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Ab Initio Study of Growth Mechanism of 4H–SiC: Adsorption and Surface Reaction of C₂H₂, C₂H₄, CH₄ and CH₃

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ABSTRACT Silicon carbide is a semiconductor material with ideal properties for high temperature and high power applications. The epitaxial layer fabrication is usually performed using CVD under a hydrogen rich atmosphere and high temperature. At such conditions the surface of the growing layer is expected to be passivated by the abundantly present hydrogen. In this work, we use quantum chemical density functional theory (B3LYP and M06-2X) and transition state theory to study surface reactions related to the deposition of carbon on the (0001) surface of 4H–SiC. We show that it is unlikely for an adsorption to occur on a passivated site unless the hydrogen termination is removed. We propose that unterminated sites can be effectively created during the CVD by an abstraction process. We provide details of the adsorption process of active carbon species, namely CH₃, CH₄, C₂H₂ and C₂H₄ gases, and their subsequent surface reactions such as desorption, abstraction of neighboring surface hydrogens

and dimer formation. The reaction rates and sticking coefficients are provided for the temperature range of 298–2500 K. Finally, entire reaction paths from adsorptions to stable surface products are presented and discussed.

Introduction

Silicon carbide is a semiconductor material with wide band gap, high thermal conductivity, high blocking voltage and high breakdown electric field. Thanks to its high breakdown electric field and thinner drift layers^{1–4}, SiC power devices withstand higher operating temperature and switching frequency in comparison to the Si devices. Among its many polytypes the 4H polytype is usually preferred for electronic applications. Homoepitaxial layers of SiC are typically grown using chemical vapor deposition (CVD) technique, which is a versatile method for depositing thin films and coatings of a wide variety of materials^{5–7}. During the process, the 4H–SiC substrate(s) is placed inside a growth chamber maintained at 1500 – 1600 °C and a pressure of 50 – 200 mbar. The precursors (such as SiH₄ and C₃H₈) diluted in hydrogen flow with/without halogen addition are fed into the chamber and generate the growth.^{5,7–9} At these conditions, it has been shown that the productions of certain carbon species are more preferable than others. Among these are acetylene (C₂H₂), ethylene (C₂H₄), methane (CH₄), and methyl radicals (CH₃)¹⁰. It is typically suggested, based on their abundancy, that these species are the main carbon contributors to the SiC growth despite the fact that there are no valid confirmations on their reactivity with the SiC surface.

To the authors' knowledge, most adsorption studies available up to date have focused on reconstructed surfaces. The adsorption energies of hydrocarbons as well as other molecules have been reported on various surface reconstructions and polytypes, such as cubic SiC^{11–14} and

hexagonal polytypes^{15,16}. However, the CVD growth is usually presumed to happen layer by layer. This scenario plus the CVD process condition are more likely to generate a surface which is terminated by hydrogen atoms. Such termination allows maintaining the SiC sp^3 structure, while at the same time passivates the adsorption sites by creating high activation barriers of adsorptions¹⁷. Unless (hydrogen) vacant sites are created, the adsorption rates are expected to be very low. It has been shown in many related systems such as silicon and graphene that the alkyne and alkene adsorptions on the surface dangling bonds (i.e. vacant sites) can generate a chain production of surface dangling bonds via a process called surface hydrogen abstraction^{18–21}. This in turn initiates a chain of growth on an otherwise H-terminated surfaces. This phenomenon is expected to occur as well on the SiC surface but whether the chain can be sustained under the hydrogen rich atmosphere is still to be seen. Nevertheless, it is important to consider first the chance of creating surface dangling bonds in the CVD where the hydrocarbon adsorptions may start.

In this work, we report *ab initio* studies of the production of surface dangling bonds via an abstraction process and the adsorption of acetylene (C_2H_2), ethylene (C_2H_4), methane (CH_4) and methyl radical (CH_3) on the unterminated sites as well as on H-terminated sites. The study is performed on the (0001) surface of 4H-SiC, which is the silicon face. When relevant, other surface reactions such as desorption, surface hydrogen abstraction and dimer formation will be discussed. The energies at 0 K and Gibbs free energies at 298 – 2500 K are provided for each process. When applicable, transition state theory is applied to determine reaction rates.

Computational Methods

Cluster Model. The 4H-SiC surface is modeled using a cluster of $\text{Si}_{19}\text{C}_{19}$. $\text{Si}_{19}\text{C}_{19}$ is composed of two unreconstructed SiC bilayers terminated with hydrogen as shown in Fig. 1. The (0001) surface, Si face, is chosen for all reactions (Fig. 1a). This surface provides two central sites (depicted by A and B in Fig. 1a and 1b) where the surface reactions are to be studied. Unlike computational approaches using periodic models, the cluster model has drawbacks due to its limited cluster size. Nevertheless, we may expect the effects of adsorptions and surface reactions to be localized due to their covalent nature. This is confirmed by the small bending in dihedral angles of the outer most C-C-C-C atoms on the bottom layer (available in supplementary material) in comparison to the reference, H-terminated cluster. The bending is shown to be small, $\sim 0.16^\circ$ in average, with the maximum of 0.38° for $\text{CH}(\text{ads})\text{-CH}_2(\text{ads})$, despite the fact that no atoms have been frozen during optimizations and hence the cluster is allowed to relaxed completely. The artefacts of cluster size are hence expected to be small.

Figure 1. Top view of the Si face (0001) (a) and side view (b) of the $\text{Si}_{19}\text{C}_{19}$ cluster. A and B mark the adsorption/reaction sites. In both pictures, the hydrogen terminations on the A and B sites have been removed to clearly show the underneath Si sites.

Energies and Barriers. All quantum chemical calculations are performed using the Gaussian 09 software.²² Geometry optimizations to the minima and saddle points are carried out using the hybrid density functional theory (DFT) B3LYP^{23,24} and the LanL2DZ basis set^{25,26} in

combination with the empirical dispersion corrections D3 from Grimme et al. 2010²⁷. Harmonic frequency calculations are carried out at the same level of theory. The transition states are verified by visualizing the vibrational displacement of the imaginary frequencies. The electronic energies are corrected using the single-point energy derived from the M06-2X functional²⁸ and the G3LargeXP basis set²⁹. Whenever the G3LargeXP fails to derive a properly converged SCF, the basis set is replaced by a slightly smaller but more stable cc-pVTZ from Dunning³⁰. The M06-2X functional has been used in place of B3LYP-D3 in the electronic energy calculations due to its superior performance in calculating barrier heights^{31,32}.

