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Step Coverage Prediction in Low-Pressure Chemical Vapor Deposition

G. B. Raupp* and T. S. Cale

Department of Chemical, Bio & Materials Engineering and Center for Solid State Electronics Research, Arizona State University, Tempe, Arizona 85287

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A mathematical model incorporating simultaneous one-dimensional Knudsen diffusion and chemical reaction is employed to analyze transient behavior during low-pressure chemical vapor deposition (CVD) in features of arbitrary geometry on patterned semiconductor wafers. For a given feature geometry and CVD reaction, the dimensionless model equations reveal that step coverage is controlled by the value of a single dimensionless parameter that represents the ratio of a characteristic deposition rate to a characteristic reactant diffusion rate. Temperature, reactant partial pressure at the feature mouth, and aspect ratio are the process parameters that may be varied to improve step coverage for a given CVD chemistry. The proper directions of change for temperature and reactant pressure are determined by the parameters of the intrinsic reaction rate expression for the particular CVD chemistry of interest. Deposition of amorphous SiO₂ from TEOS (tetraethyl silicate) is considered as a specific example. The model predicts that step coverage improves with decreasing temperature and increasing pressure of TEOS at the feature mouth, in agreement with experimental results. Calculation of reactive sticking coefficients shows that this diffusion-reaction model is consistent with the modification of the line-of-sight model that invokes low sticking coefficients to explain conformal step coverage.

Introduction

An important goal of chemical vapor deposition (CVD) of thin films in microelectronics fabrication is conformal step coverage over patterned regions of the wafer. Examples of processes in which step coverage is especially critical include deposition of insulating films between metal interconnect levels and deposition of metal, silicide, or polysilicon films for the electrical interconnections themselves. Current trends in very large scale integration (VLSI) technology make achievement of conformal step coverage increasingly important for several reasons. First, as lateral dimensions have continued to shrink, vertical dimensions have not scaled by the same factor, due primarily to materials' properties limitations.¹ Hence aspect ratios of contact holes and vias have steadily increased. Second, because chip area is largely controlled by metalization area, vertical integration in the form of multilevel interconnection has been adopted as a strategy for further shrinking of microcircuits.^{1,2} Poor step coverage and lack of planarity in underlying deposited layers will compound the problem of achieving good step coverage in subsequently deposited layers.

It has been previously reported³⁻¹⁰ that the quality of step coverage in low-pressure CVD (LPCVD) depends on deposition parameters including temperature, total gas-flow rate, reactant pressures, and growth rate as well as the substrate material and the geometry of the step. The currently accepted theory used to explain experimental observations, summarized briefly in the next section, borrows heavily from the ideas and experience of physical

vapor deposition. In this model it is presumed that LPCVD is a line-of-sight process and that therefore non-conformal step coverage can largely be explained by geometrical shadowing effects. The model in its current form cannot quantitatively predict the proper relationship between deposition parameters. Moreover, in certain instances the model incorrectly predicts even qualitative directional changes in step coverage (improvement vs degradation) as a particular parameter is varied. These major shortcomings have led to much confusion in the field and have dictated programs of development that are empirical in nature.

Alternative models for gas-solid reaction on internal surfaces exist in the literature but have not gained much attention. In 1957, Peterson¹¹ modeled atmospheric pressure carbon gasification in a long cylindrical pore with simultaneous first-order reaction and diffusion. In a series of papers published in the late 1970s, van den Brekel and

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* Author to whom correspondence should be addressed at the Department of Chemical, Bio & Materials Engineering.

co-workers¹²⁻¹⁴ modeled atmospheric pressure CVD over patterned substrates by accounting for two-dimensional diffusion and heterogeneous reaction in triangular and trapezoidal trenches. McConica and Churchill¹⁵ were the first to propose that low-pressure CVD in cylindrical contact holes could be described by pseudo-steady simultaneous reaction and one-dimensional molecular, or Knudsen, diffusion. The model was developed specifically for hydrogen reduction of tungsten hexafluoride, a reaction exhibiting zero-order kinetics in limiting reactant (WF_6). In this original model, nonuniform deposition arises due to a moving front of limiting reactant starvation as the contact hole fill proceeds. Because of the simple kinetics involved, an analytical expression for the position of the reaction front could be employed. Deposition at the hole base was not accounted for in the model boundary conditions. In a second paper, McConica et al.¹⁶ numerically simulated unsteady simultaneous zero- and first-order deposition reactions in a cylindrical contact hole; deposition at the hole base was taken into account. In this paper we extend the pseudo-steady model of McConica and co-workers to numerically simulate LPCVD processes with arbitrary deposition kinetics in features of arbitrary geometry. Here concentration gradients can arise due to mass-transfer limitations inside the contact hole and directly lead to nonconformal film growth as a function of depth. Simulation results are presented for the TEOS-SiO₂ chemistry, which follows half-order deposition kinetics. The model qualitatively predicts typically observed experimental trends. More importantly, the model reveals the interrelationship between deposition variables, and thus this model may be useful in guiding development strategies.

Accepted Theory of Step Coverage in LPCVD

The currently accepted model used to explain step coverage in LPCVD is essentially the same as that developed for physical vapor deposition (PVD). The concepts involved and modeling equations for step coverage prediction in PVD are summarized in articles by Tisone and Bindell¹⁷ and Blech.¹⁸ In LPCVD, the mean free path of reactant gas molecules is much greater than the dimensions of the contact hole, and it is therefore reasoned that deposition in the contact hole is not unlike the PVD line-of-sight process. If the *reactive* sticking coefficient of the limiting gas-phase reactant, defined as the fraction of molecules striking the surface that react, is unity, then step coverage is completely determined by geometrical shadowing effects. Within a feature, both shadowing by the opposing wall and self-shadowing due to nonuniform film growth on the wall can lead to a reduction in local deposition rate.

