Conversion of SF₆ by thermal plasma at atmospheric pressure

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Abstracts: Sulphur hexafluoride (SF₆) gas which has high global warming potential (GWP₁₀₀=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 SF₆ gas was analyzed using GC. The decomposed amount of SF₆ gas was decreased as the plasma gas flow rate was increased. Additive gases (H₂, O₂) were used to increase the decomposition of SF₆ gas. In case of adding H₂ gas, the decomposition of SF₆ gas was better than that of SF₆ for adding O₂ gas. About 99% decomposition of SF₆ gas has been achieved.

Keywords: Thermal plasma, PFCs, SF₆, decomposition

1. Introduction

Perfluorocompounds (PFCs) including CF₄, C₂F₆, C₃F₈, CHF₃, SF₆, and NF₃ 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 greenhouse 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 (CO₂, NO₂, CH₄, 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].

SF₆ 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 (GWP₁₀₀=23,900) [5].

Although the abatement of SF₆ gas is performed through thermal treatment or a catalytic process, SF₆ is difficult to be treated effectively in the gas phase [6].

In this study, we have investigated the decomposition of pure SF₆ gas which is using as an isolator of a current transformer. The additive gases, such as H₂ and O₂, were injected into the system to attain the developed decomposition of SF₆. However, the hydrocarbons, such as CH₄ or C₂H₆, were not injected because of avoiding the formation of carbon-containing compounds, such as CF₄, CO, CO₂ [7]. It has been expected that we will get better decomposition rate if diluted gas using in the semiconductor industry instead of pure SF₆ is treated by thermal plasma.

2. Experimental

The thermal plasma abatement device used to investigate the decomposition of SF₆ 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 SF₆ gas flow rate and additive gases injected. 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 SF₆ 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
amounts of SF₆ 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 SF₆ was calculated by using the equation (1).

\[
\text{Decomposition}_{\text{SF₆}}(\%) = \frac{C_{i_{\text{SF₆}}} - C_{f_{\text{SF₆}}}}{C_{i_{\text{SF₆}}}} \times 100 \tag{1}
\]

where \(C_i\) and \(C_f\) are the concentrations of the SF₆ 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 SF₆, (b) SF₆/O₂ = 1, and (c) SF₆/H₂ = 1 at atmospheric pressure. Chemical equilibrium compositions were calculated by the software program based on Gibbs free energy minimization [9]. The pure SF₆ 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 SF₆ is easily decomposed by thermal plasma. In case of adding O₂, the temperature for the decomposition of SF₆ scarcely changes. However, for adding H₂, SF₆ 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 H₂.

Fig. 3 shows that the decomposition of SF₆ was decreased as SF₆ flow rate was increased. The decomposition of SF₆ was tested over a variety of SF₆ 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 SF₆ reached up to 83.9 % at the thermal plasma power of 5 kW (200 A), Ar plasma gas flow rate of 8

<table>
<thead>
<tr>
<th>Table 2 Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input power</strong></td>
</tr>
<tr>
<td><strong>Plasma gas flow rate (Ar)</strong></td>
</tr>
<tr>
<td><strong>SF₆ gas flow rate</strong></td>
</tr>
<tr>
<td><strong>Additive gas flow rate (H₂, O₂)</strong></td>
</tr>
<tr>
<td><strong>Analysis</strong></td>
</tr>
</tbody>
</table>

Fig. 2 Thermodynamic equilibrium composition of (a) pure SF₆, (b) SF₆ and O₂, (c) SF₆ and H₂
Fig. 3 The decomposition of SF$_6$ as a function of treatment flow rate 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 (200 A), Ar plasma gas flow rate of 8 l/min and SF$_6$ 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$_2$F$_2$, 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 SF₆ in the semiconductor industry would be treated easily if the thermal plasma processing is employed.

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5. References