Nano Sensors

PhD/ MTech/ BTech
Course No.: EEL7450
L-T-P [C]: 3–0–0 [3]

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Lecture 29 dated 11th Apr 2025

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Nano Imprint 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, NIL of bulk resist (polymer sheet, pellets).

Book: Nanofabrication: principles, capabilities and limits, by Zheng Cui

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Nanoimprint lithography: Patterning by mechanical replication

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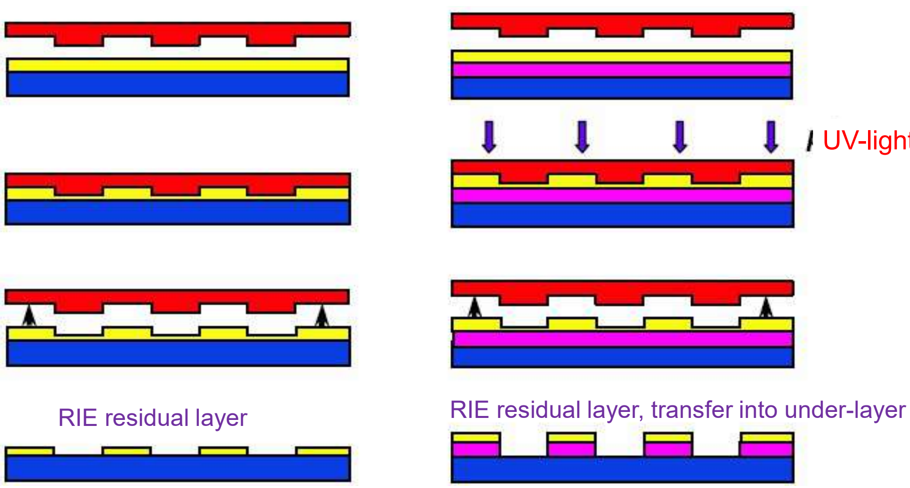
Two NIL approaches

Thermal NIL

UV-curing NIL



Heat up to soften the resist, imprint, cool down and separate

Liquid (soft) resist, hardened by UV irradiation due to cross-linking

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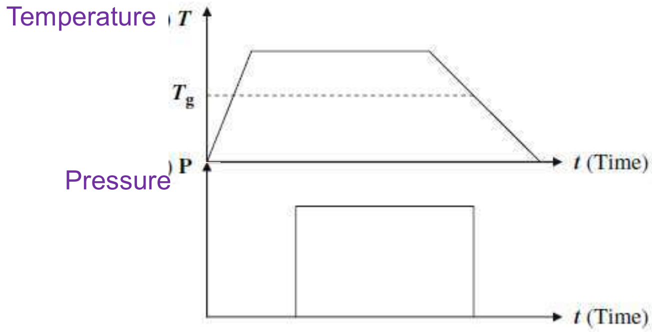
Thermal nanoimprint

Temperature and pressure evolution during thermal press nano-imprinting



- Typical temperature is 100°C – 200°C, ~30-50°C above resist's glass transition temperature.
- Typical pressure is about 20-50 atm, depends on resolution and pattern in the mold (easy for protruded feature, higher pressure for recessed feature in mold)

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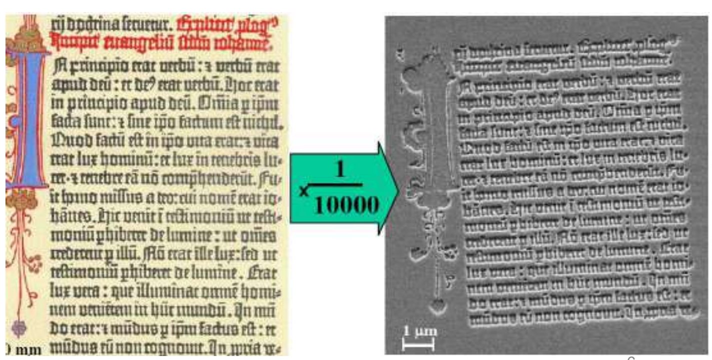
Printing: some history

1. During 1041-1048, Bi Sheng invented movable type printing technique. Hardened clay as mold.
2. 12th century *metal* type printing techniques were developed in Korea.
3. 1450 Gutenberg introduced his press. 300 two-volume bibles printed.
4. 1970´s compact disks (CD).
5. 1996, Nano-Imprint Lithography (NIL), sub-10 nm feature size, high throughput and low cost.
6. Today, NIL is one candidate (though not top candidate) for next-generation lithography for IC industry.
7. The bottom line is, NIL has the highest resolution (sub-5nm) and is fast. It will come into play when no other lithography can do the job.

Gutenberg bible (1450)



Duplicated by NIL (2000)

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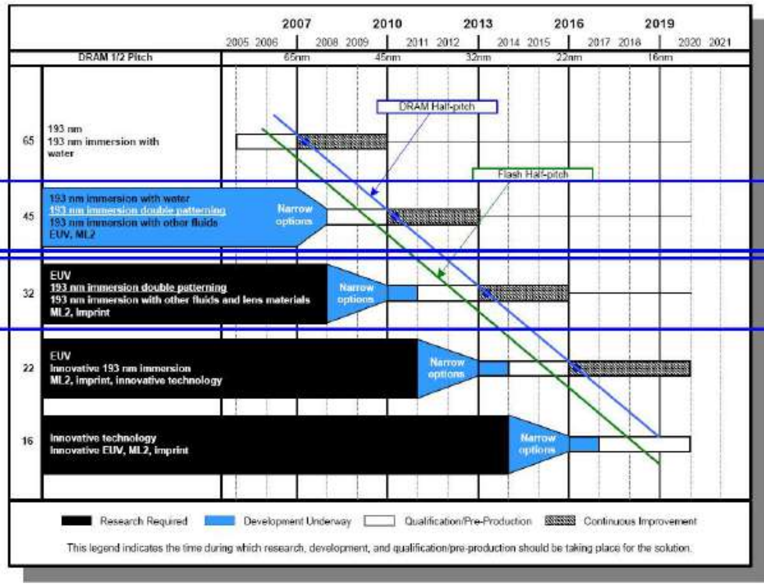
NIL not ready yet for ICs, but never excluded

ML2: maskless lithography (EBL, SPM..)



ITRS (2006) Projections for Lithography Technology 7

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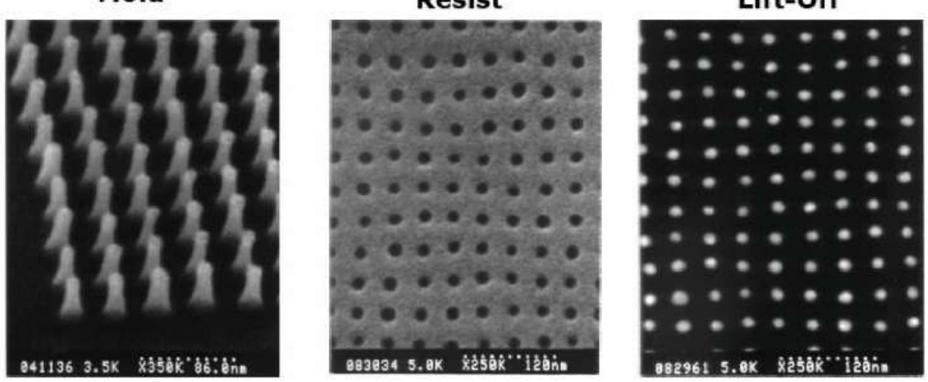
Key advantage of NIL: highest resolution

Mold | Resist | Lift-Off



10 nm dia pillar mold | 10 nm dia resist holes by imprinting | 10 nm dia metal dots by imprint and lift-off

NanoStructure Laboratory
PRINCETON UNIVERSITY

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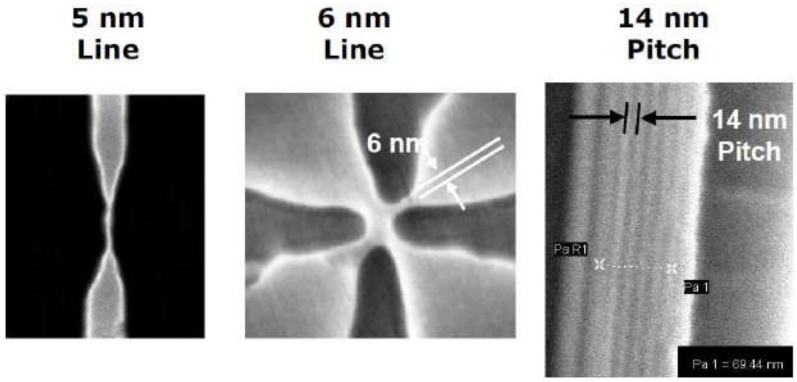
Key advantage of NIL: highest resolution

Sub-5 nm features and 14nm pitch nanoimprint



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.

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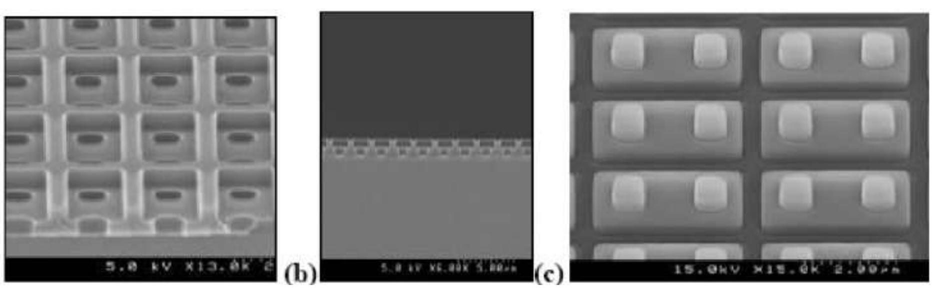
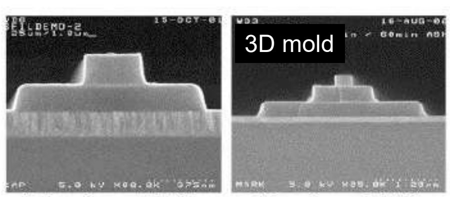
Another key advantage: 3D imprinting



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

(BEOL: back end of line)



2 tier, using oxide/ITO 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.

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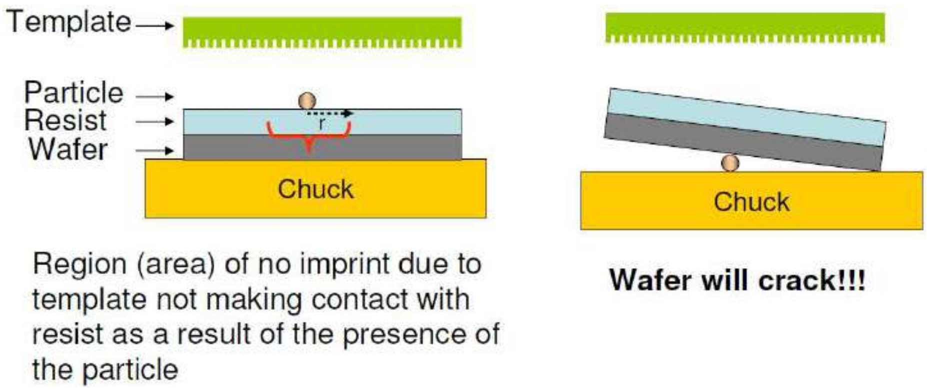
Imprinting in presence of a dust particle



- Dust is one of the most serious problems 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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Desired resist properties

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

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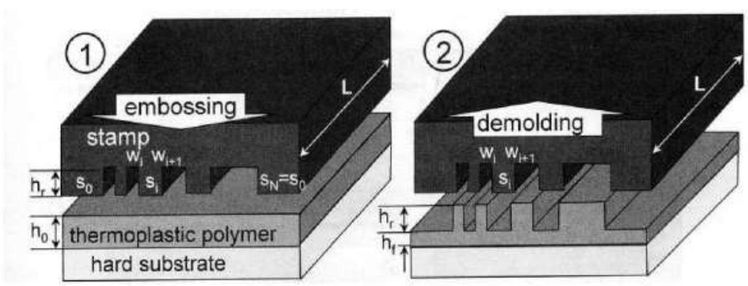
How much initial material (resist) is needed?



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

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

- 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.

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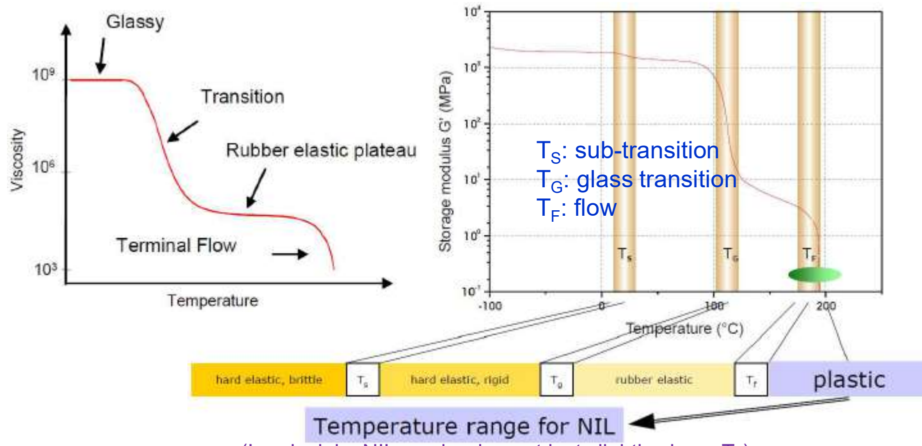
"Standard" resist for NIL: PMMA

Glass transition and flow temperature of PMMA



(In principle, NIL can be done at just slightly above T_g)

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 lithographies).

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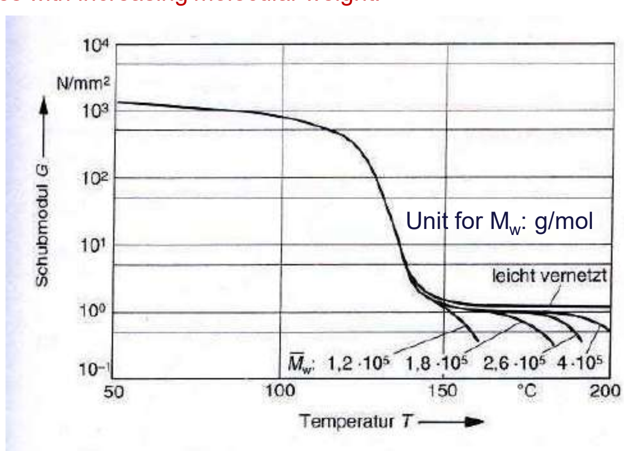
Shear modulus of different molecular weight PMMAs

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.

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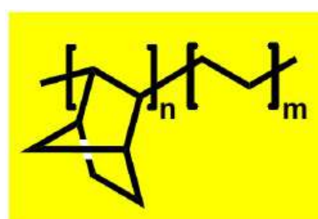
Another thermal NIL resist: TOPAS polymers

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

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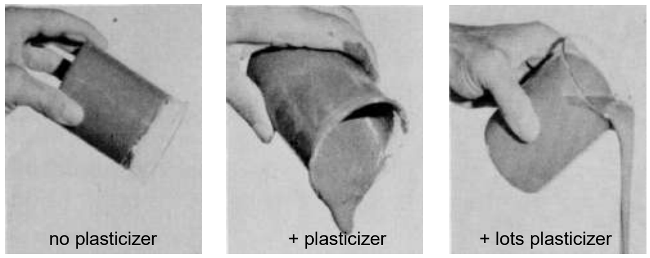
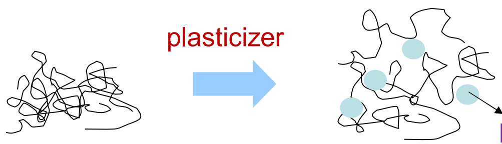
T_g **can be lowered** by adding **plasticizer** into the resist





Plasticizer: monomers, solvents, small molecules

Plasticizer: decreased chain entanglement, increased chain motion

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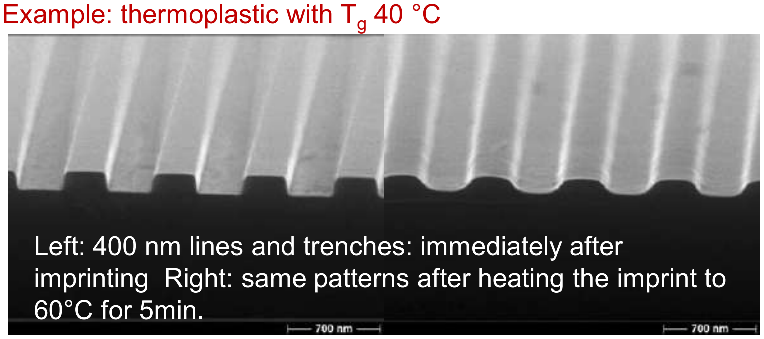
Polymer with low T_g

- Low imprint temperature
- Good polymer flow at moderate temperature
- Less problems with thermal expansion
- Shorter thermal cycle time

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.

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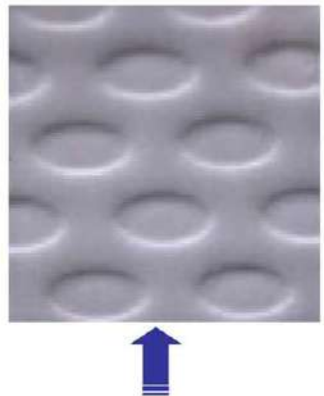
If T_g is too low…



10 days after imprinting a low T_g resist

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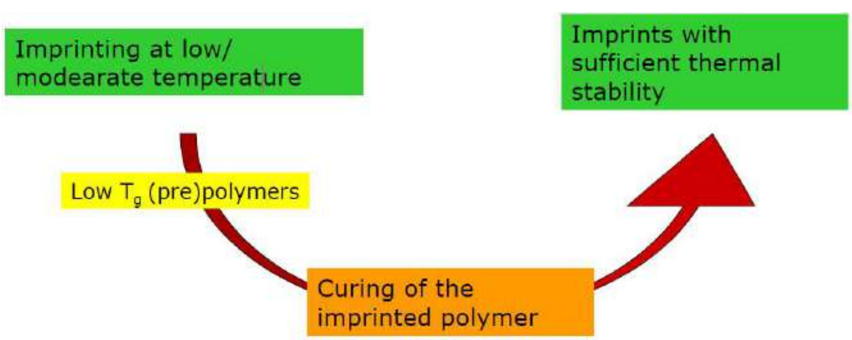
Approach to thermal stability



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

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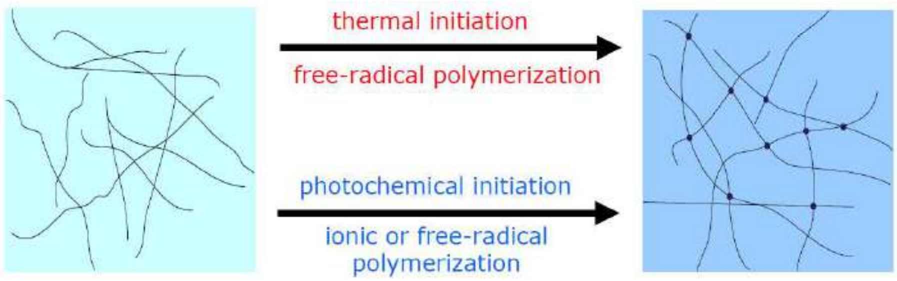
Thermal and photochemical curing



Linear or branched thermoplastic (pre)polymer

Cured polymer

Thermal curing is also called "thermal set"

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

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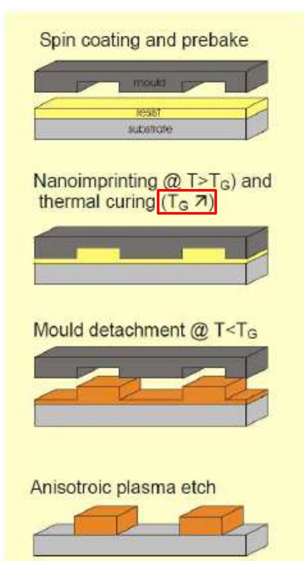
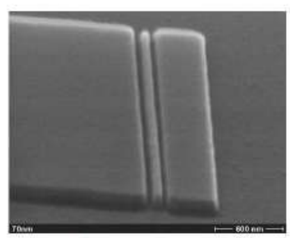
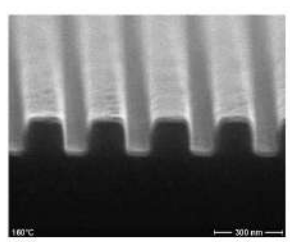
Imprinting thermally curing polymer mr-I 9000E





50 nm line and trenches



100 nm trenches

Litho 2006, Marseille 26 – 30 June 2006

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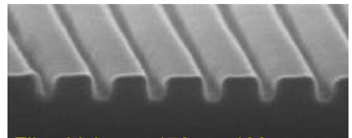
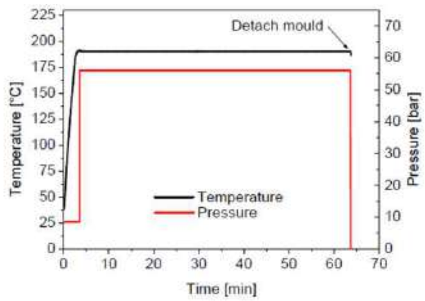
Fast iso-thermal (no thermal cycle, no cooling) nanoimprint

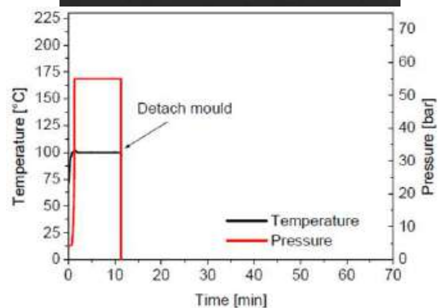
- Isothermal imprinting due to increase in T_g during imprinting (so no need to cool down).
- Reduce issues of thermal expansion.
- Decrease considerably imprint time (since no cooling).



Film thickness 170nm, 100nm trenches, 10-20nm residual layer.



Starting model system:
NIL at 190°C for 1 hour for sufficient curing.



