

# Effect of N-containing additive gases on global warming gas emission during remote plasma cleaning process of silicon nitride PECVD chamber using $C_4F_8/O_2/Ar$ chemistry

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## Abstract

In this study, remote plasma cleaning process was investigated in a silicon nitride plasma enhanced chemical vapor deposition chamber using  $C_4F_8/O_2/Ar$  and  $C_4F_8/O_2/Ar$ +additive gas. The remote plasma source used in the present experiments showed the capability of nearly complete destruction, destruction removal efficiency  $\cong 100\%$ , of  $C_4F_8$  gas with or without the additive  $N_2$ ,  $N_2O$  and  $NO$  gases. The cleaning rate of the silicon nitride layers is increased 32–40% by adding  $N_2$ ,  $N_2O$  and  $NO$  gases to the optimized  $C_4F_8/O_2$  cleaning chemistry. This is presumably due to the effective reaction of  $NO$  radicals formed in the remote plasma with  $N$  on the silicon nitride surface, followed by the effective fluorination of  $Si$  atoms. As a result, the million metric tons of carbon equivalent values could be effectively reduced due to the decreased emission of  $CF_4$  as well as the increased cleaning rate of the silicon nitride layers, comparable to those of  $NF_3/Ar$  remote plasma cleaning. For the effective reduction of global warming effects, the experimental results indicate a possibility of using the alternative gas such as  $C_4F_8$  with the N-containing additive gases for the environmentally benign remote plasma cleaning process.

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**Keywords:** Remote plasma chamber cleaning; Global warming effect; Silicon nitride;  $C_4F_8$

## 1. Introduction

During semiconductor manufacturing and flat panel display production, gasification processes of silicon, silicon dioxide and silicon nitride are required. For example, cleaning the chambers used for thin film processes or etching of the dielectric films on the wafer surface is a few gasification processes during integrated circuit manufacturing. Traditionally, these processes have been performed with PFCs, e.g.  $CF_4$  or  $C_2F_6$ . During cleaning or etching processes, the emission of recombined and non-reacted PFCs into the atmosphere has caused a growing concern in the semiconductor industry because of their potential global warming effects caused by their strong IR absorption characteristics and long atmospheric lifetime. Concern about the high global warming potential of these gases has pro-

voked investigations to achieve equivalent or better cleaning efficiencies with lower emissions of global warming gases [1].

Various ways to reduce the emission of PFCs have been investigated in the semiconductor industry by the use of alternative process chemicals, process optimization and new abatement technologies including destruction and recovery [2]. Among those, the reduction of emitted PFCs by replacing the conventional cleaning gases with alternative gases with high destruction efficiency and less emission characteristics could be a fundamental solution [2–7]. Various alternative gases such as  $C_3F_8$  [3],  $C_4F_8$  [4],  $C_4F_8O$  [5], and  $NF_3$  [6,7] with high destruction removal efficiency (DRE) have been studied to replace conventional PFCs such as  $CF_4$ ,  $SF_6$  and  $C_2F_6$  [5].

Remote plasma processing has been frequently used for chemical dry etching of various materials due to several advantages over the direct plasma etching in some applications. Since the lifetime of ions is shorter

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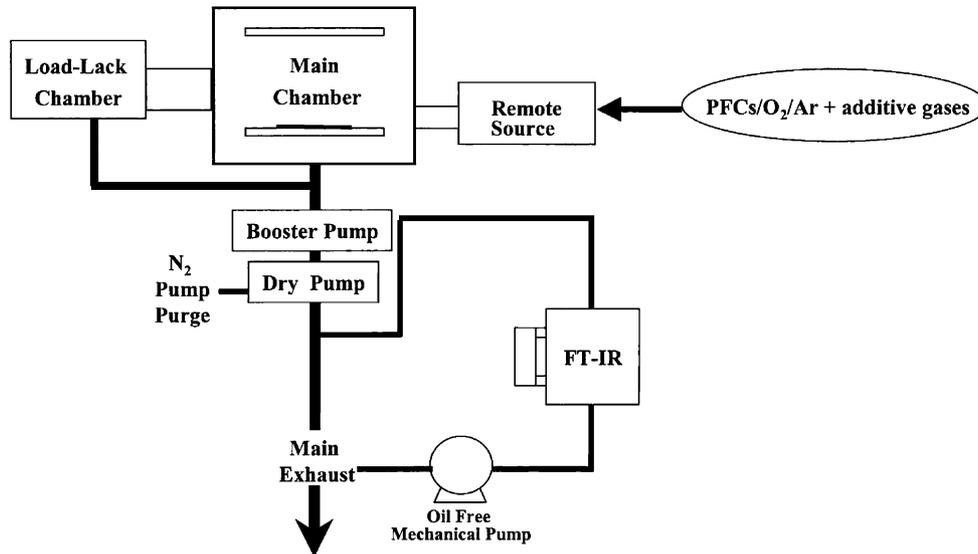