The energies of reaction (ΔE_R) and activation barriers ($\Delta E_{act}^\ddagger$) at 0 K are derived as follows:

$$\Delta E_R = (\sum E_{products}) - (\sum E_{reactants}), \quad (1)$$

$$\Delta E_{act}^\ddagger = E_{TS} - (\sum E_{reactants}) \quad (2)$$

where $E_{reactants}$ and $E_{products}$ are the energies of the reactants and products, and E_{TS} is the energy of the transition states (TS) of the reactions. When gaseous species are involved, the ground state refers to the asymptote condition where the surface and the gas are located at infinite distance apart. The asymptote is used as the reference point rather than the physisorbed state due to the fact that the latter usually turns unfavorable with positive Gibbs free energies as the temperature increases. The zero-point vibration correction is applied to all energies. At nonzero temperatures, T , the standard Gibbs free energies of reaction (ΔG°_R) and activation ($\Delta G_{act}^\ddagger$) are calculated via $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The enthalpy (ΔH°) and the entropy (ΔS°) are derived in similar manners to Eq. 1 and 2.

Reaction Rates. The conventional transition state theory (TST) is used to derive the rates of surface reactions where there exists an intrinsic transition barrier. Hence, it is assumed that the reactants and the activation complexes are in equilibrium and the equilibration is rapid. The equations used in this work have been modified from Reuter and Scheffler's³³.

Adsorption. Adsorption rate (R_{ads}) of gaseous species A on a silicon site terminated by an adsorbed species B or written as $A(g) + B(ads)-Si(s) \rightarrow \text{product}(s)$ are obtained as follows.

$$R_{ads} = A_s f_{ads} \exp(-\Delta E_{act}^\ddagger / k_B T) \cdot \Phi_A \cdot \Theta_B, \quad (3)$$

where $f_{ads} = q_{vib,el}^{TS} / (q_{2D-Trans}^{gas} \cdot q_{int}^{gas} q_{vib,el}^{surf}), \quad (4)$

and $\Phi_A = \gamma_A p / \sqrt{2\pi m_A k_B T}. \quad (5)$

The sticking coefficient of species A (S_A) which describes the probability of gaseous species A to stick on the surface per strike is defined as $S_A = R_{ads} / (A_s \cdot \Phi_A \cdot \Theta_B)$. Using Eq. 3–5, we obtain

$$S_A = f_{ads} \exp(-\Delta E_{act}^\ddagger / k_B T). \quad (6)$$

Here R_{ads} is in the unit of molecule sites⁻¹ s⁻¹. $\Delta E_{act}^\ddagger$ and Φ_A refer to the activation energy of adsorption process at 0 K and the impingement rate of species A from the kinetic theory. Θ_B is the fraction of the surface occupied by B(ads). A_s is the area per one site of surface species B and is assumed equal to the area per one lattice site of 4H-SiC (0001), 8.178×10^{-20} m² as derived from the lattice constant $3.073 \text{ \AA}$ ³⁴. f_{ads} reduces the probability to stick due to the effects of the system degrees of freedom. The partition functions of the surface states, i.e. q^{TS} of the transition state and q^{surf} of the cluster, include only the vibrational and electronic parts. For the gases,

q^{gas} includes all terms except the translation along the reaction coordinate. It is divided into two parts. The vibrational, rotational and electronic parts of the gas partition functions are present in q_{int}^{gas} . The translational part includes only 2 out of 3 degrees of freedom, $q_{2D-Trans}^{gas} = A_s \cdot 2\pi m_A k_B T / h^2$, where the area in which the gas species may reside is assumed equal to A_s if they are to strike on the surface site successfully. The actual (unknown) area may be larger than A_s as discussed in Reuter and Scheffler's work³³. This simplification hence results in an overestimation of the sticking coefficient to a certain extent. Lastly, k_B , T , γ_A , p and m_A refer respectively to the Boltzmann constant, the process temperature, mole fraction of gaseous species A, the total pressure and the mass of gaseous species A. The adsorption rates can be rewritten in the units of mole area⁻¹ time⁻¹ and length time⁻¹ via $R_{ads}/A_s N_A$ and $R_{ads} \cdot h_{ML}$ respectively, where N_A is the Avogadro constant and h_{ML} is the height of 1 SiC bilayer, for which the value of 2.5131×10^{-10} m is used.

Desorption. Following Reuter and Scheffler,³³ desorption rate (R_{de}) of the adsorbed species A, $A(ads)-Si(s) \rightarrow product(s)$, is written as

$$R_{de} = f_{de} \left(\frac{k_B T}{h} \right) \exp(-\Delta E_{de}^\ddagger / k_B T) \cdot \Theta_A, \quad (7)$$

where $f_{de} = q_{vib,el}^{TS} / q_{vib,el}^{ads}$. (8)

Similar to the adsorption, f_{de} is a factor taking care of the effects of the system degrees of freedoms and q^{ads} is the partition function of the adsorbed species plus the cluster on which it attaches. Θ_A is the fraction of surface occupied by A(ads) and $\Delta E_{de}^\ddagger$ is the activation energy of desorption at 0 K.

Surface Reactions. For on-surface reaction $A(\text{ads})\text{-Si(s)} + B(\text{ads})\text{-Si(s)} \rightarrow \text{product(s)}$, the reaction rate ($R_{on-surf}$) is obtained from

$$R_{on-surf} = f_{on-surf} \left(\frac{k_B T}{h} \right) \exp(-\Delta E^\ddagger_{on-surf} / k_B T) \Theta_{AB}, \quad (9)$$

where $f_{on-surf} = q_{vib,el}^{TS} / q_{vib,el}^{surf}$. (10)

Θ_{AB} is the fraction of surface occupied by an adjacent pair of $A(\text{ads}) + B(\text{ads})$ and $\Delta E^\ddagger_{on-surf}$ is the activation energy of the on-surface reaction at 0 K.

Results and Discussion

Results and discussion are organized as follows. First, we report and discuss surface site terminations and the possibility to produce a surface hydrogen vacancy via abstraction by atomic hydrogen. Then it is followed by adsorption of gaseous C_2H_2 , C_2H_4 , CH_4 and CH_3 on hydrogen terminated as well as on vacant sites. When relevant, the processes of desorption, surface hydrogen abstraction and dimer formations are reported and discussed. The symbol $A(\text{ads})\text{-Si(s)}$ which refers to an adsorbed species A bonded to a surface silicon site will now be shortened to $A(\text{ads})$. This should not cause any confusion as the silicon face of the 4H-SiC is used for the entire study. The energies (0 K) and the Gibbs free energies (1600 °C) of all the studied surface reactions are summarized in Table 1. The Gibbs free energies, sticking coefficients and rate constants over 298–2500 K are provided in the supplementary materials.

