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Adsorption and surface diffusion of silicon growth species in silicon carbide chemical vapour deposition processes studied by quantum chemical computations

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The effect chlorine addition to the gas mixture has on the surface chemistry in the chemical vapour deposition process for silicon carbide (SiC) epitaxial layers is studied by quantum-chemical calculations of the adsorption and diffusion of SiH₂ and SiCl₂ on the (000-1) 4H-SiC surface. SiH₂ was found to bind stronger to the surface than SiCl₂ by approximately 100 kJ mol⁻¹ and to have a 50 kJ mol⁻¹ lower energy barrier for diffusion on the fully hydrogen-terminated surface. On a bare SiC surface, without hydrogen termination, the SiCl₂ molecule has a somewhat lower energy barrier for diffusion. SiCl₂ is found to require a higher activation energy for desorption once chemisorbed, compared to the SiH₂ molecule. Gibbs free-energy calculations also indicate that the SiC surface may not be fully hydrogen terminated at CVD conditions since missing-neighbouring pair of surface hydrogens is found to be a likely type of defect on a hydrogen terminated SiC surface.

1 Introduction

During the last twenty years, the interest in silicon carbide (SiC) based electric devices has greatly increased due to the superior properties, e.g. higher operation temperature, higher thermal conductivity and higher critical electrical breakdown field [1, 2], compared to conventional silicon based devices. A critical factor holding back the development of silicon carbide technology is the significantly higher manufacturing costs compared to conventional semiconductor materials and especially compared to silicon. A substantial part of the production cost of the final device is the cost for manufacturing the active region. This region is usually manufactured as an epitaxial layer, grown with great precision, in terms of crystal quality and impurity levels, on top of a single crystalline substrate. For a long time, the method of choice for epitaxial growth of silicon carbide has been Chemical Vapour Deposition (CVD). The silicon and carbon precursors typically used in SiC CVD are high purity silane, SiH₄, and small hydrocarbon molecules, e.g. ethylene, C₂H₄, or propane, C₃H₈. These gases are diluted approximately one thousand times in a H₂ carrier gas flow that is used as solvent and is also needed for the growth chemistry. The process temperature and pressure is usually 1500-1600 °C and 100-1000 mBar,

respectively. Typically, SiC CVD processes operate with a growth rate of 5-10 $\mu\text{m/h}$ [3], to be compared to a few hundred of $\mu\text{m/h}$ for epitaxial growth of silicon [4].

To increase the growth rate of epitaxial layers of SiC, the number of silicon and carbon atoms interacting with the substrate per time unit must be increased. This is achieved by increasing the concentration of silicon and carbon in the gas mixture. However the drawback of increased gas phase concentrations is the increased probability of formation of solid aggregates in the gas phase, mainly silicon droplets, which in contact with the surface causes severe crystal defects making the epitaxial layer unusable for electric devices.

In order to avoid the formation of silicon droplets, an element can be added to the gas mixture that binds stronger to silicon than silicon itself. Good candidates for this are the halogens, where the standard bond enthalpies for the Si-Si, Si-F, Si-Cl, Si-Br and Si-I bonds are 226, 597, 400, 330 and 234 kJ mol^{-1} respectively [5]. Of these, the bromine and iodine atoms are rather large and, especially iodine forms a too weak bond to silicon. The fluorine on the other hand, binds too strongly to silicon and can also form very toxic HF gas in reactions with the hydrogen carrier gas. So the Si-Cl bond turns out to be the one with the best suited bond enthalpy. A further advantage with using chlorine as growth additive is that chlorinated silicon compounds are available in high purity since they are already commercially used in the silicon industry. The CVD process where chloride is added to the gas mixture is often called chloride-based CVD and it has been shown to be a route to achieve growth rates $>100 \mu\text{m/h}$ at otherwise standard process conditions, but it has also opened up for low temperature (1300 $^{\circ}\text{C}$) processes with growth rates around 5-10 $\mu\text{m/h}$ [6].

