

# Formation of fluorine for abating sulfur hexafluoride in an atmospheric-pressure plasma environment

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## Abstract

In this study, a large amount of toxic and reactive fluorine ( $F_2$ ) was produced in the atmospheric-pressure microwave discharge environment by adding additives to abate sulfur hexafluoride ( $SF_6$ ). When  $H_2$  was added, the selectivity of  $F_2$  was as high as 89.7% at inlet  $H_2/SF_6$  molar ratio ( $R_{H_2}$ ) = 1. Moreover, the conversion of  $SF_6$  significantly increased from 33.7% (without additive) to 97.7% ( $R_{H_2}$  = 5) at  $[SF_6]$  = 1%, and 0.8 kW because the addition of  $H_2$  inhibited the recombination of  $SF_6$ . With the addition of  $O_2$ ,  $H_2 + O_2$  or  $H_2O$ , the selectivity of  $F_2$  was still greater than 81.2%, though toxic byproducts, including  $SO_2F_2$ ,  $SOF_2$ ,  $SOF_4$ ,  $SO_2$ ,  $NO$ , and  $HF$ , were detected. From optical emission spectra,  $SF_2$  was identified, revealing the  $SF_6$  dissociation process might be carried out rapidly through an electron impact reaction:  $SF_6 \rightarrow SF_2 + 4F$ . Subsequently,  $F_2$  was formed via the recombination of F atoms.

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## 1. Introduction

Sulfur hexafluoride ( $SF_6$ ) is widely used as an etching and etching-aid gas in manufacturing very large scale integration circuits. The emission of  $SF_6$  from the semiconductor manufacturing process has recently increased greatly along with the output value of the semiconductor industry. However,  $SF_6$  has a long lifetime in the atmosphere ( $\sim 3200$  years), with a high global warming potential which is about 23,900 times higher than  $CO_2$  [1].

Although the abatement of  $SF_6$  emission is usually performed through thermal treatment or catalytic process,  $SF_6$  is difficult to burn in the gas phase and thermally stable up to 500 °C [2]. In various discharge environments [2–13],  $SF_6$  can be dissociated into lower sulfur fluorides in a low- to high-temperature reactor via a stepwise process:  $SF_x + e \rightarrow SF_{x-1} + F + e$  ( $6 \geq x \geq 1$ ) [14].

The intermediate species of dissociation,  $SF_x$  [15], tend to recombine rapidly to  $SF_6$  or reform into the highly toxic

products, such as  $S_2F_{10}$  (TLV = 0.01 ppm) and  $SF_4$  (ceiling value = 0.1 ppm) (Table 1) [16], or highly corrosive and reactive fluorine gas ( $F_2$ ) [2,5,9]. Hence, the qualitative analyses of byproducts were carried out in various plasma environments with different additives, and byproducts such as  $SOF_4$ ,  $SO_2F_2$ ,  $SOF_2$ ,  $S_2OF_{10}$ ,  $S_2O_2F_{10}$ ,  $SO_2$ ,  $SiF_4$ ,  $OF_2$ , and  $F_2$  were detected in an  $O_2$ -added radio-frequency (RF) plasma or dielectric barrier discharge (DBD) [2,12];  $S_2F_{10}$ ,  $SF_4$ ,  $SOF_2$ ,  $SOF_4$ ,  $SO_2F_2$ ,  $SO_2$ ,  $SO_3$ , and  $HF$  were produced by  $H_2O$ -added corona discharge or microwave (MW) plasma [13,17]. Air,  $H_2S$  or hydrocarbons were also added to reduce the production of sulfur oxyfluorides, but sulfur,  $CF_4$ ,  $CO/CO_2$  or  $NO/NO_2$  would be formed [12,18].

