# Global warming gas emission during plasma cleaning process of silicon nitride using $c$-$C_4F_8O/O_2$ chemistry with additive Ar and $N_2$

K. J. Kim, C. H. Oh, and N.-E. Lee[a)]
*Department of Materials Engineering and Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon, Kyunggi-do 440-746, Korea*

J. H. Kim, J. W. Bae, and G. Y. Yeom
*Department of Materials Engineering, Sungkyunkwan University, Suwon, Kyunggi-do 440-746, Korea*

S. S. Yoon
*Jusung Engineering, No. 49, Neunpyeong-ri, Opo-myeun, Kwangju, Kyunggi-do 464-890, Korea*

(Received 3 July 2002; accepted 8 December 2003; published 12 February 2004)

In this work, the cyclic perfluorinated ether ($c$-$C_4F_8O$) with very high destructive removal efficiencies (DREs) was used as an alternative process gas for cleaning of the silicon nitride chemical vapor deposition chamber. Direct plasma cleaning of silicon nitrides in a capacitively coupled plasma mode using the gas mixtures of $c$-$C_4F_8O/O_2$, $c$-$C_4F_8O/O_2$+Ar, and $c$-$C_4F_8O/O_2+N_2$ was investigated in order to evaluate the effects of additive gases (Ar and $N_2$) on the global warming. Emitted net volumes of perfluorocompounds during cleaning of silicon nitride were quantitatively measured by Fourier transform-infrared spectroscopy. The effects of additive Ar and $N_2$ on the DRE and the million metric tons of carbon equivalent (MMTCE) values were evaluated from the volumetric emission of effluents. MMTCE value for the optimized $c$-$C_4F_8O/O_2$ cleaning was decreased by ≅64% compared to that of the $C_2F_6/O_2$ chemistry as a result of decreased emission of $CF_4$. During the cleaning process using $c$-$C_4F_8O/O_2$ gas mixtures with additive Ar and $N_2$, the DRE value as high as ≅98% was obtained and MMTCE values were reduced by ≅78% and ≅81% compared to those of $C_2F_6/O_2$ cleaning, respectively, as a combined result of the decreased $CF_4$ emission and increased cleaning rate. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1645881]

## I. INTRODUCTION

Perfluorocompounds (PFCs) emissions from the semiconductor industries are suspected to contribute to global warming. To prevent further increase of global warming, the semiconductor industries are all committed to reduce the emission of PFCs 10% below the emission level of 1995 by 2010.[1] Among the semiconductor fabrication processes, the plasma cleaning process of the chemical vapor deposition (CVD) chamber for silicon dioxide and silicon nitride is known to emit the largest quantities of net PFCs. It is, therefore, necessary to develop various methods to cut down the emission of PFCs.[2,3]

For the CVD chamber cleaning processes of silicon dioxide or silicon nitride, various alternative gases such as $C_3F_8$, $c$-$C_4F_8$, and $NF_3$ having relatively low global warming potential have been studied to replace conventional PFCs such as $CF_4$, $SF_6$, and $C_2F_6$.[4–6] In particular, the cleaning process using $NF_3$ remote plasma has been developed and widely used in order to minimize the erosion and damage of chamber parts during cleaning as well as to decrease the global warming effect.[6] Use of $NF_3$/Ar cleaning chemistry, however, has some issues related to the cost of gas used and corrosion in the exhaust lines. Therefore, a cleaning process using less expensive gases including $C_4F_8$ and $C_4F_8O$ could be an alternative solution due to lower cost. Recently, $c$-$C_4F_8O$ used in this work is one of the promising alternative gases that are currently under study for cleaning of the silicon dioxide and silicon nitride CVD chamber.[7] Table I describes some of the chemical properties of $c$-$C_4F_8O$.[7]

[a)]Author to whom correspondence should be addressed; electronic mail: nelee@skku.edu

## II. EXPERIMENT

Figure 1 shows a schematic diagram of the gas sampling system used in this experiment for analyzing gas species emitted from the exhaust line during cleaning of silicon nitride layers. The plasma enhanced CVD (PECVD) system was a modified commercial capacitively coupled plasma system for 6 in. wafer processing using 13.56 MHz rf power. The distance between the sample and the top electrodes was 5 cm. The aluminum chamber with a diameter of 27 cm and height of 10 cm was evacuated using a pumping system combined with a booster pump and a dry pump to ≅1 mTorr prior to the injection of cleaning gases. The rf power was applied only to the top electrode for the plasma generation. Silicon nitride samples were located on the floated Al substrate holder without heating and without biased power. Silicon nitride layers deposited on square-shaped (5 cm×5 cm) Si (001) by low pressure CVD were used as samples for the cleaning experiment. The cleaning rate of silicon nitride was measured using an $\alpha$-step profilometer (Tencor, AS-500).

