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The Possibility of Carbonyl Fluoride as a New CVD Chamber Cleaning Gas

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Carbonyl fluoride (COF_2) has been investigated as an alternative gas for plasma-enhanced chemical vapor deposition (PECVD) chamber cleaning in order to reduce greenhouse gases emitted from the cleaning process in semiconductor manufacturing. The cleaning performance of COF_2 and the environmental impact of its exhaust gases were evaluated using an experimental plasma tool. The results indicated that the cleaning performance of COF_2 was equivalent to that of conventional C_2F_6. Furthermore, it was confirmed that the use of COF_2 would enable the reduction of global warming emissions by over 95% relative to the use of C_2F_6, and thus COF_2 is considered to be a promising alternative cleaning gas.

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Perfluorocarbons (PFCs) such as CF_4 and C_2F_6, etc., with strong infrared absorption coefficients and extremely long lifetimes in the atmosphere are, therefore, greenhouse gases and their global warming potentials (GWPs)[1] are quite high. They are mainly used for the plasma enhanced chemical vapor deposition (PECVD) chamber cleaning process in semiconductor manufacturing, and are contained in the exhaust gases from the process as well. PFCs have roughly ten thousands times more impact on global warming than carbon dioxide because of their long lifetimes and high GWP values. Accordingly, the PFC emissions pose serious problems for the global environment. With a view to reducing the quantity of greenhouse gases emitted from the cleaning process, research and development of alternative gases[2,3] and abatement systems[4] for exhaust gases have been conducted.

The objective of the present work is to research and develop alternative CVD chamber cleaning gases, which show performances equivalent to conventional gases, and thus enable a great reduction in greenhouse gas emitted from the cleaning process. At first, we searched for a substitute gas among substances that had low GWP values. However, the number of substances whose GWP values have been measured is limited. Substances that are hydrolyzed with water or moisture in the atmosphere are assumed to have short atmospheric lifetimes and low GWP values. Thus the hydrolysis property was one of important characteristics in the present search for alternative.

COF_2 is one of the by-products generated during plasma cleaning using perfluorocarbons. When a mixed gas of C_2F_6 and O_2 is used for cleaning silicon compounds, the exhaust gas is known to contain nondecomposed C_2F_6, recombined CF_4, SiF_4 produced from silicon compounds, CO_2 oxidized perfectly, which released fluorine completely, CO oxidized imperfectly, which released fluorine completely, COF_2 which released fluorine incompletely, HF and F_2 generated by the plasma but not utilized. Since COF_2, SiF_4, F_2, and HF are toxic gases, they have been abated with water scrubbers. The hydrolysis characteristic of COF_2 is well known. The cleaning performance of COF_2 has been in doubt because it is not been completely dissociated by the plasma reaction and has a small number of fluorine atoms in its molecule. However we selected COF_2 for its hydrolysis properties as the candidate of an alternative gas to study in the present work.

The toxicity index, TLV (TWA) in American Conference of Industrial Hygienists (ACGIH) of COF_2 is 2 ppm, which is larger than that of arsine (0.05 ppm) and of germane (0.2 ppm), both of which are widely used in semiconductor manufacturing. Thus, compared with these substances, the toxicity of COF_2 is considered to be moderate. In addition, COF_2 is neither explosive nor combustible. Therefore, COF_2 can be handled with the existing safety control standards for toxic gases implemented by semiconductor manufacturers. What is more, since COF_2 flows through the downstream of the chamber as the component of the exhaust during C_2F_6 cleaning, it is unlikely that COF_2 cleaning causes more trouble to the system than C_2F_6 cleaning.

