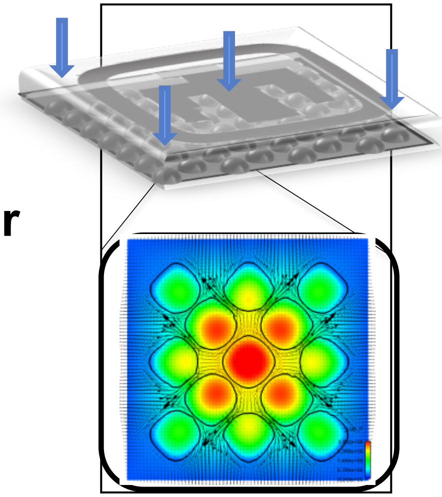
SAND2016-9512C

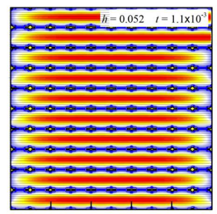
ISCST 2016 Featured/Plenary Session
Micro-/Nano-Replication Technology
Session Chairs: Shuzo Fuchigami and Satish Kumar



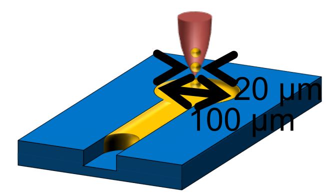
8:15 AM Randy Schunk The fundamentals of micro- and nano-replication manufacturing: challenges and opportunities

8:45 AM Benjamin Leever NextFlex: Enabling a Domestic Manufacturing Ecosystem for Flexible Hybrid Electronics

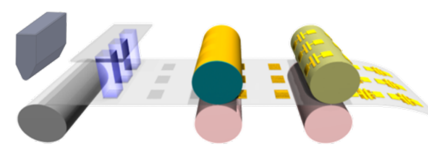
9:15 AM Roger Bonnecaze Multiscale Fluid and Solid Mechanics of UV Nanoimprint Lithography



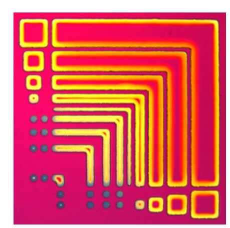
9:45 AM Break



10:20 AM Lorraine Francis Self-Aligned Capillarity-Assisted Lithography for Electronics



10:50 AM Vivek Subramanian High-speed printing of transistors: From Inks to Devices



11:20 AM Hayden Taylor Polymeric microembossing and nanoimprinting: computationally inexpensive process models for designing inline optical metrology

For Presentation at the 18th Symposium of International Society of Coating Science and Technology, 19-21 September 2016

The fundamentals of micro- and nano-replication manufacturing: challenges and opportunities

P. Randall Schunk

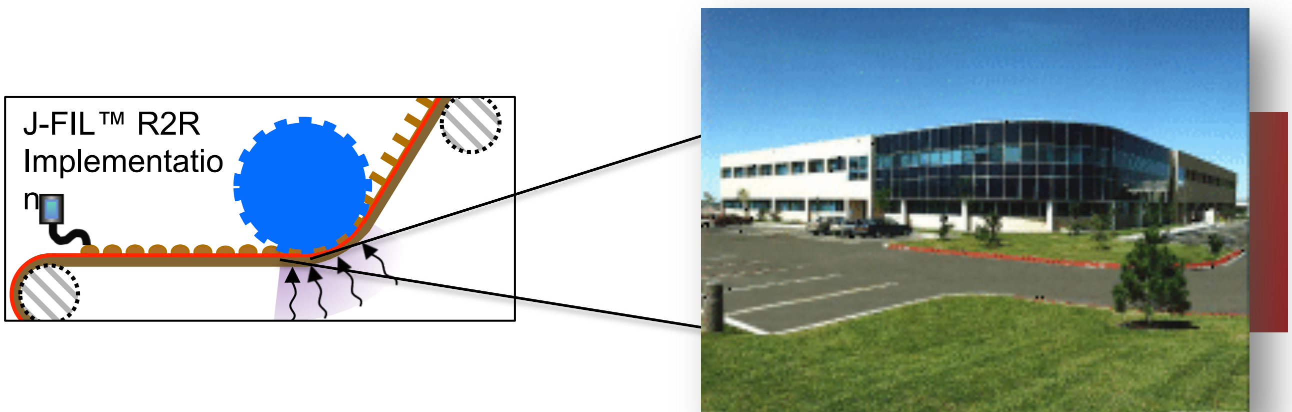
National Laboratory Professor

Department of Chemical and Nuclear Engineering

University of New Mexico

Manager, Advanced Materials Laboratory

Sandia National Laboratories



Contributions from N. Bell, T. Boyle, K. Tjiptowidjojo, A. Cochrane, S. A. Roberts, D. Hariprasad, R. Malahkov

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OUTLINE

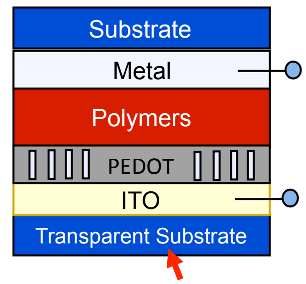
Goal: Frame this special session on micro- and nano-replication

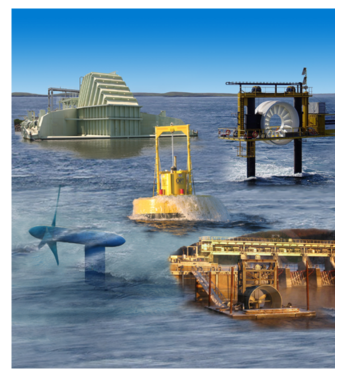
- **Advanced Manufacturing and printed electronics** *(From a Material Science point of view….)*
  - **Current roadmap elements that present technical challenges - *Leever***
  - **Micro/Nano Replication – From 3D printing to R2R**
    - ***Why R2R? –Faster***
    - ***Why nano-manufacturing - performance***
    - ***What can we learn from a century of manufacturing technology development?***
- **Science and engineering challenges**
- **Meeting some these challenges with integrated particle-to-ink-to-print lab**
- **Meeting some of these challenges with M/S.**

Energy/Mobile Computing/Sensing Technologies and Manufacturing

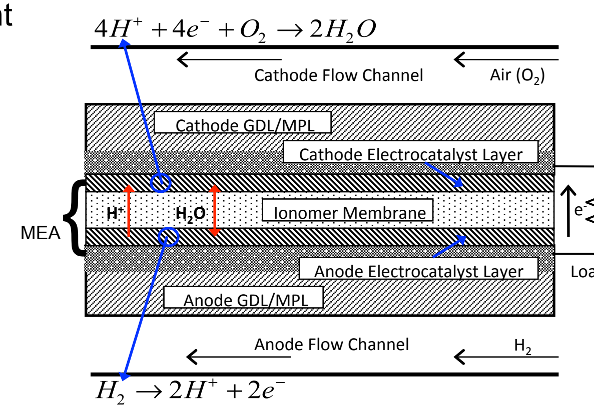
- **Materials/devices for these apps (e.g. energy storage, generation, conversion) needed <u>in volume!</u>**
- **Successful insertion (transportation, grid, whatever) often impeded by unfavorable cost model (<u>manufacturing and performance, reliability</u>)**
- **All these technologies are demanding <u>smaller feature sizes, thinner films, etc. over large areas volumes.</u>**

