Adsorption and Reaction of Si$_2$H$_5$ on Clean and H-Covered Si(100)-(2 × 1) Surfaces: A Computational Study

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ABSTRACT: A spin-polarized density functional theory calculation was carried out to characterize the adsorption and decomposition of Si$_2$H$_5$ radical on the clean and H-covered Si(100)-(2 × 1) surface. The adsorption structures and energies of Si$_2$H$_6$, Si$_2$H$_4$, SiH$_3$, and SiH$_2$ on the Si(100)-(2 × 1) surface were predicted. It was found that Si$_2$H$_6$, Si$_2$H$_4$, SiH$_3$, and SiH$_2$ preferentially adsorb at the dimer$_a$, intrarow, dimer$_b$, and in-dimer sites, respectively. Potential energy profiles for the reactions of Si$_2$H$_5$ radical on the clean and H-covered Si(100)-(2 × 1) surfaces were constructed using the nudged elastic band (NEB) method. Calculations show that the Si$_2$H$_5$ radical can easily decompose to Si$_2$H$_4$(a), SiH$_3$(a), SiH$_2$(a), and H(a) without any thermal activation, and the decomposition of Si(100)/Si$_2$H$_5$(a) → Si$_2$H$_4$(a)/SiH$_3$(a)/SiH$_2$(a)/H(a) may be the dominant mechanism on the clean Si(100) surface because of its low barrier and high exothermicity. The most likely mechanism for the reaction of Si$_2$H$_5$ on the H-covered Si(100)-(2 × 1) surface is the reaction of Si$_2$H$_5$(a) + H(a) → 2SiH$_3$(a) with an exothermicity of 2.3 kcal/mol by passing a barrier of 59.9 kcal/mol.

INTRODUCTION

Silicon chemical vapor deposition (CVD) processes, including plasma-enhanced CVD (PECVD), catalytic CVD, and thermal CVD,1—6 are extensively used for silicon-based thin film growth in the semiconductor industry. Among the variety of growth methods, generating amorphous or microcrystalline silicon films by PECVD from silane is a widespread technique because of its high potential for yielding a uniform high-quality silicon thin film on a large area substrate.1 These films have been used as promising materials for thin film transistors (TFTs) for active matrix displays, multiple junction photovoltaic solar cells, active pixels in X-ray imaging, photoreceptors, and sensing devices.7—10 CVD processes are composed of the two reaction regimes: the gas-phase reactions and the gas-surface reactions. The gas-surface reaction probability of each molecule determines the importance of precursors for thin film growth. To precisely control the property of thin film, the identification of precursors is essential.11

Except for silane (SiH$_4$), disilane (Si$_2$H$_6$) is often employed as a thin-film precursor in industry and as a dopant precursor in III—V compound semiconductors and has attracted a great amount of interest in deposition of epitaxial layers of Si$_1$—Ge$_{1-x}$12,13 Si$_1$—Ge$_{1-x}$—Sb$_x$,14—16 and SiC.16 The thermal reactions of Si$_2$H$_6$ on the Si(100) surface have been studied by using a variety of experimental techniques.17,18 A well-established mechanism is the dissociation of the Si$_2$H$_6$ molecule into two SiH$_3$ fragments especially on clean surfaces and at low temperatures.17,18 However, both Si—Si bond cleavage and Si—H bond cleavage are a priori possible for the dissociation of the Si$_2$H$_6$ molecule; if the Si—H bond dissociation leads to Si$_2$H$_4$, the latter can further decompose to SiH$_3$ and SiH$_2$ or can react with adsorbed H to produce SiH$_4$ and SiH$_2$. In addition, the disilyl radical (Si$_2$H$_5$) has received particular attention since this species has been identified to contribute significantly to the growth of Si bearing nanostructures in plasma- and photoinitiated silicon CVD.19,20

The underlying physical—chemical processes are very complex. However, it is hard to obtain the information of the detailed reaction mechanisms under very limited experimental conditions. Thus, how to obtain the detailed reaction mechanisms is vital for modeling the CVD processes. Recently, the density functional theory calculation has provided a way to obtain these reaction mechanisms accurately. In the present study, we report the detailed reaction mechanisms of Si$_2$H$_5$ on the clean and H-covered Si(100)-(2 × 1) surfaces by the density functional theory calculations.

