Influence of O_2 on the CF_4 Decomposition by Atmospheric Microwave Plasma

H. D. Xie, B. Sun, X. M. Zhu, and Y. J. Liu
College of Environmental Science and Engineering, Dalian Maritime University, China

Abstract—CF_4 decomposition was investigated by atmospheric microwave plasma experimentally. The mechanisms of CF_4 decomposition assisting with O_2 were also investigated by emission spectrum analysis. The results indicated that the destruction and removal efficiency (DRE) of CF_4 increased firstly and then decreased with the increase of O_2 concentration. There was an optimal O_2 concentration (1000ml/m^3), the CF_4 DRE was up to 99 % when the microwave power achieved 1000 W for CF_4 2000 ml/m^3 with argon as a carrier gas. The results of emission spectrum analysis indicated that the CF_4 decomposition highly depended on the electron collision in plasma, and O radicals was the assistance in the later reaction, to further oxidize CF_i to CO_2. For achieving the best DRE of CF_4 with O_2 as an additive gas, the most important key factor was to achieve optimum concentration of O_2 in inlet gas. More or less concentration of O_2 was both unsuitable for the CF_4 decomposition.

Keywords—Microwave plasma, CF_4 decomposition, Oxygen, Emission spectrum

I. Introduction

Perfluorocompounds (PFCs) are widely used in the chamber cleaning of chemical vapor deposition (CVD) and dielectric film etching processes in modern industry [1]. Because of their strong absorption of infrared radiation and long atmospheric lifetimes which cause the global warming effect, the PFCs emitted from industry need to be removed efficiently. CF_4 is one of the most stable PFCs whose decomposition is extremely difficult using traditional abatement technology. At atmospheric pressure, microwave plasma has homogeneous high electron density and therefore appears much more efficiency for the destruction of CF_4 [2]. The destruction and removal efficiency of CF_4 was 98 % using microwave power of 1.8 kW at total gas flow rate of 20 L/min, the addition of water to the reactor could promote the DRE of CF_4 [2]. However, the increase of water molar ratio above 3.5 (H_2O/C_2F_6>3.5/1) was found to affect the plasma stability. Therefore, the addition of oxygen to the gas stream was attempted, it was found that the addition of O_2 (C_2F_6/O_2=2/1) improved DRE of all species present in the gas mixture [3]. Hong et al. [4] used microwave plasma to decompose CF_4, 98.23 % of CF_4 contaminants were abated with O_2 addition. Tsai et al. [5] reported that the DRE of CF_4 was only 12.9 % using microwave plasma (CF_4/N_2) with no additives because of the rapid recombination of CF_4. With the addition of O_2, CF_4 DRE elevated and reached 84.4~89.8 % at inlet O_2/CF_4 ratio = 1~5, respectively, at 0.8 kW [5]. Because O or O atoms could react with CF_4 and its fragments, such as CF_2, then removing C atoms by forming CO_2, CO, and COF_2, inhibited the recombination of CF_4 [5]. O_2 addition could also enhance the SF_6 decomposition effectively in plasma reactor [6]. O_2 as an additive gas was widely used to enhance PFCs decomposition in plasma process [7-9], all of these studies reported that O_2 as an additive gas could promote the decomposition of PFCs, it was because O_2 could convert to O radical in plasma and cause the oxidation of PFCs to CO_2. However, the decomposition of PFCs in plasma depends on two major mechanisms, including direct electrons dissociation and reactions with O radicals which are generated from O_2 in plasma. The mechanisms of these processes need to be studied. A variety of radicals associated with CF_4 decomposition should be investigated. Emission optical spectroscopy is widely used on diagnosis of radicals in plasma [10-13]. In this study, we present that the microwave argon plasma operated at atmospheric pressure. The DRE of CF_4 with O_2 as an additive gas was investigated. The influence of O_2 concentration on the radicals' density in microwave plasma was investigated by the emission optical spectrum analysis. The mechanisms of CF_4 decomposition assisted with O_2 were studied.

Corresponding author: B. Sun
e-mail address: sunb88@newmail.dlmu.edu.cn

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II. Experiment

A schematic diagram of the experimental system was shown in Fig.1. The microwave system consisted of a microwave generator (IBF, GEM) with variable power output from 200 to 2000 W, isolator and power monitor. Microwave transported through the wave guide and produced plasma at atmospheric pressure in a quartz tube (inner diameter is 13 mm). Carbontetrafluoride (CF4 > 99.7 %), oxygen (O_2 > 99 %) and Argon (Ar > 99.9 %) were controlled by Mass flow controllers (MFC) respectively to achieve the desired concentration of CF_4 and O_2 in argon gas stream. The conditioned gas was introduced into the plasma reactor, and the gas after reaction was neutralized in wet scrubber. The gas mixtures before and after reaction were monitored online

