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Chemical vapor deposition of silicon carbide in the methyltrichlorosilane-hydrogen system

Brown, Peter William, Ph.D.
The Ohio State University, 1993
CHEMICAL VAPOR DEPOSITION
OF SILICON CARBIDE
IN THE
METHYLTRICHLOROSILANE - HYDROGEN SYSTEM

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Graduate School
at The Ohio State University

By

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1993

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To my wife, Jennifer, and son, Carl, thank you for your patience and understanding.
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NOMENCLATURE

\(a_i\) coefficient of reactant species \(A_i\) in general chemical reaction

\(A\) reaction constant

\(A_i\) general reactant species in general chemical reaction

\(b_i\) coefficient of product species \(B_i\) in general chemical reaction

\(B_i\) general product species in general chemical reaction

\(c_p\) heat capacity of gas mixture

\(D_i\) binary diffusion coefficient of species \(i\) in \(H_2\)

\(E\) activation energy

\(f\) total number of species present in physical property calculations

\(Gr\) Grashof number

\(g_z\) longitudinal component of acceleration due to gravity

\(k\) thermal conductivity

\(k_r\) forward reaction rate constant

\(K_a\) thermodynamic equilibrium constant based on concentration

\(K_p\) thermodynamic equilibrium constant based on pressure

\(k_r\) reverse reaction rate constant
L  characteristic length
M_i  molecular weight of species i
P  pressure
Pr  Prandtl number
r  cylindrical coordinate direction
R  universal gas constant
Ra  Rayleigh number
Re  Reynolds number
R_i  rate of generation of species i in general chemical reaction
R_{i,k}  production rate of species i by reaction k
R_k  rate of generation of SiC by reaction k
Sc  Schmidt number
T  absolute temperature
T_e  temperature of eastern domain boundary
T_w  temperature of western domain boundary
v_r  radial component of velocity
v_z  longitudinal component of velocity
V_\infty  bulk velocity
w_i  weight fraction of species i
z  cylindrical coordinate direction

\Delta G^0  change of Gibbs energy of the reaction under standard state conditions
α  thermal diffusivity of fluid
β  H₂:CH₃SiCl₃ molar ratio
β  thermal expansion coefficient
δ  momentum boundary layer thickness
δ_{CBL}  concentration boundary layer thickness
θ  cylindrical coordinate direction
µ  viscosity
ρ  density of gas mixture
ϕ_{ij}  dimensionless parameter used in viscosity calculations
χ_i  mole fraction of species i
CHAPTER I

INTRODUCTION

The chemical vapor deposition (CVD) of silicon carbide has been investigated for many decades. However, the complexity of the chemical reactions taking place has thwarted any precise understanding of the mechanism(s) responsible for the deposition of SiC. Literature reports of deposits grown at seemingly similar experimental conditions have yielded disparate SiC compositions and morphologies.

In addition, little effort has been made to study the CVD of SiC via the implementation of mathematical models which are capable of describing the pertinent transport phenomena and predicting deposition rates found within the CVD reactors. Such models have been applied successfully to study the CVD of Si and GaAs, due primarily to interests from the microelectronics industry. The physical properties of SiC render it a likely candidate to replace Si in high temperature electronics applications. The recently developed ability to deposit
single crystal SiC films should expedite the mathematical modeling of the CVD of SiC, in order to gain further insight into the mechanisms involved in the deposition process.

The present study was motivated by two objectives. The first was to develop and validate a two-dimensional mathematical model capable of ultimately predicting the deposition rates of SiC in the CH₃SiCl₃ (methyltrichlorosilane, MTS) - H₂ (hydrogen) system onto a variety of substrates. The second objective was to further develop the relationships existing between the morphology, composition, and growth rates of deposited SiC and the experimental variables of system temperature, pressure, and initial molar H₂:CH₃SiCl₃ ratio.

The work performed in the present study has been divided into five main categories, which are discussed in the following five chapters. Chapter II focuses on a review of the reports found in the open literature regarding the CVD of SiC, both experimental observations and any modeling efforts made thereof. A short discussion regarding the histories of SiC and CVD is also included. A discussion focusing on calculations based on thermodynamic equilibrium conditions ensues in Chapter III. Results are presented indicating relationships between system temperature, pressure, and H₂:CH₃SiCl₃ ratio on the compositions of the condensed and vapor phases.

Chapter IV briefly describes the selected method in the development of the mathematical model. Subsequently, the discussion in Chapter V is directed at the steps taken to test the aforementioned model, including the application of the model
to predict fluid flow found in driven cavity problems, as well as to predict the mass, momentum, heat, and transport of chemical species found within SiC CVD reactors using the $\text{H}_2$ - $\text{CH}_3\text{SiCl}_3$ gaseous system.

Chapter VI discusses the morphological characterization of the SiC deposits grown in the present study. Discussions regarding the dependence of the growth morphology on system temperature and $\text{H}_2$-$\text{CH}_3\text{SiCl}_3$ ratio are presented. Finally, Chapter VII includes concluding remarks and some potential future directions which may be undertaken to gain a deeper understanding of SiC-CVD.
CHAPTER II

LITERATURE REVIEW

Silicon carbide was first produced by Berzelius \(^1\) in 1824 by accident, in an attempt to synthesize diamond. Practically sixty years elapsed until the next article appeared by Schuetzenberger in 1881 \(^1\). Work surrounding the chemical vapor deposition (CVD) of silicon carbide increased sharply in the 1960’s and 1970’s, due to the recognition of the superior electronic properties of SiC. Research dropped in the late 1970’s, essentially disappearing through the early 1980’s, because of the inability to deposit thin films of single crystal SiC (implicit in this is the inability to deposit thin films of single polytype SiC). In the late 1980’s, researchers discovered methods for depositing monocrystalline films of SiC. Accordingly, the electronics industry spurred research again, and is still continuing today.

The first observance of the polytypism phenomenon in silicon carbide has been attributed to Baumhofer’s report of 1912 \(^2\), concomitant with the discovery of the application of X-ray diffraction to crystallography. Polytypes of silicon carbide
differ only in the stacking sequence of double layers of the constituent silicon and carbon atoms. Each double layer consists of a close-packed plane of silicon atoms and a close-packed plane of carbon atoms. When these double layers are stacked, the positions of the layers with respect to one another coincide with the A, B, and C sites found in traditional crystallographic nomenclature for the stacking of close-packed planes.

Another method for visualizing the structure of SiC is presented. Assume the structure is derived from Si₄C or C₄Si coordination tetrahedra which are connected through their vertices. Layers of these connected tetrahedra are formed, in which all the tetrahedra have one apex out of the bottom layer plane. The result is alternating layers of Si and C atoms. Again, the stacking sequence of these layers determines the polytype of SiC formed.

The number of observed polytypes of silicon carbide currently exceeds 200 for practical purposes, only two polytypes are of interest. One of these is β-SiC, which is the only cubic polytype of SiC, also referred to as 3C-SiC. The layer stacking sequence for β-SiC corresponds to ABCABC... The second important polytype is 6H-SiC, which is a hexagonal polytype, with a layer stacking sequence of ABCACB... The nomenclature α-SiC includes the 6H polytype, as well as all other known hexagonal (e.g. 2H, 4H, 8H) and rhombohedral (e.g. 15R, 21R, 27R, 33R) polytypes.

The cubic SiC polytype (3C) is the predominant type synthesized in temperatures below approximately 1600 °C. At temperatures above this, 6H-SiC
grows preferably. The stability of each polytype (3C or 6H) is greatly affected by the presence of impurities, especially by those elements in groups III and V of the periodic table. Group III elements tend to stabilize the hexagonal 6H structure, while group V elements stabilize the cubic structure. The underlying reasons for this phenomenon are unknown at this time.

The stacking fault formation energy for the transformation between polytypes is known to be very small \(^5\). The presence of impurities from groups III or V on the periodic table obviously disturb the electronic state of the SiC crystal in such a way that a new stacking sequence of the double layers is enhanced. The presence of impurities is not likely to be the sole cause for the stability and existence of very long period polytypes, for example the 4680R polytype \(^1\).

Several growth theories rely on a screw dislocation and the growth of SiC about it, in which the period length corresponds to the step height of the spiral growth. However, there have not been any experimental observances of such screw dislocations. Subsequently, no theory is presently able to describe the formation and stabilities of SiC polytypes.

Silicon carbide can be grown industrially in any of three different forms. One of these is in bulk form, wherein the Lely process is usually implemented. The Lely process depends on the sublimation of silicon carbide, and is implemented above 2000 °C. The result is relatively large grains of silicon carbide (several polytypes observed), which can then be ground to the desired size.
Milewski et al. \textsuperscript{[6]} devised a technique for growing silicon carbide from rice hulls. Rice hulls contain large amounts of silica (approximately 20 weight percent) in addition to carbon in the form of cellulose and other organic compounds. By the growth mechanism of the rice hulls, the silicon and carbon sources are homogeneously mixed, on a very fine scale. The silicon carbide produced by this method has finer grains than for the Lely process.

Secondly, thin films of silicon carbide can be grown, predominantly by chemical vapor deposition (CVD). Chemical vapor deposition has been implemented since around 1890, when de Lodyguine deposited tungsten films on carbon lamp filaments \textsuperscript{[7]}. CVD relies on a heterogeneous reaction taking place on a substrate, on which a deposit forms. The gas phase transports the reactants toward and product gas species away from the substrate surface.

An attractive feature of CVD is that compounds with extremely high melting temperatures (if they melt at all) may be deposited at much lower temperatures than their melting points. Examples of such materials include carbon, and several metallic carbides (SiC, TiC, WC, etc.) whose melting points are generally above 3000 °C. Various chemical vapor deposition techniques allow for the deposition of SiC, for example, at temperatures around 500 °C. Lower deposition temperatures allow for a wider selection of potential substrate materials, as well as reducing processing costs.

Seven processes which may govern any individual conventional CVD deposition system occur in the following order: (1) transport of the bulk gas via
convection into the reactor; (2) diffusion of the reactants through a boundary layer adjacent to the substrate; (3) adsorption of the deposit-forming species onto the substrate surface; (4) rearrangement of chemical bonds to form the deposit (the conversion of adsorbed species into chemisorbed species); (5) desorption of any product species off the substrate surface; (6) diffusion of the product gaseous species through a boundary layer adjacent to the substrate surface, and (7) transport of the bulk gas out of the reaction chamber. When steps (2) and/or (6) are found to be the rate-limiting step for the deposition process, the system is said to be under mass transport (diffusion) control. If the rate limiting step is found to be any of steps (3) through (5), the reaction is said to be limited by reaction kinetics.

Generally at high enough temperatures, the process becomes controlled by diffusion of the reactant. At lower temperatures, reaction kinetics may become sufficiently slow to render the process under kinetic control.

In the \( \text{CH}_3\text{SiCl}_3 - \text{H}_2 \) system for SiC deposition, the temperature above which the process is considered to be under diffusion control is approximately 1300 °C. At temperatures below 1150 °C, the process is considered to be under kinetic control. Between these two temperatures, the deposition process is controlled by a combination of the diffusive and kinetic factors. Very little is known regarding the species involved in the adsorption / recombination / desorption steps found when the system is under reaction kinetics control, because of the lack of high temperature sensors able to accurately measure the relevant species acting on the substrate surface at the deposition temperature.
Two types of conventional CVD reactors are implemented in the coating of substrates. Reactors may be categorized as either "cold-walled" or "hot-walled" types. For cold-walled reactors, only the substrate is directly heated, usually by either running an electric current through the substrate, or by applying an infrared source of energy to the substrate surface thereby heating it. Obviously resistive heating of the substrate requires a substrate material which conducts electricity, so this method is not applicable to insulating substrate materials. Hot-walled furnaces are externally heated, usually by a heated wire wound around the reactor tube. Thermal energy must travel through the furnace wall and the vapor phase before it reaches the substrate. Hence, in these furnaces, the substrate and the furnace wall get coated with the deposit.

Cold-walled furnaces generally run with higher precursor efficiencies, i.e. a higher percentage of the precursor gas is consumed solely for the coating of the substrate, compared to the hot-walled reactor. No agreement has been reached indicating the better furnace design. Cold-walled furnaces, although more efficient with respect to the amount of precursor, inherently have very steep thermal and concentration gradients within the vapor phase. The geometry of the substrate also plays a role in the determination of which type of furnace can be used. More complex models must be used to describe cold-walled systems with the same degree of accuracy as for hot-walled reactor models.

Finally, whiskers of SiC can also be grown by CVD. Whiskers are often used in the design of composite materials where they act as the reinforcing phase
embedded in a matrix. The growth process typically employed to synthesize SiC whiskers is termed the VLS process[^8,^9], wherein the acronym stands for vapor (precursor gases) liquid (catalyst) solid (crystalline whisker growth). Typical catalysts include iron and other transition metals. The underlying principle is the formation of a liquid pool which is a Si-C-X alloy, where X stands for the catalyst element. The whisker grows by the adsorption of silicon and carbon from the vapor phase through the liquid - vapor interface, and the precipitation of SiC at the liquid - solid interface, on the opposite side of the liquid droplet. The morphology of whiskers grown by the VLS process are typically 5 microns in diameter, and several thousand microns in length. The shape of the whiskers is very straight, resembling needles. Typical furnace temperatures implemented during VLS whisker growth lay between 1200 and 1400 °C. Growth rates in the longitudinal direction are of a magnitude of 1 millimeter per hour and are apparently time independent.

Due to its unique physical properties, silicon carbide has a wide range of applications, which require the production of silicon carbide by differing methods. The physical properties and potential applications of SiC are the focus of the next section.

**PROPERTIES OF BETA SILICON CARBIDE**

As mentioned above, the properties of silicon carbide cause it to be a likely candidate for many applications. SiC does not melt in the normal sense of the
word; rather, it has been experimentally found to dissociate at 2830 °C under a pressure of 35 atmospheres of argon \[^{[10]}\]. Hence it is used in high temperature environments. It has a relatively high thermal conductivity of approximately 500 W/(m·K) \[^{[10]}\]. \(\beta\)-SiC possesses a high hardness value of approximately 2800 kg/mm\(^2\) on the Knoop scale (100 g mass) \[^{[11]}\]. The energy gap of \(\beta\)-SiC is around 2.3 eV, which in addition to other properties, makes it a likely candidate for electronic applications. Silicon carbide also is highly oxidation- and corrosion-resistant up to temperatures of 1500 °C. Applications for cubic silicon carbide include abrasion / wear resistant coatings, electronic coatings, or thin films in the semiconductor field. The possible applications of SiC fall into two main categories: electronic and non-electronic, which are addressed in the following discussion.

**ELECTRONIC APPLICATIONS**

Silicon has a maximum operating temperature of around 300 °C in the electronic semiconductor industry \[^{[4]}\]. The development of aircraft engines, for example, which operate at increasingly higher temperatures and use more electronic sensing devices, mandates that a new material be developed to replace the role of silicon in these sensors. The electrical properties of \(\beta\)-SiC (wide bandgap and high electric field properties \[^{[10]}\]) permit such a replacement. The growth of thin film single crystals of \(\beta\)-SiC was achieved by Parsons *et al.* \[^{[10]}\] who synthesized single crystal \(\beta\)-SiC by using a single crystal TiC\(_x\) substrate for the epitaxial growth
process. Subsequently, others found that the epitaxial growth of β-SiC is possible on silicon substrates with vicinal (001) surfaces $^{[12,13]}$. 

The growth method of SiC for electronic applications is usually a plasma assisted (enhanced) chemical vapor deposition, known as PACVD or PECVD (also known as the glow discharge (GD) method). The use of a plasma in the CVD process allows lower temperature processing. The energy supplied to the gaseous system by the plasma replaces the thermal energy found at higher temperatures in conventional thermally activated CVD. Lower deposition temperatures are crucial in the electronic industry to maintain the desired heterogeneous distribution of dopants. Electron-assisted CVD (EACVD) has also been applied for the deposition of β-SiC $^{[14]}$. 

Amorphous silicon carbide films have also been grown successfully $^{[15-27]}$. Methods for film growth include metallorganic CVD (MOCVD) $^{[18]}$, low temperature CVD (500 - 600 °C) $^{[15,19]}$, PECVD $^{[16,17,20,23-26]}$, reactive sputtering (RS) $^{[20]}$, and pyrolysis of metal-organic polymers $^{[21]}$. Sputtered coatings generally have inferior properties to those coatings produced by PECVD $^{[20]}$. Thin films deposited by PECVD are often hydrogenated during the process. Hydrogenated silicon films have optical band gaps of approximately 1.7 eV, while hydrogenated carbon films have optical band gaps of around 4 eV. Hence, varying the ratio of silicon to carbon in the coating shifts the band gap of the coating, and this has proven to be controllable and reproducible. Examples of applications of amorphous
SiC are microwave power transistors, solar cell windows, electrolytic electrodes, sensors, and oxidation resistant coatings\textsuperscript{[22]}. A large amount of work has also examined the epitaxial growth of $\beta$-SiC thin films\textsuperscript{[13, 14, 28 - 44]}. The primary method for the growth of such films is CVD, with smaller efforts in EACVD\textsuperscript{[14]} and PECVD\textsuperscript{[32, 44]}. A two-step CVD method has also provided satisfactory results\textsuperscript{[36]}, in which polycrystalline SiC is deposited first in a very thin layer on silicon at low temperature, and a subsequent layer of SiC is deposited over a long period of time at higher temperatures on top of the first layer. This two-step approach apparently increases the probability of heteroepitaxial growth. The substrate material is single crystal silicon, with a surface orientation slightly off-axis from (001). The twenty percent lattice mismatch between silicon and silicon carbide can be eliminated by tilting the axis of the substrate surface, resulting in SiC growths which are significantly more planar in morphology, with fewer defects, and thereby enhancing single crystal growth.

Most of the research of SiC CVD for electronic applications has focused on the growth of the cubic polytype. The higher temperatures required for the hexagonal 6H-SiC stability ($> 1600 ^\circ$C) make it difficult to form such deposits for the electronic field\textsuperscript{[45 - 52]}. The extremely small sizes of current and future electronic structures (integrated circuits, heterojunctions, etc.) require sharp and distinct boundaries between neighboring layers of material doped with various elements. The high processing temperatures required for the 6H polytype do not result in such boundaries, and hence until low temperature techniques are developed
for the growth of 6H, the cubic form will continue to be the polytype most used in electronic applications. The primary application for the hexagonal polytype of SiC is in blue light emitting diodes\textsuperscript{[46]}.

NON-ELECTRONIC APPLICATIONS

Much work has been reported in the open literature regarding the study of SiC CVD for non-electronic applications. These applications include wear-resistant coatings, corrosion-resistant coatings, or the deposit of SiC in the development of composite materials, either as a fiber coating or matrix material. Another application is the deposition of SiC in the form of whiskers which thereafter are imbedded in a composite material in either an aligned or non-aligned arrangement. When silicon carbide is deposited to form the matrix material in a fiber-reinforced composite material, the fibers exist prior to the deposition in a woven preform arrangement. In these instances, the precursor gases must infiltrate the preform and deposit SiC throughout the entire preform. Chemical vapor infiltration (CVI) is the term given to these cases\textsuperscript{[53]}.

The preferred gaseous system appears to be the methyltrichlorosilane (CH\textsubscript{3}SiCl\textsubscript{3}, MTS) - hydrogen (H\textsubscript{2}) system (or other molecules containing both silicon and carbon), based on the number of reports found in the literature. Other gaseous systems contain either a silane - hydrocarbon group (e.g. SiH\textsubscript{4} - C\textsubscript{3}H\textsubscript{8}), or a silicon chloride - hydrocarbon group (e.g. SiCl\textsubscript{4} - CH\textsubscript{4}) group\textsuperscript{[54-66]}. Some work has also implemented reactive chemical vapor deposition, in which a carbon-
containing gas species (e.g. \(\text{C}_2\text{H}_4\), \(\text{C}_3\text{H}_8\), or \(\text{CH}_4\)) is used as the precursor, and the substrate material is silicon. At sufficiently high temperatures (800 - 1200 °C), the precursor decomposes and deposits a carbon coating on the substrate. The silicon and carbon subsequently react to form a layer of SiC \(^{[67]}\). The opposite scenario also seems possible, although no reports thereof have been made.

As mentioned above, many reports have been made regarding the CVD of SiC in the MTS - \(\text{H}_2\) system \(^{[24, 43, 53, 68 - 94]}\). Unfortunately, several of these reports have some pertinent parametric data missing, such as system pressure, type of furnace, gas composition, flow rates, or substrate material. Accordingly, direct comparisons between seemingly similar works become difficult.

Two methods are commonly used to deliver the source gas into the CVD reactor. At normal temperature and pressure (NTP) MTS is liquid. The boiling point of MTS at one atmosphere pressure is around 66 °C, and the vapor pressure of MTS at room temperature is approximately 200 torr \(^{[83]}\). Hence, for experiments conducted at pressures below 200 torr, the MTS bath boils at or above room temperature. One method for delivery of MTS into the furnace is the bubbling of some hydrogen through MTS. These hydrogen bubbles are widely presumed to be saturated with MTS by the time the bubbles reach the top of the MTS bottle and subsequently enter the furnace. Of course, the gas feed line between the MTS tank and the furnace must be of equal or higher temperature than the MTS tank to prevent condensation. A separate line of hydrogen is run into the furnace without
being bubbled through the tank, so that the inlet gas composition may be varied between \( \text{CH}_3\text{SiCl}_3: \text{H}_2 \) ratios of zero and the saturation of MTS in hydrogen.

An important factor in the accuracy of this delivery system is the temperature of the MTS tank through which the hydrogen is being bubbled. Quite often this issue is not discussed. Studies at different system pressures which utilize this bubbling system often neglect to discuss the issue of MTS tank temperature (and the temperature of the lines between the MTS tank and the furnace inlet). At experimental system pressures above 200 torr, the saturation of MTS in the bubbled hydrogen decreases with increasing system pressure (assuming constant MTS bath temperature). Hence, varying the proportion of hydrogen flowing through the MTS tank and the hydrogen bypassing the MTS tank does not have the same effect on the average furnace inlet gas composition at differing system pressures. Accordingly, the initial gas composition found in those reports which utilize the bubbling system should often be accepted with caution, if they fail to discuss the issue of MTS vapor pressure / temperature of the MTS bath and gas feed lines connecting the MTS source to the inlet of the furnace.

Park et al. \(^{[68]}\) investigated the effect of substrate material (with respect to the surface roughness and chemical species of the substrate) on the phase and microstructure of deposits obtained by conventional CVD in the MTS system. The substrate materials were pyrolytic carbon and polished silicon wafers. The chemical species found in the deposit did not depend on the substrate material over the range of experimental conditions tested. However, the morphology of the
coating did depend on the substrate material, and the initial surface roughness of each substrate. On the polished carbon substrate, the growth morphology resembled nodules, with a noticeable porosity obvious upon examination of the fracture surface. On the polished silicon substrate, the surface of the coating was relatively flat, with no apparent porosity within the coating. Growth of SiC on a silicon substrate ground with emery paper led to a deposit with large nodules and small bumps. Hence, the substrate material has little to do with the chemical species deposited, but the surface roughness of the substrate does play a role in determining the morphology of the SiC grown.

Besmann et al. studied the CVI of SiC in the MTS - H₂ system in Nicalon fiber bundles. The operating conditions were generally around 1100 °C. The reaction was first order with respect to reactant concentration with an activation energy for the deposition reaction of only 66 kJ/mol (± 20). The first order concentration dependence indicates that a chemical kinetic mechanism is rate controlling rather than mass transport; this should be expected at the relatively low experimental temperatures. Besmann also found the deposition process to have a zeroth order dependence on MTS concentration at reduced system pressures (3.3 kPa). The reported values of the activation energy found by Besmann range from 66 (± 20) kJ/mol [53] to 188 (± 52) kJ/mol [154]. The widely differing activation energies and reaction orders indicate the difficulty in describing SiC deposition from MTS via a single expression over a wide range of conditions.
It is generally believed that SiC formation originates from two separate silicon and carbon deposition reactions, wherein the rate limiting step for SiC growth is the deposition of carbon. Some results indicate excess silicon at lower deposition temperatures, while other results under apparently similar conditions yield no excess silicon. Besmann found that silicon deposition is significantly faster than the SiC deposition at the same temperature. Hence, at low temperatures, excess silicon is apparently indicative of a low reactivity of the carbon-containing species. The reactivity of carbon-containing species and the equilibrium concentrations of silicon-containing species are important factors in determining the composition of the condensed phase.

Several reports described the reaction kinetics of SiC growth. A maximum growth rate occurs within the temperature range 1300 - 1500 °C. Below this range, slow kinetics retard overall growth. Within this range, growth is assumed to be diffusion controlled. Above this temperature range, homogeneous nucleation has been observed \(^{[69]}\), thereby depleting the gas phase of reactant.

