Week 1-13

Thin Film Deposition, Processing and Patterning

Deposition from vapor (continued) & solution
Post-growth processing (annealing)
Device patterning

Chapter 5.4.2.4 - 5.6 (except 5.6.4)

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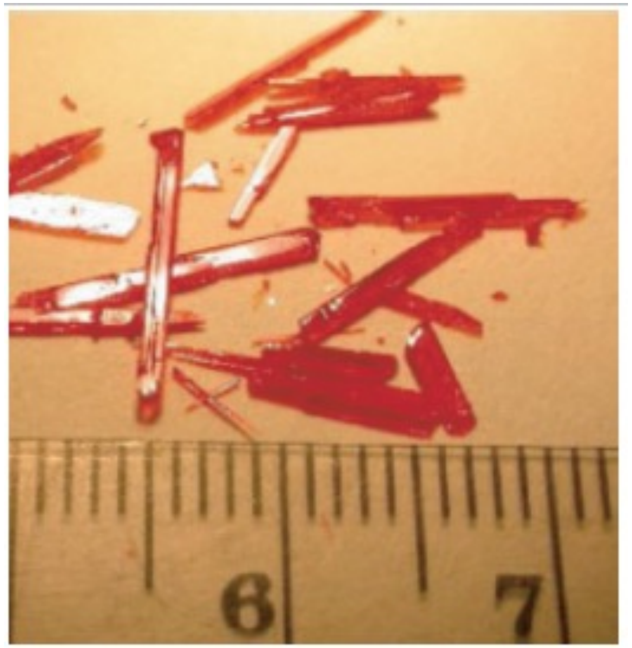
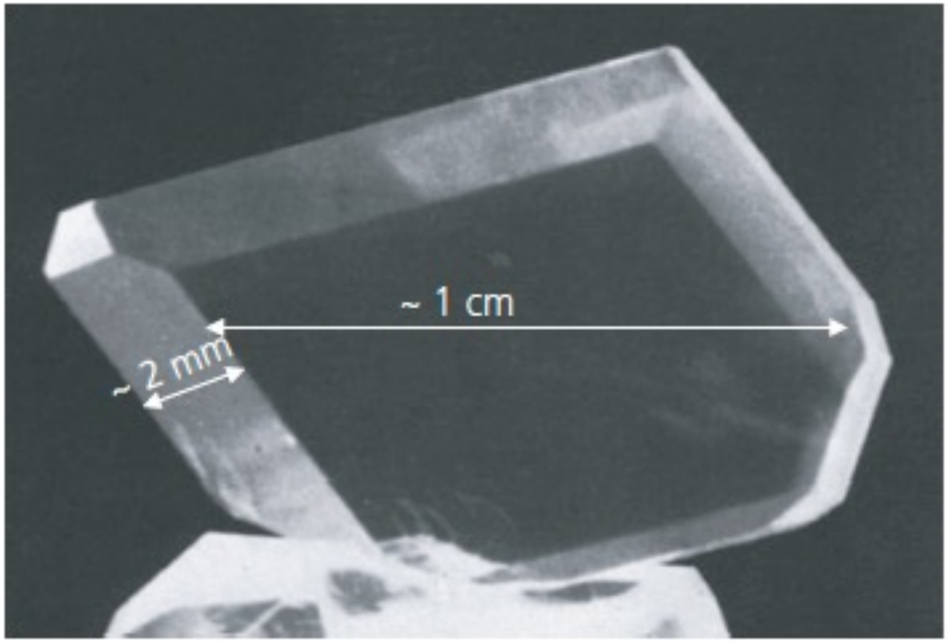
Crystal Platelets Grow on Cold Chamber Walls Via OVPD

- Same phenomenon as found in thermal gradient sublimation
- Sometimes called ”plate sublimation”



rubrene



pyrene

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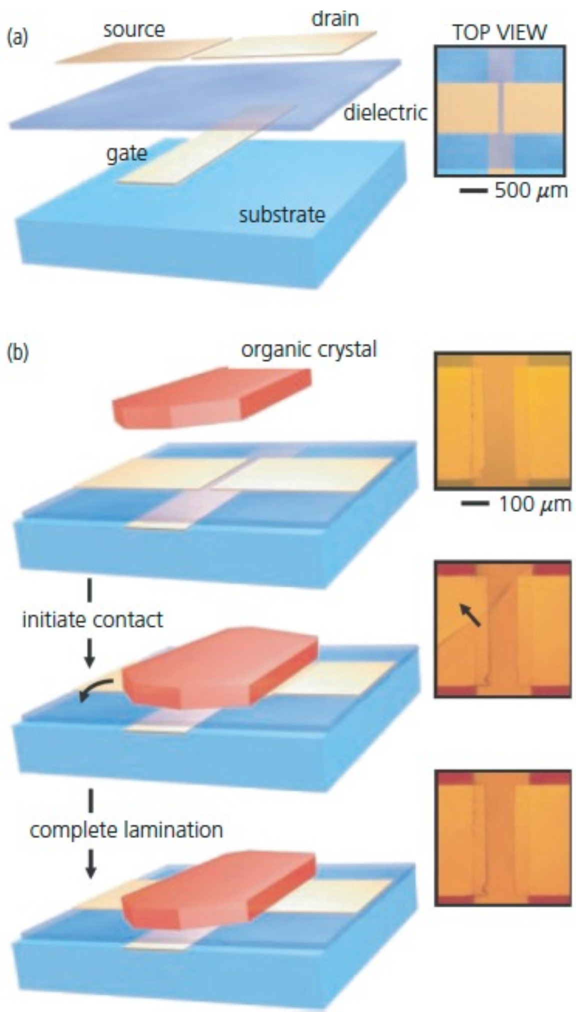
de Boer et al. Phys. Stat. Sol. (a) 201 1302 (2004)

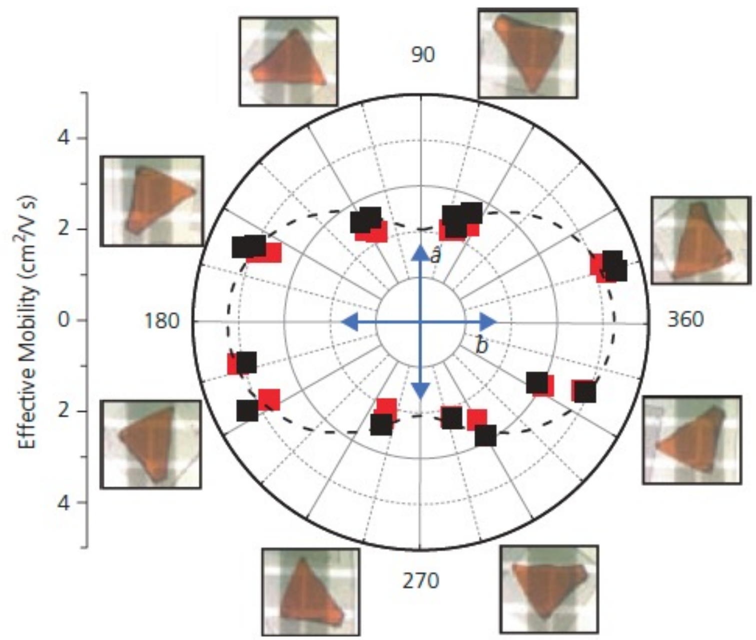
Karl, *Organic Crystals*, Springer (1980)

Single Crystal Platelets Exhibit Anisotropies Characteristic of Organics

Fabrication of OTFT by placing platelet on S and D contacts



Mobility depends on crystal direction



Sundar et al., Science 303, 1644 (2004).

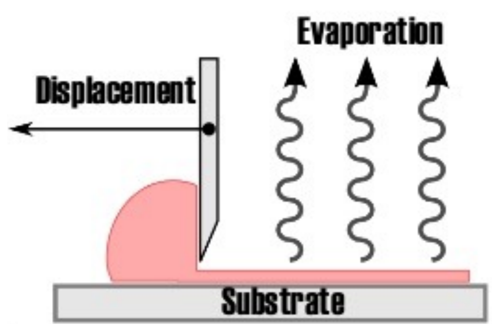
Solution Deposition: Common Methods

Drop fluid onto spinning substrate:
Excess fluid thrown off

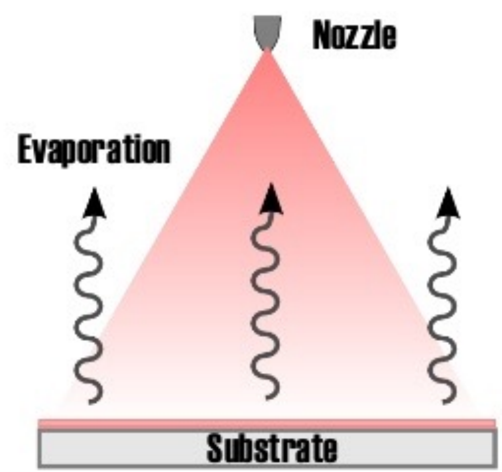
Evaporation rate = spin-off rate

Evaporation rate > spin-off rate: Film deposition complete

Spin-on

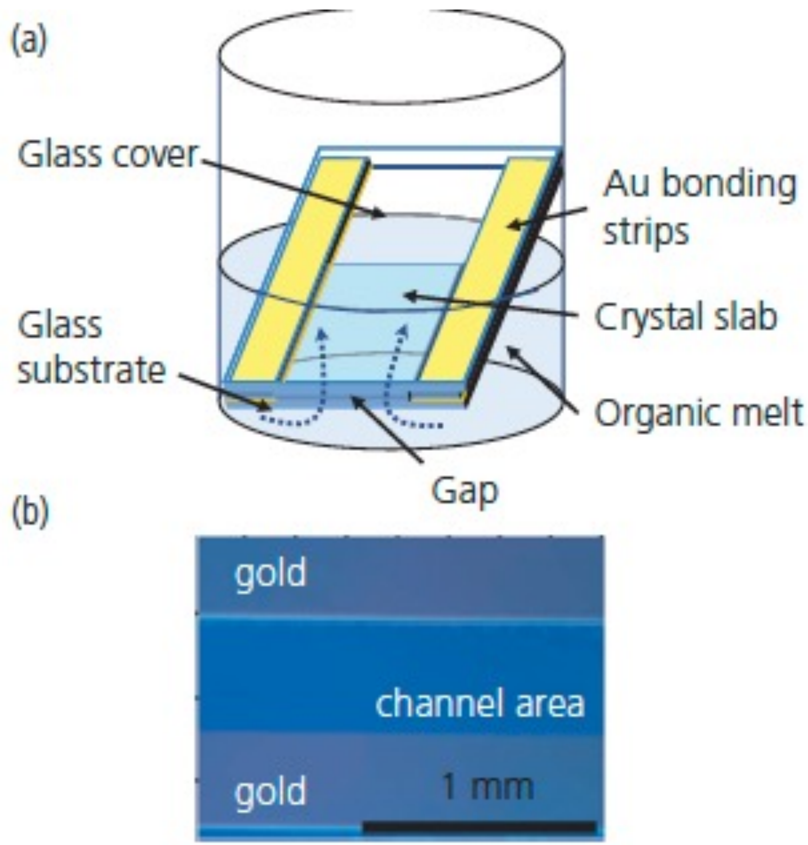


Doctor blade (Spread-on)



Spray-on

Large single crystal growth from solution



- Organic dissolved in solution
- Drawn into gap between two glass plates by capillary action
- Solution slowly evaporates leaving crystal slab between plates
- Nucleation along gold spacers used to bond plates results in single crystal growth
- If evaporation too fast, polycrystallites form

Anthracene single crystal in channel

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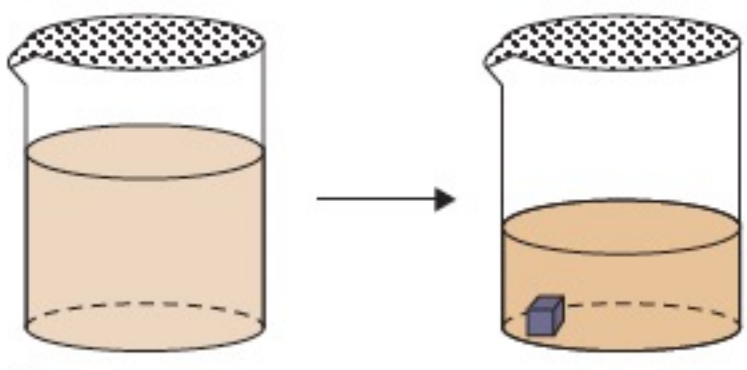
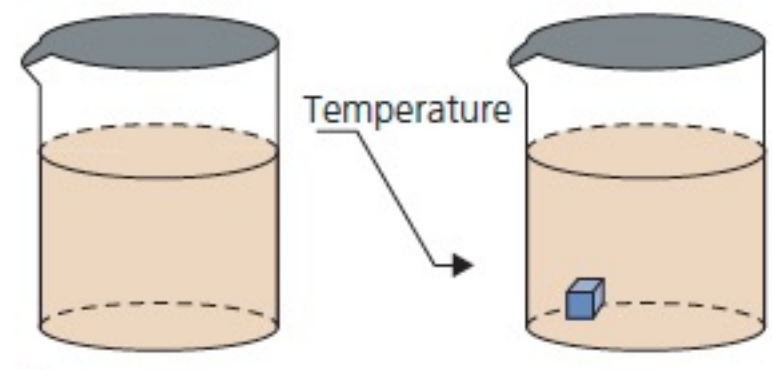
Kéna-Cohen et al. Phys. Rev. Lett., 101, 116401 (2008)

