear of the reduction device to be used as burn-wet, plasma-wet, etc.[14] In industrial sites, burn-wet scrubbers are mainly used. Research on the plasma-wet type, which has higher PFCs destruction removal efficiency (DRE) than the burn-wet type, is being actively conducted, and its utilization in the field is increasing accordingly. Plasma scrubber research was mainly

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conducted by improving the plasma torch[15] and improving the wet processing structure.[16] However, the DRE of PFCs was mainly measured and only the type of by-product gas of each PFCs was confirmed, but no study was conducted on the amount of by-product gas generated by each PFC.

In this study, the DRE and by-product gas generation rate of the Plasma-wet scrubber, which is increasingly used in the field, was measured. Plasma-wet scrubbers were divided into etch type and water film type, and the DRE and by-product gas generation rates for the two scrubber types were measured and compared.

Table 1. Global warming potential and Lifetime of greenhouse gases(AR6)[17].

Greenhouse gases	Lifetime (year)	GWP_{100}
CO_2	50–200	1
CH_4	12	27
CF_4	50 000	7 380
SF_6	3 200	24 300
C_2F_6	10 000	12 400
CHF_3	222	14 600
C_3F_8	2 600	9 290
C_4F_8	3 200	10 200
NF_3	500	17 400

2. Materials and Methods

2.1. Composition of Plasma-wet scrubber

Figure 1 shows the configuration of Plasma-wet scrubber. Plasma-wet scrubber is composed of inlet part, plasma system, pyrolysis reactor, gas quenching part and wastewater circulation tank, wet spray tower, and outlet part. When waste gas such as PFCs enters the inlet part, it comes into contact with the arc plasma generated by the plasma system and rises up in the pyrolysis reactor to decompose. The high-temperature gas is cooled in the quenching part, and by-products are treated in the wet spray tower, and the wastewater is stored in the circulation tank and discharged. The treated gas is discharged through the outlet part.[18]

Figure 2 shows the setup of the plasma-wet scrubber used in this study. Plasma-wet scrubber is divided into an etch type for waste gas treatment in the etching process and a water film type for waste gas treatment in the chemical vapor deposition (CVD) process. In the case of the etch type, water is sprayed from the gas quenching part located below the pyrolysis reactor part. In the case of the water film type, a water film is formed inside the pyrolysis reactor.

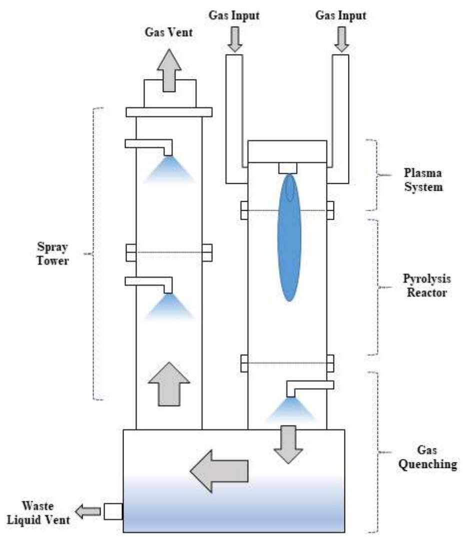

Figure 1. Schematic diagram of plasma-wet scrubber.

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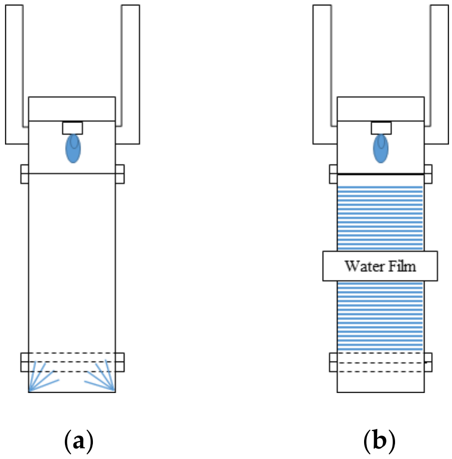

Figure 2. Schematic diagram of etch type(a) and water film type(b).

