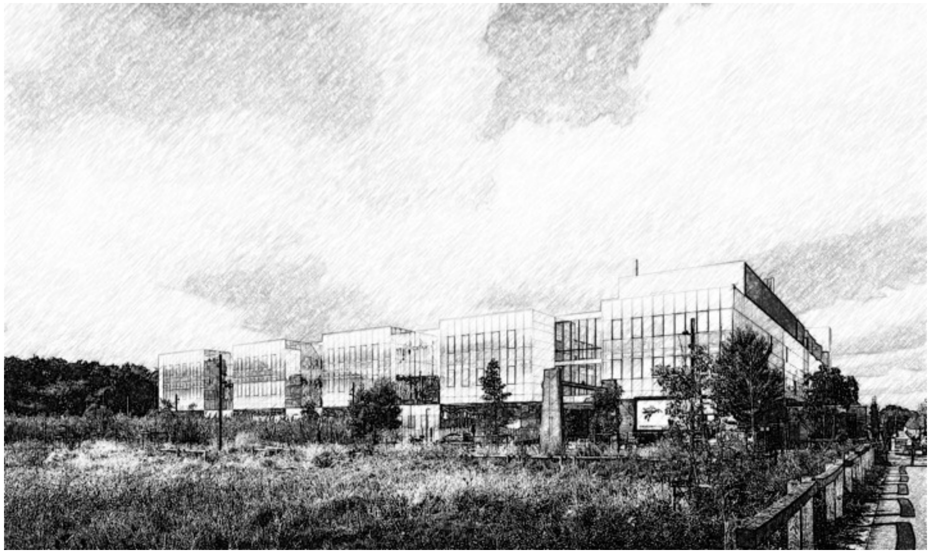
sunlit-team.eu

Nano-impression: Introduction générale

Andrea Cattoni

18th November 2021

Centre de Nanosciences et de Nanotechnologies (C2N), CNRS
Paris-Saclay University, Palaiseau (France)



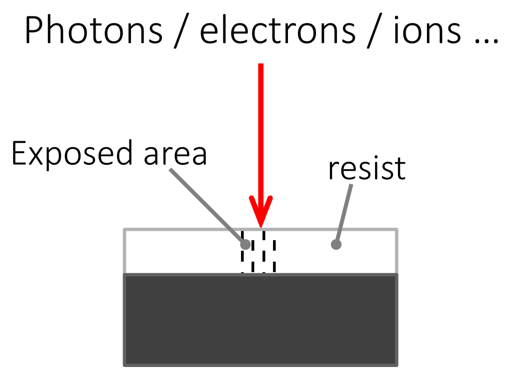
Outline

- Short introduction on lithography & nanofabrication
- Nanoimprint (NIL)
  - Thermal NIL
  - UV NIL and Step&Flash
  - Soft NIL
  - Degassing Assisted Patterning (DAP)

Lithography

is the process of printing patterns onto a thin film called a resist, using a localized interaction: photons-, electrons-, ions-beams, engraving micro-tools (tip, rigid mold…)

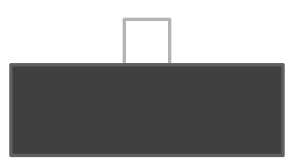
1) Localized exposure (EBL)



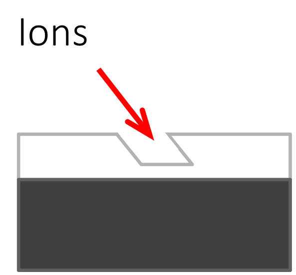
2) Development of:

Positive-tone resist

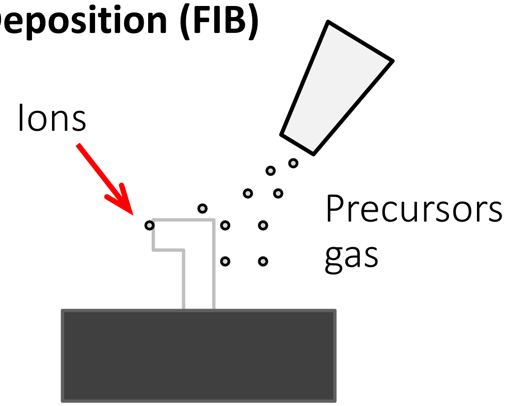
Negative-tone resist



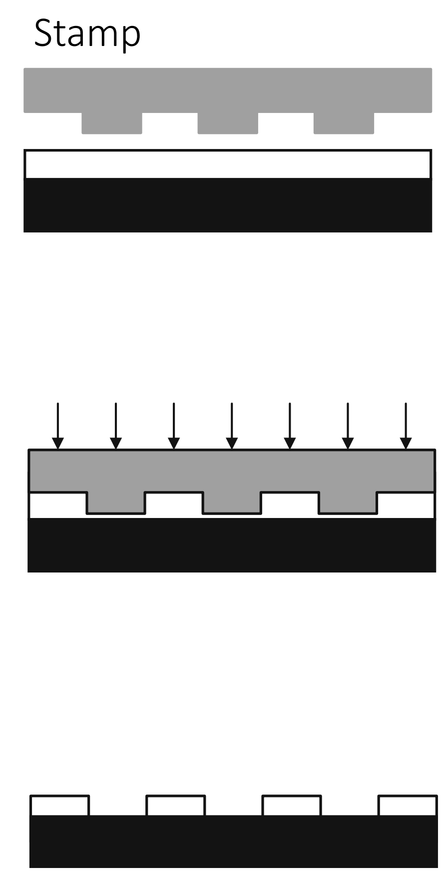
Selective ion milling (FIB)



Ion Beam Induced Selective Deposition (FIB)



Replication (NIL)



Lithography techniques

can be classified according to the type of radiation / micro-tool used to locally modify the resist:

by photons:

- Optical (projection) lithography: deep UV, extreme UV, X-ray
- Interferometric Optical Lithography, Talbot Lithography ...
- Maskless Optical Lithography
- by Scanning Probes: SNOM Lithography

by charged beams

- Electron beam lithography
- Focused ion beam (FIB)
- Charged Particles Projection Lithography
- by Scanning Probes: STM

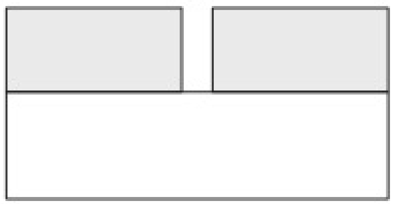
by replication (or physical transfer of material)

- Thermomechanical Indentation
- Dip-Pen Nanolithography
- Nanoimprint &Co (or print: µCP &Co)

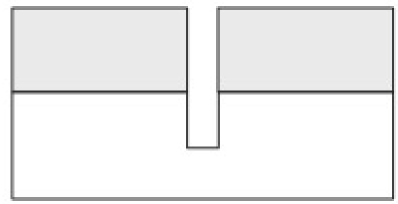
....

Pattern transfer

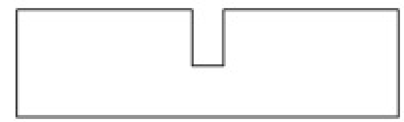
1.



a) Positive resist after development

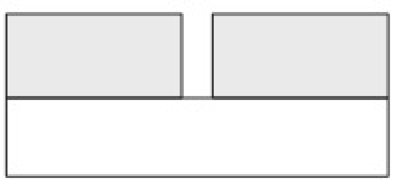


b) Anisotropic ion etching using the resist as mask

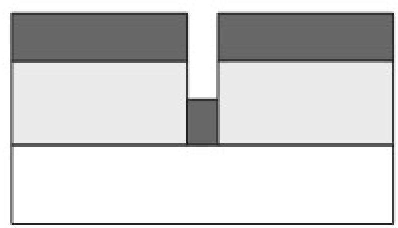


c) Removal of resist

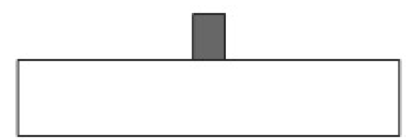
2.



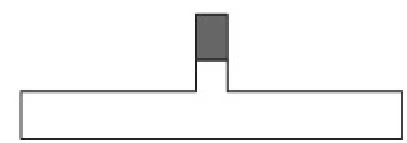
a) Positive resist after development



b) Deposition of a thin layer on the resist

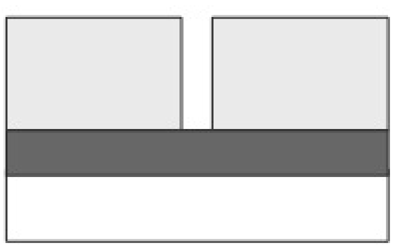


c) Dissolving the resist: lift-of

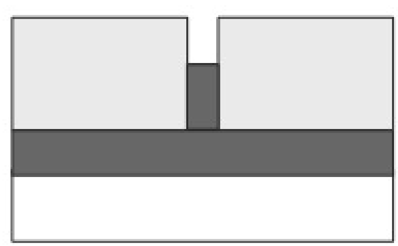


d) Anisotropic etch using the deposited film as etch mask

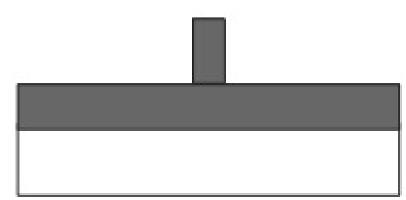
3.



a) Positive resist after development



b) Electrolytic growth from the growth base

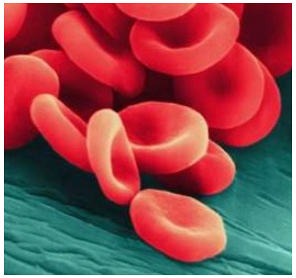


c) Removal of resist

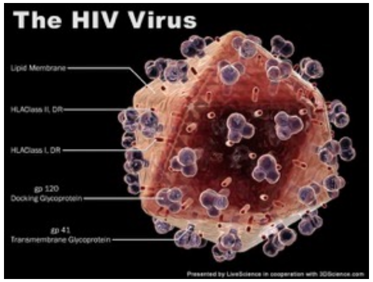
Order of magnitudes

dust mite ~200 mm

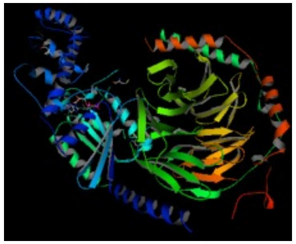
red blood cells ~ 2,5 mm



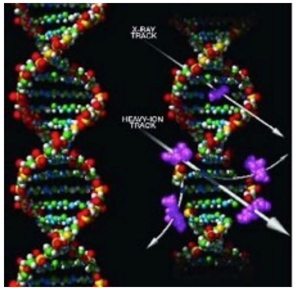
Virus ~ 50-100 nm



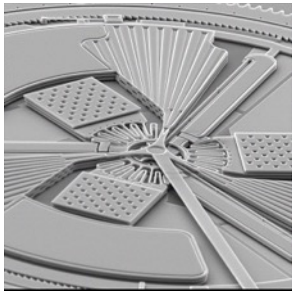
Proteins



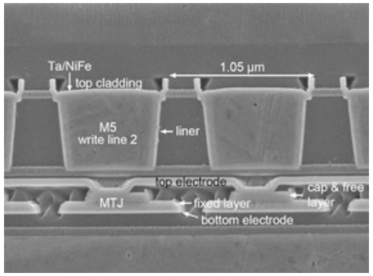
DNA ~ 2 nm



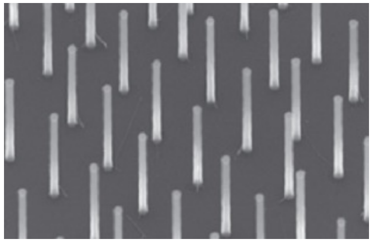
MEMS



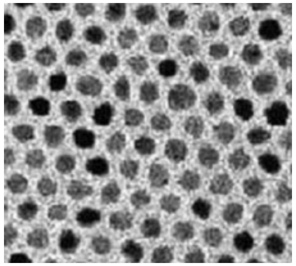
Magnetic Tunneling Junction



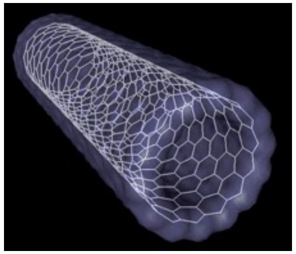
Nano wires



Mesoporous membranes



Carbon nanotube



100µm — 10µm — 1µm — 100nm — 10nm — 1nm

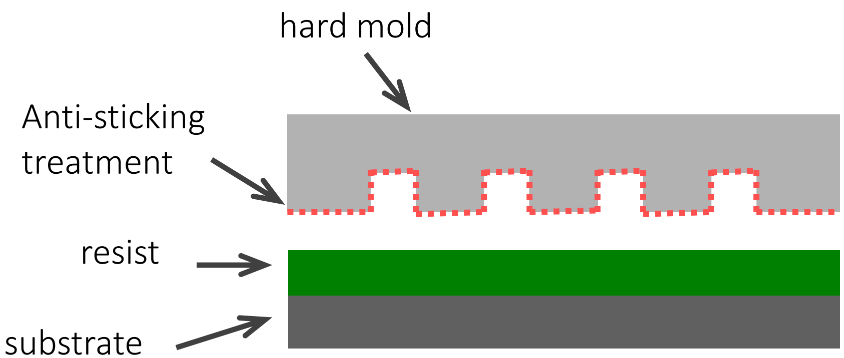
Optical Lithography

X-ray Lithography

Electron Beam Lithography & **Nanoimprint**

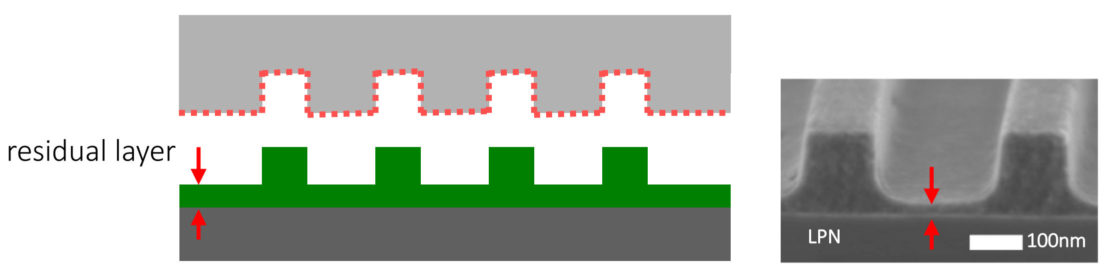
Scanning Probes Lithographies

Nanoimprint Lithography: principle



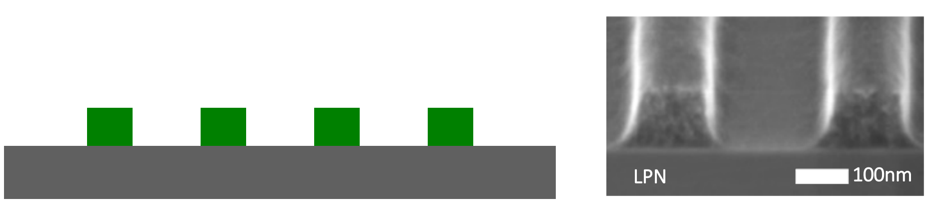
A hard mold containing nanoscale surface-relief is pressed at high temperature and pressure into a resist creating a thickness contrast.

1) Imprinting at high pressure and temperature



A thin *residual layer* is intentionally left to prevents direct impact of the hard mold on the substrate.

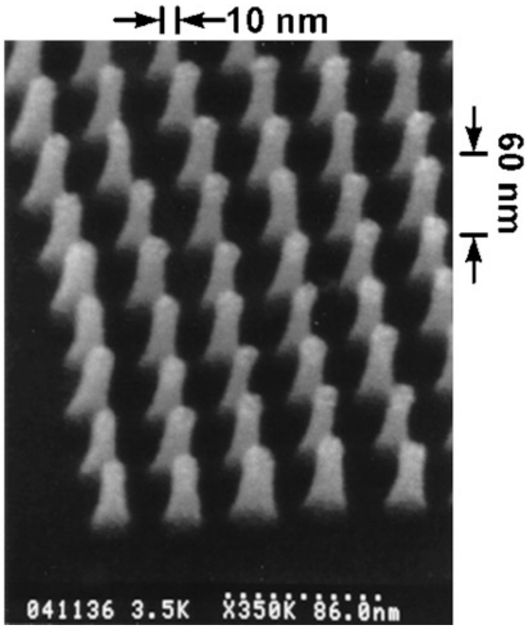
2) Pattern Transfer by Reactive Ion Etching



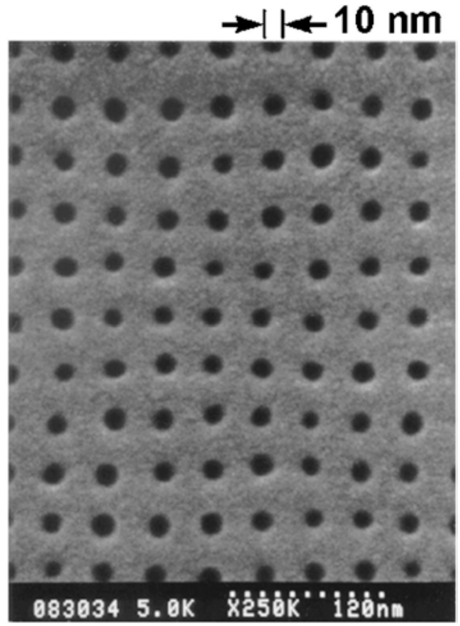
For most applications, the residual layer is removed by an anisotropic dry-etching.

S.Y. Chou et al., APL **67**, 3114 (1995)

High resolution and no proximity effects



Scanning electron microscopy (SEM) image of a fabricated mold with a 10 nm diam- eter array.



SEM image of hole arrays imprinted in poly(methyl methacrylate) by using such a mold.

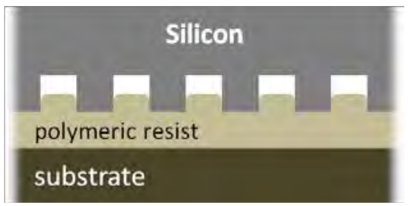
S.Y. Chou et al., J. Vac. Sci. Technol. B **15**, 2897 (1997)

Nanoimprrint demonstrated <u>ultrahigh resolutions</u> soon after its inception.

