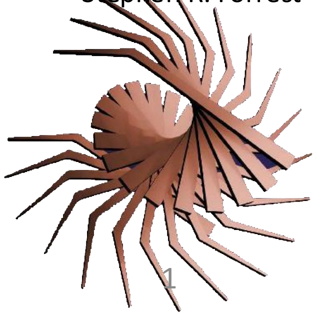
Week 7

The Art of Making Devices

Materials purification
Thin film growth
Device patterning
Packaging

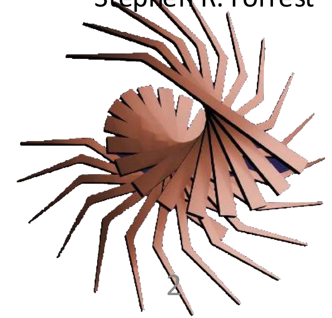
Chapter 5

Concepts in Organic Electronics
Stephen R. Forrest



Objectives

- Provide a “hands-on” description about how devices are made
- Describe material purification methods
- Describe the various techniques for high quality materials growth
  - Single crystals
  - Solution deposition
  - Vapor phase deposition
- Describe methods of device patterning



Material Purity

To achieve high quality optoelectronic properties, materials must be purified

Impurities take many different forms:

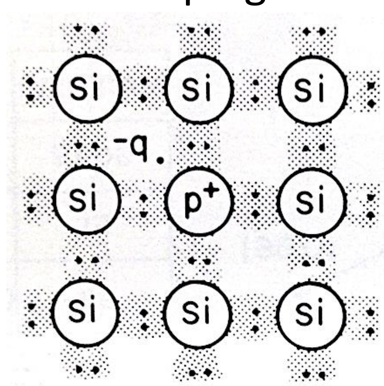
- Extrinsic defects
  - Dopants and “dirt”
  - Substitutional
  - Interstitial
- Intrinsic defects
  - Vacancies
  - Stacking faults

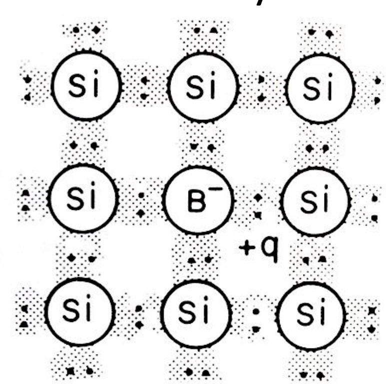
Due to lack of bonds in vdW solids, impurities have different effects

- Create stacking faults
- React with molecular constituents
  - Create unwanted bonds
  - Create fragments

In all cases, the inclusion of <u>unwanted</u> impurities leads to undesirable outcomes

This is different from doping to change the conductivity of a semiconductor

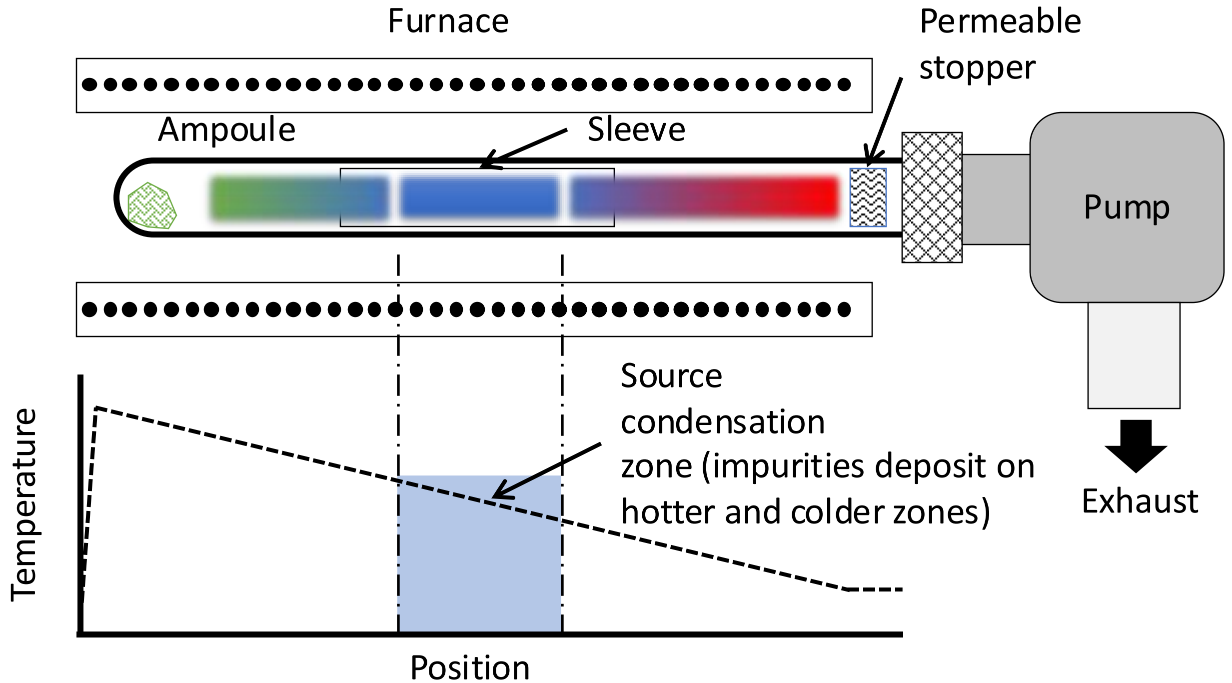


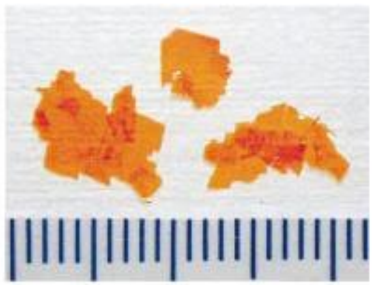


Concepts in Organic Electronics
Stephen R. Forrest

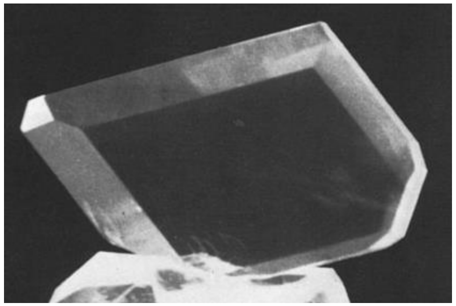
Purification by Thermal Gradient Sublimation

Useful for obtaining very high purity small molecule materials





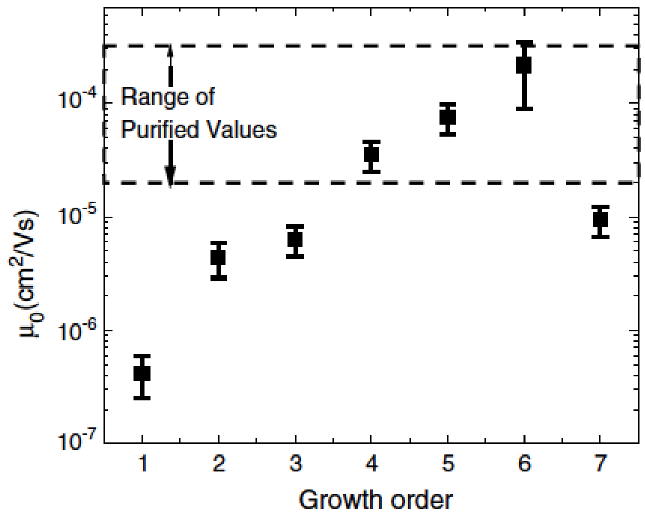
Tetracene after sublimation



Pyrene

- Reasonably fast and simple
- Material must be sublimable
- Multiple cycles result in higher purity
- Can occur in vacuum or under inert gas flow
- Small crystal growth on chamber walls possible

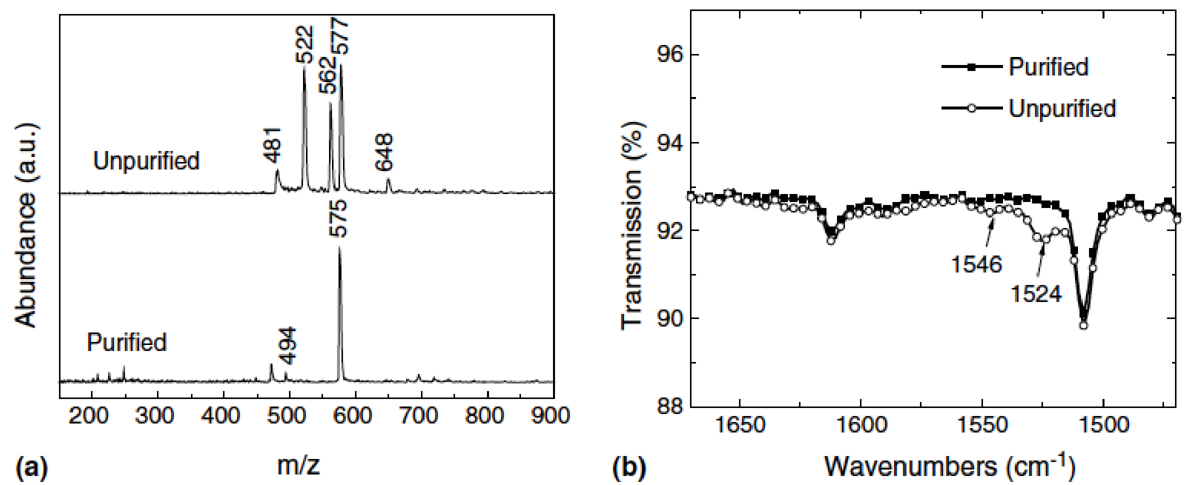
Purification of CuPc via Multi-cycle Sublimation in Vacuum