2.2. Experiment setup and methods

Figure 3 illustrates the experiment set up that was used in this study. The kinds of gas used were CF_4, SF_6, NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8, and high purity (99.999 %) was used. The flow rate of the target gas was adjusted using a mass flow meter (MFC; M3030V, LINE TECH Co., Korea), and the concentration of the PFCs gas was adjusted to 4 000 to 5 000 μmol/mol by mixing with nitrogen gas (99.999 %) to be injected into the plasma-wet scrubber (NSPW600Plus, GnBS eco, Korea). The flow rate injected into the Plasma-wet scrubber is 100, 300 L/min, which includes nitrogen and air, which are essential during scrubber operation. Plasma-wet scrubbers range in power from 6 to 11 kW. FTIR (Gasmet DX4000, Gasmet Co., USA) was used to measure the inlet and outlet concentrations of the Plasma-wet scrubber. For the gas cell of FT-IR, a 60 cm long cell was used in the inlet measurement and a 500 cm long cell was used in the outlet measurement. The inlet and outlet flow rates of the plasma-wet scrubber were measured using QMS (isepa-S, el Co., Korea). Table 2 shows the experimental operating conditions of detail.

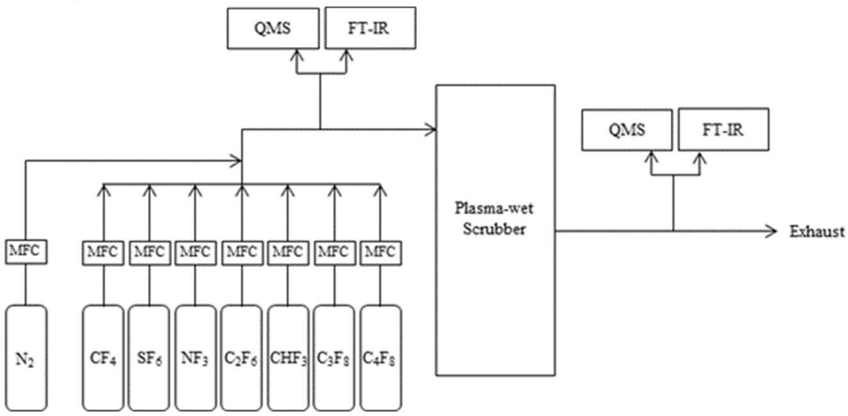

Figure 3. Schematic diagram of experiment.

Table 2. Operating conditions used experiment.

Operating condition	Parameter
Input power (kW)	6 - 11
Total gas flow rate (L/min)	100, 300
N_2 plasma gas flow rate (L/min)	40 ~ 50
Reactive injection gas(air) flow rate(L/min)	0.8 ~ 2
Concentration of PFCs (μmol/mol)	4 000 - 5 000

2.3 Calculation of PFCs

The DRE of PFCs can be defined as follows[19]:

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$$DRE\ of\ PFCs\ (\%) = (1 - \frac{V_{out}}{V_{in}}) \times 100 \quad (1)$$

$$V_{in} = C_{in} \times Q_{in} \quad (1)$$

$$V_{out} = C_{out} \times Q_{out} \quad (1)$$

Where, V_{in} : Inlet volume-flow of PFCs (L/min)
V_{out} : Outlet volume-flow of PFCs (L/min)
C_{in} : Inlet concentration of PFCs (μmol/mol)
C_{out} : outlet concentration of PFCs (μmol/mol)
Q_{in} : inlet flow of PFCs (L/min)
Q_{out} : outlet flow of PFCs (L/min)
The Generation rate of by-products can be defined as follows:

$$\text{Generation rate of By} - \text{products}\ (\%) = \frac{V_{bp}}{V_{in}} \times 100 \quad (1)$$

$$V_{bp} = C_{bp} \times Q_{out} \quad (1)$$

Where, V_b : Outlet volume-flow of by-products (L/min)
C_{bp} : Outlet concentration of by-products (μmol/mol)

