

# Silicon Chemical Vapor Deposition One Step at a Time: Fundamental Studies of Silicon Hydride Chemistry

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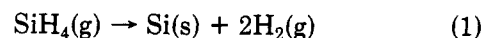
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Thin solid films of silicon, ranging in composition and crystallinity from amorphous hydrogenated Si to single-crystal epitaxial Si are vital to modern technology, finding myriad uses in areas such as solar energy conversion and state of the art microelectronics. These films are routinely fabricated from gaseous precursor molecules by a variety of empirically developed chemical vapor deposition (CVD) processes. A mechanistic understanding of these processes is clearly desirable from a practical viewpoint. Efficient optimization of film properties and growth conditions is vital in order to satisfy the demands that new technologies place on these materials. Detailed understanding of CVD processes also presents a significant and fascinating scientific challenge in the areas of physical, inorganic, surface, and solid-state chemistry. The net conversion of gaseous silane, SiH<sub>4</sub>, to solid silicon and gaseous hydrogen appears simple enough, yet the mechanism of this process can be alarmingly complex. Gas-phase, gas-surface, surface, and solid-state chemical processes can all be involved, depending on the deposition conditions.

Our approach in this Account is to discuss recent studies of elementary processes in silane chemistry. The ultimate goal of this approach is to facilitate the construction of chemically accurate deposition mechanisms from this fundamental information, one step at a time. No attempt has been made to provide comprehensive review of the enormous and diverse CVD literature. In particular, we do not discuss the practical implementation of silicon CVD, silicon growth from precursors other than the silicon hydrides, phenomenological film growth studies, in situ diagnostic studies of CVD reactors, or large-scale numerical modelling studies of CVD processes in any detail. Information on these and other topics can be found elsewhere in recent papers and review articles, for example, refs 1-11.

Reaction 1 is exothermic by 8.2 kcal/mol. Although both silane and disilane are thermodynamically unstable with respect to the elements, significant kinetic barriers exist to their decomposition. The energy re-



quired to overcome these barriers and achieve film growth at useful rates is typically provided by heat, plasma excitation, or light. Table I lists several common CVD processes for the deposition of silicon from silane or disilane. These processes are distinguished by the pressure, temperature, and method of excitation employed. Specification of these conditions, in turn, determines the type of material deposited and, more importantly for purposes of this Account, specifies which chemical processes are likely to be important.

Figure 1 schematically illustrates the potentially important elementary mechanistic steps in an arbitrary Si film growth process. These steps include interaction of the silane precursor with a surface, gas-phase dissociation of silane to produce silicon hydride radicals, gas-phase and surface reactions of these radicals, and desorption of byproducts, such as molecular hydrogen, from the growing film. Our ultimate goal is to obtain enough fundamental information on these elementary steps to determine, a priori, which steps will control deposition rates and film properties under which deposition conditions.

Separation of gas-phase and surface reaction steps is a useful approach to both the discussion and investigation of CVD chemistry. The gas-phase chemistry determines the fluxes of various species to the film growth surface. Subsequent chemistry at that surface incorporates silicon into the film. In thermal systems at very low pressures (UHVCVD in Table I), gas-phase collisions are rare compared to gas-surface collisions and unimolecular decomposition in the gas phase is unlikely. The appropriate mechanistic starting point is the interaction of silane with a hot, clean silicon surface. At higher pressures in thermal systems, gas-phase unimolecular dissociation of silane may become

