Experimental Studies on Ignition Behavior of Pure Disilane and Its Lower Flammability Limit

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This work aims to uncover the ignition behavior and explosion characteristics of disilane. An electrically controlled four-way switching valve was used to switch the parallel disilane and nitrogen flows so that disilane can be released without acceleration to the vent stub. By using mass flow controllers, the flow rate of disilane was controlled accurately to determine the critical exit velocity of pure and dilute disilane for different vent diameters. With the aid of boundary layer theory, the ignition of pure disilane always occurs in a mixture fraction of 0.61, which is called the most reactive mixture fraction. With careful control of the disilane feeding process to prevent premature ignition, premixed disilane/air mixture was successfully prepared in 20-L sphere apparatus for determination of lower flammability limit (LFL). The premixed disilane/air mixture was ignited by an electric spark with an energy of 10 J. LFL of disilane in air was determined to be 0.50 ± 0.02 vol.%. Maximum pressure rise and deflagration index of varied disilane concentrations were also characterized. Interestingly, disilane reacts spontaneously with a very lean oxygen-nitrogen mixture of 0.1 vol.%. The results in this work will be useful for risk management of disilane.
Keywords: Disilane, autoignition, jet release, lower flammability limit.

1. Introduction

Disilane is an important silicon precursor for low temperature epitaxial deposition of thin films. Disilane is considered an interesting source compared to monosilane for thermal chemical deposition (CVD) of epitaxial silicon because it requires lower process temperature that may protect the film's quality from damage. Like silane, disilane is also noted for its pyrophoric nature.

There was a typical accident occurring at a semiconductor parts factory in Tateyama, Chiba, Japan, 1995 (Itagaki & Tamura, 1995). In that case, air leaked into the exhaust piping system and reacted with residual disilane resulting in a fire that injured four workers. However, limited efforts have been made to characterize the risk of fire and explosion of disilane due to its extreme sensitivity towards air.

Eméleus and Stewart (1936) investigated the lower and upper critical explosion limits of disilane which are the sum of the pressures of disilane and oxygen in the reactor resulting in an explosion. The results implied that the flammability of silanes increases with the molecular weight. However, those results do not quantitatively assess the risk of fire and explosion of a disilane release under ordinary conditions. Tokuhashi et al. (1990) performed a burning test of premixed disilane-oxygen-nitrogen mixture at ambient conditions; the work focused more on the burning velocity of disilane and the chemical mechanism of its combustion rather than the ignition behavior.

The lower flammability limit (LFL), limiting oxygen concentration (LOC), and other fire and explosion characteristics are also very important for safety management of flammable gases or vapors. However, the existing data on disilane fire and explosion hazards are still limited and contradictory. Urano et al. (1989) reported that 0.1% disilane/N_2 ignites spontaneously in air, indicating a LFL of less than 0.1%. According to Tokuhashi et al. (1990), disilane concentration at zero burning velocity may become approximately 0.4%,

implying that the LFL can be deduced to be 0.4%. Sugawara (1992) and Kondo (1994) reported that the flammability range of disilane is from 0.5 to 100%; however, there was no reported experimental data.

In this work, tests were conducted to determine the precise conditions for prompt ignition of a disilane release into air as well as to characterize the fire and explosion parameters of disilane. The results were used to determine the ignition mechanism, providing valuable information regarding safe design and operation of equipment containing this pyrophoric substance.

2. Materials and methods

2.1 Materials

Semiconductor grade disilane with a purity of >99.998% was used. A nitrogen source containing <0.1 ppm of moisture and <1 ppm of O_2 was used after further purification by a moisture/oxygen trap (Agilent model OT3-4). Oxygen gas used for LOC testing had a purity of >99.9% with moisture content <1 ppm.

