

Diborane Addition Effect on Second Order Reactions of Si Photo-CVD under Vacuum Ultraviolet Irradiation

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We investigated the photolysis of a mixture of disilane, diborane and hydrogen gases under 160 nm and 185 to 350 nm irradiation from a deuterium lamp at room temperature. The photolysis was observed with infrared absorption spectroscopy. Comparing our results with the theoretical calculations we clarified that the dissociation of disilane is mainly due to the second-order reaction in high partial pressure. In 160 nm and 185 to 350 nm photolysis, the primary reaction which generates SiH_2 , SiH_3 and H radicals is dominant. Adding diborane suppresses the dissociation of disilane and decreases the creation efficiency of monosilane from disilane. We attribute these results to trapping of the photo-generated hydrogen atoms by diborane and catalytic enhancement of the surface chemisorption of SiH_2 onto the surface covered by boron hydride.

1. Introduction

Photochemical vapor deposition (Photo-CVD) using short-wavelength light sources is being investigated for the formation of high-quality thin films¹⁻⁵). Despite the extensive development on this technique has undergone, very little is known about the fundamental physical and chemical processes involved. This is because of the difficulty in analytically studying the photo-CVD environment. In general, silicon film is deposited at the growth surface through reactions of active species which are generated in the irradiation volume and diffuses to the surface, accompanied by many second-order reactions. Most source gases for photo-CVD absorb the UV/VUV light and decompose into intermediates. The substrate also absorbs the light and generates electron-hole pairs. Many researchers have investigated the deposition and quantitatively explained their experimental results in this manner.

Recently, we pointed out a doping impediment that occurred at a substrate temperature of 600°C under 160 nm irradiation in polysilicon CVD using a disilane, diborane, and hydrogen gas⁶). Despite the doping impediment, the growth rate was unchanged. In the present study we paid special attention to the photo-generated intermediate species and the second-order reactions that take place during the diffusion to determine the mechanism of the impediment.

2. Experiment

Our experimental set up is shown in Fig. 1. We used infrared absorption spectroscopy to determine the amount of gas without disturbing the contents in a reactor. Photolysis was carried out in a $1.9 \times 10^3 \text{ cm}^3$ cylindrical quartz White cell in which the path length of the IR probe light was 10 m. The

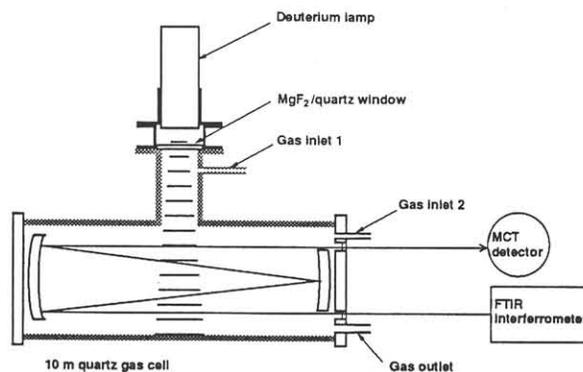


Figure 1. Schematic diagram of experimental set-up.

detection limit for our gas sample was about 1×10^{-4} Torr. A dc discharge type deuterium lamp (HAMAMATSU L1835, 150 W) irradiated the cell through a magnesium fluoride or quartz window.

Figure 2(a) shows the absorption cross sections of disilane, diborane and monosilane^{7,8}). The broad absorption spectra show that these molecules belong to the direct dissociation type in this wavelength region. It is well known that hydrogen does not absorb the light. The emission spectra from the deuterium lamp that pass through the MgF_2 and quartz windows are shown in Fig. 2(b). The spectra consist mainly of a narrow line at 160 nm and a broad one 180 to 350 nm. There is a line at 125 nm, but its power density is less than 1/20 that of the 160 nm line. Based on these spectra, we expect disilane to be effectively photodecomposed so much when the magnesium fluoride but not diborane or monosilane. The quartz window completely blocks emissions with wavelengths of less than

185 nm. With the quartz window, only disilane is expected to decompose slightly around 185 nm irradiation. Comparing the time dependence of the partial pressures of gases during the irradiation using the two windows yields a understanding of the role of 160 nm emission on photolysis.

3. Results and discussion

3.1 Dissociation of disilane

After filling the cell with a mixture of disilane and hydrogen at a constant pressure of 750 Torr, we started the irradiation through the MgF_2 window. Then we observed a gradual decrease in the amount of disilane, along with the appearance of monosilane generated by dissociation of the disilane, as shown in Fig. 3. It should be mentioned that the absorptions stopped changing immediately whenever we stopped the irradiation during the measurement, as can be seen in Fig. 3. This means that the gas composition in the cell is constant throughout, and that the characteristic of the gas mixing by diffusion is kept shorter than the time scale for the change in the gas pressure during the photolysis.

