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Effect of N_2O to C_4F_8/O_2 on Global Warming during Silicon Nitride Plasma Enhanced Chemical Vapor Deposition (PECVD) Chamber Cleaning Using a Remote Inductively Coupled Plasma Source

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For the silicon nitride plasma enhanced chemical vapor deposition (PECVD) chamber cleaning, a remote inductively coupled plasma (ICP) source was used with $C_4F_8/O_2/N_2O$ and the effects of N_2O on the silicon nitride cleaning rates and global warming were investigated. By adding 5% of N_2O to C_4F_8/O_2, the cleaning rate comparable to that of optimized Ar/NF_3 could be obtained. At the exhaust line, CF_4, C_4F_8, NF_3, etc. were detected and the significant decrease of million metric tons of carbon equivalent (MMTCE) observed by the addition of N_2O to C_4F_8/O_2 was due to the decrease of emitted CF_4. The MMTCE for the optimized $C_4F_8/O_2/N_2O$ was also similar to that for Ar/NF_3 at the highest cleaning condition. [DOI: 10.1143/JJAP.41.L1495]

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

PFC (perfluorocompound) gases such as CF_4, C_2F_6, C_3F_8, C_4F_8, and NF_3 have been used extensively in chamber cleaning and etching processing for silicon nitride or silicon dioxide.[1–3] These compounds are chemically and toxicologically benign, however, these species absorb an infrared spectrum region and have long lifetimes such as thousands times of CO_2.[4–6] Therefore, the reduction of emitted PFCs should be made by abating emitting PFCs after the processing or by replacing with the gases emitting less PFCs.

For the plasma enhanced chemical vapor deposition (PECVD) chamber cleaning, a direct plasma cleaning method which uses the PECVD plasma source or a remote plasma cleaning method which uses a separate remote plasma source could be utilized. Currently, a remote plasma source is preferred in the PECVD chamber cleaning because it can clean the chamber walls and the corners of components more easily and does not damage the chamber components compared to the direct plasma source. For the cleaning gas used with the remote plasma source, nitrogen trifluoride, NF_3, has been mainly applied and preferentially used in the cleaning of silicon dioxide or silicon nitride PECVD chamber due to its superior cleaning properties with low global warming effect. However, due to the cost, shortage of supply, and safety problem of NF_3, various remote plasma cleaning sources using alternative gases are being widely studied.

In this study, PECVD silicon nitride chamber cleaning with NF_3/Ar and C_4F_8/O_2 using an inductively coupled plasma (ICP)-type remote plasma source has been studied to investigate a possibility to use alternative gases. C_4F_8 is cheaper and safer than NF_3 for the chamber cleaning, however, it has higher global warming potential if it is not dissociated completely. Characteristics of both gas mixtures such as cleaning rate, destruction and removal efficiencies (DREs), and million metric tons of carbon equivalent (MMTCE) were compared. To improve cleaning rate and reduce PFC emission of C_4F_8/O_2, N_2O was added because NO radical dissociated from N_2O is known to increase silicon nitride etch rate significantly during the plasma etching.[7–11]

The PECVD chamber was evacuated using a pump system combined with a booster pump and a dry pump to 0.13 Pa before the introduction of 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 remote plasma source was a homemade ICP source using 13.56 MHz as the rf power. 500 W of rf power was applied to the ICP source while maintaining the PECVD chamber pressure at 40 Pa. Cleaning species generated by ICP source were injected to the side of PECVD chamber through a quartz injector. Silicon nitride samples deposited on silicon wafers were loaded at three locations of the PECVD chamber, that is, substrate center, sidewall and front wall of the chamber facing the injector. As the chamber cleaning gas mixtures, NF_3/Ar and (20 sccm)C_4F_8O/(140 sccm)O_2/N_2O were used, and the effects of gas mixing ratio on the silicon nitride cleaning rates, emitted species, and PFC emission rates were investigated. Cleaning of silicon nitride samples was conducted at room temperature.

