Week 1-14

Nanoimprint Patterning and Stamping

Roll-to-Roll Manufacturing

Device Packaging

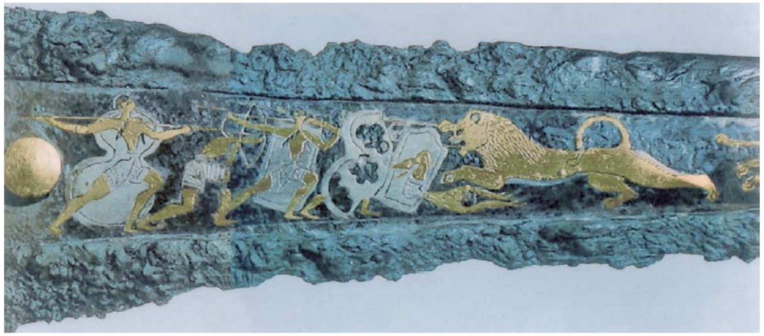
Chapter 5.6.4, 5.7-5.9

Nanoimprint Patterning

- Nanoimprinting proceeds by direct transfer of material by pressing a “stamp” to a substrate
- Completely based on dry processing – ideal for organics since no concern for solvent degradation of deposited layers
- Can have resolution in the nanometer range determined by stamp patterning constraints, yet can be applied over very large areas.
- In some cases, pressures applied can be very (prohibitively) large

Cold welding: A stamping method used through the ages

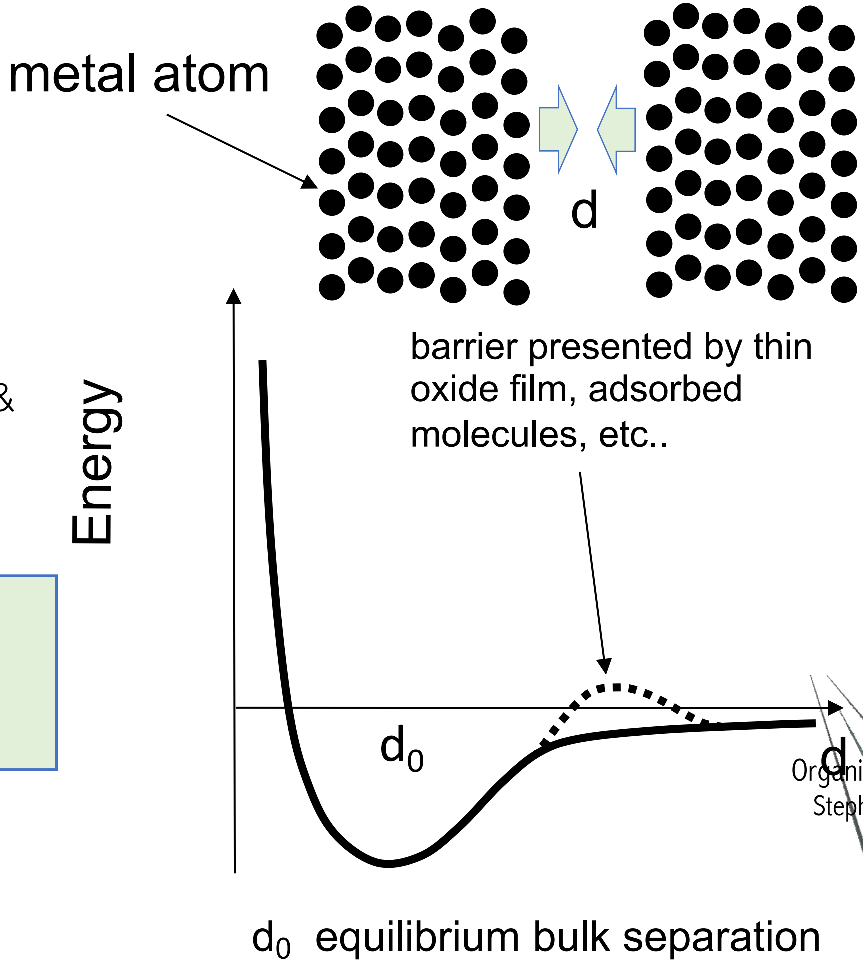
- Bring 2 clean metal surfaces together under pressure
- Atoms at surfaces eventually share outer shell electrons once any surface barriers are penetrated by pressure
- Bonding (i.e. complete sharing) of electrons occurs in ps



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

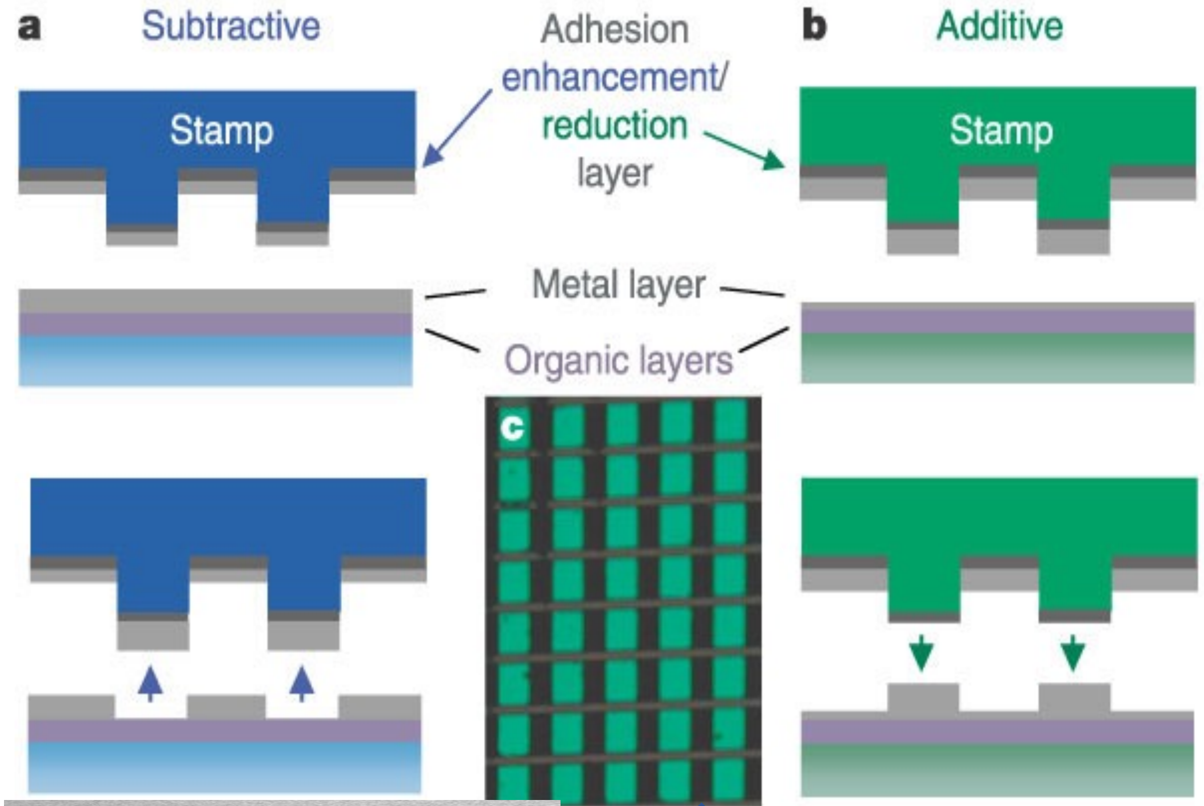
J. Haisma and GACM Spierings, Materials Science & Engineering R–Reports 37 1 (2002)

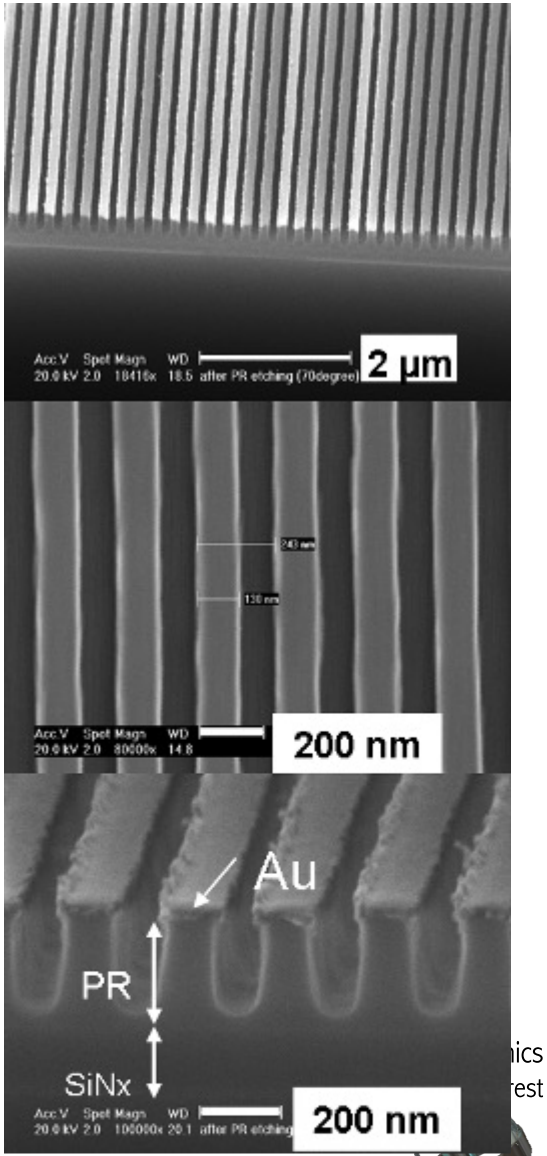
- Adhesive-free bonding of similar metals
- Useful for attaching contacts to organics, or even two organic films within a device.

