VOC Emissions Reduction from Photolithographic Processes

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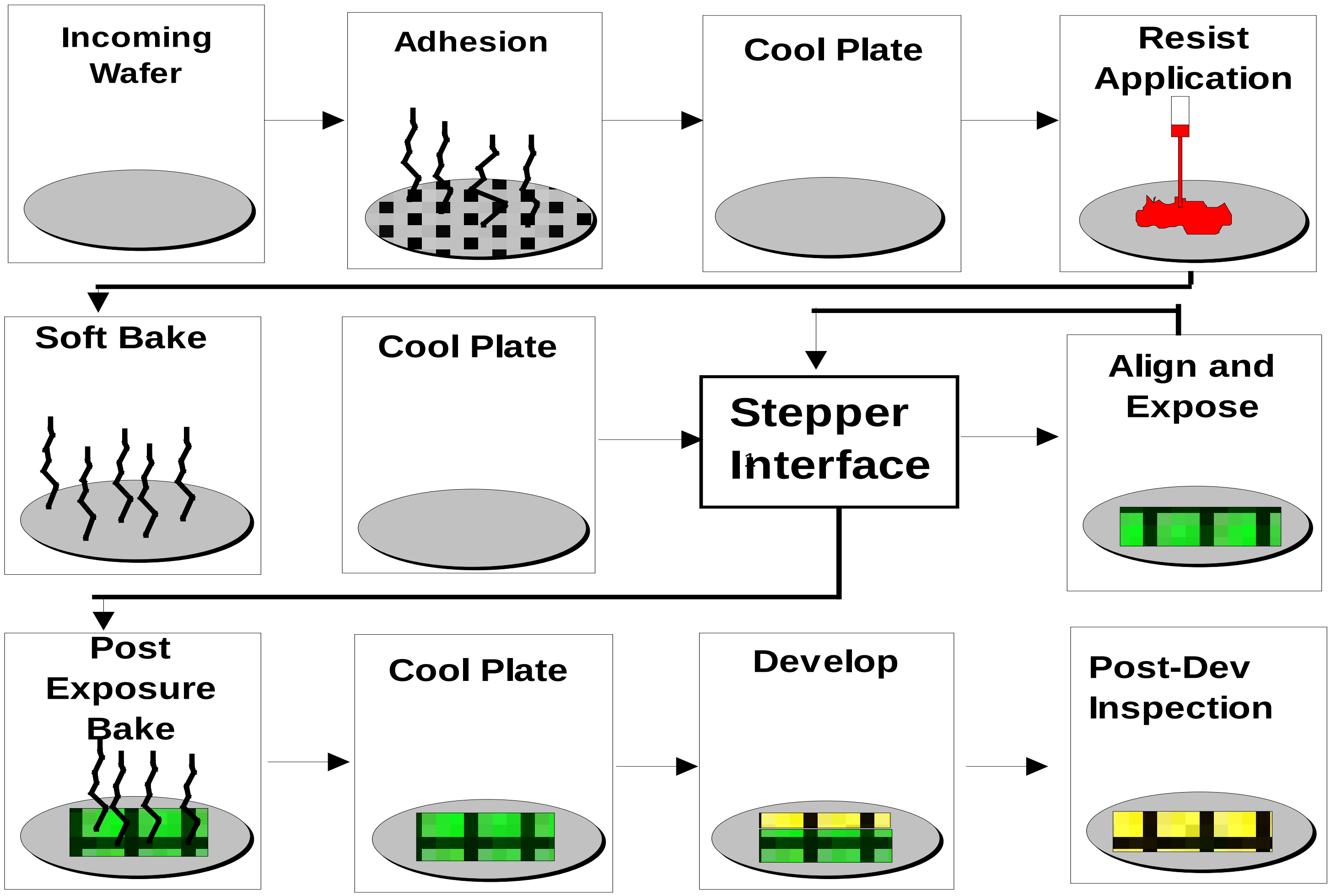
Photolithography

- Application and development of photoresist with the use of light and heat to write a pattern of microstructures on a wafer

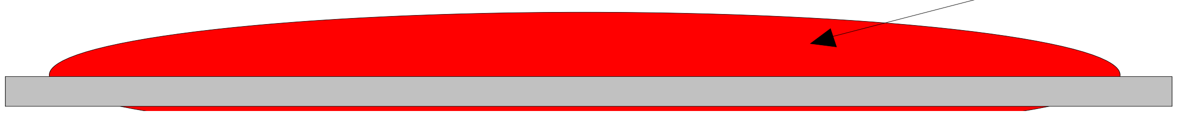
- Photoresist
  - Protective material used to form a resistant film on the wafer surface
  - Reacts chemically with areas exposed (not covered by a patterned mask) to become more or less soluble with respect to a solvent

Basic Photo Process Steps

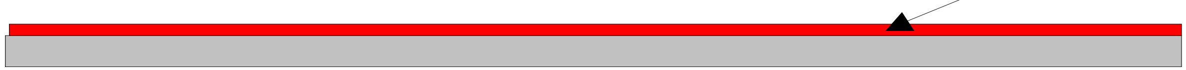


Spin-Coat Resist Usage/Waste

~ 5 ml Dispense on 200 mm Dia Wafer



1 - 2 Microns Thick
+/- 0.01 Microns



Initial Wet Volume: ~ 5 ml
Final Wet Volume: ~ .06 ml
Approx 99% Waste

Chemical Usage in the Photolithography Process

- Standard photoresist chemicals
  - Resin (*e.g. Cresol-formaldehyde {Novolac})*
  - Solvents
    - Ethyl lactate (EL) (b.p 154C)
    - Ethyl 3-ethoxypropionate (EEP)
    - Cellosolve Acetate
  - Photo-active Compounds
- Developer
- Edge Bead Remover
- Solvents

Strategies for Reducing VOC Emissions

- Switch to Water-Based Resists
  - Advantage: no VOC emissions
  - Disadvantage: line width resolution, “speed”

- Optimize Use of Current Solvent-Based Resists
  - Advantage: utilize current formulations, equipment
  - Disadvantage: no hope for eliminating VOC emissions

Benefits to Minimizing Resist Usage

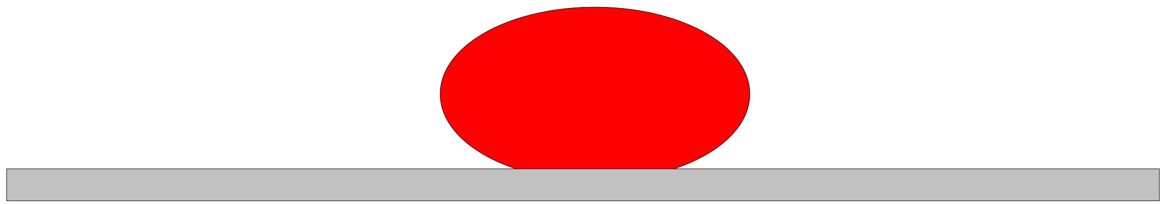
- Resist cost (~$500/gallon)
- Environmental Impact
  - Most of the Resist is "wasted", in the sense that it is spun off the wafer. The high "waste" is required to achieve uniformity in thickness and proper coverage.
  - Because of precise resist formulations, solvent evaporation during spinning, and contamination concerns, it is impossible to recycle resist that is spun from the wafer.
  - Typically, Organic Solvents are used to clean the photoresist "cups" into which the excess resist is spun. Less solvent usage leads to less emissions of Volatile Organic Compounds (VOCs).

