Conversion of SF_6 by thermal plasma at atmospheric pressure

Sung-Han Han , Hong Sun Seon , Paik-Kyun Shin , Dong Wha Park

Department of Chemical Engineering and RIC-ETTP(Regional Innovation Center for Environmental Technology of Thermal Plasma), Inha University, 253 Yonghyun-dong, Nam-gu, Incheon, 402-751, Republic of Korea

Abstracts: Sulphur hexafluoride (SF_6) gas which has high global warming potential (GWP_{100}=23,900) and long lifetime was decomposed by using thermal plasma at atmospheric pressure. Experiments were carried out at various conditions and the decomposition of SF_6 gas was analyzed using GC. The decomposed amount of SF_6 gas was decreased as the plasma gas flow rate was increased. Additive gases (H_2, O_2) were used to increase the decomposition of SF_6 gas. In case of adding H_2 gas, the decomposition of SF_6 gas was better than that of SF_6 for adding O_2 gas. About 99% decomposition of SF_6 gas has been achieved.

Keywords: Thermal plasma, PFCs, SF_6, decomposition

1. Introduction

Perfluorocompounds (PFCs) including CF_4, C_2F_6, C_3F_8, CHF_3, SF_6, and NF_3 are highly stable compounds with unique physical and chemical properties that make them useful for some specialized applications. They are heavy, inert, non-toxic, and non-flammable materials [1]. PFCs have been used in the semiconductor industry for their process performance and low impact on employee safety [2]. The existence of these gases in the air is harmful because they cause the global warming through the green house effect [3]. Table 1 shows the lifetimes and global warming potential (GWP) of PFCs gases. The need of decomposition of PFCs has arisen internationally. At the Conference of the Parties (COP3) in Kyoto, Japan, in December 1997, 159 nations participated in a treaty that would include PFCs in the basket of greenhouse gases (CO_2, NO_2, CH_4, etc) subject to emission reductions for nations that ratify the treaty. The agreement in Kyoto confirms to reduce the output of greenhouse gases by years 2008–2012 to 7% below 1990 levels [4].

SF_6 has been used in the etching and cleaning processes of the semiconductor industry. Also, it has been used as an isolator of a current transformer. But, this gas is one of the global warming gases which has the long lifetime in the atmosphere (~3200yr) with the large global warming potential (GWP_{100}=23,900) [5].

Although the abatement of SF_6 gas is performed through thermal treatment or a catalytic process, SF_6 is difficult to be treated effectively in the gas phase [6].

In this study, we have investigated the decomposition of pure SF_6 gas which is using as an isolator of a current transformer. The additive gases, such as H_2 and O_2, were injected into the system to attain the developed decomposition of SF_6. However, the hydrocarbons, such as CH_4 or C_2H_6 were not injected because of avoiding the formation of carbon-containing compounds, such as CF_4, CO, CO_2 [7]. It has been expected that we will get better decomposition rate if diluted gas using in the semiconductor industry instead of pure SF_6 is treated by thermal plasma.

Table 1
Atmospheric lifetimes GWP_{100} of greenhouse gases [8]

Greenhouse gases	Atmospheric lifetime (year)	GWP_{100}
CO_2	50-200	1
CF_4	50000	6500
C_2F_6	10000	9200
SF_6	3200	23900
C_3F_8	2600-7000	7000
CHF_3	250-390	11700
C_4F_8	3200	8700
CH_4	12	21
N_2O	120	310
NF_3	50-740	8000

2. Experimental

The thermal plasma abatement device used to investigate the decomposition of SF_6 was operated at atmospheric pressure. The cathode was a tungsten rod and the anode was a copper nozzle. Runs were performed under a variety of conditions by changing the plasma gas, the SF_6 gas flow rate and additive gases injected. Experimental system is shown schematically in Fig. 1. Experimental setup was consisted of a DC power supply, a torch, a reaction tube, a quenching tube, a scrubber and an aspirator. The reaction tube made of the stainless steel tube was 20 mm inside diameter. And the quenching tube was 8 mm inside diameter and made up of copper. Both the reaction and quenching tube were water-cooled double tubes. Pure sulphur hexafluoride, hydrogen and oxygen gas flow rate were controlled by Mass Flow Controllers (MFCs) which were used to control accurately. The injection position of the SF_6 and additive gases was set at 5 mm above from the nozzle center. Ar gas was used as a plasma gas. Ar gas flow rate was increased from 8 l/min to 12 l/min. The decomposed

