Nanometer Scale Patterning and Processing

Spring 2016

Lecture 32

Nanoimprint Lithography (NIL) – Overview and Thermal NIL Resists

Nanoimprint lithography (NIL)

1. Overview.
2. Thermal NIL resists.
3. Residual layer after NIL.
4. NIL for large features (more difficult than small one).
5. Room temperature NIL, reverse NIL, inking.
6. NIL of bulk resist (polymer sheet, pellets).

Nanoimprint: Mechanical Replication

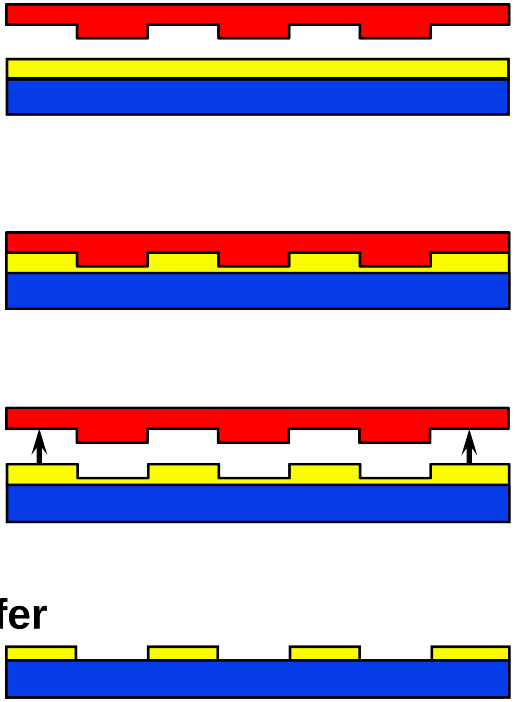
1. 1970´s compact disks (CD).
2. 1996, Nano-Imprint Lithography (NIL), sub-10 nm feature size achieved.
3. Today, NIL is one candidate (though not top candidate) for next-generation lithography for IC industry.
4. NIL has the highest resolution (sub-5nm) and is fast. It will come into play when no other lithography can do the job.

Two Approaches of NIL

Thermal-NIL (T-NIL)

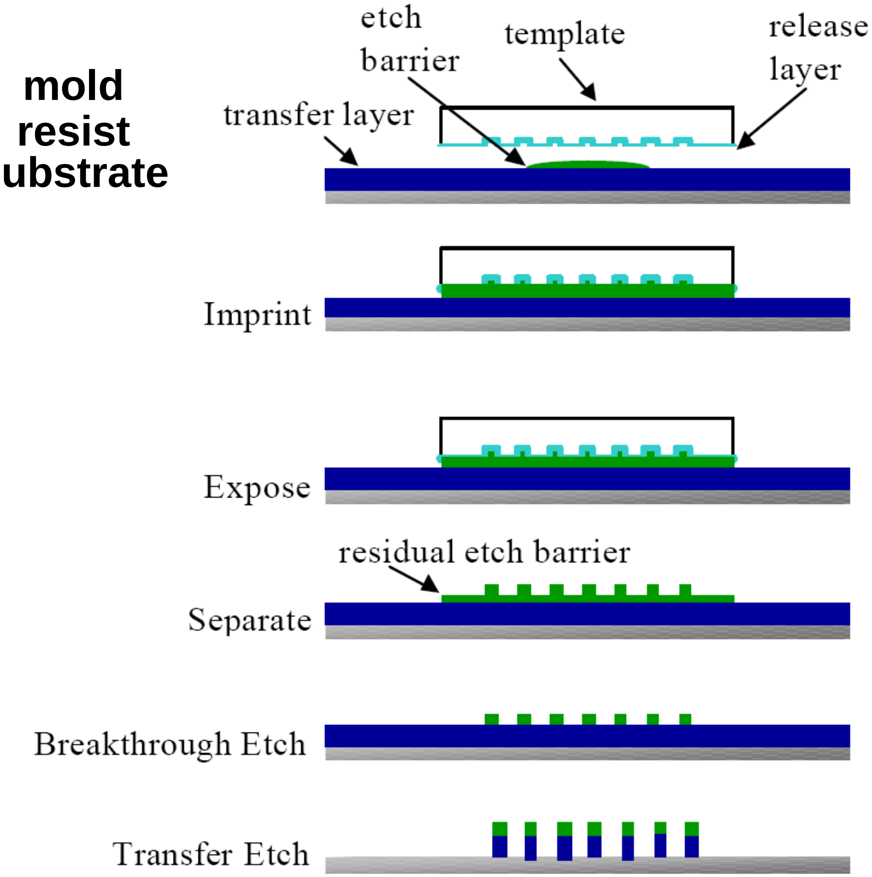
1. Imprint
- **Press Mold**
- **Remove Mold**

2. Pattern Transfer
- **RIE**



Commercial Vendor: NanoNex
(started by Prof. Stephen Chou)

Step-and-Flash NIL (SFIL)



Commercial Vendor: Molecular Imprint
(started by Prof. Grant Willson, *etc.*)

Comparison

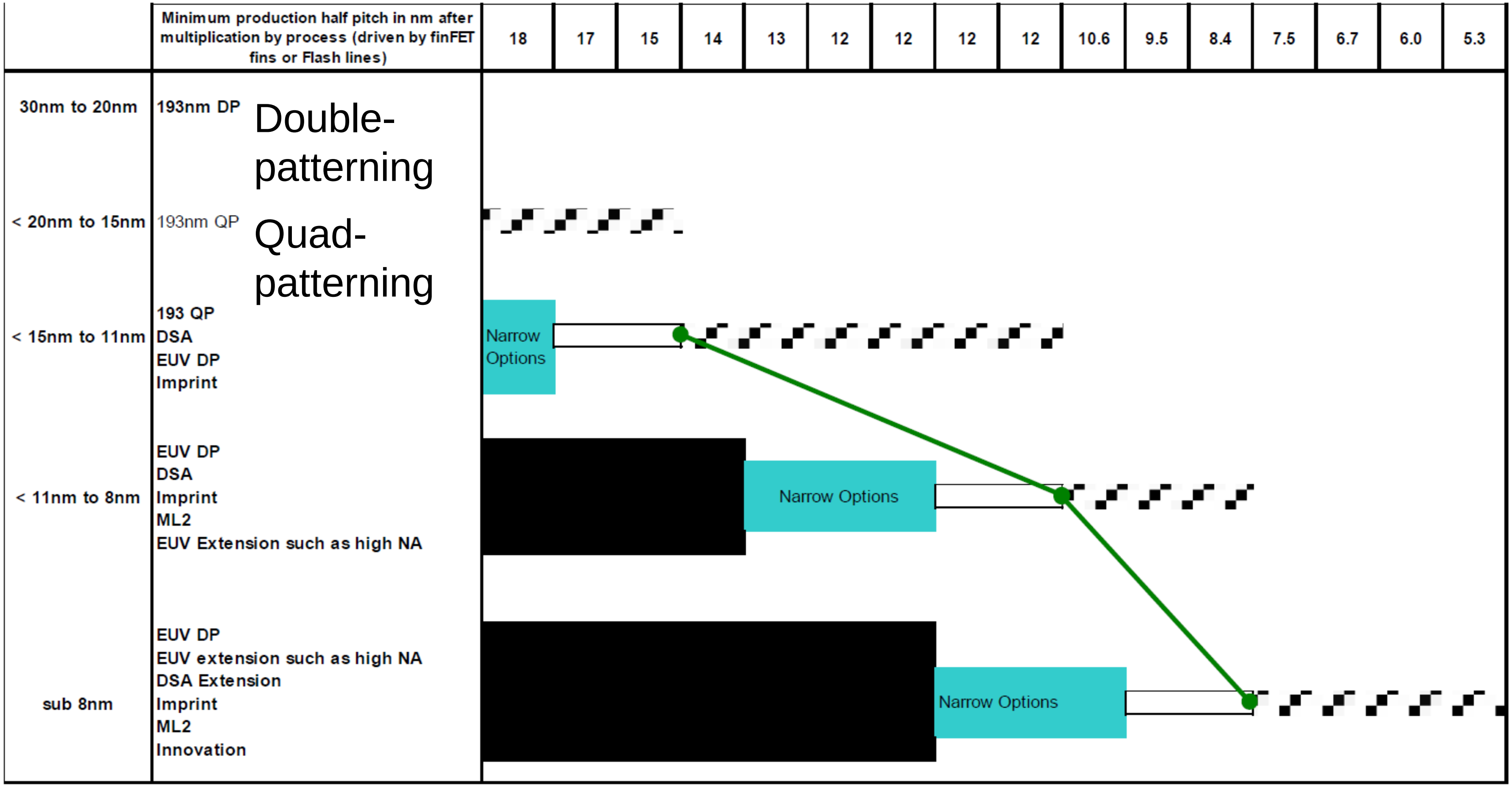
	Thermal	UV
Resist material	Thermoplastic or thermal-set (i.e. cured upon heating)	UV-sensitive monomer plus various additives
Resolution	Sub-5nm	2nm demonstrated, but volume shrinkage after cross-linking
Temperature	30-100^{o}C above T_g	Room temperature
Pressure	Normally over 10 bar	~ 1 bar, or higher
Resist application	Spin coating, easy	Spin coating or drop
Resist thickness	Up to many μm, easy for pattern transfer	Typically < 100nm, need an extra transfer layer
Cycle time	1-30 min, slow	~1 min
Large features	~100 μm, difficult	Relatively easy, low viscosity
Alignment	~ 1 μm, difficult; CTE mismatch	20nm demonstrated
Application	Broad range, simple and work with many materials	Targeted for semiconductor industry with alignment

