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Spin coating: One-dimensional model

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The model of the spin-coating process presented here accounts for variations of concentration, viscosity, and diffusivity across the thickness of the spin-coated film. The flow of the liquid is governed by a balance between centrifugal driving force and viscous resisting force. Radial variations in film thickness and concentration are neglected. The Galerkin/finite-element method is employed to solve the equation set. Film thinning slows initially due to decreasing film thickness and ceases finally due to dramatically increasing viscosity of the coating liquid as solvents evaporate. The formation of a region of extremely low solvent concentration and correspondingly high viscosity and low binary diffusivity at the free surface, i.e., a solid "skin," is predicted. Coating defects can occur if convective flow has not completely ceased when this skin forms. Skin formation can be eliminated or delayed by partially saturating the overlying gas with solvent or by using mixed solvents (having both high and low volatilities) in the coating liquid. The temperature variation in the film during coating varies negligibly from the ambient.

INTRODUCTION

Spin coating is used to deposit the photoresist films used in the lithographic stages of microelectronic manufacturing processes. With the diminishing size of microelectronic devices, it has become increasingly important to understand the interaction between liquid flow and mass transfer during spin coating. The basic principles of the fluid mechanics, solvent transport, and film formation in spin coating were presented in a preceding paper,[1] where the approximations in previous analyses were evaluated and compared. The main conclusion was that the line of mathematical modeling begun by Emslie, Bonner, and Peck[2] and advanced by Meyerhofer[3] could be substantially improved by accounting for variations of composition, viscosity, and diffusivity across the thickness of the film of liquid being spin coated. Here a mathematical model—equations of flow and convective diffusion—is put forward to account for the solvent concentration with depth within a drying film. The old approximation that the radial velocity of the liquid is determined by a balance between centrifugal driving force and viscous resisting force is retained. The model is said to be one dimensional because radial variations in solvent concentration and film thickness are ignored.

The one-dimensional model reported here allows more reliable predictions than the models that have been available. It provides insights into the mechanisms of flow and evaporation and their interaction during spin coating by representing the concentration profile across the thickness of the film. As solvent evaporates, the nonvolatile material concentrates more and more toward the free surface of the film. As concentration rises, viscosity does too. Ultimately, it rises so abruptly that the remaining material becomes practically solid. And as concentration rises, diffusivity of the remaining solvent falls. Often, it ultimately falls abruptly. These phenomena were missing from previous attempts at modeling,[3–5] which have relied on the assumption of uniform solvent concentration throughout the film at all times. There have been two previous attempts to model the concentration profile across the thickness of the thinning film. The first[6] was invalidated by an erroneous flow model (cf. Bornside, Macosko, and Scriven,[1] and Lawrence[7]). In the second,[7] the concentration in the bulk of the film is taken to be constant with the concentration variation being restricted to a boundary layer adjacent to the free surface. In the present work, no restrictions are placed on the variation of concentration across the thickness of the coated film. The effects of partially saturating the bulk of the gas overlying the spinning disk with the volatile solvent are also examined. The model is then extended to include the case of a binary solvent system where the solvents have differing volatilities. Finally, the temperature variation in the film during coating is investigated.

ONE-DIMENSIONAL MODEL

The one-dimensional model rests on the underlying physical principles of conservation of mass and momentum. Radial variations in the film thickness and solvent concentration in the liquid are ignored by this model, and the densities of the components of the coating liquid are taken to be equal and constant. The one-dimensional model allows a virtually unrestricted solvent concentration profile in the liquid. (Figure 1 shows the cylindrical coordinate system used for modeling the spin-coating process.)

Local conservation of mass of solvent within the coating liquid is expressed by the convective-diffusion equation:

$$\frac{\partial x_A}{\partial t} + w\frac{\partial x_A}{\partial z} - \frac{\partial}{\partial z}\left(D(x_A)\frac{\partial x_A}{\partial z}\right) = 0. \qquad (1)$$

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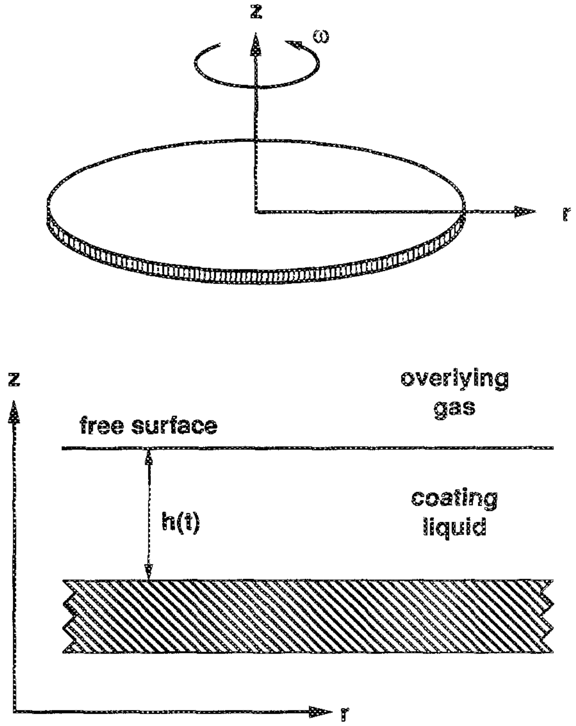

FIG. 1. Cylindrical coordinate system used for modeling the spin-coating process. Radial variations in film thickness are ignored.

x_A is the mass fraction of solvent A, t is time, z is distance above the surface of the disk, w is velocity normal to the surface of the disk, and D is binary diffusivity which generally depends on concentration. Local conservation of overall mass within the coating liquid is expressed by the continuity equation

$$\frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{\partial w}{\partial z} = 0. \tag{2}$$

r is radial position and u is the velocity in the radial direction.

