Synthesis of Polysilanes by Tunneling Reactions of H Atoms with Solid Si_2H_6 at 10 K

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Tunneling reactions of H atoms with solid Si_2H_6 at 10 K were investigated. The in situ and real-time reactions $H + Si_2H_6$ to form silane and polysilanes were monitored using FT-IR. Quantitative analysis of gaseous products was made by thermal desorption spectrometry. Monosilane and polysilanes were detected as major reaction products. The intermediate product SiH_2 was suggested to play an important role for the growth of the Si–Si network of the solid products.

The chemistry of silanes has attracted the interest of many researchers since its basic understanding is of technological importance for the formation of high quality semiconductor films using chemical vapor deposition.[1,2] The gas-phase kinetic data of silanes and the total reaction simulations of CVD (chemical vapor deposition) processes have been studied extensively.[3–7]

In our previous work,[8] the tunneling reactions of H atoms with various hydrocarbons were investigated at 10 K. It was found that the H-atom abstraction as well as recombination reactions of H with radicals plays major roles in the cryogenic tunneling reactions. In our recent work,[9] it was found that amorphous silicon was synthesized by the reaction of H with solid SiH_4 at 10 K. In the current work, we further examined the reaction of H with solid Si_2H_6 at 10 K in order to obtain further information on the mechanism for the formation of amorphous silicon at cryogenic temperature.

The experimental details were described previously.[9] Briefly, a vacuum manifold equipped with a cryocooler, a discharge tube for the generation of H atoms, and a quadrupole mass analyzer was evacuated to ca. 10^{-10} Torr. The reactant, gaseous Si_2H_6 (Nihon Sanso Corp., Si_2H_6:He = 10.5:89.5 high purity diluted gas), was deposited on a silicon wafer substrate at 10 K. After the deposition, the solid film was sprayed by H atoms produced by a dc-corona discharge. The temperature of the H atoms was kept at about 27 K. The in situ and real-time observation of tunneling reactions taking place on the solid substrate was monitored by FT-IR (Mattson Instruments, Infinity Gold) using the reflective mode. The IR signal intensities were calibrated by depositing known amounts of SiH_4 and Si_2H_6 on the silicon substrate. Quantitative analysis of polysilanes could not be made because their absorption coefficients are not available. After the H atom irradiation, the gaseous products were analyzed by thermal desorption spectrometry (TDS) using a quadrupole mass spectrometer (Leda mass, Microvision 300D).

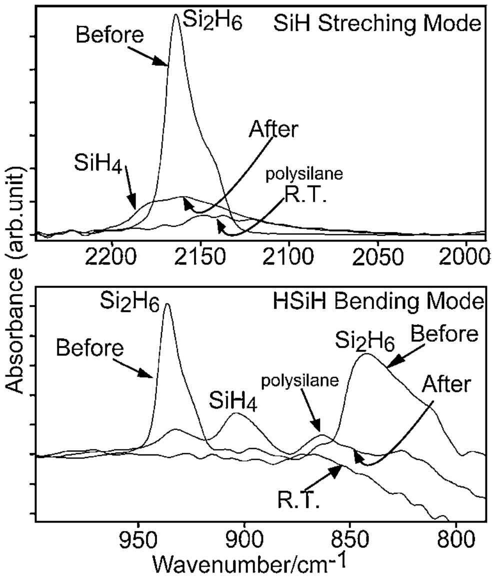

Figure 1. FT-IR spectra of 4 ML solid Si_2H_6 film before and after the reaction with H atoms for 4 h at 10 K. The upper and bottom panels show the SiH stretching and the HSiH bending modes, respectively.