Computational Details. All present calculations are performed with the density-functional theory (DFT) utilizing the Vienna ab initio simulation package (VASP).21—24 The generalized gradient approximation with the Perdew—Burke—Ernzerhof (PBE)25 functional is used for all calculations. The Brillouin zone is sampled with the Monkhorst—Pack grid with (3 × 3 × 1) mesh k-points. A 300 eV cutoff energy, which allows convergence...
The clean and H-covered Si(100)-(2×1) surface is modeled in a periodic slab geometry with six atomic silicon layers in which each layer contains 12 Si atoms (see Figure 1). The periodically repeated slabs are separated by a vacuum region of thickness greater than 10 Å which ensures no interaction between the slabs. On the top of the surface, the supercell contains six dimers which will become six dangling bonds after optimization. The dimer may play a crucial role in the molecular adsorption. The bottom surface of the slab is terminated by hydrogen atoms that form symmetric SiH2 groups. The bottom three atomic silicon layers, and eight silicon layers of the Si(100) surface are quite consistent: the difference in the calculated adsorption energy is negligible (less than 1.0 kcal/mol). Therefore, in the present study, we only used six silicon layers of the Si(100) surface.

The adsorption energies of all possible adsorbates are calculated as follows:

$$E_{\text{ads}} = E_{\text{mole/surface}} - (E_{\text{mole}} + E_{\text{surface}})$$

where $E_{\text{mole}}$ is the energy of an isolated molecule that represents SiH3, $E_{\text{surface}}$ is the energy of a clean Si(100)-(2×1) surface, and $E_{\text{mol/surface}}$ is the total energy of the same molecule adsorbed on the Si(100)-(2×1) surface. A negative value for $E_{\text{ads}}$ suggests stable adsorption.

The nudged elastic band (NEB) method30,31 is applied to map out minimum energy paths (MEP) and to locate transition structures by connecting reactants, intermediates, and products. All transition states are verified by the number of imaginary frequencies (NIMG) with NIMG = 1.

<table>
<thead>
<tr>
<th>reaction</th>
<th>spin</th>
<th>nonspin</th>
<th>expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH5→</td>
<td>61.2</td>
<td>63.7</td>
<td>55.5</td>
</tr>
<tr>
<td>SiH2 + H</td>
<td>65.5</td>
<td>81.5</td>
<td>60.5</td>
</tr>
<tr>
<td>SiH6→</td>
<td>86.7</td>
<td>118.6</td>
<td>89.3</td>
</tr>
<tr>
<td>SiH3 + SiH3</td>
<td>74.8</td>
<td>93.0</td>
<td>76.7</td>
</tr>
</tbody>
</table>
Si–Si bond lengths between Si₂H₅ and the surface are 2.36, 2.36, and 2.38 Å, respectively.

**SiH₂ and Si₂H₄ Adsorption.** The adsorption energies and structures of most stable SiH₂ and Si₂H₄ are shown in Table 2 and Figure 2. The adsorption energies for SiH₂ adsorbed on the in-dimer (first layer) and on the inter-row (first layer) turn into the configurations of SiH₂ adsorption on intrarow site, while the optimized configurations of Si₂H₄ adsorption on the inter-row (first and second layer) is dissociative and leads to co-adsorption of SiH and H. The adsorption energies of Si₂H₅ adsorbed on the in-dimer (first layer), intrarow, inter-row (first layer), and inter-row (first and second layer) sites are −84.6, −87.7, −83.9, and −49.6 kcal/mol, respectively. Similar to SiH₂ case, the optimized structure of Si₂H₄ adsorption on the in-dimer (first and second layer) site turns into the configuration of Si₂H₄ adsorption on the intrarow site.

