UNIT OPERATIONS FOR SMART NANOMANUFACTURING

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U.S. MANUFACTURING CRISIS

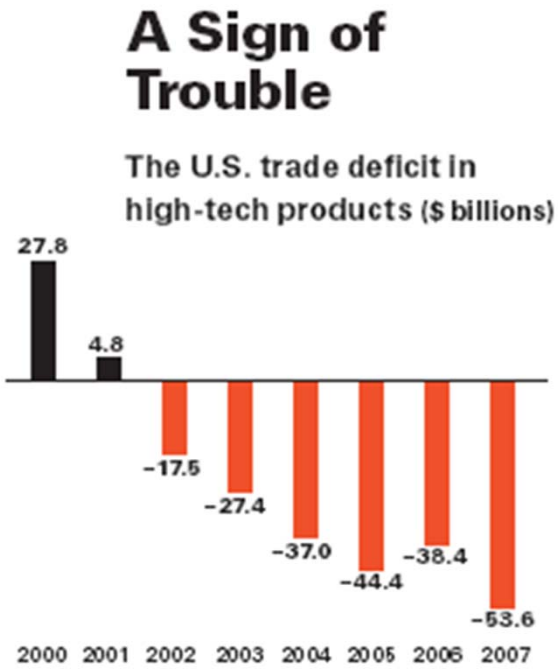
- In 2007 the Manufacturing Sector was 11.7% of US GDP and declining.

- Employment in the sector has dropped over 16% since 2000.

- The trade balance in the high-tech products has become negative since 2002.

- Outsourcing has reduced US ability to manufacture high tech products and eroded its industrial commons.

- Industrial commons needed for innovation and creation of new industries.



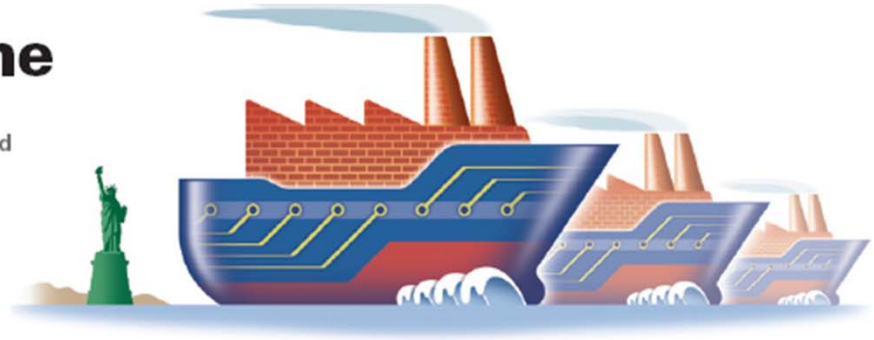
Pisano & Shih, HBR 2009

Designed in U.S. Made in China, S. Korea and Taiwan

MORE REASON FOR CONCERN…

Going…Going…Gone

Many high-tech products can no longer be manufactured in the United States because critical knowledge, skills, and suppliers of advanced materials, tools, production equipment, and components have been lost through outsourcing. Many other products are on the verge of the same fate.



Semiconductors

ALREADY LOST

"Fabless" chips

AT RISK

DRAMs

Flash memory chips

Lighting

ALREADY LOST

Compact fluorescent lighting

AT RISK

LEDs for solid-state lighting, signs, indicators, and backlights

Electronic displays

ALREADY LOST

LCDs for monitors, TVs, and handheld devices like mobile phones

Electrophoretic displays for Amazon's Kindle e-reader and electronic signs

AT RISK

Next-generation "electronic paper" displays for portable devices like e-readers, retail signs, and advertising displays

Energy storage and green energy production

ALREADY LOST

Lithium-ion, lithium polymer, and NiMH batteries for cell phones, portable consumer electronics, laptops, and power tools

Advanced rechargeable batteries (NiMH, Li-ion) for hybrid vehicles

Crystalline and polycrystalline silicon solar cells, inverters, and power semiconductors for solar panels

AT RISK

Thin-film solar cells (the newest solar-power technology)

Computing and communications

ALREADY LOST

Desktop, notebook, and netbook PCs

Low-end servers

Hard disk drives

Consumer-networking gear such as routers, access points, and home set-top boxes

AT RISK

Blade servers, midrange servers

Mobile handsets

Optical-communication components

Core network equipment

Advanced materials

ALREADY LOST

Advanced composites used in sporting goods and other consumer gear

Advanced ceramics

Integrated circuit packaging

AT RISK

Carbon composite components for aerospace and wind energy applications

Pisano & Shih, HBR 2009

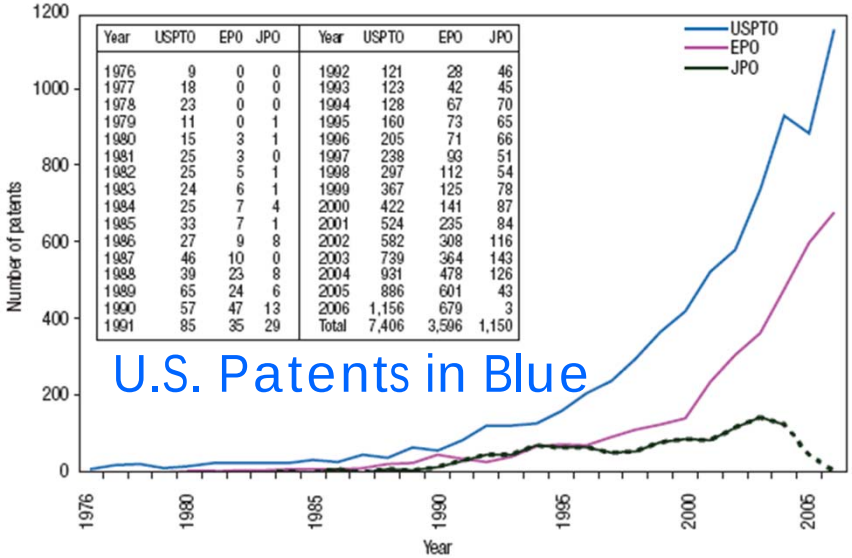
NANOMANUFACTURING – AN OPPORTUNITY

- Build on US expertise and success in nanoscience.

- Reinvigorate US manufacturing.

- Reverse trend in high-tech product trade deficit by impacting computing, communications, semiconductors, solid state lighting, electronic displays, energy storage, biomedical applications and solar cells.

- But the time to act is now.



Year	USPTO	EPO	JPO	Year	USPTO	EPO	JPO
1976	9	0	0	1992	121	28	46
1977	18	0	0	1993	123	42	45
1978	23	0	0	1994	128	67	70
1979	11	0	1	1995	160	73	65
1980	15	3	1	1996	205	71	66
1981	25	3	0	1997	238	93	51
1982	25	5	1	1998	297	112	54
1983	24	6	1	1999	367	125	78
1984	25	7	4	2000	422	141	87
1985	33	7	1	2001	524	235	84
1986	27	9	8	2002	582	308	116
1987	46	10	0	2003	739	364	143
1988	39	23	8	2004	931	478	126
1989	65	24	6	2005	886	601	43
1990	57	47	13	2006	1,156	679	3
1991	85	35	29	Total	7,406	3,596	1,150

Chen *et al.* Nature Nanotech. 2008

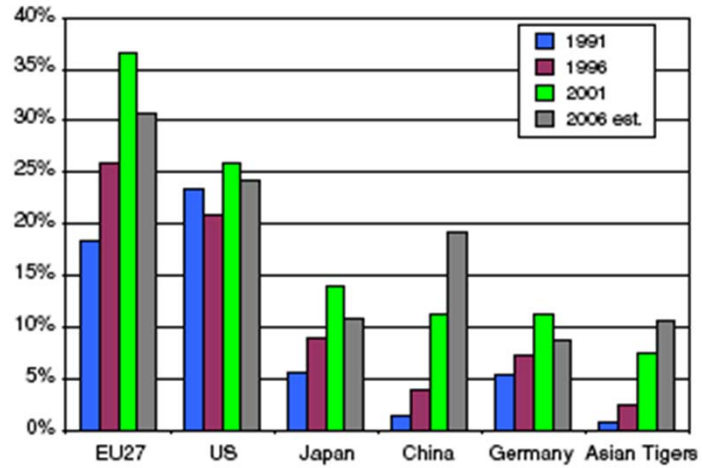


Fig. 2 Percentage of annual Nanotechnology publications by Country/Country Bloc for selected years. Source: See Fig. 1

Youtie *et al.* J. Nanopart. Res. 2008

WHAT IS NANOMANUFACTURING?

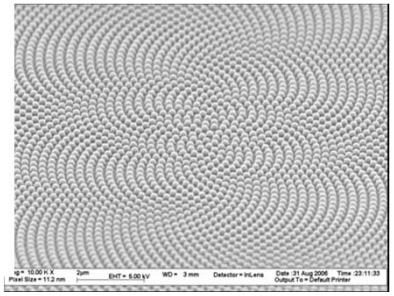
- The bridge between the discoveries in the nanosciences and real-world nanotechnology-enabled products.

- It encompasses bottom-up assembly, top-down high resolution processing, molecular systems engineering, and hierarchical integration with macro-scale systems.

