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Chemical Vapor Deposition Modeling for High Temperature Materials

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FOR HIGH TEMPERATURE MATERIALS

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SUMMARY

The formalism for the accurate modeling of chemical vapor deposition (CVD) processes has matured based on the well established principles of transport phenomena and chemical kinetics in the gas phase and on surfaces. The utility and limitations of such models are discussed in practical applications for high temperature structural materials. Attention is drawn to the complexities and uncertainties in chemical kinetics. Traditional approaches based on only equilibrium thermochemistry and/or transport phenomena are defended as useful tools, within their validity, for engineering purposes. The role of modeling is discussed within the context of establishing the link between CVD process parameters and material microstructures/ properties. It is argued that CVD modeling is an essential part of designing CVD equipment and controlling/optimizing CVD processes for the production and/or coating of high performance structural materials.

INTRODUCTION

Among the available methods for fabricating materials from the gas phase, chemical vapor deposition (CVD) provides many diverse opportunities for commercial application because it is more economical to develop and easier to scale up. Indeed, its versatility allows CVD to be routinely employed in various areas of materials science and technology. However, as the interest and demand in more sophisticated advanced materials grows to meet today's more stringent performance requirements, it is becoming clearer that the CVD technique should be better exploited.

Structural materials have not generally received the same degree of attention in terms of the precision of the CVD process during their fabrication as the electronic and optical materials. However, this is no longer the case.

A sufficient understanding of the interactive physicochemical phenomena involved in CVD is required to efficiently produce novel materials with superior properties. Therefore, modeling of such complex systems is now recognized to be an essential and integral part of CVD research.

The controlled implementation of the CVD process is an interdisciplinary effort involving many different fields of science and engineering. A comprehensive analysis should naturally include gas phase and surface chemical reaction kinetics, heat and multicomponent mass transport, fluid physics, and thermodynamics (ref. 1). The simultaneous description of the coupled phenomena in multidimensions with multireaction schemes obviously requires highly efficient computational software and hardware (ref. 2). The analysis should be fully supported by the measurement, testing and characterization techniques that are available to specialists in heat transfer, fluids, chemistry and materials science.

The modeling of the interactions of such multiparameter systems is indeed a challenge. One has only the directly controllable parameters of the system to manipulate the properties of the coated or fabricated material. These available CVD input variables can be the substrate temperature, reactor pressure, reactant gas composition, or the total flow rate. However, the factors that affect the material property more directly are the growth rate, chemical composition, doping or impurity levels, and microstructure of the deposit material, all of which are also interrelated. All of these latter factors are, in turn, influenced by the convective, thermal and chemical species' concentration fields that prevail inside CVD reactors based on the directly controlled operating parameters. The role of CVD modeling in assisting the process optimization and control is to shed some light onto the transport and chemical processes evolving inside CVD reactors and governing the key factors that determine the resulting material properties. The modest capabilities of CVD modeling today is mostly restricted to accurate growth rate and some deposit chemical composition predictions for only limited materials, and is far from being able to correctly predict doping/impurity levels in the deposit or provide an indication of evolving microstructures. Yet, before undertaking the challenge of improving the material microstructure/property at the chemical and/or materials science level, there are still many useful ways of utilizing modeling in terms of obtaining more rational flow and thermal fields inside CVD reactors. In that respect, by assisting CVD equipment manufacturers for better designs, modeling has taken the established CVD technology back almost a decade!

So far most sophisticated CVD models have been developed for electronic material applications. A review of the current status of CVD modeling is given in references 1 and 3. With increasing interest on advanced structural materials and emphasis for high temperature applications, modeling efforts addressing these issues specifically have recently started to appear in the literature. Besides the papers related to modeling chemical vapor infiltration (CVI) processes, which this paper will not discuss, examples of such efforts are the recent publications related to the CVD synthesis or coating of continuous fibers, which are used for the reinforcement of (inter)metallic and ceramic matrices (refs. 4 to 6).

Because of the emphasis on high temperature applications of structural materials, exposure of the materials to high temperatures during the CVD process is not necessarily disadvantageous. In fact, it may even be desirable to ascertain that the material/coating will survive temperatures as high as at least the intended service temperature. Therefore, some of the advantages of low temperature, such as plasma-enhanced, CVD for electronic material applications do not apply to materials which are expected to be used, for example, in the hot sections of the turbine engine for aeropropulsion applications. Therefore, this paper is limited to modeling only subatmospheric and atmospheric thermal CVD processes and excludes others such as very low pressure, plasma-enhanced or photo-assisted CVD.