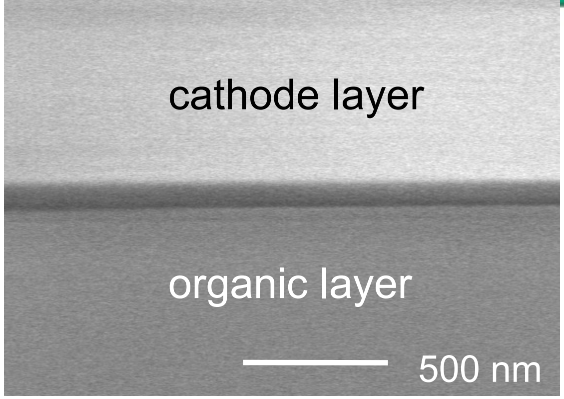


d_0 equilibrium bulk separation

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)

Subtractive vs. Additive Printing Steps

Subtractive

1. Deposit thick, similar metal of similar thickness on both hard stamp and surface
2. Press stamp to substrate until cold-welded
3. Apply greater pressure to fracture metal at edges of hard stamp (>100 MPa)
4. Lift away metal from substrate surface

- High pressure to conform to surface defects and fracture metal at edges
- Very high resolution (~10 -50 nm) determined by stamp patterning

Additive

1. Deposit a very thin (~5 nm) metal "strike layer" on the substrate surface
2. Deposit an "adhesion-reduction" layer on the soft (e.g. PDMS) stamp surface
3. Deposit a metal layer to the desired thickness of the final contact onto the stamp
4. Press stamp onto strike layer surface. Soft stamp pressures of ~ 100kPa are needed.
5. Lift of stamp, leaving behind the metal cold-welded to the strike layer.
6. Use light reactive ion (e.g. Ar+) plasma etch to remove thin strike layer between thick metal patterns

- Only low pressure needed since soft stamp can conform to surface defects
- Lower resolution than subtractive method due to soft stamp edge deformation under pressure
- Adhesion reduction layer ensures metal leaves stamp without pulling metal from substrate on stamp separation

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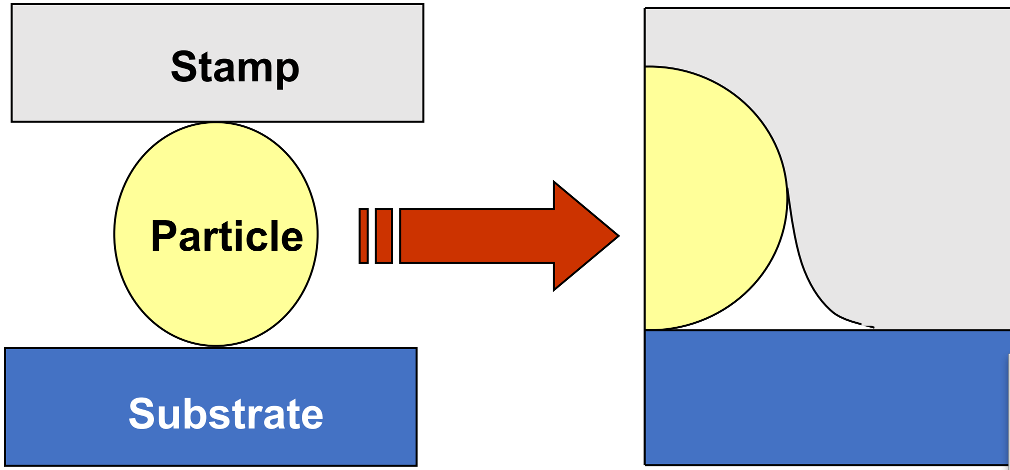
Conforming to surface defects

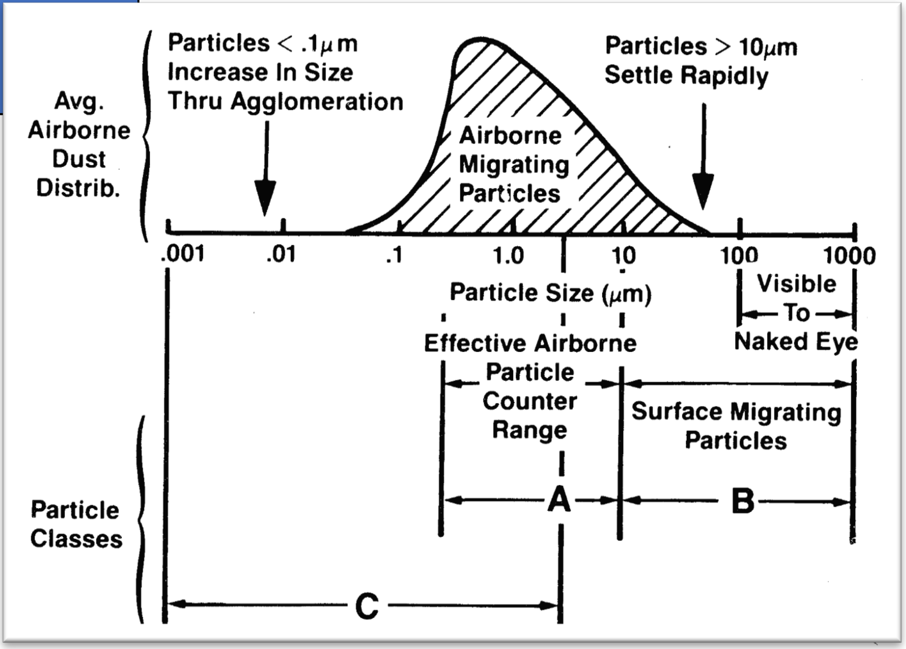
Hard Stamps Used in Subtractive Printing

Particlulate Distortions Under Stamp Require High Pressure



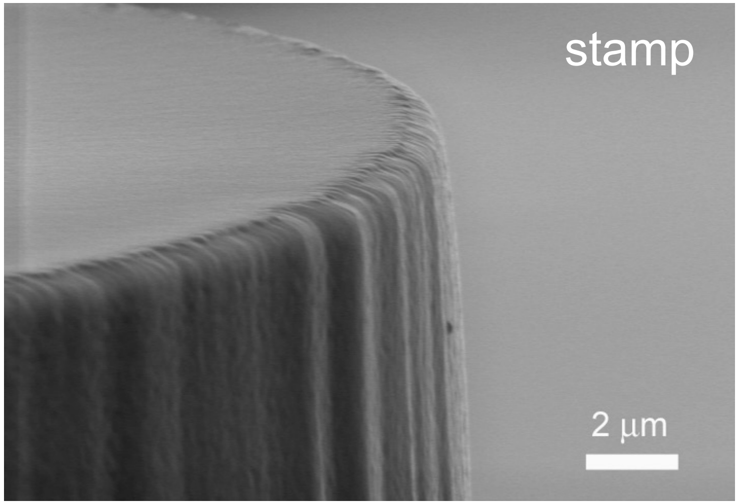
Stamp deformation required for contact: >100 MPa.

