

Unconventional bottom-up approach to nanofabrication of functional materials

Massimiliano Cavallini

M. Facchini, C. Albonetti, E. Bystrenova and F. Biscarini



**Institute for the Study of Nanostructured Materials
Bologna (ISMN)**

Nanotechnology of Multifunctional Materials Research Division

LITHO2006

Marseille (F), June 26th, 2006



EU-Integrated Project NMP4-CT-2004-500355 “NAIMO”.
Coordinator: Yves Gertz, *Univerité Libre Belgique*

Co-workers

Roberto Lazzaroni, Philippe Leclère, Mathieu Surin,
Université de Mons-Hainaut, Service de Chimie des Matériaux Nouveaux,
(Belgium)

Dag Werner Breiby, Martin M. Nielsen, Jens Wenzel Andreasen,
The Danish Polymer Centre, Risø National Laboratory Frederiksborgvej
(Denmark)

Klaus Müllen, Andrew C. Grimsdale, Prashant Sonar
Max-Planck-Institut für Polymerforschung, Mainz (Germany).

Jaume Veciana, Daniel Ruiz, Conceptio Rovira
CSIC-ICMAB Barcellona (Spain)



- Nanotechnologies are not just a matter of downscaling; instead, they provide overall flexibility and control on material response.
- The growth method determines the properties of organic thin films of functional materials.
- Long-range molecular order and a limited nucleation density of domain in organic thin films can lead to increase the charge mobility.

Aim

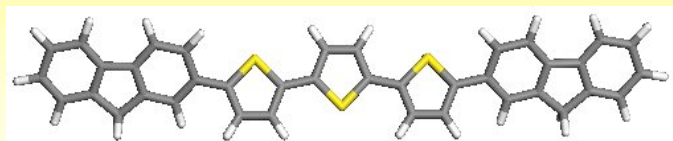
- Improvements of some physical properties of functional materials thin film (ex. charge mobility) by controlling the nanostructuration.

Strategy

The simplest strategy to achieve these results is to exploit the self-organizing properties of materials by stamp assisted deposition (Bottom-Up approach).

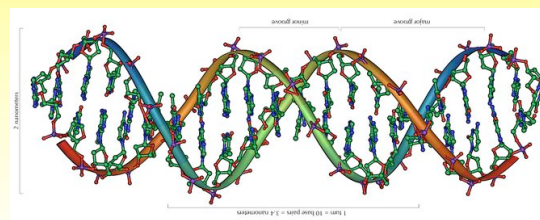


Organic Semiconductors



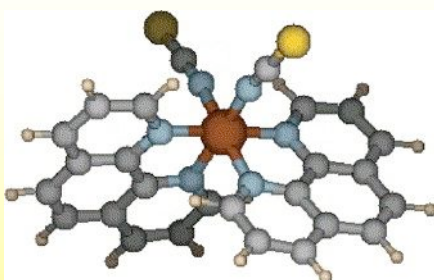
F-T3-F

Bio-Molecules



λ -DNA

Spin Crossover



Fe (Phen)₂SCN₂

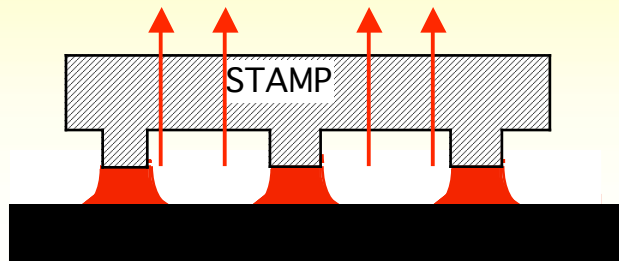
Molecular Magnets



Mn₁₂O₁₂(O₂CC₁₂H₉)₁₆(H₂O)₄



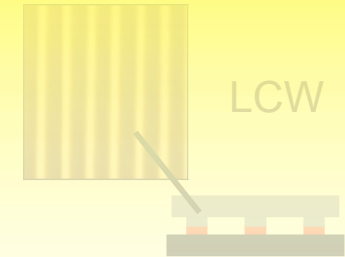
Stamp assisted self-organization



Self-Assembly Crystallization Dewetting

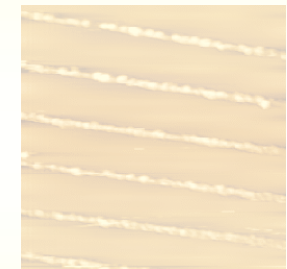
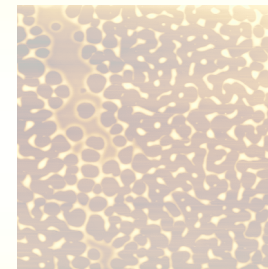


