EVOLVE

Version 5.0i.a

USER'S MANUAL

Part I Reference Manual

August 1999

EVOLVE5.0i.a is a topography-relevant process simulator. Modules exist to simulate low pressure deposition and etch (*EVLP*), high pressure deposition and etch (*EVHIP*), and thermal thin film flow (*EVFLOW*).

This user's manual for EVOLVE, Version 5.0i.a was updated in April of 1999 by Max Bloomfield and David Richards of the Process Modeling and Simulation research group at Rensselaer Polytechnic Institute.

EVOLVE5.0i.a was developed by Timothy S. Cale, Max Bloomfield, David Richards, and Sofiane Soukane, starting from previous versions. It is based on extensive work by several people, including members of the Process Simulation Laboratory in the Center for Solid State Electronics Research at Arizona State University (through 1997) and many colleagues in industry.

For more information on the history of and the contributors to EVOLVE, please see *The History of EVOLVE* section of Part II of this manual.

Users can expect to find unclear, inconsistent and even incorrect information in this manual, as it is not completed, commercial grade documentation. For example, the documentation for EVHP and EVFLOW are not as well developed as that for EVLP.

EVOLVE is under development, and we would be pleased to hear from users about potential bugs, suggestions, or novel uses for EVOLVE

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Introduction

EVOLVE is a program that simulates *low pressure transport and reaction; e.g., physical vapor deposition (PVD), low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD), high pressure chemical vapor deposition (HPCVD), thin film thermal reflow processes, and etch processes.* EVOLVE was developed to fill the need for physically based simulators for deposition/etch/reflow processes in the microelectronics industry. EVOLVE is designed for process engineers and technology CAD (TCAD) engineers who need to determine the conformality and/or composition of deposited films, or profiles of etch surfaces, as functions of process conditions.

Because critical inputs such as reaction mechanisms, chemical kinetics, and flux distributions are not available for the vast majority of processes, a common use of EVOLVE at this time is as a tool to help determine the information required for physically based deposition simulations. The determination of the required information has the additional benefit of focusing attention on understanding the transport and kinetic processes that are important to deposition/etch/reflow processes. EVOLVE is well suited for this purpose. After achieving an understanding of a given deposition process, EVOLVE can be used for predictive simulations. The strong physical basis for EVOLVE is certainly an important feature; however, EVOLVE can also be used in a 'nonphysical' or a 'semi-physical' mode; *e.g.*, if the user is forced (through lack of information) to use suggested values for sticking factors, or if EVOLVE's predictions are compared with those of other simulation packages.

EVOLVE undergoes continuous development: Current features are being improved upon and new physical phenomena included. Some major improvements to EVOLVE are:

1. Specular transport of species.
2. Improved flux integration.
3. More reliable determination of surface fractions.
4. Improved surface movement algorithm.
5. Multiple-material substrates with material-specific reactions
6. Reaction rate models have been extended.
7. User-defined flux distributions can be included via files. Input files are designed in general format for simulations of low pressure deposition, etch, high pressure deposition, or reflow processes.In order to take advantage of some of the features

in EVOLVE; user-defined flux distributions, user defined reaction rates and user defined specular re-emission models, you need to have source or object code. Standard distributions include only executable code. EVOLVE can also be used by other simulation packages; however, this requires a special distribution. Special arrangements can be made in order to use these features and/or obtain source or object code through your contact person (see page 6).

This documentation package contains:

1. This reference manual, which introduces EVOLVE, the BTRM (ballistic transport and reaction model), the CTRM (continuum transport and reaction model), the VTFM (viscous thermal flow model), and EVOLVE.
2. A user's guide, which provides guidelines for learning EVOLVE and details on how to build data files for EVOLVE. The user's guide also contains an installation guide for EVOLVE.
3. A set of examples, which contains input data files and the main graphical outputs.

Contact Person

Questions or suggestions concerning applications, options, and performance of EVOLVE as well as licensing arrangements should be directed to the attention of

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Background

EVOLVE is a process simulation framework that uses physically based, first principles, transport, reaction, and reflow models. It simulates the surface evolution process at feature scale based on fundamental physical laws represented by the following models:

- BTRM (Ballistic Transport and Reaction Model)
- CTRM (Continuum Transport and Reaction Model)
- VTFM (Viscous Thermal Flow Model)

Simple introductions to the BTRM, the CTRM, and the VTFM are presented in Appendix A. A list of publications on EVOLVE related topics is provided in Appendix B. Further descriptions of the BTRM, CTRM, and VTFM can be found in a variety of publications such as in our previous work (Appendix B), and in citations therein to our own work and the publications of other groups. Knowledge of the BTRM, CTRM, and VTFM is assumed to some extent in this guide and would certainly improve confidence in and ability to interpret and evaluate simulation results.

EVOLVE5.0i.a, is designed to simulate the following processes under various process control conditions:

- LPCVD (low pressure chemical vapor deposition)
- HPCVD (high pressure chemical vapor deposition)
- PVD (physical vapor deposition)
- PECVD (plasma enhanced chemical vapor deposition)
- Etching
- Reflow (viscous thermal flow of thin film)

EVOLVE is set up for three-dimensional simulation of material transport and surface reactions on the surfaces of long features (long into the page) or into features with locally circular cross sections. For trenches, the cross section of the surface can be very general in shape; *e.g.*, it can have multiple asymmetric features. For features of circular cross section, EVOLVE is limited to simulating deposition/etch/reflow in one feature at a time; however, this feature can be of fairly arbitrary vertical cross section.

