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High-Efficiency PFC Abatement System Utilizing Plasma Decomposition and Ca(OH)2/Cao Immobilization

High-Efficiency PFC Abatement System Utilizing Plasma Decomposition and Ca(OH)$_2$/CaO Immobilization

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Abstract—**In order to minimize contributions to global warming, it is important to develop a perfluorocompound (PFC) abatement system that can remove PFCs effectively with low electric power. We have developed a new PFC abatement system consisting mainly of a 2-MHz ICP plasma source and two Ca(OH)$_2$/CaO columns operated under a decompression pressure. Reactive fluorinated compounds including SiF$_4$ are immobilized in the Ca(OH)$_2$/CaO columns without a water scrubber. Stable compounds such as CF$_4$ are excited by the 2-MHz ICP plasma. When the emissions from an Si oxidation film etching process chamber were treated by this abatement system, F$_2$ equivalent removal efficiency was 99.6%, which was about one order of magnitude larger than that of a conventional abatement system. But the CO$_2$ equivalent removal efficiency was calculated to be 91.4% because over 95% of CO$_2$ equivalent emissions were caused by the plasma source power consumption of 2.4 kWh. It means that minimization of the plasma source power consumption, depending on PFC emissions, is a very effective method of minimizing contributions to global warming in a manner similar to improving the PFC removal efficiency.**

Index Terms—**Abatement, calcium, plasma.**

I. INTRODUCTION

PERFLUOROCOMPOUNDS (PFCs) are widely used in semiconductor manufacturing for plasma processes such as dielectric film etching and chemical–vapor deposition (CVD) chamber cleaning. Due to their long atmospheric lifetimes and high global warming potential (GWP), PFCs, such as tetrafluoromethane (CF$_4$), hexafluoroethane (C$_2$F$_6$), octofluoropropane (C$_3$F$_8$), and octofluorocyclobutane (c-C$_4$F$_8$) promote the greenhouse effect. Table I shows GWP$_{100}$, that is defined as a relative GWP value calculated for the period of 100 years against CO$_2$, and the atmospheric lifetime for typical fluorinated compounds [1]. To prevent further global warming, the semicon-

TABLE I
GLOBAL WARMING POTENTIAL FOR 100 YEARS (GWP$_{100}$) AND ATMOSPHERIC LIFETIME FOR FLUORINATED COMPOUNDS

	Lifetime (years)	GWP$_{100}$ (100 years horizon)
CO$_2$	50-200	1
CF$_4$	50,000	5,700
C$_2$F$_6$	10,000	11,900
C$_3$F$_8$	2,600	8,600
c-C$_4$F$_8$	3,200	10,000

ductor industry is committed to reducing the emission of PFCs to 10% below the emission level of 1995 by 2010 [2]. Thus, many developments of PFC emissions reduction have been performed in four general areas: process optimization, alternative chemistries, capture/recovery, and abatement [3]–[14].

On the other hand, the volume of PFCs used in semiconductor manufacturing has been increasing with the growth in production of semiconductor devices. In addition, PFCs do not completely decompose in the plasma process chambers and are generated as byproducts [5], [6]. Particularly, CF$_4$ and SiF$_4$ are generated as the byproducts in etching processes that use CF$_3$ ions and CF$_2$ radicals. They are also generated in the cleaning process for CVD chambers. Therefore, a high efficiency PFC abatement system is necessary for the reconciliation of semiconductor industry growth and global warming prevention. Combustion-type abatement systems [10] and atmospheric pressure plasma resolution-type abatement systems [11], [12] are generally utilized as point-of-use removal equipment. Tonnis *et al.* [13] and Kuroki *et al.* [14] reported on PFC abatement systems utilizing an inductively coupled plasma discharged under a decompression pressure. But the PFC removal efficiencies of these systems are about 90%–98% and are not efficient enough to prevent global warming. In addition, since the formation of deposits in the exhaust pipe, corrosion of the exhaust pipe and fluorine acid drainage are likely to occur in these systems, thus frequent maintenance and hazardous material treatments are required. To prevent these problems, a large amount of purge gas is required and, as a result, a large amount of energy is required to decompose the PFCs and the purge gases.

The focus of this paper is to develop a safe PFC abatement system that has minimal environmental impact and, at the same

time, improves productivity. This paper describes the distinguishing features and performance of a newly developed PFC abatement system. The experimental results show that the PFC abatement system can treat the emissions exhausted from a Si oxidation film etching process chamber. The removal efficiency is discussed on the basis of CO_2 equivalent emissions, which takes into account the plasma source power consumption.

