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A Quantum Chemical Exploration of SiC Chemical Vapor Deposition

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Abstract

SiC is a wide bandgap semiconductor with many attractive properties. It has attracted particular attentions in the areas of power and sensor devices as well as biomedical and biosensor applications. This is owing to its properties such as large bandgap, high breakdown electric field, high thermal conductivities and chemically robustness. Typically, SiC homoepitaxial layers are grown using the chemical vapor deposition (CVD) technique. Experimental studies of SiC CVD have been limited to post-process measuring of the layer rather than *in situ* measurements. In most cases, the observations are presented in terms of input conditions rather than in terms of the unknown growth condition near the surface. This makes it difficult to really understand the underlying mechanism of what causes the features observed experimentally. With help of computational methods such as computational fluid dynamic (CFD) we can now explore various variables that are usually not possible to measure. CFD modeling of SiC CVD, however, requires inputs such as thermochemical properties and chemical reactions, which in many cases are not known. In this thesis, we use quantum chemical calculations to provide the missing details complementary to CFD modeling.

We first determine the thermochemical properties of the halides and halohydrides of Si and C species, SiH_nX_m and CH_nX_m , for X being F, Cl and Br which were shown to be reliable compared to the available experimental and/or theoretical data. In the study of gas-phase kinetics, we combine *ab initio* methods and DFTs with conventional transition state theory to derive kinetic parameters for gas phase reactions related to Si-H-X species. Lastly, we study surface adsorptions related to SiC-CVD such as adsorptions of small C-H and Si-H-X species, and in the case of C-H adsorption, the study was extended to include subsequent surface reactions where stable surface products may be formed.

Sammanfattning

SiC är ett halvledarmaterial med stort bandgap som har många attraktiva egenskaper. Det har fått särskilt mycket uppmärksamhet inom kraftkomponenter och sensorer, men också för tillämpningar inom biomedicin och biosensorer. Detta beror på materialets stora bandgap, förmågan att klara höga elektriska fält, goda värmeledningsförmåga och kemiska stabilitet. Epitaxiska skikt av SiC för kommersiella tillämpningar tillverkas med hjälp av kemisk ångdeposition (Chemical Vapor Deposition, CVD). Experimentella studier av SiC CVD begränsas till mätningar som görs i efterhand, snarare än under processens gång. För det mesta görs observationer med utgångspunkt från processens ingångsvärden istället för från de okända tillväxtförhållandena vid ytan. Detta gör det svårt att verkligen förstå de underliggande mekanismerna för de observerade experimentella resultaten. Med hjälp av beräkningsmetoder, såsom computational fluid dynamics (CFD) kan vi utforska olika variabler som vanligtvis inte går att mäta. Dock kräver CFD-modellering av SiC CVD ingångsdata i form av termokemiska egenskaper och kemiska reaktioner, och dessa data är ofta okända. I den här avhandlingen har vi använt kvantkemiska beräkningar för att ta reda på de detaljer som saknas för fortsatt CFD-modellering.

Till att börja med har vi bestämt de termokemiska egenskaperna för halider och hydrohalider av SiH_nX_m och CH_nX_m , där X är F, Cl och Br, och som visats vara tillförlitliga data jämfört med tillgängliga experimentella och teoretiska data. För att studera gasfas-kinetik har vi kombinerat *ab initio* och DFT-beräkningar med konventionell "transition state theory" för att härleda kinetiska parametrar för gasfas-reaktioner för Si-H-X species. Slutligen har vi studerat ytadsorption relaterad till SiC CVD, såsom adsorption av små C-H och Si-H-X species, och som i fallet C-H adsorption utökats till att även inkludera efterföljande ytreaktioner där stabila ytprodukter kan bildas.

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List of included publications

Paper 1 Shortcomings of CVD modeling of SiC today

Ö. Danielsson, P. Sukkaew, L. Ojamäe, O. Kordina and E. Janzén
Theoretical Chemistry Accounts (2013) 132, 1398.

My contributions: I calculated all thermochemical properties, performed parts of CFD kinetic model and wrote part of the paper

Paper 2 Thermochemical properties of halides and halohydrides of silicon and carbon

P. Sukkaew, L. Ojamäe, O. Kordina, E. Janzén and Ö. Danielsson
ECS Journal of Solid State Science and Technology (2016) 5, P27.

My contributions: I calculated all thermochemical properties and wrote the entire paper

Paper 3 Silicon chemistry in fluorinated chemical vapor deposition of silicon carbide

P. Stenberg, P. Sukkaew, I. Farkas, O. Kordina, E. Janzén, L. Ojamäe, Ö. Danielsson and H. Pedersen
J. Phys. Chem. C, Just Accepted Manuscript
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My contributions: I calculated all surface chemistry and wrote part of the paper

Paper 4 Adsorption of silicon halides and silicon halohydrides on 4H-SiC during SiC-CVD process.

P. Sukkaew, L. Ojamäe, O. Kordina, E. Janzén and Ö. Danielsson
In manuscript.

My contributions: I calculated all surface chemistry and wrote the entire paper

Paper 5 *Ab initio* study of growth mechanism of 4H-SiC: adsorption and surface reaction of C₂H₂, C₂H₄, CH₄, and CH₃

P. Sukkaew, L. Ojamäe, O. Kordina, E. Janzén and Ö. Danielsson
J. Phys. Chem. C, Just Accepted Manuscript
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My contributions: I calculated all surface chemistry and wrote the entire paper

Paper 6 Opening the black box of silicon carbide chemical vapor deposition

P. Sukkaew, P. Stenberg, O. Kordina, E. Janzén, H. Pedersen, L. Ojamäe, and Ö. Danielsson

Submitted.

My contributions: I calculated gas-phase kinetic reactions of the Si-H-F, Si-H-Cl and Si-H-Br systems

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Chapter 1 Introduction

1.1 Silicon Carbide

SiC is a wide bandgap semiconductor with many attractive properties. As the Si technology reaches its maturity, the investment has moved on to developing new materials with physical properties superior to Si. SiC has attracted particular attentions in the areas of power and sensor devices as well as biomedical and biosensor applications. This is owing to its properties such as large bandgap, high breakdown electric field, high thermal conductivities and chemically robustness^{1–8}. Table 1 shows a summary of SiC properties at room temperature in comparison to Si and other wide bandgap semiconductors. The usage of wide bandgap semiconductors in power device applications enhance the efficiencies in energy transformations, while making it possible to produce devices in smaller sizes and be more robust in operations at high temperatures^{1,9,10}. It is also expected that SiC unipolar power devices will replace Si bipolar devices over the blocking range of 300 – 6500 V, and there is a promising future for these devices in the ultrahigh (> 10 kV) voltage range¹. The chemical robustness of Si-C bond and large Young's modulus also make SiC attractive in sensor applications featuring high temperature and hostile environments^{4,5,11} as well as biomedical and biosensor applications^{12,13}.

Table 1 Properties of SiC in comparison to Si and other wide bandgap semiconductors.

Properties	SiC			Si	GaN	Diamond
	4H	6H	3C			
Energy gap ^{1,4,14,15}	3.2	3.0	2.3	1.12	3.4	5.5
Thermal conductivity (W cm ⁻¹ K ⁻¹) ^{14,16}	4.9	4.9	3.6	1.3	1.3	20
Electron mobility (cm ² V ⁻¹ s ⁻¹) ^{4,14,17}	1000	400	800	1500	900	2200
Breakdown field (MV cm ⁻¹) ^{4,7,14}	~3	2	3.2	0.3–0.6	~3	10
Electron saturation velocity (cm s ⁻¹) ^{14,17}	2×10 ⁷	2×10 ⁷	2×10 ⁷	1×10 ⁷	2×10 ⁷	3×10 ⁷
Melting Point (K) ^{4,16}	3103	3103	3103	1690	2673	1673
Young's modulus (GPa) ⁴	300 to 500			130–180	200–300	1000
Relative dielectric constant ^{6,11,14}	10	9.7	9.6	11.9	8.9	5.7

SiC crystallizes in both cubic zincblende and hexagonal wurtzite structures and exhibits more than 200 polytypes^{18–20}. These polytypes, distinguished by the lattice types and stacking orders, are shown to have rather similar properties regarding their physical, chemical and mechanical aspects¹⁵. The differences are seen in the band gap and band structures and are shown to vary as functions of hexagonalities¹⁵, which are defined as the percentages of atoms in hexagonal positions in the unit cells. Among SiC many polytypes, the majority of research are focused on the 6H, 4H and 3C polytypes, shown in Figure 1.1. The first two polytypes are hexagonal and the last is cubic. The 6H and 4H polytypes have been used as substrates for the group III-N heteroepitaxial growth²¹, graphene²² as well as homoepitaxial growth of SiC. For GaN epitaxy, 6H and 4H SiC substrates have advantages in having small lattice constant mismatch to GaN and good thermal conductivity²¹. At present both 4H- and 6H-SiC substrates are commercially available in large size and good quality. For electronic applications, the 4H polytype is the most common owing to its technological status and physical properties. More reviews on the SiC high power applications may be found in Ref.^{1,2,6,23–25}. The 3C polytype,

Figure 1.1 Stacking orders of 3C, 4H, and 6H polytypes of SiC. The letter A, B and C refer to the three stacking positions of a closed packed structure. The 3C polytype has 3 repeated units, ABC. The 4H polytype has 4 repeated units, ABCB, and the 6H polytype has 6 repeated units, ABCACB.

on the other hand, is preferable for micro electro mechanical systems (MEMS) sensors for its ability to grow on Si wafers and hence compatible with conventional Si based MEMS processes ^{4,5}.

