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CHEMICAL KINETICS MODELS FOR SEMICONDUCTOR PROCESSING

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ABSTRACT

Chemical reactions in the gas-phase and on surfaces are important in the deposition and etching of materials for microelectronic applications. A general software framework for describing homogeneous and heterogeneous reaction kinetics utilizing the Chemkin suite of codes is presented. Experimental, theoretical and modeling approaches to developing chemical reaction mechanisms are discussed. A number of TCAD application modules for simulating the chemically reacting flow in deposition and etching reactors have been developed and are also described.

INTRODUCTION

Complex chemically reacting flow simulations are commonly employed to develop a quantitative understanding of processes and to optimize reaction conditions in microelectronics applications such as chemical vapor deposition (CVD) and plasma processing. Many coupled physical phenomena occur in deposition and etching reactors, including gas-phase chemical reactions, convective and diffusive transport to a reacting surface, heterogeneous reaction at the surface, and possibly diffusion or reaction in the solid bulk material. Although reaction conditions, geometry, and fluid flow can vary widely among such systems, they share the need for accurate, detailed descriptions of the chemical kinetics occurring in the gas-phase or on reactive surfaces.

Most TCAD tools in use today do not consider details of process chemistry. This paper will describe a general software approach to modeling process chemistry utilizing the Chemkin suite of codes. Chemkin provides a widely used interface for describing chemical reaction kinetics, either in terms of elementary reactions or global reaction mechanisms. It affords a structured approach to writing physically based TCAD modules through its reusable libraries describing gas-phase reaction kinetics, surface reaction kinetics, and transport properties.

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Application codes (TCAD modules) typically use these libraries in simulations of the coupled fluid-flow, transport, and reaction kinetics in models ranging from the reactor-scale to the microelectronic feature scale. A range of numerical models for thermal CVD and plasma processes will be described here, including: stirred-reactors, stagnation-flow / rotating-disk reactors, and multiple-stacked-wafer low-pressure CVD reactors. The basic kinetic modules in Chemkin have been extended [1] to incorporate non-thermal effects necessary for modeling plasma processes, including multiple temperatures and reaction kinetics that depend on ion-energy. A simple plasma application code will be described, a well-stirred reactor. Chemical kinetics can also control the evolution of microelectronic feature topography during deposition or etch processes.

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CHEMKIN SOFTWARE

The Chemkin software [1] was developed to aid in the incorporation of complex gas-phase chemical reaction mechanisms into numerical simulations. Currently, there are a number of simulation codes based on Chemkin which solve chemically reacting flows useful for microelectronics applications. The Chemkin interface allows the user to specify the necessary input through a high-level symbolic interpreter, which parses the information and passes it to a Chemkin application code.

To specify the needed information, the user writes an input file declaring the chemical elements in the problem, the name of each chemical species, thermochemical information about each chemical species, a list of chemical reactions (written in the same fashion that a chemist would write them, i.e., a list of reactants converted to products), and rate constant information, in the form of modified Arrhenius coefficients. The thermochemical information is entered in a very compact form as a series of polynomial coefficients describing the species entropy (S), enthalpy (H), and heat capacity (C_p) as a function of temperature. The thermochemical database is in a form compatible with the widely used NASA chemical equilibrium code [2].

Because all of the information about the reaction mechanism is parsed and summarized by the Chemkin interpreter, if the user desires to modify the reaction mechanism by adding species or deleting a reaction, for instance, they only change the interpreter input file and the Chemkin application code (for example, a rotating-disk reactor simulation code) does not have to be altered. The modular approach of separating the description of the chemistry from the set-up and solution of the reacting flow problem allows the software designer great flexibility in writing chemical-mechanism-independent code. Moreover, the same mechanism can be used in different microelectronics application codes without alteration.

The Surface Chemkin package [3,4] was designed for the complementary task of specifying mechanistic and kinetic rate information for heterogeneous chemical reactions, i.e., reactions at surfaces. Surface Chemkin was designed to run in conjunction with Chemkin and, indeed, execution of the Chemkin interpreter is required before the Surface Chemkin interpreter may be run. The user interface for Surface Chemkin is very similar to that of Chemkin, but is expanded to account for the richer nomenclature and formalism required to specify heterogeneous reaction mechanisms.

The transport package software package [5] provides for a full Dixon-Lewis, multicomponent, dilute gas treatment of the gas-phase transport properties. It also includes the effects of such phenomena as thermal diffusion. It has the capability of calculating, as a function of temperature, the pure species viscosity, pure species thermal conductivity, and binary diffusion coefficients for each gas-phase species in the mechanism.

