Combustion Characteristics of Several Flammable Gases with Chlorine Trifluoride

HIDEO OHTANI, LEE SAN GON and YOICHI UEHARA
Department of Safety Engineering, Faculty of Engineering
Yokohama National University
156 Tokiwadai, Hodogaya-Ku, Yokohama 240, Japan

ABSTRACT

There are several flammable gases used in semiconductor industries, and some oxidizing gas such as chlorine trifluoride (ClF₃) is also used in the same production apparatus. As knowledge of the combustion characteristics of flammable gases with oxidizing gases other than oxygen are lacking, an experimental study to evaluate combustion characteristics was performed. Chlorine trifluoride, the oxidizing gas used in this study was commercialized recently for etching and cleaning purposes because of its powerful oxidizing ability. As flammable gases, tetraethyl orthosilicate (TEOS:Si(OC₂H₅)₄), hydrogen (H₂) and ammonia (NH₃) were investigated. These gases are toxic, except for hydrogen, and have high reactivity, so these gases were first diluted with nitrogen separately. The diluted TEOS and ammonia gases were found to ignite spontaneously while being mixed with the diluted ClF₃ gas. On the other hand, the diluted hydrogen gas could be mixed with the diluted ClF₃ gas without spontaneous ignition. And a H₂/ClF₃/N₂ mixture could be ignited by an electric spark. Therefore, for TEOS and ammonia, "flammable limit" means the limit of spontaneous combustion, and for hydrogen the flammable limit means the usual limit of ignitability by an external ignition source.

The flammability diagrams of TEOS/ClF₃/N₂, NH₃/ClF₃/N₂ and H₂/ClF₃/N₂ mixtures were determined. And reaction kinetics between them were discussed from observed combustion characteristics.

KEYWORDS: Chlorine trifluoride, TEOS, hydrogen, ammonia, flammability diagram, spontaneous ignition.

INTRODUCTION
In semiconductor industries, many flammable gases\(^1,2\) are used for doping and so on, and several oxidizing gases are used for etching and cleaning. Explosion accidents have happened concerning silane(SiH\(_4\)) such as one at Berkeley Heights, NJ on March 17, 1988, at Kodaira, a suburban Tokyo metropolis, on December 13, 1989, and one at Osaka University on October 2, 1991. At least, the first and the third accidents suggest the possibility of accidental mixing of a flammable gas with an oxidizing gas because they are both supplied to the same gas line in the present production system of semiconductors. However, the explosive hazard of a flammable gas usually has been assessed against air or oxygen. Evaluation of combustion characteristics in other oxidizing gases is indispensable for preventing explosive accidents of semiconductor gases.

Chlorine trifluoride(ClF\(_3\)) was commercialized recently to utilize its high reactivity in an oxidizing reaction. Combustion characteristics of flammable gases with ClF\(_3\) are not known well. The evaluation of explosion hazard of ClF\(_3\) has just been started\(^3,4\). Previous studies of the combustion characteristics of SiH\(_4\) and SiH\(_2\)Cl\(_2\) with ClF\(_3\) revealed the powerful oxidizing ability of ClF\(_3\). ClF\(_3\) was powerful enough to cause spontaneous ignition of the gases. In this study, combustion characteristics of tetraethyl orthosilicate(TEOS: Si(OC\(_2\)H\(_5\))\(_4\)), ammonia(NH\(_3\)) and hydrogen(H\(_2\)) with ClF\(_3\) were investigated experimentally. These gases are also frequently used in semiconductor industries.

**EXPERIMENTAL PROCEDURE**

Experimental apparatus consisted mainly of two dilution vessels and an explosion vessel all made of stainless steel(Fig. 1), of the inner space of the explosion vessel was 10 cm in diameter and 12 cm high. First the whole experimental apparatus was evacuated. Then, both ClF\(_3\) and one of flammable gases were diluted with nitrogen in the dilution vessels.