Energy Storage/Generation Materials





Marine/hydrokinetic



Fuel Cell Technology

Mobile computing

Flexible electronics

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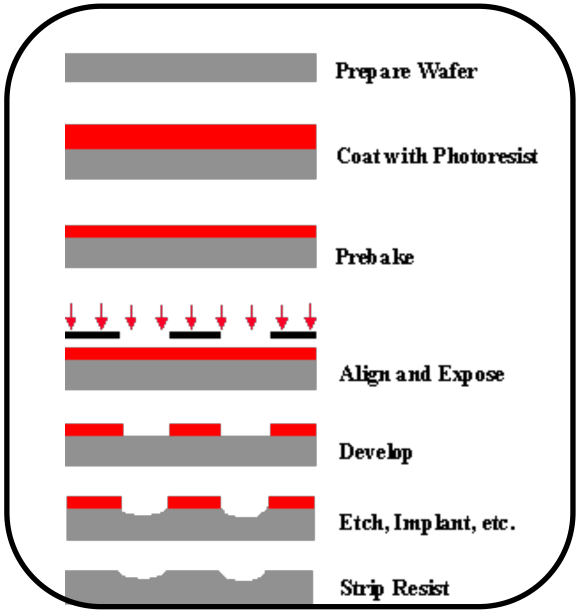
Printing vs. silicon/microfab – The motivation is obvious

Optical Lithography/Microfabrication

-Feature size/Resolution 10->50 nm (multiple-patterning, EUV)
-Material density/purity – High – Vapor deposition.
-Throughput – 1 m^2/hr
-Overlay/registration to 100 nm

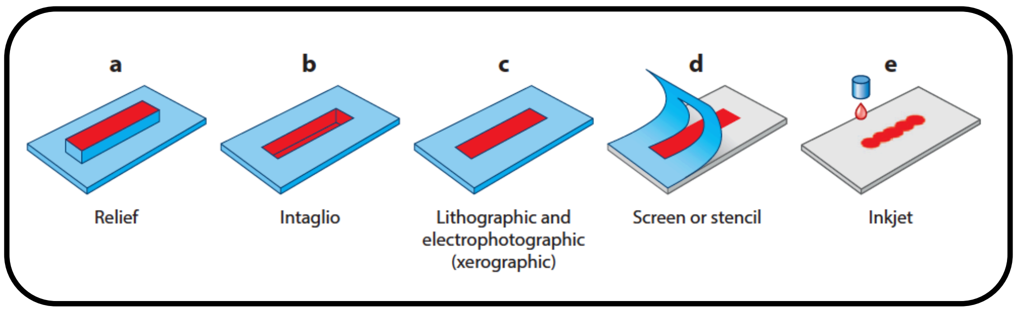


Multiple, batch steps: LELM-lift

Direct write/print Additive

-Feature size/Resolution 500 nm - 2 micron
-Material density/purity - average
-Throughput – 1000 m^2/hr
-Overlay – to 5-10 micron

Gravure, Screen, flexography, inkjet….with electrically functional conducting or optical inks…



From S. Kumar, Ann. Rev. Fluid Mech. 2015

Two Steps: Deposit, Solidify

Comes down to cost advantage (economy of scale) vs. performance

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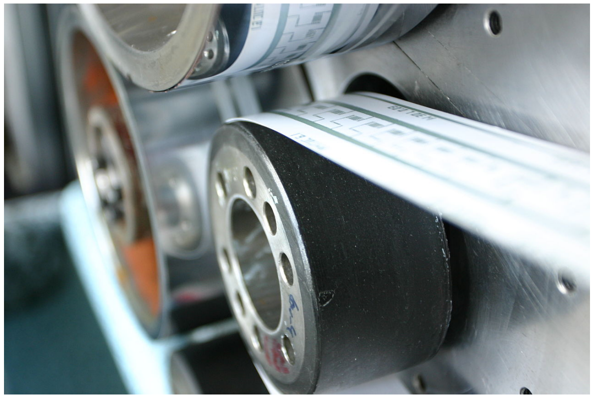
"Micro" electronics: Cost model includes performance, fab cost, durability

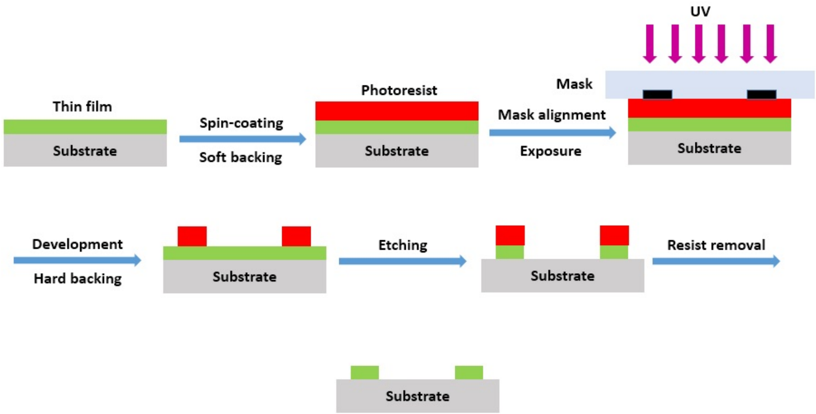
Printed Electronics
-Long switching times (clockspeed)
-Low integration density (transistors)

-Large areas
-Flexible form factors
-Simple fabrication
-Low cost

Conventional electronics
-Extremely short times (fast clockspeed)
-Extremely high integration density

-Small areas
-Rigid substrates
-Complex fabrication
-High fab cost





Materials research (breadth) in the printing realm is an unknown frontier relative to conventional electronics

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Challenges and opportunities: What do the industry roadmaps say? (printed electronics)

Key Challenges* (From the Organization of Organic and Printed Electronics - www.oe-a.org)

- Based on an analysis of the application and technology parameters, the recent progress in materials and process technology and the expected future technology development, the following key challenges ("Red Brick Walls") were identified for which major breakthroughs are needed:
  - **Processes**: resolution, registration, uniformity and characterization/ metrology –*All addressed in this session.*
  - **Encapsulation**: flexible transparent barriers at low cost
  - **Materials**: improvement of electrical performance, processability and stability
  - Development of appropriate **standards and regulations** for organic electronics