To discuss the effect quantitatively, we have to describe the rate equation of disilane. When we disregard the quartz wall area dependent dissociation⁹), the directly observable rate, dn/dt , is the sum of three terms, $(dn/dt)^{photon}$, $(dn/dt)^{radical}$ and $(dn/dt)^{surface}$. The first term is the result of the direct photo-dissociation (primary reaction) by incident photons. The second term is the contribution of the reactions between radicals generated by the primary reaction and disilane molecules. The first term is expressed using the incident photon number per unit time, N , the optical path length, l , the cell volume, V , the cross section, $S(\lambda)$, and density, n , of disilane as follows:

$$(dn/dt)^{photon} = -\sum_{\lambda} N(\lambda)/V[1-\exp(-S(\lambda)nl)],$$

where λ is the wavelength of the incident photon. Using this equation and the characteristic values for the deuterium lamp we calculated the contribution from this term. The results are shown in Figs 4(a) and 4(b) for the two windows. Figure. 4(a) shows that the primary reaction of the molecule, becomes the dominant channel of dissociation at partial pressures lower than 0.037 Torr under 185 to 350 nm irradiation. At higher pressures, dissociation by the second-order reaction becomes important. For 160 nm irradiation of disilane, the same situation was observed. The primary reaction was dominant at lower than 0.0008 Torr, as shown in Fig. 4(b). At higher pressures, the second-order reaction is dominant. At 0.06 Torr, the rate is about 20 times as large as that by the primary reaction. Our calculation shows that at 0.037 Torr and 0.0008 Torr, the loss rates in the directly irradiated volume are $4.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$ for the quartz window and $2.3 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$ for the MgF_2 window. These two rates are very close, and enable us to predict the condition where the primary reaction becomes dominant in a real photo-C system from

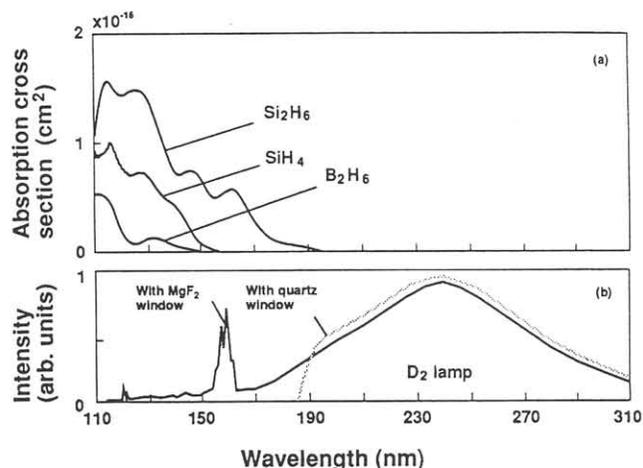


Figure 2. (a) Absorption cross section for disilane, diborane and monosilane (after refs. 7,8). (b) The emission spectra from deuterium lamp passing through fused silica (gray line) and magnesium fluoride (solid line).

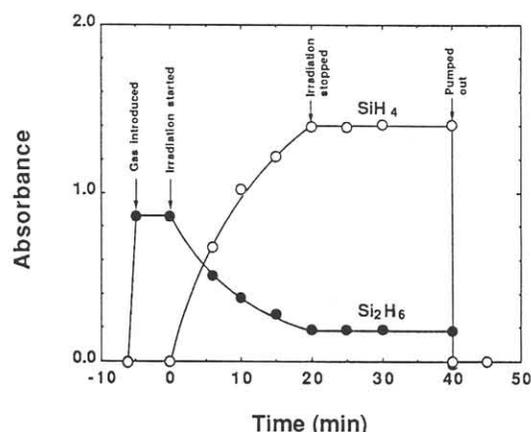


Figure 3. An example of time evolution of the absorbance of disilane and monosilane in wavelength of 2187.9 and 842.9 cm^{-1} , respectively.

the parameter in the equation.

3.2 Wavelength effect and addition of diborane

To discuss photolysis in more detail, we introduce two terms: loss rate, defined as $-dP/dt$, and creation rate, defined as dP/dt , for disilane and monosilane. These values are deduced from Fig. 4(a) and (b) for each set of irradiation conditions. Figure 5 shows the disilane loss rate dependence on disilane pressure. When no diborane is added, the loss rates increase monotonously with disilane pressure, but at different rates for irradiations. When we add diborane at 0.05 Torr (1/4 the molar fraction of disilane) with irradiation through the MgF_2 window, the loss rate decreases, especially at low disilane pressures, as indicated by the open squares in the Fig. 5. The decrease in the total photon number due to the absorption of diborane was confirmed to be negligible, and cannot explain the result of the dissociation decrease. The effect of the addition becomes noticeable at pressure lower than for adding diborane. This

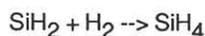
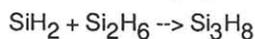
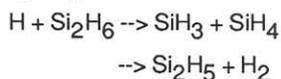
shows that the dissociation channel is affected by the diborane addition.