Crystalline Growth from Solution

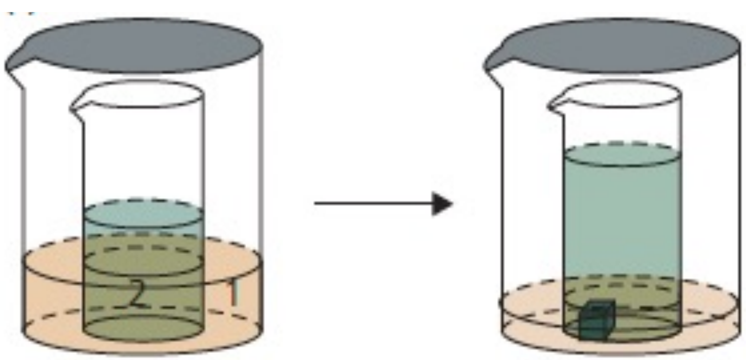
Four methods that result in supersaturation of the solute in the solvent, forcing crystallization



solvent evaporation

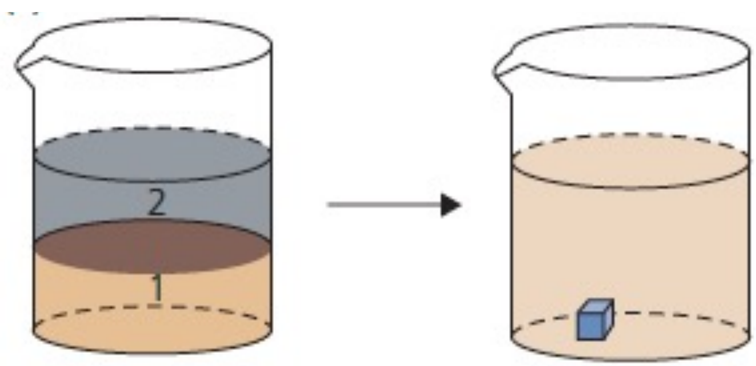


temperature reduction



vapor diffusion

- Source highly soluble in low volatility solvent 2
- Less soluble in high volatility solvent 1
- Solvent 1 concentration increases in inner ampoule, resulting in supersaturation



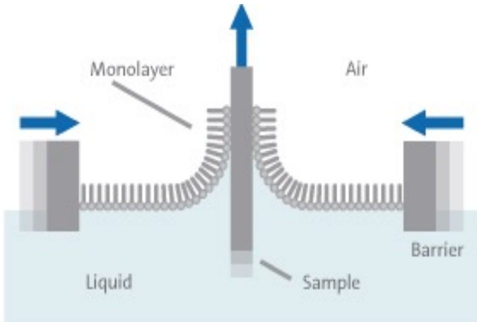
liquid interdiffusion

- Source highly soluble in solvent 2
- Less soluble in solvent 1
- Solvent 1 & 2 interdiffuse until supersaturation

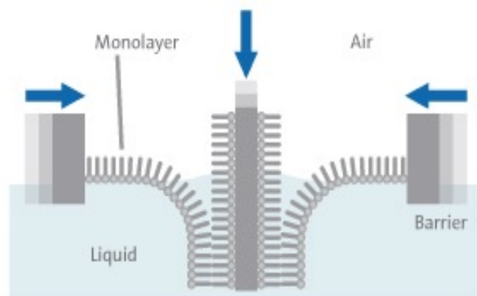
Langmuir-Blodgett Monolayer Film Deposition

- Float molecules functionalized with hydrophilic and phobic groups on opposite ends on H_2O
- Draw hydrophilic or phobic sample surface through the film to pick up molecules
- Squeeze film by bringing barriers in from edges of trough to "heal" the film hole
- Repeat for as many cycles as MLs needed

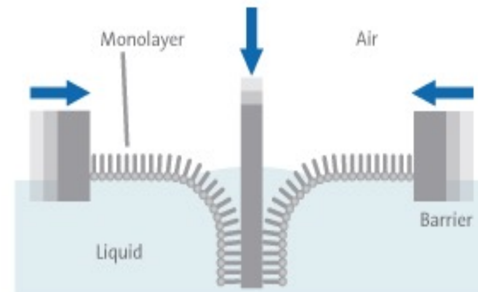
Hydrophilic surface deposition



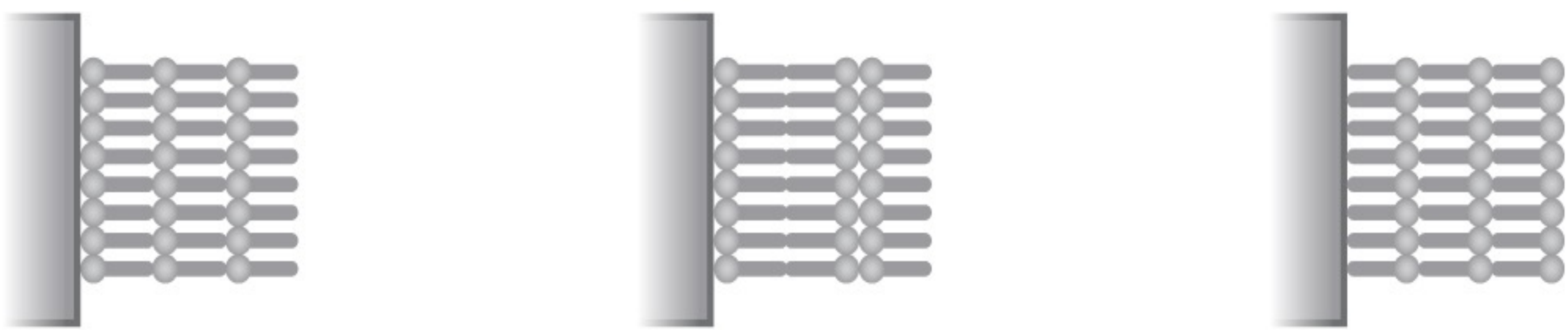
Hydrophilic surface: layer 2



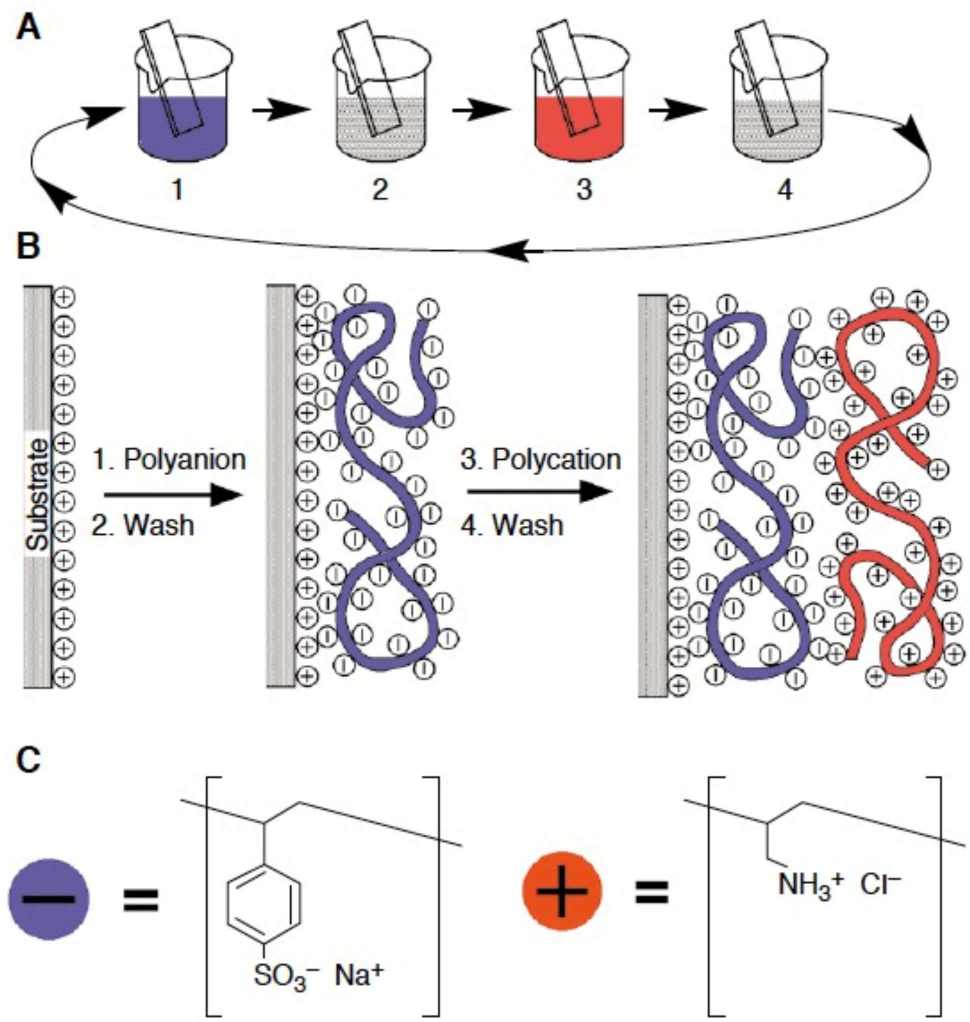
Hydrophobic surface deposition



Different configurations of 3 MLs on substrate surface



Electrostatic Monolayer Deposition

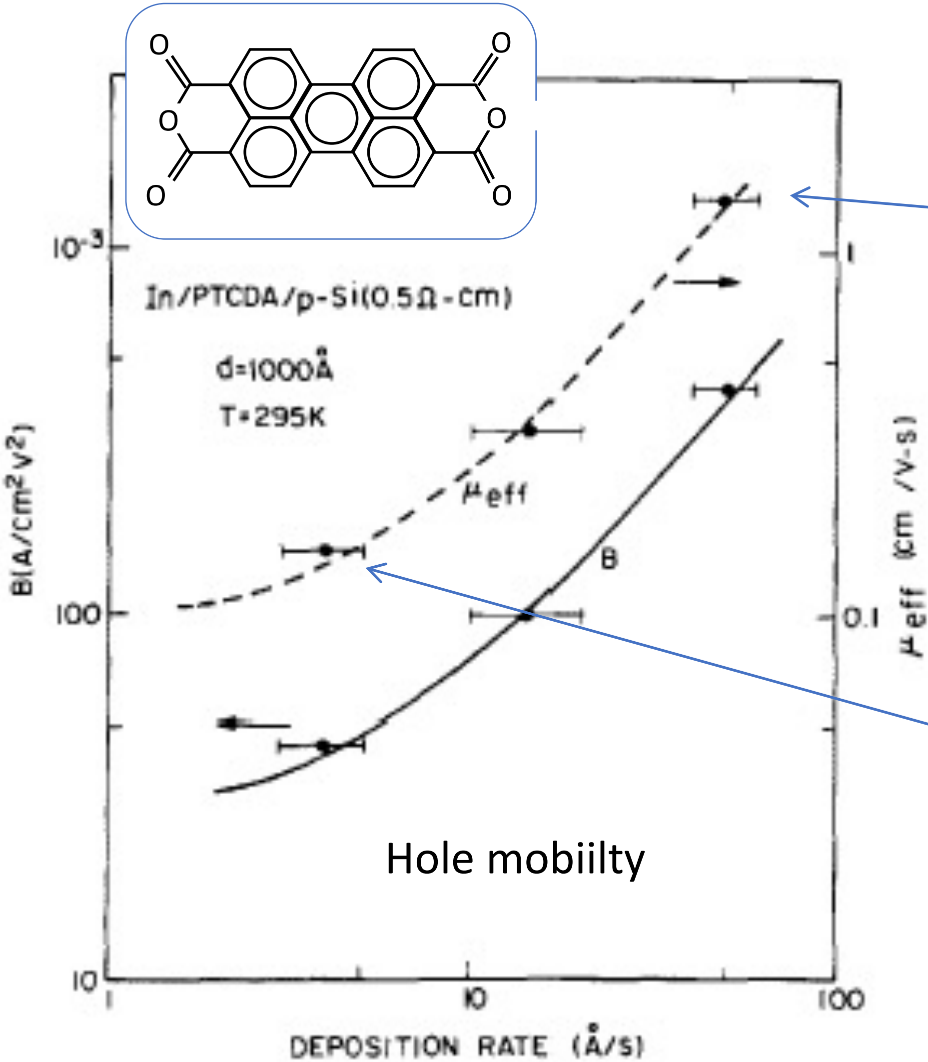


Decher, et al. SCIENCE VOL. 277, 29 AUGUST 1997, p 1233

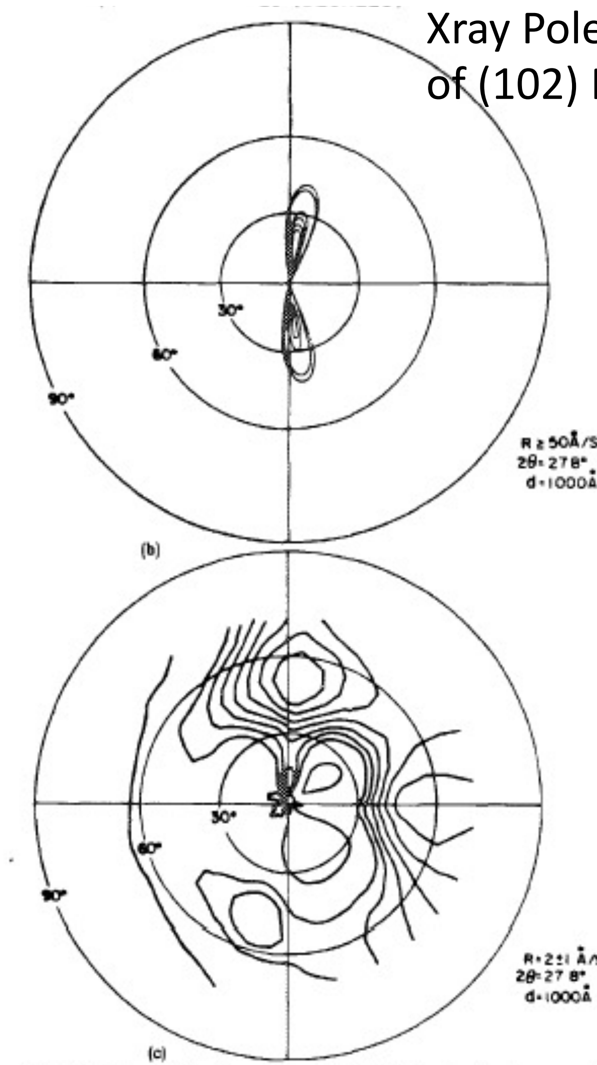
Post deposition film processing

- Some as-deposited films not in ideal morphology for device performance
- Unless growth results in the lowest energy crystalline phase, the morphology is metastable
- Adding energy to the film can help it to relax into a lower energy state:
    - polycrystalline$\rightarrow$crystalline
    - nanocrystalline$\rightarrow$microcrystalline
    - amorphous$\rightarrow$polycrystalline
- Adding energy = annealing