Fig. 1. Schematic of the remote plasma source and gas sampling system used for cleaning of the silicon nitride PECVD chamber.

than the gas travel time from the plasma to the sample in contrast to direct plasma etch, the etching mechanism is purely chemical. Therefore, damage effects, such as charging and radiation damages, can be minimized [8]. Recently, remote plasma cleaning process using  $\text{NF}_3$  has been developed in order to minimize the erosion and damage of chamber parts during cleaning as well as to decrease global warming effect [6,7]. Remote plasma cleaning using  $\text{NF}_3/\text{Ar}$  chemistry, however, has some issues related to the cost of gas and corrosion problem in the exhaust lines. Therefore, alternative remote plasma cleaning process is being developed using alternative gases such as  $\text{C}_3\text{F}_8$ ,  $\text{C}_4\text{F}_8$  and  $\text{C}_4\text{F}_8\text{O}$ .

In this work, cleaning processes of  $\text{C}_4\text{F}_8/\text{O}_2/\text{Ar}$  + additive gas were investigated for the development of the cleaning process in a commercial silicon nitride plasma enhanced chemical vapor deposition (PECVD) system using a commercial remote plasma source. Under the optimum condition, the cleaning rate of  $2330 \text{ \AA}/\text{min}$  was obtained at the room temperature. In order to improve the cleaning rate, nitrogen-containing gases such as  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}$  were used as additive gases. Even though  $\text{N}_2\text{O}$  and  $\text{NO}$  are global warming gases with low global warming potential, self-contribution was negligible due to no emission during cleaning process. Optimization of the cleaning process by adding  $\text{N}_2$ ,  $\text{N}_2\text{O}$  and  $\text{NO}$  increased the cleaning rate by the factor of approximately 1.43, 1.32 and 1.35, respectively, and decreased the million metric tons of carbon equivalent (MMTCEs) by 12.7, 25 and 23.4%, respectively, compared to those of optimized  $\text{C}_4\text{F}_8/\text{O}_2/\text{Ar}$  without additive gases. Comparing the MMTCE values obtained from the  $\text{C}_4\text{F}_8/\text{O}_2/\text{Ar}/\text{N}$ -containing additive gas and the  $\text{NF}_3/\text{Ar}$  cleaning chemistry at the optimum condi-

tions gave the comparable MMTCE values for each cleaning process.

## 2. Experimental

Fig. 1 shows a schematic diagram of the remote plasma source and the gas sampling systems used in the present experiment for cleaning of a commercial silicon nitride PECVD chamber. The remote plasma source was a commercial toroidal-type plasma source operated at the power of 6 kW AC and the frequency of 400 kHz. The PECVD chamber was evacuated down to approximately 1 mTorr using a pumping system combined with a booster pump and a dry pump, before the introduction of the mixture of cleaning gases. Square-shaped ( $2 \times 2 \text{ cm}^2$ ) silicon nitride films deposited on Si (0 0 1) were used as samples for cleaning experiments. The samples were located on the 8 inch substrate holder without heating and biased power. The plasma was ignited at the Ar flow rate of 4000 sccm. Then  $\text{C}_4\text{F}_8$  and  $\text{O}_2$  gases were injected for the cleaning experiments.