The radial velocity u is determined by requiring that centrifugal driving force and viscous resisting force balance[2]:

$$u = \int_0^z \frac{\rho\omega^2 r(h-z')}{\eta(x_A)}\,dz'. \tag{3}$$

Here ω is the spin speed, ρ is the liquid's density, and η is its viscosity, which generally depends on concentration. h is the time-dependent thickness of the film. Substituting this velocity profile into the continuity equation gives

$$\int_0^z \frac{2\rho\omega^2(h-z')}{\eta[x_A(z',t)]}\,dz' + \frac{\partial w}{\partial z} = 0. \tag{4}$$

The substrate is impenetrable, and so there is no overall mass flux or mass flux of solvent there:

$$w = 0, \quad \text{at } z = 0, \tag{5a}$$

$$\frac{\partial x_A}{\partial z} = 0, \quad \text{at } z = 0. \tag{5b}$$

At the free surface of the liquid $z = h$, the flux of solvent mass is continuous [cf. Eq. (16) in Ref. 1]:

$$\left(\frac{1}{1-x_A}D(x_A)\frac{\partial x_A}{\partial z}\right)\bigg|_{z=h} + k(x_A|_{z=h} - x_{A\infty}) = 0. \tag{6}$$

Here the mass flux of solvent A from the liquid into the adjacent gas m_A has been approximated by a mass transfer expression (for example, Cussler[8]), viz., $m_A/\rho = k(x_A|_{z=h} - x_{A\infty})$, where k is the mass transfer coefficient. This approach has the merit of accounting qualitatively for the flow of the overlying gas and allowing exploration of the effect of partially saturating the arriving gas through the parameter $x_{A\infty}$, the mass fraction of solvent in the coating liquid that would be in equilibrium with the mass fraction of solvent in the bulk gas. The flux of overall mass at the free surface $z = h$ must also be conserved; this is the so-called kinematic boundary condition [cf. Eq. (14) in Ref. 1]:

$$\frac{dh}{dt} - w|_{z=h} + k(x_A|_{z=h} - x_{A\infty}) = 0. \tag{7}$$

The preceding development has retained the possibility that viscosity η and binary diffusivity D depend upon solvent concentration. The increase of the coating liquid's viscosity with falling solvent concentration as solvents evaporate from the coating liquid is important because it determines when the convective flow of liquid ceases. If the binary diffusivity in the coating liquid decreases drastically as the concentration of solvents falls as solvents evaporate from the free surface, a steep gradient of solvent may form in the liquid film and the evaporation rate of solvent may fall. The simplification of radial uniformity (needed for the one-dimensional model) does not allow for the possibility of a viscosity that depends upon shear rate; this is treated in a sequel using an even more general two-dimensional model.

FINITE-ELEMENT FORMULATION

The one-dimensional model of spin coating is described by the system of equations (1) and (4)–(7). These form a nonlinear system of integropartial differential equations in both space and time. The system is reduced to a system of algebraic and ordinary differential equations in time by applying the finite-element method described in detail by Strang and Fix.[9] (A detailed description of the application of the finite-element method to free-surface liquid-flow problems may be found in Kistler[10] and Kistler and Scriven.[11,12]) The time derivatives are approximated with a backward difference formula (Gear[13]; also see Byrne and Hindmarsh[14]), and the resulting equation set is solved at each time step using Newton's method. The step size in time is automatically adjusted with an algorithm developed by Byrne and Hindmarsh.[15] (A detailed description of the numerical methods applied to the one-dimensional model of spin coating is available elsewhere.[16])

SINGLE-SOLVENT SYSTEM—RESULTS AND DISCUSSION

The one-dimensional model of spin coating requires viscosity and binary diffusivity as a function of concentration as well as a mass transfer coefficient. The concentration-dependent relationship for viscosity proposed by Meyerhofer[3] in his modeling study of spin coating is used here:

$$\eta = \eta_0 (1 - x_A)^4 + \eta_S . \tag{8}$$

Here $\eta_0 = 10\,000$ P and $\eta_S = 0.01$ P. Equation (8) is plotted in Fig. 2. Viscosity rises by several orders of magnitude as solvent mass fraction falls. The concentration-dependent relationship for diffusivity proposed by Flack *et al.*[6] in their modeling study of spin coating is used here:

$$D = D_0 \exp\left(\frac{x_A}{a x_A + b}\right) . \tag{9}$$

Here $D_0 = 7.8 \times 10^{-12}$ cm^2/s, $a = 0.040$, and $b = 0.043$. Equation (9) is plotted in Fig. 3. Diffusivity falls by several orders of magnitude as solvent mass fraction falls. The mass transfer coefficient k used here is the one proposed by Kreith, Taylor, and Chong[17] and Sparrow and Gregg[18,19] for laminar air flow over an open spinning disk:

$$k = 4 \times 10^{-5} (\omega / s^{-1})^{1/2} \text{ cm/s}. \tag{10}$$

Here the evaporating solvent has a molecular weight of 100 g/mole and an equilibrium vapor pressure of 0.1 atm. Both the overlying gas and the film being coated are at room temperature.

The one-dimensional model requires initial conditions for the velocity and solvent mass fraction profiles. At time $t = 0$ the substrate is taken to be spinning at its final process speed, and this spin speed does not change throughout the course of the computation. The initial solvent mass fraction is taken to be uniform across the thickness of the film. The initial profile of the velocity in the direction normal to the substrate is calculated from the continuity equation (2) and the radial velocity profile equation (3). Because the film thickness is uniform and the viscosity across the thickness of the film is initially uniform due to the initially uniform solvent mass fraction profile, the initial normal velocity profile can be derived [Eq. (13) in Ref. 1]:

$$w = \frac{\rho \omega^2}{\eta} \left(\frac{1}{3} z^3 - z^2 h \right) . \tag{11}$$

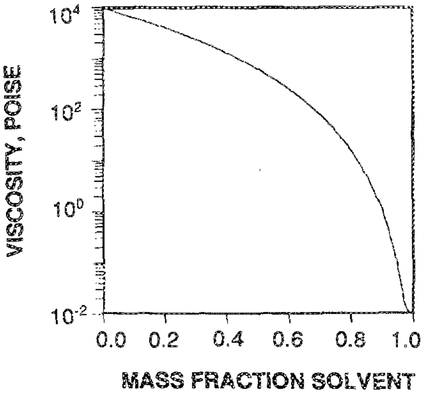

FIG. 2. Plot of Eq. (8) showing the coating liquid's viscosity as a function of concentration. Viscosity rises by several orders of magnitude as solvent mass fraction falls.

