Solvent Vapor Effects on Striation Growth in Spin Coating

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Striation defects are radially-oriented ridges with a quasi-sinusoidal thickness profile that occur during spin coating. They arise due to Marangoni forces that are established during early stages of drying of the coating. We have demonstrated in earlier work that solvent evaporation, which is concentrated at the free surface, causes surface tension differences and that this can become unstable causing the formation of the wavy surface structure. Earlier work has shown that saturating the vapor environment with the primary solvent used in the coating formula can greatly reduce the amplitude of the striations that are formed. This makes sense because it lowers the evaporation rate and therefore reduces the magnitude of the Marangoni forces. We have also shown that solvent mixtures can be used to alleviate these evaporation-induced defects [[1,2]].

In the present work we investigate the effect of vapor composition *above* the outward flowing coating solution and the vapor's influence on the formation of striations. By providing different species into the vapor environment they can be surface-active and help counteract the evaporation-driven surface-tension effects. Alternately, the extra solvent vapor can magnify this defect mode.

We have worked with a silica nanoparticle based solution in water (Ludox) and diluted it with ethanol 10:1 for our base coating solution. This gave relatively thin coatings with mild striations as a result of the relatively rapid evaporation of ethanol from the solution during coating. Ancillary solvents for the external environment were chosen from several available in the lab. Their basic surface tension and volatility characteristics are listed here (in order of increasing volatility):

	Surface Tension (mN/m)	Vapor Pressure (Pa)
Ethanol	21.97	7878
Ethyl Acetate	23.39	12466
Methanol	22.07	16838
Hexane	17.89	19840
Chloroform	27.11	20800
Acetone	23.46	30235

The air environment within the spin coater bowl was prepped for the coating runs by first drying the ambient environment using small trays of Drierite for an hour and then Petri

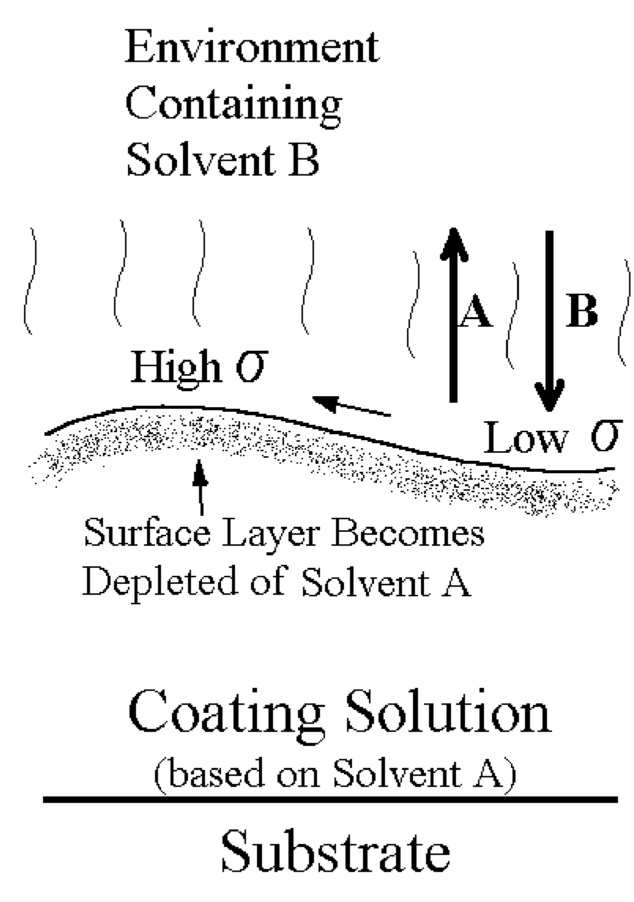
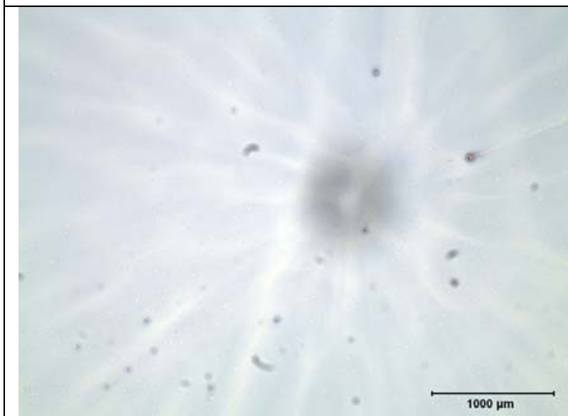


Figure 1: Schematic representation of a system with solvent flux in both directions. The coating solution has excess of solvent A (compared to its vapor pressure in the air), while the ambient is saturated in solvent B (not contained in the coating solution).

