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# Chemical Vapor Deposition Modeling—An Assessment of Current Status

Suleyman A. Gokoglu  
*Case Western Reserve University*  
*Cleveland, Ohio*

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# CHEMICAL VAPOR DEPOSITION MODELING - AN ASSESSMENT OF CURRENT STATUS

Suleyman A. Gokoglu\*  
Case Western Reserve University  
Cleveland, Ohio 44106

## Summary

This paper points out the shortcomings of earlier approaches that assumed thermochemical equilibrium and used chemical vapor deposition (CVD) phase diagrams. It demonstrates significant advancements in predictive capabilities due to recent computational developments especially those for deposition rates controlled by gas phase mass transport. The importance of using the proper boundary conditions is stressed, and the availability and reliability of gas phase and surface chemical kinetic information are emphasized as the most limiting factors. Future directions for CVD are proposed on the basis of current needs for efficient and effective progress in CVD process design and optimization.

## Introduction

Among the available gas phase processes for materials production, chemical vapor deposition (CVD) has the greatest potential for commercial applicability because it is easier to scale up and is more economical. Indeed, CVD has been routinely employed in various areas of materials science and technology. However, the conventional CVD process design (i.e., reactor geometry, gas flows, and chemistry) has often relied primarily on intuition and experience. As the interest and demand in more sophisticated advanced materials are growing to meet today's stringent performance requirements, it is becoming clear that traditional experimental approaches alone will not suffice to efficiently produce novel materials with superior properties. For confirming and enhancing our fundamental understanding of the physicochemical phenomena occurring in CVD processes, the modeling of such complex systems is now recognized as an essential part of CVD research.

The basic concept of CVD is quite simple. Source gases or vapors containing some or all of the constituent elements of the deposit material, usually mixed with a carrier gas, flow over heated surfaces on which the material will be deposited (fig. 1). The source species are transported, by diffusion and convection, to the hot surfaces while they are simultaneously heated. Usually both gas and surface chemical reactions occur, depending on the prevailing heat and mass transport and on the chemical kinetic parameters during operation. This paper is limited to subatmospheric and atmospheric thermal CVD processes and excludes others such as very low pressure, plasma-enhanced, or photo-assisted CVD. Although many of the statements made also apply to chemical vapor infiltration (CVI) processes, for the sake of brevity, no specific reference is made.

Despite its conceptual simplicity, the controlled implementation of the CVD process is truly an interdisciplinary effort which involves many different fields of science and engineering. A comprehensive analysis should, most obviously, include gas phase and surface chemical reaction kinetics, heat and multicomponent mass transport, fluid physics, and thermodynamics (ref. 1). The analysis should be fully supported by the measurement, testing, and characterization techniques that are available to specialists in heat transfer, fluids, and materials science. The modeling of the interactions of such multiparameter systems is indeed a challenge. Furthermore, the simultaneous description of the coupled phenomena in multidimensions with multireaction schemes naturally requires highly efficient computational software and hardware (ref. 2).

## Thermodynamic Approach

Not too long ago, CVD modeling only involved making gas-solid thermochemical equilibrium calculations,

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\*NASA Resident Research Associate at Lewis Research Center.



inspired by the conventional phase diagram calculation approach. Computer programs, such as those based on free-energy minimization (e.g., SOLGASMIX and NASA CEC (refs. 3 and 4), have been used 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 dynamic finite rate phenomena such as transport and/or chemical kinetics. Besides their inability to predict the rates of deposition, such approaches also fail to account for the observed shifts in the deposit material phase and composition from equilibrium predictions (refs. 5 and 6). For example, although one can predict the deposition of silicon from silane, even at room temperature, and of carbon from propane at temperatures as low as 125 °C under atmospheric pressure, these depositions do not occur in real life because of kinetic barriers. Conversely, successful deposition of silicon nitride can be accomplished from silicon tetrafluoride and ammonia under conditions that are substantially outside of the predicted region for stable silicon nitride formation. The recent success in diamond deposition is yet another counter-example to approaches based on thermochemical equilibrium assumptions. Indeed, with the increasing availability of elaborate transport models and chemical kinetic information, thermochemical equilibrium calculations can no longer be justifiably classified under CVD modeling. However, they are excellent tools for initial feasibility studies, providing guidance for the formation of possible gaseous species and condensed phases of different chemical compositions.

