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C_4F_8O/O_2/N-based Additive Gases for Silicon Nitride Plasma Enhanced Chemical Vapor Deposition Chamber Cleaning with Low Global Warming Potentials

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In this study, N_2O and NO were added as additive gases to C_4F_8O/O_2 for plasma enhanced chemical vapor deposition (PECVD) silicon nitride chamber cleaning and their effects on the emission properties of perfluorocarbon compounds (PFCs) were investigated. The cleaning rate, destruction and removal efficiencies (DREs), and million metric tons of carbon equivalent (MMTCE) were studied as a function of flow rates of PFCs and additive gases. The use of C_4F_8O/O_2 alone showed the highest cleaning rate and the lowest emission properties at the cleaning condition of 20%C_4F_8O/80%O_2, working pressure of 500 mTorr, and 13.56 MHz rf power of 350 W. By the addition of about 20% NO or 20% N_2O to the optimized C_4F_8O/O_2, the additional reduction of MMTCE higher than 50% could be obtained. The addition of NO resulted in lower MMTCE compared to that in the case of the addition of N_2O mostly due to the higher silicon nitride cleaning rate in the latter case. [DOI: 10.1143/JJAP.41.6570]

KEYWORDS: PFCs, PECVD chamber cleaning, MMTCE, DREs, GWP

1. Introduction

Perfluorocompound (PFC) gases such as CF_4, C_2F_6, C_3F_8, C_4F_8, and SF_6 have been used extensively in chamber cleaning and etching processing.[1–3] These long-lived compounds are chemically and toxicologically benign, however, these species absorb light from the infrared spectrum region and contribute to global warming.[4–6]

PFCs are emitted from certain semiconductor processes due to their relatively low utilization efficiencies and recombination of the PFCs fed for processing in these processes.[4,6] Therefore, the reduction of emitted PFCs should be performed by abating PFC emission after the processing or by using gases which emit lower levels of PFCs.

For the silicon dioxide or silicon nitride PECVD chamber cleaning processes, various gases such as C_4F_8, C_3F_8, SF_6 and NF_3 have been used. Among these gases, NF_3 showed the highest DREs of above 90% and the lowest MMTCE and is also widely applied to the commercial PECVD chamber cleaning process currently.[4,7] But the problems in the case of the NF_3 process include toxicity of the gas, the price and shortage of the gas supply, and unwanted toxic F_2 production as a byproduct.[5] Because of these problems, researchers have searched for alternatives which are less expensive, mass productive, and less toxic. One of those alternatives is cyclic perfluorinated ether(C_4F_8O), which has an appreciable global warming potential estimated to be 8700 by 3M Inc. and has been studied for use as a silicon dioxide PECVD chamber cleaning gas.[8]

In this study, the effects of N-based additive gases such as NO and N_2O to C_4F_8O/O_2 have been investigated as possible gas mixtures for silicon nitride PECVD chamber cleaning with low PFC emission and the characteristics of silicon nitride cleaning and PFC emission have been studied.

2. Experimental

Figure 1 shows the schematic diagram of the gas sampling system used in this experiment to analyze gas species emitted from the exhaust valve during the cleaning of the silicon nitride PECVD chamber. The PECVD chamber was evacuated using a pump system combined with a booster pump and a dry pump to 10^{-3} Torr before the introduction of cleaning gas mixtures. The dry pump uses N_2 as the purging gas, and the flow rate of the N_2 gas was estimated as 33.2 slm. The PECVD system was a capacitively coupled plasma system using rf power of 13.56 MHz. The distances between electrodes and the electrode radius were 5 cm and 7.5 cm, respectively. As the chamber cleaning gases, 20%C_4F_8O/80%O_2/additives (N-based) with the total flow rate of 80 sccm were used and the effects of gas mixing ratio on the silicon nitride cleaning rate, emitted species, and PFC emission rate were investigated. RF power to the chamber during the cleaning was 350 Watts and working pressure was 500 mTorr.