Mobility increases with sublimation cycle due to increased purity

Reduction of impurity signatures

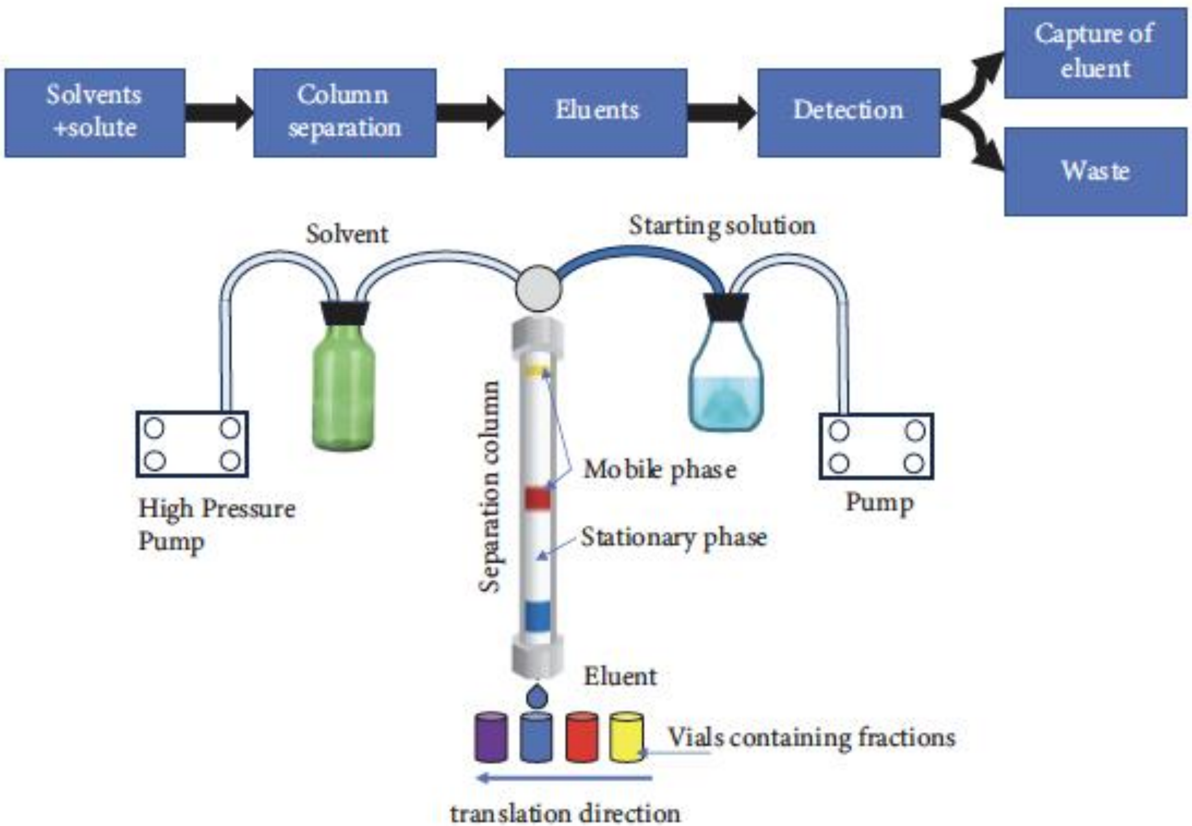
H_2Pc main impurity

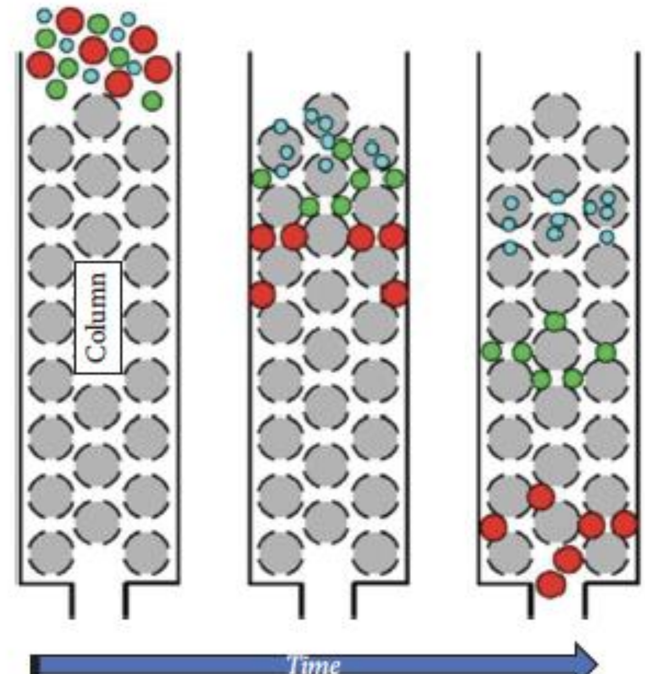


Salzman, et al., Organ. Electron. 6, 242 (2005)

Purification via Solution

Chromatography





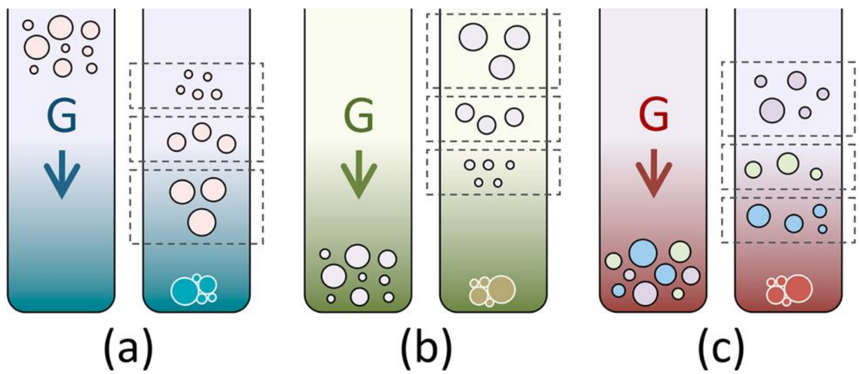
Concepts in Organic Electronics
Stephen R. Forrest

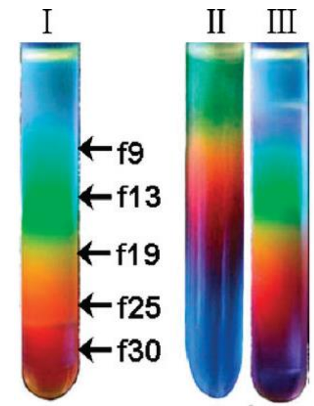
Column High Pressure Liquid Chromatography (HPLC)

Size exclusion chromatography

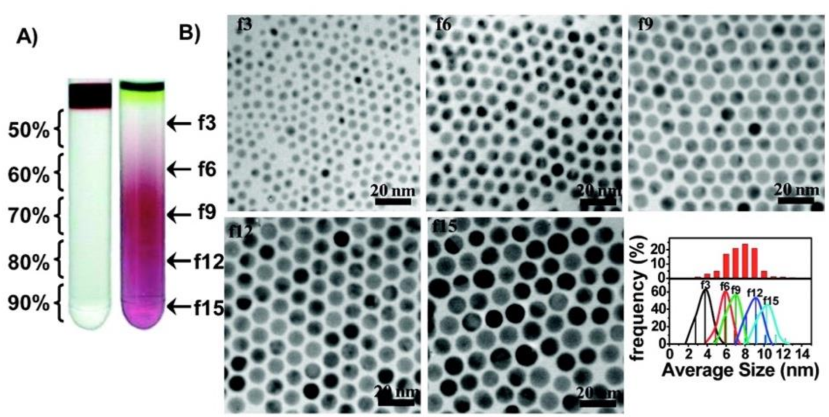
Purification via Centrifugation

Density gradient centrifugation



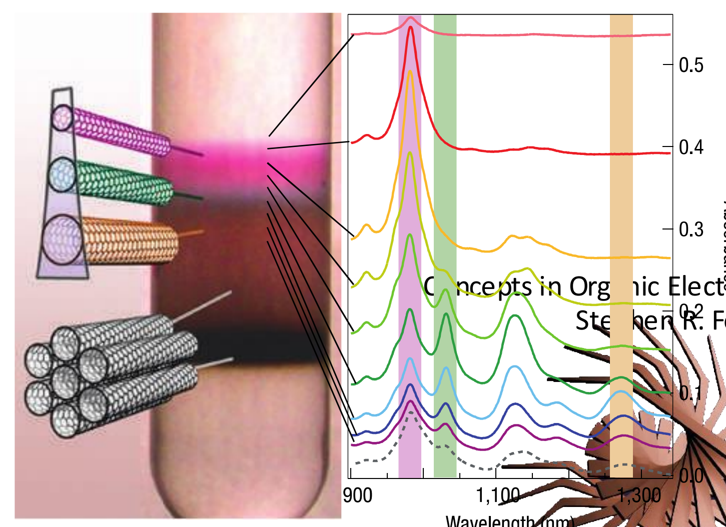


- Solvent density is graded from top (low density) to bottom (high density)
- Centripetal force (G) applied at 20 – 80K rpm. (a) Heavier particles float to bottom, (b) lighter to the top. (c) Particles of different densities separate independent of size.
- Micropipette extracts particles of desired size and density



Quantum Dots: 2 Solvent Mixture

Bai et al., J. Am. Chem. Soc. 132, 2333 (2010)



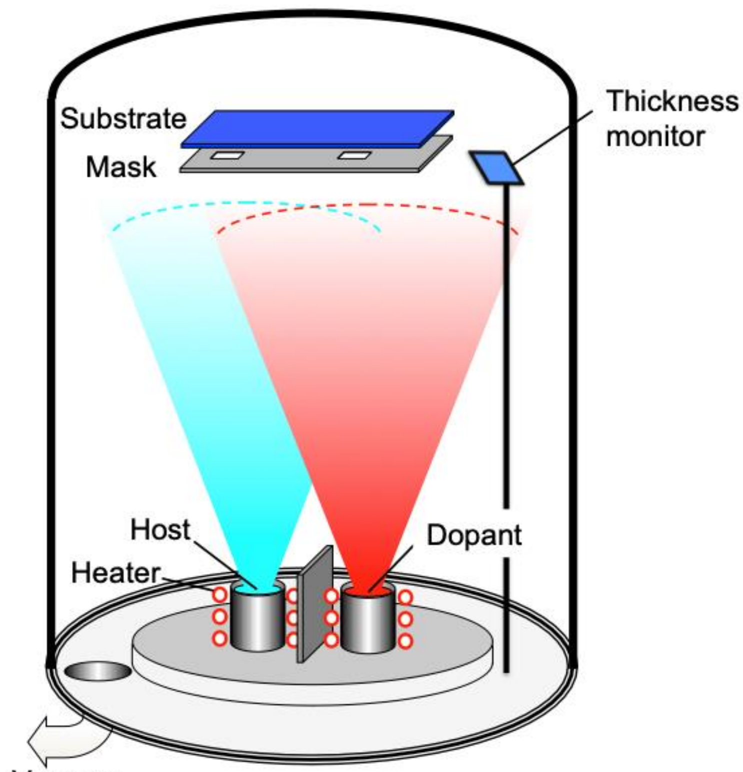
Carbon Nanotubes

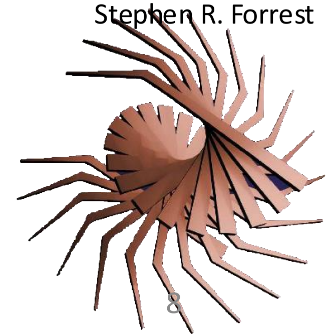
Arnold et al., Nat. Nanotech. 1, 60 (2006)

Film Deposition

Vacuum Thermal Evaporation (VTE)

- Most common method for small molecules
- Simple
- Precise
- Multilayer structures possible
- Wasteful of materials
- High vacuum: 10^{-7} torr
- Oil-free pumps

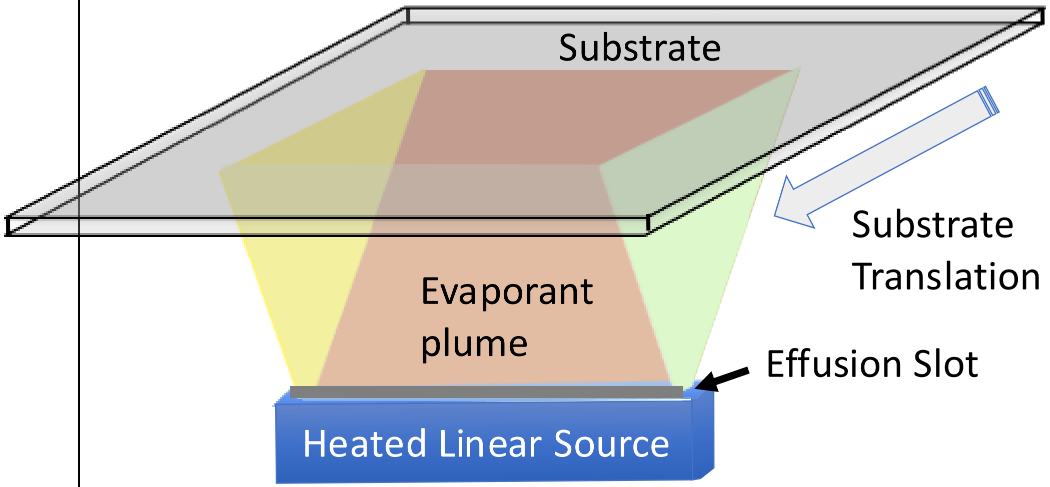




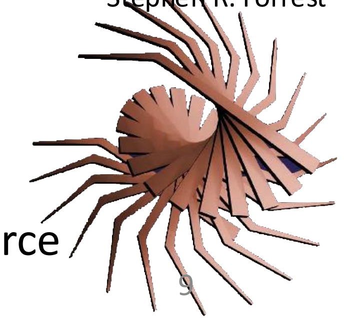
In-line VTE for Mass Production

Table 5.3: Approximate "mother" glass substrate sizes used in display manufacturing.

