

## Decomposition of Tetrafluorocarbon in Dielectric Barrier Discharge Reactor

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**Abstract**—The decomposition of CF<sub>4</sub> in dielectric barrier discharge at atmospheric pressure was examined. The effect of O<sub>2</sub> contents, N<sub>2</sub> contents, and total flow rate on CF<sub>4</sub> conversion was experimentally investigated. The maximum conversion of CF<sub>4</sub> was about 87% at 5 kV, 15 kHz for the feed gas stream containing 5 sccm CF<sub>4</sub>, 7.5 sccm O<sub>2</sub>, and 187.5 sccm Ar. CO, CO<sub>2</sub>, and COF<sub>2</sub> were the main products when O<sub>2</sub> was used as the additive gas. NO<sub>x</sub> was produced when N<sub>2</sub> was used as the additive gas. The conversion of CF<sub>4</sub> 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<sub>4</sub> was decreased with the increase of the nitrogen content.

Key words: Plasma, Barrier Discharge, CF<sub>4</sub>, COF<sub>2</sub>, Global Warming

In the semiconductor industry, perfluorocompounds (PFCs) such as CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, SF<sub>6</sub>, NF<sub>3</sub>, CHF<sub>3</sub>, and C<sub>3</sub>F<sub>8</sub> 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 warming potential (GWP) of up to 25,000 times that of CO<sub>2</sub>. 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<sub>4</sub> molecule to form CFi radicals. The radicals react with the additive gas such as O<sub>2</sub> to form products that have low GWP.

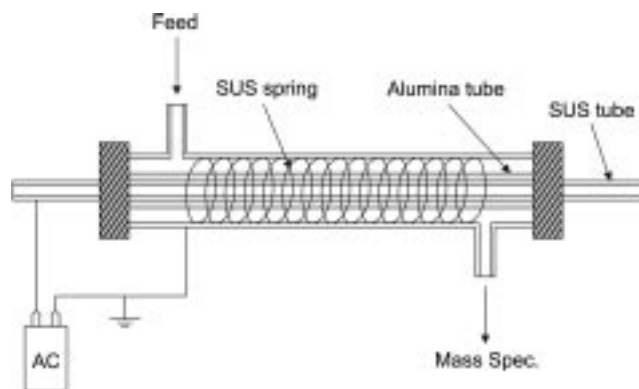


Fig. 1. Dielectric barrier discharge reactor.

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<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, 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

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The performance of the DBD reactor was described in terms of the conversion, which was defined by the fraction of  $\text{CH}_4$  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  $\text{CF}_4/\text{O}_2$  ratio on  $\text{CF}_4$  conversion was investigated. The  $\text{CF}_4/\text{O}_2$  ratio was varied from 2 to 0.25. The conversion of  $\text{CF}_4$  increased initially with the increase of  $\text{O}_2$  content and

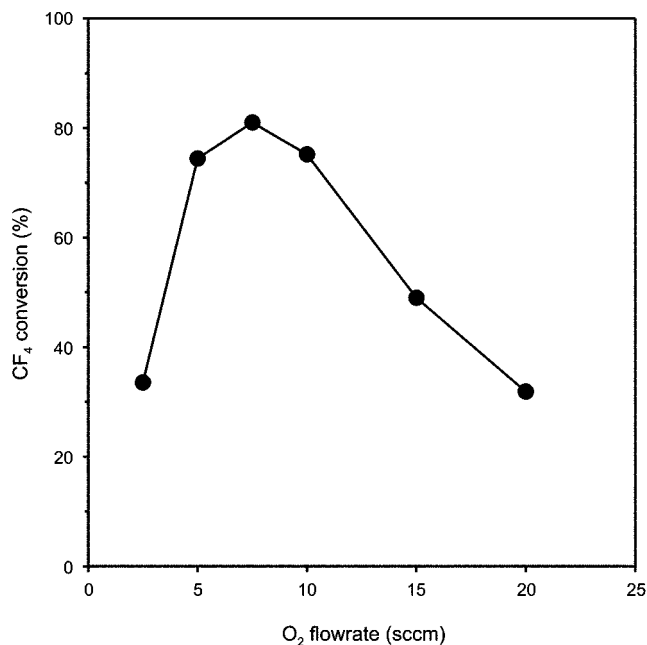


Fig. 2. Effect of  $\text{CF}_4/\text{O}_2$  ratio on  $\text{CF}_4$  conversion (total flowrate 200 sccm,  $\text{CF}_4$  5 sccm, Ar as balance; applied voltage 5 kV, frequency 15 kHz).