In order to improve the reliability of the concentration data obtained from the Fourier transform infrared spectros-

TABLE I. Chemical properties of $c$-$C_4F_8O$.

| | |
|---|---|
| Vapor pressure | 1802.7 Torr |
| Flammability | Nonflammable |
| Critical temperature | 111.85 °C |
| Critical pressure | 19 951.6 Torr |
| Freezing point | −83 °C |
| Boiling point | 0 °C |
| Toxicity | No |

TABLE II. $GWP_{100}$ values of feed and emitted gases in the present experiments.

| Gases | $GWP_{100}$ |
|---|---|
| $CO_2$ | 1 |
| $CF_4$ | 6500 |
| $C_2F_6$ | 9200 |
| $C_3F_8$ | 7000 |
| $c$-$C_4F_8O$ | 8000 |

copy (FT-IR) (MIDAC I2000) used in the present experiments, a calibration procedure for the measurements using the same calibrated mass flow controller was carried out. The cell path length of the gas cell (1 cm) used in the FT-IR was calibrated as 0.97 cm using a standard $SF_6$ gas with the volume concentration of 501 ppmv and checked regularly. Before measuring the emission of PFCs during the cleaning of silicon nitride layers, flow rate of dilution $N_2$ for purging the dry pump and linearity of feed gases and targeted gases was checked by FT-IR. The flow rate of dilution $N_2$ was 32 980 sccm in our experimental setup. This value was regularly checked to maintain the same experimental conditions for every measurement. Slopes of concentration from the calibration curve for feed and targeted gas flow rates diluted by the $N_2$ ballast at the dry pump were obtained and utilized for calculating the emitted volume of each effluent from the measured concentration data from FT-IR. F mass balances were calculated from the emitted volume of each gas.

Silicon nitride samples were cleaned with gas mixtures of $C_4F_8O/O_2$, $C_4F_8O/O_2+Ar$, and $C_4F_8O/O_2+N_2$, and the effects of additives Ar and $N_2$ were evaluated by measuring the net emitted PFCs quantitatively using FT-IR. The gas sampling system is equipped with a Teflon™ sample line with a 2 m length and 0.25 in. diameter, which was used to extract emitted gases from the exhaust of the vacuum pump line. The exhaust gas samples were extracted after the $N_2$ ballast dilution at the dry pump at near-atmospheric pressure. During the cleaning process, plasma characteristics were investigated by measuring the species in the chamber using optical emission spectroscopy (OES) (SC Technology, Model 300). Optimum conditions were obtained by controlling gas chemistry, $c$-$C_4F_8O$ feed gas flow rate, and operational pressure. The applied rf power was held constant at 350 W.

Destruction of feed gas and effects of emitted gases on global warming were quantified as destructive removal efficiencies (DREs) and 1 000 000 metric tons of carbon equivalents (MMTCEs), respectively. DREs and MMTCEs were calculated by using the volumetric concentration of the species measured by FT-IR and then by applying the formula in Eqs. (1) and (2), respectively,

$$\mathrm{DRE}(\%)=\left[1-\frac{C_o}{C_i}\right]\times 100, \tag{1}$$

where $C_i$ is gas volumetric concentration before plasma cleaning and $C_o$ is gas volumetric concentration after plasma cleaning, and

$$\mathrm{MMTCE}=\sum_i \frac{12}{44}\times\frac{Q_i\,(\mathrm{kg})\times \mathrm{GWP}_{100i}}{10^9}, \tag{2}$$

where $GWP_{100i}$ is the global warming potential of each component (integrated over a 100 yr time horizon) of the calculation and $Q_i$ is the total mass of that species (in kg) released during the process.[8] The $GWP_{100}$ values of the emitted gases included in the calculation of MMTCEs are summarized in Table II. MMTCE values were quantified based on emitted volumes of PFC gases during cleaning of the 1-$\mu$m-thick silicon nitride layer.

A quantitative assessment of the effluents was limited to the targeted species such as $CF_4$, $C_2F_6$, $C_3F_8$, $C_4F_8O$, $SiF_4$, and $COF_2$. Other species such as $CO_2$, CO, and HF were detected but not quantified for calculation of MMTCE. Because noble gases and homonuclear diatomics are not detectable via FT-IR, $F_2$ was not monitored in this study.

