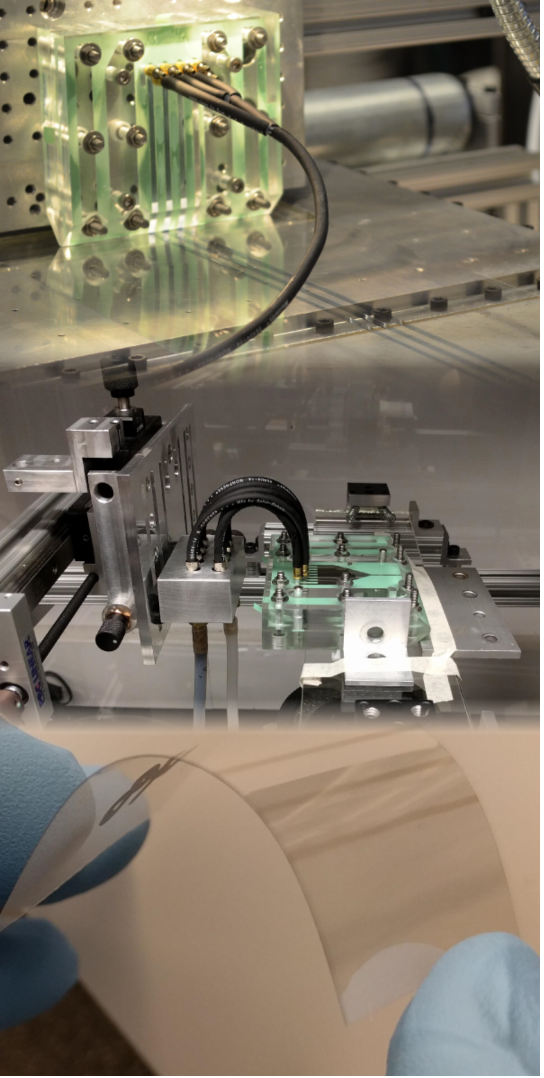


Science of Pattern Coating onto Heterogeneous Surfaces using a Hybrid Tool

Tequila A. L. Harris, Ph.D.

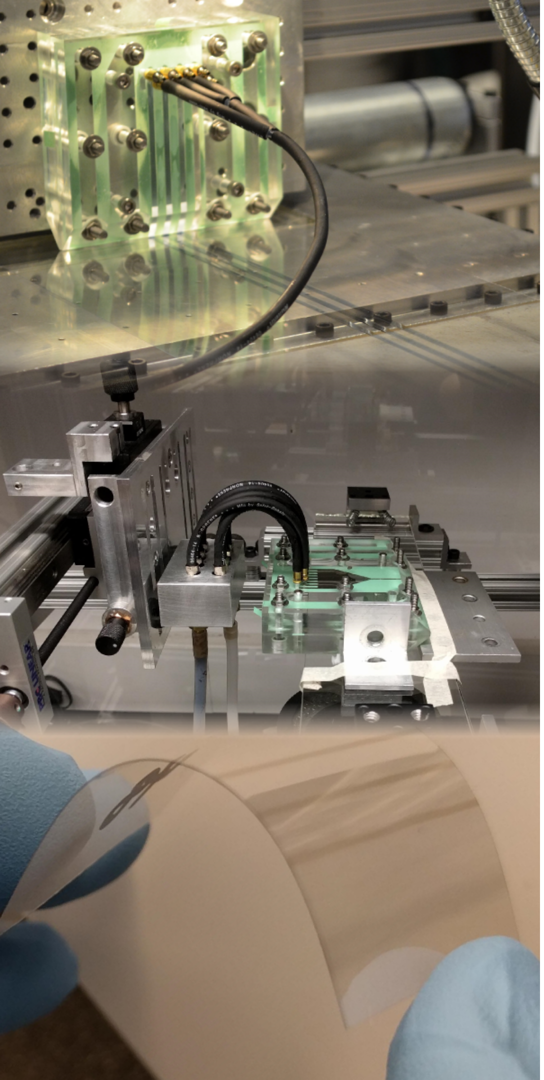
Polymer Thin Film Processing Group

Woodruff School of Mechanical Engineering

Georgia Institute of Technology

NSF

FLEX@TECH Flexible Electronics



Agenda

I. Brief Overview of Dr. Michael Varenberg's Group

II. Overview of the Harris Group

III. Background and motivation

IV. Objective

V. Materials and methods

   a. Materials

   b. Process platform and imaging setup

   c. Strategies for patterned film deposition

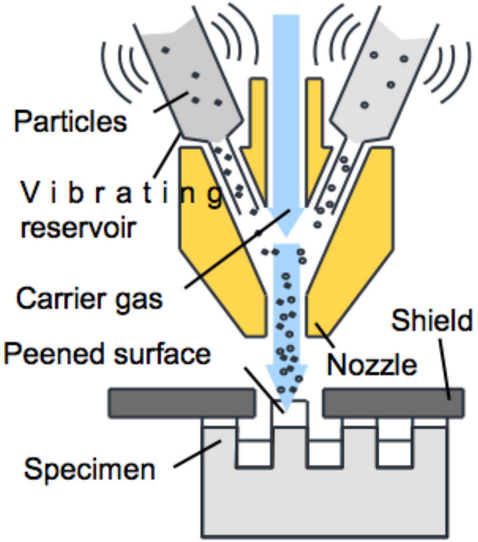
VI. Results

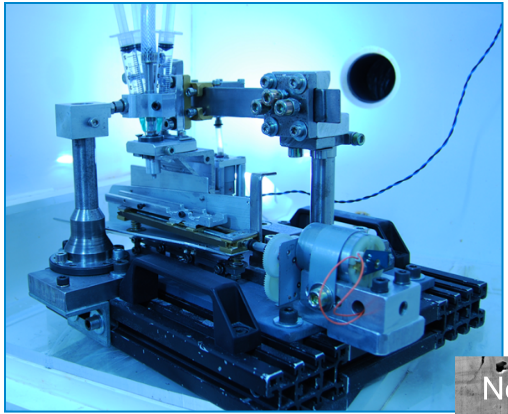
   a. Deposition flow of single coating liquid

   b. Deposition flow of two coating liquids

VII. Conclusions

Mechano-Chemical Surface Modification





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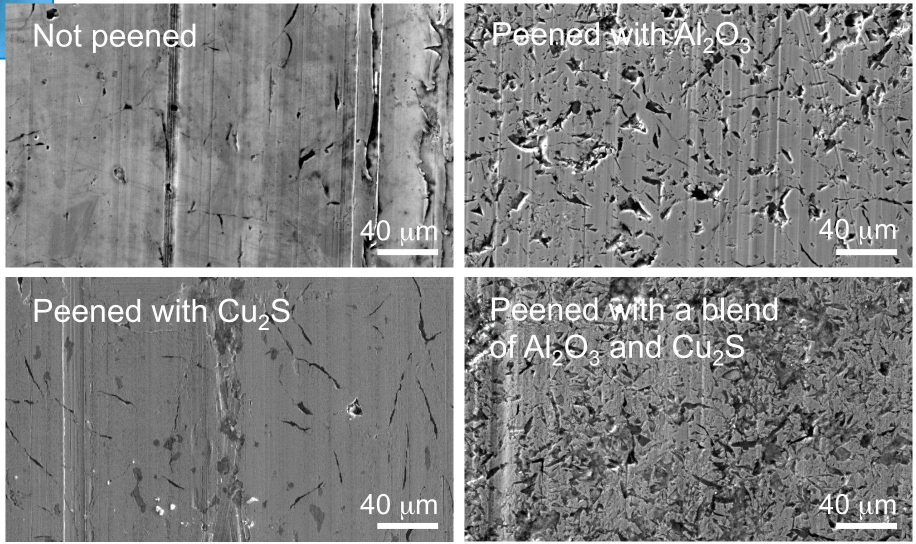
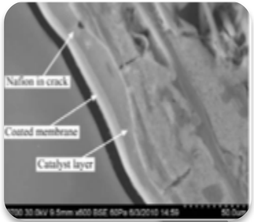


