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# Effect of Ramping-Up Rate on Film Thickness for Spin-On Processing

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## ABSTRACT

Spin-on processing is used in many industries to deposit very thin coatings on flat substrates, including silicon wafers, flat-panel displays, and precision optical components. A liquid precursor solution is first dispensed onto the surface of the substrate; this fluid then spreads out very evenly over the surface due to large rotational forces caused by spinning of the substrate. When looking for an optimum coating procedure process engineers can adjust many variables including the peak spin speed, the ramping rate to reach that speed, the spinning time, as well as allowing for dynamic solution dispense before ramping up, though most protocols focus on the peak spin speed as the primary controlling variable. Engineers often construct spin-speed versus thickness correlations that enable predictable adjustment of spin-speed to achieve a desired thickness. Yet, rather little attention has been paid to the importance of the acceleration rate used to reach the desired peak speed. We show here that ramping rate is also important in helping establish the final coating thickness. We present a numerical model of the fluid flow on a spinning wafer when the spin-speed is ramping linearly up to a desired peak speed and then held constant. It is shown that the coating may “set” into its final thickness before the spin-speed reaches its peak value. In these cases then the peak spin-speed parameter is no longer the primary variable that defines the final coating thickness. This also impacts the interpretation of critical exponents found when fitting spin-speed vs. thickness data. We perform parallel experimental measurements for different ramping-up times and confirm the results from the numerical model. Both experimental and theoretical results support use of the simplified model put forth by Meyerhofer over 25 years ago (*J. Appl. Phys.* **49** (1978) 3993-3997).

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## INTRODUCTION

Spin coating is a simple process for rapidly depositing thin coatings onto relatively flat substrates. The substrate to be covered is held by some rotatable fixture (often using a vacuum to clamp the substrate in place) and the coating solution is deposited onto the surface; the action of spinning causes the solution to spread out and leave behind a very uniform coating of the chosen material on the surface of the substrate. Typically, the coating solution contains solvent species as well as the materials being deposited onto the substrate. The spin coating process has been studied extensively in the past and much is known about the factors that control coating deposition and the final thickness of the deposit that results [1-11]. However, relatively little effort has been expended toward understanding the importance of the first few seconds of the spin-coating process: the time when the wafer is accelerating up to the peak spin-speed. One study has correlated the ramping rate with the amplitude of striation defects in photoresist and concluded that rapid ramping results in more uniform coating thickness [12]. Another study has shown that smaller center-to-edge thickness variations occur when slower ramping is used for photoresist deposition [4]. This effect was associated with the well-understood non-Newtonian fluid behavior found for some polymer solutions and particle suspensions during spin coating [7,13-16]. Still, one modeling study included the ramping rate into their simulation and found there to be no effect, though they didn't allow for solvent evaporation during the ramping phase [17].

We approach this problem here and show that significant variations in coating thickness can result from relatively small ramp-up time differences. This helps emphasize

the importance of accurate equipment speed control as well as observance of rigidly constrained processing parameter choices when reliable processing results are required.

## BACKGROUND

The physics of fluid flow on a spinning substrate has been rigorously described in the seminal work of Emslie, Bonner, and Peck [1] (hereafter referred to as “EBP”). The fluid layer is assumed to be thin enough that the radial rotational forces are exactly offset by the viscous drag imposed by the fluid. Mathematically, this force balance is expressed by this differential equation:

$$-\eta \frac{\partial^2 v}{\partial z^2} = \rho \omega^2 r \quad (1)$$

where:

- $\eta$  is the fluid’s viscosity,
- $v$  measures the radial velocity component,
- $z$  is a vertical height dimension,
- $\rho$  is the fluid density,
- $\omega$  is the rotation rate, and
- $r$  is the radius being considered.

Note, that the left hand side calculates the gradient in the shear developed by the velocity vs. depth profile and that this must exactly balance the rotational forces felt by the same volume element. When this equation was solved with the appropriate boundary conditions, EBP found the following expression for the fluid velocity profile with depth:

$$v = \frac{1}{\eta} \rho \omega^2 r \left[ hz - \frac{z^2}{2} \right] \quad (2)$$

where  $h$  is the instantaneous fluid thickness and  $z$  is ranges from  $0$  to  $h$ . By integrating they were able to determine the total fluid thinning rate and derive a function for the fluid depth versus time. Their thinning rate was found to be:

$$\frac{dh}{dt} = -2Kh^3 \quad (3)$$

where  $\mathbf{K}$  is a flow constant defined by:

$$K = \frac{\rho\omega^2}{3\eta} \quad (4)$$

EBP's treatment neglected the fact that most coating solutions have volatile solvents in the recipe, and that the evaporation of these solvents also contributes to fluid thinning. Meyerhofer [2] added this important factor into the equation. He recognized that the evaporation rate was not dependent on the physical thickness of the fluid, but rather depended on vapor diffusion through the aerodynamic boundary layer above the wafer surface. This evaporation contribution to thinning was therefore:

$$\frac{dh}{dt} = -e \quad (5)$$

where  $e$  is a function of spin-speed because the vapor boundary layer changes thickness as the rotation rate changes [2,18,19]. Thus,  $e$  is found to conform to:

$$e = C\sqrt{\omega} \quad (6)$$

where  $C$  is a proportionality constant that depends on whether airflow above the surface is laminar or turbulent, and on the diffusivity of solvent molecules in air (since it is basically limited by diffusion of the evaporating molecules through the aerodynamic boundary layer above the surface of the wafer during spinning). In prior work, we have simply determined  $C$  experimentally using a laser interferometry technique [20-22]. Others using laser interference effects have dubbed this method "optospinography" [23,24].

So, in most real spin-coating conditions, the action of *both* processes will be contributing simultaneously – and throughout the entire process. This results in the thinning rate differential equation shown here:

$$\frac{dh}{dt} = -2Kh^3 - e \quad (7)$$

This equation was the basis for fitting interferometry data to extract the  $e$  and  $K$  constants for particular coating solutions [20,21].

Meyerhofer took his analysis one step further – to allow for an estimation of the final film thickness in terms of the key physical constants. He recognized that the flow term has a cubed dependence on  $h$ , while the evaporation term is independent of fluid thickness. This indicated that for large thickness values the flow would dominate – bringing the thickness down and ultimately becoming insignificant in comparison to the evaporation rate. He defined a “cross-over” point where the two contributions would be equal. Then, he assumed that after the cross-over point (during the time when evaporation dominates) the film will form essentially by drying in place. With this approach he was able to predict the final coating thickness,  $h_f$ , in terms of the key solution parameters, according to:

$$h_f = x \left( \frac{e}{2(1-x)K} \right)^{1/3} \quad (8)$$

where,  $e$  and  $K$  are the evaporation and flow constants, defined above, and  $x$  is the fractional solids content of the solution (i.e., what would be left over when the solvents are completely removed by evaporation or baking).

The inherent dependencies of  $\mathbf{e}$  and  $\mathbf{K}$  on spin-speed then combine in equation (8) to predict that the final coating thickness will vary as the inverse square root of the spin-speed:

$$h_f \propto \omega^{-1/2} \quad (9)$$

This spin-speed exponent of  $-1/2$  has been observed in numerous experimental studies [2,3,4,8,25-38], though values that deviate somewhat from  $-1/2$  are also reported [2,4,39-43]. In earlier work, deviations from a value of  $-1/2$  were attributed to more viscous solutions or viscosity changes during spinning [44]. In fact, if no evaporation takes place then a spin-speed exponent of  $-1$  would be expected based on EBP's thickness solution [1]. Still, some experimental work has given exponents *smaller* in magnitude and neither model can explain these deviations [2,4,40,43].

In the present work, we show that the earliest stage of spinning (when the sample is still ramping up to its peak spin-speed) can influence the final coating thickness so that different spin-speed exponents can arise even when the basic process conforms to the equations given above. In the next section we describe a numerical model for exercising a spin coating process that includes the period when the fluid is ramping up to speed. Then another section describes a set of thin films that were deposited with different ramping rates to test the predictions of the numerical model.

## NUMERICAL MODEL

The numerical treatment covered here combines two basic effects. First, the flow and evaporation physics described above are assumed to be fundamental aspects of the processes we cover. Second, we will assume a time varying spin-speed – in accordance

with typical values that might be chosen when programming spin coating equipment. Equation (7) will be used exclusively to describe the combined flow and evaporation physics – without any simplification for early or late stages of the process – ie. both terms will be evaluated in all circumstances. The spin-speed dependencies for both  $\mathbf{e}$  and  $\mathbf{K}$  will be defined by equations (6) and (4), respectively – and will be adjusted with time in accordance with the time varying spin-speed. The variation of spin-speed with time will be linear at first, until the desired peak speed is reached, after which time the speed will be held constant:

$$\omega(t) = \begin{cases} \alpha t & t < t_{ramp} \\ \omega_{peak} & t > t_{ramp} \end{cases} \quad (10)$$

where,  $t_{ramp}$  is the time an operator might select for the equipment to ramp up to the peak spinning rate,  $\alpha$  is the acceleration rate during that ramping time, and  $\omega_{peak}$  is the spinning rate plateau after ramping is complete. Note that these constants are somewhat interrelated because if a linear ramp is used then the appropriate acceleration rate will be defined by the peak speed divided by the ramp time:

$$\alpha = \frac{\omega_{peak}}{t_{ramp}} \quad (11)$$

Using these basic equations, a numerical model is exercised where user-defined initial conditions are then incremented by small amounts to watch the fluid thickness evolution – and ultimately to predict the final coating thickness that will be produced by a chosen set of process parameters.



In determining the predicted final coating thickness, we must monitor when the coating fluid has reached the “cross-over” point described above. Then, we assume – as Meyerhofer did – that the final evaporation stage will freeze-in the final coating thickness from that point. The new feature that Meyerhofer didn’t consider is that the cross-over point may be reached before the spin-speed has completely ramped up to the peak speed that has been chosen for a process.

The mechanics of the numerical model were implemented in a large spreadsheet where each row represented an incremental time step starting from appropriate initial conditions in the first row. The time steps were managed so that no increment was allowed to cause more than 1% change in fluid thickness before the next time step. Contributions from flow (equation (3)) and from evaporation (equation (5)) were calculated separately to ensure that neither contribution was surpassing this gradual change criterion. The cross-over point was determined by noting the time-step at which the flow contribution first became smaller than the evaporation contribution. The spin-speed value at that time was then logged, as well as the fluid thickness. Figure 1 gives an example plot showing the fluid thickness evolution with time for ethanol ramping up to a spin-speed of 2000 RPM in a period of 1 second. The cross-over point occurs at approximately 1.65 seconds, at a time when the spin-speed has already reached 2000 RPM. After this point the fluid thinning is dominated by evaporation (and it essentially dries in place).

One observation can be made immediately: if a significantly longer ramping time had been used, then the crossover point would have been reached before the peak spin-speed had been reached. This would freeze in the final coating thickness at a different

spin-speed than had been selected as the peak rotation rate setting. This effect is shown quantitatively in Figure 2, which gives the spin-speed at the cross-over point as a function of the ramping-up time. Three different peak spin-speed choices are shown. For very short ramping-up times (e.g. 1 second) the cross-over point occurs at the intended spin speed, while at longer ramping up times (e.g. 5+ seconds) then the cross-over point occurs significantly before the rotation rate has reached the desired peak speed. And, since each spin-speed is affected differently by this offset, it is not possible to extract meaningful spin-speed exponents from samples where ramping has taken too long. Figure 3 shows predicted coating thicknesses for spin-coating protocols that have either 1-second or 5-second ramping times. The solvent chosen was ethanol and a 5% solution of the coating constituents was used for estimating final thicknesses. At slow spin-speeds then the ramping time is not a factor in determining the final coating thickness. However at higher spin-speeds a thicker coating results when a longer ramp rate is chosen. This is a consequence of reaching the cross-over point before reaching the final spin-speed – and the fact that the fluid thickness will be greater at this point than it would be if cross-over were reached at a higher speed. The next section covers an experiment designed to mimic the situations predicted in this section.

## EXPERIMENTAL PROCEDURE

Based on the results shown in Figures 2 and 3, we designed a model experiment intended to test whether these coating thickness differences were actually found for real solutions. As a coating solution, we used sol-gel precursors designed to deposit an amorphous silicon dioxide layer.

Tetra-ethoxy-silane (TEOS), ethanol, and acidified water (0.15 M HCl) were mixed in a molar ratio of 8:1:40 respectively. The ratio water:TEOS = 5 was chosen to achieve a relatively short gelation time [<sup>45</sup>]. After combining the liquids, the solution was stirred vigorously for one hour, at the end of which the solution was significantly warmer. Upon cooling, the sol was diluted with a large amount of ethanol, bringing the final solution recipe to 4:25:20. Based on this composition, the fractional solids content was estimated to be about 10%.

