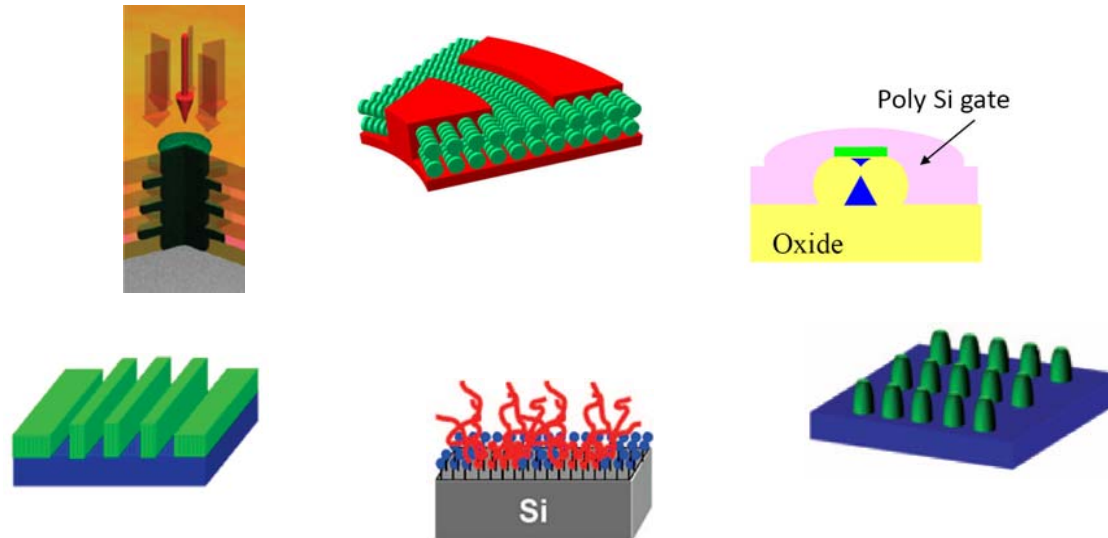
E-beam lithography and nanoimprint for polymer nanostructures



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Outline

- Introduction
- E-beam lithography
  - Principle
  - Step in top-down processes
  - Templates for bottom-up architectures
- Nanoimprint
  - Principle
  - Applications
  - NIL and EBL
- Conclusion

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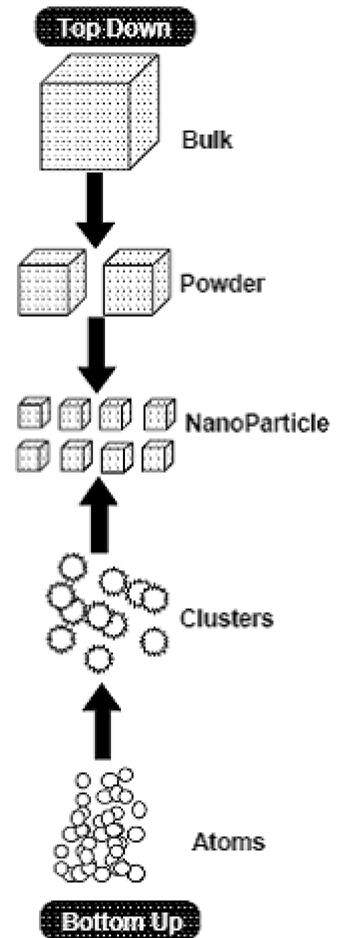
Introduction

- 2 ways of fabricating nanodevices:
  - Top-Down: from bulk material (aligned masks + etching/growth/deposition)
  - Bottom-Up: from individual species (chemical/physical self-assembly)
- Maximizing B-U makes a process cheaper
- Top-down remain necessary at some steps
- EBL can:
  - Serve as lithography step in T-D processes
  - Provide nanotemplates for B-U experiments
  - Provide mold for nanoimprint lithography



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EBL Principle

SEM column

Computer 2: lithography

Computer 1: SEM control & imaging

Beam blanker control

SE detector

e^-

Sample stage control

- beam blanker : deflection plates which drive the beam off-axis

Important parameter (for litho) : blanking time (or frequency)

E-beam instrumentation

- Modified SEM

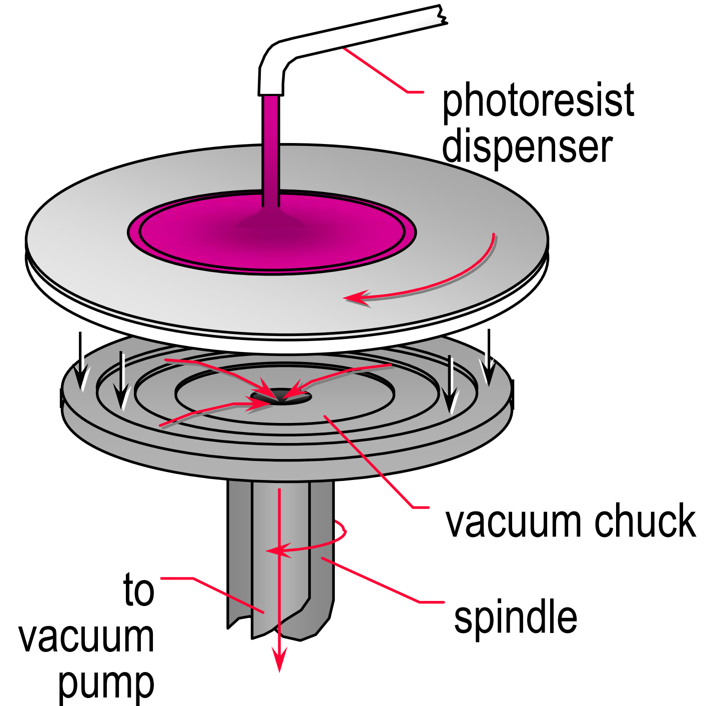
- Can be used for litho and imaging
- Acc. Voltage: 30kV
- Cheap and versatile

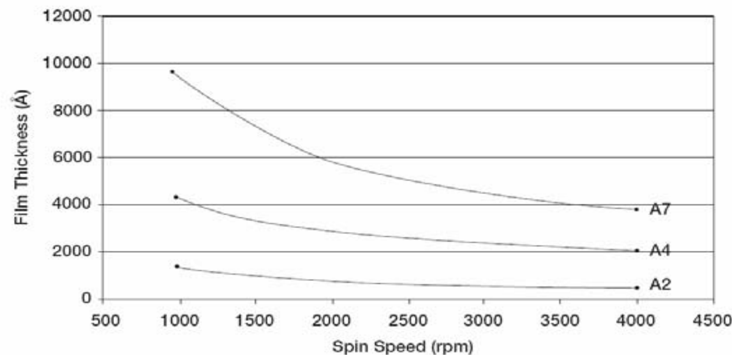
- E-beam writer

- Exclusively dedicated to EBL
- Acc. Voltage: 100kV
- Accurate and fast

Samples for EBL

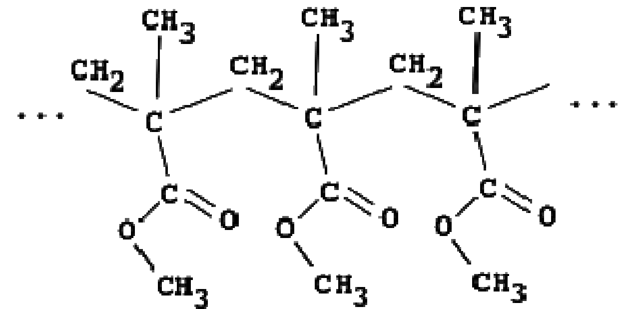
- Resist:
  - Diluted into solvent
  - Solution spin-coated on the substrate
  - Pre-baked to evaporate remaining solvent
- Substrate:
  - conductive material (to evacuate charges)
  - If not, slight metallization on top of the resist

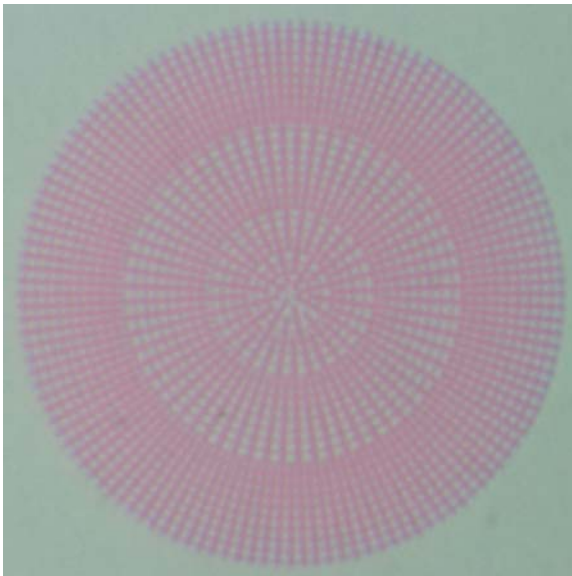




Positive resists

- Chains are broken by e-beam
- Solubility of exposed region increases
- Ex: PMMA

