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Sukkaew, P., Kalered, E., Janzén, E., Kordina, O., Danielsson, Ö., Ojamäe, L., (2018), Growth Mechanism of SiC Chemical Vapor Deposition: Adsorption and Surface Reactions of Active Si Species, *The Journal of Physical Chemistry C*, 122(1), 648-661. <https://doi.org/10.1021/acs.jpcc.7b10751>

Original publication available at:

<https://doi.org/10.1021/acs.jpcc.7b10751>

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Growth Mechanism of SiC CVD – Adsorption and Surface Reactions of Active Si Species

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ABSTRACT

Silicon carbide is a wide bandgap semiconductor ideally suitable for high temperature and high power applications. An active SiC layer is usually fabricated using halide-assisted chemical vapor deposition (CVD). In this work, we use quantum chemical density functional theory (B3LYP and M06-2X) and transition state theory to study adsorptions of active Si species in the CVD process on both the Si face and the C face of 4H-SiC. We show that adsorptions of SiCl, SiCl₂, SiHCl, SiH and SiH₂ on the Si face likely occurs on a methylene site, CH₂(ads), but the processes are thermodynamically less favorable than their reverse or desorptions. Nevertheless, the adsorbed products become stabilized with help of subsequent surface reactions to form a larger cluster. These cluster formation reactions happen with rates that are fast enough to compete with the desorption processes. On the C face, the adsorptions likely occur on a surface site terminated by a dangling bond, *(ads), and produce the products which are thermodynamically stable. Lastly, we

present the Gibbs free energies of adsorptions of Si atoms, SiX, SiX₂, SiHX, for X being F and Br. Adsorptions of Si atoms are shown to be the most thermodynamically favorable among all the species in the study. Among the halide-containing species, the Gibbs free energies ($\Delta_R G^\circ$) from smallest to largest are observed in the adsorptions of SiX, SiHX and SiX₂, for X being the halides. The results in this study suggest that the major Si contributors in SiC-CVD process are Si atoms, SiX (for X being the halide) and SiH.

Introduction

Silicon carbide (SiC) is a wide bandgap semiconductor ideally suitable for high-voltage, power devices¹⁻³ and sensors^{4,5}. Among SiC numerous polytypes, the 4H polytype is a common choice for electronic applications⁶ thanks to its superior characteristics of high breakdown electric field and high mobility¹. An active layer of 4H-SiC is usually fabricated using chemical vapor deposition (CVD). The process is performed at temperatures ~1500-1600 °C and pressures ~50-300 mbar, typically using a mixture of silane (SiH₄) and light hydrocarbons diluted in the flow of hydrogen. Addition of halides, especially chlorine, is often used to suppress the formation of silicon clusters in the gas phase so that the growth rate can be increased by increasing the precursor concentration^{7,8}. It has been shown recently that Br chemistry worked similarly well in terms of material qualities and growth rates⁸. In addition, F-chemistry was also reported to produce high quality SiC homoepitaxial layer⁹.

CVD processes involve chemical reactions in the gas phase and on the surface. During the process, active species are produced from pyrolysis before transported to the surface and become incorporated into the growing layer. For the F-, Cl- and Br-assisted SiC-CVD conditions, it was shown using thermodynamic equilibrium calculations^{8,10} that the Si species with the highest gas

phase concentrations are SiX, SiX₂, SiHX (for X referring to F, Cl and Br) as well as Si₂C and Si atoms. This suggests that these species might act as the Si growth contributors.

Surface reactions of SiH₂, SiCl₂ and SiBr₂ were recently reported ^{8,11} on the C-face of 4H-SiC. It was shown that SiCl₂ and SiBr₂ behave similarly for the reactions considered ⁸. This suggests that similar reactivity may be expected among different halides. In our recent study, we compare SiF, SiHF and SiF₂ adsorptions on the Si-face of 4H-SiC and found that SiF was the most active species in the set, while SiF₂ was the least active species ¹⁰. These studies ^{10,11} also showed that at the CVD process temperature, most adsorptions occurred with relatively large, positive Gibbs free energies ($\Delta_R G^\circ$). This means that adsorption is less favorable than its reverse.

In our previous work ¹², we presented growth mechanisms of 4H-SiC with the focus on active C-species adsorptions and their subsequent surface reactions on the Si-face of 4H-SiC. We showed that hydrocarbon adsorptions occurred with much slower rates than desorptions, but with help of subsequent reactions, the process proceeded forward and produced stable final products. In this work, we continue with adsorptions of active Si-species and their subsequent reactions on both the Si face and the C face. We consider the following Si-species: SiH, SiH₂, SiCl, SiHCl, and SiCl₂. The adsorption sites on the Si face are CH₃(ads), CH₂(ads) and C₂H₄(ads), as shown in Fig. 1a-c. We have shown in our previous work ¹² that these three surface sites can be produced from adsorptions (and subsequent reactions) of gaseous CH₃, C₂H₂ and C₂H₄ respectively. On the C face, we consider two adsorption sites: H(ads) and *(ads), referring respectively to a surface site (C site) terminated by a hydrogen atom and a dangling bond as shown in Fig. 2a and b. Lastly, we discuss adsorptions of Si atoms as well as F- and Br-chemistries and demonstrate their similarities and differences in terms of reactivity and thermodynamics.

Computational Methods

The surface of 4H-SiC is modeled using $\text{Si}_{19}\text{C}_{19}$ and $\text{Si}_{24}\text{C}_{24}$ clusters. The central surface sites (two on $\text{Si}_{19}\text{C}_{19}$ and three on $\text{Si}_{24}\text{C}_{24}$) are chosen for the study. $\text{Si}_{19}\text{C}_{19}$ is used in the calculations of adsorption and the first step of cluster formation, while $\text{Si}_{24}\text{C}_{24}$ is employed in the second step of cluster formation. To preserve the SiC bulk geometry, both clusters are terminated at the edges by hydrogen atoms. Adsorptions are studied on both the Si face and the C face of the cluster. On the Si face, we consider three adsorption sites: $\text{CH}_3(\text{ads})$, $\text{CH}_2(\text{ads})$ and $\text{C}_2\text{H}_4(\text{ads})$ as shown in

Fig. 1a – 1c, while on the C face, two adsorption sites, H(ads) and *(ads), are selected as shown in Fig. 2a and b. In this study, *(ads) refers to a surface site terminated by a dangling bond.

All ground state and transition state (TS) structures are optimized using the density functional theory (DFT) with the B3LYP functional^{13,14} and the LanL2DZ basis set^{15,16} together with the D3 dispersion corrections from Grimme et al.¹⁷. Harmonic frequency calculations are performed at the same level of theory on the optimized structures. B3LYP electronic energies are replaced with the energy calculated using the M06-2X functional¹⁸ and Dunning's basis set cc-pVTZ¹⁹. The transition state (TS) structures are verified by visualizing the vibrational displacement associated with the imaginary frequencies. Zero point energy correction is applied to all energies in the study. All quantum chemical calculations are performed using the Gaussian 09 software²⁰.

The energies and Gibbs free energies of reaction are derived using

$$\Delta_R E^\circ = (\sum E^\circ_{products}) - (\sum E^\circ_{reactants}), \quad (1)$$

$$\Delta_R G^\circ = (\sum G^\circ_{products}) - (\sum G^\circ_{reactants}). \quad (2)$$

The energies and Gibbs free energies of activation are derived using

$$\Delta_{TS} E^\circ = (\sum E^\circ_{TS}) - (\sum E^\circ_{reactants}), \quad (3)$$

$$\Delta_{TS} G^\circ = (\sum G^\circ_{TS}) - (\sum G^\circ_{reactants}). \quad (4)$$

$E^\circ_{reactants}$, $E^\circ_{products}$, E°_{TS} refer to the energies of the reactants, products and transition states, respectively. For a reaction involving gas phase species, the ground state energy is defined with respect to the asymptote condition where the surface and the gas are separated at infinite distance.

This is not to be confused with the physisorbed state, which is known to be unstable at high temperature.

Reaction Rates. The conventional transition state theory (TST) is applied to calculate the rate constant. This implies that rapid equilibrium is assumed between the reactants and activation complex. TST is applicable when a tight transition state exists between the reactant and product states ^{21,22}. Similar to our previous study ¹², we use the modified rate equations from Reuter and Scheffler's work ²³.

Adsorption. Adsorption rate (R_{ads}) of a reaction in the form, $A(g) + B(ads) \rightarrow \text{product}(ads)$, is obtained as follows.

$$R_{ads} = A_s f_{ads} \exp(-\Delta_{TS} E^\circ / k_B T) \cdot \Phi_A \cdot \Theta_B , \quad (5)$$

Here the adsorption rate R_{ads} is in the unit of molecule sites⁻¹ s⁻¹. A_s is the surface area per site of surface species B, assumed equal to the area per one lattice site on the Si face and the C face of 4H-SiC, 8.178×10^{-20} m² as derived using the lattice constant of $3.073 \text{ \AA}$ ²⁴. $\Delta_{TS} E^\circ$ is the activation energy of adsorption at 0 K. k_B and T refer to the Boltzmann constant and the process temperature, respectively. Θ_B is the surface fraction of B(ads), and Φ_A is the impingement rate of species A calculated using

$$\Phi_A = \gamma_A p / \sqrt{2\pi m_A k_B T}. \quad (6)$$

γ_A , p and m_A refer respectively to the mole fraction of gaseous species A, the total pressure and the mass of gaseous species A. The factor f_{ads} in Eq. 5 is a factor derived from the partition functions,

$$f_{ads} = q_{vib,el}^{TS} / (q_{2D-Trans}^{gas} \cdot q_{int}^{gas} q_{vib,el}^{surf}). \quad (7)$$

Here the partition function of a surface species contains only the vibrational and electronic parts, with the translational and rotational parts discarded. This applies to q^{TS} of the transition state and q^{surf} of a surface species, B(ads). The partition of the gas, q^{gas} , includes all degrees of freedom except the translation along the reaction coordinate. In Eq. 7, q^{gas} is divided into two parts. The q_{int}^{gas} contains the vibrational, rotational and electronic parts, while $q_{2D-Trans}^{gas}$ is the 2-dimensional, translational part of the partition function calculated using $q_{2D-Trans}^{gas} = A_s \cdot 2\pi m_A k_B T / h^2$. Here we assume that the gaseous species that strike on the surface site must reside within the area A_s . All partition functions are extracted from the Gaussian 09 calculations²⁰.