EVOLVE provides the opportunity for physically based deposition simulations, because its background physics is based on "first principles" models. For completely physically based simulations, you need to know or be able to estimate:

1. The heterogeneous reaction rate expressions for the reactions that result in film growth.
2. The angular distribution of reactant fluxes, both from the source volume above the wafer and from the wafer surfaces.
3. The surface diffusivities of adsorbed intermediates and components of the film.
4. The surface energies of films undergoing curvature driven surface diffusion.
5. The viscosities of films undergoing thermal reflow.
6. Homogenous reactions for high pressure transport and reaction systems.
7. Boundary conditions, perhaps in terms of operating conditions.

For simplicity in nomenclature, this group is referred to as "constitutive" relationships. They are essentially the models (submodels) required to complete the material balances that are represented by the integro-differential equations of the BTRM, and the partial differential equations of the CTRM and VTFM. Unfortunately, all of the information required for physically based simulation is available for only a limited number of deposition/etch/reflow systems. Until all of the constitutive relationships for a given deposition process are known, you will be forced to perform simulations that are not completely physically based. Of course, EVOLVE can be used to simulate deposition/etch/reflow processes for which there is little or no information, in the same manner as other deposition/etch/reflow process simulators. Nevertheless, your simulations should be as physically based as possible to maximize the usefulness of your results. EVOLVE is designed to be used as a tool in the determination of the required constitutive relationships [4,5]. In addition to providing a few standard equation forms for your convenience, EVOLVE is flexible enough to incorporate user-defined constitutive relationships (if you have source or object code).

LPCVD

To predict film profile evolution in LPCVD systems, it is usually safe to ignore surface diffusion and it is reasonable to use cosine flux distribution functions for each reactant from the source volume as well as all surfaces. Using these assumptions, physically based simulations are possible if you have information regarding the ***intrinsic kinetics*** of the deposition process. Deposition reaction kinetics have been estimated for several LPCVD systems of current interest. References 5-7 detail the type of information that is required, for blanket tungsten, tungsten silicide and silicon dioxide from TEOS, respectively. If sufficient kinetic information is not available to develop reliable rate expressions, then you may chose to run the simulator with pre-selected, constant values for sticking factor(s). Although this approach lacks physical basis, it has been used successfully (it is usually the only option) in other deposition simulation packages. If the observed aerial reaction rate (moles per second per area of surface) equation is available, this should be used in place of pre-selected values of the sticking factor. Even better would be a mechanism for the surface chemistry; unfortunately, such mechanisms have been proposed for only a few deposition systems. The models (rate expressions) used to approximate the deposition rates as a function of operating conditions for a given LPCVD chemistry should be determined from experiments. Reaction rate expressions have been proposed for many systems; however, they undergo refinement as more experimental information becomes available. Five fairly general reaction rate forms are included in EVOLVE. If the rate form you wish to use in a simulation can be written in one of these forms, then you enter the appropriate parameter values. If your rate expression cannot be written in one of these forms and you have source or object code, you may want to write your own subroutine to define the rate forms. User defined subroutines are briefly mentioned in the User's Guide.

PVD

To predict film profile evolution during PVD processes, it is often necessary to account for non-cosine flux distributions from the source gas as well as surface diffusion. On the other hand, it is often safe to ignore re-emission of the depositing species from the feature surfaces. The generalized cosine distribution [3], which contains one parameter is often used for PVD processes. It is not possible at this time to reliably predict the angular distribution of fluxes from operating conditions; therefore, simulated film profiles should be compared with experimental profiles to determine the distribution parameter. Of course, it may not be possible to fit the observed profiles using the generalized cosine distribution. If you have

object code, you may use a subroutine to define your own flux distribution function. Example 8 demonstrates how to use a file to input flux distributions; *e.g.*, from a simulator for collimated transport. For this version of EVOLVE, these flux distributions must have cylindrical symmetry with respect to the normal of the substrate. In particular, EVOLVE has been used to simulate collimated depositions [8,9].

EVOLVE is designed to handle physically based surface diffusion due to gradients in the surface concentrations of adsorbed surface species [10] and/or curvature driven surface diffusion [11]. Surface diffusion can also be included in simulations of LPCVD and PECVD processes, if desired. Concentration driven surface diffusion of adsorbed species can be incorporated only if a model for the surface chemistry is introduced which includes one or more diffusing species. It should be noted that even less is known about surface diffusion of adsorbed species than is known about deposition reaction kinetics and flux distribution functions.

PECVD

To predict film profile evolution during PECVD, both neutral and ionic species will have to be included. References 13-15 discuss the information required for PETEOS. Surface diffusion is usually not important. For neutral species, you should use the cosine distribution, unless other information is available. The normal distribution is often used for ionic species. Although progress has been made in the estimation of flux distributions from operating conditions for simple plasma systems [for examples, see references 16 and 17], they cannot yet be reliably estimated for the complex plasmas used for PECVD. Thus, it is recommended that the user compare simulated profiles with experimental film profiles and adjust the single parameter (standard deviation) of the distribution function for a given set of operating conditions. As for the case of PVD, other flux distribution functions can be defined by the user.

Little is known about the deposition kinetics for PECVD systems, because of their complexity. Completely physically based simulation of PECVD processes is less likely than for either LPCVD or PVD processes. References 14 and 15 discuss the use of EVOLVE for such semi-physical (but useful) simulations.