Further boiling down, these challenges to colloidal capillary hydrodynamics, consolidation and sintering and structural mechanics—mechanical and optical engineering

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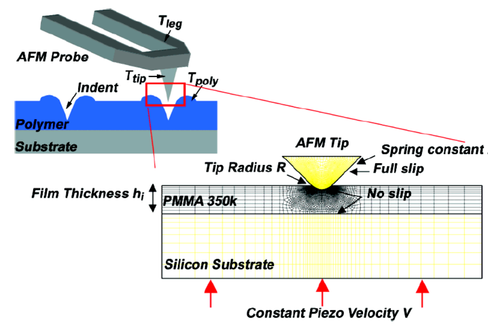
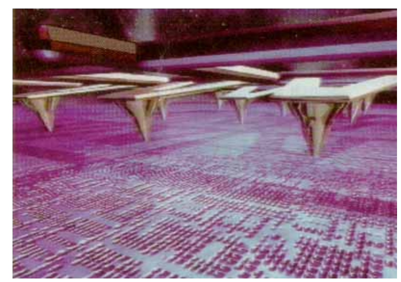
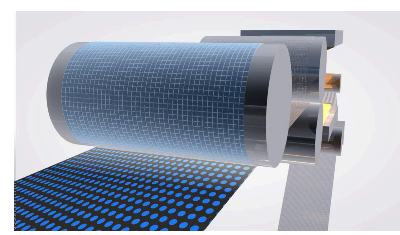
Replication Manufacturing

- **Manufacturing – "Making something practically"**
- **Replication - Achieve practicality through repetition –** *From assembly-line through continuous processing (scales of granularity)*
  - **Digital/advanced manufacturing**
    - **3D printing AM, stero-litho, ink-jet… -- Digital template**
  - **Physical/Advanced manufacturing: Lithography**
    - **Opens up to *parallel* processing single feature to multiple features over surfaces (*physical template*) – molding, printing, imprinting, embossing, optical**
  - **Continuous manufacturing (physical template)**
    - **Extrusion, coating, milling/machining…**
- *Replication with "nanocomponents" nanoparticles through chemistry – is this replication?*







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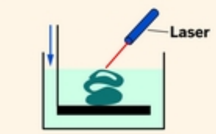
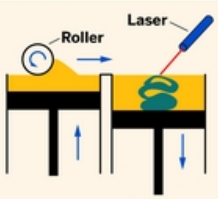
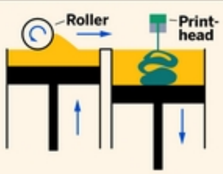
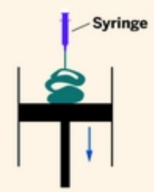
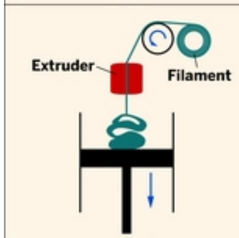
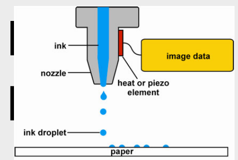
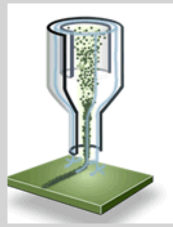
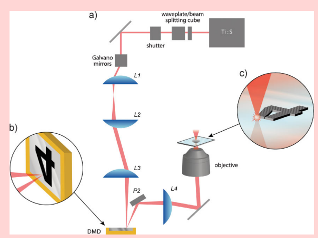
Additive Manufacturing Approaches

Digital/advanced manufacturing (digital replication)

	TECHNIQUE	SMALLEST PRINTABLE FEATURE	MATERIALS
	**Stereolithography:** Laser cures photopolymer as platform lowers into liquid vat.	1–70 µm	Photopolymers
	**Laser sintering:** Laser melts powder rolled onto platform. Platform lowers with each layer printed.	45–100 µm	Metals Polymers
	**Powder-bed ink-jet printing:** Printhead sprays liquid binder onto powder to fuse layers. Platform lowers with each layer printed.	350–500 µm	Ceramics Metals Polymers
	**Robocasting:** Syringes extrude fluid materials that harden on lowering platform.	200–400 µm	Biopolymers Some metals Food
	**Fused deposition modeling:** Heated extruder melts plastic filament, which cools on lowering platform.	260–700 µm	Thermoplastics

	**Ink-jet** Liquid droplet delivery on substrate	10-20 micron	Colloidal inks
	**Aerosol-jet** – atomized ink focused into narrow stream for precision writing	10-20 micron	Colloidal inks

	**Multiphoton Lithography (MPL)**	**<100 nm**	**Photopolymers, biopolymers, some metals and ceramics**

One manufacturing dimension not covered here is throughput!
-- Job Shop, specialty apps

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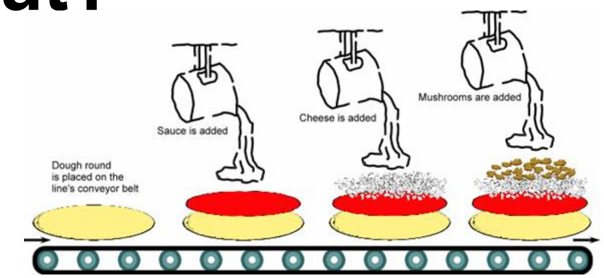
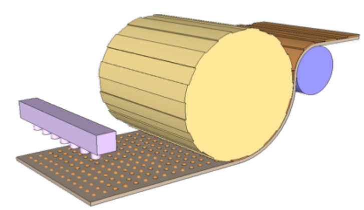
How increase throughput?

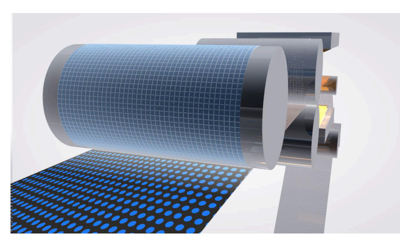


- **Conceivably, all additive approaches can be configured in a "batch-step assembly line"**
  - Semi-continuous step-by-step
- **Multiple tool heads could be configured in parallel to cover greater areas**

- **Additionally, the base could be flexible, and the features and the web can be rolled for compact storage –**
  - Could be configured R2R
- **Precision, continuous R2R using such replication best carried out with a physical template (extrusion die or patterned ink well)**



Can true nanomanufacturing be realized?