Many years of effort have produced a number of high-level Chemkin applications for chemically reacting flow simulation. These codes have been widely distributed to and used by researchers around the world. The general structure of a Chemkin application code is shown in Fig 1. The TCAD module (reactor model) contains the code needed to set up the governing equations that physically represent the reacting flow, e.g., mass, momentum, and energy conservation equations. This module is responsible for reading the user input defining the problem, such as reactor geometry, pressures, flow rates, reactant-gas composition, etc.

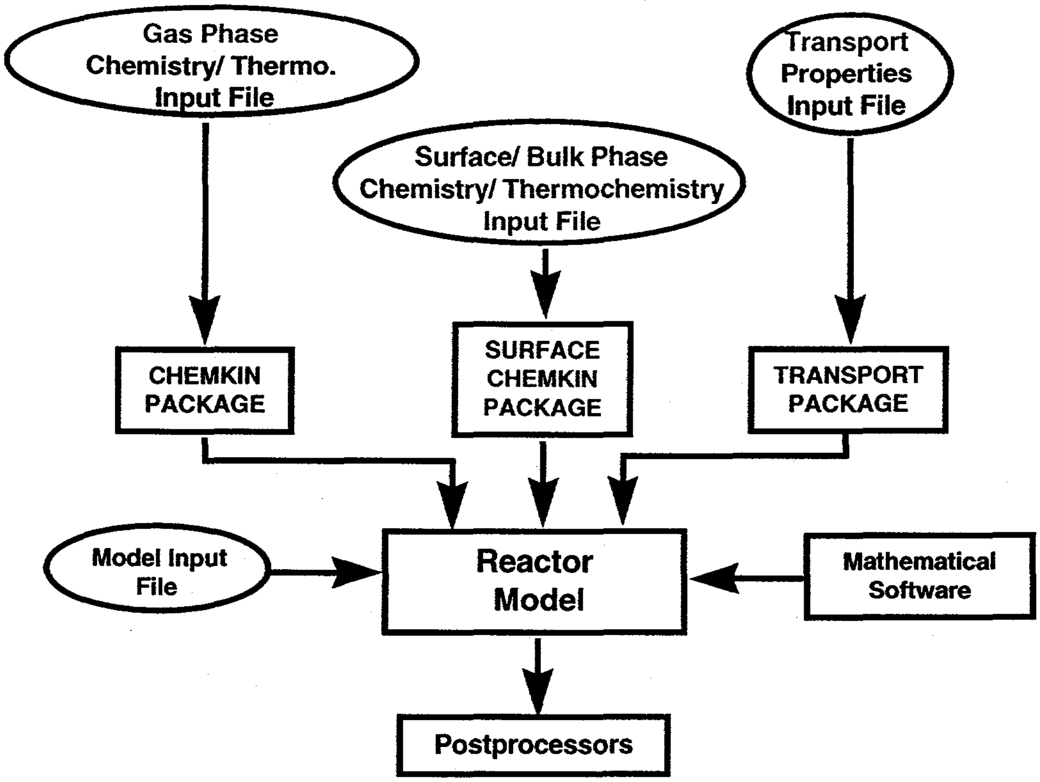

Figure 1. Relationship between software packages (boxes) and user input files (ovals) in a typical Chemkin application code.

The numerical model makes subroutine calls to the Chemkin, Surface Chemkin, and Transport libraries whenever it needs information related to the chemical or transport state of the system. These libraries can return a variety of information, such as: densities, transport properties (e.g., species diffusivities, thermal conductivity, viscosity), information about species (e.g., molecular weights, species names, chemical composition), information about reactions (e.g., local chemical reaction rates at a gas-phase node or at a surface node). The user supplies an input file describing the gas-phase chemical reaction mechanism to the Chemkin Interpreter, a separate input file describing the surface-reaction mechanism to the Surface Chemkin Interpreter, and an input file of molecular (modified Lennard-Jones) parameters for the Transport package's preprocessor.

The TCAD module (and not the Chemkin package per se) is responsible for solving the system of governing equations to describe the system being modeled. We have found it advantageous to separate the mathematical software responsible for actually solving the system of equations from the application code itself. Thus, an additional box representing Mathematical Software is included in Fig. 1, to emphasize the distinction between the tasks of setting-up the problem and its numerical solution (which can often be done using standard numerical solution packages).