Treated surfaces: Ground cast iron
Shot peening media: Al_2O_3, size 44-75 μm, and Cu_2S, size <44 μm
Carrier gas: N_2, pressure 2 bar
Outcome: Cu_2S and Al_2O_3 = ultra low friction, high wear resistance and Superior lubricity.

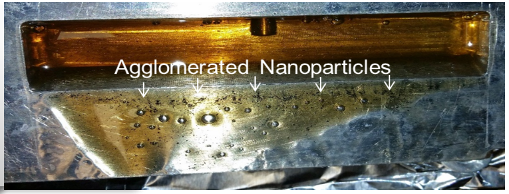
1. Varenberg, Ryk, Yakhnis, Kligerman, Kondekar and McDowell, Tribol. Lett. 64 (2016) 28

PTFP Group Research Themes

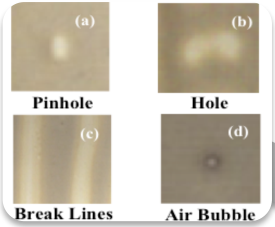


Direct Coating Porous Media

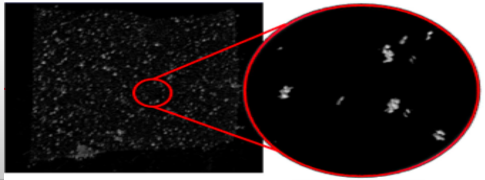
Fiber Modeling and CFD



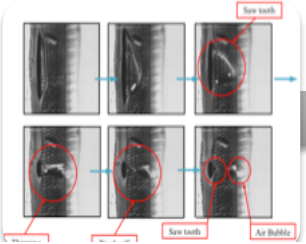
Particle Flow



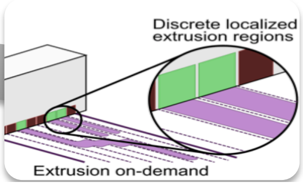
Defect Analysis



Particle Distribution



Wetting Phenomena



Novel / Advanced Manufacturing

Applications

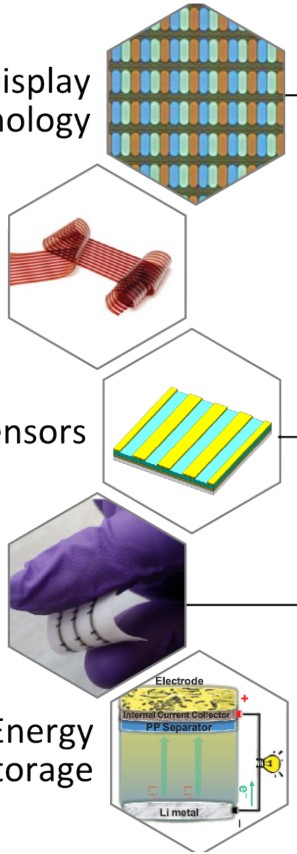
Display technology

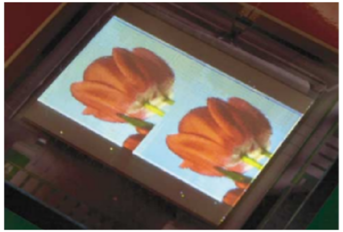
Photovoltaics

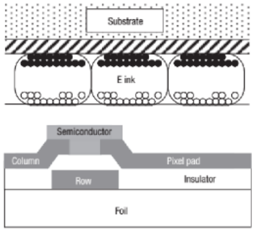
Sensors

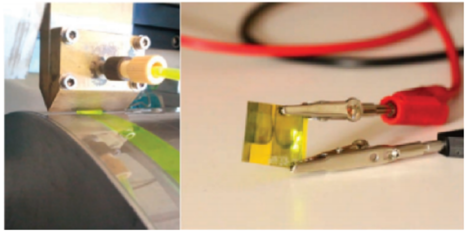
Wearables

Energy storage

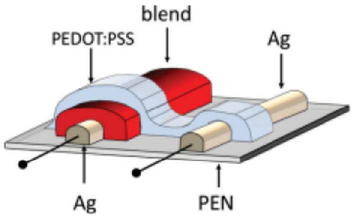


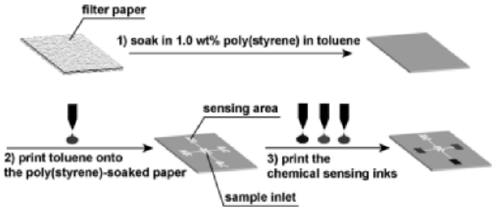




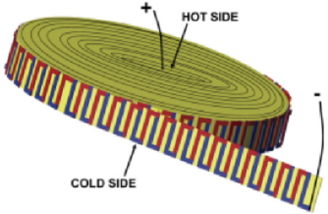


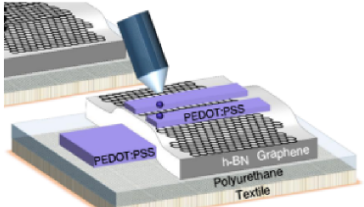
Forrest, S. R., *Nature* **2004.** Gelinck, G. H. et al. *Nat. Mater.* **2004**. Sandström, A. et al., *Nat. Commun.* **2012**.





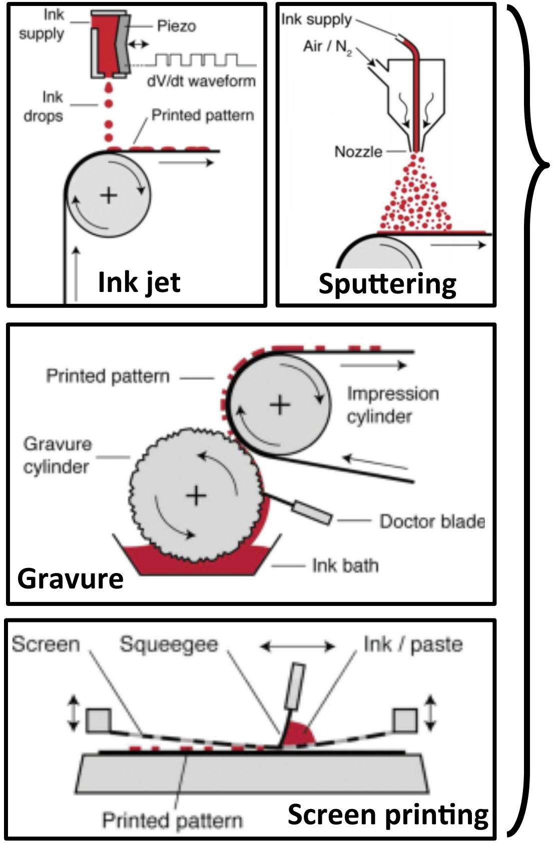
Azzellino, G. et al., *Adv. Mater.* **2013**. Abe, K.; Suzuki, K.; Citterio, D., *Anal. Chem.* **2008.**





Weber, J. et al., *Sens. Actuators, A* **2006**. Zhou, G. et al., *Adv. Mater.* **2015**. Carey, T. et al., *Nat. Comm.* **2017**.

