Lecture 2:

Chapter 1. Organic molecular beam deposition

Ref.
1. F. Schreiber, Chapter 1. organic molecular beam deposition: Growth studies beyond the 1st monolayer
2. Lecture notes by John A. Venables: Lecture notes on Surfaces and Thin Films (http://venables.asu.edu/grad/lectures.html)
3. S. R. Forrest, Ultrathin Organic Films Grown by Organic Molecular Beam Deposition and Related Techniques, Chem. Rev. 1997, 97, 1793-1896

2009. 3. 5.

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General Issues

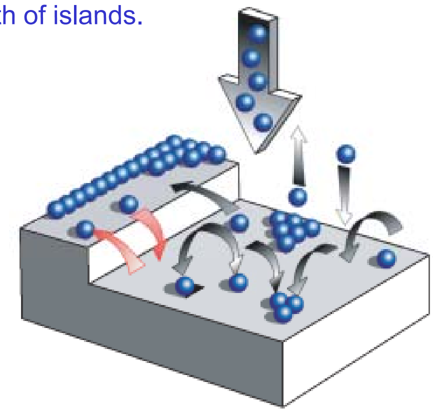
1. Definition of interfaces (degree of interdiffusion and roughness)
   (a) organic- organic (e.g. in OLED)
   (b) organic-metal (e.g. for electrical contacts)
   (c) organic-insulator (e.g. in OTFT)

2. The crystal structure
   (a) Which structure is present? (Note that polymorphism is very common in organics
   (b) Are different structures coexisting?
   (c) Orientation of the structure (epitaxy)
   (d) Is the structure strained (epitaxy)?

3. Crystalline quality/defect structure
   (a) Mosaicity
   (b) Homogeneity within a given film (density of domain boundaries etc.)
   (c) Density of defects

Schematic of processes relevant in thin film growth

- adsorption (as a result of a certain impingement rate)
- (re-)desorption,
- intra-layer diffusion (on a terrace)
- interlayer diffusion (across steps)
- nucleation and growth of islands.



F. Schreiber, phys. stat. sol. (a) 201, No. 6, 1037–1054 (2004)

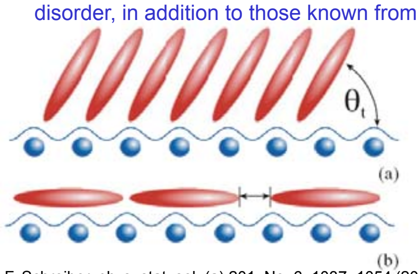
Issues specific to organic thin film growth

1. Organic molecules are 'extended objects' and thus have internal degrees of freedom (vibrational, conformational, and orientational). This is probably the most fundamental difference between growth of atomic and growth of organic systems.

2. The size of the molecules and the associated unit cells are greater than that of typical (inorganic) substrates.

(a) The effective lateral variation of the potential is smeared out (i.e., averaged over the size of the molecule), making the effective corrugation of the substrate as experienced by the molecule generally weaker than for atomic adsorbates. → More translational domains.

(b) Organics frequently crystallize in low-symmetry structures, which again can lead to multiple domains (not only translational, but also orientational domains). Importantly, both are a source of disorder, in addition to those known from inorganic systems (e.g., vacancies).



(a) *Orientational degrees of freedom*, potentially leading to orientational domains (additional source of disorder). They can also give rise to orientational transitions during growth.

(b) Molecules larger than the unit cells of (inorganic) substrates, thus leading to translational domains. Generally, this can also lead to a smearing-out of the corrugation of the substrate potential experienced by the adsorbate.

F. Schreiber, phys. stat. sol. (a) 201, No. 6, 1037–1054 (2004)

Issues specific to organic thin film growth

3. The interaction potential (molecule-molecule and molecule-substrate) is generally different from the case of atomic adsorbates, and van-der-Waals interactions are more important.

(a) The response to strain is generally different. Potentially, **more strain can be accommodated**. The different ('softer') interactions with the substrate and the corrugation of the potential have also been discussed in terms of **'van-der-Waals epitaxy'** and **'quasi-epitaxy'.**

(b) The importance of van-der-Waals interactions implies that the **relevant temperature scales (for evaporation from a crucible and also for diffusion on the substrate) are usually lower**. However, the total interaction energy of a molecule (integrated over its 'contact area' with a surface) can be substantial and comparable to that of strongly interacting (chemisorbing) atomic adsorbates.