Minato and Fukuda \(^{[71, 77]}\) deposited SiC within a fluidized bed reactor in the MTS - H\(_2\) system. His results indicate excess silicon at lower temperatures (below 1400 - 1500 °C), and stoichiometric β-SiC at higher temperatures at atmospheric pressures. The fluidized bed particles were approximately 0.001 m in diameter and consisted of microspherical nuclear fuel coated with pyrolytic carbon. The SiC coating retains fission products within the fuel particle, as well as acting as a diffusion barrier to metallic fission products, thus serving as a miniature pressure
vessel for the particle. The density of the coating decreased with decreasing temperature, corresponding to the codeposition of excess silicon. At a fixed temperature, with increasing hydrogen content in the gas mixture, the density of the coating decreased. The hardness of the deposited SiC (+Si) did not reach the inherent value of SiC until the deposition temperature of 1500 °C. At temperatures below 1300 °C, the hardness was very close to the intrinsic hardness of silicon. While his results are generally consistent with other works, the temperatures at which excess silicon was observed were significantly higher than in other reports.

Kuo et al. [74] studied the effect of CH\textsubscript{4} on CVD β-SiC grown in the MTS - H\textsubscript{2} system, with the primary objective of reducing the amounts of excess silicon found at lower deposition temperatures. For temperatures above 1450 °C and a system pressure of 35 torr, the selected substrate material was graphite. The presence of methane affected the morphology, crystallographic properties, and apparent growth mechanism of SiC. At lower temperatures, CH\textsubscript{4} reacted with excess silicon to form SiC, thereby increasing the deposition rate at these lower temperatures. The presence of methane during the growth of SiC also yielded some hexagonal polytype SiC at 1450 °C, which normally is not experimentally observed until temperatures exceed 1800 °C.

Motojima and Hasegawa [75] grew SiC layers on graphite substrates at 1100 - 1200 °C, and examined the effect of the mass flow rate and linear velocity of gas on the codeposition characteristics of excess silicon and SiC. These results indicate a dependence of the composition of the condensed phase on pressure and on gas
flow rate. For a constant mass flow rate, reductions in pressure result in higher linear velocities. Another method for increasing the velocity of the gas phase is to add chemically inert argon to the flow. These two methods affect the system in different ways. Reductions in system pressure affect the physical properties of the gas, and alter the diffusivities of the gas components. The addition of argon for changing the velocity of the gas phase results in different values for the physical properties and diffusivities compared to the pressure reduction method. Higher flow rates yielded more dense and adherent SiC coatings. Reductions in the system pressure from 760 torr to 10 torr resulted in coatings with little or no excess silicon at 1000 °C. The addition of argon to the gas stream resulted in an acceleration of SiC deposition, especially at low temperatures. An addition of argon gas to the system was effective in suppressing the codeposition of excess silicon.

Choi and Kim [76] studied the effect of temperature on the composition of the condensed phase in the MTS - H₂ system at 760 torr. Free silicon was deposited at all temperatures below 1500 °C, with stoichiometric growth of SiC above 1500 °C. The MTS mole fraction was varied between 0.005 and 0.02. The deposition rates were linear functions at the examined temperatures of 1300 and 1500 °C. At a MTS molar fraction of 0.01, the deposition rate increased with increasing (H₂ + MTS) mass flow rate over the entire temperature range studied. The apparent activation energies and reaction constants decreased with increasing temperature. The morphology of the coatings deposited at 1300 °C were fully dense and relatively smooth, while coatings obtained at 1500 °C showed a faceted surface.
So and Chun [78] grew SiC coatings at 1100 - 1400 °C at 200 torr onto graphite substrates, studying the effects of deposition temperature, system pressure, and MTS input fraction on the growth characteristics and structure of the resultant coatings. Their deposition process was reaction limited, wherein the calculated activation energy was 110 kJ/mol at 200 torr, decreasing to 55 kJ/mol at 500 torr. Homogeneous gaseous reactions were attributed to these values. No excess silicon was observed over the range of experimental conditions studied, contrary to some other reported results. At every temperature studied, the deposition rate increased with an increase in total system pressure. The total flow rate had a negligible effect on the deposition rate.

Cheng et al. [79] studied the growth of β-SiC in the MTS - H₂ system over 1250 - 1600 °C. The claimed system pressure of 0.93 MPa (> 9 atm!) was also characterized as "reduced pressure". The deposition rate was found to increase with an increase in mass flow rate. The growth rate reached a maximum at a temperature around 1450 °C, whereafter the decrease in growth rate with increasing temperature was attributed to homogeneous reactions taking place in the gas phase.

Parretta et al. [80] studied the effect of substrate material on the properties of β-SiC grown in the MTS - H₂ system between 900 and 1100 °C. The morphologies of the coatings grown on graphite substrates and on α-SiC substrates were identical at 1100 °C. The activation energies were 250 kJ/mol at 900 °C and 300 torr, and 200 kJ/mol at a pressure of 750 torr. At 1100 °C, the activation energy decreased to 125 kJ/mol for both pressures examined. The hardness of the
coatings increased as the deposition temperature increased, although this was attributed to the change in microstructure and not to composition of the coating as in other works.

Chin et al. [82] studied the effect of system temperature, pressure, and \( \text{H}_2:\text{CH}_3\text{SiCl}_3 \) ratio on the morphological, chemical, and microstructural properties of SiC. The trends observed by Chin are similar to those found in other works. Figure 1 is a schematic drawing illustrating the aforementioned dependencies.

Figure 1. Chemical composition - process relationships in the chemical vapor deposition of SiC in the MTS - H\(_2\) system [ref. 82].
The general trends indicated in Fig. 1 are in agreement with much of the published experimental results, although the accuracy of the boundaries remains in question. Strongly facetted structures were deposited under higher deposition temperatures (> 1500 °C), higher H₂:CH₃SiCl₃ ratios (> 10:1), and reduced system pressures. Smooth deposits with rounded growth features were formed at lower temperatures (< 1150 °C), low gas ratios (< 5:1), and increased pressures. The smallest changes in the morphology of the coatings were observed with changes in the pressure. A combination of the 3C and 2H polytypes were observed for all temperatures below 1500 °C. Only the cubic form of SiC was seen above 1500 °C.

Muench and Pettenpaul [83] prepared β-SiC from the MTS - H₂ system, studying the influence of flow rate, vapor pressure, and temperature on the growth rate and morphology of the deposit. All experiments were conducted at atmospheric pressure. Approximately 5 wt % excess carbon was observed at 1600 °C, and 50 wt % excess silicon was seen at 1200 °C. Stoichiometric SiC was deposited around 1500 °C. The deposition rate increased linearly with increasing temperature. Higher vapor pressures of the MTS reactant also yielded proportionately higher deposition rates.

Kobayashi et al. [84] found large amounts of excess carbon in SiC grown under conditions where other studies found excess silicon. They studied the effect of using hydrogen or argon gas as the carrier for the MTS. The amount of excess carbon increased with an increase in the amount of argon. The difference in the carbon content for using hydrogen compared to argon as the carrier was as much as
45 percent. At temperatures above 1400 °C the composition of the coating showed no dependence on the carrier gas species. At 1500 °C, the deposit was nearly stoichiometric.

Federer [88] studied the deposition of SiC on fluidized bed particles in the MTS - H₂ system. The reactant gas composition and temperature were correlated with the resultant morphology and density of the coating. The most dense coatings were obtained when the H₂:CH₃SiCl₃ ratio was around 20:1, and the temperature was in the range 1475 - 1675 °C. Lower temperatures yielded silicon - rich deposits. The density of the coatings decreased with higher growth rates, due to increased porosity. Porosity decreased with increasing H₂:CH₃SiCl₃ ratios and lower deposition temperatures, because of an increase in excess silicon.

Kemenade and Stemfoort [89] formed β-SiC by the pyrolysis of CH₃SiCl₃ in hydrogen at 1 atm pressure in the temperature range 1200 - 2000 °C. The apparent activation energy at lower temperatures was approximately 67 kJ/mol. At temperatures above 1800 °C, the activation energy was -75 kJ/mol based on mass increase rates of the coating. Excess silicon formed at the lower temperatures, but only in negligible amounts. Large quantities of excess carbon were present in the coatings formed at the high temperature range, leading to a decrease in the mass growth rate. However, radial growth rates were not affected by temperature, suggesting that a combined deposition and dissolution of silicon takes place, wherein the silicon deposits and subsequently dissolves out of the deposit by reacting with SiCl₄. The mass growth rate curves coincide with the thickness
growth rate curves when the free carbon is calculated as an equivalent amount of SiC. Hence, the theory reporting a homogeneous reaction at high temperatures which thereby reduces the deposition rates should perhaps be corrected for the mass of excess carbon.

Gulden [93] studied the CVD of β-SiC in a fluidized bed in the temperature range 1400 - 1800 °C. The deposition rate seemed largely unaffected by temperature. The deposition rate increased linearly with the MTS flux. At 1400 °C and high carrier flow rates (20,000 sccm) deposits were primarily composed of grains resembling growth cones. With increasing temperature, the grain size increased and the growth cones disappeared, to be replaced by columnar grains. At 1800 °C, some excess carbon and α-SiC was present. As in other studies, lower deposition temperatures yielded coatings with some free silicon.

Langlais et al. [94] studied the kinetics of the CVD of SiC in the MTS - H₂ system over the temperature range 750 - 1100 °C at pressures neighboring 150 torr. The deposition rate decreased with increasing H₂:CH₂SiCl₃ ratio. At temperatures below 850 °C the activation energy was approximately 165 kJ/mol. For a temperature range around 1200 K, a system pressure around 10 torr, and an initial H₂:CH₂SiCl₃ ratio between 10² and 10⁶, the following reaction process was proposed:
wherein the first of these reactions occurs homogeneously and the latter reaction occurs heterogeneously. For higher temperatures, lower pressures, and lower composition ratios, the reaction process changes according to:

\[ \text{CH}_3\text{SiCl}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{SiCl}_2 + \text{HCl} \]  

(1)

\[ \text{CH}_4 + \text{SiCl}_2 \rightarrow \text{SiC}_x + 2\text{HCl} + \text{H}_2 \]  

(2)

These sets of proposed reactions are in agreement with the experimental observations of excess silicon associated with high amounts of hydrogen in the system. According to the above reactions, the carbon-containing molecule does not require any help from the carrier hydrogen pumped into the reactor, whereas the silicon-containing species requires the presence of an atom capable of reacting with it to remove the chlorine atoms attached to the silicon. For systems previously discussed in which only argon was used as the carrier, large amounts of excess carbon were found in the coatings, which is equivalent to a lack of silicon existed in the same coating. The deposition rate reaches a peak at the system pressure of approximately 15 torr. Below this value, the reaction is presumed to be under reaction control, and above this value, the controlling mechanism may be either a zeroth-order reaction or diffusion through the boundary layer.
MATHEMATICAL MODELING

Several mathematical models have been developed to describe the conventional CVD process (not plasma nor electron assisted, but rather thermally activated) on a continuum-base level \^[90, 95 - 134]. These reports may be divided into two main categories: those which employ calculations based on well known partial differential equations believed to describe the relevant transport phenomena, and those which make fairly big assumptions in an effort to reduce the complexity of the calculations (without requiring the solution to the partial differential equations).

The models in the former category often use well established finite difference or finite element methods for solving the transport equations in either two or three spatial dimensions \^[95 - 100, 103, 105 - 107, 109, 111, 112, 114, 117, 118, 120, 121, 125, 127 - 129, 131, 132]. None of these models are implemented for the chemical vapor deposition of silicon carbide in any gaseous system. Silicon and gallium arsenide are the largest groups of deposited materials studied in these models, due to their wide use as thin films in the electronics industry. Johnson et al. \^[117] studied the CVD of ZnSe in a horizontal reactor in a two-dimensional model, utilizing the commercial code entitled TEMPEST. They conclude that in order to model CVD processes, turbulence and time dependence must be included in the calculations. This conclusion should apply only to their system, wherein the Reynolds number has been calculated to be near the laminar to turbulent threshold value of 2100. None of the experimental reports indicated a turbulent gas system within the SiC CVD vessels (Langlais \^[94] has calculated the Reynolds number to be on the order of 10 in
the hot zone of a typical CVD reactor used to deposit SiC). In addition, their conclusion may be indicative of improperly input boundary conditions. As mentioned in the model formulation section (Chapter IV), the correct implementation of boundary conditions in the usage of a mathematical model determines whether the model will yield physically realistic results (assuming the equations used in the model are able to describe the transport phenomena and reactions).

Only two models have been found in which silicon carbide is the selected coating material. Both of these however, make gross assumptions about the system at hand. Allendorf and Kee \cite{102} studied the CVD of SiC in the silane - propane - hydrogen gas system (no chlorine present) in a rotating disc reactor. However, they reduced the modeled domain to a one-dimensional system, based on the assumption of an infinitely long disc. They give no supporting data to validate their model. One-dimensional models by nature are unable to predict any convective flow within a CVD reactor, and are not able to predict changes in boundary layer thicknesses adjacent to substrate edges. Hence, their report may serve primarily as a source of kinetic data for the 83 gas phase reactions and 36 heterogeneous reactions they include in their model.

Minato and Fukuda \cite{90} provide an analytical model of SiC deposition on graphite-coated nuclear fuel particles in a fluidized bed reactor in the CH$_3$SiCl$_3$ - hydrogen system. A primary assumption in the development of their model is that the rate-limiting-step is the diffusion of the reactant to the surface of the fuel
particles. Comparison between thermodynamic calculations and their experimental results yields the observation that the reaction does not follow thermodynamic equilibrium calculations, similar to results experimentally found in all SiC CVD deposits.

Holstein and Fitzjohn [95] examined the effect of buoyancy forces and reactor orientation on fluid flow and growth rate uniformity in cold-walled CVD reactors. Their results indicate that the effect of buoyancy on uniformity of the deposit is substantially reduced for low pressure systems (0.1 atm). For studying the significance of buoyancy forces in vertically oriented CVD reactors, the ratio of the buoyancy to inertial forces influences the resultant fluid flow. This ratio is expressed by the ratio of Grashof to Reynolds numbers, $Gr / Re$, which are dimensionless numbers used to qualitatively explain flow phenomena in fluids. The Grashof and Reynolds numbers are defined according to the following expressions:

$$Re = \frac{\rho \nu_0 h}{\mu} \quad (5)$$

$$Gr = \frac{\rho^3 g h^3 \Delta T}{\mu^2 \nu} \quad (6)$$

wherein $\rho$ is the density, $\nu_0$ the average velocity, $h$ a characteristic length, $\mu$ the viscosity, $g$ the gravitational acceleration, $\Delta T$ the temperature difference occurring over the characteristic length, and $T$ the absolute temperature. The Reynolds number describes the ratio between the inertial and viscous forces within the fluid, and the $Gr / Re$ ratio indicates the proportion of the buoyancy forces to the inertial forces. Indeed, for low pressure CVD systems, the $Gr / Re$ ratio has values on the
order of unity. The onset of recirculative backflow in a vertically oriented CVD reactor in which the substrate is hotter than the furnace wall has been found to begin when the $Gr / Re$ ratio exceeds 72. Hence, for typical low pressure CVD systems, buoyancy forces are practically negligible. However, the buoyancy forces increase as $P^3$, and accordingly play a significant role in high pressure (1 atm) CVD systems. The characteristic length of the system (for example the diameter or width of the reaction chamber) also plays an important role in the resultant significance of the buoyancy forces. Accordingly, high pressure CVD models may be implemented disregarding the buoyancy effects as long as the geometry of the reactor warrants it, as pointed out by Moffat and Jensen [96] and Ouazzani et al. [97].

Other models have been developed which are capable of describing CVD processes on a more atomistic level [135 - 139]. These models often address important issues regarding surface mobilities, surface sticking coefficients, surface charge distribution, availability of surface sites, and other related topics which allow the separation of the adsorption, recombination, and desorption steps which are often collected into one "reaction kinetic" controlling step. However, these same models often neglect to include more operationally controllable parameters such as temperature, pressure, gas composition, or mass flow rates found within CVD reactors.
CONCLUSIONS

Silicon carbide has many physical properties which result in its use for many applications, ranging from those serving electronic purposes, nuclear fuel particle coatings, fiber coatings for use in fiber-reinforced composite materials, and as coatings applied for abrasion or corrosion resistance. A typical process for applying thin films of SiC to various substrates is chemical vapor deposition. Plasma-assisted CVD (PACVD) is usually implemented for instances in which the deposit will have an electronic purpose, due to the lower deposition temperatures and hence less dopant diffusion within the deposit or into adjacent substrate material.

Many gaseous systems may be used to deliver the SiC to the substrate surface. A popular selection is the CH₃SiCl₃ (MTS) - H₂ system, because of the 1:1 ratio of silicon to carbon in the precursor. MTS was developed with the thought of yielding stoichiometric coatings, due to its Si:C ratio of 1.

Strong dependencies of coating composition on substrate temperature, system pressure, and initial gas composition were found experimentally, often contradicting thermodynamic equilibrium predictions. The composition of the deposit is also known to depend on gas flow rate, linear velocity, and amount (if any) of argon present in the system. The combinations of all these dependencies make it often difficult to compare results found by different research efforts, especially when all these factors are not discussed.
The morphologies of the SiC coatings produced via CVD are affected primarily by temperature and gas composition. Increasing the system temperature results in a transition of the coating morphology from smooth and fully dense, to columnar, to angular, to facetted with interconnected porosity. Increasing the \( \text{H}_2: \text{CH}_3 \text{SiCl}_3 \) ratio or decreasing the system pressure have similar effects, albeit smaller in magnitude.

Mathematical models exist which are able to describe the transport phenomena found within conventional CVD reactors. The application of such models has been primarily in the CVD of silicon or gallium arsenide, both of which are used in the electronics industry. These models fall into two main categories: those which have solved the governing partial differential equations for describing mass, momentum, and heat transfer, usually by well established finite element or finite difference expressions, and those which have not. The latter models may be used for optimization in their specific application, but outside the experimental conditions investigated the use of these models should be severely restricted due to the usually rather bold assumptions made in order to simplify the problem mathematically.

None of the reported models falling into the former category were found to have been applied for the deposition of SiC in any gas system. The recent advances made in the experimental control of the polytype, composition, and morphology of deposited SiC now warrant the development of such a model, in order to further understand the deposition process, thereby allowing optimization of
existing SiC CVD reactors. In addition, the experimentally observed compositions and morphologies of the deposited SiC films are not consistent at apparently similar deposition conditions.

Hence, the work performed in the present study has attempted to address these issues. A two-dimensional mathematical model has been developed capable of describing the relevant transport phenomena found in the CVD of SiC in the CH₃SiCl₃ - H₂ system. A thermodynamic analysis was performed to investigate the dependence of the compositions of the gaseous and condensed phases on system temperature, pressure, and initial gas composition. The results of the thermodynamic calculations were implemented in the process of validation of the model. Several experiments were conducted in order to further develop the relationships between growth morphology and experimentally controllable parameters. Morphologies significantly different than those previously reported have been observed in the present study.
INTRODUCTION

Thermodynamic equilibrium calculations are extremely useful in the design stages of a chemical vapor deposition reaction process. If the CVD process is determined to be in a state which approximates thermodynamic equilibrium, these calculations can be implemented in a predictive manner, disclosing the operating conditions which result in the desired coating properties. The results of these computations at the very least are capable of indicating compositional trends of the condensed phase (and the vapor phase), when the system of interest is found to be limited by the reaction kinetics.

Temperature, pressure, and inlet gas composition are some of the more significant variables which control the physical properties of the deposit in the CVD process. Based on the temperature, pressure, and initial gas composition conditions, the deposition reaction may possibly yield a coating which is either stoichiometric SiC, or a deposit which contains either free silicon or carbon.
If the kinetics of the decomposition reaction are assumed to be sufficiently rapid to cause this process to be thermodynamically predictable (i.e. the system is at thermodynamic equilibrium as soon as the precursor and carrier gases come into contact with the substrate), then thermodynamic calculations in the CH$_3$SiCl$_3$ - H$_2$ system can be applied to determine which gaseous species play an important role in the deposition of SiC, in addition to determining the quantity and stoichiometry of the deposited SiC. Knowledge of the major gas constituents formed under thermodynamic equilibrium conditions can be applied in a mathematical model which ultimately is capable of predicting the deposition rates and profile along a substrate.

In the present study, a computer program entitled SOLGASMIX was first employed to calculate the thermodynamic equilibrium compositions of the gas and condensed phases in the CH$_3$SiCl$_3$ - H$_2$ system. The purpose of this portion of the study was two-fold, first to determine the stable gaseous species which should be included in the mathematical model. The other purpose was to provide (by way of calculation) CVD stability diagrams which indicate conditions for deposition of single-phase silicon carbide in given regimes of temperature, inlet gas composition, and the absolute system pressures examined via SOLGASMIX.

If the assumption of thermodynamic equilibrium is correct, then it would be prudent to determine the experimental conditions for which single-phase silicon carbide is the most stable phase (assuming single phase SiC is the desired result). Hence, the composition of the gaseous and condensed phases at equilibrium, and
therefrom CVD equilibrium stability diagrams for the CH$_3$SiCl$_3$ - H$_2$ system were calculated.

PROCEDURE

The computer code used in this study is called SOLGASMIX. This program calculates that composition which results in a minimum for the Gibbs energy of the system, under given conditions of total system pressure, temperature, and initial gas compositions. The computer code also takes into account the conservation of mass. For a more detailed description of the method by which SOLGASMIX calculates the equilibrium composition, please refer to references [140,141].

As previously mentioned, the three major input variables in SOLGASMIX are temperature, pressure and composition. Another important assumption used by SOLGASMIX is that the system is held at constant pressure, as opposed to constant volume. The system pressure was varied between 30 and 300 torr, specifically collecting data at 30, 90, 150, and 300 torr. The amount of precursor gas (CH$_3$SiCl$_3$) was held constant at 100 gm-moles. The concentration of the carrier gas (i.e. H$_2$) was varied systematically such that the ratio between the moles of methyltrichlorosilane and the moles of hydrogen ranged from 1:1 to 1:1000. The system temperature was varied between 1000 and 2200 K, in 100 degree increments. There was no diluent (e.g. Ar) gas present in the calculations, unless otherwise stated.
The chemical equilibrium of a gas phase composed initially of $\text{CH}_3\text{SiCl}_3$ and $\text{H}_2$ should take into account all of the possible chemical gaseous and condensed species composed of a combination of the atoms Si, C, H, and Cl. The gaseous species taken into account in this study included those listed in Table 1. Four condensed phases are considered in these calculations: $\alpha$-SiC, $\beta$-SiC, C, and Si. All of these species were included in every calculation since their effect on the equilibrium condensed phases was not known a priori. The formation of many of these species is obviously less probable than others; nevertheless they were included. All of the condensed phases were assumed to exhibit no tolerance for deviations from stoichiometry (i.e. line compounds).

Table 1. Gaseous species considered in the thermodynamic equilibrium calculations.

<table>
<thead>
<tr>
<th>Species</th>
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</tr>
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<tbody>
<tr>
<td>C</td>
<td>SiC</td>
<td>$\text{C}_2\text{H}$</td>
<td>$\text{C}_2\text{HCl}$</td>
<td>$\text{CCl}$</td>
</tr>
<tr>
<td>Cl</td>
<td>Si$_2$C</td>
<td>CH</td>
<td>CHCl</td>
<td>$\text{CCl}_2$</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>SiC$_2$</td>
<td>$\text{C}_2\text{H}_2$</td>
<td>$\text{CH}_2\text{Cl}$</td>
<td>$\text{CCl}_3$</td>
</tr>
<tr>
<td>H</td>
<td>SiCl</td>
<td>$\text{CH}_3$</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
<td>$\text{CCl}_4$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>SiCl$_2$</td>
<td>$\text{CH}_4$</td>
<td>$\text{CHCl}_3$</td>
<td>SiH$_2$Cl</td>
</tr>
<tr>
<td>Si$_2$</td>
<td>SiCl$_3$</td>
<td>HCl</td>
<td>SiH</td>
<td>SiH$_2$Cl$_2$</td>
</tr>
<tr>
<td>Si$_3$</td>
<td>SiCl$_4$</td>
<td></td>
<td>SiH$_4$</td>
<td>SiHCl$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CH$_3$SiCl$_3$</td>
</tr>
</tbody>
</table>
The JANAF\textsuperscript{150} tables provided the standard Gibbs energies of formation for most of the species studied. The given data for CH$_3$SiCl$_3$ was extrapolated into the temperature regime of interest. For extrapolation purposes, it was assumed $\Delta c_p$ equalled zero. The thermodynamic data for all of the SiCl$_x$'s ($x = 1-4$) were taken from Pankratz\textsuperscript{151}. It should be noted that the standard free energy of formation of $\beta$-SiC was lower for all temperatures than the $\alpha$-SiC. Hence, no $\alpha$-SiC was predicted to form throughout the tested temperature range. Also, the thermodynamic data for carbon is that for the formation of graphite. Therefore, no other forms of carbon were considered to deposit.

RESULTS AND DISCUSSION

EFFECT OF TEMPERATURE ON VAPOR PHASE COMPOSITION

Figure 2 is a typical plot of the resultant vapor pressures of the most predominant gaseous species as a function of temperature, as indicated by the thermodynamic equilibrium calculations for the conditions of $P_{\text{system}} = 90$ torr, and the initial gas composition $H_2:CH_3SiCl_3 = 10:1$. The most prevalent gaseous product species has been calculated to be HCl, as indicated in the net decomposition reaction of CH$_3$SiCl$_3$ in hydrogen:

$$CH_3SiCl_3 \rightarrow SiC + 3HCl \quad (7)$$

For a typical coating temperature of 1600 K, the next most prevalent gas species is SiCl$_2$, approximately two orders of magnitude lower in partial pressure.
than HCl. Hence, the net decomposition reaction of CH$_3$SiCl$_3$ as shown above can be considered to be a generally accurate description of the system.