This model predicts that step coverage should be a function of geometry only and thus be independent of CVD chemistry, a prediction that is clearly in opposition to experimental observation. For example, Levin and Evans-Lutterodt³ investigated the step coverage behavior of undoped and phosphorous-doped SiO₂ glass films deposited using atmospheric pressure and low-pressure CVD

with SiH₄/O₂ mixtures, using LPCVD with TEOS, and using plasma-enhanced CVD with SiH₄/N₂O mixtures. For identical trench geometries, the LPCVD TEOS exhibited markedly better step coverage than either the plasma-enhanced or thermal SiH₄-based deposition chemistries.

In most LPCVD processes, observed step coverage is markedly superior to that predicted on the basis of pure geometrical shadowing. For this reason, the original model has been modified to explain these situations. One modification allows for surface migration following adsorption. The *adsorptive* sticking coefficient, defined as the fraction of molecules striking the surface that adsorb, is assumed to be unity in this case. The adsorbed reactant molecule either will react at the original adsorption site or may migrate from site to site. According to the conventional argument, this surface diffusion serves to locally average the angular range of the source seen by different points within the contact hole. The conventional argument further reasons that because surface diffusivity increases with surface temperature, step coverage is expected to improve with increasing temperature. Recent results have shown that the *opposite* trend is observed for a number of CVD chemistries.⁴⁻⁶

A second modification relaxes the assumption of unity *reactive* sticking coefficient. Here surface diffusivity is assumed to be negligible. For sticking coefficients less than 1, a fraction of the molecules that strike the surface are inelastically scattered back into the gas phase. Every point on the internal surface then acts as a local source of reactant molecules, minimizing geometrical shadowing which would otherwise lead to nonconformal coverage. The fact that no quantitative prediction of reactive sticking coefficients based on first principles has been performed to date has limited the general applicability of this model.

The model described below incorporates simultaneous gas-phase molecular diffusion and heterogeneous reaction within a feature of arbitrary geometry. The model is consistent with the second modification of the original model described above, in that it predicts that reactive sticking coefficients are indeed low during a typical conformal hole fill and are relatively higher during a nonconformal fill. However, it is neither desirable nor necessary to deal with sticking coefficients directly, since that information is implicit in the deposition rate expression. Nonetheless, one goal of this paper is to reconcile the concepts of the model described herein with the concepts of the accepted model by showing how sticking coefficients vary in time and space during a feature fill.

Alternative Theory Development

In LPCVD, the gas density is sufficiently low so that the mean free path is orders of magnitude greater than the dimensions of a typical wafer feature. Under these conditions, continuum dynamical descriptions of gas flow must be replaced by the kinetic theory of gases and the Boltzmann equation. The Boltzmann equation is a rather complicated nonlinear integrodifferential equation whose solution for practical problems appears to be feasible only through suitable approximations.

To avoid the computational difficulties of the Boltzmann equation, we model the feature fill process as one of time-dependent simultaneous heterogeneous reaction and Knudsen diffusion¹⁹ as described by the kinetic theory of gases. Consider deposition in a feature of arbitrary cross section \mathcal{R} and depth \mathcal{H} defined spatially by a moving

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coordinate system with the origin at the center of the feature mouth. The following assumptions are crucial to the model development: (i) deposition occurs through a single heterogeneous reaction under conditions for which a single reactant is limiting; (ii) the feature is isothermal; (iii) homogeneous reactions occur to a negligible extent; (iv) surface diffusion is negligible; (v) lateral or radial concentration gradients are small. Under this set of assumptions, the concentration profile of limiting reactant *i* in the feature is governed by a one-dimensional material balance which states that the rate of accumulation of *i* in a differential volume element of the feature is defined by an imbalance between the diffusive flow rate of *i* into the element and the rate of disappearance of *i* by heterogeneous reaction, or

$$\frac{\partial\{C_i\mathcal{A}\}}{\partial t} = \frac{-\partial\{\mathcal{A}N_i\}}{\partial z} - \mathcal{R}(C_i, T) \frac{\partial a}{\partial z} \quad (1)$$

Here $\mathcal{R}(C_i, T)$ is the molar rate of disappearance of *i* due to surface reaction per unit surface area as a function of local molar concentration C_i and local temperature, T , a is the active surface area, and N_i is the molar flux of *i* given by

$$N_i = -\mathcal{D}_{K_i} \partial C_i / \partial z \quad (2)$$

where \mathcal{D}_{K_i} is the cross-sectional area averaged Knudsen diffusivity. In general, variables are functions of position and time. Note that expression 2 is applicable for all CVD reactions carried out at low pressure, even those in which there is a change in the number of gas-phase molecules, since in free molecular flow component gases diffuse independently of each other. Appropriate spatial boundary conditions for $t > 0$ are

$$C_i(0, t) = C_{i0} \quad (3a)$$

$$N_i(\mathcal{H}, t) = \mathcal{R}(C_i(\mathcal{H}, t), T) \quad (3b)$$

where C_{i0} is the concentration of *i* at the feature mouth. Boundary condition 3b states that at the feature base the surface chemical reaction rate must be balanced by the rate of molar diffusive flux of limiting reactant to the solid surface. A constant concentration of limiting reactant at the feature mouth, condition 3a, implies that the deposition reactor is operated under steady conditions. A number of different initial conditions can be envisioned depending on reactor startup procedures.