The sample matrix included RPM values of 1000, 2000, and 3000. And, ramping times of either 1-second or 5-seconds were used. The coating solutions were deposited in large enough quantity to flood the 100mm silicon wafers that we used as substrates (3-4 ml). Wafers were subjected to 30 seconds of spinning at the peak speed (substantially longer than the expected cross-over times). After deposition, coatings were treated at 260°C for 3 minutes to drive off residual solvents and consolidate the silicate sol-gel coatings. Coating thicknesses were measured using ellipsometry near the center of the wafer. Data represent averages of 10 data points taken from two wafers coated under identical conditions. Standard deviations in thickness for each sample were typically less than 2% of absolute thickness.

## RESULTS

Average thickness values for the six different spinning protocols are shown in Figure 4. The basic shape of the thickness versus spin-speed plots is the same as found from the numerical model. When longer ramp times are used then the coatings are thicker (indicating that they coatings had “set” before reaching the peak spin-speed). When the

data are fitted to get a power-law dependence on spin-speed we find a value of  $-0.52$  for 1-second ramping and a value of  $-0.23$  for the 5-second ramping protocols. Again, this is consistent with the exponents found when fitting the values determined by the numerical model ( $-0.50$  and  $-0.27$ , respectively). It is interesting that 1-second ramping times appear to be fast enough to match the behavior predicted by Meyerhofer; the substrates are accelerated fast enough to reach the peak spin-speed before the key coating thickness development stage is reached.

## DISCUSSION

One of the key ways of adjusting final coating thickness for any particular precursor solution is to adjust the spin-speed used to apply it to a wafer. This adjustment is calibrated by running a thickness versus spin-speed master plot, fitting the data to a power law and calculating what spin-speed will deliver the desired coating thickness. The present work has shown that this procedure of calibrating a process to predict the optimum spin-speed is also strongly dependent on other aspects of a typical spinning protocol – in this case the time taken to accelerate up to the desired spin-speed. For the conditions tested, a 1 second ramp time appears to be satisfactory in getting the wafer/fluid up to speed fast enough that the flow/evaporation physics are characteristic of that peak spin-speed.

There are other aspects of spin-on processing protocols that might also be problematic with respect to making repeatable and predictable coating thickness depositions. For example, many wafer spinners provide for more than one ramp+hold interval and often a relatively slow “dispense” cycle is used to help conserve coating

solution and apply it uniformly on the wafer before accelerating up to the peak speed. It is possible that this step could allow the coating fluid to reach the cross-over point prematurely.

Previous literature reports [<sup>2,4,40,43</sup>] of spin-speed exponents that have deviated from the ideal  $-0.5$  value might also be a result of slow ramping up to speed. In many cases these exponents are more like the exponents we found here for 5-second ramping times. Unfortunately, authors in these previous reports have not specified their ramping up protocols, nor other aspects of their spinning procedures.

Our comparison between the thinning model and experiment involve coating solutions with a relatively volatile solvent (ethanol). This is typical for sol-gel derived coatings for depositing oxide or nanocomposite layers [<sup>45</sup>]. The timing of the crossover point is strongly dependent on the solvent's volatility with less volatile solvents reaching cross-over later in the process. However, as spin-coating protocols may be adjusted to have longer ramping up times (e.g. to avoid non-Newtonian flow effects) then there is a greater likelihood that the coatings will have “set” before reaching the targeted peak spin-speed. Specific details of solvent volatility and viscosity will need to be considered for individual systems to gauge the importance of the ramping-up rate. For example, it is very possible, even likely, that more viscous solutions will behave significantly differently, especially since the higher viscosity implies a slower solvent diffusion within the coating fluid and a breakdown of the evaporation rate-limiting-step as identified by Meyerhofer and others. However, the experiment and model that we have developed here is simple enough that it could be usefully applied to some of these other situations. We expect to extend our work in this direction in future studies.

## CONCLUSIONS

The process of coating development for spin-on processing has been examined in detail for process protocols that include a short period of programmed ramping-up to a target spin-speed. It was found that in some cases the evaporation process takes over before the peak spin-speed has been reached. This causes the coating to “set” before the peak speed is even reached and creates thicker than expected coatings. This also perturbs the key spin-speed exponent and may make it difficult to ensure portability of coating deposition protocols between equipment or researchers. Great care must be exercised to specify our coating protocols well enough that reproducible coatings will result.

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## FIGURE CAPTIONS

Figure 1: Fluid thickness evolution with time for ethanol ramping up to a spin-speed of 2000 RPM in a period of 1 second and then holding. The fluid started at 100 microns thick at time zero and reached the cross-over point at about 1.65 seconds from the initiation of ramping.