Drop casting

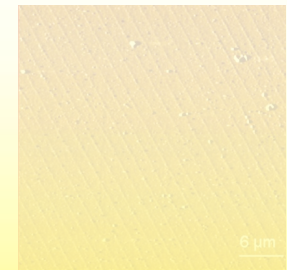


LCW

Partial wetting
(Alq3 on Si)



Self-organization
P3HT fibrills



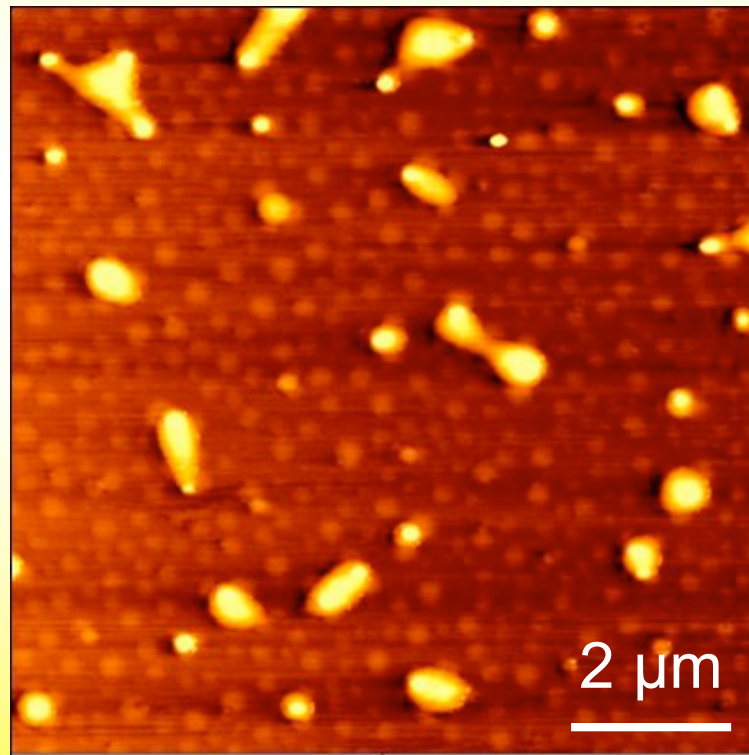
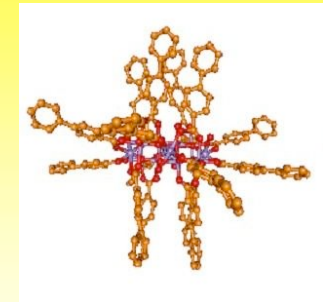
Dewetting
(SMM on SiO_x)



* EU Patent PCT: EP03/10242 16/9/2003 and
M.Cavallini, F.Biscarini *Nano Letters* 3, 1269 (2003).

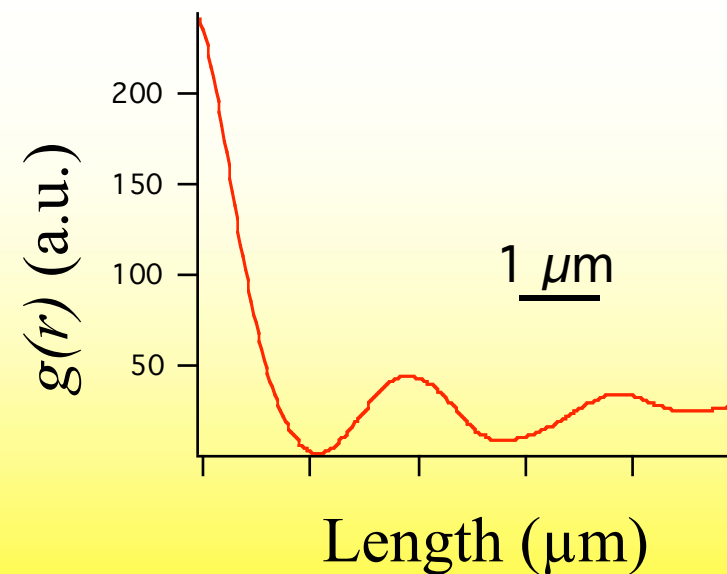
Dewetting of Mn12 SMM on Si/SiO_x (native)