Combining eq 1 and 2 with $\partial a / \partial z = \mathcal{P}(z, t)$, where $\mathcal{P}(z, t)$ is the instantaneous local feature perimeter, the material balance becomes

$$\frac{\partial}{\partial t} \{C_i(z, t) \mathcal{A}(z, t)\} = \frac{\partial}{\partial z} \left\{ \mathcal{A}(z, t) \mathcal{D}_{K_i}(z, t) \frac{\partial C_i}{\partial z} \right\} - \mathcal{P}(z, t) \mathcal{R}(C_i(z, t), T) \quad (4)$$

To clarify the relationship between deposition parameters and to facilitate translation of model results to a spectrum of CVD chemistries, we rewrite the model equations in dimensionless form by referencing all variables except axial distance to conditions at the feature mouth at time zero. This development differs from those of McConica and co-workers, which reference variables to instantaneous conditions at the feature mouth, yielding equations whose parameters are time dependent.^{15,16,20} If we define the following dimensionless parameters:

dimensionless time

$$\tau = t \mathcal{D}_{K_{i0}} / \mathcal{H}_0^2$$

dimensionless axial distance

$$\xi = z / \mathcal{H}$$

dimensionless feature depth

$$H(\tau) = \mathcal{H}(\tau) / \mathcal{H}_0$$

dimensionless cross section

$$A(\xi, \tau) = \mathcal{A}(\xi, \tau) / \mathcal{A}_0$$

dimensionless perimeter

$$P(\xi, \tau) = \mathcal{P}(\xi, \tau) / \mathcal{P}_0$$

dimensionless concentration

$$\Theta(\xi, \tau) = C_i(\xi, \tau) / C_{i0} \quad (5)$$

dimensionless diffusivity

$$D_K(\xi, \tau) = \mathcal{D}_{K_i}(\xi, \tau) / \mathcal{D}_{K_{i0}}$$

dimensionless reaction rate

$$G(\xi, \tau) = \mathcal{R}(\xi, \tau) / \mathcal{R}_0$$

step coverage modulus

$$\Phi = \frac{\mathcal{H}_0^2 \mathcal{P}_0 \mathcal{R}_0}{\mathcal{A}_0 \mathcal{D}_{K_{i0}} C_{i0}}$$

where subscript zero refers to conditions at the feature mouth at time zero, the differential equation 5 becomes

$$\frac{\partial \Theta}{\partial \tau} = -\frac{\Theta}{A} \frac{\partial A}{\partial \tau} + \frac{1}{AH^2} \frac{\partial}{\partial \xi} \left\{ AD_K \frac{\partial \Theta}{\partial \xi} \right\} - \Phi \cdot G \cdot P / A \quad (6)$$

The boundary conditions are transformed to

$$\Theta(0, \tau) = 1 \quad (7a)$$

$$\partial \Theta / \partial \xi(1, \tau) = -\beta \Phi H(\tau) G(1, \tau) / D_K(1, \tau) \quad (7b)$$

where β is equal to the ratio of initial cross-sectional area to initial sidewall area, or $\mathcal{A}_0 / \mathcal{P}_0 \mathcal{H}_0$. For a given geometry, β can be written as a function of feature aspect ratio.

The first term on the right-hand side of the equation can be shown to be negligible by rewriting the partial derivative as

$$\partial A / \partial \tau = -\Phi P(\xi, \tau) G(\xi, \tau) / \rho \quad (8)$$

where ρ is the ratio of deposited film molar density to the molar density of gaseous reactant *i*. Upon substitution and rearrangement, eq 6 becomes

$$\frac{\partial \Theta}{\partial \tau} = \frac{1}{AH^2} \frac{\partial}{\partial \xi} \left\{ AD_K \frac{\partial \Theta}{\partial \xi} \right\} - \Phi \frac{G \cdot P \cdot [1 - \Theta / \rho]}{A} \quad (9)$$

In LPCVD processes, solid density ρ is typically more than 6 orders of magnitude greater than gas density, and hence Θ / ρ can be set equal to zero without meaningful loss of model accuracy.

For the results presented in this paper, the model equations were solved numerically for a cylindrical contact hole by using the so-called "pseudo-steady-state" approximation ($\partial \Theta / \partial \tau \approx 0$). Physically, this assumption implies that concentration profiles adjust rapidly to the gradual movement of the solid film front during deposition so that at any particular instant in time, the gas-phase concentration profile in the feature is the steady-state profile that would exist for the reaction conditions prevailing at that instant. Although this assumption simplifies solution of the equations, it may not be appropriate under certain conditions. McConica and Inamdar²⁰ have recently solved the unsteady equations for a zero-order reaction in a cylindrical contact hole and have concluded that the pseudo-steady model is appropriate only for conditions in

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which there is no significant depletion of reactant in the feature. We have solved the full-time dependent partial differential equation for a number of cases and found little discrepancy between unsteady and pseudo-steady predictions for process conditions that lead to good step coverage ($\geq 95\%$).²¹ Successively greater divergence between the two predictions results as Φ is increased. We are currently working to quantitatively define the regime for which the pseudo-steady approximation is not valid.

The approximate form of the differential equation 9 was cast in finite difference form by dividing the contact hole length into 100 equal-size segments and using central finite difference approximations for the derivative terms. Newton's method was used to linearize the equations about a trial solution and subsequently to solve the linearized simultaneous algebraic equations for the pseudo-steady-state concentration profiles. At time zero the analytical profile obtained for a zeroth order reaction²² was utilized as the trial profile. At subsequent times the previously converged profile was used as an initial guess. The tri-diagonal matrix of partial derivatives was inverted by using a modified Gauss-Jordan reduction algorithm to yield the correction vector for dimensionless concentrations. We found it necessary to employ a fractional correction of 0.5 to avoid oscillation around and divergence from the actual profiles. Iteration continued until concentrations at all points changed less than 0.001% from one iteration to the next. The total deposition time to achieve closure at the hole mouth was divided into 100 equal-size steps. The results were affected neither by tighter convergence tolerances nor by the use of a greater number of increments in distance or time. Following convergence, local growth rates were calculated assuming a nominal SiO₂ density of 2.27 g/cm³. These growth rate profiles were used to update the sidewall profile for the next time step. Although reaction at the contact hole base is accounted for in the boundary condition, to simplify the computations the changing length of the contact hole was not taken into account. In this regard, one should note that in conformal hole fills the contact hole depth is not changed since deposition at the base is offset by deposition on the external surfaces of the wafer at the hole mouth. Thus for conformal fills this approximation introduces little error. In nonconformal fills the hole length increases as deposition proceeds, and the approximation becomes progressively poorer.