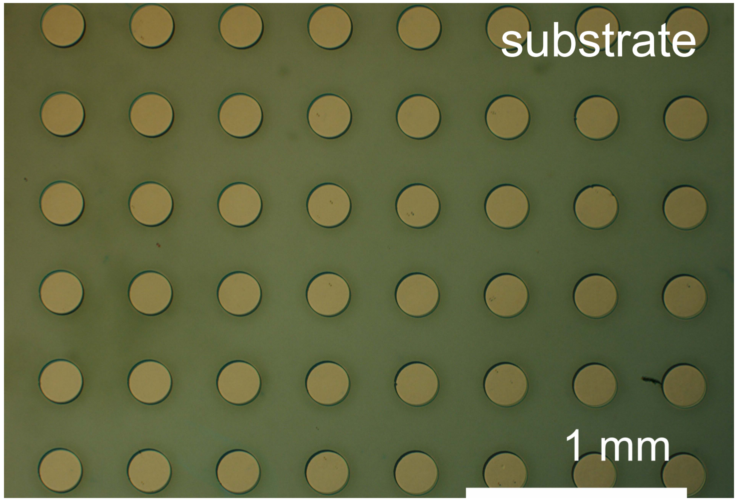
⇒ soft stamp advantage

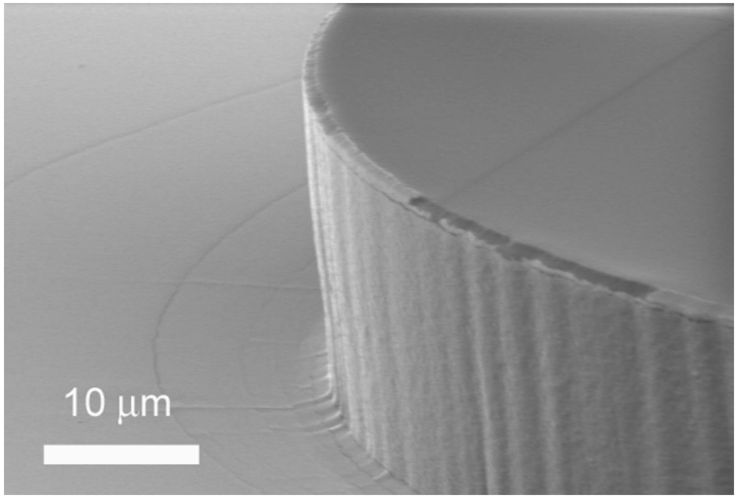


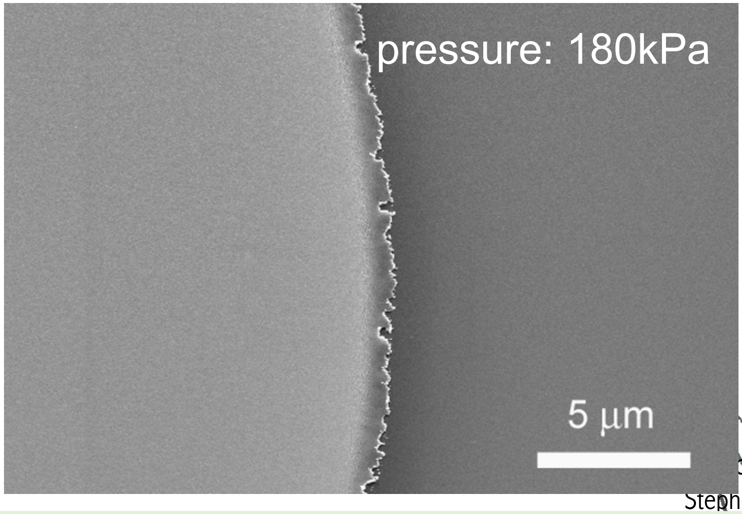
Fabrication of OLEDs Using PDMS stamps

1000x pressure reduction from hard stamps







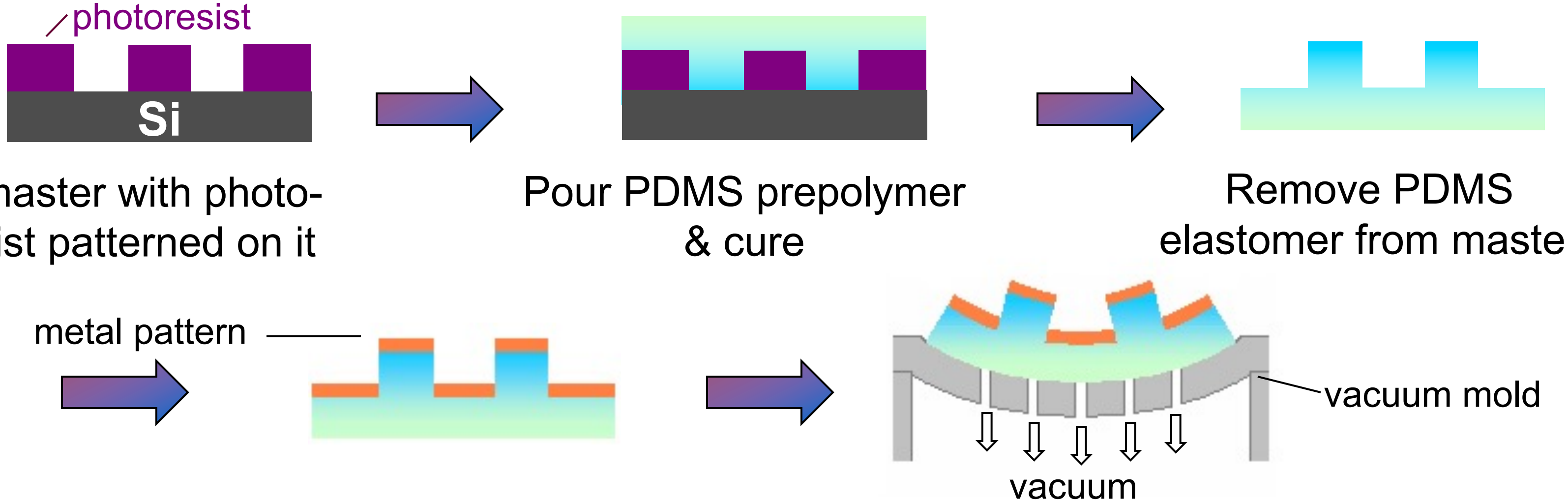


Surface roughness due to round soft stamp edges reproduced on transferred pattern

Kim & Forrest, *Adv Mater*. **15**, 541, 2003

3D Hemisphere Patterning by Stamping

Step 1) Formation of 3D stamps



Si master with photoresist patterned on it

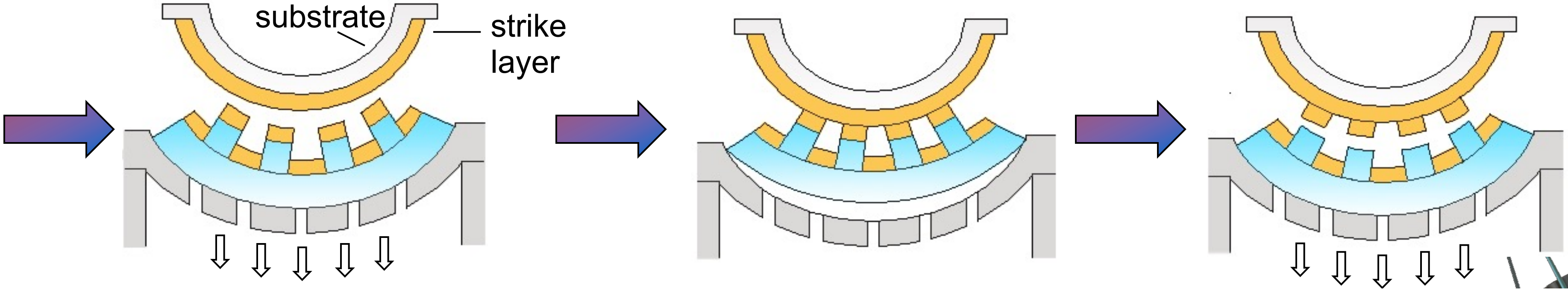
Pour PDMS prepolymer & cure

Remove PDMS elastomer from master

Evaporate metal on PDMS stamp

Deform PDMS + metal using hemispherical mold

Step 2) Transfer materials by stamping



Bring hemisphere to stamp

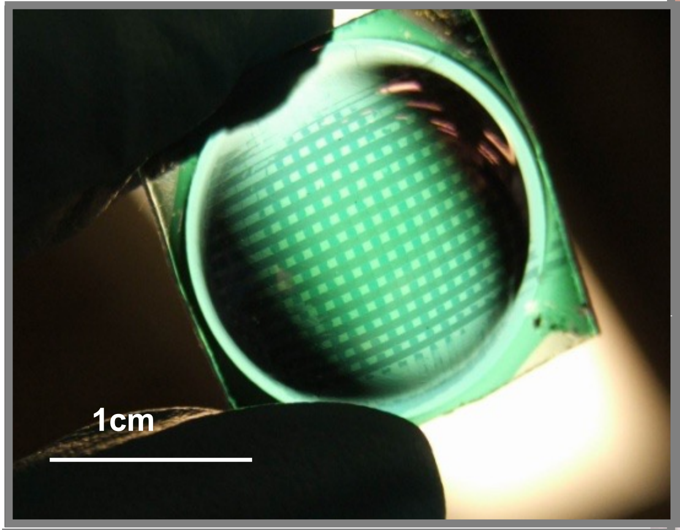
Release vacuum "snap the suspenders"

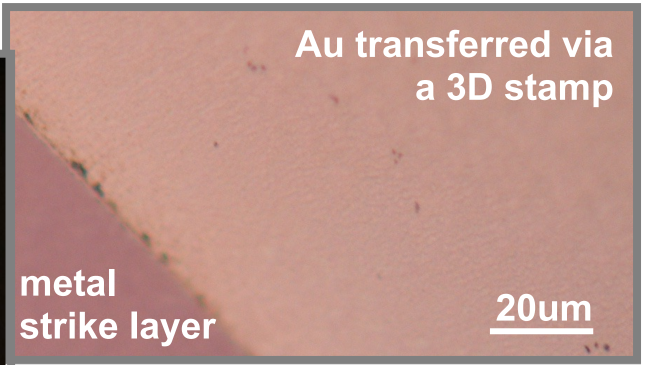
Withdraw stamp from substrate

tronics
Forrest

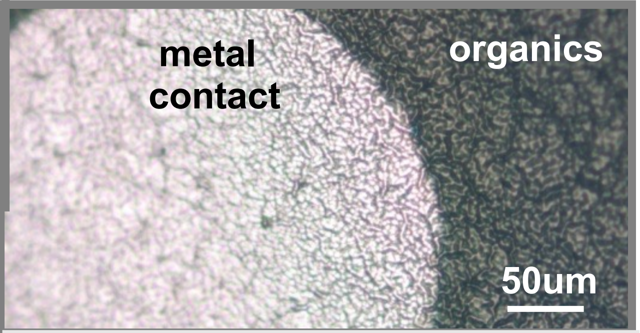
Organic Photodiode Array Contacts Stamped on Hemispherical Substrate