Mobility Increases with Order



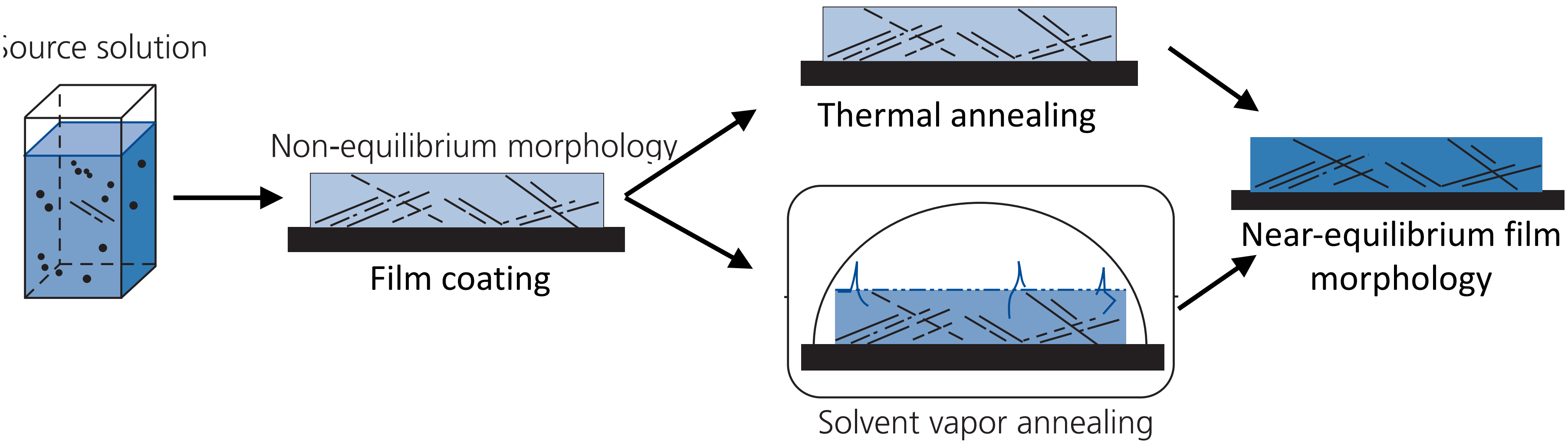
Xray Pole Figures of (102) PTCDA



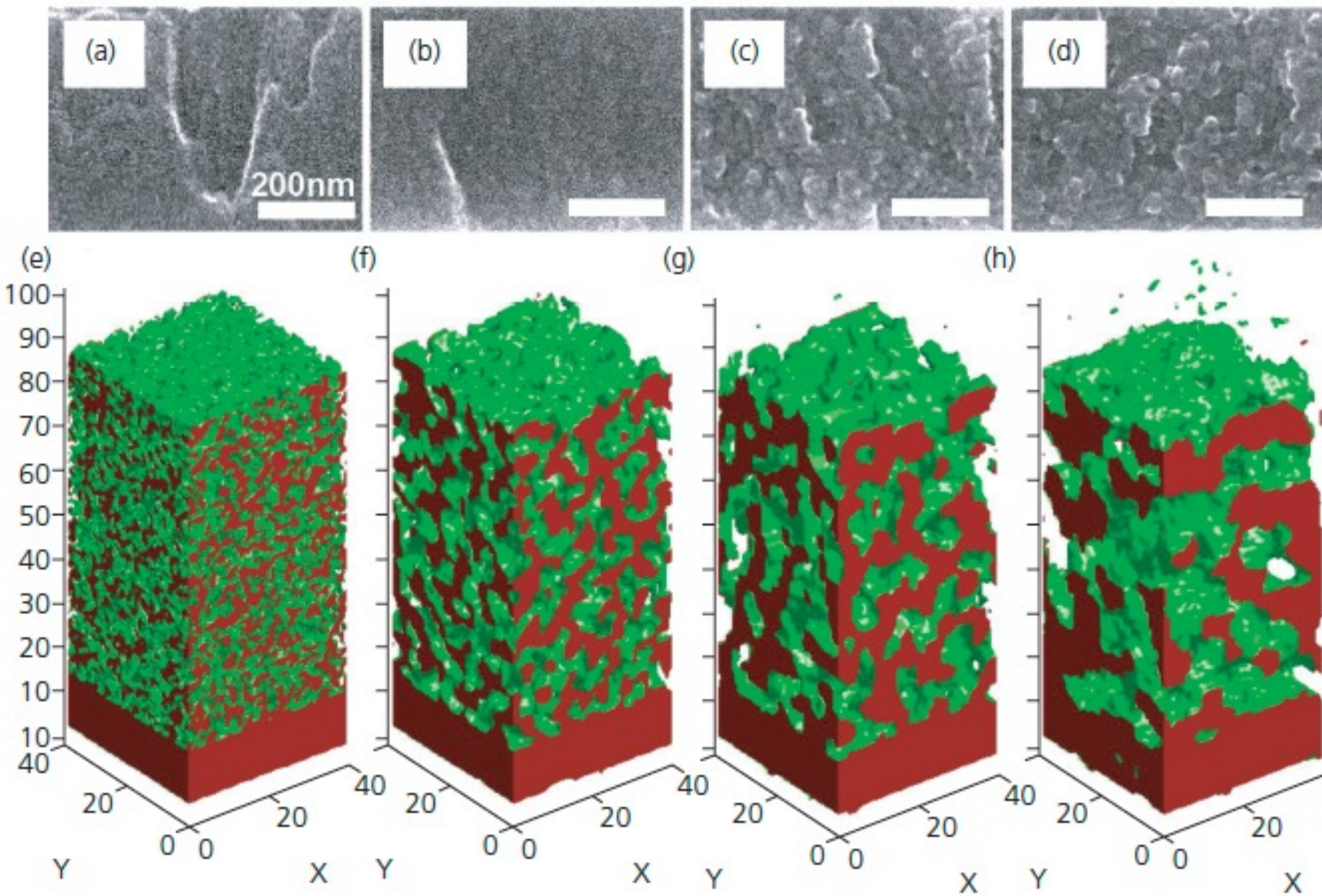
S. R. Forrest, M. L. Kaplan, and P. H. Schmidt, J. Appl. Phys. **56**, 543 (1984).

Film Annealing Processes

Increase molecular mobility within the film by
- Adding heat
- Introducing small solvent molecules



Thermal annealing can be constrained with a capping layer



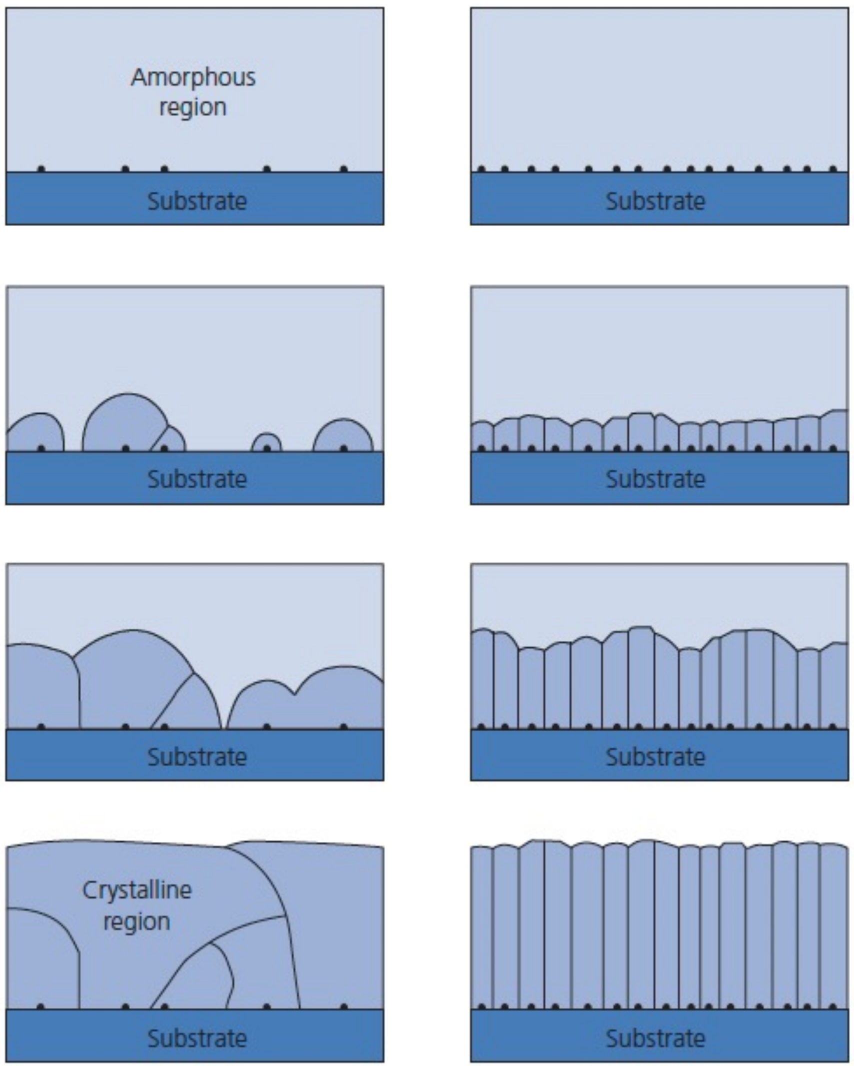
CuPc:PTCBI 4:1

atom-atom potential structure calculation

as-deposited 450K 500 K 550K

15 min anneal with Ag cap to hold top surface flat

Solvent vapor annealing gives molecules spatial mobility to crystallize



Verploegen et al., Adv. Func. Mater., 20, 3519 (2010)

<u>Two cases</u>

1. Sparse nuclei lead to large crystals
2. Closely spaced nuclei lead to closely packed and small crystals

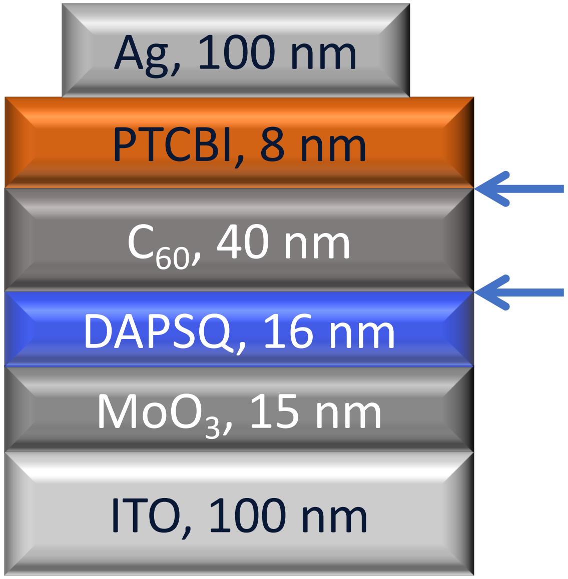
Crystal growth terminates when it grows into its neighbors