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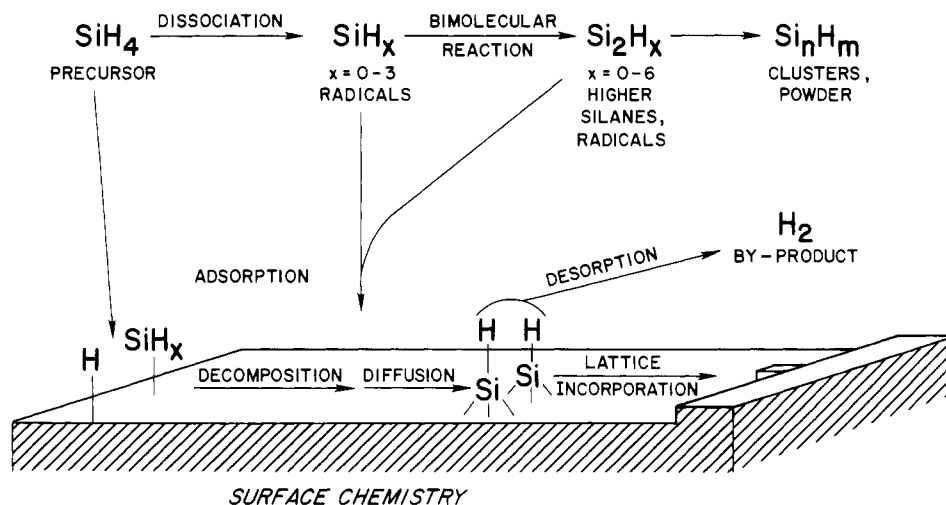
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**Table I**  
Some Common Silicon CVD Processes Using Silane or Disilane

method	pressure, Torr	temperature, K	comments
ultrahigh-vacuum CVD (UHVCVD)	$10^{-3}$ – $10^{-2}$	775–1000	epitaxial silicon from thermal decomposition of $\text{SiH}_4$ for microelectronics
low-pressure CVD (LPCVD)	0.1–1	900–1000	polycrystalline silicon from thermal decomposition of $\text{SiH}_4$ or $\text{Si}_2\text{H}_6$ for microelectronics
atmospheric-pressure CVD (APCVD)	760	1100–1400	epitaxial silicon from thermal decomposition of $\text{SiH}_4$ in $\text{H}_2$ or He buffer gas for microelectronics
plasma-enhanced CVD (PECVD)	$10^{-3}$ –1	300–600	amorphous hydrogenated silicon from plasma decomposition of $\text{SiH}_4$ or $\text{Si}_2\text{H}_6$ for solar cells
photochemical CVD (PHOTOCVD)	0.1–10	300–600	amorphous hydrogenated silicon from Hg-sensitized photolysis of $\text{SiH}_4$ or direct photolysis of $\text{Si}_2\text{H}_6$ for solar cells

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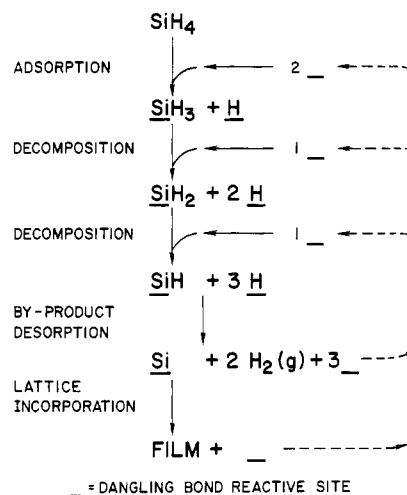
**Figure 1.** Schematic mechanism of Si film growth by a generalized CVD process, starting with  $\text{SiH}_4$  precursor gas. Elementary mechanistic steps and important classes of reactive intermediates are shown.

important. The appropriate questions are, what are the dissociation products and what is their chemistry? In plasma or photochemical systems, multiple dissociation channels may lead to the production of a variety of gas-phase radical species. The appropriate questions are, which species are produced and what is their role in the deposition chemistry?

### Epitaxial Si Growth from $\text{SiH}_4$

Surface reaction processes contributing to film growth are shown in Figure 1 and include adsorption, surface decomposition (conversion of surface species), lattice incorporation, and byproduct desorption. Surface diffusion plays an active role at high growth temperature ( $T$ ), but a lack of data leaves the role of diffusion at lower  $T$  an area for speculation and future research. A recent innovation<sup>12</sup> in Si CVD growth is the use of both atomically clean substrates and a  $\text{SiH}_4$  pressure of  $\approx 10^{-3}$ – $10^{-2}$  Torr. This approach, UHVCVD, embodies the simplest chemistry of the Si CVD processes: surface decomposition of  $\text{SiH}_4$  is the only path. Note that the term UHVCVD refers to the design of the apparatus, not the film deposition pressure.

