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Abatement of perfluorocompounds with microwave plasma in atmospheric pressure environment

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ABSTRACT

Perfluorocompounds emitted by the semiconductor industry are global warming gases. These gases need to be removed efficiently because of their strong absorption of infrared radiation and long atmospheric lifetimes which cause the global warming effect. In this study, microwave argon plasma operating at atmospheric pressure was investigated experimentally for various operating conditions including microwave power, total gas flow rate, initial concentration, and additive gas. The mechanisms of perfluorocompounds decomposition were studied by the plasma emission spectrum. Under the optimum condition, the destruction and removal efficiency of CF_4 could reach up to 98.4%. The emission spectrum analysis indicated that the existence of the O or OH radicals could enhance the CF_4 decomposition by adding suitable volume of O_2 or H_2O. The mechanisms of CF_4 decomposition are that the electron, O and OH radicals all associated with CF_4 conversion, it has the sequence that enough effective electrons reacted with CF_4 to form CF_i radicals, O and OH radicals further reacted with CF_i radicals to convert CF_4 into CO_2 and HF.

1. Introduction

Recently, the emission of global warming gases has become an important environmental problem all over the world. The original greenhouse gases in atmosphere include water vapor, carbon dioxide, methane, nitrous oxide, and ozone. And the man-made greenhouse gases include chlorofluorocarbons, hydrofluorocarbons and perfluorocompounds, which are generated in a variety of industrial processes. The perfluorocompounds including CF_4, C_2F_6 and C_3F_8, are widely used as etching and cleaning gases in semiconductor manufacturing processes. These gases have been identified as potential global warming gases, because of their strong infrared absorption and long atmospheric lifetimes, which can be longer than 50,000 years for CF_4. As shown in Table 1, the global warming potentials (GWP_{100}) and atmospheric lifetime of perfluorocompounds are many times higher than those of the original greenhouse gases, such as CO_2, CH_4, and N_2O.

There are four main routes to reduce the perfluorocompounds emission: the application alternative chemical compounds, process optimization, recycle, and abatement. However, there are some obstacles to the implementation of the first three routes considering the cost and technology of the semiconductor manufacturing. Thus, the abatement method seems to be the most cost-effective solution [1].

The abatement technologies of perfluorocompounds emissions from semiconductor industry include catalytic decomposition, combustion, and plasma processes. The catalytic oxidation method can remove perfluorocompounds efficiently. However, since the solid reagents are depleted with reaction time, the packed reactant bed should be replaced frequently, which makes this process inadequate for treating a large flux of perfluorocompounds gases [2,3]. A simulated high temperature air combustion furnace had been used to decompose CF_4, but the result showed that the destruction and removal efficiency of CF_4 was only 16%, with the problem of generating NO_x [4]. In addition, the cost associated with fuels was expensive in combustion processing.

Recently, the plasma technologies used in the abatement of perfluorocompounds include dielectric barrier discharges, inductively coupled plasma and microwave plasma [5–15]. Microwave plasma has high electron temperature and high electron density which is more efficient to perfluorocompounds abatement than other plasma technology. Wofford et al. [11] carried out CF_4 decomposition using atmospheric pressure microwave plasma with 1.95 kW of microwave power at flow rate of 0.3 L/min, and achieved 99% removal efficiency of CF_4. Microwave plasma, used to decompose perfluorocompounds, was also described by Radoiu [12], and 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. Although lots of efforts have been done on perfluorocompounds decomposition by microwave plasma and deduced the reactions of perfluorocompounds decomposition [11–15], the mechanisms of decomposition and the active radicals generated in microwave plasma need to be

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Table 1
Global warming potentials (100 years horizon) and atmospheric lifetime of some greenhouse gases.

Greenhouse gases	GWP_{100}	Atmospheric lifetime (year)
CO_2	1	5–200
CH_4	23	12
N_2O	296	120
CF_4	5700	50,000
C_2F_6	11,900	10,000

further investigated in detail. In this paper, the characteristics of microwave plasma operated at atmospheric pressure were investigated for the destruction and removal efficiency of CF_4. Specifically, the active radicals in plasma were identified by the emission spectrum, and the reaction mechanisms of the active radicals were discussed for the removal of CF_4. The destruction and removal efficiency of CF_4 for various operating conditions including microwave power, total flow rate, initial CF_4 concentration, and additive gas was also investigated.