Avrami Equation predicts the volume rate of growth of the crystallites:

$$V(t) = V(0)\left[1 - e^{-(kt^n)}\right]$$

n=1-3 is the dimensionality of the crystallites
k=reaction (growth) rate

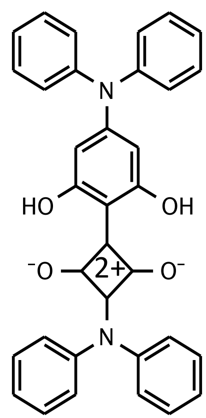
Controlling Morphology Via Annealing



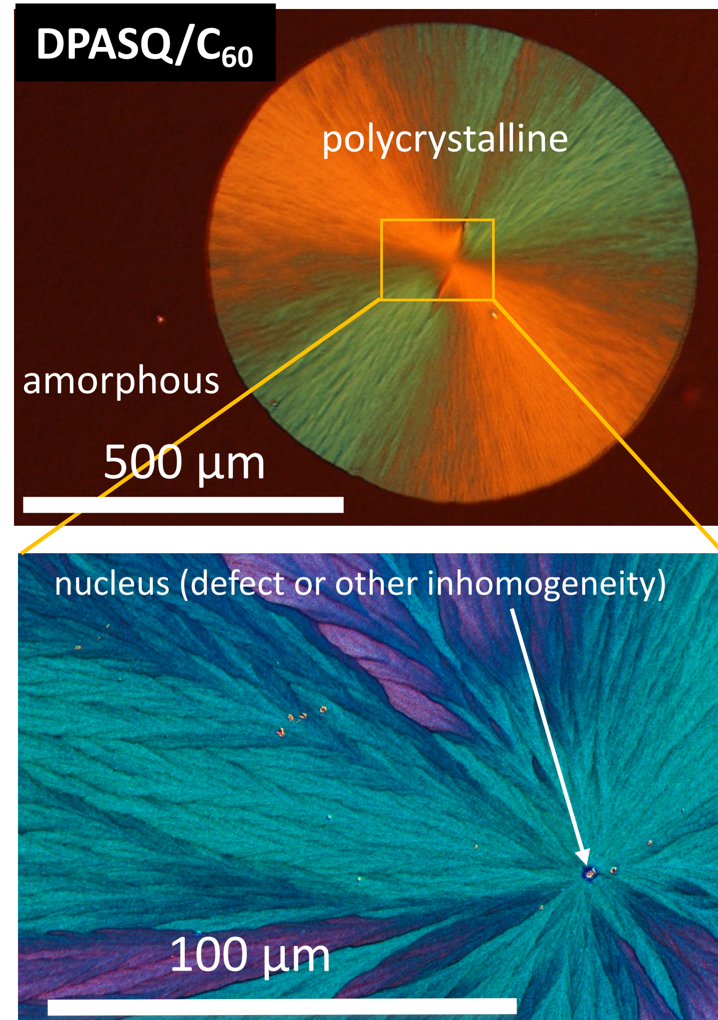
Conventional organic solar cell

SVA:
Post-C_{60}
Pre-C_{60}

DPASQ



SVA Post-C_{60}



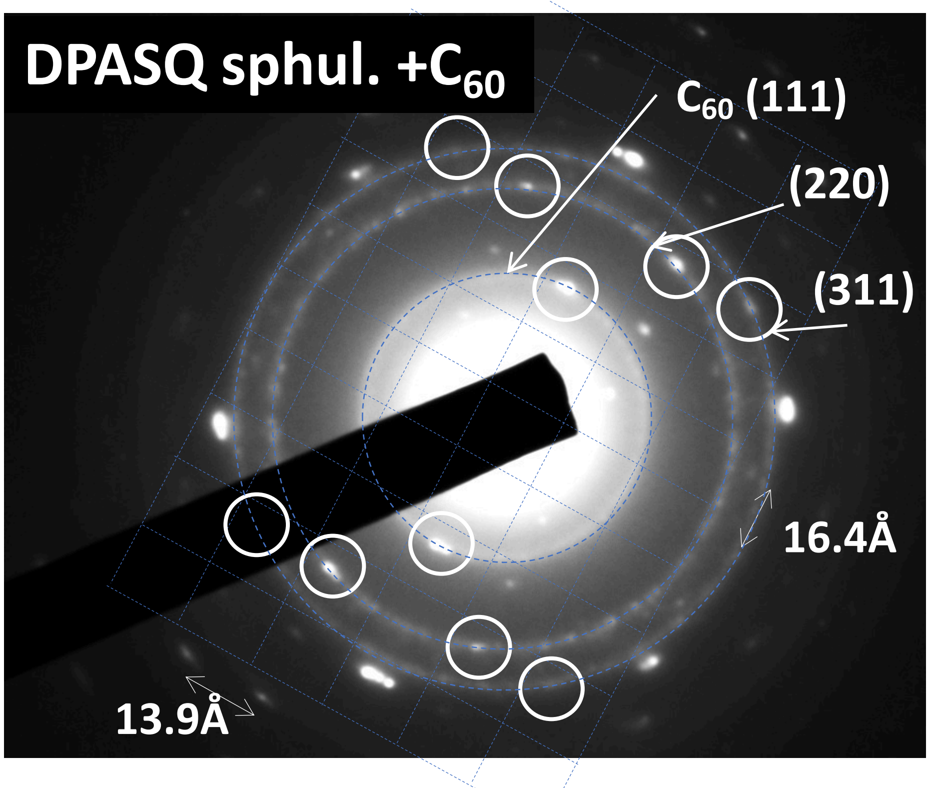
DPASQ (asymmetric squaraine)
- ❑ Crystallizes easily.
- ❑ Solvent vapor annealed (in DCM)

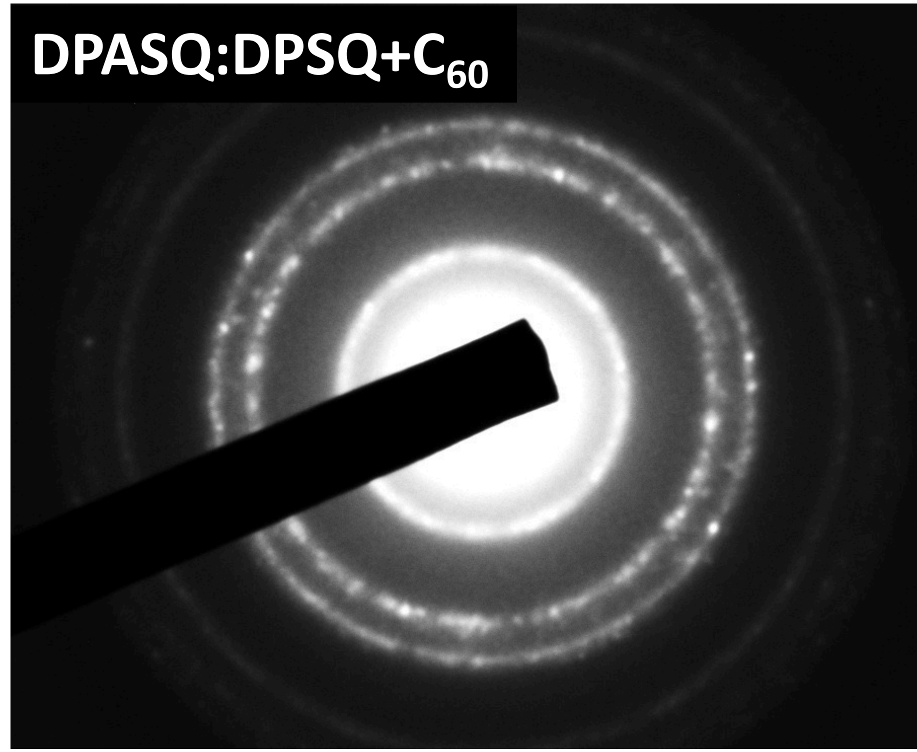
- Spherulite crystallization
  - –Large driving force for amorphous⇒crystal transition
  - –Highly asymmetric crystallization rates.
  - –Low-angle branching or splitting of crystallites.
  - –Grow until reaching energetically relaxed (crystallized) region.
  - –Nucleation at free surface⇒ nucleation sites reduced for SVA post-C_{60}.

Zimmerman et al., ACS Nano, 7, 9268 (2013)

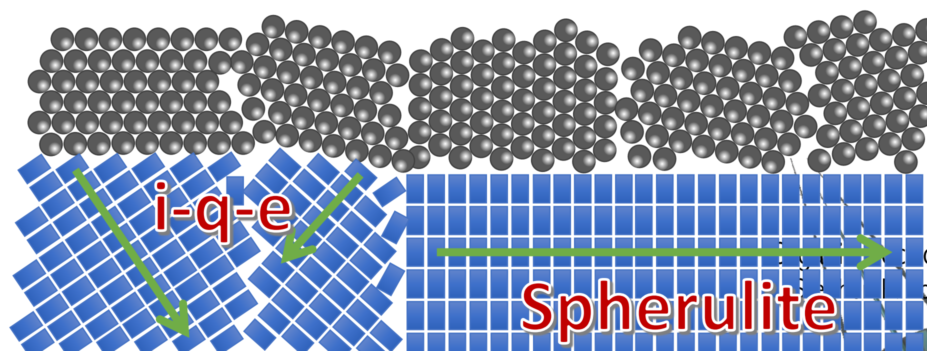
Understanding the Annealed Structure

Selected Area Electron Diffraction (SAED)



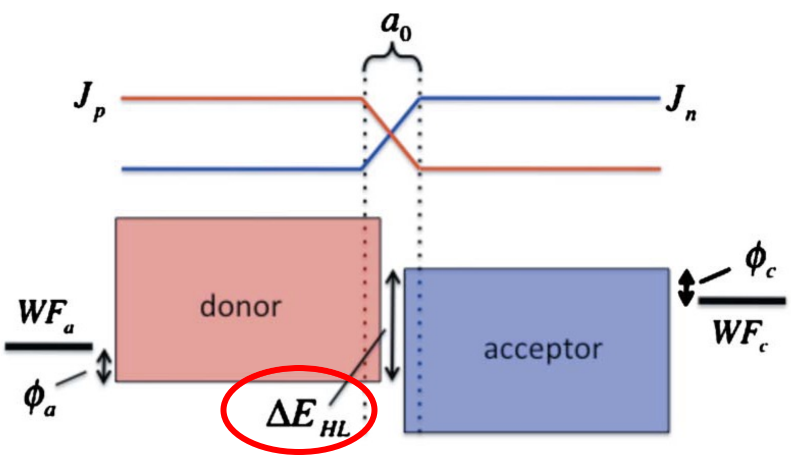


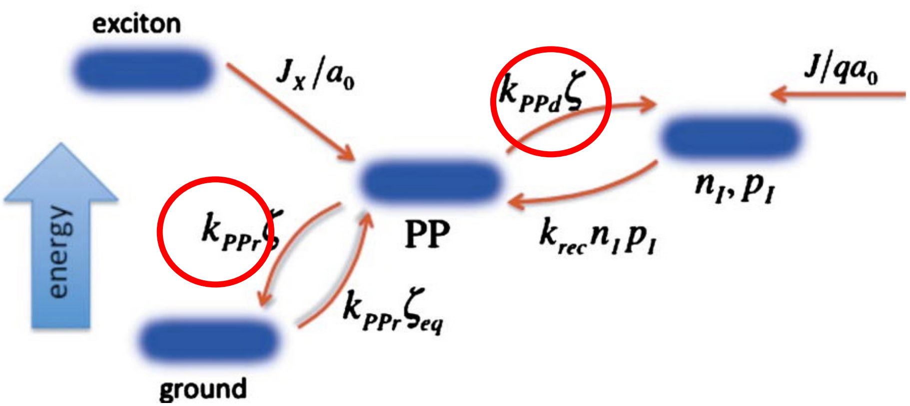
- Micron-scale crystals of DPASQ.
- Mesh: 13.9 Å by 16.4 Å, α=90°.
- "Inverse quasi epitaxy": DPASQ crystallization seeded by C_{60} interface.



Zimmerman et al., ACS Nano, 7, 9268 (2013)

Controlling Open-circuit Voltage via Interface Recombination



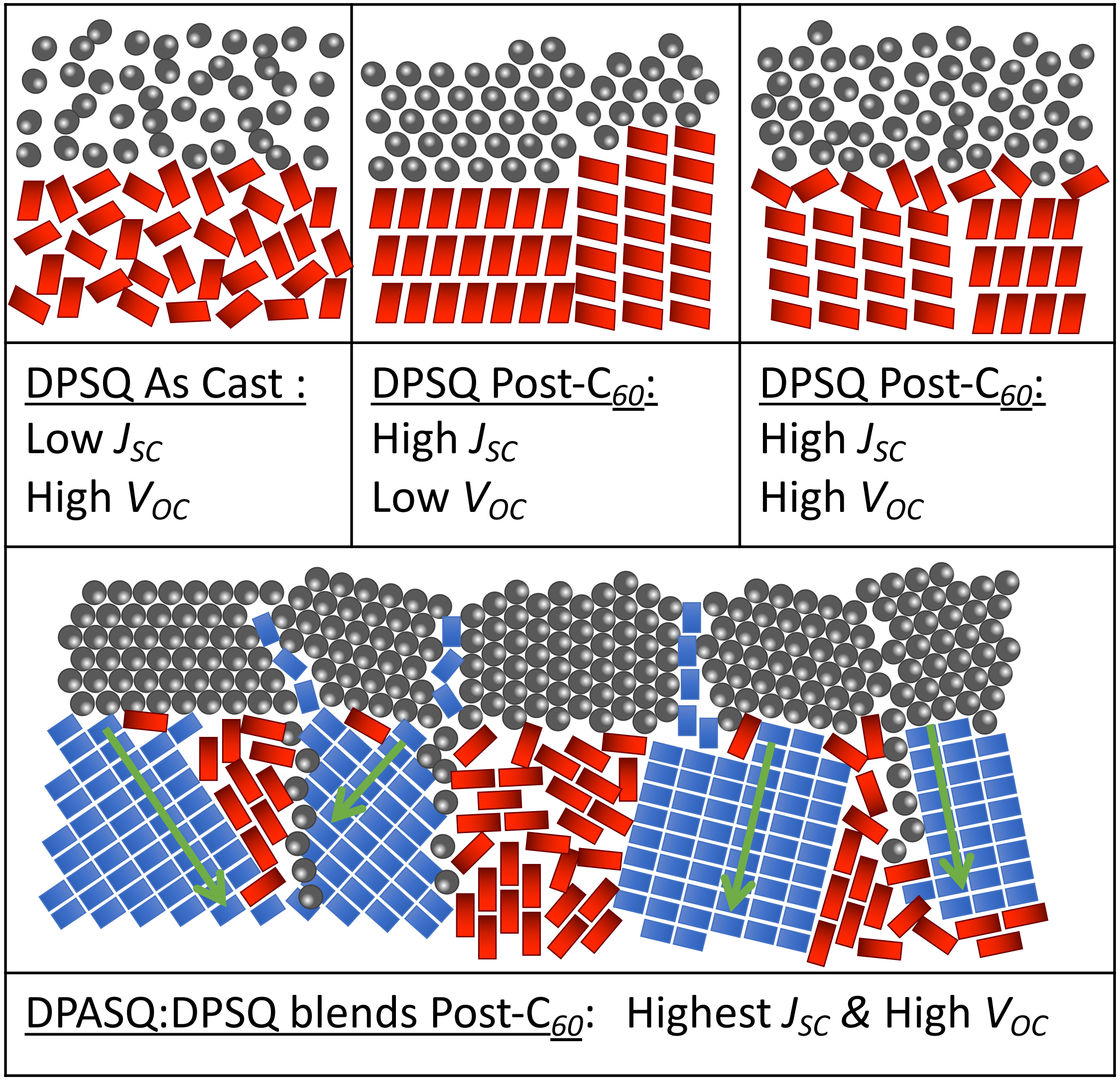


$$qV_{OC} = \Delta E_{HL} - nk_B T \ln\left[\frac{k_{PPr}}{k_{PPd}}\frac{k_{rec}N_L N_H}{J_X/\alpha_0}\right].^*$$

