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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 SiF₄ as Si precursor†

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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 homoepitaxial growth of SiC. Comparing CH₄, C₂H₄ and C₃H₈ as carbon precursors to the SiF₄ silicon precursor, CH₄ 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 onto.

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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 over material quality and precise control over the incorporation of impurities is required. Of paramount importance for upscaling any CVD process in a device production are 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.¹ The uniformity in a CVD process is therefore dependent on both the 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.² A CVD process with large-area uniformity is required for the commercial realization of SiC devices. The growth of homoepitaxial SiC layers using CVD – based on SiH₄ and C₂H₄ or C₃H₈ – has already been commercialized,³ but lately much interest has been directed towards using a halogenated CVD chemistry, mainly by adding chlorine, to allow a higher growth rate on account of the eliminated gas phase nucleation.⁴ Since the halogens F, Cl and Br bind more strongly to Si than Si itself – the binding strengths for F, Cl, Br and Si to Si are 576, 417, 358 and 310 kJ mol^{−1}, respectively⁵ – higher partial pressures of Si species can be used in SiC CVD with a halogenated CVD chemistry without the formation of Si droplets in the gas phase.

Both chlorinated⁴ and brominated⁶ chemistries have been shown to behave very similarly to the standard, non-halogenated chemistry, albeit with a 5–20 times higher deposition rate. SiC CVD using a fluorinated chemistry was first demonstrated in 2012 by Rana *et al.*⁷ Lately, it has been shown that a fluorinated chemistry, using SiF₄ and C₂H₄ 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 μm h^{−1} compared to 100 μm h^{−1} or more for a chlorinated or brominated chemistry.⁸ We hypothesize that this

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behavior is due to the low reactivity of the SiF_4 molecule given its very strong Si–F bonds and the slower kinetics of the Si precursor, which is not matched to the faster kinetics of the C_2H_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_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° off-cut from the (0001) axis in the (11–20) direction. As a carrier gas, palladium membrane purified hydrogen (H_2) was used. The precursors used were SiF_4 or a mixture of SiF_4 and SiH_4 as Si precursor and either CH_4 , C_2H_4 or C_3H_8 as C precursors, which were diluted in the carrier gas to the inlet concentrations $\text{Si}/\text{H}_2 = 0.25\%$ and $\text{C}/\text{H}_2 = 0.125\%$, respectively. The use of SiF_4 renders $\text{F}/\text{Si} = 4$ but when a mixture of SiF_4 and SiH_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 when growth rate was of interest when 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 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 the surface morphology could be studied. It should be noted that the optical microscopy images cannot at the same time show both 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 were 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 H_2 , H and HF, 11 hydrocarbon species and 10 fluorosilanes were taken into account, plus SiH_4 , SiH_2 and Si. The full reaction scheme is listed in ESI,† Table S1. Backward rates were calculated from the equilibrium constant, if not explicitly written out. Hydrocarbon reactions are taken from the literature, while reactions of fluorosilanes were obtained using quantum chemical calculations. The ground state and transition state structures were optimized using the hybrid density functional theory (DFT) B3LYP^{9,10} 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) computation.¹³ The electronic energies were calculated using CCSD(T) single point calculations^{14,15} and cc-pVnZ basis sets from Dunning^{11,16} for $n = D, T$ and Q before extrapolation to the values at the complete basis set limit by,¹⁷

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

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 software.¹³

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 set^{18–20} with Grimme dispersion correction^{12,21} for the optimization. Single point calculations were done with the M062X Minnesota functional,²² using the GTLargeXP basis set.²³ 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 system²⁴ using a MATLAB code.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.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_2H_4 , CH_4 and C_3H_8) at the growth temperature $T = 1600^\circ\text{C}$, and otherwise the same process parameters, it can be seen (Fig. 1) that the onset of epitaxial growth