The features generated by dewetting can have complex distribution but often they are **NOT** randomly distributed!

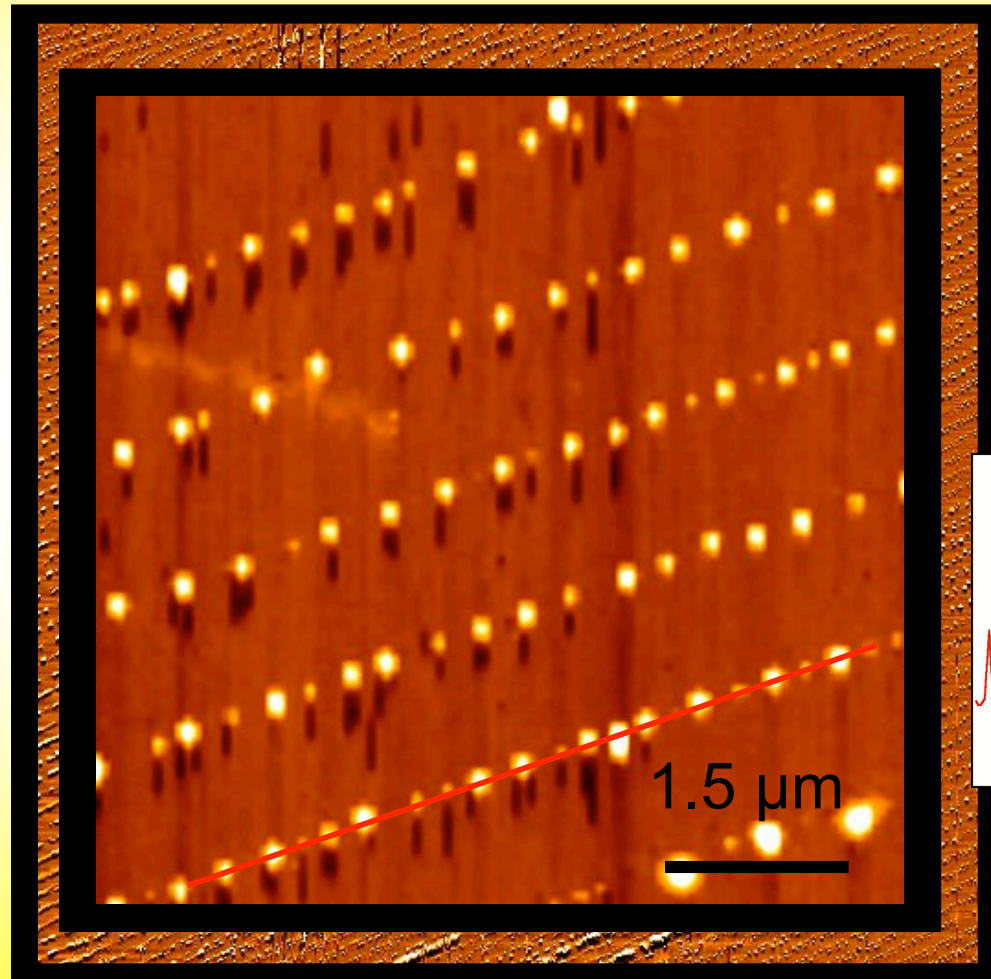


Z scale: 25 nm

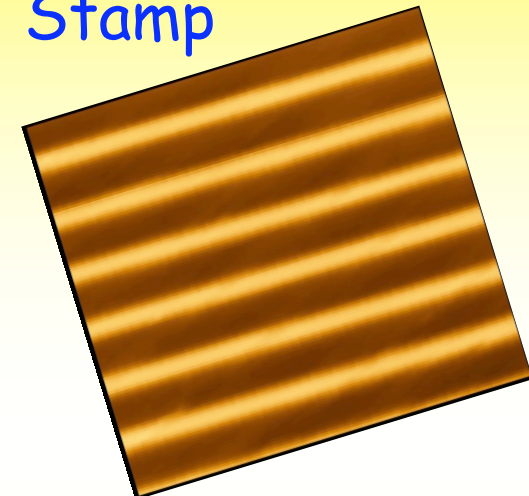
2D height-height
correlation function $g(r)$
(radial distribution)



