

# EXPERIMENTAL STUDY ON FLAMMABILITY CONCENTRATION AREAS OF CO/F<sub>2</sub>/N<sub>2</sub> AND SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> MIXTURES

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## ABSTRACT

Recently, a variety of gases have been used in advanced technological industries, such as a semiconductor industry. There are several highly reactive gases among them. Fluorine is one of the representative gases which have very high reactivity. Its high reactivity has been known qualitatively for a long time. But its quantitative hazard has not been assessed yet.

In this study, a flammability area of a CO/F<sub>2</sub>/N<sub>2</sub> mixture was determined experimentally, and designated in a triangular diagram. And, a flammability area of a SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture was also determined and designated in a triangular diagram. CF<sub>3</sub>OF is a product of a reaction between CO and F<sub>2</sub>, which are components of the first mixture, and used as an etching or a cleaning gas in a semiconductor industry. Namely, there is a possibility of accidental mixing between SiH<sub>4</sub> and CF<sub>3</sub>OF. SiH<sub>4</sub> is a material of silicon based semiconductors. The flammability diagrams obtained in this study are indispensable for safe handling of these gases.

**KEYWORDS:** Semiconductor material gases, Flammability, Explosion

## INTRODUCTION

Recently, many kinds of gases have been used in semiconductor industries. There are several gases, which have not been used widely, so their flammability characteristics are not known well. The author and co-workers had studied several such gases and reported their flammability characteristics already<sup>1-5</sup>. However, there are many gases remained unknown and improvement of semiconductor technologies is refreshing a list of their gas storage.

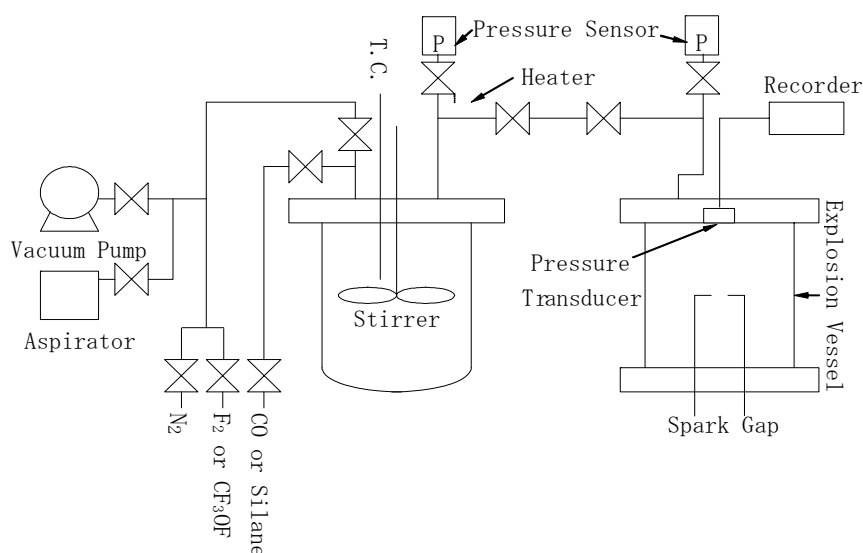
In this study, flammability of CO with F<sub>2</sub> in nitrogen atmosphere was investigated at first. They are mixed when producing CF<sub>3</sub>OF and sometimes explosion occurred while mixing. However, quantitative evaluation of their flammability had not been conducted. Then, flammability of a SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture was also evaluated. CF<sub>3</sub>OF is a product of the first mixture, and used as an etching or a cleaning gas in a semiconductor industry. On the other hand, SiH<sub>4</sub> is the most frequently used gas for semiconductor production. Namely, there is a possibility of accidental mixing between SiH<sub>4</sub> and CF<sub>3</sub>OF.

The above facts can be drawn qualitatively from the fundamental chemical knowledge, but they are not enough for preventing explosion hazard. Combinations of these gases must not be avoided. These gases must be used together for producing some semiconductors. Quantitative evaluation of their flammability diagram should be done for reducing explosion hazard in such industries.

## EXPERIMENTAL

### Experimental Apparatus

Fig. 1 illustrates overall view of an experimental apparatus. The explosion vessel was made from a stainless steel cylinder. Its inner diameter was 100mm, and height was 100 mm. There was another stainless vessel used for mixing gases before introducing them into the explosion vessel. A couple of tungsten spark plugs were set at ca. 50mm above the bottom of the vessel. Pressure history after ignition was measured by a pressure transducer, and recorded by a digital storage oscilloscope.