Experimental

The performance of the cleaning gas is usually evaluated at the time of cleaning the deposits on the entire inside of the chamber after the actual PECVD process. In the present study, the cleaning performances and the environmental impact of its exhaust gases were evaluated using the experimental plasma tool (manufactured by Anelva Corporation) and the system as shown in Fig. 1a. The chamber is equipped with circular parallel plate electrodes (the upper electrode with a diameter of 44 cm, and lower electrode with a diameter of 42 cm). To the showerhead-type upper electrode, radio frequency (rf) power of 13.56 MHz was applied. The mass flow controller (MFC) set the flow rates of the tested gas and the additive gas. The gases were introduced into the chamber through the upper electrode showerhead. To dilute the exhaust from the chamber, nitrogen was fed at the inlet of the dry pump at 15.5 L/min. SiO_2 and SiN_x are the major insulation films deposited by CVD in the semiconductor large scale integration (LSI) process. In the present paper, SiO_2 film or/and a quartz plate were selected as samples because SiO_2 was revealed to requires longer time for an etching reaction than SiN_x in the preliminary experimental evaluation.

The cleaning performances was evaluated by two kinds of etch rates, the etch rate on the lower electrode and the etch rate toward the chamber wall without the pattern. For the measurement of the etch rate on the lower electrode, approximately 10,000 Å SiO_2 thin film deposited in advance on a 15 cm diam silicon wafer was etched as a sample as shown in Fig. 1a. The film thickness was measured at 9 fixed points on the wafer by a spectroscopic reflectometric film thickness measuring instrument (model 3000 manufactured by Nanometorics, Japan) before and after the plasma discharged. Etch rates were calculated by the differences in the film thickness and etching times. As well as the etch rate, within-wafer uniformity was obtained by the following formula. Poor uniformity means that the

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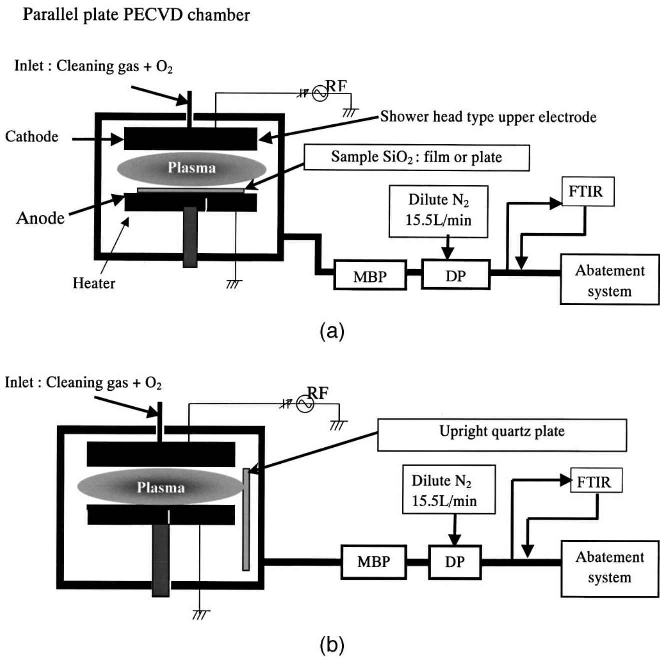

Figure 1. (a, top) Schematic diagram of experimental setup. (b, bottom) Quartz plate setting for etch rates toward chamber wall.

plasma is irratically generated, which is not desirable in the CVD chamber cleaning process.

$$\langle \text{Within-wafer uniformity}(\%) = (\text{maximum etch rate} - \text{minimum etch rate}) / (\text{maximum etch rate} + \text{minimum etch rate}) \times 100 \rangle \quad [1]$$

Analysis of the exhaust gases from the etching reaction between the cleaning gas and quartz plate was performed by the Fourier transform infrared (FTIR) spectroscopy (Infinity Gold by Mattson) with a 2 cm absorption cell with barium fluoride windows. As shown in Fig. 1a, a 15 cm quartz plate was placed on the lower electrode and exhaust gases from the chamber were fed into the FTIR spectroscope through the dry pump outlet with dilute nitrogen. Quantitative analysis of FTIR for the exhaust gas components was conducted using the calibration curve measured with the reference gas. The low values of the concentrations are attributable to dilution with nitrogen at 15.5 L/min, and the concentration values were measured during continuous etching while absorption peaks (concentrations of components) were constant.

