Micro/Nano-structured Functional Surfaces & Components

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Section Head Nanoscale Technology

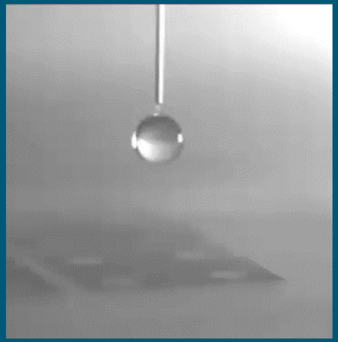
Why surface nanostructuring?

Optics

US 8,542,442 B2

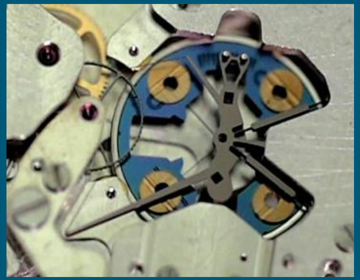
- Anti-counterfeiting OVDs
- Structural & plasmonics colours
- Light trapping (PV)

Wettability & anti-icing



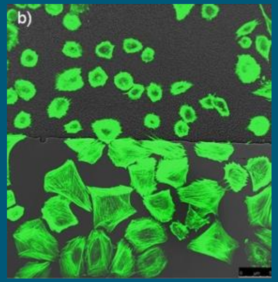
- Controlled wetting
- Oleophobicity
- Anti-icing

Adhesion & friction



- Dry-adhesion
- COF and wear control

Sensing & biology



- Sensitive sensor
- Biodiagnostic platform
- Control cell-substrate interactions

Trends & Objectives

Global trends

- Nanostructured, functional and responsive surfaces find applications in many different sectors: bio- and med-tech, medicine, sensors, agriculture, energy, ICT, transportation but surface modification processes should meet the standard set by industry (cost efficiency, reproducibility, robustness, 2&3D surface)
- Smart coatings capable of actively responding to its environment in a functional and predicatable manner become reality; main challenge here is to allow the production of thin films with controlled morphology at the nm scale, improved adhesion and long term performances.

Long-term objectives

- Reliable structuring and functionalization processes for the modification of surface properties (anti-stiction, hydro-phobic/philic, metal plating) or for the elaboration of functional mesoporous thin films with extended range of porosity and composition (sensing)
- From 2D surface to complex 3D components: alternative coating techniques
- Broadened material and structuring techniques portfolio (multi sectorial application domains)
- Upscaling (large area/high throuput surface modification): automated surface modification processes

Objective and strategy

Origination of Micro-/Nano-structures and

Self- Assembly eg. Nanosphere lithography Sol-gel processes

→

Upscaling or Replication

Dry etching
Hot embossing
UV nanoimprint
Injection Molding
Slot Die Coating

→

Surface functionalization

Molecular vapor deposition (SAMs, metal oxide thin films)
Dye or Enzyme Encapsultation

→

Characterization & Integration

Performance evaluation

Demo: Nanostructured functional components

Agenda

- Introduction to Self –Assembly: definition and some "historical examples"
- Fabrication of Nanostructured Surfaces and Component using Nanosphere Lithography
- Functional Surfaces: self-assembled nanolayers for substrate metallization
- Responsive Surfaces: mesoporous sol-gel layer for sensing application
- Extension to new patterning/printing techniques for sensing

Introduction to Self-Assembly

Self-Assembly, some pioneers

Science, 1991, Vol.254, p.1312

Molecular Self-Assembly and Nanochemistry: A Chemical strategy for the Synthesis of Nanostructures

George M. Whitesides, John P. Mathias, Christopher T. Seto

- **Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by noncovalent bonds**
  - weaker and less directional bonds such as ionic, hydrogen bonds and van der Waals interactions (0.1 to 5 kcal/mol) relative to covalent bonds (40 to 100 kcal/mol) and comparable to thermal energies (RT=0.6 kcal/mol at 300K)
  - Stability achieved when molecules in self-assembled structures are joined by many of these weak noncovalent interactions (e.g. via large molecular area in VdW contact, multiple hydrogen bonds)

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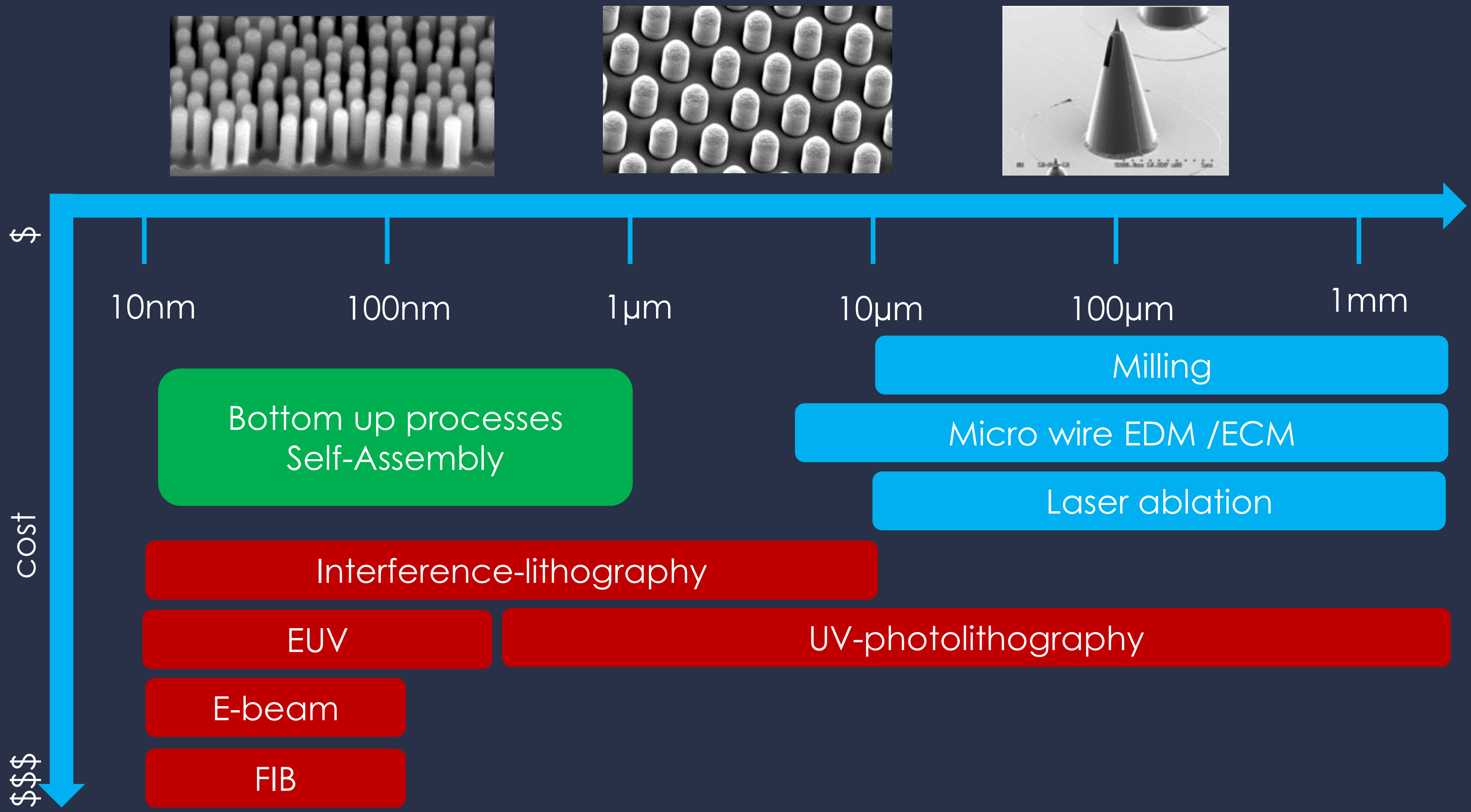
Self-Assembly, some pioneers

- Self-assembly is also emerging as a new strategy in chemical synthesis, with the potential of generating structures with dimensions of 1 to 10^2 nanometers (with molecular weights of 10^4 to lo10^{10} daltons). Structures in the upper part of this range of sizes are presently inaccessible through chemical synthesis

- The ability to prepare them would open a route to structures comparable in size (and perhaps complementary in function) to those that can be prepared by microlithography and other techniques of microfabrication.

Fabrication techniques for micro & nano-structuration

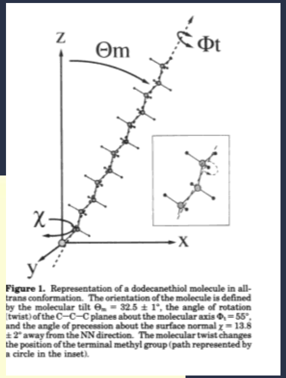


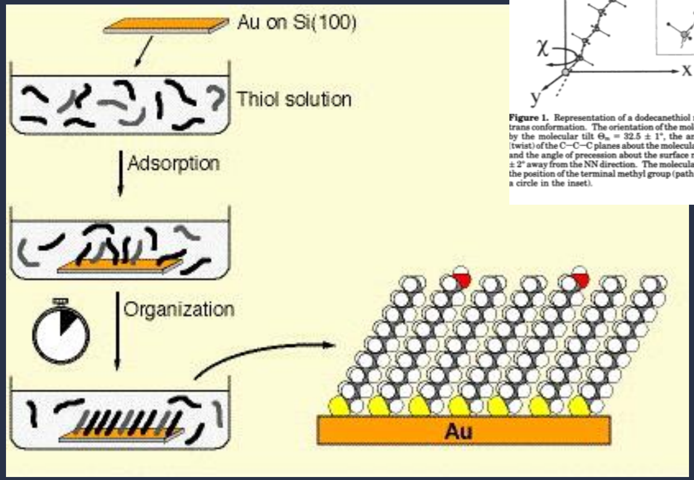
Example 1: SAMs of functionalized alkanethiols on gold

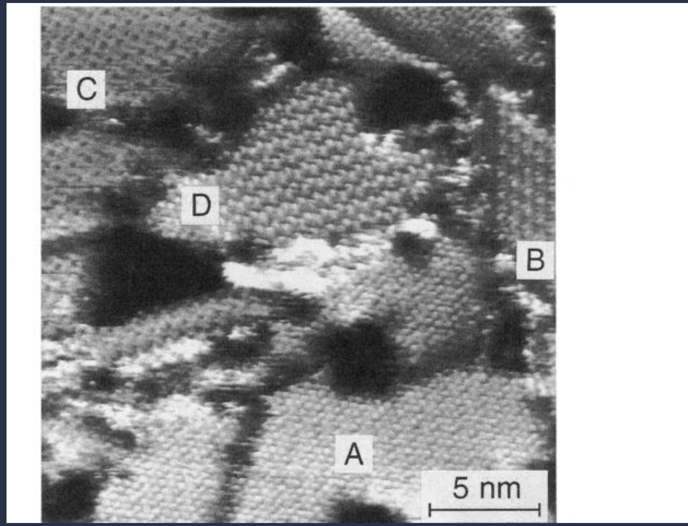
- Initial adsorption is fast (seconds) but 15 hours needed to obtain well-ordered defect free SAMs. Multilayers do not form

- The structure results from a balance of the S-Au chemisorption, S-S interaction and interaction between neighboring alkyl chains (Transm. Elect. Diffraction, XRD, molecular dynamics simulation)

- Different superlattices with several molecular conformations. Thermal annealing improves molecular packing







Langmuir **1994**, *10*, 2869
Real-Space Observation of Nanoscale Molecular Domains in Self-Assembled Monolayers
E. Delamarche et al.

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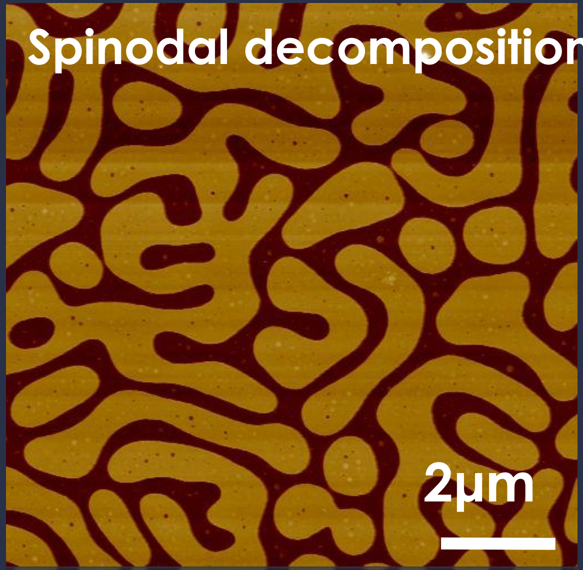
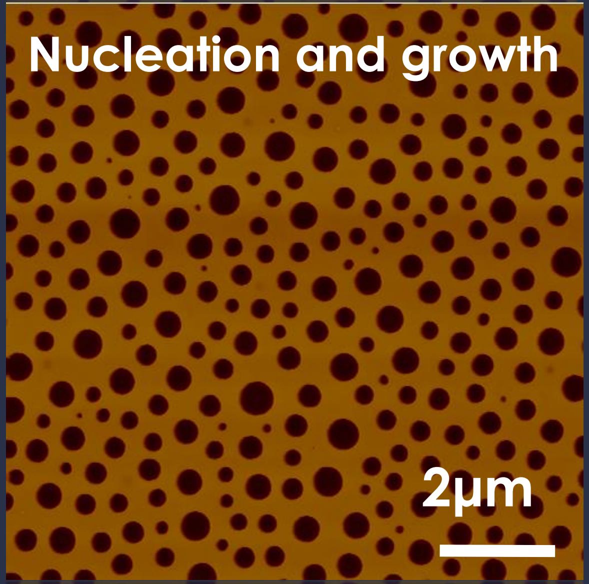
Example 2: Polymer self-assembly based structures

- The structures are larger than the length of the polymer chain (µm and sub-µm range) and have peculiar morphologies (dots or worm-like) depending on the blend composition and processing conditions

- The structures are stochastic with respect to shape and order but present well-defined length-scale

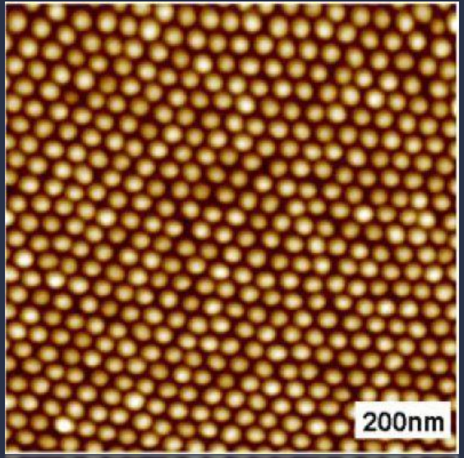
- Tunable size, depending on e.g. the polymers' size, their weight ratio, the solvent , the surface energy of the substrate, the humidity rate .



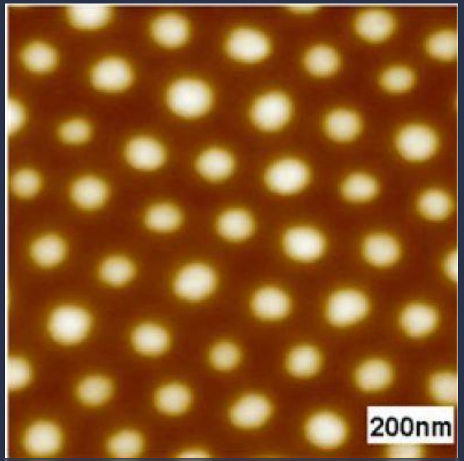


Example 3: Block-copolymer self-assembly

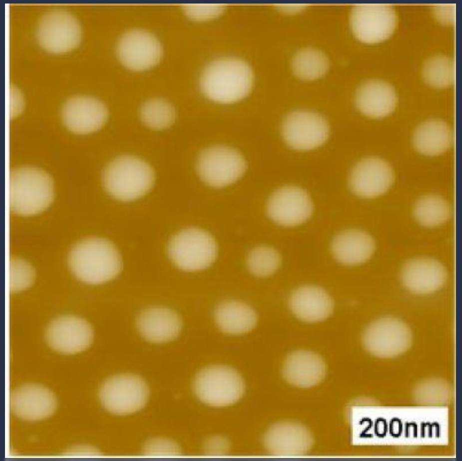
- Periodicity and size can be easily tuned by adjusting polymer molecular weight, block-ratio and deposition parameters (e.g. PS-b-PVP)