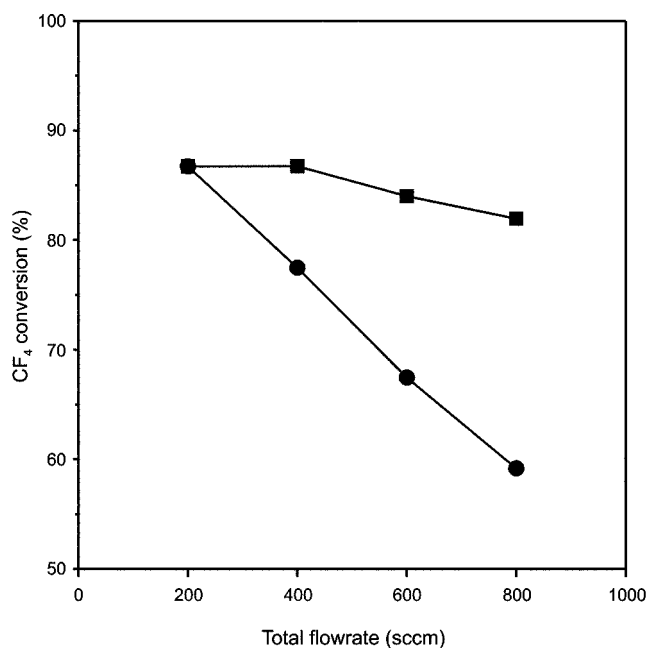


Fig. 3. Effect of residence time on  $\text{CF}_4$  conversion (Applied voltage 5 kV, frequency 15 kHz; ■  $\text{CF}_4 : \text{O}_2 : \text{Ar} = 1 : 1.5 : 37.5$ , ●  $\text{CF}_4$  5 sccm,  $\text{O}_2$  7.5 sccm, Ar as balance).

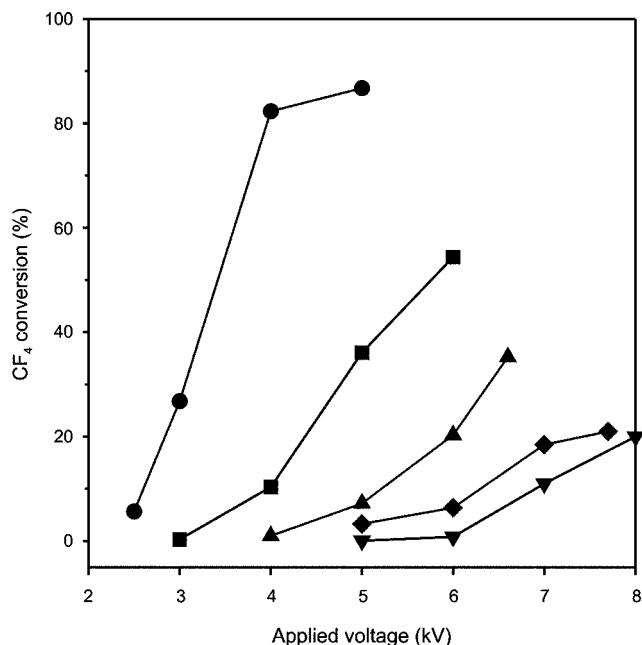


Fig. 4. Effect of  $\text{N}_2$  concentration on  $\text{CF}_4$  conversion (total flowrate 200 sccm,  $\text{CF}_4$  5 sccm,  $\text{O}_2$  7.5 sccm, Ar as balance, frequency 15 kHz; ●  $\text{N}_2$  0 sccm, ■  $\text{N}_2$  40 sccm, ▲  $\text{N}_2$  87.5 sccm, ◆  $\text{N}_2$  170 sccm, ▼  $\text{N}_2$  187.5 sccm).

showed the maximum value at  $\text{CF}_4/\text{O}_2 = 3/2$  as shown in Fig. 2. The additional increase of  $\text{O}_2$  content resulted in the decrease of the  $\text{CF}_4$  conversion.

