Deposition and Patterning Techniques for Organic Materials

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Organic Electronics: principles, devices and applications

Milano, November 24th, 2015

Overview

COATING

PATTERNING

Organic materials

Soluble

- Drop casting
- Spin coating
- Doctor Blade
- Dip coating
- Langmuir-Blodgett
- Spray coating

- Screen printing
- Soft Lithography
- NIL/Embossing
- Physical Delamination
- Photopatterning
- Printing

M. Caironi

Non-soluble

- Compression molding
- Vacuum Thermal Evaporation
- Organic Vapor Phase Deposition (OVPD)
- Organic Molecular Beam Deposition (OMBD)

- Shadow masking
- Vapor Jet Printing

Choice of the deposition technique

Uniformity

Waste of material

Thickness Ex. solar cells
- organic BHJ ~ hundreds nm
- dye-sensitized ~ µm

Nanomorphology
(molecules relative arrangement in the solid state)

sol
- solvent evaporation

non-sol
- deposition rate

- post-processing

Material
- solubility
- polarity
- polymer or small molecule
- single or mix

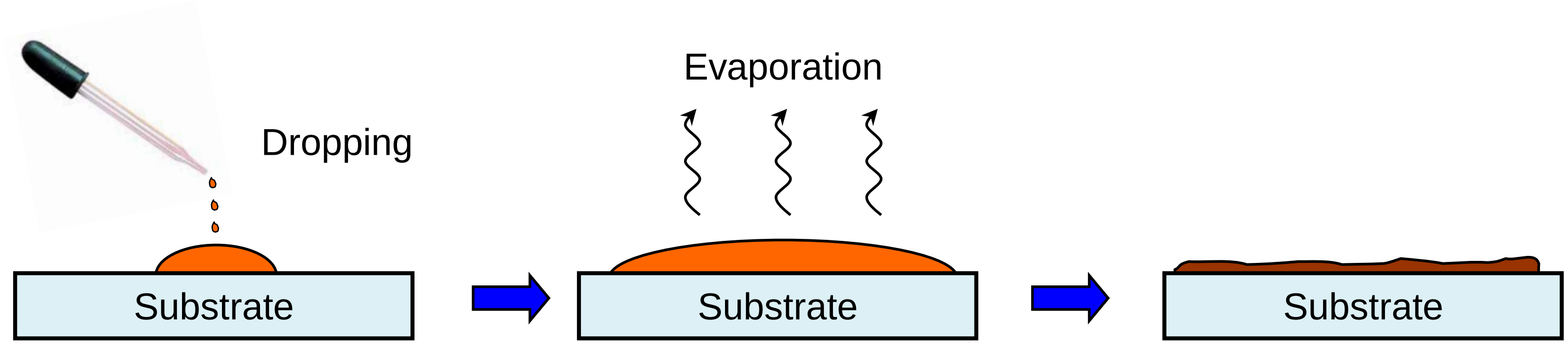
Substrate
- shape
- dimension
- surface features: roughness, wettability

Solution processable materials: deposition techniques

- Drop casting
- Spin coating
- Dip coating
- Langmuir-Blodgett
- Spray coating

Drop Casting

Dropping of solution and spontaneous solvent evaporation



Film thickness $\propto$ solution concentration

✓ Very simple
✓ Low waste of material

X Limitations in large area coverage
X Thickness hard to control
X Poor uniformity

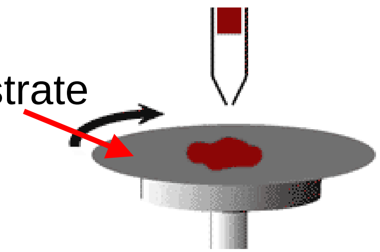
Tricks...

- **Combination of solvents**
- **Solvents evaporation time**: heating of the substrate to speed up the evaporation process and improve film morphology

Spin Coating I

Dropping on spinning substrate

substrate



Film thickness: dependent on many controllable parameters dω/dt, ω, t, solution viscosity,…

- ✓ Good uniformity
- ✓ Reproducibility
- ✓ Good control on thickness

down of 10nm or less

- X Waste of material
- X No large area
- X Film dries fast → less time for molecular ordering

Tricks...

Chang et Al.
Chem. Mater.,16, 23, (2004)

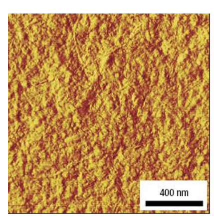
	bp (°C)	mobility ($cm^2/(V\ s)$)
chloroform	60.5−61.5	0.012
thiophene	84	
xylene	138−139	0.042
CHB	239−240	0.022
TCB	218−219	0.12

P3HT-based TFTs

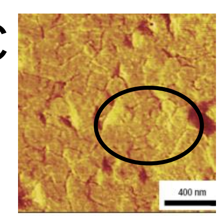
•Solvent evaporation time

•Additives

McCulloch *et Al.*,
Nat. Mater., 5, 328, (2006)



180ºC



larger crystallinity

POST-PROCESSING

•Thermal annealing

•Vapor annealing

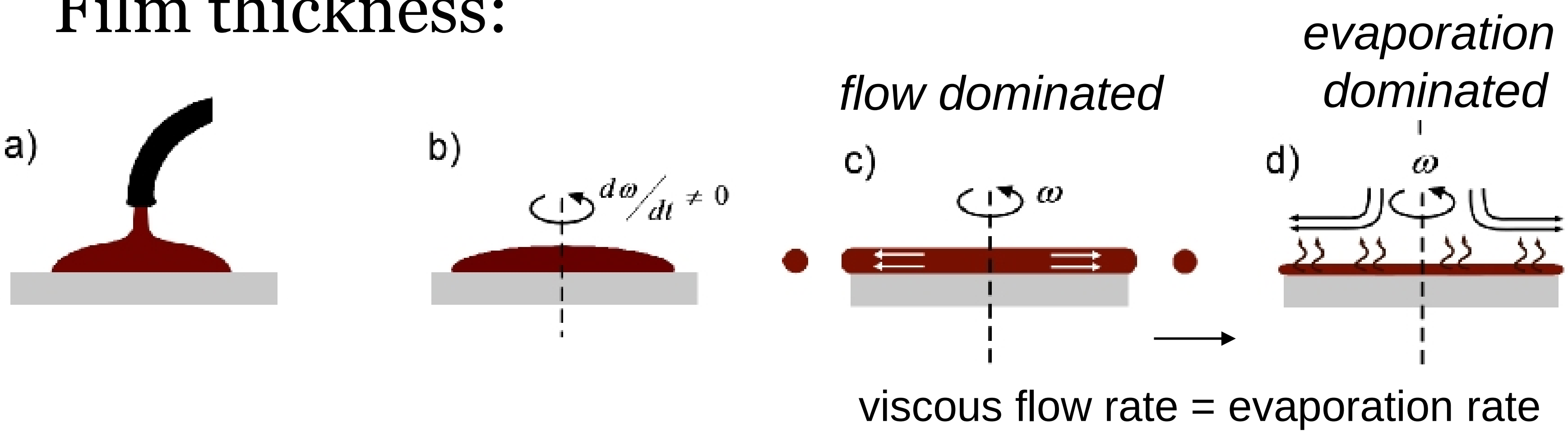
Y. Wang, J. Solar Energ. Eng., 2012, 134, 011017

Z. Zhao et al., Microel. Realiab., 2013, 53, 123

L.M. Chen et al., Adv. Mater., 2009, 21, 1434

Spin Coating II

Film thickness:



$$h_{FIN} = k \cdot c_0 (1 - c_0)^{-1/3} \omega^{-1/2} (\mu_0 / \rho_0)^{1/3}$$

c_0 solids concentration (by volume)
μ_0 viscosity
ρ_0 liquid density

most commonly reported experimental relationship between thickness and rotational speed

- Independent from radial coordinate
- Valid under certain approximation (e.g. Newtonian fluid)

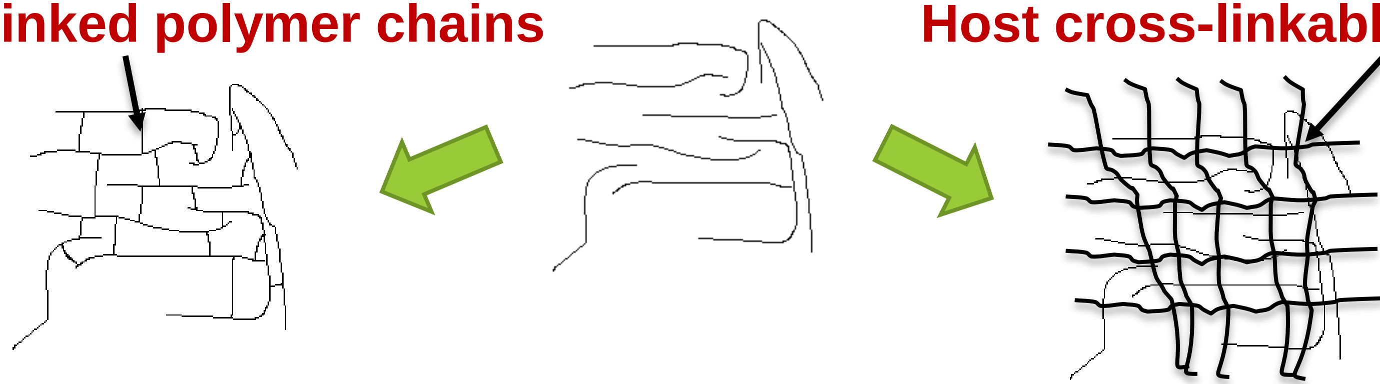
S. L. Hellstrom, "Basic Models of spin-coating", http://large.stanford.edu/courses/2007/ph210/hellstrom1/

How to handle multilayer deposition?

Post-deposition film insolubilization

Polymer cross-linking — Thermally / UV-light — activated

Cross-linked polymer chains **Host cross-linkable polymer**



- ✓ Stable, high degree of control
- X Polymer intrinsic properties are affected

- ✓ Appliable to any kind of polymer (small molecule?)
- ✓ Doesn't affect polymer intrinsic properties
- X Less "deterministic"

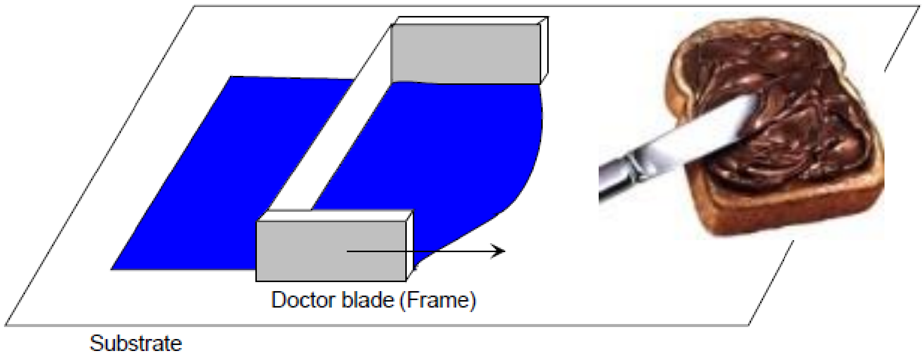
X Film properties are affected

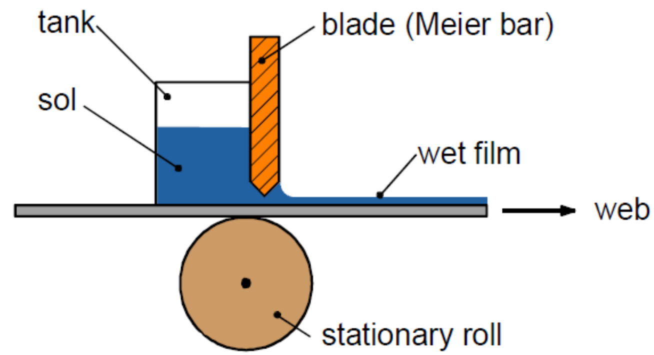
P. Keivanidis et al.,
Appl. Phys. Lett. 94, 173303, 2009.
S.H. Khong et al.,
Adv. Funct. Mater., 17, 2490, 2007

Binda et al.,
Appl. Phys. Lett. 98, 073303, 2011.
J. Lì et al.,
J. Appl. Phys., 100, 034506, 2006

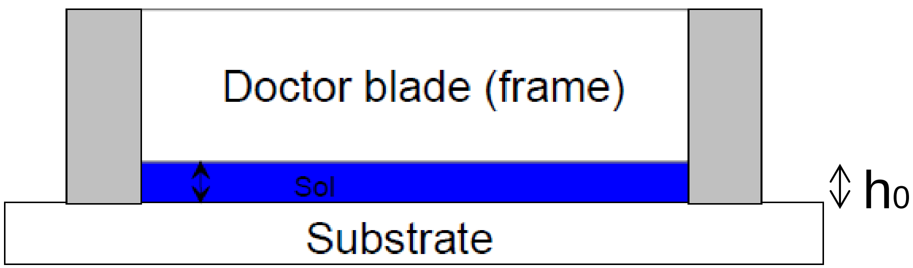
Doctor Blading I

Spreading through a moving blade onto a stationary substrate
stationary moving





Film thickness:



Film thickness: 20 – 200 nm

$h_{fin}\downarrow$

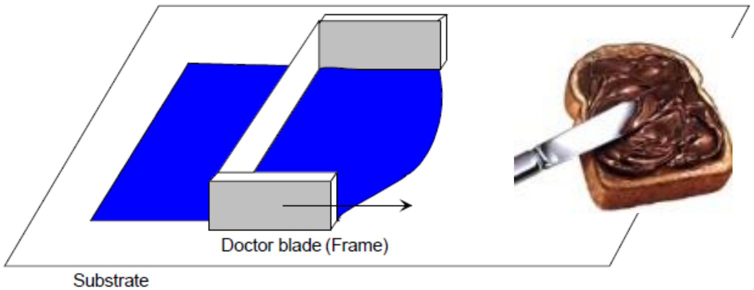
$\downarrow$	c	concentration
$\uparrow$	U	deposition speed
$\downarrow$	h_0	height of the gate

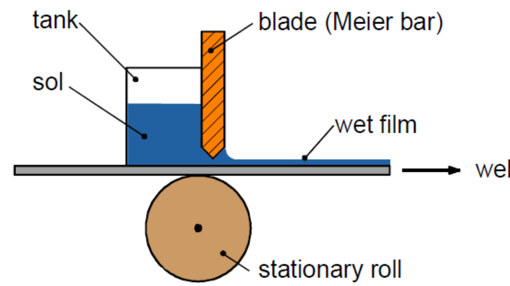
Theoretical height of the wet layer thickness: surface tension, wetting, viscosity, coating speed,...

http://scidok.sulb.uni-saarland.de/volltexte/2011/3076/pdf/sm200405.pdf
Y. Chou et al., J. Am. Ceram. Soc., 70,10, 1987.