Although the etch rate toward chamber wall can be measured directly by placing a SiO_2 film wafer piece on the chamber inner wall,[7] another way was designed for the present study. The etch rate of SiO_2 film on the electrode and the SiF_4 concentration analyzed in the exhaust gas is proportional.[8] SiF_4 is also produced by the etching reaction between the cleaning gas and the quartz plate placed upright near the chamber wall as shown in Fig. 1b. Therefore, the SiF_4 flow rate can be considered to be proportional to the etch rate toward the chamber wall. The flow rates were obtained by converting the SiF_4 concentrations into the mmol/min unit.

In order to evaluate the environmental impacts of the cleaning gases, as the index of global warming gas emissions during the etching of the quartz plate, kilograms of carbon equivalent per minute (kgCE/min) was used, which has been defined with the following formula

$$kgCE = \Sigma(12/44)(Q_i/\text{min})(GWP_{100i}) \quad [2]$$

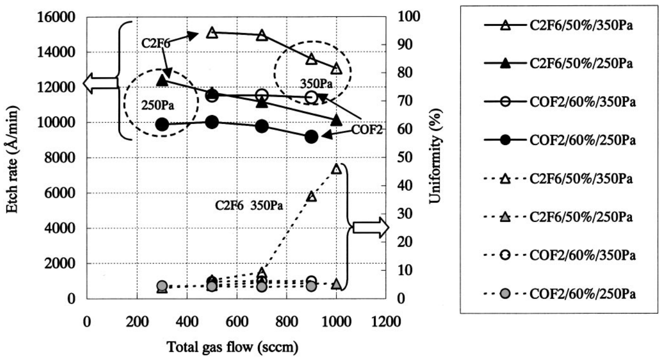

Figure 2. Etch rate and uniformity *vs.* total gas flow.

where i indexes gases in the exhaust, Q_i/min is the mass flow in kilogram/min during etching, and GWP_{100i} is the 100 year integrated global warming potential of the gas. GWP_{100i} values in the present paper were used the following values revised in 2001: CF_4, 5700; C_2F_6, 11900; C_3F_8, 8600; c-C_4F_8 10,000; CO_2, 1. Although the GWP of COF_2 has not been estimated, they react with water very quickly and produce CO_2 and HF. Their contribution to global warming is as same as CO_2 at most. Thus the GWP values in this present paper were assumed to be the same with that of CO_2 (=1).

Tested gas dissociation efficiencies was defined with the following formula

$$\text{Dissociation efficiency}(\%) = 100 - \text{tested gas concentration during etching} / \text{tested gas concentration before etching} \times 100 \quad [3]$$

The items common to the experimental conditions are the tested gases, COF_2, candidate substitute gas; and C_2F_6, C_3F_8, c-C_4F_8 reference gas for evaluation. Oxygen is the additive gas. RF power is 750 W (power density: 0.96 W/cm^2). The lower electrode temperature is 300°C. The interelectrode distance is 50 mm. The etching (discharge) time is 30 s for etch rate measurement using SiO_2 film on silicon wafer and about 200 s for the exhaust gas analysis using a quartz plate by FTIR. Total gas flow rate (tested gas + oxygen) and pressure value were recorded for each experiment.

Results and Discussions

As mentioned in the introduction, hydrolysis characteristics of COF_2 were attractions to survey the performance as an alternative for PECVD chamber cleaning gas of low GWP value. In order to clarify the performance, a few experiments were performed.