- Material choice determines:
  - ΔE_{HL} (HOMO-LUMO Gap)
  - Steric hindrance (MO overlap)
- Device processing/morphology can limit V_{OC} losses:
  - k_{PPd} (PP dissociation)
  - k_{PPr} (PP recombination)

*Giebink *et al.* PRB 2010

Solution Processing Phenomena



- To maximize V_{OC} in OPVs:
    - Disorder at HJ.
- To maximize J_{SC}:
    - Ordered bulk.
    - Finger-like BHJ structure.
- DPSQ maintains interface disorder on SVA Post-C_{60}.
- DPASQ undergoes "inverse quasi-epitaxy" and inter-diffusion on SVA Post-C_{60}.
- Blending DPASQ and DPSQ eliminates tradeoff between V_{OC} and J_{SC} and maximizes η_P.

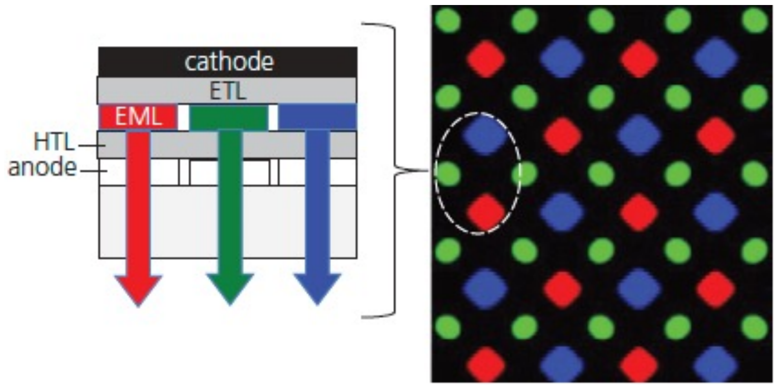
Zimmerman et al., ACS Nano, 7, 9268 (2013)

Device and Film Patterning

Primary purpose is to define the device area, suited to its function

- Requirements
  - Simple
  - Non-destructive of the materials forming the device
  - Adaptable to large substrate areas
  - Adaptable to flexible substrates
  - Rapid (for large scale manufacturing)

- Methods
  - Shadow masking
  - Direct printing (Ink jet and OVJP)
  - Photolithography
  - Stamping and nanopatterning
  - LITI



Example: Pixel micro-patterning in OLED displays

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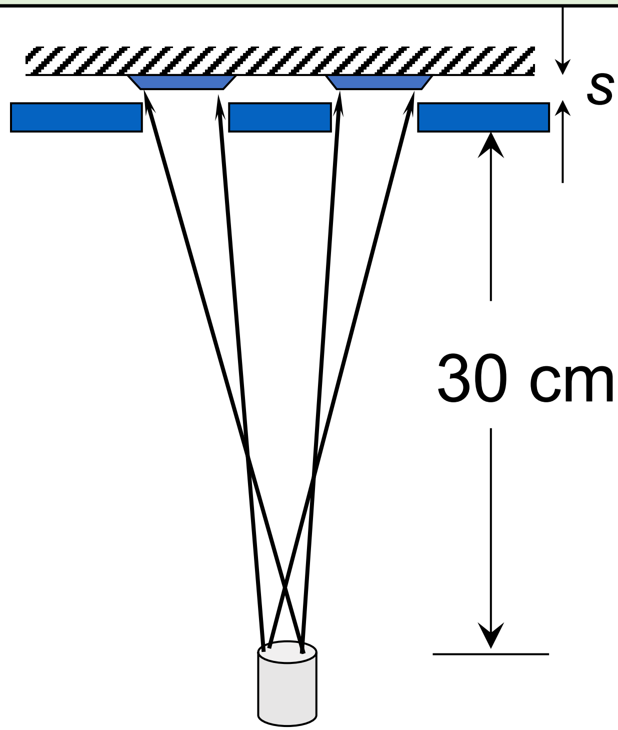
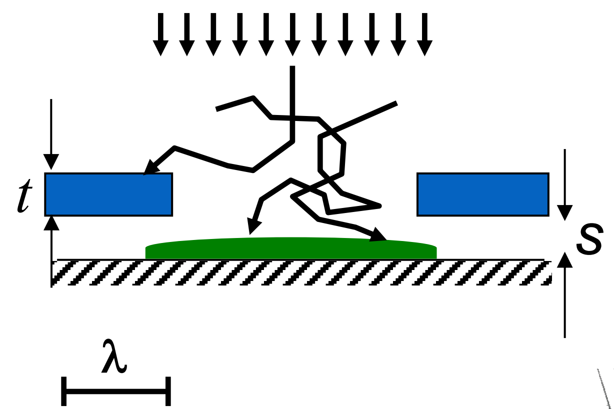
Shadow mask patterning in the kinetic and diffusive film growth regimes

- Shadow mask patterning is the most common form of organic device electrode definition
- Used for producing OLED displays for small mobile and large TV applications

Vacuum Evaporation vs. Vapor Phase Deposition



$$\lambda = \frac{k_B \cdot T}{\sqrt{2} \cdot \sigma \cdot P}$$ Mean free path

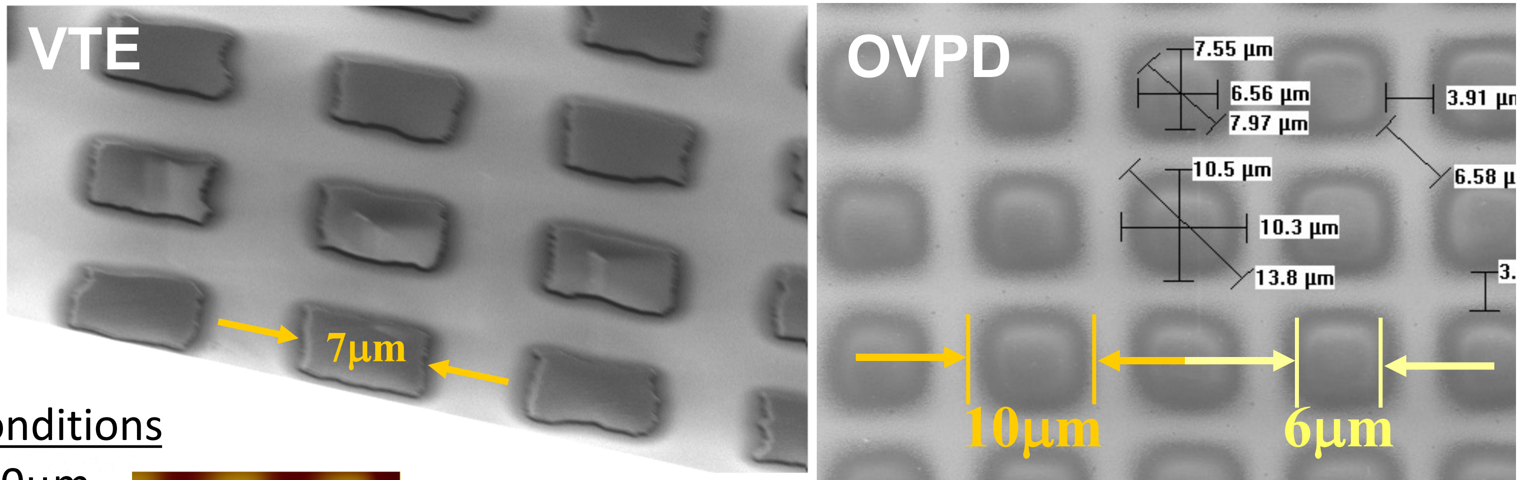


10^{-5} – 10^{-10} Torr

10^{-1} – 10 Torr

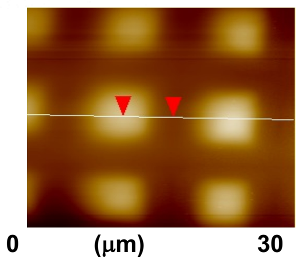
M. Shtein et al. J. Appl. Phys., 93, 4005, (2003)