## Transport Phenomena and Boundary Conditions

Beyond thermochemical equilibrium, the next level of complexity is the incorporation of transport phenomena into the model (refs. 1 and 7). Over the past decade remarkable advancements have been made in the field of computational fluid dynamics (CFD) for aerospace vehicles (ref. 8). Such progress certainly had a considerable impact on CVD modeling as well. Indeed oversimplified "stagnant layer" or boundary layer descriptions are being increasingly replaced by CVD modelers in favor of multidimensional analyses. However, special conditions pertaining specifically to CVD require more attention than the mostly turbulent, high-speed applications that modern CFD codes were developed for. Although the statement that most CVD situations result in laminar flows may connote a simpler case than for the flows encountered in CFD applications, such low-speed flows require a careful and complex treatment of buoyancy-driven free convection.

Thus, the so-called Boussinesq approximation, which is usually employed to simplify the gravitational body force term in the momentum conservation equations, can no longer be justified for CVD where the temperature gradients can be as steep as 1000 K/cm. Therefore, the temperature dependence of gas density, just like every other gas transport and thermodynamic property, should be explicitly treated.

There are CVD situations where the prevailing conditions result in traveling wave flow instabilities that require a time-dependent treatment (ref. 9). Furthermore, the presence of comparable forced and free convection in many CVD systems requires three-dimensional analyses of the resulting flow structures (refs. 10 to 13). The effects of buoyancy-driven convection in a typical atmospheric pressure, horizontal CVD reactor are depicted in figure 2 (ref. 10). It has a rectangular-channellike entrance region (fig. 2(a)). The hot susceptor extends further downstream and has steps on both sides. The flow conditions are given in the figure caption. The calculations incorporated the conjugate heat transfer to account for the heating of the quartz blocks both upstream of the constant temperature susceptor and under it. Figure 2(b) shows the results of a numerical flow visualization study when the trajectories of particles introduced into the stream at 0.3 cm above the susceptor level are calculated in the absence of gravity. However, under terrestrial conditions (fig. 2(c)), the flow structure is dramatically different, resulting in a corkscrewlike behavior, which no two-dimensional analysis (e.g., boundary layer description) can be expected to correctly describe.

As another consequence of steep temperature gradients, a mass transfer mechanism different from Fickian diffusion, namely Soret diffusion, has been demonstrated to be nonnegligible in CVD systems involving species with disparate molecular weights (ref. 14). Hence, CVD models neglecting Soret diffusion cannot provide the level of precision required for today's complex coatings.

Besides the temperature dependence, the compositional dependence of gas properties must also be accounted for, even if the reactive gases in the mixture are dilute, because many CVD applications use a mixture of gases. In cases where reactive gases form a considerable portion of the overall mixture, additional energy flux terms must be included in the energy conservation equation because of concentration gradients and disparate heat capacities of species. Furthermore, nondilute reactive species environments naturally necessitate the incorporation of the heat of reactions in the gas phase and on the surface and the incorporation of nonzero normal gas velocity on the deposition surface.



The proper treatment of the boundary conditions required for the solution of modeling equations has recently been demonstrated to be critical in many cases (refs. 12, 13, and 15). The use of either constant temperature or adiabatic wall conditions does not correctly describe the role of radiation or the coupled interaction of the environment with the CVD system. Asymmetric and other unexpected flow and temperature fields are observed and can be predicted by using more realistic boundary conditions (ref. 16). Moreover, under typical microgravity conditions, even when continuum approximations hold, it has been shown that along nonisothermal walls the so-called no-slip boundary condition does not apply, and there is considerable side-wall gas creep (ref. 17). 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. For example, the effect of wafer boat and cage design on the uniformity of growth has been recently demonstrated for low-pressure CVD applications (ref. 18).

## 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. 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 now being increasingly employed for the required thermochemistry. For the relatively well studied atmospheric CVD chemistry of silicon from silane, encouraging predictions of deposition rates have been accomplished under fairly complicated conditions as shown by figure 3 (ref. 10). This demonstrates the capabilities of current sophisticated computer codes whenever deposition rates are governed by gas phase reactions and mass transport. The ability to account for reactive species inventories and depletion rates is essential for both cold wall and (especially) hot wall processes. However, even for silicon deposition from silane, which has been studied for over 20 years, a consensus has still not been reached on many questions related to reaction pathways and kinetics in the gas phase (ref. 19).

Depending on the pressures, temperatures and concentrations in CVD systems, the prevailing supersaturation levels can lead to particle formation due to gas phase nucleation. Although there are a few cases where particle-aided and/or modified CVD may be desired

and intentionally introduced (refs. 20 and 21), in most CVD applications gas phase nucleation is detrimental to deposit quality. Therefore, for most conventional CVD situations, this phenomenon need not be included in CVD modeling, except to define the safe operation boundaries to preclude the usually very sudden onset of gas phase nucleation.