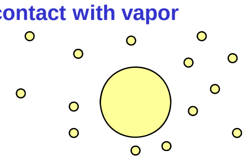
(c) Since we are concerned with closed-shell molecules and van-der-Waals-type crystals, there are **no dangling bonds at the organic surface**, and thus the surface energies are usually weaker than for inorganic substrates.

(d) If the surface of the substrate is 'strongly interacting', diffusion is limited and thus the evolution of well-ordered films is hampered. In the extreme case of a 'very reactive' surface (e.g., with dangling bonds available), the molecules may even dissociate upon adsorption.

F. Schreiber, phys. stat. sol. (a) 201, No. 6, 1037–1054 (2004)

Nucleation and Growth

Droplet in contact with vapor



Surface tension
= Free Energy per unit area of interface

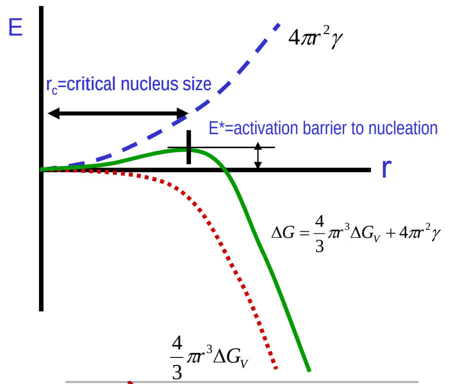
$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

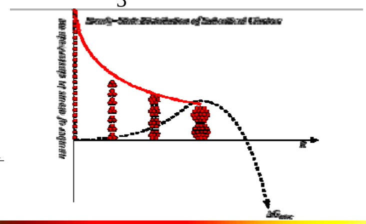
Free energy change per unit volume

Free energy change per unit area of surface

$$\frac{\partial \Delta G}{\partial r} = 0 \rightarrow r_{critical} = \frac{-2\gamma}{\Delta G_V}$$

$$\Delta G^*_{critical} = \frac{16\pi\gamma^3}{3(\Delta G_V)^2} \qquad \frac{dN}{dt} = \omega n_s A^* \exp\frac{-\Delta G^*_{critical}}{kT}$$

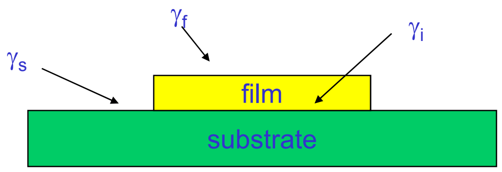




Film growth on the substrate

γ: the surface energies

The relative contributions of the free substrate surface, γ_s, the film surface, γ_f , and the film-substrate interface, γ_i are related to the different growth modes:



$$\Delta G_{\text{interface}} \propto \gamma_s - \gamma_f + \gamma_i$$

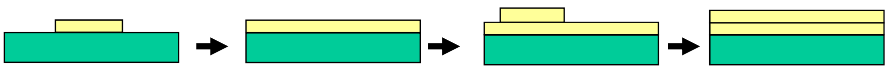
3 growth modes

1) Frank-Van der Merwe Growth: $\gamma_f > \gamma_s + \gamma_i$

The atoms of the deposit material are more strongly attracted to the substrate than they are to themselves.

Growing layer reduces surface energy; "wets" the surface completely

→ **smooth, layer-by-layer growth**



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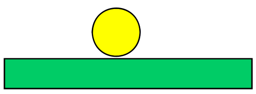
2) Vollmer-Weber Growth ("V-W"): $\gamma_f < \gamma_s + \gamma_i$

Growing layer wants to minimize interface energy and its own surface energy

→**islands starting at the first monolayer:**

The deposit atoms are more strongly bound to each other than they are to the substrate.



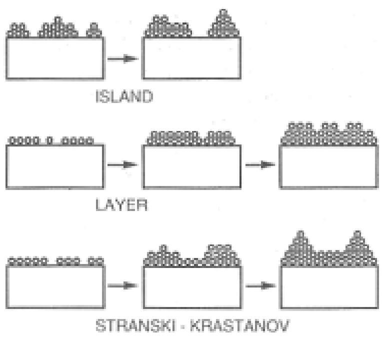
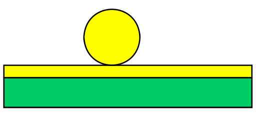


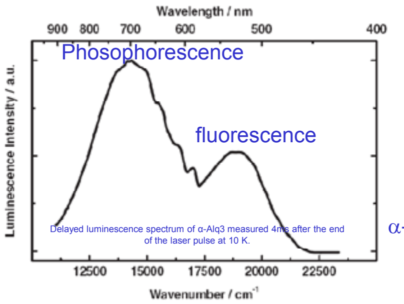
Figure Basic modes of thin-film growth.