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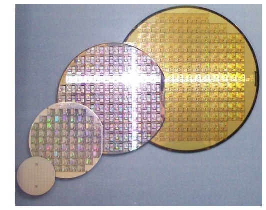
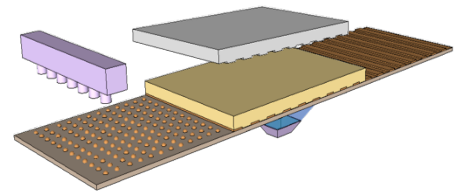
<u>Additive/subtractive</u> Manufacturing for Volume Production

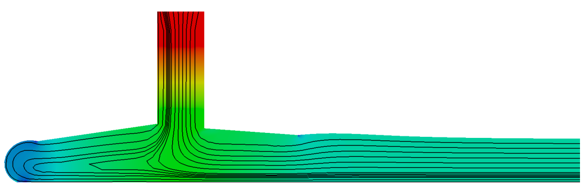
- **Wafer-scale or step-and-process roll-scale lines**
  - **Configurations involving solution deposition, etching, vapor deposition, optical litho, etc.. – *Microelectronics industry!***

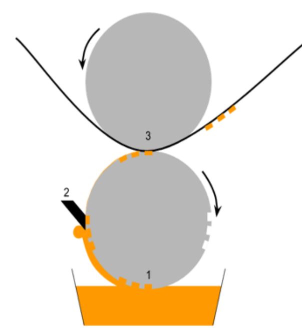


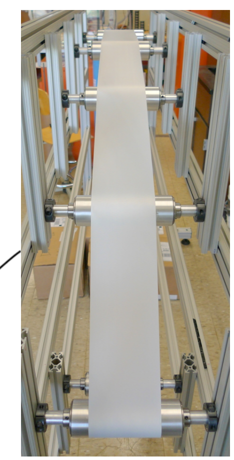
- **Wafer-scale and roll-scale Imprint lithography**
  - **Imprint/contact print** Bonnecaze et al.
  - **Embossing/etching** Taylor et al.
    - *Only with this class of manufacturing routes can nano-scale features be achieved without particles – See Bonnecaze et al.*



- **Continuous R2R-scalable techniques (truly "additive"!)**
  - **Printing/lithography – "Mechanical replication"**
    - **microGravure, flexography, aerosol, screen** Subramanian et al.
  - **Continuous Coating (Extrusion, slide, roll)**







How does one push these into "nanomanufacturing" scales?

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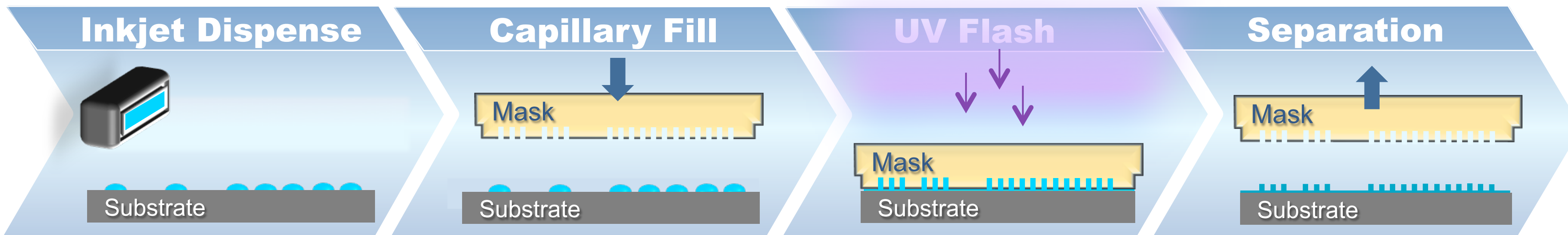
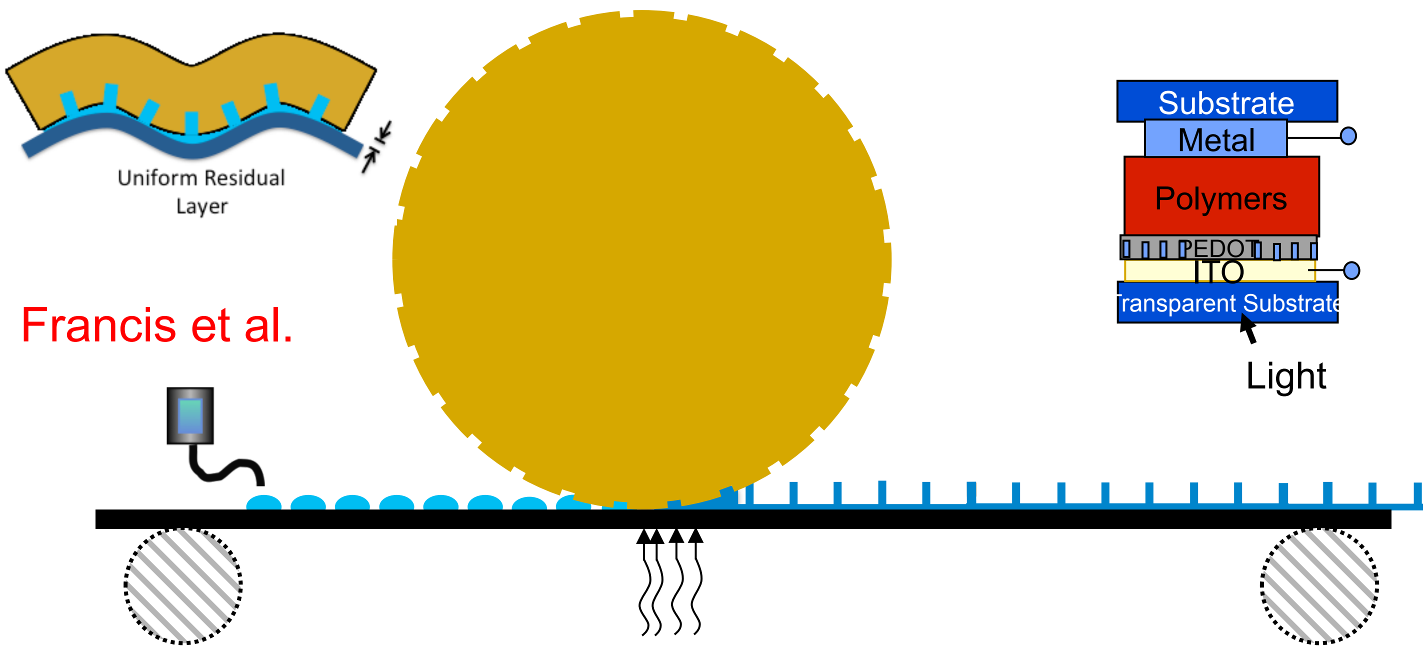
Subtractive and Hybrid Additive/Subtractive Manufacturing

Jet Flash Imprint Lithography™ (J-FIL™)



Courtesy of MolecularImprints

Roll-to-Roll Nanoimprint Lithography (R2R_NIL)