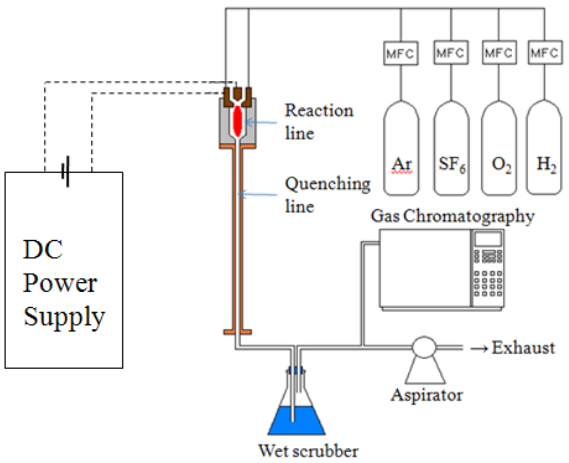

Fig.1 Experimental Setup

amounts of SF_6 were analyzed by GC. Exhausted gases, fluorine and hydrofluorine were removed through the scrubber and discharged by the aspirator. The arc current was 200 A and the plasma power was 5 kW. Table 2 shows the experimental conditions in this study in detail. The decomposed amount of SF_6 was calculated by using the equation (1).

$$\text{Decomposition}_{SF_6}(\%) = \frac{C_{i_{SF6}} - C_{f_{SF6}}}{C_{i_{SF6}}} \times 100 \qquad (1)$$

where C_i and C_f are the concentrations of the SF_6 before and after the abatement device, respectively.

3. Results and Discussion

Fig. 2 shows the equilibrium amounts of species in the system of (a) pure SF_6, (b) SF_6/O_2 = 1, and (c) SF_6/H_2 = 1 at atmospheric pressure. Chemical equilibrium compositions were calculated by the software program based on Gibbs free energy minimization [9]. The pure SF_6 needs the temperature above 1,500 K to be decomposed. Generally the plasma temperature at the nozzle is about 10,000K [10]. Therefore, it could be expected that pure SF_6 is easily decomposed by thermal plasma. In case of adding O_2, the temperature for the decomposition of SF_6 scarcely changes. However, for adding H_2, SF_6 rapidly started to be decomposed from the low temperature region. The main by-product is HF. Through these results, it is expected that the decomposition efficiency would be enhanced in case of adding H_2.

Table 2 Experimental conditions

Input power	5kW
Plasma gas flow rate (Ar)	8, 10, 12 l/min
SF_6 gas flow rate	100, 300, 500, 1000 SCCM
Additive gas flow rate (H_2, O_2)	0.1 l/min
Analysis	GC

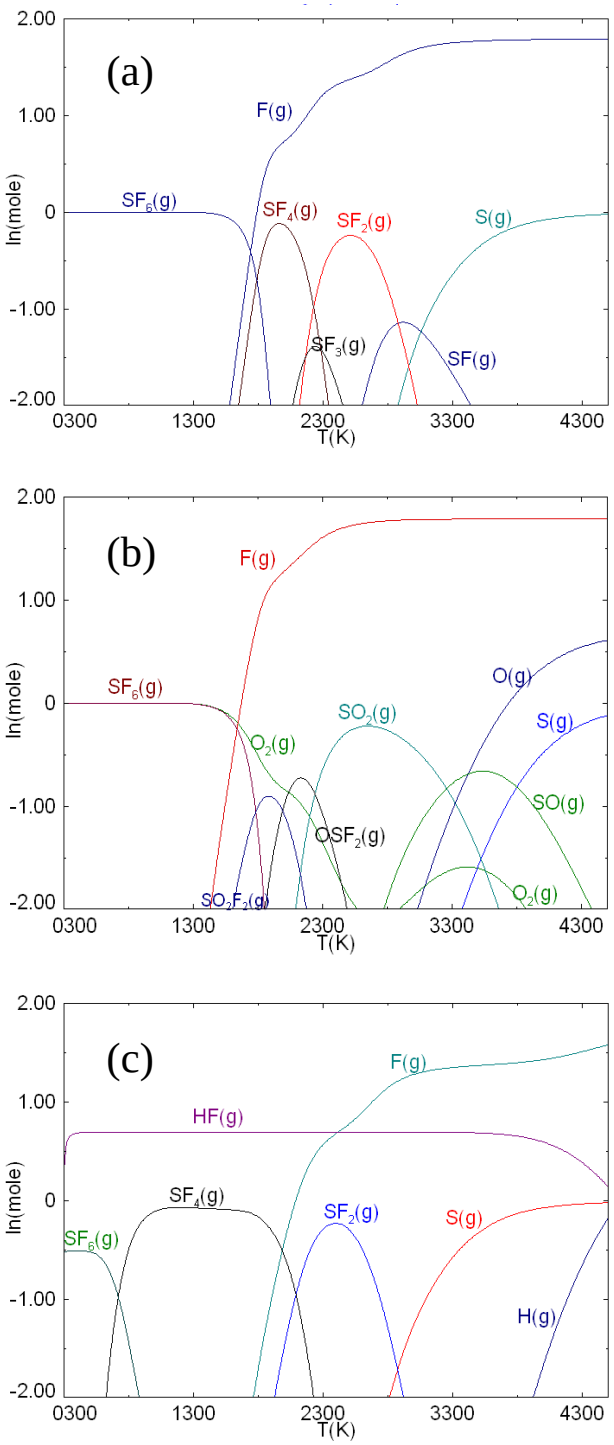

Fig.2 Thermodynamic equilibrium composition of (a) pure SF_6, (b) SF_6 and O_2, (c) SF_6 and H_2