Figure 1 shows the FT-IR spectra of the 4 ML (equivalent monolayers) thick solid Si_2H_6 film before and after 4 h of reaction with H atoms at 10 K. The intensities of peaks for Si_2H_6 (ca. 2165, ca. 2145, ca. 940, ca. 840, and ca. 820 cm^{-1}) decreased with the reaction time. These decreases were accompanied by concomitant increases of monosilane (SiH_4, ca. 2187(ν_1), ca. 2191(ν_3), and ca. 900(ν_4) cm^{-1}),[9] other products with a broad tailing extending to lower wavenumber of Si_2H_6 (2150–2050 cm^{-1}), and a peak at ca. 860 cm^{-1} designated as "polysilane." The spectrum designated as "R.T." corresponds to that for polysilane obtained after the substrate temperature was increased to room temperature. The intermediate radical species were not detected in the present experiments, possibly because they were quickly annihilated by the reactions with H atoms sprayed over the film and/or with the neighboring reactant, Si_2H_6.

Figure 2 shows the relationship between the amounts of the reaction products and the reaction time. The amounts of Si_2H_6 and SiH_4 are displayed as equivalent monolayers (ML). It should be noted that the initial decrease of Si_2H_6 is accounted for by the increases of the products, SiH_4 and polysilane. The formation of SiH_4 as a major product strongly suggests the occurrence of reaction (1).

$$Si_2H_6 + H \rightarrow SiH_4 + SiH_3 \ (\Delta H^0 = -64\,\mathrm{kJ\,mol^{-1}})^{10} \quad (1)$$

The possible competing reaction (2):

$$Si_2H_6 + H \rightarrow Si_2H_5 + H_2 \ (\Delta H^0 = -64\,\mathrm{kJ\,mol^{-1}})^{10} \quad (2)$$

has almost the same enthalpy change as that for reaction (1).

Dobbs et al. made the theoretical calculations on $Si_2H_6 + H$ for three configurations of the transient states.[11] They predicted that the barrier (E_a) for the "frontside" attack to a Si–Si bond by a H atom is $E_a = 3.0\,\mathrm{kcal\,mol^{-1}}$ ($1\,\mathrm{kcal\,mol^{-1}} = 4.184\,\mathrm{kJ\,mol^{-1}}$) for reaction (1). They further reported that the barrier height of H atom abstraction for reaction (2) is even lower as

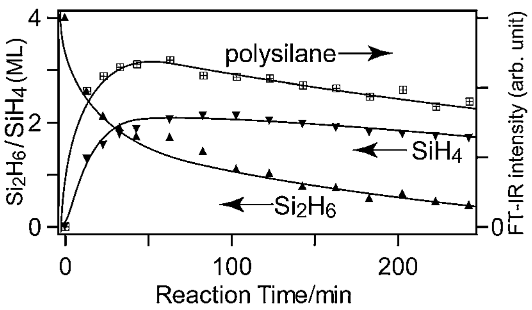

Figure 2. The relationship between the amounts of the reaction products and the reaction time. The amounts of Si_2H_6 and SiH_4 were displayed as equivalent monolayers (ML).

$2.4\,kcal\,mol^{-1}$. Because the reactions at 10 K should proceed via tunneling processes, the reactions with lower barriers may take place more favorably. The formation of SiH_4 clearly indicates that reaction (1) is one of the major processes for the reaction $H + Si_2H_6$. The discrepancy between the theoretical predict and our result exists possibly because the reactions (1) and (2) competes, but the Si_2H_5 produced by reaction (2) is quickly annihilated by the recombination $H + Si_2H_5 \rightarrow Si_2H_6$.