Reducing pressure and temperature will suppress buoyancy effects as well as gas phase decomposition and nucleation. Deposition is then controlled only by surface kinetics, which improves uniformity but slows rates. Yet, the mechanisms and kinetics of surface phenomena - such as adsorption, diffusion, nucleation, incorporation (reaction pathways), and desorption - which must appear as boundary conditions in such numerical simulations - are scarcely known for many of the systems of interest to the CVD community. Again, even for silicon deposition from silane, experimentally observed reaction efficiencies can vary by more than two orders of magnitude for nominally identical conditions; similarly, deposition rates at low temperatures and very low pressures can be comparable to those obtained at high temperatures and atmospheric pressure (ref. 22). In addition, explanations of the dependence of deposition rate, deposit material phase, and morphology on different substrate materials, crystallographic orientations, or surface coverage are not consistent. Such uncertainties inevitably create controversy and confusion. Therefore, the key to being able to relate the controllable CVD process parameters to the rate and uniformity of deposition as well as to the deposit material microstructure, defects, and other factors (resulting in certain material properties) lies in solving the mysteries of surface chemical reaction mechanisms (pathways) and their associated energetics and kinetics.

Efficient incorporation of such fundamental information on gas phase and (especially) surface chemical kinetics into existing computer codes is not simple. New constraints need to be satisfied: for example, the mass balance of species at the surface (gas-solid interface) should account for their transport, generation and destruction rates both in gas and solid phases, and the total number of active surface sites does not need to be conserved and should be allowed to evolve with time. Furthermore, when chemical kinetics are incorporated into transport models, 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. The expected difficulties in CVD may not be circumvented by the schemes and algorithms usually developed for CFD of high-speed, chemically reacting flows. The demand for "smarter" methodologies, not only relying on numerical



techniques but also exploiting the available physico-chemical information, will indeed be growing as a larger variety of chemical systems are modeled.

Depending on the prevailing molecular mean free path and the characteristic dimensions of interest (e.g., wafer spacing), molecular trajectories in free molecular flow can be calculated. In cases where the mean free path is comparable to, say, the trench width or height for an electronic device, the Monte Carlo direct simulation method is a powerful technique which is being utilized increasingly (ref. 23).

## Closing Remarks

In summary, CVD modeling currently employs powerful computational tools, hardware and software, which provide invaluable insights into the complex physicochemical phenomena taking place in CVD reactors (as exemplified by figs. 2 and 3). These tools can go beyond research purposes and be confidently used for improved design and optimization of future CVD reactors provided that (1) the transport, thermodynamic, and chemical kinetic data fed to such codes are of utmost quality, and that (2) they can be verified with carefully controlled experiments. Refinement of such input information can be more efficiently obtained via more focused 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 - 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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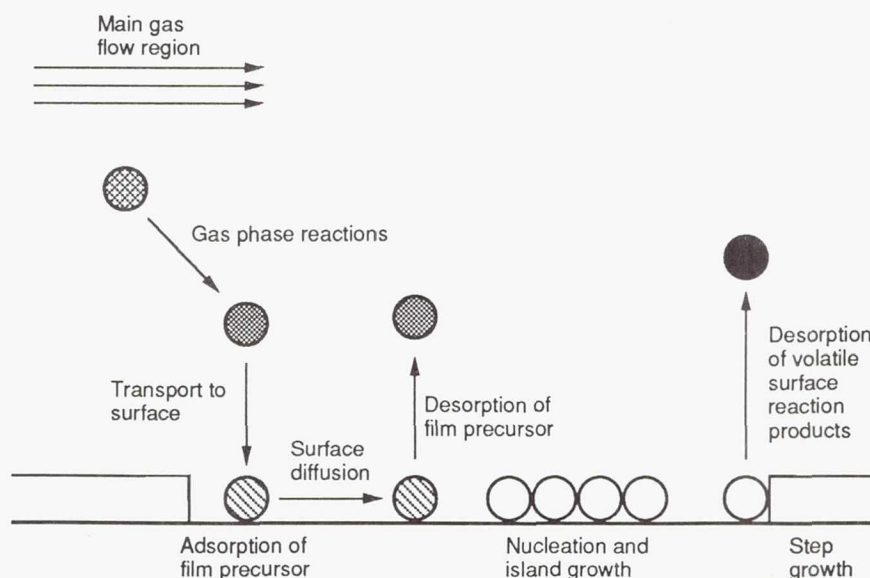
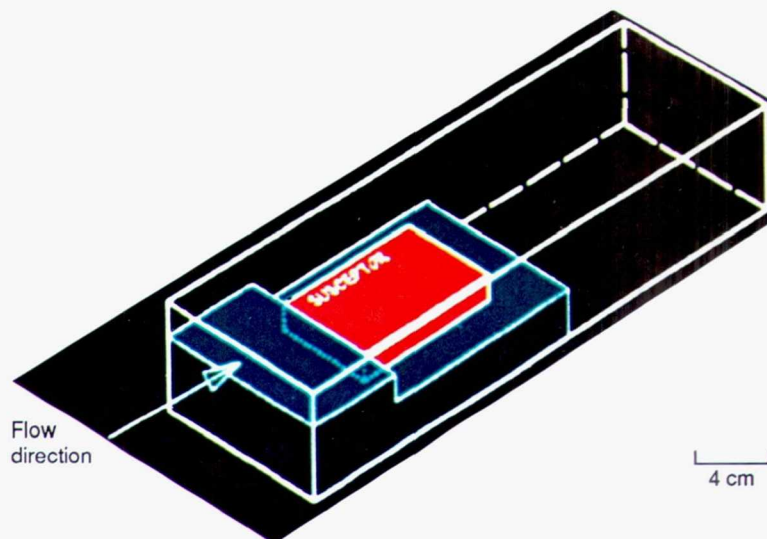


