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Matching precursor kinetics to afford a more robust CVD chemistry: a case study of the C chemistry for silicon carbide using SiF$_4$ as Si precursor

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Abstract

Chemical Vapor Deposition (CVD) is one of the technology platforms forming the backbone of the semiconductor industry and is vital in the production of electronic devices. To upscale a CVD process from the lab to the fab, large area uniformity and high run-to-run reproducibility are needed. We show by a combination of experiments and gas phase kinetics modeling that the combinations of Si and C precursors with the most well-matched gas phase chemistry kinetics gives the largest area of of homoepitaxial growth of SiC. Comparing CH$_4$, C$_2$H$_4$ and C$_3$H$_8$ as carbon precursors to the SiF$_4$ silicon precursor, CH$_4$ with the slowest kinetics renders the most robust CVD chemistry with large area epitaxial growth and low temperature sensitivity. We further show by quantum chemical modeling how the surface chemistry is impeded by the presence of F in the system which limits the amount of available surface sites for the C to adsorb.
Introduction

Chemical vapor deposition (CVD) is one of the most important techniques in semiconductor manufacturing, typically employed to make the active region of the device structures where a very high control on material quality and precise control over the incorporation of impurities is required. Of paramount importance for upscaling any CVD process in a device production is the large scale uniformity and run to run reproducibility, both of which depend on the spatial and temporal uniformity of the CVD chemistry. The CVD chemistry for most semiconductor materials relies on gas phase chemical reactions to form reactive species from the precursor molecules and subsequent surface chemical reactions to form the material. The uniformity in a CVD process is therefore dependent on both gas phase and surface chemistry of the employed precursor system. The uniformity in an industrial CVD reactor is typically controlled by carefully designing the gas flow patterns in the CVD reactor. However, a well-chosen overall robust CVD chemistry, which is not affected by minor temperature fluctuations and gas flow disturbances, is also a prerequisite for highly uniform CVD. The CVD chemistry should, ideally, render high concentrations of the reactive species with very similar spatial and temporal distributions.

Here we use silicon carbide (SiC) as a model system to explore the effect of precursor kinetics on the overall CVD chemistry. SiC is a semiconductor with a wide band gap, high saturation electron drift velocity and high energy of the optical phonons which renders a high electric field breakdown strength, which makes SiC very well suited for high power devices. A CVD process with large area uniformity is required for commercial realization of SiC devices. The growth of homoepitaxial SiC layers using CVD – based on SiH₄ and C₂H₄ or C₃H₈ – is already commercialized, but lately much interest has been directed towards using a halogenated CVD chemistry, mainly by adding chlorine, to allow a higher growth rate on the account of eliminated gas phase nucleation. Since the halogens F, Cl and Br binds stronger to
Si than Si itself – the binding strengths for F, Cl, Br and Si to Si are 576, 417, 358 and 310 kJ/mol, respectively\textsuperscript{5} – higher partial pressures of Si species can be used in SiC CVD with a halogenated CVD chemistry without formation of Si droplets in the gas phase.

Both chlorinated\textsuperscript{4} and brominated\textsuperscript{6} chemistries have been shown to behave very similar to the standard, non-halogenated chemistry, albeit with a 5-20 times higher deposition rate. SiC CVD using a fluorinated chemistry was first demonstrated 2012 by Rana et al.\textsuperscript{7} Lately, it has been shown that a fluorinated chemistry, using SiF\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} as precursors, renders a CVD chemistry that is very sensitive to the C/Si ratio of the growth species impinging the surface and with a deposition rate of only around 30 \(\mu\)m/h compared to 100 \(\mu\)m/h or more for a chlorinated or brominated chemistry.\textsuperscript{8} We hypothesize that this behavior is due to a low reactivity of the SiF\textsubscript{4} molecule given its very strong Si-F bonds and a slower kinetics of the Si precursor which is not matched to the faster kinetics of the C\textsubscript{2}H\textsubscript{4} precursor, rendering a less robust CVD chemistry as manifested by the sensitivity to the impinging C/Si ratio. We test this hypothesis by kinetic modeling combined with experimental SiC deposition from SiF\textsubscript{4} and different hydrocarbons and show that the best matched gas phase chemical kinetics renders the most robust SiC CVD.