APPROACHES TO CVD MODELING

The sophistication levels of the approaches taken to model CVD processes vary depending on the objectives of the effort, the level of complexity, and the availability of thermodynamic, transport and/or chemical kinetic data. Generally, CVD modeling efforts can be categorized as either approaches based on thermochemical equilibrium calculations or dynamic approaches where rate issues are addressed based on the transport and chemical kinetic phenomena.

Thermochemical Equilibrium

Inspired by the conventional phase diagrams, thermochemical equilibrium calculations are used to obtain "CVD phase diagrams." Computer programs, such as those based on free-energy minimization (e.g., SOLGASMIX and NASA CEC (refs. 7 and 8)), are utilized frequently to predict possible windows of operation to deposit the desired materials for given parameter ranges of temperature, pressure and elemental composition.

The limitations and reliability of such an equilibrium-based approach are, naturally, due to finite rate phenomena such as gas phase transport and/or chemical kinetics. Besides their inability to predict the rates of deposition, such approaches also fail to account for the shifts of the deposit material from the equilibrium phases and compositions. A trivial example of the deficiency of the method can be given as follows: although one can predict the deposition of silicon from silane even at room temperature, it does not occur in real life because of kinetic barriers. Conversely, successful deposition of silicon nitride can be accomplished from silicon tetrafluoride and ammonia precursors as demonstrated at the United Technologies Research Center: here conditions that are substantially outside the predicted region for stable silicon nitride formation have been used (ref. 9). Numerous other examples of such departures from equilibrium behavior are observed and reported in the literature.

However, thermochemical equilibrium calculations can still be useful tools for initial feasibility studies, providing guidance for the formation of possible gaseous species and condensed phases of different chemical composition. In fact, their capability to explain the observed deposit chemical composition variation along the deposition surface has been demonstrated, if judiciously applied by considering the **local** variations of temperature, pressure and gas composition (ref. 10). Such treatments are expected to be even more accurate at higher temperature thermal CVD applications, i.e., for high temperature structural materials, where chemical equilibria are approached. Furthermore, it may be the only available rational approach for complex multicomponent chemical systems, as is the case for the deposition of superconducting materials (refs. 11 and 12) or the codeposition of different compounds (ref. 13). The severe lack of chemical kinetic information for many systems of interest and the uncertainties associated with the available kinetic data render the equilibrium approach still very useful.

Gas Phase Transport Phenomena

With the increasing availability of elaborate transport models based on the well established principles of fluid dynamics, heat, and mass transfer, accurate predictions of flow, thermal and concentration fields in complex shaped CVD reactors are quite possible today (ref. 14). In fact, the capability to predict flow and thermal fields in reactors with steep temperature gradients (~1000 K/cm) has probably been the largest contribution of CVD modeling in helping the equipment manufacturers design better reactors. Providing answers to such questions as the proper location of gas inlet and exit ports, the proper positioning of the substrate, the proper operating conditions and geometrical considerations to avoid buoyancy-driven free convection flows, and the proper heating and cooling of the reactor system to obtain more uniform thermal fields around the substrate are only a few examples where modeling has had a considerable impact to improve performances of different CVD reactors.

Figure 1 is a demonstration of how a computational fluid dynamics code may be used to predict the complex flow structures that can develop in a laboratory-scale cold-wall reactor with an inductively heated rectangular substrate. It is shown (by the presence (top case) and absence (bottom case) of the terrestrial gravitational field) that gravitationally-induced free convection flows are responsible for both the recirculation cell created in front of the substrate and the three-dimensional helical flow around the substrate. It is interesting to note that the incoming flow is directed towards the bottom of the hot substrate by the presence of the recirculation cell and will, therefore, supply uneven amounts of source gases to top and bottom surfaces, which will lead to asymmetric deposit thickness profiles.