The sticking coefficient (S_A), which is defined as the probability (from 0 to 1) that the gaseous species A will stick on the surface per strike, is calculated using $S_A = R_{ads} / (A_s \cdot \Phi_A \cdot \Theta_B)$. From Eq. 5–7, we obtain

$$S_A = f_{ads} \exp(-\Delta_{TS} E^\circ / k_B T). \quad (8)$$

Desorption. Desorption rate (R_{de}) of a reaction in the form, A(ads) $\rightarrow$ product(s), is obtained using

$$R_{de} = f_{de} \left(\frac{k_B T}{h} \right) \exp(-\Delta_{TS} E^\circ / k_B T) \cdot \Theta_A. \quad (9)$$

$\Delta_{TS} E^\circ$ is the activation energy of desorption at 0 K. Θ_A is the fraction of surface occupied by A(ads). f_{de} is the factor derived from the partition functions,

$$f_{de} = q_{vib,el}^{TS} / q_{vib,el}^{ads}. \quad (10)$$

where q^{TS} and q^{ads} are the partition functions of the transition state and the adsorbed species, A(ads).

On-surface Reaction. Reaction rate of an on-surface reaction in the form, A(ads) + B(ads) $\rightarrow$ product(s), is obtained using

$$R_{on-surf} = f_{on-surf} \left(\frac{k_B T}{h} \right) \exp(-\Delta_{TS} E^\circ / k_B T) \Theta_{AB}. \quad (11)$$

$\Delta_{TS} E^\circ$ is the activation energy of the on-surface reaction at 0 K. Θ_{AB} is the surface fraction of a pair of A(ads) + B(ads). $f_{on-surf}$ is the factor derived from the partition functions,

$$f_{on-surf} = q_{vib,el}^{TS} / q_{vib,el}^{surf}. \quad (12)$$

where q^{TS} and q^{surf} are the partition functions of the transition state and the pair of A(ads) + B(ads).

Results and Discussion

This section is divided into three parts. The first and second parts are focused on the adsorptions of SiH, SiH₂, SiCl, SiHCl and SiCl₂ and their subsequent surface reactions on the Si face and on the C face of 4H-SiC. The last subsection is focused on the adsorptions of Si atoms and of SiX, SiHX and SiX₂ for X being F and Br, which leads to the discussion of the similarities and dissimilarities between the different CVD chemistries.

1 Adsorptions and surface reactions on the Si face of 4H-SiC.

1.1 Adsorptions. We consider three types of adsorption sites on the Si face: CH₃(ads), CH₂(ads) and C₂H₄(ads), which are the products of surface reactions of CH₃, C₂H₄ and C₂H₂ gases as reported in our previous work ¹².

Adsorptions on CH₃(ads) of SiH, SiH₂, SiCl, SiHCl, and SiCl₂ gases occur by breaking a C-H bond in CH₃(ads) and forming a new C-Si bond and Si-H bond. Fig. 3a and b show the transition state and the product of SiH adsorption on CH₃(ads). Adsorptions of SiH, SiH₂, SiCl, SiHCl, and SiCl₂ gases all produce large energy barriers ($\Delta_{TS}G^\circ$) and positive changes in the Gibbs free energies, $\Delta_R G^\circ$, at 1600 °C which is the temperature typically used in SiC CVD process. Large energy barriers ($\Delta_{TS}G^\circ$) lead to very low sticking coefficients for all species, as shown for R1 – R5 in Table 1. The positive $\Delta_R G^\circ$ indicate that desorption, i.e. the reverse of the adsorption reaction, is thermodynamically more favorable and that desorption rates are faster than adsorption rates, as shown in Table 2.

The reactivity of CH₃(ads) can be enhanced, for example by abstraction of an H atom

which occurs with $\Delta_R G^\circ$ and $\Delta_{TS} G^\circ$ of -82 and 248 kJ/mol at 1600 °C ¹². The H-abstraction process R16 creates a dangling bond on the C site and thereby increasing its reactivity. As a result, adsorptions of Si species on CH₂(ads) are more favorable than on CH₃(ads) as shown in R6 – R10 in Table 1. In addition, adsorptions of Si species on CH₂(ads) also occur without the presence of transition states. However, their $\Delta_R G^\circ$ are positive, meaning that desorptions are again more favorable and occur with faster rates, as shown in Table 2.

Now let us move on to adsorptions of Si species on a C₂H₄(ads) molecule. A C₂H₄(ads) molecule is a product of C₂H₂ adsorption and its subsequent reactions¹². Similar to CH₃(ads), the C₂H₄(ads) molecule has no surface dangling bond. Thus, adsorptions on C₂H₄(ads) species require breaking of the C-C bond in the molecule before new Si-C bonds can be formed. Figure 4a and b show the transition state and the product of SiH adsorption on a C₂H₄(ads) molecule. Similar to the adsorptions on CH₃(ads), adsorptions of Si species on C₂H₄(ads) species create large energy barriers ($\Delta_{TS}G^\circ$) at 1600 °C. It should be noted that despite $\Delta_R G^\circ$ being negative in some cases, all transition barriers $\Delta_{TS}G^\circ$ are significantly larger than the other adsorption sites considered previously. This is likely due to the species itself being more stable. As a result, the sticking coefficients of the Si species are the lowest on C₂H₄(ads) species. C₂H₄(ads) species is thus the least active adsorption site considered here. In addition, their large transition barriers also make it hard for desorptions to occur via the direct reverse of R11 – R15. The formation of two Si-C bonds thus helps stabilizing the surface species.

Similar to CH₃(ads), the reactivity of C₂H₄(ads) species can be enhanced by interacting with a hydrogen atom,

which occurs with $\Delta_R G^\circ$ and $\Delta_{TS}G^\circ$ of 1 and 295 kJ/mol at 1600 °C, as shown in Table 1. Reaction R17 breaks the C-C bond within the species and creates a dangling bond on one of the C atoms. Adsorptions of Si species on the newly created CH₂(ads) occur without the presence of a transition state and their products are accompanied by an adjacent CH₃(ads).

In conclusion, from the sticking coefficients listed in Table 1, we find that the adsorption processes with the largest sticking coefficients (S) are as follows: adsorption of SiH on CH₃(ads) ($S =$

3×10^{-4}), adsorption of SiCl on CH₃(ads) ($S = 4 \times 10^{-5}$), adsorption of SiH₂ on CH₃(ads) ($S = 3 \times 10^{-5}$) and adsorption of SiH on C₂H₄(ads) species ($S = 9 \times 10^{-6}$). The growth rate V_H associated with each adsorption can be obtained using $V_H = R_{ads} \cdot h_{ML}$, with h_{ML} being the height of one SiC bilayer, $\sim 2.5131 \times 10^{-10}$ m. We assume Θ of 1.0 for both CH₃(ads) and C₂H₄(ads) species which are their maximum values. The molar fractions, Φ , of the Si-species were taken from thermodynamic equilibrium calculations at 1600 °C ($\Phi \sim 10^{-5}$ for SiH and SiH₂, $\Phi \sim 10^{-3}$ for SiCl and SiCl₂ and $\Phi \sim 10^{-4}$ for SiHCl⁸). We obtain the following growth rates: ~ 0.25 $\mu\text{m}/\text{hour}$ for SiCl on CH₃(ads), ~ 0.08 $\mu\text{m}/\text{hour}$ for SiCl on C₂H₄(ads) species, ~ 0.03 $\mu\text{m}/\text{hour}$ for SiH on CH₃(ads) and ~ 0.002 $\mu\text{m}/\text{hour}$ for SiH₂ on CH₃(ads). These growth rates are much too low to contribute significantly to the growth rate observed experimentally, ~ 100 $\mu\text{m}/\text{hour}$ ⁷. Instead, we may speculate that adsorptions occur more efficiently on CH₂(ads) from their much smaller $\Delta_R G^\circ$ and lacking of transition states. By assuming the sticking coefficients of the Si species to be 1.0 on CH₂(ads) and using Θ equal to 1.0 together with the same molar fractions of the Si species as before, we obtain the growth rates of 84 $\mu\text{m}/\text{hour}$ for SiH, 82 $\mu\text{m}/\text{hour}$ for SiH₂, $\sim 6 \times 10^3$ $\mu\text{m}/\text{hour}$ for SiCl and SiHCl, and ~ 455 $\mu\text{m}/\text{hour}$ for SiCl₂. These growth rates are much larger than the experimental value because we have assumed Θ of CH₂(ads) equal to 1.0, which is the maximum value possible, and we have so far neglected the effects of desorptions. In fact, with their $\Delta_R G^\circ$ being positive, adsorptions on CH₂(ads) are expected to occur with the rates which are significantly smaller than their desorptions.

Table 1 The energies (0 K), standard Gibbs free energies (1600 °C) and sticking coefficients of SiH, SiH₂, SiCl, SiHCl and SiCl₂ on CH₃(ads), CH₂(ads) and C₂H₄(ads) species pre-deposited on the Si face of 4H-SiC. The (free) energies are presented in the unit of kJ/mol, calculated with respect to the energy of the reactant state at asymptote condition.