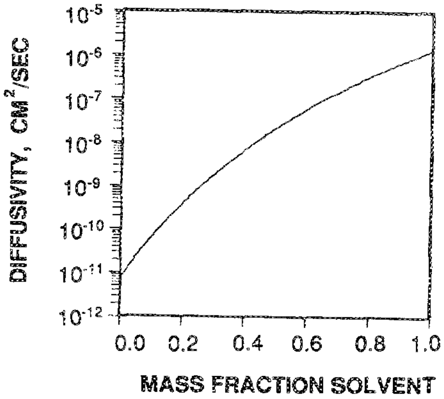

FIG. 3. Plot of Eq. (9) showing the coating liquid's diffusivity as a function of its concentration. Diffusivity falls by several orders of magnitude as solvent mass fraction falls.

The one-dimensional model of spin coating is checked by comparing it with two limiting cases. The first case is Emslie and co-worker's[2] solution for film thinning by convective outflow only, i.e., having an unbounded external or gas-phase resistance to mass transfer. Evaporation is suppressed by setting the mass transfer coefficient k to zero. The evolution of the film thickness is compared with Emslie and co-worker's prediction for the thinning of an initially uniform film that thins uniformly.

The second limiting case against which the one-dimensional model is tested is for simultaneous film thinning by convective outflow and evaporation with negligible internal resistance to mass transfer, which corresponds to an unbounded binary diffusivity. This is imposed by setting the binary diffusivity $D(x_A)$ to a large number. Meyerhofer[3] first proposed that the coupled flow and mass transfer that occurs during spin coating could be approximated by neglecting the internal resistance to mass transfer. This approximation implies that the solvent concentration profile across the film remains uniform as the solvent concentration falls due to evaporation. Meyerhofer assumed that the rate of solvent evaporation is constant. Sukanek[5] extended Meyerhofer's model by introducing a mass transfer expression to account for the rate of evaporation; i.e., the rate of evaporation is taken to be equal to a mass transfer coefficient—which accounts roughly for gas-phase resistance to solvent transport—times the difference between the solvent concentration at the free surface and in the bulk gas. The evolution of the film thickness and the uniform solvent mass fraction predicted with the one-dimensional model are compared with predictions made from solving the appropriate differential equations [Eqs. (21), (22), and (23) in Ref. 1] developed by Meyerhofer and Sukanek.

In both cases the one-dimensional model compares well; the discrepancy is limited only by the error tolerance for choosing time steps and by the degree of mesh refinement, i.e., the number and distribution of elements. These are therefore chosen so that the solutions computed with the one-dimensional model differ from those computed with the simpler models by less than 1%. The one-dimensional model of spin coating is also checked for global conservation of mass when convective outflow is suppressed so that film thinning occurs solely by evaporation of solvent. When the centrifugal driving force for flow is suppressed, the dry thickness computed with the one-dimensional model equals the initial film thickness times the initial mass fraction of solids in the liquid film:

$$h_d = h_i(1 - x_{A_i}). \tag{12}$$

Here h_d is the dry film thickness, h_i is the initial wet thickness, and x_{A_i} the initial solvent mass fraction.

It is a well-known property of the spin-coating process that dry film thickness is independent of the initial volume of coating liquid dispensed (Daughton and Givens[20]). Therefore, the one-dimensional model of spin coating can be tested by computing the dry film thickness over a range of spin speeds for two different initial thicknesses. The dry thickness is taken to be the fraction of solids in the film multiplied by the film thickness when the rate of thinning by evaporation becomes 100 times greater than film thinning by radial convective outflow (the computed dry thickness changes by less than 0.1% if the computation is carried beyond this point). The dry thickness versus spin speed is compared for initial thicknesses of 0.1 and 1 mm in Fig. 4. The initial solvent mass fraction is taken to be 0.9 uniformly throughout the film. x_{A_∞}, the mass fraction of solvent in the liquid that would be in equilibrium with the gas supplied, is zero. Figure 4 clearly shows that the one-dimensional model predicts no apparent difference in dry film thickness for these two initial thicknesses. Because the rate of film thinning by convective outflow is proportional to film thickness cubed [see Eqs. (5) and (6) in Ref. 1], the 1-mm-thick film thins by convective outflow at a rate 1000 times greater than the 0.1-mm-thick film. Initially, film thinning is primarily by radial convective outflow and the free-surface region where solvent concentration is lowered by evaporation is quickly swept away before solvent from below can diffuse into it. The film initially 1 mm thick therefore thins to 0.1 mm with its initial concentration practically unchanged and so yields the same dry thickness as the film that is initially 0.1 mm thick.

It is of course possible to begin the simulation with a film so thin that the initial rate of film thinning by convection does not completely overwhelm that by evaporation. Because there is then an immediate interaction between radial convective outflow—which is proportional to the cube of film thickness—and solvent evaporation, the final film thickness becomes a strong function of the initial thickness. Figure 5 shows the dry thickness as a function of the initial thickness at spin speeds of 1000, 3000, and 10 000 rpm for a coating liquid with an initial solvent mass fraction of 0.90 and where the concentration of solvent in the bulk of the overlying gas is zero, i.e., $x_{A_\infty} = 0$. The three curves join where the initial film is so thin that the initial rate of evaporation completely overwhelms that of convective outflow. (Hereafter the initial film thickness is taken to be 0.1 mm.)

The one-dimensional model is tested over the range of spin speeds from 1000 to 10 000 rpm for initially uniform solvent mass fractions of 0.85, 0.90, and 0.95 (see Fig. 6). The bulk of the overlying gas is again taken to be solvent free. As the initial, uniform solvent mass fraction is increased from 0.85 to 0.95 (and hence viscosity decreased), a thinner dry film is obtained for two reasons. First, the initial amount of solids present decreases with increasing solvent mass fraction. Second, the rate of convective outflow increases as the liquid's viscosity decreases: Equations (5) and (6) in Ref. 1 predict that film thinning by radial convective outflow is inversely proportional to the liquid's viscosity. Thus more liquid flows off the disk as solvent concentration is increased.