Table 1 Summary of energies at 0 K and standard Gibbs free energies at 1600 °C of the surface reactions on 4H-SiC (0001). The energies and free energies are presented in the unit of kJ/mol with respect to the energy of the reactant state.

	$\Delta E_{\text{act}}^{\ddagger \text{ } 1)}$ (0 K)	$\Delta E_{\text{ads/R}}^{\text{ } 2)}$ (0 K)	$\Delta G_{\text{act}}^{\ddagger \text{ } 1)}$ (1600 °C)	$\Delta G_{\text{ads,R}}^{\circ \text{ } 2)}$ (1600 °C)
Gaseous Adsorptions				
$\text{CH}_3(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{CH}_3(\text{ads}) + \text{H}(\text{g})$	120	7	400	96
$\text{CH}_4(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{CH}_3(\text{ads}) + \text{H}_2(\text{g})$	362	9	620	37
$\text{C}_2\text{H}_2(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{C}_2\text{H}_3(\text{ads})$	214	120	481	394
$\text{C}_2\text{H}_4(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{C}_2\text{H}_5(\text{ads})$	322	-106	566	203
$\text{CH}_3(\text{g}) + *(\text{ads}) \rightarrow \text{CH}_3(\text{ads})$	-	-357	-	-33
$\text{CH}_4(\text{g}) + *(\text{ads}) \rightarrow \text{CH}_3(\text{ads}) + \text{H}(\text{g})$	190	71	436	129
$\text{C}_2\text{H}_2(\text{g}) + *(\text{ads}) \rightarrow \text{C}_2\text{H}_2(\text{ads})$	10	-96 ³⁾	245	170 ³⁾
$\text{C}_2\text{H}_4(\text{g}) + *(\text{ads}) \rightarrow \text{C}_2\text{H}_4(\text{ads})$	4 ³⁾	-77	259 ³⁾	207
Surface hydrogen Abstractions				
$\text{H}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{H}_2(\text{g}) + *(\text{ads})$	12	-62	165	-93
$\text{CH}_3(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_2(\text{ads}) + \text{H}_2(\text{g})$	52 ³⁾	-25	248 ³⁾	-82
$\text{CH}_2(\text{ads}) + \text{H}(\text{ads}) \rightarrow \text{CH}_3(\text{ads}) + *(\text{ads})$	95 ³⁾	-40	146 ³⁾	-11
$\text{C}_2\text{H}_2(\text{ads}) + \text{H}(\text{ads}) \rightarrow \text{C}_2\text{H}_3(\text{ads}) + *(\text{ads})$	33 ³⁾	-77 ³⁾	73 ³⁾	-66 ³⁾
$\text{C}_2\text{H}_4(\text{ads}) + \text{H}(\text{ads}) \rightarrow \text{C}_2\text{H}_5(\text{ads}) + *(\text{ads})$	47 ³⁾	-42	86 ³⁾	-30
Carbon group transfers				
$\text{C}_2\text{H}_3(\text{ads}) + *(\text{ads}) \rightarrow \text{CH}(\text{ads})\text{--CH}_2(\text{ads})$	63	-39	128	7
$\text{C}_2\text{H}_5(\text{ads}) + *(\text{ads}) \rightarrow \text{CH}_2(\text{ads}) + \text{CH}_3(\text{ads})$	265 ³⁾	-19	268 ³⁾	-35
$\text{C}_2\text{H}_5(\text{ads}) \rightarrow \text{CH}_2(\text{ads}) + \text{CH}_3(\text{g})$	-	322	-	-45
Recombination with hydrogen atom				
$\text{C}_2\text{H}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{C}_2\text{H}_3(\text{ads})$	-	-430	-	-174
$\text{C}_2\text{H}_4(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{C}_2\text{H}_5(\text{ads})$	-	-392	-	-133
$\text{CH}(\text{ads})\text{--CH}_2(\text{ads}) + \text{H}(\text{g}) \rightarrow \text{CH}_2(\text{ads})\text{--CH}_2(\text{ads})$	-	-384	-	-132

¹⁾ Energies and free energies of activation, ²⁾ energies and free energies of adsorption/reaction, ³⁾ cc-pVTZ basis set has been used for the single point energy correction.

1 Surface site terminations. In the study of surface adsorption to follow, two types of surface terminations will be considered as adsorption sites. The first is a Si site terminated by a hydrogen atom, denoted by H (ads), and the other is a vacant site on which a dangling bond is exposed, denoted by *(ads). To create the surface dangling bond, or a vacant site, we consider an abstraction process of the type $\text{H}(\text{g}) + \text{H}(\text{ads}) \leftrightarrow \text{H}_2(\text{g}) + *(\text{ads})$.

At 0 K the activation barrier is found to be 12 kJ/mol with respect to the energy of the reactants. The reaction is found to be exothermic with the reaction energy of -62 kJ/mol. At 1600 °C the Gibbs free energy of reaction (ΔG°_R) is found to be -93 kJ/mol. This implies that the reaction is favorable going forward to produce $H_2(g) + *(ads)$. The Gibbs free energy of activation ($\Delta G^\ddagger_{act}$) is shown to increase significantly from the value at 0 K to 165 kJ/mol. The increase is found to mainly be due to the entropy term ($T\Delta S$). From ΔG°_R we derive the surface fractions of $*(ads)$ and $H(ads)$, $\Theta_X = [X(ads)]/[total]$, by assuming that the system has reached the equilibrium condition. At 100 mbar, 1600 °C and the mole fractions of $H(g)$ and $H_2(g)$ of $\sim 10^{-3}$ and 1.0 respectively¹⁰, we obtain Θ_* and Θ_H of 0.28 and 0.72. This suggests that at the SiC-CVD condition there exists a significant amount of surface dangling bonds.

Using Eq. 3–6, we obtain a sticking coefficient for $H(g)$ on $H(ads)$ of 1.9, which is above the maximum value of 1.0. This overestimation is likely due to the breakdown of the simple TST³⁵. Nevertheless, this method allows us to gain qualitative measure on the correct value of the sticking coefficient. Similarly, the sticking coefficient of $H_2(g)$ on $*(ads)$ is found to be 6.9×10^{-3} . Using the values of Θ_* and Θ_H obtained earlier, the forward and reverse rates are found to be $\sim 2.6 \times 10^4$ and $\sim 1.8 \times 10^5$ molecule sites⁻¹ s⁻¹ which are fast enough to maintain the equilibrium condition we have assumed.