23500-b-25500 g/mol



91500-b-105000 g/mol



190000-b-190000 g/mol

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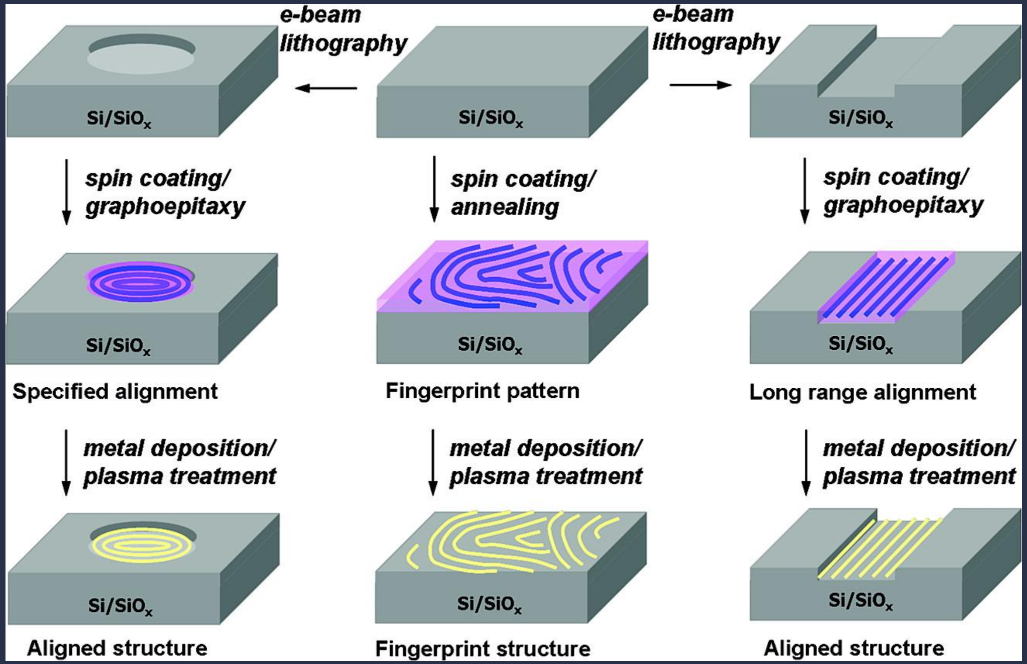
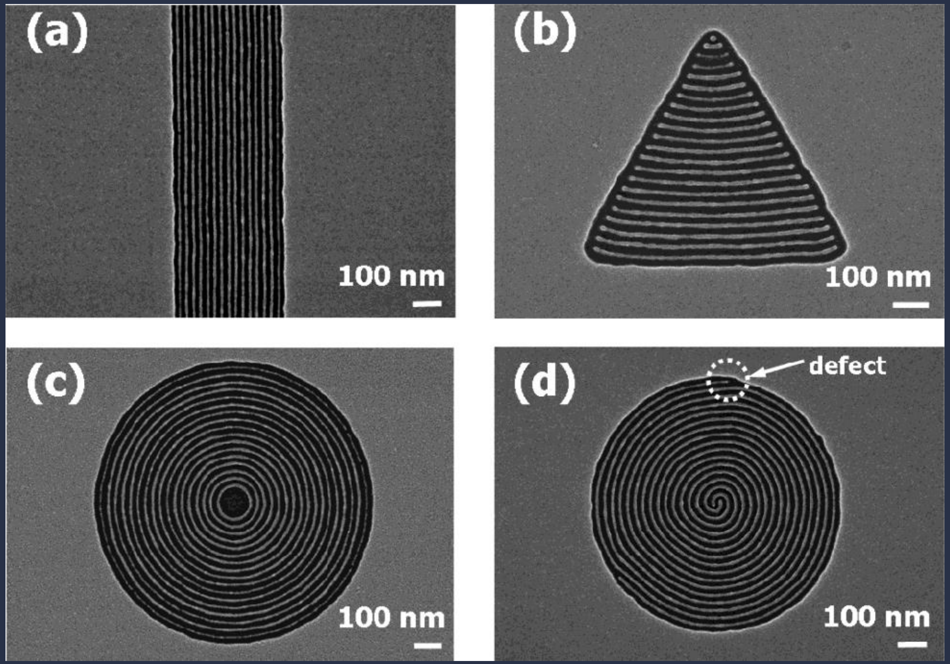
Krishnamoorthy *et al.* *Adv.Funct.Mat.* 2006, *16*, 1469

Example 4: Guided Self Assembly to improve ordering

- **Graphoepitaxy:** use prepatterned surfaces to improve ordering of the self assembled structures (eg. for application in Optics)





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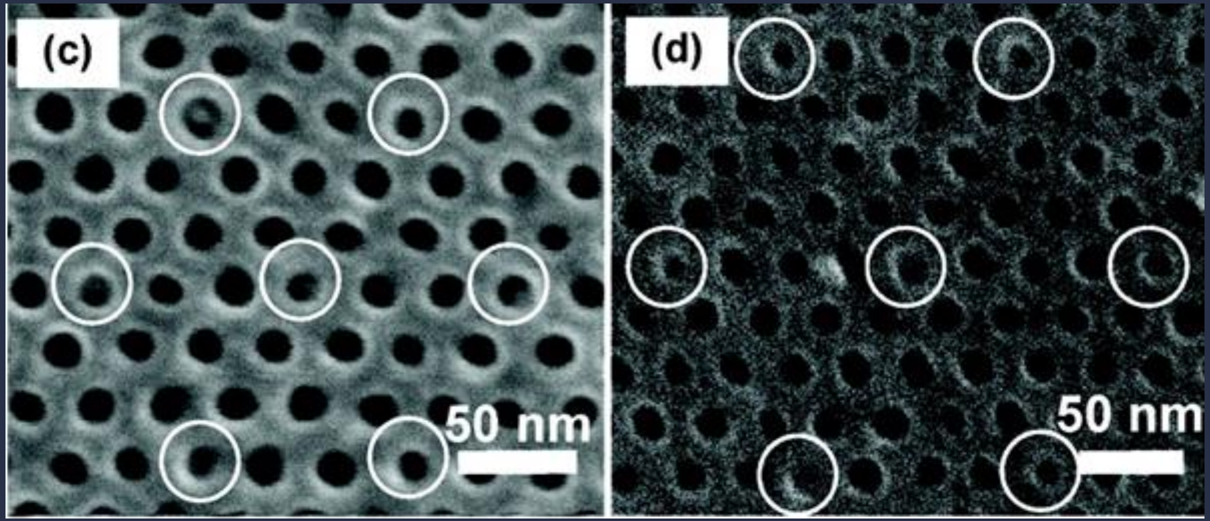
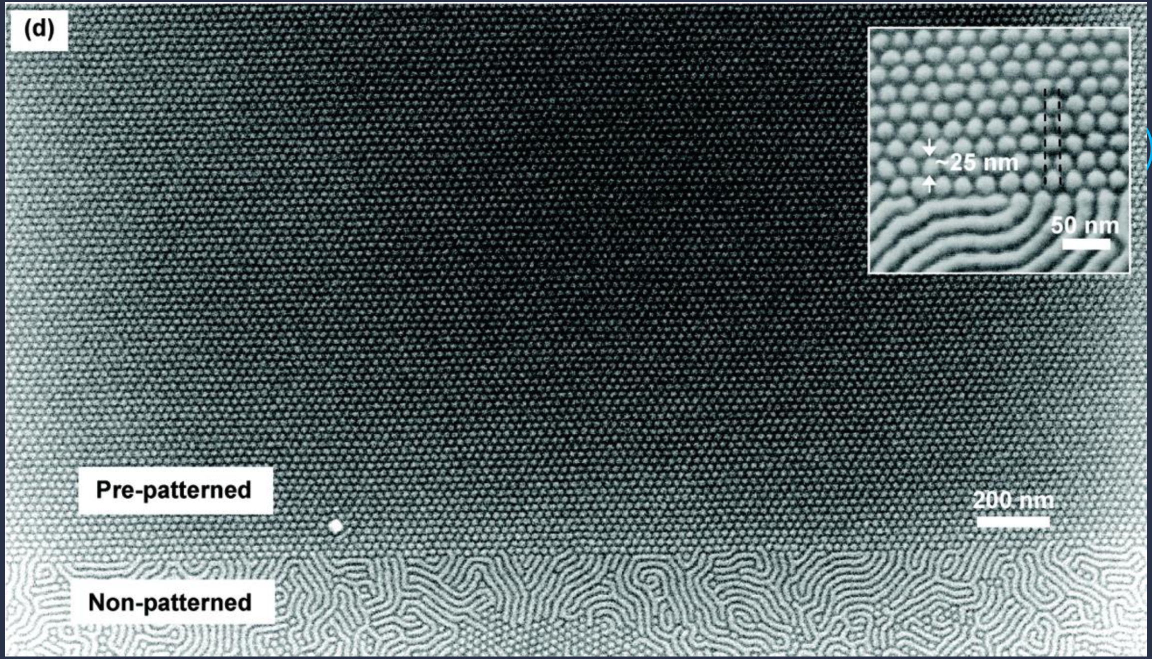
Example 5: Guide Self-Assembly to improve ordering

- Use e-beam to pre-structure the substrate (Seagate/Hitachi)
- Application: New patterned media at 1Tbit/in2 and beyond

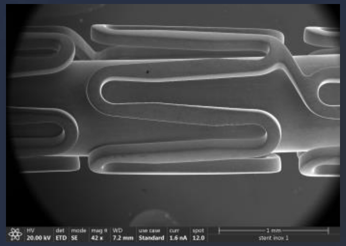




Wan et al, Langmuir, 2009, Seagate research centre

Fabrication of Nanostructured Surfaces and Component using Nanosphere Lithography

Which process for which surface ?

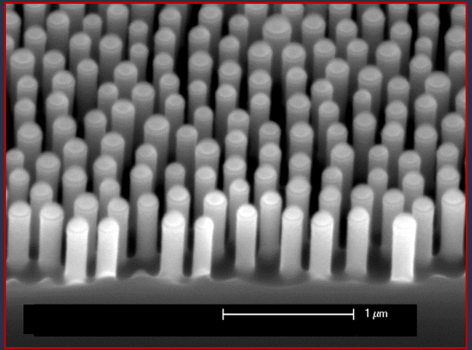


Surface nanostructuring
Etch mask fabrication + etching

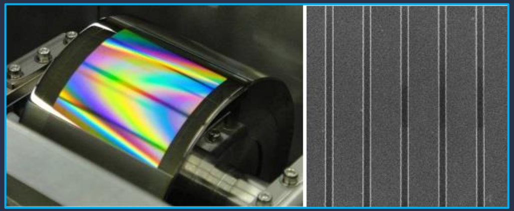
2D Planar
- *Photo-lithography*
- *NIL*
- *Spin coating*
- *PVD/CVD/ALD*
- *Dry/wet etching*
- *Pre-post-processes*

3D Freeform
- *Self limiting deposition*
- *Nanosphere lithography*
- *ALD*
- *Pre-post-processes*
- *Wet/vapor etching*

2.5D Curved Multilevel
- *NIL-flex stamp*
- *Pre-post-processes*
- *Dip-Spray-coating*
- *Special dry/wet etching*
- *Special photo-lithography*
- *PVD/CVD/ALD*



Glass surface structuring



Seamless roller (www.asahi-kasei.co.jp)

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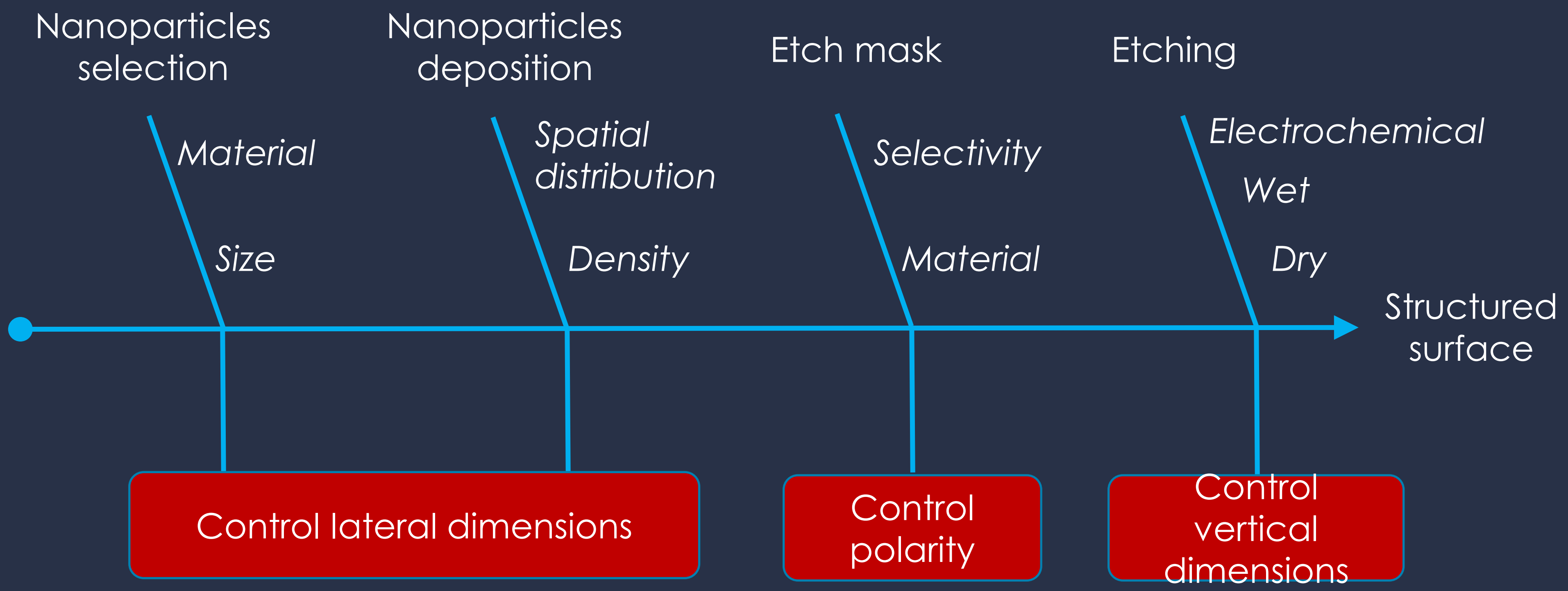
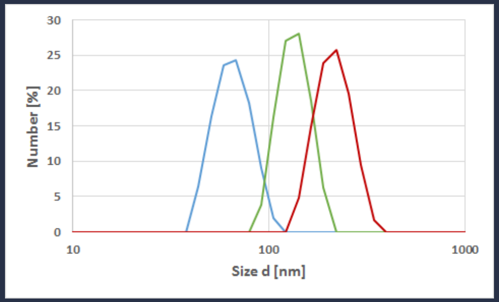
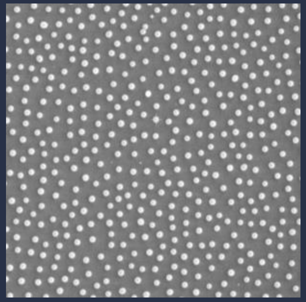
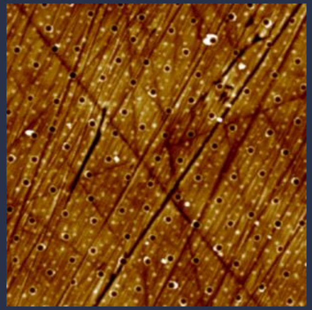
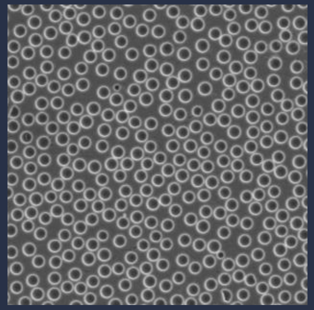
Nanosphere Lithography / Process flow



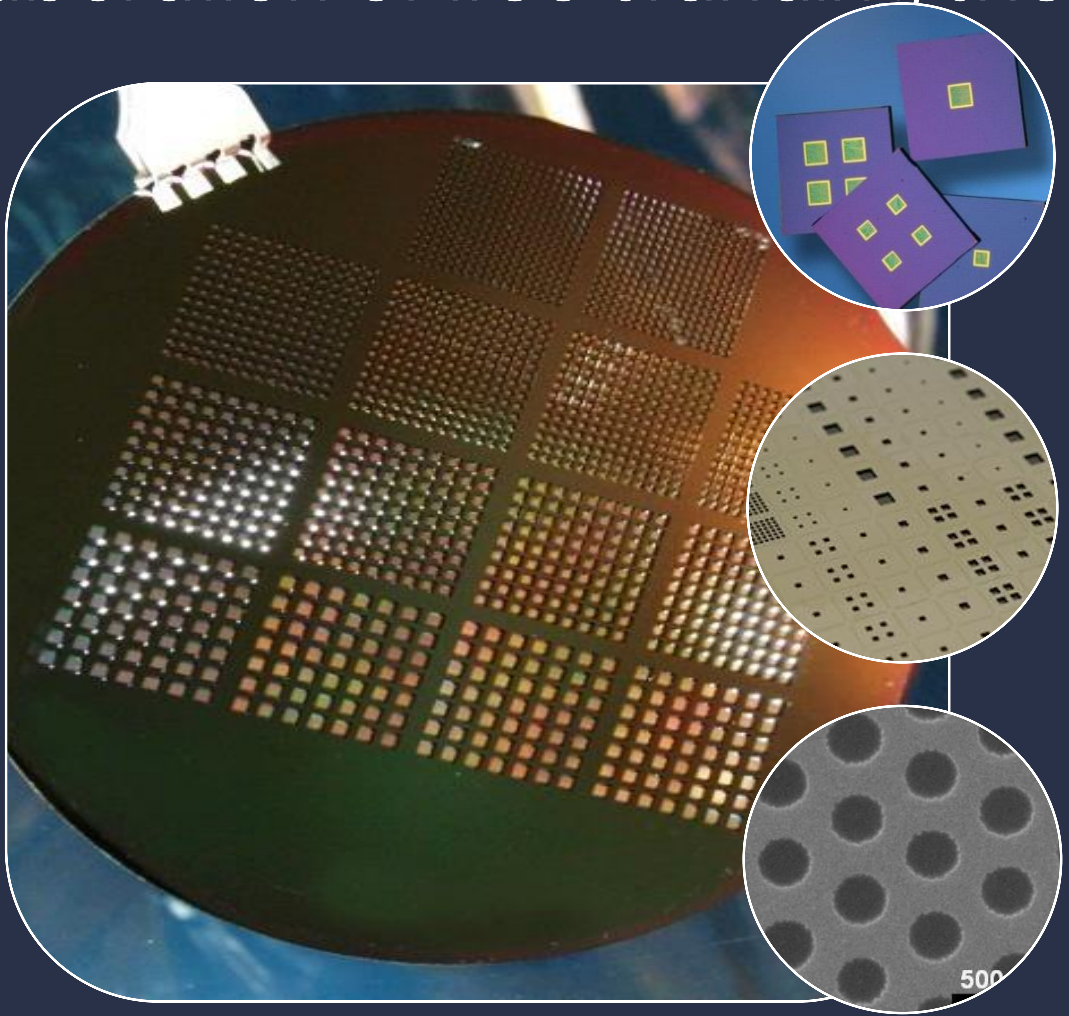








Hybridation with standard microfabrication process for the elaboration of free-standing silicon nitride membranes



