

Effect of O₂(CO₂)/C₄F₈O gas combinations on global warming gas emission in silicon nitride PECVD plasma cleaning

B.H. Oh^{a,*}, J.W. Bae^a, J.H. Kim^a, K.J. Kim^a, Y.S. Ahn^a, N.-E. Lee^a, G.Y. Yeom^a, S.S. Yoon^b, S.-K. Chae^c, M.-S. Ku^a, S.-G. Lee^c, D.-H. Cho^c

^aDepartment of Materials Engineering, Sungkyunkwan University, Jangan-Gu, Chunchun-Dong 300, Suwon, South Korea

^bR&D Division, Jusung Engineering Co Ltd, #49 Neungpyeong-Ri, Opo-Myeun, Kwangju-Gun, Kyunggi-do, South Korea

^cSamsung Electronics Co Ltd, san #24 Nongseo-Ri, Kiheung-Eup, Yongin, South Korea

Abstract

In this study, O₂/C₄F₈O and CO₂/C₄F₈O have been used as the chemicals for plasma-enhanced chemical vapor deposition (PECVD) chamber-cleaning of silicon nitride, and the effects of gas mixture and operational pressure on the silicon-nitride cleaning rate and emission properties, such as emission species, destruction and removal efficiencies (DREs), and million metric tons of carbon equivalent (MMTCE), have been investigated. O₂/C₄F₈O generally showed a higher silicon-nitride cleaning rate compared to CO₂/C₄F₈O, possibly due to the removal of fluorine by carbon in CO₂. The highest silicon-nitride cleaning rate obtained with O₂/C₄F₈O was approximately 600 nm/min for 80% O₂/20% C₄F₈O at 66.7 Pa (500 mtorr), 40 sccm, 150 W of 13.56-MHz RF power, and without substrate heating. Emission species, such as CF₄, COF₂ and CO₂, were observed through the exhaust line during silicon nitride cleaning, in addition to the undestructured remaining feed gases. The quantities of these emission species were higher than that of C₄F₈O fed through the cleaning chamber. With 80% O₂/20% C₄F₈O, the highest DREs and the lowest MMTCE obtained were 92% and 3 × 10⁻¹⁰, respectively. In the case of CO₂/C₄F₈O, silicon nitride cleaning rates were lower, the DRE was lower and MMTCEs were higher than those of O₂/C₄F₈O. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Global warming gas; Perfluorocompound; Plasma-enhanced chemical vapor deposition (PECVD)

1. Introduction

Perfluorocompounds (PFCs) emitted by industry are known to cause serious global warming effects. To prevent further increases in global warming, members of the semiconductor industry have decided to reduce the emission of PFCs responsible for global warming by 10% until 2010 [1]. Among semiconductor fabrication processes, the plasma-chamber cleaning process during chemical vapor deposition (CVD) is known to emit the largest quantities of PFC gases. Therefore, it is necessary to develop various methods to drastically reduce the emission of PFC gases using the development of replacement gases, recovery and reuse, or abatement [2,3].

For silicon dioxide or silicon nitride CVD chamber-cleaning processes, various gases, such as C₄F₈, C₃F₈, NF₃, etc., which have low global-warming potential have been studied by many researchers to replace conventionally used PFCs, such as CF₄, SF₆, C₂F₆, etc. Among these, NF₃ has shown to have more than 90% DRE, and is also currently applied to commercial PECVD chamber-cleaning processes. Some of the problems with the NF₃ process are the price, the shortage of the gas, and unwanted F₂ production as a by-product [3]. Recently, other replacement gases, which are available at low price and in large quantity, have also been widely studied. C₄F₈O is one of the gases which is currently under study as a replacement in the cleaning of a silicon oxide PECVD chamber.

In this study, a silicon nitride PECVD chamber was cleaned with O₂/C₄F₈O and CO₂/C₄F₈ and the effects on chamber cleaning and PFC emission properties were

* Corresponding author. Tel.: +82-31-290-7418; fax: +82-31-290-7410.

E-mail address: visionbh@netian.com (B.H. Oh).