Substrate Generation[a]	Dimensions (in mm)[b]
1	300×400
2	400×500
3	550×650
4	680×880 or 730×920
5	1000×1200 or 1100×1300
6	1500×1800
7	1900×2200
8	2200×2400
9	2400×2800
10	2850×3050
11	3200x3600

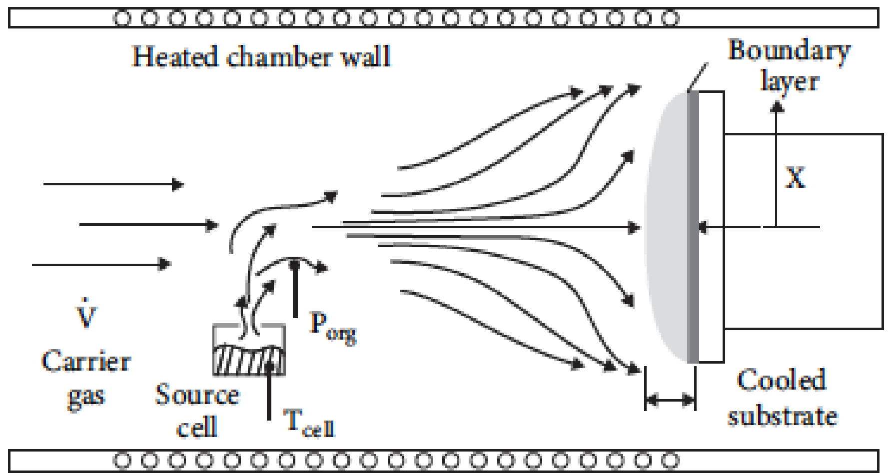


- Display manufacturing lines ~100-125 m in length!
- Glass substrate thickness ~0.3-0.7 mm
- Precise doping requires coincident fluxes from >1 linear source



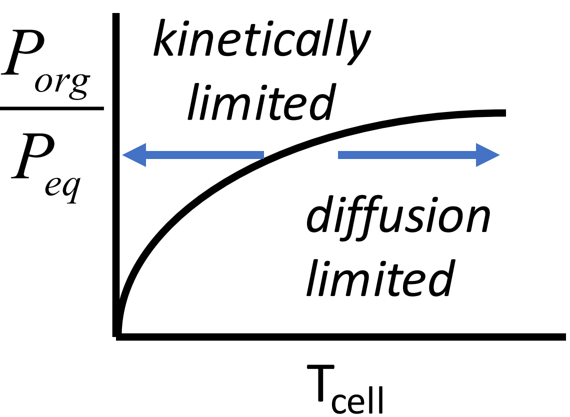
Organic Vapor Phase Deposition: Concept

0.1 - 10 Torr

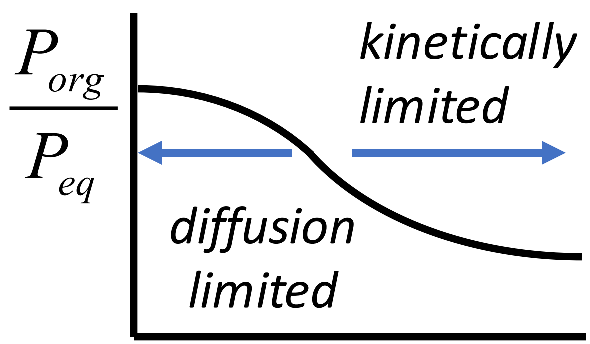


- Controlled and accurate doping (gas saturated with organics ~ equilibrium)
- Dust free chamber
- Efficient materials use
- Control of film crystal structure

Constant Flow Rate



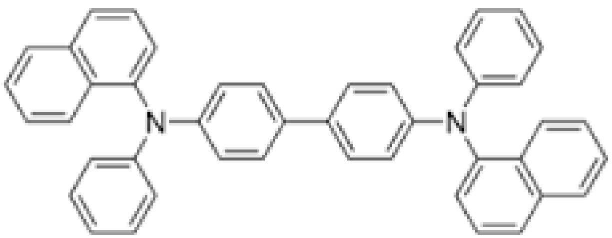
Constant Temperature



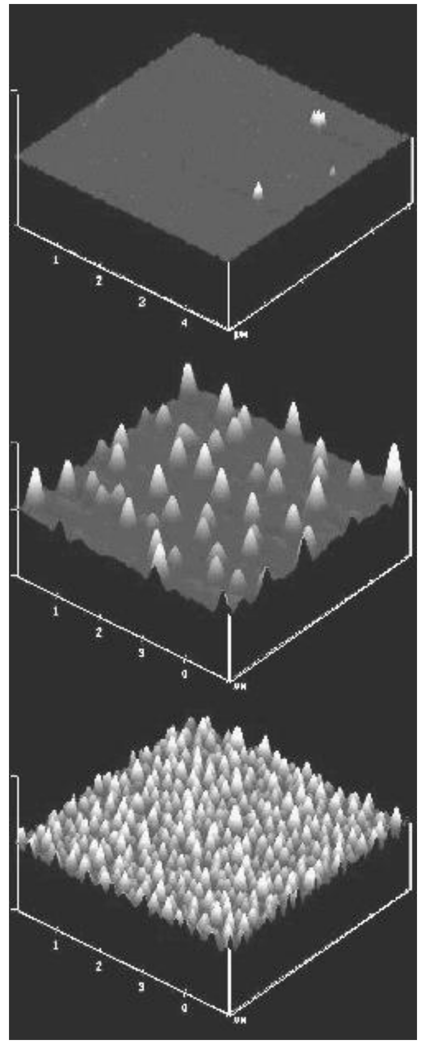
$$r_{out} = \frac{\dot{V}}{RT_{cell}} \frac{P_{org}\exp(-\frac{\Delta H}{RT_{cell}})}{1 + \dot{V}\delta / D_{org}}$$

M. Shtein, et al., J. Appl. Phys., 89, 1470 (2001).

Morphology Controlled by Gas Flow and Temperature Conditions



α-NPD
(hole conductor)



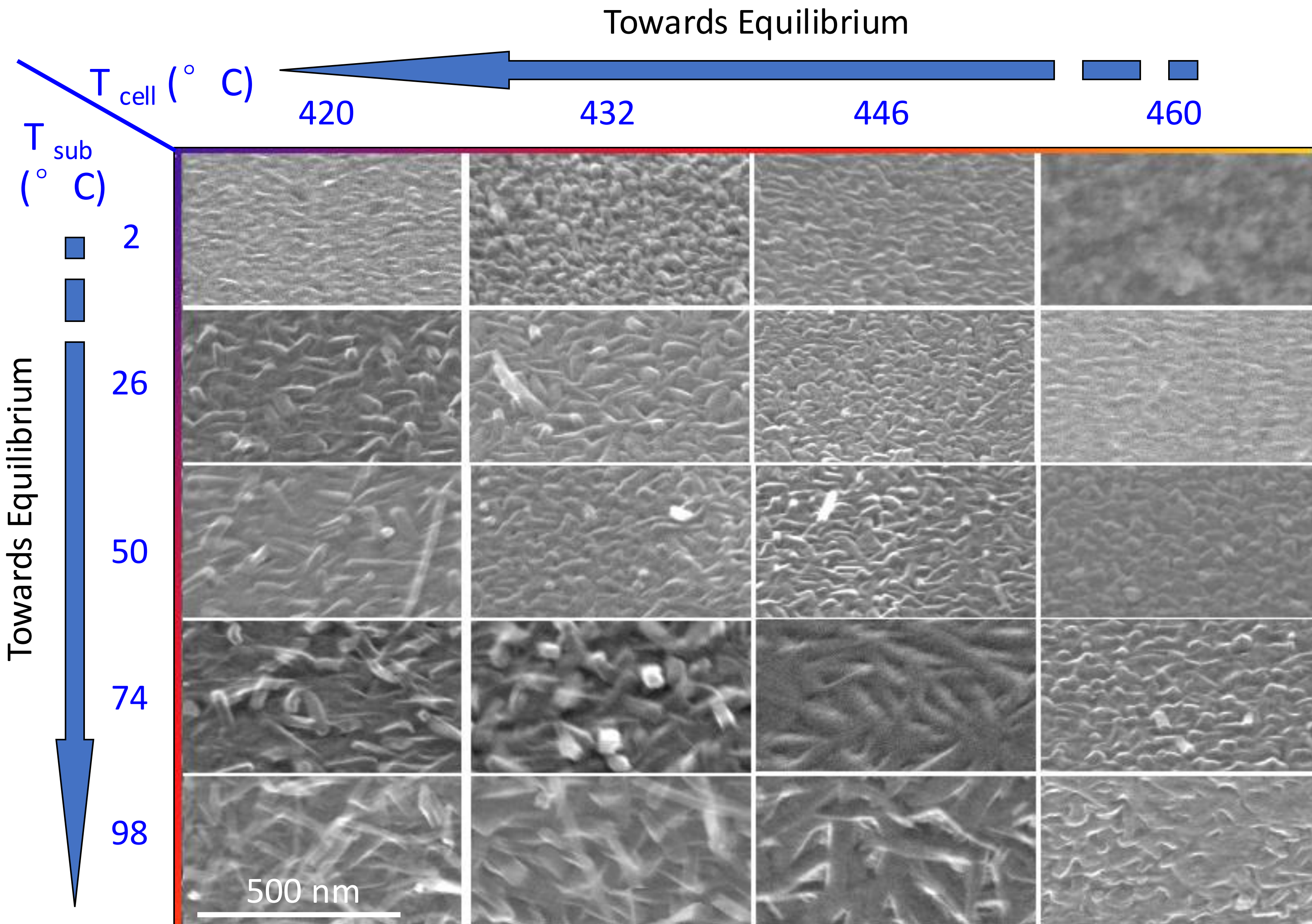
0.8 nm/s

1 nm/s

Gas phase nucleation ensues at high deposition rates ("snowing")