1.2 Chemical Vapor Deposition (CVD) of SiC

The progress in SiC technology has sped up drastically since the emergence of high quality and large SiC wafers grown by seed sublimation method ^{26,27}. Active layer of SiC is commonly carried out homoepitaxially using chemical vapor deposition (CVD) technique ^{28,29}. Chemical vapor deposition (CVD) as its name suggests is a process where deposition occurs via chemical reactions from vapor phase precursors ³⁰. The process has been utilized to grow various kinds of materials as reviewed by Ref. ³¹. The quality of homoepitaxial layers depends directly on the ability to control the uniformity, layer thickness and doping density while at the same time suppressing the formation of defects and, particularly in SiC homoepitaxy, avoiding polytype mixing. The polytype mixing can be reduced or completely eliminated by a method called “step-controlled epitaxy” ³². This technique uses surface steps to replicate the substrate polytype to the layers. By cutting a substrate at a slight off angle from the usual *c*-plane, more steps are produced on the surface with narrower terraces lying in between. As the widths of terraces become narrower, the species adsorbed somewhere on the terraces can now migrate on the surface to reach the step edges and the growth occurs steadily from the step edges as a result. This way of growth ensures that the stacking order of the substrate is passed on to the growing layer resulting in a single crystal. In this way it is possible to achieve stable growth at lower temperature of polytypes that otherwise would require very high temperature such as 4H and 6H at a lower temperature ³².

CVD of 4H polytypes is usually carried out at the temperature between 1500 to 1600 °C and the pressure of 100-300 mbar. Typically, the process proceeds using precursors such as silane (SiH₄) and light hydrocarbons such as ethylene (C₂H₄) or propane (C₃H₈). Alternatively, usage of precursors such as methyl-trichlorosilane (CH₃SiCl₃) have also been reported ^{28,29}. During the process, the precursors are pre-diluted with a carrier gas (usually hydrogen) and fed into the heated growth chamber where the substrate is placed and well heated. When heated sufficiently, the precursor molecules start to react via pyrolysis reactions producing reactive gaseous species which when reaching the surface will get adsorbed into a new layer. The standard chemistry of SiC CVD is carried out with only the precursors and the carrier gas in the gas flow. How-

ever, problems occur when attempting to increase the growth rate by feeding in more precursors, i.e. by increasing the precursor concentrations. It is observed that when high concentrations of precursors have been used so-called silicon droplets start to form in the gas and damage the growing surface when they get into contact²⁹. This can be suppressed by adding halogen into the system to dissolve the droplets. With halogen addition, the growth rate can be increased significantly, as high as a few hundred micrometers per hour²⁹. In most cases, Cl has been used for this purpose. Recent research also found that Br and F chemistries are applicable to SiC CVD^{33–35}.

Experimental studies of SiC CVD have been limited to post-process measuring of the layer rather than *in situ* measurements. In most cases, the observations are presented in terms of input conditions at the inlet and reactor setup such as precursor flow rates, C/Si ratios, doping agent flow rates, process temperature etc. rather than in terms of the actual condition on the surface. It should be noted that the inlet conditions are not necessarily the same as the condition just above the surface. Most importantly, the conditions at the inlet and on the surface might not be related via linear relationships³⁶. Without knowing the actual surface condition, it is difficult to elucidate the underlying mechanism. This can be remedied by using various modeling methods.

1.3 Present Status of SiC-CVD Process Modeling

Computational modeling can be used to study what is happening inside the CVD growth chamber. Modeling of CVD-related phenomena has been carried out by many different methods, depending on the time and length scales of the phenomena. For calculations in macroscale (reactor scale), computational fluid dynamic (CFD) is a powerful method which has been applied to various types of CVD processes and materials allowing predictions of heat and flow distributions inside the growth chamber, types and concentration profiles of gaseous molecules and radicals, profiles of growth rates and doping^{37–40}. Usage of CFD ranges from designing of reactor geometry to process control. CFD studies of SiC CVD were reported in Ref^{38,41–43}.

For CVD calculations, CFD requires detailed input of all aspects ranging from material properties in heat and mass transports to elementary chemical reactions occurring in the process. The methods for solving the mass and heat transport equations are well developed and the calculations are reliable^{38,42}. The chemical reactions occurring during CVD can be divided into a gas-phase

part and a surface part. For SiC deposition, the gas phase part involves C-Si-H-halide containing species. The reactions involving C-H and Si-H species, both experimental and theoretical data, are available in the literature ^{38,41,44–47} and recently Cl-related reactions ^{48–51} have also become available based on *ab initio* and density functional theory (DFT) calculations. The data have been used extensively in CFD modeling ^{36,51–53}. As the calculation cost is high, it is preferable to preselect only the important reactions rather than using the entire extensive set. In this way the computational cost can be reduced without losing important details. However, for SiC CVD such reduced reaction sets are shown to work well only within limited conditions and need to be generalized to cover wider process conditions in order to be useful ⁵³. Alternatively, it is possible to predict the gas phase compositions directly from their thermodynamic properties ^{39,54,55}. The derived compositions are the condition as the system reaches its thermodynamic equilibrium and hence when its total Gibbs free energy is the lowest. It is a useful way to explore the effects of changes in process conditions on the species formations both in gas phase and condensed phase. For this to be reliable it is important to include all important species including the short-lived radicals where thermodynamic properties are usually not available in the commonly used databases. Quantum chemical calculations such as *ab initio*, DFT and their composites are great tools to derive such properties, especially for short-lived species which are hard to measure experimentally ^{55–57}.

The details of surface reactions are much less studied than the gas phase. Due to necessity surface models for CFD in the literature usually combine experimental results carried out under different conditions than the CVD ^{58–63}. Computational studies on adsorptions on SiC surfaces are also rare and unsystematic ^{64–70}. A useful model for thin film growth needs to include kinetics occurring at different positions (step edge, terrace, surface configuration, etc.). Surface adsorption studies, as well as studies of kinetics and thermochemistry, have been performed extensively using DFT. DFT has its strength in its accuracy and costs compared to other *ab initio* methods ^{71,72}. Time and length scales for DFT are in the order of 1 ps to 1 ns and 1 Å to a few nm respectively ⁷³. With DFT kinetic barrier heights can be obtained with high accuracy and together with transition state theory the actual rate can be calculated. It should also be noted that each DFT calculation provides information for a certain reaction on a certain surface configuration. To build up a surface model for CFD requires multiple DFT calculations covering a wide range of reactions and surface configurations.

Alternative methods to simulate micro to mesoscale such as molecular dynamics (MD) and kinetic Monte Carlo (kMC) can also be applied to study surface phenomena^{65,72,74–76}. These types of methods allow much larger coverage in time and length scales than DFT. MD length scale ranges from a few nm to 100 nm and time scale of a few μs to 1 ms⁷³, while kMC time scale is in the order of a few ms to seconds and at a length scale of 100 nm to 1 μm ⁷³. Unless combined with atomic level method such as DFT as in the case of *ab initio* MD, empirical data will be used to determine the time evolution in such studies. Evolution of atoms and molecules in MD is directed by the use of effective force fields. However, at the present time, MD empirical force fields are not yet suitable for semiconductor growth applications due to their lack of parameters for the details to predict correct chemical reactions involved in the process. A compromising way to solve this problem is to add a quantum mechanical method such as DFT to calculate chemical reactions at a certain, fixed interval of time. This *ab initio* MD however has its drawback in its limited time and length scales due to the usage of DFT. As the time scale is shortened, the chance of actually observing chemical reactions happening during the run is also small, especially for reactions with large energy barriers. kMC can also be empirical based but different from MD in the methods describing time evolution. Using kMC the system is allowed to evolve based on probability and transition rate of events⁷³. The calculations can be performed at a time scale more appropriate to growth and at the same time cover a large number of atoms and molecules. In this way, surface morphology can be taken into account and surface evolution at each positions can be observed. But a drawback with atomistic simulation techniques such as MD and kMC are that lengthy separate simulations need to be performed for e.g. each temperature or pressure. More analytic kinetic simulation techniques like CFD are exceedingly more efficient when it comes to e.g. predicting concentrations and their time-dependence of different species, which are the quantities most of interest in order to understand the CVD process.

Chapter 2 Quantum Chemical Calculations

2.1 Introduction

Quantum chemical calculations apply quantum theory to study chemical related processes. The goal is to determine electronic structures of atoms and molecules, from which the energies and equilibrium geometries can be derived. At atomic level, the particles are described in term of wave functions which are governed by the Schrödinger equation. The non-relativistic, time-independent Schrödinger equation in atomic units is written as

$$H\Psi = E\Psi, \quad (2.1)$$

where

$$\begin{aligned} H &= T_e + T_n + V_{en} + V_{ee} + V_{nn} \\ &= -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \sum_n \frac{1}{M_n} \nabla_n^2 - \sum_i \sum_n \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} \\ &\quad + \frac{1}{2} \sum_{ij, i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{n, m, n \neq m} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|} \end{aligned}$$

The Hamiltonian H is the energy operator containing (listed from left to right) the electron kinetic term (T_e), the nuclei kinetic term (T_n), the electron-nuclei interaction (V_{en}), the electron-electron interaction (V_{ee}) and lastly the nuclei-nuclei interaction (V_{nn}). Ψ is the wave function describing the system.