2. Materials and methods

A schematic diagram of the experimental system is shown in Fig. 1. The microwave system consisted of wave guide and a microwave generator (IBF, GEM) with variable power output from 200 to 2000 W. The microwave transported through the wave guide and the plasma could be generated in a quartz tube (diameter 15 cm) at atmospheric pressure. The flow rate of carbon tetrafluoride (CF_4, >99.7%), argon (Ar, >99.9%) and oxygen (O_2, >99%) were controlled by mass flow controllers (MFC). The flux passed through a mixing reactor where water vapor was added by an exact minim flux pump controller and a water vapor generator. The conditioned gas was then introduced into the plasma reactor, and the gas after reaction was neutralized through a wet scrubber. The gas mixtures before and after reaction was monitored online by the gas chromatography (GC-2010,SHIMADZU). The radicals in plasma were identified by the multi-channel photonic analyzer (PMA-11, HAMAMATSU). The destruction and removal efficiency (DRE) of CF_4 was calculated from:

$$\mathrm{DRE}\,(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (1)$$

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.

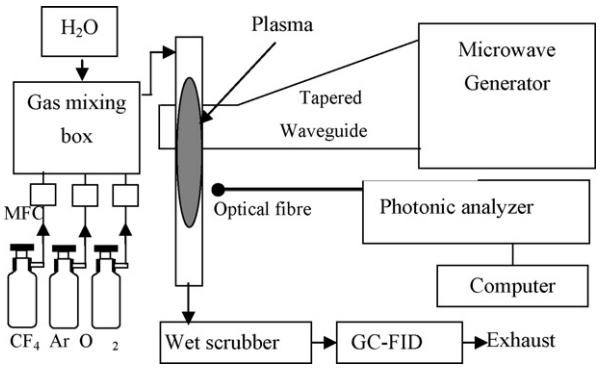

Fig. 1. Schematic diagram of the experimental system.

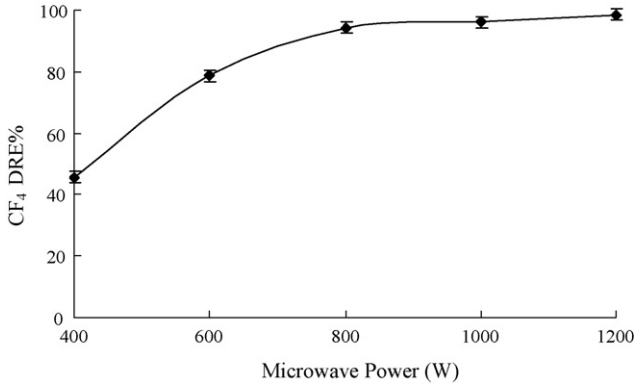

Fig. 2. Effect of microwave power on the DRE of CF_4. Total flow rate is 4 L/min; CF_4 concentration is 5000 mL/m^3.

3. Results and discussion

3.1. Effect of microwave power on the DRE of CF_4

Fig. 2 shows the DRE of CF_4 as a function of microwave power. The destruction efficiency increased with the increase of microwave power. It is considered that the CF_4 decomposition mainly depend on its collision with energetic electrons, the CF_i radicals can be generated by electron collision as described in reaction (1)–(6):

$$e + CF_4 \rightarrow CF_3 + F^- \quad (1)$$

$$e + CF_3 \rightarrow CF_2 + F^- \quad (2)$$

$$e + CF_4 \rightarrow CF_2 + 2F + e \quad (3)$$

$$e + CF_3 \rightarrow CF + 2F + e \quad (4)$$

$$e + CF_4 \rightarrow CF + F + F_2 + e \quad (5)$$

$$e + CF_2 \rightarrow CF + F + e \quad (6)$$

$$R = k[e]^x[CF_4]^y \quad (7)$$

As described in reaction (7), increasing the electrons density could increase the reaction rate. The electron density increased with the increase of microwave power, as shown in Fig. 3 (The electron density was calculated by Stark widths of the neutral argon spectral lines in 4s–4p transitions). Therefore, increasing microwave power can increase the electron density, resulting in the increase of the CF_4 decomposition. However, it can be found from Fig. 3 that the electron density at 1000 W is smaller than that at 800 W. It may be the reason of the increase of electron temperature. In our experiment, the electron density and the electron temperature were measured simultaneously. It had been found they were all influenced by the

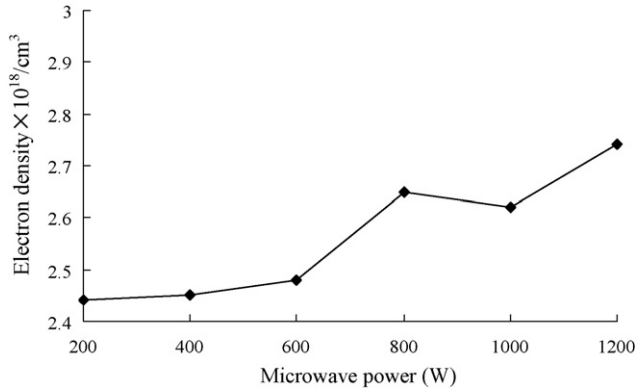

Fig. 3. Effect of microwave power on electron number density.

