Effect of Solvent Evaporation Rate on "Skin" Formation During Spin Coating of Complex Solutions

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ABSTRACT

Spin coating can often be used to create highly uniform coatings on flat substrates using sol-gels and other precursor solutions. Typically, fluid flow considerations dominate the early part of spinning while solvent evaporation controls the behavior at later stages. However, even though evaporation does not control the early stages, it is still occurring throughout the entire process and evaporation-related issues can arise during the flow-dominated stage that may ultimately become coating thickness non-uniformities in the final product. Striation defect formation is a good example of this. During the spin coating process the evaporation of solvent takes place at the top surface of the flowing fluid, thus a concentration profile for the solute species will exist within the flowing solution. Since the solute species in sol-gel solutions are often prone to condensation or cross-linking reactions, it is possible for this top surface to experience a rapid increase in viscosity and potentially to act as a barrier to further evaporation. This top layer could be equivalent to the skin layer on drying paint.

In this paper we explore the effect of solvent depletion in the near-surface-region by closely analyzing the flow and evaporation rates for real solutions, both sol-gel and polymer, during spinning. We report interferometrically measured fluid thickness data that are analyzed to directly extract the net material evaporation rate. Data are compared for different spin speeds, thus directly adjusting the evaporation rate and potential solvent depletion effect at the surface. It is found that the evaporation rate applicable through the entire first stage of spin coating is nearly the same as that for pure solvent. Thus the top surface composition does not deviate greatly from its starting value until very near the end of coating formation process, when flow has effectively ceased and the coating drying stage begins.

Keywords: Spin coating, evaporation, sol-gel, interferometry, PMMA.

INTRODUCTION

Spin coating is a simple and effective manner in which to deposit thin, uniform films across planar substrates. The film solution generally consists of volatile solvents in solution with effectively non-volatile solutes. This solution is dispensed onto a planar surface that is then accelerated to a predetermined rotation rate. Evaporation of the volatile constituents occurs from the top surface of the solution, while simultaneously the rotation forces the fluid to flow uniformly outward (subject to a no-slip condition where the substrate is wetted by the solution). The solution's thinning rate attributed to viscous flow varies as the cube of solution thickness (and the square of spin speed)[1], so this dominates the early stage of spinning. The solution's thinning rate contributed by solvent evaporation is independent of solution thickness because it occurs only at the top surface and is limited by diffusion of the evaporated solvent molecules through a laminar vapor boundary layer above the solution/air interface[2]. Since the laminar boundary layer thickness depends on the square root of spin speed, then the evaporation rate also carries this dependence[3,4]. Equation (1) summarizes these effects:

$$\frac{\partial h}{\partial t} = -2Kh^3 - e \tag{1}$$

where:

$$K = \frac{\rho\omega^2}{3\eta} \quad \text{and} \quad e = C_e\sqrt{\omega}$$

In these equations ρ, η, ω, and h are the fluid density, viscosity, rotation rate, and instantaneous thickness, respectively. The evaporation rate, e, is described using a scaling constant, C_e, which implicitly includes such effects as the solvent's vapor pressure over the solution, diffusion rate in the air, and parameters that control the vapor boundary layer thickness (e.g. the viscosity of air). However, since none of these parameters are explicitly adjusted in our work, we parameterize the evaporation rate with this single constant.

Evaporation of solvents occurs throughout the entire spin coating process. This evaporation occurs as mass transfer of solvents at the fluid/vapor interface. A concentration profile must develop within the thinning fluid to feed the evaporation at the top surface. And, since the non-volatile components are not removed, there must be a net buildup of these solutes near the fluid/vapor interface. It would be possible for this increase in solute concentration at the fluid surface to lead to a local increase in the fluid viscosity and the formation of a skin layer. On the other hand, if diffusion of the solvent is fast in the solution then this surface enrichment might not be large enough to impact the viscosity and subsequent evaporation.

The question we address in this paper is whether this skin layer is thick enough or forms early enough to interfere with the thinning behavior described in equation (1) above. If such a skin forms, then it could act as a diffusion barrier to any further solvent evaporation thereby changing the physics of coating formation and thus altering the expected final film profile and potentially contributing to defects in the final coating. The next section describes the use of laser interferometry to measure the flow and evaporation constants, *K* and *e*, given above. Then, various coating solutions have been studied with this technique with a direct attention to whether evaporation rate changes give evidence for skin formation during spinning. Finally the results are discussed and conclusions are presented.

