Abatement of CF₄ and CHF₃ emitted from semiconductor manufacturing processes using low-pressure plasmas generated by annular-shaped electrodes

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Abstract:
A plasma abatement system operating at low pressures is set up with the aim of treating CF₄ and CHF₃ emitted from the semiconductor industry. The abatement device has a tube-shaped reactor wrapped in metal electrodes, which allows for easy connection to a pre-existing pipeline in the semiconductor industry. With respect to RF and AC power supplies, the destruction and removal efficiencies (DREs) for CF₄ are compared by varying the pressure. In addition, the influences of O₂ and H₂O additions on the CHF₃ abatement are investigated based on the spectra measured with a Fourier transform infrared (FTIR) spectroscopy. Then, the gas condition for suppressing the recombination of CHF₃ fragments into CF₄ is proposed. Finally, the DREs for a mixture of CF₄ and CHF₃ are measured as a function of input power to demonstrate the feasibility of our device for abatement of perfluorinated compounds (PFCs) emitted from the semiconductor industry.

Keywords: Abatement of perfluorinated compounds (PFCs), low-pressure plasmas, annular-shaped electrodes

1. Introduction
Perfluorinated compounds (PFCs) are extensively used in the semiconductor industry for plasma etching and chamber cleaning because of their prominent chemical property and low toxicity. The emission of PFCs is, however, regulated because of their very high global warming potential (GWP) and long atmospheric lifetimes compared to CO₂ [1]. Together with the rapid growth of the semiconductor industry, the quantity of PFCs emitted from the semiconductor manufacturing processes has greatly increased as well, and this is now a significant concern.

PFCs are now often thermally abated using combustion at atmospheric condition after the vacuum pumps. Combustion is, however, not effective in sense that it abates PFCs after they are significantly diluted in N₂ gas through the vacuum pumps. The dilution of PFCs in N₂ gas not only requires significant amounts of natural gas but also produces second pollutants such as NO and NO₂.

Recently, low-pressure plasmas have received a great attention to the abatement of PFCs emitted from semiconductor manufacturing processes due to their high destruction and removal efficiency (DRE). Low-pressure plasmas provide abundant reactive species, which can easily break down chemical C-F and C-H bonds of PFCs. In addition, the abatement of PFCs before their dilution in N₂ gas allows for the high DRE without the production of secondary pollutants.

Conventional plasma abatement devices developed so far are based on a radio frequency (RF) inductive coupled plasma (ICP) [2-4] or microwave plasma generating system [5]. However, installation of these systems in pre-existing vacuum pipelines in the semiconductor industry is not simple and is relatively costly. This work aims to find an alternative plasma abatement device with a simpler structure and cheaper installation cost.
2. Experimental

As shown in Fig. 1, our plasma abatement device has a simple cylindrical shape, which allows it to be easily combined with pre-existing vacuum pipelines in the semiconductor industry. The reactor basically consists of two quartz tubes divided by a metal part. Each quartz tube is wrapped in a copper electrode which is annular in shape. The metal part placed between the two quartz tubes is grounded and has converging parts from periphery to center with a view to obtaining more uniform plasmas in space. The stainless steels connected to the reactor edge are also grounded, and they will be replaced by pre-existing pipelines in the semiconductor industry in practical applications. AC and RF waveforms are applied to the two copper electrodes on the quartz tubes.

![Figure 1. A schematic of experimental system.](image)

The plasma reactor is placed upstream of a vacuum pump (Lotvacuum, HD 1200). Although the plasma density is expected to increase with decreasing reactor diameter, the inner diameter of quartz is set to 100 mm to guarantee the vacuum conductance. It is known that RF plasmas provide higher plasma density than AC plasmas while AC power supplies are several times cheaper than RF supplies at same power levels. In this work, the DREs for CF

3. Results and discussion

Figure 2 shows a difference in DREs for CF

between AC and RF operations at a same power of 800 W. The pressure is varied from 40 to 200 mTorr, and the flow rates of Ar, CF

and O

are all fixed at 50 sccm. It is seen that AC operation achieves higher DREs for CF

than RF operation. Under the same power, RF plasmas have a higher current but lower voltage than AC plasmas. This difference leads to the high electron densities and thus high gas temperatures but low electron energies of RF plasmas compared to those of AC plasmas. CF

abatement is initiated by the electron impact dissociation. Because CF

is very stable gas, dissociation of CF

into CF

requires electrons with high energies. Because of higher voltage, AC plasmas produce more energetic electrons than RF plasmas, and this is the reason why AC plasmas are more effective for the decomposition of stable gases such as CF