LCW works at large area (mm²)by dewetting



Stamp



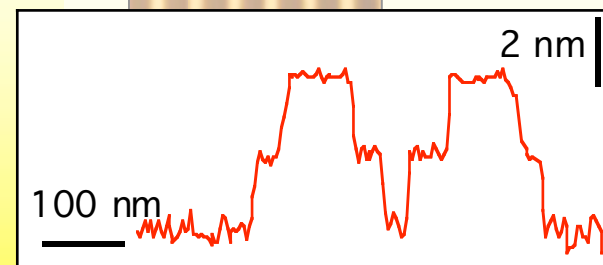
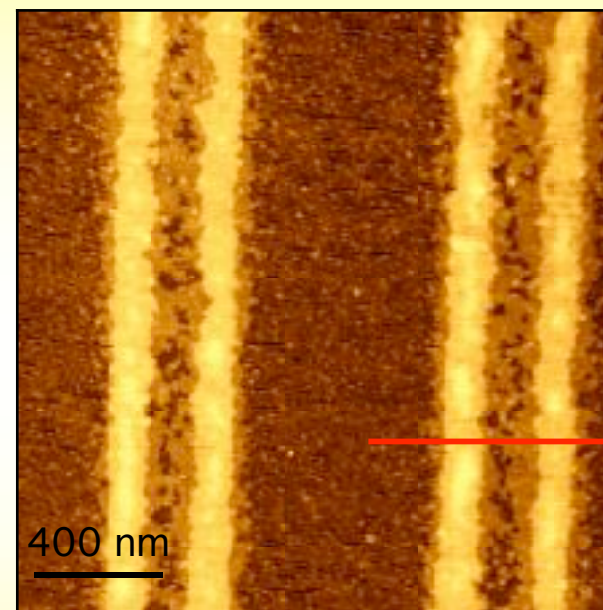
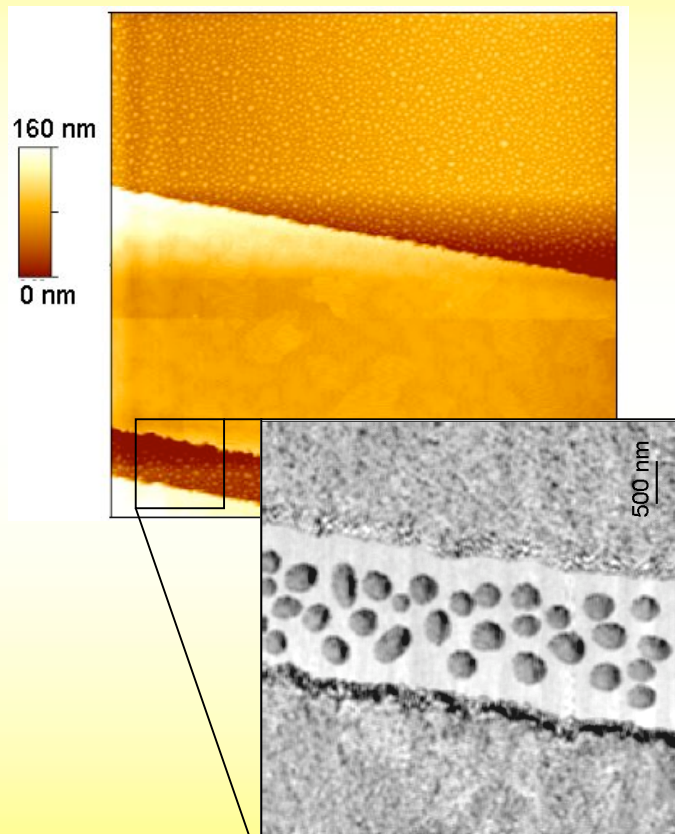
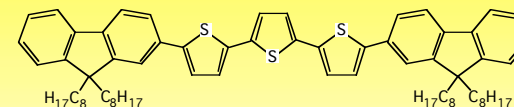
Diam. \approx 200 nm