The dry film thickness computed with the concentration-dependent diffusion coefficient in Eq. (9) is compared to that computed with an unbounded binary diffusivity, i.e., no internal resistance to evaporation, in Fig. 7. Initially the

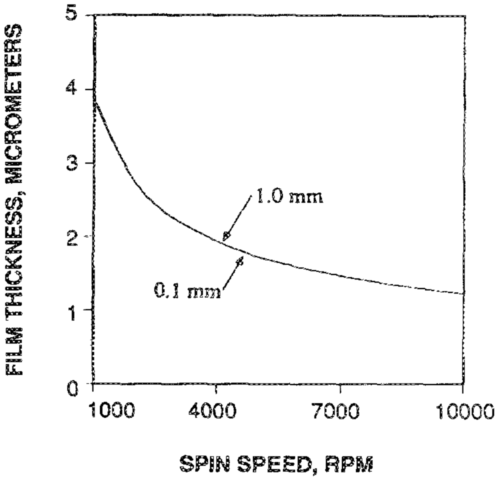

FIG. 4. Dry thickness as a function of spin speed for two different initial thicknesses of 0.1 and 1 mm. The initial solvent mass fraction is 0.9, and the concentration of solvent in the bulk of the overlying gas x_{A_∞} is zero. There is no apparent difference in the dry thickness over a range of spin speeds from 1000 to 10 000 rpm.

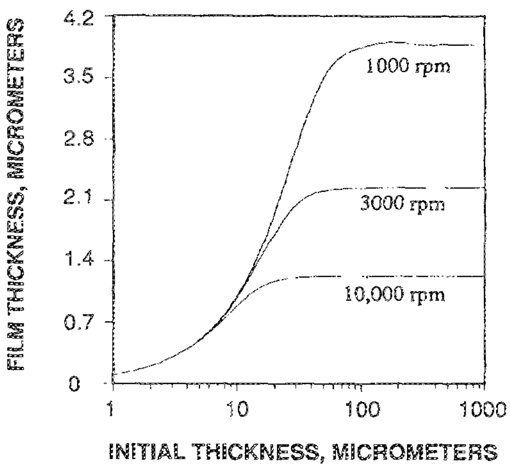

FIG. 5. Dry thickness as a function of initial thickness at spin speeds of 1000, 3000, and 10 000 rpm. The initial solvent mass fraction is 0.9, and the concentration of solvent in the bulk of the overlying gas x_{A_∞} is zero. The three curves join at 10 μm where the initial film is so thin that the initial rate of evaporation completely overwhelms that of convective outflow.

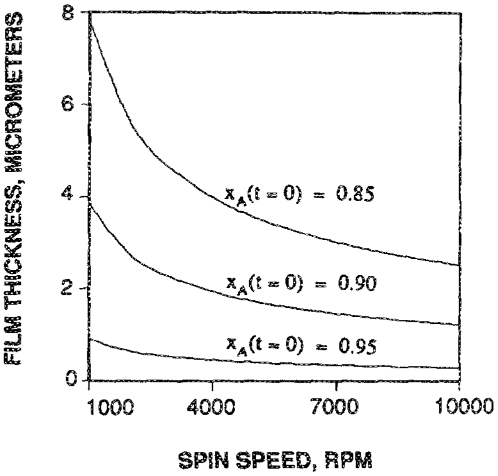

FIG. 6. Dry thickness as a function of spin speed at initial solvent mass fractions of 0.85, 0.90, and 0.95. The initial film thickness is 0.1 mm, and the concentration of solvent in the bulk of the overlying gas $x_{A\infty}$ is zero. Dry film thickness falls with increasing solvent concentration.

solvent mass fraction is 0.9 throughout the film. The bulk of the overlying gas is solvent free. When there is no internal resistance to evaporation (viz., the binary diffusivity is unbounded), a thicker dry film is obtained. When the binary diffusivity is unbounded, the average solvent concentration across the thickness of the film decreases earlier, the liquid's viscosity rises sooner, and hence flow ceases before it does when the diffusivity falls with solvent concentration. More solids are thus left on the disk at the cessation of flow when the binary diffusivity is unbounded than when the diffusivity falls with solvent concentration.

Controlling the concentration of solvent in the bulk of the overlying gas gives greater control over the dry film thickness. Dry thicknesses obtained by spinning under a solvent-saturated atmosphere for different lengths of time are compared in Fig. 8. Initially, the solvent mass fraction is 0.9 throughout the film. The solvent concentration in the bulk of the overlying gas is held in equilibrium with the solvent in the liquid, i.e., $x_{A\infty} = 0.9$, during the first 1, 3, 10, or 30 s of spinning, after which time the solvent concentration in the bulk of the overlying gas is taken to be zero, i.e, $x_{A\infty} = 0$. The dry film thickness decreases with increasing spin time under the saturated atmosphere because more liquid can flow off the disk.