Add initiator + plasticizer:
Imprint at 100°C for 10min, no cooling.
(Initiator to increase curing speed; plasticizer to lower imprint temperature)

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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)

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

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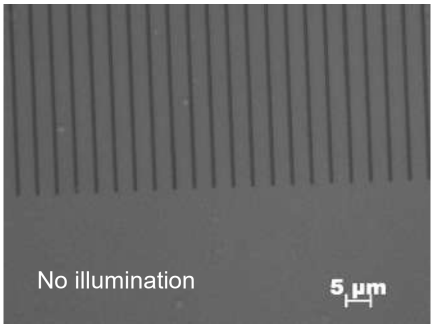
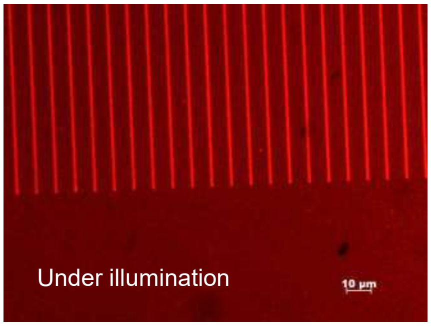
Imprinting on luminescent nano-crystal/ PMMA based co-polymer composites





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

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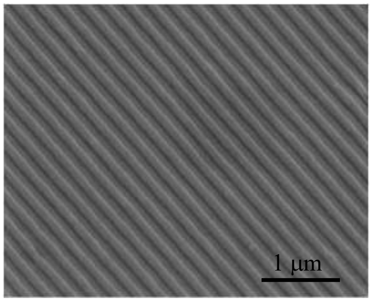
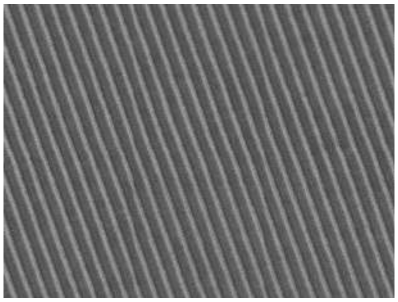
Functional “resist”: semiconducting polymer

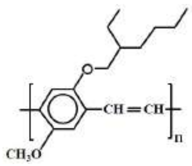
SEM image of 200nm period MEH-PPV grating



R-P3HT grating with 200nm period



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



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

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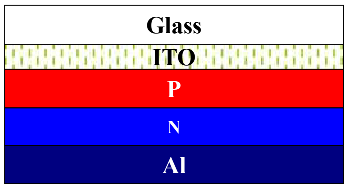
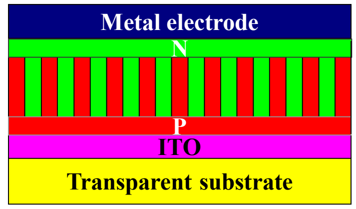
Application: nanostructured plastic solar cell

MEH-PPV is a popular p-type semiconducting polymer for plastic solar cell.
(The n-type material is Alq3, http://en.wikipedia.org/wiki/Tris(8-hydroxyquinolinato)aluminium)



Classic planar p-n junction, low junction area, low efficiency



Nanostructured junction, high junction area, high efficiency

- Plastic solar cells: flexible, light weight, tunable electrical properties, and potential lower fabrication cost.
- Limitation: low energy conversion efficiency due to low carrier mobility.
- Method to increase efficiency: increase the interface area by nano-patterning the p-n junction.

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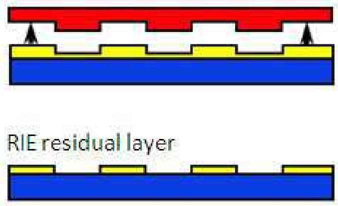
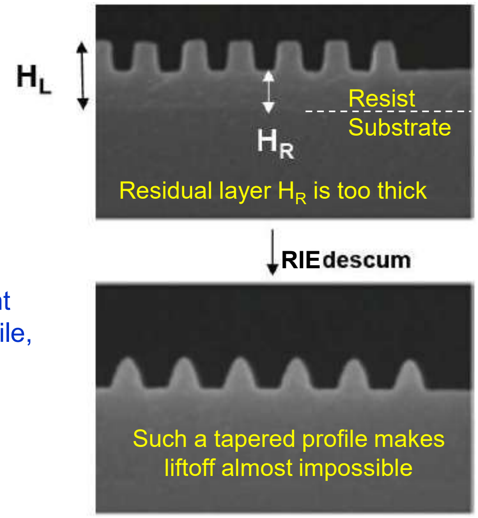
Residual layer: thinner is better for easier pattern transfer





- Too thick residual layer makes subsequent RIE more demanding: hard to control profile, pattern size shrinkage (CD loss).
- So, resist thickness should be << pattern height of mold.
- CD: critical dimension.

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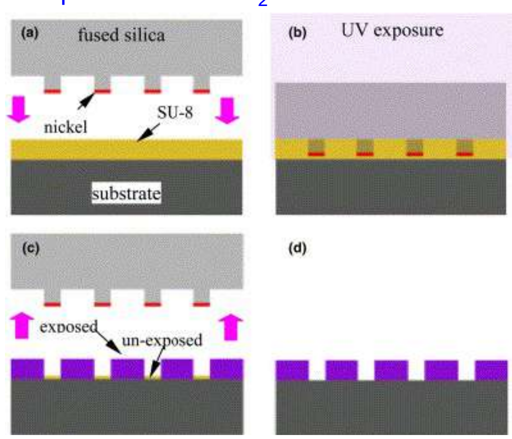
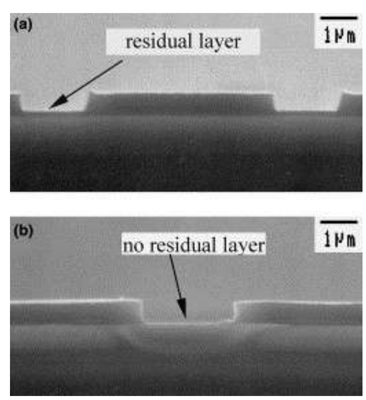
How to get rid of residual layer (thermal NIL aided by UV exposure)

Add light-blocking metal layer (here Ni), and use resist developer **instead** of O_2 RIE to remove the residual layer.



Un-exposed area developed (since SU-8 is negative resist)



Comparison of residual layers in micro-scale resist pattern obtained by: (a) conventional NIL; (b) the current technique where no residual layer is left.

Cheng and Guo, "A combined-nanoimprint-and-photolithography patterning technique", MEE, 2004.

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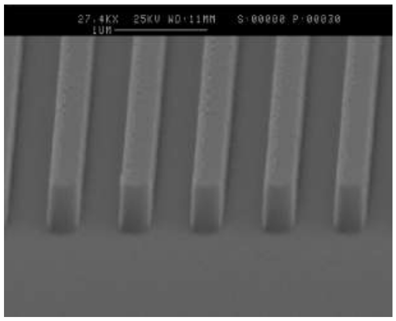
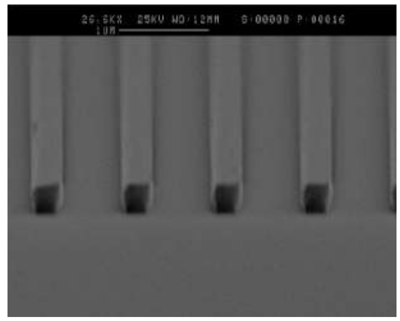
ICP etching of residue layer

ICP: inductively coupled plasma, high plasma density and etching rate, better control

(According to an ICP tool seller, usually very difficult to get such etching result)
ICP provides the best performance for etching residual layer:

- Low pressure processing minimizes isotropic (lateral) etching and loss of profile.
- Lower temperature processing also helps.
- Low bias processing minimizes faceting at the top of the lines.





Polystyrene residue removal on Al. 200nm residual removed in 2 minutes using a pure O_2 ICP plasma – linewidth remains constant at 0.35μm and sidewall is vertical.

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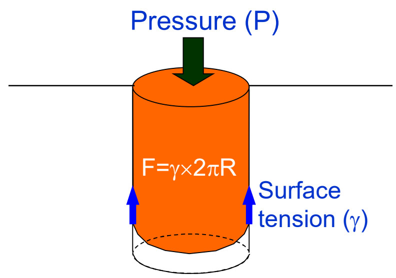
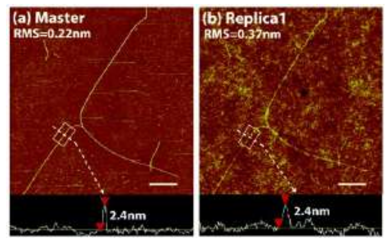
NIL for small features/ high resolution (<10nm)

Press liquid into a nano-hole



$$P = \frac{\gamma \times 2\pi R}{\pi R^2} = \frac{2\gamma}{R} \propto \frac{1}{R}$$



UV-curable NIL, **2nm** carbon nanotube mold

- Pressure ∝ 1/diameter.
- But for protruded mold features (pillars…), local pressure at the pillar is much higher than average - easy to imprint.

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Hua … Rogers, "Polymer imprint lithography with molecular-scale resolution", Nano Lett. 2004

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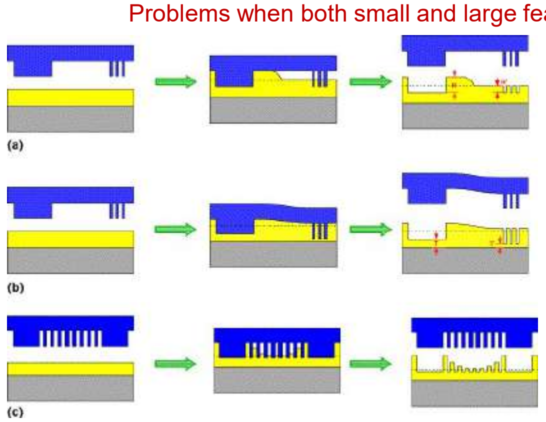
NIL for large features (>100 μm) - simultaneous pattern duplication of large and small features

- Application: large features are needed to connect small ones to the outside world (electrodes…).
- Challenge: more polymer must be displaced over longer distances.
- A popular approach: two-step process - small features by NIL, large ones by photolithography with alignment.

Problems when both small and large features are present



Schematics of pattern failure mechanisms in NIL as a result of: (a) non-uniform pattern height; (b) non-uniform residual layer thickness; (c) incomplete nano-pattern replication.

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Cheng, "One-step lithography for various size patterns with a hybrid mask-mold", Microelectronic Engineering 71, 288–293 (2004).

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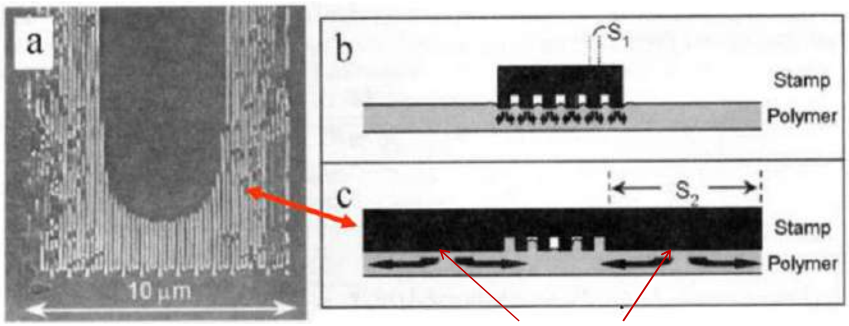
NIL pattern uniformity



Etch some dummy holes/trenches here

- Different "fill factors" across mold lead to different sinking rates.
- Mold bending leads to non-uniform residual layer on substrate.
- One solution: fabricate "dummy" cavities/protrusions to create constant fill factor.

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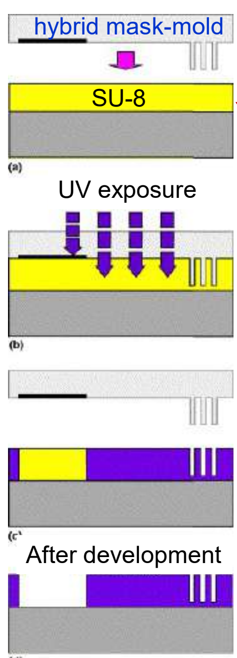
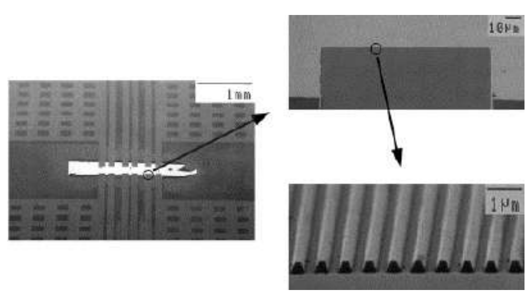
Combined photo- (for macro) and nanoimprint lithography (for nano)

Using a hybrid mask-mold for one-step lithography of both large- and nano-patterns



Here SU-8 is used *both* as a photo-resist and thermal NIL resist.

(SU-8 is a photo-resist, but not a UV-curing NIL resist as it is hard to imprint at room temperature. Instead, it can be used as a thermal NIL resist, T_g~50°C)



SEM micrograph of resist patterns obtained by the technique with hybrid mask-mold.

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Cheng, "One-step lithography for various size patterns with a hybrid mask-mold", Microelectronic Engineering 71, 288–293 (2004).

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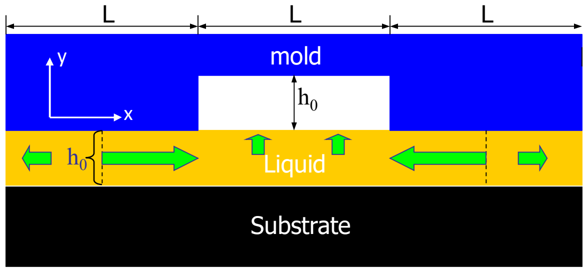
Modeling of liquid flow for large features (>>pattern depth)



Assumptions:
- Periodic mold structure (period 2L)
- Ignore inertial, gravitational force and surface tension
- Resist film thickness = mold trench depth = h_0

$$L = \frac{2h_0}{3}\sqrt{\frac{p\,\tau}{\mu}} \propto \left(\frac{p\,\tau}{\mu}\right)^{1/2}$$

L: achievable feature size
p: pressure
τ: imprinting time
μ: viscosity
h_0: film thickness

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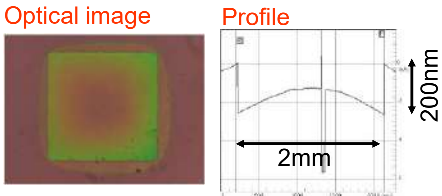
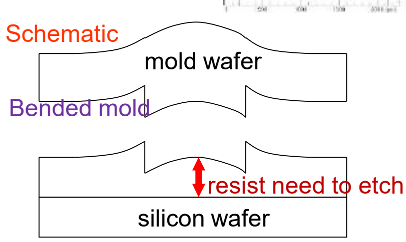
Problems of imprinting simultaneously large (mm) and small (nm) features

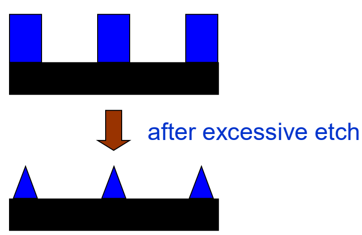
Square (mm) imprinted into PMMA



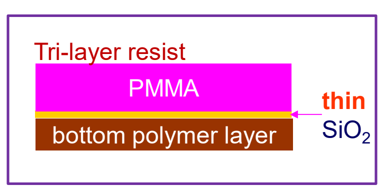


Due to mold bending, need excessive etch to remove the thick residual resist at the square center

But for nanoscale features…



Such a profile makes liftoff difficult.
Solution: use tri-layer resist system



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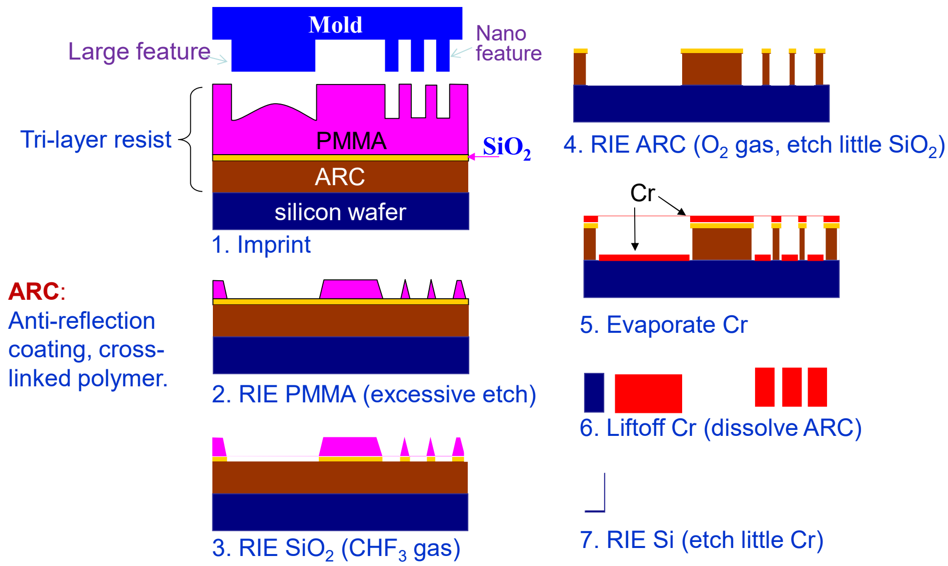
Fabrication process flow



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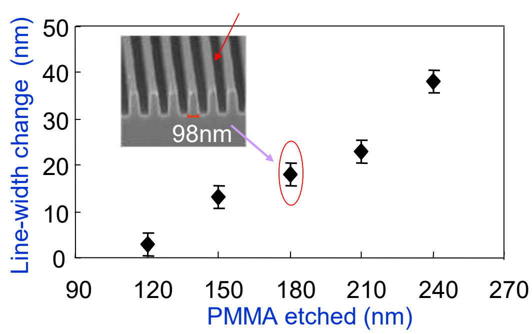
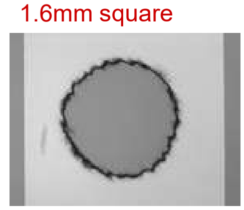
Result of simultaneous imprinting large and small features

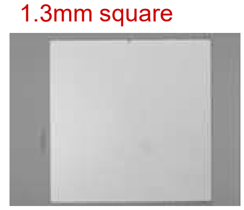
Line-width in the mold is 80nm
Line-width in the duplicated pattern is 98nm



1.6mm square



1.3mm square



(RIE PMMA 180nm)

Summary:
For small features, line-width increased by ~18nm.
For large features, 1.3mm squares were faithfully duplicated.

Cui and Veres, "Pattern replication of 100 nm to millimeter-scale features by thermal nanoimprint lithography", MEE, 2006

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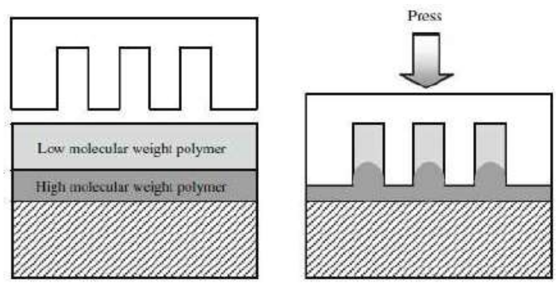
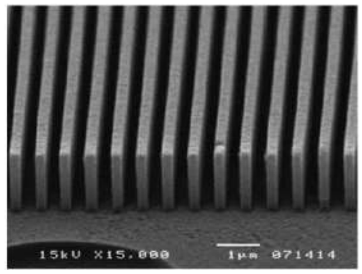
NIL of high aspect ratio structures

- Low molecular weight (M_w) has low viscosity, so is easy to imprint.
- But it also has low shear modulus, which makes the pattern easily broken during separation if the pattern is of high aspect ratio.
- The solution is a double-layer resist stack, bottom layer high M_w for its strength (not easily broken) and top layer low M_w for its good flow capability.



Schematic of double-layer nano-imprinting



High-aspect-ratio pattern imprinted using double-layered polymer process.
Top layer: PMMA (M_w=15kg/mol), 0.7μm;
Base layer: PMMA (996kg/mol), 1.5μm.
170°C, 150bars, 250nm lines; pattern height: 1.3μm.

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Nano Sensors

PhD/ MTech/ BTech
Course No.: EEL7450
L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL
ELECTRICAL ENGINEERING
IIT JODHPUR

Lecture 32-33 dated 13th Apr 2025

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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, NIL of bulk resist (polymer sheet, pellets).

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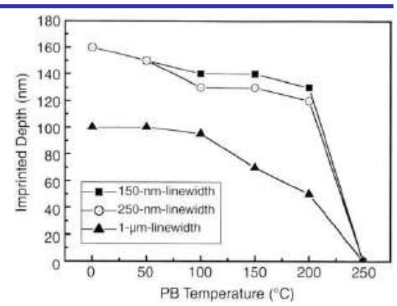
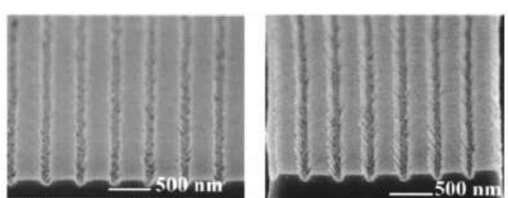
Room temperature ("Thermal") NIL

Use special material, such as hydrogen silsequioxane (HSQ), or ultrahigh pressure.

Pre-baking is important:
- The effect of prebaking HSQ is to remove the solvent in it.
- The hardness of HSQ increases at around 150°C (so don't bake at higher T).



Influence of prebaking temperature on imprinted depth in HSQ (imprinting pressure: 220 bars)



Non-postbaking
(a)

150°C
(b)

Room temperature NIL is possible, but not popular.

FIG. 5. HSQ replicated patterns with 100 nm linewidth after postbaking. (a) No postbaking and (b) baking temperature of 150 °C.

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"Nanoimprint and nanocontact technologies using hydrogen silsequioxane", JVST B, 2005

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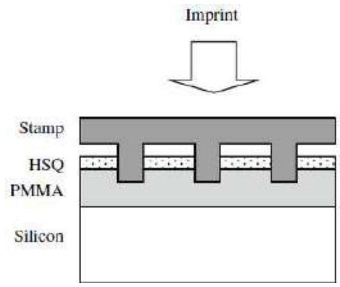
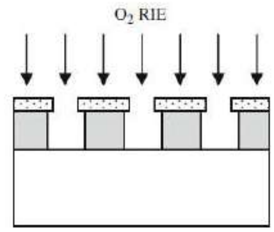
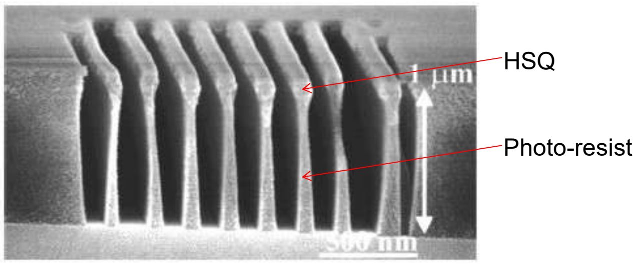
RT-NIL into HSQ/ Polymer bi-layer

Bi-layer resist:

Hard to spin thick HSQ. It is like SiO_2, so is good etching mask when RIE the polymer under-layer using O_2 gas.