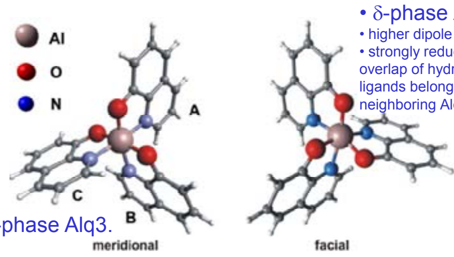
3) Stranski-Krastanov ("SK") Growth

Balance of forces changes during growth:
Typically, first layer wets surface but subsequent layers do not.
Change in balance of forces is often due to strain in the growing layer, typically due to a mismatch in lattice constants between substrate and film.



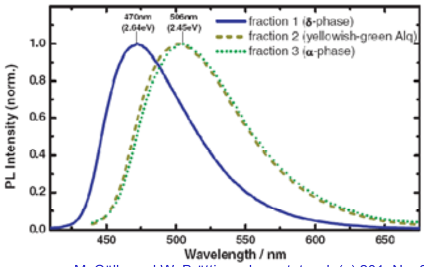
Purification of Alq3 and some optical properties

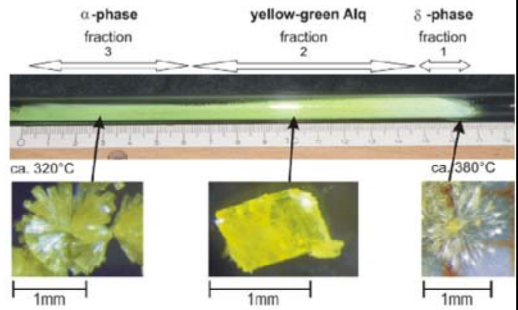




α-phase Alq3.

- δ-phase Alq3.
  - higher dipole moment
  - strongly reduced π-orbital overlap of hydroxyquinoline ligands belonging to neighboring Alq3 molecules





M. Cölle and W. Brütting, phys. stat. sol. (a) 201, No. 6, 1095–1115 (2004).

Purification and Crystal Growth

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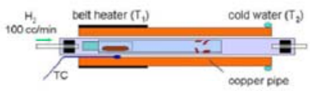
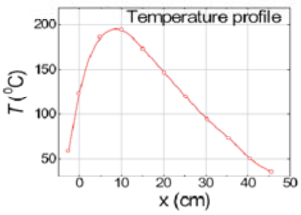
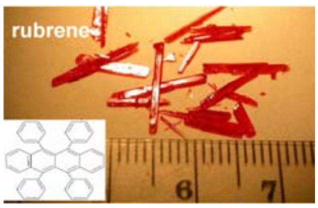
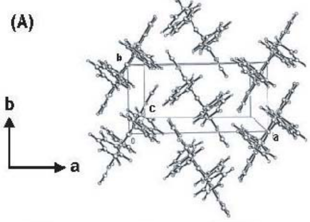
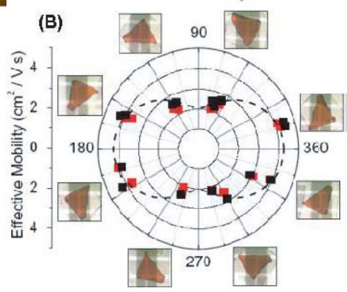




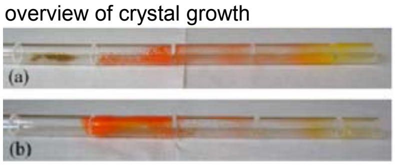
The angular dependence of the mobility for a rubrene crystal, measured at room temperature.







