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Current understanding of the halogenated deposition chemistry for chemical vapor deposition of SiC

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Abstract

The deposition rate of silicon carbide (SiC) in chemical vapor deposition (CVD) can be boosted by addition of chlorine. This has been explored and applied for hard coatings and electronic grade SiC. We briefly summarize the recent research done in the field of SiC CVD and discuss the understanding of the CVD chemistry with addition of halides. We seek to improve a previous statement that SiCl_2 is the main silicon species for growth of SiC. Recent experiments and modeling suggest that SiCl_2 , and its fluorinated and brominated analogues, are inactive and that $\text{SiF}/\text{SiCl}/\text{SiBr}$ are the main halogenated species for growth.

Introduction

Silicon carbide (SiC) is both a hard material and a wide bandgap semiconductor with high thermal conductivity. This has made it a very interesting material for power electronics as well as hard coatings, both applications require film deposition. The preferred method for depositing thin films of SiC is chemical vapor deposition (CVD). While CVD of SiC for hard coatings applications typically use the single-source precursor methyl trichlorosilane, CH_3SiCl_3 (MTS),¹ CVD of electronic grade SiC typically uses silane, SiH_4 , and either ethylene, C_2H_4 , or propane, C_3H_8 , as precursors with a possibility to vary the C/Si ratio in the gas mixture.² In both cases, the precursors are diluted in a carrier gas; the hard coatings industry often uses nitrogen for low cost and safety, while the electronics industry uses hydrogen since nitrogen is a n-type dopant in SiC. CVD of SiC for hard coatings is typically done at 1000-1400 °C¹ while CVD for epitaxial SiC films require higher temperatures of

1500-1700 °C.²

Motivated by the need for thick, 50-200 µm epitaxial layers for power device applications,³ there has been considerable research efforts during the past 15-20 years to use a chlorinated CVD chemistry also for electronic grade SiC. CVD of SiC using SiH₄ and C₂H₄/C₃H₈ could 20 years ago only afford growth rates of 5-10 µm/h.⁴ The deposition was here limited by the low partial pressure of SiH₄ possible in the process; too high partial pressure of SiH₄ resulted in homogeneous gas phase nucleation of silicon droplets, detrimental to the SiC surface morphology making the epitaxial layer useless for device fabrication. The addition of an excess of Cl to the CVD chemistry prevents the formation of Si–Si bonds (bond enthalpy 226 kJ mol⁻¹ or 2.34 eV)⁵ since the stronger Si–Cl bonds (bond enthalpy 400 kJ mol⁻¹ or 4.15 eV)⁵ are thermodynamically more favored. The use of chlorinated CVD chemistry affords deposition rates for epitaxial SiC films of 100-200 µm/h.⁶

We reviewed the field of chlorinated CVD chemistry for electronic grade SiC 2012⁶ and discussed then the understanding of the CVD chemistry up to that point in time. The research in the field has since then expanded to include also fluorinated and brominated CVD chemistry for epitaxial SiC films.^{7,8} These works and more detailed modelling of the chlorinated CVD chemistry for SiC has shifted our understanding of the chemical mechanisms in halogenated CVD of SiC. In this paper we therefore summarize the current understanding of halogenated CVD chemistry for SiC and point out the need for more detailed modeling in CVD coupled with careful experiments for a better understanding of CVD chemistry in general.

Current Status

In our 2012 review we drew the conclusion that SiCl₂ is the most important species for the deposition of SiC, i.e. the major silicon species contributing to growth of SiC.⁶ This was based on the result that it was always the Si species with the highest concentration in the gas phase in all thermochemical models; regardless of the chemical approach to chlorinated CVD chemistry, i.e. if chlorinated silanes, chlorinated hydrocarbons, MTS or HCl-addition was used for a chlorinated CVD chemistry. This was also analogous to the current understanding that SiH₂ is the most important species in standard, non-chlorinated, CVD chemistry for

electronic grade SiC. We also argued for using the formation path of SiCl_2 from the precursor molecules as a guide to understand the differences in precursor utilization between the approaches to chlorinated CVD chemistry: The lower growth rate for the same amount of precursor supplied for the approach to use SiH_4 with added HCl compared to HSiCl_3 could be explained by a less complicated chemical path to form SiCl_2 from HSiCl_3 compared to $\text{SiH}_4 + 2 \text{HCl}$.⁹