PROPERTIES

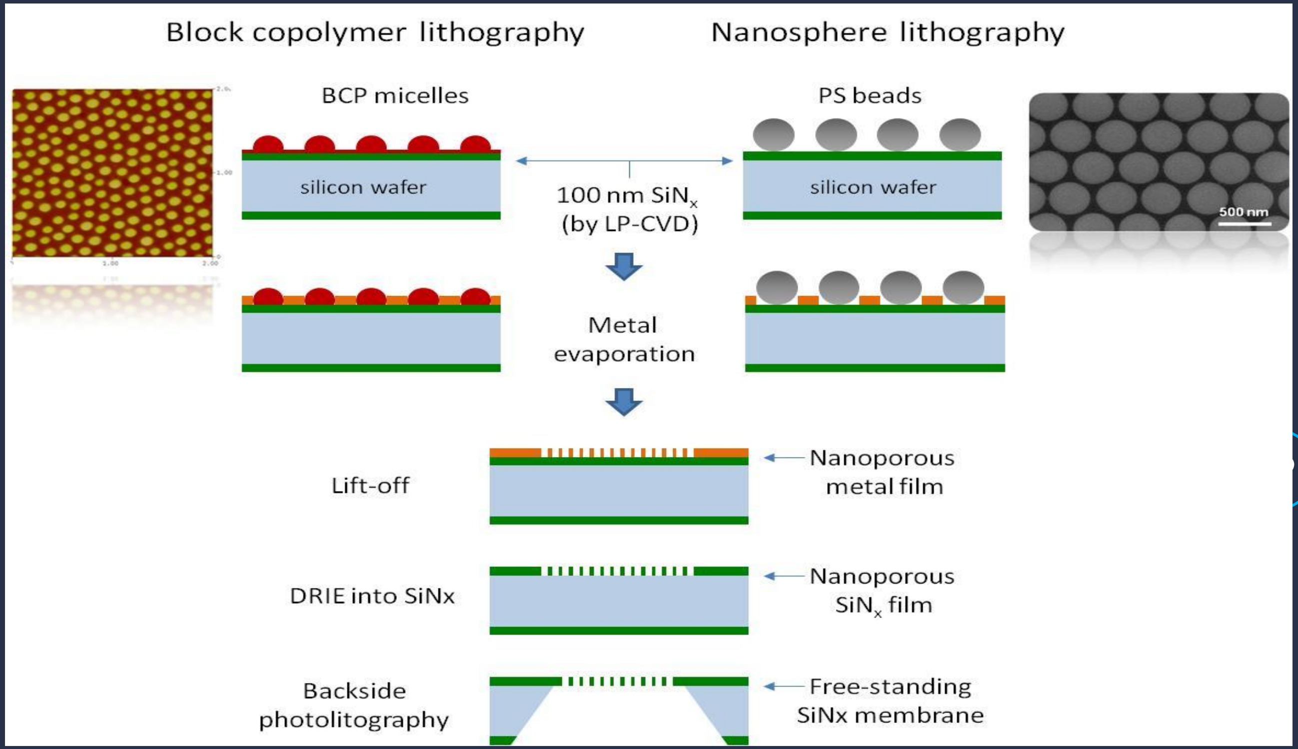
- highly selective membranes
- fast transport rates
- minimum sample loss
- chemical and thermal stability
- facile post-functionalization

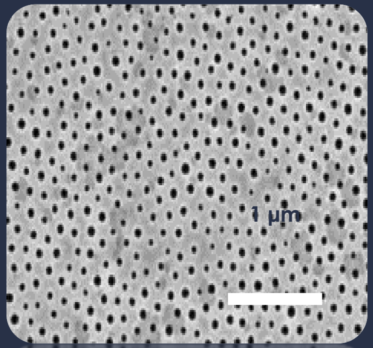
MEMBRANE SPECIFICATIONS

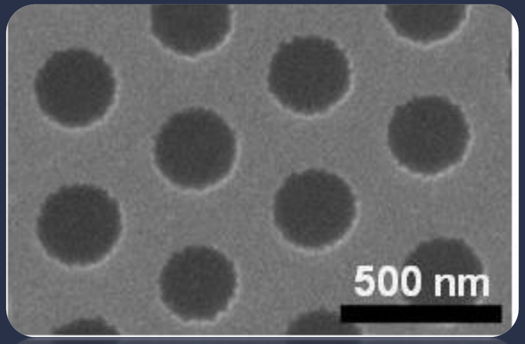
- pore size range: 10 nm up to several µm
- narrow pore size distribution
- high pore density. up to 10^{10} cm^2
- ultrathin SiN films: 100-500 nm (adjustable)
- autoclavable, reusable

Self-assembly processes for nanopatterning

- Ultrathin nanoporous SiN produced combining self-assembly at the nanoscale and micro-fabrication techniques.
- Ability to adjust independently nanopore size **(10-500 nm)**, porosity and membrane thickness
- Automated bead deposition process: reproductibility and homogeneity demonstrated on 150 mm wafer

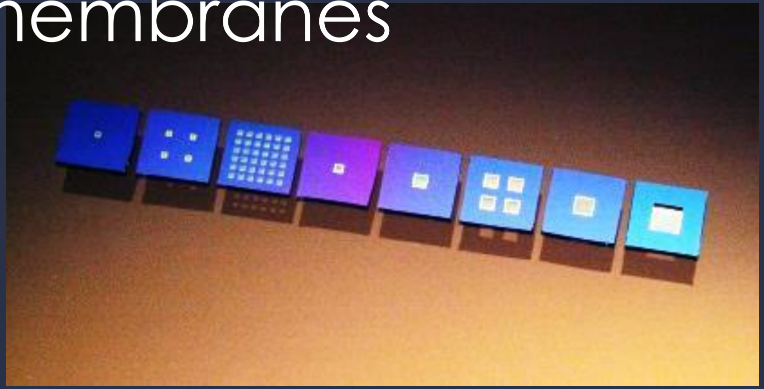


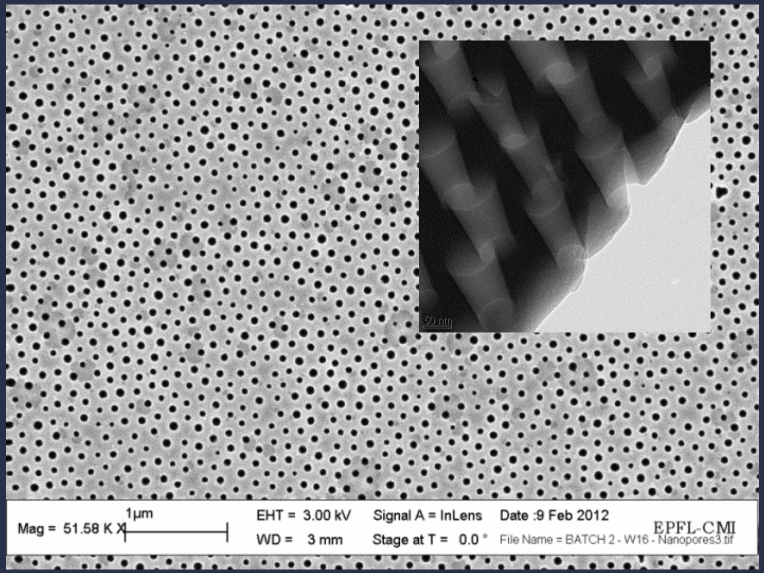




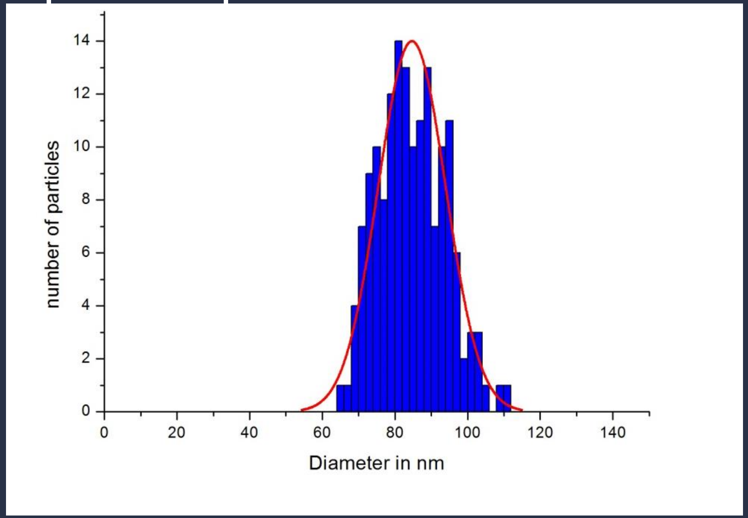
Morphological properties of nanoporous membranes

- 100 -200nm thick free standing nanoporous SiN film.
- Nanopore diameter = 85nm.
- Nanopore density ≈ 4.10^9 pores/cm^2.
- Membrane size 300x300µm^2 up to 2x2mm^2.





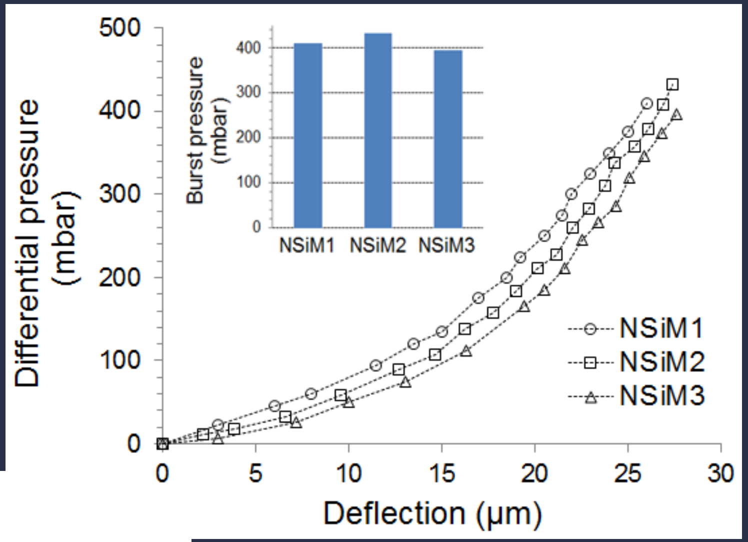
SEM & TEM images of nanopores

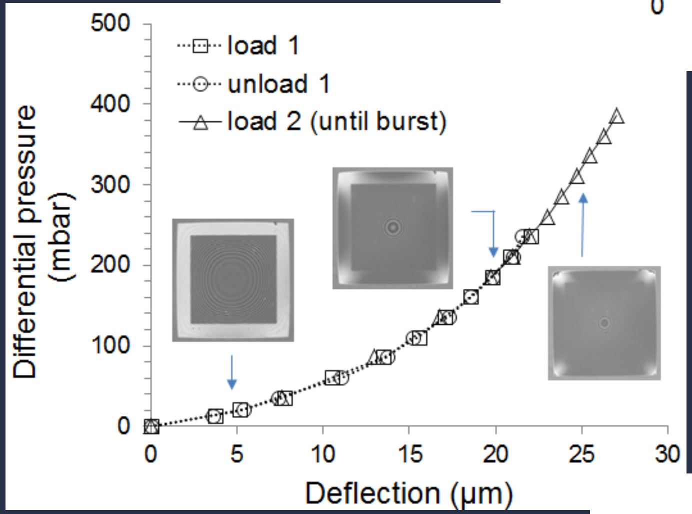


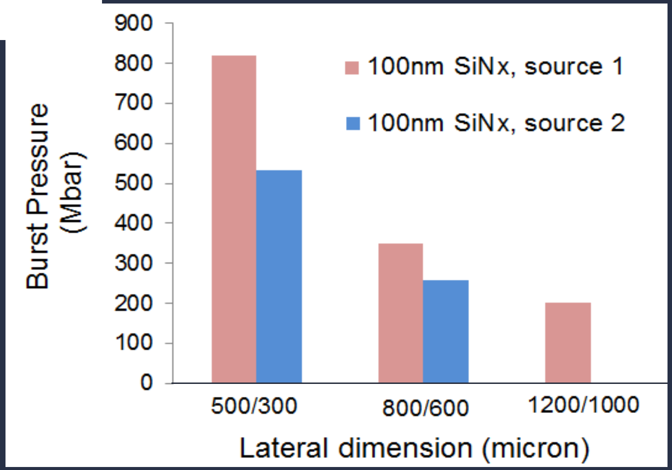
Size distribution analysis of nanopore diameter

Mechanical stability

- No hysteresis.
- Reversible & elastic membrane deformation.
- Very good repeatability of the measurements
- Large influence of membrane dimensions, SiN type, thickness & porosity on burst pressure







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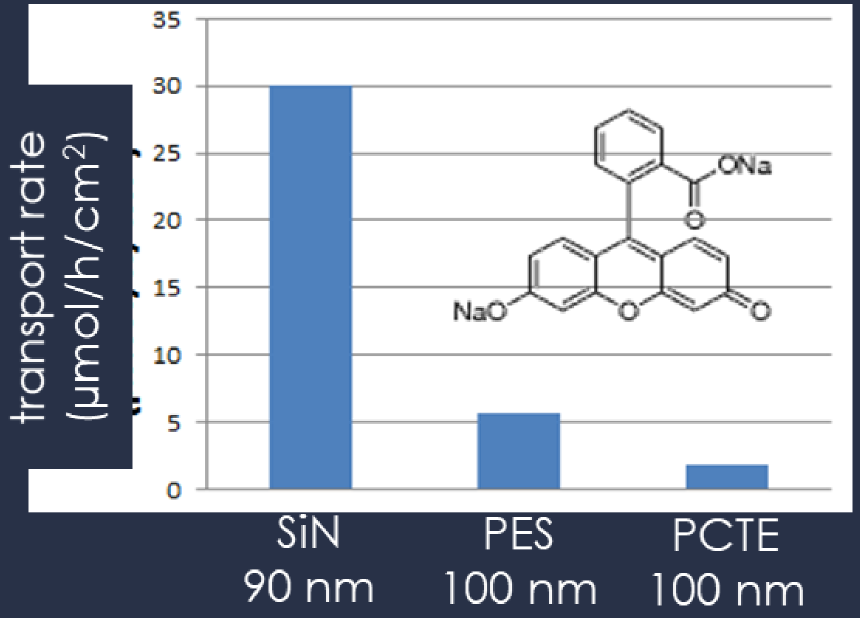
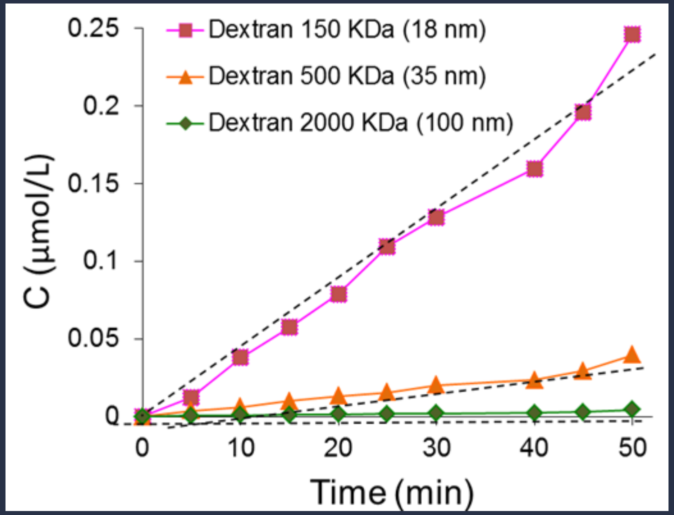
Nanoporous membrane transport and separation properties

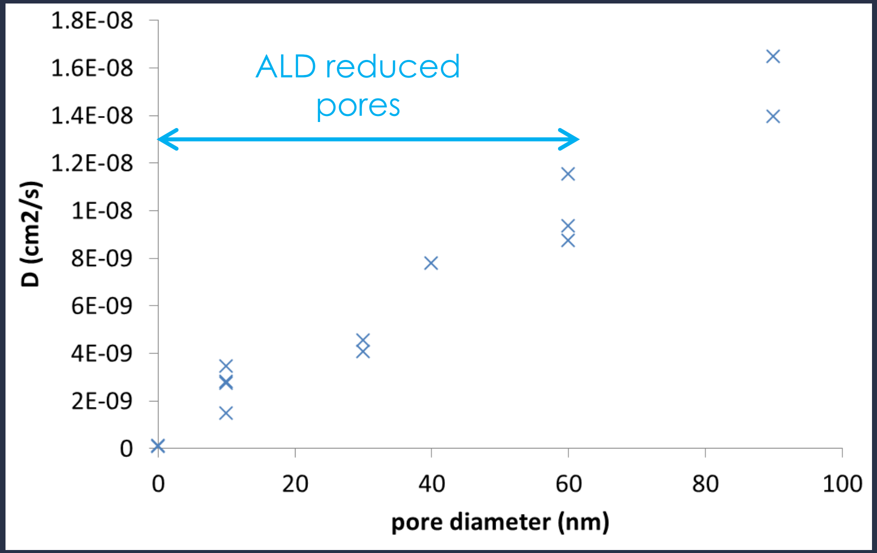
- Comparison with commercial PES and track-etched PC membranes.
  - 6 to 15-fold higher transport rate on SiN membranes
- Size-based separation
  - Tested with dextrans of various MW
  - Pore size 90nm
  - Excellent selectivity

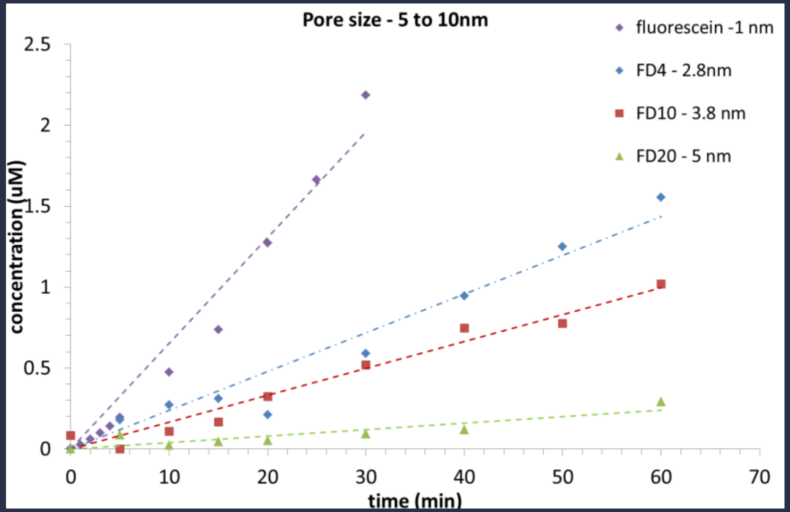




Pore size reduction using Atomic Layer Deposition (ALD)

- Pore size control (r<40nm) is achieved via Atomic Layer Deposition of Al_2O_3.
  - Diffusion of sodium fluorescein shows the effect of the pore constriction
- Reduced pore size (5-10nm) – ALD 40nm
  - C_0 = 500 µM
  - Size-based filtration of very small biomolecules e.g. unbound anticancer drugs





