

# Photoinduced Reaction of Disilane with the Si(111) Surface

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The photoinduced reaction of disilane on Si(111) using ultraviolet (UV) irradiation has been studied using temperature-programmed desorption (TPD). Hydrogen and silane desorption yields were used to determine the reactivity of disilane on Si(111) with and without UV irradiation. Photoinduced reaction of disilane was accomplished either through simultaneous exposure of disilane and UV irradiation or by UV irradiation of a physisorbed disilane layer after exposure to disilane. These two methods of photoexcitation were compared to the thermal reaction of disilane with clean Si(111). UV irradiation during or after dosing of the crystal surface at 110 K greatly enhanced the reactivity of disilane on Si(111) compared to similar disilane exposures without UV irradiation. UV irradiation *during* disilane exposure of Si(111) at low temperatures results in greater Si deposition than does UV irradiation *following* disilane exposure. The mechanism of the photoinduced disilane reaction has been studied using clean, partially deuterated, and fully deuterated Si(111) surfaces. Thermally, the reactivity is controlled by the surface dangling bonds, whereas the photoinduced chemistry appears to primarily involve insertion by the photogenerated diradical, silylene. Evidence was found for the existence of a molecular physisorbed precursor state that interacts directly with the dangling bonds of Si(111).

## 1. Introduction

As demands on semiconductor device performance continue to rise, more highly controlled thin film growth methods are needed. One method to achieve device quality epitaxial growth is ultrahigh-vacuum chemical vapor deposition (UHV-CVD).<sup>1</sup> The primary goal in UHV-CVD is reduction of the contaminants (carbon, oxygen, etc.) in the processing environment in order to obtain high-quality Si film growth at moderate temperatures. Another potential growth method at low to moderate temperatures is photoassisted chemical vapor deposition (photo-CVD). In photoassisted CVD, deposition is enhanced through excitation of the gas, excitation of the substrate, or rapid heating of the near surface region. Photoexcitation of the deposition precursor often results in highly reactive species. These reactive species are often short-lived, reacting with other precursor molecules or with the surface. Deposition can often be enhanced if carried out under conditions where the precursor is adsorbed (physisorbed or chemisorbed) on the surface prior to or during photoexcitation, thereby reducing loss of photogenerated radical species through gas-phase reactions. Under low-pressure conditions, this is achieved only at low temperatures. The benefit of a low-temperature deposition method is that undesirable solid-state reactions and diffusion can be reduced, thereby lowering the number of defects. Combining photoassisted deposition with a UHV environment can provide the proper combination of conditions necessary for growing high-quality films at low temperatures. Our objective in this research is to determine to what extent photoassisted CVD, under UHV conditions, facilitates thin film growth of Si on the Si(111) surface and to determine the mechanisms associated with this growth process.

Disilane has qualities that are desirable for CVD, including a higher sticking coefficient<sup>2</sup> and a lower dissociation energy

than silane.<sup>3</sup> The thermal interaction of disilane with the Si(111), Si(100), and Ge(111) surfaces has been studied by a variety of surface probes such as multiple internal reflection infrared spectroscopy (MIRIRS),<sup>4–9</sup> electron energy loss spectroscopy (EELS),<sup>10,11</sup> ultraviolet photoelectron spectroscopy (UPS),<sup>12,13</sup> scanning tunneling microscopy (STM),<sup>14–16</sup> and molecular beam scattering.<sup>17–19</sup> On Si(111) it is believed that disilane adsorbs both molecularly and dissociatively on dangling bond sites to produce a mixed overlayer of Si<sub>2</sub>H<sub>6</sub> and SiH<sub>3</sub>-(ads) species at temperatures around 120–140 K. Complete Si–Si bond scission to form a SiH<sub>3</sub>(ads) monolayer occurs for adsorption near 150 K. Above 200 K, SiH<sub>3</sub>(ads) further decomposes to form di- and monohydride species. Similar chemistry occurs on the more reactive Si(100) surface, but at lower temperatures.<sup>9,20</sup> The thermal reaction of disilane with Si surfaces requires dangling bond sites in order for dissociative adsorption to occur.<sup>9</sup> Furthermore, the growth of silicon from disilane and silane under thermal conditions is rate limited by the desorption of hydrogen.<sup>21–23</sup> Elevated temperatures are required to desorb hydrogen and to liberate surface sites for further film growth.

Disilane has also been used as a precursor for the low-temperature photochemical vapor deposition of Si using excimer lasers as the excitation source.<sup>24–28</sup> The absorption cross section for disilane in the UV region is greater than that for silane, and the disilane absorption band is more accessible (cutoff at 220 nm for disilane; 160 nm for silane),<sup>29</sup> making disilane a good candidate for photo-CVD processes. Photoassisted CVD of Si from disilane is based on the principle that photolysis of disilane produces a wide variety of radical species<sup>30</sup> that are more reactive toward silicon surfaces than is molecular disilane, which can accelerate film growth. Also, the presence of these reactive species under growth conditions can reduce processing temperatures by eliminating the need for thermal removal of surface

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hydrogen. For example, silyl and disilyl radicals can abstract surface hydrogen, thereby freeing occupied surface sites and generating dangling bonds for further reaction. Silylene type diradicals, in comparison, could insert into existing Si–H surface bonds, resulting in greater deposition of silicon. Photoassisted CVD can be done at high or low precursor gas pressure. Under high-pressure conditions, gas-phase chemistry will dominate, while at low pressures surface photochemistry will become dominant and surface–gas interaction will become the rate-limiting step. Low-pressure and low-temperature conditions can allow growth with a high degree of control.