Doctor Blading II

Spreading through a moving blade onto a stationary substrate
stationary moving





- ✓ Large area
- ✓ No waste of material
- ✓ Good uniformity
- ✓ Precise thickness control
- ✓ Fast – R2R

- X Micrometric precision of blade regulation
- X Not suitable for very thin films (nm)

Example: bladed organic solar cells (P3HT/PCBM)

Device performance.

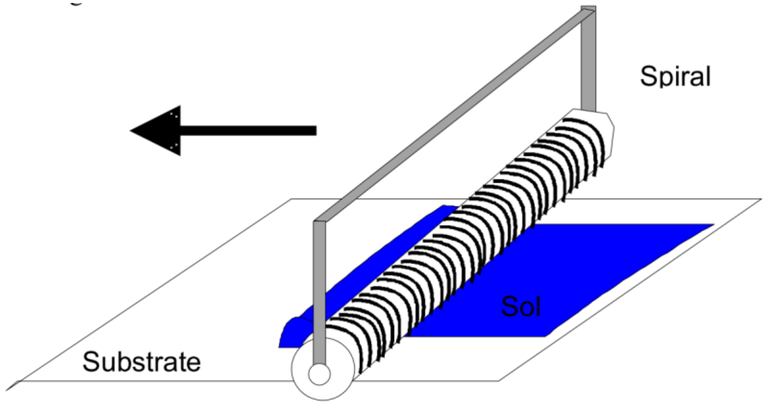
Method	Voc [V]	Jsc [mA/cm^2]	FF	PCE [%]
Spin-coated	0.58	8.91	0.62	3.16
Bladed	0.59	9.40	0.64	3.56

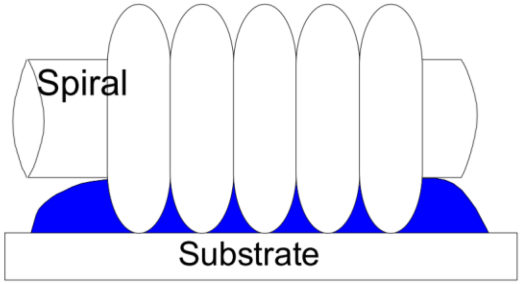
Doctor bladed active material in comparison with spin-coated (~200nm)

W.-B. Byun et al., Current Applied Physics 11 (2011)

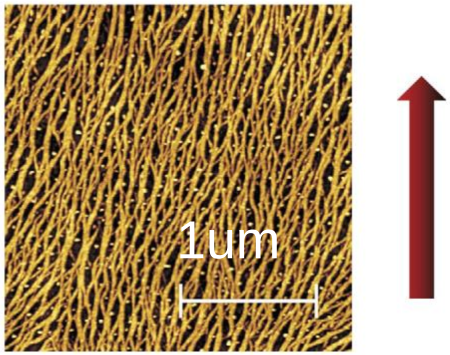
Bar coating

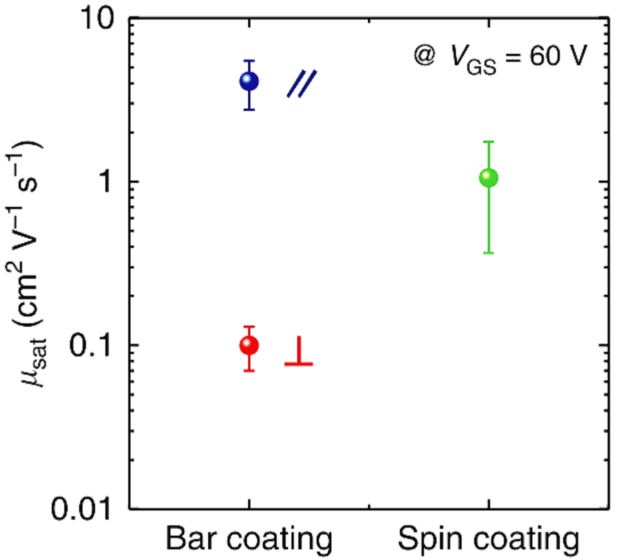
Same principle of doctor blading, but with spiral film applicator





✓ Allows directional printing

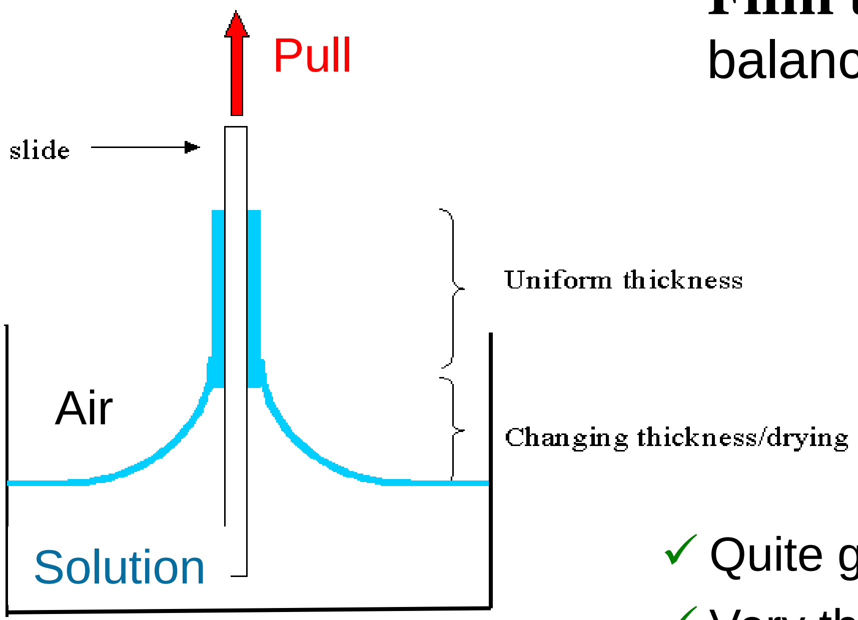




S.G. Bucella et al., Nat. Comm., 6, 8394, 2015

Dip Coating

The substrate is dipped into the solution and then withdrawn at a controlled speed.



Film thickness (H): determined by the balance of forces at the liquid-substrate interface

Landau and Levich equation: $H = \dfrac{0.94(\mu v)^{2/3}}{\gamma^{1/6}(\rho g)^{1/2}}$

μ= fluid viscosity v = withdrawal speed
ρ= fluid density g = gravitational acceleration
γ= surface tension (liquid-air)

- ✓ Quite good uniformity
- ✓ Very thin layers
- ✓ Large area coverage
- ✓ Easy process

- X Waste of material
- X Time consuming
- X Double side coverage
- X Very thin layers

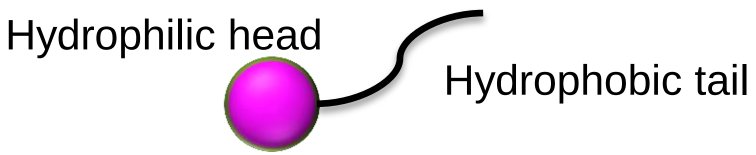
Example: TFT based on P3HT in xylene → single monolayer ≈ 2 nm thick with π-π stacking oriented in favorable transport direction

Sandberg *et Al.*, *Langmuir,* 18, 26, 2002.

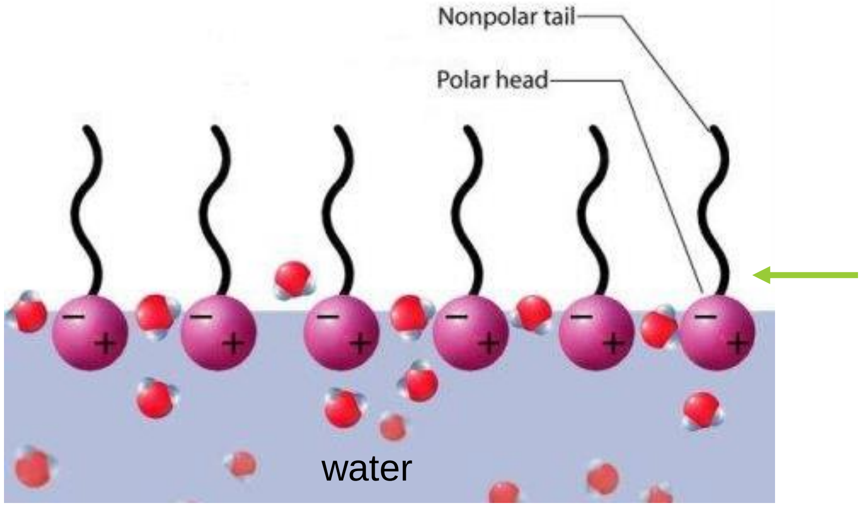
Extreme thickness control: Langmuir-Blodgett I

Transfer a Langmuir film to a substrate preserving density

Based on hydrophobicity/hydrophilicity

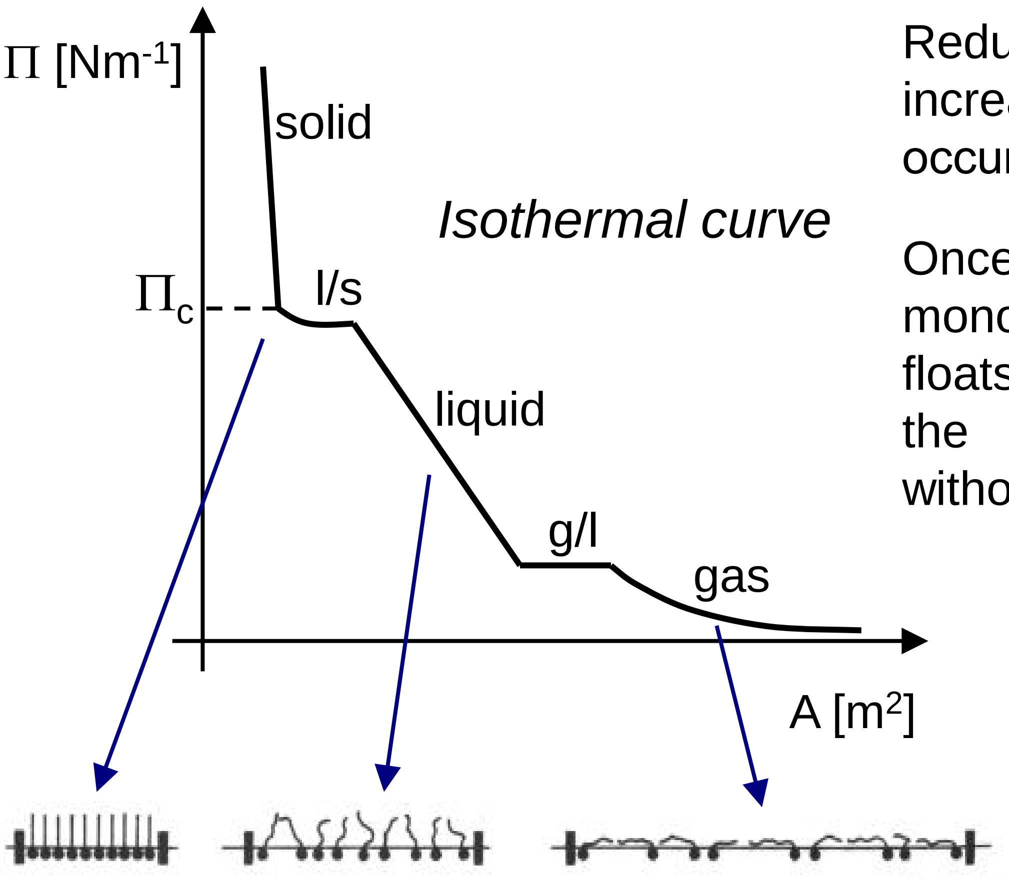


Amphiphilic molecules



Langmuir film:
Molecules move as in a bi-dimensional ideal gas, with a well defined surface pressure Π, area A, and density