Before measuring the emission of PFCs during cleaning of silicon nitride layers using  $\text{C}_4\text{F}_8$  gas, flow rate of dilution  $\text{N}_2$  for purging of dry pump and linearity of feed gas and targeted gas were checked by a Fourier transform infrared spectroscopy (FT-IR; MIDAC, I2000). The flow rate of dilution  $\text{N}_2$  was 32 980 sccm in our experimental setup. This value was regularly checked to maintain the same experimental condition for every measurement. Slope of concentration for feed gas and targeted gas flow rate diluted by  $\text{N}_2$  ballast at dry pump was measured and used for calculating emitted volumes in the present experiment.

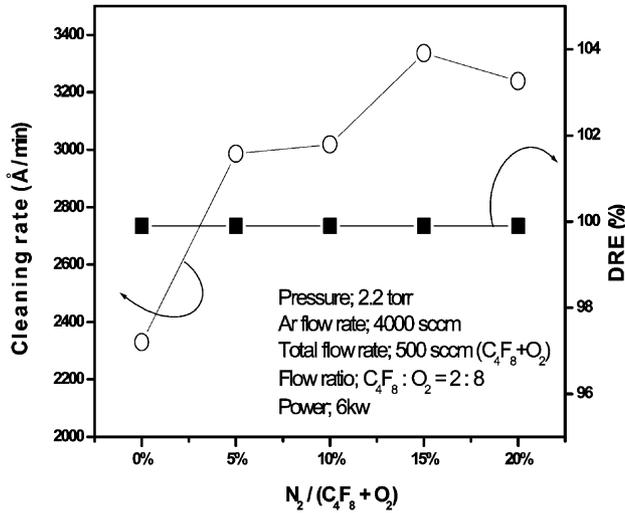


Fig. 2. The cleaning rate of silicon nitride and the DRE of  $C_4F_8$  as a function of  $N_2/(C_4F_8 + O_2)$ . The Ar flow rate was fixed at 4000 sccm during the cleaning experiments.

Silicon nitride samples were cleaned with the gas mixtures of  $C_4F_8/O_2/Ar$ ,  $C_4F_8/O_2/Ar + N_2$ ,  $C_4F_8/O_2/Ar + N_2O$  and  $C_4F_8/O_2/Ar + NO$ . The effects of additive  $N_2$ ,  $N_2O$  and  $NO$  on the cleaning rate, DREs and MMTCEs were quantitatively analyzed. Cleaning rate of silicon nitride layers was measured using an  $\alpha$  step-profilometer (Tencor, AS-500). The volumetric concentration of the species was measured by FT-IR. Optimum condition was obtained by controlling the flow rate ratio of  $C_4F_8/O_2/Ar/additive$  gases and the flow rate of  $C_4F_8$  feed gas. The applied AC power was kept at 6 kW and working pressure at 2.2 Torr.

Destruction of feed gas and the effect of emitted gases on global warming were quantified as DREs and MMTCEs, respectively. DRE and MMTCE values were calculated by using Eqs. (1) and (2), respectively;

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

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

$$MMTCE = \sum_i \frac{12}{44} \frac{Q_i}{10^9} \frac{(kg)GWP_{100i}}{10^9} \quad (2)$$

where  $GWP_{100i}$  is the global warming potential of each component (integrated over a 100 year time horizon) and  $Q_i$  is the total mass of that species (in kg) released during the process [9].  $Q_i$  can be calculated from the volumetric concentration data measured by FT-IR. Effects of the additive  $N_2$ ,  $N_2O$  and  $NO$  gases on the MMTCE values were quantified based on the emitted

volumes of PFC gases during cleaning of the 1  $\mu$ m-thick silicon nitride layer.

### 3. Results and discussion

An optimum condition for the system was obtained by controlling the flow ratio of input gases and the total flow. The optimum condition was obtained at the total flow of 500 sccm, the flow ratio of  $C_4F_8/O_2 = 100$  sccm/400 sccm, the working pressure of 2.2 Torr at the fully open valve position of the system. Under this condition, DRE and MMTCE values are approximately 100% and  $6.07 \times 10^{-11}$ , respectively.