In this paper we report our findings on the photoassisted reaction of disilane with the Si(111) surface at 110 K, including the nature of the physisorbed state at the surface and the mechanism of the photoreaction. In addition, our findings for the photoreaction of disilane with Si(111) will be compared to those previously determined in our laboratory for the photoreaction of disilane with Si(100).<sup>20</sup>

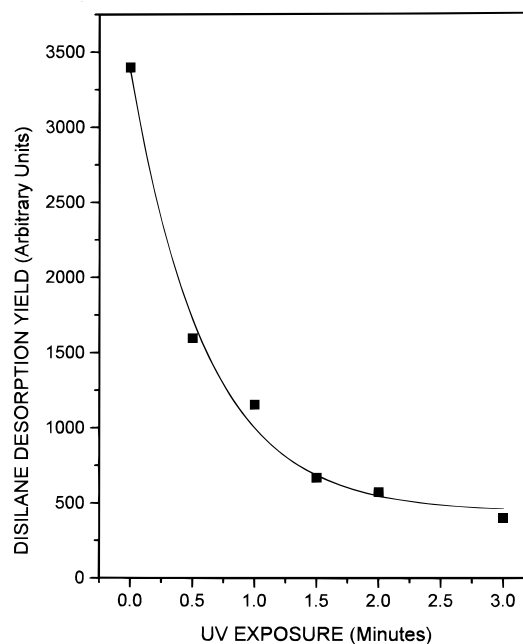
## 2. Experimental Procedures

Experiments were performed in an ultrahigh-vacuum chamber with a base pressure of approximately  $1 \times 10^{-10}$  Torr. Details of the chamber design have been described previously.<sup>31</sup> The Si(111) samples were cut from n-type Si(111) wafers, of 5–20 m $\Omega$ ·cm resistivity. The temperature was measured by a chromel–alumel thermocouple that was spot-welded to a small ( $\sim 2 \times 2$  mm<sup>2</sup>) Ta tab that was attached to the back of the crystal by a ceramic adhesive (Ultra-Temp 516, Aremco Products, Inc.). The adhesive was cured under vacuum at a high temperature (ca. 1350 K) under an applied pressure supplied by tantalum tabs. The ceramic adhesive served to electrically isolate the thermocouple and Ta tab from the crystal, while the Ta tab should help prevent the diffusion of unwanted impurities into the Si crystal. Routine cleaning of the silicon sample before each experiment was performed by Ar<sup>+</sup> ion bombardment (1 keV, 2.5  $\mu$ A) at 575 K followed by annealing at 1140 K for 3 min. Surface cleanliness was checked by Auger electron spectroscopy (AES) using a cylindrical mirror analyzer (CMA), and impurities (carbon and oxygen) after preparation were below the noise level of the spectrometer.

TPD studies were performed by resistively heating the Si crystal at a rate of 3 K/s (using a Eurotherm temperature controller with a high current/high voltage power supply) while it was positioned within a few millimeters of the orifice of a shielded quadrupole mass spectrometer (QMS). The temperature and the mass/charge ratios were monitored during the desorption using a computer interfaced to the QMS.

A tungsten spiral filament heated to  $\sim 1760$  K and placed  $\sim 5$  cm from the crystal surface was used to produce atomic deuterium and atomic hydrogen during exposure of D<sub>2</sub> (Linde, 99.5%) and H<sub>2</sub> (Liquid Air Corp., research grade, 99.9999% purity), respectively. Commercial disilane (Matheson, 99.99% purity) was used as purchased without purification. All exposures are given in langmuirs (1 langmuir =  $10^{-6}$  Torr·s) of the molecular source gas and are uncorrected for ion gauge sensitivity.

A commercially available D<sub>2</sub> lamp with a MgF<sub>2</sub> window (Hamamatsu Photonics, L879, 30 W, spectral range 115–300 nm, peak emission at 161 nm) was used as the UV light source. The lamp was positioned inside the vacuum chamber and fully encased in a copper mount. To minimize outgassing due to the temperature rise of the lamp during illumination, the mount was cooled by ice from the outside via a solid copper feedthrough. No change in the background pressure occurred



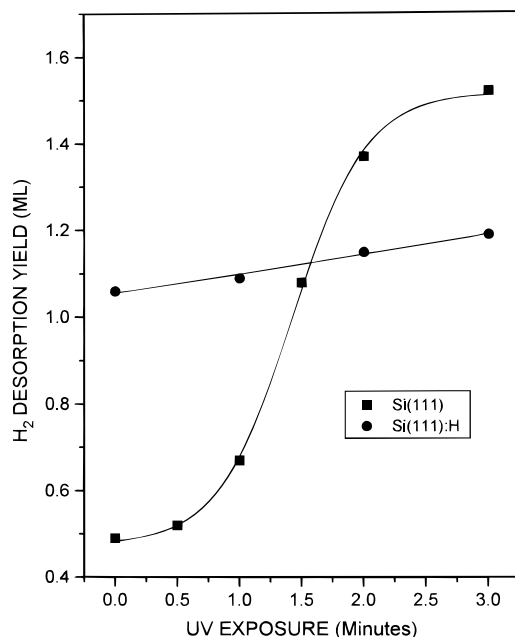
**Figure 1.** A plot of TPD yields of  $m/e = 60$  ( $\text{Si}_2\text{H}_4^+$ ) from a 5 langmuir disilane dose at 110 K after various post-UV exposures.

during the illumination periods utilized ( $\leq 500$  s.). During illumination, the Si crystal was placed approximately 2 cm from the lamp's MgF<sub>2</sub> window, in a vertical position. Disilane dosing pressures were of the order of  $1 \times 10^{-7}$  Torr.

## 3. Results

**3.1. Physisorbed Disilane.** The studies presented here of the photoinduced reaction of disilane with Si(111) have been performed at low temperatures. At such temperatures (below ca. 120 K), disilane predominantly exists on the Si(111) surface as a molecular species.<sup>4,11</sup> Epitaxial growth studies involving disilane have suggested that formation of a physisorbed precursor state is the first step in the thermal decomposition mechanism.<sup>2,32–34</sup> Uram et al.<sup>4</sup> and Imbihl et al.<sup>11</sup> measured a small apparent negative activation energy for low-temperature adsorption of disilane on Si(111) using vibrational spectroscopy.