High density storage

Courtesy of Akhilesh Jain

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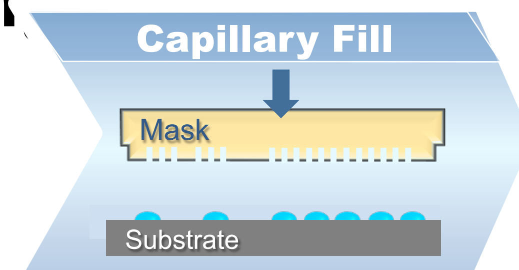
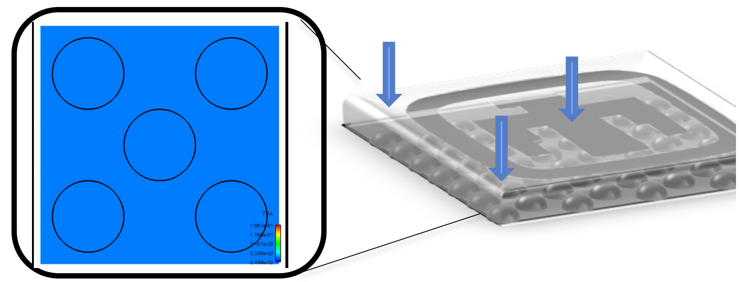
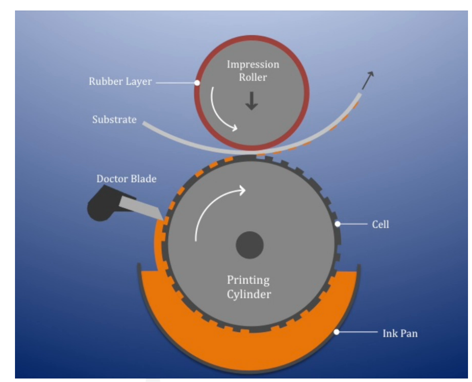
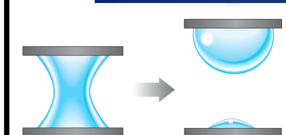
The goals/challenges of patterning by imprinting or printing

- Imprinting (press or stamp) – Low viscosity/high viscosity – really mold filling or forming
  - Achieving a **uniform RLT** over wide areas
  - Minimizing trapped-gas defects (**gas matters!**)
- Printing lithography – Additive
  - Ink **printability** (operating window)
    - Feature size limited by lack of control of capillary fluid mechanics, rheology, wettability









> ***Uniformity, printability, entrainment…***
> ***Sound familiar? To get to sub-micron featured, patterned, functional prints at scale?***

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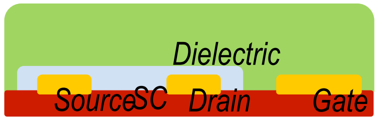
Challenges of print/imprint, continued

– **Multilayer registration (exponentially more difficult the smaller the feature). Easy for 3D printing due to larger feature size….**



  - *Not an issue for coating. Francis et al. for printing*

– **Delivery of nano-colloid materials for controlled structures**

  - *Fluid mechanical/tribological challenges both printing and coating*
    - *– Addressed by Subramanian (reference), others.*
  - *Solidification challenges –densification for function – Many, E.G. Advanced Materials Laboratory, SNL*

– **Process science challenges remain – Devices/ functions often need thinner (sub micron), higher resolution.**

  - *Metrology challenges at the 100 nm scale and less- Coating and printing (addressed by Taylor, others)*
  - *Surface science (substrate, liquid, colloidal)*

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What are these challenges in liquid thin liquid film coating?

Goal – *"Thin" functional films with long range uniformity (low defect rate), possibly at high speed*

- **Coatability**
  - Continuous thin uniform wet film over wide areas
    - Common defects – Ribbing, barring, air entrainment, mottle, interfacial instabilities
- **Uniformity**
  - Solidification and uniform microstructure/thickness over wide areas
    - Common defects – marangoni, starry night, etc.
  - Quality control (on-line/at line defect detection)

The underpinning physical barriers to success are the same!

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To surmount challenges requires fundamentals

- **Printing/imprinting: smaller features, faster**
  - *Capillary hydrodynamics of delivery and transfer (Kumar)*
  - *Two phase flow (gas matters)*
  - *Structural mechanics (gravure and flexography) – Thin structure and bulk structure and elastohydrodynamics*
- **Bottom-up/Top-down - Delivering nanomaterials**
  - *Ink design*
    - *Rheology*
    - *Stability*
    - *Wettability*
  - *Drying/solidification control for function*

Coatability – thinner/faster

- *Capillary hydrodynamics*
- *Dynamic Wetting and spreading (dewetting)*
- *Air entrainment*
- *Rheology – Colloidal/ polymer*
- Structural mechanics (tension web)

Uniformity

- *Drying/solidification science*
- *Polymerization*
- *Colloidal stability/ directed assembly*

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Meeting these challenges at Sandia's Advanced Materials Laboratory

Functional Materials
- Nano-patterned materials
- Nano-patterned surfaces

Underpinning Science
- Bottom-up (self assembly, self organization*)
  - Exp.: Brinker, Fan, et al.
  - M/S: Schunk, Grest, et al.
- Top-Down: Nano Patterning
  - Exp: Talin, Bogart
  - M/S: Schunk, Reedy, Chandross et al.

Manufacturing "Science"
- Schunk, Kaehr, Boyle, Brinker, et al. (AML)

Large Throughput Processing Fundamentals
-Coating, Molding, Embossing (AML, CRMPC, UT)

Nano-Particle Fundamentals
-Drying (NPFC, Schunk et al.)
-Rheology (NPFC, Bell et al.)
-Phase and Thermo (NPFC, Brinker et al.)

Nan -Patterning Fu
-Imp
-Other Lithography

Nanoink development

Machine Design
-Summit V, MESA
(UT partner)