Here the under-layer is 1μm-thick AZ photo-resist (not PMMA).

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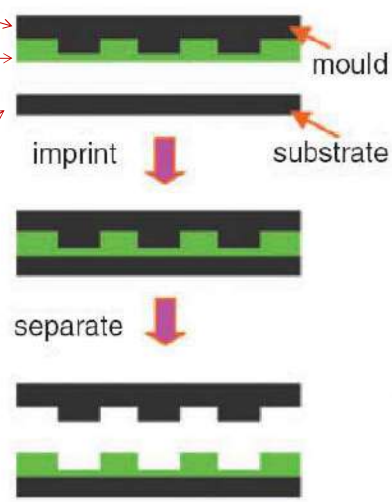
Reverse NIL

Mold with low surface energy

Polymer spun-coated or poured on mold and baked

Substrate with relatively high surface energy (i.e. no anti-adhesion treatment)



L. J. Guo, J. Phys. D 37, R123 (2004)

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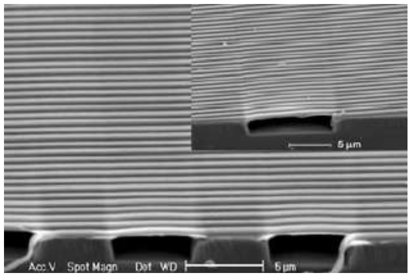
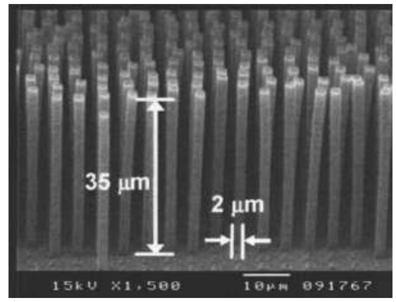
Reverse NIL: result



Polycarbonate grating imprinted across 5µm and 10µm (insert) gaps in silicon.



High-aspect-ratio PMMA pillars replicated by cast molding (reverse NIL).

- PMMA is dissolved in toluene (or chloroform) that "wets" the mold treated with **anti-stick** low surface energy layer.
- Since they **wet each other**, resist solution goes into the mold pattern by capillary force.
- The separation (de-molding) is actually easier than regular imprint, since now there is no external force applied to squeeze the polymer into cavity, and thus there is no shear stress in the molded polymer structures. (shear stress makes separation more difficult)

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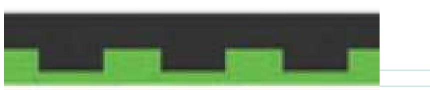
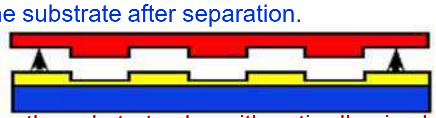
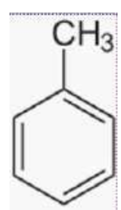
Reverse NIL by squeezing the polymer into mold cavity



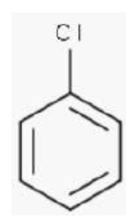
- The residual layer can be thinner than spin-coating or pouring polymer onto mold, and polymer surface is flat.
- For normal NIL, the mold is treated with anti-stick layer, so resist stay at the substrate after separation.



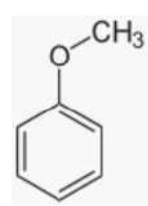
- By treating the substrate also with anti-adhesion layer, resist may stay on the mold after separation since the mold is patterned whereas the substrate is flat.
- However, since the substrate with anti-adhesion layer has low surface energy and is very un-polar, one has to use a solvent that is un-polar, such as toluene.
- Otherwise, if using common (PMMA) solvent like chloro-benzene or anisole, the resist solution will form droplets on or slip off the low-surface energy substrate during spin-coating, rather than forming a continuous thin film.



Toluene (un-polar)



Chlorobenzene (polar)



Anisole (polar)

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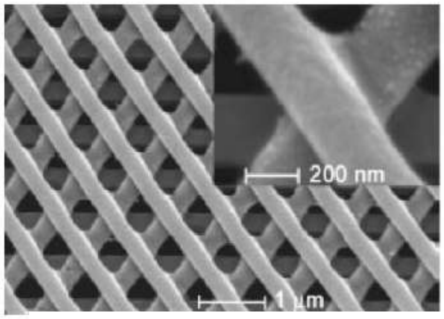
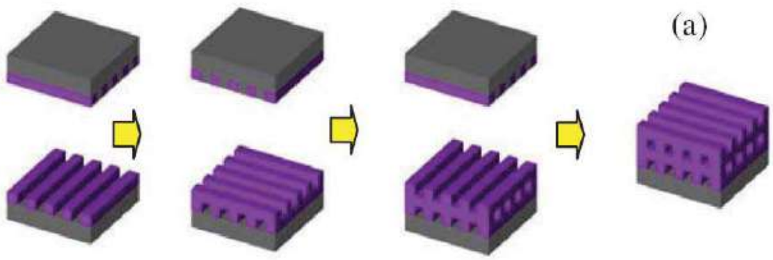
Layer-by-layer NIL (repeated reverse NIL)



The glass transition temperatures of the polymers must be **lower for later/ upper** layers. Here the residual layer has been dry-etched.



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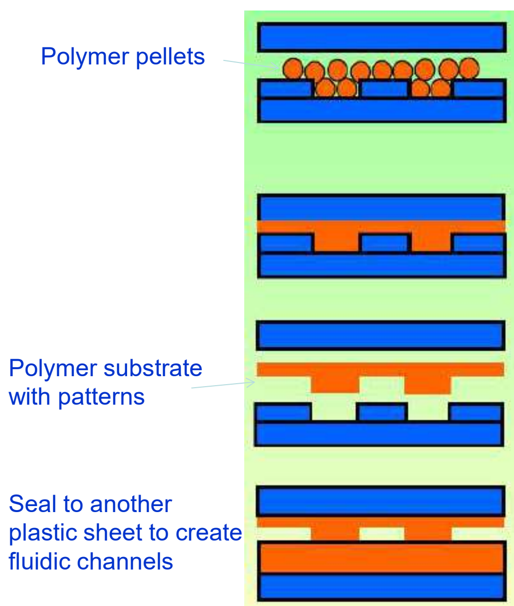
Hot embossing pellets



V. Studer, A. Pépin, Y.Chen, Appl. Phys. Lett. 80, 3614 (2002)

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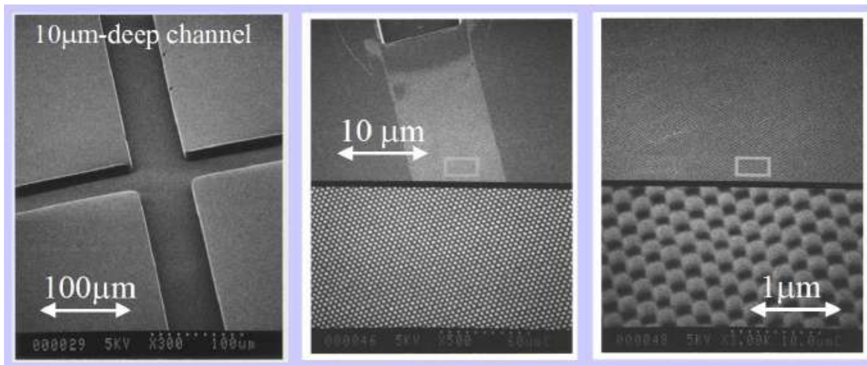
Hot embossing PMMA pellets: result

NIL at 180°C, 50bar pressure for ~10 min



For fabricating micro- and nano-fluidic channels in thermoplastic polymers.

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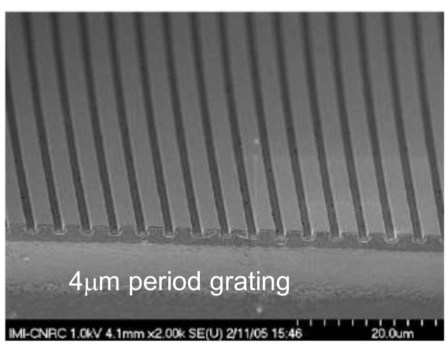
Hot embossing polystyrene pellets

Polystyrene is bio-compatible (cell culturing Petri-dish is made of polystyrene, perhaps plus some additives).

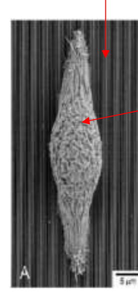


Application: contact guidance of cell growth

- Definition: anisotropic topographic features induce cells to align along the direction of the anisotropy.
- Importance: in tissue engineering, if tissue is to be repaired, the new cells must be aligned and positioned correctly.

grating substrate

cell



Journal of Cell Science 118 (10)

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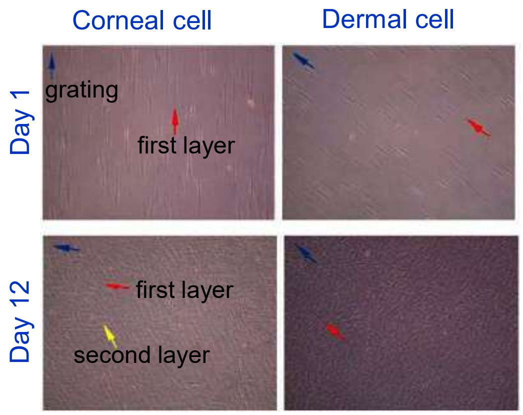
Tissue engineering: corneal and dermal cell growth



- First layer: both cells aligned with the grating (as expected).
- Second layer:
    Corneal cells - oriented at 60° relative to first layer, as in a native cornea
    Dermal cells - no orientation

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Questions/ comments …

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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, NIL of bulk resist (polymer sheet, pellets).
6. UV-curing NIL.
7. Resists for UV-NIL.
8. Mold fabrication for thermal and UV-NIL.

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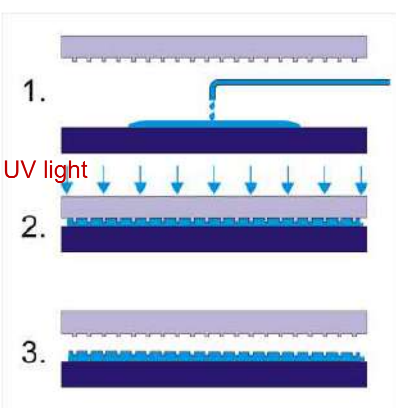
UV-curing NIL

UV-curing NIL is a mechanical molding process, like thermal NIL; but very different from photolithography that is a chemical process, though they both use UV light.

UV-NIL using dispensing resist



- Room temperature, low pressure (1 - few atm).
- *Liquid* resist consisting **monomer**, photo-initiator, coupling agent, surfactant, solvent…
- Resist cross-link (become solid) upon UV illumination.
- Mold (or substrate) must be transparent to UV. Most popular mold material is quartz.
- Easier for alignment than thermal NIL (thermal expansion destroys alignment), closer to optical lithography.
- But resist side, thermal NIL resist is closer to optical lithography resist. For example, PMMA and SU-8 is both a photo-resist (PMMA for DUV lithography) and thermal NIL resist.
- In fact, UV-NIL resist is closer to UV-curable glue.

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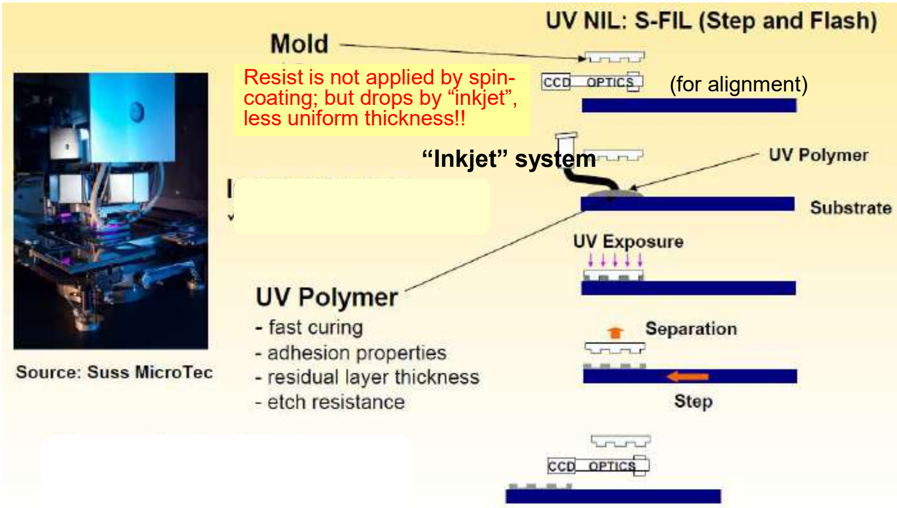
Step and flash UV-NIL



- Technology commercialized by Molecular Imprint Inc.
- Resembles deep UV stepper, die by die patterning (no need of a BIG expensive mold).
- Favored by the semiconductor industry or wherever mold is too expensive.

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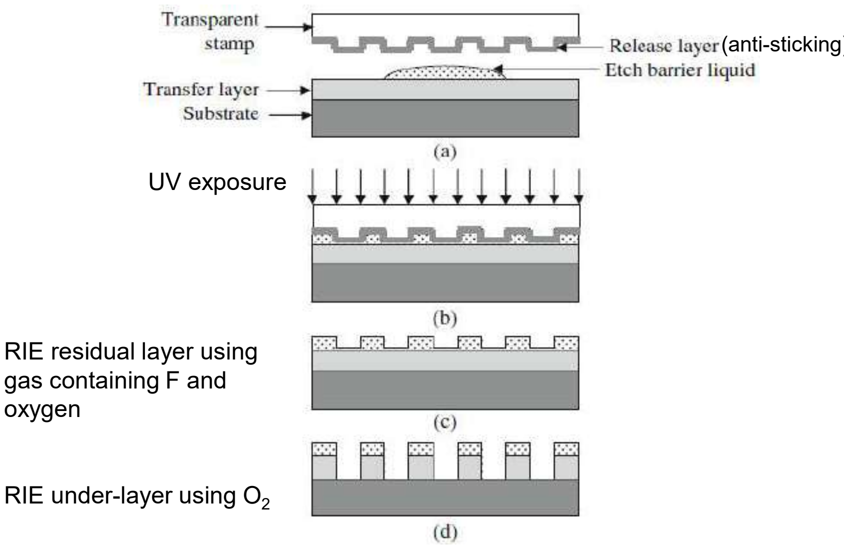
Step and flash UV-NIL using bi-layer resist



The UV resist can be very thin but contains Si that is resistant to O_2 RIE, then a polymer under-layer can be used for pattern transfer.

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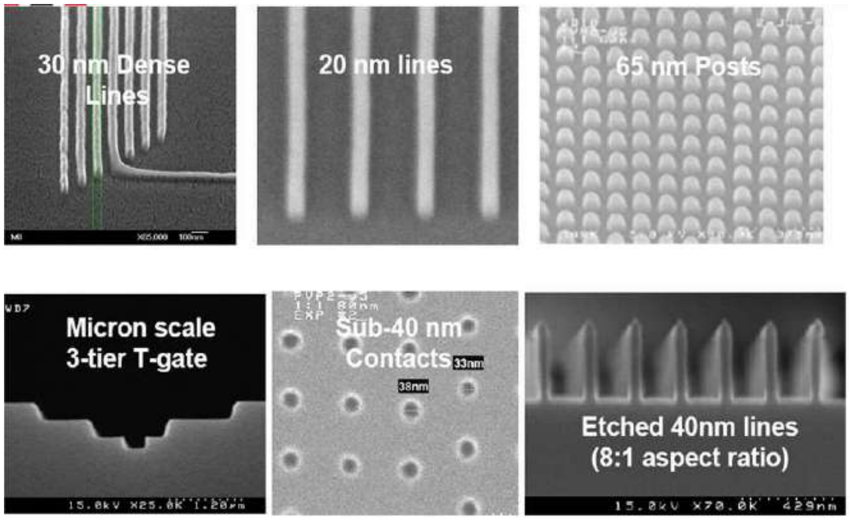
Some examples of step and flash NIL



In principle, UV-NIL has lower resolution than thermal NIL due to resist shrinkage (~10%) upon cross-linking. In practice, UV-NIL has demonstrated similar resolution to thermal NIL.

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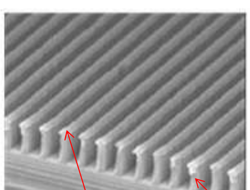
UV-NIL using spin-on resist (uniform thickness)

NXR-2000 Series, Photo-Curable Resists

- Sub-5 nm demonstrated resolution and wafer-scale uniformity
- Room temperature operation
- Super-low viscosity
- Spin-on or resist-drop dispensing
- Excellent etching resistance
- Low UV-curing dosage

Nanonex



UV-resist   Under-layer (PMMA, ARC…, also called transfer layer)

- Typically bi-layer system, thin UV-resist layer to minimize shrinkage effects.
- Resist contains Si, so can be used as a hard mask for etching under-layer with O_2 plasma.
- Spin-on resist is not suitable for step-and-flash NIL, because the entire film must be imprinted quickly in one shot (liquid resist not as stable as thermal NIL resist in air, and it takes in dust quickly).
- A big expensive mold is needed, but the throughput is also higher.
- For R&D, spin-on resist is much more reliable than step-and-flash NIL, because the amplitude and uniformity of residual layer thickness is a big issue for drop-dispensed resist.

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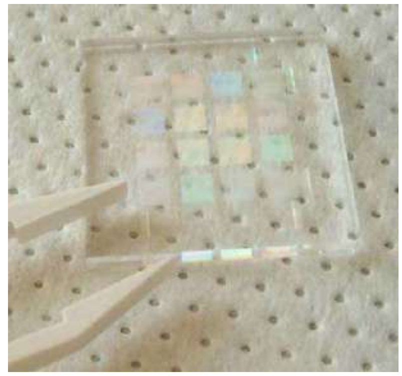
PDMS mold for UV-NIL

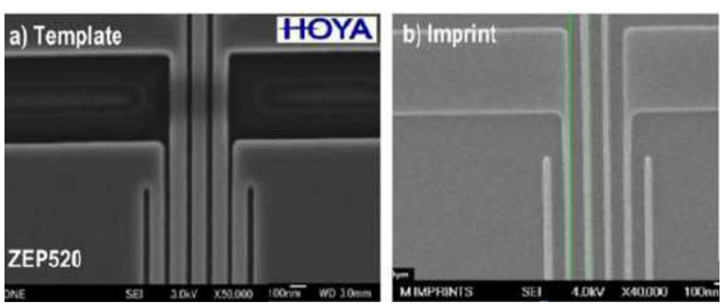
- Unlike quartz, PDMS is flexible and soft for conformal contact to non-flat substrate.
- But not for high resolution (<100nm), because PDMS is not hard enough and thus its nanostructure will deform under pressure.
- One solution is using bi-layer, pattern in *hard*-PDMS or PMMA, which is spun on (regular soft) PDMS.
- After oxygen plasma treatment, PDMS surface is like SiO_2, so it is easy for silane anti-sticking treatment.



Transparent mold (also called stamp or template) in PDMS

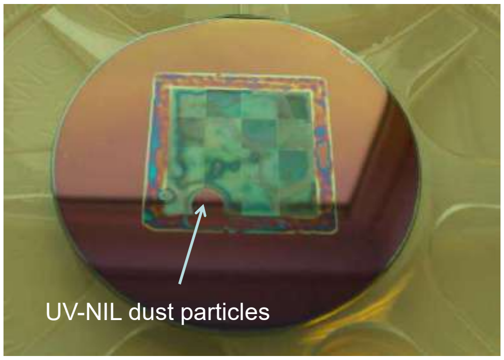
ZEP-520 mold (ZEP is an e-beam lithography resist)

- Because UV-NIL uses low pressure and room temperature, thermoplastic EBL resist such as PMMA and ZEP-520 can be used as a mold right after EBL and development.
- However, one may need anti-sticking surface treatment with silane, yet the silane treatment is not reliable on ZEP or PMMA, or other thermoplastic polymers.
- Therefore, thermoplastic polymers are not popular mold materials.



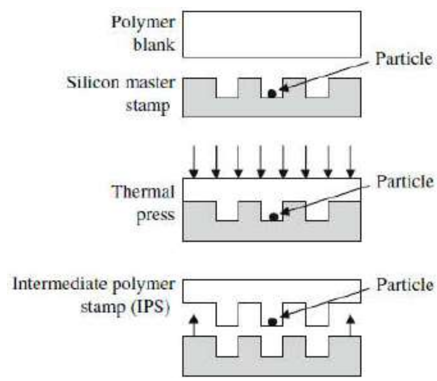
Mold in ZEP-520 with line-width 50nm   Imprint result into a UV-curing resist

Dust



Dust is a bigger issue for UV-NIL than for thermal NIL because:

- The *liquid* resist takes in dust easily from air, and the dust cannot be blown away.
- The pressure is lower, leading to larger defect area with same size of dust particle.
- So sometimes, UV-NIL is done at higher pressure to reduce defect area.



Self-cleaning process: dust particles on the "master mold" can be trapped to the polymer replicate, which can be used as a mold for UV-NIL (called "daughter mold").

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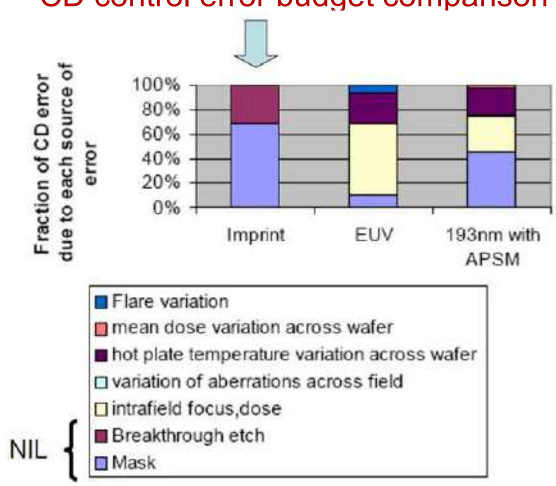
Critical dimension (CD) control in NIL

UV-NIL is one candidate for next generation lithography to replace 193nm lithography.