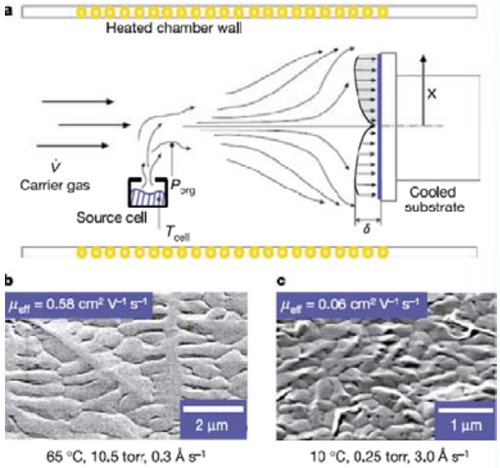
Schematic overview of crystal growth

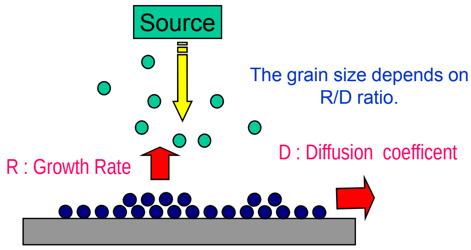


(a) Result after first regrowth of as-purchased organic material..
(b) At the end of the second regrowth no dark residue is present at the position of the source material, which demonstrate the purifying effect of the growth process.

R. W. I. de Boer, M. E. Gershenson, A. F. Morpurgo, and V. Podzorov, phys. stat. sol. (a) 201, No. 6, 1302–1331 (2004).

Pentacene Thin Film

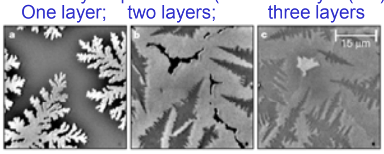




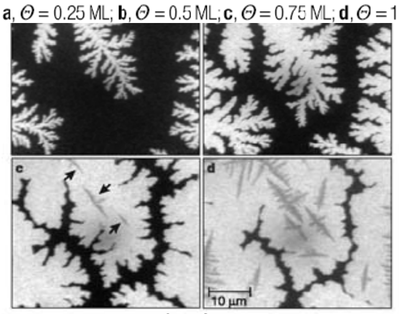
S. R. Forrest, Nature **428**, 911 (2004).

Growth dynamics of pentacene thin films

Development of the pentacene layer-by-layer contrast during deposition on Si(001) during growth at a rate of 10^{-2} monolayers per minute (one monolayer (ML) ~15 Å).
One layer; two layers; three layers



Evolution of the dendritic shape of pentacene islands on cyclohexene-saturated Si(001).
a, $\Theta = 0.25$ ML; **b**, $\Theta = 0.5$ ML; **c**, $\Theta = 0.75$ ML; **d**, $\Theta = 1$ ML.



Diffusion-limited aggregation
T. A. Witten, L. M. Sander, Phys. Rev. B 27, 5686 (1983).

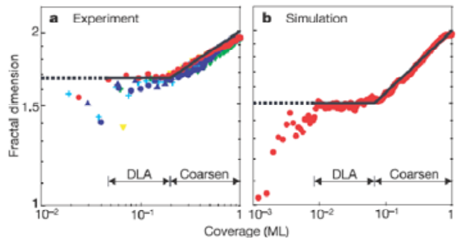
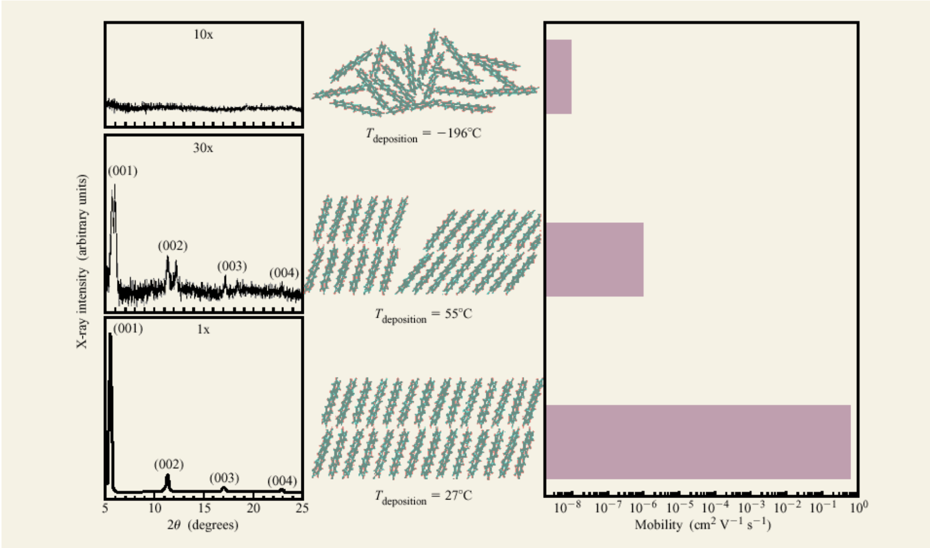


Figure 4 Coverage-dependent fractal dimension of single-molecular-layer pentacene islands on cyclohexene-saturated Si(001). **a**, Experiment; **b**, modified DLA (diffusion-limited aggregation) simulation. Independently of the experimental conditions, including growth rate variations and substrate surface preparation as illustrated by the different colours and symbols, the fractal dimension follows a universal curve.

