



# Study on plasma characteristics and gas analysis before and after recovery using liquid-fluorocarbon precursor

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## ARTICLE INFO

### Keywords:

L-FC(Liquid-Fluorocarbon)  
Etching  
GWP  
Plasma

## ABSTRACT

Perfluorocarbon (PFC) gas is a representative greenhouse gas with high global warming potential (GWP) and is mainly used in the etching processes applicable to the manufacture of semiconductor devices. High capacity and high integration have been achieved in recent years as semiconductor device structures have been replaced by vertical layer structures, and the consumption of PFC gas has exploded due to the increase in high aspect ratio and patterning processes. In this study, the etching and recovery process were performed using  $C_5F_8$  in L-FC which is in liquid phase at room temperature. This is because the ratio of F and C constituting  $C_4F_8$ , which is a PFC gas used for conventional etching, is similar. In addition, the recovered  $C_5F_8$  was injected back into the chamber to confirm its reusability, and the electron temperature, plasma density, and ion energy distribution were analyzed. In addition, based on these data, the Si and  $SiO_2$  etching process requiring high selectivity was applied using the gas obtained before and after recovery. An analysis of the surface composition of Si and  $SiO_2$  after the etching process confirmed the possibility of recovering and reusing the exhaust gas during the process.

## 1. Introduction

Perfluorocarbon (PFC) gases such as  $CF_4$ ,  $C_2F_6$ ,  $C_3F_8$ , and  $C_4F_8$  are typical gases used in the semiconductor and display industries. Especially in the semiconductor process, this is a representative greenhouse gas that is primarily used during the etching process in the manufacture of ultra-scale integrated circuits (ULSIs) and in cleaning after the Chemical Vapor Deposition (CVD) process [1–13]. In recent years, the structure of semiconductor devices has been changing rapidly: the use of vertical layers for high capacity and high integration, and PFC gas consumption is exploding due to the increase of high aspect ratio processes and processes requiring patterning. These gases are physicochemically stable and have high Global Warming Potential (GWP). They are classified as representative greenhouse gases that promote global warming. Therefore, many researchers have been working on how to decompose, recover, and reuse the gas after the etching process to reduce the emissions of PFC gas [12–14]. Marilena Roduiu group discusses how to treat greenhouse gases by plasma decomposition [15]. In this method, secondary byproducts that may cause additional environmental pollution are generated. In particular, because it decomposes even the pure gas that is exhausted without reacting in the process, it is limited by the huge loss incurred in terms of cost. The Kim group also discusses the recovery of unreacted pure gases

using membranes [16]. In this case, manufacturing a membrane for the selective separation of high PFC gas is difficult. The requirement of a variety of expensive pressurization and additional devices for the separation is a disadvantage. James J. Spivey conducted a study aimed at recovering the gases generated during the plasma process by adsorption [17]. The advantage of this method is that the structure of the adsorption module is relatively simple and high-purity process gas can be recovered. However, the application of this method is difficult when using a conventional PFC gas with a very low boiling point, and the method is limited by low efficiency. However, this problem can be solved by the Fluorocarbon Precursor, which is liquid at room temperature due to its high boiling point, resulting in better adsorption at higher temperatures compared to conventional PFC gases. Thus, research on liquid fluorocarbon (L-FC) in liquid phase at room temperature has been carried out not only in terms of adsorption and reuse, but also in a bid to replace existing PFC gas with high GWP. Among the L-FCs,  $C_5F_8$  gas has a high C/F ratio; similar to that of the  $C_4F_8$  gas, which is a conventional PFC gas. Thus, as an alternative, many studies have proposed the use of  $C_5F_8$  gas for etching due to its high selectivity of  $SiO_2$  to Si [18–20].