The effect of the total flow rate, which was related to the residence time of  $\text{CF}_4$  in the reactor, was examined. Fig. 3 shows the changes of  $\text{CF}_4$  conversion according to the various flow rates at the applied voltage of 5 kV and frequency of 15 kHz. The conversion of  $\text{CF}_4$  decreased with the increase of total flow rate. The increase of flow rate reduced the residence time of  $\text{CF}_4$  in the reactor, which resulted in reducing the chance of  $\text{CF}_4$  molecules to collide with electrons which had enough energy to destroy the carbon-fluoride bond.

Fig. 4 shows the effect of applied voltage and  $\text{N}_2$  concentration on  $\text{CF}_4$  conversion at fixed experimental conditions at the total flow rate of 200 sccm,  $\text{CF}_4$  flow rate of 5 sccm, the applied voltage of 2.5–8 kV, and the frequency of 15 kHz.  $\text{CF}_4$  conversion decreased with the increase of  $\text{N}_2$  concentration. Nitrogen seemed to prevent  $\text{CF}_4$  molecules from reacting with electrons and absorb the plasma energy. With increasing the applied voltage,  $\text{CF}_4$  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  $\text{CF}_4$  are shown in Fig. 5. Fig. 5(a) shows the components in the feed stream containing  $\text{CF}_4$ ,  $\text{O}_2$ , and Ar prior to applying the plasma. The baseline spectra of  $\text{CF}_4$  were 12( $\text{C}^+$ ), 19( $\text{F}^+$ ), 31( $\text{CF}^+$ ), 50( $\text{CF}_2^+$ ), 69( $\text{CF}_3^+$ ), those of  $\text{O}_2$  were 16( $\text{O}^+$ ), 32( $\text{O}_2^+$ ), and those of Ar were 20( $\text{Ar}^{2+}$ ), 40( $\text{Ar}^+$ ). When the plasma was applied, peak intensities of 16, 32, 50, and 69 decreased substantially and the peak intensities of 28( $\text{CO}^+$ ), 44( $\text{CO}_2^+$ ), 47( $\text{COF}^+$ ), and 66( $\text{COF}_2^+$ ) increased. Comparing Fig. 5(a) with 5(b),  $\text{CO}_2$  was produced as a primary product, including a small amount of CO and  $\text{COF}_2$ .

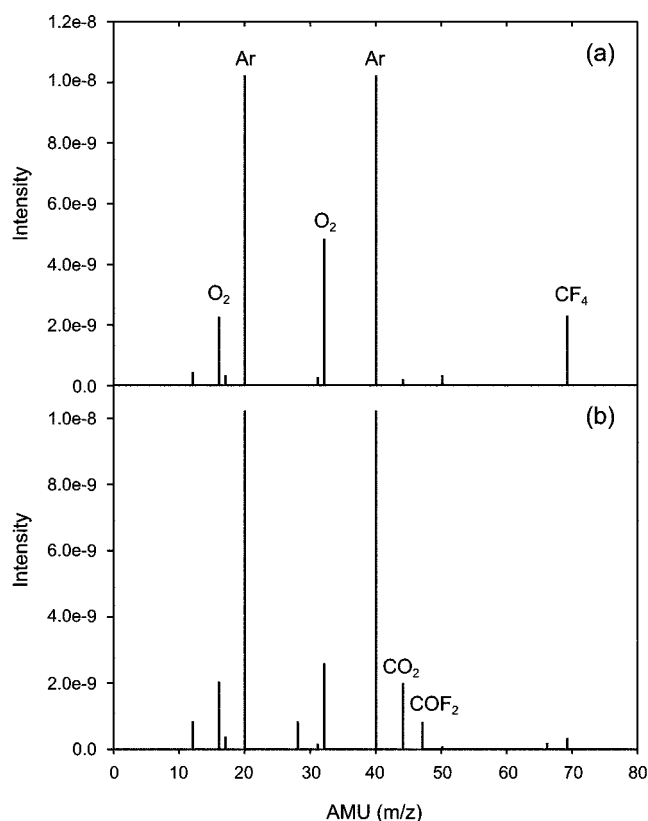


Fig. 5. QMS spectra at applied voltage 5 kV, frequency 15 kHz,  $\text{CF}_4$  5 sccm,  $\text{O}_2$  7.5 sccm, Ar 187.5 sccm; (a) plasma off (b) plasma on.