The effects of the total gas flow rate (the tested gas and the additive gas, O_2) on the etch rate are shown in Fig. 2. In this experiment, C_2F_6 and COF_2 were fixed at 50 and 60% concentration and at pressures of 250 and 350 Pa, respectively. Although the maximum etch rate of C_2F_6 was higher than that of COF_2, the results of both gases show the same tendency that the etching performance for C_2F_6 and COF_2 decrease slightly as the total gas flow rate is increased. The etch rates were higher at a pressure of 350 Pa than at 250 Pa. However, in the case of only C_2F_6 at 350 Pa, the uniformity deteriorated when the total flow rate was 700 standard cubic centimeters per minute (sccm) or more and the plasma generation became unstable. Meanwhile, in the case of COF_2 at 350 Pa, the uniformity was maintained even at 900 sccm. This indicates that COF_2 achieves more stable plasma generation than C_2F_6, which is advantageous for the actual cleaning condition. Based on these experimental results, basic experimental conditions were fixed at a total gas flow rate of 300 sccm and at pressure of 250 Pa.

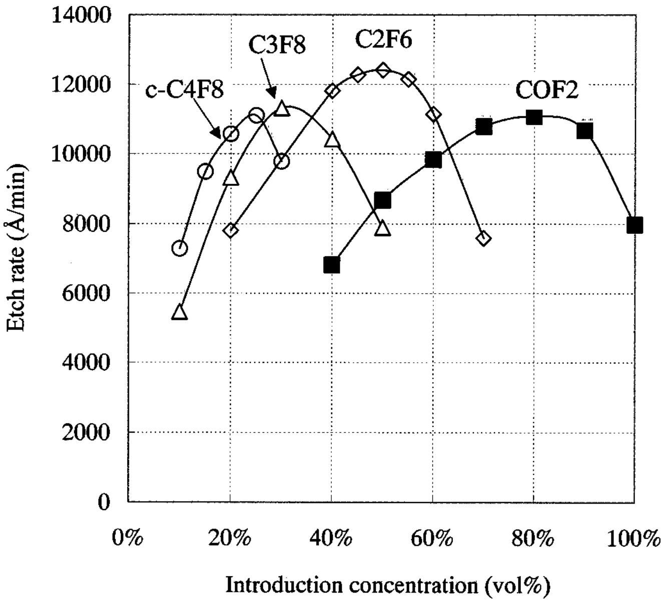

Figure 3. Etch rate *vs.* gas concentration (%).

The effects of the introductory concentrations on etch rates are shown in Fig. 3. The gases were COF_2, C_2F_6, and C_3F_8. In this evaluation, the total gas flow rate and chamber pressure were fixed at 300 sccm and 250 Pa. The maximum etch rate on the electrode of COF_2 was slightly lower than C_2F_6 and roughly the same level compared with C_3F_8 and c-C_4F_8.[4,5] The etch rate formed curves with an upper convex peak in relation to the concentration. The maximum etch rates occurred at approximately 50% concentration for C_2F_6, at approximately 80% concentration for COF_2, at approximately 30% concentration for C_3F_8, and at approximately 25% concentration for c-C_4F_8. The concentrations at which the peaks appeared depended on the number of carbon atoms; when the number of carbon atoms increases from 1 to 4, more oxygen is required, lowering the concentration at which the peak appears.[6] The effects of the introductory concentration on the exhaust gas components are shown in Fig. 4 for C_2F_6 and Fig. 5 for COF_2. The total gas flow rate was fixed at 300 sccm, and the chamber pressure was fixed at 250 Pa. The exhaust gas from the plasma reaction with the quartz plate on the lower electrode was analyzed by FTIR. The percentage part is small because the exhaust gas is diluted with 15.5 L/min nitrogen. The components' percentage does not add up to 100% because nitrogen, oxygen, and fluorine are not analyzed by FTIR without their infrared absorption. When Fig. 4 and Fig. 5 were compared, it was found that the exhaust gases by using COF_2 did not include C_2F_6, and that the CF_4 concentration is extremely low in the case of COF_2 rather than that of C_2F_6. It seems that the amount of CF_4 produced as by-product is slight in the case of COF_2 for the plasma reaction because of the large binding energy of C=O in COF_2 molecules. Although the dissociation ratio of COF_2 is equivalent to that of C_2F_6, COF_2 in the exhaust reacts with water easily and can be removed by an existing scrubber. This suggests that the amount of greenhouse gas emitted will be reduced greatly, when COF_2 is used for cleaning. It is also points out that compared with exhaust gases emitted from the actual CVD cleaning process in the manufacturing line, the C_2F_6 and SiF_4 concentrations are low. The low C_2F_6 concentration and the high dissociation efficiency were attributable to the small amount of total gas flow rate. The low SiF_4 concentration was attributable to a small etching area because only one quartz plate was placed on the lower electrode. The concentration of CO was also low because it was estimated that the oxidation was well done in this plasma tool and/or more COF_2 was recombined with surplus fluorine attributable to a small etching area. (CO reacts with F_2 very quickly.) As shown in Fig. 4 and Fig. 5, the increase in introduction concentration of the tested gas led to the increase in the CF_4 concentration in the exhaust. Carbons containing cleaning gases are finally oxidized producing CO_2 and fluorine radicals. However, side reaction of CF_4 consumes fluorine radicals in vain to cleaning purpose. Thus, the decrease in the introductory oxygen concentration was seen to cause the decrease of CO_2 and the increase of CF_4 and finally the decrease in fluorine radicals and lowering in the etch rate.