CD control error budget comparison

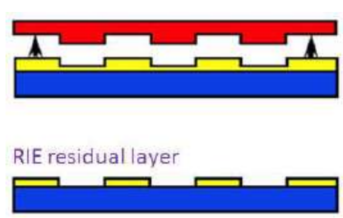


Advantage of NIL for CD control:

- No diffraction or proximity effects.
- No lens aberrations.

Disadvantage of NIL for CD control:

- 1× mask, so CD error on mask is printed onto resist without reduction.
- Need a breakthrough etch of the residual layer, which adds CD error due to lateral etch.
- But this error could be compensated in mask (mold) design.



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Summary: comparison between thermal and UV NIL

	Thermal	UV
Resist material	Thermoplastic or thermal-set (i.e. cured upon heating)	Monomer, photo-initiator plus various additives
Resolution	Sub-5nm	2nm demonstrated, but volume shrinkage after cross-linking
Temperature	30-100°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, since 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

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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, NIL of bulk resist (polymer sheet, pellets).
6. UV-curable NIL.
7. Resists for UV-NIL.
8. Mold fabrication for thermal and UV-NIL.

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Resist for UV-NIL

Overview:
- UV-NIL resist has little in common with photo-resist, which resembles more thermal NIL resist.
- In principle, any material that is soft (thus can be imprinted) and becomes hard upon UV exposure, can be used as UV-NIL resist.
- For example, UV-glue and dental UV sealant, are UV-NIL resists.

Component of UV-NIL resist:
- Vinyl ethers that are the key ingredient for photoploymerization.
- Organic acrylate monomer that provides low viscosity.
- Organic cross-linker for thermal stability and mechanical strength.
- Additives: silicon-containing acrylate monomer (to increase dry etching resistance), flourinated compounds (to lower surface energy for easy separation).
- Photoinitiator: cationic or free radical photoinitiator.

Photoinitiators:
(dissociate upon UV irradiation to form radicals that promote polymerization process)
- Cationic photoinitiator:
  Insensitive to oxygen, but low curing rates; and acids and heavy metals are harmful to semiconductors.
- Free radical photoinitiator: (more popular at present)
  Great variety, high curing rates, but sensitive to oxygen, need vacuum or N_2 environment curing.

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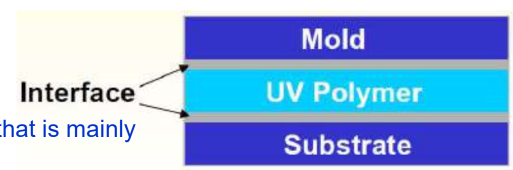
Adhesion mold/ UV polymer/ substrate

Ideally:
No adhesion between mold/UV-polymer.
Strong adhesion between substrate/UV polymer.

Interface reaction:
Mechanical adhesion, wetting, specific adhesion that is mainly caused by inter-molecular bindings.



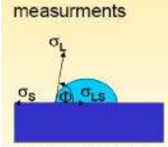
σ is surface tension (N/m), also called surface energy (energy/m^2=N/m)

For **substrate** (Si, Si/HMDS, Si/ARC), **low contact angle** (small Φ) is **better**.

For **mold**, **high** is **better**.
But here, all resists still "wet" the mold (Φ<90^o)

Wetting:

Contact angle measurments



$\sigma_S = \sigma_{LS} + \sigma_L \cdot \cos\Phi$

*ARC: Anti Reflective Coating

**Mold: Quartz treated with FTCS

	Contact angle (°)			
Resist	Si	Si / HMDS	Si / ARC*	Mold**
NOA 61	23,7	41,8		68,3
Helioseal	15	26,7		66,2
Inoflex RP+	14,9	31,9	✓8	67,9
PAK 01	✓9,4	20,3	✓8,7	66,5
NIF 2	16,3	12,3	✓6,1	33,7
NIF 1	15,8	11,4	✓5,9	34,2
Z Resist	✓6,3	25,8	10,6	65,4

Note: those resists are just examples, none of them are popular – in fact currently there is no single UV-resist that gains enough popularity.

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Holger Schmitt, Christoph Lehrer

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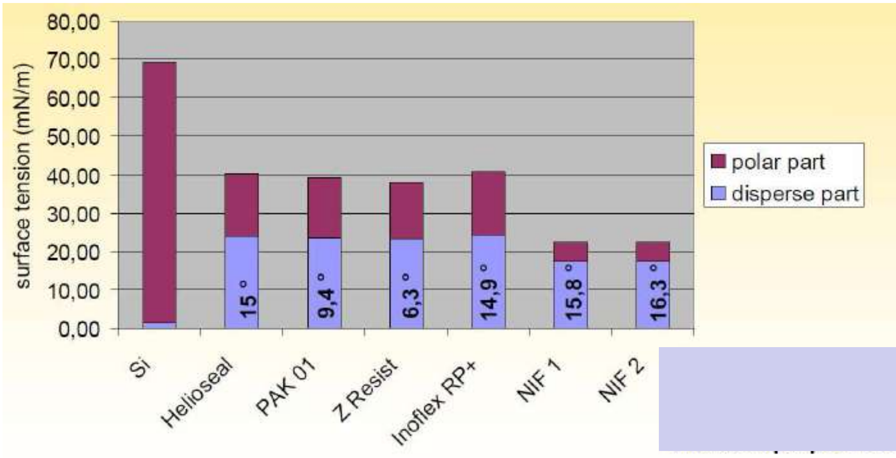
Surface tension of various materials



Contribution to total surface tension: polar and disperse part.

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Residual layer thickness

For drop-dispensed resist (not spin coating)

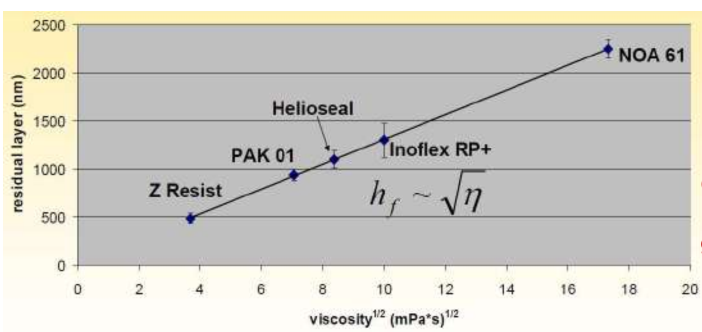
$$if \quad h_f << h_0$$

$$h_f = \sqrt{\frac{s^2 \cdot t_f}{2p}} \cdot \sqrt{\eta}$$

$$\Rightarrow h_f \sim \sqrt{\eta}$$

h_f: final thickness
h_0: initial thickness
s: distance
t_f: imprint time
p: pressure
η: viscosity

Thin (<<100nm) residual layer leads to less dimensional accuracy loss, so low viscosity (high flow rate) is desired.



Conclusion:
UV sealant and UV glue not appropriate.

Certainly, residual layer thickness also depends on initial dispensed drop volume.

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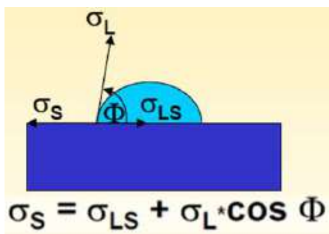
Summary for resist

Curing chemistry: ideally it should be compatible with oxygen, so no need of vacuum.

Curing speed: higher is better for faster imprint, typically few seconds curing time.

Viscosity: lower is better, to fill large features faster, to have thinner residual layer.

Surface energy: since the resist has to "wet" the mold (contact angle <90 degree) for imprint using low pressure, both the mold and the resist have to have low surface energy for easy separation. Low surface energy resist may not adhere (wet) the Si substrate, making spin coating difficult or leading to resist peel off upon separation. One strategy is to coat an under-layer (PMMA, PMGI, ARC…) that binds well with the resist having low surface energy.



If mold is coated with mold release agent (very low surface energy), the resist may still "wet" the mold if it also has low surface energy. (i.e. all the σ in the equation is small, one can still have Φ<90°)

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Mold for thermal and UV-curing NIL

Mold: also called template, stamp, master.
Mold release agent: also called releasing layer, anti-sticking coating.
Separation: also called de-molding, de-embossing, release.

Overview:
- Usually fabricated from Si, quartz or nickel, though polymer mold is becoming more popular and available.
- Feature fabrication at 1x vs. 4x for optical projection lithography, and critical dimension (CD) control at 1x is more challenging.
- For instance, photomask needs ~250 nm resolution to print 65 nm features; NIL mold needs to be 65nm.

Desired properties:
- Compatible to mold release agent coating.
- Mechanically durable (for reuse).
- Chemically durable (for cleaning).
- Low CTE mismatch with substrate (coefficient of thermal expansion).

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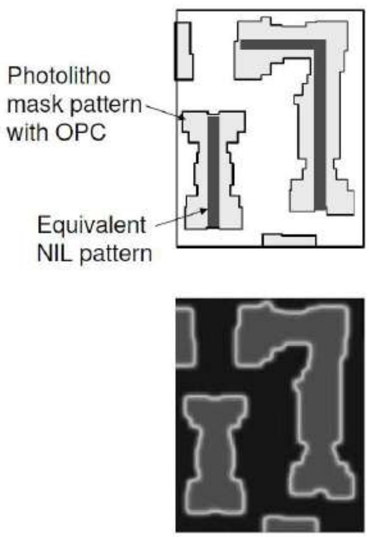
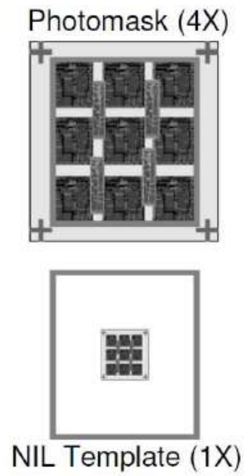
Comparison with photomask

Optical projection lithography mask with OPC & equivalent NIL mold.





OPC: optical proximity correction

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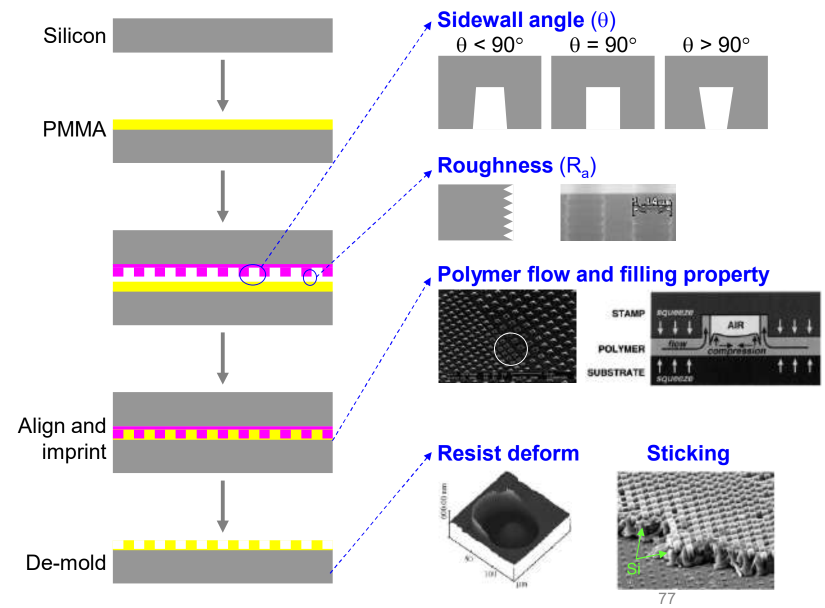
Mold issues: profile, roughness, sticking



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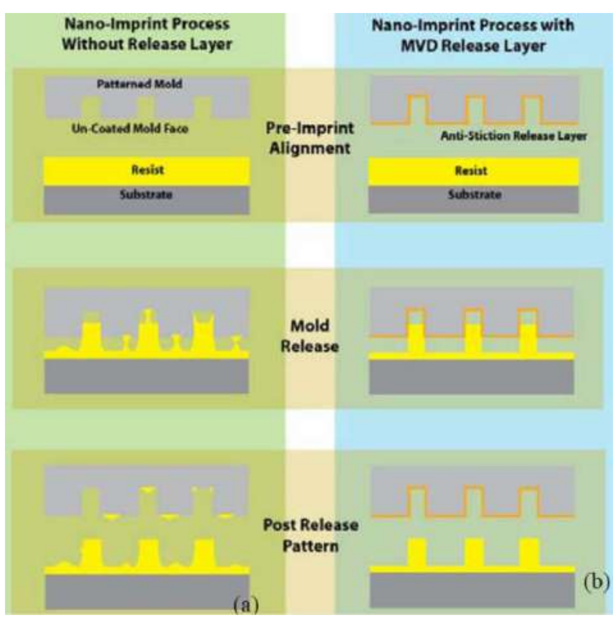
Importance of anti-stick coating



NIL using a mold without (top) and with (bottom) anti-stick coating

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Mold release agent: teflon-like coating

Same idea as anti-stick cooking ware coating, but mono-layer.

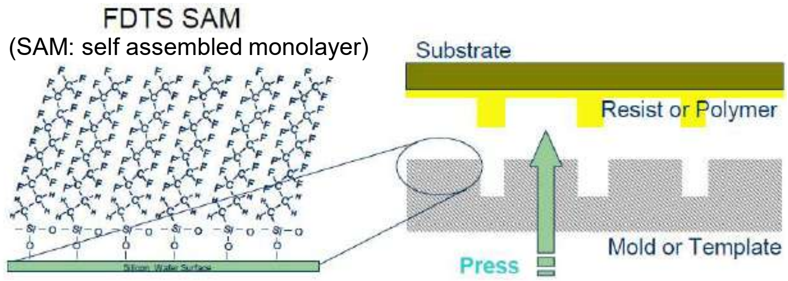

Fig. 2 SAMs used as a low energy release layer

FDTS: (1H,1H,2H,2H)-Perfluoro decyl trichloro silane, works with SiO_2 surface

Coatings are 100% conformal and extremely uniform.

Silane treatment by simple vacuum coating:
Clean wafer by oxygen plasma, put wafer and a drop of silane inside a container, and vacuum the container. After >5 hours, take wafer out and bake 150°C for 20min to stabilize the silane coating.

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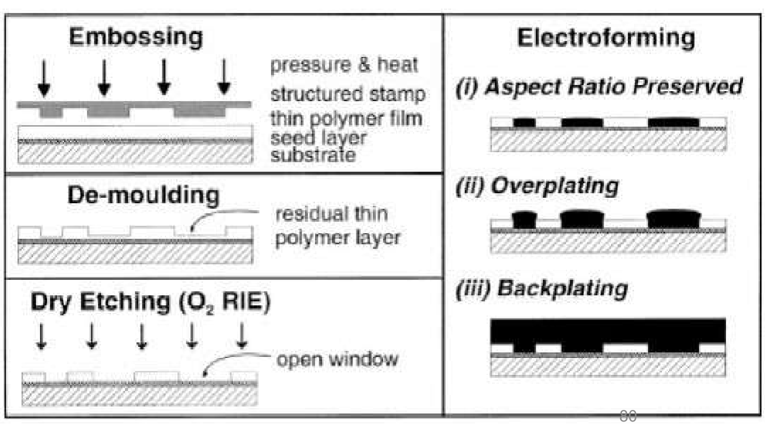
Ni mold

- Si or SiO_2 mold is most popular, but they are brittle.
- Metal mold is more robust and durable, used for making CD/DVDs.
- More difficult to fabricate, takes days for electroplating to 100s μm thick.
- Thickness is not uniform: much thicker (>2×) plating near wafer edges, need polishing back.
- Direct silane anti-stick coating to Ni not working, needs sputtering a thin (10nm) SiO_2.
- More used for hot-embossing onto thick plastic sheets for micro/nano-fluidics applications.



Source: Microelectron. Eng. 57-58 (2001) 375-380

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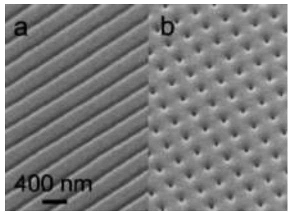
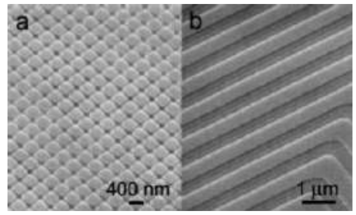
SEM images of Ni molds

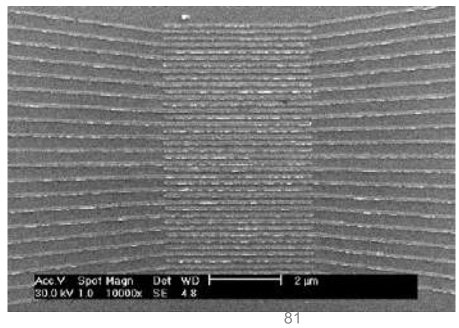
Mold by electroplating





Mold by e-beam lithography and liftoff

Easier to pattern metal by liftoff.
But metal structure by lift-off doesn't have vertical profile (Δ-shaped), and is of low height.
The underneath Si is still brittle.



SEM image a of Ni/Si mold showing 90nm channel-length inter-digited electrodes.

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Soft PDMS/ PMMA (rigid) mold for UV-NIL

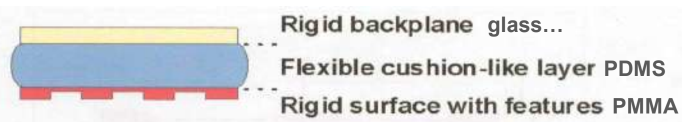
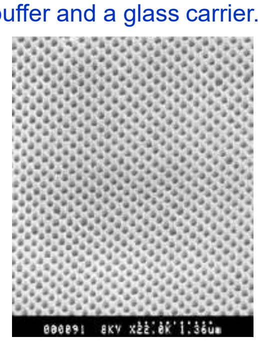
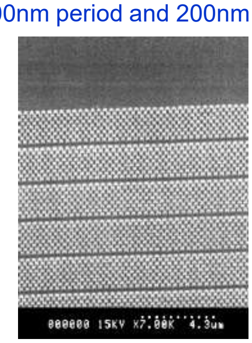


Figure 7: schematic overview of a possible multi-layer-stamp design, a flexible cushion like layer between a rigid backplane and a thin, rigid surface with the imprint structures

Mold: PMMA top layer cast and bonded on a PDMS buffer and a glass carrier.

Resist pattern: 0.1atm imprint pressure, triangular lattices of 300nm period and 200nm pillar diameter.





PDMS alone can be used as UV-NIL mold, but its nanostructure is not hard enough and will bend/collapse during NIL even at low pressure. It is good for µm-feature size UV-NIL.

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Roy, "Enhanced UV imprint ability with a tri-layer stamp configuration", MEE 2005

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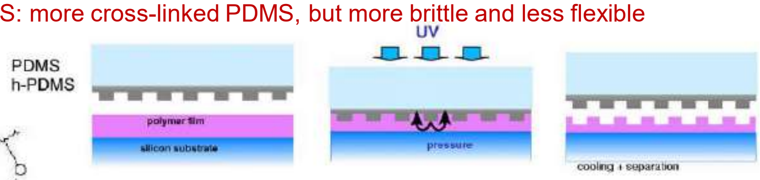
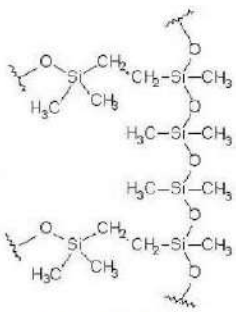
Soft PDMS/hard PDMS mold for UV-NIL

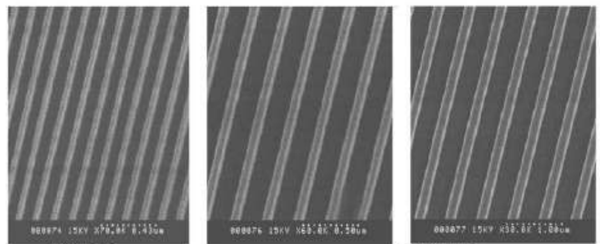
Hard PDMS: more cross-linked PDMS, but more brittle and less flexible





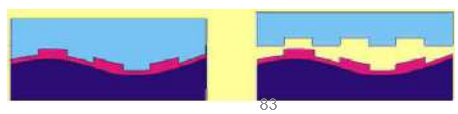
PDMS

Images of line gratings after NIL



70 nm 120 nm

Use of a flexible mold :
for conformal contact,
even on patterned substrates
with surface irregularities



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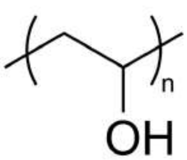
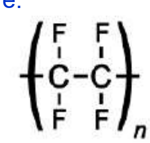
Other polymer mold materials

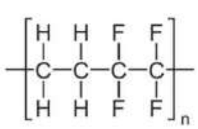
PVA (polyvinyl alcohol): water soluble, can be one-time use mold (imprint and dissolve the mold with water)



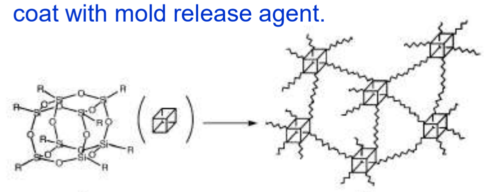
PTFE (Teflon, polytetrafluoroethylene): can be molded using a silicon mold at high temperature (>250^{o}C). Low surface energy (no need for mold release agent), high strength, can do thermal NIL at high temperature.



ETFE (ethylene tetrafluoroethylene): similar to PTFE, but mold is easier to fabricate from a master mold.



SSQ (silsesquioxane): similar to HSQ. After cross-linking the material is like SiO_2, which is easy to coat with mold release agent.



In principle, all cross-linked polymer can be used as NIL mold; however, most of them cannot be treated with mold release agent.

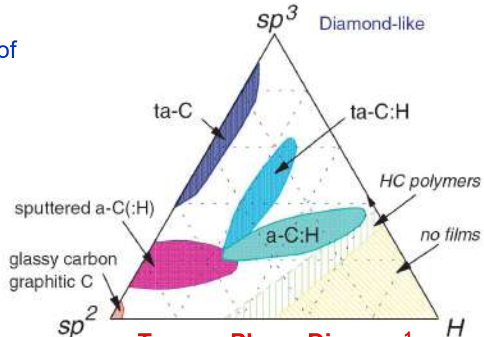
Barbero, "High resolution nanoimprinting with a robust and reusable polymer mold" (ETFE), Advanced Functional Materials, 2419 (2007)

84

Diamond mold

Diamond is hardest, but too expensive. Use diamond like carbon (DLC) *film* instead for mold.

- DLC is a synthetic meta-stable form of carbon.
- Amorphous network consisting of various fractions of hydrogen, SP^2 and SP^3 hybridized carbon.
- Common synthesis techniques
  - Pulsed laser deposition
  - Ion beam deposition
  - Plasma enhanced chemical vapor deposition (PECVD)
  - And many other techniques
- PECVD deposition uses hydrocarbon plasma in the presence of energetic ion bombardment.