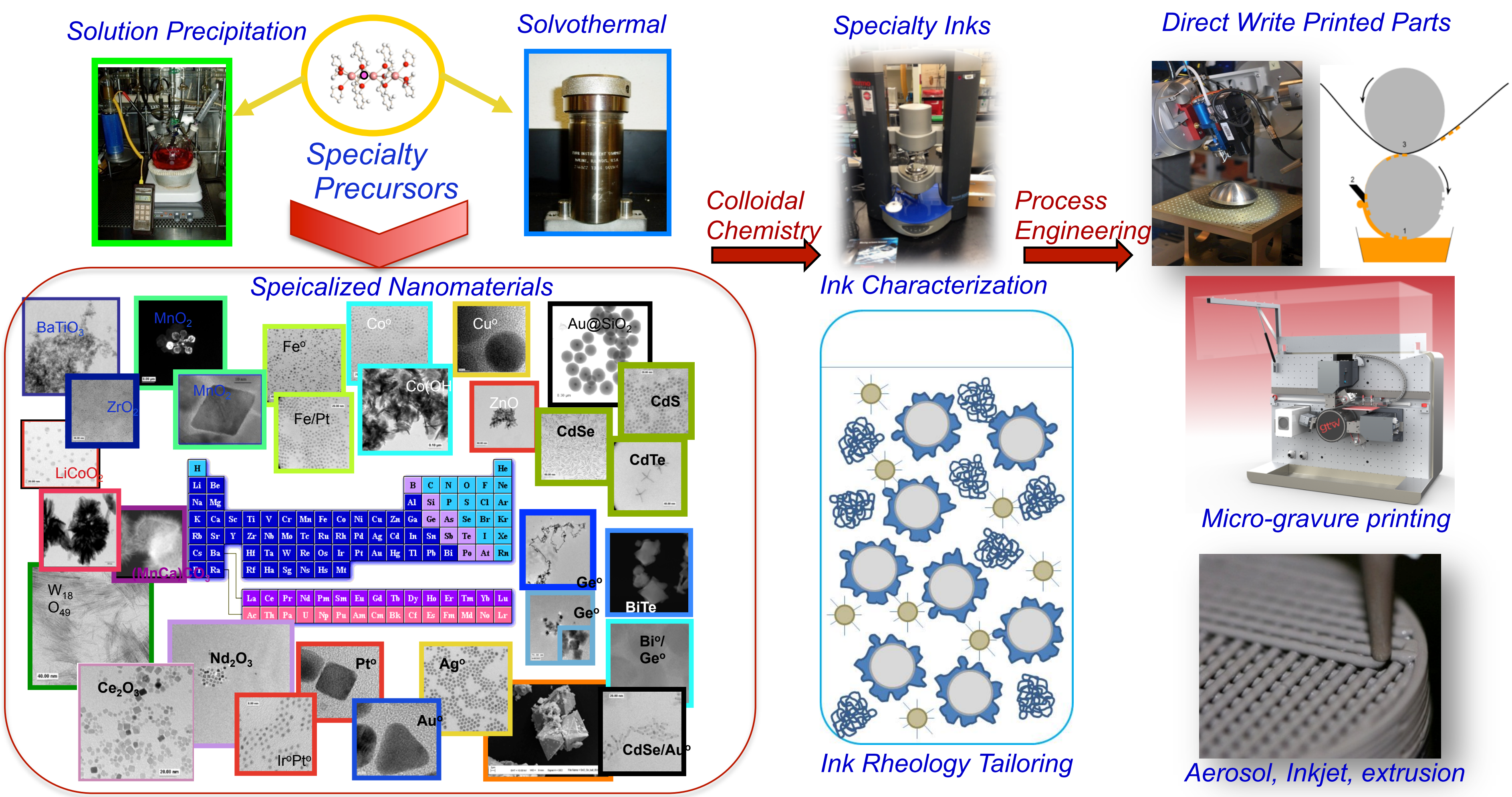
Template Fab.
-MESA
(UT partner)

NanoParticle Fab.
-Boyle et al., AML

Re evant, On oing Activities
-Fluc uating fluids
-Imprint, release
-Long range order
-filling at 30 nm

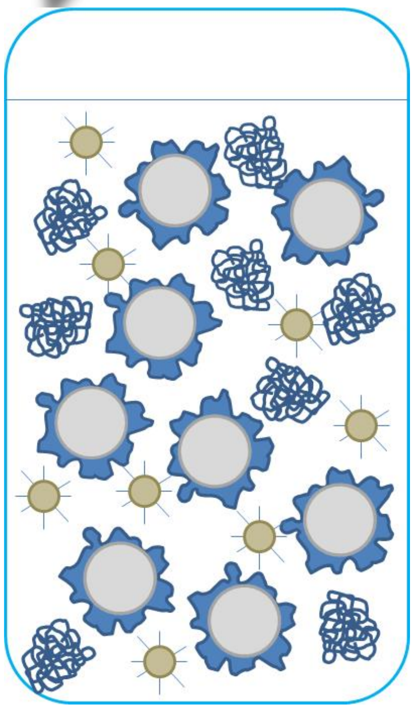
*Made practical by Pre-Processing to Concentrated form, before thermo takes over

From nano-materials to components at the AML



From specialized, tailored nano-materials to process-able inks requires chemical synthesis, colloidal chemistry, rheology/characterization, process engineering

Development of Ink Compositions for Printing



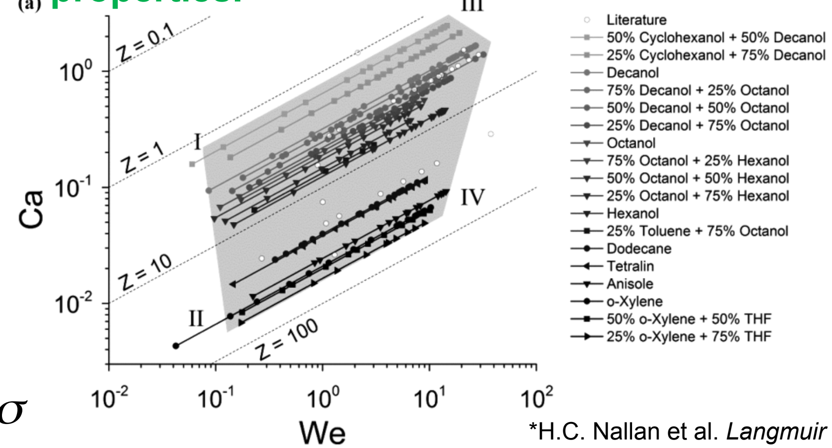
Ink Systems are formed from multiple components:

- Solvents (s), wetting agents, soluble polymers or micelles, & nanoparticle(s)
- Control over viscosity, surface tension, drying rate, and wetting are required.

$$Ca = \mu V/\sigma$$

$$We = \rho V^2 d/\sigma$$

A. Develop solvent compositions within the printing window of fluid properties.*



*H.C. Nallan et al. *Langmuir* **30** (2014) 13470.

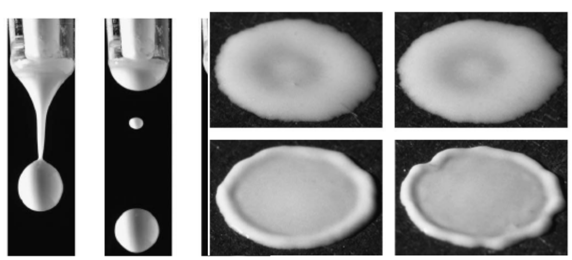
B. Effective dispersion is critical for printing using DOD or gravure/ flexo printers.