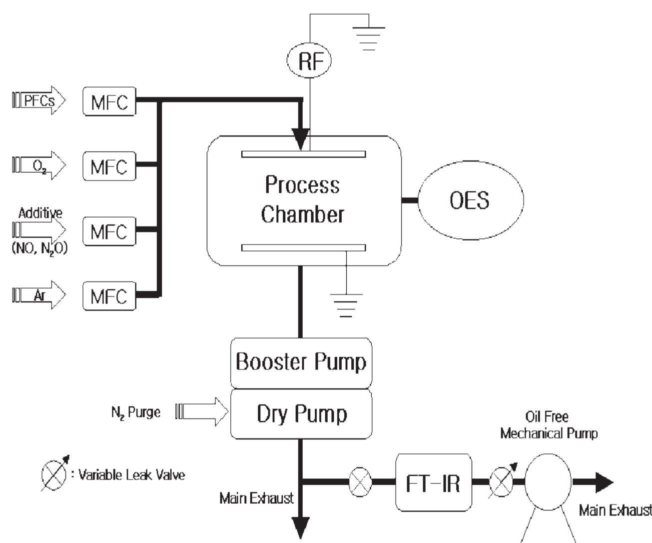

Fig. 1. Schematic diagram of the PFC gas sampling system used in this experiment.

The gas analysis tools used in this experiment were a Fourier transform-infrared spectrometer (FT-IR, MIDAC I2000) and optical emission spectroscopy (OES, SC Tech.). The FT-IR was connected to the exhaust line while OES was

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installed at the chamber window. The intensities of each of the molecules detected by FT-IR were calibrated using various calibration gases. The destruction of feed gases and the amount of the emitted global warming gases were estimated as DREs and MMTCE, respectively. To estimate silicon nitride cleaning rates, silicon nitride films deposited on silicon wafers were located at the substrate holder at room temperature and the cleaning rate was measured using a step-profilometer.

3. Results and Discussion

Before the introduction of NO and N_2O to C_4F_8O/O_2, the effect of gas mixing ratio of C_4F_8O/O_2 on silicon nitride cleaning rate, DREs, and MMTCE was investigated. DREs were estimated by eq. (1) shown below. In the equation, V_{on} and V_{off} are the emitted average volume of C_4F_8O at the exhausted line with plasma-on and -off without silicon nitride samples, respectively. Equation (2) was used for the calculation

$$\frac{V_{\text{off}} - V_{\text{on}}}{V_{\text{off}}} \times 100\,(\%) \tag{1}$$

$$\text{MMTCE} = \frac{Q\ (\text{kg}) \times GWP_{100}}{10^9} \tag{2}$$

of MMTCE. Here, Q (kg) means total mass in kg of global warming species released during processing for 2 min and GWP stands for global warming potential.[4] Emitted volumes and Q were estimated from the volume concentration measured by FT-IR. The result revealed the highest silicon nitride cleaning rate of 6000 Å/min. Generally, in the etching or cleaning using fluorocarbon gases, polymerization of the form $(CF_2)_n$ is unavoidable. However, in this experiment, possibly due to the sufficient O_2 supply, the polymerization did not occurr and relatively high cleaning rates were obtained. Also, 98% of DREs, and 3.6×10^{-10} of MMTCE could be obtained with $20\%C_4F_8O/80\%O_2$, 80 sccm of total flow rate at 500 mTorr of working pressure and 350 W of rf power.

While maintaining the optimum condition of $20\%C_4F_8O(16\,\text{sccm})/80\%O_2(64\,\text{sccm})$, NO or N_2O was introduced into the chamber from 0 to 25% and the effects of NO and N_2O on the cleaning rate, DREs, MMTCE and so forth. were investigated by the same method mentioned above. Figure 2 shows the effects of NO and N_2O on silicon nitride cleaning rates, F atom density (F/Ar), and the destruction efficiencies of C_4F_8O. As shown in the figure, the silicon nitride cleaning rate increased rapidly with the increase of NO and N_2O up to 10–15% and the further increase of NO and N_2O nearly saturated the silicon nitride cleaning rate. If the effects on the silicon nitride cleaning rates are compared between NO and N_2O, the addition of NO to C_4F_8O/O_2 resulted in higher silicon cleaning rates compared to the addition of N_2O. The factors affecting the silicon nitride etch rate could be summarized as the surface arrival rate of fluorine which is the main etchant of silicon,[9–11] the removal of nitrogen from the surface, and the surface oxidation due to oxygen existing in the plasma during the etching.[14–17]

The amount of fluorine in the plasma can be estimated using OES and the results are also shown in Fig. 2. Ar