“eye size” imager



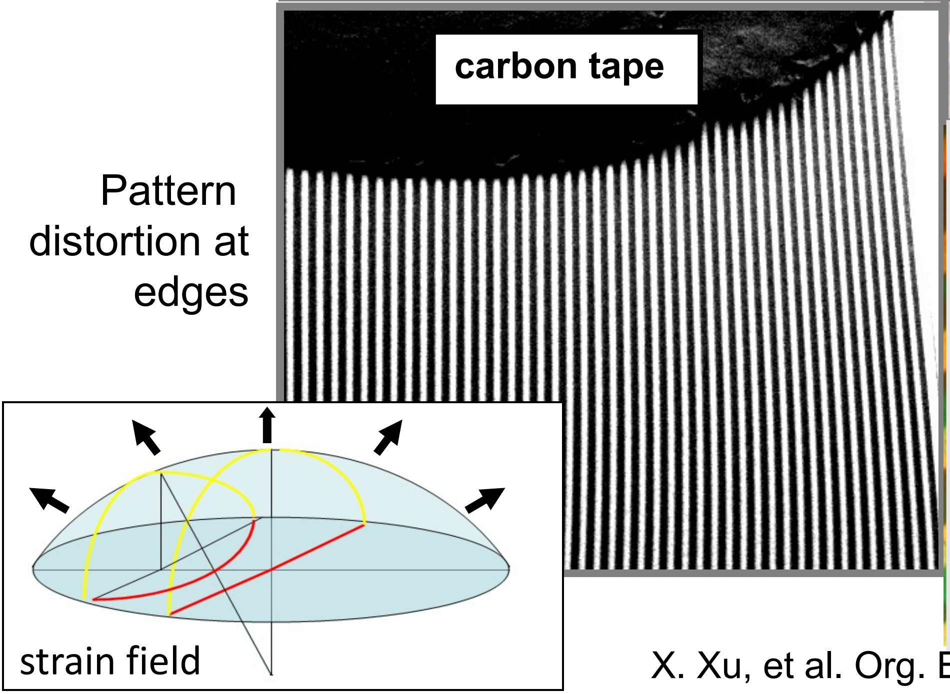


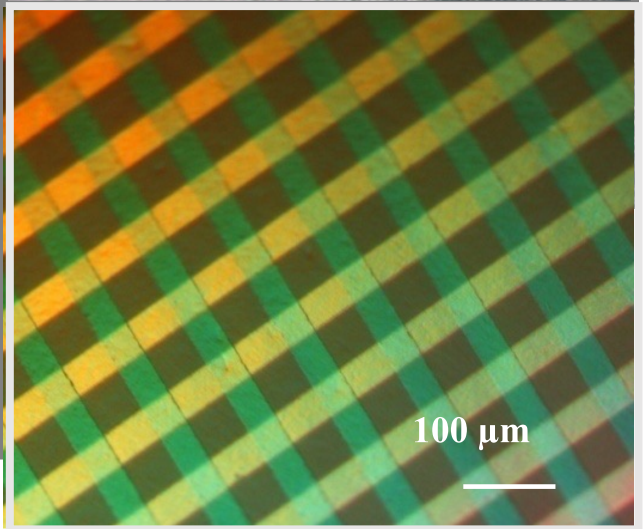
Defect-free Pattern transfer



Metal cracks if stretched on plastic

Pattern distortion at edges

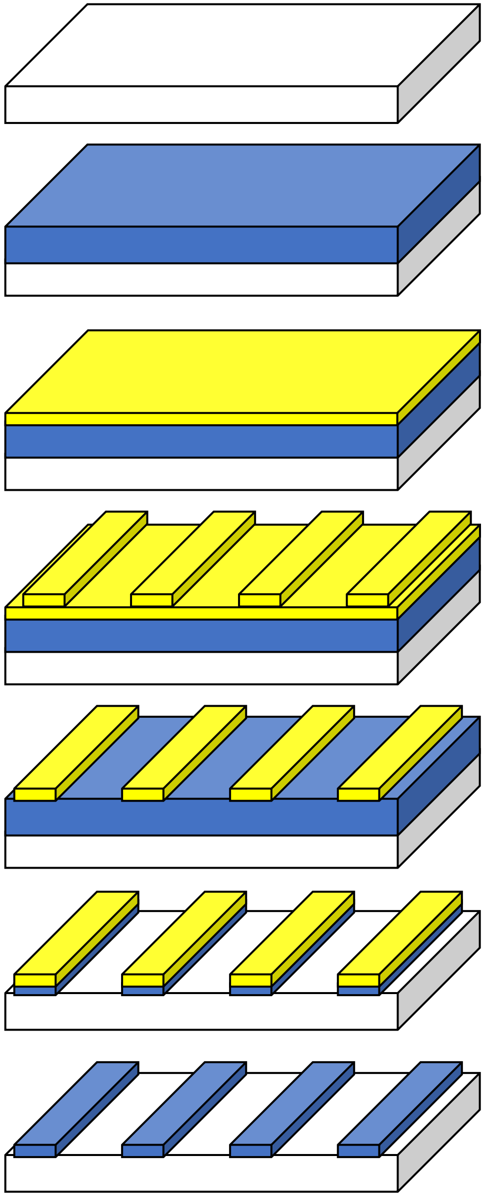




Completed array

X. Xu, et al. Org. Electron., 9, 1122 (2008)

Patterning Brittle ITO on Hemispherical Surface requires additional mask transfer steps



PETg Substrate

1. ITO Deposition (800A)

2. Metal Strike Layer (150A)

3. Transfer of Au (500A)
Pattern via PDMS Stamp

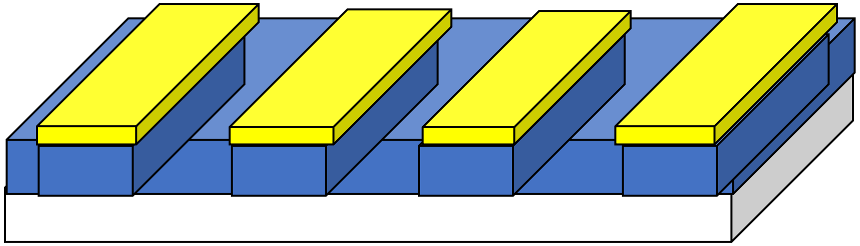
4. Etching of Strike Layer

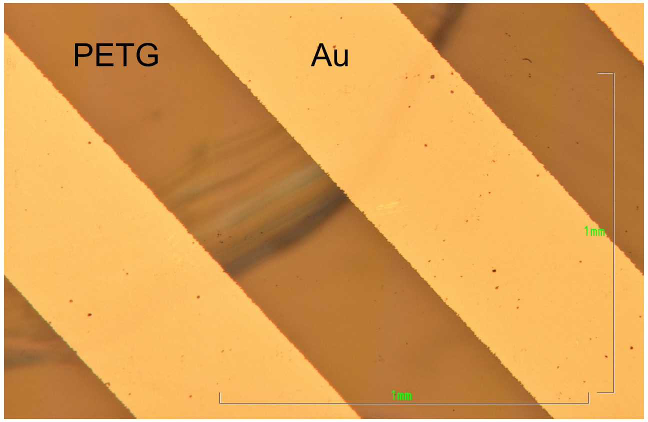
5. ITO Etching

   0.05M Oxalic Acid (100A/min)