H \approx 40 nm

100 μm × 100 μm



The nature of the substrate strongly influence the morphology of thin film (layered growth vs. droplets)



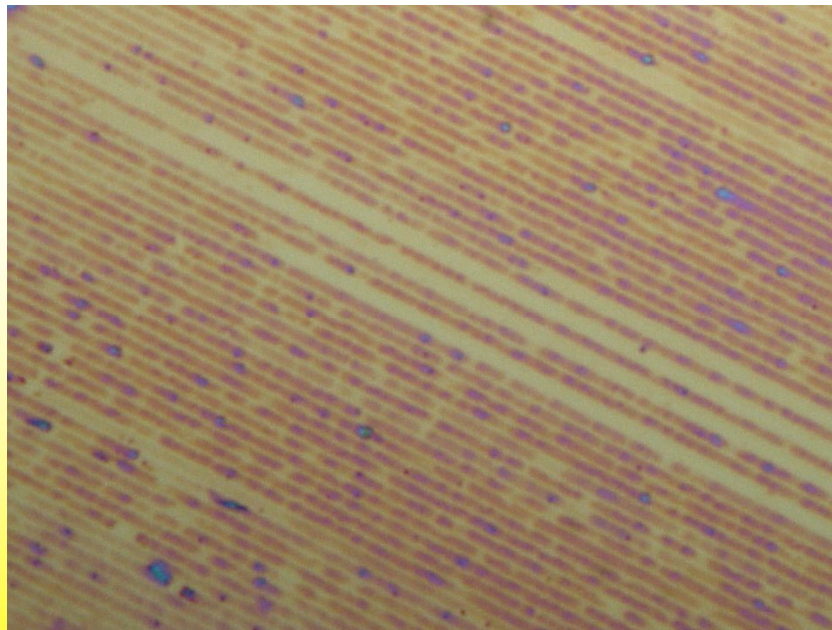
Thin film does not work in FET!
Thick films (>250 nm) FET works
 $\mu = 1.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$

Optical microscopy on sub-micrometric stripes

Optical micrographs of a thin deposit of nanostructured F-T3-F on a SiO_x Stripes thicker than 25 nm (pitch $> 1\mu\text{m}$) are visible by optical microscope. These aligned stripes are made of crystallites of F-T3-F which are birefringent under crossed polars.