The typical Chemkin user takes advantage of TCAD modules describing the physical system of interest, which have been developed by a much smaller number of software designers. The challenge for most users has been converted from software development to that of developing realistic reaction mechanisms that accurately describe the chemical system of interest. Aspects of constructing a realistic reaction mechanism describing the chemical system of interest are discussed in the next section.

DEVELOPING CHEMICAL REACTION MECHANISMS

Information about heterogeneous reaction kinetics that is required to construct a numerical model for use in a microelectronics equipment simulation can range from simple reactive sticking coefficients (probabilities) to very detailed, elementary surface reaction mechanisms. The experimental and theoretical methodologies for studying chemical reaction mechanisms in the gas phase are quite mature and well-established. However, relatively less is known about heterogeneous surface reactions, and the techniques to study them are not in as mature a state. This section summarizes the experimental, theoretical and numerical modeling approaches that can be used to develop heterogeneous reaction mechanisms needed in semiconductor equipment models.

In recent years, the surface science approach has led to a dramatic increase in our knowledge of the surface chemistry and kinetics of some key deposition and etching processes related to microelectronics. Some of the work regarding surface science has been summarized in reviews and book chapters [6,7]. Processes that have been studied using the surface science approach include the deposition and etching of semiconductors (e.g., Si, Ge, GaAs), metals (e.g., W, Cu, Al), and insulators (e.g., SiO_2). The information gained from these studies may be both mechanistic and kinetic in nature.

The general philosophy behind the surface science approach is to study a surface or surface process in a well characterized and controlled environment, whenever feasible. This usually (but not always) requires that the study (or a portion of the study) be performed in an ultra-high vacuum (UHV) system. The most commonly used surface science experiments fall into two broad categories. The first category of techniques (e.g., AES, XPS, LEED, etc.) directly probe some characteristic of the surface using charged particles and/or photons. Such techniques generally yield elemental, chemical, or structural information. The second category of techniques (e.g., temperature programmed desorption) monitor neutral atoms, radicals, or molecules that have desorbed or scattered from the surface. These techniques yield information regarding the surface chemical reaction kinetics and mechanisms. In addition to temperature programmed desorption (TPD), there are a wide number of variations of techniques aimed at examining surface reaction kinetics and mechanisms, ranging from sophisticated modulated molecular beam scattering techniques to simple reactant gas backfilling or flow experiments at pressures of 10^{-9}-10^{-5} Torr. The techniques for measuring and modeling surface reaction kinetics have also been reviewed in detail elsewhere [8-18].

In the traditional surface science approach the surface chemistry and physics are examined in a UHV chamber at reactant pressures (and sometimes surface temperatures) that are normally far from the actual conditions of the process being investigated (e.g., catalysis, CVD, etching etc.). This so-called "pressure gap" has been the subject of much discussion and debate for surface science studies of heterogeneous catalysis [19], and most of the critical issues are also relevant to the study of microelectronic systems. By going to lower pressures and temperatures it is sometimes possible to isolate reaction intermediates and perform a stepwise study of a surface chemical mechanism. Reaction kinetics (particularly unimolecular kinetics) measured at low pressures often extrapolate very well to "real-world" conditions.

There are often some important chemical issues that cannot be addressed solely by low pressure studies and the traditional surface science approach. For these situations the capability of exposing the surface to realistic or near realistic pressures is needed. This is normally achieved by transferring the sample (under vacuum) from the UHV analysis chamber into a separate chamber that can be operated at higher pressures. In addition to the knowledge obtained from any of the surface science techniques, it is very desirable to have a reliable set of growth rate data that accurately represents the surface chemical kinetics at, or near, actual growth conditions. This allows reliable comparison of the reaction kinetics measured at low pressures ("surface science kinetics") to the growth rates measured at typical operating conditions ("reactor kinetics").

There are several methods of obtaining surface kinetic information that are normally not considered to be a subset of "surface science." One class of measurements involves determination of the deposition topography on top of (or inside of) small features intentionally fabricated on (or in) a surface. This information is compared to models of growth using various proposed chemical mechanisms and rate constants (or sometimes simply sticking probabilities). This technique of "feature-scale" modeling has been used to back out surface kinetic parameters for some CVD reactions. (See work by Cale [20] and McVittie [21] as representative examples.)

