

## **Flammability limits of silane/perfluorocarbon/nitrogen mixtures**

Hideo OHTANI

Corresponding author: Hideo OHTANI

Academic degree: Dr. of Engineering

Position: Associate Professor

Professional or Academic affiliation: Yokohama National University

Mailing address: 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN

Phone: +81-339-3982

Fax: +81-339-4011

E-mail address: hohtani@ynu.ac.jp

**Paper No.031201; JLPPI**

## **Abstract**

Perfluorocarbons are known to react with silane because silane is a very strong reducing agent. However, quantitative information on their explosion limits are not known. So, in this study, flammability of silane/perfluorocarbon/nitrogen was examined experimentally. Their flammability areas were revealed quantitatively as triangular flammability diagrams, and the fact that perfluorocarbon reacts with silane was ascertained.

## **1. Introduction**

Recently, many kinds of gas have been used in semiconductor industries. There are several gases, which have not been used widely, so their flammability characteristics are not known well. Lee, Ohtani, Uehara, & Aramaki (1992) and Ohtani, Lee, & Uehara (1994) studied a few gases and reported their flammability characteristics already. However, there are many gases remaining to be examined. In this study, a combination of silane and perfluorocarbon was studied.

As one of semiconductor material gases, halogenated hydrocarbons are known to react with silane. Perfluorocarbons are included in such gases. In this case, as silane is a strong reductant, perfluorocarbon is considered to act as an oxidizer. Reactivity of a combination of chemical materials depends on relative stability of reactants and products. If there were any more stable products than reactants, reaction may occur. In the case of perfluorobutane and silane, methane and silicon tetrafluoride ( $\text{SiF}_4$ ) are estimated as products and they are more stable than reactants.

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.

Then, in this study, flammability diagrams of  $C_mF_{2m+2}$  with silane are evaluated quantitatively.

## 2. Experimental procedure

### (1) Experimental apparatus.

The same experimental apparatus described in Lee et al. (1992) was used. It consists of an explosion vessel, a mixing vessel, a vacuum pump, and piping between them.

The explosion vessel was made from a stainless steel cylinder. Its inner diameter was 100mm, and height was 100mm. 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.

### (2) 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. The mixture was ignited in the explosion vessel with ignition energy of 300J (15kV, 20mA, 1s) supplied by a neon transformer-type power supply. Pressure history after ignition was recorded by a digital storage oscilloscope. Occurrence of explosion was judged from the maximum pressure exceeded 0.01 MPa or not.

### (3) Sample gases.

Tested mixture was composed of silane ( $SiH_4$ ),  $C_mF_{2m+2}$  and nitrogen ( $N_2$ ). As  $C_mF_{2m+2}$ ,

perfluoroethane (C<sub>2</sub>F<sub>6</sub>), perfluorobutane (C<sub>4</sub>F<sub>10</sub>), perfluorohexane (C<sub>6</sub>F<sub>14</sub>), and perfluorooctane (C<sub>8</sub>F<sub>18</sub>) were used.

### 3. Flammability areas

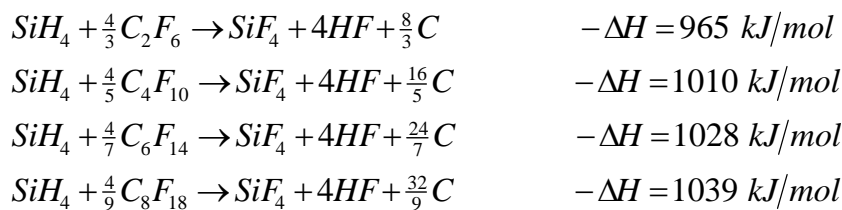
Figures 1-4 show triangular flammability diagrams of SiH<sub>4</sub>/C<sub>2</sub>F<sub>6</sub>/N<sub>2</sub>, SiH<sub>4</sub>/C<sub>4</sub>F<sub>10</sub>/N<sub>2</sub>, SiH<sub>4</sub>/C<sub>6</sub>F<sub>14</sub>/N<sub>2</sub>, and SiH<sub>4</sub>/C<sub>8</sub>F<sub>18</sub>/N<sub>2</sub> mixtures. Straight lines in the triangular diagrams show chemical stoichiometric composition for each mixture. Reaction equation of each mixture will be discussed later. It should be noted that scale of each diagram is different.