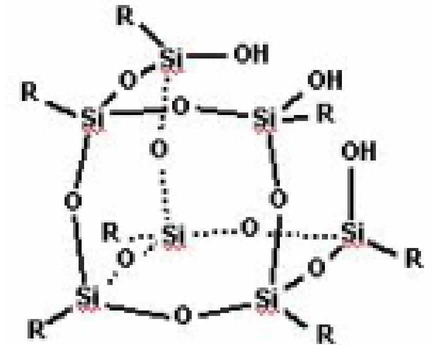


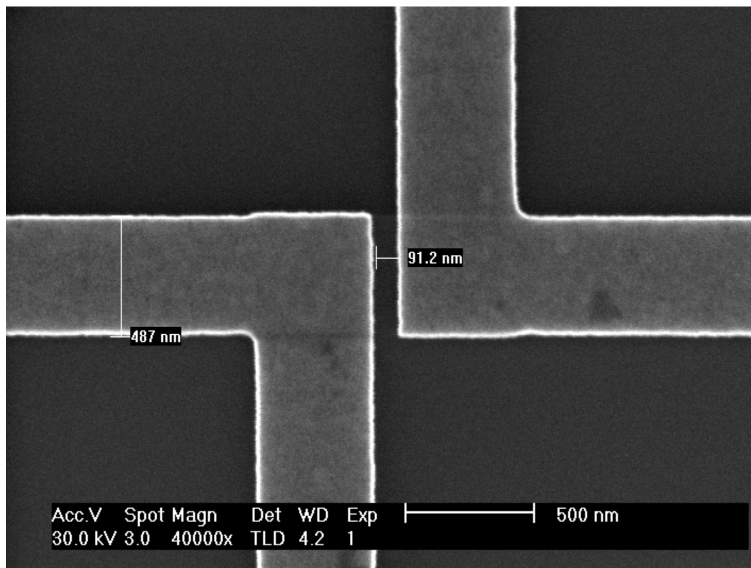


- Solvent: Chlorobenzene, anisole
- Dose type: 100-300 µA/cm²
- Développeur: MIBK

Negative resists

- Chains are cross-linked by e-beam
- Solubility of exposed regions decreases
- Ex: Hydrogen Silsesquioxane (HSQ)





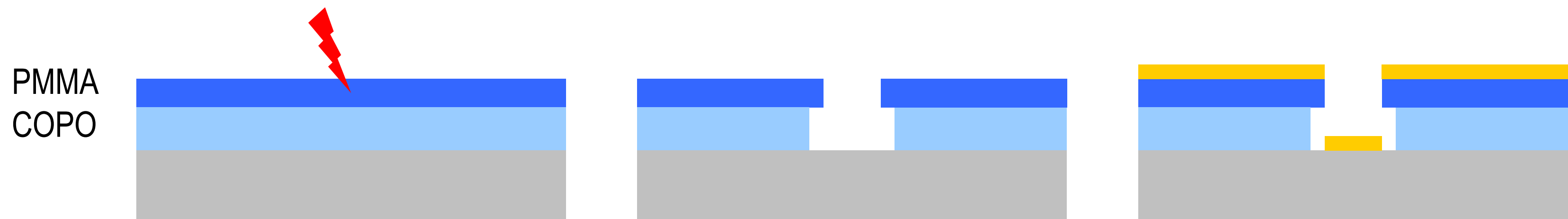
Courtesy of N. Reckinger

- Solvent: MIBK
- Dose type: 400µA/cm²
- Developer: TMAH

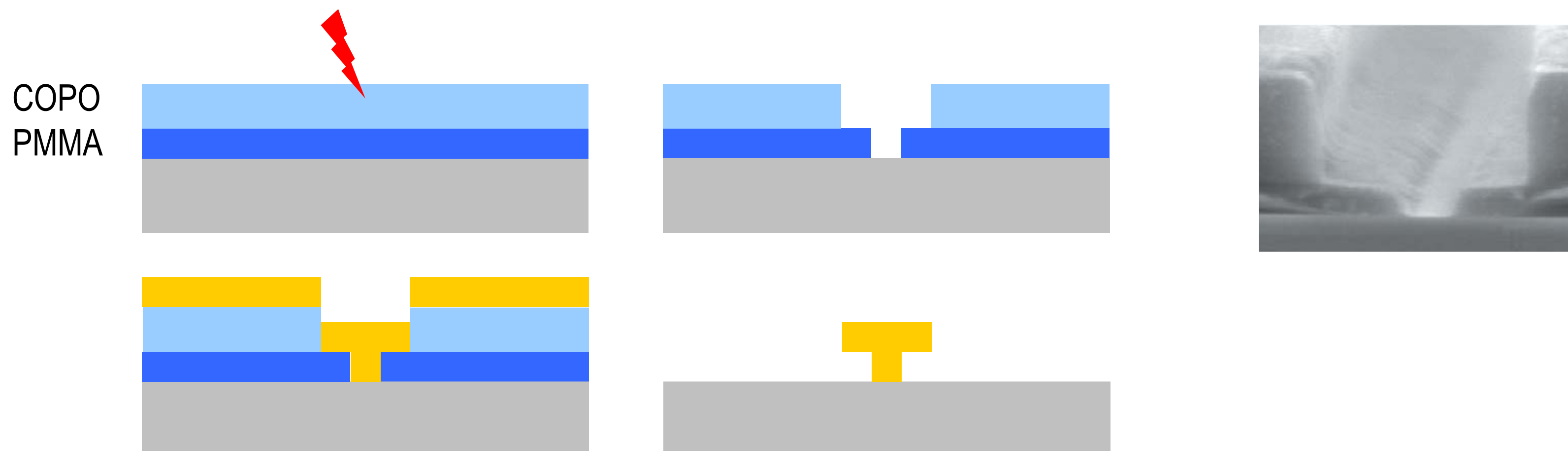
Multilayer process

PMMA / co-MMA) stacks allows z-modulated openings

- To improve lift-off of metals



- For 3D-nanoshapes



Dose

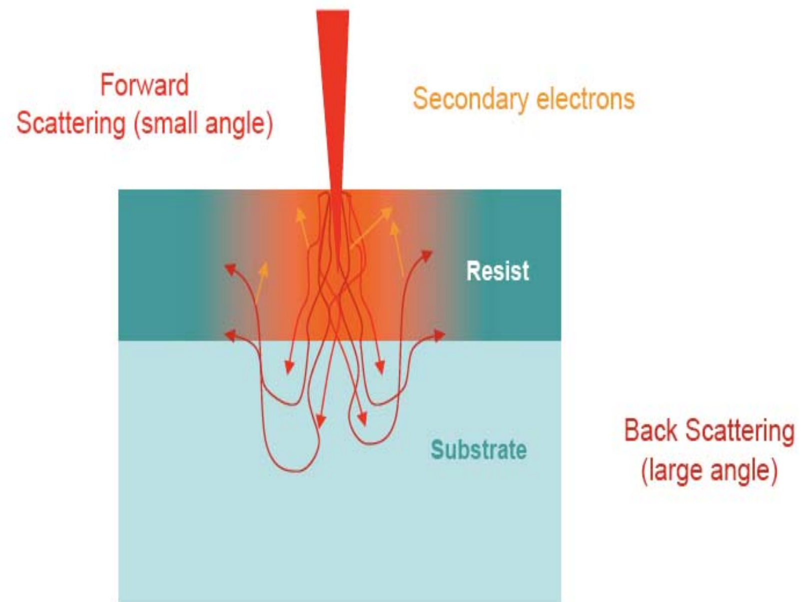
- Charge per unit surface necessary to expose a given resist film.