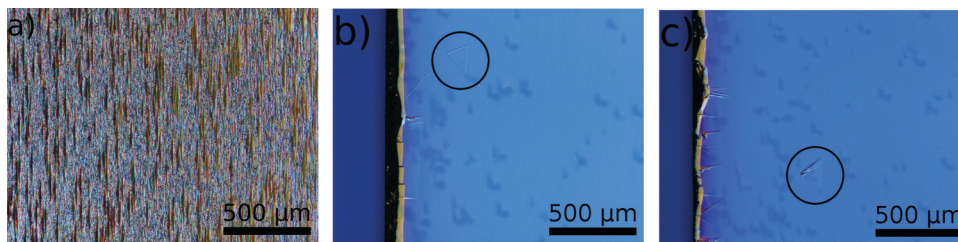


Fig. 1 Optical microscopy images of the SiC surface grown with $T = 1600\text{ }^{\circ}\text{C}$ and different C precursors. (a) 10 cm from the inlet using C_2H_4 showing a rough surface indicative of polycrystalline growth with no onset of epitaxial growth. (b) 3 cm from the inlet using CH_4 showing a smooth surface with a triangular surface defect (circled) indicative of epitaxial growth. (c) 3 cm from the inlet using C_3H_8 showing a smooth surface with a triangular surface defect (circled) indicative of epitaxial growth.

differs between the precursors. C_2H_4 shows no onset of epitaxial growth within 10 cm from the inlet, while both CH_4 and C_3H_8 had their onset of epitaxial growth upstream of the most upstream sample, placed 3 cm from the inlet.

The results shown in Fig. 1 display no difference between CH_4 and C_3H_8 . Lowering the temperature to $T = 1550\text{ }^{\circ}\text{C}$ (Fig. 2) reveals that C_3H_8 has no onset of epitaxial growth within 10 cm from the inlet, while CH_4 shows epitaxial growth at the most upstream sample placed 3 cm from the inlet.

Simulations of the gas phase composition for the three different carbon precursors in combination with SiF_4 were done using kinetic modelling. Concentrations of the main gas phase species with respect to time are shown in Fig. 3 and 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.

CH_3 and C_2H_2 have been identified as the carbon-containing growth species in SiC CVD²⁶ and SiF has previously been suggested to be the main Si growth species in fluorinated SiC CVD.⁸ Here we can 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_2H_2 is highest when using C_2H_4 , and lowest when using CH_4 . The CH_3 concentration is very similar for C_3H_8 and CH_4 as precursors, while it is at least three orders of magnitude lower when C_2H_4 is used.

Discussion

The decomposition chemistry of SiF_4 , leading to more usable Si-containing species for SiC growth, is slow compared to the decomposition of C_3H_8 and C_2H_4 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 SiF_4 precursor decomposes on its way through the susceptor. Changes in the C/Si ratio will influence the growth conditions for

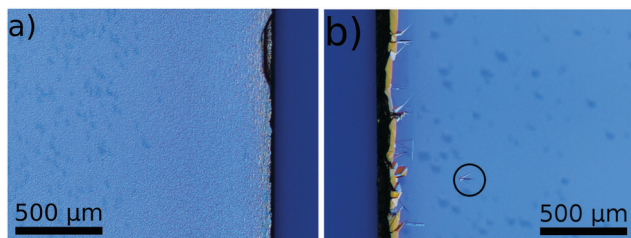


Fig. 2 Optical microscopy images of the SiC surface grown with $T = 1550\text{ }^{\circ}\text{C}$ and different C precursors. (a) 10 cm from the inlet using C_3H_8 showing a rough surface indicative of no growth and no onset of epitaxial growth, (b) 3 cm from the inlet using CH_4 showing a smooth surface with a triangular surface defect (circled) indicative of epitaxial

