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Silicon Chemistry in Fluorinated Chemical Vapor Deposition of Silicon Carbide

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Abstract

The use of chlorinated chemical vapor deposition (CVD) chemistry for growth of homoepitaxial layers of silicon carbide (SiC) has diminished the problem of homogenous gas phase nucleation, mainly the formation of Si droplets, in CVD of SiC by replacing Si-Si bonds with stronger Si-Cl bonds. Employing the even stronger Si-F bond could potentially lead to an even more efficient CVD chemistry, however, fluorinated chemistry is very poorly understood for SiC CVD. Here, we present studies of the poorly understood fluorinated CVD chemistry for homoepitaxial SiC layers using SiF₄ as Si precursor. We use a combination of experimental growth studies, thermal equilibrium calculations of gas phase composition and quantum chemical computations (i.e. hybrid density functional theory) of the surface chemistry to probe the silicon chemistry in the CVD process. We show that while growth rates on the order of 35 $\mu\text{m/h}$ can be achieved with a fluorinated chemistry, the deposition chemistry is very sensitive to the mass flows of the precursors and not as robust as the chlorinated CVD chemistry which routinely yields 100 $\mu\text{m/h}$ over wide conditions. By using the position for the onset of epitaxial growth along the gas flow direction as a measurable, together with modeling, we conclude that SiF is the main Si growth species with SiHF as a minor Si species contributing to growth.

1. Introduction

The material properties of silicon carbide (SiC) make it suitable for high power semiconductor devices,^{1,2} where its wide band gap (3.26 eV for the 4H-SiC polytype) and high electric breakdown field strength ($2 \cdot 10^6$ V/cm) make it possible to block high voltages. Chemical vapor deposition (CVD) is by far the most suitable technique to produce the high quality, thick, low doped epitaxial layers needed for these devices. CVD of epitaxial SiC films is typically done at high temperatures (1500 – 1750 °C) with the Si and C precursor molecules heavily diluted in a hydrogen carrier gas. A limiting factor for the increase in growth rate by increasing the amount of precursor, is the onset of homogeneous gas phase nucleation – typically formation of silicon clusters – at too high concentrations of precursors in the gas mixture. This limitation can be circumvented by adding chlorine (Cl) to the process,³ since it binds stronger to Si (Si-Cl 417 kJ/mol⁴) than Si to Si (Si-Si 310 kJ/mol⁴), thereby hindering silicon clustering and allowing for a higher precursor concentration and an increased growth rate of epitaxial SiC layers. This chemical route has been thoroughly investigated and developed.⁵ It has recently been shown that bromine (Br) also has the effect of hindering silicon cluster formation and that the growth rate can be further increased by substituting Cl with Br. The Si-Br bond (Si-Br 358 kJ/mol⁴) is stronger than the Si-Si bond but weaker than the Si-Cl bond. The somewhat weaker Si-Br bond is believed to lead to lower activation barriers in the gas phase and surface chemistry, leading to the somewhat higher growth rate observed for brominated CVD chemistry compared to chlorinated CVD chemistry.⁶ Further, it has been shown by Rana et al.⁷ that silicon clusters can be fully eliminated by using SiF₄ as the Si precursor. This report (Ref. 7) is the first report on using SiF₄ as Si precursor for CVD of SiC but does not discuss the possible chemistry in a fluorinated CVD route to SiC. The Si-F bond is the strongest Si-halogen bond (Si-F 576 kJ/mol⁴) which makes SiF₄ a very stable molecule. The

mechanisms behind growth with such a stable molecule therefore become interesting, why we here further investigate the fluorinated chemistry. We employ a combination of CVD experiments and thermochemical and quantum chemical modelling in an effort to elucidate the chemistry of the silicon species in fluorinated CVD of SiC. In the extension, these results will be important for an overall understanding of halogenated CVD of SiC.

2. Methods

Experimental details.

SiC samples were grown using an inductively heated horizontal hot wall CVD system. The precursors SiF_4 and C_2H_4 were diluted in Pd membrane purified H_2 and introduced through a quartz liner connected *via* a graphite continuation to the susceptor. The susceptor, 190 mm long, 78 mm wide and 24 mm high in inner dimensions, was positioned in an RF heated graphite container which on the outside was isolated with rigid graphite. The whole package was then placed in a quartz tube. SiC substrates of 4H Si-face 4° off-cut in the (11-20) direction, $16 \times 16 \text{ mm}^2$ in size, were placed at certain positions along the center line of the susceptor bottom. For the experiments, the temperatures were 1600 °C and 1650 °C, the pressure was 100 mbar and the carrier gas flow was 25 standard l/min (SLM) as well as 37.5 SLM where explicitly written. The precursor gas flow ratios Si/ H_2 and C/Si were varied between 0.125 % – 1.0 % and 0.125 – 1.2, respectively. To emphasize that these ratios are determined from the flow of precursors, controlled by electronic mass flow controllers going into the growth chamber, they will be referred to as inlet ratios throughout this paper.

As SiF_4 is used together with hydrogen, the formation of hydrogen fluoride (HF) inside the quartz tube is inevitable. Security precautions related to HF as a byproduct from the process is discussed in the Supporting information.⁸ No etching of the reactor's quartz tube could, however, be seen, which is well in line with previous findings, that quartz is not etched by HF unless water is present⁹ and the temperature of the quartz is below $\sim 700^\circ\text{C}$ ¹⁰. Detailed CFD simulations show that the temperature on the quartz tube, and the gas close to it, downstream of the susceptor, is around 200°C , even though the gas leaving the susceptor has a much higher temperature. This is because of the vortices created in the gas at the susceptor exit, which leads to a good mixing of hot and cool gas closer to the quartz tube wall, and the slow backflow of cool gas closest to the quartz tube wall that is an effect of the vortices created. The thickness of the epitaxial layers was measured from the sample cross section in a scanning electron microscope (SEM) after the sample had been cleaved. Approximately 2 mm from each side of the sample were excluded to avoid edge effects.

Thermodynamic equilibrium modelling.

