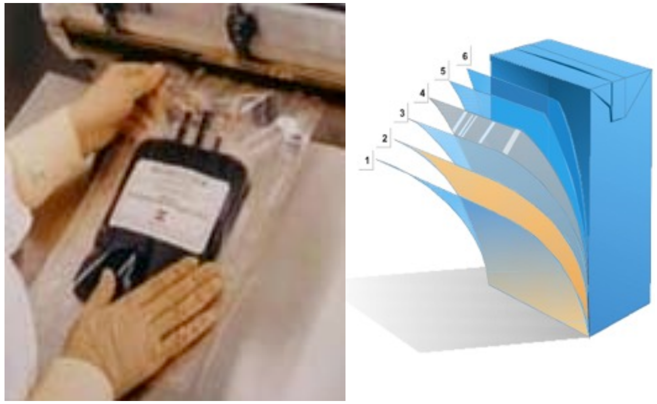
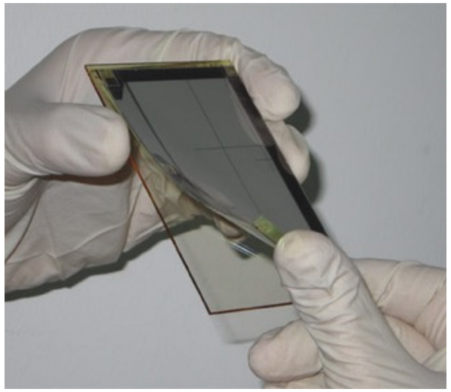
APPLICATION TO SURFACES, NANOSTRUCTURES AND DEVICES

UV-CURABLE POLYMER-BASED MATERIALS AT LPAC

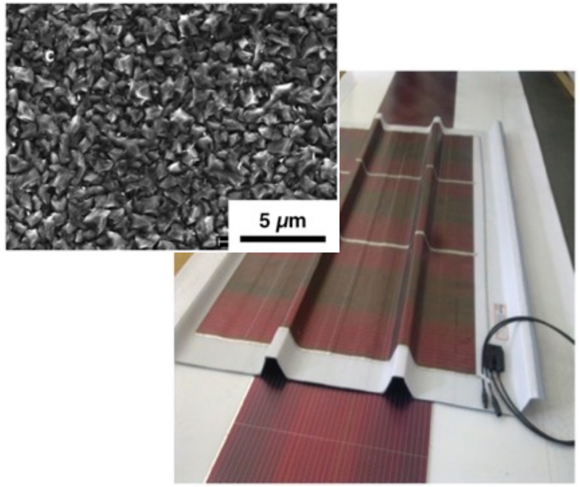
UV inks and gas-barrier films
Food & pharma packaging



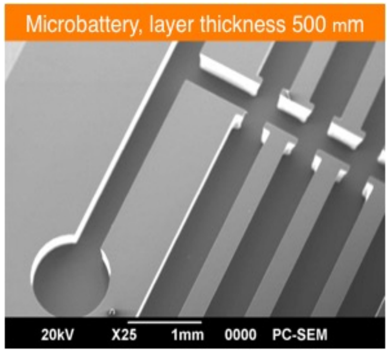
Encapsulation ‘hard-coats’
Flexible displays



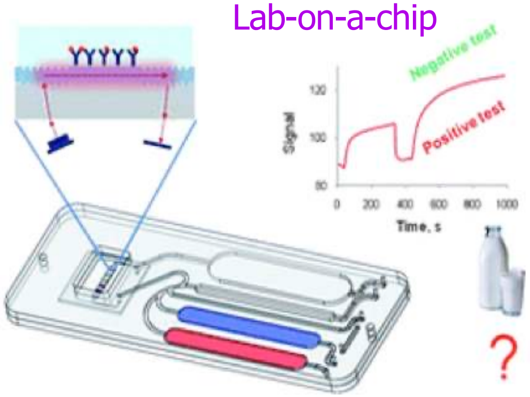
Bioinspired surfaces
Light-trapping textures
for solar cells



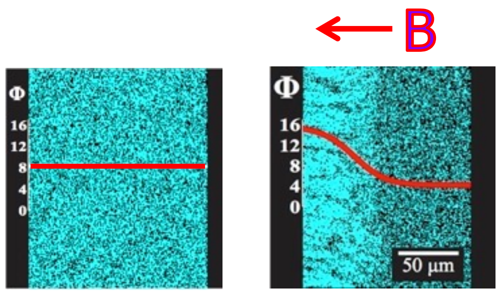
Low-stress UV resists
Microdevice structures



Optical polymer sensors
Lab-on-a-chip



Functionally graded composites
Antibacterial surfaces & ε-FGM insulators



Nanostructured devices

- Technologies
- Process methods

Application examples

- optical biosensors

Valérie Geiser

- bioinspired surfaces

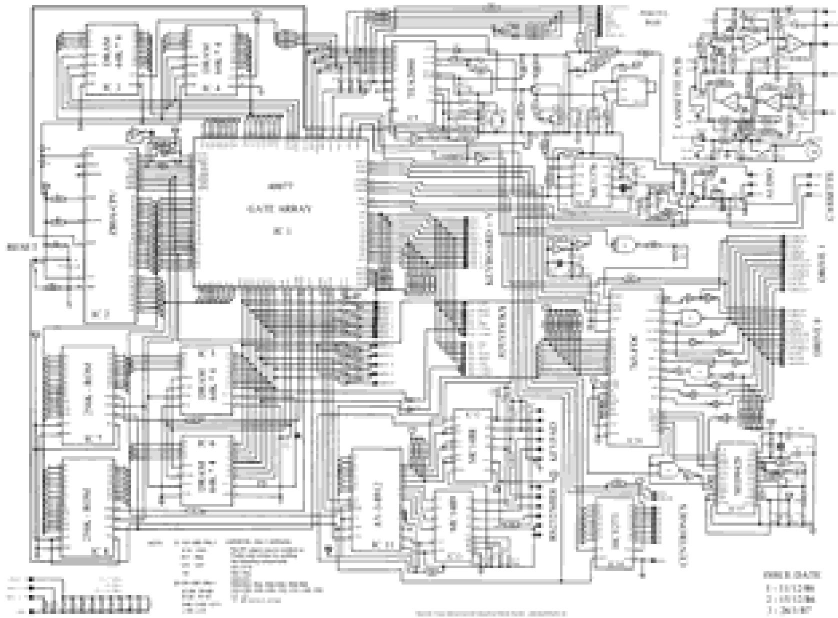
Marina Gonzalez Lazo

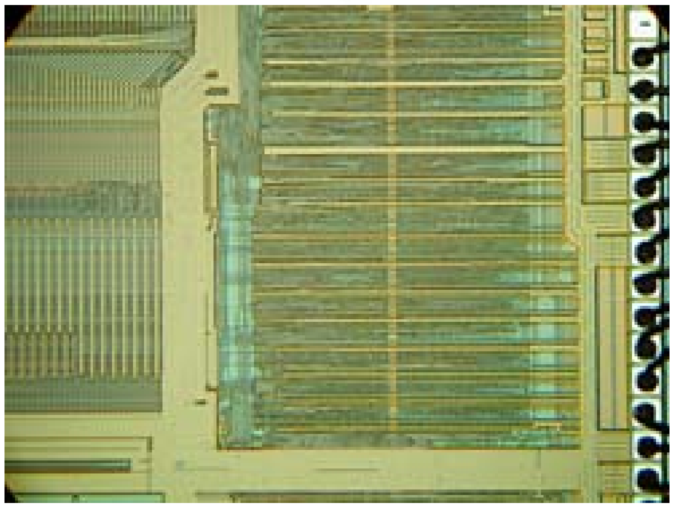
Lionel Wasser

Luca Mueller

Feyza Karasu

NANOSTRUCTURED DEVICE TECHNOLOGIES



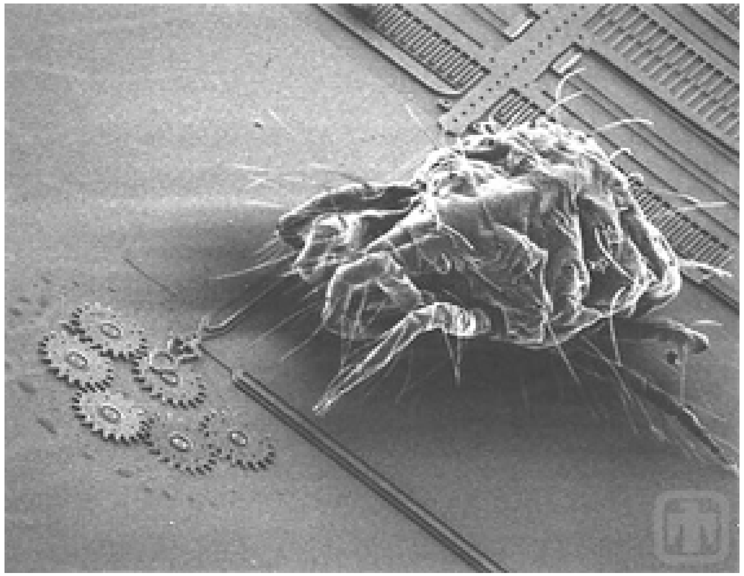


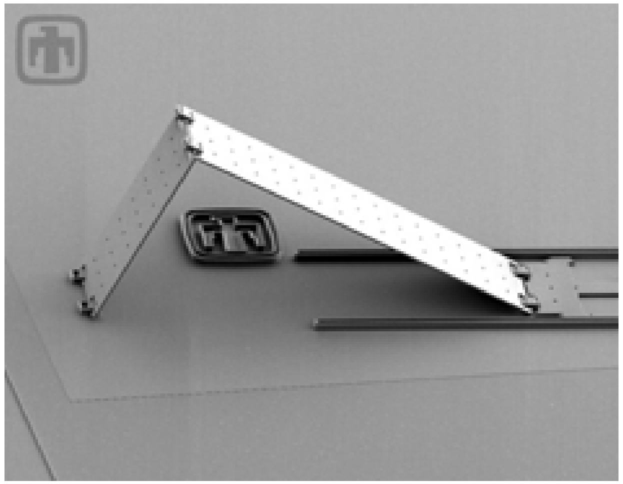
SSI : small-scale integration (early 60's)
MSI : medium-scale integration (late 60's)
LSI : large-scale integration (mid 70's)
VLSI : very large-scale integration (80's)

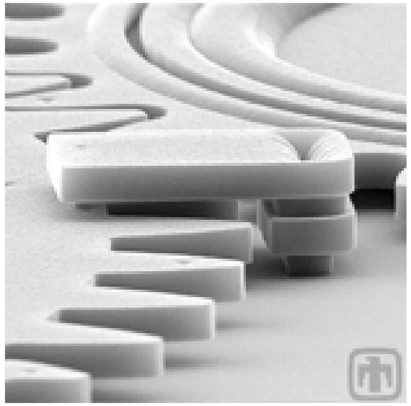
ULSI (ultra large-scale integration),
WSI (wafer-scale integration)
SOC (system-on-chip)

NANOSTRUCTURED DEVICE TECHNOLOGIES

- Micro(Nano) Electro Mechanical System
- Micromachine / Micro System Technology (MST)
- *Electrical comp.+Mechanical comp.* based on CMOS process
- Application: G-MEMS (inertia MEMS) – accelometer, gyro, etc.
  Optical MEMS – communication, display, etc.
  Bio MEMS – DNA chip, lab-on-a-chip, etc.

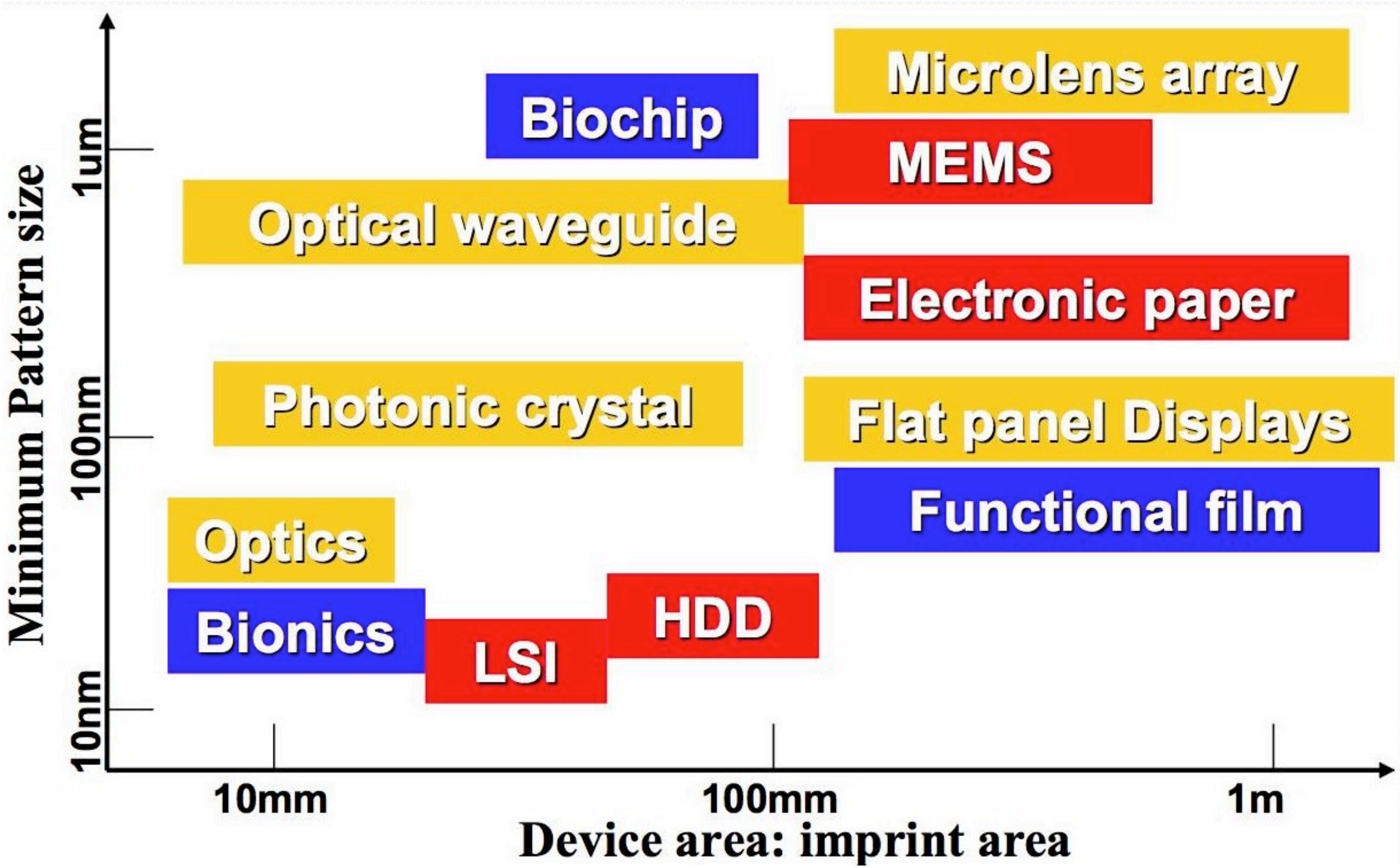






Pictures from Sandia National Laboratory
http://mems.sandia.gov/gallery/images.html

NANOSTRUCTURED DEVICE TECHNOLOGIES

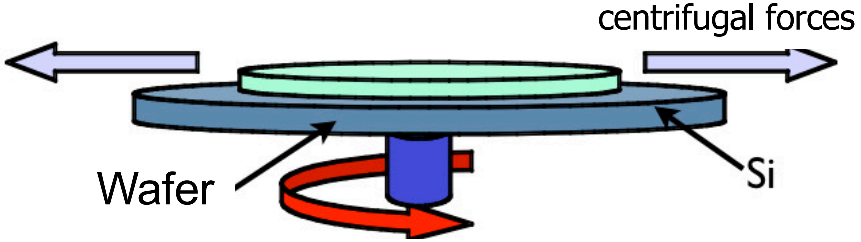


Sakai, J. Photopolym Sci Technol (2009)