Ternary Phase Diagram[1]

Why DLC is a good mold material?

- Excellent hardness and wear resistance → 30-35 Gpa.
- Low energy surface → 35-50mN/m, may not need anti-stick coating.
- Controllable band gap → 1 to 3.5eV, for UV transparency.
- High chemical and corrosion resistance.
- Can be deposited on both Quartz and Si.

However, DLC deposition is very challenging, not very available.

J. Robertson, Materials Science and Engineering R 37 (2002), 129-281

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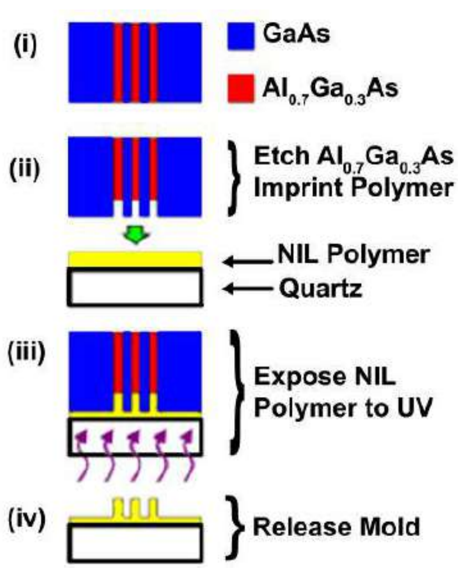
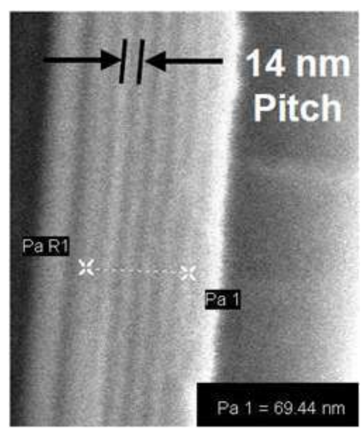
Mold by MOCVD and selective wet-etching





Precise control of pitch and line-width.

By far the highest resolution (~6nm) NIL is demonstrated using such a mold.

Otherwise, it is very difficult to write 14nm pitch grating using e-beam lithography.

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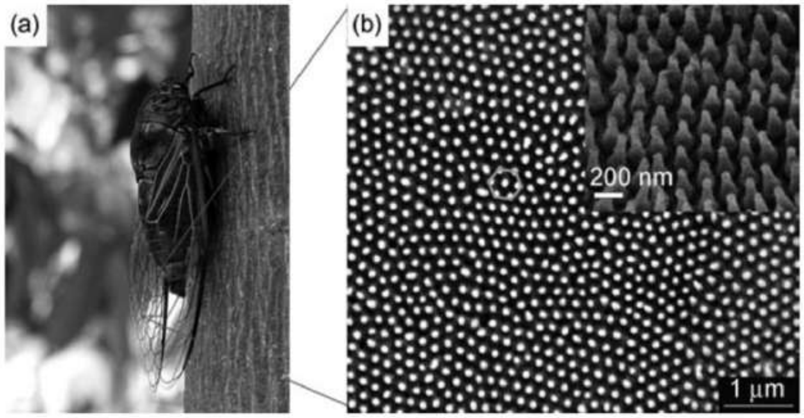
Mold fabricated by nature

Cicada Wings: a mold from Nature



The cicada wings consist of ordered hexagonal close-packed arrays of pillars with a spacing of about 190nm.

The height of the pillars is about 400nm and the diameters at the pillar top and bottom are about 80nm and 150nm, respectively.

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Properties of cicada wings

- Cicada wings have sufficient stiffness, chemical stability and low surface tension for NIL.
- These properties originate from the arrangement of highly crystalline chitin nano-fibers embedded in a matrix of protein, polyphenols and water, with a small amount of lipid.
- Crystalline chitin interacts with the protein matrix via hydrogen bonding, which gives stiffness and chemical stability to the structure.
- The Young's modulus of these cicada wings can be as high as 7–9GPa. Although far lower than silicon (up to 131GPa), it is sufficient for imprinting into PMMA.
- There is a layer of wax on the surface of the wings, which contains esters, acids, alcohols, and hydrocarbons. This layer gives low surface tension, so no need of anti-stick coating.

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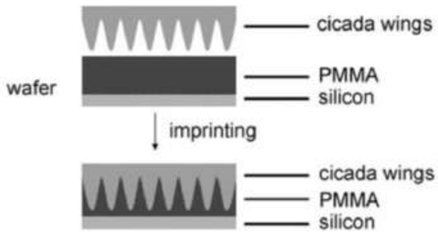
Results of NIL using cicada wing mold



Pressure ~40 bar; temperature ~190℃, 70℃ higher than the T_g of PMMA; imprint time 3min.

The pitch between the wells is about 190nm, the well diameter is about 150nm, and the depth is found to be about 400nm; these are consistent with the mold.

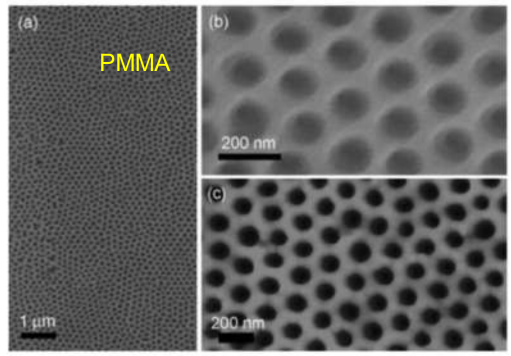


Figure 3. Results after imprinting using cicada wings as the stamp. (a) and (b) are SEM images of patterned PMMA with different scales. (c) is an AFM image of the patterned PMMA surface.

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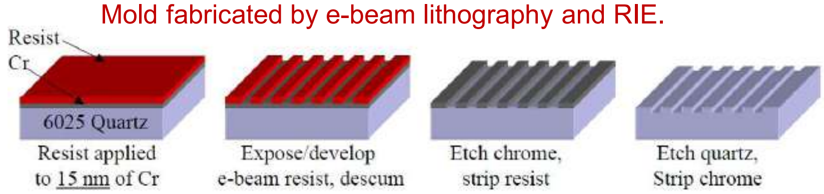
Mold fabricated by engineer

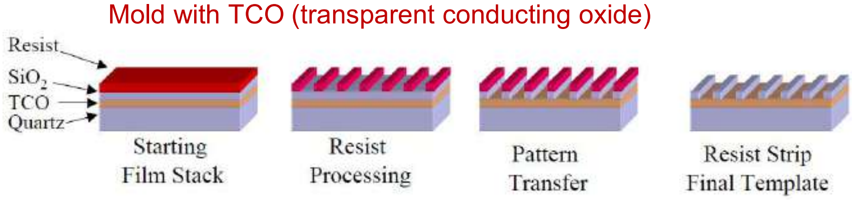
Mold fabricated by e-beam lithography and RIE.



RIE gas Chemistry: Cr – Cl_2/O_2; SiO_2 – CF_4/O_2

If no Cr RIE etch facility (no Cl_2 gas), Cr can be patterned readily by liftoff.

Mold with TCO (transparent conducting oxide)



Incorporating TCO film in the mold has the following advantages:
- Mold written by EBL without charge build-up.
- Final molds are easily inspected with SEM (no charging).
- It is still transparent for UV-NIL.

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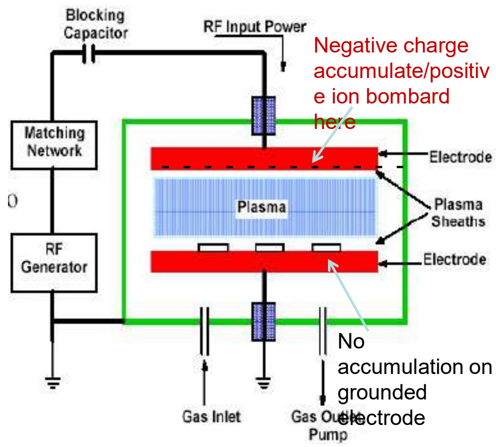
Parallel plate etchers (regular RIE, low density plasma)

- Both chemical reaction and physical sputtering process occur.
- Plasma etch mode:
  - Pressure: 100 – 1000mTorr
  - Voltage drop (self-bias) 10 - 100V
- Reactive ion etch (RIE) mode:
  - Pressure: 10 - 100mTorr
  - Voltage drop 100 - 700V
- RIE has high voltage drop, so is more directional/anisotropic than plasma etch.



Parallel plate etcher is low density plasma system: most gas molecules are NOT ionized or excited, so the reactive species and ions have very low density, leading to low etch rate.

This is *sputter* deposition configuration; for etching, the two electrodes need to be reversed, and wafer put on the electrode not grounded.

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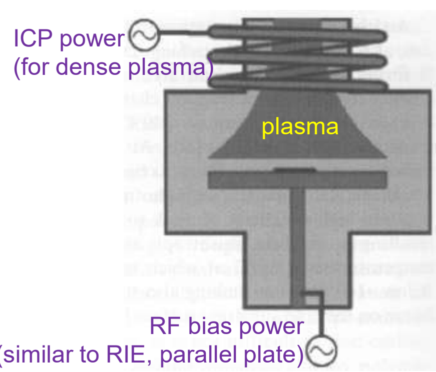
High density plasma system

Inductively coupled plasma (ICP)
(four systems at Waterloo)



Picture of an analytical ICP viewed through green welder's glass

- High AC magnetic field in the coil, so electrons move in circles with long path, leading to higher collision and ionization probability.
- Plasma density 10^{11} - 10^{12} ions/cm^3.
- Independent control of RF bias (ion energy, directionality) and ion density (ICP plasma density, chemical etching rate).
- High etching rate than RIE, but may be less anisotropic due to increased chemical etching.
- ICP etcher can be used as a pure RIE etcher by turning off the ICP component.

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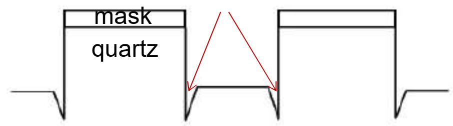
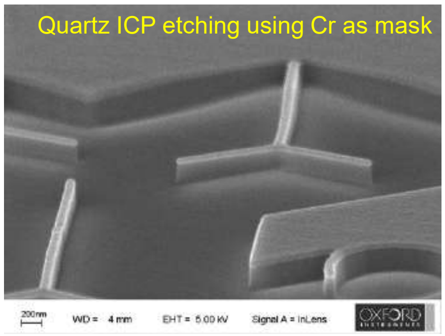
Etching issues for mold fabrication

- Etch should be vertical or very near vertical.
- NO negative slope allowed
- Trenching undesirable
- Smooth sidewalls desirable
- Uniform depth
- Uniform critical dimension (CD)



ICP etching offers better process control
(ICP-inductively coupled plasma)



- Cr mask etch followed by quartz etch.
- 200nm depth for 30nm features (aspect ratio 7:1)
- Etch rate 85nm/min.
- Selectivity over Cr >170:1 (very high).
- 89-90°profile (very vertical)
- Smooth and trenching free.

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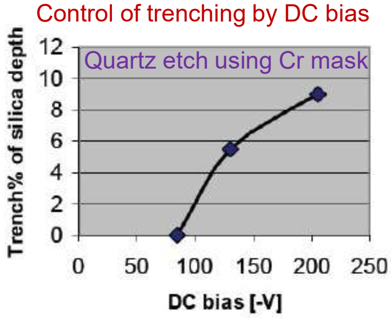
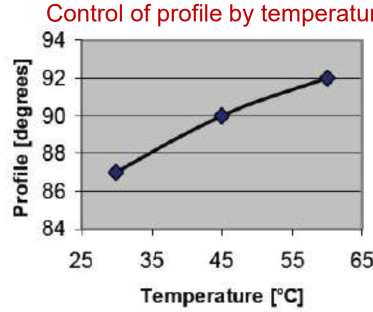
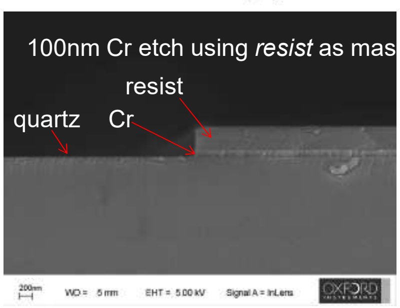
ICP quartz mold etch: process control

Control of trenching by DC bias



Control of profile by temperature





Process gases: Cl_2, O_2 (+He).
Cr etch rate >15nm/min.
Uniformity <±4% (200mm wafer)
Profile >85°.
Delta CD<50nm.
CD control < ±1%.
Selectivity Cr : resist > 0.5 : 1 (resist dependent)

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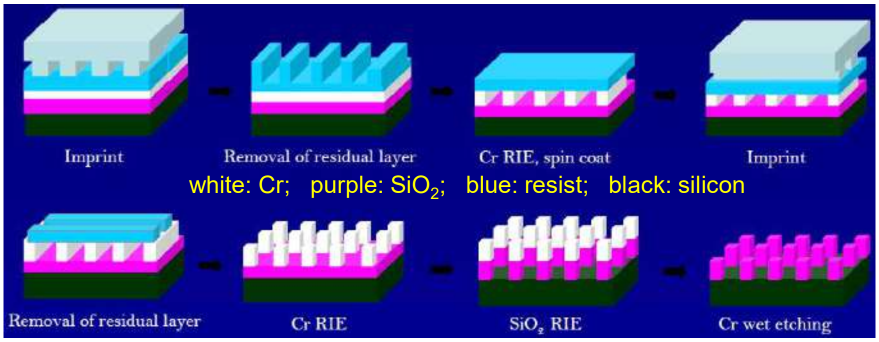
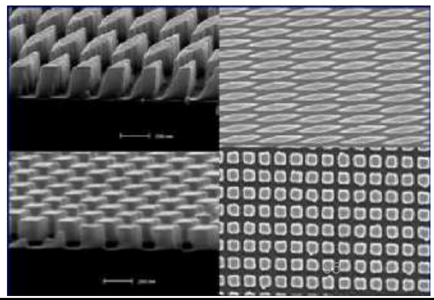
Pillar array mold fabrication from a grating mold



Grating mold over large (up to 4" wafer with 200nm period) can be fabricated by interference lithography



Pillar array (2D) mold fabricated from grating (1D) mold by two NILs (at orthogonal directions or not)

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Nanoimprint lithography (NIL)

1. UV-curable NIL.
2. Resists for UV-NIL.
3. Mold fabrication for thermal and UV-NIL.
4. Alignment.
5. NIL into metals.
6. NIL systems (air press, roller, roll-to-roll, EFAN…)
7. NIL applications

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END of NIL

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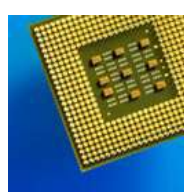
Alignment (overlay)

- Electronic devices such as transistors/chips require multiple levels of materials and processing.
- For NIL, there is no distortion due to lens since no lens is used.

Challenges for sub-100nm alignment:

- Smaller error budget for mold pattern placement since it is 1×.
- Alignment mark fabrication error has to be <10nm.
- Features are too small to be seen optically ~10nm.
- Alignment is sensitive to the gap between mold and substrate.
- Mold distortion/drift due to pressure, temperature and defects is big problem.
- Generally, alignment for NIL is much more difficult than other lithographies.
- Thermal NIL is worse due to thermal expansion mismatch.

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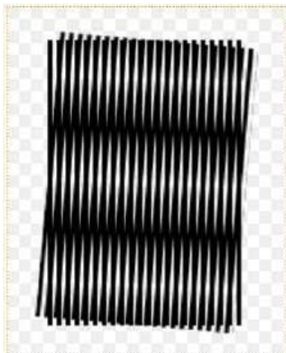
Possible alignment methods

- Direct imaging, as in optical lithography.
- Amplitude-sensitive schemes.
- Phase-sensitive schemes.
  - Spatial phase detecting – Moiré pattern (simple, insensitive to gap)



A moiré pattern, formed by two sets of parallel lines, one set inclined at an angle of 5° to the other.

(Wikipedia) In physics, a moiré pattern is an interference pattern created, for example, when two grids are overlaid at an angle, or when they have slightly different mesh sizes.

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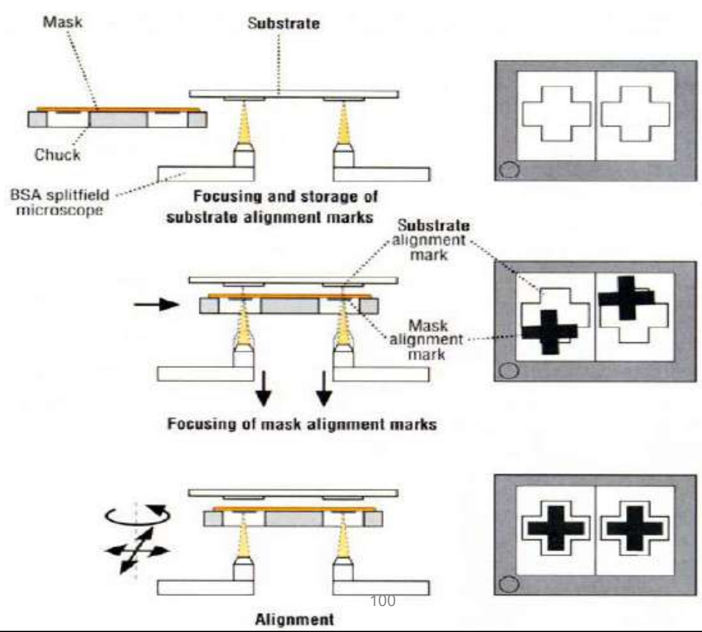
Direct imaging

- Backside alignment because silicon substrates are not transparent to visible light.
- Sub-micron precision is demonstrated.
- Precision is limited by optical resolution and thermal, mechanical noises.
- For thermal (or UV) NIL that requires high pressure, alignment is easily destroyed due to lateral drift of mold or substrate.



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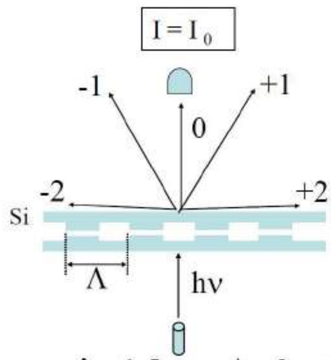
Amplitude sensitive alignment scheme

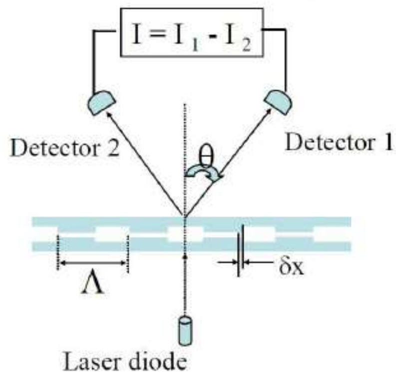
•**Method-1**: Measure the zero order diffraction patterns of two gratings with the same period



e.g., λ= 1.5 µm, Λ= 3 µm

Maximum signal when aligned.

•**Method-2**: Measure the first order diffraction patterns of two gratings with the same period



Minimum signal when aligned (I_1=I_2)

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William Moreno, Princeton

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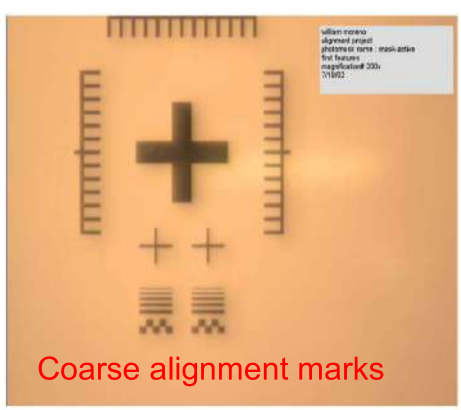
Two step alignment using cross marks and Moiré patterns

Moiré patterns: optical image of superposition of two patterns.
Advantage: slight displacement of one of the objects creates a magnified change in their Moiré patterns.
For sub-100nm alignment:

Coarse alignment using cross marks and boxes or circular gratings.
Fine alignment using interferometric spatial phase matching (Moiré).



Optical image (200x)

- Same as alignment in contact/proximity optical lithography.
- Cross mark provide alignment of ~0.5µm.
- Cross marks are relatively big and easy to locate.

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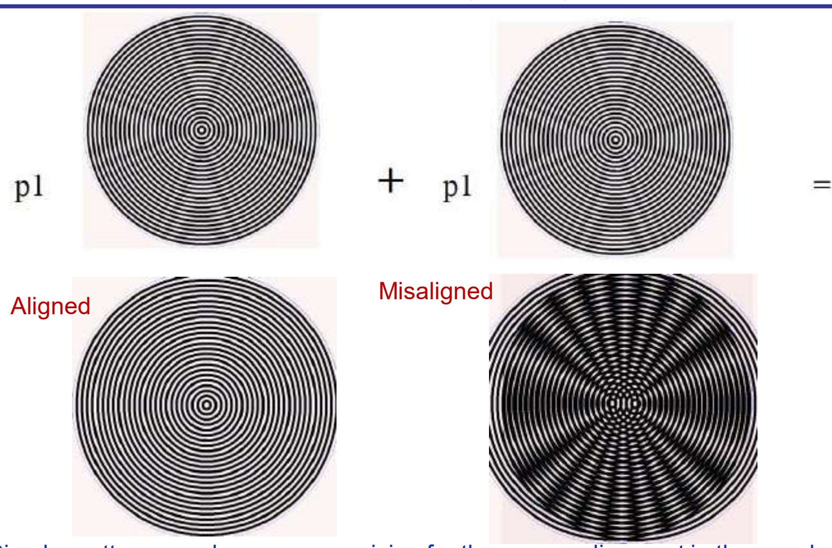
Circular gratings



Circular patterns produce more precision for the coarse alignment in the x and y axis.
They are more sensitive to displacement than cross marks.
M. King and D. Berry were the first who start alignment using moiré concentric circles in 1972 (Appl. Opt.11. 2455).