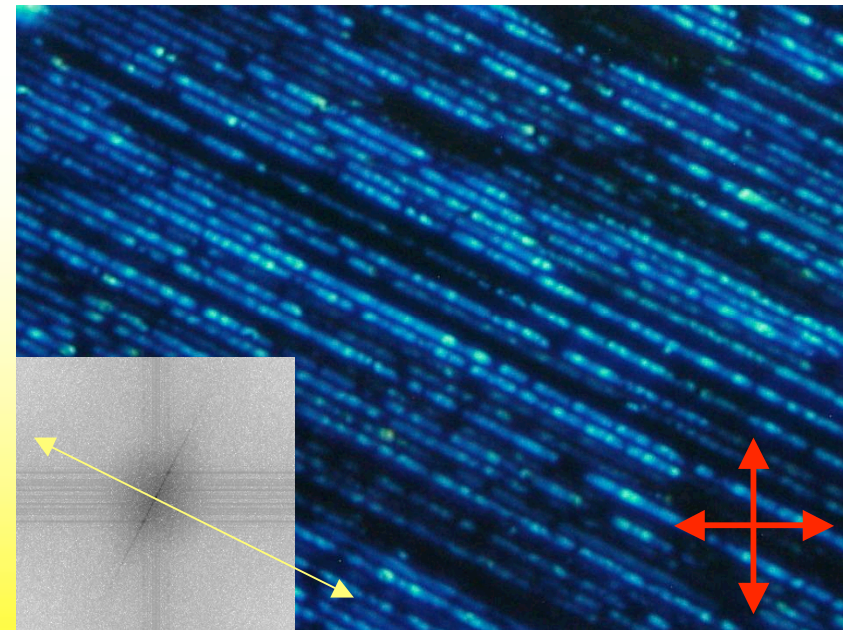
Under natural light

Mean size of domains:
 $6.1 \pm 1.0 \mu\text{m}$



$60 \times 90 \mu\text{m}^2$

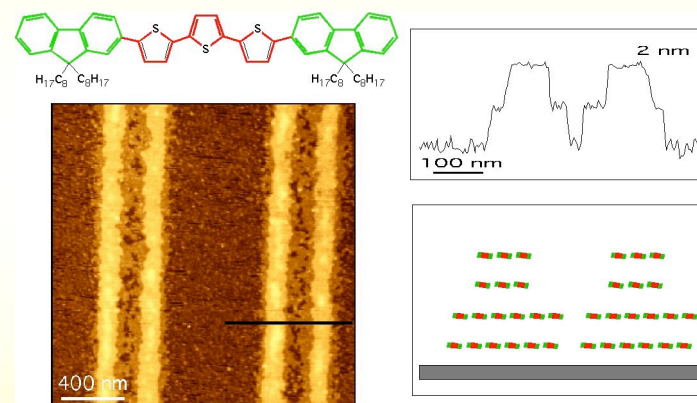
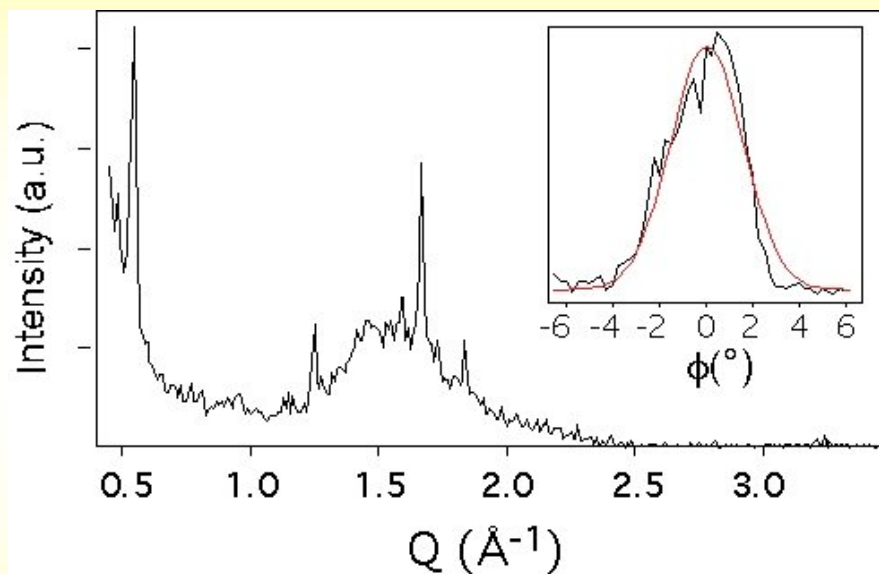
LITHO2006



$60 \times 90 \mu\text{m}^2$



Sharply defined reflection was observed at $Q=1.51 \text{ \AA}^{-1}$, along the direction of F-T3-F stripes.