Temperature-programmed desorption spectra were recorded after a combination of a 5 L disilane exposure of Si(111) at 110 K followed by post-UV irradiation of the surface in vacuum. The TPD yields for molecular disilane are presented as a function of the post-UV exposure in Figure 1. The first observation is that there is a decrease in the amount of molecular disilane desorption (Figure 1) with increasing (post) UV exposure. There are three main channels that can lead to depletion of molecular disilane from the surface: photoinduced dissociative chemisorption, thermal desorption caused by the heat generated by the UV lamp, and direct photodesorption. Temperature rises of up to 4 K were measured at the back of the crystal during UV irradiation, but the temperature rise at the crystal face is certainly greater. The cumulative effect of the three possible disilane-depletion channels increases with increasing UV exposure, causing a reduction in the measured amount of molecular disilane left on the surface at higher UV exposures. Hydrogen TPD yields, which are a measure of the extent of disilane reaction with the Si(111) surface, were also recorded for the experiments presented in Figure 1 and are presented in Figure 2. Initially, the H<sub>2</sub> yield slowly increases upon low exposures to UV irradiation, but then rapidly increases with intermediate UV exposures, leveling off at approximately



**Figure 2.** TPD yields, in units of H monolayers, of  $m/e = 2$  ( $H_2^+$ ) from a 5 langmuir disilane dose of Si(111) (squares) and a saturation disilane dose of Si(111):H at 110 K (circles) after various post-UV exposures.

1.5 ML at higher UV exposures. Saturation of the  $H_2$  yield at high UV exposures coincides with depletion of molecular disilane desorption (cf. Figure 1 and Figure 2).

Closer examination of Figures 1 and 2 reveals that at low UV exposures very little additional  $H_2$  desorbs from the surface, while significant disilane depletion is observed. This suggests that, initially, UV irradiation causes little additional reaction of disilane (beyond that occurring thermally at these temperatures) but causes significant desorption. It is uncertain whether this disilane depletion is caused by direct photodesorption or by thermal desorption induced by photothermal surface heating. It is observed, however, that these changes occur over a relatively short time scale where no measurable change in the surface temperature is observed. In the intermediate UV exposure regime, there is a sharp increase in the  $H_2$  desorption yield and a significant decrease in the amount of disilane that remains. This indicates that photoinduced dissociative chemisorption becomes important in this exposure regime. At high UV exposure, the amount of disilane physisorbed on the surface becomes significantly depleted, limiting further photoreaction and resulting in a saturation of the  $H_2$  yield (dependent upon the particular disilane exposure initially used).

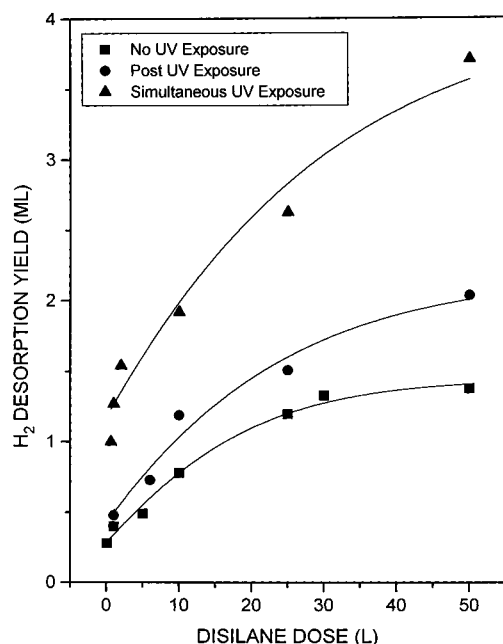
For multilayer disilane adsorption on Si(111) at 110 K, it is expected that there are at least two types of weakly bound disilane. The first type of physisorbed disilane is in direct contact with the Si(111) surface and the exposed dangling bonds and is presumably more tightly bound to the surface than the second and subsequent layers of physisorbed disilane. This second layer is weakly interacting with the chemisorbed hydride ( $H$  or  $SiH_x$ ,  $x = 1-3$ ) species or with the physisorbed disilane species present in the first monolayer. The interaction between physisorbed disilane and the surface silicon dangling bonds is expected to be stronger than that between physisorbed disilane and the adsorbed species ( $H$ ,  $SiH_x$ , and  $Si_2H_6$ ) present in the first layer.

If the outermost layers efficiently absorb the UV irradiation, then there are two explanations that could account for the observations presented in Figures 1 and 2. The initial surface

at 110 K consists of multiple layers containing both physisorbed and chemisorbed disilane. Post-UV irradiation could cause molecular desorption of disilane from the more weakly bound outermost physisorbed layers, while inducing dissociation of those molecules more tightly bound near the reactive dangling bonds of the Si surface. Such behavior would account for the rapid decrease in the amount of adsorbed disilane with post-UV exposure while also explaining the initial induction period observed prior to significant disilane dissociation. An alternative explanation of the data also involves efficient absorption of the UV irradiation by the outermost layers but exclusively involves UV-induced photoreaction. Absorption of UV irradiation by disilane can generate mono- and diradical  $Si_xH_y$  species. In the outermost molecular layers, the monoradicals ( $\cdot H$ ,  $\cdot SiH_3$ , and  $\cdot SiH_2SiH_3$ ) could abstract a hydrogen from other nearby disilane molecules and generate molecular species ( $H_2$ ,  $SiH_4$ , and  $Si_2H_6$ , respectively) and another monoradical or could react with each other to produce similar molecular species. In comparison, the diradicals  $\cdot SiH_2$  and  $\cdot SiHSiH_3$  could react with disilane to generate the higher order silanes,  $Si_3H_8$  and  $Si_4H_{10}$ , respectively. Such photoreactions would initially generate volatile molecular species that would result in depletion of adsorbed disilane with no initial Si deposition. Once these outermost volatile layers are removed, the UV irradiation can induce similar chemistry between radicals and either the surface itself or adsorbed  $SiH_x$  species. Such layer-by-layer photochemistry would additionally account for our observations.