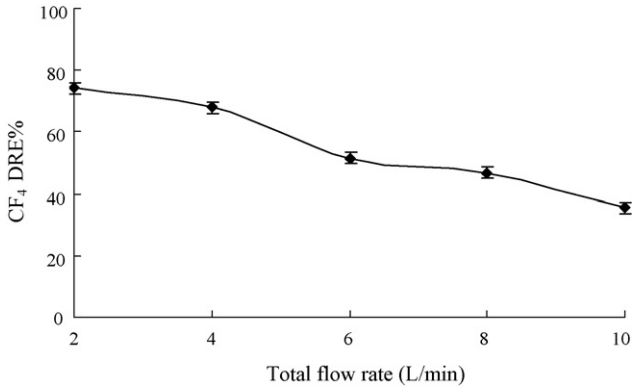

Fig. 4. Effect of total flow rate on DRE of CF_4.

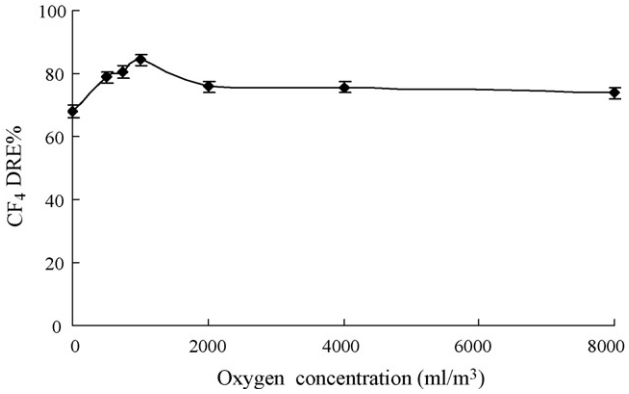

Fig. 6. Effect of O_2 as an additive gas on DRE of CF_4.

microwave power. The variety of electron temperature (calculated by Boltzmann Plot Method) was not obvious (4100–4350 K) when the microwave power increased from 200 to 800 W. However, the electron temperature (4776 K) at 1000 W was much higher than that (4139 K) of 800 W. It might be that the power was mainly used on increasing the temperature of electrons when the power up to 1000 W. It means that the power of 1000 W enhance the energy of each electron, and has little effect on increasing electron density.

3.2. Effect of total flow rate on DRE of CF_4

Dependence of CF_4 destruction on the total flow rate ranged from 2 to 10 L/min, as shown in Fig. 4. The applied microwave power was controlled at 0.4 kW. The CF_4 initial concentration was 2000 mL/m^3. The DRE of CF_4 increased with decrease of total flow rate. This implied that the DRE of CF_4 was determined by the residence time of the reactant in the plasma reactor. Increasing the residence time in reactor would increase the probability of collision between CF_4 molecules and electrons, resulting in a higher DRE of CF_4.

3.3. Effect of CF_4 initial concentration in the inlet gas on DRE of CF_4

The dependence of DRE of CF_4 on CF_4 initial concentration in the inlet gas was shown in Fig. 5. The total flow rate was 4 L/min and the applied microwave power was 0.4 kW. The initial concentration was ranged from 1000 to 5000 mL/m^3. The DRE of CF_4 decreased with increasing of CF_4 concentration, and the electron concentration relative to the CF_4 concentration decreased with the increase of CF_4 concentration with the same microwave power. Higher initial

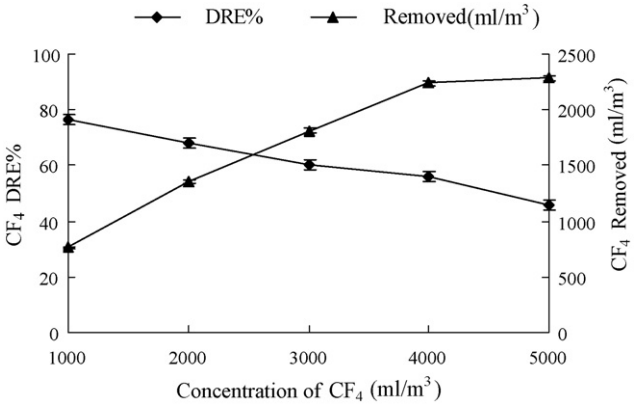

Fig. 5. Effect of CF_4 initial concentration on DRE of CF_4.