Fig. 2 shows the cleaning rate of the silicon nitride layers and DREs as a function of  $N_2$  flow added to  $C_4F_8/O_2/Ar$  cleaning chemistry. The injection of  $C_4F_8$  and  $O_2$  after the ignition of the plasma using Ar was followed by  $N_2$  gas injection.  $N_2$  was added to the optimized  $C_4F_8/O_2/Ar$  chemistry by 5–20%. The percentage of  $N_2$  gas in the paper indicates the gas flow ratio of  $N_2/(C_4F_8 + O_2)$ . Cleaning rate was increased by the factor of  $\approx 1.43$  and showed a maximum at the 15% addition of  $N_2$ . Interestingly,  $N_2$  was most effective in increasing the cleaning rate of the silicon nitride layers among the additive gases. The DRE values were  $\approx 100\%$  at the AC power of 6 kW regardless of the process conditions in the present experiment.

Cleaning rate and DRE values during the cleaning using the  $C_4F_8/O_2/Ar$  chemistry with the addition of  $N_2O$  additive gas were shown in Fig. 3. With the 15% addition of  $N_2O$ , the cleaning rate of the silicon nitride layer was increased by the factor of  $\approx 1.32$ , from 2330 to 3075  $\text{\AA}/\text{min}$  at the AC power of 6 kW, compared to the case of the optimized  $C_4F_8/O_2/Ar$  chemistry. The

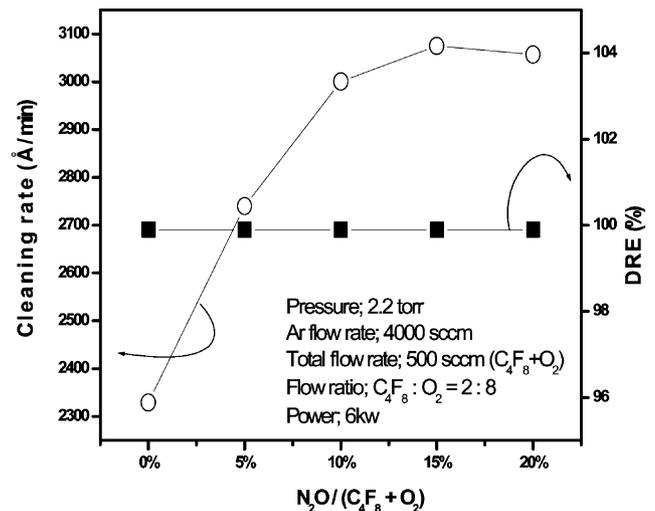


Fig. 3. The cleaning rate of silicon nitride and the DRE of  $C_4F_8$  as a function of  $N_2O/(C_4F_8 + O_2)$ . The Ar flow rate was fixed at 4000 sccm during the cleaning experiments.

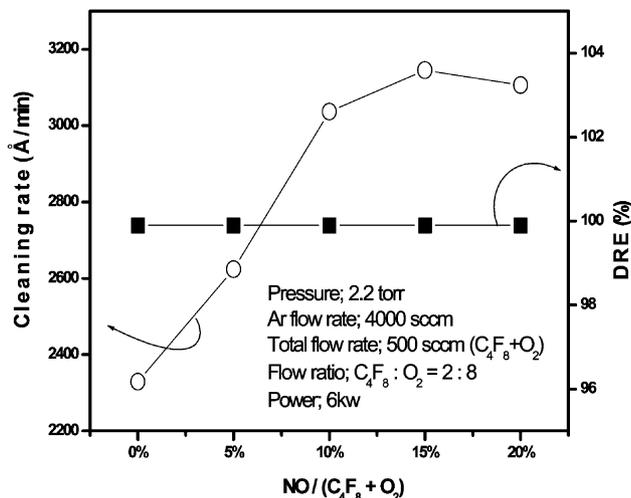


Fig. 4. The cleaning rate of silicon nitride and the DRE of C<sub>4</sub>F<sub>8</sub> as a function of NO/(C<sub>4</sub>F<sub>8</sub> + O<sub>2</sub>). The Ar flow rate was fixed at 4000 sccm during the cleaning experiments.

DRE values of C<sub>4</sub>F<sub>8</sub> gas are  $\cong 100\%$ , which indicates the near complete destruction of C<sub>4</sub>F<sub>8</sub> feed gas.