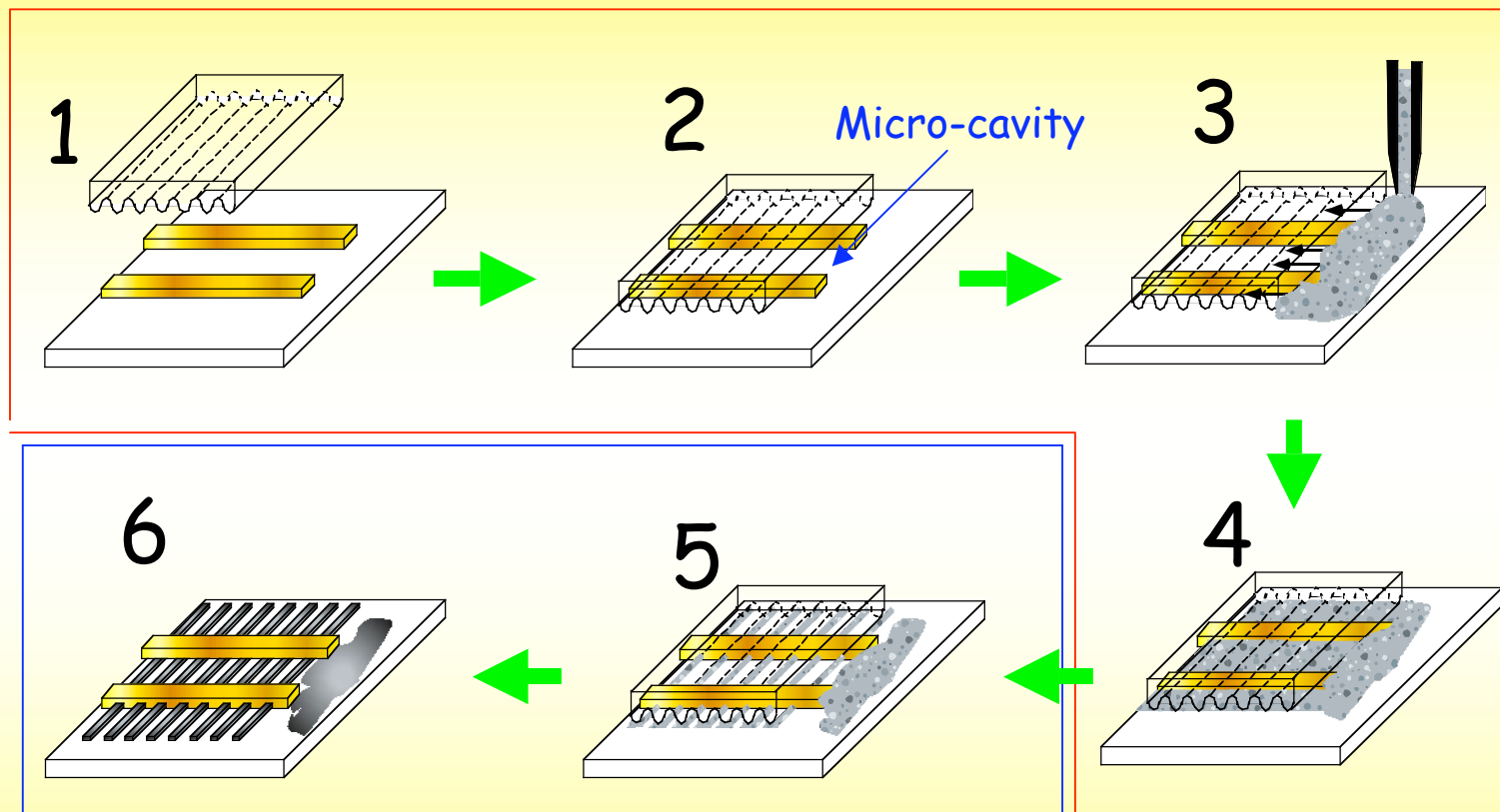
Q scan along the stripes direction, inset displays the in-plane rocking scan at $Q=1.51 \text{ \AA}^{-1}$. $\Phi=0$ corresponds to the direction of the stripes.

F-T3-F stripes results crystalline and highly oriented, the π -stacking direction being along the stripes.

ISMN-Bologna Combined Micromolding in Capillaries and Lithographically Controlled Wetting