Photoresist Dispense Optimization

- Objective
  - Coverage of given thickness
  - Coverage of given uniformity
- Control Variable(s)
  - Resist properties (viscosity, solvent mass fraction, *amount dispensed*)
  - Spin speed
  - Spin recipe
  - Temperature, RH

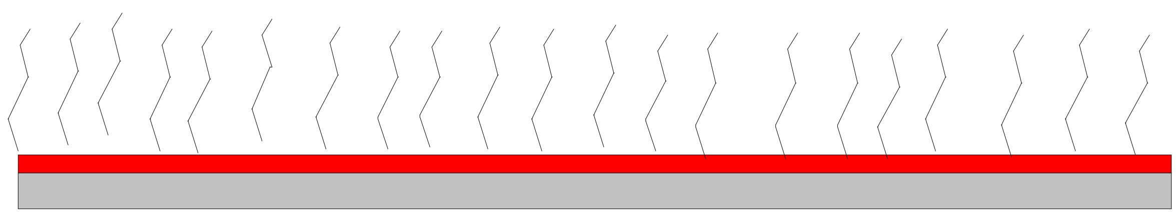
Three Steps to Coating Process

Surface Tension



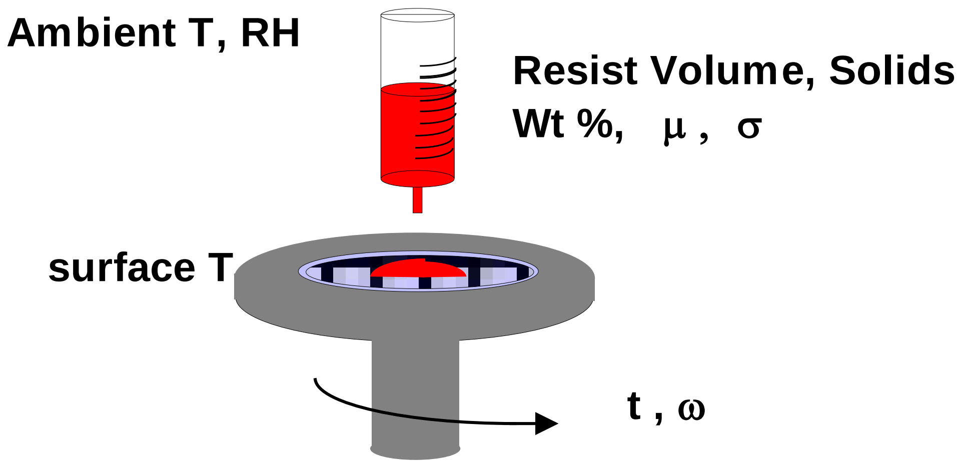
Viscosity

Solvent Evaporation



Spin-Coat Operating Parameters

- Spin Speed (rpm)
- Spin Time (sec)
- Surface Temperature
- Room Temperature
- Room Humidity
- Resist Volume
- Resist Viscosity
- Resist Solid Mass Fraction



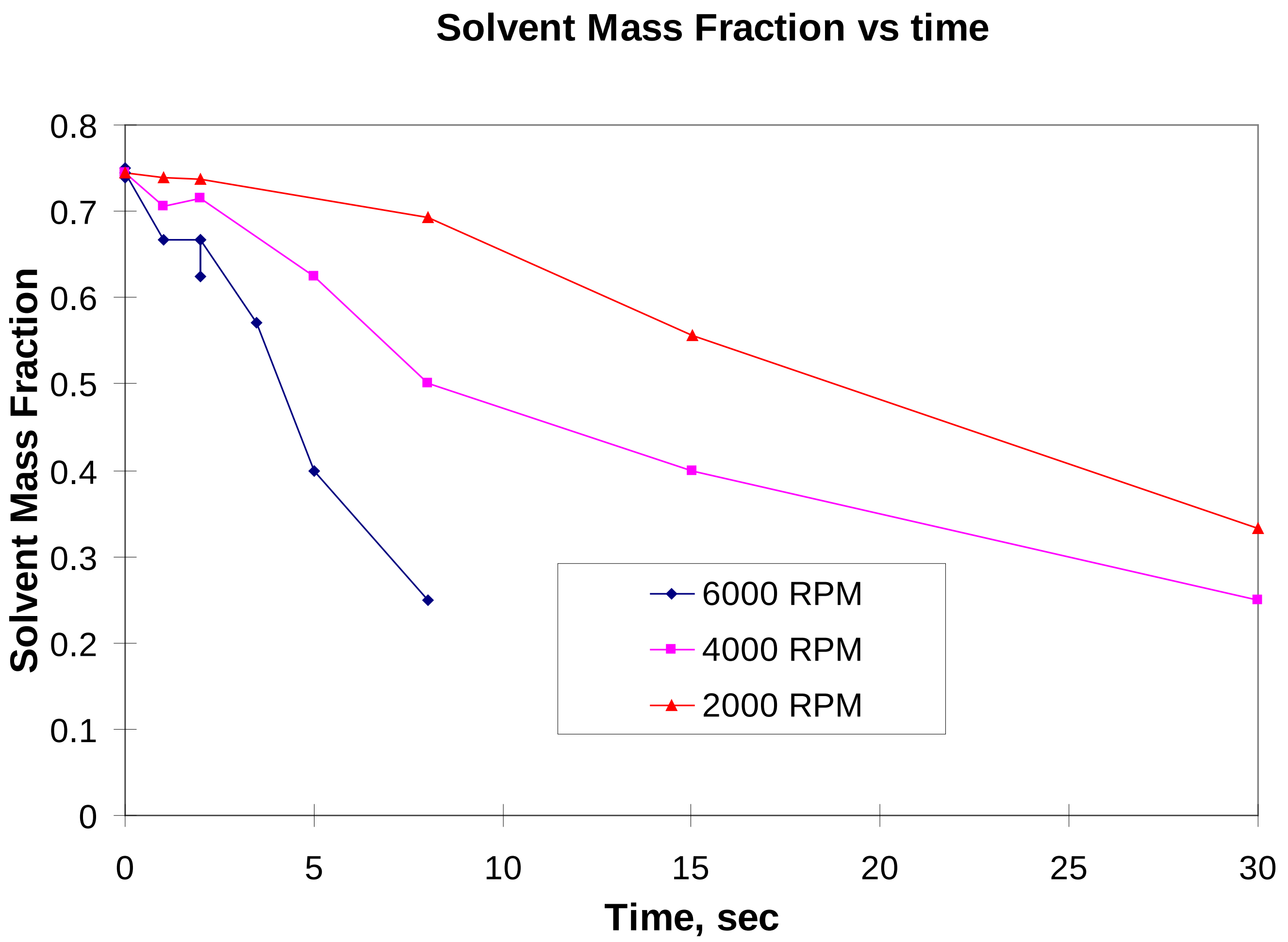
Properties of Photoresist

- Initial Viscosity: 5 to 100 cP
- Solvent Mass Fraction (SMF): 70-90%
- Photoresist viscosity for the experiments presented:
  - 560 Resist - 17 cP
  - 500 Resist - 40 cP
- Typical Viscosity Changes: 0.01 to 10,000 Poise as SMF goes from 1.0 to 0.0
- Typical Diffusivity Changes: 10^{-6} to 10^{-12} cm^2/sec as SMF goes from 1.0 to 0.0