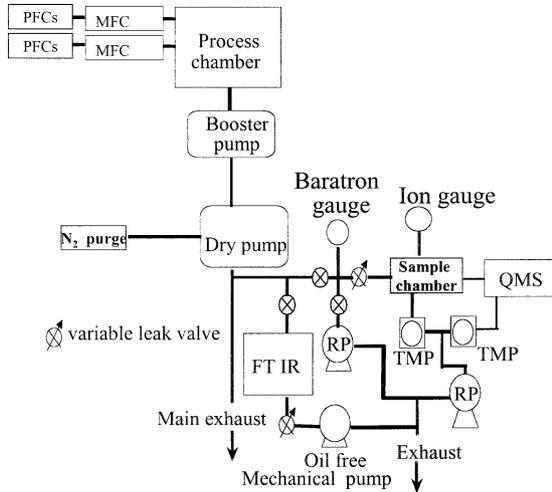


Fig. 1. Schematic diagram of the PFC gas sampling system used in this experiment.

studied using a quadrupole mass spectrometer and Fourier-transform infrared spectroscopy.

2. Experimental

Fig. 1 shows the gas sampling system used in this experiment to analyze gas species emitted from the exhaust valve during cleaning of the silicon nitride PECVD chamber. The CVD chamber was evacuated using a pump system consisting of a booster pump and a dry pump to 0.13 Pa (10^{-3} torr) before introduction of the cleaning gases. The dry pump uses N_2 as the purging gas, and the flow rate of the purging gas was estimated as 33.2 slm. The CVD system was a home-made capacitively coupled PECVD system using 13.56 MHz for the RF power. As the chamber cleaning gases, O_2/C_4F_8O and CO_2/C_4F_8O were used, and the effects of gas mixing ratio and operational pressure on the silicon nitride cleaning rate, emission species and PFC emission rate were investigated. RF power to the chamber during cleaning was 150 W and the total flow rate was fixed at 40 sccm.

The gas analysis tools used in this experiment were a quadrupole mass spectrometer (QMS; Hiden Analytical Inc, HAL IV 201) and a Fourier-transform infrared spectrometer (FTIR; MIDAC I2000) and they were connected to the exhaust line. Mass peaks of the quadrupole mass spectrometer and the intensity of each molecule detected by FTIR were calibrated using various calibration gases. The destruction of feed gas and the amount of the emitted global warming gases were estimated as DRE and MMTCE, respectively. Silicon nitride samples were located on the substrate without heating and the silicon nitride cleaning rate was measured using a step profilometer.

3. Results and discussion

Fig. 2a,b shows the effect of gas mixing ratio and operational pressure on the silicon nitride cleaning rate, respectively. In Fig. 2a, oxygen in O_2/C_4F_8O was varied from 40 to 90% and CO_2 in CO_2/C_4F_8O from 50 to 90%, while maintaining the operational pressure at 66.7 Pa (500 mtorr). In Fig. 2b, the operational pressure of the cleaning process was varied from 5.3 (40 mtorr) to 93.3 Pa (700 mtorr), while keeping the gas ratio at 80% $O_2/20%$ C_4F_8O and 90% $CO_2/10%$ C_4F_8O , respectively. The RF power and gas flow rate were maintained at