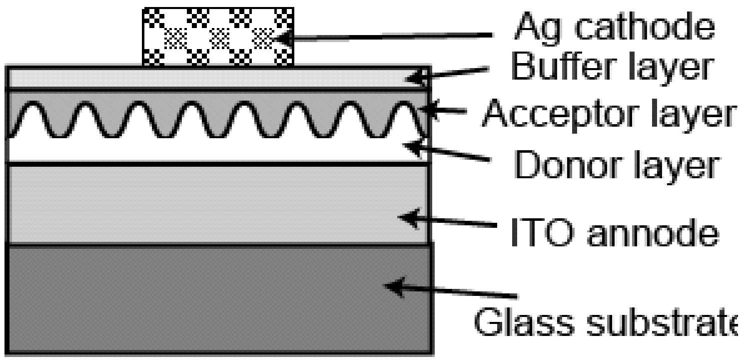
1.2 nm/s

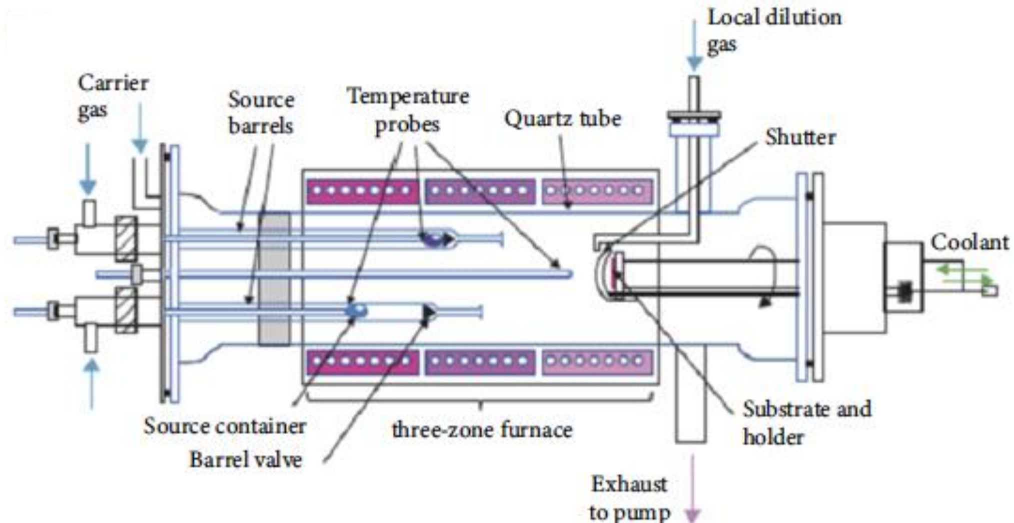
Nanomorphology control by temperature



(flowrate = constant, pressure = constant)

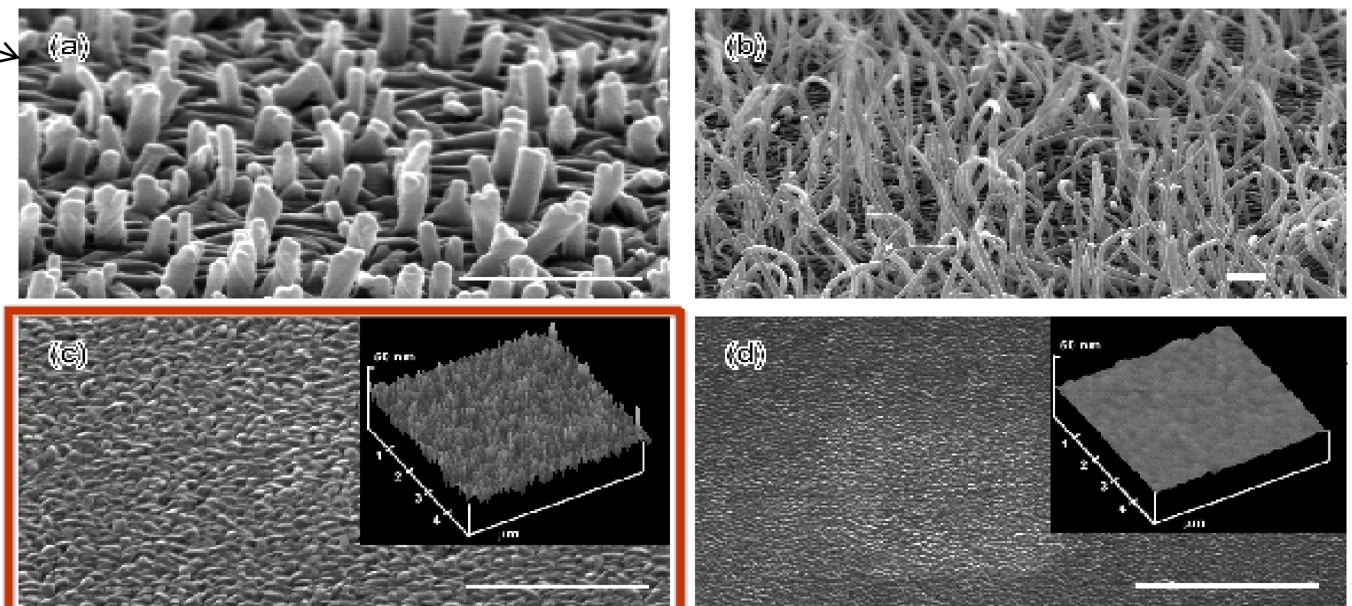
Controlled growth of a Bulk HJ by OVPD





Stranski-Krastonow growth

F. Yang, et al. Nature Mater., **4**, 39 (2005)



OVPD rms~3.5nm

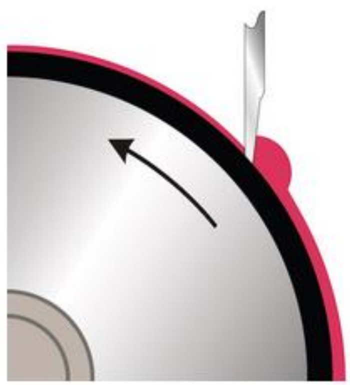
VTE rms~0.3nm

Different strain and growth conditions result in different structures

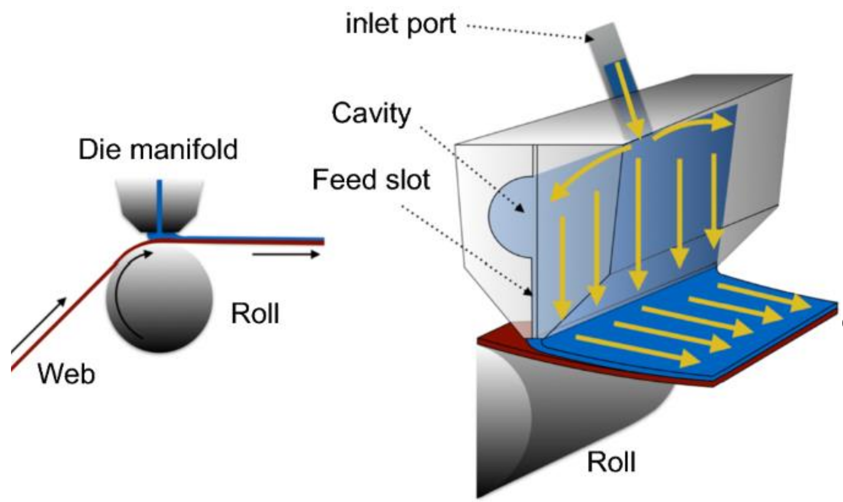
Film deposition from solution

Spin-on

Doctor blade

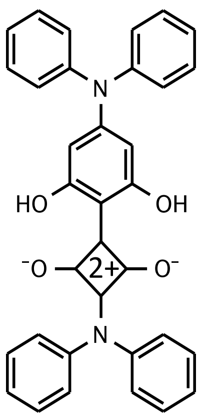


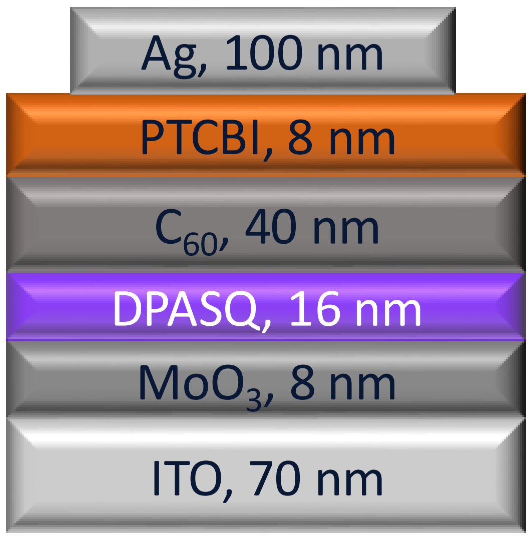
Slot-dye coating



Controlling Morphology Via Solvent Vapor Annealing

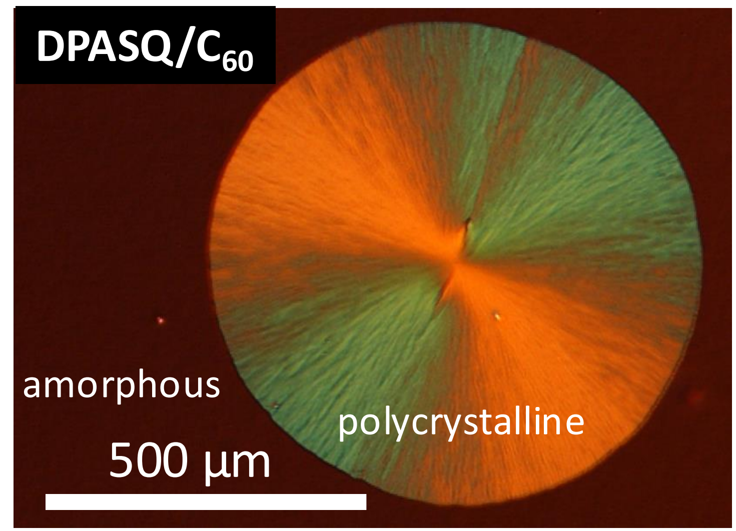
DPASQ





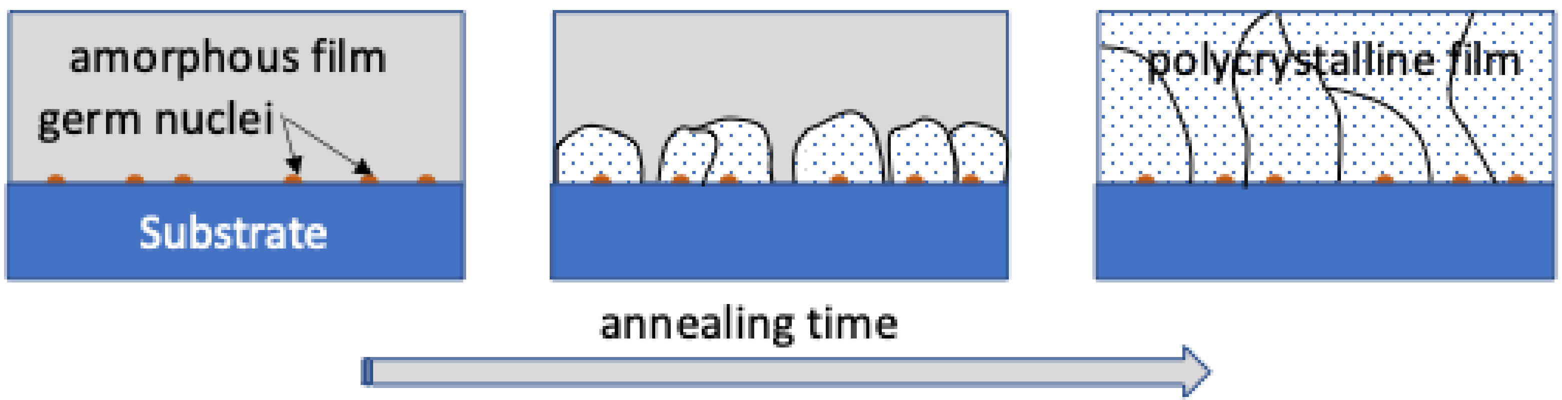
Conventional organic solar cell

Spherulite formation



- DPASQ (asymmetric)
  - Crystalizes easily.
    - Solvent vapor annealed (dichloromethane, DCM)