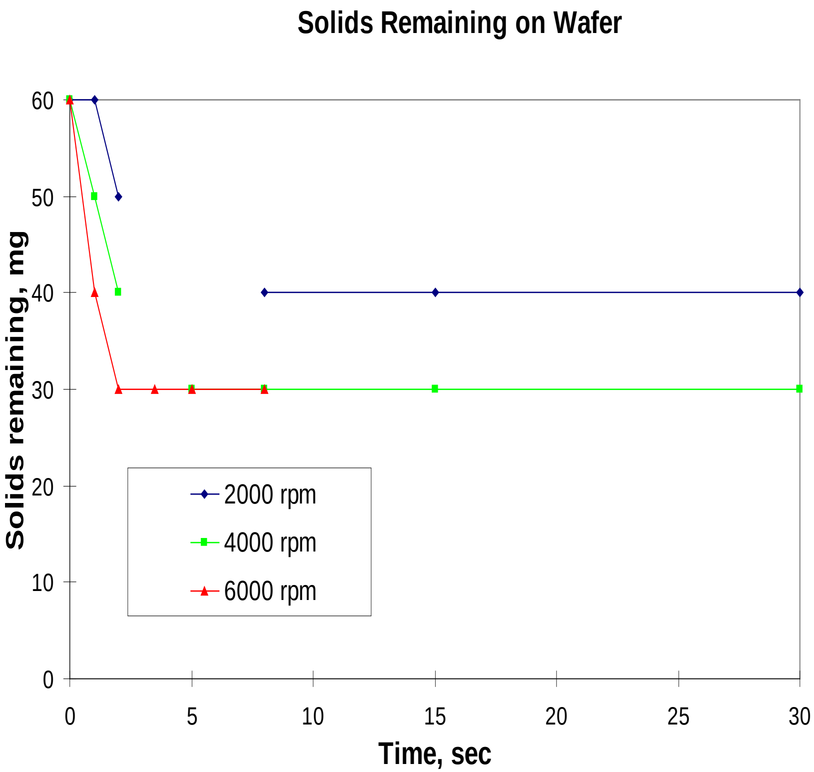
Coating Process Overview

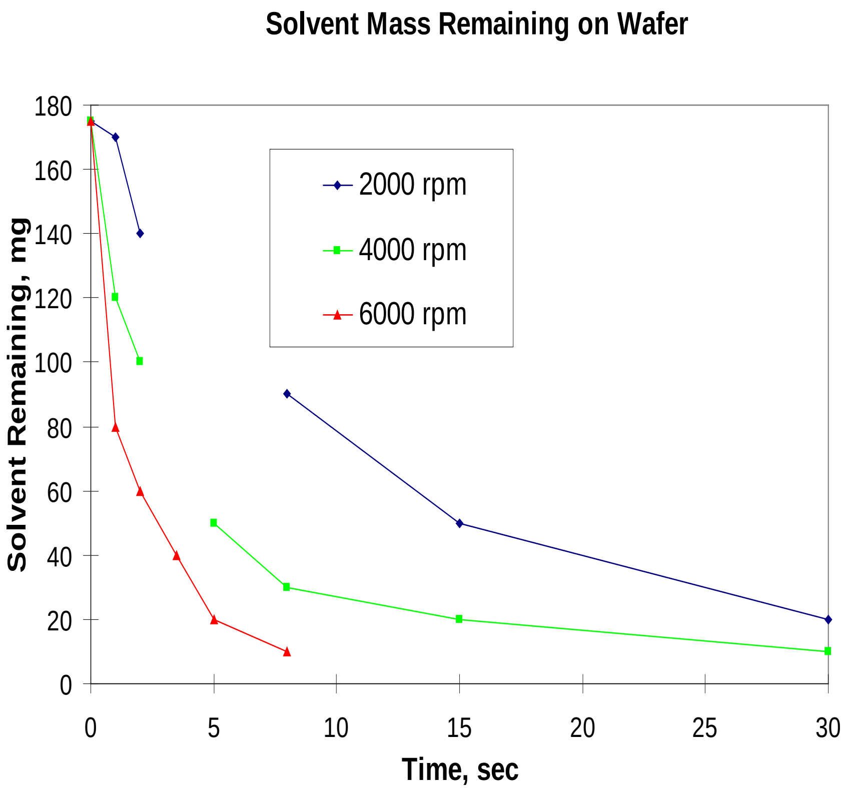
- Current Practice
  - At slow speed (usually ~2000 rpm) dispense 3-5 cc resist and spin for less than 2 seconds
  - Ramp up speed (~3000 rpm) and spin for 20-30 seconds
  - Apply Edge Bead Remover
  - Fraction Resist "spun off": typically 97-99%
- Ultra Casting Pre-dispense (UCP)
  - At very high speed (6000 rpm) dispense 1 cc resist and spin for 1 second
  - Decelerate to 2000 rpm and apply second dispense of 1 cc
  - Accelerate to 3000 rpm and spin for 20-30 seconds
  - Apply Edge Bead Remover
  - Fraction Resist "spin off": typically 95-97%

How Fast Does the Solvent Evaporate?