BACKGROUND

To analyze evaporation rates during spin coating, a previously developed interferometry technique is used[5,6,7] A low power laser is aimed at the center of a silicon wafer during the spin coating process. The beam is reflected from both the film surface and the surface of the silicon wafer, causing interference, and the resulting beam is directed into a linear optical power meter which converts the optical intensity readings into voltages. The data are logged by a computer and are processed after the spinning run has been completed. An example interference pattern is shown in Figure 1. In keeping with the practice of Horowitz[5], we call these interferograms "optospinograms." With knowledge of the index of refraction for the solution, the fluid thickness *h* can be deduced at each interference maximum and minimum position in an optospinogram (starting at the time when the fluid is thinnest and working backwards). With these thickness values as well as the corresponding time values it is possible to determine $\Delta h/\Delta t$ and thereby directly plot $-\Delta h/\Delta t$ vs. $2h^3$. Figure 2 shows this plot for the optospinogram given in Figure 1. The evaporation rate, *e,* is the Y-intercept point of the resulting linear regression and the slope gives the constant K, both defined above in equation (1).
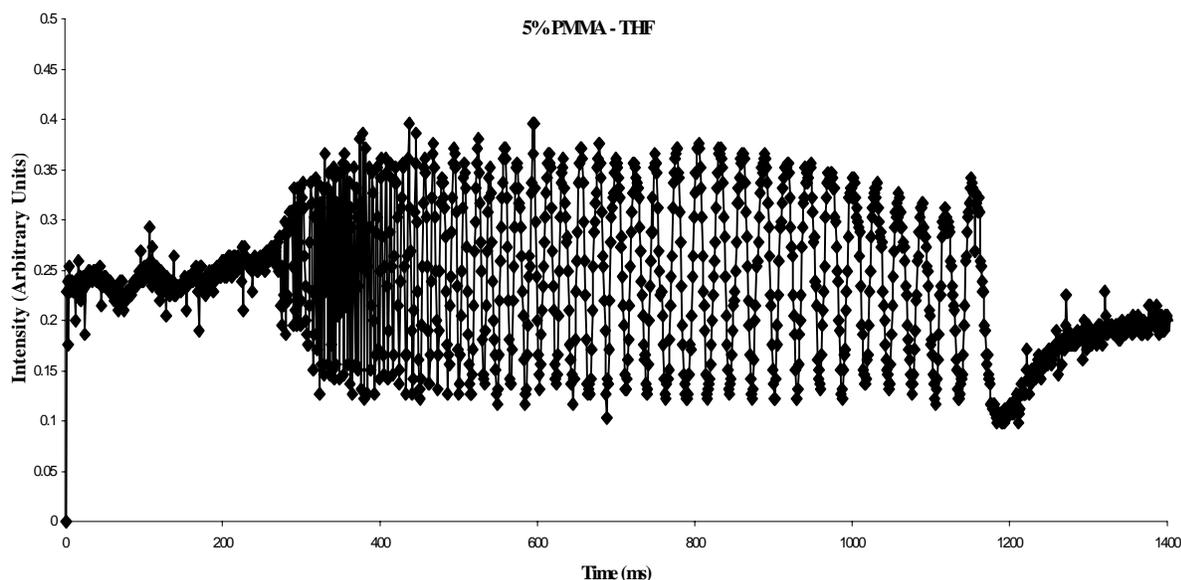

Fig. 1: Typical intensity vs. time plot or "optospinogram" for a spun-on solution. The peak and trough positions correspond to ¼ wavelength changes in fluid thickness. This 5% PMMA – THF solution was spun at 4000 rpm.
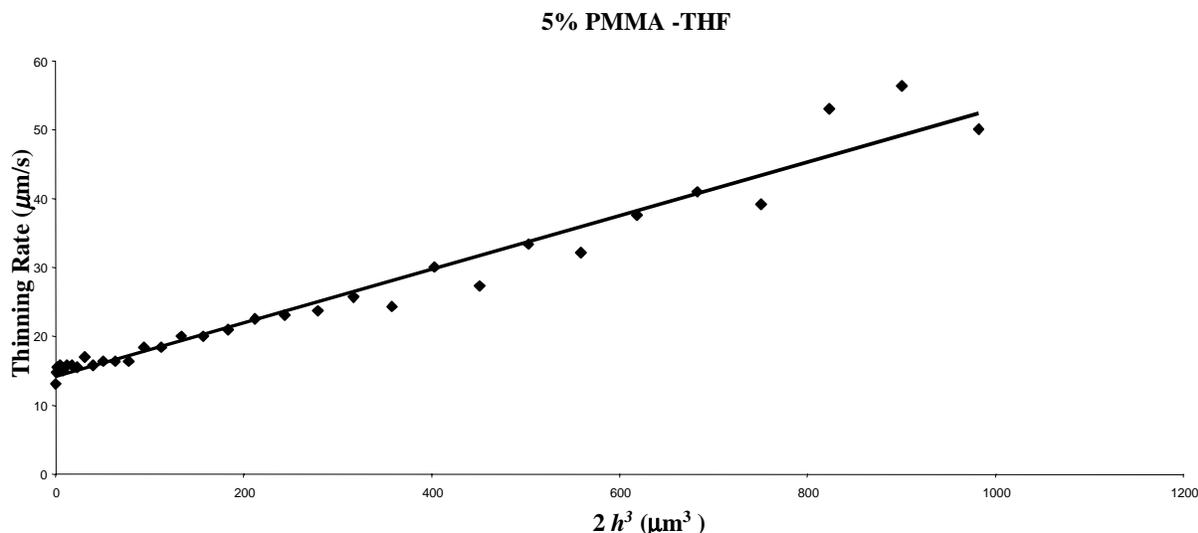
5% PMMA -THF