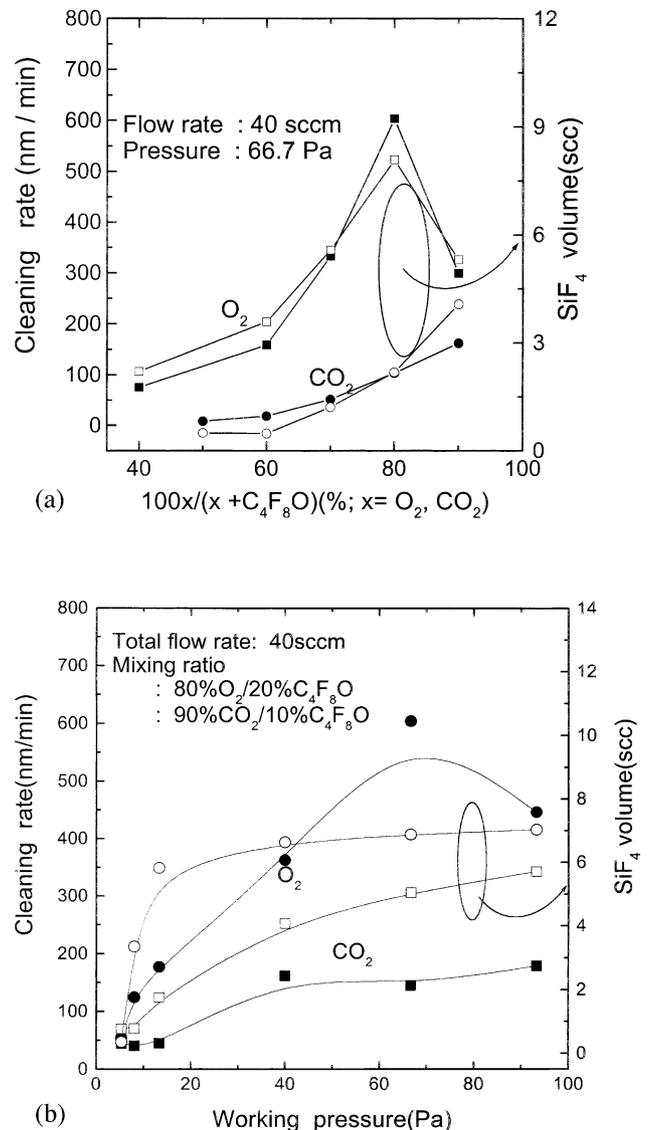


Fig. 2. Silicon nitride cleaning rate and SiF_4 volume emitted as a function of: (a) gas mixing ratio of O_2 (CO_2)/[$C_4F_8O + O_2$ (CO_2)] at 66.7 Pa (500 mtorr); and (b) the operational pressure at gas mixing ratios of 80% $O_2/20%$ C_4F_8O and 90% $CO_2/10%$ C_4F_8O . Total pressure and flow rate were maintained at 66.7 Pa (500 mtorr) and 40 sccm, respectively.

150 W and 40 sccm, respectively. As shown in Fig. 2a, the silicon nitride cleaning rate initially increased with increasing oxygen up to 80% in the O_2/C_4F_8O gas mixture, and a further increase in oxygen decreased the cleaning rate. The increase in cleaning rate with increasing O_2 appears to originate from the release of more fluorine by the formation of CO in the plasma during cleaning, even though the partial pressure of C_4F_8O decreases with increasing O_2 in the mixture. The decrease in cleaning rate above 80% O_2 reflects a decrease in fluorine in the gas mixture. In the case of CO_2/C_4F_8O , the cleaning rate continuously increased with increasing CO_2 in the gas mixture; however, the cleaning rate was much lower than that of O_2/C_4F_8O , possibly due to the additional formation of CF_x by carbon in CO_2 [4,5]. If silicon nitride is etched, SiF_4 is released through the exhaust line, and therefore the flow rates of SiF_4 measured by FTIR were also included in the figures. As shown, the flow rates of SiF_4 showed the same trends as the cleaning rates, similar to the results of other researchers [6–8]. The highest cleaning rate obtained in the experiment was approximately 600 nm/min with 20% $O_2/80%$ C_4F_8O at 66.7 Pa (500 mtorr).

Using FTIR and QMS, the species emitted through the exhaust line during cleaning were monitored and the results are shown in Fig. 3 for FTIR and Fig. 4a for QMS. In fact, QMS data were cracking patterns of parent molecules sampled at the exhaust line, and therefore to obtain partial pressure values of parent molecules, cracking patterns of each possible parent molecule had to be previously measured and calculated. On the other hand, the data obtained by FTIR were from the molecules themselves. Therefore, it was easier to calculate DREs and MMTCEs from the FTIR data. As shown in Fig. 3a,b for 80% $O_2/20%$ C_4F_8O (Fig. 3a is with silicon nitride cleaning and Fig. 3b is with plasma decomposition in the absence of silicon nitride; COF_2 is not shown for the case with silicon nitride cleaning) and Fig. 3c for 90% $CO_2/10%$ C_4F_8O with silicon nitride cleaning, the species with largest volumetric parts per million (ppmv) observed was CF_4 , followed by COF_2 . Also, a large quantity of CO_2 was observed for 80% $O_2/20%$ C_4F_8O . In the case of 90% $CO_2/10%$ C_4F_8O , due to the large quantity of CO_2 in the feed gas, it was difficult to estimate recombined CO_2 during cleaning. In fact, as shown in the figures, the ppmv of CF_4 formed from C_4F_8O was 2.5-fold higher than that of C_4F_8O for 80% $O_2/20%$ C_4F_8O and six-fold higher for 90% $CO_2/10%$ C_4F_8O . The COF_2 and CO_2 emitted were also considerably higher than C_4F_8O for 80% $O_2/20%$ C_4F_8O . Other possible recombinations of PFC gases, such as C_2F_6 , C_3F_8 and C_4F_8 , were not observed during cleaning using $O_2(CO_2)/C_4F_8O$. Fig. 4b shows the cracking pattern of O_2/C_4F_8O measured by QMS without generating a plasma, and as