Extreme thickness control: Langmuir-Blodgett II



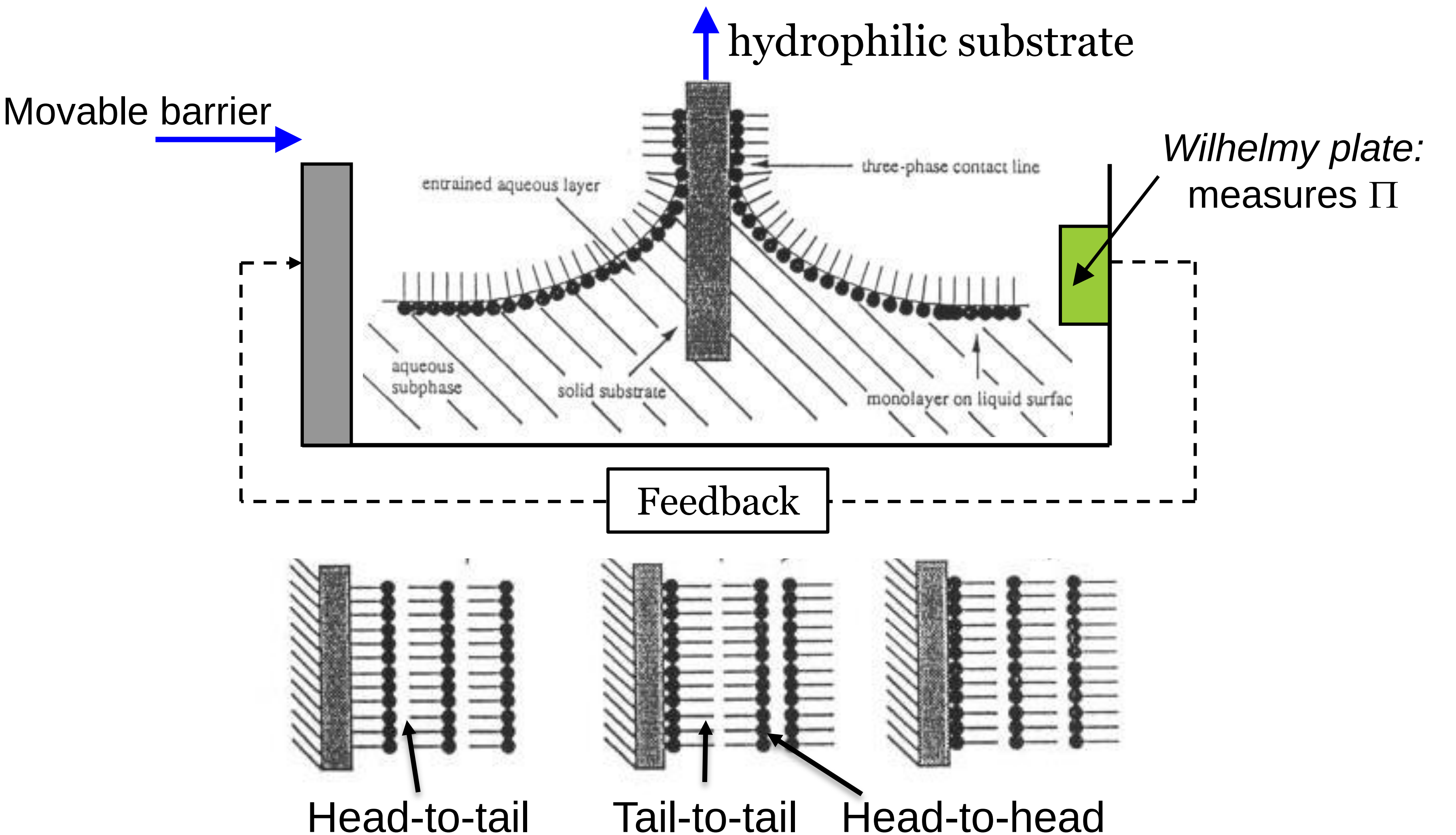
Reducing the available area, pressure increases and eventually a phase-change occurs: “gas” → “liquid” → “solid”

Once Π_C is reached, a compact molecular mono-layer is formed (”solid” state) and floats on the water surface. At this stage the area cannot be further reduced without destroying the mono-layer.

http://www.biolinscientific.com/technology/l-lb-ls-technique/

Extreme thickness control: Langmuir-Blodgett III

Langmuir-Schaefer: horizontal deposition

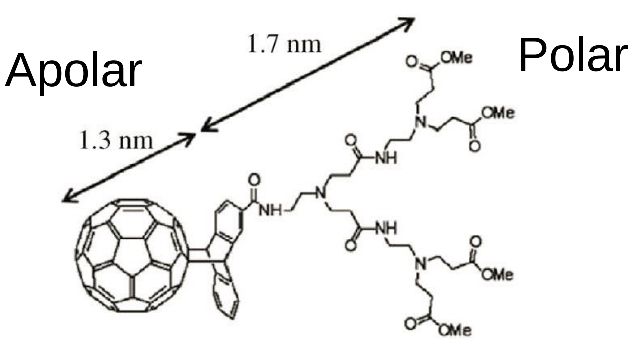


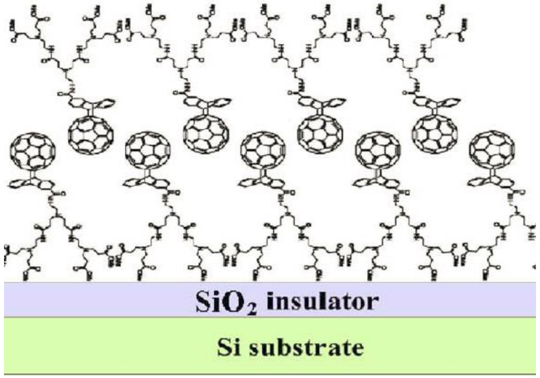
Extreme thickness control: Langmuir-Blodgett IV

- ✓ Excellent control of thickness.
  An ideal monolayer can be grown
- ✓ Homogeneity over large areas
- ✓ Multilayer structures with varying layer composition
- ✓ Control on the packing density
- ✓ Low sensibility to molecular structure

- X Only amphyphilic molecules can be deposited
- X Non trivial setup
- X Thin films

Example: C60 dendrimer – n-type TFT





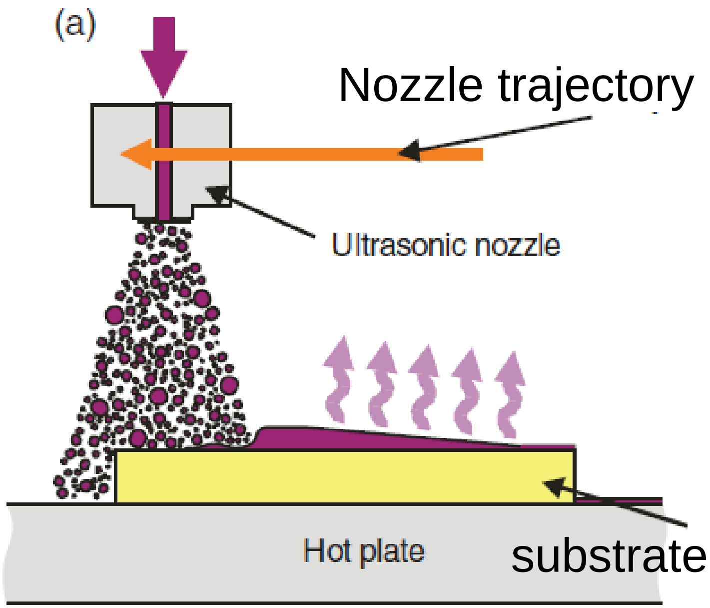
LB film: 5 layers ≈ 15nm

Higher mobility than spin-coated film → higher morphological order (on 30 nm length)

Kawasaki *et al.,* Appl. Phys. Lett. 91, 243515, 2007.

Spray Coating

Substrate is hit by a vaporized solution flux



The **film thickness** and morphology can be controlled by:

- air pressure
- solution viscosity
- solvent properties (evaporation rate,…)
- gun tip geometry
- distance between nozzle and substrate

✓ Large area coverage

✓ On many different substrates

✓ Fast – R2R compatible

? Waste of material

single pass technique: wet droplets merge on the substrate into a full wet film before drying

↓

smooth and uniform films analogous to spin-coating

multiple pass technique: droplets dry independently

↓

rougher films, but topology and wettability issues can be overcome and thickness can be adjusted

Spray Coating

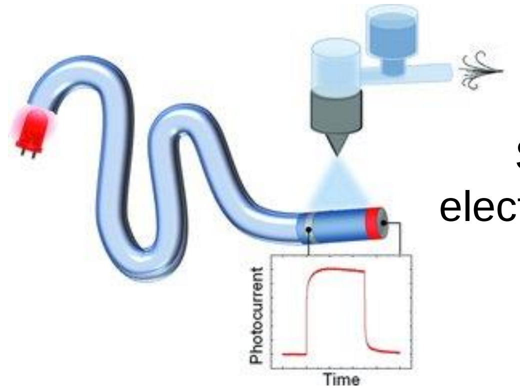
Example: Spray-coated organic solar cells

Girotto et al. Adv. Funct. Mater. 2011, 21, 64–72

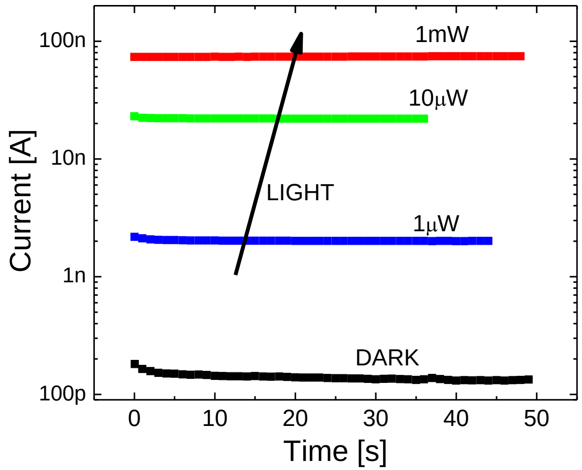
sample (PEDOT:PSS–P3HT:PCBM)	PCE [%]	J_{SC} [mA cm^{-2}]	FF [%]	V_{OC} [mV]
spin–spin	3.62	9.37	65	595
spray–spin	3.65	9.08	68	587
spin–spray	3.53	8.84	69	575
spray–spray	3.52	8.79	70	573

Example: Organic light sensor directly deposited onto a Plastic Optical Fiber

Binda et al., Adv.Mater.2013,25, 4335–4339

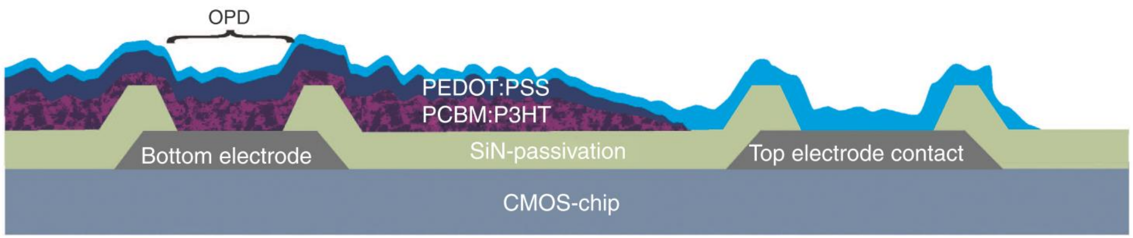


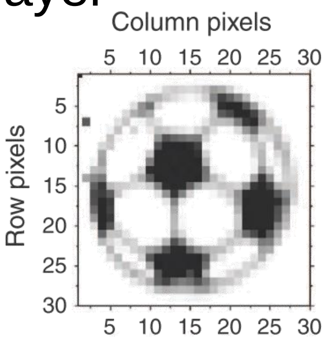
Spray coated bottom electrode and active material



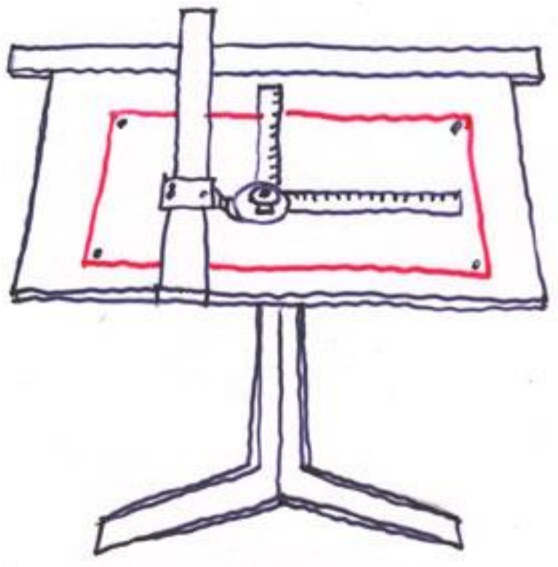
Example: Hybrid CMOS-imager with sprayed photoactive layer

D. Baierl et al., Nat. Comm., 2012





Solution processable materials: patterning techniques

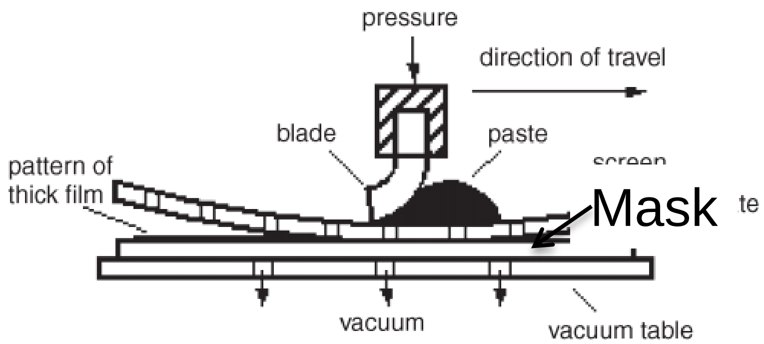


through a mask

- Shadow masking
- Photopatterning
- Soft Lithography
- NIL/Embossing
- Physical Delamination
- Atomic force nanolithography

Screen Printing + Shadow masking

The solution of the active material is squeezed by a moving blade through a screen mask onto the substrate surface



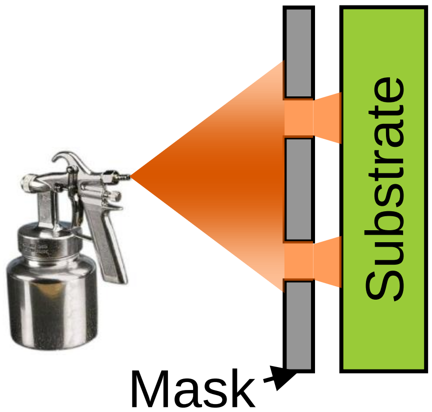
Z. Bao et al., A. J. *Chem. Mater. 9*, 1299-1301, 1997.