		0 K		1600 °C		
		$\Delta_R E^\circ$	$\Delta_{TS} E^\circ$	$\Delta_R G^\circ$	$\Delta_{TS} G^\circ$	S
Adsorptions on CH₃(ads)						
R1	SiH(g) + CH ₃ (ads) → SiH ₂ -CH ₂ (ads)	-157	82	94	325	3×10^{-4}
R2	SiH ₂ (g) + CH ₃ (ads) → SiH ₃ -CH ₂ (ads)	-203	88	91	364	3×10^{-5}
R3	SiCl(g) + CH ₃ (ads) → SiHCl-CH ₂ (ads)	-124	106	146	358	4×10^{-5}
R4	SiHCl(g) + CH ₃ (ads) → SiH ₂ Cl-CH ₂ (ads)	-185	123	132	422	7×10^{-7}
R5	SiCl ₂ (g) + CH ₃ (ads) → SiHCl ₂ -CH ₂ (ads)	-134	190	177	492	8×10^{-9}
Adsorptions on CH₂(ads)						
R6	SiH(g) + CH ₂ (ads) → SiH-CH ₂ (ads)	-320	-	15	-	-
R7	SiH ₂ (g) + CH ₂ (ads) → SiH ₂ -CH ₂ (ads)	-247	-	65	-	-
R8	SiCl(g) + CH ₂ (ads) → SiCl-CH ₂ (ads)	-306	-	37	-	-
R9	SiHCl(g) + CH ₂ (ads) → SiHCl-CH ₂ (ads)	-226	-	113	-	-
R10	SiCl ₂ (g) + CH ₂ (ads) → SiCl ₂ -CH ₂ (ads)	-183	-	128	-	-
Adsorptions on C₂H₄(ads)						
R11	SiH(g) + C ₂ H ₄ (ads) → SiH-(CH ₂) ₂ (ads)	-275	140	-11	379	9×10^{-6}
R12	SiH ₂ (g) + C ₂ H ₄ (ads) → SiH ₂ -(CH ₂) ₂ (ads)	-327	206	-28	460	5×10^{-8}
R13	SiCl(g) + C ₂ H ₄ (ads) → SiCl-(CH ₂) ₂ (ads)	-245	148	36	388	7×10^{-6}
R14	SiHCl(g) + C ₂ H ₄ (ads) → SiHCl-(CH ₂) ₂ (ads)	-312	234	7	517	2×10^{-9}
R15	SiCl ₂ (g) + C ₂ H ₄ (ads) → SiCl ₂ -(CH ₂) ₂ (ads)	-273	275	50	552	2×10^{-10}
Hydrogen abstraction						
R16	CH ₃ (ads) + H(g) → CH ₂ (ads) + H ₂ (g) ^{a)}	-25 _{a)}	52 ^{a)}	-82 ^{a)}	248 ^{a)}	-
R17	C ₂ H ₄ (ads) + H(g) → CH ₂ (ads) + CH ₃ (ads)	-138	96	1	295	-

^{a)} Ref. ¹².

Table 2 The adsorption and desorption rate constants at 1600 °C of SiH, SiH₂, SiCl, SiHCl and SiCl₂ on CH₃(ads) and C₂H₄(ads) pre-deposited on the Si face of 4H-SiC.

	Adsorption rate constant ^{a)}	Desorption rate constant ^{b)}

Adsorptions on CH₃(ads)			
R1	SiH(g) + CH ₃ (ads) → SiH ₂ -CH ₂ (ads)	3×10^{-1}	1×10^7
R2	SiH ₂ (g) + CH ₃ (ads) → SiH ₃ -CH ₂ (ads)	2×10^{-2}	1×10^6
R3	SiCl(g) + CH ₃ (ads) → SiHCl-CH ₂ (ads)	3×10^{-2}	5×10^7
R4	SiHCl(g) + CH ₃ (ads) → SiH ₂ Cl-CH ₂ (ads)	4×10^{-4}	3×10^5
R5	SiCl ₂ (g) + CH ₃ (ads) → SiHCl ₂ -CH ₂ (ads)	4×10^{-6}	6×10^4
Adsorptions on C₂H₄(ads)			
R11	SiH(g) + C ₂ H ₄ (ads) → SiH-(CH ₂) ₂ (ads)	2×10^{-2}	5×10^2
R12	SiH ₂ (g) + C ₂ H ₄ (ads) → SiH ₂ -(CH ₂) ₂ (ads)	9×10^{-5}	9×10^{-1}
R13	SiCl(g) + C ₂ H ₄ (ads) → SiCl-(CH ₂) ₂ (ads)	8×10^{-3}	6×10^3
R14	SiHCl(g) + C ₂ H ₄ (ads) → SiHCl-(CH ₂) ₂ (ads)	2×10^{-6}	2×10^{-1}
R15	SiCl ₂ (g) + C ₂ H ₄ (ads) → SiCl ₂ -(CH ₂) ₂ (ads)	2×10^{-7}	4×10^{-1}

a) The adsorption rate constants, $R_{ads}/p\gamma_g\Theta_s$, are calculated using Eq. 5-8. Here, the adsorption rate (R_{ads}) is in molecule per site per second. The total pressure (p) is in Pascal. The gaseous molar fraction (γ_g) and the surface fraction (Θ_s) are unitless. The surface area per site of CH₃(ads) is assumed equal to $8.178 \times 10^{-20} \text{ m}^2$ which is the area per one lattice site on the Si-face of 4H-SiC. The area per site of C₂H₄(ads) is assumed equal to $1.636 \times 10^{-19} \text{ m}^2$ which is the area per two lattice sites.

b) The desorption rate constants, R_{de}/Θ_s , are calculated using Eq. 9-10. Here, the desorption rate (R_{de}) is in molecule per site per second. The surface fraction (Θ_s) is unitless.

1.2. Cluster formations. In the previous subsection, we showed that based on the rate derived it is unlikely for adsorptions on $CH_3(ads)$ and on $C_2H_4(ads)$ species to contribute significantly to the growth. It could be that the main adsorption route occurs mainly via $CH_2(ads)$. We also show that adsorptions on $CH_3(ads)$, $C_2H_4(ads)$ and $CH_2(ads)$ all occur with positive $\Delta_R G^\circ$. Thus, for all processes considered, desorptions are more favorable than adsorptions. In order for the growth to proceed in the forward direction, it is thus necessary that there are subsequent reaction path(s)

following adsorptions which helps reducing the total $\Delta_R G^\circ$ and stabilizing the final products. In addition, this path(s) should occur with a rate that is fast enough, at least comparable to that of the desorption rate. We propose that one route for this is by formation of larger surface species, or a cluster.

In the first step following adsorptions, let us consider a bonding process between the adsorbed species and an adjacent $\text{CH}_3(\text{ads})$, as shown in R18-R22 in Table 3. In Figure 5a-c, we show an example of $\text{SiH-CH}_2(\text{ads})$, which is the product of SiH adsorption on $\text{CH}_2(\text{ads})$, forming a bond with its adjacent $\text{CH}_3(\text{ads})$. This process occurs by breaking a C-H bond in $\text{CH}_3(\text{ads})$ and forming new C-Si and Si-H bonds. As shown in Table 3, the processes R18-R22 are thermodynamically preferable with negative $\Delta_R G^\circ$ at 1600 °C. In addition, their transition barriers are relatively small, especially for the interactions R18 and R20, resulting in the forward rate constants as high as 10^9 molecule site⁻¹ second⁻¹ as shown in Table 4. These rates are fast enough to compete with desorption processes. From the rate constants shown in Table 4, it should be noted that R19, R20 and R22 which are the subsequent reactions following the adsorptions of SiH_2 , SiHCl and SiCl_2 , are ~100-1000 times slower than R18 and R20 which are the subsequent reactions following the adsorptions of SiH and SiCl . This together with the fact that $\Delta_R G^\circ$ of SiH_2 , SiHCl and SiCl_2 adsorptions are much more positive than $\Delta_R G^\circ$ of SiH and SiCl adsorptions implies that the growth contributions from SiH_2 , SiHCl and SiCl_2 are likely much less than from SiH and SiCl .

Following this step, the surface species can be stabilized further by forming another Si-C bond with another $\text{CH}_3(\text{ads})$ via R23-R26 shown in Table 3. An example of an interaction between $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$ and an adjacent $\text{CH}_3(\text{ads})$, which is the reaction following R18, is shown in Fig. 6a-c. Via these two steps, SiC growth via SiH adsorption may proceed as follows,

These steps produce $\text{SiH-(CH}_2)_3(\text{ads})$ as the final product and produces a total change in $\Delta_R G^\circ$ of -366 kJ/mol at 1600 °C. The step-by-step change in the Gibbs free energy is depicted in Fig 7. Similarly, SiH_2 adsorption and subsequent reactions are as follows

and

This leads to the production of $\text{SiH-(CH}_2)_3(\text{ads})$ with a total change in $\Delta_R G^\circ$ of -238 kJ/mol at 1600 °C.

SiCl adsorption and subsequent reactions may occur via two different routes, as shown in Fig. 8.

and

or

The product $\text{SiH}-(\text{CH}_2)_3(\text{ads})$ occurs via the combination of R8, R20 and R24 with a total change in $\Delta_R G^\circ$ of -260 kJ/mol at 1600 °C, while the product $\text{SiCl}-(\text{CH}_2)_3(\text{ads})$ occurs by replacing R24 with R25 and produces a total change in $\Delta_R G^\circ$ of -318 kJ/mol at 1600 °C. It should be noted that $\Delta_{TS} G^\circ$ of R24 and R25 are relatively similar (269 and 289 kJ/mol). Thus, the two processes are highly competitive to each other.

SiHCl adsorption and subsequent reactions occurs as follows,

(R21)

and

or

The product $\text{SiH}-(\text{CH}_2)_3(\text{ads})$ occurs via the combination of R9, R21 and R24 with a total change of -138 kJ/mol in $\Delta_R G^\circ$ at 1600 °C, while the product $\text{SiCl}-(\text{CH}_2)_3(\text{ads})$ occurs by replacing R24 with R25 producing a total change in $\Delta_R G^\circ$ of -196 kJ/mol at 1600 °C.

Adsorption of SiCl_2 and its subsequent reactions produce $\text{SiCl}-(\text{CH}_2)_3(\text{ads})$ with the change in $\Delta_R G^\circ$ of -139 kJ/mol at 1600 °C. This happens via

and

Let us now consider reactions R27 and R28,

and

which help creating a surface dangling bond, $\text{Si}^*\text{-(CH}_2)_3(\text{ads})$, which was shown to be important for hydrocarbon adsorptions for the next layer ¹². As shown in Table 3 and 4, it is more difficult to remove Cl-termination in comparison to H-termination. Nevertheless, as the CVD process condition is known to produce a significant amount of H atoms in the gas phase ²⁵, the rates of R27 and R28 likely occur much faster than adsorptions.

Table 3 The energies (0 K) and standard Gibbs free energies (1600 °C) of the clustering process.

The (free) energies are presented in the unit of kJ/mol.