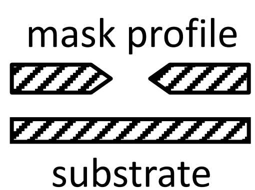
Resolution limits for shadow-masking

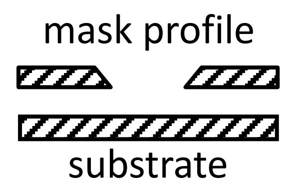


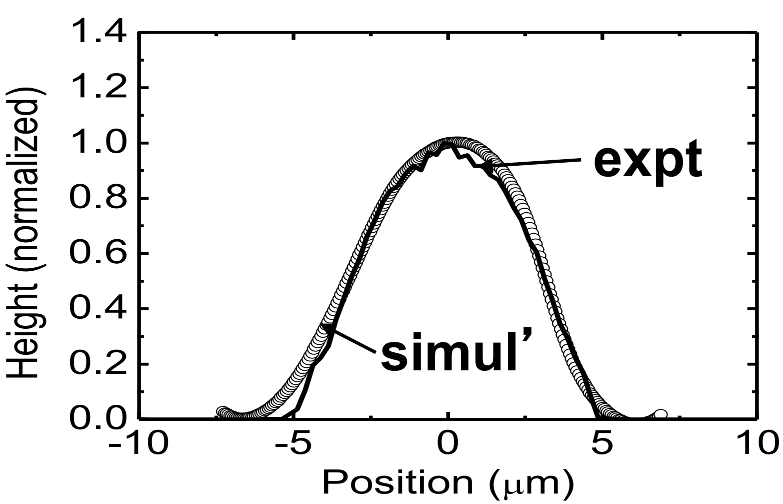
OVPD Conditions

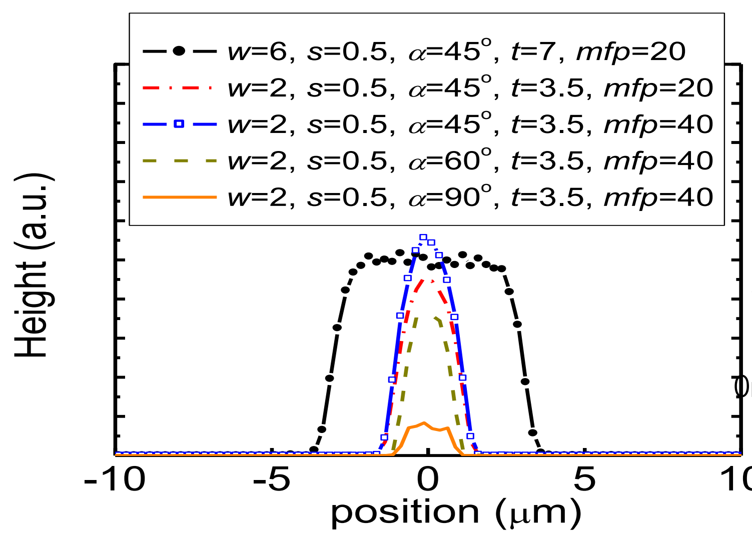
λ = 20µm
s=0.5µm
t=3.5µm
w=6µm











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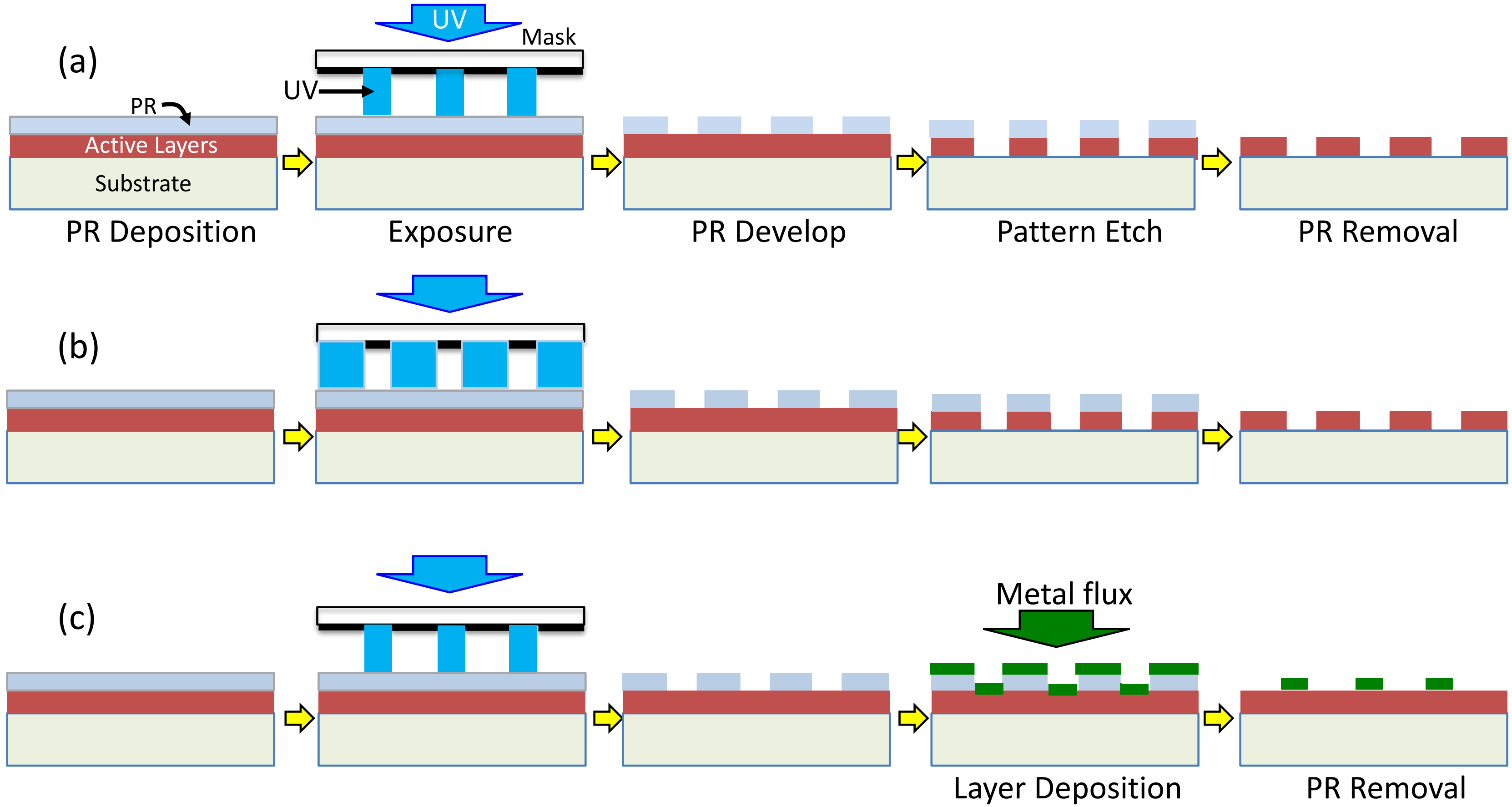
M. Shtein et al. J. Appl. Phys., 93, 4005, (2003)

Photolithography: Common Method for Patterning Inorganic Semiconductor Devices

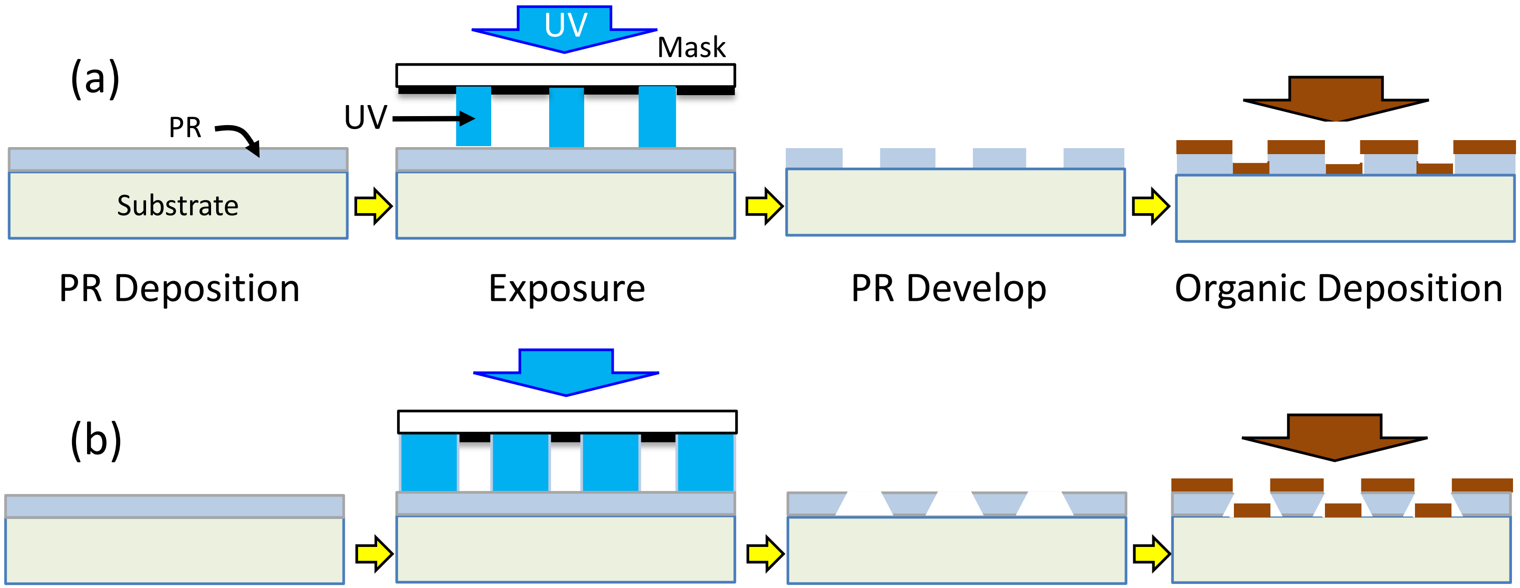
Photolithographic processes employ solutions (polymer resists, developers, etc.) that can damage organic active layers

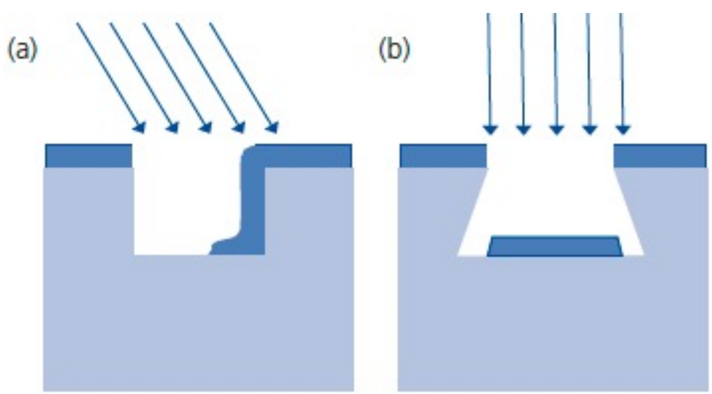
⇒ More adaptable to substrate (e.g. electrode, feature) definition



Three (of many) variations shown: (a) positive photoresist, (b) negative photoresist, (c) liftoff

Use Photoresist to Create Surface Topography to Pattern Subsequently Deposited Organics

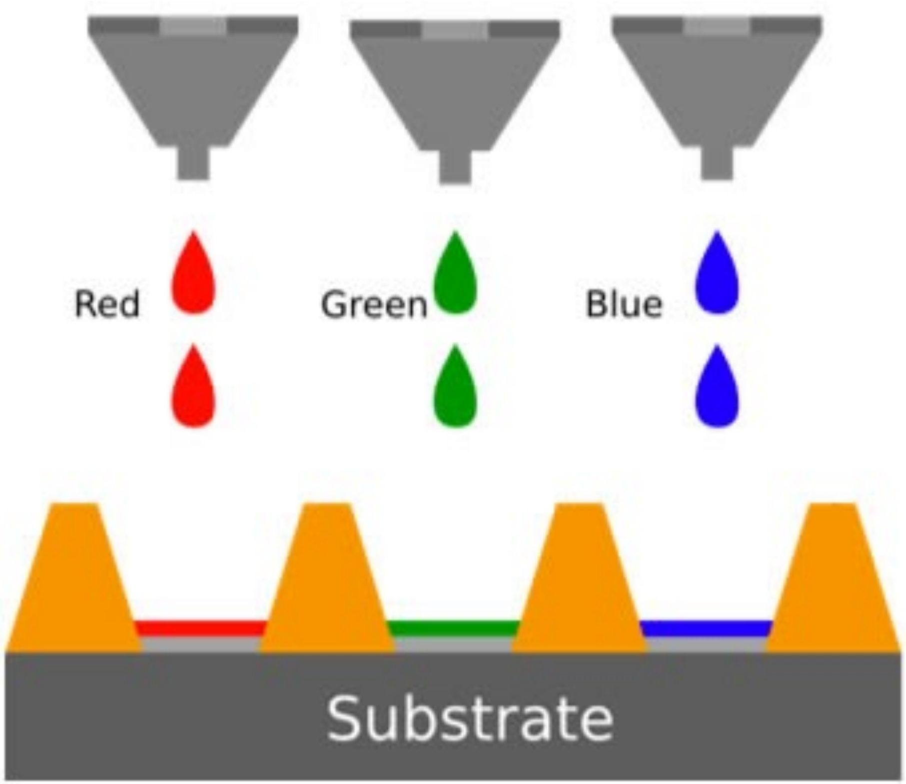


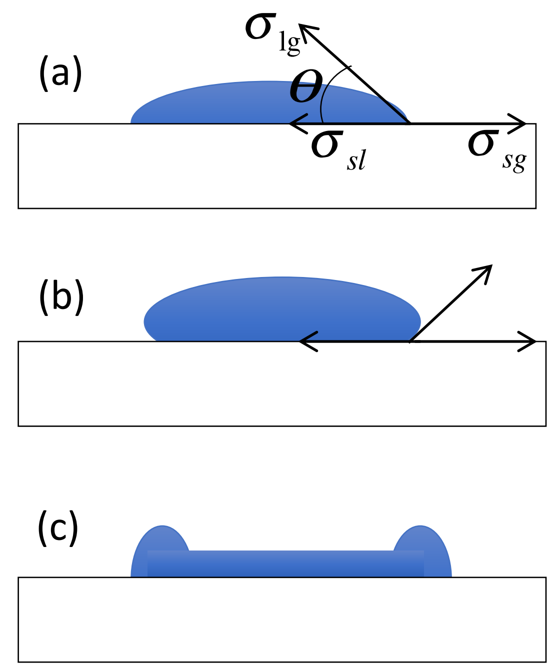


- Deposition of the organic in vacuum
- Shape of pattern on substrate depends on direction of the source to substrate

- Avoid exposure to wet chemistry in photolithography
- Resolution defined by photolith limits.
- The pattern left in the polymer provides a near-field “shadow mask” for the deposit

Inkjet Printing

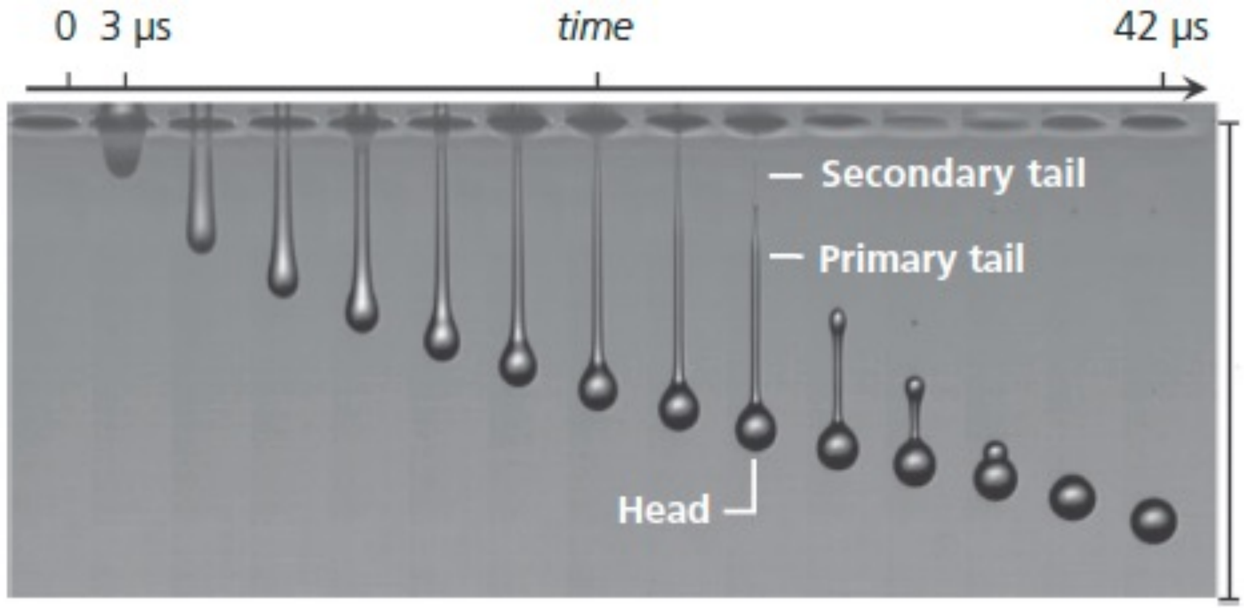




- Organic semiconductors similar to inks used in printing
- Organics must be soluble
- Droplets injected into wells formed by polymer walls

- Film cross section depends on its rheological properties and relative energy with substrate surface
- “Coffee stain effect” encourages piling up of deposit near edges – can result in non-uniform device performance