T_g: glass transition temperature CTE: coefficient of thermal expansion

International Technology Roadmap for Semiconductors (ITRS)

- An industry consortium that guides or dictates the semiconductor technologies
- http://public.itrs.net/
- Latest Roadmap can be downloaded at: http://www.itrs.net/Links/2013ITRS/Home2013.htm

NIL always a candidate for IC Manufacturing



	Minimum production half pitch in nm after multiplication by process (driven by finFET fins or Flash lines)	18	17	15	14	13	12	12	12	12	10.6	9.5	8.4	7.5	6.7	6.0	5.3
30nm to 20nm	193nm DP Double-patterning																
< 20nm to 15nm	193nm QP Quad-patterning																
< 15nm to 11nm	193 QP DSA EUV DP Imprint	Narrow Options															
< 11nm to 8nm	EUV DP DSA Imprint ML2 EUV Extension such as high NA					Narrow Options											
sub 8nm	EUV DP EUV extension such as high NA DSA Extension Imprint ML2 Innovation								Narrow Options								

Legend indicates the time frame in which research, development, and qualification/pre-production should be taking place for a given half pitch rangefor the solution.

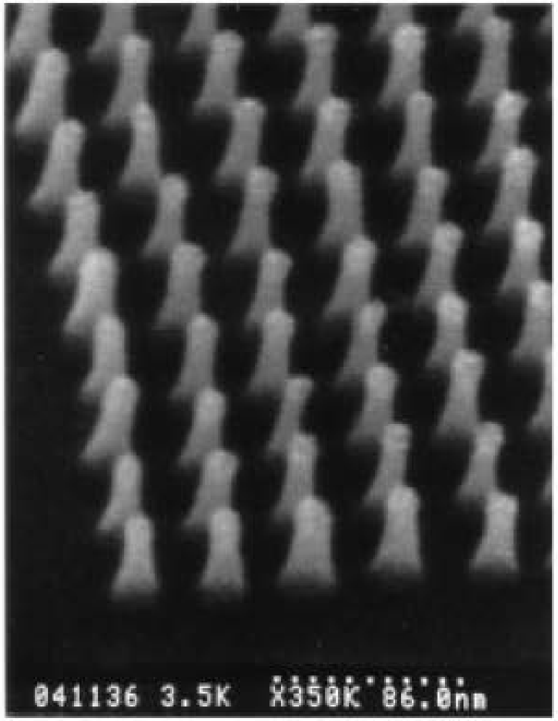
Research Required ■
Development Underway 🟦
Qualification / Pre-Production ☐
Continuous Improvement ▞

ITRS (2013) Projections for Lithography Technology

DSA: Directed self-assembly, ML2: maskless lithography (EBL, SPM..)

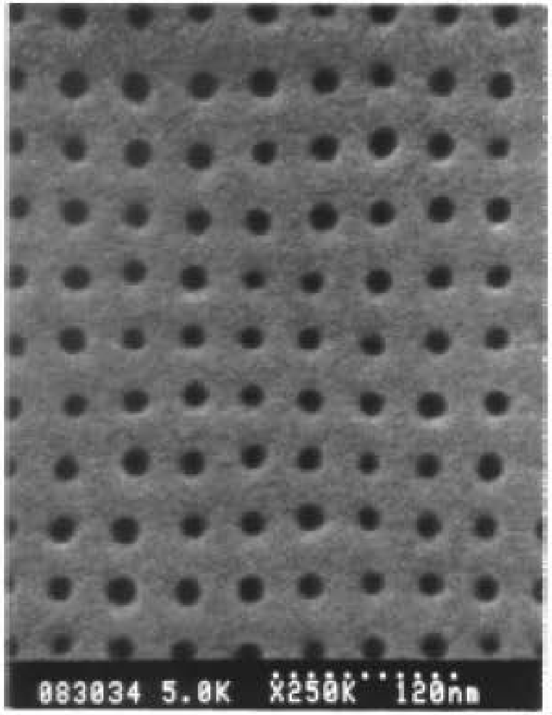
Key advantage of NIL: highest resolution

Mold



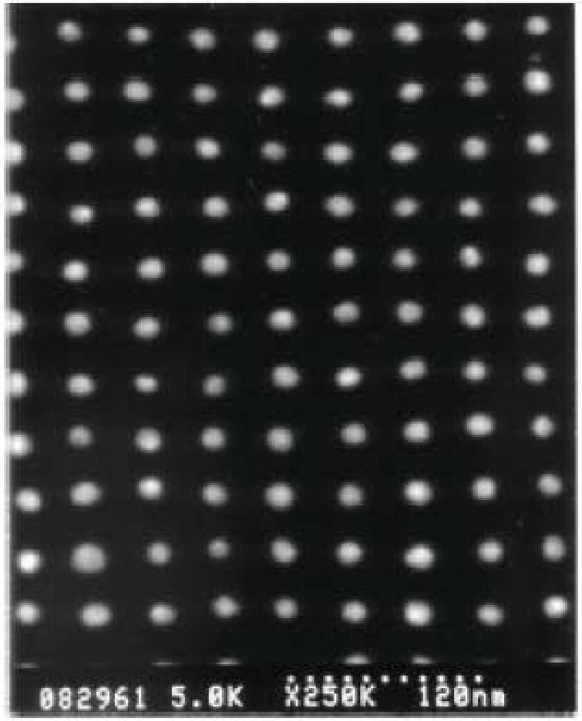
10 nm dia pillar mold

Resist



10 nm dia resist holes by imprinting

Lift-Off

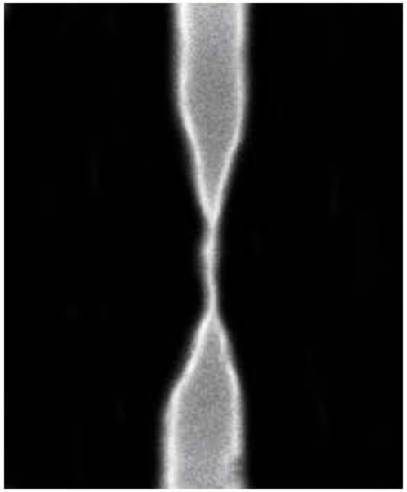


10 nm dia metal dots by imprint and lift-off

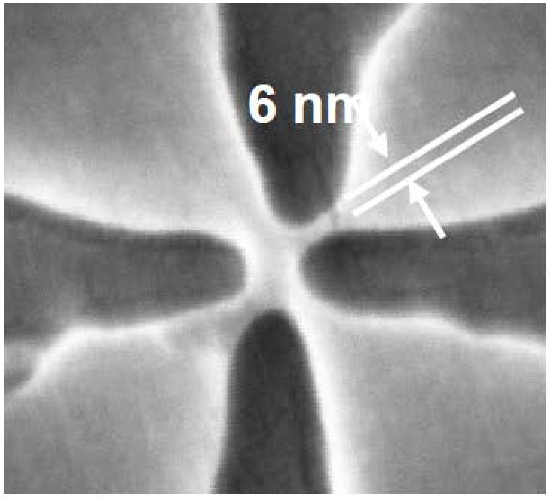
Key advantage of NIL: extremely high resolution