To understand the SiC growth process better, various modeling methods can be used to estimate the composition of the gas mixture at the growth surface, which species contribute to growth, and the rate of surface reactions that determine *e.g.* the growth rate. The composition of the gas mixture is a result of a vast number of gas phase reactions. It is in principle possible to compose a model with all these reactions and simulate the concentrations of each species in the gas for a realistic representation of the CVD reactor, using *e.g.* Computational Fluid Dynamics (CFD). However, the necessary input data for such a model, such as reaction rate constants or activation energies, are not easily obtained or found in literature. On the other hand, temperatures in the SiC CVD process are very high and thus gas phase reactions will be fast. The typical mean time for the gas phase

reactions is of the order of nanoseconds, while the residence time for the gas in the hot zone of the reactor is of the order of 0.1 seconds at typical growth conditions. This means that, as an approximation, we can use thermodynamic equilibrium calculations to estimate the gas phase composition at various process conditions.

Here, thermodynamic equilibrium in the Si-C-F-H system was calculated by minimization of Gibbs free energy for the conditions $T = 1600\text{ }^{\circ}\text{C}$, $p = 100\text{ mbar}$, inlet $\text{Si}/\text{H}_2 = 0.25\%$, inlet $\text{C}/\text{Si} = 1.0$, inlet $\text{F}/\text{Si} = 4.0$. Then, one parameter at a time was varied, while keeping the others constant at their standard value. Since one can choose which species that are allowed to form in such calculations, there is a risk that wrong conclusions might be drawn if the set of molecules is too limited. Here, we have allowed in total 153 different species to form, with their thermochemical properties taken from recent and updated literature sources. The set of allowed species include hydrocarbons and silicon hydrides with up to five carbon or silicon atoms, organosilicon species with one and two silicon atoms and up to four carbon atoms,¹¹ pure carbon and silicon molecules from C to C_6 and Si to Si_6 , and all Si_xC_y where $2 \leq x+y \leq 6$,¹² as well as the complete sets of the SiH_nF_m and CH_nF_m molecules ($n + m \leq 4$).¹³ No condensed phases were allowed to form, a common approach for probing the gas-phase composition before it reaches the substrate, but the larger Si and Si-C molecules (such as Si_6 or Si_5C) could be thought of as embryos to solid particles in the gas.

The equilibrium calculations give the approximate composition of the gas phase at the selected conditions. However, there is a concentration gradient towards the surface caused by the deposition of species, and the mass transport to the surface is driven by this gradient. Therefore the concentration at the surface will not be the same as further above the surface, even if the temperatures are the same. One commonly used approach to estimate the concentrations of each

species at a surface is by using the Maxwell-Boltzmann velocity distribution, so that the number of moles striking the surface per unit area and unit time is

$$\Phi_i = \frac{p_i}{\sqrt{2\pi M_i RT}} \quad (\text{Eq. 1})$$

where p_i is the partial pressure of species i , and M_i its molar mass. This expression provides a reasonably good approximation, and it has been used for the analysis below to derive the variation in impingement rate depending on temperature, inlet Si/H₂ ratio and inlet C/Si ratio.

Surface chemistry modelling.

Thermodynamic equilibrium computations enable prediction of the gas phase composition as the system approaches equilibrium and gives us an idea of which species that are likely to be present in the gas phase. To determine whether or not these species actively participate in the growth, and if so to what degree, requires the knowledge of the process Gibbs free energies. For this, we have used quantum chemical hybrid density functional theory (DFT) to study the gas species reactions with the surface, where we modeled the adsorption process using a SiC cluster, Si₁₃C₁₃H₃₂, which consists of two Si-C bilayers. The perfect symmetry of a SiC slab has been retained by terminating the dangling bonds near the edges with hydrogen atoms. The Si face of the cluster, namely the (0001) surface, was chosen as the adsorption surface which provided a planar area of 3 interconnected hexagonal SiC rings. The correct Si-C stoichiometry has been imposed for all cases. To accommodate the landing of a Si species we assumed the presence of either a methyl (-CH₃) or a methylene (CH₂) group already attached to the surface as the adsorption site.

The quantum chemical calculations were performed using the Gaussian 09 software.¹⁴ The equilibrium structures as well as transition states were optimized using the B3LYP functional^{15,16}

and the LanL2DZ basis set^{17,18} with dispersion correction (D3)¹⁹. The systems were allowed to fully relax during the optimization. Harmonic vibrational frequencies were calculated using the same functional, basis set and dispersion correction. To improve the accuracy of energy prediction, we replaced the B3LYP electronic energies with single-point calculated energies using the M06-2X functional²⁰ together with the G3LargeXP basis set from the Gaussian-4 theory.²¹ All transition states were verified by visualizing the displacement from the imaginary frequency vibration or following the intrinsic reaction coordinates to the reactant and product states. The changes in free energies were defined with respect to the reactants in the ground state. From the free energy difference between the transition state (saddle point) and the reactant state, the classical transition state theory provides prediction of the forward reaction rate constant and, as a consequence, the molecular sticking coefficients which is the probability of a molecule to deposit per hit (see Supporting information for detailed derivation⁸). The Si₁₃C₁₃H₃₂ cluster has been tested against a larger cluster (Si₂₂C₂₂H₄₄) where it has been shown to provide results in good agreements to the larger cluster for the adsorptions on a methyl group at the same level of calculations as used here in this study. Differences of less than 3 kJ/mol for the Gibbs free energies of reactions and less than 10 kJ/mol for the Gibbs free energies of activation were observed in between the two different cluster sizes over the temperature range of 400 – 2200 °C.⁸

3. Results

We note experimentally that the growth rate along the gas flow direction in the susceptor always assumes a profile, schematically shown in Fig. 1.

Figure 1. Schematic growth rate versus position in the susceptor, *i.e.* distance from the inlet.

From the susceptor inlet and a short distance into the susceptor the growth rate is zero or only a few $\mu\text{m/h}$ until a certain position where an abrupt increase to the maximum growth rate is observed. The spatial extension of the increase, which depends on the process parameters, is typically 1–3 cm along the susceptor. From the position after this short extension the growth rate slowly decreases along the susceptor. This decrease is similar to what has been observed for chlorinated SiC CVD.^{22,23} After the growth rate increase, at the same position as the growth rate reaches its maximum, the growth also becomes epitaxial. This transition to epitaxial growth is such abrupt that the position for it is easily recognized. This position will in the following be referred to as the onset of epitaxial growth. Prior to the onset of epitaxial growth, the surface is completely covered with triangular surface defects of different sizes and shapes. The onset of the epitaxial growth at the sides of the susceptor is situated closer to the inlet. Here we will discuss the onset position as where it is most downstream observed, *i.e.* in the middle of the susceptor. The following sections will describe how the position for the onset of epitaxial growth shifts depending of process parameters, *i.e.* precursor concentrations and temperature.