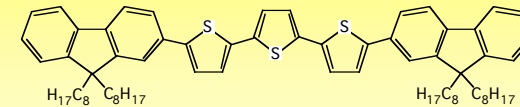
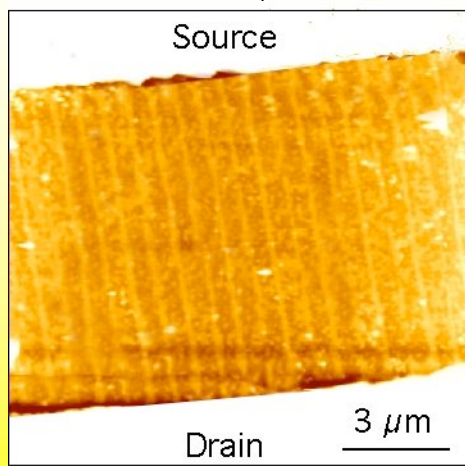
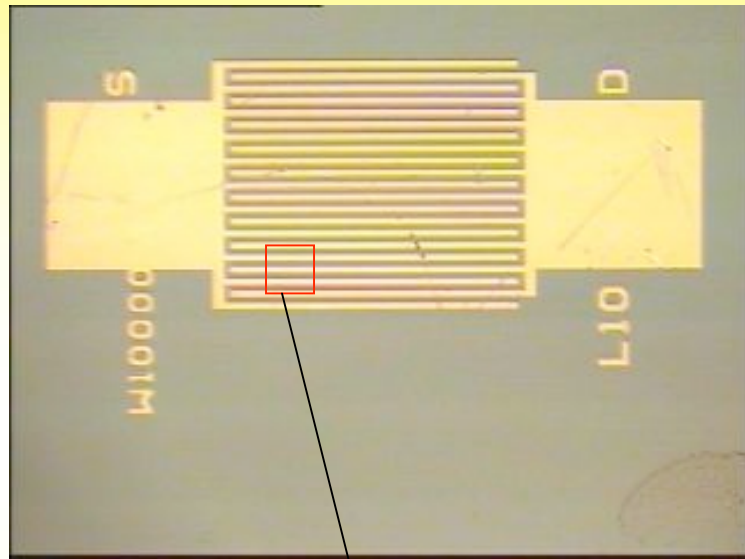


Micromolding in capillaries*

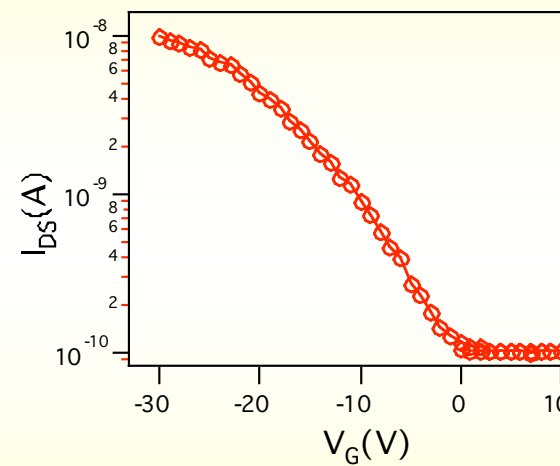


Lithographically Controlled Wetting**

Timing using DMF solution:
Steps 1→4: <5 s
Steps 4→6: ~12 hrs



Transfer characteristics



FET based on nanostripes work!

$$\mu = 0.5 \times 10^{-4} \text{ cm}^2/\text{Vs}$$

Vacuum sublimated films (>250 nm) FET
mobility

$$\mu = 1.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$$



- LCW exploits spontaneous properties of materials.
- It allows the **fabrication of layered nanostripes or nanopattern** of functional materials.
- It can induce oriented crystallization of nanostructures at large area.
- **The FET based on nanostripes works!**
- **FETs based on nanostripes exhibit charge mobility (measured along nano stripes) two orders of magnitude larger than vacuum-sublimed thin films.**



- Fabio Biscarini (Research Scientist, Head)
- Massimiliano Cavallini (Research Scientist)
- Antonietta Rizzo (Research Scientist)
- Chiara Dionigi (Research Scientist)
- Silvia Milita (Research Scientist)
- Eva Bystrenova (Postdoc in Physics)
- Cristiano Albonetti (Postdoc in Physics)
- Rajendra Kshirsagar (Postdoc in Physics)
- Sunnia Dutta (Postdoc in Physics)
- Pablo Stoliar (Postdoc in Physics)
- Massimo Facchini (Ph. D. Student in Chemistry)
- Jean-Crispin Kengne (Ph. D. Student in Chemistry)
- Pierpaolo Greco (Ph. D. Student in Chemistry)
- Matei Costantin Iacobini (Ph. D. Student in Physics)
- Anderas Straub (Student in Physics)
- Paolo Annibale (Student in Physics)
- Annalisa Calò (Student in Chemistry)