Appendix A contains all additional figures of similar content, in which the partial pressures of the most prevalent equilibrium gas species are depicted as functions of temperature, and each plot containing data for a particular system pressure and initial gas composition (H$_2$:CH$_3$SiCl$_3$ ratio).

In the procedure section above, thermodynamic equilibrium calculations were performed over the temperature range 1000 - 2200 K at 100 K intervals. Inspection of most of the data presented in Appendix A (as well as in Fig. 2) results in the observation that data are not present at each 100 degree interval. The inability of SOLGASMIX to calculate the equilibrium composition at these specific temperatures, pressures, and H$_2$:CH$_3$SiCl$_3$ ratios is the cause of the lack of data. The reason for this lack of data is not known.
Figure 2. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a H$_2$:CH$_3$SiCl$_3$ molar ratio of 10:1.
Two regions are generally distinguishable on these figures, based on the temperature at which equilibrium is reached. The first region occurs throughout the temperature range of 1000 to about 1600 K, in which the major equilibrium gas species are SiCl₂, SiCl₃, SiCl₄, CH₄, and SiHCl₃ (other than H₂ and HCl). In the second temperature range (about 1600 to 2200 K), the dominant gaseous species become H, Cl, SiCl₂, and SiCl₃.

The absence of any significant amounts of gaseous species containing both silicon and carbon is noteworthy. This observation concurs with those results found in other efforts. The relative instability (high reaction rate) of those gas species (i.e. relatively weak silicon / carbon bond [143]) is indicated by the absence of gas species containing both Si and C. An example of this is the complete decomposition of the CH₃SiCl₃ molecule, whose equilibrium vapor pressure was sufficiently low to warrant its exclusion from the vapor phase equilibrium figures. Therefore, the silicon and carbon atoms seem to deposit in separate yet dependent reactions, and subsequently recombine on the substrate surface to form SiC.

As the temperature is increased, lighter (lower molecular weight) gas species become more stable in relation to the heavier molecules. Similar temperature dependencies were also found at the other pressures (30, 150, and 300 torr) studied.

Keeping in mind that the thermodynamic calculations obey mass conservation, a reduction in the silicon content of the vapor phase is concomitant with a silicon increase in the condensed phase. Hence, at the lower end of the temperature range, the predominant equilibrium vapor phase components were
silicon-containing species; significant amounts of excess carbon were determined to exist in equilibrium in the condensed phase. A parallel statement can be made regarding the vapor and condensed phases toward the upper end of the evaluated temperature range.

The method of presenting data in the form of "stability diagrams" for the condensed phase is quite common \cite{142,143}. Stability diagrams indicate regions in (temperature / pressure / gas composition) space, and the resultant condensed phase constituents contained therein. However, this method mandates that no information regarding the quantities of each species (i.e. graphite and SiC) in the condensed phase be given. However, sometimes this information is useful, as is the case when a specific amount of second phase is desirable. Accordingly, figures 3 through 5 include information pertaining to the quantities of both SiC and graphite present in the deposited phase, including the variations of the quantities of the condensed phase constituents with temperature, pressure, and initial gas composition.

**EFFECT OF TEMPERATURE ON CONDENSED PHASE COMPOSITION**

Figure 3 is a schematic of the variation of the composition of the condensed phase with temperature, comparing the results for system pressures of 30, 90, 150, 300, and 760 torr. The mass of lines abutting the top of the figure represents the number of moles of SiC determined to be in equilibrium in the condensed phase. Likewise, the data near the bottom of the figure represent the quantity of excess carbon (in the form of graphite) in the deposit.
The total number of moles of silicon (and of carbon, since each molecule of \( \text{CH}_3\text{SiCl}_3 \) contains the same quantity of C and Si atoms) in the system for all calculations has been held constant at 100, since the amount of \( \text{CH}_3\text{SiCl}_3 \) has been held constant at 100 gm-moles. From figure 3, under the assumed conditions (\( \text{H}_2:\text{CH}_3\text{SiCl}_3 \) ratio of 10:1), excess carbon is predicted to exist in equilibrium with the co-deposited SiC for all temperatures and pressures.

The quantity of excess carbon seems to be relatively insensitive to the system pressure, especially for temperatures above 1600 K. This is coincidentally also the approximate temperature at which there is a minimum in the carbon content of the condensed phase (approximately 5% excess carbon).

Appendix B contains plots of a similar nature, although for differing gas ratios. By inspection of the figures in Appendix B, two observations can readily be made: (1) the composition of the condensed phase becomes slightly more pressure-sensitive for lower initial gas ratios (more enriched solutions of \( \text{CH}_3\text{SiCl}_3 \) in hydrogen); (2) reduction in the \( \text{CH}_3\text{SiCl}_3 \) partial pressure results in a reduction of the carbon content in the condensed phase.
Figure 3. Composition of condensed phase as a function of temperature, for a \( \text{H}_2: \text{CH}_2\text{SiCl}_3 \) ratio of 10:1, for all examined pressures.
EFFECT OF SYSTEM PRESSURE

Figure 4 shows the aforementioned dependence of carbon content in the condensed phase on the CH$_3$SiCl$_3$ partial pressure. The composition of the condensed phase is plotted against temperature, for all the examined H$_2$:CH$_3$SiCl$_3$ ratios, and a constant system pressure of 90 torr. For ratios above 50:1, the excess carbon content in the solid phase essentially disappears, except for temperatures above 2000 K.

Appendix C contains figures of a similar nature, for the other examined system pressures. Scrutiny of these plots reveals the lack of any significant pressure sensitivity on the excess carbon content.
Figure 4. Variation of the condensed phase composition as a function of temperature, for the system pressure of 90 torr, and all evaluated $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratios.
EFFECT OF MTS CONCENTRATION

Figure 5 is a schematic of the variation of the condensed phase composition as a function of H\textsubscript{2}:CH\textsubscript{3}SiCl\textsubscript{3} ratio, based on the thermodynamic equilibrium calculations, for 1600 K. Each pair of SiC and graphite lines in the figure represent one of the evaluated system pressures. Those lines near the top of the figure represent the number of moles of SiC calculated to be in the condensed phase. Similarly, data near the bottom of the figure represent the calculated equilibrium amount of graphite to exist in the deposit.

For H\textsubscript{2}:CH\textsubscript{3}SiCl\textsubscript{3} ratios above 100:1, no graphite is predicted to exist in the condensed phase, for all the pressures studied (except 760 torr, see below). Increasing the H\textsubscript{2}:CH\textsubscript{3}SiCl\textsubscript{3} gas ratio tends to decrease the amount of graphite in equilibrium in the deposit. By inspection of figures 57 through 63 (refer to Appendix A), this observation coincides with the apparent increase in the methane (CH\textsubscript{4}) content in the equilibrium vapor phase with an increase of the H\textsubscript{2}:CH\textsubscript{3}SiCl\textsubscript{3} ratio. Methane is the most prevalent source of carbon in the vapor phase, and observing trends of how the CH\textsubscript{4} vapor pressure varies in relation to the predominant silicon-containing vapor species, results in complementary trends found in the composition of the condensed phase.

It must be emphasized at this point that the data for 760 torr included a significant amount of argon in the calculations (10 gm-moles). Previous data\textsuperscript{[142]} have indicated a substantial effect of argon on the condensed phase in thermodynamic equilibrium. Higher amounts of argon included in either the
experimental trials \cite{43, 75, 84} or the thermodynamic calculations yield higher amounts of excess carbon (or less amounts of excess silicon) in the deposit. For constant pressure systems, the presence of argon effectively reduces the H2:CH3SiCl3 ratio, which increases the amount of excess carbon in the condensed phase.
Figure 5. Composition of condensed phase as a function of $H_2:CH_3SiCl_3$ ratio, for the evaluated temperature of 1600 K, and all examined pressures.
CVD STABILITY DIAGRAMS

Figures 6 through 9 show the stability diagrams from the thermodynamic equilibrium calculations by SOLGASMIX for the 30, 90, 150, and 300 torr total pressures, respectively. The temperature range studied was 1000 - 2200 K. The triangularly shaped points indicate the conditions where SiC and C were predicted to co-deposit. Similarly, the rectangularly shaped points indicate those conditions under which it is predicted that only SiC will deposit. Hence, there exists a boundary between the two regions. Implementation of SOLGASMIX for determining a precise location of the boundary between a deposit containing only SiC, and a deposit containing both SiC and graphite, is beyond the scope of the present study. Doing so would involve a substantial increase in the number of SOLGASMIX calculations made for data not necessarily relevant to the implementation of these results within the mathematical modeling portion of the present study.

At high H₂:MTS ratios and low temperatures, only SiC should deposit according to the calculated equilibrium conditions. On the other hand, at low H₂:MTS ratios and high temperatures, carbon should deposit simultaneously with the SiC. As the pressure is increased, the boundary shifts slightly toward lower H₂:MTS ratios and towards higher temperatures. For example, at the total pressure of 30 torr (refer to figure 6), the lowest H₂:MTS ratio at which only SiC deposits is approximately 50:1, at approximately 1400 K. However, at an increased total
system pressure of 300 torr (refer to figure 9), single-phase SiC is predicted to
deposit at a minimum ratio of only about 20:1, at the same temperature of 1400 K.
Figure 6. CVD condensed phase stability diagram, based on thermodynamic equilibrium calculations, for a total system pressure of 30 torr.
Figure 7. CVD condensed phase stability diagram, based on thermodynamic equilibrium calculations, for a total system pressure of 90 torr.
Figure 8. CVD condensed phase stability diagram, based on thermodynamic equilibrium calculations, for a total system pressure of 150 torr.
Figure 9. CVD condensed phase stability diagram, based on thermodynamic equilibrium calculations, for a total system pressure of 300 torr.
THERMODYNAMIC PREDICTION COMPARISON

The results of the thermodynamic analysis presented in this study agree well with other thermodynamic predictions [142, 143], although these other works do not include information about the quantities of the condensed phase constituents. Similar results could be expected, however, since all of the calculations used the JANAF tables as a source for the thermodynamic data. Little work has been done regarding a sensitivity analysis of the predicted results on the Gibbs energy data implemented, although Bernard and Madar [144] indicate such an analysis may be warranted.

THERMODYNAMIC PREDICTIONS VS. EXPERIMENTAL OBSERVATIONS

The thermodynamic predictions presented in this research, and in references [142] and [143], indicate that no co-deposition of silicon should be expected over the examined range of temperature, pressure, and gas composition. The experimental results found by Heaney [87] conflict with the thermodynamic predictions. They have found excess silicon (5 atomic percent excess) to deposit under the following conditions: $T = 1300 \, ^\circ\text{C}$, $P = 100 \, \text{torr}$, $H_2:CH_3SiCl = 5:1$. By reducing the $H_2:CH_3SiCl$ ratio to 1:1, Heaney has found large quantities of excess carbon (97 atomic percent excess). Similar results were found by Chin et al. [82], although excess silicon was not observed until the $H_2:CH_3SiCl$ ratio reached a value of 20:1, compared to 5:1 for Heaney.
Muench and Pettenpaul [83] and Gulden [93] observed the deposition of non-stoichiometric silicon carbide, although under conditions different from Heaney [87] and Chin [82]. Free silicon was found to deposit at temperatures below 1300 °C, and free carbon deposited at system temperatures above 1600 °C.

Kobayashi et al. [84], Popper and Riley [85], and the results in the present study contradict the aforementioned experimental results. Excess carbon was found in the deposited phase for temperatures in the range 1000 - 1400 °C. No free silicon was detected (via X-ray diffraction) in any of the samples coated in the present study. These results appear to be in agreement with the thermodynamic calculations.

The existence of conflicting experimental data in the literature indicates that the deposition of silicon carbide via MTS and hydrogen is a relatively complex system (contrary to Gulden’s conclusion [93] that the deposition is very simple!), and potentially dependent on the specific apparatuses used for the deposition process.

The comparison of thermodynamic equilibrium calculations to experimentally obtained results demands that two criteria are satisfied: (1) the Gibbs energy data used in the calculations are accurate; (2) the system can be accurately represented by equilibrium conditions. The former criterion is assumed to be satisfied, as well accepting the method for calculating thermodynamic equilibrium compositions. Therefore, the thermodynamic equilibrium calculations obtained in the present study are believed to accurately represent the thermodynamic equilibrium conditions within the studied system.
Those experimental results from the literature which do not agree with thermodynamic equilibrium calculations apparently have other factors imposing on the deposition process in such a way that the system is no longer able to be described by thermodynamic equilibrium. These factors may include the MTS delivery system -- for example, if the MTS is delivered to the reactor via bubbling of hydrogen through a bottle of MTS, the actual amount of delivered MTS may differ from the amount thought to enter the CVD reactor. Other factors may include geometrical considerations involving the path and history of the MTS before entering the furnace.
CONCLUSIONS

CVD equilibrium stability diagrams were calculated for β-SiC formation from the CH₃SiCl₃ - H₂ system at various temperatures, system pressures, and initial gas compositions. The results indicate that the single phase SiC field (in temperature / H₂:CH₃SiCl₃ space) coincides with higher initial gas ratios, and an optimal operating temperature around 1600 K. At temperatures above or below this, slightly higher H₂:CH₃SiCl₃ ratios are required for single phase β-SiC deposition. These results are not particularly sensitive to the system pressure. However, β-SiC deposition is strongly dependent upon the operating temperature and the amount of hydrogen carrier gas.

Of the 36 possible product gas species considered in these thermodynamic calculations, just a few dominant product gas species are normally present in the thermodynamically equilibrated vapor phase. For the operating conditions in the experimental portion of this project, HCl is the dominant product gas species formed, with the partial pressure of the next most prevalent gas species at least one order of magnitude lower. For temperatures around 1500 K and lower, the prevalent equilibrium gaseous species are the silicon chlorides, methane, and SiHCl₃ (other than H₂ and HCl). At temperatures around 1700 K and above, the dominant gaseous species become H, Cl, SiCl₂, and SiCl₃. Gaseous species containing both silicon and carbon have been shown to be relatively unstable, and hence exist only in very low concentrations under thermodynamic equilibrium.
The composition of the condensed phase has been shown to be relatively insensitive to the system pressure, especially above 1600 K. Below 1600 K, higher pressures yield a deposit with a higher amount of excess carbon (in the form of graphite) co-deposited with the SiC. Hence, single phase SiC deposition at low temperatures is favored by lower system pressures.

The composition of the condensed phase is sensitive to the $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio in such a way that higher ratios yield deposits with lower amounts of excess carbon. $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratios of 100:1 or higher generally resulted in single phase SiC deposition, except for very high temperatures (greater than 2000 K).

These thermodynamic calculations can provide a useful insight in describing the composition of the condensed phase and of the equilibrium vapor phase for such a chemical vapor deposition process, or at least the trends to expect in the condensed phase composition. Thermodynamic analysis can assist in the development stages of CVD processes by guiding research efforts toward the operating conditions resulting in coatings with the desired properties.

The thermodynamic equilibrium calculations obtained in the present study are in agreement with those previously reported in the literature. A general lack of precise agreement exists between thermodynamic predictions and experimentally reported condensed phase compositions. However, the results of these calculations are applicable to the experimentally observed trends in the condensed phase composition found in the CVD of SiC in the $\text{H}_2 - \text{CH}_3\text{SiCl}_3$ system, although some reported data conflict strongly with the thermodynamic predictions. Hence,
reported data on the composition of the condensed phase for apparently similar CVD systems are also conflicting. This observation is obviously not the result of faulty thermodynamic calculations, but rather is probably indicative of some pertinent factors not taken into consideration in those systems whose data conflict with thermodynamic predictions. An obvious cause is the deposition reaction not being governed by thermodynamics as much as by kinetics. Other possibilities center around imprecise process control (i.e. imprecise temperature control, mass flow control, pressure control). The control of the deposition by kinetic processes forces other factors into any predictive capability as of yet not discussed -- namely knowledge of the flow field adjacent to the substrate, as well as the concentrations of gases important to the overall reaction. The development of such a predictive model is the focus of the next chapter.
CHAPTER IV

DEVELOPMENT OF TRANSPORT PHENOMENA MODEL

INTRODUCTION

The phenomena of interest are the transfer of mass, momentum, and heat through a vertically oriented CVD cylindrical reactor tube. Each of these transport phenomena can be described accurately by a partial differential equation. The purpose of this section is to briefly describe the method by which these partial differential equations are implemented in the transport phenomena modeling.

In their basic forms, the aforementioned governing partial differential equations contain several dependent variables. The first step taken in the model formulation was to minimize the number of terms in these equations, in order to sufficiently simplify them (while still maintaining an accurate description of the system), thereby facilitating their use in the mathematical model. The following assumptions were made in the model formulation in order to reduce the terms in the governing equations:
ASSUMPTIONS

The basic assumptions made in the initial stages of the model formulation are presented in the following list:

(1) All relevant dependent variables studied were considered to behave symmetrically about $\theta$, the axis in cylindrical coordinates which rotates perpendicularly around the longitudinal axis. Hence the mathematical model was developed using a maximum of two independent spatial variables, namely $r$ and $z$, the radial and longitudinal directions as prescribed in the cylindrical coordinate system notation.

(2) The flow in the reactor was considered to be laminar. This is a valid assumption since the flow conditions during the deposition process were such that the calculated Reynolds number for the system was in the laminar range for all cases.

(3) The diffusion coefficients in this study were assumed to be binary in nature. Although the system under consideration has more than two species present in the gas phase, this is still a valid assumption since $H_2$ (the carrier gas in this system) was always the predominant gas phase constituent. In addition, the imprecision in the reported calculated diffusion coefficient data $^{152, 153}$ did not warrant the additional computational efforts to calculate multi-species diffusional coefficients.

(4) The effect of radiative heat transfer was neglected.
(5) Diffusion of gaseous species due to temperature gradients (Soret diffusion) was considered to be negligible and hence was disregarded. Experimentally, the type of CVD reactor used falls within the "hot-walled" category of furnaces. Consequently, the temperature gradients in the radial direction were determined to be extremely small (a few K difference between the temperature of the wall and the temperature measured along the centerline of the furnace), and hence this becomes a reasonable assumption.

(6) The calculated values used for viscosity, thermal conductivity, and specific heat were based on a mixture of the three relevant gases (MTS, H₂, and HCl) in their proportionate amounts in each control volume, and the temperature. The diffusivities of the reactant and product gases were calculated assuming that hydrogen was the carrier (diluent) gas. These physical properties were assumed to be dependent on temperature, and each property was defined as a function of temperature based on a user-defined temperature dependence expression. Appendices E through H contain all the relevant expressions for the heat capacity, thermal conductivity, viscosity, and diffusivity, respectively, for each of the gas phase components (H₂, HCl, and CH₂SiCl₃), expressions for calculating these properties for a general gas mixture containing 2 or more of the components, as well as tables of values of each of these thermo-physical properties for each gas component.

Physical property data for the gas phase components were estimated using
the methods prescribed in reference [152]. The general viscosity expression was obtained from Geiger and Poirier [148].

(7) Transient effects in the present CVD system were neglected and hence only steady-state solutions were considered.

(8) Viscous dissipation terms in the energy balance equation were considered to be negligible and therefore were omitted from the calculations.

(9) The chemical reaction taking place in the system was considered to be heterogeneous, occurring on all surfaces found within the modeled domain. For the deposition of silicon carbide, the following reaction was assumed to proceed:

\[
\text{CH}_2\text{SiCl}_3 \rightarrow \text{SiC} + 3\text{HCl}
\]

with hydrogen acting as a carrier gas (essentially inert in this case).

GOVERNING PARTIAL DIFFERENTIAL EQUATIONS

Under the above assumptions, the system can be described by the following governing partial differential equations, in cylindrical coordinates:

(1) Continuity equation (only \(r\) and \(z\) components, since the flow field is presumed to be independent of \(\theta\), the angle of rotation about the longitudinal axis):
\[ \frac{1}{r} \frac{\partial}{\partial r}(r \nu_r) + \frac{\partial}{\partial z}(\rho \nu_z) + \sum_{k=1}^{k} R_k = 0 \]  

(9)

in which \( \rho \) is the density of the gas phase, \( \nu_r \) is the radial velocity component, \( \nu_z \) is the longitudinal velocity component, and \( R_k \) is a term which accounts for the mass (in the form of SiC) lost from the gas phase via the deposition reaction. The value of \( R_k \) is zero everywhere except along all the surfaces on which the deposition reaction is proceeding.

(2) Conservation of momentum (for a Newtonian fluid) in the radial direction:

\[ \nu_r \frac{\partial}{\partial r}(\rho \nu_r) + \nu_z \frac{\partial}{\partial z}(\rho \nu_z) = -\frac{\partial P}{\partial r} \]

\[ + \frac{\partial}{\partial r}\left( \mu \frac{1}{r} \frac{\partial}{\partial r}(r \nu_r) \right) + \frac{\partial}{\partial z} \mu \frac{\partial \nu_r}{\partial z} \]  

(10)

wherein \( P \) is the relative pressure, and \( \mu \) is the viscosity of the gas mixture.

(3) Conservation of momentum (for a Newtonian fluid) in the longitudinal direction:

\[ \nu_r \frac{\partial}{\partial r}(\rho \nu_r) + \nu_z \frac{\partial}{\partial z}(\rho \nu_z) = -\frac{\partial P}{\partial z} \]

\[ + \frac{1}{r} \frac{\partial}{\partial r} \mu \frac{\partial \nu_z}{\partial r} + \frac{\partial}{\partial z} \mu \frac{\partial \nu_z}{\partial z} + \rho g_z \]  

(11)

wherein \( g_z \) is the longitudinal component of the acceleration due to gravity.

Since the longitudinal axis of the system in consideration is presumed to be parallel to the direction of gravitational acceleration, \( g_z \) equals the full magnitude of the gravitational constant, i.e. \( g_z = 9.81 \text{ m/s}^2 \).
(4) Conservation of thermal energy:

\[ v_x \frac{\partial}{\partial x} (\rho C_p T_x) + v_z \frac{\partial}{\partial z} (\rho C_p T_z) = \frac{1}{\rho} \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + \frac{\partial}{\partial z} (k \frac{\partial T}{\partial z}) \]  \hspace{1cm} (12)

in which \( C_p \) is the heat capacity of the gas mixture, \( T \) is the absolute temperature, and \( k \) is the thermal conductivity of the gas mixture.

The net MTS decomposition reaction is endothermic according to data from the JANAF \[^{[150]}\] tables (\( \Delta H^0_{\text{rxn}} = 230 \text{ kJ/mol} \)). Hence, as the reaction proceeds, a local temperature drop in the gas phase will reduce the reaction rate. Based on the heat capacity values in Appendix E, the energy required to heat the gases to 1300 °C is approximately 1,013 kJ/mol.

Energy supplied by the furnace wall is the only driving force for a continued reaction. In addition, the overall small reaction rates (1 mol of MTS is experimentally introduced into the furnace every 44,800 seconds) result in very small energy contributions from the reaction in comparison to the heat supplied by the furnace element. Thus, it is assumed the enthalpy of reaction (and other terms not shown) is negligible in comparison to the energy input into the system by the furnace wall, and hence is disregarded from the energy balance calculations.
(5) Conservation of mass for each gaseous species:

\[
\nabla \cdot \left( \nu \frac{\partial \omega_i}{\partial x} + \nu \frac{\partial \omega_i}{\partial z} \right) = \frac{1}{r} \frac{\partial}{\partial r} r D_i \frac{\partial \omega_i}{\partial r} + \frac{\partial}{\partial z} D_i \frac{\partial \omega_i}{\partial z} + \sum_{k=1}^{k} R_{ik} \tag{13}
\]

where \( \omega_i \) is the mass fraction of the gaseous species \( i \), \( D_i \) is the diffusion coefficient of gaseous species \( i \) diluted in hydrogen, and \( R_{ik} \) represents the production rate of species \( i \) based on the kinetics of reaction \( k \). For the case of hydrogen, which is considered to act only as an inert carrier, the term \( R_{ik} \) is zero. For the reactant (\( \text{CH}_2\text{SiCl}_3 \)), \( R_{ik} \) is negative; accordingly, for the product gas species (HCl), \( R_{ik} \) is positive. The term \( R_{ik} \) is zero except along the surfaces on which deposition and streaming is taking place.

The density of the gas mixture, \( \rho \), was calculated from the ideal gas law using the mass fraction, \( \omega_i \), and the molecular weight, \( M_i \), of each species in the mixture. When the system pressure, \( P \), is reduced, the density of the gas mixture is reduced according to:

\[
\rho = \frac{P}{RT \sum_{i=1}^{i} \frac{\omega_i}{M_i}} \tag{14}
\]

where \( R \) is the universal gas constant and \( T \) is the absolute temperature.

In order to include the heterogeneous reaction into the mathematical model, a method for calculating the reaction kinetics was needed. According to the literature, the reaction kinetics for the decomposition of \( \text{CH}_2\text{SiCl}_3 \) in hydrogen to form SiC can be adequately described by assuming the kinetics follow an Arrhenius
type behavior. The following is a description of how the reaction kinetics may be calculated under the above conditions.

