Growth Mechanism of SiC CVD: Surface Etching by H-2, H Atoms, and HCl

Pitsiri Sukkaew, Örjan Danielsson and Lars Ojamäe

The self-archived postprint version of this journal article is available at Linköping University Institutional Repository (DiVA):

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-147115>

N.B.: When citing this work, cite the original publication.

Sukkaew, P., Danielsson, Ö., Ojamäe, L., (2018), Growth Mechanism of SiC CVD: Surface Etching by H-2, H Atoms, and HCl, *Journal of Physical Chemistry A*, 122(9), 2503-2512.

<https://doi.org/10.1021/acs.jpca.7b10800>

Original publication available at:

<https://doi.org/10.1021/acs.jpca.7b10800>

Copyright: American Chemical Society

<http://pubs.acs.org/>

Growth Mechanism of SiC CVD – Surface Etching by H₂, H Atoms and HCl

Pitsiri Sukkaew, Örjan Danielsson and Lars Ojamäe*.*

Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden.

ABSTRACT

Silicon carbide is a wide bandgap semiconductor with unique characteristics suitable for high temperature and high power applications. Fabrication of SiC epitaxial layers is usually performed using chemical vapor deposition (CVD). In this work, we use quantum chemical density functional theory (B3LYP and M06-2X) and transition state theory to study etching reactions happening on the surface of SiC during CVD in order to combine etching effects to the surface kinetic model for SiC CVD. H₂, H atoms and HCl gases are chosen in the study as the most likely etchants responsible for surface etching. We consider etchings of four surface sites, namely CH₃(ads), SiH₃-CH₂(ads), SiH₂-(CH₂)₂(ads), SiH-(CH₂)₃(ads), which represent four subsequent snapshots of the surface as the growth proceeds. We find that H atoms are the most effective etchant on CH₃(ads) and SiH₃-CH₂(ads), which represent the first and second steps of the growth. HCl and H₂ are shown to be much less effective than H atoms and produce the etching rate constants which are $\sim 10^4$ and $\sim 10^7$ times slower. In comparison to CH₃(ads), SiH₃-CH₂(ads) is shown to be less stable and more

susceptible to etchings. Unlike the first and second steps of the growth, the third and fourth steps (i.e. $\text{SiH}_2\text{-(CH}_2\text{)}_2\text{(ads)}$ and $\text{SiH-(CH}_2\text{)}_3\text{(ads)}$) are stable and much less susceptible to any of the three etchants considered. This implies that the growth species become more stable via forming Si-C bonds with another surface species. The formation of a larger surface cluster thus helps stabilizing the growth against etchings.

Introduction

Silicon carbide is a wide bandgap semiconductor with unique characteristics such as chemical and mechanical robust, high thermal conductivity, high carrier mobilities and high breakdown electric field. These characteristics make SiC ideally suitable for applications dealing with high power, high temperature and harsh environments¹⁻³. For electronic applications, 4H polytype has been used most frequently. Fabrication of epitaxial SiC layers is usually performed using chemical vapor deposition (CVD)^{4,5}. The standard recipe is to use a mixture of silane and light hydrocarbons as the precursors. An addition of halides such as chlorine to the process, either in the form of HCl or as chlorinated precursors, has been established as the most promising route for high growth rate SiC CVD⁴.

In CVD, the growth happens via interactions between the growing surface and the active species in the gas phase. In our previous studies we presented the growth mechanisms of SiC starting from hydrocarbon adsorptions, followed by Si-species adsorptions and finished at the formation of a SiC surface cluster^{6,7}. So far we have not considered the effects of etching in the growth. *In situ* etching of SiC has been reported by several groups to have significant effects in altering the surface morphology⁸⁻¹⁰. While most studies reported microscopically change of the surface morphology before and after etching, very few studies actually provide detailed mechanisms or activation

energies of the process (for an example, the reader is referred to Ref. ^{9,11}). Among those studies, a study by Kojima et al., who investigated H₂ etching of 4H-SiC over the temperature range of 1500 – 1650 °C, reported the activation energy of 123.0 kcal/mol, or 515 kJ/mol, on the C face of 4H-SiC and the author mentioned observing similar trend on the Si face ¹⁰. We will show later that this experimental activation energy agrees well with our calculations.

For chloride-assisted SiC CVD, etchings are likely resulted from H₂, H atoms and HCl gases. Hydrogen, H₂, is usually employed as a carrier gas for CVD processes and is often used as a surface etchant during *in situ* surface preparation prior to growth. Hydrogen atoms, on the other hand, is not added directly into the process but is commonly produced in a significant amount via gas-phase and surface reactions during the growth. We have shown in our previous work that H atoms effectively help creating dangling bonds on the surface during the growth and thereby facilitates surface adsorptions of the active growth species ^{6,7}. HCl is often introduced in the SiC-CVD process to suppress the formation of silicon droplets, which are known to deteriorate the surface upon contact.

There are several studies in the literature of H₂, H atoms and HCl reactions on semiconductor surfaces such as Si ^{12–17}, c-SiC ^{16,18–21} as well as h-SiC ^{22–24}. In most cases, the focus was placed on reconstructed surfaces, both clean and hydrogenated, known to exist in a near vacuum atmosphere. In this work, we focus instead on the effects of etching during the growth which likely happens in a layer by layer fashion ⁹. We will thus consider etching reactions happening at each steps of the growth, starting from etching of the newly adsorbed species on the surface to etching of the final SiC surface cluster. The objective is to combine etching effects to the growth model we have already established in order to build up a detailed surface kinetic model for SiC CVD.

Methods

The surface is modeled using $\text{Si}_{24}\text{C}_{24}$ cluster. All the edges of the cluster are terminated by hydrogen atoms to preserve the SiC bulk geometry. Etching reactions will be studied on four surface sites corresponding to four steps of SiC growth on the surface of 4H-SiC, namely $\text{CH}_3(\text{ads})$, $\text{SiH}_3\text{-CH}_2(\text{ads})$, $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$, $\text{SiH-(CH}_2)_3(\text{ads})$. These four surface sites are shown in Fig. 1a-d.

Figure 1 Side views and top views of a) $\text{CH}_3(\text{ads})$, b) $\text{SiH}_3\text{-CH}_2(\text{ads})$, c) $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$ and d) $\text{SiH-(CH}_2)_3(\text{ads})$

Similar to the previous work ^{6,7}, optimizations and harmonic frequency calculations are performed using the density functional theory (DFT) with the B3LYP functional ^{25,26} and the LanL2DZ basis set ^{27,28} together with the D3 dispersion corrections from Grimme et al. ²⁹. The B3LYP electronic energy is corrected by a single point energy calculated using the M06-2X functional ³⁰ and

Dunning's basis set cc-pVTZ³¹. The transition state (TS) structures are verified by visualizing the vibrational displacement associated with the imaginary frequencies. The zero point energy correction is applied to all energies in the study. All quantum chemical calculations are performed using the Gaussian 09 software³².

The energies ($\Delta_R E^\circ$) and Gibbs free energies ($\Delta_R G^\circ$) of reactions are calculated 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 calculated using

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

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

In Eq. 1 and 3, the $E^\circ_{reactants}$, $E^\circ_{products}$, E°_{TS} refer to the energies (i.e. the sum of electronic energies and zero-point vibrational energies from the quantum-chemical calculations or, in other words, the internal energies U° at 0 K) of the reactants, products and transition states, respectively. The Gibbs free energies G° in Eq. 2 and 4 are related to the energy E° via $G^\circ = H^\circ - TS^\circ$ where H° and S° are the enthalpy and the entropy of the species, both derived from the partition function, which is a function of the geometry-optimized structures and vibrational frequencies from the quantum-chemical computations^{32,33}. T refers to the temperature considered. For a reaction involving gas phase species, the ground state energy refers to the energy when the gaseous species and the surface are placed at an infinite distance apart.

Reaction Rates. The conventional transition state theory (TST) is applied in the calculation of the reaction rate constants. Similar to our previous study ⁶, we used the modified rate equations from Reuter and Scheffler's work ³⁴.

We consider an etching reaction of the form $A(g) + B(ads) \rightarrow \text{products}$, where the etchant $A(g)$ reacts with the adsorbed species $B(ads)$ and thereby either directly removes the whole or part of B from the surface, or transforms it into another species, that is removed in subsequent reaction or etching steps. Likewise $A(g)$ may initially be adsorbed and later (in whole or in part) be removed. The etching rate (R_{etch}) of a reaction, $A(g) + B(ads) \rightarrow \text{product}$, in the unit of molecule sites⁻¹ s⁻¹ is calculated using conventional transition state theory (TST),

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

Here A_s and Θ_B are the surface area per site and the surface fraction of $B(ads)$ respectively. $\Delta_{TS} E^\circ$ is the activation energy of the etching reaction at 0 K. Φ_A is the impingement rate of the etching gas A ,

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

where γ_A and m_A refer to the mole fraction and mass of the etching gas A . p is the total pressure and k_B and T are the Boltzmann constant and the temperature. The factor f_{etch} in Eq. 5 is derived from the partition functions using

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

In Eq. 7, following Reuter and Scheffler's work ³⁴ the partition function related to a surface species contains only the vibrational and electronic parts. This applies to q^{TS} of the transition state and

q^{surf} of a surface species. On the other hand, the partition of the gas, q^{gas} , includes all the degrees of freedom except the translation along the reaction coordinate. In Eq. 7, q^{gas} is separated into q_{int}^{gas} , which contains the vibrational, rotational and electronic parts, and $q_{2D-Trans}^{gas} = A_s \cdot 2\pi m_A k_B T / h^2$, which refers to the 2-dimensional, translational part of the partition function. A_s is assumed equal to the area per site of the surface species.

The reverse of the etching reaction can be written as $A(ads) \rightarrow \text{product}$. The reaction rate (R_{rev}) in the unit of molecule sites⁻¹ s⁻¹ is calculated using

$$R_{rev} = f_{rev} \left(\frac{k_B T}{h} \right) \exp(-\Delta_{TS} E^\circ / k_B T) \cdot \Theta_A. \quad (8)$$

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

$$f_{rev} = q_{vib,el}^{TS} / q_{vib,el}^{surf}. \quad (9)$$

Here q^{surf} refers to the partition function of the surface adsorbed species, $A(ads)$. Similar to the Eq 7, the partition function of surface species contains only the vibrational and electronic parts.

Results and Discussion

1. Etching of $CH_3(ads)$, the 1st step of the growth

First, we consider etchings of $CH_3(ads)$, which is a representative of the etching process during the starting point of the growth. $CH_3(ads)$ is shown in Fig 1a and 2a. The energies at 0 K and the Gibbs free energies at 1600 °C of H_2 , H atoms and HCl etchings of $CH_3(ads)$ are summarized in Table 1.

H₂ etching of CH₃(ads),

occurs via the transition state shown in Fig. 2b. The process is thermodynamically favorable with negative $\Delta_R E^\circ$ (0 K) of -9 kJ/mol and $\Delta_R G^\circ$ (1600 °C) of -35 kJ/mol. However, the transition barrier height at 1600 °C is found to be relatively high, 574 kJ/mol. This is likely due to the relatively inert nature of H₂. This results in an extremely low etching rate constant at 1600 °C as shown in Table 2.

H atom etching of CH₃(ads) can produce two possible sets of products depending on the position where the H atom is to be incorporated,

where $*(\text{ads})$ refers to a surface site terminated by a surface dangling bond. In Figure 2c and 2d, we show the transition state structures for reactions R2a and R2b, respectively. From thermodynamic point of view, both processes are favorable with negative $\Delta_R G^\circ$ at 1600 °C. The transition barriers (317 kJ/mol for R2a and 311 kJ/mol for R2b at 1600 °C) are only half the size of H₂ etching reaction, R1 (574 kJ/mol). As a result, the etching rate constants of R2a and R2b are $\sim 10^7$ times larger than H₂ etching, R1.

HCl etching of CH₃(ads) can produce two sets of products depending on the positions where the H and Cl atoms are to be incorporated,

The transition states of R3a and R3b are shown in Fig. 2e and 2f, respectively. Reaction R3a is thermodynamically favorable with $\Delta_R E^\circ$ (0 K) and $\Delta_R G^\circ$ (1600 °C) of -106 and -94 kJ/mol and occurs with a transition barrier of 464 kJ/mol at 1600 °C. This results in the rate constant which is $\sim 10^3$ time faster than H_2 etching (R1) but $\sim 10^4$ time slower than H atom etching (R2a and R2b). Reaction R3b, on the other hand, is thermodynamically unfavorable at 1600 °C with $\Delta_R G^\circ$ of 50 kJ/mol. The process also produces a large transition barrier (708 kJ/mol) at 1600 °C resulting in a rate constant which is $\sim 10^7$ time slower than the first process.

