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Global Warming Gas Emission during Plasma Cleaning Process of Silicon Nitride Using c-C_4F_8O Feed Gas with Additive N_2

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Abstract

In this work, the cyclic perfluorinated ether (c-C_4F_8O) with very high destructive removal efficiency (DRE) than other alternative gases, such as C_3F_8, c-C_4F_8 and NF_3 was used as an alternative process chemical. The plasma cleaning of silicon nitride using gas mixtures of c-C_4F_8O/O_2 and c-C_4F_8O/O_2+N_2 was investigated in order to evaluate the effects of adding N_2 to c-C_4F_8O/O_2 on the global warming effects. Under optimum condition, the emitted net perfluorocompounds (PFCs) during cleaning of silicon nitride were quantified and then the effects of additive N_2 by obtaining the destructive removal efficiency (DRE) and the million metric tons of carbon equivalent (MMT-CE) were calculated. DRE and MMTCE were obtained by evaluating the volumetric emission using Fourier transform-infrared spectroscopy (FT-IR). During the cleaning using c-C_4F_8O/O_2+N_2, DRE values as high as ≅ 98 % were obtained and MMTCE values were reduced by as high as 70 % compared to the case of C_2F_6/O_2. Recombination characteristics were indirectly investigated by combining the measurements of species in the chamber using optical emission spectroscopy (OES), before and after the cleaning, in order to understand any correlation between plasma and emission characteristics as well as cleaning rate of silicon nitride.

1. INTRODUCTION

Perfluorocompounds (PFCs) emitted by the semiconductor industries are known to cause global warming. To prevent further increase of global warming by emitted PFCs, the members of semiconductor industries have decided to reduce the emission of PFCs responsible for global warming to 10 % 1995 level by 2010[1]. Among the semiconductor fabrication processes, silicon dioxide and silicon nitride CVD chamber cleaning process is known to emit the largest quantities of net PFCs. Therefore it is necessary to develop various methods to cut down the emission of the PFCs[2, 3].

For cleaning the silicon dioxide or silicon nitride

CVD chamber, various alternative gases such as C_3F_8, c-C_4F_8, and NF_3 having low global warming potential have been studied to replace conventional PFCs such as CF_4, SF_6, and C_2F_6. The c-C_4F_8O used in this work is one among gases that are currently under study for the cleaning of silicon dioxide and silicon nitride CVD chamber[4]. Table 1 describes some of the chemical properties of this compound[4].

Table 1. Chemical properties of c-C_4F_8O

Vapor pressure	1802.7 Torr
Flammability	Nonflammable
Critical temperature	111.85 ℃
Critical pressure	19951.6 Torr
Freezing point	− 83 ℃
Boiling point	0 ℃

2. EXPERIMEMT

Figure 1 shows a schematic diagram of gas sampling system used in this experiment to analyze gas species emitted from the exhaust line 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 ≅ 1 mTorr before the injection of cleaning gases. The PECVD system was a home-made capacitively coupled plasma system using 13.56 MHz rf power. Square-shaped

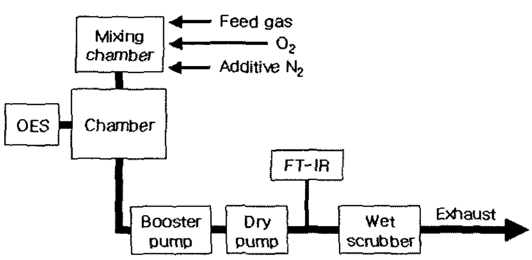

Fig. 1 A schematic of gas sampling system

(5 cm × 5 cm) silicon nitride which was deposited on Si (001) was used as cleaning samples. MMTCE values were quantified based on the cleaning of 1 (m-thick silicon nitride.