**Decomposition of Si₂H₅ on a Clean Si(100)-(2 × 1) Surface.** To study the basic mechanism of Si₂H₅ with the clean Si(100)-(2 × 1) surface, we constructed the potential energy surface (PES) of Si₂H₅ + Si(100) surface using the NEB method. For this purpose, we have selected energetically the most stable adsorption of Si₂H₅, SiH₅, SiH₄, and H. These PESs include the following elementary reactions:

\[
\text{Si₂H₅(g)} + \text{Si(100)} \rightarrow \text{Si₂H₅(a)}/\text{Si(100)}
\]

As seen from Figure 3, the adsorption of Si₂H₅ on the surface is exothermic giving rise to the dimer_a and dimer_b intermediates, which lie 54.4 and 53.1 kcal/mol below the reactants, respectively. These processes take place by variational transition states without intrinsic barriers.

Let us discuss reaction pathways starting from these two intermediates separately. The first decomposition of Si₂H₅ adsorption from dimer_a leads to Si₂H₄(a)/Si(100)/H(a) with the co-adsorption of Si₂H₄(a) and H(a) at the intrarow; see Figure 3a. This process is found to be exothermic by 36.4 kcal/mol and requires a barrier of 14.1 kcal/mol at transition-state TS1. In TS1, the broken Si–H bond length is about 1.864 Å which is 0.353 Å longer than that in the reactant. The second decomposition starts from dimer_a and leads to SiH₃(a)/Si(100)/SiH₂(a) with the co-adsorption of SiH₃(a) and SiH₂(a) at the intrarow; see Figure 3a. This process occurs with a barrier of 34.4 kcal/mol at TS4 and is exothermic by 17.6 kcal/mol. The broken Si–Si bond is 3.708 Å in the transition-state TS4. The overall reactions of the first and second decompositions are calculated to be exothermic by 36.4 and 70.7 kcal/mol, respectively, and both do not require thermal activation energy.

In summary, our calculations have shown that the Si₂H₅ radical can easily dissociate to Si₂H₄(a), SiH₃(a), SiH₂(a), and H(a) without any thermal activation on the clean Si(100) surface. The reaction mechanism of Si(100)/Si₂H₅(a) → Si₂H₄(a)/Si(100)/H(a) may dominate on the clean Si(100) surface because of its low barrier and high exothermicity.

**Decomposition of Si₂H₅ on the H-Covered Si(100)-(2 × 1) Surface.** In this section, we describe the interactions of the Si₂H₅ radical with the H-covered Si(100)-(2 × 1) surface in detail. These reaction mechanisms are important and require detailed analysis since they occur during the initial stages of growth. The H-covered Si(100)-(2 × 1) surface, which the Si₂H₅ radical cannot attach to, is shown in Figure 1d. The dangling bonds are passivated on the film surface when the H concentration is high. Formation of reactive adsorption sites requires removal of H.
atoms from the surface to expose the dangling bonds of the underlying Si atoms to incoming reactive radicals. Abstraction of surface hydrogen by the Si₂H₅ radical occurs first to create the dangling bonds and can be represented as

\[
\text{Si}_2\text{H}_5(g) + \text{H}(s) \rightarrow \text{Si}_2\text{H}_6(g) + \text{H}(s)\text{-surface with one adsorption site}
\]

The calculated activation barrier and the reaction energy for the abstraction reaction are 1.6 and −8.3 kcal/mol, respectively. Our results are in close agreement with the calculated results of the abstraction of surface hydrogen by the SiH₃ radical (activation barrier of ∼2.08 kcal/mol and an exothermic reaction energy of 5.77−8.07 kcal/mol).³²,³³

