Characteristics of resist films produced by spinning

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A model is presented for the description of thin films prepared from solution by spinning. Using only the centrifugal force, linear shear forces, and uniform evaporation of the solvent, the thickness of the film and the time of drying can be calculated as functions of the various processing parameters. The model is compared with experimental results obtained on positive photoresists and excellent agreement is obtained. When adequate care is taken, the liquid forms a level surface during spinning, and the film thickness becomes uniform and independent of the size of the substrate. The film thickness $h$ shows the following dependence on spin speed $f$, initial viscosity $\eta_i$ and evaporation rate $\epsilon$: $h \propto f^{-\frac{3}{2}} \eta_i^{1/3} \epsilon^{1/3}$, and $\epsilon$ is proportional to $f^{1/2}$.

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INTRODUCTION

Production of thin organic films, such as photoresist, by centrifugal spinning from solution on rotating disks is a simple technique which is widely used. A thick layer of solution is applied to the disk. During rotation, the solution flows radially outward. As the liquid layer thins, evaporation of the solvent increases the concentration of the solids causing increased viscosity and formation of the solid film. This technique can lead to very uniform films of well-controlled thickness. Despite its wide usage, no complete description of the process appears in the literature explaining the uniformity of the films and the dependence of the process on material parameters. This report attempts such a description and compares it with experimental results on films of positive-working photoresists.

The first description of the flow of a viscous liquid on a rotating disk was given by Emslie, Bonner, and Peck. They showed that, for a Newtonian fluid (linear relationship between shear stress and shear rate), the solution of the hydrodynamic equations leads asymptotically to a layer of uniform thickness, independent of the liquid profile at the start of the rotation. The thickness, of course, decreases continuously with time as material is spun away. Acarvis, Shah, and Petersen extended this calculation to non-Newtonian liquids and showed that the film no longer approached a uniform-thickness condition. The effect only becomes significant for large deviations from linearity. Neither of these papers, nor any others that the author is aware of, examines the real situation in which evaporation of a solvent is taken into account so that, at the end of the procedure, a solid film remains with a predetermined thickness profile.

Because of the widespread use of the spinning technique, numerous measurements of profile and film thickness have been reported. They are well represented by the results of Damon on Kodak photoresists. He observed that the following equation described the dependence of the final film thickness $h$ on spinner rotation rate $f$ and on initial solids concentration $c_0$ for the various resist materials he investigated:

$$h = kc_0^{1/2}f^{1/2}. \quad (1)$$

The constant $k$, which must be a function of the polymer-solvent system, was also found to depend on the equipment used.

MODEL OF THE SPINNING PROCESS

In order to calculate the hydrodynamics of the spin-coating process, we first assume as a starting point that a layer of polymer solution of uniform thickness $h_0$ is applied on the horizontal surface of a circular substrate. At time $t = 0$, the substrate is spun at a rotation rate $f$. If the solution has approximately Newtonian character, then Emslie et al. have shown that the hydrodynamics are governed by the following equations:

Force balance:

$$-\eta \frac{\partial^2 v}{\partial z^2} = \rho \omega^2 r; \quad (2)$$

continuity:

$$\frac{\partial h}{\partial t} = -\frac{1}{r} \frac{\partial (r\rho v)}{\partial r}. \quad (3)$$

Here the $z$ axis is the rotation axis, $r$ is the radial direction, and cylindrical symmetry is assumed. Thus the velocity $v(z)$ is in the $r$ direction. Gravitational and Coriolis forces are neglected, $\eta$ is the viscosity, $\rho$ is the density, $\omega = 2\pi f$, and we define the kinematic viscosity $\nu = \eta/\rho$. The total radial flow per unit circumference is given by

$$q = \omega^2 rh^3/3\nu. \quad (4)$$

The solution of these equations when there is no evaporation (no change in $\nu$) is that the profile remains uniform and that $h$ decreases as

