# Week 7

# Growth and Patterning

Materials purification
Thin film growth
Device patterning
Packaging

Chapter 5

# 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:

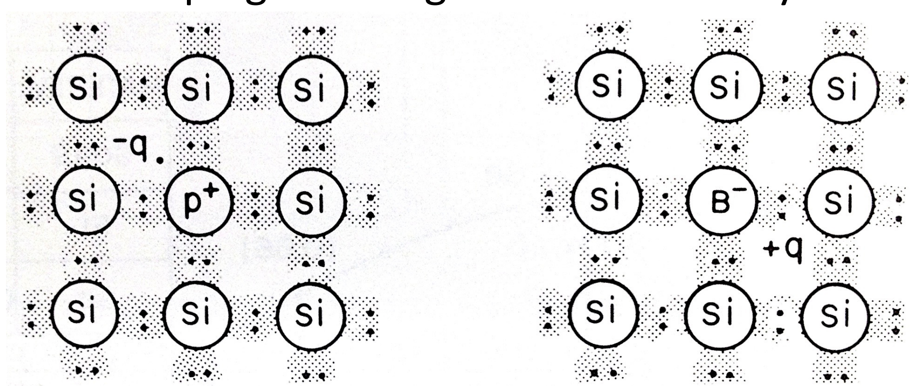
- Extrinsic defects
    - Dopants and “dirt”
    - Substitutional
    - Interstitial
- Intrinsic defects
    - Vacancies
    - Stacking faults

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

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

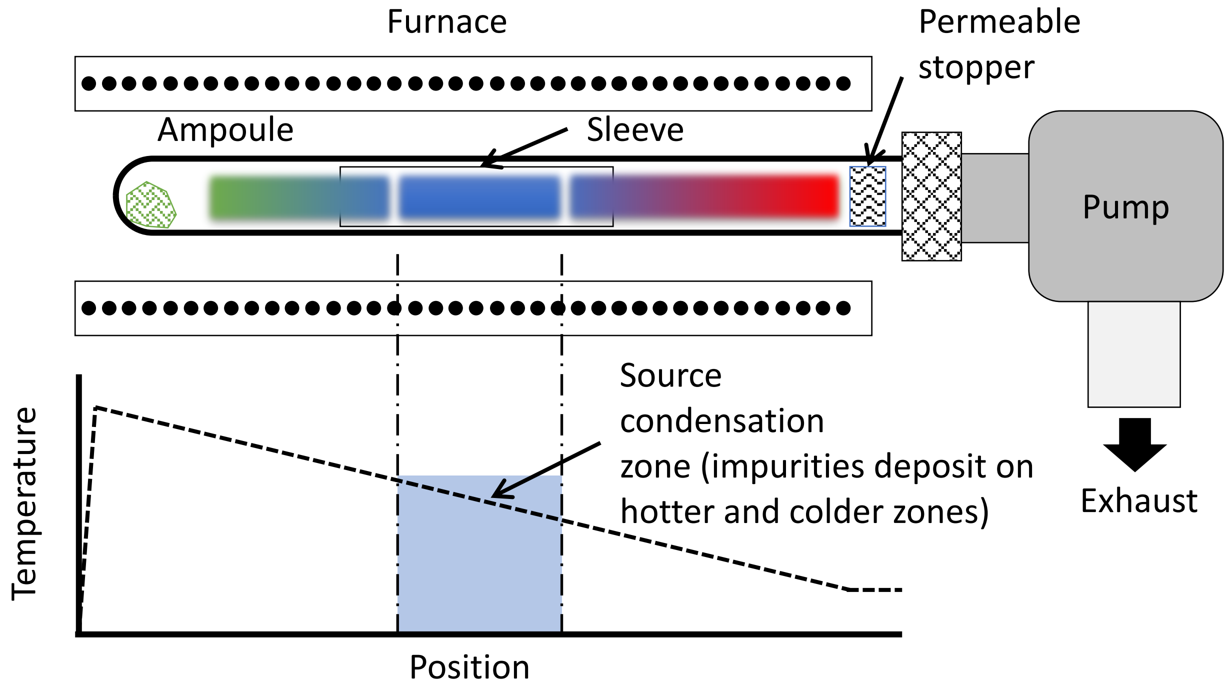
In all cases, the inclusion of <u>unwanted</u> impurities leads to undesirable outcomes

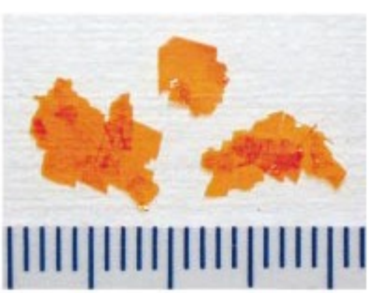
This is different  from doping to change the conductivity of a semiconductor



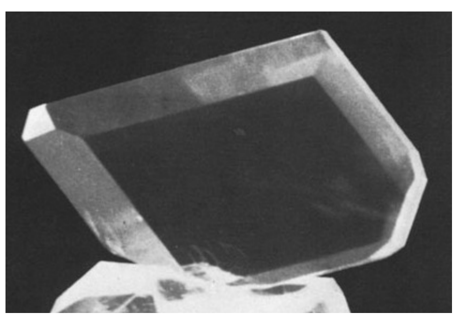
# Purification by Thermal Gradient Sublimation

Useful for obtaining very high purity small molecule materials



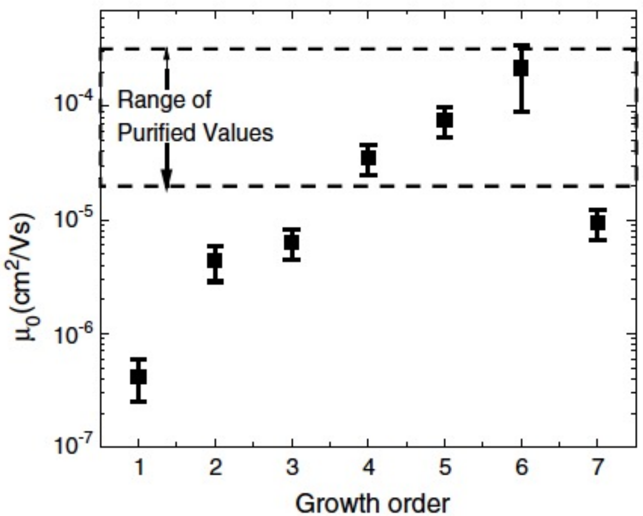
Tetracene after sublimation



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

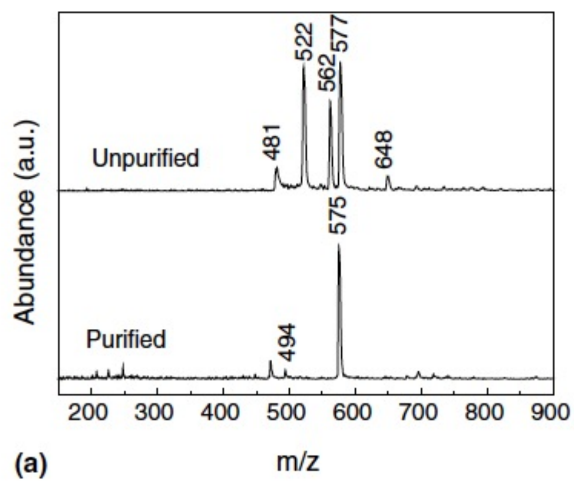
# Purification of CuPc via Multi-cycle Sublimation in Vacuum

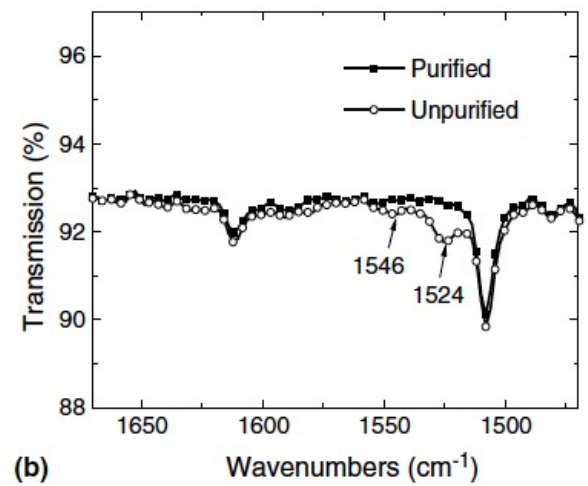



Mobility increases with sublimation cycle due to increased purity

reduction of impurity signatures

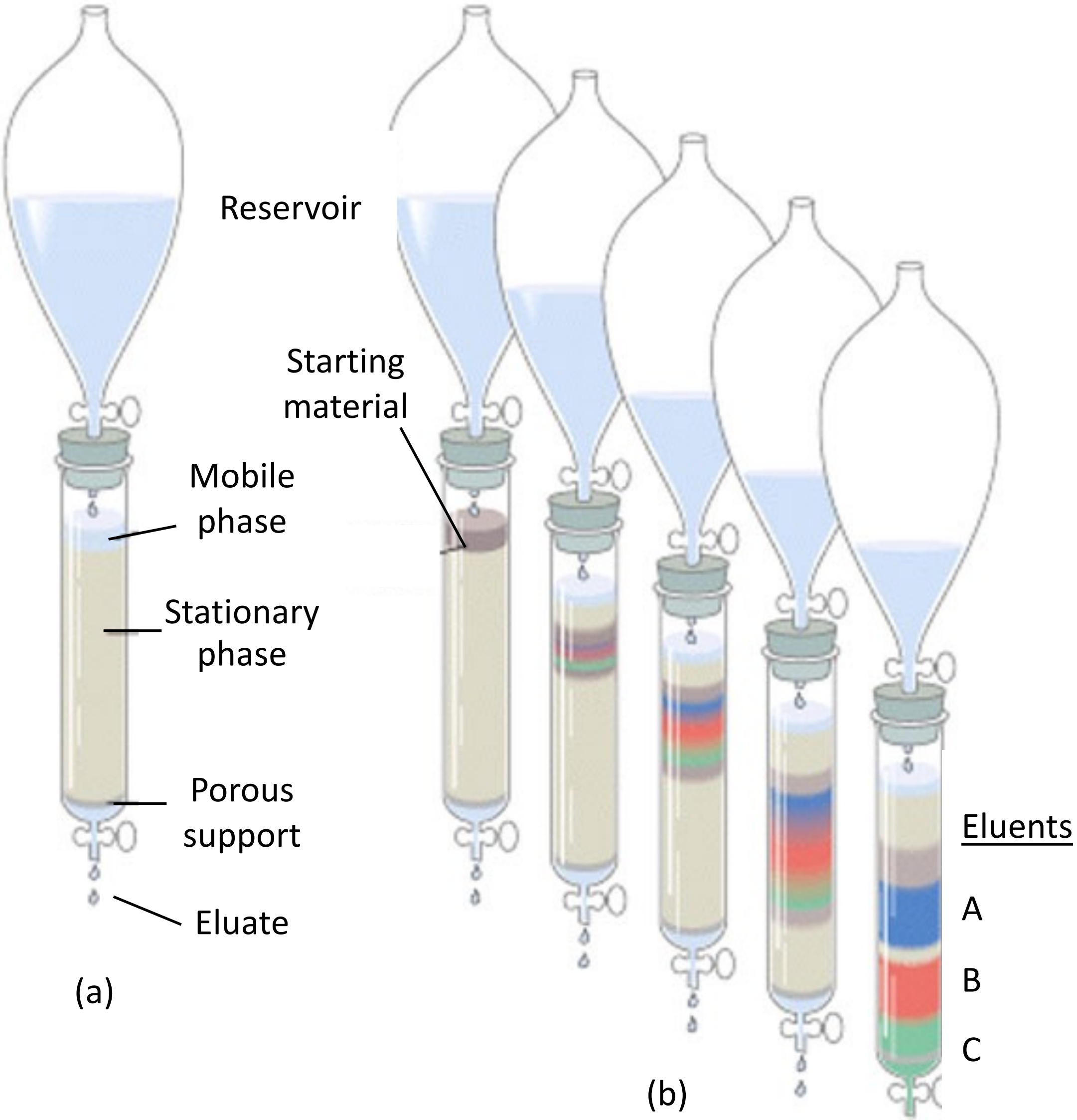
$H_2Pc$ main impurity



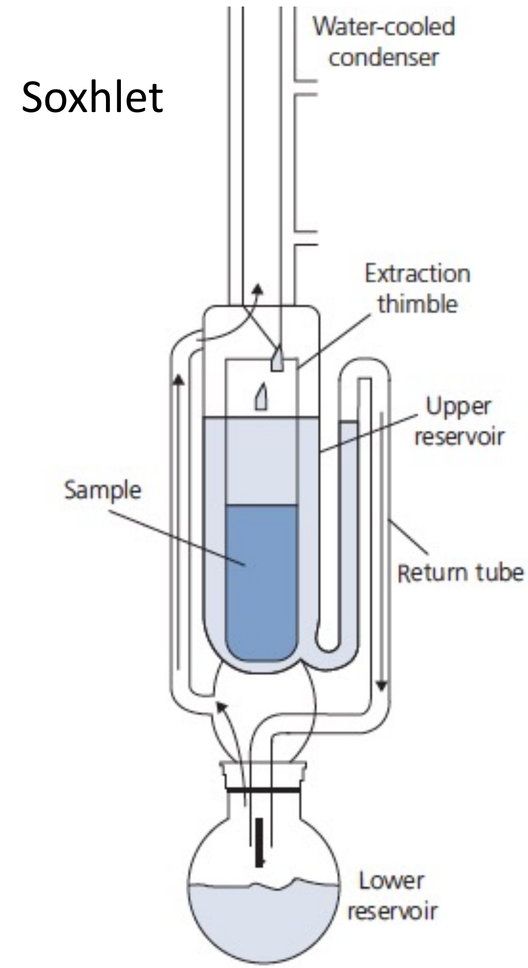




Salzman, et al., Organ. Electron. 6, 242 (2005)

# Purification via Solution



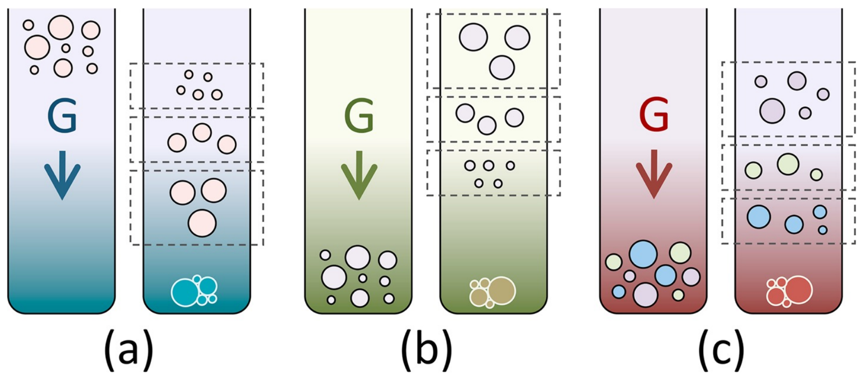

Column High Pressure Liquid Chromatography (HPLC)