Sub-5 nm features and 14nm pitch nanoimprint

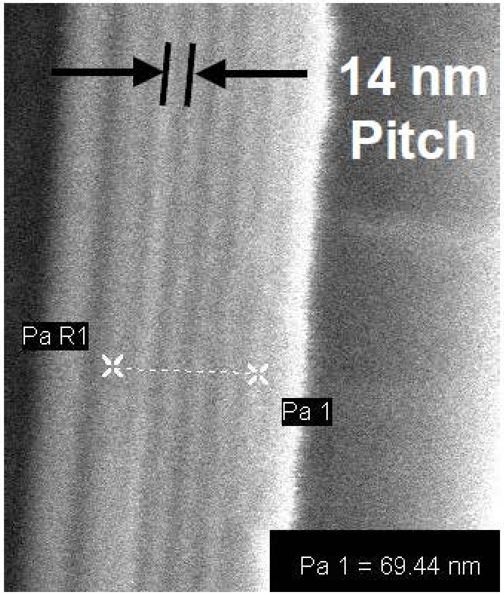
5 nm
Line



6 nm
Line



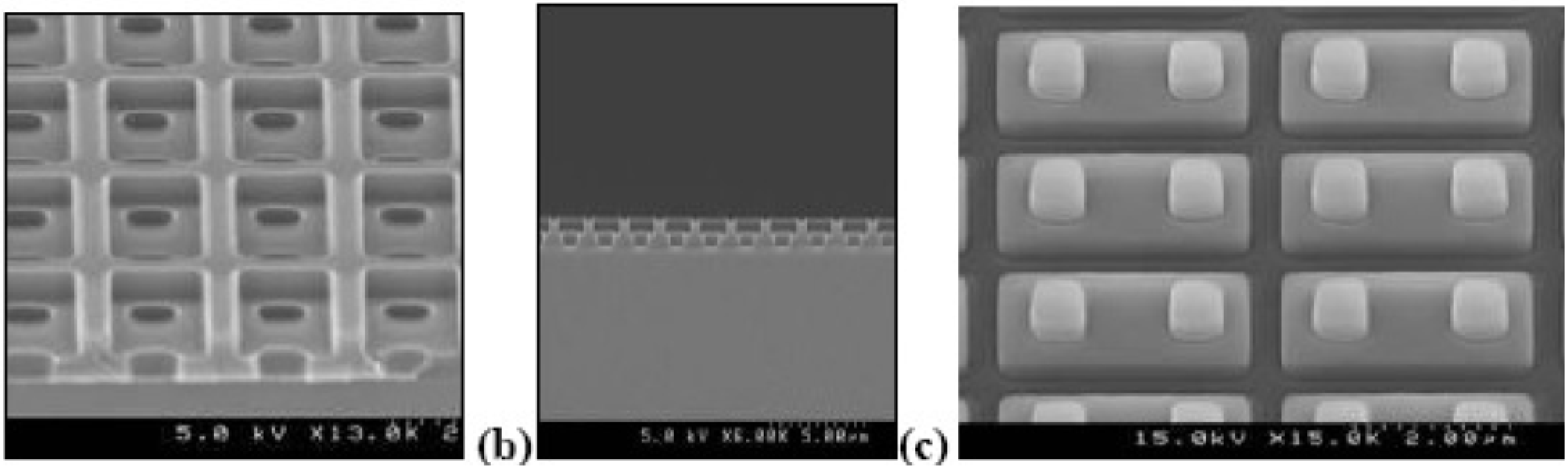
14 nm
Pitch



Yet, feature size and pitch still limited by mold making. They can go smaller.

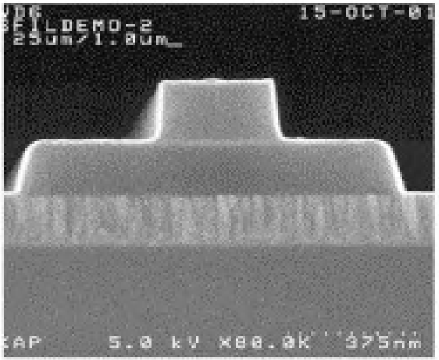
No more light diffraction limit, charged particles scattering, proximity effect…
Sub-10nm feature size, over a large area with high throughput and low cost.

Another key advantage: 3D imprinting

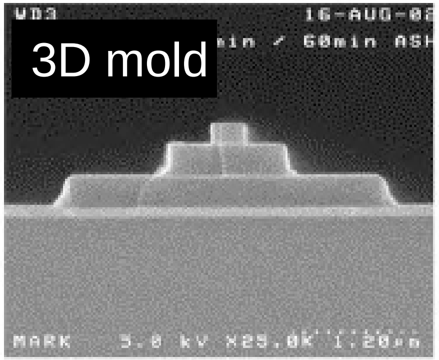


- Patterning of the via and interconnect layers simultaneously, in CMOS BEOL .
- Potentially reduces the number of masking levels needed in BEOL.

(BEOL: back end of line)



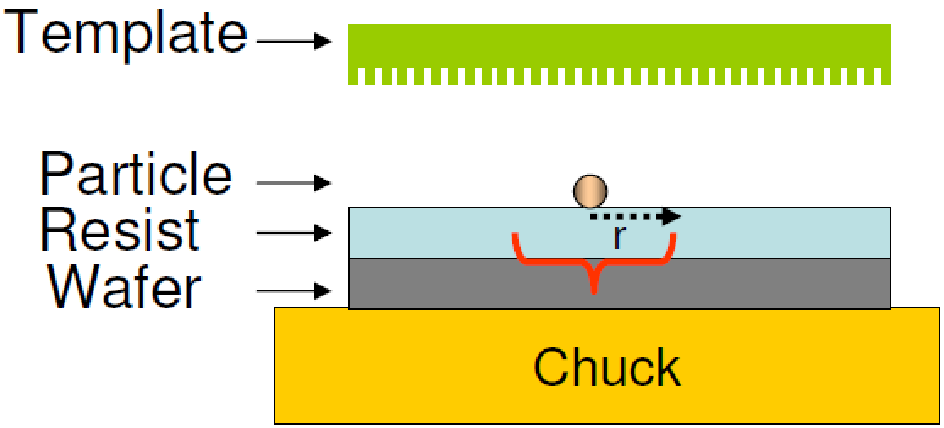
2 tier, using oxide/ITO


3D mold

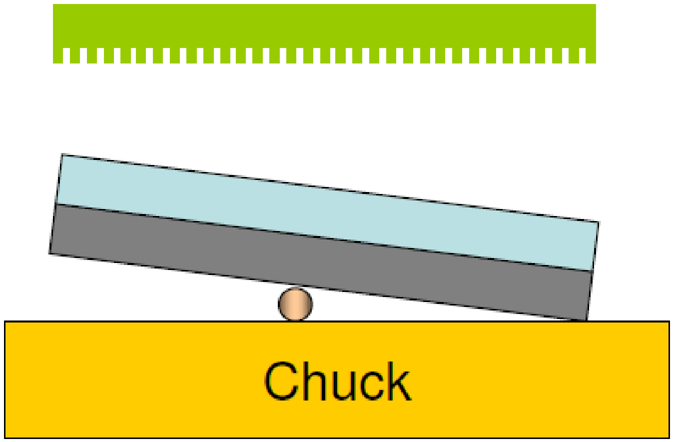
3 tier using oxide/ITO

Wikipedia: **Back end of line** (**BEOL**) is the portion of integrated circuit fabrication line where the active components (transistors, resistors, etc.) are interconnected with wiring on the wafer. BEOL generally begins when the first layer of metal is deposited on the wafer. It includes contacts, insulator, metal levels, and bonding sites for chip-to-package connections.

Imprinting in presence of a dust particle



Region (area) of no imprint due to template not making contact with resist as a result of the presence of the particle



Wafer will crack!!!

Dust is one of the most serious problem for NIL, defect area>>>>>dust size.

To prevent mold wafer breaking, sandwich the mold/substrate stack with something soft, such as a paper or plastic.

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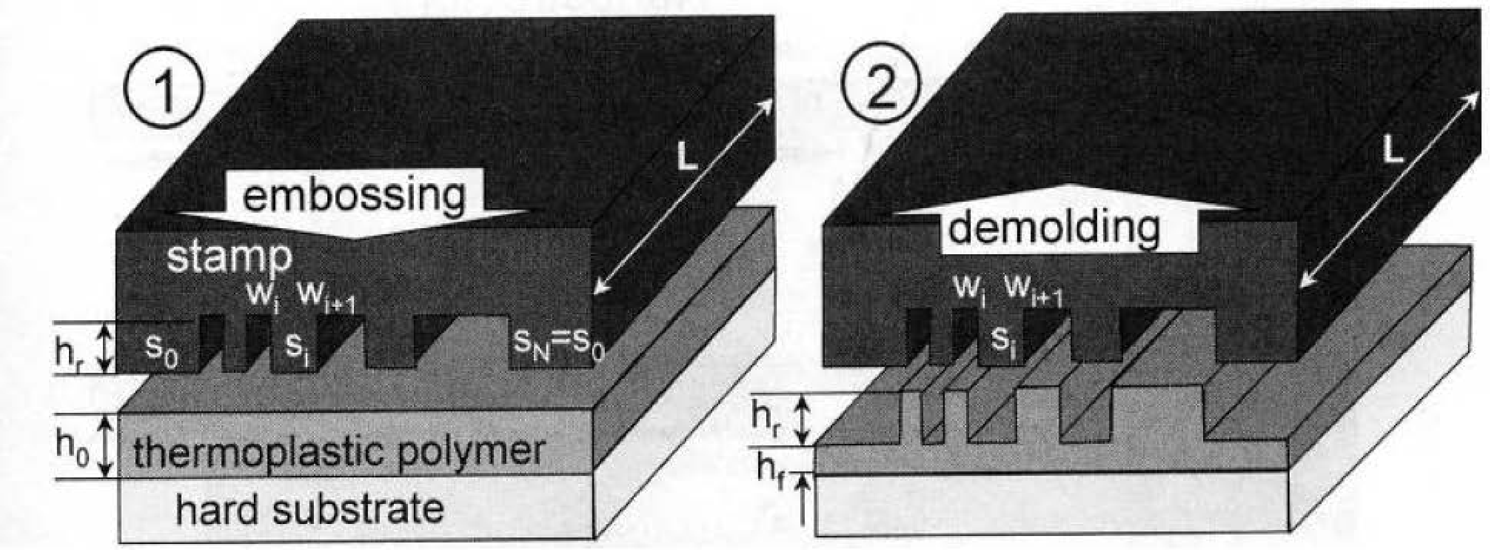
- Section 1