The Schrödinger equation is a many-body equation and thus it is impractical to solve directly unless the system under study is extremely small. To remedy this, approximations are usually made. The first approximation considered here is the Born-Oppenheimer (BO) approximation, which states that the electrons adjust themselves to the motion of the nuclei or in other words the nucleus movement is separable from that of the electrons. The BO assumption is based on the fact that the nuclei are much heavier than the electrons. It has been shown to work well unless two (or more) solutions come close in energies. With BO approximation, the Schrödinger equation can be separated into two parts, the first describing the electronic wave function and the latter de-

scribing the nucleus wave function. The electronic Schrödinger equation is written as

$$H_e \Psi_e(\mathbf{R}, \mathbf{r}) = E_e(\mathbf{R}) \Psi_e(\mathbf{R}, \mathbf{r}), \quad (2.2a)$$

where
$$H_e = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_n \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{2} \sum_{i,j, i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and the nucleus Schrödinger equation is

$$(T_n + V_{nn} + E_e(\mathbf{R})) \Psi_n(\mathbf{R}) = E_{Tot} \Psi_n(\mathbf{R}) \quad (2.2b)$$

where $T_n = -\frac{1}{2} \sum_n \nabla_n^2$ and $V_{nn} = \sum_i \sum_j \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}$.

The Eq. 2.2a and 2.2b satisfy the total Schrödinger equation,

$$H_{Tot} \Psi_{Tot} = E_{Tot} \Psi_{Tot}, \quad (2.2c)$$

where
$$H_{Tot} = H_e + T_n + V_{nn},$$

$$\Psi_{Tot}(\mathbf{R}, \mathbf{r}) = \Psi_n(\mathbf{R}) \Psi_e(\mathbf{R}, \mathbf{r}).$$

It should be noted that, in the electronic Schrödinger equation, Eq. 2.2a, the nuclei positions are treated as fixed parameters, while in the nuclear wave function equation, Eq. 2.2b, the presence of electrons are treated as a potential acting on the nuclei. It is clear by comparing Eq. 2.1 and Eq. 2.2a - 2.2c that the BO approximation removes the coupling terms between the kinetics of nuclei and electrons.

2.2 Hartree-Fock Approximation

The Hartree-Fock (HF) method⁷⁷⁻⁸⁰ reduces the N -particle Schrödinger equation, Eq. 2.2a, into a one-particle equation by treating V_{ee} as an average field acting on each electron. The HF method uses a Slater determinant as a trial wave function,

$$\Psi^{HF} = \frac{1}{\sqrt{N!}} \det |\varphi_1(1) \dots \varphi_N(N_e)|. \quad (2.3)$$

Here φ_i is a single-electron wave function, called spinorbital, which is a product of a spatial orbital and a spin function. N_e is the number of electrons in the system. The determinant formulation ensures that the wave function is anti-symmetric with respect to an interchange between two electron coordinates. With the wave function written this way, it is inherently assumed that the wave functions can be separated into a product of single-electron spinorbitals. Moreover, by using a single determinant as a solution, HF entirely neglects the effects of electron correlation.

With the Slater determinant ansatz, Eq. 2.3, the electron-electron repulsion in Eq. 2.2a is separated into two terms,

$$\begin{aligned} v_{ee} &= \frac{1}{2} \sum_{ij, i \neq j} \left[\left\langle \Psi \left| \frac{1}{|r_i - r_j|} \right| \Psi \right\rangle \right], \\ &= \frac{1}{2} \sum_{ij} \left[\left\langle \varphi_i \varphi_j \left| \frac{1}{|r_i - r_j|} \right| \varphi_i \varphi_j \right\rangle - \left\langle \varphi_i \varphi_j \left| \frac{1}{|r_i - r_j|} P_{ij} \right| \varphi_i \varphi_j \right\rangle \right], \\ &= \frac{1}{2} \sum_{ij} [J_{ij} - K_{ij}] \end{aligned} \quad (2.4)$$

The first term (J_{ij}) is the classical Coulomb interaction, and the second term (K_{ij}) is the exchange interaction between two electrons. By choosing φ_i to be orthonormal to each other, the exchange term is nonvanished only for the spinorbitals with the same spins. Using variation method, the one-electron HF equation is written as

$$f_i \varphi_i = \varepsilon_i \varphi_i, \quad (2.5)$$

where

$$f_i = h_i + \sum_j [J_j - K_j],$$

$$h_i = -\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|r_i - R_n|},$$

$$J_j \varphi_i = \left[\int d\mathbf{r} (2) \varphi_j^* \frac{1}{|\mathbf{r}(1) - \mathbf{r}(2)|} \varphi_j \right] \varphi_i,$$

and

$$K_j \varphi_i = \left[\int d\mathbf{x} (2) \varphi_j^* \frac{1}{|\mathbf{r}(1) - \mathbf{r}(2)|} \varphi_i \right] \varphi_j,$$

where $\mathbf{r}$ and $\mathbf{x}$ refer to the spatial coordinate and the spatial plus the spin coordinate respectively. The operator f_i is called the Fock operator. The operator h_i is a one-electron Hamiltonian containing the electron kinetics and the potential from the nuclei.

With the HF orbitals given by Eq. 2.5, the HF wave function can be formulated using Eq. 2.3 with the energy derived from the electronic Schrödinger equation Eq. 2.2a,

$$E^{HF} = \left\langle \Psi^{HF} \left| -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_n \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{2} \sum_{i,j,i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \Psi^{HF} \right\rangle. \quad (2.6a)$$

Alternatively E^{HF} can be written in term of HF orbital energy, ε_i , as

$$E^{HF} = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} [J_{ij} - K_{ij}]. \quad (2.6b)$$

It should be noted that the total energy, E^{HF} , is not equal to the sum of the orbital energies, $\sum_i \varepsilon_i$. The sum of the orbital energies, $\sum_i \varepsilon_i$, has in fact counted the repulsion effects twice and thus needs to be corrected with the term $J - K$.

HF requires an initial guess of orbitals to start with, and from there the calculation continues iteratively until the wave function and energy remain unchanged, or in other words until the self-consistency is reached. As it is based on the variational method, HF energy is guaranteed to be either equal to or larger than the exact value. Despite HF's limitation in neglecting electron correlations, HF orbitals can be used to build up a trial wave function for other methods such as MP2 and CC, as well as to provide an exchange energy for hybrid DFTs.

From the HF determinant, a new trial wave function can be built by adding more determinants to the HF wave function. This can be achieved by, for example, using a linear combination of determinants as in configuration interac-

tion (CI) method. The additional determinants can be built by replacing one or more orbitals in the HF determinant with virtual ones, and they are thus called excited Slater determinants. In a “frozen core” approximation, only the valence electrons are allowed to be excited. The excited determinants are classified from the number of excited electrons. When one, two or three electrons are excited, the determinants are called respectively as singly, doubly, triply excited determinants. The virtual orbitals are generally obtained from an HF calculation whenever a basis set larger than a minimum set has been used. To get a reasonable description of the wave function, however, the number of virtual orbitals should not be too small. From the new trial wave function, electron correlations can now be taken into account by solving for a wave function that are a solution to the Schrödinger equation.

2.3 Møller-Plesset Many-Body Perturbation Theory

Correlation effects can be recovered using many-body perturbation theory⁷⁷ where the Hamiltonian, H , is written in terms of a reference Hamiltonian, $H^{(0)}$, and a perturbed Hamiltonian, $H^{(1)}$, with λ being a parameter determining the strength of perturbation,

$$H = H^{(0)} + \lambda H^{(1)}. \quad (2.7)$$

The perturbed Schrödinger equation is

$$H\Psi = [H^{(0)} + \lambda H^{(1)}]\Psi = E\Psi. \quad (2.8)$$

with the energy (E) and wave function (Ψ) written using Taylor expansion as follows,

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots, \quad (2.9a)$$

$$\text{and} \quad \Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots. \quad (2.9b)$$

Substitute Eq. 2.9a and 2.9b into Eq. 2.8, the Schrödinger equation becomes

$$[H^{(0)} + \lambda H^{(1)}][\Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots]$$

$$= [E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots], [\Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \dots] \quad (2.10)$$

By mapping the terms with the same power of λ , we obtain the n^{th} -order perturbation equations. These equations provide formula for the n^{th} -order energy corrections and the n^{th} -order wave function corrections.