Etching

Etch process simulations could be done in previous versions of EVOLVE; however, the surface moving algorithm since 4.1a has been written with etching in mind. The reaction and

transport options are essentially the same as in previous versions. There is very little known about the fundamental chemical reactions that occur during etch processing. EVOLVE's role will largely be to help develop kinetic and transport models for various etching processes.

HPCVD

HPCVD processes are described using a two-dimensional continuum transport-reaction model appropriate for intrinsically two-dimensional features. EVOLVE solves the model governing equations to predict species concentration distributions inside the solution domain. The species considered include reactants, possible by-products and inert carrier gases. Special efforts have been made to improve the previously reported model boundary conditions at the top of the solution domain. The boundary conditions consist of species concentrations at the flat wafer surfaces, which may be estimated by feature scale models based on known reaction kinetics and experimental growth rate data or by reactor scale models. The height of the solution domain is selected such that its effect on the final simulator predictions is negligible.

A rather simple method of estimating effective species diffusivities is used in EVHIP. Another main challenge remaining in the CTRM applications is the estimation of species concentrations on the flat wafer surfaces, which are the requirements of the boundary conditions and generally unavailable from experimental measurements. For simple surface reactions, reactant concentrations can be predicted based on experimental film growth rates and compositions, if surface reaction kinetics are known. However, the concentrations of reaction by-product and carrier gases cannot be estimated in this way, although they affect the composition of the gas phase mixture and perhaps the rates of homogeneous reactions. Reactor scale simulations are highly recommended in those situations to accurately predict the reactant partial pressures at the wafer surface.

Reflow

The reflow part of EVOLVE is based on a viscous thermal flow model. The model is extended to infinitely long trenches with arbitrary cross sections and axisymmetric contacts/vias, for which two dimensional profile evolution is appropriate. The governing equations are the two dimensional Navier-Stokes equations and the continuity equation for incompressible fluids. Since the Reynolds number, which is the ratio of a characteristic inertial force to a characteristic viscous force, is smaller than 10^{-8}, the inertial forces are neglected. For a fixed anneal time, two parameters determine the film profile; surface

tension and viscosity. Gravity does not play a significant role during the processes. Fairly good agreement is found between EVOLVE predictions and experimental SEMs in BPSG/PSG thermal flow and Au laser melting processes. After the viscosity of the PSG films is modeled as a function of temperature and phosphorus pentoxide concentration using an Arrhenius type equation, the surface tension of the PSG films is estimated using experimental film profiles.

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Appendix A: BTRM, CTRM, VTFM and EVOLVE

EVOLVE, the deposition/etch/reflow process simulator, consists of two basic parts; 1) a process (transport, reaction, and viscous flow) model solver and 2) a surface movement algorithm. At any time, the surface is discretized into a finite number of geometric elements that contain information about the location and geometry of the surface. The process model solver solves the process model's governing equations on the discretized surfaces to get growth rates as functions of location at each time step. These local growth rates are used by the surface movement algorithm to update the film surface. After the surface is updated the surface representation is refined. This procedure is repeated until desired film thickness, feature closure or deposition time is reached.

This appendix contains brief descriptions of the BTRM, CTRM and VTFM, intended to help users understand more about the fundamental models employed by EVOLVE. All references referred to can be found in the publication list in Appendix B.

Ballistic Transport and Reaction Model (BTRM)

The BTRM was developed by Cale and coworkers. It is applicable to typical low pressure film deposition and etch processes that occur under conditions where the characteristic lengths are significantly smaller than the mean free path—that is, for Knudsen numbers $K_n \gg 1$. Advantages of the BTRM include the facts that the integro-differential equations of the BTRM are valid over the entire range of sticking factor from unity to zero and that local deposition rates may be obtained by solving the BTRM governing equations as determined by operating conditions and intrinsic kinetics.

Non-cosine, but cylindrically symmetric flux distributions were introduced into the BTRM to account for non-isotropic velocity distributions in the source volume. The flux of particles (η_i) of the *i*-th species to the surface depends on position, in general. The flux of the *i*-th species to a point *A* on the surface is expressed in terms of the volume number density n_i of the *i*-th species in the gas and velocity distribution function p_i. Assuming that any angular dependence of velocity can be factored, the velocity distribution function is the product of angular distribution function $g(\theta)$ and velocity magnitude distribution function p'. The flux of the *i*-th species passing through $d\mathbf{A}$ in the solid angle $d\omega$ can be written

$$\eta(\theta,\phi) = n_i\, g(\Omega)\cos\Omega\, d\omega \int_0^\infty p'(v)\,dv \qquad \text{(A1.1)}$$

In Equation A1.1, it is assumed that the velocity distribution through (or from) a point has cylindrical symmetry. *p'(v)* is an integration constant for a given speed distribution function.