- Parallel process
- No diffraction-limited
- No proximity effects

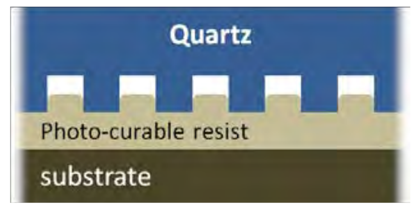
Nanoimprint Lithography: variations on a Theme

T NIL



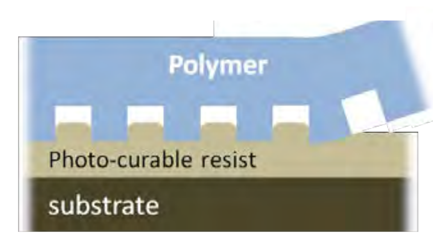
- High Pressure
- Hight Temperature

UV NIL / Step&Flash

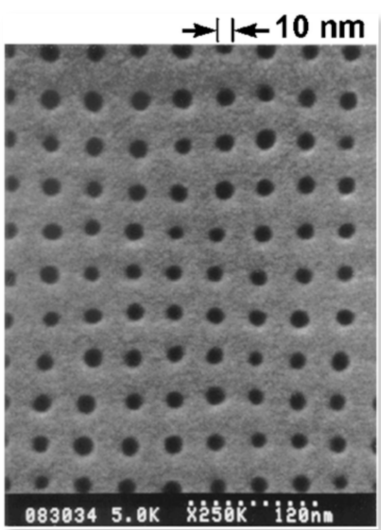


- Lower Pressure (< 1 atm)
- Room Temperature

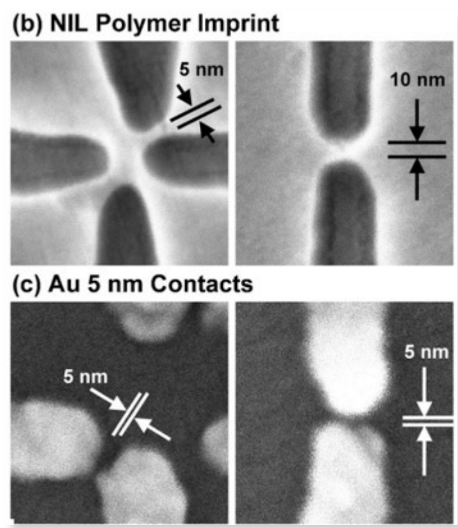
Soft UV NIL



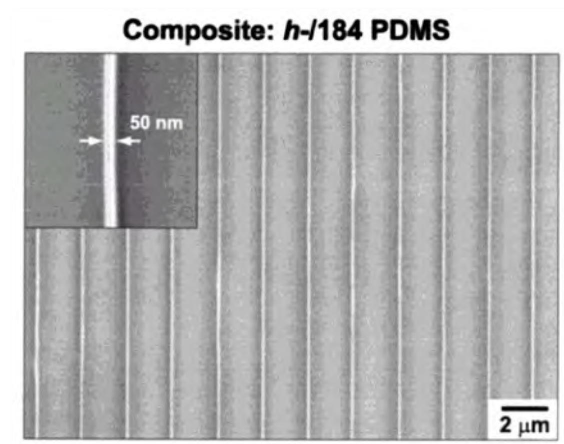
- Low Pressure (≪ 1 atm)
- Room Temperature
- Cheap
- Flexible/curved substr.



J. Vac. Sci. Tech. B **15**, 2897 (1997)



APL **84**, 5299 (2004)



Langmuir **18**, 5314 (2000)

Thermal Nanoimprint

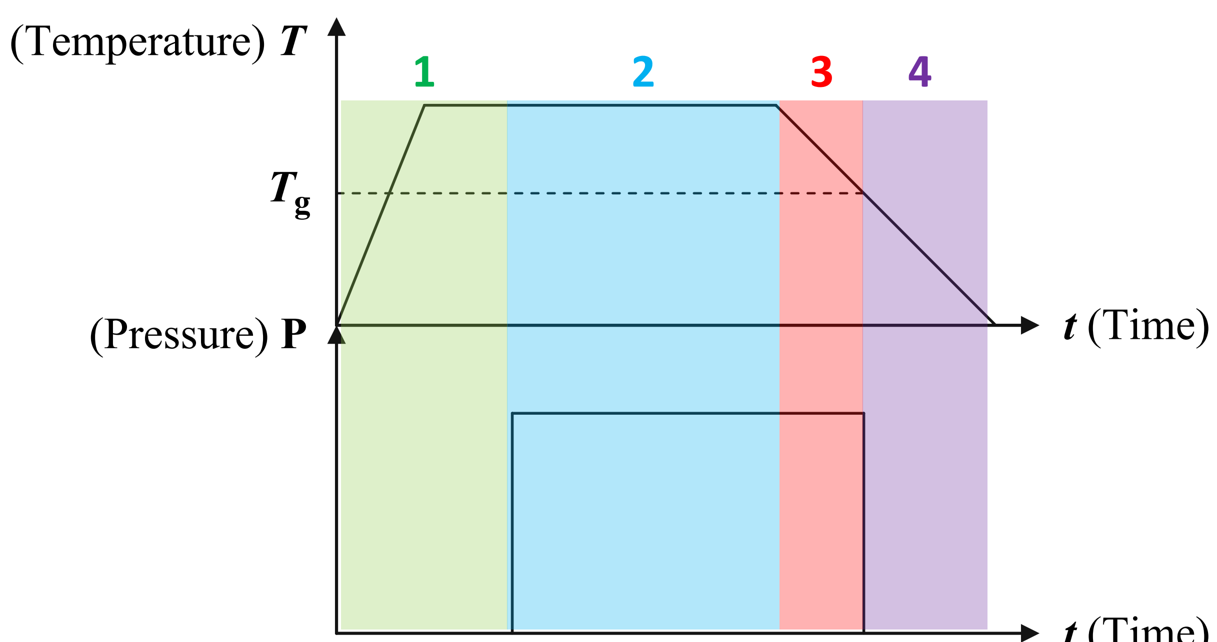
First proposed by Stephen Y. Chou in 1995 [APL 67, 3114 (1995)]

1) Substrate with a Thermoplastic resist is heated above its glass transition temperature (Tg)

2) Stamp is pressed into the resist at pressure around 50-100 bars

3) While maintaining the pressure the substrate is cooled under Tg

4) Pressure is remove and the stamp and the imprinted sample are separated.

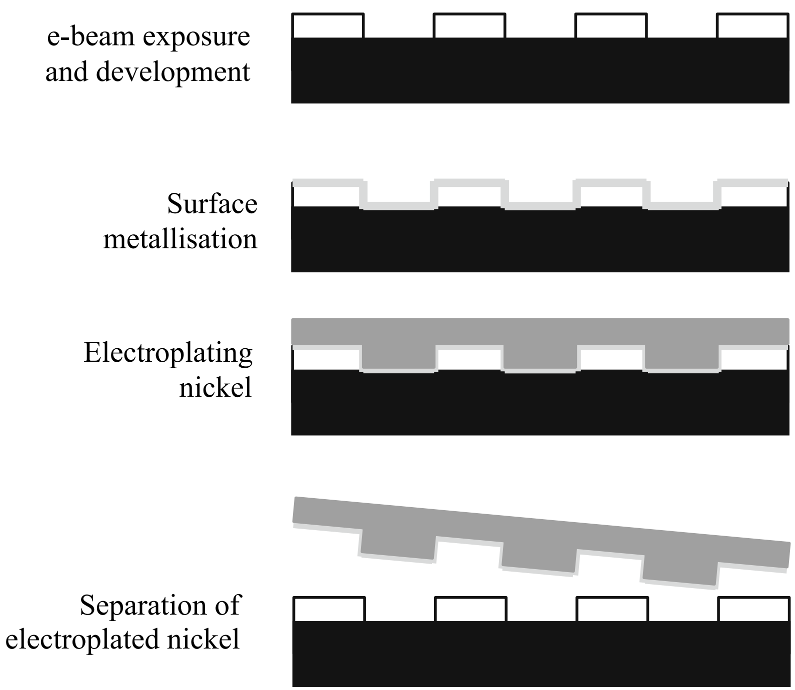


The stamp: fabrication

Stamp materials: Si, SiO_2, SiN (brittle).

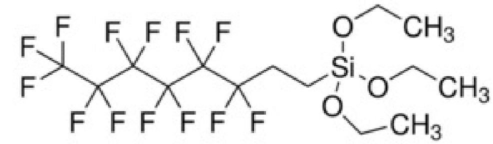
Most durable stamp are made of Nickel.

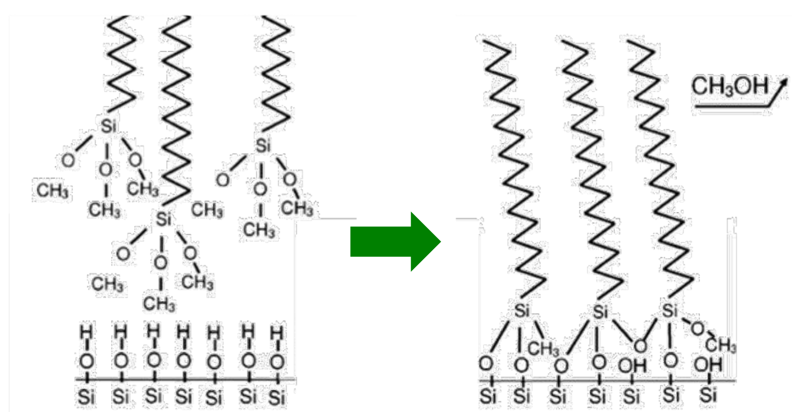
Process for fabricating nickel stamp



Nano-structuration **increases the total surface area** → strong resist-mold adhesion!

- Incorporate internal release agents into the resist formulation (surfactants)
- Use low surface energy materials for the mold (Polymers, see Soft UV NIL)
- **Anti-sticking treatments:** SAM of a Fluorosilane on the mold surface

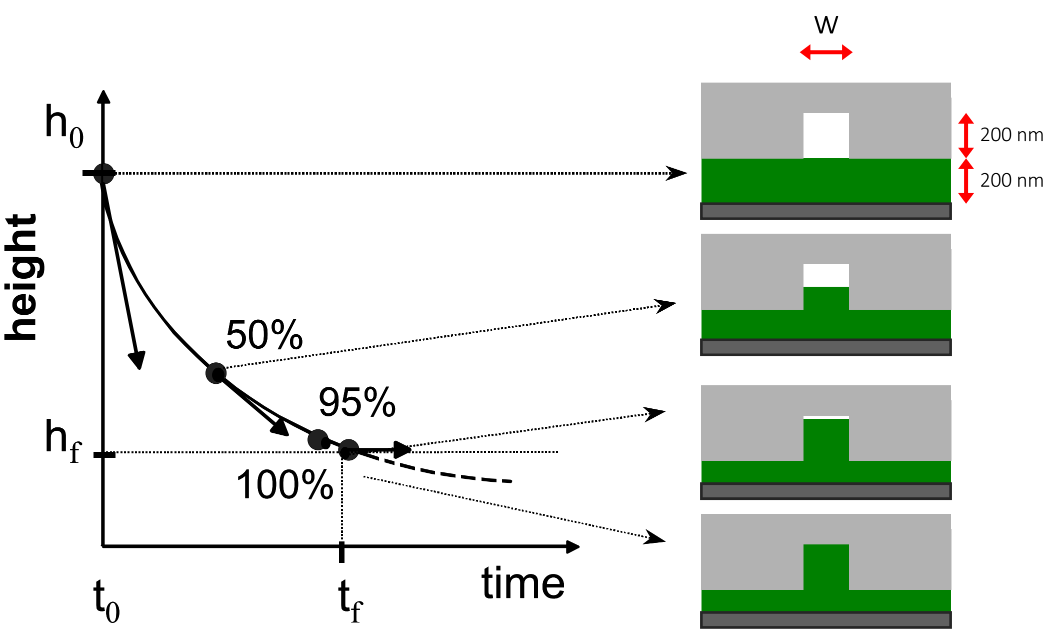


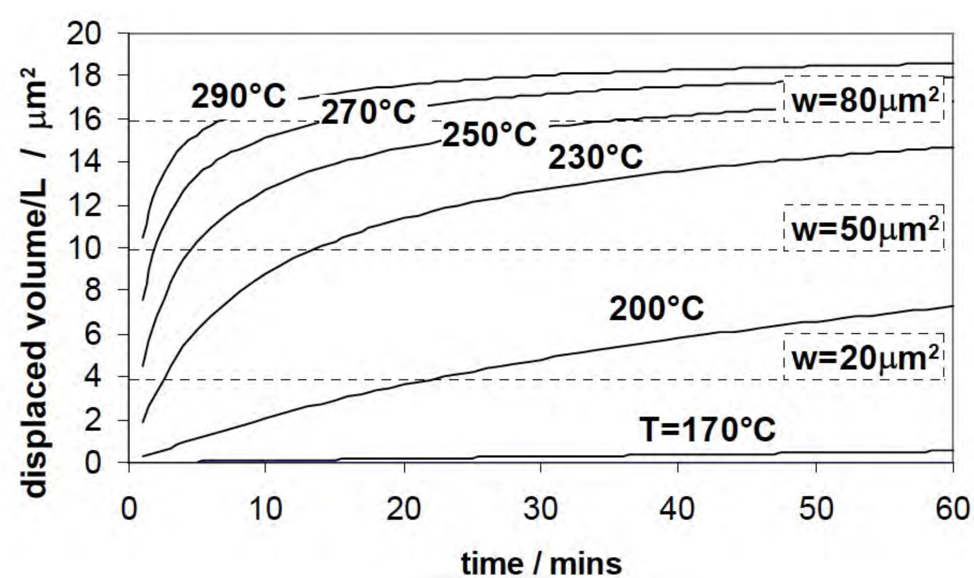


Nanoimprint resists

- **Low glass transition temperature:** low imprinting temperature is always preferred
- **Low viscosity:** to facilitate easy flow of polymer during filling stamp cavities
- **Low shrinkage:** after imprinting to maintain pattern fidelity
- **High resistance to dry etching:** if used as mask for pattern transfer by dry-etching
- **Soluble in a solvent:** if used for lift-off

i.e. Polymer viscosity depends on its molecular weight and <u>heating temperature</u>:
→ imprinting time may be completed in a few seconds at 200 ℃ or take hours at 140 ℃





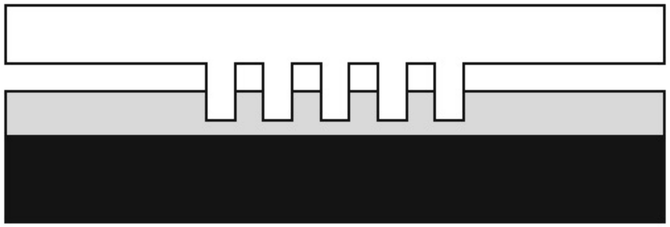
Alternative Lithography, C.M.S. Torres, Editor. 2003, Kluwer Academic

P=3.6 × 106 Nm^{-2} (35,5 atm), viscosity = 2648 Pa × s

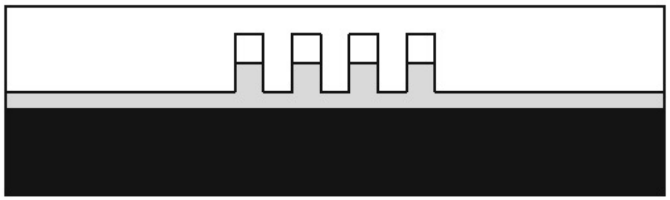
Resist displacement

“Positive” stamp structure causes much less displacement of polymer during imprint, compared to the negative stamp structures.

Positive stamp



Negative stamp

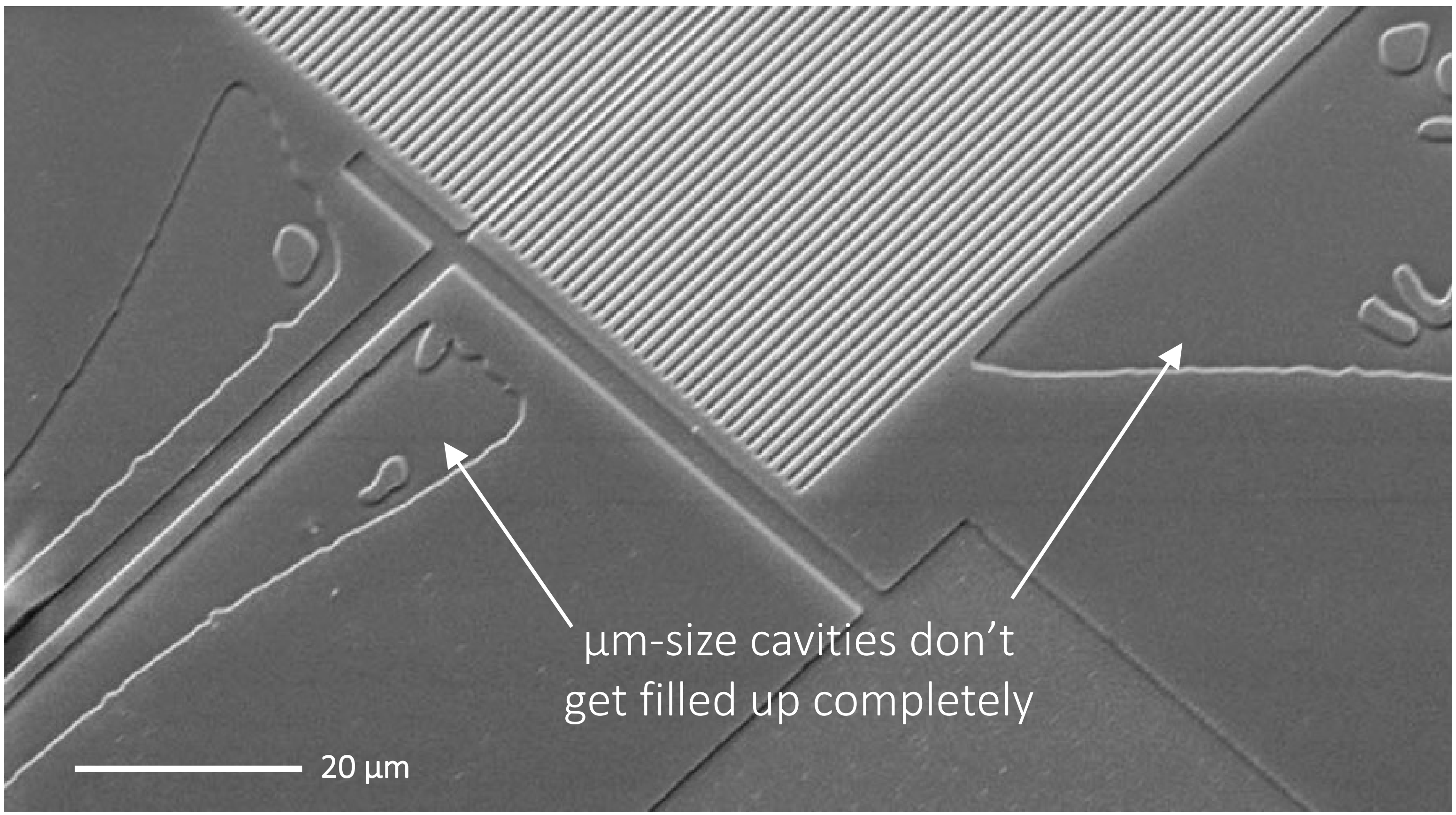


Pattern design for NIL stamps should make sure that the cavities and protrusions are uniformly distributed over the entire stamp area, to avoid large difference in polymer squeezing flow distance.