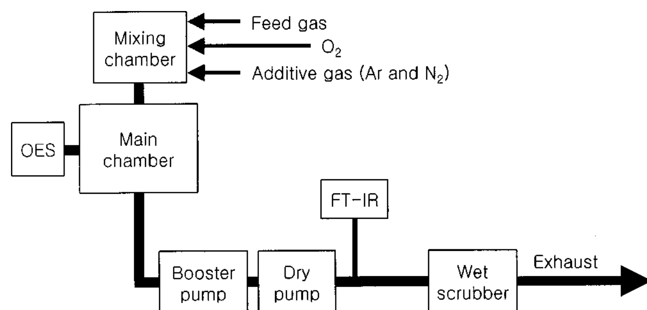


FIG. 1. Schematic of gas sampling system.

## III. RESULTS

In this experiment, evaluation of the effects of additive Ar and $N_2$ on global warming during the cleaning of silicon nitrides using $c$-$C_4F_8O$-based feed gas was referenced to the cleaning rate and the MMTCE value obtained at an optimum condition of the cleaning process using $C_2F_6/O_2$ in the same test chamber. An optimum condition with the maximum cleaning rate of silicon nitrides for $C_2F_6/O_2$ cleaning chemistry was determined by varying the $C_2F_6/O_2$ flow ratio, total flow, and operation pressure at the fixed rf power of 350 W. The cleaning rate of ≅480 nm/min was obtained at the optimum condition (operating pressure: 400 mTorr, $C_2F_6$ flow rate: 22 sccm, and $O_2$ flow rate: 22 sccm). Under the optimum condition for $C_2F_6/O_2$ chemistry, the MMTCE and DRE values obtained were $7.3\times10^{-10}$ and 68%, respectively.

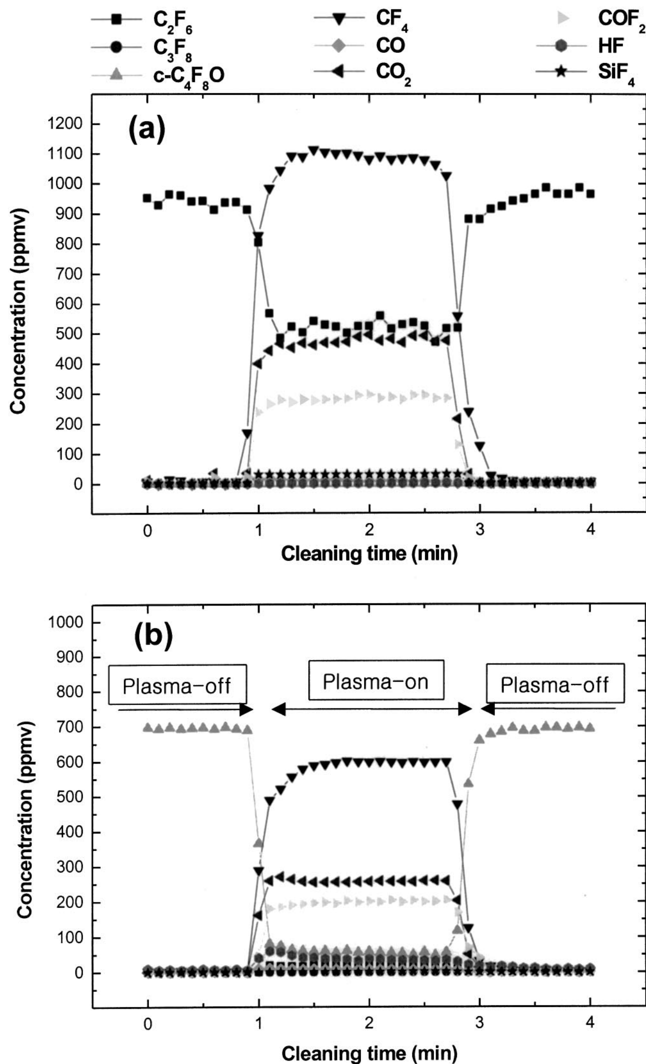


FIG. 2. Extractive FT-IR monitoring data during silicon nitride cleaning using $C_2F_6/O_2$ (a) and $c$-$C_4F_8O/O_2$ chemistry (b).

Similarly to the case of the $C_2F_6/O_2$ chemistry, the cleaning rate during cleaning using $c$-$C_4F_8O/O_2$ chemistry obtained at an optimum condition (operating pressure: 500 mTorr, $c$-$C_4F_8O$ flow rate: 16 sccm, and $O_2$ flow rate: 64 sccm) was ≅508 nm/min. The DRE value obtained under this optimum condition was 98.4%, indicative of nearly complete decomposition of $c$-$C_4F_8O$ feed gas. The MMTCE value obtained for $c$-$C_4F_8O/O_2$ cleaning was $2.6\times 10^{-10}$ and was decreased by ≅64% as compared to that of optimized $C_2F_6/O_2$ chemistry.

