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SHORT COMMUNICATION

Decomposition of Tetrafluorocarbon in Dielectric Barrier Discharge Reactor

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Abstract−The decomposition of CF_4 in dielectric barrier discharge at atmospheric pressure was examined. The effect of O_2 contents, N_2 contents, and total flow rate on CF_4 conversion was experimentally investigated. The maximum conversion of CF_4 was about 87% at 5 kV, 15 kHz for the feed gas stream containing 5 sccm CF_4, 7.5 sccm O_2, and 187.5 sccm Ar. CO, CO_2, and COF_2 were the main products when O_2 was used as the additive gas. NO_x was produced when N_2 was used as the additive gas. The conversion of CF_4 was increased while the applied voltage and the residence time were increased. When nitrogen was added to argon as the diluent gas, the conversion of CF_4 was decreased with the increase of the nitrogen content.

Key words: Plasma, Barrier Discharge, CF_4, COF_2, Global Warming

In the semiconductor industry, perfluorocompounds (PFCs) such as CF_4, C_2F_6, SF_6, NF_3, CHF_3, and C_3F_8 are widely used for chemical vapor deposition chamber cleaning, plasma-assisted chamber cleaning processes, and dielectric film etching. These gases are mostly inert and extremely long-lived compounds that have the ability to stay in the atmosphere for very long times [Ravishankara et al., 1993]. PFCs are greenhouse or global warming gases since they are strong absorbers of infrared radiation and have a global worming potential (GWP) of up to 25,000 times that of CO_2. Despite the global warming potential, the PFCs usage in the semiconductor industry is steadily increasing and, therefore, the emission of PFCs must be tightly regulated in the near future.

The reduction of the PFC emission is approached by finding replacement gases, optimizing the process to minimize gas use, capturing and recycling of the PFCs in the effluent, and decomposing the PFCs by abatement process [Mohindra et al., 1997]. While process modification may be desirable from an environmental aspect, the complexity and diversity of the semiconductor manufacturing process make it difficult to be implemented and there are few alternative chemicals to replace PFCs. The capture and recycle approach is appropriate when large quantities of the specific PFCs are used. The abatement methods involve combustion, and thermal-chemical or plasma-assisted abatement. Combustion is the most developed technology, but the cost for effluent treatment is high. Thermal/chemical methods, such as catalyst application, are limited by the bed capacity. Thus, plasma-assisted abatement seems to be the most appropriate tool for reducing the PFC emission.

Plasma-assisted technologies, such as a surface wave plasma and a microwave plasma, have recently been developed [Hartz et al., 1998; Wofforo et al., 1999; Liao et al., 1999; Cho et al., 1998; Savinov et al., 1999; Jeong et al., 2001; Lee et al., 2001]. These papers are related with the effective conversion of perfluorocarbon using dielectric barrier discharge, which could generate effective electrons enough to fragment CF_4 molecule to form CFi radicals. The radicals react with the additive gas such as O_2 to form products that have low GWP.

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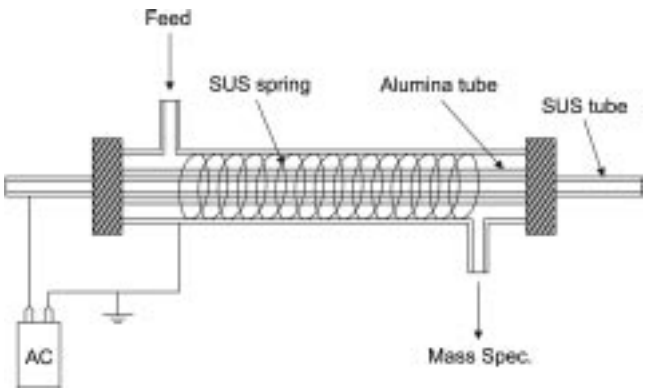

Fig. 1. Dielectric barrier discharge reactor.

The dielectric barrier discharge (DBD) reactor is shown in Fig. 1. The DBD reactor was made of stainless steel tube with an inner diameter of 16 mm. The inner electrode was stainless steel tube with an outer diameter of 4 mm and was inserted into an alumina tube, which was a dielectric material. The outer electrode was a stainless steel spring with an outer diameter of 1.2 mm and was welded on the inner wall of the DBD reactor. The feed gas was composed of CF_4, N_2, O_2, and Ar. The flow rates of gases were controlled with Mass Flow Controllers. A high frequency AC power supply was connected to the DBD reactor to generate plasma. The specification of AC power supply is represented in Table 1. Quadrupole mass spectrometer (Balzers, QMS 200) with Quadstar 421 software was used for the qualitative and quantitative analysis of the reactants and products.