Local Knudsen diffusivities were estimated by using the theoretical expression for holes of infinite length combined with an empirical correction factor for tubes of finite length:²³

$$\mathcal{D}_{Ki} = \left\{ \frac{20 + 8(\mathcal{H}/2R)}{20 + 19(\mathcal{H}/2R) + 3(\mathcal{H}/2R)^2} \right\} \mathcal{H} / 4 \cdot (8k_B T / \pi m_i)^{1/2} \quad (10)$$

where k_B is Boltzmann's constant, T is absolute temperature, m_i is the molecular mass of i , and R is the instantaneous local hole radius. The square-root term is the mean molecular velocity estimated assuming a Maxwell distribution function. Similar expressions are available for other feature geometries.

Results and Discussion

The dimensionless model equations reveal that for a given feature geometry, step coverage is controlled by the step coverage modulus Φ and the deposition reaction concentration dependence G . For an n th order deposition reaction, G is equal to Θ^n . Thus step coverage behavior is determined uniquely by the parameters Φ , n , and feature geometry, as discussed previously by Cale et al.²¹ For equal values of Φ , increasing order n leads to successively poorer step coverages since greater dependence on concentration magnifies deposition nonuniformity in the feature. Aspect ratio exerts only a minor effect on step coverage for equivalent Φ , since aspect ratio appears explicitly as an independent parameter only in the second boundary condition. For equivalent aspect ratios, cylindrical contact holes represent a more severe test of step coverage than do rectangular trenches of infinite length.

Before discussion of results of the complete model including time evolution of sidewall profiles, it is instructive to consider the effect of step coverage modulus on reactant concentration profiles. Physically, the meaning of this dimensionless parameter can be revealed by rewriting Φ as

$$\Phi = \frac{[\mathcal{H}_0 \mathcal{P}_0] \cdot \mathcal{R}(C_{i0})}{\mathcal{A}_0 \cdot \mathcal{D}_{Ki0} [C_{i0} - 0] / \mathcal{H}_0} \quad (11)$$

The step coverage modulus can be seen to represent a ratio of characteristic rates. The numerator is the rate of heterogeneous reaction of the limiting reactant i on the feature sidewall in the complete absence of mass-transfer limitations. The denominator is the rate of diffusion of limiting reactant i under conditions of a linear concentration profile with zero concentration of i at the feature base. A large value of the step coverage modulus will therefore result in a severe concentration gradient and nonuniform deposition throughout the contact hole. Conversely, a small value will yield a mild concentration gradient and relatively uniform deposition. Clearly processing strategies aimed at improving step coverage should seek to decrease the step coverage modulus.

The power of the step coverage modulus concept is that the correct interrelationship between process variables becomes evident. For n th order kinetics and a cylindrical contact hole

$$\Phi = \frac{2\mathcal{H}_0^2 (R_g T)}{R_0 \mathcal{D}_{Ki0}} k_0 \exp[-E/R_g T] p_{i0}^{n-1} \quad (12)$$

Expression 12 combined with expression 10 for Knudsen diffusivity reveals that for a given CVD chemistry, only three process parameters control step coverage. These three parameters are temperature T , partial pressure p_{i0} of the limiting reactant at the feature mouth, and the contact hole geometric aspect ratio $\mathcal{H}_0/2R_0$. All other deposition processing parameters such as flow rate, total pressure, and reactor configuration are important only inasmuch as they affect these three key parameters.

Temperature appears explicitly in the numerator of the step coverage modulus, in the reaction rate constant, and in the Knudsen diffusivity. For chemical reactions with typical apparent activation energies in the range 80–200 kJ/mol, the strongest temperature dependence of the various factors is manifested in the rate constant. Indeed, for the TEOS-SiO₂ chemistry the apparent activation energy is 195 kJ/mol,²⁴ and increasing temperature markedly increases the step coverage modulus and leads

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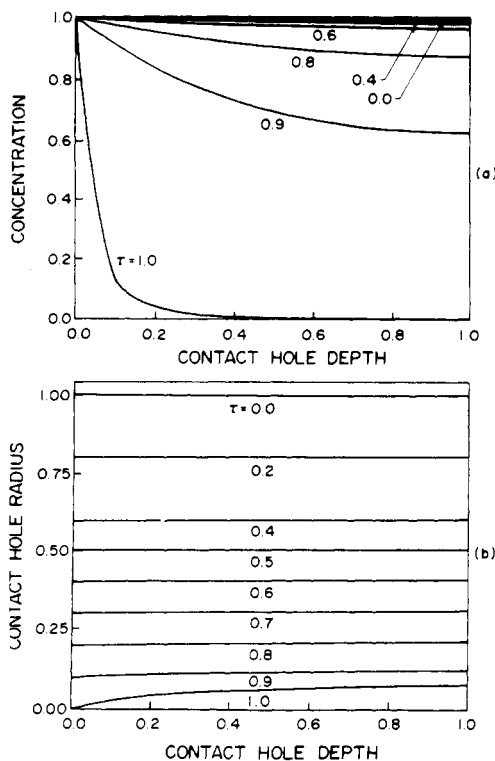


Figure 1. Time evolution of TEOS dimensionless concentration profiles and contact hole sidewall profile for reaction conditions that yield good step coverage. Model parameters were $\Phi = 0.013$, $n = 0.5$, and aspect ratio = 12.5. Dimensionless time τ refers to fractional time to hole closure.

to a degradation in step coverage.