Chloride was mainly introduced in SiC CVD to circumvent the formation of the silicon droplets, however, the introduction also means that the chemistry, both the gas phase chemistry and the surface chemistry, in the process changes. According to thermophysical studies of the gas-phase chemistry, the actual molecules interacting with the surface are mainly SiCl_2 in chloride-based CVD [7-9] as compared to mainly SiH_2 in conventional CVD [7, 9]. For a better understanding of the impact of the chloride-based chemistry on the growth, the differences in how the SiCl_2 and SiH_2 molecules interact with the SiC surface are of great interest. Here we probe the surface chemistry of SiCl_2 and SiH_2 to study differences crucial to their behaviour in a CVD process.

Quantum-chemical calculations have previously been used to study the surface chemistry in silicon carbide CVD [10-13]. Larsson et al. [10] have studied adsorption and abstraction of hydrogen on hydrogen-terminated (0001) and (000-1) surfaces on 4H-SiC and found that the two hydrogen-terminated surfaces are stable enough to

endure temperatures up to 2300°C even in presence of hydrogen or halogen radicals [10]. Reconstruction of the unterminated (0001) and (000-1) surfaces upon adsorption was investigated [11] and it was found that the (0001) surface obtained a (1×2) reconstruction whereas the (000-1) surface retained its initial (1×1) structure. Both surfaces gained parameters closer to the bulk parameters when species, i.e. C₂H₂ and Si, were adsorbed on the surface [11]. A study by Wachowicz and Kiejna [12] shows that hydrogen-termination of a naked 4H-SiC cluster suppresses the surface relaxation.

In this work hybrid ab initio – DFT calculations was performed using a cluster model to investigate adsorption and diffusion of SiH₂ and SiCl₂ on the (000-1) 4H-SiC surface. Both fully hydrogen-terminated surfaces and surfaces with hydrogen vacancy sites were studied with the purpose to investigate the difference in growth behaviour in the CVD process using standard and chlorinated growth chemistry.

2 Method

The interaction between the hydrogen-terminated 4H-SiC (000-1) surface, also denoted as the carbon face, or C-face of a SiC wafer, and the two molecules SiH₂ and SiCl₂ were investigated using quantum-chemical calculations. The surface was modelled using a cluster of atoms, cut from the bulk crystal structure. 4H-SiC crystallize in a hexagonal structure with space group P6₃mc and the lattice parameters $a = 3.08 \text{ \AA}$ and $c = 10.08 \text{ \AA}$ [13]. The clusters were cut in such a way that the number of unsaturated bonds was minimized and the atom coordination was maximized. Clusters with various sizes, ranging from 26 to 400 atoms, were constructed and their structures relaxed (i.e. geometry optimized) [14] to find the local energy-minima structures. The clusters were studied both with and without hydrogen saturating the dangling bonds at the surfaces.

The quantum-chemical calculations were mainly performed using the B3LYP hybrid ab initio-density functional theory method [15,16] with a double zeta basis set (DZ) [17, 18] used for initial geometry-optimization calculations and the larger 6-31G(d,p) basis set [19] for final optimizations and for property calculations. In geometry-optimization calculations on the molecules occurring in this study, the additional ab initio electron correlation-corrected methods MP2 [20] and QCISD(T) [21] were also used, as well as the large basis set 6-311++G(2df,2pd) [22]. The quantum-chemical program Gaussian 09 [23] was employed. The use of a cluster model facilitates the application of hybrid ab initio - DFT calculations.

When calculating the Gibbs free energy via a vibrational normal mode computation in the Gaussian 09 program, a temperature of 1870 K and partial pressures according to table 1 were used. The temperature and pressure used are based on common parameters in CVD processes of silicon carbide [6].

Transition-state energies and structures were obtained using the Synchronous Transit-Guided Quasi-Newton (STQN) method [24, 25] in the Gaussian 09 program, which uses a quadratic synchronous transit (QST) approach [26] followed by a quasi-Newton algorithm.

Table 1. The partial pressure used in the calculations of thermodynamical properties.