Controlling Morphology Via Thermal Annealing



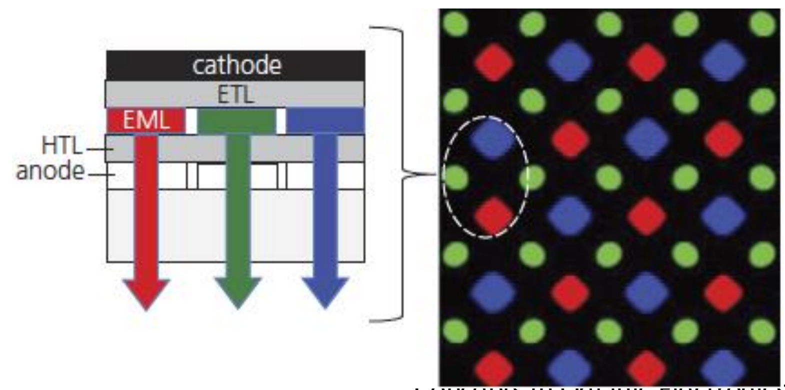
D. E. Motaung, et al. 2009. *Journal of Materials Science,* 44**,** 3192

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

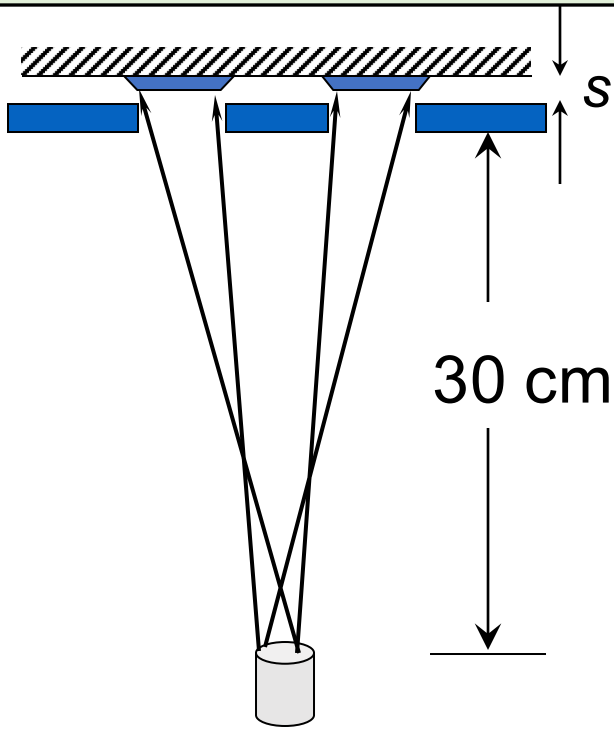


Example: Pixel micro-patterning in OLED displays

Shadow mask patterning in the kinetic and diffusive film growth regimes

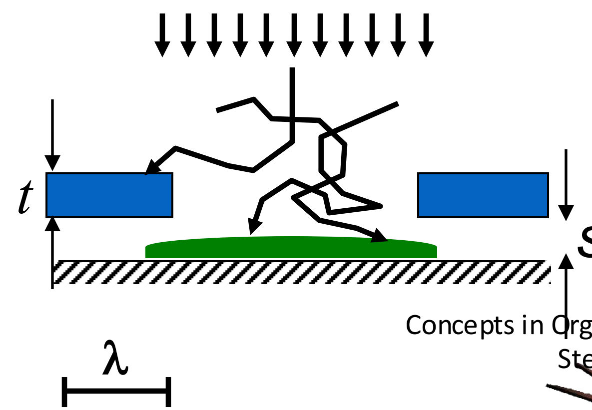
- Shadow mask patterning is the most common form of organic device electrode definition
- Used for producing OLED displays for small mobile and large TV applications

Vacuum Evaporation vs. Vapor Phase Deposition



$10^{-5} – 10^{-8}$ Torr

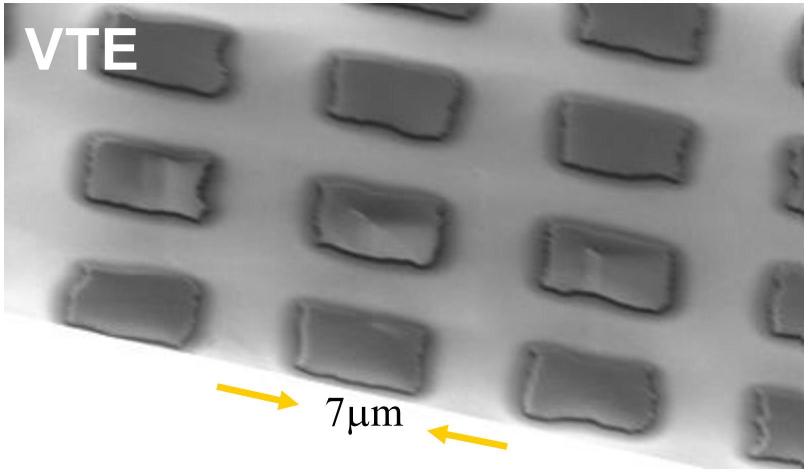
$$\lambda = \frac{k_B \cdot T}{\sqrt{2} \cdot \sigma \cdot P}$$ Mean free path

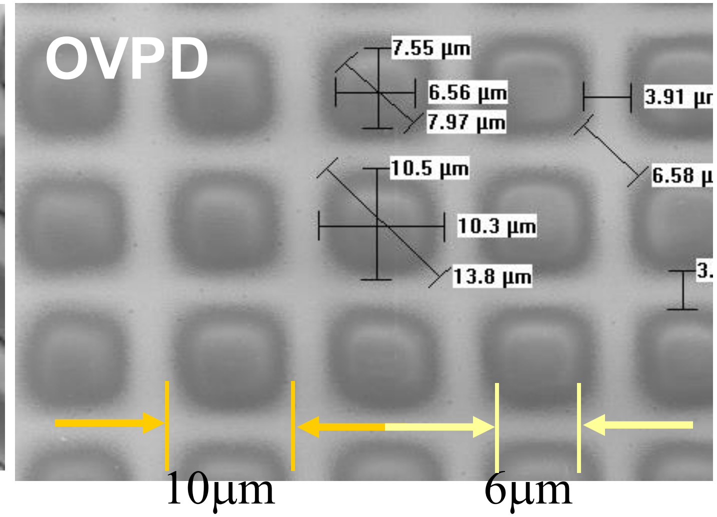


10^{-1} – 1 Torr

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

Resolution limits for shadow-masking





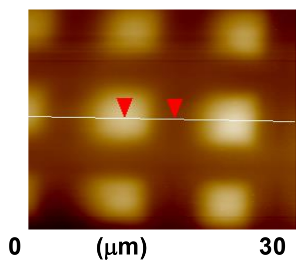
<u>OVPD Conditions</u>

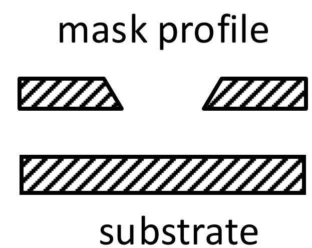
λ = 20μm

s=0.5μm

t=3.5μm

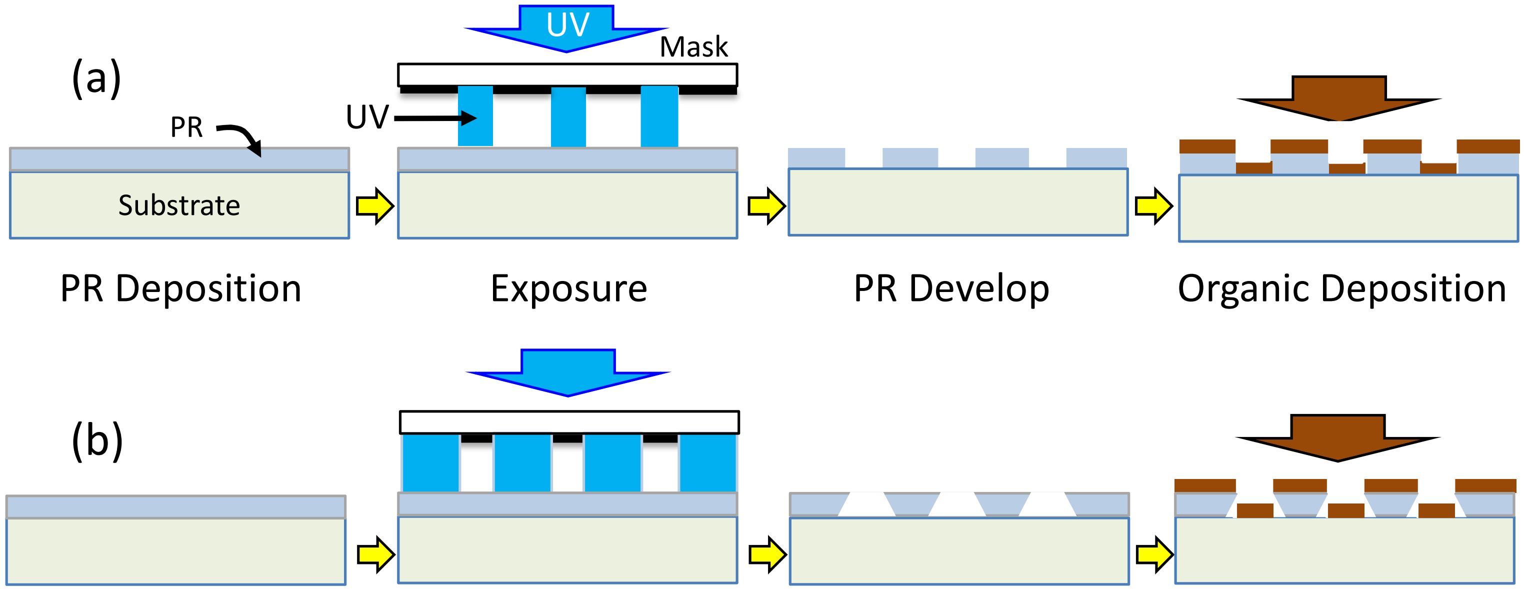
w=6μm

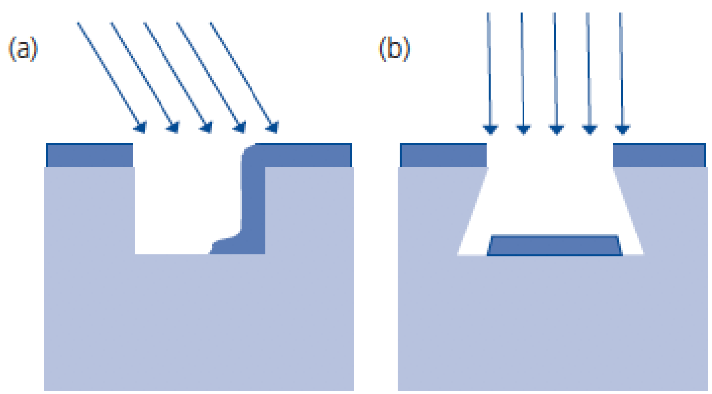




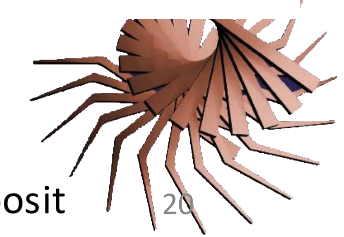
M. Shtein et al. J. Appl. Phys., **93**, 4005, (2003)