The exponent of the reactant partial pressure term arises due to a mismatch between the functional dependences of the reaction rate (order n) and of the diffusive flux (first order) on reactant pressure. On this basis, we can formulate several "rules of thumb" for improving step coverage for a given CVD chemistry of known reaction order. For reaction orders less than 1, increased pressure of limiting reactant at the feature mouth will improve step coverage. Step coverage is independent of reactant pressure for first-order reactions. For reaction orders greater than 1, decreased partial pressures will improve step coverage. In application of these rules it must be emphasized that the salient partial pressure is that at the contact hole mouth, which, under conditions of nondifferential conversion or due to the effects of thermal diffusion and other complicating factors, could be very different from the reactor inlet value. This fact alone might be responsible for much of the confusion in this field regarding the effects of such deposition parameters as total flow rate, total pressure, and reactant partial pressures on observed step coverages. Indeed, careful consideration must be given to all potential gradients in a given reactor,²⁵ including axial and radial flow velocity, temperature, and concentration gradients before unequivocal conclusions on the effects of a given parameter on step coverage can be made.

Figure 1 presents the time-varying nature of the dimensionless concentration profiles and sidewall profile for a temperature of 973 K, pressure of TEOS at the contact hole mouth of 0.25 Torr, and initial geometric aspect ratio equal to 12.5 (50- μm depth and 4- μm diameter); for these

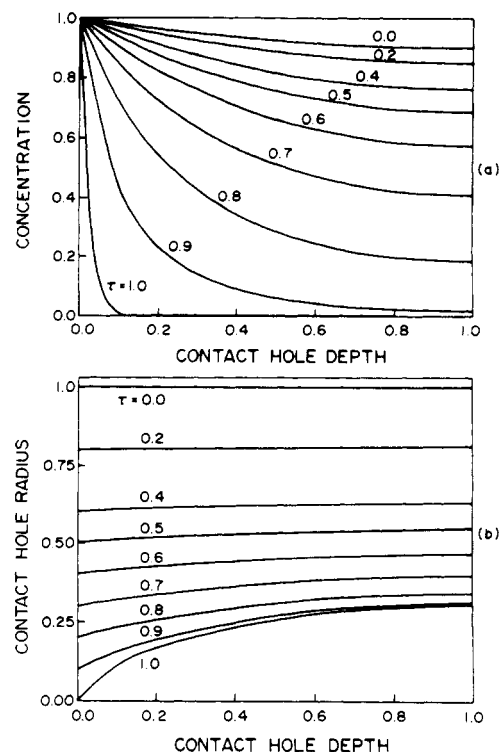


Figure 2. Time evolution of TEOS dimensionless concentration profiles and contact hole sidewall profile for reaction conditions that yield poor step coverage. Model parameters were $\Phi = 0.19$, $n = 0.5$, and aspect ratio = 12.5. Dimensionless time τ refers to fractional time to hole closure.

process parameters Φ equals 0.013. A reaction order of $1/2$ was employed in our simulations; this value was based on the data of Adams and Capio²⁴ from which we have derived a value for the rate parameter of $38.77 \text{ mol}/(\text{cm}^2\cdot\text{s}\cdot\text{Torr}^{1/2}) \exp\{-195 \text{ kJ}\cdot\text{mol}^{-1}/R_g T\}$. For these conditions and deposition kinetics, the model predicts step coverages at hole closure of $SC_{\text{base}} = 92.4\%$ and $SC_{\text{half}} = 93.7\%$, where these values are evaluated as ratios of the final film thickness at the base and half the contact hole depth, respectively, to film thickness at the feature mouth. Figure 1a shows that at 0.8 of the way to hole closure, concentration gradients are relatively mild with base concentration remaining above 87% of the mouth concentration. Corresponding deposition is nearly conformal, as shown in the time-dependent contact hole radial profiles in Figure 1b. As the radii decrease, instantaneous step coverage aspect ratios increase and Knudsen diffusivities decrease. Both factors serve to increase the severity of the instantaneous deposition conditions, and thus concentration gradients become more severe as deposition proceeds. However, even at 90% closure, concentration at the base remains well above zero, and hence ultimate step coverage is fairly high.

The behavior described above can be contrasted with that for conditions in which a much lower step coverage is achieved ($SC_{\text{base}} = 67\%$) by comparing Figure 1 to Figure 2. In this simulation temperature is higher (1023 K) and TEOS pressure is lower (0.01 Torr) than for the previous case ($\Phi = 0.19$); both factors contribute to lower step coverage. Significant concentration gradients are present even at time zero and become progressively more severe, leading to fairly nonconformal deposition as early as halfway through the contact hole fill. By the time hole closure is achieved, internal mass-transfer limitations have become so severe that the bottom half of the contact hole is literally starved for reactant.

The model was used to predict step coverages as a function of the three key process parameters. Figure 3

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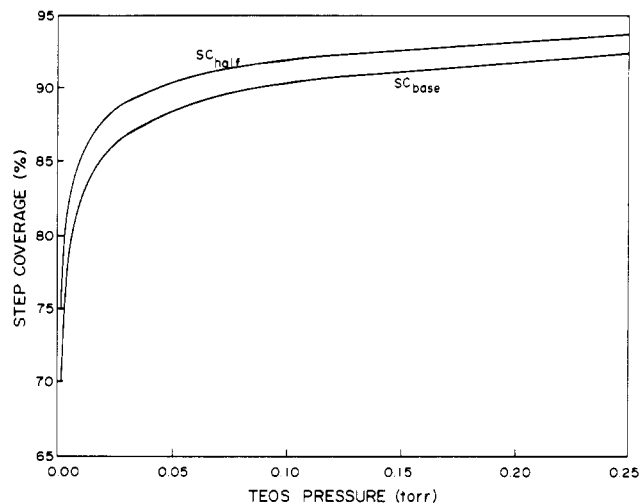


Figure 3. Effect of TEOS partial pressure at the contact hole mouth on step coverage.