From the results in this section, it is clear that even though most of these processes are favorable thermodynamically, they are all limited by kinetics especially for H_2 and HCl etching. From the three etchants studied, it is evident that H atoms are the most successful etchant on $\text{CH}_3(\text{ads})$ and that $\text{CH}_3(\text{ads})$ is not susceptible to H_2 and HCl etchings. Whether this conclusion is still valid for other carbon groups on the surface will be left for further investigations.

It is worth noting that adsorptions of CH_3 gas on the surface site with a dangling bond occur with $\Delta_R G^\circ$ of -33 kJ/mol at 1600 °C without any transition state ⁶. It is likely, as a result, that the sticking coefficient of CH_3 gas on the surface is close to 1.0. Here we define the sticking coefficient as the probability (from 0 to 1) that the gaseous species will stick on the surface per strike. Therefore, if we assume the sticking coefficient CH_3 gas to be 1.0 and use the surface areas per site of SiC of $8.178 \times 10^{-20} \text{ m}^2$, we will obtain the adsorption rate of CH_3 gas to be $\sim 10^3 \cdot p \gamma_g \Theta_s$ molecule per site per second. Here, the unit of the pressure (p) is in pascal, and the gaseous molar fraction (γ_g) and the surface fraction (Θ_s) are unitless. From Table 2, we see that the etching rates of H atoms on $\text{CH}_3(\text{ads})$ via R2a and R2b are $\sim 1 \cdot p \gamma_g \Theta_s$. As a result, unless the gas phase concentration of

H atoms is much larger ($>10^3$) than that of CH_3 radicals, the etching rates will be much lower than the adsorption and a significant amount of $\text{CH}_3(\text{ads})$ likely survives the etchings.

a)

b)

c)

d)

e)

f)

Figure 2 Structures of a) $\text{CH}_3(\text{ads})$, b) transition state of $\text{H}_2(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{CH}_4(\text{g}) + \text{H}(\text{ads})$, c) transition state of $\text{H}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{ads})$, d) transition state of $\text{H}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{CH}_4(\text{g}) + *(\text{ads})$, e) transition state of $\text{HCl}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{CH}_4(\text{g}) + \text{Cl}(\text{ads})$ and f) transition state of $\text{HCl}(\text{g}) + \text{CH}_3(\text{ads}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{H}(\text{ads})$.

Table 1 The energies at 0 K and standard Gibbs free energies at 1600 °C in the unit of kJ/mol of etching reactions by H_2 , H atoms and HCl. Here $*(\text{ads})$ refers to a surface site terminated by a surface dangling bond.

		0 K		1600 °C	
		$\Delta_R E^\circ$	$\Delta_{TS} E^\circ$	$\Delta_R G^\circ$	$\Delta_{TS} G^\circ$
Etching of $\text{CH}_3(\text{ads})$					
R1	$\text{CH}_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}(\text{ads})$	-9	354	-35	574
R2a	$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + *(\text{ads})$	-73	146	-135	317
R2b	$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{ads})$	-6	116	-93	311
R3a	$\text{CH}_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{Cl}(\text{ads})$	-106	227	-94	464
R3b	$\text{CH}_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{H}(\text{ads})$	76	521	50	708
Etching of $\text{SiH}_3\text{-CH}_2(\text{ads})$					
R4	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_3(\text{ads})$	-17	309	-62	514
R5a	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3(\text{g}) + \text{CH}_3(\text{ads})$	-57	124	-114	285
R5b	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2(\text{ads})$	-41	59	-104	245
R6a	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_3\text{Cl}(\text{g}) + \text{CH}_3(\text{ads})$	-89	159	-131	410
R6b	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2\text{Cl}(\text{ads})$	84	428	70	652
Etching of $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$					
R7	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	16	321	195	547
R8a	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	-58	151	83	326
R8b	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2(\text{ads})$	-10	72	123	265

R9a	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{HCl(g)} \rightarrow \text{SiH}_2\text{Cl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	-65	179	143	430
R9b	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{HCl(g)} \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2\text{Cl(ads)}$	112	432	334	687
Etching of SiH-(CH₂)₃(ads)					
R10	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	34	326	223	532
R11a	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{SiH-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	-29	155	84	329
R11b	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H(g)} \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_2(\text{ads})$	-5	75	120	247
R12a	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)} \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	-59	171	157	426
R12b	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl(g)} \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_2\text{Cl(ads)}$	134	469	359	704

Table 2 The forward and reverse rate constants of etching reactions by H₂, H atoms and HCl.

		Forward rate constants	Reverse rate constants
Etching of CH₃(ads)			
R1	$\text{CH}_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H(ads)}$	$4 \times 10^{-8} \text{ a)}$	$4 \times 10^{-9} \text{ a)}$
R2a	$\text{CH}_3(\text{ads}) + \text{H(g)} \rightarrow \text{CH}_4(\text{g}) + \text{* (ads)}$	$6 \times 10^{-1} \text{ a)}$	$1 \times 10^{-4} \text{ a)}$
R2b	$\text{CH}_3(\text{ads}) + \text{H(g)} \rightarrow \text{CH}_3(\text{g}) + \text{H(ads)}$	$8 \times 10^{-1} \text{ a)}$	$2 \times 10^{-3} \text{ a)}$
R3a	$\text{CH}_3(\text{ads}) + \text{HCl(g)} \rightarrow \text{CH}_4(\text{g}) + \text{Cl(ads)}$	$4 \times 10^{-5} \text{ a)}$	$1 \times 10^{-7} \text{ a)}$
R3b	$\text{CH}_3(\text{ads}) + \text{HCl(g)} \rightarrow \text{CH}_3\text{Cl(g)} + \text{H(ads)}$	$6 \times 10^{-12} \text{ a)}$	$1 \times 10^{-10} \text{ a)}$
Etching of SiH₃-CH₂(ads)			
R4	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_3(\text{ads})$	$2 \times 10^{-6} \text{ a)}$	$3 \times 10^{-8} \text{ a)}$
R5a	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H(g)} \rightarrow \text{SiH}_3(\text{g}) + \text{CH}_3(\text{ads})$	4 a)	$2 \times 10^{-3} \text{ a)}$
R5b	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H(g)} \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2(\text{ads})$	$6 \times 10^1 \text{ a)}$	$6 \times 10^{-2} \text{ a)}$
R6a	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{HCl(g)} \rightarrow \text{SiH}_3\text{Cl(g)} + \text{CH}_3(\text{ads})$	$1 \times 10^{-3} \text{ a)}$	$2 \times 10^{-7} \text{ a)}$
R6b	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{HCl(g)} \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2\text{Cl(ads)}$	$2 \times 10^{-10} \text{ a)}$	$2 \times 10^{-8} \text{ a)}$
Etching of SiH₂-(CH₂)₂(ads)			

R7	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	$4 \times 10^{-7} \text{ }^{\text{a)}}$	$6 \times 10^3 \text{ }^{\text{b)}}$
R8a	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	$6 \times 10^{-1} \text{ }^{\text{a)}}$	$6 \times 10^6 \text{ }^{\text{b)}}$
R8b	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2(\text{ads})$	$3 \times 10^1 \text{ }^{\text{a)}}$	$4 \times 10^9 \text{ }^{\text{b)}}$
R9a	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_2\text{Cl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	$7 \times 10^{-4} \text{ }^{\text{a)}}$	$4 \times 10^5 \text{ }^{\text{b)}}$
R9b	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$	$4 \times 10^{-11} \text{ }^{\text{a)}}$	$6 \times 10^3 \text{ }^{\text{b)}}$
Etching of SiH-(CH₂)₃(ads)			
R10	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	$2 \times 10^{-6} \text{ }^{\text{a)}}$	$1 \times 10^5 \text{ }^{\text{b)}}$
R11a	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	$3 \times 10^{-1} \text{ }^{\text{a)}}$	$6 \times 10^6 \text{ }^{\text{b)}}$
R11b	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_2(\text{ads})$	$5 \times 10^1 \text{ }^{\text{a)}}$	$1 \times 10^{10} \text{ }^{\text{b)}}$
R12a	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	$1 \times 10^{-3} \text{ }^{\text{a)}}$	$1 \times 10^6 \text{ }^{\text{b)}}$
R12b	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$	$2 \times 10^{-11} \text{ }^{\text{a)}}$	$9 \times 10^3 \text{ }^{\text{b)}}$

^{a)} Calculated using Eq. 5-7. 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 areas per site of $\text{CH}_3(\text{ads})$ and $\text{SiH}_n\text{X}_m\text{-CH}_2(\text{ads})$ are 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, representing the areas per two and three lattice sites on the Si-face of 4H-SiC.

^{b)} Calculated using Eq. 8-9. 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.

2. Etching of $\text{SiH}_3\text{-CH}_2(\text{ads})$, the 2nd step of the growth

In the second step of the growth, we assume that a Si-species is successfully bonded with the surface C-group. The simplest product of this step is thus a species containing only one Si and C atoms. From the H-rich atmosphere of the CVD, we assume further that the dangling bonds of the surface species are fully saturated by hydrogen atoms. As a result, we arrive at $\text{SiH}_3\text{-CH}_2(\text{ads})$ as a representative of this growth step, as shown in Fig. 1a and 3a. The energies at 0 K and Gibbs free energies at 1600 °C of etching reactions by H_2 , H atoms and HCl are summarized in Table 1.

H_2 etching of $\text{SiH}_3\text{-CH}_2(\text{ads})$,

occurs via the transition state shown in Fig. 3b. From a thermodynamic point of view, this process is favorable with $\Delta_R E^\circ$ of -17 kJ/mol at 0 K and $\Delta_R G^\circ$ of -63 kJ/mol at 1600 °C. However, similar to H_2 etching of $\text{CH}_3(\text{ads})$ in reaction R1, the transition barrier of R4 is relatively large (514 kJ/mol) at 1600 °C. The forward rate constant of R4 shown in Table 2, despite being $\sim 10^2$ time faster than that of R1, is still much slower than that of H atoms etchings as to be discussed below.

H atom etching of $\text{SiH}_3\text{-CH}_2(\text{ads})$ can produce two different products as follows,

R5a and R5b occur via the transition states shown in Fig. 3c and 3d respectively. Both processes are thermodynamically favorable at 1600 °C, with $\Delta_R G^\circ$ of -114 and -104 kJ/mol. The transition barrier of R5a (285 kJ/mol) is slightly larger than that of R5b (245 kJ/mol). Both are only half the size of the barrier of R4. Thus, the etching rate constants from H atoms are $\sim 10^6$ - 10^7 time faster

than H₂. In comparison to H atom etching of CH₃(ads), these etching rate constants are ~10² time faster suggesting that SiH₃-CH₂(ads) is more vulnerable to H atom etchings than CH₃(ads).

HCl etching of SiH₃-CH₂(ads) can produce two sets of products,

The transition states of R6a and R6b are shown in Fig. 3e and 3f respectively. From a thermodynamic perspective, only R6a is favorable 1600 °C with negative $\Delta_R G^\circ$ of -131 kJ/mol. We find the transition barrier to be 410 kJ/mol at 1600 °C. The reaction R6b is thermodynamically unfavorable at 1600 °C with positive $\Delta_R G^\circ$ of 70 kJ/mol and a much larger transition barrier (652 kJ/mol) at 1600 °C. As a result, R6a is ~10³ time faster than H₂ etching R4, but ~10⁴ time slower than H atom etchings, R5a and R5b. In comparison to HCl etching of CH₃(ads), etching reactions R6a and R6b are ~10² time faster, which again suggests that SiH₃-CH₂(ads) is more vulnerable to etchings than CH₃(ads).