Figures 2(a) and 2(b) show the time dependence of the concentration of byproducts derived from the FT-IR analysis. The results in Figs. 2(a) and 2(b) were for optimized cleaning conditions for $C_2F_6/O_2$ and $c$-$C_4F_8O/O_2$ cleaning gas chemistry, respectively. Emitted volumes, F mass balances, and MMTCE values are summarized in Table III. A main PFC effluent is $CF_4$ gas that primarily contributes to the global warming effect due to its high global warming potential. The data in Fig. 2 and Table III indicate that the emitted volume of $CF_4$ during $c$-$C_4F_8O/O_2$ cleaning is smaller than that during $C_2F_6/O_2$ cleaning. Other effluents with global warming potential in this study are $C_2F_6$, $C_3F_8$, and $CO_2$. For MMTCE calculation, $C_2F_6$ and $C_3F_8$ were also included. However, their contribution to the global warming effect during $c$-$C_4F_8O$ processes was found to be negligibly small. F mass balances were calculated for $C_2F_6/O_2$ and $c$-$C_4F_8O/O_2$ cleaning chemistries. Fluorine mass from $F_2$ was not included because of the difficulty of measurement by FT-IR. F mass balance values obtained (F mass in effluents/F mass in influents), as shown in Table III, were 1.21 and 0.68 for $C_2F_6/O_2$ and $c$-$C_4F_8O/O_2$ cleaning chemistries, respectively. The F balance values for $C_2F_6/O_2$ cleaning chemistries show the values off from 100%, possibly due to the errors in obtaining a large dynamic range (i.e., linearity) in the $CF_4$ calibration curve in the concentration range of measurement and difficulty of $F_2$ measurement in FT-IR in this experiment.

TABLE III. Calculated volumetric emissions of effluents by FT-IR and fluorine mass balance (in grams) for optimized $C_2F_6/O_2$ and $c$-$C_4F_8O/O_2$ cleaning chemistries during cleaning of the 1-$\mu$m-thick silicon nitride layer. Fluorine mass from $F_2$ was not included due to the difficulty of measurement by FT-IR.

| | Cleaning chemistry | | | |
|---|---|---|---|---|
| | $C_2F_6/O_2$ | | $c$-$C_4F_8O/O_2$ | |
| | Volume (scc) | Grams (F only) | Volume (scc) | Grams (F only) |
| Influents | | | | |
| $C_2F_6$ | 52.6 | 0.254 | — | — |
| $c$-$C_4F_8O$ | — | — | 28.7 | 0.18 |
| Effluents | | | | |
| $C_2F_6$ | 28.2 | 0.135 | 1.06 | 0.005 |
| $C_3F_8$ | 0 | 0 | 0 | 0 |
| $c$-$C_4F_8O$ | 0 | 0 | 4.44 | 0.030 |
| $CF_4$ | 47.0 | 0.151 | 23.1 | 0.074 |
| CO | 0.41 | — | 0.31 | — |
| $CO_2$ | 20.24 | — | 9.80 | — |
| HF | 0.04 | 0 | 1.56 | 0.001 |
| $COF_2$ | 12.10 | 0.019 | 7.41 | 0.013 |
| $SiF_4$ | 1.30 | 0.002 | 1.35 | 0.004 |
| F mass | | 1.21 | | 0.68 |
| MMTCE | $8.2\times 10^{-10}$ | | $3.3\times 10^{-10}$ | |

In order to investigate the possibility of reducing MMTCE values further by increasing cleaning rate and/or reducing the amount of emitted gases with high GWPs such as $CF_4$, the effects of additives Ar and $N_2$ during $c$-$C_4F_8O/O_2$ cleaning were investigated. Addition of Ar does not expect to produce any byproducts because of the inertness of Ar, but expects to change dissociation characteristics of cleaning gases in the chamber and thereby recombination characteristics of reacting radicals leading to change in the volume of emitted gases. Even though addition of $N_2$ to PFC gases, for example $CF_4$, was reported to help to increase etch rate of silicon nitride,[8–10] the effects on global warming have not been reported. These additive gases are nontoxic and not expensive compared to most of the PFCs.