Silicon nitride cleaning rate was measured using a step-profilometer. The gas analysis tool used in this experiment was a fourier transform - infrared spectrometer (FT-IR, MIDAC I2000) connected to the exhaust line. The intensities of each molecules detected by FT-IR were calibrated using various calibration gases. The destruction of feed gases and the amount of the emitting global warming gases during the cleaning process were estimated as DREs[12] and MMTCE,[4] respectively.

Figure 1 shows the effect of NF_3/Ar gas mixture ratio on the silicon nitride cleaning rates for the three different locations of the chamber and the DREs of the NF_3 measured at the exhaust line. The flow rate of NF_3 was maintained at 20 sccm and the flow rate of Ar mixed to NF_3 was varied. The chamber pressure was kept at 40 Pa. As shown in the figure, the addition and increase of Ar to NF_3 initially increased the silicon nitride cleaning rate until the ratio of Ar/NF_3 is 0.5 and the further increase of Ar decreased the cleaning rate. The highest silicon nitride cleaning rate obtained was about 310 nm/min at 0.5 of Ar/NF_3. Also, the differences in the cleaning rates among the three locations were less than 10%, therefore, were similar for all of Ar/NF_3 ratios. The DREs for all of the investigated Ar/NF_3 were higher than 95%, therefore, most of fed NF_3 gas was destructed. The high DREs for all of Ar/NF_3 ratios appears to be from the high dissociation efficiency of NF_3 at the high rf power. The increase of silicon nitride cleaning

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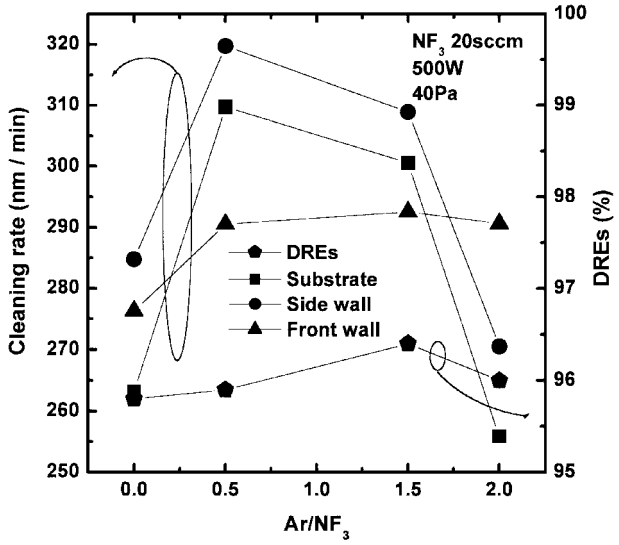

Fig. 1. The effect of NF_3/Ar gas mixture ratio on the silicon nitride cleaning rates for the three different locations of the chamber and the DREs of the NF_3 measured at the exhaust line. (NF_3 flow rate: 20 sccm, operating pressure: 40 Pa).

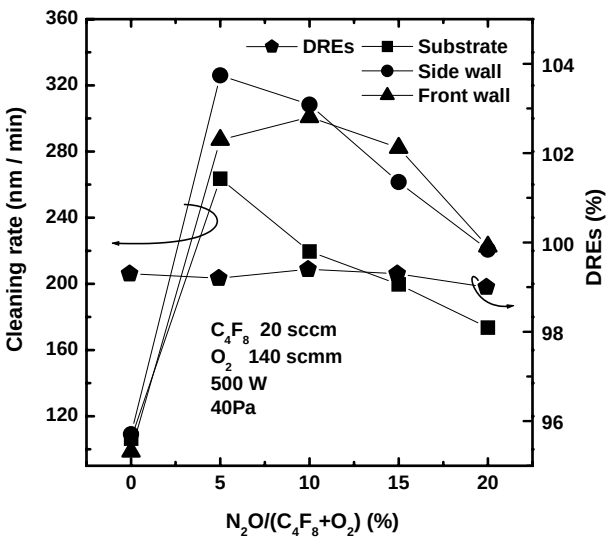

Fig. 2. The effect of N_2O to C_4F_8(20 sccm)/O_2(140 sccm) on silicon nitride cleaning rate for the three different locations of the chamber and DREs of C_4F_8 measured at the exhaust line. (Flow rates of C_4F_8 and O_2: 20 sccm and 140 sccm, respectively, operating pressure: 40 Pa).

rate by the addition of Ar to 0.5 of Ar/NF_3 is probably related to the further dissociation of NF_x ($x < 3$) to have more F radicals available for silicon nitride etching by increasing electron density due to the low ionization potential of Ar. However, the decrease of silicon nitride cleaning rate above 1.5 of Ar/NF_3 ratio appears to be related to the loss of F radicals to the pump without reacting with silicon nitride due to the lower residence time at high total flow rates.