The silicon hydride species observed under ultrahigh vacuum (UHV, pressures  $\leq 10^{-9}$  Torr) conditions for the decomposition of  $\text{SiH}_4$  on the  $\text{Si}(100)$ – $(2 \times 1)$  surface<sup>13</sup> are shown in Figure 2. (The standard surface structure



**Figure 2.** Mechanism of surface decomposition of  $\text{SiH}_4$  on the  $\text{Si}(100)$ – $(2 \times 1)$  surface, emphasizing the silicon hydride intermediates and the role of dangling bonds on surface Si atoms.

notation<sup>14</sup> is used). This scheme outlines the growth chemistry for UHVCVD. The dashed arrows at the right represent a feedback loop in the kinetics of the overall film-growth reaction. Dangling bonds on surface Si atoms (denoted  $\_$ ) are consumed in the adsorption and decomposition steps and are produced only by the desorption of  $\text{H}_2$ . This feedback loop allows byproduct ( $\text{H}_2$ ) desorption kinetics to influence or completely

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control the film growth rate (GR). In the case of CVD from silane, the GR is controlled by the rate of the reaction  $2\text{H} \rightarrow 2\text{H}_2 + \text{H}_2(\text{g})$  at temperatures below roughly 900 K. Generally, for CVD processes the GR equals the adsorption rate, provided that etching or evaporation of film atoms does not occur. This applies to the silicon hydride system below about 1100 K (the detectable onset of Si atom desorption). Factors controlling the rate of  $\text{SiH}_4$  adsorption are therefore central to understanding the growth kinetics. It is the coverage of dangling bonds that governs the adsorption rate at low  $T$ .

The reactive sticking probability,  $S^R$ , is the number of dissociatively adsorbed molecules produced per molecule-surface collision, and the R superscript emphasizes that bond breaking and formation must occur. An indirect method of evaluating  $S^R$  involves equating the film growth rate (GR) with the adsorption rate and calculating molecules (Si atoms) adsorbed from film thickness. The molecule-surface collisions are calculated from pressure and time data. The ubiquitous  $\text{Si}_2\text{H}_6$  impurity in commercially available  $\text{SiH}_4$  makes these evaluations upper limits on  $S^R$  of silane. Comparison of GR data from six different laboratories places an upper limit of  $3 \times 10^{-4}$  for  $S^R$  of  $\text{SiH}_4$  on both Si(100) and Si(111) surfaces.<sup>15,16</sup>

The initial slope of a plot of molecules adsorbed per square centimeter versus exposure per square centimeter is a direct measure of  $S^R$ . Measuring calibrated  $\text{H}_2$  temperature programmed desorption (TPD) areas after calibrated  $\text{SiH}_4$  exposures, we have evaluated  $S^R$  with UHV conditions maintained during surface preparation and after the exposure.<sup>17-19</sup> Because we must assume that no  $\text{H}_2$  desorbs from the surface during the exposure, the slope is a lower limit on  $S^R$ . Thus, a lower limit of  $3 \times 10^{-5}$  on the Si(100)-(2×1) surface at  $T_s = 675$  K was determined by using highly purified silane.<sup>17</sup> Rigorous limits on  $S^R$  of  $\text{SiH}_4$  are  $3 \times 10^{-5} < S^R < 3 \times 10^{-4}$ . An enhancement of  $S^R$  for  $\text{SiH}_4$  on ion-bombardment Si(111)-(7×7) surfaces (compared to the annealed surface)<sup>18</sup> suggests that details of surface structure may also affect the rate of silane adsorption.