Silicon nitride samples were cleaned with the gas mixtures of C_4F_8O/O_2 and C_4F_8O/O_2+N_2. The effects of additive N_2 and the net emitted PFCs were quantitatively measured using Fourier transform infrared spectroscopy (FT-IR; MIDAC, I2000). The gas sampling system consisted of a 2 m, 1/4 inch Teflon$_{TM}$ sample line, which was used to extract emitted gas from the exhaust of vacuum pump line. The exhaust gas samples were extracted after the N_2 ballast dilution at the dry pump at near-atmospheric pressure. During the cleaning process, recombination characteristics were indirectly investigated by measuring of species in the chamber using optical emission spectroscopy (OES; SC Technology, Model 300). Optimum condition was obtained by controlling gas chemistry, c-C_4F_8O flow rate, and operational pressure. The applied rf power held constant at 350 W and the PECVD chamber wasn't heated.

The destruction of feed gas and the amount of the emitted global warming gases were quantified as destructive removal efficiency (DRE) and million metric tons of carbon equivalent (MMTCE), respectively. DRE and MMTCE values were calculated by using the concentration of species measured FT-IR and then by applying the formula in Equation (1) and (2);

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

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

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

where GWP_{100i} is the global warming potential of each component (integrated over a 100 year time horizon) of the calculation and Q_i is the total mass of that species (in Kg) released during the process[5]. Silicon nitride samples were located at the substrate without heating and the silicon nitride cleaning rate was measured using an (step-profilometer (Tencor, AS-500).

A quantitative assessment of the effluent was limited to the targeted species CF_4, C_2F_6, C_3F_8, SiF_4, and COF_2. Other species such as CO_2, CO, and HF were detected but not quantified. Noble gases and homonuclear diatomics are not detectable via FT-IR, therefore F_2 was not monitored in this study.

3. RESULTS AND DISCUSSION

Before studying the global warming effect during silicon nitride cleaning using c-C_4F_8O feed gas, dry pump dilution N_2 flow rate as well as linearity of feed gas and targeted gas were checked by FT-IR. Dilution N_2 flow rate was 32,979.72 sccm in our system. We checked this value to maintain the same condition for every measurement. A slope of concentration to feed gas and targeted gas flow rate is 30.23 ppmv/sccm in this experiment.

Through cleaning of silicon nitride using C_2F_6 reference feed gas, the cleaning rate of 484.0 nm/min was obtained at an optimum condition (400 mTorr, C_2F_6: 22 sccm, O_2: 22 sccm). MMTEC value was 1.22×10^{-9} and DRE of C_2F_6 feed gas was 68.14 %.

The cleaning rate obtained at an optimum condition (500 mTorr, c-C_4F_8O: 16 sccm, O_2: 64 sccm)

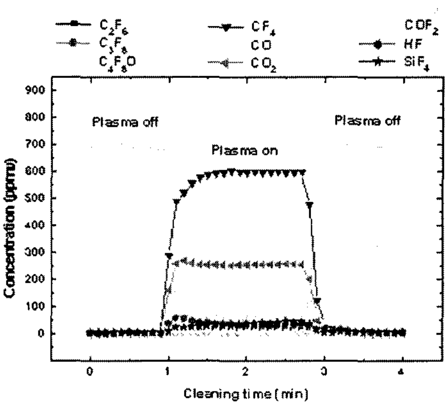

Fig. 2 Extractive FT-IR monitoring during silicon nitride cleaning using c-C_4F_8O/O_2

was 507.7 nm/min during c-C_4F_8O/O_2 cleaning. Under this condition, DRE of c-C_4F_8O feed gas was 98.38 %, and most of the feed gas was exhausted after being decomposed. MMTEC value was 3.58×10^{-10}. This value corresponds to the reduction of MMTCE by about 70% as compared to the case of C_2F_6/O_2 cleaning. Comparing DRE values of two cases, the reduction of emitted feed gas that was exhausted without participating during cleaning process explains to the observed decrease in MMTCE values. Figure 2, however, shows that the emission of CF_4 is increased for the case of c-C_4F_8O/O_2 cleaning.

CF_4 is a representative by-product that affects on global warming. The FT-IR analysis did include C_2F_6 and C_3F_8 in the MMTCE values calculations; however, the amount of either of these compounds produced from c-C_4F_8O feed gas processes was found to be negligible or zero in all case.