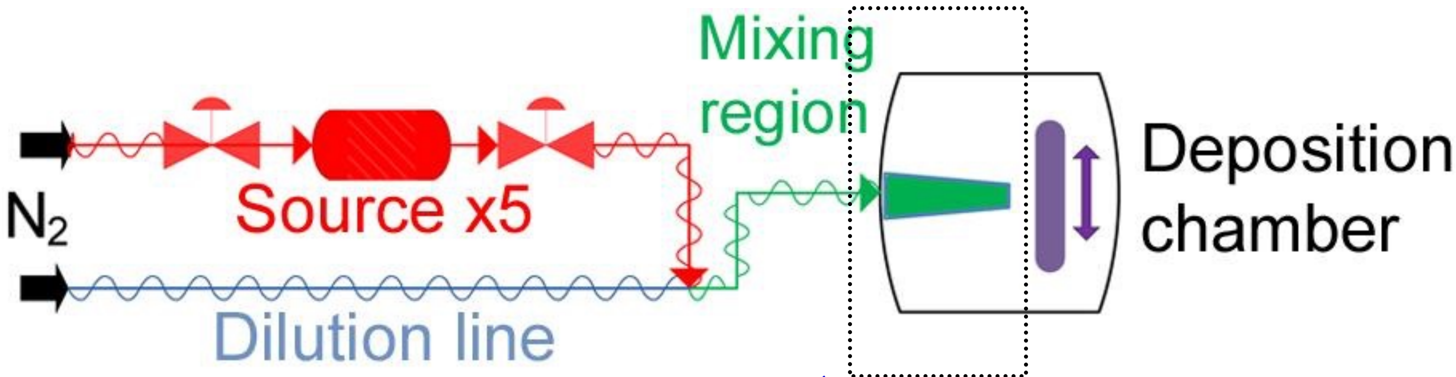
Inkjet Droplet Formation in Real Time

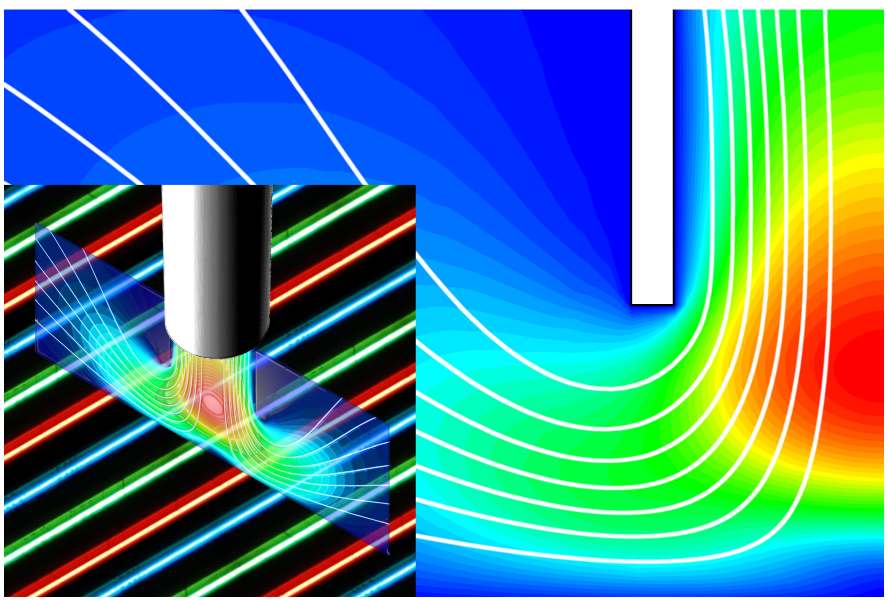


- Droplet shape depends on viscosity and volume of the droplet
- Want to avoid separation of of secondary and primary tails
- Speed limited by fluid properties

van der Bos et al. Phys. Rev. Applied, 1 014004 (2014)

Printing an R-G-B WOLED Using Organic Vapor Jet Deposition

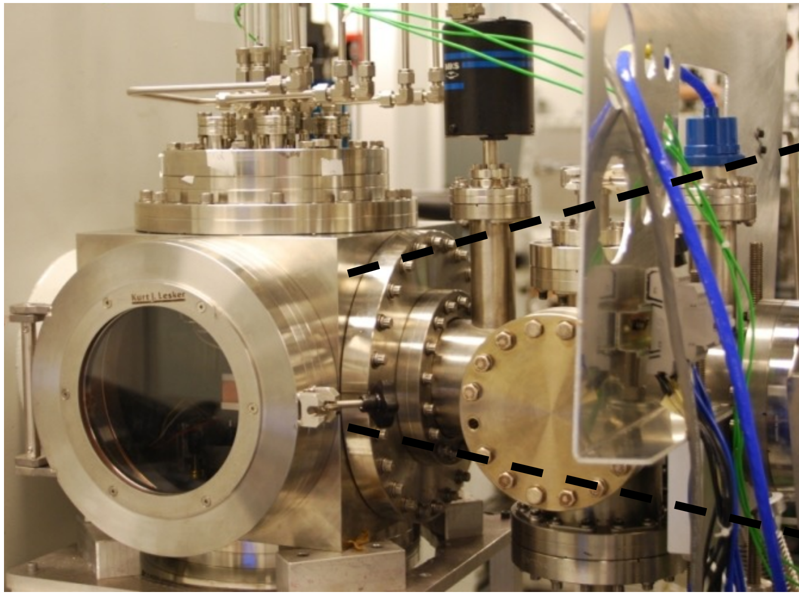


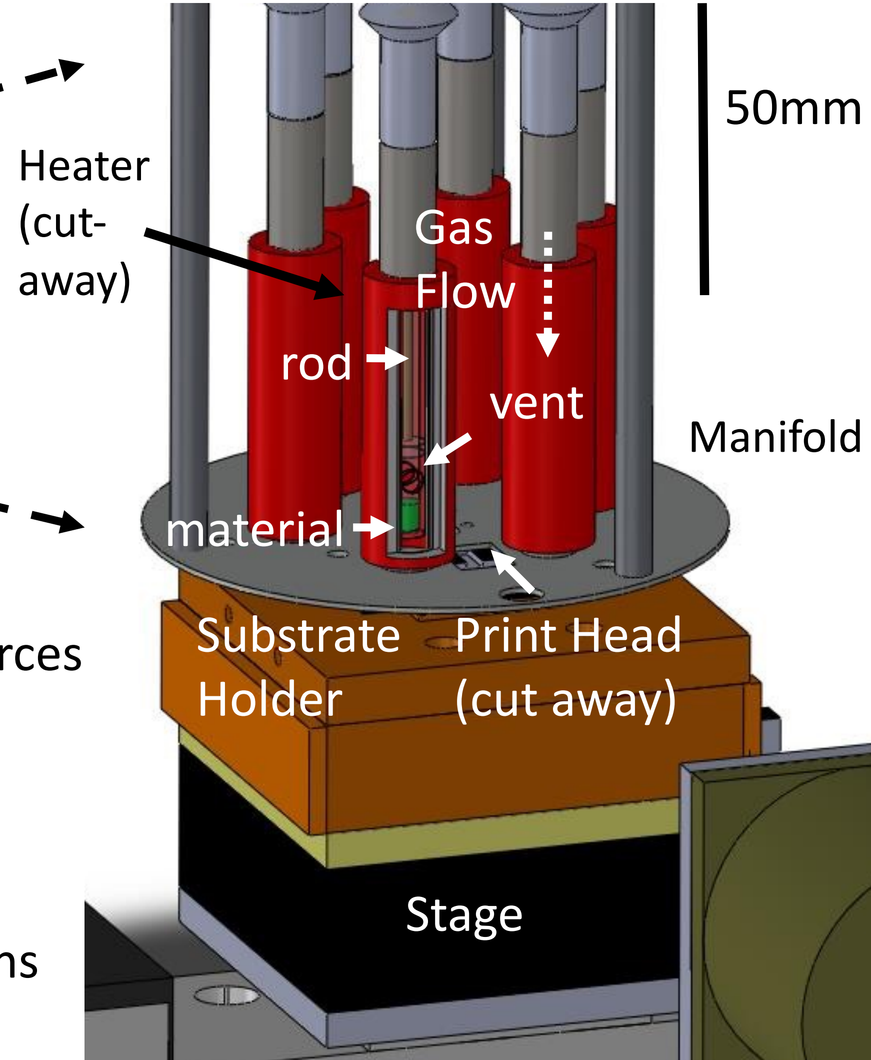


- Optimized R-G-B OLEDs can be combined to form a WOLED
- Each color separately optimized by choosing guest/host combinations
- Tunable color balance
- Motion stage beneath nozzle
- Nozzle creates high speed vapor jet

Arnold et al. Appl. Phys. Lett., 92, 053301 (2008)

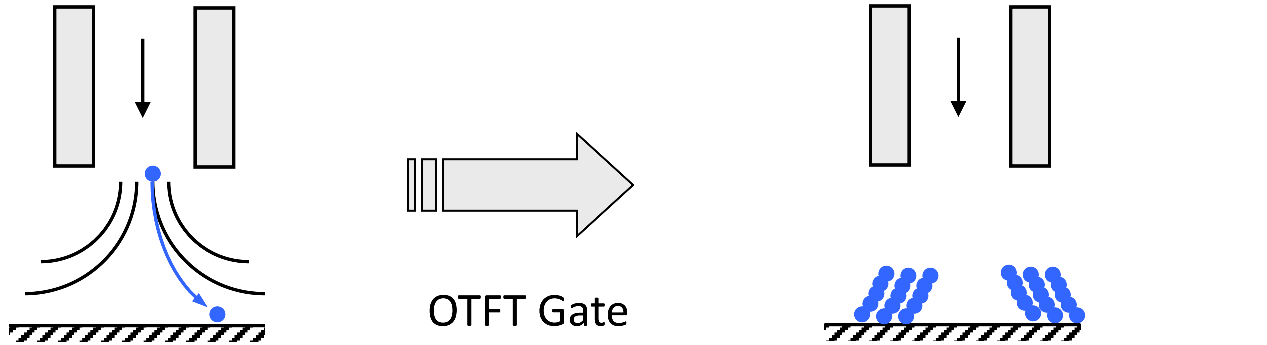
Laboratory Printer

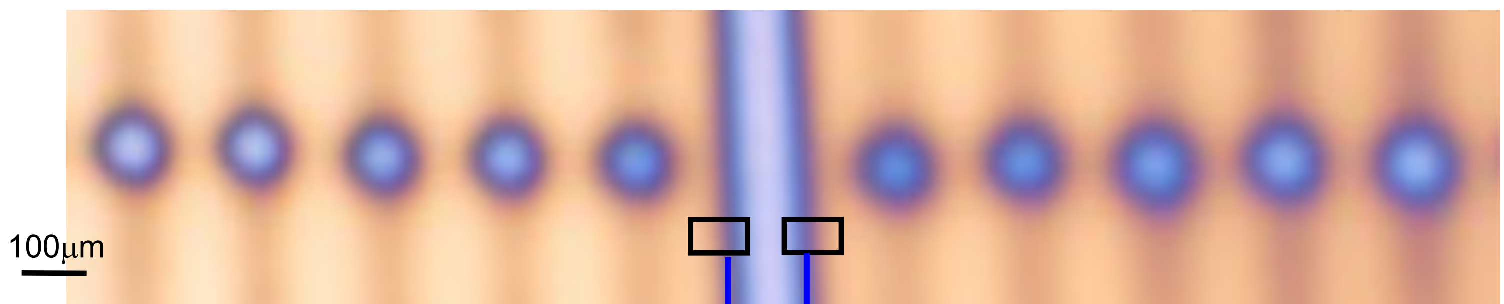


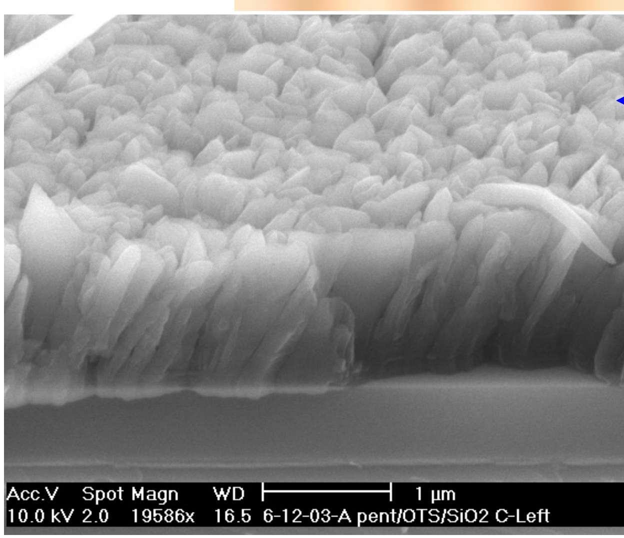


- Manifold w/ independently heated sources
- High vacuum chamber
- Chilled substrate holder
- Glove box loading
- Minimal pressure drops and tube lengths