The conclusion that the photodecomposition requires surface dangling bonds is supported by an additional series of measurements that were performed and are also plotted in Figure 2. The dangling bonds on the Si(111) surface were "consumed" by exposing the surface to hydrogen atoms that were generated by dissociation of  $H_2$  on a hot tungsten filament. The surface was exposed to atomic hydrogen at a surface temperature of 600 K to produce a Si(111):H surface containing ca. 1.0 monolayer of hydrogen. In this way, we are able to follow the photoinduced reaction of disilane on a surface in which the first physisorbed layer was not in direct contact with the dangling bonds. We find that when dangling bonds are not available, the photoreactivity is greatly suppressed (see Figure 2). Note that the  $H_2$  TPD yield begins at ca. 1.0 ML since the surface initially has one monolayer of H preadsorbed. This result would also suggest that the molecules in direct contact with the dangling bonds are mainly responsible for the photoreactivity of disilane seen here.

The presence of a weakly bound molecular disilane adsorption state on Si(111) has been previously observed by others. Uram and Jansson found that at 120 K on Si(111) disilane both molecularly adsorbs and partially dissociates.<sup>4</sup> The above result is also consistent with an EELS study by Imbihl et al.<sup>11</sup> in which, upon adsorbing disilane at 80 K and annealing to 170 K, the molecular disilane was removed and a small amount of hydrogen containing species ( $SiH_x$ ) remained. It is difficult to determine from TPD what fraction of the physisorbed phase will chemisorb at 110 K, as this number can also be altered by reactions that occur during the TPD temperature ramp. However, it should be noted that for a 0–3 min post-UV exposure the  $H_2$  TPD yield varies from 0.5 to 1.5 ML. As this is close to the saturation limit observed for the thermal reaction of atomic hydrogen (1.4 ML) or of disilane (1.4 ML) with the Si(111) surface, it suggests that the dangling bonds are saturated by the photoinduced reaction process, even for an initial 5 langmuir disilane exposure. Furthermore, this result indicates that, for post-UV exposure of a low-temperature disilane layer, the Si



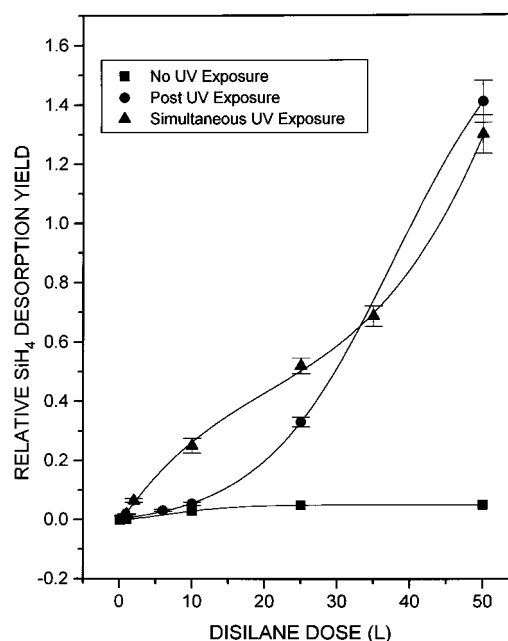
**Figure 3.**  $H_2$  TPD yields for Si(111) as a function of disilane dosage at 110 K. Each curve was plotted for a type of UV exposure: no UV (squares), post-UV (circles), and simultaneous UV (triangles).

dangling bonds play an important role in the photochemistry that occurs. These points will be discussed further below.

**3.2. Effect of UV Irradiation on the Reactivity of Disilane with Si(111).** The effect of UV irradiation on the reaction of disilane with Si(111) was examined under two types of UV exposure conditions. First, for the process discussed above, termed *post-UV exposure*, the Si(111) crystal is dosed with a specified amount of disilane at  $1 \times 10^{-7}$  Torr and then exposed under vacuum to UV light for the same amount of time as the disilane dosing period. The second type of UV exposure process, termed *simultaneous UV exposure*, involves exposing the Si(111) surface to UV irradiation while the crystal is being dosed with disilane. The same pressure was used for all disilane doses ( $1.0 \times 10^{-7}$  Torr). In addition to the UV-induced reaction processes, we also examined the thermal reactivity of disilane on Si(111) (i.e., the extent of dissociative disilane adsorption without UV irradiation).

For disilane decomposition on Si(111), the amount of hydrogen and silane desorbing from the surface during TPD is an indication of the extent of reaction. To quantify the  $H_2$  yield, a hydrogen monolayer was prepared by exposing the Si(111) surface to 300 langmuirs of  $H_2$  ( $10^{-6}$  Torr  $\times$  300 s) near a hot tungsten filament (1760 K) at a crystal temperature of 600 K. The crystal was elevated to this temperature in order to minimize etching of the Si surface during H atom adsorption.<sup>35</sup> The resulting  $H_2$  TPD yield is then used to quantify the subsequent photoreaction studies. The  $H_2$  yield from this surface corresponds to 1.0 ML and is exactly that due to saturation of the  $\beta_1$ - $H_2$  TPD feature.