In conclusion, etching of SiH₃-CH₂(ads) occurs most effectively by H atoms. We have also noted that the etching rate constants are ~100 times larger than that on CH₃(ads). As a result, SiH₃-CH₂(ads) is much more susceptible to etching than CH₃(ads). In addition, in our previous work ⁷ we show that adsorptions of SiH and SiH₂ gases on CH₃(ads) and CH₂(ads) surface sites all occur with positive $\Delta_R G^\circ$ at 1600 °C meaning that these adsorptions are thermodynamically less favorable than their reverses or desorptions. This plus the fact that SiH₃-CH₂(ads) is 100 times more susceptible to H atom etching implies that this step of the growth is more critical than the first.

a)

b)

c)

d)

Figure 3 Structures of a) $\text{SiH}_3\text{-CH}_2(\text{ads})$, b) transition state of $\text{H}_2(\text{g}) + \text{SiH}_3\text{-CH}_2(\text{ads}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_3(\text{ads})$, c) transition state of $\text{H}(\text{g}) + \text{SiH}_3\text{-CH}_2(\text{ads}) \rightarrow \text{SiH}_3(\text{g}) + \text{CH}_3(\text{ads})$, d) transition state of $\text{H}(\text{g}) + \text{SiH}_3\text{-CH}_2(\text{ads}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2(\text{ads})$, e) transition state of $\text{HCl}(\text{g}) + \text{SiH}_3\text{-CH}_2(\text{ads}) \rightarrow \text{SiH}_3\text{Cl}(\text{g}) + \text{CH}_3(\text{ads})$, and f) transition state of $\text{HCl}(\text{g}) + \text{SiH}_3\text{-CH}_2(\text{ads}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2\text{Cl}(\text{ads})$,

3. Etching of $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$, the 3rd step of the growth

In this step of the growth, we assume that the surface group from the previous step, $\text{SiH}_3\text{-CH}_2(\text{ads})$, forms another Si-C bond with an adjacent $\text{CH}_3(\text{ads})$ and produces $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$, shown in Fig 1a and 4a. The energies and Gibbs free energies of etching of $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$ by H_2 , H atoms and HCl are summarized in Table 1.

H_2 etching of $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$,

occurs with the transition state shown in Fig. 4b. The transition barrier at 1600 °C is 547 kJ/mol. This produces an etching rate constant of roughly the same magnitude compared to H₂ etching of CH₃(ads) and SiH₃-CH₂(ads) at 1600 °C as shown in Table 2. However, unlike reactions R1 and R4, R7 is thermodynamically much less favorable than its reverse with $\Delta_R G^\circ$ at 1600 °C of 195 kJ/mol. This results in the forward rate constant which is $\sim 10^{10}$ time slower than its reverse indicating that H₂ etching of SiH₂-(CH₂)₂(ads) via reaction R7 is highly unlikely.

H atom etching of SiH₂-(CH₂)₂(ads) can produce two different products as follows,

Reactions R8a and R8b occur via the transition states shown in Fig. 4c and 4d, with the barrier height for R8a slightly larger than R8b. The forward rate constants of R8a and R8b are roughly of the same magnitude as H atom etchings of CH₃(ads) and SiH₃-CH₂(ads). However, again the reactions R8a and R8b are thermodynamically less favorable than their reverses as the temperature rises toward 1600 °C, with $\Delta_R G^\circ$ of 83 and 123 kJ/mol respectively. As a result, at 1600 °C the reverse rate constants of both process are 10^7 - 10^8 time faster than the forward rate constants as shown in Table 2. This indicates that H atom etching of SiH₂-(CH₂)₂(ads) is unlikely.

HCl etching of SiH₂-(CH₂)₂(ads) can produce two different products,

The reactions R9a and R9b occur via the transition state structures shown in Fig. 4e and 4f. The transition barriers of R9a and R9b at 1600 °C are 430 and 687 kJ/mol. The rate constants of R9a and R9b are roughly the same magnitude compared to HCl etchings of CH₃(ads) and SiH₃-CH₂(ads) at 1600 °C as shown in Table 2. At 1600 °C, both R8a and R8b are thermodynamically much less favorable than their reverses, with $\Delta_R G^\circ$ of 143 and 334 kJ/mol respectively. The reverse rate constants are, as a result, 10⁹-10¹⁴ time faster than the forward rate constants as shown in Table 2. This again indicates that etching of SiH₂-(CH₂)₂(ads) is unlikely.

In conclusion, this section shows that at 1600 °C SiH₂-(CH₂)₂(ads) is not susceptible to any of the three etchants considered. From the previous section, we show that SiH₃-CH₂(ads) is susceptible to both H atom etchings and desorptions. It is thus clear that SiH₃-CH₂(ads) become more stable by forming an Si-C bond with an adjacent CH₃(ads) and producing SiH₂-(CH₂)₂(ads). This is in fact consistent with our previous study ⁷ where we show that SiH-CH₂(ads) and SiH₂-CH₂(ads) also become more stable by forming an Si-C bond with an adjacent CH₃(ads). This Si-C bond formation is shown to happen with the rates that are fast enough to compete with dissociative desorptions of SiH-CH₂(ads) and SiH₂-CH₂(ads) ⁷. These findings thus confirm the important of this growth step in stabilizing the surface species and causing the growth to proceed in the forward direction.

Figure 4 Structures of a) $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$, b) transition state of $\text{H}_2(\text{g}) + \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$, c) transition state of $\text{H}(\text{g}) + \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$, d) transition state of $\text{H}(\text{g}) + \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2(\text{ads})$, e)

transition state of $\text{HCl(g)} + \text{SiH}_2\text{-(CH}_2\text{)}_2\text{(ads)} \rightarrow \text{SiH}_2\text{Cl-CH}_2\text{(ads)} + \text{CH}_3\text{(ads)}$, and f) transition state of $\text{HCl(g)} + \text{SiH}_2\text{-(CH}_2\text{)}_2\text{(ads)} \rightarrow \text{SiH}_3\text{-CH}_2\text{(ads)} + \text{CH}_2\text{Cl(ads)}$. In these pictures, neighboring Si-C atoms have been removed to clearly show the transition state structures.

4. Etching of $\text{SiH-(CH}_2\text{)}_3\text{(ads)}$, the 4th step of the growth

In this fourth step, we assume that the surface group from the previous step, $\text{SiH}_2\text{-(CH}_2\text{)}_2\text{(ads)}$, has formed another Si-C bond with an adjacent $\text{CH}_3\text{(ads)}$ and produced a surface cluster, $\text{SiH-(CH}_2\text{)}_3\text{(ads)}$, shown in Fig 1a and 5a. This is the last step of the growth to be considered here. The energies and Gibbs free energies of etching reactions of $\text{SiH-(CH}_2\text{)}_3\text{(ads)}$ by H_2 , H atoms and HCl are summarized in Table 1.

H_2 etching of $\text{SiH-(CH}_2\text{)}_3\text{(ads)}$,

occurs via the transition structure shown in Fig. 5b. This creates a transition barrier of 532 kJ/mol at 1600 °C. This produces an etching rate constant of roughly the same magnitude compared to H_2 etching of $\text{CH}_3\text{(ads)}$, $\text{SiH}_3\text{-CH}_2\text{(ads)}$ and $\text{SiH}_2\text{-(CH}_2\text{)}_2\text{(ads)}$ at 1600 °C as shown in Table 2. However, reaction R10 is thermodynamically unfavorable at any temperatures considered here, with $\Delta_R E^\circ$ (0 K) and $\Delta_R G^\circ$ (1600 °C) of 34 and 223 kJ/mol. This results in the forward rate constant which is $\sim 10^{11}$ time slower than its reverse, indicating that the etching is highly unlikely.

H atom etching on $\text{SiH-(CH}_2\text{)}_3\text{(ads)}$ can produce two different products through

Reactions R11a and R11b occur via the transition structures shown in Fig. 5c and 5d, respectively. The transition barriers at 1600 °C of R11a and R11b are 329 and 247 kJ/mol respectively. The barriers produce the forward rate constants which are roughly of the same magnitude as H atom etchings of CH₃(ads), SiH₃-CH₂(ads) and SiH₂-(CH₂)₂(ads) at 1600 °C. However, as R11a and R11b are thermodynamically less favorable than their reverses, with $\Delta_R G^\circ$ of 83 and 123 kJ/mol respectively, their reverse rate constants of both process are 10⁹-10¹⁴ time faster than the forward rate constants, again indicating the etching processes to be unlikely.

HCl etching of SiH-(CH₂)₃(ads) can produce two different products,

Reactions R12a and R12b occur via the transition structures shown in Fig. 5e and 5f. The transition barriers at 1600 °C of R12a and R12b are 426 and 704 kJ/mol respectively. The barriers produce the forward rate constants roughly of the same magnitude as HCl etchings of CH₃(ads), SiH₃-CH₂(ads) and SiH₂-(CH₂)₂(ads) at 1600 °C. Reactions R11a and R11b are thermodynamically less favorable than their reverses, with $\Delta_R G^\circ$ of 157 and 359 kJ/mol respectively. The reverse rate constants are 10⁹-10¹⁴ time faster than the forward rate constants, again indicating that the etching processes are unlikely.

Thus similar to SiH₂-(CH₂)₂(ads), SiH-(CH₂)₃(ads) is not susceptible to any of the three etchants considered. This confirms the previous conclusion that the surface species become more stable by forming a larger cluster.

a)

b)

c)

d)

e)

f)

Figure 5 Structures of a) $\text{SiH}-(\text{CH}_2)_3(\text{ads})$, b) transition state of $\text{H}_2(\text{g}) + \text{SiH}-(\text{CH}_2)_3(\text{ads}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$, c) transition state of $\text{H}(\text{g}) + \text{SiH}-(\text{CH}_2)_3(\text{ads}) \rightarrow \text{SiH}-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$, d) transition state of $\text{H}(\text{g}) + \text{SiH}-(\text{CH}_2)_3(\text{ads}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_2(\text{ads})$, e) transition state of $\text{HCl}(\text{g}) + \text{SiH}-(\text{CH}_2)_3(\text{ads}) \rightarrow \text{SiHCl}-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$, and f) transition state of $\text{HCl}(\text{g}) + \text{SiH}-(\text{CH}_2)_3(\text{ads}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$,

5. Summary and Comparison to Experimental Findings

In the previous subsections, we showed that etching is most preferable on $\text{CH}_3(\text{ads})$ and $\text{SiH}_3\text{-CH}_2(\text{ads})$, which are the first and second steps of the growth, but etching of $\text{SiH}_2-(\text{CH}_2)_2(\text{ads})$ and $\text{SiH}-(\text{CH}_2)_3(\text{ads})$, which are the third and last steps of the growth, is thermodynamically unfavorable. This finding indicates that the surface species become more stable by forming more Si-C bonds with adjacent $\text{CH}_3(\text{ads})$ groups. Thus, bonding with an adjacent surface group helps stabilizing the growth species against etchings. It also implies that etching is unlikely to happen in the middle of a terrace where each surface species are fully bonded with the layer underneath. Rather, it suggests that etching is more likely to occur near the edges where the atoms hold fewer Si-C bonds with its neighbors, which agrees well with what usually observed experimentally.

Among the three etchants studied here, we show that H atoms are the most powerful etchant, followed by HCl and H_2 respectively. We noted that the etching by H atoms and HCl can produce two possible products, depending on whether the H atom is to be incorporated. For H atom etchings, it is apparent that the process can happen in both ways, with one being 1-100 times faster than the other. However, the situation is markedly different in the HCl etching where one of the

case is now highly dominant over the other. In this case, we show that it is almost certain that the H atom is to be bonded to the C species and the Cl atom to the Si species.

Figure 6 presents a complete etching pathway by $\text{H}_2(\text{g})$. It should be noted that such a scheme including also the H and HCl etchings is not as easy to illustrate due to the numerous reactions. Nevertheless, figure 6 presents a common trait observed in all three cases, i.e. etchings are most preferable at the 1st and 2nd steps of the growth but not on the 3rd and 4th step.

Interestingly, our $\Delta_{TS}G^\circ$ of H_2 etchings calculated at 1600 °C (514-574 kJ/mol) is close to the experimental activation energy (515 kJ/mol) reported by Kojima et al. who made measurements over the temperature range of 1500 – 1650 °C¹⁰. This experimental value was however reported for H_2 etching on the C face, and not on the Si face as in our study, although the authors stated that they observed a similar trend on the Si face. In addition, our results as well as the activation energy of 515 kJ/mol from Kojima et al. are both consistent with the activation energy required to decompose the hexagonal SiC crystal to C and Si, which was reported to be 466 ± 69 kJ/mol by R. N. Ghoshtagore³⁵. Thus our calculated data agrees well with experiments, and can be applied with reliability to SiC CVD modeling.

Figure 6 Reaction scheme of H_2 etching on 4H-SiC at 1600 °C. Etchings are preferable on the 1st and 2nd steps of the growth but not on the 3rd and 4th steps.