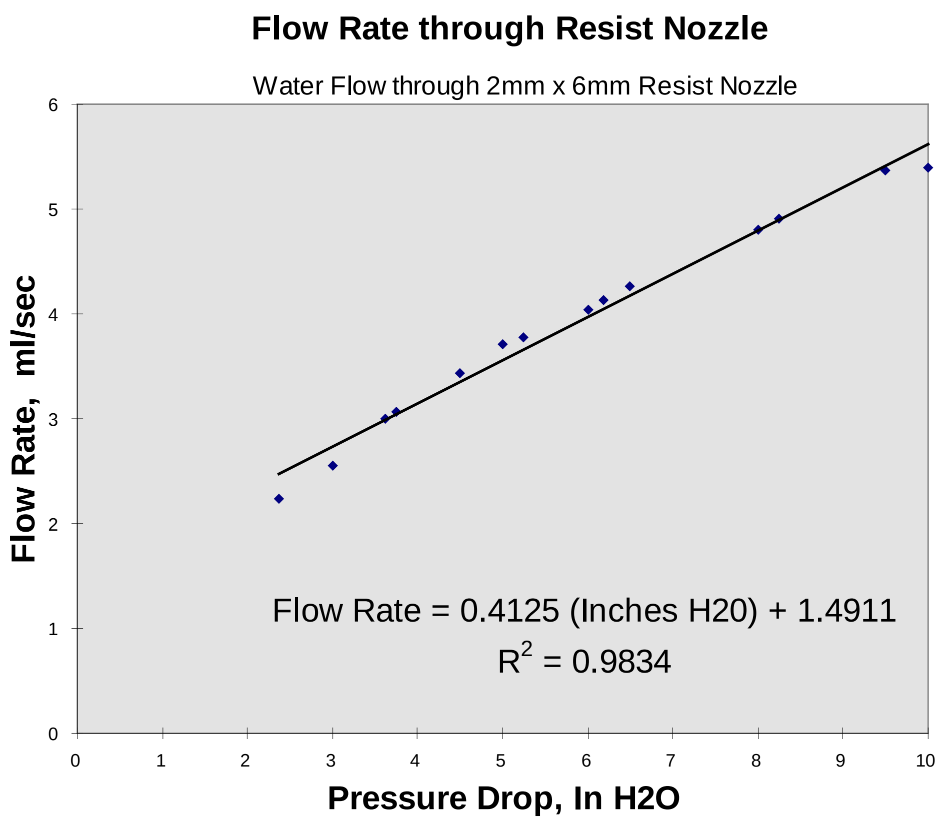


Solid and Solvent Mass Remaining on Wafer

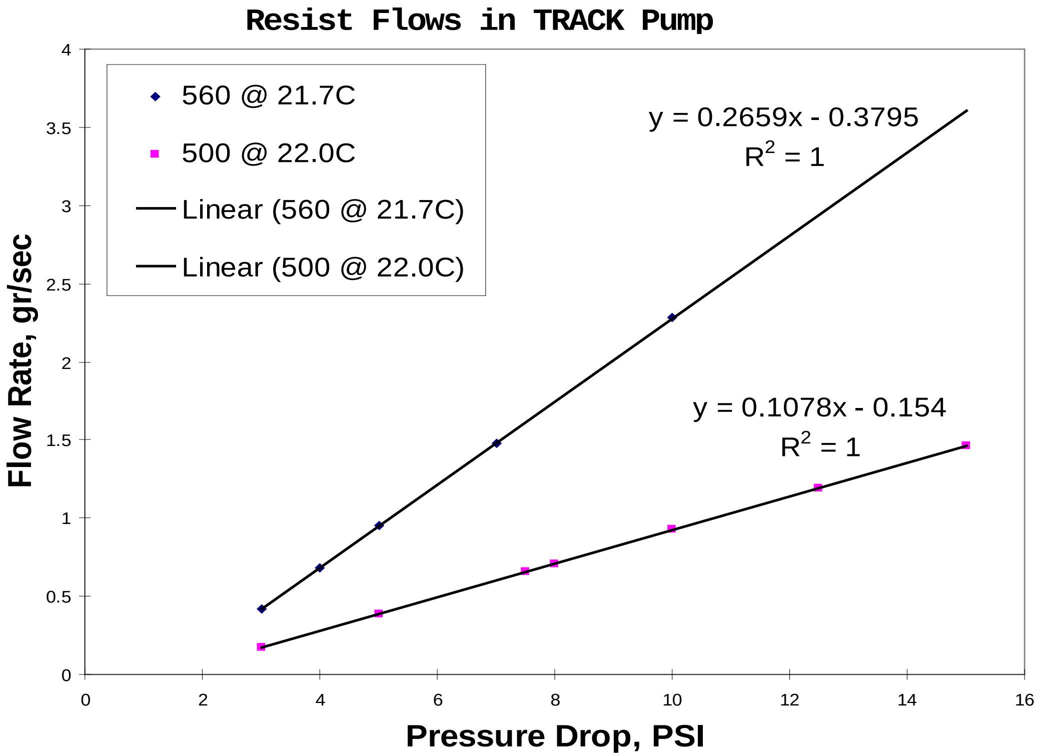




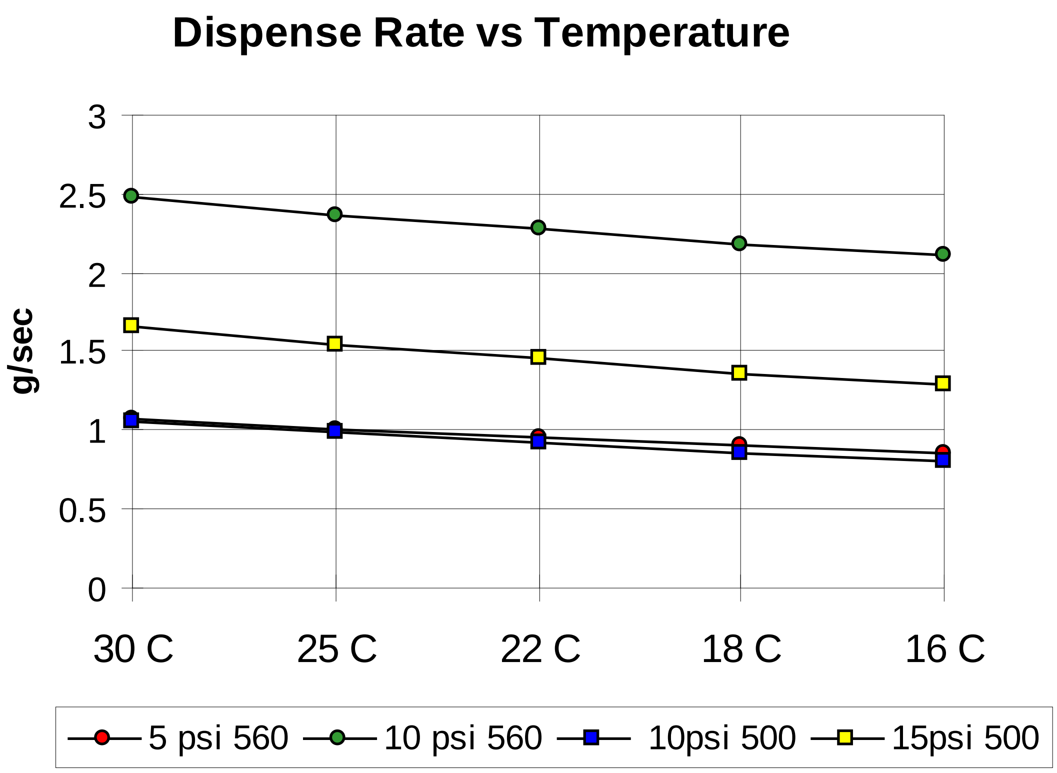
Flow Characteristics: Resist Dispense Nozzle



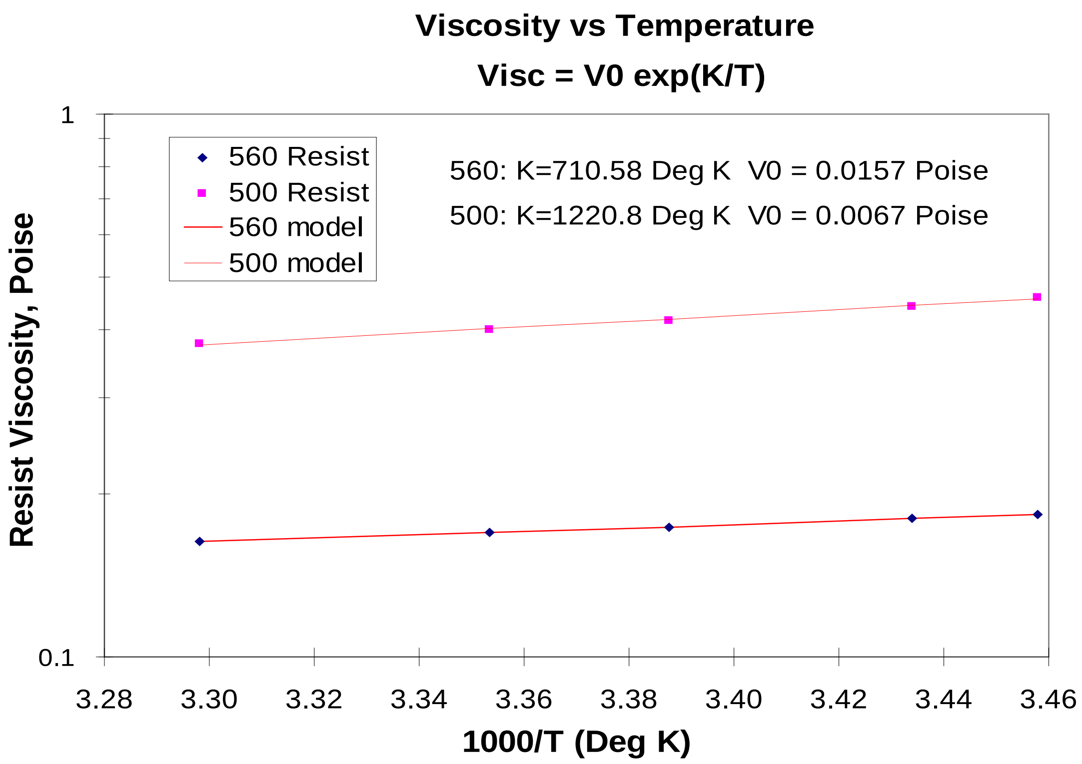
Resist Flows vs. Pressure Drop in TRACK Pump



Dispense Rate vs. Temperature



Temperature Dependence of Resist Viscosity



Theory of Spin Coating

Conservation of solvent

$$\frac{\partial x_A}{\partial t} + \frac{\partial x_A}{\partial z} - \frac{\partial}{\partial z}(D(x_A)\frac{\partial x_A}{\partial z}) = 0$$