In this study, the etching process was performed using  $C_5F_8$  gas in L-FC, and the unreacted etching gas produced after the process was adsorbed and recovered through the adsorption module. The plasma and

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<https://doi.org/10.1016/j.apsusc.2020.147358>

Received 2 March 2020; Received in revised form 9 July 2020; Accepted 23 July 2020

Available online 01 August 2020

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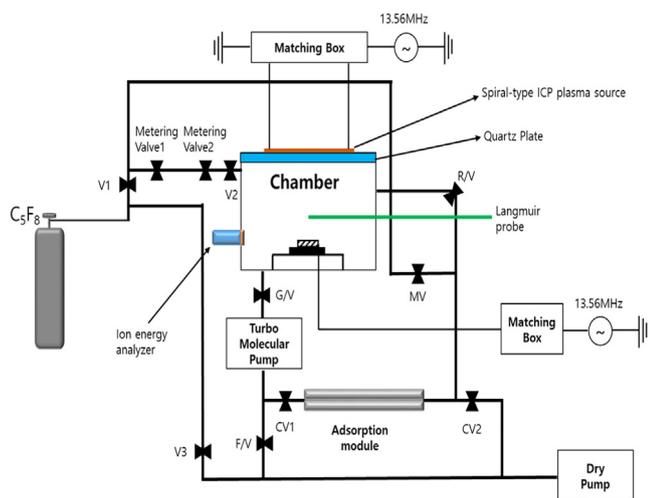


Fig. 1. Schematic diagram of an ICP etching system with adsorption and recovery modules installed.

the surface composition of the wafer etched by the plasma was analyzed after the use of C<sub>5</sub>F<sub>8</sub> gas before and after recovery. Based on these experimental data, the reliability of the etch processes performed through the recovered C<sub>5</sub>F<sub>8</sub> gas was evaluated, and the possibility of reusing the recovered C<sub>5</sub>F<sub>8</sub> gas was confirmed.

## 2. Experimental

Fig. 1 shows a schematic of an inductively coupled plasma (ICP) etching system with adsorption and recovery modules installed. The chamber is cylindrical, with an inner diameter of 260 mm and a height of 400 mm. A spiral-type antenna with a diameter of 7 mm was used as a source of plasma discharge, and 20 mm thick quartz was used between the plasma and the antenna for stable power transfer. The distance between the plasma source and the substrate was 115 mm and the diameter of the substrate was 125 mm. The installed adsorption module was 200 cm long and consisted of a heater for vaporization, a liquid nitrogen inlet for adsorption, and six thermocouple gauges for temperature measurement. By simultaneously operating the liquid nitrogen and the heater to control the optimum adsorption temperature for various gases, the temperature of the adsorption module could be maintained within  $-200\text{ }^{\circ}\text{C}$  and  $200\text{ }^{\circ}\text{C}$ . C<sub>5</sub>F<sub>8</sub> was used as the process gas in this experiment. Compared to the conventional PFC gas, the boiling point is relatively high; therefore, L-FC which exists in the liquid phase at room temperature has the advantage of being easily recovered by adsorption. The boiling points for various PFC gases and L-FCs are shown in Table 1.

C<sub>4</sub>F<sub>8</sub>, which is widely used for selective etching of Si and SiO<sub>2</sub>, is

Table 1  
PFCs and L-FCs according to boiling and melting points.

PFC	Chemical name	Chemical Formula	Melting Point(°C)	Boiling Point (°C)
	Carbon Tetrafluoride	CF <sub>4</sub>	-183.6	-127.8
	Hexafluoroethane	C <sub>2</sub> F <sub>6</sub>	-100.6	-78.2
	Octafluoropropane	C <sub>3</sub> F <sub>8</sub>	-183	-36.7
	Perfluorocyclobutane	c-C <sub>4</sub> F <sub>8</sub>	-40.1	-5.8
	Trifluoromethane	CHF <sub>3</sub>	-155.2	-82.1
L-FC	Chemical name	Chemical Formula	Melting Point(°C)	Boiling Point (°C)
	Perfluorocyclopentene	C <sub>5</sub> F <sub>8</sub>	-70	27
	Octafluorotoluene	C <sub>7</sub> F <sub>8</sub>	-65.6	104.8
	Perfluorobutyl iodide	C <sub>4</sub> F <sub>9</sub> I	-68	67
	Hexafluorobenzene	C <sub>6</sub> F <sub>6</sub>	5.2	80.2
	2H,3H-Decafluoropentane	C <sub>5</sub> H <sub>2</sub> F <sub>10</sub>	-80	55