2.2 Release

The system and procedure used was the same steady-state release configuration as Tsai et al. (2010) which is described in Figure 1. The flow rate of disilane and nitrogen could be controlled accurately by using a set of mass flow controllers (MFC). A four-way switching valve was used to establish a parallel, steady flow of disilane into a burn box and nitrogen into the release line. When switched, the disilane flowed steadily at the desired flow rate through the stainless-steel vent stub of 1/8-in or 1/16-in Swagelok® port connectors with inner diameters of 2.032 and 0.762 mm, respectively. The port connector was changed for every test. The ignition behavior and flame kernel were recorded directly by using a high-speed video camera with a recording rate of 5000 frames/second. The steady release tests were carried out at an air temperature of 31 ± 2 °C. The difference between the disilane source temperature and the air temperature was normally less than 1 °C. The relative air humidity was 66 ± 6%.
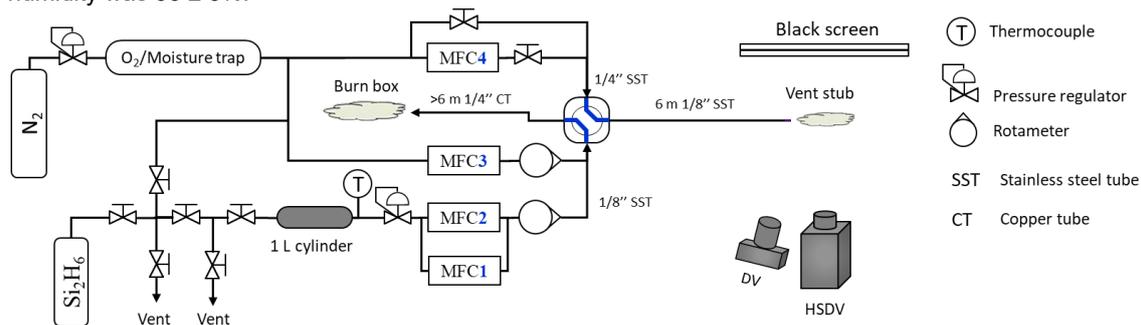

Figure 1: Schematic diagram for steady release test

2.3 Flammability limit testing

The LFL, LOC and other explosion severity parameters including overpressure (P_{max}), and rate of maximum pressure rise $(dP/dt)_{max}$ were determined using a 20-L sphere apparatus (Kühner AG) as shown in Figure 2. The measuring range of the system is 20 bar. The test chamber is a hollow sphere made of stainless steel with a volume of 20.1118 ± 0.0008 liters that was recalibrated by water. A water jacket serves to dissipate the heat of explosions and to maintain thermostatically controlled test temperature at 27-28 °C using a temperature circulator. A permanent electric spark igniter with an energy of 10 J installed at the center of the test chamber was used as the ignition source.
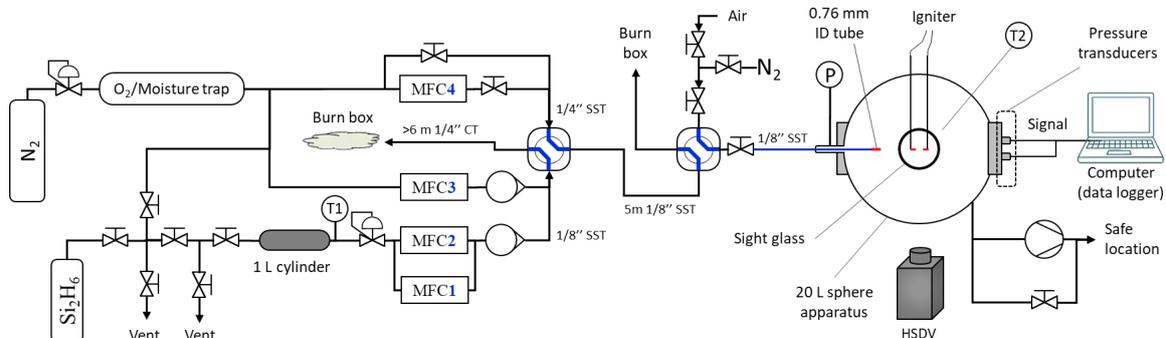