Nanoimprint "proximity effect"

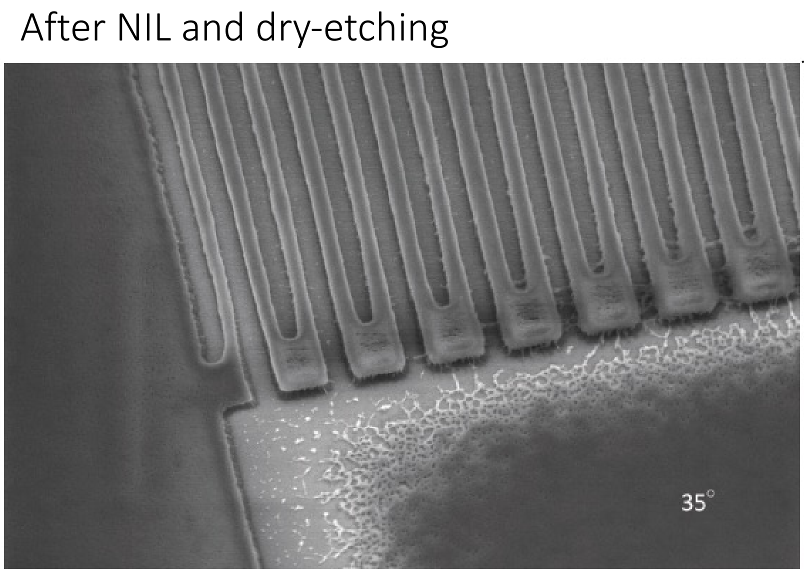
! Smaller features are easier to imprint than larger features because the squeezing flow distance of polymer is much less.

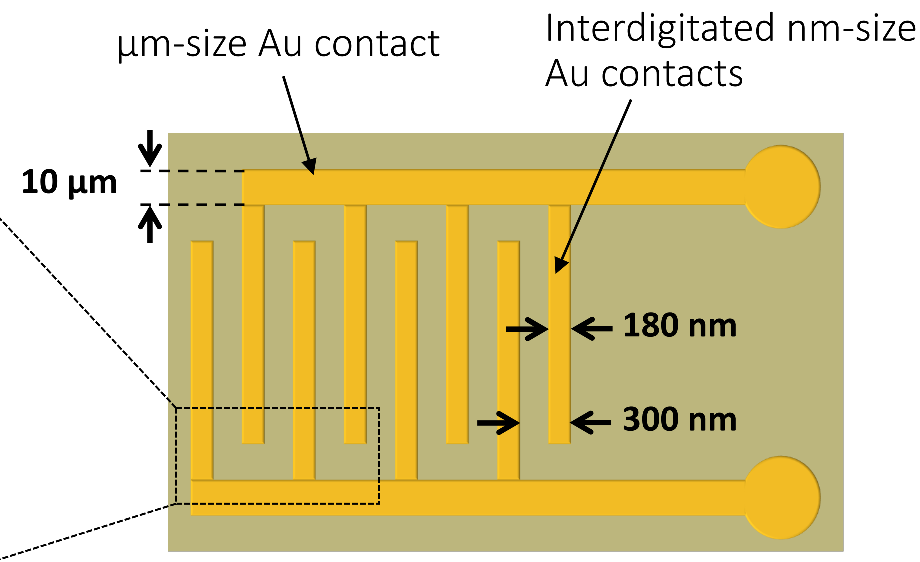
→ Imprint µm/nm-size features in the same mold is challenging

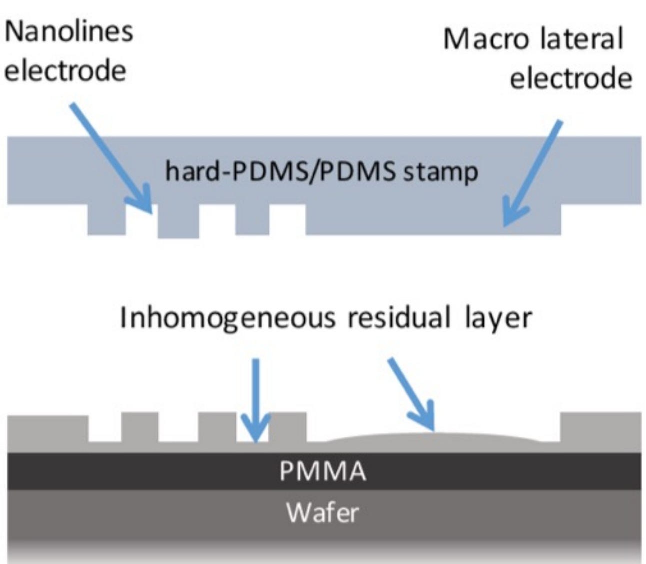


Scheer et al., J. Vac. Sci. Technol. B **16**, 3917 (1998)

Nanoimprint “proximity effect”





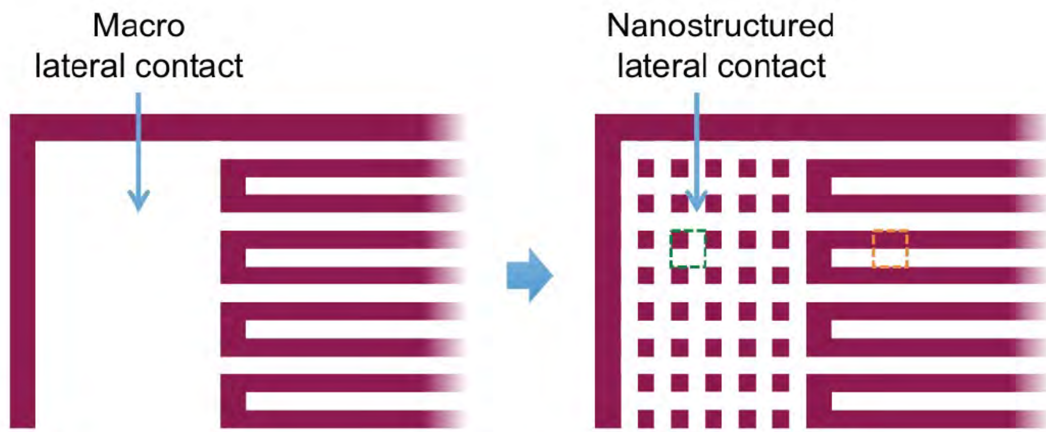


- Lateral displacement of resist material is problematic µm-sized feature

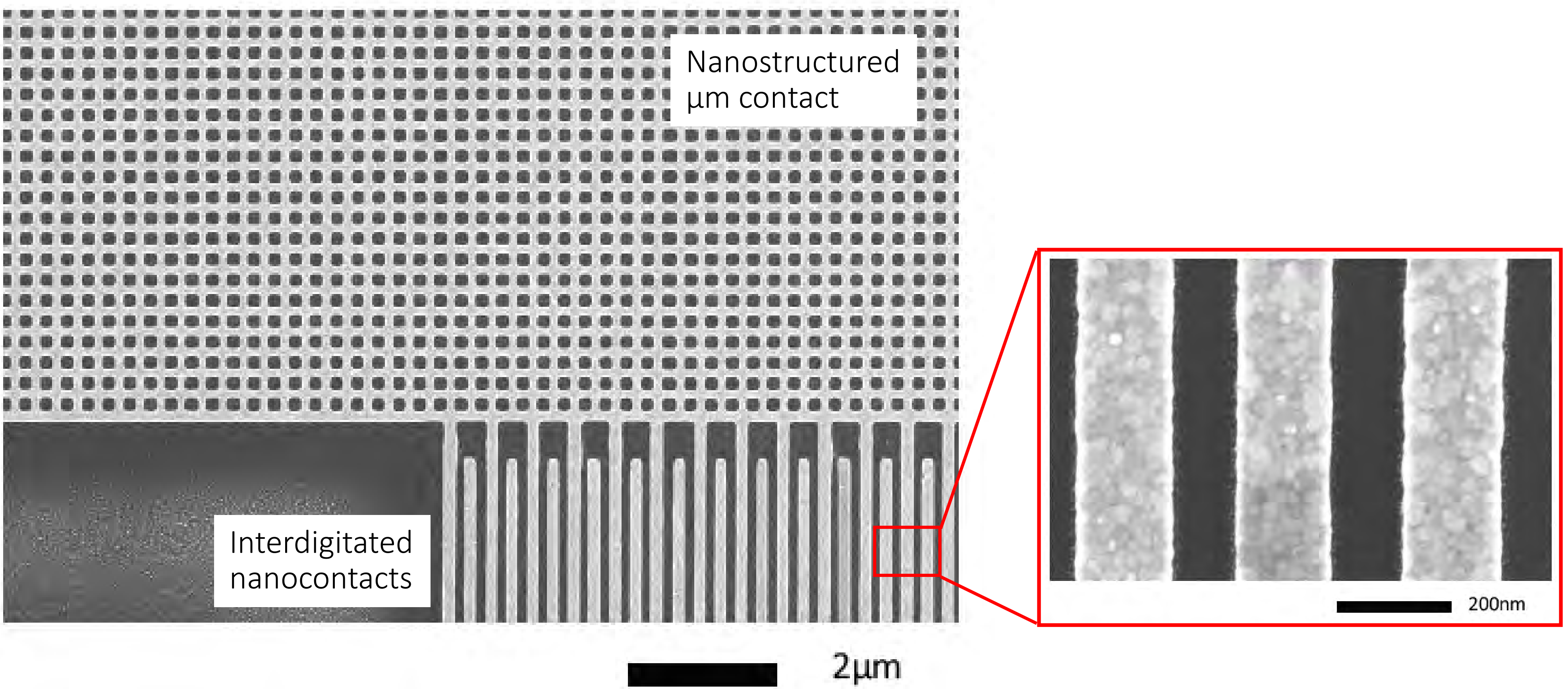
→ Different residual layer in nm- / µm-size features

- Over etching result in a distortion of the nanometric features

(Possible) solution: nanostructured macro-contacts

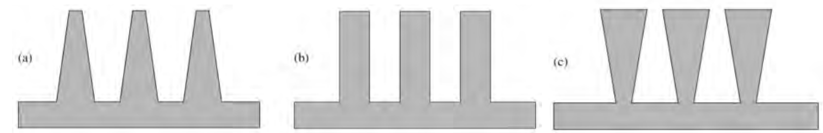


After Au lift-off



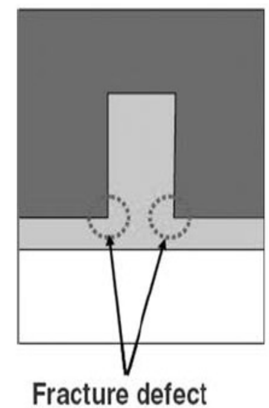
Demolding of high aspect ratio structure

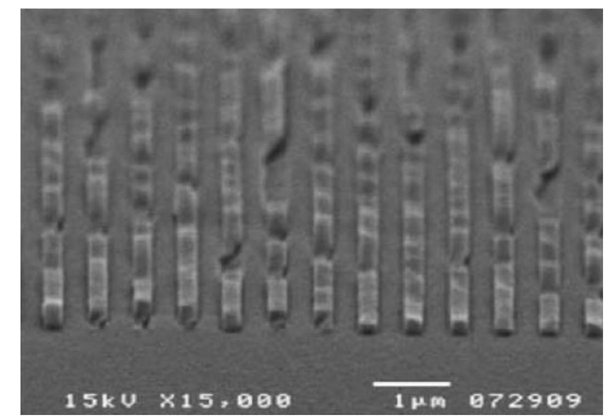
- Demolding a rigid mold from a rigid substrate is critical
- Especially for structures with high aspect ratio (> 3)
- Especially using large surface area molds



Low-molecular-weight (Mw) facilitates imprinting: low viscosity but also low shear modulus (brittle!)

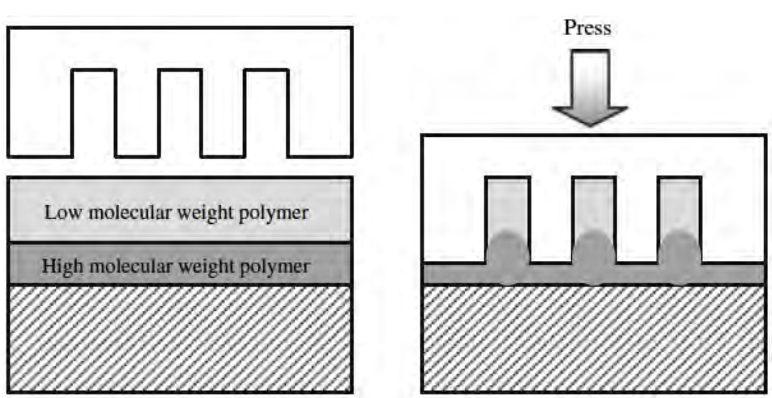
Stress is concentrated at the base area of polymer pattern → **Fracture!**

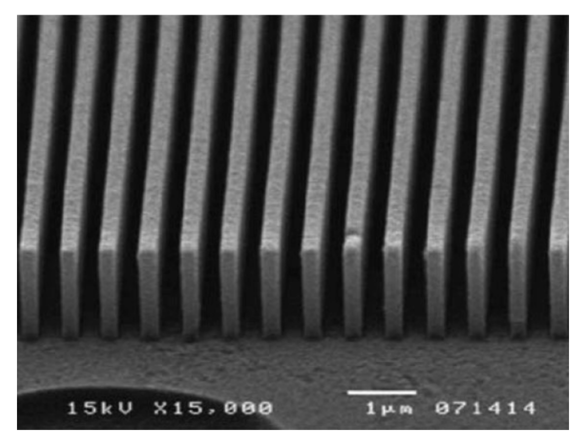




Konishi et al., Microelect.. Eng. 83, 869 (2006)

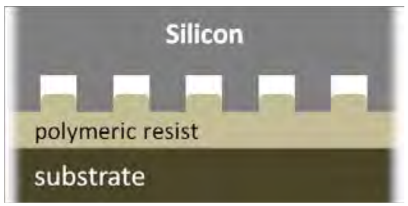
For high aspect ratio structures: High Mw + Low Mw



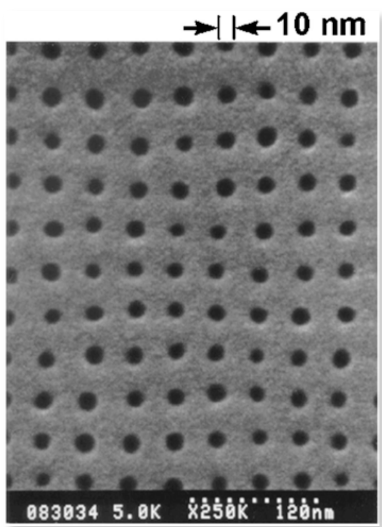


Nanoimprint Lithography: variations on a Theme

T NIL

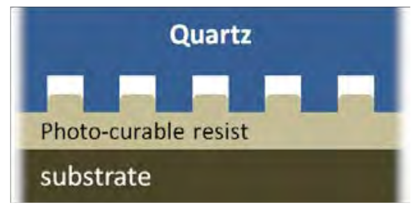


- High Pressure
- Hight Temperature

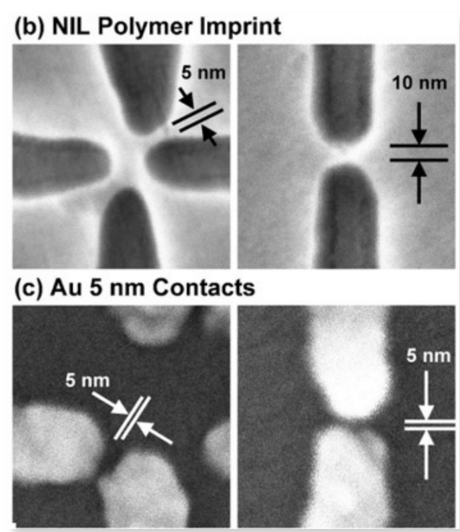


J. Vac. Sci. Tech. B **15**, 2897 (1997)

UV NIL / Step&Flash

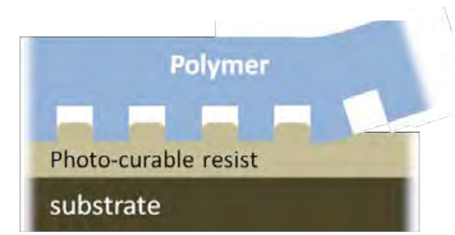


- Lower Pressure (< 1 atm)
- Room Temperature

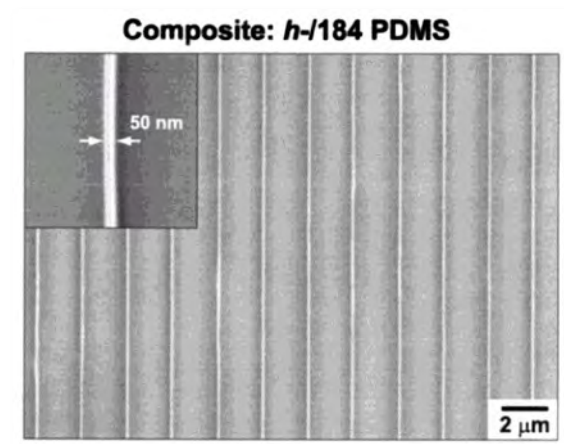


APL **84**, 5299 (2004)

Soft UV NIL

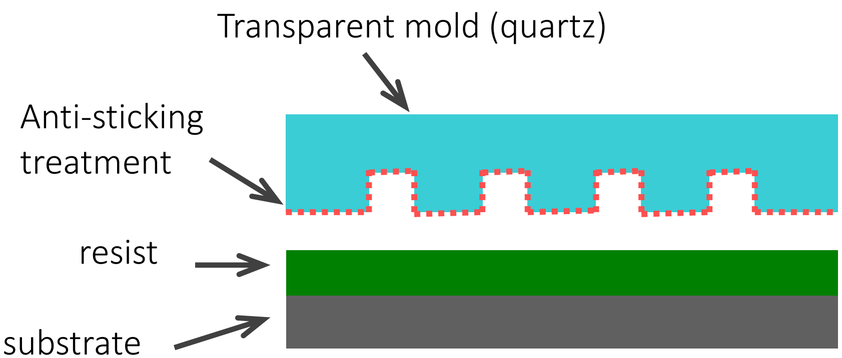


- Low Pressure (≪ 1 atm)
- Room Temperature
- Cheap
- Flexible/curved substr.

