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Effect of N-based Gases to C_3F_8/O_2 on Global Warming during Silicon Nitride PECVD Chamber Cleaning Using a Remote Plasma Source

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Silicon nitride cleaning of plasma enhanced chemical vapor deposition (PECVD) chamber was carried out by NF_3 and C_3F_3/O_2 using a remote plasma source. The effects of cleaning gases on the silicon nitride cleaning and perfluorocompounds (PFCs) emission properties were studied. To improve the cleaning properties with C_3F_8/O_2, N-based gases such as N_2, N_2O, and NO were added to an optimized condition of C_3F_8/O_2 (that is, C_3F_8 : O_2= 3:7).The silicon nitride cleaning rate was increased by about 70 % from 260 to 440 nm/min by mixing 5 to 10 % of N-based gases to C_3F_8(30 %) /O_2(70 %). Million metric tons of carbon equivalents (MMTCEs) were investigated and MMTCEs were decreased from 1.5×10^{-10} to 8×10^{-11} by the addition of 5 to 10 % N-based additive gases to C_3F_8(30 % /O_2(70 %). In the case of NF_3, silicon nitride cleaning rate was 900 nm/min and the MMTCE was lower than 5×10^{-11} at 600 sccm of NF_3. Even though N-based gas with added C_3F_8/O_2 shows a higher MMTCE and a lower silicon nitride cleaning rate than those by NF_3, it is believed that N-based gas with added C_3F_8/O_2 is replaceable to NF_3 due to such advantages as relatively low price and low F_2 emission.

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I. INTRODUCTION

Fluorinated gas discharges are widely used in the semiconductor industry to etch silicon, silicon oxide, and silicon nitride films, and to clean chemical vapor deposition (CVD) reactors or plasma-enhanced chemical vapor deposition (PECVD) reactors that deposit these films. [1–4] Perfluorocompounds (PFCs) such as C_2F_6, C_3F_8, CF_4, C_4F_8, NF_3, *etc.* are exhausted as non-destructed or regenerated PFC species during the above processing. These species have high global warming potentials (GWPs), since they absorb an infrared spectrum region and have long lifetimes over thousands times of CO_2. [1,5,6] PFCs that have long lifetimes contribute to global warming evaluated by million metric tons of carbon equivalent (MMTCE) [1]. Despite of these properties, the use of PFCs has increased in the semiconductor industry in last years even though semiconductor industry is making efforts to reduce PFCs emission through the several councils and by replacing with PFCs having low global warming effects or by the abatement of the emitted PFCs. [1,6] C_3F_8 and NF_3 have shorter life times and higher destruction removal efficiencies (DREs) [7] than other PFCs such as C_2F_6, CF_4, etc. [6] Especially, NF_3 is currently being used as a low global warming gas with a remote plasma source for PECVD chamber to reduce the damages to the process chamber parts and to clean the chamber more thoroughly. However, the use of NF_3 shows problems such as cost, shortage of supply, and safety compared to other PFCs. In this study, silicon nitride samples deposited by PECVD were etched with NF_3, C_3F_8/O_2, and N-based gas added to C_3F_8/O_2 using a remote plasma source and the characteristics of silicon nitride etch rate, destruction and removal efficiency (DRE), and MMTCE were compared to investigate a possibility of C_3F_8-based gases to replace NF_3 as remote plasma cleaning gases for PECVD chambers. In fact, the addition of N-based gases to PFCs is known to increase silicon nitride etch rates for the plasma etching study using microwave remote plasma sources. [8–12] Therefore, in this experiment, the effects of N-based gases to C_3F_8/O_2 on the global warming in addition to silicon nitride cleaning were investigated using a remote plasma source.