Molecular beam / surface scattering methods for measuring the reactivity of stable molecules [22] and radical intermediate species [23,24] at a deposition surface are often used. In the first type of experiment the reactive sticking coefficient (probability) for silane and disilane was determined. The reaction probability has a complex dependence upon both the surface temperature and the flux of the molecules at the surface. This flux dependence explains some seemingly inconsistent low-pressure CVD deposition rate data in the literature.

In the second type of experiment, denoted IRIS [23,24] (Imaging of Radicals Interacting with Surfaces), a molecular beam of a radical intermediate species is produced from a plasma, and these radicals impinge upon a surface. Spatially resolved laser-induced fluorescence (LIF) is used to monitor the difference in the incident and scattered fluxes of a species, and thus determine the fraction which reacts at the surface of the growing film

In addition to experiments, a range of theoretical techniques are available to calculate thermochemical information and reaction rates for homogeneous gas-phase reactions. These techniques include ab initio electronic structure calculations and various semi-empirical approximations, transition state theory, RRKM theory, quantum mechanical reactive scattering, and the classical trajectory approach. Although still computationally intensive, such techniques have proven themselves useful in calculating gas-phase reaction energies, pathways, and rates. Some of the same approaches have been applied to surface kinetics and thermochemistry, but with necessarily much less rigor.

In constructing a numerical model of a CVD or etching process for simulations, it will always be necessary to supply some information about the heterogeneous chemistry. Even if the chemistry is not specified in a very elementary manner, one still must ensure that the surface reactions specified "balance" in a chemical sense, in order that mass in the system will be conserved. The information about heterogeneous reactions required to construct a numerical model for use in an equipment simulation can range from simple reactive sticking coefficients (probabilities) to very detailed, elementary surface reaction mechanisms.

Although use of sticking coefficients as the description of heterogeneous chemistry is the simplest approach possible, there can still be a great deal of information required from the modeler as input to the simulation. For every gas-phase species, ranging from just a small number (in the case that detailed gas-phase chemistry is not included) up to dozens (when detailed gas-phase chemistry is considered), one must specify the probability that the species will react upon collision with a surface. Moreover, the surface reaction probability will often depend upon the surface temperature, or perhaps, the pressure. It may also depend upon the coverage of other species on the surface, i.e., site-blocking. For each species surface sticking (reaction) probability, the user must also specify what byproducts are produced by the reaction and whether the reaction proceeds reversibly. Describing surface reactions via sticking probabilities is by far the most common method employed in semiconductor chemistry models.

Heterogeneous reaction rates are often expressed in terms of a Langmuir-Hinshelwood mechanism. The analytical functional form of the rate expression obtained accounts for the competition for open reactive sites on a surface. It often provides the correct dependence upon reactant partial pressures. Representative examples using such analytical rate expressions can be found for Si deposition [25,26], and for Si_3N_4 deposition [27,28].

An alternate approach is to specify an elementary chemical reaction mechanism at the surface. In this case one can have reactions between gas-phase species and surface species, as well as reactions between adsorbed species. At this level of specification, surface reaction mechanisms often become very complex, including dozens of elementary reactions. Such complex surface chemistry reaction mechanisms have been used in models for GaAs MOCVD [29-31], tungsten CVD [32], and diamond CVD [33-36], for example.

For each reaction in a surface chemistry mechanism, one must provide a temperature dependent reaction probability or a rate constant for the reaction in both the forward and reverse directions. (The user may specify that a reaction is irreversible or has no temperature dependence, which are special cases of the above general statement). In order to simulate the heat consumption or release at a surface due to heterogeneous reactions, the (temperature-dependent) endothermicity or exothermicity of each reaction must also be provided. In developing a surface reaction mechanism, one may choose to specify independently the forward and reverse rate constants for each reaction. An alternative would be to specify the change in free energy (as a function of temperature) for each reaction, and compute the reverse rate constant via the reaction equilibrium constant.