concentration of CF_4 meant less energy was available for decomposing each CF_4 molecule, resulting in lower DRE of CF_4. The absolute value of decomposed CF_4 molecules increased with the increase of initial concentration of CF_4. This result indicated that the effect of decreasing electrons density was greater than that of increasing CF_4 concentration on the DRE of CF_4, namely "x" is greater than "y" in reaction $R = k[e]^x[CF_4]^y$.

3.4. Effect of O_2 concentration on DRE of CF_4

The O radicals are essential for converting CF_i to CO_2. Adding O_2 in the inlet gas will generate O radicals in plasma, so that it affects the CF_4 decomposition. The effect of concentration of O_2 in the inlet gas on DRE of CF_4 is shown in Fig. 6. The total flow rate was 4 L/min, the concentration of CF_4 was 2000 mL/m^3, and the applied microwave power was 0.4 kW. The results indicated that the DRE of CF_4 increased firstly and then decreased with further increasing the concentration of O_2. The highest DRE of CF_4 was achieved with the O_2 concentration of 1000 mL/m^3. A variety of radicals in $CF_4/O_2/Ar$ plasma were diagnosed by the emission spectrum, as shown in Fig. 7. Fig. 7(a) shows the O_2 (1000 mL/m^3) with argon as carrier gas without CF_4; Fig. 7(b) shows the O_2 (1000 mL/m^3) and CF_4 (2000 mL/m^3) with argon as carrier gas. The peak with the wavelength at 763.51 nm indicated atomic argon (Ar^*). 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 atom appeared at near 250 nm when CF_4 and O_2 were used. The presence of Si peak was due to the etching of an inner wall of quartz tube by F, which was produced by CF_4 decomposition.

As the existence of O_2, the effective electrons reacted with CF_4 and O_2 to form CF_i and O radicals in plasma, and the O radicals further reacted with CF_i radicals to convert CF_4 into CO_2. These processes can be described by reaction (8)–(13):

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

$$CF_3 + O \rightarrow COF_2 + F; \quad (9)$$

$$CF_2 + O \rightarrow CFO + F; \quad (10)$$

$$CFO + O \rightarrow CO_2 + F; \quad (11)$$

$$CF + O \rightarrow CO + F; \quad (12)$$

$$COF_2 + O \rightarrow CO_2 + F_2 \quad (13)$$

The O radicals' density dependent on O_2 concentration in argon plasma in the process of CF_4 composition was shown in Fig. 8. The highest DRE of CF_4 had been achieved, and the O radicals had the minimum number intensity when the concentration of O_2 was

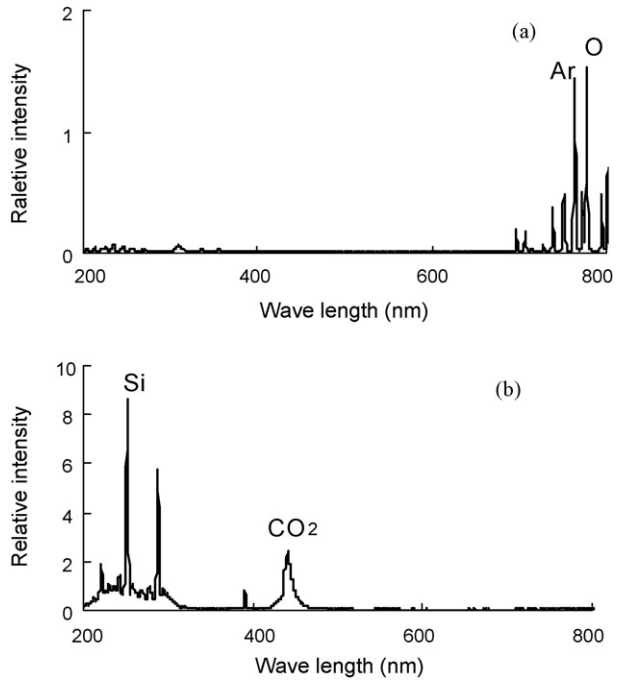

Fig. 7. Spectra of microwave plasma emission spectrum. (a) Ar with O_2; (b) Ar with O_2 and CF_4.