II. CONCEPT OF PFC ABATEMENT SYSTEM

A. Newly Developed $Ca(OH)_2/CaO$

The basic concept of the PFC abatement system is to decompose PFCs with lower plasma source power consumption and immobilize reactive fluorinated compounds by utilizing a solid reactant. To implement this concept, the PFC abatement system was operated under a decompression pressure to introduce fluorinated compounds, that retain their energetic state, into the column filled with newly developed $Ca(OH)_2/CaO$ as the solid reactant.

There are three reasons for utilizing the $Ca(OH)_2/CaO$ admixture which is made by dehydration of $Ca(OH)_2$. One reason is that the resulting product, CaF_2, is nonhazardous and stable and another reason is that a water scrubber is not required. The latter eliminates the need for fluorine acid drainage treatments. Thus, this abatement system using $Ca(OH)_2/CaO$ is not only safer than the conventional system but also suitable for semiconductor manufacturing facilities that are limited in water supply. The third reason is explained by the reaction mechanisms

$$Ca(OH)_2 + COF_2 \rightarrow CaF_2 + CO_2 + H_2O \qquad (1)$$
$$CaO + H_2O \rightarrow Ca(OH)_2. \qquad (2)$$
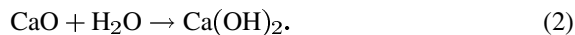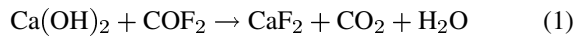
Although $Ca(OH)_2$ is necessary to react with the fluorinated compound, a significant amount of moisture is generated by the reaction shown by (1). As shown by (2), the generated H_2O reacts with CaO and generates another $Ca(OH)_2$. Thus, H_2O is used as an intermediate for the fluorination reaction of CaO and only a small amount of moisture is exhausted downstream.

A reactant with a high specific surface area should be used to promote the reaction mentioned above because it would raise the collision probability between gases and $Ca(OH)_2/CaO$. In addition, the grain diameter should be several millimeters to reduce the pressure loss. Unfortunately, the specific surface area of conventional $Ca(OH)_2/CaO$ is only 0.1–10 m^2/g when its grain diameter is 2–6 mm [15]. On the other hand, the newly developed $Ca(OH)_2/CaO$ has many micropores in the range of 10 to 100 nm as shown in Fig. 1. This structure allows the developed $Ca(OH)_2/CaO$ to have a specific surface area of 60–70 m^2/g and a grain diameter of 2–6 mm simultaneously. This means that the specific surface area of the developed $Ca(OH)_2/CaO$ is about two orders of magnitude larger than that of conventional $Ca(OH)_2/CaO$.

B. System Configuration

Fig. 2 shows a schematic diagram of the PFC abatement system that mainly consists of a 2-MHz ICP plasma source (LG3000, Landmark Technology Corporation), two
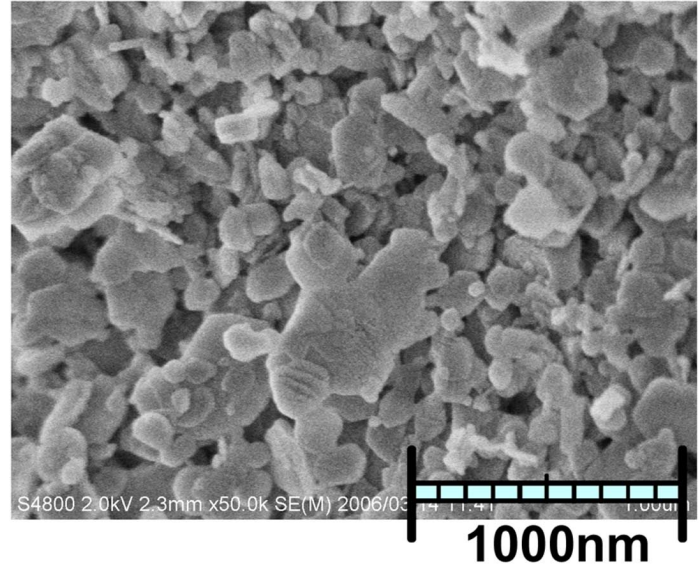