Molecule	Pressure [atmospheres]
H ₂	0.1
SiCl ₂	0.0004
SiH ₂	0.0004
HCl	0.0016

The influence from spin multiplicity on the molecular energies was investigated for the two molecules SiH₂ and SiCl₂, see table 2. As can be seen, the energy for the singlet state is lower than the energy for the triplet state for both SiH₂ and SiCl₂. Henceforth the singlet state is used as default state for these molecules. Similar result for the SiCl₂ molecule was reported in [27]. From table 2 it is seen that the agreement is good between the B3LYP/6 31G(d,p) results and the results using MP2 or CCSD(T) together with a large basis set.

Table 2. Bond length, angles and energy difference between singlet and triplet states for SiH₂ and SiCl₂ using different methods and basis set. X denotes Cl and H respectively. E_t – E_s is the difference between the triplet state and singlet state energies.

Structure	Method	Si–X [Å]		XSiX angle [°]		E _t – E _s [kJ mol ⁻¹]
		Singlet	Triplet	Singlet	Triplet	
SiH ₂	B3LYP/DZ	1.56	1.50	91.2	118.7	73
	B3LYP/6-31G(d,p)	1.53	1.49	91.3	118.4	83
	B3LYP/6 311++G(2df,2pd)	1.52	1.49	91.6	118.6	86
	MP2/6-311++G(2df,2pd)	1.51	1.47	92.2	118.2	67
	QCISD(T)/6-311++G(2df,2pd)	1.52	1.48	92.3	118.3	83
SiCl ₂	B3LYP/DZ	2.24	2.22	101.8	120.4	221
	B3LYP/6-31G(d,p)	2.11	2.08	102.3	119.1	222
	B3LYP/6 311++G(2df,2pd)	2.10	2.07	101.8	118.6	223
	MP2/6-311++G(2df,2pd)	2.08	2.05	101.3	118.6	213
	QCISD(T)/6-311++G(2df,2pd)	2.09	2.06	101.6	117.6	221

3 Results and Discussion

3.1 SiC clusters

3.1.1 Structures and cohesive energies

For hydrogen-terminated clusters (Fig. 1), the silicon-carbon bond lengths were found to be 1.915 ± 0.01 Å in the bulk and 1.895 ± 0.01 Å at the surface after geometry optimization. The angles between silicon-carbon bonds were $109.4^\circ \pm 0.2^\circ$ for bonds inside the cluster and somewhat larger ($110.5^\circ \pm 0.5^\circ$) for angles between silicon-carbon bonds at the surface. Thus the bond lengths and angles of the clusters are close to the initial bond-lengths of 1.89 Å and the bond angles of 109.5° calculated from the experimental lattice parameters.

Fig. 1 The different hydrogen-terminated clusters used, a-f: two layer triangular shape, g-i: two layer round shape, j-m: four layer triangular shape, n-p: six layer triangular shape. The cluster pictures were drawn using Moviemol [28].

If the clusters in Fig. 1 were geometry-optimized without the hydrogen termination the structures were significantly deformed. The silicon-carbon bond lengths varied to a large extent, i.e. 1.80-1.96 Å. More important, the angles between silicon-carbon bonds deviated from the crystal angle of 109.5° by up to 5° inside the clusters and up to 30° between bonds at the surface. The two-layer clusters obtained cage-like structures and the silicon-carbon bond length decreased to an average of 1.83 Å. An example of this is shown in Fig. 2 for the cluster from Fig. 1b stripped of its hydrogens. The same behaviour has been observed in GaN clusters [29]. The large surface relaxation in clusters covered with dangling bonds makes them less suitable as models for the

crystal surface when studying the adsorption processes; in the present study the H-terminated clusters (in some cases with one or two H vacancies) were used.

Fig. 2 The $\text{Si}_{22}\text{C}_{22}$ structure, a two-layer cluster without hydrogen termination after the geometry was relaxed.