Signs that the importance of SiCl_2 was insufficient

Encouraged by early results comparing MTS with the brominated analogue methyltribromosilane, CH_3SiBr_3 (MTBS) showing a higher deposition rate and lower activation energy of epitaxial SiC from MTBS compared to MTS,¹⁰ we did a direct comparison between brominated and chlorinated CVD chemistry for SiC by adding either HBr or HCl to SiH_4 and C_2H_4 .⁷ The Si–Br bond has a bond enthalpy of 330 kJ mol^{-1} or 3.42 eV .⁵ We showed reproducibility of the higher deposition rate for a brominated chemistry compared to a chlorinated chemistry. When we did thermochemical modeling to compare the brominated and chlorinated chemistries, we found that the brominated analogue to SiCl_2 , SiBr_2 , was formed in lower amounts than SiCl_2 . This was a puzzling result as it was expected that the higher observed deposition rate of SiC with addition of HBr, compared to addition of HCl, should be explained by a higher concentration of SiBr_2 , compared to SiCl_2 . We therefore concluded that the understanding of the importance for SiCl_2 , then expanded also to SiBr_2 , was likely insufficient.⁷ That is, the major Si containing gas species is inactive for the growth of SiC.

In parallel we started quantum chemical modeling of the surface chemistry of SiC CVD, studying the differences between SiH_2 and SiCl_2 to probe the origins of the higher deposition rate afforded with a chlorinated chemistry.¹¹ It was expected that the SiCl_2 species should have a more favorable surface chemistry compared to the SiH_2 species to explain the tenfold increase in deposition rate with a chlorinated CVD chemistry. We found that the SiH_2 species had a higher adsorption energy and lower activation energy for adsorption compared to SiCl_2 .¹¹ SiH_2 was also found to diffuse more easily on the SiC surface than SiCl_2 .¹¹ These results did not support the experimental results that the chlorinated CVD chemistry gives a

higher deposition rate. When this modeling was extended to also include SiBr_2 , it was found that the difference in adsorption energies between SiCl_2 and SiBr_2 on the SiC surface is very small,⁷ which does not support the experimental observations that brominated CVD chemistry gives higher deposition rate than chlorinated CVD chemistry.

To complete the investigations of the halogens in SiC CVD we undertook studies of fluorinated CVD chemistry using SiF_4 . We demonstrated that SiF_4 can be used for CVD of epitaxial SiC films, but the deposition rate achieved were only about $30 \mu\text{m/h}$.⁸ This can be expected from the bond enthalpy, the very strong Si–F bonds (597 kJ mol^{-1} or 6.19 eV)⁵ should render a much slower kinetics resulting in fewer growth species. Through combined thermochemical modeling and careful experiments, we showed that the fluorinated SiCl_2 analogue, SiF_2 , cannot be a growth species, but instead SiF is likely the main growth species, possibly with minor contributions from SiHF .⁸

Future Needs and Prospects

A better understanding through better modeling

The concentration of gas phase species above the surface is not the only factor of importance for the deposition chemistry. We have recently described a systematic modeling approach for CVD that combine quantum chemical calculations with computational fluid dynamics for multi scale modeling of CVD processes.¹² In short, the approach is a seven step protocol where the controlling phenomena/factors are identified through a system and time scale analysis and a model for the gas phase reaction mechanisms and determine reaction rate constants utilizing quantum-chemical computations or other methods is constructed. The gas phase kinetic model is verified by performing gas phase kinetics simulations and species concentration trends are evaluated from the kinetic model and compare with experiments to determine growth species. A surface reaction mechanism is then constructed and used to determine reaction rate constants. Computational Fluid Dynamics (CFD) is then used to simulate the CVD process with the gas phase and surface kinetics included. Finally the CFD model is validated against experiments. In this modeling approach, the reaction kinetics were modelled taking both concentrations and reaction free energy barriers into account. The latter case often using the Eyring formula (which leads to the Arrhenius equation). For the details

of the calculations, we refer to Ref ¹². To demonstrate this modeling approach, we used SiC as a model system and deduced a detailed chemical model for CVD of SiC without using correction factors to fit experimental data. The model can explain several phenomena in CVD of epitaxial SiC:

The amount of surface-active carbon species controls the nitrogen doping in SiC.¹³ It is known that the nitrogen doping does not vary much with temperature between 1500-1600°C.¹⁴ Our recent modeling shows that the concentrations of C₂H₂ and CH₃ remain constant between 1400-1700°C, while CH₄ and C₂H₄ decrease.

When varying the concentrations of carbon, i.e. the C/Si ratio, species with more than two silicon atoms (silicon clusters) decrease with increasing C/Si, while species with more than three carbon atoms increases to significant levels. The degree of step bunching can be controlled by changing the C/Si ratio, and it is suggested that step bunching is caused by either Si or C clusters on the surface.¹⁵ The modeling results support the presence of such species at these conditions.