**FIGURE 1.** Experimental apparatus for examining flammability area

### Experimental Procedure

The explosion vessel, the mixing vessel, and piping were vacuumed at first, and then each component was introduced into the mixing vessel as each gas had predetermined partial pressure. Composition of the mixture was determined from partial pressures of each gas. Then it was transferred to the explosion vessel as the mixture had atmospheric pressure. There was possibility that the gases evaluated in this study might cause auto-ignition while mixing. Therefore, a diluted flammable gas was transferred to the explosion vessel at first. Then, a diluted oxidizing gas was introduced into the explosion vessel. Pressure history while introducing the oxidizing gas was recorded for judging the mixture cause auto-ignition or not. Occurrence of auto-ignition was judged from deviation of the pressure history from which recorded for introducing 100% nitrogen. When there was no auto-ignition, the mixture was ignited in the explosion vessel with ignition energy of 300 J (15 kV, 20 mA, 1 s) supplied by a neon transformer-type power supply. Pressure history after ignition was also recorded by a digital storage oscilloscope. Occurrence of explosion was judged from the maximum pressure exceeded 0.01 MPa or not.

### Sample Gases

The first mixture tested was composed of carbon monoxide (CO), fluorine (F<sub>2</sub>) and nitrogen. In this mixture, CO, F<sub>2</sub> and N<sub>2</sub> are flammable, oxidizing and inert gases, respectively. The second mixture was composed of silane (SiH<sub>4</sub>), CF<sub>3</sub>OF and nitrogen. In this case, SiH<sub>4</sub>, CF<sub>3</sub>OF and N<sub>2</sub> are flammable, oxidizing and inert gases, respectively.

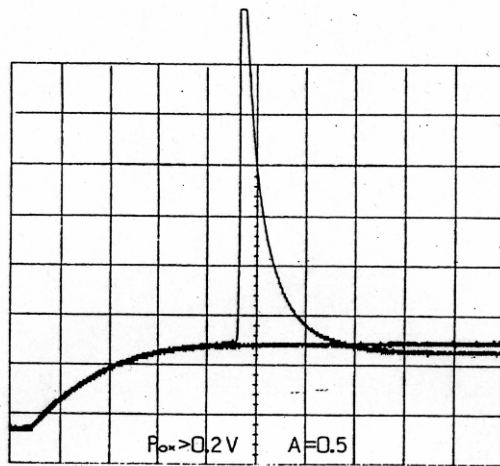
## RESULTS AND DISCUSSION

### CO/F<sub>2</sub>/N<sub>2</sub> Mixture

Reactivity of the CO/F<sub>2</sub>/N<sub>2</sub> mixture has revealed to have three regimes. They are auto-ignition regime, flammable regime and no-reaction regime. In the auto-ignition regime, auto-ignition occurs while mixing the flammable gas with the oxidizing gas. In the flammable regime, an explosion occurs when the CO/F<sub>2</sub>/N<sub>2</sub> mixture was ignited. Of course, no reaction occurs in the no-reaction regime.

#### 1) Pressure history

Three types of pressure history were observed in the auto-ignition regime.



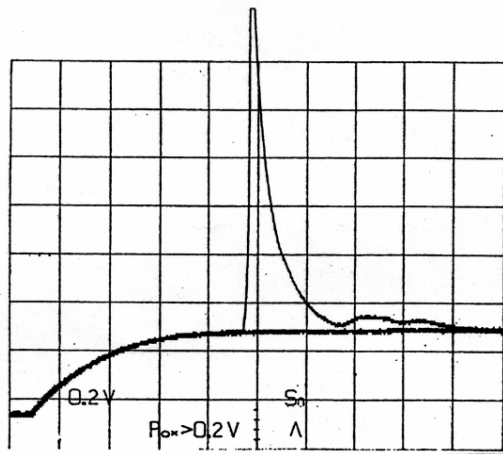
**FIGURE 2.** Pressure history of the 1st type auto-ignition

Fig. 2 shows a pressure history recorded during the mixture cause the first type auto-ignition. There are two curves. The first one is for a real test run, and another is for a blank run. The pressure history of the blank run shows pressure increased gradually and approached the atmospheric pressure.

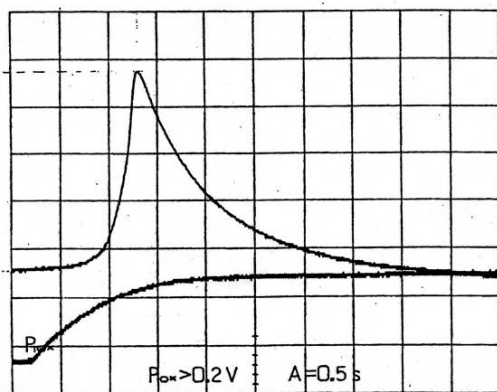
As seen from Fig. 2, pressure history of the real test run shows deviation from the blank run. Auto-ignition occurred at the time when whole oxidizing gas was introduced into the explosion vessel. It is apparent from sudden increase of pressure near the center line. After the auto-ignition pressure went down under the blank run. It means decrease of molecule number after the auto-ignition.