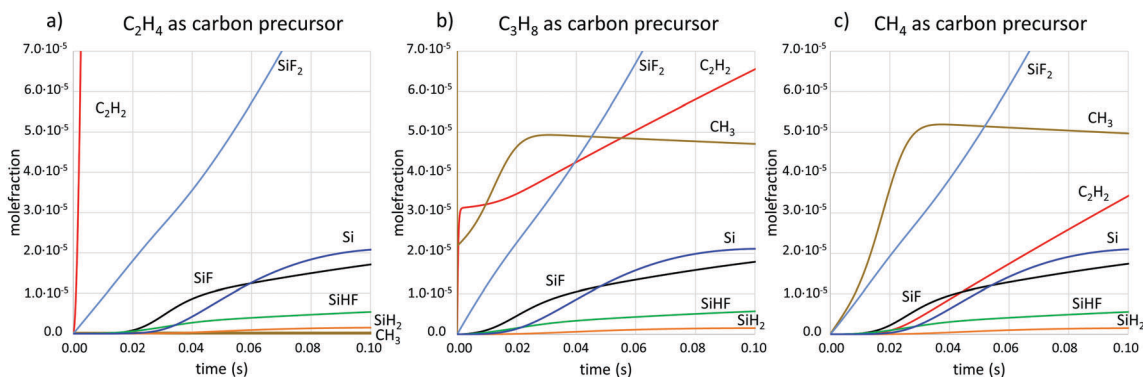


Fig. 3 Concentrations of main gas phase species at $T = 1600\text{ }^{\circ}\text{C}$ from kinetic simulations when the carbon precursor is (a) C_2H_4 , (b) C_3H_8 , (c) CH_4 .

growth.



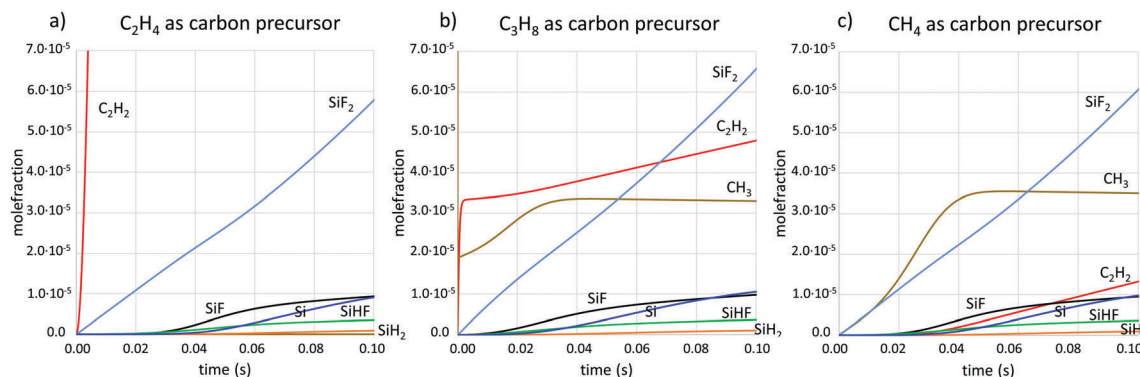


Fig. 4 Concentrations of main gas phase species at $T = 1550\text{ }^{\circ}\text{C}$ from kinetic simulations when the carbon precursor is (a) C_2H_4 , (b) C_3H_8 , (c) CH_4 .

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, SiF_4 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. CH_4 , which is not normally used in the CVD of SiC just because of its slow decomposition chemistry, is an excellent partner in this respect.

The experimental results (Fig. 1 and 2) show that the kinetics for forming carbon-bearing growth species for SiC differs between different carbon precursors. When using SiF_4 together with C_2H_4 , the combination of resulting growth species does not lead to epitaxial growth along the studied area in the susceptor. With C_3H_8 or CH_4 , on the other hand, the growth is already epitaxial at the most upstream part of the susceptor at $T = 1600\text{ }^{\circ}\text{C}$, 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 $T = 1550\text{ }^{\circ}\text{C}$, 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 at this temperature.

The experimental results are supported by the chemical kinetic calculations, where it can be 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 forms a third C–C bond to form C_2H_2 , the decomposition product of CH_4 is mainly CH_3 , which may then 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.²⁶ 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 be readily 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,