summarizes step coverage dependence on partial pressure of TEOS at the contact hole mouth, holding temperature and geometric aspect ratio constant at 973 K and 12.5, respectively. The predictions exhibit the expected trend that step coverage is monotonically degraded with decreasing reactant partial pressure, in qualitative agreement with experimental observations. However, the model significantly overestimates quantitative values of observed step coverage; under the conditions of the simulations, Levin and Evans-Lutterodt reported that step coverage decreased from 54 to 41%.³ There exist several possible reasons for this lack of quantitative agreement. First, it is unlikely that the quoted total pressures³ are identical with the actual TEOS partial pressures at the contact hole mouth. On the basis of *average* reported deposition rates³ compared to deposition rates predicted by the intrinsic kinetic rate expression developed by Adams and Capio,²⁴ we estimate that actual *average* TEOS pressures were anywhere from 14 to 40% of the reported total pressures. This discrepancy may be due to reactant depletion along the length of the CVD reactor. In this case TEOS pressure will be a function of position in the reactor and could well be over an order of magnitude less than the reported inlet pressure if the contact hole of interest was located near the reactor gas flow exit. If TEOS pressures in the reactor were indeed significantly less than the values reported, quantitative agreement between the model and experiment might be closer than the numerical comparison above suggests. In addition, decomposition products may affect local deposition rates and contribute to further deposition nonuniformity. Clearly, differential reactant conversions are desired if the model is to be experimentally validated.

A second reason for step coverage overestimation lies in the approximate nature of the model itself. The pseudo-steady-state assumption appears to be a poor approximation for conditions that yield poor step coverage.^{20,21} In addition, several approximations are inherent in the expression for Knudsen diffusivity. This average diffusivity was derived assuming a mild pressure gradient in a cylindrical contact hole of infinite length by integrating the flow over a cross section of the tube. Depending on prevailing reaction conditions, reactant partial pressure profiles may be steep. In addition, flow is not uniform across the flow area. One can show that flow down the contact hole axis is 18% greater than the average flow, whereas flow at the wall is only 75% of the average. The radial averaging process employed here greatly simplifies modeling but fails to account for nonuniform flow which

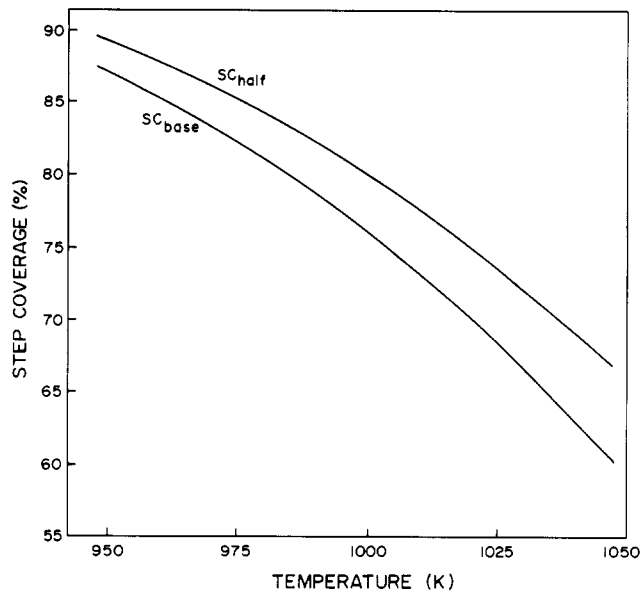


Figure 4. Effect of temperature on step coverage.

could contribute to nonuniform deposition. Moreover, the use of the average Knudsen diffusivity for cylindrical geometries fails to account for the fact that contact hole sidewalls are not vertical during deposition. In light of these factors, lack of quantitative agreement between model and experiment is understandable.

The effect of temperature on step coverage for a constant TEOS pressure of 0.01 Torr is shown in Figure 4. Step coverage depends strongly on temperature; coverage rapidly degrades as temperature is increased above 1000 K. This degradation is a direct result of the fact that for TEOS, the rate of heterogeneous decomposition increases much more rapidly than the rate of diffusion as temperature is increased.

Decreased step coverage with increasing temperature is observed for most CVD chemistries in which the effect has been investigated, including deposition of Si from disilane or silane,⁵ of W from tungsten hexafluoride and hydrogen,^{4,6} and of W from silane, tungsten hexafluoride, and hydrogen mixtures.⁶ An exception to this temperature-step coverage trend is the deposition of SiO₂ from silane/oxygen or disilane/oxygen mixtures.⁵ For this particular chemistry, the apparent activation energy for film deposition is uncommonly low. Baliga and Gandhi²⁶ report an apparent activation energy of only 2.8 kJ/mol. In a more recent publication Maeda and Nakamura²⁷ isolated the surface reaction rate parameter from the adsorption parameters; from their data one can conclude that under certain conditions (low surface coverages by reactants) the apparent activation energy may actually be *negative*. For this reaction we therefore expect that diffusivity will increase more rapidly than reaction rate with increasing temperature, and hence observed step coverage dependence on temperature is consistent with the expectations of the model.

Figure 5 shows the effect of increasing aspect ratio $H_0/2R_0$ on step coverage at constant TEOS pressure and temperature. The model predicts that step coverage decreases in a nearly linear fashion with increasing aspect ratio. McConica et al.¹⁶ have suggested that step coverage varies linearly with the square of the aspect ratio. Our predictions show that although step coverage modulus increases as the aspect ratio squared, this dependence is

(26) Baliga, B. J.; Gandhi, S. K. *J. Appl. Phys.* 1973, 44, 990.

(27) Maeda, M.; Nakamura, H. *J. Appl. Phys.* 1981, 52, 6651.