In Figure 2, the amount of SiH_4 shows a steep initial increase that is followed by a gradual decrease. The decrease in SiH_4 should be attributed to its conversion to polysilane. The gradual decrease in polysilane after about 50 min should be due to the growth of a Si–Si bond network, i.e., decrease in the IR absorption for Si–H bonds. The formation of SiH_4 as a major product in Figure 2 indicates that the rate-controlling step for the formation of polysilane is the reaction of H with SiH_4 but not the reaction $H + Si_2H_6$. As for the hydrogen abstraction from SiH_4, a theoretical study by Yu et al.[12] predicted $E_a = 5.54\,kcal\,mol^{-1}$ for $SiH_4 + H \rightarrow SiH_3 + H_2$, which is significantly higher than $E_a = 3.0\,kcal\,mol^{-1}$ for $Si_2H_6 + H \rightarrow Si_2H_5 + H_2$.[11] The considerably smaller bond energy of $H_2Si\text{–}H$ ($D_0 = 291\,kJ\,mol^{-1}$)[10] than that of $H_3Si\text{–}H$ ($D_0 = 384\,kJ\,mol^{-1}$)[10] may argue for the favorable H-atom abstraction reaction, $H + SiH_3 \rightarrow SiH_2 + H_2$. The H-atom abstraction by a H atom ($RH\bullet + H \rightarrow R\colon + H_2$) competes with the recombination of a H atom and radicals ($RH\bullet + H \rightarrow RH_2$), which is discussed in the previous reports.[8d,8e] Since the most important reactive intermediate for the formation of polysilane is SiH_2 as reported in our previous paper,[9] the rate-controlling step may be $H + SiH_4 \rightarrow SiH_3 + H_2$. The highly reactive SiH_2 generated by H-atom abstraction reaction $H + SiH_3 \rightarrow SiH_2 + H_2$ should play the most important role for the growth of the Si–Si bond network as was reported previously.[9] That is, the barrierless insertion reactions of silylene (SiH_2 $^1A_1$) produced by $SiH_3 + H \rightarrow SiH_2 + H_2$ to Si–Si and Si–H bonds lead to the formation of the Si–Si bond network.

Figure 3 shows the TDS spectra for the sample reacted with H atoms for 4 h. Figure 3a shows the appearances of unreacted Si_2H_6 and reaction product SiH_4 desorbing at ca. 90 and ca. 60 K, respectively. A small desorption peak at ca. 75 K is possibly due to the desorption of SiH_4 trapped in the reactant Si_2H_6 matrix. Figure 3b shows the TDS spectra of higher silanes, Si_nH_{2n+2}. Among them, the signal intensity of Si_4H_{10} is much stronger than those with $n = 3$ and 5. This species may be formed by the recombination reaction, $2Si_2H_5 \rightarrow Si_4H_{10}$.

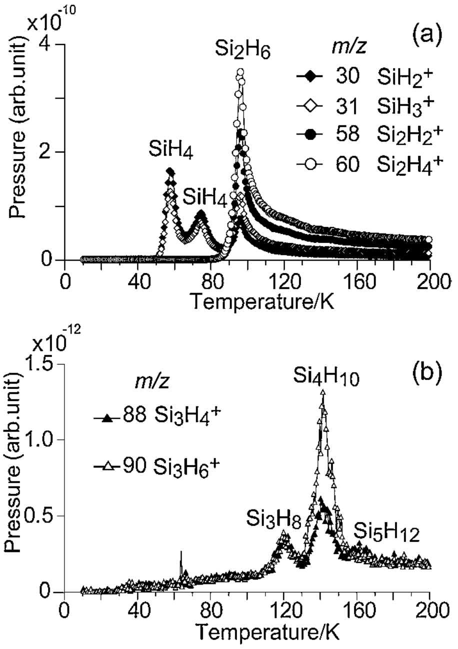

Figure 3. TDS spectra of the Si_2H_6 film reacted with H atoms for 4 h at 10 K. Panel (a) shows the mass signals tuned for the ions containing 1 and 2 Si atoms. Panel (b) shows the mass signals for the ions containing 3–5 Si atoms.

In summary, the cryogenic synthesis of polysilane by the tunneling reaction of H with solid Si_2H_6 at 10 K is investigated. It was found that the major reaction channel is the cleavage of the Si–Si bond of Si_2H_6, i.e., reaction (1). The highly reactive intermediate product SiH_2 inserts to Si–Si and also to Si–H bonds of neighboring reactants, resulting in the growth of Si–Si bond networks for polysilane and ultimately for amorphous silicon.

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