To investigate a possibility of alternative gases for silicon nitride cleaning using the remote plasma source, gas mixtures of $C_4F_8/O_2/N_2O$ were used and its silicon nitride cleaning rate was investigated. Before the addition of N_2O to C_4F_8/O_2, the effect of C_4F_8/O_2 gas mixtures on silicon nitride cleaning rate was investigated by varying oxygen flow rate while maintaining the flow rate of C_4F_8 at 20 sccm same as NF_3 flow rate in Fig. 1 (not shown). The highest silicon nitride cleaning rate could be obtained at C_4F_8(20 sccm)/O_2 (140 sccm), however, its cleaning rate was about 35% of the optimized condition of Ar/NF_3 in Fig. 1. Therefore, N_2O was added to the optimized C_4F_8(20 sccm)/O_2(140 sccm) to improve the silicon nitride cleaning rate. Figure 2 shows the effect of N_2O to C_4F_8(20 sccm)/O_2(140 sccm) on silicon nitride cleaning rate for the three different locations of the chamber and DREs of C_4F_8 measured at the exhaust line. The pressure was also maintained at 40 Pa and the flow rates of C_4F_8 and O_2 were kept at 20 sccm and 140 sccm, respectively. As shown in the figure, the addition of N_2O to C_4F_8/O_2 up to 5% increased the silicon nitride cleaning rate drastically, however, the further increase of N_2O decreased the etch rate slowly. The highest silicon nitride cleaning rate obtained at 5% N_2O was about 300 nm/min similar to that of Ar/NF_3 obtained in Fig. 1. At this condition, the differences in the cleaning rates among the three locations were also about 10% similar to the case of Ar/NF_3. As shown in the figure, the DREs of C_4F_8 were higher than 99% for all of the conditions, therefore, almost all of the feed gas was destructed.

The increase of silicon nitride cleaning rate by the small addition of N_2O shown in Fig. 2 appears to be from NO dissociated from the N_2O from the reaction (1) shown below.

$$N_2O + O \rightarrow 2NO \quad (1)$$

$$N_2O + O \rightarrow N_2 + O_2 \quad (2)$$

In fact, the reaction (2) is known to be more dominant than reaction (1),[10] however, from the reactions of $N_2 + O \rightarrow NO + N$, NO radicals can be made again in the plasma.[13] The NO radicals generated in the reactions will be used to remove nitrogen from the silicon nitride surface by the reactions (3)–(5) and promote the reaction rate between remaining silicon on silicon nitride and fluorine to form volatile SiF_x.[7–11]

$$2NO + 2N(s) \rightarrow 2N_2 + O_2 \quad (3)$$

$$NO + N(s) \rightarrow N_2O \quad (4)$$

$$NO + N(s) \rightarrow N_2 + O \quad (5)$$

Therefore, the increase of silicon nitride cleaning rate with the small addition of N_2O is believed to be from the enhanced surface reaction not from the increase of fluorine by the increased dissociation of C_xF_y. The slow decrease of silicon nitride cleaning rate with the further increase of N_2O indicates the sufficient supply of NO to the silicon nitride surface and is possibly from the loss of fluorine radicals to the pump without the reaction due to the increase of total flow rate.

Because the silicon nitride cleaning rates and cleaning uniformities are similar each other for the optimized conditions of Ar/NF_3 and $C_4F_8/O_2/N_2O$, the NF_3 gas system might be replaced by the C_4F_8 gas system for the silicon nitride cleaning using a remote ICP source if total global warming effect of emitted PFC gases at the exhaust line is also comparable each other.