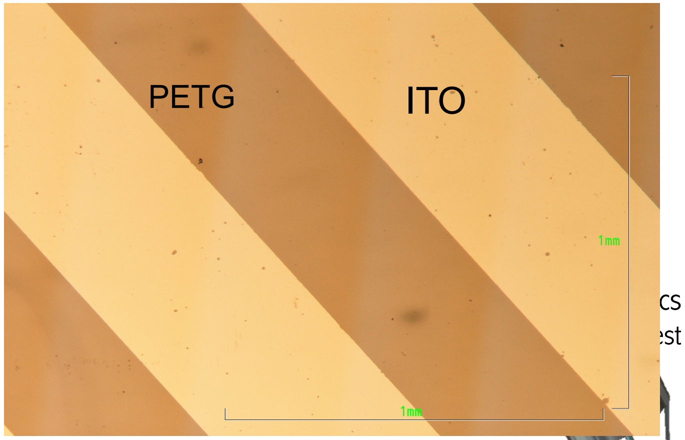
6. Au Removal

Patterned ITO



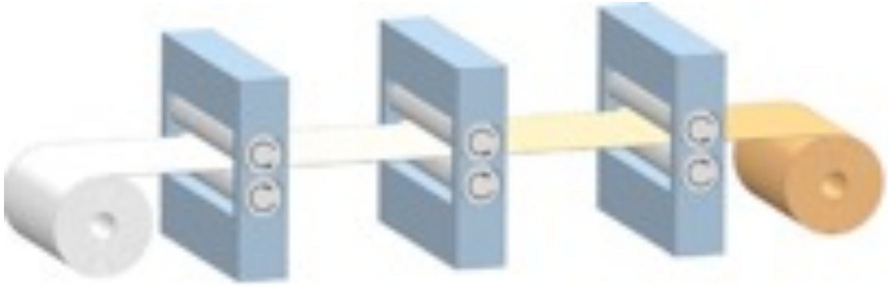


After Step 5



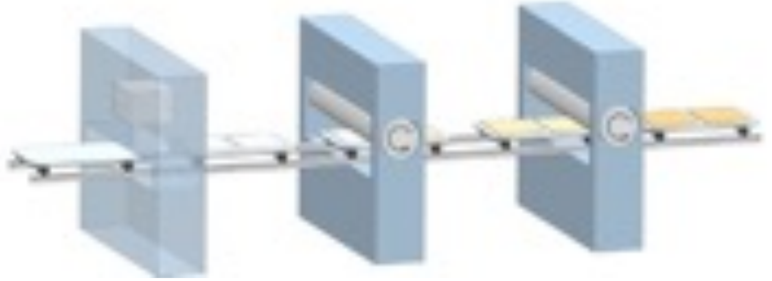
After Step 6

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

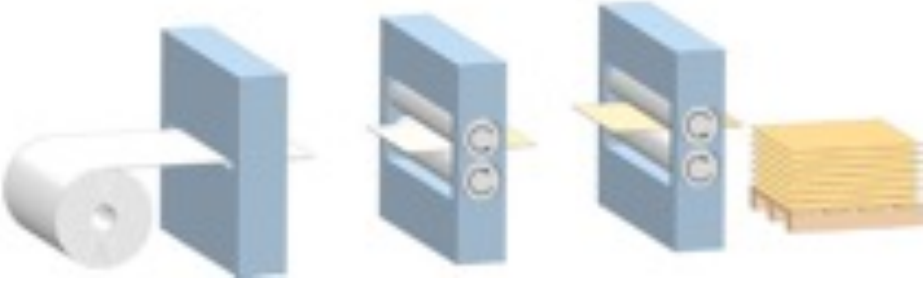


Roll-to-roll

Sheet-to-sheet



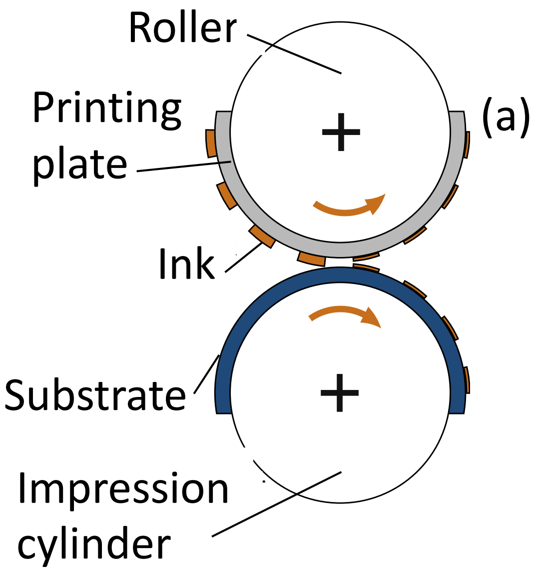
Sheet-to-carrier

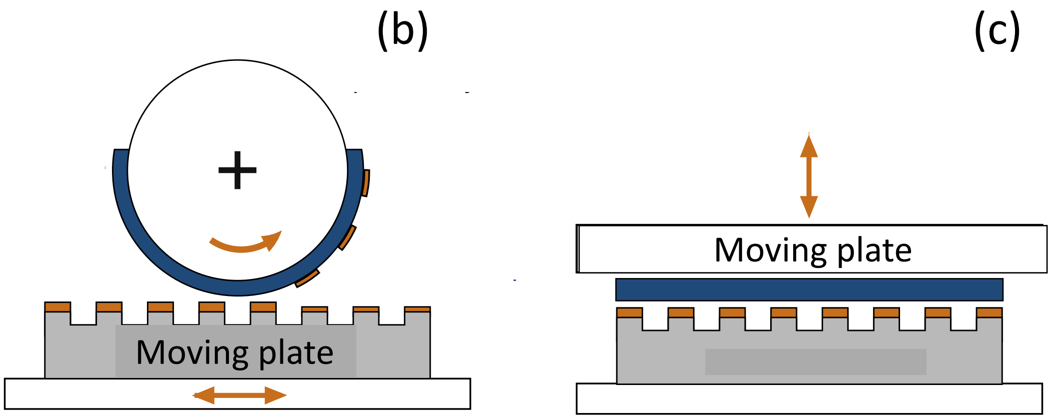


Roll-to-Sheet

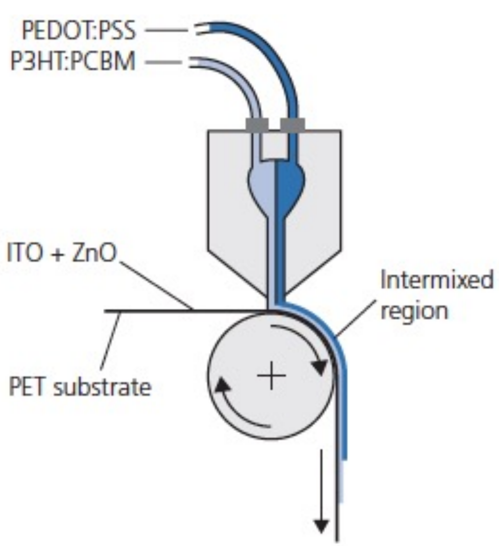
- Roll-based production requires flexible substrates
- Solution or vapor deposition of films possible
- Requires very clean (i.e. inert) gas environment