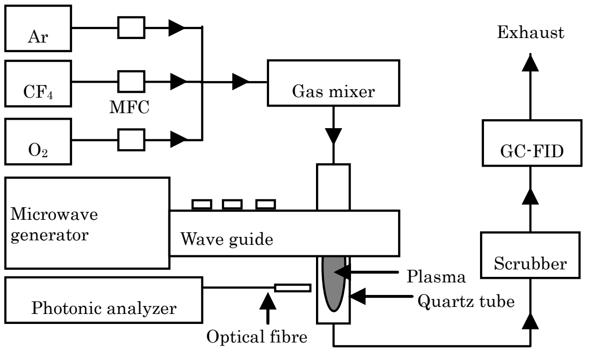

Fig. 1. Schematic diagram of experiment.

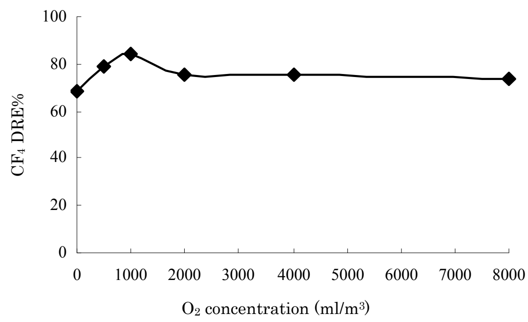

Fig. 2. Effect of O_2 concentration on DRE of CF_4.

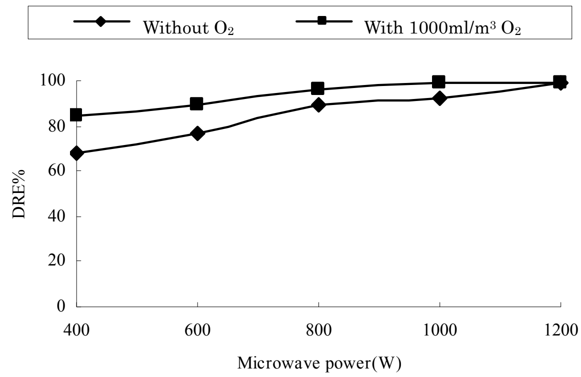

Fig. 3. CF_4 DRE% with 1000 ml/m^3 O_2 compared with that without O_2.

by gas chromatography (Shimadzu GC-2010; capillary column, molecular sieve 13X; FID). Radicals in plasma were monitored using the multi-channel photonic analyzer (PMA-11, Hamamatsu).The destruction and removal efficiency (DRE) was calculated:

$$DRE \quad (\%) \quad = \frac{C_{in} - C_{out}}{C_{in}} \times 100$$

Where C_{in} is the initial concentration of CF_4 input reactor and C_{out} is its final concentration after the plasma treatment out of the reactor.

III. Results and discussions

A. *Effect of O_2 concentration on the DRE of CF_4*

To find an optimal condition of the O_2 addition, CF_4 DRE for various O_2 concentrations have been investigated. The total gas flow rate was 4 L/min containing Ar, CF_4 and O_2. The concentration of CF_4 was 2000 ml/m^3. The concentration of O_2 was ranged from 0 to 8000 ml/m^3. The results showed that there was an optimal O_2 concentration for maximizing the CF_4 removal efficiency. As shown in Fig. 2. The DRE of CF_4 increased firstly and then decreased with increasing of O_2 concentration. The highest DRE of CF_4 for 400 W was 83.6 % with O_2 concentration of 1000 ml/m^3, and the energy density was 30 kJ/L. Kim et al. [14] investigated the role of the O_2 concentration on CF_4 removal using DBD and remarked that the removal efficiency also reached a maximum (32 %) for an O_2 concentration around 500-1000 ml/m^3, and the energy density was 45 kJ/L.

At the condition of various microwave power, CF_4 removal test with 1000 ml/m^3 O_2 addition was performed, in contrast to that without O_2 addition, as shown in Fig. 3. The DRE of CF_4 with 1000 ml/m^3 O_2 addition was higher than that without O_2 addition with any given inputting power. The DRE of CF_4 with 1000 ml/m^3 O_2 addition was up to 99 % when the microwave power was up to 1000 W.