Figure 3 shows the cleaning rate of the silicon nitride layer using $c$-$C_4F_8O/O_2+Ar\,(N_2)$ cleaning gases as a func-

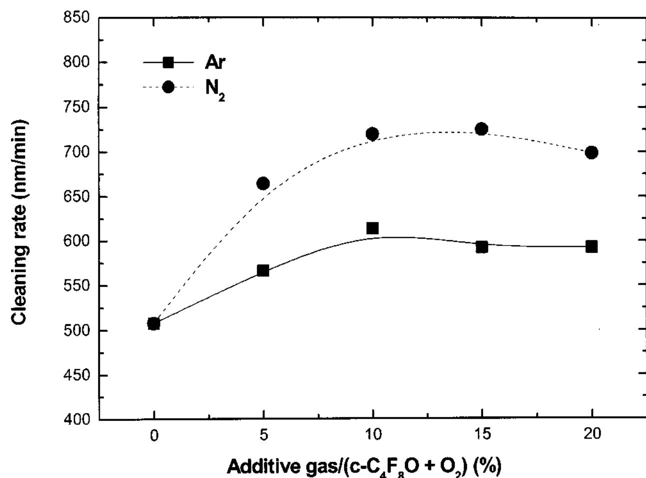


FIG. 3. Cleaning rates of silicon nitride as a function of flow rate ratio of additive gases to ($c$-$C_4F_8O+O_2$).

tion of flow rate ratio of additives Ar and $N_2$ to ($c$-$C_4F_8O+O_2$), respectively. Effects of additives Ar and $N_2$ on the cleaning rate were investigated only by changing the flow rate of additive gases under the optimized condition of $c$-$C_4F_8O/O_2$ cleaning (operating pressure: 500 mTorr, $c$-$C_4F_8O$ flow rate: 16 sccm, and $O_2$ flow rate: 64 sccm). The total flow of $c$-$C_4F_8O/O_2$+Ar and $c$-$C_4F_8O/O_2+N_2$ was changed from 80 to 100. As shown in the data in Fig. 3, cleaning rates of silicon nitride were increased gradually with Ar and $N_2$ added and then were saturated at $\cong$10% of added gases. The addition of $N_2$ gas to $c$-$C_4F_8O/O_2$ chemistry increases the cleaning rate more effectively than the addition of Ar, as seen in Fig. 3. The cleaning rates are increased by $\cong$20% and 33% compared to the case of cleaning without additives Ar and $N_2$, respectively. When more than 10% of $N_2$ is added, the cleaning rate tends to be saturated, which is similar to the case of adding Ar. Adding $N_2$ during the cleaning of silicon nitride helps decrease the global warming effect because an increase in the cleaning rate can reduce the use of feed gas used for cleaning of samples with the same thickness.

The volumes of gases emitted during cleaning of 1-$\mu$m-thick silicon nitride layers were obtained from the volumetric concentration measured by FT-IR and are shown in Fig. 4. Figure 4(a) shows that the emitted volume of $CF_4$ was decreased and slightly increased again as additive Ar flow increases. The emitted volume of $CF_4$ was decreased by $\cong$34% with 10% of Ar added compared to the case of no Ar added. The volume of other emitted gases was not changed significantly with Ar added, as seen in Fig. 4(a). In the case of $N_2$ addition [see Fig. 4(b)], the emitted volume of $CF_4$ was decreased by $\cong$50% at the condition with $N_2\geqslant$10% added compared to the case of no $N_2$ added. Even though one can see that the emission of $COF_2$ and HF slightly increases contrary to the decrease of the emission of $CF_4$, a large decrease in the $CF_4$ emission should be balanced by an increase in emission of other byproducts containing fluorine in terms of F mass closure. Experimental proof cannot be provided here, but processes such as increase in the $F_2$ emission or increase in polymerization in the chamber might be responsible for this. One can also observe much increased emission volume of CO and $CO_2$. In particular, increase of emission volume of $CO_2$ can be suggested as the result of forbidden polymerization on the surface of the cleaning sample. Among byproducts, GWPs of $CO_2$ have lower emission volume than those of $CF_4$, and $COF_2$ and HF can be removed by a wet scrubber.[7]