Use Photoresist to Create Surface Topography to Pattern Subsequently Deposited Organics





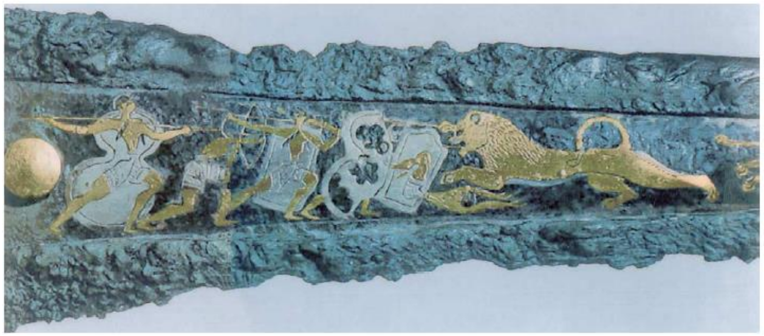
- Deposition of the organic in vacuum
- Shape of pattern on substrate depends on direction of the source to substrate



- 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

Cold welding: A stamping method used through the ages

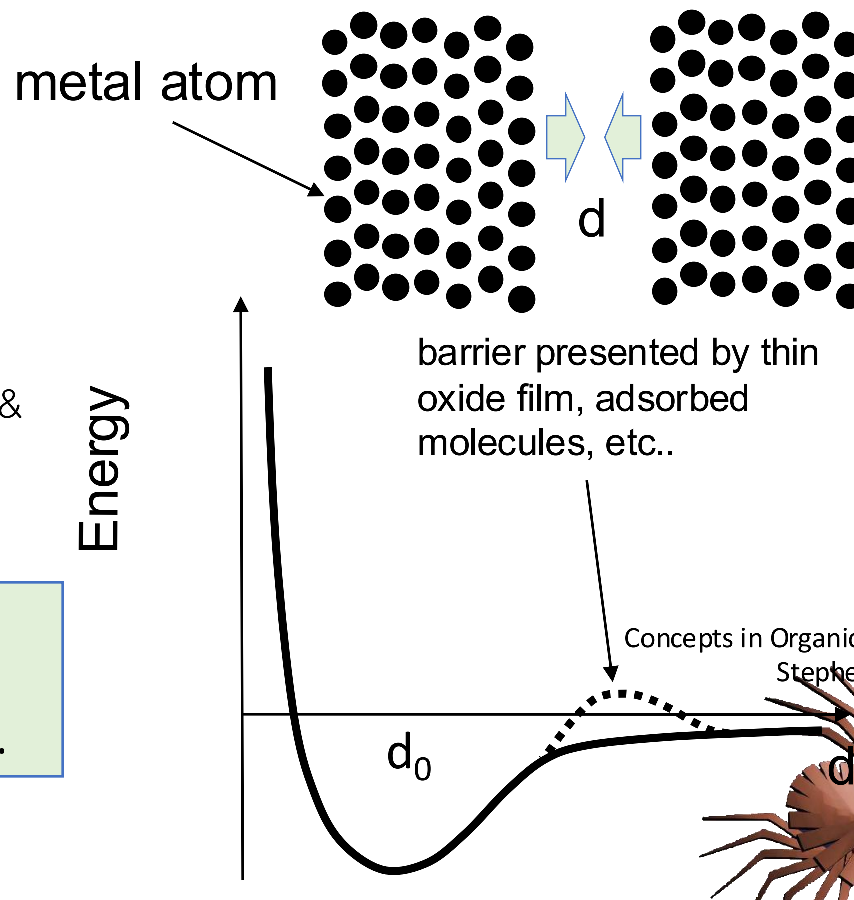
- Bring 2 clean metal surfaces together under pressure
- Atoms at surfaces eventually share outer shell electrons once any surface barriers are penetrated by pressure
- Bonding (i.e. complete sharing) of electrons occurs in ps



Bronze dagger blade with cold-welded gold and silver decorations. From Mycena, Greece; 2nd or 1st millennium B.C.

J. Haisma and GACM Spierings, Materials Science & Engineering R–Reports 37 1 (2002)

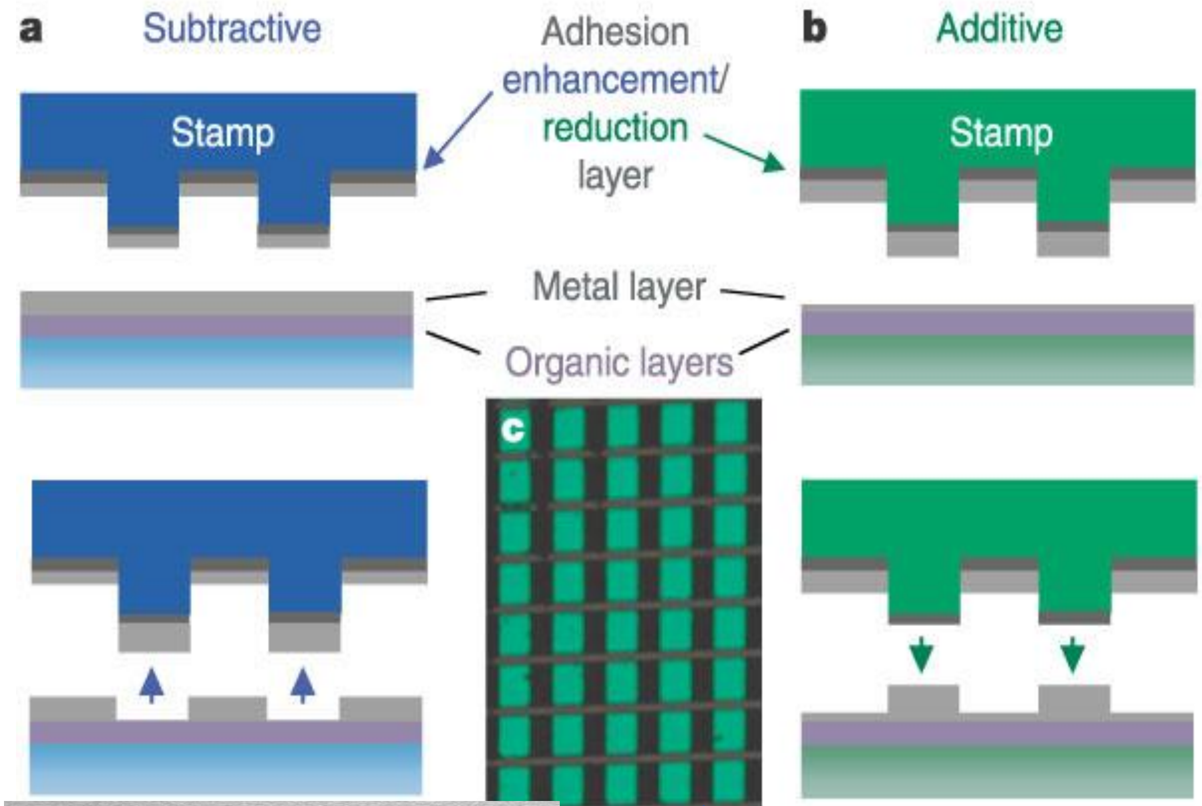
- Adhesive-free bonding of similar metals
- Useful for attaching contacts to organics, or even two organic films within a device.