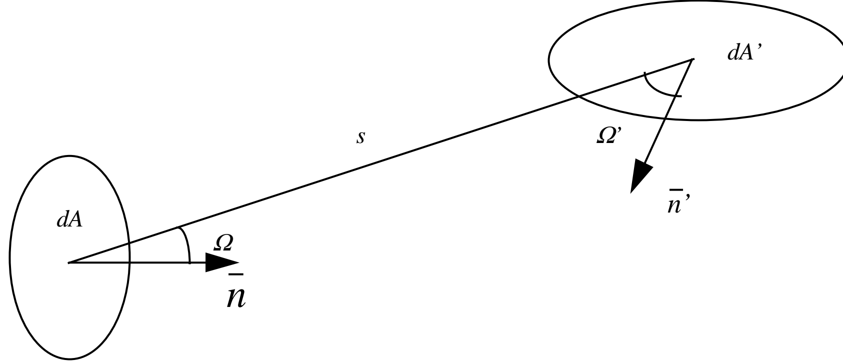

Figure 1: The geometry for determining the ballistic transport from *dA* to *dA'*

Assume that particles re-emit diffusely from the feature surfaces. As shown in **Figure 1**, the rate at which particles of the *i*-th species leave the differential surface area *dA* and strike the differential area *dA'* inside a feature is

$$\kappa_{AA'}\eta_{iA}^{l}\left[g_{iA}(\Omega)/G_{iA}\right]\cos\Omega\cos\Omega' dAdA'/\left(\pi s^2\right) \tag{A1.2}$$

where the differential areas are connected by a line segment of length *s* and their normal vectors form angles of Ω and Ω' with respect to this connecting line, $\kappa_{AA'}$ is the visibility factor that is unity if *dA* and *dA'* can see each other, zero if they cannot and *G* is the normalization constant for a specified *g*. G_{iA} can be expressed as

$$G_{iA} = 2\pi\int_0^{\pi/2} g_{iA}(\Omega)\cos\Omega\sin\Omega d\Omega \tag{A1.3}$$

The superscript *l* indicates flux leaving *dA*. A similar expression represents the flux of particles between the gas source and any position in the feature. For convenience, the transmission probability between *dA'* and *dA* is introduced

$$q(A;A') = \kappa_{AA'}\cos\Omega\cos\Omega'/s^2 \tag{A1.4}$$

The total flux to a point *A'* on the surface consists of all of fluxes leaving from other areas of the feature and the fluxes from the gas source volume:

$$\eta_{iA'}^{a} = \int_{source}\eta_{iA}^{l}\left[g_{iA}(\Omega)/G_{iA}\right]q(A;A')dA + \int_{surface}\eta_{iA}^{l}\left[g_{iA}(\Omega)/G_{iA}\right]q(A;A')dA \tag{A1.5}$$

where the integrations are over the feature surface and the source volume, as indicated. To incorporate deposition into the analysis, the local sticking factor is introduced. The sticking factor σ_{iA} is the probability that a particle of the *i*-th species, after colliding with the surface,

becomes physically incorporated into the wall or reacts to become part of a growing film. The flux of species *i* leaving a point *A* on the surface is related to its incoming flux by

$$\eta_{iA}^{l} = (1 - \sigma_{iA})\eta_{iA}^{a} \tag{A1.6}$$

The subscript *a* indicates incoming flux. The local total deposition rate is decided by

$$R(x, y, z, t) = r(x, y, z, t)v(x, y, z, t) \tag{A1.7}$$

where *r* is the rate of formation of the solid product and *v* is the molar volume of the deposited solid film.

For PVD and CVD systems, one angular distribution function of the flux from the source to the feature that has been used for fluxes of depositing materials is

$$g(\theta) = \frac{1}{\rho\, sin^2\,\theta + cos^2\,\theta} \tag{A1.8}$$

where ρ is the generalized cosine parameter. If ρ=1 then g=1 and the source is isotropic (cosine distribution). A function that has been used for ions in plasma systems is the normal distribution

$$g(\theta) = \frac{1}{\sqrt{2\pi\sigma}}\, exp\left(-\frac{\theta^2}{2\sigma^2}\right) \tag{A1.9}$$

where the width of the distribution is specified by σ and depends on the number of collisions of ions with other particles in the sheath, which in turn depends on operation conditions. In principle angular distribution function or σ and ρ can be estimated using Monte Carlo simulations. For example, Lin and Cale simulated angular flux distributions from hexagonal collimators using the Monte Carlo method. Myers *et al.* presented results of ion energy and angular distributions in single and dual frequency plasmas. They first solved a dual frequency sheath model to predict the potential as a function of position and time and the sheath thickness as a function of time. Then, Monte Carlo simulations were performed to determine the energy and angular distribution functions for the ions, taking into account a variety of collision types.

The above analysis assumes that particles are re-emit diffusely from surfaces. More detailed treatments of gas-solid interactions may be found in the references.

Continuum Transport and Reaction Model (CTRM)

Besides the basic feature scale models for simulating low pressure deposition processes inside the features, there is a different transport and reaction regime for low

Knudsen number (K_n<<1). This is modeled by the continuum transport regime where gas phase molecule-molecule collisions result in potential homogeneous reactions, which are not important inside features in lower pressure deposition processes.