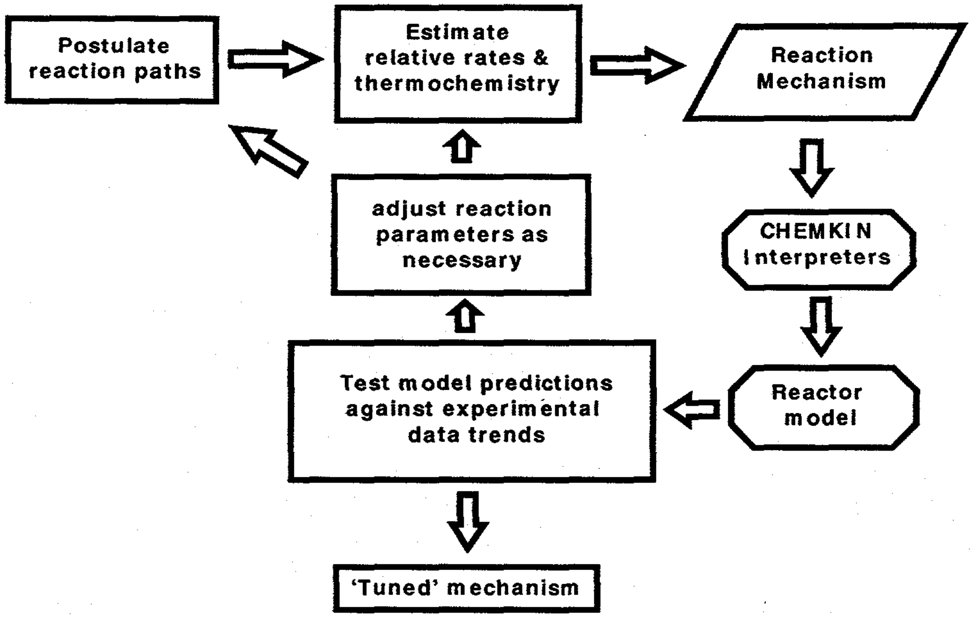

Figure 2. Illustration of the iterative process to develop a complete reaction mechanism.

The energetics of forming and breaking surface bonds is needed to describe the thermochemistry of surface chemical reactions. This information provides the enthalpy change for a reaction. However, the change in entropy is also necessary to determine the reaction change in Free Energy and thus the equilibrium constant. It is more useful to deal with surface thermochemistry in terms of the contributions from the individual surface and gas-phase reactant and product species, rather than on the more global basis of the net change in a reaction (although, of course, the two are related). In practice, one can algebraically manipulate a series of reaction ΔH and ΔS values to obtain a self-consistent set of heats of formation and standard-state entropies for the surface species. This information on individual surface species would fit most logically into standard Thermodynamic Equilibrium programs which minimize Free Energy.

Putting together a complete reaction mechanism to describe the complex chemistry in a deposition or etching system is typically an iterative process, as illustrated in Fig. 2.

Experimental rate information for all possible chemical reactions will not be available. Thus, some information, such as reaction rate constants or species heats of formation, will necessarily have to be estimated. In the best case, predictions of the reactor simulation will not be too sensitive to values of parameters that have been "guessed." However, one must always be aware of the uncertainties introduced through such parameter estimation. Typically a reaction mechanism is deduced after a number of cycles of running a reactor simulation, comparing output with experimental data, adjusting the values of some of the parameters in the model, and testing numerical predictions again with experiment. The output of this process is a reaction mechanism which, as a whole, has been "tuned" to give a realistic description of the process of interest. It is very rare that some tweaking of rate parameters is not needed in order to match the experimental training set. Of course, then one must exercise caution in extrapolating code predictions too far outside the parameter space for which the model has been validated.

APPLICATION CODES

A range of application codes for simulating deposition processes have been written at Sandia National Laboratories, based on the Chemkin software. This section describes three such TCAD modules. The first is a zero-dimensional perfectly stirred reactor model, AURORA, which has primarily been used to model chemistry, deposition and etching in plasma reactors. The second code, SPIN, is one-dimensional and models the gas-phase chemistry, transport and surface reactions in a rotating-disk or stagnation-point-flow reactor. The third, OVEND, models the chemistry and transport in a multiple-stacked-wafer low-pressure CVD (LPCVD) reactor.

AURORA

The AURORA Software is a FORTRAN computer program that predicts the steady-state or time-averaged properties of a well mixed or perfectly stirred reactor for plasma or thermal chemistry systems. AURORA allows modeling of non-thermal plasma reactors with the determination of ion and electron concentrations and the electron temperature, in addition to the neutral radical species concentrations. Well stirred reactors are characterized by a reactor volume, residence time or mass flow rate, heat loss or gas temperature, surface area, surface temperature, the incoming temperature and mixture composition, as well as the power deposited into the plasma for non-thermal systems. The model accounts for finite-rate elementary chemical reactions both in the gas phase and on the surface. The governing equations are a system of nonlinear algebraic relations. The program solves these equations using a hybrid Newton/time-integration method embodied by the software package TWOPNT [37]. The program runs in conjunction with the new Chemkin-III [1] and Surface Chemkin-III [3] packages, which handle the chemical reaction mechanisms for thermal and non-thermal systems. Chemkin-III allows for specification of electron-impact reactions, excitation losses, and elastic-collision losses for electrons.