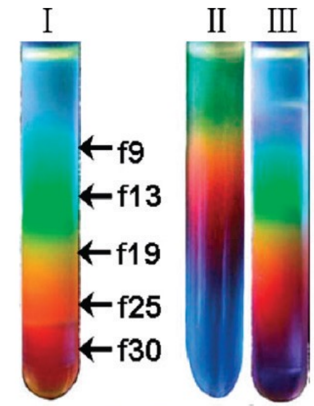



Solvent Washing

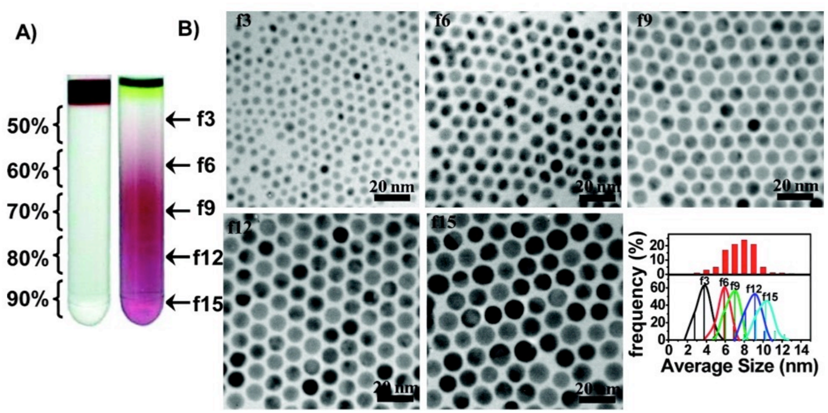
# Purification via Centrifugation

Density gradient centrifugation



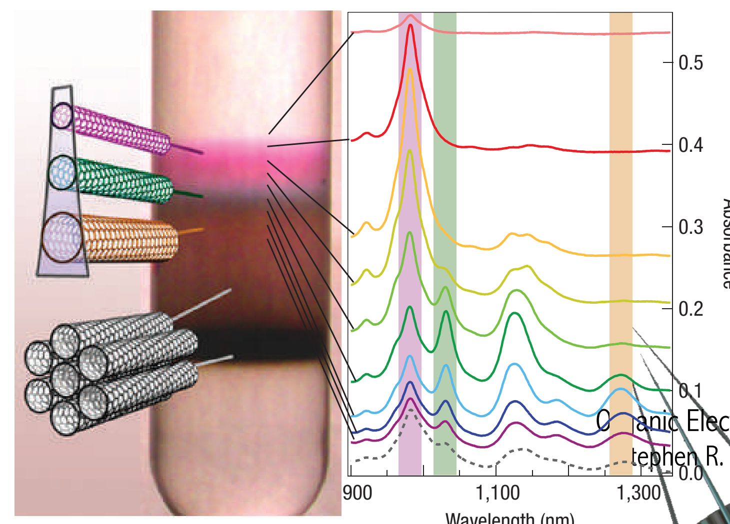




- Solvent density is graded from top (low density) to bottom (high density)
- Centripetal force (G) applied at 20 – 80K rpm. (a) Heavier particles float to bottom, (b) lighter to the top. (c) Particles of different densities separate independent of size.
- Micropipette extracts particles of desired size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




Quantum Dots: 2 Solvent Mixture

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



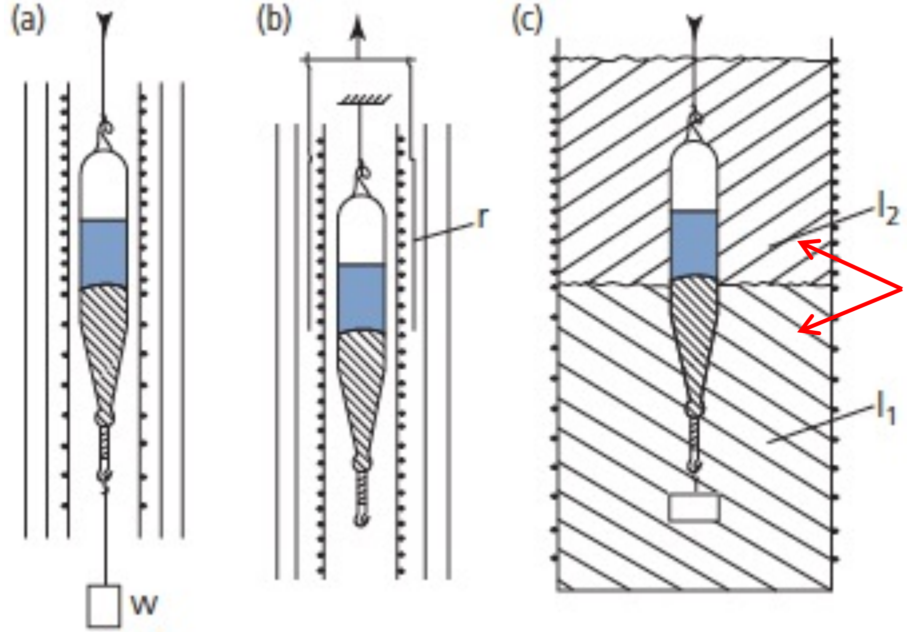

Carbon Nanotubes

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

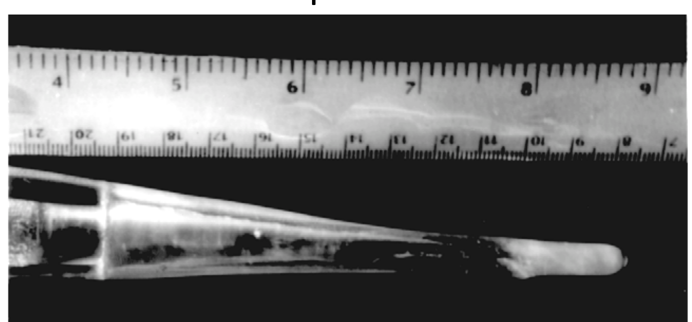
# Crystal Growth: Bridgeman Process

Material has to have a solution (melt) phase

Growth front moved from position of seed




Three ways to manage the growth front temperature
(a) bias-wound heating coil, (b) reflective shield around top coils, (c) immersion into a fluid with two immiscible liquids to conduct heat



anthracene single crystal

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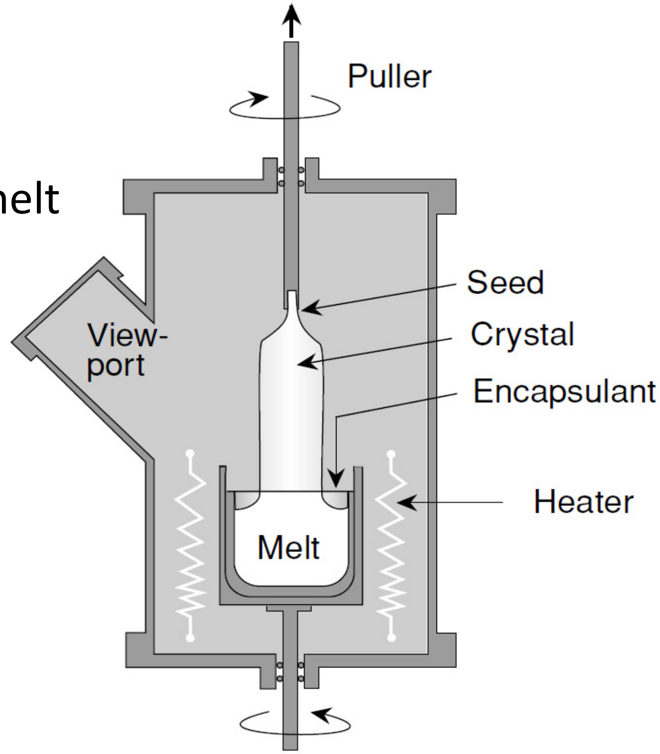
# Crystal Growth: Czochralski Process

Material has to have a solution (melt) phase

Seed slowly pulled from melt



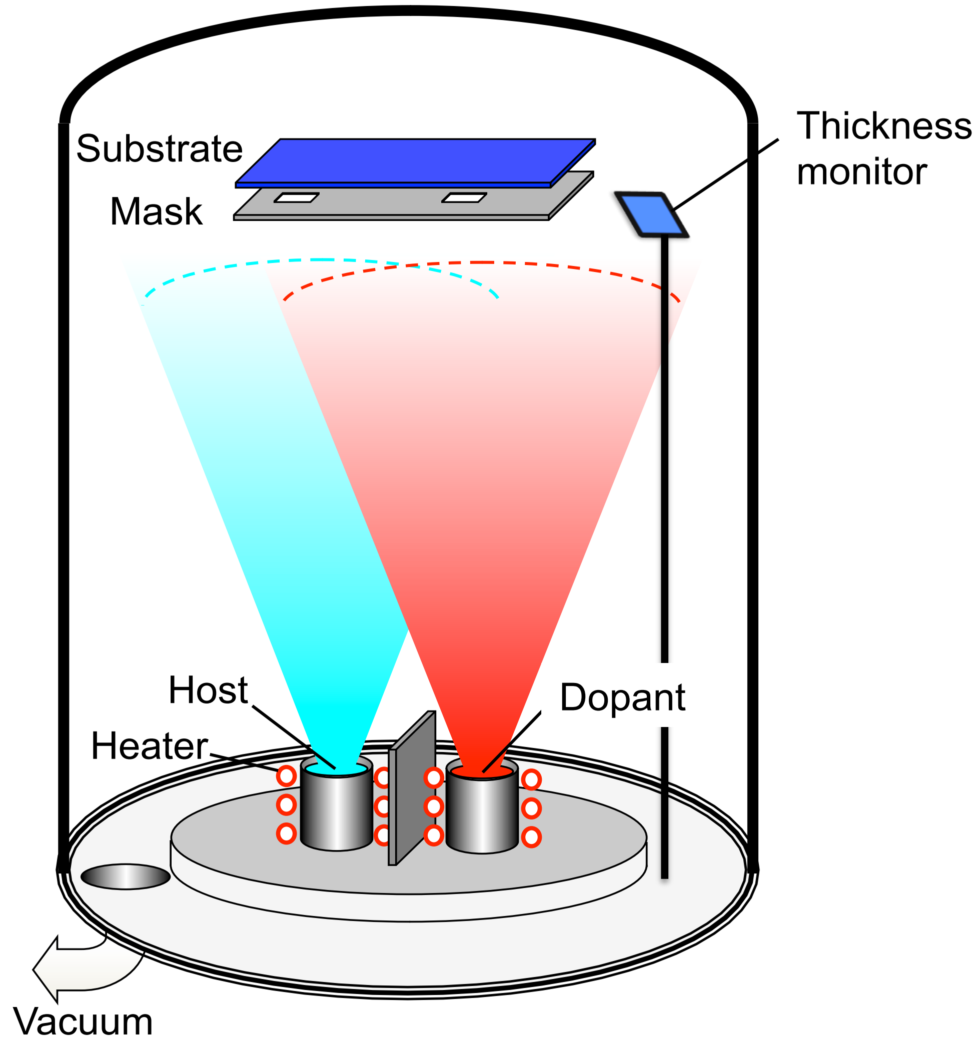

Benzophenone crystal boules

Sankaranarayanana and Ramaswamy J. Cryst. Growth 280, 467 (2005)

# Film Deposition

## Vacuum Thermal Evaporation (VTE)

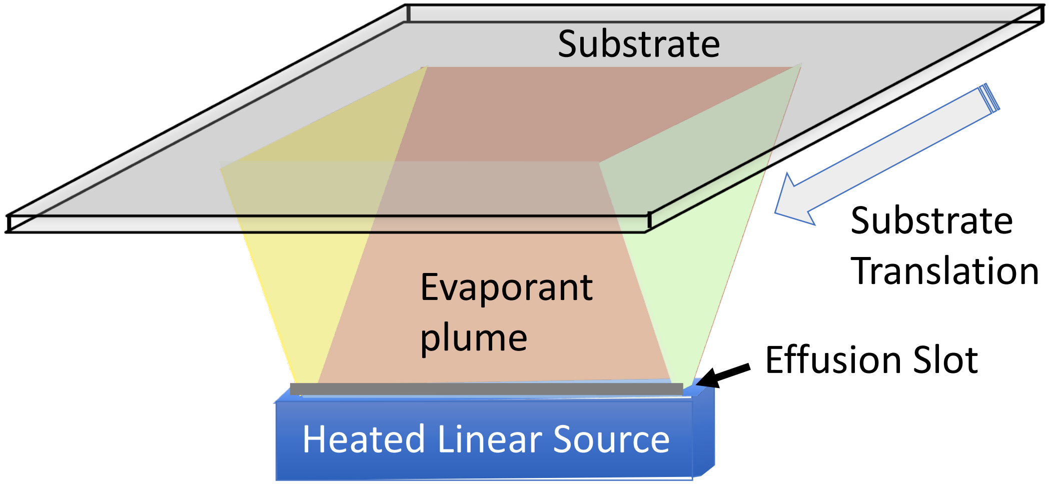
- Most common method to date
- Simple
- Precise
- Multilayer structures possible
- Small molecules, not polymers
- Wasteful of materials
- High vacuum: $10^{-7}$ torr
- Oil-free pumps



# In-line VTE for Mass Production

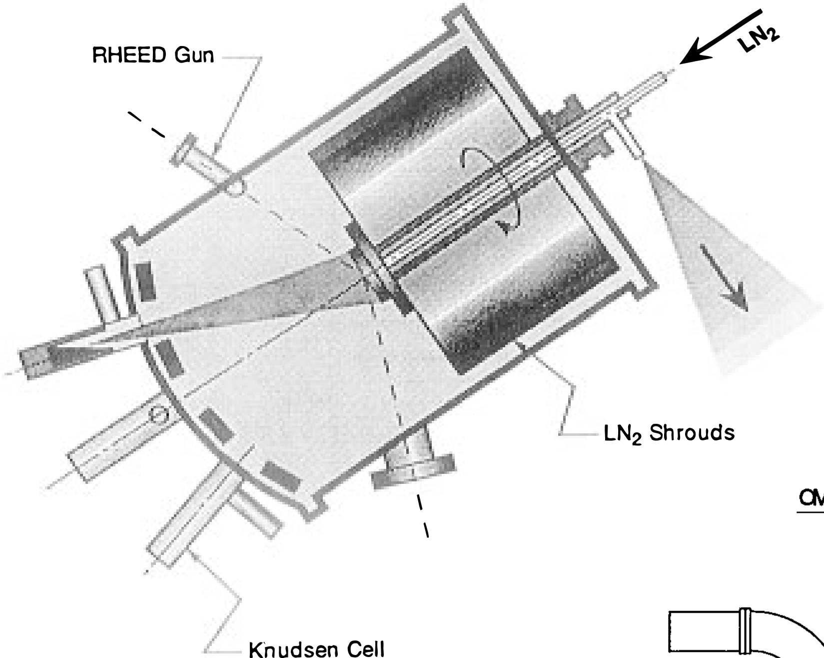
Table 5.3: Approximate "mother" glass substrate sizes used in display manufacturing.

| 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 |

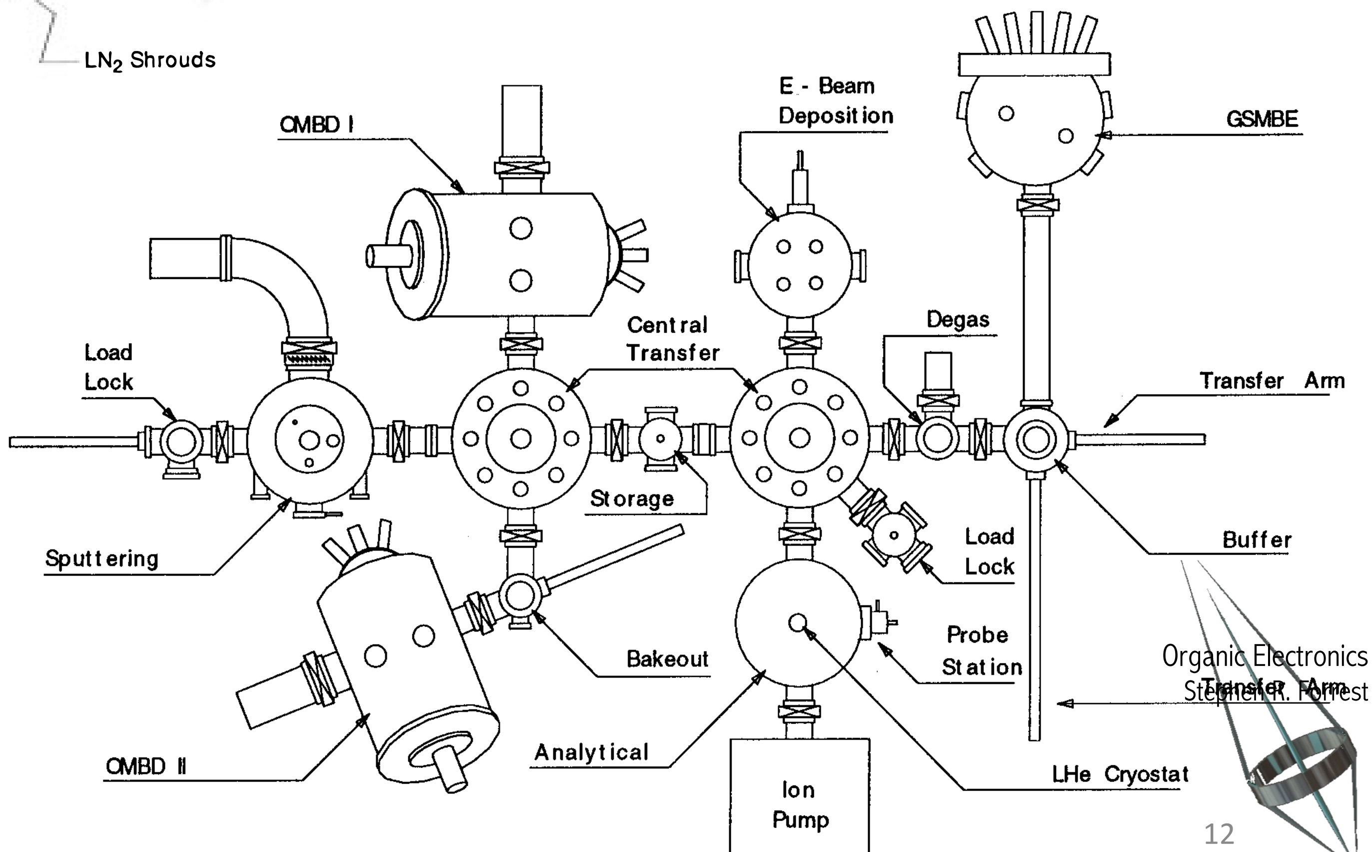



- Display manufacturing lines ~100-125 m in length!
- Glass substrate thickness ~0.3-0.7 mm
- Precise doping requires coincident fluxes from >1 linear source