Table 1. Specification of the AC power supply

Model	A1831, Auto electric, Korea
Frequency	0-15 kHz
Voltage	0-10 kV
Current	0-100 mA
Power	0-1 kW

The performance of the DBD reactor was described in terms of the conversion, which was defined by the fraction of CH_4 converted into the products. The additive gas was helpful to produce a lower GWP gas. Oxygen was used primarily to oxidize the carbon molecules. The effect of CF_4/O_2 ratio on CF_4 conversion was investigated. The CF_4/O_2 ratio was varied from 2 to 0.25. The conversion of CF_4 increased initially with the increase of O_2 content and showed the maximum value at CF_4/O_2=3/2 as shown in Fig. 2. The additional increase of O_2 content resulted in the decrease of the CF_4 conversion.

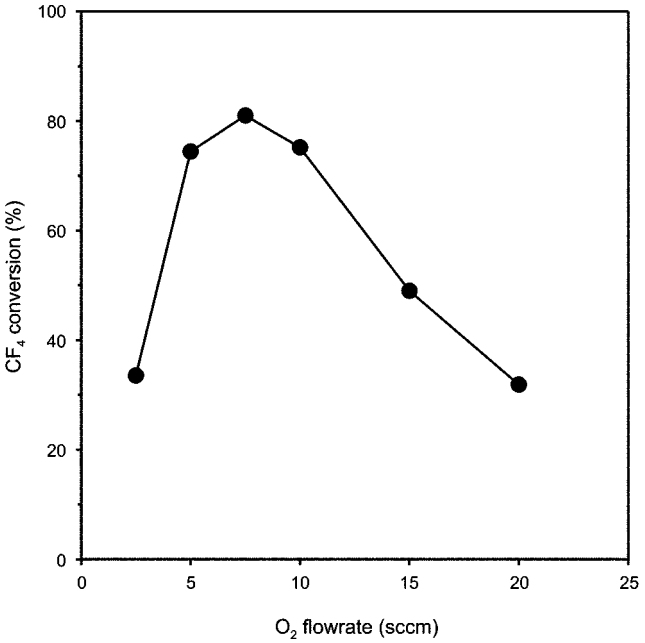

Fig. 2. Effect of CF_4/O_2 ratio on CF_4 conversion (total flowrate 200 sccm, CF_4 5 sccm, Ar as balance; applied voltage 5 kV, frequency 15 kHz).

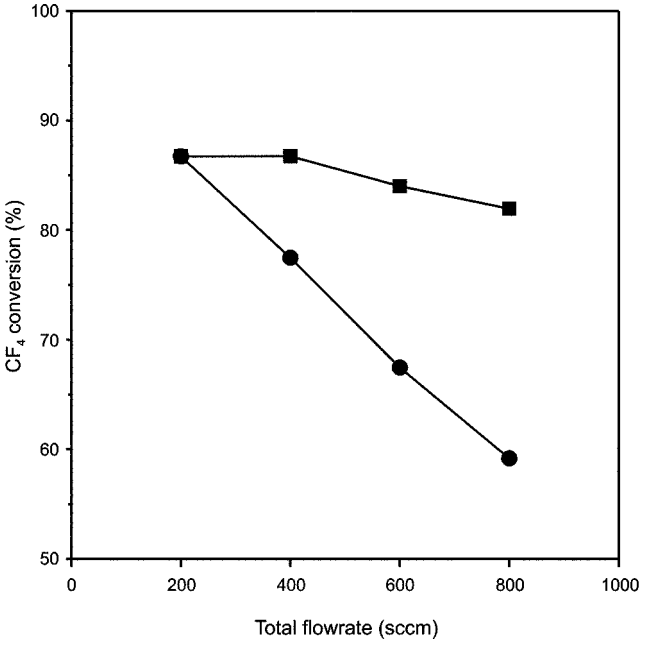

Fig. 3. Effect of residence time on CF_4 conversion (Applied voltage 5 kV, frequency 15 kHz; ■ $CF_4 : O_2 : Ar$=1 : 1.5 : 37.5, ● CF_4 5 sccm, O_2 7.5 sccm, Ar as balance).