clearly difficult to recover because it exists in a gaseous state at room temperature and has a boiling point of  $-6\text{ }^{\circ}\text{C}$ . On the other hand, L-FC, such as C<sub>5</sub>F<sub>8</sub> is easy to recover because it exists in the liquid phase at room temperature owing to its boiling point ( $26\text{ }^{\circ}\text{C}$ ). Considering these characteristics, research on adsorption and recovery using C<sub>5</sub>F<sub>8</sub> was conducted. A dry pump (Ebara, 20 × 40) was used to create a low vacuum of  $2 \times 10^{-3}$  Torr and a TMP (Turbo-molecular pump, Varian, ATH 1600 M) was used as a secondary pump to create a high vacuum of  $5 \times 10^{-6}$  Torr. For accurate pressure measurement during the process, three baratron gauges were installed. The first gauge was mounted on the side of the chamber, the second and third gauges were mounted before and after the adsorption module to measure the pressure change caused by gas adsorption. The module was cooled with liquid nitrogen while the specimen heaters maintained accurate localized temperature control. In order to find the optimum temperature for adsorption, the temperature of the adsorption module was increased by intervals of  $20\text{ }^{\circ}\text{C}$  starting from  $-140\text{ }^{\circ}\text{C}$  and the pressure change before and after the adsorption module was observed. A study on adsorption was carried out while the plasma etching process using C<sub>5</sub>F<sub>8</sub> gas was performed in order to observe the adsorption characteristics caused by impurities generated during the etching process. Ar was mixed with C<sub>5</sub>F<sub>8</sub> etching gas for stable discharge. Etching was performed for 5 min under process conditions of 10 mTorr, 100 W of source power (13.56 MHz of rf generator, Dressler Cesar 1330) and  $-100\text{ V}$  DC Bias voltage (13.56 MHz of RF generator, Youngshin RF, YSR-06MF). After the etching process, the adsorption module was isolated using the valves before and after, and the C<sub>5</sub>F<sub>8</sub> gas adsorbed during the etching process was recovered to the chamber through vaporization using a heater. In order to evaluate the applicability and reliability of the recovered gas to the process, characteristic analysis through the plasma and etching process according to various input power changes and DC bias voltage changes was conducted.

Residual Gas Analyzer (RGA, Extorr XT300) was used to compare the component analysis of pure C<sub>5</sub>F<sub>8</sub> gas and adsorbed gas during the plasma etching process. In addition, Langmuir probe (Impedans Inc.) was used for characterization such as plasma density and electron temperature according to the etching gas before and after recovery. In order to analyze the ion energy distribution before and after recovery, an ion energy analyzer (Impedans, Semion) was installed and measured. The sensor of the ion energy analyzer was located at the center of the substrate. In addition, SiO<sub>2</sub> and Si samples of size  $10\text{ mm} \times 10\text{ mm}$  were used to analyze the surface characteristics of wafers etched with plasma using C<sub>5</sub>F<sub>8</sub> gas before and after recovery. After the etching process, XPS (X-ray Photoelectron Spectrometer, Thermo Fisher Scientific K-Alpha + XPS) was used to compare the chemical composition of the surface and the thickness of the CF polymer layer.

## 3. Results and discussion

Fig. 2 shows the experimental results of pressure change with temperature of the adsorption module using C<sub>5</sub>F<sub>8</sub> gas. The process pressure was varied from 5 to 15 mTorr to investigate the change in adsorption characteristics. In order to find the optimum temperature for adsorption, the temperature of the adsorption module was increased starting from  $-140\text{ }^{\circ}\text{C}$  to  $-100\text{ }^{\circ}\text{C}$  and the pressure change of the adsorption module was observed with baratron gauges.

