

Shear Alignment of Particles During Spin Coating

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Spin coating is a process for applying uniform coatings to a wide variety of substrates. The final film thickness depends on viscosity, drying rate, percentage of solids, and surface tension and many of these influencing factors have been investigated. Our recent research has been focused on alignment of anisotropic particles being deposited by spin coating. One key aspect of spin coating is the shear forces that are experienced by the fluid before solvent evaporation takes over and freezes in a final particle arrangement. We have calculated the shear experienced by the particles during all stages of the process and tracked the fluid flow to determine the individual particle trajectories. A small fraction of fluid that starts near the center of the wafer contributes to the final coating while the majority of the fluid is flung off. From our calculations, it is evident that the particles away from the center of the wafer are more aligned toward the flow direction due to the higher shearing effect they experienced. Less alignment of particles is found near the center of the wafer as shear is significantly lower at the center. Alignment of the particles in the final coating can be advantageous for various optical, electrical and magnetic applications.

Fluid flow on spinning wafers is usually constrained by a no-slip condition at the fluid/substrate contact and a condition at the free surface that is nearly free of shear imposed by the external airflow. If the fluid thickness is uniform and the viscosity is a constant value then relatively simple flow equations result^[1]:

$$v_r = 3K(-0.5rz^2 + rhz) \quad h = \frac{h_o}{(1 + 4Kh_o^2 t)^{0.5}} \quad K = \frac{\rho\omega^2}{3\eta}$$

where v_r is the velocity in the r direction. r is the radial position component, z is the height position component, the distance from the solid/liquid surface to the point in question. h is the instantaneous height of the fluid, h_o is the original height of the fluid. t is time. K is a constant, combining the density ρ , the viscosity η , and the spin speed ω .

If we consider the velocity gradient from the substrate to the free surface (through $v_r(z)$) then we recognize that particles that are embedded in this moving solution will experience shear – and will have the potential for shear alignment during the coating process. We have investigated the cumulative shear that individual particles will experience as they flow during a complete spinning run. We have had to include a full tracking of where the specific particle is during the process ($r(t)$, $z(t)$), within a coating of height, $h(t)$). A simple example of this tracking process is illustrated in Figure 1.

The cumulative shear is calculated according to the following equation:

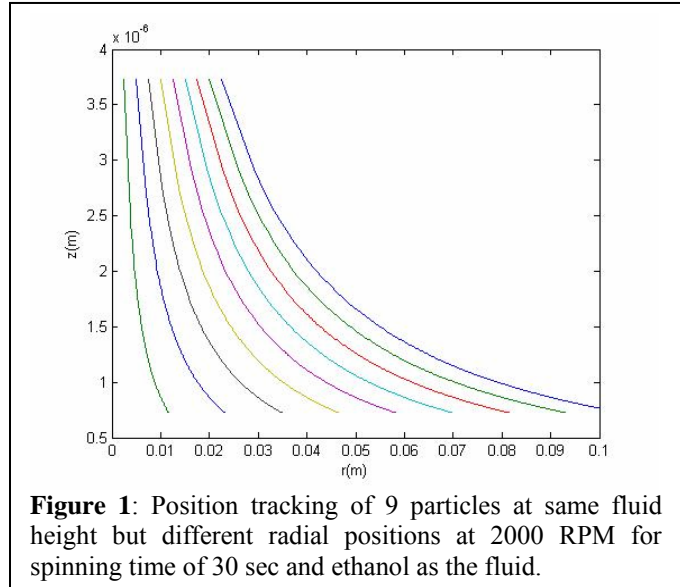


Figure 1: Position tracking of 9 particles at same fluid height but different radial positions at 2000 RPM for spinning time of 30 sec and ethanol as the fluid.

$$\int_0^{t_f} \tau_z dt = \int_0^{t_f} \left[3K(r-2z) \left(\frac{h_0}{\sqrt{1+4Kh_0^2 t}} \right) + 3Kz(z-r) \right] dt$$

where the variables have been defined above. The time is integrated from a fluid height associated with the initial dispense of fluid to the top surface of the wafer up to a point when the fluid reaches a thickness where it will start to be dried by evaporation into a static film – and thus freezing the particles into their final location. Figure 2 shows a contour map of this shear integration.