- Solids loading increased by proper dispersant choice, up to ~15-20%
- Surface tensions are low : between 15 – 40 mN/m
- Viscosity vary from 1-10 mPas.
- Surfactant concentrations tailored to surface area

$$\mu_{rel}=\mu_{\sigma\upsilon\sigma\pi}/\mu_{\sigma o\lambda}=(1-\phi/\phi_m)^{-n}$$

C. Adjust wetting and drying agents to minimize satellite drops and surface wetting concerns.

Dependent on surface interactions with substrate, and drying rate.



R. Guo et al. *JECerS* **23** (2003) 115-122.
X. Zhao, et al. *Ceram.Intl.* **29** (2003) 887-892.
N. Ramakrishnan, et al. J. Mat. Proc. Tech. 169 (2005) 372-381.
P.S.R. Krishna Prasad et al. *J. Mat. Proc. Tech.* **176** (2006) 222-229.

All experimental capabilities and SMEs exist at the AML!

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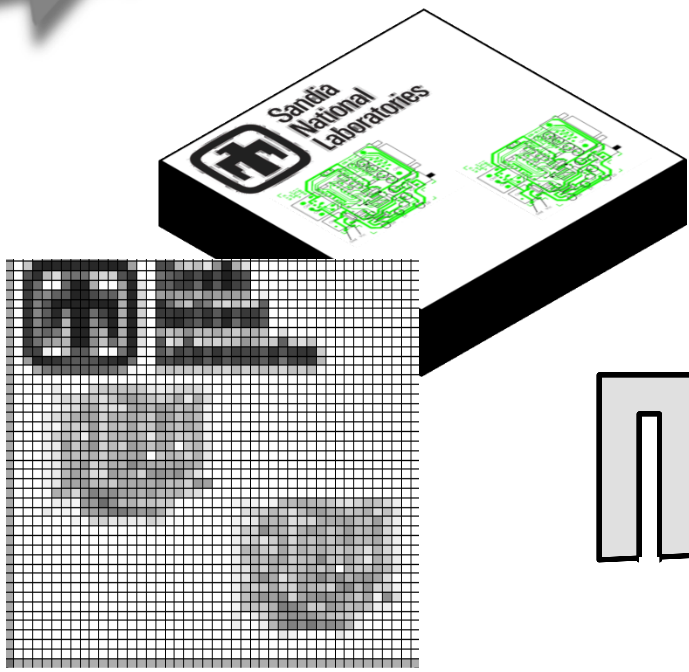
Bridging multiple scales

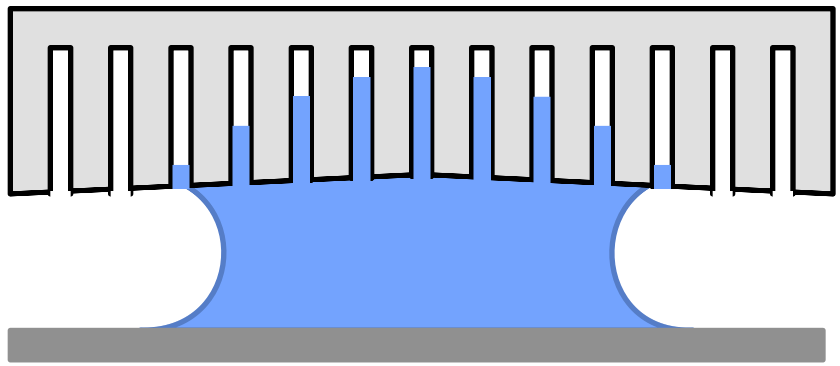
Important features:

- Six orders of magnitude difference in length scales
- Different physics at each scale



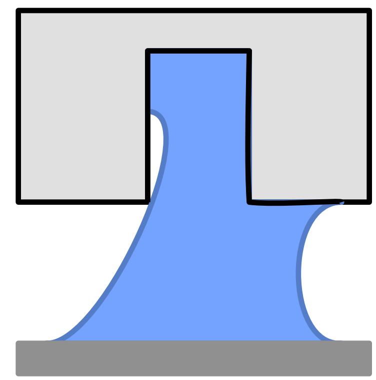
Machine-scale model

- 3-D Shell FEM
- Coarse-grained models
- Highly-parallel simulations
- 10 cm



Meso-scale model

- 3-D FEM
- Analytical model development
- Effective medium approach
- 1 µm



Feature Scale

- 3-D FEM
- Atomistics
- 10 nm

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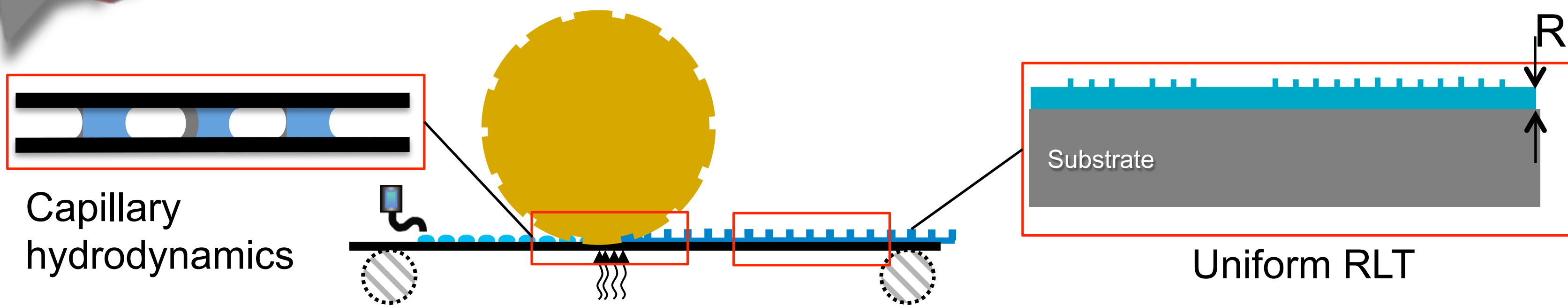
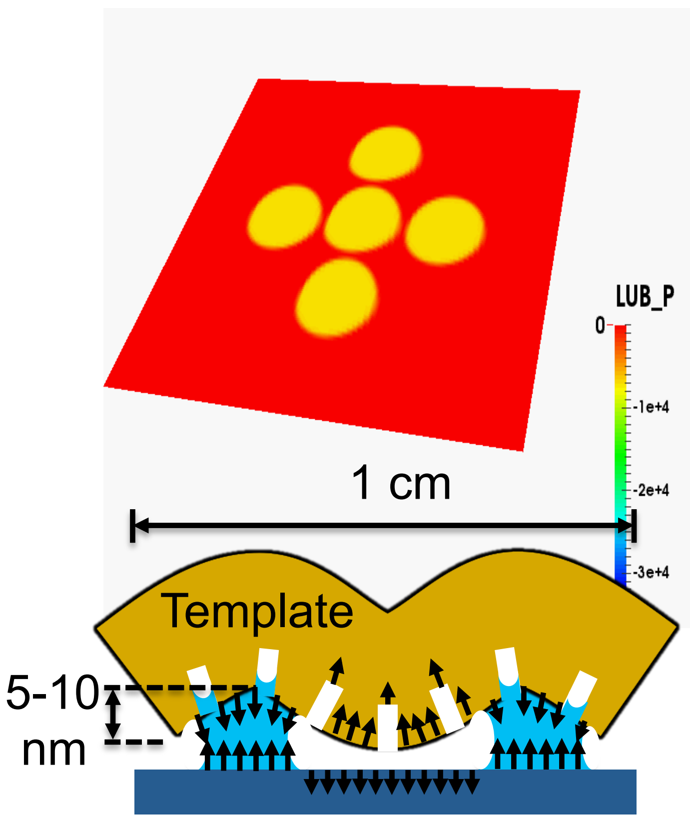
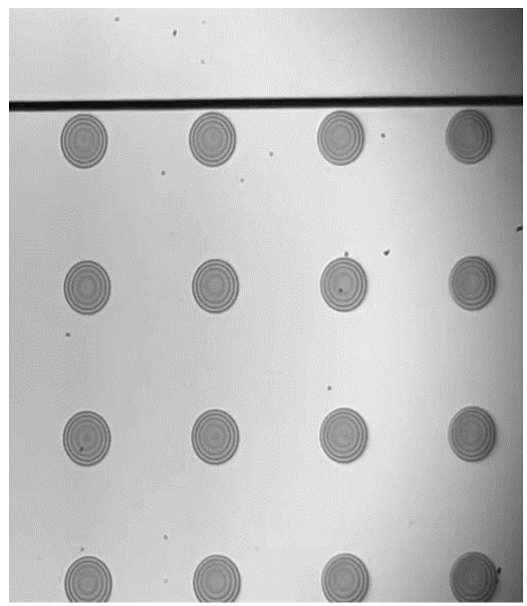
NIL: Gas and Structural Mechanics Matter!