II. EXPERIMENTAL

Figure 1 shows the schematic diagram of a silicon nitride PECVD deposition system, a remote plasma source, and a measurement system used in this experiment. The PECVD deposition system was a commercially available system (EUREKA 2000) made by Jusung Engineering Co., Ltd. The remote plasma source for the silicon nitride cleaning was a transformer-coupled type source. To clean the chamber, the PECVD sys-

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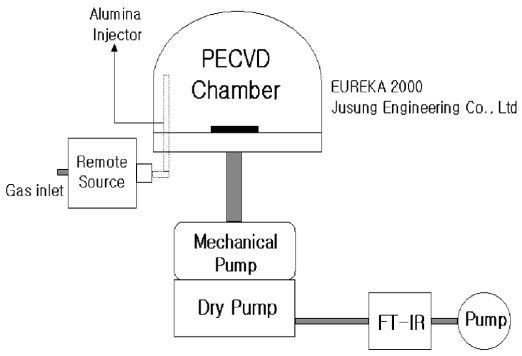

Fig. 1. Schematic diagram of a silicon nitride PECVD chamber, a remote plasma cleaning source, and a measurement system used in this experiment.

tem was evacuated using a pump system combined with a booster pump and a dry pump to 7.5 mTorr. The remote source was pre-ignited by 4 slm Ar before the introduction of cleaning gas mixtures such as NF_3, C_3F_8/O_2, and C_3F_8/O_2/N-based additives (N_2, N_2O, NO). The dry pump uses N_2 as a purging gas. The flow rate of the N_2 gas was estimated as 33.2 slm. Cleaning species generated by the remote source were uniformly injected through the alumina injector at the bottom of PECVD chamber. Silicon nitride samples deposited on silicon wafers were loaded at the center of the PECVD chamber. 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 for 2 minutes. Silicon nitride cleaning rate was measured using a step-profilometer. The gas analysis tool used in this experiment was a Fourier transform-infrared absorption 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 global warming potential by the emitted gases during the cleaning process were estimated as DRE and MMTCE, respectively. The DRE was calculated by taking the ratio of the PFC gas volume fed to the chamber to the emitted PFC feed gas volume at the exhaust line. The calculation of MMTCE from the emitted PFC gases can be found elsewhere. [6]

III. RESULTS AND DISCUSSION

Figure 2 shows the effects of NF_3 and C_3F_8/O_2 on silicon nitride cleaning rate as a function of NF_3 flow rate from 200 to 600 sccm and as a function of C_3F_8/O_2 ratio at 500 sccm of flow rate (C_3F_8 + O_2), respectively. The power to the remote plasma source was 6 kW. The source was pre-ignited using 4 slm of Ar. The cleaning gases were introduced to clean the silicon nitride in addition to 4 slm of Ar. Total pressure to the PECVD chamber

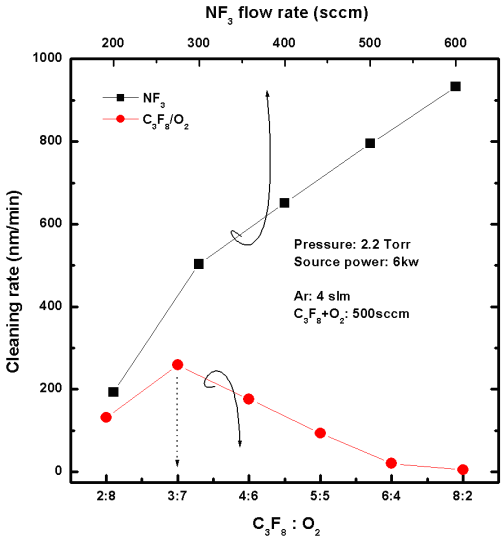

Fig. 2. Silicon nitride cleaning rate measured as functions of NF_3 flow rate and C_3F_8/O_2 ratio.