So far, most plasma-abated studies have addressed the effective removal of fluorine compounds. In this study, the selectivity of byproducts, especially  $F_2$ , in the effluents were measured and compared by using an atmospheric-pressure plasma with essential high electron density to abate  $SF_6$ . Moreover, various additives, such as  $H_2$ ,  $O_2$ ,  $H_2/O_2$ , and  $H_2O$ , were added into the mixtures to enhance the abatement capacity of  $SF_6$ , while hydrocarbons, such as  $C_2H_4$  or  $CH_4$ , were not added to avoid the formation of carbon-containing compounds ( $CF_4$ ,  $COF_2$ ,  $CO$  or  $CO_2$ ). In addition, the selectivity of other byproducts,

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Table 1

Threshold limit value (TLV) of the concentration of byproducts possibly produced from the abatement of SF<sub>6</sub> [16]

Compound	TLV or TWA <sup>a</sup>	Compound	TLV or TWA <sup>a</sup>
S <sub>2</sub> F <sub>10</sub>	0.01 ppm	COF <sub>2</sub>	2 ppm
SF <sub>4</sub>	0.1 ppm (ceiling)	HF	3 ppm
SOF <sub>2</sub>	0.7 ppm	SO <sub>2</sub> F <sub>2</sub>	5 ppm
SiF <sub>4</sub>	0.8 ppm	NO	25 ppm
F <sub>2</sub>	1 ppm	SOF <sub>4</sub>	— <sup>b</sup>
SO <sub>2</sub>	2 ppm		

<sup>a</sup> TWA: time-weighted average.

<sup>b</sup> (–) No data.

including HF, SO<sub>2</sub>F<sub>2</sub>, SOF<sub>2</sub>, SOF<sub>4</sub>, SO<sub>2</sub>, and sulfur, as well as the conversion of SF<sub>6</sub>, were also compared.

## 2. Experimental

The experimental setup is shown schematically in Fig. 1. An electrodeless atmospheric microwave torch plasma system is assembled by using a commercially available magnetron (National Electronics YJ-1600, 2.45 GHz) with maximum stationary power of 5 kW in a continuous-wave mode. The microwave radiation passes through a circulator and a three-stub tuner, and is then fed into a waveguide (ASTEX WR340), which is connected laterally with a resonant auxiliary cavity. A quartz tube (3.3-cm-o.d.) was located one-quarter wavelength from the shortened end of the waveguide and intersected with the waveguide and the resonator perpendicularly. In addition, the microwave plasma was ignited by inserting a tungsten wire into the resonant cavity from the top of the reactor and sparking in the waveguide.

The flow rate of high purity reactants that were supplied from compressed gas cylinders was adjusted with calibrated mass flow controllers, introduced into a gas mixer, and then injected into the top and side of the quartz tube. The well-mixed working gas passed through the quartz tube and entered the discharge zone of the reactor that equipped an outer cooling tube with water passed in the opposite direction, enabling the stabilization of the

plasma torch. After completing the plasma-chemical reactions, the effluents flowed through the reactor. The final gas mixtures were then analyzed and exhausted at atmospheric pressure.

The composition of the reactants and products were mainly identified and quantified by an on-line Fourier transform infrared spectrometer (Nicolet, Avator 370). The FTIR analysis conditions were set as follows: spectral range = 4000–740 cm<sup>−1</sup>, resolution = 0.5 cm<sup>−1</sup>, number of scans = 8, gain = 4. The gas cell and transfer line from the reactor to FTIR were constantly heated in order to avoid condensation. The mole fraction of the product species was determined by a comparison with the response of the peak height of standard gas at the same wavenumber. However, no SF<sub>4</sub> and S<sub>2</sub>F<sub>10</sub> were found in the effluents, and concentrations of H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O were not measured. In addition, the qualitative analysis of F<sub>2</sub> was carried out by a residual gas analyzer (Extorr, XT200), while the mole fraction of F<sub>2</sub> was calculated via a mass balance by assuming unquantified F atoms were all converted into F<sub>2</sub> [19]. Moreover, the amount of sulfur deposition was also estimated by the mass balance of S atoms.

The experimental conditions are summarized as follows: the additives were H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> + O<sub>2</sub>, H<sub>2</sub>O; inlet additive/SF<sub>6</sub> molar ratios were: H<sub>2</sub>/SF<sub>6</sub> (*R*<sub>H<sub>2</sub></sub>) and O<sub>2</sub>/SF<sub>6</sub> (*R*<sub>O<sub>2</sub></sub>) = 0/1–5/1, H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> (*R*<sub>H<sub>2</sub>/O<sub>2</sub></sub>) = 1/1/1, 1/3/1, and 2/2/1, and H<sub>2</sub>O/SF<sub>6</sub> (*R*<sub>H<sub>2</sub>O</sub>) = 1/1 and 4/1; system pressure (*P*) was operated at 101.3 kPa; applied MW power was 0.8 or 1.3 kW; the feeding concentration of SF<sub>6</sub> ([SF<sub>6</sub>]) was kept at 1%; N<sub>2</sub> was the carrier gas, the temperature of the feed was at 303 K; total flow rate was at 20 or 10 slm (standard L/min).