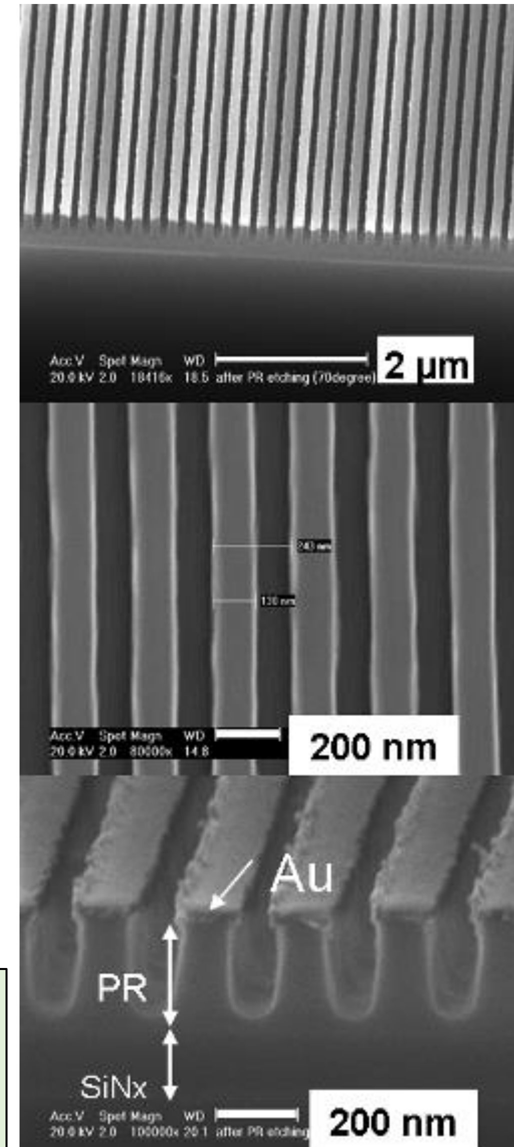


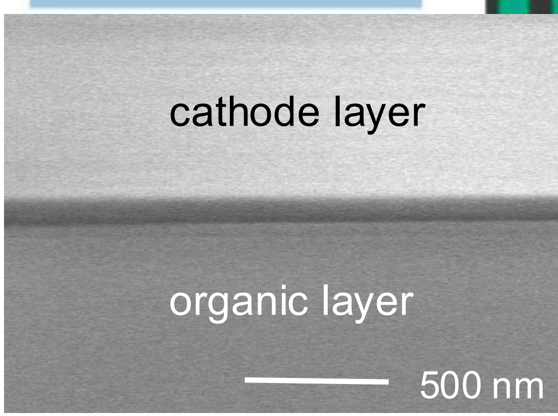
d_0 = equilibrium bulk separation

Concepts in Organic Electronics
Stephen R. Forrest

Cold-Welding Row and Column Electrodes







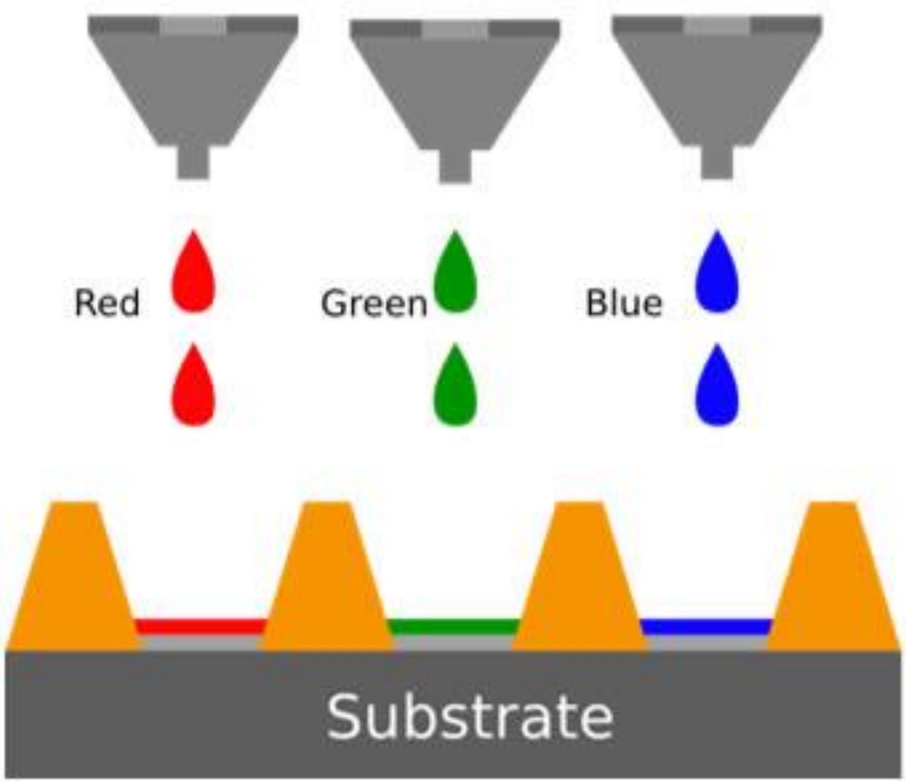
Nanoscale resolution

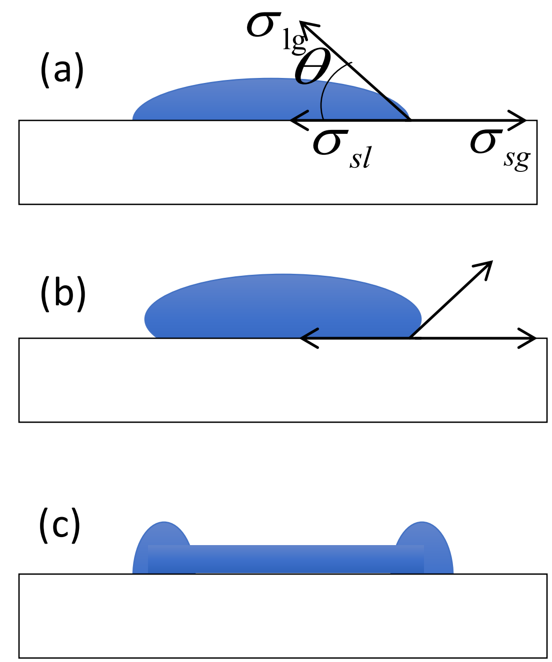
OLED Display with cold-welded cathode contacts

Two methods:
Subtractive (requires high pressure)
Additive (lower pressure)

C. Kim et al., Science **288** 832 (2000)

Inkjet Printing

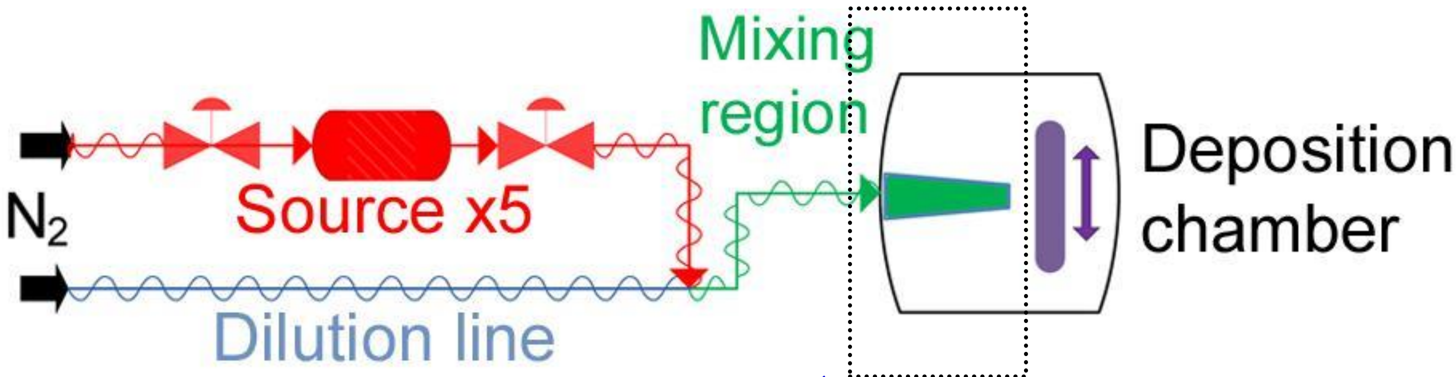


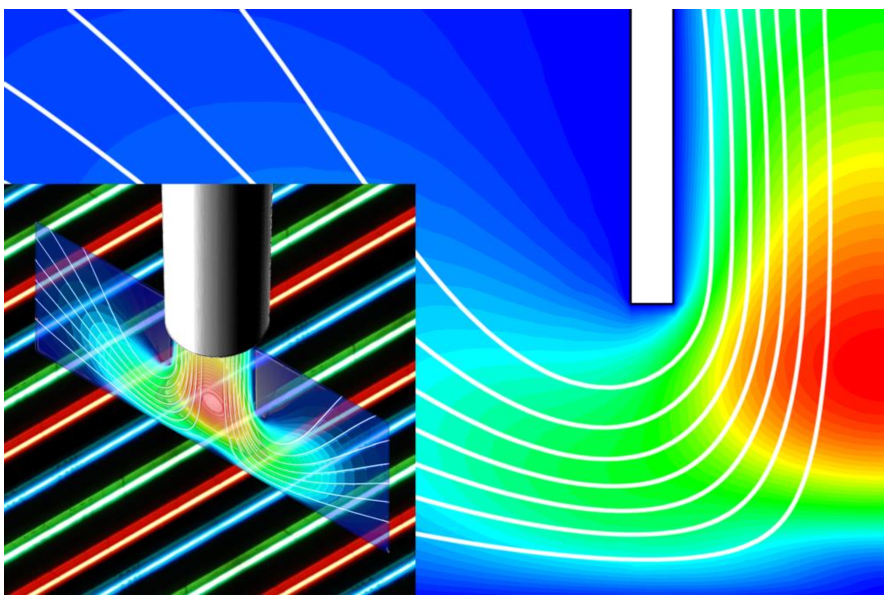


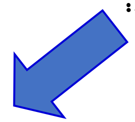
- Organic semiconductors similar to inks used in printing
- Organics must be soluble
- Droplets injected into wells formed by polymer walls

- 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

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



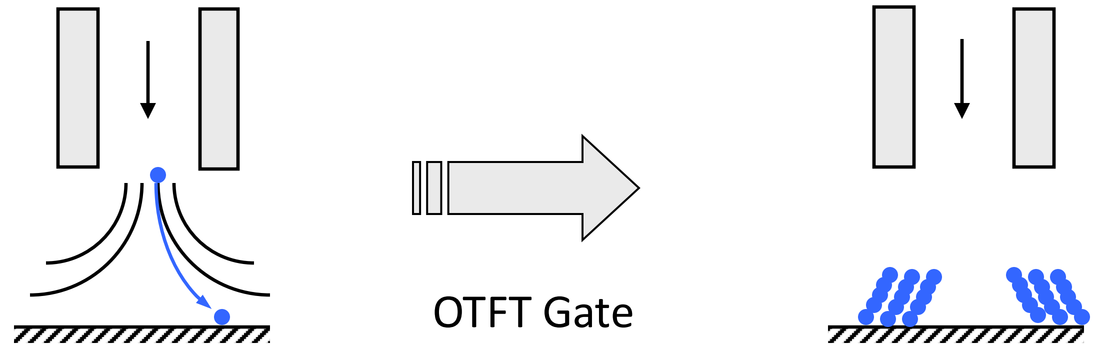


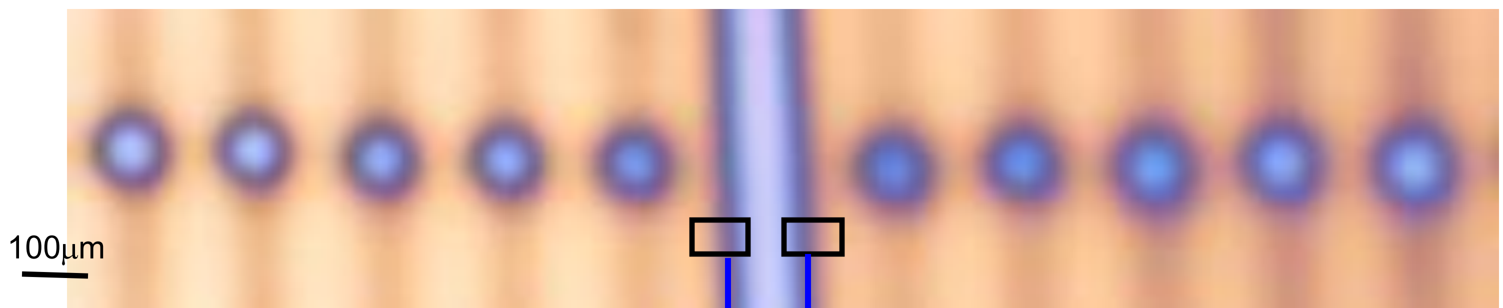


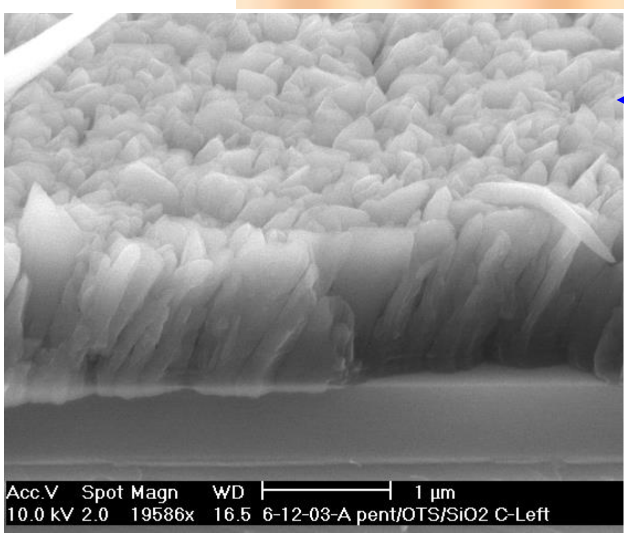
- Optimized R-G-B OLEDs can be combined to form a WOLED
- Each color separately optimized by choosing guest/host combinations
- Tunable color balance
- Motion stage beneath nozzle
- Nozzle creates high speed vapor jet