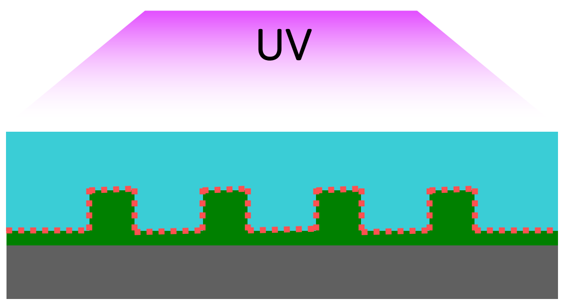


Langmuir **18**, 5314 (2000)

UV Nanoimprint Lithography (UV-NIL)



1) Imprint at RT and low pressure



2) Pattern Transfer by Reactive Ion Etching

- For some applications, the substrate materials cannot withstand high pressure and/or temperature.
- For T-NIL the cool down step consumes most of the time of the imprinting cycle (low throughput)

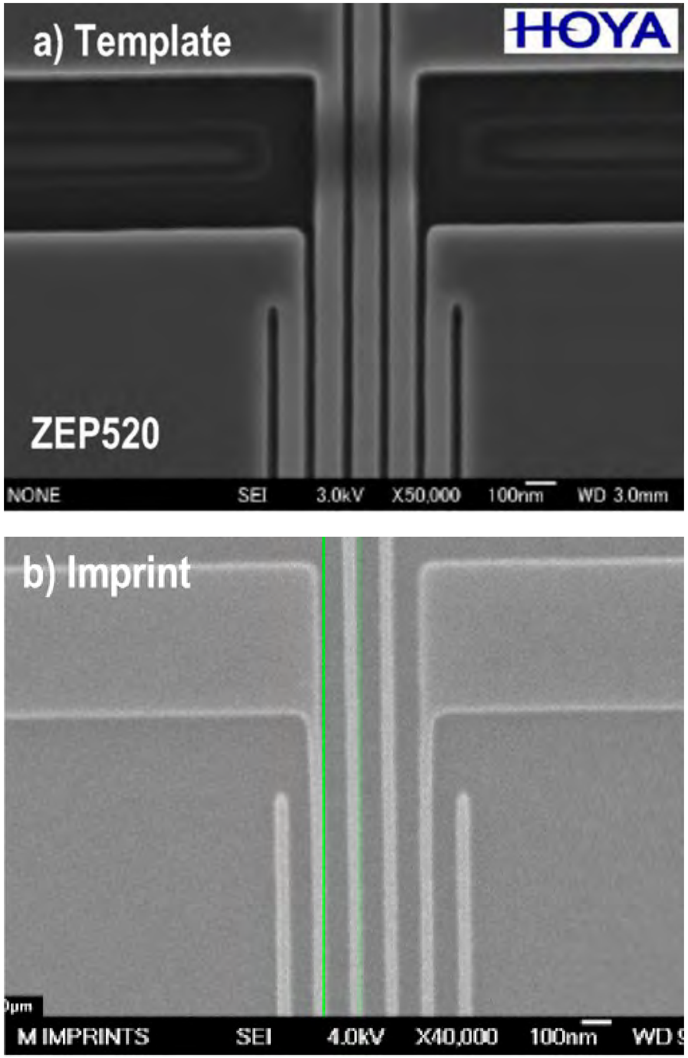
Transparent mold (quartz)

UV-curable liquid precursor (50-200 mPa*sec)

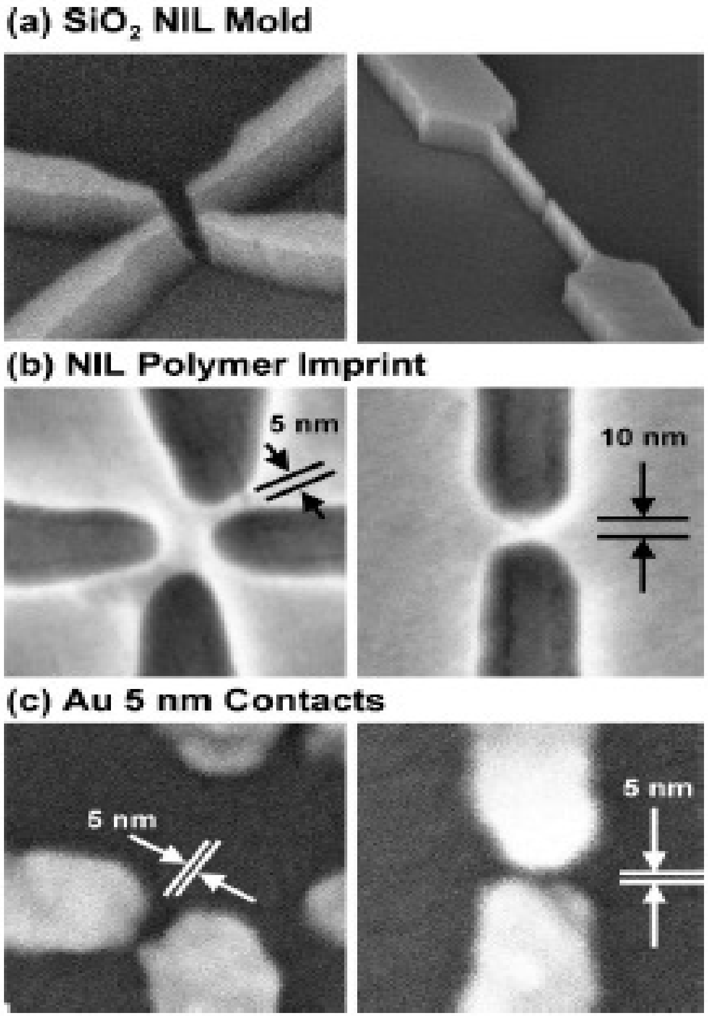
→ RT, Low P (< 1 bar)

S.Y. Chou et al., APL 67; 3114 (1959)

UV Nanoimprint Lithography (UV-NIL)



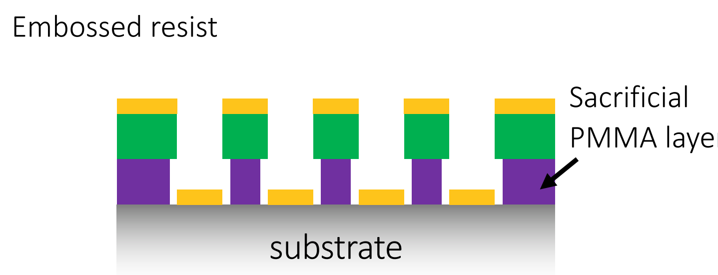
Microel. Engineer. 85, 856 (2008)



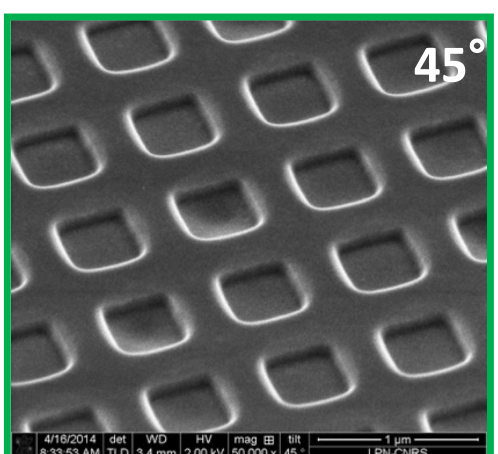
Austin et al., APL **84,** 5299 (2004)

UV-Curable resists

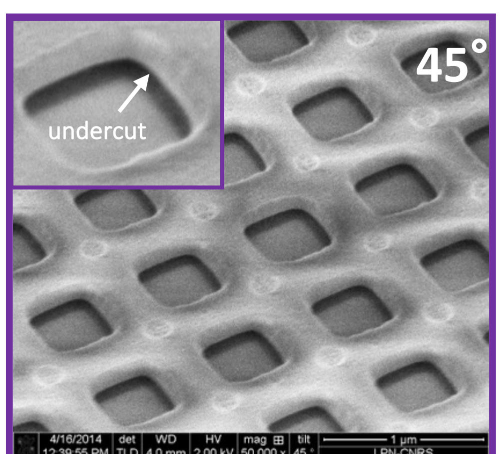
- **Low viscosity:** few tens of mPa*sec (for T-NIL is about 10^4 Pa*sec)
- **Fast UV curing:** with few hundreds of mJ cm^{-2} curing time is a few seconds to a minute
- **Low shrinkage:** to ensure pattern fidelity (typically 5–15% volume shrinkage)
- **High dry etch selectivity:** to ensure reliable pattern transfer into substrate materials
- **Typically insoluble in solvents:** double resist is used for for lift-off



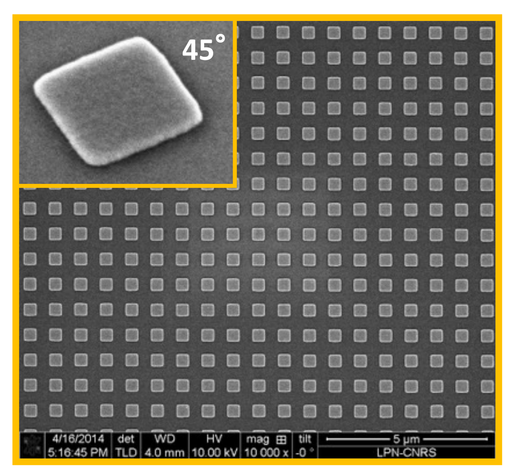
Nanoimprint of the UV-curable resist

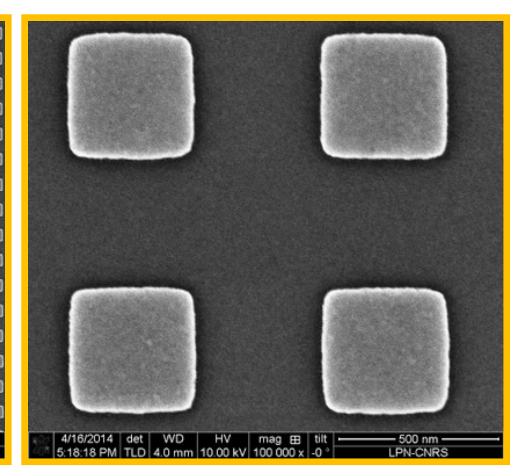


Dry-etching of residual layer + pattern transfer in PMMA



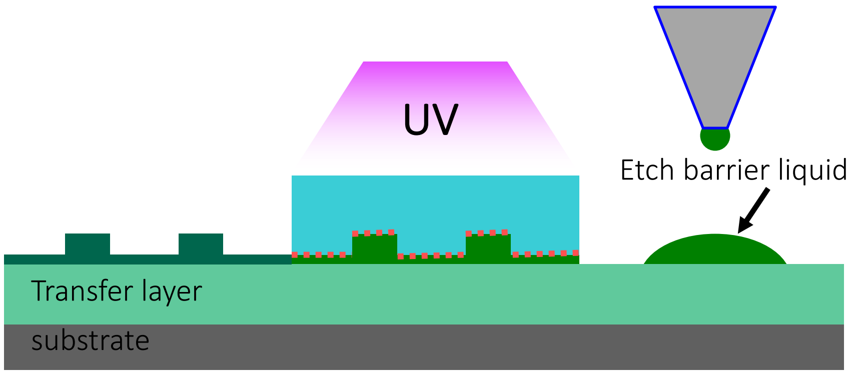
Ge-Au deposition and lift-off of PMMA





Step&Flash Lithography (SFIL)

Drop of etch barrier liquid / imprint / UV curing



Dry-etching of “etch barrier” residual layer and pattern transfer in the “transfer layer”

Molecular imprint
Imprio 300
Low Cost CMOS Nanoimprint system

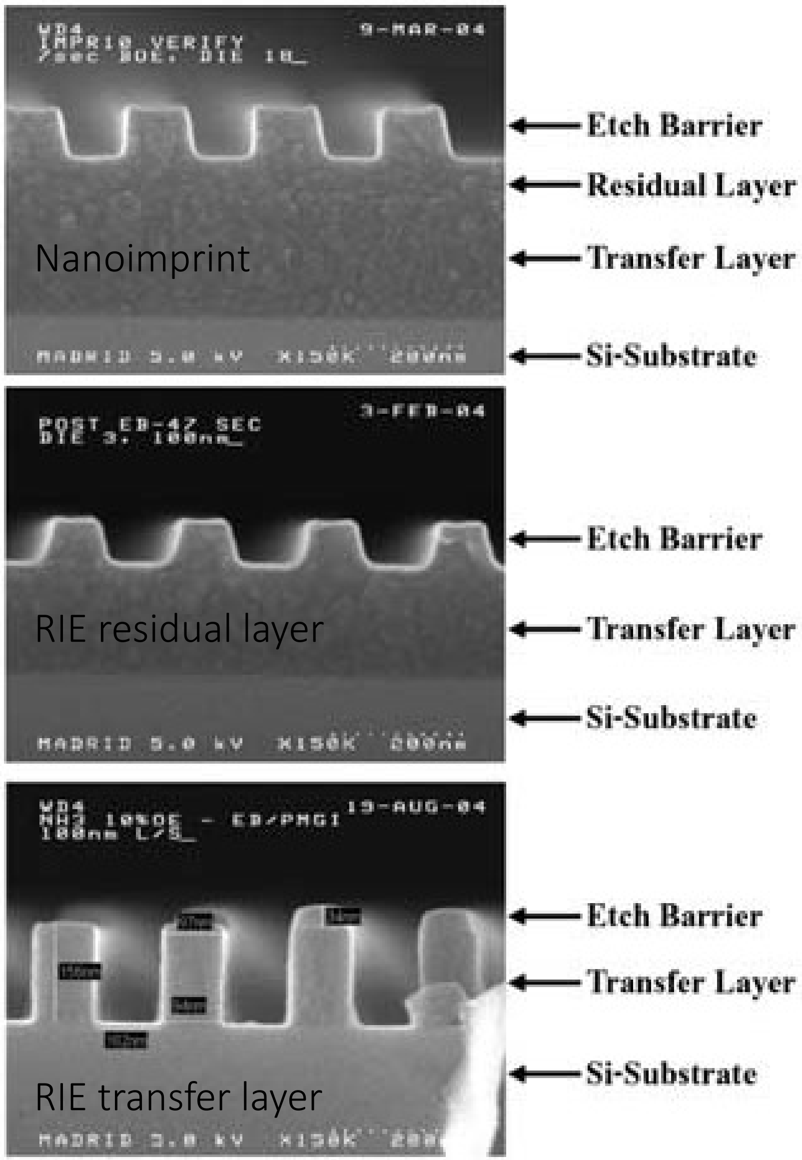
Quartz stamps:

- Difficult to fabricate (expensive)
- Fragile!
- Difficult to demold over large surface areas

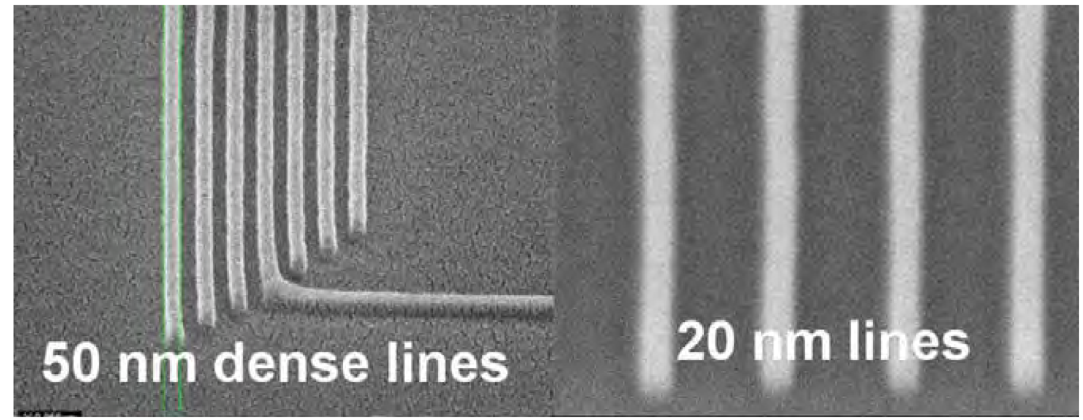
Step&Flash (stamp 1 cm^2)

1. Wafer covered with the **“Transfer layer”** (sacrificial polymer layer)
2. **“Etch barrier”** (low viscosity, UV-curable liquid polymer liquid containing Si) <u>locally dispensed</u>
3. Stamp in contact: the liquid polymer fills the stamp cavities by <u>capillary action</u>
4. Short UV-curing
5. <u>Repeat the sequence</u> to cover the wafer area
6. Dry-etching transfers the pattern into the transfer layer (which serves for further pattern transfer into the substrate)

Step-and-Flash Imprint Lithography

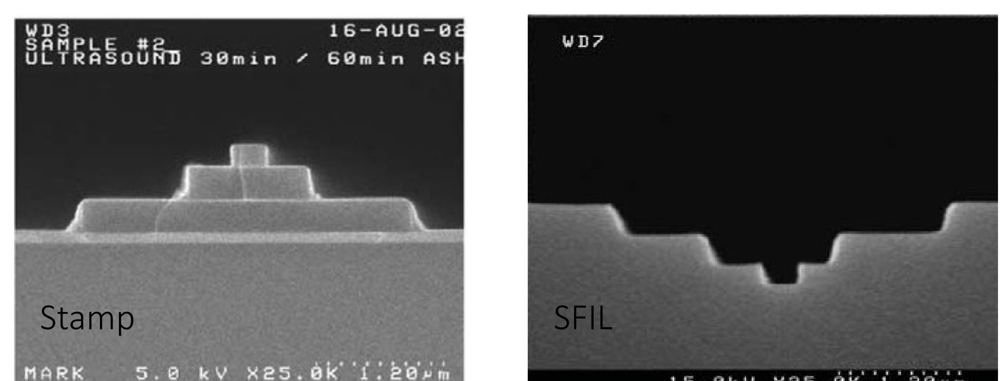


Resnick et al., Proc. SPIE 4688, 205 (2002)



Resnick et al., Mater. Today **8**, 34 (2005)

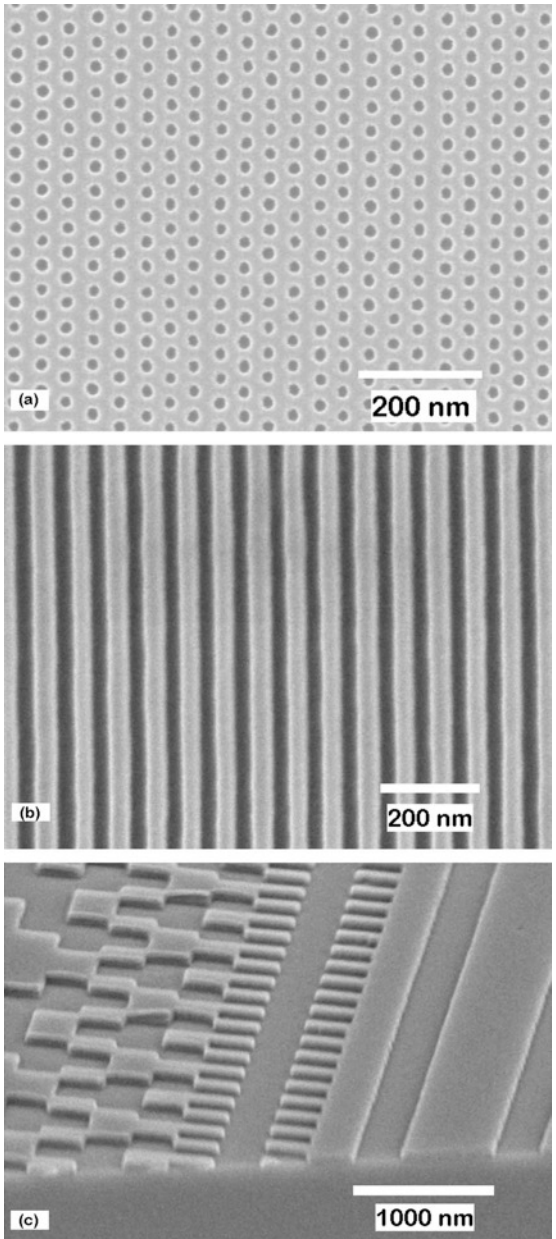
The template can be made in to three-dimensional shape through multi-level or grey scale lithography process.