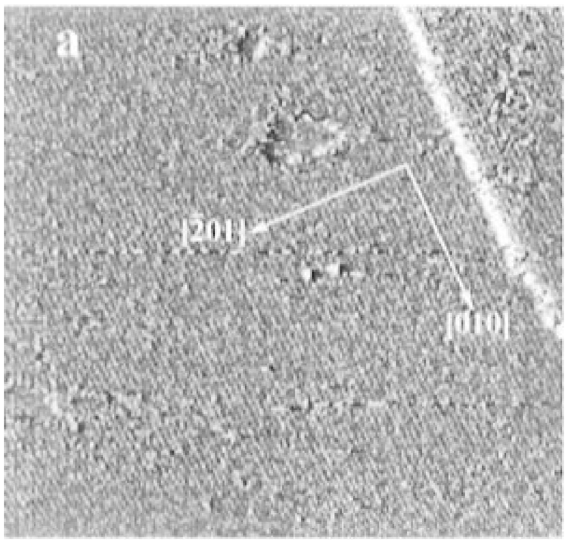
# Organic Molecular Beam Deposition (OMBD)



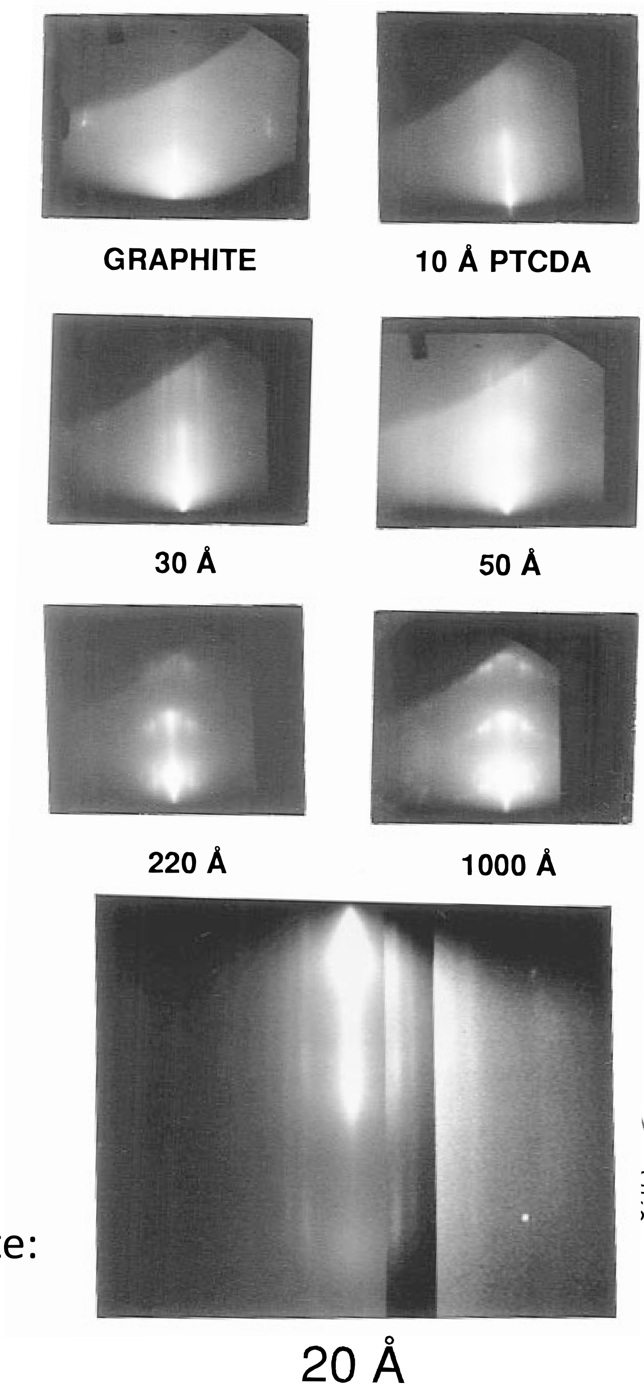

Ultrahigh Vacuum Environment: ~$10^{-10}$ torr
Extremely low impurity concentrations
Scientific exploration
Monolayer growth control
In-situ diagnostics
- RHEED, PES, I-V…



# Near Perfect Growth by OMBD



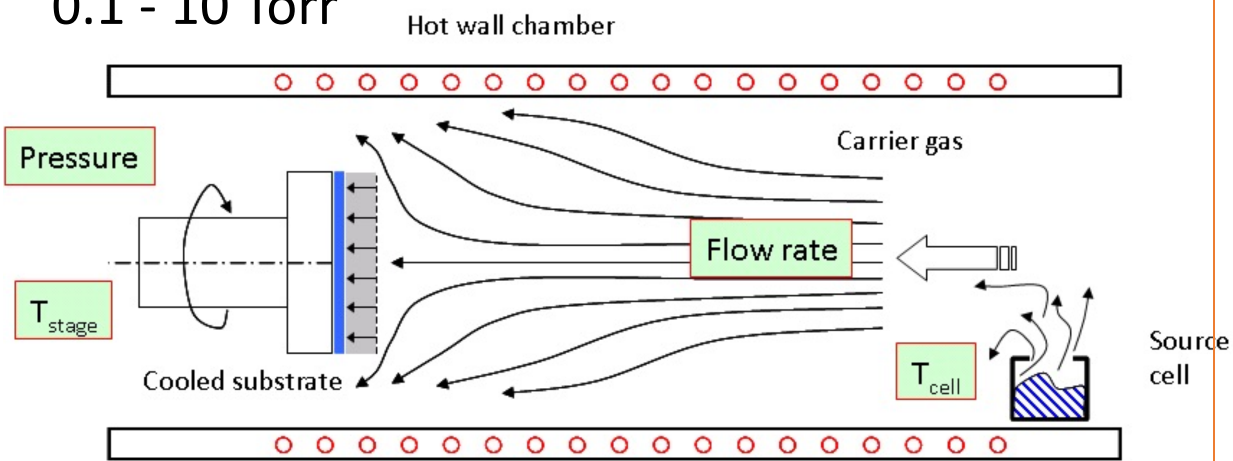

STM image of PTCDA on Graphite:
Layer by layer growth without epitaxial matching




RHEED of PTCDA on Graphite:
Flat and ordered

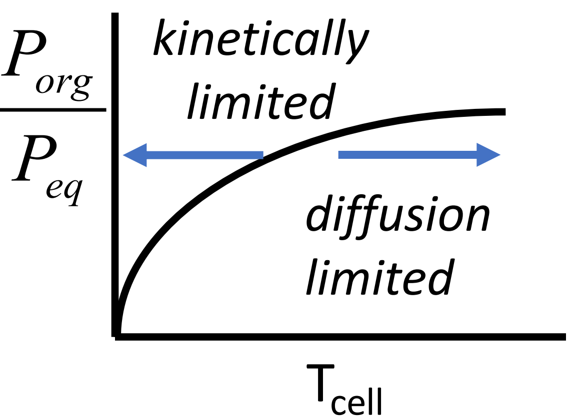
# Organic Vapor Phase Deposition: Concept

0.1 - 10 Torr

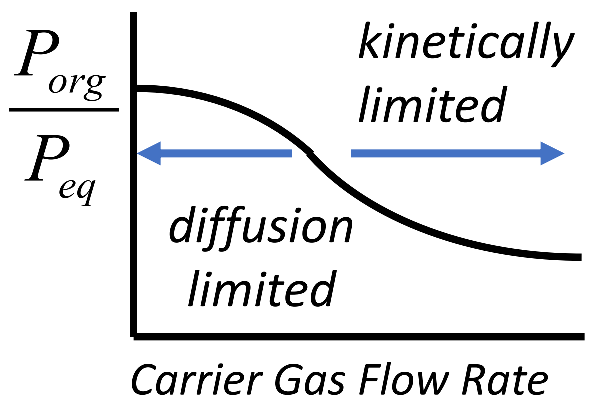



- **Controlled and accurate doping (gas saturated with organics ~ equilibrium)**
- **Dust free chamber**
- **Efficient materials use**
- **Control of film crystal structure**

*Constant Flow Rate*




*Constant Temperature*

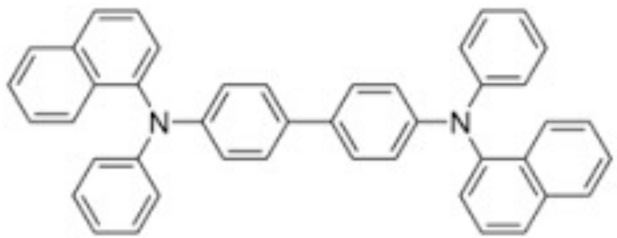



$$r_{out} = \frac{\dot{V}_{src}}{RT_{cell}} \cdot \frac{P_0 \exp(-\Delta H / RT_{cell})}{1 + \dot{V}_{src} / A_{evap} D_{org}}$$

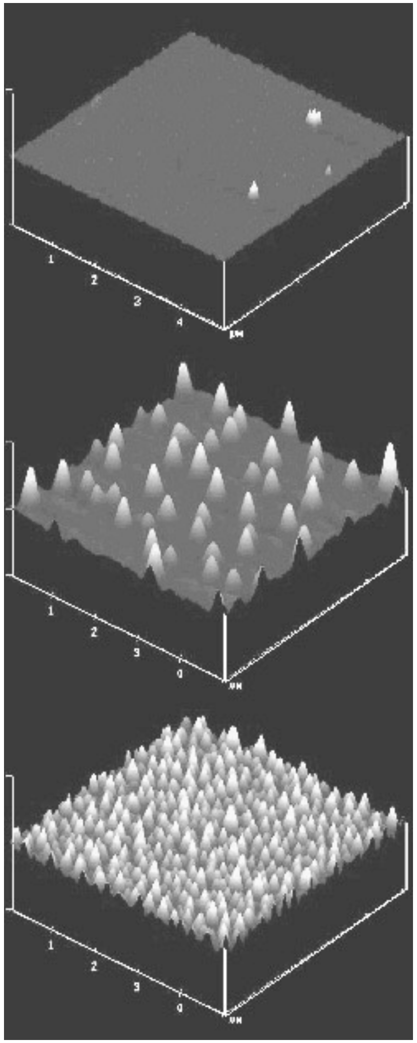
Stephen R. Forrest

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

1.2 nm/s

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

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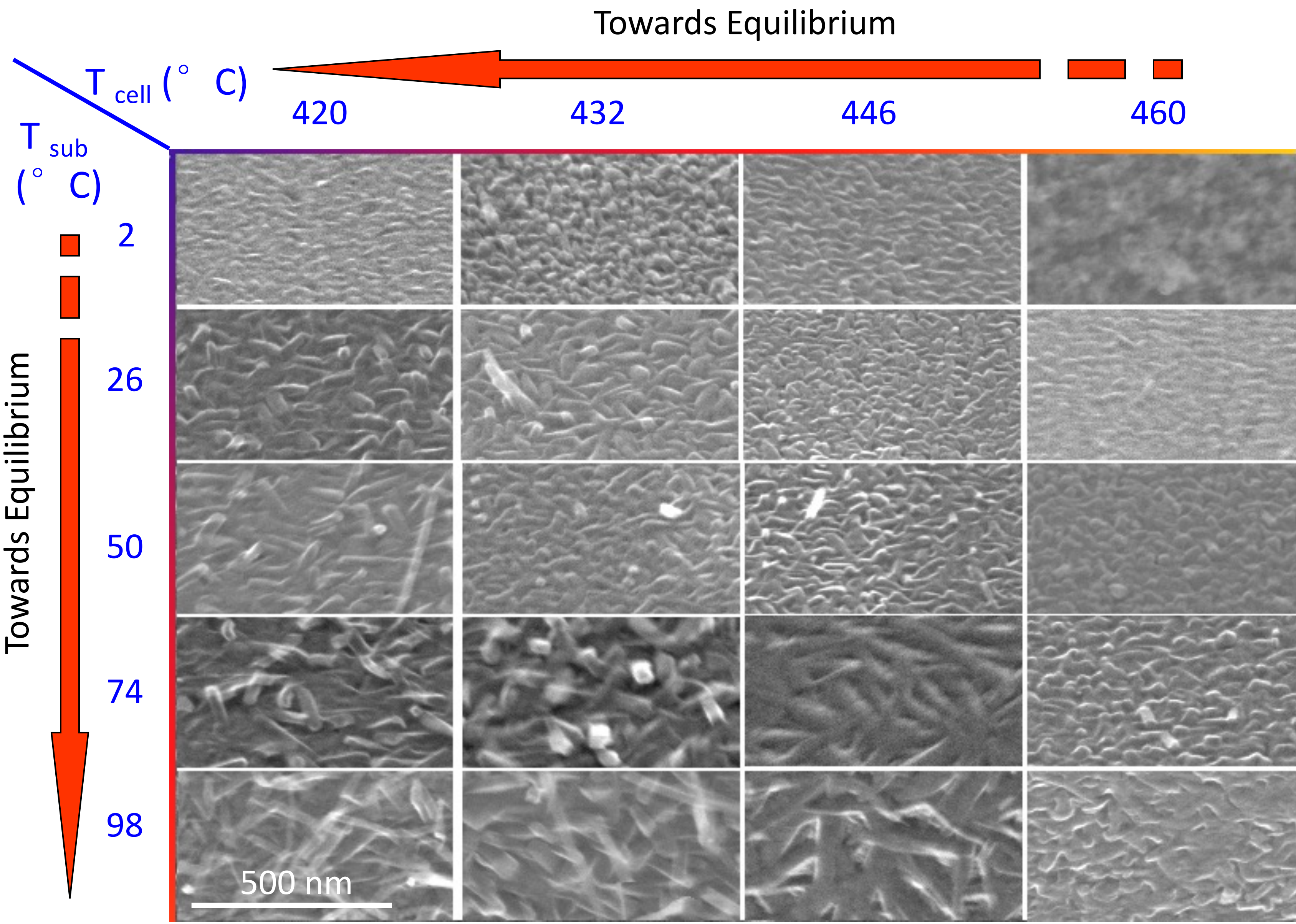
# Nanomorphology control by temperature

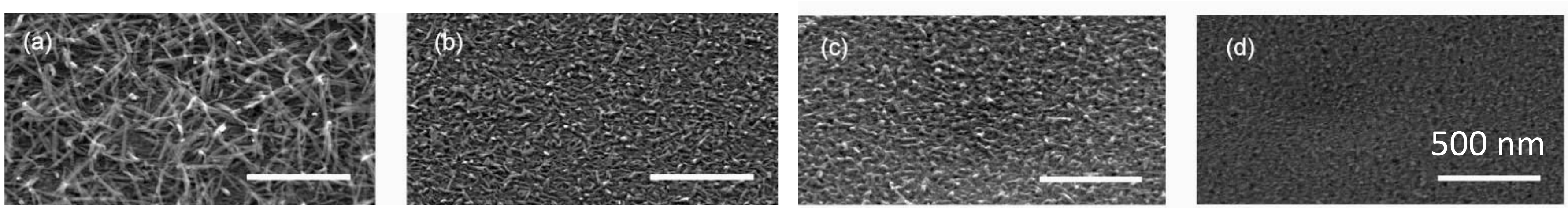



(flowrate = constant, pressure = constant)