Fig. 4 shows the results of cleaning rate and DRE measurements during the cleaning with added NO gas. NO gas was added from 5 to 20% to the optimized C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar chemistry. In the case of adding 15% of NO to C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar, the cleaning rate was increased by the factor of  $\cong 1.35$ , from 2330 to 3145 Å/min. Similarly to the case of adding N<sub>2</sub> and N<sub>2</sub>O, the DRE values were  $\cong 100\%$  for all experimental conditions.

Increase in the cleaning rate of silicon nitride layers with the addition of N<sub>2</sub>, N<sub>2</sub>O and NO gases to the optimized C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar cleaning chemistry can be explained by the surface reaction of NO radicals formed in the plasma with the silicon nitride layers [6,8,10–14]. It has been suggested that the reaction of NO radicals with N on the surface of silicon nitride results in the effective removal of nitrogen on the surface of the silicon nitride. In turn the increased reaction rate of F radicals with Si in the silicon nitride layer leads to the increase in the cleaning rate [6,8,10–14]. The reason for the slight decrease in the cleaning rate at 20% of N<sub>2</sub>, N<sub>2</sub>O and NO is not clear at this point because of the complicated nature of plasma reactions and the surface reactions. The continued increase of additive gases may dilute the concentrations of F density in the plasma. For a reference, cleaning performance of NF<sub>3</sub>/Ar chemistry was evaluated and the results of cleaning rate and DRE are shown in Fig. 5. The injection flow of NF<sub>3</sub> gas into the remote plasma source was increased from 200 to 600 sccm following the plasma ignition using the Ar flow rate of 4000 sccm. As seen from the data in Fig. 5, cleaning rate increases linearly with NF<sub>3</sub> flow. DRE values of NF<sub>3</sub> were also close to 100% at the AC power of 6 kW.

The cleaning rate of silicon nitride layers using NF<sub>3</sub>/Ar at the flow rate of 300 sccm was 5030 Å/min. It was higher than the cleaning rate using C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar chemistry at the C<sub>4</sub>F<sub>8</sub> flow rate of 100 sccm with the additive N<sub>2</sub>, N<sub>2</sub>O and NO gases. The flow rate of NF<sub>3</sub> during NF<sub>3</sub>-based cleaning is higher than that during C<sub>4</sub>F<sub>8</sub>-based cleaning. The lower cleaning rate observed during the C<sub>4</sub>F<sub>8</sub>-based cleaning with additive gases is attributed to the limited C<sub>4</sub>F<sub>8</sub> flow rate (about one third of NF<sub>3</sub> flow rate) due to the limited AC power applied to the remote plasma source used in the experiments. If the flow rate of C<sub>4</sub>F<sub>8</sub> can be increased to the level of NF<sub>3</sub> flow rate by using larger AC power source, similar or higher cleaning rate is expected for the C<sub>4</sub>F<sub>8</sub>-based cleaning chemistry.

Fig. 6a–c show the average concentration of the emitted gases during the cleaning experiments using C<sub>4</sub>F<sub>8</sub>-based chemistry with N<sub>2</sub>, N<sub>2</sub>O, NO additive gases, respectively. The emitted volume of NO and N<sub>2</sub>O during cleaning was negligible. An interesting observation from the data is that the emitted volume of CF<sub>4</sub> was negligible and, as a result, this decrease in the emission of CF<sub>4</sub> leads to the decrease of the MMTCE value. The volume of emitted COF<sub>2</sub> is quite large compared to the other gases. The concentrations of emitted CO<sub>2</sub> and COF<sub>2</sub> obtained as a function of the percentage of added gases do not show a clear consistency even though the concentration of COF<sub>2</sub> decreased at 5% of added gases and then remains almost the same except for the case of NO addition. But, COF<sub>2</sub> was not included in the calculation of MMTCE because COF<sub>2</sub> gas can be easily removed by a wet scrubber [5].