MATERIAL AND MECHANISM OF THERMAL NANOIMPRINT

Desired Resist Properties for NIL

- No adhesion to the mold during separation.
- Low viscosity during imprinting.
  - Low imprint pressure and temperature.
- Sufficient thermal stability in subsequent processes, e.g. RIE, lift-off.
  - High plasma etch resistance for pattern transfer into under-layers.
- Minimal shrinkage (for UV and thermal curable resist).
- Other general lithography requirements
  - Good adhesion to the substrate, uniform film thickness, easy spinning.
  - High pattern transfer fidelity
  - Soluble in non-toxic solvents, deposition by spin-coating.
  - Mechanical strength and tear resistance.

Initial Resist Thickness



$$h_0\sum_{i=1}^{N}(s_i+w_i) \;=h_f\sum_{i=1}^{N}(s_i+w_i)+h_r\sum_{i=1}^{N}w_i$$

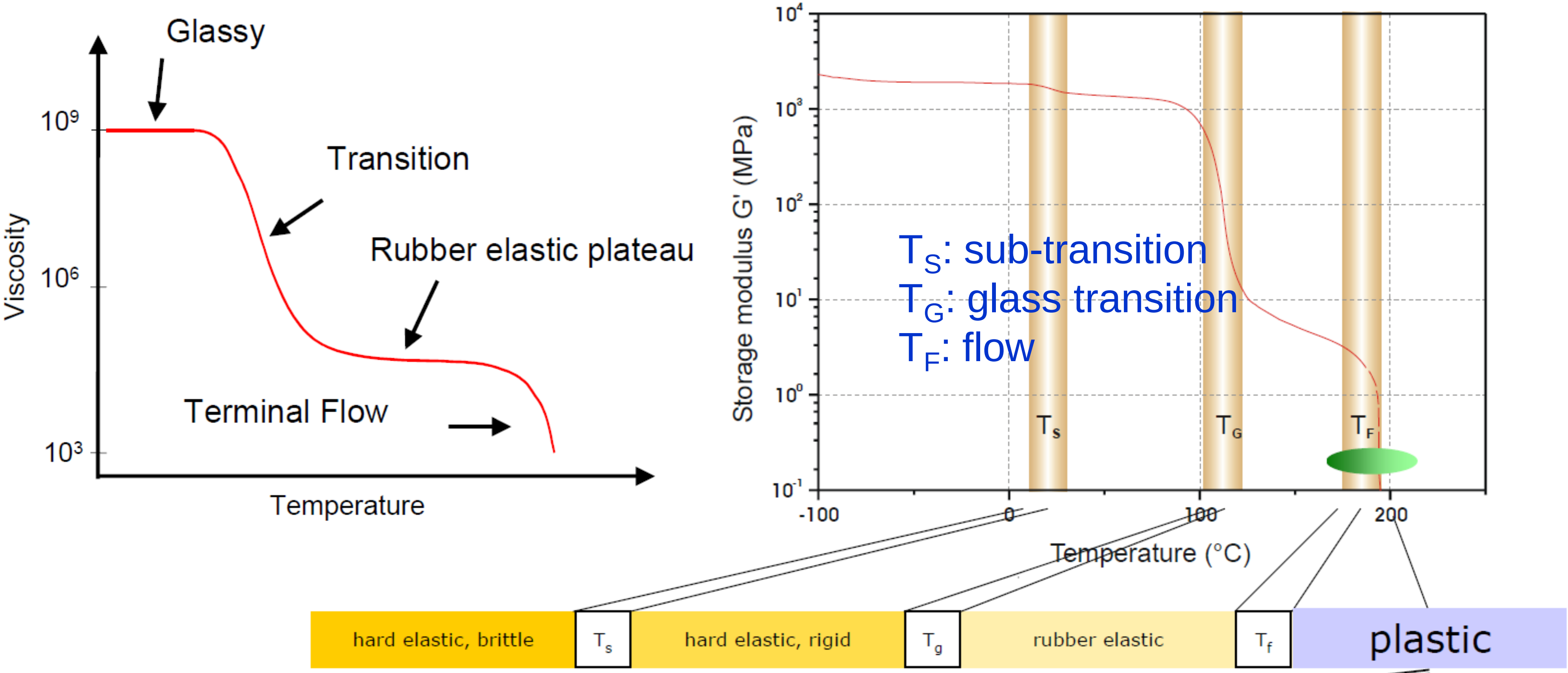
$$h_0=h_f+\frac{h_r}{\sum_{i=1}^{N}(s_i+w_i)}\sum_{i=1}^{N}w_i$$

- Polymer is not compressible, so conservation of volume.
- Too thick h_0 leads to large h_f, difficult for pattern transfer.
- Too thin h_0 increases mold wear and damage.

Alternative Lithography: Unleashing the Potentials of Nanotechnology (book), 2003.

First Resist for NIL: PMMA

Glass transition and flow temperature of PMMA

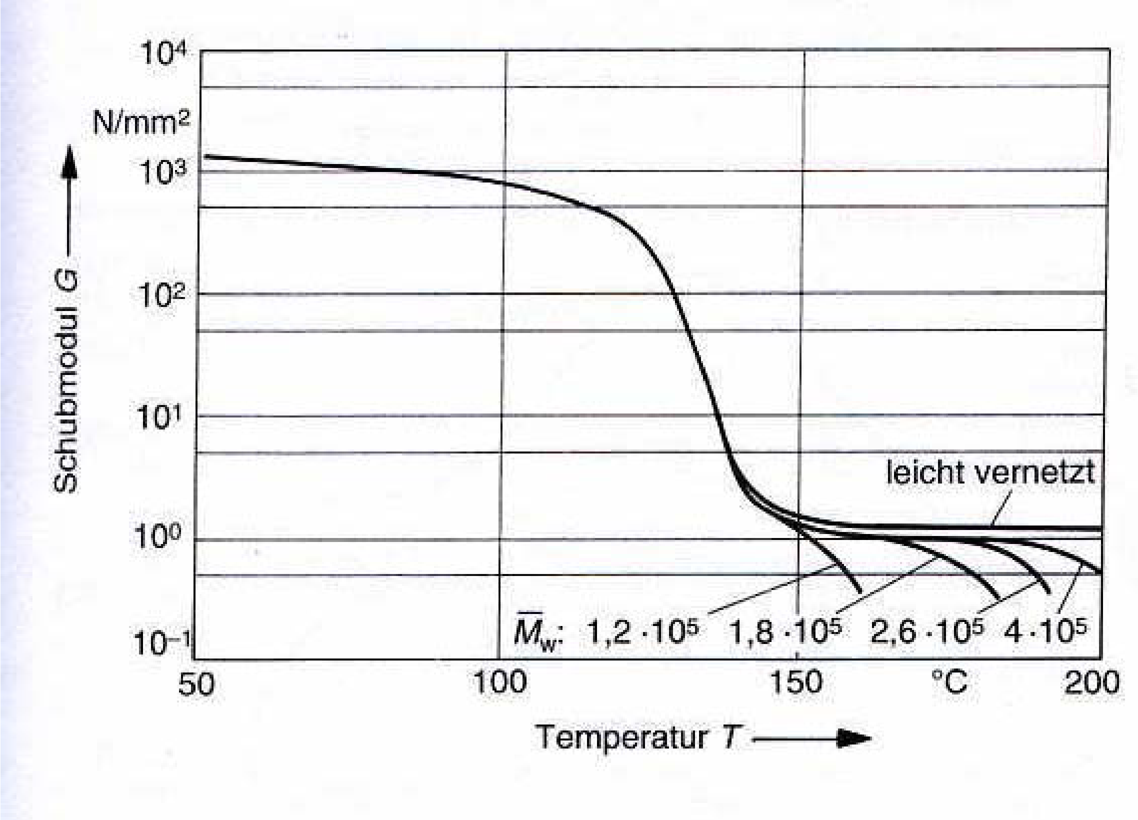


Temperature range for NIL

However, PMMA is far away from being an ideal NIL resist. It is popular simply because people are familiar with it (since it is resist for many other lithography).