Despite the maturity of the computational transport codes, one has to still be very cautious of the assumptions involved for their application to each specific case. The validity of using the Boussinesque approximation (versus using the explicit temperature dependence of gas density in the gravitational body force term of the momentum conservation equation), the treatment of the dependence of the fluid transport and thermodynamic properties on temperature and composition, the inclusion of the effects of Soret diffusion, and the proper accounting for radiative heat transfer are typical questions to be addressed for evaluating the suitability of available models. Also, for nondilute source gas mixtures, one has to consider the heats of reaction for both gas phase and surface reactions, as well as the nonzero gas velocity normal to the deposition surface, the so-called Stefan flow. Such additional complications naturally make the models more cumbersome and increase the coupling among the momentum, energy and species mass conservation equations. As a consequence, one pays a severe penalty in computational complexity and time. It is, therefore, imperative to select the level of sophistication of the model judiciously.

Sophisticated models can give quite inaccurate solutions because of the improper implementation of boundary conditions. Therefore, it is critical to realize, for example, that the use of constant temperature or adiabatic wall boundary conditions does not correctly describe the role of radiation or the coupled interaction of the environment with the CVD system (ref. 15). Asymmetric and other unexpected flow and temperature fields are observed and can be predicted by using more realistic boundary conditions (ref. 16). For a correct description of the temperature distribution on the solid surfaces inside a CVD reactor, conjugate heat transfer analyses (where the coupled gas and solid phase temperature profiles are simultaneously solved) are becoming increasingly necessary.

In the case of CVD processing of fibers, continuous operation is a practical consideration to produce economically feasible quantities of continuous lengths. Therefore, models should be capable of treating the time-dependent growth process coupled with the associated dimensional changes of the fiber.

In cases where the prevailing molecular mean free path becomes comparable to the characteristic dimensions of interest (e.g., fiber diameter), the applicability of the transport equations based on the continuum approximations starts becoming questionable. This is analogous to the Knudsen diffusion situation for CVI processes where the pore size becomes comparable to or smaller than the molecular mean free path. Considering the increasing interest in CVD processing of smaller diameter fibers ($<\sim 25$ μm), especially for ceramic matrix composites, it is doubtful if conventional models can accurately describe the transport processes in high temperature and low pressure CVD systems involving such small diameter fibers. For such cases, molecular trajectory calculation techniques can be utilized by employing, for example, the Monte Carlo direct simulation method.

Gas Phase and Surface Chemical Kinetics

The availability and reliability of gas phase and surface kinetic information are currently the most limiting factors in CVD modeling. The mechanisms, pathways and kinetics of many of the reaction systems of interest to the CVD community are scarcely known. Yet, models should be able to account for reactive species inventories and depletion rates in the gas phase. Surface phenomena such as adsorption, diffusion, nucleation, incorporation, or desorption must appear as boundary conditions in such simulations. Because of the difficulties associated with obtaining experimental kinetic data for the extensive sets of possible reactions under relevant conditions, theoretical techniques utilizing quantum chemistry and electronic structures are being increasingly employed for the required thermochemistry. Table I lists the number of gas phase and surface reactions that have been used in recent CVD models for some of the material systems of interest. Excess hydrogen is the carrier gas for all cases.

As can be seen from table I, the number of simultaneous gas phase and surface reactions, and therefore, the species, necessary to properly model even single element deposit materials can be as high as tens to hundreds. The kinetic rate expressions of these reactions are obtained from theoretical calculations. Usually, the numerical difficulties associated with significant differences among the characteristic times of reactions and transport processes (the so-called "stiff" systems) have been known to create additional challenges. Such expected difficulties in CVD cannot always be circumvented by the schemes and algorithms usually developed for the computational fluid dynamics of high-speed, chemically reacting flows. Furthermore, unlike the simpler geometries used by the references listed in table I, most realistic industrial applications will involve three-dimensional systems demanding prohibitive computer power, which even today's "personal" Cray's cannot meet with so many species and reactions! Therefore, the demand for "smarter" methodologies, not only relying on numerical techniques but also exploiting the available physicochemical information, will indeed be growing. To that effect, an approach, for example, utilizing a statistical design of computational experiments can be used in order to reduce the excessively large sets of reactions down to a more feasible and manageable size which can mimic the actual behavior of the chemical system (ref. 22).