Consider deposition in a feature on a patterned wafer that is exposed to a gas mixture under deposition conditions typical of high pressure CVD. Through heterogeneous chemical reactions, solid species are deposited on the flat wafer surface and on the sidewall and base surfaces of the feature. In order to develop a mathematical model for such processes, the following assumptions have been made:

1. The gas phase obeys the ideal gas law: At the conditions of pressure and temperature used in CVD reactors (pressure ≈ 1 atm), this is a reasonable assumption.
2. The effect of surface diffusion on deposited film conformality is neglected. According to the investigations of Oh et. al. on the deposition of thin films using high pressure CVD processes, the effect of surface diffusion is usually negligible on the deposited film conformality. Experimental studies of tungsten and tungsten silicide depositions concluded similar results.
3. The solution domain is isothermal: Since the features considered are on the micron scale, it seems to be a good assumption to neglect the heat transfer inside the films, and on the scale of features.
4. The key reactant is sufficiently dilute that the total volume change with reaction approaches zero under the deposition conditions considered: high pressure CVD processes generally have a large ratio of carrier (inert) gases to the reactant gases (> 100) in the system. The reaction-induced molar volume changes do not have significant effects on the total pressure.
5. Since the solution domain is near the wafer surface (within several microns), convective transport of species can be neglected. The height of the solution domain in the model is on the order of microns above the wafer surfaces. Because the tangential velocities of the species are zero at the wafer surface and the reactants and gaseous by-products are diluted in carrier gases, the convective transport of species in the solution domain is neglected.
6. The height of the solution domain is large enough in order that the species horizontal concentration gradients can be neglected at the top of the domain.

Any or all of these assumptions can be related or modified, if appropriate to a specific system. **Figure 2** shows a schematic feature, which represents a cross section of an infinitely long trench or an axisymmetric via. In this work, the *z*-axis is chosen to be the vertical axis. However, the selection of the origin of the rectangular or cylindrical coordinates is rather arbitrary, with the *x (r)* axis pointing from left to the right and the *z*-axis pointing from the bottom to the top of the paper, as shown in **Figure 2**.

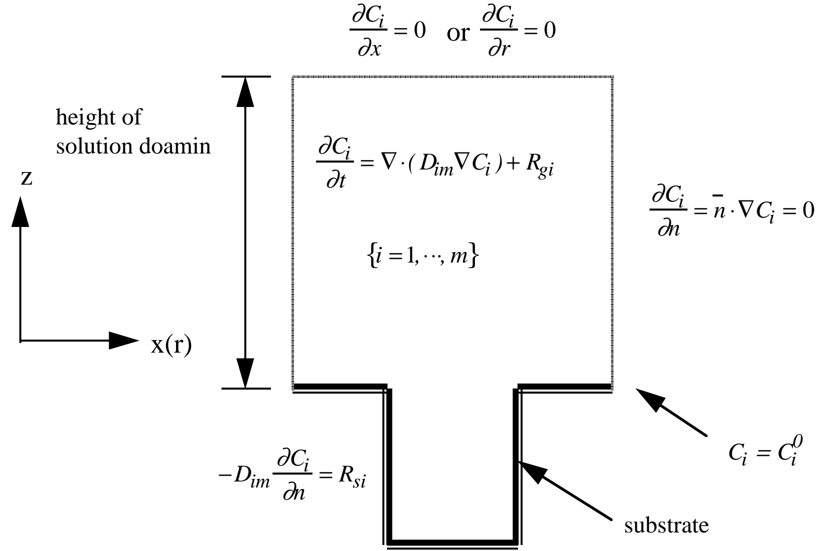

Figure 2 : Sample domain for governing equations and boundary conditions

Under assumptions (1) to (6), the governing equations are species balances; *i.e.*, time-dependent diffusion-reaction equation for each species,

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_{im} \nabla C_i) + R_{gi} \tag{A2.1}$$

in which for infinite trenches with no gradients in the *y*-direction:

$$\nabla \cdot (D_{im} \nabla C_i) = \frac{\partial}{\partial x}(D_{im} \frac{\partial C_i}{\partial x}) + \frac{\partial}{\partial z}(D_{im} \frac{\partial C_i}{\partial z}) \tag{A2.2a}$$

and for axisymmetric vias with no gradients in the azimuthal direction:

$$\nabla \cdot (D_{im} \nabla C_i) = \frac{1}{r} \frac{\partial}{\partial r}(D_{im} r \frac{\partial C_i}{\partial r}) + \frac{\partial}{\partial z}(D_{im} \frac{\partial C_i}{\partial z}) \tag{A2.2b}$$

C_i is the molar concentration of the species *i*, D_{im} is the effective diffusivity of species *i* in the mixture and R_{gi} is the homogeneous rate of generation the *i*-th species (moles/time/volume). Boundary conditions used in this study are:

I. Surface (heterogeneous) reaction on the wafer

$$-D_{im}\frac{\partial C_i}{\partial n} = R_{si} \quad \text{(A2.3a)}$$

II. At the top of the domain (in the source volume) for trenches and vias respectively

$$\frac{\partial C_i}{\partial x} = 0 \quad \text{(A2.3b)}$$

$$\frac{\partial C_i}{\partial r} = 0 \quad \text{(A2.3c)}$$

III. At the domain side wall

$$\frac{\partial C_i}{\partial n} = \bar{n} \cdot \nabla C_i = 0 \quad \text{(A2.3d)}$$

IV. At the flat wafer surfaces well away from the feature considered

$$C_i = C_i^0 \quad \text{(A2.3e)}$$

In above expressions, $\bar{n}$ is the local unit normal vector along the boundary given by

$$\bar{n} = \frac{-e_x \frac{\partial z}{\partial x} + e_z}{\sqrt{1 + (\partial z / \partial x)^2}} \quad \text{(A2.3f)}$$

or

$$\bar{n} = \frac{-e_r \frac{\partial z}{\partial r} + e_z}{\sqrt{1 + (\partial z / \partial r)^2}} \quad \text{(A2.3g)}$$

where e_x, e_r and e_z are unit vectors along x, r, and z directions, respectively. R_{si} is heterogeneous generation rate of the species i (moles/time/area) and C_i^0 is the concentration of the i-th species at the end of the solution domain on the flat wafer surface, as shown in **Figure 2**.