2 Adsorption of C_2H_2 on $H(ads)$. Reaction of $C_2H_2(g)$ on $H(ads)$ produces $C_2H_3(ads)$ as the only products. At 0 K the activation barrier ($\Delta E^\ddagger_{act}$) and adsorption energy (ΔE_{ads}) are found to be relatively high, 214 and 120 kJ/mol respectively, with respect to the reactants. At 1600 °C, the standard Gibbs free energies of activations ($\Delta G^\ddagger_{act}$) and adsorptions (ΔG°_{ads}) have increased from the values at 0 K to 481 and 394 kJ/mol. Using Eq. 3–6, we obtain an extremely low

sticking coefficient of 1.4×10^{-8} . The desorption rate derived from Eq. 7–8 is shown to be $1.4 \times 10^{11} \cdot \Theta_{C_2H_3(ads)}$ molecule sites $^{-1}$ s $^{-1}$. This rate of adsorption is indeed too low to generate the growth rates observed in the CVD.

3.1 Adsorption of C_2H_2 on $*(ads)$ and Hydrogen Abstraction. The C_2H_2 chemisorption on $*(ads)$ produces $C_2H_2(ads)$ as their sole product. The $C_2H_2(ads)$ is found to be stable in two different geometrical structures. The structure with lower energy, and hence more stable, has its dangling bond pointed toward the adjacent surface hydrogen atom. The activation and adsorption energies are found to be 10 and -96 kJ/mol at 0 K. At 1600 °C, $\Delta G^\ddagger_{act}$ increases to 245 kJ/mol while ΔG°_{ads} becomes 170 kJ/mol. The positive ΔG°_{ads} means that the process is not favorable

thermodynamically. The sticking coefficient at 1600 °C is found to be of 5.2×10^{-2} , which is much larger than the adsorption on H (ads). Interestingly, the calculated sticking coefficient is remarkably close to the value of 0.02 – 0.03 reported by Mogab and Leamy³⁶ as the net sticking coefficient of C₂H₂ on Si(111) at 800 – 1100 °C and pressure below 10^{-5} torr. Nevertheless, the rate constant for the reverse process (desorption) is shown to be much larger, giving the desorption rate of $\sim 3.2 \times 10^{11} \cdot \Theta_{C_2H_2(ads)}$ molecule sites⁻¹ s⁻¹. The adsorption process and the Gibbs free energies at 1600 °C are illustrated in Fig. 2 (from A to C).

Even though the rate constant of desorption process is very large, the process still needs to compete with the next reaction, namely the surface hydrogen abstraction shown in C to E in Fig. 2. The latter process happens via an interaction between the hydrogen atom of an adjacent H (ads) and the dangling bond residing at the outer carbon atom of the C₂H₂ (ads). We obtain the activation barrier ($\Delta E^\ddagger_{act}$) of 33 kJ/mol and the reaction energy (ΔE_R) of -77 kJ/mol with respect to the reactant state. During the process, the H atom of H (ads) is transferred to C₂H₂ (ads) leaving a dangling bond on the surface and producing C₂H₃ (ads). At 1600 °C, $\Delta G^\ddagger_{act}$ and ΔG°_R become respectively 73 and -66 kJ/mol. Using Eq. 9–10, we obtain the forward and reverse rate of $\sim 3.6 \times 10^{11} \cdot \Theta_{C_2H_2(ads)+H(ads)}$ and $5.2 \times 10^9 \cdot \Theta_{C_2H_3(ads)+*(ads)}$ molecule sites⁻¹ s⁻¹, respectively. Hence, the abstraction process is slightly faster than the desorption and some of the C₂H₂ (ads) are successfully changed into C₂H₃ (ads). The product of C₂H₃ (ads) + *(ads) is shown to be much more stable than the C₂H₂ (ads) + H (ads) with the Gibbs free energy reduced by ~ 66 kJ/mol. Nevertheless, the Gibbs free energy of C₂H₃ (ads) + *(ads) is ~ 104 kJ/mol larger than that of the starting reactants, C₂H₂ (g) + *(ads), plus an adjacent H (ads).

3.2 Hydrogen Atom Recombination. Figure 2 positions A to E summarize and illustrate the surface reactions we have discussed so far starting from $C_2H_2(g)$ adsorption on $*$ (ads) to the production of hydrogen abstraction process, $C_2H_3(ads) + *(ads)$. However, by this, we have assumed that the dangling bond on $C_2H_2(ads)$ remains active and not consumed by recombination process with atomic hydrogen shown in C–F' in Fig. 2. The latter process is shown to occur without an intrinsic barrier and reduce the Gibbs free energy by -175 kJ/mol. The product of $C_2H_3(ads) + H(ads)$ is therefore more stable with -6 kJ/mol in the Gibbs free energy in comparison to the starting point of $C_2H_2(g) + *(ads)$, plus an adjacent $H(ads)$. Since there is no intrinsic barrier between the reactant, $C_2H_3(ads) + *(ads)$, and the product, $C_2H_3(ads) + H(ads)$, Eq. 3–6 are no longer suitable for this case. Nevertheless, it is possible to compare the maximum rate of the process C–F' to that of the abstraction in C–E in Fig. 2. By assuming the maximum sticking coefficient of 1.0, we obtain the maximum rate of the process C–F' at $\sim 5 \times 10^7 \cdot \gamma_H \Theta_{C_2H_2(ads)+H(ads)}$ molecule sites⁻¹ s⁻¹ at 100 mbar and 1600 °C. This is certainly smaller than the forward rate of the abstraction process C–E, $\sim 3.6 \times 10^{11} \cdot \Theta_{C_2H_2(ads)+H(ads)}$ molecule sites⁻¹ s⁻¹.

3.3 $CH_2(ads)$ – $CH_2(ads)$ Dimer formation. From point E in Fig. 2, the pair of $C_2H_3(ads)$ and $*$ (ads) may also react with each other to form a rather unstable $CH(ads)$ – $CH_2(ads)$ dimer, shown as E to G. At 1600 °C, the ΔG°_R and $\Delta G^\ddagger_{act}$ are shown to be 7 and 128 kJ/mol, which implies that the reverse is more favorable than the forward process. Using Eq. 9 and 10, we obtain the forward rate of $1 \times 10^{10} \cdot \Theta_{C_2H_3(ads)+*(ads)}$ molecule sites⁻¹ s⁻¹ and $2 \times 10^{10} \cdot \Theta_{CH(ads)-CH_2(ads)}$ molecule sites⁻¹ s⁻¹ for the reverse. The product $CH(ads)$ – $CH_2(ads)$ is shown to be less stable with 111 kJ/mol of Gibbs free energy larger than the process starting point, $C_2H_2(g)$ and $*$ (ads). Nevertheless, a recombination between the dangling bond residing on the CH side of the

CH(ads)–CH₂(ads) and a hydrogen atom can reduce the Gibbs free energy by -132 kJ/mol and produce a stable CH₂(ads)–CH₂(ads) dimer, Fig 2 (from G to H). The latter process has the same maximum rate as the recombination discussed earlier. The recombination process is therefore the rate-limiting step for producing stable products, C₂H₃ (ads) + H (ads) and CH₂(ads)–CH₂(ads).