Another issue of concern for CVD modeling is the degree of uncertainty regarding the chemical kinetic parameters of reaction systems. Besides the questions related to the low pressure limits of the rate constants, one also has to be careful about the temperature ranges of applicability of the reported rate constants for high temperature CVD systems because many of these values are obtained for lower temperature electronic material applications. Even for the most studied case of silicon deposition from silane, there seems to be no consensus on the reaction kinetics of either gas phase or surface kinetics. Table II lists the different rate constants reported only in the most recent literature for the gas phase dissociation of silane into silylene and hydrogen in a hydrogen bath gas.

Similar to gas phase chemistry, the controversies and inconsistencies related to surface kinetics for silicon deposition from silane have been recently discussed by reference 26, i.e., the experimentally observed reaction efficiencies vary by more than two orders of magnitude for nominally identical conditions and the deposition rates obtained at low temperatures and very low pressures are comparable to those obtained at high temperatures and atmospheric pressure. The disagreements have continued in 1990 and 1991 as evidenced by the different expressions published by references 25 and 27 for the reactive sticking coefficients of SiH_4 and Si_2H_6 on silicon surfaces.

Under the circumstances, expecting CVD models to be able to accurately predict the minute levels of dopant or impurity concentrations evolving in the deposit material during their in-situ deposition is currently unrealistic. Yet, it should be mentioned that the limitation is not due to the lack of a plausible formalism to incorporate such treatments into CVD models but is due to the unavailability and/or uncertainty of chemical kinetic information.

It seems that CVD modeling can be most helpful in areas where chemical kinetic limitations due to gas phase and/or surface reactions are minimal, i.e., in the gas phase mass transport controlled regime. After all, it would certainly be desirable to operate under such conditions where the deposition rates and source gas utilization would be maximized. The limitations of chemical kinetic barriers can be circumvented by increasing CVD temperatures. In principle, this should be less of a concern for high temperature materials (cf., electronic materials) up to their intended service temperatures or the limit of endurance for the substrate material. Provided the kinetic barriers are overcome, one can then use thermochemical equilibrium calculations at surface conditions to define the chemical composition of the deposit and the boundary conditions for the species mass transport equations (ref. 28).

However, at higher temperatures one has to consider another potential problem of gas phase powder formation. The prevailing supersaturation levels can be sufficiently high for the reactive precursors created at high temperatures to lead to gas phase nucleation and particle formation. Therefore, one needs to define the safe operation boundaries to preclude the usually very sudden onset of gas phase nucleation (ref. 29).

AN EXAMPLE CASE: FIBER CVD

CVD modeling of thin fibrous substrates encompasses specific problems that are not encountered for other typical substrates with flat surfaces (refs. 4 to 6). The chemical and structural complexity of the Textron SCS-6 SiC fiber grown by a continuous CVD process, as is schematically depicted in figure 2, is a good example of how changes in CVD conditions may lead to cross-sectional variations in chemical compositions and microstructures (ref. 30). In an endeavor to study the relationships between process variables and deposit compositions, microstructures and properties, we modeled a miniature Textron CVD reactor built in our laboratory. It is an upflow batch reactor made of a quartz tube of 1.8 cm I.D. and adjustable length. The monofilament is resistively heated. Silicon deposition from silane is chosen because of its better studied gas phase and surface chemistry and relevance to other silicon-based CVD materials of high temperature interest. The results are presented for the first 20 cm from the inlet. A more detailed discussion is given reference 6.

The axisymmetric geometry of the reactor with a thin hot fiber at the center creates very steep temperature gradients (~10000 K/cm versus 1000 K/cm in conventional geometries) near the fiber surface. This results in such atypical Soret diffusion effects that Soret becomes one of the primary gas transport mechanisms, i.e., predicted growth rates change by a few hundred percent with and without its inclusion in the model (fig. 3). Hence, accurate information for such transport coefficients is essential for the reliability of fiber CVD models. Furthermore, the sensitivity of predicted rates on fiber temperature indicates that the accurate measurement and control of fiber temperature is of utmost importance to controlling rates.

The higher temperature region within ~250 μm from the fiber surface is also the chemically active region where most of the SiH_2 production, which governs the deposition rate of silicon, occurs. Therefore, the above discussed uncertainties of the chemical kinetic parameters, which may not give significant differences in predicted Si deposition rates for conventional flat plate-like geometries, result in unacceptably magnified rate predictions depending on whose data is used from table II (ref. 6).