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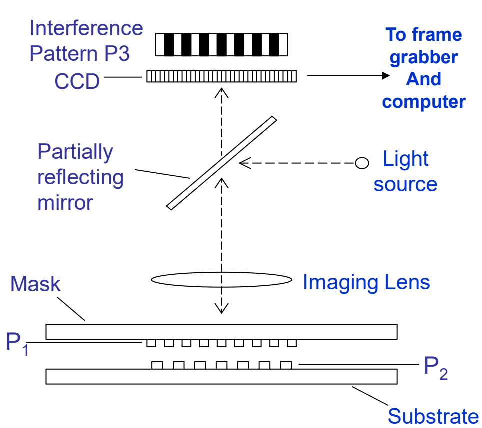
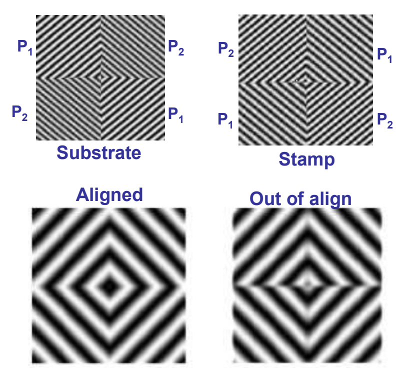
Fine alignment using Moiré: concept and simulation

Sub-10 nm alignment accuracy





Simulations of alignment/misalignment

$$P_3 = (P_1 \times P_2) / |P_1 - P_2|$$

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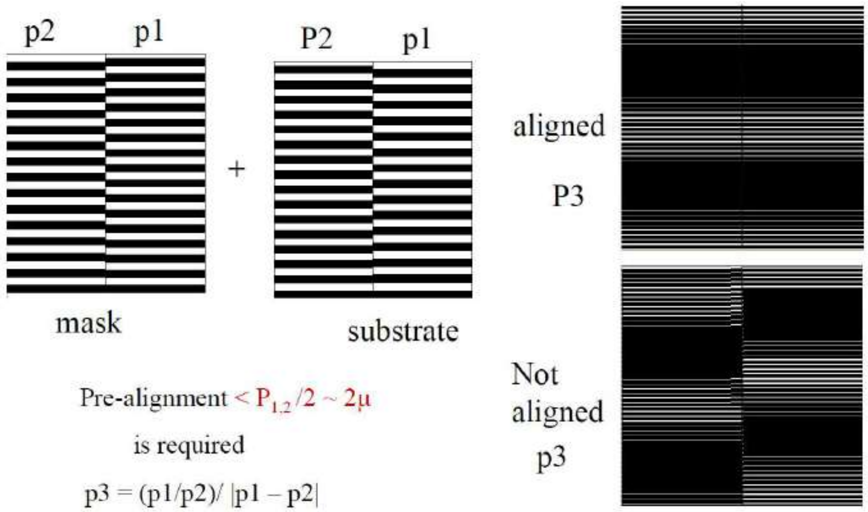
Interferometric spatial phase matching of linear gratings



Challenges:

- Precise alignment in tilting.
- Grating fabrication error need to be very small, smaller than 10nm.

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E. Moon, J. Vac. Sci. Tech. 1993A. MoelJ. Vac. Sci.

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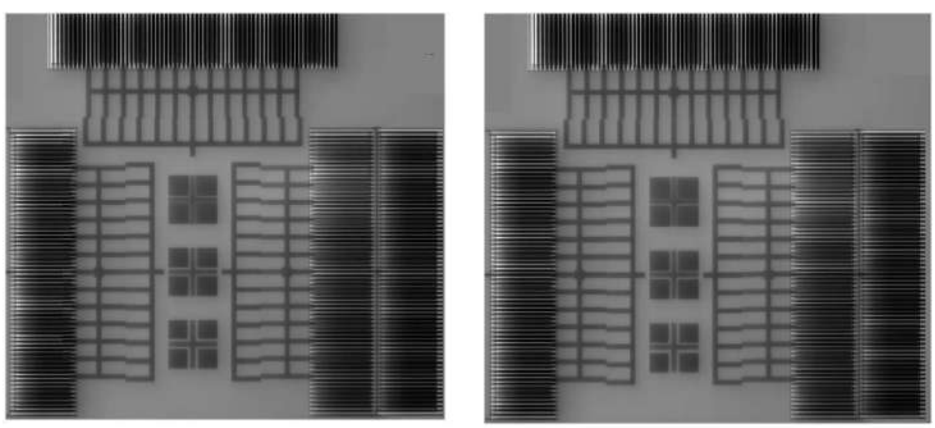
Moiré alignment marks for NIL



aligned misaligned

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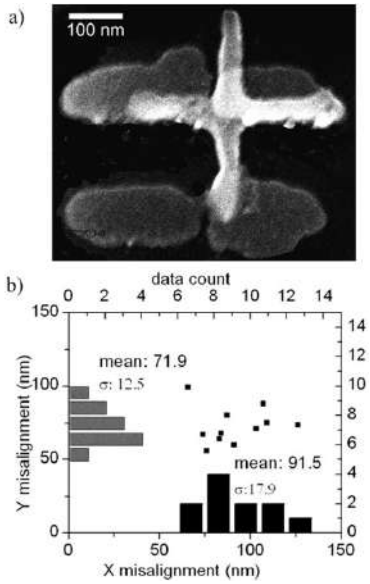
Result of sub-100nm alignment in NIL



For UV-NIL, sub-100nm alignment can be achieved readily, but this is still too far away from requirement for IC production (few nm).

"Sub-20-nm Alignment in Nanoimprint Lithography Using Moiré Fringe", Li, Nano Lett., 2006.

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Nanoimprint lithography (NIL)

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5. NIL into metals.
6. NIL systems (air press, roller, roll-to-roll, EFAN…)

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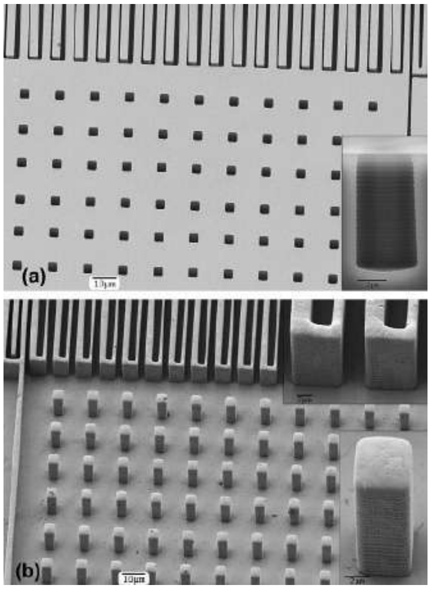
NIL directly into metals



Silicon mold (inset: cross-section) produced by ICP-DRIE (26 cycles), with line-width 1 or 2µm (depth 6µm) and holes with edge length 4µm (depth 8µm).

Microstructured silver plate after forming at 400°C with a pressure of 300MPa, and Si mold removal by KOH etching.
(Typical thermal NIL pressure is 2MPa)

"Metal direct nanoimprinting for photonics", Buzzi, MEE 2008

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NIL directly into metals: bi-layer and sharp mold

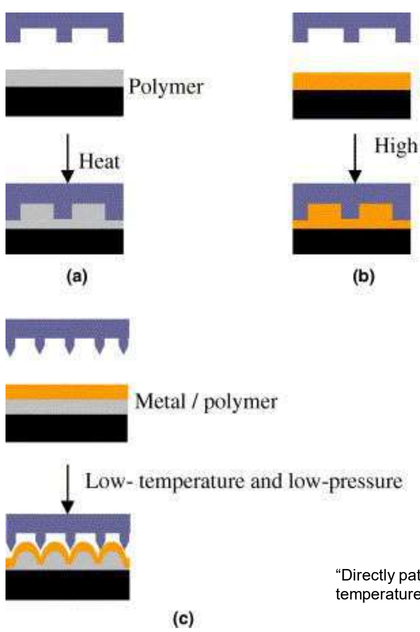

Fig. 1. Schematic diagrams of imprint technologies.
(a) Conventional nanoimprint lithography.
(b) Direct imprint metal films.
(c) Nanoimprint in metal/polymer bi-layer.

"Directly patterning metal films by nanoimprint lithography with low-temperature and low-pressure", Chen, MEE 2006

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Results

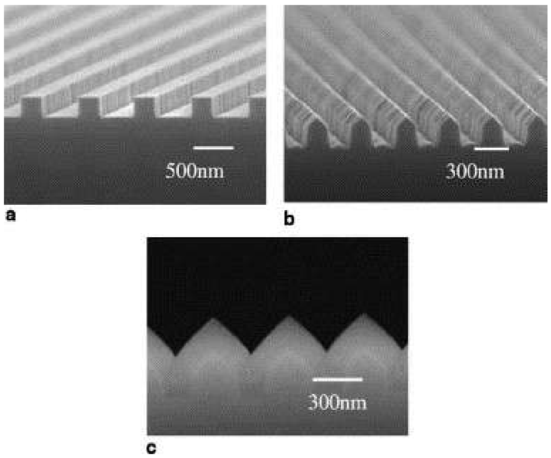

Fig. 2. SEM images of molds (a) conventional binary mold with flat top, (b) sharp mold, (c) triangle mold.

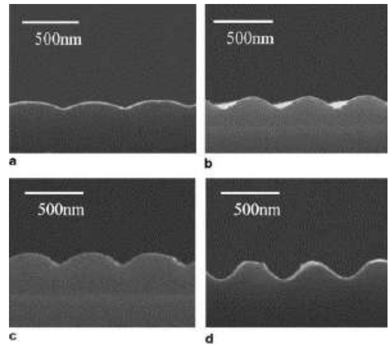

Fig. 5. The depth of surface-profile in metal films can be tuned by using different imprint pressure (a) 7 MPa, (b) 12 MPa, (c) 14 MPa, (d) 17 MPa.

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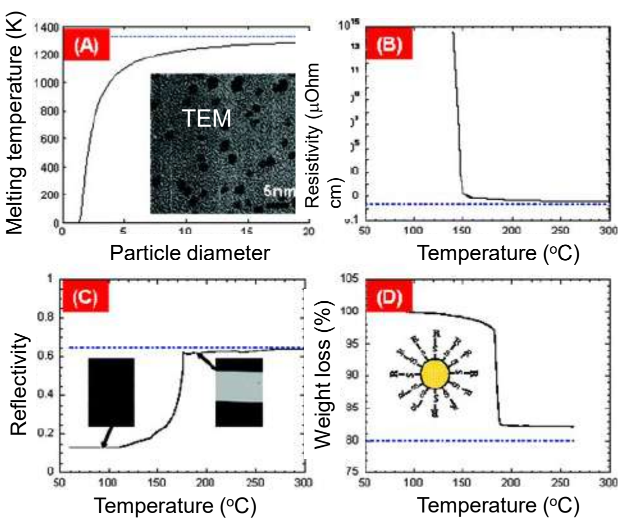
NIL into metal nano-particles at low temperature & pressure

Thermal (melting) characteristics of SAM-protected Au nano-particles (NPs).
NP can be melted/imprinted at rather low temperature. (SAM: self assembled monolayer)



(A)Melting temperature of Au NPs with different sizes.

(B)Resistivity (dotted line represents bulk gold resistivity 2.65μΩ·cm). Melt to form continuous film with low resistivity.

(C)Reflectivity at 514.5nm wavelength. Insets represent the optical images of NP film before (left) and after (right) the melting.

(D)Mass change at various heating temperatures.

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"Direct Nanoimprinting of Metal Nanoparticles for Nanoscale Electronics Fabrication", Ko, Nano Lett. 2007

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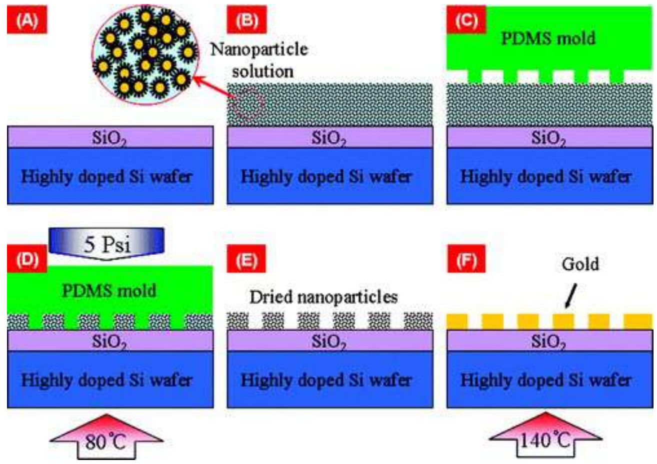
NIL into Au nano-particles and melting of NPs



(A, B) Dispensing NP solution on Si wafer.
(C, D) Pressing PDMS mold on NP solution under 5psi pressure at 80°C (1atm=14psi).
(E, F) Removal of mold and induce NP melting on hot plate at 140°C.
The SAM-protected NPs are suspended in an organic solvent that is extremely viscous (like a solid) at room temperature, but its viscosity drops drastically with temperature.

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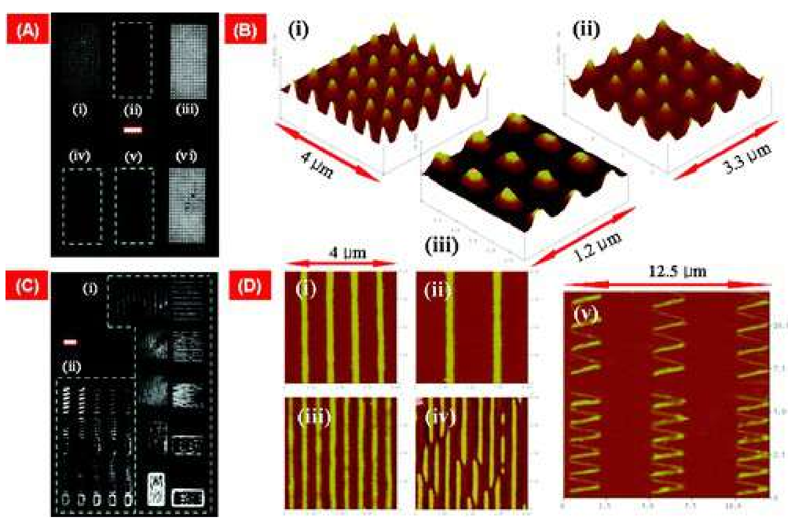
Results of NIL into Au



Optical dark field images of (A) nanodots and (C) nanowires (scale bar is 5 μm).
AFM topography images of (B) nanodots; (D(i–iv)) straight nanowires, and (D(v)) serpentine nanowires.

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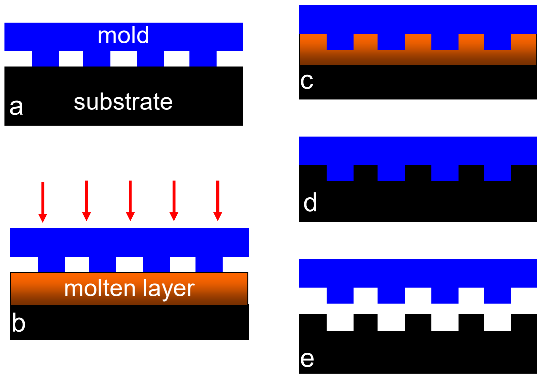
Laser-assisted direct imprint (LADI) of metals

Metal can be easily melted and patterned by a pulsed laser.



One-step patterning process:

Replaces the steps of resist patterning, pattern transfer by etching, and resist removal all into one single step. And this step takes only order 100 ns!

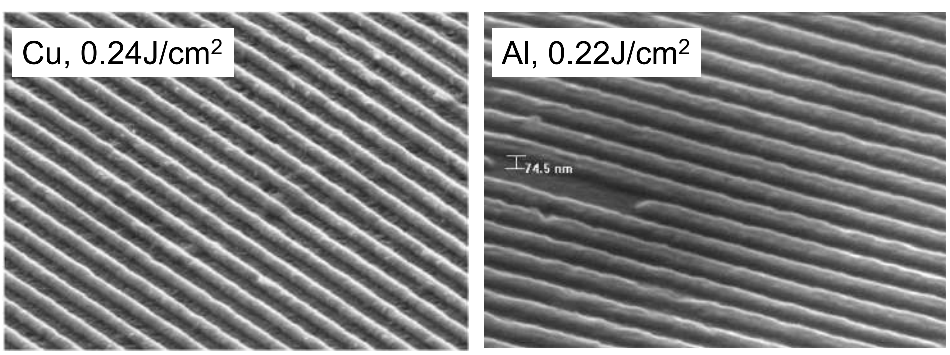
Minimal heating of the substrate

Mold and substrate can have different thermal expansion.

Application:

IC interconnect, flexible/durable NIL metal mold.

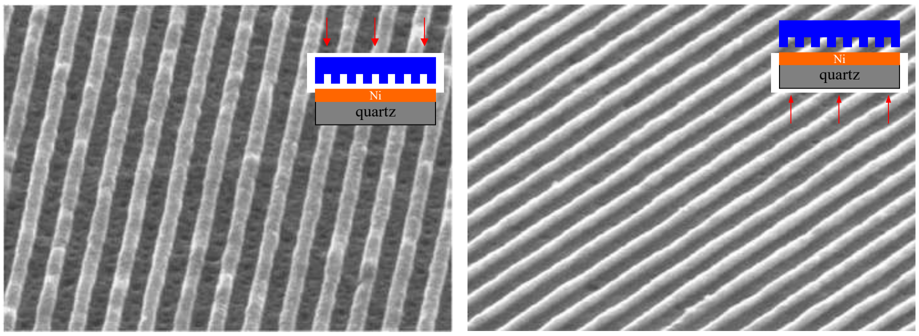
200 nm period grating patterned by LADI



Pattern height: 100 nm.
XeCl excimer laser, λ=308nm, 20ns pulse, laser fluence 0.24J/cm^2 = 12MW/cm^2
Line was rounded due to surface tension and volume shrinkage upon solidification.

200 nm period grating patterned by LADI: Ni

Front side illumination, 0.41 J/cm^2 — Back side illumination, 0.60 J/cm^2



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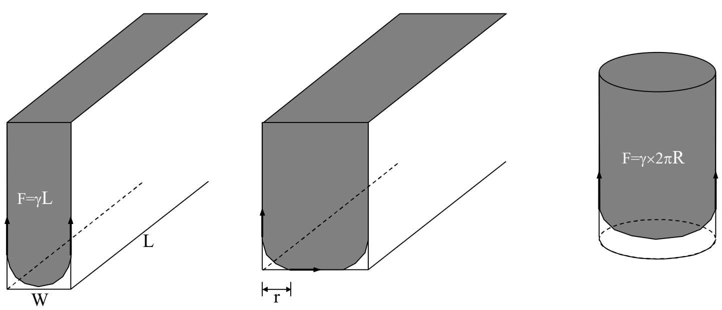
How much pressure needed



$$P = \frac{2\gamma L}{WL} = \frac{2\gamma}{W} \qquad P = \frac{2\gamma L \cos 45^o}{\sqrt{2} rL} = \frac{\gamma}{r} \qquad P = \frac{\gamma \times 2\pi R}{\pi R^2} = \frac{2\gamma}{R}$$

- Pressure $\propto$ surface tension / dimension.
- Order 10^2 atm is needed for 100 nm feature size, due to the high surface tension of metals.
- The surface tension of metals are order 1N/m, as compared to 0.07N/m for water.

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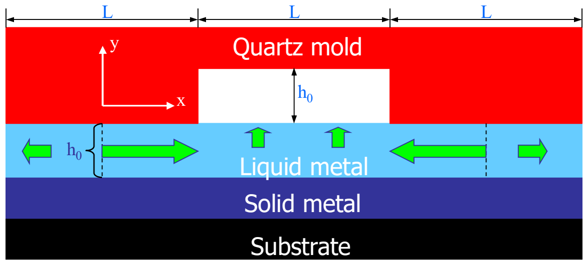
How big feature can be patterned
(how far the liquid can flow before it freezes)



$$L = \frac{2h_0}{3}\sqrt{\frac{p\tau}{\mu}}$$

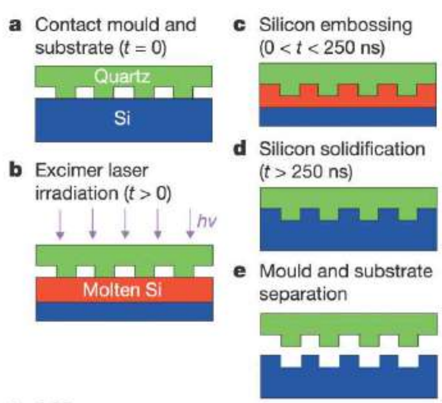
Inertial force is ignored.
p: pressure.
τ: melting time.
μ: viscosity.

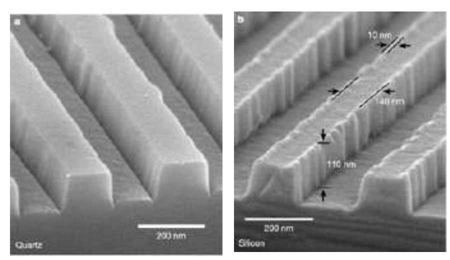
Material	L	Assume:
Cu	4.9 μm	P=400atm
Ni	4.2 μm	τ=100ns
Si	12.0 μm	h_0=200nm

Experiment: 17 μm Si has been patterned, but failed for several tens of μm.

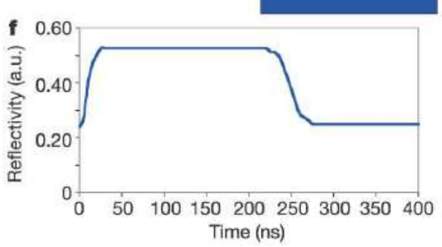
Viscosity for molten metals are comparable to that of water at room temperature (0.00091 Pa·sec, or 0.91 centipoises), much lower than polymer.

Direct imprint into Si





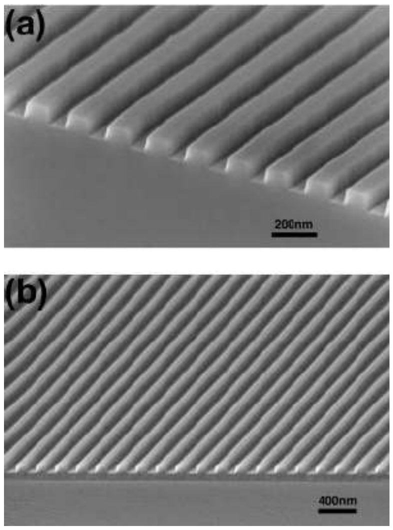
Faithful duplication of sub-10nm features in the quartz mold due to RIE trenching effect.



The reflectivity of a HeNe laser beam from the silicon surface versus the time, when the silicon surface is irradiated by a single laser pulse with 1.6mJ/cm^2 fluence and 20ns pulse duration.
Molten Si, becoming a metal, gives a higher reflectivity. The measured reflectivity shows the silicon in liquid state for about 220ns.