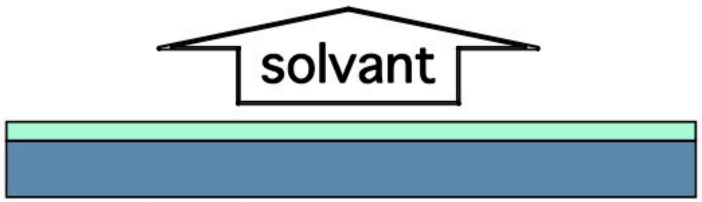
PHOTOLITHOGRAPHY

Photoresist = monomer + photoinitiator + solvent

1. Spin coating (500-8'000 rpm)

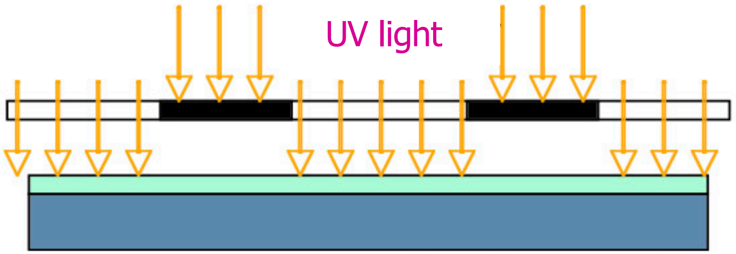


2. Soft bake (90-120° C, minutes)



A. Bertsch, EPFL

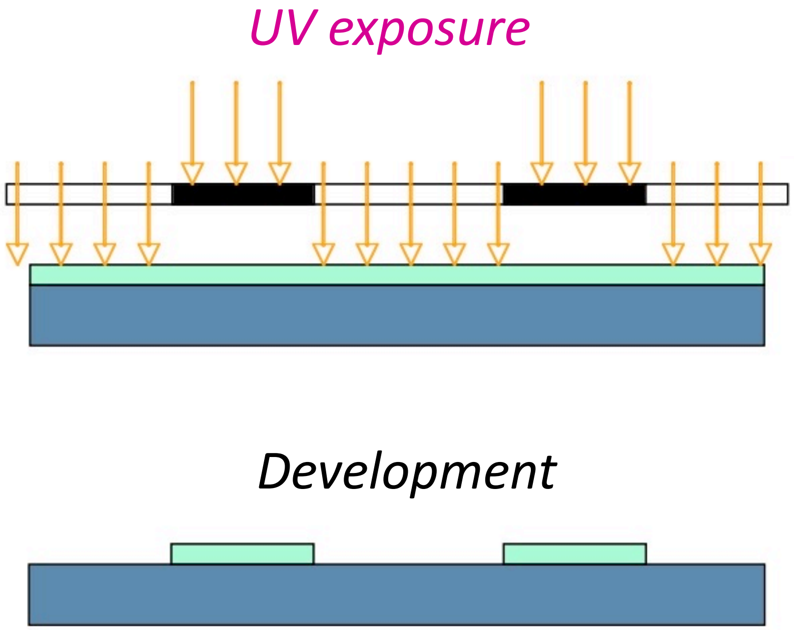
3. Exposure (seconds)



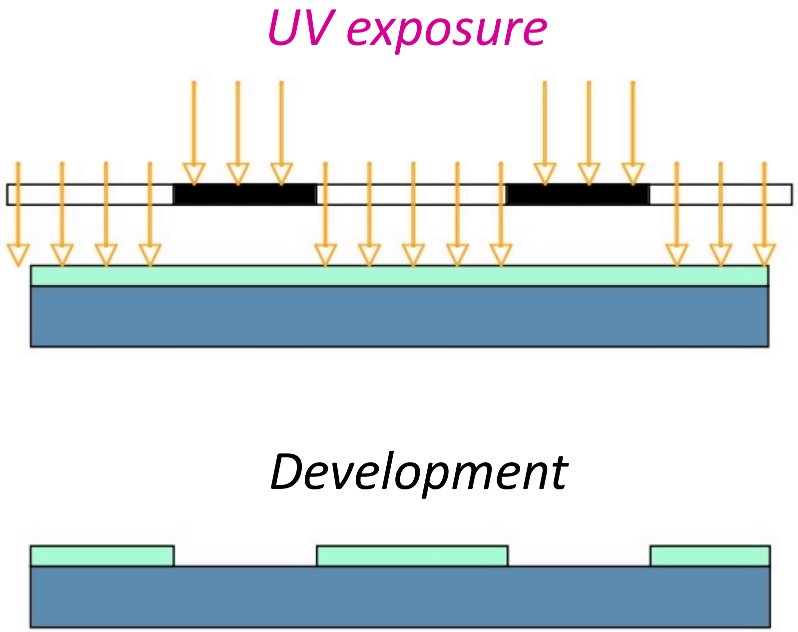
4. Development

POSITIVE VS NEGATIVE RESISTS

Positive photoresist:
UV-induced chain scission
Exposed parts become soluble



Negative photoresist:
UV-induced chain polymerization
Non-exposed parts become soluble



A. Bertsch, EPFL

POSITIVE VS NEGATIVE RESISTS

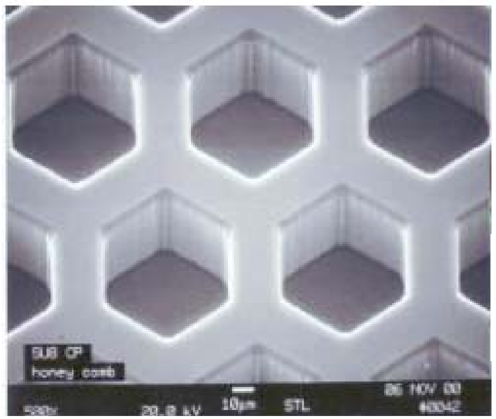
Characteristic	Positive	Negative
Adhesion to Silicon	Fair	Excellent
Relative Cost	More Expensive	Less Expensive
Developer Base	Aqueous	Organic
Minimum Feature	0.5 μm and below	± 2 μm
Step Coverage	Better	Lower
Wet Chemical Resistance	Fair	Excellent
Resin type	Novolac	Epoxy (SU-8)

Madou, Fundamentals of Microfabrication (2002)

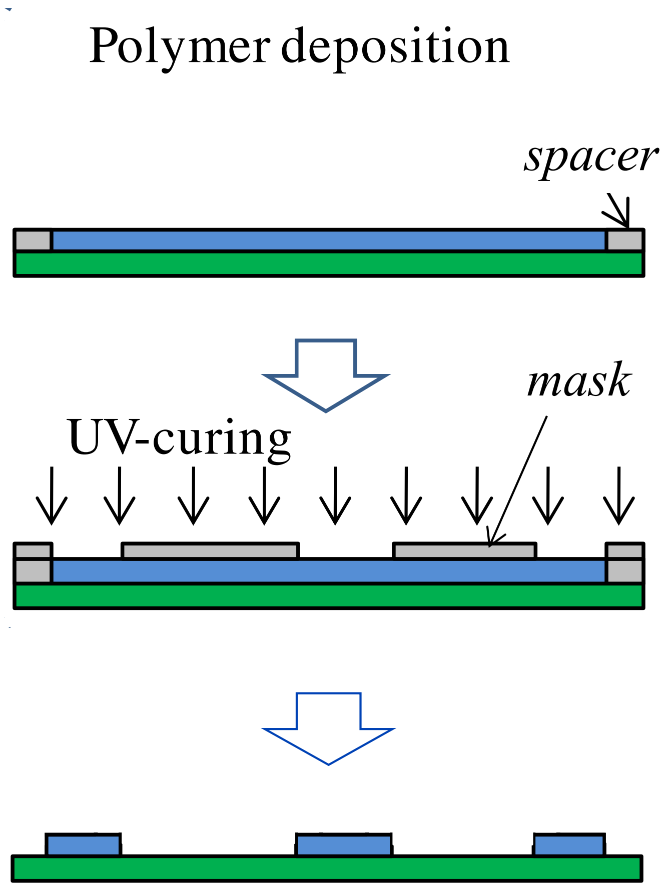
PHOTOLITHOGRAPHY: SU-8

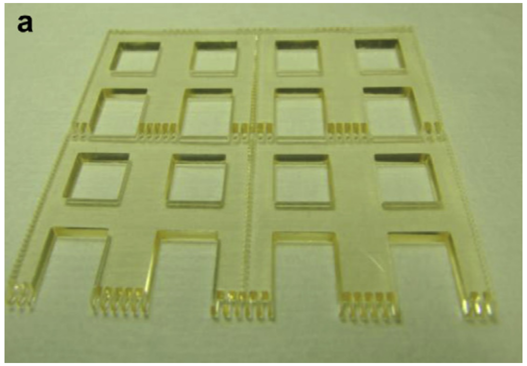
- epoxy-based negative tone photoresist
- Commercially available from Microchem and Gersteltec.
- for thick polymer microstructures with high aspect ratio
- Process flow

  substrate pretreatment ⇒ coating ⇒ soft bake ⇒ expose
  ⇒ post expose bake ⇒ development ⇒ rinse & dry
  ⇒ hard bake (optional)
- Process time: > 30 min. up to several hours.
- High resolution, high aspect ratio (+)
- High internal stress, cracks (-)

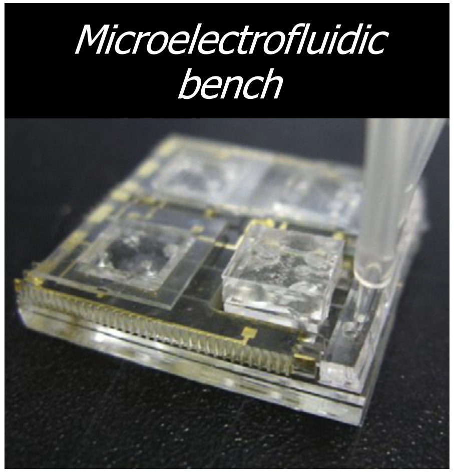


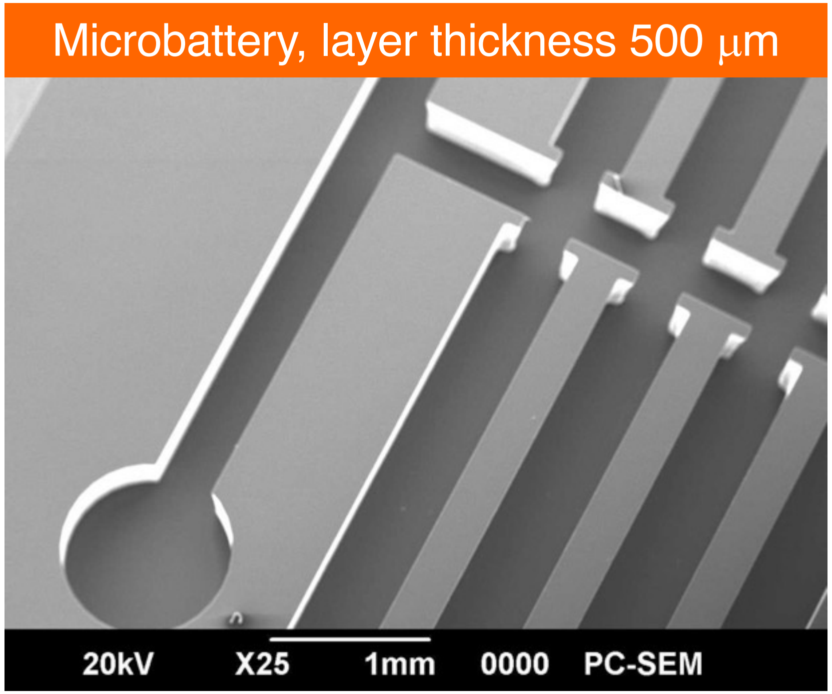
DIRECT PATTERNING





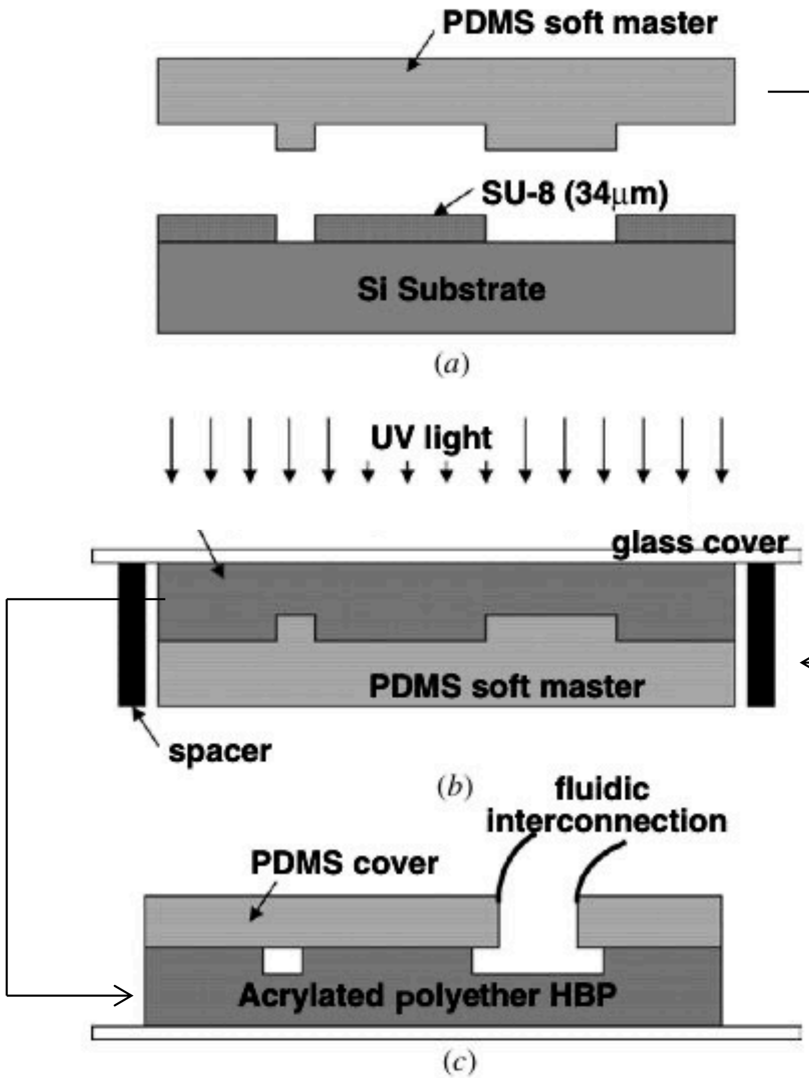
Doh et al., Current Appl Phys (2012)

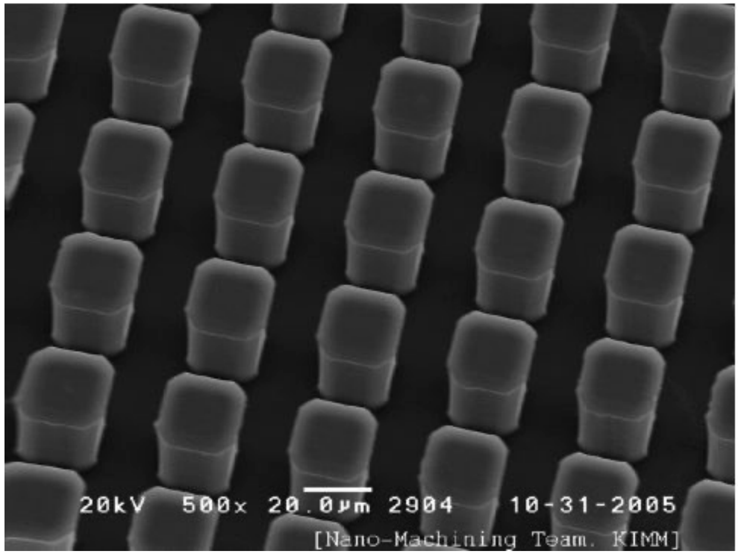


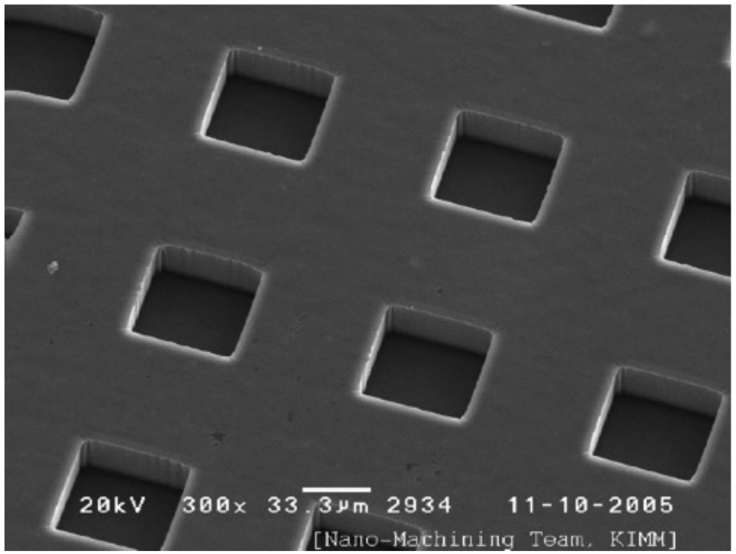


Schmidt, L.-E., J Micromech Microeng 2008

UV-MICROMOLDING





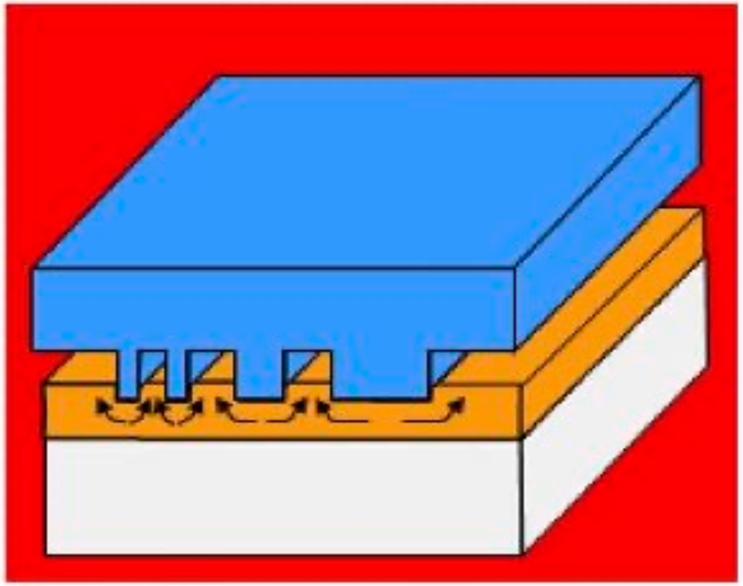


Jin, et al., J Micromech Microeng 2007

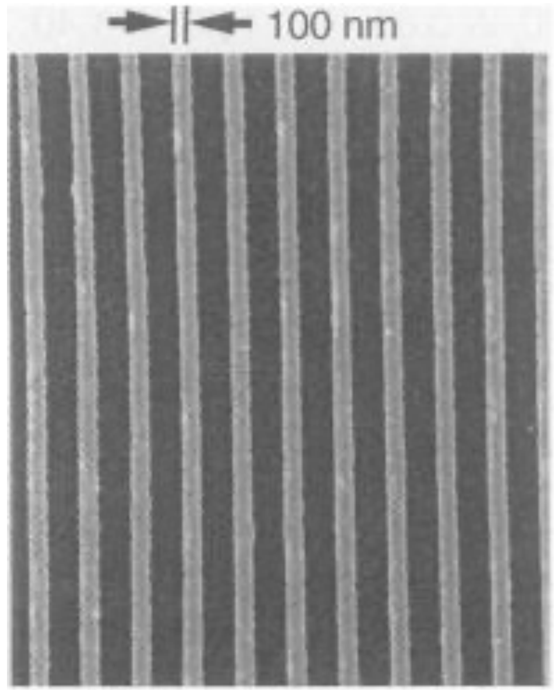
NANO-IMPRINT LITHOGRAPHY (NIL)