✓ Simple

X Limited **resolution: ≈ 50-100 μm**

X Waste of material

X Only viscous solutions

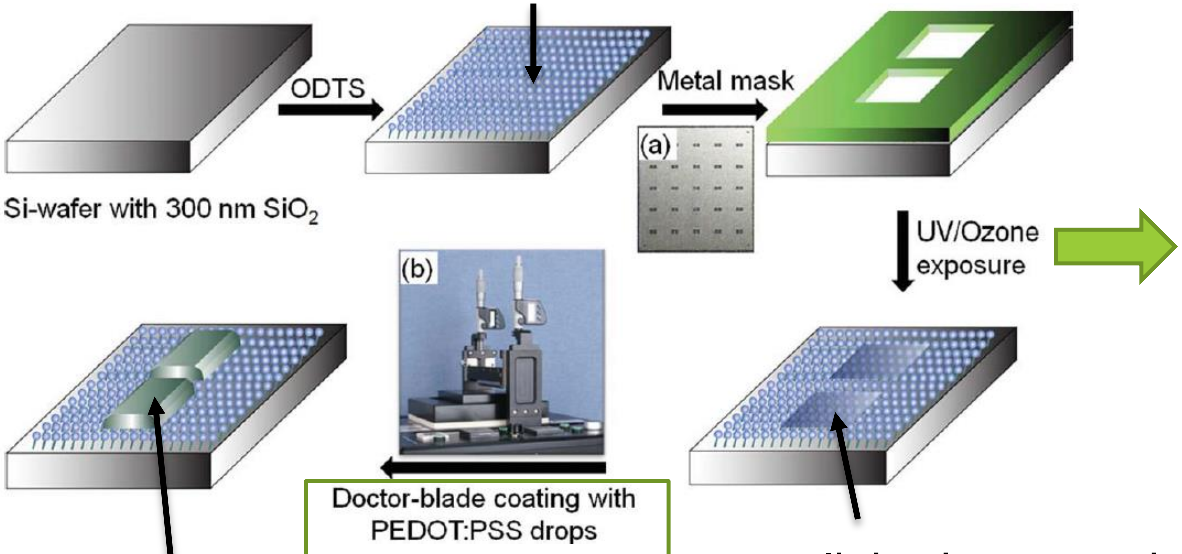


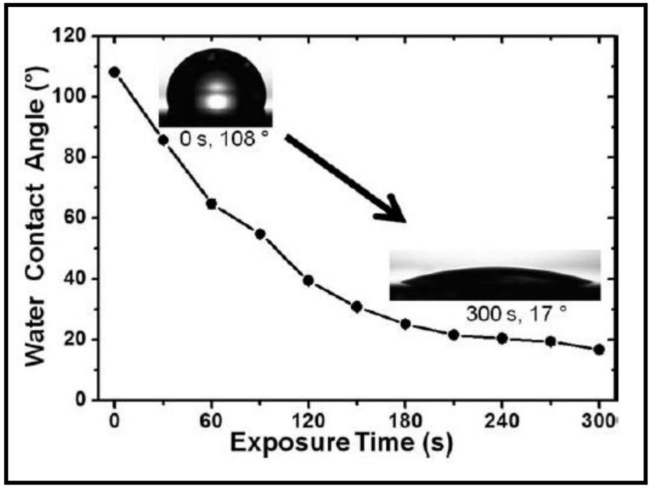
Masking applied to spray coating:
shadow masking

Shadow masking+selective wettability

Exploiting the difference in wettability between hydrophobic surfaces and hydrophilic surfaces to make the patterns

Hydrophobic SAM
(Self Assembled Monolayer)



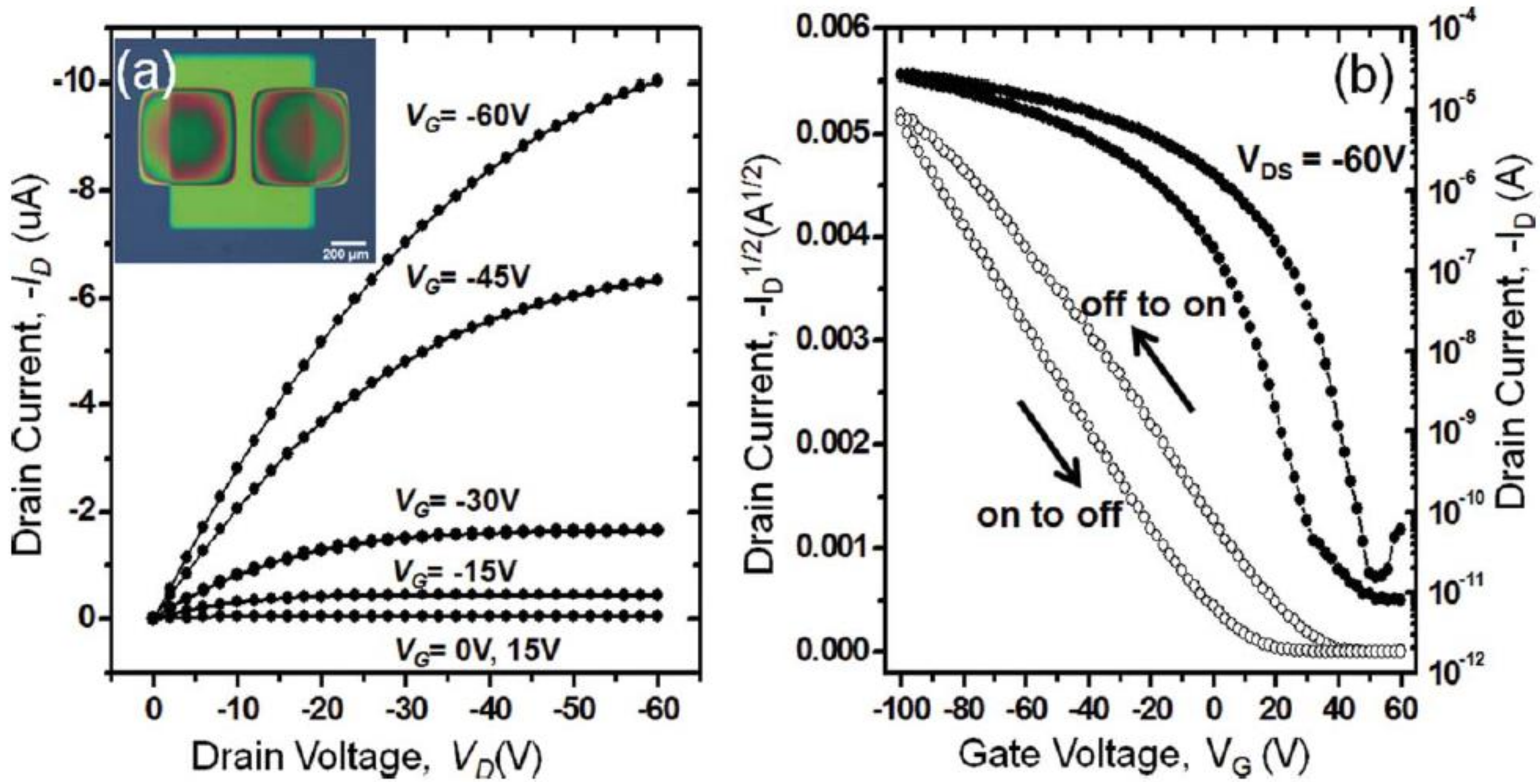


UV-light damages the ODTS film

PEDOT/PSS: conductive polymer from aqueous suspension

Journal of Polymer Science B: Polymer Physics, 49, 1590–1596, 2011

Shadow masking+selective wettability

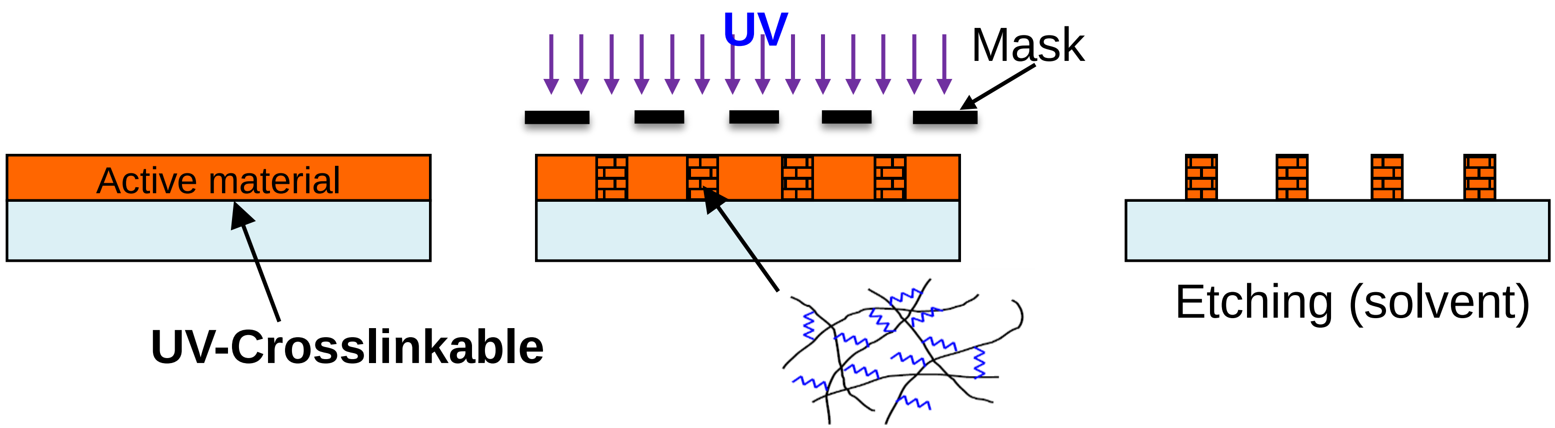


Journal of Polymer Science B: Polymer Physics, 49, 1590–1596, 2011

Photopatterning

Same principles and equipement of standard photo-lithography

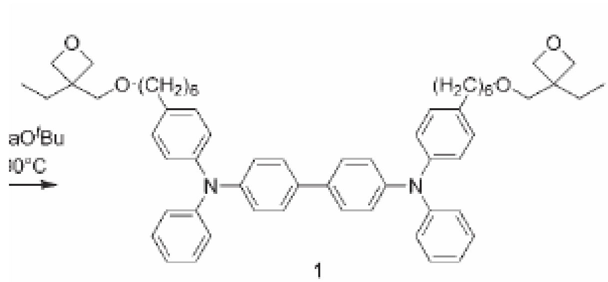
→ resist is the active material!

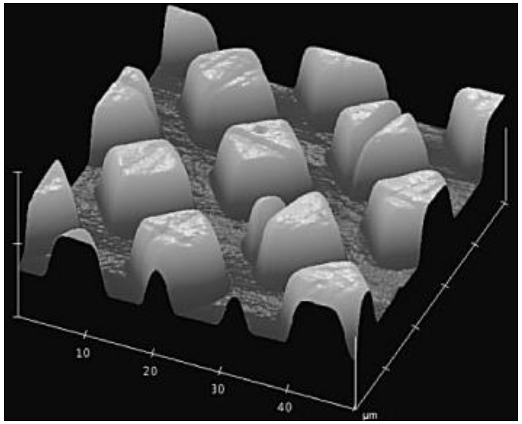


Example: patterning of pixels in OLED display:

Patterning of the hole transport layer

Feature size ≈ 5 μm





Nuyken *et Al*., Macromol. Rapid Commun., 25, 1191–1196, 2004.