$$h = h_0[1 + (4\omega^2/3\nu)\nu f^2]^{-1/2}. \quad (5)$$

In order to produce a solid film, the solvent must evaporate. At the start of the spinning, the concentration of the solute is uniform. The solvent evaporates uniformly over the entire surface area causing the solids concentration $c$ to increase. As $h$ is independent of $r$ [Eq. (5)], $c$ will also be independent of $r$ (while there will be some change of $c$ with $z$, this can be neglected in these thin films). In order to simplify the discussion, we assume that both solute and solvent...
have density unity, and that the volume of the solution is equal to the volume of the solvent \( (L) \) plus the volume of the solids \( (S) \) that would exist after the evaporation of all the solvent. While real solutions do not obey this assumption, the difference is small over the concentration ranges used and does not affect the final results. We define \( L \) and \( S \) per unit area and thus obtain

\[
c(t) = \frac{S}{(S + L)}
\]

and

\[
h = S + L.
\]

The change in concentration affects the hydrodynamics through the dependence of viscosity on concentration. Because there is no dependence on \( r \), the film thickness will continue to reduce uniformly, but the rate is different from that given by Eq. (5). We write the rate of change of \( S \) and \( L \) due to outflow and evaporation (at a rate \( e \)):

\[
\frac{dS}{dt} = -c \frac{2}{r} \frac{\partial (r \rho)}{\partial r} = -c \frac{2 \omega^2 h^3}{3 v}, \tag{7}
\]

\[
\frac{dL}{dt} = -(1 - c) \frac{2 \omega^2 h^3}{3 v} - e. \tag{8}
\]

The equations are expressed in terms of rate of change of volume per unit area \( (m/s) \). The two coupled equations can be integrated from the initial thickness and concentration values to the point where \( L = 0 \), i.e., only the solid film remains. At that point, the final film thickness \( h_f = S_f \).

This calculation was performed numerically in order to determine the dependence of the final thickness and the time to drying on the various parameters. The viscosity of many of these solutions has been reported to be a power-law function of the concentration, and, for the purposes of calculation, we use the relationship

\[
c(t) = S/(S + L)
\]

and

\[
h = S + L.
\]

FIG. 1. Calculated time dependence during spinning of the volume of solids \( (S) \) and solvent \( (L) \) per unit area normalized to the initial values. The parameter values used are initial thickness \( h_0 = 30 \mu m \), initial concentration \( c_i = 0.10 \), spin speed \( = 4500 \text{ rpm} \), viscosity \( \nu = (4 \times 10^{-6} \text{ cm}^2/\text{s}) \), initial value \( \nu_i = 1 \times 10^{-5} \text{ m}^2/\text{s} \), evaporation rate \( e = 1 \times 10^{-6} \text{ m}/\text{s} \).

FIG. 2. Calculated film thickness as function of spin speed. The parameter values are the same as in Fig. 1, except as indicated.

\[
\nu = \nu_{\text{solvent}} + \nu_{\text{solid}} c^\gamma.
\]

The exponent \( \gamma \) typically has values around 2.5 for photoresist solutions. The value of \( e \) is taken to be constant with time, because we are not able to measure or calculate its actual value. However, allowing \( e \) to vary during the integration produces only small changes in \( h_f \).

The result of a typical integration is shown in Fig. 1. Both volume of solvent and volume of solids relative to their initial values are plotted as a function of time. The values of the parameters used are indicated in Fig. 1. The curves show that, at the start, the outflow dominates and the concentration does not change much. When \( h \) has dropped to about \( \frac{1}{2} h_0 \), evaporation takes over and \( S \) rapidly reaches its final value. Flow has ceased completely due to the high viscosity and the reduced liquid thickness. Only evaporation continues.

Figure 2 shows the calculated final film thickness as the spin speed is varied. The values of the parameters used are listed in Fig. 2. Three different values of initial thickness of the solution are shown. If \( h_0 = 10 \mu m \), then, at the lower speeds, there is no outflow at all and only evaporation down to a thickness of \( S_f = c h_0 \). On the other hand, it is shown that, at high enough speeds, there is no dependence on the initial height of the liquid. There, the thickness is proportional to the \( -\frac{1}{3} \) power of the speed. Inspection of Fig. 2 shows that this relationship applies for \( S_0 = c_0 h_0 > 2 h_f \).