Chou, "Ultra fast and direct imprint of nanostructures in silicon", Nature,

Ultrafast (order 100ns) thermal NIL into polymer resist (not metal) using laser pulse



LAN: laser assisted nanoimprint lithography.
Polymer resist need to be dye-doped for optical energy absorption (transparent otherwise).

(a) Scanning electron microscope (SEM) image of 200 nm period grating quartz mold.
(b) NPR-69 (a NIL resist) gratings on a Si substrate produced by LAN with a single laser pulse of 0.4J/cm^2. The gratings have a line-width of 100nm and height 90nm.

Here the UV light is just to melt the resist, rather than curing it.

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“Ultrafast patterning of nanostructures in polymers using laser assisted nanoimprint lithography”, Xia,

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6. NIL systems (air press, roller, roll-to-roll, EFAN…)

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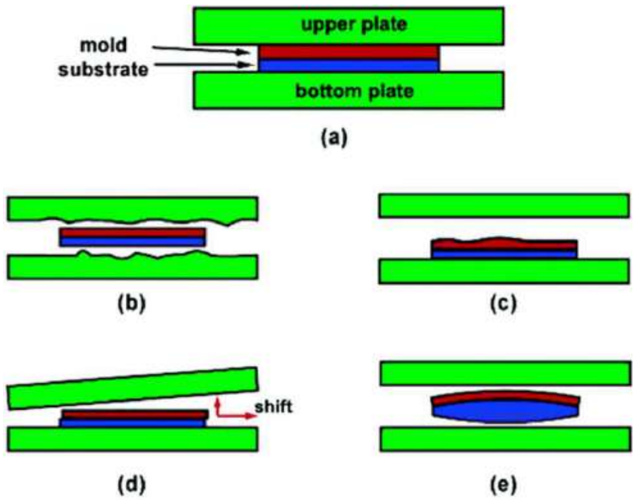
Limitations of solid parallel plate (SPP) press



(a) Ideal SPP
(b) Imperfect plate surfaces
(c) Uneven mold/substrate backside
(d) Non-parallelism between plates
(e) Curved sample surfaces

Fortunately, most of the problems can be solved by putting a piece of clean room paper, plastics, or graphite sheet above/below mold/substrate.

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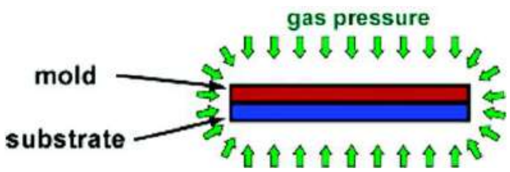
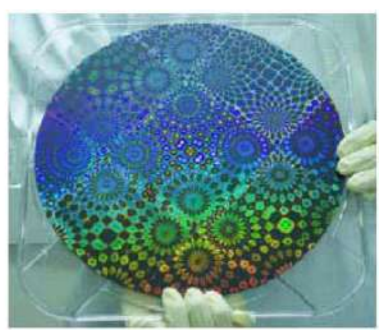
Air cushion press (ACP) nanoimprint



Mold/substrate sealed between plastic sheets/membranes

8-in pressure indicating papers (gas pressure= 5kg/cm^2). Uniform color means uniform pressure.



A 12-inch imprinted wafer

One can get similar imprint result using solid plate press, but needs higher pressure to make sure the pressure is high enough everywhere across the wafer.

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J. Vac. Sci. Technol. A, Vol. 23, No. 6, pp. 1687-1690,

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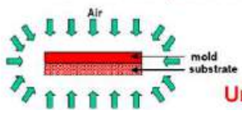
NIL tools: air-press

P_{max} = 500 PSI (34 bars)
T_{max} = 220 °C
UV : 200 W, 320-390 nm

* Full-wafer (up to 4") nanoimprinting tool
* Sub-micron overlay alignment accuracy

Air Cushion PressTM (ACP)
for ultimate nanoimprint uniformity

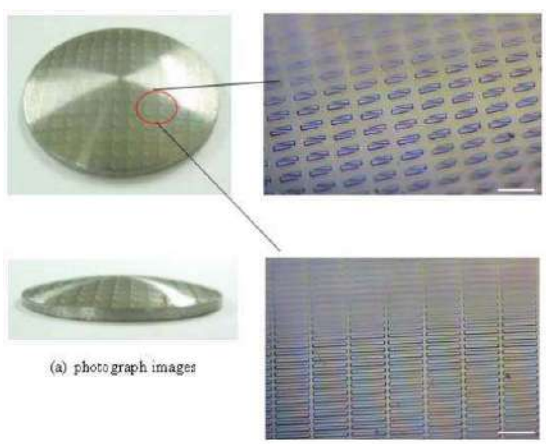


Uniform pressure applied by the 2 membranes

Air press has uniform pressure, but for most applications parallel plate press can also achieve good result (may need something soft like a paper for more uniform pressure).

“Air Cushion Press for Excellent Uniformity, High Yield, and Fast Nanoimprint Across a 100 mm Field”, Nano Lett. 2006.

NIL onto curved surface



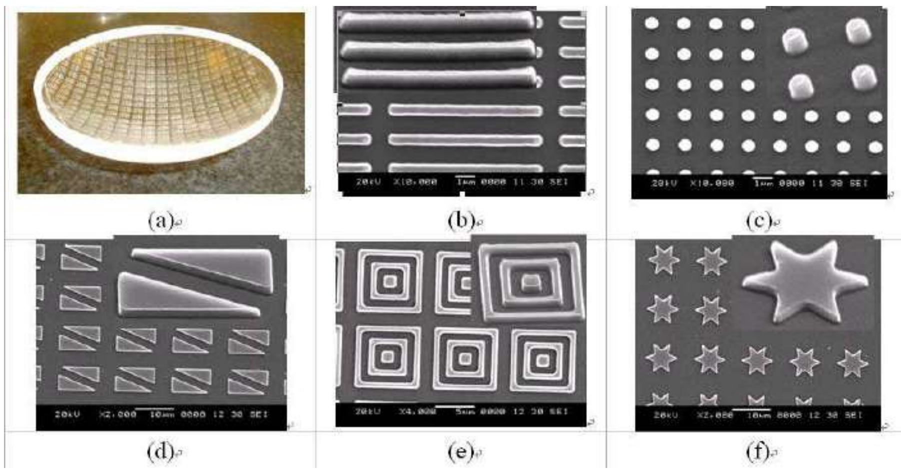
(a) photograph images

(b) OM images, scale bar is 15 μm

- Imprinted patterns on 2-inch convex surface.
- Using flexible PDMS mold and uniform gas pressure, the patterns can be transferred onto curved surface successfully.

Curved surface imprint

SEM images of detailed imprinted patterns on curved substrate.



J. Vac. Sci. Technol. B, Vol. 24, No. 4, Jul/Aug, pp. 1724-1727, Nov. 2006.

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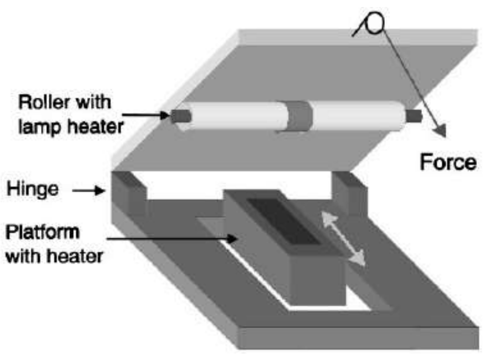
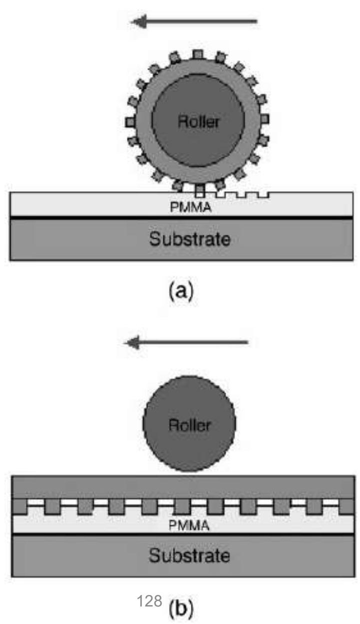
Roller NIL



(a)Imprints using a cylinder mold.
(b)Imprints using a flat mold: putting the mold directly on the substrate, and rotating the roller on top of the mold.

- For schema (a), infinitely large surface area can be imprinted using one (small) mold.
- For schema (b), NIL can be done at very low force.



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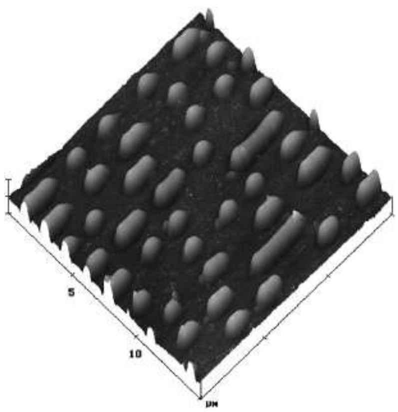
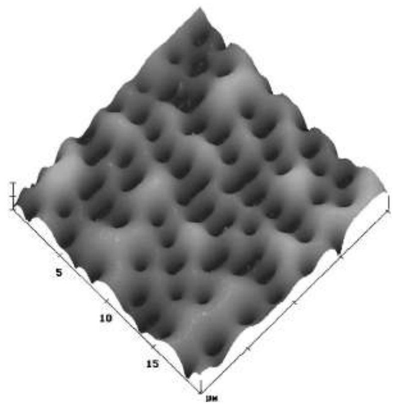
Results of roller NIL



AFM graph of a compact disk mold before bent into a cylinder: 700nm tracks pattern on the surface of compact disk.



PMMA imprinted by a cylinder mold, showing sub-100nm accuracy in pattern transfer.

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“Roller nanoimprint lithography”, Tan, JVST B, 1998.

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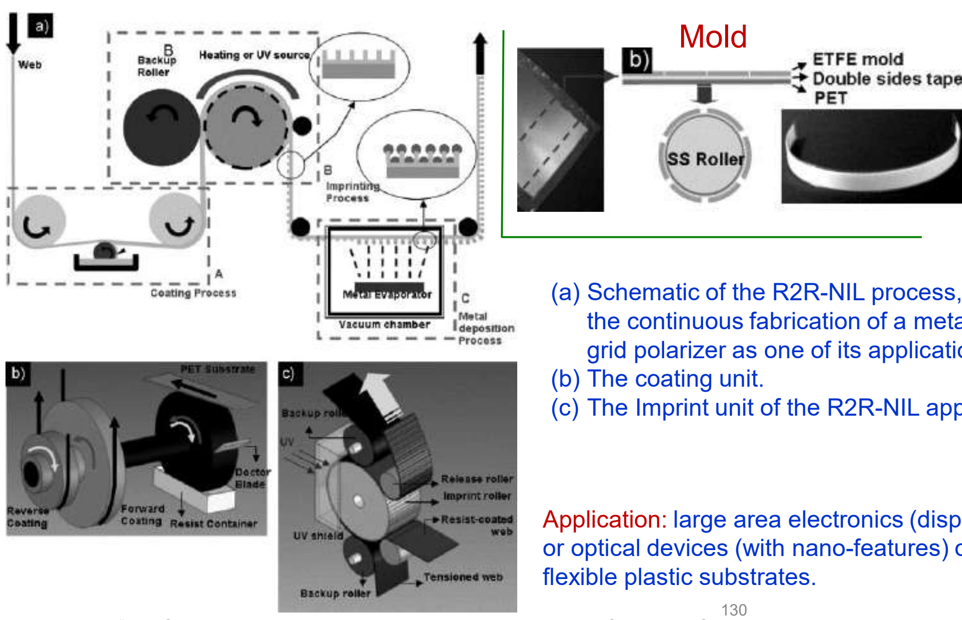
Roll-to-roll (R2R) nanoimprint lithography



(a) Schematic of the R2R-NIL process, and the continuous fabrication of a metal wire-grid polarizer as one of its applications.
(b) The coating unit.
(c) The Imprint unit of the R2R-NIL apparatus.

Application: large area electronics (display…) or optical devices (with nano-features) on flexible plastic substrates.

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“High-Speed Roll-to-Roll Nanoimprint Lithography on Flexible Plastic Substrates”, Guo, Adv. Mater. 2008.

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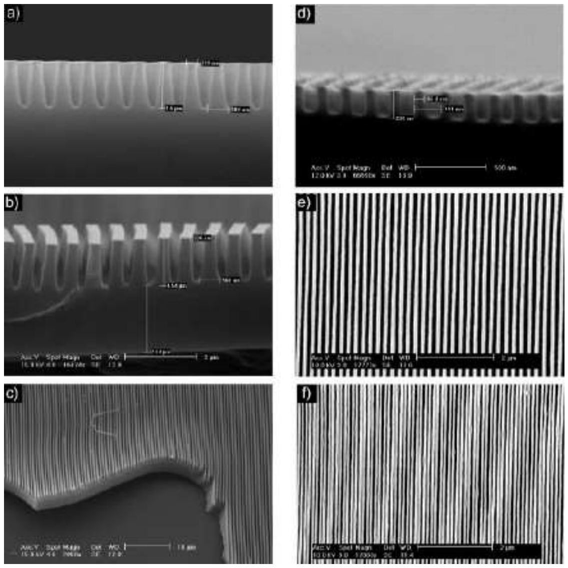
Results of roll-to-roll imprint



a) The original Si mold.

b-c) Epoxy-silicone gratings replicated from the ETFE mold.

d,e) SEM pictures of 200nm period 70nm line- width epoxy-silicone pattern.

f) 100nm period 70nm line-width epoxy-silicone pattern

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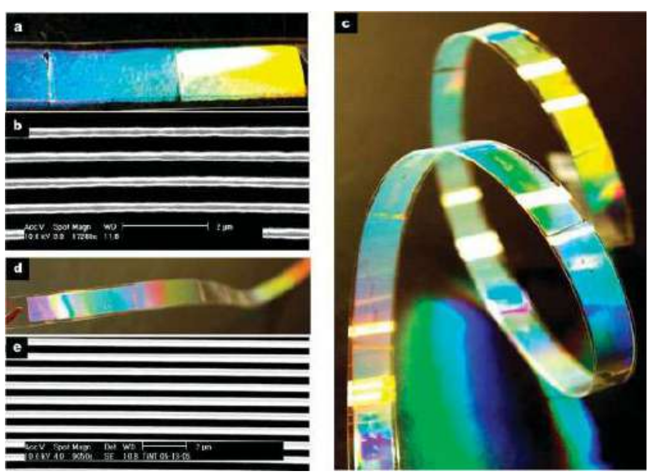
Results of roll-to-roll imprint



- Thermal R2R-NIL results: a-b) photograph and SEM of a 700nm period 300nm line-width PDMS grating pattern imprinted on PET strip.
- UV R2R-NIL results: c-e) photographs and SEM of 700nm period 300nm line-width epoxy-silicone grating pattern imprinted on PET strip, showing bright light diffraction. Total length is 570mm.

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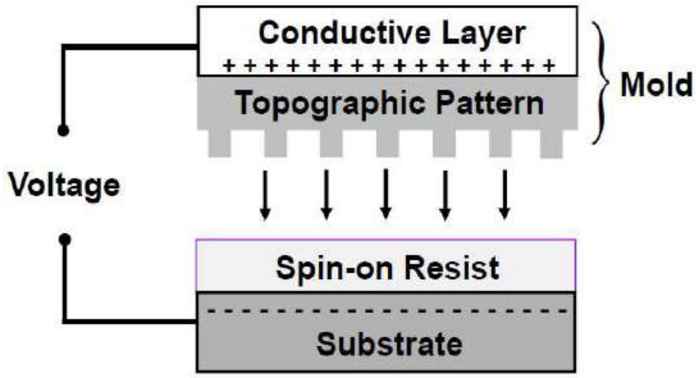
Electric field assisted NIL (EFAN)



Principle of EFAN: a voltage is applied between the conductive layers on the mold and the substrate, generating an electrostatic force to press the mold into the resist layer.

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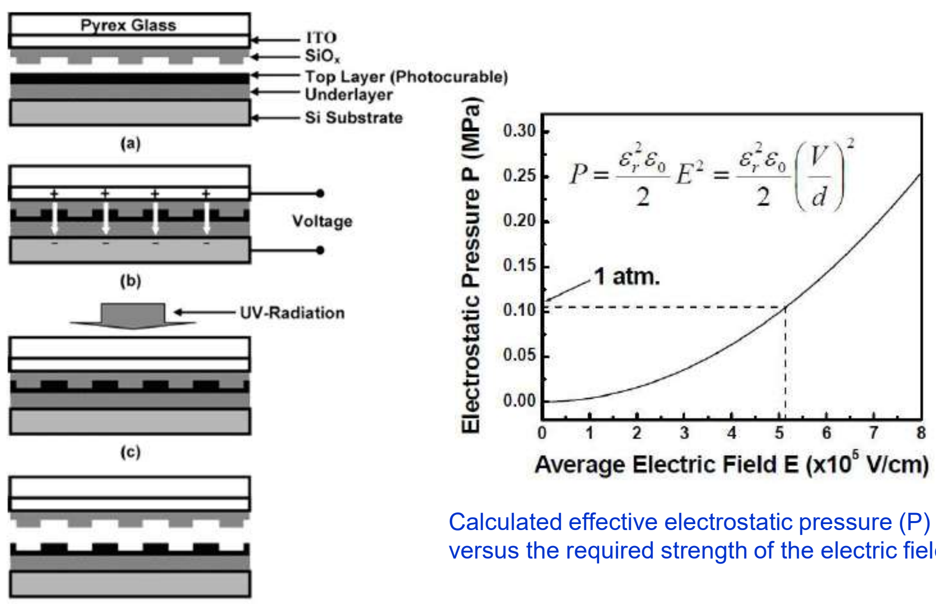
EFAN process flow



Calculated effective electrostatic pressure (P) versus the required strength of the electric field.

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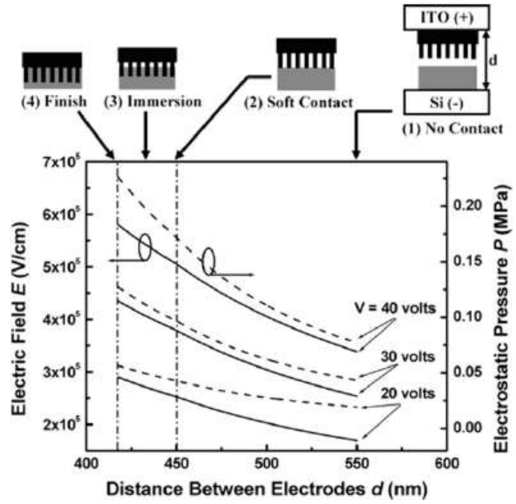
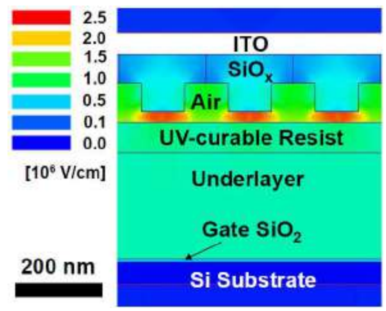
A more accurate calculation





A 2D simulation of EFAN, which adds complete details of dielectric structures into the calculation of electric field.

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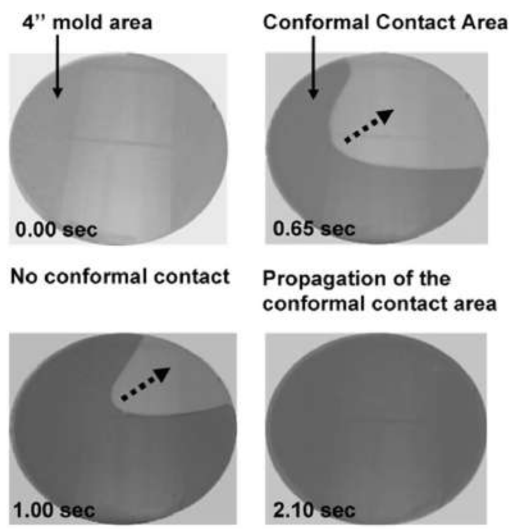
Propagation of contact area and imprint results

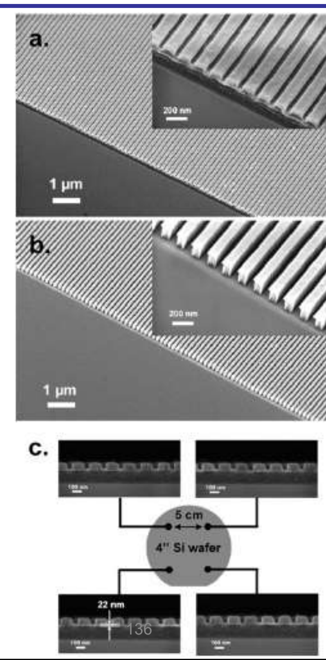


No conformal contact

Propagation of the conformal contact area

Propagation at t = 1 sec

Fully imprinted wafer at t = 2.1 sec



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Nanoimprint lithography (NIL)

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NIL applications: overview

- Basically, NIL can be used for virtually any applications involving nanofabrication.
- In fact, it would be the only choice for high volume production of nano-devices except those in IC (integrated circuit) industry and those don't need precise patterning (i.e. no need of long range ordering, they can then be patterned by cheap chemical synthesis or self assembly, namely "bottom –up" methods).
- This is simply because other nano-lithographies (EBL, FIB, scanning probe…) don't have the throughput needed for mass production.
- The major challenges for NIL: mold fabrication (1×), alignment, defect control. It still has a long way to go for IC manufacturing.