Thermal nanoimprint lithography (NIL, T-NIL)
–
also called

Hot embossing lithography (HEL)



Process: Compression of thin thermoplastic film between hard stamp and substrate and molding by squeeze flow



Chou et al., Science (1996)

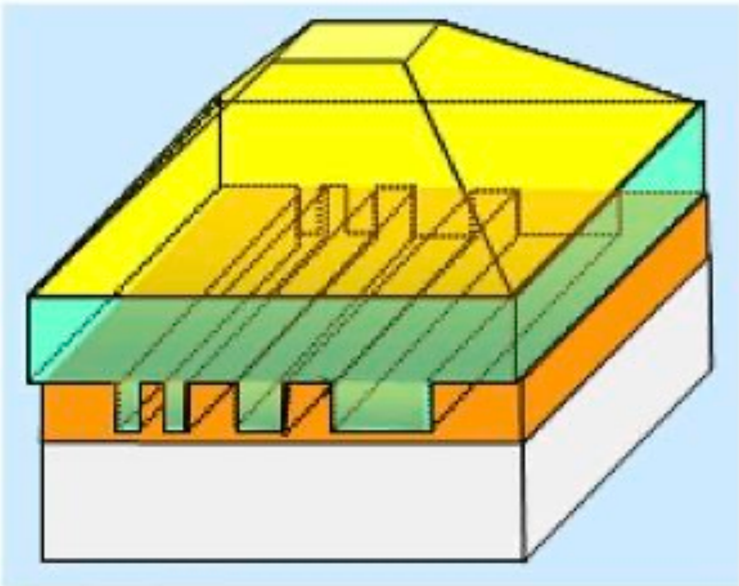
H. Schift, J. Vac. Sci. Technol. B (2008)

NANO-IMPRINT LITHOGRAPHY (NIL)

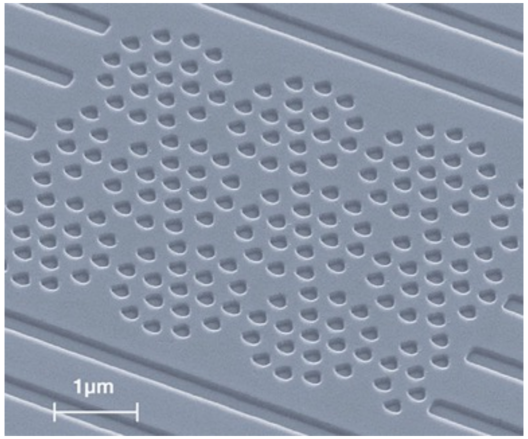
UV-nanoimprint lithography (UV-NIL)

(a) Hard stamp lithography

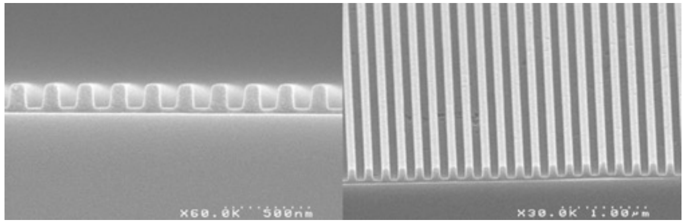
(b) Soft (stamp) lithography (SL)



Process: Low pressure filling of liquid resin at room temperature by capillary action and hardening by UV-exposure through the stamp; coating by dispensing or spin coating of precursor



Suss.com



LTM-CNRS

H. Schift, J. Vac. Sci. Technol. B (2008)

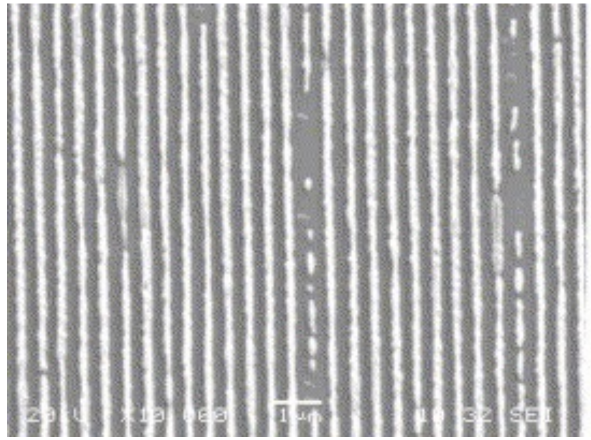
DEMOLDING AND CLOGGING!

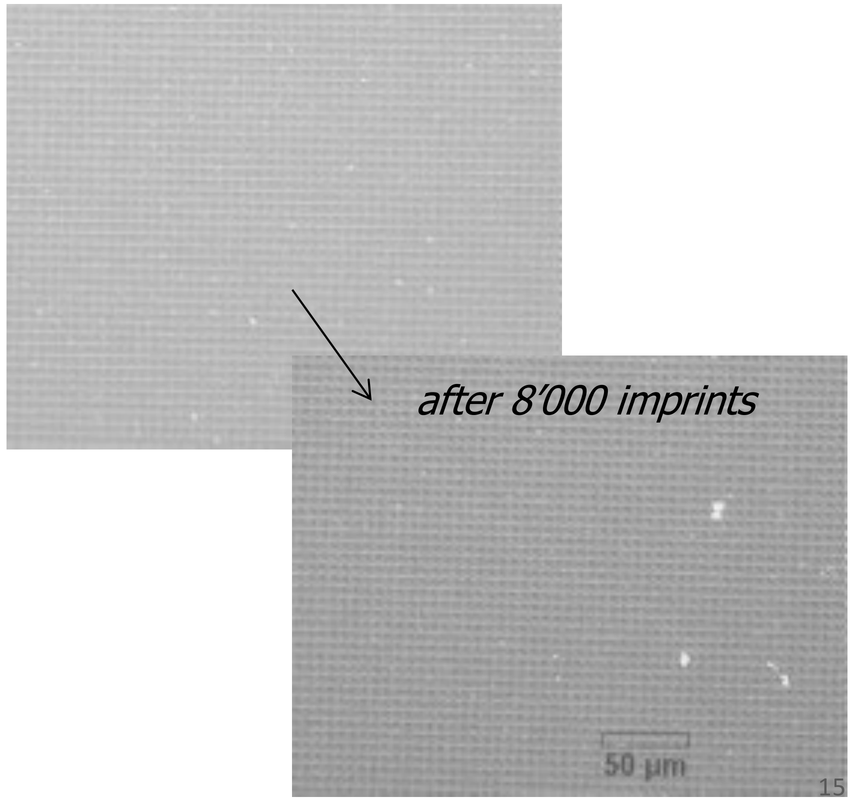
Problems:

- adhesion at the surface
- friction due to surface roughness
- shrinkage - stress
- trapping of the polymer in concave geometry

Solutions:

- mold surface treatment (e.g. fluorinated silanes)
- mold design (clearance angle)
- sacrificial layers (SiO_2 …)
- mold (solvent) cleaning
- mold filling simulation (viscoelasticity and stress effects)





Merino et al., Microelectronic Eng (2007)
Eriksson et al., Microelectronic Eng (2011)

Nanostructured devices

- Technologies
- Process methods

Application examples

- optical biosensors


Valérie Geiser

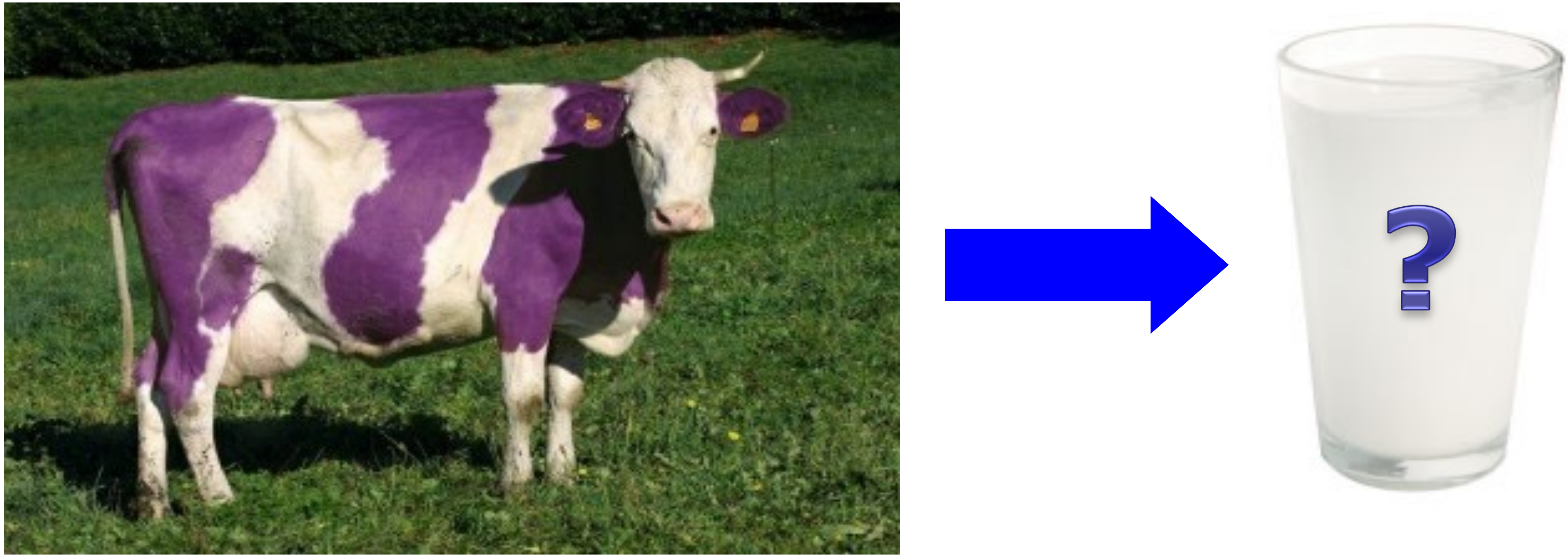
- bioinspired surfaces


Marina Gonzalez Lazo


Lionel Wasser


Luca Mueller


Feyza Karasu



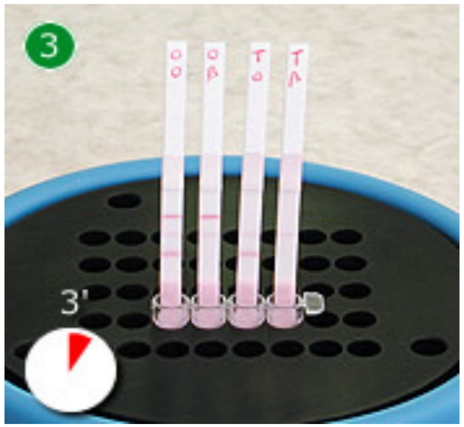
MOTIVATION – FOOD SAFETY

Conventional techniques

- high-screening ☺
- quantitative analysis ☺
- semi-automatic 😐
- skilled user ☹
- lab. environment ☹
- expensive ☹

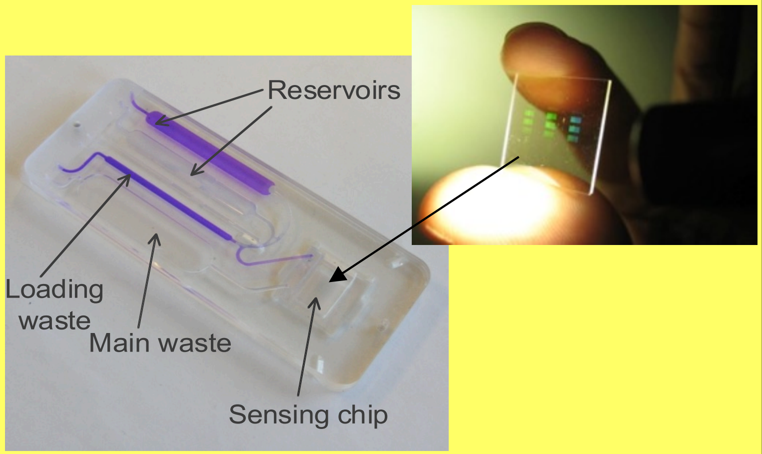
Strip tests

- cheap ☺
- fast ☺
- field environment ☺
- quite easy to use 😐
- max 2 antibiotic families ☹



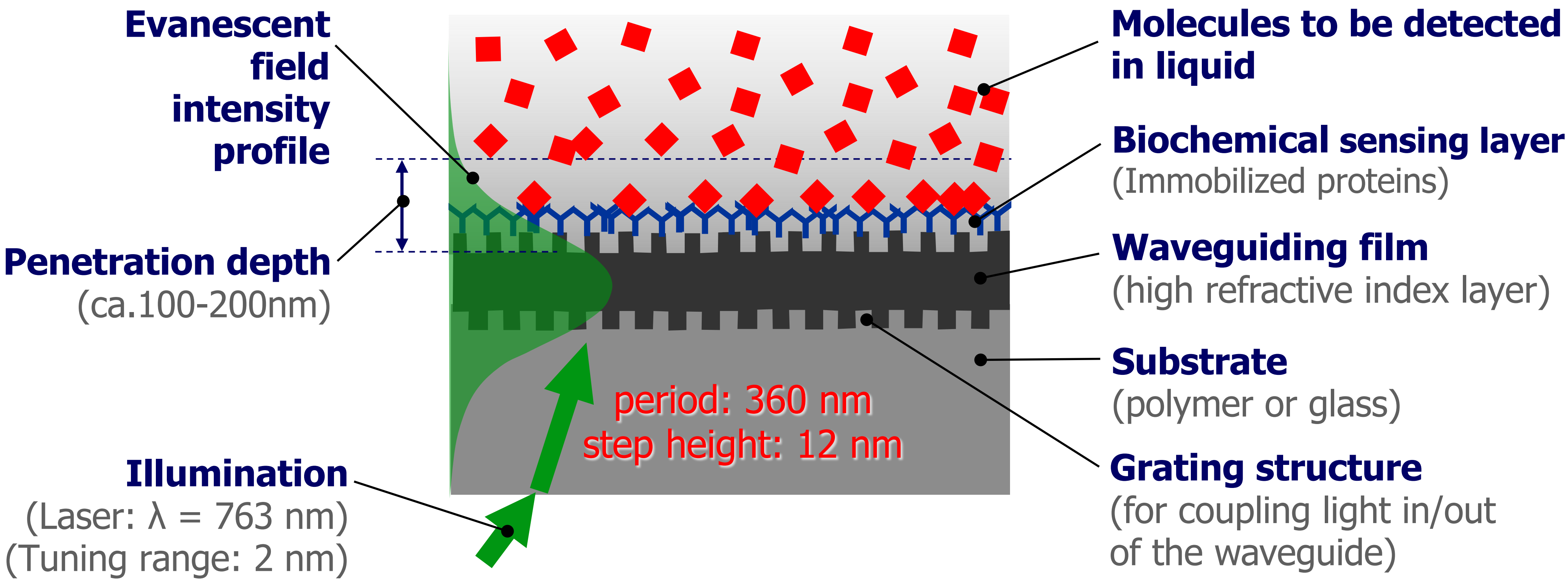
Lab-on-a-chip

- **semi-quantitative ☺**
- **easy to use ☺**
- **cheap ☺**
- **fast ☺**
- **fully-automated ☺**
- **field environment 😐**



