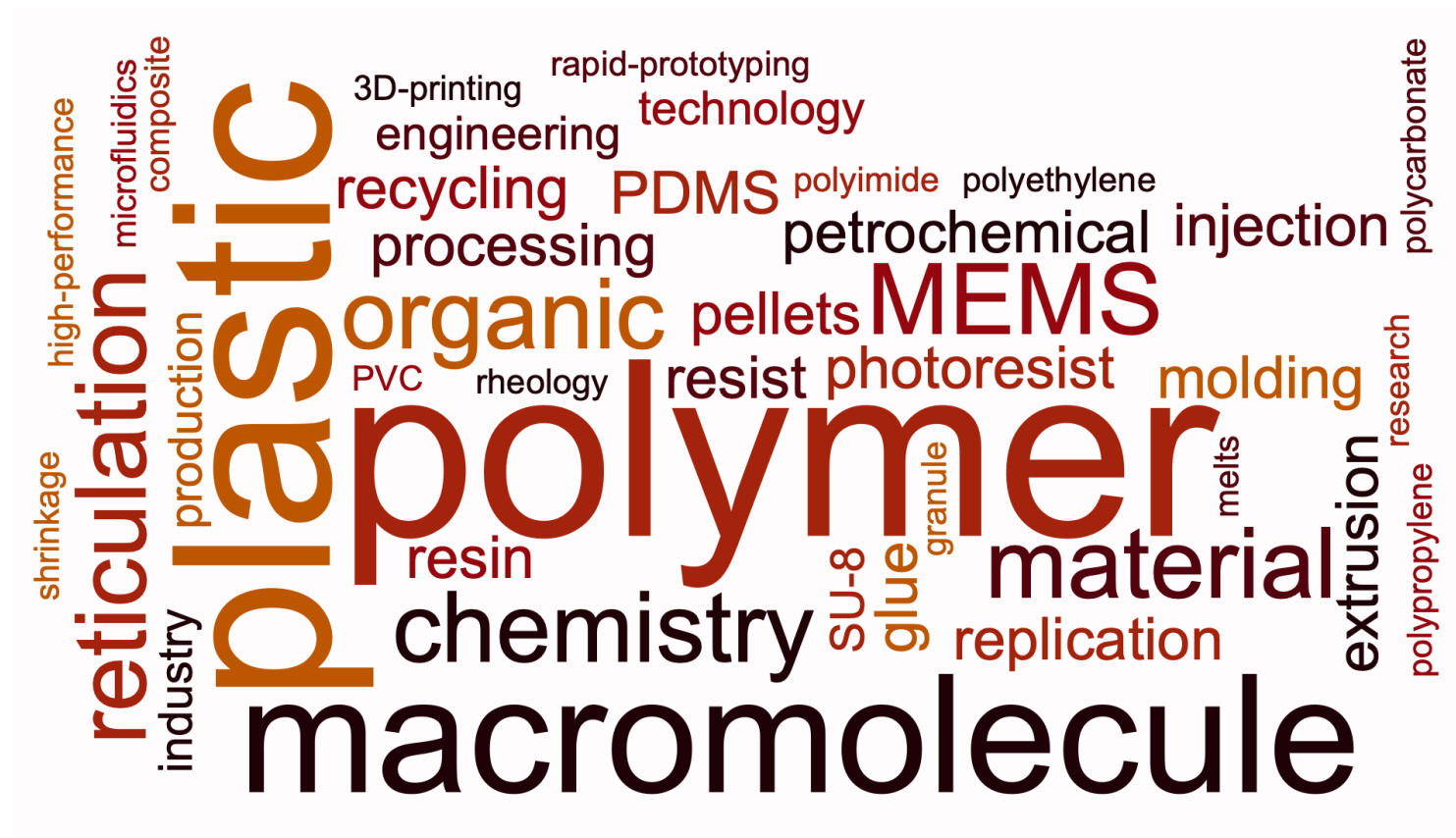




Polymers & MEMS

Polymers: Definition

Substances composed of very large molecules, called macromolecules, that are multiples of simpler chemical units called monomers.
(Encyclop. Britanica)

Natural / Synthetic

Homopolymers / Copolymers

Linear / Branched / Crosslinked / Hyperbranched

Nylon
Nitrile rubber
ABS
DNA
Proteins
PET
Bakelite
Epoxy resin
Vulcanized rubber
Glycogen
Cellulose
PDMS
Etc..

Why polymers for MEMS?

MEMS were initially developed to produce **micromechanical** systems (microphones, accelerometers, gyroscopes, pressure sensors, etc.) using Si, SiO₂, metals

Polymers will not replace Si and traditional MEMS materials, but their characteristics will allow to widen the application domains of MEMS

In the last 15 years, new applications have emerged for MEMS in **life science** and **biomedical** domains, where polymers play a key role.

Why polymers for MEMS?

The **advantages of polymers**:

- **Material properties:** not brittle, withstand large strains, low thermal expansion, some are optically transparent, with low fluorescence, chemically inert, biocompatible
- **Can be processed with a wide range of techniques:** Photo-patterning, wet and plasma etching, molding, laser ablation, 3D printing, screen printing, hot embossing, imprinting, plasma and fusion bonding, surface modification, etc..
- **Can be mixed with other materials:** (fibers, nanotubes, particles) to make composite materials and tune their properties.
- **Cost effective, cleanroom not always needed**

1- Resists / Photoresists

- **Temporary mask in photolithography process**
- **Direct fabrication of micro-components**
- **High Aspect Ratio components**
- **Multi-level components**
- **3D printing (stereolithography, micro-stereolithography, TPP, etc..)**

2- Thermoplastics (plastics that can be melted)

- **Injection molding**
- **Imprinting (nano-imprint)**
- **Excimer laser fabrication of 3D structures (also with thermosetting polymers)**

3- Elastomers (plastic material with elastic properties)

- **Rapid prototyping**
- **Molding**
- **Microfluidic applications**

4- “Special” polymers

- Vapor phase deposition (CVD)
- Conformal deposition
- Biocompatibility
- Optical films

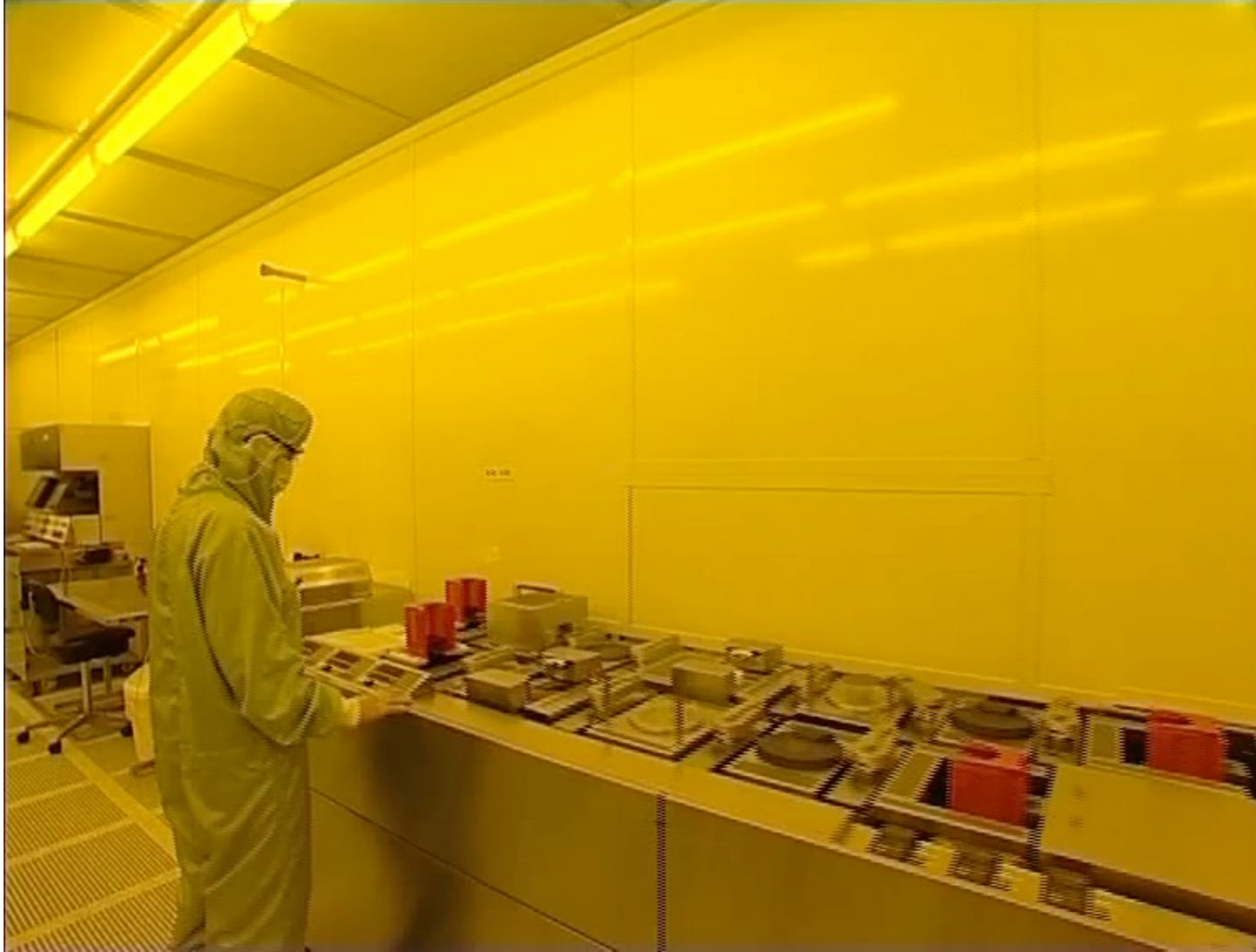


1- Resists / Photoresists

The most used polymers for manufacturing MEMS

Photoresist =
{Polymer + Solvent + Photoinitiator}

Spin coating / Photolithography





**Photoresists
used as
temporary
masks**

Photoresists:

Generally used for **masking** during wet chemical or plasma etching, **later removed**.

Example: photolithography, SiO_2 as mask for KOH etching

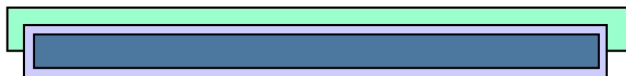
1- Si wafer



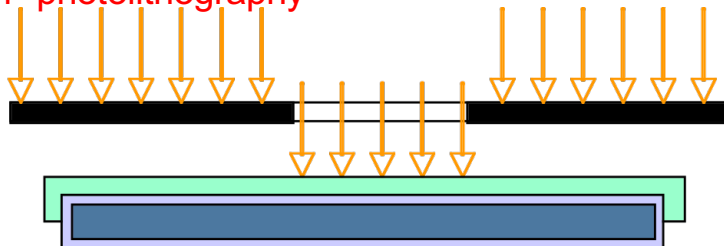
2- oxydation (1micron)



3- positive resist



4- photolithography



5- development



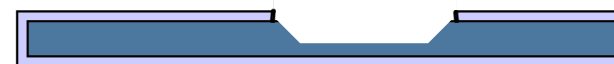
6- Wet etching of SiO_2 ($\text{HF}/\text{NH}_4\text{F}$)



7- photoresist removal
(solvent or plasma)