- Exposure time = Area x dose / beam current

Ex: for a 1 cm^2 square to expose in a resist layer with a sensitivity of 300 $\mu Cb/cm^2$, and a beam current of 1 nA

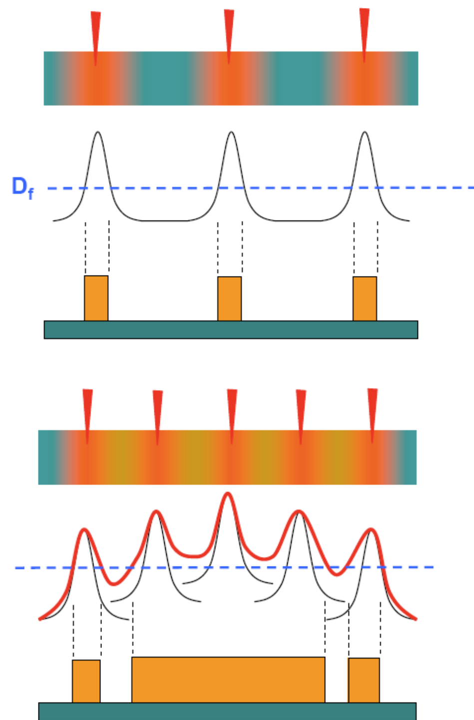
=> 3.5 days !

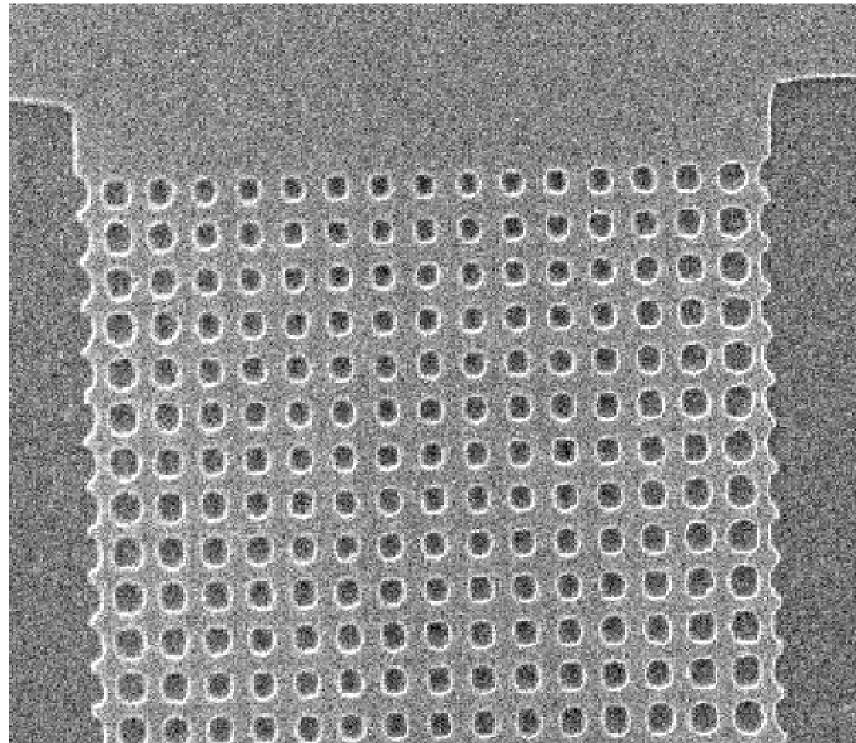
  - Low throughput technique ! use only for small patterns
  - Back-scattered electrons also expose the resist



Proximity effect

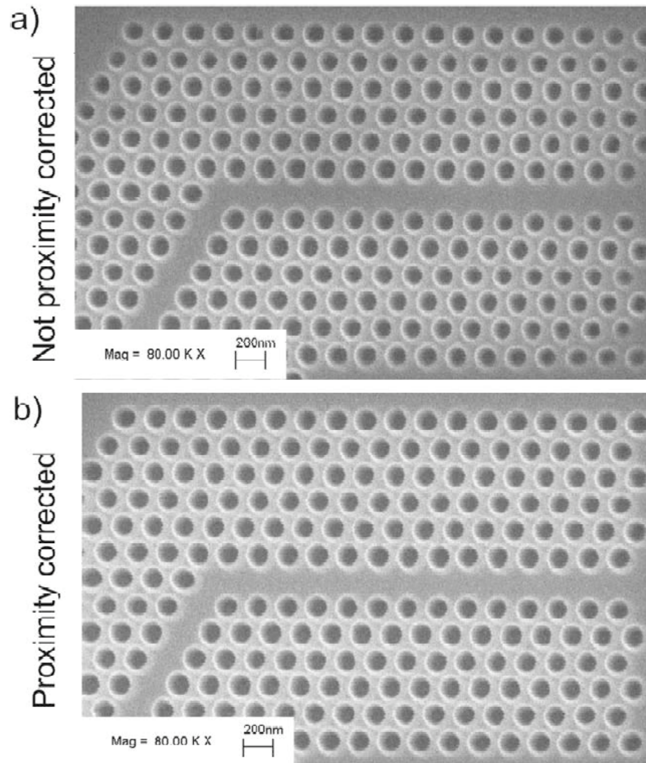
- Illustration: array of 100 nm wide/spaced lines in negative resist) :





- Correction: lower dose in the middle of the array

Proximity effect corrections



- Without correction : external holes are smaller that internal holes
- With Correction : Higher dose on external holes=> narrower distribution of size

  (possible to adjust with Monte-Carlo simulations)
- Other ways to limit proximity effect:
  - use thin resist & thin substrate,
  - adjust the geometry of the pattern,
  - adjust the acceleration voltage.

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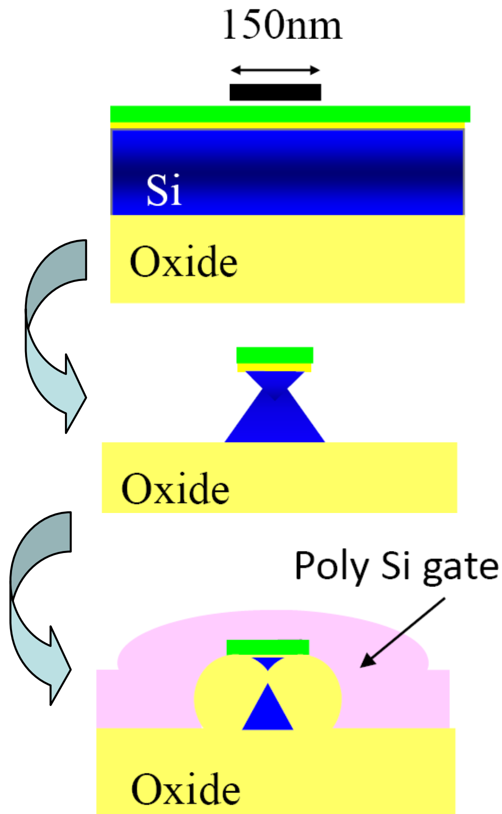
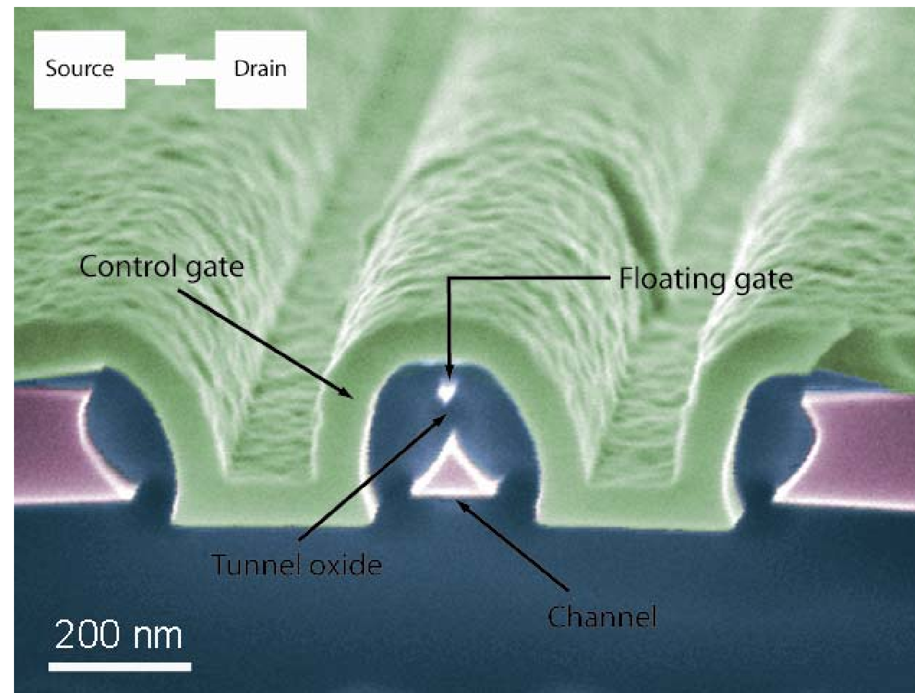
Floating gate transistors