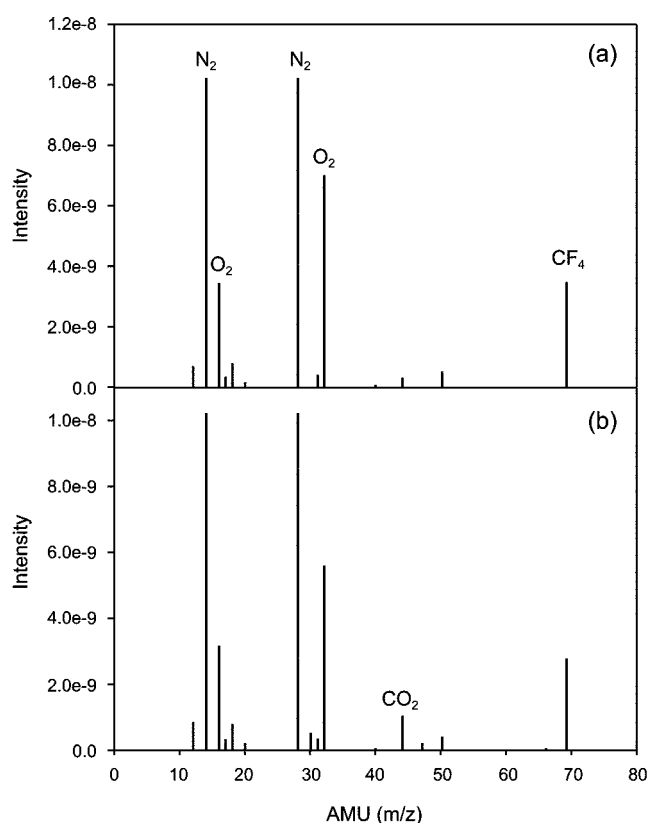


Fig. 6. QMS spectra at applied voltage 5 kV, frequency 15 kHz,  $\text{CF}_4$  5 sccm,  $\text{O}_2$  7.5 sccm,  $\text{N}_2$  187.5 sccm; (a) plasma off (b) plasma on.

Fig. 6(a) shows the components in the feed stream containing  $\text{CF}_4$ ,  $\text{O}_2$ , and  $\text{N}_2$  prior to the plasma being applied. When the plasma was applied, peak intensities of 50, and 69 decreased and the peak intensities of 30( $\text{NO}_x$ ), 44( $\text{CO}_2$ ), and 47( $\text{COF}^+$ ) increased as shown in Fig. 6(b).  $\text{CO}_2$  was mainly produced, and a small amount of CO,  $\text{COF}_2$ , and  $\text{NO}_x$  was generated. Analysis of QMS spectra showed that the major products in the DBD reactor were  $\text{CO}_2$ , CO, and  $\text{COF}_2$ , and  $\text{NO}_x$  was produced with  $\text{N}_2$  as the additive gas. However, the conversion of  $\text{CF}_4$  decreased dramatically when  $\text{N}_2$  was added to the reactant stream. This is a very interesting phenomenon, which needs to be studied more to explain the effect of  $\text{N}_2$  addition to the decomposition of  $\text{CF}_4$ .

The performance of  $\text{CF}_4$  conversion in the dielectric barrier discharge at atmospheric pressure was studied. The dielectric barrier discharge could generate effective electrons enough to fragment  $\text{CF}_4$  molecules to form  $\text{CF}_i$  radicals that react with additive gases such as  $\text{O}_2$ . The effect of  $\text{O}_2$  content, nitrogen content, and total flow rate on  $\text{CF}_4$  conversion was experimentally investigated. The maximum conversion of  $\text{CF}_4$  was about 87% at 5 kV, 15 kHz for the feed gas stream containing 5 sccm  $\text{CF}_4$ , 7.5 sccm  $\text{O}_2$ , and 187.5 sccm Ar. CO,  $\text{CO}_2$ , and  $\text{COF}_2$  were produced as primary products with  $\text{O}_2$  as the additive gas and  $\text{NO}_x$  was produced with  $\text{N}_2$  as the additive gas. The conversion of  $\text{CF}_4$  increased with applied voltage and residence time. When nitrogen was added to argon as the diluent gas, the conversion of  $\text{CF}_4$  was decreased with the increase of the nitrogen content. From the above results, the dielectric barrier discharge was adequate for reducing the  $\text{CF}_4$  emission.

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