Conclusion

Density functional theory (B3LYP and M06-2X) and transition state theory are used to study etching reactions by H_2 , H atoms and HCl gases occurring on the surface of SiC during chemical vapor deposition (CVD). Four surface sites on the Si face of 4H-SiC, namely $\text{CH}_3(\text{ads})$, $\text{SiH}_3\text{-CH}_2(\text{ads})$, $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$, $\text{SiH-(CH}_2)_3(\text{ads})$, are chosen for the study. These surface sites represent four subsequent growth steps of 4H-SiC. On the first and second steps of the growth, represented by $\text{CH}_3(\text{ads})$ and $\text{SiH}_3\text{-CH}_2(\text{ads})$, we show that H atoms are the most successful etchant, while HCl and H_2 etchings, despite thermodynamically favorable, are shown to produce much slower etching rate constants and thereby limited by kinetics. Etchings of $\text{SiH}_3\text{-CH}_2(\text{ads})$ occur with the rate constants which are ~ 100 times larger than that of $\text{CH}_3(\text{ads})$. As a result, $\text{SiH}_3\text{-CH}_2(\text{ads})$ is less stable and more susceptible to etching than $\text{CH}_3(\text{ads})$. Etchings of third and fourth steps of the growth, $\text{SiH}_2\text{-(CH}_2)_2(\text{ads})$ and $\text{SiH-(CH}_2)_3(\text{ads})$, are shown to be thermodynamically unfavorable and produce the etching rate constants which are much smaller than that of their reverses. This suggests that the surface species become more stable by forming more Si-C bonds with adjacent $\text{CH}_3(\text{ads})$ and that this helps stabilizing the growth species against etchings.

Supporting Information

Gibbs free energies, 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>.

Corresponding Authors

*Emails: pitsu@ifm.liu.se and lars@ifm.liu.se.

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.

REFERENCES

- (1) Kimoto, T. Material Science and Device Physics in SiC Technology for High-Voltage Power Devices. *Jpn. J. Appl. Phys.* **2015**, *54*, 040103.
- (2) Castellazzi, A.; Fayyaz, A.; Romano, G.; Yang, L.; Riccio, M.; Irace, A. SiC Power MOSFETs Performance, Robustness and Technology Maturity. *Microelectron. Reliab.* **2016**, *58*, 164–176.
- (3) Phan, H. P.; Dao, D. V.; Nakamura, K.; Dimitrijević, S.; Nguyen, N. T. The Piezoresistive Effect of SiC for MEMS Sensors at High Temperatures: A Review. *J. Microelectromech. Syst.* **2015**, *24*, 1663–1677.
- (4) Pedersen, H.; Leone, S.; Kordina, O.; Henry, A.; Nishizawa, S.; Koshka, Y.; Janzén, E. Chloride-Based CVD Growth of Silicon Carbide for Electronic Applications. *Chem. Rev.* **2012**, *112*, 2434–2453.
- (5) Choy, K. L. Chemical Vapour Deposition of Coatings. *Prog. Mater. Sci.* **2003**, *48*, 57–170.
- (6) Sukkaew, P.; Danielsson, Ö.; Kordina, O.; Janzén, E.; Ojamäe, L. Ab Initio Study of Growth Mechanism of 4H-SiC: Adsorption and Surface Reaction of C₂H₂, C₂H₄, CH₄, and CH₃. *J. Phys. Chem. C* **2017**, *121*, 1249–1256.
- (7) Sukkaew, P.; Kalered, E.; Janzén, E.; Danielsson, Ö.; Ojamäe, L. Growth Mechanism of SiC CVD – Adsorption and Surface Reactions of Active Si Species. *J. Phys. Chem. C* **2018**, *122*, 648–661.
- (8) Hassan, J.; Bergman, J. P.; Henry, A.; Janzén, E. In-Situ Surface Preparation of Nominally on-Axis 4H-SiC Substrates. *J. Cryst. Growth* **2008**, *310*, 4430–4437.
- (9) Glass, S.; Reis, F.; Bauernfeind, M.; Aulbach, J.; Scholz, M. R.; Adler, F.; Dudy, L.; Li, G.; Claessen, R.; Schäfer, J. Atomic-Scale Mapping of Layer-by-Layer Hydrogen Etching and Passivation of SiC(0001) Substrates. *J. Phys. Chem. C* **2016**, *120*, 10361–10367.
- (10) Kojima, K.; Kuroda, S.; Okumura, H.; Arai, K. Effect of Additional Silane on In Situ H₂ Etching Prior to 4H-SiC Homoepitaxial Growth. *Mater. Sci. Forum* **2007**, *556–557*, 85–88.
- (11) Borovikov, V.; Zangwill, A. Step Bunching of Vicinal 6H-SiC{0001} Surfaces. *Phys. Rev. B* **2009**, *79* (24), 245413.
- (12) Longo, R. C.; Owen, J. H. G.; McDonnell, S.; Ballard, J. B.; Wallace, R. M.; Randall, J. N.; Chabal, Y. J.; Cho, K. Ab Initio Study of H₂ Associative Desorption on Ad-Dimer Reconstructed Si(001) and Ge(001)-(2×1) Surfaces. *J. Phys. Chem. C* **2014**, *118*, 10088–10096.

- (13) Cavallotti, C. Reactivity of Silicon Surfaces in the Presence of Adsorbed Hydrogen and Chlorine. *Chem. Vap. Deposition* **2010**, *16*, 329–335.
- (14) Brenig, W.; Pehlke, E. Reaction Dynamics of H₂ on Si. Ab Initio Supported Model Calculations. *Prog. Surf. Sci.* **2008**, *83*, 263–336.
- (15) Dürr, M.; Höfer, U. Dissociative Adsorption of Molecular Hydrogen on Silicon Surfaces. *Surf. Sci. Rep.* **2006**, *61*, 465–526.
- (16) Peng, X.; Krüger, P.; Pollmann, J. Adsorption Processes of Hydrogen Molecules on SiC(001), Si(001) and C(001) Surfaces. *New J. Phys.* **2008**, *10* (12), 125028.
- (17) Kunioshi, N.; Anzai, K.; Ushijima, H.; Fuwa, A. Effects of Cluster Size on Calculation of Activation Energies of Silicon Surface Reactions with H₂ and HCl. *J. Cryst. Growth* **2015**, *418*, 115–119.
- (18) Pollmann, J.; Peng, X.; Wieferink, J.; Krüger, P. Adsorption of Hydrogen and Hydrocarbon Molecules on SiC(001). *Surf. Sci. Rep.* **2014**, *69*, 55–104.
- (19) Derycke, V.; Fonteneau, P.; Pham, N. P.; Soukiassian, P. Molecular-Hydrogen Interaction with β -SiC(100)3 $\times$ 2 and c (4 $\times$ 2) Surfaces and with Si Atomic Lines. *Phys. Rev. B* **2001**, *63*, 201305(R).
- (20) Trabada, D. G.; Flores, F.; Ortega, J. Hydrogenation of Semiconductor Surfaces: Si-Terminated Cubic SiC(100) Surfaces. *Phys. Rev. B* **2009**, *80*, 075307.
- (21) Deák, P.; Aradi, B.; Knaup, J. M.; Frauenheim, T. Hydrogen Adsorption and Etching on the Si-Rich 3C-SiC(001) 3 $\times$ 2 Surface: First-Principles Molecular Dynamics Calculations. *Phys. Rev. B* **2009**, *79*, 085314.
- (22) Wachowicz, E.; Kiejna, A. Structure and Energetics Changes during Hydrogenation of 4H-SiC{0001} Surfaces: A DFT Study. *J. Phys.: Condens. Matter* **2012**, *24*, 385801.
- (23) Seyller, T. Passivation of Hexagonal SiC Surfaces by Hydrogen Termination. *J. Phys.: Condens. Matter* **2004**, *16*, S1755-S1782.
- (24) Olander, J.; Larsson, K. M. E. An Ab Initio Study of 4H-SiC(0001) and (000 $\bar{1}$) Surface Processes at Experimental Temperatures. *Thin Solid Films* **2004**, *458*, 191–196.
- (25) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (26) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (27) Dunning, T. H.; Hay, P. J. Gaussian Basis Sets for Molecular Calculations. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Springer US: Boston, MA, 1977; pp 1–27.
- (28) Wadt, W. R.; Hay, P. J. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for Main Group Elements Na to Bi. *J. Chem. Phys.* **1985**, *82*, 284–298.
- (29) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (30) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (31) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

- (32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
- (33) McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Mill Valley, California, 2000.
- (34) Reuter, K.; Scheffler, M. First-Principles Kinetic Monte Carlo Simulations for Heterogeneous Catalysis: Application to the CO Oxidation at RuO₂. *Phys. Rev. B* **2006**, 73, 045433.
- (35) Ghoshtagore, R. N. Decomposition of Single Crystal Silicon Carbide. *Solid-State Electron.* **1966**, 9, 178–180.

TOC graphic

Supporting Information for

Growth Mechanism of SiC CVD – Surface Etching by H_2 , H Atoms and HCl

*Pitsiri Sukkaew**, *Örjan Danielsson* and *Lars Ojamäe**

Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

*Emails: pitsu@ifm.liu.se and lars@ifm.liu.se.

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	$\text{CH}_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}(\text{ads})$	1.052E-12	-8.051E-09	2.407E-05	-3.579E-02	-1.242E+01
R2a	$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + *(\text{ads})$	2.926E-13	-3.892E-09	1.993E-05	-5.741E-02	-7.493E+01
R2b	$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{ads})$	-5.827E-13	2.420E-09	2.471E-06	-5.446E-02	-8.666E+00
R3a	$\text{CH}_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{Cl}(\text{ads})$	4.451E-13	-3.502E-09	1.183E-05	-7.267E-03	-1.044E+02
R3b	$\text{CH}_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{H}(\text{ads})$	3.175E-13	-2.537E-09	8.588E-06	-2.119E-02	7.255E+01
R4	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_3(\text{ads})$	8.580E-13	-6.687E-09	2.054E-05	-4.269E-02	-2.120E+01
R5a	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3(\text{g}) + \text{CH}_3(\text{ads})$	3.241E-13	-4.593E-09	2.530E-05	-6.297E-02	-5.868E+01
R5b	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2(\text{ads})$	5.256E-14	-2.268E-09	1.746E-05	-5.723E-02	-4.390E+01
R6a	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_3\text{Cl}(\text{g}) + \text{CH}_3(\text{ads})$	-4.216E-15	-7.573E-10	5.837E-06	-2.875E-02	-9.213E+01
R6b	$\text{SiH}_3\text{-CH}_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2\text{Cl}(\text{ads})$	2.036E-13	-1.687E-09	6.238E-06	-1.410E-02	8.347E+01
R7	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	2.433E-12	-1.512E-08	3.014E-05	7.546E-02	1.770E+01
R8a	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2\text{-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	1.478E-12	-9.760E-09	2.311E-05	5.434E-02	-5.428E+01
R8b	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2(\text{ads})$	1.166E-12	-7.169E-09	1.479E-05	5.938E-02	-6.849E+00
R9a	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_2\text{Cl-CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	1.670E-12	-9.795E-09	1.666E-05	1.000E-01	-5.912E+01
R9b	$\text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_3\text{-CH}_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$	1.766E-12	-1.009E-08	1.576E-05	1.098E-01	1.178E+02
R10	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	2.621E-12	-1.640E-08	3.330E-05	7.798E-02	3.579E+01
R11a	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	1.375E-12	-9.180E-09	2.218E-05	4.084E-02	-2.678E+01
R11b	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2\text{-(CH}_2)_2(\text{ads}) + \text{CH}_2(\text{ads})$	1.155E-12	-7.212E-09	1.522E-05	5.465E-02	-2.166E+00
R12a	$\text{SiH-(CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiHCl-(CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	1.787E-12	-1.056E-08	1.851E-05	1.031E-01	-5.342E+01