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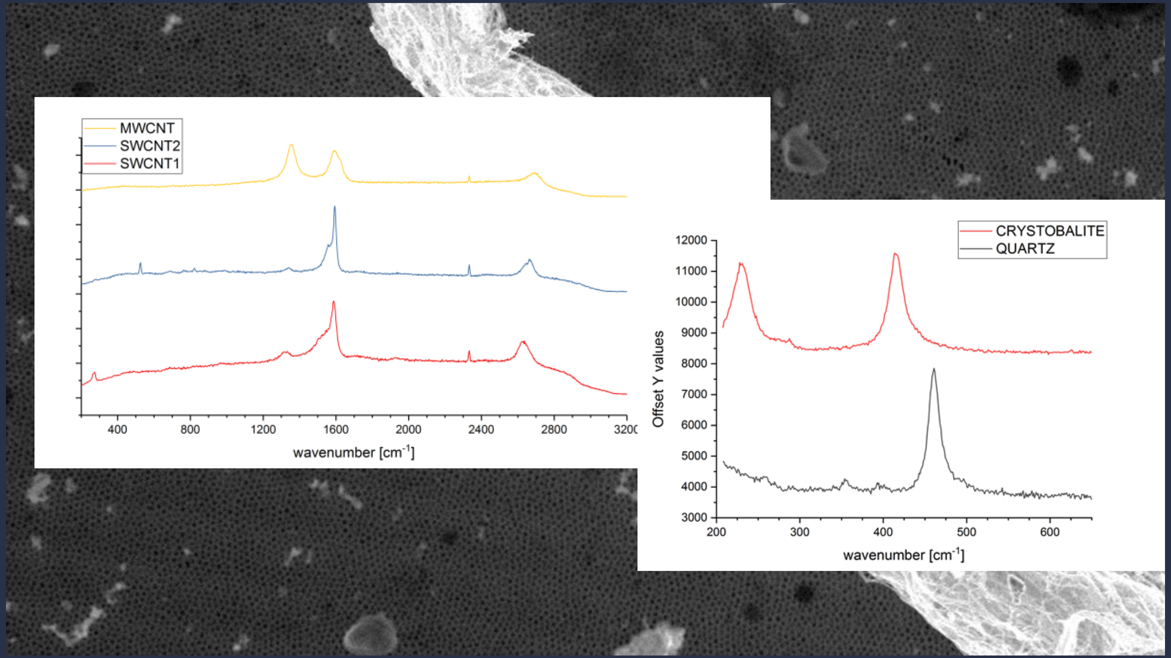
NSiMs for monitoring exposure to nps

- Stat Peel original detection device is specifically designed to monitore exposure to potentially harmful fibers and platelets
- Membranes are integrated in a filtration slides to gather particles from the filtered air
- Full Raman spectra allow to classify the detected material and thus calculate its mass.
- Detection limits: sub ng for SWCNTs, a few ng for MWCNT, graphene, respirable crystalline silica, TiO_2, metal oxides



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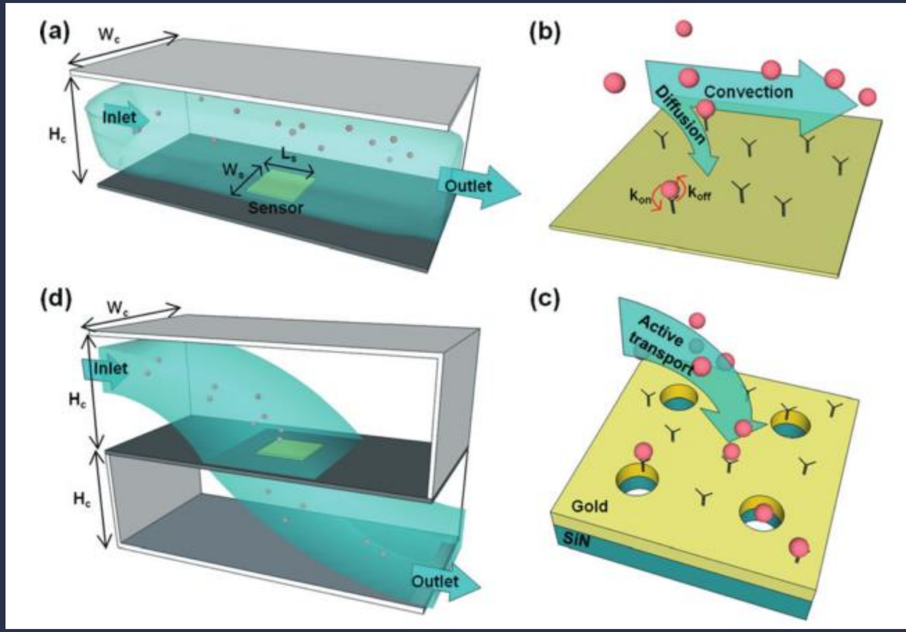
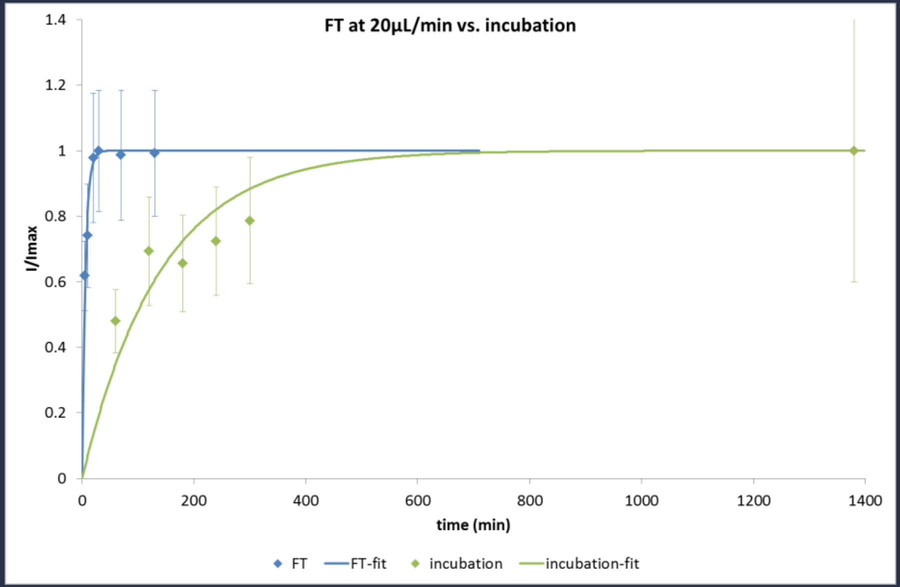
Flow through micropores decreases significantly the response time





1st order kinetics fit

$$\frac{I}{I_{max}} = 1 - e^{-t/t_0}$$

	t_0
Incubation	126-140 min
5µL/min flow	49 min
20µL/min flow	6 min
50µL/min flow	1min
100µL/min flow	2min

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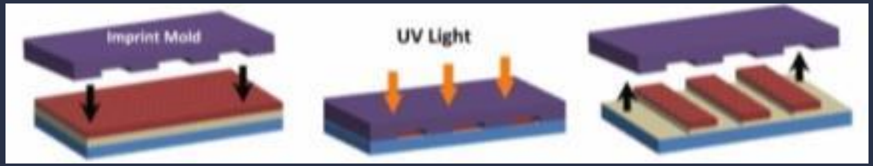
Surface structuring using micro/nanoreplication techniques

- UV Nanoimprint
  - Rapid prototyping
  - High accuracy
  - UV-curable resins (PUA, sol-gel)
- Hot embossing
  - Small series production
  - Thermoplastic & thermosetting materials
- Injection molding
  - High throughput
  - Large series production



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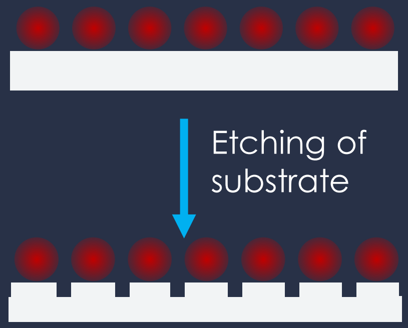
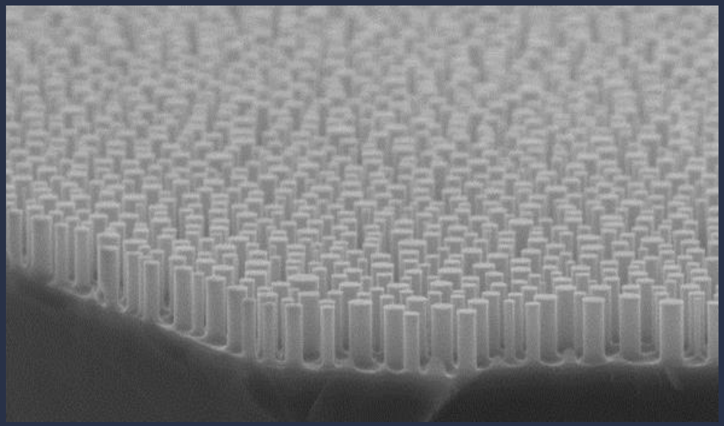
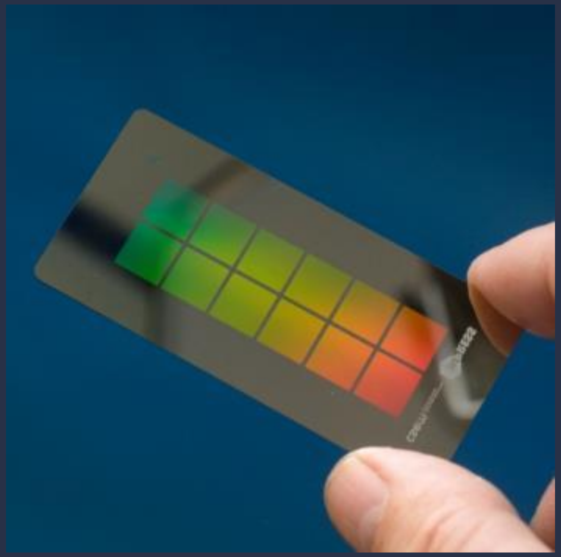
Fabrication of different replication tools, Ni shims

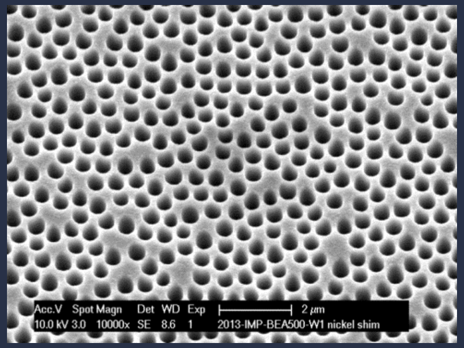
- Processing of silicon-based materials





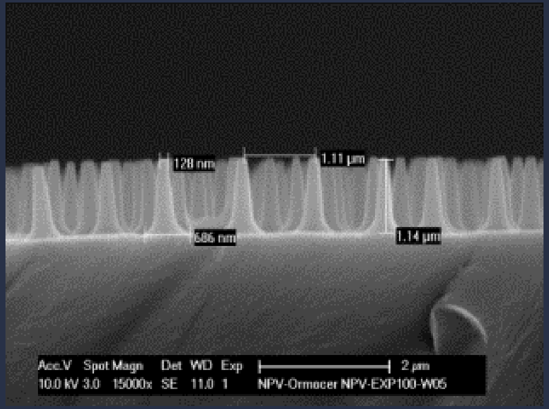
- Fabrication of nanostructured Ni shims
  - Silicon insert used as template for electroforming

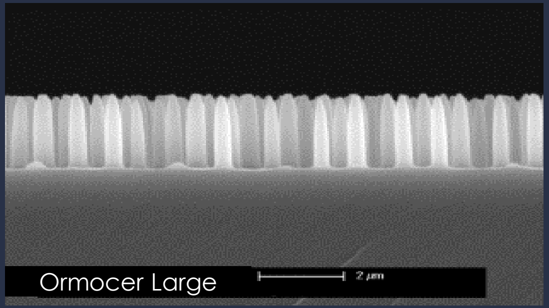


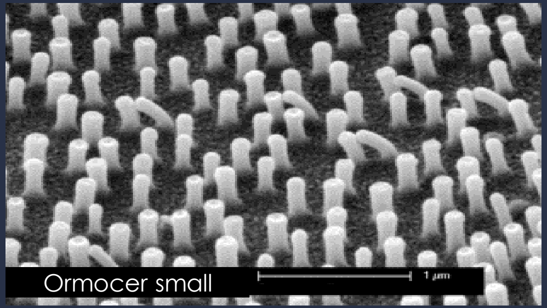


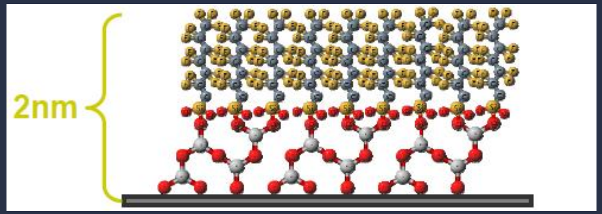
Controlled wettability of surfaces using nanostructuring

- Replication of micro/nanostructures by hot embossing (PC) or UV nanoimprint.
- Deposition of perfluorinated SAM on plastic or UV curable resin
- Wettability characterization: dynamic water contact-angles, videos of drop impacts









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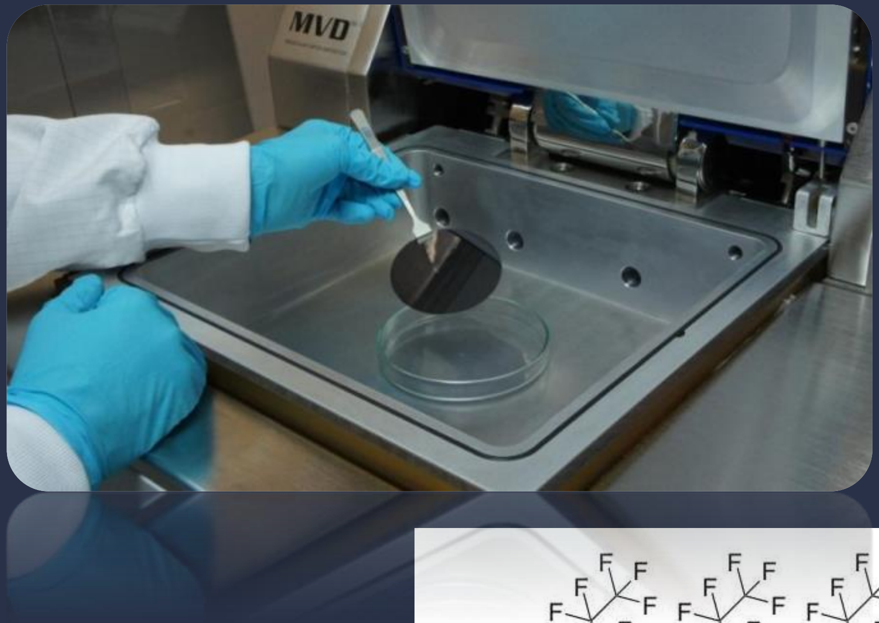
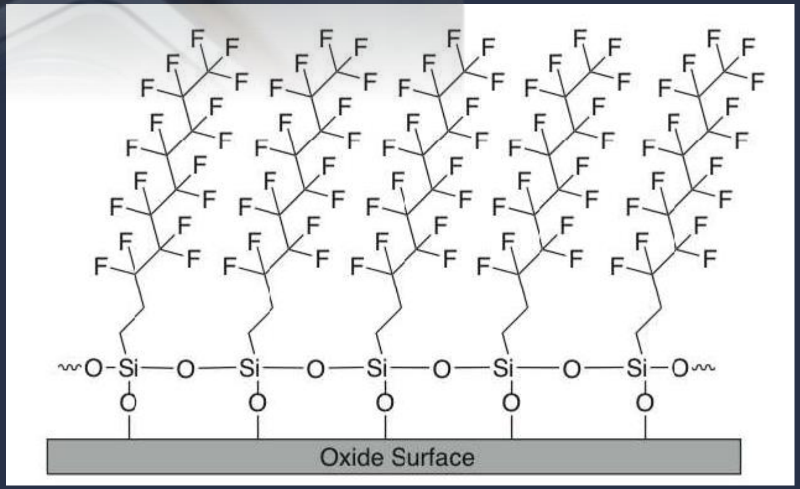
Superhydrophobic surface by Molecular Vapor Deposition

- Conformal coating down to nm scale
- Precise layer thickness control
- Deposition on temperature sensitive materials-polymers
- Know-how of intermediate layer creation;
- Wide choice of chemicals





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Contact angle measurements

- To describe correctly surfaces wettability, both dynamic contact-angles are necessary (advancing **and** receding contact angle)

Advancing contact angle (θ_a) Receding contact angle (θ_r)

Contact-angle hysteresis $\Delta\theta = \theta_a - \theta_r$

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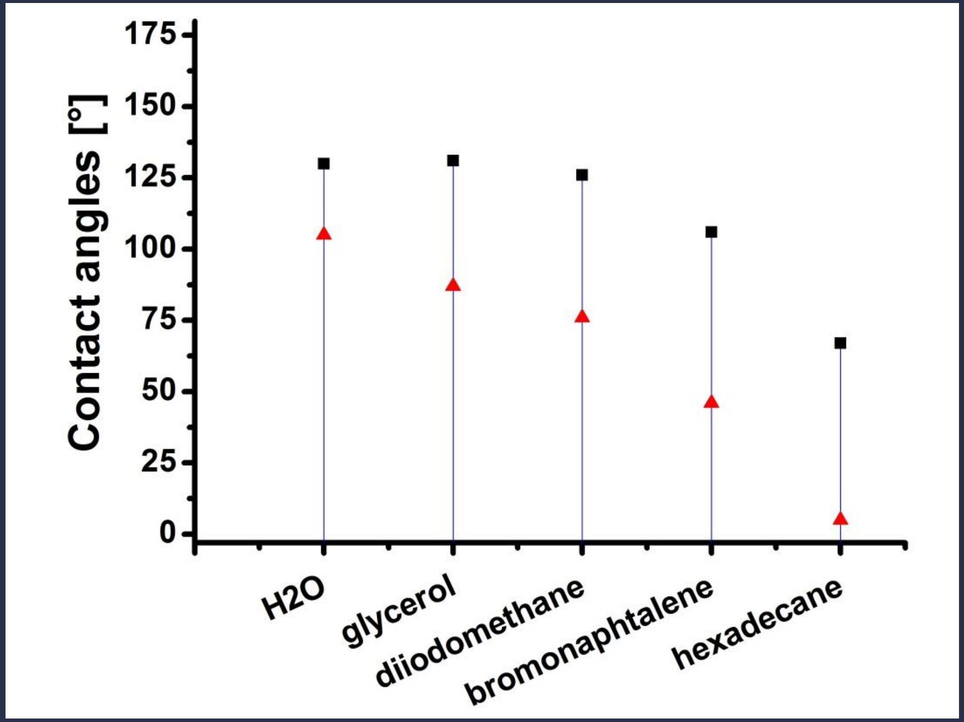
Stability of the superhydrophobic states