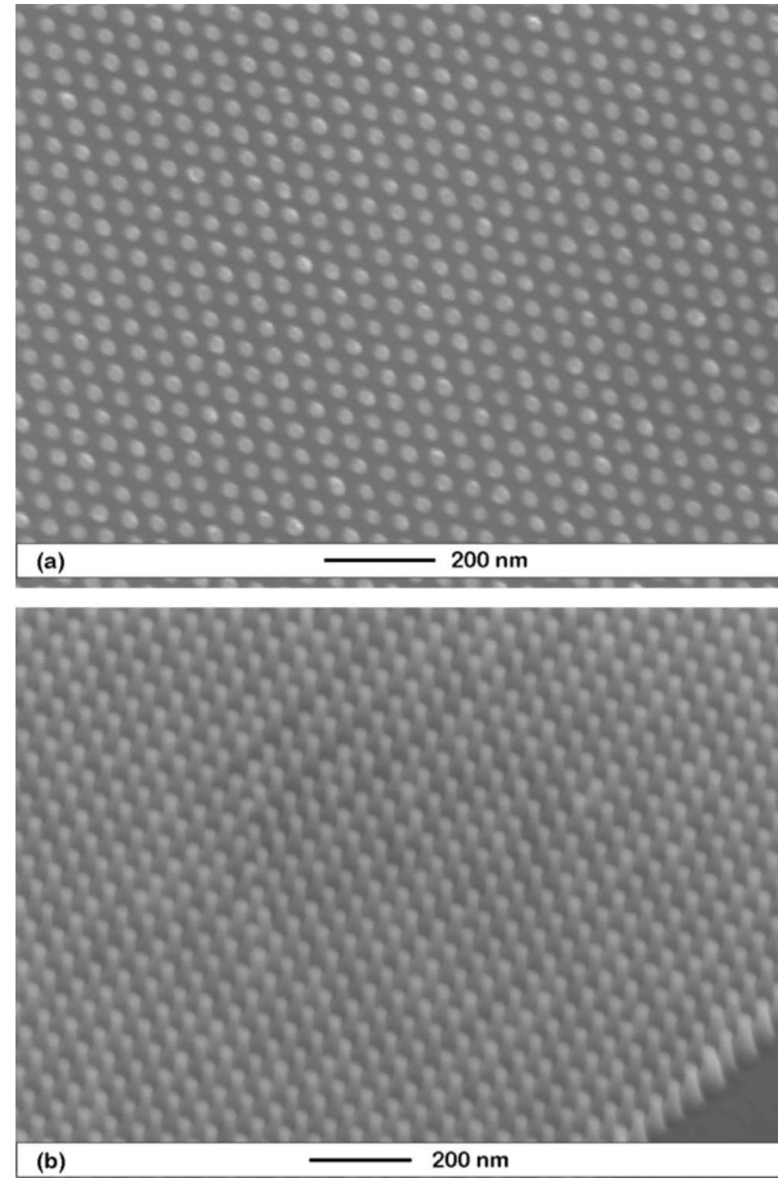
Johnson et al., Microelectron. Eng. 67-68, 221 (2003)

Step-and-Flash Imprint Lithography

(from J. Vac. Sci. Technol. B **27**, 573 (1999)



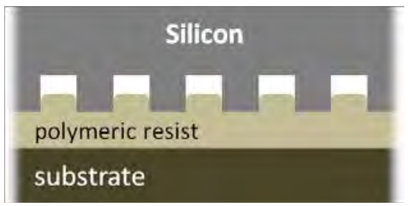
(a) SEM images of imprinted resist patterns. (a) BPM patterns at 40 nm pitch 0.4 Tbit/in^2, (b) DTR track patterns at 70 nm pitch, and (c) a tilt image from a servo pattern region.



Pattern transfer by lift-off: (a) Cr dots after lift-off and (b) tilt image of fused silica topography after etching.

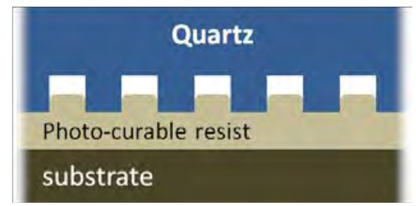
Nanoimprint Lithography: variations on a Theme

T NIL



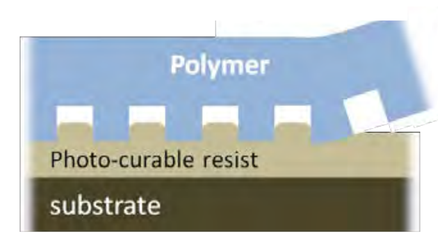
- High Pressure
- Hight Temperature

UV NIL / Step&Flash

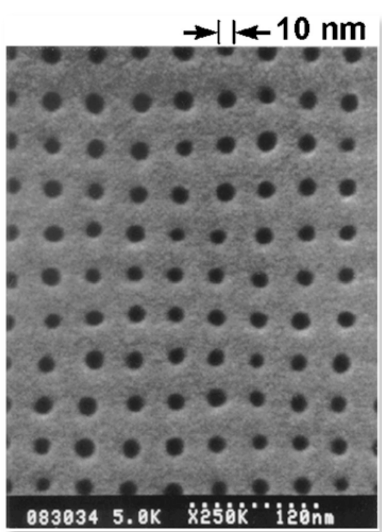


- Lower Pressure (< 1 atm)
- Room Temperature

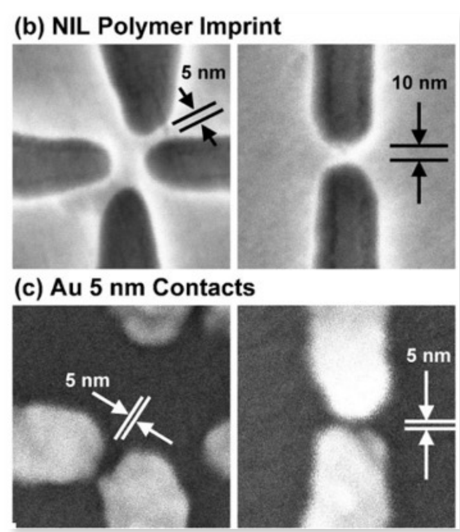
Soft UV NIL



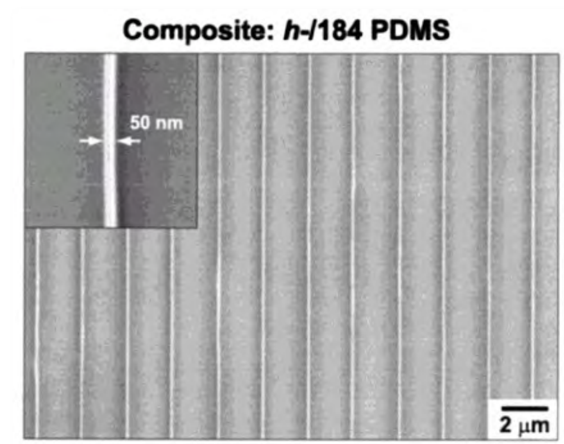
- Low Pressure (≪ 1 atm)
- Room Temperature
- Cheap
- Flexible/curved substr.



J. Vac. Sci. Tech. B **15**, 2897 (1997)



APL **84**, 5299 (2004)



Langmuir **18**, 5314 (2000)

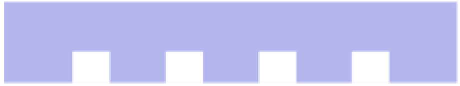
Soft UV Nanoimprint Lithography

- Flexible, cheap, transparent polymeric stamp are replicated from a single (expensive) Si master fabricated by (expensive) electron beam lithography.
- The flexibility of the polymeric stamp ensures conformal contact with the surface substrate on large surfaces at low pressures (≪ 1 atm, even zero!), also on uneven, curved or flexible substrates.

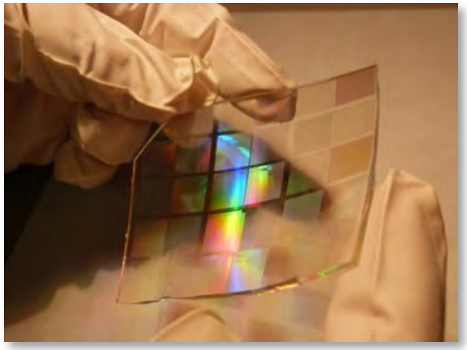
Pre-polymers (PDMS, Ormostamp)

Pre-polymer casting on Si master

Reusable (up to ∽80 times*)



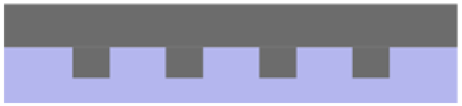
Thermal/UV-curing & peel-off of the polymer stamp



hard-PDMS/PDMS stamp (C2N)

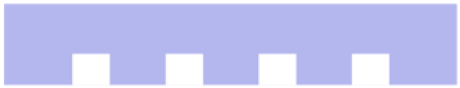
*Schmitt et al., Microelec. Engineer. 98, 275 (2012)

Polymer foils (IPS from Obducat)

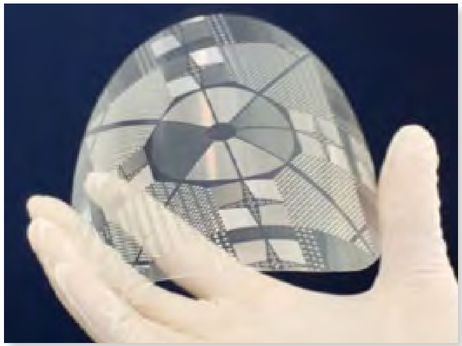


T-NIL in flexible polymer foil

Single use



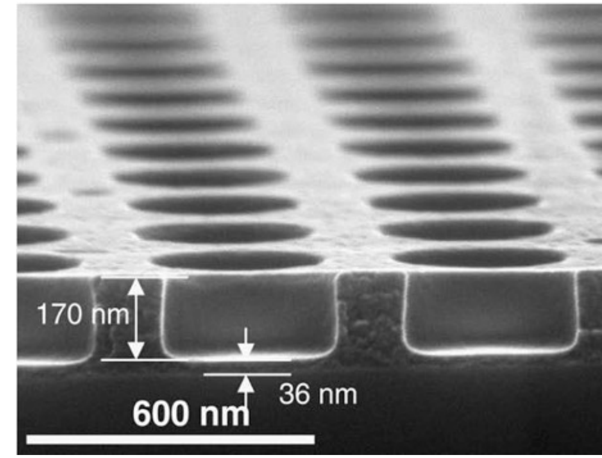
Peel-off of the polymer foil

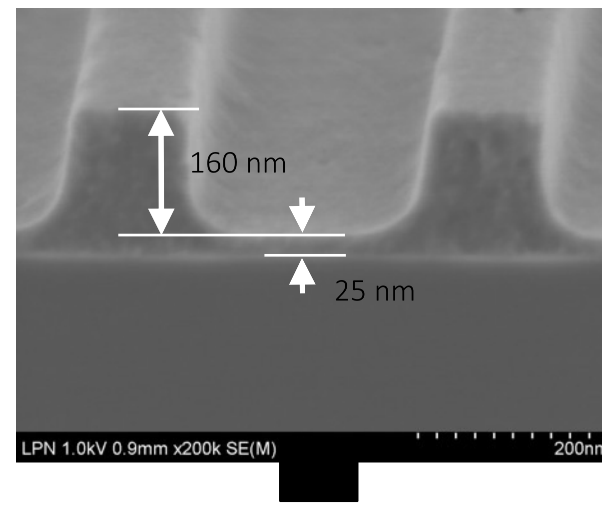


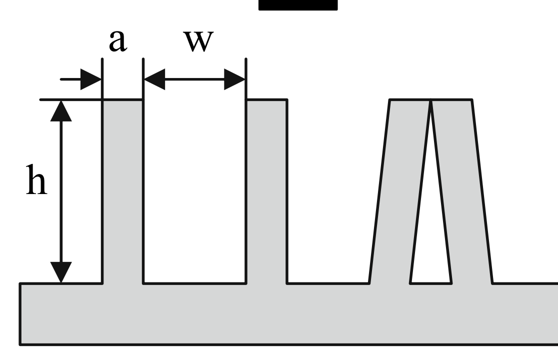
IPS Polymer (Obducat)

PDMS-based stamps

Polydiméthylsiloxane (PDMS) ordinally proposed for Microcontact Printing [G. Whitesides, Applied Physics Letter 1993]







- **Elastomer:** conformal contact with a nonplanar surface without applying any pressure
- **Low surface energy:** (22 mJ m^{-2}) → easy peel off
- **Chemically inert** to many diluted acids and solvents
- **Optically transparent** down to wavelength of 300 nm

Drawbacks:

- Low Young's modulus (≈2 MPa) lead to pattern collapse of high aspect ratio features
- PDMS stamps fail to replicate sub 100-nm structures

“Hard-PDMS”

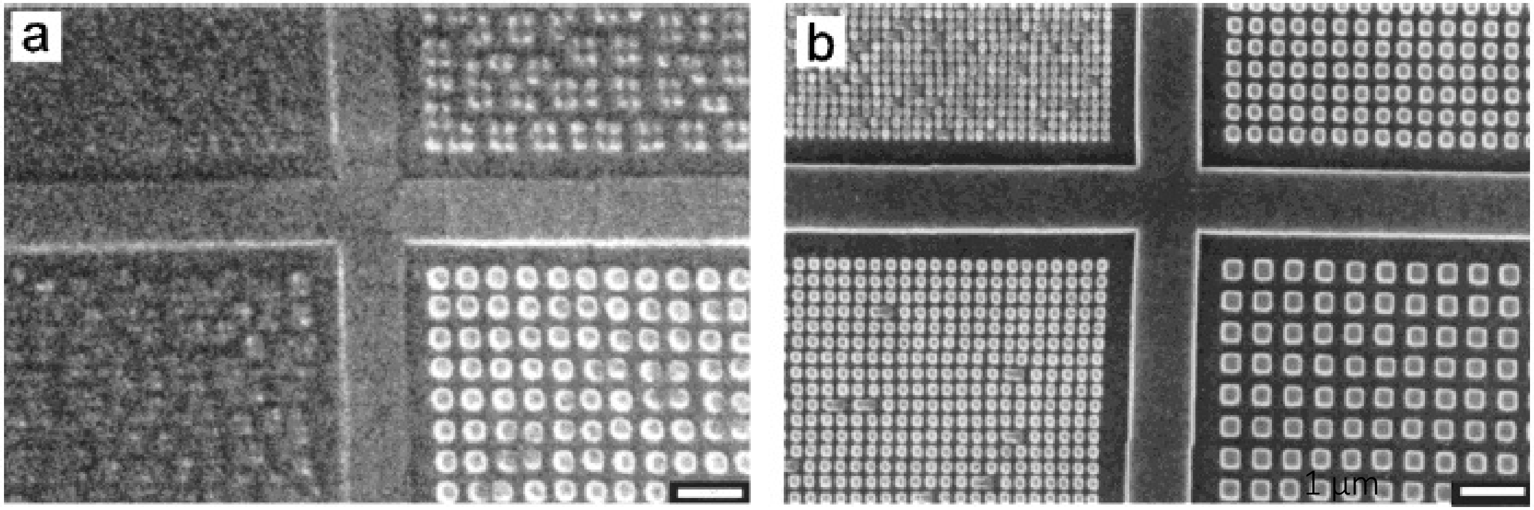
Lower Mw pre-polymer:

→ Lower viscosity pre-polymer: better replication of the Si master nm-size features

→ Once cured has high Young's modulus (more brittle)

PDMS (Sylgard 184)
(compression modulus of 2 N/mm^2)

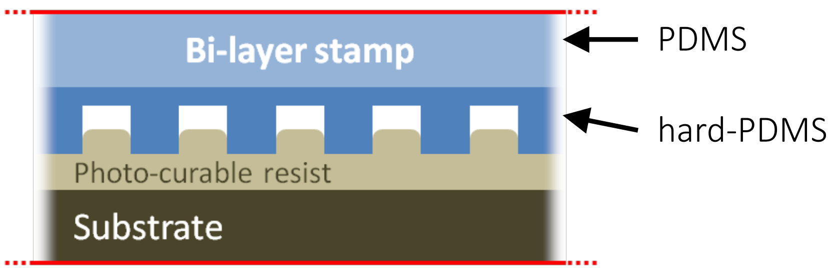
Hard-PDMS
(compression modulus of 9.7 N/mm^2)



H. Schmid, B. Michel, Macromolecules 2000, 33, 3042.

Bi-layer hard-PDMS/PDMS stamp

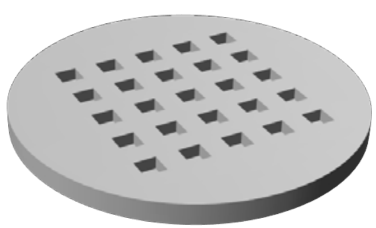
T. Odom et al. Langmuir 18, 5314 (2000)