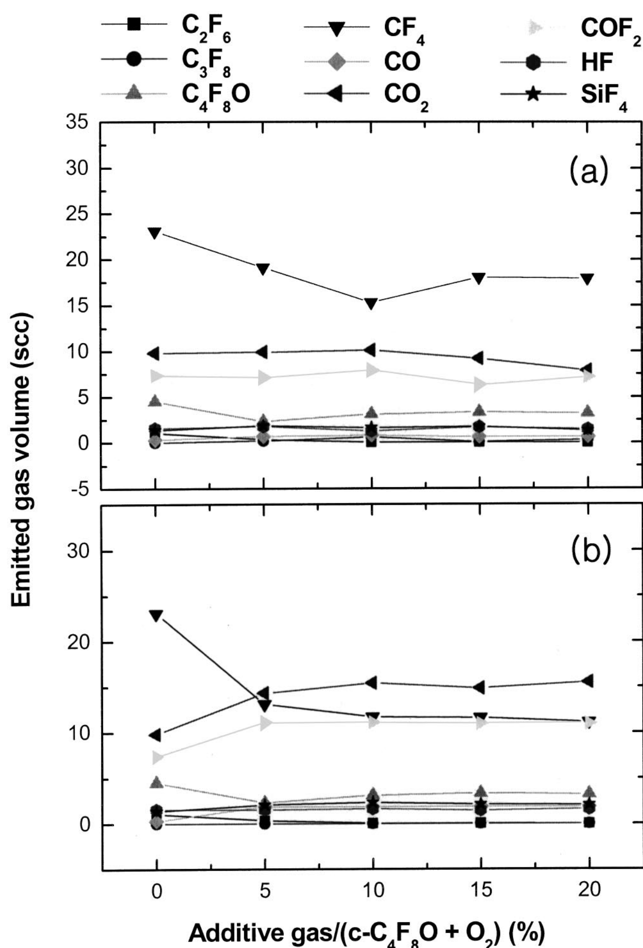


FIG. 4. Emitted gas volume during silicon nitride cleaning as a function of flow rate ratio of additive gases: (a) Ar and (b) $N_2$ to ($c$-$C_4F_8O+O_2$).

Figure 5 shows DRE values of feed gas as a function of flow rate of additive Ar and $N_2$ gases. DRE values, as seen in Fig. 5, were increased from 98.38 to 99.56 as Ar increases from 0 to 10 sccm and then decreased gradually with Ar >10% added. In the case of $N_2$ addition, DRE values were not changed significantly with increase in $N_2$. An interesting observation is that Ar addition is more effective than $N_2$ addition in increasing DRE values. This may indicate differences in mechanisms of increasing cleaning rate and reducing MMTCE values (as shown in Fig. 7) for Ar and $N_2$ addition.

In order to understand the increase of cleaning rate during cleaning with additive $N_2$, OES measurements were carried out. In Fig. 6, OES analyses data during glow discharges

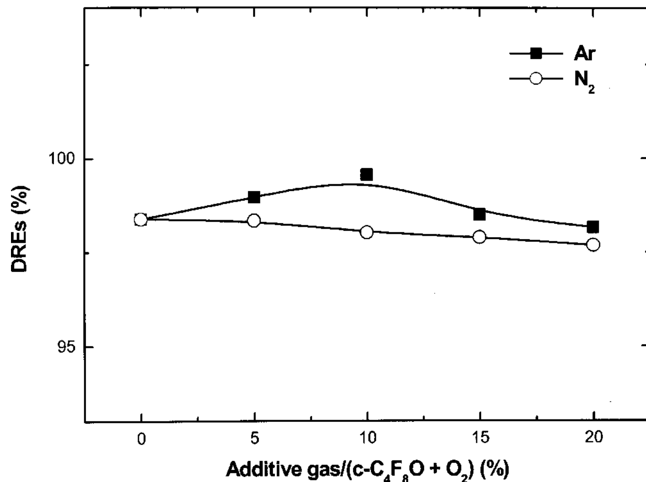


FIG. 5. DREs of $c$-$C_4F_8O$ feed gas as a function of flow rate ratio of additive gases to $(c$-$C_4F_8O+O_2)$.

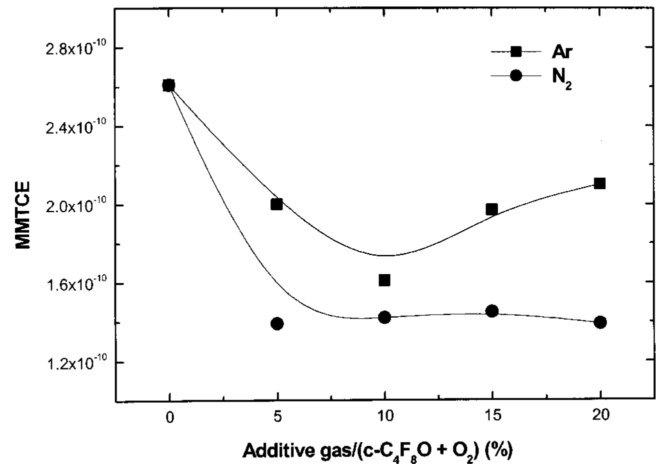


FIG. 7. MMTCE values during silicon nitride cleaning as a function of flow rate ratio of additive Ar and $N_2$ to $(c$-$C_4F_8O+O_2)$.

with additive $N_2$ without a cleaning sample inside the chamber, indicate the creation of a NO molecule from the observed peaks at wavelengths of 653.6 and 656.9 nm. The F peak position at 703.7 nm was indicated in Fig. 6. Similarly to the case of 624, 685.6, and 690.2 nm, however, the peak at 703.7 nm was not clearly detected. We suppose that the intensity of the peak at 703.7 nm corresponding to the F radical is not apparently detected due to its low intensity and overlapping with other neighboring peaks from, for example, $N_2$.