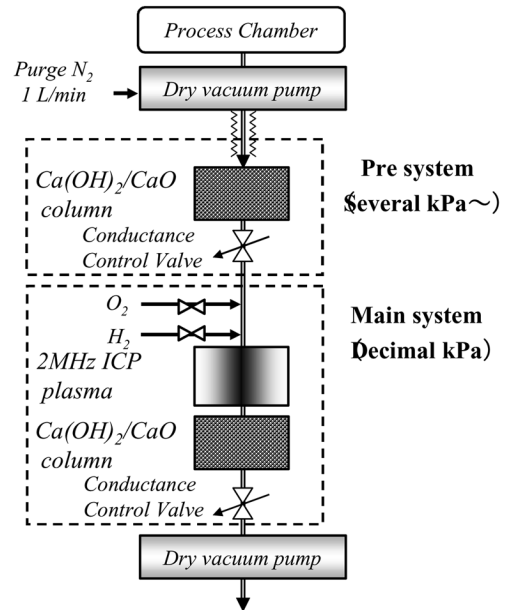Fig. 1. Scanning electron microscopy image of $Ca(OH)_2/CaO$.

Fig. 2. Schematic diagram of the newly developed PFC abatement system.

$Ca(OH)_2/CaO$ columns, two conductance control valves, and two dry vacuum pumps. We call the upstream column a presystem and the plasma source and the downstream column a main system.

In the presystem, $Ca(OH)_2/CaO$ in the upstream column immobilizes reactive fluorinated compounds, such as F_2, HF, COF_2, and SiF_4, which are included in emissions exhausted from a process chamber. Deposition caused by SiF_4 and corrosion caused by F_2 and/or HF are efficiently prevented because the pressure between the upstream pump and the presystem is under a decompression pressure range of over several kPa. Thus, the presystem serves to reduce the maintenance frequency of the pipe connected between the main system and the presystem. By the same token, a reduction of the purge gas flow rate introduced into the dry vacuum pump is also possible.

In the main system, stable compounds, such as CF_4, C_2F_6, and C_3F_8, which pass through the presystem, are excited by the 2-MHz ICP plasma and are immobilized by $Ca(OH)_2/CaO$ in the downstream column under a decompression pressure range of several hundred Pa. The gas temperature in the plasma is several hundred K under this operational pressure range and increases when this pressure is increased. Thus, preventive measures against the chamber's thermal fracture are made easier in comparison with atmospheric pressure plasma resolution-type abatement systems. An additional advantage is that the excited compounds can be introduced into the $Ca(OH)_2/CaO$ column while maintaining their energetic state because the collision frequency between excited compounds is comparatively small under this operation pressure. PFC removal efficiencies can be over 99% because recombination of CF_4 is prevented by this feature. However, it is difficult to utilize $Ca(OH)_2/CaO$ effectively because the collision frequency between the excited compound and the $Ca(OH)_2/CaO$ is comparatively small under this operation pressure. It is necessary to utilize the column with a large diameter to decrease the velocity of gases in the column as this measure. In addition, the plasma source power consumption can be lower than that of the atmospheric pressure plasma source because the utilization of the power supply frequency of 2 MHz decreases circuit losses. Since there is a direct correspondence between electric power consumption and CO_2 equivalent emission, this suggests that CO_2 emissions can be decreased by minimizing the electric power consumption. However, because the differential pressure caused by the column is different depending on the amount of $Ca(OH)_2/CaO$ in the column, it is necessary to control the pressure at the column by using the conductance control valve after exchanging the $Ca(OH)_2/CaO$.

III. EXPERIMENT

The PFC abatement system was built as described in the preceding section. It is imperative that SiF_4 is removed at the presystem to treat the emissions exhausted from an Si oxidation film etching process chamber because SiF_4 decomposition in the plasma source generates SiO_2.

First, the reactivity of $Ca(OH)_2/CaO$ was evaluated by using SiF_4 since it has a large bond dissociation energy of 6.03 eV and a small free energy of formation of -16.7 eV and is, thereby, one of the least reactive gases. In this experiment, a sample gas of $3vol\%SiF_4/Ar$ (Ar as balanced gas) was introduced into a $Ca(OH)_2/CaO$ column and was exhausted out through a conductance control valve by utilizing a dry vacuum pump until SiF_4 was detected with a nondispersive infrared (ND-IR)-type gas monitor. Fig. 3 shows a schematic diagram for this experiment. The pressure in the $Ca(OH)_2/CaO$ column was maintained at 1.3 kPa. The sample gas passed through the $Ca(OH)_2/CaO$ column at a velocity of 10.3 cm/s. The lower detection limit for SiF_4 concentration was approximately 1000 parts per million by volume (ppmv) for a minimum signal-to-noise ratio of 3:1 under a pressure of 1.3 kPa.