The product compositions are based on molar concentrations of the effluent. The conversion of SF<sub>6</sub> (*C*<sub>SF<sub>6</sub></sub>) and the selectivity of byproducts (SF for F atoms and SS for S atoms) in this study are defined as follows:

$$C_{\text{SF}_6} = \frac{(\text{SF}_6 \text{ converted})}{(\text{SF}_6 \text{ fed to the reactor})} \times 100\%$$

SF<sub>A</sub> (or SS<sub>A</sub>) = the fraction of F atoms (or S atoms for SS<sub>A</sub>) from abated-SF<sub>6</sub> converting into product A (%)

For example, selectivity of F<sub>2</sub> = ([F<sub>2</sub>] × 2)/([SF<sub>6</sub>] × *C*<sub>SF<sub>6</sub></sub> × 6) × 100%

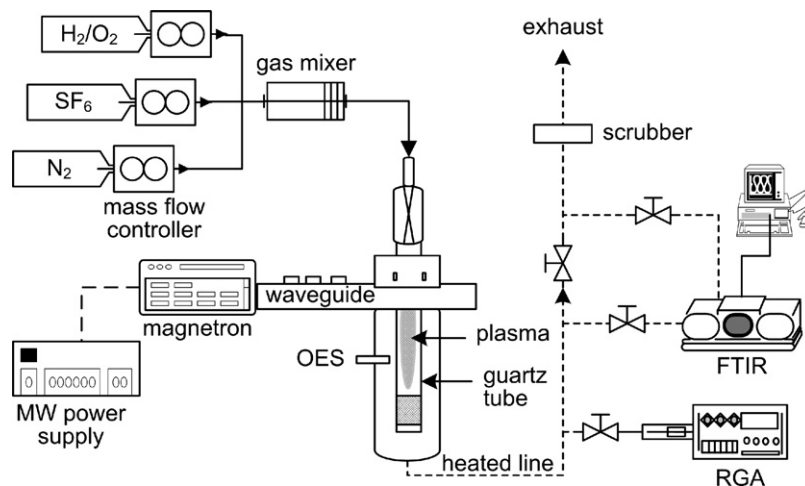


Fig. 1. Schematic of the atmospheric-pressure plasma system.

Table 2

Comparisons of byproducts using different plasma approaches and adding various additives

Plasma	Additive	Byproducts	Reference
MW	H <sub>2</sub>	F <sub>2</sub> , Sulfur, HF	This study
RF <sup>a</sup>	H <sub>2</sub>	HF, SiF <sub>4</sub> , sulfur, SO <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , SOF <sub>2</sub> , SOF <sub>4</sub> , S <sub>2</sub> F <sub>10</sub> , S <sub>2</sub> OF <sub>10</sub> , S <sub>2</sub> O <sub>2</sub> F <sub>10</sub>	[18]
MW	O <sub>2</sub>	F <sub>2</sub> , sulfur, SO <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , SOF <sub>2</sub> , SOF <sub>4</sub> , NO <sub>x</sub>	This study
MW	O <sub>2</sub>	F <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , SO <sub>2</sub>	[1]
MW	O <sub>2</sub>	SiF <sub>4</sub> , SO <sub>2</sub> F <sub>2</sub> , SOF <sub>2</sub> , FNO, FNS	[10]
DBD	O <sub>2</sub>	OF <sub>2</sub> , F <sub>2</sub> , SOF <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , SO <sub>2</sub> , O <sub>3</sub>	[12]
MW	H <sub>2</sub> + O <sub>2</sub>	F <sub>2</sub> , sulfur, SO <sub>2</sub> , HF, SO <sub>2</sub> F <sub>2</sub> , SOF <sub>2</sub> , SOF <sub>4</sub> , H <sub>2</sub> O	This study
MW	H <sub>2</sub> O	F <sub>2</sub> , sulfur, SO <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , HF, SOF <sub>2</sub> , SOF <sub>4</sub>	This study
MW	H <sub>2</sub> O	SO <sub>2</sub> , SO <sub>3</sub> , HF	[13]
Corona	H <sub>2</sub> O	S <sub>2</sub> F <sub>10</sub> , SF <sub>4</sub> , SOF <sub>2</sub> , SOF <sub>4</sub> , SO <sub>2</sub> F <sub>2</sub> , SiF <sub>4</sub> , COF <sub>2</sub> , CF <sub>4</sub> , HF, CO	[17]
Spark	H <sub>2</sub> O	SO <sub>2</sub> F <sub>2</sub> , SOF <sub>2</sub> , SO <sub>2</sub> , SiF <sub>4</sub>	[3,4]
RF <sup>a</sup>	H <sub>2</sub> S	SiF <sub>4</sub> , SO <sub>2</sub> , SO <sub>2</sub> F <sub>2</sub> , HF, SOF <sub>2</sub> , SOF <sub>4</sub> , sulfur	[20]