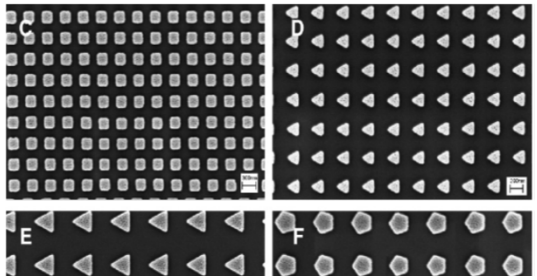
- The commercially successful manufacture of materials/products with nanoscale (1-100 nm) components.
  - Microelectronics industry is already there and often provides foundation/driver for these efforts

POTENTIAL USEFUL PRODUCTS

Photonics for LEDs



Nanoscale Drug Carriers



High Speed Roll to Roll Coating

Photovoltaics

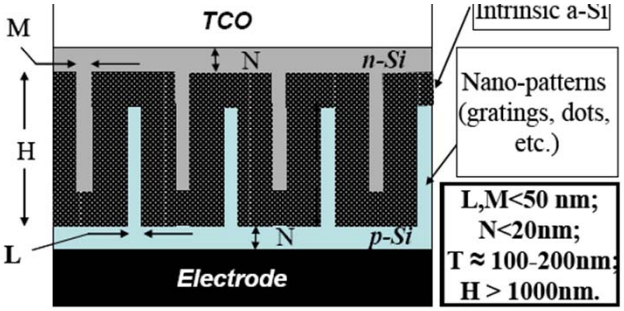
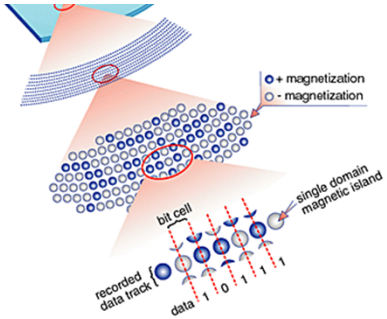


Figure 3: Proposed (NP) a-Si solar cell

Konarka



Hitachi Global Storage Technologies

THE SIMULATION CHALLENGE

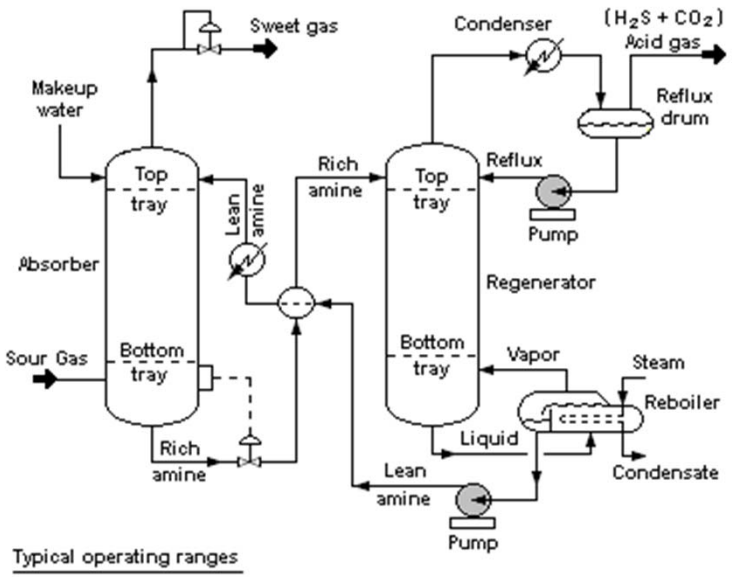
- Bridge the chasm between promising nano-technological advances at the laboratory scale and commercially viable nanomanufacturing.

- Aid the design and optimization with models and simulations of the unit operations of nanomanufacturing.
  - Production rate, defectivity

- Mitigate risk in transforming a promising lab result to a viable manufacturing process in the early stages by modeling the system.

- Use knowledge to create a vibrant nanomanufacturing sector in the US and rebuild the industrial commons

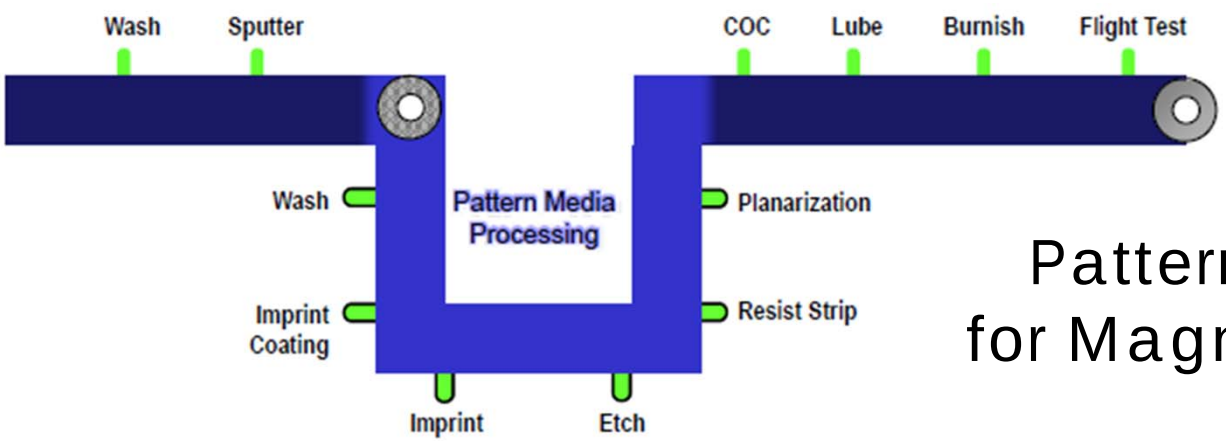
UNIT OPERATIONS



Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure at tower bottom

Gas Sweetener



Patterned Media for Magnetic Memory

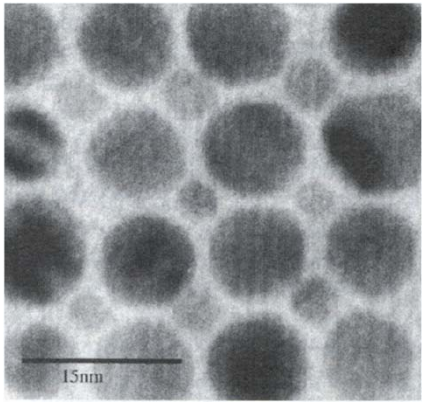
SOME PROPOSED UNIT OPERATIONS FOR NANOPATTERNING

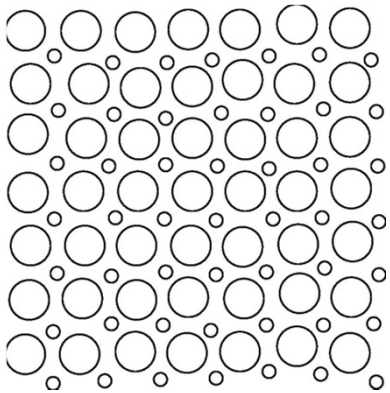
BOTTOM-UP	**TOP-DOWN**
MATERIAL FORMULATION	**WRITING**
Nanoparticle synthesis -Size, shape, composition Nanoparticle formulation - Processability	Focused Jets Dip Pen Direct Write Heated Probe Tip Nanosculpting
SELF-ASSEMBLY	**IMPRINT**
Thermal / Equilibrium Directed /Templated Kinetically Limited Evaporation Induced	Thermal Imprint / Molding UV Imprint Electrochemical machining Contact Transfer Printing

SELF-ASSEMBLY (SA)