Because SiF_4 reacts with $Ca(OH)_2/CaO$ at the upstream side of the column, there is a transient zone of reaction in which a gradient in the number of immobilized F atoms is formed as shown in Fig. 4. The horizontal axis and the vertical axis show
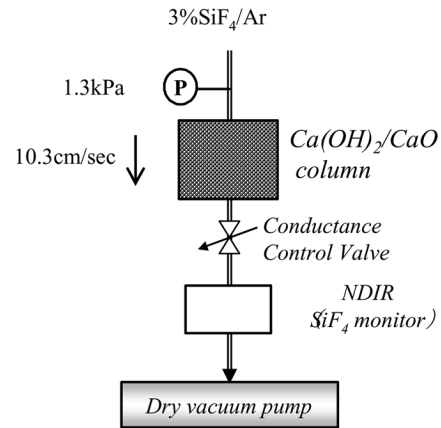

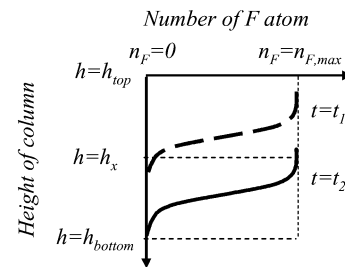Fig. 3. Schematic diagram of experiment to evaluate the reactivity of $Ca(OH)_2/CaO$.

Fig. 4. Schematic diagram of the progress state of the reaction in the $Ca(OH)_2/CaO$ column.

the number of F atoms and the height of column, respectively. As an example, the number of F atoms at a height of H_x is almost zero at $t = t_1$ and is $n_{F,max}$ at $t = t_2$. Similarly, the number of F atoms at $t = t_2$ is zero at $H = H_{bottom}$ and $n_{F,max}$ at $H = H_x$. Thus, the height of $Ca(OH)_2/CaO$ quantity, which is one of the conditions, has no influence on the length of the transient zone of reaction, which is generally called the mass transfer zone (MTZ). Therefore, the utilization efficiency was defined as the ratio of the removed number of F_2 equivalent molecules to Ca atom number in the reaction zone, which is the area outside of MTZ.

Next, the PFC removal efficiency of the main system was evaluated by using the CF_4 which could pass through the presystem. Fig. 5 shows a schematic diagram for this experiment. The plasma source power consumption was kept constant at 3.6 kWh. The sample gas, a mixture of $CF_4/O_2/Ar/H_2$ was pumped through a plasma source, a $Ca(OH)_2/CaO$ column, and a conductance control valve by utilizing a dry vacuum pump. The total flow rate, the CF_4 flow rate and the pressure in the plasma source were 1000–1600 cm^3/min, 50–200 cm^3/min, and 300 Pa, respectively. When the total flow rate was 1600 cm^3/min, the sample gas flowed to the $Ca(OH)_2/CaO$ column from the plasma source within a time of 130 ms and passed through the $Ca(OH)_2/CaO$ column at a velocity of 17 cm/s.

Lastly, the performance of the PFC abatement system shown in Fig. 1 was evaluated by using the emissions exhausted from a Si oxidation film etching process chamber. C_4F_6 and C_4F_8 were introduced into the etching chamber as process gases at a
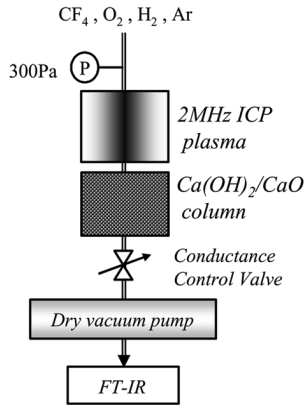
Fig. 5. Schematic diagram of experiment to evaluate CF_4 removal efficiency of main system.

Fig. 6. Specific surface area dependence of reaction efficiency.

flow rate of 4 and 18 cm^3/min, respectively. The plasma source power consumption was 2.4 kWh.

The emissions were measured by a Fourier transform infrared (FT-IR) absorption spectrometer which was positioned at the downstream side of the dry vacuum pump. The FT-IR mainly consists of ZeSe cell windows, KBr optics, a 10-cm path length gas cell, and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The lower detection limit for CF_4 concentration was approximately 1 ppmv at a minimum signal-to-noise ratio of 3:1. This means that this FT-IR is capable of detecting CF_4 with a flow rate of 0.001 cm^3/min when the total gas flow rate is 1000 cm^3/min. Thus, if the initial CF_4 flow rate is 100 cm^3/min, it is possible to determine a 99.99% removal efficiency.