**Methods**

**Experimental details**

A horizontal hot wall CVD reactor was used for the growth of epitaxial SiC on 4H-SiC substrates with 4\(^\circ\) off-cut from the (0001) axis in the (11-20) direction. As carrier gas, palladium membrane purified hydrogen (H\textsubscript{2}) was used. The precursors used were SiF\textsubscript{4} or a mixture of SiF\textsubscript{4} and SiH\textsubscript{4} as Si precursor and either CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4} or C\textsubscript{3}H\textsubscript{8} as C precursors, which were diluted in the carrier gas to the inlet concentrations Si/H\textsubscript{2} = 0.25 % and C/H\textsubscript{2} = 0.125 %, respectively. The use of SiF\textsubscript{4} renders in F/Si = 4 while when the mixture of SiF\textsubscript{4} and SiH\textsubscript{4} was
used the F/Si ratio varied from 0 to 4. 25 standard liters per minute (SLM) of carrier gas was used at the process pressure \( p = 100 \) mbar except from when growth rate was of interest where 37.5 SLM was used as well as \( \text{Si}/\text{H}_2 = 0.125 \% \). The temperatures were either \( T = 1550 \) or 1600 °C. The SiC coated graphite susceptor used in the experiments was 190 mm long with a gas cross section of 78 mm in width and 24 mm in height, in which 16×16 mm pieces of SiC substrates were placed at 3, 6 and 9 cm from the inlet. The upstream direction was connected to a broadened SiC coated graphite inlet connected to a quartz liner for the process gases. Heating of the susceptor was made via an RF heated graphite cylinder surrounding the susceptor. The graphite cylinder and susceptor were insulated with rigid graphite insulation, which was purged with argon – instead of \( \text{H}_2 \) – to improve its thermal insulation properties. The whole setup was encapsulated in a quartz tube. The grown SiC films were characterized using a Nomarski differential interference contrast optical microscope from which surface morphology could be studied. It should be noted that the optical microscopy images cannot at the same time both show the surface of the whole 16×16 mm samples and the surface features in detail. As the surface features are indicative of epitaxial film growth, we show only detailed micrographs to point out surface features.

**Modeling**

Simulations of chemical kinetics were done using a one-dimensional transient model to evaluate the gas phase composition with respect to time at constant temperature and constant pressure. The initial gas mixture at time \( t = 0 \) was set to the same concentrations as in the experiments, and calculations were done for the three different carbon precursors. The kinetic model consisted of 89 elementary reaction steps, whereof 57 steps for hydrocarbon reactions. No reactions between silicon and carbon species are accounted for in the model. This is motivated by the low amounts of Si-C species found at thermodynamic equilibrium in the Si-C-H-F system\(^8\). Apart from \( \text{H}_2 \), H and HF, 11 hydrocarbon species and 10 fluorosilanes.
were taken into account, plus SiH₄, SiH₂ and Si. The full reaction scheme is listed in Supporting Table 1. Backward rates were calculated from the equilibrium constant, if not explicitly written out. Hydrocarbon reactions are taken from literature, while reactions of fluorosilanes were calculated using quantum chemical calculations. The ground state and transition state structures were optimized using the hybrid density functional theory (DFT) B3LYP⁹, ¹⁰ and Dunning’s cc-pVTZ basis set¹¹ together with the dispersion energy corrected by D3 correction from Grimme et al.¹². Harmonic frequencies were calculated at the same level of theory. Transition states were verified by either visualizing the displacement of the imaginary frequencies or by tracing the reaction path from the transition state to the product and reactant states using the intrinsic reaction coordinate (IRC) computation¹³. The electronic energies were calculated using CCSD(T) single point calculations¹⁴, ¹⁵ and cc-pVnZ basis sets from Dunning¹¹, ¹⁶ for n = D, T and Q before extrapolated to the values at the complete basis set limit by,¹⁷

\[ E(n) = E(\infty) + Be^{-(n-1)} + Ce^{-(n-1)^2}. \]  

(1)

Transition state theory was applied to derive the rate constants. For a reaction with no transition state, the barrier height was approximated to be equal to the reaction energy when the energy was positive (uphill), and to be zero when the energy was negative (downhill). All calculations were performed using the Gaussian 09 software¹³.