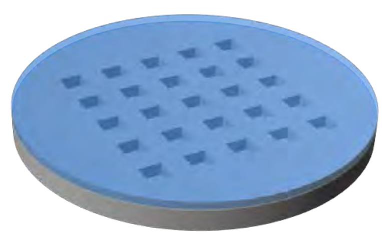
Thin rigid hard-PDMS to ensure replication of the sub-100 nm nanostructures

Thick PDMS top layer maintains a global flexibility and conformal contact at low imprint pressure

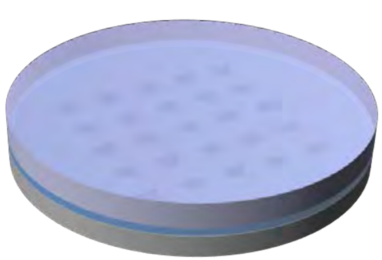
1) Si master mold by EBM



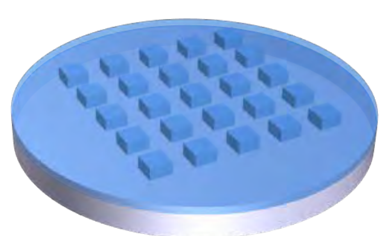
2) Spin-coating of pre-polymer hard-PDMS

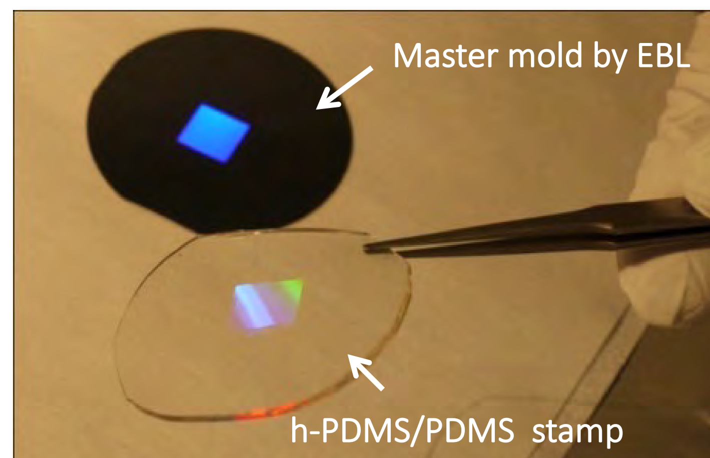


3) Casting of PDMS and soft baking (1 day 60 ° C)



4) Demolding, anti-sticking treatment



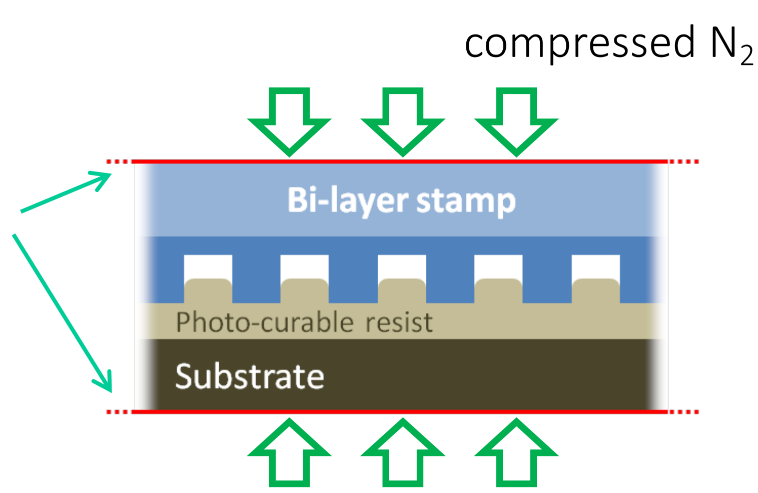


A. Cattoni, et al., in "Recent advances in Nanofabrication Techniques and Application" edited by Bo Cui, Intech (2011)

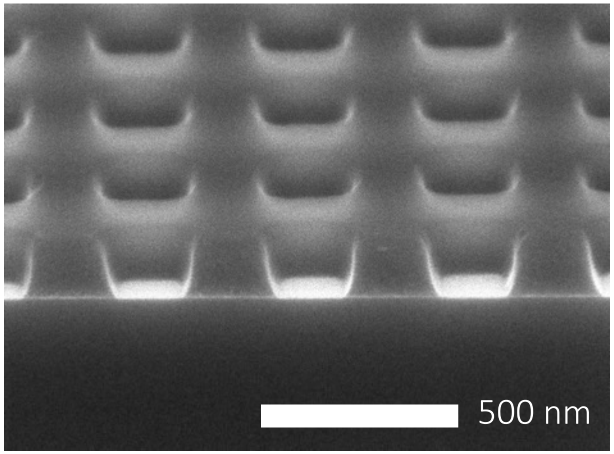
Soft UV NIL with bi-layer stamp

Nanonex NX2500

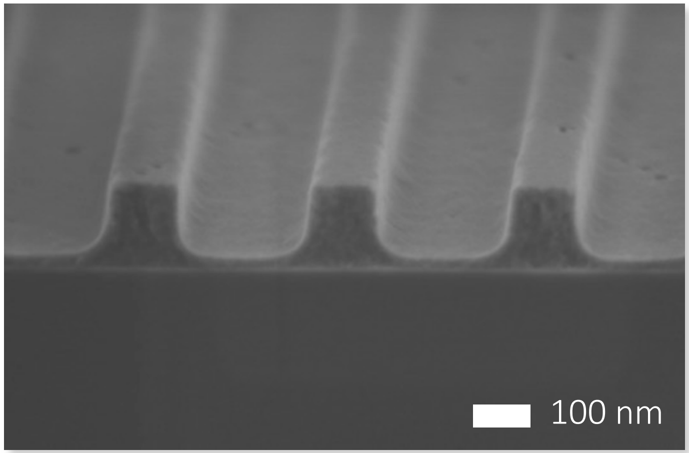
- Uniform pressure applied by transparent membranes
- Low Pressure (< 1 atm)
- up to 4 inches



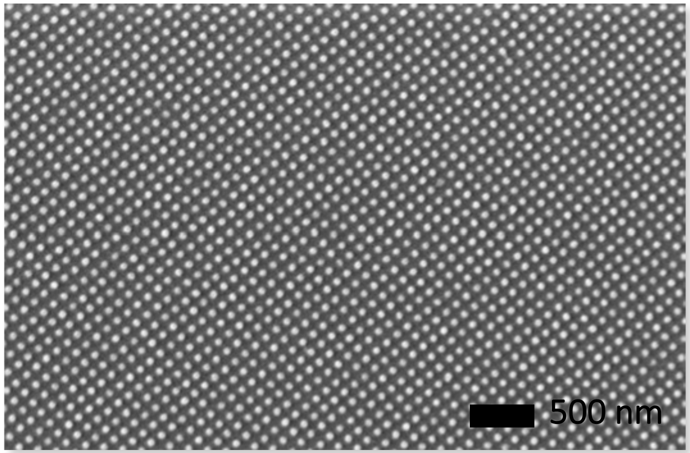
Squared holes: 200 nm, 400 nm pitch



Lines: 120 nm, 400 nm pitch



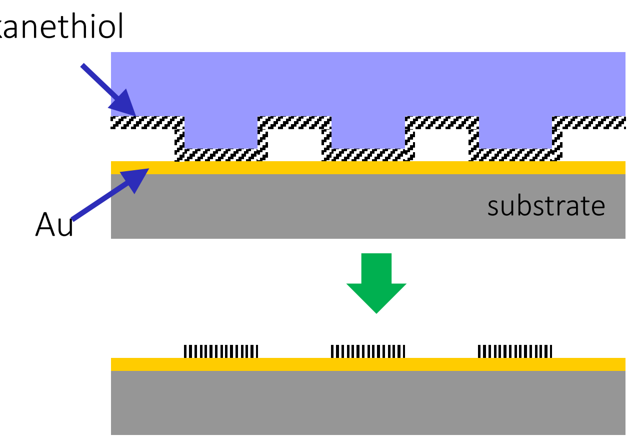
Pillars: 50 nm, 100 nm pitch

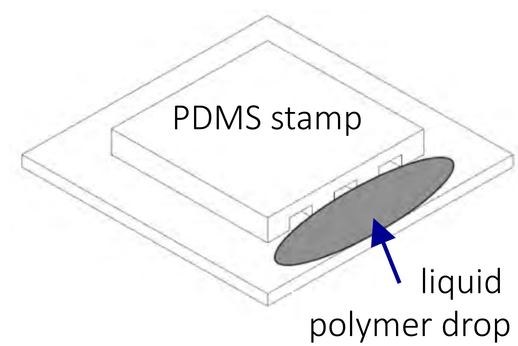


“Soft Lithographies”

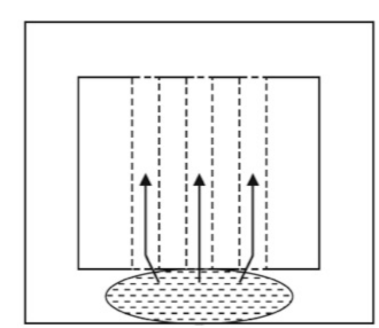
> based on PDMS stamps no imprinter machine

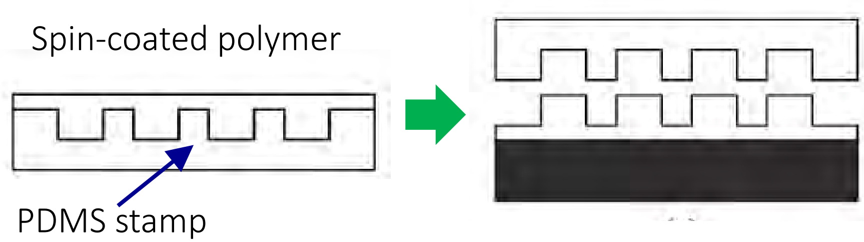
- Microcontact printing [Whitesides - Applied Physics Letter 1993]
- Nanoimprinting Lithography (Soft UV NIL) [Chou - APL 1995]
- Micromolding in capillaries [Whitesides - Nature 1995]
- Replica molding [Whitesides - Science 1996,]
- Microtransfer molding [Whitesides – Adv. Mat. 1996]
- Solvent-assisted micromolding [Whitesides – Adv. Mat. 1997]
- Micro-aspiration assisted lithography [Chen – Mic. Eng. 2007]
- **Degassing-Assisted Patterning** [Cattoni/Chen - Biot.&Bioeng. 2010]





Filling of the stamp
µchannels by capillary forces

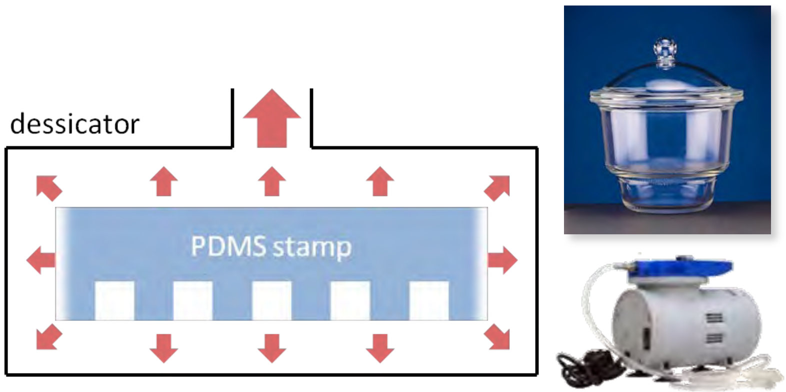




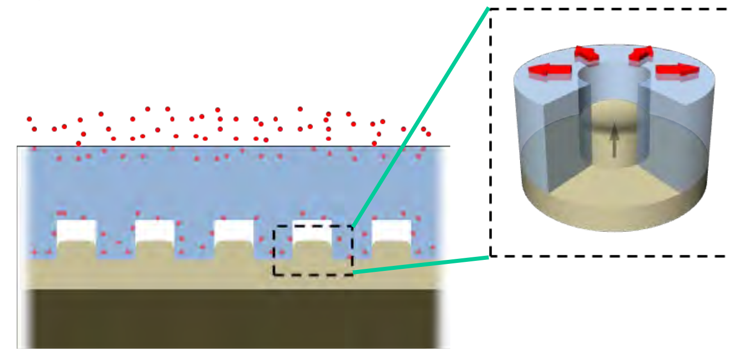
see for example: “Soft Lithography”, Y. Xia and G. M. Whitesides, Angew. Chem. Int. Ed. 37, 550 (1998)

Degassing Assisted Patterning (DAP)

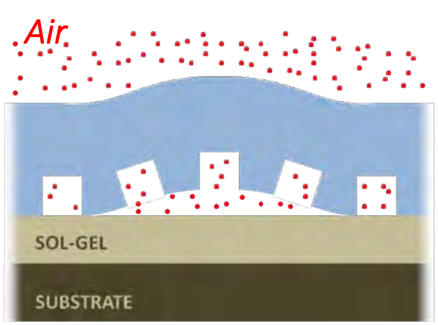
1) Degassing (τ ≈ 5 min)



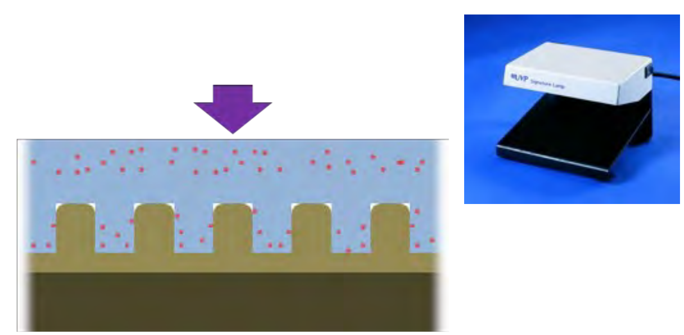
3) ΔP → the resist is aspirated into the stamp nanocavities



2) eventual macroscopic bubble are removed in few seconds



4) UV/thermal curing and demolding

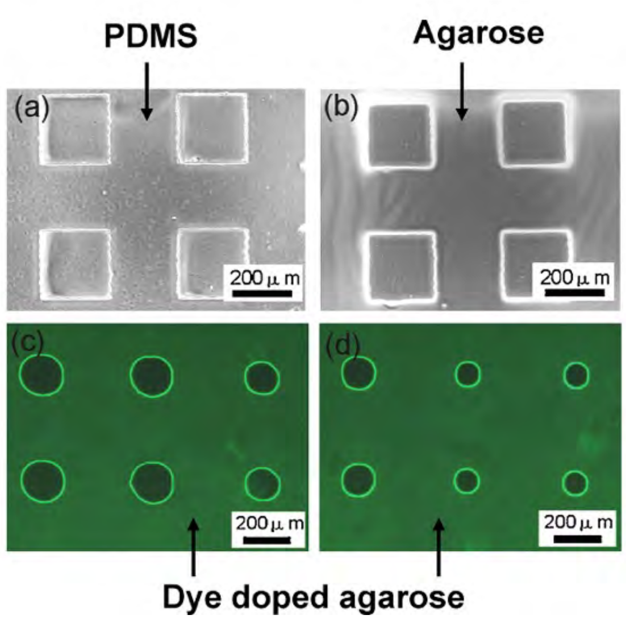


Cattoni et al., MNE 2010

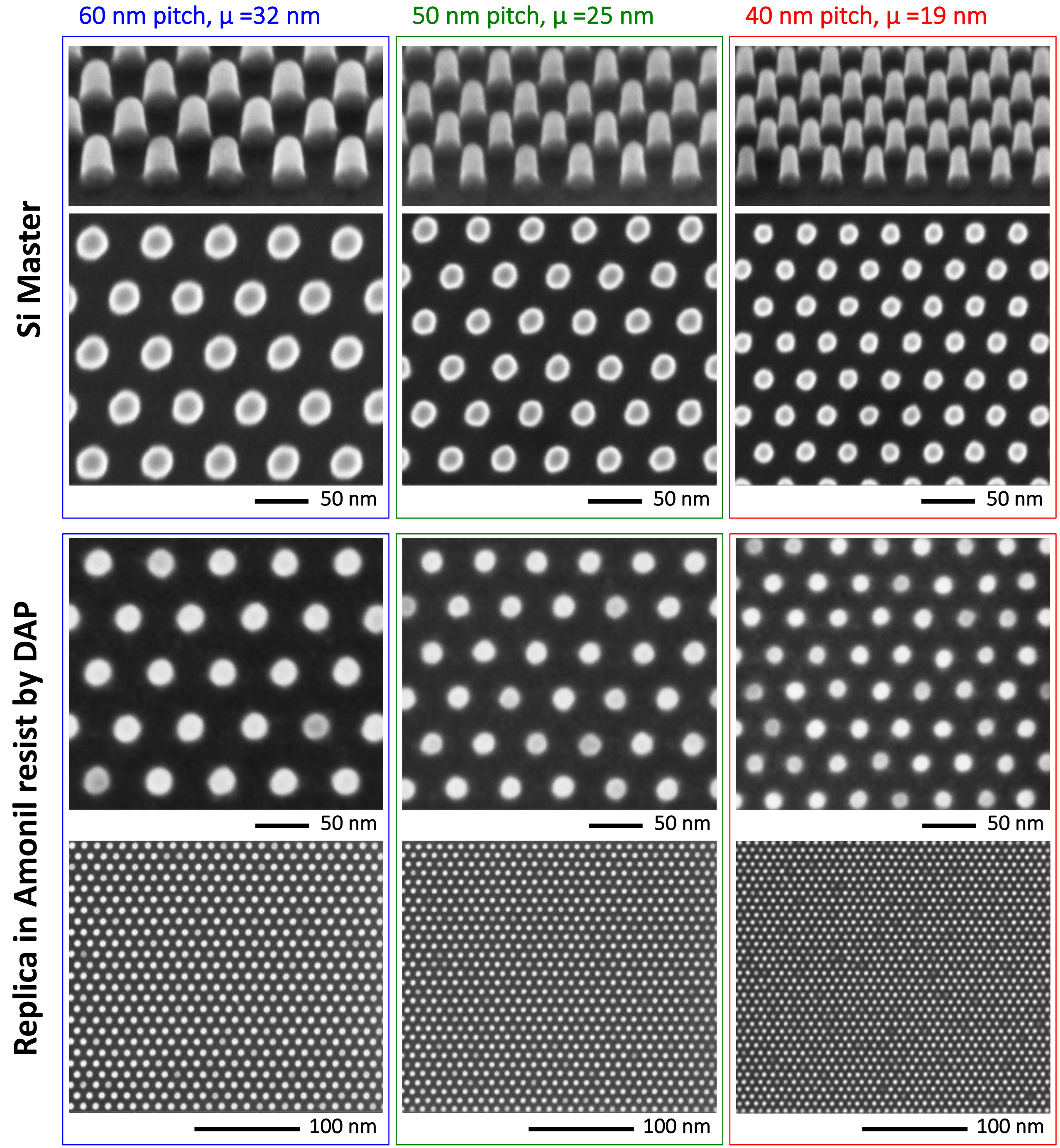
Biotech. and Bioeng. 105, 854 (2010)