Because a primary reason for modeling any process is to gain an understanding of the underlying physics that governs it, the one-dimensional model of spin coating is used to examine the interactions during the spinning process. As a representative test case, a disk spinning at 3000 rpm having a coating liquid with an initially uniform mass fraction of 0.9 is chosen. The concentration of solvent in the bulk of the overlying gas is taken to be zero throughout. Figure 9 shows a comparison between cumulative loss of film thickness due to radial convection and to evaporation. Figure 10 shows the corresponding loss rates by convective outflow and by solvent evaporation relative to the initial rate of film thinning. These figures reveal that there is a large and rapid initial thinning due to radial convective outflow during which film thinning due to evaporation of the volatile solvent is unimportant. However, the convective outflow continuously slows during the first second of spinning after which it falls dramatically as evaporation of solvent becomes the sole mechanism for film thinning. The dotted line in Fig. 10 is the corresponding result from the prediction by Emslie and coworkers[2] for the thinning without evaporation of a uniform film having a constant viscosity—the viscosity is calculated from Eq. (8) with the solvent mass fraction x_A equal to 0.9. For the first second of spinning the one-dimensional model's prediction for convective outflow parallels that of Emslie

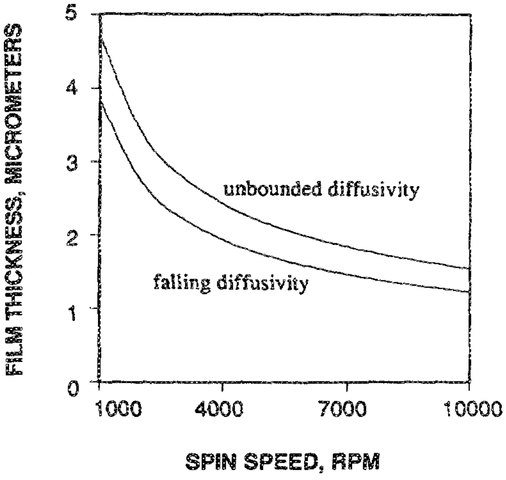

FIG. 7. Dry thickness as a function of spin speed computed with the falling diffusivity model Eq. (9) and with an unbounded binary diffusivity, i.e., no resistance to mass transport within the coated film. The initial film thickness is 0.1 mm, the initial solvent mass fraction is 0.9, and the concentration of solvent in the bulk of the overlying gas $x_{A\infty}$ is zero.

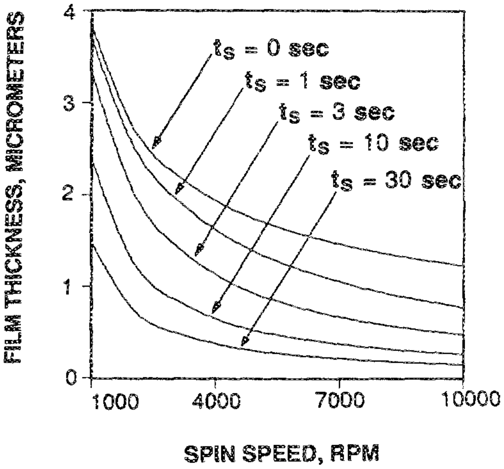

FIG. 8. Dry thickness as a function of spin speed computed by spinning for specified times t_s under an atmosphere having a solvent concentration in equilibrium with the solvent concentration in the liquid. After t_s seconds the overlying atmosphere is rapidly changed to solvent free as the disk continues to spin. The initial film thickness is 0.1 mm, and the initial solvent mass fraction is 0.9.

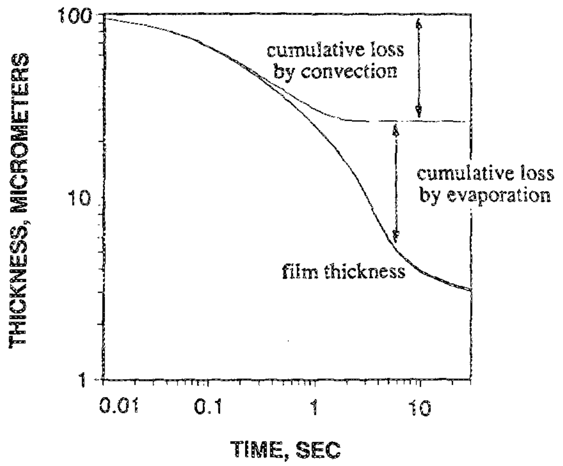

FIG. 9. Comparison between evaporative and convective losses for a coating liquid that is initially 0.1 mm thick with an initially uniform solvent mass fraction of 0.9. The disk spins at 3000 rpm, and the concentration in the overlaying gas $x_{A\infty}$ is zero. The greatest loss of film thickness is by convective flow and occurs initially.

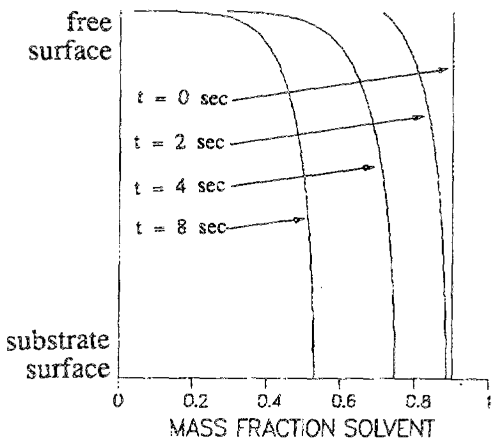

FIG. 11. Solvent concentration profiles at 0, 2, 4, and 8 s after the onset of spinning corresponding to Figs. 9 and 10. A region of low solvent concentration, i.e., a solid "skin," forms at the free surface during drying.

and co-workers. In both, liquid flow slows because the rate of convective outflow is proportional to film thickness cubed [see Eqs. (5) and (6) in Ref. 1]. The mass fraction of solvent at the free surface—and hence the rate of evaporation—remains nearly constant during this period because the surface is continuously swept away. When the rate of convective outflow has fallen to approximately the rate of evaporation, the convective rate drops dramatically because the growing effect of solvent evaporation causes viscosity to skyrocket.

The corresponding solvent concentration profiles at selected times are in Fig. 11. These profiles show that a region of extremely low solvent concentration and correspondingly high viscosity and low binary diffusivity, in brief a solid "skin," ultimately forms at the free surface. Because the rate of evaporation depends upon the solvent flux to the free surface, this skin acts to retard solvent evaporation. The ratio of the free-surface solvent mass fraction to the average solvent mass fraction across the thickness of the film (a measure of the degree of "skin" formation) is compared with the ratio of convective to evaporative loss in Fig. 12. This comparison indicates that in this case the free-surface skin does not form until well after flow ceases (throughout this paper the cessation of flow is taken to occur when the ratio of convective to evaporative loss drops below 0.01).