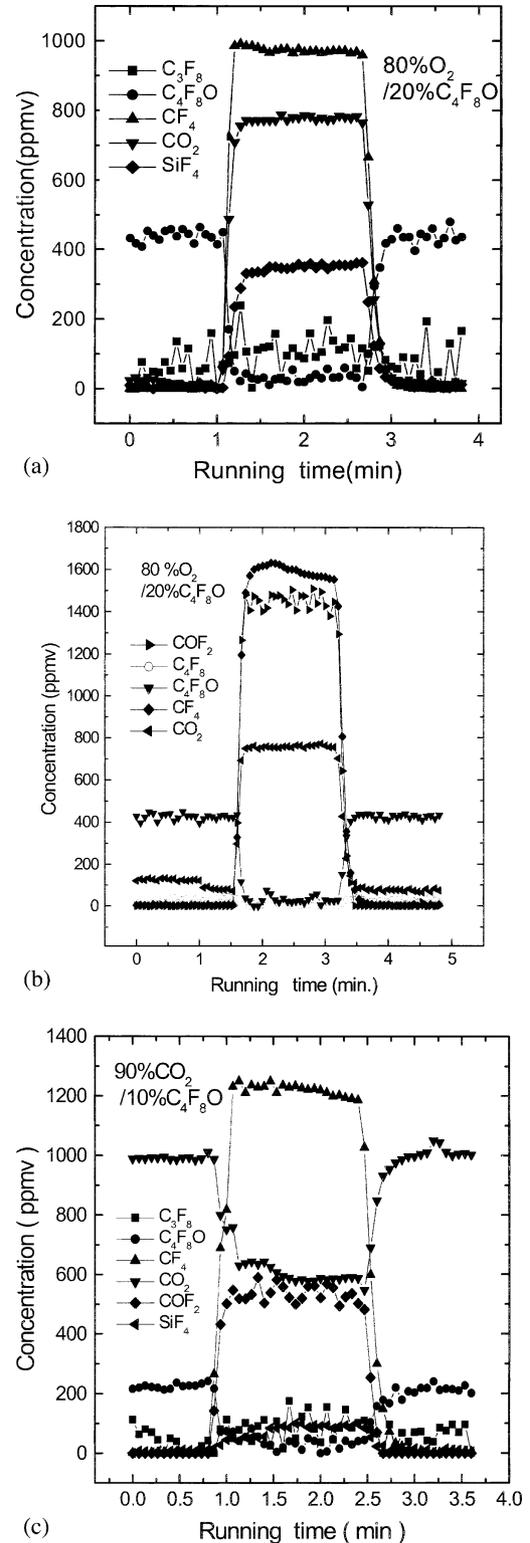


Fig. 3. FTIR data of gas concentration emitted during the silicon nitride cleaning process with process conditions of 80% $O_2/20%$ C_4F_8O : (a) with silicon nitride cleaning; (b) with plasma decomposition in the absence of silicon nitride; and (c) with process conditions of 90% $CO_2/10%$ C_4F_8O with silicon nitride cleaning. Total pressure and flow rate were maintained at 66.7 Pa (500 mtorr) and 40 sccm, respectively.