# Nanomorphology control by flow rate

(fixed source and substrate temperatures)

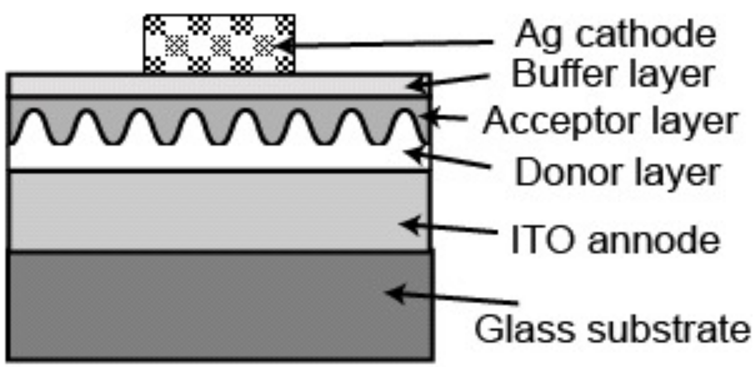
$N_2$ flow rate: 100 sccm | 125 sccm | 150 sccm | 200 sccm

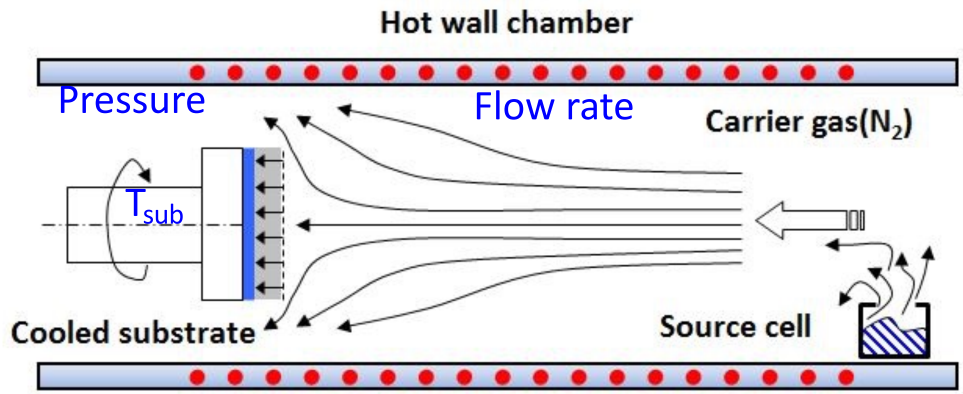



Increasing carrier gas flow rate

| Crystals | Needle morph. Long, large | Flat morph. Uniaxial, small |
|---|---|---|
| Source temperature | Low | High |
| Substrate temperature | High | Low |
| Carrier gas flow rate | Low | High |
| Chamber pressure | Low | High |

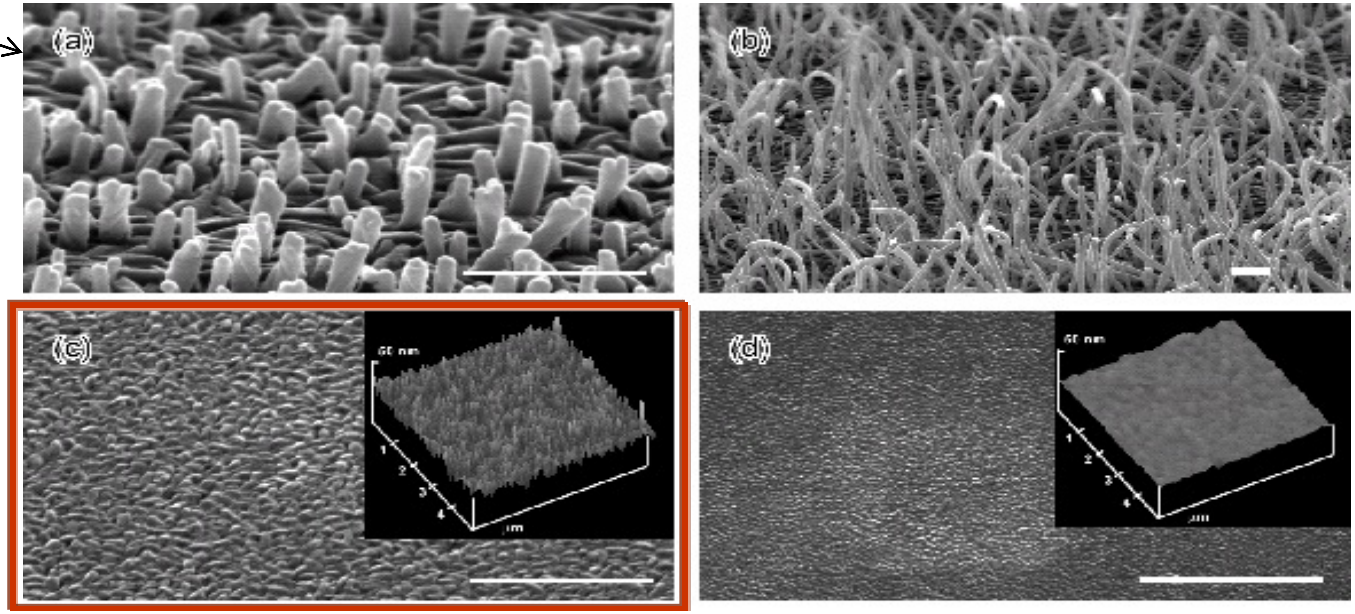
# Controlled growth of a Bulk HJ by OVPD




Stranski-Krastonow growth

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



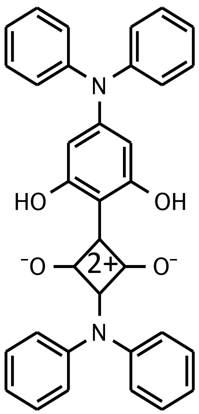

**OVPD**
**rms~3.5nm**

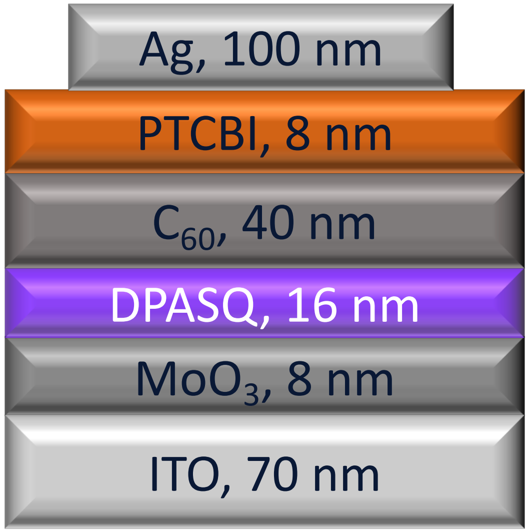
**VTE**
**rms~0.3nm**

Different strain and growth conditions result in different structure

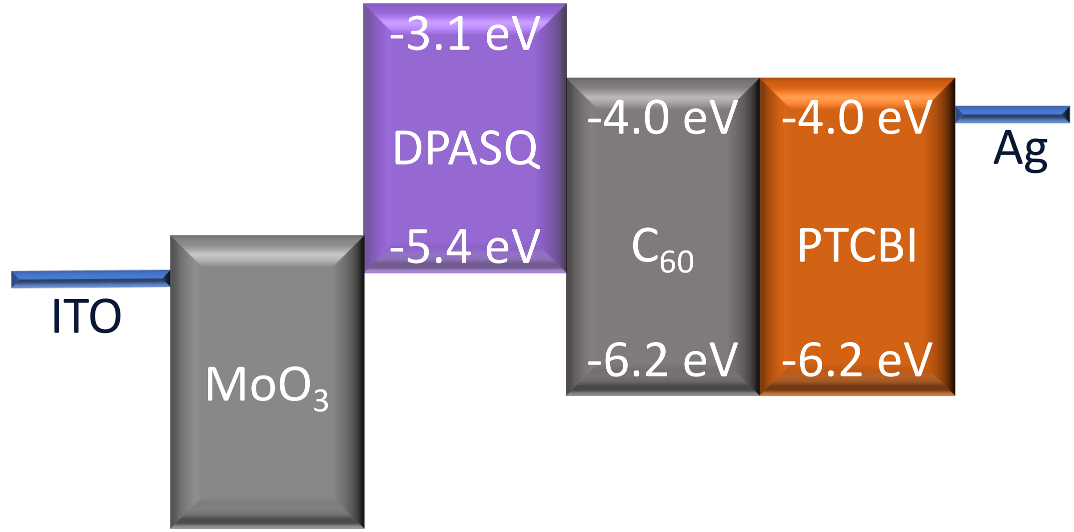
# Controlling Morphology Via Annealing

DPASQ



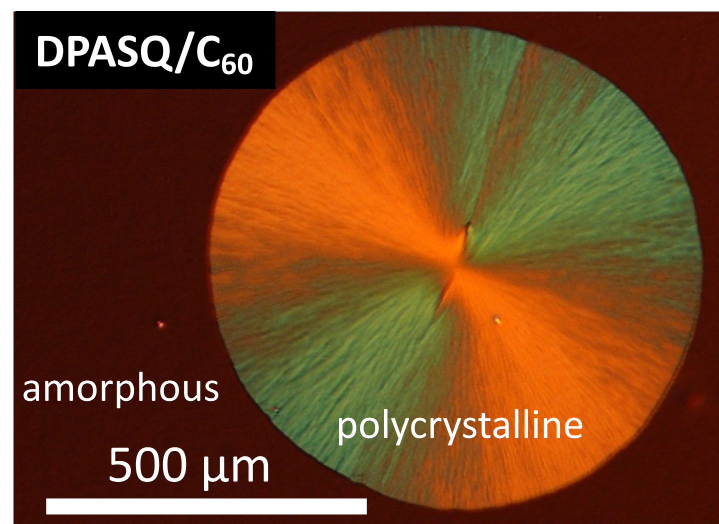




Conventional organic solar cell



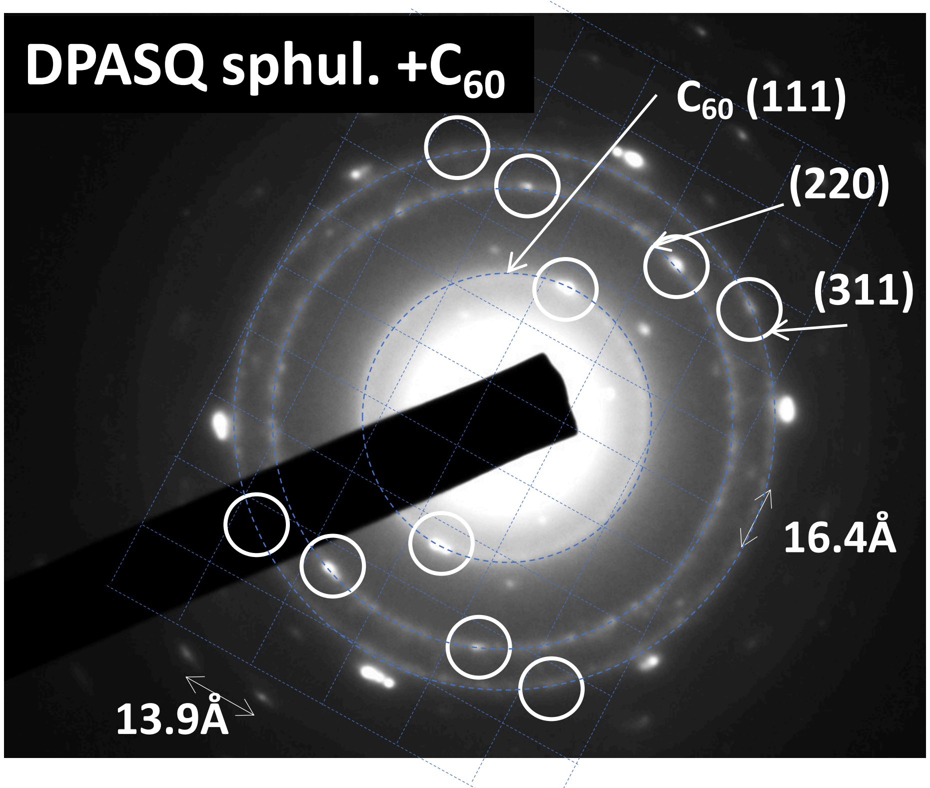

- DPASQ (asymmetric)
  - Crystalizes easily.
    - Solvent vapor annealed (dichloromethane, DCM)

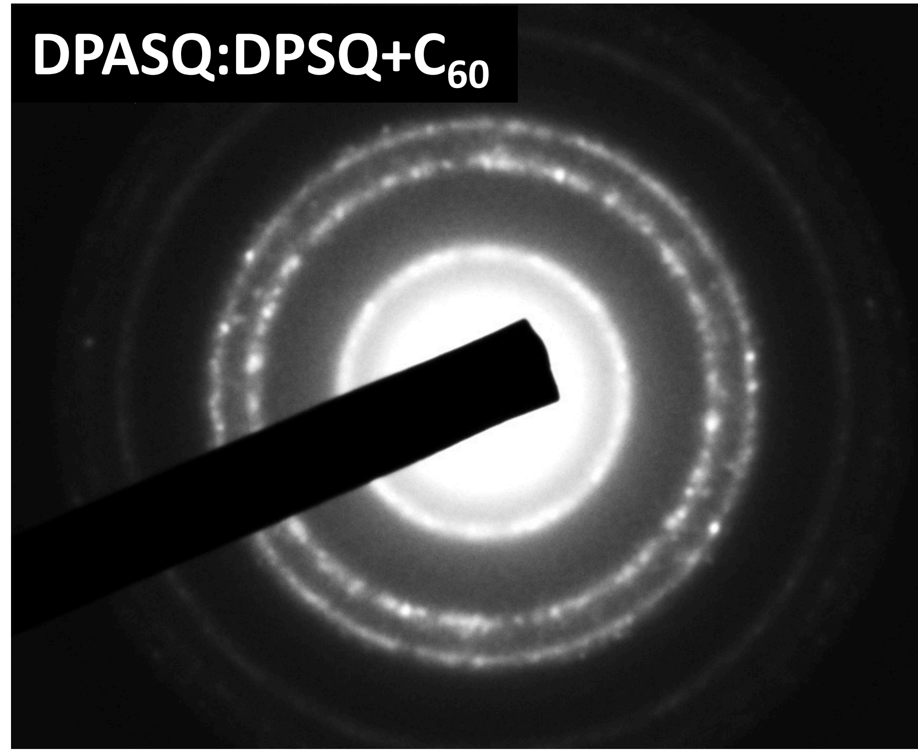
Spherulite formation



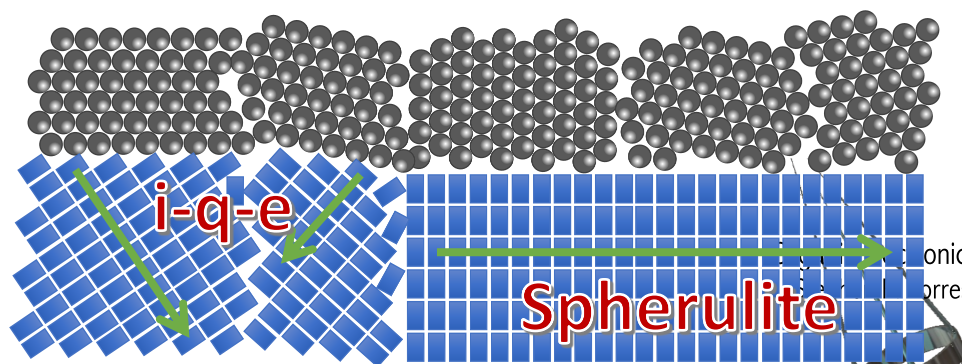
# Understanding the Annealed Structure

## Selected Area Electron Diffraction (SAED)

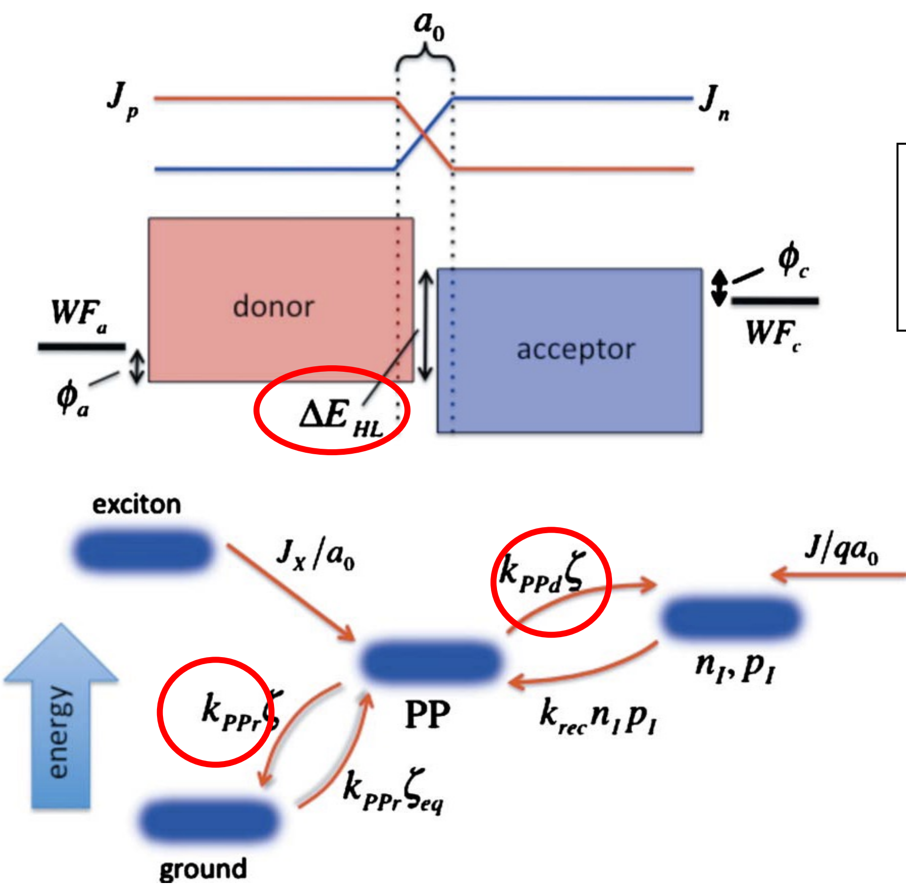



- Micron-scale crystals of DPASQ.
- Mesh: 13.9 Å by 16.4 Å, α=90°.
- "Inverse quasi epitaxy": DPASQ crystallization seeded by $C_{60}$ interface.