Equilibrium SA

Kiely et al. Adv. Mater. 2000

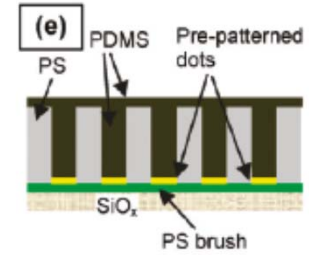


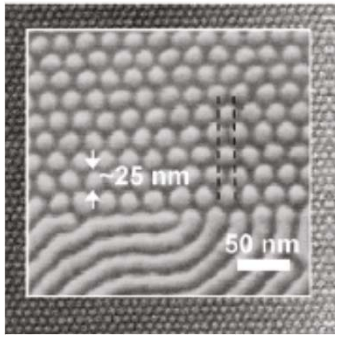


Rabideau & Bonnecaze Langmuir 2006

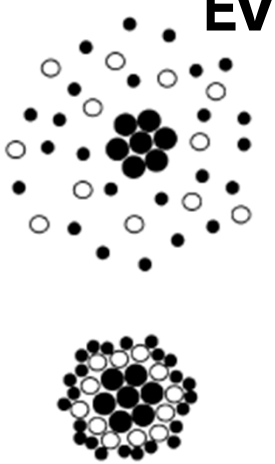
Directed SA

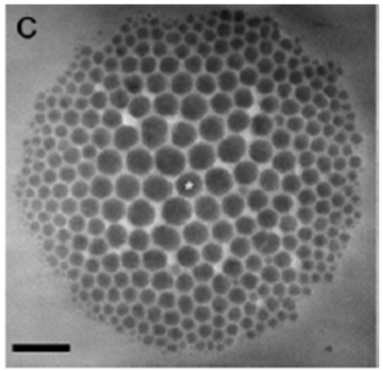
Wan & Yang Langmuir 2009





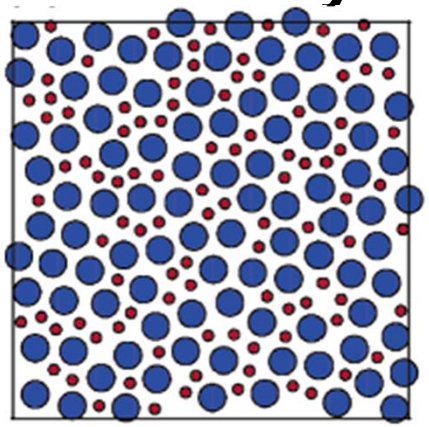
Evaporation Inducted SA





Rabideau et al. Langmuir 2007

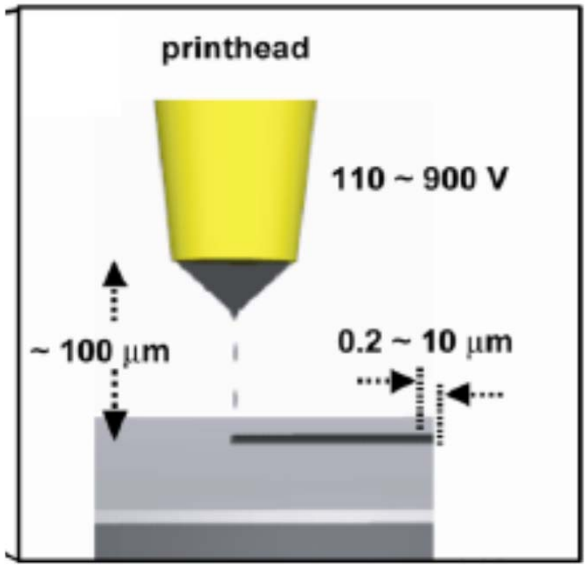
Kinetically Limited SA



Rabideau & Bonnecaze Langmuir 2005

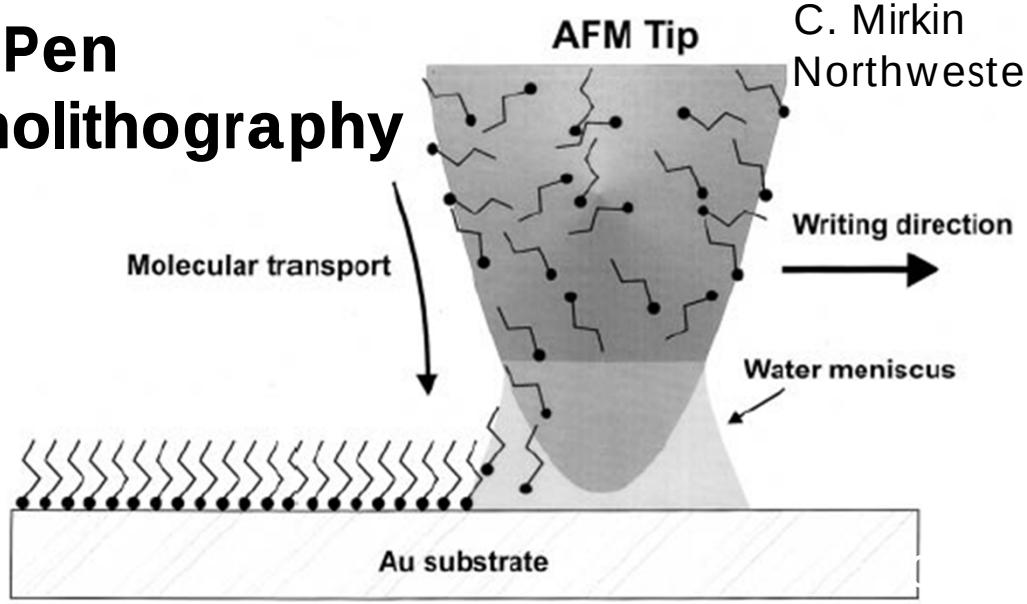
WRITING

E-Jet Printing

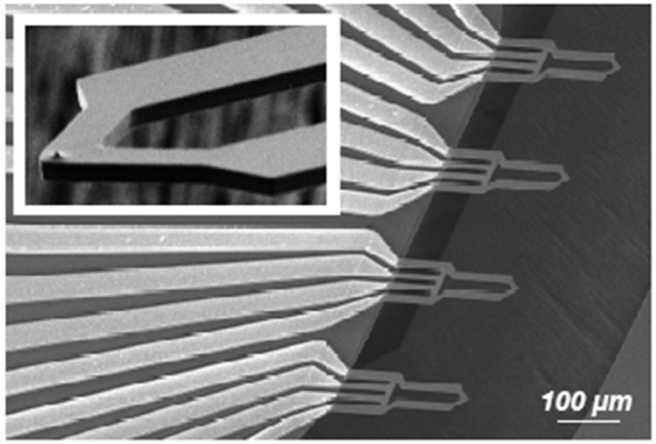


J. Rogers UIUC

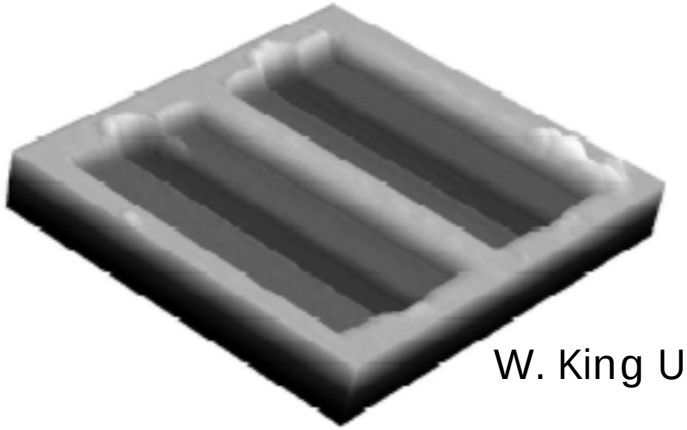
Dip Pen Nanolithography



C. Mirkin Northwestern



Multiplexed Nanosculpting

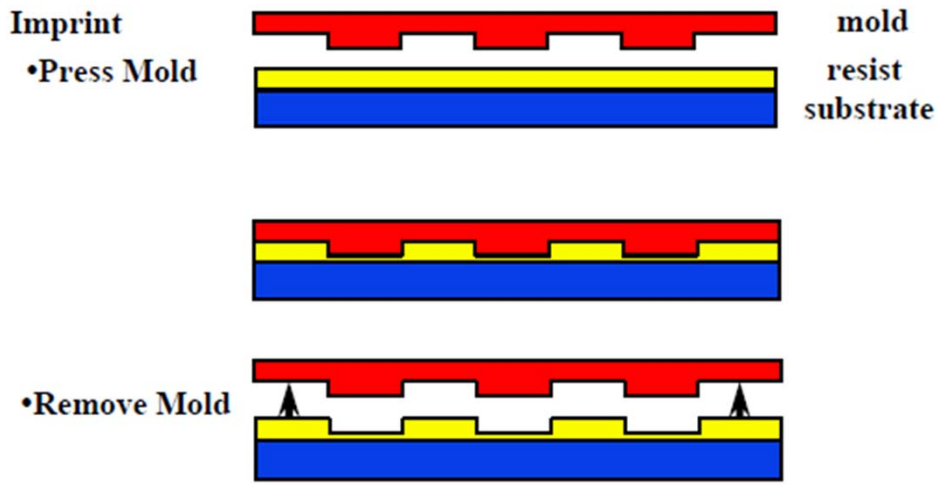


W. King UIUC

IMPRINT

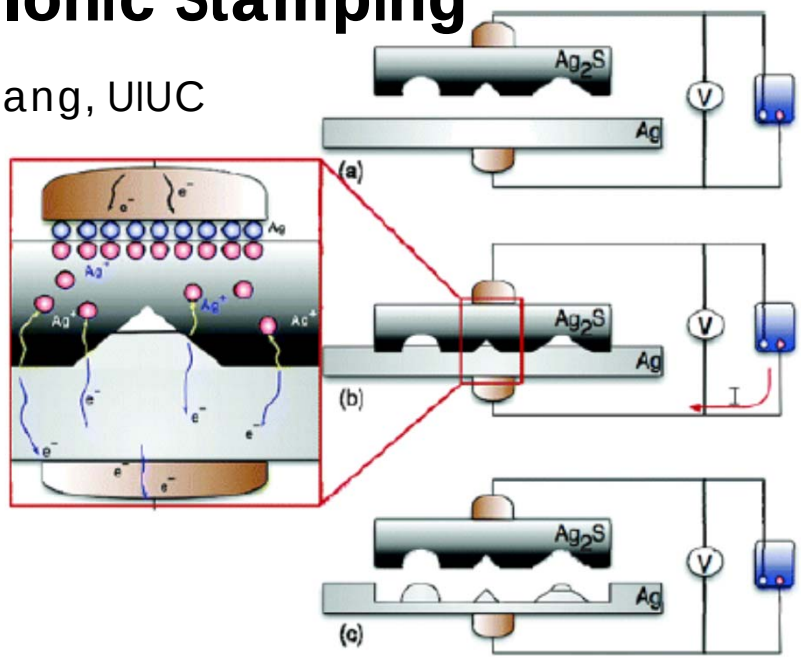
Thermal Imprint

Chou, Princeton