Related to this, we also note that by changing the temperature and precursor gas flow rates we can also change the height (*i.e.* maximum growth rate) and slopes of this profile. Changes in carrier

gas flow did not seem to impact on the position for the onset of epitaxial growth. The growth rates achieved are typically $\sim 20 \mu\text{m/h}$ when similar experimental setup and parameters in the brominated and the chlorinated chemistries of SiC CVD yields $\sim 100 \mu\text{m/h}$.^{6,24}

The dependence on the inlet C/Si ratio.

It has been shown for fluorinated CVD of SiC on on-axis 4H SiC (0001) substrates that the growth rate is limited by the amount of carbon containing species (C-limited) for higher inlet C/Si ratios.²⁵

We find, however, that the onset of epitaxial growth also changes with the inlet C/Si ratio as shown in Fig. 2, where the onset of epitaxial growth shifts downstream in the susceptor for increased inlet C/Si ratio.

Figure 2. Growth rate profiles for different inlet C/Si ratios (labels) at $T = 1650 \text{ }^\circ\text{C}$ and inlet $\text{Si/H}_2 = 0.125 \%$ with $Q = 25 \text{ SLM}$. The onset of epitaxial growth shifts with inlet C/Si ratio. For inlet $\text{C/Si} = 1.2$ the onset of epitaxial growth is at $\sim 9 \text{ cm}$ from the inlet, for inlet $\text{C/Si} = 1.05$ it is at $\sim 4 \text{ cm}$ and for inlet $\text{C/Si} \leq 0.9$ it is at $< 3 \text{ cm}$. The decline in growth rate after the onset is $\sim 0.5 \mu\text{m/h/cm}$.

When increasing the inlet C/Si ratio to ≥ 1.5 , the onset of epitaxial growth does not appear within the susceptor length. Also, when lowering the inlet C/Si ratio to 0.9 the onset of epitaxial growth

appears upstream of the used sample positions. The C/Si ratio is not found to affect the rate of decrease in growth rate which is $\sim 0.5 \mu\text{m/h/cm}$ at 1650°C and inlet $\text{Si}/\text{H}_2 = 0.125\%$.

The dependence on the inlet Si/H_2 ratio.

The Si/H_2 ratio reflects the amount of precursors in the inlet gas mixture which, for SiC CVD, typically affects the growth rate. Here, we also find that the onset of epitaxial growth is shifted downstream when the inlet Si/H_2 is increased, keeping the inlet C/Si ratio constant, as seen in Fig. 3. The decline in growth rate in the epitaxial growth region increases with increased Si/H_2 ratio, but is here typically in the range of $1\text{--}2 \mu\text{m/h/cm}$.

Figure 3. Growth rate profiles for different inlet Si/H_2 ratios (labels) at $T = 1650^\circ\text{C}$ and inlet $\text{C}/\text{Si} = 0.5$ with $Q = 25$ SLM. The position for the onset of epitaxial growth shifts with inlet Si/H_2 ratio. For inlet $\text{Si}/\text{H}_2 = 0.125\%$ the position is < 3 cm from the inlet, for inlet $\text{Si}/\text{H}_2 = 0.25\%$ and 0.3125% it is ~ 4 cm and ~ 6 cm respectively. For inlet $\text{Si}/\text{H}_2 = 0.375\%$ position for the onset of epitaxial growth is not observed within 13 cm.

The combined dependence of the inlet Si/H_2 and C/Si ratio.

The onset of epitaxial growth is shifted downstream for both an increase in the inlet Si/H₂ ratio at a given inlet C/Si ratio and an increase in the inlet C/Si ratios at a given inlet Si/H₂ ratio. The onset of epitaxial growth can in other words be kept at the same position by decreasing one parameter and increasing another. The positions for the onset of epitaxial growth are tabulated in Table 1 and plotted in Fig. 4 for varied inlet Si/H₂ and inlet C/Si ratios at T = 1600 °C.

Inlet Si/H ₂ ratio (%)	Inlet C/Si ratio (1)	Position for Onset of epitaxial growth (cm)
0.125	0.8	6
0.125	0.9	8
0.125	1.0	>12
0.25	0.45	6
0.25	0.50	11
0.375	0.30	5
0.375	0.33	8
0.50	0.25	6
1.0	0.125	<2
1.0	0.135	4

Table 1. Listed positions for the onset of epitaxial growth at temperature 1600 °C for different combinations of inlet Si/H₂ and inlet C/Si ratios.

Figure 4. The position for the onset of epitaxial growth as labels in the unit of cm from the susceptor inlet depending on inlet Si/H₂ and inlet C/Si ratios at 1600 °C and Q = 25 SLM. Lines are inserted to connect the points with the same position for the onset of epitaxial growth (6 cm and 8 cm). Note the log₂ scale of the axes. The onset of epitaxial growth can be kept constant by changing the two ratios simultaneously.

Here it can be noticed that there are growth parameters that give the same position for the onset of epitaxial growth; two positioned at ~8 cm for [inlet Si/H₂, inlet C/Si] = [0.125 %, 0.9] and [inlet Si/H₂, inlet C/Si] = [0.375 %, 0.33], as well as three points having the same position for the onset of epitaxial growth at ~6 cm for the [inlet Si/H₂, inlet C/Si] ratio values [0.125 %, 0.8], [0.25 %, 0.45] and [0.50 %, 0.25]. These two lines, seen in Fig. 4, connecting the same positions exemplify that these positions are changed upstream for both a lower inlet Si/H₂ ratio and lower inlet C/Si ratio, *i.e.* towards the lower left corner in the figure. At the same time it is possible to see that small changes in the inlet ratios causes significant shifts in these positions. To keep the onset of epitaxial growth constant, the two parameters have to be changed almost oppositely.