Because surface  $\text{SiH}_3$  and  $\text{SiH}_2$  groups are relatively unstable, surface hydrogen is present only in the form of SiH for  $T_s \geq 675$  K. These SiH groups block the reactive dangling bond sites required for  $\text{SiH}_4$  chemisorption, causing  $S^R$  to be a strongly decreasing function of H coverage.<sup>17,18</sup> at this temperature. This defines the lower limit in temperature for strictly thermal Si growth.

Identification and quantification of surface SiH,  $\text{SiH}_2$ , and  $\text{SiH}_3$  species when they coexist on Si surfaces have proved to be a persistent problem in silicon hydride surface chemistry.<sup>20,21</sup> Infrared absorption spectroscopy

using a Si multiple internal reflection element<sup>22</sup> provides structure and stoichiometry information, but long signal-averaging times have prohibited kinetic studies. We have applied static secondary ion mass spectrometry (SSIMS) to this problem and have demonstrated that surface  $\text{SiH}_x$  moieties are sputtered intact as the corresponding  $\text{SiH}_x^+$  secondary ions under mild  $\text{Ar}^+$  ion bombardment conditions.<sup>20</sup> Referring to Figure 2, adsorbed  $\text{SiH}_3$  and SiH were directly observed by SSIMS after  $\text{SiH}_4$  adsorption on Si(100)-(2×1), and the  $\text{SiH}_2$  intermediate was detected by using the  $\text{SiH}_2$  decomposition peak in TPD.<sup>13</sup>

Decomposition kinetics for surface species may be extracted from temperature-programmed SIMS, as developed by White and co-workers.<sup>23</sup> By performing the  $\text{SiH}_4$  adsorption<sup>13</sup> and atomic H adsorption<sup>20</sup> in separate studies, we have adjusted the coverage of dangling bonds and SiH coexisting with  $\text{SiH}_3$  and found the trihydride to be unstable in the presence of dangling bonds which participate in the reaction  $\text{SiH}_3 + \text{H} \rightarrow \text{SiH}_2 + \text{H}$ . Trihydride decomposition by this reaction occurs between 150 and 350 K on the clean surface (high dangling-bond coverage). For essentially zero dangling-bond coverage (high coverage of coadsorbed SiH),  $\text{SiH}_3$  is stabilized up to  $\approx 675$  K. The preexponential factor for this reaction decreases with decreasing coverage of dangling bonds, while the activation energy is small ( $\approx 2$  kcal/mol) and constant.<sup>13</sup> Subsequent  $\text{SiH}_2$  decomposition involves two mechanisms, and the competition of these is also controlled by the dangling-bond coverage. On the clean surface, abundant dangling bonds favor  $\text{SiH}_2 + \text{H} \rightarrow \text{SiH} + \text{H}$ . A second-order mechanism is observed at low dangling-bond (high-SiH) coverage:  $2\text{SiH}_2 \rightarrow \text{H}_2(\text{g}) + 2\text{SiH}$ .

Two trends summarize the surface decomposition of  $\text{SiH}_x$  groups. First, SiH is the most stable, and the rank order of stability of the surface hydrides is  $\text{SiH} > \text{SiH}_2 > \text{SiH}_3$ . Second, the stability of  $\text{SiH}_2$  and  $\text{SiH}_3$  is controlled by the local surface environment, specifically by the availability of dangling bonds. Dangling bonds are needed as reactive sites to bind the H atoms produced by di- and trihydride decomposition.

We have constructed a kinetic model for CVD growth of epitaxial Si from  $\text{SiH}_4$  based on the scheme in Figure 2. Our measurements of the first two steps (adsorption followed by  $\text{SiH}_3$  decomposition) are combined with literature data<sup>24,26</sup> for the  $\text{SiH}_2$  and SiH decomposition steps. The essence of this model<sup>15,16</sup> is an expression for the Si GR in terms of the  $\text{SiH}_4$  adsorption rate coefficient,  $k_A$ , the silane flux to the surface ( $\text{SiH}_4$ ), and the coverage of surface dangling-bond sites ( $\_$ ). This expression is  $\text{GR} = 2k_A(\text{SiH}_4)\_$ , which accurately predicts the Si GR between about 725 and 1275 K (the practical limits of the data). The Si GR exhibits a trend