The local deposition rate (length/time) is determined from

$$G(x, y, t) = R_{solid}(x, y, t)v \quad \text{(A2.4)}$$

where v is the molar volume of the deposited solid film and R_{solid} represents the rate of formation of the solid product on the wafer surface (moles/time/area).

There are several parameters in addition to the physical properties of each species, which need to be determined before the model equations can be solved. First, there are the species concentrations at the flat wafer surface (Equation A2.3e). Experimental approaches,

however, are generally not able to measure those concentrations. Reactor scale models are usually required in those situations. One exception is that it is possible to use feature scale models to estimate surface concentrations based on known surface reaction kinetics and film growth rates for simple reaction systems. The second parameter is the height of the solution domain, which is an adjustable parameter in the model.

In order to complete the model equations for high pressure CVD processes, species transport properties need to be estimated. In general, the transport properties (diffusivities) are functions of local temperature, pressure, and composition of the gas mixture. Theoretical and empirical methods are used to calculate the species effective diffusivities.

The binary gas phase diffusivity at low to moderate pressure is calculated using kinetic theory. This theory gives expressions for the transport coefficients in terms of the intermolecular potential energy of interaction φ between a pair of molecules as a function of their separation distance *r*. A widely used empirical potential energy function for non-polar molecules is the Lennard-Jones potential, given by

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{A2.9}$$

in which σ is the collision diameter of the molecule and ε is a characteristic energy of interaction between the molecules. The Lennard-Jones potential of species *i* is characterized by σ_i and ε_i, usually given as ε_i / k, where *k* is Boltzmann's constant. These parameters may be estimated from experimental data or from empirical relations as functions of the critical properties of the species.

The binary diffusivity D_{ij} of the gas pair *i* and *j* is a function of temperature and pressure, but is virtually independent of gas composition, *viz*

$$D_{ij} = 0.0018583\frac{\sqrt{T^3\left(\frac{1}{m_i}+\frac{1}{m_j}\right)}}{P\sigma_{ij}^2\Omega_{D,ij}} \tag{A2.10}$$

with *T* in Kelvin, *P* in atm and σ_{ij} in Angstrom. In Equation A2.10, m_i and m_j are molecular weights of species *i* and *j*, respectively, σ_{ij} is the characteristic Lennard-Jones length and $\Omega_{D,ij}$ is the diffusion collision integral, which is a dimensionless function of the temperature and of the intermolecular potential field for one molecule of *i* and one of *j*. The Lennard-Jones parameters σ_{ij} and ε_{ij} could, in principle, be determined from accurate measurements of D_{ij} over a wide range of pressure and temperature. With somewhat greater difficulty, other measured properties of mixtures of *i* and *j* could be used, such as viscosity and thermal

diffusivity. However, suitable data are rare; therefore σ_{ij} and ε_{ij} usually have to be estimated. A method that is widely used to estimate the mean values is to use the mixing rules

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{A2.11a}$$

and

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \tag{A2.11b}$$

The collision integral $\Omega_{D,ij}$ is a function of temperature only and is given by

$$\Omega_{D,ij} = \frac{1.06036}{\bar{T}^{0.15610}} + \frac{0.19300}{exp(0.47635\bar{T})} + \frac{1.03587}{exp(1.52996\bar{T})} + \frac{1.76474}{exp(3.89411\bar{T})} \tag{A2.12}$$

with the reduced temperature $\bar{T}$ given by

$$\bar{T} = \frac{kT}{\varepsilon_{ij}} \tag{A2.13}$$

where k is Boltzmann's constant.

By assuming that the i-th species diffuses through a stagnant multicomponent mixture, the effective diffusivity of the i-th species in the mixture D_{im} is calculated from

$$D_{im} = (1 - x_i)\left(\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}} \right)^{-1} \tag{A2.14}$$

where x_i is the molar fraction of i-th species. The assumption of the stagnant multi-component mixture may become doubtful when the system has fast surface reactions. In those cases, the D_{im} should be estimated by solving Stefan-Maxwell equations, namely,

$$\frac{1}{D_{im}} = \frac{\sum_{j=1}^{n} \left(1/D_{ij}\right)\left(x_j N_i - x_i N_j\right)}{N_i - x_i \sum_{j=1}^{n} N_j} \tag{A2.15}$$

where N is the species local flux. Equation A2.14 is an approximate solution of Equation A2.15 in a stagnant mixture. Assuming that reactants and gaseous by-products are diluted in carrier gas j, D_{im} is equal to the binary diffusivity D_{ij}. This result can be derived from both Equations A2.14 and A2.15.