Figure 3 shows the spectra measured with the FTIR spectroscopy for CHF

(50 sccm) by adding O

and H

at a fixed power (600 W) and pressure (120 mTorr). CHF

is weakly bonded, so that it is more easily decomposed than CF

. It is, however, noted that in the case of the only CHF

injection, the CHF

fragments are substantially recombined into CF

. The CHF

decomposition is more activated by the addition of O

, which, however, can’t suppress the CF

production. Similar tendency is found in Xu et al.’s and Vitale et al.’s works [2], [3], and this is because CF

is a very stable gas. As seen in Fig. 3,
the recombination of CHF$_3$ fragments into CF$_4$ is only suppressed by the addition of H$_2$O. Electron dissociation of H$_2$O produces O, H, and OH radicals, which react on CHF$_3$ fragments into stable gases such as CO, CO$_2$, and HF. These reactions prevent CHF$_3$ fragments from recombining into CF$_4$.

Increasing the H$_2$O flow rate. On the contrary, the decomposition rate of CHF$_3$ greatly decreases with an increase in H$_2$O flow rate. It is derived from this result that H$_2$O acts as a sink to absorb the electrical energy. Thus, it can be said that the optimization of H$_2$O flow rate is very important for effective abatement of CHF$_3$.

Figure 2. Comparison of destruction and removal efficiency (DRE) for CF$_4$ between AC and RF operations measured as a function of pressure at a fixed power of 800 W.

Figure 3. Influence of O$_2$ and H$_2$O additions on the FTIR spectra for CHF$_3$ abatement.

Figure 4. Influence of H$_2$O addition on the FTIR spectra for CHF$_3$ abatement.

Figure 5. Destruction & Removal efficiency (DRE) for a mixture of CF$_4$ (5 sccm) and CHF$_3$ (50 sccm) measured as a function of power.

To demonstrate the feasibility of our device for the abatement of PFCs, the DREs for a mixture of CF$_4$ and CHF$_3$ are measured as a function of power. Experiment is performed under similar conditions.
previously tested for the RF ICP abatement system in SEMATECH [4]. The pressure is set to 120 mTorr, and the flow rates of CF$_4$, CHF$_3$, and H$_2$O are fixed at 5, 50, and 50 sccm. By consulting Xu et al.’s work [2], the DRE for a mixture of PFCs is defined as the sum of the output flow rate of C$_x$F$_y$ species divided by the input flow rate;

$$\text{DRE} = \left(1 - \frac{\sum_i f_i(C_xF_y)_{\text{out}}}{\sum_i f_i(C_xF_y)_{\text{in}}}\right) \times 100\%,$$

where $f_i$ is the flow of the $i$th C$_x$F$_y$ species in sccm.

The DREs measured as a function of power is plotted in Fig. 5. The DRE sharply increases by 800 W, and then an increasing intensity slows down with the power. A DRE of 90% is achieved at a power of 800 W. Although the DREs obtained in this work are slightly lower than those reported in other previous works, the main reason seems to be caused by the use of a larger reactor diameter in our case.

4. Conclusions

We demonstrate the feasibility of a low-pressure plasma reactor for the abatement of CF$_4$ and CHF$_3$. The device has a simple cylindrical shape, which allows for easy connection to pre-existing vacuum pipelines in the semiconductor industry. The abatement results obtained with AC and RF power supplies show that AC operation is better for the treatment of stable gases such as CF$_4$ than RF operation. CHF$_3$, which has weak bonds, is easily decomposed by plasmas, but undesirable CF$_4$ is produced as a product. The decomposition rate of CHF$_3$ is increased by the addition of O$_2$, which, however, does not suppress the CF$_4$ production. The addition of H$_2$O prevents CHF$_3$ fragments from recombining into CF$_4$, but the decomposition rate greatly decreases with the H$_2$O flow rate. At a power of 800 W, a DRE of 90% is achieved for a mixture of CF$_4$ (5 sccm) and CHF$_3$ (50 sccm) by adding H$_2$O (50 sccm).

References