In Figure 3,  $H_2$  TPD yields, in units of H atom monolayers, are plotted versus disilane adsorption for three different reaction conditions: upon simultaneous UV exposure, upon post-UV exposure, and upon no UV exposure. The UV exposure (in seconds) is 10-fold greater than the disilane exposure (in langmuirs). Thus, a 10 langmuir disilane dose corresponds to a post-UV or simultaneous UV exposure of 100 s. We observe that both types of UV exposure *enhance* the amount of hydrogen desorbing from the Si(111) surface, in comparison to a similar disilane dosage without UV exposure. Moreover, the hydrogen

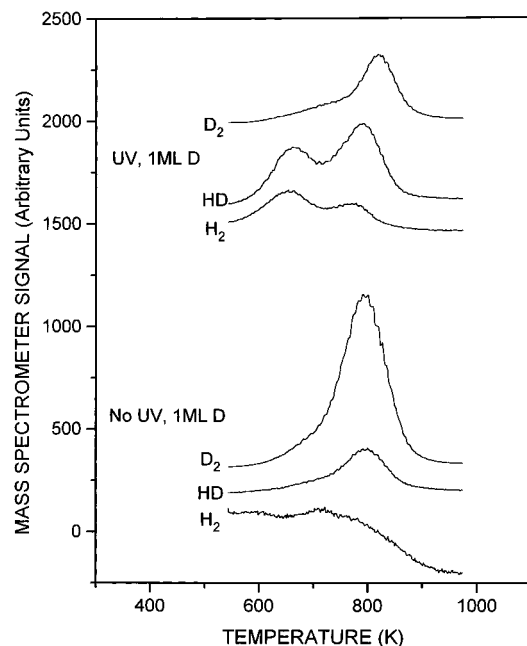


**Figure 4.** TPD areas of  $m/e = 30$  ( $SiH_2^+$ ) for Si(111) as a function of disilane dosage at 110 K and different UV conditions: no UV (squares), post-UV (circles), and simultaneous UV (triangles). The fragment  $SiH_2^+$  ( $m/e = 30$ ) was used to measure silane yields. The TPD areas are normalized to the silane desorption area from a hydrogen-saturated Si-(111) surface.

yield is greater under simultaneous UV exposure conditions versus post-UV irradiation conditions, for a given disilane dose. In addition, UV irradiation greatly enhances the silane ( $SiH_4$ ) TPD yields over that for the nonirradiated surface (see Figure 4). Again, we observe that simultaneous UV irradiation increases reactivity more than post-UV exposure, except at very large disilane doses, where silane yields for both irradiation methods are comparable. The increase in TPD yield for silane caused by UV exposure is much more pronounced than the increase in hydrogen yield when compared to the yield of these products from a nonirradiated surface. This can be explained by the fact that as further reaction is induced by UV irradiation, a greater percentage of the surface is covered by higher hydrides ( $SiH_2$ ,  $SiH_3$ , and possibly  $Si_2H_5$ ). It is these latter two hydrides,  $SiH_3$  and  $Si_2H_5$ , that are thought to be responsible for silane production. This is discussed below after details of the reaction mechanism are presented.

**3.3. Photoreaction Mechanism.** The main reaction pathway for the photoinduced reaction of disilane with Si(111) was studied using partially and fully monodeuterated Si(111) surfaces. A similar study was performed in our lab on Si(100) and is described in detail elsewhere.<sup>20</sup> The main features of our studies on Si(111) are presented here.

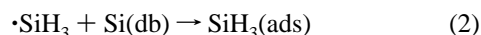
The desorption of hydrogen species ( $H_2$ , HD, and  $D_2$ ) from a monodeuterated surface exposed to disilane (25 langmuirs) was studied under simultaneous UV and non-UV reaction conditions (Figure 5). Under non-UV conditions the main desorption products are the  $D_2$  monolayer that was preadsorbed plus a small amount of HD, but no  $H_2$  desorption. The small amount of HD is likely due to dissociation and exposure of the surface to a partial pressure of hydrogen during D atom exposure caused by the residual hydrogen background in the chamber. Under simultaneous UV exposure and subsequent TPD, we observe substantial desorption of both  $H_2$  and HD, with significant  $\beta_2$  features (in addition to the  $\beta_1$  features). In addition, we observe minor desorption of  $D_2$  with a slight  $\beta_2$  feature. The observation of both  $\beta_1$  and  $\beta_2$  features in the  $H_2$ ,



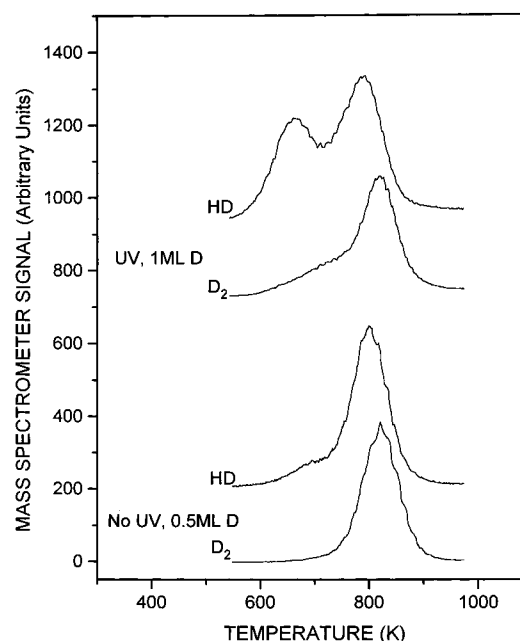
**Figure 5.** Mixed deuterohydrides from the reaction of disilane with Si(111):D under simultaneous UV reaction conditions and thermal conditions.

HD, and D<sub>2</sub> TPD spectra indicates that the photoreaction gives rise to the production of the following five different surface hydrides and deuterides: SiH, SiD, SiH<sub>2</sub>, SiD<sub>2</sub>, and SiHD. A model study was done to see whether silyl radicals could explain these results.