F.-J. M. z. Heringdorf, M. C. Reuter and R. M. Tromp, *Nature* **412**, 517-520 (2001)

Correlation between morphology and mobility

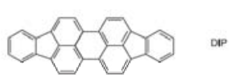


J. M. Shaw, P. F. Seidler, *IBM J. Res. & Dev*., **45**, 3 (2001)

More complex heterostructures and technical interfaces

The controlled deposition of metals on organics ('top electrode') is non-trivial. In order to reduce problems related to interdiffusion (and ultimately short-circuiting) and traps related to surface states, different strategies can be pursued.

1. Deposition at low temperatures to 'freeze in' the interdiffusion;
2. Deposition at (moderately) high rates with the idea that the metals are quickly forming larger aggregates which are then less mobile and diffuse less far into the organic film;
3. Use of 'suitably reactive' metals and/or organics, so that a strong interaction at the top layer(s) of the organic material prevents interdiffusion;
4. 'Soft deposition' by 'thermalising' or at least reducing the energy of the impinging metal atoms by 'baffling' these using a noble gas or other means;
5. Miscellaneous other non-thermal deposition strategies including, e.g., electrochemical deposition may be attempted.



Diindeno(1,2,3,-cd,1',2',3'-lm)perylene ($C_{32}H_{16}$, DIP, a red dye)

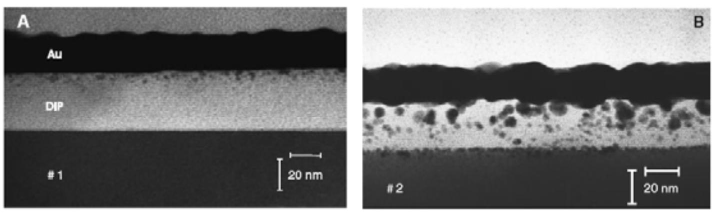
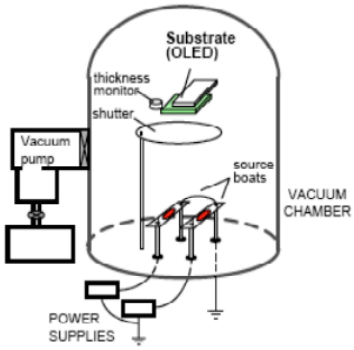


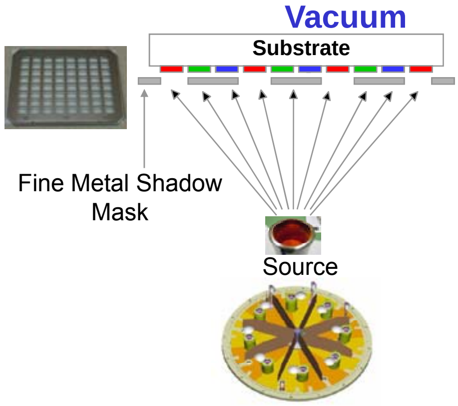
Fig. 8 Cross-sectional TEM images of two Au/DIP/siliconoxide heterostructures. While the Au contact prepared at −120 °C and a rate of 23 Å/min (left) exhibits rather well-defined interfaces, the Au contact prepared at 70 °C and a rate of 0.35 Å/min (right) shows strong interdiffusion. Note that individual lattice planes of the DIP film can be resolved. From Ref. [50] with permission.

F. Schreiber, phys. stat. sol. (a) 201, No. 6, 1037–1054 (2004)

Vacuum Deposition: Low molecular mass dyes

• Best way to deposit small molecules into thin films.
• Advantages are that multilayer thin films can be built up. This is not easily achievable using solution processing - as each layer tends to dissolve underlying layers.
• Vacuum deposited films are often of very high purity having very low contaminant levels.





