Modeling of Striation Development in Spin Coating

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Lateral surface tension variations drive the development of "striation" defects in spin coating. The evaporation of solvents causes a surface enrichment of the coating-forming constituents that reaches a point of instability when the evaporation is too rapid. We develop and exercise a numerical model of the evaporation of solvent in spin coating and the surface tension changes that result. Different wavelength perturbations are then initiated and these influence the composition changes and striation growth (or damping). The behavior is governed by two counteracting physical effects: one that always tends toward leveling (based on the nominal average surface tension value) and one that tends toward roughening (based on the surface tension gradients that develop under the influence of evaporation). To complicate matters further, the variation in fluid thickness with time often forces conditions that satisfy both "thin film" and "thick film" limits when trying to solve for the composition profile with depth at various times. We consider different solvent characteristics and examine the importance of volatility, surface tension value, and viscosity.

The striations are driven by Marangoni forces that develop on the surface of the drying coating. Figure 1 shows a schematic of the phenomenon and illustrates the competition of forces that the coating experiences. The curvature of the surface drives a leveling process, but lateral differences in the surface tension can lead to an imbalance where thicker regions continue to grow thicker by pulling in coating solution from neighboring spots.

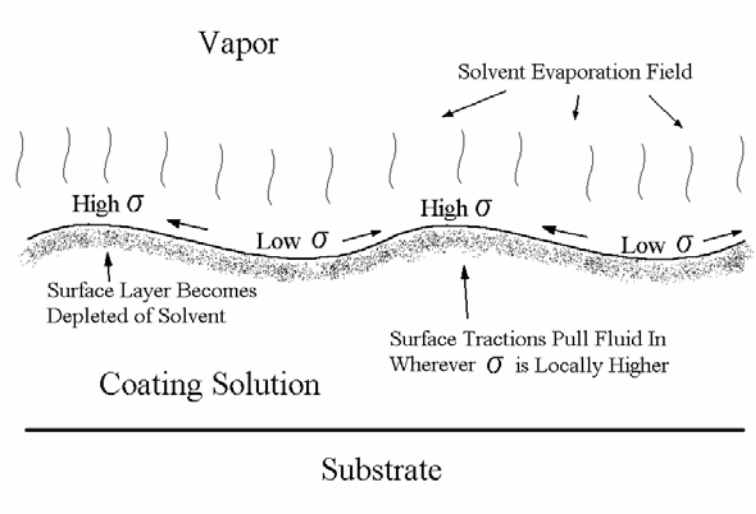

Figure 1: Simple schematic depicting the development of a striation pattern within a coating during drying. The lateral differences in surface tension can lead to an imbalance. The concentration of solute at the surface is governed by the balance between diffusion within the solution and the evaporation rate into the surrounding air; locations with different thickness then establish a different local composition at the surface, and therefore have different surface tension.

We developed a numerical model for spin coating that uses the established fluid thinning model and incorporates the solvent evaporation with time based on Meyerhofer's early work[1]. Then we apply, for every incremental time step, the solution for the lateral fluid motions indicated in the adjoining figure.

Simultaneously, we examine the evaporation of solvent and the effect that this has on the surface composition within the coating solution. This surface composition defines what the local surface tension will be for the coating solution and different thickness locations will have slightly different composition and therefore slightly different surface tensions. The numerical approach we have taken starts with a small perturbation in thickness at an early time when coating flow is dominated by viscous thinning and allows the perturbation to develop with time – and the local compositional fluctuations to change accordingly. This equation defines the amplification or damping of perturbations in thickness:

$$\frac{\partial A}{\partial t} = -\frac{Ak^4}{3\eta}\left[(H_o + A)^3(\Sigma_o + 2B) + (H_o - A)^3(\Sigma_o - 2B)\right] \quad +$$

$$\frac{Bk^2}{2\eta}\left[(H_o + A)^2 - (H_o - A)^2\right] + \frac{\eta_{air}\,\omega}{\delta}\left[(H_o + A)^2 - (H_o - A)^2\right]$$

where **A** is the thickness perturbation amplitude around an average solution thickness, $\mathbf{H_0}$, and **B** is the surface tension perturbation around the average surface tension value, $\mathbf{\Sigma_0}$. The perturbation wavenumber, **k**, has a strong influence on the amplification or damping of any perturbation. Shear effects imposed by the nearby air are included in the third term, though this is negligibly small for the conditions we find in our samples.