		0 K		1600 °C	
		$\Delta_R E^\circ$	$\Delta_{TS} E^\circ$	$\Delta_R G^\circ$	$\Delta_{TS} G^\circ$
1 st step of cluster formation process					
R18	$\text{SiH-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	-219	95	-158	151
R19	$\text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	57	177	-80	246
R20	$\text{SiCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	-182	142	-140	176
R21	$\text{SiHCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{H(g)}$	46	167	-94	235
R22	$\text{SiCl}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	43	189	-100	228
2 nd step of cluster formation process					
R23	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	-34	292	-223	309
R24	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	59	231	-157	269
R25	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	-44	266	-215	289
R26	$\text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	37	243	-167	288
Surface dangling bond creation					
R27	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	-63	12	-77	181
R28	$\text{SiCl-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	40	90	-19	258

Table 4 The forward and reverse rate constants of subsequent reactions at 1600 °C in the unit of molecule per site per second.

		Forward rate constants	Reverse rate constants
1 st step of cluster formation process			
R18	$\text{SiH-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	$2 \times 10^9 \text{ }^{\text{a)}}$	$9 \times 10^4 \text{ }^{\text{a)}}$
R19	$\text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	$5 \times 10^6 \text{ }^{\text{a)}}$	$6 \times 10^{-1} \text{ }^{\text{b)}}$
R20	$\text{SiCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	$5 \times 10^8 \text{ }^{\text{a)}}$	$6 \times 10^4 \text{ }^{\text{a)}}$
R21	$\text{SiHCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{H(g)}$	$1 \times 10^7 \text{ }^{\text{a)}}$	$5 \times 10^{-1} \text{ }^{\text{b)}}$
R22	$\text{SiCl}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	$2 \times 10^7 \text{ }^{\text{a)}}$	$5 \times 10^{-1} \text{ }^{\text{b)}}$
2 nd step of cluster formation process			
R23	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	$1 \times 10^5 \text{ }^{\text{a)}}$	$2 \times 10^{-6} \text{ }^{\text{b)}}$
R24	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	$1 \times 10^6 \text{ }^{\text{a)}}$	$1 \times 10^{-3} \text{ }^{\text{b)}}$
R25	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	$3 \times 10^5 \text{ }^{\text{a)}}$	$3 \times 10^{-6} \text{ }^{\text{b)}}$
R26	$\text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	$4 \times 10^5 \text{ }^{\text{a)}}$	$6 \times 10^{-5} \text{ }^{\text{b)}}$
Surface dangling bond creation			
R27	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	$3 \times 10^4 \text{ }^{\text{b)}}$	$7 \times 10^1 \text{ }^{\text{b)}}$
R28	$\text{SiCl-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	$7 \times 10^1 \text{ }^{\text{b)}}$	$2 \times 10^1 \text{ }^{\text{b)}}$

^{a)} Calculated using Eq. 9-10. The rate constant is defined as R/Θ_s where R is the reaction rate in molecule per site per second and Θ_s is the surface fraction which is unitless.

^{b)} Calculated using Eq. 5-8. The rate constant is defined as $R/p\gamma_g\Theta_s$ where the reaction rate (R) is in molecule per site per second, the total pressure (p) is in pascal, and the gaseous molar fraction (γ_g) and the surface fraction (Θ_s) are unitless. The surface area per site of $\text{SiH}_n\text{X}_m\text{-CH}_2(\text{ads})$ is assumed equal to $8.178 \times 10^{-20} \text{ m}^2$ which is the area per one lattice site on the Si-face of 4H-SiC.

The areas per site of $\text{SiH}_n\text{X}_m\text{-(CH}_2)_2(\text{ads})$ and $\text{SiX-(CH}_2)_3(\text{ads})$ are assumed equal to 1.636×10^{-19} and $2.453 \times 10^{-19} \text{ m}^2$ respectively, which are the areas per two and three lattice sites on the Si-face of 4H-SiC.

Figure 5 Top view and side view of a) the reactants, b) the transition state, and b) the product of 1st step of cluster formation between SiH-CH₂(ads) and an adjacent CH₃(ads).

Figure 7 Reaction scheme of SiC growth from SiH(g) adsorption and cluster formation

Figure 8 Reaction scheme of SiC growth from SiCl(g) adsorption and cluster formation.

2 Adsorptions on the C face of 4H-SiC. Here we consider two types of surface sites: H(ads) and *(ads), which refer respectively to a surface site on the C face terminated by an H atom and by a dangling bond. Adsorptions of the Si-species on H(ads) occurs by breaking a C-H bond and forming a Si-H bond and a Si-C bond as shown in Fig. 9a and b. The processes are present with large energy barriers ($\Delta_{TS}G^\circ$) together with large positive $\Delta_R G^\circ$ as shown in Table 5. This results in low sticking coefficients for all adsorbing species. As shown in Table 5, the sticking coefficients on H(ads) from largest to smallest are $\text{SiH} > \text{SiCl} > \text{SiH}_2 \gg \text{SiHCl} \gg \text{SiCl}_2$. With the growth rate V_H obtained using $V_H = R_{ads} \cdot h_{ML}$, with h_{ML} being 2.5131×10^{-10} m, and using Θ equal to 1.0 together with the same molar fractions of the Si species similar to section 1.1, we obtain the adsorption rates (from highest to lowest) to be ~ 1.1 $\mu\text{m}/\text{hour}$ for SiCl; ~ 0.2 $\mu\text{m}/\text{hour}$ for SiH; ~ 0.005 $\mu\text{m}/\text{hour}$ for SiH₂; and smaller for the rest. These rates are again too low to contribute to the growth rate observed experimentally.

Adsorptions of the Si-species on *(ads), on the other hand, occurs with much smaller $\Delta_R G^\circ$ and without transition states due to the presence of the surface dangling bond. *(ads) can be created from H(ads) via an interaction with a hydrogen atom,

which occurs with $\Delta_R G^\circ$ and $\Delta_{TS}G^\circ$ of -46 and 211 kJ/mol at 1600 °C. Unlike adsorptions on the Si face, adsorptions of SiH, SiH₂ and SiCl on *(ads) occur with negative $\Delta_R G^\circ$ at 1600 °C, as shown in Table 5. This indicates that the adsorbed species on the surface are stable without any help from subsequent reactions. From $\Delta_R G^\circ$, we might expect the following trend of the adsorption rates (from largest to smallest): $\text{SiH} > \text{SiCl} > \text{SiH}_2 \gg \text{SiHCl} \gg \text{SiCl}_2$, which is the same order as above for H(ads). Since adsorptions on *(ads) occur without transition states, we might speculate

fast adsorption rates on $\ast(\text{ads})$. If we assume the sticking coefficients to be 1.0 for all the Si species on $\ast(\text{ads})$ and use Θ equal to 1.0 together with the same molar fractions as used in section 1.1, we will obtain the same growth rates as shown in section 1.1 which are too high in comparison to the experimental values. As we have discussed previously, the exaggeration in the growth rate is likely due to the following facts. 1) Θ has been assumed equal to its maximum value ($\Theta = 1.0$) and 2) we have not taken desorption processes into account.

Table 5 The energies at 0 K and standard Gibbs free energies at 1600 °C of the adsorption processes and sticking coefficients on H(ads) and $\ast(\text{ads})$ on the C face of 4H-SiC. The (free) energies are presented in the unit of kJ/mol and calculated with respect to the energy of the reactant state at asymptote condition.

		$\Delta_R E^\circ$ ^{a)} (0 K)	$\Delta_{TS} E^\circ$ ^{b)} (0 K)	$\Delta_R G^\circ$ ^{a)} (1600 °C)	$\Delta_{TS} G^\circ$ ^{b)} (1600 °C)	S ^{c)} (1600 °C)
R29	$\text{SiH}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiH}_2(\text{ads})$	-194	47	63	292	3×10^{-3}
R30	$\text{SiH}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiH}_3(\text{ads})$	-238	61	56	350	6×10^{-5}
R31	$\text{SiCl}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiHCl}(\text{ads})$	-149	77	133	336	2×10^{-4}
R32	$\text{SiHCl}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiH}_2\text{Cl}(\text{ads})$	-207	116	123	422	8×10^{-7}
R33	$\text{SiCl}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiHCl}_2(\text{ads})$	-153	192	186	506	4×10^{-9}
R34	$\text{SiH}(\text{g}) + \ast(\text{ads}) \rightarrow \text{SiH}(\text{ads})$	-341	-	-51	-	-
R35	$\text{SiH}_2(\text{g}) + \ast(\text{ads}) \rightarrow \text{SiH}_2(\text{ads})$	-301	-	-1	-	-
R36	$\text{SiCl}(\text{g}) + \ast(\text{ads}) \rightarrow \text{SiCl}(\text{ads})$	-338	-	-25	-	-
R37	$\text{SiHCl}(\text{g}) + \ast(\text{ads}) \rightarrow \text{SiHCl}(\text{ads})$	-267	-	66	-	-
R38	$\text{SiCl}_2(\text{g}) + \ast(\text{ads}) \rightarrow \text{SiCl}_2(\text{ads})$	-212	-	129	-	-

^{a)} Energies and free energies of reaction, ^{b)} energies and free energies of activation, ^{c)} sticking coefficients.

Table 6 The adsorption and desorption rate constants at 1600 °C of SiH, SiH₂, SiCl, SiHCl and SiCl₂ on H(ads) on the C face of 4H–SiC.

		Adsorption rate constant ^{a)}	Desorption rate constant ^{b)}
R29	SiH(g) + H(ads) → SiH ₂ (ads)	2	2×10^7
R30	SiH ₂ (g) + H(ads) → SiH ₃ (ads)	5×10^{-2}	2×10^5
R31	SiCl(g) + H(ads) → SiHCl(ads)	1×10^{-1}	8×10^7
R32	SiHCl(g) + H(ads) → SiH ₂ Cl(ads)	4×10^{-4}	2×10^5
R33	SiCl ₂ (g) + H(ads) → SiHCl ₂ (ads)	2×10^{-6}	5×10^4

^{a)} The adsorption rate constants, $R_{ads}/p\gamma_g\Theta_s$, are calculated using Eq. 5-8. Here, the adsorption rate (R_{ads}) is in molecule per site per second. The total pressure (p) is in pascal. The gaseous molar fraction (γ_g) and the surface fraction (Θ_s) are unitless. The surface area per site of H(ads) is assumed equal to $8.178 \times 10^{-20} \text{ m}^2$ which is the area per one lattice site on the C-face of 4H–SiC.