The significance of the steep temperature gradients near the fiber surface and, consequently, the amplified importance of Soret diffusion and chemical kinetics increase even more as the fiber diameter gets smaller. Therefore, the correct prediction of temperature fields inside the cold wall fiber reactor becomes of paramount importance. In predicting the wall temperatures for typical operating conditions of our fiber CVD reactor, it is determined that radiation has a strong contribution especially for low thermal conductivity gases (fig. 4). However, if radiation is fully accounted for, accurate predictions of wall temperatures are indeed possible (ref. 31).

Radial growth rates on the fiber will vary with respect to the fiber diameter. However, besides this expected change, which should scale with the available deposition surface area, there are other less obvious interactions of growth rate with fiber diameter as a consequence of the above mentioned temperature profile, Soret and chemistry effects (fig. 5).

The specific issues pertaining to cold wall fiber CVD for high temperature applications creates more challenges for CVD modeling, for both batch and continuous modes of reactor operation. Furthermore, with increasing interest in smaller diameter fibers, most of these issues, such as the atypical importance of Soret diffusion, the unusually stringent accuracy requirement for the chemical kinetic parameters, or the complex interaction of deposition rates with fiber diameter, get even more difficult to tackle.

FUTURE RECOMMENDATIONS AND CLOSING REMARKS

Despite the present limitations of CVD modeling in providing immediate solutions to the complex problems associated with various reactors, different chemical systems and applications, the utility of CVD modeling cannot be disputed in assisting the resolution of many existing issues. It can provide invaluable insights into the complex physicochemical phenomena taking place inside CVD reactors, provided that one is conscientious about its current capabilities and cognizant of its anticipated future challenges. It is certainly helpful for confirming and enhancing our understanding of the process. CVD models can be routinely used for designing more efficient reactor geometries and optimizing gas inlet, outlet and substrate configurations. They can go beyond predicting qualitative trends and are increasingly being used to obtain accurate quantitative predictions of deposition rates and deposit chemical compositions.

The usefulness and beauty of presenting information in a “universal” format, for example by using dimensionless variables, have long been recognized by scientists and engineers. The use of CVD phase diagrams is partly such an approach which condenses the various operating conditions of different systems into a general form by utilizing the fundamentals of equilibrium thermodynamics. The limitations of such an approach due to transport and chemical kinetic phenomena are discussed above. Attempts have been made in the literature to incorporate the effects of transport-induced shifts into CVD phase diagrams (ref. 32). However, their inability to give information about rates and be applicable to different reactor geometries still limit their utility for practical applications. The growing volume of CVD literature is certainly increasing the burden of gleaning useful information from publications to apply to a different situation. Currently, technical papers related to CVD are being published at a rate of about two articles a day. The need to find more general ways of reporting information in the CVD literature is greater than ever today. Such an approach is also essential for scaling up laboratory research to industrial size production. In an attempt to unify the efforts to establish the link between process parameters and material microstructures, it is suggested that a generic plot, as is shown in figure 6, be explored, at least for the same material systems using the same chemical precursors as source gases. It is inspired by the structural zone model proposed by Thornton (ref. 33) for physical vapor deposition systems. The suggested coordinates could be, for example, the local growth rates normal to the deposition surface and the surface temperature, which could be nondimensionalized with respect to the activation energy of the relevant surface phenomenon. A similar graph is given in reference 9. Even if the data of different investigators fail to collapse into a common form when cast into such a format, it is anticipated that the differences will be reduced and the analysis will be simplified. Once, and if, such a "universal" diagram is constructed for a chemical system by complimentary experimentation, then the loop would be closed by reducing the goal of CVD modeling to accurate rate and deposit composition predictions which is more feasible.

The accuracy and reliability of CVD models will undoubtedly depend on their verification by carefully controlled experiments and the quality of the transport, thermodynamic and chemical kinetic data supplied to them. Thus, developing high fidelity models and improving the confidence levels for their use are directly coupled with experimentation for testing the models and refining such input information. This can be more efficiently accomplished via more focused and synergistic theoretical and experimental efforts. Modeling geared to address specific aspects of a complex phenomenon, where the analyses are justifiably reduced to a more manageable size with a negligible sacrifice in information, will indeed be more effective. Similarly, smaller scale experimental efforts in better defined environments, set up to provide answers to individual thermochemical questions, can be more meaningful. Future CVD research should, therefore, include both experiments and modeling as integral parts of a coordinated program.