The contents of a well mixed or stirred reactor are assumed to be very uniform spatially due to high diffusion rates or forced turbulent mixing. In other words, the rate of conversion of reactants to products is controlled by chemical reaction rates and not by mixing processes. Thus, the reactor is considered to be "limited" by reaction kinetics. This is a very good assumption for the very low pressure, highly diffuse operating conditions of most plasma reactors and some thermal CVD systems. An essential element of the stirred reactor model is the assumption that the reactor is sufficiently mixed to be described well by spatially averaged or bulk properties. For low-pressure processes (1 Torr and below), the dominance of species diffusion renders this assumption valid in many practical applications. The major advantage of the well stirred approximation lies in the relatively small computational demands of the mathematical model. Such a model allows investigators with only moderate computational resources to easily consider and analyze large, detailed chemical reaction mechanisms.

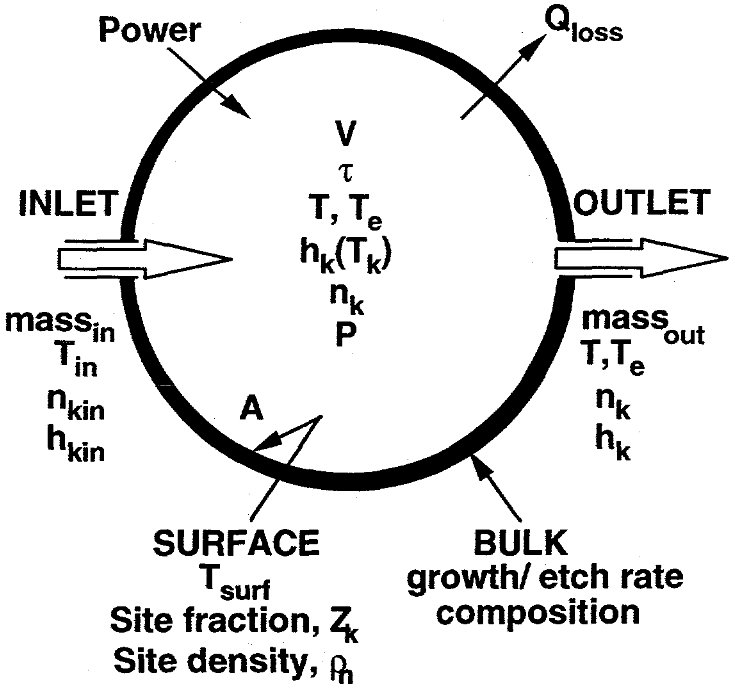

Figure 3. Schematic representation of a well stirred reactor.

In addition to fast mixing, the modeling of well-stirred reactors requires several assumptions. First, mass transport to the reactor walls is assumed to be infinitely fast. Therefore, the relative importance of surface reactions to gas-phase reactions is determined only by the surface-to-volume ratios of each material and the relative reaction rates. Second, the flow through the reactor must be characterized by a nominal residence time, which can be deduced from the flow rate and the reactor volume. The treatment of plasmas requires that power is deposited uniformly into the plasma bulk or, alternatively, that the electrons' diffusion and thermal conduction transport processes are fast relative to the rates of electron-driven chemical kinetics. In addition, we assume that the chemical reaction rate coefficients are independent of reactor conditions. This assumption may be violated in the case where the electron energy distribution function deviates significantly from Maxwellian conditions [38]. However, modeling plasma systems in this manner still provides important insight into the reactor chemistry [38-42]. Finally, the characterization of a quasineutral bulk plasma depends on a thin-sheath approximation, where the sheath thickness is much smaller than the reactor-chamber dimensions.