Figure 2: Spin-speed at the cross-over point as a function of ramping time for ethanolic solutions. Peak spin-speeds of 1000, 2000, and 3000 RPM are shown, but if the ramping time is too long then cross-over is reached before the peak spin-speed is achieved.

Figure 3: Predicted final coating thickness as a function of spin-speed and ramping time (on Log-Log scale). Fluid parameters for ethanol were used with 5% of the solution being coating-forming constituents. The fitted spin-speed exponent for the 1-second ramp samples was  $-0.50$ , while the 5-second ramp samples yielded an exponent of  $-0.27$ .

Figure 4: Measured final coating thickness as a function of spin-speed and ramping time. An ethanolic sol-gel solution was used, as described in the text. The fitted spin-speed exponent for the 1-second ramp samples was  $-0.52$ , while the 5-second ramp samples yielded a value of  $-0.23$ .

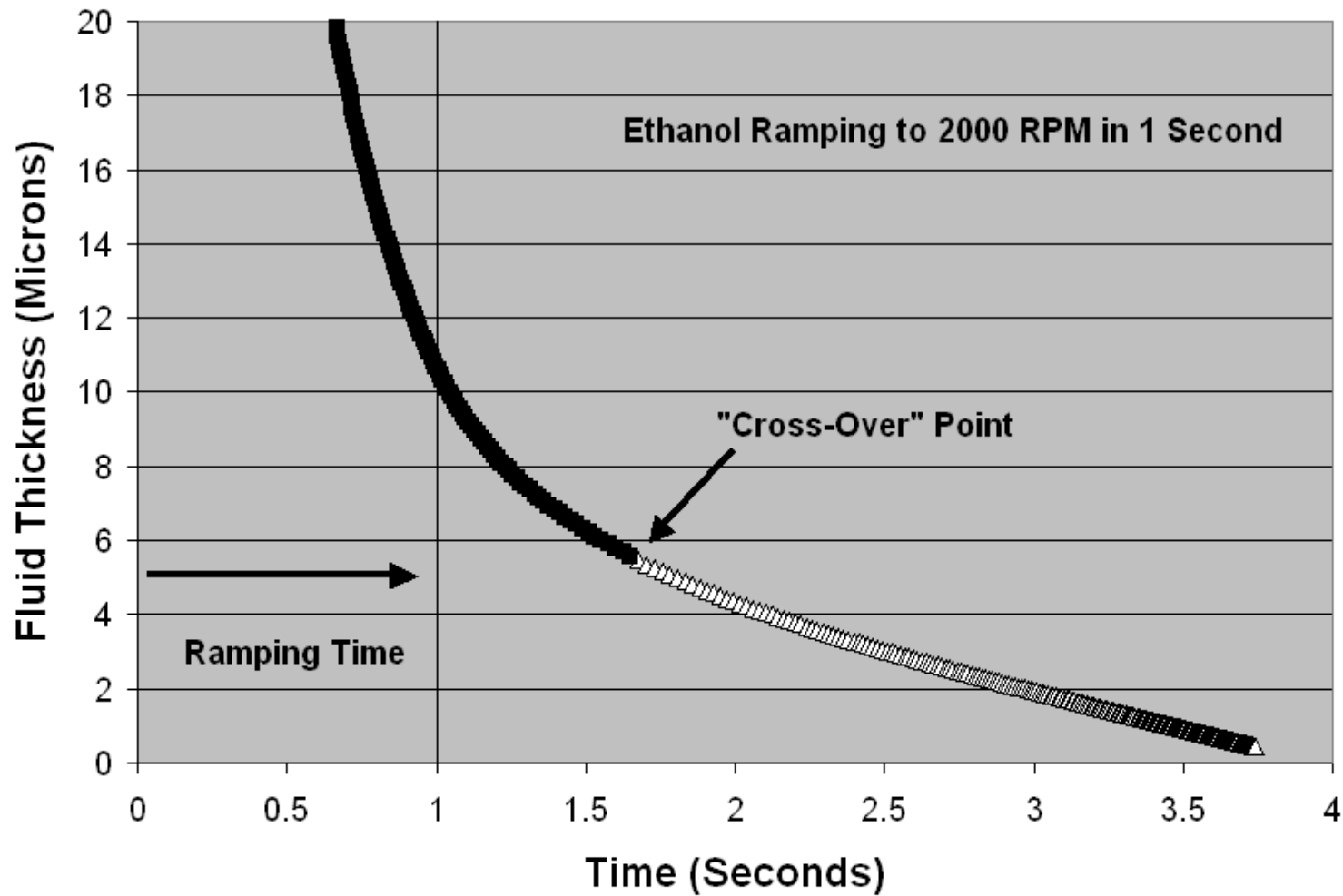
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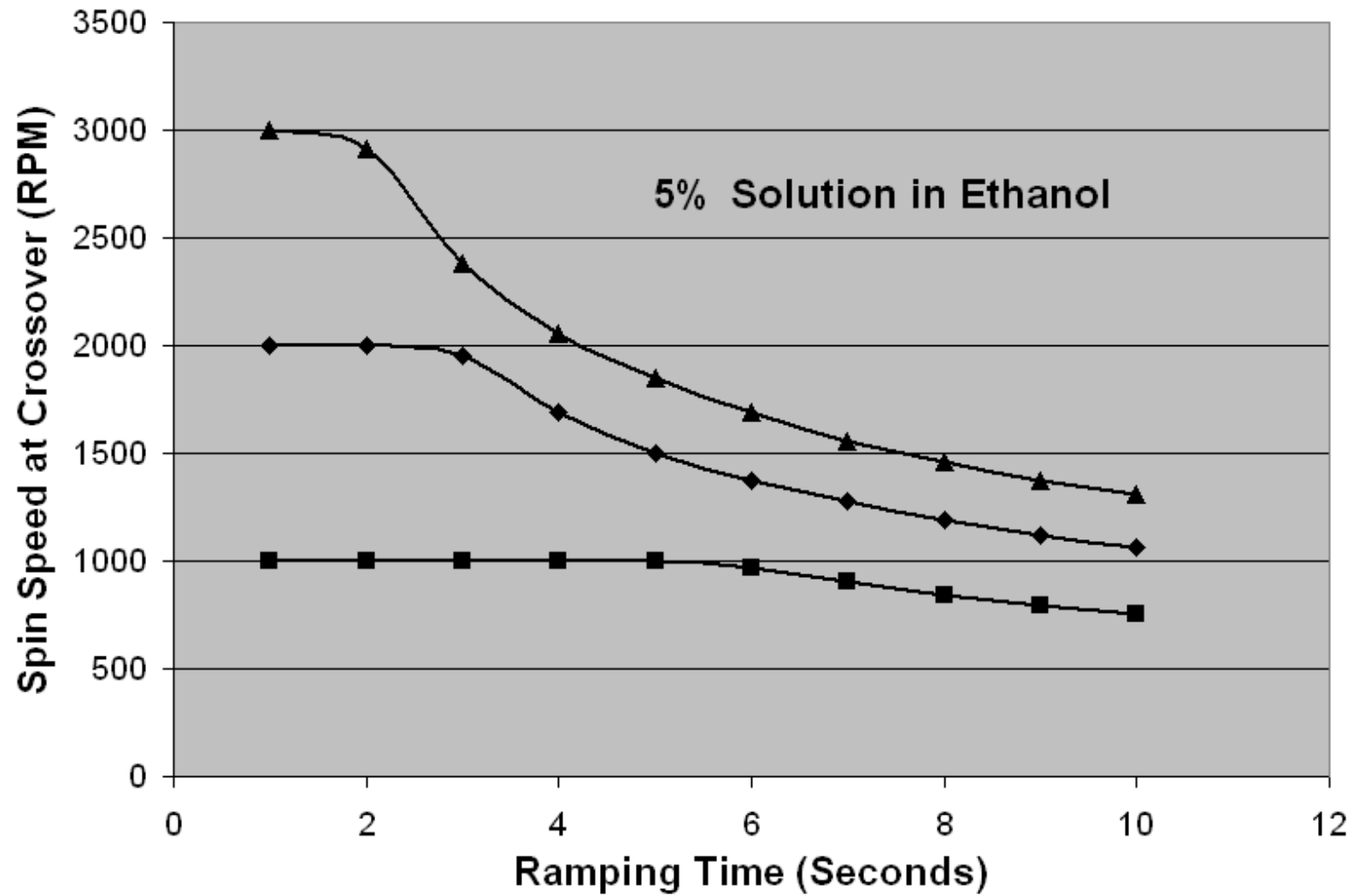