Peak of the flammability area is not clear for the C<sub>2</sub>F<sub>6</sub> mixture. It looks like to have two heads. Peak of the flammability area for the C<sub>4</sub>F<sub>10</sub> mixture is rather clear than that for the C<sub>2</sub>F<sub>6</sub> mixture.

Although there is a little quantitative difference, flammability areas of C<sub>6</sub>F<sub>14</sub> mixture and C<sub>8</sub>F<sub>18</sub> mixture had almost the same shapes with that of the C<sub>4</sub>F<sub>10</sub> mixture. Peak concentrations and observed lowest concentrations of each component along the flammability area for the SiH<sub>4</sub>/C<sub>m</sub>F<sub>2m+2</sub>/N<sub>2</sub> mixtures are summarized in Table 1.

### 4. Reaction equations

Reaction equations are estimated as follows by using computer program CHETAH (ASTM (1994)), which conducts thermodynamic calculation.



These reaction equations were ascertained indirectly by facts that there remained carbon deposit in the explosion vessel after explosion, and peaks of their flammability areas are close to the lines showing stoichiometry for the reaction equations.

These large heats of reaction are related with differences in heats of formation between reactants and products. Related bond energies are Si-H(319kJ/mol), C-F(484kJ/mol), Si-F(592kJ/mol), H-F(567 kJ/mol), and C-H(411kJ/mol). Namely, Si is more stable when it combines with F than H, and F is more stable when it combines with H than C. Therefore, the products are expected from the reactants.

Adiabatic flame temperatures at boundaries of the flammability area for the second type mixtures were calculated by using Gibb's free energy. The adiabatic flame temperatures for C<sub>4</sub>F<sub>10</sub>, C<sub>6</sub>F<sub>14</sub>, and C<sub>8</sub>F<sub>18</sub> mixtures are all 1500 K. However, the adiabatic temperature for C<sub>2</sub>F<sub>6</sub> mixture is 1800 K. The difference of the adiabatic flame temperatures comes from difference in C-C bond energy between C<sub>2</sub>F<sub>6</sub> and others. Namely, bond dissociation energy of CF<sub>3</sub>-CF<sub>3</sub> bond (410kJ/mol) is larger than other normal C-C bond (354kJ/mol).

## 5. Conclusion

Flammability characteristics of silane in perfluorocarbon atmosphere were examined experimentally in this study. Flammability diagrams several silane/perfluorocarbon/nitrogen mixtures and their peak concentrations were obtained quantitatively. It will be useful to avoid explosion incidents in using silane and some perfluorocarbon simultaneously.

## References

Lee, S.G., Ohtani, H., Uehara, Y., & Aramaki, M. (1992), Experimental Study on

Flammability Limit of Chlorine Trifluoride/Dichlorosilane/Nitrogen Mixture. In *Journal of Loss Prevention in Process Industries*, 5, 192-195.

Ohtani, H., Lee, S.G., & Uehara, Y. (1994), Combustion Characteristics of Several Flammable Gases with Chlorine Trifluoride. In *Proceedings of the Fourth International Symposium on Fire Safety Science*, Ottawa, Canada, 493-502.

ASTM (1994), CHETAH ver.7.0 The ASTM Computer Program for Chemical Thermodynamic and Energy Release Evaluation (NIST Special Database 16), 3<sup>rd</sup>. Ed., In ASTM Data Series DS 51B, ASTM, Philadelphia.

## List of Table and Figures

TABLE 1 Peak concentrations of  $N_2$  and lowest flammable concentrations of  $SiH_4$  and  $C_mF_{2m+2}$  for  $SiH_4/C_mF_{2m+2}/N_2$  mixture.

FIGURE 1 Flammability areas of  $SiH_4/C_2F_6/N_2$  mixture.

FIGURE 2 Flammability areas of  $SiH_4/C_4F_{10}/N_2$  mixture.

FIGURE 3 Flammability areas of  $SiH_4/C_6F_{14}/N_2$  mixture.

FIGURE 4 Flammability areas of  $SiH_4/C_8F_{18}/N_2$  mixture.

TABLE 1 Peak concentrations of N<sub>2</sub> and lowest flammable concentrations of SiH<sub>4</sub> and C<sub>m</sub>F<sub>2m+2</sub> for SiH<sub>4</sub>/C<sub>m</sub>F<sub>2m+2</sub>/N<sub>2</sub> mixture.