In the n^{th} -order Møller-Plesset (MP) many-body perturbation theory, MP n , the reference Hamiltonian is chosen to be the sum of the Fock operators ⁸¹,

$$H^{(0)} = \sum_i f_i = \sum_i [h_i + \sum_j [J_j - K_j]]. \quad (2.11)$$

With the parameter λ set to 1, the perturbed Hamiltonian is

$$H^{(1)} = H_e - H^{(0)} = \frac{1}{2} \sum_{ij, i \neq j} \frac{1}{|r_i - r_j|} - \sum_{ij} [J_j - K_j]. \quad (2.12)$$

Here H_e is the electron Hamiltonian Eq (2.2a). The 0th-order wave function, $\Psi^{(0)}$, is the HF determinant and the i^{th} -order wave function, $\Psi^{(i)}$, in Eq. 2.9b is written in terms of the excited Slater determinants. For MP0 and MP1 levels, the energies are simply $\sum_i \varepsilon_i$ and E^{HF} respectively. The correlation correction starts from MP2 level with the energy correction,

$$\begin{aligned} E^{(2)} &= \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{vir} \frac{[\langle \Psi^{(0)} | H^{(1)} | \Psi_{ij}^{ab} \rangle - \langle \Psi_{ij}^{ab} | H^{(1)} | \Psi^{(0)} \rangle]^2}{E^{(0)} - E_{ij}^{ab}} \\ &= \frac{1}{4} \sum_{ij}^{occ} \sum_{ab}^{vir} \frac{[\langle \varphi_i \varphi_j | \varphi_a \varphi_b \rangle - \langle \varphi_i \varphi_j | \varphi_b \varphi_a \rangle]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}. \end{aligned} \quad (2.13)$$

Here, Ψ_{ij}^{ab} is an excited determinant in which φ_i and φ_j occupied orbitals are replaced by φ_a and φ_b virtual orbitals. The summations $\sum_{ij}^{occ}$ and $\sum_{ab}^{vir}$ run over all occupied and virtual orbitals respectively. The reader is referred to a review paper by D. Cremer ⁸² for explicit forms of MP n . It should be noted that the energies derived from MP n do not always converge monotonically toward the limiting value, as shown in Fig. 2.1a. Instead, it could oscillate around the value as n increases, as shown in Fig. 2.1b ^{82,83}. Nevertheless, for a

well behaved system, acceptable results can be expected between MP3 and MP4 ⁷⁷.

Figure 2.1 Correlation (single point) energies of the MP_n methods in the unit of Hartree of a) CH_4 and b) HF calculated using cc-pVnZ basis sets, for $n = D, T, Q$ and 5. The correlation energies are calculated based on equilibrium structures optimized using CCSD(T) level and cc-pVDZ basis set.

2.4 Coupled Cluster Theory

The coupled-cluster (CC) theory ^{77,84} introduces an ansatz of the form,

$$\Psi_{cc} = e^T \Psi_0, \quad (2.14)$$

where
$$e^T = \sum_n \frac{1}{n!} T^n.$$

The operator T is called the cluster operator and written as $T = T_1 + T_2 + T_3 + \dots + T_N$. The operator T_i produces the i^{th} -excited Slater determinant for the HF wave function, Ψ_0 , such as

$$T_1 \Psi_0 = \sum_i^{occ} \sum_a^{vir} t_i^a \Psi_i^a$$

and

$$T_2 \Psi_0 = \sum_{ij}^{occ} \sum_{ab}^{vir} t_{ij}^{ab} \Psi_{ij}^{ab}.$$

with the summations $\sum_{ij}^{occ}$ and $\sum_{ab}^{vir}$ running over all occupied and virtual orbitals respectively.

With the CC ansatz the Schrödinger becomes $H\Psi_{cc} = He^T\Psi_0 = E_{cc}\Psi_0$. As it is not possible to include all terms in the expansion, the operators which create higher excited states are usually abandoned in the calculation. When T includes only the single (T_1) and double (T_2) excitations, the method is called CCSD. In CCSD, the cluster operator T produces

$$e^{T_1+T_2} = 1 + (T_1 + T_2) + \frac{1}{2}(T_1 + T_2)^2 + \frac{1}{3!}(T_1 + T_2)^3 + \dots \quad (2.15)$$

Figure 2.2 Correlation (single point) energies of a) HF and b) CH4 calculated using CCSD in comparison to MP4. The correlation energies (in Hartree) are shown as functions of cc-pVnZ basis sets, for $n = D, T, Q$ and 5. The correlation energies are calculated based on equilibrium structures optimized using CCSD(T) level and cc-pVDZ basis set.

The exponential function e^T thus includes not only the single and double excitations, T_1 and T_2 , but also their disconnected products T_1T_1, T_1T_2, T_2T_2 , etc.

An addition of connected T_3 to CCSD results in CCSDT but this is usually too costly for most applications. Nevertheless, connected T_3 excitation is usually important ⁷⁷. As shown in Figure 2.2a and 2.2b, the correlation energy from CCSD is inadequate in comparison to the correlation energies derived from MP4. There are various methods derived to approximate an addition of the triple excitation. Among these, the most popular one is the CCSD(T) ⁸⁵, in which the triple excitation is included by perturbation. CCSD(T) is shown to give a good compromise between the cost and accuracy, and in fact found to be more accurate than CCSDT by error cancelations between the overestimation of triple contribution and the error of truncations of higher excitations ^{86,87}.

2.5 Density Functional Theory (DFT)

DFT is similar to HF in reducing the many-body equation into a single-particle equation. It is based on the theorem by Hohenberg and Kohn ⁸⁸ (HK) which demonstrates that the ground state energy of electronic system, as well as other properties at ground state, are unique functionals of the electron density, $E = E[n(r)]$. In the same article ⁸⁸, HK also introduced a “universal” functional of electron density which can be used together with *any* external potential in order to derive the electronic energy and demonstrated that the correct density is obtained by minimizing the energy functional.

Kohn and Sham ⁸⁹ (KS) expanded the work of HK and formulated a set of one-particle Schrödinger equations similar to the Hartree approach. They proposed that the problem of N interacting particles can be solved using an auxiliary system of N uninteracting particles subjected to a potential V . The potential V is in fact a term describing the particle interactions. The auxiliary system can then be described using,

$$\left[-\frac{1}{2}\nabla^2 + V\right]\Psi_i = E\Psi_i \quad (2.16)$$

where $-\frac{1}{2}\nabla^2$ is the kinetic energy of non-interacting particles and $V = V_{ext} + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + E_{XC}$ is the potential resulting from the particles interactions.

The potential V is composed of 1) V_{ext} which is an external potential from the nuclei, 2) the term $\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ which is a potential created by an electronic density $n(\mathbf{r}')$ and 3) E_{XC} which is a new potential containing all N -particle interactions. In this way, Eq. 2.16 puts all the complexities into the unknown exchange-correlation term, E_{XC} ⁹⁰. Up to this point, KS formulation is exact and with the correct exchange-correlation term it provides the density. Similar to HF, DFT has the advantage in its low computational cost in comparison to wave function-based electron correlation methods such as MP n and CC.

The quest in DFT formulation has been to obtain the unknown E_{xc} . KS⁸⁹ presented the first E_{xc} using the homogeneous electron gas assumption, which is valid only for a slowly varying density $n(\mathbf{r})$. The E_{xc} thus depends only on the density $n(\mathbf{r})$ and is called the local density approximation (LDA). The spin generalized case of LDA, called the local spin density approximation (LSDA), assumes that E_{xc} is a function of both spin densities, $n^\alpha(\mathbf{r})$ and $n^\beta(\mathbf{r})$. This type of E_{xc} typically underestimates the exchange part of E_{xc} by 5-10%⁹¹. An improvement by including density gradients ∇n leads to the second type of functionals called the generalized gradient approximation or GGA. GGA functionals are shown to provide improvement over LDA in the energy accuracy, but similar to LDA, GGA suffers from overbinding tendency but with smaller amounts than LDA⁹¹. There are many gradient corrected functions available in the literature. The famous GGA functionals are B88⁹², PW86⁹³, PBE⁹⁴ and LYP⁹⁵.

For quantum chemical calculations in which chemical bonding and thermochemistry are the main focus, hybrid DFTs and their descendants such as meta hybrids have been used extensively and with high success. Hybrid E_{xc} includes the HF exact exchange, E_X^{HF} , to LDA or GGA functional to reduce the overbinding tendency⁹⁶. The most popular hybrid function is B3LYP, which uses the B3 exchange functional from E_{XC}^{B3PW91} ⁹⁶ and the correlation functional from LYP⁹⁵. B3LYP has been used intensively in quantum chemistry with more than 60,000 citations^{91,97}. It was shown to be reliable for determining geometries and calculating thermochemical properties for small organic

molecules ^{98,99}. At the present, there are new functionals available which outperform B3LYP in some aspects especially for kinetic barrier heights ^{100,101} but at the same time more expensive ¹⁰². For a system with many electrons, a compromise then has to be made between the cost and accuracy.

2.6 Basis Sets

In solving the Schrödinger equation using *ab initio* methods, an orbital is usually written as a linear combination of known functions, called basis sets. For these basis functions to describe an orbital correctly, they should form a complete set. In practice, a finite basis set is used and the accuracy thus depends on how well these functions can represent the orbitals and how many functions are included. In general, there are two error sources in *ab initio* methods: 1) the method inherited error and 2) the error due to lack of basis set convergence.