Processing from solution

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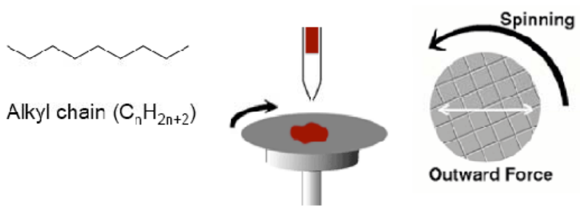
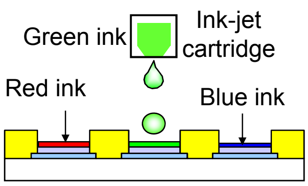
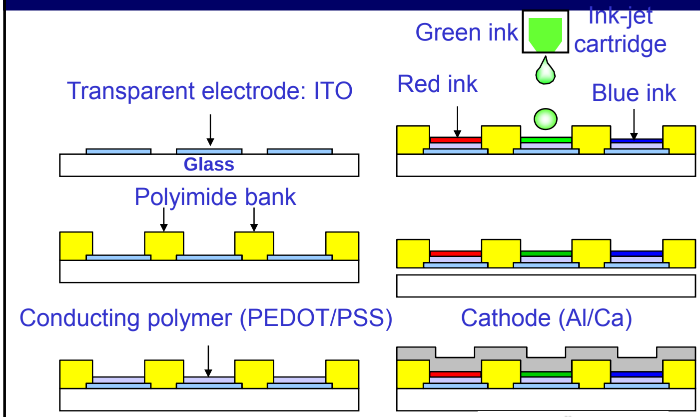
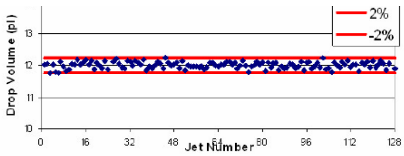
• Depositing materials from solution is very cheap. Large areas can be covered. Expensive vacuum systems are not needed.
• To process macromolecules, it is important to maintain material solubility - generally achieved by incorporation of bulky alkyl (unsaturated) side-groups. These groups are un-conjugated (no
delocalised electrons - contain σ bonds only). However they are important for macromolecules (polymers), as they permit the solvent molecules to solubilize the molecule.
• Macromolecules are usually spin-cast or dip-cast into thin films.

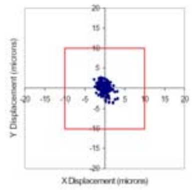


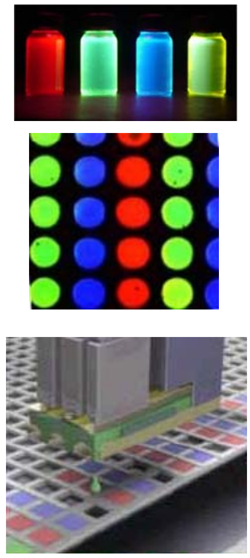


Inkjet printing

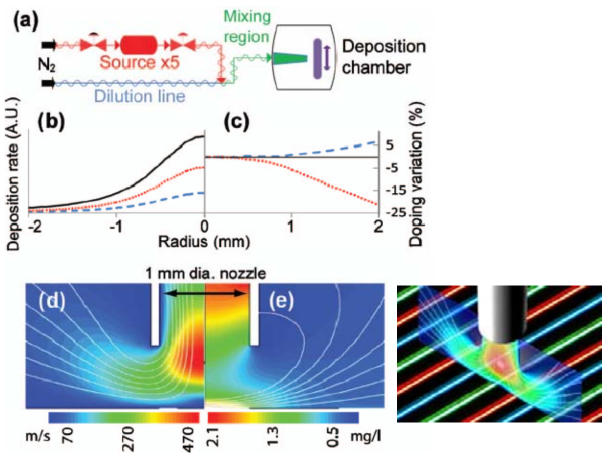


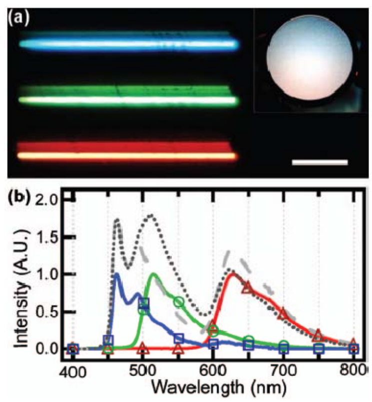






Organic vapor jet printing (OVJP)