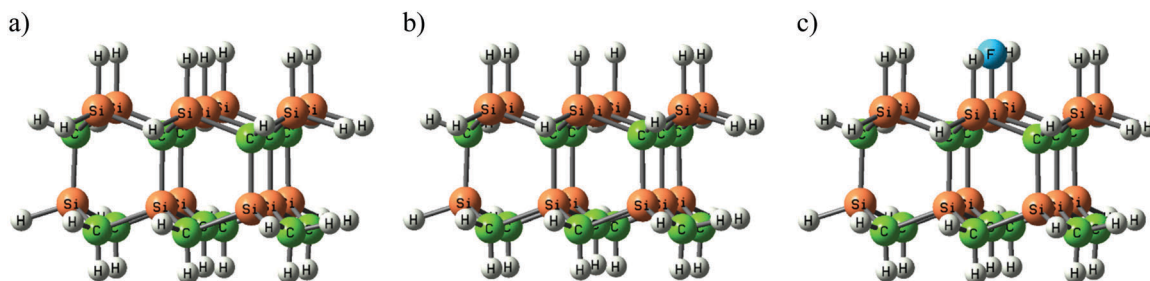


Fig. 5 The SiC cluster models used in this study of (a) the completely hydrogen-terminated surface – H (s), (b) the cluster with a dangling bond – X (s) and (c) the single fluorine-terminated structure – F (s).



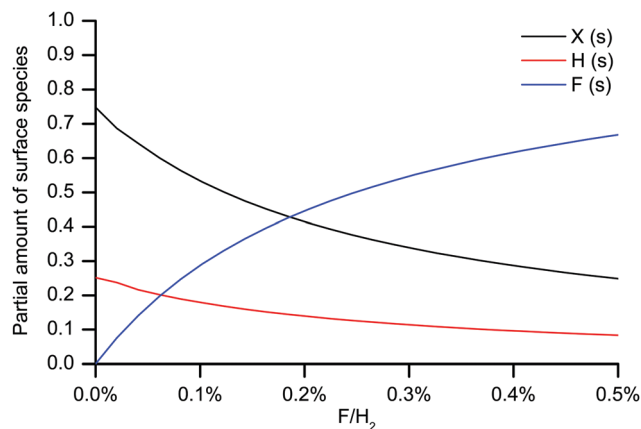


Fig. 6 Equilibrium composition of the surface species at different F/H_2 ratios from quantum-chemical modeling. H (s) denotes hydrogen termination, X (s) denotes surface vacancy, F (s) denotes fluorine termination.

F (s), with increasing F gas phase concentration are shown in Fig. 6. The fluorine termination increases with fluorine concentration at 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 would also increase the amount of fluorine-terminated surface sites downstream.

To verify the dependence of the amount of surface vacancies on the SiC growth, experiments were conducted 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 an 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

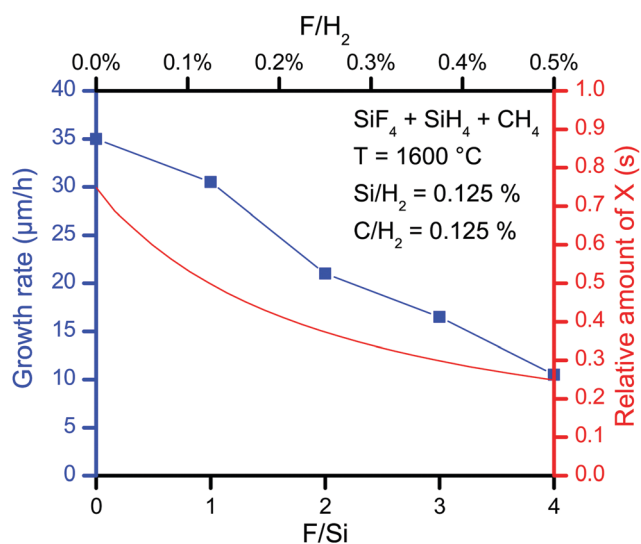


Fig. 7 The relative amount of surface vacancies available for chemisorption of C-bearing growth species and the growth rate obtained for various F/Si or F/H_2 ratios.

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 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, and thereby reducing the growth rate even more than if a lower Si/ H_2 ratio had 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_2H_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_2H_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_2H_4 and C_3H_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 onto. We show that the slow kinetics of the CH_4 molecule matches the slow kinetics of the SiF_4 molecule while the C_2H_4 and C_3H_8 molecules have faster kinetics, leading to a 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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