Degassing Assisted Patterning (DAP)

- Originally proposed for patterning µm-scale biological matter (↓)
- Extended to imprint of organic/inorganic resist (→)



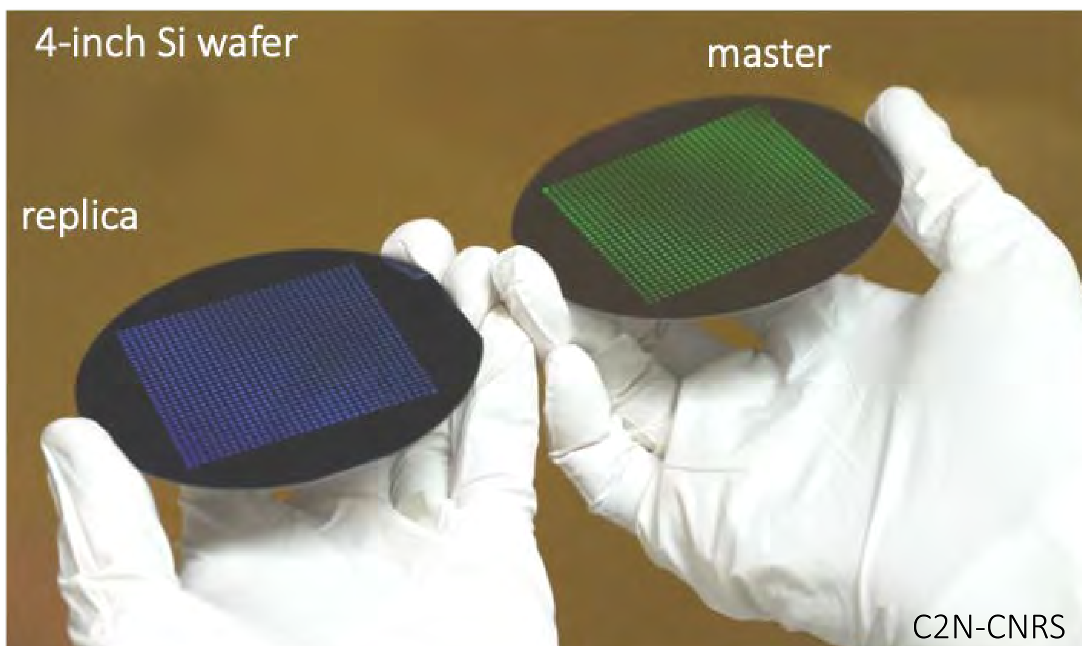
Biotech. & Bioeng. (2010) 105 856



Degassing Assisted Patterning (DAP)

- Higher resolution as compare conventional Soft UV Nanoimprint (up to 20 nm)
- No imprinter machine (dessicator + pump + UV lamp)
- No pressure → no long-range deformations
- Bubble-defects-free
- It can be integrated in UV mask aligner
- Still large area imprint

1024 fields of 1 mm²

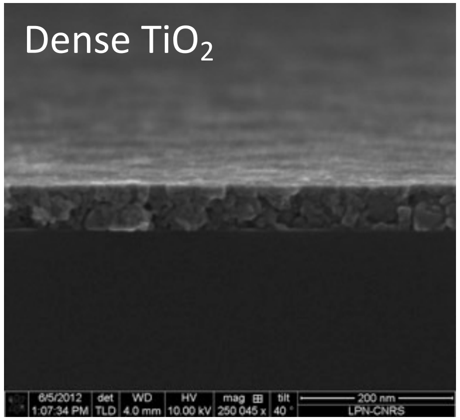


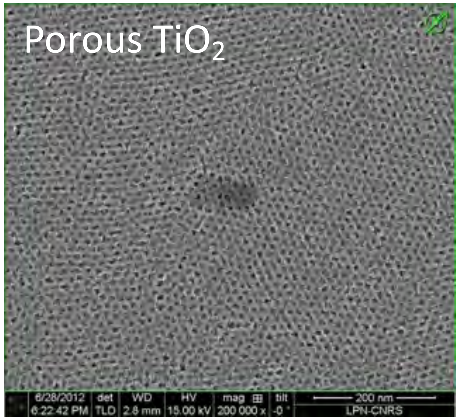
DAP for direct embossing of sol-gel derived films

Resist → liquid sol-gel precursor

- Titanium alkoxide
- Ethanol
- Water
- (surfactants → porosity)

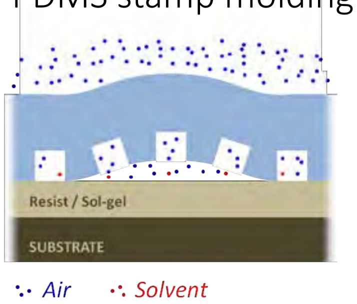
Spin or dip-coating → amorphous film
Thermal processing (450 ℃) → crystal phase (TiO_2 Anatase)



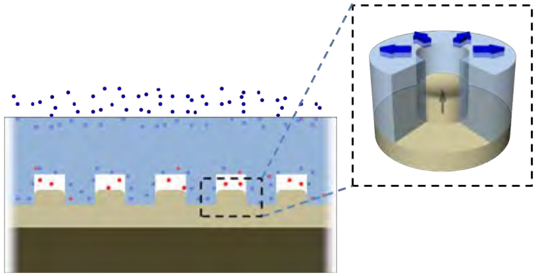


Direct embossing of TiO_2 derived sol-gel films:

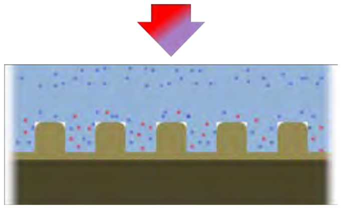
1) PDMS stamp degassing ($\tau \approx 10$ min)
2) Sol-gel spin-coating
3) PDMS stamp molding



4) ΔP → air/resist/solvents (1 min)



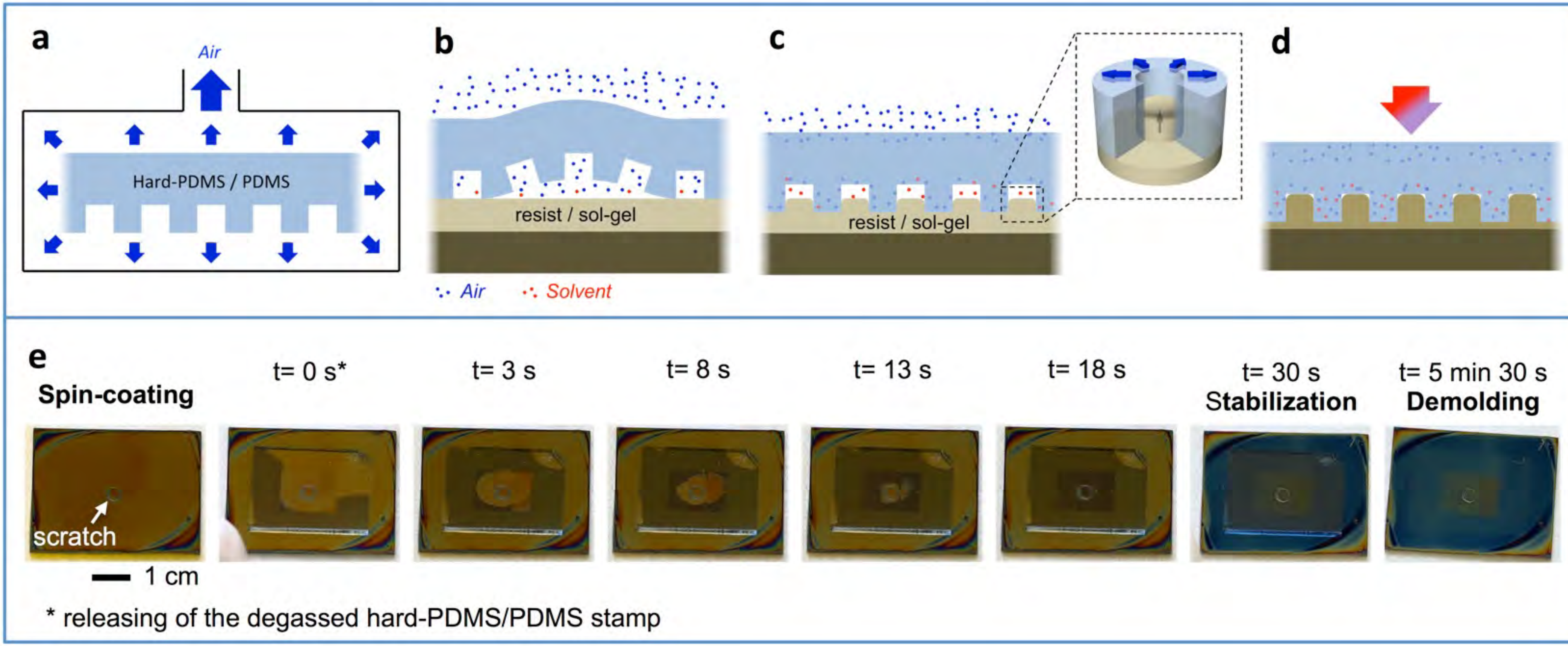
5) Sol-gel stabilization (T = 110 ℃, 3 min)



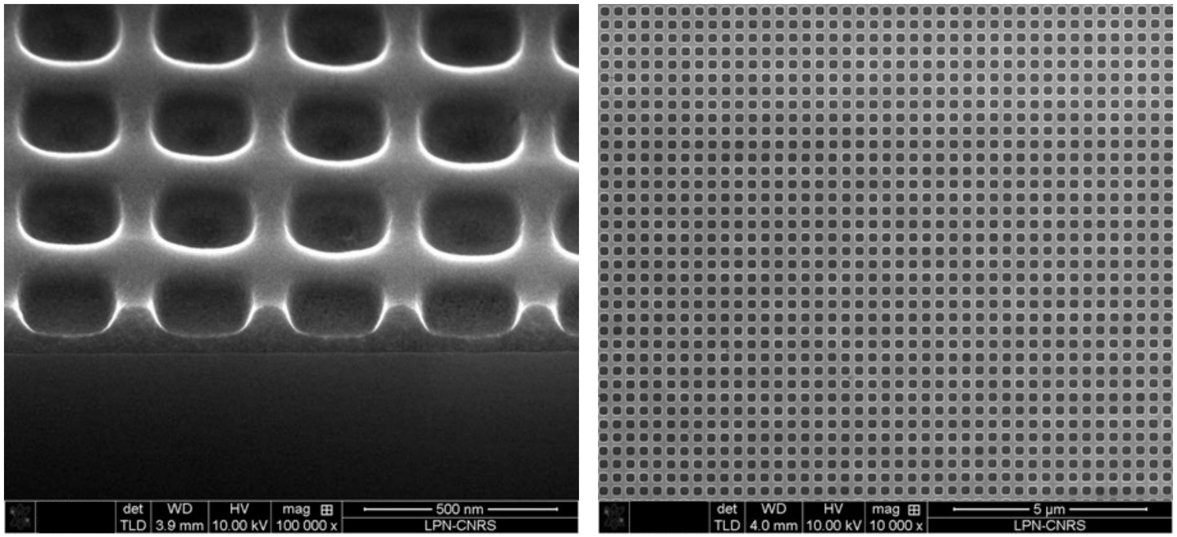
6) Sol-gel crystallization (T = 450 ℃)

(Anatase, n = 1.8 ⟶ 2.4)

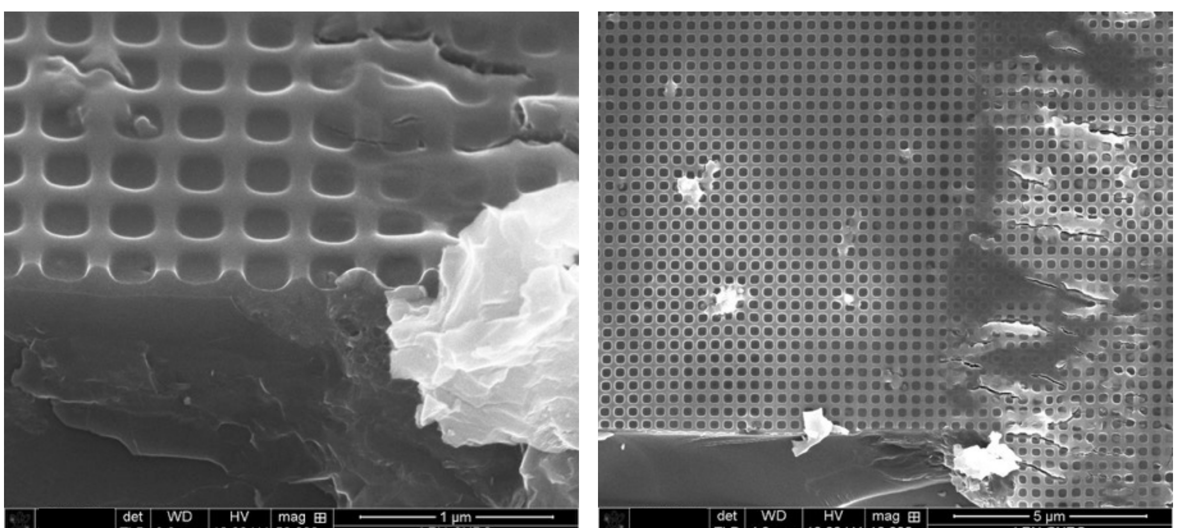
DAP TiO_2 (Video)



Resulted pattern



SEM images of the embossed TiO_2 inside the circular inscription stabilized at 110 ℃.

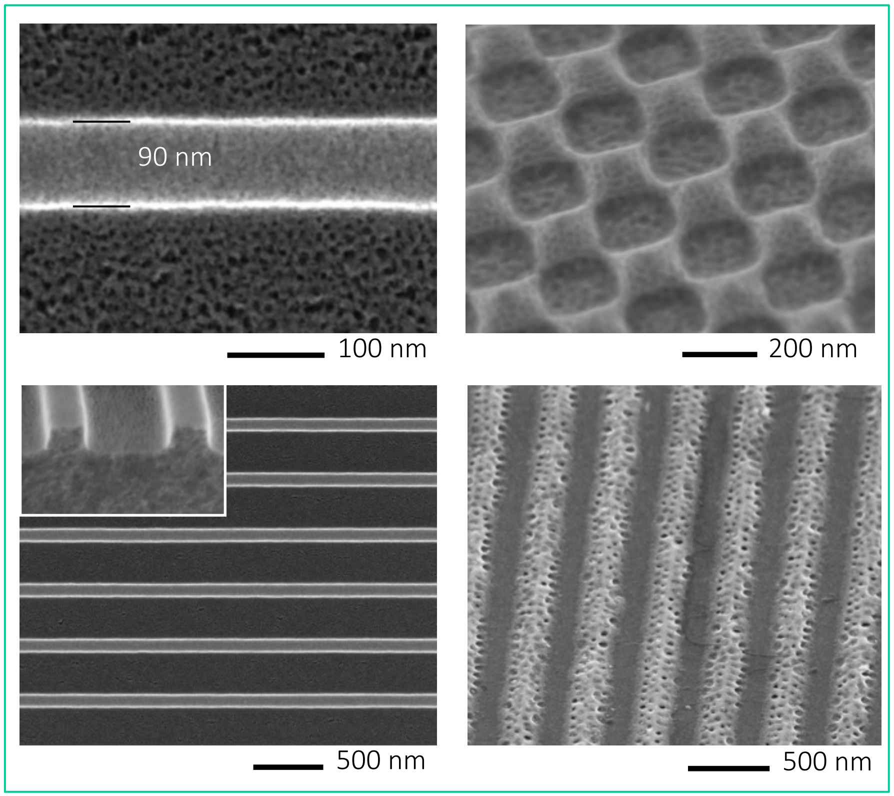


SEM images of the embossed TiO_2 in proximity of the circular inscription stabilized at 110 ℃.