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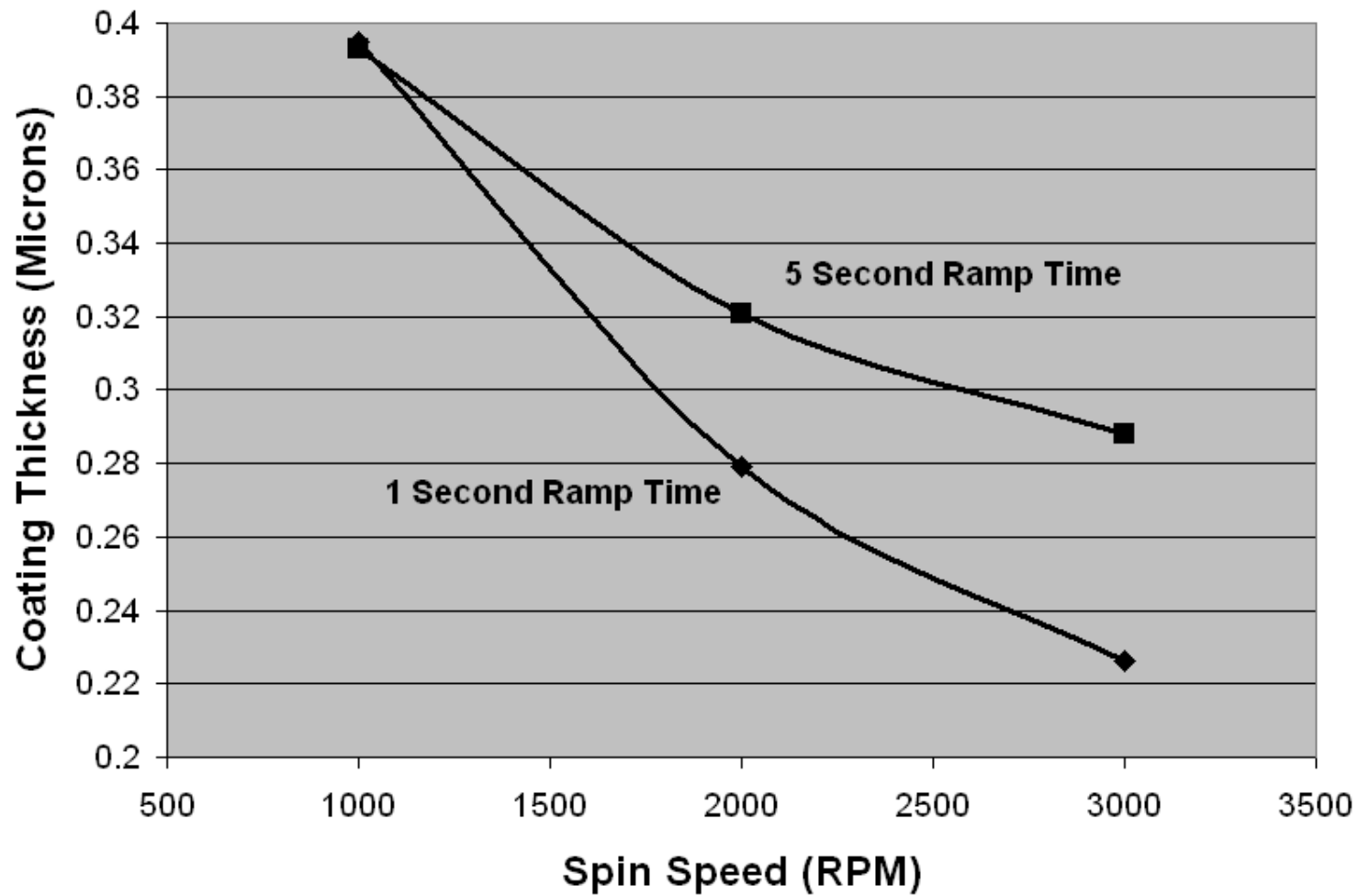
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**Figure 1:** Fluid thickness evolution with time for ethanol ramping up to a spin-speed of 2000 RPM in a period of 1 second and then holding. The fluid started at 100 microns thick at time zero and reached the cross-over point at about 1.65 seconds from the initiation of ramping.



**Figure 2:** Spin-speed at the cross-over point as a function of ramping time for ethanolic solutions. Peak spin-speeds of 1000, 2000, and 3000 RPM are shown, but if the ramping time is too long then cross-over is reached before the peak spin-speed is achieved.