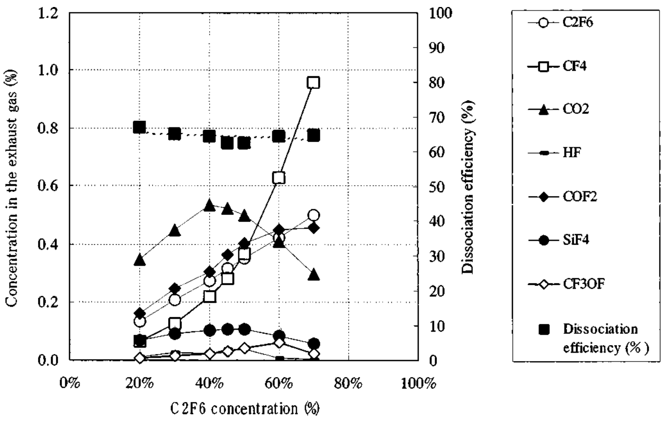

Figure 4. Exhaust gas analysis of C_2F_6 *vs.* gas concentration.

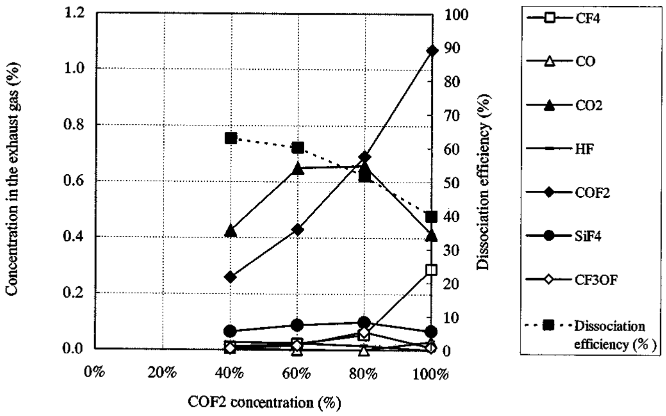

Figure 5. Exhaust gas analysis of COF_2 *vs.* gas concentration.

Comparison of kgCE/min in the exhaust gases is shown in Fig. 6. Specifically, we set the concentration of C_2F_6 at 50%, C_3F_8 at 30%, c-C_4F_8 at 25%, and the concentration of COF_2 at 60 and 80%. On this evaluation, the total gas flow rate and chamber pressure were fixed to be 300 sccm and at 250 Pa. The plasma reaction with SiO_2 using COF_2 reduced the kgCE/min of greenhouse gases emitted by over 95% relative to using of C_2F_6. COF_2 generated hardly any CF_4 as by-products during the plasma cleaning reaction compared with those generated by using C_2F_6. Greenhouse gases emissions were reduced by using less C_3F_8 and c-C_4F_8 than by using COF_2 because C_3F_8 and c-C_4F_8 could not avoid recombining with CF_4 and high GWP gases themselves were not decomposed perfectly. Moreover, as shown in Fig. 3, the COF_2 maximum etch rate appeared when the concentration was 80%. When the concentration was lowered to 60%, the etch rate fell by only approximately *ca.* 10% from the maximum whereas the CF_4 quantity in the exhaust gas dropped by approximately 50% as shown in Fig. 6. Thus, it was concluded that the optimum concentration of COF_2 is around 60% in this study. The C_2F_6 maximum etch rate appeared when the concentration was