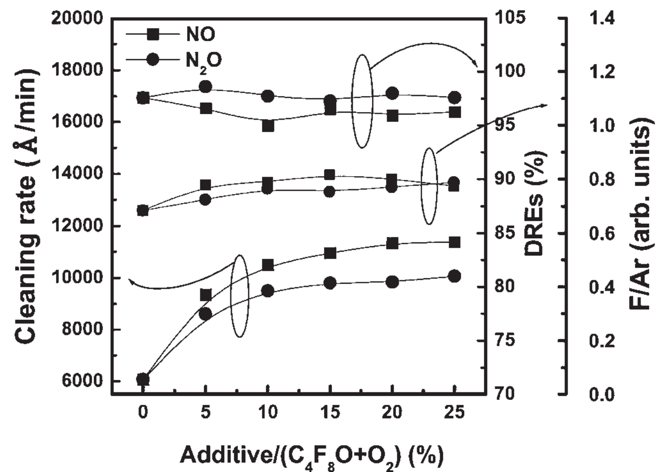

Fig. 2. Silicon nitride cleaning rate, F atom density (F/Ar) and destruction efficiency C_4F_8O as a function of the flow rate of NO and N_2O additive gases.

actinometry[12,13] was used to estimate the concentration of fluorine in the plasma. As shown in the figure, the addition of a small amount of NO or N_2O to C_4F_8O/O_2 slightly increased the fluorine concentration in the plasma and the addition of NO resulted in a higher fluorine concentration compared to the addition of N_2O. However, no significant increase of fluorine as a function of NO or N_2O which can affect the initial sharp increase of the silicon nitride cleaning rate shown in Fig. 2 could be observed. Therefore, the increase of the silicon nitride cleaning rate with the addition of NO or N_2O in Fig. 2 appears not to be related significantly to the increase of the fluorine amount in the plasmas.

Figure 2 also shows the destruction efficiency of C_4F_8O as a function of NO and N_2O measured by FT-IR at the exhaust line. As shown in the figure, the destruction efficiencies were generally in the range from 95–99% and the addition of NO or N_2O did not affect the DREs significantly. The results from F/Ar and the destruction efficiency may suggest that the silicon nitride cleaning rates as a function of NO and N_2O to C_4F_8O/O_2 are more related to the nitrogen and oxygen removal from the surface rather than the reaction of silicon with fluorine in our experimental conditions. Kastenmeier and coworkers[16,17] reported that the efficient form of nitrogen in increasing silicon nitride etch rate in the etching of $CF_4/O_2/N_2$ was NO from the following reactions with silicon nitride.

$$\text{Si–N} + \text{NO} \rightarrow \text{Si} + \text{N}_2\text{O} \tag{3}$$

$$\text{N} + \text{O} \rightarrow \text{NO} \tag{4}$$

$$\text{Si–O} + \text{NO} \rightarrow \text{Si} + \text{NO}_2 \tag{5}$$

$$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \tag{6}$$

Among these reactions, the surface reaction (3) is the fastest reaction and is related to the nitrogen removal rate from the surface by NO. The reactions from (4) and (6) are related to the formation of NO and reaction (5) is related to the rate of removal of oxygen from the surface. The increase of silicon nitride cleaning rate with the increase of NO and N_2O amounts in our experimental conditions is also probably related to the concentration of NO arriving at the

surface. It is because sufficient fluorine radicals removing silicon from the silicon nitride surface could be supplied to the surface through the nearly full dissociation of C_4F_8O. When NO concentrations were measured qualitatively by OES for the addition of N_2O and NO to C_4F_8O/O_2, a higher NO concentration was measured for NO naturally and a lower NO concentration was measured for N_2O (not shown). Therefore, the silicon nitride cleaning rate in our experimental conditions is believed to be related to the NO concentration on the surface because the Si–O or Si–O–F layer formed on the surface decreases the cleaning rate.