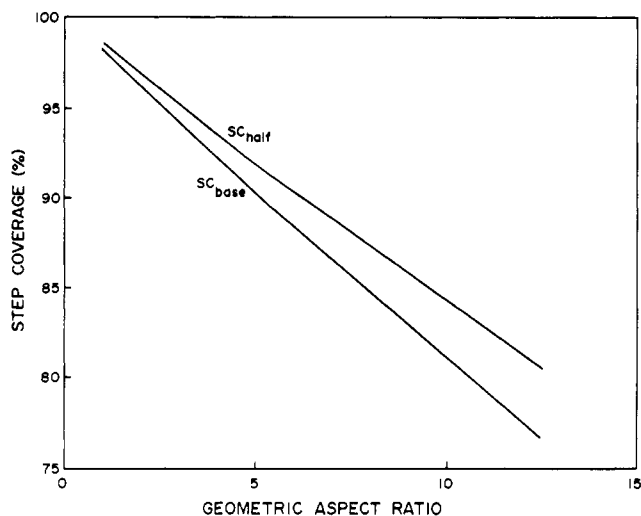


Figure 5. Effect of contact hole aspect ratio on step coverage.

not carried through linearly to the arbitrarily defined step coverage.

In summary, the model presented here correctly predicts all expected qualitative trends in experimental step coverage behavior. With further sophistication (e.g., an unsteady model, a two-dimensional model) and careful experimentation better agreement between experiment and theory should be achieved. Even without further improvement, the alternative model is a significant improvement over the accepted line-of-sight model in that semiquantitative predictions can be made on the basis of readily measurable data. Indeed, all that is required is an intrinsic reaction rate expression and the feature geometry. No assumptions need be made concerning numerical values of surface diffusivity or sticking coefficient.

The present model is consistent with the modification of the line-of-sight model, which suggests the idea that low sticking coefficients lead to conformal step coverage. To demonstrate this fact for the current model, we have calculated the time evolution of reactive sticking coefficient profiles for the converged concentration profiles in the contact hole fills simulated in Figures 1a and 2a. Reactive sticking coefficients are simply calculated as a ratio of reaction rate per unit area divided by collision rate per unit area. Collision frequencies Z may be estimated from the kinetic theory of gases assuming an ideal gas, or

$$Z = C_i(k_B T / 2\pi m_i)^{1/2} \quad (13)$$

where all variables are as previously defined. For an n th-order deposition reaction

$$\mathcal{R} = k_0 \exp(-E/R_g T) C_i^n \quad (14)$$

where the rate of reaction is in molecules/(cm²·s) and E is the apparent activation energy, the reactive sticking coefficient becomes

$$S = k_0(2\pi m_i/k_B T)^{1/2} \exp(-E/R_g T) C_i^{n-1} \quad (15)$$

Note that the behavior of the sticking coefficient with varying T or C_i mimics that of the step coverage modulus. The sticking coefficient may either decrease or increase with increasing T depending on the apparent activation energy E ; for activated reactions, S increases with T . For negative apparent activation energies S decreases with increasing T . For first-order reactions S is independent of reactant concentration. For n less than 1, S decreases with increasing reactant concentration; S increases with increasing concentration for reactions with n greater than 1.

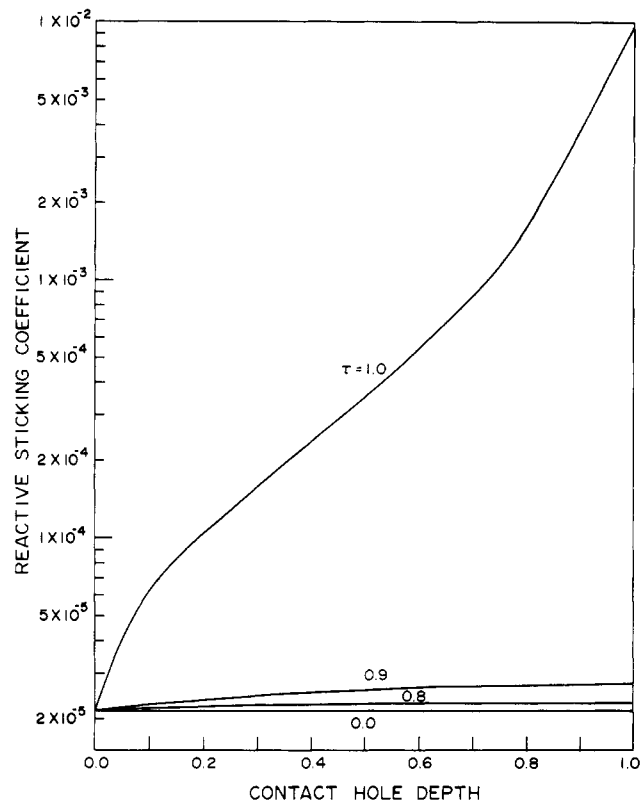


Figure 6. Time evolution of sticking coefficient profiles for the conditions of Figure 1. Dimensionless time τ refers to fractional time to hole closure.

Figure 6 presents the time evolution of the reactive sticking coefficient profiles for the conditions of the contact hole fill simulation represented in Figure 1. Reactive sticking coefficients are initially low, on the order of 10^{-5} , and are uniform through the depth of the contact hole. Sticking coefficients remain essentially uniform as the fill proceeds up until 80% closure; this uniformity in sticking coefficient reflects the conformal film deposition at the initial stages of contact hole fill. As deposition proceeds and concentration gradients become more severe, S values increase with contact hole depth and become nonuniform. Consequently, film deposition in the latter stages of the fill becomes increasingly nonconformal.

Figure 7 shows the corresponding reactive sticking coefficient profiles for the simulation represented in Figure 2. Initial sticking coefficients are more than an order of magnitude higher than in the previous case. The steeper gradients in sticking coefficient reflect the steeper gradients in TEOS concentration. The fact that S approaches unity at the contact hole base at closure is consistent with the idea that here deposition is nearly completely controlled by the rate of internal mass transfer.