The CF_4 decomposition depended on the O_2 concentration and the microwave power. The primary step of converting CF_4 to CF_i (including CF_3, CF_2, and CF) radicals was electrons collision, as shown in reactions (1-6),

$$e + CF_4 \rightarrow CF_3 + F^- \qquad (1)$$
$$e + CF_3 \rightarrow CF_2 + F^- \qquad (2)$$
$$e + CF_4 \rightarrow CF_2 + 2F + e \qquad (3)$$
$$e + CF_3 \rightarrow CF + 2F + e \qquad (4)$$
$$e + CF_4 \rightarrow CF + F + F_2 + e \qquad (5)$$
$$e + CF_2 \rightarrow CF + F + e \qquad (6)$$

On the other hand, the diatomic oxygen ions or molecules, which are ionized in the microwave plasma with electrons collision, undergo dissociative recombination or attachment to create oxygen radicals [4], as shown in reactions (7-8).

$$O_2 + e \rightarrow O + O^- \qquad (7)$$
$$O_2^+ + e \rightarrow O + O \qquad (8)$$

Then the resulting CF_i radicals react with O radicals to form CO_2, COF_2 and CO, as shown in reactions (9-14).

$$CF_3 + O \rightarrow COF_2 + F \qquad (9)$$
$$CF_2 + O \rightarrow CFO + F \qquad (10)$$
$$CFO + O \rightarrow CO_2 + F \qquad (11)$$
$$CF_2 + O_2 \rightarrow COF_2 + O \qquad (12)$$
$$CF + O \rightarrow CO + F \qquad (13)$$
$$COF_2 + O \rightarrow CO_2 + F_2 \qquad (14)$$

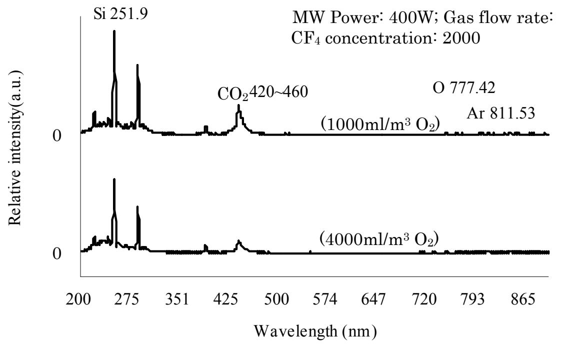

Fig. 4. The emission spectra of Ar/CF_4 plasma with 1000 ml/m^3 O_2 and 4000 ml/m^3 O_2.

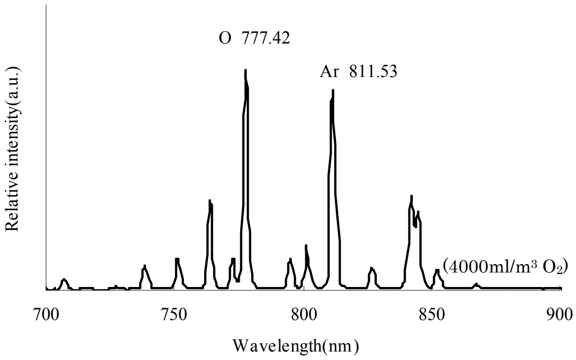

Fig. 5. The zoom of the spectrum (700-900 nm) in Fig. 4.

The O_2 molecules adsorbed the electrons to excite and ionize as reactions (7-8), while the CF_4 conversion highly depended on electrons collision as reactions (1-6) at the same time. For inputting given microwave power 400 W, more than 1000 ml/m^3 O_2 concentration meant less electrons was obtained by CF_4 molecule and less CF_i radicals formed as reactions (1-6). In addition, extreme higher inlet O_2 concentration would make for instability of plasma. So it leaded to lower DRE of CF_4. For these reasons, optimum O_2 concentration was essential for the best destruction and remove efficient of CF_4, lower and higher concentration of O_2 were both unsuitable to the decomposition of CF_4.

B. Emission spectroscopy analysis

Emission spectra of Ar/CF_4 plasma with 1000 ml/m^3 and 4000 ml/m^3 O_2 were shown in Fig. 4. As the O and Ar peaks in Fig. 4 were not visible, a zoom of this region of the spectrum was shown in Fig. 5. The peak with the wavelength at 811.53 nm indicated atomic argon, Ar^*, and the peak with the wavelength at 777.42 nm indicated atomic oxygen, O^*. The peaks of CO_2 appeared in the region of 421-461 nm and the peak of Si appeared at near 250 nm when CF_4 used. As Si peak was not appeared without CF_4 adding, the Si peak appeared due to etching of an inner wall quartz tube by F, which was generated by CF_4 decomposition, so the density of Si can denote the density of F. Similar results have been described by T. Kuroki et al. [1], for the optical emission spectrum analysis, with CF and O, they also observed the peaks of O, and Si.

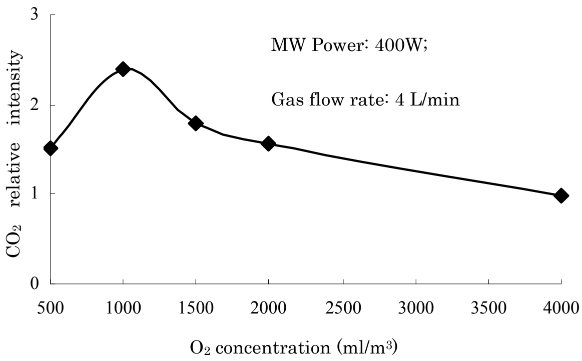

Fig. 6. Effect of O_2 concentration on the CO_2 intensity.