Figure 6 shows the relation between the loss rate of disilane, R_L , and the creation rate of monosilane, R_C . The relationship between these rates when no diborane is added are well expressed by the linear equation, $R_C = R_L$. This means that one monosilane is generated from one disilane, in the gas phase through the second-order reactions in a wide rate region. It is noted that this relation is valid at 3.5×10^{-5} Torr/min, where the primary reaction is dominant. However, when the diborane is added, lower creation rates are obtained, as shown by the open squares. The equation is expressed as $R_C = CR_L$, where $C = 0.6 \pm 0.2$. The addition of diborane has a more obvious effect on the creation efficiency of monosilane. Fig. 7 shows the creation efficiency of monosilane, defined as the ratio of monosilane pressure to loss disilane pressure, as a function of disilane pressure under the same conditions as above. When diborane is added, the efficiency decreases from 1 to about 0.7, showing that diborane has an important effect on monosilane creation from disilane dissociation.

3.3 Dissociation model

We formulated an explanation of the dissociation process based on our experimental results. The radicals generated by the primary reaction between a disilane and a photon with a wavelength of 147 nm were reported as neutral SiH_2 , SiH_3 , SiH_3SiH , Si_2H_5 and H atoms¹⁰.

To consider the second-order reaction, we have to know its probability of occurrence. It is a reasonable assumption in our pressure condition that the most important second-order reactions are those in which stable hydrogen atom in hydrogen ambient and SiH_2 attack disilane and hydrogen molecule as follows:¹¹⁻¹³



The reaction velocity of the last reaction is reported to be very small, $1.0 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ¹²). However, since the pressure of hydrogen gas in the cell is 750 Torr, this equation becomes the main path for the creation of stable monosilane. Other stabilized reaction of the radicals which should be considered are



These equations account for the solid growth at the wall.

In very low disilane pressure, we have to consider the primary reactions. In these reactions the creation of monosilane is governed by the presence of SiH_2 , which becomes monosilane when it collides with hydrogen

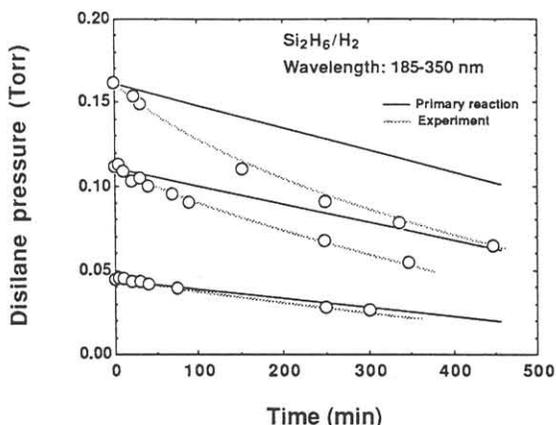


Figure 4(a). Partial pressure of disilane as a function of time under deuterium lamp irradiation through a quartz window with initial pressures of 0.16, 0.11 and 0.045 Torr. The solid lines are obtained from calculations based on the primary reaction for the dissociation.

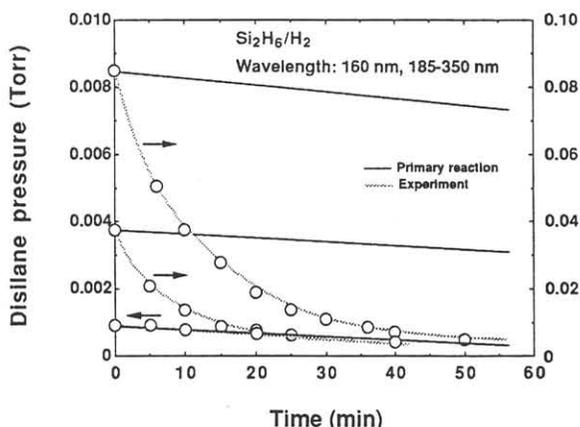


Figure 4(b). Partial pressure of disilane as a function of time under irradiation through a MgF_2 window with initial pressures of 0.084, 0.038 and 0.001 Torr. The solid line shows the primary reaction.