Fig. 3 shows a pressure history recorded during the mixture cause the second type auto-ignition. In this case also, auto-ignition occurred at the time when whole oxidizing gas was introduced into the explosion vessel. But there is difference in the pressure history from which of the first type auto-ignition after the auto-ignition occurred. There was fluctuation of pressure after the auto-ignition, and pressure approached the atmospheric one. Namely, in the case of second type auto-ignition, no change occurred in molecule number before and after auto-ignition.

Fig. 4 shows a pressure history recorded during the mixture cause the third type auto-ignition. In this case, auto-ignition occurred at several tens seconds to several minutes after whole oxidizing gas was introduced into the explosion vessel. The upper curve follows the right end of the lower curve. This shows reaction rate of the auto-ignition process is rather slow, and no change in molecule number occurs before and after the auto-ignition.



**FIGURE 3.** Pressure history of the 2nd type auto-ignition



**FIGURE 4.** Pressure history of the 3rd type auto-ignition

## 2) Flammability diagram

Fig. 5 shows the flammability diagram of the  $\text{CO}/\text{F}_2/\text{N}_2$  mixture. The flammability area includes the explosion regime and the auto-ignition regime. The explosion regime locates at the outermost area of the flammability area. The auto-ignition regime is enveloped by the explosion regime. In the auto-ignition regime, the first and the second type auto-ignition locates at the inner of the third type auto-ignition. Moreover, the first type auto-ignition looks to locate and the second type looks to locate upper the line which shows ratio of  $\text{F}_2$  concentration to  $\text{CO}$  concentration is 1. It gives valuable information for estimating reaction equations occurred at the first and the second type auto-ignitions.

## 3) Gas analysis

Table 1 shows gas components before and after reaction. As seen in this table, major product of auto-ignition reaction is  $\text{COF}_2$ . Because  $\text{F}_2$  is very active,  $\text{F}_2$  did not remain after reaction even if  $\text{F}_2$  was rich. But  $\text{CO}$  remained after reaction if  $\text{CO}$  was rich. Existence of  $\text{CO}_2$  suggests that there should be oxidation of  $\text{CO}$  to  $\text{CO}_2$  in these reactions.

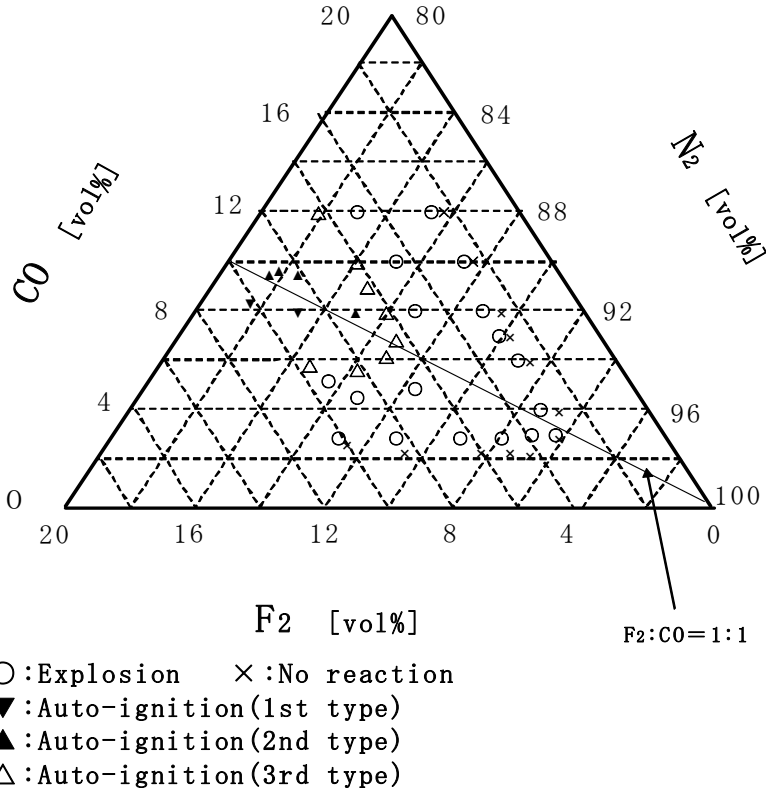


FIGURE 5. Flammability diagram of the CO/F<sub>2</sub>/N<sub>2</sub> mixture

TABLE 1. Gas concentration after reaction

	Conc. (vol %)	Run 1	Run 2	Run 3	Analyzer
Before mixing	F <sub>2</sub>	7.06	13.82	2.29	
	CO	13.22	7.27	12.61	
	N <sub>2</sub>	79.72	78.91	85.1	
Regime name		2nd type auto-ignition	1st type auto-ignition	Explosion	
After mixing	CO	11.25	—	9.65	FT-IR
	CF <sub>4</sub>	0.01	0.17	—	GC-MS
	CO <sub>2</sub>	0.55	0.38	1.93	GC-MS
	COF <sub>2</sub>	7.08	6.57	1.56	GC-MS
	CF <sub>3</sub> OF	—	0.7	—	GC-MS
	F <sub>2</sub>	—	—	—	GC-MS
	N <sub>2</sub>	—	—	—	

#### 4) Reaction schemes

Reaction between CO and F<sub>2</sub> is supposed to be as follows.