Viscous Thermal Flow Model (VTRM)

The equations that represent the thin film viscous flow model are a set of coupled partial differential equations that describe the momentum and mass balances along with appropriate boundary conditions. Several assumptions behind the model used are:

1. The deposited film is isothermal: Since the thicknesses of the films are on the order of a micron, heat transfer inside the films is neglected.
2. The physical properties of the film are not a function of position (isotropic): The viscosity and surface tension of the film are functions of film compositions and annealing temperatures, and they are not easily controlled properties. The isotropic assumption may become doubtful when steep dopant concentration gradients exist inside the films.
3. The melted films are incompressible: This is a valid assumption for the films considered here, which generally have high densities and viscosities and are glass-like liquids.
4. The melted film is Newtonian: The shear stress-shear rate behavior of many liquids can be described by Newton’s law, *i.e.*, shear stress-shear rate relation is linear. A Newtonian fluid is a good starting point, considering the lack of data to accurately define the shear stress-shear rate relationship.
5. The flow is laminar: The Reynolds numbers in thin film thermal flow processes are extremely small ($<10^{-8}$).

Figure 3 shows schematic as-deposited film and substrate profiles. The feature geometries considered include infinitely long trenches or an axisymmetric vias, for which two-dimensional profile evolution is appropriate. In this work, the z-axis is chosen to be the vertical axis. The selection of the origin of the rectangular or cylindrical coordinate system is rather arbitrary, with x (r) axis pointing from left to the right and z axis pointing from bottom to the top of the paper.

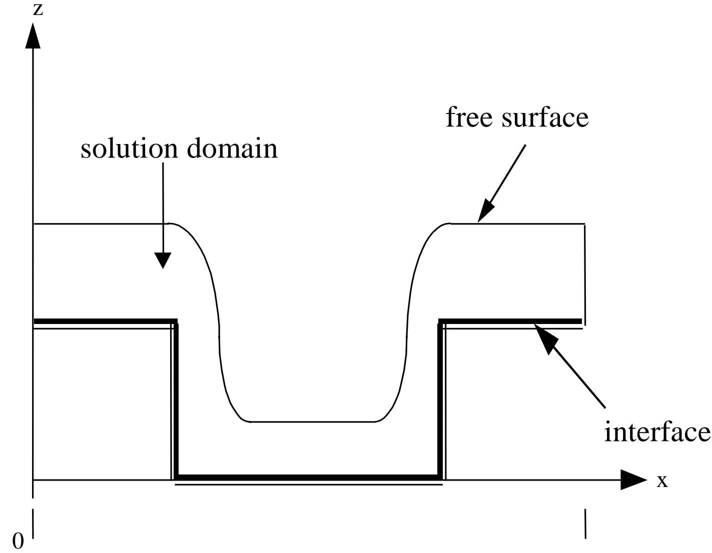

Figure 3: Coordinate systems used in the viscous flow model

With assumptions and geometries discussed above the process can be modeled as a two-dimensional, incompressible, free-boundary problem. The location of the free boundary, $B(x,z,t)$ or $B(r,z,t)$, is unknown and must be determined as it changes over time. The other unknowns are the velocity and pressure distributions in the film. The governing equations are the continuity equation and the Navier-Stokes equations for the incompressible fluid. The continuity equation simply describes the conservation of mass. The Navier-Stokes equations express the momentum balances in the x, r and z directions. According to the assumptions 2 and 4, the melted film has constant density and viscosity and the shear stress-shear rate relation is linear (Newtonian fluid). The governing equations are:

for infinitely long trenches (rectangular coordinates):

continuity equation:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial z} = 0 \qquad \text{(A3.1)}$$

x-momentum balance:

$$-\frac{\partial p}{\partial x} + \mu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial z^2}\right) = 0 \qquad \text{(A3.2)}$$

z-momentum balance:

$$-\frac{\partial p}{\partial z} + \mu\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2}\right) - \rho g = 0 \qquad \text{(A3.3)}$$

and for axisymmetric contacts/vias (cylindrical coordinates):

continuity:

$$\frac{\partial u}{\partial r}+\frac{u}{r}+\frac{\partial v}{\partial z}=0 \tag{A3.4}$$

r-momentum:

$$-\frac{\partial p}{\partial r}+\mu\left[\frac{\partial^2 u}{\partial r^2}+\frac{1}{r}\frac{\partial u}{\partial r}-\frac{u}{r^2}+\frac{\partial^2 u}{\partial z^2}\right]=0 \tag{A3.5}$$

z-momentum:

$$-\frac{\partial p}{\partial z}+\mu\left[\frac{\partial^2 v}{\partial r^2}+\frac{1}{r}\frac{\partial v}{\partial r}+\frac{\partial^2 v}{\partial z^2}\right]+\rho g=0 \tag{A3.6}$$

Here u and v are the vertical and horizontal velocities, respectively, corresponding to coordinates x and z or r and z, p is the pressure, ρ is the film density and μ is viscosity.

The flow field satisfies conditions of no slip and no penetration at the interface of the flowing film and the substrate:

$$u=0 \text{ (no slip)} \tag{A3.7a}$$

$$v=0 \text{ (no penetration)} \tag{A3.7b}$$

On the free surface the flow satisfies the normal and shear stress balance as well as the kinematic boundary condition at $z=h(x)$ or $z=h(r)$:

normal stress balance:

for trenches

$$\frac{\partial h}{\partial x}\left(-p+2\mu\frac{\partial u}{\partial x}\right)-\mu\left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial z}\right)=\sigma\frac{\partial h}{\partial x}\frac{1}{R_1} \tag{A3.8a}$$

for vias

$$\frac{\partial h}{\partial r}\left(-p+2\mu\frac{\partial u}{\partial r}\right)-\mu\left(\frac{\partial u}{\partial r}+\frac{\partial v}{\partial z}\right)=\sigma\frac{\partial h}{\partial r}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \tag{A3.8b}$$