Continuous Printing Methods

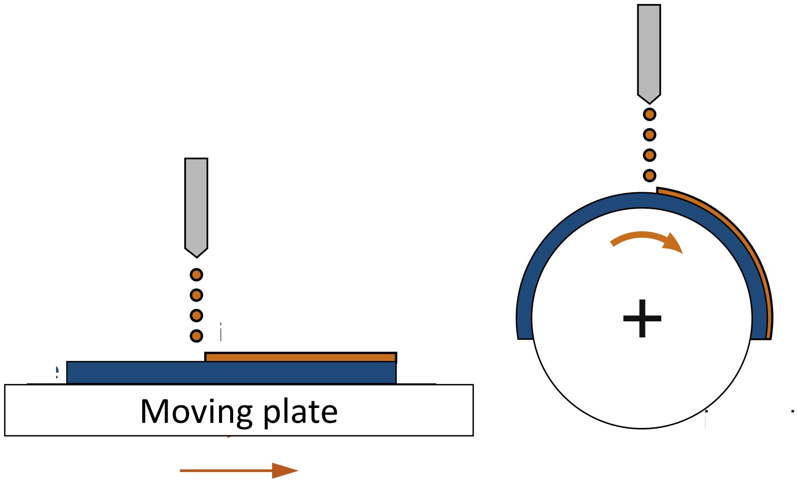




Embossing/stamping

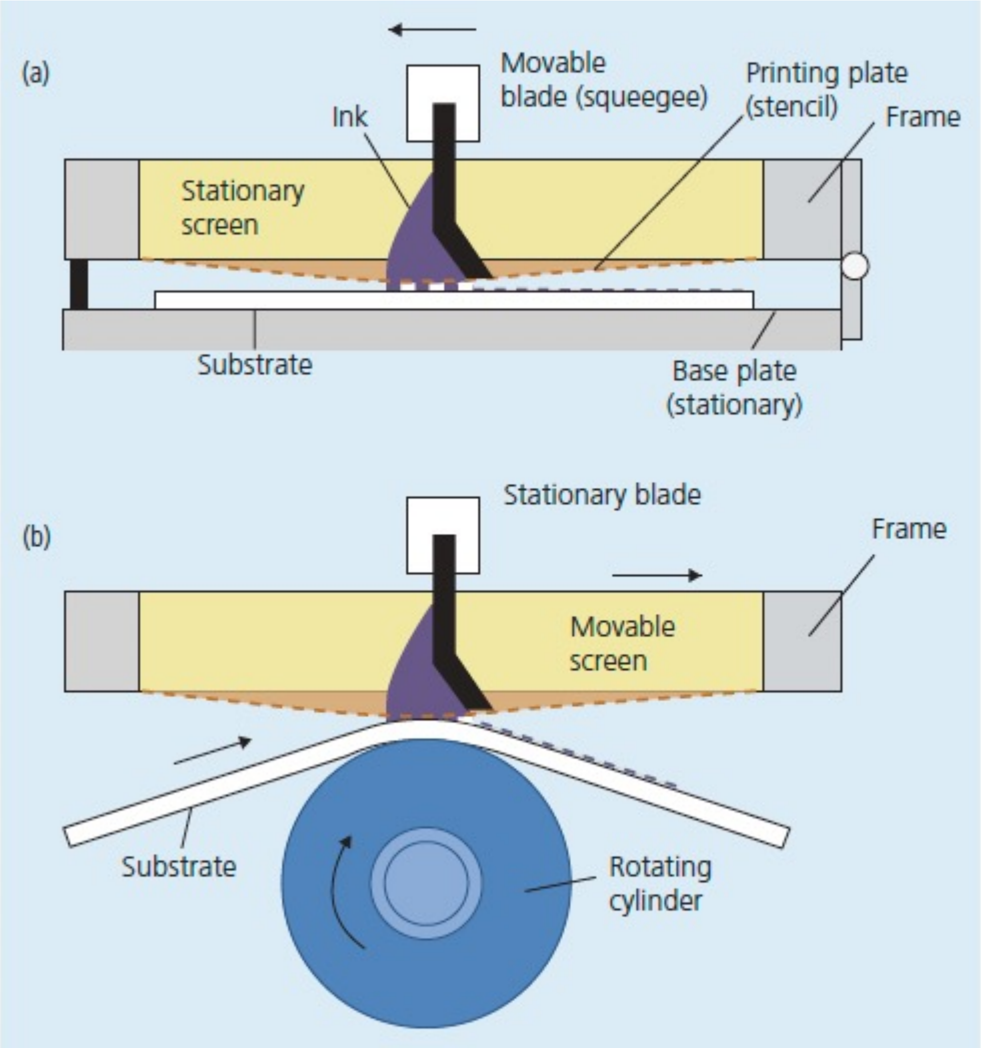


Slot dye coating



Inkjet printing

Low Resolution, Rapid Patterning

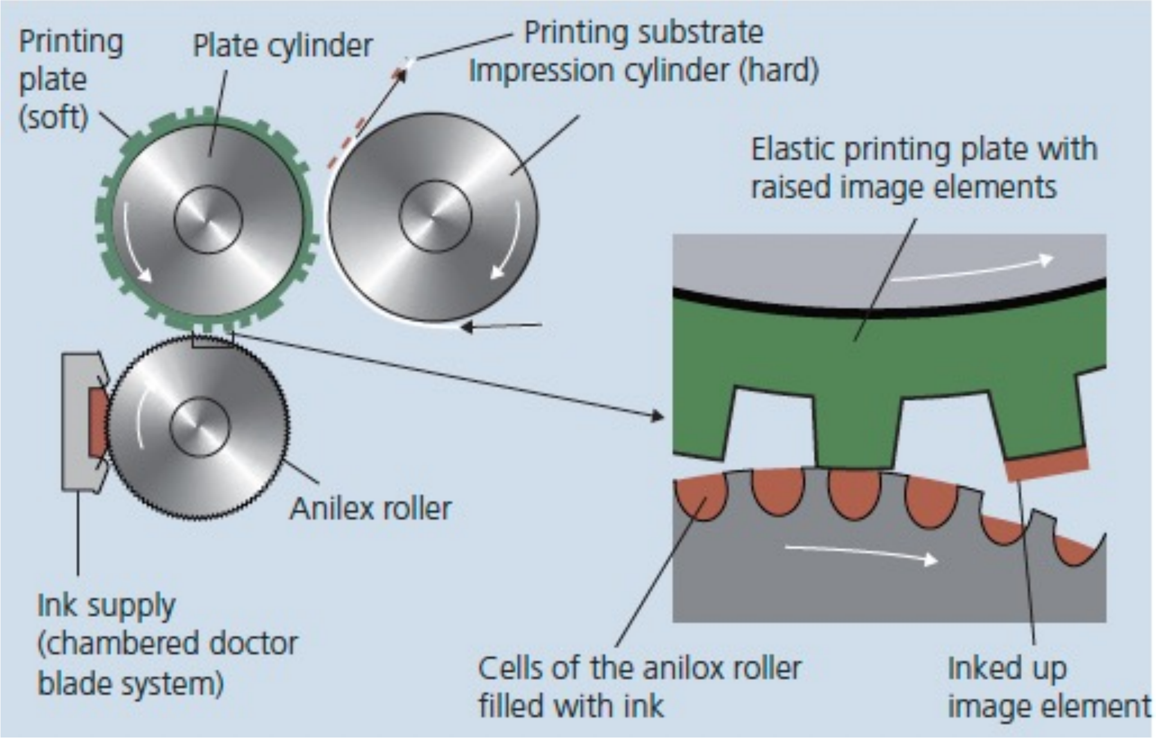


Kipphan *Handbook of Print Media*, Springer (2001)

Screen printing

- Pattern on fine-mesh screen (silk) allows penetration of “ink” on selective areas of substrate
- Resolution ~ 100 µm
- Speed ~ 2-3 m^2/s

Low Resolution, Rapid Patterning

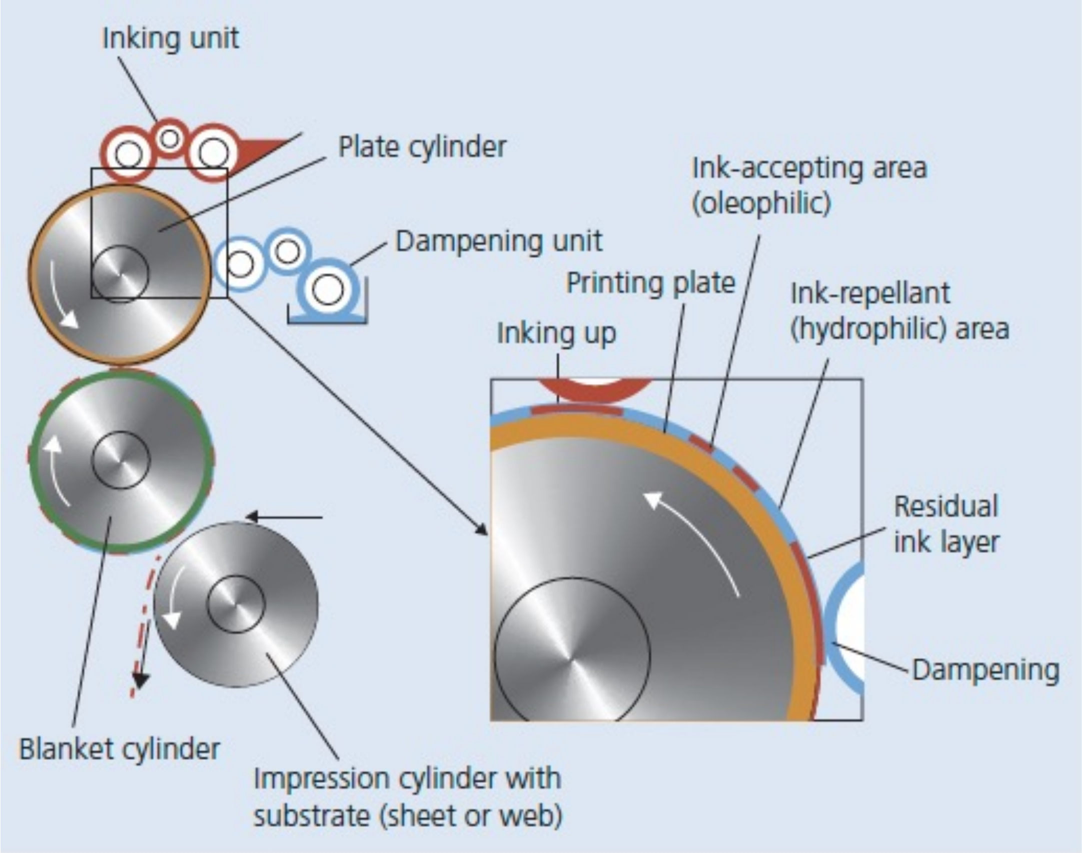


<u>Flexographic printing</u>

- Wells etched into anilox roller
- Ink spread onto roller from a supply chamber
- Roller transfers ink by contact with raised regions of substrate
- Resolution ~ 100 µm
- Speed ~ 10 m^2/s

Kipphan *Handbook of Print Media*, Springer (2001)

Moderate Resolution, Rapid Patterning

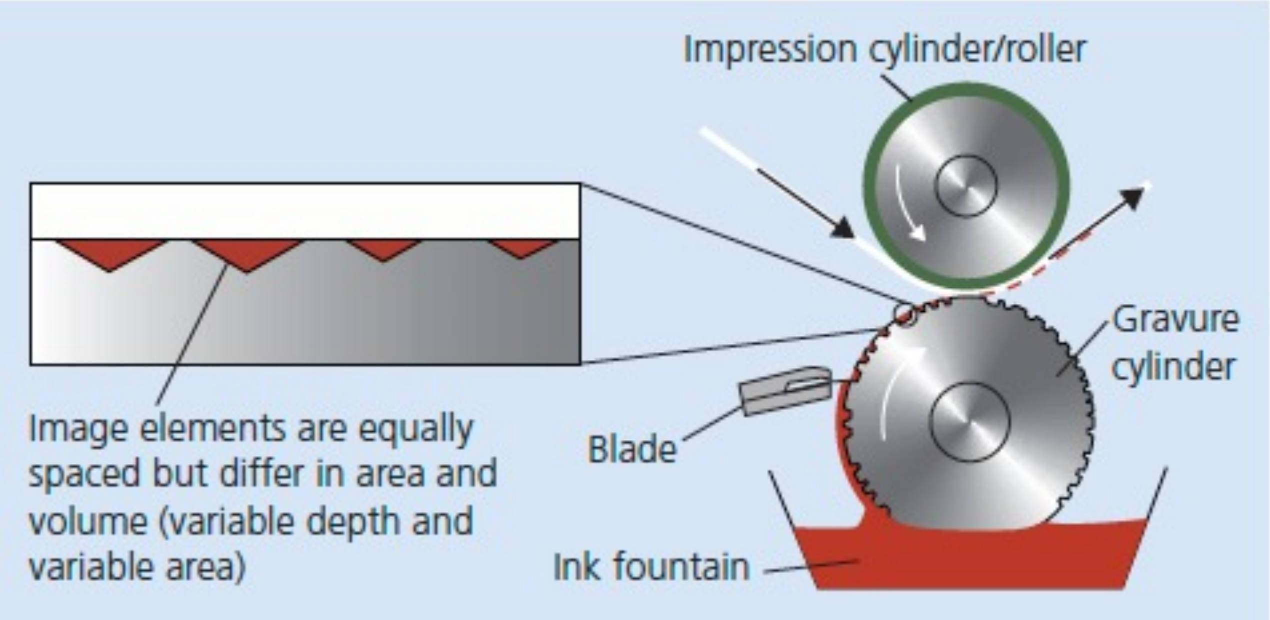


Offset printing

- Pattern etched into roller with selective oliophilic and hydrophilic regions
- Ink spread onto roller from a second roller to fill wells
- Roller transfers ink by contact with substrate
- Resolution ~ 10-50 µm
- Speed ~ 5-30 m^2/s