Due to the large amount of dangling bonds in a cluster without hydrogen termination its favoured spin state is not obvious. The effect of spin multiplicity on the cluster energy was investigated for one cluster without hydrogen termination (Fig 2). Geometry optimizations using different spin states showed that the singlet state was lower in energy than the triplet state by 49 kJ mol^{-1} , and the energy increased for higher spin multiplicities.

The cohesive energies per SiC unit for the hydrogen-terminated clusters were calculated using two different methods. The first method uses the following formula to calculate the cohesive energy per SiC unit:

$$\Delta E_{coh} = \frac{E_{tot} - n(E_{Si} + E_C) - m \frac{E_{H_2}}{2}}{n} \quad (1)$$

E_{tot} is the total potential energy of the geometry-optimized hydrogen-terminated SiC cluster, obtained from the quantum-chemical calculation (i.e. the sum of the electron-electron, nuclei-nuclei and electron-nuclei potential energies plus the electron kinetic energies). n is the number of SiC units, E_{Si} is the energy for a free silicon atom, E_C is the energy for a free carbon atom, m is the number of hydrogen atoms. E_{H_2} is the energy for a hydrogen molecule.

In the second method, the energy contributions from the hydrogen atoms at the surface were subtracted. The idea was to thereby remove the surface energy from the cohesive energies. The following formula was used:

$$\Delta E_{coh} = \frac{E_{tot} - n(E_{Si} + E_C) - mE_{H,surf}}{n} \quad (2)$$

E_{tot} is the total electronic energy (i.e. the potential energy of the nuclei) for the hydrogen-terminated SiC cluster as before. m is the number of hydrogen atoms. $E_{H,surf}$ is estimated from the energy difference between a fully

hydrogen terminated cluster and a cluster with one hydrogen atom removed, averaged over different hydrogen atoms.

The cohesive energy variation with respect to size of the cluster is displayed in Fig. 3. Presuming that the cluster energy depends approximately linearly on both surface area and on the volume the relationship between total energy per SiC unit and number of SiC units can be derived.

$$\frac{E_{tot}}{n} = a \cdot n^{-1/3} + b \quad (3)$$

where a and b are constants and n is the number of SiC units. Thus the trend will be that the cohesive energy per SiC unit (ΔE_{coh}) will depend approximately linearly on the number of units raised to the power of minus one third ($n^{-1/3}$).

In Fig. 3, both methods for estimating the cohesive energy are shown using a subset of clusters that increase in size simultaneously in three dimensions, see fig 1 a-c. As Fig. 3 shows, both methods extrapolate to the same value of the cohesive energy per SiC unit, $\sim 1700 \text{ kJ mol}^{-1}$, when the cluster size approaches infinity. That the two formulas extrapolate to the same value is to be expected since the surface effects are negligible for very large clusters.

Fig. 3 Cohesive energy per SiC unit versus number of SiC units raised to minus one third. The two different methods used are described in the text, equation (1) and (2). The clusters used are shown in Figs. 1a, 1l and 1p.

3.1.2 Band gap

The band-gap energies for the clusters were estimated from the energy differences between the highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs), see Fig. 4. The band gap is relatively large for the small clusters which can be attributed to the quantum confinement effect [30] and decreases with increasing cluster size. In Fig. 5, band gap energies for a subset of clusters, chosen to increase simultaneously in size in all three dimensions, are plotted. The extrapolated value of the band gap as the cluster size grows toward infinity is 4.17 eV, which may be a rather crude estimation since only three data points were used in the extrapolation. For comparison the experimental value for the band gap in 4H-SiC is 3.2 eV [31].

Fig. 4 Band gap energies plotted versus cluster size. The B3LYP functional and the basis set 6-31G(d,p) were used. The cluster structures are displayed in Fig. 1.

Fig. 5 Band gap versus number of SiC units to the power of -0.53 for a set of clusters whose sizes were uniformly increased in three dimensions, see Figs. 1a, 1l and 1p.