While Eqs. (7)-(9) cannot be solved analytically, we can use the results of Fig. 1 and 2 to derive an approximate value of \( h_f \) in the range \( S_f > 2 h_f \). We assume that, at the outset, evaporation is negligible and that this condition applies until the liquid film thins to a value \( h_{f2} \) at which the evaporation and outflow contributions in Eq. (8) are equal.

\[
S_f / S_0 = L_f / L_0
\]

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where \( c = c_0 \) and \( \nu = \nu_0 \). We further assume that, from this point on, the outflow is negligible compared to the evaporation, so that

\[
h_f = S_f c_0 \nu_0 \left( \frac{1}{3} \right)^{1/3} c_0 \nu_0 \left( 1 - c_0 \right)^{1/3} \omega^{1/3} \nu_0^{1/3} e^{1/3}
\]

for \( S_f \geq 2h_f \). This relationship shows the same dependence on spin speed as the exact calculation (Fig. 2), so that we can compare the two quantitatively. Using the values of \( c_0, \nu_0, \) and \( e \) given in Fig. 1, Eq. (11) gives \( h_f \) at 4500 rpm to be 0.42 \( \mu \)m compared to the exact value 0.54 \( \mu \)m (Fig. 2). Additional calculations show that in the high-\( h_f \)/high-\( \omega \) range \( h_f \) depends on \( \nu_0 \) and on \( e \) exactly as is given by Eq. (11). Thus, the simple assumptions used provide a remarkably good approximation in this range. One of the reasons for this is that the calculated \( h_f \) does not depend strongly on the exact form and values of Eq. (9).

For example, varying \( \gamma \) from 2 to 6 while keeping \( \nu_0 \) constant only causes \( h_f \) to vary from 0.50 to 0.60 \( \mu \)m in the above case.

**EXPERIMENTAL RESULTS**

The predictions of the spinning model were tested on some positive-working photoresists. We used both Shipley AZ-1350 and Mark II', a similar mixture. Various concentrations were prepared by dissolving both starting materials in methyl cellosolve acetate.

In order to justify the approximations of the model, it was necessary to use adequately flat and horizontal substrates and a high acceleration whirler. A Headway Research 1-EC101-R285 spinner was used and carefully leveled. Square glass substrates, 5 x 5 cm, were held flat on a special vacuum chuck of the same size, with vacuum holes only at the four corners (even small vacuum holes distort a 1-mm thick glass slide to the point where small differences in film thickness over the holes can be seen after spinning). The solution was applied to cover the entire substrate with a thickness of at least 1 mm and then the spinner was turned on. Acceleration to full speed takes place in a small fraction of a second, and the speed is accurately controlled by a servomechanism. Spinning was continued until the films were visually dry.

The topography of the surface of the solution was observed visually during spinning. After the first fraction of a second, the surface appeared completely flat and remained so. As the layer thinned out, interference colors were observed to change uniformly through the various orders. This confirms the predictions of the model of Emslie et al. The kinds of instabilities in the flow described by Damon ("waves of liquid moving from the center out") can be observed when the acceleration is not rapid enough (of the order of 0.2 \( s \) or larger) or when the solution is applied very nonuniformly, and particularly at low spin speeds.

The uniformity of our solid films was established by determining the thickness at a number of different points on the film. We measured the interference spectrum over the visible range and determined the thickness from the interference extrema to a precision of approximately \( \pm 2 \) nm. On a typical 5 x 5 cm slide, the central 2.5 x 2.5 cm had a total thickness variation of 5 nm out of 860 nm. We have observed a similar degree of uniformity over much larger areas when spin coating circular substrates as large as 35 cm in diameter. Furthermore, at a given spin speed, the absolute film thickness on the largest substrates was found to be the same as on the 5 x 5 cm squares.