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

Flow anisotropy: Non-equilibrium crystallization & molecular ordering





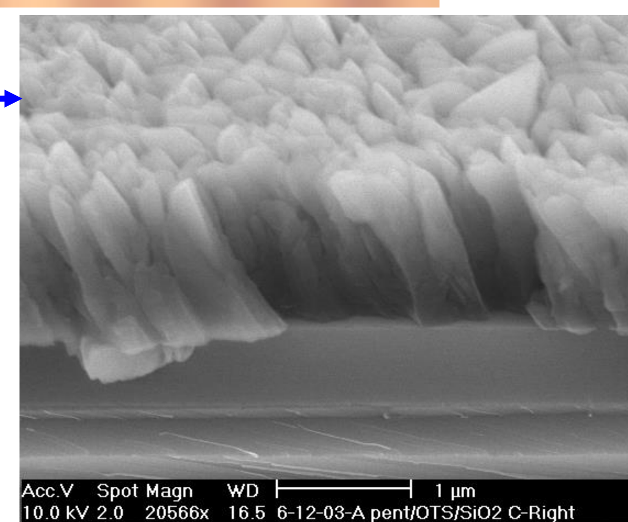


Local deposition rate: 700 Å/s

μ= 0.25 $cm^2/V \cdot s$

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

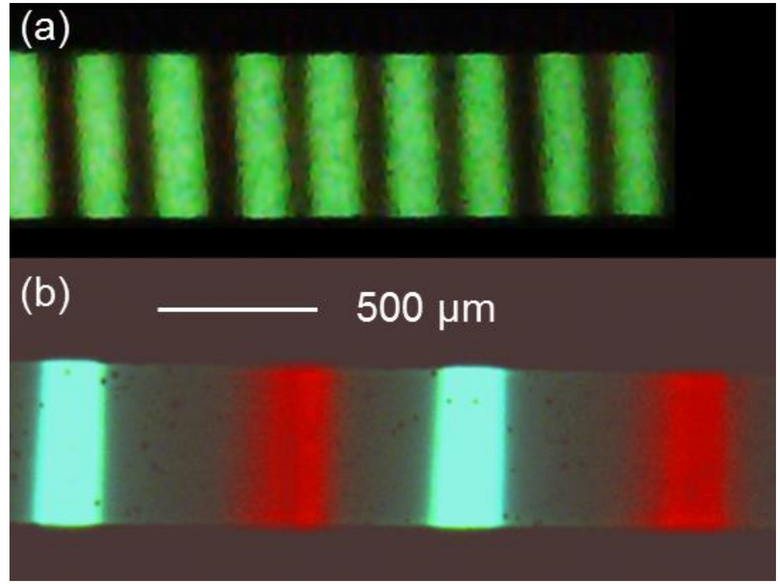
V_t = 17, 10 V



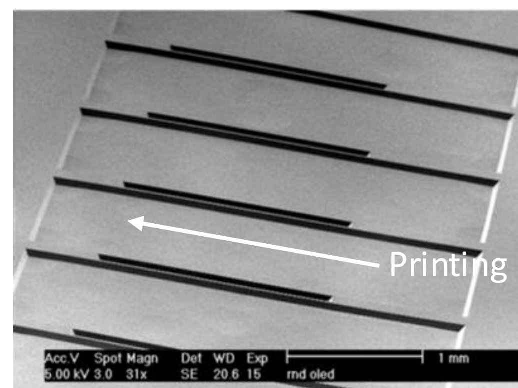
Printed R–G Pixel Arrays

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)

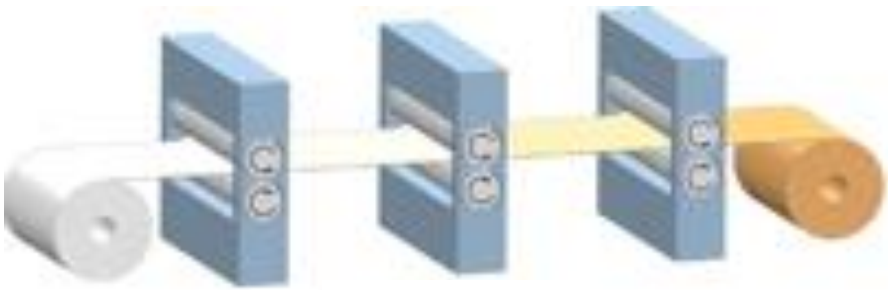


MEMS Nozzle Array

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

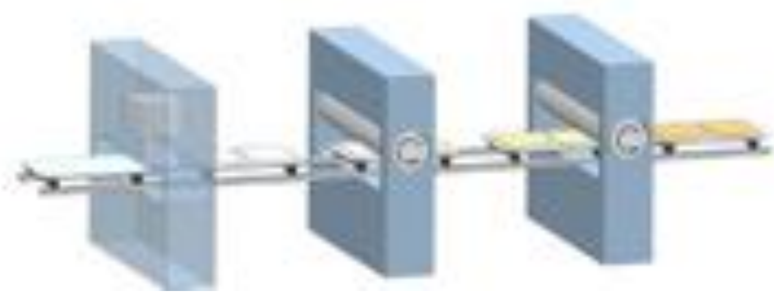
McGraw, et al. *App. Phys. Lett.* **8** 013302 (2011)

R2R Manufacturing Processes Useful for Rapid, Large-scale OE Device Production



Roll-to-roll

Sheet-to-sheet

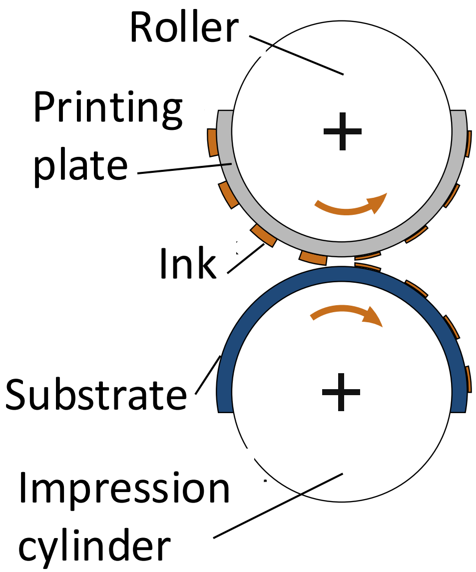


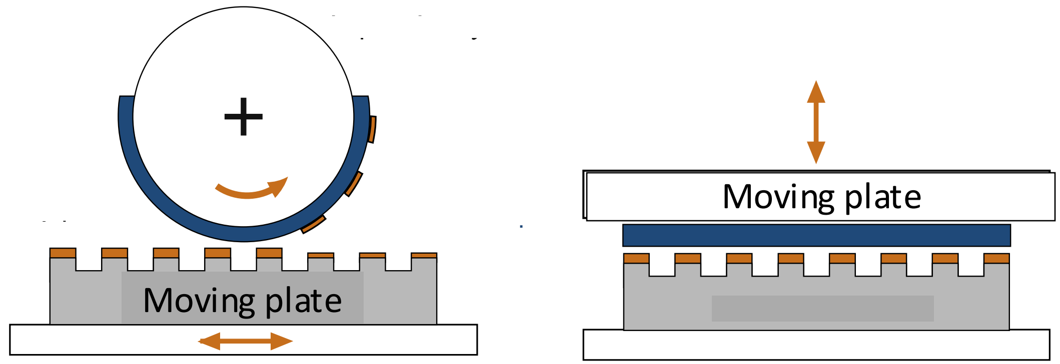
Sheet-to-carrier

Roll-to-Sheet

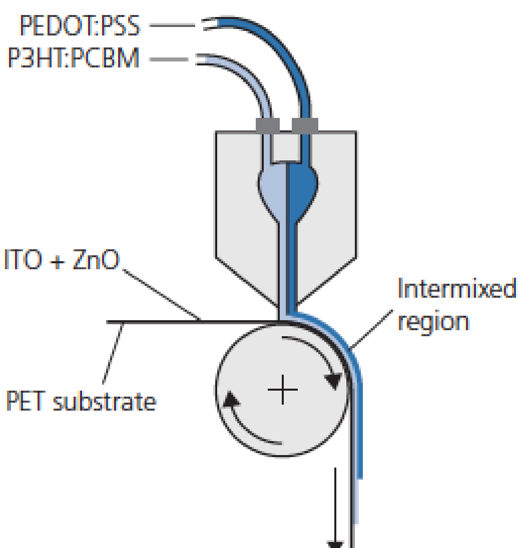
- Roll-based production requires flexible substrates
- Solution or vapor deposition of films possible
- Requires very clean (i.e. inert) gas environment

Continuous Printing Methods

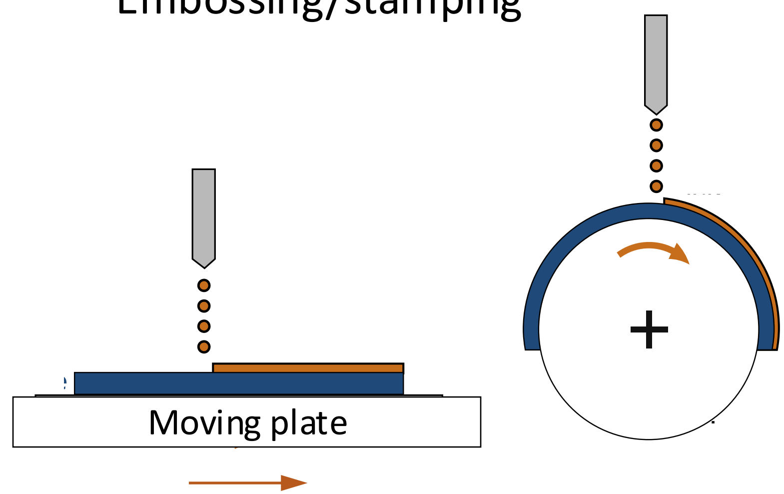




Embossing/stamping



Slot dye coating



Inkjet printing

What we learned

- Purity must be at the highest level to assure optimum device performance and lifetime
  - ➢ Purity obtained by distillation of materials according to their molecular weights
  - ➢ Small molecules more easily purified due to weight monodispersity
- Crystal growth in the bulk and thin film possible for materials by growth process and/or by post-growth annealing
  - ➢ Controlled, uniform growth by solution and vapor phase possible
- Patterning methods developed that can provide nanoscale features but avoid exposure of layers to destructive wet chemistry
  - ➢ Many patterning process adapted from the print industry (inkjet, screen, gravure, etc.)
- Rapid R2R manufacturing of very large areas of devices a nearly unique advantage of organic electronics
  - ➢ But manufacturing must be done in clean, oxygen and contaminant-free environment
- Devices must be packaged to be protected from the environment