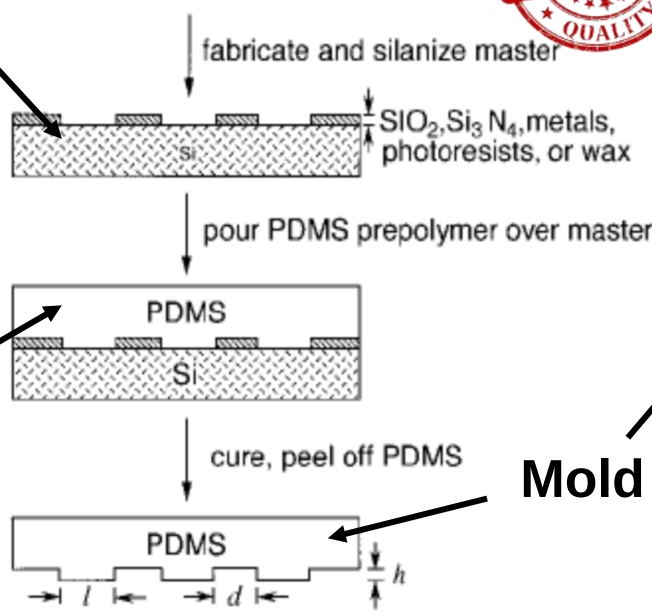
Soft Lithography

Earliest motivation: overcome cost of photolithography for sub μm features

Basic idea: replicate patterns generated by photolithography through an *elastomeric* mold.

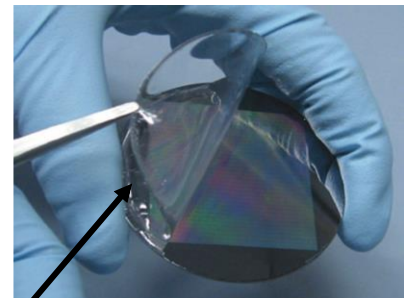
Master

- Photolithography
- X-Ray Litho
- EB Litho
- FIB writing…



Elastomer

Mold



Critical aspect ratios

✓ Conformal

✓ Fast – R2R

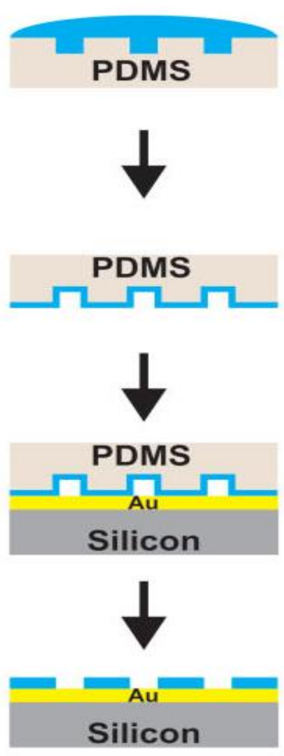
Review: Whitesides *et al*., Angew. Chem. Int. Ed. 1998, 37, 550 -575.

	Resolution
soft lithography	
microcontact printing (μCP)	35 nm
replica molding (REM)	30 nm
microtransfer molding (μTM)	1 μm
micromolding in capillaries (MIMIC)	1 μm
solvent-assisted micromolding (SAMIM)	60 nm

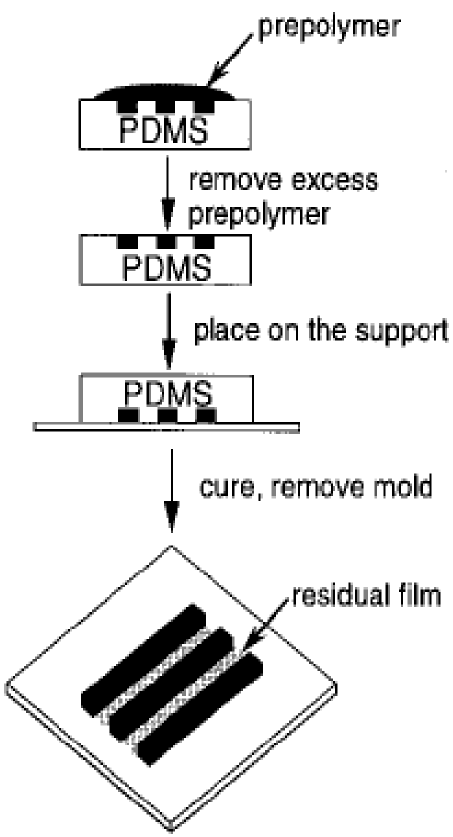
Soft Lithography

Printed material has to adhere to the substrate while the interaction with the mold has to be minimal

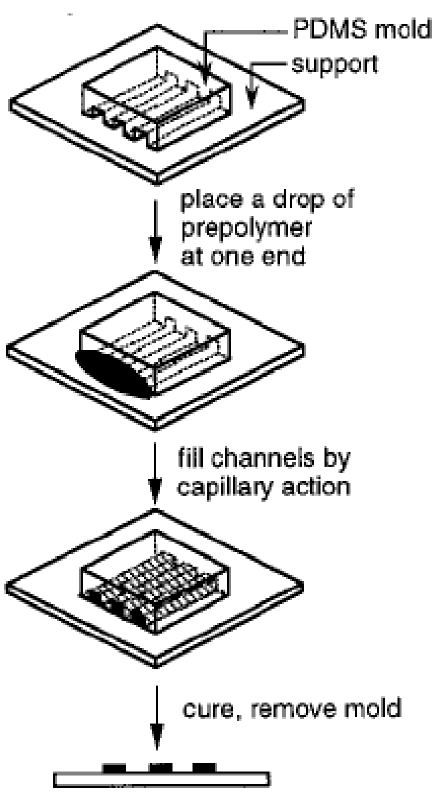
Micro Contact Printing (μCP)



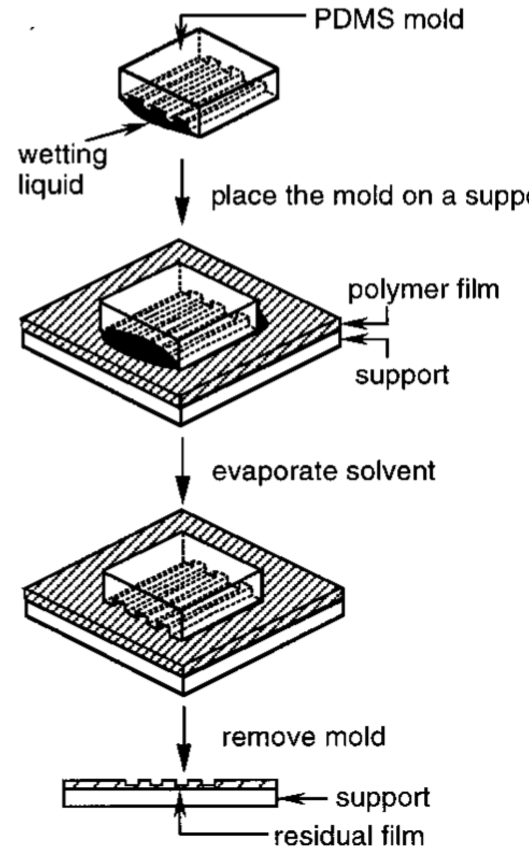
Micro Transfer Molding (μTM)



Micromolding in Capillaries (MIMIC)



Solvent-assisted Micromolding (SAMIM)



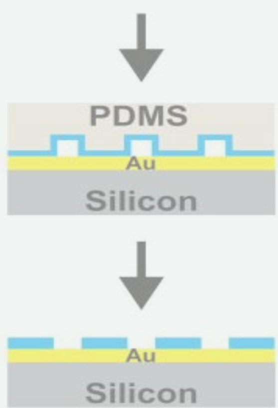
Soft Lithography

Printed material has to adhere to the substrate while the interaction with the mold has to be minimal

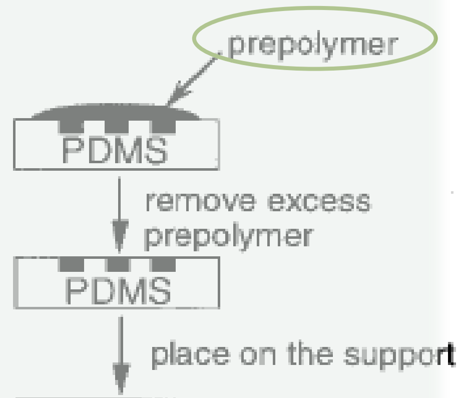
Micro Contact Printing (μCP)

Appl. Phys. Lett. **88**, 063513, 2006.

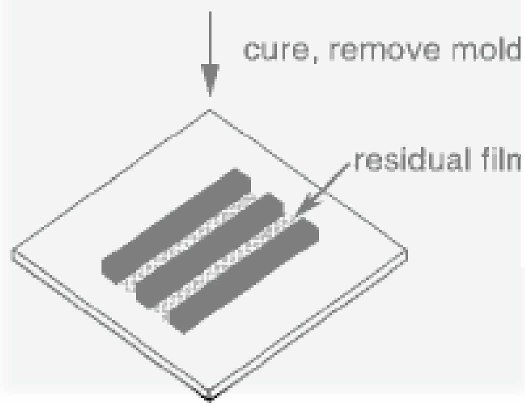
Org. Elec. 8,94–113, 2007.
(film grown by LBL onto the mold)



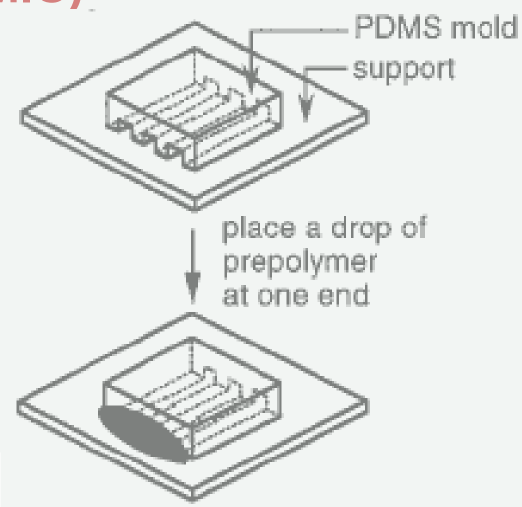
Micro Transfer Molding (μTM)



Angew. Chem. Int. Ed. 1998, 37, 550 -575



Micromolding in Capillaries (MIMIC)



Adv. Mater. 14, 1565, (2002)

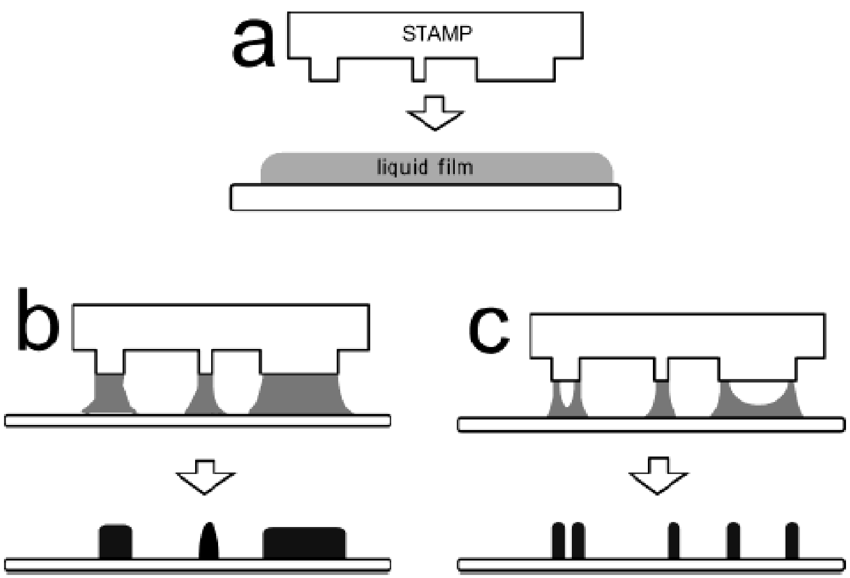
Organic Electronics 8, 389–395, (2007)

Organic Electronics 10, 527–531, (2009)

Micro-Contact Printing (μCP) III

Subtractive

As the stamp is placed in contact with a liquid thin film spread on a substrate, capillary forces drive the solution to form menisci under the stamp protrusions

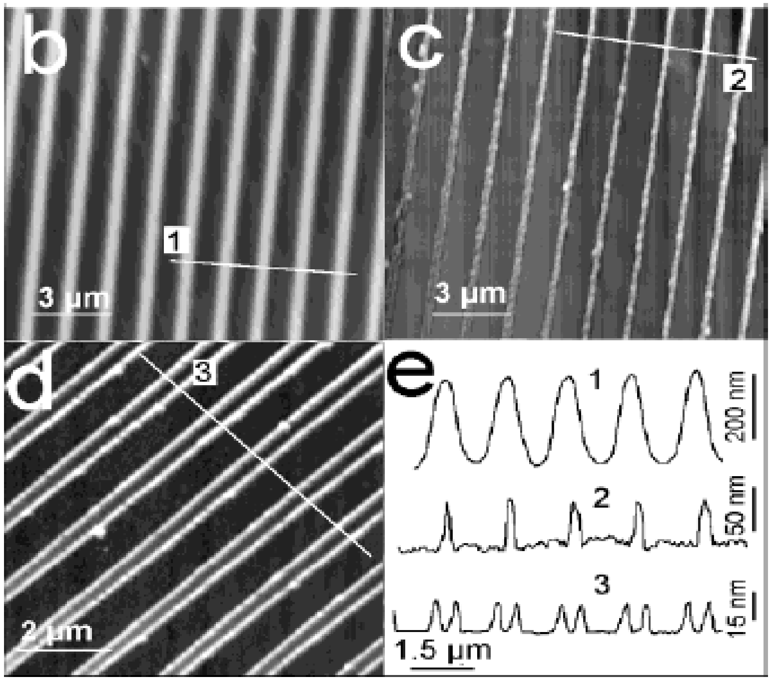


Dilute solution

Very dilute solution

↓

Solution pinned to the edges



b) AFM image of the stamp; c) printed AlQ_3 film using dilute solution; d) very dilute solution; e) line profile of stamp and films

Cavallini, *Nano Lett.*, Vol. 3, No. 9, 2003.