was maintained at 2.2 Torr. As shown in the figure, the increase of NF_3 flow rate from 200 to 600 sccm increased the silicon nitride cleaning rate almost linearly in the case of NF_3. At 600 sccm, the silicon nitride etch rate was close to 900 nm/min. The further increase of NF_3 flow rate was not possible due to the increase of reflected power. The increase of silicon nitride cleaning rate with the increase of NF_3 flow rate appears to be from the increase of fluorine atoms to the PECVD chamber. DREs for the range from 200 to 600 sccm of NF_3 were higher than 99 % (not shown). In the case of C_3F_8/O_2, the increase of oxygen percent in the C_3F_8/O_2 initially increased the silicon nitride cleaning rate, however, oxygen added more than 70 % in C_3F_8/O_2 decreased thecleaning rate. Oxygen is required to remove the carbon on the silicon nitride surface due to the high polymerization on the silicon nitride surface by the carbon in C_3F_8. [13,14] Oxygen is known to release fluorine atoms from fluorocarbon gases, therefore, the addition of oxygen to C_3F_8 increased the silicon nitride cleaning rate.

However, the increase of oxygen percentage over 30 % in C_3F_8/O_2 decreases the C_3F_8 concentration in the feed gas mixture. Therefore, it will finally decrease silicon nitride cleaning rate due to the lack of fluorine source gas, that is, C_3F_8. The highest silicon nitride cleaning rate obtained was 260 nm/min at C_3F_8(30 %)/O_2(70 %). At this condition, DRE was also higher than 99 % (not shown). To increase the silicon nitride cleaning rate, N-based gases such as N_2, N_2O, and NO were added to the optimized C_3F_8/O_2. The addition of N-based gases to fluorocarbon gases is known to increase the silicon nitride etch rates for the plasma etching studies using microwave remote plasma etching systems. [8–12] It is also confirmed in our previous study in the cleaning of a silicon nitride PECVD system using a direct capacitively

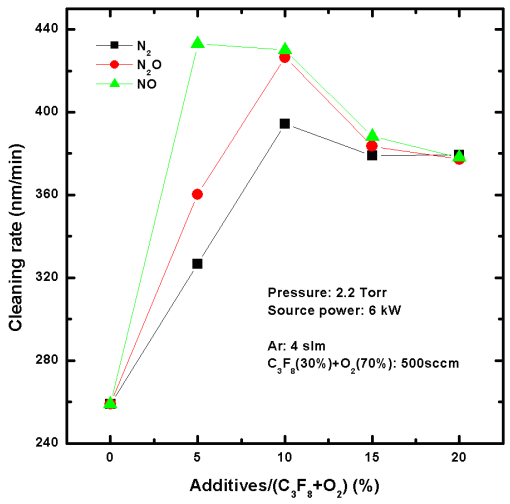

Fig. 3. Silicon nitride cleaning rate measured as a function of N-based additive gases such as NO, N_2O, and N_2 to C_3F_8(150 sccm)/O_2(350 sccm)

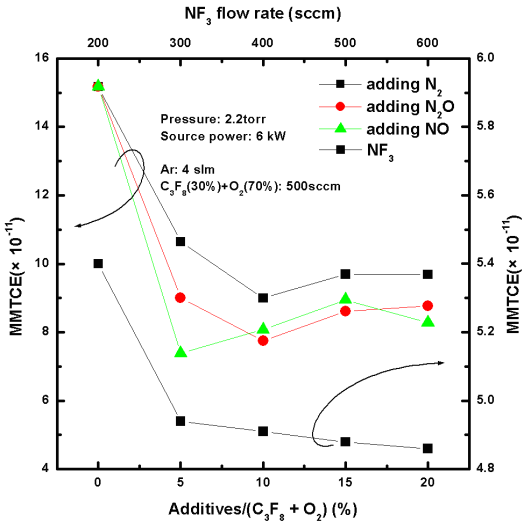

Fig. 4. Normalized MMTCEs as functions of NF_3 flow rate and N-based additive gases to C_3F_8(150 sccm)/O_2(350 sccm).

coupled plasma source. [15] Figure 3 shows the effect of N-based gases to C_3F_8(30 %)/O_2(70 %) on the cleaning rate of silicon nitride using a remote plasma source. The remote plasma source power and total pressure were kept at 6 kW and 2.2 Torr, respectively. Ar flow rate and flow rate of C_3F_8/O_2 were also maintained at 4 slm and 500 sccm, respectively.