This relationship between the parameters can also be visualized by relating the C precursor flow to inlet H₂ flow as inlet C/H₂ instead of to the inlet Si/H₂ flow as inlet C/Si. The inlet C/H₂ flow is related to the inlet Si/H₂ and inlet C/Si as

$$\text{inlet } \frac{C}{H_2} = \text{inlet } \frac{Si}{H_2} \times \text{inlet } \frac{C}{Si}, \quad (\text{Eq. 2})$$

which remains constant if one parameter is doubled and the other halved. This is shown in Fig. 5, where the positions for the onset of epitaxial growth are plotted as inlet Si/H₂ versus inlet C/H₂.

Figure 5. The position for the onset of epitaxial growth. The labels indicate distance in cm from the susceptor inlet depending on inlet Si/H₂ and inlet C/H₂ ratios at 1600 °C for Q = 25 SLM. Lines are inserted to connect the points with the same position for the onset of epitaxial growth (6 cm and 8 cm). The inlet C/H₂ axis is linear and the inlet Si/H₂ axis is in log₂ scale. Note the narrow scale of the inlet C/H₂ compared to inlet Si/H₂. The positions for the onset shift upstream for increased inlet Si/H₂ at constant inlet C/H₂ and downstream for increased inlet C/H₂ at constant inlet Si/H₂.

The figure shows for the position of onset of epitaxial growth at 6 cm that the amount of C precursor should be increased by only 25 % while the amount of Si precursor should be increased by 400 % to maintain the position, and thereby how much more sensitive the position for the onset of epitaxial growth is to changes in the amount of C precursor compared to the amount of Si precursor, and also that the inlet C/H₂ has to be reduced if the inlet Si/H₂ is reduced to maintain a constant onset of epitaxial growth position.

The dependence on temperature.

The influence of temperature on the position for the onset of epitaxial growth at temperatures T = 1600 °C and T = 1650 °C is shown in Fig. 6, where it is seen that the onset shifts upstream for higher temperatures.

Figure 6. Onset of epitaxial growth positions when

temperature and inlet C/Si are varied for inlet Si/H₂ = 0.125 % and Q = 25 SLM. The positions for the onset of epitaxial growth are shifted upstream with increased temperature for comparable parameters.

The growth rate.

Since the growth rate decreases along the gas flow direction, and the position where the growth rate has its maximum also varies for varying process parameters, it is difficult to find suitable values/positions for comparing growth rates at different conditions. By increasing the carrier gas flow rate by 50 % (from 25 SLM to 37.5 SLM), the slope of the decreasing growth rate along the gas flow direction was reduced, while maintaining the maximum growth rate for the same precursor flow rates. Fig. 7 shows the maximum growth rates vs. inlet Si/H₂ ratio at T = 1600 °C. Here, the inlet C/H₂ = 0.125 % was used. The variation in the growth rate shown here is not linear, although increasing for higher inlet Si/H₂ ratios. Based on the growth rate and amount of precursors used, we estimate the precursor utilization to be approximately 10 %.

Figure 7. Measured maximum growth rates for different inlet Si/H₂ ratios at T = 1600 °C and Q = 37.5 SLM.

Thermodynamic equilibrium calculations.

Under the assumptions made in the methods section we used thermodynamic equilibrium calculations to predict the gas phase composition and the impingement rates of each species (derived using Eq. 1), when varying temperature at constant inlet Si/H₂ and C/Si ratios of 0.25 % and 0.5, respectively, and when varying inlet Si/H₂ ratio at constant temperature and inlet C/Si ratio of 1600 °C and 0.5, respectively, as well as when varying inlet Si/H₂ ratio at constant inlet C/H₂ ratio and temperature of 0.125 % and 1600 °C, respectively. The species with the highest impingement rates are shown in Fig. 8.

Experimentally, growth rates were shown to be in the range of ~5 – 35 μm/h. 10 μm/h corresponds to an adsorption rate of $\sim 2 \cdot 10^{-4}$ mol/m²/s for each element.⁸ Therefore, all gas species with an impingement rate lower than $2 \cdot 10^{-5}$ mol/m²/s, corresponding to a maximum growth rate of ~1 μm/h, are excluded in the further discussion, since their contribution to the growth is considered to be less important. Gas species with an impingement rate higher than $2 \cdot 10^{-5}$ mol/m²/s at these conditions are, ordered by impingement rate, SiF₂, C₂H₂, CH₄, SiF, SiHF, CH₃, Si, SiF₄, SiHF₃,

C_2H_4 , SiH_2 , Si_2C , SiCH_2 , SiH , SiF_3 and SiC_2 . To clarify, species with two C or Si atoms, *e.g.* C_2H_2 and Si_2C , need half the impingement rate compared to a species with one C and/or Si species, *i.e.* $1 \cdot 10^{-5} \text{ mol/m}^2/\text{s}$, to provide a C or Si impingement rate on the surface of $2 \cdot 10^{-5} \text{ mol/m}^2/\text{s}$.

Figure 8. Impingement rates derived from thermodynamic equilibrium concentrations. a) and b) show the dependence on temperature. c) and d) show the dependence on inlet Si/H₂ when the inlet C/Si = 0.5, *i.e.* varying also C/H₂. e) and f) show the dependence on inlet Si/H₂ when inlet C/H₂ = 0.125 %. a), c) and e) show the species

without C, while b), d) and f) the species containing C. $F/Si = 4$ in all calculations. The impingement rate scales in the plots are $\log_{10}$ and the inlet Si/H_2 scales are $\log_2$.

Summary of the results.

The position for the onset of epitaxial growth is significantly dependent on the inlet C/H_2 ratio at $T = 1600\text{ }^{\circ}\text{C}$, but not significantly dependent on the inlet Si/H_2 ratio. The position for the onset of epitaxial growth is also dependent on temperature. Higher inlet C/H_2 ratios and lower temperature shifts the position for the onset of epitaxial growth downstream. There is a weak dependence of the growth rate on the inlet Si/H_2 ratio. Thermodynamic equilibrium calculations show that several species have enough impingement rate to ascribe for the observed growth rate.