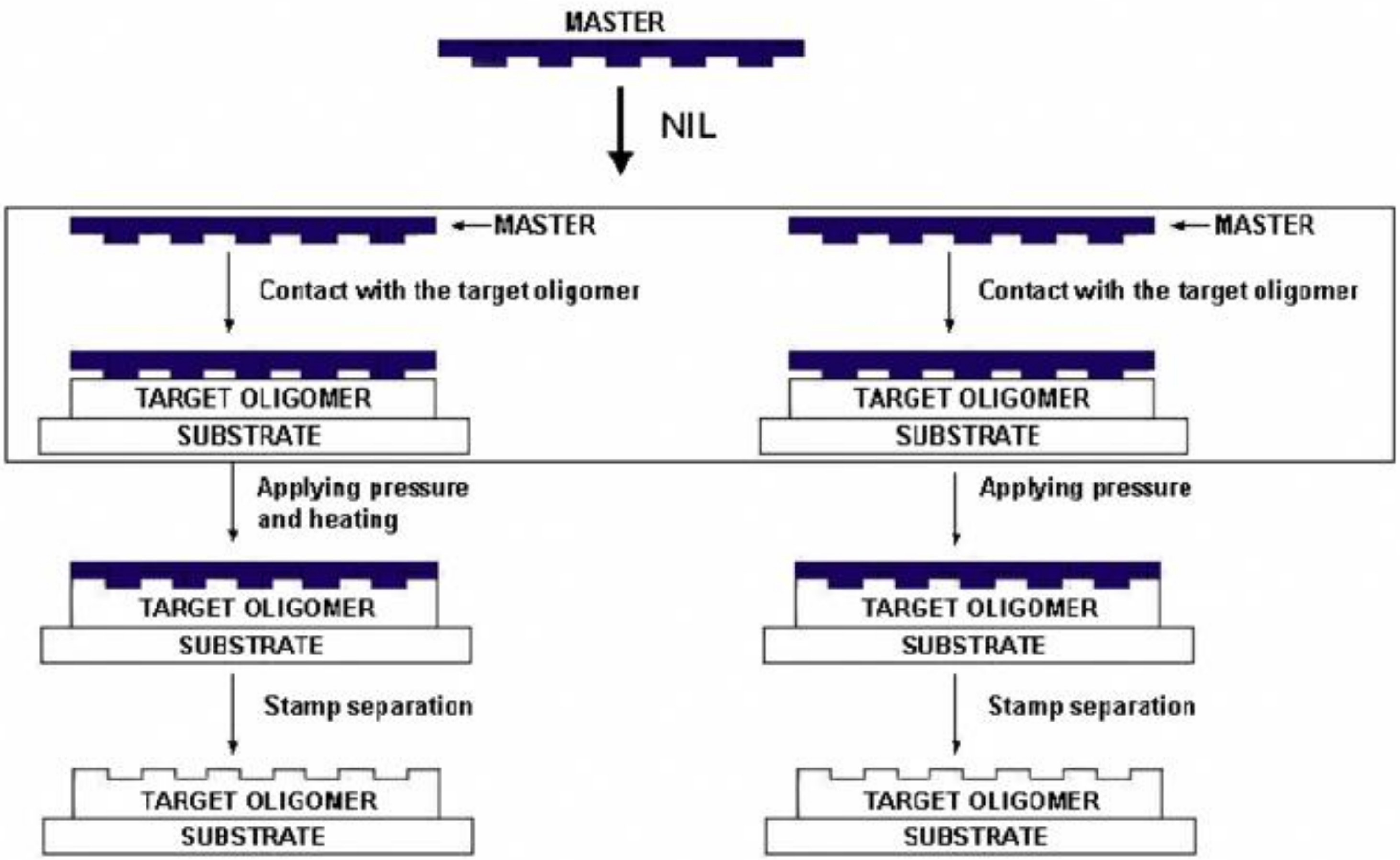
Nano Imprint Lithography/Embossing I

Similar to SL but based on **hard** mold/stamp.

It allows obtaining smaller features (≈10 nm)

T>Tg

Tg: polymer glass phase transition



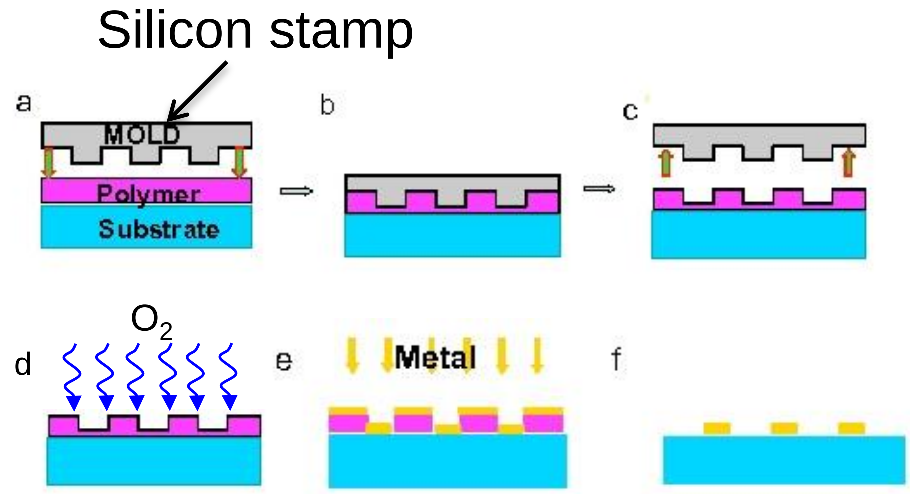
Hot Embossing

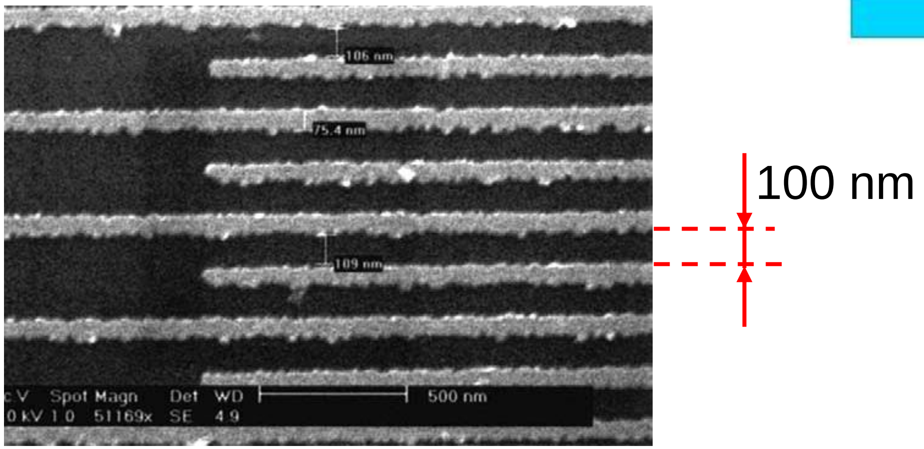
Room Temperature NIL

Nano Imprint Lithography/Embossing II

Example: Nanometer-sized electrodes for OTFTs

- Nanoimprint of photoresist (a,b,c)
- Dry etching in O_2 plasma (d)
- Metallization Au/Ti (e)
- Lift-off in acetone (f)

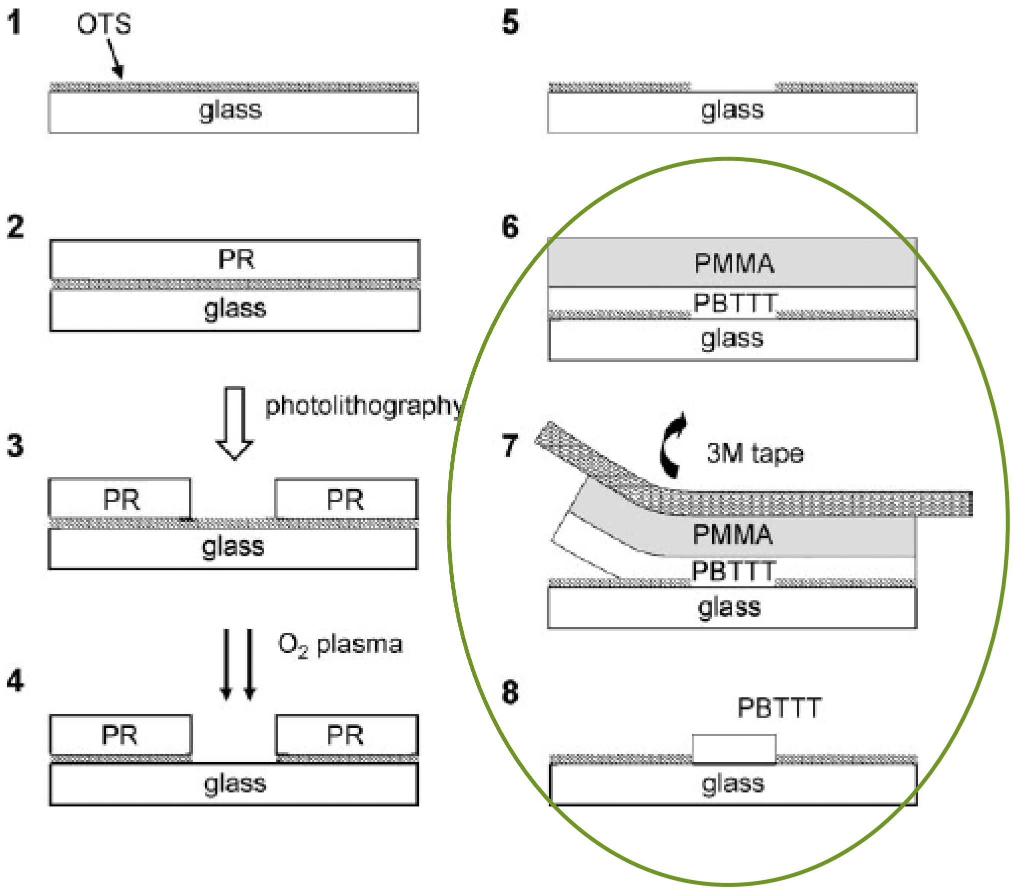




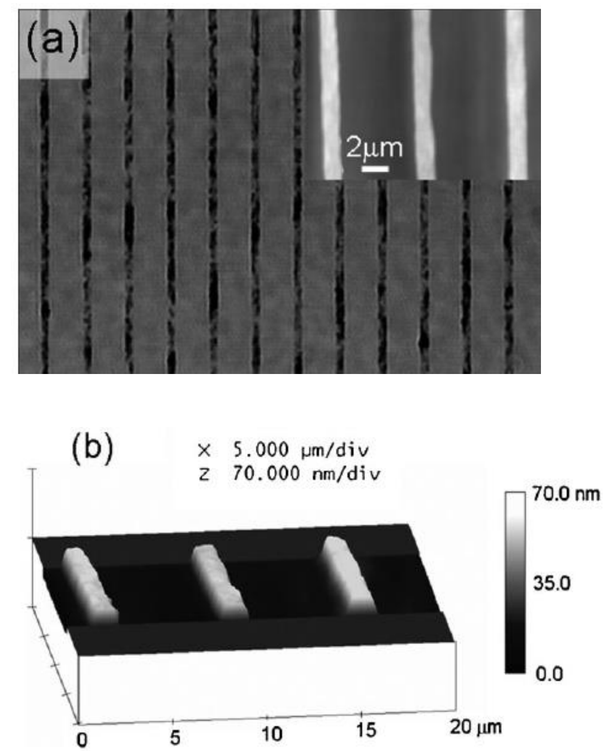
Kam *et al*., Microelectronic Engineering, 73, 809–813, 2004.

Physical Delamination

Based on a photolithographic process previous to semiconductor deposition



Polymer adhere to the substrate where OTS is not present



Optical and AFM images of patterned PBTTT

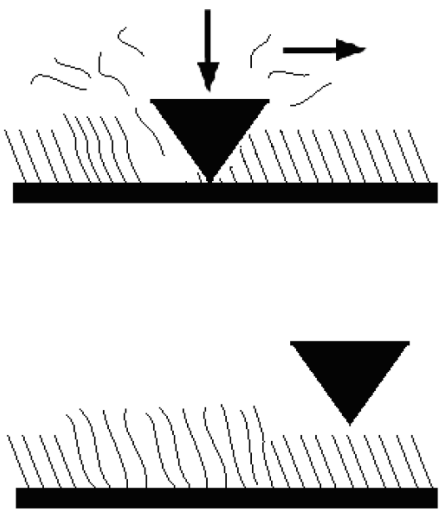
Sirringhaus, Adv. Mater., 21, 1–6, 2009.