However, if either the mass transfer coefficient is larger, the diffusion coefficient is smaller, or both, then skinning can occur before flow ceases. For example, if the mass transfer coefficient in Eq. (10) is made five times larger and the diffusion coefficient in Eq. (9) is made five times smaller, the ratio of the mass fraction of solvent at the free surface to the average solvent mass fraction across the thickness of the film drops below 0.1 well before flow ceases (see Fig. 13). Flow beneath a surface skin stretches the skin and so could lead to serious coating defects such as radial cracking. One way to

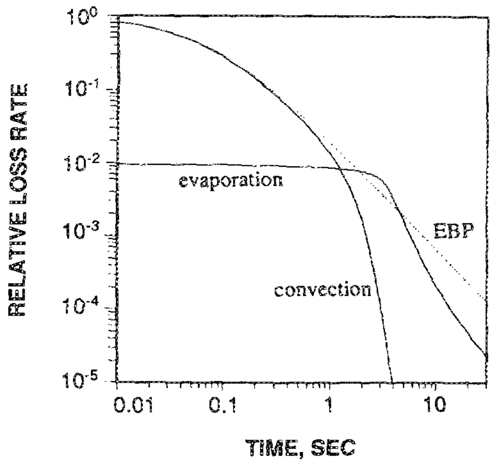

FIG. 10. Instantaneous loss rates by convection and evaporation corresponding to Fig. 9. The dotted line labeled EBP [Emslie and co-workers (Ref. 2)] is for liquid flow only and is a plot of the derivative with respect to time of Eq. (8) in Ref. 1.

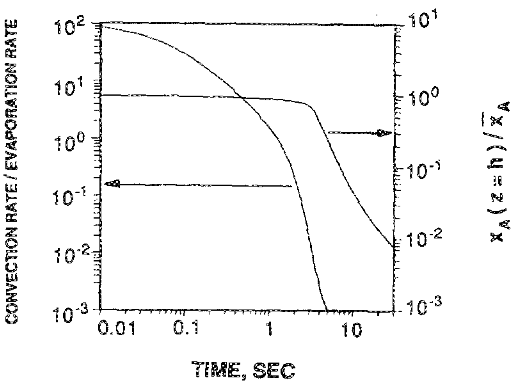

FIG. 12. The ratio of convection to evaporation compared to the ratio of the free-surface solvent mass fraction x_A $(z=h)$ to the average solvent mass fraction across the thickness of the film $\bar{x}_A$. The conditions are the same as those of Figs. 9–11.

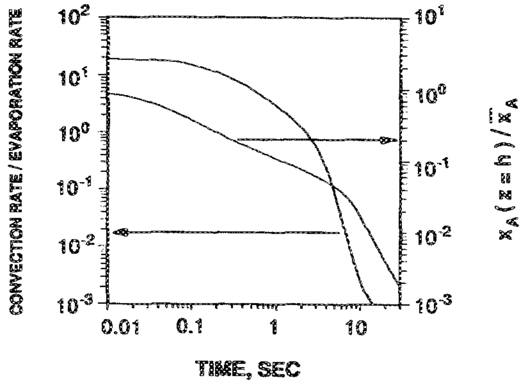

FIG. 13. The ratio of convection to evaporation compared to the ratio of the free-surface solvent mass fraction x_A $(z=h)$ to the average solvent mass fraction across the thickness of the film $\bar{x}_A$. The mass transfer coefficient is five times greater than Eq. (10), and the diffusivity is five times less than Eq. (9). The conditions are otherwise the same as in Figs. 9–12. The ratio of the mass fraction of solvent at the free surface to the average mass fraction of solvent across the thickness of the film drops below 0.1 well before flow ceases, i.e., when the ratio of convection to evaporation drops below 0.01.

reduce this problem is to partially saturate the bulk of the overlying gas with solvent. For example, if the concentration of solvent in the bulk of the overlying gas is fixed at a value that would be in equilibrium with a liquid mass fraction of 0.4, i.e., $x_{A\infty} = 0.4$, then the skinning problem is eliminated (see Fig. 14). Another way to reduce the skinning problem is to coat with a mixed solvent system where the solvents have differing volatilities. This is developed below for a binary-solvent system.

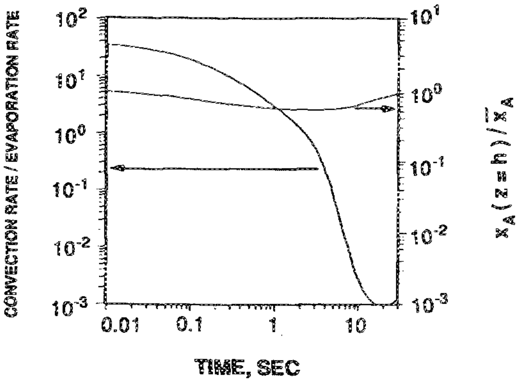

FIG. 14. The ratio of convection to evaporation compared to the ratio of the free surface solvent mass fraction x_A $(z=h)$ to the average solvent mass fraction across the thickness of the film $\bar{x}_A$. The mass transfer coefficient is five times greater than Eq. (10) and the diffusivity is five times less than Eq. (9). The concentration of solvent in the bulk of the overlying gas $x_{A\infty}$ is 0.4. The conditions are otherwise the same as in Figs. 9–12. The skinning problem is eliminated.