3. Results

3.1. Decomposition of PFCs in etch type

Figure 4(a) shows the DREs of CF_4, SF_6, CHF_3, C_2F_6, C_3F_8, and C_4F_8 when the flow rate is 100 L/min in the etch type. The DREs of SF_6, NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 were maintained above 99 % regardless of power change. The DRE of CF_4 increased from 72.45 % at 8 kW to 95.60 % at 11 kW with increasing power, but the DRE was lower compared to other gases.

Figure 4(b) shows the DREs of SF_6, CHF_3, C_2F_6, C_3F_8, and C_4F_8 when the flow rate is 300 L/min in the etch type. As the power is higher, the DRE of SF_6 increases from 96.57 % to 99.99 %, and the DRE is 99.99 % at the power of 8 kW, maintaining the DRE up to 11 kW. The DRE of NF_3 increases from 49.32 % to 95.57 % as the power increases, and from 10 kW, the DRE is over 90 %. The DRE of C_4F_8 increases from 94 % to 98.59 % as the power increases, and from 6 kW, the efficiency is higher than 90 %. In the case of CHF_3, C_2F_6, and C_3F_8, as the power increased, the DRE increased from 62.42 %, 49.17 %, and 38.35 % to 87.06 %, 70.74 %, and 81.45 %, respectively.

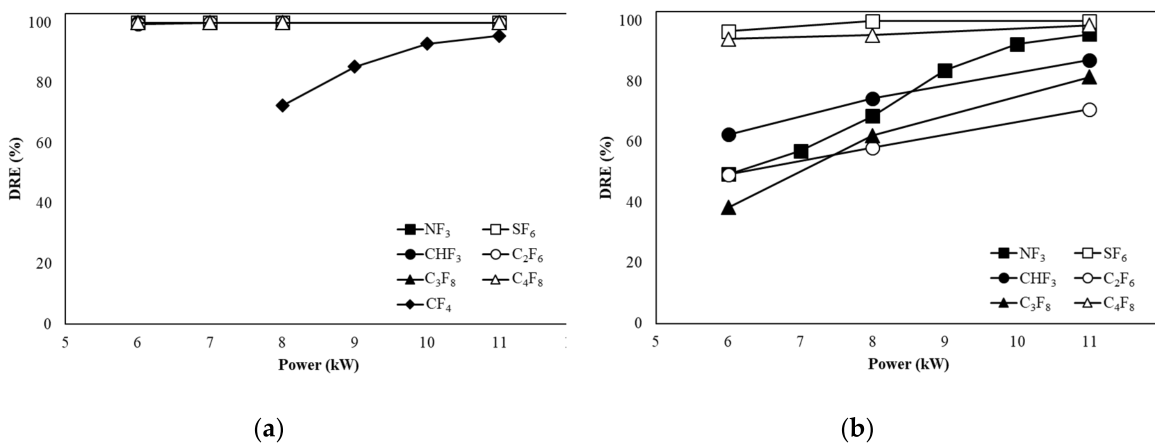

Figure 4. In the etch type, decomposition of PFCs with power change at a flow rate of 100 L/min(a) and at a flow rate of 300 L/min(b).