Conservation of mass, energy, and species describe a well mixed reactor including net generation of chemical species within the reactor volume, and net loss of species and mass to surfaces in the reactor. The stirred reactor consists of a chamber, which may or may not be thermally insulated, having inlet and outlet ducts. Figure 3 illustrates the conceptual representation of a generic reactor chamber. A steady flow of reactants is introduced through the inlet with a given species composition and temperature. The mass flow rate into the reactor may not be equal to the mass flow rate out of the reactor, due to deposition on or etching of surface materials. In the AURORA model, the reactor pressure is specified, so that the conservation equations determine the volume outflow. Although Fig. 3 depicts a single surface in the reactor, an actual reactor may contain many different material surfaces, such as reactor walls, silicon wafer, substrate holder, etc. Each of these materials may have a different set of reaction kinetics associated with it. For this reason, we have included the capability of defining multiple surface materials [3] that represent different fractions of the total surface area, with corresponding surface chemistry mechanisms.

SPIN

The SPIN computer code [43] models the reactive flow in a rotating-disk reactor (RDR), represented schematically in Fig. 4. In a RDR, a heated substrate spins (at typical speeds of 1000 rpm or more) in an enclosure through which the reactants flow. The rotating disk geometry has the important property that in certain operating regimes [44] the species and temperature gradients normal to the disk are equal everywhere on the disk. The equations describing the complex three-dimensional spiral fluid motion can be solved by a separation-of-variables transformation [45,46] that reduces the equations to a system of ordinary differential equations.

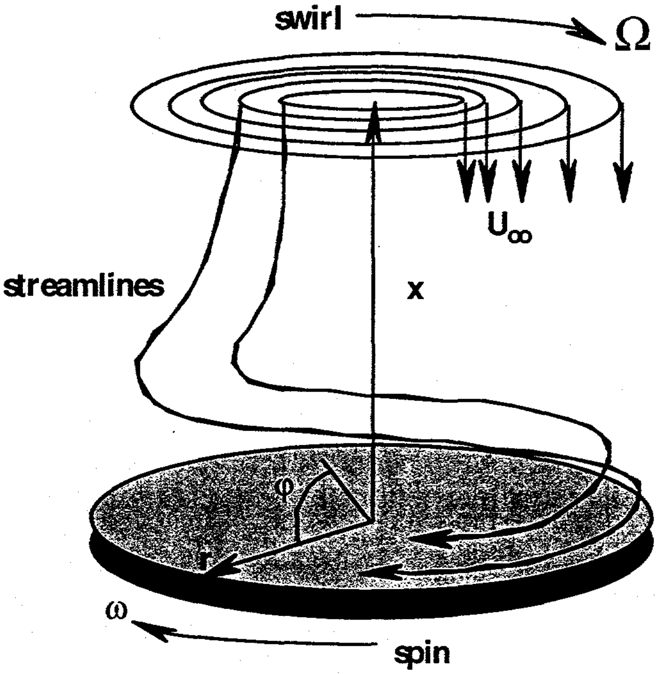

Figure 4. Schematic representation of the flow in a rotating-disk

Strictly speaking, the transformation is only valid for an unconfined infinite-radius disk and buoyancy-free flow. Furthermore, only some boundary conditions are consistent with the transformation (i.e., temperature, gas-phase composition, and approach velocity are all specified to be independent of radius at some distance above the disk). However, the transformed equations still provide a very good practical approximation to the flow in a finite-radius reactor over a large fraction of the disk (up to ~90% of the disk radius) when the reactor operating parameters are properly chosen, e.g., high rotation rates [44]. In the limit of zero rotation rate, the rotating disk flow reduces to a stagnation-point flow, for which a similar separation-of-variables transformation is also available. Such flow configurations ("pedestal reactors") also find use in microelectronics applications.

The SPIN computer code relies on the transformation (which is valid for either the rotating disk or stagnation-point flow) derived by Evans and Greif [47] and then extends the analysis to include the coupling of fluid flow with chemical kinetics [48]. In addition to the fluid mechanics, the model formulation includes the production and depletion of species due to reactions in the gas phase and at the surface, convective and diffusive transport of species in the gas phase, and transport to the deposition surface. The model predicts deposition rates and gas-phase chemical species density profiles, surface coverages, gas velocities, and temperature profiles as a function of process parameters such as disk temperature, rotation rate, pressure, and flow rates.

OVEND

The OVEND [49] reactor model for deposition and species-transport is represented schematically in Fig. 5 for a horizontal multiple-stacked-wafer LPCVD configuration. The wafers are placed concentrically within the reactor tube so that they lie perpendicular to the main direction of the flow. The user input defines the number of wafers, their spacing, dimension, etc.

The model is formed by coupling basic mass- and energy-transport submodels for the "intra-wafer" and "annular flow" regions of the reactor. Formulating the problem as a set of coupled "one dimensional" intra-wafer and annular-flow problems leads to very significant computational savings compared to solving the two-dimensional problem directly.