Shear modulus of different molecular weight PMMAs

Flow temperature of PMMA (and other amorphous polymers) increases with increasing molecular weight.



Comments:

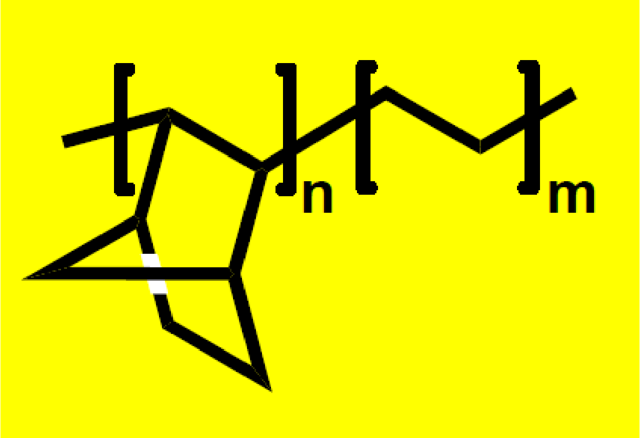
PMMA is the choice for beginners, not optimized for NIL. T_g=105°C, NIL at >150°C.

Polystyrene (T_g close to PMMA) is slightly better – easy separation due to lower surface energy.

Poly(vinyl phenyl ketone) is comparable to polystyrene but with T_g only 58°C. NIL at 95°C.

Another thermal NIL resist: TOPAS polymers

TOPAS: Cyclic olefinic copolymer (norbornene and ethylene)



Attractive properties:

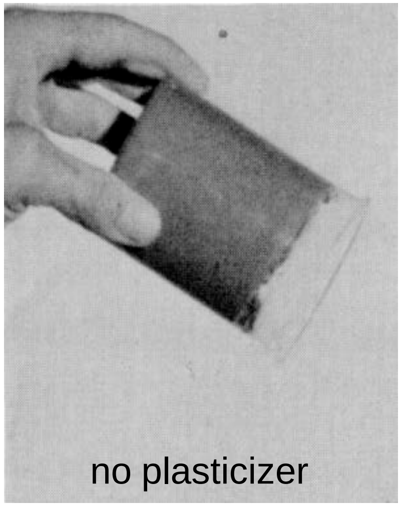
- very un-polar
- very low water absorption
- high optical transparency (>300 nm)
- high chemical resistance
- low surface energy
- high plasma etch resistance

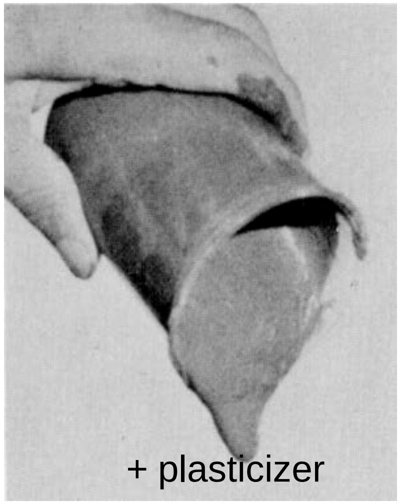
But finding solvent system giving homogeneous and stable solutions is not an easy task (chemical resistance, hard to dissolve)

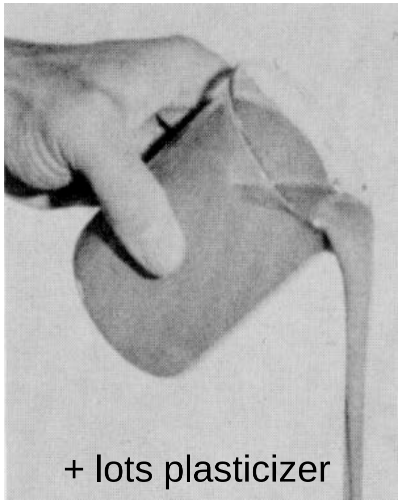
Applications: lab-on-a-chip micro-fluidic system…

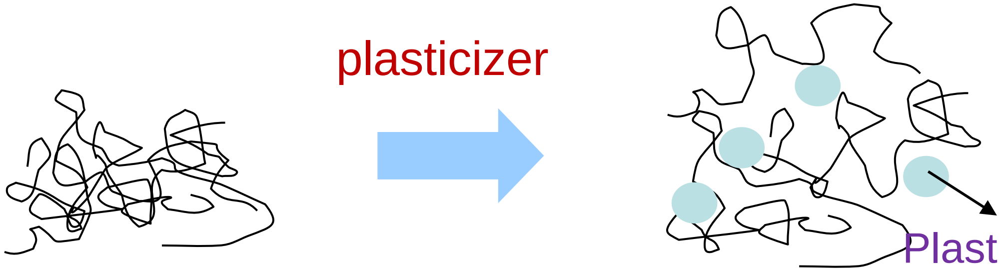
Commercial Topas solutions: (from Micro-Resist)
  mr-I T85 with Topas grade 8007
  mr-I T65 with Topas grade 9506
Similar product: Zeonor from Zeon or Zeonex

T_g can be lowered by adding plasticizer into the resist


no plasticizer


+ plasticizer


+ lots plasticizer


plasticizer

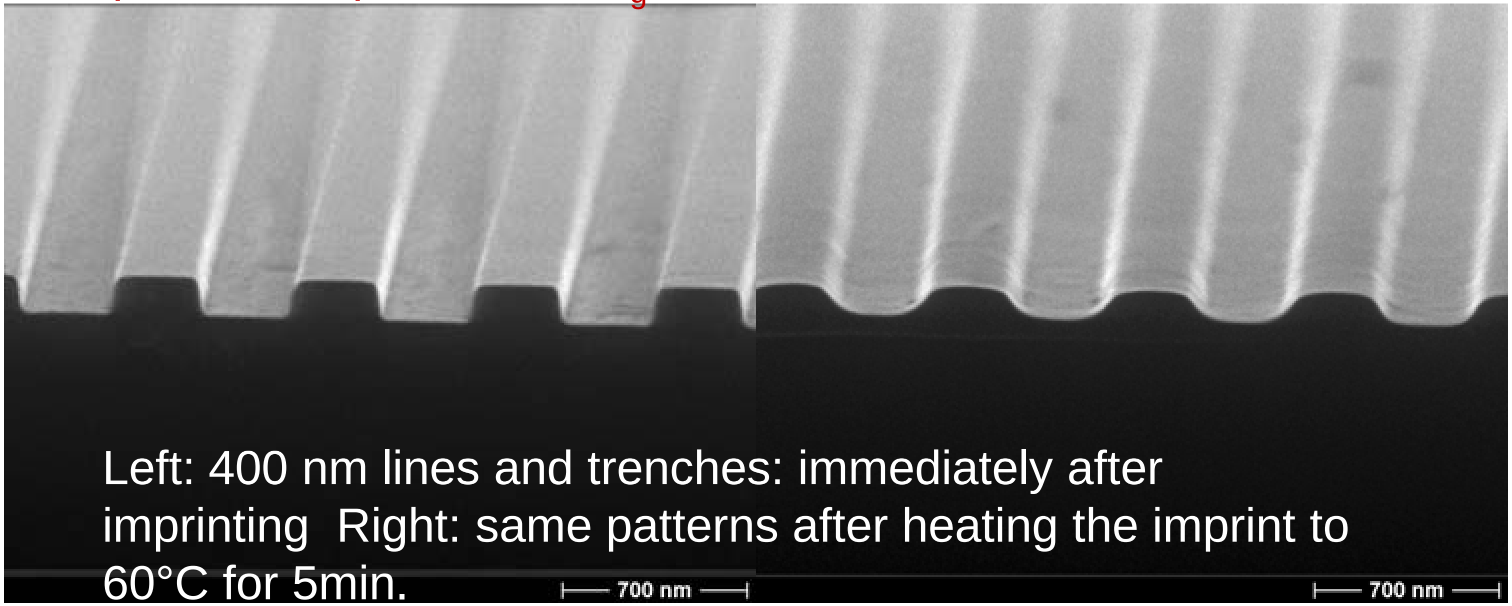
Plasticizer: monomers, solvents, small molecules

Plasticizer: decreased chain entanglement
increased chain motion

Polymer with low T_g

- Low imprint temperature
- Good polymer flow at moderate temperature
- Less problems with thermal expansion
- Shorter cycle time due to faster reaching the imprint temperature (?)
- Not always, cooling to ambient temperature takes long time, not heating.