8- KOH etching

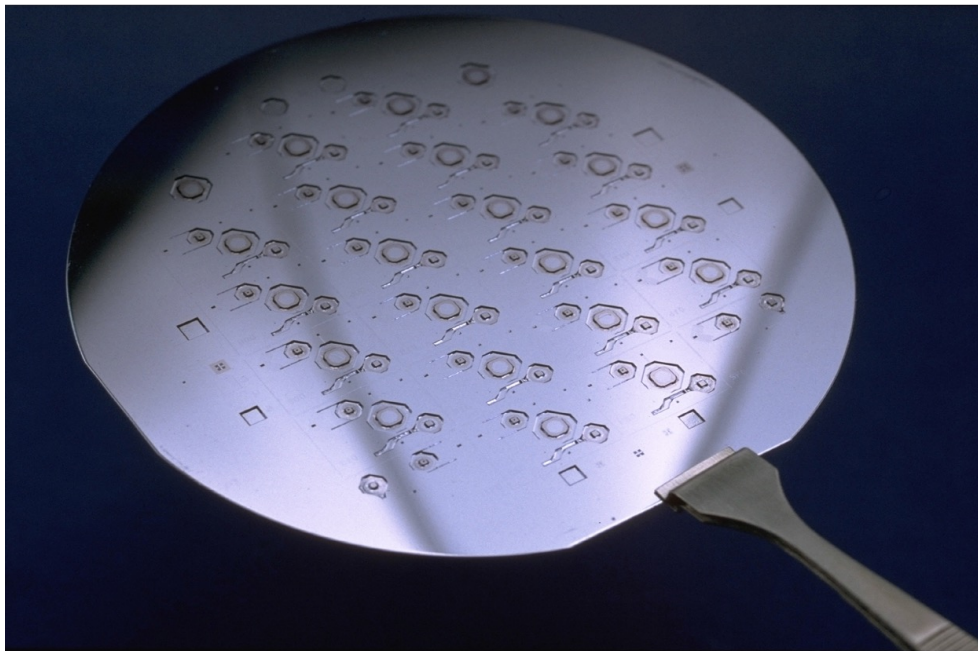


→ KOH etches Si, but not SiO_2

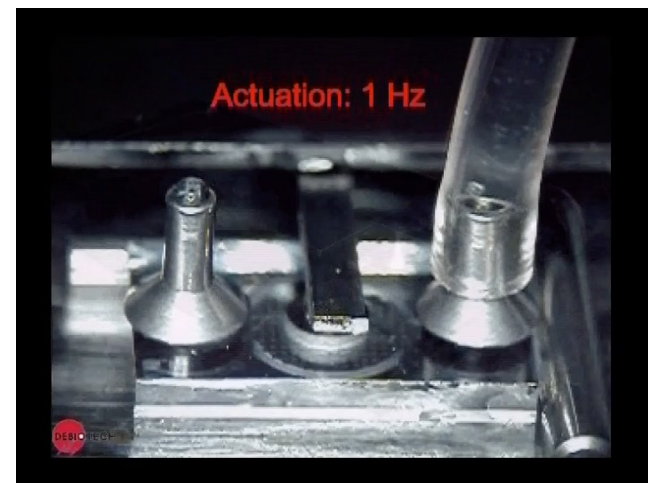
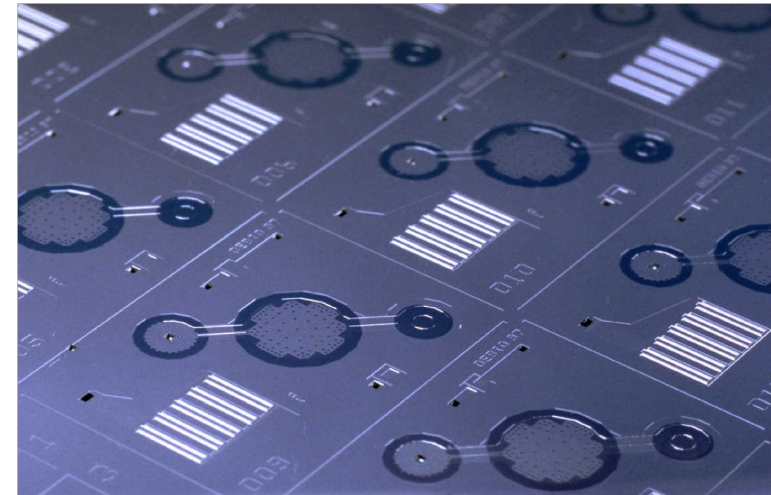
Photoresists:

Generally used for **masking** during wet chemical or plasma etching, **later removed**.

Example: photolithography of SiO₂



The first micro-pumps were manufactured using this process



More than 20 photoresists are available at CMi

Fundamental principles

Data Preparation

Ebeam Resists

MMA / PMMA

ZEP 520A

CSAR 62

HSQ / FOX16

nLOF

Electra 92

Operation Manuals

Tips

Ebeam – Resists

Following ebeam resists are currently available to users at CMi. Only these resists are authorized to be exposed in the Raith EBPG5000 tool, and to be processed on the processing equipment in zone 7 of CMi cleanroom. Please, do not introduce any other material without consulting CMi staff first.

MMA / PMMA

Positive tone. Polymer. Primarily used for lift-off, primary choice for wet etch, can be used for dry etch as well.

See more

ZEP 520A

Positive tone. Primarily used for lift-off, primary choice for wet etch, can be used for dry etch as well.

See more

HSQ / FOX16

Positive tone. Polymer. Primarily used for lift-off, primary choice for wet etch, can be used for dry etch as well.

See more

nLOF

Positive tone. Polymer. Primarily used for lift-off, primary choice for wet etch, can be used for dry etch as well.

See more

Mask Fabrication

Photoresists available in CMi

AZ 1512 HS

AZ ECI 3007

AZ ECI 3027

AZ 10XT-07

AZ 10XT-20

AZ 10XT-60

AZ 40XT

LOR 5A / AZ 1512 HS

AZ NLOF 2020

AZ 15nXT

SU-8

M108Y

M35G

PI 2610 & PI 2611

Photolithography Nomenclature

HMDS

Photoresists available in CMi

Introduction :

To do a smart choice of photoresist (PR), first answer the following questions:

- What are the layout critical dimensions (CD), i.e. minimum pattern size ?
- If the next step is subtractive (etching), what is the etching chemistry and what is the etching selectivity with the PR ?
- If the next step is additive (lift-off), what is the thickness of the material to be deposited and which equipment is used ?
- Do you have any existing topography on the wafer ?

Then, find a suitable photoresist from the list of i-line resists (to expose on CMi's mask-aligners and laser writers) or DUV resists (to expose on CMi's DUV stepper).

Positive i-line ($\lambda = 365\text{nm}$) resists :

AZ 1512 HS / Positive tone / Recommended for general use, wet etching, surface protection (dicing)

AZ ECI 3007 / Positive tone / Recommended for dry etching (etching, surface protection)

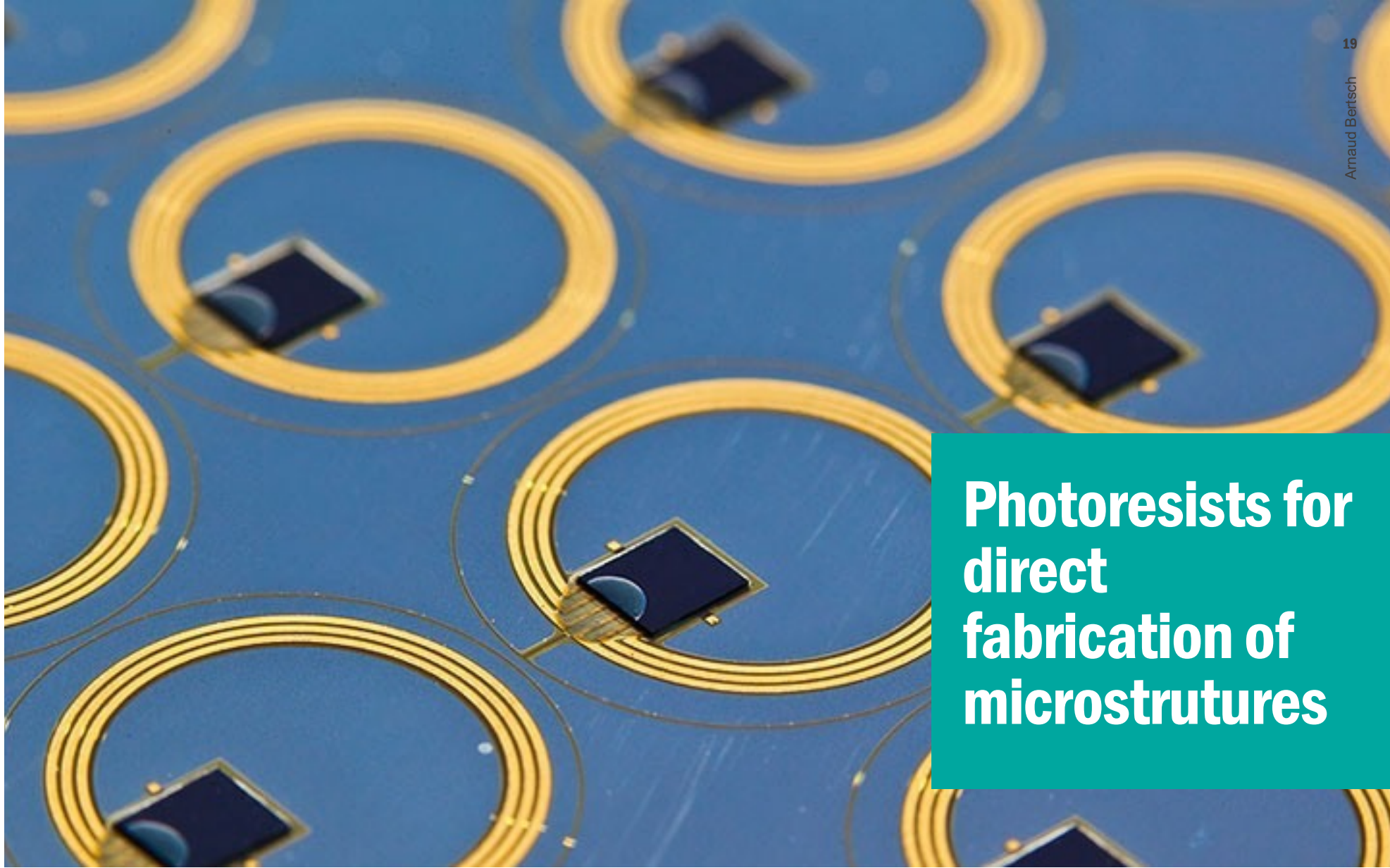
Choose wisely a photoresist for your application

1- Resolution requirements: UV, Deep UV, e-beam ?

2- Resolution requirements: Higher resolutions require thinner photoresist layers

3- Chemical compatibility: Make sure all the previously structured materials are compatible with the chosen photoresist, adhesion promoter, developer, and stripper. If it is used for lift-off, make sure the photoresist is compatible with the subsequent process steps.

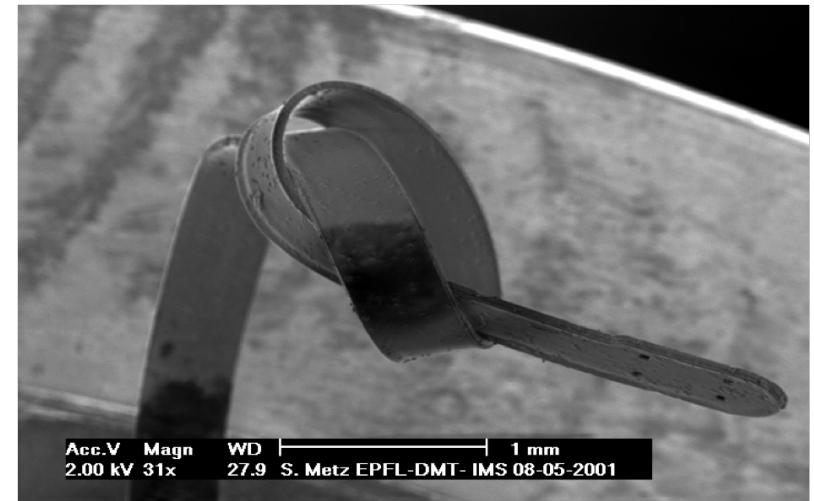
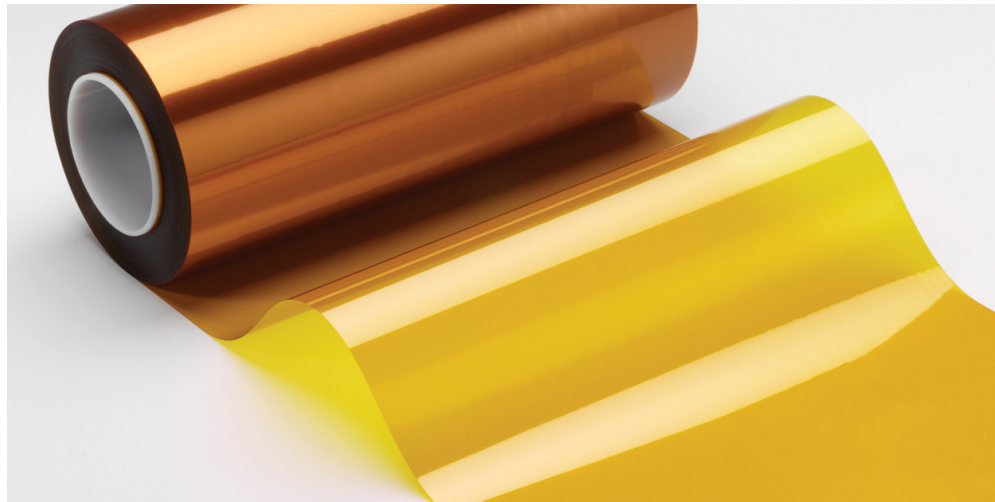
4- Function of the photoresist: Make sure the photoresist is adapted to the application: Thick photoresist layers are generally needed for deep etching processes. Some applications require vertical sidewalls, other do not. Some are etched isotropically in plasmas, others are not.