4. Discussion

To determine what species are involved in the growth, *i.e.* growth species, the experimentally observed positions for the onset of epitaxial growth and growth rates are compared to calculated C/Si impingement ratios of plausible combinations of species and impingement rates of species. From combinations where a good agreement is found we achieve growth species candidates. As the thermodynamic equilibrium calculations made here only consider the gas phase, we investigate the surface reactivity of these candidates using density functional theory. This “sorting-out” strategy will tell what Si species are involved in the growth in the fluorinated chemistry.

We have observed experimentally that epitaxial growth starts at a certain position in the susceptor – referred to as the onset of epitaxial growth. This is a phenomenon, to our knowledge, not previously discussed in SiC CVD. To discuss the origin of this we first summarize what influences

the position for the onset of epitaxial growth. We have observed that the position for the onset of epitaxial growth is influenced by the inlet C/Si ratio, and by the inlet Si/H₂ ratio (Fig. 4). Fig 9 sketches the growth rate at a constant position in the susceptor for changed inlet C/Si (or C/H₂) ratio at a constant inlet Si/H₂ ratio observed by us (marked by “Experimental range” in the figure) together with what is normally seen for SiC CVD at low C/Si ratios i.e. C and Si limited regimes.

Figure 9. Sketch of growth rate for different amounts of C precursor marked with different growth regimes.

We speculate in that the non-epitaxial growth (approaches 0 $\mu\text{m/h}$) is related to a surface passivation related to the impingement of C growth species – probably by a H-termination of the surface originating from that the H is still bound to its C from the C_xH_y growth species, now adsorbed on the surface.

Since the changes to the inlet precursor concentrations also influence the gas phase composition, and thereby the impingement rate of the different C and Si species, a connection between the onset of epitaxial growth and the C/Si impingement ratio is expected. The position of the onset of epitaxial growth is also influenced by the inlet Si/H₂ ratio for constant inlet C/Si ratio, and therefore it is likely that the C/Si impingement ratio of the species contributing to the growth, referred to as the C/Si impingement ratio, can change, even if the inlet C/Si ratio is constant. Since the inlet Si/H₂

and inlet C/Si ratio can be altered to hold a constant onset of epitaxial growth position, we can assume that the C/Si impingement ratio is approximately the same for a certain position for the onset of epitaxial growth at the same time as the impingement rates of these species correlate to growth rate trends. By comparing trends in experimental growth rates and positions for the onset of epitaxial growth to trends in calculated impingement rates of different species when varying the CVD process conditions, it is possible to tie specific species to the experimental observations. The trajectory in parameter space at which the position for the onset of epitaxial growth can be kept constant will be used to identify growth species candidates.

Experiments show that the growth rate increases with increased inlet Si/H₂ ratio for a constant C/H₂ ratio (Fig. 7). The impingement rates of the growth species are therefore not expected to decrease with increased Si/H₂ ratio. From the equilibrium calculations we see that the atomic Si, SiH, SiH₂, SiCH₂, Si₂C and SiC₂ species all decrease with increased inlet Si/H₂ ratio (Fig. 8e-f) and they are therefore not expected to be growth species in the fluorinated chemistry for SiC CVD. Further, SiF₃, SiHF₃ and SiF₄ increase fast with increased inlet Si/H₂ ratio to a rate which does not scale to the observed growth rate change (Fig. 7). Furthermore SiHF₃ and SiF₄ are closed-shell molecules and are hence less reactive while SiF₃ impingement rate decreases with increased temperature and is well below $2 \cdot 10^{-4}$ mol/m²/s for inlet Si/H₂ = 0.125 %, indicating that these species are not growth species either. Candidates for being Si growth species based on their impingement, impingement rate trends for varying inlet Si/H₂ ratio and reactivity can thus only be SiF₂, SiF and SiHF.

The different C containing species can be evaluated in a similar manner as the Si species. The impingement rates for the species SiC₂, Si₂C and SiCH₂ decrease with increased inlet Si/H₂ ratio to well below an impingement rate of $2 \cdot 10^{-4}$ mol/m²/s and are therefore excluded as candidates for

being C growth species. Remaining C growth species candidates are thus C_2H_2 , CH_4 , CH_3 and C_2H_4 , which all show similar trends when varying inlet C/Si (and/or inlet Si/ H_2) at growth temperature 1600 °C, although with different impingement rates. Therefore any of the C growth species candidates can be used in this study to determine the C/Si impingement ratio trends for the Si growth species candidates, even though some discussion can be of interest. CH_4 is a stable closed-shell molecule and therefore not particularly surface reactive compared to CH_3 , which on the other hand has a lower impingement rate than CH_4 . C_2H_4 has an impingement rate about ~1000 times lower than C_2H_2 , fairly close to an impingement rate of $1 \cdot 10^{-4}$ mol/ m^2 /s. C_2H_2 and CH_3 both follow the same trends in temperature and concentrations, although the impingement rate of C_2H_2 is ~125 times higher than the impingement rate of CH_3 . For the sake of simplicity, we will use C_2H_2 in the further discussion in the comparison to the Si species. If CH_4 would have been used, the C/Si impingement ratio would have been scaled by ~0.15; for CH_3 by ~0.008 and for C_2H_4 by ~0.001.

Three species combinations will now be discussed further; $C_2H_2 + SiF_2$, $C_2H_2 + SiF$ and $C_2H_2 + SiHF$. The impingement of SiF_2 varies with the inlet Si/ H_2 , for inlet C/ H_2 = 0.125 % as shown in Fig. 8e *i.e.* it does not follow the trends of the four C species discussed above, which have approximately constant impingement rate, independent of inlet Si/ H_2 shown in Fig. 8f. This gives a C/Si impingement ratio trend that is significantly dependent on the inlet Si/ H_2 ratio at constant inlet C/ H_2 ratio, which is in contradiction to what is shown in Fig. 5, where experiments show that the onset of epitaxial growth is not strongly dependent on the inlet Si/ H_2 ratio at constant inlet C/ H_2 ratio. Due to the poor agreement between the onset of epitaxial growth and the C/Si impingement ratio, we therefore do not believe that SiF_2 is a Si growth species. This is similar to chlorinated and brominated chemistries in which neither $SiCl_2$ nor $SiBr_2$ are considered to be a

significant Si growth species.⁶ That SiF₂ does not seem to take part in growth – even though it has a high impingement rate – is further discussed below when the surface reactions are analyzed by quantum-chemical computations.