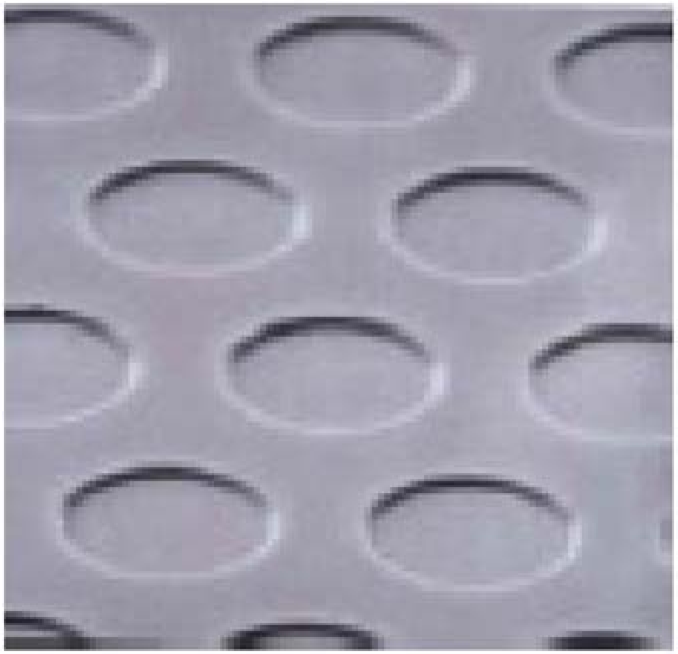
Example: thermoplastic with T_g 40 °C



Left: 400 nm lines and trenches: immediately after imprinting Right: same patterns after heating the imprint to 60°C for 5min.

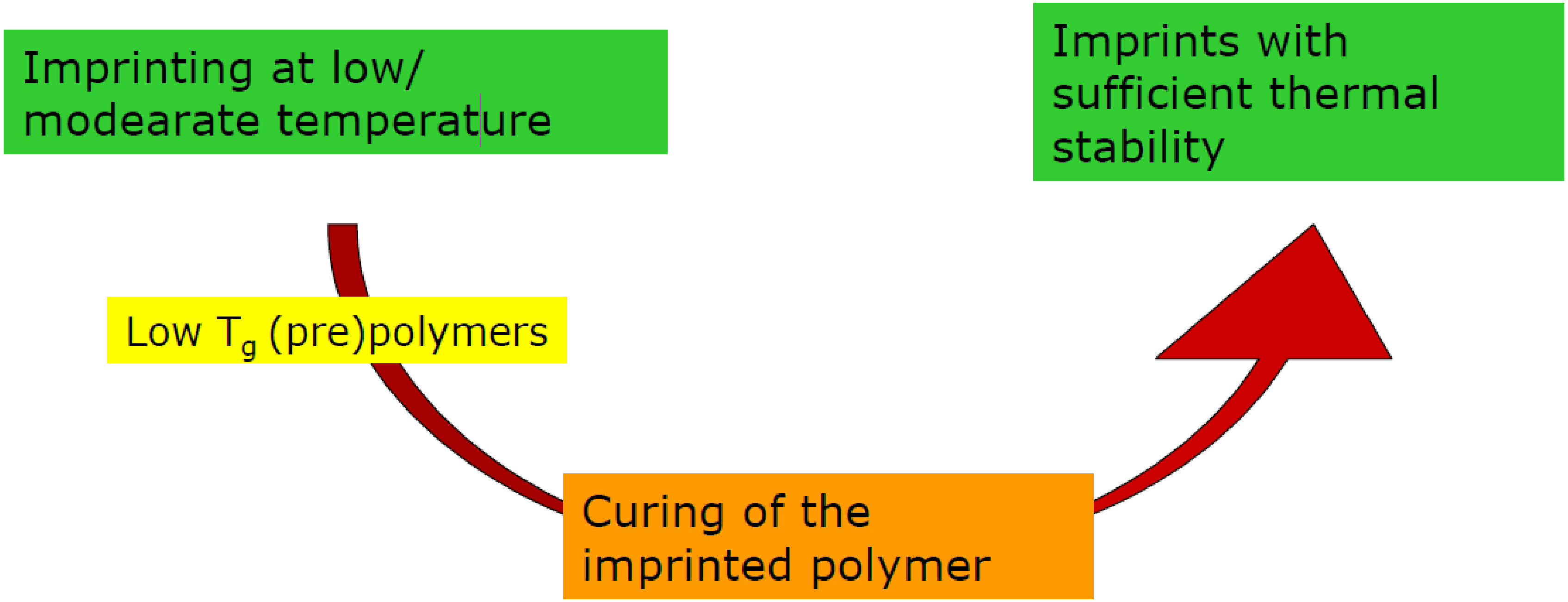
- Thermal stability of imprinted patterns (deterioration by thermal flow) is determined by the glass transition temperature.
- Sufficient thermal stability of imprinted patterns is necessary in subsequent processes such as metal evaporation for liftoff or plasma etching.

If T_g is too low…



10 days after imprinting a low T_g resist

Approach to thermal stability



Imprinting at low/ modearate temperature

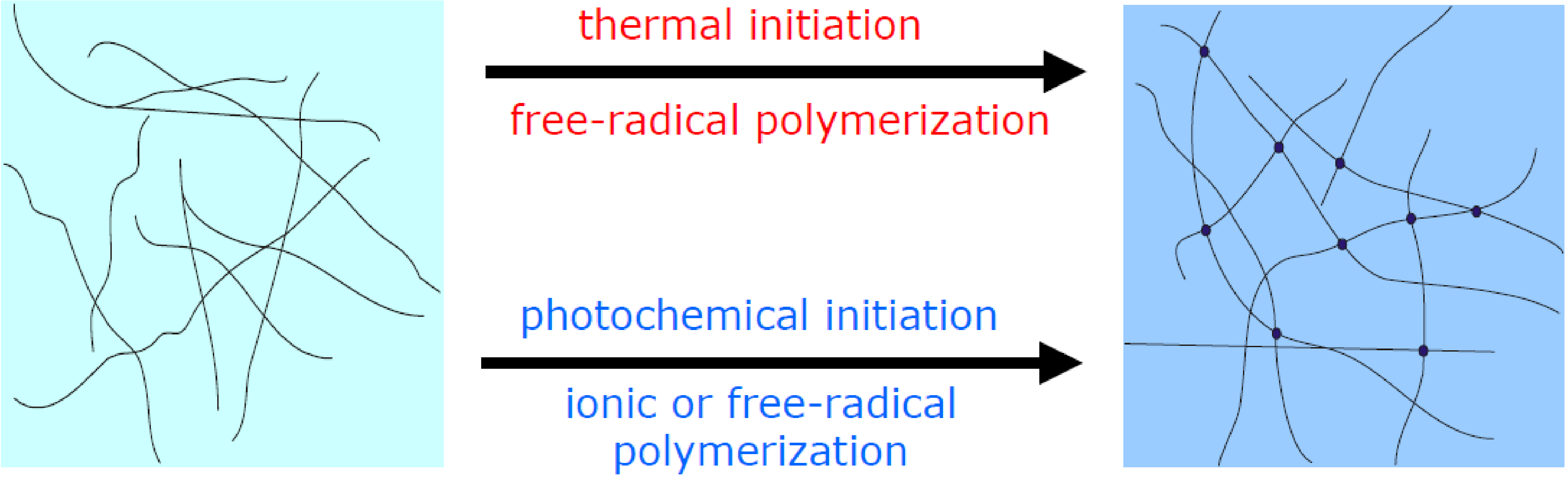
Low T_g (pre)polymers

Curing of the imprinted polymer

Imprints with sufficient thermal stability

Thermal-set/curable resist: polymer is cured (cross-linked) upon heating, making it stable at very high temperatures.