Photoresists for direct fabrication of microstructures

Photoresists for the direct fabrication of polymer micro-components

Example photosensitive polyimide (PI) (it is a negative photoresist)



First used as a dielectric material for microelectronics, it is also used as a flexible material for the direct fabrication of MEMS.

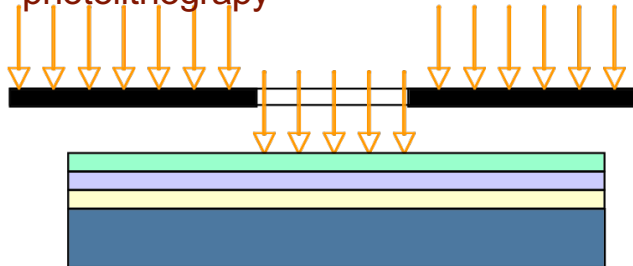
Photoresists for the direct fabrication of polymer micro-components

Example of NON photosensitive polyimide (biocompatible and implantable)

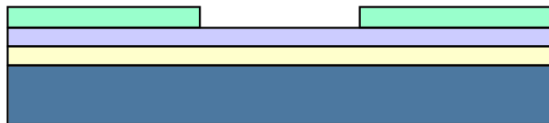
1- Si wafer + PI
+ SiO₂ + positive photoresist



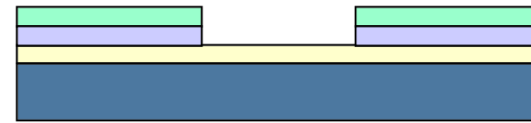
2- photolithography



3- development



4- HF etching of SiO₂



5- photoresist removal

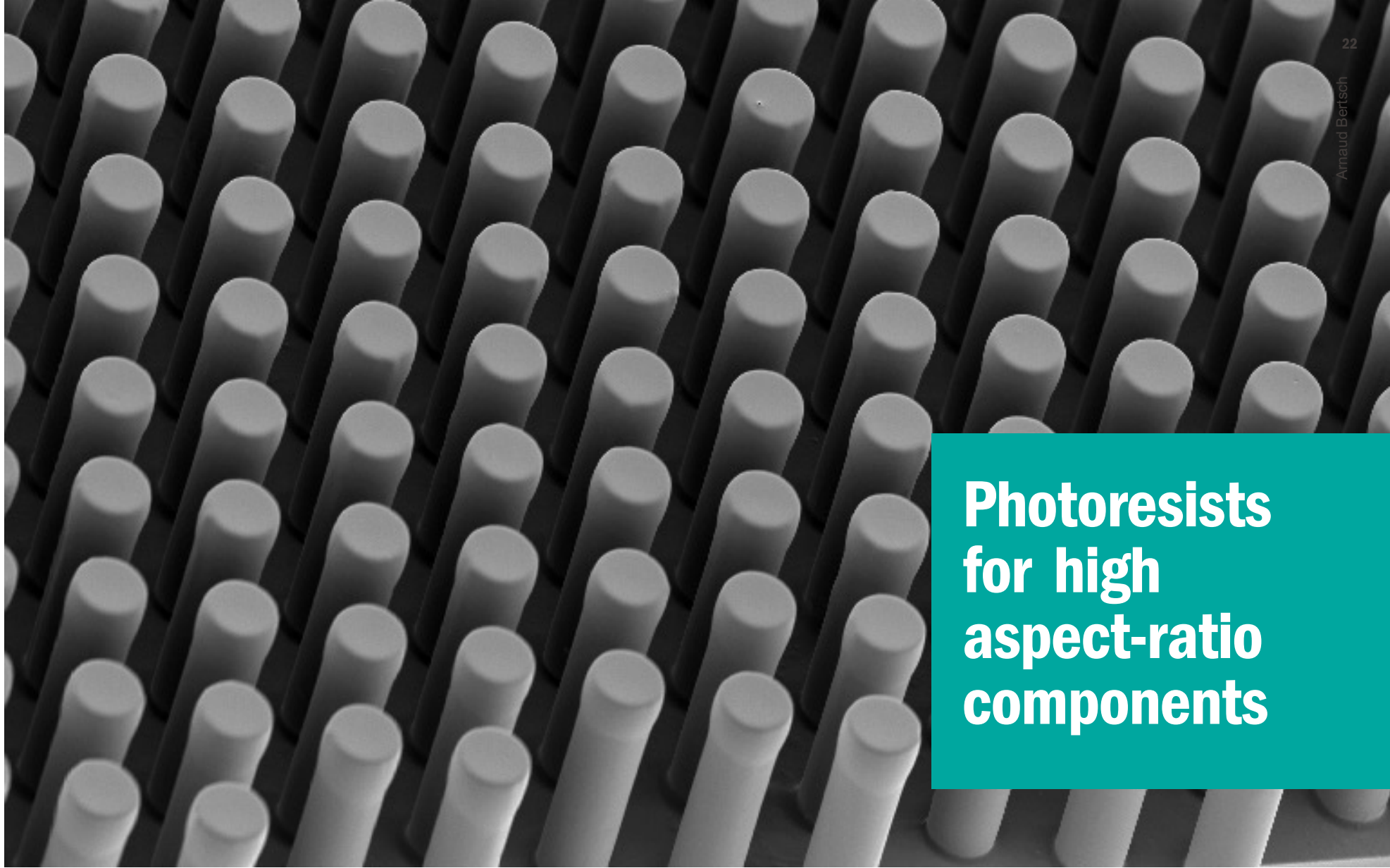


6- O₂ plasma etching



7- SiO₂ removal (HF)



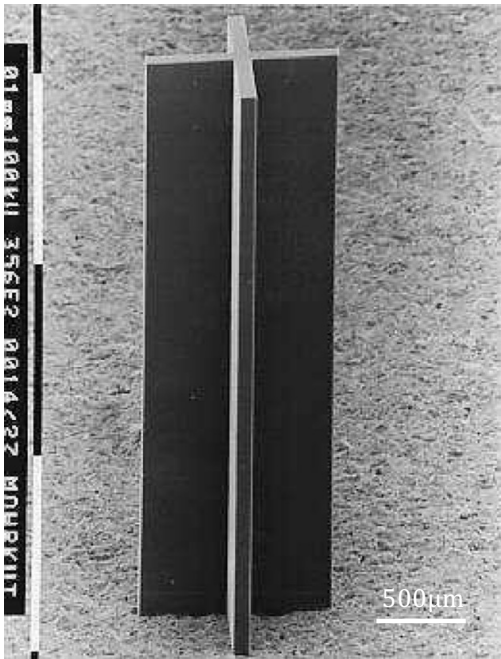


**Photoresists
for high
aspect-ratio
components**

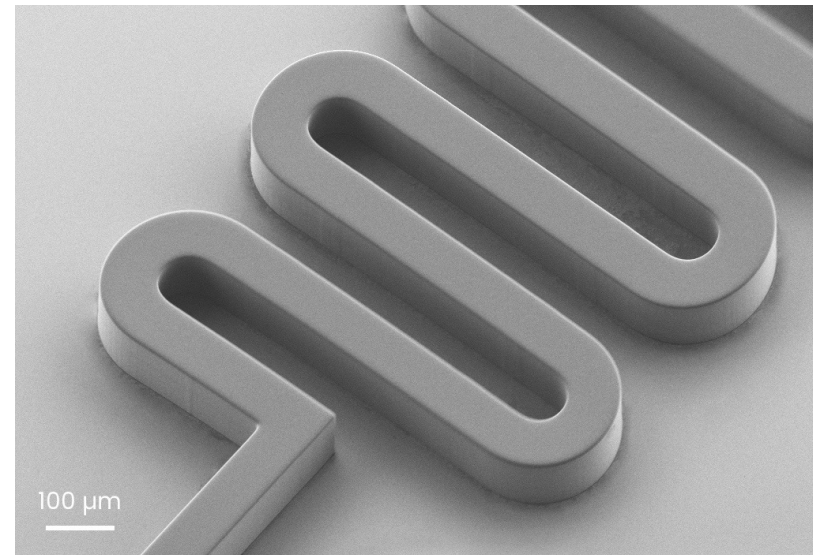
Photoresists for high aspect ratio components

Aspect ratio:

It is the ratio between the vertical and the lateral dimensions of an object



high aspect ratio



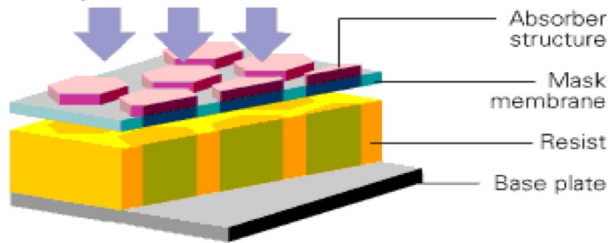
low aspect ratio

German acronym : *Lithographie, Galvanoformung, Abformung*

Initially, the LIGA process was developed to manufacture microstructures used for uranium enrichment.

1. Irradiation

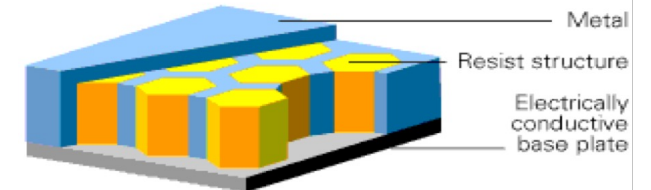
Synchrotron irradiation



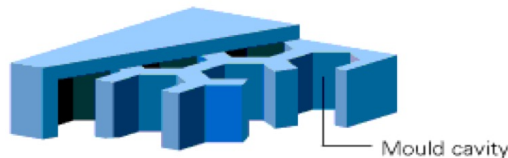
2. Development



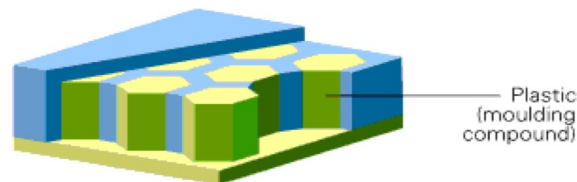
3. Electroforming



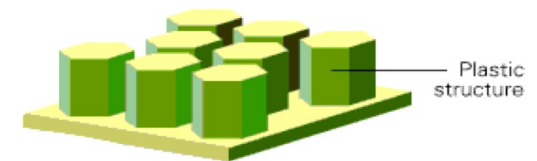
4. Mould insert



5. Mould filling

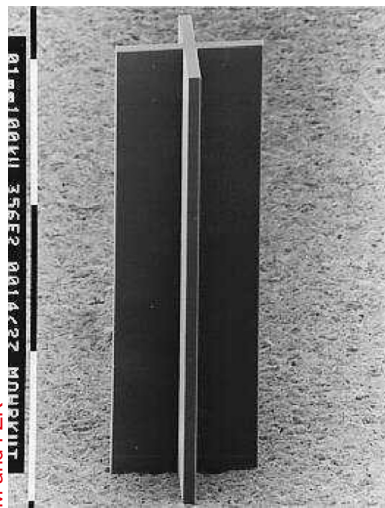


6. Mould release

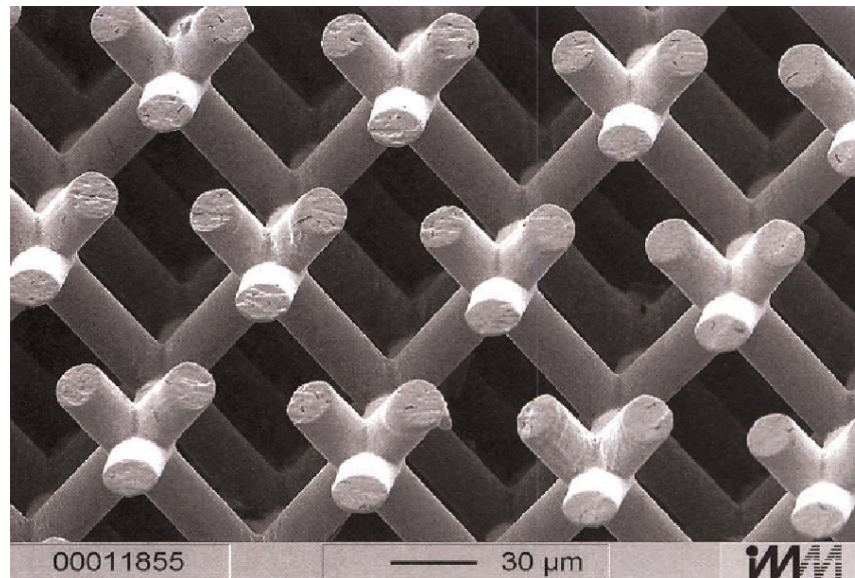


- Resolution better than one micron (200 nm)
- Layer thickness larger than 1 mm
- Very high aspect ratios (up to 500)
- PMMA, SU-8
- After molding: Metals, ceramics, polymers
- But: You need a synchrotron