# Controlling Open-circuit Voltage via Interface Recombination

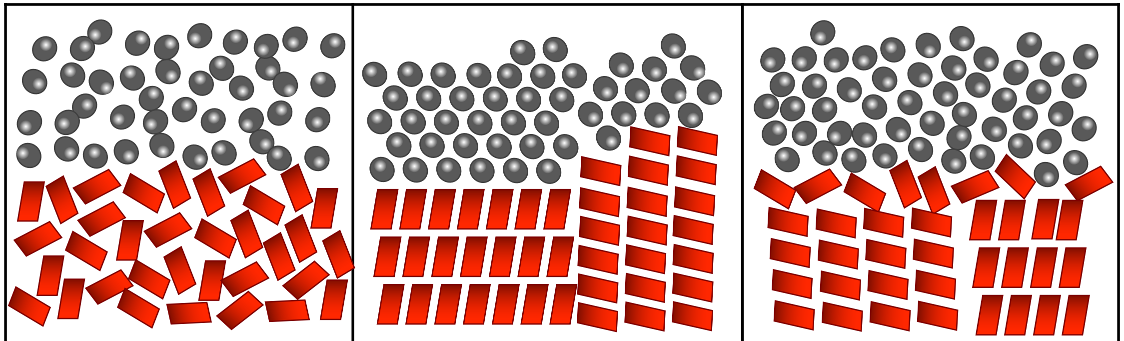



$$qV_{OC} = \Delta E_{HL} - nk_B T \ln\left[\frac{k_{PPr}}{k_{PPd}} \frac{k_{rec} N_L N_H}{J_X / \alpha_0}\right].^*$$

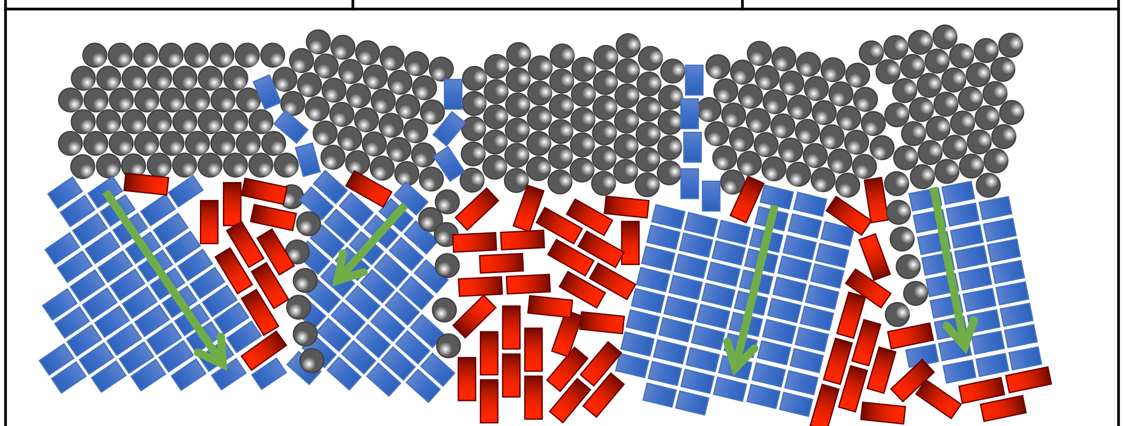
- Material choice determines:
  - $\Delta E_{HL}$ (HOMO-LUMO Gap)
  - Steric hindrance (MO overlap)
- Device processing/morphology can limit $V_{OC}$ losses:
  - $k_{PPd}$ (PP dissociation)
  - $k_{PPr}$ (PP recombination)

*Giebink *et al.* PRB 2010

# Solution Processing Phenomena



| | | |
|---|---|---|
| DPSQ As Cast : Low $J_{SC}$ High $V_{OC}$ | DPSQ Pre-$C_{60}$: High $J_{SC}$ Low $V_{OC}$ | DPSQ Post-$C_{60}$: High $J_{SC}$ High $V_{OC}$ |



DPASQ:DPSQ blends Post-$C_{60}$: Highest $J_{SC}$ & High $V_{OC}$

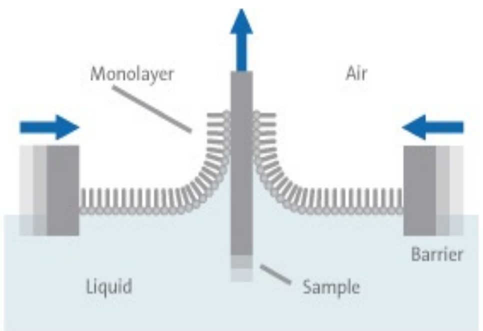
- To maximize $V_{OC}$ in OPVs:
  - Disorder at HJ.
- To maximize $J_{SC}$:
  - Ordered bulk.
  - Finger-like BHJ structure.
- DPSQ maintains interface disorder on SVA Post-$C_{60}$.
- DPASQ undergoes "inverse quasi-epitaxy" and inter-diffusion on SVA Post-$C_{60}$.
- Blending DPASQ and DPSQ eliminates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

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

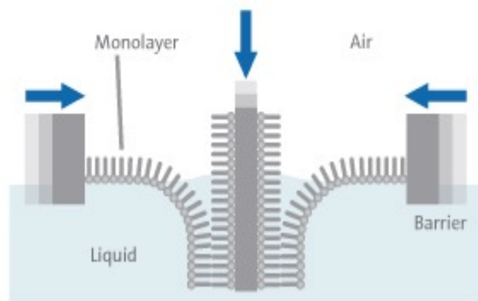
# Langmuir-Blodgett Monolayer Film Deposition

- 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

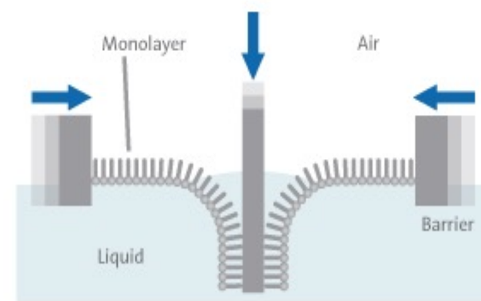
Hydrophilic surface deposition



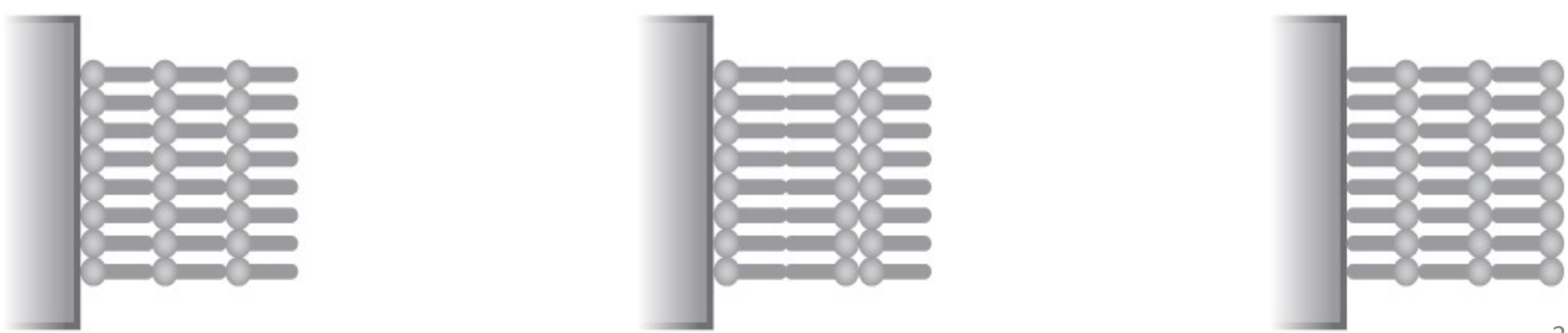

Hydrophilic surface: layer 2



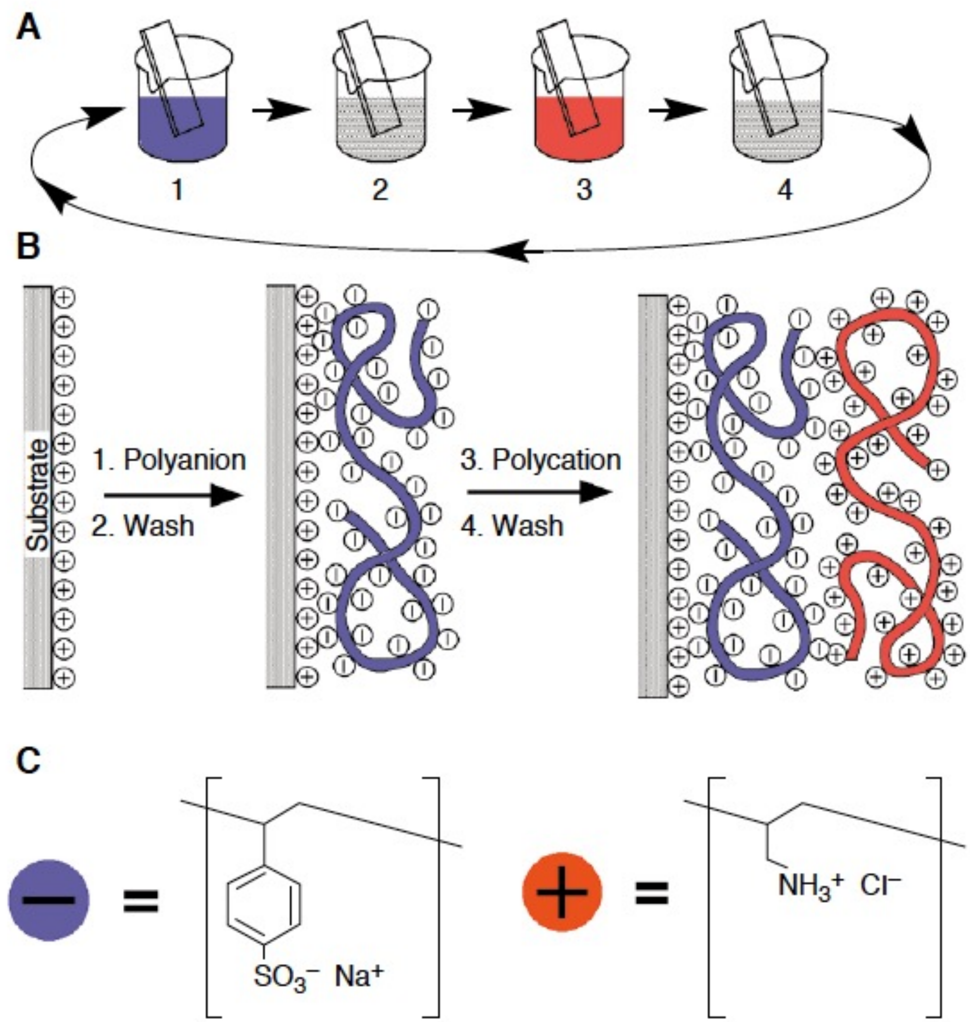

Hydrophobic surface deposition




Different configurations of 3 MLs on substrate surface



# Electrostatic Monolayer Deposition

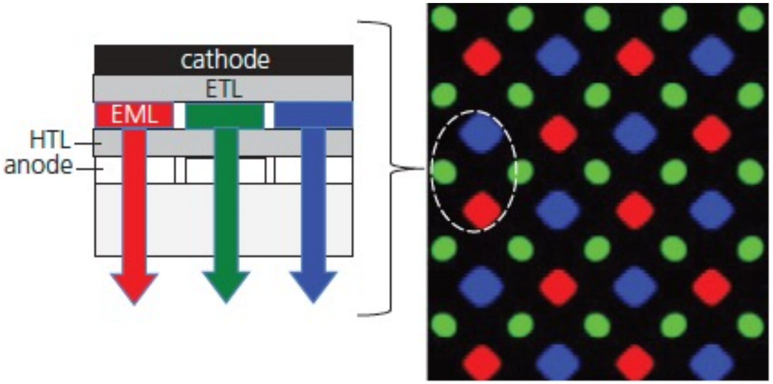



Decher, et al. SCIENCE VOL. 277, 29 AUGUST 1997, p 1233

# 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

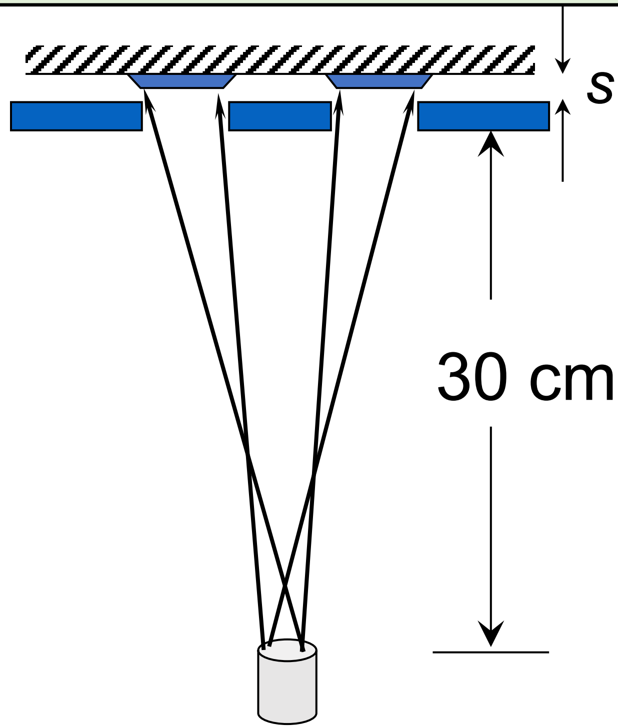



Example: Pixel micro-patterning in OLED displays

# Shadow mask patterning in the kinetic and diffusive film growth regimes

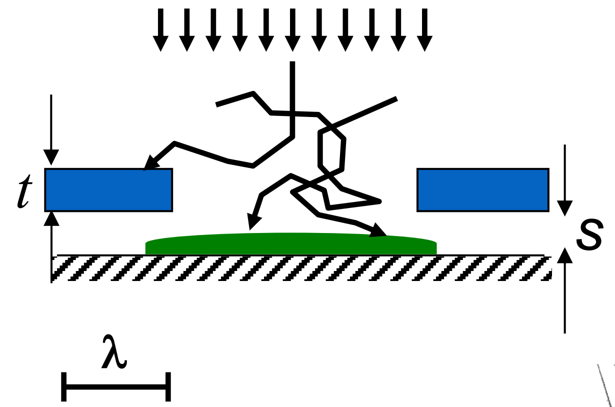
- Shadow mask patterning is the most common form of organic device electrode definition
- Used for producing OLED displays for small mobile and large TV applications