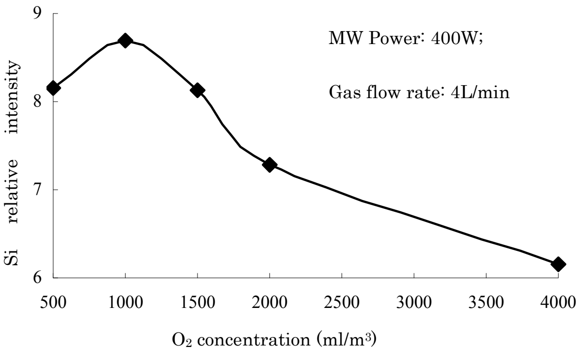

Fig. 7. Effect of O_2 concentration on the Si intensity

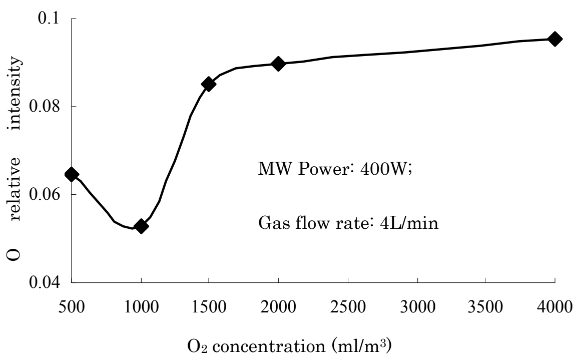

Fig. 8. Effect of O_2 concentration on the O radicals intensity

The relative intensity of CO_2, Si, and O with the increase of O_2 concentration was shown in Fig. 6, Fig. 7 and Fig. 8, respectively.

The CO_2 and Si had the maximum intensity and the O radicals had the minimum intensity with 1000 ml/m^3 O_2. It is might be the following reasons: When the highest DRE of CF_4 was achieved with 1000 ml/L O_2 addition, the most of CF_4 was decomposed. The more CF_4 decomposed the more CO_2 and F generated. On the other hand, the O radicals combined with C to convert to CO_2, the more CF_4 decomposed and CO_2 generated, the more O radicals consumed. So in the reaction (15):

$$CF_i + O \rightarrow CO_2 + F \quad (15)$$

CO_2 and F as resultant had the highest intensity and O radicals as reactant had the lowest intensity when the highest DRE of CF_4 achieved. When the O_2 concentration was more than 1000 ml/m^3, the DRE of CF_4 was decreased, the density of CO_2 and Si was also decreased. The density of O radicals was increased with the increase of O_2 concentration. It is might be the following reasons: O_2 converted to O radicals with electron collision in plasma, resulted in no enough electrons for the reactions (1-6). If the first step reactions (1-6) had not occurred availability, there was not enough CF_i produced, so there was no CO_2 and F produced in later reactions (9-14). The increase of O radicals is because that the O radicals were more and more generated as reactions (7-8) with the increase of O_2 concentration, meanwhile there was not enough CF_i to react with O radicals, so the O radicals accumulated to more and more high density. The results indicated that CF_4 decomposition highly depended on the electron collision as described in reactions (1-6) in plasma, O radicals was the assistance in later reaction, to further oxidize CF_i to CO_2. In the processing of O radicals formation, O_2 absorbed much of electrons, which was adverse to CF_4 convert to CF_i by electron collision. For achieving the best DRE of CF_4 with O_2 as an additive gas, the most important key factor was to have an optimum concentration of O_2 in gas stream. More or less O_2 adding was both unsuitable to CF_4 decomposition.

V. CONCLUSION

The atmospheric microwave plasma was successfully applied to CF_4 decomposition with O_2 as an additive gas. The influence of O_2 on the CF_4 decomposition was investigated by diagnosis of radicals in plasma. As results, the DRE of CF_4 increased firstly and then decreased with increase of O_2 concentration. The highest DRE of CF_4 was 83.6 % with O_2 concentration of 1000 ml/m^3 using the 400W microwave power. The DRE was up to 99% when the microwave power over 1000 W. CF_4 decomposition highly depended on the electron collision. O radicals were the assistance in later reaction, for CF_i to be oxidized into CO_2. During the formation of O radicals, electron was captured by O_2, which decreased collision probability between CF_4 molecule and electron. There might be a competition between the increments of O radicals to react with CF_i fragments and the decrements of electron for collision with CF_4 molecule. For decomposing CF_4 in microwave plasma with O_2 as an additive gas, the most important key was to control the concentration of O_2 in gas stream. The optimum concentration of O_2 was essential to achieve the highest DRE of CF_4.

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