3.2 Surface Reactions

Reactions for SiH_2 and SiCl_2 at the SiC surface were studied. Also the reaction energy for removal of hydrogen from the surface was investigated. The cluster used to model the SiC (000-1) surface was the hydrogen-saturated triangular shaped $\text{H}_{60}\text{Si}_{33}\text{C}_{33}$ cluster shown in Fig. 1c.

3.2.1 Subtraction of surface hydrogen

An initial study was carried out of the energetics of subtraction of hydrogen from the surface of the hydrogen-terminated SiC cluster:

The reaction energy ΔE for the removal of one surface hydrogen was found to be 198 kJ mol⁻¹. Removal of a second, adjacent, hydrogen corresponded to the reaction energy 309 kJ mol⁻¹. (If instead the product is the radical $\text{H}(\text{g})$ rather than the molecular hydrogen, the reaction energy for removal of the first hydrogen is 432 kJ mol⁻¹ and for the second 543 kJ mol⁻¹. These can be compared to the internal energy reaction energies 367 and 587 kJ mol⁻¹ obtained in Ref. [10].)

The reaction Gibbs free energies for removal of one surface hydrogen to form molecular hydrogen was found to be 40 kJ mol⁻¹ at the H_2 pressure in table 1. Interestingly, for removal of the second hydrogen the free energy

difference is -40 kJ mol⁻¹, which means that Gibbs free energy difference when two neighbouring hydrogen are removed is about 0 kJ mol⁻¹. The reaction Gibbs free energy for removal of all hydrogen on the (000-1) surface of the cluster is about 42 kJ mol⁻¹ per hydrogen atom, i.e. the bare surface is thermodynamically less stable than the hydrogenated surface in agreement with the result in Ref. [10]. But the close to zero reaction Gibbs free energy for the removal of a pair of hydrogen indicates that this kind of missing-neighbouring pair of hydrogens might be a not uncommon type of defect at CVD growth conditions.

3.2.2 Adsorption of SiH₂ and SiCl₂

Adsorption of SiH₂ and SiCl₂ was studied by allowing the molecules to replace one adsorbed hydrogen atom, see reaction 1 and 2 in table 3 and Fig. 6a, or allowing them to replace two adsorbed hydrogen atoms to form a Si bridge between two carbon atoms in the surface, see reaction 3 and 5 in table 3 and Fig. 6b. An alternative studied adsorption mechanism is to let two SiH₂ or SiCl₂ molecules replace two adsorbed hydrogen atoms, forming two Si-C bonds to two carbon atoms in the surface, see reaction 4 and 6 in table 3 and Fig. 6c. H₂(g) is formed as byproduct in the reactions above. Further, adsorption was also studied by letting a SiH₂ or SiCl₂ replace one adsorbed hydrogen atom, forming a Si-C bond, and then transfer the hydrogen to the Si atom, forming an additional Si-H bond, see reaction 7 and 8 in table 3.

Table 3. The adsorption reaction energies for various adsorption types for SiH₂ and SiCl₂ on the model SiC (000-1) surface in Fig. 1c. The Gibbs free energy was calculated using a temperature of 1870 K and pressures according to table 1. The functional B3LYP together with the basis set 6-31G(d,p) was used.

	Reaction	Adsorption reaction energy	
		ΔE [kJ mol ⁻¹]	ΔG [kJ mol ⁻¹]
1.	SiH ₂ (g) + H(ads) → SiH ₂ (ads) + ½H ₂ (g)	-57	199
2.	SiCl ₂ (g) + H(ads) → SiCl ₂ (ads) + ½H ₂ (g)	27	305
3.	SiH ₂ (g) + 2H(ads) → SiH ₂ (ads) + H ₂ (g)	-14	146
4.	2SiH ₂ (g) + 2H(ads) → 2SiH ₂ (ads) + H ₂ (g)	-395	219
5.	SiCl ₂ (g) + 2H(ads) → SiCl ₂ (ads) + H ₂ (g)	105	261
6.	2SiCl ₂ (g) + 2H(ads) → 2SiCl ₂ (ads) + H ₂ (g)	-184	447
7.	SiH ₂ (g) + H(ads) → SiH ₃ (ads)	-214	206
8.	SiCl ₂ (g) + H(ads) → SiCl ₂ H(ads)	-123	334

Fig. 6 The adsorbed molecules in reaction 1, 3 and 4. The corresponding structures for SiCl_2 are very similar and are therefore not shown.