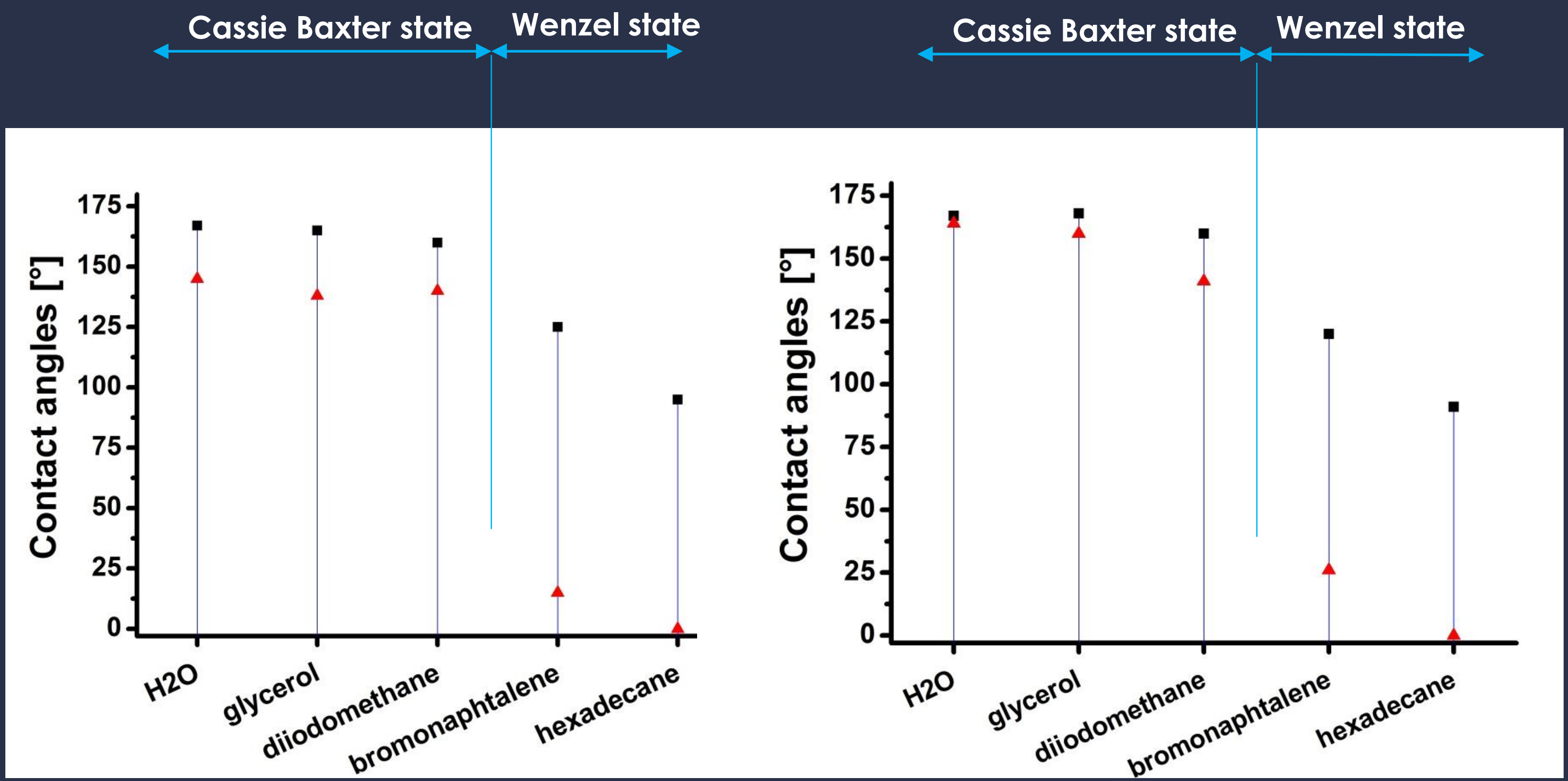
- Dynamic contact angles for flat Ormocer surface treated with a perfluorosilane layer



Liquid	Surface tension [mN/m]
Water	72.8
Glycerol	64
Di-iodomethane	50.8
a-Bromonaphtalene	44.4
n-hexadecane	27.5

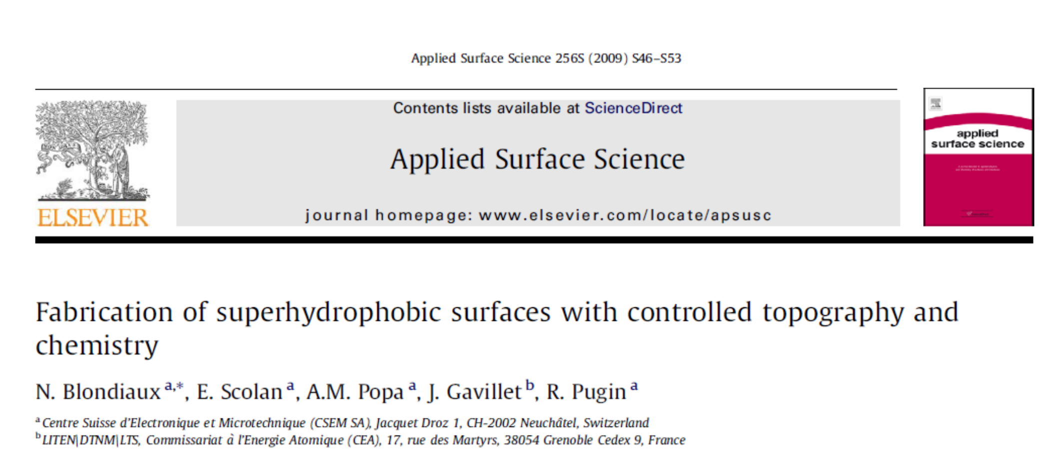
Stability of the superhydrophobic states

- Dynamic contact angles for **structured Ormocer** samples treated with a perfluorosilane layer



Ormocer Small

Ormocer Large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Fabrication of superhydrophobic surfaces with controlled topography and chemistry

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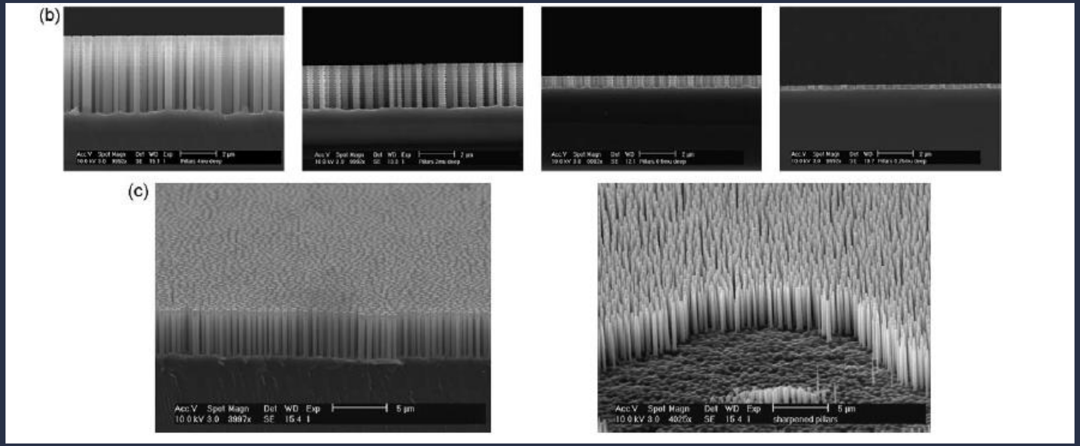
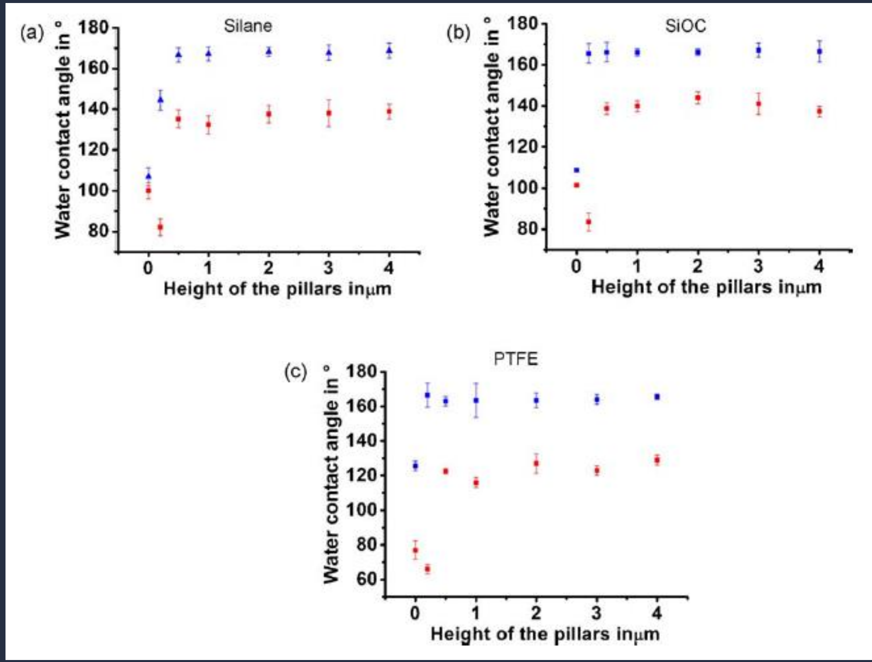
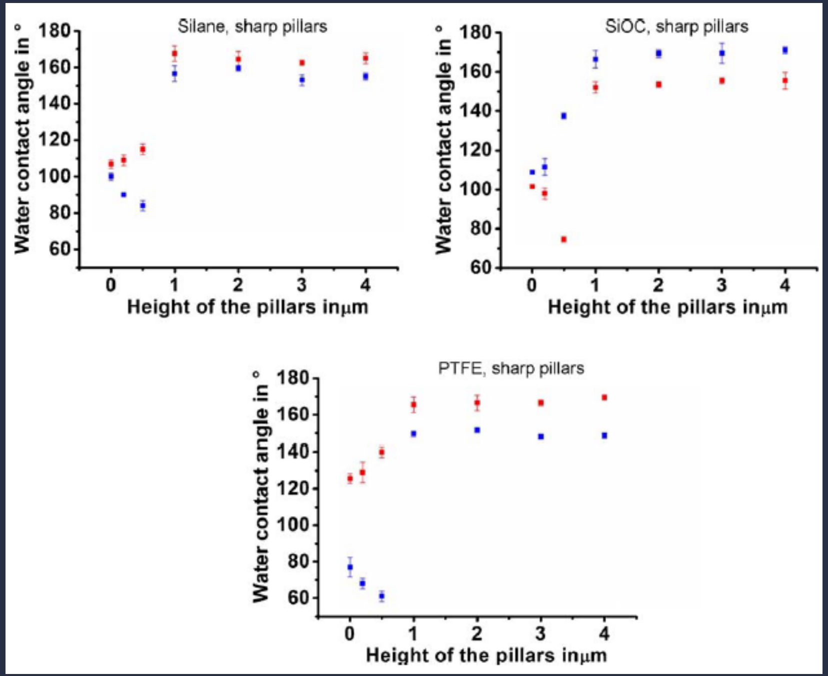
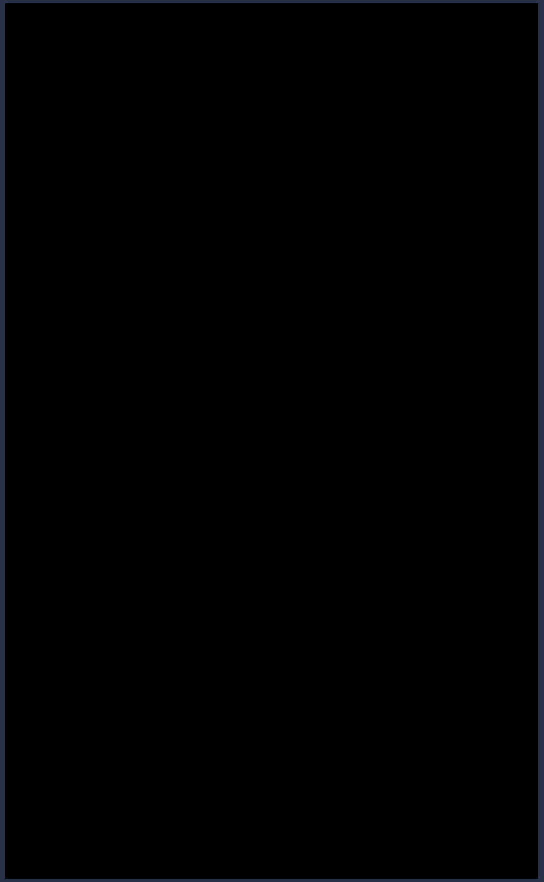






Superhydrophobic surfaces

- High speed video records of water drops impacts on superhydrophobic surfaces:



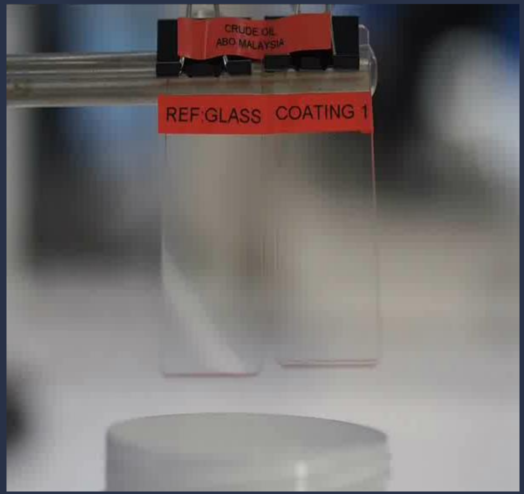
Flat

Structure 1

Structure 2

Oleophobic surfaces

Superhydrophobic surfaces (water)



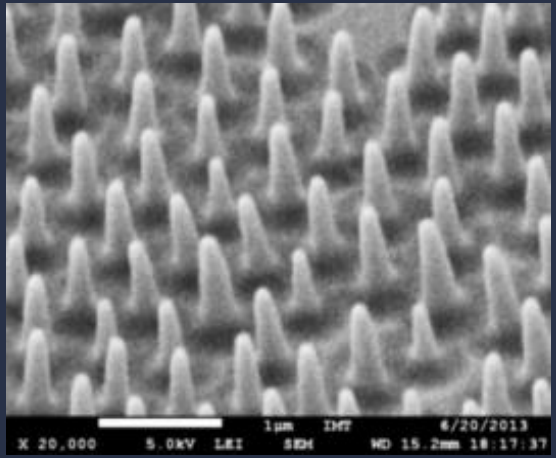
Easy to clean oleophobic coating (crude oil)

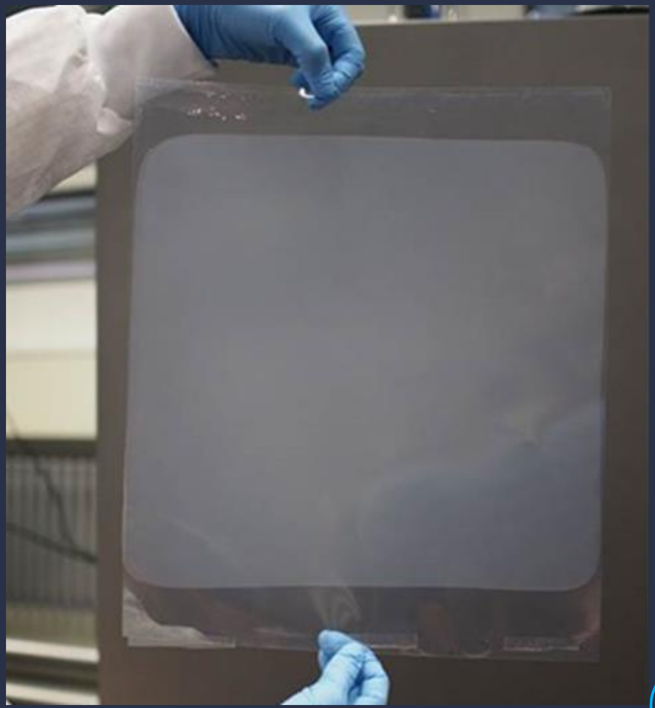
Deposition of crude oil + immerse in water

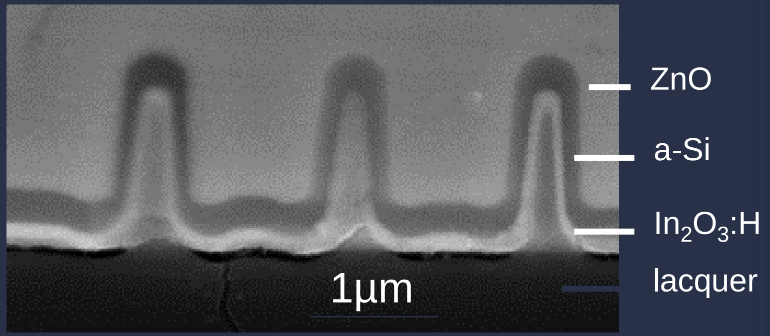
Underwater oleophobic coating

Nanostructured foils for Photovoltaic solar cell

- Nanostructured substrate for flexible PV cell
- Nanoeplication on 30x30 cm2
- The substrate & coating should withstand the solar cell deposition process (vacuum, temperature)
- Development of a temperature resistant primer for polymer foils
- Process applied on thin foils (down to 25µm)