For the other two combinations C₂H₂ + SiF and C₂H₂ + SiHF it can be noted from Fig. 8e that the impingement rate from SiF and SiHF are nearly constant with respect to inlet Si/H₂ (in contrast to the impingement rate of SiF₂), which is also the case for the four hydrocarbons, shown in Fig 8f. The behaviors of the species combinations C₂H₂ + SiF and C₂H₂ + SiHF are almost identical to each other and clearly different from the C₂H₂ + SiF₂ combination. The most prominent difference between the two is that the C/Si impingement ratio is ~3 times higher for C₂H₂ + SiHF compared to C₂H₂ + SiF. Fig. 10 plots the calculated C/Si impingement ratios for SiF and SiHF in combination with C₂H₂ for different inlet Si/H₂ and inlet C/Si ratios.

Figure 10. C/Si impingement ratio calculated by thermal equilibrium calculations at $T = 1600$ °C for the species combinations a) C₂H₂ + SiF and b) C₂H₂ + SiHF. The labels next to the lines indicate the inlet C/Si ratio. The calculations show that the C/Si impingement ratio increases with increased inlet Si/H₂ ratio, even though the inlet C/Si is constant. Lines are guidance for the eye. The scales for the C/Si impingement ratio are cut at 200 and 600, respectively.

To correlate the calculated C/Si impingement ratios to the positions of the onset of epitaxial growth (Fig. 4), Fig. 11 shows the positions of the onset of epitaxial growth superimposed on an interpolated color representation of the calculated C/Si impingement ratios.

Figure 11. The positions of the onset of epitaxial growth from experiments and the C/Si impingement ratio from thermal equilibrium calculations at $T = 1600\text{ }^{\circ}\text{C}$ for the species combinations a) $\text{C}_2\text{H}_2 + \text{SiF}$ and b) $\text{C}_2\text{H}_2 + \text{SiHF}$. Note the different color scales.

Both species combinations show an agreement between the C/Si impingement ratio and position for the onset of epitaxial growth for different experimental parameters. When the C/Si impingement ratio becomes low enough, the growth of SiC is epitaxial. This observation is supported by the classical CVD structure/property/process relationship described by Blocher²⁶ where a low precursor concentration and a high temperature is deemed necessary for epitaxial growth.

To understand why the position of the onset of epitaxial growth is changed when the inlet C/H₂ is varied we recall the temperature dependence of the Si and C growth species around the growth process temperature. The impingement of C₂H₂ is almost constant from 1400 °C and upwards, while the Si growth species increase their impingement with increased temperature, decreasing the C/Si impingement ratio as the temperature increases. The changed position of the onset of epitaxial

growth with changed inlet C/H₂ ratio (or inlet C/Si ratio for a specific inlet Si/H₂ ratio) is likely an effect of slow kinetics of the SiF₄ precursor molecule to form Si growth species compared to the formation of C-species from C₂H₄ together with the temperature gradient in the susceptor (*i.e.* cooler at the inlet and hotter further downstream) and the gas mixture (*i.e.* cooler at the inlet as well as towards the middle of the gas flow and hotter further downstream as well as closer to surfaces). Here it should be emphasized that the reactor is designed in such way that susceptor in plane temperature gradients are minimized by designing inlet, front- and rear insulation to have steep temperature gradients. The heating of the gas inside the susceptor is compensated by thermal radiation at the rear of the susceptor. The susceptor temperature is therefore constant compared to the increasing temperature of the gas providing more growth species. This results in a steadily decreasing C/Si impingement ratio by the increasing amount of Si growth species. If the ratio decreases enough, below the threshold limit, there will be epitaxial growth, and thereby an onset of epitaxial growth.

Reactivities of SiF, SiHF and SiF₂ were studied via the adsorption processes modelled by the quantum chemical methods. The species were assumed to react with two types of surface carbon groups: first a C site without a dangling bond and then a C site including a dangling bond. These two cases were represented respectively by a methyl (-CH₃) and a methylene (-CH₂) group which have been pre-attached to the surface Si atom prior to the adsorption. Based on this scenario, we obtained the Gibbs free energies of adsorption and activation (if a saddle point exists).

It is observed that the Gibbs free energies of adsorption increase monotonically with the rise of the process temperature. The relations between the process temperature and the Gibbs free energies of adsorption over 400 to 2200 °C are shown in Fig. 12a-b. At room temperature the adsorptions starts with negative values for all cases but then changes signs when the temperature reaches the

following values: 1763 °C, 1023 °C and 613 °C for the SiF, SiHF and SiF₂ on a methylene site and 504 °C, 850 °C and 524 °C for SiF, SiHF and SiF₂ on a methyl site. This means that approaching the growth temperature, the Gibbs energies have all become positive for the adsorptions on a methyl site as well as the adsorptions of SiHF and SiF₂ on a methylene site. The only exception is the SiF adsorption on a methylene site, at least when the temperature is less than 1763 °C.

Figure 12. Relations between the temperature and the Gibbs free energies of adsorption ($\Delta G^\circ_{\text{ads}}$) of the SiF (solid), SiHF (dash) and SiF₂ (dot) on a) a methyl (-CH₃) site and b) a methylene (-CH₂) site. The Gibbs free energies as functions of temperature were derived using density functional theory as described in the methods, surface chemistry modelling subsection.

The positive Gibbs energies calculated for the surface reactions suggest that the adsorptions are thermodynamically unfavorable in comparison to the reverse, namely surface desorptions via the same pathway. However, a positive ΔG° simply implies that the numerical value of the equilibrium constant is below one, i.e. the reaction is shifted to the left. We can see that SiF has the largest equilibrium constant followed by SiHF and then by SiF₂ for adsorption on methylene, and that the equilibrium constant is even larger than one (negative ΔG°) for SiF, at typical growth temperatures. It is worth noting that the presence of a dangling bond residing at the methylene group, CH₂(ads)

on the surface helps lowering the Gibbs energies of adsorptions. The most significant reduction is in the SiF adsorption on methylene which is a radical-radical reaction.