The basis functions used in this thesis are based on the Gaussian type orbitals (GTOs),

$$\chi_{\zeta,n,l,m}(r, \theta, \varphi) = NY_{l,m}(\theta, \varphi)r^{2n-2-l}e^{-\zeta r^2}, \quad (2.17a)$$

or
$$\chi_{\zeta,l_x,l_y,l_z}(r, \theta, \varphi) = Nx^{l_x}y^{l_y}z^{l_z}e^{-\zeta r^2}. \quad (2.17b)$$

In Eq. 2.17a, the function is written in spherical coordinates. The integers n , l , m are the principle, angular and magnetic quantum numbers respectively. ζ is the exponent parameter determining the radial extent (how loose or tight) of the orbital. $Y_{l,m}$ is spherical harmonic functions. In Eq. 2.17b, the function is written in Cartesian coordinate and l_x, l_y, l_z are parameters determining the types of orbital, i.e. s , p , d , etc.

The smallest possible set of basis functions has one s -function for the first row atoms, two s -functions for Li and Be, and two s -functions and a set of p -functions ($2p_x, 2p_y, 2p_z$) for the rest of the second row, etc. If the number of the functions is doubled, tripled or quadrupled, with different exponents ζ in each set, the new basis sets are called a double zeta (DZ), a triple zeta (TZ), and a quadruple zeta (DZ), respectively. As it is known that the core electrons are much less involved in chemical reactions than the valence, an addition of

Figure 2.3 Basis set convergence for correlation (single point) energies of CCSD, CCSD(T) and MP4. The figures a) to d) show the correlation energies of ^3C , ^4N , ^3O , and ^2F respectively. The correlation energies are shown as functions of cc-pVnZ basis sets, for $n = \text{D, T, Q}$ and 5 together with the values at the complete basis set limits, shown as DTQ and TQ5. The basis set limits are extrapolated using the relation $E(n) = E(\infty) + B e^{-(n-1)} + C e^{-(n-1)^2}$ from Peterson et al. 1994²⁹. The value at DTQ uses the energies from the cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets and TQ5 uses the energies from the cc-pVTZ, cc-pVQZ and cc-pV5Z basis sets.

basis functions can be done only for the valence electrons, which is called a spilt valence basis.

The functions with larger exponents, ζ , are appropriate in describing tighter bonds such as σ bonds, while those with smaller exponents allow the orbital to be more diffuse and are needed when the electrons are loosely bound. In most cases, basis functions with higher angular momentum are also needed to properly describe electron distribution along the bond, i.e. describing polarization. They are especially important in describing electron correlation.

In adding more basis functions into the set, it is also important to consider the balance of basis sets. As a rule of thumb, the number of added functions should be maximum at the function with the lowest angular momentum, i.e. s . The number of the next lowest angular momentum function, p , should be one less and so on. For example, a balance basis is $5s4p3d2f1g$. But as the functions f and g are much less important, they might also be left out, thus leaving the basis simply as $5s4p3d$.

In most cases, the computational speed can be improved by contracting the primitive basis sets into contracted basis sets. Contraction combines the primitive basis functions into smaller groups of *fixed* linear combinations. A linear combination of these groups are then used in place of the primitive set. This introduces a new set of expansion coefficients, the number of which are much smaller than those of the primitive set. With the number of variables (expansion coefficients) reduced, so does the computational cost. Contraction is found to be useful especially for inner electrons which are much less involved in the chemical process and thus less effected by the environment. Contracted basis sets are for example Pople basis sets and Dunning-Huzinaga basis sets.

An important consideration for choosing a basis set is the error it may produce in comparison to the value at the complete basis set (CBS) limit. Without a well-define path to the CBS value, it is difficult to predict the error and determine from where it derives. This leads to constructions of correlation consistent basis sets and their descendants^{103–105}. With these types of basis sets, the correlation energies converge smoothly to a limiting value with increasing in the size of the basis sets⁸⁷, as shown in Figs. 2.3. The smooth, converging behavior of the correction energies allow mathematical prediction of the CBS values, as shown in Figs. 2.3^{87,106}.

2.7 Composite Methods

In general, despite the demand in accuracy, it is impractical to perform a high level calculation together with a basis set close to the basis set limit. Alternatively, a combination of different levels of theory (i.e. different methods and basis sets) can be used to improve the accuracy but in a way that reduces the cost in comparison to a direct calculation at a high level. For example, the geometry optimization is less sensitive to the level of theory than the energy⁷⁷. Hence, to reduce the calculation cost, a lower level of theory can be used for geometry optimization and from there the energy is then calculated. Various composite methods have been proposed in the literature, the choice of which depends on the level of accuracy and cost. Among these are the Gaussian-*n* theory^{107–110}, the complete basis-set method (CBS)^{111–115}, HEAT^{116,117} and the Weizmann-*n* theories^{118–120}. In this thesis, the Gaussian-4 theory and the Weizmann-1 theory are used to calculate the thermochemical properties of gases.

The Gaussian-4 theory (G4)¹¹⁰ provides predictions of thermochemical data by combining a series of *ab initio* calculations with empirical corrections. The method was designed to be computationally relatively light so that its application covers not only small molecules but also those of intermediate sizes. The *ab initio* parts of the theory contain a series of single point calculations at the CCSD(T), MP4, MP2 and HF levels and various basis sets. The HF energy is extrapolated to the value at the CBS limit. The G4 uses empirical corrections (called higher level corrections) to take into account the remaining deficiencies. These corrections were derived from experimental data (the *Gn* sets) containing enthalpies of formation, ionization energies and electron and proton affinities from various types of molecules. The theory was shown to produce an average absolute deviation of 0.83 kcal/mol for 454 energies in the test set¹¹⁰.

The Weizmann-1 theory (W1), unlike the Gaussian-*n* theories, include no empirical correction terms. It has been designed for the first- and second-row molecules and has been shown to produce an average absolute deviation of 0.30 kcal/mol¹²¹. The method^{118,121} uses extrapolations to the CBS values for the HF, CCSD as well as (T) corrections. W1 also includes *ab initio* calculations for core correlation and scalar relativistic effects^{118,121,122}. With a CBS extrapolation at the CCSD(T) level, a large portion of correction effects is expected to be recovered. This however causes the method to be computationally much heavier than the *Gn*.

Chapter 3 Quantum Chemistry in CVD Modeling

3.1 Optimization and Normal Mode Vibration

Applications of quantum chemistry to the study of CVD allows plenty of structural and dynamical information to be obtained. Main tasks are to determine the geometrical structure and the energy of the molecule, as well as those of the transition state. The equilibrium structure of the molecule and the structure of the transition state are present on a potential energy surface (PES) as stationary points. Mathematically, they are described by the vanishing of the energy gradients with respect to all geometrical parameters. For a molecule, the stationary point forms a minimum on the PES, while for a transition state it forms a saddle point which is characterized by a maximum along the reaction coordinate linking two minima which are the reactant and the product states.

A method to locate a minimum on a PES is called a geometry optimization. An optimization process requires a guess of an initial structure from which the first and second derivatives of energy, called the gradient and the force matrix or Hessian, are derived with respect to the internal coordinates such as bond lengths, or alternatively to the Cartesian coordinates of each constituent atoms. During the optimization, a new structure is created from the initial gradient and Hessian matrix. This new structure is then used to create a new gradient and Hessian, which then leads to a prediction of a new structure. The process continues iteratively until the stationary point is located ⁷⁷.

Once the structure is found, the Hessian is calculated, diagonalized and mass weighted. From the Hessian, normal mode frequencies can be derived, which for a stationary point being a minimum on a PES should all be positive values. For a transition state, on the other hand, one frequency is required to be imaginary due to the force constant being negative. For a correct transition state, the directional movement associated to the imaginary frequency should depict structural change along the intrinsic reaction coordinate to the product state or in the opposite direction to the reactant state. Once the normal mode frequencies and the geometrical structure are known, we can then proceed to calculate the partition function, which is a central function to thermodynamics.

3.2 Partition Functions

It is known from statistical thermodynamics ¹²³ that the probability, p_i , of finding the system in the state with an energy E_i is determined by the Boltzmann factor, $e^{-E_i/k_B T}$, where k_B and T are the Boltzmann constant and temperature respectively. The normalization constant to p_i is called the partition function, given by $Q = \sum_i e^{-E_i/k_B T}$. It is Q which determines other thermodynamic properties and thus lies at the heart of thermochemistry.