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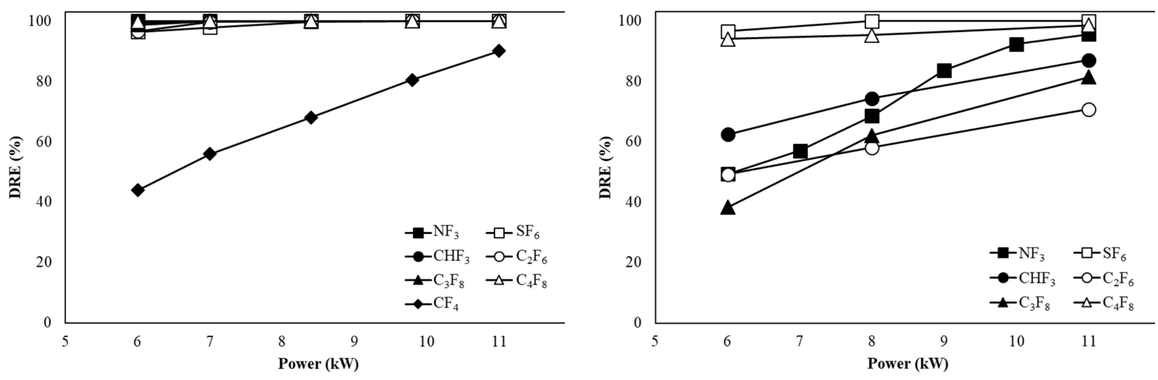
3.2. Decomposition of PFCs in WF type

Figure 5(a) shows the DREs of CF_4, SF_6, CHF_3, C_2F_6, C_3F_8, and C_4F_8 when the flow rate is 100 L/min in the water film(WF) type. As the power increased, the DREs of SF_6, CHF_3, C_2F_6, C_3F_8, and C_4F_8 increased from 96.44 %, 99.30 %, 96.60 %, 98.74 %, and 99.93 % to 99.99 %, respectively. In the case of CF_4, the DRE value increased from 43.96 % to 90.06 % as the power increased from 6 to 11 kW, but the DRE was lower compared to other gases. In the case of NF_3, the DRE was 99.99 % from 6 kW regardless of the power increase.

Figure 5(b) shows the DREs of SF_6, CHF_3, C_2F_6, C_3F_8, and C_4F_8 when the flow rate is 300 L/min in the WF type. In the case of SF_6, it increased from 88.91 % to 94.39 % as the power increased. In the case of NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8, the DRE at 6 kW was as low as 60.21 %, 58.21 %, 54.08 %, 32.67 %, and 46.60 %. However, the DREs of NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 at 11 kW were 99.80 %, 95.34 %, 85.38 %, 88.49 %, and 98.22 %, respectively.



(a) (b)

Figure 5. In the WF type, decomposition of PFCs with power change at a flow rate of 100 L/min(a) and at a flow rate of 300 L/min(b).

3.3. DRE of etch and WF type

Figure 6 shows the DRE of CF_4 in the etch type and WF type when the flow rate is 100 L/min. When CF_4 is decomposed, it requires a high temperature. In the case of the WF type, the temperature inside the reactor is lower than that of the etch type due to the water film, so the decomposition of CF_4 did not occur well.

Figure 7 shows the DRE of SF_6, NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 in the etch type and WF type when the flow rate is 300 L/min and the power is 11 kW. In the case of SF_6, the DRE of the etch type was higher than that of the WF type. In the WF type, due to the water film, the temperature inside the reactor was lower than that of the etch type, which inhibited the decomposition of SF_6, which requires a high temperature for decomposition. In the case of NF_3, CHF_3, C_2F_6, and C_3F_8, DRE was higher in the WF type than in etch type. The water film prevented recombination of each gas and the conversion to HF occurred well. In the case of C_4F_8, the DREs of the etch type and the WF type were similar.

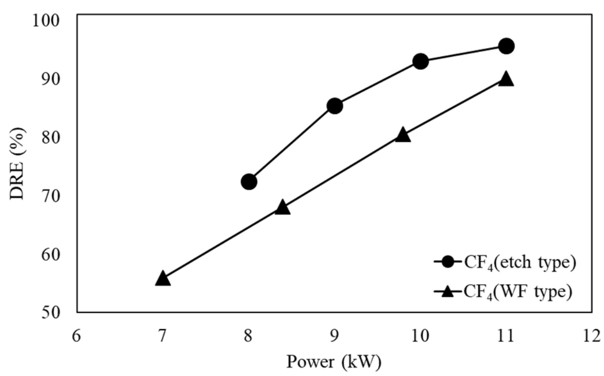


Figure 6. Decomposition of CF_4 in etch type and WF type.