Kipphan *Handbook of Print Media*, Springer (2001)

High Resolution, Rapid Patterning

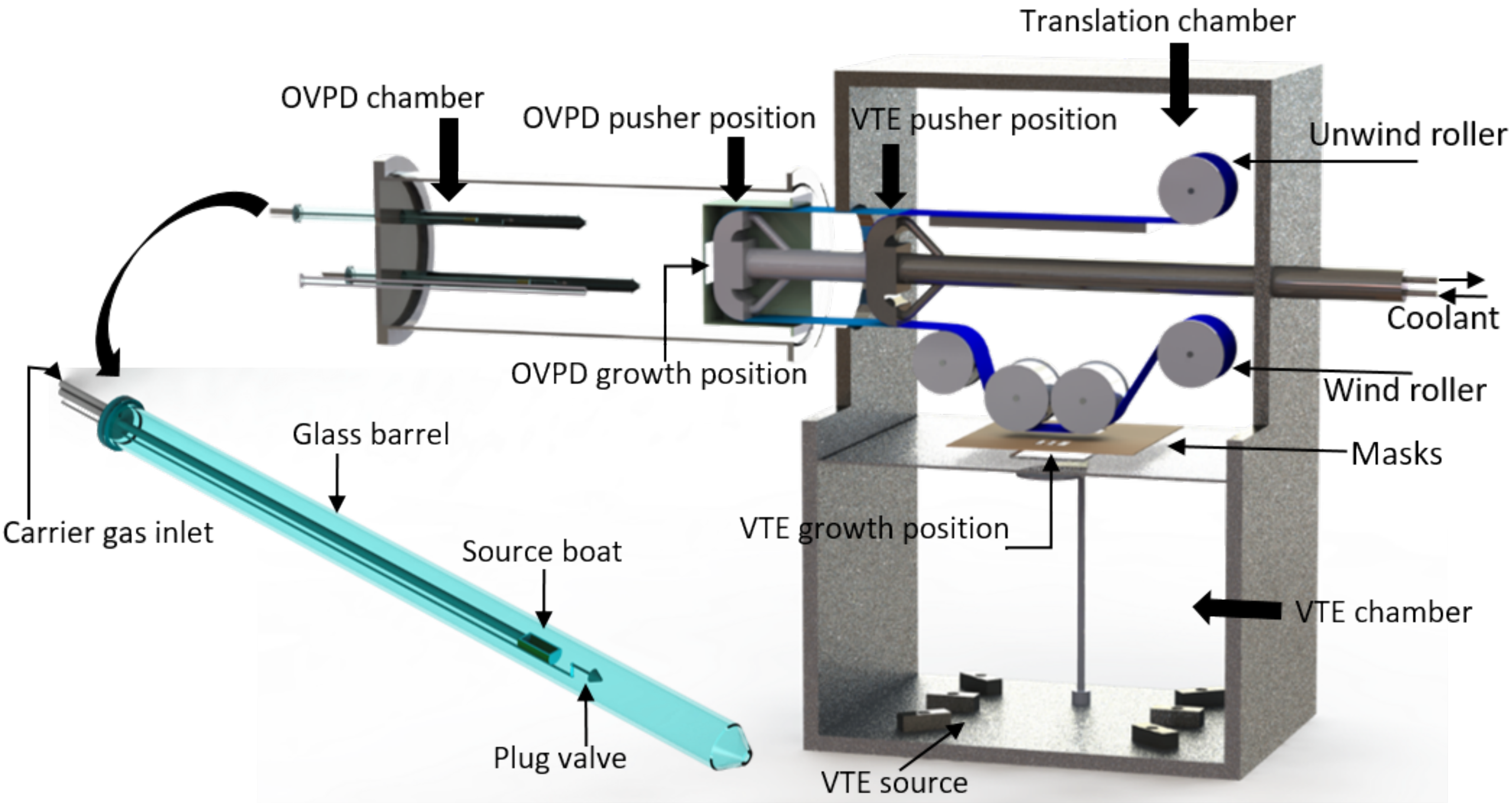


Gravure printing

- Wells engraved into gravure cylinder
- Ink picked up for a trough (ink fountain)
- Excess ink removed using doctor blade
- Substrate pressed between gravure and soft impression cylinder transfers ink
- Resolution ~ 1 µm
- Speed ~ 50 m^2/s

Kipphan *Handbook of Print Media*, Springer (2001)

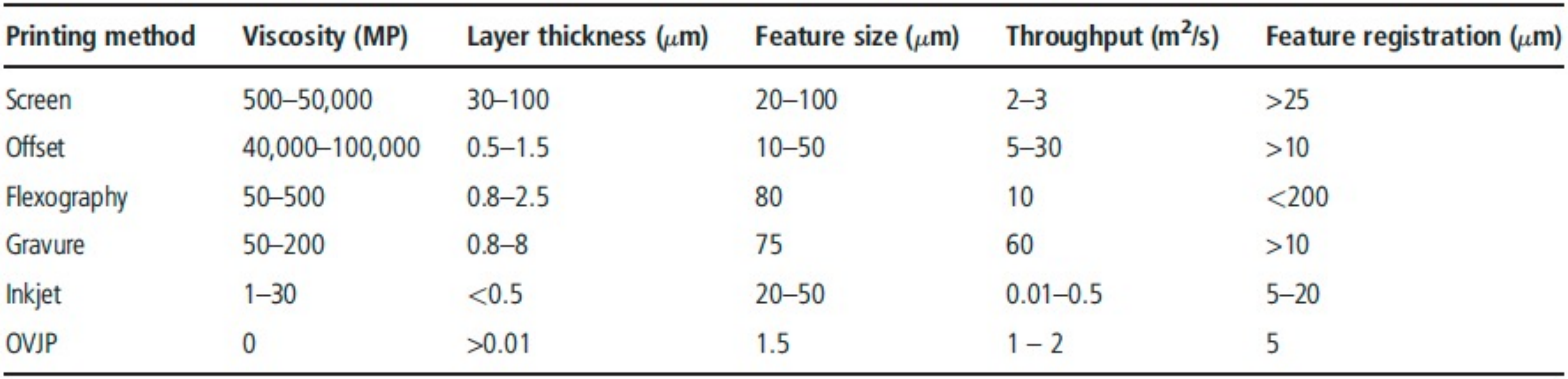
Combination VTE and OVPD Deposition in R2R Environment



R2R can be done in vacuum as well as with solution
System used for organic solar cells and OLEDs

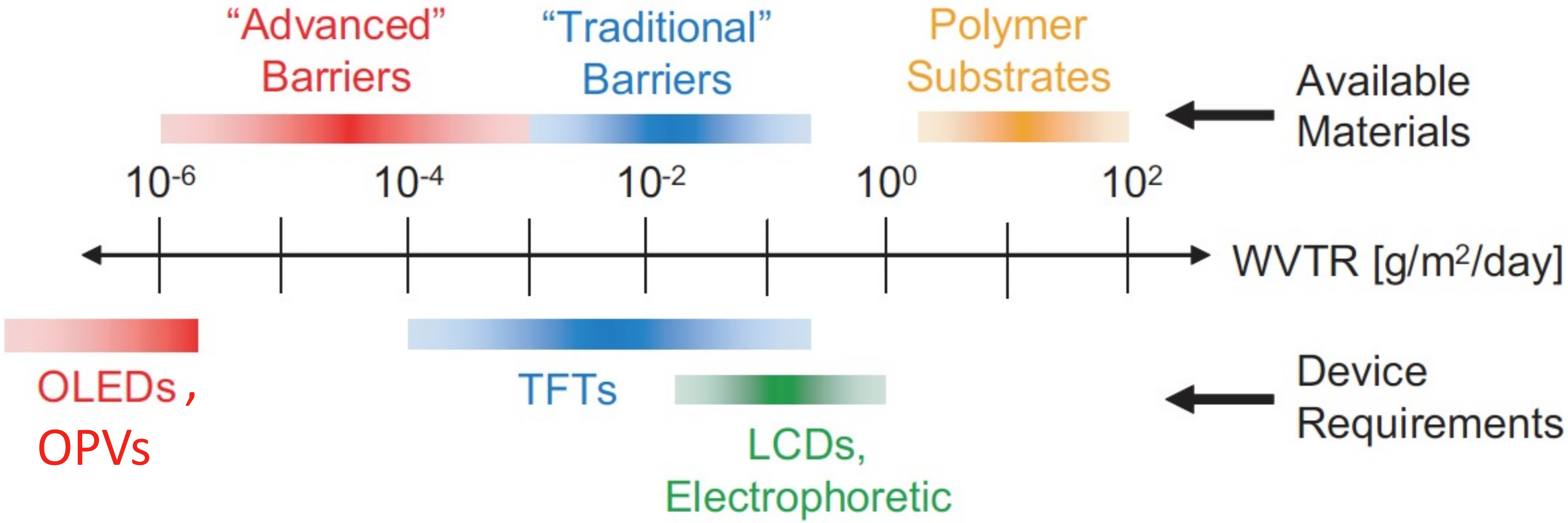
Qu & Forrest, Appl. Phys. Lett., 113, 053302 (2018)