The model study was performed by preparing a partially deuterated Si(111) surface (0.5 ML) and subsequently exposing this surface to disilane (25 langmuirs). The partially deuterated surface was prepared by dosing the surface with deuterium (100 langmuirs) at 740 K. This model study was performed to help determine to what extent the silyl radical may be responsible for the observed photochemistry. If the radical  $\cdot\text{SiH}_3$  is a primary contributor to the photochemistry, and if under simultaneous UV conditions disilane was exposed to a monodeuterated surface, then the following reactions would be expected:



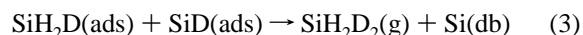
A partially monodeuterated Si(111) surface subsequently exposed to disilane at low temperatures would be a suitable model for examining a mechanism on a fully monodeuterated surface that is dominated by photogenerated silyl radicals. Abstraction of deuterium atoms by photogenerated  $\cdot\text{SiH}_3$  radicals would leave behind dangling bonds, which a partially monodeuterated Si(111) surface appropriately models. Reaction of these dangling bonds with disilane at low temperatures will predominantly result in cleavage of the Si-Si bond, thereby producing a model surface composed of silyl species and monodeuteride species. All the reactants needed to simulate a silyl-dominated photoreaction mechanism on a deuterated surface are present: SiH<sub>3</sub>, SiD, and Si dangling bonds. TPD spectra for HD and D<sub>2</sub> desorption from such a Si(111) surface (i.e., following the reaction of disilane with a partially monodeuterated surface) show predominantly a  $\beta_1$ -peak for both D<sub>2</sub> and HD but a very slight  $\beta_2$ -HD feature (Figure 6). The absence of any significant HD or D<sub>2</sub> desorption from the  $\beta_2$  state suggests that the partial SiD layer does not react with disilane under these



**Figure 6.** Comparison of deuterohydride products from the photoinduced reaction of disilane with Si(111):D to those from the thermal reaction of disilane with Si(111):0.5D.

reaction conditions. More importantly, it indicates that a surface composed initially of SiH<sub>3</sub> and SiD does not generate the observations made for a monodeuterated surface exposed to disilane and UV light. For the latter surface involving simultaneous UV irradiation, a large amount of HD is observed to desorb with a strong  $\beta_2$  feature, as well as some  $\beta_2$ -D<sub>2</sub> desorption. *This indicates that the silyl radical is likely not the dominant photoinduced reactive intermediate leading to Si deposition.* Similar observations were made for the Si(100) surface previously.<sup>20</sup>

We also examined the desorption spectra for the various cracking fragments expected for silane and its isotopic analogues. Under UV irradiation conditions involving the reaction of disilane with a fully monodeuterated Si(111) surface,  $m/e = 33$  and  $34$  were observed, whereas for reaction of disilane with the partially monodeuterated Si(111) surface without UV irradiation,  $m/e = 33$  was observed but  $m/e = 34$  was not. The presence of  $m/e = 34$  is best explained by the following reaction.



The absence of  $m/e = 34$  from the partially monodeuterated surface suggests the absence of SiH<sub>2</sub>D(ads) on this model surface. Furthermore, the lack of any significant  $\beta_2$ -HD and  $\beta_2$ -D<sub>2</sub> features shows that SiD species are preserved for the model surface following disilane reaction. In comparison, in both the studies presented here on Si(111) and in the previous studies on Si(100),<sup>20</sup> silane-*d*<sub>2</sub> was observed to desorb from a Si surface presaturated with monodeuterides and subsequently exposed to disilane and UV irradiation simultaneously. Thus, reaction of disilane under simultaneous UV conditions with fully monodeuterated Si(111) generates the surface species SiH<sub>2</sub>D-(ads) and hence involves the reaction of SiD species with a photoreactive intermediate other than the silyl radical. This species is either the diradical  $\cdot\text{SiH}_2$  or the diradical  $\cdot\text{Si}(\text{SiH}_3)\text{H}$ .

#### 4. Discussion

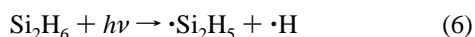
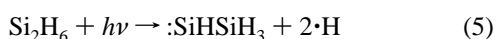
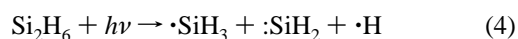
**4.1. Summary of Our Results.** The reactivity of disilane on Si(111) at ca. 110 K under various UV irradiation conditions is summarized below.

1. With UV irradiation, the reaction of disilane with Si(111) is enhanced with respect to the thermal reaction, as determined from the quantitative desorption yields of hydrogen and silane using TPD. Simultaneous UV irradiation gave greater reaction enhancement than post-UV irradiation under the adsorption conditions used for both studies.

2. There is evidence for a molecular physisorbed precursor state that interacts directly with the dangling bonds of Si(111). This state does not lead to significant dissociative chemisorption upon exposure at 110 K followed by subsequent heating of the Si(111) surface but does lead to substantial decomposition upon UV irradiation at 110 K.

3. The photoinduced reaction pathway for disilane is distinct from the thermal reaction pathway. Observations for the photoinduced reaction suggest that silyl radicals are not the primary species leading to enhanced reaction and deposition of silicon.

**4.2. Photochemistry of Disilane and the Nature of the Photogenerated Intermediates.** Photolysis of disilane at 147 nm has been studied previously by Perkins and Lampe.<sup>30</sup> They found that disilane photolysis occurred at this wavelength via the following reactions:



The quantum yields of reactions 4–6 are 0.61, 0.18, and 0.21, respectively.<sup>30</sup> All three reactions are energetically accessible with the broad-band emission source used in our study. Emission from our D<sub>2</sub> lamp is centered at 161 nm. It is also known that the diradical  $\cdot\text{SiH}_2$  can insert into SiH bonds of silane and disilane in the gas phase.<sup>36</sup>

In this and our previous study<sup>20</sup> of the photoinduced reaction of disilane with Si(100), we found that when the surface was parallel to the light beam during simultaneous exposure of disilane, no enhancement in disilane reactivity was observed compared to the thermal reactivity at that temperature. Furthermore, in a related study, the effect of simultaneous UV irradiation during disilane exposure of Si(100) at 160 and 200 K was previously examined.<sup>20</sup> At these elevated temperatures (which are in fact above the molecular desorption temperature for disilane from Si(100)), no photoenhancement was observed.<sup>20</sup> From these previous studies and from the similarities reported here for the photoinduced reaction of disilane with Si(111), we believe that condensed-phase photolysis is occurring.