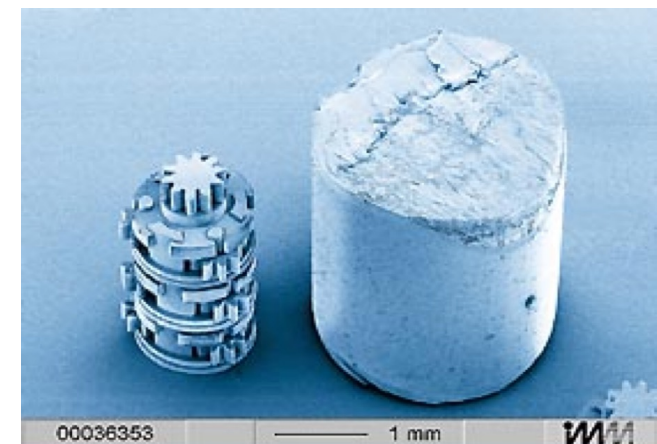
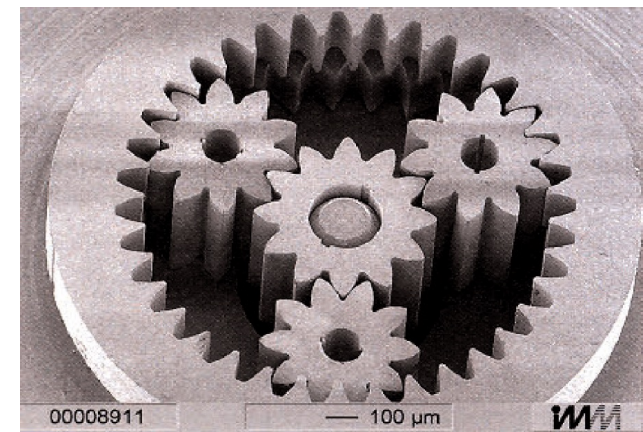
LIGA -X : Examples



PMMA

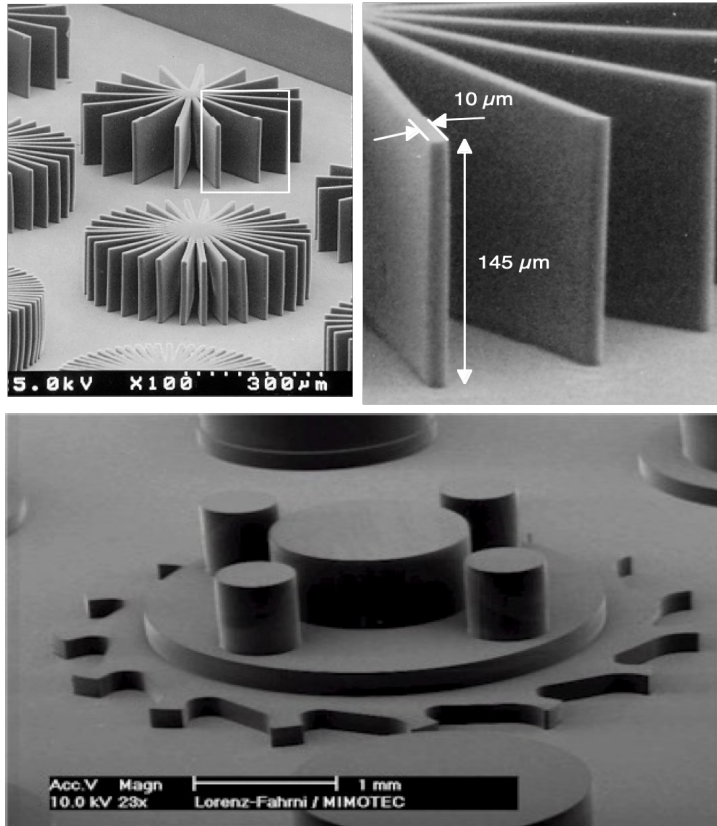


Negative resist
photonic bandgap material



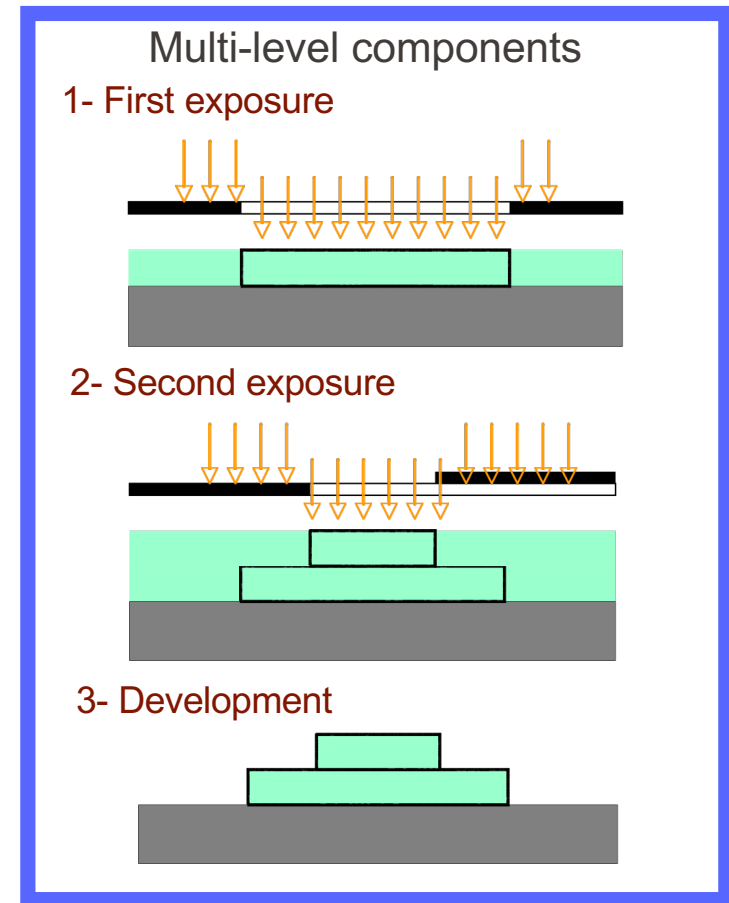
POM (Polyoxymethylene)
Molding

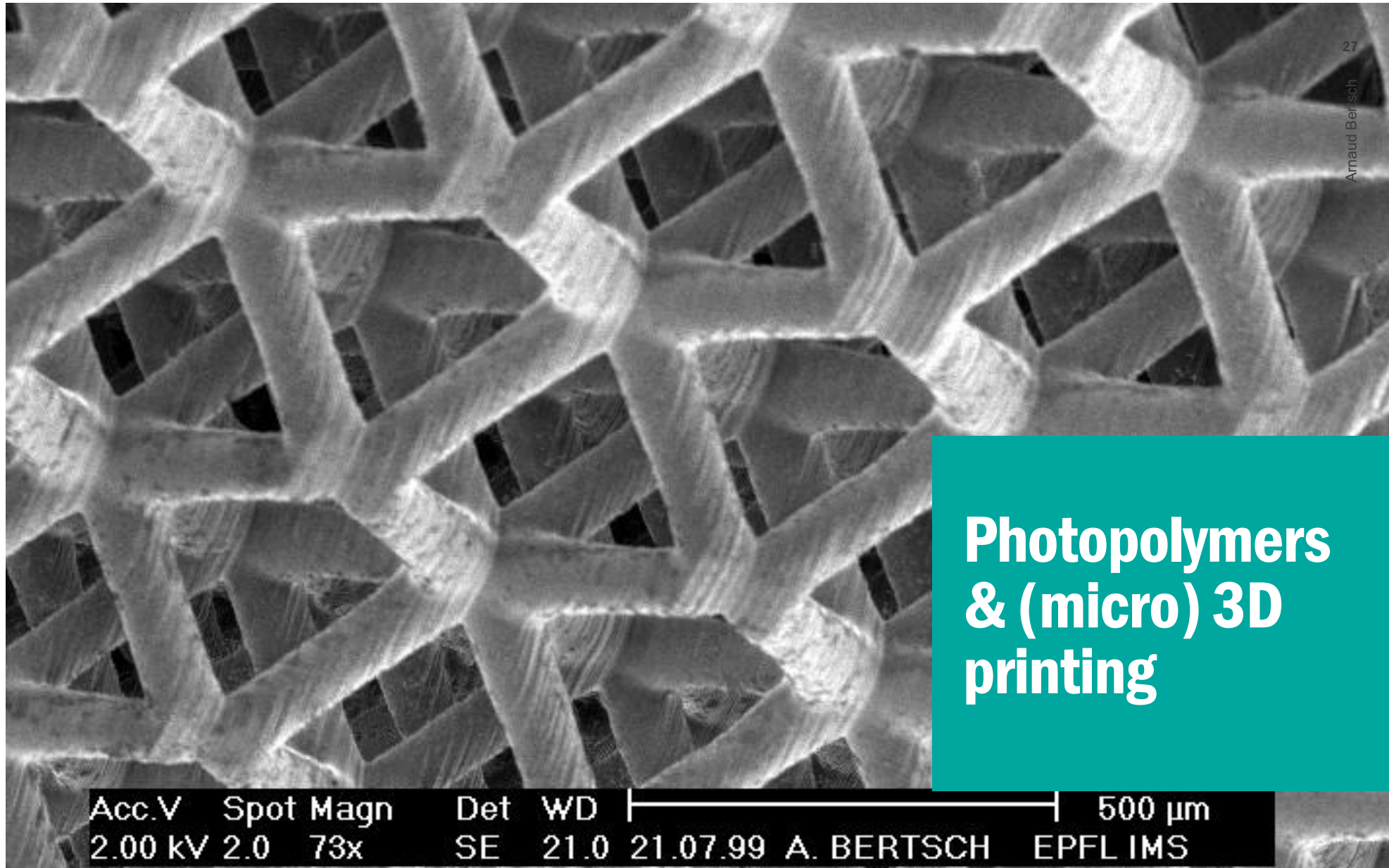
UV - LIGA : The SU-8 resist



- Negative resists (in particular SU-8)
- Resolution: 2 to 3 microns

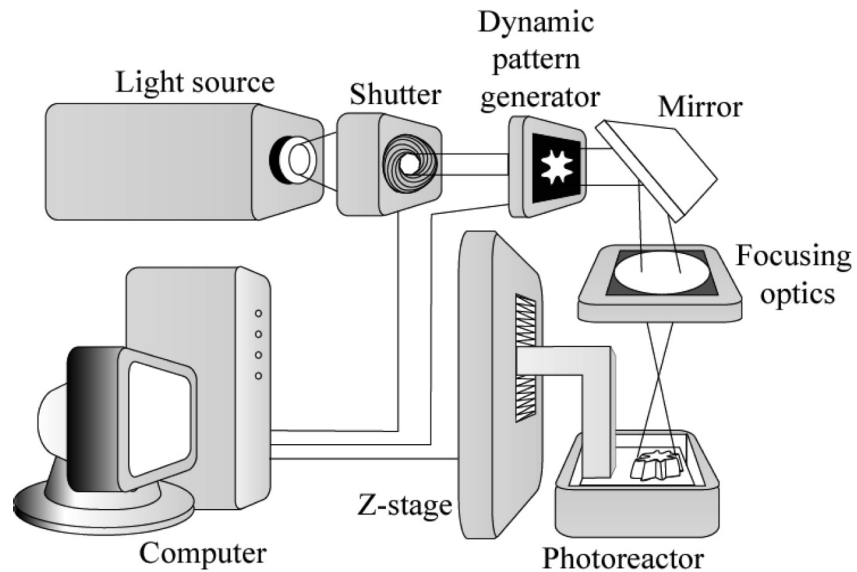
- Resist thickness: 1 to 500 microns
- Aspect ratio: up to 40