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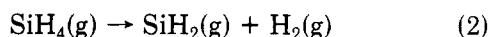
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commonly observed in Arrhenius behavior of CVD processes: the rate-limiting step changes with  $T$ . A large activation energy ( $E_A$ ) is observed at low  $T$ , and a small  $E_A$  is observed at high  $T$ , with a curved transition region between. The large  $E_A$  observed at low  $T$  is due to growth rate limitation by the byproduct desorption reaction,  $2\text{H} \rightarrow 2_+ + \text{H}_2(\text{g})$ , with  $E_A = 47$  kcal/mol measured by Sinniah et al.<sup>24</sup> The feedback loop indicated in Figure 2 (dashed lines) is responsible for kinetic control of the adsorption rate by the product desorption step. The small  $E_A$  (3 kcal/mol) observed at high  $T$  is due to  $\text{SiH}_4$  adsorption being the rate-limiting step, and this is the activation energy observed<sup>18</sup> for  $S^R$  of  $\text{SiH}_4$  in our studies on  $\text{Si}(111)-(7\times 7)$ . Measurements of the H coverage versus  $T$  during growth are also accurately predicted by this expression.<sup>16</sup>

### Silicon Growth from $\text{SiH}_4$ at Higher Pressures

At higher total pressures in thermal systems (LPCVD and APCVD conditions), gas-phase collisions become important and provide energy for the unimolecular decomposition of silane. Silane pyrolysis has been studied by static<sup>27,28</sup> and flow pyrolysis,<sup>29-31</sup> shock tube,<sup>32</sup> and laser powered homogeneous pyrolysis<sup>33</sup> techniques. The initial step in this process has been a source of considerable controversy,<sup>27-33</sup> as has the role of heterogeneous decomposition in pyrolysis studies.<sup>31,33-37</sup> It is now generally agreed that *when* silane decomposes in the gas phase, the primary dissociation is given by reaction 2, three-center elimination of molecular hydrogen to form silylene. This species has recently been directly detected by intracavity dye laser absorption spectroscopy during the pyrolysis of silane.<sup>38</sup> There



is also some information on the pressure-temperature-surface conditions that favor homogeneous decomposition and those that favor heterogeneous decomposition.<sup>36,37</sup> Lower total pressures and lower reaction temperatures favor the heterogeneous reaction, while higher total pressures and higher reaction temperatures favor the homogeneous reaction. It is important to realize that *both* processes may be occurring, especially under LPCVD conditions.

Accurate incorporation of the homogeneous decomposition step into CVD models is complicated by the fact that silane is a small molecule with no low-frequency vibrational motions. Thus, its unimolecular decomposition is never in the high-pressure limit under

CVD conditions. This requires that Rice-Ramsperger-Kassel-Marcus theory (RRKM) modelling be used to calculate the appropriate decomposition rate for a given set of reaction conditions.<sup>39</sup> Significant progress has been made in RRKM modelling of silane decomposition;<sup>40</sup> however, experimental data in the appropriate pressure regime and with the appropriate bath gases are still lacking.

Given that the reactive species  $\text{SiH}_2$  is formed in the gas phase, it is necessary to understand its chemistry. Does it react rapidly with other gas-phase molecules such as silane and molecular hydrogen which are likely to be present in a CVD system, or does it diffuse to surfaces, stick, and contribute directly to film growth? Prior to 1985, arguments were frequently made that the latter process dominated. This was because the available kinetic data for the reactions of silylene, estimated from competitive rate studies, suggested that it was rather unreactive with molecules such as hydrogen, silane, and disilane.<sup>41</sup> In 1985 Inoue and Suzuki<sup>42</sup> and Jasinski<sup>43</sup> independently devised flash photolysis/laser spectroscopic techniques for studying silylene kinetics directly in real time. The results of these studies, carried out at room temperature, were surprising. Both groups found that silylene was orders of magnitude more reactive with hydrogen, silane, and disilane than previously thought. In particular, silylene reacts by insertion at nearly the gas kinetic rate (i.e., a rate constant of approximately  $10^{-10}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>) with silane and disilane. These results and subsequent more complete studies<sup>44,45</sup> have qualitatively and quantitatively changed much of our understanding of the mechanistic role of silylene in CVD systems. The kinetic studies also provided the first experimental evidence that *ab initio* predictions for the heat of formation of silylene<sup>46-48</sup> were far more accurate than the accepted experimental value<sup>49</sup> and confirmed *ab initio* predictions of the reactivity of silylene with hydrogen.<sup>50</sup> Finally, the kinetic results led to a reevaluation<sup>51,52</sup> of the pyrolysis data for disilane<sup>53</sup> which resolved further thermochemical discrepancies.