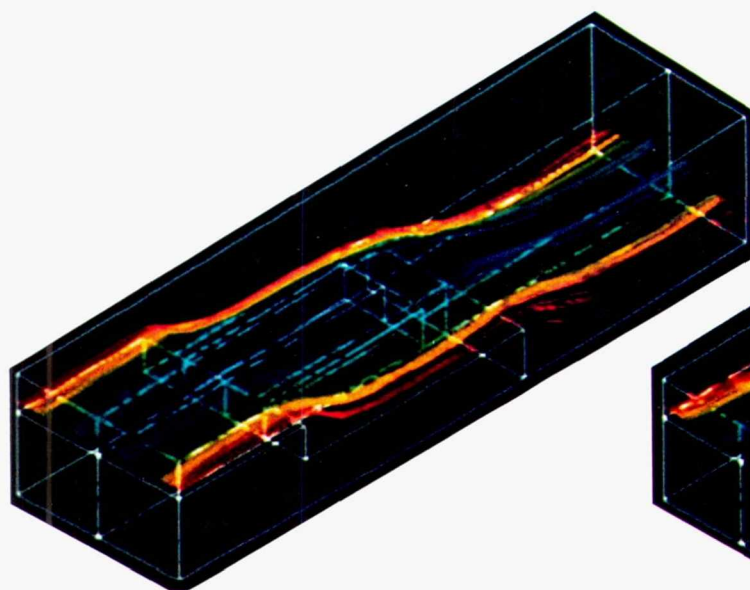
Figure 1.—Transport and reaction processes underlying chemical vapor deposition (CVD) (from ref. 1).

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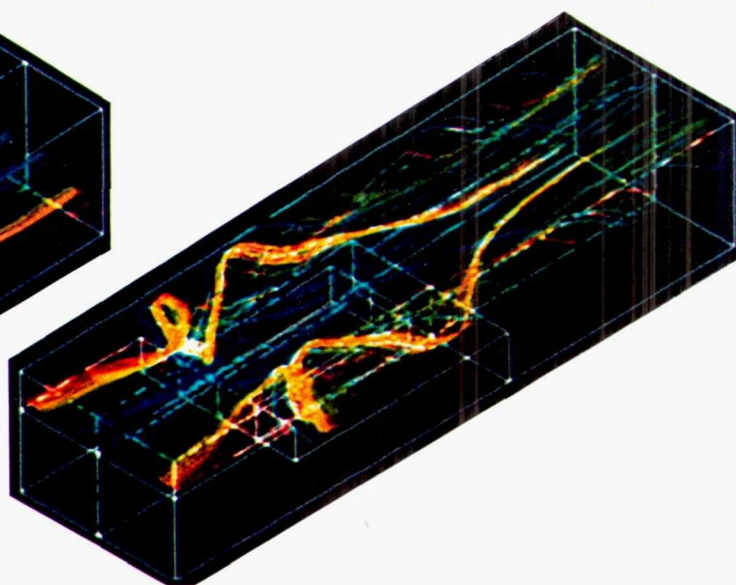




(a) Modeled portion of reactor.



(b) No gravitational acceleration.