The adsorption reaction energies were calculated according to the formula $\Delta E_{\text{ads}} = \Sigma E(\text{products}) - \Sigma E(\text{reactants})$.

This definition of adsorption reaction energy gives a negative value for the adsorption energy when there is a decrease in total energy for the system, implying an exothermic process and an energetically favourable adsorption, or attraction. The adsorption reaction energies are shown in table 3.

In reaction 1 and 2, one molecule is adsorbed and one half hydrogen molecule is removed. The adsorption reaction energies (ΔE) are -57 kJ mol^{-1} for SiH_2 and 27 kJ mol^{-1} for SiCl_2 and the position of the silicon atom of the molecule is close to that of a crystal lattice position. The silicon-carbon bond length ($1.89 \text{ \AA}$) to the adsorbed silicon is $0.02 \text{ \AA}$ shorter than the mean value for silicon-carbon bond lengths for both SiH_2 and SiCl_2 . The adsorbed silicon is negligible tilted for the SiH_2 molecule and for the SiCl_2 molecule roughly 6° tilted compared to the geometry optimized crystal structure. There is a negligible deformation in the cluster and thereby insignificant strain.

The adsorption reaction energies are low for reaction 3 and even positive for reaction 5. In reaction 3 and 5, the molecules are adsorbed by forming bonds to two adsorption sites and thereby saturating its dangling bonds, but the surface structure is deformed in the adsorption process, since the two adsorption sites are brought closer together, see Fig. 6 b. The deformation creates a strain in the cluster which increases its total energy.

In reactions 4 and 6, two molecules adsorb at two adjacent sites. The adsorption energies indicate that these reactions are more favourable compared to reactions 3 and 5. Also, for this adsorption mode, the silicon positions at the surface are more similar to those in the crystal structure. In this structure the two silicon atoms in the adsorbed molecules have one unsaturated bond each which leads to an attraction between the two molecules,

resulting in a silicon-silicon bond. Thereby the silicon atoms obtain standard sp^3 hybridizations, see Fig. 6 c.

This type of reaction creates none, or only a very small, deformation on the cluster, therefore no significant strain is present.

In reaction 7 and 8 there is no release of hydrogen molecules. Instead the hydrogen atom is transferred to the $SiH_2/SiCl_2$ molecule, creating an adsorbed SiH_3 and $SiCl_2H$ molecule respectively, which chemisorbs at the site where the hydrogen was initially located. Reactions 7 and 8 result in the largest adsorption reaction energy magnitudes per adsorbed molecule. These reactions result in structures where the silicon atom in the adsorbed molecule is situated close to the expected crystal lattice location. There is negligible deformation in the cluster. Also, due to the formation of the additional Si-H bond, the adsorbed silicon atom has no dangling bonds.

To study the influence of cluster size on the reaction energies, reactions 7 and 8 were also modelled on the larger $H_{72}Si_{46}C_{46}$ cluster (Fig. 1k) with the resulting adsorption reaction energies ΔE -211 kJ mol^{-1} and -116 kJ mol^{-1} , respectively. These values agree favourably with the energies in Table 3 where the smaller cluster $H_{60}Si_{33}C_{33}$ (Fig. 1c) was employed.

At typical SiC CVD temperatures, the surface has been reported to be hydrogen terminated [10]. However, as shown above in section 3.2.1, the formation of hydrogen vacancies in the surface termination is thermodynamically favourable. If the hydrogen termination is not complete, there are a number of free adsorption sites available on the surface and an alternative form of adsorption reaction, similar to reaction 1-6 but without the abstraction of hydrogen, would be possible. These types of reactions will not break any C-H bonds. As a result these reactions will give much stronger adsorption energies compared to reactions 1-6, where two C-H bonds are broken and one H-H bond is created, see table 4.