Comparison of R2R Deposition/Printing Methods



Printing method	Viscosity (MP)	Layer thickness (μm)	Feature size (μm)	Throughput (m^2/s)	Feature registration (μm)
Screen	500–50,000	30–100	20–100	2–3	>25
Offset	40,000–100,000	0.5–1.5	10–50	5–30	>10
Flexography	50–500	0.8–2.5	80	10	<200
Gravure	50–200	0.8–8	75	60	>10
Inkjet	1–30	<0.5	20–50	0.01–0.5	5–20
OVJP	0	>0.01	1.5	1 – 2	5

Packaging: Keeping the Device Safe from its Environment



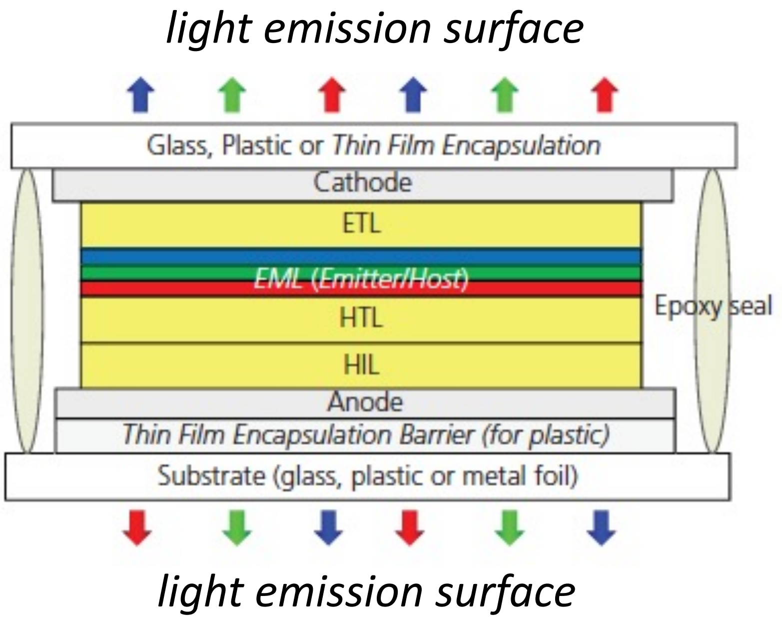
Water vapor transfer rate determines package quality and use

Organic Electronics
Stephen R. Forrest

Lewis, Mater. Today, 9, 38 (2006)

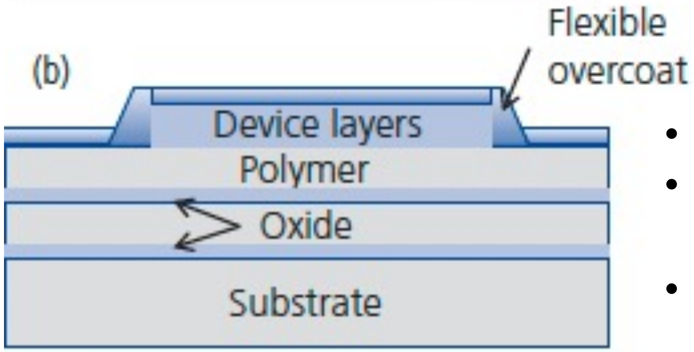
The Best Package Substrate and Lid are Impermeable to Moisture and Oxygen

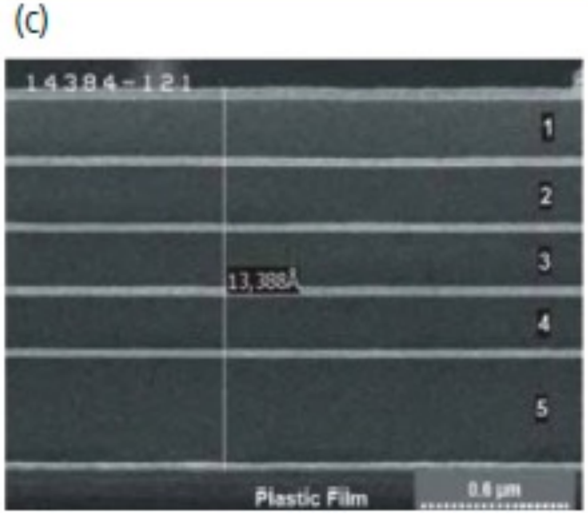
- Glass, metal ideal but they are not flexible
- Photonic devices require at least one transparent package surface



Common OLED epoxy sealed packaging scheme

Multlayer Inorganic/polymer barrier layer substrates provide flexibility





Lewis, Mater. Today, 9, 38 (2006)

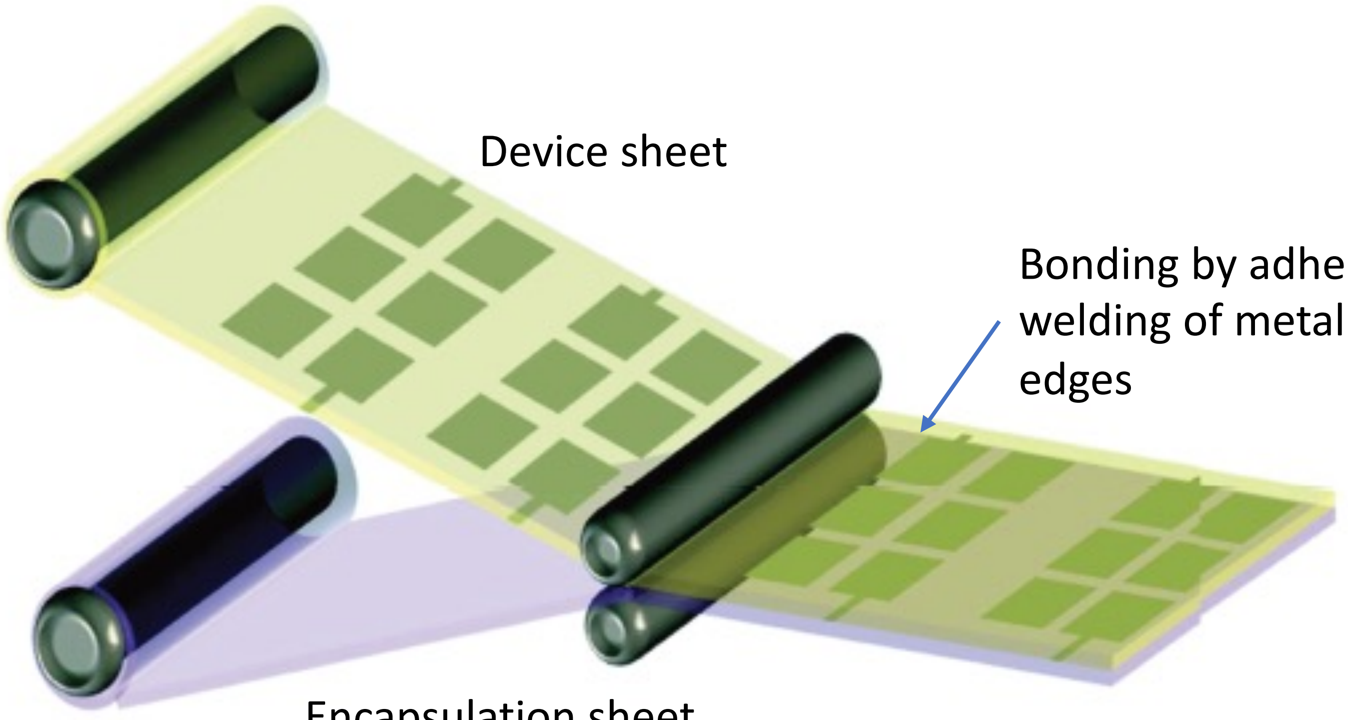
- Plastic alone is very permeable to oxygen, water
- Layering a thin inorganic glassy layer between polymer to form laminate
- Can delay ingress of contaminants into device cavity in package
  - ➢ Small defects in inorganic layers not aligned, so molecules diffuse in long, circuitous paths to reach device layers
  - ➢ Glassy layers deposited using plasma, atomic layer dep. (ALD)
- Laminate layer thicknesses 10s – 100s nm
- Pairs of polymer/glass called dyads

No. of dyads	WVTR (g/m^2/day)
0	4.7
1	0.07
2	<0.005
3	<0.005
4	<0.005
5	~10^{-6}

Dyad: 0.3 µm PMMA/37 nm AlO_x

Graff et al. J. Appl. Phys. 96, 1849 (2004)

Encapsulation Can Be Adapted to R2R Manufacturing



Device sheet

Bonding by adhesive or cold-welding of metal stripes at edges

Encapsulation sheet

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

Organic Electronics: Where we've been (and what's next)

You now have learned about

- structure
- growth and layering
- optical properties
- electronic properties of organic materials

These are all the basics needed to fully understand and analyze all OE devices and phenomena