^{b)} The desorption rate constants, R_{de}/Θ_s , are calculated using Eq. 9-10. Here, the desorption rate (R_{de}) is in molecule per site per second. The surface fraction (Θ_s) is unitless.

3 Adsorptions of SiH_xF_y , SiH_xBr_y and Si atoms. The Gibbs free energies ($\Delta_R G^\circ$) of adsorptions of SiH_xF_y , SiH_xBr_y and Si atoms on both the Si face and the C face of 4H-SiC are shown in Table 7 and 8. Similar to the previous sections, adsorptions are more favorable on a surface site with the presence of a dangling bond, i.e. $\text{CH}_2(\text{ads})$ and $\ast(\text{ads})$.

Adsorptions of Si atoms are shown to be the most thermodynamically favorable among all the Si species in the study. On the Si face, the Gibbs free energies ($\Delta_R G^\circ$) of Si atom adsorptions on $\text{CH}_3(\text{ads})$ and $\text{CH}_2(\text{ads})$ are 24 and -48 kJ/mol at 1600 °C, which are the lowest $\Delta_R G^\circ$ among the set. Similarly, on the C face, $\Delta_R G^\circ$ of Si atom adsorptions on $\text{H}(\text{ads})$ and $\ast(\text{ads})$ are also smallest among the set, with $\Delta_R G^\circ$ of -7 and -109 kJ/mol at 1600 °C. Due to the change in the spin states, these reactions are spin-forbidden and the calculation of the reaction rates is beyond the scope of this study.

For the halide systems, the Gibbs free energies ($\Delta_R G^\circ$) from smallest to largest are observed in the adsorptions of SiX , SiHX and SiX_2 , for X being the halides. This is similar to what we previously

observed in the adsorptions of the Cl chemistry. As a result, we propose that SiX (for X being F, Cl and Br) are the major growth contributors to SiC among the SiH_xX_y species.

Table 7 The energies (0 K) and standard Gibbs free energies (1600 °C) of the adsorption processes of Si atoms, SiF, SiHF, SiF₂, SiBr, SiHBr and SiBr₂ on CH₃(ads) and CH₂(ads) pre-deposited on the Si face of 4H–SiC. The (free) energies are presented in the unit of kJ/mol, calculated with respect to the energy of the reactant state at asymptote condition.

		$\Delta_R E^{\circ \text{ a)}}$ (0 K)	$\Delta_R G^{\circ \text{ a)}}$ (1600 °C)
R40	$^3\text{Si(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-CH}_2(\text{ads})$	-217	24
R41	$\text{SiF(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiHF-CH}_2(\text{ads})$	-127	139
R42	$\text{SiHF(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{F-CH}_2(\text{ads})$	-192	120
R43	$\text{SiF}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHF}_2\text{-CH}_2(\text{ads})$	-138	167
R44	$\text{SiBr(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiHBr-CH}_2(\text{ads})$	-120	135
R45	$\text{SiHBr(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{Br-CH}_2(\text{ads})$	-180	133
R46	$\text{SiBr}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHBr}_2\text{-CH}_2(\text{ads})$	-130	184
R47	$^3\text{Si(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{Si-CH}_2(\text{ads})$	-320	-48
R48	$\text{SiF(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiF-CH}_2(\text{ads})$	-316	19
R49	$\text{SiHF(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiHF-CH}_2(\text{ads})$	-225	110
R50	$\text{SiF}_2(\text{g}) + \text{CH}_2(\text{ads}) \rightarrow \text{SiF}_2\text{-CH}_2(\text{ads})$	-163	162
R51	$\text{SiBr(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiBr-CH}_2(\text{ads})$	-304	35
R52	$\text{SiHBr(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiHBr-CH}_2(\text{ads})$	-224	101
R53	$\text{SiBr}_2(\text{g}) + \text{CH}_2(\text{ads}) \rightarrow \text{SiBr}_2\text{-CH}_2(\text{ads})$	-189	139

^{a)} Energies and free energies of reaction.

Table 8 The energies (0 K) and standard Gibbs free energies (1600 °C) of the adsorption processes of Si atoms, SiF, SiHF, SiF₂, SiBr, SiHBr and SiBr₂ on H(ads) and *(ads) on the C face of 4H–SiC. The (free) energies are presented in the unit of kJ/mol, calculated with respect to the energy of the reactant state at asymptote condition.

		$\Delta_R E^{\circ \text{ a)}}$ (0 K)	$\Delta_R G^{\circ \text{ a)}}$ (1600 °C)
R54	$^3\text{Si(g)} + \text{H(ads)} \rightarrow \text{SiH(ads)}$	-222	-7
R55	$\text{SiF(g)} + \text{H(ads)} \rightarrow \text{SiHF(ads)}$	-161	107
R56	$\text{SiHF(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{F(ads)}$	-225	100
R57	$\text{SiF}_2\text{(g)} + \text{H(ads)} \rightarrow \text{SiHF}_2\text{(ads)}$	-175	156
R58	$\text{SiBr(g)} + \text{H(ads)} \rightarrow \text{SiHBr(ads)}$	-148	135
R59	$\text{SiHBr(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{Br(ads)}$	-204	134
R60	$\text{SiBr}_2\text{(g)} + \text{H(ads)} \rightarrow \text{SiHBr}_2\text{(ads)}$	-142	194
R61	$^3\text{Si(g)} + \text{*(ads)} \rightarrow \text{Si(ads)}$	-351	-109
R62	$\text{SiF(g)} + \text{*(ads)} \rightarrow \text{SiF(ads)}$	-355	-44
R63	$\text{SiHF(g)} + \text{*(ads)} \rightarrow \text{SiHF(ads)}$	-275	44
R64	$\text{SiF}_2\text{(g)} + \text{*(ads)} \rightarrow \text{SiF}_2\text{(ads)}$	-215	108
R65	$\text{SiBr(g)} + \text{*(ads)} \rightarrow \text{SiBr(ads)}$	-335	-10
R66	$\text{SiHBr(g)} + \text{*(ads)} \rightarrow \text{SiHBr(ads)}$	-268	67
R67	$\text{SiBr}_2\text{(g)} + \text{*(ads)} \rightarrow \text{SiBr}_2\text{(ads)}$	-211	133

Summary and Conclusion

The density functional theory (B3LYP and M06-2X) and transition state theory are used to study adsorption processes of active Si species on the Si face and the C face of 4H–SiC. On the Si face,

we show that adsorptions of SiCl, SiCl₂, SiHCl, SiH and SiH₂ occurs more likely on a methylene site, CH₂(ads). The processes are shown to occur without the presence of transition states and thus relatively large sticking probabilities should be expected. The $\Delta_R G^\circ$ from smallest to largest are SiH > SiCl > SiH₂ > SiHCl > SiCl₂. Adsorptions on a methyl site, CH₃(ads), and on an ethylene site, C₂H₄(ads), both occur with relatively large activation barriers at the CVD process condition resulting in small sticking probabilities of all Si species considered. The adsorptions on CH₂(ads), CH₃(ads) as well as C₂H₄(ads) are all shown to be thermodynamically less favorable than their reverse, i.e. desorptions. The adsorbed products are shown to be stabilized by reacting with adjacent methyl sites and forming a larger cluster. These subsequent processes happen with rates that are fast enough to compete with desorption processes. On the C face, the adsorptions likely occur on a surface site terminated by a dangling bond, *(ads), which are shown to occur without the presence of transition states and produce stable products. The $\Delta_R G^\circ$ from smallest to largest are SiH > SiCl > SiH₂ > SiHCl > SiCl₂. Lastly, we present the Gibbs free energies of adsorptions of Si atoms, SiX, SiX₂, SiHX, for X being F and Br. Again, it is observed that adsorptions on the Si face occurs most likely on a methylene site, CH₂(ads), while adsorptions on the C face occur on a surface site terminated by a dangling bond, *(ads). Adsorptions of Si atoms are shown to be the most thermodynamically favorable among all the species in the study. Among the halide-containing species, the Gibbs free energies ($\Delta_R G^\circ$) from smallest to largest are observed in the adsorptions of SiX, SiHX and SiX₂, for X being the halides. From the results obtained in this study we conclude that the major Si contributors in the SiC-CVD process are Si atoms, SiX (for X being the halide) and SiH. This is unlike Si-CVD processes in which SiH₂ was predicted to be the most important species contributing to Si deposition^{26,27}. The results also imply that SiX₂ is not a major contributor to SiC growth, in contrast to previous assumptions.

Supporting Information

Gibbs free energies, sticking coefficients, rate constants at the temperature range of 298 – 2500 K and molecular coordinates. This material is available free of charge via the internet at <http://pubs.acs.org>.

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Acknowledgment

The authors acknowledge financial support from the Swedish Foundation for Strategic Research, from the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO Mat LiU No 2009 00971), and from the Swedish Research Council (VR Grant No. 2016-05137_4). Supercomputer resources were provided by the Swedish National Infrastructure for Computing (SNIC) and the National Supercomputer Centre (NSC), Linköping University.