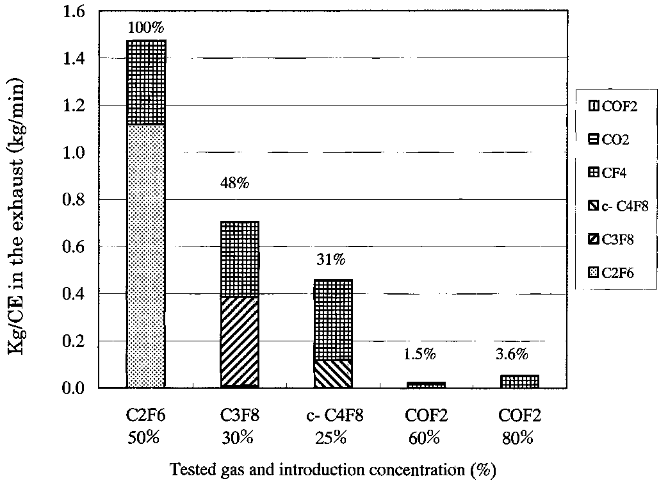

Figure 6. Comparison of kgCE/min in the exhaust gases.

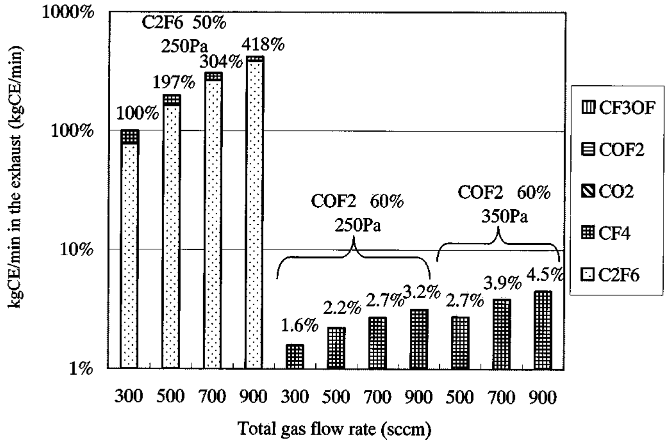

Figure 8. The kgCE/min *vs.* the total gas flow rate.

50%, and many cleaning recipes adopt this concentration. Thus, we set the concentration of C_2F_6 at 50% as the reference.

Comparison of the effects of the total gas flow rate on the dissociation efficiency is shown in Fig. 7. The increase in the total gas flow rate from 300 to 900 sccm led to similar decreases in dissociation efficiency of both C_2F_6 and COF_2 from 60 to 40%. The decrease in etch rates due to the increase in the total gas flow rate as shown in Fig. 2 is also due to the decrease in dissociation efficiency. The decrease in dissociation efficiency seems attributable to a shorter time during which gas molecules receive discharge energy, due to the increase in the total gas flow rate.

Comparison of the effects of the total gas flow rate on the kgCE/min is shown in Fig. 8. Even when the total gas flow rate of COF_2 increased, CF_4 was generated, and the kgCE/min remained slight because the GWP value of nondecomposed COF_2 was estimated to be the same as that of CO_2. In contrast, the increase in the total gas flow rate of C_2F_6 resulted in the decrease in the dissociation efficiency, which led to an increase in nondecomposed C_2F_6 and in the kgCE/min. The decrease in dissociation efficiency due to the increase in the total gas flow rate further consolidated the superiority of COF_2 to C_2F_6 in terms of environmental impact.