Table 4. The adsorption reaction energies for SiH₂ and SiCl₂ reacting with the hydrogen-terminated SiC surface with one or two H(surf) vacancies. The Gibbs free energy was calculated using a temperature of 1870 K and pressures according to table 1. The functional B3LYP together with the basis set 6-31G(d,p) was used.

	Reaction	Adsorption reaction energy	
		ΔE [kJ mol ⁻¹]	ΔG [kJ mol ⁻¹]
9.	SiH ₂ (g) + [single H(surf) vacancy] → SiH ₂ (ads)	-255	159
10.	SiCl ₂ (g) + [single H(surf) vacancy] → SiCl ₂ (ads)	-170	265
11.	SiH ₂ (g) + [double H(surf) vacancies] → SiH ₂ (ads)	-529	146
12.	2SiH ₂ (g) + [double H(surf) vacancies] → 2SiH ₂ (ads)	-905	220
13.	SiCl ₂ (g) + [double H(surf) vacancies] → SiCl ₂ (ads)	-426	261
14.	2SiCl ₂ (g) + [double H(surf) vacancies] → 2SiCl ₂ (ads)	-724	448

When considering all reactions 1-8 in table 3 one can see that the SiH₂ molecule overall has lower adsorption reaction energy, roughly 100 kJ mol⁻¹ per adsorbed molecule lower compared to the SiCl₂ molecule, i.e. it is more favourable to adsorb SiH₂ than SiCl₂. The same results are obtained when letting the two molecules adsorb at vacancy sites, see table 4.

When studying the Gibbs free energies for all reactions in table 3 and 4 one can notice a large difference from the behaviour of the ordinary adsorption energies. The low concentration of SiH₂ and SiCl₂ compared to H₂ and the low overall pressure in the chamber results in low partial pressures for these two molecules and therefore they are favoured to exist as free particles in the reactions. This leads to a positive value of the adsorption reaction Gibbs free energy, which means that these equilibrium distributions are heavily displaced toward the reactants.

For reaction 7 and 8 (table 3), the transition states between physisorbed and chemisorbed configurations were located and the activation energies for the adsorption were computed, see table 5. The reaction paths are visualized in Fig. 7. At the transition state, the Si(molecule)-C(surface) distances are 2.38 Å for SiH₃ and 2.39 Å for SiCl₂H. The H(molecule)-C(surface) distances at the transition state are 1.57 Å for SiH₃ and 1.62 Å for SiCl₂H. At the chemisorbed state the corresponding numbers are 1.93, 1.90, 2.85, 2.87 Å.

Table 5. The local-minimum energies for SiH₂(ads), SiCl₂(ads) and their transition state energies relative the free molecules in kJ mol⁻¹. The B3LYP functional and the 6-31G(d,p) basis set were used.

Molecule	ΔE		
	Physisorbed state	Transition state	Chemisorbed state
SiH ₂	-11	77	-214
SiCl ₂	-18	216	-123

Fig. 7 Reaction paths for the conversion between physisorbed and chemisorbed adsorption states of SiH₂ (red) and SiCl₂ (green).

As can be seen in Fig. 7 and table 5 the adsorption reaction of SiH₂ has a lower activation energy (88 kJ mol⁻¹) than the corresponding reaction with SiCl₂ (234 kJ mol⁻¹) has, implying faster adsorption rates for SiH₂ than for SiCl₂. One can also notice that the physisorption is stronger for the SiCl₂ molecule (7 kJ mol⁻¹ stronger), implying a greater tendency to stick to the surface, which is important to initialize the reaction. (It should be noted here that the physisorption energies obtained by B3LYP are uncertain due to the incomplete description of dispersion interactions by this functional. But since the physisorption energies anyhow will be small, this does not influence the discussion significantly.) Further, one can also notice that when the two molecules have been adsorbed (i.e. chemisorbed) it requires larger activation energy to desorb the SiCl₂ molecule (339 kJ mol⁻¹)

compared to the SiH_2 molecule (291 kJ mol^{-1}). The chloride-based CVD chemistry thus seems to provide a more stable surface chemistry during growth, in that once chemisorbed the SiCl_2 molecule should have a lower tendency to desorb than the SiH_2 molecule.