The concentration of each compound was calculated based on the absorption intensities measured at the appropriate wavelength for each compound. The flow rate of each compound was obtained by multiplying the total flow rate by the concentration of each compound. F_2 equivalent removal efficiency, useful as a general figure of merit, was calculated based on the F_2 equivalent flow rate at the inlet and outlet of the PFC abatement system.

IV. RESULTS

A. SiF₄ Removal by Presystem

Fig. 6 shows the Ca utilization efficiency of $Ca(OH)_2$/CaO evaluated by using 3vol% SiF_4/Ar (Ar as balanced gas) under a pressure of 1.3 kPa and a velocity of 10.3 cm/s. The horizontal axis and the vertical axis show the specific surface area of $Ca(OH)_2$/CaO and the Ca utilization efficiency, respectively. The Ca utilization efficiency increased proportionally with the specific surface area. As an example, the Ca utilization efficiency was around 16% when the specific surface was 60 m^2/g. This figure shows that the presystem can remove SiF_4.

Furthermore, it was confirmed that the Ca utilization efficiency could be improved by raising the reaction pressure. When the pressure was 13 kPa, the Ca utilization efficiency of $Ca(OH)_2$/CaO, which had a specific surface area of 60 m^2/g, was around 25%. In addition, it was confirmed that the Ca utilization efficiency could be improved to about 85% by using F_2
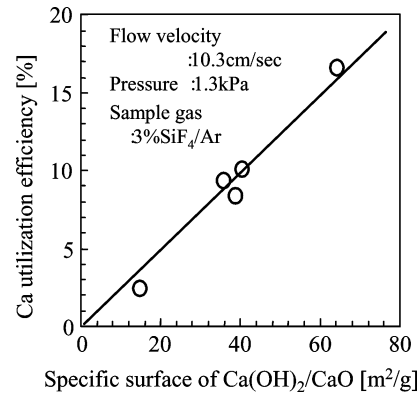

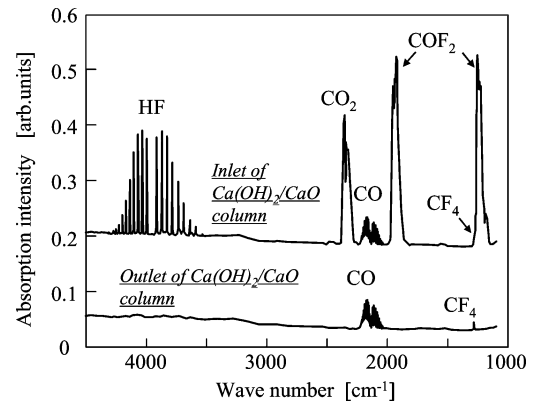
Fig. 7. Infrared absorption spectra at the inlet and outlet of the $Ca(OH)_2$/CaO column.

instead of SiF_4. This suggests that the Ca utilization efficiency depends strongly on the gas element.

B. CF₄ Removal by Main System

CF_4 removal efficiency of the main system was evaluated by using a CF_4/O_2/Ar/H_2 gas mixture under a plasma source power consumption of 3.6 kWh and a pressure of 300 Pa. The flow rates of CF_4, O_2, H_2, and Ar were 100, 300, 150, and 450 cm^3/min, respectively. Fig. 7 shows the infrared absorption spectra measured by FT-IR at the inlet and outlet of the $Ca(OH)_2$/CaO column. The horizontal axis and the vertical axis show the wave number and the absorption intensity, respectively. COF_2, CO_2, and HF were detected only at the inlet as byproducts. In other words, this figure shows that only CF_4 among the fluorinated compounds passed through the $Ca(OH)_2$/CaO column.