	C <sub>2</sub> F <sub>6</sub>	C <sub>4</sub> F <sub>10</sub>	C <sub>6</sub> F <sub>14</sub>	C <sub>8</sub> F <sub>18</sub>
Peak concentration of N <sub>2</sub> (vol%)	58	83.8	87.3	87.4
Lowest SiH <sub>4</sub> concentration (vol%)	18	9.8	8.8	9.0
Lowest C <sub>m</sub> F <sub>2m+2</sub> concentration (vol%)	14	4.8	3.0	2.6



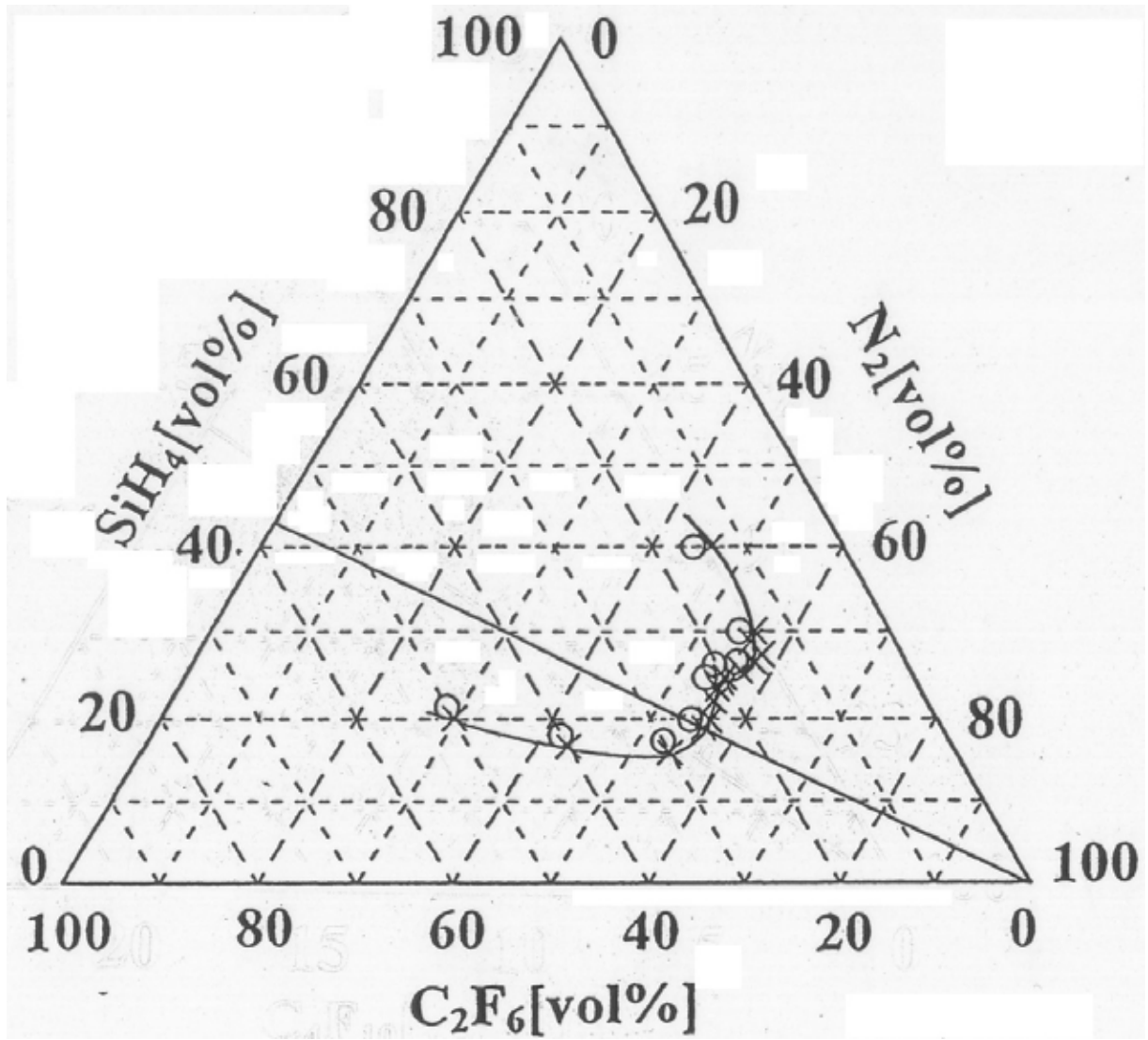


FIGURE 1 Flammability areas of SiH<sub>4</sub>/C<sub>2</sub>F<sub>6</sub>/N<sub>2</sub> mixture.