**FIGURE 1.** Schematic diagram of the experimental apparatus.
respectively. Concentrations of the diluted flammable gas and the diluted ClF₃ gas were
determined from partial pressures in the dilution vessels. The diluted flammable gas was
introduced first into the explosion vessel, at pressure up to 50 kPa. The diluted ClF₃ gas
was injected into the explosion vessel containing the diluted flammable gas by pressure
difference between the dilution and the explosion vessels up to 100 kPa. In a case of
TEOS or ammonia as flammable gas ignition occurred spontaneously by the injection of
the diluted ClF₃ gas when compositions of the diluted gases were in flammable range. In a
case of hydrogen as a flammable gas spontaneous ignition did not occur, so an electric
spark was applied after the diluted ClF₃ gas was well mixed in the explosion vessel. The
pressure and temperature histories during the injection of the diluted ClF₃ gas into the
explosion vessel or after an electric spark was applied were measured by using a pressure
transducer and a sheathed CA-thermocouple having 0.5 mm sheath diameter. Their
outputs were recorded by a storage oscilloscope (HITACHI VC-6045). No appreciable
temperature variation was observed near the flammable limit in a case of the spontaneous
ignition. Therefore, discussion in the following section will be focused on the pressure
history.

The tested gases were supplied as follows. ClF₃ was supplied as a liquefied gas in a 1 litre
cylinder. TEOS is liquid at the room temperature, so its vapor was drawn from a flask
containing liquid TEOS. Ammonia and hydrogen were supplied in 10 litre cylinders.

EXPERIMENTAL RESULTS AND DISCUSSION

Pressure History

Figure 2 shows an example of the pressure history after the initiation of the diluted ClF₃
gas injection into the explosion vessel. A pressure history labeled as blank in the figure
shows the history for the blank test in which pure N₂ was injected into the explosion vessel.
The pressure histories for the diluted ClF₃ gas differ obviously from the blank curve. As
mentioned before spontaneous ignition occurred when the diluted TEOS or ammonia gas
was in the explosion vessel and pressure histories for them show larger values than the
blank curve. The difference between these curves was considered to be caused by heat
release of the oxidation reaction meaning that the tested composition is in the flammable
range. As the actual composition at a point where the reaction started was unknown
because ignition occurred during injection, concentration of ClF₃ and TEOS or ammonia
will be represented by the values in the dilution vessels.

It should be noted that in case of TEOS the pressure increment appeared after the diluted
ClF₃ gas had been injected completely into the explosion vessel. But the pressure
increment was relatively small when the concentration of TEOS was low (TEOS 1). A
distinct pressure peak appeared when concentration of TEOS was relatively high (TEOS 2).
Although spontaneous ignition occurred similarly in case of the diluted ammonia gas, the
pressure increment appeared just after the initiation of the diluted ClF₃ gas injection. On
the other hand, no spontaneous ignition occurred with hydrogen as a flammable gas.
Therefore the pressure history for hydrogen was identical with the blank curve until the
well mixed hydrogen/ClF₃/N₂ mixture was ignited electrically. Accordingly, the flammable composition for the mixture in the explosion vessel was determined clearly in a case of hydrogen.

**Tetraethyl Orthosilicate (TEOS)**

Figure 3 shows relation between pressure increment and concentration of the diluted ClF₃ gas which was injected into the explosion vessel. In this figure the pressure increment means the maximum difference between pressure histories for the actual and the blank tests. Concentration of the diluted TEOS gas which was introduced into the explosion vessel before the injection of the diluted ClF₃ gas was set to 0.5 vol% and 0.25 vol%. This figure shows there are apparently three regimes. No pressure increment appears in the first regime under 0.9 vol% of ClF₃, i.e. the first regime is out of the flammable range. In the second regime between 0.9 vol% and 2.5 vol% of ClF₃, a little pressure increment was observed. The pressure increment was constant independently of the concentration of ClF₃. In the third regime over 2.5 vol% of ClF₃, the pressure increment increased linearly with the increase of ClF₃ concentration. Some chemical reaction occurred in the second and the third regimes, but the reaction was limited to some extent in the second regime, and more complete reaction occurred in the third regime.