Radial momentum/continuity

$$\int_0^z \frac{2\rho\omega^2(h-z')}{\eta[x_A(z',t)]}dz' + \frac{\partial w}{\partial z} = 0$$

where

x_A mass fraction of solvent in resist

D Diffusivity of solvent

ρ density of resist

ω spin speed

h resist thickness

η viscosity of resist

Boundary Conditions

$$(\frac{1}{1-x_A})D(x_A)\frac{\partial x_A}{\partial z} + k(x_A - x_{A\infty}) = 0 \quad \text{at } z = h$$

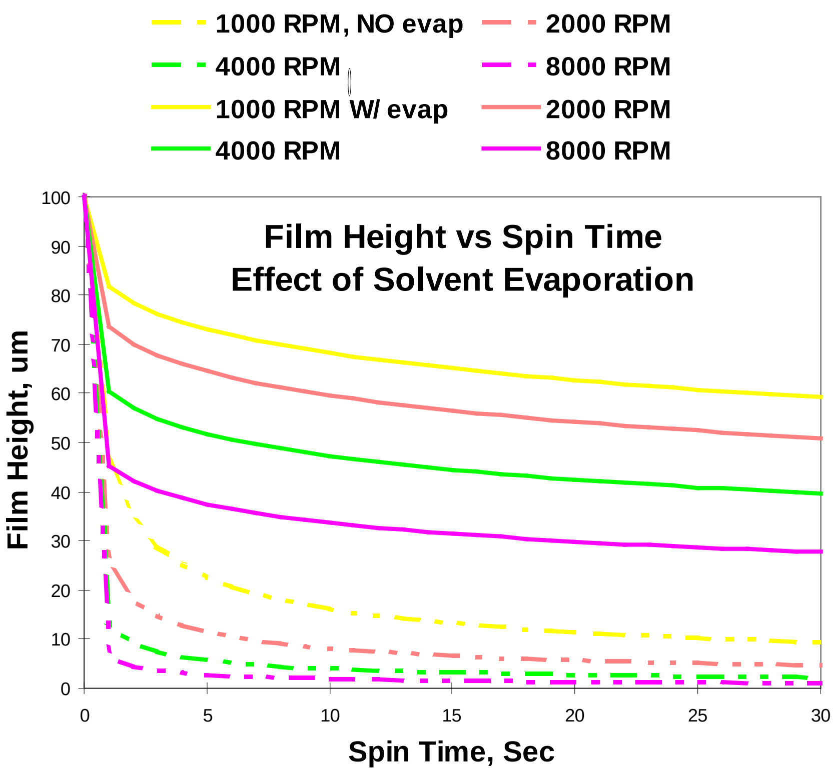
$$w = 0 \quad and \quad \frac{\partial x_A}{\partial z} = 0 \quad \text{at } z = 0$$

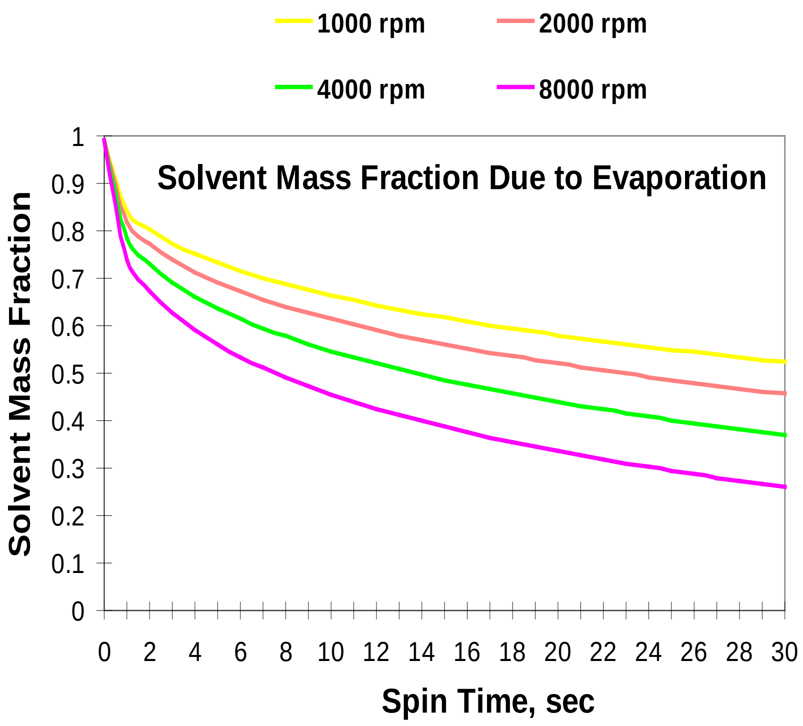
$$\frac{dh}{dt} - w(z=h) + k(x_A(z=h) - x_{A\infty}) = 0$$

Can show theoretically that

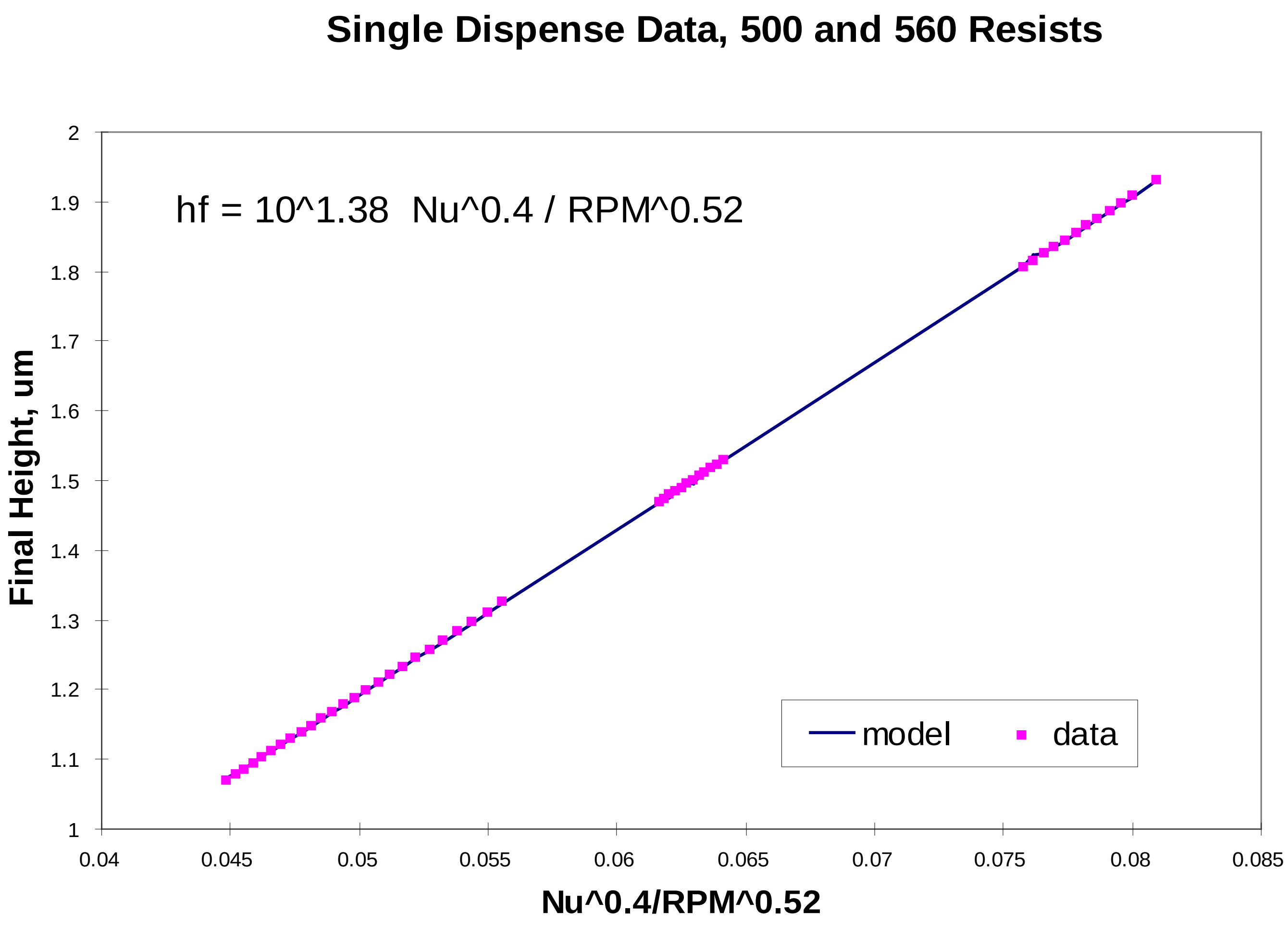
$$h = h(\omega, \eta) = K\,\eta^{0.25}/\omega^{1/2}$$