shear stress:

long trenches

$$\left(-p+2\mu\frac{\partial v}{\partial z}\right)-\mu\left(\frac{\partial u}{\partial z}+\frac{\partial v}{\partial x}\right)\frac{\partial h}{\partial x}=\sigma\frac{1}{R_1} \tag{A3.8c}$$

for vias

$$\left(-p+2\mu\frac{\partial v}{\partial z}\right)-\mu\left(\frac{\partial u}{\partial z}+\frac{\partial v}{\partial r}\right)\frac{\partial h}{\partial r}=\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \quad \text{(A3.8d)}$$

where σ is the surface tension. R_1 and R_2 are radii of curvature, which are given by [83]

$$\frac{1}{R_1}=\frac{\partial^2 h/\partial x^2}{\left[1+(\partial h/\partial x)^2\right]^{3/2}} \text{ or } \frac{1}{R_1}=\frac{\partial^2 h/\partial r^2}{\left[1+(\partial h/\partial r)^2\right]^{3/2}} \quad \text{(A3.8e)}$$

$$\frac{1}{R_2}=\frac{\partial h/\partial r}{\sqrt{r\left(1+\left(\partial^2 h/\partial r^2\right)^2\right)}} \quad \text{(A3.8f)}$$

The two radii of curvature for a general three-dimensional surface (axisymmetric via/contact) are combined as follows. One erects a normal to the surface at the point in question and then passes a plane through the surface and containing the normal. The line of intersection in general will be curved, and the radius of curvature is that for a circle tangent to the line at the point involved. The second radius of curvature is obtained by passing a second plane through the surface, also containing the normal, but perpendicular to the first plane. This gives a second line of intersection and a second radius of curvature. If the first plane is rotated through a full circle, the first radius of curvature will go through a minimum. However, the sum $1/R_1+1/R_2$ is independent of how the first plane is oriented.

For distinguishing purposes, h is used to represent the z-coordinates of the points on the free surfaces. The normal stress boundary condition states that the jump in pressure across the boundary is equal to the surface tension times the mean curvature of the surface. The shear stress states that the jump in shear stress across the boundary is equal to the gradient of the surface tension along the surface. The kinematic boundary condition, *i.e.*, the condition that there is no mass flux across the free surface ($B(x, z, t)$ or $B(r, z, t)$) is:

for trenches

$$\bar{n}\cdot\left(e_x u+e_z v-\frac{\partial B(x,z,t)}{\partial t}\right)=0 \quad \text{(A3.9a)}$$

for vias

$$\bar{n}\cdot\left(e_r u+e_z v-\frac{\partial B(r,z,t)}{\partial t}\right)=0 \quad \text{(A3.9b)}$$

where $\bar{n}$ is the outward pointing unit normal vector at the free surface, as expressed in Equations A2.3f and A2.3g. At the solution domain side wall, the boundary conditions are that the same features and film structures appear periodically on the substrate; *i.e.*,

$$\frac{\partial v}{\partial n}=0 \quad \text{(A3.10a)}$$

and

$$u = 0 \tag{A3.10b}$$

Appendix B Articles on EVOLVE Related Topics

Updated Feb. 04, 1997

"Physically Based Modeling of Selective Deposition and Etch Processes", V. Mahadev, Z. Tang and T. S. Cale, in preparation.

"Integrated Modeling and Simulation of Dual Frequency Plasma Deposition Processes", F. R. Myers and T. S. Cale, in preparation.

"Control Aspects of Programmed Rate Chemical Vapor Depostion of Tungsten", J. Kristof, L. Song, K. S. Tsakalis and T. S. Cale, in preparation.

"Nonuniformity in CMP Processes Due to Stresses", D. Wang, S. M. Chandrashekar, S. P. Beaudoin and T. S. Cale, to be published in Proceedings of the Second International Conference on Chemical-Mechanical Polish Planarization for ULSI Multilevel Interconnection, VMIC, 1997, in press.

"Multi-Scale Simulations for Thermal Chemical Vapor Deposition Processes", M., K. Gobbert, T. Merchant, L. J. Borucki and T. S. Cale, **J. Electrochem. Soc.**, submitted.

(Invited) "Feature Scale Transport and Reaction During Low Pressure Deposition Processes", T. S. Cale and V. Mahadev, in **Thin Films**, Vol. 22, S. Rossnagel and A. Ulman (eds.), Academic Press, 1996, p. 175.

(Invited) "Topography Evolution During Semiconductor Materials Processing", T. S. Cale, V. Mahadev, Z. Tang, G. Rajagopalan and L. J. Borucki, in Plasma Processing of Semiconductors, F. Williams (ed.), Kluwer Academic Publishers, 1997, in press.

(Invited) "Introduction to Plasma Enhanced Chemical Vapor Deposition", T. S. Cale, G. B. Raupp, B. R. Rogers, F. R. Myers and T. E. Zirkle, in Plasma Processing of Semiconductors, F. Williams (ed.), Kluwer Academic Publishers, 1997, in press.

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"Simulation of Collimated Titanium Nitride Physical Vapor Deposition using EVOLVE", A. J. Toprac, S.-Q. Wang, J. Schlueter, and T. S. Cale, to be published by MRS.

"Transport Through Multicomponent Dual Frequency Plasma Sheaths", F. R. Myers, M. W. Peters, M. Ramaswami and T. S. Cale, **Thin Solid Films**, accepted.

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