Fig. 2: Plot used for determining evaporation rate of a solvent during the spin coating process

EXPERIMENTAL PROCEDURE

Data are presented below for both sol-gel and non-sol-gel solutions. Sol-gel solutions for depositing PZT and WO$_3$ were used, following published synthesis routes[8,9]. The PZT sol-gel contains several alcohol types (because the synthesis uses titanium isopropoxide, zirconium n-butoxide, and methanol as a solvent). In addition, each of these forms its corresponding acetate ester during the condensation reactions[8,10]. The WO$_3$ sol-gel is simpler, with a preponderance of ethanol in the solution[9]. To provide a more controlled solution for purpose of comparison, polymer solutions were also studied using PMMA (5% by weight of MW = 120,000) dissolved into two common solvents, chlorobenzene (CB) and tetrahydrofuran (THF). These solutions provided a much more controlled evaluation of the evaporation rate effects imposed by the evaporation of solvent during the spinning process and are interesting when compared with the effects seen for the sol-gel materials described first. The sol-gel solutions were characterized at 2000 and 3000 RPM, while the polymer solutions were measured at a wider variety of spin speeds. The wider range of spin speeds allowed a more accurate fit of the evaporation proportionality constant, C_e. In addition, optospinograms were gathered for the spin application of pure chlorobenzene and THF solutions at various spin speeds in order to determine the C_e values applicable for each pure solvent alone for comparison against the C_e values of the two mixed solutions.

RESULTS

Solvent evaporation rates were extracted by fitting optospinograms for the solutions described above. For polymer-solvent mixtures the findings are presented in Table 1 while the data for sol-gel solutions are given in Table 2. Several spin speeds were evaluated for each mixture (and each pure solvent) so that appropriate C_e values could be determined in each case. These constants are given in Table 3. It is immediately apparent that the evaporation constants for the coating solutions (both polymeric and sol-gel) were extremely close to the values for their corresponding pure solvents. The fact that the pure-solvent and solution values were so close is an indication that the evaporation process did not leave behind a surface layer that impeded further solvent evaporation. In other words, the amount of solvent evaporation is not large enough to change the permeability of the top surface layer of material, at least for the majority of the coating regime (as visible using the optical interferometry technique).

DISCUSSION

Solvent evaporation is a critical component of depositing thin films using spin coating. As pointed out previously by Meyerhofer[2], the evaporation rate defines a relative time scale by which the radial fluid flow is metered. Faster evaporation results in thicker final film thickness, while slower evaporation leaves more time for fluid out-flow and gives a thinner final coating. When evaporation is so important in determining the final coating thickness, it is interesting to note that the quantitative evaporation rates determined interferometrically are not that different from the related pure-solvent values (see Table 3). Thus, the evaporation is not fast enough to markedly change the chemistry of the solution during most of the coating process. It is not fast enough to deplete the solvent from the top surface of the solution, thereby creating a dense skin

layer during the dynamic coating process. Two other independent lines of reasoning also support this conclusion. First, the spin-speed dependence of the evaporation rate indicates that the evaporation is rate-limited by diffusion through the hydrodynamic boundary layer in the air just above the fluid surface rather than within the solution. The evaporative removal of solvent is a multi-step process. Solvent diffuses to the surface, it converts at the interface from the fluid phase to the vapor phase, and finally it diffuses through the boundary layer into the distant air surroundings. Only the diffusion through the boundary layer will have a square-root of spin-speed dependence (because the width of this region follows this same power). This finding is further supported by a simple back-of-the-envelope calculation of the diffusion distance that solvent molecules might naturally experience during a typical spinning run. Our experience shows (from measuring the interferometric behavior of numerous solutions) that the fluid-flow dominated phase lasts only a couple of seconds. So, for reasonably fluid and volatile solvents, the molecules will have diffusion distances on the order of 100 µm within this time frame, whereas the evaporation rate through the exterior boundary layer is occurring at only about 10-15 µm/sec even when considering an extremely volatile solvent (e.g., Table 1 shows data for THF).