<sup>a</sup> At 1.33 kPa (others are at 101.3 kPa).

### 3. Results and discussion

#### 3.1. Byproducts by adding various additives

Table 2 listed the comparisons of byproducts using different plasma approaches and adding various additives. With the addition of H<sub>2</sub>, the byproducts were only F<sub>2</sub>, HF and yellow sulfur deposition. Fig. 2A shows the typical FTIR spectra before and after the abatement of SF<sub>6</sub> at 0.8 kW in mixtures of H<sub>2</sub>/SF<sub>6</sub>/N<sub>2</sub> at  $R_{H_2} = 1$ . Without SF<sub>4</sub>, S<sub>2</sub>F<sub>10</sub>, SiF<sub>4</sub>, and sulfur oxyfluorides were detected in this study, though they have been identified in a low-pressure RF plasma glass reactor with the addition of H<sub>2</sub> or H<sub>2</sub>S [18,20] (Table 2).

When O<sub>2</sub> was added in SF<sub>6</sub>/N<sub>2</sub> mixtures at  $R_{O_2} = 1$  (Fig. 2B), F<sub>2</sub>, sulfur oxyfluorides (including SO<sub>2</sub>F<sub>2</sub>, SOF<sub>2</sub>, and SOF<sub>4</sub>), and

trace NO (in some cases) were produced. Though HF was not produced due to the H<sub>2</sub>-free environment, the toxicity equivalents of decomposed byproducts were sometimes higher using O<sub>2</sub> as the additive as opposed to using H<sub>2</sub>. Similar results have been reported in an RF plasma reactor [21]. However, FNS and FNO that were found in the O<sub>2</sub>-containing MW plasma [10] as well as OF<sub>2</sub> and O<sub>3</sub> that were detected in the O<sub>2</sub>-rich DBD reactor [12], were not found (Table 2).

Using a method of adding H<sub>2</sub>O into the SF<sub>6</sub>/N<sub>2</sub> mixtures, more and complex byproducts, including F<sub>2</sub>, HF, sulfur oxyfluorides, and elemental sulfur were formed because of both the H and O atoms involved in the reactions. However, SF<sub>4</sub> and S<sub>2</sub>F<sub>10</sub> that were yielded in the H<sub>2</sub>O-added corona discharge [17] were not found (Table 2).

In order to change the inlet H/O atom ratio, H<sub>2</sub> and O<sub>2</sub> were added simultaneously. At a lower feeding concentration of H<sub>2</sub>, such as at H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> = 1/1/1, similar byproducts were found with the addition of H<sub>2</sub>O. However, when the feeding of H<sub>2</sub> was elevated, causing the H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> ratio to reach 3/1/1, the formation of SO<sub>2</sub>F<sub>2</sub>, SOF<sub>2</sub>, and SOF<sub>4</sub> were suppressed via the formation of more SO<sub>2</sub>.

#### 3.2. Selectivity of F<sub>2</sub> and other byproducts

Table 3 shows that the most abundant F- and S-containing byproducts were F<sub>2</sub> and elemental sulfur (expressed as S<sub>1</sub>), respectively, regardless of which additive (H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> + O<sub>2</sub>, or H<sub>2</sub>O) was added. The selectivity of F<sub>2</sub> for adding various additives was very high and at least about 81% and was far greater than that of HF. Moreover, a majority of S atoms were converted to polysulfur via the aggregation of S or S<sub>2</sub> during subsequent quenching in the afterglow zone.