1000 mL/m^3. It could be described as the follow reaction:

$$CF_i + O \rightarrow CO_2 + F \quad (14)$$

$$k = [CO_2][F]/[CF_i][O] \quad (15)$$

When the highest DRE of CF_4 had been achieved with O_2 concentration of 1000 mL/m^3, the maximum reaction rate was got, the CO_2 and F as resultant reached the highest number intensity and O radicals as reactant got to the lowest number intensity. With further increasing concentration of O_2, the DRE of CF_4 decreased gradually, and the density of CO_2 and Si decreased (not shown in the figure). The O radicals increased with the increase of O_2. It is because that O_2 convert to O radicals with electron collision during plasma discharge, resulting in no enough electrons for the reactions (1)–(6). If in the first step reactions (1)–(6) have not occurred availability, there is not enough CF_i produced. So there is no CO_2 and F produced in the later reactions (9)–(13), although more O radicals produced in reaction (8) with the increase of O_2 concentration. The result indicated that CF_4 decomposition highly depended on the electron collision as described in reactions (1)–(6). O radicals were the assistance in later reaction, for CF_i to be oxidized into CO_2.

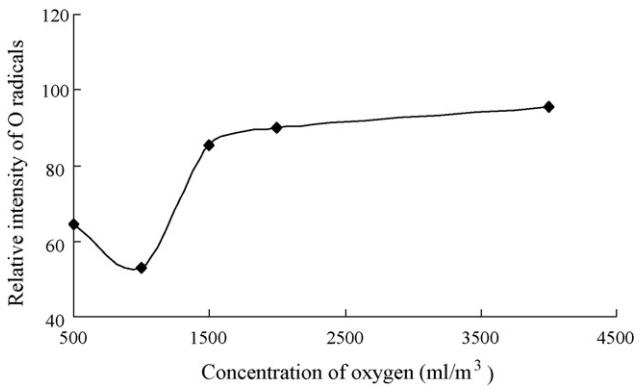

Fig. 8. Relative intensity of O radicals as a parameter of the O_2 concentration.

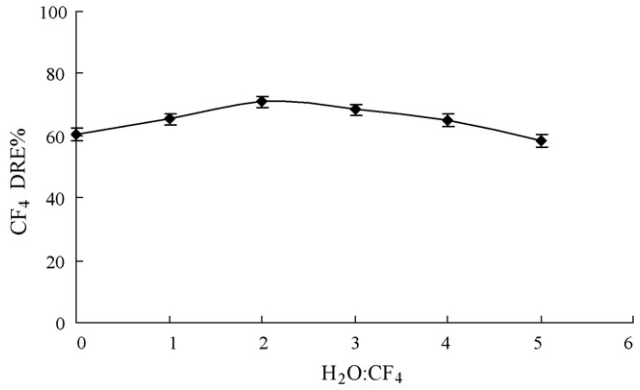

Fig. 9. Effect of molar ratio of H_2O to CF_4 on DRE of CF_4.

During the formation of O radicals, electron collision was needed, which decreased CF_4 colliding with electron. For decomposing CF_4 in microwave plasma with O_2 as addictive gas, the most important key was to control the concentration of O_2 in gas stream. The suitable concentration of O_2 is essential to achieve the highest DRE of CF_4.

3.5. *Effect of molar ratio of H_2O to CF_4 (H_2O:CF_4) on the DRE of CF_4*

The addition of water vapor to the microwave plasma reactor was attempted to promote the DRE of CF_4 with the O, H and OH radicals. The DRE of CF_4 in microwave plasma in the presence of water was shown in Fig. 9. The flow rate was 4 L/min containing CF_4 3000 mL/m^3 with the applied microwave power of 0.4 kW, the molar ratio of H_2O to CF_4 was ranged from 0 to 5. The DRE of CF_4 increased firstly and then decreased with further increasing of the molar ratio of H_2O to CF_4. The highest DRE of CF_4 was observed at the molar ratio of H_2O to CF_4 was 2 to 1.

The emission spectrum indicated that the OH radicals were generated and further reacted with CF_i during plasma discharge. The plasma emission spectrum with water vapor in gas stream is shown in Fig. 10. Fig. 10(a) shows the microwave argon plasma emission spectrum with water vapor without CF_4; Fig. 10(b) shows the molar ratio of H_2O to CF_4 was 2 to 1 with argon as carrier gas. When water vapor was added into the plasma, the peak with the wave length near 309 nm indicated the existence of hydroxyl radicals (OH^*). The peaks of Ar^*, and O^* also appeared. The peak of Si did not appear with H_2O/Ar, and the Si peak appeared in Fig. 10(b) due to the etching of inner wall of quartz tube by the F or HF which is generated by the CF_4 decomposition.