For an ideal gas system, the total energy, E , can be written as a sum of the energies from each molecule, ε . This implies that for an ideal gas system, Q can also be written as a function of the partition functions of individual molecules, q . For a system of N indistinguishable molecules, $Q = q^N/N!$ ¹²³ where the factor $N!$ derives from the indistinguishability of the molecules. The molecular partition function, q , can also be separated into four parts according to the molecular degrees of freedom, i.e. translational, q_t , rotational, q_r , vibrational, q_v , and electronic, q_e . We now write the partition function, Q , following the method used in the Gaussian software ¹²⁴ as ^{123,125}

$$Q = q^N/N!, \quad (3.1)$$

where $q = q_t q_r q_v q_e$,

$$q_t = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V,$$

$$q_r = \frac{8\pi^2 I k_B T}{\sigma h^2} \quad \text{for a linear molecule,}$$

$$q_r = \frac{1}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \sqrt{I_x I_y I_z} \quad \text{for a nonlinear molecule,}$$

$$q_v = \prod \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/2T}}$$

$$q_e = \sum g e^{-\varepsilon_i/k_B T} \cong g.$$

Here m , V , P , h are the mass of the molecule, the volume, the pressure and the Planck constant. I and σ are the molecule moment of inertia and symmetry

index respectively. $\Theta_v = hv/k_B$ is the vibrational temperature of vibrational mode v , and g is the spin multiplicity of the molecule. In the derivation of q , we have assumed that the molecule is an ideal gas, a rigid rotor and a harmonic oscillator. The model is defined with respect to the bottom of the well, and thus q_v includes the zero-point vibrational mode by definition. The approximation $q_e \cong g$ derives from the assumption that the energy difference between the ground state (ε_0 defined as zero) and the first excited state, ε_1 , is much larger than $k_B T$. Hence, all excited states are inaccessible and only the ground state energy, $\varepsilon_0 = 0$, contributes to q_e . This then reduces the summation $\sum g e^{-\varepsilon_i/k_B T}$ to g .

Once the partition function is obtained, other thermodynamic functions can be calculated using the following relations ¹²³

$$E(T) - E(0) = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad (3.2)$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q, \quad (3.3)$$

$$H = E + pV, \quad (3.4)$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} \text{ and } C_P = \left(\frac{\partial H}{\partial T} \right)_{N,P}, \quad (3.5)$$

$$A = E - TS, \quad (3.6)$$

$$G = A + pV, \quad (3.7)$$

$$\mu = \left(\frac{\partial A}{\partial n} \right)_{T,V}. \quad (3.8)$$

Here E , S , H , C_V , A , G and μ are the energy, entropy, enthalpy, heat capacity, Helmholtz free energy, Gibbs free energy and chemical potential respectively.

3.3 Thermochemistry

From the partition functions, Q , we can now derive thermochemical properties related to the SiC-CVD process. Most reactor scale modeling requires the enthalpy, entropy and heat capacity of all species involved in the process. These are usually written in the form of 7-coefficient NASA polynomials fitted over a specified temperature range,

$$\frac{C_p^\circ}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4, \quad (3.9)$$

$$\frac{H^\circ}{RT} = a_1 + \frac{a_2 T}{2} + \frac{a_3 T^2}{3} + \frac{a_4 T^3}{4} + \frac{a_5 T^4}{5} + \frac{a_6}{T}, \quad (3.10)$$

$$\frac{S^\circ}{R} = a_1 \ln T + a_2 T + \frac{a_3 T^2}{2} + \frac{a_4 T^3}{3} + \frac{a_5 T^4}{4} + a_7. \quad (3.11)$$

where a_1 to a_7 are the fitting coefficients, and H° is the *absolute* enthalpies defined as $H^\circ = \Delta H_f^\circ(298 \text{ K}) + H^T - H^0$.

The entropy and heat capacity are readily available from *ab initio* calculations using Eq. 3.3 and 3.5. The enthalpy function, H° , however requires more calculations. This is due to the presence of $\Delta H_f^\circ(298 \text{ K})$, the standard enthalpy of formation of the molecule at 298 K which requires empirical atomic properties. The standard enthalpy of formation, ΔH_f° , is the enthalpy change at the standard condition (1 bar) when the molecule is formed from its constituent atoms in their reference states, i.e. their most stable form at 1 bar. $\Delta H_f^\circ(298 \text{ K})$ is derived from the standard enthalpy of formation at 0 K, or $\Delta H_f^\circ(0 \text{ K})$, and the thermal correction at 298 K, or $H^{298} - H^0$ as

$$\begin{aligned} \Delta H_f^\circ(298) &= \Delta H_f^\circ(0 \text{ K}) + [H^{298} - H^0]_{\text{molecule}} \\ &\quad - \sum_{\text{atom}} [H^{298} - H^0]_{\text{atom}} \end{aligned} \quad (3.12)$$

$$\text{where} \quad \Delta H_f^\circ(0 \text{ K}) = \sum_{\text{atom}} \Delta H_f^\circ(0 \text{ K}) - \sum D_0, \quad (3.13)$$

$$\text{and} \quad \Sigma D_0 = \Sigma_{atom} E - E_{molecule}. \quad (3.14)$$

The thermal correction at 298 K, $H^{298} - H^0$, can be derived from *ab initio* calculations, Eq. 3.4. ΣD_0 is the atomization energy at 0 K, which is defined as the difference in the energy at 0 K between the constituent atoms and the molecule and can be derived from the partition functions, Q , of the molecules and the relevant atoms. The data of atomic ΔH_f° and atomic thermal correction $H^{298} - H^0$ are usually available from databases such as NIST-JANAF ¹²⁶ and NIST-CCCBDB ¹²⁷ as presented in Table 3.1.

Table 3.1 Atomic ΔH_f° and $H^{298} - H^0$ relevant to SiC CVD obtained from databases and literature.

	ΔH_f° at 0 K (kJ/mol)	$H^{298} - H^0$ (kJ/mol)
Si	446 ± 8 ¹²⁶ , 448.5 ± 0.8 ¹²⁸	3.218 ¹²⁶
C	711.19 ± 0.46 ¹²⁶	1.051 ¹²⁶
H	216.035 ± 0.006 ¹²⁶	4.234 ¹²⁶
F	77.28 ± 0.30 ¹²⁶	4.413 ¹²⁶
Cl	119.621 ± 0.006 ¹²⁶	4.591 ¹²⁶
Br	117.92 ± 0.06 ¹²⁶	12.255 ¹²⁶

3.4 Gibbs Free Energy Minimization

From the Gibbs free energies of the molecules, we can predict the gas phase species composition as the system reaches equilibrium by minimizing the total Gibbs free energy. This method is simple as it does not require any kinetic inputs. To obtain reliable results, all relevant species should be included in the minimization. The derived gas phase species composition is thus the composition which minimizes the Gibbs free energies of the system at the temperature and pressure of consideration. By repeating the process over a range of temperatures (and/or pressures), a diagram of compositional change can be obtained as a function of temperature and pressure.

In general, the change in the total Gibbs free energy is written as ¹²³

$$dG = -SdT + VdP + \sum \mu_i dn_i, \quad (3.15)$$

with S , T , V , P , μ_i and n_i being the entropy, temperature, volume, pressure, chemical potential and the amount (mole) of species i , respectively. The minimization of the Gibbs free energy with respect to all species must be subjected to the conservation of species, $\sum n_i a_{ij} = b_j$, where a_{ij} is the number of atoms of element j contained in species i , and b_j is the total number (mole) of element j in the system. For the process that takes place at constant pressure and temperature, the change in the Gibbs free energy becomes simply $dG = \sum \mu_i dn_i$.

3.5 Conventional Transition State Theory

In this section, we summarize the calculation method for kinetic parameters using *ab initio* calculations together with conventional transition state theory (TST). TST provides a method to estimate reaction rate constants when there exists a transition state between the reactants and products. The transition state (TS) is a saddle point on the PES with a maximum along the reaction coordinate between the reactant and product as depicted in Fig. 3.1. The TS structure produces one imaginary normal mode frequencies, $\nu^\ddagger$, corresponding to the directional movement along the intrinsic reaction coordinate to the product state or in the opposite direction to the reactant state as shown in Fig. 3.2. TST assumes that a thermal equilibrium is maintained between the reactant state and the transition state, which at high pressure with many collisions, can be fulfilled. At other pressures, the theory cannot account for the pressure dependent effects on chemical reactions. It is also assumed that once the system has crossed the barrier at TS it will reach the product state without recrossing back to the reactant state. When recrossing happens, TST predicts an overestimation of the true rate.

3.5.1 Gas Phase Kinetics

For a reaction $A + B \rightleftharpoons TS \rightarrow C$, the assumption of equilibrium between the reactants and TS leads to ¹²⁹

Figure 3.1 Illustration of potential energy from the reactant state to the transition state (TS) and to the product state of the reaction, $\text{SiCl}_3(\text{g}) + \text{HCl}(\text{g}) \leftrightarrow \text{SiCl}_4(\text{g}) + \text{H}(\text{g})$. The transition state corresponds to a saddle point in energy, in contrast to the reactant and product states which are minima on the PES.