Surface vacancies on SiC were probed by quantum-chemical calculations of SiC clusters consisting of 13 carbon and 13 silicon atoms, terminated by hydrogen atoms. The B3LYP functional⁹ was used together with the LANL2DZ basis set¹⁸,¹⁹,²⁰ with Grimme dispersion correction¹², ²¹ for the optimization. Single point calculations were done with the M062X Minnesota functional²², using the GTLargeXP basis set²³. The thermodynamic data from the DFT calculations have been utilized to compute the total Gibbs free energy, which was
minimized with respect to the distribution of the species to get the thermodynamically most stable (i.e. the equilibrium) composition of the system\textsuperscript{24} using a MATLAB code.\textsuperscript{25}

**Results**

It has previously been shown that epitaxial growth of SiC using a fluorinated chemistry is possible if the effective C/Si impingement ratio, i.e. the C/Si impingement ratio from the growth species, which changes along the susceptor, is low enough.\textsuperscript{8} The position at which the C/Si impingement ratio is low enough and the epitaxial growth begins is referred to as the onset of epitaxial growth. When comparing three different carbon precursors (C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}) at the growth temperature T = 1600 °C, and otherwise same process parameters, it is seen (Fig. 1) that the onset of epitaxial growth differs between the precursors. C\textsubscript{2}H\textsubscript{4} shows no onset of epitaxial growth within 10 cm from the inlet, while both CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8} had their onset of epitaxial growth upstream of the most upstream placed sample, placed 3 cm from the inlet.

![Optical microscopy images](image)

**Figure 1.** Optical microscopy images of the SiC surface grown with T = 1600 °C and different C precursors. a) 10 cm from the inlet using C\textsubscript{2}H\textsubscript{4} showing a rough surface indicative of polycrystalline growth with no onset of epitaxial growth. b) 3 cm from the inlet using CH\textsubscript{4} showing a smooth surface with a triangular surface defect (circled) indicative of epitaxial growth, c) 3 cm from the inlet using C\textsubscript{3}H\textsubscript{8} showing a smooth surface with a triangular surface defect.
defect (circled) indicative of epitaxial growth.

The results shown in Fig. 1 display no difference between CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}. Lowering the temperature to T = 1550 °C (Fig. 2) reveals that C\textsubscript{3}H\textsubscript{8} has no onset of epitaxial growth within 10 cm from the inlet, while CH\textsubscript{4} shows epitaxial growth at the most upstream placed sample 3 cm from the inlet.

![Figure 2](image)

**Figure 2.** Optical microscopy images of the SiC surface grown with T = 1550 °C and different C precursors. a) 10 cm from the inlet using C\textsubscript{3}H\textsubscript{8} showing a rough surface indicative of no growth and no onset of epitaxial growth, b) 3 cm from the inlet using CH\textsubscript{4} showing a smooth surface with a triangular surface defect (circled) indicative of epitaxial growth.

Simulations of the gas phase composition for the three different carbon precursors in combination with SiF\textsubscript{4} were done using kinetic modelling. Concentrations of the main gas phase species with respect to time are shown in Fig. 3 and Fig. 4 at two different temperatures. The time frame of interest is in the range 0.01-0.1 s as it is in this time range that the precursors pass through the susceptor.
Figure 3. Concentrations of main gas phase species at $T = 1600^\circ$C from kinetic simulations when the carbon precursor is a) $C_2H_4$, b) $C_3H_8$, c) $CH_4$.