During the adsorption process, the chamber pressure remained nearly constant regardless of the temperature of the adsorption module. However, a sudden pressure change in the adsorption module was observed when the temperature of the module was approximately  $-100\text{ }^{\circ}\text{C}$  to  $-80\text{ }^{\circ}\text{C}$ . This shows that adsorption begins within the temperature range of approximately  $-80\text{ }^{\circ}\text{C}$ . In addition, when the process pressure was 15 mTorr rather than 5 mTorr, a severe pressure change of more than 10% was observed in the adsorption module. This confirmed that more process gas was adsorbed as the process pressure increased. Thus, the higher the process pressure, the shorter the mean

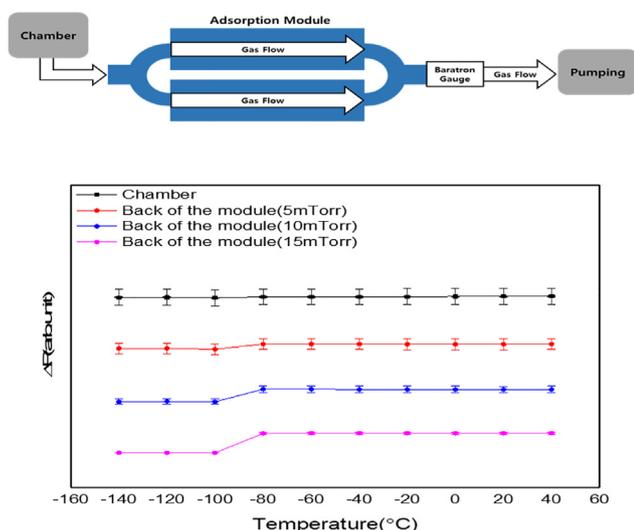


Fig. 2. Pressure change with temperature of adsorption module using C<sub>5</sub>F<sub>8</sub> gas.

free paths of the gas, resulting in many collisions with the surface of the adsorption module and improvement in the adsorption efficiency.

In general, many etching byproducts and various decomposition species are generated during the etching process. However, if they are adsorbed to the adsorption module used in this study, their reuse is expected to be extremely problematic. Fig. 3 shows the results of the RGA analysis of the residual gas in the chamber before and after recovery to determine whether pure C<sub>5</sub>F<sub>8</sub> gas was selectively recovered by adsorption. Since the gas adsorbed and recovered during the etching process may contain etching by-products compared to pure gas, the adsorption and recovery processes were performed by etching Si and SiO<sub>2</sub> samples under the conditions of 10 mTorr of operation pressure with C<sub>5</sub>F<sub>8</sub> and Ar 1: 9 mixed and 200 W of input power. The RGA analysis before and after recovery were performed under the same conditions without plasma. As can be seen in the figure, the main peaks of C<sub>5</sub>F<sub>8</sub> are amu 93, 143, 162, 193, and 212, and the related peaks were detected in the etching gas both before and after recovery. In addition, the peaks of the other components except C<sub>5</sub>F<sub>8</sub> were confirmed to be the same in the analysis results of the gas before and after recovery. These results confirmed that only the relatively pure C<sub>5</sub>F<sub>8</sub> etching gases could be selectively adsorbed and recovered by controlling the temperature of the adsorption module.