Photopolymers & (micro) 3D printing

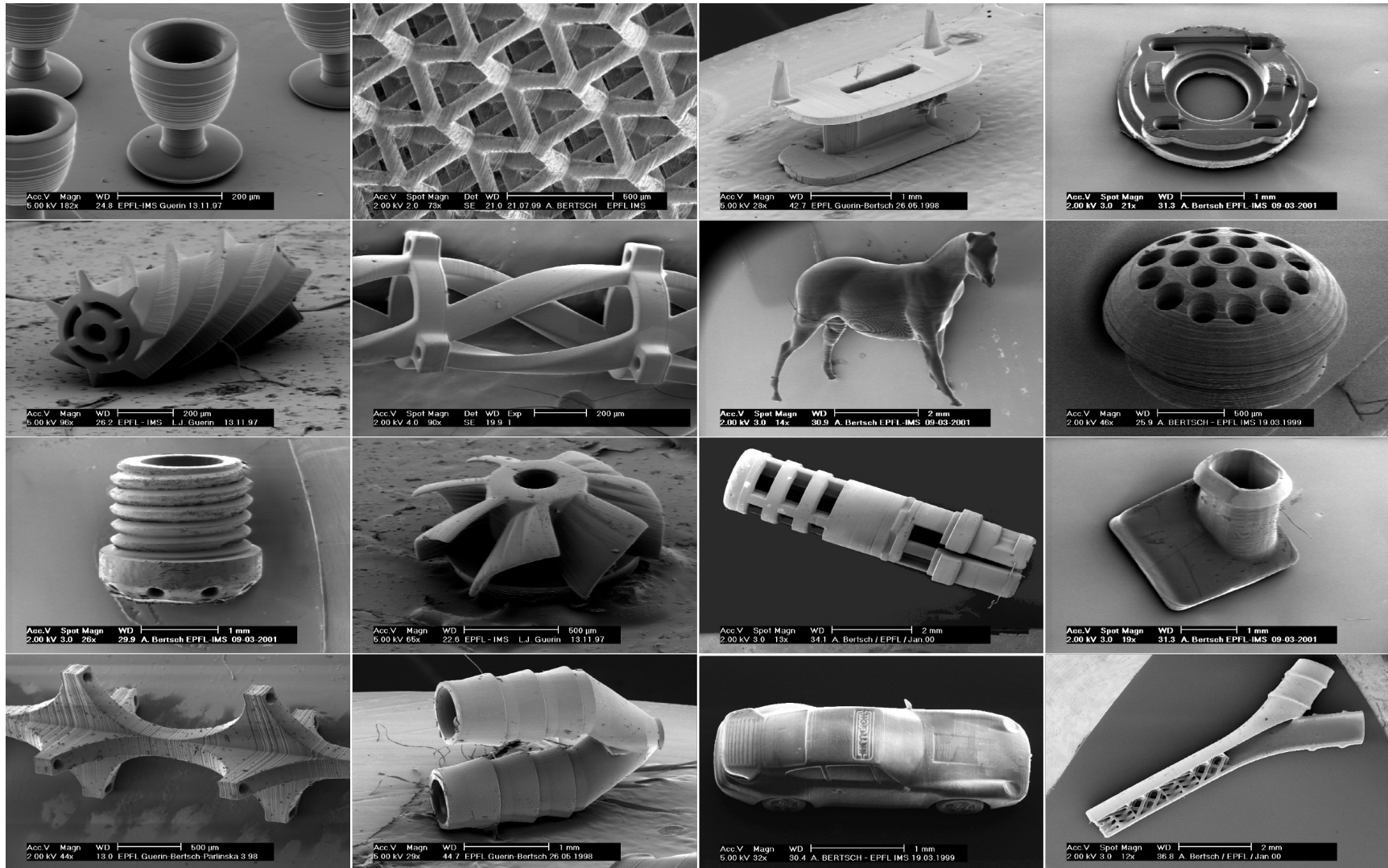
Photopolymers for stereolithography



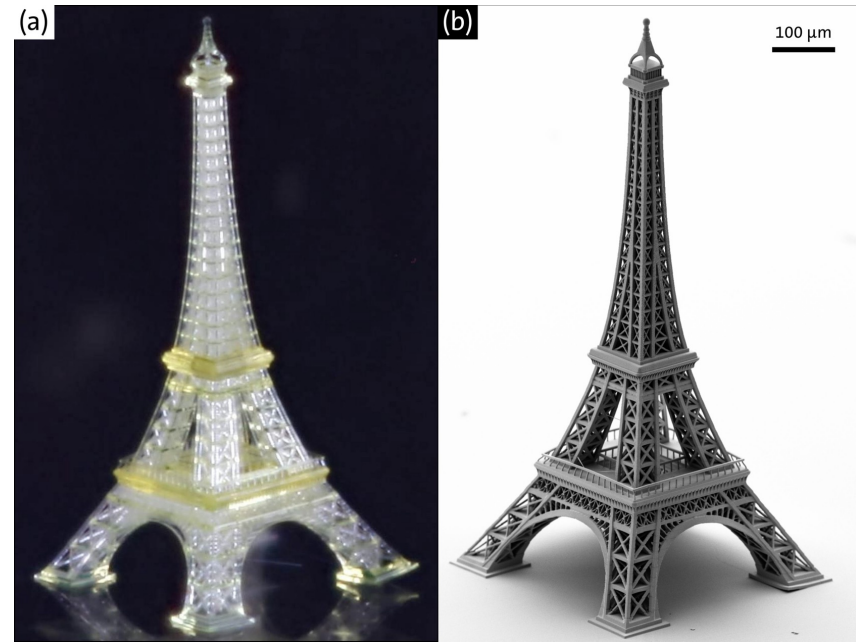
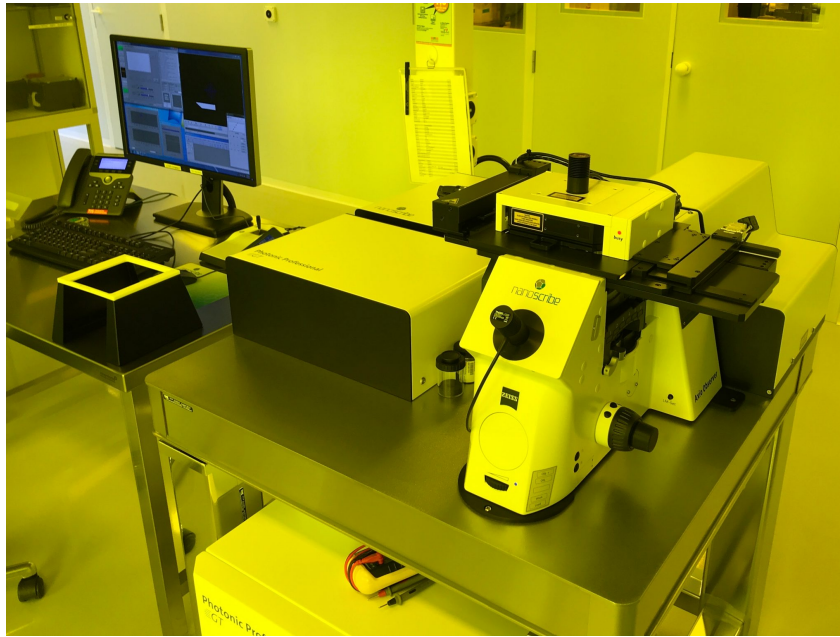
- Layer by layer fabrication
- The image of the layer being manufactured is projected on the liquid resin surface, which induces local polymerization.
- Once the irradiation of one layer is done, the object is moved vertically in the photoreactor, and a layer of liquid resin is spread on the last fabricated layer.
- The fabrication process is repeated until all layers are manufactured.

- 3D objects (really)
- Resolution: 200nm to 10 microns, depending on the process
- Limited choice of materials
- 3D components are unlikely to be used for molding
- Not wafer-compatible

Microstereolithography



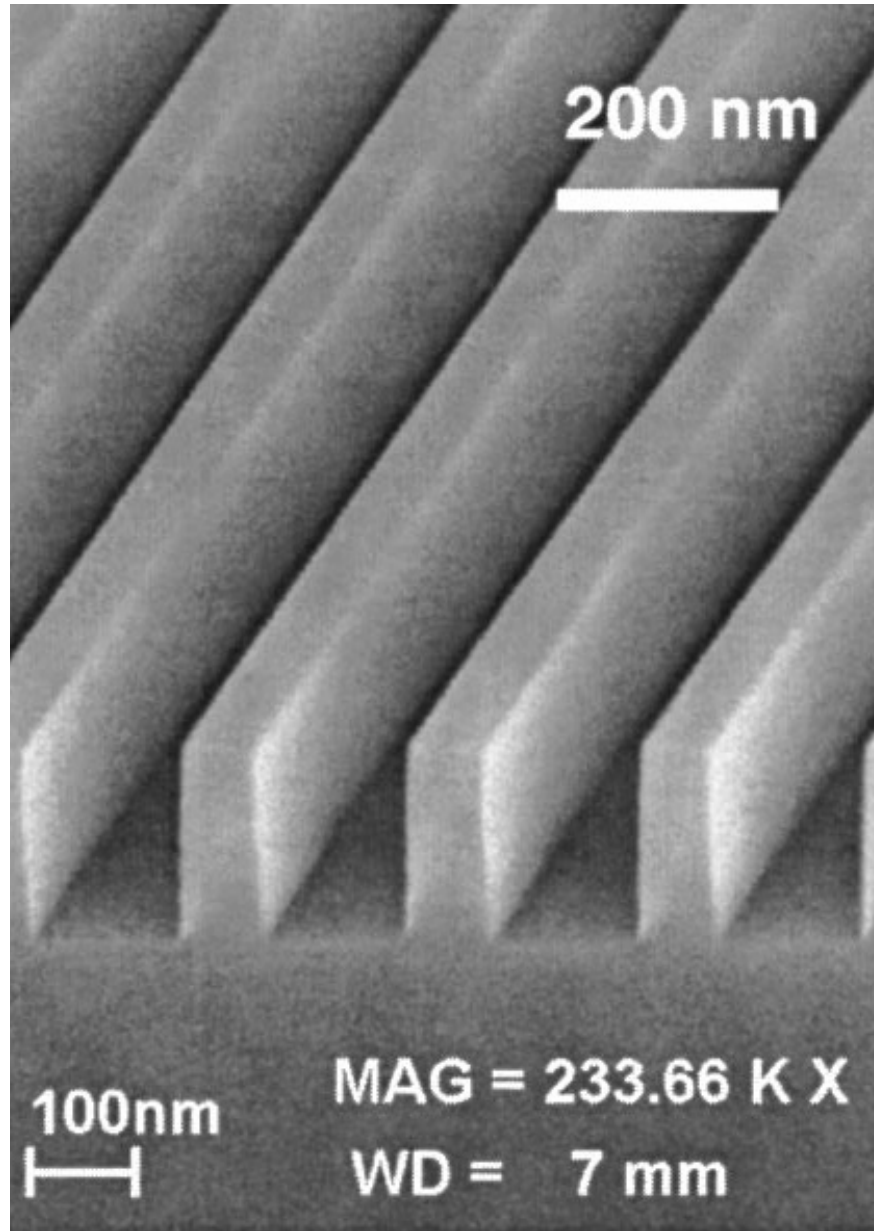
TPP: Two-photon stereolithography (nanoscribe)



Fabricated

CAD model

- The two-photon absorption requires that the combined energy of two photons matches the transition energy between the ground and excited states of the photoinitiator, it has a quadratic dependence on the light intensity, which confines this phenomenon to the area of the focal point, and allows to obtain polymerized volume elements of sub-micron resolutions.
- Printing speed: 1 to 10mm³ per hour.