Total global warming effect of emitted PFC gases at the exhaust line is estimated by MMTCE.[4] When Ar/NF_3 was used in the cleaning of silicon nitride, only small un-destructed NF_3 was detected as the emitted PFC affecting global warming. Figure 3 shows the calculated MMTCEs for the experiments with Ar/NF_3 and $C_4F_8/O_2/N_2O$ in Figs. 1 and 2. "As is" means the MMTCE calculated with the emitted PFC

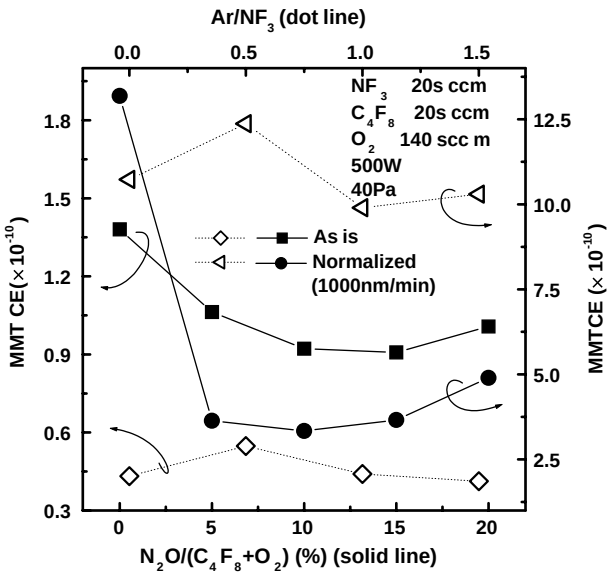

Fig. 3. The MMTCEs calculated for experiments in Figs. 1 and 2 as a function of Ar/NF_3 ratio and adding N_2O to C_4F_8(20 sccm)/O_2(140 sccm). ("As is": the MMTCE calculated with the emitted PFC species during the cleaning for the period of 2 min, "normalized": the MMTCE re-calculated for the time to remove 1000 nm of silicon nitride).

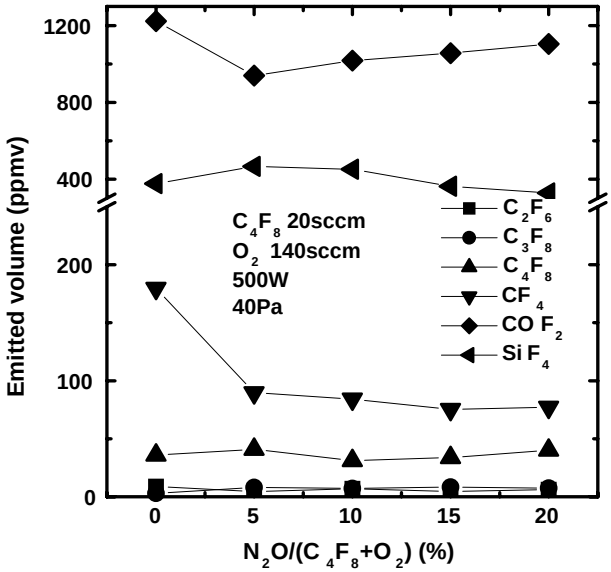

Fig. 4. The emitted PFC volumes and other detected species by FT-IR at the exhausted line as a function of N_2O to C_4F_8(20 sccm)/O_2(140 sccm).

species during the cleaning for the period of 2 min and "normalized" means the MMTCE re-calculated for the time to remove 1000 nm of silicon nitride. As shown in the figure, the MMTCE of "as is" for Ar/NF_3 was not significantly dependent on Ar/NF_3 ratio because the PFCs being involved to MMTCE calculation is only NF_3 and the DREs of NF_3 is in the range from 95 to 97% for the investigated Ar/NF_3. Also, the normalized MMTCE was not significantly dependent on Ar/NF_3 because the variation of silicon nitride cleaning rates was less than 20% for the investigated Ar/NF_3 ratios. The normalized MMTCE for the highest silicon nitride cleaning condition was 1.8×10^{-10}.