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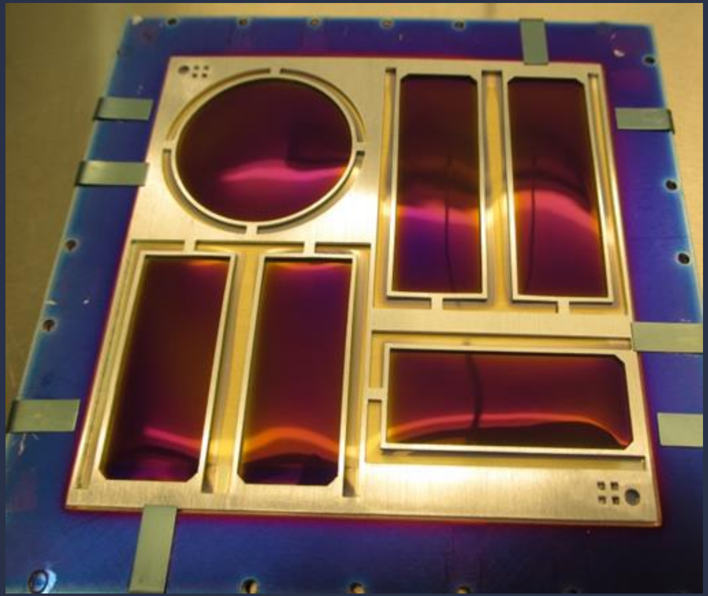
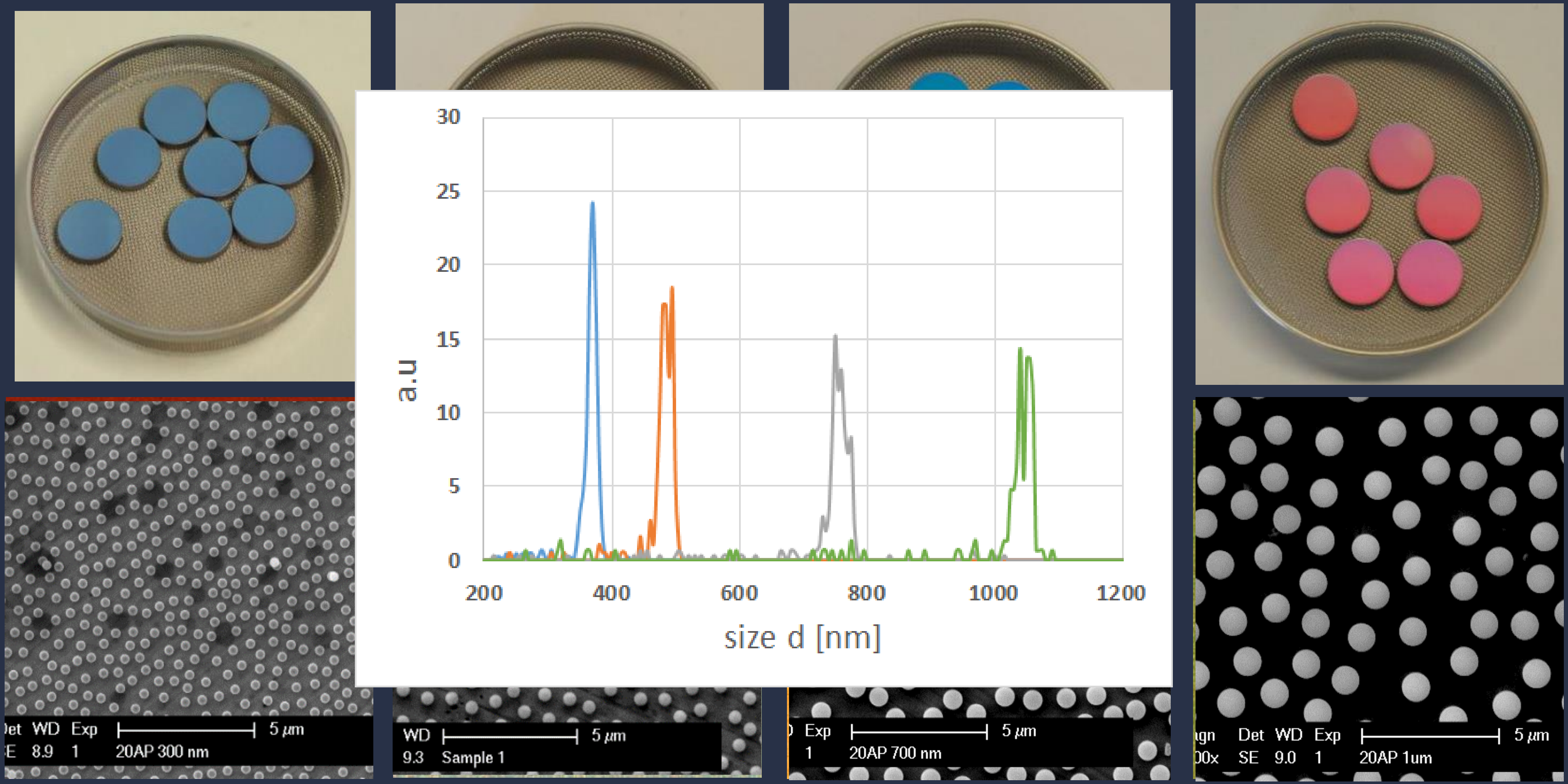
Nanostructured foils for Photovoltaic solar cell

- Integrate PV cells in a wristband
- outstanding PV performance at ultra-low illumination
- Application: wearable devices



Steel tool structuring for embossing and injection molding



Ø300nm particles Ø500nm particles Ø700nm particles Ø1µm particles

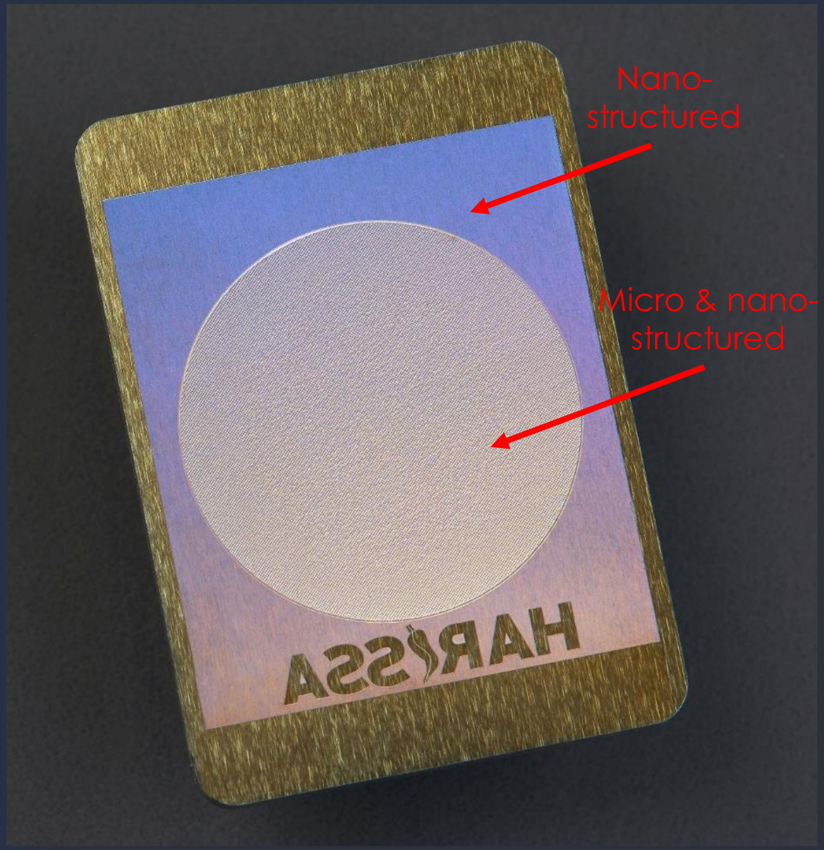
Fabrication of different replication tools, hard steel tools

- Fabrication of «hard steel tools» for embossing and injection molding
- Microstructuring by electrochemical micromachining

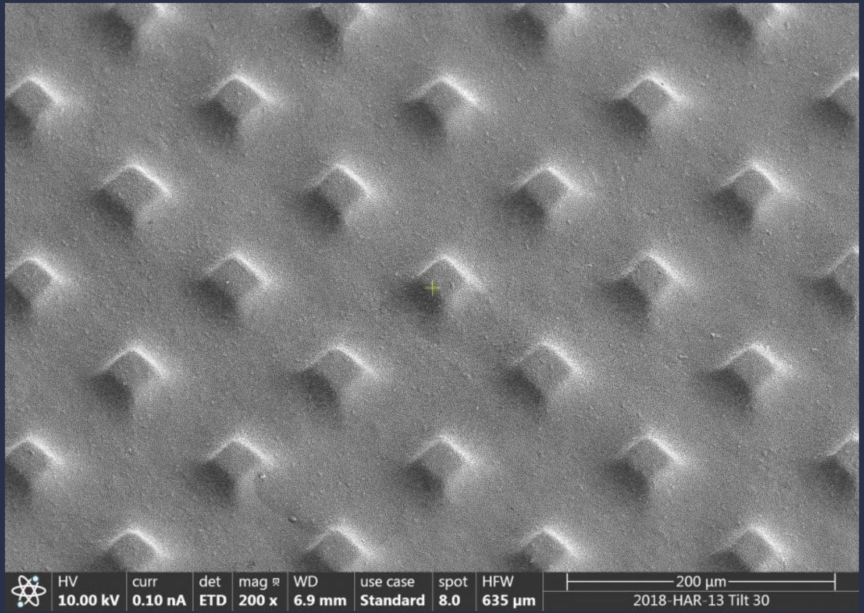
microposts, size: 30µm, pitch: 110µm, height: 15µm

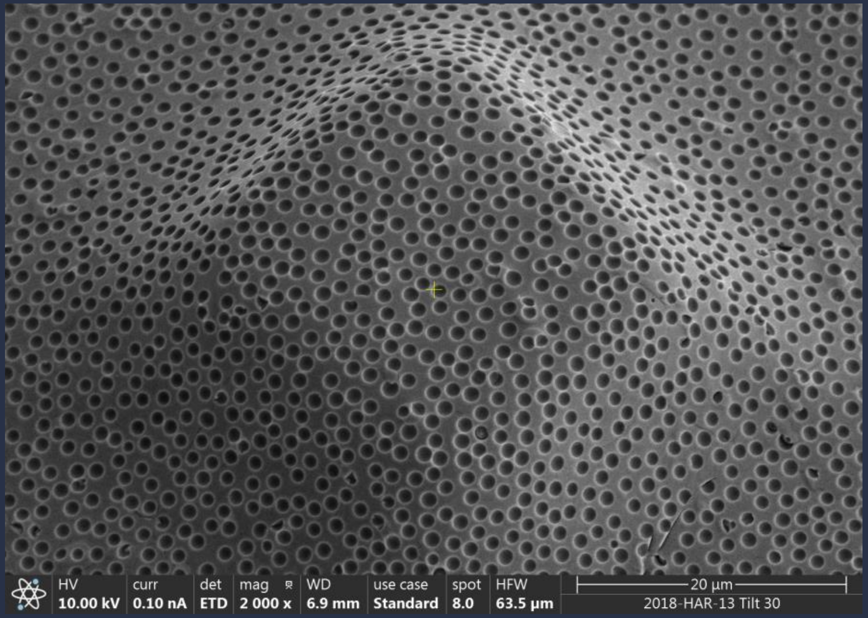
- Nanostructuring by nanosphere lithography + electrochemical etching

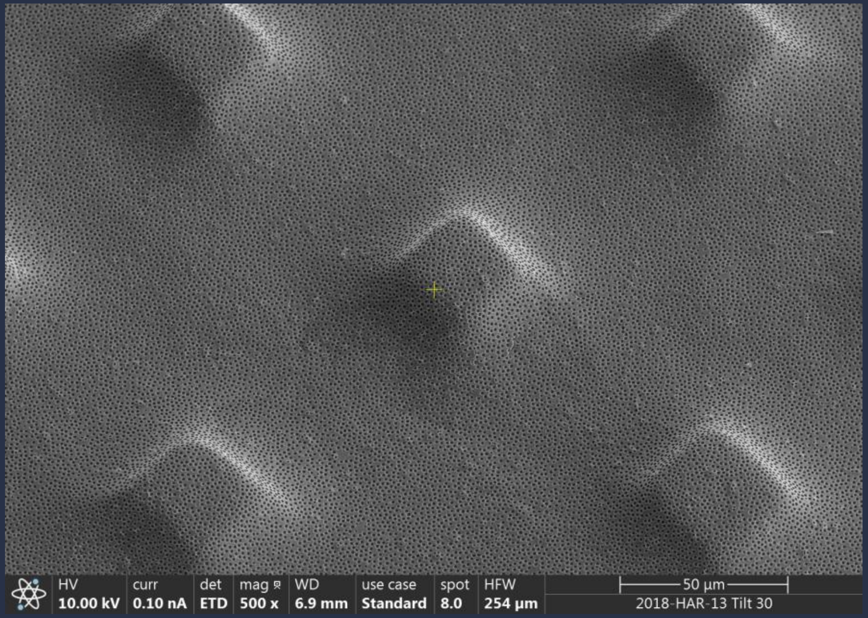
hemispherical cavities, Ø1µm



Fabrication of different replication tools, hard steel tools







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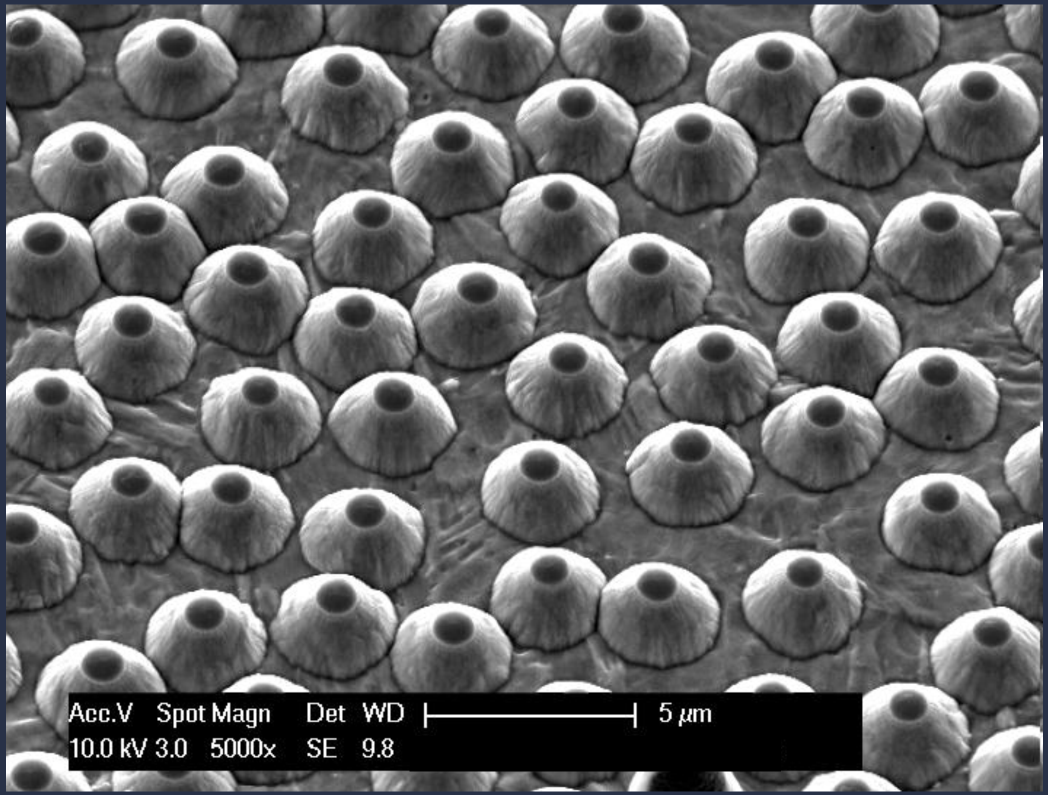
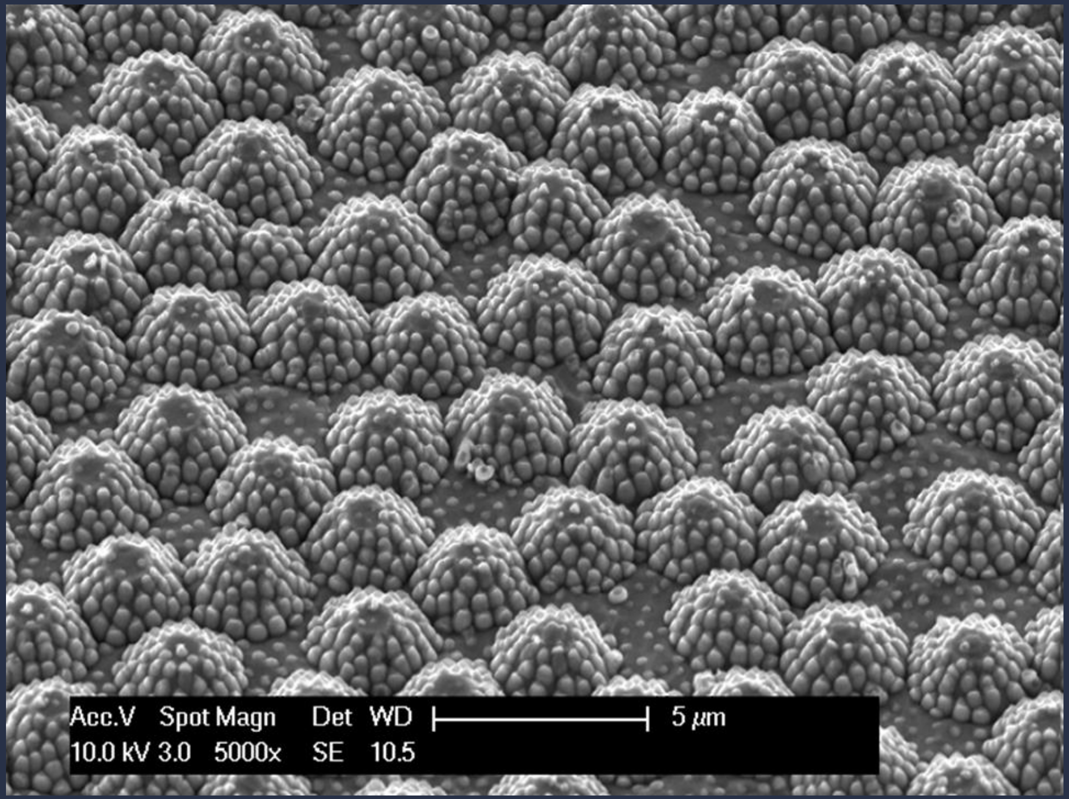
Hierarchical structuring at a smaller scale, in steel