Figure 3.2 Illustration of vibrational movement corresponding to the imaginary frequency of the transition state of the reaction, $\text{SiCl}_3(\text{g}) + \text{HCl}(\text{g}) \leftrightarrow \text{SiCl}_4(\text{g}) + \text{H}(\text{g})$.

$$K_P^\ddagger = \frac{P_{TS}P^\circ}{P_A P_R} = e^{-\Delta G^\ddagger/RT}. \quad (3.16)$$

where $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ is the Gibbs free energy of activation of the reaction and $P^\circ = 1$ bar. For $n = 1$ mole, and using the molar partition function, $q_m \equiv \frac{q}{n} = q$, the equilibrium constant can be written in terms of the molar partition functions, q , which is shortened from q_m , as ¹²⁹

$$K_P^\ddagger = \frac{N_A q_{TS}}{q_A q_B} e^{-\Delta_r E^\ddagger(0 \text{ K})/RT}, \quad (3.17)$$

where $\Delta E^\ddagger = E^{TS} - \sum_{\text{reactants}} E$. The rate $R_{\rightarrow}$ of converting TS into the product C depends on the frequency, $\nu^\ddagger$, and the probability of its success, κ ,

$$R_{\rightarrow} = \kappa \nu^\ddagger [TS]. \quad (3.18)$$

This gives the forward rate as $R_{\rightarrow} = k_r [A][B]$ where $k_r = \frac{RT}{P^\circ} \kappa \nu^\ddagger K_P^\ddagger$. The factor RT derives from the relation $P_A = RT[A]$. The probability κ is called the transmission coefficient. It introduces tunnelling effects and recrossing probability into the rate constant. It is sometimes assumed to be 1. It can be shown that for $h\nu^\ddagger/k_B T \ll 1$, the rate constant can be written as¹²⁹

$$k_r = \kappa \frac{RT}{P^\circ} \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}, \quad (3.19)$$

or
$$k_r = \kappa \frac{RT}{P^\circ} \frac{k_B T}{h} \frac{N_A q^{TS}}{q^A q^B} e^{-\Delta E^\ddagger/RT}. \quad (3.20)$$

where in Eq. 3.19, the vibrational mode corresponding to $\nu^\ddagger$ is discarded from $\Delta G^\ddagger$ and the same is applied to q^{TS} in Eq. 3.20. The rate constant from Eq. 3.19 and 3.20 can also be fitted to the Arrhenius form, $k_r = A e^{-E_a/RT}$, with the parameter E_a being the activation energy.

3.5.2 Surface Kinetics

A solid surface can be modeled from a surface of a cluster, provided that the cluster is not too small. To model a solid surface, we follow the method of Reuter and Scheffler¹³⁰ where the cluster translational and rotational degrees of freedom are removed, and so as their partition functions, q_t and q_v . This adjustment is applied to the transition states as well as to the cluster with adsorbed species. Hence, only two parts, i.e. the vibrational and electronic parts, of the partition function of the cluster are included in the calculation,

$$q^{surf} \cong q_v^{cluster} \cdot q_e^{cluster}, \quad (3.21)$$

where $q_v^{cluster}$ and $q_e^{cluster}$ are derived from Eq. 3.1. Following Reuter and Scheffler¹³⁰, the partition function of gaseous molecules related to a surface reactions are written as

$$q^{gas} = q_{t,2D}^{gas} \cdot q_r^{gas} \cdot q_v^{gas} \cdot q_e^{gas}. \quad (3.22)$$

It should be noted that q^{gas} is similar to Eq. 3.1 except that the translational degree of freedom along the reaction coordinate has been removed, leaving only 2 out of 3 translational degrees of freedom. The 2 dimensional, translational partition function is written as

$$q_{t,2D}^{gas} = A_s \cdot \left(\frac{2\pi mk_B T}{h^2} \right). \quad (3.23)$$

Here A_s is the area in which the gas species may reside in order to react successfully with the surface. In our study, the value of A_s is assumed equal to the area per one surface site or equally the area per one lattice site. For a surface site on the (0001) surface of 4H-SiC, the area is equal to $8.178 \text{ \AA}^2$, calculated using the 4H lattice constant of $3.073 \text{ \AA}$ ¹³¹.

Adsorption rate. Using TST, we can derive adsorption rate of gaseous species A , corresponding to the reaction $A(g) + B(s) \rightarrow \text{products}$, to be¹³⁰

$$R_{ads} = A_s \frac{q^{TS}}{q^{A(g)} \cdot q^{B(s)}} \exp(-\Delta E^\ddagger / k_B T) \cdot \Phi_A \cdot \Theta_B, \quad (3.24)$$

Here R_{ads} is written in the unit of molecule sites⁻¹ s⁻¹. Alternatively, the adsorption rates can also be rewritten in the unit of mole area⁻¹ time⁻¹ by using $R_{ads}/A_s N_A$ and also in the unit of length time⁻¹ by using $R_{ads} \cdot h_{ML}$ respectively. Here N_A is the Avogadro constant and h_{ML} is the height of 1 SiC bilayer. $\Delta E^\ddagger$ is the activation energy of adsorption process at 0 K. q^{TS} and $q^{B(s)}$ are defined similar to Eq. 3.21 and $q^{A(g)}$ is defined by Eq. 3.22. Here A_s refers to the area per one lattice site on the surface and Θ_B is the fraction of surface occupied by $B(s)$. Φ_A is the impingement rate of species A from the kinetic theory,

$$\Phi_A = \gamma_A P / \sqrt{2\pi m_A k_B T}, \quad (3.25)$$

where γ_A is the mole fraction of gaseous species A and P is the total pressure such that the product $\gamma_A P$ produces the partial pressure of species A , and m_A is the mass of gaseous species A .

We can also define the sticking coefficient of species A , or S_A , using the relation, $S_A = R_{ads,A}/(A_S \cdot \Phi_A \cdot \Theta_B)$ which produces

$$S_A = \frac{q^{TS}}{q^{gas} \cdot q^{cluster}} \exp(-\Delta E^\ddagger/k_B T) . \quad (3.26)$$

The sticking coefficient of species A describes the probability of the species A to stick on the surface per strike.

Desorption rate. Using TST, the desorption rate, R_{de} , of an adsorbed species A described by a reaction, $A(s) \rightarrow B(g) + B(s)$, is shown to be

$$R_{de} = \frac{k_B T}{h} \left(\frac{q^{TS}}{q^{A(s)}} \right) \exp(-\Delta E^\ddagger/k_B T) \cdot \Theta_A , \quad (3.27)$$

This reaction is the reverse of adsorption process. q^{TS} and $q^{A(s)}$ are defined similar to Eq. 3.21, and $\Delta E^\ddagger$ is the activation energy of desorption process. Θ_A is the fraction of surface occupied by adsorbed species $A(s)$.

Surface Reactions. For an on-surface reaction, $A(s) + B(s) \rightarrow \text{product}$, the reaction rate derived from TST is

$$R_{on-surf} = \frac{k_B T}{h} \left(\frac{q^{TS}}{q^{A(s)B(s)}} \right) \exp(-\Delta E^\ddagger/k_B T) \Theta_{AB} , \quad (3.28)$$

where q^{TS} , $q^{A(s)B(s)}$ are defined following Eq. 3.21. Here $q^{A(s)B(s)}$ is the partition function of a cluster on which an adjacent pair of $A(s)$ and $B(s)$ resides. Θ_{AB} is the fraction of surface occupied by such a pair. $\Delta E^\ddagger$ is the activation energy of the reaction at 0 K.

Chapter 4 Results and Summary

An understanding of SiC CVD is crucial to the improvement and design of process conditions. Computational modeling has become a useful tool for such purposes due to a lack of available *in situ* measurements. A reactor scale modeling such as computational fluid dynamic (CFD) requires details of kinetics and thermochemistry in order to calculate the gas mixtures, the dominant gas-phase species as well as the growth and doping profiles. The needed information however is not always available as we have pointed out in **Paper 1**. Firstly, thermochemical properties of organosilicons are usually missing from the common databases. When they are available, they sometimes contain relatively large errors. We showed this by comparing the data provided from the CHEMKIN database to our results derived from *ab initio* calculations. We showed that the heat capacity (C_p) of $\text{CH}_3\text{SiH}_2\text{SiH}(\text{g})$ from the CHEMKIN database was highly erroneous and unphysical, and that the use of this data could lead to the conclusion that this particular species was the main Si growth contributor at atmospheric pressure. Instead, when using the results from *ab initio* calculations we predicted that there was no significant growth contribution from this particular organosilicon species based on the kinetic model being used. However, whether it is possible to generalize and conclude that the organosilicon does not take part in the growth at all depends directly on how correct and how well the kinetic model is in explaining the growth mechanism of SiC CVD.

Most kinetic models in the literature at the time were focused on the Si-limited growth of SiC CVD. Thus, the kinetics of the hydrocarbon chemistry was less well investigated. Moreover, experimental results performed by our group¹³², showed that there were difference in the growth rates and surface roughness when different hydrocarbons were used as precursors. This led us to study the gas-phase kinetics of hydrocarbons presented in the literature. In this study, we selected two models from the literature, one from Allendorf and Kee⁴¹ and the other from de Persis *et al.*¹³³, as well as a model compiled by one of the authors. The simulation conditions were kept the same for all three and no depositions were allowed. We chose to compare the results when three different hydrocarbon precursors, CH_4 , C_2H_4 , C_3H_8 , were used. The studies showed that under the same condition the three models predicted relatively different profiles of concentrations of the most abundantly produced hydrocarbon species and atomic H. Thus, it is clear that more improvement must be made in kinetic models before we can expect reliable and realistic results.

Researchers, due to lack of kinetic data, usually chose to adopt and modify the surface kinetic model presented by Allendorf and Kee⁴¹. This model however was shown to predict C-limited growth which conflicted to the Si-limited growth observed in experiments. Kinetic studies performed by one of the authors using the gas phase and surface kinetics from Allendorf and Kee⁴¹ showed that the C-limited mode was constantly predicted for at least up to the C/Si ratio of 2.0, with no transition to the Si-limited mode near C/Si =1 as observed in experiments. Thus, it is clear that not only the gas phase model but also the surface kinetics are needed in order to build a more reliable model.