A rough surface is an indication of high carbon concentrations (high C/Si ratio), and experiments show that high Si/H₂ requires lower input C/Si to maintain a SiC film with smooth morphology.¹⁶ With increasing silicon concentrations (high Si/H₂, maintaining C/Si ratio), a saturation in growth rate, along with a roughening of the surface is observed experimentally.¹⁷ This indicates that at some Si concentration level, species that do not contribute to the growth are formed instead of the growth species. Modeling results show concentration saturations of Si, SiH, and SiH₂ above Si/H₂ = 0.1 %. SiCl and SiBr increase at least up to Si/H₂ = 1.0 %, and concentrations level out beyond Si/H₂ > 1.0 %, while SiF (and SiHF) remain constant at Si/H₂ > 0.05 %. In the standard Si-C-H system, larger Si-containing species (clusters) are formed instead of the smaller active growth species. In the chlorine and bromine cases, some of the silicon goes to forming the clusters, and some form halogenated silicon species, which reduces the amount of gas phase nucleation. In the fluorine case, the silicon goes almost exclusively to SiF₂ and SiF_{4-n}H_n (n = 0-3).

The model also shows that SiCl₂ is not a species active for growth since the concentration of SiCl₂ increases with higher Cl/Si ratio in the inlet CVD gas mixture and decreases with increasing temperature while the experimental deposition rates show opposite trends.^{18,19}

Using the same modeling approach for brominated and fluorinated chemistries in CVD of SiC, we also see lower concentrations of Si-Br species as compared to Si-Cl species and higher concentrations of Si-C and Si-H species in the Br chemistry as compared to Cl. Since the growth rate is about 10% higher using the Br chemistry,⁷ this would indicate that the halogenated species do not have a positive effect on the growth rate. In the fluorinated chemistry, the concentrations of Si-C and Si-H species are at least one order of magnitude lower, as compared to the other chemistries. This could indicate that there are fewer number of different active growth species in the F chemistry, and we speculate that this could lead to fewer structural defects.

The current understanding of halogenated CVD chemistry for SiC

Gas phase chemistry

The high temperatures used for CVD of electronic grade SiC ensures that chemical equilibrium establishes faster than the residence time for the gas in the reactor. Since the residence time, i.e. the time the gas spends in the deposition zone of the CVD reactor, is of the order of 0.1 – 1.0 s, this means that the highly reactive radicals that are created have enough time to react and form more stable species. Therefore, we could expect that species with high concentrations at thermodynamic equilibrium will also be present in relatively high concentrations in the SiC CVD reactor, even though concentration levels may be different. Therefore, we use the approach to analyzing changes in concentrations of the high-concentration species at equilibrium with different modelled process conditions to get an idea of the behavior of the chemistry involved, which helps us building a kinetic reaction model with all the relevant reaction paths.

It is then concluded that species with concentrations high enough to provide sufficient material to SiC deposition are: CH₃, CH₄, C₂H₂, C₂H₄, Si, SiH₂, Si₂C, Si₃C, SiCH₂, SiC₂, SiCl₂, SiCl, SiHCl (or the corresponding Br and F species). Some of these species are more stable than others and will therefore not contribute to the deposition of SiC.

In previous literature, species with the highest concentrations were automatically assumed to be the ones contributing to the growth. Therefore, SiCl₂ was expected to contribute the most to the growth of SiC.⁶ Following the same reasoning, SiBr₂ and SiF₂ would contribute the

most when chlorine is substituted for bromine or fluorine. However, the growth rate is higher when using bromine compared to chlorine, while it is lower when using fluorine.^{7,8} Here, we present modeling of the gas phase chemistry using the systematic modeling method for CVD¹². These results show an opposite trend of the relative SiX_2 concentrations, both with temperature (Fig. 1) and with increasing halogen to silicon ratio in the gas mixture (Fig. 2). As explained above, the difference in adsorption rates is too small to account for the difference in growth rates.

Another noteworthy approach to an increased understanding of the CVD chemistry for deposition of SiC is the study by Shima et al.²⁰ where high aspect ratio structures combined with mass spectrometry was used to reveal the importance of the CH_2SiCl_3 species when using the common precursor methyl trichlorosilane, CH_3SiCl_3 (MTS).

Surface chemistry

During CVD, dangling bonds on the SiC surface will, to a large extent, be passivated. Deposition of SiC is suggested to be highly dependent on the creation of vacancies, i.e. sites with dangling bonds in the surface passivation layer.²¹ For the standard, non-halogenated CVD chemistry, the surface will be passivated by hydrogen atoms. In halogenated CVD chemistry, halogen atoms are also available for surface passivation. Given the high bond enthalpy of halogens–silicon and halogen–carbon, it is not surprising that halogenated CVD chemistry renders a lower probability to form vacancies in the surface passivating layer.²² For example, in Ref. ²² it was found that the surface Si dangling bond ratio fell from about 0.75 to about 0.3 when the F/H₂ ratio was increased from 0 to 0.5% at typical CVD conditions, based on first-principles calculations. The SiC deposition can to some extent be regarded as inhibited by the presence of halogen atoms on the surface. This explains the often observed decrease in deposition rate with higher halogen to silicon ratio in the inlet CVD gas mixture; higher partial pressure of halogen atoms in the gas phase lowers the probability to form vacancies in the surface passivating layer which hinders the deposition of SiC. We argue that this surface passivating effect is more probable to explain the reduction in deposition rate with higher partial pressure of halogen, than the often-suggested increased competing etching of the SiC film. In addition, the etching efficiency of HCl molecules were computationally

found to be subpar as compared to that of H atoms, which of course are present in both halogenated and non-halogenated CVD.²³