There are two ways of reducing MMTCE values; increasing cleaning rate using the same amount of feed gas or reducing emitted gases with high global warming potential such as CF_4. In order to decrease MMTCE values further, the effects of additive N_2 during c-C_4F_8O/O_2 cleaning

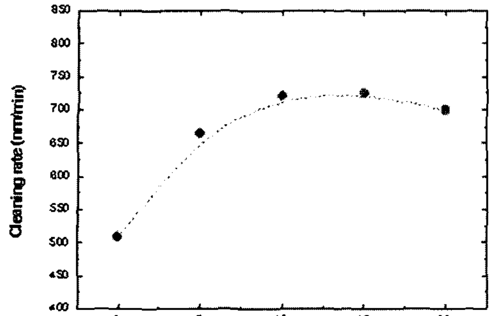

Fig 3 Cleaning rates of silicon nitride as a function of additive N_2 flow rate ratio

were investigated. Adding N_2 have been reported to help increase of silicon nitride etch rate[6, 7]. Figure 3 shows the silicon nitride cleaning rate when N_2 was added. The cleaning rate is increased as much as by 32.5 %. When N_2 is added over 10 %, the cleaning rate tends to be saturated. This result will be helpful for suppressing the global warming because it can decrease the use of feed gas to clean the same thickness of silicon nitride layer.

Figure 4 shows DRE values as a function of additive N_2 flow rate. This result is contrary to the trend of cleaning rate. In order to understand this result, OES measurements were carried out. Figure 5, OES analyses data during glow discharges with addictive N_2 without cleaning sample inside chamber, indicates the creation of NO molecule from observed peaks at the wavelength of 653.6 nm and 659.9nm ($N^2\Delta - C^2\Pi$ system). Extensive researches have been done on the production on NO in discharges containing N_2 and O_2[8]. The increased cleaning rate by additive N_2 can be attributed to increase in cleaning rate due to the NO molecules created in glow discharge plasma during silicon nitride cleaning[9]. The presence of NO in the gas phase facilitates silicon nitride etching of silicon nitride by F atom[7]. NO molecule or the energetic metastable NO* can promote etching actively as a reactive species or passively as the source of activation energy for the etching reaction, through the formation of volatile SiF_4. Also, because the etch rate of silicon nitride without biasing at substrate between those of silicon and silicon dioxide[10], N_2 in this experiment contributes to increase in the cleaning rate by suppressing the creation of silicon dioxide[11].

As seen in Figure 6, we can see that the increased emission of COF_2 and HF in inversely proportional to the decrease in the emission of CF_4. It

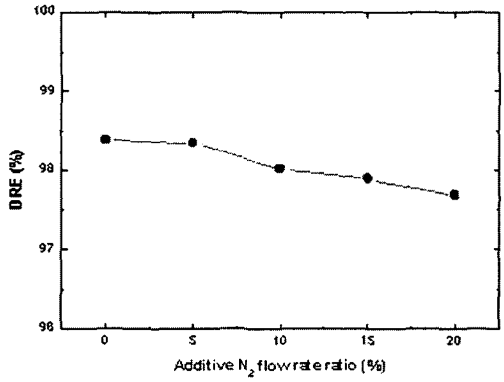

Fig. 4 DRE of c-C_4F_8O feed gas as a function of additive N_2 flow rate ratio

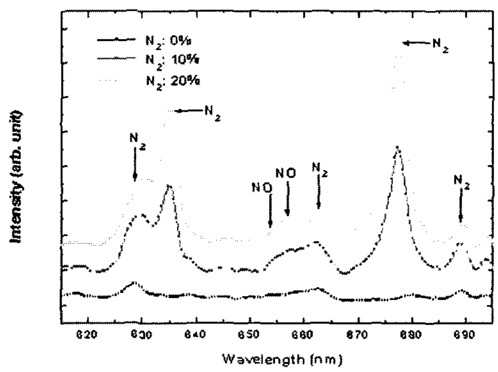

Fig 5 OES spectra of glow discharge of c-C_4F_8O/O_2+N_2 without silicon nitride sample