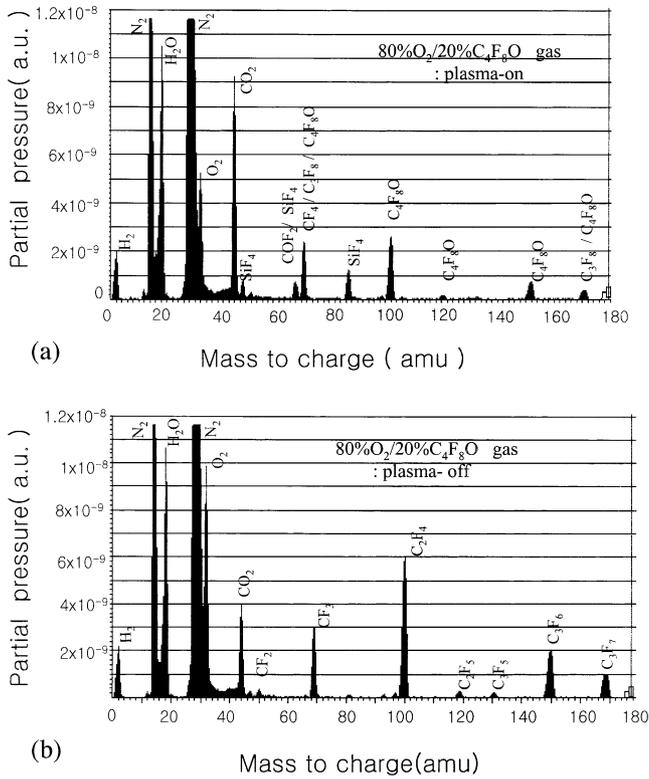


Fig. 4. QMS data of gases emitted during silicon nitride cleaning by O₂/C₄F₈O with (a) plasma-on and (b) plasma-off. Process conditions: 66.7 Pa (500 mtorr) of operational pressure, 80% O₂/20% C₄F₈O gas mixing ratio and 40 sccm total flow rate.

shown in the figure, large CF₃ and C₂F₄ peak intensities cracked from C₄F₈O were measured. Therefore, these peaks may be responsible for the high CF₄ and COF₂ emission at the exhaust line for O₂(CO₂)/C₄F₈O by the recombination process [9].

The DREs of C₄F₈O were measured as a function of the gas mixture for CO₂/C₄F₈O and O₂/C₄F₈O at 66.7 Pa (500 mtorr) and as a function of operating pressure for 90% CO₂/10% C₄F₈O and 80% O₂/20% C₄F₈O. The results are shown in Fig. 5a,b for the gas mixing ratio and the operational pressure, respectively. As shown in Fig. 5a, the DREs of C₄F₈O increased from 80 to 92% with an increase in O₂ in O₂/C₄F₈O from 40 to 80%, and further increase in O₂ decreased the DREs. In the case of CO₂/C₄F₈O, the DREs remained similar at 80%, regardless of the change in CO₂ percent in CO₂/C₄F₈O. As shown in Fig. 5b, when the operational pressure was varied from 8 (60 mtorr) to 66.7 Pa (500 mtorr), the DREs for 80% O₂/20% C₄F₈O increased from 85 to 92%; however, further increase in operating pressure to 120 Pa (900 mtorr) did not change the DREs. In the case of 90% CO₂/10% C₄F₈O, the DRE was approximately 80% and did not show any significant change with changes in operating pressure, similar to the case for the gas mixing ratio. The higher

DREs for O₂/C₄F₈O appear to be related to the dissociation efficiency of O₂ and CO₂. The binding energy of O₂ is 119.11 kcal/mol, and that of CO₂ is 127.2 kcal/mol. Therefore, O₂ is more easily dissociated and releases oxygen radicals, which could be used to combine with carbon in C₄F₈O and help it to dissociate faster [10].

MMTCE was also measured as a function of gas mixture and operating pressure to estimate the degree of global warming potential of the specific cleaning process. The results are shown in Fig. 6a,b for gas mixture and operating pressure, respectively. The other