BINARY-SOLVENT SYSTEM—MODEL DEVELOPMENT

The underlying physical principles that govern the spin coating of a binary-solvent system are the same as those for the single-solvent system. The mathematical expressions for conservation of overall mass within the film—the continuity equation (4), for no overall mass flux at the substrate Eq. (5a), and for no mass flux of solvent at the substrate Eq. (5b) (enforced for each solvent)—remain unchanged. Local conservation of mass of each solvent species across the thickness of the film is expressed by a convective-diffusion equation for each species (Onsager[21]; also see Toor[22]):

$$\frac{\partial x_A}{\partial t} + w\frac{\partial x_A}{\partial z} - \frac{\partial}{\partial z}\left(D_{AA}\frac{\partial x_A}{\partial z} + D_{AB}\frac{\partial x_B}{\partial z}\right) = 0, \tag{13}$$

$$\frac{\partial x_B}{\partial t} + w\frac{\partial x_B}{\partial z} - \frac{\partial}{\partial z}\left(D_{BA}\frac{\partial x_A}{\partial z} + D_{BB}\frac{\partial x_B}{\partial z}\right) = 0. \tag{14}$$

x_A and x_B are the mass fractions of solvents A and B. D_{AA} and D_{BB} are the main-term diffusion coefficients, and D_{AB} and D_{BA} are the cross-term diffusion coefficients. In liquids the cross-term diffusion coefficients are often 10% or less of the main-term diffusion coefficients (Cussler[8]). Continuity of flux of overall mass at the free surface is enforced by the kinematic boundary condition, which must account for evaporation of both solvents:

$$\begin{aligned}\frac{dh}{dt} - w|_{z=h} + k_A(x_A|_{z=h} - x_{A\infty})&\\ + k_B(x_B|_{z=h} - x_{B\infty}) = 0.&\end{aligned} \tag{15}$$

k_A is the mass transfer coefficient for solvent A, and k_B is the mass transfer coefficient for solvent B. Continuity of solvent mass flux at the free surface must also be enforced for each solvent:

$$\begin{aligned}&\left(D_{AA}\frac{\partial x_A}{\partial z} + D_{AB}\frac{\partial x_B}{\partial z}\right)\Bigg|_{z=h}\\ &\quad + k_A(x_A|_{z=h} - x_{A\infty})(1 - x_A|_{z=h})\\ &\quad - k_B(x_B|_{z=h} - x_{B\infty})x_A|_{z=h} = 0,\end{aligned} \tag{16}$$

$$\begin{aligned}&\left(D_{BA}\frac{\partial x_A}{\partial z} + D_{BB}\frac{\partial x_B}{\partial z}\right)\Bigg|_{z=h}\\ &\quad + k_B(x_B|_{z=h} - x_{B\infty})(1 - x_B|_{z=h})\\ &\quad - k_A(x_A|_{z=h} - x_{A\infty})x_B|_{z=h} = 0.\end{aligned} \tag{17}$$

A detailed development of Eqs. (16) and (17) can be found elsewhere.[16]

BINARY-SOLVENT SYSTEM—RESULTS AND DISCUSSION

A binary-solvent system having high- and low-volatility solvents can be used to delay the onset of skin formation in spin coating until after flow has ceased. A solution of nonvolatile solids dissolved in two solvents is coated at 3000 rpm. The concentration-dependent function for viscosity Eq. (8) is taken to depend on total solvent concentration:

$$\eta = \eta_0(1 - x_A - x_B)^4 + \eta_S.$$

The main-term diffusion coefficients D_{AA} and D_{BB} are taken to be equal and to depend on the total solvent concentration. Each diffusion coefficient is taken to be five times less than the one in Eq. (9):

$$D_{AA} = D_{BB} = \frac{1}{5} D_0 \exp\left(\frac{x_A + x_B}{a(x_A + x_B) + b}\right).$$

The cross-term diffusion coefficients D_{AB} and D_{BA} are neglected. The mass transfer coefficient of solvent A is taken to be five times greater than the coefficient in Eq. (10). However, the mass transfer coefficient of solvent B is taken to be 20 times less than that of solvent A; hence solvent B is 20 times less volatile than solvent A. Initially, the mass fraction of each solvent is taken to be 0.45 throughout the film and the bulk of the overlying gas is taken to be solvent free. Figure 15, which is a comparison between the ratio of the free-surface solvent mass fraction to the average solvent mass fraction across the thickness of the film and the ratio of convective to evaporative loss, demonstrates that the onset of skinning at the free surface is dramatically delayed with this binary solvent system (cf. Fig. 13).

SINGLE-SOLVENT SYSTEM—THERMAL ENERGY EFFECTS

The temperature variation in the liquid film during spin coating is estimated by applying the principle of energy conservation simultaneously with those of mass and momentum conservation. The coating liquid has only one solvent. A large temperature decrease during spinning due to evaporative cooling could significantly affect the coating liquid's viscosity and internal resistance to mass transfer, thus affecting the quality and thickness of the final film.

Local energy conservation within the film is expressed by the equation of thermal energy conservation:

$$\rho C_p\left(\frac{\partial T}{\partial t} + w\frac{\partial T}{\partial z}\right) - k_t\frac{\partial^2 T}{\partial z^2} = 0. \tag{18}$$

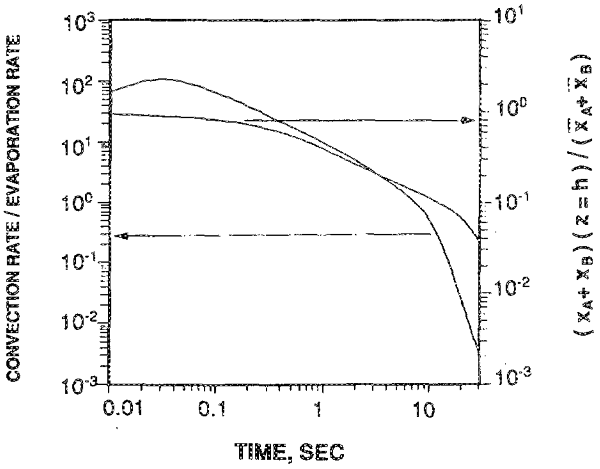

FIG. 15. Mixed solvents: the ratio of convection to evaporation compared to the ratio of the free surface mass fraction of total solvent $(x_A + x_B)$ $(z = h)$ to the average mass fraction of total solvent across the thickness of the film $\bar{x}_A + \bar{x}_B$. The disk spins at 3000 rpm. The film thickness is initially 0.1 mm and the initial mass fraction of each solvent is taken to be 0.45 throughout the film. The overlying gas is taken to be solvent free. There is no free surface skinning problem.