In the case of $C_4F_8/O_2/N_2O$, the detected PFCs at the exhaust line were C_2F_6, C_3F_8, CF_4, etc. in addition to the undestructed C_4F_8. Some of the emitted species such as C_2F_6, C_3F_8, CF_4, C_4F_8, COF_2 and SiF_4 at the exhaust line for (20 sccm) C_4F_8/(140 sccm)O_2/N_2O during the silicon nitride cleaning are shown in Fig. 4 as a function of N_2O percentage. As shown in Fig. 3, the MMTCE of "as is" decreased with the increase of N_2O percentage until 15% of N_2O was added to $N_2O/C_4F_8/O_2$. The decrease of MMTCE with the increase of N_2O was mainly attributed to the decrease of CF_4 with the increase of N_2O percentage because other PFC gases such as C_2F_6, C_3F_8, and C_4F_8 were not significantly changed with N_2O percentage as shown in Fig. 4. The decrease of CF_4 with the addition and increase of N_2O is not clear, however, it might be related to 1) the formation of CO_x or COF_x by the recombination of O from N_2O and CF_x or 2) the formation of CN or NF_x by the recombination of CF_x and N from N_2O. However, the measured COF_2 was not increased with the increase of N_2O percentage as shown in Fig. 4 and there are enough O available in the C_4F_8/O_2 plasmas even without N_2O, therefore, the case of 2) might be more feasible. To compare MMTCE with the case with Ar/NF_3, the MMTCE was also normalized and the result is shown in Fig. 3. As shown in the figure, due to the significant increase of silicon nitride cleaning rate by the addition of N_2O, the decrease of normalized MMTCE was as large as 75% by the addition of 5% of N_2O to C_4F_8/O_2. When the highest silicon nitride cleaning conditions of Ar/NF_3 and $N_2O/C_4F_8/O_2$ were compared, the normalized MMTCE of $N_2O/C_4F_8/O_2$ was about 3.5×10^{-10} while the normalized MMTCE of Ar/NF_3 was 1.8×10^{-10}. Because these normalized MMTCEs of Ar/NF_3 and $N_2O/C_4F_8/O_2$ are not significantly different while the silicon nitride cleaning rates and cleaning uniformities are similar each other, it is believed that NF_3-based gas mixtures can be replaceable to C_4F_8-based gas mixtures for the silicon nitride PECVD chamber cleaning using a remote ICP source if an additive gas such as N_2O is added. The other gases such as NO or N_2 which generates NO when added to C_4F_8/O_2 are also believed to be useable as additive gases.

Using a remote ICP source, characteristic of silicon nitride PECVD chamber cleaning were investigated for Ar/NF_3 and $C_4F_8/O_2/N_2O$. When gas mixtures of C_4F_8/O_2 were used, the silicon nitride cleaning rates were much lower than those by Ar/NF_3, however, by the addition of 5% of N_2O to C_4F_8/O_2, the silicon nitride cleaning rate comparable to that of optimized Ar/NF_3 could be obtained with the chamber cleaning uniformity less than 20%. The increase of silicon nitride cleaning rate with the addition of 5% N_2O to C_4F_8/O_2 is believed to be from the removal of N on silicon nitride by NO dissociated from N_2O, therefore, enhancing the formation of volatile SiF_x formation by the reaction of exposed silicon on silicon nitride with fluorine. MMTCEs of Ar/NF_3 and $C_4F_8/O_2/N_2O$ during the silicon nitride cleaning were also compared. The PFC gases detected by FT-IR at the exhaust line during the silicon nitride cleaning were C_2F_6, C_3F_8, CF_4, and un-destructed C_4F_8 for $C_4F_8/O_2/N_2O$ and un-destructed NF_3 for Ar/NF_3. No significant change of MMTCE was observed for different Ar/NF_3 gas mixtures, however, significant decrease of MMTCE was observe by the addition of small N_2O to C_4F_8/O_2 for $C_4F_8/O_2/N_2O$ due to the decrease of CF_4 with the addition of N_2O at the exhaust line. The MMTCEs at the highest silicon nitride cleaning condition were not signif-

icantly lower for Ar/NF_3 compared to that for $C_4F_8/O_2/N_2O$, therefore, it is believed that NF_3-based gas mixtures can be replaceable to C_4F_8-based gas mixtures for the silicon nitride PECVD chamber cleaning using a remote ICP source if an additive gas such as N_2O is added.

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