Fig. 4 shows the results of plasma density and electron temperature measured to investigate plasma characteristics using recovered gas. For comparison analysis, the recovery was measured under 10 mTorr of a process pressure using C<sub>5</sub>F<sub>8</sub>/Ar mixed gas before and after recovery. Plasma density and electron temperature were measured using

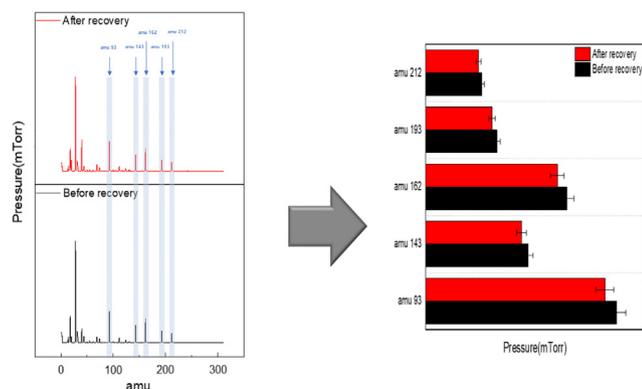


Fig. 3. RGA analysis of the residual gas in the chamber before and after recovery.

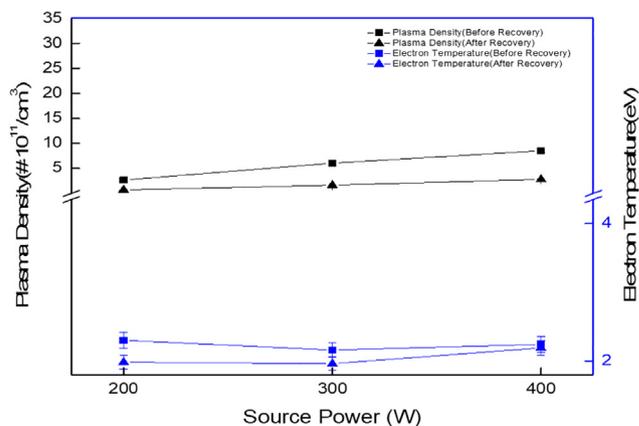


Fig. 4. Plasma density and electron temperature measured to investigate plasma characteristics using recovered gas.

Langmuir probe with increasing ICP source power from 100 W to 300 W.

Overall, plasma density increased linearly with increasing ICP source of power and a high density of  $1.3 \times 10^{11}/\text{cm}^3$  was obtained. No significant change was observed in the case of electron temperature and approximately 2.4 eV according to the ICP source power, was maintained. In addition, both pure C<sub>5</sub>F<sub>8</sub> gas and recovered C<sub>5</sub>F<sub>8</sub> gas exhibited the same tendency, and it was confirmed that a slight difference in measurement values converged within the measurement error range of the Langmuir probe. This indicates that C<sub>5</sub>F<sub>8</sub> plasma has the same characteristics before and after recovery.

Although it was confirmed that the measured electron temperature and plasma density were almost the same before and after recovery, if the ion energy distribution was changed by the small difference of electron temperature, the species of ion generated by decomposition in plasma could be changed. As this may be an unwanted variable in the nano-process requiring precise etching, the ion energy distribution of C<sub>5</sub>F<sub>8</sub> plasma was measured before and after recovery using of an ion energy analyzer.

Fig. 5 shows the result of ion energy distribution measured with varying input power from 100 W to 300 W and 10 mTorr of C<sub>5</sub>F<sub>8</sub>/Ar mixed gas before and after recovery. Evidently, the ion energy distribution of the C<sub>5</sub>F<sub>8</sub> plasma before and after recovery showed that the peak intensity and energy band were identical within the error. In addition, as the source power increased, the peak intensity and the energy band exhibited the same trend. Through this, the species of ions generated by decomposition in C<sub>5</sub>F<sub>8</sub> plasma before and after recovery is similar, and the same etch results will be shown because they are incident on the substrate with similar energy distribution.