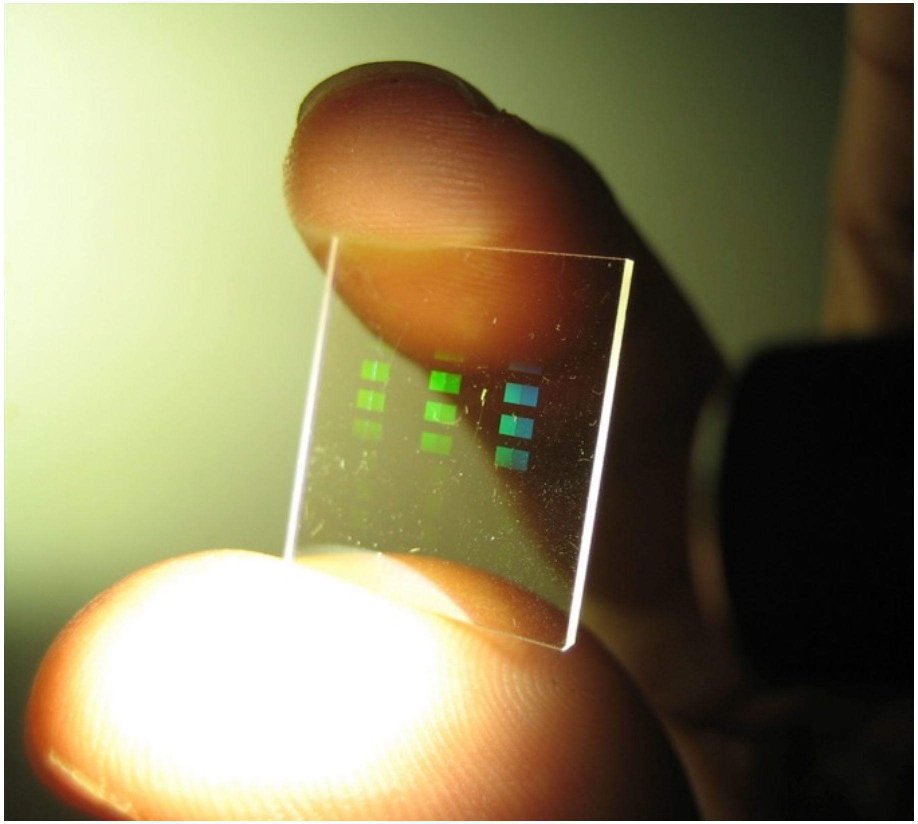
WAVELENGTH INTERROGATED OPTICAL SENSOR

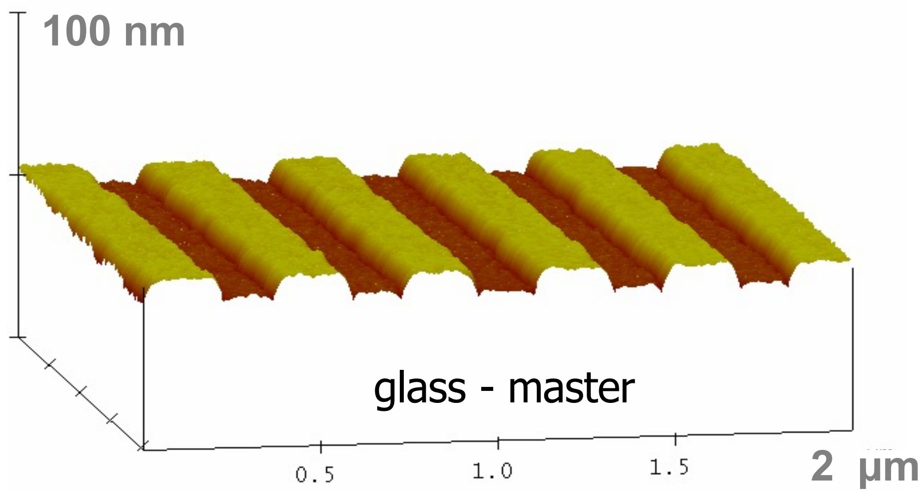
Evanescence field is highly sensitive to changes in refractive index.
Device sensitivity: pg/mm²



Cottier, Sensor Actuat A **2003,** 91 (1), 241

WAVELENGTH INTERROGATED OPTICAL SENSOR



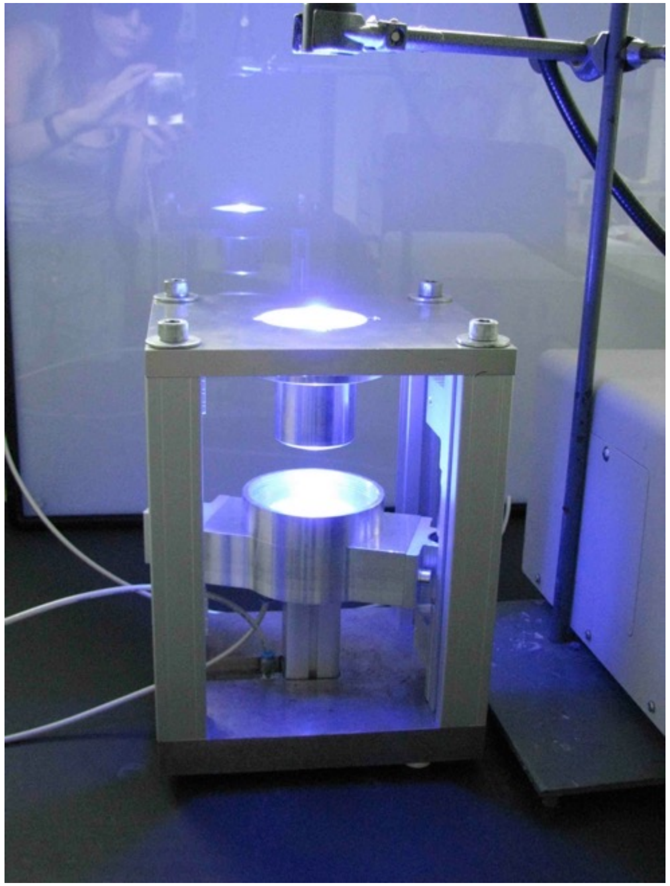


DYNETIX BIOSYSTEMS

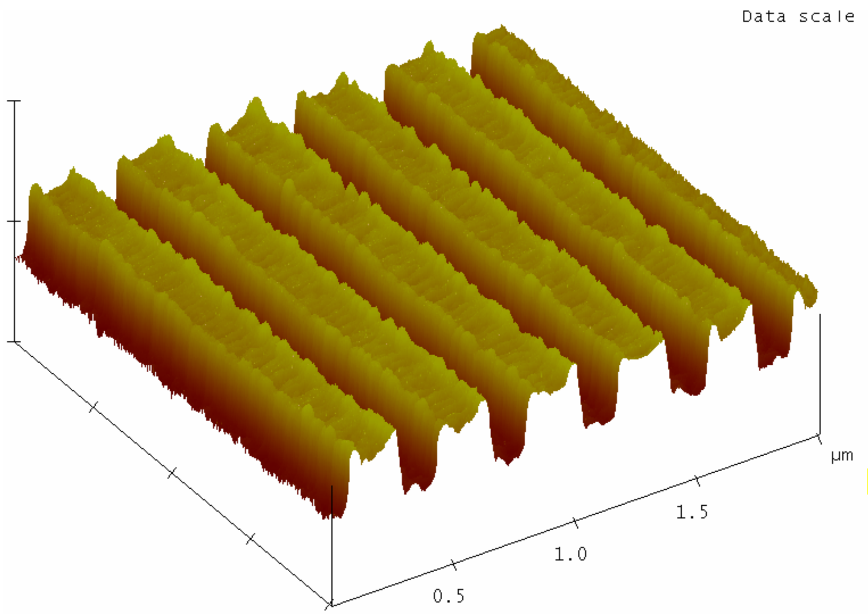
csem centre suisse d'électronique et de microtechnique

Cottier, Sensor Actuat A **2003,** 91 (1), 241

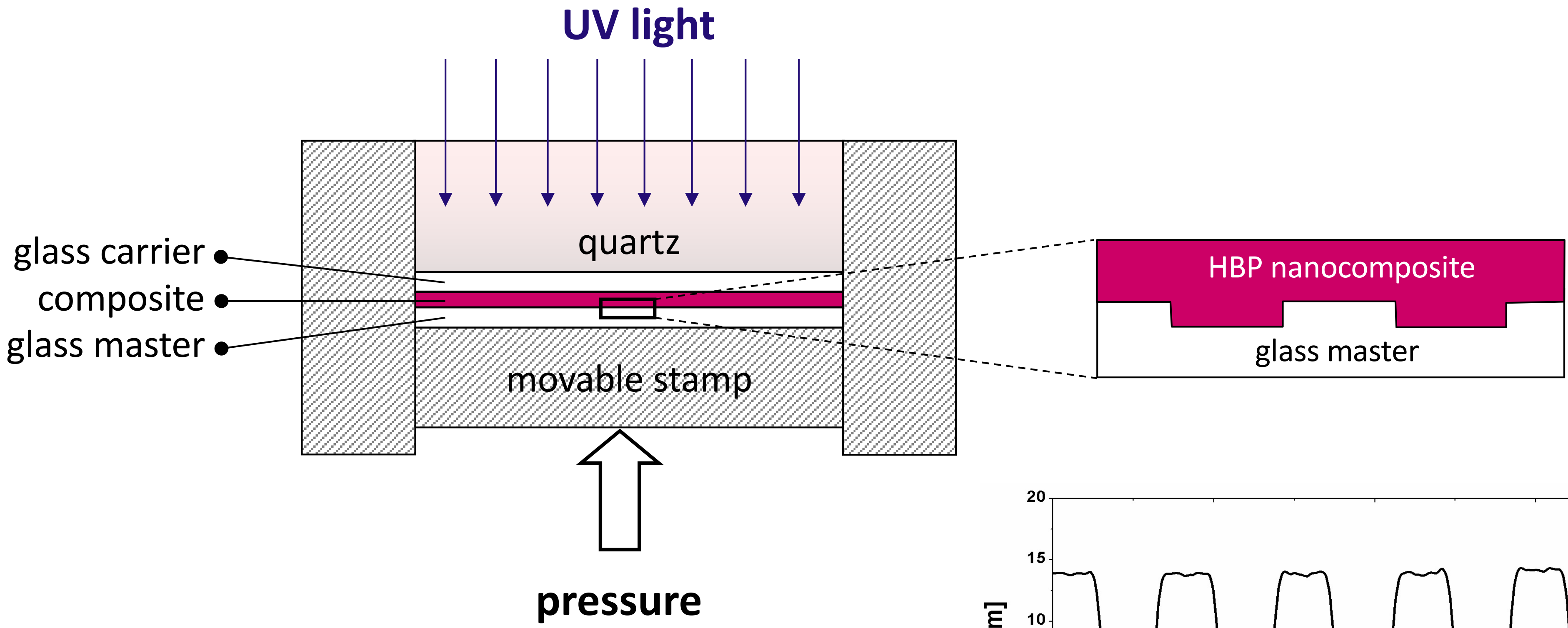
UV-NANOIMPRINT LITHOGRAPHY (UVNIL)

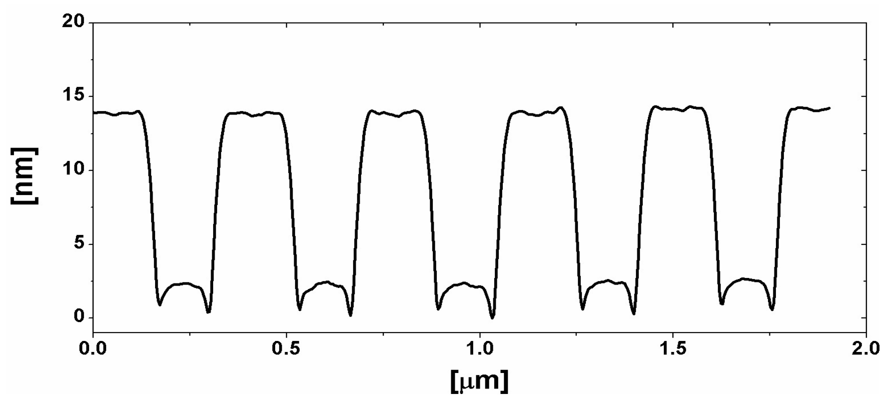


Polymer nanogratings for optical waveguide devices



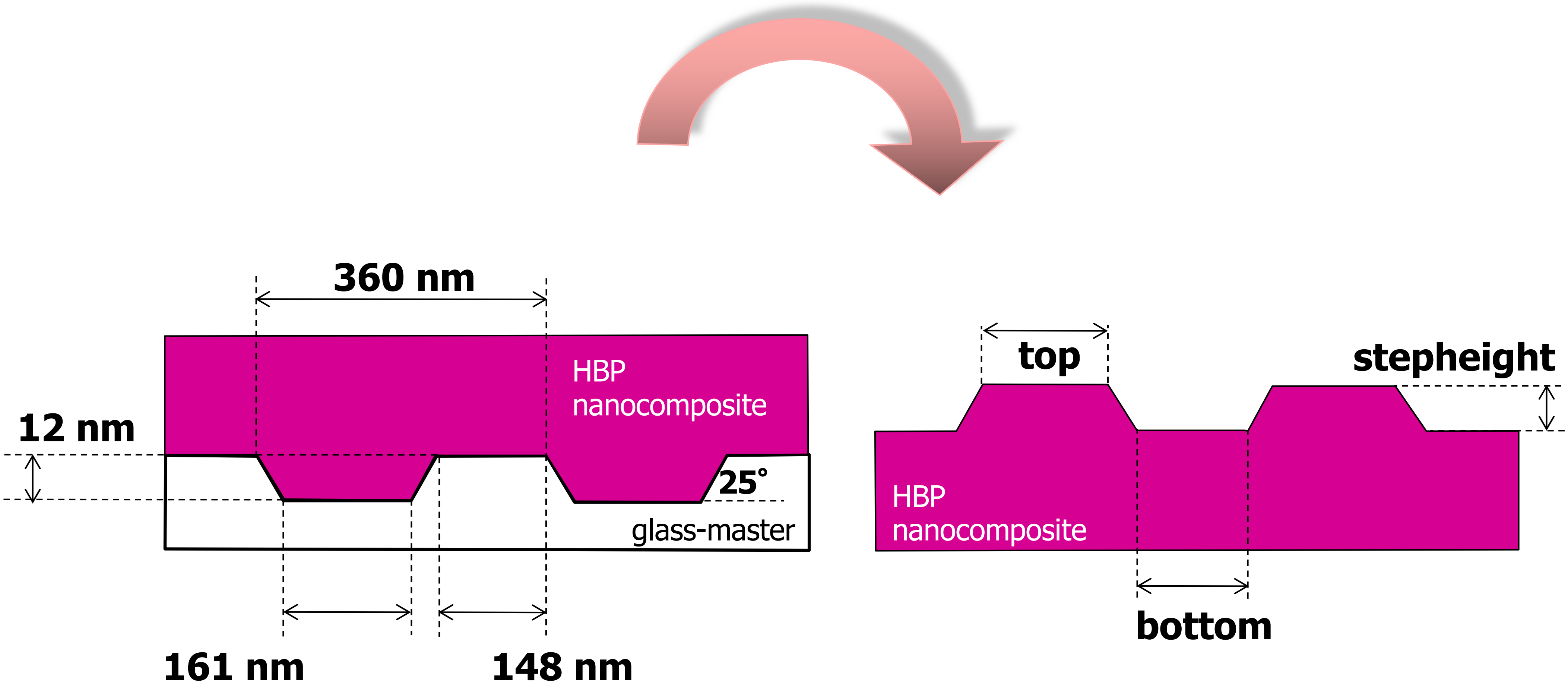
UVNIL SET-UP



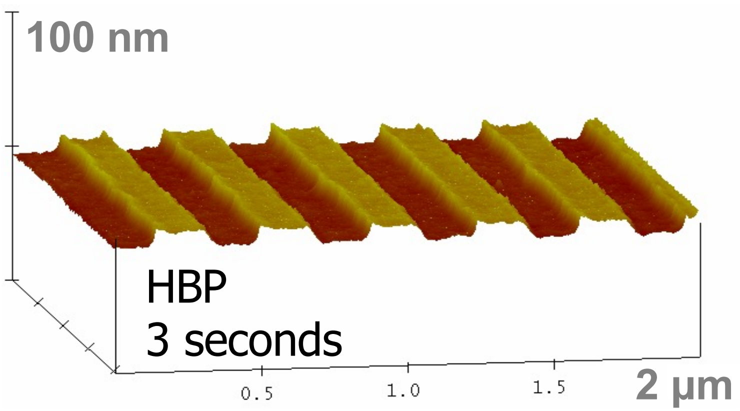


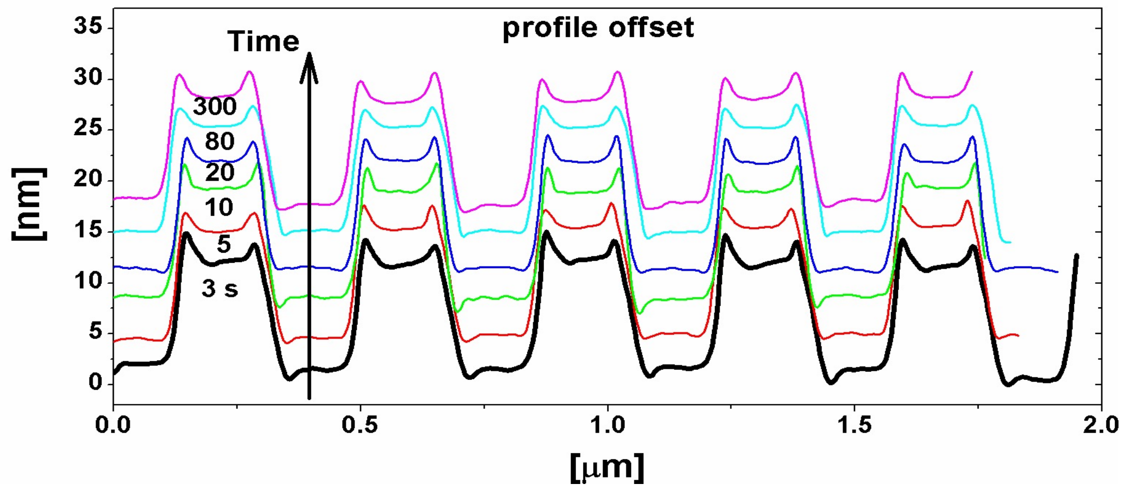
Chou et al., Appl Phys Lett (1995)
Geiser et al., Macromol Sympos (2010)