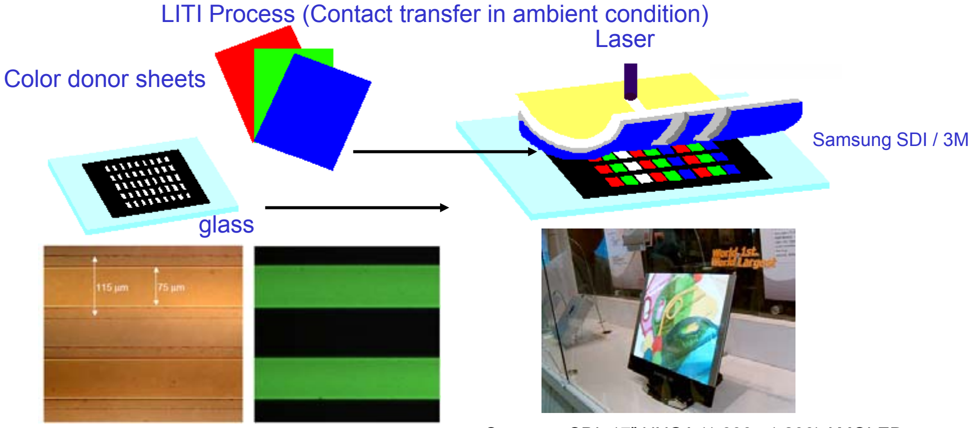




M. S. Arnold, G. J. McGraw, S. R. Forrest, and R. R. Lunt, Appl. Phys. Lett. (2008) 92, 053301.
Cordelia Sealy. Materials Today, 2008. 3. 20 (http://www.materialstoday.com/archive/2008/11-04/news05.html

LITI (Laser Induced Thermal Imaging)

LITI Process (Contact transfer in ambient condition)

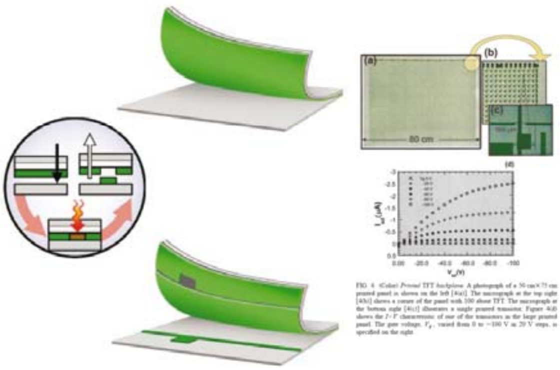


Samsung SDI, 17” UXGA (1,600×1,200) AMOLED

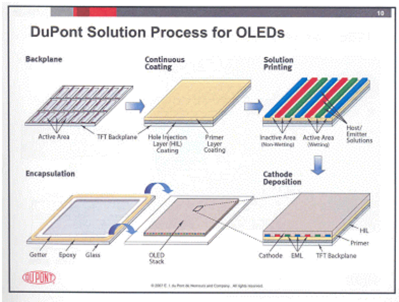
- RGB 유기 물질이 도포된 도너기판 (donor film)을 AMOLED backplane 기판에 밀착시킨 후, 레이저를 필름 뒤에서 조사하여 유기물질을 필름에서 기판으로 전사시킴으로써 RGB pattern을 얻는 방법.
- 상온/상압에서 도너필름을 기판에 밀착시키며 정렬 정밀도가 매우 높고, 레이저빔 크기에 따라 소형기판의 초미세 패턴으로부터 대형기판의 균일한 화소형성 패턴에까지 형성 가능.

DuPont’s patterning process

DuPont’s laser patterning process



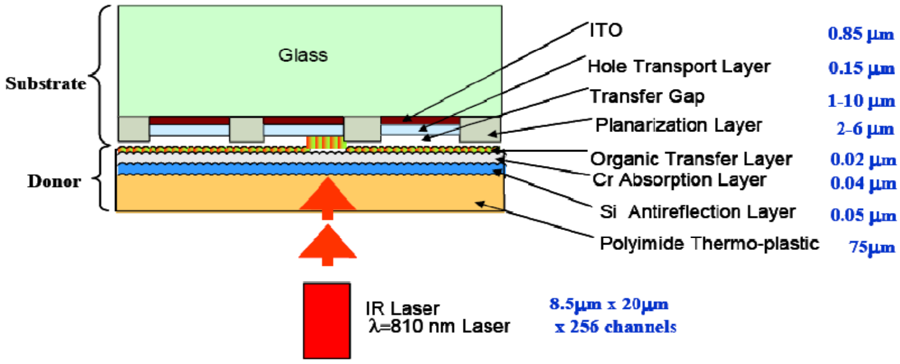
DuPont’s solution process



- 두개의 필름 (donor/receiver)를 붙인 다음 적외선 레이저를 스캔하여 도너필름쪽의 얇은 흡수층에서 발생되는 열에 의한 gas bubble이 전도성 고분자의 패턴을 형성하는 기술
- 유기반도체의 대면적 제조공정에 응용이 가능