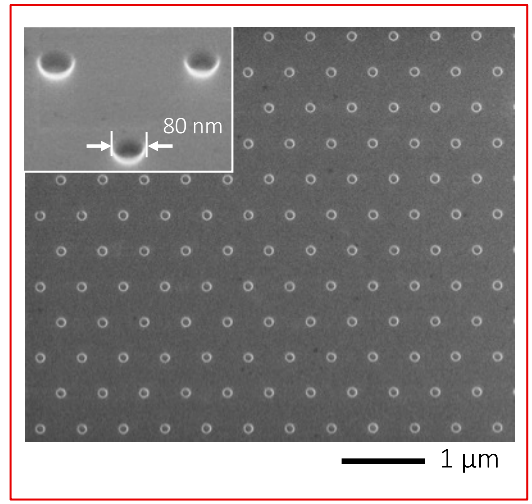
Extension to SiO_2, Al_2O_3, IrO_2 sol-gels or NPs

- One step process: no more lithography + pattern transfer!
- Porosity can be tuned using different surfactants in the sol-gel solution

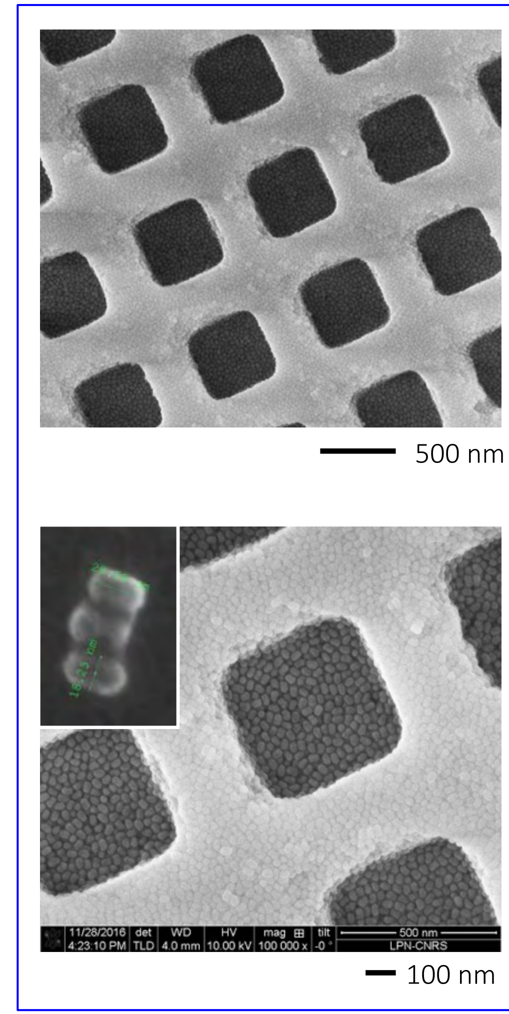
MesoporousTiO_2



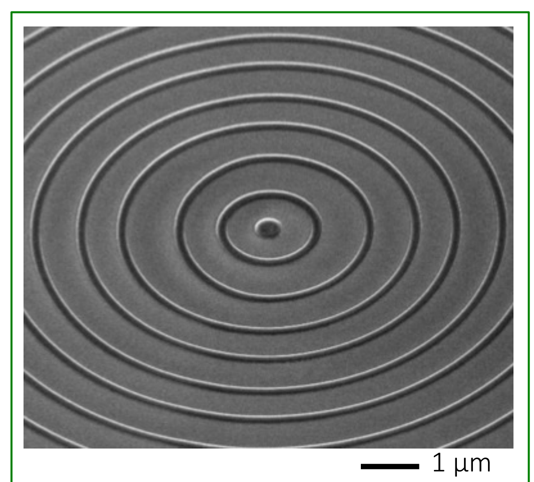
Dense SiO_2

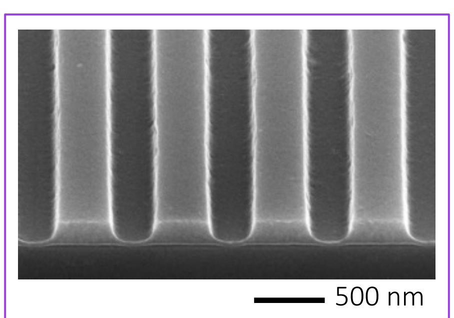


$NaYF_4$ (Er/Yb) NPs



Dense Al_2O_3



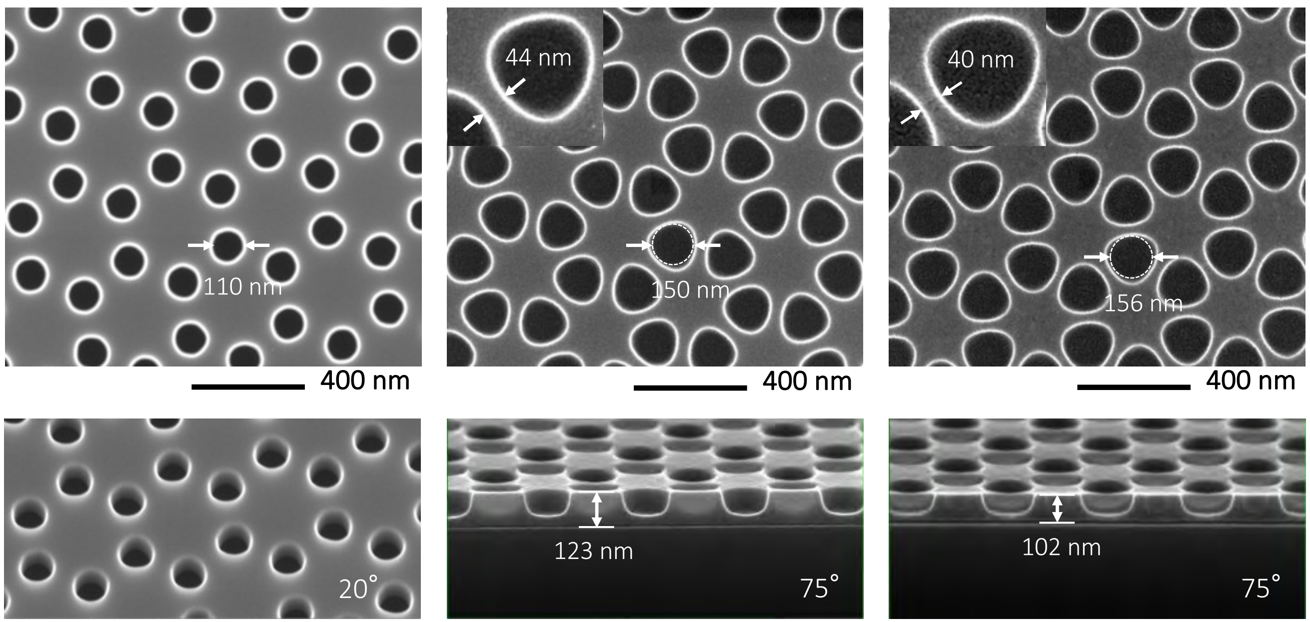


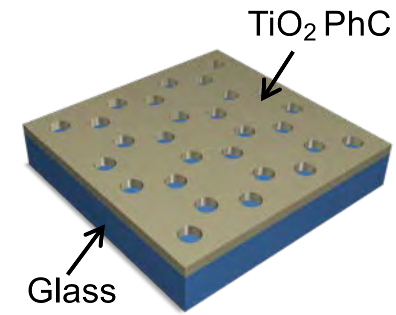
Dense IrO_2

2D Photonic Crystals by direct imprint of TiO_2

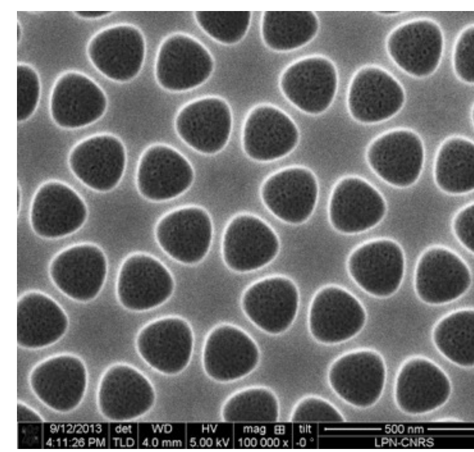
Patterned area: 5 mm x 5 mm.

Silicon Master mold | Embossed TiO_2 amorphous(n=1.9) | Embossed TiO_2 Poly-crystalline (n=2.35)





Embossed TiO_2
amorphous(n=1.9)
on glass

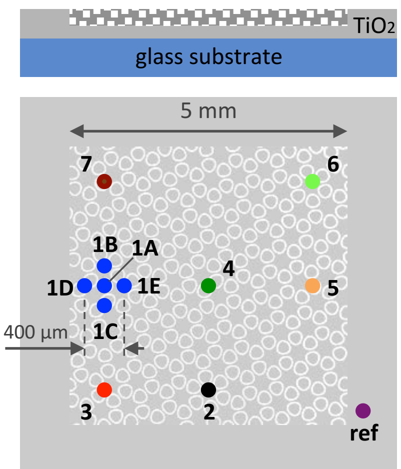


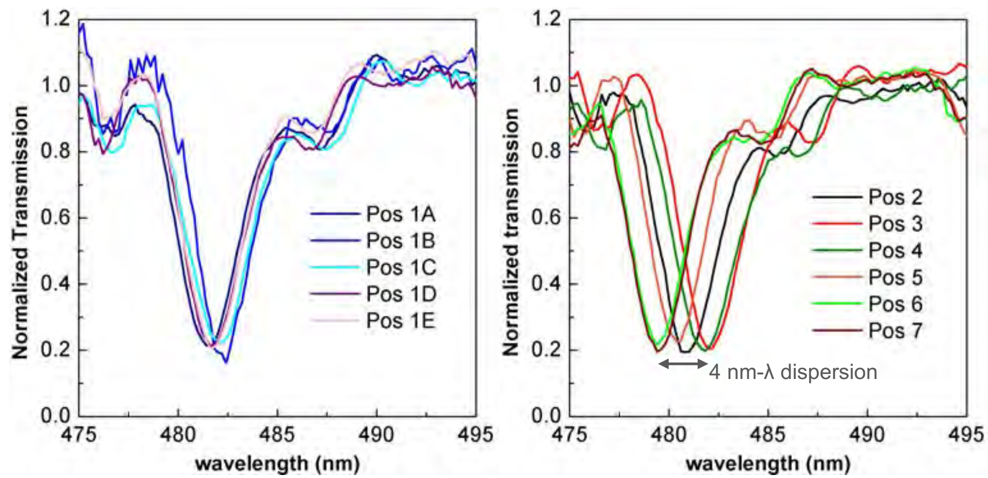
Volumetric losses:

47% induced by solvents removal (stabilization at 110 ℃)

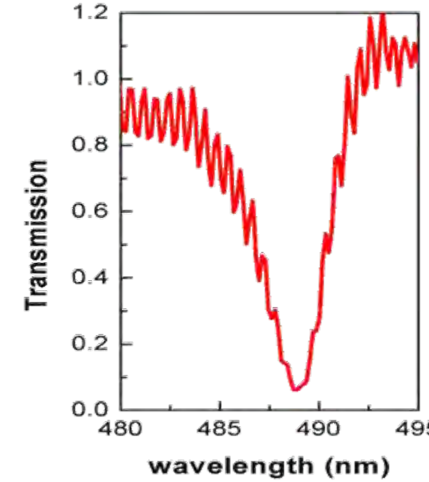
+ 3% lateral, 17% out of plane (calcination at 450 ℃)

Transmission spectra





SiN/glass (Ref.)



- Good contrast comparable to conventional SiN/glass and e-beam + dry etching process
- Extremely low short/long-range deformation:

$\Delta\lambda/\lambda \approx \Delta L/L$ $\quad \lambda = 482$ nm, $\Delta\lambda = 4$ nm $\Big\}$ long-range deformation (ΔL) $\leq$ 1,25 nm!

Light-trapping in ultra-thin GaAs solar cell

Record GaAs solar cell (1.5 µm)

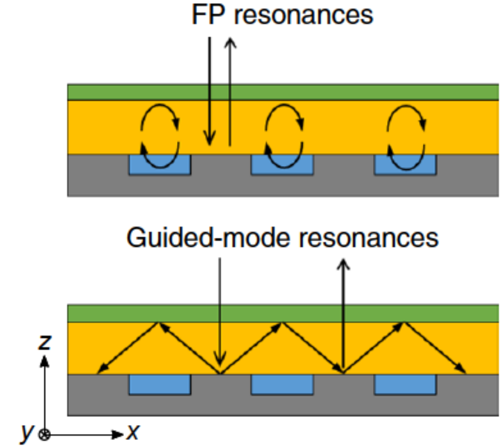
$J_{SC}^{Exp.} = 29.7\ mA/cm^2$

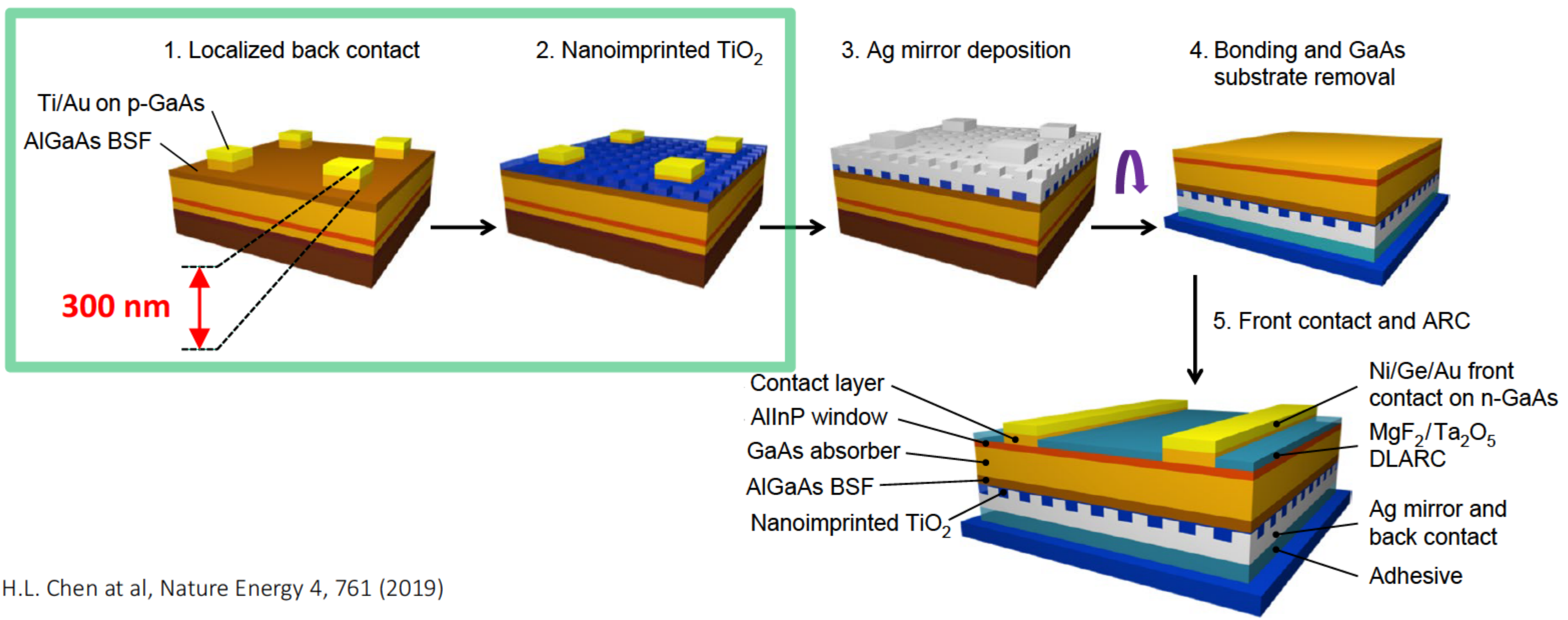
Ultra-thin GaAs solar cell (200 nm)

$J_{SC}^{Num} = 16.7\ mA/cm^2$

With Light-trapping (TiO_2/Ag mirror)

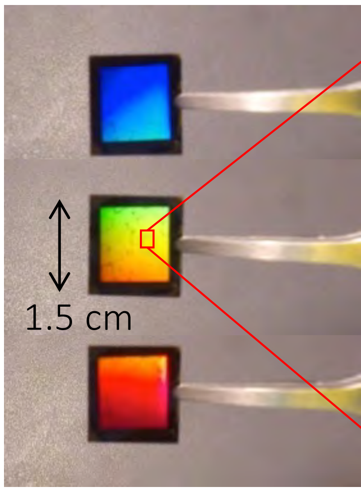
$J_{SC}^{Num} = 25.6\ mA/cm^2$ (+ 53%)



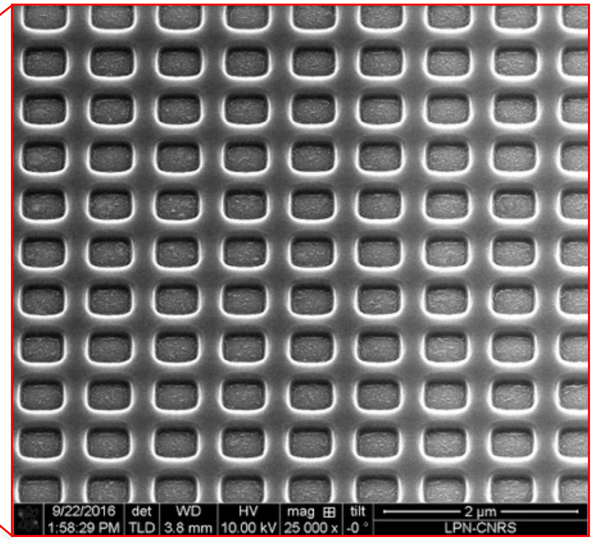


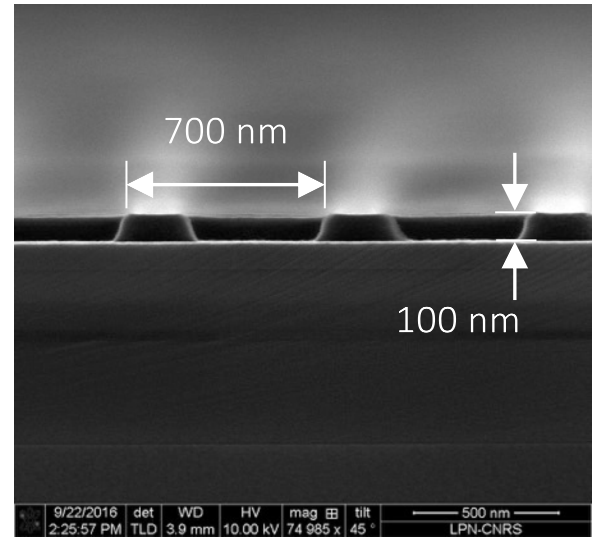
H.L. Chen at al, Nature Energy 4, 761 (2019)

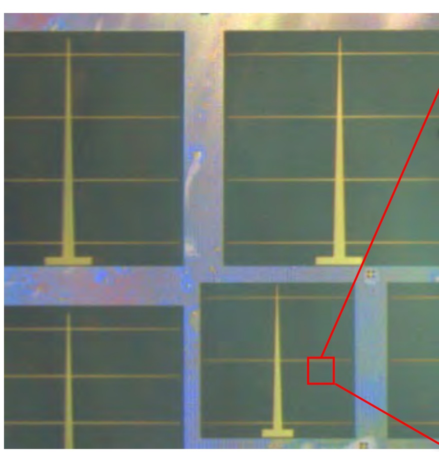
Light-trapping in ultra-thin GaAs solar cell

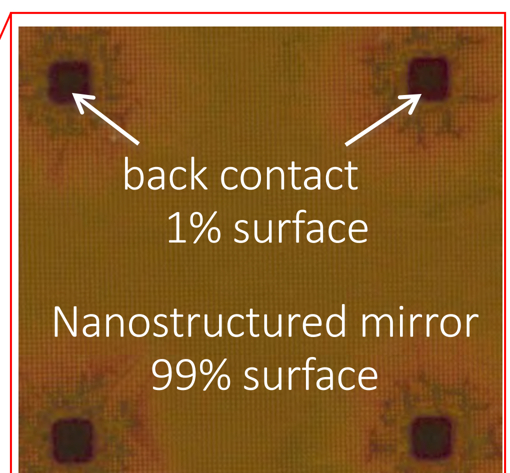


Embossed TiO_2 before Ag deposition









Predicted: J_{SC} = 25.6 mA/cm^2

Experimental J_{SC} = 24.8 mA/cm^2

ΔJ_{SC} 0.8 mA/cm^2

(State of the art certified efficiency 19.9%)

Outlook

Advantages

- Parallel technique: low-cost, large surface area
- High resolution, no diffraction-limited
- Suitable for uniformly distributed cavities/protrusions (arrays)
- Ideal to couple top-down with bottom up approaches (sol-gel, NPs, BCP, MOF etc.):
  → Direct nano-structuration of the material of interest

Disadvantages

- Demanding optimization process (pattern distortion)
- Difficult replication of µm-/nm-sizes features in the same stamp
- Limited aspect ratio (∽ 3)