Figure 3 shows FT-IR spectra of C_4F_8O, C_3F_8 (1247.0–1281.2 cm^{-1}), C_2F_6 (1233.5–1268.0 cm^{-1}), CF_4 (1275.4–1288.0 cm^{-1}), COF_2 (1877.0–1988.5 cm^{-1}, 934.8–999.4 cm^{-1}) and so forth. measured at the exhaust line with the condition of C_4F_8O(16 sccm)/O_2(64 sccm), 350 W and 500 mTorr. Figure 3(a) shows mainly the spectrum of C_4F_8O which has wave numbers in the ranges of 952.5–975.5 cm^{-1}, 1017.8–1049.6 cm^{-1}, 1077.9–1111.4 cm^{-1}, 1190.0–1219.2 cm^{-1} and 1240.3–1279.1 cm^{-1} with plasma-off. Figure 3(b) shows the spectrum of the species regenerated and produced with plasma-on. As shown in the figure, C_4F_8O was destructed completely with plasma-on. Also, the CF_4 peak was relatively higher than other peaks. SiF_4 (1014.3–1042.7 cm^{-1}) peak, which is an etch product, was relatively weak due to the small size of the sample used in the experiment. Peaks from H_2O were not considered in the calculation.

Figure 4 shows MMTCE estimated from the FT-IR measured at the exhaust line. The MMTCE was calculated by eq. (2) from the emitted gases exhibiting global warming potential such as C_4F_8O, C_3F_8, C_2F_6 and CF_4. As shown in the figure, the MMTCE decreased with the addition of NO and N_2O to C_4F_8O/O_2. The decrease of MMTCE with the addition of NO and N_2O was attributed to the decrease of

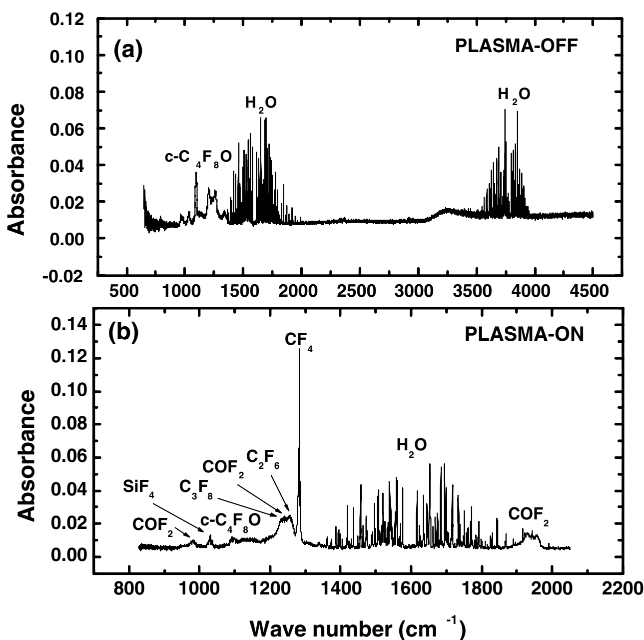

Fig. 3. Spectra of the species detected by FT-IR at the condition of C_4F_8O(16 sccm)/O_2(64 sccm), 350 W and 500 mTorr. (a) Plasma-off, (b) Plasma-on.

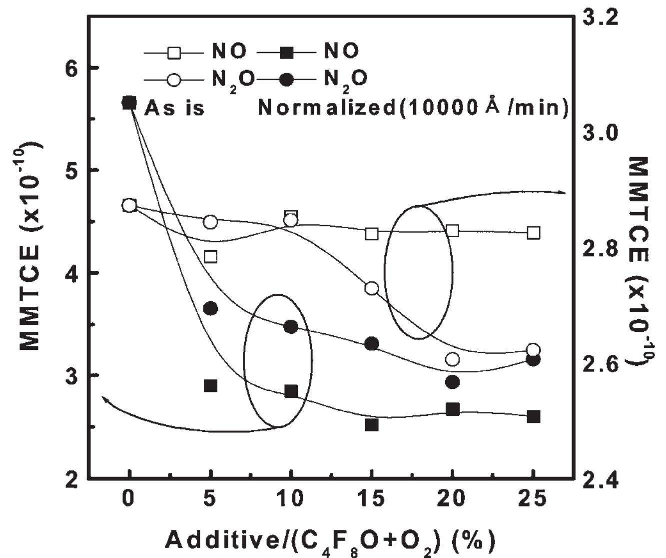

Fig. 4. Variations of as is and normalized MMTCE as a function of the flow rate of NO and N_2O additive gases.