Because the kinetics are so rapid, the major role of silylene in CVD systems is to insert into the Si-H bonds

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of silanes and produce disilane and higher homologues. Modelling of this process is complicated by the fact that the insertion reactions of silylene are three-body association reactions.<sup>44,45</sup> Therefore, the apparent bimolecular reaction rate constant is dependent on the total pressure and nature of the buffer gas used. Preliminary results on the temperature dependence of silylene insertion reactions suggest that there is little or no activation barrier for insertion into molecular deuterium<sup>54</sup> and that the apparent activation barrier for insertion into Si-H bonds may be negative.<sup>55</sup>

While the chemistry of silane pyrolysis has been studied directly as far as formation and reaction of silylene, the remainder of the chemistry is largely speculative. Several groups have attempted to model and explore the full mechanism, including understanding the apparent rate acceleration at later reaction times, the role of heterogeneous processes, and the formation of larger silicon hydride molecules and "silicon soot" particles.<sup>5,32,36,37,56</sup> The pyrolysis of disilane and of tri- and tetrasilane, which also produces silylenes, has also been explored.<sup>52,57</sup>

### Silicon Growth under Plasma and Photochemical Conditions

PECVD and PHOTOCVD are typically performed at low enough temperatures that direct surface decomposition or thermal unimolecular dissociation of the precursor can be ignored. The deposition process is initiated by the production of gas-phase silicon hydride radicals. Under PECVD conditions these radicals can be formed by electron-impact processes, and it is reasonable to expect that all possible radicals, SiH, SiH<sub>2</sub>, and SiH<sub>3</sub> will be formed, in addition to atomic silicon and hydrogen.<sup>58</sup> Direct measurements of the electron impact dissociation cross sections for the formation of each of these species from silane have not yet been made, however.<sup>8,59</sup> Direct photolysis of silane is rarely used in CVD, because silane has no appreciable absorption cross section at wavelengths longer than 160 nm.<sup>60,61</sup> Under Hg-sensitized conditions, there is ample evidence that silyl radicals are formed.<sup>62-64</sup> In the case of disilane, direct photolysis at 193 nm is quite efficient, but the photochemistry is complex and remains to be understood in detail.<sup>65-68</sup>

As in the case of thermal production of silylene, discussed above, it is necessary to understand the gas-phase kinetics of the remaining silicon hydride radicals. Direct kinetic studies of SiH and SiH<sub>3</sub> have been undertaken in recent years. Preliminary results<sup>69-71</sup> for SiH, at room temperature, show that it is less reactive than silylene with hydrogen, but reacts gas kinetically with silane. The rate constant for the reaction of SiH with silane also appears to be pressure dependent, suggesting that the product is Si<sub>2</sub>H<sub>5</sub>. A variety of techniques have been developed to study silyl kinetics directly.<sup>72-76</sup> Infrared diode laser kinetic studies of silyl demonstrate that it is unreactive with SiD<sub>4</sub> (and hence, presumably, with SiH<sub>4</sub>) and with Si<sub>2</sub>H<sub>6</sub> at room temperature.<sup>77</sup> These studies have provided preliminary values for the rate constant for reaction of silyl with itself. Two groups have reported values for the recombination rate constant of silyl radicals.<sup>75,76</sup> As might be expected, the rate constants are near gas kinetic, but a factor of 2 discrepancy remains between the measured values.