Solution Processing Approach and Needs

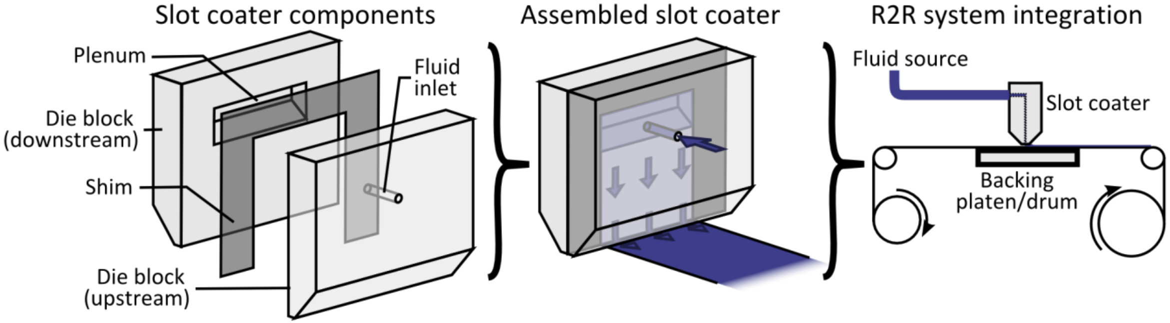


Recurring challenges:

- Mask/master-free patterning
- Material formulation
- Waste reduction
- Process complexity
- Tool clogging
- Scalability

Slot coating advantages:

- + Selective deposition
- + Broad viscosity range
- + Low waste
- + Wide-area



[1] Søndergaard, R. R.; Hösel, M.; Krebs, F. C., *J. Polym. Sci., Part B: Polym. Phys.* **2013**. [2] Krebs, F. C., *Sol. Energy Mater. Sol. Cells* **2009**.

Research objective

Objectives:

To develop and implement a slot coating-inspired approach for **heterogeneous micro-scale pattern features**, without subtractive steps, masks, or pre-patterning of the substrate, by studying the effects of liquid bridge behavior, fluid properties, and wetting and diffusion of one or more fluid species.

Key Questions:

1. What are the **physical mechanisms** enabling pattern formation?
2. How does the process drive and/or limit **material formulation**?
3. What physical limits exist on **minimum feature size**?

Materials – Fluids, Substrates, and Tooling

Coating fluids (Primary)

1. Polyvinyl alcohol (**PVA**), Mowiol® 4-88, aqueous solution
2. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (**PEDOT:PSS**), Clevios™ PH1000 doped with 1% Triton X-100 and 6% ethylene glycol

Coating fluids (Secondary)

3. Polydimethylsiloxane (**PDMS**)
4. **Glycerol**, 95% aqueous solution
5. Vacuum pump oil (**VPO**), KMP Corp. L340

Solid phases

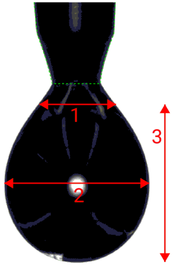
6. Polyethylene terephthalate (**PET**), film substrate and shim stock
7. Polymethyl methacrylate (**PMMA**)

Materials – Rheology and Wetting

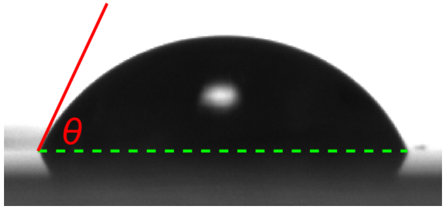
Material	μ (cP)	σ (mN/m)	θ on PET film (°)	θ on cast PMMA (°)
PVA (10% aq.)	29	44	56	59
PVA (15% aq.)	107	43	58	62
PVA (20% aq.)	392	42	60	65
PVA (24% aq.)	1057	42	--	--
PDMS	970	20	--	--
PEDOT:PSS	29	32	17	17
Glycerol	400	63	--	--
[illegible]	64	31	--	--

Viscosity

Surface tension (σ)

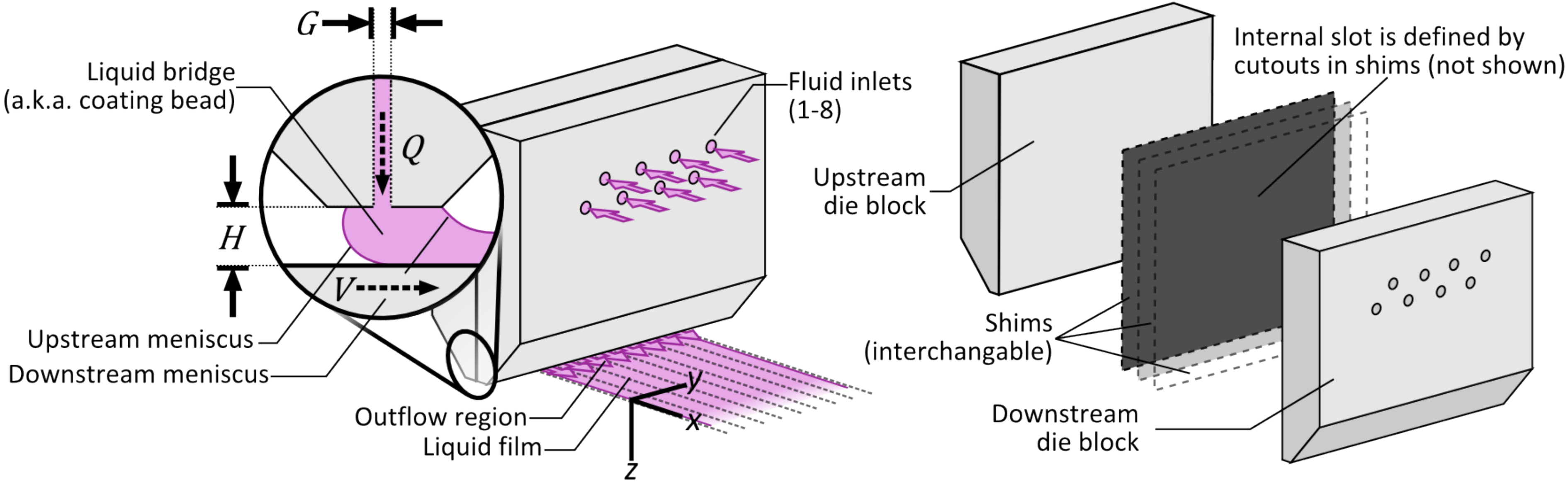


Contact angle (θ)