Fig. 8 shows the CF_4 removal efficiency of the main system. The plasma source power consumption and the pressure were 3.6 kWh and 300 Pa, respectively. The CF_4 flow rate was 50–200 cm^3/min, and the O_2 and H_2 flow rates were both three times larger than the CF_4 flow rate. Ar was added to make the total flow rate 1600 cm^3/min. The horizontal axis and the vertical axis show the initial CF_4 flow rate and the CF_4 emissions, respectively. The CF_4 emissions increased with increasing initial CF_4 flow rate. Dotted lines in this figure show a removal efficiency of 99.9% or 99.99%. In the range where the initial CF_4 flow rate was less than 200 cm^3/min, the removal efficiency was over 99.9%. Furthermore, when the
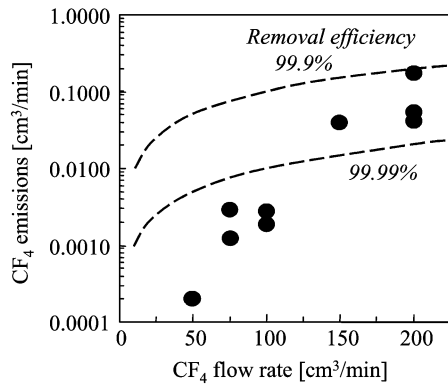
Fig. 8. CF_4 removal efficiency of the main system. The CF_4 flow rate was 50–200 cm^3/min.
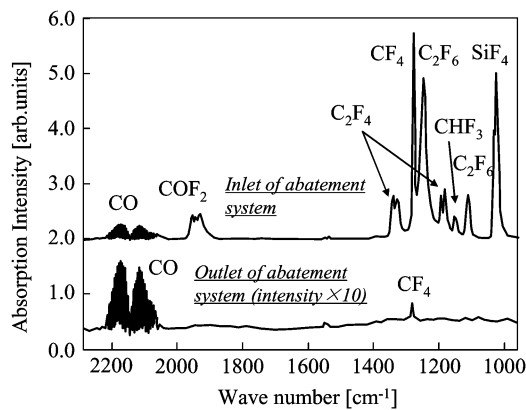

Fig. 9. Infrared absorption spectra at the inlet and outlet of the abatement system.

initial CF_4 flow rate was less than 100 cm^3/min, the removal efficiency was over 99.99%.

C. Performance of PFC Abatement System

Fig. 9 shows the infrared absorption spectra measured by FT-IR at the inlet and outlet of the PFC abatement system positioned at the exhaust line of an Si oxidation film etching process chamber. The horizontal axis and the vertical axis show the wave number and the absorption intensity, respectively. With the exception of CO and CF_4, most compounds, such as COF_2, C_2F_4, C_2F_6, CHF_3, and SiF_4, were detected only at the inlet side. In other words, this figure shows that all fluorinated compounds except for CF_4 were removed by the PFC abatement system. The PFC removal efficiency of the PFC abatement system was evaluated by comparison of the total amount of detected compounds. The average flow rates of F_2 equivalent emissions at the inlet and outlet of the PFC abatement system were calculated to be 46.84 and 0.17 cm^3/min, respectively. The removal efficiency based on the F_2 equivalent emissions was calculated to be 99.6%, which is about one order of magnitude larger than that of a conventional abatement system. As mentioned above, this system does not use water for C–F species stabilization and does not emit H_2O. This means that the water scrubber to treat the hydrogen fluoride drainage could be eliminated.
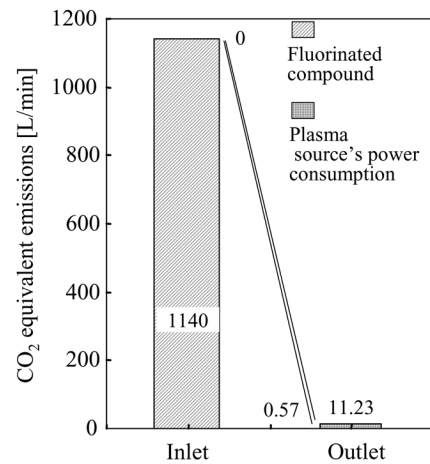

Fig. 10. CO_2 equivalent emissions at the inlet and outlet of the $Ca(OH)_2$/CaO column. The flow rate of CF_4, O_2, H_2, and Ar were 200, 600, 600, and 400 cm^3/min, respectively. Plasma source power consumption was 3.6 kWh.

V. DISCUSSION

In order to view this problem from the perspective of global warming prevention, the removal efficiency should be described using CO_2 equivalent emissions. In this case, CO_2 equivalent emissions are calculated based on the sum of each compound's emission origin and the electric power consumption origin. The former is given by multiplying the flow rate of each compound by each GWP_{100}. The latter is given by multiplying the electric power consumption by the CO_2 equivalent factor of 0.368 kg-CO_2/kW, when electricity supplied by Tokyo Electric Corporation is used [16]. The CO_2 equivalent factor is equal to a one-hour average of a CO_2 equivalent flow rate of 3.12 L/min. For example, Hattori *et al.* showed that a plasma source power consumption of 5.9 kWh was needed to decompose CF_4 at 96.5% removal efficiency by utilizing the atmospheric pressure plasma abatement system [11]. Because the plasma source power consumption of 5.9 kWh was calculated to have a CO_2 equivalent flow rate of 18.41 L/min, reducing electric power consumption is as important as reducing PFC emissions.