- Nanoscaled 1-electron gate for memory devices



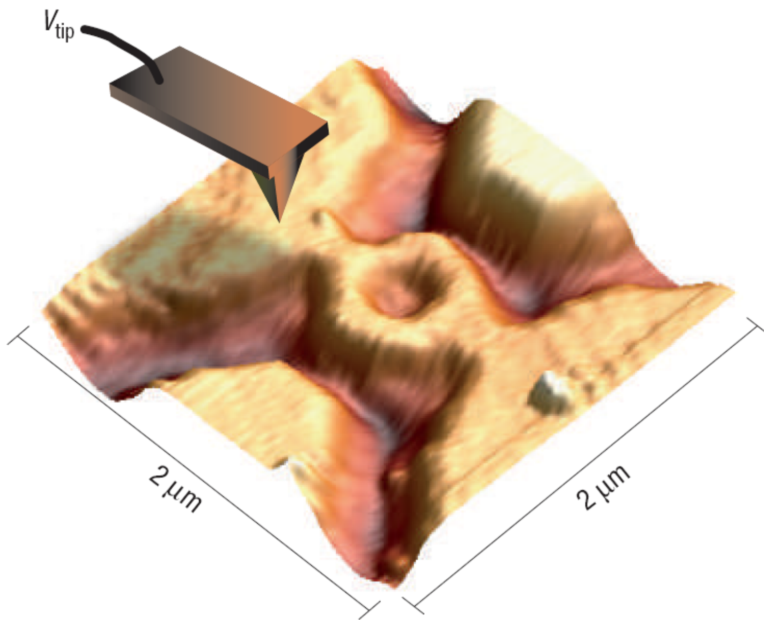
- Substrate SOI (Silicon on insulator)

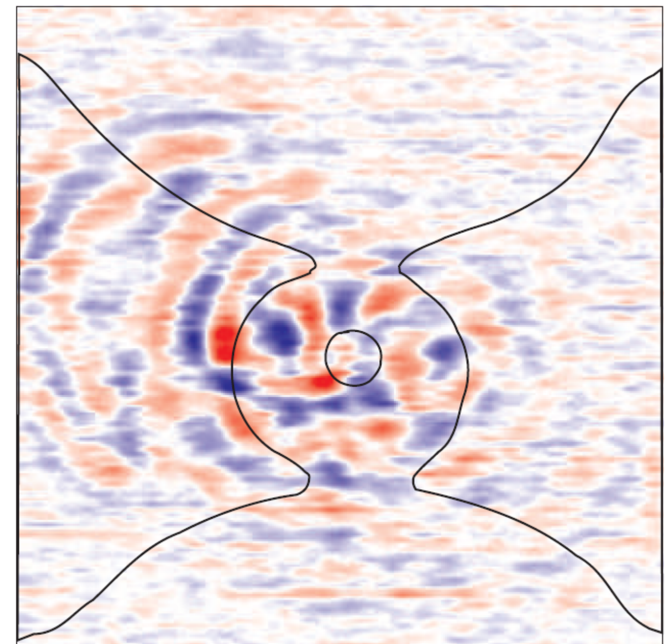


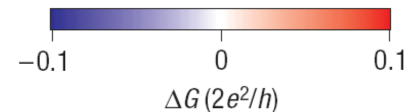
X. Tang et al., *IEEE trans on nanotechnology* **2006**, 5, pp. 649-656.

Quantum ring

- Etching of InGaAs/InAlAs through PMMA mask
- Electronic transport in such small rings is ballistic
- AFM tip modulates the ring transductance



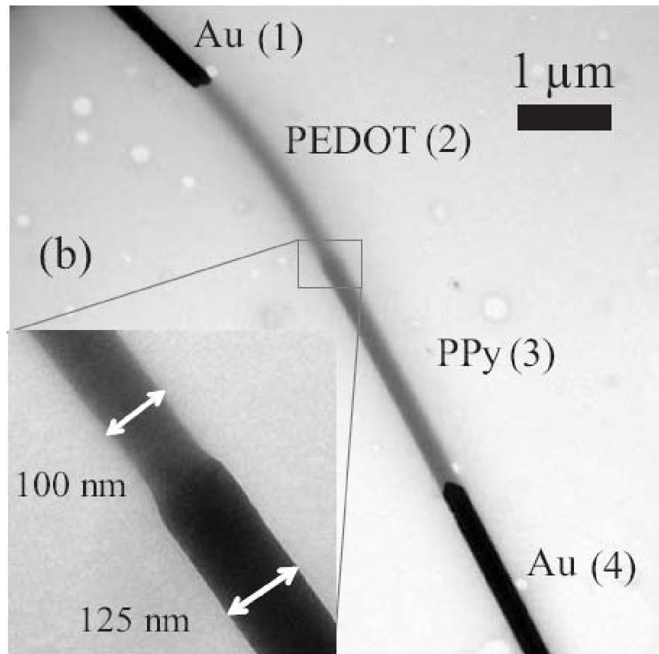


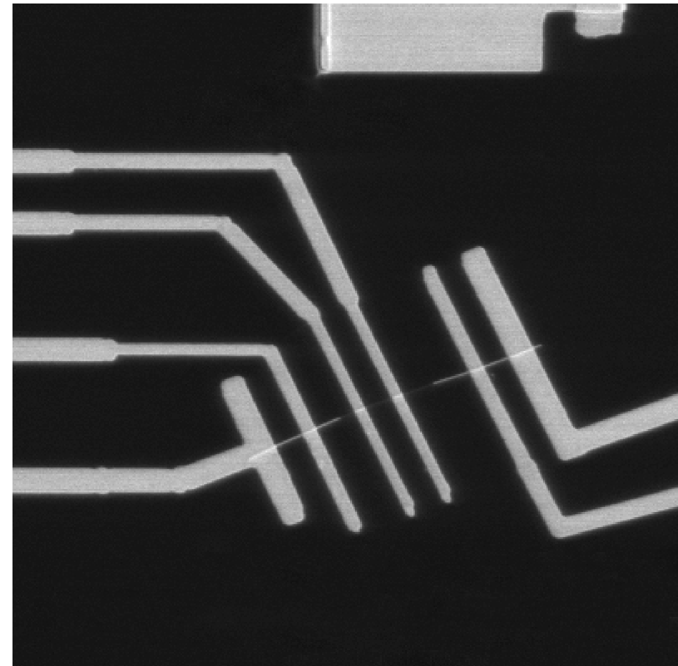


B. Hackens *et al, Nature Phys.* **2006**,2, pp. 826-829

Functional nanowires

- Registration needed in respect to the nanowires
- Metal lift-off on PMMA
- 4 wires measurement of metal-polymer nanowires





L. Gence et *al., Nanowires Science and Technology* 2010, pp243-268

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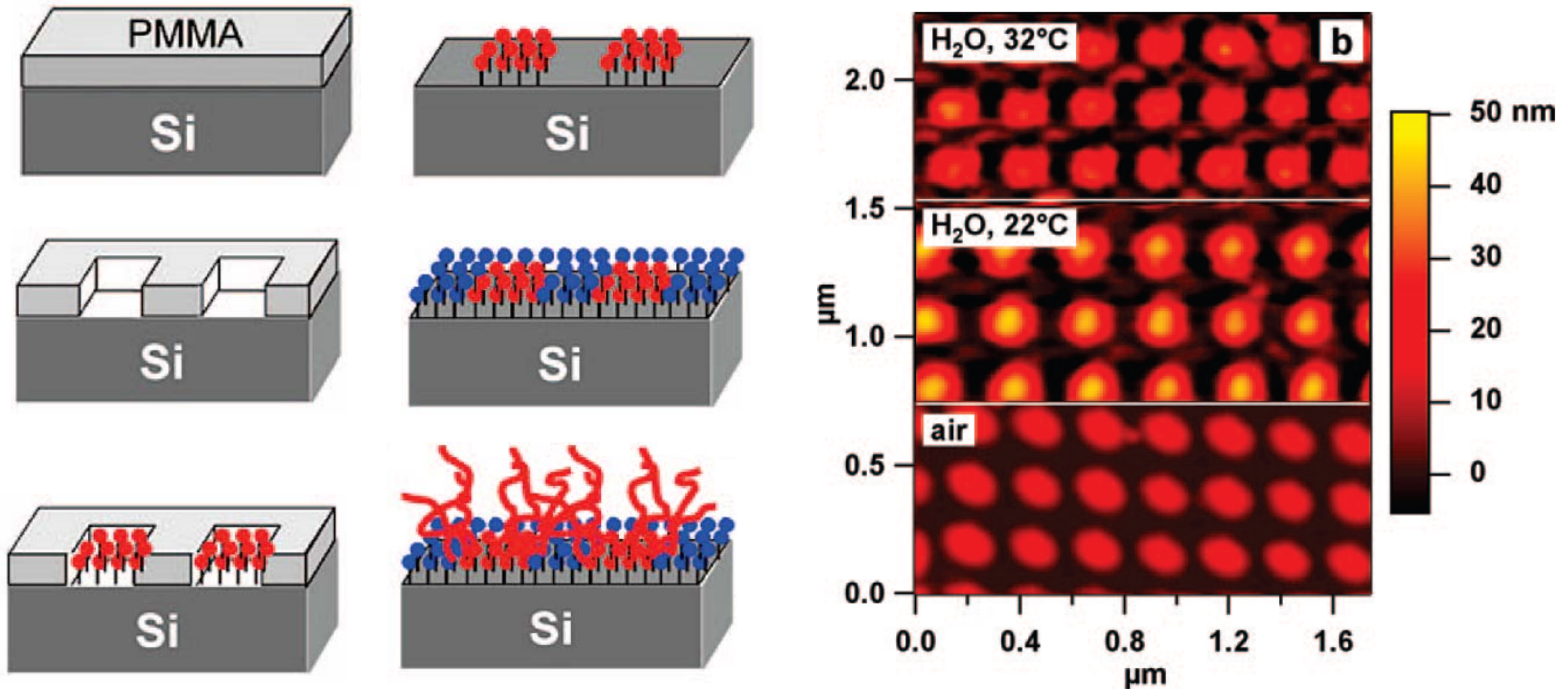
Thermo-responsive polymer brushes