Figure 4 shows variation of the elapsed time to reach the maximum pressure increment shown in Fig. 3. This figure shows the same three regions as Fig. 3. The maximum pressure increment appeared about 5 seconds after the initiation of the injection in the second region. At the boundary between the second and the third regions, the elapsed time was delayed slightly. Then the elapsed time decreased as the ClF₃ concentration increased in the third region. It took about one second to inject the prescribed amount of the diluted ClF₃ gas into the explosion vessel. Therefore, the main part of the reaction between ClF₃ and TEOS occurred after the injection terminated.
Concentration of ClF$_3$ [vol%]

**FIGURE 3.** Relation between the pressure increment and the ClF$_3$ concentration for TEOS. Concentration of the diluted TEOS gas was 0.5 vol%($\Delta$) or 0.25 vol%($\bigcirc$).

**FIGURE 4.** Relation between the elapsed time to reach the maximum pressure increment and the ClF$_3$ concentration for TEOS. Concentration of the diluted TEOS gas was 0.5 vol%($\Delta$) or 0.25 vol%($\bigcirc$).

From the result shown in Figs. 3 and 4, several reaction mechanisms between ClF$_3$ and TEOS were supposed and discussed. However, any clear image of the reaction mechanism could not be attained. The most important finding is that the reaction phenomena can be classified at the same concentration of ClF$_3$ independently of the TEOS concentration. This is considered to mean that a decomposition reaction of ClF$_3$ alone governs the whole reaction. But this supposition can not the explain presence of the second region. In the second region the ClF$_3$ concentration did not affect the maximum pressure increment and the elapsed time. To confirm the reaction mechanism between ClF$_3$ and TEOS, a more thorough investigation is indispensable.
Besides, the complete combustion reaction between them is expressed as
\[ Si(OC_2H_5)_4 + 12Cl\ell F_3 \rightarrow SiF_4 + 8CF_4 + 12HCl + 4H_2O, \quad \Delta H = -6493.2 \text{ kJ/mol} \]

But Stein\(^5\) reported that CIF\(_3\) decomposed at 220 °C like
\[ Cl\ell F_3 \rightarrow F_2 + Cl\ell F, \quad \Delta H = 108.7 \text{ kJ/mol} \]

This decomposition reaction was considered to occur before the complete combustion reaction. Taking this decomposition reaction into account and assuming that relatively stable C\(_1\)F\(_{12}\) did not react with TEOS, the complete combustion reaction was modified like
\[ Si(OC_2H_5)_4 + 24Cl\ell F_3 \rightarrow SiF_4 + 8CF_4 + 12HF + 4H_2O + 24Cl\ell F, \quad \Delta H = -7934.4 \text{ kJ/mol} \]

According to this reaction, TEOS can react with twofold amount of CIF\(_3\) compared with the complete combustion reaction, and release larger heat than the complete combustion reaction.

Figure 5 shows the flammability diagram for the TEOS/CIF\(_3\)/N\(_2\) mixture. Strictly speaking, this flammable range is that where the spontaneous ignition occurred. It is different from the usual flammable range where a flammable mixture is ignitable externally. However, an electric spark could not ignite a mixture out of the flammable range in Fig. 5, so the flammable range in Fig. 5 is believed to coincide with the usual flammable range. Open circles means the data belong to the second region (TEOS 1), and solid circles means those belong to the third region (TEOS 2). The lower limiting concentration for CIF\(_3\) and TEOS are ca. 0.6 vol\% and ca. 0.2 vol\%, respectively.

**Ammonia**

Figure 6 shows variations of the pressure increment and the elapsed time to reach the maximum pressure increment vs. the concentration of CIF\(_3\). The concentration of the diluted NH\(_3\) gas was kept at 1.45 vol\%. The minimum concentration of CIF\(_3\) at which the

![Figure 5](image-url)  
**FIGURE 5.** Flammability diagram of the TEOS/CIF\(_3\)/N\(_2\) mixture.
pressure increment appeared was 0.28 vol%. Above the limit concentration the pressure increment increased and the elapsed time decreased linearly as the ClF₃ concentration increased.