Before measuring the film thickness, we determined the dependence of viscosity on the concentration of solids in the solution. The result for Mark II' resist is shown in Fig. 3. The curve for Shipley AZ-1350 (starting either with 1350J or 1350B) is very similar and slightly steeper at concentrations above 0.20.

**FIG. 3.** Viscosity of Mark II' solutions at 25°C (1 \( \times 10^{-6} \) m\(^2\)/s =1 cP).

**FIG. 4.** Measured film thickness as function of spin speed (in rpm) and solute concentration.
The curve is described by Eq. (9) over the range from $c=0.025$ to $0.20$:

$$v = (1.18 \times 10^{-6} + 1.0 \times 10^{-4}e^{2.4}) \text{ m}^3/\text{s}. \quad (12)$$

The measured values of Mark II' film thickness as function of spin speed and concentration are shown in Fig. 4. Except for the very dilute solution, all curves follow a $f^{-0.5}$ dependence over the entire range within experimental error. This is in agreement with Eq. (1) and many other observations on resists. Other measurements have shown that the power law extends down to spin speeds of 100 rpm for Shipley AZ-1350. It does not agree with the $r^{2/3}$ dependence calculated (Fig. 2) unless it is assumed that $e$ depends on spin speed as $e \propto f^{1/2}$.

A spin dependence of $e$ is also supported by the fact that $e$ depends very strongly on how fast the vapor phase above the liquid is removed. If, e.g., the spinner is enclosed in a housing, the film thickness produced decreases to an extent which indicates a change in $e$ of a factor of 2–3. We are not able to measure $e$ independently to determine the dependence on $f$. However, the rate of evaporation must be related to the air flow over the spinning disk, a problem that has been solved for the case of an infinitely large disk. There, it was found that the rate of fresh air flowing onto the disk per unit area from above is uniform and proportional to $f^{1/2}$. The simplest model suggests that the rate of evaporation is proportional to the rate of airflow over the surface, so that $e \propto f^{1/2}$ in agreement with the above deduction.

![Graph](image-url)

**FIG. 5.** Film thickness produced at $f=1000$ rpm as function of the initial concentration of solute Mark II'. The curve is calculated using the parameter values given by Eqs. (12) and (13). The points are experimental.

The different slope of the most dilute solution in Fig. 4 cannot be explained readily. The thickness values are quite small, and less accurate, but the effect appears to be real and has been confirmed on large substrates at about the same concentration.

By fitting one point of the Fig. 4 to a corresponding calculated value, we obtain a numerical value of the evaporation rate per unit area ($f$ is in rpm):

$$e = 6.32 \times 10^{-9} f^{1/2} \text{ m/s}. \quad (13)$$

With this value, we recalculate the predicted film thickness as function of initial concentration. A comparison with the experiment is shown for 1000 rpm in Fig. 5, with good agreement.

As a final check on the model we have been using, we investigated the time it takes for $h_f$ to be reached. The film was observed for changes in interference colors during spinning. The drying time was taken as that point where the color stops changing. This is a subjective measurement which we could reproduce with 1–2 s variation. In Fig. 6, the experimental data are shown compared to the curve calculated using the appropriate value of $e$ [Eq. (13)]. There is some difference in the absolute values of time, but the speed dependence is well reproduced, lending further support to the model.

In conclusion, we have described a model of spinning films from solution. It is based on the equations of Emslie et al. with the addition of the evaporation of the solvent. The experimental data are well described by this model if the evaporation rate is assumed to vary as the square root of the spin speed.

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A recent paper by B.D. Washo [IBM J. Res. Develop. 21, 190 (1977)] attempts to calculate the thickness of spun films without taking evaporation into account. This is done by making an unrealistic approximation of no or little outward flow. It results in a radial dependence of the thickness [Eq. (8) of their paper], whereas the exact calculation of the fluid distribution without evaporation predicts a uniform thickness (Ref. 1).


A. E. Bell (private communication).

L. P. Fox (private communication).