Fig. 7 shows the MMTCE values calculated from Eq. (2) using the emitted volume data in Fig. 6. Due to the

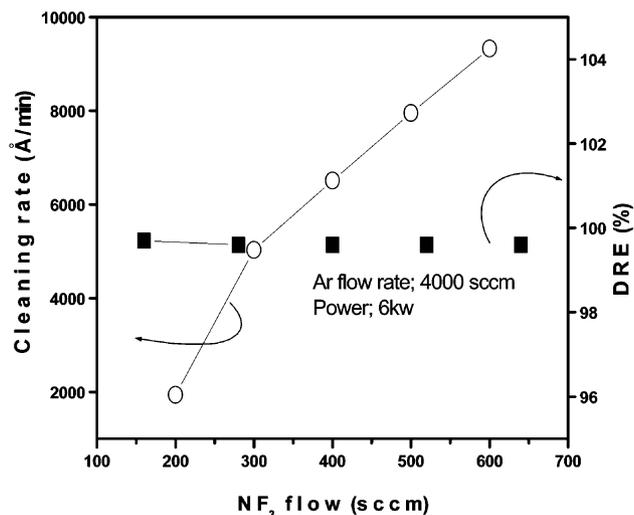


Fig. 5. The cleaning rate of silicon nitride and the DRE as a function of NF<sub>3</sub> flow rate. The Ar flow rate was fixed at 4000 sccm during the cleaning experiments.

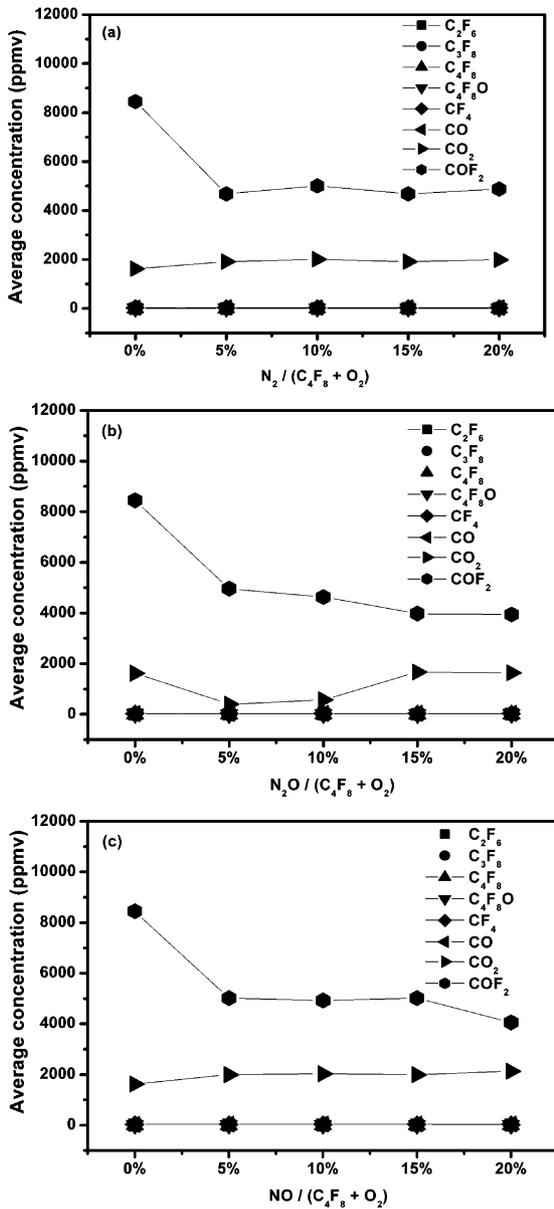


Fig. 6. The average concentrations of exhausted species as a function of the percentage of (a)  $N_2$ , (b)  $N_2O$  and (c)  $NO$  during the remote plasma cleaning using  $C_4F_8/O_2/Ar$  chemistry.

negligible emitted volume of  $N_2O$  and  $NO$ , those gases were not included in the calculation of MMTCEs. As seen in Fig. 7, MMTCE values were decreased due to the increase in the cleaning rate with the addition of  $N_2$ ,  $N_2O$  and  $NO$  as well as the decrease in the emitted volume of  $CF_4$ . For comparison, the values obtained from the  $NF_3/Ar$  cleaning chemistry are also shown in Fig. 7. With the addition of 15% of  $N_2$ ,  $N_2O$  and  $NO$  gases, the MMTCE values were reduced by 12.7, 25 and 23.4%, respectively. In the case of adding over 15% of  $N_2O$  and  $NO$  to  $C_4F_8/O_2/Ar$  cleaning chemistry, the obtained MMTCE values were smaller than those of  $NF_3/Ar$  cleaning chemistry. The present experimental

results indicate that remote plasma cleaning using alternative gases such as  $C_4F_8$  with very high DREs can possibly replace the  $NF_3$ -based remote plasma chamber cleaning processes.