G. B. Blanchet, Y. L. Loo, J. A. Rogers, F. Gao, and C. R. Fincher, Appl. Phys. Lett. 82, 463 (2003).(Du Pont)

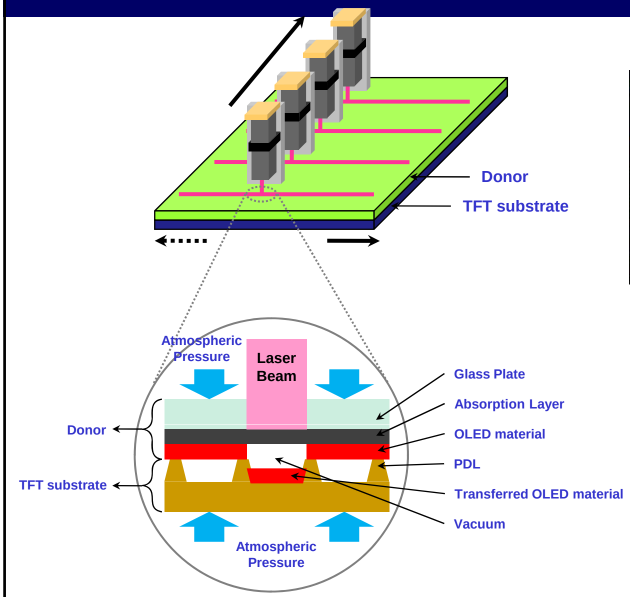
RIST (Radiation Induced Sublimation Transfer)



도너필름과 기판 간격이 일정하게 유지되도록 1-10μm 의 spacer를 삽입하며, 40 nm의 크롬 흡수층을 포함하는 도너필름에 고에너지의 레이저빔을 스캔하여 진공 중에서 도너필름에 도포된 유기물질이 승화되어 기판으로 이동되도록 하는 기술

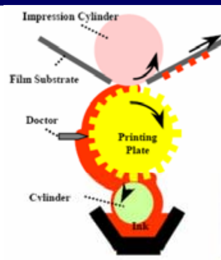
Color patterning method without shadow mask: transfer in a vacuum chamber
Boroson et al. SID 2005 Digest p172 (Eastman Kodak)

LIPS (Laser Induced Pattern-wise Sublimation)



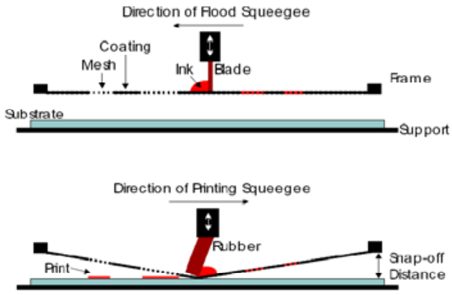
- Sony에서 2007년 SID학회에 발표한 27인치급 AMOLED 제조 방식
- diode laser를 사용하여 microcrystalline Si TFT backplane을 제조했고, 이 레이저 스캔기술을 동일하게 RGB 유기물질의 대면적 patterning에 적용함.
- LITI와 비슷한 개념이지만, 진공 중에서 전사가 이루어지고 필름 대신 기판을 도너로 사용했다는 점이 다름.

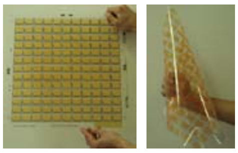
Other Printing Methods: Gravure, Screen or R2R Printing



Gravure Printing

(Dai Nippon Printing Co, *SID 05 DIGEST, pg. 1196 (2005)*





Screen Printing

H. Antoniadis (OSRAM), IMID'05

D. A. Pardo, G. E. Jabbour, N. Peyghambarian, Advanced Materials, 12, 1249 (2000).

Roll-to-Roll Process