4 Adsorption of C₂H₄ on H (ads). Reaction of C₂H₄ gas on H (ads) produces C₂H₅ (ads) as their sole product. At 0 K the activation barrier ($\Delta E^{\ddagger}_{\text{act}}$) and adsorption energy (ΔE_{ads}) are 322 and -106 kJ/mol with respect to the reactants. At 1600 °C the standard Gibbs free energies of activation ($\Delta G^{\ddagger}_{\text{act}}$) and adsorption ($\Delta G^{\circ}_{\text{R}}$) both become very large, 566 and of 203 kJ/mol. Using Eq. 3–6, we obtain an extremely low sticking coefficient of $\sim 6 \times 10^{-11}$ similar to what previously observed in C₂H₂ adsorption on H (ads).

5.1 Adsorption of C₂H₄ on * (ads) and Hydrogen Abstractions. The C₂H₄ (g) chemisorption on *(ads) produces the surface species C₂H₄ (ads). The activation energy ($\Delta E^{\ddagger}_{\text{act}}$) and adsorption energy (ΔE_{ads}) at 0 K become 4 and -77 kJ/mol with respect to the reactants. Hence, similar to C₂H₂ the activation energy drops significantly for the adsorption on *(ads). At 1600 °C, the standard Gibbs free energies of activation ($\Delta G^{\ddagger}_{\text{act}}$) and adsorption ($\Delta G^{\circ}_{\text{R}}$) are 259 and 207 kJ/mol, respectively. Using Eq. 3–6, the sticking coefficient of 2.1×10^{-2} is obtained. Similar to C₂H₂, the positive $\Delta G^{\circ}_{\text{ads}}$ means that the process is not favorable in the forward direction. The desorption rate, given by Eq. 7–8, is again shown to be relatively large at $\sim 1.4 \times 10^{12} \cdot \Theta_{\text{C}_2\text{H}_4(\text{ads})}$ molecule sites⁻¹ s⁻¹. The adsorption process and the Gibbs free energies at 1600 °C are illustrated in Fig. 3 (from A to C).

Similar to C₂H₂, C₂H₄ (ads) can abstract an adjacent surface hydrogen from H (ads), as shown in Fig. 3 C to E. At 0 K, the activation barrier ($\Delta E^{\ddagger}_{\text{act}}$) is 47 kJ/mol and the reaction energy (ΔE_{R}) is -42 kJ/mol with respect to the reactant state. Similar to C₂H₂, the H atom from H (ads) is transferred to the C₂H₄ (ads) leaving a dangling bond on the surface and forming C₂H₅ (ads). At 1600 °C, $\Delta G^{\ddagger}_{\text{act}}$ and $\Delta G^{\circ}_{\text{R}}$ are 86 and -30 kJ/mol, respectively. Using Eq. 9–10, the forward and reverse rates are $\sim 1.6 \times 10^{11} \cdot \Theta_{\text{C}_2\text{H}_4(\text{ads})+\text{H}(\text{ads})}$ and $2.1 \times 10^{10} \cdot \Theta_{\text{C}_2\text{H}_5(\text{ads})+*(\text{ads})}$ molecule sites⁻¹ s⁻¹, respectively. Hence, unlike C₂H₂, for C₂H₄ the rate of the abstraction process is ~10 times slower than the desorption rate meaning that the C₂H₄ deposition is less effective than C₂H₂.

5.2 Hydrogen Atom Recombination. Similar to what previously observed in C₂H₂, the surface dangling bond in C₂H₄ (ads) may also be consumed by atomic hydrogen via a recombination process producing C₂H₅ (ads), as shown in Fig 3 C to H. Recombination process C to H has no intrinsic barriers and results in a reduction of the Gibbs free energy by -133 kJ/mol. The

maximum rate, i.e. with 1.0 sticking coefficient, is found to be $\sim 5 \times 10^7 \cdot \gamma_H \Theta_{C_2H_4(ads)+H(ads)}$ molecule site⁻¹ s⁻¹, which is much slower than the desorption and abstraction rates. The product of the recombination, despite being less stable than the product of the desorption, is much more stable than that of the abstraction. In addition, by releasing the dangling methyl group (–CH₃), the C₂H₅ (ads) will be transformed to CH₂ (ads) and reduces the Gibbs free energy even further by -45 kJ/mol, as shown in Fig. 3 I. Nevertheless, this pathway is limited by the slow rate of the recombination process.

5.3 Surface Reaction. From the C₂H₅ (ads) and * (ads) in Fig. 3 E, a transfer of the methyl group (–CH₃) to the adjacent * (ads) or E to G in Fig. 3 is shown to happen via a relatively large reaction barrier of 265 kJ/mol at 0 K. This produces a pair of surface species CH₂ (ads) + CH₃ (ads). At 1600 °C, the $\Delta G^\ddagger_{act}$ and ΔG°_R are shown to be 268 and -35 kJ/mol. Using Eq. 9 and 10, we obtain the forward and reverse rates of $1.3 \times 10^6 \cdot \Theta_{C_2H_5(ads)+*(ads)}$ and $1.7 \times 10^5 \cdot \Theta_{CH_3(ads)+CH_2(ads)}$ molecule sites⁻¹ s⁻¹. On the other hand, the surface dangling bond *(ads) in Fig 3 E may instead recombine with a hydrogen atom (E to H in Fig. 3) and follows the path H to I in Fig. 3 producing CH₂ (ads) as discussed earlier. The process E to H has the maximum rate of $5 \times 10^7 \cdot \gamma_H \Theta_{C_2H_5(ads)+*(ads)}$ molecule sites⁻¹ s⁻¹ which is slower than the reaction rate E to H but nevertheless producing a more stable product, CH₂ (ads).