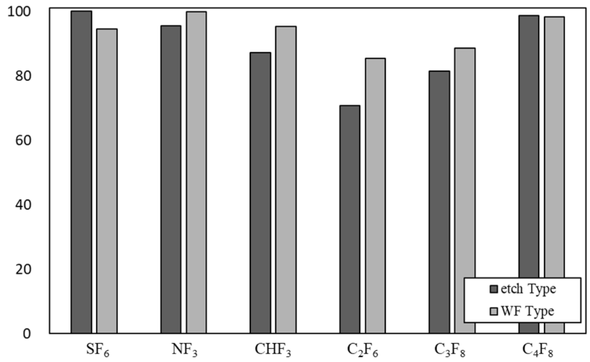


Figure 7. Decomposition of PFCs in etch type and WF type.

3.4. Rate of by-product gas generation

The rate of by-product gas generation was calculated by the amount of by-product gas generation for C_2F_6, CHF_3, C_3F_8, and C_4F_8 where F gases such as CF_4 and C_2F_6 are generated as by-product gases. The amount of by-product gas generation was measured at a flow rate of 100 L/min and power of 7 kW. Figure 8(a) shows the by-product gas generation rate of CHF_3 in the etch type. The pure DRE calculated considering the by-product gas generation rate was 89.54 %, and the by-product gas generation rate was confirmed to be 10.40 %. As for by-product gas, CF_4 was high at 99.92 % of the by-product gas generation rate, and C_2F_6 was generated as little as 0.08 %. Figure 8(b) shows the by-product gas generation rate of CHF_3 in WF type. It was confirmed that the pure DRE calculated considering the by-product gas generation rate was 99.93 % and the by-product gas generation rate was 0.002 %, showing a very low generation rate. A small amount of CF_4 was generated as a by-product gas.

Figure 9(a) shows the by-product gas generation rate of C_2F_6 in the etch type. The pure DRE calculated considering the by-product gas generation rate was 65.21 %, and the by-product gas generation rate was confirmed to be 34.76 %. Only CF_4 was generated as a by-product gas. Figure 9(b) shows the by-product gas generation rate of C_2F_6 in WF type. It was confirmed that the pure DRE calculated considering the by-product gas generation rate was 99.62 % and the by-product gas generation rate was 0.06 %, showing a very low generation rate. A small amount of CF_4 was generated as a by-product gas even in the WF type.

Figure 10(a) shows the by-product gas generation rate of C_3F_8 in the etch type. The by-product gas generation rate of C_3F_8 is 130.58 %, and more by-product gas is generated than the amount of injected C_3F_8. As for by-product gas, CF_4 was high at 99.92 %, C_2F_6 was 0.05 %, and CHF_3 was low at 0.001 %. Figure 10(b) shows the by-product gas generation rate of C_3F_8 in WF type. The by-product gas generation rate of C_3F_8 was 0.09 %, and the pure DRE calculated considering the by-product gas generation rate was confirmed to be 99.76 %. In the WF type, a small amount of CF_4 was generated as a by-product of C_3F_8.

Figure 11(a) shows the by-product gas generation rate of C_4F_8 in the etch type. The by-product gas generation rate of C_4F_8 is 146.95 %, and more by-product gas is generated than the amount of injected C_4F_8. Among the by-product gases, CF_4 was high at 99.97 % and C_2F_6 was low at 0.03 %. Figure 11(b) shows the by-product gas generation rate of C_4F_8 in WF type. The by-product gas generation rate of C_4F_8 was 20.19 %, which was less than that of the etch type, and the pure DRE calculated considering the by-product gas generation rate was confirmed to be 79.80 %. In the WF type, as a by-product gas of C_4F_8, CF_4 was generated at 99.99 % and C_2F_6 at 0.01 % among the by-product gas generation rates. The rate of by-product gas generation in the WF type is significantly lower than that of the etch type. In the WF type, the water film prevents the recombination of PFCs, which generate a lot of by-product gases, and facilitates conversion to HF, so that the generated by-products can be treated well.