Figure 2: Schematic diagram for LFL and LOC testing

The amount and concentration of disilane flowing into 20-L sphere was controlled accurately by using an MFC and managing the feeding time. Before feeding disilane, the sphere was evacuated to about 0.5 bar. To prevent premature ignition during mixture preparation, a premixed 2.5 to 10 vol.% disilane/N_2 mixture was introduced into the test chamber with a high flow velocity up to 164.8 m/s through a 0.762 mm ID tube. The feeding time started counting as soon as switching both 4-way valves at which time dilute disilane was introduced into the sphere. The first 4-way valve was switched back when the desired amount of disilane was fed; while the second was maintained for 10 more seconds prior to switching back. This procedure allows the gas feeding process to be ended with the same flow velocity of N_2 which helps avoid the ignition at the vent stub when directly shutting off disilane flow. To ensure uniform mixing, air was rapidly added last into the chamber to achieve atmospheric pressure, and the mixture was left for 10 minutes prior to ignition by the electric spark.

The criteria for flammability in this work is a pressure rise of ≥7 % above the initial absolute test pressure in accordance with ASTM standard ASTM E918−19 (2020) and ASTM E2079−19 (2019). Flame morphology was captured using a high-speed camera through the sight glass. The test chamber was visually inspected and cleaned after every trial.

3. Results and Discussion

3.1 Ignition behavior of disilane release into ambient atmosphere

In the release test, there were two main behaviors observed, prompt and delayed ignitions. Disilane can be released indefinitely into air without ignition when the flow velocity is higher than a certain value, the so-called critical exit velocity. Lower than the critical exit velocity, prompt ignition always occurs. Figure 3 shows some typical clips from high-speed video for pure disilane release from a 2.032 mm ID vent stub with an exit velocity of 30.8 m/s. The ignition is initiated downstream of the jet center as can be seen at 0.5 ms and is similar to the prompt ignition behavior of monosilane observed by Tsai et al. (2010).

Figure 4 summarizes the critical exit velocity of pure and dilute disilane through different vent diameters. The critical exit velocity of disilane increased with disilane concentration. With 2.032 mm ID vent stub, the critical exit velocity increased from 2.7 to 39.2 m/s with a concentration from 1.1 to 16.6 vol.%, respectively; for 0.762 mm ID vent stub, it increased from 29.2 to 56.0 m/s with a disilane concentration from 13.3 to 100 vol.%, in that order. Additionally, the critical exit velocity of disilane increased with an increase in vent diameter which agrees with the observation for silane release performed by Tsai et al. (2010).
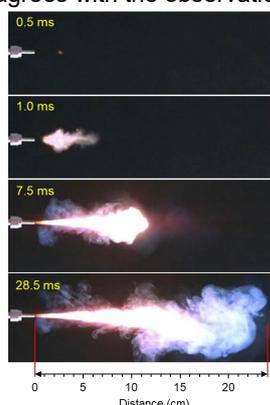

Figure 3: Clips from high-speed video for a typical prompt ignition release. Vent size: 2.032 mm. Disilane exit velocity 30.8 m/s, Re = 16776
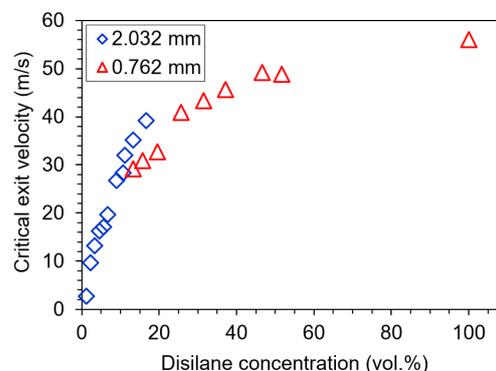
Figure 4: Critical exit velocities of pure and diluted disilane

It should be noted that similar to monosilane release, it is still possible to observe finite delayed ignition for a gas flow above the critical exit velocity of disilane. The finite delayed ignitions are mostly as a result of a flow disturbance or particle contamination in the ambient air or the vent tubing (Ngai et al., 2007).