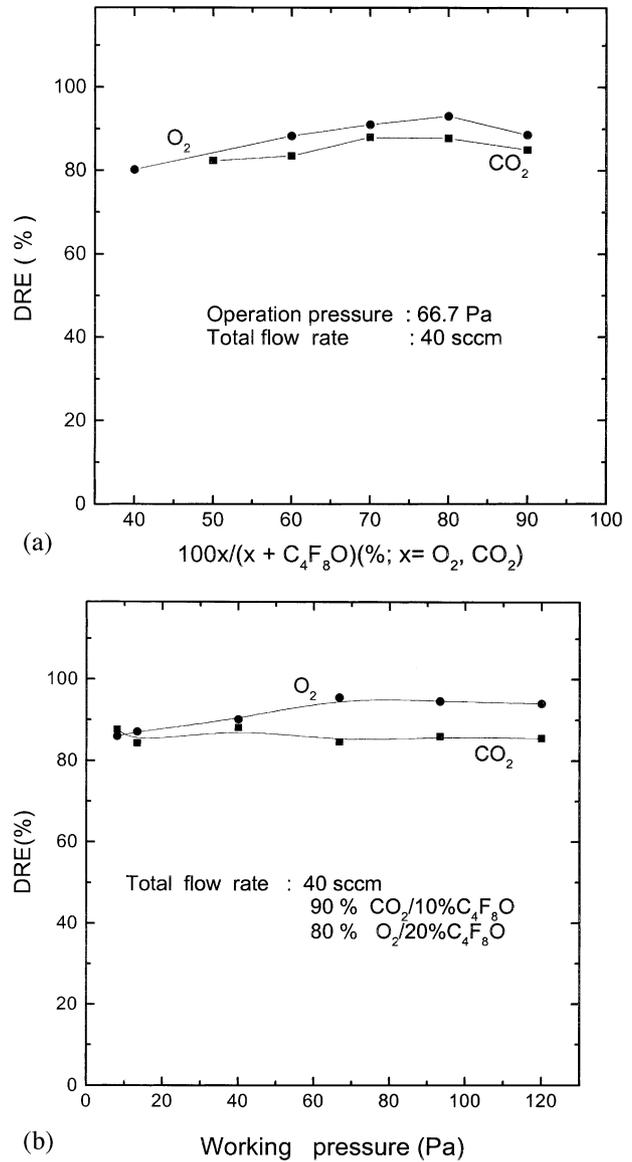


Fig. 5. DREs of O₂ (CO₂)/C₄F₈O mixing gas as a function of (a) gas mixing ratio at 66.7 Pa (500 mtorr) and (b) operation pressure at 80% O₂/20% CO₂ and 90% CO₂/10% C₄F₈O ratios. Total pressure and flow rate were maintained at 66.7 Pa (500 mtorr) and 40 sccm, respectively.

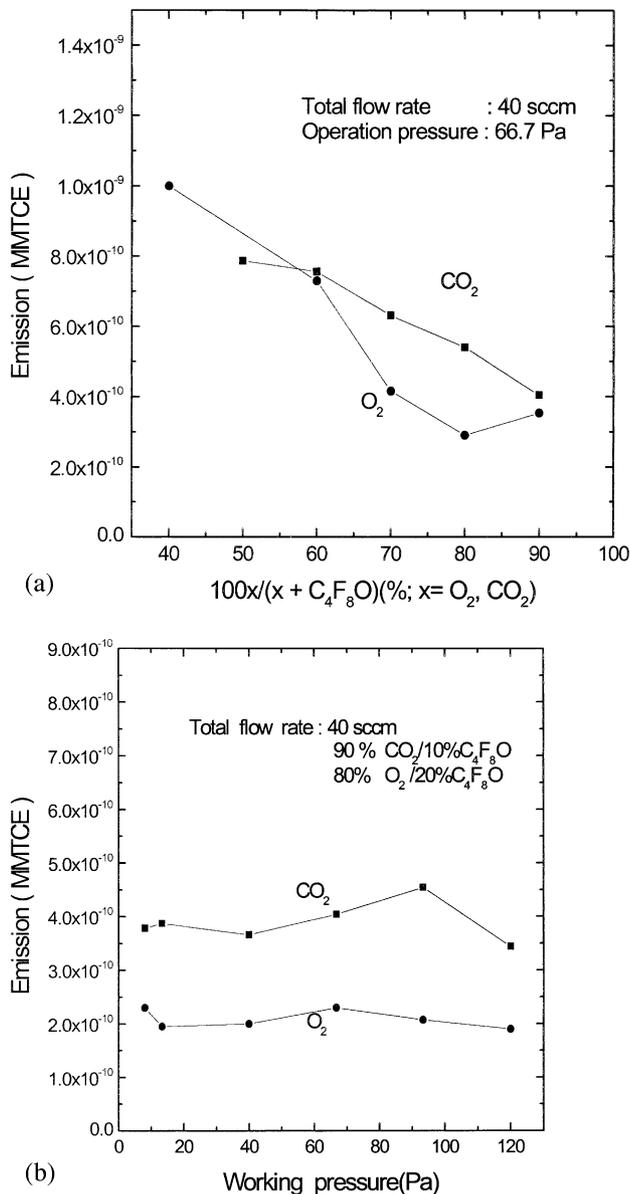


Fig. 6. MMTCEs during silicon nitride cleaning process as a function of (a) gas mixing ratio of O_2 (CO_2)/ C_4F_8O and (b) operational pressure at 80% O_2 / 20% CO_2 and 90% CO_2 / 10% C_4F_8O gas ratios. Total pressure and flow rate were maintained at 66.7 Pa (500 mtorr) and 40 sccm, respectively.