**Vacuum Evaporation vs. Vapor Phase Deposition**




**$10^{-5} – 10^{-10}$ Torr**

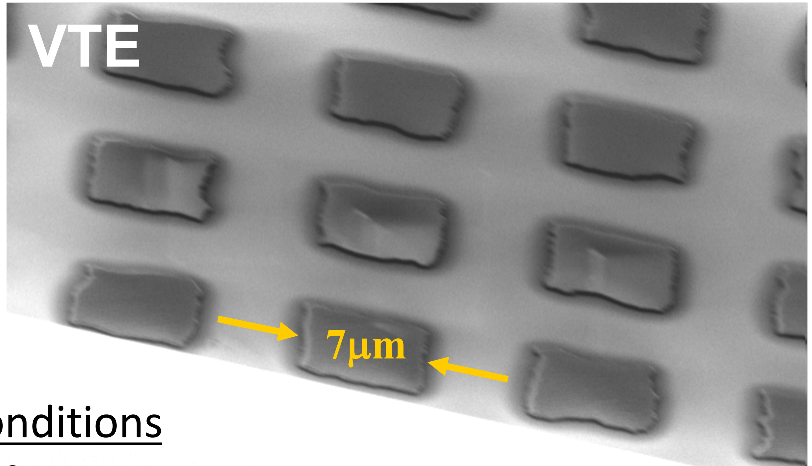
$$\lambda = \frac{k_B \cdot T}{\sqrt{2} \cdot \sigma \cdot P}$$ Mean free path

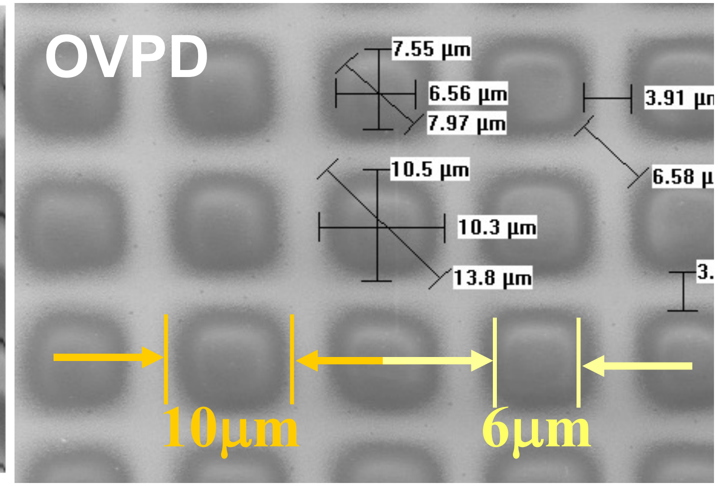



**$10^{-1}$ – 10 Torr**

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

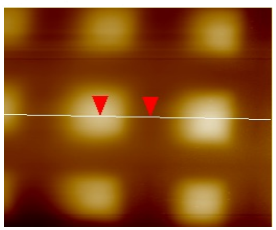
# Resolution limits for shadow-masking

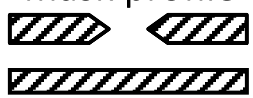


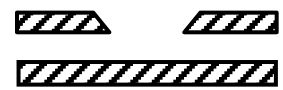



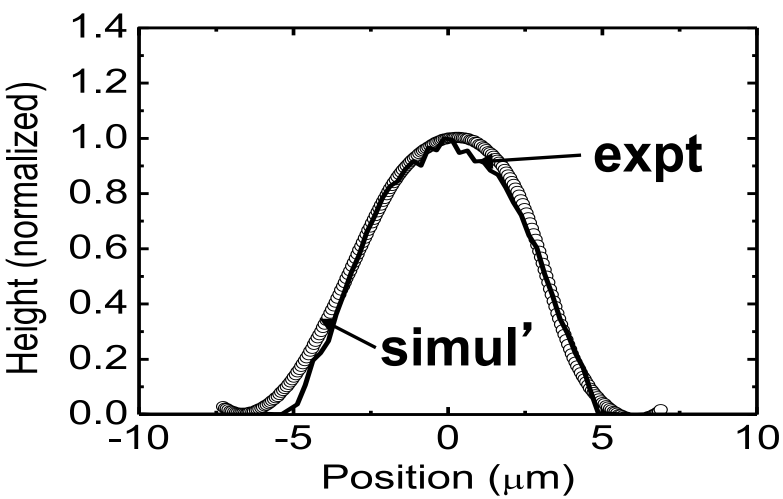

<u>OVPD Conditions</u>

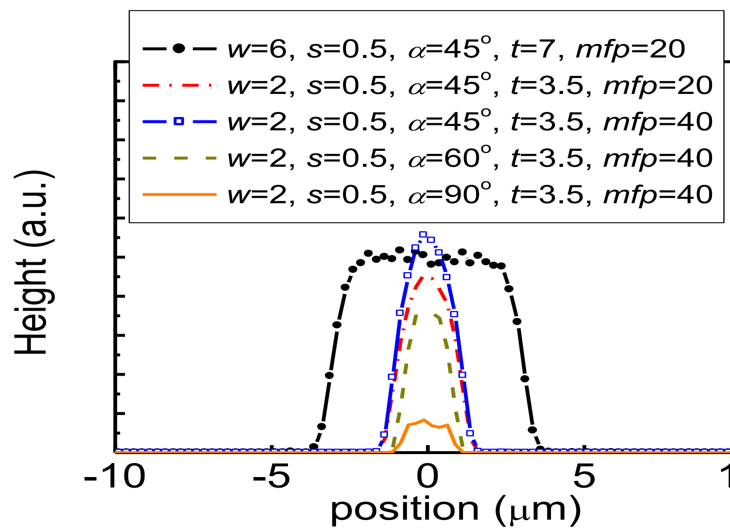
$\lambda$ = 20µm
*s*=0.5µm
*t*=3.5µm
*w*=6µm



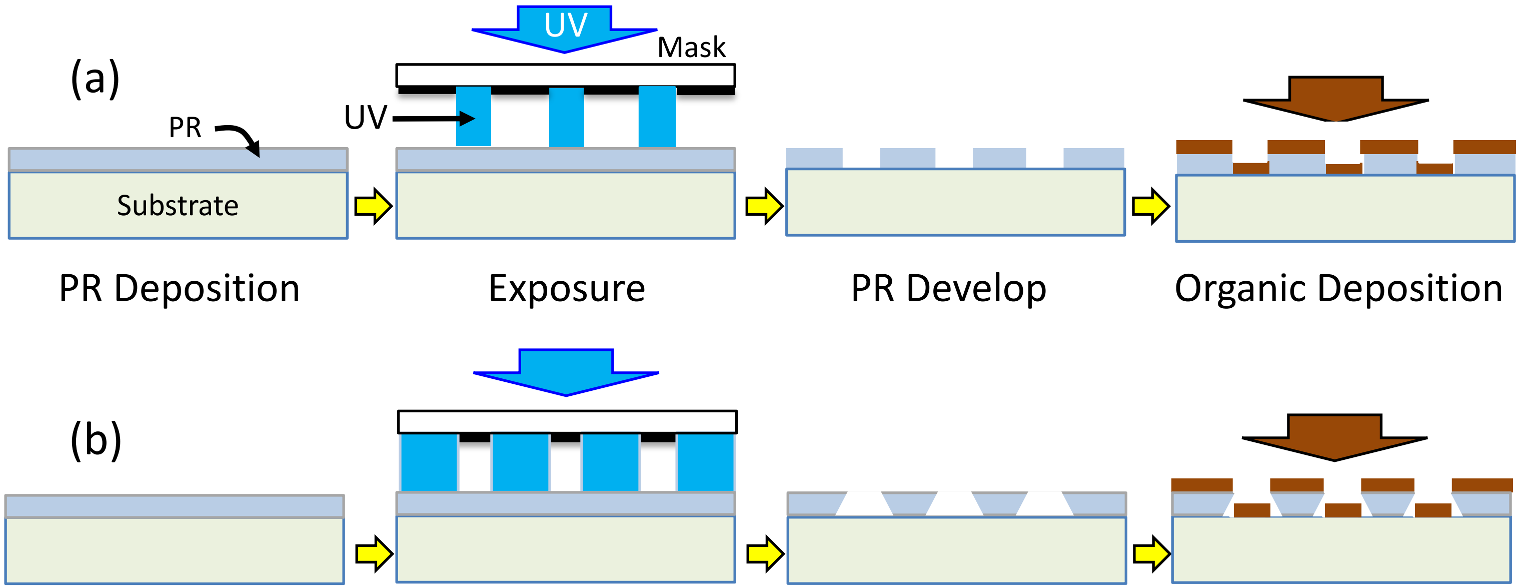



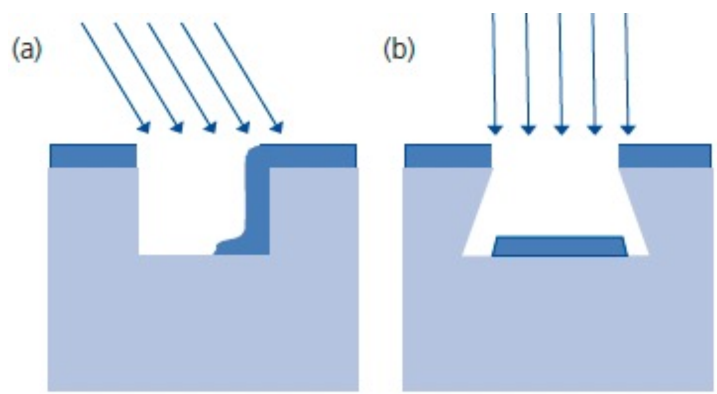




M. Shtein et al. J. Appl. Phys., 93, 4005, (2003)

# Use Photoresist to Create Surface Topography to Pattern Subsequently Deposited Organics

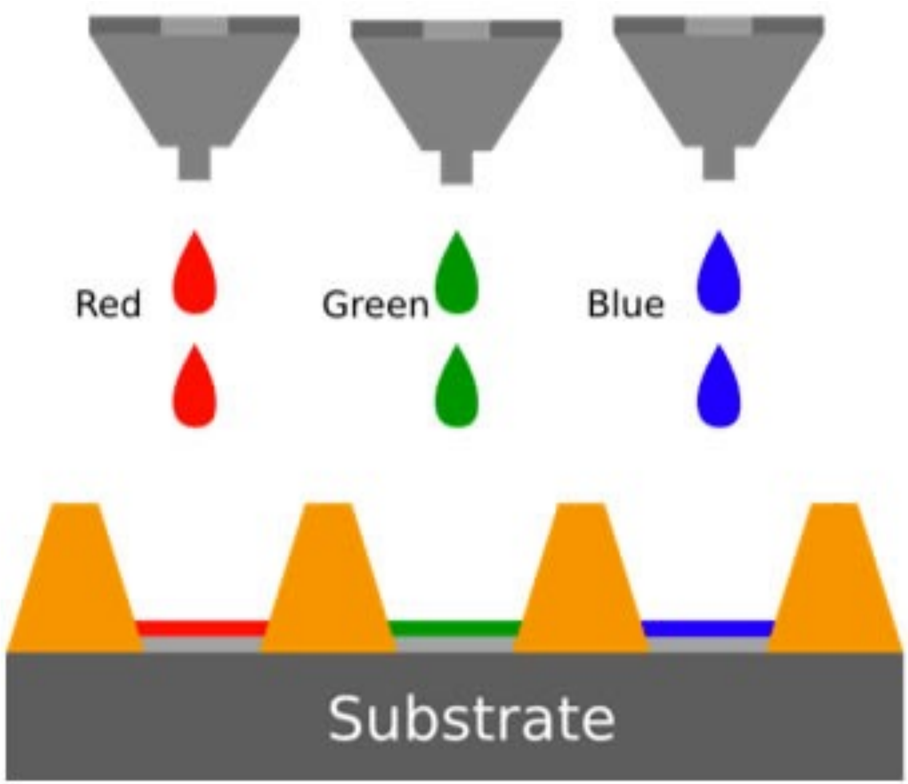


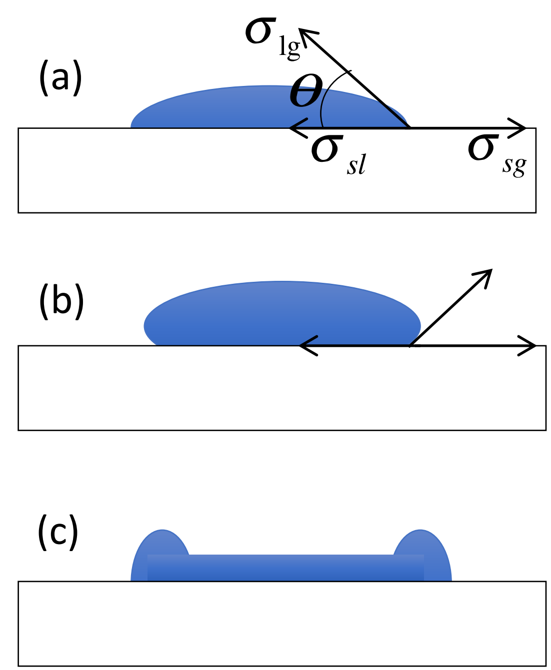




- Deposition of the organic in vacuum
- Shape of pattern on substrate depends on direction of the source to substrate

- 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

# Inkjet Printing

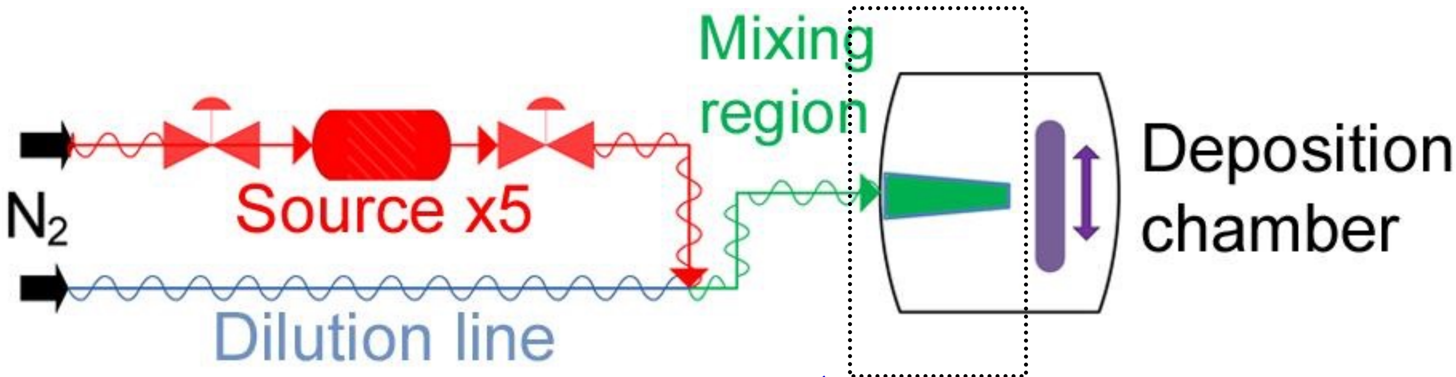


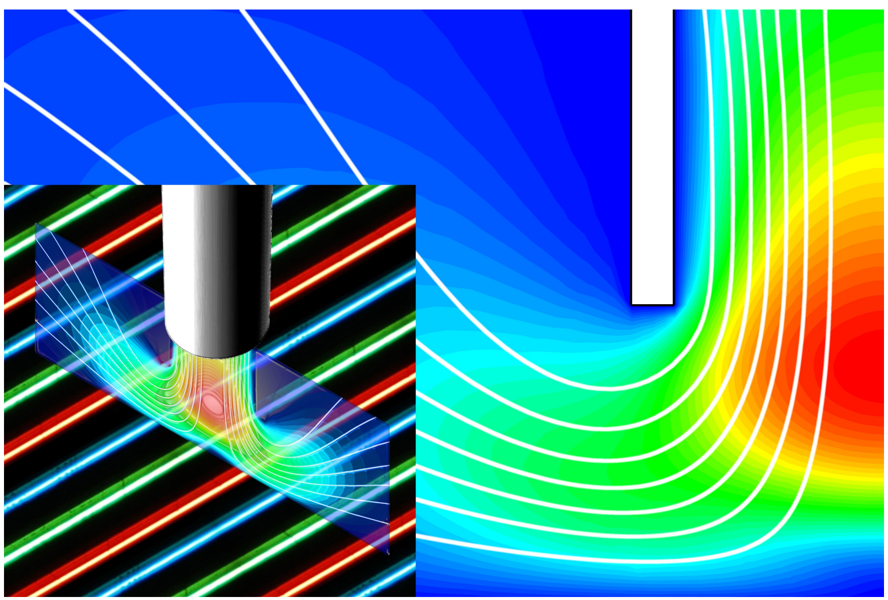




- Organic semiconductors similar to inks used in printing
- Organics must be soluble
- Droplets injected into wells formed by polymer walls