Comparison of the etch rates toward the chamber wall are shown in Fig. 9. The quartz plate was placed upright near the chamber wall. For the gases tested at the fixed concentrations, the chamber pressure and the total gas flow rate were varied as below, and SiF_4 in the exhaust was analyzed by FTIR. In addition, the etch rates (quartz plate) on the lower electrode are also shown in Fig. 10 under the same experimental conditions. They showed the pressure dependencies of the SiF_4 quantity produced. C_2F_6 with a concentration of 50% and COF_2 with a concentration of 60% were tested.

The total gas flow rate was 300, 500, 700, 900 (sccm) and the chamber pressure was 150, 250, 350 (Pa).

It was found that the etch rates toward the chamber wall of COF_2 were 20 to 25% higher than that of C_2F_6, although the etch rates on the electrode of COF_2 was approximately 10% lower than that of C_2F_6 at the same pressure. As shown in Fig. 9 and 10, the COF_2 cleaning performance at 350 Pa was equivalent to that of C_2F_6 at 250 Pa in consideration the etch rates both on the electrode and toward the chamber wall. For amount of SiF_4 quantity, the etch rates toward the chamber wall were smaller than the etch rates on the lower electrode because the quartz plate accounts for only approximately one-tenth of the entire chamber wall circumference and only the 50 mm edge portion of the 15 cm quartz plate upright was exposed between the electrodes.

In the case of C_2F_6 and COF_2, the effect of the total flow rate on both etch rates was slight, but the effect of the chamber pressure was great. Specifically, as the chamber pressure decreased, the etch rate toward the chamber wall increased whereas the etch rate on the electrode decreased. Although it is difficult to identify substances to be cleaned in the case that they are distributed unevenly, it is effective to set a pressure for the cleaning recipe optimized for deposition conditions and for uneven distribution.

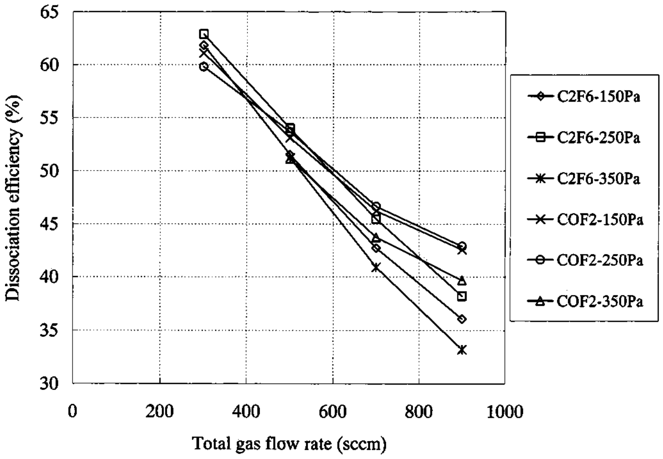

Figure 7. The dissociation efficiency *vs.* total gas flow rate.

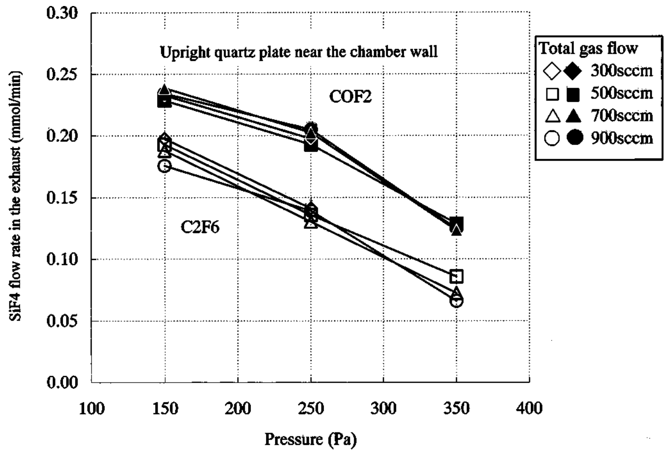

Figure 9. Comparison of the etch rates toward chamber wall.