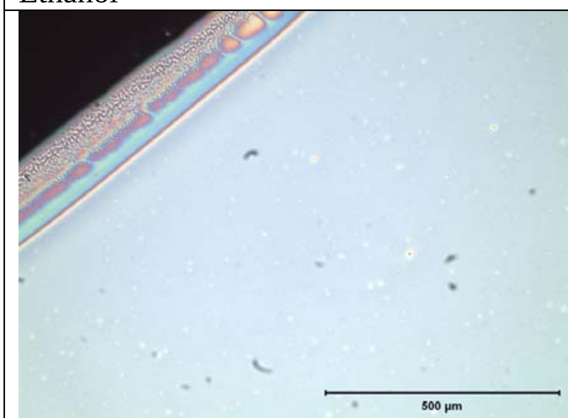
dishes placed within the spin bowl containing the extra solvent – and also let to evaporate for an hour before the coating solution was spun. After spin coating, the samples were examined with optical microscopy to evaluate the quality of the coatings that had been formed and to correlate the behavior in terms of the external solvent characteristics.

Representative optical micrographs are shown below. The middle picture shows the extremely flat coating that results when the external environment contains the *same* solvent as the majority volatile species within the coating solution (ethanol). This reduces the evaporation rate and therefore it lowers the driving force for the development of Marangoni force instabilities. Both acetone and methanol are higher volatility solvents. Their net rate of diffusion through the vapor boundary layer is expected to be higher than the escape rate for the ethanol. They were anticipated to be able to modify the surface tension characteristics of the system during the spin coating process. Methanol has a surface tension nearly identical to ethanol's so its incorporation during spinning is expected to help offset some of the evaporation-driven instability. On the other hand, the acetone is somewhat higher surface tension, so might be expect to amplify the effect. Certainly both of these coatings still exhibit striation defects (as shown in the top and bottom pictures), however no substantial difference in striation pattern or magnitude is detected in our experiments for these two solvents. When ethyl acetate was used (not shown) we achieved much flatter coatings and this is consistent with its utility as a co-solvent in making spin-coating formulations in earlier studies [2]. On the other hand the humidity level in the ambient is known to have a strong effect on coating quality in these situations. We will discuss these variations in coating quality with solution and ambient solvent chemistry in further detail in our presentation.

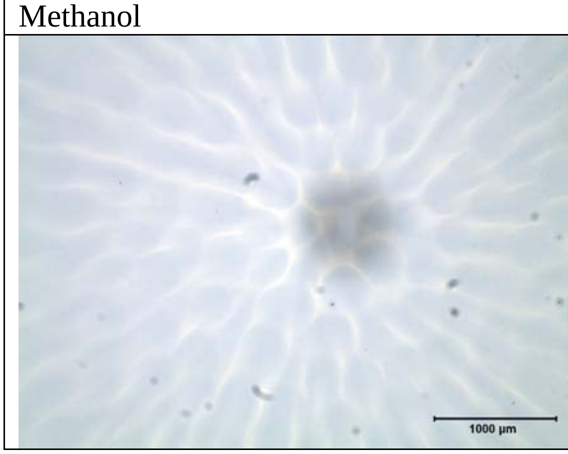
Acetone



Ethanol



Methanol



[1] D. P. Birnie, III, "Rational Solvent Selection Strategies to Combat Striation Formation during Spin Coating of Thin Films", J. Materials Research, **16** (4), 1145-54 (2001)

[2] D. J. Taylor and D. P. Birnie, III, "Striation Prevention by Targeted Formulation Adjustment: Aluminum Titanate Sol-Gel Coatings", Chemistry of Materials, **14**, 1488-1492 (2002)

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