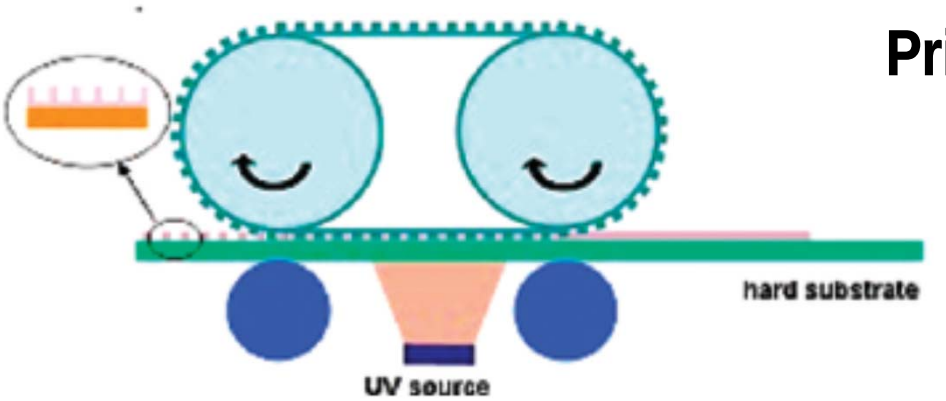


(S4) Ionic Stamping

Fang, UIUC

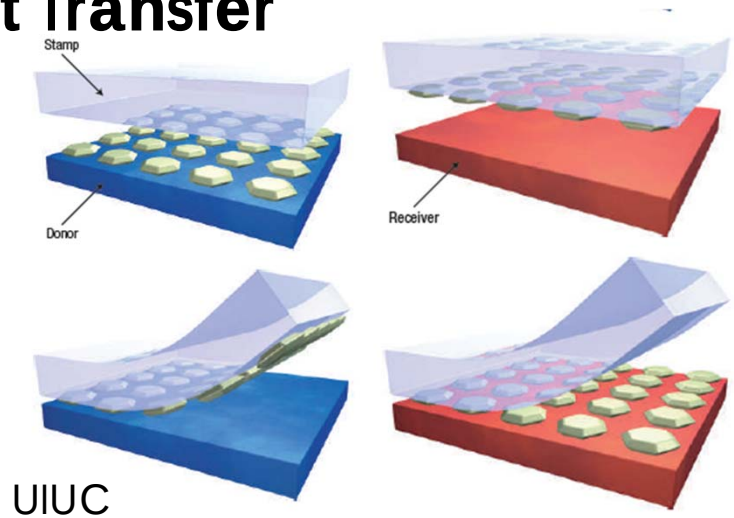


Roll-to-Roll UV Imprint



Guo, Michigan

Contact Transfer Printing

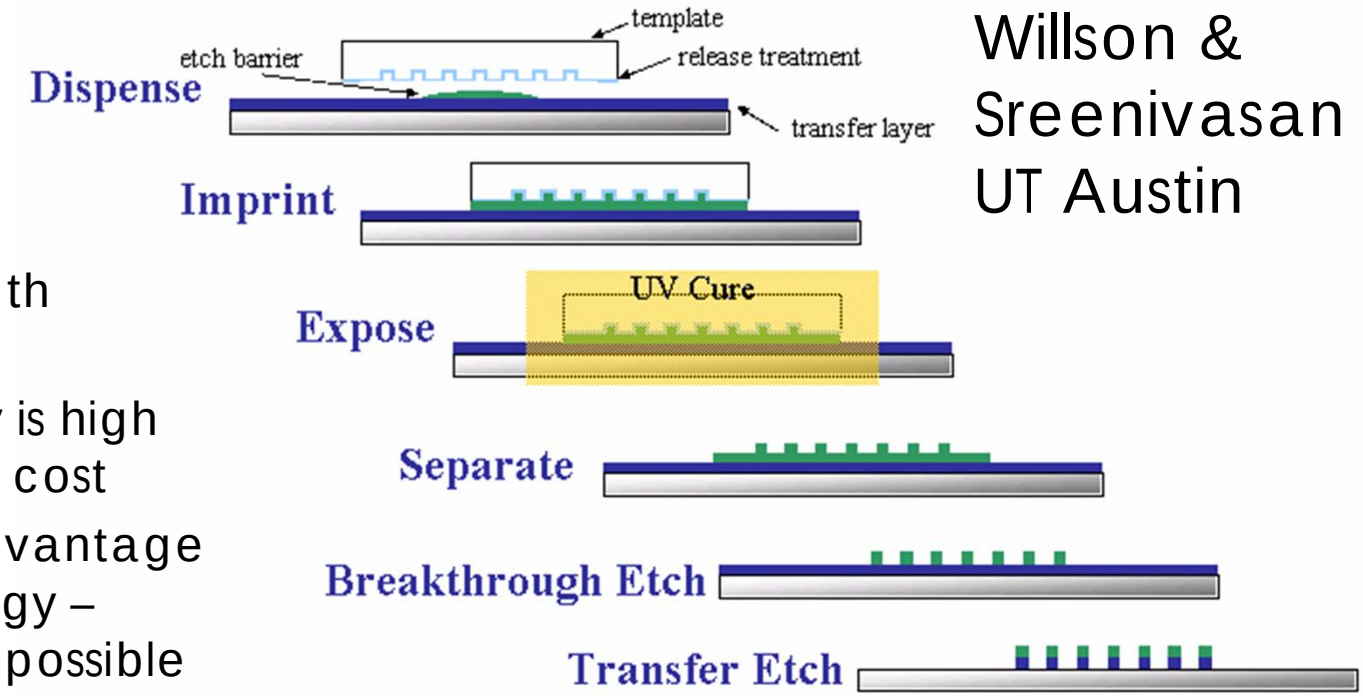


J. Rogers UIUC

UV IMPRINT LITHOGRAPHY

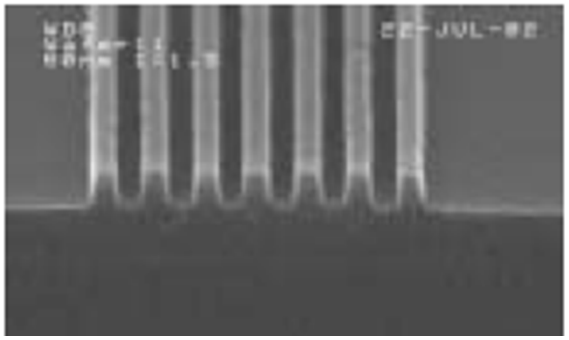
UV Imprint Lithography

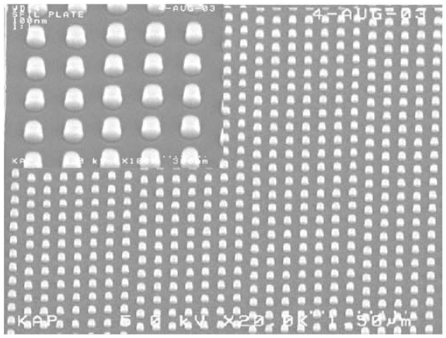
- Photolithography requires expensive optics systems & is limited by wavelength of light
- Imprint lithography is high throughput and low cost
- Template takes advantage of E-beam technology – smaller features are possible



Willson & Sreenivasan UT Austin

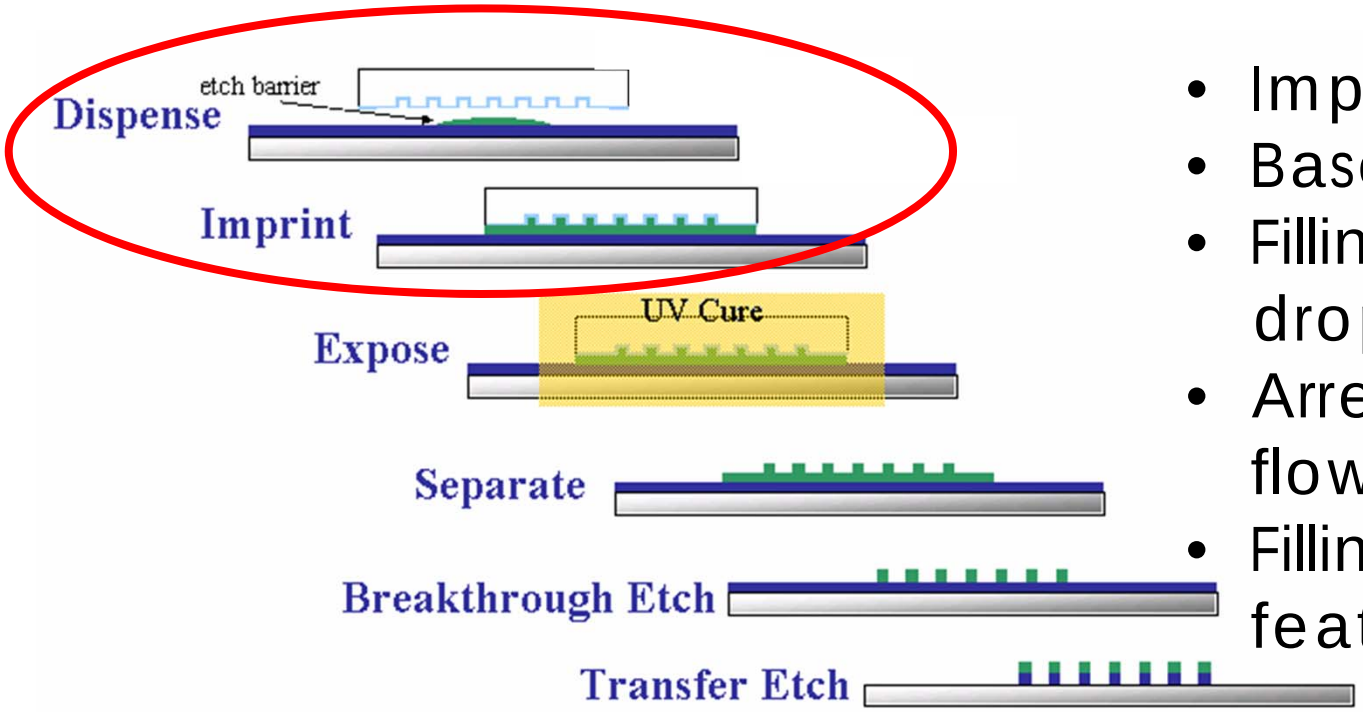
60 nm lines Todd Bailey et. al. University of Texas at Austin, TX



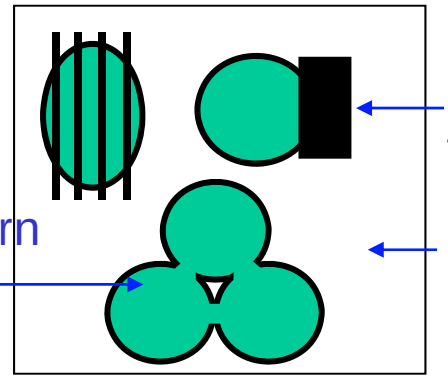


100 nm pillars Douglas J. Resnick and William J. Daukser, Motorola Labs Tempe, AZ