The results of these kinetic studies provide a reasonably simple picture of the fate of the monosilicon hydride radicals under most PECVD and PHOTOCVD conditions. SiH and SiH<sub>2</sub> react rapidly with silane, while SiH<sub>3</sub> reacts rapidly only with other radical species. Since the concentration of radical species is typically much lower than the concentration of stable molecules, SiH and SiH<sub>2</sub> are rapidly consumed in the gas phase while SiH<sub>3</sub> is long-lived.<sup>78</sup> This explains the observation that silyl is by far the dominant radical at steady state in silane plasmas<sup>58</sup> and makes silyl a viable candidate to transport silicon to growth surfaces. Whether silyl is the only species involved in deposition under plasma conditions or significant deposition occurs from species containing more than one silicon atom is a matter of present controversy.<sup>79-81</sup>

An understanding of the chemistry of the disilicon radicals is necessary to complete the picture that has been presented thus far. Direct studies of these fascinating species are presently hampered by a complete lack of optical spectroscopic information on any disilicon species other than Si<sub>2</sub>. Ab initio calculations suggest that species such as Si<sub>2</sub>H<sub>2</sub> and Si<sub>2</sub>H<sub>4</sub> have novel structures that are quite different from acetylene and ethylene.<sup>82-85</sup> Also lacking from a complete picture of

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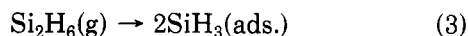
PECVD growth is definition of the rates of processes removing surface H at the low temperatures that are used. Abstraction of surface hydrogen (or deuterium) by incident D(H) atoms producing HD has been observed under well-defined conditions.<sup>24,86</sup> Hydrogen atom desorption processes induced by both electron and low energy ion impact may also occur in the plasma environment, and the electron impact induced regeneration of dangling bonds from hydrogenated Si surfaces is well documented.<sup>87</sup>

### Surface Reactions of Higher Silanes and SiH<sub>x</sub> Radicals

Whenever gas-phase chemistry occurs, silicon hydride radicals and higher silanes are generated. Some of these species are sufficiently long-lived in the gas phase to diffuse to film growth surfaces. The surface chemistry of the higher silanes such as di- and trisilane and of the silicon hydride radicals must, therefore, be understood. Even though they may be produced only in small quantities relative to silane, the  $S^R$  of silane is so low that minority gas-phase species, if they chemisorb efficiently, may account for all or an appreciable fraction of silicon deposited.

An intriguing observation in the chemisorption behavior of silanes is that  $S^R$  on a clean Si surface increases by 3–4 orders of magnitude for Si<sub>2</sub>H<sub>6</sub> (compared to SiH<sub>4</sub>) due to addition of the Si–Si bond and the increased molecular weight. Trisilane shows similar behavior to disilane: both exhibit  $S^R \approx 10^{-1}$  or greater on clean Si at room  $T$ .<sup>19</sup> Studies on Si(111)–(7×7)<sup>19,88,89</sup> and Ge(111)<sup>90</sup> agree that Si<sub>2</sub>H<sub>6</sub> adsorbs through a molecular precursor state weakly interacting with the surface, and limited data suggest a similar mechanism for Si<sub>3</sub>H<sub>8</sub>.<sup>19</sup> The surface residence time<sup>91</sup> of molecular Si<sub>2</sub>H<sub>6</sub> at room  $T$  on a hydrogen-terminated Si(111)–(7×7) surface is roughly 50 μs. The molecule interacts with the surface dangling bonds, remaining physisorbed on the dangling bond terminated surface at temperatures up to 110 K, but desorbing<sup>88</sup> from the hydrogen-terminated surface at lower  $T$  ( $\approx 80$  K).