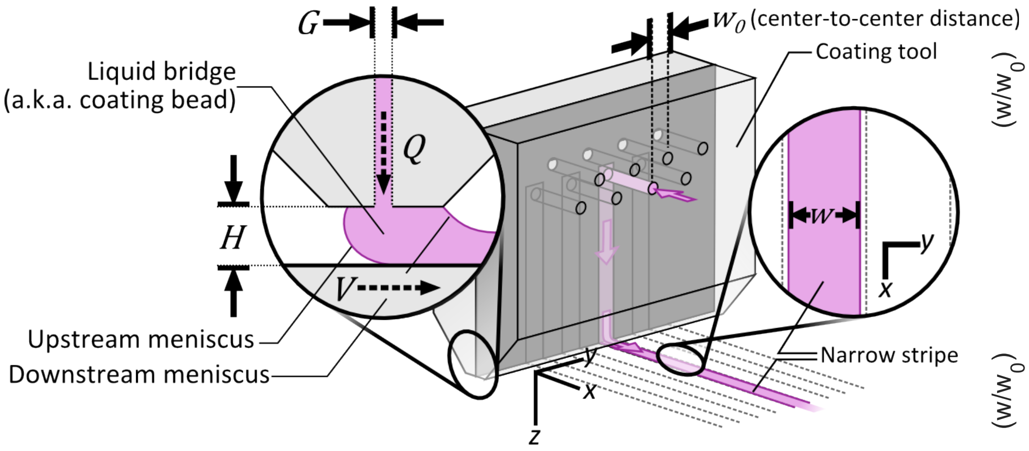
Methods: Slot coating tool and techniques

- Multiple inlet ports can accept multiple coating fluid species (some can be unused)
- Shims with cutouts implement internal geometry (multiple shims can be used)
- Localized outflow regions can be actuated independently



[1] Parsekian, A. W. and Harris, T. A. L., US Provisional Patent Application No. 62/593,323 (2017)

Process control – one fluid phase



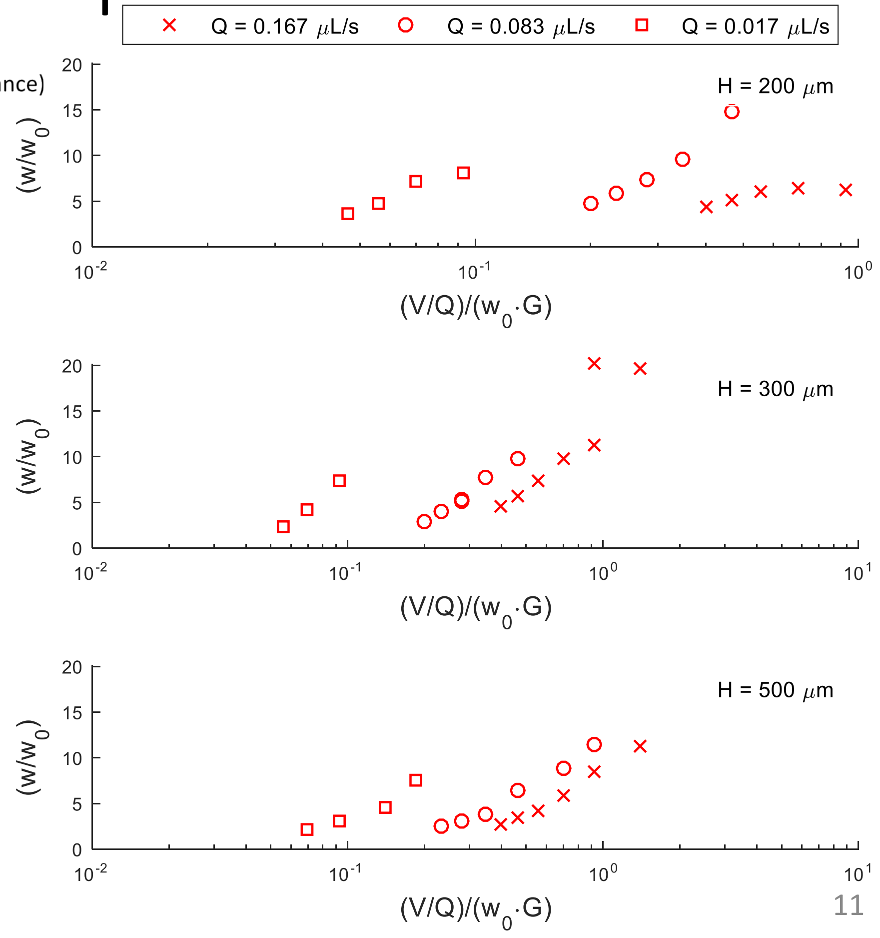
Coating fluid:

Polyvinyl alcohol (PVA), 10% aqueous

(ρ = 1.023 g/mL μ = 26 cP, σ = 44 mN/m)

Parameters:

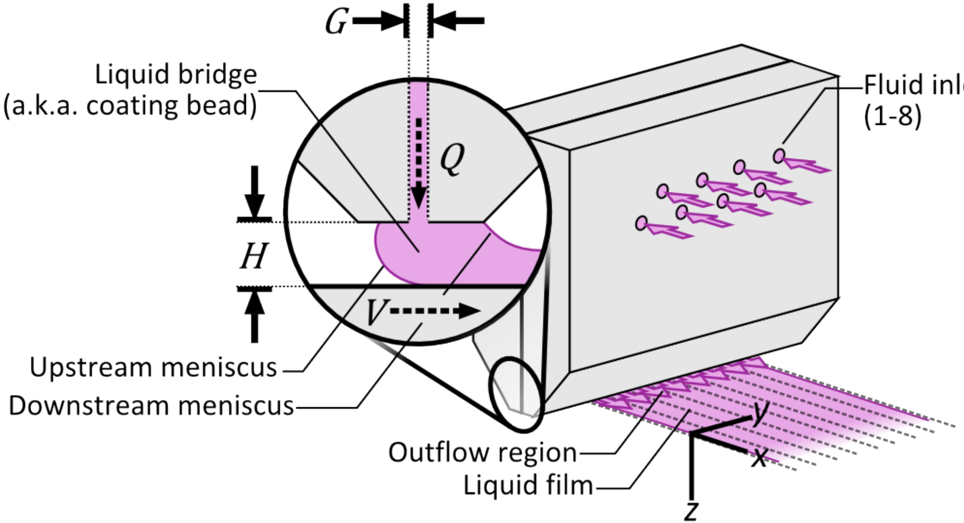
Q	volumetric flow-rate	G	slot gap
V	substrate velocity	w_0	slot width
H	coating gap	w	width of coated stripe



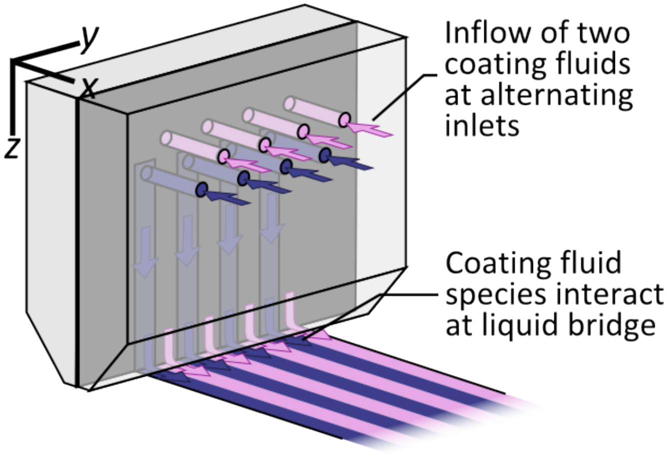
Parsekian and Harris, *Chem. Eng. Proc.* **109**, 2016.