operational conditions were the same as shown in Fig. 5. When O_2 was increased from 40 to 80% in O_2 / C_4F_8O , MMTCE decreased from 1×10^{-9} to 3×10^{-10} , and further increase in O_2 increased the MMTCE slightly. The silicon-nitride cleaning rate, DREs, and MMTCEs were also measured using NF_3 to compare with the results of O_2 / C_4F_8O [11]. The lowest MMTCE and the highest cleaning rate obtained in this experiment with O_2 / C_4F_8O were similar to those obtained with NF_3 in our experimental set-up (not shown). In the

case of CO_2 / C_4F_8O , an increase in CO_2 in CO_2 / C_4F_8O from 50 to 90% decreased the MMTCE continuously from 8×10^{-10} to 4×10^{-10} ; however, MMTCEs of CO_2 / C_4F_8O were generally higher than those of O_2 / C_4F_8O . When MMTCEs were measured as a function of the operating pressure for 80% O_2 / 20% C_4F_8O and 90% CO_2 / 10% C_4F_8O , the values did not change significantly with operating pressure for either of the gas combinations. However, the MMTCE for 90% CO_2 / 10% C_4F_8O was approximately two-fold higher than that for 80% O_2 / 20% C_4F_8O . The higher MMTCE for CO_2 / C_4F_8O is mainly related to the emission of more CF_4 during the cleaning process, as shown in Fig. 3a,b.

4. Summary

In this study, C_4F_8O has been used with O_2 and CO_2 as additive gases, and the effects of gas mixture and operating gas pressure on the silicon nitride plasma-enhanced CVD chamber cleaning and global warming potential have been investigated.

The gas combination of CO_2 / C_4F_8O showed lower silicon nitride cleaning rates compared to O_2 / C_4F_8O , possibly due to the removal of fluorine by carbon in CO_2 . The highest silicon nitride cleaning rate for O_2 / C_4F_8O was approximately 600 nm/min at 80% O_2 / 20% C_4F_8O , 66.7 Pa (500 mtorr), 40 sccm, 150 W of 13.56 -MHz RF power and without substrate heating. The main emission species measured at the exhaust line were CF_4 , COF_2 and CO_2 , and the quantities of these species were higher than that of C_4F_8O fed through the cleaning chamber.

The DRE and MMTCE values measured for the optimal condition of O_2 / C_4F_8O were 92% and 3×10^{-10} , respectively, and were similar to values we obtained for silicon nitride cleaning with NF_3 . In the case of CO_2 / C_4F_8O , not only was the cleaning rate, but the DRE was also lower and the MMTCE was higher.

References

- [1] Semiconductor Industry Association, International Technology Roadmap for Semiconductors, International SEMATECH, Austin, Texas, 1999, p. 248.
- [2] A. Grill, Cold Plasma in Materials Fabrication, IEEE Press, New York, 1993, p. 180.
- [3] W. Worth, B. Duffin, L. Modrey, Tool Perfluorocompound (PFC) Emission Data Report, SEMATECH, 1997, p. 8, Report 96073156B-ENG.
- [4] R. Xu, J. Kushner, J. Vac. Sci. Technol. A 18 (1) (2000) 213.
- [5] C.C. Allgood, M.T. Mocella, Proceedings of the Semicon West Seminar: Improving Environmental Performance of Wafer Manufacturing Processes, 2000, Session A, paper 3.
- [6] B.E.E. Kastenmeier, P.J. Matsuo, G.S. Oehrlein, J. Vac. Sci. Technol. A 16 (4) (1998) 2047.
- [7] B.D. Pant, U.S. Tandon, Plasma Chem. Plasma Process. 19 (4) (1999) 545.

- [8] M.Y. Liao, K. Wong, J.P. McVittle, K.C. Saraswat, *J. Vac. Sci. Technol. B* 17 (6) (1999) 2638.
- [9] V. Mohindra, Characterization of Perfluorocompound Emission and Abatement Kinetics in Plasma Processes, MIT, Department of Chemical Engineering, 1996, PhD thesis.
- [10] P. Brown, L. Mendicino, V. Vartanian, *Proc. Electrochem. Soc.* 99 (8) (1999) 52.
- [11] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 72nd, CRC Press, Boston, 1992, pp. 6–116.