Once weakly adsorbed, the molecular state may simply desorb, or it may chemisorb via Si–Si bond scission. Formation of adsorbed silyl groups, reaction 3, is observed<sup>88–90</sup> below room  $T$ , and may be the favored low- $T$  reaction. Specific atomic sites on the Si(111)–(7×7)



surface have been identified as the initial SiH<sub>3</sub> chemisorption sites, while other sites are preferred for SiH decomposition product formation.<sup>92</sup> Under CVD growth conditions ( $T > 775$  K), an alternative chemisorption process is also observed,<sup>91</sup> reaction 4. The



$T$ -dependent competitive rates of reactions 3 and 4 remain to be studied. Surface decomposition of disilane can be described<sup>91</sup> by using three regimes of surface  $T$ . Below 675 K, adsorption is via the molecular precursor and dangling bonds are required for reaction 3 or 4 to occur. In a narrow  $T$  window from 700 to 750 K, growth of hydrogenated Si by an unidentified insertion reaction into surface Si–H or Si–Si bonds (dangling bonds not required) is observed. Above 775 K, reaction 4 is observed, and epitaxial Si growth occurs.

Direct studies of  $S^R$  for silicon hydride radicals are in their infancy. Perrin and Broekhuizen<sup>93</sup> have used film growth rates under Hg-sensitized photolysis conditions to estimate a sticking coefficient for SiH<sub>3</sub>. They estimate  $S^R$  for SiH<sub>3</sub> to be 0.1–0.2, although they conclude that only 40% of the radicals that initially stick are incorporated into film and that 60% recombine and desorb as disilane. Thus, they estimate that  $S^R$  is about 0.04–0.08 for silyl on a hydrogenated silicon surface. Ho et al.<sup>94</sup> have used laser-induced fluorescence spectroscopy to measure the amount of SiH, produced in a molecular beam by plasma decomposition of silane, that survives a collision with a heavily hydrogenated amorphous silicon surface. They conclude that  $S^R$  for SiH on this surface is 0.94. Robertson and Rossi<sup>95</sup> have used infrared multiphoton dissociation to produce SiH<sub>2</sub> and resonance enhanced multiphoton ionization spectroscopy to measure its loss rate to hydrogenated silicon and silicon–carbon surfaces in a bulb. They conclude that  $S^R$  for silylene on a hydrogenated silicon surface is 0.15.

Based on the gas-phase chemistry of the radicals, discussed above, one might expect that SiH and SiH<sub>2</sub>, which insert rapidly into Si–H bonds, would stick efficiently to a hydrogenated silicon surface, while SiH<sub>3</sub>, which cannot insert into Si–H bonds, would require a dangling bond site in order to stick. This expectation for relative reactivities agrees with available experimental results. Truly direct measurements of  $S^R$  for the silicon hydride radicals, in which a single radical species interacts with a well-defined surface and the amount that sticks is directly measured, provide a significant experimental challenge that has yet to be realized.

The chemistry of adsorbed radicals is largely unexplored. A very mobile, weakly bound state has been proposed for the SiH<sub>3</sub> radical.<sup>96</sup> This speculation is consistent with the ability of low-power SiH<sub>4</sub> PECVD to produce conformal amorphous hydrogenated Si films.<sup>96</sup>

### Conclusions

The chemical pathways that lead to film growth in silicon CVD processes are clearly diverse and complicated. Some aspects of these pathways have now been revealed in detail, and we have presented a discussion of the recent work that provides much of this detail. It is also clear that much work remains if our stated goal of a complete understanding of this relatively simple

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CVD system at the level of elementary chemical steps is to be achieved. We have pointed out some of the areas where more work is required, such as the characterization of silicon hydride radicals containing more than one silicon atom and direct studies of radical-surface chemistry. Examples of additional areas that provide a wealth of challenging problems are the role of surface structure and defects on adsorption, diffusion, nucleation, and lattice incorporation and an understanding of gas-phase nucleation and formation of particulates. A great deal of progress has been made

in piecing together the chemistry underlying silicon CVD in the last five years. A predictive understanding of the relationship between this chemistry and the materials properties of the deposited films lies ahead.

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