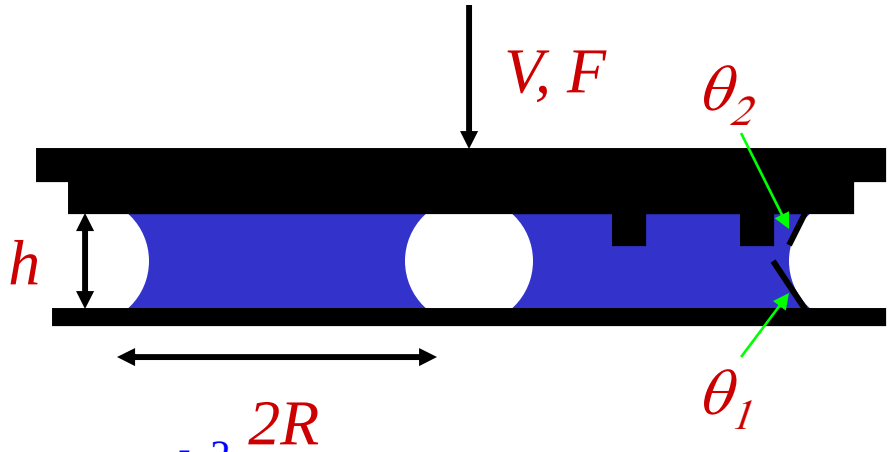
Fluid Management in UV Imprint Process



- Imprint time
- Base layer thickness
- Filling by multiple drops
- Arresting of droplet flow front
- Filling of template features



Multi-Drop Squeeze Flow



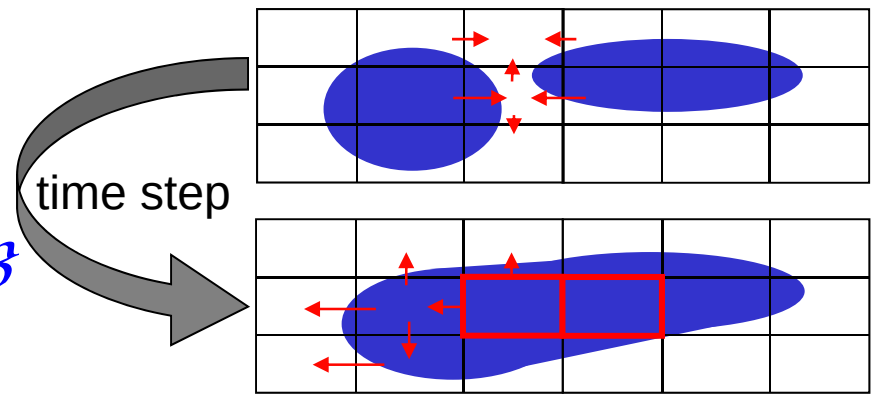
$$\langle \mathbf{u} \rangle = \frac{-h^2}{12\mu} \nabla p$$

$$\nabla \cdot \left(h^3 \nabla p \right) = -12 \mu V$$

$$p = p_{atm} - \frac{\gamma \left(\cos\theta_1 + \cos\theta_2 \right)}{h} \quad @\mathcal{B}$$

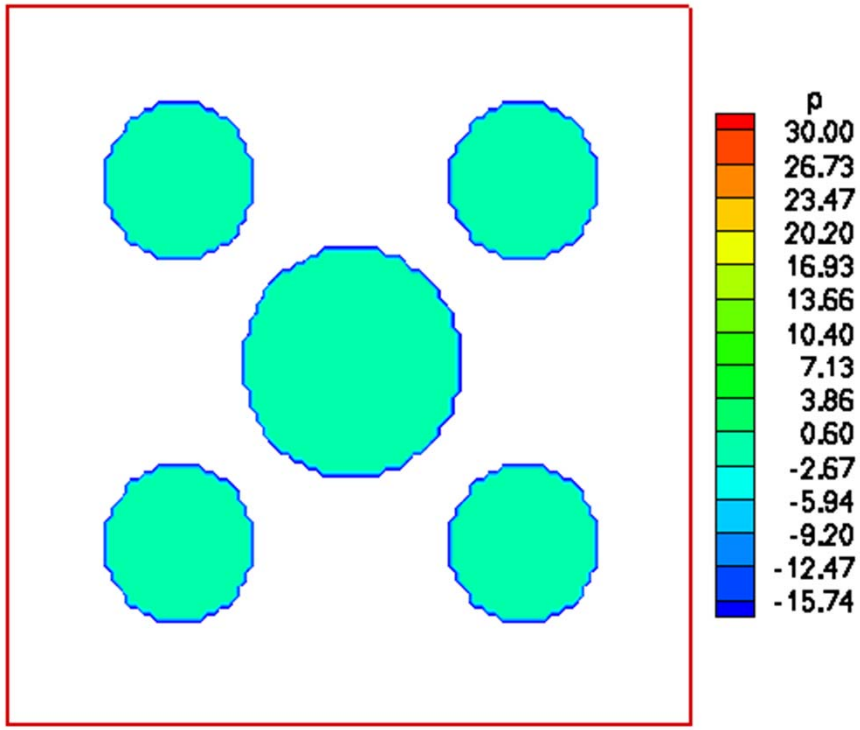
$$\frac{\mathrm{d}h}{\mathrm{d}t} = -V \text{ for constant } V \text{ or } F$$

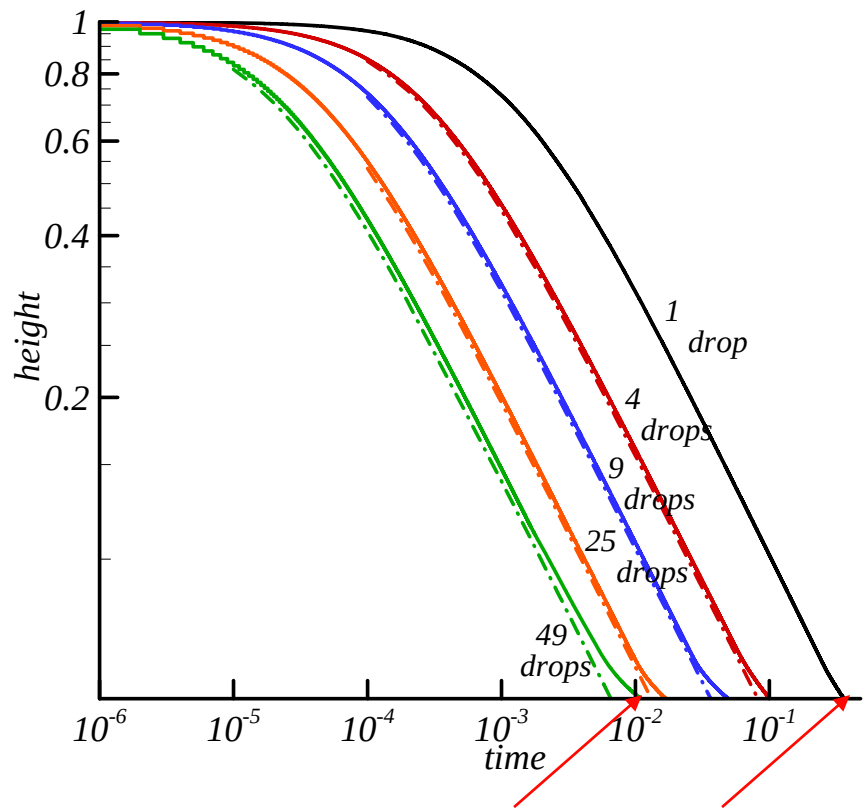
- Strong capillary and viscous forces
- Model as flat plate and with template edge and few features
- Solve multi-drop evolution via VOF method



Change boundary conditions and do it again!

Multiple Drop Filling

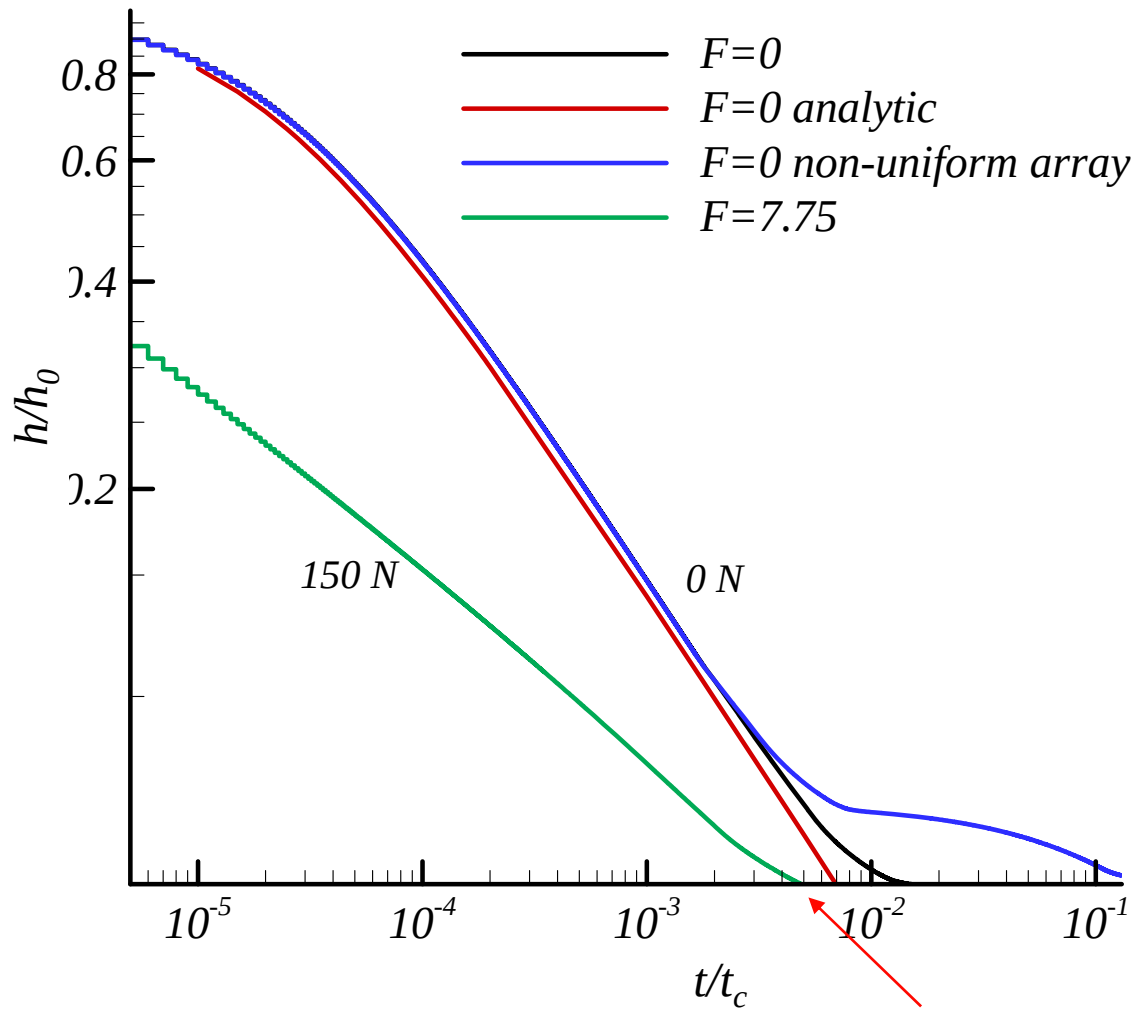




$t_{imprint}$ ~3 s vs. 65 s for h= 50 nm

$$h \sim \left(\frac{3\mu Q}{4\pi\hat{\gamma}N}\right)^{1/2} t^{-1/2} \qquad t_{imprint} \sim \left(\frac{3\mu L^2}{4\pi\hat{\gamma}N}\right)\frac{1}{h_f}$$