Fig.3 shows that the decomposition of SF_6 was decreased as SF_6 flow rate was increased. The decomposition of SF_6 was tested over a variety of SF_6 flow rates. In this case the plasma gas flow rate was 8 l/min and the arc current was 200 A. The decomposition of pure SF_6 reached up to 83.9 % at the thermal plasma power of 5 kW (200 A), Ar plasma gas flow rate of 8

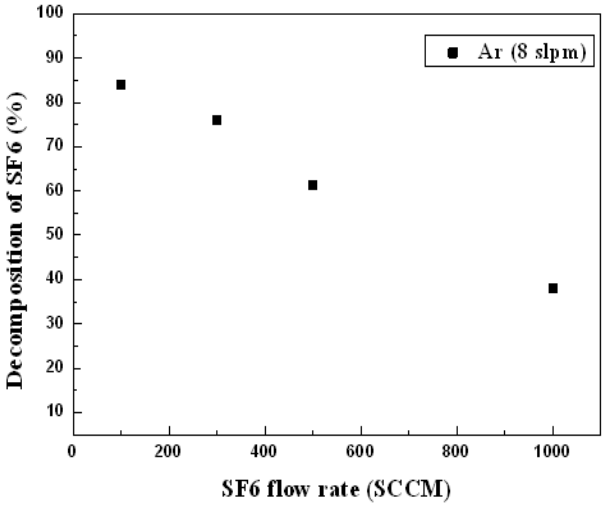

Fig.3 The decomposition of SF_6 as a function of treatment flow rate

l/min and SF_6 flow rate of 100 SCCM.

Fig.4 presents the trend of SF_6 decomposition with changing the treatment gas flow rate. The decomposed amount of SF_6 was decreased by increasing the plasma gas and SF_6 gas flow rate. It was due to the short residence time as increasing the gas flow rate. It seems that the decomposed amount of SF_6 is greatly influenced by the gas flow rate. The decomposition of SF_6 had gone down to about 10% at thermal plasma power of 5 kW (200 A), Ar plasma gas flow rate of 12 l/min and SF_6 flow rate of 1000 SCCM.

The decomposition of SF_6 in the presence of O_2 and H_2 fixed at 100 SCCM was tested over the same range of gas flow rates. The Fig.5 presents the increase of the SF_6 decomposition efficiency by adding H_2 and O_2. The decomposition of SF_6 was quite increased when H_2 and O_2 were added. Especially when H_2 was injected, the decomposition rate of SF_6 was better. The decomposition rate of SF_6 was 99.2% at thermal plasma power of 5 kW