In general, the higher the thickness of the CF polymer layer deposited on the etched sample surface, the higher the selectivity of SiO<sub>2</sub> to Si has been reported through many previous studies [21–25]. As such, the thickness of the CF polymer layer has great influence on

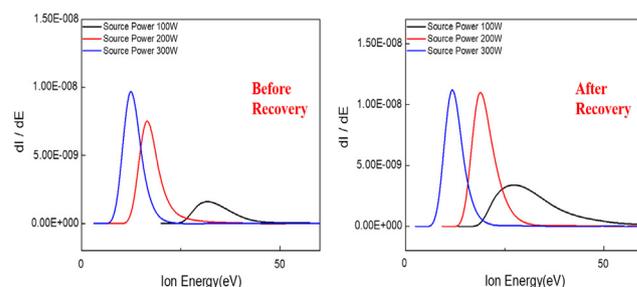


Fig. 5. IEDF measured with varying input power from 100 W to 300 W and 10 mTorr of C<sub>5</sub>F<sub>8</sub>/Ar mixed gas before and after recovery.

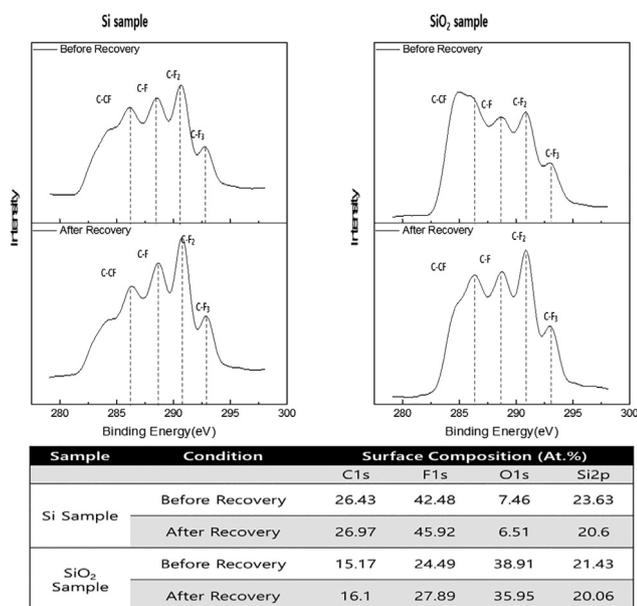


Fig. 6. XPS analysis of Si and SiO<sub>2</sub> samples etched with C<sub>5</sub>F<sub>8</sub>/Ar mixed gas before and after recovery.

etching characteristics such as selectivity. In this regard, the surface of the sample after etching for the Si and SiO<sub>2</sub> samples was analyzed using C<sub>5</sub>F<sub>8</sub> etching gas before and after recovery. Fig. 6 shows the results of XPS analysis of the surface of Si and SiO<sub>2</sub> samples etched with C<sub>5</sub>F<sub>8</sub>/Ar mixed gas before and after recovery. The experimental conditions were etched for each sample for 5 min at 100 W of ICP source power and -100 V of bias voltage at 10 mTorr of process pressure with C<sub>5</sub>F<sub>8</sub>/Ar mixed gas. As a result of irradiating the etched sample surface with XPS, the chemical composition of the Si sample surface etched by the C<sub>5</sub>F<sub>8</sub>/Ar mixed gas before and after recovery are equal within the error range, and the same was true for the SiO<sub>2</sub> sample.

In the case of the Si sample, the intensity of C-CF (286.6 eV), C-F (288.8 eV), C-F<sub>2</sub> (290.1), and C-F<sub>3</sub> (293.2 eV) was much higher than that of the SiO<sub>2</sub> sample. In the case of SiO<sub>2</sub>, the C component of the etching gas reacts with O in SiO<sub>2</sub> and is outputted in the form of CO and CO<sub>2</sub>, but in the case of Si, it was deposited in the form of CF polymer. Upon calculating the CF polymer layer thickness from the photoemission intensities of the etched Si and SiO<sub>2</sub> sample surfaces, the CF polymer layer thickness of Si was about 68% thicker than that of SiO<sub>2</sub>. These results suggest that the use of a new type of precursor, C<sub>5</sub>F<sub>8</sub>, will enable the high selectivity etching of SiO<sub>2</sub>/Si as in previous studies [21–25].