Radial variations in temperature are neglected, and the liquid's density is taken to be constant. The viscous dissipation term, which accounts for heat generated by friction during flow and so acts to increase temperature, is also neglected. T is absolute temperature. C_p is the heat capacity, and k_t is the thermal conductivity. At the substrate surface there are two possible boundary conditions. Either the temperature remains constant, i.e., the substrate is isothermal,

$$T = T_0, \quad \text{at } z = 0, \tag{19a}$$

or there is no heat transfer from the substrate to the coating liquid, i.e., the substrate is insulating,

$$\frac{\partial T}{\partial z} = 0, \quad \text{at } z = 0. \tag{19b}$$

At the free surface the principle of continuity of energy flux is imposed:

$$k_t \frac{\partial T}{\partial z}\bigg|_{z=h} + h_t(T|_{z=h} - T_\infty) + k\rho\Delta\hat{H}_{\text{vap}}(x_A|_{z=h} - x_{A\infty}) = 0. \tag{20}$$

The first term accounts for conductive heat flux to the free surface from the liquid, the second term for convective heat transfer from the overlying gas, and the third term for evaporative cooling. h_t is the coefficient of convective heat transfer from the gas to the free surface of the liquid, and $\Delta\hat{H}_{\text{vap}}$ is the heat of vaporization of solvent per unit mass.

The single-solvent one-dimensional model with the added equations of energy conservation is tested for a coating liquid with an initially uniform solvent mass fraction of 0.9. The disk spins at 3000 rpm, and the bulk of the overlying gas is solvent free. The viscosity, mutual diffusivity, and mass transfer coefficient are given in Eqs. (8)–(10), respectively. The convective heat transfer coefficient h_t from the bulk of the overlying gas to the coating liquid is taken from the same sources as is the mass transfer coefficient (Kreith and coworkers[17] and Sparrow and Gregg[18,19]). The coating liquid's thermal conductivity k_t, heat capacity C_p, and heat of vaporization $\Delta\hat{H}_{\text{vap}}$ are approximated with those of room-temperature benzene. The coating liquid is initially at room temperature T_∞, which is here taken to be 300 K.

When the temperature of the substrate is constant [Eq. (19a)], the maximum free-surface temperature drop is 0.5 K and occurs 0.06 s after spin-off begins. When the substrate is insulating [Eq. (19b)], the maximum free-surface temperature drop is 0.7 K and occurs 0.5 s after spin-off begins. The cooling of the coating liquid at the free surface as solvent evaporates is counteracted by conductive heat transfer from below and convective heat transfer from the overlying gas: The spinning disk acts as a centrifugal pump drawing air toward then across its surface. Equation (20) can also be used to obtain an order of magnitude estimate of the thermal effects in spin coating. If the film thickness is taken to be 100 μm, the temperature profile across the thickness of the film to be linear, and the substrate to be at the ambient temperature T_∞; then $T_\infty - T|_{z=h}$ is 2.4 K.

CONCLUSIONS

A one-dimensional model of spin coating with film thinning by both convective outflow and solvent evaporation is presented. This model removes the assumption made by previous authors of no internal resistance to mass transport within the coating film. Film thinning is shown to diminish initially due to decreasing film thickness (convective outflow is proportional to film thickness cubed for a Newtonian coating liquid) but to cease finally due to dramatically increasing viscosity as solvents evaporate. The formation of a solid "skin" at the free surface is predicted; coating defects could occur if convective flow has not completely ceased when this skin forms. Two approaches are proposed to delay the onset of this skinning. The first is to saturate partially the overlying gas with solvent. The second is to use a coating liquid having both high- and low-volatility solvents. The temperature variation during spin coating is found to be negligible.

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[1] D. E. Bornside, C. W. Macosko, and L. E. Scriven, J. Imag. Technol. **13**, 122 (1987).
[2] A. G. Emslie, F. T. Bonner, and L. G. Peck, J. Appl. Phys. **29**, 858 (1958).
[3] D. Meyerhofer, J. Appl. Phys. **49**, 3993 (1978).
[4] S. A. Jenekhe, Ind. Eng. Chem. Fundam. **23**, 425 (1984).
[5] P. C. Sukanek, J. Imag. Technol. **11**, 184 (1985).
[6] W. W. Flack, D. S. Soong, A. T. Bell, and D. W. Hess, J. Appl. Phys. **56**, 1199 (1984).
[7] C. J. Lawrence, Phys. Fluids **31**, 2786 (1988).
[8] E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems* (Cambridge University, Cambridge, 1984).
[9] G. Strang and G. J. Fix, *An Analysis of the Finite Element Method* (Prentice Hall, Englewood Cliffs, NJ, 1973).
[10] S. F. Kistler, Ph.D. thesis, University of Minnesota, Minneapolis, 1983.
[11] S. F. Kistler and L. E. Scriven, in *Computational Analysis of Polymer Processing*, edited by J. R. A. Pearson and S. M. Richardson (Applied Science, London, 1983), p. 243.
[12] S. F. Kistler and L. E. Scriven, Int. J. Numer. Methods Fluids **4**, 207 (1984).
[13] C. W. Gear, IEEE Trans. Circuit Theory **18**, 89 (1971).
[14] G. D. Byrne and A. C. Hindmarsh, J. Comput. Phys. **70**, 1 (1987).
[15] G. D. Byrne and A. C. Hindmarsh, ACM Trans. Math. Software **1**, 71 (1975).
[16] D. E. Bornside, Ph.D. thesis, University of Minnesota, Minneapolis, 1988.
[17] F. Kreith, J. H. Taylor, and J. P. Chong, J. Heat Transfer **81**, 95 (1959).
[18] E. M. Sparrow and J. L. Gregg, J. Heat Transfer **81**, 249 (1959).
[19] E. M. Sparrow and J. L. Gregg, J. Heat Transfer **82**, 294 (1960).
[20] W. J. Daughton and L. F. Givens, J. Electrochem. Soc. **129**, 173 (1982).
[21] L. Onsager, Ann. NY Acad. Sci. **46**, 241 (1945).
[22] H. L. Toor, AIChE J. **10**, 448 (1964).