CALCULATION OF HETEROGENEOUS REACTION KINETICS

Generally speaking, for a chemical reaction such as,

\[ a_1A_1 + a_2A_2 + \ldots + a_mA_m = b_1B_1 + b_2B_2 + \ldots + b_mB_m \]  \hspace{1cm} (15)

the net rate of generation of species \( i \), \( R_i \), is given by

\[ R_i = -k_r \prod_{j=1}^{n} [A_j]^{a_j} + k_f \prod_{j=1}^{n} [B_j]^{b_j} \]  \hspace{1cm} (16)

where \( k_f \) and \( k_r \) are the forward and reverse reaction rate constants, respectively.

The forward reaction rate constant, \( k_f \), for a particular reaction is expressed as

\[ k_f = A \exp \left( -\frac{E}{R \cdot T} \right) \]  \hspace{1cm} (17)

where \( A \) (reaction constant) and \( E \) (activation energy of the reaction) are experimentally determined. The values reported in the literature of \( \ln A \) and \( E \) for the reaction considered in this study were 5.7 (± 5.1) kg/m²-s, and 188 (± 53) kJ/mol as found in reference [154]. The thermodynamic equilibrium constant for reaction (15) may be expressed as
\[ K_p = \exp \left( -\frac{\Delta G^0}{R \cdot T} \right) \]  

(18)

where \( \Delta G^0 \) is the change of Gibbs free energy of the reaction under standard state conditions ([=] J/mol), \( R \) is the universal gas constant ([=] J/mol-K), and \( T \) is the absolute temperature ([=] K).

For reaction (15), \( \Delta G^0 \) may be determined according to the following relation:

\[ \Delta G^0 = \sum_{i=1}^{n} b_i \Delta G^0_{b_i} - \sum_{j=1}^{m} a_j \Delta G^0_{a_j} \]  

(19)

Furthermore,

\[ K_c = K_p \cdot P^n \]  

(20)

wherein \( P \) is the total pressure of the system, and the superscript \( n \) represents the number of moles destroyed in the gas phase subtracted from the number of moles produced in the gas phase, and can be calculated according to the following relation:

\[ n = \sum_{i=1}^{n} b_i - \sum_{j=1}^{m} a_j \]  

(21)

The equilibrium constant for a reaction based on concentration can be expressed as:
\[ K_c = \frac{k_f}{k_r} \] (22)

The above relation allows for the calculation of the reverse reaction constant \( k_r \). The net rate of generation or destruction for each individual species from the chemical reaction (15) can be calculated from equation (16). The rate of a species being produced or consumed at any particular location of the reactor depends on the local temperature and concentration of species involved in the reaction. The rate term appears as a source term \((R_a)\) in the partial differential equations for species conservation, as shown above.

**SOLUTION PROCEDURE**

The governing partial differential equations as shown above are highly nonlinear in nature, in addition to the strong dependence each dependent variable has on all the other dependent variables. Hence, collectively they are unsolvable in their differential form by any known direct method. Thus, a different approach must be taken to solve the equations.

Two prerequisites exist for the development of a sound mathematical model. The first of these is that the formulation and ensuing numerical algorithm be "well-posed". This means that small changes in the input conditions should not lead to extraordinarily large changes in the resultant solution. The second (equally important) of these is that the computer code should be numerically stable -- problems in the solution procedure due to round-off errors, and the number of
significant figures, for example, should be minimized. If the model is numerically unstable, the results of the calculations tend to be unreliable, even for a well-posed formulation. Therefore, the above governing partial differential equations must be manipulated in such a way that the relations developed in the partial differential equations remain valid, and the solution method does not intrude on these relations such that the problem becomes numerically unstable.

Another important concept of a mathematical model is the efficiency of the algorithm used to solve the equations. The efficiency of a code can be related to the overall time required to obtain a reasonably accurate solution to the proposed problem. This depends largely on the understanding of (1) the algorithm itself, and (2) how a computer performs calculations. A low level of knowledge in either of these two factors (especially the former) can only result in a less efficient model, excluding good fortune.

One of the first steps taken in the development of the model is to discretize the governing partial differential equations. The continuous information contained within the partial differentials becomes discontinuous. The values of the dependent variables (i.e. \(v_1, v_2, P, T, w_i\)) become known only at discrete points (as defined by the user) within the domain. The governing partial differential equations are transformed via the discretization method into a set of linear algebraic equations, for which a solution is significantly easier to determine.

The discretization method employed in the present study treats as unknowns the values of the dependent variables at some discrete points (hereafter referred to
as "grid points", "nodes", or "cells"). For a more elaborate and detailed description of the discretization method employed here, see reference [155].

A discretized partial differential equation is a linear algebraic relation which connects the values of a dependent variable between neighboring grid points. In deriving the discretized equations, some assumptions must be made regarding the local profile of the dependent variable.

The discretization method employed in the present study is often referred to as the "control volume" or "finite difference" method. The control volume method is so named because the calculation domain is divided into non-overlapping control volumes, with one grid point located in each control volume. The interfaces between adjacent control volumes form an orthogonal network. For instances in which only one or two spatial dimensions need to be examined, the magnitudes of the discrete distances in the coordinate directions not discretized assume values of unity for the sake of simplicity. Each partial differential equation is integrated over each control volume.

The solution of the discretized equations in one dimension is achieved by employing a standard Gaussian elimination method. This method will be referred to hereafter as the tridiagonal matrix algorithm, or TDMA. This rather appropriate name was given to the algorithm because when the coefficients of the discretized equations are placed in a matrix form, the only non-zero terms in the matrix fall on the main diagonal and the diagonals directly above and below it. One significant advantage of the TDMA method over direct methods is its comparatively low
demand on both computer time and memory, both of which are proportional to the number $N$ of grid points in the system for TDMA, as opposed to $N^2$ or $N^3$ for direct methods.

For two-dimensional problems, as in the present study, TDMA requires some slight modifications in order to solve the equations while still using the same amount of computer storage. The implementation method of the modified TDMA plays a significant role in the efficiency of the model. This modified TDMA routine is also known as the line-by-line method.

For a two-dimensional grid, there are two important factors to consider in the application of the line-by-line method. The first of these is the direction of the TDMA. The second of these is the direction that the (one-dimensional) TDMA line moves across the 2-D domain (called the sweep direction). The rate at which information from the boundaries enters the middle of the calculated domain (hence the rate of convergence) depends largely on the direction of the line-by-line sweep direction, as well as the direction of the TDMA.

This is especially true for flow fields which behave essentially parabolically (spatially). If for example the sweep direction is from downstream to upstream, convergence will be much slower than for the opposite case, because all the flow determining information is squeezed into a less load-bearing term, and the upstream variables will not have been updated for any particular sweep.

The above factors also hold true for cases in which the aspect ratios of the grids differs significantly from one. For a two-dimensional system, the grid aspect
ratio is defined as the ratio between the lengths of the grid surfaces sharing a common corner. The ability of information to be mathematically transferred (i.e. rate of convergence) through an extremely small grid interface is significantly reduced compared to the rate of information transfer across an interface with a relatively large surface area. Hence for systems which consist primarily of "spaghetti" grids, the efficiency of the algorithm is reduced, due to the need for more iterations to be made to get the boundary condition information into the bulk of the domain.

To effectively combat this numerical phenomenon, in the present study TDMA was applied in four separate directions, each originating from one of the boundaries of the domain. By doing so, all information contained in the boundary conditions were transferred as quickly as possible into the middle of the domain, thereby significantly reducing computational time.

Each discretized equation represents the relation of a dependent variable to the other variables, both dependent and independent. Discretized equations have been developed which describe the transfer of momentum in each of the cylindrical coordinate directions (r and z), overall continuity (pressure field), temperature, and conservation of each gas species, modeled within the system domain. Since the total weight fraction of all the gaseous species always equals unity, there are \((n-1)\) discretized equations for a fluid containing \(n\) species.

To solve the system of interlinked, non-linear, discretized equations, an iterative procedure has been developed. The name given to this solution procedure
is SIMPLE, which is an acronym for semi-implicit method for pressure linked equations. The guiding principles utilized in SIMPLE are the conservation of mass, thermal energy, and momentum. In each iteration the intermediate solution for the velocity field is adjusted by an amount required to satisfy the continuity equation. Subsequent to this, the thermal and species mass fraction equations are solved. One cycle of satisfying the conservation of continuity, momentum, heat, and species constitutes one iteration. Iterations continue in the mathematical model until certain convergence criteria are met, as discussed briefly below.

CONVERGENCE CRITERIA

The degree of convergence of the system of discretized equations is measured according to the magnitude of residual source terms. Each dependent variable possesses its own residual source term. A residual source term is an indicator of the absolute magnitude of the difference between the "solution" for that discretized equation after a particular iteration, and the value of the dependent variable required to maintain the conservation principle applied to the dependent variable.

Typically, these residual source terms are "normalized", which indicates the ratio of the residual source term to the amount of mass, momentum, or heat entering the system, depending on which dependent variable is being examined. Therefore, as the residual source terms approach zero, the overall solution to the set of discretized equations is being approached. For simple problems, such as an...
isothermal, non-reactive, flow of one gaseous species through a straight tube, meaningful normalized residual source terms on the order of $10^8$, or even zero (since some round off error is introduced by the computer itself), are obtained. However, for the problem at hand, a reasonable convergence criterion is that all normalized residual source terms are on the magnitude $10^3$ or smaller. For all practical purposes, the time required for convergence beyond $10^3$ is not warranted by the more precise solution obtained, due to the underlying assumptions made in the formulation of the model, as well as the inaccuracy of the physical, thermodynamic, and kinetic data relevant to the system.

UNDER-RELAXATION FACTORS

Due to the highly non-linear interdependencies between the dependent variables, the mathematics in the problem may become unstable, and either oscillate around or diverge away from the exact solution. One method for reducing the probability of the aforementioned instabilities is to dampen the amount of change of each dependent variable between successive iterations. This procedure is commonly referred to as under-relaxation.

Under-relaxation factors are assigned to each dependent variable. An under-relaxation factor of unity allows 100% of the calculated change in the value of a particular dependent variable between iterations be applied to that particular dependent variable. Similarly, an under-relaxation factor of zero will allow 0%
change in the value of the dependent variable in consideration between successive iterations.

If the system of discretized equations was at the exact solution to the governing partial differential equations, the change of the dependent variables between iterations would be zero, implying no significance to the magnitude of the under-relaxation factors. However, during all the intermediate iterations between the initial guess and the solved set of equations, the magnitudes of the under-relaxation factors play a key role in the mathematical stability of the problem in consideration.

A new technique was introduced here. When the initial conditions were far from the solution, the required under-relaxation factors for convergence were quite small ($\approx 0.01$), especially with the non-linear relationships between the dependent variables. Similarly, for cases which were initially close to the solution, higher under-relaxation factors were tolerated ($\approx 0.7$) in the process without causing numerical divergence.

Consequently, a technique was developed by which the under-relaxation factors were permitted to change between successive iterations, depending on the rate of convergence (or divergence) for each individual dependent variable. The rate of convergence (or divergence) was determined for each variable based on a comparison of its normalized residual source term between successive iterations. For cases in which the normalized residual source terms decreased in magnitude, it was assumed that the solution was being approached, and vice versa. For
dependent variables which were converging on their solutions, the under-relaxation factors were increased to increase the overall computational efficiency. Likewise, those variables which were diverging had their under-relaxation factors reduced, to minimize the magnitude of the oscillation about the solution. The overall affect of the implementation of this technique was a substantial increase in the computational efficiency, by as much as a factor of 10.

BOUNDARY CONDITIONS

In the discussion about the workings of TDMA, the input of accurate boundary conditions used for each discretized equation determines whether the mathematical model yields the desired results. The following deliberation describes the choice of boundary conditions implemented within the modeled domain.

The first and most important consideration with regard to the implementation of boundary conditions is that the modeled system reflects well what is actually occurring in the real system. The most obvious example is that the geometry input into the mathematical domain describe the geometry of the real system with a reasonable amount of accuracy.

The proper choice of boundary conditions is necessary for the model to function properly (i.e. the converged solution accurately represents the system of interest). The results of the SOLGASMIX computations were employed in this respect. Based on these calculations, there are three major components in the gas phase: \( \text{H}_2 \), \( \text{HCl} \), and \( \text{CH}_3\text{SiCl}_3 \). At the chosen system operating conditions, there are
approximately two orders of magnitude difference between the HCl concentration and the next most prevalent gaseous species, SiCl\textsubscript{2}. The net decomposition reaction (see page 38) therefore represented the system reasonably well, and hence this large difference in equilibrium vapor pressures permitted the omission of these lower vapor pressure species from the calculations.

At the inlet, the velocity of the gas mixture was specified in the axial direction as plug flow, and the radial component of velocity was considered to be zero. Also, the gas composition at the inlet, as well as the temperature of the inlet gas, were considered to be known and hence were considered as boundary conditions.

At the outlet, gradients of all variables with respect to the longitudinal direction were prescribed as zero.

Zero gradient conditions in the radial direction for all dependent variables were prescribed along the symmetry axis. Due to the axisymmetric nature of the problem, only one radial length was modeled to save computational time.

The side wall temperature was fixed according to the measured temperature profile. All other surfaces in the system were considered to be adiabatic. No mass was permitted to permeate through gas / solid interfaces.

In addition, due to the heterogeneous reaction taking place, the continuity equation becomes adjusted by the amount of mass leaving the gas phase as the silicon carbide deposited on the furnace wall, the substrate, and all other surfaces incorporated within the model domain.
Table 2 lists all the relevant parameters and boundary conditions for the system under consideration.

Table 2. Operating parameters for the model.

| Reactor Dimensions (m): |  
|-------------------------|---
| Diameter                | 0.019 |
| Height                  | 0.4572 |

| Substrate Dimensions (m): |  
|---------------------------|---
| Diameter                  | 0.003 |
| Length                    | 0.4572 |

| Temperatures (K): |  
|------------------|---
| Inlet Gas        | 315, 298 |
| Wall Set Point   | 1373, 1473, 1573 |

| Pressures (torr): |  
|------------------|---
| Total System Pressure | 100, 150 |

(760 torr = 1.01325 x 10^5 Pa)

| Inlet Gas Compositions: |  
|-------------------------|---
| H₂:MTS = 2:1 - 20:1 |

| Inlet Volumetric Flow Rate (sccm): |  
|------------------------------------|---
| FR_{MTS} varied inlet gas comp.)   | FR_{H₂} = 300 |

CONCLUSIONS

A two-dimensional, steady-state mathematical model has been developed which is capable of describing the mass, momentum, and thermal transport phenomena found within a CVD reactor. The governing partial differential equations are found to be unsolvable using any direct method due to their non-linearities and strong interdependencies. Hence these equations were discretized
into linear algebraic relations, and the solution technique known as SIMPLE was employed on these algebraic equations to find solutions to the velocity, temperature, and species fields within the modeled domain.

The following three factors may be used to determine whether a model is worth implementing: (1) accurate description of the system of interest; (2) numerical stability of solution method, and (3) computational efficiency of algorithm. The model developed in the present study addresses all three issues.

Since the underlying partial differential equations are believed to accurately describe the aforementioned transport phenomena in general, a key determinant in the accurate solution to the proposed problem is the proper implementation of boundary conditions. If the boundary conditions are input in such a way that they do not represent the system well, then the algorithm presented may indeed find a solution, albeit to either the wrong problem or a non-physical problem. Hence, introducing the boundary conditions properly is essential in obtaining the desired results. Therefore, the model must be tested and shown to be able to predict accurate solutions. Accordingly, the focus of the next chapter deals primarily with the verification of the mathematical model developed in the present study.
CHAPTER V

VERIFICATION OF MATHEMATICAL MODEL

INTRODUCTION

After a mathematical model has been developed, the next natural step is to validate the code. Three factors should be considered in the validation of a mathematical model: (1) if the governing equations have been discretized properly; (2) if the selected algorithm used to solve the set of discretized equations yields a converged solution, and (3) whether the developed mathematical model is appropriate for solving the proposed problem. The first two factors may be addressed using the driven cavity problem. The third factor may only be known when the first two factors have been satisfactorily met, and the model is applied to the problem of interest (i.e. CVD of SiC in the CH₃SiCl₃ - H₂ system in a vertically-oriented hot-walled reactor).

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DRIVEN CAVITY PROBLEM

The standard test for validating a mathematical model is to examine the fluid flow within a square cavity \cite{145}. The first test in the present study examines the fluid flow in an isothermal square cavity. The results of this test are compared to those obtained by FLUENT, which is a commercially marketed computational fluid dynamics modeling package (marketed by Creare, Inc.). The square cavity has dimensions of 1.00 m on each side. The flow inside the cavity is considered to be laminar. The chamber is filled with a fluid which has physical properties consistent with those of air at normal temperature and pressure. The top wall in this square cavity is assumed to be moving horizontally at a constant rate. Computations were carried out for two different velocities of the top boundary, namely 0.001 m/s and 0.01 m/s, wherein a positive velocity indicates a boundary moving from left to right. Twenty one nodes were used in the calculations for both coordinate directions by both of the computer codes. The solution was assumed to have been reached when the residual source terms $\leq 10^{-3}$.

Figure 10 shows schematics of the computed fluid flow fields for the model developed in the present study (figure 10, top) and the results obtained by FLUENT (figure 10, bottom). The velocity of the moving boundary was fixed at 0.001 m/s for the results shown in this figure. In each of these schematics the length of the arrow is directly proportional to the calculated velocity. The lengths of the longest vectors in each plot are noticeably different; however, the velocities corresponding to the longest vectors in each plot differ only by approximately 5 percent. Figure
11 shows schematics for the case in which the top boundary was assumed to be moving at a rate of 0.01 m/s, wherein again the plot in the top of the figure represents the calculations obtained by the model developed in the present study and the plot in the bottom of the figure represents the results of FLUENT. Again, excellent agreement is found in comparing the results of the two codes. Hence, it appears the partial differential transport phenomena equations have been correctly discretized in the mathematical model developed in the present research. In addition, the method employed to solve the equations is valid for the case of a driven cavity.
Figure 10. Predicted velocity profiles within similar driven cavities for (top) model developed in present study, (bottom) FLUENT. The top boundary is moving at a fixed rate of 0.001 m/s.
Figure 11. Predicted velocity profiles within similar driven cavities for (top) model developed in present study, (bottom) FLUENT. The top boundary is moving at a fixed rate of 0.01 m/s.
Another square cavity problem was examined to study the capability of the model developed in the present study to accurately calculate the fluid flow field dominated by buoyancy forces (i.e. natural convection). The solution found in 1983 by de Vahl Davis [145] for buoyancy driven (natural) convective flow within a square cavity is considered to be a benchmark solution, and has been repeated by several other modeling efforts.

The problem considered is that of a case of natural convection in a square cavity of a Boussinesq fluid. A Boussinesq fluid is one which exhibits incompressibility except that produced from thermal expansion, resulting in a significant buoyancy force. This buoyancy force is represented by the term \( g\cdot\beta\cdot\Delta T \), wherein \( g \) is the gravitational acceleration constant, \( \beta \) is the thermal expansion coefficient, and \( \Delta T \) is the relative temperature difference of neighboring units of fluid [146].

The physical properties and other parameters in this case have been made dimensionless. Non-dimensionalizing the problem has two primary advantages: (1) it indicates the dominant physical phenomena for a specific case, and (2) it enhances the ability of the selected solution method to reach the solution by reducing problems associated with calculations of numbers differing by several orders of magnitude. The resulting relevant dimensionless parameters employed in the present study are the Rayleigh number \( (Ra) \) and the Prandtl number \( (Pr) \), which are defined according to the following expressions:
\[ Ra = \frac{\rho \beta g (T_e - T_w) L^3}{\mu \alpha} \]  
\[ Pr = \frac{\mu C_p}{k} \]

wherein \( \rho \) is the density of the fluid, \( \beta \) is the volume expansion coefficient, \( g \) is the gravitational acceleration constant, \( L \) is the length of the side of the square, \( \mu \) is the viscosity of the fluid, \( \alpha \) is the thermal diffusivity of the fluid, \( c_p \) is the heat capacity of the fluid, and \( k \) is the thermal conductivity of the fluid. Non-dimensionalizing the problem requires the physical properties of the fluid to be set to the following values: \( k=1, \beta=1, g=1, \mu=1, c_p=Pr, \) and \( \rho=\sqrt{Ra/Pr}. \)

The top (northern) and bottom (southern) walls of the cavity are assumed to behave adiabatically. The left (western) wall is held constant at a temperature \( T_w \) and the right (eastern) boundary is held at a temperature \( T_e \), wherein \( T_e > T_w \). Assuming the density of the fluid decreases with increasing temperature, the resultant flow field should be driven in a counter-clockwise direction.

The boundary condition for temperature was defined as the following; \( T_w=T_e-1 \). The top and bottom walls were assumed to behave adiabatically. The velocity boundary conditions were prescribed by a conductance of mass equalling zero at the boundaries, which resulted in the velocities obtaining values of zero at the domain boundaries. The number of nodes in each coordinate direction was set at 27 for the present study. Convergence of the solution was assumed to be satisfied when all the residual source terms \( \leq 10^{-3} \).
Three cases were compared in the present work. The Prandtl number was held constant at 0.71. The Rayleigh number was held at $10^3$, $10^4$, and $10^5$. Variations of the Rayleigh number were obtained by varying the length of the side of the square. Figure 12 shows the results for the calculated velocity fields for the model developed in the present study and for a commercially marketed computational fluid dynamics code named FIDAP. The Rayleigh number for the results in this figure is $10^3$. Figures 13 and 14 show similar plots for $Ra$ numbers of $10^4$ and $10^5$, respectively. As the Rayleigh number increases, the central point about which the fluid is spinning bifurcates into two separate recirculation pools.

Figures 15 through 17 indicate the temperature fields found within the studied systems wherein $Ra$ equaled $10^3$, $10^4$, and $10^5$, respectively. Again, the plots on the top of each figure represent the results found by the model developed in the present study, and the plots found in the bottom of the figure represent the results obtained by FIDAP. The vertical axis in the top plot of figures 15 through 17 represents the dimensionless temperature of the system. The bottom most corner of the same plots coincides with the southwest corner of the domain. As the Rayleigh number increases, the amount of heat transported by convection becomes greater in comparison to the amount of heat transported by conduction, which is apparent from examining the Rayleigh number expression. If the heat were transported solely by conduction, the temperature profile would be linear between the western and eastern walls throughout the entire domain. Deviations from a
linear profile indicate the presence of thermal transport by convection. Another observation stemming from an increase in the $Ra$ number is increased thermal gradients neighboring the vertical walls.

The results as shown above for both types of driven cavities are in very good agreement. Hence, the mathematical model developed in the present study is capable of describing both forced and natural convection, and the algorithm implemented to solve the set of discretized equations is satisfactorily validated. The only remaining question now is whether the developed model is able to accurately describe the transport phenomena found within a CVD reactor, which is the focus of the following section.
Figure 12. Predicted velocity profiles for similar thermal driven cavities of (top) model developed in present study and (bottom) FIDAP, in which $Ra=1000$ and $Pr=0.71$. 
Figure 13. Predicted velocity profiles for similar thermal driven cavities of (top) model developed in present study and (bottom) FIDAP, in which $Ra=10000$ and $Pr=0.71$. 
Figure 14. Predicted velocity profiles for similar thermal driven cavities of (top) model developed in present study and (bottom) FIDAP, in which $Ra=100000$ and $Pr=0.71$. 
Figure 15. Predicted temperature contours for similar thermal driven cavities of (top) model developed in present study and (bottom) FIDAP, in which $Ra=1000$ and $Pr=0.71$. 
Figure 16. Predicted temperature contours for similar thermal driven cavities of (top) model developed in present study and (bottom) FIDAP, in which $Ra=10000$ and $Pr=0.71$. 
Figure 17. Predicted temperature contours for similar thermal driven cavities of (top) model developed in present study and (bottom) FIDAP, in which $Ra=100000$ and $Pr=0.71$. 
The results in the driven cavity section indicated that the governing equations had been discretized properly, as well as a sound algorithm used to solve the equations. The next step taken in the validation of the computer code developed in the present study was to compare the deposition profiles of experimentally deposited SiC to those profiles as determined by the model.

Two experimental reactor geometries were selected for this purpose. Both geometries included the use of a vertically-oriented hot-walled reactor. The first of the geometries studied was one in which the substrate was a graphite disc, suspended from the top, and located in the center of the reactor. The deposition zone of interest was the bottom surface of the disc, whose normal was parallel to the longitudinal axis of the furnace. The second geometry studied was one in which the substrate was a graphite rod, suspended approximately along the longitudinal axis of the reactor. The following section discusses the experimental apparatus implemented throughout all the trials.

EXPERIMENTAL SETUP

Figure 18 depicts a schematic of the experimental apparatus used for the CVD experiments. For vacuum generation and pressure control, a mechanical pump is located downstream from the reactor. To control pressure, a ballast valve is incorporated into the vacuum line downstream of the furnace, through which excess argon is pumped, effectively slowing the pump down to attain the desired
pressure in the reaction chamber. The main pressure sensor (indicated by the P symbol in the figure) acting in unison with the ballast valve maintained the set pressure within 0.2 torr. The low pressure gauge (indicated by mP in the figure) was used only after the apparatus was setup after cleaning, primarily for leak testing. Due to the reactive (explosive) nature of hydrogen, all oxygen must be purged from the system and all leaks eliminated from the gas delivery plumbing before the flow of hydrogen is started.