Courtesy of Molecular Imprints and Dr. Shrawan Singhal, UT

Just like many high-speed, ultra-thin film coating systems

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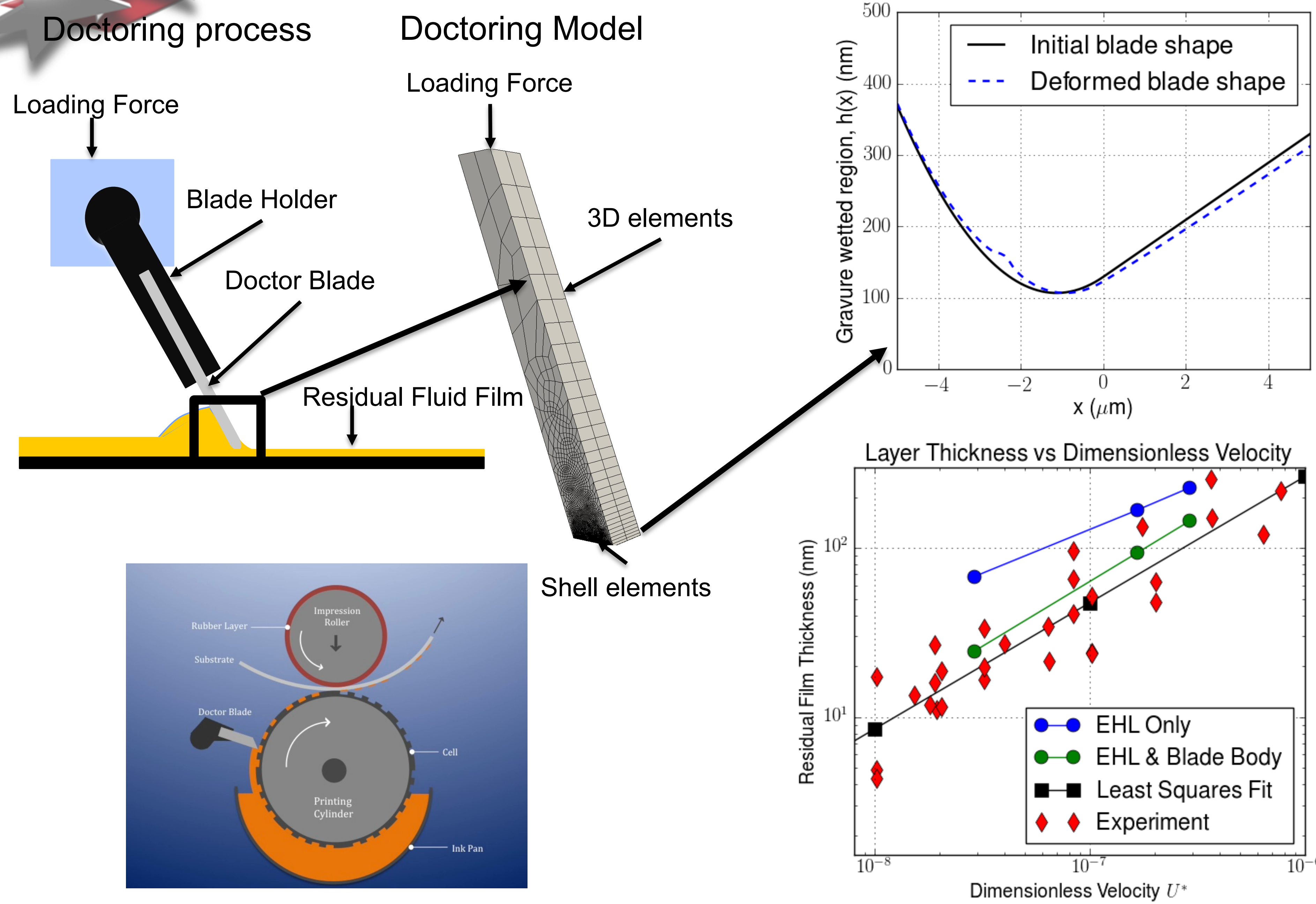
Doctoring in gravure printing



Summary & Future Work

- Micro-/Nano-replication in R2R remains topical:
  Unprecedented feature resolution (< 1 micron inks, <100 nm imprint) define the research challenges

- Printing (liquid-bridge or liquid drop transfer) and imprinting (mold filling and release) share common goals with thin liquid film coating
  Uniform film (RLT), material microstructure for intended properties, etc.

- Physical barriers to higher throughput and smaller features are rooted in
  - Capillary hydrodynamics
  - Wetting and spreading
  - Structural mechanics (thin sheet)
  - Metrology (on-line/at-line)
  - Colloidal dispersion dynamics
  - Solidification and microstructure

- The following presentations will address many of these barriers and challenges and then some (multilayer registration)