The conditions for growth or shrinking of the thickness perturbation are strongly affected by the wavenumber, **k**, so it is instructive to find the condition where maximum amplification to the perturbation is experienced. This is found where the differential above is maximized:

$$\frac{\partial}{\partial k}\frac{\partial A}{\partial t} = 0 = -\frac{4Ak^3}{3\eta}\left[(H_o + A)^3(\Sigma_o + 2B) + (H_o - A)^3(\Sigma_o - 2B)\right] + \frac{Bk}{\eta}\left[(H_o + A)^2 - (H_o - A)^2\right]$$

At any instantaneous average thickness, the perturbation that is amplified the most will be found at this wavenumber:

$$k_{peak} = \left(\frac{3B}{2\Sigma_o}\right)^{1/2}\frac{1}{H_o}$$

We have exercised our numerical model and established final relative roughness values that combine these effects through time and test the importance of different solution variables (viscosity, surface tension value, and evaporation rate). Figure 2 shows two example roughness results as a function of inverse wavenumber. These graphs illustrate that some particular wavelength of perturbation is most amplified in the final coating – as is well known in the striation patterns that develop experimentally. More graphs of this type will be presented to illustrate the influence of the key experimental parameters in our coating solutions.

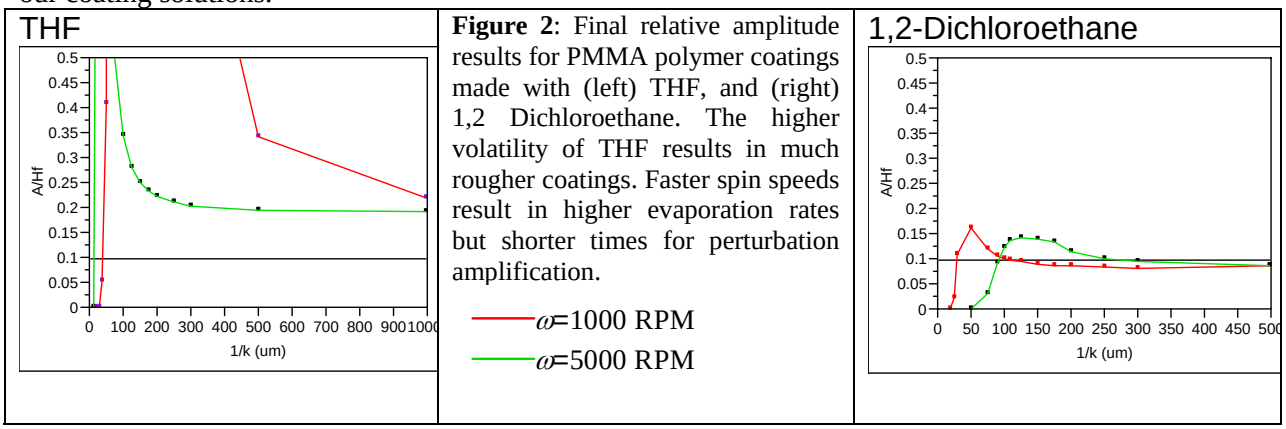

Figure 2: Final relative amplitude results for PMMA polymer coatings made with (left) THF, and (right) 1,2 Dichloroethane. The higher volatility of THF results in much rougher coatings. Faster spin speeds result in higher evaporation rates but shorter times for perturbation amplification.

[1] D. Meyerhofer. "Characteristics of resist films produced by spinning," *J. Appl. Phys.* **49** [7] 3993-7 (1978).

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