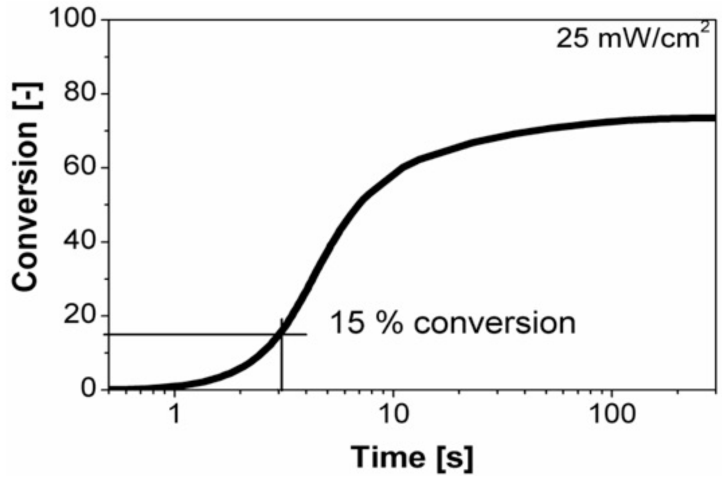
GRATING DIMENSIONS

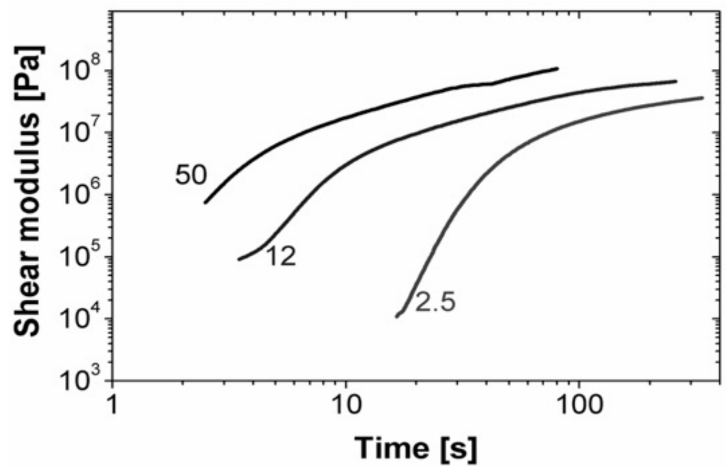


INFLUENCE OF ILLUMINATION TIME



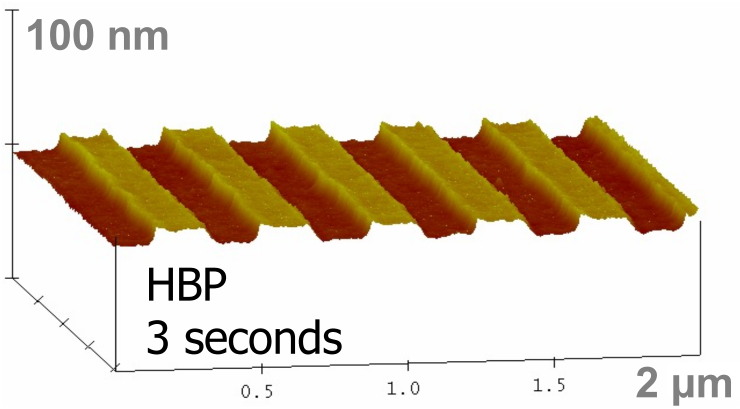


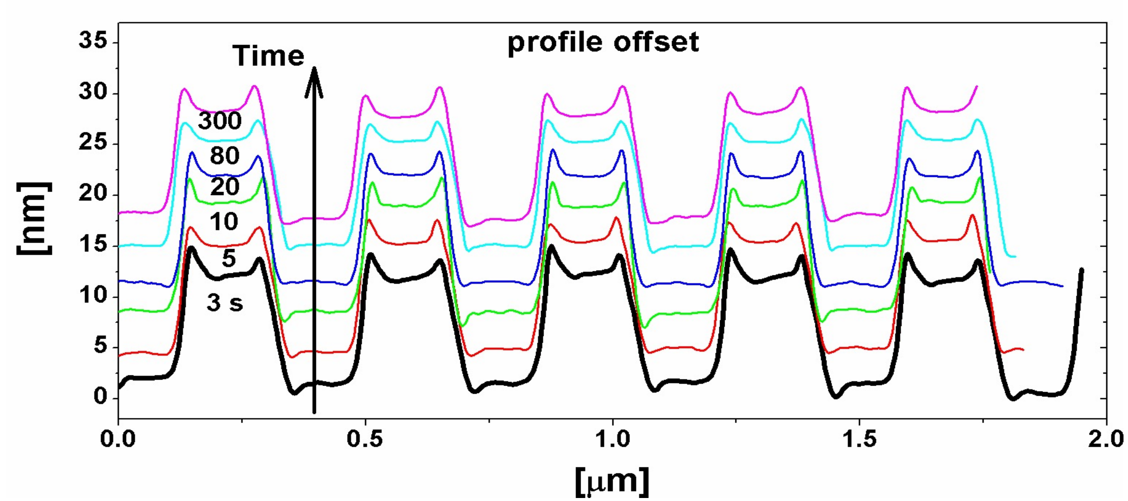


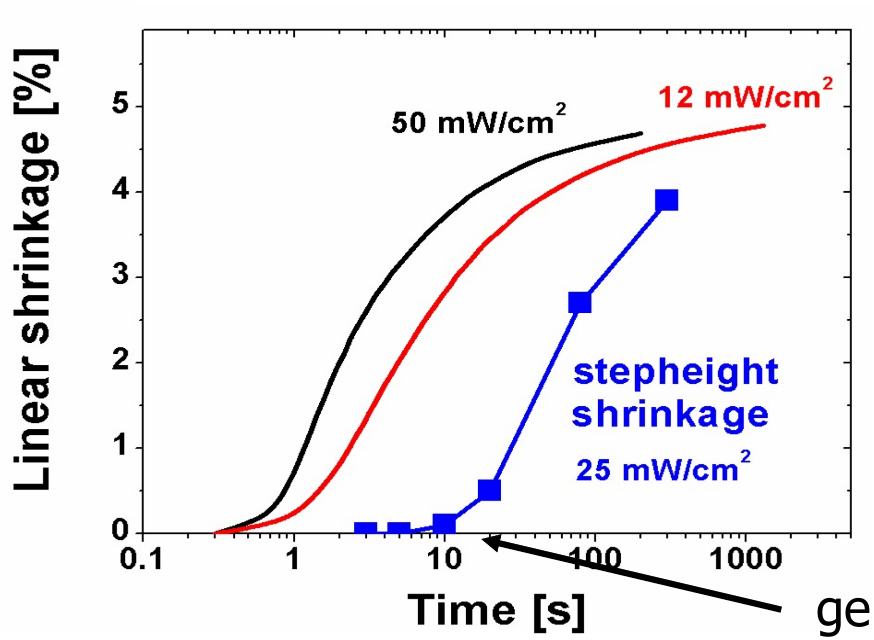


after 3 seconds:
15 % conversion
1 MPa shear modulus

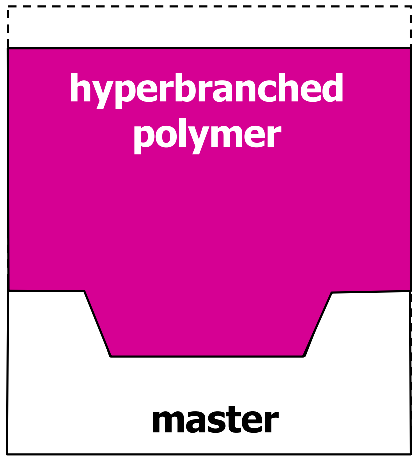
INFLUENCE OF ILLUMINATION TIME



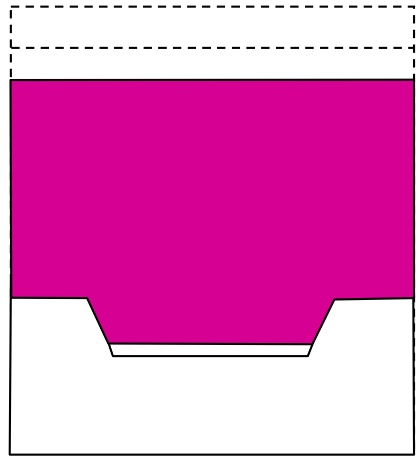




gelation

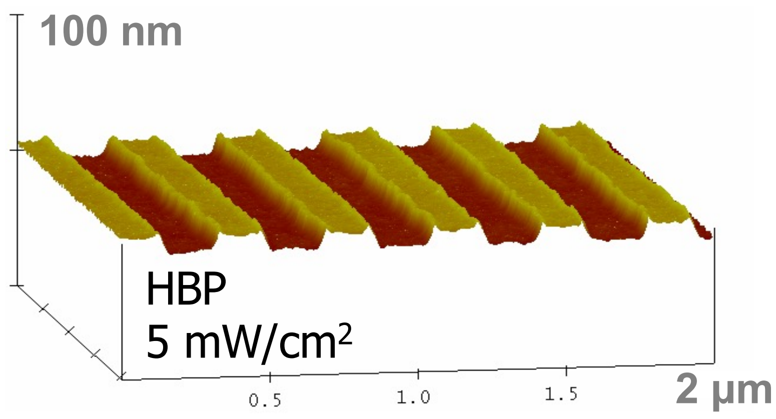


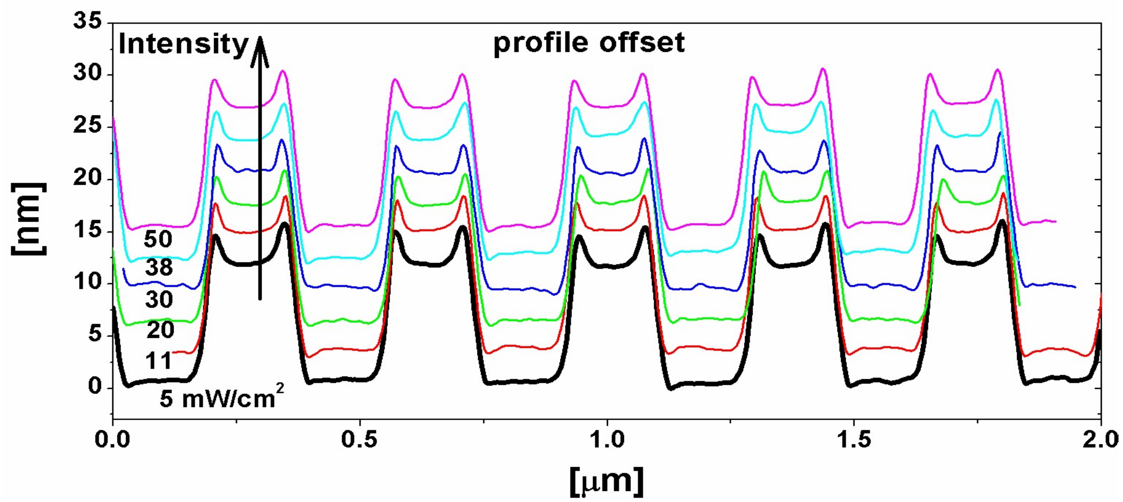
before
gelation

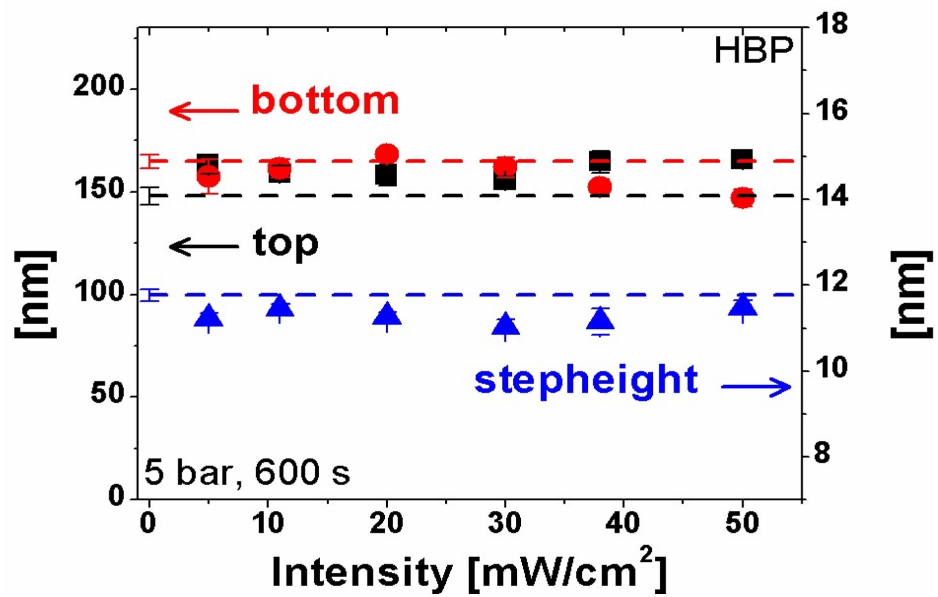


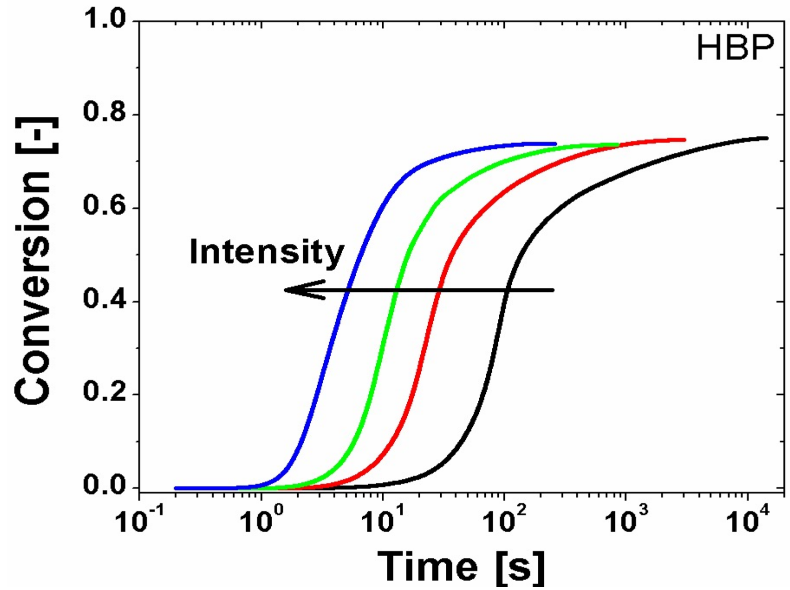
after
gelation

INFLUENCE OF UV-LIGHT INTENSITY