CH$_3$ and C$_2$H$_2$ have been identified as the carbon containing growth species in SiC CVD$^{26}$ and SiF has previously been suggested to be the main Si growth species in fluorinated SiC CVD.$^8$

Figure 4. Concentrations of main gas phase species at $T = 1550^\circ$C from kinetic simulations when the carbon precursor is a) $C_2H_4$, b) $C_3H_8$, c) $CH_4$.

Here we also see that the amount of atomic silicon is available at similar concentrations as SiF. Atomic silicon should be very reactive and is most likely also contributing to the growth. Comparing the concentrations of the two hydrocarbon growth species for the three different carbon precursors, we note that the concentration of C$_2$H$_2$ is highest when using C$_2$H$_4$, and
lowest when using CH₄. The CH₃ concentration is very similar for C₃H₈ and CH₄ as precursors, while it is at least three orders of magnitude lower when C₂H₄ is used.

**Discussion**

The decomposition chemistry of SiF₄, leading to more usable Si-containing species for SiC growth, is slow compared to the decomposition of C₃H₈ and C₂H₄ and their usable C-containing decomposition products (Fig. 3a and b). This leads to unmatched concentrations of carbon and silicon in the susceptor, with potentially large C/Si ratios upstream that do not promote epitaxial growth conditions, and with a constantly changing C/Si ratio along the flow direction as the SiF₄ precursor decomposes on its way through the susceptor. Changes in the C/Si ratio will influence the growth conditions for e.g. dopant incorporation, which is dependent on the amount of available C on the surface, ²⁷ or shift the growth mode from C limited to Si limited, thereby changing the spatial growth rate profile and thickness of the final layer. We have recently shown that a too high C/Si leads to a surface poisoning of carbon which prevents epitaxial growth. ⁸ To achieve a robust CVD chemistry that gives epitaxial growth over large areas, SiF₄ needs to be matched to a carbon precursor with an equally slow chemistry so that the C/Si impingement ratio can be kept at low enough levels. CH₄, which is not normally used in CVD of SiC just because of its slow decomposition chemistry, is an excellent partner in this respect.

The experimental results (Figs. 1 and 2) show that the kinetics for forming carbon bearing growth species for SiC differs between different carbon precursors. When using SiF₄ together with C₂H₄, the combination of resulting growth species does not lead to epitaxial growth along the studied area in the susceptor. With C₃H₈ or CH₄, on the other hand, the growth is epitaxial already at the most upstream part of the susceptor at T = 1600 °C, suggesting that the C/Si impingement ratio is low enough for epitaxial growth. The difference in the kinetics
between precursors is further demonstrated by the results at $T = 1550 \, ^\circ\text{C}$, when the case where $C_3H_8$ is used does not lead to epitaxial growth even at the most downstream position studied, while $CH_4$ renders epitaxial growth at all positions also at this temperature.

The experimental results are supported by the chemical kinetic calculations, where it is seen that the production of $C_2H_2$ is very fast when $C_2H_4$ is used as precursor, while it is relatively slow for $CH_4$ as precursor. Indeed, the decomposition paths for the hydrocarbons differ significantly. While $C_2H_4$ breaks two C-H bonds and form a third C-C bond to form $C_2H_2$, the decomposition product of $CH_4$ is mainly $CH_3$, which then may react to form $C_2H_6$, which in turn will undergo further reactions that eventually lead to $C_2H_2$. The latter reaction path contains more reaction steps, each with some energy barrier to climb, which makes the production of $C_2H_2$ slow in comparison to the first reaction path. The production rate of $C_2H_2$ in the $CH_4$ case matches well the production rate of SiF and Si, which would help keep the C/Si ratio at the SiC surface at levels suitable for epitaxial growth.