As previously mentioned, the type of furnace used in these experiments was a tube type resistance furnace. The furnace chosen is a platinum wound single zone furnace approximately 0.46 meters in length. This selection implies that the CVD furnace is a hot-walled type of reactor, which further implies that deposition will proceed on both the substrate and the furnace wall. The temperature is controlled by an electronic controller and a single thermocouple located lengthwise in the center of the furnace. Figure 19 indicates temperature profiles obtained from three set point temperatures.

Flow control of the CH$_3$SiCl$_3$ vapor and H$_2$ gas was achieved via a two channel flow network up to the point of entry into the furnace. The hydrogen source material was a compressed gas. The CH$_3$SiCl$_3$ source material is in the liquid state. Accordingly, the MTS supply tank and the flow channel were heated with thermal tape to a sufficiently high temperature (approximately 40 °C) to achieve a high equilibrium vapor pressure and to prevent condensation of the source vapor in the gas delivery tubing. Electronic mass flow controllers (indicated in Fig.
18 by MFC) measured and controlled the flow rate of the source gases, maintaining three significant figures in the delivery rate. Solenoid driven pneumatic valves (represented by PV in Fig. 18) regulate the path of the source gases. In the initial stages of each trial, the source gases were directed through the furnace bypass plumbing lines, thereby filling the delivery tubing (initially filled with argon) with the source gas. This was most important for the accurate delivery of MTS, due to the relatively slow flow rates during the experiments concomitant with the duration of the trial (30 minutes of MTS flow directed through the reactor).

The precursor and carrier gases are introduced into the bottom of the reactor, flow in an upward fashion through the furnace, and exit through the top of the furnace. After exiting the reactor, the gas stream is passed through the pump and subsequently treated. The exhaust is first passed through a moist scrubber system which neutralizes any acidic gases. The remaining gases (primarily \( \text{H}_2 \) and \( \text{Ar} \)) are subsequently passed through a heated SiC burner element, in which the residual hydrogen gas is combusted. After exiting the hydrogen burner, the remaining gases are exhausted into the atmosphere.
Figure 18. Schematic of the vertical hot-walled CVD experimental apparatus.
Figure 19. Measured temperature profile along the center of the furnace for three different set points, as measured from the outlet (top) of the furnace.
EXPERIMENTAL DEPOSITION

Table 3 indicates the operating parameters for the CVD reactor for the experiments conducted to validate the model using a graphite rod as the substrate, located approximately along the longitudinal axis of the furnace.

Table 3. Operating parameters for the CVD reactor, in which the substrate was a graphite rod.

<table>
<thead>
<tr>
<th>Reactor dimensions (m):</th>
<th>0.019</th>
</tr>
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<tbody>
<tr>
<td>Diameter:</td>
<td></td>
</tr>
<tr>
<td>Height:</td>
<td>0.46</td>
</tr>
<tr>
<td>Substrate dimensions (m):</td>
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</tr>
<tr>
<td>Diameter:</td>
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<tr>
<td>Length:</td>
<td>0.3</td>
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<tr>
<td>Temperatures (K):</td>
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<tr>
<td>Inlet gas stream</td>
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</tr>
<tr>
<td>Furnace set point</td>
<td>1573</td>
</tr>
<tr>
<td>System pressure (torr):</td>
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</tr>
<tr>
<td>Inlet gas H₂:CH₃SiCl₃ ratio:</td>
<td>10:1</td>
</tr>
<tr>
<td>Inlet flow rates (sccm):</td>
<td></td>
</tr>
<tr>
<td>H₂:</td>
<td>300</td>
</tr>
<tr>
<td>CH₃SiCl₃</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 20 depicts a schematic of the reactor/substrate geometry used for validation purposes. A graphite rod approximately 0.3 meters long was placed such that the bottom of the rod was suspended 0.1 meters from the inlet. The gas flow direction is from bottom to top in the diagram. After the set point temperature of 1573 K was achieved, the temperature was allowed to equilibrate for approximately
two hours before beginning the precursor gas flow. During the equilibration time, a steady flow of 30 sccm of Ar gas is maintained through the furnace at the set system pressure of 150 torr.

At the onset of the experiment, hydrogen gas is allowed to flow through the furnace for 30 minutes, during which the MTS flow is directed through the reactor bypass tubing. The MTS flow is subsequently directed into the gas stream directed into the furnace. The flow of MTS through the reactor occurs for 30 minutes, after which time the hydrogen and MTS supplies are rapidly cut off.

The furnace pressure is rapidly dropped to approximately 1 torr with argon flowing through the furnace, to evacuate the chamber of residual MTS and hydrogen. The reaction chamber is subsequently filled to 1 atm pressure of argon, and pumped to below 10 torr (this cycle is repeated ten times) to remove any MTS, thereby stopping any coating processes. The power supply to the furnace is cut off, and the sample is allowed to cool down within the CVD reactor to room temperature.

The graphite rod was removed from the furnace and subsequently cut into = 0.1 meter lengths. The cross-sectional thickness of the coating was examined with a scanning electron microscope (SEM). The measured thickness was assumed to accurately represent the average growth rate of SiC by dividing the measured thickness by the total time of deposition (30 minutes). Figure 21 represents the measured average growth rate of SiC in relation to the distance from the inlet for a total of three trials. The highest deposition rate appears at the bottom of the
substrate, and quickly drops off. The peak in the deposition rate occurs in that portion of the furnace found within the ramp up section of the temperature profile, and not within the isothermal section of the furnace. By the time the gases reach the beginning of the isothermal section of the furnace, the reaction is practically over, indicating that a temperature much less than 1300 °C is required for the thermal decomposition of MTS in hydrogen. The temperature coinciding with the maximum deposition rate is approximately 1200 °C, as determined by the temperature profiles found in figure 19.
Figure 20. Schematic of the reactor/substrate geometry for experiments conducted with the graphite rod substrate (dimensions in meters).
Figure 21. Experimentally measured deposition profiles along the length of the graphite rod.
Experiments were also conducted on another form of substrate to validate the model. In the following discussion, the substrate used was a graphite disc, approximately 0.013 meters (0.5 inches) in diameter, and was located midway along the length of the furnace. Table 4 indicates the operating parameters selected for this set of experiments.

Table 4. Operating parameters for the CVD reactor, in which the substrate was a graphite disc.

<table>
<thead>
<tr>
<th>Reactor dimensions (m):</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>0.019</td>
</tr>
<tr>
<td>Height</td>
<td>0.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate dimensions (m):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>0.013</td>
</tr>
<tr>
<td>Distance from inlet</td>
<td>0.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperatures (K):</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Inlet gas stream</td>
<td>298</td>
</tr>
<tr>
<td>Furnace set point</td>
<td>1573, 1373</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System pressure (torr):</th>
<th>100</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Inlet gas H₂:CH₃SiCl₃ ratio:</th>
<th>10:1</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Inlet flow rates (sccm):</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>300</td>
</tr>
<tr>
<td>MTS</td>
<td>30</td>
</tr>
</tbody>
</table>

The system pressure was reduced for these cases to eliminate the need for heating the MTS supply tank and delivery tubing. Figure 22 shows a schematic of the experimental geometry used for graphite disc substrates. As in the previous cases, the main gas flow direction is from bottom to top.
Unfortunately, the furnace previously used for the graphite rod experiments burned out, necessitating the installation of a new furnace. The new furnace was also the hot-walled tube type, platinum-wound with a single zone. Figure 23 depicts the measured temperature profile along the length of the new furnace for a set point of 1300 °C. The temperature profile of the new furnace lacked the isothermal section found in the furnace previously used. However, the profile is rather symmetric about the middle position of the furnace. The hottest temperature found in the new furnace was approximately 70 °C higher than the set point. The graphite disc was suspended at the midway position along the length of the furnace, which coincides with the hottest position found in the furnace.
Figure 22. Schematic of the reactor/substrate geometry found in the validation experiments in which a graphite disc was implemented as the substrate (dimensions in meters).
Figure 23. Measured temperature profile along the longitudinal axis of the furnace, as measured from the bottom (inlet), for a set point of 1300 °C.
Experiments were conducted at two different temperatures, namely 1300 and 1100 °C set points. The same experimental procedure was used for the deposition trials on disc substrates as for the deposition on the graphite rods. At the conclusion of each coating run, the SiC coated graphite discs were fractured along two perpendicular diameters of the disc, resulting in four pie pieces each containing an approximate 90 degree arc length. Scanning electron micrographs were taken along the fracture surfaces, and the thicknesses of the coatings were measured as a function of position along the diameter of the disc. The overall growth rate was assumed to be time independent, so that an average deposition rate could be calculated by dividing the measured growth thickness by the total time of MTS flow through the furnace (30 minutes).

Figure 24 indicates the measured deposition profile found along the bottom disc surface for the experiments conducted at a set point of 1300 °C. The apparent scatter in the data results from the nodular morphology of the coating. The data average to approximately 1.4 μm/min. Plate I is a representative SEM micrograph of the fracture surface of the SiC growth, in which the nodular growth morphology is apparent.

Figure 25 indicates the measured growth rates along the bottom surface of the disc substrate for the experiments conducted at a set point of 1100 °C. The average deposition rate has fallen to approximately 0.3 μm/min, presumably due to the lower temperature and the subsequently lower reaction kinetics. Plate II is a representative SEM micrograph of the fractured surface of the SiC growth. The
morphology of the deposit formed at lower temperatures is similar to that of the higher temperature deposited growth.
Figure 24. Measured deposition profile along the bottom surface of the disc substrate for a set point temperature of 1300 °C.
Plate I. Representative SEM micrograph of the fractured surface of the SiC deposited at a set point of 1300 °C.
Figure 25. Measured deposition profile along the bottom surface of the disc substrate, for a set point temperature of 1100 °C.
Plate II. Representative SEM micrograph of the fractured surface of the disc substrate, for the set point temperature of 1100 °C.
The deposition of SiC at two different temperatures allows the calculation of the kinetic parameters relevant to the deposition process, namely the reaction constant $A$ and the activation energy $E$, as denoted in Chapter III. Assuming that the deposition reaction may be expressed according to the following type of reaction,

$$\text{Rate} = A \exp \left( - \frac{E}{RT} \right)$$

(25)

wherein $R$ is the universal gas constant (J/mol-K), $T$ is the absolute temperature (K), and Rate is the deposition rate ($\mu$m/min), the corresponding values of $\ln A$ and $E$ become 11.43 ($A = 91,828$ ($\mu$m/min)) and 151,266 [J/mol], respectively. These values fall within the literature reported ranges of the kinetic parameters, wherein $\ln A$ has been reported to be 5.7 ($\pm$ 5.1), and $E$ has been reported to be 188,000 ($\pm$ 53,000) (the margins of error based on other reports are actually larger than those reported in reference [154]). These calculations assume the actual temperatures of the reactions are 70 °C higher than the set points, as determined by the experimentally measured temperature profile. The values of $A$ and $E$ determined by the present study have been implemented in the mathematical modeling portion of the validation process.
MATHEMATICAL MODELING

SUBSTRATE: GRAPHITE ROD

The physical domain modeled was similar to that shown in Figure 20, although only one radial length was modeled due to the axisymmetric nature of the problem. The length of the modeled rod was assumed to run the entire length of the CVD reactor, since experimentally the highest deposition rate was at the bottom edge of the graphite rod, and it was not known if potentially higher deposition rates were located at a position closer to the inlet.

The input boundary conditions in the model were as follows. The experimentally measured temperature profile was input along the furnace wall. The surface of the rod was assumed to behave adiabatically. The composition, temperature, and velocity of the gas mixture through the inlet were known. The reaction kinetic data as obtained from the disc experiments were input into the reaction kinetics expressions. Zero gradients were imposed along the outlet boundary as well as the symmetry axis, in relative perpendicular directions to each boundary. No mass was permitted to permeate through either the furnace wall nor the graphite rod surface.

The physical domain was divided into 30 cells in the radial direction and 52 cells in the longitudinal direction. The grid was practically uniform throughout the domain in the radial direction, except for the region neighboring the substrate, in which the grid size was reduced to 500 microns. The grid spacing in the longitudinal direction was constant. This grid arrangement was found to reach a
solution which was independent of the radial grid size. The solution was assumed to have been reached when the magnitudes of all of the normalized residual source terms \( \leq 10^{-3} \). Iterations continued through the computer code until the specified convergence criteria were met. A typical number of iterations needed for convergence was \( 2 \times 10^4 \).

Figure 26 shows the predicted velocity profile found within the CVD reactor. The inlet of the reactor corresponds to the bottom of the figure, and the outlet coincides with the top of the figure. Accordingly, the furnace wall is found along the right side of the figure, and the symmetry axis appears along the left boundary of the plot, and is marked "SYM". The surface of the graphite rod appears just to the right of the symmetry axis. The length to height ratio in the figure has been drastically reduced from the actual geometry to distinguish any characteristics found in the velocity plot. The relative lengths of the arrows indicate linearly proportional velocities, in which the lengths of the arrows found in the inlet correspond to a velocity of 0.09 m/s. The velocity of the gas increases as it approaches the hot zone of the furnace, as well as the increase in the volume of the gas related to the chemical reaction taking place, in which one mole of \( \text{CH}_3\text{SiCl}_3 \) is replaced with three moles of HCl.
Figure 26. Predicted velocity profile found within the CVD reactor in which the substrate was a graphite rod.
Figure 27 is a schematic of the predicted temperature field found throughout the modeled domain. The vantage point of the figure is from above the southeast corner of the domain (the fourth quadrant as defined in cartesian coordinate space). Practically no temperature gradient exists in the radial direction. This feature was experimentally found to be true, in which only 3 or 4 Kelvin separated the measured temperatures along the furnace wall and those measured along the longitudinal axis of the furnace.
Figure 27. Predicted temperature field within the modeled domain, in which the substrate was a graphite rod.
Figure 28 indicates the predicted field for the weight fraction of MTS throughout the domain. The vantage point of this figure is from above the northeast corner of the domain (the first quadrant). The strip of cells along the back right edge of the figure correspond to those grids embedded within the substrate, and accordingly have no MTS within them. The reaction appears to be reaction-kinetics limited toward the inlet, as indicated by the lack of depletion of MTS. Once a critical temperature is reached, corresponding to a position approximately 0.09 meters from the inlet, the reaction kinetics speed up markedly until the reaction becomes limited by the diffusion of the reactant to the substrate and furnace wall. The exiting gas contains only about 10% of the original amount of MTS entering the system.

Figure 29 is a schematic of the weight fraction of HCl found within the modeled domain. The vantage point for this figure is from above the southeast corner (the fourth quadrant). The gas entering the system has no HCl in it. At the same point of rapid depletion of the gas phase of MTS, there is a rapid increase in the content of the gas phase of HCl.

Figure 30 indicates the field of weight fraction of hydrogen throughout the domain, of which the vantage point is found above the southeast corner of the domain (the fourth quadrant). As the reaction proceeds and the gas phase moves through the reactor, the weight fraction of hydrogen increases, due to the loss of the SiC mass from the gas phase.
Figure 28. Predicted weight fraction of CH$_3$SiCl$_3$ throughout the modeled domain, in which the vantage point of the figure is above the northeast corner of the domain.
Figure 29. Predicted weight fraction of HCl throughout the modeled domain, in which the vantage point of the figure is above the southeast corner of the domain.
Figure 30. Predicted weight fraction of $\text{H}_2$ throughout the modeled domain, in which the vantage point of the figure is above the southeast corner of the domain.
Figure 31 represents a comparison between the experimentally measured deposition profile and the mathematically predicted deposition profile, as a function of distance from the inlet. The deposition reaction does not proceed until the gas mixture gets hot enough for the reaction to proceed, which coincides with a position approximately 0.08 meters from the inlet. The peak deposition rate is found to be around 1.5 μm/min, at a position of 0.1 meters from the inlet (which coincidentally was the position of the bottom edge of the graphite rod). Deposition essentially comes to a stop beyond positions of 0.3 meters from the inlet, due to depletion of MTS from the gas phase as well as decreasing temperatures as the gases approach the outlet. Scatter in the experimentally measured data arose primarily from the nodular morphology of the coating, as shown previously. The model assumed a completely dense ($\rho_{\text{sic}} = 3.21 \times 10^3$ kg/m$^3$), completely planar growth. Good agreement exists between the two plots, which is indicative of (1) proper discretization of the governing partial differential equations, (2) appropriate solution method for the proposed problem, (3) valid assumptions regarding the reaction kinetics of the system.
Figure 31. Comparison between experimentally measured and mathematically predicted deposition profiles along the length of the graphite rod substrate.
SUBSTRATE: GRAPHITE DISC

As mentioned previously, another substrate form was selected for further validation purposes of the model. Graphite discs were suspended in the furnace, wherein the geometry of the system is similar to that shown in figure 22. The modeled domain neglected much of the furnace downstream of the disc to reduce CPU time. The modeled domain is only 0.3 meters in length, wherein the disc is found 0.24 meters from the inlet. The domain was divided into 30 cells in the radial direction and 62 cells in the longitudinal direction. The grid spacing is predominantly constant in the radial direction. The grid spacing in the longitudinal direction is very non-uniform to accommodate the flow characteristics surrounding the disc substrate. Cells adjacent to the substrate were 500 μm in length normal to the substrate. Boundary conditions were similar in nature to those used in the solution of the graphite rod substrate cases. The same convergence criteria were implemented in these cases as were used in the solution to the rod cases.

Figure 32 indicates the predicted velocity profile found within the modeled domain. The bottom boundary of the figure coincides with the inlet of the system, the top boundary corresponds to the outlet of the system, the right side of the plot corresponds to the furnace wall, and the left side of the plot corresponds to the symmetry axis, and is labelled as "SYM". The length of the arrows found in the inlet correspond to a velocity of 0.14 m/s. Again, as the gas mixture gets heated from the wall and as the reaction proceeds to increase the volume of the gas, velocities of the gas increase. No recirculative flow pattern is predicted to exist on
the downstream side of the disc, which could be expected from the very laminar behavior of the flow field (the maximum Reynolds number is only of the order of 10, and a value of approximately 2100 is required for the transition from laminar to turbulent flow to take place).

Figure 33 indicates the predicted temperature field within the modeled domain for a set point of 1300 °C. As in the graphite rod case, practically no temperature gradient is predicted to exist in the radial direction of the reactor.
Figure 32. Predicted velocity field within the modeled domain wherein the substrate is a graphite disc, and the set point temperature is 1300 °C.
Figure 33. Predicted temperature field within the modeled domain wherein the substrate is a graphite disc, and the set point temperature is 1300 °C.
Figure 34 is a schematic of the predicted MTS weight fraction field within the modeled domain for a set point temperature of 1300 °C. The vantage point of the figure is from above the northeast corner of the domain (the first quadrant). The gas phase remains less depleted upstream of the disc in comparison to the rod case, due to the absence of a reactive surface (other than the furnace wall) below the substrate. Hence a higher deposition rate may be predicted at the same position in the furnace for the deposition onto a disc substrate in comparison to deposition on the rod substrate. The weight fraction of MTS decreases as the gas mixture flows in the radial direction along the substrate surface due to the ongoing deposition reaction.

Figures 35 and 36 are the predicted HCl weight fraction field and the predicted H₂ weight fraction field, for a set point of 1300 °C. The bottoms of the figures correspond to the inlet of the reactor, and accordingly, the top boundaries of the figures represent the outlet of the modeled domain. Similarly, the right boundary of each figure corresponds to the furnace wall, and the left boundary of the figure coincides with the symmetry axis of the furnace. As the gas flows through the reactor, HCl is produced concomitant with the CH₃SiCl₃ depletion. Again, the overall weight fraction of hydrogen increases as the gas mixture flows through the system due to depletion of mass from the gas phase in the form of SiC deposited.
Figure 34. Predicted MTS weight fraction field, wherein the set point temperature is 1300 °C, and the vantage point of the figure is above the northeast corner of the domain.
Figure 35. Predicted HCl weight fraction field, wherein the set point temperature is 1300 °C.
Figure 36. Predicted hydrogen weight fraction field, wherein the set point temperature is 1300 °C.
Figure 37 depicts a comparison between the experimentally determined deposition profile and the mathematically predicted deposition profile for a set point of 1300 °C. Both sets of data show little dependence of deposition rate on radial position. The average deposition rate is approximately 1.4 μm/min.
Figure 37. Comparison between mathematically predicted and experimentally measured deposition profiles along the disc substrate surface, for a set point of 1300 °C.
Experiments were also conducted at a set point of 1100 °C, and accordingly, the model was executed for similar conditions. Figure 38 is a schematic of the MTS weight fraction field within the domain for a set point of 1100 °C. The orientation of this figure is such that the vantage point is from above the northeast corner of the domain (first quadrant). Less depletion of MTS from the gas phase has occurred in this case in comparison to the higher temperature set point data, due to slower reaction kinetics and slower diffusivities of MTS and HCl.

Figure 39 is a comparison between the experimentally determined and mathematically predicted deposition profiles along the graphite disc substrate for a set point of 1100 °C. Again, little variation of the deposition profile is seen with respect to the radial position. The average deposition rate is approximately between 0.3 and 0.4 μm/min under these conditions.
Figure 38. Predicted MTS weight fraction field for a set point of 1100 °C, where the vantage point is from above the northeast corner of the domain.
Figure 39. Comparison between the experimentally determined and mathematically predicted deposition profile along the surface of the graphite disc substrate, with a set point temperature of 1100 °C.
The comparisons between the experimentally determined deposition profile and the mathematically predicted deposition profiles indicate good agreement between the modeling results and the experimentally observed results for the two system geometries studied. As mentioned above, this is indicative of (1) proper discretization of the governing equations, (2) appropriate solution method employed, and (3) valid assumptions regarding the reaction kinetics. The rather large uncertainty in the values of the reaction kinetics parameters $A$ and $E$, as well as the large uncertainty in the diffusivity data for MTS, warrants an analysis of the dependence of the predicted results on variations in these quantities, which is the focus of the following section.

EFFECT OF PROCESS PARAMETERS

Figure 40 shows a schematic of the variation of the deposition profile along the rod substrate as a function of the reaction constant $A$ (denoted as $Rc$ in the figure legend). As expected from the reaction rate expression, decreasing the value of $A$ results in a lower peak deposition rate, as well as shifting the peak to positions further from the inlet, and vice versa. The value of $E$ was held constant for these trials at 188 kJ/mol.

Figure 41 shows a schematic of the variation of the deposition profile as a function of the reaction activation energy $E$ (denoted as $Ea$ in the figure legend), along the surface of the rod substrate. The value of $A$ was held constant at 859 for these trials. As the activation energy of the reaction is increased, the deposition
rate decreases in addition to the peak rate moving further downstream. The reaction kinetics are more sensitive to changes in $E$ than in $A$, which should be expected from the linear dependence on $A$ and the exponential dependence on $E$.

For all of these cases the set point temperature was maintained at 1300 °C, the system pressure was held at 100 torr, the inlet gas composition was $\text{H}_2:\text{CH}_3\text{SiCl}_3 = 10:1$, and the diffusivity of MTS varied according to the expression found in Appendix D. Although varying the reaction parameters has no physical significance (nature has fixed these values), doing so may allow researchers to reduce the uncertainty in these experimentally determined values. For instance, examination of the figures results in the conclusion that the activation energy is unlikely to be above 200 kJ/mol, although values up to 235 have been reported. These high $E$ values simply do not allow the reaction to proceed at rates corresponding to the observed deposition rates. Similarly, extremely low values of $A$ (below 1000) appear to be improbable for similar reasons.
Figure 40. Effect of variations in the reaction constant $A$ on the predicted deposition profile along the length of the rod substrate.
Figure 41. Effect of variations in the reaction activation energy $E$ on the deposition profile along the rod substrate.
Figure 42 shows the dependence of the deposition profile along the length of the graphite rod substrate on the magnitude of the diffusivity of MTS in hydrogen. The set point temperature was 1300 °C, the total system pressure was held at 150 torr, the inlet gas composition was maintained at a H$_2$:CH$_3$SiCl ratio of 10:1. The reaction constant $A$ and the activation energy $E$ were held at the values determined in the present study, i.e. 91,828 ([$\equiv$] µm/min) and 151,266 ([$\equiv$] J/mol), respectively.