Let us consider the photoreactions 4–6 described above. The types of species generated in reaction 4 are hydrogen atoms, silyl radicals, and silylene diradicals. If any of these photogenerated species encounter a bare Si surface atom with a dangling bond, they will react to form SiH, SiSiH<sub>3</sub>, and SiSiH<sub>2</sub> $\cdot$ , respectively. The latter species, SiSiH<sub>2</sub> $\cdot$ , would likely insert into a neighboring Si–Si bond to generate a bridging SiH<sub>2</sub> species. If these photogenerated species encounter an SiH surface species, they could react to abstract the H atom and form H<sub>2</sub>(g), SiH<sub>4</sub>(g), and  $\cdot\text{SiH}_3$ (g), respectively. Alternatively, the silylene diradical could insert into the Si–H bond rather than abstracting the H atom, thus producing SiSiH<sub>3</sub>. Notice that reaction of  $\cdot\text{H}$  or  $\cdot\text{SiH}_3$  with SiH via abstraction would generate relatively unreactive gas-phase species and result in formation of a surface dangling bond. Hence, abstraction by these two photogenerated species would regenerate a bare surface. Alternatively, upon encountering an SiH species, the

three type of photogenerated species produced in reaction 4 may insert into one of the three Si–Si back-bonds (i.e., react with Si–SiH) to form SiH<sub>2</sub>, Si(SiH<sub>3</sub>)H, and Si(SiH<sub>2</sub>)SiH, respectively. If these photogenerated species encountered an SiH<sub>2</sub> surface species, they could abstract a hydrogen atom to form a surface dangling bond and H<sub>2</sub>(g), SiH<sub>4</sub>(g), and  $\cdot\text{SiH}_3$ (g), respectively. Alternatively, the photogenerated radicals could react with one of the two Si–Si back-bonds of SiSiH<sub>2</sub> to generate SiH<sub>3</sub>, Si<sub>2</sub>H<sub>5</sub>, and Si(SiH<sub>2</sub>)SiH<sub>2</sub>, respectively. If these photogenerated species encountered a SiH<sub>3</sub> surface species, they could abstract a hydrogen atom to form a surface dangling bond and the same H<sub>2</sub>(g), SiH<sub>4</sub>(g), and  $\cdot\text{SiH}_3$ (g) species, respectively, similar to that expected for reaction of these species via abstraction with SiH or SiH<sub>2</sub>. Alternatively, the photogenerated radicals could react with the lone Si–Si back-bond of SiSiH<sub>3</sub> to generate a surface dangling bond and SiH<sub>4</sub>(g), a surface dangling bond and Si<sub>2</sub>H<sub>6</sub>(g), and Si<sub>2</sub>H<sub>5</sub>, respectively.

The types of species thus generated from reaction of an  $\cdot\text{H}$  atom with the disilane exposed Si surface is either (i) a surface dangling bond and an unreactive gas-phase species such as H<sub>2</sub> or SiH<sub>4</sub> or (ii) a surface bound Si hydride, e.g., SiH, SiH<sub>2</sub>, or SiH<sub>3</sub>. Likewise, reaction of the silyl radical  $\cdot\text{SiH}_3$  with the disilane exposed Si surface will generate either (i) a surface dangling bond and a Si-containing gas-phase species (namely SiH<sub>4</sub> and Si<sub>2</sub>H<sub>6</sub>, and possibly higher order silanes such as Si<sub>3</sub>H<sub>8</sub> if Si<sub>2</sub>H<sub>5</sub> is a prevalent surface species) or (ii) a surface bound Si hydride (e.g., SiH<sub>3</sub>, Si(H)SiH<sub>3</sub>, Si<sub>2</sub>H<sub>5</sub>, etc.). Reaction of the diradical  $\cdot\text{SiH}_2$  with the disilane exposed Si surface will generate either (i) other gas-phase radicals such as  $\cdot\text{SiH}_3$  or  $\cdot\text{Si}_2\text{H}_5$ , or (ii) surface bound Si hydrides (e.g., SiH<sub>2</sub>, SiH<sub>3</sub>, Si<sub>2</sub>H<sub>5</sub>, Si(SiH<sub>2</sub>)SiH, etc.). Note that, in general, reaction of the monoradical species  $\cdot\text{H}$  or  $\cdot\text{SiH}_3$  can lead to significant removal of surface bound species (i.e., etching), whereas the diradical species  $\cdot\text{SiH}_2$  leads primarily to addition of surface bound Si-containing species (i.e., deposition).

The photogenerated species produced in reactions 5 and 6 are substitutional analogues of those produced in reaction 4, where a hydrogen atom has been replaced by a silyl group, and hence the products they would generate would be similar, but of higher order. For example, reaction of  $\cdot\text{Si}_2\text{H}_5$  would be similar to that of  $\cdot\text{SiH}_3$ . However, whereas  $\cdot\text{SiH}_3$  would react via abstraction with SiH or SiH<sub>3</sub> to produce SiH<sub>4</sub> or Si<sub>2</sub>H<sub>6</sub>,  $\cdot\text{Si}_2\text{H}_5$  would produce Si<sub>2</sub>H<sub>6</sub> or Si<sub>3</sub>H<sub>8</sub>, respectively.