Atomic force nanolithography

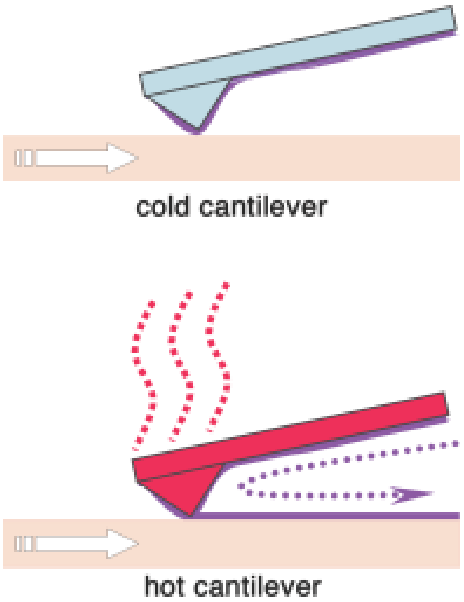
Transplant the concept of writing with a pen to the nanoscale

Resolution < 100 nm... but on 100x100 μm area!

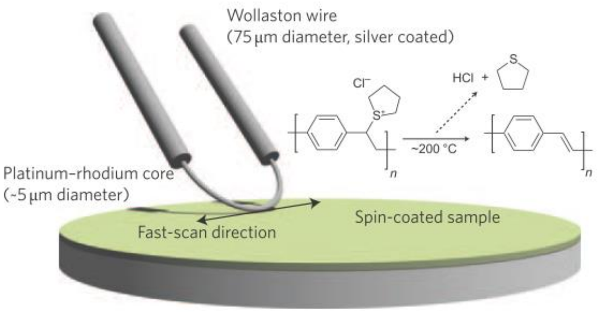
Nanoshaving, Nanografting

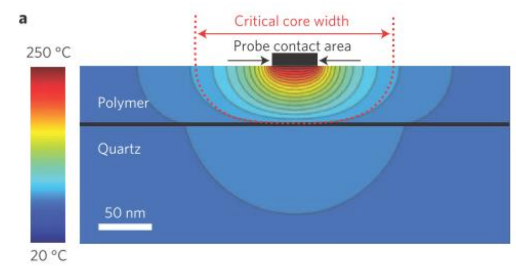


Dip-pen



Thermo/elettro-chemically patterning





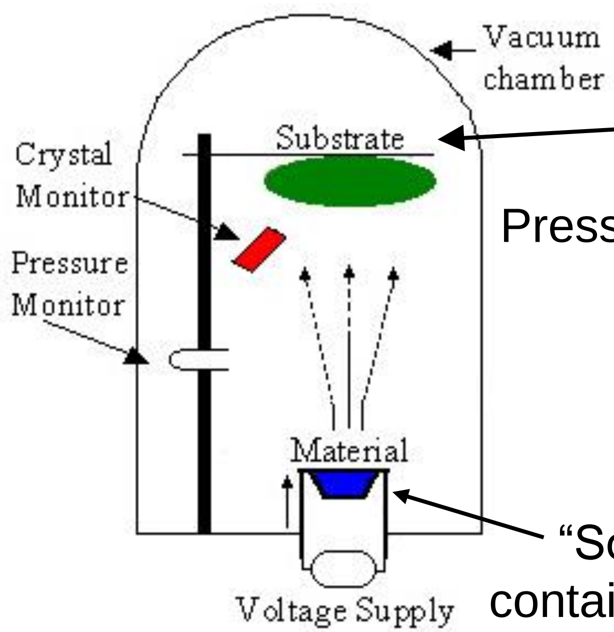
J. Phys.: Condens. Matter 21 (2009) 483001
Nature Nanotech, 4, 664 - 668 (2009)

Non-soluble materials: deposition techniques

- Vacuum Thermal Evaporation
- Organic Vapor Phase Deposition (OVPD)
- Organic Molecular Beam Deposition (OMBD)
- Compression molding

Vacuum Thermal Evaporation I

Sublimation of molecules due to high-vacuum and high temperature



Substrate holder

Pressure 10^{-5}-10^{-7} torr → Molecules mean free path: tens of cm - m

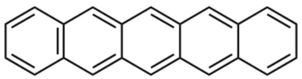
"Source boat": contains the material and it is heated at hundreds of °C

- Evaporated molecules travel in straight lines inside the chamber and they condense on the substrate
- Growth rate controlled by tuning the temperature of the source boat

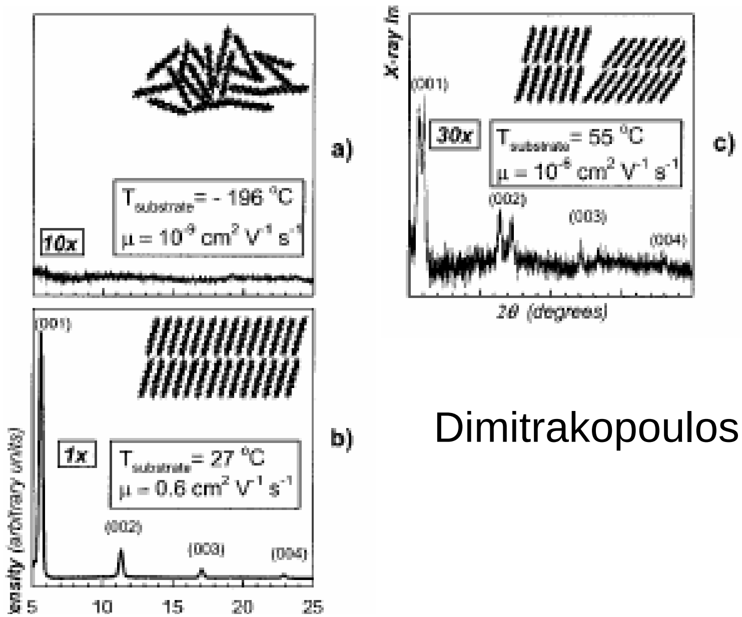
Thickness of the film is monitored with the *crystal microbalance* (change of the resonating frequency of a piezo resonator).

Vacuum Thermal Evaporation II

Growth rate and substrate temperature affect film morphological order



Pentacene on SiO_2



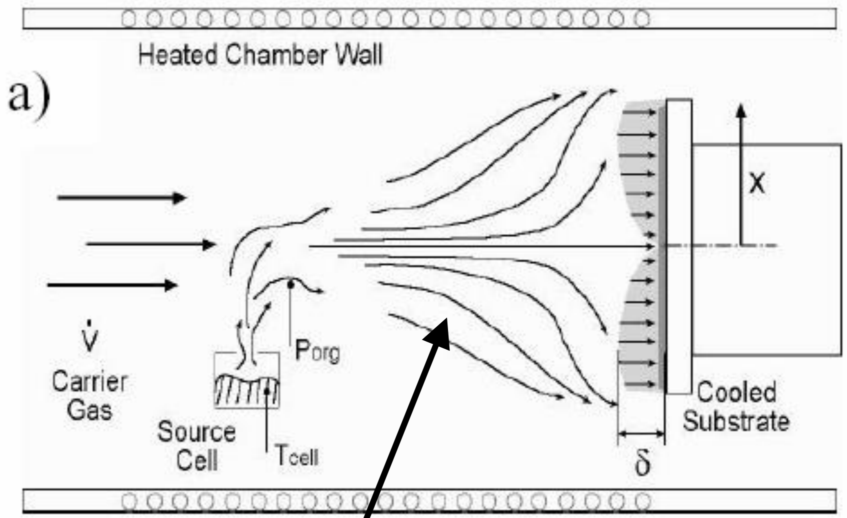
Dimitrakopoulos, Adv. Mater., 14, 99, (2002)

- ✓ High quality, ordered thin films
- ✓ Good control and reproducibility of film thickness
- ✓ Multilayer deposition and co-deposition of several organic materials

- X Waste of material
- X Expensive equipments
- X Very low throughput → high production costs
- X No large area coverage

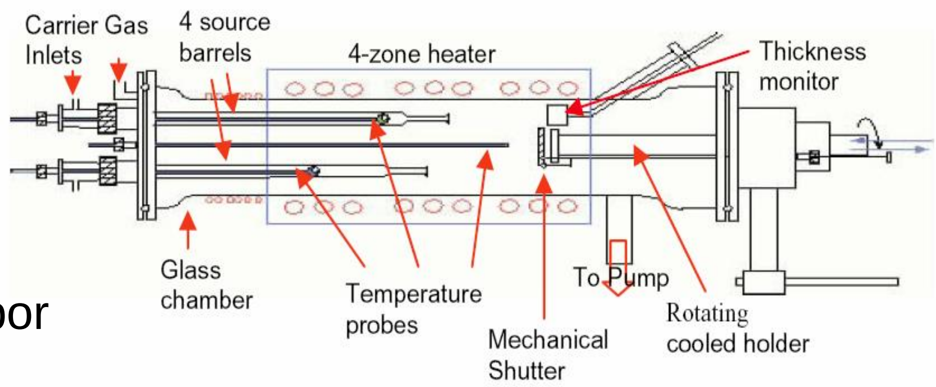
Organic Vapor Phase Deposition I

Based on *low pressure* carrier gas instead of high vacuum



Hot inert carrier gas (Ar, N_2) transport source material to the cooled substrate where condensation occurs

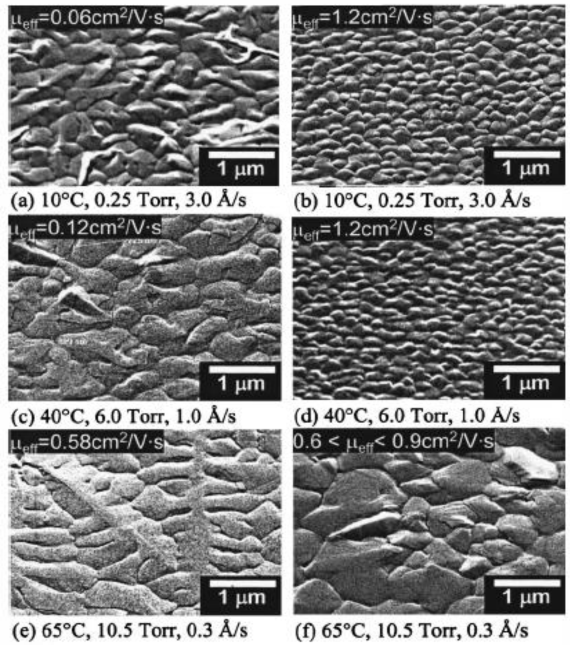
Heated walls → vapor does not condense



Organic Vapor Phase Deposition II

Example: TFT based on Pentacene

SiO$_2$ SiO$_2$-OTS



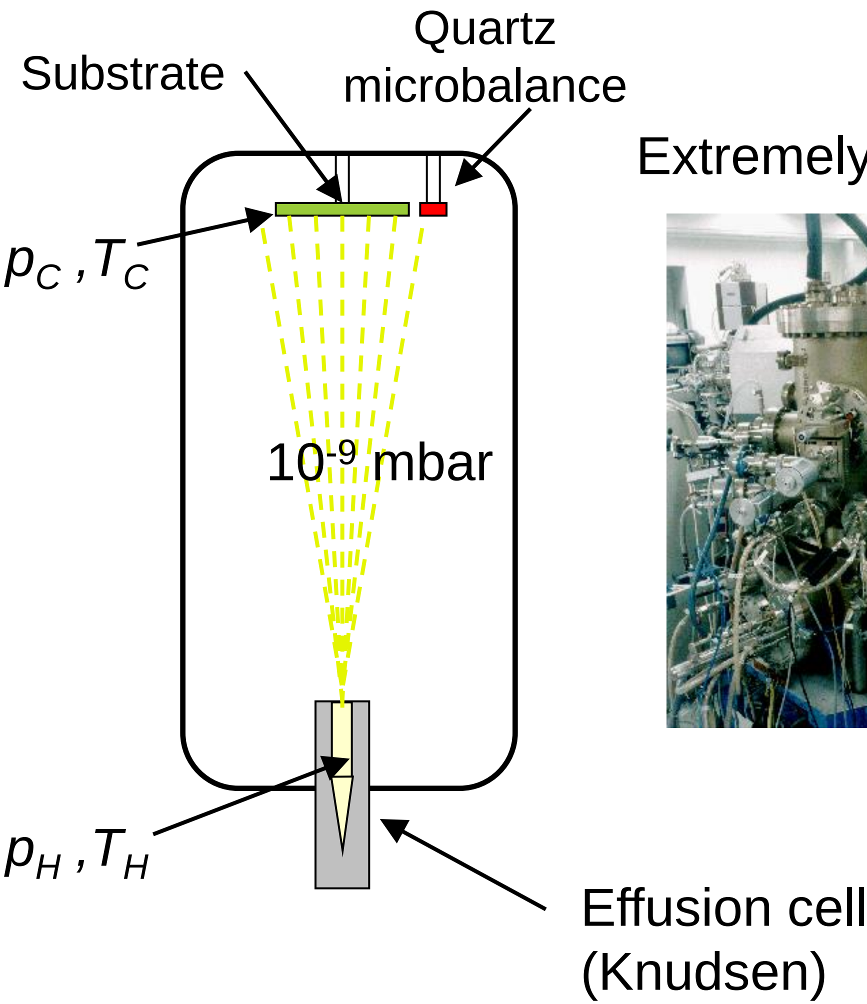
Shtein *et al*. Appl. Phys. Lett., 81, No. 2 (2002)

Advantages over standard VTE:

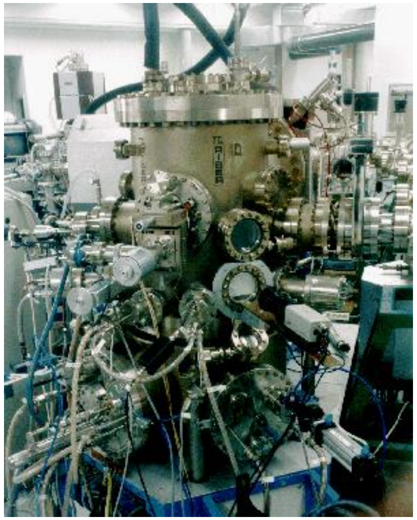
- ✓ Higher deposition rates
- ✓ Less waste of material (no condensation on the internal walls)

Organic Molecular Beam Deposition

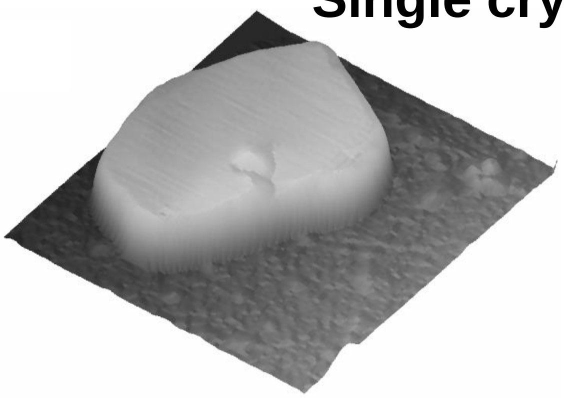
Flow of focalized molecules in ultra high vacuum

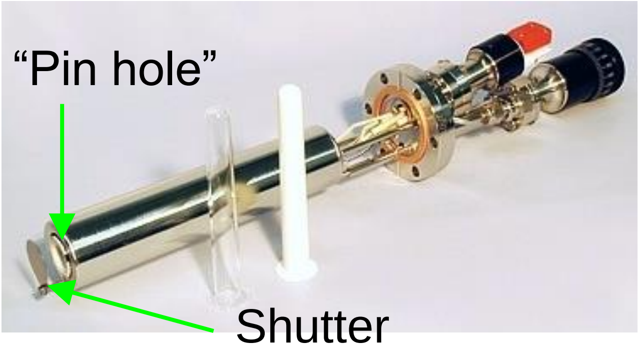


Extremely slow deposition rate → *epitaxial* growth



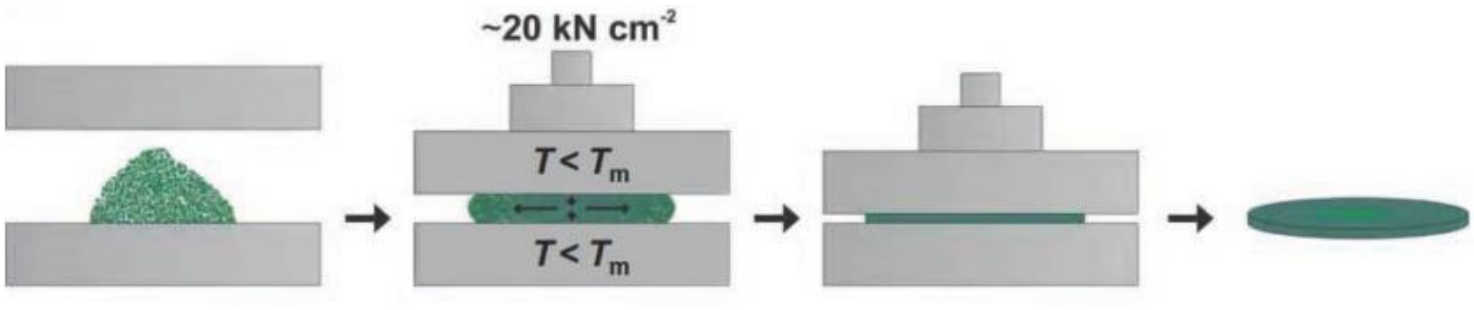
Single crystal





Compression molding

Solid, powdered material placed in a hot press and compressed well below the melting temperatures of the species



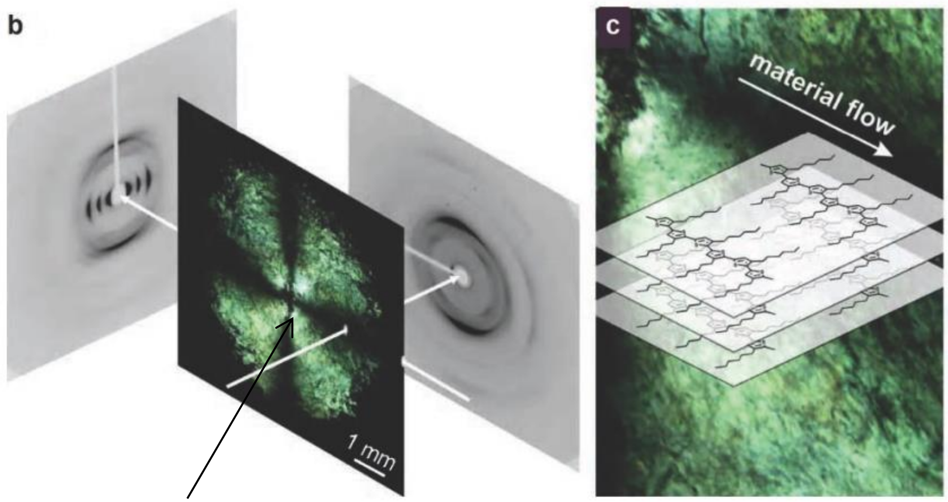
- ✓ Medium area
- ✓ Applicable to wide range of materials
- ✓ No waste of material
- ✓ Good uniformity
- ✓ Mechanical robustness
- ✓ Highly ordered films

X Thickness 1-200µm

Baklar et al. Adv. Mater. 2010, 22, 3942–3947

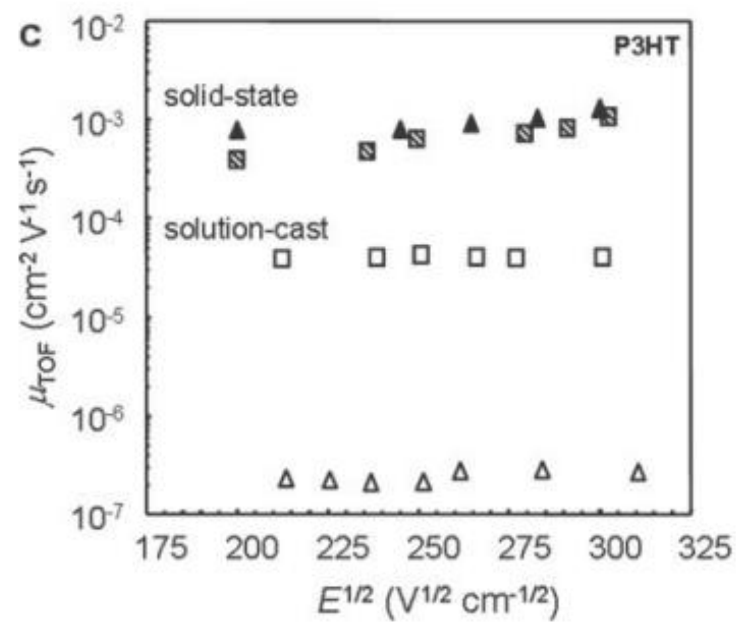
Compression molding

Radial molecular flow during compression molding



Material anisotropy X-ray diffraction

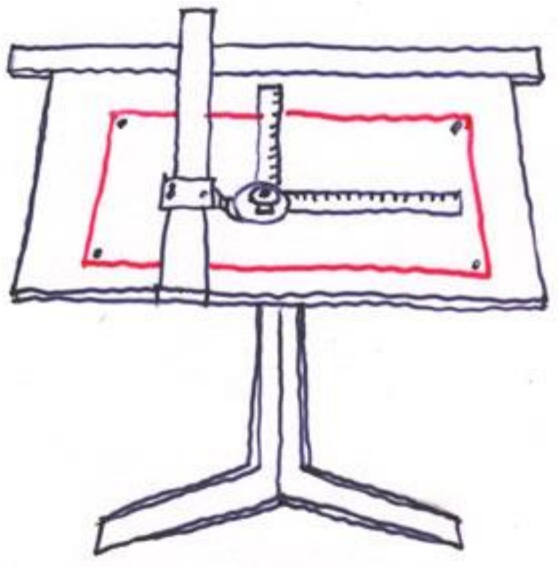
Free-standing flexible film



- TFT performances comparable with optimized solution processes devices

Baklar et al. Adv. Mater. 2010, 22, 3942–3947

Non-soluble materials: patterning techniques

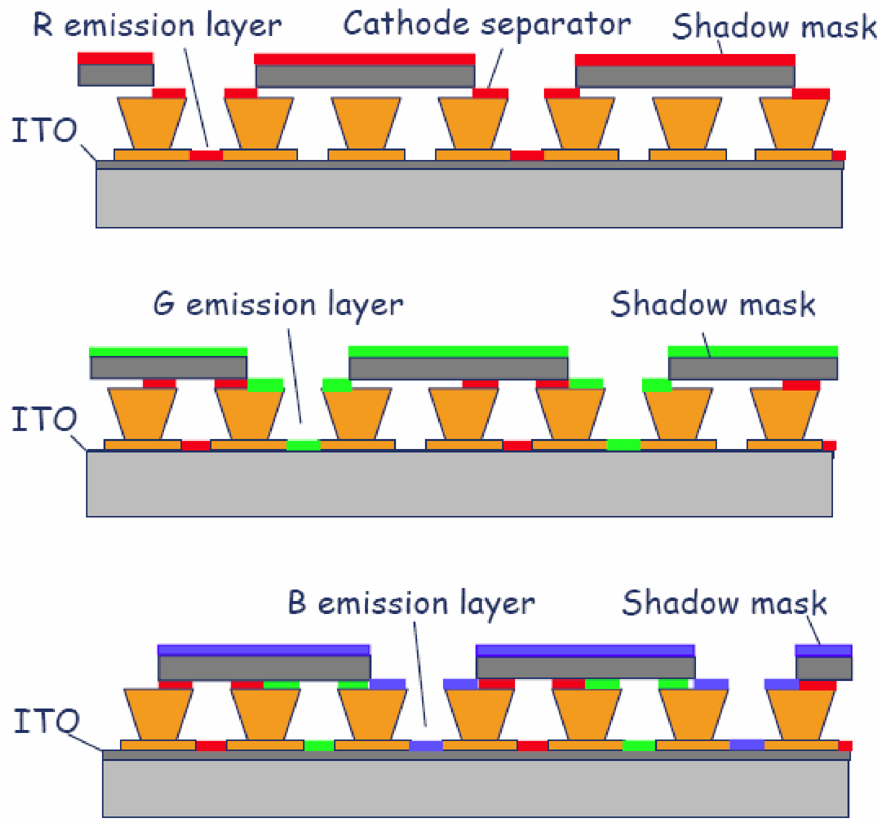


- Shadow masking
- Vapor Jet Printing

Patterning of vacuum deposited materials

Shadow mask (same principle of screen printing).
Resolution limited to tens of μm.

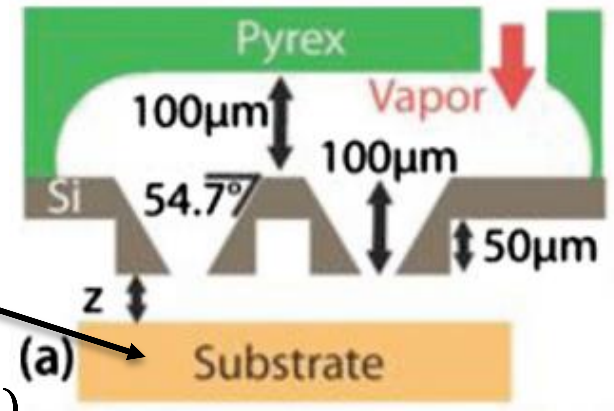
Example: Patterning of RGB sub-pixels in OLED displays



Fukuda *et Al.*, Synthetic Metals, 111–112 (2000)

Organic Vacuum Jet Printing (OVJP)

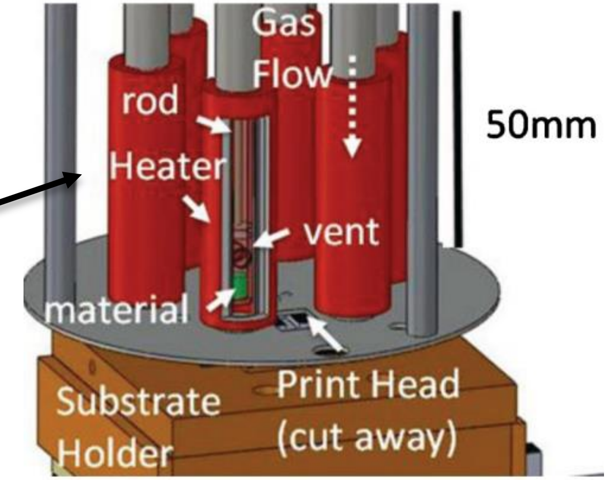
Organic small molecule material carried by hot inert gas to a nozzle array that collimates the flow into jets



Condensation onto a proximally located cold substrate, that can moove relatively to the print-head for patterning

For high resolution (~20µm):

•Narrow nozzles ~10µm (MEMS processing)
•Low gas flow rate



6 tubes with different source material

✓ No solvent

✓ No shadow mask

Thickness: 30 nm

G.J. McGraw, Appl. Phys. Lett. 98, 013302, 2011