Thermal and photochemical curing



thermal initiation

free-radical polymerization

photochemical initiation

ionic or free-radical polymerization

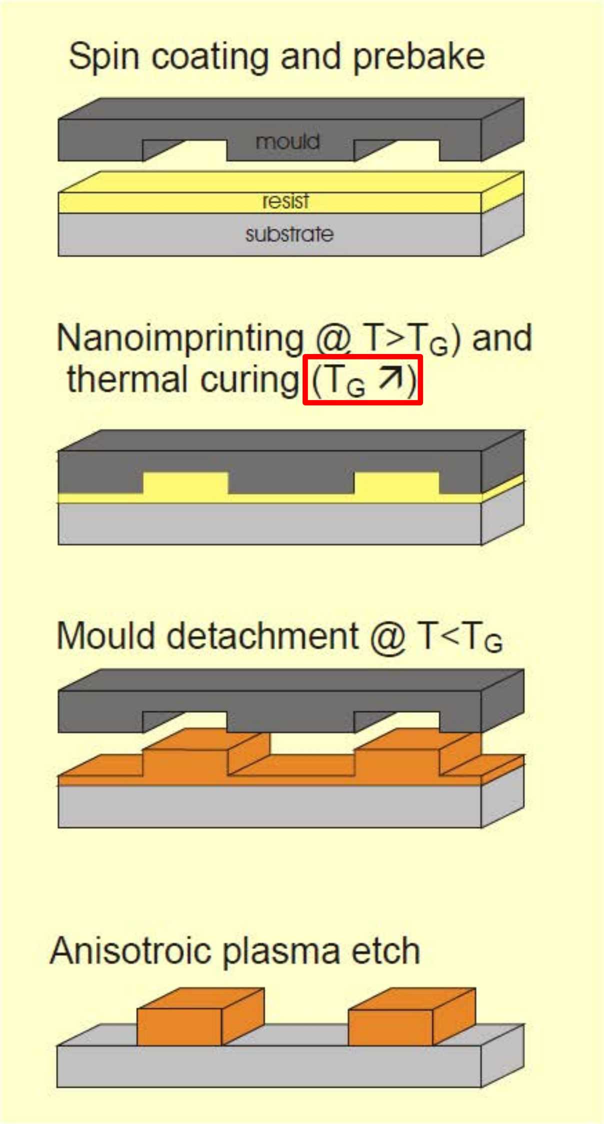
Linear or branched thermoplastic (pre)polymer

Cured polymer

Curing:

Cross-linking of the macromolecules, generation of a spatial macromolecular network.

Imprinting thermally curing polymer mr-I 9000E

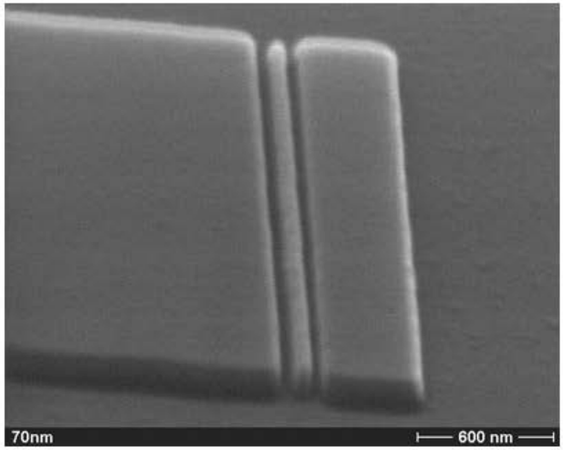


Spin coating and prebake

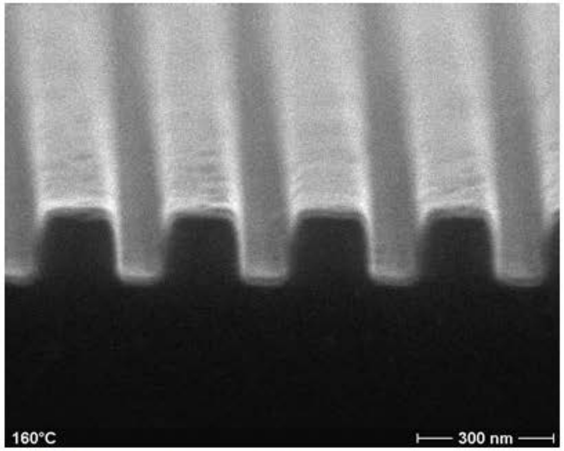
Nanoimprinting @ $T>T_G$) and thermal curing (T_G ↗)

Mould detachment @ $T<T_G$

Anisotroic plasma etch



50 nm line and trenches

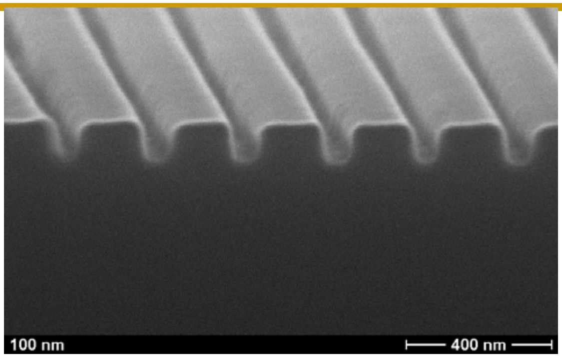


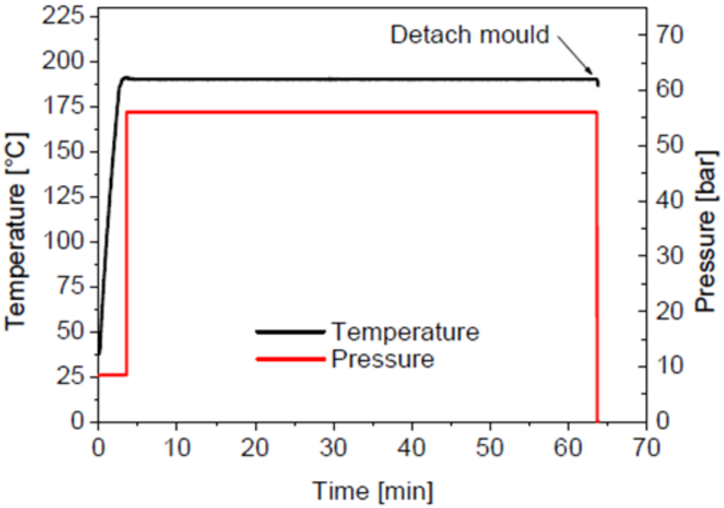
100 nm trenches

Litho 2006, Marseille 26 – 30 June 2006

Fast iso-thermal nanoimprint lithography (NIL without thermal cycle)

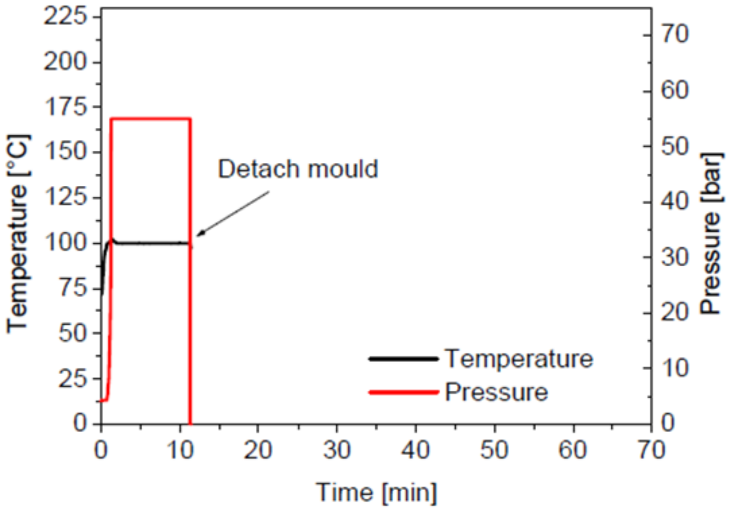
- Isothermal imprinting due to increase in T_g during imprinting.
- Reduce issues of thermal expansion.
- Decrease considerably imprint time (since no cooling).





Starting model system:

Best imprint results (no displacement of patterns) when mold is detached at imprint temperature (i.e. no cooling).
NIL at 190°C for 1 hour (sufficient curing) necessary for excellent patterns



Add initiator A + plasticizer 1:

Imprint at 100°C for 10min, no cooling.
Film thickness 170nm, 100nm trenches, 10-20nm residual layer.
(Initiator to increase curing speed; plasticizer to lower imprint temperature)

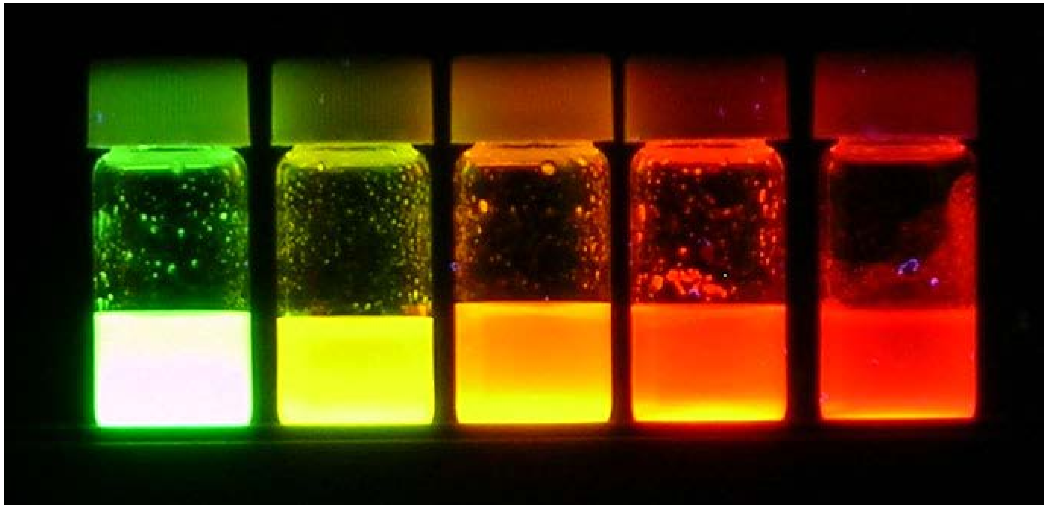
micro resist technology

Functional resist: nano-crystal(NC)/polymer based materials

Synthesis and functionalisation of colloidal nano-particles for incorporation into thermoplastic or thermal-curing (i.e. thermal-set) polymers.