3.2 Analysis of most reactive ignition kernel

Figure 5 shows the overlapping of the ignition location for all cases of prompt ignitions from two different vent diameters. Surprisingly, the normalized ignition distance, defined as the ratio of ignition distance to vent diameter, appears to depend linearly on the disilane flow velocity, regardless of the vent diameter, up to a certain flow velocity (Figure 5b). As the disilane release is in the form of a jet, it is possible to check the amount of air entrained into the disilane jet. In a laminar, axisymmetric jet flow into a static medium, the flow rate created by the jet is given by the following analytical expression (Schlichting, 1979):

$$Q = \frac{8\pi\mu\chi}{\rho} \tag{1}$$

where Q is the volumetric flow rate of air entrained, χ is the downstream distance in the jet, μ is the viscosity of air, and ρ is the density of air. It should be noted that the air entrainment expression of Eq. (1) only holds for laminar flows. The entrainment of ambient air depends only on the downstream distance of the jet. It is found that the volumetric flow ratio of air entrainment to the disilane flow at the ignition location is scattered around a constant of 0.643 ± 0.123 (Figure 6a). The constant volumetric flow ratio of air entrainment to the disilane flow suggests that the most reactive ignition kernel occurs when the average disilane concentration in the jet reaches about 1/(1+0.643) or 61 vol.% (Figure 6b). The results on the critical exit velocity for indefinitely delayed ignition and the most reactive fraction for prompt ignition should be useful in validating suitable disilane ignition and flow interaction models.
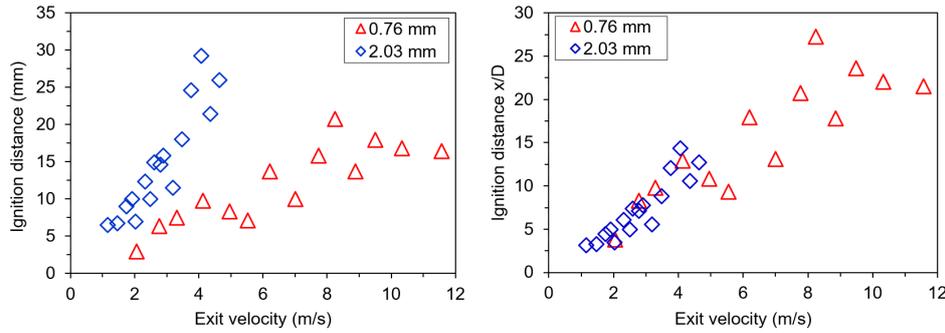

Figure 5: Ignition distance for prompt ignitions of pure disilane release from two different vent diameters
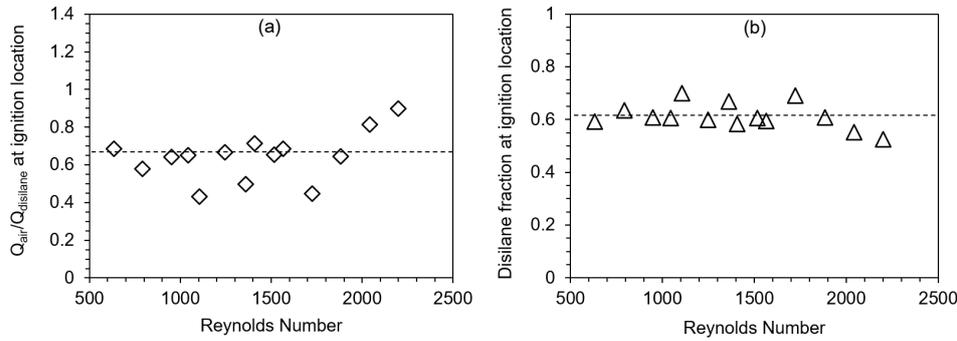

Figure 6: (a) Volumetric flow ratio of air entrainment to the disilane flow and (b) the most reactive fraction at the ignition location

3.3 Disilane flammability limit

The stable mixture of disilane/air only existed up to about 2.14 vol.% disilane. There was no reaction during a period of 10 minutes that was confirmed by the constant temperature and pressure inside the testing chamber. Above 2.14 vol.%, the mixtures were metastable and automatically ignited after a certain delay during the mixture preparation. The stable mixture was then ignited by the electric spark ignitor.

