Deposition and Patterning Techniques for Organic Materials

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Organic Electronics: principles, devices and applications
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Overview

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

**PATTERNING**
- Screen printing
- Soft Lithography
- NIL/Embossing
- Physical Delamination
- Photopatterning
- Printing
  - M. Caironi
- Shadow masking
- Vapor Jet Printing

**Organic materials**

- Soluble
- Non-soluble
Choice of the deposition technique

**Uniformity**

**Waste of material**

**Thickness**

- Ex. solar cells

**Nanomorphology**

- (molecules relative arrangement in the solid state)
  - solvent evaporation
  - deposition rate
  - post-processing

**Material**

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

**Substrate**

- shape
- surface features: roughness, wettability
- dimension
Solution processable materials: deposition techniques

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

Dropping of solution and spontaneous solvent evaporation

- Very simple
- Low waste of material
- Limitations in large area coverage
- Thickness hard to control
- Poor uniformity

Film thickness $\propto$ solution concentration

- 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

- Good uniformity
- Reproducibility
- Good control on thickness

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

Film thickness: dependent on many controllable parameters $d\omega/dt$, $\omega$, $t$, solution viscosity, ...

down of 10nm or less


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


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Tricks...

- Solvent evaporation time
- Additives

P3HT-based TFTs

POST-PROCESSING
- Thermal annealing
- Vapor annealing

180ºC

larger crystallinity

<table>
<thead>
<tr>
<th>bp (ºC)</th>
<th>mobility (cm²/(V·s))</th>
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<tbody>
<tr>
<td>chloroform</td>
<td>60.5–61.5</td>
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<tr>
<td>thiophene</td>
<td>84</td>
</tr>
<tr>
<td>xylene</td>
<td>138–139</td>
</tr>
<tr>
<td>CHB</td>
<td>239–240</td>
</tr>
<tr>
<td>TCB</td>
<td>218–219</td>
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</table>
Spin Coating II

Film thickness:

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

- \( c_0 \) solids concentration (by volume)
- \( \mu_0 \) viscosity
- \( \rho_0 \) 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
- Applicable to any kind of polymer (small molecule?)
- Doesn’t affect polymer intrinsic properties
- Does’t affect polymer intrinsic properties

- Polymer intrinsic properties are affected
- Less “deterministic”
- Film properties are affected


J. Lì et al., J. Appl. Phys., 100, 034506, 2006
Doctor Blading I

Spreading through a moving blade onto a stationary substrate

Film thickness:

Film thickness: 20 – 200 nm

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


Doctor Blading II

Spreading through a moving blade onto a stationary substrate

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

**Example:** bladed organic solar cells (P3HT/PCBM)

<table>
<thead>
<tr>
<th>Method</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF</th>
<th>PCE [%]</th>
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<tbody>
<tr>
<td>Spin-coated</td>
<td>0.58</td>
<td>8.91</td>
<td>0.62</td>
<td>3.16</td>
</tr>
<tr>
<td>Bladed</td>
<td>0.59</td>
<td>9.40</td>
<td>0.64</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Micrometric precision of blade regulation

Not suitable for very thin films (nm)

Not suitable for very thin films (nm)

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

\[
H = \frac{0.94(\mu v)^{2/3}}{\gamma^{1/6}(\rho g)^{1/2}}
\]

- \( \mu \) = fluid viscosity
- \( v \) = withdrawal speed
- \( \rho \) = fluid density
- \( g \) = gravitational acceleration
- \( \gamma \) = surface tension (liquid-air)

- ✔ Quite good uniformity
- ✔ Very thin layers
- ✔ Large area coverage
- ✔ Easy process
- ✗ Waste of material
- ✗ Time consuming
- ✗ Double side coverage
- ✗ Very thin layers

**Example:** TFT based on P3HT in xylene → single monolayer ≈ 2 nm thick with \( \pi-\pi \) stacking oriented in favorable transport direction

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 $\Pi$, area $A$, and density
Extreme thickness control: Langmuir-Blodgett II

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

Once $\Pi_c$ 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

- Movable barrier
- Hydrophilic substrate
- Wilhelmy plate: measures \( \Pi \)
- Langmuir-Schaefer: horizontal deposition

- Feedback
- Head-to-tail
- Tail-to-tail
- Head-to-head
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 amphiphilic 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)

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

**Example:** Organic light sensor directly deposited onto a Plastic Optical Fiber  
Binda et al., Adv Mater. 2013, 25, 4335–4339

**Example:** Hybrid CMOS-imager with sprayed photoactive layer  
D. Baierl et al., Nat. Comm., 2012

<table>
<thead>
<tr>
<th>sample (PEDOT:PSS–P3HT:PCBM)</th>
<th>PCE [%]</th>
<th>JSC [mA cm^-2]</th>
<th>FF [%]</th>
<th>VOC [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>spin–spin</td>
<td>3.62</td>
<td>9.37</td>
<td>65</td>
<td>595</td>
</tr>
<tr>
<td>spray–spin</td>
<td>3.65</td>
<td>9.08</td>
<td>68</td>
<td>587</td>
</tr>
<tr>
<td>spin–spray</td>
<td>3.53</td>
<td>8.84</td>
<td>69</td>
<td>575</td>
</tr>
<tr>
<td>spray–spray</td>
<td>3.52</td>
<td>8.79</td>
<td>70</td>
<td>573</td>
</tr>
</tbody>
</table>
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.


- Simple
- Limited resolution: $\approx 50$-$100$ $\mu$m
- Waste of material
- 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)

1. Si-wafer with 300 nm SiO₂
2. ODTS coating
3. Metal mask
4. UV/Ozone exposure
5. PEDOT/PSS from aqueous suspension
6. Doctor-blade coating with PEDOT:PSS drops

PEDOT/PSS: conductive polymer
UV-light damages the ODTs film

*Journal of Polymer Science B: Polymer Physics, 49, 1590–1596, 2011*
Shadow masking + selective wettability
Photopatterning

Same principles and equipment 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

Soft Lithography

Earliest motivation: overcome cost of photolithography for sub $\mu$m 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


**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)

Micro Transfer Molding (μTM)

Micromolding in Capillaries (MIMIC)


(film grown by LBL onto the mold)


**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.

Nano Imprint Lithography/Embossing I

Similar to SL but based on **hard** mold/stamp. It allows obtaining smaller features ($\approx 10$ nm)

$T > T_g$

$T_g$: polymer glass phase transition

Hot Embossing

Room Temperature NIL
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)

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

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

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**

- 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

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

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

Pentacene on SiO$_2$

Organic Vapor Phase Deposition I

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

Hot inert carrier gas (Ar, N₂) transport source material to the cooled substrate where condensation occurs.

Heated walls \(\rightarrow\) vapor does not condense.
**Organic Vapor Phase Deposition II**

**Example:** TFT based on Pentacene

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

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

\[ p_C, T_C \]
\[ p_H, T_H \]

Effusion cell (Knudsen)

Quartz microbalance

Extremely slow deposition rate → epitaxial growth

Single crystal

"Pin hole"

Shutter
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
Compression molding

Radial molecular flow during compression molding

Material anisotropy  X-ray diffraction

- TFT performances comparable with optimized solution processes devices

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

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 move relatively to the print-head for patterning

For high resolution (~20μm):

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

✓ No solvent
✓ No shadow mask
Thickness: 30 nm