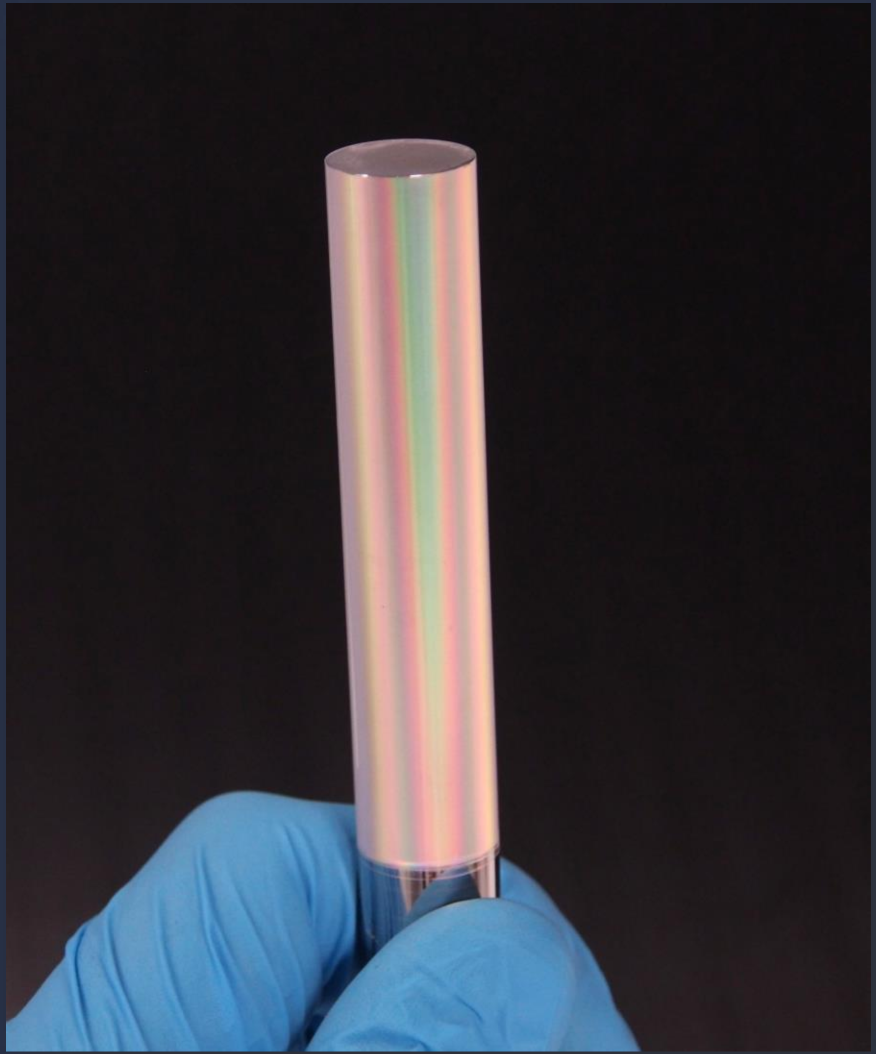
Single scale structure
2µm structures, RMS : 450nm



Hierarchical structuring
2µm + 200nm structures

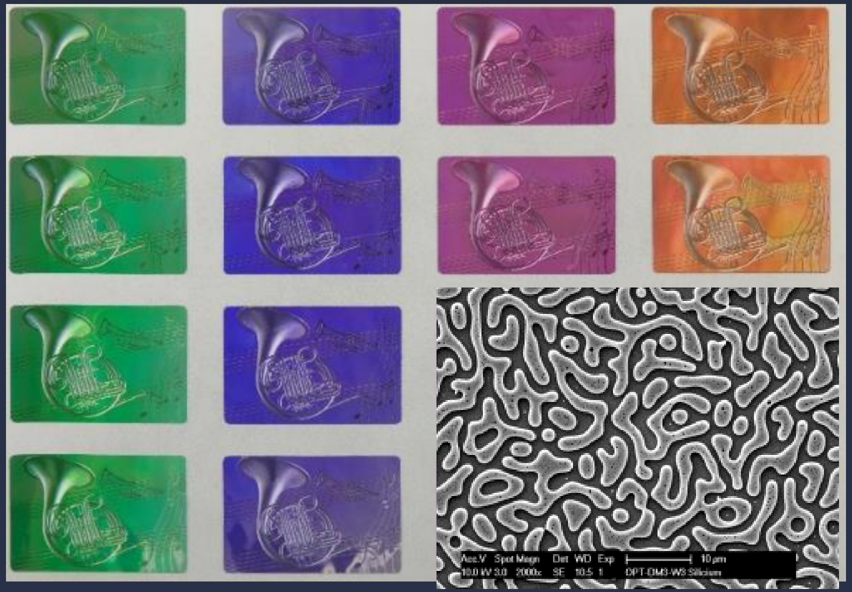
Structuring complex 3D steel parts

- The particle deposition and electrochemical etching processes were optimized to structure homogeneously cylindrical parts
- Compatible with macro and microparts
- Exemples: steel cylinder, mirror polished, Ø14mm length 80mm



Replicated nanostructures for anticouterfeiting

- Complex holograms (eg. binary depth profile) or stochastic structures as new security features
- Fabrication of structured tools for replication
- Unique (10 CSEM patents)
- Unique color effects for banknotes, forgery proof documents, packaging and brand protection
- Compatible with existing manufacturing processes (R2R, S2S, injection molding)
- Partnership for industrialisation established



Replicated nanostructures for anticouterfeiting

- Structured steel tools for embossing & injection molding)
- Security element is directly part of the final product
- Embossing security features on pills
- Several industrial application

Multi Level to high Security

- Multi security levels designs, combination of up to 3 different security levels
- Easy to check, laser pointer, Moiré screen... But difficult to reproduce
- QR code can be hidden in a DOE structures -Track & trace
- Smartphone readable
- Color switch effects for Passport and Banknotes DID®

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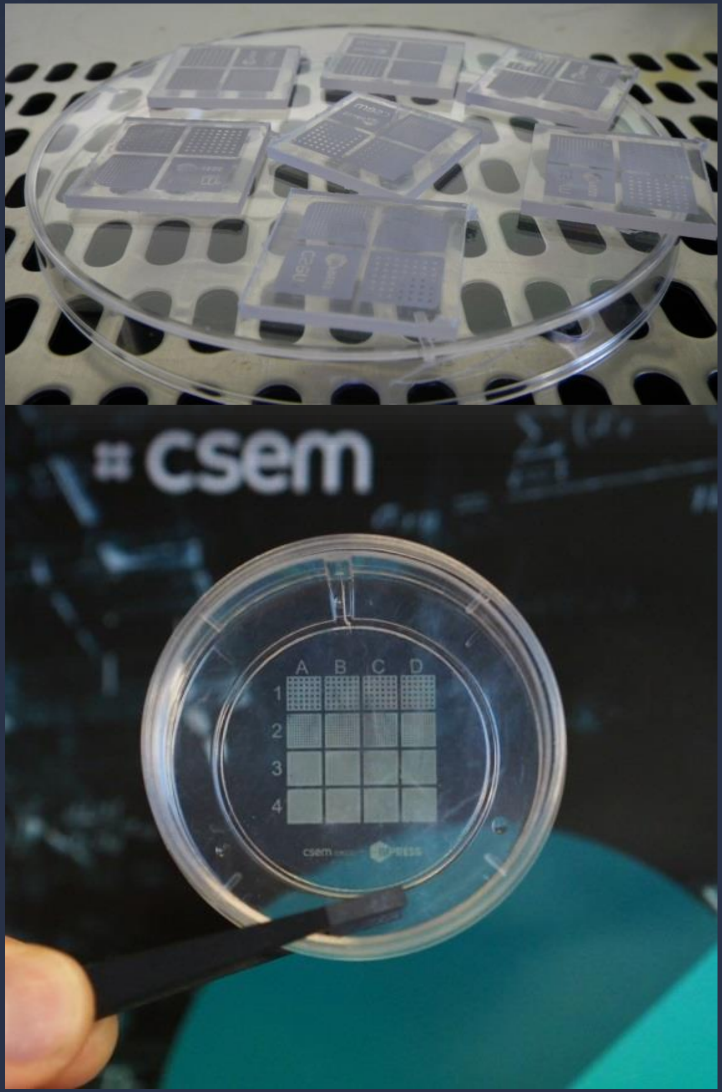
Nanostructured surface for biological cell growth

- Fabrication of nanostructured surfaces with a **controlled growth of adherent cells**
- Fabrication of **cell-adhesion/cell repellent patterns** using topography
  - Grow eukaryotic cells on flat and structured surfaces
  - Analyse the morphology of the cells after 3days
  - Characterize the adhesion of cells on flat/structured surfaces



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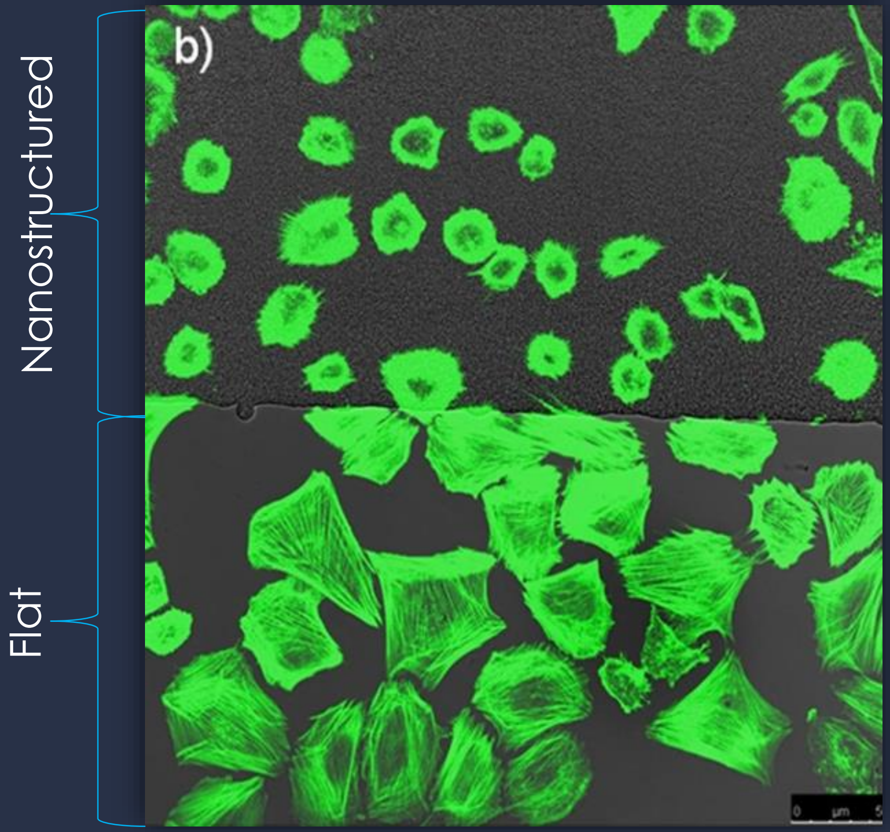
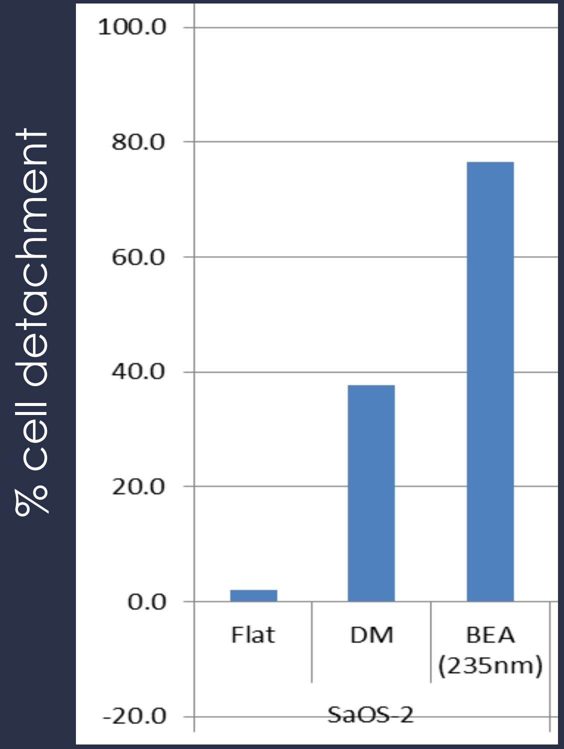
Results cell detachment & cell morphology:

Bone cells (SaOS 2)





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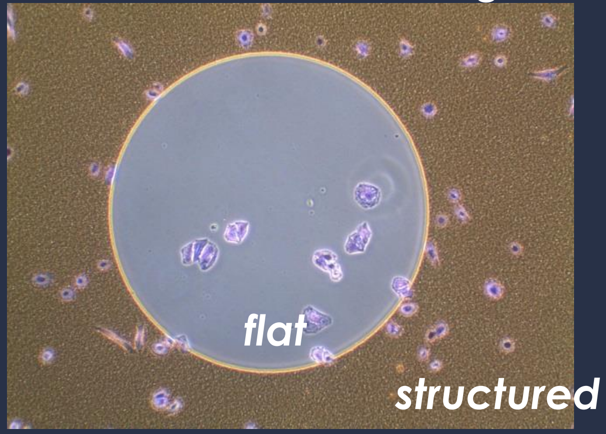
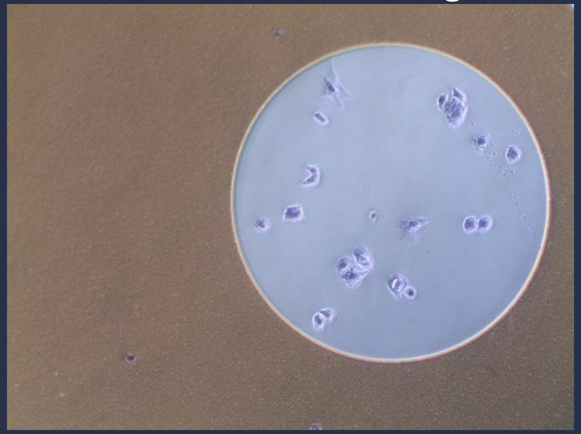
Cell detachment on various materials

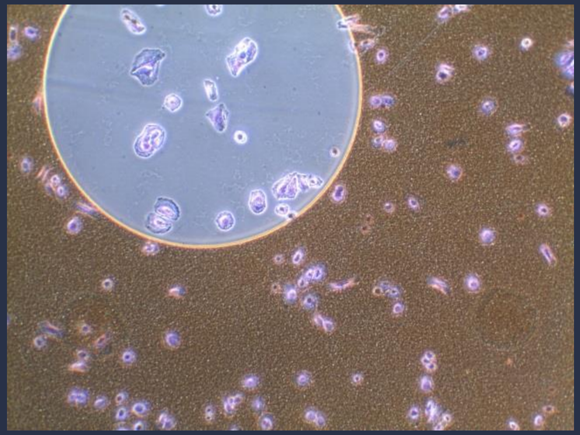
Before washing | *After washing*

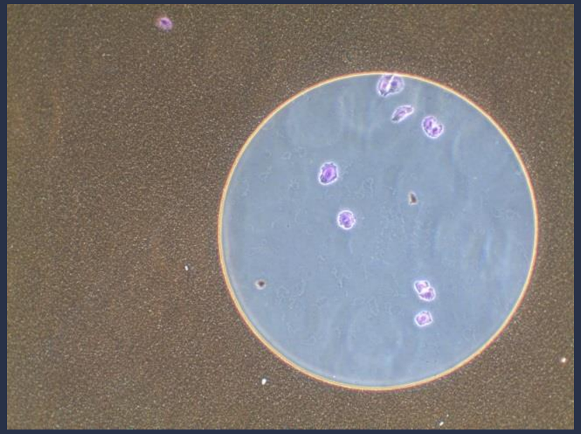
UV-curable resin





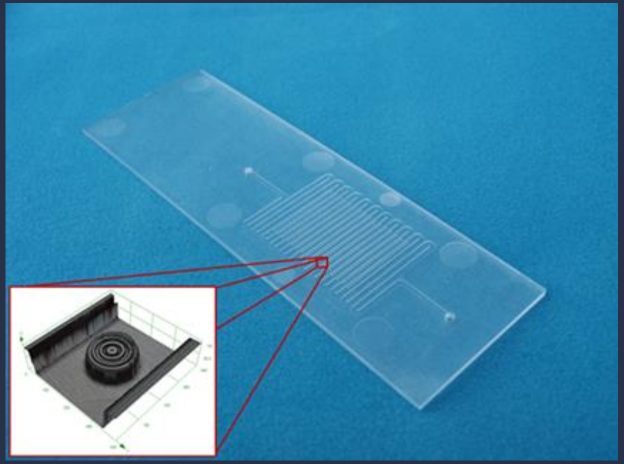
Hot embossed polycarbonate

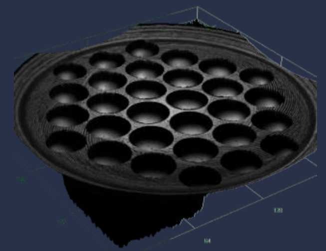


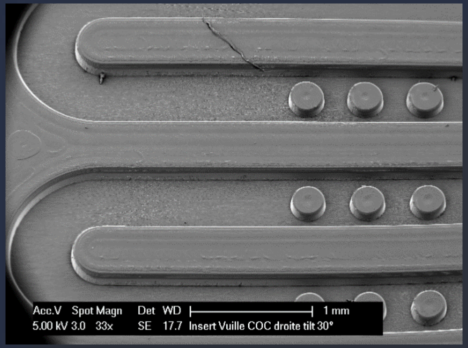


Nanostructured biodiagnostic platform

- Objectives: Improve sensitivity of injection-molding bio-diagnostic platform with nanostructuration
  - Control of the wettability of detection spots
  - Improve signal quality and homogeneity
- Tooling: fabrication of nanostructures on a mold insert presenting micro-channels and micropins
- Replication : optimization of the replication process for nanostructured micromolds