Figure 7 shows the maximum pressure rise of the disilane explosion. The pressure rises in the tests of 0.12 to 0.47 vol.% disilane/air mixture increase from 0.01 to 0.04 bar. The LFL of disilane was determined to be 0.50 ± 0.02 vol.% as it gives a pressure rise of ≥ 0.07 bar which is ≥ 7% pressure rise from absolute ambient pressure in accordance with ASTM E918−19 (2020). The test was repeated at least twice to verify the LFL value. The LFL result is consistent with 0.5 vol.% reported by Sugawara (1992) and Kondo (1994).
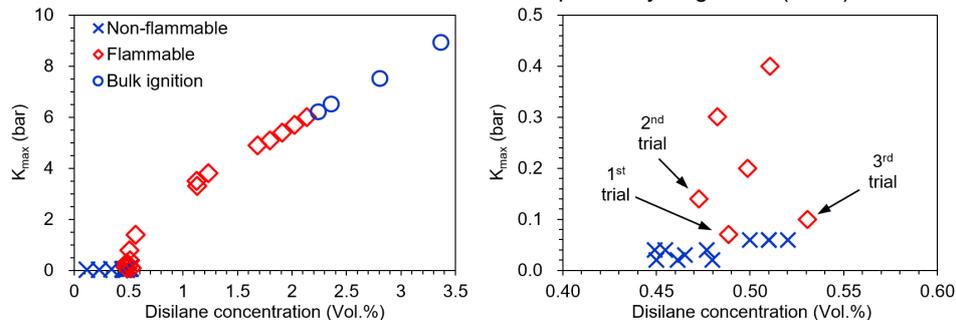

Figure 7: Disilane/air explosion overpressure at 1 bar and 27°C

The deflagration index (K_G) of disilane/air explosion can be calculated as (Bartknecht, 1981):

$$K_G = \left(\frac{dP}{dt}\right)_{max} \times V^{1/3} \tag{2}$$

Where, P is the pressure (bar), t is time (s), V is the volume of a testing chamber (m^3), and K_G is the deflagration index (bar-m/s).

Figure 8 shows that for the 1.9 vol.% disilane/air mixture, the maximum rate of pressure rise and deflagration index were found to be 2310 bar/s and 627 bar-m/s which are similar to those of a stoichiometric hydrogen explosion (Senecal & Beaulieu, 1998).
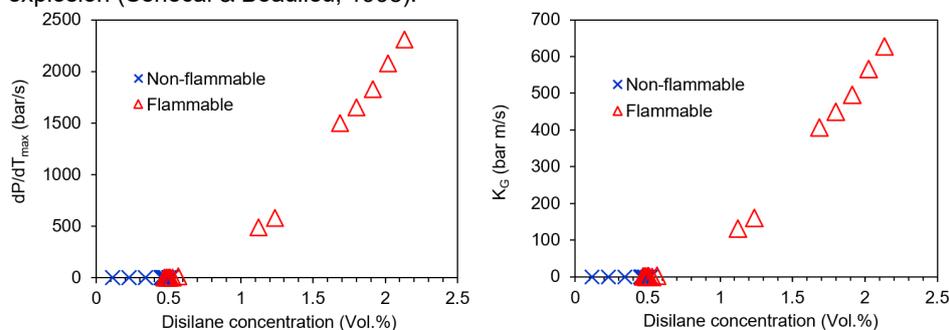

Figure 8: (a) Maximum rate of pressure rise and (b) deflagration index of disilane/air explosion