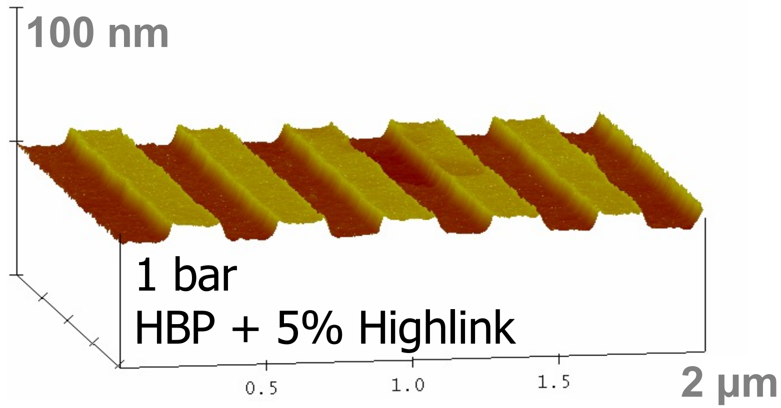


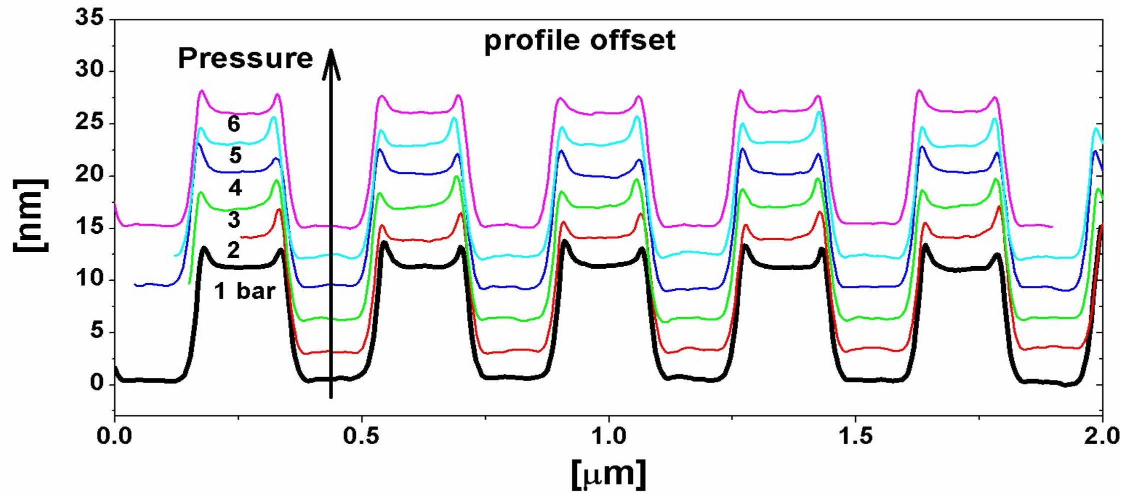


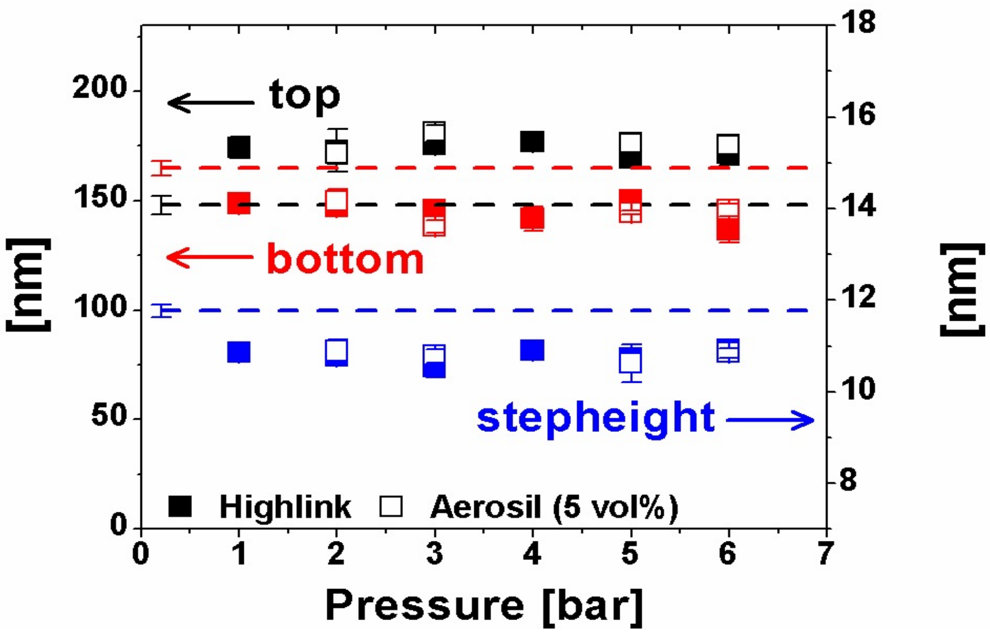


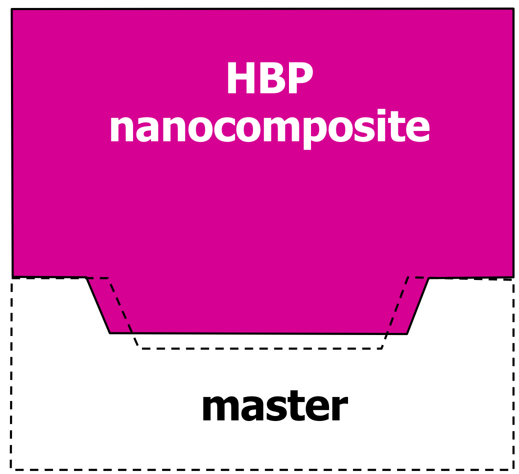
Dalle Vacche et al., Polymer (2010)

INFLUENCE OF PRESSURE

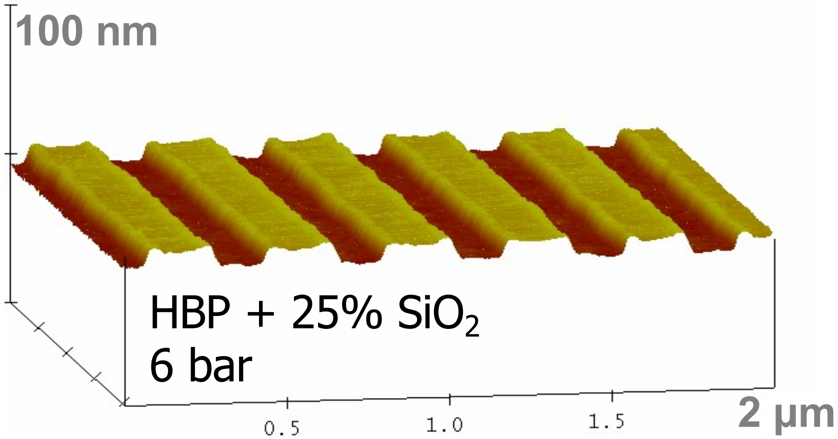


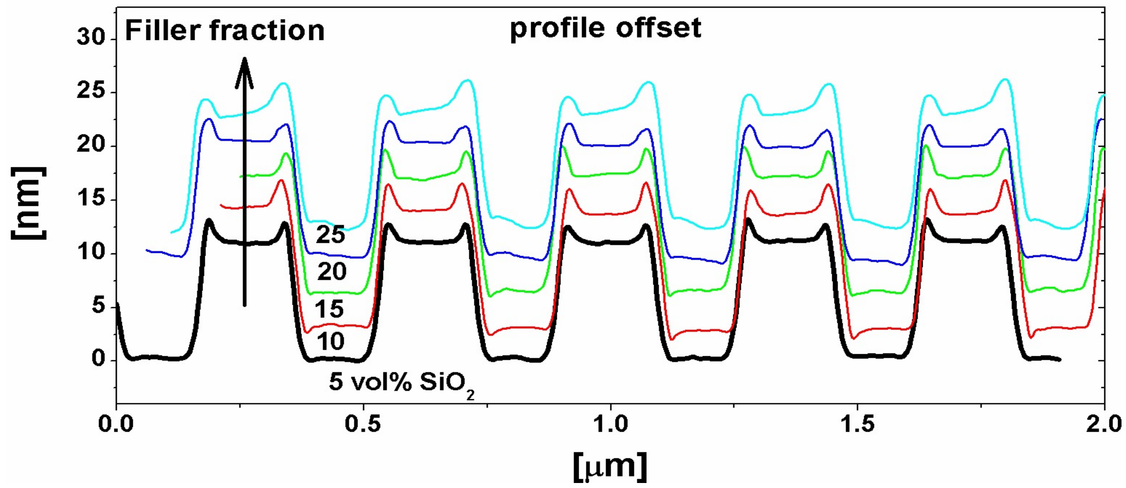


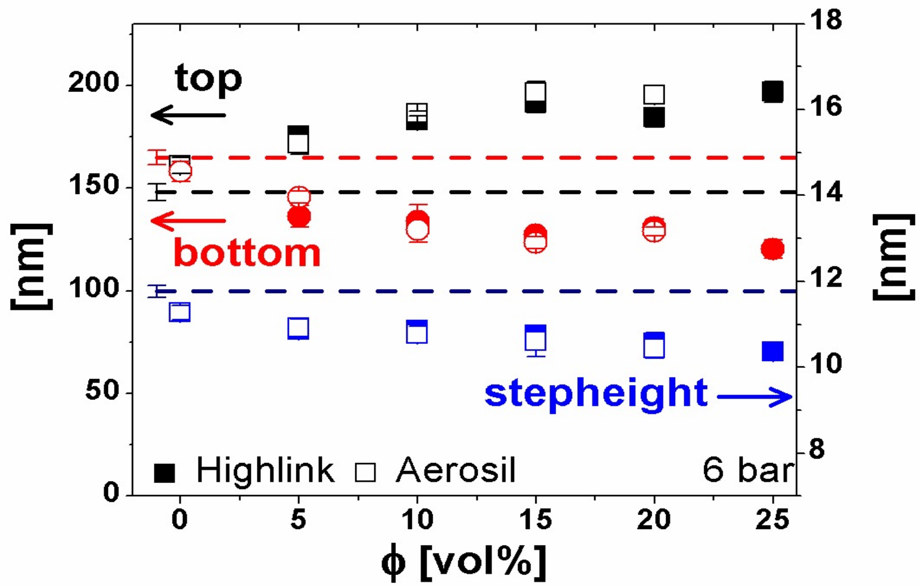


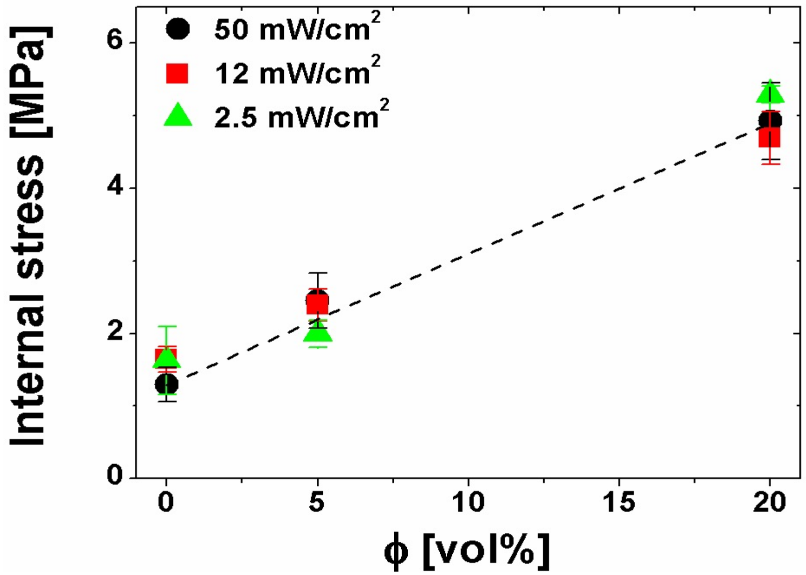


INFLUENCE OF NANOPARTICLES

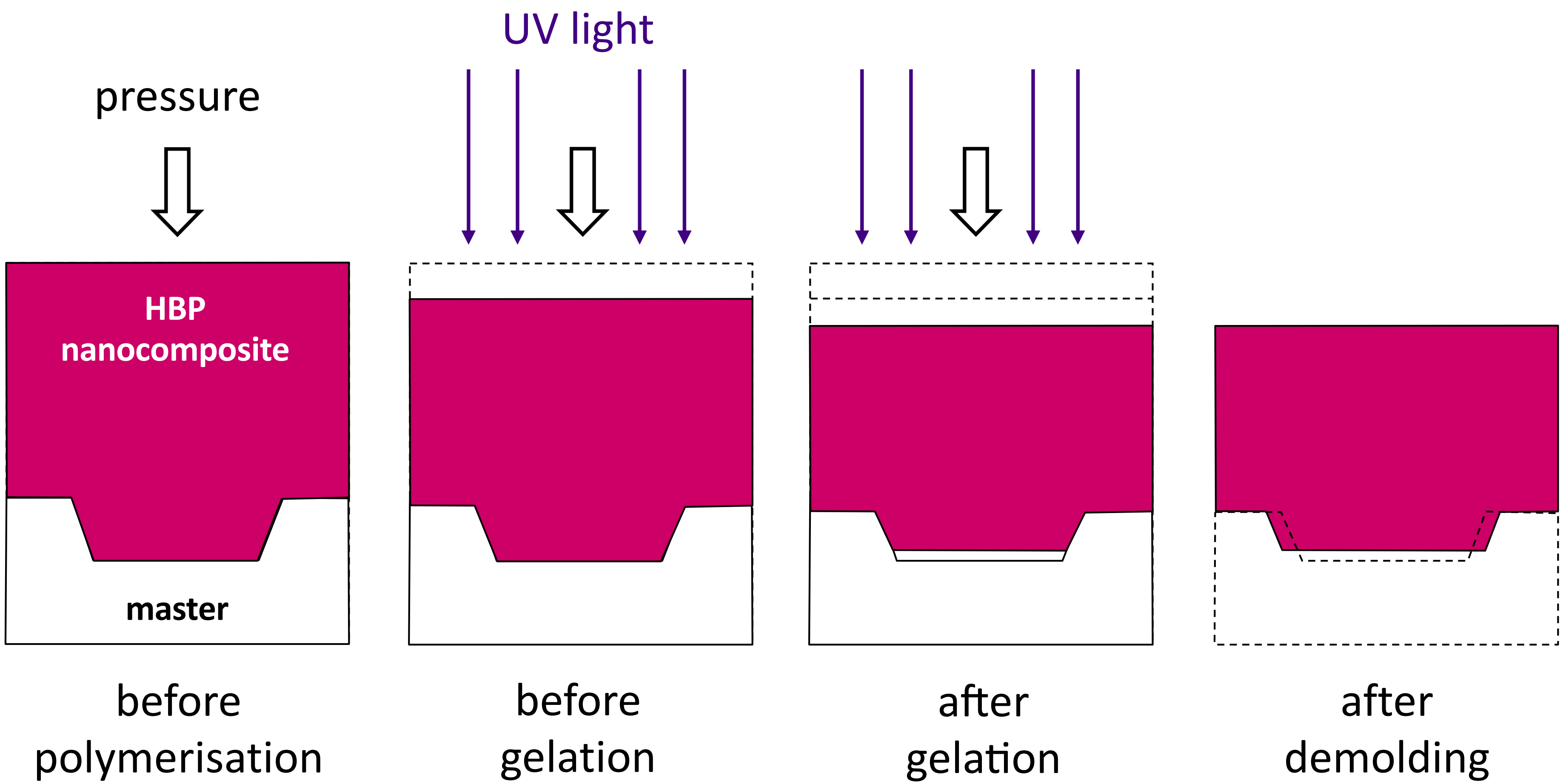






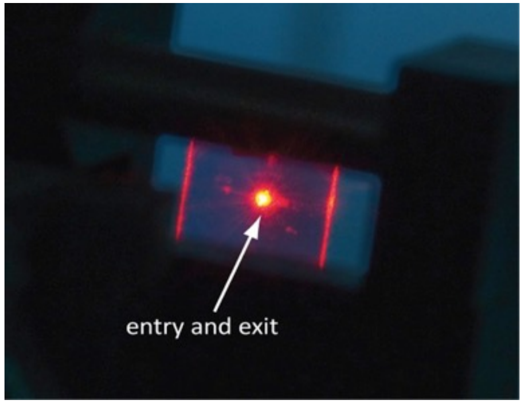


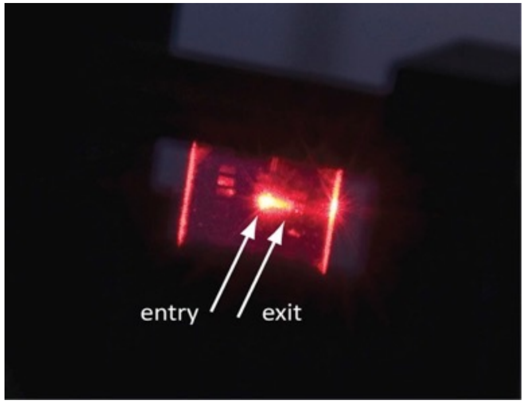
UVNIL SUMMARY

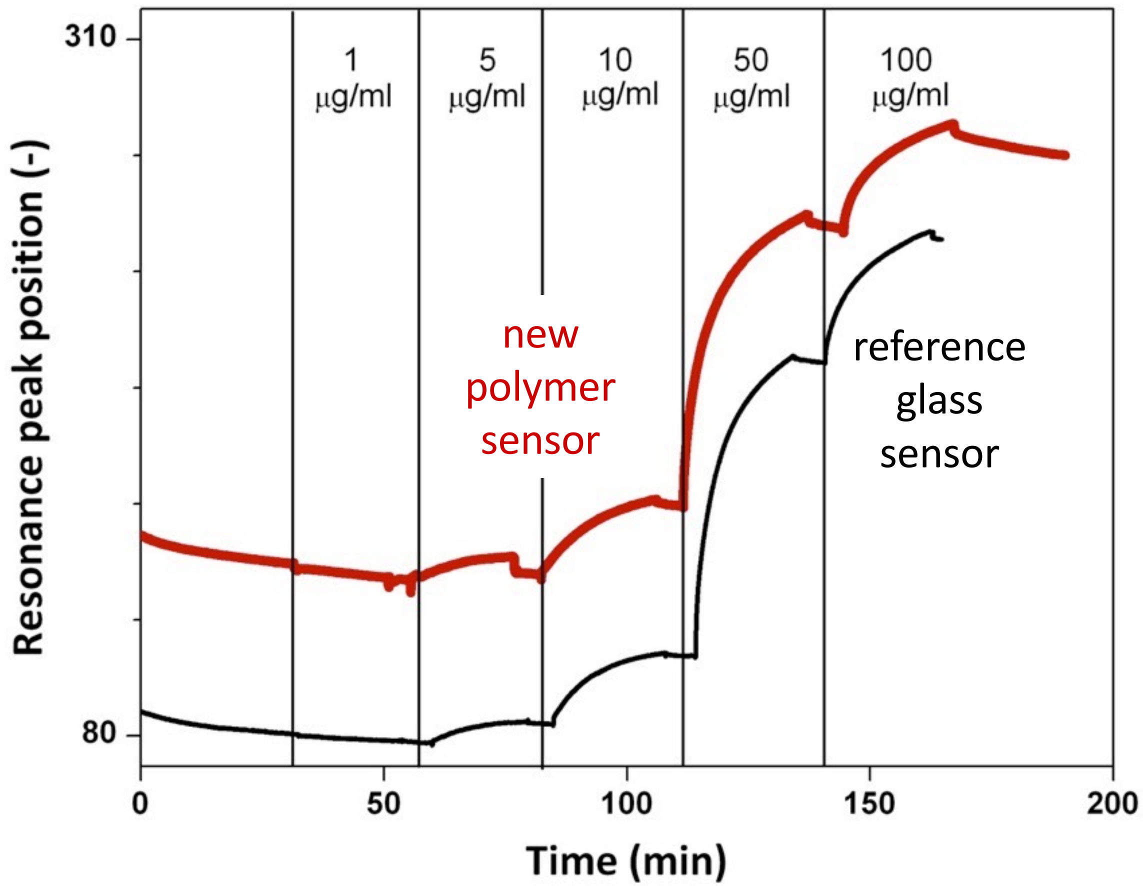


Geiser et al, MRS spring meeting 2010, Macromol Sympos (2010)