Imprint Time – Applied Force



Improve imprint time by:

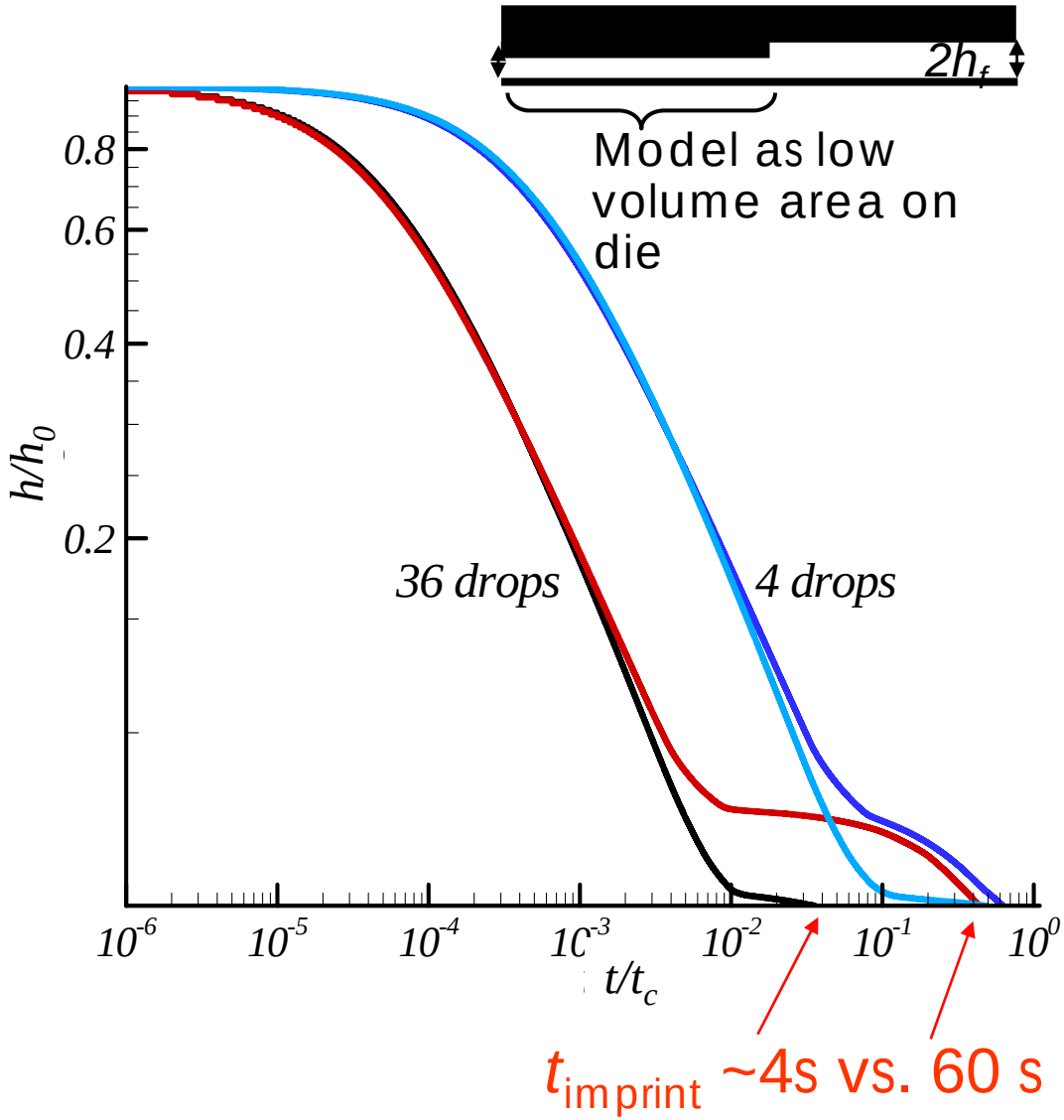
- Uniform drop placement
- Applied Force – Causes higher fluid pressures (3 MPa vs. 450 kPa)

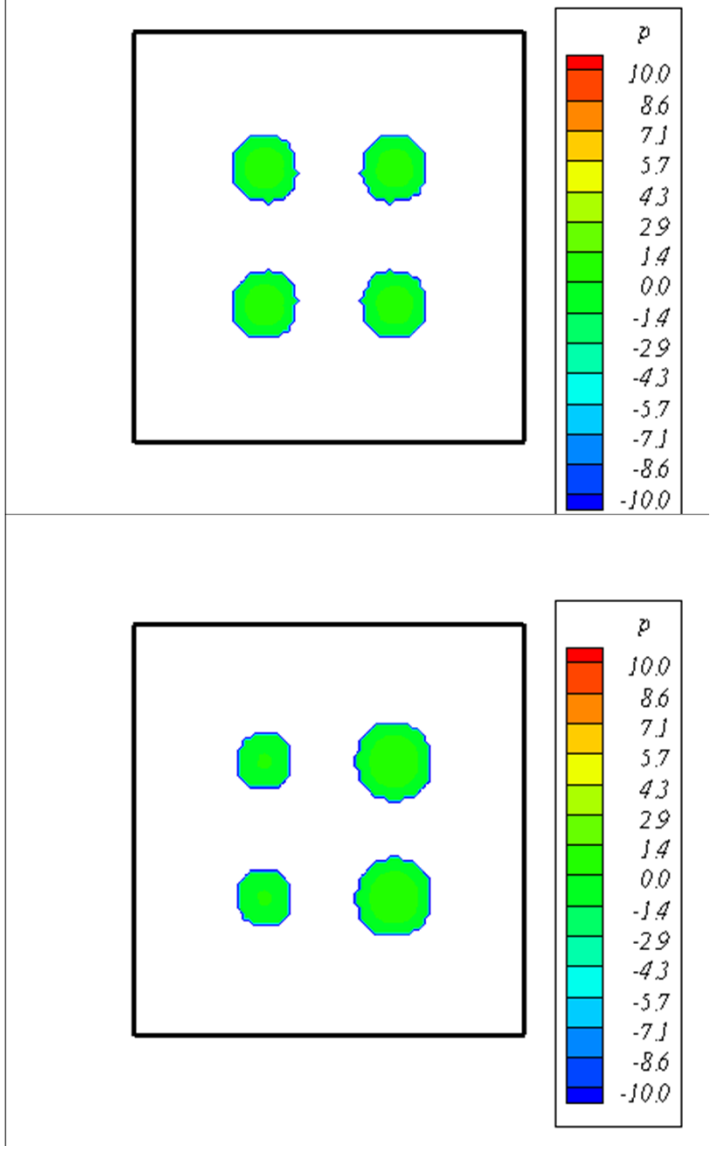
$$h \sim \left(\frac{3\mu Q^2}{8\pi F_{Applied} N} \right)^{1/4} t^{-1/4}$$

$$t_{imprint} \sim \left(\frac{3\mu L^2}{8\pi F_{Applied} N} \right) \frac{1}{h_f^2}$$