The LOC of disilane is defined to be the lowest oxygen concentration below which autoignition of disilane is not able to occur. In this work, the LOC of disilane was determined by feeding pure disilane (0.2 L/min) into the 20-L sphere containing 0.1 vol.% O$_2$/N$_2$ at ambient pressure. Figure 9 illustrates temperature and pressure profiles during 60 seconds of pure disilane addition. Temperature increases from 27 to 30.8 °C at second 30 and pressure rise to 1042 mbar at second 26 compared to 1006 of calculated pressure rise in the case of no ignition occurring , indicating the occurrence of spontaneous ignition of disilane. Therefore, the LOC of disilane in dry medium is expected to be less than 0.1 vol.%, which is much lower than that of monosilane of 0.7 vol.% (Baratov et al., 1969). The result suggests that disilane seems to react with any O$_2$ in the environment. In addition, since bulk ignition always occurred during the preparation of a disilane/air mixture with concentration higher than 2.14 vol.%, the upper flammability of disilane is expected to be close to 100 vol.%, which agrees with Sugawara (1992) and Kondo (1994) although no upper flammability limit (UFL) measurement was performed.
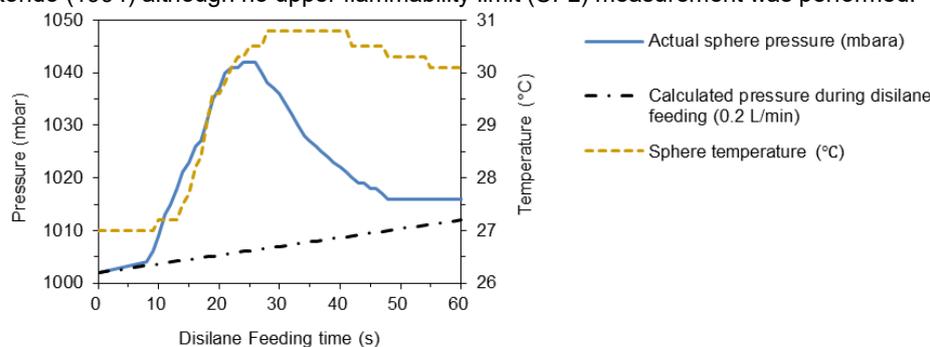

Figure 9: Pressure and temperature evolution during pure disilane feeding into a 20-L sphere containing 0.1 vol.% O$_2$/N$_2$ at 1 bar

3.4 Discussion

The extreme sensitivity of disilane compared to monosilane may be derived from the weaker Si-H bonds and the presence of Si-Si bond in the disilane structure. Goumri et al. (1993) determined the dissociation enthalpy of Si-H bond in disilane of 373.7 kJ/mol, which is smaller than that in monosilane (384.1 kJ/mol) (Seetula et al., 1991). In addition, bond dissociation energy of Si-Si bond in disilane was determined to be 340.2 kcal/mol (Steele & Stone, 1962), which is smaller than that of Si-H bond. Therefore, it is much easier for O$_2$ to attack the weaker Si-Si bond instead of the stronger Si-H bond. Delayed ignition of a silane release may cause the ignition at end of the release resulting in a fatal vapor explosion (Peng et al., 2008). The formation of a metastable mixture of silane/air resulting from a silane release with indefinitely delayed ignition is considered the most dangerous case due to the unpredictable behavior and potential for a violent explosion. With a very low flammability limit and very high critical exit velocity, in the case of disilane leaks, there is higher probability that prompt ignition with smooth fire may occur instead of explosion as compared to a leak of monosilane. Therefore, from the safety point of view, disilane can be considered safer than monosilane because disilane is pyrophoric at very low concentrations and

tends to ignite spontaneously upon contact with air. In reality, bulk autoignition resulted from the metastable disilane/air mixture very rarely happens when disilane releases into open space as it only occurs with a well-mixed mixture (Britton, 1990). However, care must also be taken to prevent the accumulation of unignited disilane to avoid a potential vapor explosion through the use of forced ventilation or open air storage.

4. Conclusions

This work has presented experimental results on the autoignition behaviors of a steady jet release of disilane into static air and explosion characteristics of disilane/air mixtures. Like silane, indefinitely delayed, finite delayed and prompt ignition behaviors were observed in disilane release tests. The critical exit velocity of pure disilane release through 0.762 mm I.D. tube was determined to be 56.0 m/s. The LFL of disilane/air mixture was measured to be 0.50 ± 0.02 vol.%. The values of K_{max} and K_G of 2.14 vol.% disilane/air were determined to be 5.7 bar and 627 bar-m/s, respectively which are close to those of a stoichiometric H_2 explosion. The mixture of higher disilane/air concentrations (> 2.14 vol.%) was metastable and automatically ignited in a certain delay. Reported data are useful for risk management of disilane in the industry. Further work is still required to investigate the effect of moisture on the ignition behavior of disilane.

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