Slot coating tool for alternating-stripe patterns

- Localized outflow regions correspond to an array of inlets
- Internal geometry manipulates flow for each inlet-outlet pair, and assists feature size scaling
- Flow through each inlet can be sourced independently, or left unused



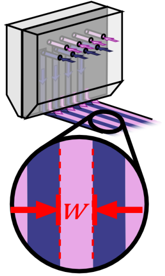
Slot coating tool – processing parameters



Alternating-stripe coating configuration

[1] Parsekian, A. W. and Harris, T. A. L., US Provisional Patent Application No. 62/593,323 (2017)

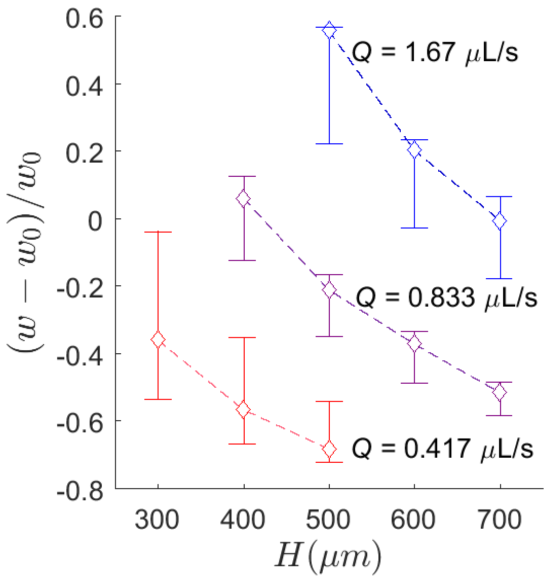
Process control – Two Fluid Phases

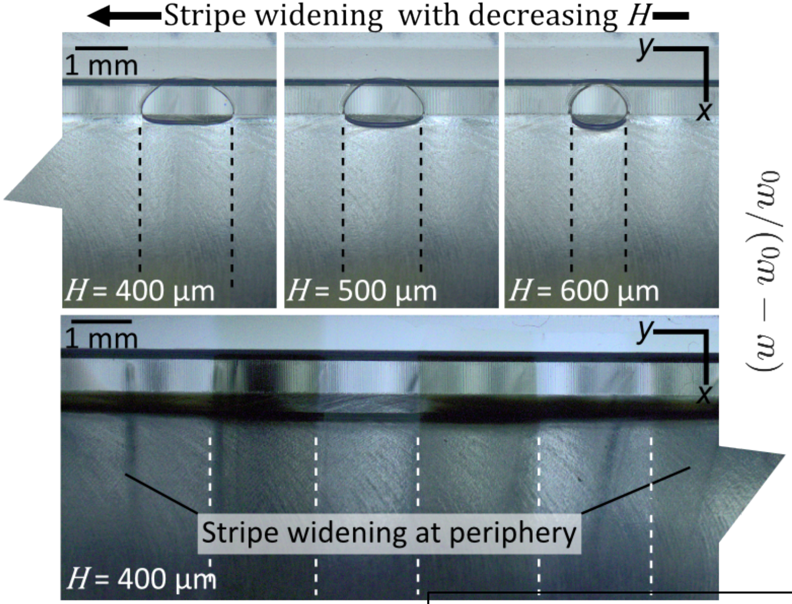


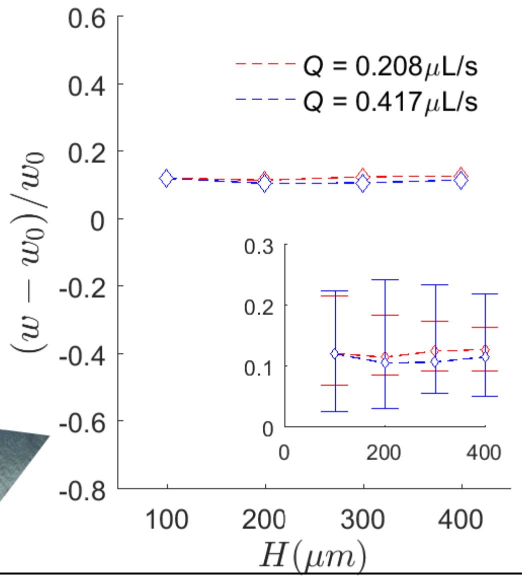
Coating fluids: PVA, 10% aqueous (transparent) and with >2% dye added (dark)

Single coating fluid (separate coating beads)

Two coating fluids (interaction within coating bead)





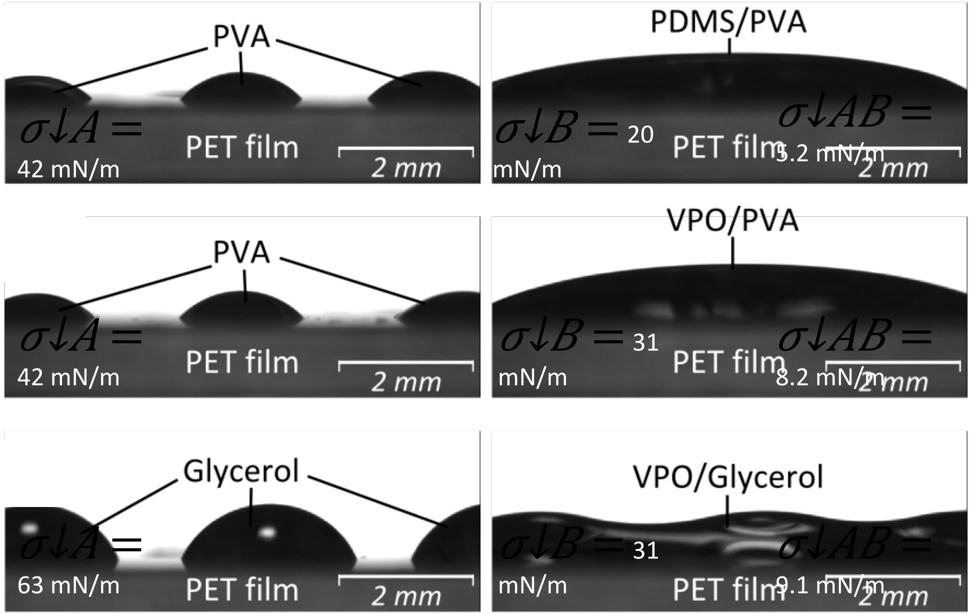


Coating fluids:

1. Polyvinyl alcohol (PVA), 10% aqueous (transparent)
2. PVA, 10% aqueous, with >2% dye added (dark)

Wetting transition in immiscible stripes

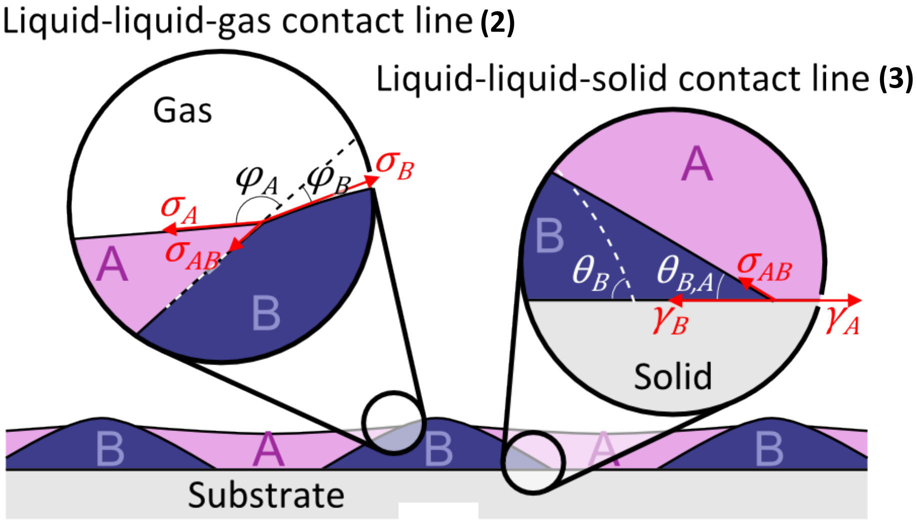
Single coating fluid | **Interacting immiscible fluids**



$$0 = \sigma_{AB} - \sigma_A \cos\varphi_A + \sigma_B \cos\varphi_B \quad \text{(1a)}$$

$$0 = \sigma_A \sin\varphi_A - \sigma_B \sin\varphi_B \quad \text{(1b)}$$

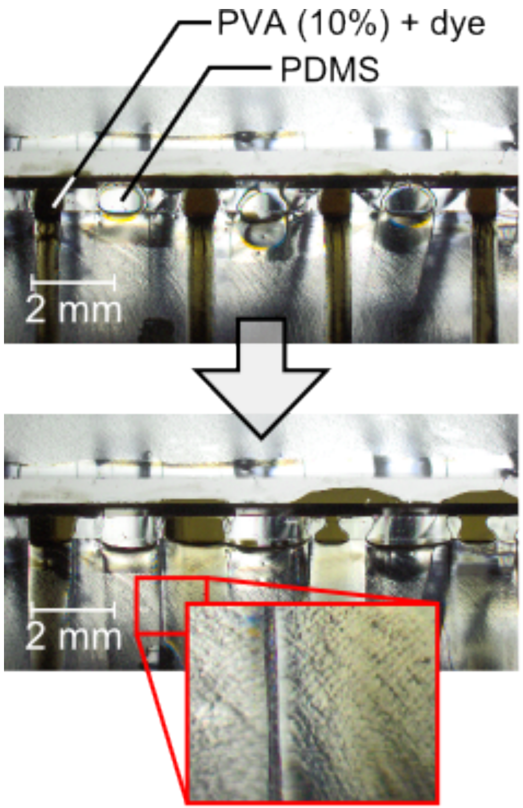
$$0 = -\gamma_A + \gamma_B + \sigma_{AB} \cos\theta_{B,A} \quad \text{(2)}$$



Liquid phases:

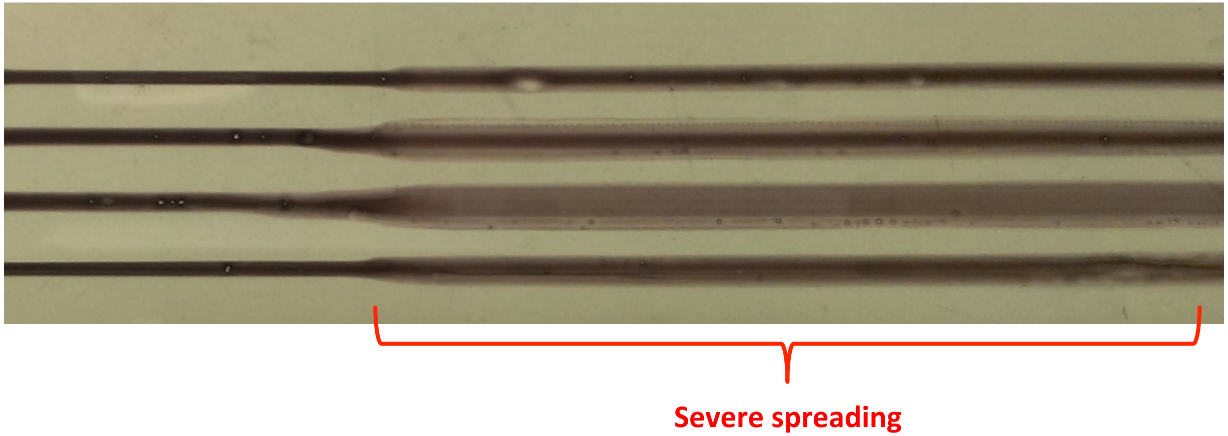
- PVA – Polyvinyl alcohol (PVA), 24% aqueous
- PDMS – Polydimethylsiloxane
- VPO – Vacuum pump oil L430

Wetting transition for immiscible fluid phases

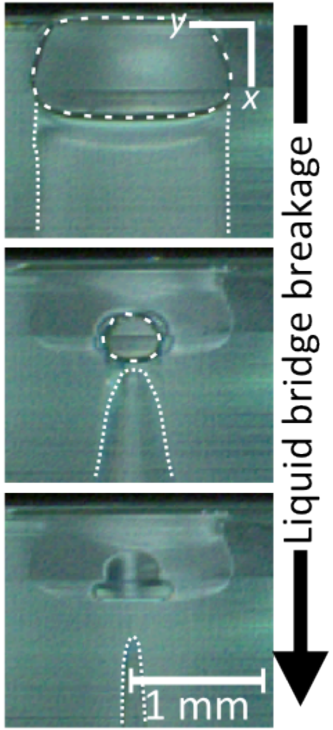


Coating fluids:

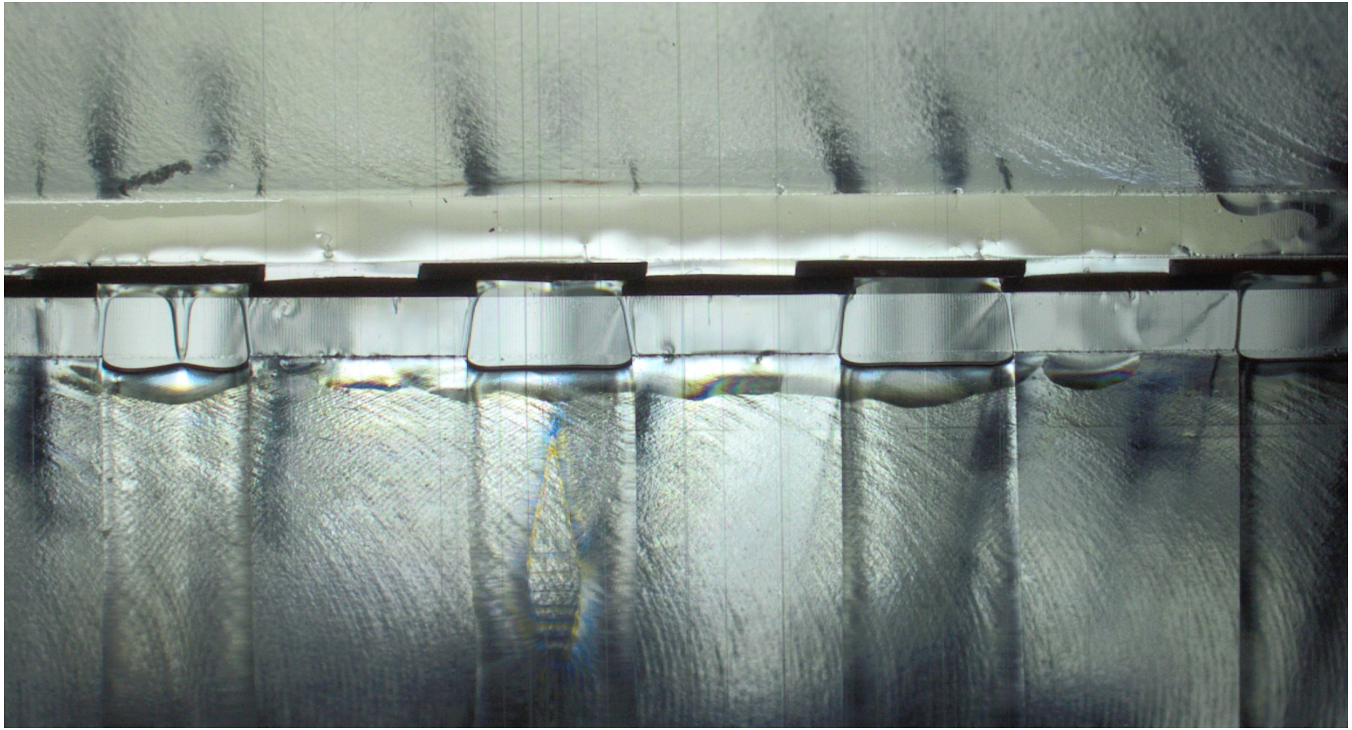
1. Polydimethylsiloxane (PDMS)
2. Polyvinyl alcohol (PVA), 24% aqueous, with >2% dye added



Feature size limitation for single fluid phase



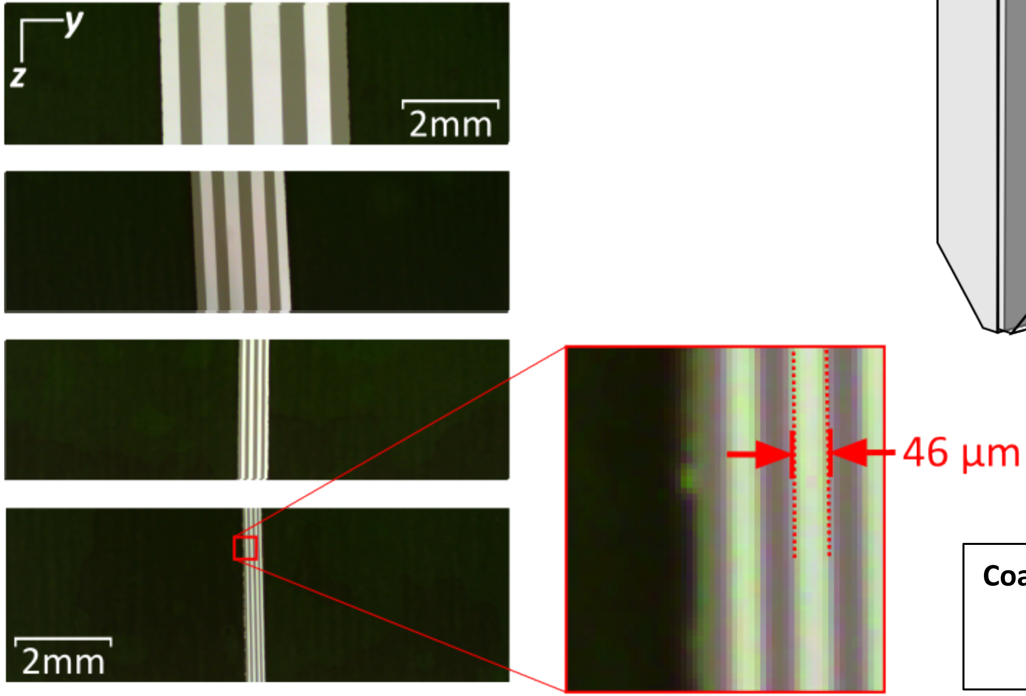
[1]

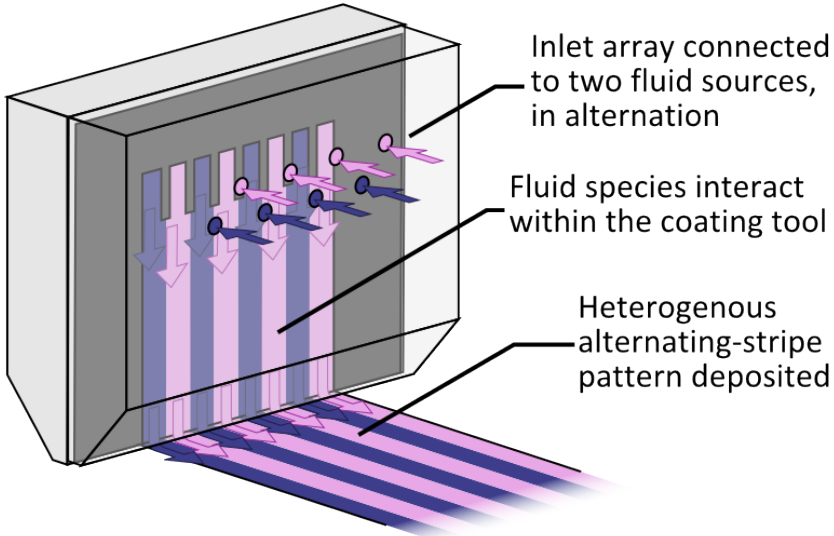


Liquid bridge breakup event defines a minimum feature size (w_{crit}) for narrow-stripe slot coating

[1] Parsekian and Harris, *Chem. Eng. Proc.* **109**, 2016.