R12b	SiH-(CH ₂) ₃ (ads) + HCl(g) → SiH ₂ -(CH ₂) ₂ (ads) + CH ₂ Cl(ads)	1.871E-12	-1.079E-08	1.753E-05	1.102E-01	1.391E+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	CH ₃ (ads) + H ₂ (g) → CH ₄ (g) + H(ads)	2.926E-12	-1.809E-08	3.746E-05	9.148E-02	3.536E+02
R2a	CH ₃ (ads) + H(g) → CH ₄ (g) + *(ads)	1.978E-12	-1.273E-08	3.013E-05	6.558E-02	1.474E+02
R2b	CH ₃ (ads) + H(g) → CH ₃ (g) + H(ads)	2.295E-12	-1.474E-08	3.526E-05	7.458E-02	1.165E+02
R3a	CH ₃ (ads) + HCl(g) → CH ₄ (g) + Cl(ads)	1.979E-12	-1.189E-08	2.329E-05	1.089E-01	2.323E+02
R3b	CH ₃ (ads) + HCl(g) → CH ₃ Cl(g) + H(ads)	6.593E-13	-2.704E-09	-5.936E-07	1.029E-01	5.272E+02
R4	SiH ₃ -CH ₂ (ads) + H ₂ (g) → SiH ₄ (g) + CH ₃ (ads)	2.857E-12	-1.767E-08	3.649E-05	8.436E-02	3.086E+02
R5a	SiH ₃ -CH ₂ (ads) + H(g) → SiH ₃ (g) + CH ₃ (ads)	1.802E-12	-1.139E-08	2.635E-05	6.409E-02	1.255E+02
R5b	SiH ₃ -CH ₂ (ads) + H(g) → SiH ₄ (g) + CH ₂ (ads)	1.971E-12	-1.251E-08	2.940E-05	7.448E-02	6.033E+01
R6a	SiH ₃ -CH ₂ (ads) + HCl(g) → SiH ₃ Cl(g) + CH ₃ (ads)	2.142E-12	-1.262E-08	2.383E-05	1.173E-01	1.636E+02
R6b	SiH ₃ -CH ₂ (ads) + HCl(g) → SiH ₄ (g) + CH ₂ Cl(ads)	1.298E-12	-6.825E-09	9.038E-06	1.158E-01	4.327E+02
R7	SiH ₂ -(CH ₂) ₂ (ads) + H ₂ (g) → SiH ₃ -CH ₂ (ads) + CH ₃ (ads)	3.123E-12	-1.927E-08	3.987E-05	9.298E-02	3.208E+02
R8a	SiH ₂ -(CH ₂) ₂ (ads) + H(g) → SiH ₂ - CH ₂ (ads) + CH ₃ (ads)	1.963E-12	-1.243E-08	2.873E-05	6.933E-02	1.530E+02
R8b	SiH ₂ -(CH ₂) ₂ (ads) + H(g) → SiH ₃ - CH ₂ (ads) + CH ₂ (ads)	2.178E-12	-1.401E-08	3.353E-05	7.433E-02	7.375E+01
R9a	SiH ₂ -(CH ₂) ₂ (ads) + HCl(g) → SiH ₂ Cl-CH ₂ (ads) + CH ₃ (ads)	2.189E-12	-1.310E-08	2.559E-05	1.147E-01	1.841E+02
R9b	SiH ₂ -(CH ₂) ₂ (ads) + HCl(g) → SiH ₃ -CH ₂ (ads) + CH ₂ Cl(ads)	1.787E-12	-1.012E-08	1.701E-05	1.256E-01	4.369E+02
R10	SiH-(CH ₂) ₃ (ads) + H ₂ (g) → SiH ₂ - (CH ₂) ₂ (ads) + CH ₃ (ads)	2.861E-12	-1.769E-08	3.652E-05	8.482E-02	3.261E+02

R11a	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	2.130E-12	-1.346E-08	3.077E-05	6.831E-02	1.556E+02
R11b	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_2(\text{ads})$	1.940E-12	-1.256E-08	3.035E-05	6.565E-02	7.649E+01
R12a	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiHCl}-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	2.316E-12	-1.418E-08	2.921E-05	1.131E-01	1.765E+02
R12b	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$	1.679E-12	-9.420E-09	1.562E-05	1.159E-01	4.736E+02

Table S3 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
R1	$\text{CH}_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}(\text{ads})$	-3.651	1.157	344.560	-17.477	2.762	353.525
R2a	$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + *(\text{ads})$	6.289	0.316	143.673	-16.140	2.718	211.613
R2b	$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{ads})$	4.915	0.266	111.212	-11.349	1.654	114.781
R3a	$\text{CH}_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{Cl}(\text{ads})$	-6.257	1.397	224.831	-13.400	2.418	326.663
R3b	$\text{CH}_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{H}(\text{ads})$	-10.843	2.433	519.369	-17.131	3.063	445.906
R4	$\text{SiH}_3-\text{CH}_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_3(\text{ads})$	-4.250	1.350	298.042	-16.486	2.592	317.823
R5a	$\text{SiH}_3-\text{CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3(\text{g}) + \text{CH}_3(\text{ads})$	5.255	0.529	121.383	-23.444	3.766	170.401
R5b	$\text{SiH}_3-\text{CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2(\text{ads})$	4.143	0.459	55.527	-20.412	3.115	90.899
R6a	$\text{SiH}_3-\text{CH}_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_3\text{Cl}(\text{g}) + \text{CH}_3(\text{ads})$	-9.669	1.704	153.929	-18.806	2.551	243.375
R6b	$\text{SiH}_3-\text{CH}_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_4(\text{g}) + \text{CH}_2\text{Cl}(\text{ads})$	-11.177	2.144	424.431	-16.304	2.701	339.764
R7	$\text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_3-\text{CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	-4.764	1.328	309.659	22.740	0.717	302.122
R8a	$\text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2-\text{CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	4.624	0.582	147.799	22.157	0.897	206.430
R8b	$\text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_3-\text{CH}_2(\text{ads}) + \text{CH}_2(\text{ads})$	5.465	0.314	68.559	26.299	0.139	80.055
R9a	$\text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_2\text{Cl}-\text{CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	-7.897	1.572	174.703	24.374	0.549	243.134
R9b	$\text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_3-\text{CH}_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$	-11.540	2.010	427.308	24.036	0.681	320.086

R10	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{H}_2(\text{g}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	-3.174	1.347	315.582	24.110	0.798	290.510
R11a	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	3.726	0.601	149.913	19.628	0.997	180.329
R11b	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_2(\text{ads})$	6.029	0.331	72.049	26.551	0.220	78.588
R12a	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiHCl}-(\text{CH}_2)_2(\text{ads}) + \text{CH}_3(\text{ads})$	-6.022	1.342	167.321	26.110	0.359	230.330
R12b	$\text{SiH}-(\text{CH}_2)_3(\text{ads}) + \text{HCl}(\text{g}) \rightarrow \text{SiH}_2-(\text{CH}_2)_2(\text{ads}) + \text{CH}_2\text{Cl}(\text{ads})$	-9.360	1.951	464.763	25.615	0.678	336.471

Table S4 Molecular Coordinates in Z-matrix form

$\text{CH}_3(\text{ads})$

H						
Si	1	B1				
Si	2	B2	1	A1		
H	3	B3	2	A2	1	D1
C	2	B4	1	A3	3	D2
C	2	B5	1	A4	5	D3
C	3	B6	2	A5	1	D4
H	7	B7	3	A6	2	D5
H	5	B8	2	A7	1	D6
H	5	B9	2	A8	1	D7
H	7	B10	3	A9	2	D8
H	6	B11	2	A10	1	D9
Si	5	B12	2	A11	1	D10
Si	7	B13	3	A12	2	D11
Si	6	B14	2	A13	1	D12
C	13	B15	5	A14	2	D13
C	15	B16	6	A15	2	D14
C	15	B17	6	A16	2	D15
C	14	B18	7	A17	3	D16
H	16	B19	13	A18	5	D17
H	19	B20	14	A19	7	D18
H	16	B21	13	A20	5	D19
H	17	B22	15	A21	6	D20
H	18	B23	15	A22	6	D21
H	19	B24	14	A23	7	D22
Si	16	B25	13	A24	5	D23
Si	17	B26	15	A25	6	D24
Si	18	B27	15	A26	6	D25
Si	19	B28	14	A27	7	D26
H	26	B29	16	A28	13	D27
H	29	B30	19	A29	14	D28
H	27	B31	17	A30	15	D29
H	28	B32	18	A31	15	D30
H	28	B33	18	A32	15	D31
C	28	B34	18	A33	15	D32
C	29	B35	19	A34	14	D33

C	26	B36	16	A35	13	D34
Si	36	B37	29	A36	19	D35
Si	37	B38	26	A37	16	D36
Si	35	B39	28	A38	18	D37
H	38	B40	36	A39	29	D38
H	39	B41	37	A40	26	D39
C	38	B42	36	A41	29	D40
C	39	B43	37	A42	26	D41
H	43	B44	38	A43	36	D42
H	44	B45	39	A44	37	D43
H	44	B46	39	A45	37	D44
H	43	B47	38	A46	36	D45
Si	28	B48	18	A47	15	D46
Si	15	B49	6	A48	2	D47
Si	27	B50	17	A49	15	D48
Si	51	B51	27	A50	17	D49
Si	49	B52	28	A51	18	D50
Si	52	B53	51	A52	27	D51
Si	49	B54	28	A53	18	D52
Si	53	B55	49	A54	28	D53
Si	55	B56	49	A55	28	D54
Si	54	B57	52	A56	51	D55
Si	57	B58	55	A57	49	D56
Si	56	B59	53	A58	49	D57
C	54	B60	52	A59	51	D58
C	55	B61	49	A60	28	D59
C	56	B62	53	A61	49	D60
C	58	B63	54	A62	52	D61
C	60	B64	56	A63	53	D62
C	58	B65	54	A64	52	D63
C	54	B66	52	A65	51	D64
C	53	B67	49	A66	28	D65
C	56	B68	53	A67	49	D66
C	55	B69	49	A68	28	D67
C	52	B70	51	A69	27	D68
C	57	B71	55	A70	49	D69
H	49	B72	28	A71	18	D70
H	50	B73	15	A72	6	D71
H	51	B74	27	A73	17	D72
H	52	B75	51	A74	27	D73
H	53	B76	49	A75	28	D74
H	54	B77	52	A76	51	D75
H	55	B78	49	A77	28	D76
H	56	B79	53	A78	49	D77
H	57	B80	55	A79	49	D78
H	67	B81	54	A80	52	D79
H	69	B82	56	A81	53	D80
H	68	B83	53	A82	49	D81
H	70	B84	55	A83	49	D82
H	72	B85	57	A84	55	D83
H	71	B86	52	A85	51	D84
H	52	B87	51	A86	27	D85

H	57	B88	55	A87	49	D86
H	55	B89	49	A88	28	D87
H	54	B90	52	A89	51	D88
H	56	B91	53	A90	49	D89
H	53	B92	49	A91	28	D90
C	59	B93	57	A92	55	D91
H	94	B94	59	A93	57	D92
H	94	B95	59	A94	57	D93
H	58	B96	54	A95	52	D94
H	60	B97	56	A96	53	D95
H	94	B98	59	A97	57	D96

B1	1.4919325
B2	3.1543471
B3	1.4919333
B4	1.9021379
B5	1.9098387
B6	1.9021373
B7	1.0993573
B8	1.0993583
B9	1.1004839
B10	1.1004846
B11	1.1029646
B12	1.9034846
B13	1.9034901
B14	1.9189440
B15	1.9031319
B16	1.9084116
B17	1.9084139
B18	1.9031328
B19	1.0993411
B20	1.0993426
B21	1.1004909
B22	1.1042187
B23	1.1042187
B24	1.1004898
B25	1.9021293
B26	1.9112126
B27	1.9112131
B28	1.9021314
B29	1.4920279
B30	1.4920265
B31	2.4811811
B32	2.4767624
B33	2.4811840
B34	1.9064993
B35	1.9089740
B36	1.9089786
B37	1.9093208
B38	1.9093222
B39	1.9132713

B40	1.4920114
B41	1.4920123
B42	1.9008211
B43	1.9008217
B44	1.1005613
B45	1.1005610
B46	1.0990006
B47	1.0990000
B48	3.1319546
B49	3.1402170
B50	3.1319536
B51	3.1235216
B52	3.1235189
B53	3.1213690
B54	3.1415474
B55	3.1213758
B56	3.1307271
B57	3.1137512
B58	3.1348474
B59	3.1137481
B60	1.9102005
B61	1.9113946
B62	1.9102007
B63	1.9150719
B64	1.9150706
B65	1.9158306
B66	1.9049275
B67	1.9047881
B68	1.9049291
B69	1.9059308
B70	1.9047896
B71	1.9059309
B72	1.4903197
B73	1.4908871
B74	1.4903193
B75	1.4895646
B76	1.4895655
B77	1.4893714
B78	1.4886434
B79	1.4893714
B80	1.4886446
B81	1.1011678
B82	1.1011671
B83	1.1012180
B84	1.1012544
B85	1.1012542
B86	1.1012189
B87	1.4908119
B88	1.4908117
B89	1.4908104
B90	1.4908379
B91	1.4908375