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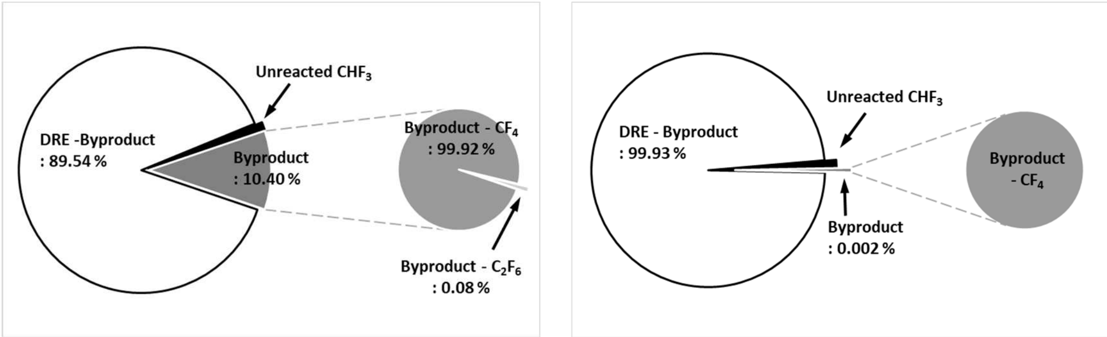
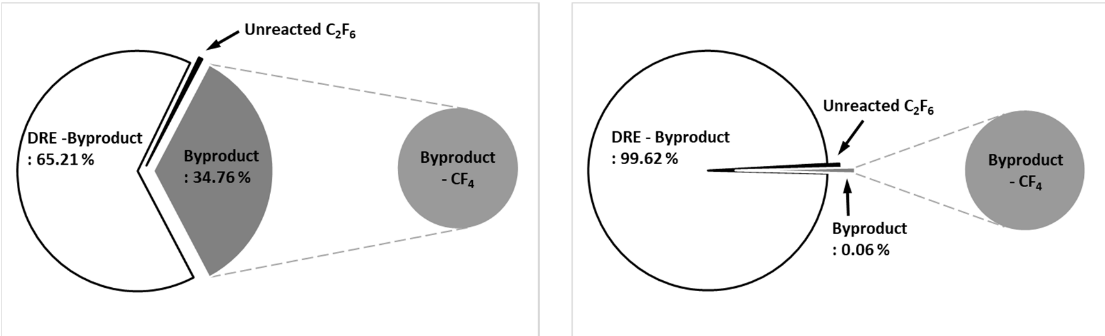


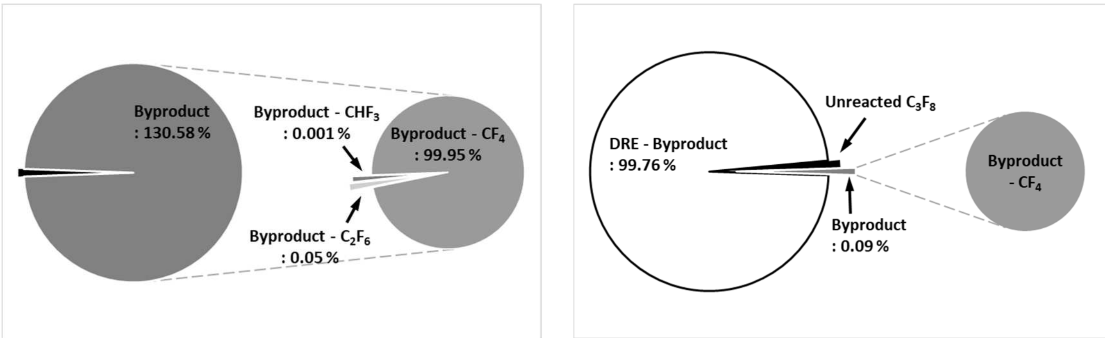
(a) (b)

Figure 8. By-product generation rate of CHF_3 in etch type(a) and WF type(b).