A recent paper by Rana et al. found a route to graphene synthesis on SiC by a surface treatment by SiF₄ where the SiF₄ is suggested to etch Si from the SiC surface.²⁴ One must remember that the surface passivation that we discuss is, like any atomic layer at temperatures above 1000 °C dynamic – it will lose atoms, forming vacancies and new atoms will arrive to the surface to fill the vacancies. If one does not provide the chemical species for material growth, as in the study by Rana et al, etching of surface silicon will be significant. It is important to note that in the study by Rana et al. they etch away silicon to form graphene one does not need a high etching rate to remove one to two atomic layers of silicon in a minute. If the drop in deposition rate seen when using SiF₄ as Si-precursor is going to be explained only by a higher etching rate, then the etching rate must be in the order of 70 µm/h and would also require the etching of carbon. The adsorption process on the silicon face of SiC by precursors such as Si, SiH, SiH₂, SiHX and SiX₂ have been investigated by quantum-chemical calculations.²⁵ It was found that the adsorption had the highest adsorption energy at methylene sites, where it occurs without activation energy barriers. Comparing H- and Cl-chemistries, the most favorable (i.e. lowest) reaction Gibbs free energy was for Si adsorption, followed by SiH, SiCl, SiH₂, SiHCl and SiCl₂. Looking at F- and Br-chemistries, the internal ordering was SiX, SiHX and SiX₂. Similar results were prior obtained for F in Ref. ⁸. This indicates that the most potent Si contributors to the growth process are the species Si, SiHX and SiH. Plausible reaction mechanisms for bulk formation starting from SiH respective SiCl were also investigated, and it can be noted that for the reaction step with the highest energy barrier the Gibbs free activation energy was 309 and 269 kJ/mol, respectively, indicating SiCl to be kinetically favored over SiH.

The surface reaction scheme from Ref. ²⁵ was used in the microkinetic simulation segment of the CFD simulations of CVD growth using SiH₄ and C₂H₄ as precursors in Ref. ¹². Si and SiH as silicon precursors was found to be sufficient to reproduce the experimentally observed growth rate, which at the very least shows that it is possible that SiH is one of the most important growth species. Further and more extensive studies are needed in order to unambiguously predict the dominant growth species from simulations alone. Such studies

should also include edge and terrace effects. A systematic and thorough scanning of more of the multitude of possible reaction paths together with sensitivity analyses for the computed growth rates would be desirable, possibly using machine learning tools.

Conclusions

In this paper we have tried to update our understanding of chlorinated CVD chemistry of SiC from ten years ago and in doing that give a fuller description of the chemistry in the CVD process. We briefly review more recent results to point out that our former understanding with the SiCl_2 species as the most important species for deposition of SiC is insufficient. Recent modeling suggests this, the major Si containing gas phase species, to be inactive for the deposition and rather function as a gas phase reservoir for Si. Instead, recent findings point towards SiCl as the most important Si species for SiC deposition with C_2H_2 as the most important C species. These results also extend to fluorinated and brominated CVD of SiC. Recent findings also point to a change in surface chemistry in halogenated CVD compared to standard CVD where the SiC surface is believed to be halogen terminated rather than hydrogen terminated, posing an alternative explanation than enhanced etching for the decrease in deposition rate with higher halogen to Si ratio.

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Figures and Figure Captions

Fig. 1 Molefractions of halogenated silicon species at equilibrium when varying the temperature ($\text{Si}/\text{H}_2 = 0.25\%$, $\text{C}/\text{Si} = 1.0$, $\text{X}/\text{Si} = 4.0$ where $\text{X} = \text{Cl}$, Br or F). Solid lines represent a chlorinated CVD chemistry, dashed lines a brominated CVD chemistry and dotted lines a fluorinated CVD chemistry.

Fig. 2 Molefractions of halogenated silicon species at equilibrium when varying the X/Si ratio ($T = 1600^{\circ}\text{C}$, $\text{Si}/\text{H}_2 = 0.25\%$, $\text{C}/\text{Si} = 1.0$). Solid lines represent a chlorinated CVD chemistry, dashed lines a brominated CVD chemistry and dotted lines a fluorinated CVD chemistry.