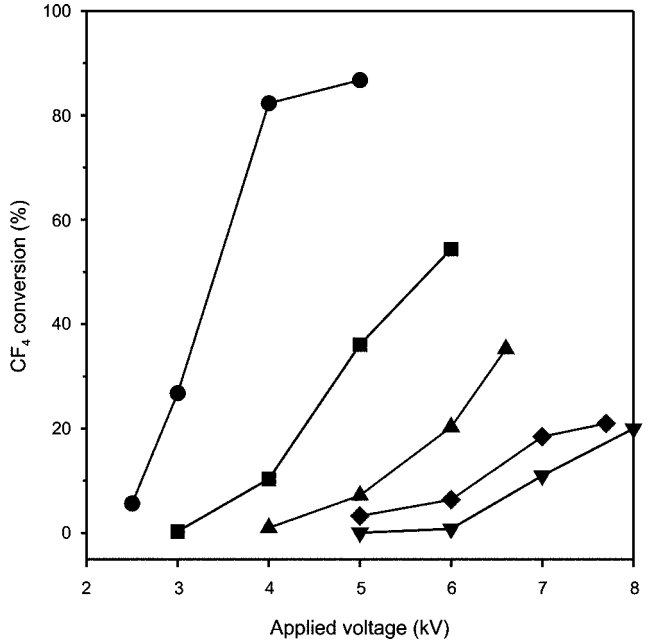

Fig. 4. Effect of N_2 concentration on CF_4 conversion (total flowrate 200 sccm, CF_4 5 sccm, O_2 7.5 sccm, Ar as balance, frequency 15 kHz; ● N_2 0 sccm, ■ N_2 40 sccm, ▲ N_2 87.5 sccm, ◆ N_2 170 sccm, ▼ N_2 187.5 sccm).

The effect of the total flow rate, which was related to the residence time of CF_4 in the reactor, was examined. Fig. 3 shows the changes of CF_4 conversion according to the various flow rates at the applied voltage of 5 kV and frequency of 15 kHz. The conversion of CF_4 decreased with the increase of total flow rate. The increase of flow rate reduced the residence time of CF_4 in the reactor, which resulted in reducing the chance of CF_4 molecules to collide with electrons which had enough energy to destroy the carbon-fluoride bond.

Fig. 4 shows the effect of applied voltage and N_2 concentration on CF_4 conversion at fixed experimental conditions at the total flow rate of 200 sccm, CF_4 flow rate of 5 sccm, the applied voltage of 2.5-8 kV, and the frequency of 15 kHz. CF_4 conversion decreased with the increase of N_2 concentration. Nitrogen seemed to prevent CF_4 molecules from reacting with electrons and absorb the plasma energy. With increasing the applied voltage, CF_4 conversion increased. The increase of applied voltage represented increasing the number of the effective electrons and the internal energy of system.

QMS spectra of the conversion of CF_4 are shown in Fig. 5. Fig. 5(a) shows the components in the feed stream containing CF_4, O_2, and Ar prior to applying the plasma. The baseline spectra of CF_4 were 12(C^+), 19(F^+), 31(CF^+), 50(CF_2^+), 69(CF_3^+), those of O_2 were 16(O^+), 32(O_2^+), and those of Ar were 20(Ar^{2+}), 40(Ar^+). When the plasma was applied, peak intensities of 16, 32, 50, and 69 decreased substantially and the peak intensities of 28(CO^+), 44(CO_2^+), 47(COF^+), and 66(COF_2^+) increased. Comparing Fig. 5(a) with 5(b), CO_2 was produced as a primary product, including a small amount of CO and COF_2.