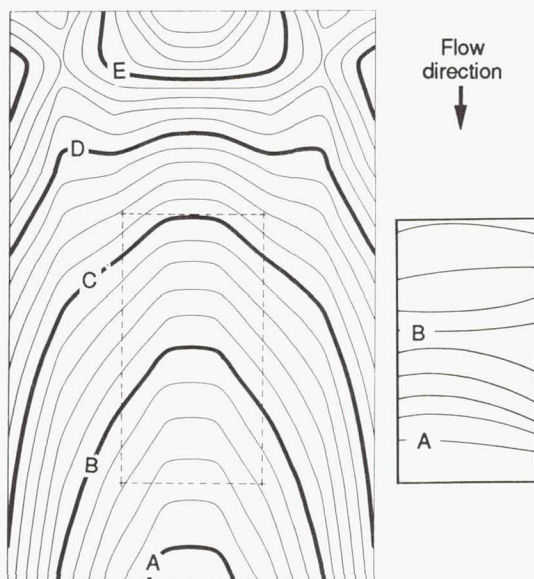


(c) Earth gravitational acceleration.

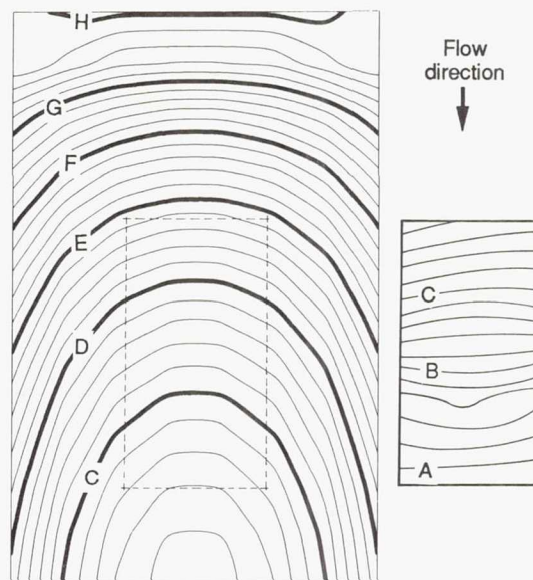
Figure 2.—Effects of buoyancy-driven convection in an atmospheric pressure chemical vapor deposition (CVD) reactor. Susceptor temperature, 1373 K; inlet gas temperature, 300 K; gas flowrate, 4 slm; gas composition, 75 mol %  $H_2$  and 25 mol % Ar. Trajectories are for particles introduced 0.3 cm above the surface at the entrance.



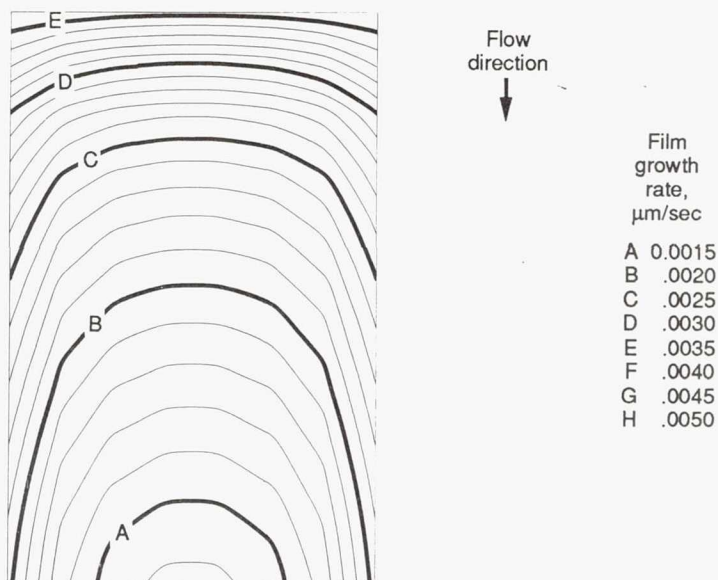
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(a) Buoyancy-driven flows present. Gas composition, 75 mol %  $H_2$  and 25 mol % Ar; Earth gravity.



(b) Buoyancy-driven flows suppressed. Gas composition, 75 mol %  $H_2$  and 25 mol % He; Earth gravity.



(c) Buoyancy-driven flows absent. Gas composition, 75 mol %  $H_2$  and 25 mol % Ar; zero gravity.

Figure 3.—Comparison of silicon film growth rates obtained from model predictions and experiments. Experimental contours generated from 12 data points measured at intersections of four equally spaced rows and three equally spaced columns (section outlined in central region of susceptor). Susceptor temperature, 1373 K; inlet gas temperature, 300 K; gas flowrate, 4 slm.



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