3.2.3 Diffusion

Apart from surface adsorption, surface diffusion is also highly important for a CVD process, especially for epitaxial growth processes. One possible diffusion path on a hydrogen-terminated SiC surface would be the reaction path described in Fig. 7 if both forward and backward directions are combined. An adsorbed molecule would become desorbed by going in the backward reaction path direction. Then the molecule is free to move near the surface to a new position where it readsorbs, which is equivalent to going in the forward reaction path direction. This diffusion path would, using the chemisorption and transition state energies in table 5, have activation energies of 291 kJ mol^{-1} for SiH_2 and 339 kJ mol^{-1} for SiCl_2 . Hence SiH_2 should diffuse more easily on the surface according to this reaction path.

Diffusion of SiH_2 and SiCl_2 on a bare surface was also studied. A diffusion transition state was found for SiCl_2 located symmetrically in between the initial and final states seen in Fig. 8, with an activation energy of 107 kJ mol^{-1} . For the SiH_2 molecule this conformation was actually a shallow minimum, with two symmetrically located transition states between the initial/final and shallow minimum structure. The activation energy of SiH_2 is 121 kJ mol^{-1} (the energy of the shallow minimum is 118 kJ mol^{-1}).

Fig. 8 Visualization of the reaction path for SiCl_2 diffusion. The corresponding path for SiH_2 is visually very similar.

The diffusion activation energies for SiH_2 and SiCl_2 are thus similar with a slightly lower value for SiCl_2 . These activation energies are considerably smaller compared to the activation energy for diffusion on a hydrogen-terminated surface described earlier, 121 compared to 291 kJ mol^{-1} for SiH_2 , and 107 compared to 339 kJ mol^{-1}

for SiCl_2 . Thus in this model, SiH_2 and especially SiCl_2 diffuse more easily on a bare surface than on a hydrogen-terminated surface.

4 Conclusions

Studies of the adsorption of SiH_2 and SiCl_2 on the SiC (000-1) surface showed that the SiH_2 molecule generally adsorbed roughly 100 kJ mol^{-1} more strongly than the SiCl_2 molecule. The activation energy for adsorption of SiH_2 on a fully hydrogen-terminated surface was roughly 140 kJ mol^{-1} lower than corresponding activation energy for SiCl_2 . It should be noted that these activation energies also implies that once adsorbed, the SiCl_2 molecule has a lower tendency to desorb than the SiH_2 molecule. Another observation was that the SiCl_2 molecule physisorbed somewhat stronger than the SiH_2 molecule on the hydrogen terminated surface. This might be an important property to initialize the adsorption reaction.

For surface diffusion of SiH_2 and SiCl_2 on the fully hydrogen-terminated SiC surface, the activation energy for SiH_2 was 50 kJ mol^{-1} lower compared to that for the SiCl_2 molecule. On a SiC surface without hydrogen termination, these activation energies were significantly lower: 121 compared to 291 kJ mol^{-1} for SiH_2 and 107 kJ mol^{-1} compared to 339 kJ mol^{-1} for SiCl_2 . On the bare surface the SiCl_2 molecule has the lowest activation energy by 14 kJ mol^{-1} . Thus SiH_2 will diffuse more easily compared to SiCl_2 on a fully hydrogen terminated surface. Both molecules will diffuse more easily on a bare surface and here the SiCl_2 molecule diffuses slightly more easily than the SiH_2 molecule.

Since the silicon growth specie in a chloride-based SiC CVD process, SiCl_2 , once chemisorbed has a lower tendency to desorb than SiH_2 , this implies that with a chlorinated chemistry the chemisorbed Si atoms are more likely to build up the SiC epitaxial layer. Thus, these results suggest that chlorinated chemistry constitutes a good choice for CVD growth of SiC epitaxial layers.

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