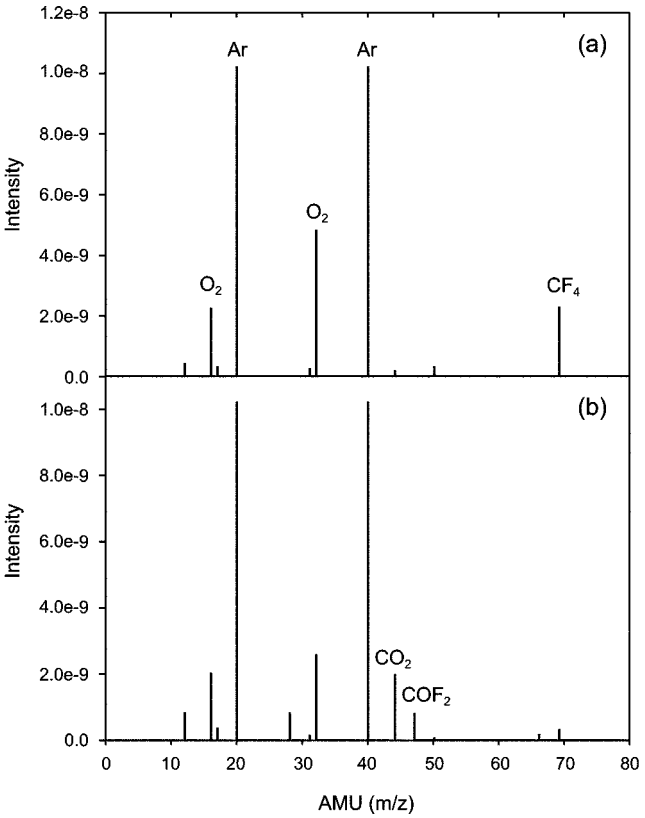

Fig. 5. QMS spectra at applied voltage 5 kV, frequency 15 kHz, CF_4 5 sccm, O_2 7.5 sccm, Ar 187.5 sccm; (a) plasma off (b) plasma on.

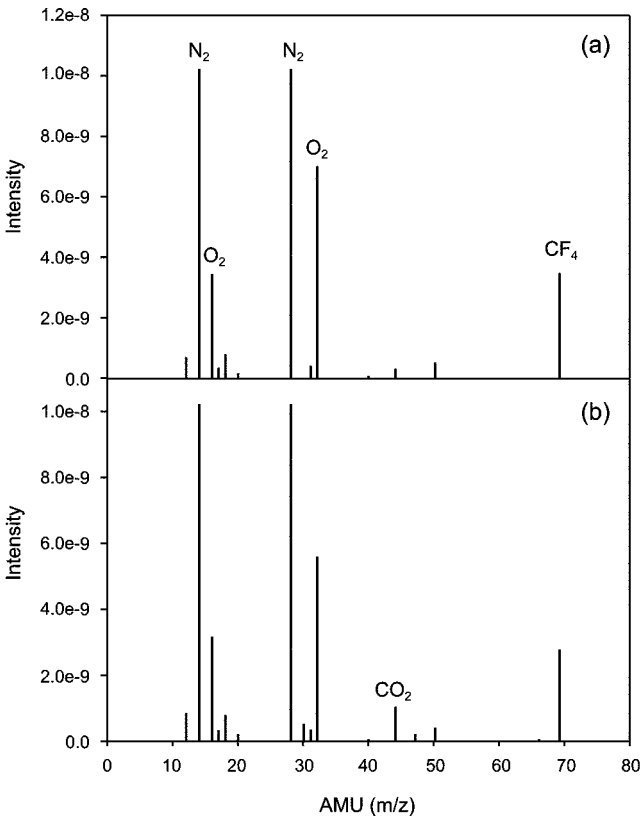

Fig. 6. QMS spectra at applied voltage 5 kV, frequency 15 kHz, CF_4 5 sccm, O_2 7.5 sccm, N_2 187.5 sccm; (a) plasma off (b) plasma on.

Fig. 6(a) shows the components in the feed stream containing CF_4, O_2, and N_2 prior to the plasma being applied. When the plasma was applied, peak intensities of 50, and 69 decreased and the peak intensities of 30(NO_x), 44(CO_2^+), and 47(COF^+) increased as shown in Fig. 6(b). CO_2 was mainly produced, and a small amount of CO, COF_2, and NO_x was generated. Analysis of QMS spectra showed that the major products in the DBD reactor were CO_2, CO, and COF_2, and NO_x was produced with N_2 as the additive gas. However, the conversion of CF_4 decreased dramatically when N_2 was added to the reactant stream. This is a very interesting phenomenon, which needs to be studied more to explain the effect of N_2 addition to the decomposition of CF_4.

The performance of CF_4 conversion in the dielectric barrier discharge at atmospheric pressure was studied. The dielectric barrier discharge could generate effective electrons enough to fragment CF_4 molecules to form CFi radicals that react with additive gases such as O_2. The effect of O_2 content, nitrogen content, and total flow rate on CF_4 conversion was experimentally investigated. The maximum conversion of CF_4 was about 87% at 5 kV, 15 kHz for the feed gas stream containing 5 sccm CF_4, 7.5 sccm O_2, and 187.5 sccm Ar, CO, CO_2, and COF_2 were produced as primary products with O_2 as the additive gas and NO_x was produced with N_2 as the additive gas. The conversion of CF_4 increased with applied voltage and residence time. When nitrogen was added to argon as the diluent gas, the conversion of CF_4 was decreased with the increase of the nitrogen content. From the above results, the dielectric barrier discharge was adequate for reducing the CF_4 emission.

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