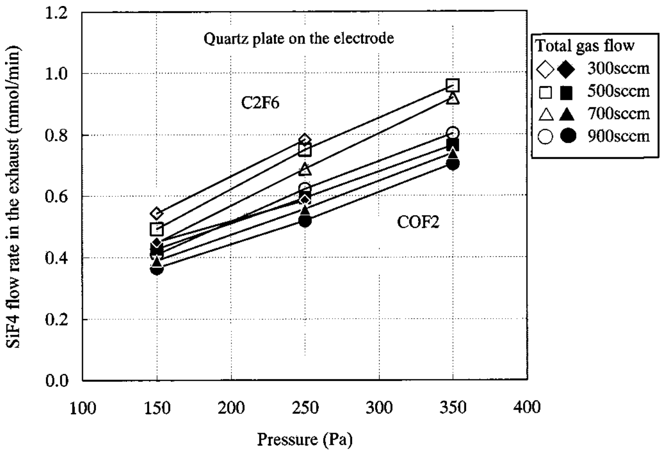

Figure 10. Etch rate on the lower electrode *vs.* the chamber pressure.

Conclusion

The CVD chamber cleaning performances of COF_2 and C_2F_6 were evaluated by measuring the etch rates on the lower electrode for SiO_2 film and the etch rates toward the chamber wall for the quartz plate placed upright. The results showed that the performance of COF_2 was equivalent to that of C_2F_6 in consideration of the etch rates both on the electrode and toward chamber wall. It was also confirmed that the generation of plasma is more stable and the plasma tended to expand more toward the chamber wall in the case of COF_2 than in the case of C_2F_6.

Their environmental impacts during the cleaning were evaluated by the kgCE/min of global warming gas based on exhaust gases analysis. It was found that the kgCE in the case of COF_2 was greatly reduced compared to that in the case of C_2F_6 because the by-product, CF_4, was remarkably low and the GWP of nondecomposed COF_2 was estimated to be the same as that of CO_2 for its hydrolysis property.

Thus, in view of the characteristics of COF_2, it was concluded that COF_2 is a strong candidate to replace C_2F_6 and that the use of COF_2 would enable a great reduction in greenhouse substances generated during cleaning. Provided adequate safety measures are implemented, the use of COF_2 as a cleaning gas would greatly reduce the greenhouse gas emission from the semiconductor industry.

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References

1. *The Science of Climate Change* IPCC Climate Change, (1995).
2. W. Entley, W. Hennessy, and J. Langan, *Electrochem. Solid-State Lett.*, **3**, 99 (2000).
3. L. Pruette, S. Karecki, R. Reif, L. Tousignant, W. Reagan, S. Kesari, and L. Zazzera, *J. Electrochem. Soc.*, **147**, 1149 (2000).
4. C. Allgood, M. Mocella, H. Chea, and H. Sawin, *J. Electrochem. Soc.*, **150**, G112 (2003).
5. Y. Mitsui, Y. Kosano, T. Takaichi, T. Beppu, and A. Sekiya, in *Proceedings of 8th Annual International Semiconductor Environmental Safety and Health (ISESH) Conference*, Kenting, Taiwan (2001).
6. Y. Kosano, Y. Mitsui, T. Takaichi, A. Sekiya, and T. Beppu, in *Proceedings of 7th Annual International Semiconductor Environmental Safety and Health (ISESH) Conference*, Dresden, Germany (2000).
7. S. Suzuki, E. Wani, T. Sunada, K. Shibata, T. Morimura, Y. Mitsui, Y. Kosano, T. Takaichi, T. Beppu, and A. Sekiya, in *The Global Climate Change: A Coordinated Response by Electrochemistry and Solid-State Science and Technology*, A. Wieckowski, Editor, PV 2000-20, p. 231, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
8. T. Yonemura, K. Fukae, Y. Ohira, Y. Mitsui, T. Takaichi, A. Sekiya, and T. Beppu, *J. Electrochem. Soc.*, **150**, G707 (2003).