##### 3.2.1. Addition of hydrogen

With the addition of H<sub>2</sub> in SF<sub>6</sub>/N<sub>2</sub> mixtures at H<sub>2</sub>/SF<sub>6</sub> = 1, the selectivity of F atoms for F<sub>2</sub> (SF<sub>2</sub>) was as high as 89.7%, with the selectivity of S atoms for elemental sulfur being 100%, and the minor byproduct was HF with F-atom selectivity of 10.3% (Table 3). It should be noted that the characteristics of byproducts resulting from the addition of H<sub>2</sub> to abate SF<sub>6</sub> in MW plasma are rarely cited in the literature, because it seems to be expected

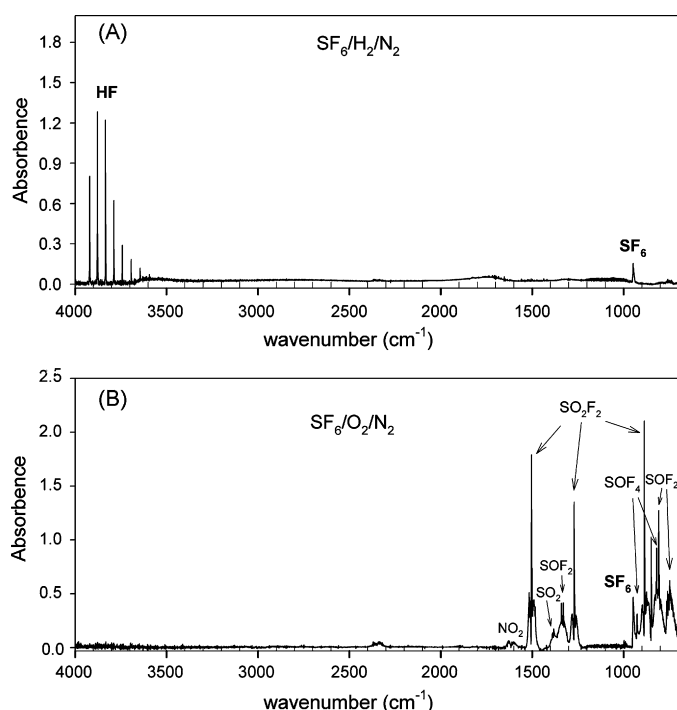


Fig. 2. Typical FTIR spectra after the plasma abatement of SF<sub>6</sub> at inlet H<sub>2</sub>/SF<sub>6</sub> molar ratio = 5 (A) and inlet O<sub>2</sub>/SF<sub>6</sub> molar ratio = 5 (B) at 0.8 kW.

Table 3

Selectivities of byproducts resulting from SF<sub>6</sub> abatement for various inlet mixtures ([SF<sub>6</sub>]<sub>in</sub> = 1%, 10 slm, 0.8 kW)

$R_{H_2}^a$	$R_{O_2}$	$R_{H_2O}$	Selectivity of F atoms (%)					Selectivity of S atoms (%)				
			[F <sub>2</sub> ]	[HF]	[SO <sub>2</sub> F <sub>2</sub> ]	[SOF <sub>2</sub> ]	[SOF <sub>4</sub> ]	[S <sub>1</sub> ]	[SO <sub>2</sub> ]	[SO <sub>2</sub> F <sub>2</sub> ]	[SOF <sub>2</sub> ]	[SOF <sub>4</sub> ]
0	0	0	100.0	0	0	0	0	100.0	0	0	0	0
1			89.7	10.3	0	0	0	100.0	0	0	0	0
5			82.2	17.8	0	0	0	100.0	0	0	0	0
	1		90.8	0.0	7.4	0.43	1.39	47.9	26.6	22.1	1.3	2.1
	5		81.3	0.0	15.6	0.78	2.27	13.8	33.6	46.9	2.3	3.4
1	1		83.9	9.3	5.8	0.33	0.65	63.8	16.8	17.5	1.0	1.0
3	1		85.5	14.5	0	0	0	61.7	38.3	0	0	0
		1.0	87.4	7.3	4.6	0.19	0.45	60.2	24.7	13.8	0.6	0.7
		4.0	81.2	12.9	5.3	0.33	0.22	58.8	24.0	15.9	1.0	0.3

<sup>a</sup>  $R_{O_2}$  = inlet O<sub>2</sub>/SF<sub>6</sub> ratio;  $R_{H_2}$  = inlet H<sub>2</sub>/SF<sub>6</sub> ratio;  $R_{H_2O}$  = inlet H<sub>2</sub>O/SF<sub>6</sub> ratio.

that a large amount of HF will be produced, while this has not been found to be the case in this study. For example, the F atoms were converted mainly into HF with almost no F<sub>2</sub> being detected in the glass-made RF plasma reactor [18].