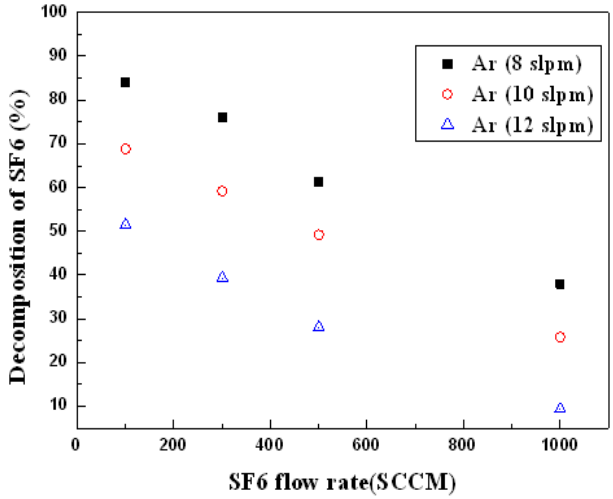

Fig.4 The decomposition of SF_6 as a function of the gas flow rate

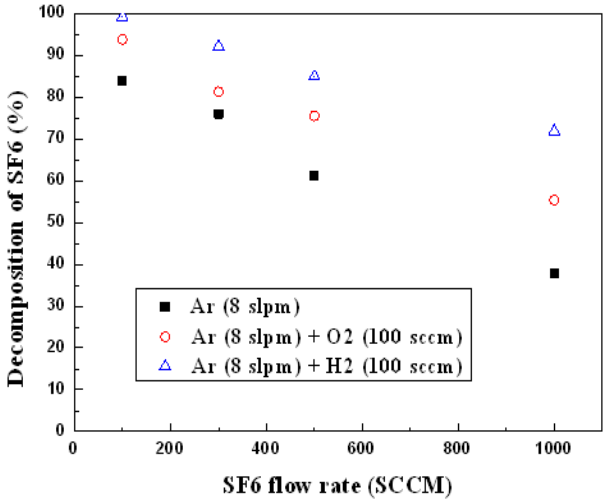

Fig.5 The decomposition of SF_6 as a function of adding gases

(200 A), Ar plasma gas flow rate of 8 l/min and SF_6 flow rate of 100 SCCM and H_2 flow rate of 100 SCCM when H_2 was used as the additive gas.

When H_2 and O_2 were added, the decomposition of SF_6 was elevated at the each case. In case of adding H_2, it appears that H_2 was easily decomposed into active species such as H atoms and then reacted with SF_6. The active fragments from H_2 form highly stable products, mainly F_2, HF, etc. This result was not only a significant improvement in the decomposition of SF_6, but also an inhibition of the recombination of SF_6. And when O_2 was added, SF_6 and its fragments react with O_2 and O atoms to form SO_2 and sulfur oxyfluorides, such as SO_2F_2, SOF_2, and SOF_4 which could inhibit the recombination of SF_6.

4. Conclusions

An experimental investigation has been performed for decomposition of SF_6 using a thermal plasma system. The decomposition of process gases was conducted at atmospheric pressure. The plasma gas and the SF_6 gas flow rates were employed as the main operating variables. Since decomposition efficiency was related to the residence time, the decomposed amount of SF_6 was decreased as the Ar and SF_6 gases flow rates were increased. Moreover, the decomposition of SF_6 was enhanced by adding the additive gases. The results show that decreasing the gas flow rate and adding the additive gases can produce the most effective decomposition of SF_6. In addition, adding hydrogen was better than adding oxygen as the auxiliary gas. When using H_2 as the additive gas, the decomposition of SF_6 gas has been achieved up to 99.2 % at 5 kW.

The pure SF_6 gas is in common used as an isolator of a current transformer. The results of the decomposition efficiency in this study indicated that thermal plasma processing could be applied successfully for the decomposition of pure SF_6. Therefore, it is expected that

the diluted PFCs including SF_6 in the semiconductor industry would be treated easily if the thermal plasma processing is employed.

Acknowledgments

This work was supported by the Regional Innovation Center for Environmental Technology of Thermal Plasma (ETTP) at Inha University designated by MKE (2009).

5. References

[1] Wen-Tien Tsai, Horng-Ping Chen and Wu-Yuan Hsien, A review of uses, environmental hazards and recovery/recycle technologies of perfluorocarbons (PFCs) emissions from the semiconductor manufacturing processes, *Journal of Loss Prevention in the Process Industries* 15, 2 (2002)

[2] Kunihihiko, Koike, Tatsu Fukuda, Schizuichi Fujikaa and Manabu Saeda, *Jpn. J. Appl. Phys.* **36**, p. 5274, (1993)

[3] Dong-yun Kim and Dong Wha Park, Decomposition of PFCs by steam plasma at atmospheric pressure, *Surface and Coatings Technology* 202, 22-23 (2008).

[4] Kyoto Protocol, Climate Change Conference, Kyoto, Japan, Dec. 1–10 (1997).

[5] F. Dentener, R. Derwent, E. Dlugokencky, E. Holland, I. Isaksen, V. Kirchhoff, P. Matson, M. Midgley and M. Wang, Climate change: the scientific basis. In: J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. Van der Linden, X. Dai, K. Maskell and C.A. Johnson, Editors, *Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change* 1, Cambridge University Press, New York, pp. 239-288, (2001).

[6] R.J. Van Brunt, J.T. Herron, Fundamental process of SF6 decomposition and oxidation in glow and corona discharge, *IEEE Trans. Electr. Insul.* 25, 75-93 (1990)

[7] Cheng-Hsien Tsai, Jen-min Shao, Formation of fluorine for abating sulfur hexafluoride in an atmospheric-pressure plasma environment, *Journal of Hazardous Materials*, 157, 1 (2008).

[8] J.T. Houghton, L.G. Meira Filho, B.A. Callander, N, Harris, A. Kattenberg, K. Maskell, Climate Change 1995-The Science of Climate Change, Cambridge University Press, New York, p. 121, (1996).

[9] Chemsage, software program, Version 3.2, GTT-Technologies, Germany.

[10] Park, Dong Wha, Doc, Thesis, Dept. of Chem. Eng., Tokyo Institute of Technology (1988).