$t_{imprint}$ ~0.6 s vs. 14 s for h= 50 nm

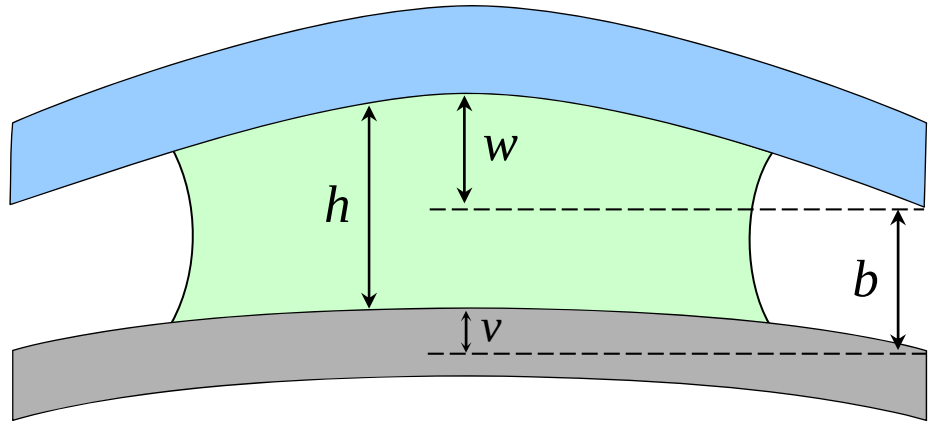
Imprint Time - Feature Density





TEMPLATE DEFORMATION

Simultaneously model template deformation and pressure inside fluid



template bending

$$D\nabla^4 w = P$$

downward motion of template

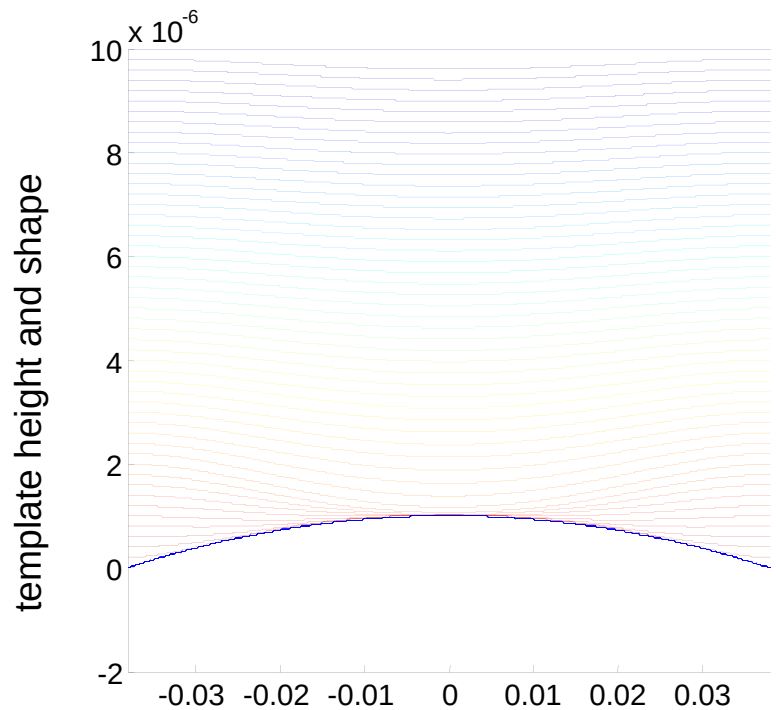
pressure from viscous resistance

$$\frac{\partial h}{\partial t} = \nabla \cdot \left(\frac{1}{12\mu} h^3 \nabla P - \frac{1}{2} \mathbf{u} h \right)$$

horizontal motion during alignment

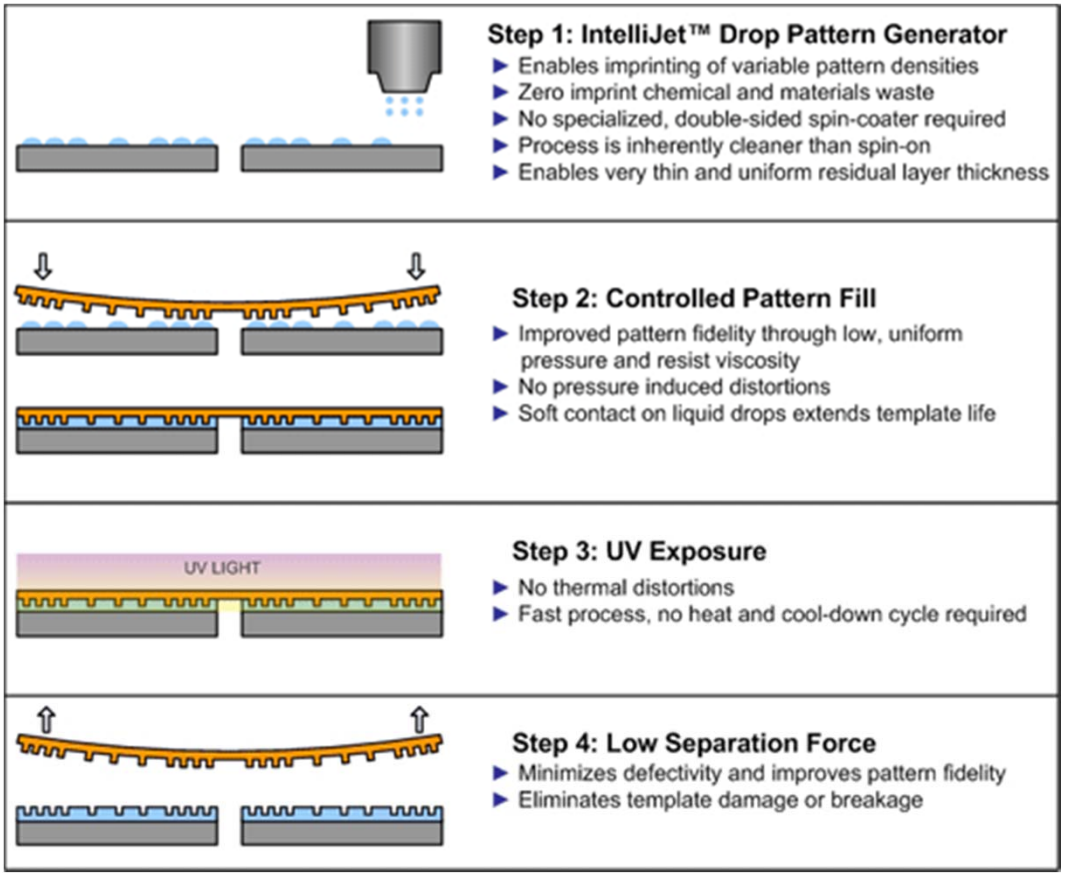
$P = -\frac{\gamma'}{h}$ at droplet edge ← capillary pressure