With the Gibbs free energies of adsorption we arrive at the prediction of how likely the process may occur. To explicitly determine the reaction rates or the sticking coefficients would invoke the knowledge of both the Gibbs energies of adsorption as well as the potential energy surface along the reaction coordinates. For the adsorptions on a methyl site, there exists a saddle point between the reactant and the product states for which the Gibbs free energies of activation over the range of 400 to 2200 °C is shown in Fig. 13.

Figure 13. Relations between the temperature and the Gibbs free energies of activation ($\Delta G^\ddagger$) of the SiF (solid), SiHF (dash) and SiF₂ (dot) on a methyl (-CH₃) site. The Gibbs free energies as functions of temperature were derived using density functional theory as described in the methods, surface chemistry modelling subsection.

At 1600 °C these barrier heights become relatively high in energy in comparison to the reactant ground state as depicted in Fig. 14a. Using transition state theory we extracted the sticking coefficients at 1600 °C to be $\sim 7.4 \cdot 10^{-5}$ for SiF, $\sim 1.0 \cdot 10^{-6}$ for SiHF and $\sim 3.3 \cdot 10^{-9}$ for SiF₂. The barriers of desorption via the same pathway are smallest in SiF (194 kJ/mol), followed by SiHF

(296 kJ/mol) and SiF_2 (333 kJ/mol). Hence, it is easier for the adsorbed SiF to desorb back into gas phase than for the adsorbed SiHF or SiF_2 species. Adsorptions on a methylene site do not occur with saddle points between the reactants and products as presented in Fig. 14b. It is therefore not suitable to use conventional transition state theory to derive the rate constants or sticking coefficients for adsorption process on a methylene. Nevertheless, we expect all sticking coefficients to be relatively large. As shown in Fig. 14b, adsorption of SiF occurs with negative Gibbs free energies at 1600 °C, in contrast to SiHF and SiF_2 . This suggests that for SiF the process of adsorption is preferable over desorption via the same pathway. Hence, among these three species SiF is likely the most active growth contributor. Unlike SiF, both SiHF and SiF_2 prefer the process of desorption to adsorption. The larger positive Gibbs free energy of adsorption suggests that desorption is more favorable for SiF_2 than for SiHF. Hence, SiHF will likely contribute to growth more effectively than SiF_2 . From these facts it is clear that SiF_2 is much less likely to contribute to the growth than SiF and SiHF. This could also be viewed as support for a suggested etching mechanism where SiF_4 etches away Si by forming two SiF_2 , which leave the surface.²⁷ This coincides with the experimental results between the onset of epitaxial growth and the C/Si impingement ratio.

Figure 14. Gibbs free energies of activation and adsorption at $T = 1600^\circ\text{C}$ of the $\text{SiF}(\text{g})$, $\text{SiHF}(\text{g})$ and $\text{SiF}_2(\text{g})$ on a) a methyl ($-\text{CH}_3$) site and b) a methylene ($-\text{CH}_2$) site. The Gibbs free energies as functions of temperature were derived using density functional theory as described in the methods, surface chemistry modelling subsection.

In general, the results from the quantum chemical modeling show that it is unlikely for the Si-species to get adsorbed on a fully bonded carbon site located on a smooth H-terminated Si terrace. However, when a dangling bond is introduced on the carbon site, adsorption of SiF species become thermodynamically favorable. Even though adsorptions of SiHF and SiF_2 on $\text{CH}_2(\text{ads})$ occur with positive Gibbs free energies, we believe that the system can be stabilized even further by subsequently bonding the Si group to another adjacent C group. If this is the case, then adsorption at steps will definitely have advantages over terraces since adjacent C groups are available at step while it is not always the case for terraces. The non-epitaxial growth upstream of the onset of epitaxial growth could be a result of a $\sim 100\%$ CH_3 terminated surface from the high C/Si impingement ratio. The triangular surface defects can then be a result of growth at steps under carbon rich conditions, although this is only speculations, which require a more thorough investigation.

5. Conclusion

By using a combination of growth experiments, thermochemical and quantum chemical modeling we can now present a better understanding of the CVD chemistry for CVD of SiC using SiF₄ as Si precursor. The experiments use the onset of epitaxial growth as the observable for how the C/Si ratio of the impinging species. The difference in C and Si chemistry in the fluorinated chemistry makes the C/Si impingement ratio strongly dependent on the temperature and precursor concentrations. It is observed that a process generating a high C/Si impingement ratio hinders the growth of SiC. When the C/Si impingement ratio is low enough, the growth of SiC is epitaxial.

Thermochemical calculations shows that the possible Si bearing species for growth are SiF₂, SiF and SiHF. By modeling the observed changes in onset of epitaxial growth we conclude that SiF is the main Si bearing species for SiC growth with minor contribution from SiHF. SiF₂ is concluded not to contribute to the SiC growth. This conclusion is further supported by quantum chemical modeling where SiF is the only Si species with a favorable adsorption Gibbs free energy.

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Supporting Information

Further details on the onset of growth, quantum-chemical calculations with a larger SiC cluster, derivation of the impingement rate needed for a certain growth rate, impingement rates of other C and Si species and safety precautions for working with the risk of residual HF vapors from a CVD process with SiF₄ are available free of charge via the Internet at <http://pubs.acs.org>.

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TOC image

Supporting Information for

Silicon Chemistry in Fluorinated Chemical Vapor Deposition of Silicon Carbide

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Cluster model.

The $\text{Si}_{13}\text{C}_{13}\text{H}_{32}$ cluster has been tested against a larger cluster, $\text{Si}_{22}\text{C}_{22}\text{H}_{44}$, for adsorption process of gaseous SiF, SiHF and SiF₂ on a methyl group. The Gibbs free energies of reaction ($\Delta_R G^\circ$) and of activation ($\Delta G^\ddagger$) were calculated and compared as shown in Table S1 below.