Conclusions

The model presented here correctly predicts qualitative trends typically observed in LPCVD on patterned wafers. Moreover, the model demonstrates that for given CVD chemistry, only three process variables control step coverage. These key parameters are reactant partial pressure at the feature mouth, temperature, and feature aspect ratio. The relationship between these variables is revealed through the dimensionless parameter we have called the step coverage modulus Φ . The greater the step coverage modulus, the greater the deposition nonuniformity. Thus, in development of LPCVD processes in which step coverage must be improved, deposition parameters should be

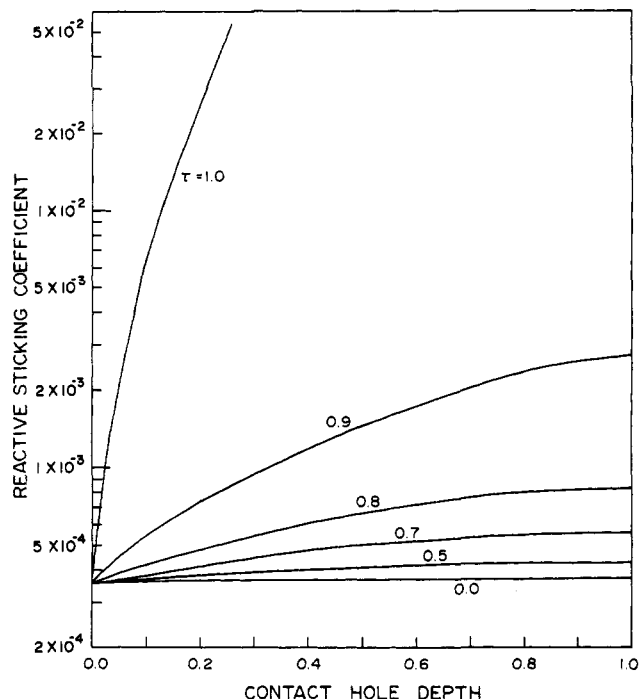


Figure 7. Time evolution of sticking coefficient profiles for the conditions of Figure 2. Dimensionless time τ refers to fractional time to hole closure.

adjusted so that the step coverage modulus is decreased.

For a given aspect ratio, either temperature or reactant pressure or both may be adjusted to enhance step coverage. The proper direction of parameter adjustment depends on the partial pressure dependence and apparent activation energy of the intrinsic deposition kinetics for the particular CVD chemistry of interest. Using the step coverage modulus as a guideline, the following rules of thumb may be used in parameter adjustment: (i) increase reactant partial pressure for reactions of order less than 1; (ii) decrease reactant partial pressure for reactions of order greater than 1; (iii) reactant partial pressures will not effect step coverage for first-order reactions; (iv) decrease temperature for activated or nonactivated reactions (activation energies ≥ 0); (v) increase temperature for negative apparent activation energies.

When viewed in context of the model presented here, many apparent inconsistencies in experimental step coverage data can easily be explained. For example, consider the TEOS-SiO₂ deposition chemistry. Kern et al.²⁸ and Levin and Evans-Lutterodt³ have independently concluded that deposition rate is not an important step coverage parameter since in some cases increasing deposition rate improved step coverage, whereas in other cases increasing deposition rate degraded step coverage. The model shows that what is important is not the absolute deposition rate but the relative rates of deposition and internal mass transfer by diffusion, as manifested in the step coverage modulus. The model demonstrates that increased TEOS partial pressure increases deposition rate and improves step coverage. This improvement is due to the fact that the diffusion rate increases faster than the reaction rate,

which increases only as the square root of concentration. On the other hand, increased temperature also increases deposition rate but in this case decreases step coverage. Because the TEOS reaction is highly activated, deposition rate increases much more rapidly than diffusion with increasing temperature.

Finally, we note that the alternative model is not in opposition to the version of the generally accepted model which attempts to explain step coverage observations in terms of nonunity reactive sticking coefficients. Rather, the model presented in this paper serves to formalize this idea and provide a vehicle by which sticking coefficients may be directly estimated as functions of position and time.

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Nomenclature

A	feature cross sectional area, cm ²
A_0	feature initial cross sectional area, cm ²
A	dimensionless feature cross-sectional area
a	active surface area for deposition, cm ²
C_i	molar volumetric concentration of i , mol/cm ³
C_{i0}	concentration of i at the feature mouth, mol/cm ³
D_{Ki}	average Knudsen diffusivity of i , cm ² /s
D_{Ki0}	average Knudsen diffusivity of i at time zero, cm ² /s
D_K	dimensionless Knudsen diffusivity
E	activation energy, kJ/mol
G	dimensionless reaction rate
k_0	preexponential factor for rate parameter k
k_B	Boltzmann's constant
\mathcal{H}	feature depth, μm
\mathcal{H}_0	initial depth of feature, μm
H	dimensionless feature depth
m_i	molecular mass of i , g/molecule
n	reaction order with respect to limiting reactant
N_i	molar flux of limiting reactant i , mol/(cm ² ·s)
P_{i0}	partial pressure of limiting reactant at feature mouth
\mathcal{P}	feature perimeter, cm
\mathcal{P}_0	initial perimeter of feature, cm
P	dimensionless feature perimeter
R	radius of contact hole, μm
R_0	initial radius of contact hole, μm
R_g	gas constant, cal/(mol·K)
\mathcal{R}	intrinsic specific heterogeneous reaction rate of i , mol/(cm ² ·s)
S	reactive sticking coefficient, dimensionless
SC_{base}	step coverage based on film thickness at feature base, percent
SC_{half}	step coverage based on film thickness at one-half feature depth, percent
t	time, s
T	temperature, K
z	axial distance, μm
Z	collision frequency, molecules/(cm ² ·s)

Greek Characters

β	ratio of initial cross-sectional area to initial sidewall area
θ	dimensionless concentration of limiting reactant i
ξ	dimensionless axial distance
ρ	ratio of deposited film molar density to molar density of gaseous reactant i
τ	dimensionless time
Φ	dimensionless step coverage modulus

Registry No. SiO₂, 7631-86-9.

(28) Kern, W.; Vossen, J. L.; Schnable, G. L. *Annu. Proc., Reliab. Phys.* [Symp.] 1973, 11th, 214.