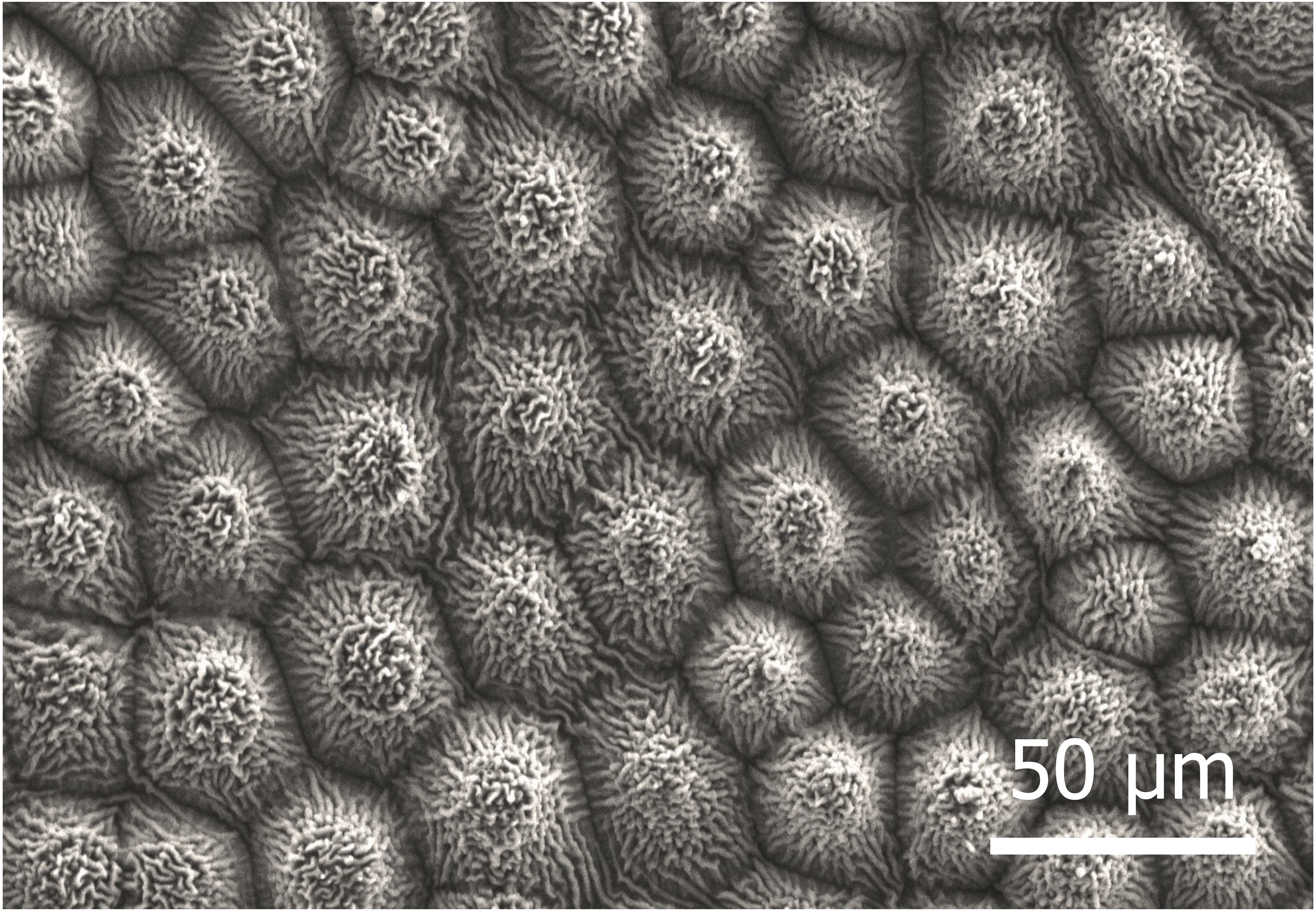
WAVELENGTH-INTERROGATED OPTICAL SENSOR WIOS



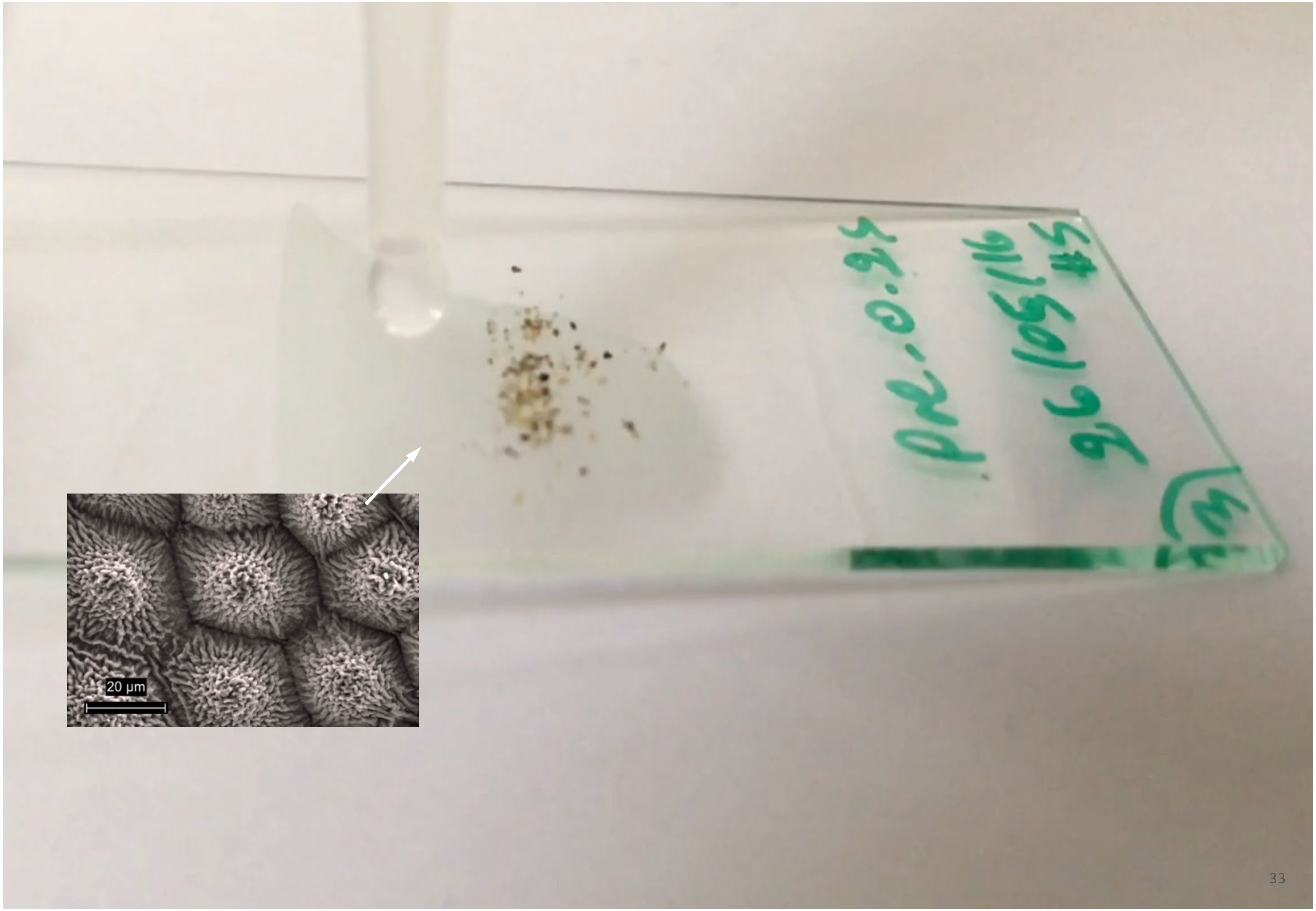




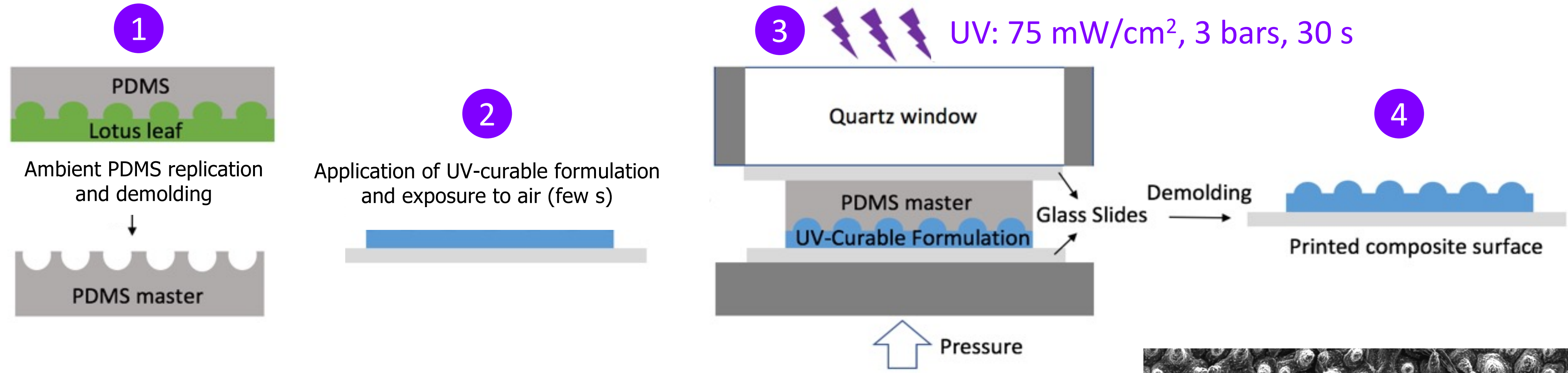
Suarez et al., Lab-on-a-chip (2009)
Geiser et al, Macromol Sympos (2010)


50 µm

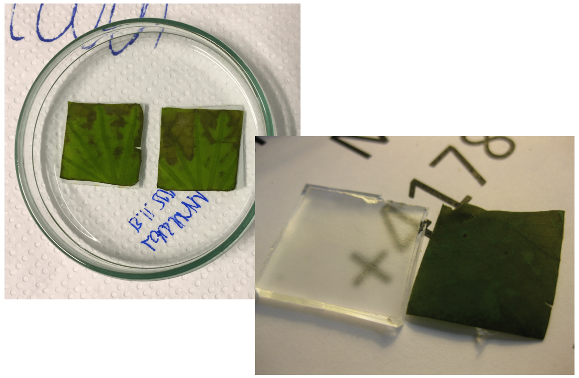
http://www.webmultiple.net/roses-originales.html

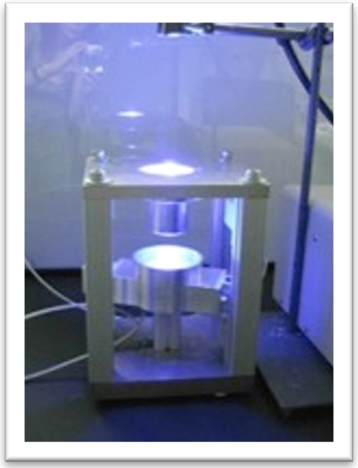

20 µm

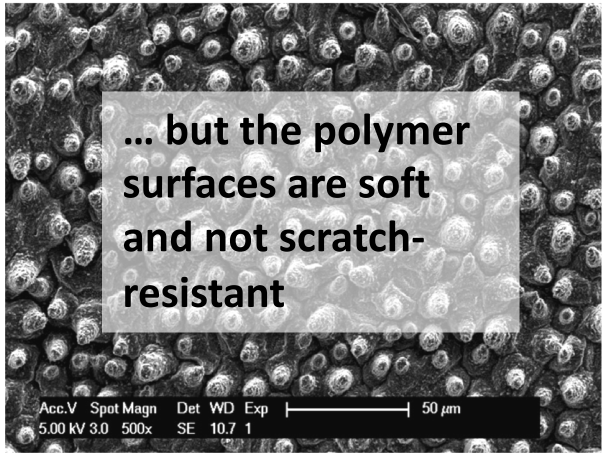
UV nanoimprint lithography process steps



Lausanne botanical garden

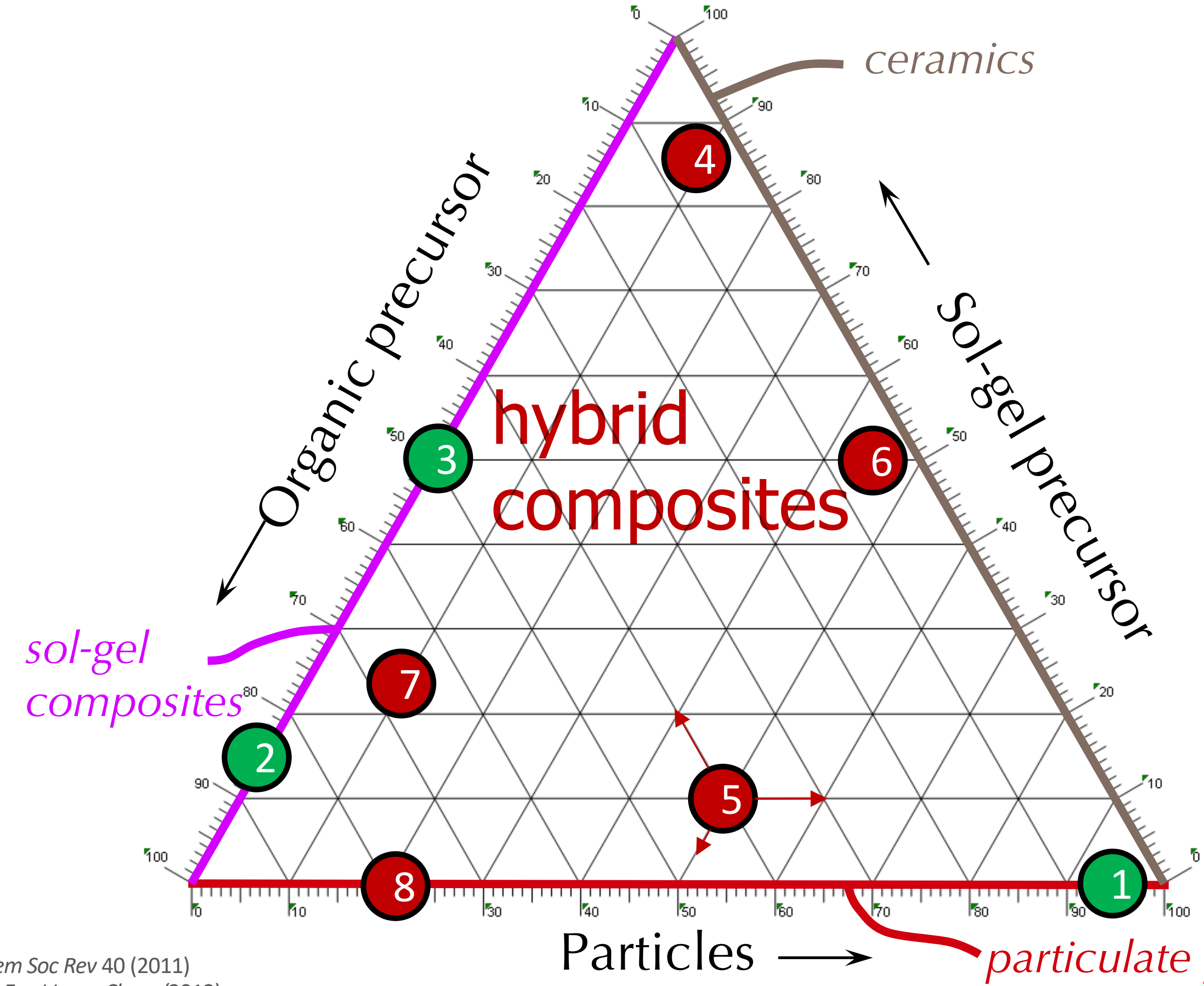






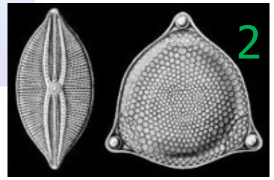
Wasser, Leterrier, et al., Coatings, 8, 436 (2018)