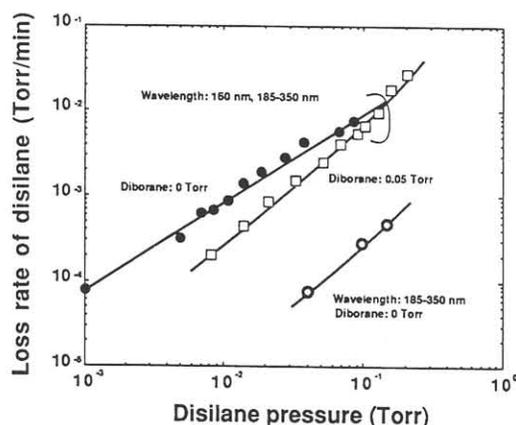
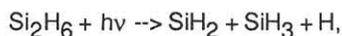


Figure 5. The effect of diborane addition on photodissociation in a disilane and hydrogen gas system.

molecules. If no diborane is added the efficiency is observed as 1, as stated before. We can now conclude that the quantum yield of the primary process,



is about 1. The result differs from that observed in 147 nm photolysis by Perkins at al¹⁰). Their value is 0.7 for the process. We think this is reflected by the different characters of excitation states for 160 and 147 nm photons¹⁴).

The effects of diborane addition are a gradual decrease in the loss rate of disilane with decreasing pressure, and a decrease in the creation efficiency of monosilane. The most probable explanation is as follows: As discussed before, disilane dissociation in the second-order reaction region is due to H and SiH₂ attacking the disilane. It is therefore natural to make a model in which hydrogen atom reacts with diborane molecule, exchange hydrogen atom and these reaction keep equilibrium. The equilibrium condition is necessary because we did not observe any enhancement of diborane dissociation in the disilane/diborane/hydrogen gas system. The reaction is expressed by



This also qualitatively explains the increase of the difference in the disilane loss rates with decreasing partial pressure in Fig. 5. Our experiment suggests another reaction path, $\text{SiH}_2 + \text{-BH}_x(\text{Wall}) \rightarrow \text{Solids}$,

which lead the decrease of the creation efficiency of monosilane, in addition to the reaction path where SiH₂ and H₂ becomes monosilane in hydrogen ambient. Physical meaning is that the boron-hydrogen complex at the wall surface enhances the chemisorption of SiH₂ and leads to the well-known enhanced growth rate of boron-doped hydrogenated amorphous silicon¹). In the IR absorption experiment, we were unable to detect SiBH complex in the gas phase. This might be because of low vapor pressure of SiBH complex at the low temperature surface. At high temperature of 600°C, the complex is easy to desorb from the surface and thus does not contribute the growth rate but impede the boron doping. We believe this is the mechanism of the doping impediment observed at 600°C surface.

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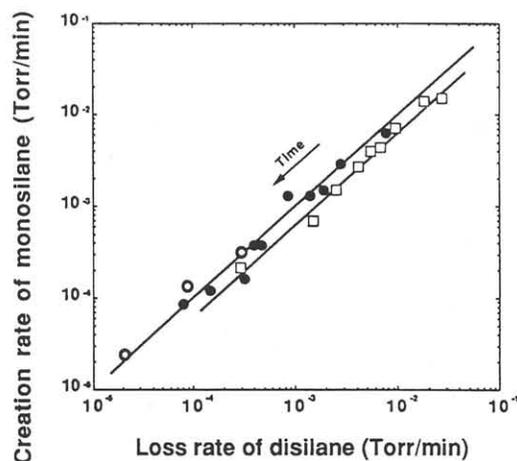


Figure 6. The creation rate of monosilane, $dP_{\text{monosilane}}/dt$, versus the loss rate of disilane, $-dP_{\text{disilane}}/dt$. The marks are defined in figure 5.

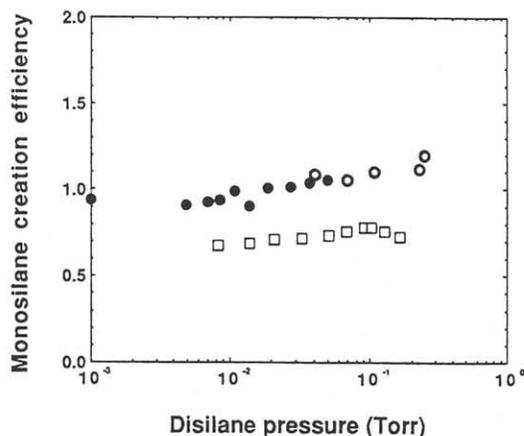


Figure 7. The creation efficiency of monosilane, defined as the ratio of monosilane to the loss rate of disilane, as a function of disilane partial pressure. The marks are defined in figure 5.