B92	1.4908106
B93	1.8992727
B94	1.0954851
B95	1.0954860
B96	1.4909321
B97	1.4909319
B98	1.0957292
A1	89.7071888
A2	89.7069214
A3	111.2721293
A4	110.3623182
A5	142.5255649
A6	110.6601769
A7	110.6597925
A8	109.1537485
A9	109.1538996
A10	108.3064824
A11	111.6015898
A12	111.6016322
A13	110.6922674
A14	112.1692649
A15	111.2996738
A16	111.2997116
A17	112.1688868
A18	110.1973316
A19	110.1974030
A20	108.3104717
A21	107.7115402
A22	107.7113778
A23	108.3105414
A24	111.5489360
A25	111.2381622
A26	111.2381004
A27	111.5485779
A28	111.1864193
A29	111.1865507
A30	97.7556710
A31	98.0404668
A32	97.7555352
A33	111.0626108
A34	108.4296973
A35	108.4295799
A36	111.4355286
A37	111.4359120
A38	111.3153592
A39	110.4643148
A40	110.4640489
A41	108.2169691
A42	108.2174403
A43	109.2046992
A44	109.2050461
A45	110.7413939

A46	110.7414230
A47	121.6839523
A48	72.8194725
A49	121.6839423
A50	90.2642460
A51	90.2642717
A52	120.4183678
A53	90.1270035
A54	120.4182787
A55	120.1882366
A56	59.9578120
A57	60.0435772
A58	59.9578933
A59	35.2215768
A60	90.3834261
A61	35.2214764
A62	145.8600212
A63	145.8597789
A64	90.3277507
A65	143.6776193
A66	35.0948352
A67	143.6777180
A68	34.6541262
A69	35.0949235
A70	143.4930117
A71	145.9701337
A72	145.1638033
A73	145.9697845
A74	89.2631709
A75	89.2632811
A76	89.7627246
A77	90.8249356
A78	89.7627803
A79	90.6747680
A80	108.1918145
A81	108.1919807
A82	108.1610108
A83	108.1070400
A84	108.1071780
A85	108.1612625
A86	145.6878671
A87	89.9906350
A88	145.1387520
A89	90.2564355
A90	90.2565379
A91	145.6878025
A92	90.4591107
A93	111.4364968
A94	111.4370075
A95	87.5612444
A96	87.5615540
A97	110.7617791

D1	0.0000000
D2	-148.1755829
D3	120.1535006
D4	-126.1321382
D5	173.7537150
D6	-53.8306221
D7	63.4382394
D8	56.4843115
D9	-62.5629524
D10	-176.8272240
D11	-63.2498490
D12	179.9963704
D13	179.8558804
D14	55.7254077
D15	-179.6793220
D16	-179.8561430
D17	-56.6090461
D18	56.6090518
D19	59.9060485
D20	62.6807630
D21	-62.6812683
D22	-59.9062058
D23	-179.8463094
D24	-179.9071843
D25	179.9072076
D26	179.8462907
D27	176.9256111
D28	-176.9256810
D29	-157.1361466
D30	77.8185125
D31	157.1359452
D32	55.5486273
D33	61.5140512
D34	-61.5142533
D35	178.3320573
D36	-178.3322628
D37	179.4506906
D38	-56.2903874
D39	56.2905596
D40	-178.4028369
D41	178.4029821
D42	57.6190070
D43	-57.6193993
D44	-174.9392040
D45	174.9385775
D46	-98.4017152
D47	-61.9769821
D48	98.4013209
D49	13.6257944
D50	-13.6255173
D51	-54.4463601
D52	165.3644100

D53	54.4461666
D54	-54.4291937
D55	0.4179598
D56	-0.7061206
D57	-0.4178114
D58	37.1099667
D59	-35.0922809
D60	-37.1095886
D61	32.8796368
D62	-32.8796929
D63	161.6425217
D64	36.3185856
D65	-87.8398816
D66	-36.3187538
D67	88.1110346
D68	87.8400640
D69	35.5442189
D70	75.0079389
D71	180.0000000
D72	-75.0080373
D73	-143.8576882
D74	143.8580881
D75	-89.1472756
D76	-145.6896846
D77	89.1472912
D78	-91.3460690
D79	179.7484064
D80	-179.7481751
D81	-117.3254504
D82	117.6908428
D83	-179.7809568
D84	117.3255531
D85	95.1158762
D86	161.6585984
D87	92.1653230
D88	163.3214804
D89	-163.3212587
D90	-95.1152772
D91	-90.2649765
D92	-30.2705224
D93	90.1929784
D94	-89.4524059
D95	89.4529637
D96	-150.0387421

SiH₃-CH₂(ads)

H						
Si	1	B1				
Si	2	B2	1	A1		
H	3	B3	2	A2	1	D1

C	2	B4	1	A3	3	D2
C	3	B5	2	A4	1	D3
C	3	B6	2	A5	1	D4
H	7	B7	3	A6	2	D5
H	5	B8	2	A7	1	D6
H	5	B9	2	A8	1	D7
H	7	B10	3	A9	2	D8
H	6	B11	3	A10	2	D9
Si	5	B12	2	A11	1	D10
Si	7	B13	3	A12	2	D11
Si	6	B14	3	A13	2	D12
C	13	B15	5	A14	2	D13
C	15	B16	6	A15	3	D14
C	15	B17	6	A16	3	D15
C	14	B18	7	A17	3	D16
H	16	B19	13	A18	5	D17
H	19	B20	14	A19	7	D18
H	16	B21	13	A20	5	D19
H	17	B22	15	A21	6	D20
H	18	B23	15	A22	6	D21
H	19	B24	14	A23	7	D22
Si	16	B25	13	A24	5	D23
Si	17	B26	15	A25	6	D24
Si	18	B27	15	A26	6	D25
Si	19	B28	14	A27	7	D26
H	26	B29	16	A28	13	D27
H	29	B30	19	A29	14	D28
H	27	B31	17	A30	15	D29
H	28	B32	18	A31	15	D30
H	28	B33	18	A32	15	D31
C	28	B34	18	A33	15	D32
C	29	B35	19	A34	14	D33
C	26	B36	16	A35	13	D34
Si	36	B37	29	A36	19	D35
Si	37	B38	26	A37	16	D36
Si	35	B39	28	A38	18	D37
H	38	B40	36	A39	29	D38
H	39	B41	37	A40	26	D39
C	38	B42	36	A41	29	D40
C	39	B43	37	A42	26	D41
H	43	B44	38	A43	36	D42
H	44	B45	39	A44	37	D43
H	44	B46	39	A45	37	D44
H	43	B47	38	A46	36	D45
Si	28	B48	18	A47	15	D46
Si	15	B49	6	A48	3	D47
Si	27	B50	17	A49	15	D48
Si	51	B51	27	A50	17	D49
Si	49	B52	28	A51	18	D50
Si	52	B53	51	A52	27	D51
Si	40	B54	35	A53	28	D52
Si	53	B55	49	A54	28	D53

Si	40	B56	35	A55	28	D54
C	54	B57	52	A56	51	D55
C	57	B58	40	A57	35	D56
C	53	B59	49	A58	28	D57
C	51	B60	27	A59	17	D58
C	49	B61	28	A60	18	D59
C	50	B62	15	A61	6	D60
C	54	B63	52	A62	51	D61
C	53	B64	49	A63	28	D62
C	56	B65	53	A64	49	D63
C	55	B66	40	A65	35	D64
C	52	B67	51	A66	27	D65
C	57	B68	40	A67	35	D66
H	64	B69	54	A68	52	D67
H	66	B70	56	A69	53	D68
H	65	B71	53	A70	49	D69
H	67	B72	55	A71	40	D70
H	69	B73	57	A72	40	D71
H	68	B74	52	A73	51	D72
H	52	B75	51	A74	27	D73
H	57	B76	40	A75	35	D74
H	55	B77	40	A76	35	D75
H	54	B78	52	A77	51	D76
H	56	B79	53	A78	49	D77
H	53	B80	49	A79	28	D78
H	57	B81	40	A80	35	D79
H	56	B82	53	A81	49	D80
H	55	B83	40	A82	35	D81
H	54	B84	52	A83	51	D82
H	53	B85	49	A84	28	D83
H	52	B86	51	A85	27	D84
H	51	B87	27	A86	17	D85
H	50	B88	15	A87	6	D86
H	49	B89	28	A88	18	D87
Si	63	B90	50	A89	15	D88
Si	62	B91	49	A90	28	D89
Si	62	B92	49	A91	28	D90
H	92	B93	62	A92	49	D91
H	55	B94	40	A93	35	D92
H	93	B95	62	A94	49	D93
H	92	B96	62	A95	49	D94
H	92	B97	62	A96	49	D95
C	92	B98	62	A97	49	D96
Si	99	B99	92	A98	62	D97
H	93	B100	62	A99	49	D98
H	91	B101	63	A100	50	D99

B1	1.4919152
B2	3.1538073
B3	1.4919460
B4	1.9015629

B5	1.9095821
B6	1.9012774
B7	1.0992611
B8	1.0993343
B9	1.1005464
B10	1.1005288
B11	1.1029760
B12	1.9037314
B13	1.9034461
B14	1.9188534
B15	1.9023399
B16	1.9072614
B17	1.9066766
B18	1.9030897
B19	1.0993498
B20	1.0993636
B21	1.1004371
B22	1.1041784
B23	1.1042207
B24	1.1005022
B25	1.9025336
B26	1.9122510
B27	1.9116159
B28	1.9013539
B29	1.4919478
B30	1.4919244
B31	2.4775970
B32	2.4712735
B33	2.4748718
B34	1.9026836
B35	1.9087752
B36	1.9085594
B37	1.9098449
B38	1.9089967
B39	1.9100898
B40	1.4918630
B41	1.4918788
B42	1.8999087
B43	1.9000579
B44	1.1005335
B45	1.1005419
B46	1.0987484
B47	1.0988525
B48	3.1191610
B49	3.1399715
B50	3.1248291
B51	3.1235358
B52	3.1184992
B53	3.1233739
B54	3.1394886
B55	3.1256454
B56	3.1330032

B57	1.9108804
B58	1.9127060
B59	1.9110366
B60	1.9193956
B61	1.9211941
B62	1.9173516
B63	1.9049905
B64	1.9058760
B65	1.9058512
B66	1.9079260
B67	1.9049570
B68	1.9061878
B69	1.1011942
B70	1.1011861
B71	1.1012740
B72	1.1013059
B73	1.1012891
B74	1.1013316
B75	1.4908531
B76	1.4906890
B77	1.4909552
B78	1.4909414
B79	1.4908903
B80	1.4908959
B81	1.4888535
B82	1.4890825
B83	1.4851330
B84	1.4893038
B85	1.4891120
B86	1.4897018
B87	1.4895644
B88	1.4906797
B89	1.4828551
B90	1.9135542
B91	1.9249849
B92	1.9173873
B93	2.4512582
B94	3.6525214
B95	3.6808188
B96	4.5949582
B97	2.4577404
B98	1.9203714
B99	1.9027097
B100	1.4882780
B101	1.4915733
A1	89.7503002
A2	89.6869013
A3	111.1816806
A4	34.3333315
A5	142.4181554
A6	110.7582185
A7	110.7059174

A8	109.1163315
A9	109.1349272
A10	108.2904190
A11	111.5960482
A12	111.6128851
A13	110.6688096
A14	112.2104028
A15	111.3505942
A16	111.4452912
A17	111.8288931
A18	110.2065840
A19	110.2384653
A20	108.3761087
A21	107.7052373
A22	107.8041158
A23	108.1639624
A24	111.4811547
A25	111.1589025
A26	111.2939881
A27	111.5028270
A28	111.2001616
A29	111.2951889
A30	97.3192838
A31	97.6477529
A32	97.0910454
A33	110.8114298
A34	108.5527236
A35	108.4570462
A36	111.5673072
A37	111.4032793
A38	111.1815900
A39	110.5450496
A40	110.6162728
A41	108.2127066
A42	108.1862372
A43	109.3258551
A44	109.2944801
A45	110.9130706
A46	110.7839320
A47	121.9475563
A48	72.8514463
A49	121.8923322
A50	90.2081144
A51	90.2730940
A52	120.5390331
A53	121.1103500
A54	120.7488875
A55	121.2539775
A56	35.1890192
A57	36.1369072
A58	91.2582341
A59	36.0941190