The deposition profile is strongly dependent on $D_{MTS}$. Varying the value of $D_{MTS}$ is achieved by altering the value of the coefficient "$R$" (denoted as $D$ in the figure caption) in the expression for the diffusivity of MTS in hydrogen as shown in Appendix H. Reducing the value of $R$ does not substantially move the position of the peak deposition rate. However, reducing $R$ does allow for higher deposition rates further downstream due to slower diffusion to the reaction site, and hence less depletion of the reactant when compared to higher values of $R$. As was the case for $A$ and $E$, varying $R$ has little physical meaning other than to reduce the rather large uncertainty in the calculated magnitude of $D_{MTS}$. 
Figure 42. Effect of varying the diffusivity of MTS in hydrogen on the predicted deposition profile along the length of a graphite rod substrate.
The effect of varying the set point temperature on the deposition profile along the length of a graphite rod substrate was also examined. Figure 43 shows a schematic of this dependence for three different set point temperatures, namely 1100, 1200, and 1300 °C. The average values of the kinetic parameters were used in these calculations. The $R$ coefficient in the $D_{MTS}$ expression was held at $0.395 \times 10^7$. Raising the set point temperature has much the same effect as reducing the activation energy. Altering the temperature directly affects the physical properties of the gas mixture, whereas changing the activation energy alone does not do this. In spite of this, the resultant deposition profiles shift in similar directions for increased temperatures and reduced activation energies. Increasing the set point shifts the onset and peak deposition toward the inlet, and reduces deposition further downstream.

Figure 44 shows the effect of changing the system pressure on the deposition profile along the length of a graphite rod. The set point temperature remained at 1300 °C. The inlet gas composition was held at a $\text{H}_2: \text{CH}_3\text{SiCl}_3$ ratio of 10:1. The value of the coefficient $R$ in the $D_{MTS}$ expression was held at $0.395 \times 10^7$. With increased pressures, the deposition rate decreases overall, probably due to the dependency of diffusivities on pressure.
Figure 43. Effect of varying set point temperature on the deposition profile along the length of a graphite rod substrate, for a system pressure of 150 torr, and an inlet gas ratio H_{2}:CH_{3}SiCl_{3} = 10:1.
Figure 44. Effect of varying system pressure on the deposition profile along the length of a graphite rod substrate, for a set point temperature of 1300 °C, and an inlet gas ratio of $\text{H}_2\text{CH}_3\text{SiCl}_3 = 10:1$. 
CONCLUSIONS

Two types of driven cavity problems were addressed in order to validate the mathematics of the model developed in the present study. The first type involved an isothermal square cavity whose top boundary was sliding, with the other three walls stationary. The results of the presently developed model were compared to those of a commercially available computational fluid dynamics code entitled FLUENT. The agreement between the results obtained from the two codes was excellent, indicating that the governing partial differential equations had been correctly discretized, and that the chosen solution method was appropriate for the proposed problem.

The second type of driven cavity problem involved the buoyancy driven flow of a Boussinesq fluid within a square cavity. The results of the model developed in the present study were compared to those of another commercially available code entitled FIDAP. Solutions were obtained for the dimensionless fluid characteristics of Prandtl number = 0.71 constant, while the Rayleigh number varied between $10^3$, $10^4$, and $10^5$. Good agreement was attained between the results, indicating that the model developed in the present study accurately models natural and forced convection and heat transfer under the specified conditions.

The model was subsequently applied to the main problem of interest, namely the CVD of SiC in the CH$_3$SiCl$_3$ - H$_2$ system. Two simple system geometries were investigated, in which the experimentally measured deposition profiles were compared to those obtained via the mathematical model. The first of
these geometries studied was that of deposition onto a graphite rod suspended along the longitudinal axis of the vertically oriented hot-walled tube furnace. Agreement between the experimental data and the predicted deposition profile was very good.

The second set of experiments were conducted on graphite discs suspended in a similar furnace. These experiments were conducted at two different temperatures in order to experimentally determine the reaction kinetics parameters of reaction constant $A$ and activation energy $E$. The values of said parameters were determined to be $91,828$ (=[μm/min) and $151,266$ (=[J/mol), respectively, which fall within the reported error margins for these parameters.

An analysis was carried out to determine the degree to which the predicted deposition profiles were affected by varying the values of the reaction constant, activation energy, and the diffusivity of MTS in hydrogen. All three of these parameters have rather large degrees of uncertainty within the literature reports. Deposition profiles were most affected by varying the activation energy or the diffusivity, and were least affected by changing the reaction constant over the ranges investigated. Changing the set point temperature also had a large effect of the predicted deposition profiles, in much the same way as changing the activation energy. The system pressure affected the deposition profiles only slightly, probably due to changes in the calculated diffusivities of MTS and HCl.

The model as developed seems well suited for studying the deposition of SiC in the CH$_3$SiCl$_3$ - H$_2$ system. The application of the model in its current form is limited to CVD conditions which result in fully dense, relatively planar growths
of silicon carbide, similar to those coatings applied in the electronics industry as well as fiber coatings for use in fiber reinforced composite materials. Implementation of the model may result in the ability to reduce the amount of uncertainty in the values of various process parameters as reported in the open literature, such as diffusivities and reaction kinetic data. Proper usage of the model may also expedite the optimization and/or the scale-up procedures in existing CVD reactors, or accelerate the design stages of new CVD systems.
CHAPTER VI

MORPHOLOGICAL CHARACTERIZATION OF DEPOSITED SiC

INTRODUCTION

As previously mentioned, the morphology of the grown silicon carbide has been found to depend on the process parameters of temperature, initial inlet gas composition, and the system pressure. In this study, the system temperature and inlet gas $\text{H}_2: \text{CH}_3\text{SiCl}_3$ ratio were varied in order to develop the underlying relationships. The examined ranges of these parameters differed from those already evaluated and reported in the literature. Gross morphological changes occur with changes in the gas composition, while the morphologies found were independent of temperature over the range studied.

Two types of substrates were selected for the present study: rods, positioned along the longitudinal axis of the reaction chamber, and discs, suspended from the top and positioned in the center of the furnace. All of the rods were made of graphite, while the discs used were either graphite (usually) or alumina.
SUBSTRATE: GRAPHITE ROD

The graphite rods used were 0.46 meters long and 0.003 meters in diameter. Carbon yarn was used to suspend the rods in position. They were positioned along the longitudinal axis of the furnace, such that the bottom of the graphite rod coincided with the bottom (inlet) of the reaction chamber, and the rods ran the entire length of the furnace.

Three sets of experimental conditions were selected in the present study, and are outlined in Table 5. Each experiment was conducted on two separate samples. The length of time for each coating run was maintained at 30 minutes.

Table 5. Experimental conditions used in the coating of the graphite rods.

<table>
<thead>
<tr>
<th>CASE</th>
<th>T (K)</th>
<th>P (torr)</th>
<th>α (= H\textsubscript{2}:CH\textsubscript{4}:SiCl\textsubscript{4} ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1573</td>
<td>100</td>
<td>10:1</td>
</tr>
<tr>
<td>2</td>
<td>1473</td>
<td>100</td>
<td>10:1</td>
</tr>
<tr>
<td>3</td>
<td>1573</td>
<td>100</td>
<td>2:1</td>
</tr>
</tbody>
</table>

The volumetric flow rate of hydrogen was held constant at 300 sccm. These experiments were conducted in the furnace which yielded the temperature profile indicated in Fig. 19 (see page 102). The same experimental procedure was used for all of these runs, similar to that discussed in the previous chapter. Once coated, the graphite rods were fractured into ≈ 0.02 meter lengths. Each of these pieces was
subsequently examined via scanning electron microscopy (SEM), in which micrographs were taken of the fracture surfaces of the samples and of the top surface of the coating.

CASE 1 COATINGS

Six distinct "morphological zones" (MZ) were found on the samples coated using the first set of conditions listed in Table 5. The first of these zones was closest to the inlet, and extended for approximately 0.025 meters downstream, where no detectable coating was found.

The second MZ consisted primarily of SiC characterized as nodules with small whiskers. A representative micrograph of this zone is depicted in Plate III. The magnification in the micrograph is 1000x. This zone extended for approximately 0.025 m. The coating at this location consists primarily of a nodular growth, with a small fractional coverage of the whiskers. These whiskers were typically about 5 μm in diameter and 20 μm in length. The cross section of the small whiskers is cycloidal in nature, although the shape of the whiskers overall is rather twisted.

The next (third) MZ consisted of a nodular growth with the absence of any small whiskers. Plate IV is a representative micrograph of the growth found in this region, which extended approximately 0.065 m. The magnification in the photo is 1300x. Plate IV is a micrograph of the fracture surface found at the 0.10 meter position as measured from the bottom of the furnace (inlet). The graphite substrate
can be seen in the right portion of the micrograph, and the SiC coating appears in the left side of the picture.

The nodular growth found along the length of the graphite rod undergoes some transitions over the next two morphology zones. The fourth MZ consisted of nodules, with a significant portion thereof characterized as "extended nodules". Plate V is a representative micrograph of the surface morphology of the coatings found in this section. The magnification in the micrograph is 100x. The delineation between "small whiskers" and "extended nodules" is rather subjective. The gradual transition from a nodular growth to one consisting primarily of distinct whiskers should be kept in mind. Extended nodules were classified as such because these growths usually are much straighter and larger in size than those growths characterized as small whiskers. These extended nodules are approximately 100 \( \mu \text{m} \) in diameter and 300 to 400 \( \mu \text{m} \) in length. As was the case for the small whiskers, the cross sectional shape of the extended nodules is cycloidal. The extended nodules are rather straight overall, in contrast to the small whiskers. Hence, the primary difference between coatings characterized as extended nodules and those characterized as whiskers is the characteristic shape and size of the growths. Extended nodules appear much larger in diameter and much straighter than whiskers.

These extended nodules undergo a transition around the 0.15 meter position. The nodules grown in the range 0.15 - 0.30 meter from the inlet are characterized as rough nodules and are classified into the fifth MZ. Plate VI depicts a
micrograph of a representative portion of these rough nodules. The magnification in the micrograph is 1700×. The surface of the nodules has become less smooth than those grown further upstream, including the extended nodules.

Finally, the last and sixth MZ found along the lengths of the graphite rods grown under the first set of experimental conditions consists of very small whiskers. Plate VII is a representative micrograph of the coating found in this region. The magnification of this photo is 2700×. The micrograph is of the fractured surface, in which the graphite substrate is visible in the left portion, and the SiC is found in the right side of the photo. This region begins at about the 0.3 meter position. The coating gradually tapers off toward the outlet, due to the lower temperatures found near the outlet portion of the furnace.
Plate III. SEM photomicrograph of a representative section of the coating found in the second morphology zone for case 1. Magnification = 1000×.
Plate IV. SEM photomicrograph of a representative section of the SiC coating found in the third morphology zone for case 1. Magnification = 1300×.
Plate V. SEM photomicrograph of a representative section of the SiC coating found in the fourth morphology zone for case 1. Magnification = 100x.
Plate VI. SEM photomicrograph of a representative section of the SiC coating found in the fifth morphology zone for case 1. Magnification = 1700x.
Plate VII. SEM photomicrograph of a representative section of the SiC coating found in the sixth morphology zone for case 1. Magnification = 2900×.
CASE 2 COATINGS

The morphologies found on those samples coated under case 2 conditions were somewhat similar to those found in the first set of experimental conditions. The only difference between the two conditions is that the set point temperature in the second condition was 100 K lower than in the first condition set. The morphology zones of the deposit formed in the second set were essentially pushed downstream in comparison to those in case 1, to positions in the furnace which were at the same temperature as those for the higher set point. The first MZ (no noticeable deposition) extended from the inlet to a position 0.075 m from the inlet. The coating found in the second morphology zone of the samples coated in case 2 consisted primarily of a nodular growth, with a very small fractional coverage of small whiskers, as is shown in Plate VIII. The magnification of the photo is 600×.

The morphology of the growth for the majority of the length of the rod was nodular, as shown in Plate IX. This zone (third MZ) began at around the 0.10 m position, and ended around the 0.35 m position. Occasionally extended nodules were found along the length of the rod in this region, but not enough to warrant a separate morphological classification. The size of the nodules decreased as the position of the coating became closer to the outlet.

A transition in the morphology of the coating occurs around the 0.35 m position. As was the case for the coatings deposited in the first set of experimental conditions, the morphology of the coating nearest the outlet consisted primarily of very small whiskers. Plate X is a representative micrograph of the whiskers. The
magnification of the photo is 8000×. The whiskers are on the order of 0.1 μm in diameter, and 2 - 4 μm in length. The cross-sectional shape of the whiskers is again cycloidal, and the entire whisker is rather twisted. The length required for the transition between nodular growth and very small whisker growth is approximately 0.05 m.

The reduction in the set point temperature effectively eliminated the appearance of extended nodules and of the rough nodules, by comparison of the two cases discussed above. In addition, the onset of deposition occurs further downstream for the lower set point temperature case, at positions which have the same temperature by examination of the temperature profile. A lower reactor temperature may induce a different set of gas phase reactions, which consequently results in the lack of the varying nodular growth.

The onset of the very small whisker growth region for the above two cases occurs at slightly different positions in the reactor. This growth region begins at a position further upstream for the higher set point temperature case, indicating that the formation of these whiskers may be due to depletion of reactant. If the whisker growth neighboring the outlet depended primarily on temperature, then the growth of whiskers in the lower set point temperature case would have occurred further upstream than for the high set point case, which is in conflict with the results.
Plate VIII. SEM photomicrograph of a representative section of the coating found in the second morphology zone for case 2 deposits. Magnification = 600x.
Plate IX. SEM photomicrograph of a representative section of the coating found in the third morphology zone for case 2 deposits. Magnification = 600×.
Plate X. SEM photomicrograph of a representative section of the coating found in the fourth morphology zone for case 2 deposits. Magnification $= 8000 \times$. 
CASE 3 COATINGS

The experimental conditions in case 3 differ from those found in case 1 only in α. The resultant morphologies found along the case 3 substrates differ significantly from those found in either case 1 or 2. The onset of any deposition occurs in case 3 trials around the 4 cm position. Instead of the morphology of the coating consisting of nodules with a low fractional coverage of small whiskers, as in case 1, the morphology in the second MZ is found to be nodular in nature, with no small whiskers present, as shown in Plate XI. Plate XI depicts the fracture surface of the substrate and coating, in which the substrate is found in the left portion of the photo, and the deposit is found on the right. The magnification of the photo is 1600×. The thickness of the coating is around 3 μm. The appearance of nodules is seen to the 0.07 m position.

Plate XII depicts a representative section of the top surface of the coating found in the next morphology zone, characterized as the shiny section. The magnification of the photomicrograph is 600×. This section appears almost mirror-like to the naked eye -- extremely shiny and reflective. The coating found in this section was the smoothest of all coatings obtained in the present study, which is apparent in plate XII. The shiny section extends from the 0.07 m position to the 0.10 m position along the length of the substrate.

Plate XIII depicts the morphology of the coating found in the next zone, which is a predominant nodular growth, reminiscent of the other nodular growths
shown previously. The magnification of the photomicrograph is 600×. These nodules covered the substrate up to the 0.19 m position.

A dramatic morphological alteration takes place at approximately the 0.20 m position. The nodular growth found in the previous MZ transforms into very long whiskers, as shown in Plate XIV. The magnification of the photomicrograph is 1000×. The graphite substrate can be seen in the left portion of the plate. The diameter of the whiskers is around 3 μm, and their lengths often exceed 100 μm. The cross-sectional thickness of the whiskers is cycloidal. The whiskers themselves are very curved in nature. Their main growth direction is not necessarily normal to the substrate surface, but rather they twist around almost randomly in direction. The thickness of the bed of whiskers is approximately 50 microns. A base thickness of SiC exists on the substrate on the order of 2 μm.

The morphology of the coating along the length of the rod undergoes one final small transformation. These relatively large whiskers are replaced by very small whiskers, similar to those found in cases 1 and 2. Plate XV depicts a representative section of the coating found within the small whisker region of the coating neighboring the outlet. The magnification in this plate is 600×. The onset of the small whisker region begins around the 0.30 m position, which is at a position further upstream than in the previous 2 cases.
Plate XI. SEM photomicrograph of a representative section of the coating found in the second morphology zone in case 3. Magnification = 1600×.
Plate XII. SEM photomicrograph of a representative section of the coating found in the third morphology zone in case 3. Magnification = 600×.
Plate XIII. SEM photomicrograph of a representative section of the coating found in the fourth morphology zone in case 3. Magnification = 600×.
Plate XIV. SEM photomicrograph of a representative section of the coating found in the fifth morphology zone in case 3. Magnification = 1000x.
Plate XV. SEM photomicrograph of a representative section of the coating found in the sixth morphology zone in case 3. Magnification = 600×.
Figure 45 is a summary of the morphological regions found along the lengths of the graphite rod substrates for the three cases examined. The appearance of the shiny section and of the relatively large whiskers in case 3 differentiate it from cases 1 and 2. The lack of the extended nodules and rough nodules from case 3 coatings should also be noted.

The actual demarcation between neighboring morphology zones is not accurately represented by a separation line as indicated in the figure. Adjacent morphology zones share a transitional zone, which varies in length along the rod for different morphology zone boundaries. All transition zones are at most 0.02 meters in length, the shortest of which is found abutting the shiny section zone in case 3, wherein the transition between neighboring morphologies is much more abrupt, on the order of 0.003 m.

The existence of vapor phase compositional gradients and temperature gradients along the length of the reactor result in a fairly complex problem regarding the determination of the factors controlling the morphology of the coating. Accordingly, another set of experiments was conducted wherein the rod substrates were replaced by disc substrates, which is the focus of the following section.
Note: The following schematics are not to scale.

**Figure 45.** Schematic of the morphology zones obtained along graphite rod substrates under experimental conditions outlined in cases 1, 2, and 3, from top to bottom.
SUBSTRATE: GRAPHITE DISC

The geometry of the system in which disc substrates were used has been discussed previously in Chapter IV. Table 6 indicates the selected processing conditions for the disc substrate trials. The temperature profile corresponding to the furnace used in the coating of all the disc substrates is as shown in Fig. 23 (see page 111). The experimental procedure as discussed in Chapter IV was applied to these trials. The hydrogen flow rate was held constant at 300 sccm. At least two samples were coated in cases 1 through 3; only one sample was coated in cases 4 through 13.

To suspend the graphite discs upside down in the furnace, a small hole was drilled completely through each substrate, and a graphite rod (with a slightly larger diameter than the hole) was forced into the hole until the end of the rod was flush with the bottom surface of the disc. Colloidal carbon paint was dabbed into and around the fitting, both on the top and bottom surfaces of the substrate. The friction between the graphite support rod and the disc, as well as the presence of the carbon paint, was sufficient to prevent the disc from falling off the supporting rod.
Table 6. Operating conditions for the cases in which a graphite disc was used as the substrate.

<table>
<thead>
<tr>
<th>Case</th>
<th>T (K)</th>
<th>P (torr)</th>
<th>α</th>
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<tr>
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<tr>
<td>13</td>
<td>1573</td>
<td>100</td>
<td>2:1 → 10:1</td>
</tr>
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</table>

The morphology of the coating obtained for case 1 is shown in Plate I (see page 115). This morphology is characterized by its nodular growth. The morphology is consistent across the entire substrate surface, and the deposited thickness is relatively uniform. The color of the deposit as seen by the naked eye was gray/silver.

Coatings obtained under case 2 conditions yielded quite different results. The morphology of the coatings here is represented in Plate XVI, as shown below (magnification = 800×). The graphite substrate is located toward the top of the photomicrograph. The coating morphology is characterized by a predominance of relatively large whiskers. These whiskers are similar in size and shape to those
found in the third morphology zone of the deposited SiC on a case 3 graphite rod ($\alpha = 2:1$). The diameter of the whiskers is approximately 3 or 4 \( \mu \text{m} \), and the length is on the order of 100 \( \mu \text{m} \). Again, the whiskers appear cycloidal in cross-sectional shape, and the overall shape of the whiskers is curved. The bed of whiskers is approximately 50 \( \mu \text{m} \) deep. The color of the deposit was brown/yellow.

The morphology of the coatings obtained under case 3 conditions was similar to those obtained under case 2 conditions. Plate XVII depicts the typical morphology found on case 3 discs (magnification = 1000\(*\)). The characteristics of the whiskers are the same as in case 2, including the color.
Plate XVI. SEM photomicrograph of the coating obtained under case 2 conditions when the substrate is a graphite disc. Magnification = 800x.
Plate XVII. SEM photomicrograph of the coating obtained under case 3 conditions when the substrate is a graphite disc. Magnification = 1000x.
Cases 4 through 10 were executed in order to analyze the trend in the deposit morphology through the transition of whisker $\rightarrow$ nodular $\rightarrow$ whisker as $\alpha$ increases from 2:1 to 20:1 with dilution of the MTS. Plate XVIII is an SEM photomicrograph of the coating obtained in case 4 ($\alpha = 4:1$). The magnification of this plate is 2000×. The resultant morphology is whisker-like, although the whiskers are substantially straighter than in previous trials. The color of the deposit is brown/yellow.

Plate XIX indicates a whisker morphology when a $\alpha$ value of 6:1 is used. The magnification in this photomicrograph is 1000×. The whiskers obtained in case 5 are significantly shorter and smaller than those found in case 4. The color of the deposit obtained under case 5 conditions is brown/yellow.

Plate XX indicates the typical morphology of the deposit obtained when $\alpha = 8:1$ (case 6). The magnification of the micrograph is 1000×. The morphology may be described as angular, resembling the nodular coatings much more than the whiskers. The color of the deposit is gray/silver.

Plate XXI shows an SEM photomicrograph of the surface of the deposit formed under case 7 conditions ($\alpha = 12:1$). The magnification of the micrograph is 1000×. The morphology resembles that which has previously been classified as extended nodular. The color of the coating to the naked eye is gray/silver.

Plate XXII represents an SEM photomicrograph of the deposit obtained under case 8 conditions ($\alpha = 14:1$). The magnification is 1000×. The morphology seems to be in a transitional state between extended nodules and whisker growth.
Some whiskers may already be observed, such as the whisker spiraling away from the substrate surface in the left portion of the micrograph. The color of the coating was a combination gray/silver and brown/yellow, with no particular color dominating.

Plate XXIII indicates an SEM micrograph of the coatings formed under case 9 conditions (α = 16:1). The magnification is 1000×. The morphology is dominated by whisker growth. The diameter of these whiskers is similar to those obtained at α values of 2:1 and 20:1. However, the average length of the whiskers is only around 20% of those grown at 2:1 or 20:1. In addition, the whisker growth direction is more normal to the substrate surface than the growth direction of the 2:1 and 20:1 grown whiskers. The color of the deposit formed on this specimen was brown/yellow.

Plate XXIV shows an SEM photomicrograph of the deposit obtained under case 10 conditions (α = 18:1). The magnification of this photo is 100×. The morphology of the coating is best characterized by extended nodules, although a few stray whiskers are seen growing on the substrate surface. The predominant color seen on this deposit is gray/silver.
Plate XVIII. Representative SEM photomicrograph of the deposit formed under case 4 conditions ($\alpha = 4:1$). Magnification = 2000x.
Plate XIX. Representative SEM photomicrograph of the deposit formed under case 5 conditions ($\alpha = 6:1$). Magnification = 1000×.
Plate XX. Representative SEM photomicrograph of the deposit formed under case 6 conditions ($\alpha = 8:1$). Magnification = 1000x.
Plate XXI. Representative SEM photomicrograph of the deposit formed under case 7 conditions ($\alpha = 12:1$). Magnification = 1000x.
Plate XXII. Representative SEM photomicrograph of the deposit formed under case 8 conditions ($\alpha = 14:1$). Magnification = 1000×.
Plate XXIII. Representative SEM photomicrograph of the deposit formed under case 9 conditions ($\alpha = 16:1$). Magnification = 1000x.
Plate XXIV. Representative SEM photomicrograph of the deposit formed under case 10 conditions ($\alpha = 18:1$). Magnification = 100x.
The general trend as seen from cases 4 through 10 corresponds to the keystone trials of $\alpha$ values of 2:1, 10:1, and 20:1, in which nodular deposits are formed at and around $\alpha$ of 10:1, and whiskers grow at $\alpha$ values near both 2:1 and 20:1. This phenomenon has not been reported in the open literature.

The two most common rationalizations for whisker growth are the following: (1) diffusion-controlled growth, and (2) metallic impurities. For diffusion-controlled growth, whisker growth is induced by a very dilute reactant supply, according to the following scenario. Assume initially a planar growth of SiC under kinetically limited conditions of reactant diffusion control. Impose a small local growth perturbation in which a portion of the growing vapor / solid interface extends beyond the surrounding interface. As a direct result of this, the outermost tip of the perturbation is exposed to a higher concentration of reactant in comparison to its surroundings. Accordingly, the tip of the perturbation continues to grow at a higher rate than the initially planar growth behind it, assuming diffusion control (implicit in this is an infinitely fast surface reaction rate). Hence, the initially small perturbation yields a whisker.

The other common explanation for whisker growth has been the introduction of metallic impurities into the system, usually iron or other transition elements (e.g. Co or Ni are also common). The whisker growth mechanism occurs by what is known as the VLS mechanism, which was outlined in Chapter I.

Neither of these mechanisms is able to explain the observed pattern of whisker and nodular growth morphologies. The transition from nodular growth to
whisker growth as the $\alpha$ value increases from 10:1 to 20:1 may be explained by the
diffusion controlled mechanism for whisker growth. However, this mechanism can
not explain the observed whisker growth at more enriched MTS vapor sources.
Metallic impurities may explain the observed whisker growth at the lower end of
the examined $\alpha$ ratios, for the lack of any other potential mechanism. However, all
other reports of intentional metallic impurity introductions into the reaction chamber
have resulted in morphologies of whiskers significantly different than those found
in the present study [8, 9].