#### 4. Conclusions

In this study, an etching process using C<sub>5</sub>F<sub>8</sub> in L-FC was carried out and the etch gas was adsorbed and recovered. The composition and plasma and surface characteristics of the etched sample were analyzed. A mixture of C<sub>5</sub>F<sub>8</sub> and Ar gases was used to recover the etching gas exhausted during the plasma process, and the RGA was used to confirm that the gas before and after the recovery was pure, containing no etching by-products or impurities. In addition, as a result of analyzing the characteristics of the C<sub>5</sub>F<sub>8</sub> plasma before and after the recovery, the plasma characteristics before and after the recovery were the same within the error range, and the etching characteristics could be expected to be similar. Based on these results, the etching gas before and after the recovery was applied to an etching process requiring high selectivity such as Si and SiO<sub>2</sub>, and the analysis of the surface residue after etching was measured using XPS. XPS analysis results confirm that the chemical composition of the sample surface etched by C<sub>5</sub>F<sub>8</sub> before

and after recovery is the same. This study confirmed the possibility of selectively recovering and reusing post-etch process C<sub>5</sub>F<sub>8</sub> through use of the adsorption module proposed in this study. The use of low GWP L-FC as virgin or recycled gas, or when mixed with high GWP PFC, will help to slow global warming.

#### CRedit authorship contribution statement

**Junyoung Park:** Investigation, Writing - original draft.  
**Byoungmoon Oh:** Kyongnam Kim: Methodology, Conceptualization.  
**Dain Sung:** Visualization, Formal analysis. **Geunyoung Yeom:** Supervision, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

In this work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20172010105910), and also supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government (MSIT). (No. 2020R1A2C2007532).