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TABLE I.—NUMBER OF REACTIONS USED IN RECENT CVD MODELS

Material	Source gases/H_2	Gas phase	Surface	Reference/ Year
Si	SiH_4	27	13	17/1989
GaAs	TMG+AsH_3	232	115	18/1989
SiC	$SiH_4+C_3H_8$	166	36	19/1991
Diamond	CH_4+O_2	158	52	20/1991
W	WF_6	8	65	21/1991

TABLE II.—REPORTED RATE CONSTANTS, k, FOR SILANE DISSOCIATION,

$SiH_4 \rightarrow SiH_2 + H_2$

$[k = AT^{\beta}\exp(-E/RT)]$

A, sec^{-1}	β	E, kcal/mole	Reference/ Year
1.09×10^{25}	-3.37	61.2	17/1989
3.3×10^{15}	-0.5	55.9	23/1990
6.67×10^{29}	-4.795	63.45	19/1991
6.17×10^{15}	0	59.99	24/1991
5.2×10^{13}	0	52.54	25/1991

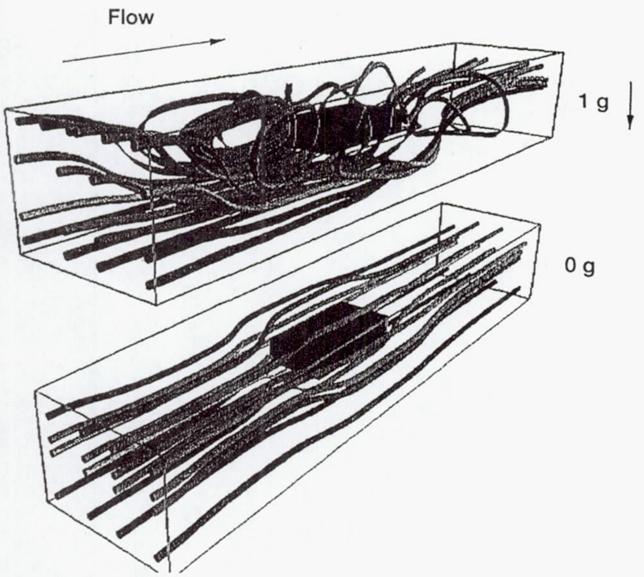

Figure 1.—Schematic of flow patterns in a cold-wall CVD reactor with an inductively heated rectangular substrate. The 3-dimensional complex flows in the presence of gravity is due to bouyancy-driven free convection flows.

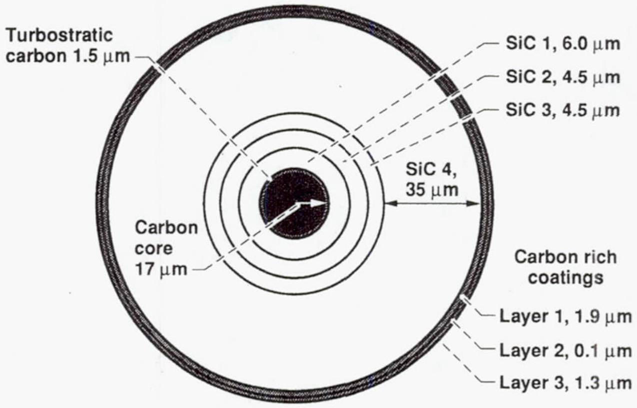

Figure 2.—Schematic of Textron's SCS-6 silicon carbide fiber microstructure [30].

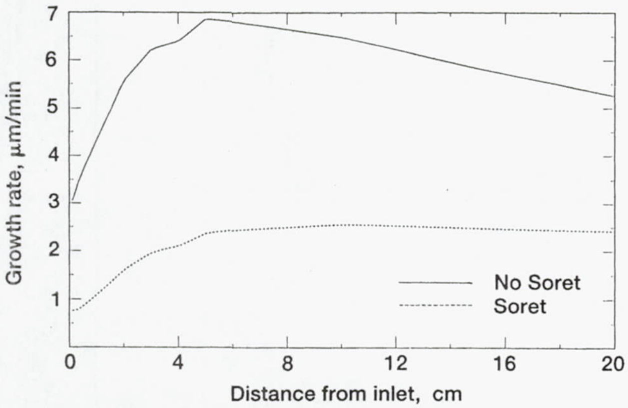

Figure 3.—Predicted silicon growth rates with and without Soret diffusion versus axial distance along fiber [6].