Then, the Si₂H₅ adsorbs on the H(s)-surface with one adsorption site giving rise to Si₂H₅(s)−Si(g) + H(g)−Si(g) intermediate with an exothermicity of 63.4 kcal/mol as shown in Figure 4. The process takes place by variational transition state without intrinsic barrier. Starting from the Si₂H₅(s)−Si(g) + H(g)−Si(g) intermediate, the first reaction path passes the transition-state TS5 producing SiH₃(g)−Si(g) + SiH₄(g). The dissociation process of SiH₃(g) occurs by abstraction of one surface H with a high barrier of 78.4 kcal/mol and is endothermic by 55.8 kcal/mol. The second reaction path, shown in Figure 4, occurs by abstraction of one surface H forming Si₂H₆(g) with one dangling bond left. This process requires a barrier of 68.9 kcal/mol and is endothermic by 54.4 kcal/mol. The third reaction path, the most likely pathway, occurs by cleavage of the Si−Si bond of Si₂H₅(s) to produce 2SiH₃(a) adsorbed on the surface with an exothermicity of 2.3 kcal/mol by passing TS7, which is 3.5 kcal/mol below the reactants.

In addition, we also study the decomposition of Si₂H₆ on the H(s)-surface with one dangling bond. As seen in Figure 5, the barrier of Si₂H₆ dissociation by cleavage of the Si−Si bond leading to 2SiH₃(a) is only 0.3 kcal/mol higher than that of Si₂H₅ dissociation by cleavage of the Si−H bond producing Si₂H₅(a) and H(a) indicating that the cleavages of the Si−Si bond and the Si−H bond of Si₂H₆ are competitive on a hydrogenated Si surface. The results can be interpreted as evidence for the conflict of different experimental results in which some showed that the disilane adsorption occurs via the mechanism of Si−Si bond dissociation³⁴,³⁵ and some have been interpreted as evidence for the mechanism of Si−H bond dissociation.³⁶,³⁷ The adsorbed SiH₃ can further dissociate by reacting with surface H to produce the gas-phase SiH₄ and H₂. The emission of H₂(g) can be negligible because of its high barrier (90.8 kcal/mol). The emission of SiH₄(g) may take place by passing TS9 which is 8.0 cal/mol below the reactants; see Figure 5.
CONCLUSIONS

The adsorption and decomposition of Si₂H₅ radical on the clean and H-covered Si(100)-(2 × 1) surface have been studied by the spin-polarized density functional theory. It was found that Si₂H₆, Si₂H₄, SiH₃, and SiH₂ preferentially adsorb at the dimer a, intrarow, dimer b, and in-dimer sites, respectively, with adsorption energies of 54.2, 87.7, 57.0, and 77.0 kcal/mol, respectively. Potential energy profiles for the reactions of Si₂H₅ radical on the clean and H-covered Si(100)-(2 × 1) surfaces were constructed using the nudged elastic band (NEB) method. Calculations show that the Si₂H₅ radical can easily dissociate to the adsorption of Si₂H₄(a), SiH₃(a), SiH₂(a), and H(a) without any thermal activation on the clean Si(100) surface and that the reaction mechanism of Si(100)/Si₂H₅(a) → Si₂H₄(a)/Si(100)/H(a) may dominate on the clean Si(100) surface because of its low barrier and high exothermicity. The most likely reaction pathway of Si₂H₅ on the H-covered Si(100)-(2 × 1) surface occurs by cleavage of the Si–Si bond of Si₂H₅(a) to produce 2SiH₃(a) adsorption on the surface with an exothermicity of 2.3 kcal/mol by passing a barrier of 59.9 kcal/mol. The emission of silane (SiH₄) takes place with a very high barrier of 78.4 kcal/mol indicating that the adsorbed Si₂H₅(a) does not directly react rapidly with the coadsorbed H(a) to desorb SiH₄(g) on the H-covered Si(100)-(2 × 1) surface. However, the emission of SiH₄(g) may occur from the adsorbed SiH₃(a) reacting with the coadsorbed H(a) on the H-covered Si(100)-(2 × 1) surface.

Figure 4. Schematic potential energy profiles for the decomposition of Si₂H₅ on the H-covered Si(100)-(2 × 1) surface.

Figure 5. Schematic potential energy profiles for the decomposition of Si₂H₆ on the H-covered Si(100)-(2 × 1) surface.
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