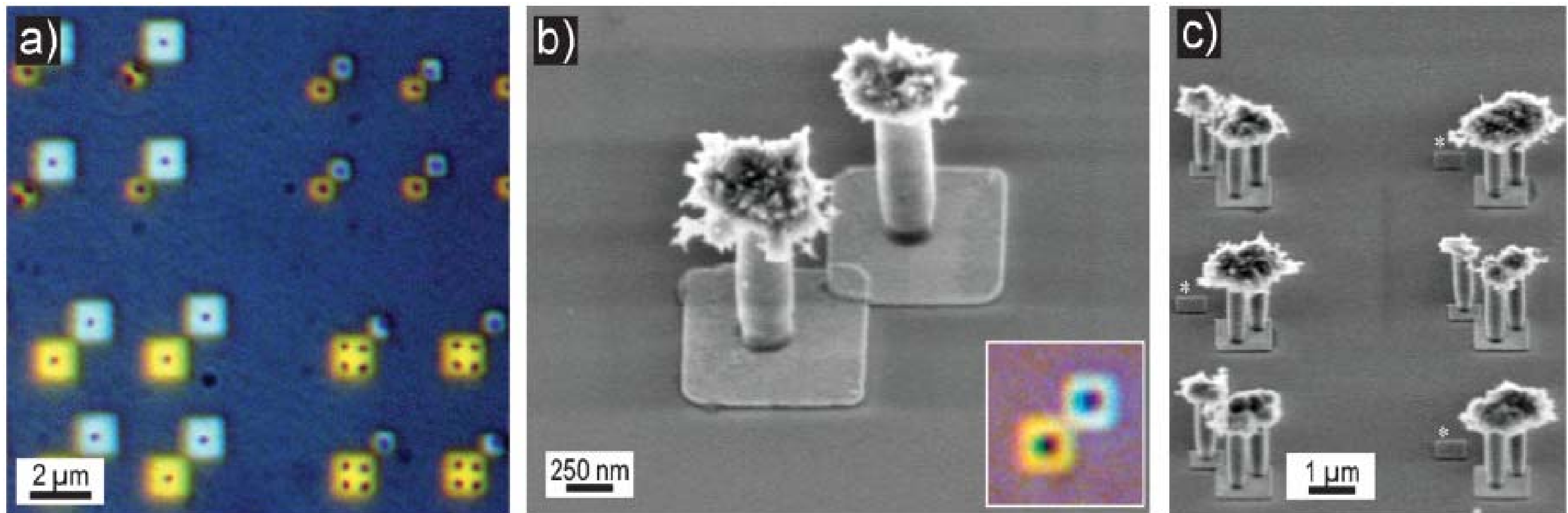
- Nanobrushes of PMEO2MA grafted on ATRP initiator



A. M. Jonas *et al., Nano Lett.* 2008, 8, 3819-3824

Transfer of catalytic growth

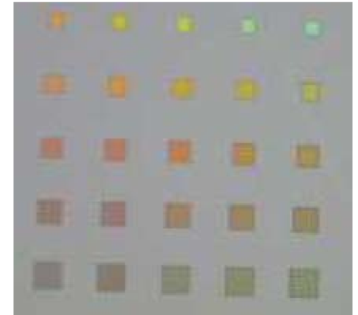
- Template: cylinder openings in PMMA
- PANI growth catalyzed by Pd pads
- This growth still yields for Au pads adjacent to Pd.



A. Vlad *et al., Small* 2010, *6*, pp. 627 - 632.

3D photonic crystals

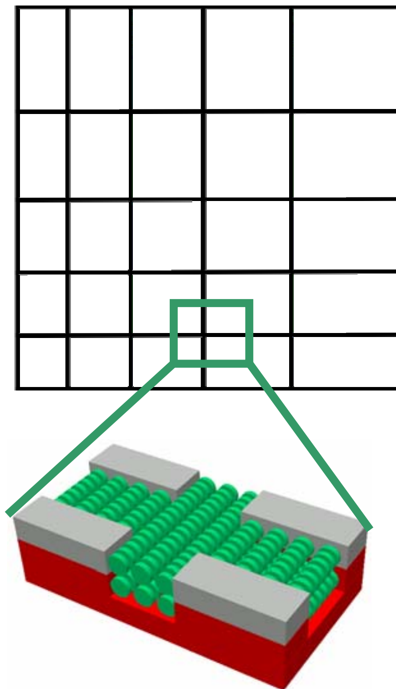
- Litho of dots into a PMMA/copo multilayer matrix
- PANI growth in the obtained structure
- Dissolution of the matrix

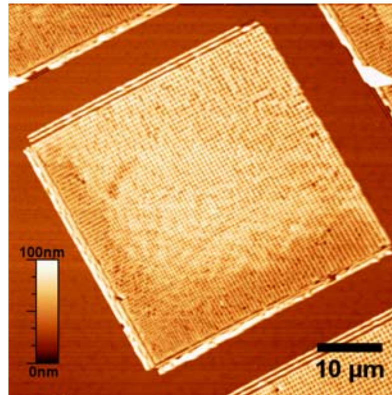


Vlad *et al.*, *Nano Lett.* **2009**, *9*, pp. 2838-2843

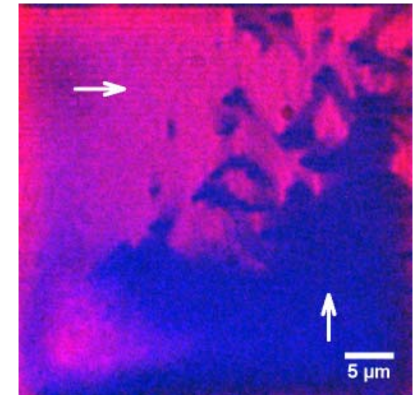
Columnar LC alignment

- PMMA patterned with grooves increasingly spaced
- Grapho-epitaxic alignment of LCs
- Transition between alignments yields the interfacial tension γ





AFM/TM, height image

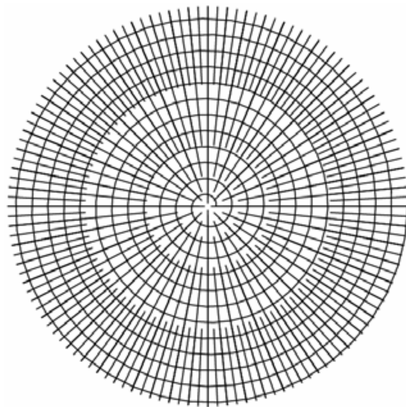


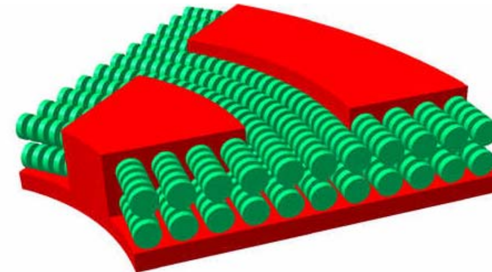
ICM image

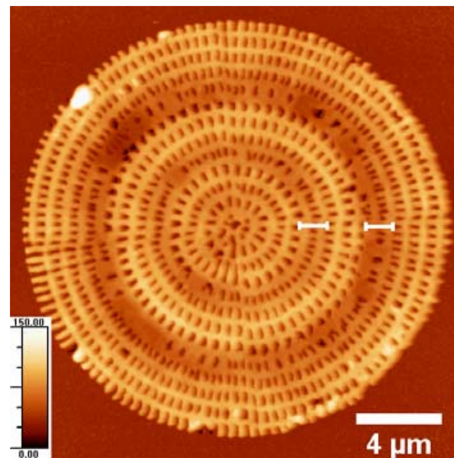
P-O Mouthuy *et al.,* Nano Lett. **2007**, 7, pp. 2627-2632