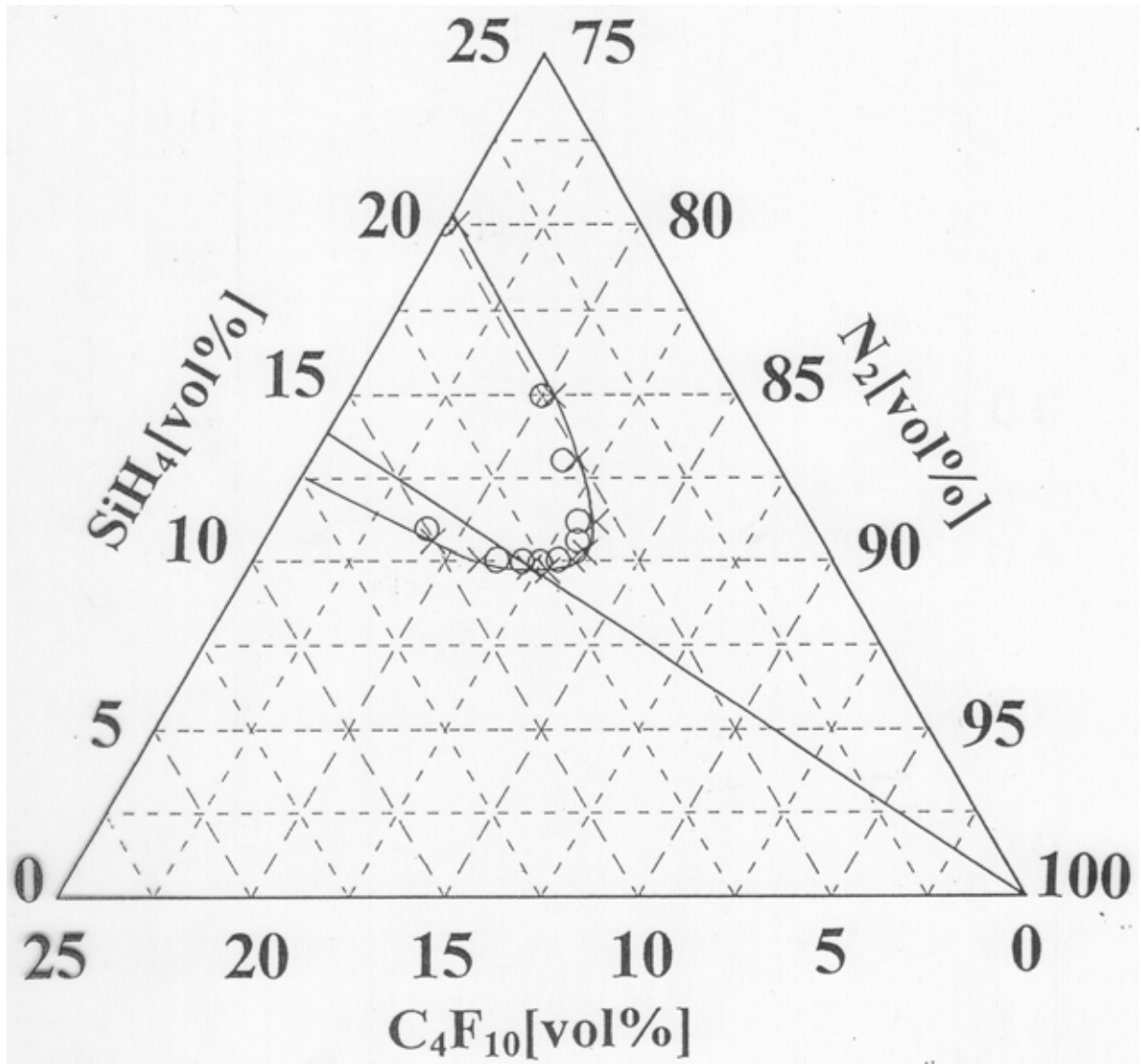


FIGURE 2 Flammability areas of  $\text{SiH}_4/\text{C}_4\text{F}_{10}/\text{N}_2$  mixture.