Effect of Evaporation on Film Height During Spinning

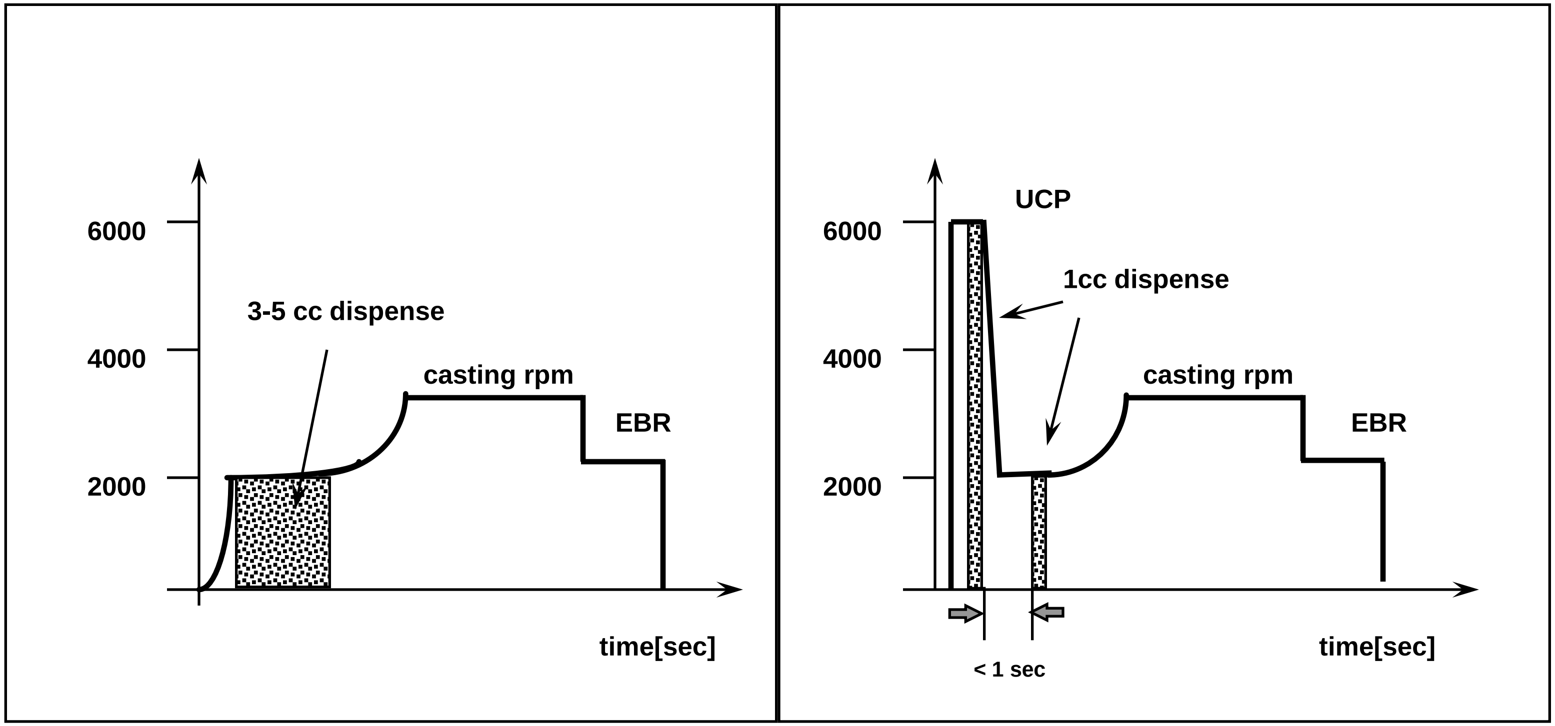




Final Film Thickness: Single Dispense



Ultra Casting Predispense Technique

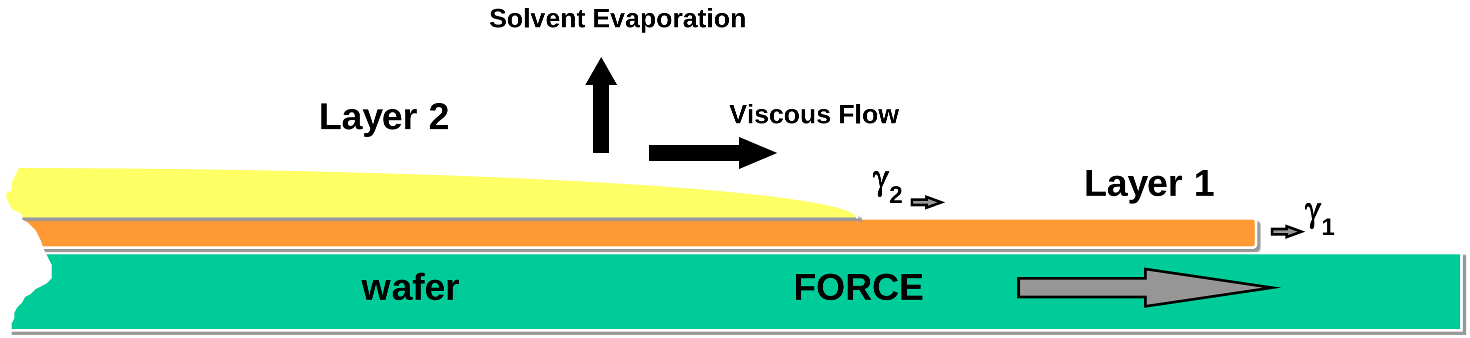


conventional dispense

UCP dispense

Note: All dispenses achieve complete coverage of the wafer with coating solution (Resist) ; the process that forms the final thickness and uniformity is at the same rpm in both cases !