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Supporting Information for

Growth Mechanism of SiC CVD – Adsorption and Surface Reactions of Active Si Species

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Table S1 Gibbs free energies of reaction (ΔG°_R) in kJ/mol at the temperature range of 298 – 2500 K.

$$\Delta G^\circ_R = a_1 T^4 + a_2 T^3 + a_3 T^2 + a_4 T + a_5 \text{ for temperature (T) = 298 – 2500 K.}$$

		a_1	a_2	a_3	a_4	a_5
R1	$\text{SiH(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads})$	-2.87E-13	2.95E-09	-1.42E-05	1.54E-01	-1.61E+02
R2	$\text{SiH}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads})$	-1.37E-13	2.03E-09	-1.31E-05	1.79E-01	-2.09E+02
R3	$\text{SiCl(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-CH}_2(\text{ads})$	-4.63E-13	4.20E-09	-1.76E-05	1.67E-01	-1.27E+02
R4	$\text{SiHCl(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{Cl-CH}_2(\text{ads})$	-3.29E-13	3.35E-09	-1.65E-05	1.93E-01	-1.89E+02
R5	$\text{SiCl}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl}_2\text{-CH}_2(\text{ads})$	-5.67E-13	5.03E-09	-2.10E-05	1.93E-01	-1.36E+02
R6	$\text{SiH(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiH-CH}_2(\text{ads})$	5.36E-13	-2.93E-09	1.84E-06	1.86E-01	-3.28E+02
R7	$\text{SiH}_2(\text{g}) + \text{CH}_2(\text{ads}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads})$	3.17E-13	-1.36E-09	-3.24E-06	1.79E-01	-2.54E+02
R8	$\text{SiCl(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiCl-CH}_2(\text{ads})$	2.12E-13	-7.33E-10	-3.66E-06	1.93E-01	-3.10E+02
R9	$\text{SiHCl(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiHCl-CH}_2(\text{ads})$	2.58E-13	-9.36E-10	-4.42E-06	1.94E-01	-2.31E+02
R10	$\text{SiCl}_2(\text{g}) + \text{CH}_2(\text{ads}) \rightarrow \text{SiCl}_2\text{-CH}_2(\text{ads})$	-5.17E-14	1.23E-09	-1.01E-05	1.82E-01	-1.85E+02
R11	$\text{SiH(g)} + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiH-(CH}_2)_2(\text{ads})$	-3.25E-13	2.92E-09	-1.28E-05	1.60E-01	-2.80E+02
R12	$\text{SiH}_2(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	-2.19E-13	2.35E-09	-1.28E-05	1.80E-01	-3.33E+02
R13	$\text{SiCl(g)} + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_2(\text{ads})$	-6.34E-13	5.07E-09	-1.83E-05	1.72E-01	-2.47E+02
R14	$\text{SiHCl(g)} + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	-5.08E-13	4.35E-09	-1.79E-05	1.94E-01	-3.15E+02
R15	$\text{SiCl}_2(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads})$	-7.43E-13	5.97E-09	-2.21E-05	1.98E-01	-2.75E+02
R17	$\text{C}_2\text{H}_4(\text{ads}) + \text{H(g)} \rightarrow \text{CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	-1.55E-13	7.55E-10	-1.21E-06	7.50E-02	-1.38E+02
R18	$\text{SiH-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	3.94E-13	-2.44E-09	5.02E-06	3.13E-02	-2.23E+02

R19	$\text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	-3.20E-13	2.56E-09	-7.37E-06	-6.61E-02	5.72E+01
R20	$\text{SiCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	3.17E-13	-1.88E-09	3.42E-06	2.25E-02	-1.86E+02
R21	$\text{SiHCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{H(g)}$	-4.83E-13	3.65E-09	-1.01E-05	-6.65E-02	4.76E+01
R22	$\text{SiCl}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	-5.09E-13	3.82E-09	-1.05E-05	-6.73E-02	4.43E+01
R23	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	-8.77E-13	5.67E-09	-1.02E-05	-9.83E-02	-2.98E+01
R24	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	1.69E-13	-1.51E-09	7.59E-06	-1.26E-01	6.02E+01
R25	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	-8.65E-13	5.58E-09	-9.89E-06	-8.92E-02	-3.91E+01
R26	$\text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	3.23E-13	-2.60E-09	1.05E-05	-1.22E-01	3.80E+01
R27	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	-3.24E-13	1.42E-09	1.89E-06	-1.56E-02	-5.99E+01
R28	$\text{SiCl-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	7.10E-13	-5.66E-09	1.94E-05	-5.25E-02	3.94E+01
R29	$\text{SiH(g)} + \text{H(ads)} \rightarrow \text{SiH}_2(\text{ads})$	-3.13E-13	2.98E-09	-1.36E-05	1.56E-01	-1.98E+02
R30	$\text{SiH}_2(\text{g}) + \text{H(ads)} \rightarrow \text{SiH}_3(\text{ads})$	-1.34E-13	1.91E-09	-1.23E-05	1.77E-01	-2.43E+02
R31	$\text{SiCl(g)} + \text{H(ads)} \rightarrow \text{SiHCl(ads)}$	-5.63E-13	4.71E-09	-1.81E-05	1.73E-01	-1.51E+02
R32	$\text{SiHCl(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{Cl(ads)}$	-3.38E-13	3.29E-09	-1.57E-05	1.98E-01	-2.10E+02
R33	$\text{SiCl}_2(\text{g}) + \text{H(ads)} \rightarrow \text{SiHCl}_2(\text{ads})$	-5.34E-13	4.68E-09	-1.94E-05	2.06E-01	-1.55E+02
R34	$\text{SiH(g)} + *(\text{ads}) \rightarrow \text{SiH(ads)}$	-7.35E-14	1.18E-09	-8.24E-06	1.69E-01	-3.45E+02
R35	$\text{SiH}_2(\text{g}) + *(\text{ads}) \rightarrow \text{SiH}_2(\text{ads})$	-1.57E-13	1.90E-09	-1.15E-05	1.79E-01	-3.06E+02
R36	$\text{SiCl(g)} + *(\text{ads}) \rightarrow \text{SiCl(ads)}$	-3.19E-13	2.83E-09	-1.23E-05	1.83E-01	-3.39E+02

R37	$\text{SiHCl(g)} + *(\text{ads}) \rightarrow \text{SiHCl(ads)}$	-2.87E-13	2.79E-09	-1.37E-05	1.98E-01	-2.70E+02
R38	$\text{SiCl}_2(\text{g}) + *(\text{ads}) \rightarrow \text{SiCl}_2(\text{ads})$	-4.28E-13	3.77E-09	-1.62E-05	2.03E-01	-2.14E+02
R40	$^3\text{Si(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-CH}_2(\text{ads})$	-2.19E-13	2.22E-09	-9.63E-06	1.43E-01	-2.21E+02
R41	$\text{SiF(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiHF-CH}_2(\text{ads})$	-4.91E-13	4.40E-09	-1.81E-05	1.65E-01	-1.30E+02
R42	$\text{SiHF(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{F-CH}_2(\text{ads})$	-3.15E-13	3.26E-09	-1.63E-05	1.90E-01	-1.96E+02
R43	$\text{SiF}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHF}_2\text{-CH}_2(\text{ads})$	-5.03E-13	4.60E-09	-1.99E-05	1.89E-01	-1.41E+02
R44	$\text{SiBr(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiHBr-CH}_2(\text{ads})$	-5.81E-13	5.02E-09	-1.97E-05	1.60E-01	-1.22E+02
R45	$\text{SiHBr(g)} + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{Br-CH}_2(\text{ads})$	-3.78E-13	3.69E-09	-1.74E-05	1.91E-01	-1.83E+02
R46	$\text{SiBr}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHBr}_2\text{-CH}_2(\text{ads})$	-5.41E-13	4.85E-09	-2.05E-05	1.94E-01	-1.32E+02
R47	$^3\text{Si(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{Si-CH}_2(\text{ads})$	4.86E-13	-3.00E-09	5.37E-06	1.45E-01	-3.25E+02
R48	$\text{SiF(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiF-CH}_2(\text{ads})$	1.93E-13	-6.01E-10	-4.02E-06	1.90E-01	-3.21E+02
R49	$\text{SiHF(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiHF-CH}_2(\text{ads})$	2.03E-13	-5.51E-10	-5.41E-06	1.92E-01	-2.30E+02
R50	$\text{SiF}_2(\text{g}) + \text{CH}_2(\text{ads}) \rightarrow \text{SiF}_2\text{-CH}_2(\text{ads})$	3.17E-14	6.66E-10	-8.71E-06	1.89E-01	-1.67E+02
R51	$\text{SiBr(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiBr-CH}_2(\text{ads})$	1.38E-13	-2.18E-10	-5.01E-06	1.92E-01	-3.07E+02
R52	$\text{SiHBr(g)} + \text{CH}_2(\text{ads}) \rightarrow \text{SiHBr-CH}_2(\text{ads})$	1.53E-13	-2.05E-10	-6.31E-06	1.87E-01	-2.28E+02
R53	$\text{SiBr}_2(\text{g}) + \text{CH}_2(\text{ads}) \rightarrow \text{SiBr}_2\text{-CH}_2(\text{ads})$	3.83E-14	6.19E-10	-8.57E-06	1.90E-01	-1.91E+02
R54	$^3\text{Si(g)} + \text{H(ads)} \rightarrow \text{SiH(ads)}$	-3.74E-13	3.06E-09	-1.08E-05	1.28E-01	-2.23E+02
R55	$\text{SiF(g)} + \text{H(ads)} \rightarrow \text{SiHF(ads)}$	-5.59E-13	4.70E-09	-1.82E-05	1.65E-01	-1.63E+02
R56	$\text{SiHF(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{F(ads)}$	-2.88E-13	2.93E-09	-1.48E-05	1.95E-01	-2.29E+02
R57	$\text{SiF}_2(\text{g}) + \text{H(ads)} \rightarrow \text{SiHF}_2(\text{ads})$	-4.21E-13	3.89E-09	-1.74E-05	2.00E-01	-1.78E+02
R58	$\text{SiBr(g)} + \text{H(ads)} \rightarrow \text{SiHBr(ads)}$	-5.95E-13	4.93E-09	-1.86E-05	1.73E-01	-1.49E+02
R59	$\text{SiHBr(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{Br(ads)}$	-3.01E-13	3.02E-09	-1.50E-05	2.01E-01	-2.07E+02

R60	$\text{SiBr}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiHBr}_2(\text{ads})$	-6.27E-13	5.30E-09	-2.10E-05	2.05E-01	-1.43E+02
R61	$^3\text{Si}(\text{g}) + *(\text{ads}) \rightarrow \text{Si}(\text{ads})$	-7.90E-14	7.76E-10	-3.78E-06	1.35E-01	-3.54E+02
R62	$\text{SiF}(\text{g}) + *(\text{ads}) \rightarrow \text{SiF}(\text{ads})$	-2.90E-13	2.63E-09	-1.18E-05	1.82E-01	-3.58E+02
R63	$\text{SiHF}(\text{g}) + *(\text{ads}) \rightarrow \text{SiHF}(\text{ads})$	-3.09E-13	2.95E-09	-1.42E-05	1.90E-01	-2.78E+02
R64	$\text{SiF}_2(\text{g}) + *(\text{ads}) \rightarrow \text{SiF}_2(\text{ads})$	-4.33E-13	3.79E-09	-1.64E-05	1.94E-01	-2.17E+02
R65	$\text{SiBr}(\text{g}) + *(\text{ads}) \rightarrow \text{SiBr}(\text{ads})$	-2.20E-13	2.13E-09	-1.05E-05	1.88E-01	-3.37E+02
R66	$\text{SiHBr}(\text{g}) + *(\text{ads}) \rightarrow \text{SiHBr}(\text{ads})$	-3.02E-13	2.89E-09	-1.40E-05	1.98E-01	-2.71E+02
R67	$\text{SiBr}_2(\text{g}) + *(\text{ads}) \rightarrow \text{SiBr}_2(\text{ads})$	-4.78E-13	4.10E-09	-1.70E-05	2.05E-01	-2.12E+02