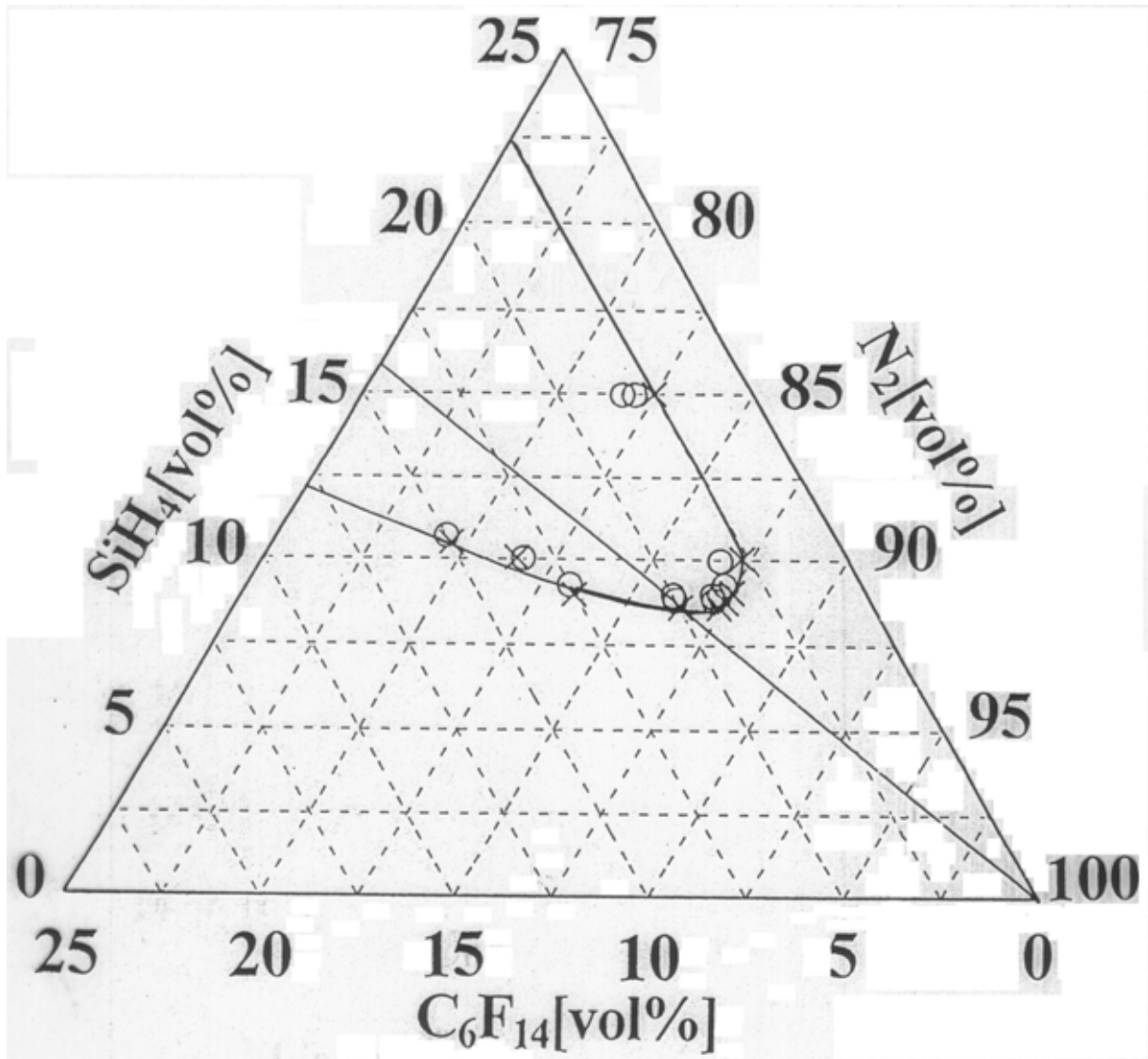


FIGURE 3 Flammability areas of  $\text{SiH}_4/\text{C}_6\text{F}_{14}/\text{N}_2$  mixture.