UCP Resist Coating - 2 Layer Model

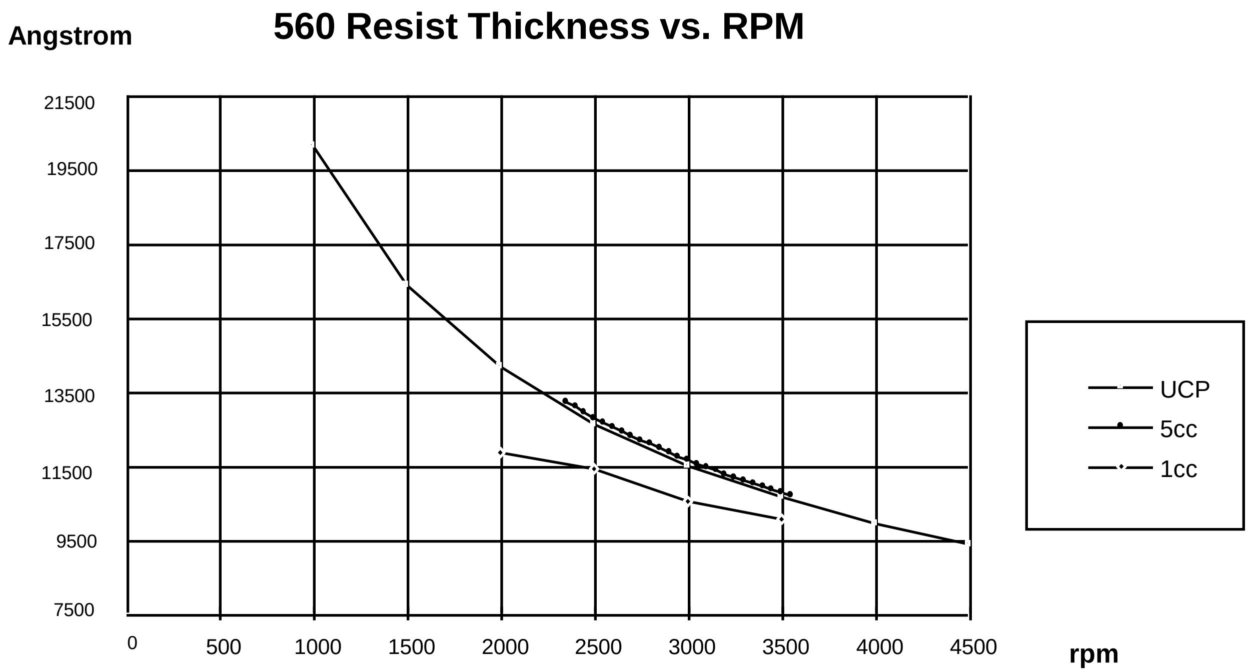


$\gamma_2 <<< \gamma_1$

Step 1: (1cc) **Overcome surface tension**
Use radial force (ultra casting rpm, 5000-6000 rpm)
Create interface

Step 2: (1cc) **Dispense at or below casting rpm,**
Minimal resist needed because very little resistance from surface tension