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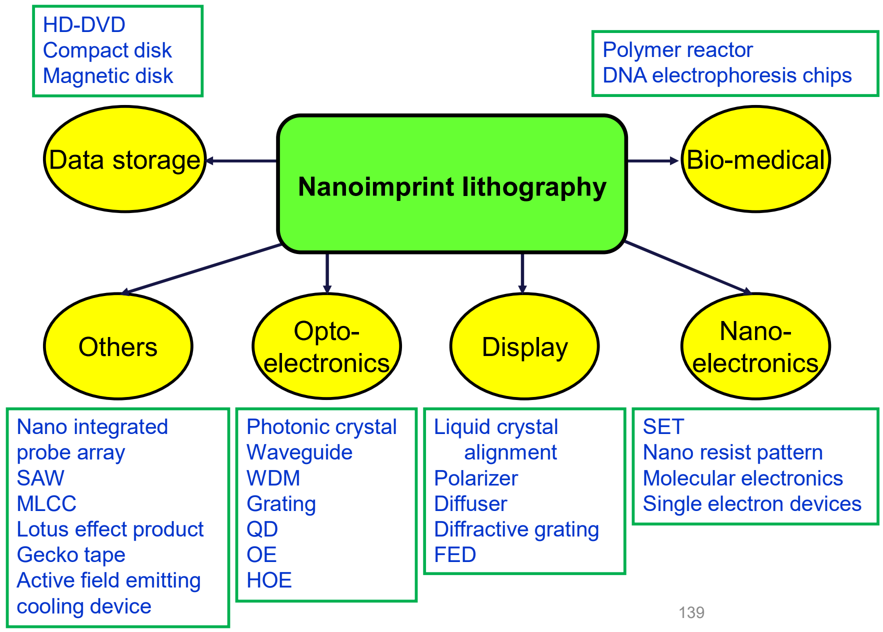
NIL applications



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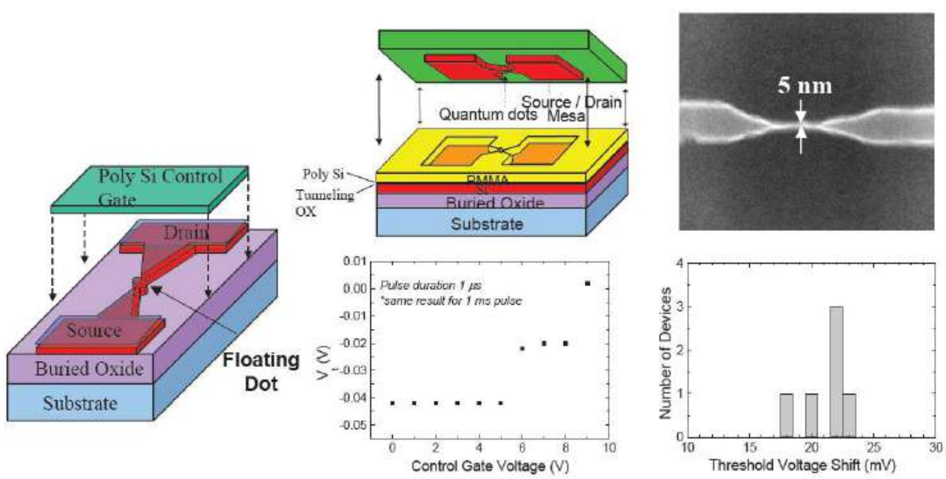
First single-electron memory with 8nm dot using NIL



For single electron devices, the size of the quantum dot is very critical. It is achieved by e-beam lithography and size shrinkage techniques, which has very low yield. By using NIL, once the “right” size is achieved, it can be duplicated many times faithfully.

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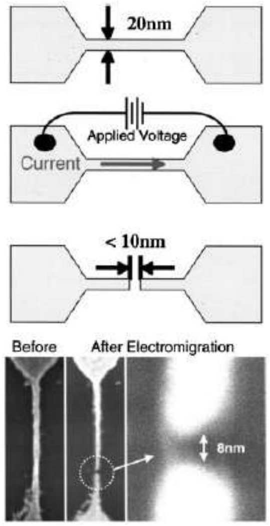
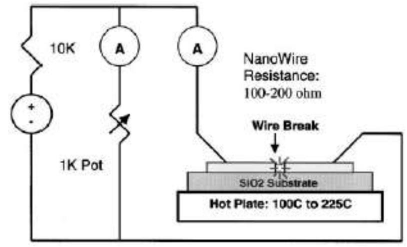
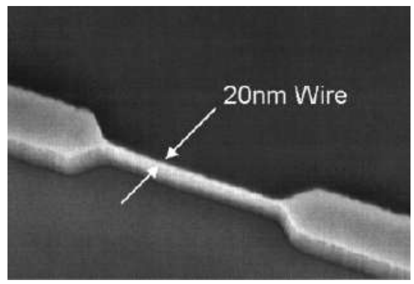
Nano-contact for molecular electronics







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Austin and Chou, “Fabrication of nanocontacts for molecular devices using nanoimprint lithography”, J. Vac. Sci. Technol. B, 20,

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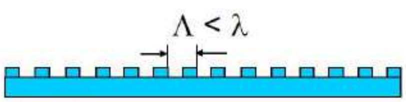
Sub-wavelength optical elements – optical chips by NIL

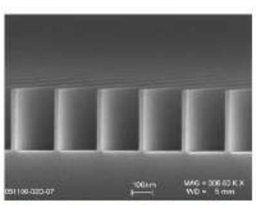


Key Uniqueness:

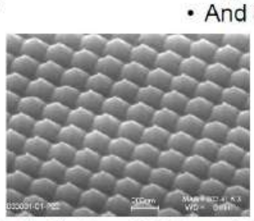
- New functions unavailable in bulk optics
- Ultra-thin (e.g., < 1 μm)
- Different optical functions by the same materials but different nanopatterns
- Large-scale monolithic integration on-chip
- Low cost, mass production

Examples of SOEs

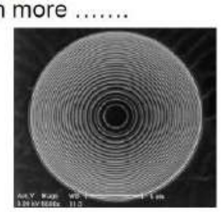
- Antireflective surfaces
- Waveplates
- Polarizers
- Filters
- Add/drop channel switches (tunable)
- Couplers
- Subwavelength binary lenses and zone plates
- Photonic crystals
- High-speed photodetectors
- High-speed lasers
- And much more ....



Waveplate with 20 nm fins



Antireflection of 200 nm pitch



Zone plate of 70 nm min. feature

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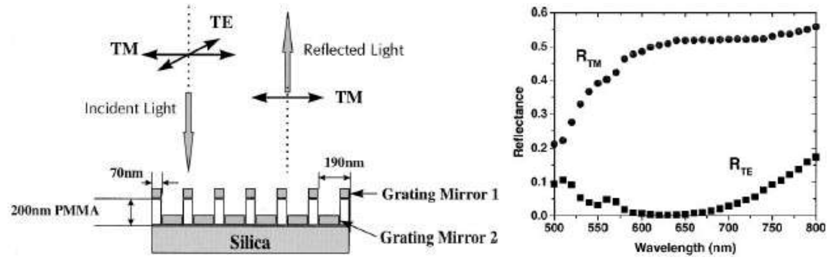
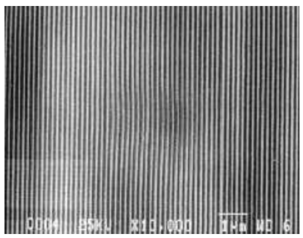
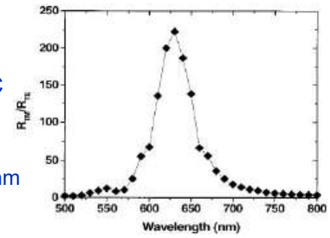
Thin film reflective polarizer





Resist: 15k PMMA
200nm-thick
Temperature: 175°C
Metal grating
5nm-Cr/70nm-Au
Grating pitch: 190nm
Line-width: 70nm
Depth: 200nm



Yu and Chou, "Reflective polarizer based on a stacked double-layer subwavelength metal grating structure fabricated using nanoimprint lithography", Appl. Phys. Lett. 77, 927-929 (2000).

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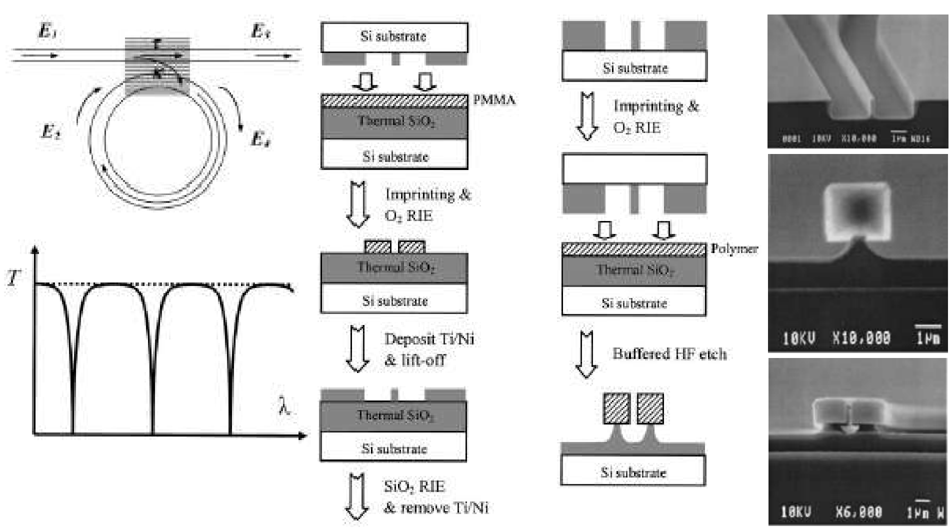
Micro-ring resonator



Resonant condition: optical path of the ring = nλ

Chao and Guo, "Polymer microring resonators fabricated by nanoimprint technique" J. Vac. Sci. Technol. B, 20, 2862-2866 (2002)

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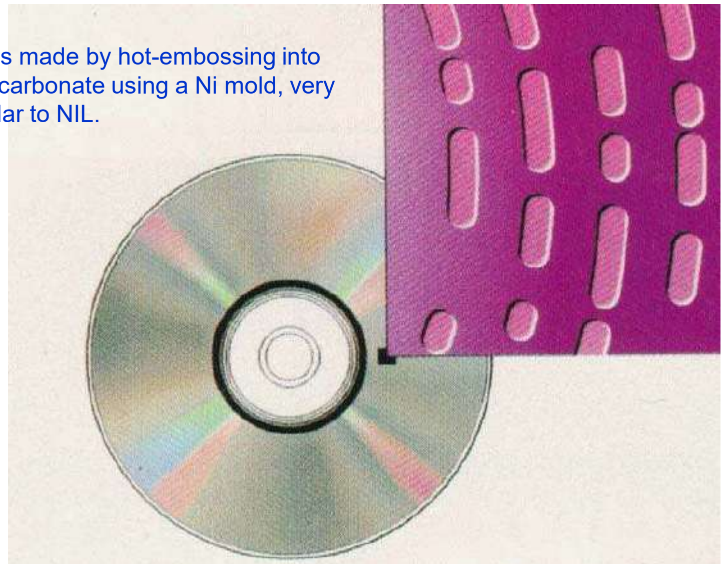
Commercial CD

CD is made by hot-embossing into polycarbonate using a Ni mold, very similar to NIL.



Compact Disc 650 MB, 48 Mbit/cm^2

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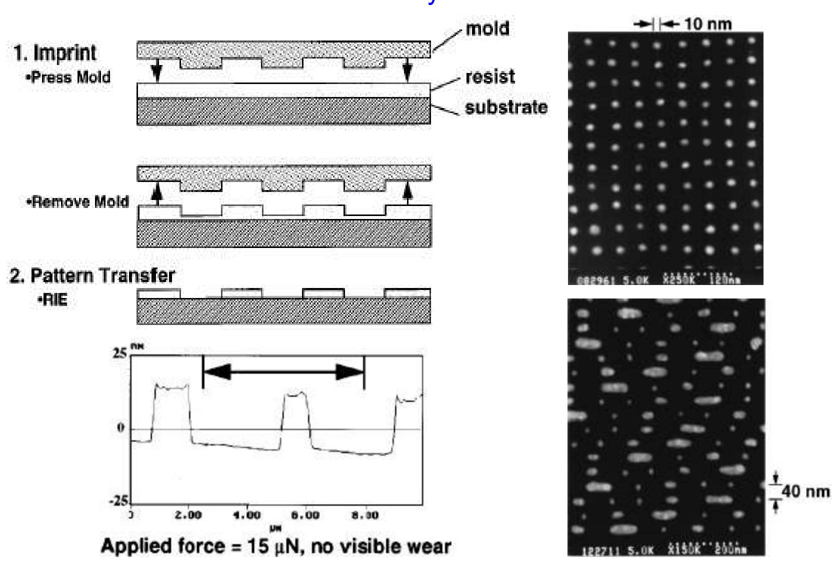
Nano-CD

CD areal density: 400 Gbit/in^2



Krauss and Chou, "Nano-compact disks with 400 Gbit/in^2 storage density fabricated using nanoimprint lithography and read with proximal probe", Appl. Phys. Lett. 71, 3174-3176 (1997).

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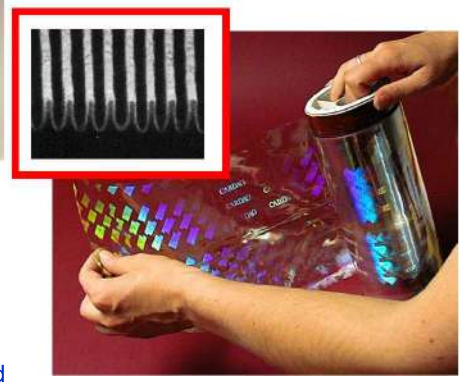
Application: diffractive security elements

Example for diffractive colors:
Tropical butterflies



Periodic diffractive elements produced by “roll-embossing” to be laminated into credit cards, bank notes etc.

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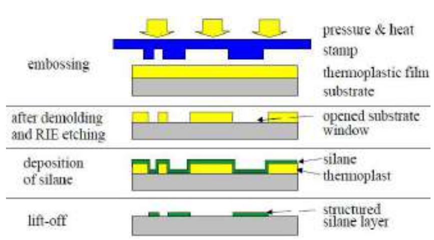
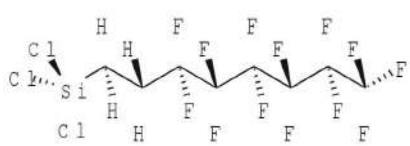
Chemical patterning by liftoff for liquid crystal displays



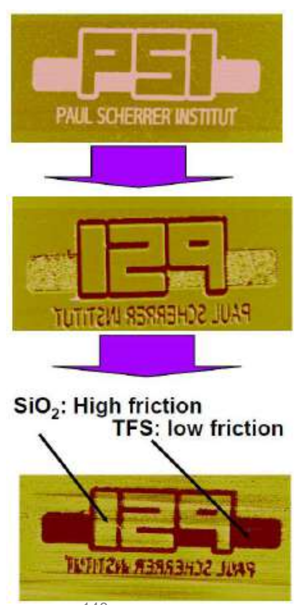


tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (TFS)

Stamp: *AFM image*

Embossed structure: *AFM image*

Chemical patterns after lift-off: *LFM image*



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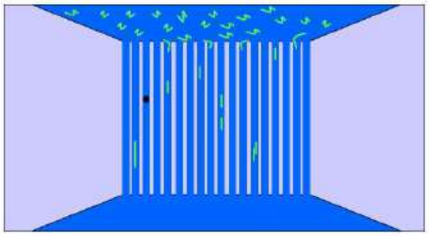
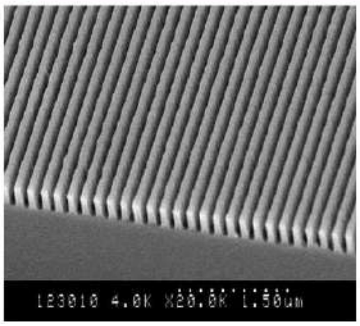
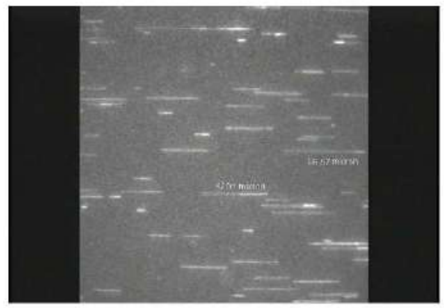
Nano-channel DNA sorter by NIL



- Channel width (>50 nm)
- Narrower than DNA Persistent length
- DNA automatically stretch DNA molecules straight
- DNA length = DNA molecular weight





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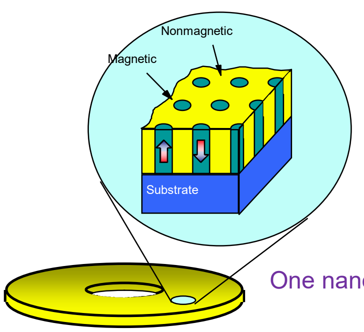
Bit-patterned magentic recording media



Advantage over conventional thin film disk:
- Overcome super-paramagnetic limit thus capable of ultra-high density recording.
- Smooth transition hence low media noise
- All-or-nothing writing process, thus can tolerate large head-field gradient.
- Robust and precise tracking through patterning.

One nanostructure = one bit

- Nanoimprint lithography is invented when Dr. Chou was asked how to make patterned magnetic media in a cheap way.
- Interestingly, first large scale application for NIL is likely on magnetic data storage.

(or it may be on large area electronics for display, but then it is not very “nano”)
- This is because no other lithography can do the job (25nm×25nm for 1Tbits/in^2).
- Currently, data storage companies like Seagate is working on this.
- The most likely solution for even higher density (>4Tbits/in^2) is guided self-assembly, where self-assembly is guided by NIL-created patterns.
- However, the mold still need to be made by the slow e-beam lithography, take ~month to fabricate.

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Who invented nanoimprint lithography?

Dr. Chou from Princeton

- It is well recognized that Dr. Stephen Chou invented nanoimprint lithography in 1995 (result published in Science in 1996).
- Dr. Grant Wilson from University of Texas at Austin invented what is now called as UV-curing NIL.
- However, it is recently revealed that Japanese scientists invented NIL (both thermal and UV-curing) in 1970s, with a few patents and publications (all in Japanese) covering many aspects.
- But 30 years ago, nobody noticed or cared about this invention.

Japanese Journal of Applied Physics 48 (2009) 06FH01 **REVIEW PAPER**

Fine Pattern Fabrication by the Molded Mask Method (Nanoimprint Lithography) in the 1970s

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Received November 28, 2008; accepted February 9, 2009; published online June 22, 2009

Nanoimprint lithography has recently been attracting the attention of many researchers in the field of nanofabrication technology. Although the study of nanoimprint lithography was initiated by Chou *et al.* around 1995, a fine-pattern fabrication technology, whose concept is similar to nanoimprint lithography, had been proposed and studied at NTT Laboratories in Japan as early as in the 1970s. The technology was based on the combination of the molding of plastic film on a substrate and dry etching of the molded film and substrate surface. It is considered that most of the basic concepts in current nanoimprint lithography were included in this early study. Some demonstration experiments using diffraction gratings, microsized test patterns, LSI patterns and microlenses were carried out to verify the feasibility of the technology at that time. The key point of the technology to fabricate fine patterns accurately was the fluidity of the plastic film. It was called the "Molded Mask Method" and this paper introduces the study on the molded mask method of those days.

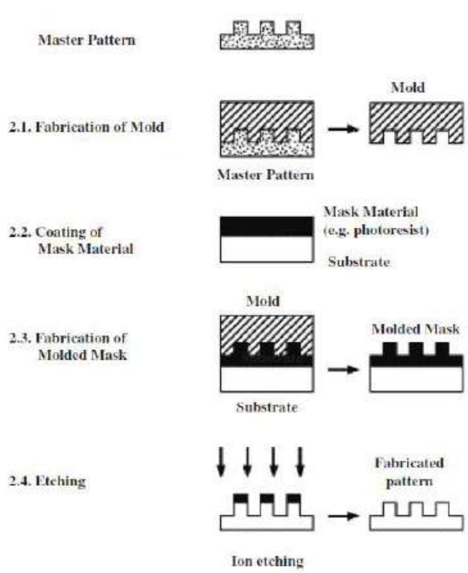

Fig. 1. Concept of the molded mask method, reported in 1976.[8]

8) M. Kondo, H. Yasuda, K. Kubodera, and S. Fujimori: Ext. Abstr. (37th Autumn Meet., 1976); Japan Society of Applied Physics, Vol. 2, p. 404 [in Japanese].

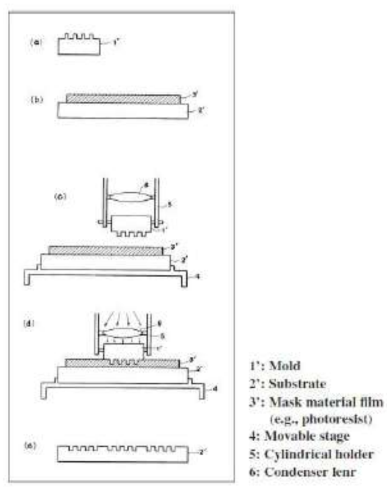

Fig. 2. Step-and-repeat method in molding and UV exposure in molded mask fabrication process, described in the patent filed in 1975.[12] The processes of (c) alignment of the substrate with the mold and (d) UV exposure to harden the mask material film pressed by the mold are repeated in the step-and-repeat manner. Multiple sets of patterns are obtained on the substrate after the etching process, as shown in (e).

12) S. Fujimori and M. Kondo: Japan Patent 947244 (1975) [in Japanese].

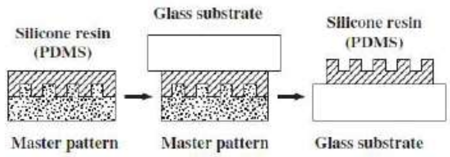

Fig. 3. Preparation of PDMS resin mold.[14] It corresponds to the process of 2.1. Fabrication of Mold in Fig. 1.

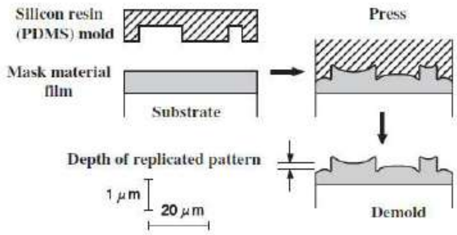

Fig. 8. Schematic of distortion of pattern shape in the molded mask fabrication process.[14]

14) S. Fujimori: NTT Lab. Res. Rep. No. 12815 (1978) [in Japanese].

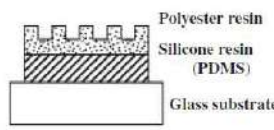

Fig. 11. Schematic of the mold with polyester resin on the surface supported by PDMS resin.[14]

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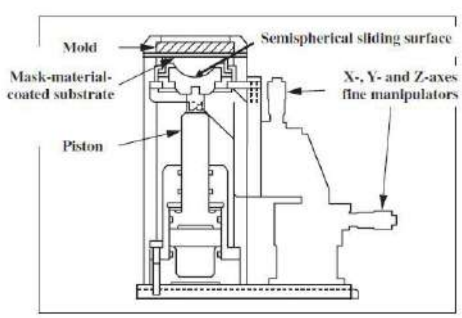

Fig. 16. Schematic of the pressing machine for molded mask fabrication process.[14]

Fig. 17. (Color online) Samples fabricated by molded mask method in the 1970s. From left to right: master pattern, mold, molded mask, and pattern fabricated on Si wafer substrate. Top: microsized test pattern. Bottom: diffraction grating.

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End of NIL

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