- 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

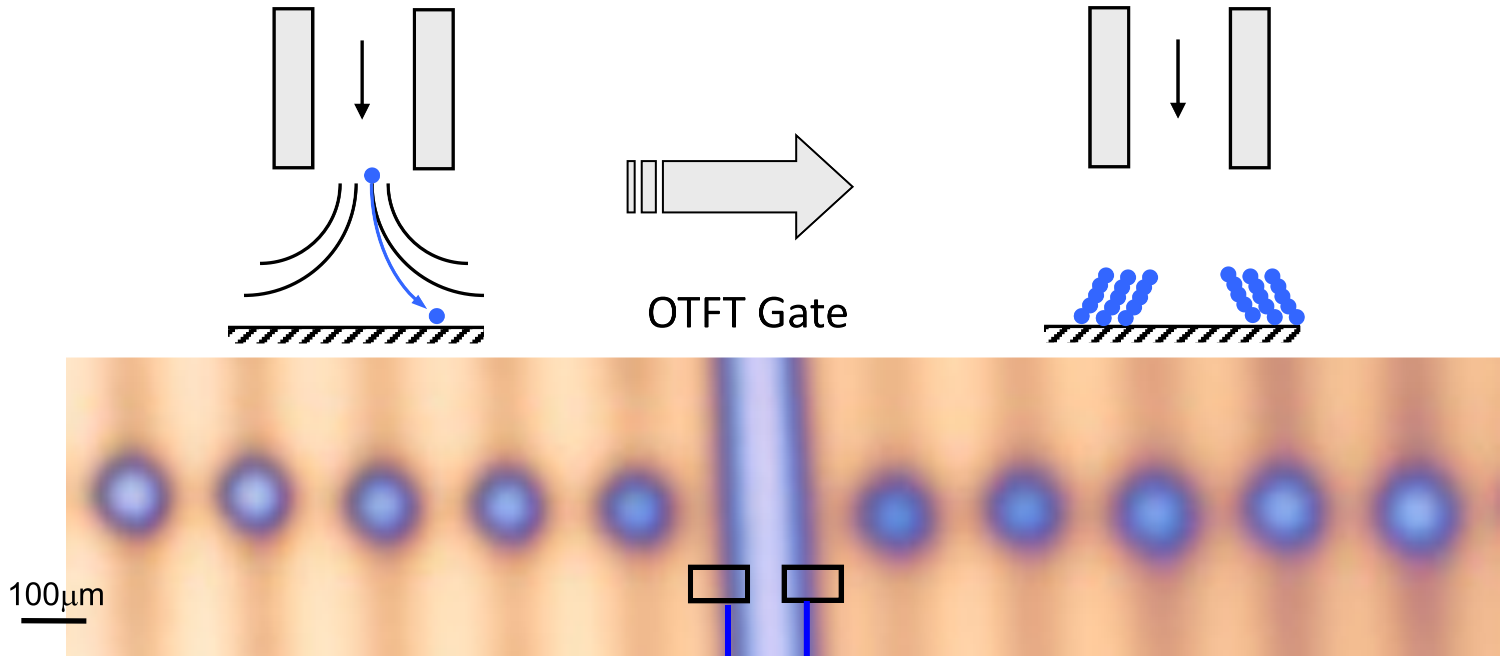


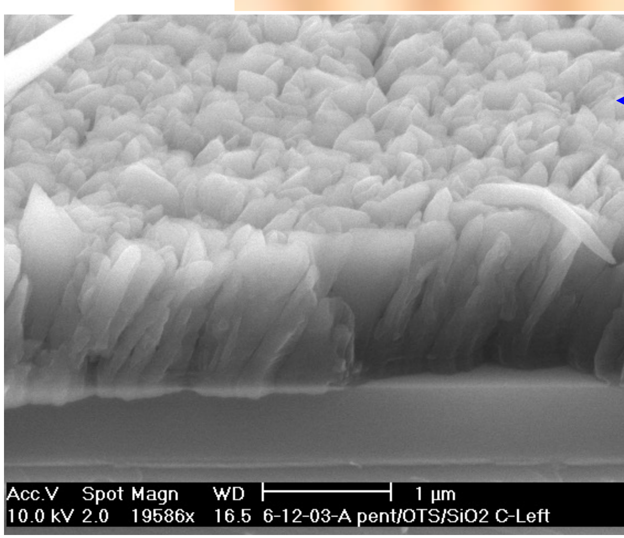



- Optimized R-G-B OLEDs can be combined to form a WOLED
- Each color separately optimized by choosing guest/host combinations
- Tunable color balance
- Motion stage beneath nozzle
- Nozzle creates high speed vapor jet

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

# Flow anisotropy: Non-equilibrium crystallization & molecular ordering



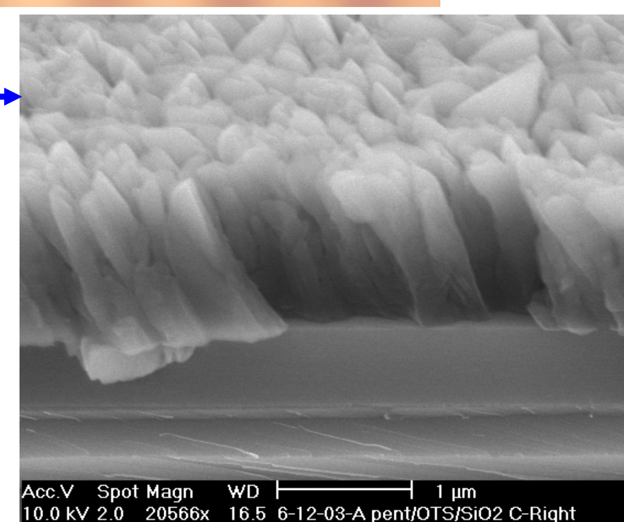




Local deposition rate: 700 Å/s

$\mu$= 0.25 $cm^2/V\cdot s$

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

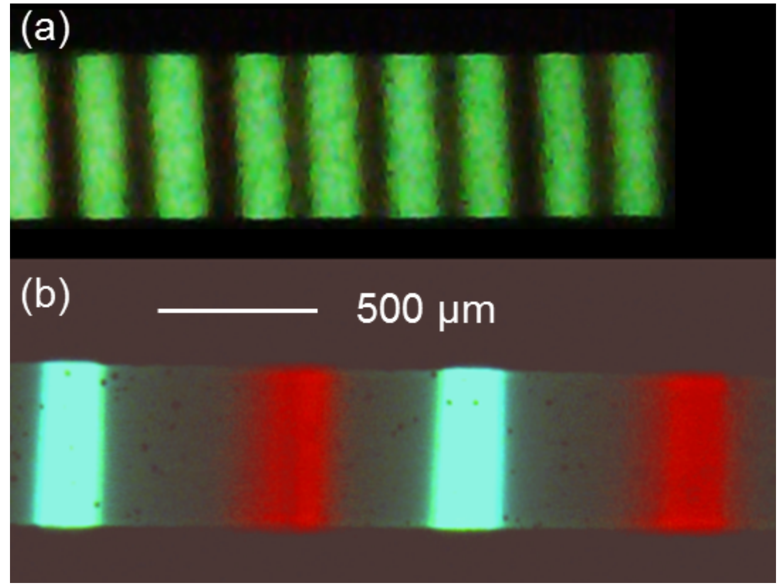
$V_t$ = 17, 10 V



# Printed R–G Pixel Arrays

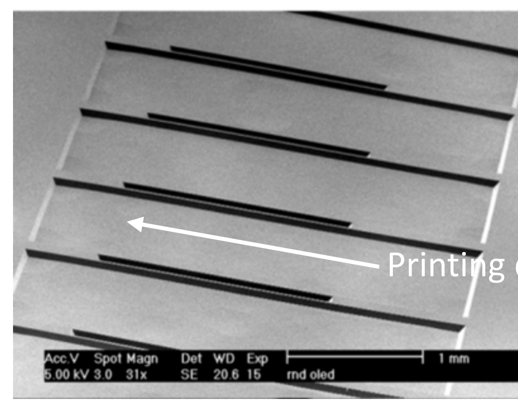
Red-Green devices printed
at nozzle substrate distance*:* 20 μm

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) |

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

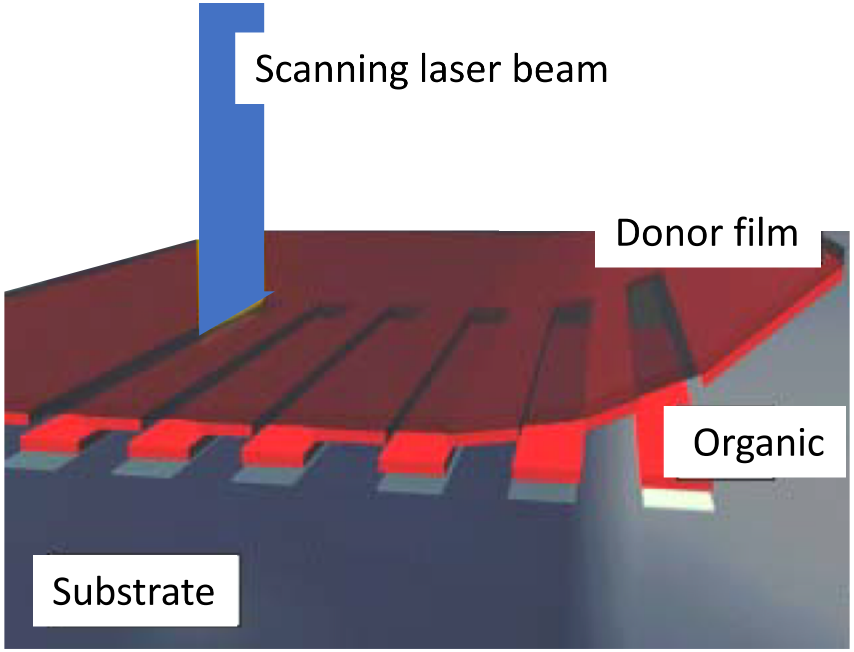



MEMS Nozzle Array

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

# Laser Induced Thermal Imaging (LITI)

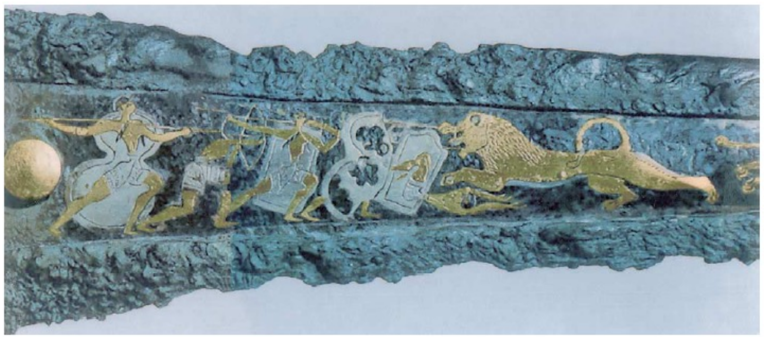
- High power laser beam absorbed in the donor film preloaded with the organic to be transferred
- Donor film placed in contact with substrate
- Heat generated by laser volitalizes organic that transfers to the substrate in the desired pattern




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

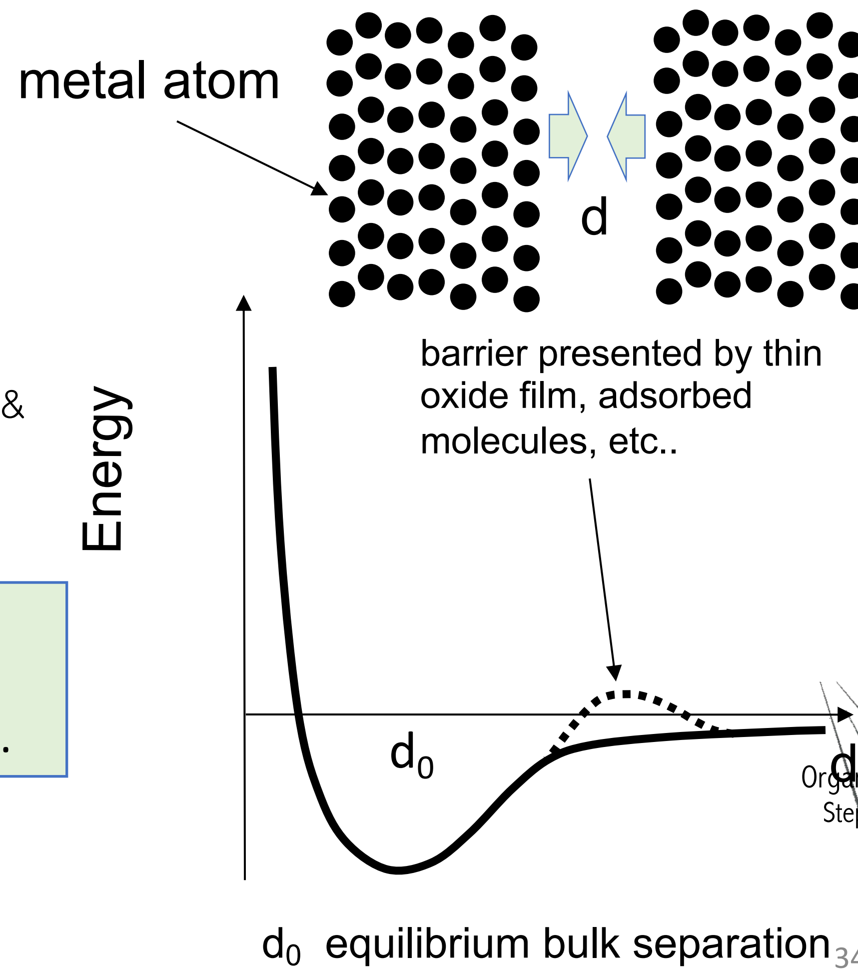
# Cold welding: A stamping method used through the ages

- 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



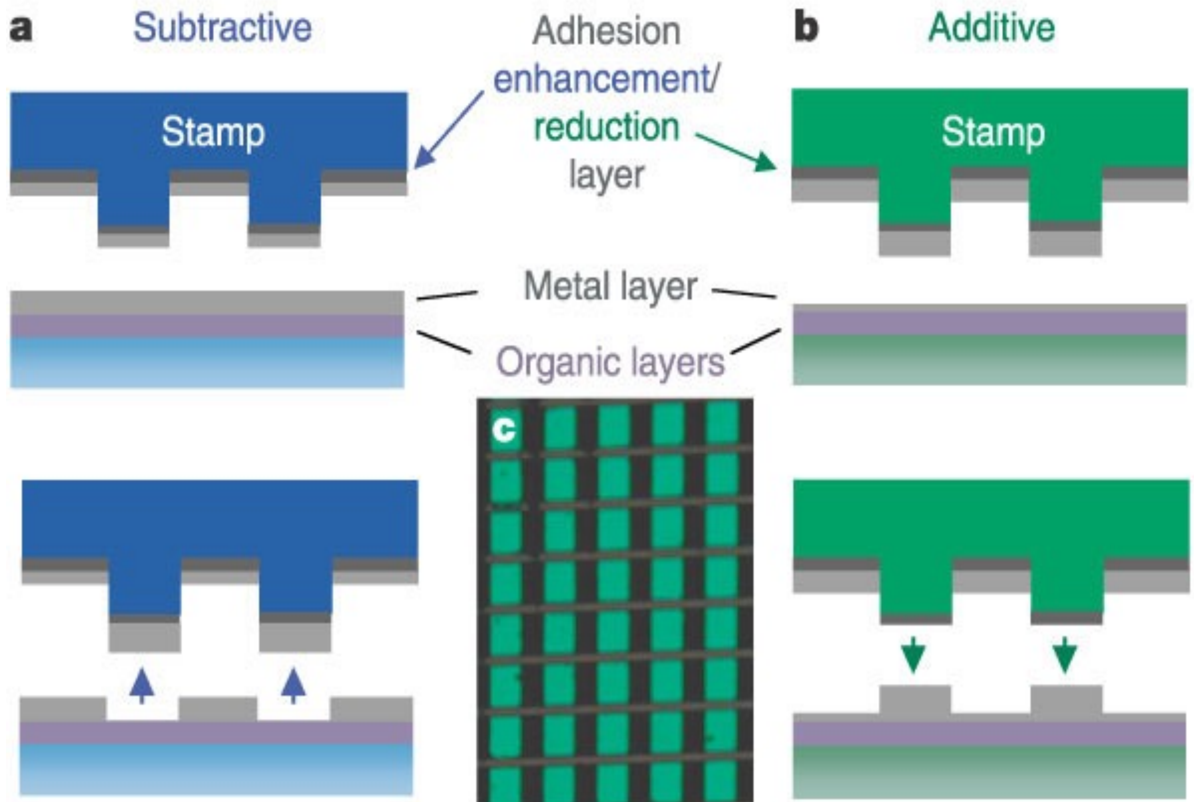
Bronze dagger blade with cold-welded gold and silver decorations. From Mycena, Greece; 2nd or 1st millennium B.C.