#### 4. Summary

In this study, nitrogen-containing gases such as  $N_2$ ,  $N_2O$  and  $NO$  were added to the optimized  $C_4F_8/O_2/Ar$  cleaning chemistry of silicon nitride PECVD chamber. Their effects on the cleaning rate, the emission characteristics of PFCs and global warming effects were investigated. The self-contribution of added  $NO$  and  $N_2O$  on global warming was negligible due to their low global warming potential compared to the other emitted PFCs and no emission during cleaning.  $NF_3/Ar$  cleaning chemistry that is currently used for PECVD chamber cleaning, was also investigated with the remote plasma source in order to compare with the results of  $C_4F_8/O_2/Ar/N$ -based additive gas mixtures.

Adding  $N_2$ ,  $N_2O$  and  $NO$  additive gases to the optimized  $C_4F_8/O_2/Ar$  cleaning chemistry increased the cleaning rate of the silicon nitride layers by 32–40%. The increase in the cleaning rate is presumably attributed to the reaction of  $NO$  radicals formed in the remote plasma with  $N$  on the silicon nitride surface resulting in the effective removal of  $N$  and then effective fluorination of  $Si$  atoms on the surface. DRE values during the remote  $C_4F_8/O_2/Ar$  plasma cleaning using the remote plasma source used in the present experiments were  $\cong 100\%$ , which indicates the near complete destruction

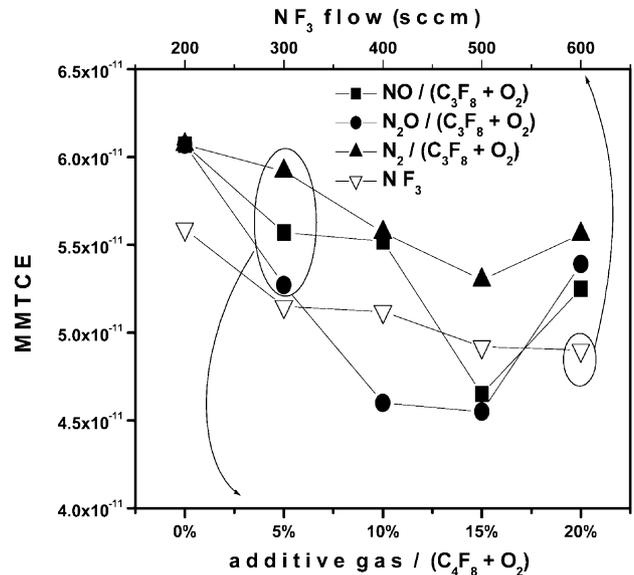


Fig. 7. MMTCE during silicon nitride cleaning as a function of the percentage of  $N_2$ ,  $N_2O$  and  $NO$  during the remote plasma cleaning using  $C_4F_8/O_2/Ar$  chemistry. For comparison, MMTCE values during  $NF_3/Ar$  remote plasma cleaning are also shown as a function of the flow of  $NF_3$ .

of  $C_4F_8$  feed gas with or without the additive gases. MMTCEs could be effectively reduced due to the decreased emission of  $CF_4$  and the increased cleaning rate of the silicon nitride layers.

Comparing MMTCE values of  $C_4F_8/O_2/Ar/N$ -based additives and  $NF_3/Ar$  chemistry in the optimum conditions, we could obtain similar MMTCE values for each gas mixture. The experimental results from the present experiments show the possible replacement of  $NF_3$ -based remote plasma cleaning processes with the remote plasma cleaning process using alternative gas such as  $C_4F_8$  if one can obtain the very high destruction efficiency using an effective remote plasma source.

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