Figure 7 shows the flammability diagram of the NH₃/ClF₃/N₂ mixture. From this diagram the lower limiting concentration for NH₃ is 0.07 vol% and that for ClF₃ is 0.14 vol%. On the other hand, the complete combustion reaction between ClF₃ and NH₃ is expressed as

\[ \text{NH}_3 + \frac{3}{4} \text{ClF}_3 \rightarrow 2\frac{1}{4} \text{HF} + \frac{3}{4} \text{HCl} + \frac{1}{2} \text{N}_2. \]
\[ \Delta H = -516.1 \text{ kJ/mol} \]

Previously mentioned ratio for the limiting concentrations of NH₃ and ClF₃ is 1:2. The ratio is much smaller than that of the complete combustion reaction, i.e. 4:3.

With the assumption that ClF₃ decomposed before the combustion reaction as mentioned above, the former complete combustion reaction was modified as

\[ \text{NH}_3 + \frac{3}{2} \text{ClF}_3 \rightarrow 3\text{HF} + \frac{3}{2} \text{ClF} + \frac{1}{2} \text{N}_2. \]
\[ \Delta H = -604.1 \text{ kJ/mol} \]

This reaction has larger heat of reaction than the complete combustion reaction, and a ratio of concentrations for NH₃ and ClF₃ has closer value with the experimental one than the complete combustion reaction.

**Hydrogen**

Figure 8 shows variations of the maximum pressure and the elapsed time to reach the maximum pressure vs. the concentration of ClF₃. In the case of hydrogen no spontaneous

![Figure 6](image)

**FIGURE 6.** Variation of the pressure increment and the elapsed time to the maximum pressure increment with the ClF₃ concentration for ammonia. Concentration of ammonia was 1.45 vol%.
ignition occurred, so the maximum pressure was attained after an electric spark was applied to the H₂/ClF₃/N₂ mixture stirred well in the explosion vessel. In this case, the concentration for each composition is that for the mixture in the explosion vessel, not in the dilution vessel. The concentration of H₂ was kept at 3.0 vol% and the initial pressure in the explosion vessel was 0.05 MPa. In this figure, the maximum pressure means the difference between the absolute maximum pressure and the initial pressure. The minimum concentration of ClF₃ at which an explosion occurred was 1.7 vol%. Beyond the limit concentration, the pressure increment increased and the elapsed time decreased linearly as the ClF₃ concentration increased up to 3.0 vol% ClF₃. Higher concentrations of ClF₃ caused little effect on the maximum pressure and the elapsed time. This means that ClF₃...
reacts with \( \text{H}_2 \) at the equivalent molar ratio. From this result, the reaction between them was expected as

\[
\text{ClF}_3 + \text{H}_2 \rightarrow 2\text{HF} + \text{ClF}.
\]

\( \Delta H = -433.8 \text{ kJ/mol} \)

This is not the so-called complete combustion reaction. This reaction also includes the decomposition reaction of ClF₃ implicitly, and relatively stable ClF still remains after the combustion reaction.

Figure 9 shows the flammability diagram of the \( \text{H}_2/\text{ClF}_3/\text{N}_2 \) mixture. Solid circles mean explosions occurred at an initial pressure 0.05 MPa, and open circles mean explosions occurred at an initial pressure 0.1 MPa. The lower limiting concentrations for ClF₃ and \( \text{H}_2 \) are 1.7 vol% and 0.9 vol% at 0.05 MPa, and 1.2 vol% and 0.5 vol% at 0.1 MPa, respectively.

**CONCLUSION**

The combustion reactions of TEOS, ammonia, and hydrogen in chlorine trifluoride were investigated experimentally. TEOS was found to ignite spontaneously after mixing well with ClF₃. Ammonia ignited spontaneously at contacted with ClF₃. Hydrogen did not ignite spontaneously, but explosions occurred in a wide concentration range by application of an electric spark to a mixture with ClF₃. From discussion on the limiting flammable concentrations, ClF₃ was considered to decompose before reacting with the flammable gas, and the active \( \text{F}_2 \) reacts alone with the fuel.

**ACKNOWLEDGMENT**

The authors wish to thank Messrs. M. Aramaki and T. Enomoto of the Central Glass Corporation for their technical and financial support.
REFERENCES