In addition to this theoretical analysis, we have synthesized micron sized ZnO rods by a hydrothermal route and used them as markers of coating flow alignment effects during spin coating. Figure 3 shows the histogram of our particle deposition process. This demonstrates that the high cumulative shear that we have calculated *does* contribute to an alignment of rod-shaped particles during the spin coating process. Because of the very high cumulative shear, we might have expected a greater amount of alignment, but the calculation doesn't account for the full 3D range of orientation effects and the full tumbling action that particles may experience during flow. Our experiments also show that there is a marked radial increase in alignment of the rods as we move further from the center of the wafer. This is also consistent with the calculation showing higher shear at larger radius values.

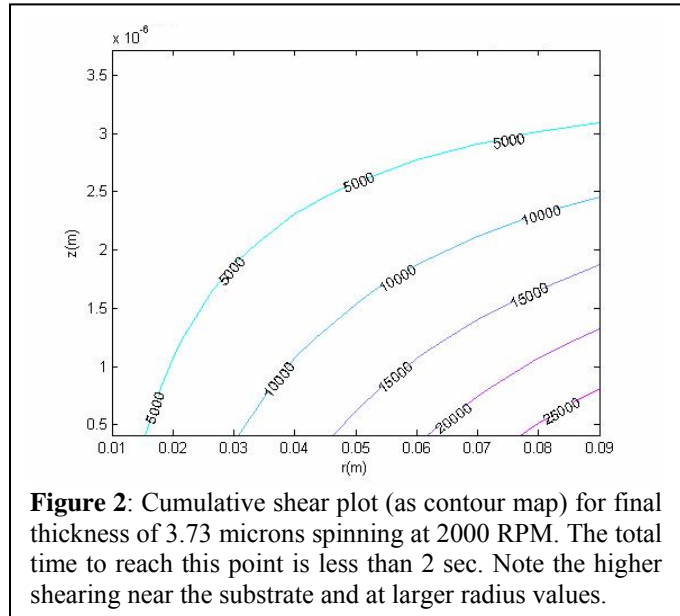


Figure 2: Cumulative shear plot (as contour map) for final thickness of 3.73 microns spinning at 2000 RPM. The total time to reach this point is less than 2 sec. Note the higher shearing near the substrate and at larger radius values.

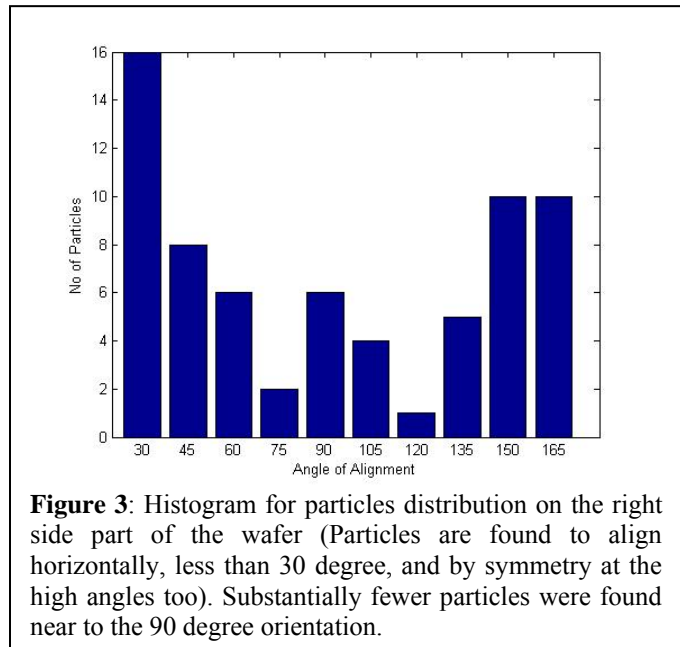


Figure 3: Histogram for particles distribution on the right side part of the wafer (Particles are found to align horizontally, less than 30 degree, and by symmetry at the high angles too). Substantially fewer particles were found near to the 90 degree orientation.

¹ A.G.Emslie, F.T. Bonner & C.G. Peck. “Flow of a Viscous Liquid on a Rotating Disk,” *J. Appl. Phys.* **29** [5] 858-62 (1958)

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