Feature size improvement with two fluids



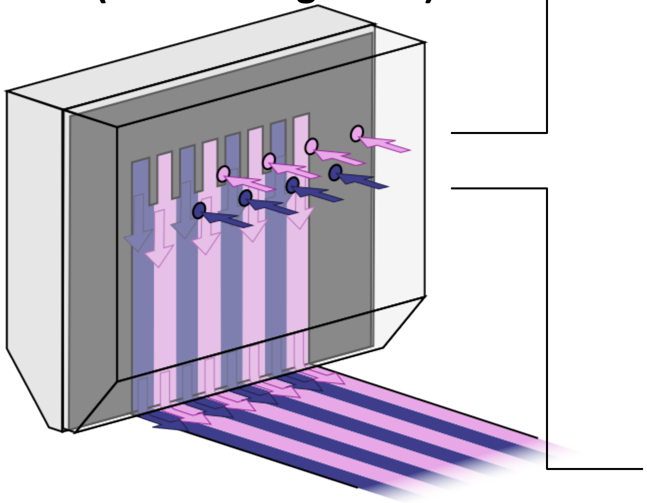


Slot coating tool

Coating fluids:
1. Polyvinyl alcohol (PVA), 10% aqueous (light)
2. PVA, 10% aqueous, with >2% dye added (dark)

Conclusions

Alternating-stripe slot coating (two coating fluids)



Material formulation

- De-wetting issues mitigated
- Miscibility of coating fluids required to circumvent unique wetting issue
- Mixing phenomena must be minimized to ensure pattern fidelity

Process capability

- Independent control over pattern geometry (stripe width and spacing), and film thickness
- Micro-scale pattern features demonstrated

Acknowledgements

National Science Foundation (NSF) for
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Peter Griffiths

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Bethany Tate
Undergraduate

Yuhan Xiao
Undergraduate

References

1. Forrest, S. R., The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* **2004,** *428* (6986), 911-918.
2. Gelinck, G. H.; Huitema, H. E. A.; van Veenendaal, E.; Cantatore, E.; Schrijnemakers, L.; van der Putten, J. B. P. H.; Geuns, T. C. T.; Beenhakkers, M.; Giesbers, J. B.; Huisman, B.-H.; Meijer, E. J.; Benito, E. M.; Touwslager, F. J.; Marsman, A. W.; van Rens, B. J. E.; de Leeuw, D. M., Flexible active-matrix displays and shift registers based on solution-processed organic transistors. *Nat. Mater.* **2004,** *3* (2), 106-110.
3. Sandström, A.; Dam, H. F.; Krebs, F. C.; Edman, L., Ambient fabrication of flexible and large-area organic light-emitting devices using slot-die coating. *Nat. Commun.* **2012,** *3*, 1002.
4. Azzellino, G.; Grimoldi, A.; Binda, M.; Caironi, M.; Natali, D; Sampietro, M., Fully Inkjet-Printed Organic Photodetectors with High Quantum Yield. *Adv. Mater.* **2013**, *25,* 6829–6833.
5. Abe, K.; Suzuki, K.; Citterio, D., Inkjet-Printed Microfluidic Multianalyte Chemical Sensing Paper. *Anal. Chem.* **2008,** *80* (18), 6928-6934.
6. Weber, J.; Potje-Kamloth, K.; Haase, F.; Detemple, P.; Völklein, F.; Doll, T., Coin-size coiled-up polymer foil thermoelectric power generator for wearable electronics. *Sens. Actuators, A* **2006,** *132* (1), 325-330.
7. Zhou, G.; Li, L.; Wang, D.-W.; Shan, X.-y.; Pei, S.; Li, F.; Cheng, H.-M., A flexible sulfur-graphene-polypropylene separator integrated electrode for advanced Li–S batteries. *Adv. Mater.* **2015,** *27* (4), 641-647.
8. Carey, T.; Cacovich. S.; Divitini, G.; Ren, J.; Mansouri, A.; Kim, J. M; Wang, C.; Ducati, C.; Sordan, R.; Torrisi, F., Fully inkjet-printed two-dimensional material field effect heterojunctions for wearable and textile electronics. *Nat. Comm.* **2017**, *8*, 1202.

References (Continued)

9. Søndergaard, R. R.; Hösel, M.; Krebs, F. C., Roll-to-Roll fabrication of large area functional organic materials. *J. Polym. Sci., Part B: Polym. Phys.* **2013,** *51* (1), 16-34.
10. Krebs, F. C., Fabrication and processing of polymer solar cells: A review of printing and coating techniques. *Sol. Energy Mater. Sol. Cells* **2009,** *93* (4), 394-412.
11. Wen, S.-H.; Liu, T.-J., Extrusion die design for multiple stripes. *Polym. Eng. Sci.* **1995,** *35* (9), 759-767.
12. Zhang, J.; Zhao, Y.; Fang, J.; Yuan, L.; Xia, B.; Wang, G.; Wang, Z.; Zhang, Y.; Ma, W.; Yan, W.; Su, W.; Wei, Z., Enhancing Performance of Large-Area Organic Solar Cells with Thick Film via Ternary Strategy. *Small* **2017,** *13* (21), 1700388
13. Lin, C.-F.; Wang, B.-K.; Lo, S.-H.; Wong, D. S.-H.; Liu, T.-J.; Tiu, C., Operating windows of stripe coating. Asia-Pac. J. Chem. Eng. 2014, 9 (1), 134-145.
14. Choinski, E. J. Method and apparatus for patch coating printed circuit boards. US Patent 4 938 994, July 3, 1990, 1990.
15. Schmitt, M.; Scharfer, P.; Schabel, W., Slot die coating of lithium-ion battery electrodes: investigations on edge effect issues for stripe and pattern coatings. *J. Coat. Technol. Res.* **2014,** *11* (1), 57-63.
16. Parsekian, A. W.; Harris, T. A. L., Extrusion on-demand pattern coating using a hybrid manufacturing process. *Chem. Eng. Process.* **2016,** *109*, 20-31.
17. T.A.L. Harris, B. Brown, Patent US 2014/0186530 A1, **2014**.
18. A. W. Parsekian, T. A. L. Harris., Patent Application US 62/593,323, **2017**.

Thank you
for your attention!

Publications

Journal Articles

1. Parsekian, A. W.; Harris, T. A. L., Extrusion on-demand pattern coating using a hybrid manufacturing process. Chem. Eng. Process. 2016, 109, 20-31.
2. Parsekian, A. W.; Harris, T. A. L., Multi-Material Patterning Using a Coating/Extrusion-on-Demand Technique: Role of Miscibility in Alternating-Stripe Films. *In preparation*

Conference Presentations

3. Parsekian, A. W.; Harris, T. A. L., Extrusion-on-Demand of Patterned Flims. *Presented at ASME International Converence on Nanochannels, Microchannels, and Minichannels*, Washington, DC, July 10–14, 2016.
4. Parsekian, A. W.; Harris, T. A. L., Extrusion Method for 2D-Patterned Films. *presented at 18th International Coating Science and Technology Symposium*, Pittsburgh, PA, September 28–21 , 2016.
5. Parsekian, A. W.; Harris, T. A. L., Hybrid Additive Process for Slot Coating of Alternating-Stripe Films, *presented at 2017 FLEX,* Monterey, CA, June 19–22, 2017

Patents

6. Parsekian, A. W. and Harris, T. A. L., US Provisional Patent Application No. 62/593,323 (2017)