At first, the CO_2 equivalent removal efficiency of the main system was evaluated in the case where the initial CF_4 flow rate was 200 cm^3/min, which is shown in Fig. 8. Fig. 10 shows the calculation result of the CO_2 equivalent emissions at the inlet and outlet of $Ca(OH)_2$/CaO column. Because the only greenhouse gas in the emissions was CF_4, of which GWP_{100} was 5700, CO_2 equivalent flow rate of emissions origin at the inlet and outlet of the main system were calculated to be 1140 and 0.57 L/min, respectively. In addition, a CO_2 equivalent flow rate of 11.23 L/min, which was derived from the plasma source power consumption of 3.6 kWh, was added to that of the outlet. Thus, the average flow rates of CO_2 equivalent emissions at the inlet and outlet of the PFC abatement system were calculated to be 1140 and 11.80 L/min, respectively. Based on this, the CO_2 equivalent removal efficiency was calculated to be 99.0%.

Next, the CO_2 removal efficiency of the PFC abatement system was evaluated for the case shown in Fig. 9. Fig. 11 shows the calculation result of the CO_2 equivalent emissions at the inlet and outlet of the PFC abatement system. CO_2 equivalent flow rate of emissions origin at the inlet and outlet of the PFC abatement system were calculated to be 89.16 and
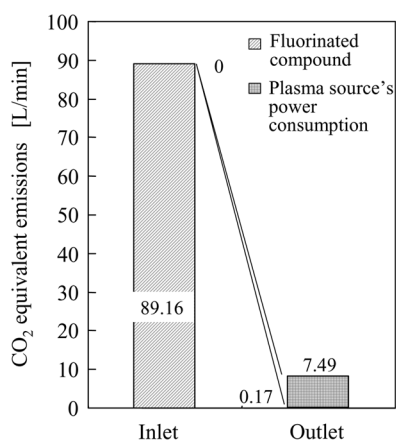
Fig. 11. CO_2 equivalent emissions at the inlet and outlet of the abatement system. C_4F_6 and C_4F_8 were introduced into the process chamber at a flow rate of 4 and 18 cm³/min, respectively. Plasma source power consumption was 2.4 kWh.

0.17 L/min, respectively. In addition, the CO_2 equivalent flow rate of 7.49 L/min, which was derived from the plasma source power consumption of 2.4 kWh, was added to that of the outlet. Thus, the average flow rates of CO_2 equivalent emissions at the inlet and outlet of the PFC abatement system were calculated to be 89.16 and 7.66 L/min, respectively. Based on this, the CO_2 equivalent removal efficiency was calculated to be 91.4%.

These results show that the ratio of the plasma source power consumption origin in CO_2 equivalent flow rate is more than 95% in both cases and the ratio in the case of Fig. 9 is comparatively larger. It means that minimization of the plasma source power consumption, depending on PFC emissions, is a very effective means for minimizing contributions to global warming in a manner similar to improving the PFCs removal efficiency. In other words, the development of a more efficient plasma source is very important for the resolution of this problem.

VI. CONCLUSION

We have developed a PFC abatement system consisting mainly of a 2-MHz ICP plasma source and two $Ca(OH)_2$/CaO columns and is operated under a decompression pressure. The presystem immobilizes reactive fluorinated compounds, which include SiF_4, by utilizing a $Ca(OH)_2$/CaO reactant with a specific surface area of 60 m²/g in the upstream column and reduces the frequency of exhaust pipe maintenance required. The main system, that excites stable compounds which pass through the presystem by utilizing a 2-MHz ICP plasma and immobilizes these excited compounds by $Ca(OH)_2$/CaO in the downstream column, could remove CF_4 with F_2 equivalent removal efficiency of over 99.9%, which was one order of magnitude larger than that of a conventional system. When the emissions exhausted from an Si oxidation film etching process chamber were treated by this PFC abatement system, the F_2 equivalent removal efficiency and the CO_2 equivalent removal efficiency were 99.6% and 91.4%, respectively. The discrepancy between the two efficiencies was attributed to the fact that over 95% of CO_2 equivalent emissions were caused by the plasma source power consumption of 2.4 kWh.

This PFC abatement system can treat the emissions exhausted from an Si oxidation film etching process chamber without a water scrubber and provides a way to have minimal environmental impact and, at the same time, improve productivity.