As shown in Fig. 3, the increase of N-based gases to the optimized C_3F_8/O_2 increased the silicon nitride cleaning rates. In the case of NO, the addition of 5 % NO showed the highest increase of silicon nitride cleaning rate of about 70 % from 260 nm/min to 440 nm/min. It was followed by N_2O (10 %: 430 nm/min) and N_2 (10 %: 400 nm/min). The increase of silicon nitride cleaning rate with the addition of N-based gases to fluorocarbon gases is from the increase of NO radicals in the plasma. The NO radical increases the surface reactions such as $2NO+2N_{surface} \rightarrow N_2 \uparrow + O_2 \uparrow$ and $NO+N_{surface} \rightarrow N_2O \uparrow$, therefore, it removes nitrogen from the silicon nitride surface and activates silicon atom on the silicon nitride surface to be etched by fluorine atoms. [8,9] The abundance of NO radicals in the plasma is as follows; NO>N_2O>N_2, [9] which is similar to the sequence of the silicon nitride cleaning rates. DREs for all of the conditions were also higher than 99 %. (not shown)

Figure 4 shows the MMTCEs calculated for NF_3 in Fig. 2 and N-based gas added C_3F_8/O_2 in Fig 3. The operational conditions were the same as those in the respective figures. The MMTCEs were calculated by measuring emitted PFC gas volumes such as NF_3, C_2F_6, C_3F_8, C_4F_8, CF_4, etc. at the exhaust line during the processing and by putting the PFC gas volumes into the equation used to calculate MMTCE [6]. The PFC gas volumes were measured by FT-IR for two minutes. The MMTCE shown in the figure was normalized to the silicon nitride cleaning rate of 1000 nm/min. As shown in Fig. 4, the increase of NF_3 flow rate decreased the MMTCE slightly from 5.4×10^{-11} to 4.9×10^{-11} and the addition of N-based gases to C_3F_8/O_2 about 5 to 10 % decreased the MMTCE from 1.5×10^{-10} to lower than 8×10^{-11}. The decrease of MMTCE with the increase of NF_3 is related to the increase of silicon nitride cleaning rate because no other PFCs are emitted for NF_3 except for NF_3 itself. DREs are higher than 99 % for all of the NF_3 flow rates. However, in the case of N-based gas with added C_3F_8/O_2, PFC gases such as CF_4, C_2F_6, etc. are emitted at the exhaust line. Therefore, these emitted PFC volumes will affect the MMTCE in addition to the silicon nitride cleaning rate. Figure 5 shows the emitted PFC volumes at the exhaust line as a function of N-based gas to C_3F_8/O_2. The operation conditions were the same as those in Figure 3. The PFC volumes were measured by FT-IR for 2 minutes. As shown in Fig. 5, the emitted C_3F_8 gas was almost 0 sccm due to the DRE higher than 99 %. The PFC species detected by noticeable amount were CF_4 and C_2F_6 as shown in Fig. 5. The emitted CF_4 volume was decreased with the increase of N-based gases possibly due to the formation of CN and NOF, therefore, by decreasing the possibility to form recombined CF_4.

The decrease of emitted CF_4 volumes with the addition of N-based gas was in the sequence of NO>N_2O>N_2 similar to that of silicon nitride cleaning rate. Therefore, the decrease of emitted CF_4 volumes with the increase of N-based gases appears to be related to the increase of silicon nitride cleaning rate and NO radicals. C_2F_6 appears to show the similar trend as CF_4 even though the emitted volumes are smaller. Therefore, the decrease of MMTCE with the increase of N-based gases to C_3F_8/O_2 shown in Fig. 4 appears to be mostly from the increase of silicon nitride cleaning rate and the decrease of emitted CF_4 vol-