Flow anisotropy: Non-equilibrium crystallization & molecular ordering





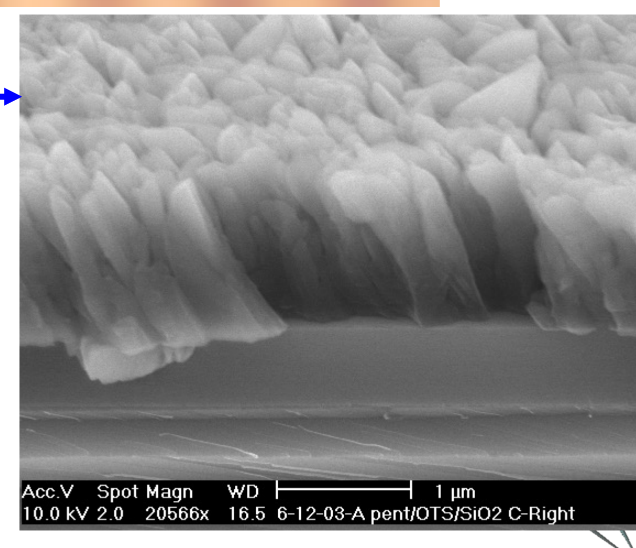


Local deposition rate: 700 Å/s

μ= 0.25 $cm^2/V \cdot s$

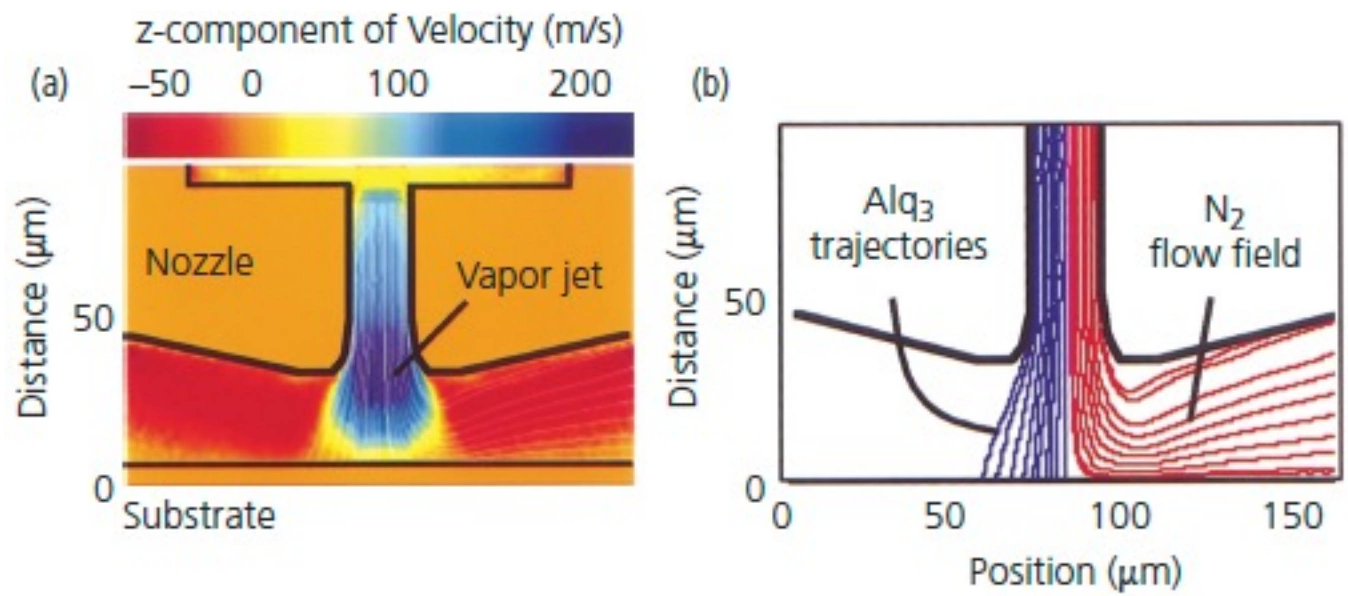
On/off = $7 \cdot 10^5$

V_t = 17, 10 V



Flow Dynamics That Govern OVJP Deposit Shape

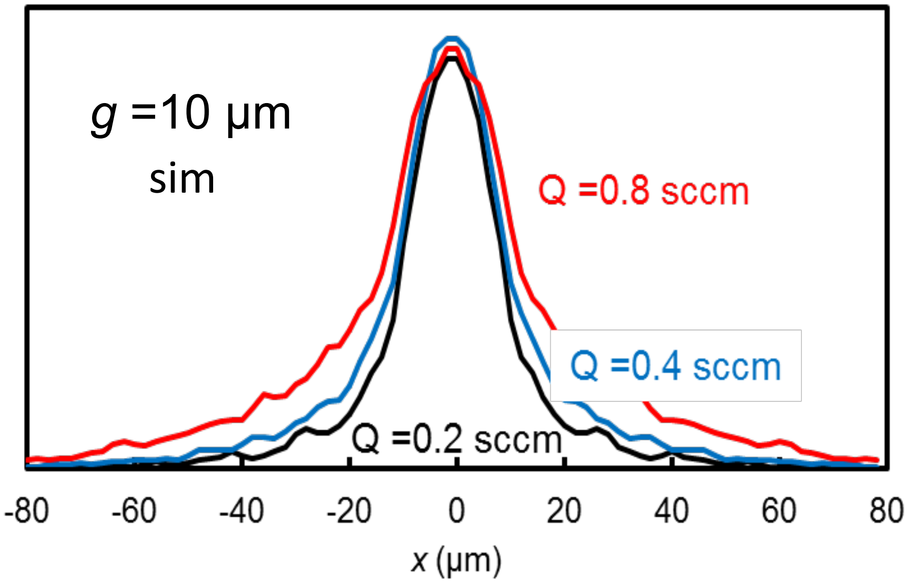
- Nozzles "focus" molecular plus carrier gas flows toward the substrate
- Heavier molecules (Alq_3 in this example) take straigher trajectories and deposit nearly directly under nozzle
- Lighter carrier gas (N_2) exhausts laterally
- Flow rates are 100's of m/s creating a high dynamic pressure beneath the nozzle



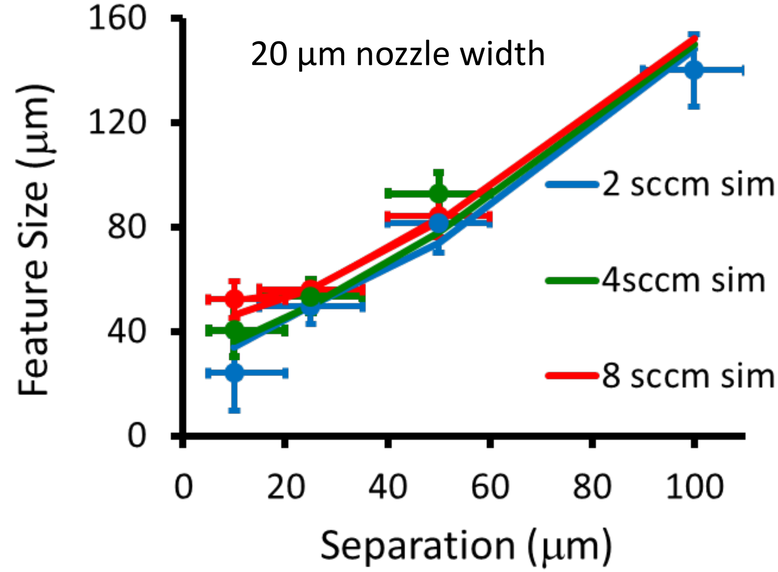
Shtein et al., J. Appl. Phys. **93**,4005 (2003)

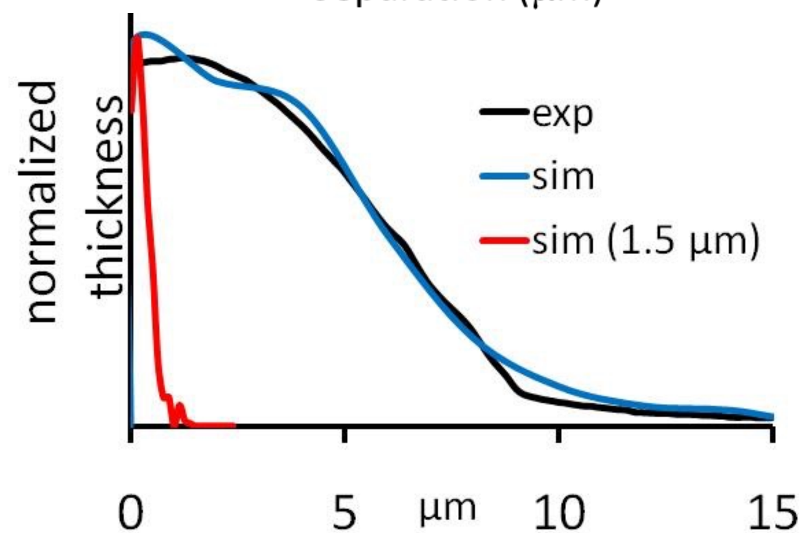
Deposition Profiles

Resolution Limits



g=nozzle-substrate distance





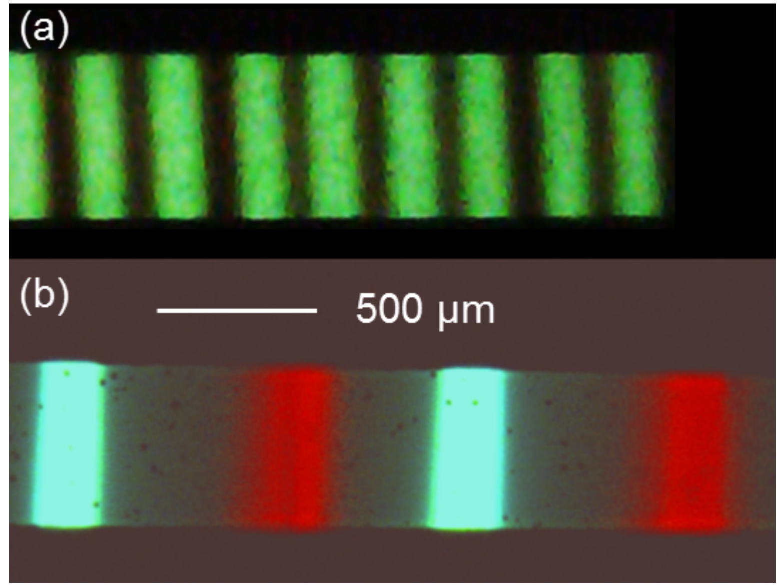
- deposit width increases with nozzle-substrate distance: *g*
- width increases with flow rate, Q, for small *g*
- Shape of deposition profile accurately reproduced by Monte Carlo simulations
- **1.5 µm features possible**

McGraw, et al. *App. Phys. Lett.* **98** 013302 (2011)

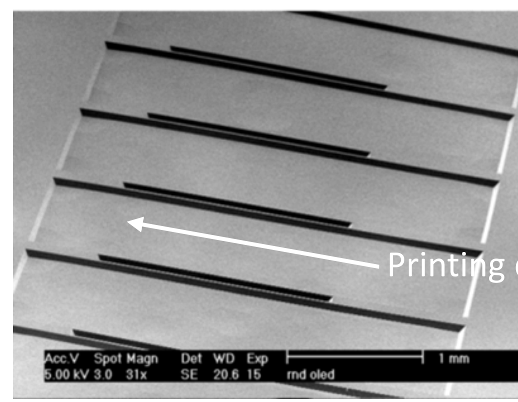
Printed R–G Pixel Arrays

Red-Green devices printed
at nozzle substrate distance*:* 20 μm

BAlq electron blocking
/emissive layer



g (μm)	Green	Red
VTE	(0.27, 0.63)	(0.66, 0.32)
10	(0.27, 0.63)	(0.66,0.33)
100	(0.32, 0.61)	(0.66,0.33)



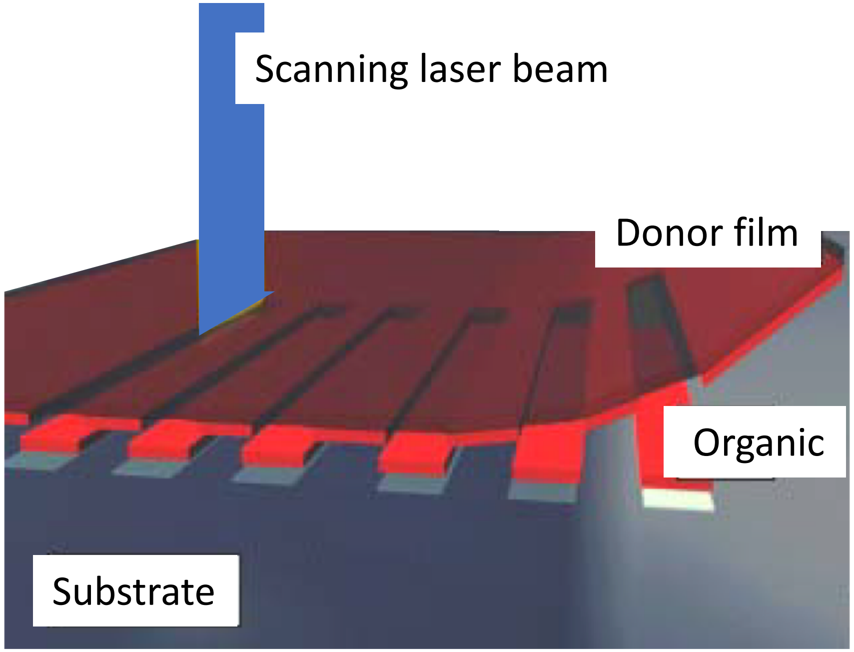
MEMS Nozzle Array

100 μm subpixels printed on 500 μm centers show
no detectible color cross-talk between pixels

McGraw, et al. *App. Phys. Lett.* **98** 013302 (2011)

Laser Induced Thermal Imaging (LITI)

- High power laser beam absorbed in the donor film preloaded with the organic to be transferred
- Donor film placed in contact with substrate
- Heat generated by laser volitalizes organic that transfers to the substrate in the desired pattern



- Donor film must be replaced after each printing
- Useful for sublimable materials (small molecules)
- Radiation damage must be controlled by appropriate absorbing layer