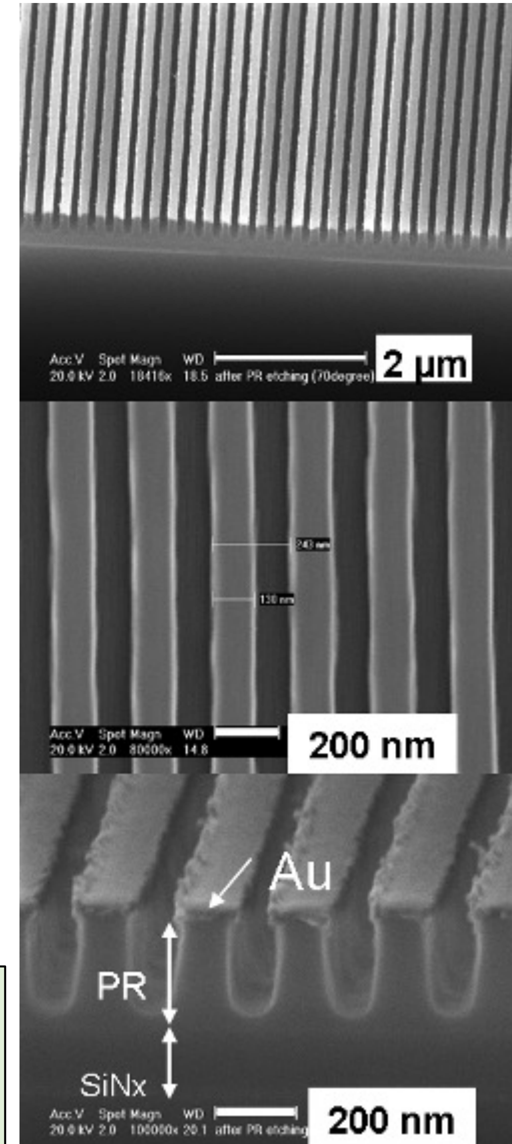
J. Haisma and GACM Spierings, Materials Science & Engineering R–Reports 37 1 (2002)

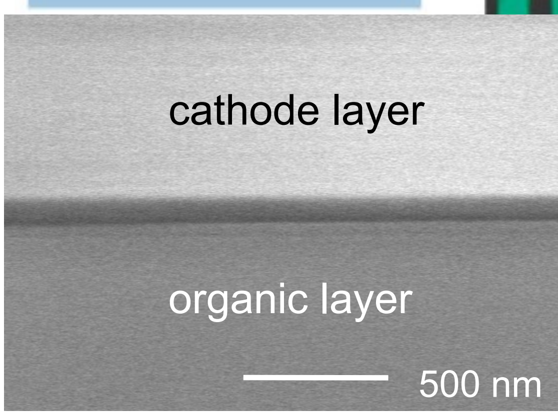



- Adhesive-free bonding of similar metals
- Useful for attaching contacts to organics, or even two organic films within a device.

# Cold-Welding Row and Column Electrodes



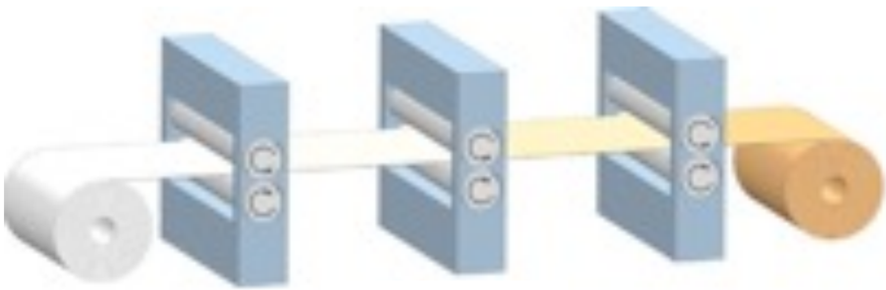

Nanoscale resolution

OLED Display with cold-welded cathode contacts

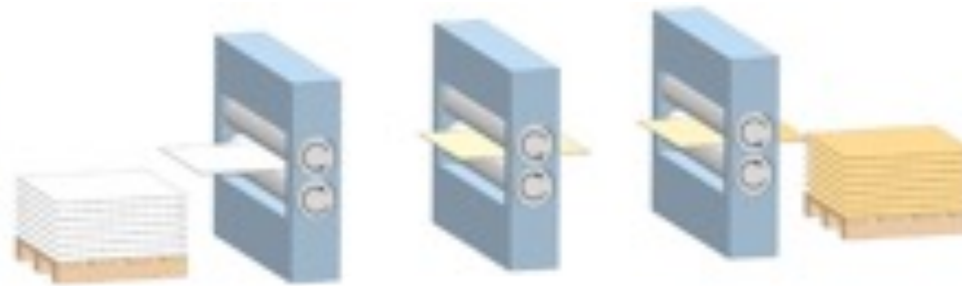
Two methods:
Subtractive (requires high pressure)
Additive (lower pressure)

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

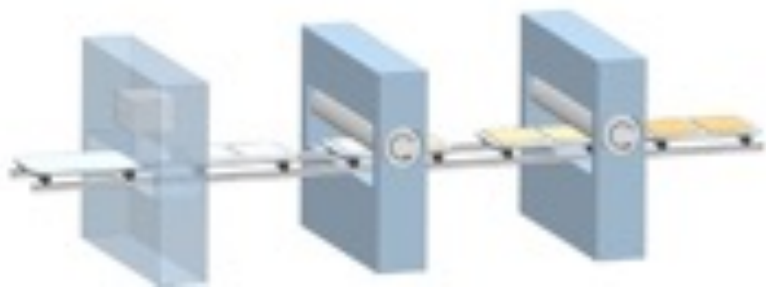
# R2R Manufacturing Processes Useful for Rapid, Large-scale OE Device Production



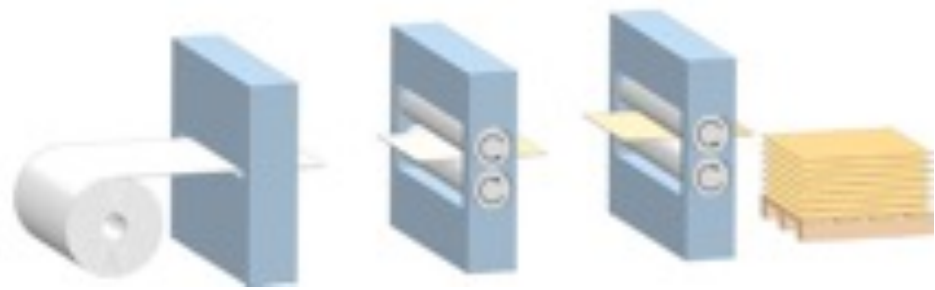
Roll-to-roll



Sheet-to-sheet



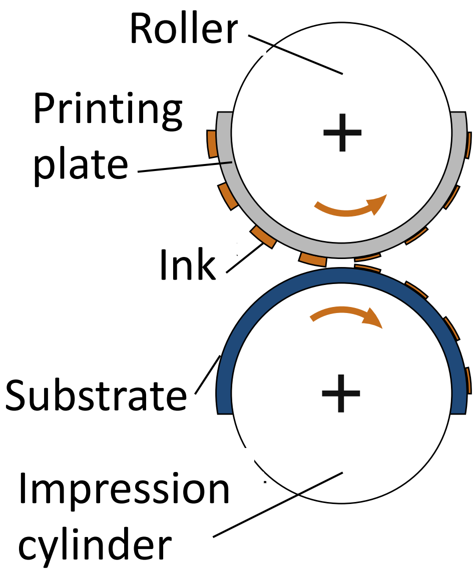
Sheet-to-carrier

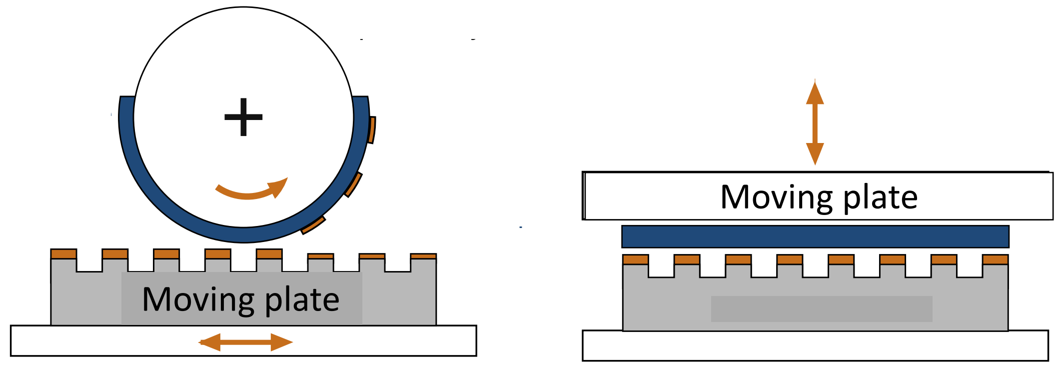


Roll-to-Sheet

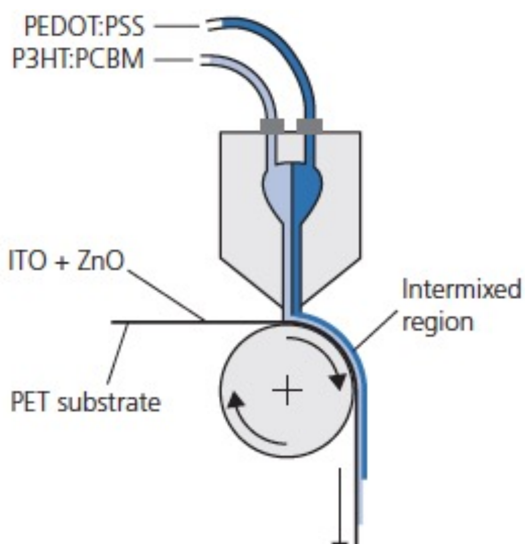
- Roll-based production requires flexible substrates
- Solution or vapor deposition of films possible
- Requires very clean (i.e. inert) gas environment

# Continuous Printing Methods

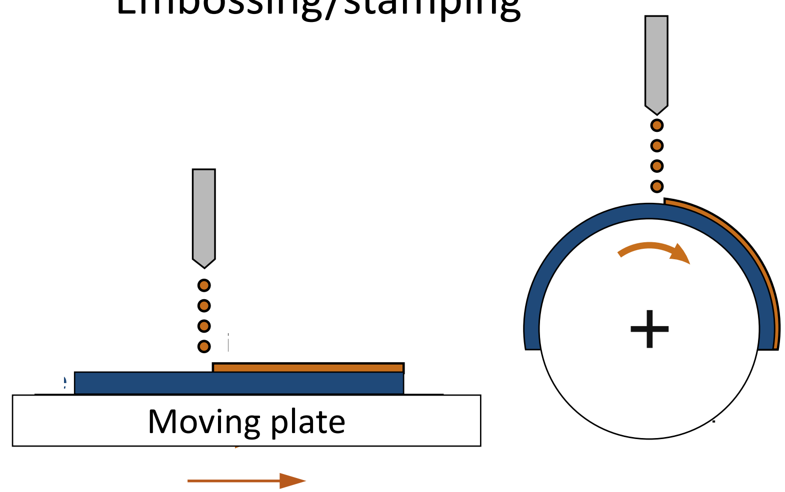



Embossing/stamping

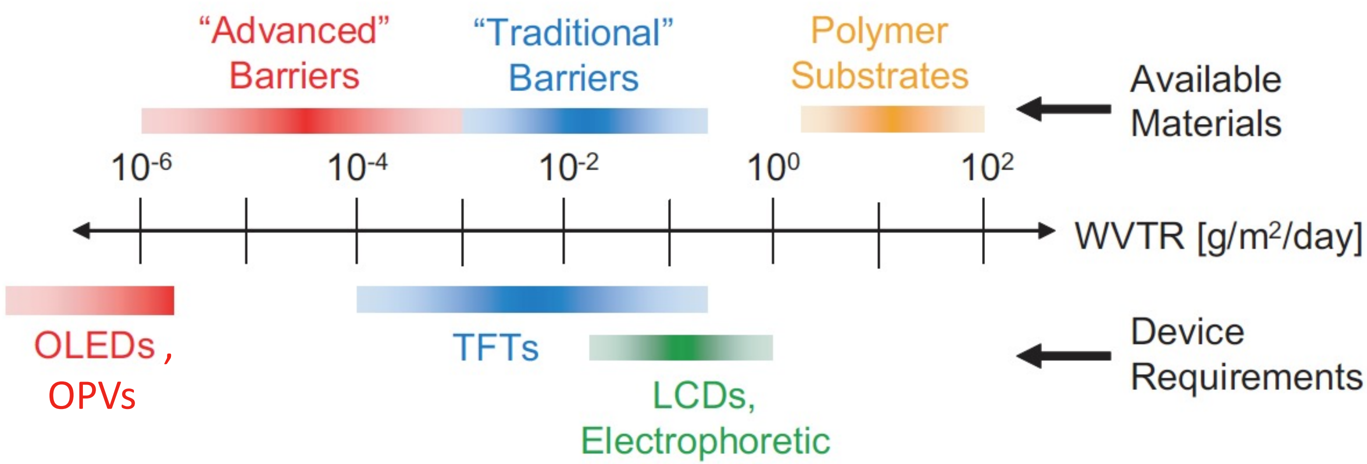



Slot dye coating

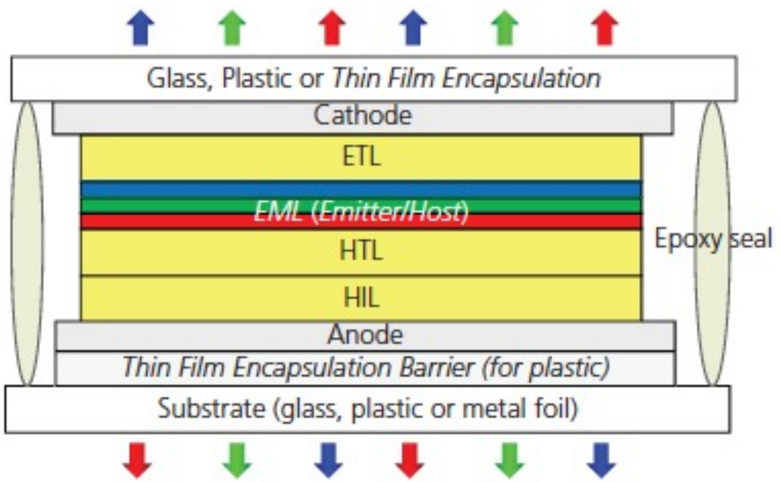



Inkjet printing

# Packaging




Water vapor transfer rate determines package quality and use




Common OLED epoxy sealed packaging scheme

Organic Electronics
Stephen R. Forrest

# 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