No SF<sub>4</sub> and S<sub>2</sub>F<sub>10</sub> could be detected in the H<sub>2</sub>/SF<sub>6</sub>/N<sub>2</sub> environment, because the SF<sub>6</sub> dissociation reaction process was possible carried out mainly through an electron impaction reaction: SF<sub>6</sub> → SF<sub>2</sub> + 4F [14,22]. The optical emission spectrum (Fig. 3A) in this H<sub>2</sub>/SF<sub>6</sub>/N<sub>2</sub> discharge showed that weak emission peaks of SF<sub>2</sub> (X<sup>1</sup>A<sub>1</sub> → C<sup>1</sup>A<sub>2</sub> transition, at 304.3, 320.4, 336.7, 360.7 nm) [23–24] were identified. SF<sub>5</sub> and SF<sub>4</sub> species were also produced, although they disappeared quickly via the Penning dissociation reaction or the electron impact dissociation reaction, such as SF<sub>5</sub> → SF<sub>4</sub> + F and SF<sub>4</sub> → SF<sub>3</sub> + F [14–15], resulting in no S<sub>2</sub>F<sub>10</sub> and SF<sub>4</sub> being found in the effluents. However, large amounts of F atoms resulted in the formation of F<sub>2</sub>, which was formed primarily in and immediately downstream of the discharge zone via the reaction of 2F + M → F<sub>2</sub> + M, with M representing the third body or wall [19,25].

The selectivity of S<sub>1</sub> was almost 100%, since no other S-containing compounds could be detected. Yellow depositions were yielded, as well as weak emission peaks of active S<sub>2</sub> (at 283.0, 286.5, 289.5, 295.5 nm) (Fig. 3A) and S (at 850–930 nm) [26–27], indicating elemental sulfur was formed via the polymerization of S or S<sub>2</sub>.

### 3.2.2. Addition of oxygen

With the addition of O<sub>2</sub>, Table 3 shows a similar selectivity of F<sub>2</sub> was found than when H<sub>2</sub> was added, ranging from 8.3% to 90.8%, while the selectivity of F atoms for SO<sub>2</sub>F<sub>2</sub>, SOF<sub>2</sub>, and SOF<sub>4</sub> increased with elevated  $R_{O_2}$  and reached 15.6%, 0.78%, and 2.27%, respectively, at  $R_{O_2}$  = 5. Moreover, a higher selectivity of S<sub>1</sub> and SO<sub>2</sub> was found at a lower  $R_{O_2}$ , 47.9% and 26.6%, respectively, at  $R_{O_2}$  = 1 (Table 3). In addition, it should be noted that a trace of NO was formed via N<sub>2</sub> reacting with O<sub>2</sub> in an O<sub>2</sub>-containing environment.

An optical emission spectrum in the O<sub>2</sub>/SF<sub>6</sub>/N<sub>2</sub> discharge (Fig. 3B) showed that the emission of SF<sub>2</sub>, N<sub>2</sub>, and S<sub>2</sub>. SF<sub>2</sub> is not only a major precursor just in the H<sub>2</sub>-added condition in the sequence of reactions following the dissociation of SF<sub>6</sub>, but is also an important precursor in the formation of SO<sub>2</sub>F<sub>2</sub> [22]. However, since O<sub>2</sub> is an efficient quencher, resulting in some electronically excited species, ionic molecular nitrogen, atomic N or O cannot be identified [28].

In Fig. 3, observation of the representative emission spectrum in both H<sub>2</sub>- and O<sub>2</sub>-containing SF<sub>6</sub>/N<sub>2</sub> discharge also shows that active N<sub>2</sub> played an important role in the translation of energy. N<sub>2</sub> from the second positive band (C<sup>3</sup>Π → B<sup>3</sup>Π transition, at 300–550 nm) and N<sub>2</sub> from the first positive band (B<sup>3</sup>Π → A<sup>3</sup>Σ transition, at 550–900 nm), were clearly identified [29–33].