Whiskers reportedly grown by the VLS process are approximately 6 $\mu$m in
diameter and 5 - 100 mm long. The cross-section of the 3C whiskers grown is
rounded triangular in shape. The overall shape of the VLS whiskers is extremely
straight, with periodic ridges along the length of the whiskers, resembling bamboo.
The tip of the VLS whisker is often much larger in diameter than the rest of the
whisker. Hence, the following discussion focuses on efforts in the present study to
identify any metallic impurities present in the system.

SEARCH FOR IMPURITIES

The first test done in order to find the source of any metallic impurities
present was to examine the whiskers with energy dispersive spectroscopy (EDS).
The nodular growth, the sides of the whiskers, the tips of the whiskers, and virgin
graphite substrates were all examined using EDS. The results indicated no
detectable level of iron or any other transition metal at levels above the background
signal from the stainless steel chamber in which the samples were placed for EDS examination.

X-ray diffraction (XRD) was used to examine the deposits of nodular growth and whisker growth obtained from the trials conducted under $\alpha$ values of 10:1 and 2:1. The results of this test are tabulated in Table 7, shown below. Two conclusions may be drawn from the results obtained via XRD: (1) both the whisker and nodular growths appear to be of the same polytype, *i.e.* 3C, and (2) no trace of iron (or other transitional elements) was found in the coatings.
Table 7. Comparison of Diffraction Data for Planar SiC, Whisker SiC, and JCPDS Data.

<table>
<thead>
<tr>
<th>Peak d spacing ([Å])</th>
<th>6H-SiC (JCPDS)</th>
<th>3C-SiC (JCPDS)</th>
<th>Planar growth</th>
<th>Whisker growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.621</td>
<td>2.511</td>
<td>2.520</td>
<td>2.5108</td>
<td>2.5097</td>
</tr>
<tr>
<td>2.352</td>
<td>2.174</td>
<td>2.180</td>
<td>2.1255</td>
<td>2.1234</td>
</tr>
<tr>
<td>1.537</td>
<td>1.418</td>
<td>1.5411</td>
<td>1.5356</td>
<td>1.5386</td>
</tr>
<tr>
<td>1.311</td>
<td>1.286</td>
<td>1.3140</td>
<td>1.3113</td>
<td>1.3093</td>
</tr>
<tr>
<td>1.256</td>
<td>1.087</td>
<td>1.2583</td>
<td>1.2298</td>
<td>1.2299</td>
</tr>
<tr>
<td>1.042</td>
<td>1.004</td>
<td>1.0893</td>
<td>0.9999</td>
<td>0.9930</td>
</tr>
<tr>
<td>0.9727</td>
<td>0.8876</td>
<td>0.9936</td>
<td>0.889</td>
<td></td>
</tr>
</tbody>
</table>

The peaks belonging to the cubic polytype with d spacings of 0.8895 and 0.8387 were not observed because these peaks were outside the examined 2θ range. The peak corresponding to the d spacing of 1.0893 was not found, although this is not necessarily alarming, due to its low relative intensity of 5 (assuming the most intense peak has a relative intensity magnitude of 100). The cubic polytype was expected to be the type grown under the conditions used in the present study, as indicated in the literature (6H, the next most common polytype, is not stable below 1700 °C unless the deposit is doped with group III elements).
The following experiments were conducted to answer the question of whether the (if any) iron source was within the graphite substrate. All of the graphite disc substrates were prepared in an identical fashion as previously. Accordingly, if the substrate were the source of iron, then the continued observation of nodular growth at $\alpha$ of 10:1, and whiskers at $\alpha$ of 2:1 and 20:1 should not have occurred. The conditions as shown in Table 6 under the heading of case 11 were selected for the following test. Approximately one half of the graphite disc substrate was submerged into a bath of $\text{HNO}_3$ acid of pH $= 1$, for 2 hours at a temperature elevated slightly above room temperature. The other half of the substrate was left unexposed to the acid bath. The sample portion soaked in the acid bath was subsequently rinsed in ultrapure water (less than ppb levels of impurities) and thereafter rinsed in methanol to expedite drying. This acid treatment is presumed to have dissolved any metallic impurities present on the substrate surface capable of resulting in the growth of whiskers via the VLS mechanism.

The sample was then subjected to experimental conditions which had previously resulted in a whisker morphology of the coating. Plate XXV is a representative SEM photomicrograph of the resultant coating on the portion of the disc which was given the acid soak treatment. The magnification of the original micrograph was 1000×. Whiskers grew on both portions of the disc, and the whisker morphology of the coating for both portions of the sample were indiscernible from one another. The whiskers grown on this sample are notably
smaller than those grown previously at $\alpha$ of 2:1. This is attributed to the lower set point temperature used in this trial. A lower temperature was required by the implementation of a reaction tube made of Vycor, which has a lower softening point than fused silica, the material usually used. This was the only trial which utilized a Vycor reaction tube. Hence, the graphite substrate material is not supplying the system with the iron necessary for the whisker mechanism to proceed.

In addition, in all cases in which whiskers were observed, whiskers also grew on top of the carbon paint used to fasten the disc to the supporting rod. Presumably, the carbon paint is free from any significant amounts of iron, and in accordance with the aforementioned conclusion, the substrate does not appear to be the source of any iron which may be responsible for the growth of whiskers.

Ammonium hydroxide was subsequently added to the acid used for soaking the substrate, in order to precipitate any metallic impurities out of solution. If any metal such as iron were present in the acid solution, the result would be a gelatinous mixture of acid neutralized by the basic addition, and the metal salt precipitate (cause of the gelatin like nature of the fluid). No precipitates were observed, indicating no noticeable amounts of iron were present in the acid after soaking the substrate.
Plate XXV. SEM micrograph of the acid-soaked portion of the sample coated under case 11 conditions. Magnification = 1000x.
Two final tests were conducted in order to determine the metallic content of the whiskers. A portion of the graphite disc sample previously coated at an $\alpha$ value of 2:1 (resulting in whisker growth) was immersed in a 1 mL HNO$_3$ bath of pH = 1 for 9 days. Any iron present in the surface of the whiskers would have dissolved out of the SiC whiskers and into the acid bath. This acid was subsequently analyzed using X-ray fluorescence (XRF) using a Kevex Corporation Model 770 Delta Analyst. The results of this test indicated no detectable levels of iron or other metallic impurities. The acid was also subjected to a trace metal analysis by the Inductively Coupled Argon Plasma Emission Spectrometry (ICP) method. None of the aforementioned metallic impurities were present above the detectable limit (low ppb) of the apparatus.

Two other experiments were conducted in which the substrate material was a graphite disc. The conditions used in these trials are listed in Table 6 as cases 12 and 13. Under case 12 conditions, the substrate was coated for 30 minutes in a 10:1 $\alpha$ gas composition. Immediately thereafter, $\alpha$ was switched to a value of 2:1 in situ, and deposition was carried out for an additional 30 minutes. All other experimental procedures (including sample preparation) in case 12 and 13 were identical to those in the previous cases. The purpose of the 10:1 $\rightarrow$ 2:1 case was to eliminate any effects the substrate has on the deposit by initially growing a relatively smooth SiC layer and subsequently subjecting the substrate to conditions which previously resulted in coatings with a whisker morphology. Any metallic
impurities originally on the substrate surface were presumed to have been trapped under the nodular growth occurring in the first portion of the case.

For the substrate coated under case 13 conditions, the introduction of the aforementioned gas ratios into the reactor were reversed, all other conditions remaining the same. The purpose of the $2:1 \rightarrow 10:1$ trial was to determine the possibility of growing a fully dense layer of SiC on the edge of the bed of the previously grown whiskers, thereby incorporating into the final coating a layer consisting of a whisker bed, with the substrate on one side and the subsequent growth of fully dense SiC on the other. The applications for such a "functionally gradient" material include optimal sites for crack deflection / propagation in fiber reinforced composite materials, or thermal barrier coatings on jet engine components, for example.

Plate XXVI is an SEM photomicrograph of the resultant surface morphology after the case was completed. The morphology is dominated by nodular growth, with a low fractional area coverage of whisker growth. The apparent color of the coating was gray / silver, with no brown / yellow tints noticeable, which previously has indicated nodular growth. The size and shape of the few whiskers present are similar to those grown under single $\alpha$ case 2 conditions. The results of this case may indicate two possible causes for the appearance of only a few whiskers. The first cause may be that indeed metallic impurities originating from the substrate surface are responsible for the whisker growth, and the initial nodular growth was able to trap most of the metallic impurities below its surface, thereby preventing
whisker growth in the second portion of the case. The other possible cause may be that the whiskers do not require a metallic impurity from the substrate surface, but that an activation energy exists for the transition between nodular growth and whisker growth, and the experimental conditions used in this case were not sufficient to overcome this activation energy (for the most part). The latter of these possibilities is considered to be the most likely, due to the results discussed above for the case in which the graphite substrate was partially soaked in nitric acid.
Plate XXVI. SEM photomicrograph of the deposit surface subjected to case 12 conditions, in which $\alpha$ is varied from 10:1 to 2:1. Magnification = 80×.
The second of these double $\alpha$ cases (case 13) used the same $\alpha$ values as in the previous case, but the order of their implementation was reversed, such that the initial growth was carried out with an $\alpha$ value of 2:1, and the second portion of the case used an $\alpha$ of 10:1. A typical surface morphology of the resultant coating can be seen in Plate XXVII. The dominant feature of the morphology is whisker growth. The color of the coating was predominantly brown / yellow, with a noticeable tint of gray / silver. The overall size and shape of the whiskers grown in this case are similar to those grown under single $\alpha$ 2:1 or 20:1 conditions.

The density of whiskers is apparently lower than in the single $\alpha$ cases. In addition, the apparent depth or thickness of the bed of whiskers is lower than in those single $\alpha$ cases. These two observations may be a result of the following scenario: in the initial 2:1 growth portion of the case, a bed of whiskers grew, similar to those grown in single $\alpha$ 2:1 conditions. During the 10:1 $\alpha$ portion of this case, nodular SiC began to backfill the bed of whiskers by growing out from the substrate surface. The 10:1 portion did not contribute to the overall length or size of the whiskers. Accordingly, only those whiskers which had grown more in the radial direction during the 2:1 portion of the case than the amount of radial growth in the 10:1 portion are visible in the photo. Hence, the results of this case reinforce the concept of whisker growth dependent on $\alpha$. 
Plate XXVII. An SEM photomicrograph of the surface of the SiC grown under case 13 conditions, in which the $\alpha$ was varied \textit{in situ} from 2:1 to 10:1. Magnification = 100$\times$. 
SUBSTRATE: ALUMINA DISC

Alumina discs were used as substrates for two cases, as indicated in the following table. The purpose of these experiments was primarily to determine the effect of the substrate material on the growth rates and morphologies of the resultant SiC deposits.

Table 8. Experimental growth conditions in which the substrates were alumina discs.

<table>
<thead>
<tr>
<th>Case</th>
<th>T (K)</th>
<th>P (torr)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1573</td>
<td>100</td>
<td>10:1</td>
</tr>
<tr>
<td>2a</td>
<td>1573</td>
<td>100</td>
<td>20:1</td>
</tr>
</tbody>
</table>

The furnace and corresponding temperature profile used in these trials were the same as those for the cases in which graphite discs were coated. The experimental procedure was the same for the deposition onto alumina discs as onto graphite discs. The alumina discs were the same diameter (13 mm) as the graphite discs, and the alumina discs were positioned at the same location in the furnace as in the graphite disc cases. The alumina discs were machined from an alumina rod by cutting with a diamond edged saw. Subsequent to this, the samples were ultrasonically cleaned in acetone and methanol to degrease the substrate surface and to remove any residual impurities from the fabrication process.
Plate XXVIII is a representative SEM photomicrograph of the resultant growth morphology obtained under case 1a conditions, which were the same as those in the graphite disc cases which led to nodular growth. The morphology of the coating grown on alumina discs in case 1a conditions may be characterized by nodular growth with an inclination toward extended nodules. The apparent color of the growth was gray / silver. The magnification in the original photo was 1000×. The size of the nodules grown are much smaller than those grown on graphite discs under similar conditions.

Plate XXIX is an SEM photomicrograph of the coating obtained under case 2a conditions, which previously led to whisker growth on graphite substrates. The morphology of the coating shown in this plate is dominated by whisker growth. The color of the deposited SiC was brown / yellow. The magnification in the plate is 1000×. The shape of the whiskers is similar to those grown under similar conditions on graphite discs, but the size is significantly smaller.

The overall thickness of the coating was extremely thin compared to those grown on graphite discs under similar conditions, with an estimated thickness on the order of 0.1 μm. This observation in conjunction with the aforementioned observations regarding the relatively small sizes of the morphological features indicates a substantial nucleation barrier to the formation of SiC on alumina.
Plate XXVIII. SEM photomicrograph of the SiC coating obtained under case 1a conditions ($\alpha = 10:1$, alumina disc). Magnification = 1000×.
Plate XXIX. SEM photomicrograph of the SiC coating obtained under case 2a conditions (α = 20:1, alumina disc). Magnification = 1000×.
The apparent adhesive bond strength was substantially weaker between the SiC and the alumina disc in comparison to the adherence between the SiC and the graphite discs. On removal of the coated alumina discs from the reactor, at least half of the coating spalled off from each sample. This is thought to arise from the mismatch in coefficients of thermal expansion (ΔCTE) between alumina and β-SiC. Table 9 indicates average values for the coefficients of thermal expansion of graphite, silicon carbide, and alumina.

Table 9. Average values of the coefficients of thermal expansion for C, SiC, and Al₂O₃ [reference 147].

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE (×10⁶/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.8</td>
</tr>
<tr>
<td>SiC</td>
<td>4.7</td>
</tr>
</tbody>
</table>

The ΔCTE between alumina and SiC results in the SiC coating existing in a state of compression in the plane parallel to the substrate surface as the sample is cooled from the deposition temperature to room temperature. The magnitude of ΔCTE is approximately equal for the SiC / graphite disc cases, but the SiC is in a state of tension for those cases upon a reduction in the temperature of the substrate and deposit.
The morphologies of the coatings obtained using an alumina substrate were similar to those obtained using graphite substrates. The concept of $\alpha$ being the controlling factor in determining the morphology of the coating is reinforced by the similar morphological results obtained using different substrate materials. Silicon carbide whisker growth dependent on $\alpha$ has not been previously reported in the literature, which indicates a potentially different cause for the whisker growth observation, although none of the reported data examined the specific experimental conditions studied in the present research. Most reported SiC deposition studies evaluated substantially more dilute gas streams. However, all analytical tests performed in the present study were unable to contradict the observed $\alpha$ dependent whisker growth phenomenon.

POTENTIAL GROWTH MECHANISM

As previously mentioned, the identical morphologies of the coatings grown at the extreme $\alpha$ values of 2:1 and 20:1 suggest one mechanism governing the growth of both whisker deposits. The metallic impurity mechanism appears to not be the likely cause for the growth of said whiskers, for the reasons given above. The mechanism discussed in the following section seems capable of describing the experimentally observed morphologies.

Assume that the diffusion of reactant to the substrate surface is controlling the kinetics of the deposition process (the experimental observations and modeling results indicate this to be the case at 1300 °C). At the high end of the examined $\alpha$
ratio (20:1 — most dilute MTS concentration in the inlet), the diffusion controlled growth of SiC is observed. The MTS supply is relatively dilute, and the MTS must diffuse through hydrogen to reach the substrate and deposit SiC.

At the low end of the examined $\alpha$ ratios (2:1 — most enriched supply of MTS into the reactor), the same whisker morphology is observed. The conclusion that this system is also controlled by the diffusion of MTS to the substrate surface is not intuitive nor expected. However, experimental results indicate this to be the case, and it may be explained according to the following scenario. Three significant factors are different for the 2:1 case than in the 20:1 case. The first of these is the diffusion of MTS is no longer through hydrogen, but rather MTS must diffuse through a gas mixture dominated by HCl. For complete decomposition of CH$_3$SiCl$_3$, each mole of MTS produces three moles of HCl vapor. Accordingly, for the initial conditions of 2 moles H$_2$ to 1 mole CH$_3$SiCl$_3$, the composition of the gas phase after significant MTS depletion approaches 2 moles H$_2$ to 3 moles HCl. Consequently, MTS must diffuse primarily through HCl and not H$_2$. Diffusion rates through HCl are significantly slower than through H$_2$.

The second significant factor which may explain the diffusion controlled growth mechanism at 2:1 $\alpha$ conditions is termed the "streaming effect". Higher MTS concentrations result in higher deposition rates. Higher deposition rates correspond to higher MTS depletion rates, and higher HCl production rates. The net positive change in the number of moles in the gas phase at the substrate surface results in a velocity component perpendicular from the substrate surface. Hence,
the large amounts of HCl produced at the substrate must be transported away from
the substrate surface via convection and diffusion. The direction of MTS transport
is opposite to that of the HCl transport and convective flow resulting from the
increase in number of moles present in the gas phase. Hence, the combination of
slower diffusivity of MTS through HCl and the streaming effect may be large
enough to cause the reaction to be controlled by the rate at which MTS reaches the
substrate surface.

Another contribution may be the change in boundary layer thickness $\delta$
resulting from the different inlet volumetric flow rates for the different $\alpha$ cases and
the streaming effect. For the flow over and around the disc substrate may be
analogous to flow over a flat plate, the boundary layer thickness is proportional to
the fluid properties and velocity field according to the following expression:

$$\delta \propto \sqrt{\frac{\rho}{\mu V_*}}$$

(26)

where $\delta$ is the boundary layer thickness, $\rho$ is the density of the fluid, $\mu$ is the
viscosity of the fluid, and $V_*$ is the bulk velocity.

An assumption must be made regarding the density of the gas mixture
adjacent to the substrate surface. Assume the MTS concentration is zero. Hence,
for the 2:1 $\alpha$ case, the gas phase neighboring the substrate consists of 2 parts H$_2$
and 3 parts HCl. For the 10:1 case, the surface gas composition changes to 10
parts hydrogen and 3 parts HCl, and in the 20:1 $\alpha$ case, the surface gas composition
becomes 20 parts hydrogen to 3 parts HCl.
A mass transfer coefficient \( k \) may be defined as the diffusive contribution to the total flux of a particular species in a gas phase, and is expressed as \( k \propto (D_i / \delta) \), where \( D_i \) is the mass diffusivity of species \( i \) and \( \delta \) is the boundary layer thickness. Appendix H indicates some representative diffusivity values for MTS in hydrogen. The diffusivity of MTS through HCl is not known. However, it may be estimated according to the following expression:

\[
D_{\text{MTS in HCl}} \propto D_{\text{MTS in H}} \sqrt{\frac{\text{MW}_{\text{H}}}{\text{MW}_{\text{HCl}}}}
\]  

(27)

Based on this expression, the diffusivity of MTS through HCl is approximately 0.23\( \times \) as fast as MTS diffusing through hydrogen.

The expression presented above for the boundary layer thickness evaluated the thickness of the momentum boundary layer. The expression for the ratio between the concentration boundary layer thickness \( \delta_{\text{CBL}} \) and \( \delta \) is approximated according to the following relationship:

\[
\frac{\delta_{\text{CBL}}}{\delta} = \frac{1}{1.026 \sqrt{\text{Sc}}} \quad (28)
\]

where \( \text{Sc} \equiv \mu / \rho D \) and is called the Schmidt number. The Schmidt number is a dimensionless number representing the proportion between kinematic viscosity and molecular diffusivity. This expression assumes flow over a flat plate. The streaming effect distorts the apparent \( \delta_{\text{CBL}} \) proportionate to the amount of MTS introduced into the reactor.
The flux of MTS toward the substrate surface may be represented by the following expression: \( J_{MTS} = k_{CBL} \cdot \Delta C \), where \( J_{MTS} \) is the flux of MTS, \( k_{CBL} \) is the mass transfer coefficient with respect to the concentration boundary layer, and \( \Delta C \) is the MTS concentration difference between the bulk gas and the gas neighboring the substrate surface. Assuming the concentration of MTS adjacent to the substrate is zero, \( \Delta C \) becomes equal to the concentration of MTS introduced into the reactor.

Based on all the above assumptions and expressions, the flux of MTS may be calculated as a function of \( \alpha \). Figure 46 indicates the relative flux of MTS toward the substrate as a function of the inlet \( \text{H}_2:\text{CH}_3\text{SiCl}_3 \) molar ratio. A local maximum in the flux of MTS occurs at an \( \alpha \) approximately \( 10^{25}:1 \). Accordingly, at concentrations more enriched than this, \( J_{MTS} \) decreases due to primarily two effects: (1) streaming effect, and (2) slower diffusivity through HCl than through \( \text{H}_2 \). At more dilute MTS concentrations, the flux approaches zero due to the lack of MTS.

At concentrations at and near the maximum MTS flux concentration, the arrival rate of MTS may be sufficiently high to result in a rate limiting step comprised of both the diffusion of MTS, and the reaction kinetics (mixed control). The degree to which the deposition reaction is under mixed control may be sufficient to result in a nodular growth morphology.

In contrast, at MTS concentrations not adjacent to the maximum MTS flux concentration (i.e. more dilute or more enriched), the deposition reaction may be predominantly governed by the diffusion of MTS, with little control from the reaction kinetics. Accordingly, this is able to qualitatively explain the whisker
morphology at the extreme $\alpha$ values examined, while observing a nodular growth at an intermediate $\alpha$.

The data shown in Fig. 46 assume all the MTS introduced into the reactor react and deposit SiC only on the substrate. In reality, though, some of the MTS is depleted from the gas phase along the reactor wall upstream of the substrate. Hence, the amount of MTS present adjacent to the substrate is actually lower than that indicated in the inlet $\alpha$ ratio. Accordingly, the effective $\text{H}_2\text{CH}_3\text{SiCl}_3$ ratio neighboring the substrate surface is higher than the $\alpha$ ratio in the inlet. The apparent disparity ($\approx 1.5$ orders of magnitude) between the calculated $\alpha$ ratio coinciding with the maximum flux and the experimentally observed $\alpha$ ratio coinciding with the nodular growth may be further reduced by taking MTS depletion into account.
Figure 46. Relative MTS flux toward the substrate surface as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ molar ratio.
CONCLUSIONS

Three types of substrates (graphite rods, graphite discs, and alumina discs) were used to examine the dependence of the growth characteristics on temperature and reactant dilution ratios. For the graphite rod cases, reductions in the set point temperature from 1573 to 1473 K did not drastically affect the morphology of the resultant coatings along the length of the rod. Near the outlet, small whisker growth is observed on all the rod cases. Lowering the set point temperature shifted all of the morphology zones downstream to equivalent temperatures according to the known temperature profile within the reactor. The predominant morphology of the deposited SiC throughout the reactor is characterized as nodular. The region of small whisker growth neighboring the outlet is believed to be a result of depletion of the reactants from the gas stream and the concomitant change on the reaction rate controlling step from reaction kinetic control to reactant diffusion control.

The maximum growth rate is observed at a position close to the inlet, indicating diffusion controlled growth throughout most of the reactor. Hence there exists a critical reactant gas concentration under reactant diffusion control, above which the morphology of the coating is found to be nodular, and below which the whisker morphology is observed.

Decreasing α from 10:1 to 2:1 under the examined conditions caused substantial changes in the resulting morphology along the length of the rod. Relatively large and non-straight whiskers were observed at positions in the reactor which previously yielded nodular growth.
Graphite discs were also coated under similar experimental conditions used for the coating of the graphite rods. The morphologies found on the discs were the same as those found on the rods at equivalent positions within the reactor. At $\alpha$ values of 2:1, the predominant feature of the grown SiC was whiskers, similar in size and shape to those grown on the rods. At $\alpha$ values at and surrounding 10:1, the morphology of the coatings on the graphite discs became nodular. Increasing $\alpha$ to 20:1 resulted in whisker growth, again similar in size and shape to those found on the rods at equivalent positions in the reactor.

The morphologies of the SiC coatings obtained on alumina discs were similar to those obtained on graphite discs. The primary difference in the deposits formed on the different substrate materials (graphite or alumina discs) was the absolute magnitude of the sizes of the morphological features, wherein the SiC grown on alumina was significantly smaller than that grown on graphite. This is attributed to a relatively large nucleation barrier for the formation of SiC on alumina.

Metallic impurities may be the cause for all the whiskers grown. However, since all substrates were prepared using identical methods, the recurring observation of nodular growth at and around the intermediate $\alpha$ cases is in conflict with the proposed metallic impurity theory. In addition, under conditions which led to the formation of the whisker morphology, similar whiskers grew on portions of the substrates which were coated with carbon paint, which contains no metallic impurities.
A possible source of any metallic impurities is the MTS source. MTS may interact with the inner lining of the stainless steel bottle after several years of contact \(^{[149]}\). The byproducts of this interaction may be transition metal chlorides in the vapor phase. Hence, at the low (dilute) MTS vapor supply cases, the diffusion control of reactant through the boundary layer may be responsible for the growth of whiskers, while at the high MTS concentrations, the concomitant higher amounts of iron (for example) chlorides present in the supplied MTS stream may be above some critical amount of iron necessary for the growth of whiskers. However, for all MTS flow rates it is likely that the proportion between the MTS vapor and the impurity iron chloride vapor remains relatively constant. Hence, this scenario seems unlikely. If the impurity metal chloride vapor were present in constant proportion with the supplied MTS vapor, it is more probable that either whiskers would form all of the time or none of the time.