2- Thermoplastics

Used in industrial production of MEMS, with replication techniques

Generally used thermoplastics:
PMMA, PC, POM, PEEK

Micro replication

Master



Si micro-manufacturing

or



High aspect ratio
component

or



Almost any
microfabrication technique

Insert



Electrodeposition
(for example Nickel)



Planarisation

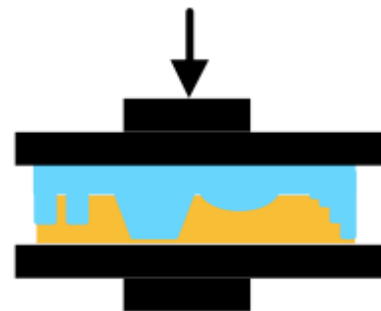


Release

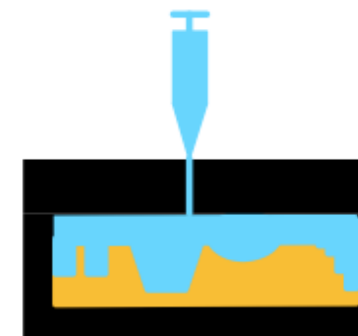
Replication



Molding



Imprinting

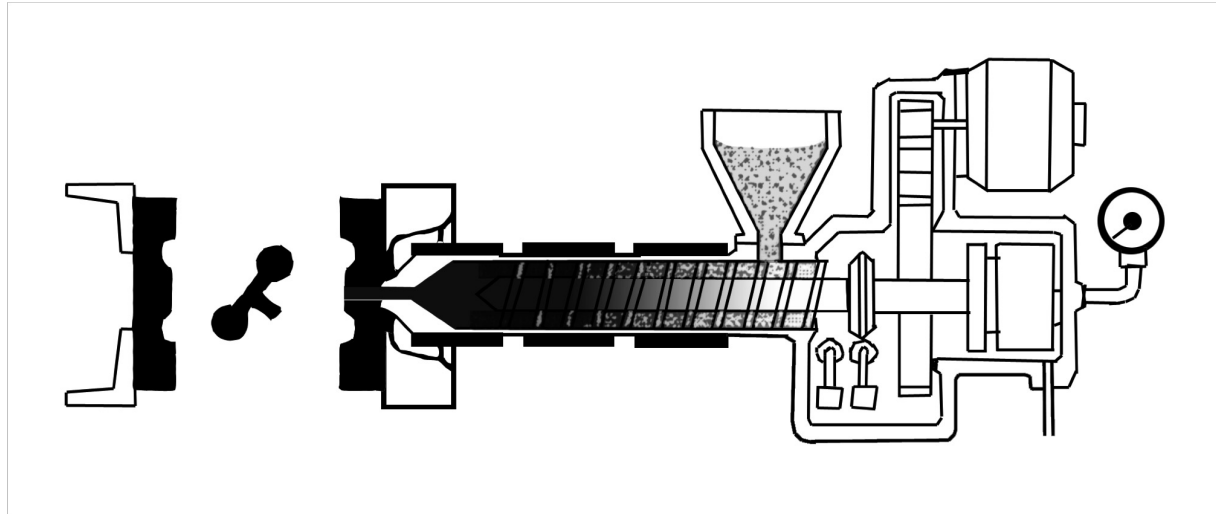


Injection molding

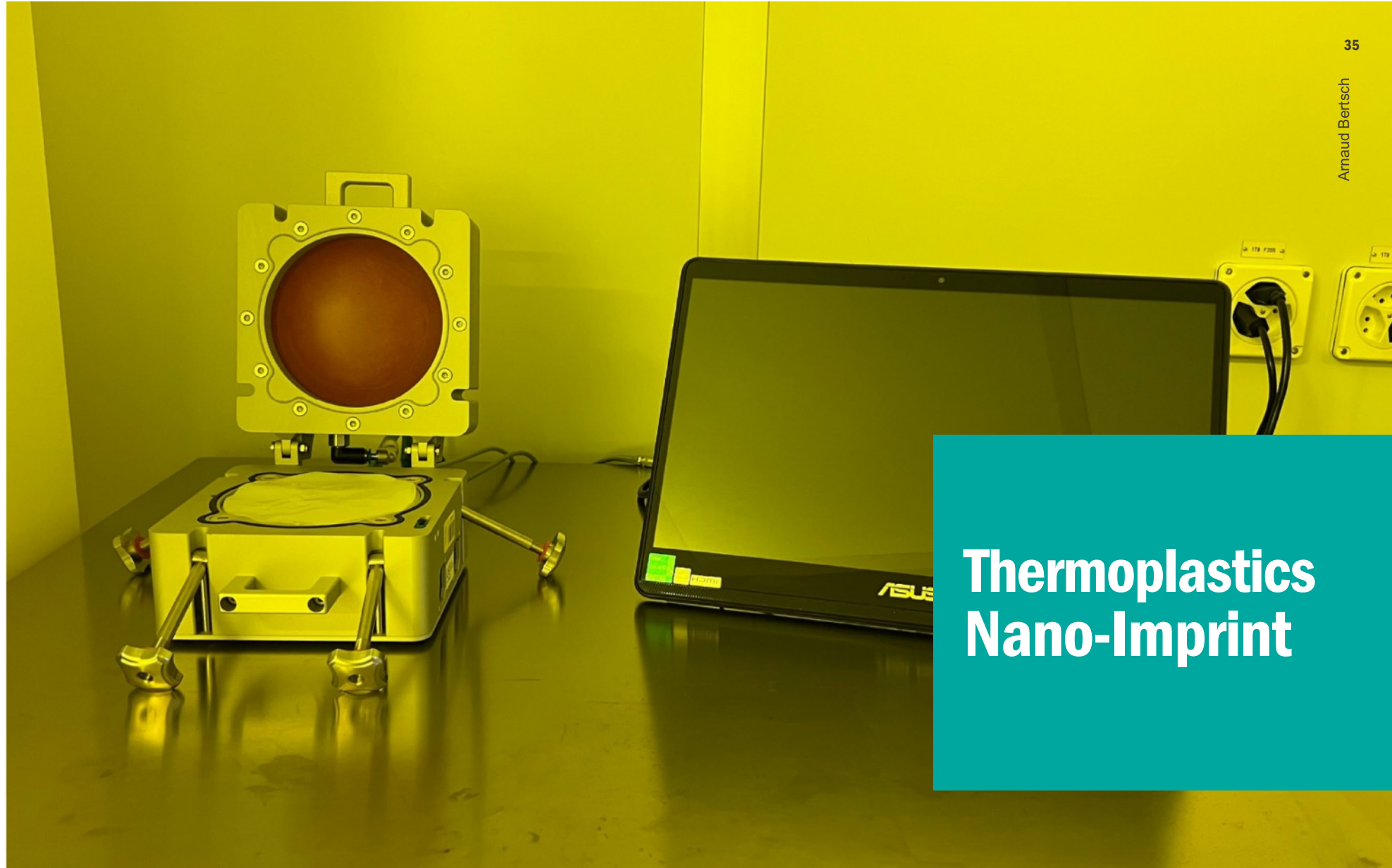


Thermoplastics Injection molding

Micro Injection Molding

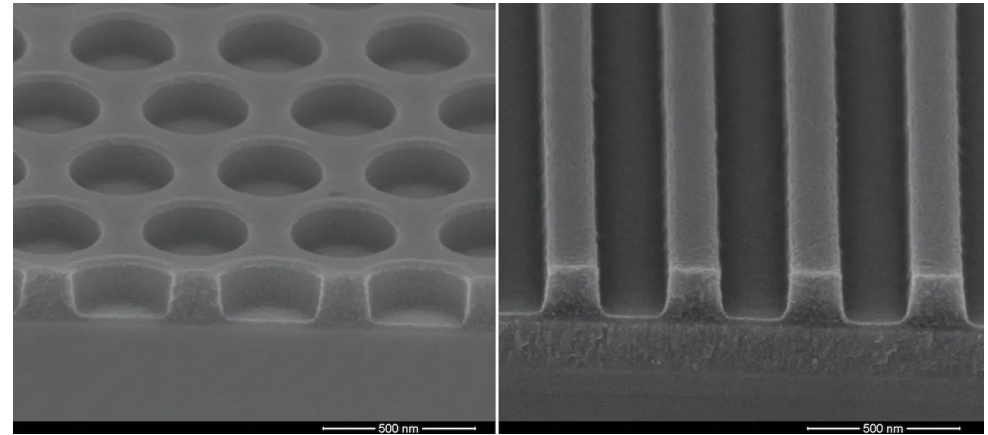
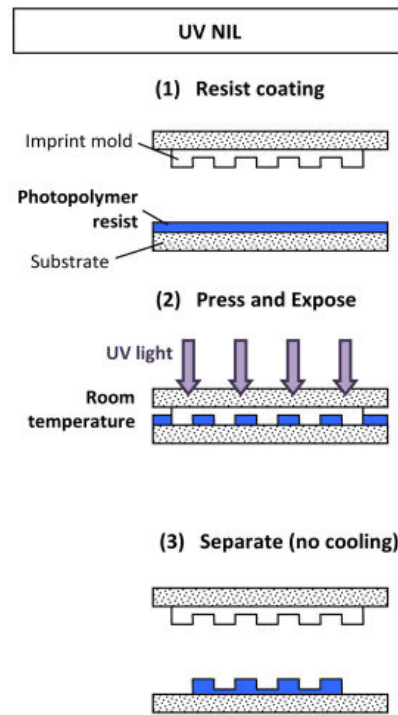
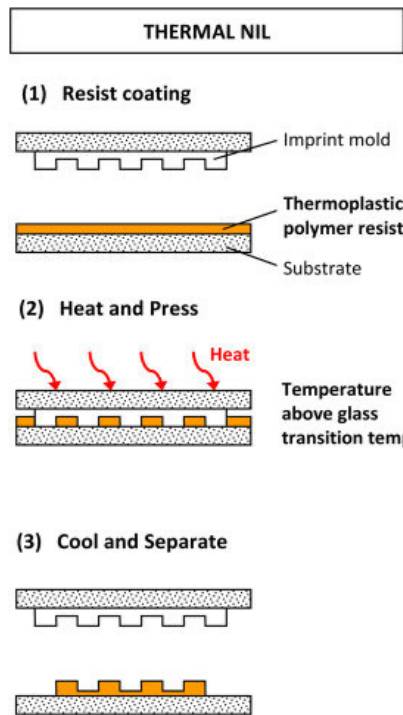


- Micro Injection Molding uses the same machine as standard injection molding
- BUT mold inserts are adapted for microcomponents (adapted mold design, systematic use of molds with multiple cavities, shorter cycle durations, etc.)
- Molds can be manufactured by diverse micromanufacturing methods (Si micro-manufacturing, RIE X-LIGA, UV-LIGA, laser ablation, micro EDM, etc.)
- Generally used thermoplastics: PMMA, PC, POM, PA12, PSU, PEEK, LCP, etc.
- Aspect ratios: up to 30 / Details down to 0.9 microns / walls down to 20 microns



Thermoplastics Nano-Imprint

Nano-Imprint (hot embossing)



www.imec-int.com

- Replication of very fine details (resolution of a few nanometers)
- Large choice of materials (all thermoplastics)
- Molds can be fabricated by many microfabrication methods (Si micromachining, RIE, X-LIGA, UV-LIGA, laser ablation, micro EDM, etc.)
- Many applications (micro-optics, displays, high-density nanopatterns for DNA analysis, genomics,...)