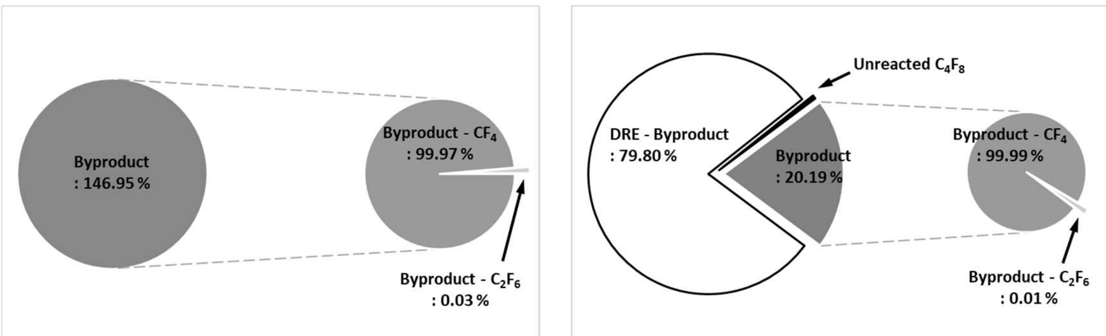
(a) (b)

Figure 9. By-product generation rate of C_2F_6 in etch type(a) and WF type(b).



(a) (b)

Figure 10. By-product generation rate of C_3F_8 in etch type(a) and WF type(b).



(a) (b)

Figure 11. By-product generation rate of C_4F_8 in etch type(a) and WF type(b).

4. Conclusions

In this study, in order to find out the decomposition characteristics of each type of plasma-wet scrubber, an experiment was conducted to find the DRE and by-product gas generation rate according to the parameter change of the etch type and WF type plasma-wet scrubbers. At 100 L/min and 11 kW in the etch type, the DRE of CF_4 was 95.60 %, and the other gases maintained 99.99 % from 6 to 11 kW. At 300 L/min and 11 kW, the reduction efficiencies of SF_6, NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 were 99.99 %, 95.57 %, 87.06 %, 70.74 %, 81.45 %, and 98.59 %, respectively. At 100 L/min and 11 kW in the WF type, the DRE of CF_4 was 90.06 % and the DRE of SF_6 was 96.44 %, and most of the other gases showed a DRE of 99.99 %. In addition, at 300 L/min and 11 kW, the DREs of SF_6, NF_3, CHF_3, C_2F_6, C_3F_8, and C_4F_8 were 94.39 %, 99.80 %, 95.34 %, 85.38 %, 88.49 %, and 98.22 %, respectively.

In the etch type, the DRE of CF_4 and SF_6 was smaller than that of the WF type. It seems that the temperature inside the reactor is lower than that of the etch type, so that decomposition does not occur properly, and the DRE is lowered. In addition, the DRE of WF was high at the total gas flow rate of 300 L/min. It seems that recombination was prevented by the water film and the DRE was increased. Therefore, in the process using CF_4 and SF_6, the etch type is considered, and in the process using other gases, the WF type is considered.

It was confirmed that the by-product gas generation rate showed a significant decrease in the WF type compared to the etch type. This seems to have reduced the generation of by-product gases by converting to HF before being decomposed into by-product gases such as CF_4 and C_2F_6 due to water film, and by-products being treated. Therefore, in the case of a process using C_3F_8 and C_4F_8, which generate a lot of by-product gas, the use of the WF type is considered. The performance of each type of plasma scrubber was confirmed, and it is thought that it can be used as basic data for carbon neutrality in the semiconductor and display industries.

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