Table S2 Gibbs free energies of activation in kJ/mol at the temperature range of 298 – 2500 K.

$$\Delta G^\ddagger = a_1 T^4 + a_2 T^3 + a_3 T^2 + a_4 T + a_5 \text{ for temperature (T) = 298 – 2500 K.}$$

		a_1	a_2	a_3	a_4	a_5
R1	$\text{SiH}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads})$	-4.57E-13	3.78E-09	-1.32E-05	1.46E-01	7.82E+01
R2	$\text{SiH}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads})$	-3.76E-13	3.31E-09	-1.32E-05	1.65E-01	8.32E+01
R3	$\text{SiCl}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-CH}_2(\text{ads})$	-7.22E-13	5.60E-09	-1.79E-05	1.54E-01	1.05E+02
R4	$\text{SiHCl}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{Cl-CH}_2(\text{ads})$	-5.83E-13	4.75E-09	-1.70E-05	1.80E-01	1.20E+02
R5	$\text{SiCl}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl}_2\text{-CH}_2(\text{ads})$	-7.00E-13	5.60E-09	-1.94E-05	1.83E-01	1.89E+02
R11	$\text{SiH}(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiH-(CH}_2)_2(\text{ads})$	-6.81E-13	4.99E-09	-1.48E-05	1.44E-01	1.38E+02
R12	$\text{SiH}_2(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	-8.40E-13	6.23E-09	-1.94E-05	1.57E-01	2.04E+02
R13	$\text{SiCl}(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_2(\text{ads})$	-9.03E-13	6.49E-09	-1.85E-05	1.45E-01	1.49E+02

R14	$\text{SiHCl(g)} + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	-9.87E-13	7.22E-09	-2.18E-05	1.73E-01	2.34E+02
R15	$\text{SiCl}_2(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads})$	-1.20E-12	8.65E-09	-2.53E-05	1.71E-01	2.78E+02
R18	$\text{SiH-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	2.85E-13	-2.08E-09	7.37E-06	2.31E-02	9.17E+01
R19	$\text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	1.72E-13	-1.03E-09	3.51E-06	3.51E-02	1.73E+02
R20	$\text{SiCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	1.75E-13	-1.30E-09	5.24E-06	1.27E-02	1.41E+02
R21	$\text{SiHCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{H(g)}$	1.05E-13	-5.95E-10	2.48E-06	3.52E-02	1.63E+02
R22	$\text{SiCl}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	9.10E-15	2.02E-10	-2.47E-07	2.16E-02	1.87E+02
R23	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	1.06E-13	-4.55E-10	1.42E-06	8.37E-03	2.90E+02
R24	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	2.71E-13	-2.01E-09	7.14E-06	1.33E-02	2.29E+02
R25	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	1.16E-13	-6.45E-10	2.42E-06	9.80E-03	2.65E+02
R26	$\text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	5.25E-13	-3.65E-09	1.09E-05	1.45E-02	2.40E+02
R27	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	1.95E-13	-1.46E-09	5.04E-06	8.58E-02	9.45E+00
R28	$\text{SiCl-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	3.24E-13	-2.40E-09	7.67E-06	8.36E-02	8.60E+01
R29	$\text{SiH(g)} + \text{H(ads)} \rightarrow \text{SiH}_2(\text{ads})$	-3.92E-13	3.16E-09	-1.09E-05	1.44E-01	4.48E+01
R30	$\text{SiH}_2(\text{g}) + \text{H(ads)} \rightarrow \text{SiH}_3(\text{ads})$	-3.15E-13	2.75E-09	-1.11E-05	1.70E-01	5.73E+01
R31	$\text{SiCl(g)} + \text{H(ads)} \rightarrow \text{SiHCl(ads)}$	-6.32E-13	4.81E-09	-1.51E-05	1.54E-01	7.82E+01
R32	$\text{SiHCl(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{Cl(ads)}$	-6.07E-13	4.72E-09	-1.60E-05	1.82E-01	1.15E+02

R33	$\text{SiCl}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiHCl}_2(\text{ads})$	-7.37E-13	5.66E-09	-1.86E-05	1.88E-01	1.92E+02
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Table S3 Sticking coefficients, $S = AT^n \exp(-E/RT)$, at the temperature range of 298 – 2500 K. The energy (E) is in the unit of kJ/mol.

		S (1600 °C)	298 – 2500 K		
			ln (A)	n	E
R1	$\text{SiH}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads})$	3.02E-04	-22.215	2.524	76.516
R2	$\text{SiH}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads})$	2.60E-05	-25.921	2.727	80.711
R3	$\text{SiCl}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-CH}_2(\text{ads})$	4.33E-05	-23.879	2.716	103.288
R4	$\text{SiHCl}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{Cl-CH}_2(\text{ads})$	7.03E-07	-28.371	2.889	117.891
R5	$\text{SiCl}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl}_2\text{-CH}_2(\text{ads})$	8.15E-09	-29.411	3.018	186.254
R11	$\text{SiH}(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiH-(CH}_2)_2(\text{ads})$	9.48E-06	-20.860	2.397	136.556
R12	$\text{SiH}_2(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	5.31E-08	-24.845	2.795	202.007
R13	$\text{SiCl}(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_2(\text{ads})$	6.61E-06	-21.531	2.533	147.736
R14	$\text{SiHCl}(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	1.68E-09	-27.043	2.883	231.808
R15	$\text{SiCl}_2(\text{g}) + \text{C}_2\text{H}_4(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads})$	1.98E-10	-27.388	3.019	275.674
R29	$\text{SiH}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiH}_2(\text{ads})$	2.62E-03	-20.912	2.355	43.270
R30	$\text{SiH}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiH}_3(\text{ads})$	6.35E-05	-25.508	2.572	55.036
R31	$\text{SiCl}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiHCl}(\text{ads})$	1.88E-04	-22.666	2.523	76.678
R32	$\text{SiHCl}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiH}_2\text{Cl}(\text{ads})$	7.69E-07	-27.618	2.754	112.348
R33	$\text{SiCl}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{SiHCl}_2(\text{ads})$	3.67E-09	-28.940	2.881	189.888

Table S4 Rate constants in forward and reverse directions. A and E are in the units of molecules per site per second and kJ/mol.

		Forward rate constants			Reverse rate constants		
		ln (A)	n	E	ln (A)	n	E
R18	$\text{SiH-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads})$	25.088	0.334	93.129	28.915	0.381	316.595
R19	$\text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	21.913	0.629	173.923	3.526	0.450	116.164
R20	$\text{SiCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads})$	25.760	0.442	141.871	28.983	0.405	328.009
R21	$\text{SiHCl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{H(g)}$	21.767	0.663	163.960	3.809	0.382	115.888
R22	$\text{SiCl}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{H(g)}$	22.261	0.859	187.453	6.906	0.240	145.684
R23	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	24.102	0.799	290.502	-3.375	1.370	316.249
R24	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	26.089	0.362	230.300	-6.274	1.372	167.938
R25	$\text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	24.630	0.688	266.089	-2.919	1.274	301.090
R26	$\text{SiCl}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads}) \rightarrow \text{SiCl-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	25.932	0.311	241.019	-7.590	1.435	201.034
R27	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g})$	6.449	0.603	10.898	-3.942	1.654	66.495
R28	$\text{SiCl-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{Si}^*\text{-(CH}_2)_3(\text{ads}) + \text{HCl(g)}$	6.141	0.492	87.315	-8.998	1.959	45.603
R29	$\text{SiH(g)} + \text{H(ads)} \rightarrow \text{SiH}_2(\text{ads})$	-10.563	1.884	43.884	29.320	0.393	244.838
R30	$\text{SiH}_2(\text{g}) + \text{H(ads)} \rightarrow \text{SiH}_3(\text{ads})$	-15.192	2.103	55.638	28.581	0.428	302.576
R31	$\text{SiCl(g)} + \text{H(ads)} \rightarrow \text{SiHCl(ads)}$	-12.736	2.056	77.259	30.230	0.372	230.536
R32	$\text{SiHCl(g)} + \text{H(ads)} \rightarrow \text{SiH}_2\text{Cl(ads)}$	-17.679	2.285	112.951	29.360	0.486	326.841

R33	SiCl ₂ (g) + H(ads) → SiHCl ₂ (ads)	-19.224	2.413	190.480	29.782	0.449	349.358
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Table S4 Molecular Coordinates in Z-matrix form

CH₃(ads)

Si						
Si	1	B1				
Si	1	B2	2	A1		
Si	2	B3	1	A2	3	D1
Si	2	B4	1	A3	3	D2
Si	5	B5	2	A4	1	D3
Si	3	B6	1	A5	6	D4
Si	2	B7	1	A6	3	D5
Si	2	B8	1	A7	3	D6
Si	7	B9	3	A8	1	D7
Si	9	B10	2	A9	1	D8
Si	3	B11	1	A10	6	D9
C	6	B12	5	A11	2	D10
C	1	B13	3	A12	12	D11
C	2	B14	1	A13	14	D12
C	12	B15	3	A14	1	D13
C	11	B16	9	A15	2	D14
C	10	B17	7	A16	3	D15
C	7	B18	3	A17	1	D16
C	12	B19	3	A18	1	D17
C	7	B20	3	A19	1	D18
C	9	B21	2	A20	1	D19
H	1	B22	14	A21	3	D20
H	2	B23	1	A22	14	D21
H	3	B24	1	A23	14	D22
H	5	B25	2	A24	1	D23
H	16	B26	12	A25	3	D24
H	6	B27	5	A26	2	D25
H	17	B28	11	A27	9	D26
H	18	B29	10	A28	7	D27
H	19	B30	7	A29	3	D28
H	20	B31	12	A30	3	D29
H	21	B32	7	A31	3	D30
H	22	B33	9	A32	2	D31
C	4	B34	2	A33	1	D32
C	3	B35	1	A34	14	D33
Si	20	B36	12	A35	3	D34
Si	19	B37	7	A36	3	D35
C	38	B38	19	A37	7	D36
Si	36	B39	3	A38	1	D37
H	39	B40	38	A39	19	D38
H	39	B41	38	A40	19	D39
H	40	B42	36	A41	3	D40
H	40	B43	36	A42	3	D41