The present work has focused on the evaporation rate of solvents from solution during spin coating. However, the evaporation of solvent has also been implicated in the formation of defects called striations[11,12]. Interestingly, striation defects were observed for some samples and not others in the present work. The wafers coated with the 5% PMMA - THF solution exhibit severe striations whereas those coated by the PMMA - chlorobenzene solution appear uniform and smooth. And, all of the sol-gel coatings studied here had minor striation defects. Chlorobenzene is substantially less volatile than tetrahydrofuran thus it appears that the volatility of the solvent selected plays a factor in determining the uniformity of the final film. The appearance of striation defects is associated with Marangoni forces experienced in the top layer of the solution during coating, which includes a delicate balance between evaporation and surface tension effects[13,14]. Typically this is driven by a composition difference at the surface and these are linked to a composition gradient near the surface. The evaporation rate data shown above demonstrate

Table 1: Measured evaporation rates as a function of spin speed for PMMA solutions and related solvents.

Solution	Spin Speed RPM	Evaporation Rate µm/s
Chlorobenzene	1000	0.55
Chlorobenzene	2000	0.90
Chlorobenzene	3000	1.04
5% PMMA - Chlorobenzene	2000	0.71
5% PMMA - Chlorobenzene	3000	0.85
5% PMMA - Chlorobenzene	4000	1.10
Tetrahydrofuran	1500	9.3
Tetrahydrofuran	2000	10.3
Tetrahydrofuran	2500	11.6
5% PMMA - THF	2000	10.5
5% PMMA - THF	3000	12.3
5% PMMA - THF	4000	13.5

Table 2: Measured evaporation rates as a function of spin speed for various sol-gel solutions and related solvents.

Solution	Spin Speed RPM	Evaporation Rate µm/s
PZT	2000	0.42
PZT	3000	0.52
PLZT	2000	0.39
PLZT	3000	0.57
WO_3	2000	2.24
WO_3	3000	2.74
Ethanol	2000	1.94
Ethanol	3000	2.26

Table 3: Derived evaporation rate constants for pure solvents and for those in solution with PMMA.

Solution	Evaporation Constant C_e [µm/s · RPM$^{-1/2}$]
Pure Chlorobenzene	0.018
Chlorobenzene in 5% PMMA	0.017
Pure Tetrahydrofuran	0.24
THF in 5% PMMA	0.22
Pure Ethanol	0.04
WO_3 sol-gel solution (ethanol based)	0.05

that we are in a "slow evaporation" regime. When experiencing relatively slow evaporation then the surface solvent concentration deviates only slightly from the interior of the solution, but still it deviates enough to feed the constant flux of solvent being removed from the surface. The diffusion equation satisfying this boundary condition[15] illustrates that although having only a small solvent depletion at the surface, the deviation will be linearly dependent on the evaporation rate. And the local composition gradient within the solution near the surface will also depend linearly on the solvent evaporation rate. Although the differences in capillary forces for the different solvents and coating materials are unknown, it is interesting that the PMMA is flat when coated using the much less volatile solvent.

Although the solvent evaporation behavior measured in this paper exhibit no explicit formation of a surface "skin" during the coating regime, it is possible that other solutions do experience such an effect. In fact, sol-gel solutions might be especially susceptible to this effect since moisture from the surrounding environment can diffuse to the surface and react into the coating solution during the spinning process. If the water causes chemical cross-linking within the solution then it is possible that it could become dramatically more resistant to diffusion of the solvent outward through this surface reaction layer. The sol-gel solutions examined in the present work were completely hydrolyzed in their starting state so did not experience this effect. Future work will attempt to examine this effect.

CONCLUSIONS

Interferometrically measured solvent evaporation rates have been determined for a variety of solutions during spin coating. These evaporation rates are found to be slow enough that the majority of the coating process is governed by the properties of the starting coating solution: the solvent evaporation is not strong enough to deplete the body of the solution until the very end of the coating process when the last drying and solvent removal occurs. This finding is supported by other lines of reasoning, including the square-root dependence of the evaporation rate on spin-speed that is typically found, and the comparison between the evaporation rate and typical diffusion rates within solution.

ACKNOWLEDGEMENTS

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