5.4 Surface Hydrogen Abstraction by CH₂ (ads) and Recombination. Similar to C₂H₂ (ads) and C₂H₄ (ads), the dangling bond in CH₂ (ads) can also abstract a surface hydrogen from an adjacent H (ads) and produce a surface dangling bond. At 0 K, this process has an activation barrier ($\Delta E^\ddagger_{act}$) and an adsorption energy (ΔE_{ads}) of 95 and -40 kJ/mol, respectively. At 1600 °C, $\Delta G^\ddagger_{act}$ and ΔG°_R are found to be 146 and -11 kJ/mol, and the forward and reverse rates become

$3.4 \times 10^9 \cdot \Theta_{CH_2(ads)+H(ads)}$ and $1.4 \times 10^9 \cdot \Theta_{CH_3(ads)+*(ads)}$ molecule sites⁻¹ s⁻¹. The negative Gibbs free energy of reaction suggests that the products CH₃ (ads) + * (ads) become slightly more stable than the reactants CH₂ (ads) + H (ads). A recombination by hydrogen atom with CH₂ (ads) would reduce the Gibbs free energy further by -140 kJ/mol at 1600 °C and results to the final products of CH₃ (ads) + H (ads). The maximum rate of the recombination process is $5 \times 10^7 \cdot \gamma_H \Theta_{CH_2(ads)}$ molecule sites⁻¹ s⁻¹, which is smaller than the abstraction rate and hence the rate limiting step of this pathway.

6 Adsorption of CH₄ and CH₃ on H (ads). Reactions of CH₄ and CH₃ gases on H (ads) both produce surface species CH₃ (ads). The adsorption of CH₄ has activation barrier ($\Delta E^\ddagger_{act}$) and adsorption energy (ΔE_{ads}) of 362 and 9 kJ/mol. At 1600 °C $\Delta G^\ddagger_{act}$ and ΔG°_R are found to be 620 and 37 kJ/mol respectively. This barrier is extremely large for both forward and reverse directions. We obtain an extremely low sticking coefficient of 1.5×10^{-12} and a slow desorption rate of $2 \times 10^{-4} \cdot \gamma_{H_2} \Theta_{CH_3(ads)}$ molecule sites⁻¹ s⁻¹, assuming the desorption happens via the same pathway. The adsorption of CH₃ is present with much smaller activation barrier ($\Delta E^\ddagger_{act}$) and adsorption energy (ΔE_{ads}) of 120 and 7 kJ/mol. At 1600 °C $\Delta G^\ddagger_{act}$ and ΔG°_R are found to be 400 and 96 kJ/mol. We obtain a sticking coefficient of 2.0×10^{-6} and the desorption rate of $1 \times 10^4 \cdot \gamma_H \Theta_{CH_3(ads)}$ molecule sites⁻¹ s⁻¹, assuming the desorption happens via the same pathway. As a result, both processes produce adsorption rates which are too low to account for the CVD deposition rates.

7 Adsorption of CH₄ and CH₃ on * (ads) The chemisorptions of CH₄ and CH₃ gases on * (ads) both produce the surface species CH₃ (ads). When a dangling bond is present, the activation barrier ($\Delta E^\ddagger_{act}$) and the energy of adsorption (ΔE_{ads}) become significantly smaller,

similar to the C₂H₂ and C₂H₄ cases. For CH₄, $\Delta E_{\text{act}}^{\ddagger}$ and ΔE_{ads} are 190 and 71 kJ/mol, while at 1600 °C $\Delta G_{\text{act}}^{\ddagger}$ and $\Delta G_{\text{R}}^{\circ}$ are found to be 436 and 129 kJ/mol. This results in a sticking coefficient of 2.0×10^{-7} and the desorption rate of $1 \times 10^4 \cdot \gamma_H \Theta_{\text{CH}_3(\text{ads})}$ molecule sites⁻¹ s⁻¹, assuming the desorption happens via the same pathway. Hence, even on a *(ads), the sticking coefficient of CH₄ is still too low to generate the reasonable growth rate for the SiC deposition.

On the other hand, the adsorption of CH₃ on *(ads) occurs with no intrinsic barriers between the reactant and the product state. The adsorption energy (ΔE_{ads}) at 0 K is found to be -357 kJ/mol while at 1600 °C $\Delta G_{\text{R}}^{\circ}$ becomes -33 kJ/mol. The rate determining methods, Eq. 3–6, are not suitable to derive for the sticking coefficient and the desorption rate for this case.

In Fig. 4, we summarize the entire process where we start from a hydrogen abstraction by an atomic hydrogen (A to C), to an adsorption of gaseous CH₃ (C to D), a hydrogen abstraction from CH₃ (ads) (D to F) and lastly a surface hydrogen abstraction (F to H). The process D to F, a hydrogen abstraction from CH₃ (ads), may happen via interaction with atomic hydrogen with $\Delta G_{\text{act}}^{\ddagger}$ and $\Delta G_{\text{R}}^{\circ}$ of 248 and -82 kJ/mol at 1600 °C respectively. Using Eq. 3–6, the forward and reverse rates are obtained to be $\sim 5 \times 10^5 \cdot \gamma_H \Theta_{\text{CH}_3(\text{ads})}$ and $3 \times 10^3 \cdot \gamma_{\text{H}_2} \Theta_{\text{CH}_2(\text{ads})}$ molecule sites⁻¹ s⁻¹, respectively. As discussed previously in section 5.4, the dangling bond on a CH₂ (ads) may be transferred to an adjacent site via surface hydrogen abstraction (Fig. 4, F to H) with the forward and reverse rates of $3.4 \times 10^9 \cdot \Theta_{\text{CH}_2(\text{ads})+\text{H}(\text{ads})}$ and $1.4 \times 10^9 \cdot \Theta_{\text{CH}_3(\text{ads})+*(\text{ads})}$ molecule sites⁻¹ s⁻¹, respectively, or may instead recombine with a hydrogen atom to produce a CH₃ (ads) again with the rate of $5 \times 10^7 \cdot \gamma_H \Theta_{\text{CH}_2(\text{ads})}$ molecule sites⁻¹ s⁻¹.

Conclusion. The density functional theory (B3LYP and M06-2X) and transition state theory are used to study surface reactions related to the deposition of carbon on the (0001) surface of 4H-SiC during the CVD process. Under the hydrogen rich atmosphere and high temperature of the CVD, the growing surface is likely passivated by the abundantly present hydrogen. We show that adsorptions on hydrogen passivated sites happen with extremely large activation barriers, while the barriers are reduced significantly with the presence of surface dangling bonds. We propose that a surface dangling bond can be effectively created by an abstraction reaction with a hydrogen atom, -93 kJ/mol of $\Delta G^\circ_{\text{R}}$ and 165 kJ/mol of $\Delta G^\ddagger_{\text{act}}$ at 1600 °C. The adsorption of CH_3 , CH_4 , C_2H_2 and C_2H_4 gases on the (0001) surface are presented as well as their subsequent surface reactions such as desorptions, abstractions of neighboring surface hydrogens,

recombination with hydrogen atoms and dimer formations. We show that adsorptions of gaseous C_2H_2 and C_2H_4 are not favorable thermodynamically and desorptions happen rather fast via the same path. Nevertheless, it is shown that subsequent surface reactions help stabilizing the product(s) and the process can occur successfully but inefficiently. It is expected that C_2H_2 contributes to growth with higher efficiency than C_2H_4 . The end products of both processes are determined by the arrival of hydrogen atoms. Unlike C_2H_2 and C_2H_4 , adsorption of CH_3 gas on a dangling bond is shown to be favorable thermodynamically. The process occurs with no barrier and negative ΔG°_R . CH_4 gas, on the other hand, is shown to be inactive toward growth.