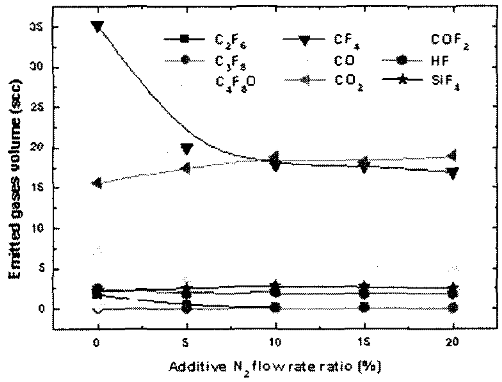

Fig. 6 Emitted gas volume during silicon nitride cleaning as a function of additive N_2 flow rate ratio

shows that the creation of CF_4 was suppressed by formation of by-products. We can also see the increase in emitted rates of CO and CO_2 resulting in reduced polymerization on the surface of silicon nitride layer. Among by-products, GWPs of CO_2 are lower than CF_4 those of, and COF_2 and HF which can be removed by a wet-scrubber[4].

MMTCE values by additive N_2 as shown in Figure 7, show a similar trend to the decrease of the emitted CF_4. It suggests that decrease in the emitted CF_4 contributed to the decrease in MMTCE values.

To reduce emission CF_4, a use of feed gases or

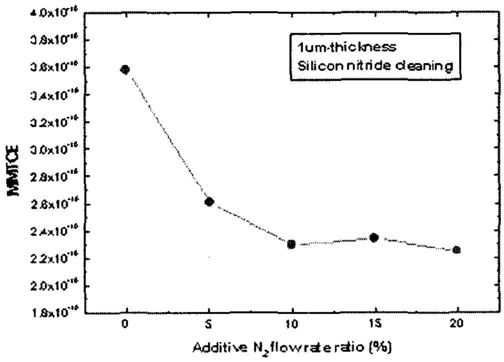

Fig. 7 MMTECE during silicon nitride cleaning as a function of additive N_2 flow rate ratio

the emission of recombined CF_4 must be inhibited from in the chamber. Adding N_2 during c-C_4F_8O/O_2 cleaning is effective, in increasing the cleaning rate as well as reducing the emitted CF_4. Because of increase in the cleaning rate and at the same time reduction in the use of feed gas, the total emission of CF_4 was decreased during cleaning silicon nitride sample with the same thickness film. After all, these contributed to the reduction in the global warming. Consequently when 10 % N_2 is added, MMTCE was decreased by 38.0 % compared with c-C_4F_8O/O_2 cleaning. Compared with c-C_4F_8/O_2 cleaning (MMTCE$\cong$1.22 × 10^{-9}), furthermore MMTCE value was decreased by 81.8 %.

4. SUMMARY

An alternative c-C_4F_8O-based PECVD chamber cleaning chemistry was evaluated as a potential replacement for C_2F_6 cleaning process currently in use. In the case of cleaning using c-C_4F_8O/O_2, MMTCE was reduced to 70.7 % but emitted CF_4 was higher than the case of C_2F_6/O_2 chemistry. Use of less feed gas and reduction of emitted CF_4 during cleaning process is effective in reducing global warming.

In this work, addition of N_2 leads to the reduction of global warming effects through increase in cleaning rate and decrease in emission of CF_4. In case of adding N_2 to c-C_4F_8O/O_2 chemistry, significant increase in cleaning rate contributes to further decrease in MMTCE values together with reduction of emitted CF_4 with high global warming potential by the reduction of feed gas used to cleaning the same thickness of silicon nitride layer. This increase in cleaning rate by additive N_2 seems to be caused by newly formed NO molecules that help to clean by increased F density. Supprssion of silicon dioxide formation by additive N_2 also effectively increases cleaning rate. In this work, when N_2 is added by 10% of total flow, MMTCE was further decreased by 38.0% compared with c-C_4F_8O/O_2 chemistry. Compared to C_2F_6/O_2 cleaning (MMTCE $\cong 1.22 \times 10^{-9}$), MMTCE value was decreased down to 81.8 %.

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