A60	36.4735811
A61	35.5882216
A62	143.5831509
A63	35.1945895
A64	143.5859568
A65	88.6125951
A66	35.1258045
A67	88.8484693
A68	108.1768477
A69	108.1626444
A70	107.9765060
A71	107.8931166
A72	108.0238369
A73	108.0787415
A74	145.6682138
A75	89.9154581
A76	90.1919510
A77	90.4248971
A78	90.2063599
A79	145.6016274
A80	147.1937741
A81	89.9550296
A82	146.4621510
A83	89.6267855
A84	88.9764580
A85	89.0651490
A86	146.3958332
A87	145.1290014
A88	147.0446154
A89	109.6890935
A90	110.4946035
A91	111.0925436
A92	112.6993376
A93	132.7229215
A94	82.7785669
A95	105.6602840
A96	138.0177805
A97	114.8422733
A98	130.0429706
A99	109.6536562
A100	108.7351017
D1	0.0081257
D2	-148.1562696
D3	-128.6184945
D4	-126.0164172
D5	173.5162299
D6	-53.7871994
D7	63.4565296
D8	56.2365702
D9	118.9834199
D10	-176.8039346
D11	-63.3994125

D12	-123.5140240
D13	179.7974190
D14	179.6198040
D15	-55.6925944
D16	179.8495513
D17	-56.7150923
D18	56.7366786
D19	59.8232289
D20	62.9404378
D21	-63.1800797
D22	-59.6770662
D23	-179.9203081
D24	-179.8106774
D25	179.7339401
D26	-179.9950557
D27	177.0223287
D28	-177.1199744
D29	-156.9047699
D30	78.0091658
D31	156.4286092
D32	55.7720687
D33	61.1069113
D34	-61.3087895
D35	178.0775608
D36	-178.0595551
D37	179.1323971
D38	-55.8094422
D39	55.9967587
D40	-178.1451579
D41	178.3652648
D42	57.7816747
D43	-57.3459495
D44	-174.8627783
D45	175.2653787
D46	-99.4281354
D47	61.9069120
D48	98.6133136
D49	13.3594113
D50	-12.6189948
D51	-54.2377079
D52	26.3921470
D53	53.8240801
D54	98.0011252
D55	37.2511437
D56	-75.1812555
D57	33.6621166
D58	-76.1458112
D59	76.6135888
D60	-179.9350631
D61	35.9436308
D62	-87.9015477
D63	-36.3673974

D64	-49.7792499
D65	87.7799667
D66	49.2627742
D67	-179.9862185
D68	-179.5029471
D69	-116.7908781
D70	-150.6006429
D71	150.6605963
D72	117.0948700
D73	95.7185256
D74	159.7314718
D75	-159.9765633
D76	163.0704701
D77	-163.0294891
D78	-95.8500790
D79	-78.6937906
D80	89.4140400
D81	77.5541671
D82	-89.3844517
D83	143.5178178
D84	-143.5683216
D85	-74.8132982
D86	179.8959904
D87	75.0961442
D88	-119.0676474
D89	120.1098853
D90	-117.7160720
D91	93.0810588
D92	41.5716541
D93	-55.5336877
D94	58.9144342
D95	51.6024696
D96	65.1088040
D97	-32.8750267
D98	-62.0820776
D99	-58.0528806

SiH₂-(CH₂)₂(ads)

H						
Si	1	B1				
Si	2	B2	1	A1		
H	3	B3	2	A2	1	D1
C	2	B4	1	A3	3	D2
C	2	B5	1	A4	5	D3
C	3	B6	2	A5	1	D4
H	7	B7	3	A6	2	D5
H	5	B8	2	A7	1	D6
H	5	B9	2	A8	1	D7
H	7	B10	3	A9	2	D8
H	6	B11	2	A10	1	D9

Si	5	B12	2	A11	1	D10
Si	7	B13	3	A12	2	D11
Si	6	B14	2	A13	1	D12
C	13	B15	5	A14	2	D13
C	15	B16	6	A15	2	D14
C	15	B17	6	A16	2	D15
C	14	B18	7	A17	3	D16
H	16	B19	13	A18	5	D17
H	19	B20	14	A19	7	D18
H	16	B21	13	A20	5	D19
H	17	B22	15	A21	6	D20
H	18	B23	15	A22	6	D21
H	19	B24	14	A23	7	D22
Si	16	B25	13	A24	5	D23
Si	17	B26	15	A25	6	D24
Si	18	B27	15	A26	6	D25
Si	19	B28	14	A27	7	D26
H	26	B29	16	A28	13	D27
H	29	B30	19	A29	14	D28
H	27	B31	17	A30	15	D29
H	27	B32	17	A31	15	D30
H	28	B33	18	A32	15	D31
C	27	B34	17	A33	15	D32
C	29	B35	19	A34	14	D33
C	26	B36	16	A35	13	D34
Si	36	B37	29	A36	19	D35
Si	37	B38	26	A37	16	D36
Si	35	B39	27	A38	17	D37
H	38	B40	36	A39	29	D38
H	39	B41	37	A40	26	D39
C	38	B42	36	A41	29	D40
C	39	B43	37	A42	26	D41
H	43	B44	38	A43	36	D42
H	44	B45	39	A44	37	D43
H	44	B46	39	A45	37	D44
H	43	B47	38	A46	36	D45
Si	28	B48	18	A47	15	D46
Si	15	B49	6	A48	2	D47
Si	27	B50	17	A49	15	D48
Si	51	B51	27	A50	17	D49
Si	14	B52	7	A51	3	D50
Si	52	B53	51	A52	27	D51
Si	40	B54	35	A53	27	D52
Si	53	B55	14	A54	7	D53
Si	55	B56	40	A55	35	D54
Si	52	B57	51	A56	27	D55
Si	57	B58	55	A57	40	D56
Si	56	B59	53	A58	14	D57
C	52	B60	51	A59	27	D58
C	57	B61	55	A60	40	D59
C	56	B62	53	A61	14	D60
C	58	B63	52	A62	51	D61

C	49	B64	28	A63	18	D62
C	58	B65	52	A64	51	D63
C	54	B66	52	A65	51	D64
C	53	B67	14	A66	7	D65
C	56	B68	53	A67	14	D66
C	55	B69	40	A68	35	D67
C	52	B70	51	A69	27	D68
C	57	B71	55	A70	40	D69
H	49	B72	28	A71	18	D70
H	50	B73	15	A72	6	D71
H	51	B74	27	A73	17	D72
H	52	B75	51	A74	27	D73
H	53	B76	14	A75	7	D74
H	54	B77	52	A76	51	D75
H	55	B78	40	A77	35	D76
H	56	B79	53	A78	14	D77
H	57	B80	55	A79	40	D78
H	67	B81	54	A80	52	D79
H	69	B82	56	A81	53	D80
H	68	B83	53	A82	14	D81
H	70	B84	55	A83	40	D82
H	72	B85	57	A84	55	D83
H	71	B86	52	A85	51	D84
H	52	B87	51	A86	27	D85
H	57	B88	55	A87	40	D86
H	55	B89	40	A88	35	D87
H	54	B90	52	A89	51	D88
H	56	B91	53	A90	14	D89
H	53	B92	14	A91	7	D90
C	60	B93	56	A92	53	D91
C	59	B94	57	A93	55	D92
Si	95	B95	59	A94	57	D93
H	94	B96	60	A95	56	D94
H	94	B97	60	A96	56	D95
H	95	B98	59	A97	57	D96
H	95	B99	59	A98	57	D97
H	58	B100	52	A99	51	D98
H	96	B101	95	A100	59	D99
H	96	B102	95	A101	59	D100

B1	1.4920086
B2	3.1536861
B3	1.4920071
B4	1.9014725
B5	1.9082983
B6	1.9004597
B7	1.0990187
B8	1.0993096
B9	1.1004617
B10	1.1005590
B11	1.1029876

B12	1.9024170
B13	1.9033341
B14	1.9186574
B15	1.9024171
B16	1.9092471
B17	1.9051931
B18	1.9042675
B19	1.0993100
B20	1.0987992
B21	1.1004628
B22	1.1042745
B23	1.1040062
B24	1.1006333
B25	1.9014714
B26	1.9092482
B27	1.9064965
B28	1.9008092
B29	1.4920085
B30	1.4920092
B31	2.4793534
B32	2.4747981
B33	2.4794089
B34	1.9051929
B35	1.9070170
B36	1.9082980
B37	1.9070179
B38	1.9087575
B39	1.9108218
B40	1.4920100
B41	1.4920069
B42	1.9008067
B43	1.9004603
B44	1.1006341
B45	1.1005591
B46	1.0990172
B47	1.0988001
B48	3.1231316
B49	3.1286796
B50	3.1286793
B51	3.1280973
B52	3.1379395
B53	3.1216020
B54	3.1379407
B55	3.1339273
B56	3.1339287
B57	3.1119118
B58	3.1304670
B59	3.1304681
B60	1.9103333
B61	1.9118782
B62	1.9118768
B63	1.9158793

B64	1.9170658
B65	1.9158797
B66	1.9050798
B67	1.9059470
B68	1.9070810
B69	1.9059458
B70	1.9050801
B71	1.9070797
B72	1.4917116
B73	1.4910209
B74	1.4910219
B75	1.4893775
B76	1.4887483
B77	1.4893766
B78	1.4887481
B79	1.4883699
B80	1.4883699
B81	1.1012672
B82	1.1012736
B83	1.1012214
B84	1.1012215
B85	1.1012736
B86	1.1012667
B87	1.4908836
B88	1.4906921
B89	1.4905020
B90	1.4908840
B91	1.4906917
B92	1.4905023
B93	1.9060354
B94	1.9060354
B95	1.9058210
B96	1.0977547
B97	1.0978499
B98	1.0978502
B99	1.0977560
B100	1.4868101
B101	1.4862591
B102	1.4913231
A1	89.7008780
A2	89.6306161
A3	111.1846265
A4	110.4867686
A5	142.4127945
A6	110.7951175
A7	110.6187249
A8	109.2040125
A9	109.2117025
A10	108.3571782
A11	111.5463221
A12	111.5335400
A13	110.7745702

A14	112.2183070
A15	110.8480534
A16	110.9727923
A17	111.5684527
A18	110.1402837
A19	110.4095534
A20	108.4165404
A21	107.4117262
A22	107.6580816
A23	107.9136865
A24	111.5462993
A25	111.1416438
A26	111.2235027
A27	111.5916453
A28	111.1846021
A29	111.3917223
A30	97.8151854
A31	97.7746908
A32	97.5110641
A33	110.9070057
A34	108.1709206
A35	108.3616467
A36	111.3617970
A37	111.4225040
A38	111.2834654
A39	110.5544217
A40	110.4701480
A41	108.1709627
A42	108.1561578
A43	109.0975737
A44	109.2117150
A45	110.7951782
A46	110.8697876
A47	121.8162714
A48	72.9390186
A49	121.6399053
A50	90.1942111
A51	125.1929492
A52	120.3393403
A53	120.9805388
A54	60.3397281
A55	60.3397056
A56	60.4435132
A57	60.3441489
A58	60.3441759
A59	90.9337909
A60	34.9732066
A61	34.9732376
A62	90.5305177
A63	36.0419699
A64	146.2640956
A65	143.6510567

A66	89.0099401
A67	143.5187134
A68	89.0099047
A69	34.9916109
A70	143.5187426
A71	145.8150803
A72	146.1109659
A73	146.1109911
A74	89.4533732
A75	146.8688212
A76	89.7841920
A77	146.8687652
A78	91.0788625
A79	91.0788346
A80	108.1405799
A81	108.0204658
A82	108.0729308
A83	108.0729738
A84	108.0204563
A85	108.1406910
A86	145.5056074
A87	89.6441173
A88	90.1266950
A89	90.2222995
A90	89.6441563
A91	90.1266158
A92	89.0612230
A93	89.0611832
A94	120.2469302
A95	107.2506004
A96	108.4744454
A97	108.4744222
A98	107.2506100
A99	87.2283865
A100	109.4105637
A101	107.9767540
D1	0.1085043
D2	-148.2445509
D3	120.3616982
D4	-126.0143625
D5	173.4486597
D6	-53.9357825
D7	63.2870025
D8	56.0714720
D9	-62.9993934
D10	-176.8978018
D11	-63.3822653
D12	179.7090308
D13	179.8687428
D14	55.9664305
D15	179.6718508
D16	179.4717737