**Figure 3:** Predicted final coating thickness as a function of spin-speed and ramping time. Fluid parameters for ethanol were used with 5% of the solution being coating constituents. The fitted spin-speed exponent for the 1-second ramp samples was  $-0.50$ , while the 5-second ramp samples yielded a value of  $-0.27$ .

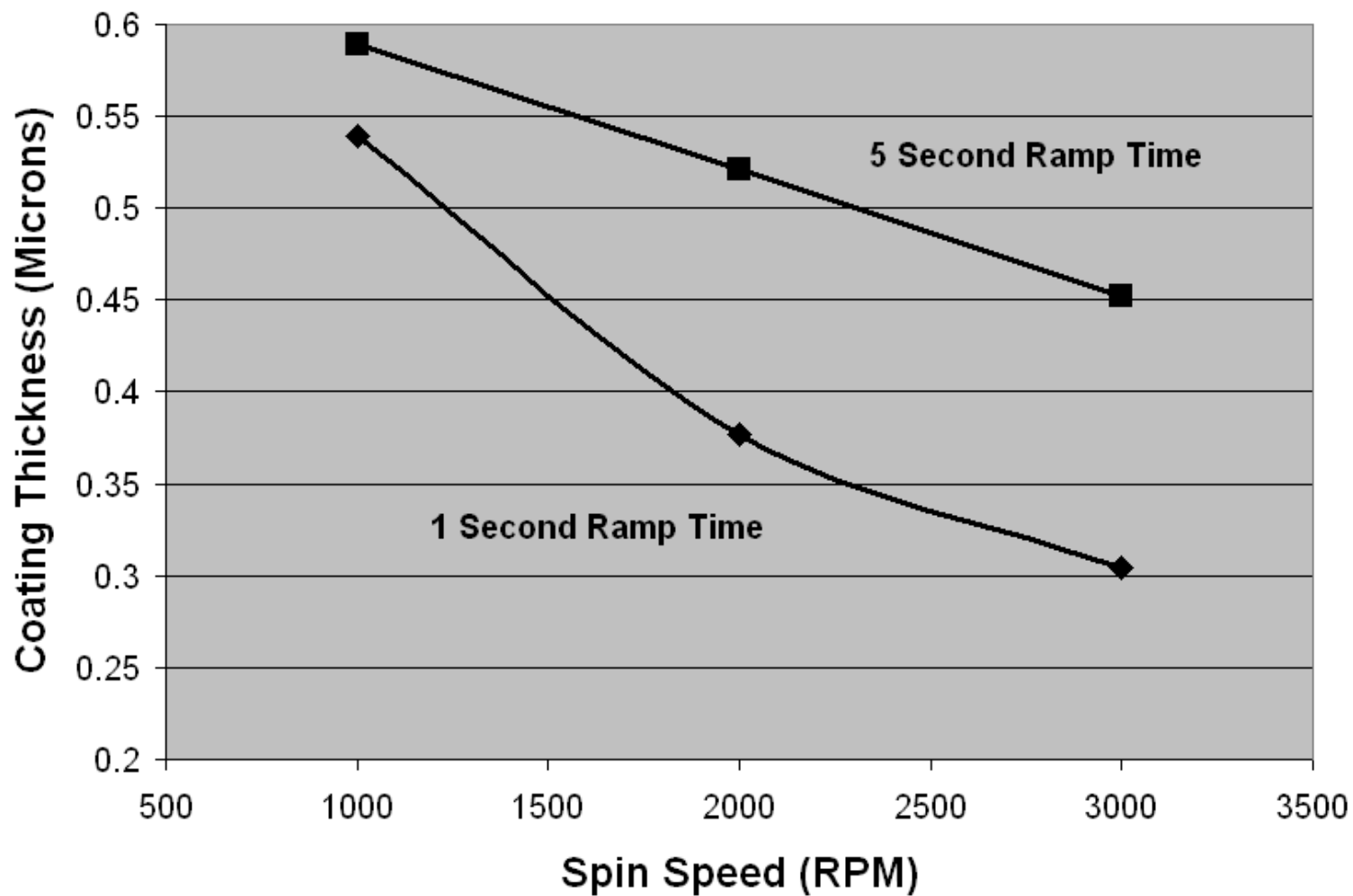


Figure 4: Measured final coating thickness as a function of spin-speed and ramping time. An ethanolic sol-gel solution was used, as described in the text. The fitted spin-speed exponent for the 1-second ramp samples was  $-0.52$ , while the 5-second ramp samples yielded a value of  $-0.23$ .