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

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TOC Graphic

Supporting Information for

***Ab Initio* Study of Growth Mechanism of 4H–SiC: Adsorption and Surface Reaction of C₂H₂, C₂H₄, CH₄ and CH₃**

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Table S1 Gibbs free energies of reaction 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
$\text{H(g)} + \text{H(ads)} \rightarrow \text{H}_2\text{(g)} + \text{* (ads)}$	-2.911E-13	1.198E-09	2.471E-06	-2.476E-02	-5.922E+01
$\text{CH}_3\text{(g)} + \text{H(s)} \rightarrow \text{CH}_3\text{(s)} + \text{H(g)}$	-4.155E-13	3.725E-09	-1.569E-05	6.716E-02	5.634E+00
$\text{CH}_4\text{(g)} + \text{H(s)} \rightarrow \text{CH}_3\text{(s)} + \text{H}_2\text{(g)}$	-1.463E-12	1.054E-08	-2.933E-05	4.149E-02	1.064E+01
$\text{C}_2\text{H}_2\text{(g)} + \text{H(s)} \rightarrow \text{C}_2\text{H}_3\text{(s)}$	2.003E-13	-7.271E-10	-3.439E-06	1.558E-01	1.163E+02
$\text{C}_2\text{H}_4\text{(g)} + \text{H(s)} \rightarrow \text{C}_2\text{H}_5\text{(s)}$	1.851E-14	4.674E-10	-6.902E-06	1.779E-01	-1.093E+02
$\text{CH}_3\text{(g)} + \text{* (s)} \rightarrow \text{CH}_3\text{(s)}$	5.316E-13	-2.783E-09	1.251E-07	1.826E-01	-3.637E+02
$\text{CH}_4\text{(g)} + \text{* (s)} \rightarrow \text{CH}_3\text{(s)} + \text{H(g)}$	-1.172E-12	9.341E-09	-3.180E-05	6.625E-02	6.986E+01
$\text{C}_2\text{H}_2\text{(g)} + \text{* (s)} \rightarrow \text{C}_2\text{H}_2\text{(s)}$	-2.592E-14	1.009E-09	-8.685E-06	1.570E-01	-9.977E+01
$\text{C}_2\text{H}_4\text{(g)} + \text{* (s)} \rightarrow \text{C}_2\text{H}_4\text{(s)}$	-6.950E-13	5.765E-09	-2.213E-05	1.789E-01	-8.041E+01
$\text{CH}_3\text{(s)} + \text{H(g)} \rightarrow \text{CH}_2\text{(s)} + \text{H}_2\text{(g)}$	-8.787E-13	5.586E-09	-1.029E-05	-2.699E-02	-2.105E+01
$\text{CH}_2\text{(s)} + \text{H(s)} \rightarrow \text{CH}_3\text{(s)} + \text{* (s)}$	5.766E-13	-4.312E-09	1.255E-05	3.514E-03	-4.040E+01
$\text{C}_2\text{H}_2\text{(s)} + \text{H(s)} \rightarrow \text{C}_2\text{H}_3\text{(s)} + \text{* (s)}$	4.454E-13	-3.439E-09	1.051E-05	-5.217E-03	-7.637E+01
$\text{C}_2\text{H}_3\text{(s)} + \text{* (s)} \rightarrow \text{CH(s)}\text{--}\text{CH}_2\text{(s)}$	1.016E-13	-4.997E-10	4.106E-07	2.665E-02	-4.213E+01
$\text{C}_2\text{H}_4\text{(s)} + \text{H(s)} \rightarrow \text{C}_2\text{H}_5\text{(s)} + \text{* (s)}$	6.346E-13	-4.723E-09	1.362E-05	-6.881E-03	-4.157E+01
$\text{C}_2\text{H}_5\text{(s)} + \text{* (s)} \rightarrow \text{CH}_2\text{(s)} + \text{CH}_3\text{(s)}$	-8.676E-13	6.067E-09	-1.582E-05	4.966E-03	-1.835E+01
$\text{CH(s)}\text{--}\text{CH}_2\text{(s)} + \text{H(g)} \rightarrow \text{CH}_2\text{(s)}\text{--}\text{CH}_2\text{(s)}$	1.411E-12	-1.004E-08	2.638E-05	1.146E-01	-3.903E+02

Table S2 Gibbs free energies of activation 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
$\text{H(g)} + \text{H(ads)} \rightarrow \text{H}_2\text{(g)} + \text{* (ads)}$	2.247E-13	-1.654E-09	5.503E-06	7.701E-02	9.977E+00