In **Paper 2**, we derived thermochemical properties of the halides and halohydrides of Si and C species, SiH_nX_m and CH_nX_m , for X being F, Cl and Br. These properties are needed for CFD modeling as well as for thermodynamic equilibrium calculation of halide-assisted SiC-CVD. We chose two composite methods, namely the Gaussian-4 (G4)¹¹⁰ and the Weizmann-1 theories^{118,121} as modified by Barnes et al.¹²² (W1RO), for the calculations. Due to limits in the design of the method, W1RO was not applied to the study of Br-containing species. With these two methods, we derived the atomization energies, enthalpies of formation and entropies of the molecules listed above. We showed that the experimental data from the databases are highly inconsistent to each other as well as to the theoretical data. For example, we observed discrepancies in the atomization energies as large as 15–40 kJ/mol between the experimental and theoretical data for SiF, CHF, SiH_3F and CH_3F . On the other hand, theoretical data from the literature and our calculations agreed well. Both methods worked nicely for the molecules in the set.

Paper 3 combined the growth studies of SiC-CVD, in which SiF_4 was used as the Si precursor, together with theoretical studies of thermodynamic equilibrium calculations and surface kinetic *ab initio* calculations. The results from thermochemical calculations performed under the same condition as the experiments suggested that the main candidates for Si growth contributors are SiF_2 , SiF and SiHF. This was concluded from the concentration levels of these species and whether they are capable of contributing to the growth at the rate observed experimentally. Secondly, we studied the change in the species concentrations vs. temperatures as well as the reactivity of the molecules. Based on the experimental growth rate profiles, these two points narrowed down the set of candidates into the three species listed above.

The part which I was mainly concerned with was the *ab initio* calculations of the surface kinetic of the three species. The study was performed on the (0001) surface of 4H-SiC modeled by a cluster of $\text{Si}_{13}\text{C}_{13}$, shown in Fig. 4.1a. The cluster was completely passivated by hydrogen atoms on all sides to preserve the SiC bulk symmetry. The choice of surface passivation was justified by the typical operating conditions of SiC-CVD, i.e. a temperature of $\sim 1600^\circ\text{C}$ in a hydrogen rich atmosphere. We chose two types of surface sites on which the Si-species were assumed to adsorb. The first site was a fully coordinated C site and the second was a C site with the presence of one dangling bond. The reason that we chose C sites as the adsorption sites, instead of Si sites, was because we were more interested in the growth with correct stoichiometry. It should be noted that the (0001) surface of 4H-SiC is a Si face. Thus, these carbon sites were obtained by pre-attaching a hydrocarbon group on a Si face before adsorption occurred. The choice of surface C groups to act as the adsorption sites were made by choosing the simplest and smallest hydrocarbon group. Thus, a methyl group, CH_3 , was chosen to represent a fully-bonded C site and a methylene group, CH_2 , was chosen for a C site with the presence of one dangling bond.

We then used DFTs to determine for the Gibbs free energies of adsorption, ΔG°_R , of the three Si-species on these two sites over a temperature range well covering the experimental conditions. The calculated ΔG°_R at the temperature corresponding to the experimental condition were shown to be positive for all cases, except for the SiF adsorption on a methylene site. This suggested, with the exception of SiF on a methylene site, that the products of adsorptions were less stable than the reactants. The adsorptions on the methyl site were shown to occur with the presence of transition state barriers for all cases. These transition barriers were shown to be relatively high and led to sticking coefficients which were too low to explain the experimental results. Thus we concluded that it was unlikely for the three Si-species to contribute to the growth by adsorbing on a fully bonded C site. On the other hand, the adsorptions on the methylene showed no transition barriers between the reactant and product states. Furthermore, from the negative ΔG°_R we concluded that SiF was likely to contribute to the growth. The positive ΔG°_R of SiHF and SiF₂ made the two species less likely to contribute in comparison to SiF. And since ΔG°_R was less positive for SiHF in comparison to SiF₂, we concluded that the chance of SiHF to overcome the positive ΔG°_R is higher than for SiF₂.

Paper 4 was an extension of the study from **Paper 3** where we included the adsorption of SiH, SiH₂, SiX, SiHX, SiX₂ for X being F, Cl and Br. Also, both the C-face and the Si-face were considered. The surfaces of 4H-SiC were

modeled using the $\text{Si}_{19}\text{C}_{19}$ cluster, shown in Fig. 4.1b. Again, the adsorption was assumed to take place with correct stoichiometry. On the Si-face the adsorptions were studied as in the previous case, i.e. on a fully bonded site (a methyl group) and a site with the presence of one dangling bond (a methylene group). In this study, ΔG°_R of adsorption were all positive at 1600 °C, unlike the results from the $\text{Si}_{13}\text{C}_{13}$ cluster. With the presence of a dangling bond, the adsorption with the lowest positive ΔG°_R was observed in SiH and SiX (with ΔG°_R less than ~40 kJ/mol), followed by SiH_2 with $\Delta G^\circ_R \sim 65$ kJ/mol. When no dangling bond was present at the site, the lowest ΔG°_R of adsorption was observed in SiH and SiH_2 with $\Delta G^\circ_R \sim 90$ kJ/mol. This plus the fact that the adsorptions occurred with the presence of transition states suggested that adsorption on a fully-saturated site was unlikely, which was similar to what previously observed using a smaller cluster in **Paper 3**. We concluded that adsorption of Si-species was more likely to occur on a site with the presence of a dangling bond with SiH, SiH_2 and SiX being the main Si growth contributors. Lastly, possible routes to create a C site with a dangling bond were suggested based on the value of the Gibbs free energies of reaction.

Figure 4.1 a) $\text{Si}_{13}\text{C}_{13}$ cluster and b) $\text{Si}_{19}\text{C}_{19}$ cluster.

On the C-face, adsorptions were assumed to occur directly on the C face with and without hydrogen terminations. These represented a fully bonded C site and a C site with the presence of a dangling bond, respectively. Similar to the Si side, adsorptions on the carbon face on a fully bonded C site occurred with positive ΔG°_R for all cases. Again, the lowest ΔG°_R were observed in SiH and SiH₂. When a dangling bond was present, ΔG°_R was shown to be negative for SiH, SiX and SiH₂ adsorptions, followed by SiHX with $\Delta G^\circ_R \sim 45\text{-}70$ kJ/mol. Thus, similar to the Si face, adsorptions of Si-species on the C face were more likely to occur when a dangling bond was present at the site, with SiH, SiH₂ and SiX being the main Si growth contributors for SiC CVD. As ΔG°_R of adsorption of SiHX species were not very large, SiHX might also contribute to the growth. Similar to the Si face, we suggested possible routes to create a C site with a dangling bond based on the value of the Gibbs free energies of reaction.

Paper 5 was a study of hydrocarbon adsorption on the Si face of 4H SiC. The study was performed using the same cluster as in **Paper 4** and the adsorption was assumed to occur with correct stoichiometry as before. The gaseous hydrocarbon species included in the study were C₂H₂, C₂H₄, CH₃ and CH₄. These species were chosen due to their high gas phase concentrations as predicted by the kinetic study in **Paper 1**. We showed that it was again unlikely for the adsorption to occur on a hydrogen terminated site. This was concluded from the large positive Gibbs free energies of reaction and large barrier heights. When a dangling bond was present, adsorption of C₂H₂ and C₂H₄ occurred with the presence of transition barriers and with positive Gibbs free energies of reaction. The sticking coefficients calculated using transition state theory were shown to be ~ 0.05 for C₂H₂ adsorption and ~ 0.02 for C₂H₄ adsorption on a Si site. However, the desorptions via the same pathway were shown to be faster than the adsorptions in both cases and that the adsorbed products were less stable than the reactant states. Nevertheless, subsequent surface reactions helped stabilizing the products by reducing the Gibbs free energy of the system. Adsorption of CH₄ was shown to occur with a very low sticking coefficient of $\sim 10^{-7}$, even with the presence of a surface dangling bond. Thus it was concluded that CH₄ was not an active species in the growth of SiC. With the presence of a dangling bond, adsorption of CH₃ was shown to occur readily with negative Gibbs free energy and without the presence of a transition state. Thus, it is likely that CH₃ contributes actively to the growth.

Paper 6 was a thorough analysis of the SiC-CVD process. Four chemistries have been included in this study: Si-C-H, Si-C-Cl-H, Si-C-Br-H and Si-C-F-H. The analysis was first performed by thermodynamic equilibrium calculations

over a wide range of process conditions to determine which species were likely to be present in the gas and could therefore act as active growth species. The results suggested that the main Si contributors were Si, SiH_x , SiX and SiHX and not SiX_2 as previously suggested in the literature. The main C contributors were suggested to be C_2H_2 and CH_3 . The organosilicons, Si_2C and S_3C , may also contribute to the growth. Secondly we proposed chemical reaction schemes leading to the formation of these species which were also shown, after “infinite” time, to reproduce the concentration profiles derived from equilibrium calculation. It was also shown from kinetic models that the residence time of the gases in the system (< 0.5 second) was long enough to reproduce the composition close to the values obtained at equilibrium condition. This implied that the thermodynamic equilibrium calculation was applicable as an analysis tool to determine gas phase composition.

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