Unterminated surface sites are necessary for an efficient chemisorption of carbon growth species. Without halogen addition to the SiC CVD process, the SiC surface is only partially terminated by hydrogen at the growth conditions studied, and there are unterminated surface sites available for the growth to proceed. When SiF$_4$ is used as precursor, HF is formed in the gas phase as a by-product from the SiF$_4$ decomposition. The presence of HF could lead to Si-H bonds on the surface being replaced by Si-F bonds, and unterminated surface sites may readily be saturated by fluorine, considering the very strong bond energy between Si and F. A SiC surface saturated by Si-F bonds, rather than Si-H bonds, would lead to an inhibited growth due to the stronger Si-F bond. The surface saturation has been studied by quantum-chemical computations using a SiC cluster model (Fig. 5). The amount of hydrogen termination, $H (s)$, unterminated surface sites, $X (s)$, and fluorine termination, $F (s)$, with increasing F gas phase concentration is shown in Fig. 6. The fluorine termination increases
with fluorine concentration on the expense of hydrogen termination and unterminated surface sites. Due to the slow kinetics of the SiF$_4$ molecule, the gas phase concentration of HF increases further into the susceptor, which then also would increase the amount of fluorine terminated surface sites downstream.

**Figure 5.** The SiC cluster models used in this study of a) the completely hydrogen terminated surface – H (s), b) the cluster with a dangling bond – X (s) and c) the single fluorine terminated structure – F (s).

**Figure 6:** Equilibrium composition of the surface species at different F/H$_2$ ratios from
quantum-chemical modeling. H (s) denotes hydrogen termination, X (s) denotes surface vacancy, F (s) denotes fluorine termination.

To verify the dependence of the amount of surface vacancies on the SiC growth, experiments were made where the F/Si ratio was controlled by mixing SiH$_4$ and SiF$_4$ as Si precursors. The F/Si ratio could then be varied between 0 and 4. As for the other CVD experiments in this study, H$_2$ was in great excess in the experiments, with the inlet ratio of the SiH$_4$ + SiF$_4$ and H$_2$ of 0.125%. Hence, the F/H$_2$ for the experiments were between 0 and 0.5%. The temperature was T = 1600 °C and the carrier gas flow was 37.5 SLM. In Fig. 7 the maximum growth rate is plotted against the F/H$_2$ ratio and compared with the amount of surface vacancies, X (s). The growth rate declines with the F/H$_2$ ratio, following the decline in surface vacancies. We therefore speculate that the growth rate is limited by the growth of the C layers due to the F terminated surface from the use of SiF$_4$ as Si precursor. But also the decreasing amount of possible Si bearing growth species (SiF, SiHF and Si) decreases with increasing F/H$_2$. Increasing the Si/H$_2$ ratio could therefore give a high growth rate upstream before more F is released terminating the surface downstream thereby reducing the growth rate even more than if a lower Si/H$_2$ ratio would have been used. That the growth rate decreases faster along the flow direction with a higher Si/H$_2$ using SiF$_4$ has been shown previously.$^8$
So while the fluorinated CVD chemistry for SiC is problematic, we show that there is a better match between SiF$_4$ and CH$_4$ than between SiF$_4$ and C$_2$H$_4$. This is opposite to when CH$_4$ is used in chlorinated SiC CVD, where good growth conditions are confined to a narrower C/Si ratio window than when using C$_2$H$_4$ as the C precursor.$^{28}$ The different rates at which growth species are formed from the precursors also suggests that combining different amounts of different precursors could be a way of controlling the spatial profile of the growth species impingement rate, and thereby the spatial profile of the C/Si impingement ratio.

**Conclusions**

We show that matching the kinetics of the silicon and carbon precursors in a SiC CVD process is necessary for achieving large area homoepitaxial growth of SiC. We show this by comparing CH$_4$, C$_2$H$_4$ and C$_3$H$_8$ as carbon precursors to the SiF$_4$ silicon precursor where CH$_4$ with the slowest kinetics renders the most robust CVD chemistry with large area epitaxial
growth and low temperature sensitivity. It is also shown how the amount of F in the system affects the surface for further growth and that the growth rate could be limited by the amount of available surface sites for the C to adsorb. We show the slow kinetics of the CH$_4$ molecule matches the slow kinetics of the SiF$_4$ molecule while the C$_2$H$_4$ and C$_3$H$_8$ molecules have faster kinetics leading to reduced process temperature window. We suggest that this precursor kinetics matching is a generic approach to choosing suitable combinations of CVD chemistries.

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