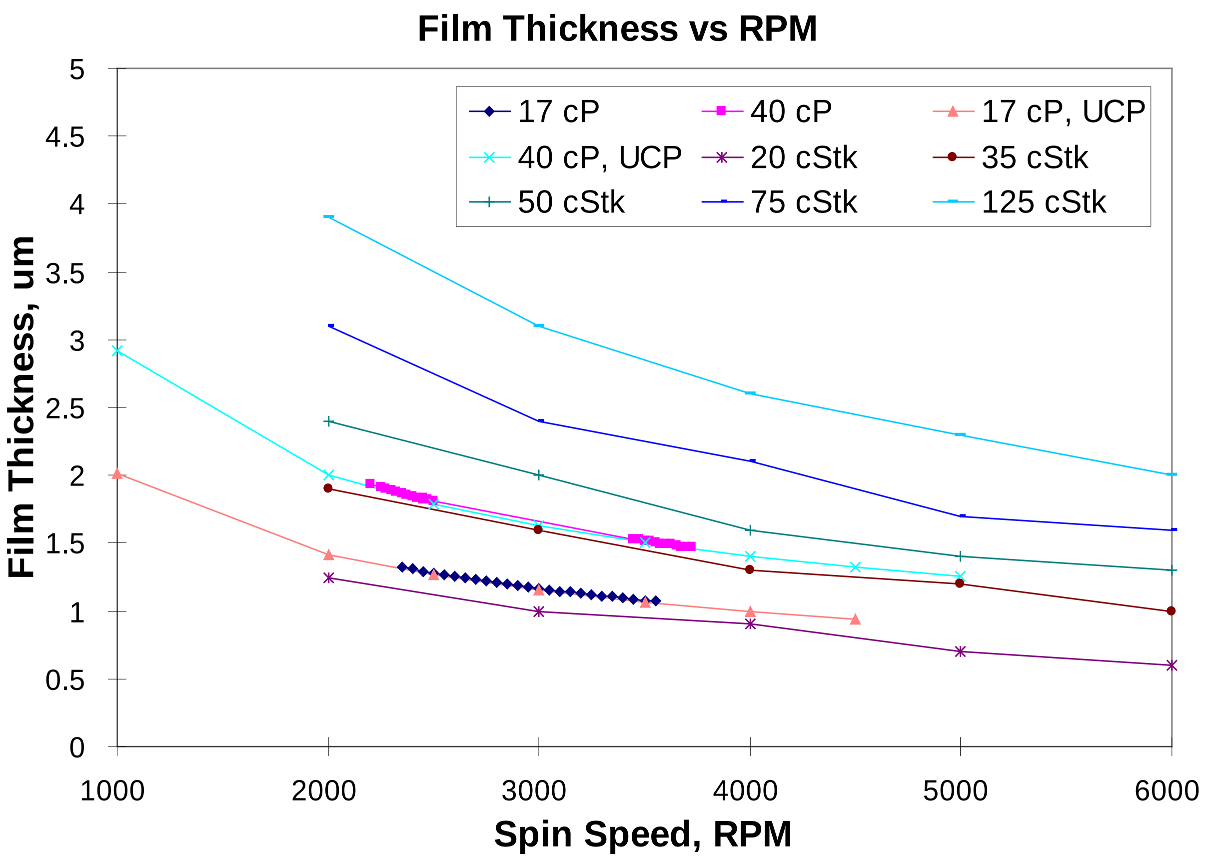
Resist Thickness vs. RPM



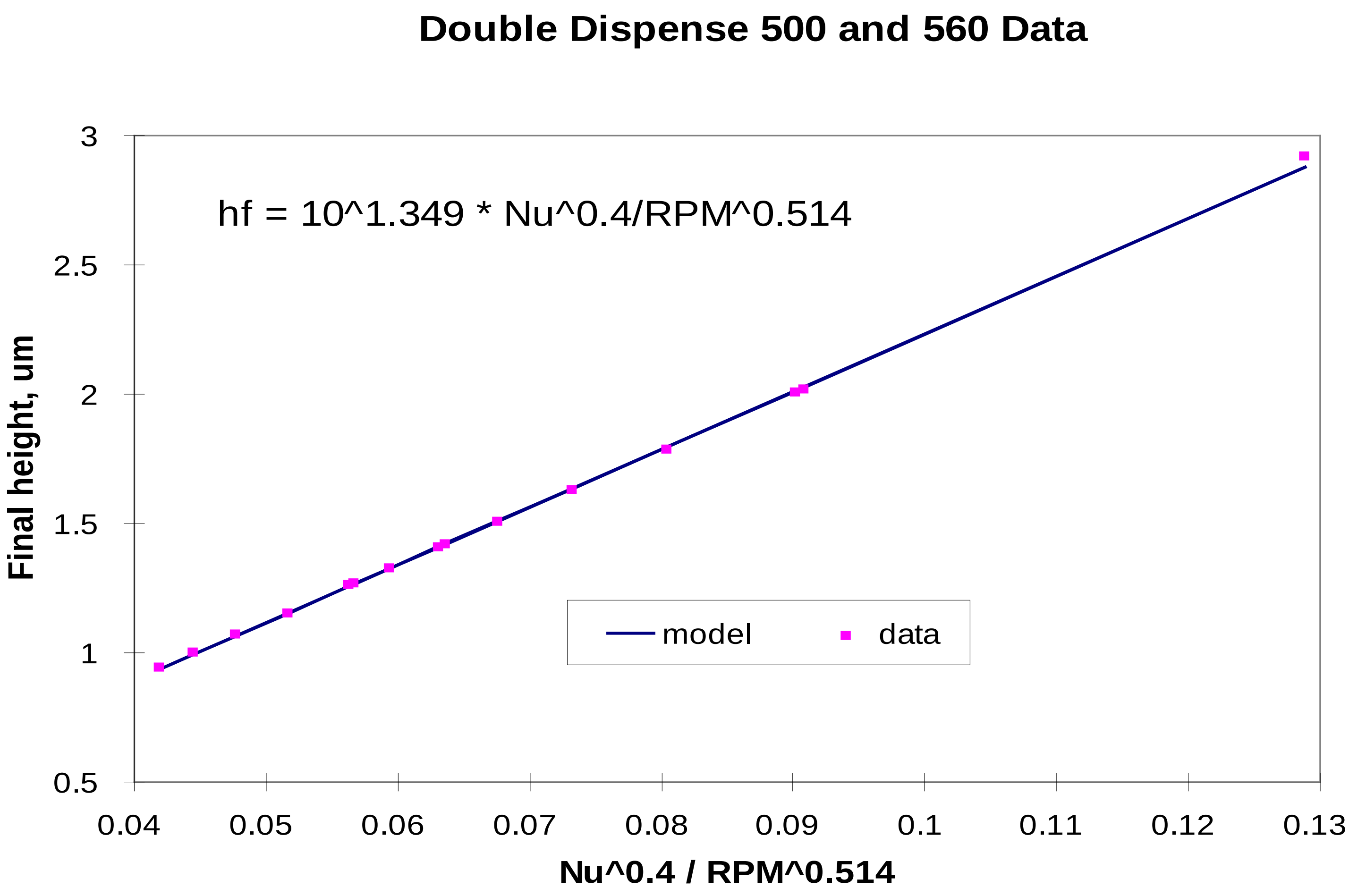
*** Once surface is wetted, only a small additional amount is needed to built thickness.**

*** Key concept: initial wetting at ultra casting rpm, second dispense at or below casting**

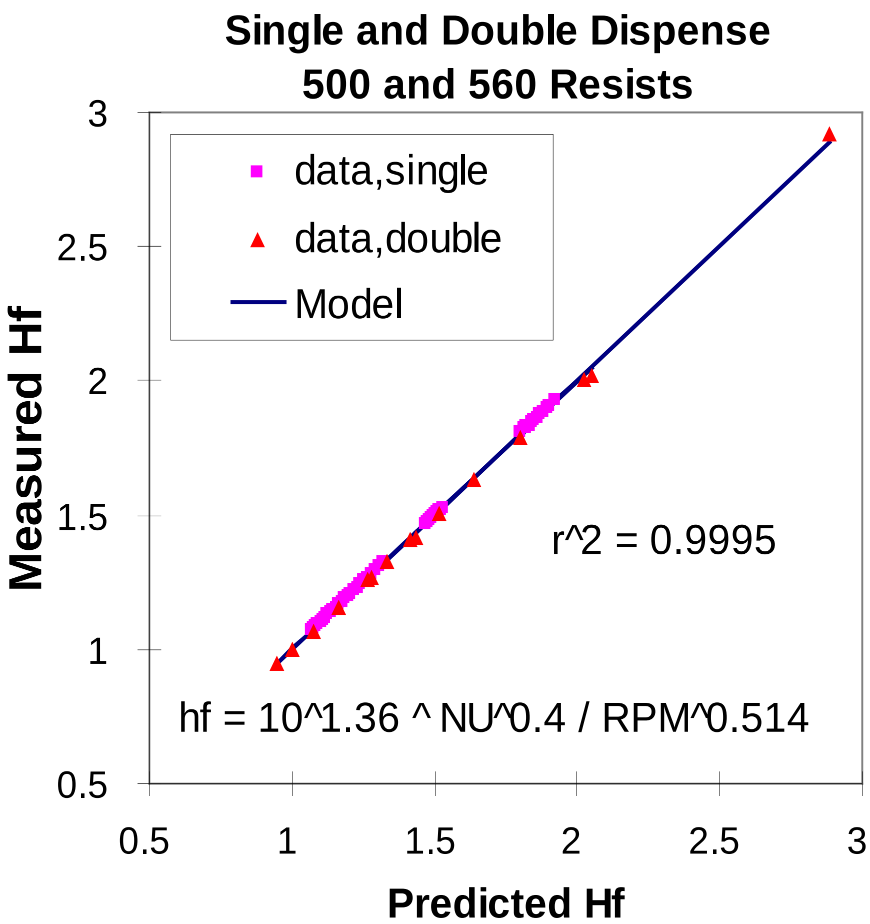
Resist Thickness vs. RPM
ALL DATA

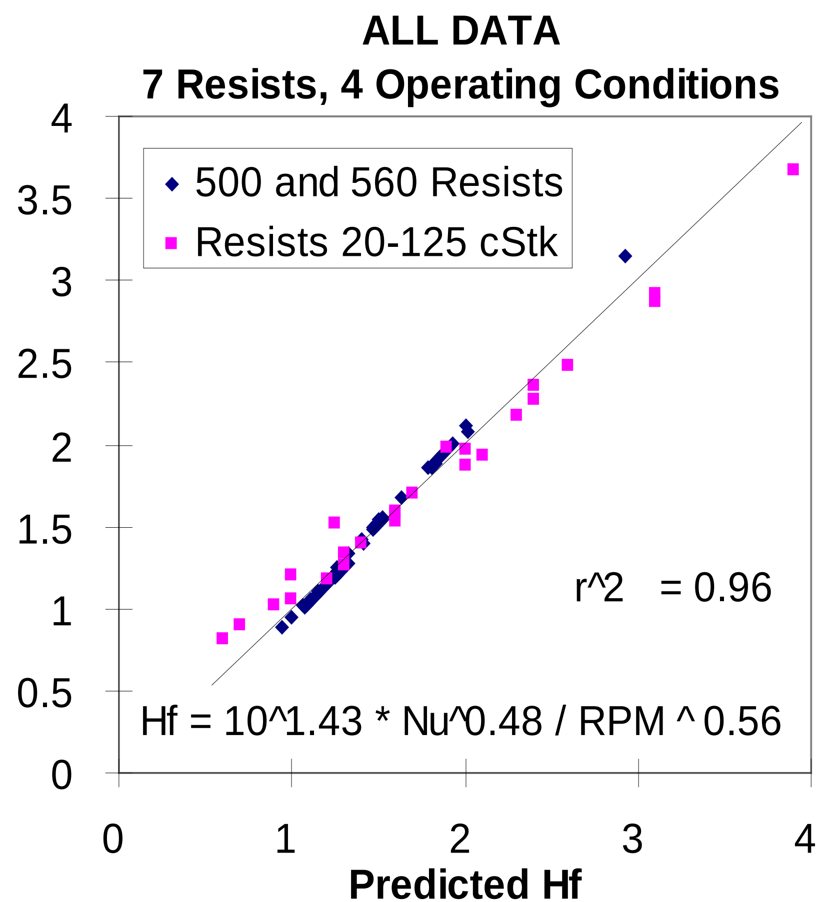


Final Film Thickness: Double Dispense Data



Final Height:
Single and Double Dispense





Conclusions

- Resist usage:
  - ~5ml for single dispense
  - ~2ml for UCP method
- Resist thickness and uniformity: identical for both methods
- Comparison to theoretical models: identical for both methods; slightly stronger viscosity dependence than predicted theoretically
- Resist and solvent usage reduction yields substantial reduction in VOC emissions

Acknowledgments

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  - Tom Roche
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