Figure 7 shows the MMTCE data obtained using Eq. (2). In this work, when 10% Ar and $N_2$ were added, MMTCE values were decreased by ≅38% and ≅46%, respectively, compared to the case of cleaning without additive gases. As compared to $C_2F_6/O_2$ cleaning (MMTCE$\cong 7.3\times 10^{-10}$), MMTCE values were decreased by ≅78% and ≅81%, respectively, when 10% Ar and $N_2$ were added.

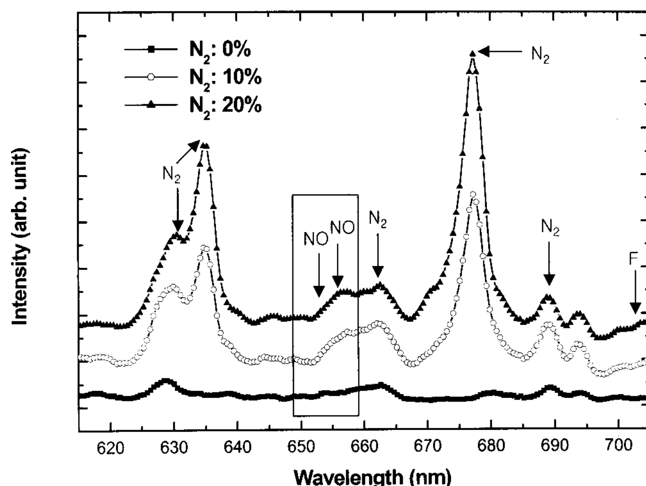


FIG. 6. OES spectra of glow discharge of $c$-$C_4F_8O/O_2+N_2$ without silicon nitride sample.

## IV. DISCUSSION

Reduction of MMTCE values by ≅38% in the cleaning experiment using $c$-$C_4F_8O/O_2$ chemistry with additive Ar is attributed to the reduction of emitted $CF_4$ by ≅34% and at the same time an increase in the cleaning rate of silicon nitride layers by ≅20% at the Ar flow rate of 10 sccm. Reduction in cleaning time by increased cleaning rate will contribute to the decrease in MMTCE values due to a reduction in the use of feed gas and decrease in total emitted volume. Reduced cleaning time for the same thickness of silicon nitride layers also contributes to the higher throughput for the production.

A slight increase in the cleaning rate of silicon nitride by adding Ar to $c$-$C_4F_8O/O_2$ chemistry is presumably attributed to increased density of F atoms from redecomposition of byproducts such as $CF_4$. In the case of adding Ar, the increase in F (703.7 nm) peak intensity was verified by the OES analyses (not shown here). The increase in DRE values shown in Fig. 5 is closely related to the increased F density in the chamber due to the change in plasma reaction chemistry. Effects of other radicals such as $CF_x$ $(x=1-3)$ were not conclusive here because the peaks of $CF_x$ radicals below 290.0 nm ranges were not detectable due to the detection limit (290.0–770.0 nm) of the OES system used in this experiment.

MMTCE values by additive Ar, as shown in Fig. 7, indicate a trend similar to the decrease of the emitted $CF_4$, as seen from the data in Fig. 4. It suggests that decrease in the emitted volume of $CF_4$ contributes to the reduction of the MMTCE values. Decrease in $CF_4$ emission may be closely related to the change in plasma reaction chemistry and recombination characteristics of radicals in the plasma chamber. Further study will be required to understand the correlation between plasma characteristics in the chamber and emission characteristics in the exhaust line. Emission characteristics are expected to depend upon plasma reactions in the chamber and recombination in the exhaust as well as inside the chamber.

Adding $N_2$ during $c$-$C_4F_8O/O_2$ cleaning is more effective than adding Ar in increasing the cleaning rate as well as in reducing the emitted volume of $CF_4$. Reduction of MMTCE values by ≅46% in the cleaning experiment using $c$-$C_4F_8O/O_2$ chemistry with additive $N_2$ is attributed to the reduction of emitted $CF_4$ by ≅50% and at the same time the increase in cleaning rate of silicon nitride layers by ≅33% at the 10% $N_2$ flow rate.

MMTCE data by the additive $N_2$ shown in Fig. 7 also show a trend similar to the decrease of the emitted $CF_4$ with high GWPs, as seen from the data in Fig. 4. In addition, an increase in the cleaning rate leading to less use of the feed gas and shorter cleaning time contributes to the reduced emission of $CF_4$ during cleaning of the silicon nitride sample with the same film thickness. It can be concluded, therefore, that a significant reduction of emitted $CF_4$ by the effects of additive $N_2$ and at the same time a reduction in the use of feed gas due to increased cleaning rate contribute to the decrease in MMTCE values for cleaning of the same thickness of silicon nitride sample.