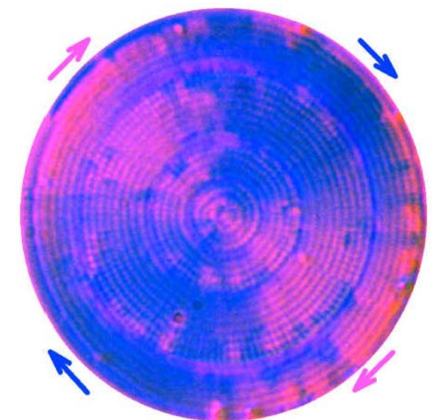
LC Physical properties measurement

- Columnar LC poured into curved PMMA grooves,
- Energetic competition between bending and tangential alignment
- Tangential misalignment gives the bending modulus *K*









P-O Mouthuy *et al.*, *Small* 2008, pp 728-732

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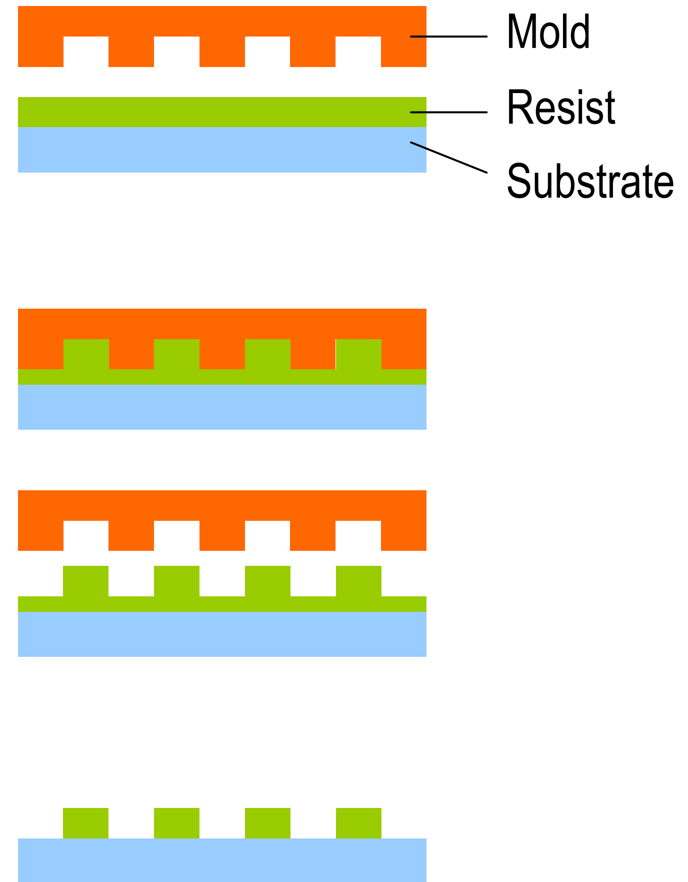
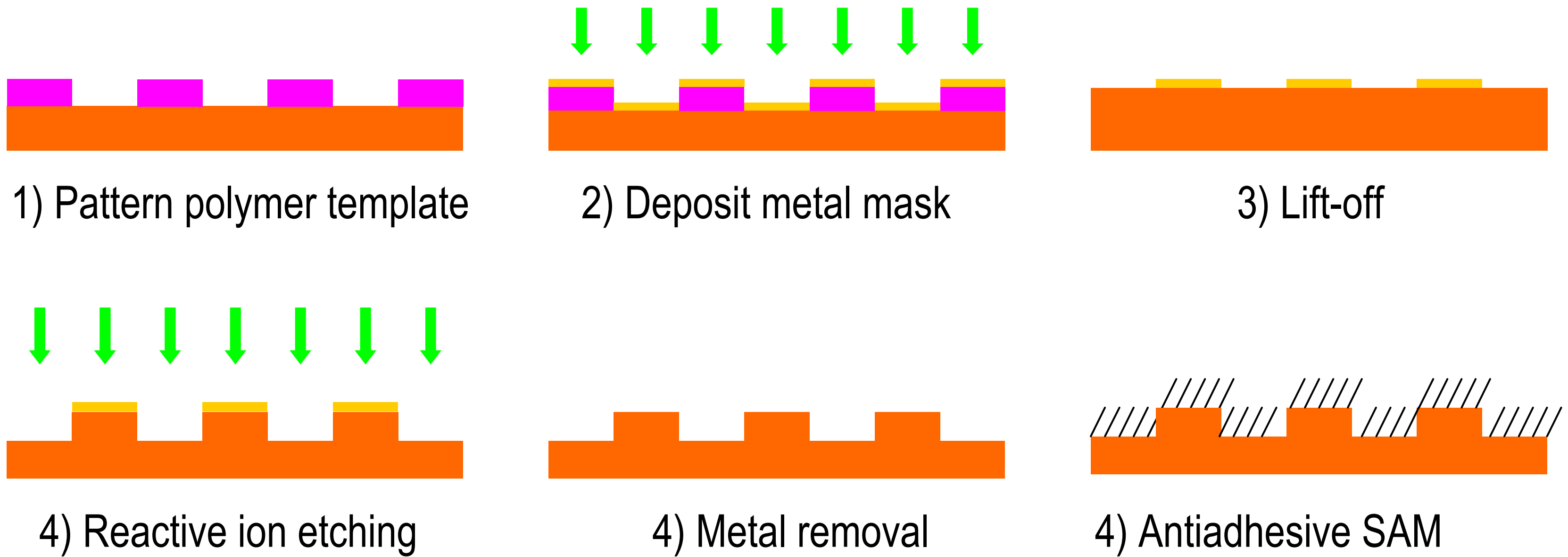
Nanoimprint lithography (NIL)

- A mold with nano-protrusions/holes prints a resist
- Thermal annealing and/or UV curing applied to shape the resist
- Mold is removed
- Pattern transfer by etching the residual layer



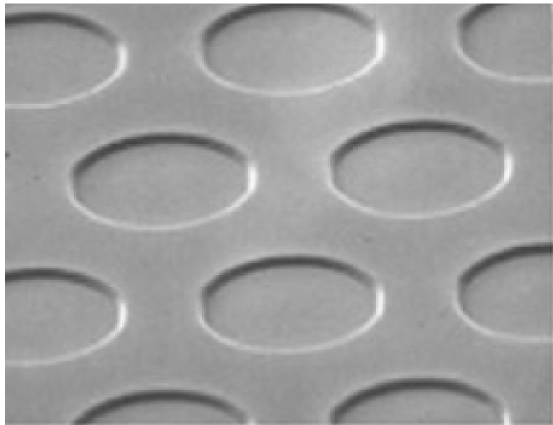
NIL molds fabrication

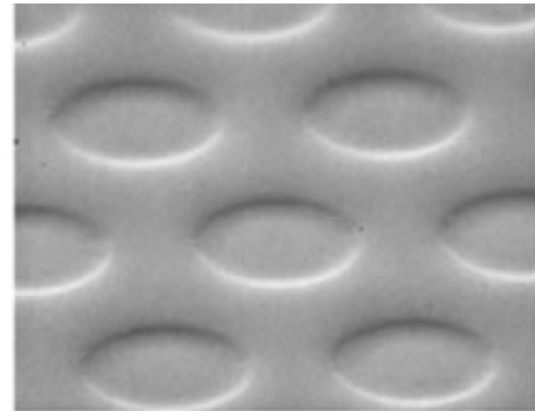
- Master mold patterned using EBL or FIB
- Antiadhesive coating (perfluorosilane) helps demolding
- Replication possible with NIL



Nanoimprint resists

- Resist must satisfy
  - Young's modulus $E_{resist} < E_{mold}$
  - Viscosity η low at imprint temperature
- Imprint pressure > shear modulus G_{resist}
- T_g > room temperature



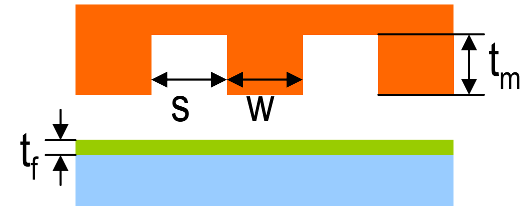


- Usual thermal resists: PMMA, PS

Full confinement

- FC if no residual layer:

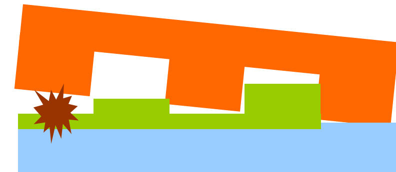
$$t_m > t_f \frac{W+S}{S}$$



- Prerequisite for graphoepitaxial alignment

- To avoid breaking the protrusions during imprint :

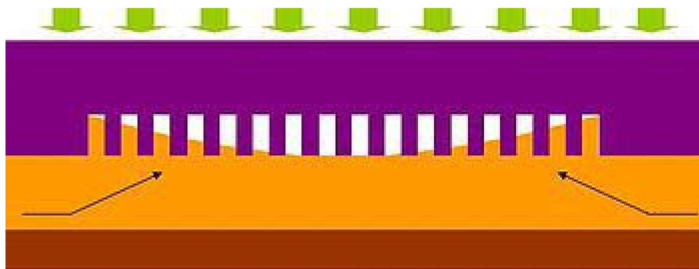
$$t_m = t_f \frac{W+S}{S}$$

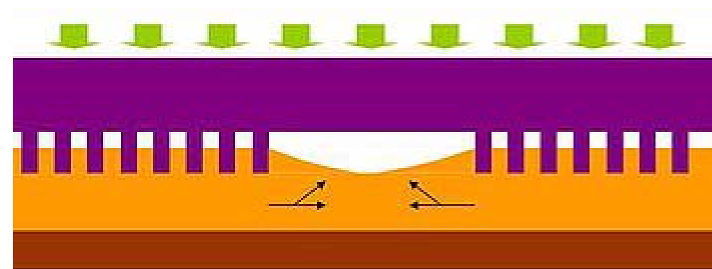


- Cleanness of the substrate critical

NIL proximity effects

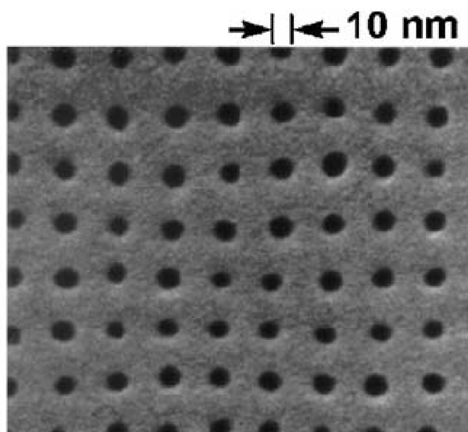
- Protrusions displace polymer => problems over long distances !
- Proximity effects for
  - Wide protrusions (imprint time $\propto \eta \times w^2$)
  - Mix of narrow and wide protrusions
  - Gaps between protrusions arrays
- To avoid proximity effects:
  - Periodic array of identical small protrusions

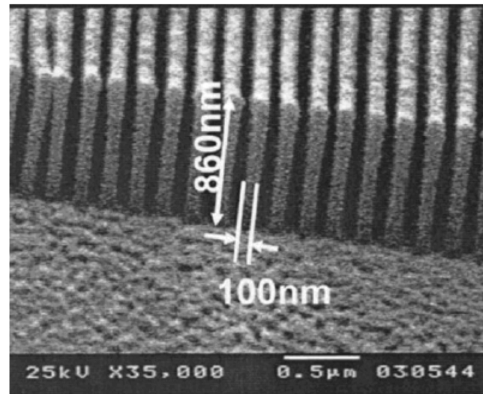


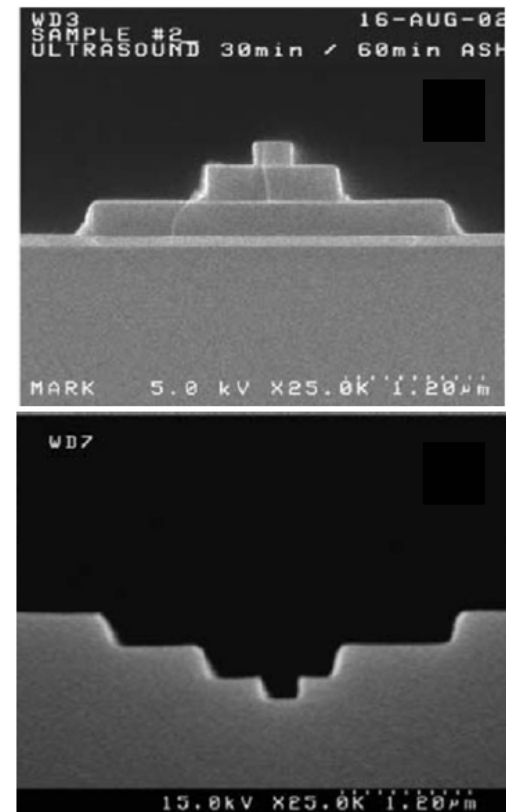


Nanoimprint advantages

- Resolution down to 10 nm
- High aspect ratio nanostructures
- 3D architectures in one step/resist
- No limitation to the imprint area
- Broad range of resists







J. Guo *et al., Adv. Mater.* **2007**, 19, pp 495–513

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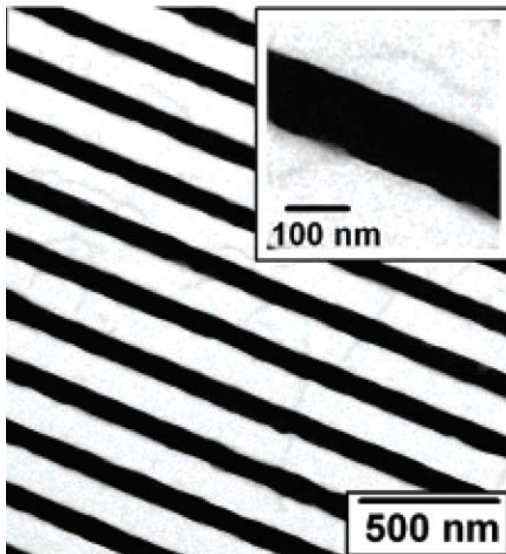
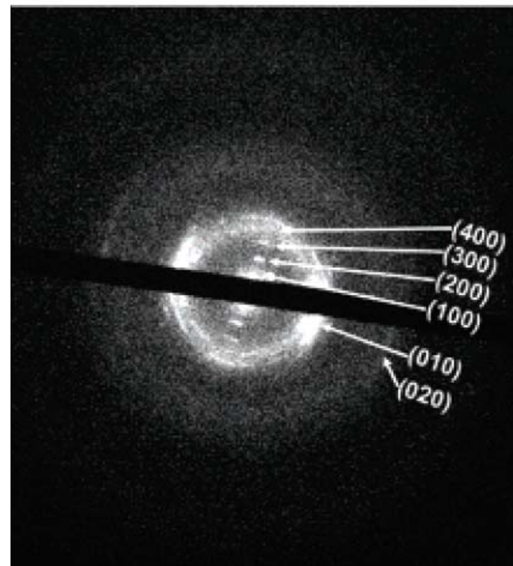
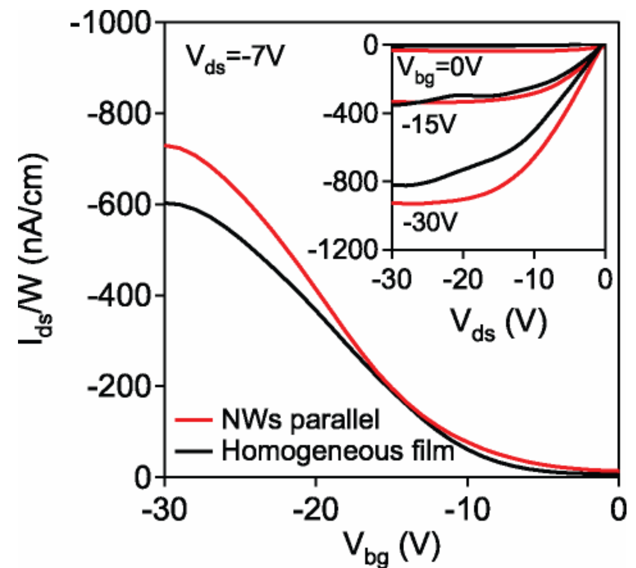
π-conjugated polymers

- Resist: PQT
- Mold: 200nm-wide lines
- Imprint: aligned PQT chains with enhanced field effect