$\Delta_R G^\circ$	$\text{Si}_{13}\text{C}_{13}\text{H}_{32}$				$\text{Si}_{22}\text{C}_{22}\text{H}_{44}$			
	400 °C	1000 °C	1600 °C	2200 °C	400 °C	1000 °C	1600 °C	2200 °C
SiF adsorption	-15	71	152	231	-15	70	150	228
SiHF adsorption	-74	24	117	207	-74	24	118	208
SiF ₂ adsorption	-21	78	170	260	-19	78	170	258
$\Delta G^\ddagger$								
SiF adsorption	197	273	347	419	192	268	341	413
SiHF adsorption	231	324	413	501	232	325	416	504
SiF ₂ adsorption	325	416	503	588	326	420	510	598

Table S1. The Gibbs free energies derived using the $\text{Si}_{13}\text{C}_{13}\text{H}_{32}$ cluster in comparison to the results calculated from a larger cluster, $\text{Si}_{22}\text{C}_{22}\text{H}_{44}$. Here, $\Delta_R G^\circ$ and $\Delta G^\ddagger$ refer to the Gibbs free energies of reaction and of activation, respectively. The results are shown for adsorption process of gaseous SiF, SiHF and SiF₂ on a methyl group ($-\text{CH}_3$). The Gibbs free energies are shown in kJ/mol unit.

Surface chemistry modelling.

Based on a simplified work of Reuter and Scheffler's¹, the adsorption rate (R_{ads}) can be written as

$$R_{ads} = \Phi \cdot \Theta \cdot A_s f_{ads} \exp(-\Delta E_{ads}/k_B T), \quad (\text{Eq. S1})$$

where

$$f_{ads} = q_{vib,el}^{TS} / (q_{2D-Trans}^{gas} \cdot q_{int}^{gas} q_{vib,el}^{surf}), \quad (\text{Eq. S2})$$

and

$$\Phi = \gamma_A p / \sqrt{2\pi m_A k_B T}. \quad (\text{Eq. S3})$$

Here Φ is the molecular impingement flux in the unit of molecule $\text{area}^{-1} \text{time}^{-1}$ where γ_A , p , m_A , k_B and T are respectively the molar fraction of the adsorbing molecule A in gas phase, the total pressure, the mass of molecule A, the Boltzmann constant, and temperature in Kelvin. Θ is the surface fraction of the adsorption sites. A_s is the area per site.

f_{ads} contains the contributions from the partition functions (q). The partition functions related to the surface (*i.e.* those of the transition state ($q_{vib,el}^{TS}$) and the surface ($q_{vib,el}^{surf}$)) include only the vibrational and electronic parts, while for the gases, all parts are included except translation along the reaction coordinates. The translational part of the gas partition function is written separately as $q_{2D-Trans}^{gas}$, to highlight the fact that only 2 out of 3 dimensions are included, while the vibrational, rotational and electronic parts are included together in the term q_{int}^{gas} . Lastly ΔE_{ads} is the adsorption barrier at 0 K with the zero point correction energy included.

From the adsorption rate and the impingement flux, we can then define the sticking coefficient (S_A) by $S_A = R_{ads} / \Phi \cdot \Theta$. Hence we obtain

$$S_A = f_{ads} \exp(-\Delta E_{ads}/k_B T). \quad (\text{Eq. S4})$$

Adsorption rate to achieve ~10μm/h.

Adsorption rate, Φ , is the number of hits per unit second per unit area. That can be formulated as

$$\Phi = v/A \quad (\text{Eq. S5})$$

where v is the hit rate (1/s) and A the area (m^2).

To achieve a growth rate of 10μm/h we first recall that the height of the 4H-SiC unit cell is $c = 1.0053 \cdot 10^{-9} \text{ m}$ gives the distance between two bilayers; $2.5131 \cdot 10^{-10} \text{ m}$. That gives us the growth rate as

$$10 \mu\text{m/h} = 10 \cdot 10^{-6} \text{ m/h} = 3.979 \cdot 10^4 \text{ bilayers/h} = 11.05 \text{ bilayers/s} \quad (\text{Eq. S6})$$

Therefore, for the area A of a surface site the hit rate

$$v = 11.05/\text{s} \quad (\text{Eq. S7})$$

The area for a surface site in the hcp structure for 4H-SiC in the c-plane to which v applies is 3 sites per hexagon with side lengths a , which gives the area of 1 site as 2 triangles with side lengths a

$$A = 2 \cdot \frac{1}{2} \cdot a^2 \cdot \sin 60^\circ = 2 \cdot \frac{1}{4} \cdot \sqrt{3} \cdot (3.0730 \cdot 10^{-10} \text{ m})^2 = 8.178 \cdot 10^{-20} \text{ m}^2 \quad (\text{Eq. S8})$$

where a is the in plane lattice constant. That gives the needed adsorption rate

$$\begin{aligned} \Phi = v/A &= (11.05/\text{s}) / (8.178 \cdot 10^{-20} \text{ m}^2) = 1.351 \cdot 10^{20} / \text{m}^2/\text{s} = \\ &= 2.2 \cdot 10^{-4} \text{ mol/m}^2/\text{s} \end{aligned} \quad (\text{Eq. S9})$$

C/Si impingement rate for other species combinations.

For a comparison to what the C/Si impingement ratio would have looked like with SiF₂ being the Si growth species, Fig S1 shows the behavior together with the growth onset positions. The correlation between the C/Si impingement ratio and the position for the onset of epitaxial growth is weak.

Security precautions regarding HF as a byproduct from the process.

As SiF₄ is used together with hydrogen, the formation of hydrogen fluoride (HF) is inevitable. Traces of HF bound in the parasitic deposition downstream of the susceptor can evaporate into the air and form HF (aq) upon reacting with the moisture in the air. To avoid that personnel get exposed to HF when opening the CVD reactor, a point exhaust at the loading flange is found to prevent most HF from spreading to the surroundings. A handheld detector is used to monitor the concentration of HF in the air. Concentrations higher than 0.3 ppm can be detected, which is below NIOSH time weight averaged Recommended Exposure Limits of 3 ppm for a 10 hour exposure.²

No detectable concentrations of HF (< 0.3 ppm) is found when the point exhaust is placed at the pump line downstream of the flange, which cannot be cleaned in run-to-run cleaning. This indicates that the HF is released from parasitic deposition, especially when the parasitic deposition has built up during a long time, and that no HF is released from the graphite parts in the hot zone. To further protect personnel, gas mask and gloves with 5 minutes breakthrough time for 48 % HF (aq) are used during the cleaning of the cell. When parts with parasitic deposition were cleaned using ethanol, HF was normally released, which could be detected when the hand hold detector was placed close to the part being cleaned. If the parts had been exposed to air for circa one minute, no detectable HF was released upon cleaning with ethanol.

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