O radicals were the precursors for perfluorocompounds remediation, however, the OH radicals can also remediate perfluorocompounds both by oxidizing CF_i and by preventing its resuscitation to make CF_4 [11]. The main reactions are shown in (16)–(22):

$$e + CF_4 \rightarrow CF_3 + F^- \quad (16)$$

$$e + H_2O \rightarrow H + OH^- \quad (17)$$

$$CF_3 + OH \rightarrow COF_2 + HF \quad (18)$$

$$CF_2 + O \rightarrow COF + HF \quad (19)$$

$$CF + OH \rightarrow CO + HF \quad (20)$$

$$COF + OH \rightarrow CO_2 + HF \quad (21)$$

$$F + H_2O \rightarrow OH + HF \quad (22)$$

Since the OH radicals can remediate perfluorocompounds both by oxidizing CF_i and by preventing its resuscitation to make CF_4, the

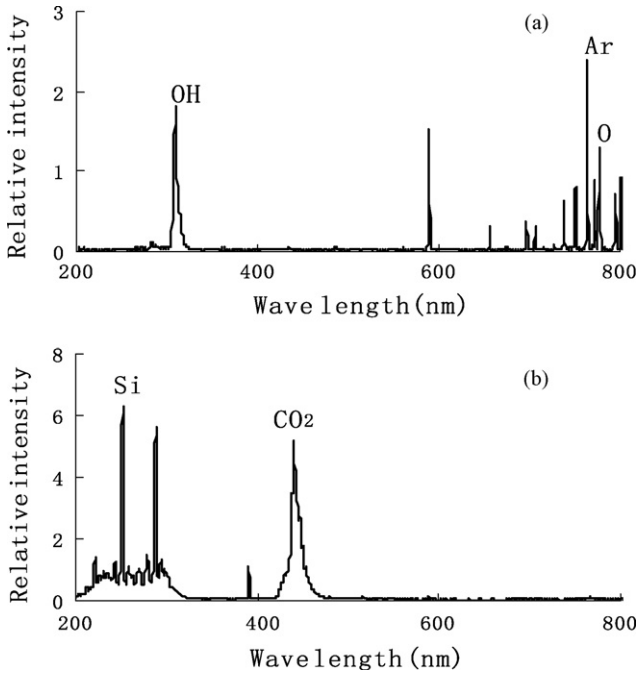

Fig. 10. Spectra of microwave plasma emission spectrum. (a) Ar with H_2O; (b) Ar with H_2O and CF_4.

adding of H_2O can promote the CF_4 decomposition efficiently. However, the water vapor is the electronegative gas, the H_2O molecules will capture the electron in plasma, which leads to decrease of electron density, so that more H_2O may quench the plasma. Then, there might be a competition between the increments of OH radicals to react with CF_i fragments and the decrements of electron for decomposition of CF_4. Therefore, the suitable molar ratio of H_2O and CF_4 is essential for achieving best DRE of CF_4.

4. Conclusions

The CF_4 decomposition and optical emission spectrum analysis were performed using microwave plasma at atmospheric. When concentration of CF_4 was 5000 mL/m^3 in gas stream, the DRE of CF_4 was 98.4%. The DRE of CF_4 was highly dependent on microwave power and total flow rate. Adding O_2 and H_2O can promote CF_4 decomposition in microwave plasma. The most important key was to control the adding mount of O_2 and H_2O. The concentration of O_2 should be 1000 mL/m^3 in gas stream for the highest DRE of CF_4 in this experiment. When the H_2O existed, the optimum ratio of H_2O to CF_4 was 2 to 1 for the highest DRE of CF_4. The optical emission spectrum analysis showed that the radicals of O^* and OH^* were generated and reacted with CF_i fragment, and CO_2 as the resultant were observed. The Si peak appeared due to etching of inner wall quartz tube by the F or HF which is generated by the CF_4 decomposition. The mechanisms of CF_4 decomposition is that the microwave plasma generated enough effective electrons to react with CF_4 to form CF_i radicals, then O and OH radicals reacted with CF_i radicals to convert CF_4 into CO_2 and HF.

Acknowledgment

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