An increased cleaning rate by additive $N_2$ gas can be attributed to the increase in the NO molecules created in glow discharge plasma during silicon nitride cleaning.[11] Extensive research has been done on the production of NO in PFC discharges containing $N_2$ and $O_2$.[11] The NO molecule or the energetic metastable NO* can facilitate etching reaction on the surface as a reactive species by splitting the Si–N bond on the surface leading to the formation of volatile $N_2O$ or as a source of activation energy for NO–N attachment leading to the formation of volatile $N_2$.[10] The presence of NO in the gas phase is also known to allow silicon nitride to be etched efficiently by F atoms.[10] Similarly to the previously reported results, NO molecules present in the plasma are expected to promote the etching reaction of silicon nitride, leading to the formation of $SiF_4$, $N_2O$, and $N_2$. The detection of NO in the exhaust was below the detection limit of FT-IR used in the present experiment.

## V. SUMMARY

An alternative $c$-$C_4F_8O$-based cleaning chemistry for the silicon nitride PECVD chamber was evaluated as a potential replacement for $C_2F_6/O_2$ cleaning chemistry currently used in many fabs. In the case of cleaning using $c$-$C_4F_8O/O_2$ feed gas, MMTCE was reduced by ≅64% compared to that of optimized $C_2F_6/O_2$ chemistry.

Use of less feed gas and reduction in the emitted volume of $CF_4$ during the cleaning process are found to be very effective in reducing global warming effects. In this work, addition of Ar or $N_2$, especially $N_2$, leads to the reduction of global warming through increase in cleaning rate as well as reduction in emission of $CF_4$.

Reduction of global warming effects by additive Ar is primarily attributed to the reduction of emitted $CF_4$ with high GWPs. In the case of adding $N_2$ to $c$-$C_4F_8O/O_2$ chemistry, a significant increase in cleaning rate contributes to the further decrease in MMTCE values, together with a reduction in the emission of $CF_4$, leading to the reduced input of feed gas used for cleaning the same thickness of the silicon nitride sample.

In summary, when Ar and $N_2$ are added by 10% of total flow, MMTCE values were decreased by ≅34% and ≅50%, respectively, compared to those without additive gases. As compared to $C_2F_6/O_2$ plasma cleaning, MMTCE values for $c$-$C_4F_8O/O_2$ chemistry with the addition of Ar and $N_2$ were decreased by ≅78% and ≅81%, respectively.

## ACKNOWLEDGMENTS

This work was supported by the Clean Technology Development Program of the Ministry of Commerce, Industry, and Energy. This work is also supported in part by the BK21 program of the Ministry of Education and by the ERC program of Korea Science and Engineering Foundation (KOSEF). The authors thank S.-K. Chae, S.-G. Lee, D.-H. Cho, and K.-S. Hong at Samsung Electronics and C. J. Lee at Jusung Engineering for their help.

[1]International Technology Roadmap for Semiconductors, 1999, p. 248.
[2]W. Worth, International Environment, Safety, and Health (IESH) Conference Processing, Milan, Italy, 23–26 June 1997.
[3]W.-T. Tsai, H.-P. Chen, and W.-Y. Hsien, J. Loss Prevention Process Industries **15**, 66 (2002).
[4]S. M. Karecki, L. C. Pruette, and R. Reif, J. Vac. Sci. Technol. A **16**, 755 (1998).
[5]L. C. Pruette, S. M. Karecki, and R. Reif, J. Vac. Sci. Technol. A **16**, 1577 (1998).
[6]S. Raoux *et al.*, J. Vac. Sci. Technol. B **17**, 477 (1999).
[7]L. Pruette, S. Karecki, R. Reif, L. Tousignant, W. Reagan, S. Kesari, and L. Zazzera, J. Electrochem. Soc. **147**, 1149 (2000).
[8]M. G. Blain, T. L. Meisenheimer, and J. E. Stevens, J. Vac. Sci. Technol. A **14**, 2151 (1996).
[9]B. E. E. Kastenmeier, P. J. Matsuo, J. J. Beulens, and G. S. Oehrlein, J. Vac. Sci. Technol. A **14**, 2802 (1996).
[10]B. E. E. Kastenmeier, P. J. Matsuo, G. S. Oehrlein, R. E. Ellefson, and L. C. Frees, J. Vac. Sci. Technol. A **19**, 25 (2001).
[11]J. Dulak, B. J. Howard, and C. Steinbrüchel, J. Vac. Sci. Technol. A **9**, 775 (1991).