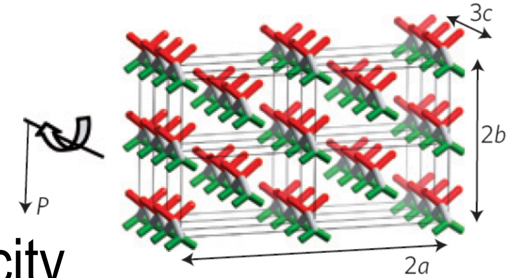


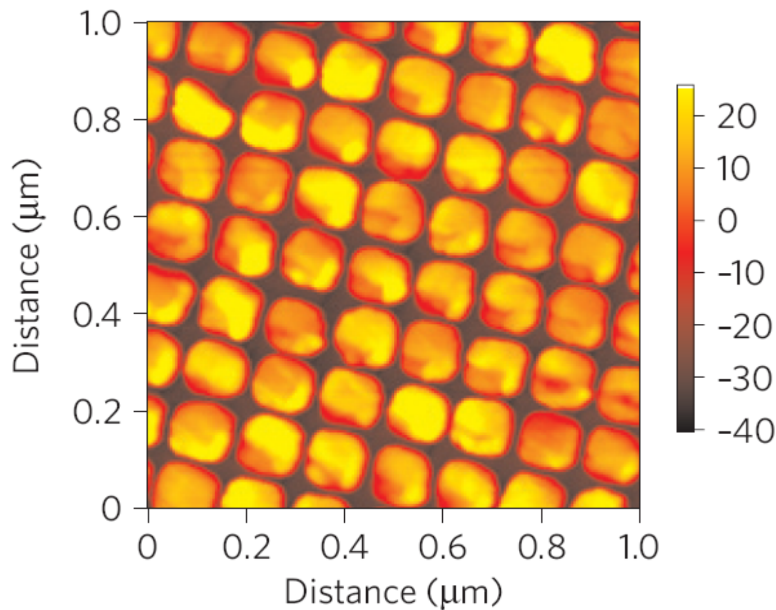


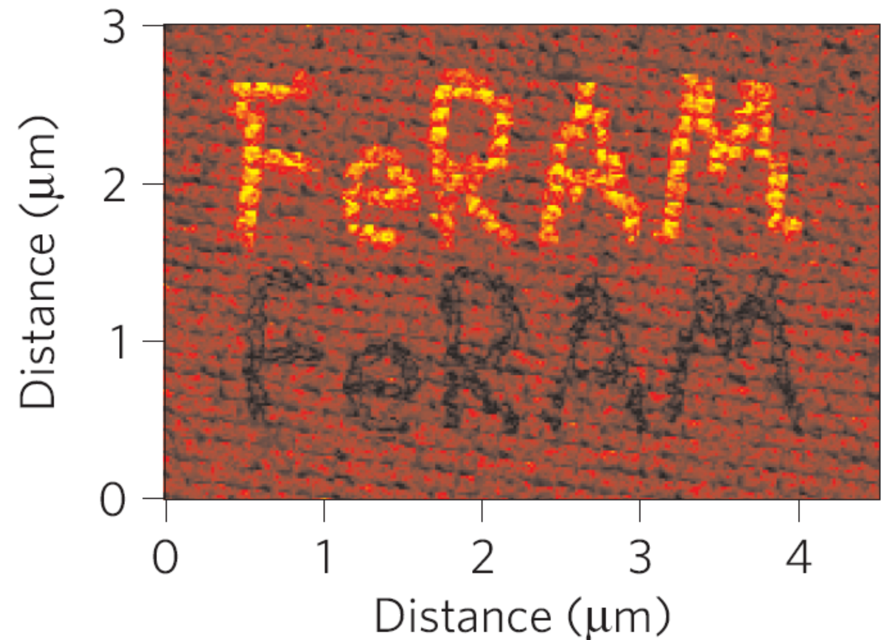
Z. Hu *et al., Nano Lett.* **2007**, 7, pp.3639 – 3644.

Ferroelectric memories

- Resist = PVDF (poly-vinylidenefluoride)
- Mold = square 100nm x 100nm nanocavities
- Imprint = monodomains with increased ferroelectricity







Z. Hu *et al., Nature Mat.* **2009**, 8, pp 62-67

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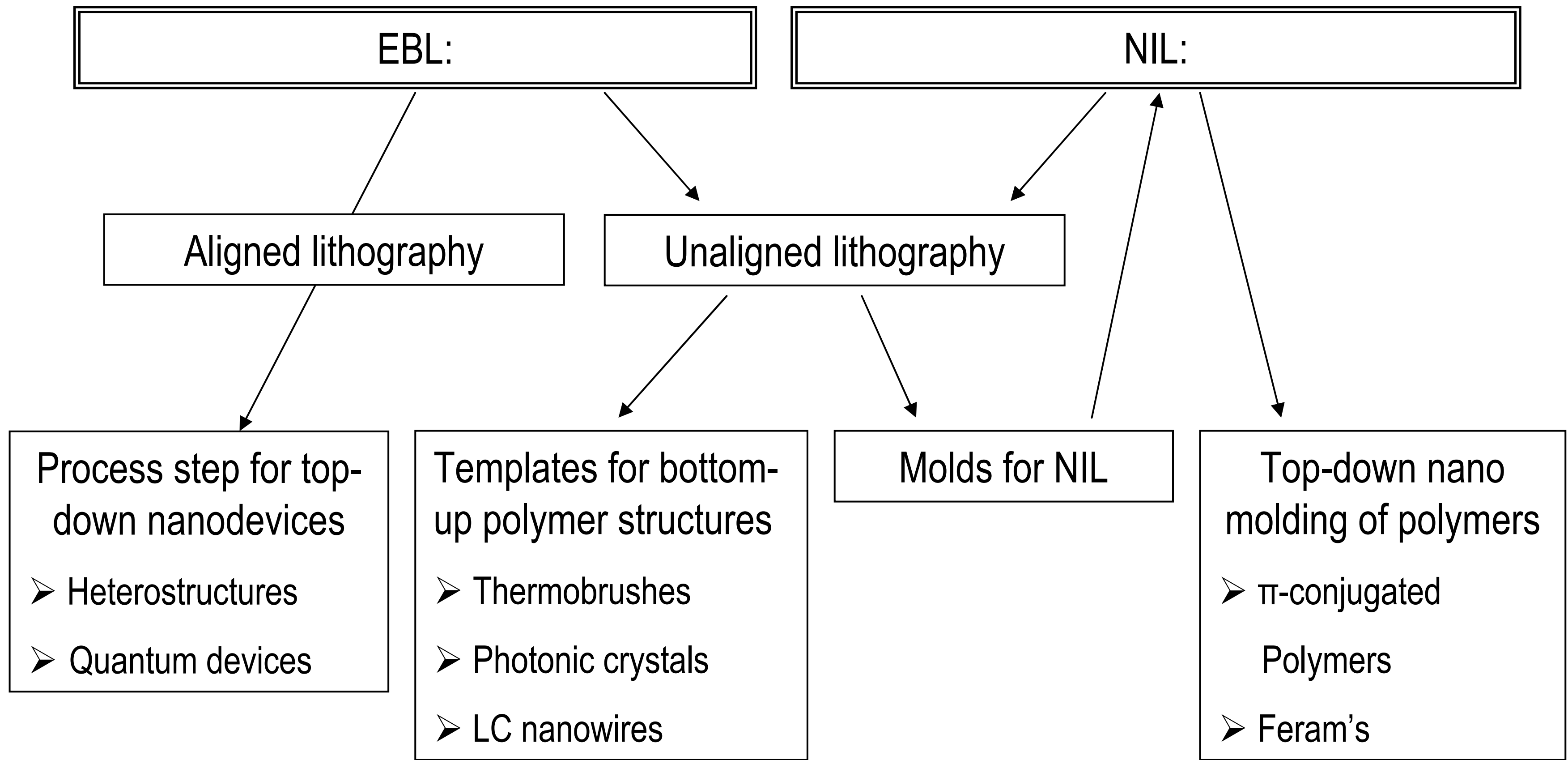
EBL and NIL for polymers



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Conclusion

EBL:	NIL:
👍 Software-generated pattern	👎 Master mold required
👍 Easy to align	👎 Difficult to align
👎 Very slow	👍 Fast (down to 15min/wafer)
👎 Cost > 500k€	👍 Cost > 100k€

- EBL and NIL are highly complementary for top-down nanofabrication
  - Time
  - Physic of writing process
  - Flexibility pattern/resist

Acknowledgements

- A. Jadin, from Certech ASBL
- POLY & DICE labs
- IMCN institute
- Winfab Cleanroom facilities
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- Slide n°8: F. Montaigne
- FNRS fundings
- You for your attention