H	38	B44	19	A43	7	D42
H	7	B45	3	A44	1	D43
H	36	B46	3	A45	1	D44
H	14	B47	1	A46	3	D45
H	13	B48	6	A47	5	D46
H	11	B49	9	A48	2	D47
C	1	B50	14	A49	3	D48
C	2	B51	1	A50	14	D49
C	3	B52	1	A51	14	D50
Si	53	B53	3	A52	1	D51
H	5	B54	2	A53	1	D52
H	2	B55	1	A54	14	D53
H	22	B56	9	A55	2	D54
H	17	B57	11	A56	9	D55
H	21	B58	7	A57	3	D56
H	18	B59	10	A58	7	D57
H	6	B60	5	A59	2	D58
H	1	B61	14	A60	3	D59
Si	15	B62	2	A61	1	D60
Si	35	B63	4	A62	2	D61
C	37	B64	20	A63	12	D62
C	8	B65	2	A64	1	D63
H	63	B66	15	A65	2	D64
H	64	B67	35	A66	4	D65
H	64	B68	35	A67	4	D66
H	63	B69	15	A68	2	D67
C	64	B70	35	A69	4	D68
H	65	B71	37	A70	20	D69
H	65	B72	37	A71	20	D70
H	66	B73	8	A72	2	D71
H	66	B74	8	A73	2	D72
Si	66	B75	8	A74	2	D73
H	76	B76	66	A75	8	D74
H	71	B77	64	A76	35	D75
C	4	B78	2	A77	1	D76
H	79	B79	4	A78	2	D77
H	79	B80	4	A79	2	D78
H	54	B81	53	A80	3	D79
H	79	B82	4	A81	2	D80

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B9	3.14880025
B10	3.15449541
B11	3.13241433

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B20	1.90315855
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D63	165.2435101
D64	-59.02971388
D65	-178.6207151
D66	-60.52071304
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D79	-60.9034913
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CH₂(ads)

Si						
Si	1	B1				
Si	1	B2	2	A1		
Si	2	B3	1	A2	3	D1
Si	2	B4	1	A3	3	D2
Si	5	B5	2	A4	1	D3
Si	3	B6	1	A5	6	D4
Si	2	B7	1	A6	3	D5
Si	8	B8	2	A7	1	D6
Si	7	B9	3	A8	1	D7
Si	9	B10	8	A9	2	D8
Si	3	B11	1	A10	6	D9
C	6	B12	5	A11	2	D10
C	1	B13	3	A12	4	D11
C	2	B14	1	A13	14	D12
C	12	B15	3	A14	1	D13
C	11	B16	9	A15	8	D14
C	10	B17	7	A16	3	D15
C	7	B18	3	A17	1	D16
C	12	B19	3	A18	1	D17
C	7	B20	3	A19	1	D18
C	9	B21	8	A20	2	D19
H	1	B22	14	A21	3	D20
H	2	B23	1	A22	14	D21

H	3	B24	1	A23	14	D22
H	5	B25	2	A24	1	D23
H	16	B26	12	A25	3	D24
H	6	B27	5	A26	2	D25
H	17	B28	11	A27	9	D26
H	18	B29	10	A28	7	D27
H	19	B30	7	A29	3	D28
H	20	B31	12	A30	3	D29
H	21	B32	7	A31	3	D30
H	22	B33	9	A32	8	D31
C	4	B34	2	A33	1	D32
C	3	B35	1	A34	14	D33
Si	20	B36	12	A35	3	D34
Si	19	B37	7	A36	3	D35
C	38	B38	19	A37	7	D36
Si	36	B39	3	A38	1	D37
H	39	B40	38	A39	19	D38
H	39	B41	38	A40	19	D39
H	40	B42	36	A41	3	D40
H	40	B43	36	A42	3	D41
H	38	B44	19	A43	7	D42
H	7	B45	3	A44	1	D43
H	36	B46	3	A45	1	D44
H	14	B47	1	A46	3	D45
H	13	B48	6	A47	5	D46
H	11	B49	9	A48	8	D47
C	1	B50	14	A49	3	D48
C	2	B51	1	A50	14	D49
C	3	B52	1	A51	14	D50
Si	53	B53	3	A52	1	D51
H	5	B54	2	A53	1	D52
H	2	B55	1	A54	14	D53
H	22	B56	9	A55	8	D54
H	17	B57	11	A56	9	D55
H	21	B58	7	A57	3	D56
H	18	B59	10	A58	7	D57
H	6	B60	5	A59	2	D58
H	1	B61	14	A60	3	D59
Si	15	B62	2	A61	1	D60
Si	35	B63	4	A62	2	D61
C	37	B64	20	A63	12	D62
C	8	B65	2	A64	1	D63
H	63	B66	15	A65	2	D64
H	64	B67	35	A66	4	D65
H	64	B68	35	A67	4	D66
H	63	B69	15	A68	2	D67
C	64	B70	35	A69	4	D68
H	65	B71	37	A70	20	D69
H	65	B72	37	A71	20	D70
H	66	B73	8	A72	2	D71
H	66	B74	8	A73	2	D72
Si	66	B75	8	A74	2	D73

H	76	B76	66	A75	8	D74
H	71	B77	64	A76	35	D75
C	4	B78	2	A77	1	D76
H	79	B79	4	A78	2	D77
H	79	B80	4	A79	2	D78
H	54	B81	53	A80	3	D79

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B11	3.13836119
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B16	1.90539133
B17	1.90657123
B18	1.9096806
B19	1.90777412
B20	1.90354238
B21	1.89963673
B22	1.4897187
B23	1.4885418
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B25	1.48931876
B26	1.10471142
B27	1.48940192
B28	1.10076809
B29	1.1007567
B30	1.10294982
B31	1.10460165
B32	1.10052632
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B34	1.93481672
B35	1.91026996
B36	1.9128069
B37	1.91023303
B38	1.90285581
B39	1.90681209
B40	1.09914228
B41	1.10058363
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B52	1.91833739
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D50	-123.3956914
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D76	89.04232718
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D78	105.0392254

C₂H₄(ads)

Si						
Si	1	B1				
Si	1	B2	2	A1		
Si	3	B3	1	A2	2	D1
Si	2	B4	1	A3	3	D2
Si	5	B5	2	A4	1	D3
Si	3	B6	1	A5	6	D4
Si	2	B7	1	A6	3	D5

Si	2	B8	1	A7	3	D6
Si	1	B9	3	A8	4	D7
Si	10	B10	1	A9	3	D8
Si	7	B11	3	A10	1	D9
C	5	B12	2	A11	1	D10
C	3	B13	1	A12	6	D11
C	2	B14	1	A13	14	D12
C	12	B15	7	A14	3	D13
C	9	B16	2	A15	1	D14
C	11	B17	10	A16	1	D15
C	7	B18	3	A17	1	D16
C	12	B19	7	A18	3	D17
C	7	B20	3	A19	1	D18
C	8	B21	2	A20	1	D19
H	1	B22	14	A21	3	D20
H	2	B23	1	A22	14	D21
H	3	B24	1	A23	14	D22
H	5	B25	2	A24	1	D23
H	16	B26	12	A25	7	D24
H	6	B27	5	A26	2	D25
H	17	B28	9	A27	2	D26
H	18	B29	11	A28	10	D27
H	19	B30	7	A29	3	D28
H	20	B31	12	A30	7	D29
H	21	B32	7	A31	3	D30
H	22	B33	8	A32	2	D31
C	4	B34	3	A33	1	D32
C	3	B35	1	A34	14	D33
Si	20	B36	12	A35	7	D34
Si	19	B37	7	A36	3	D35
C	38	B38	19	A37	7	D36
Si	36	B39	3	A38	1	D37
H	39	B40	38	A39	19	D38
H	39	B41	38	A40	19	D39
H	40	B42	36	A41	3	D40
H	40	B43	36	A42	3	D41
H	38	B44	19	A43	7	D42
H	7	B45	3	A44	1	D43
H	36	B46	3	A45	1	D44
H	14	B47	3	A46	1	D45
H	13	B48	5	A47	2	D46
H	11	B49	10	A48	1	D47
C	6	B50	5	A49	2	D48
C	2	B51	1	A50	14	D49
C	12	B52	7	A51	3	D50
Si	53	B53	12	A52	7	D51
H	5	B54	2	A53	1	D52
H	2	B55	1	A54	14	D53
H	22	B56	8	A55	2	D54
H	17	B57	9	A56	2	D55
H	21	B58	7	A57	3	D56
H	18	B59	11	A58	10	D57

H	6	B60	5	A59	2	D58
H	1	B61	14	A60	3	D59
Si	15	B62	2	A61	1	D60
Si	35	B63	4	A62	3	D61
C	37	B64	20	A63	12	D62
C	8	B65	2	A64	1	D63
H	63	B66	15	A65	2	D64
H	64	B67	35	A66	4	D65
H	64	B68	35	A67	4	D66
H	63	B69	15	A68	2	D67
C	63	B70	15	A69	2	D68
H	65	B71	37	A70	20	D69
H	65	B72	37	A71	20	D70
H	66	B73	8	A72	2	D71
H	66	B74	8	A73	2	D72
Si	65	B75	37	A74	20	D73
H	76	B76	65	A75	37	D74
H	71	B77	63	A76	15	D75
C	4	B78	3	A77	1	D76
H	79	B79	4	A78	3	D77
H	79	B80	4	A79	3	D78
C	79	B81	4	A80	3	D79
H	82	B82	79	A81	4	D80
H	82	B83	79	A82	4	D81

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B22	1.49038285
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B26	1.10448565

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