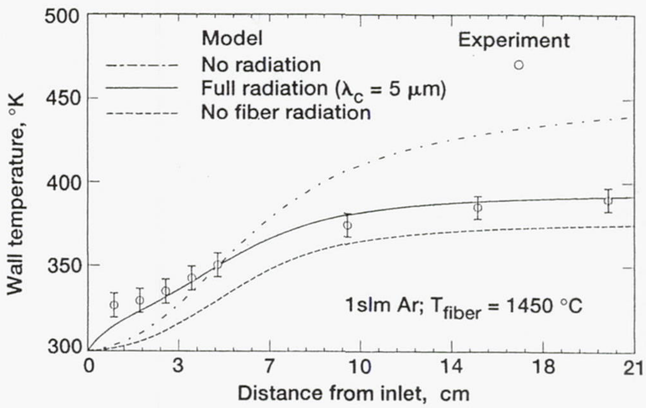

Figure 4.—Experimentally measured and predicted reactor wall temperatures for fiber CVD [31]. A sophisticated radiation model is necessary for improved accuracy.

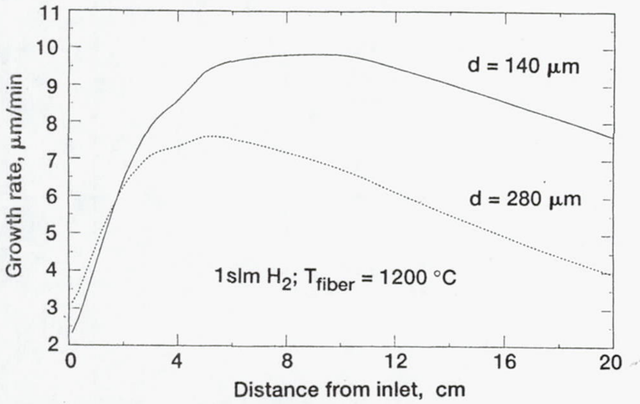

Figure 5.—Predicted silicon growth rates versus axial distance along fiber for two fiber diameters [6].

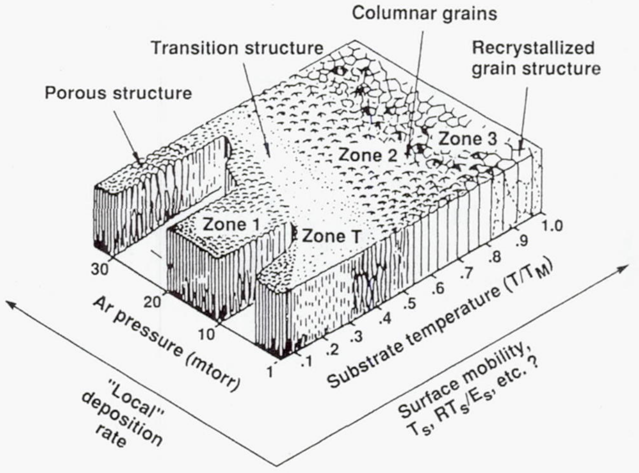

Figure 6.—Application of Thornton Structural Zone Model [33] (developed for PVD) to CVD by recommended new coordinates.

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13. ABSTRACT ***(Maximum 200 words)***

The formalism for the accurate modeling of chemical vapor deposition (CVD) processes has matured based on the well established principles of transport phenomena and chemical kinetics in the gas phase and on surfaces. The utility and limitations of such models are discussed in practical applications for high temperature structural materials. Attention is drawn to the complexities and uncertainties in chemical kinetics. Traditional approaches based on only equilibrium thermochemistry and/or transport phenomena are defended as useful tools, within their validity, for engineering purposes. The role of modeling is discussed within the context of establishing the link between CVD process parameters and material microstructures/properties. It is argued that CVD modeling is an essential part of designing CVD equipment and controlling/optimizing CVD processes for the production and/or coating of high performance structural materials.

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