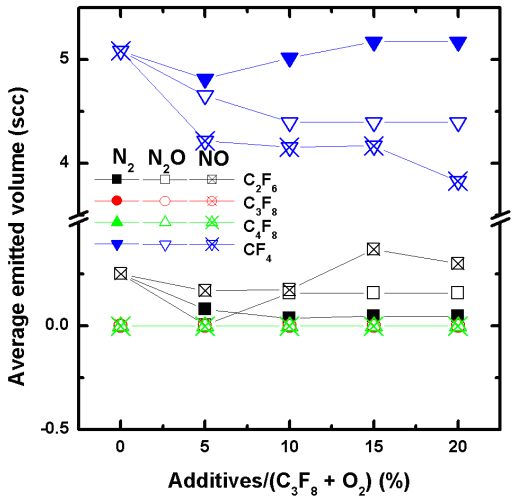

Fig. 5. Average emitted volume of detected PFCs species at the exhaust line measured as a function of N-based additive gases such as NO, N_2O, and N_2 to C_3F_8(150 sccm)/O_2(350 sccm).

ume. If MMTCEs for the various gases are compared, NF_3 (600 sccm: 4.9×10^{-11}) showed the lowest MMTCE and it was followed by $C_3F_8/O_2/NO$(5 %: 7.4×10^{-11}), $C_3F_8/O_2/N_2O$(10 %: 7.8×10^{-11}), and $C_3F_8/O_2/N_2$(10 %: 9.0×10^{-11}) in sequence. Therefore, the MMTCE for the optimized $C_3F_8/O_2/NO$ is 1.5 times higher than that of NF_3. Also, the silicon nitride-cleaning rate by the optimized NF_3 is about 2.0 times higher than that by optimized $C_3F_8/O_2/NO$. However, due to the shortage and high cost of NF_3 in addition to the possible emission of hazardous F_2 [16], the replacement of NF_3 to low global warming PFC gases as remote plasma cleaning gases for the PECVD chamber cleaning has been requested by the semiconductor manufacturing industry. Even though the optimized $C_3F_8/O_2/NO$ shows a lower silicon nitride cleaning rate and a higher MMTCE than the optimized NF_3, it is believed that the optimized $C_3F_8/O_2/NO$ could be applied to the silicon nitride PECVD chamber cleaning using a remote plasma source due to its lower cost and safety.

IV. CONCLUSIONS

In this study, a possibility of C_3F_8-based gases as the gases of a remote plasma source that can replace NF_3 for the silicon nitride PECVD chamber cleaning has been investigated by studying silicon nitride cleaning rates and MMTCE. When C_3F_8 was mixed with O_2, the silicon nitride cleaning rate showed the maximum at C_3F_8(30 %):O_2(70 %). The addition of N-based additive gases such as N_2, N_2O, and NO about 5 to 10 % to the optimized C_3F_8(30 %):O_2(70 %) increased the silicon nitride cleaning rate up to 70 %. The addition of 5 % NO to the optimized C_3F_8/O_2 showed the highest silicon nitride cleaning rate. The increase of silicon nitride cleaning rate by the addition of N-based gases to the optimized C_3F_8/O_2 was as follows; NO(5 %)>N_2O(10 %)>N_2(10 %). The increase of silicon nitride cleaning rate was related to the concentration of NO in the plasma and the NO radicals increased the silicon nitride cleaning rate by removing N from the silicon nitride surface by the formation of N_2O. CF_4 was the main PFC detected at the exhaust line for C_3F_8-based gases and the addition of NO decreased the emitted CF_4 volume. Therefore, the addition of NO to C_3F_8/O_2 not only increased the silicon nitride-cleaning rate but also decreased the MMTCE. The optimized NF_3 showed 2 times higher silicon nitride cleaning rate and 1.5 times lower MMTCE, however, if the problems of NF_3 such as high cost, shortage, and formation of hazardous F_2 are considered, it is believed that the optimized $C_3F_8/O_2/NO$ could be applicable as the replacement of NF_3.

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