REFERENCES

[1] J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. Van Der Linden, X. Dai, K. Maskell, and C. A. Johnson, *Climate Change 2001: The Scientific Basis* Cambridge Univ., , Cambridge, Rep. of IPCC, 2001, p. 47, Contribution of Working Group 1 to the Third Assess.
[2] International Technology Roadmap for Semiconductors 1999, p. 248.
[3] L. Beu, P. T. Brown, J. Latte, J. U. Rapp, T. Gilliland, T. Tamayo, J. Harrison, J. Davison, A. Cheng, J. Jewett, and W. Worth, "Perfluoro-compound (PFC) emissions reduction," *Int. SEMATECH Technology Transfer #98053508A-TR*, 1998.
[4] L. Beu and P. T. Brown, "Motorola's strategy for reducing PFC emissions," in *Proc. Electron. Manuf. Technol. Symp.*, 1998, pp. 277–285.
[5] I. Namose, "Optimization of gas utilization in plasma processes," in *Proc. 2002 Int. Symp. Semiconductor Manufacturing*, Tokyo, Japan, 2002, pp. 261–264.
[6] E. M. Chan, G. Loh, and C. C. Allgood, "Process optimization and PFC emission reduction using a c-C_4F_8 chamber cleaning process on a novellus concept 1 dielectric PECVD tool," *IEEE Trans. Semicond. Manuf.*, vol. 17, no. 4, pp. 497–503, Nov. 2004.
[7] S. Nakamura, M. Itano, H. Aoyama, K. Shibahara, S. Yokoyama, and M. Hirose, "Comparative studies of perfluorocarbon alternative gas plasmas for contact hole etch," *Jpn. J. Appl. Phys.*, vol. 42, no. 9A, pp. 5759–5764, Sept. 2003.
[8] Y. Tajima, T. Futatsuki, T. Abe, and S. Tazawa, "PFC recycling system by continuous gas chromatography," *IEEE Trans. Semicond. Manuf.*, vol. 18, no. 4, pp. 495–500, Nov. 2005.
[9] V. Vartanian, L. Beu, T. Stephens, J. Rivers, B. Perez, E. Tonnis, M. Kiehlbauch, and D. Graves, "Long-term evaluation of the litmas "blue" plasma device for point-of-use (POU) perfluorocompound and hydrofluorocarbon abatement," *Int. SEMATECH Technology Transfer #99123865B-ENG*, 2000.
[10] W. Worth, T. A. Tamayo, P. E. , and R. F. Cambio, "Analysis of data for perfluorocompound (PFC) emission control systems," *Int. SEMATECH Technology Transfer #95062847A-ENG*, 1995.
[11] K. Hattori, K. Sakurai, N. Watanabe, H. Mangyou, S. Hasaka, and K. Shibuya, "Application of atmospheric plasma abatement system for exhausted gas from MEMS etching process," in *Proc. 2006 Int. Symp. Semiconductor Manufacturing*, Tokyo, Japan, 2006, pp. 39–42.
[12] M. T. Radoiu, "Studies on atmospheric plasma abatement of PFCs," *Radiation Physics and Chemistry*, vol. 69, no. 2, pp. 113–120, Feb. 2004.
[13] E. J. Tonnis and D. B. Graves, "Inductively coupled, point-of-use plasma abatement of perfluorinated compounds and hydrofluorinated compounds from etch processes utilizing O_2 and H_2O as additive gases," *J. Vac. Sci. Technol.*, vol. A18, no. 2, pp. 393–400, Mar./Apr. 2000.
[14] T. Kuroki, J. Mine, M. Okubo, T. Yamamoto, and N. Saeki, "CF_4 decomposition using inductively coupled plasma: Effect of power frequency," *IEEE Trans. Ind. Appl.*, vol. 41, no. 1, pp. 215–220, Jan./Feb. 2005.
[15] K. Kawabata, H. Yoshimatsu, K. Suzuki, A. Osaka, Y. Miura, and H. Kawasaki, "CO_2 fixation by $Ca(OH)_2$ at high temperature," *J. Ceram. Soc. Jpn.*, vol. 102, no. 12, pp. 1173–1176, Dec. 1994.
[16] "Ministry of the environment Japan.," Manual for Calculating and Reporting the Amount of Greenhouse Gas Emissions 2006, pp. 1125–1126 [Online]. Available: http://www.env.go.jp/earth/ghg-santeikohyo/manual/index.html, Available

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