$\text{CH}_3(\text{g}) + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{H}(\text{g})$	2.523E-13	-1.083E-09	-1.635E-06	1.573E-01	1.147E+02
$\text{CH}_4(\text{g}) + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{H}_2(\text{g})$	-4.474E-13	4.166E-09	-1.697E-05	1.605E-01	3.567E+02
$\text{C}_2\text{H}_2(\text{g}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_3(\text{s})$	1.057E-13	-3.637E-10	-1.585E-06	1.470E-01	2.121E+02
$\text{C}_2\text{H}_4(\text{g}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_5(\text{s})$	-7.228E-13	5.475E-09	-1.767E-05	1.492E-01	3.210E+02
$\text{CH}_4(\text{g}) + *(\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{H}(\text{g})$	-7.042E-13	5.898E-09	-2.117E-05	1.577E-01	1.844E+02
$\text{C}_2\text{H}_2(\text{g}) + *(\text{s}) \rightarrow \text{C}_2\text{H}_2(\text{s}),$ S1,S2	-2.292E-13	1.835E-09	-6.617E-06	1.336E-01	8.670E+00
$\text{C}_2\text{H}_4(\text{g}) + *(\text{s}) \rightarrow \text{C}_2\text{H}_4(\text{s})$	-4.300E-13	3.445E-09	-1.246E-05	1.515E-01	1.975E+00
$\text{CH}_3(\text{s}) + \text{H}(\text{g}) \rightarrow \text{CH}_2(\text{s}) + \text{H}_2(\text{g})$	3.175E-13	-1.989E-09	4.957E-06	1.033E-01	4.630E+01
$\text{CH}_2(\text{s}) + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + *(\text{s})$	4.372E-13	-3.236E-09	1.084E-05	1.693E-02	9.208E+01
$\text{C}_2\text{H}_2(\text{s}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_3(\text{s}) + *(\text{s})$	2.834E-13	-2.187E-09	8.204E-06	1.292E-02	3.114E+01
$\text{C}_2\text{H}_3(\text{s}) + *(\text{s}) \rightarrow \text{CH}(\text{s})-\text{CH}_2(\text{s})$	3.634E-13	-2.832E-09	1.029E-05	2.487E-02	5.968E+01
$\text{C}_2\text{H}_4(\text{s}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_5(\text{s}) + *(\text{s})$	4.645E-13	-3.404E-09	1.115E-05	9.892E-03	4.489E+01
$\text{C}_2\text{H}_5(\text{s}) + *(\text{s}) \rightarrow \text{CH}_2(\text{s}) + \text{CH}_3(\text{s})$	-4.402E-13	2.746E-09	-4.150E-06	2.405E-03	2.652E+02

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
$\text{H}(\text{g}) + \text{H}(\text{ads}) \rightarrow \text{H}_2(\text{g}) + *(\text{ads})$	1.882E+00	-6.696E+00	1.064E+00	1.076E+01
$\text{H}_2(\text{g}) + *(\text{ads}) \rightarrow \text{H}(\text{g}) + \text{H}(\text{ads})$	6.982E-03	-1.570E+01	1.995E+00	6.701E+01
$\text{CH}_3(\text{g}) + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{H}(\text{g})$	2.038E-06	-2.265E+01	2.224E+00	1.123E+02
$\text{CH}_3(\text{s}) + \text{H}(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{s})$	2.612E-04	-6.165E+00	6.607E-01	1.100E+02
$\text{CH}_4(\text{g}) + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{H}_2(\text{g})$	1.503E-12	-2.762E+01	3.066E+00	3.536E+02
$\text{CH}_3(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}(\text{s})$	6.065E-12	-1.570E+01	1.587E+00	3.439E+02
$\text{C}_2\text{H}_2(\text{g}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_3(\text{s})$	1.360E-08	-1.926E+01	1.948E+00	2.107E+02
$\text{C}_2\text{H}_4(\text{g}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_5(\text{s})$	5.945E-11	-2.395E+01	2.773E+00	3.190E+02
$\text{CH}_4(\text{g}) + *(\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{H}(\text{g})$	2.028E-07	-2.786E+01	3.199E+00	1.815E+02

$\text{CH}_3(\text{s}) + \text{H}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + *(\text{s})$	2.206E-04	-6.943E+00	7.890E-01	1.156E+02
$\text{C}_2\text{H}_2(\text{g}) + *(\text{s}) \rightarrow \text{C}_2\text{H}_2(\text{s})$	5.161E-02	-1.804E+01	2.065E+00	7.574E+00
$\text{C}_2\text{H}_4(\text{g}) + *(\text{s}) \rightarrow \text{C}_2\text{H}_4(\text{s})$	2.082E-02	-2.319E+01	2.564E+00	-6.986E-02
$\text{CH}_3(\text{s}) + \text{H}(\text{g}) \rightarrow \text{CH}_2(\text{s}) + \text{H}_2(\text{g})$	9.324E-03	-1.118E+01	1.259E+00	4.651E+01
$\text{CH}_2(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_3(\text{s}) + \text{H}(\text{g})$	7.412E-05	-1.665E+01	1.495E+00	6.421E+01

Table S4 Rate constants in forward (k_{fwd}) and reverse (k_{rvs}) directions. A and E are in the units of molecules per site per second and kJ/mol.

	k_{fwd} (298 – 2500 K)			k_{rvs} (298 – 2500 K)		
	ln (A)	n	E	ln (A)	n	E
$\text{C}_2\text{H}_3(\text{s}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + \text{H}(\text{s})$	28.430	0.466	97.580	-	-	-
$\text{C}_2\text{H}_5(\text{s}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{H}(\text{s})$	27.790	1.050	431.823	-	-	-
$\text{C}_2\text{H}_2(\text{s}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + *(\text{s})$	31.493	0.277	110.563	-	-	-
$\text{C}_2\text{H}_4(\text{s}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + *(\text{s})$	33.037	0.035	82.595	-	-	-
$\text{CH}_2(\text{s}) + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + *(\text{s})$	26.974	0.129	93.697	23.657	0.814	135.749
$\text{C}_2\text{H}_2(\text{s}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_3(\text{s}) + *(\text{s})$	26.974	0.229	32.781	22.805	0.862	107.825
$\text{C}_2\text{H}_3(\text{s}) + *(\text{s}) \rightarrow \text{CH}(\text{s})-\text{CH}_2(\text{s})$	26.343	0.091	61.494	30.149	0.005	103.946
$\text{C}_2\text{H}_4(\text{s}) + \text{H}(\text{s}) \rightarrow \text{C}_2\text{H}_5(\text{s}) + *(\text{s})$	27.769	0.133	46.452	23.017	0.857	88.925
$\text{C}_2\text{H}_5(\text{s}) + *(\text{s}) \rightarrow \text{CH}_2(\text{s}) + \text{CH}_3(\text{s})$	26.092	0.685	266.968	29.949	0.028	282.473

Table S5 Dihedral angles C1-C2-C3-C4 of the outer most carbon atoms on the bottom layer after adsorptions and surface reactions have occurred. See Figure S1 for depiction of the four carbon atoms. The angles are shown in comparison to the reference value from the H-terminated cluster, H(ads) + H(ads).

	Dihedral C1-C2-C3-C4
H(ads) + H(ads) (reference)	179.999°
H(ads) + *(ads)	179.963°

$\text{CH}_2(\text{ads}) + \text{H}(\text{ads})$	179.837°
$\text{CH}_3(\text{ads}) + *(\text{ads})$	179.946°
$\text{CH}_3(\text{ads}) + \text{H}(\text{ads})$	179.900°
$\text{C}_2\text{H}_2(\text{ads}) + \text{H}(\text{ads})$	179.994°

Figure S1 Depiction of the carbon atoms C1 to C4 on the H-terminated cluster. The hydrogen atoms bonded to the four carbons have been removed to clearly show the carbon atoms underneath.