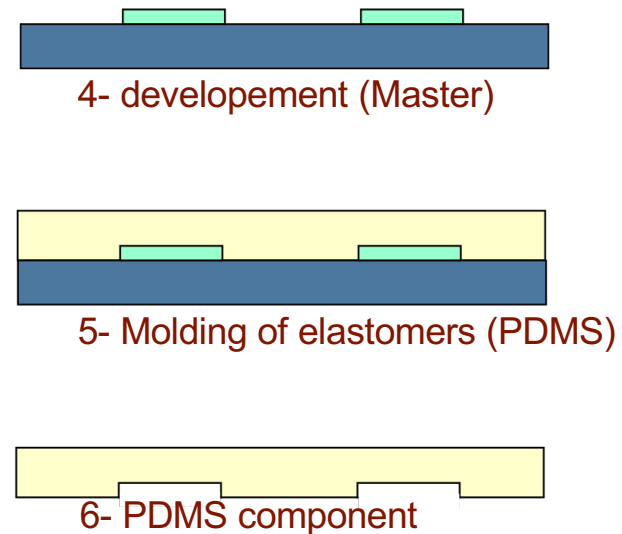
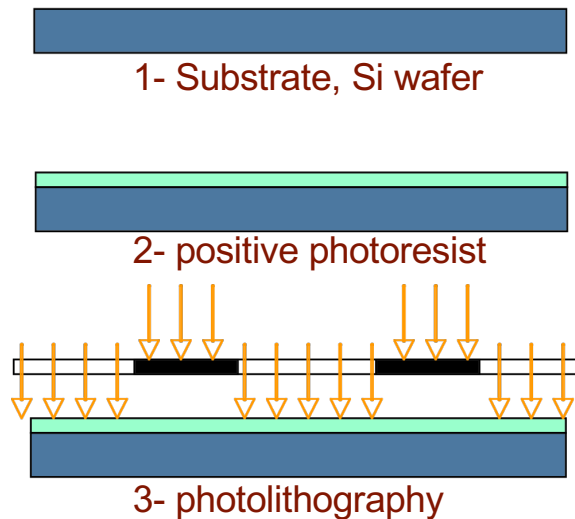
3- Elastomers

Molding

Polydimethylsiloxane (PDMS)

Rapid prototyping of Microfluidic devices

Molding of elastomers (PDMS)



- PDMS molding can be performed on a large variety of microstructured masters.
- PDMS can be irreversibly bonded to glass or pyrex by simple O₂ plasma activation
- PDMS is very flexible and transparent
- Used for microfluidic prototyping (almost always)
- Often used for making wearable devices

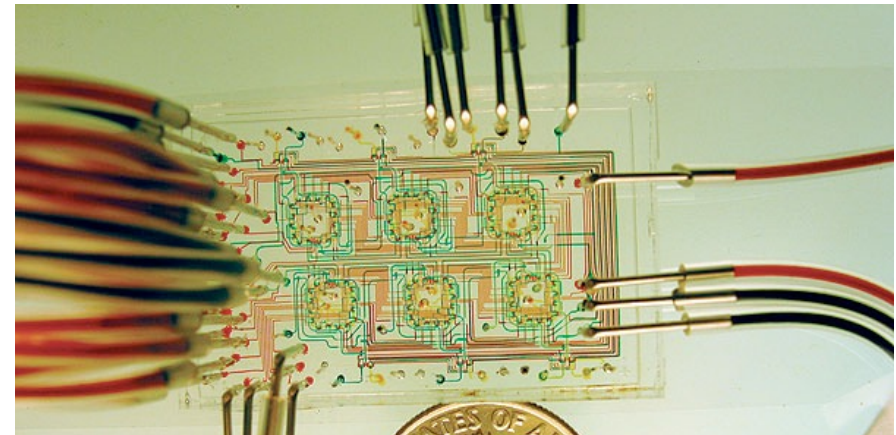
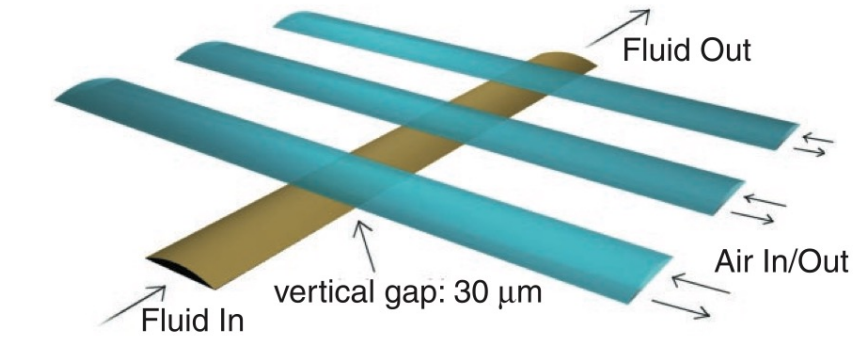
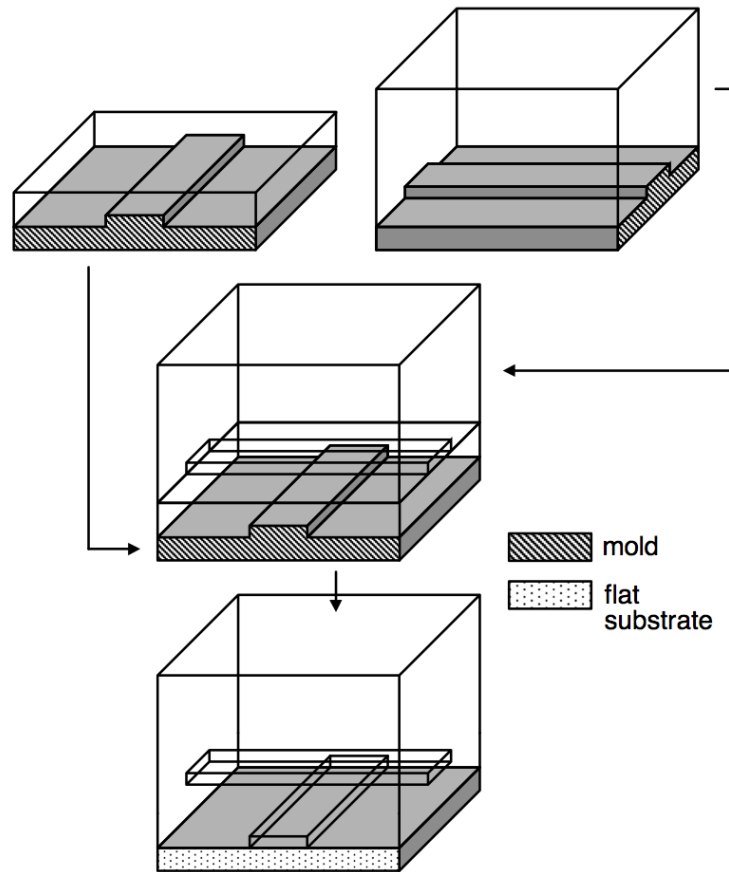
PDMS, the advantages

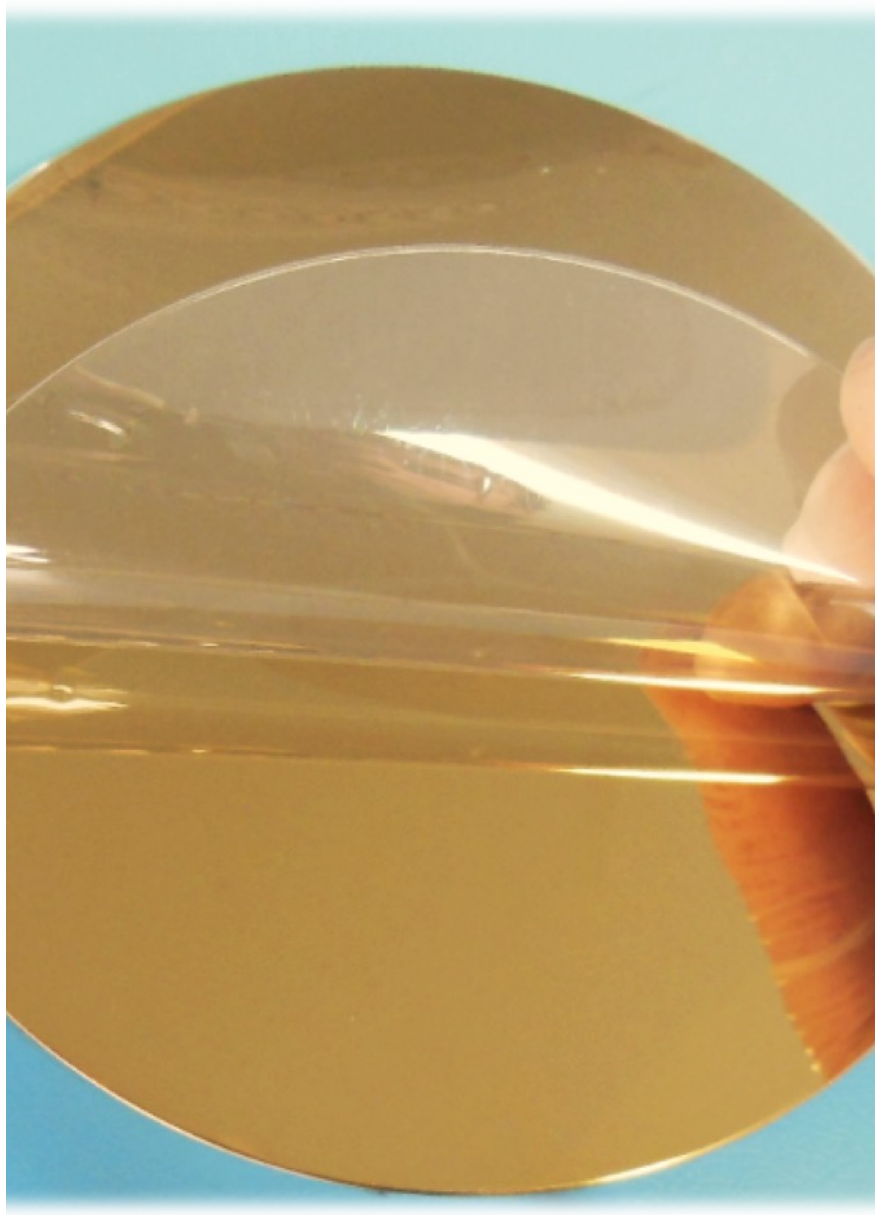
- Easy molding of fluidic channels down to details of microns in dimensions
- Rapid fabrication, easy and low cost
- Very flexible material, but mechanically strong
- Optically transparent (from 240nm to 1100nm), which is valuable for optical microscopy
- Very permeable to gases

PDMS, the limitations

- Very permeable to water (evaporation), and to many gases.
- Highly hydrophobic (which is a problem for cell culture)
- Permeable to a large number of organic molecules. Swells when exposed to a large number of solvents.
- Chemically inert surface

Multilayer PDMS





4- Special polymers

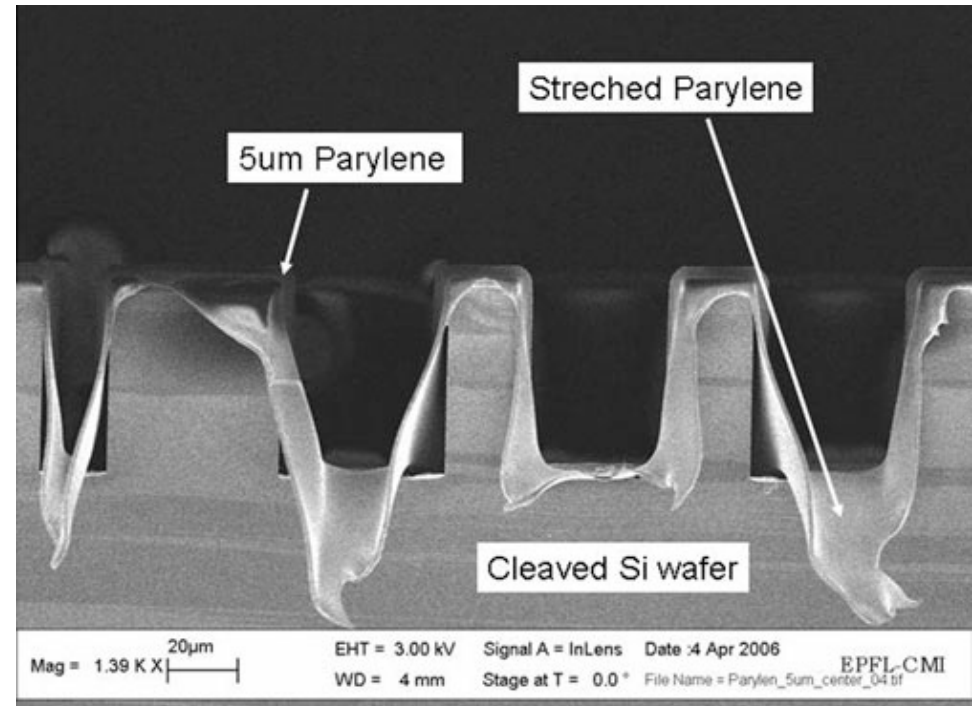
Thin films

Biocompatibility

Optical films

Parylene

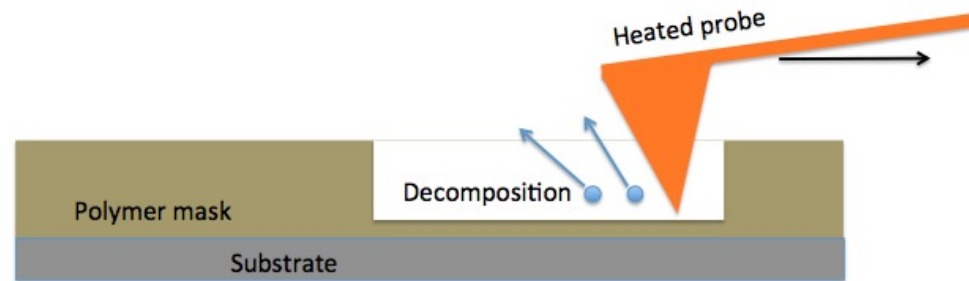
- Gas-phase deposition (CVD)
- Conformal deposition
- Low dielectric constant
- Optically clear
- Bio-compatible
- Moisture barrier
- Does not induce constraints
- Electrical insulation
- Room temperature deposition



Used in an increasing number of applications (electronics, medical, aerospace, defense, automotive, telecom, etc..)