### 3.2.3. Addition of H<sub>2</sub>/O<sub>2</sub> or steam

In order to simulate a different inlet H/O atom ratio, H<sub>2</sub> and O<sub>2</sub> were added simultaneously. When less H<sub>2</sub> was added with a H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> ratio of 1/1/1, the byproduct species were similar to those when H<sub>2</sub>O was added. The major byproducts were F<sub>2</sub>, sulfur and SO<sub>2</sub>, and the minor species was SO<sub>2</sub>F<sub>2</sub>, with traces of HF, SOF<sub>2</sub> and SOF<sub>4</sub>. The selectivity of F<sub>2</sub> was 83.9%, and the selectivity of S<sub>1</sub> and SO<sub>2</sub> were 63.8% and 16.8%, respectively

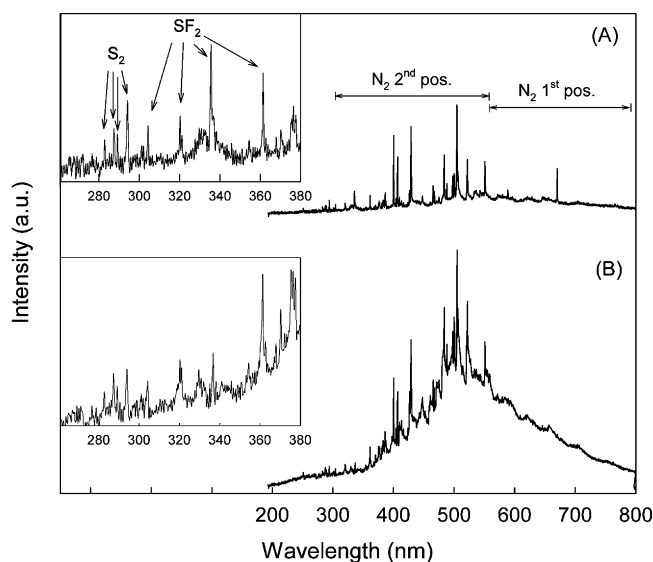


Fig. 3. Optical emission spectra of the H<sub>2</sub>(5%)/SF<sub>6</sub>/N<sub>2</sub> (A) and O<sub>2</sub>(5%)/SF<sub>6</sub>/N<sub>2</sub> (B) plasmas.



Table 4  
Conversion of SF<sub>6</sub> for various inlet mixtures ([SF<sub>6</sub>]<sub>in</sub> = 1%, 10 slm, 0.8 kW)

Mixtures	Conversion of SF <sub>6</sub> (%)	Mixtures	Conversion of SF <sub>6</sub> (%)
Without additive	33.7		
H <sub>2</sub> /SF <sub>6</sub> = 1/1	93.8	H <sub>2</sub> /O <sub>2</sub> /SF <sub>6</sub> = 1/1/1	95.9
H <sub>2</sub> /SF <sub>6</sub> = 5/1	97.7	H <sub>2</sub> /O <sub>2</sub> /SF <sub>6</sub> = 3/1/1	96.9
O <sub>2</sub> /SF <sub>6</sub> = 1/1	91.4	H <sub>2</sub> O/SF <sub>6</sub> = 1/1	96.9
O <sub>2</sub> /SF <sub>6</sub> = 5/1	94.5	H <sub>2</sub> O/SF <sub>6</sub> = 4/1	92.0

(Table 3). However, the addition of less H<sub>2</sub> with O<sub>2</sub> or H<sub>2</sub>O resulted in the most complicated effluents in the SF<sub>6</sub> plasma abatement system.

When adding more H<sub>2</sub> to reach a H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> ratio of 3/1/1, sulfur oxyfluorides disappeared but a large amount of F<sub>2</sub> and sulfur remained as a result of the formation of more HF and SO<sub>2</sub>, with the selectivities of F- and S-atoms being 14.5% and 38.3%, respectively (Table 3). The results show that a higher concentration of H<sub>2</sub> than O<sub>2</sub> not only elevated the SF<sub>6</sub> conversion, but also inhibited the formation of sulfur oxyfluorides in an H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> environment.