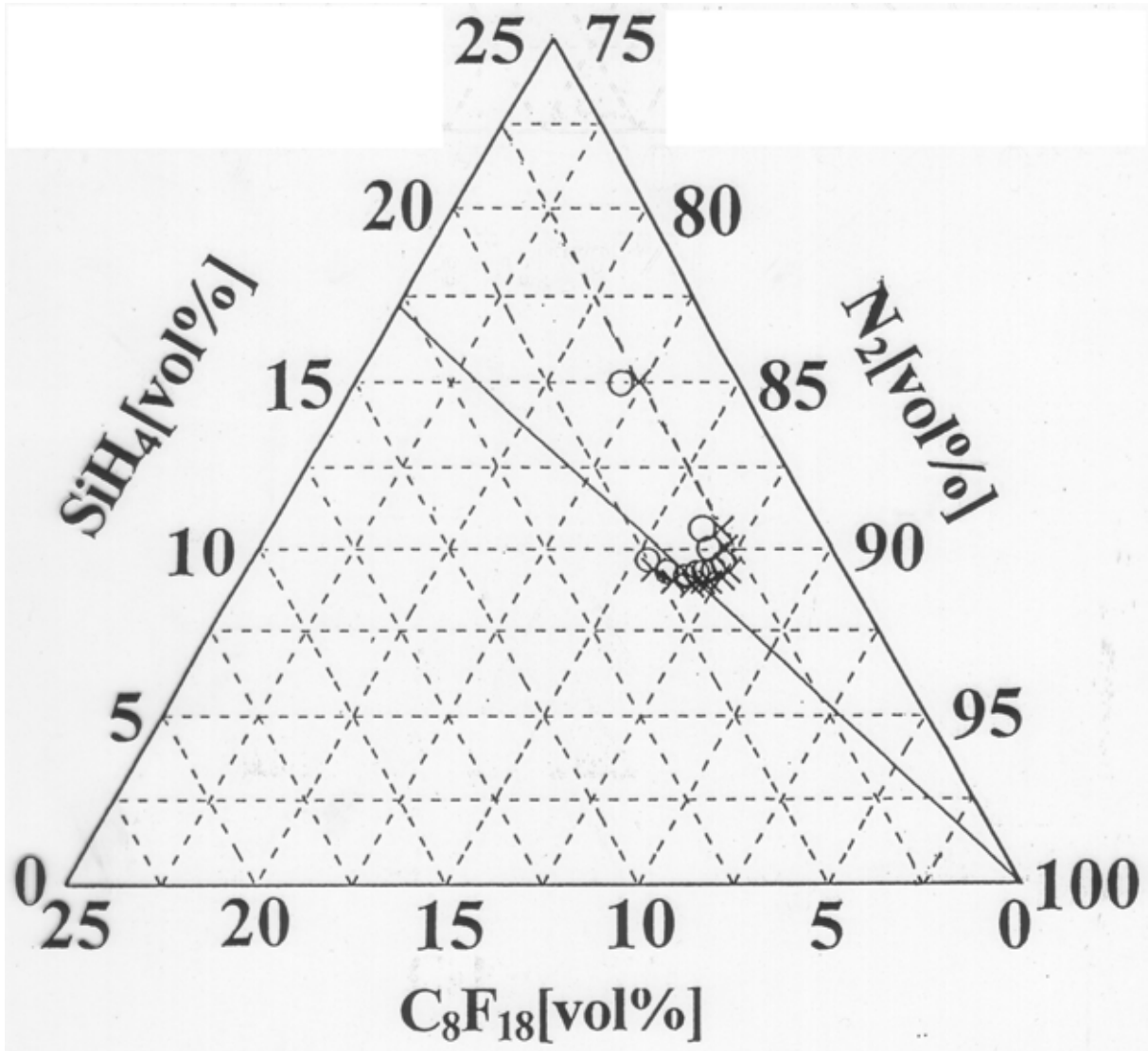


FIGURE 4 Flammability areas of  $\text{SiH}_4/\text{C}_8\text{F}_{18}/\text{N}_2$  mixture.

## Replies to the reviewer's comments

1. "Explosion limits" is used in the title, but "flammability limit or area" is used throughout the text. It is suggested to either be used.

According to this comment, the title was changed as "Flammability limits of silane/perfluorocarbon/nitrogen mixtures".

2. "Tetrafluorosilane(SiF<sub>4</sub>)" may be "silicon tetrafluoride(SiF<sub>4</sub>)".

As pointed out, "silicon tetrafluoride" is used in the CAS registry. So that term was changed to silicon tetrafluoride.