Integrative dual-cure synthesis of hybrid composites

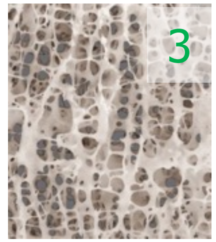


1) Nacre

2) Diatom



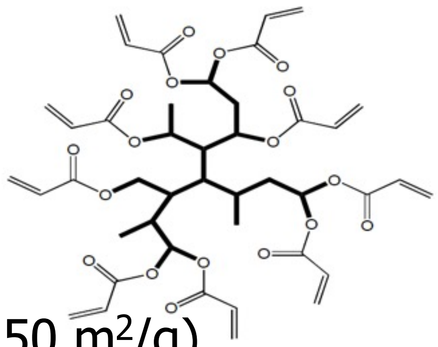
3) Bone



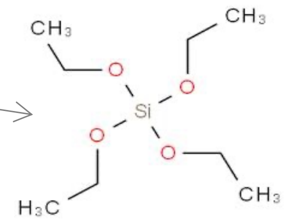
4) Ophthalmic lenses *(multilayer hybrid coatings)*
5) Dental restoration *(silica nanocomposites)*
6) Cancer treatment *(core-shell nanoparticles)*
7) Solar cells (*diffusion barrier layers*)
8) Tires *(clay and silica nanocomposites)*

Sanchez et al., *Chem Soc Rev* 40 (2011)
Drisko & Sanchez, *Eur J Inorg Chem* (2012)
Geiser, Leterrier, Månson, Macromol. Mater. Eng., 297, 155-166 (2012)

INTEGRATIVE SYNTHESIS OF HYBRID COMPOSITES



- Organic precursor: Acrylated polyester HBP (low shrinkage)
  Schmidt et al., J Micromech Microeng 18 (2008), Geiser et al., J Appl Polym Sci 114 (2009)
  Geiser et al., Macromol Sympos 296 (2010), Macromol Mater Eng 297 (2012)
- Photoinitiator: Diphenyl-(2,3,4-trimethylbenzoyl)-phosphine oxide
- SiO_2 nanoparticles: Methacrylated fused silica (12 nm, aggregates, 150 m^2/g)
- Organometal precursor: tetraethylortho-silicate (TEOS)
- Coupling agent: methacryloxypropyl-trimethoxysilane (MEMO)

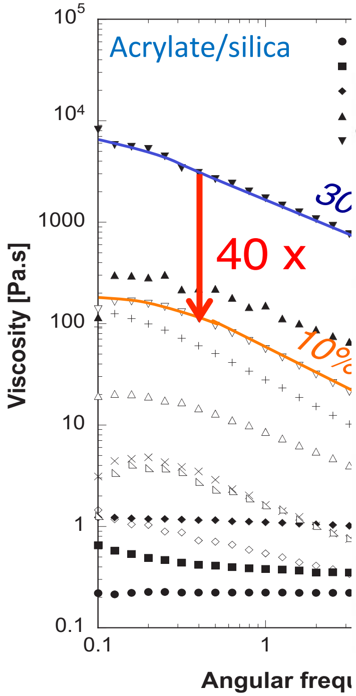


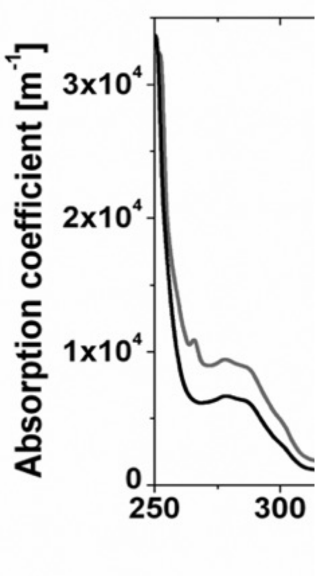
1. Sonication of silica nanoparticles + isopropanol
2. Mixing of nanoparticles/isopropanol with HBP (1 hour at 25° C)
3. Evaporation of isopropanol at 70° C
4. Addition of MEMO (mixing 10 min at 25° C)
5. Addition of TEOS (mixing 10 min at 25° C)
6. Addition of HCl 1M (mixing 10 min at 25° C)
7. Stirring at 25° C for 30 min
8. Dual-cure: condensation (1h; 4h) + photopolymerization (3 min before, after, or during condensation)

timing of the dual-cure process!

Why hybrid composites

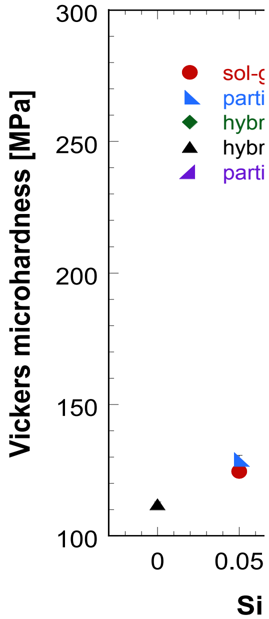
Low viscosity



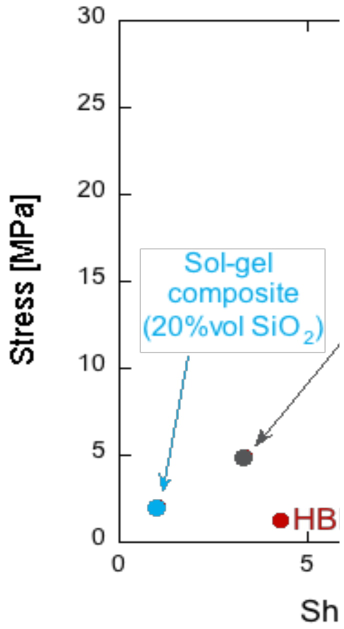


Transparency

Hardness



Shrinkage and Stress

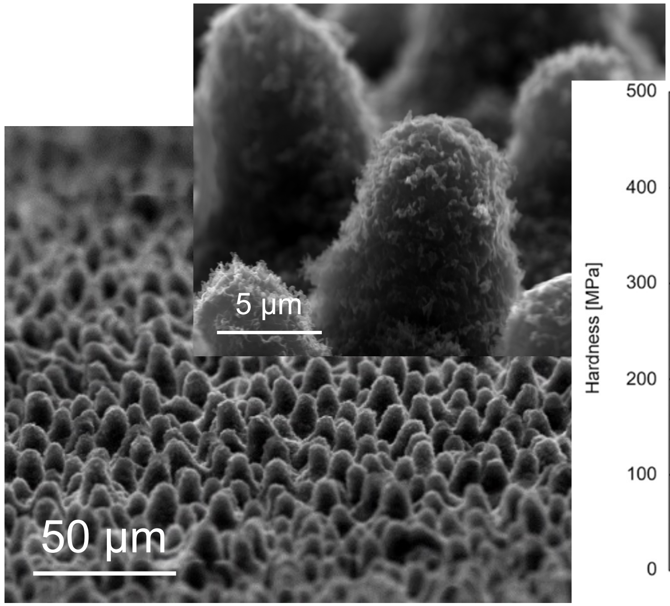


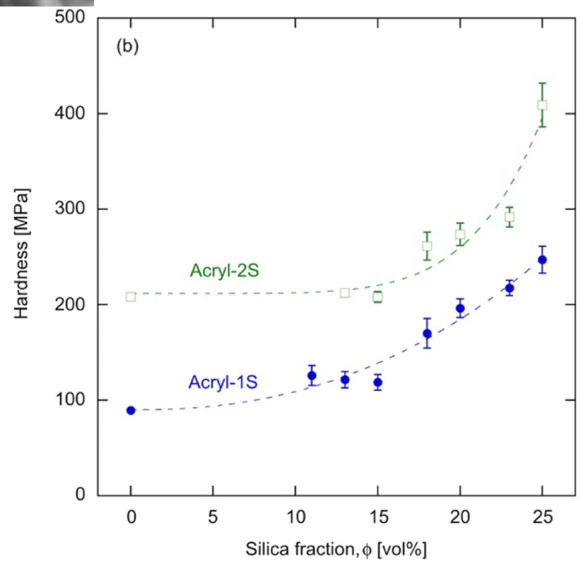
Cost effective R2R processing

Geiser, Leterrier et al., Macromol. Sympos. 296, 144 (2010)
Gonzalez Lazo, Leterrier et al., Polymer 54, 6177 (2013)

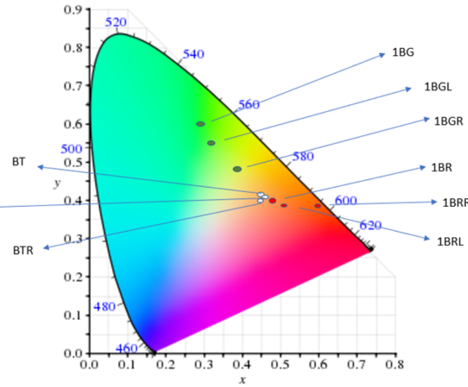
Scratch resistant and colored self-cleaning surfaces

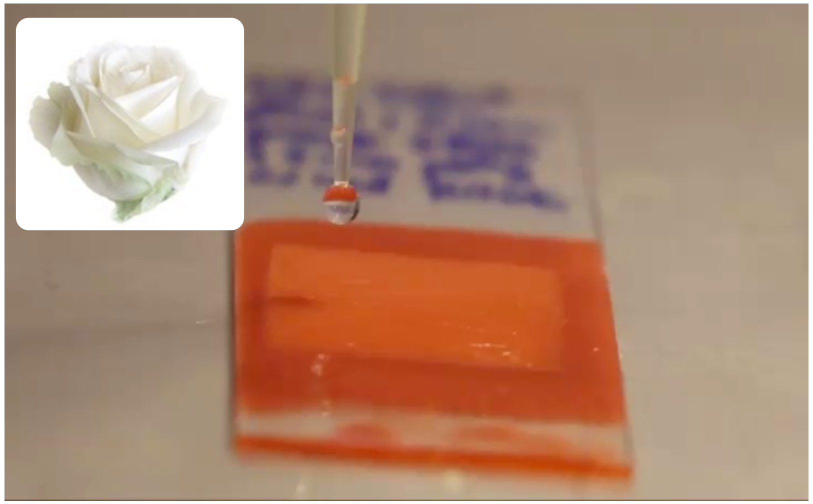
Scratch resistant: no change in WCA > 150° of hybrid composite lotus surface after 7000 sand abrasion cycles (ASTM F735–17)





Synthetic, vermillion-colored, superhydrophobic white rose petal surface



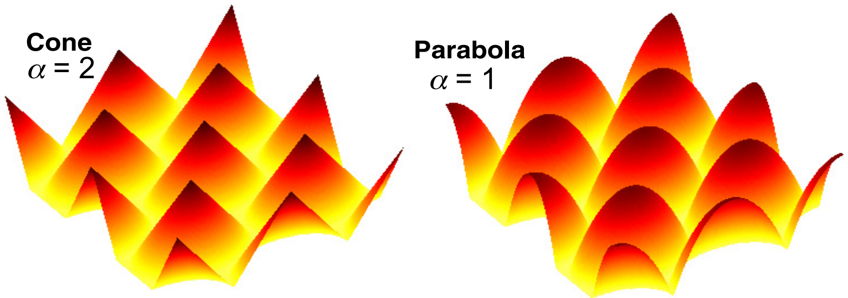


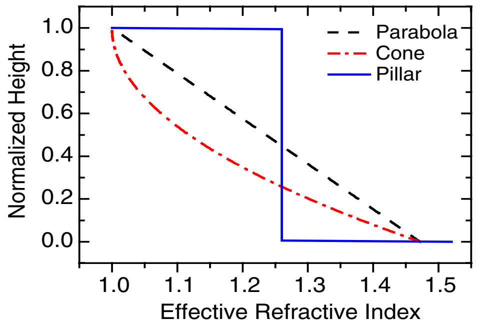

Acc.V Spot Magn Det WD 1 µm
10.0 kV 3.0 20000x SE 10.3
Reflectivity
< 1%
8%

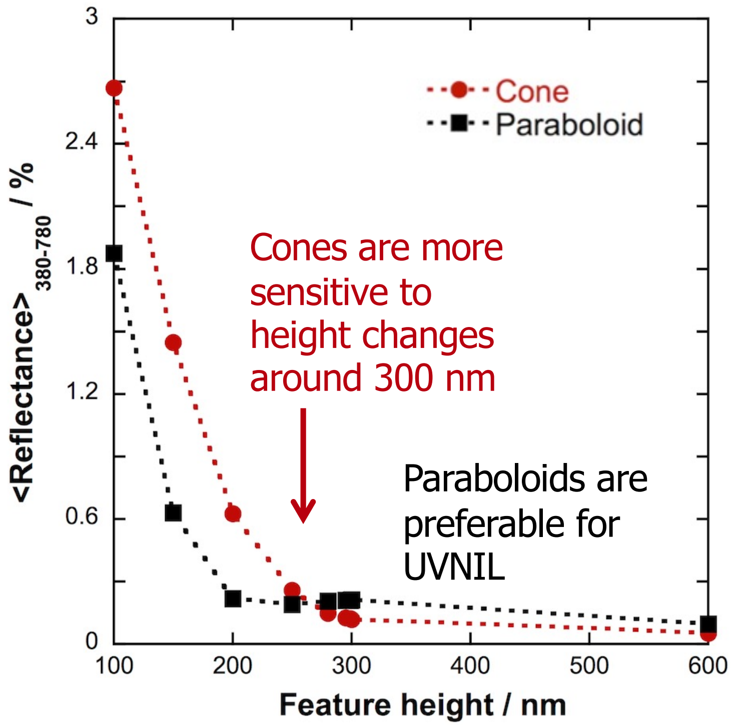
Superhard antireflective 'moth-eye' surfaces

Optical modeling of cones and paraboloid arrays:
45 layers with effective refractive index from 1 to 1.5

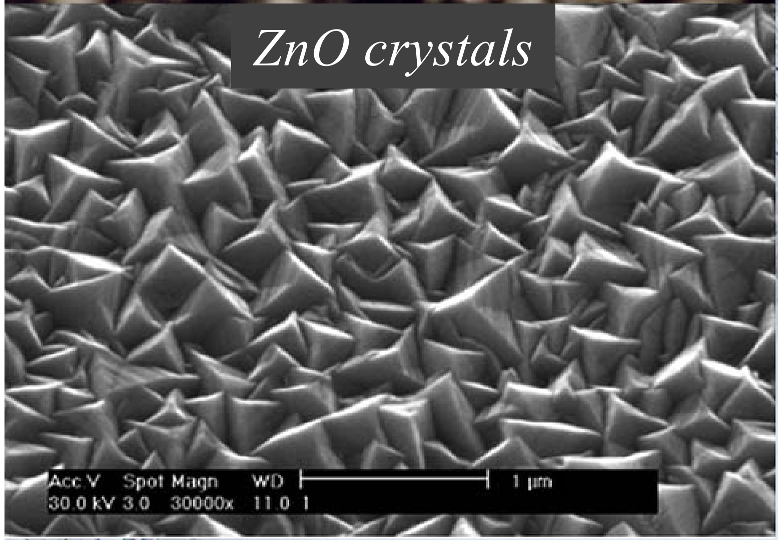
$$n_e(h) = \frac{\pi}{2\sqrt{3}} \times \left(1 - \frac{h}{h_0}\right)^{\alpha} \times (n_m - 1) + 1$$







Dewan, R., et al., Bioinspiration Biomimetics 7 (2012)
Stavenga, D.G., et al.. Proc Roy Soc B: Biol Sci 273 (2006)
Gonzalez Lazo et al., Energy Technology (2015)



Specular reflection on Ag-coated flat surface

Diffuse reflection on Ag-coated synthetic replica of ZnO surface

http://phobia.wikia.com/wiki/Chionophobia?file=Snow.jpg

Summary

Photopolymerization enables numerous developments in nanostructured device technologies

- fast, simple, room temperature process
- various fabrication techniques adapted to applications / materials
- potential for 3D structures

Integrative synthesis of hybrid composites and functionally graded composites

- combination of improved process stability and thermomechanical endurance
- unique cost-performance ratio

Still, many challenges!

- optimization of filling and demolding processes
- stability of hybrid suspensions
- shape fidelity vs. process conditions
- mass production tools & materials (e.g., injection molding)

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