The above discussion leads us to a better understanding of our observations. Photoexcitation of physisorbed disilane likely generates all of the species observed by Perkins and Lampe.<sup>30</sup> However, our mechanistic studies on Si(111) and previously on Si(100) point to the diradical species as being the major contributor to the reaction process, since it is the only species that can account for our observations. These observations include (i) production of silane-*d*<sub>2</sub>,  $\beta$ <sub>2</sub>-D<sub>2</sub>, and  $\beta$ <sub>2</sub>-HD upon simultaneous UV irradiation and disilane exposure following preparation of a saturated monodeuteride layer, (ii) the absence of the above products for a layer modeling the silyl radical reaction and consisting of a mixture of SiH<sub>3</sub>, SiH<sub>2</sub>, and SiD, and (iii) production of an  $\alpha$ -D<sub>2</sub> and an  $\alpha$ -HD state due to desorption of deuterium-containing species from Ge atoms upon post-UV irradiation of a digermane exposed Si(100) surface saturated with a monodeuteride (SiD) layer (i.e., a Si(100)-2  $\times$  1:D layer).<sup>37</sup> Our observations are dominated by the diradical reactions since these are the main processes leading to deposition. It is likely that the monoradical species are equally involved in the chemistry, but their primary effect is to cause

etching, and hence are not measured by our subsequent characterization of the resulting surface.

**4.3. Comparison with Photochemical Studies of Disilane on Si(100).** Dippel et al.<sup>28</sup> have recently studied the photoinduced reaction of disilane on deuterium terminated Si(100) at 110 K upon irradiation with 193 or 248 nm UV light from an excimer laser. The photoinduced reaction chemistry was followed by vibrational spectroscopy using high-resolution electron energy loss spectroscopy (HREELS), while the time-of-flight velocity distributions were measured upon photoinduced desorption using a mass spectrometer. The authors observed production of Si–H stretching and bending vibrations upon photolysis of a condensed Si<sub>2</sub>H<sub>6</sub> overlayer on a D-passivated Si(100) surface. Furthermore, they observed H<sub>2</sub>, SiH<sub>4</sub>, and Si<sub>2</sub>H<sub>6</sub> desorption but no other ions or radicals. The products hydrogen and silane show fast and slow components in a bimodal velocity distribution and were only observed upon irradiation at 193 nm, whereas the disilane displayed a single (partially accommodated) velocity distribution that occurred at both 193 and 248 nm. From these studies the authors concluded that H<sub>2</sub> and SiH<sub>4</sub> are generated upon photoexcitation of condensed disilane in a direct step that does not involve accommodation or collision with the surface and in a mechanism by which it is fully accommodated. However, neither mechanism involved abstraction from a Si–D bond, as no deuterium incorporation was found in any of the products. The authors concluded that as there is little evidence for reactions that abstract deuterium from the surface, the likely mechanism leading to Si deposition involves insertion of :SiH<sub>2</sub> radicals into Si–H (Si–D) bonds at the surface. These results, using single wavelength laser excitation, agree well with our broad-band UV studies on Si(111), as presented here, and with our previous studies on Si(100).<sup>20</sup>

Dippel et al.<sup>28</sup> also observed disilane desorption upon excitation at either 193 or 248 nm, even though the optical absorption of disilane has a threshold of 220 nm. Furthermore, they have shown that the disilane desorption flux is linear with laser fluence.<sup>38</sup> From these results, the authors suggested that the mechanism for disilane desorption involves light absorption by the Si substrate to produce hot carriers which lead to disilane desorption. Such behavior, in combination with photoexcitation of disilane to produce the mono- and diradicals discussed previously, would also account for our results (presented in Figures 1 and 2).

Dippel et al.<sup>28</sup> did not address the issue of physisorption at dangling bond sites, as their studies were performed on a Si–D layer. Furthermore, such studies are not readily feasible on Si(100) due to the higher reactivity of this surface.<sup>39</sup> It is interesting to note that Dippel et al.<sup>28</sup> observed significant photoreaction upon post-UV irradiation of disilane condensed onto a saturated Si(100):D surface using an excimer laser, whereas we only observed significant photoreaction previously on Si(100):D<sup>20</sup> upon simultaneous UV exposure using our broad-band D<sub>2</sub> UV source. Similar behavior is observed again here for Si(111), as shown in Figure 2, where only minor photoreaction is induced upon post-UV irradiation of a condensed disilane layer physisorbed on a saturated Si(111):H surface. The differences observed between their studies on Si(100):D<sup>28</sup> and our studies on Si(100):D<sup>20</sup> and Si(111):H (this work) must be related to the different sources of photoexcitation used and their relative intensity at various wavelengths.

## 5. Conclusions

Various aspects of the reaction of disilane on Si(111) were investigated using temperature-programmed desorption mass

spectrometry. The reactivity of disilane was compared under thermal reaction conditions and under UV photoexcitation conditions, both during and after disilane adsorption. Potential reaction mechanisms were examined by generating Si(111) surfaces with specific isotopically labeled reaction intermediates or by following the disilane photochemistry on a monodeuteride passivated Si(111) surface.

Under UV irradiation, disilane is more reactive on Si(111) than that induced thermally at approximately 110 K. Ultraviolet irradiation during or after disilane exposure enhanced the desorption yields of silane and hydrogen, thus increasing the amount of silicon deposited on the surface. This enhanced reactivity can go well beyond the first monolayer, as evidenced by H<sub>2</sub> desorption yields approaching 4.0 ML (see Figure 3). Examination of TPD yields of H<sub>2</sub> and Si<sub>2</sub>H<sub>6</sub> from Si(111) under thermal and various post-UV exposures indicated the existence of a physisorbed precursor that is in direct contact with the dangling bonds of Si(111).

We conclude that the thermal chemistry of disilane is mediated by the surface dangling bond density and the electronic and structural nature of the surface. In contrast, the photoreactivity is mediated by the inherent photochemistry of molecular disilane at the wavelength and fluence utilized. Our results indicate that the primary ultraviolet photoreaction channel leading to Si deposition and formation of surface hydrides involves the insertion of silylene diradicals.

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