D17	-56.6339239
D18	56.2751943
D19	59.8524138
D20	62.3751022
D21	-61.8851686
D22	-60.0923540
D23	-179.8687839
D24	179.6015319
D25	-179.5573319
D26	-179.9419718
D27	176.8977556
D28	-176.6500689
D29	-157.3302223
D30	-78.0715403
D31	156.9487286
D32	-55.8583625
D33	61.6519381
D34	-61.4924857
D35	178.2540514
D36	-178.1383613
D37	-179.3095970
D38	-56.0415595
D39	55.9603368
D40	-178.2540444
D41	178.1066224
D42	57.4973918
D43	-57.8198972
D44	-175.1971756
D45	174.8256616
D46	-98.5328316
D47	-62.0872027
D48	98.1052572
D49	13.8823853
D50	-93.0912101
D51	-54.4108498
D52	-98.2880565
D53	40.9771653
D54	109.8116152
D55	-54.0265885
D56	-71.4874502
D57	71.4874561
D58	-34.0080531
D59	-35.6097073
D60	35.6097330
D61	18.0171878
D62	75.8421083
D63	147.3283822
D64	36.2727345
D65	-159.7796503
D66	33.7812771
D67	-49.4315906
D68	87.8923762

D69	-33.7813190
D70	75.8420847
D71	178.9918174
D72	-74.6225706
D73	-143.8408238
D74	72.6389972
D75	-89.2401954
D76	78.1496989
D77	161.3562879
D78	-161.3563430
D79	179.7743083
D80	-178.9259985
D81	150.4483105
D82	-150.4483204
D83	178.9260171
D84	117.3024090
D85	94.8716410
D86	91.5363121
D87	-159.8552342
D88	163.1849192
D89	-91.5363400
D90	-49.3560158
D91	89.7455380
D92	-89.7455222
D93	-170.5267778
D94	-67.5741277
D95	46.0287913
D96	-46.0288778
D97	67.5740160
D98	-91.2249687
D99	105.6207332
D100	-138.1273767

SiH-(CH₂)₃(ads)

H						
Si	1	B1				
Si	2	B2	1	A1		
H	3	B3	2	A2	1	D1
C	2	B4	1	A3	3	D2
C	2	B5	1	A4	5	D3
C	3	B6	2	A5	1	D4
H	7	B7	3	A6	2	D5
H	5	B8	2	A7	1	D6
H	5	B9	2	A8	1	D7
H	7	B10	3	A9	2	D8
H	6	B11	2	A10	1	D9
Si	5	B12	2	A11	1	D10
Si	7	B13	3	A12	2	D11
Si	6	B14	2	A13	1	D12
C	13	B15	5	A14	2	D13

C	15	B16	6	A15	2	D14
C	15	B17	6	A16	2	D15
C	14	B18	7	A17	3	D16
H	16	B19	13	A18	5	D17
H	19	B20	14	A19	7	D18
H	16	B21	13	A20	5	D19
H	17	B22	15	A21	6	D20
H	18	B23	15	A22	6	D21
H	19	B24	14	A23	7	D22
Si	16	B25	13	A24	5	D23
Si	17	B26	15	A25	6	D24
Si	18	B27	15	A26	6	D25
Si	19	B28	14	A27	7	D26
H	26	B29	16	A28	13	D27
H	29	B30	19	A29	14	D28
H	27	B31	17	A30	15	D29
H	27	B32	17	A31	15	D30
H	28	B33	18	A32	15	D31
C	27	B34	17	A33	15	D32
C	29	B35	19	A34	14	D33
C	26	B36	16	A35	13	D34
Si	36	B37	29	A36	19	D35
Si	37	B38	26	A37	16	D36
Si	35	B39	27	A38	17	D37
H	38	B40	36	A39	29	D38
H	39	B41	37	A40	26	D39
C	38	B42	36	A41	29	D40
C	39	B43	37	A42	26	D41
H	43	B44	38	A43	36	D42
H	44	B45	39	A44	37	D43
H	44	B46	39	A45	37	D44
H	43	B47	38	A46	36	D45
Si	28	B48	18	A47	15	D46
Si	15	B49	6	A48	2	D47
Si	27	B50	17	A49	15	D48
Si	51	B51	27	A50	17	D49
Si	49	B52	28	A51	18	D50
Si	52	B53	51	A52	27	D51
Si	49	B54	28	A53	18	D52
Si	53	B55	49	A54	28	D53
Si	55	B56	49	A55	28	D54
Si	52	B57	51	A56	27	D55
Si	55	B58	49	A57	28	D56
Si	53	B59	49	A58	28	D57
C	52	B60	51	A59	27	D58
C	55	B61	49	A60	28	D59
C	53	B62	49	A61	28	D60
C	51	B63	27	A62	17	D61
C	49	B64	28	A63	18	D62
C	50	B65	15	A64	6	D63
C	54	B66	52	A65	51	D64
C	53	B67	49	A66	28	D65

C	56	B68	53	A67	49	D66
C	55	B69	49	A68	28	D67
C	52	B70	51	A69	27	D68
C	57	B71	55	A70	49	D69
H	49	B72	28	A71	18	D70
H	50	B73	15	A72	6	D71
H	51	B74	27	A73	17	D72
H	52	B75	51	A74	27	D73
H	53	B76	49	A75	28	D74
H	54	B77	52	A76	51	D75
H	55	B78	49	A77	28	D76
H	56	B79	53	A78	49	D77
H	57	B80	55	A79	49	D78
H	67	B81	54	A80	52	D79
H	69	B82	56	A81	53	D80
H	68	B83	53	A82	49	D81
H	70	B84	55	A83	49	D82
H	72	B85	57	A84	55	D83
H	71	B86	52	A85	51	D84
H	52	B87	51	A86	27	D85
H	57	B88	55	A87	49	D86
H	55	B89	49	A88	28	D87
H	54	B90	52	A89	51	D88
H	56	B91	53	A90	49	D89
H	53	B92	49	A91	28	D90
C	60	B93	53	A92	49	D91
C	59	B94	55	A93	49	D92
Si	94	B95	60	A94	53	D93
H	94	B96	60	A95	53	D94
H	94	B97	60	A96	53	D95
H	95	B98	59	A97	55	D96
H	96	B99	94	A98	60	D97
C	96	B100	94	A99	60	D98
H	101	B101	96	A100	94	D99
H	101	B102	96	A101	94	D100
H	95	B103	59	A102	55	D101

B1	1.492128
B2	3.154912
B3	1.492128
B4	1.900322
B5	1.908823
B6	1.900322
B7	1.099053
B8	1.099053
B9	1.100531
B10	1.100531
B11	1.102909
B12	1.903316
B13	1.903316
B14	1.920247

B15	1.903316
B16	1.907565
B17	1.907565
B18	1.903316
B19	1.099053
B20	1.099053
B21	1.100531
B22	1.104039
B23	1.104039
B24	1.100531
B25	1.900322
B26	1.907565
B27	1.907565
B28	1.900322
B29	1.492128
B30	1.492128
B31	2.481743
B32	2.476685
B33	2.481743
B34	1.907565
B35	1.908823
B36	1.908823
B37	1.908822
B38	1.908822
B39	1.912449
B40	1.492128
B41	1.492128
B42	1.900323
B43	1.900323
B44	1.100531
B45	1.100531
B46	1.099053
B47	1.099053
B48	3.123759
B49	3.123760
B50	3.123759
B51	3.138811
B52	3.138811
B53	3.132974
B54	3.138810
B55	3.132974
B56	3.132974
B57	3.129596
B58	3.129596
B59	3.129596
B60	1.911142
B61	1.911143
B62	1.911142
B63	1.917336
B64	1.917336
B65	1.917336
B66	1.906424

B67	1.906423
B68	1.906424
B69	1.906423
B70	1.906423
B71	1.906423
B72	1.491025
B73	1.491025
B74	1.491025
B75	1.488998
B76	1.488998
B77	1.488998
B78	1.488998
B79	1.488998
B80	1.488998
B81	1.101251
B82	1.101251
B83	1.101251
B84	1.101251
B85	1.101251
B86	1.101251
B87	1.490687
B88	1.490688
B89	1.490688
B90	1.490687
B91	1.490687
B92	1.490687
B93	1.904732
B94	1.904732
B95	1.900503
B96	1.098030
B97	1.098030
B98	1.098029
B99	1.492232
B100	1.900503
B101	1.098030
B102	1.098030
B103	1.098029
A1	89.766727
A2	89.766727
A3	111.327743
A4	110.517972
A5	142.572137
A6	110.728457
A7	110.728457
A8	109.254497
A9	109.254497
A10	108.358699
A11	111.560964
A12	111.560964
A13	110.636616
A14	111.600414
A15	110.808913

A16	110.808913
A17	111.600414
A18	110.276952
A19	110.276952
A20	108.082884
A21	107.638071
A22	107.638071
A23	108.082884
A24	111.560945
A25	111.205753
A26	111.205753
A27	111.560945
A28	111.327711
A29	111.327711
A30	97.722628
A31	97.897028
A32	97.722628
A33	110.988797
A34	108.323667
A35	108.323667
A36	111.461876
A37	111.461876
A38	111.367995
A39	110.517986
A40	110.517986
A41	108.323681
A42	108.323681
A43	109.254442
A44	109.254442
A45	110.728413
A46	110.728413
A47	121.736961
A48	72.950100
A49	121.736961
A50	90.191558
A51	90.191558
A52	120.248396
A53	90.191563
A54	120.248396
A55	120.248398
A56	60.287839
A57	60.287841
A58	60.287839
A59	90.541127
A60	90.541121
A61	90.541127
A62	36.028787
A63	36.028787
A64	36.028783
A65	143.502267
A66	34.726396
A67	143.502267

A68	34.726404
A69	34.726396
A70	143.502258
A71	146.404122
A72	146.404114
A73	146.404122
A74	90.538224
A75	90.538224
A76	90.725394
A77	90.538256
A78	90.725394
A79	90.725395
A80	108.075752
A81	108.075752
A82	108.075725
A83	108.075746
A84	108.075746
A85	108.075725
A86	145.198873
A87	89.987624
A88	145.198873
A89	89.987619
A90	89.987619
A91	145.198873
A92	91.315743
A93	91.315728
A94	112.118962
A95	109.703903
A96	109.703914
A97	109.703924
A98	110.825004
A99	108.084165
A100	109.395338
A101	109.395311
A102	109.703924
D1	0.000000
D2	-148.311878
D3	120.429489
D4	-126.378294
D5	173.685557
D6	-53.488827
D7	63.841987
D8	56.354743
D9	-62.993513
D10	-176.715872
D11	-63.087398
D12	179.707108
D13	-179.678951
D14	56.152723
D15	179.818701
D16	179.678951
D17	-56.837508

D18	56.837508
D19	59.545258
D20	61.670251
D21	-61.670251
D22	-59.545258
D23	179.678933
D24	179.341966
D25	-179.341966
D26	-179.678933
D27	176.715856
D28	-176.715856
D29	-157.156591
D30	-78.007937
D31	157.156591
D32	-55.779316
D33	61.570616
D34	-61.570616
D35	178.362830
D36	-178.362830
D37	-179.367938
D38	-56.153139
D39	56.153139
D40	-178.362827
D41	178.362827
D42	57.871522
D43	-57.871522
D44	-175.202281
D45	175.202281
D46	-98.344649
D47	-62.014288
D48	98.344649
D49	13.870177
D50	-13.870177
D51	-54.188556
D52	165.242936
D53	54.188556
D54	-54.188556
D55	-54.891174
D56	-54.891174
D57	54.891174
D58	-34.815779
D59	-34.815783
D60	34.815779
D61	-75.686353
D62	75.686353
D63	180.000000
D64	35.762942
D65	-88.206207
D66	-35.762942
D67	88.206207
D68	88.206207
D69	35.762942

D70	75.686332
D71	180.000000
D72	-75.686332
D73	-145.342250
D74	145.342250
D75	-91.046190
D76	-145.342263
D77	91.046190
D78	-91.046223
D79	179.994409
D80	-179.994409
D81	-117.599326
D82	117.599318
D83	179.994401
D84	117.599326
D85	92.800084
D86	161.884328
D87	92.800105
D88	161.884316
D89	-161.884316
D90	-92.800084
D91	89.940219
D92	-89.940220
D93	-149.955551
D94	-28.198469
D95	88.287325
D96	-88.287342
D97	180.000000
D98	-58.376499
D99	-63.557036
D100	-179.689998
D101	28.198450