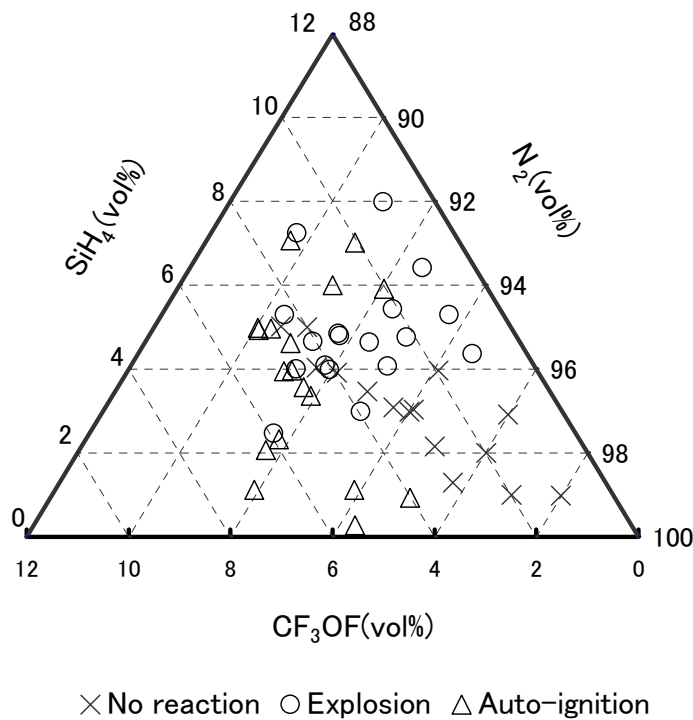


These reactions are both exothermic reactions. From observations mentioned above, major reaction occurred in the 2nd type auto-ignition regime (CO rich) and the explosion regime is reaction equation [1]. In the 1st type auto-ignition regime (F<sub>2</sub> rich), reaction equation [2] occurs in addition to reaction equation [1].

From consideration of gas components shown in table 1, another possible reaction is reaction equation [3].



Produced carbon reacts with fluorine if there was remaining fluorine.



**FIGURE 6.** Flammability diagram of the SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture

All reactions mentioned are those in which molecule number decreases. However, pressure decrease after reaction was observed just for the 1st type auto-ignition. Reaction equation (2) occurs only in the 1st type auto-ignition, and molecule number decrease is the largest. As a result, molecule number decrease in the 1st type auto-ignition regime is larger than the other regimes.

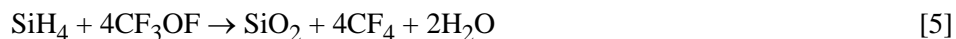
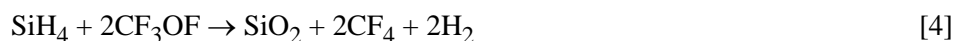
### SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture

#### 1) Flammability diagram

Fig. 6 shows the flammability diagram of the SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture. The SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture also causes auto-ignition and explosion. However, their occurrence in this experiment was very probabilistic. There was no clear regime observed. Only thing it can be said is that no reaction occurs if N<sub>2</sub> concentration in the mixture was very high.

## 2) Reaction schemes

Reaction between SiH<sub>4</sub> and CF<sub>3</sub>OF is supposed to be as follows.



Products of these reactions could not be identified quantitatively. However, there remained solid products in the explosion vessel after each test run. Their colors were white, yellow and black. Powder of SiO<sub>2</sub> should have white color. So there were other solid products which were not expected from above equations.

## CONCLUSIONS

Flammability characteristics of the CO/F<sub>2</sub>/N<sub>2</sub> mixture and the SiH<sub>4</sub>/CF<sub>3</sub>OF/N<sub>2</sub> mixture were examined experimentally in this study. These mixtures show auto-ignition in some conditions and explosion in some other conditions. Reaction schemes occurred in the former mixture was revealed rather clearly, but that in the later mixture was not clear. Their flammability diagrams were shown quantitatively.

## ACKNOWLEDGEMENT

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