#### References

- [1] S.S. Suh, N.G. Ahn, B.K. Na, Adsorption and desorption characteristics of CF<sub>4</sub> on fixed bed column, Korean J. Chem. Eng. 25 (2008) 1518–1523.
- [2] Kazushi Fujita et al., Novel process for SiO<sub>2</sub>/Si selective etching using a novel gas source for preventing global warming, J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom., 17, 1999, p. 957.
- [3] Shingo Nakamura, et al., Comparative Studies of Perfluorocarbon Alternative Gas Plasmas for Contact Hole Etch, Jpn. J. Appl. Phys. 42 (2003) 5759–5764.
- [4] Inwoo Chun, et al., A comparative study of CF<sub>4</sub>/O<sub>2</sub>/Ar and C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar plasmas for dry etching applications, Thin Solid Films. 579 (2015) 136–143.
- [5] M.B. Chang, J.S. Chang, Abatement of PFCs from Semiconductor Manufacturing Processes by Nonthermal Plasma Technologies: A Critical Review, Ind. Eng. Chem. Res. 45 (2006) 4101–4109.
- [6] N. Krishnan, et al., Alternatives to reduce perfluorinated compound (PFC) emissions from semiconductor dielectric etch processes: meeting environmental commitments while minimizing costs, IEEE Int. Symposium Electronics Environ. (2003) 19–24.
- [7] Hiromasa Ohmi, et al., PFC-Free Dry Etching Method for Si Using Narrow-Gap VHF Plasma at Subatmospheric Pressure, J. Electrochem. Soc. 157 (2010) D85–D89.
- [8] K.Y. Kim, et al., Comparative Study of Global Warming Effects during Silicon Nitride Etching Using C<sub>3</sub>F<sub>6</sub>O/O<sub>2</sub> and C<sub>2</sub>F<sub>6</sub>/O<sub>2</sub> Gas Mixtures, Electron. Mater. Lett. 11 (2015) 93–99.
- [9] A.D. Johnson, R.G. Ridgeway, P.J. Maroulis, Reduction of PFC emissions to the environment through advances in CVD and etch processes, IEEE Trans. Semiconductor Manufact. 17 (2004) 491–496.
- [10] D. Andrew, et al., Reducing PFC gas emissions from CVD chamber cleaning, Solid State Technology. 43 (2000) 103.
- [11] R.A.J.U. Ramasamy, et al., Warming Potential Reduction of C<sub>4</sub>F<sub>8</sub> Using Inductively Coupled Plasma, Jpn. J. Appl. Phys. 42 (2003) 280–285.
- [12] K. Suzuki, et al., High-Efficiency PFC Abatement System Utilizing Plasma Decomposition and Ca(OH)<sub>2</sub>/CaO Immobilization, IEEE Trans. Semiconductor Manufact. 21 (2008) 668–675.
- [13] Y. Tajima, T. Futatsuki, T. Abe, S. Tanzawa, PFC recycling system by continuous gas chromatography, IEEE Trans. Semiconductor Manufact. 18 (2005) 495–500.
- [14] S.E. Nam, A. Park, Y.I. Park, Separation and Recovery of F-gases, Korean Membr. J. 23 (2013) 189–203.
- [15] Marilena Radoiu, Shahid Hussain, Microwave plasma removal of Sulphur hexafluoride, J. Hazard. Mater. 164 (2009) 39–45.
- [16] J.E. Kim, et al., Study on Application of Membrane for Separation in Perfluorocompound Gas(SF<sub>6</sub>), J. Korea Soc. Waste Manage. 30 (2013) 173–180.
- [17] J. James, Spivey, Recovery of volatile organics from small industrial sources, Environ. Prog. 7 (1988) 31–40.
- [18] Hideki Motomuraa, Shin-ichi Imaib, Kunihide Tachibana, Difference between C<sub>4</sub>F<sub>8</sub> and C<sub>5</sub>F<sub>8</sub> plasmas in surface reaction processes for selective etching of SiO<sub>2</sub> over Si<sub>3</sub>N<sub>4</sub>, Thin Solid Films. 374 (2000) 243–248.
- [19] G.H. Kim, S.B. Kim, C.I. Kim, Selective etching of SiO<sub>2</sub> over Si<sub>3</sub>N<sub>4</sub> in a C<sub>2</sub>F<sub>6</sub>/O<sub>2</sub>/Ar plasma, Microelectron. Eng. 83 (2006) 2504–2509.
- [20] Hideki Motomuraa, Shin-ichi Imaib, Kunihide Tachibana, Surface reaction

- processes in  $C_4F_8$  and  $C_5F_8$  plasmas for selective etching of  $SiO_2$  over photo-resist, *Thin Solid Films*, 390 (2001) 134–138.
- [21] K. H. R. Kirmse et al.,  $SiO_2$  to Si selectivity mechanisms in high density fluorocarbon plasma etching, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom.*, 14(1996) 710.
- [22] F. Gaboriau et al., Etching mechanisms of Si and  $SiO_2$  in inductively coupled fluorocarbon plasmas: Correlation between plasma species and surface etching, *J. Vac. Sci. Technol., A*, 23(2005) 226.
- [23] Miyako Matsui, Tetsuya Tatsumi, Makoto Sekine, Observation of surface reaction layers formed in highly selective  $SiO_2$  etching, *J. Vacuum Sci. Technol. A Vacuum Surf. Films* 19 (4) (2001) 1282–1288, <https://doi.org/10.1116/1.1383064>.
- [24] C.H. Lee, C.K. Park, N.-E. Lee, Comparison of etching characteristics of  $SiO_2$  with ArF photoresist in  $C_4F_6$  and  $C_4F_8$  based dual-frequency superimposed capacitively coupled plasmas, *Microelectron. Eng.* 84 (2007) 165–172.
- [25] Nobuyuki Kuboi, et al., Modeling and Simulation of Plasma-Induced Damage Distribution during Hole Etching of  $SiO_2$  over Si Substrate by Fluorocarbon Plasma, *Appl. Phys. Express*, 5 (2012) 126201.