$h = b + w - v$ ← overall height between template and wafer



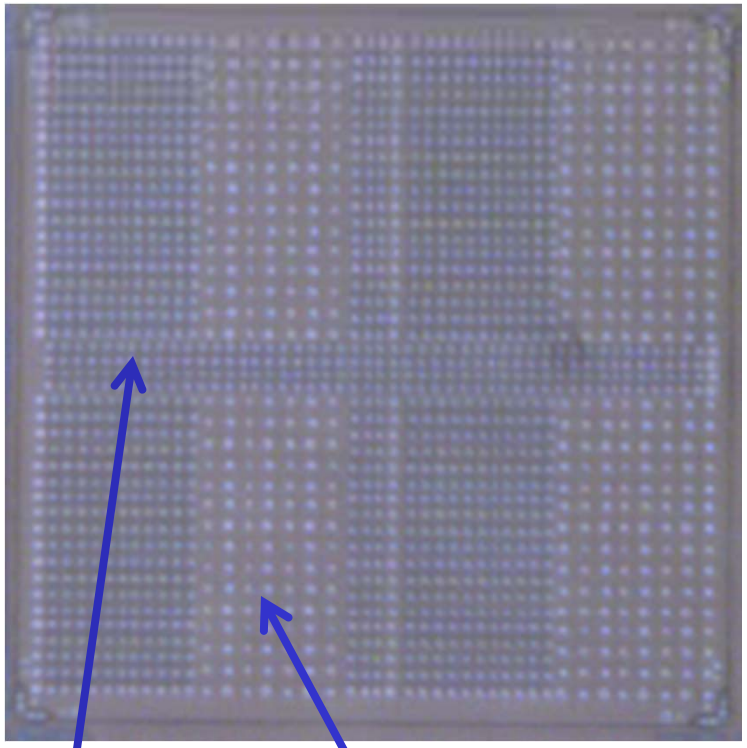
UV Imprint in Practice

Molecular Imprints J-FIL Process for
UV Imprint Lithography



www.molecularimprints.com

Controlled Pattern Filling

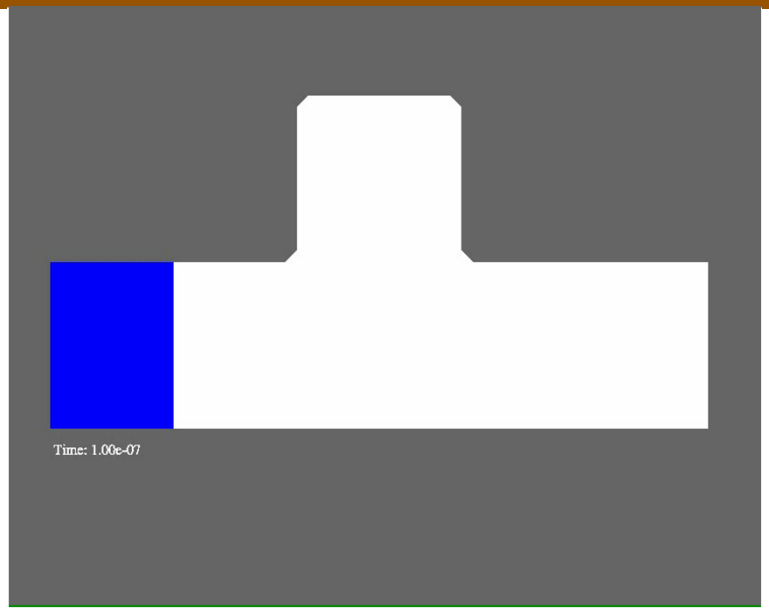


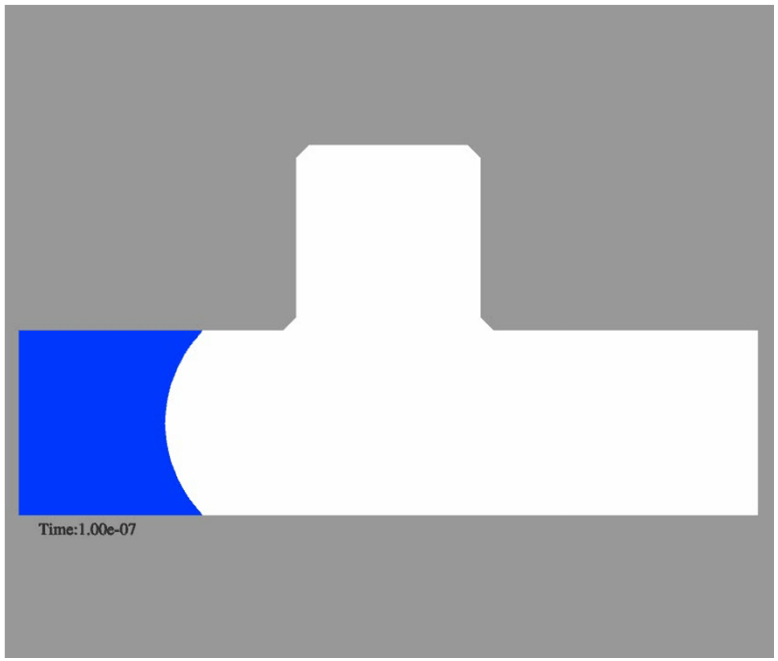
Densest features Sparsest features

INTERFACE MOTION THROUGH FEATURES

- Understand mechanism for feature filling and possible gas trapping

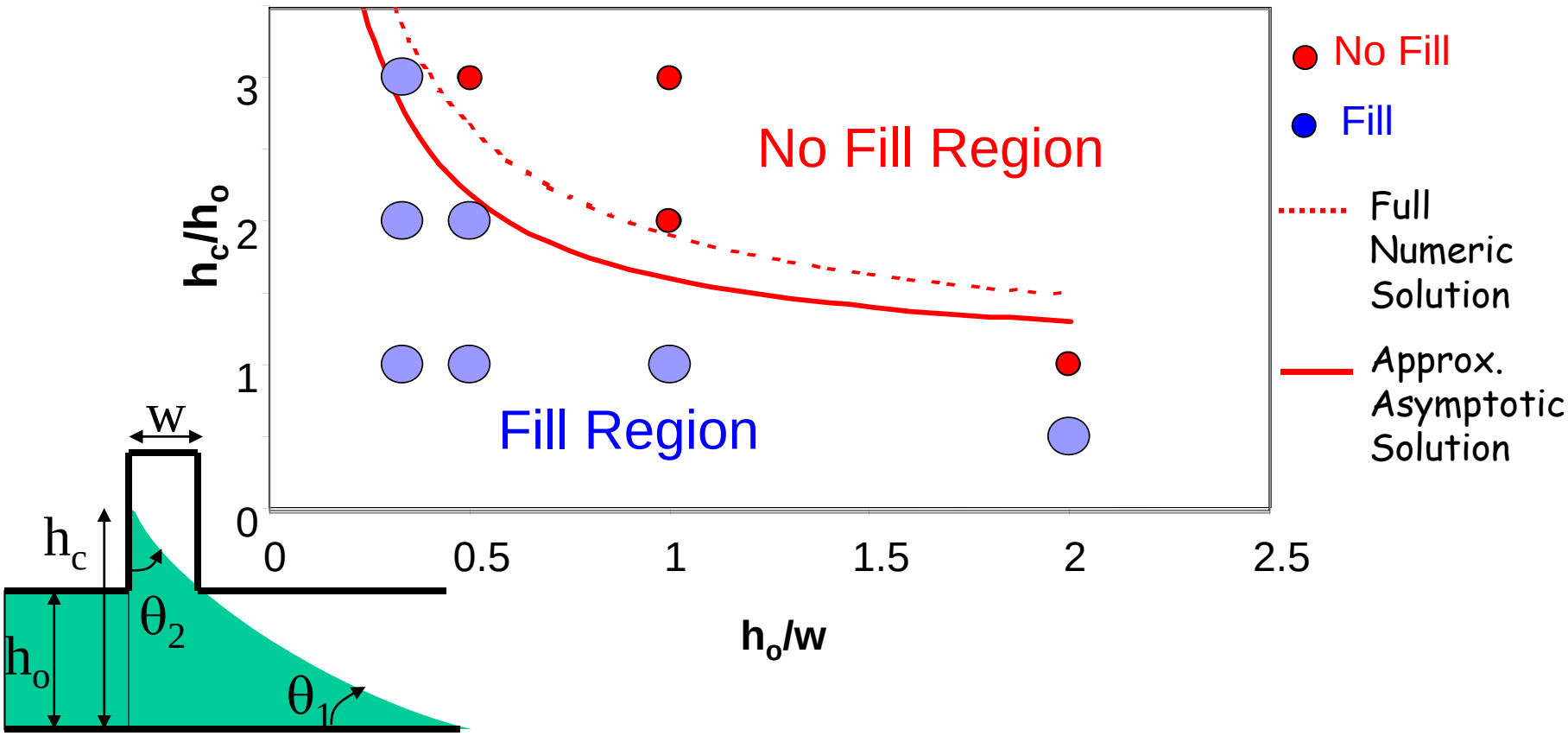
- Predict parameters that may cause air entrapment in features





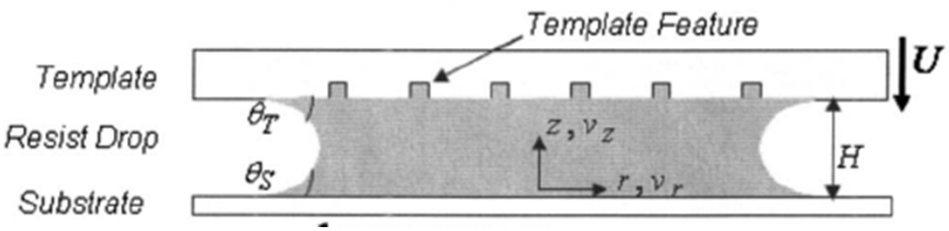
FILL – NO FILL MODEL

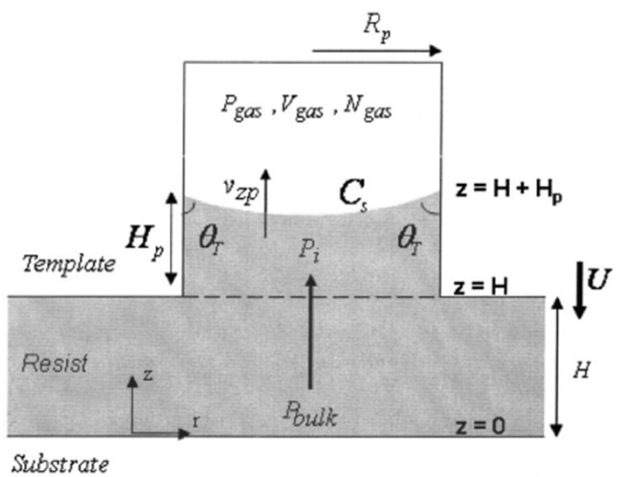
Geometry of feature and contact angles determine fill or no fill condition

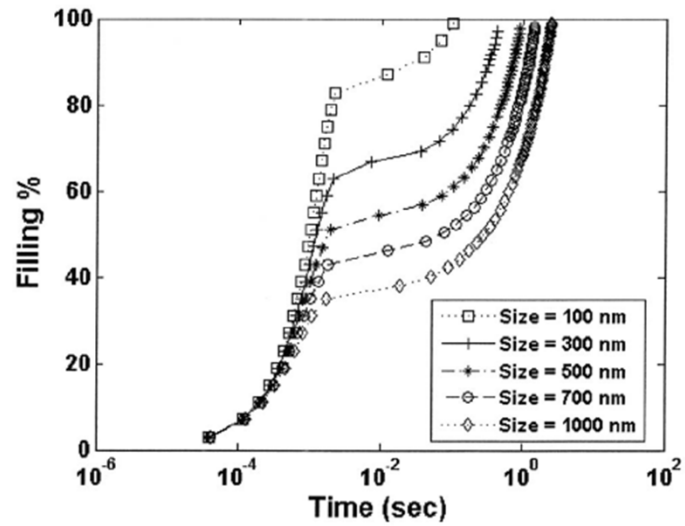


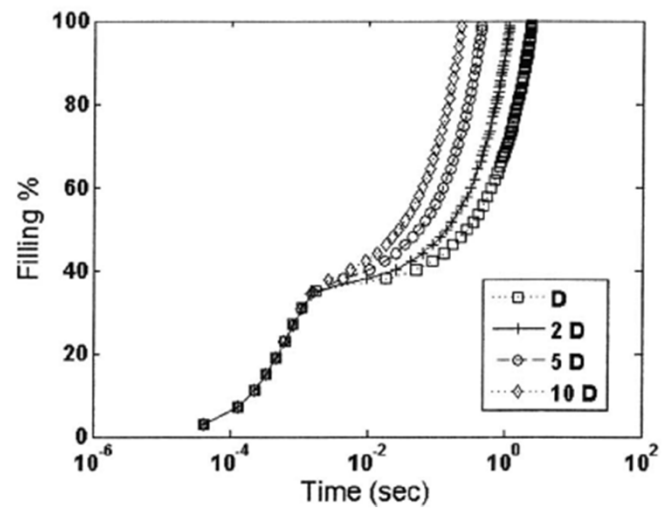
GAS TRAPPING

Feature Filling Faster for Smaller Pores and Larger Gas Diffusivity









UV Imprint for High Density Memory

Imprio HD2220 at Molecular Imprints, Austin, TX
For High Density Patterned Magnetic Media

CONCLUDING REMARKS

UNIT OPERATIONS BENEFITS TO NANOMANUFACTURING

- Scale-up methodology for nanomanufacturing
  - Large area
  - High speed
  - Low defectivity

- Enable process exploration and innovation
  - Topological and parameter optimization
  - Mitigation of risk

- Provide frame work for real-time decision making
  - Need for large area, fine resolution metrology

- Accelerate time to market from lab bench to manufactured product

THE ROLE OF CHEMICAL ENGINEERS

- Unit operations perspective can provide a useful framework to rapidly develop nanomanufacturing processes.

- Strong academic-industrial collaboration may be best for model/simulation development

- Development of the models and simulations interdisciplinary, and chemical engineering brings valuable skills
  - System level analysis
  - Multiscale perspective
  - Transport phenomena
  - Thermodynamics
  - Reaction engineering

- Nanomanufacturing offers a great opportunity for chemical engineers.

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QUESTIONS?