Tuning of functional properties:

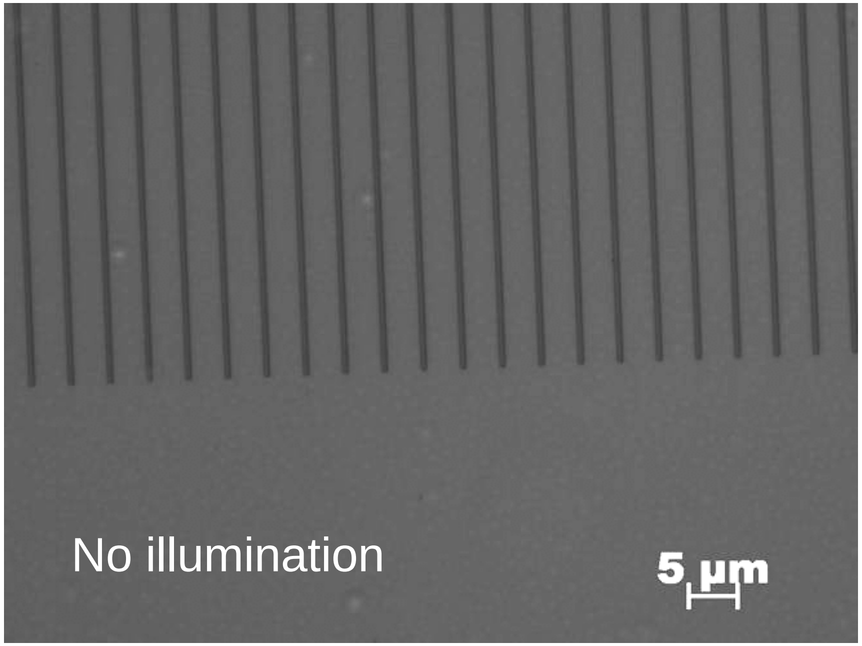
- Optical absorption and emission
- Mechanical Stability
- Conductivity
- Processability…

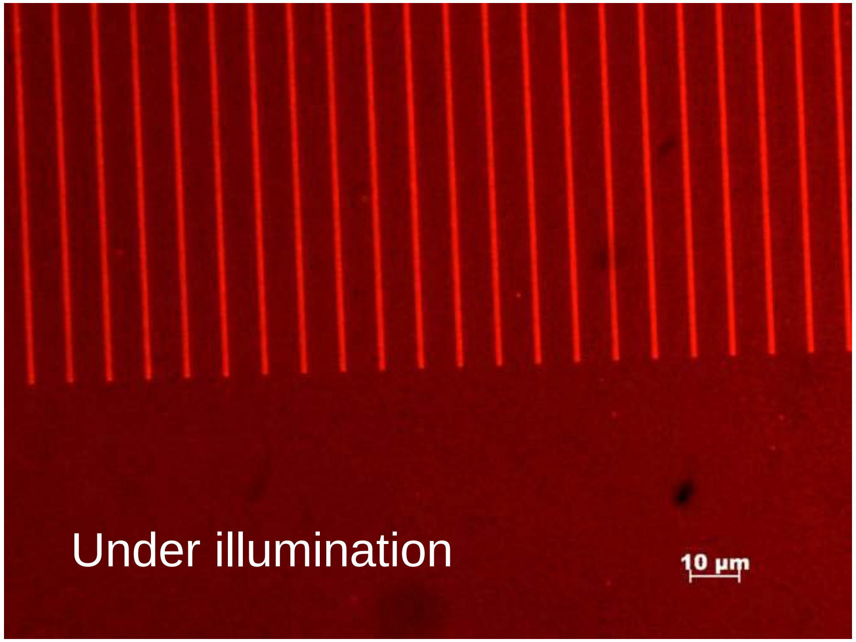


Size dependent luminescent CdSe NCs (quantum dot)

http://en.wikipedia.org/wiki/Cadmium_selenide

Imprinting on luminescent nano-crystal/PMMA based co-polymer composites

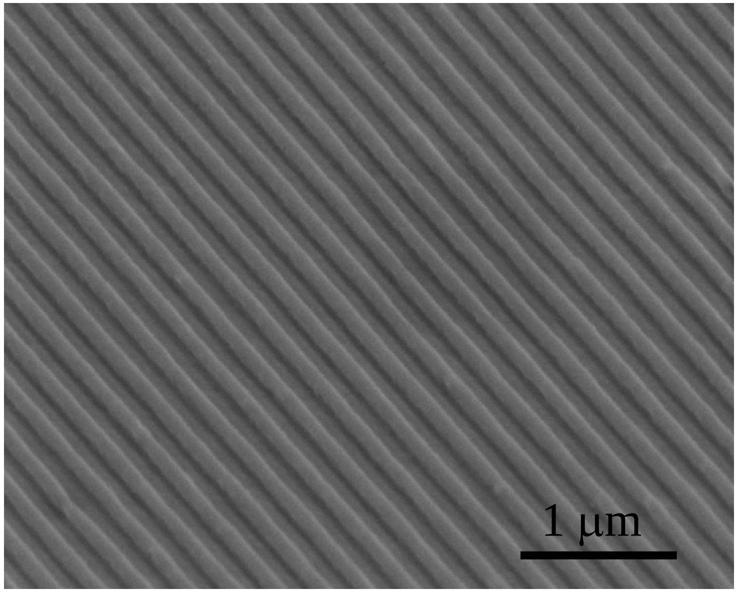




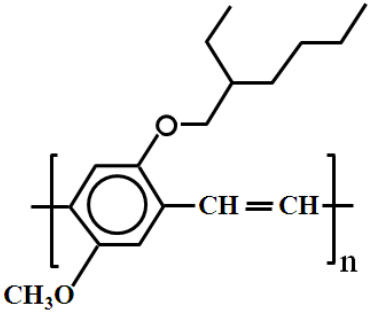
CdSe@ZnS nano-crystals (NC) in PMMA modified co-polymer.
Homogeneous distribution of NCs inside the polymer matrix.

Functional “resist”: semiconducting polymer

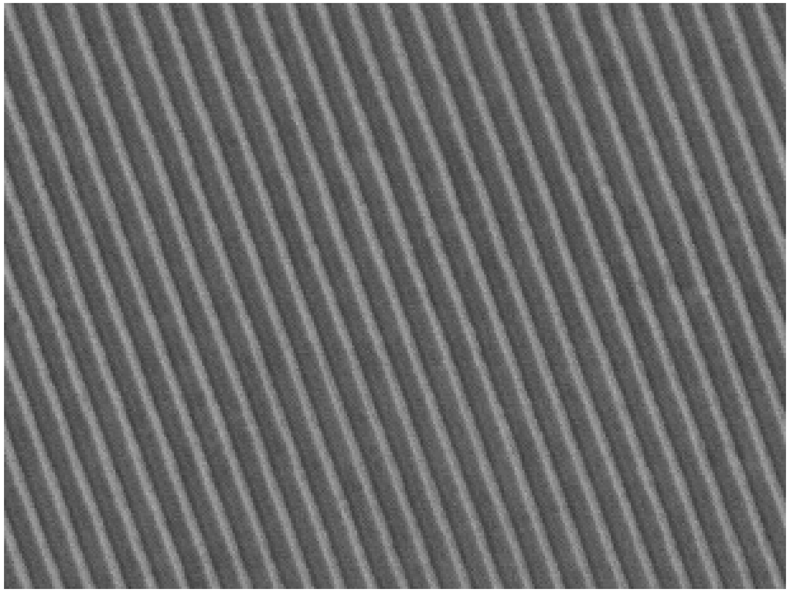
SEM image of 200nm period MEH-PPV grating



MEH-PPV T_g=65°C.
Hot embossing at 120°C and 20bar.
MEH-PPV spun on a PEDOT/ITO/glass.



R-P3HT grating with 200nm period



R-P3HT 200nm period grating.
NIL at 160°C and 35 bar.
Strong physical bond, high transition temperature.