Polymers for Thermal Scanning Probe (t-SPL)

- Sublimation of polymers
- No residues after polymer degradation
- Nano-meter thick structures
- Non planar substrates
- Printing in 2.5D



- PAA (Phthalaldehyde)
- Polycarbonates (for ex. Polyethylenecarbonate)
- PETN (Pentaerythritol tetranitrate, explosive)

In the future, which new trends in polymers for microfabrication?

- **Bioresponsive Polymers** (Change with pH or in the presence of specific bio-molecules, useful for bio-sensing or drug delivery systems)
- **Stimuli-Responsive Polymers and shape-memory polymers** (Change of properties when subjected to an external stimuli, such as light, heat, electric field gradient. Can be used as actuators or valves)
- **Self-healing polymers** (Self heal in case of cracks or damage)
- **Biodegradable polymers** (For medical applications and environmental use)
- **Conductive polymers** (For example PEDOT:PSS can be used in soft electronics systems, for wearable electronics)
- **Bioactive polymers** (For example polymers which favor or inhibit cell adhesion, antiviral, anticancer, and antimicrobial activities etc.)
- **Multifunctional polymers** (both functional and structural material)
- **Sustainable polymers** (sustainably sourced, recyclable, etc.)

5- Applications

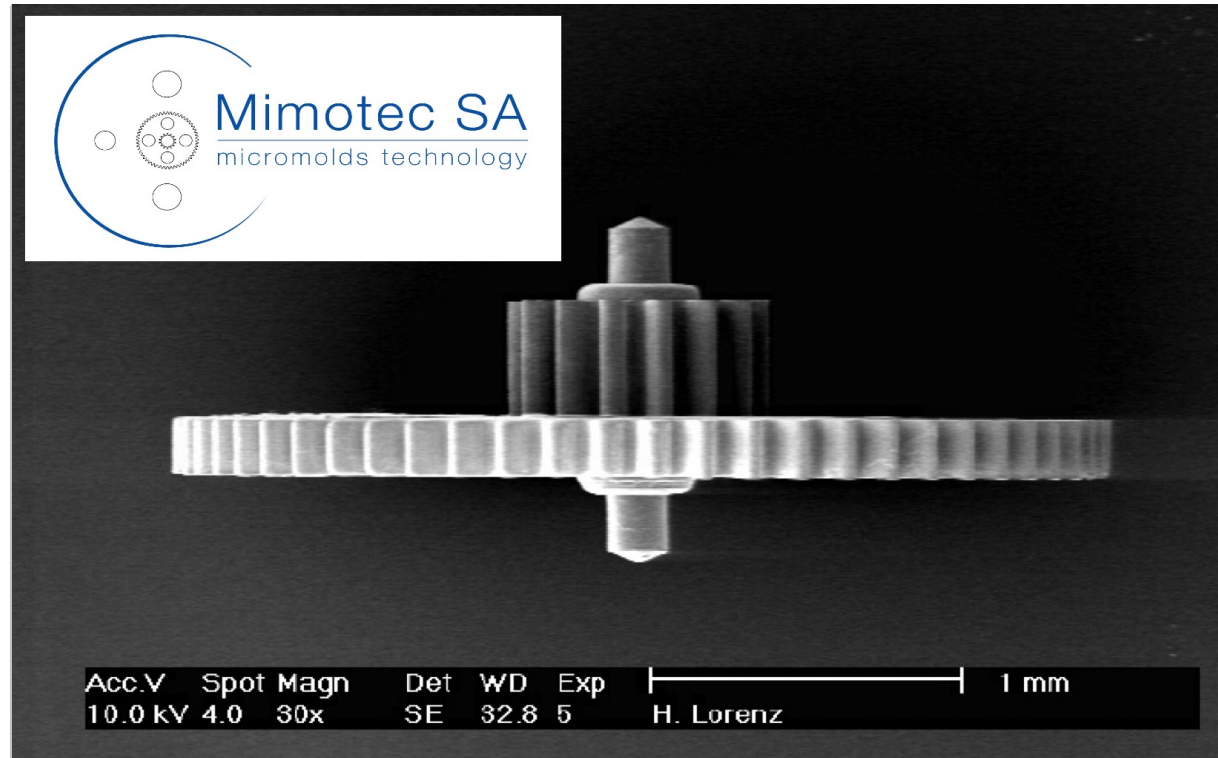
Directional deep brain stimulation electrode



aleva
NEUROTHERAPEUTICS

- Non-photosensitive polyimide
- Biocompatible elastomers

Watch components

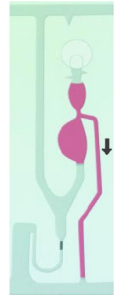


- UV-LIGA
- Injection molded for components production

Micro Fluidics: Centrifugal microfluidics on a disk

- Injection molded disk
- Capillarity to enter fluids
- Centrifugal forces

Overflow channel
activated, 2 000 rpm
for 2 seconds.



Structure filled by
capillary action.

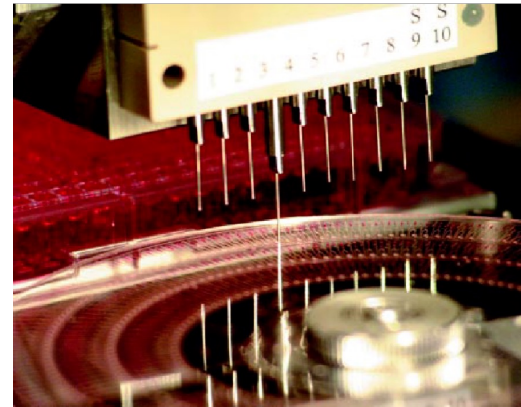
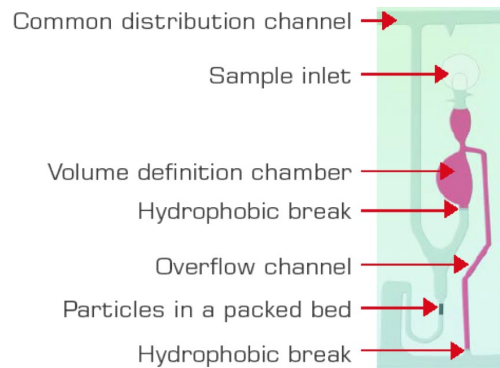
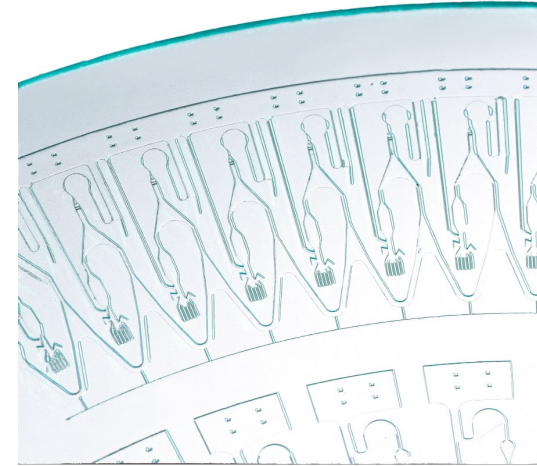


Volume defined within
the chamber.



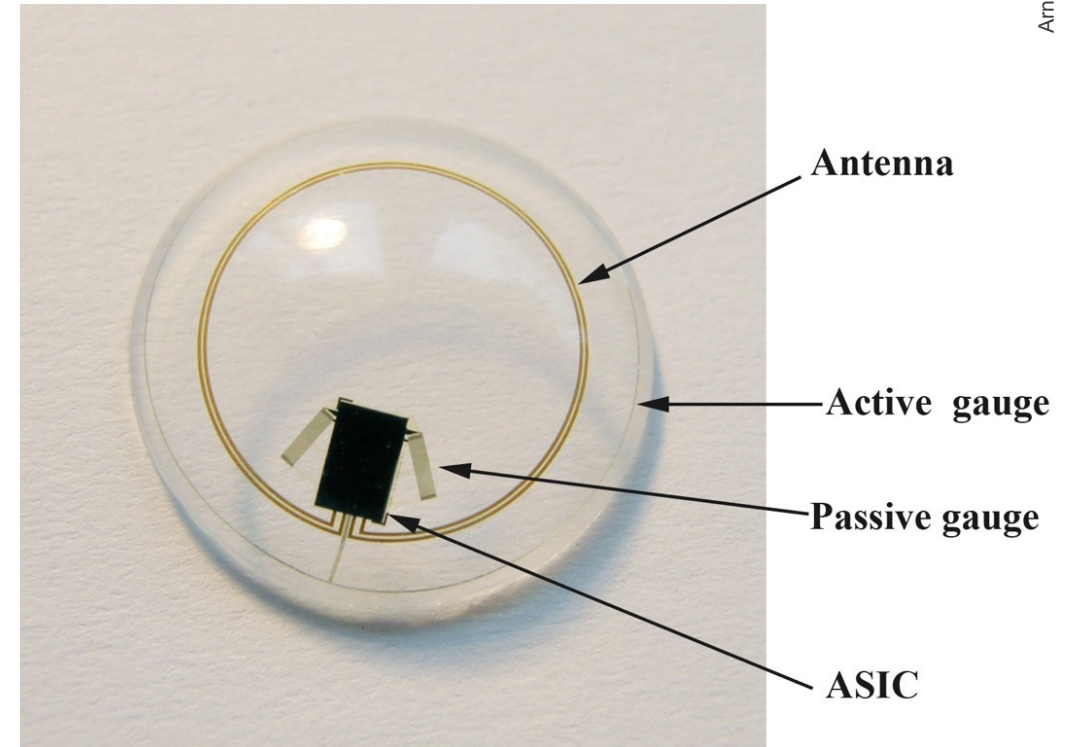
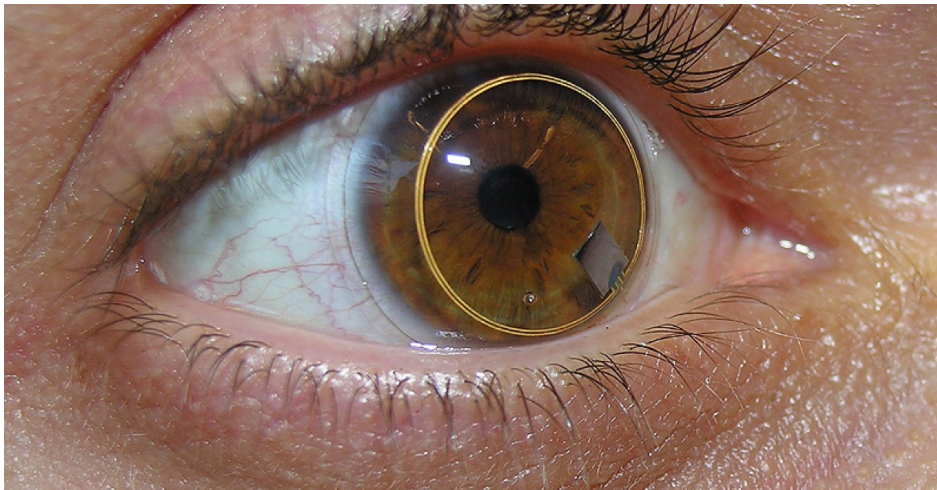
Sample loading onto
packed bed, controlled
flow for 2 minutes.

GYROS



A soft contact lens for Glaucoma detection

- Non photosensitive Polyimide
- Molding of biocompatible elastomers
- Two-step molding



Conclusion

- **Polymers** will not replace silicon.
- They open the way for new applications fields of MEMs.
- High volume production of MEMS by replication
- Biomedical applications
- Cell-based applications
- Microfluidics

EPFL