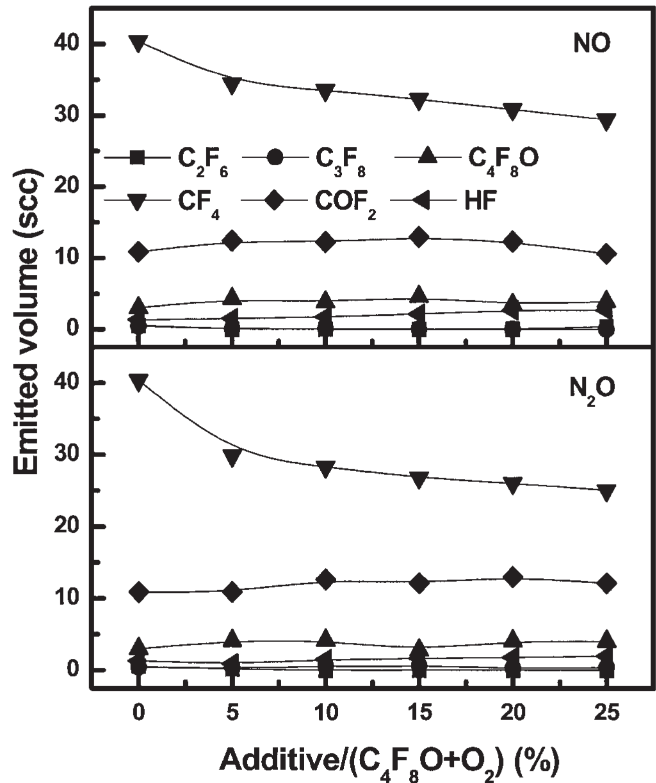

Fig. 5. Volume variation of detected species at exhaust line as a function of the flow rate of NO and N_2O additive gases.

CF_4 emission concentration which is detrimental to global warming prevention as shown in Fig. 5. In fact, CF_4 was emitted at the exhaust line with the highest concentration among the detected species such as CF_4, COF_2, C_4F_8, C_3F_8, and C_2F_6 and, by the addition of NO and N_2O. A more significant decrease of CF_4 emission was observed for N_2O addition as shown in Fig. 5. Therefore, the lower MMTCE for N_2O was mainly from the lower CF_4 emission. The possible reasons for the lower CF_4 concentration with NO and N_2O appear to be from the formation of additional CO_x

by the increase of dissociated oxygen in the plasma and the formation of CN or NF_x by the recombination of CF_x and N from N_2O. The MMTCE normalized to 10000 Å/min of the silicon nitride cleaning rate is also shown in Fig. 4. Even though MMTCE (as is) was higher for the NO addition to C_4F_8O/O_2, the normalized MMTCE was lower for the NO addition due to the higher silicon nitride cleaning rate because MMTCE is reversibly proportional to the cleaning rate. The normalized MMTCEs by the addition of 15% NO and 15% N_2O changed from 5.66×10^{-10} to 2.52×10^{-10} and to 3.31×10^{-10}, respectively.

4. Conclusion

In this study, the effects of N-based additive gases such as NO and N_2O to the optimized C_4F_8O/O_2 on the silicon nitride cleaning rate and global warming effect have been investigated for silicon nitride PECVD chamber cleaning.

By the addition of small amounts of NO and N_2O, a significant increase of silicon nitride cleaning rates could be obtained and the addition of NO resulted in a higher cleaning rate compared to N_2O addition. The increase of the silicon nitride cleaning rate in our experimental conditions appears to be related to the NO reaction with the nitrogen on the silicon nitride surface. MMTCE was calculated by measuring concentrations of global warming gas molecules emitted to the exhaust line during the cleaning process. The addition of NO and N_2O to C_4F_8O/O_2 also decreased the MMTCE due to the significant decrease in CF_4 emission. The MMTCE (as is) was lower for the N_2O addition due to the lower CF_4 emission, however, the MMTCE normalized to the 10000 Å/min silicon nitride cleaning rate was lower for the NO addition due to the higher silicon nitride cleaning rate. The normalized MMTCE by the addition of 15% NO and 15% N_2O to C_4F_8O changed from 5.66×10^{-10} to 2.52×10^{-10} and to 3.31×10^{-10}, respectively. And the DREs for these conditions were higher than 95%.

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