### 3.3. Conversion of SF<sub>6</sub>

Table 4 shows that adding the additive to the SF<sub>6</sub>/N<sub>2</sub> mixture and the inlet additive/SF<sub>6</sub> molar ratios apparently enhances the conversion of SF<sub>6</sub> (C<sub>SF<sub>6</sub></sub>). The enhancement level of various additives on C<sub>SF<sub>6</sub></sub> can be listed in the following order: +H<sub>2</sub> > +O<sub>2</sub> >> no additive. C<sub>SF<sub>6</sub></sub> was only 33.7% with no additives because of the recombination of SF<sub>6</sub> in the discharge environment.

When H<sub>2</sub> was added, C<sub>SF<sub>6</sub></sub> increased significantly and reached 93.8% and 97.7% when the inlet H<sub>2</sub>/SF<sub>6</sub> molar ratio was 1 and 5, respectively, at 0.8 kW (Table 4). Because H<sub>2</sub> was easily dissociated into active species, such as H atoms, reacting with SF<sub>6</sub> and its fragments to form highly stable products, mainly F<sub>2</sub>, HF, and sulfur, the result was not only a significant improvement in C<sub>SF<sub>6</sub></sub>, but also an inhibition of the recombination of SF<sub>6</sub>.

With the addition of O<sub>2</sub>, C<sub>SF<sub>6</sub></sub> also apparently elevated and reached 91.4–94.5% at inlet O<sub>2</sub>/SF<sub>6</sub> ratio = 1–5, respectively, at 0.8 kW (Table 4), because SF<sub>6</sub> and its fragments react with O<sub>2</sub> and O atoms to form SO<sub>2</sub> and sulfur oxyfluorides (such as SO<sub>2</sub>F<sub>2</sub>, SOF<sub>2</sub>, and SOF<sub>4</sub>), which could inhibit the recombination of SF<sub>6</sub>.

H<sub>2</sub>O was also used as an additive, and the C<sub>SF<sub>6</sub></sub> reached 96.9% when the inlet H<sub>2</sub>O/SF<sub>6</sub> ratio (R<sub>H<sub>2</sub>O</sub>) was 1, while it was slightly decreased to 92.0% at R<sub>H<sub>2</sub>O</sub> = 4 because a large amount of H<sub>2</sub>O resulted in a reduction of electron mean energy and plasma density. In addition, two inlet molar ratios of H<sub>2</sub>/O<sub>2</sub> were performed in order to alter the inlet H/O atom ratio, and a little higher C<sub>SF<sub>6</sub></sub> was found when compared to adding only H<sub>2</sub> (at R<sub>H<sub>2</sub></sub> = 1) or O<sub>2</sub> (at R<sub>O<sub>2</sub></sub> = 1), reaching 95.9% and 96.9% for H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> = 1/1/1 and 3/1/1, respectively (Table 4).

Finally, when a higher total flow rate with a higher applied power was also examined, the C<sub>SF<sub>6</sub></sub> was as high as 99.9% at 20 slpm with 1.3 kW of power at H<sub>2</sub>/O<sub>2</sub>/SF<sub>6</sub> = 2/2/1. Hence, this

microwave plasma torch can effectively destroy high concentrations of SF<sub>6</sub> at a higher flow rate with the addition of proper additives at a high enough power.

## 4. Conclusions

In this study, a large amount of F<sub>2</sub> was found from the SF<sub>6</sub> plasma abatement process when H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> + O<sub>2</sub>, or H<sub>2</sub>O was added into the mixtures to enhance the removal efficiency of SF<sub>6</sub>. However, complicated byproducts, such as SO<sub>2</sub>, sulfur oxyfluorides, and NO were formed in the O atom-containing (O<sub>2</sub>, H<sub>2</sub> + O<sub>2</sub>, or H<sub>2</sub>O) discharge environment, resulting in the only H<sub>2</sub>-added discharge system was a simpler and better alternative. Because only F<sub>2</sub>, HF and elemental sulfur were produced in the H<sub>2</sub>/SF<sub>6</sub>/N<sub>2</sub> mixtures, and because SF<sub>6</sub> was abated with the addition of H<sub>2</sub>, the sequential chemical absorption of F<sub>2</sub> within a single, dry plasma/absorber hybrid reactor is possible. The treatment of waste gases from the abatement of SF<sub>6</sub> emission is currently carried out via a pipe-end wet scrubber. However, an in-situ process for removing toxic or reactive byproducts, such as F<sub>2</sub>, in the same reactor should be preferred, because the process can reduce the corrosion of transportation pipes and reduce the loading of wastewater treatment.

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