Boundary conditions for the intra-wafer problem are defined at the symmetry axis and the outer edge of the wafers. At the outer edge of the wafers the values of the scalar dependent variables are taken to be equal to their values in the "annular region" of the reactor at the particular axial location of the wafer. These values are determined as part of a coupled simultaneous solution of the annular flow problem and the many "intra-wafer" problems. At the symmetry line of the wafers the convective and species diffusion velocities are set to zero.

The inlet flow of reactant gases to the reactor occurs through a number of "injectors" placed at different axial locations along the annular-flow region. Mass and energy addition from these injectors is included by adding a source term to the cell in which an injector is located. The user has the capability to specify an arbitrary number of injectors at different axial locations. The user is also allowed to specify the reactant gas composition, flow rate, and gas temperature for each injector.

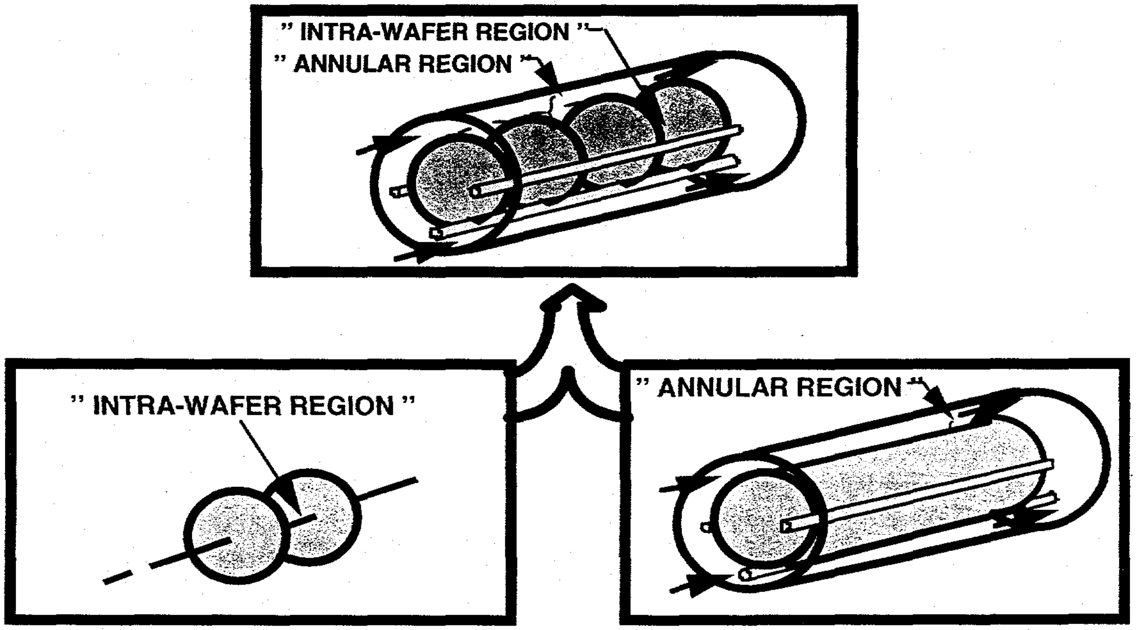

Figure 5. Schematic representation of the OVEND formulation as multiple "one-dimensional" problems

Temperature boundary conditions for the reactor walls and wafer surfaces are calculated using a separate, stand-alone application code, TWAFER [50]. This code solves the coupled radiant and convective heat transfer problem on the solid surfaces to obtain the steady-state temperature profiles. When the transport equations are integrated over the control cells in the intra-wafer and annular-flow regions, a system of coupled nonlinear algebraic equations results. This system of equations is solved by the hybrid Newton/time-integration procedure TWOPNT [37].

SUMMARY

The coupled gas-phase chemical kinetics, surface reaction rates, and species transport determine the concentrations and fluxes of species arriving at reactive surfaces in most deposition and etching systems used in the microelectronics industry. Numerical simulation TCAD tools are useful in modeling these systems for process understanding, design, optimization, and control. The Chemkin suite of software facilitates modeling of arbitrarily complex chemical reaction mechanisms within application codes written to simulate deposition and etching systems. A limitation in such modeling continues to be the availability of elementary reaction mechanisms describing the kinetics of the wide range of chemical systems of interest for the fabrication of microelectronic devices.

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