One possible scenario is that the whiskers grown at 20:1 are governed by the diffusion of the reactant through the boundary layer adjacent to the substrate, and the whiskers grown at 2:1 are controlled by the presence of metallic impurities. However, the whiskers grown at 2:1 and at 20:1 \(\alpha\) cases are remarkably similar in size and general shape. If different mechanisms are responsible for the whiskers observed at the two extreme \(\alpha\) ratios, the characteristics of the whiskers would be different, which is not the case. In addition, reports in the literature of whisker growth induced by the intentional addition of metallic impurities result in morphologies of whiskers much different than those grown in the present study.
Hence, one mechanism (not involving a metallic impurity) is believed to govern the growth of the whiskers at both the high and low $\alpha$ ratios studied.

The following scenario is believed to be responsible for the observed morphology - $\alpha$ relationship. Whiskers grown at both extreme $\alpha$ ratios tested grew under the control of diffusion of MTS to the substrate surface. At the higher $\alpha$ examined, the flux of MTS is retarded primarily as a result of two phenomena: (1) slower diffusion through HCl than through H$_2$, and (2) the streaming effect.

In contrast, at the lower $\alpha$ tested, the flux of MTS decreases primarily due to the low concentrations of MTS present. Hence, at an $\alpha$ of approximately $10^{2.5}$:1, a maximum MTS flux is predicted. This maximum MTS flux may be sufficient to cause the deposition reaction to be controlled by a combination diffusion of MTS, and reaction kinetics. The partial control of the deposition reaction by the reaction kinetics may be enough to result in the observed nodular growth. At either more dilute or more enriched MTS solutions, the flux of MTS is deficient enough the cause the deposition reaction to be governed predominantly by the diffusion of MTS, thereby resulting in the observed whisker growth.

Further work needs to be done in order to more precisely determine the growth mechanism(s) involved. For example, the SiC whiskers grown at the extreme ratios may be dissolved using any standard SiC etchants (KOH or NaOH @ 900 °C result in etch rates between 1.5 and 7 $\mu$m/min $^{[156]}$). Subsequent chemical analysis may be performed on these etchants, searching for iron or other elements thought to induce whisker growth. Alternatively, additional experiments
may be conducted at the same \( \alpha \) ratios previously examined, but using different (higher) flow rates. The flow rates may be adjusted by either flowing higher amounts of hydrogen and MTS, or by leaving those flow rates constant and introducing an inert flow of Ar into the reactor.

Increasing volumetric flow rates should alter the boundary layer thicknesses without affecting the diffusivity of MTS in the system, allowing for the examination of boundary layer thickness (and the concomitant MTS flux) on observed growth morphologies. Introducing Ar into the system, such that the total flow rates remain equivalent to those previously used, should affect the diffusivity of MTS more than the boundary layer thickness, and hence could be used to examine the effect of MTS diffusivity on the observed growth morphology.
CHAPTER VII

CONCLUSIONS

Thermodynamic equilibrium calculations were carried out on the Si - C - H - Cl system over a wide range of system temperature, pressure, and composition. The most prevalent gas species in the vapor phase were H₂ and HCl at the selected operating conditions, indicating that the net decomposition of CH₂SiCl₃ to form SiC and HCl adequately describes the system. CVD stability diagrams were calculated, indicating the composition of the condensed phase as a function of T, P, and gas composition. Increased temperatures or H₂:CH₂SiCl₃ volumetric ratios result in decreased amounts of C co-deposition.

A two-dimensional mathematical model was developed to predict the transport of mass, momentum, heat, and gas species within a vertically-oriented hot-walled CVD reactor. Deposition profiles were predicted along the surfaces of substrates in the form of either rods or discs, and compared to experimentally determined deposition profiles. The reaction constant and activation energy were deter-
determined for an Arrhenius type behavior of the MTS decomposition reaction. Good
agreement was obtained between the experimental and predicted deposition profiles.

Experiments were conducted to determine the relation between the morphology of the deposited SiC and the experimentally controllable parameters of temperature and \( \text{H}_2\text{CH}_3\text{SiCl}_3 \) ratio. The morphology of the SiC was essentially independent of temperature over the examined range. A strong dependence of SiC morphology on \( \text{H}_2\text{CH}_3\text{SiCl}_3 \) ratio was observed. Nodular SiC formed under intermediate gas compositions, while contorted whiskers grew at high and low gas ratios. The growth of whiskers in the enriched and dilute MTS gas trials is explained according to a diffusion-controlled growth mechanism.

FUTURE WORK

The nature of the governing mechanism(s) for whisker or nodular growth is not precisely known from the existing data. Further work needs to be done to isolate the growth mechanism(s) involved. For example, the SiC whiskers grown at the extreme ratios may be dissolved using any standard SiC etchants. Subsequent chemical analysis may be performed on these etchants, searching for iron or other elements thought to induce whisker growth.

Future experimental work could include the implementation of high temperature gas sensors capable of identifying the gas species adjacent to the substrate and hence responsible for the deposition of SiC. Other future experiments could include using the same \( \alpha \) ratios previously studied, but using different volumetric
flow rates. The flow rates may be adjusted by either increasing the amounts of H₂ and CH₂SiCl₃ by the same proportion, or by introducing an inert gas stream into the reactor along with the original flow rates of hydrogen and MTS. These experiments could identify whether the diffusivities and chemical boundary layer thicknesses are significant determinants of the resultant SiC morphology.

Two areas could be addressed regarding the enhancement of the mathematical model. The first of these is the enhancement of the rate of convergence. The grid generation and solution method used in the present study are known to be inferior to other methods already developed, although these other methods are typically much more difficult to encode [256]. Implementation of these newer algorithms would require starting the development of an entirely new model, which is beyond the scope of the present study.

The second area for enhancement would be the incorporation of homogeneous reactions. This step requires the knowledge of the kinetic data and physical property data for the newly included gas species, which often are missing from existing databases. The inclusion of homogeneous reactions into the current model would result in the ability to predict the composition of the deposited SiC (or whatever the CVD system of interest is). In addition, modeling of homogeneous reactions would allow the model to be applied in non-CVD systems, e.g. combustion chambers in jet or automobile engines. Results obtained by further experimentation and modeling can be applied toward the development of a model able to predict the morphological characteristics of coatings obtained via CVD.
APPENDIX A

EQUILIBRIUM VAPOR PHASE COMPOSITIONS vs. TEMPERATURE

Vapor phase compositions, as functions of temperature, based on the thermodynamic equilibrium calculations, at the examined system pressures and H₂:CH₃SiCl₃ molar ratios.
Figure 47. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a \( \text{H}_2:\text{CH}_3\text{SiCl}_3 \) molar ratio of 1:100.
Figure 48. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a \( \text{H}_2: \text{C}_2\text{H}_4 \text{SiCl}_3 \) molar ratio of 1:10.
Figure 49. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a $\text{H}_2:\text{CH}_3\text{SiCl}_3$ molar ratio of 1:1.
Figure 50. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a H₂:CH₃SiCl₃ molar ratio of 2:1.
Figure 51. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a $\text{H}_2$:$\text{CH}_3\text{SiCl}_3$ molar ratio of 5:1.
Figure 52. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a H₂:CH₃SiCl₃ molar ratio of 10:1.
Figure 53. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a H₂:CH₃SiCl₃ molar ratio of 20:1.
Figure 54. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a $\text{H}_2$:CH$_3$SiCl$_3$ molar ratio of 50:1.
Figure 55. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a H₂:CH₃SiCl₃ molar ratio of 100:1.
Figure 56.  Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 30 torr, and a H₂:CH₃SiCl₃ molar ratio of 1000:1.
Figure 57. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a $\text{H}_2\cdot\text{CH}_3\text{SiCl}_3$ molar ratio of 1:1.
Figure 58. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a H₂:CH₃SiCl₃ molar ratio of 2:1.
Figure 59. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a \( \text{H}_2: \text{CH}_3\text{SiCl}_3 \) molar ratio of 5:1.
Figure 60. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a $\text{H}_2\text{CH}_3\text{SiCl}_3$ molar ratio of 20:1.
Figure 61. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a $\text{H}_2$:$\text{CH}_3\text{SiCl}_3$ molar ratio of 50:1.
Figure 62. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a H₂:CH₃SiCl₃ molar ratio of 100:1.
Figure 63. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 90 torr, and a H₂:CH₃SiCl₃ molar ratio of 1000:1.
Figure 64. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a $\text{H}_2\cdot\text{CH}_3\text{SiCl}_3$ molar ratio of 1:1.
Figure 65. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a H₂:CH₃SiCl₃ molar ratio of 2:1.
Figure 66. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a $\text{H}_2: \text{CH}_3\text{SiCl}_3$ molar ratio of 5:1.
Figure 67. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a H₂:CH₃SiCl₃ molar ratio of 10:1.
Figure 68. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a H$_2$:CH$_3$SiCl$_3$ molar ratio of 20:1.
Figure 69. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a H₂:CH₃SiCl₃ molar ratio of 50:1.
Figure 70. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a \( \text{H}_2 \cdot \text{CH}_3\text{SiCl}_3 \) molar ratio of 100:1.
Figure 71. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 150 torr, and a H$_2$:CH$_3$SiCl$_3$ molar ratio of 1000:1.
Figure 72. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a H₂:CH₃SiCl₃ molar ratio of 1:1.
Figure 73. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a H₂:CH₃SiCl₃ molar ratio of 2:1.
Figure 74. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a $\text{H}_2:\text{CH}_3\text{SiCl}_3$ molar ratio of 5:1.
Figure 75. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a $\text{H}_2$:CH$_3$SiCl$_3$ molar ratio of 10:1.
Figure 76. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a $H_2:CH_3SiCl_3$ molar ratio of 20:1.
Figure 77. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a $\text{H}_2:\text{CH}_3\text{SiCl}_3$ molar ratio of 50:1.
Figure 78. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a H$_2$:CH$_3$SiCl$_3$ molar ratio of 100:1.
Figure 79. Variation in the calculated thermodynamic equilibrium composition of the vapor phase as a function of temperature, for a total system pressure of 300 torr, and a $\text{H}_2:\text{CH}_3\text{SiCl}_3$ molar ratio of 1000:1.
APPENDIX B

EQUILIBRIUM CONDENSED PHASE COMPOSITIONS vs. TEMPERATURE

Variation in composition of condensed phase with temperature, based on the thermodynamic equilibrium calculations, in which each plot represents a specific $\text{H}_2$:$\text{CH}_3\text{SiCl}_3$ ratio, for all examined pressures.
Figure 80. Composition of condensed phase as a function of temperature, for a
$\text{H}_2$:$\text{CH}_3\text{SiCl}_3$ ratio of 1:1, for all examined pressures.
Figure 81. Composition of condensed phase as a function of temperature, for a $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio of 2:1, for all examined pressures.
Figure 82. Composition of condensed phase as a function of temperature, for a $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio of 5:1, for all examined pressures.
Figure 83. Composition of condensed phase as a function of temperature, for a $\text{H}_2$:$\text{CH}_3\text{SiCl}_3$ ratio of 20:1, for all examined pressures.
Figure 84. Composition of condensed phase as a function of temperature, for a $\text{H}_2\cdot\text{CH}_3\cdot\text{SiCl}_3$ ratio of 50:1, for all examined pressures.
Figure 85. Composition of condensed phase as a function of temperature, for a 
$\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio of 100:1, for all examined pressures.
Figure 86. Composition of condensed phase as a function of temperature, for a \( \text{H}_2:\text{CH}_3\text{SiCl}_3 \) ratio of 1000:1, for all examined pressures.
EQUILIBRIUM CONDENSED PHASE COMPOSITIONS vs. PRESSURE

Variation of condensed phase composition versus temperature, based on the thermodynamic equilibrium calculations, in which each plot displays data for a specific pressure, for all H₂:CH₃SiCl₃ ratios examined.
Figure 87. Variation of the condensed phase composition as a function of temperature, for the system pressure of 30 torr, and evaluated $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratios in the range 1:100 - 5:1.
Figure 88. Variation of the condensed phase composition as a function of temperature, for the system pressure of 30 torr, and all evaluated \( \text{H}_2: \text{CH}_3\text{SiCl}_3 \) ratios in the range 10:1 - 1000:1.
Figure 89. Variation of the condensed phase composition as a function of temperature, for the system pressure of 150 torr, and all evaluated $H_2:\text{CH}_3\text{SiCl}_3$ ratios.
Figure 90. Variation of the condensed phase composition as a function of temperature, for the system pressure of 300 torr, and all evaluated H₂:CH₃SiCl₃ ratios.
Appendix D

Equilibrium Condensed Phase Compositions vs. H$_2$\textcdot$\text{CH}_3$SiCl$_3$ Ratio

Variation in the condensed phase composition as a function of the H$_2$\textcdot$\text{CH}_3$SiCl$_3$ ratio, based on the thermodynamic equilibrium calculations, in which each plot represents a specific temperature of evaluation, for all tested pressures.
Figure 91. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1000 K, and all examined pressures.
Figure 92. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1100 K, and all examined pressures.
Figure 93. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1200 K, and all examined pressures.
Figure 94. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1300 K, and all examined pressures.
Figure 95. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1400 K, and all examined pressures.
Figure 96. Composition of condensed phase as a function of $\text{H}_2\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1500 K, and all examined pressures.
Figure 97. Composition of condensed phase as a function of $H_2:CH_3SiCl_3$ ratio, for the evaluated temperature of 1700 K, and all examined pressures.
Figure 98. Composition of condensed phase as a function of $\text{H}_2: \text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1800 K, and all examined pressures.
Figure 99. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 1900 K, and all examined pressures.
Figure 100. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 2000 K, and all examined pressures.
Figure 101. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 2100 K, and all examined pressures.
Figure 102. Composition of condensed phase as a function of $\text{H}_2:\text{CH}_3\text{SiCl}_3$ ratio, for the evaluated temperature of 2200 K, and all examined pressures.
APPENDIX E

HEAT CAPACITY EXPRESSIONS

Heat capacity expressions for the gas phase components, units J/kg-K.

The heat capacity for hydrogen can be expressed as

\[ C_{p, \text{H}_2} = 27.14 + 0.927 \times 10^{-2} \cdot T \\
- 0.138 \times 10^{-4} \cdot T^2 + 0.765 \times 10^{-8} \cdot T^3 \]  (29)

Similar expressions have been evaluated for the heat capacities for HCl and CH₃SiCl₃, as shown by

\[ C_{p, \text{HCl}} = 30.67 - 0.720 \times 10^{-2} \cdot T \\
+ 0.125 \times 10^{-4} \cdot T^2 - 0.390 \times 10^{-8} \cdot T^3 \]  (30)

and
The heat capacity for the gas of a general composition was calculated based on the following expression:

$$C_{p, \text{(ave)}} = \sum_{i=1}^{f} m_i C_{p,i}$$

(32)

where $m_i$ is each component's mass fraction, $C_{p,i}$ is the heat capacity for each individual component and $f$ is the total number of species present in the calculations (in this case $f=3$).

Table 10, shown below, gives a few examples of some representative values for the heat capacities of each individual component species.
Table 10. Heat Capacity Values for the Studied Gas Phase Components, [J/kg·K].

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$H_2$</th>
<th>HCl</th>
<th>CH$_2$SiCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$3.025\times10^1$</td>
<td>$3.203\times10^1$</td>
<td>$7.741\times10^2$</td>
</tr>
<tr>
<td>1200</td>
<td>$3.159\times10^1$</td>
<td>$3.323\times10^1$</td>
<td>$7.666\times10^2$</td>
</tr>
<tr>
<td>1400</td>
<td>$3.404\times10^1$</td>
<td>$3.431\times10^1$</td>
<td>$7.606\times10^2$</td>
</tr>
<tr>
<td>1600</td>
<td>$3.793\times10^1$</td>
<td>$3.508\times10^1$</td>
<td>$7.543\times10^2$</td>
</tr>
</tbody>
</table>
APPENDIX F

THERMAL CONDUCTIVITY EXPRESSIONS

Thermal conductivity calculations for use in the mathematical model, units J/m·s·K.

The temperature dependent thermal conductivity for hydrogen can be expressed as

\[ k_H = 0.810 \times 10^{-2} + 0.669 \times 10^{-3} \cdot T - 0.416 \times 10^{-4} \cdot T^2 + 0.156 \times 10^{-9} \cdot T^3 \]  \hspace{1cm} (33)

Similar relationships have been made for the temperature dependencies of the thermal conductivities of HCl and CH₃SiCl₃, and are given by
\[ k_{NCl} = -0.109 \times 10^{-3} + 0.531 \times 10^{-4} \cdot T \]
\[ - 0.105 \times 10^{-7} \cdot T^2 + 0.670 \times 10^{-12} \cdot T^3 \]  
(34)

and

\[ k_{(CH_4,Cl_2)} = -0.346 \times 10^{-2} + 0.450 \times 10^{-4} \cdot T - 0.116 \times 10^{-7} \cdot T^2 \]
\[ + 0.491 \times 10^{-12} \cdot T^3 + 0.475 \times 10^{-15} \cdot T^4 \]  
(35)

An average thermal conductivity for a gas mixture may be calculated according to the following expression:

\[ k_{\text{ave}} = \frac{\sum_{i=1}^{f} [k_i \cdot \chi_i \cdot (M_i)^{\frac{1}{3}}]}{\sum_{i=1}^{f} [\chi_i \cdot (M_i)^{\frac{1}{3}}]} \]  
(36)

where \( \chi_i \) is the mole fraction of species \( i \), \( M_i \) is the molecular weight of species \( i \), \( k_i \) is the thermal conductivity of species \( i \), and \( f \) is the number of species present in the gas phase (in this case \( f=3 \)).

Table 11 as shown below gives examples of the characteristic values obtained from the expressions above for the thermal conductivity of the individual species at various temperatures.
Table 11. Thermal conductivity values for each of the individual gas species at various temperatures, units [\(\text{J/m-s-K}\)].

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>(\text{H}_2)</th>
<th>(\text{HCl})</th>
<th>(\text{CH}_3\text{SiCl}_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>4.170x10^{-1}</td>
<td>4.315x10^{-2}</td>
<td>3.090x10^{-2}</td>
</tr>
<tr>
<td>1200</td>
<td>4.820x10^{-1}</td>
<td>4.964x10^{-2}</td>
<td>3.567x10^{-2}</td>
</tr>
<tr>
<td>1400</td>
<td>5.580x10^{-1}</td>
<td>5.549x10^{-2}</td>
<td>3.997x10^{-2}</td>
</tr>
<tr>
<td>1600</td>
<td>6.540x10^{-1}</td>
<td>6.074x10^{-2}</td>
<td>4.395x10^{-2}</td>
</tr>
</tbody>
</table>
APPENDIX G

VISCOSITY EXPRESSIONS

Viscosity calculations for use in the mathematical model, units kg/m·s.

The following expression may be used for calculating the viscosity of hydrogen:

\[
\mu_{H_2} = 0.217 \times 10^{-5} + 0.255 \times 10^{-7} \cdot T - 0.108 \times 10^{-19} \cdot T^2 \\
+ 0.439 \times 10^{-14} \cdot T^3 - 0.767 \times 10^{-18} \cdot T^4
\]  \( (37) \)

where \( \mu_{H_2} \) is the viscosity of hydrogen and \( T \) is the absolute temperature in Kelvin. Similar expressions were derived to show the temperature dependencies of HCl and \( \text{CH}_2\text{SiCl}_3 \); these are shown in the following two relationships:
\[ \mu_{HCl} = -0.147 \times 10^{-3} + 0.583 \times 10^{-7} \cdot T - 0.146 \times 10^{-10} \cdot T^2 \]

\[ + 0.114 \times 10^{-14} \cdot T^3 + 0.397 \times 10^{-18} \cdot T^4 \]  \hspace{1cm} (38)

and

\[ \mu_{CH_4,Cl_1} = -0.102 \times 10^{-5} + 0.443 \times 10^{-7} \cdot T - 0.116 \times 10^{-10} \cdot T^2 \]

\[ + 0.104 \times 10^{-14} \cdot T^3 + 0.290 \times 10^{-18} \cdot T^4 \]  \hspace{1cm} (39)

respectively.

In order to determine the average viscosity of a gas containing multiple species inside any particular control volume, the following equations are used:

\[ \mu_{mix} = \sum_{i=1}^{f} \sum_{j=1}^{f} x_i \cdot x_j \cdot \Phi_{ij} \]  \hspace{1cm} (40)

in which

\[ \Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-\frac{1}{2}} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left( \frac{M_i}{M_j} \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} \]  \hspace{1cm} (41)

where \( f \) is the number of chemical species in the mixture, \( x_i \) and \( x_j \) are the mole fractions of species \( i \) and \( j \), \( \mu_i \) and \( \mu_j \) are the viscosities of species \( i \) and \( j \) at that particular temperature and pressure, and \( M_i \) and \( M_j \) are the molecular weights of species \( i \) and \( j \). It should be noted that \( \Phi_{ij} \) is dimensionless, and when \( i = j \), \( \Phi_{ij} = 1 \).
The following table (Table 12) shows representative values of the viscosities of the individual gas phase mixture components at the same temperatures as the preceding tables located in the Appendix section.

Table 12. Representative viscosity values for the individual gas phase mixture species at various temperatures, units [=] kg/m·s.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Component</th>
<th>( \text{H}_2 )</th>
<th>HCl</th>
<th>( \text{CH}_3\text{SiCl}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td></td>
<td>( 2.205 \times 10^{-4} )</td>
<td>( 4.381 \times 10^{-5} )</td>
<td>( 3.307 \times 10^{-5} )</td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td>( 2.642 \times 10^{-4} )</td>
<td>( 5.032 \times 10^{-5} )</td>
<td>( 3.792 \times 10^{-5} )</td>
</tr>
<tr>
<td>1400</td>
<td></td>
<td>( 3.175 \times 10^{-5} )</td>
<td>( 5.625 \times 10^{-5} )</td>
<td>( 4.234 \times 10^{-5} )</td>
</tr>
<tr>
<td>1600</td>
<td></td>
<td>( 3.840 \times 10^{-5} )</td>
<td>( 6.179 \times 10^{-5} )</td>
<td>( 4.647 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
APPENDIX H

DIFFUSIVITY EXPRESSIONS

Diffusivity expressions and representative values for each of the solute gas species present in this study, i.e. HCl and CH₂SiCl₃, units m²/s.

A major assumption here is that the diffusion coefficients as calculated are binary coefficients; that is, the concentration magnitude of the solute gases is sufficiently dilute such that the diffusion coefficients have no dependence on the other solute gases present. The solute species are assumed to not interact with each other in such a way as to alter the diffusivities of said species. With this in mind, the diffusivities of HCl and CH₂SiCl₃ are assumed to only depend on temperature and pressure (and of course the solvent species). Accordingly, the expression which describes the diffusivity of HCl in hydrogen can be written as:
\[ D_{\text{HCl},T} = \left( 0.800 \times 10^{-7} - 0.648 \times 10^{-9}T + 0.308 \times 10^{-11}T^2 \right) \]
\[ \times \left( + 0.228 \times 10^{-14}T^3 - 0.201 \times 10^{-18}T^4 \right) \frac{0.112 \times 10^5}{\text{Pressure}^{0.7}} \] (42)

Along these same lines, an expression which describes the diffusivity of CH\textsubscript{3}SiCl\textsubscript{3} in hydrogen can be written as:

\[ D_{\text{CH}_3\text{SiCl}_3,T} = \left( -0.152 \times 10^{-7} + 0.233 \times 10^{-9}T + 0.403 \times 10^{-12}T^2 \right) \]
\[ \times \left( -0.950 \times 10^{-16}T^3 + 0.141 \times 10^{-19}T^4 \right) \frac{R}{\text{Pressure}} \] (43)

wherein the value of R has been estimated to be \(0.395 \times 10^7\). In both of these expressions the pressure has units of Pascal, and the diffusivities have units of m\textsuperscript{2}/s.

Based on these expressions, the following table (Table 13) shows some representative values for the diffusivities of both HCl and CH\textsubscript{3}SiCl\textsubscript{3} in H\textsubscript{2}, for the same selected temperatures as in the tables above.
Table 13. Representative binary diffusion coefficient values of HCl and CH$_3$SiCl$_3$ solutes in hydrogen (diluent), units [=] m$^2$/s.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>HCl</th>
<th>CH$_3$SiCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>5.012x10^{-5}</td>
<td>1.065x10^{-4}</td>
</tr>
<tr>
<td>1200</td>
<td>7.926x10^{-5}</td>
<td>1.400x10^{-4}</td>
</tr>
<tr>
<td>1400</td>
<td>1.167x10^{-4}</td>
<td>1.764x10^{-4}</td>
</tr>
<tr>
<td>1600</td>
<td>1.632x10^{-4}</td>
<td>2.155x10^{-4}</td>
</tr>
</tbody>
</table>


77. Minato, K. and Fukuda, K., "Structure of Chemically Vapour Deposited Silicon Carbide for Coated Fuel Particles".


149. Private communication with Sankar Sambasivan, May, 1993.


158. J. Guth from WL/MLLM, Wright-Patterson Air Force Base, performed these experiments and measured the SiC deposit thickness.