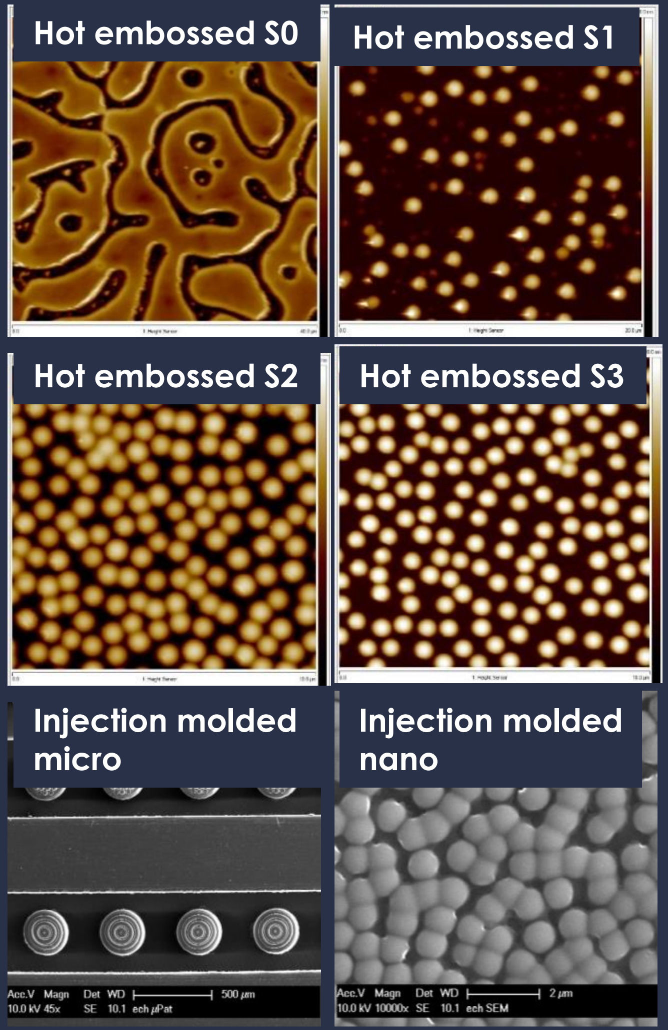






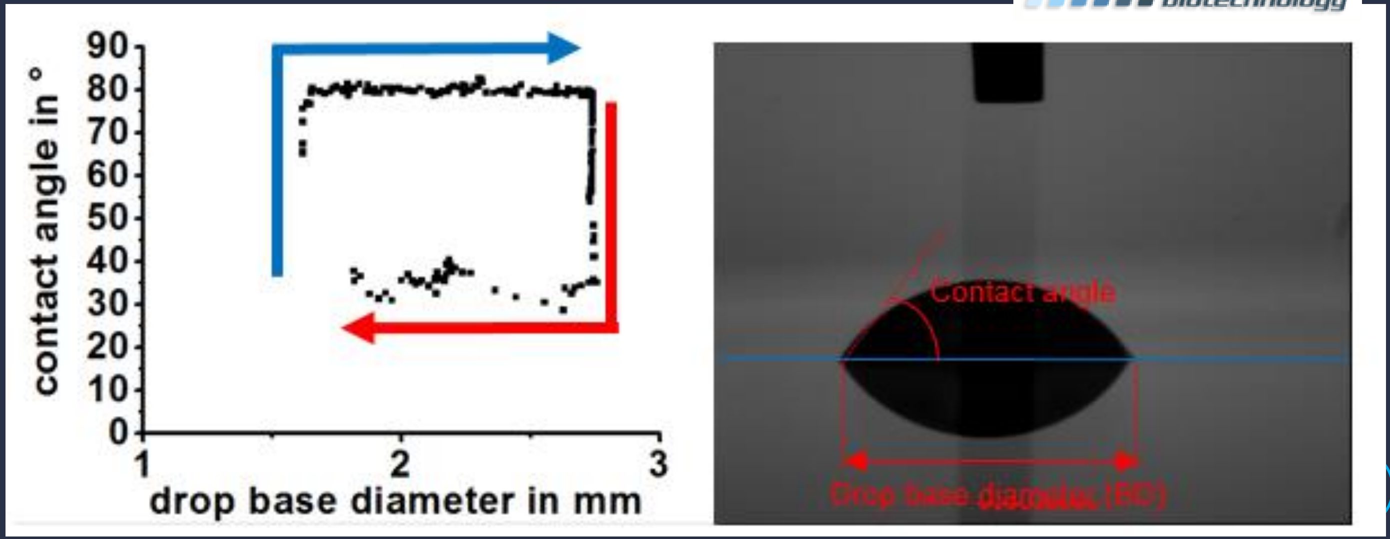
Characterisation of the micro/nanostructures

- Origination of nanostructures by beads and polymer self-assembly
- Replication into plastic, fabrication of nanostructured biodiagnostic platform:
  - Hot embossing and Injection molding: PC parts with four different structures
- Characterization:
  - Influence of structuring on wettability
  - Biodiagnostic platform : fluorescence immunoassay

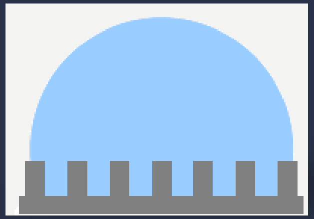


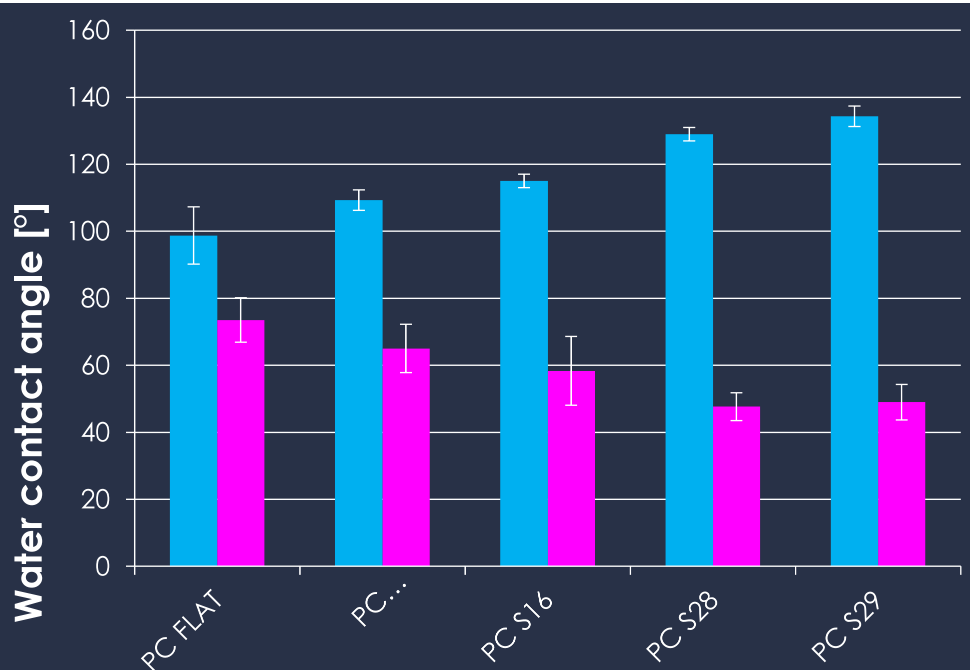
Influence of structuring on wettability

- Dynamic contact angles of water measured on the four types of hot embossed structures and, as a contro



  - Advancing water contact angle and contact angle hysteresis significantly increased
  - Wetting mode : Wenzel type (sticky drops)





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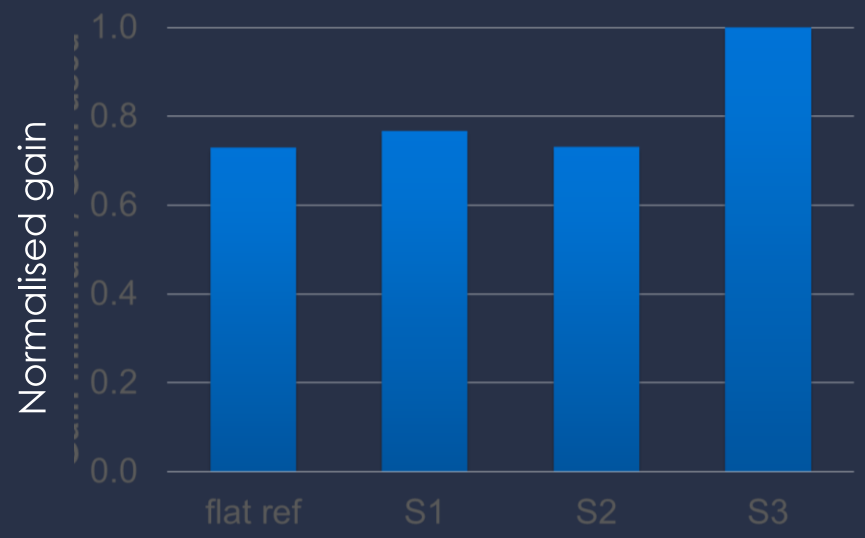
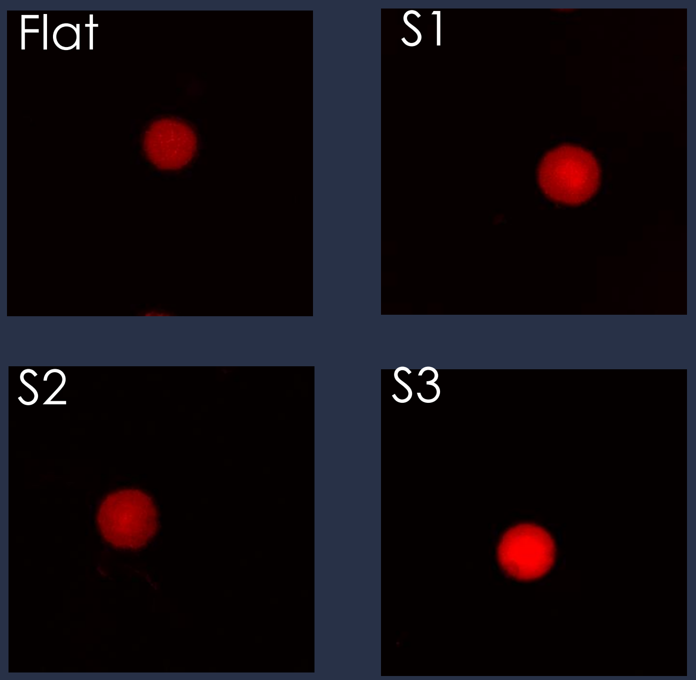
Tests using a model immunoassay

- In these tests, the antibody used for detection is inkjet-printed on the spots of the bio-diagnostic platform.
- The fluorescent spots were imaged using a confocal microscope
- Better spot homogeneity: no coffee-ring effect after spotting
- 30% increase in fluorescence for structure S3 (increase in specific surface, different roughness, possible scattering of the emitted light)





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Functional Surfaces:
Self-assembled nanolayers for substrate metallization

Metallization of 3D printed plastic parts

- Stereolithography (SLA)
  - Complex shapes
  - High resolution, even at microscale
  - Metallization adds functionality (electrodes, sensors, …) and can improve characteristics (aesthetic, resistance to chemicals/corrosion)
- Challenge of metallization
  - smooth surface (AFM roughness ≤ 5nm)
  - polymeric substrate (T_g = 111°C)
  - With >>> high adhesion

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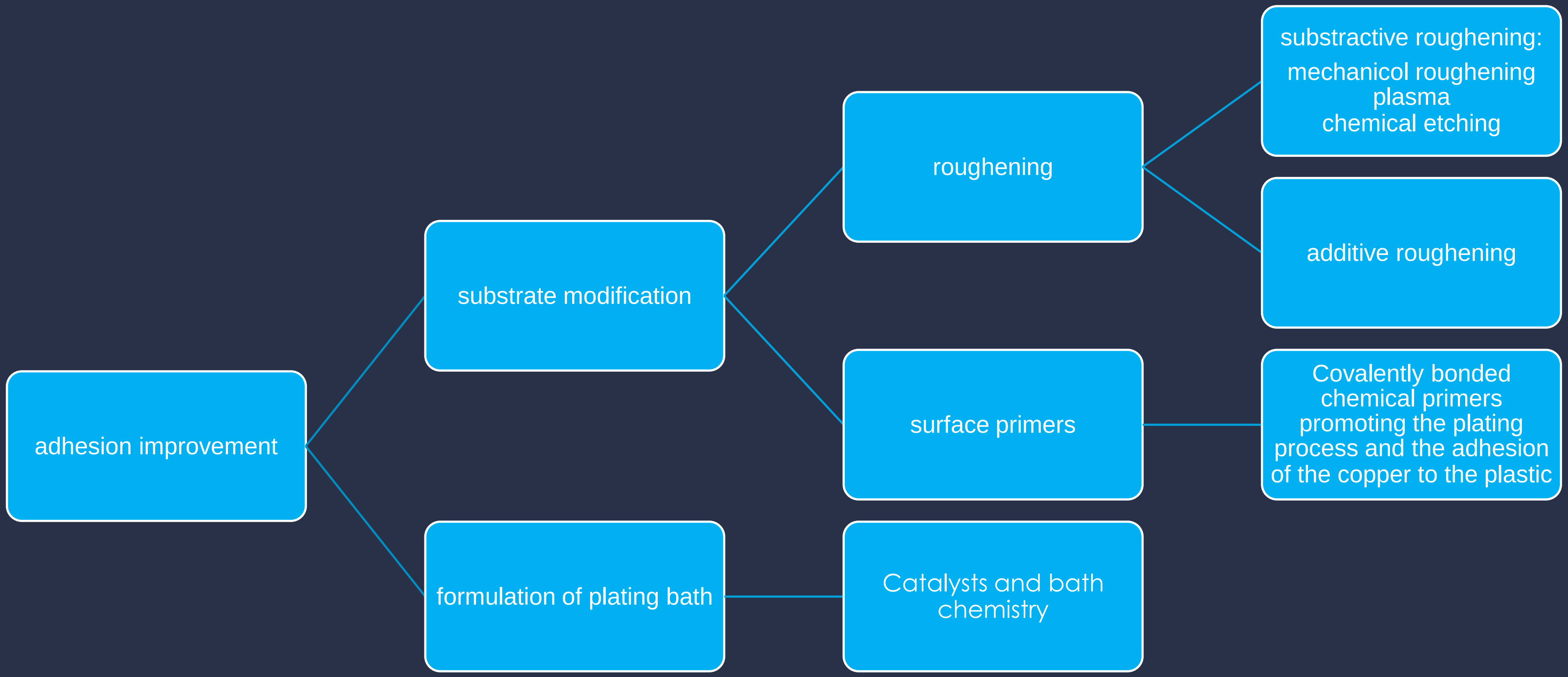
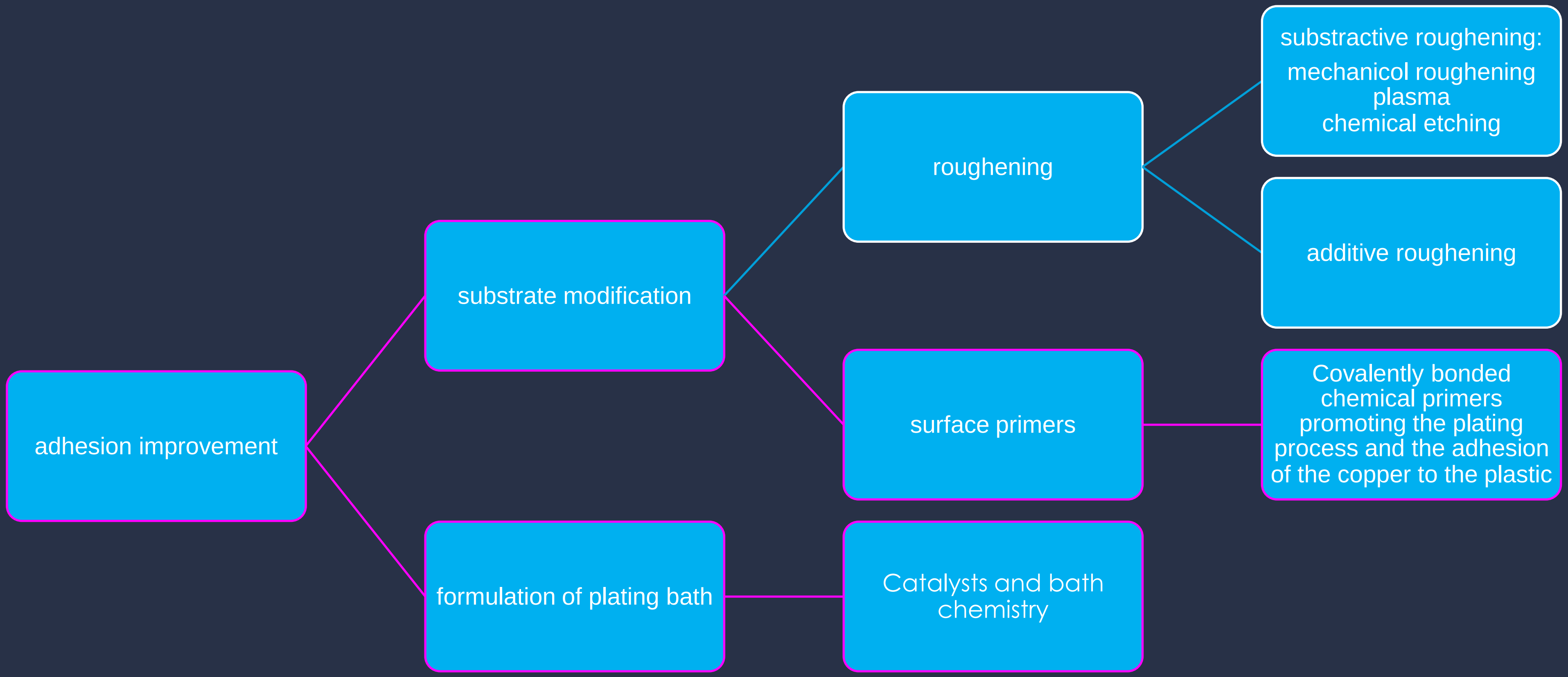
Adhesion improvement strategies

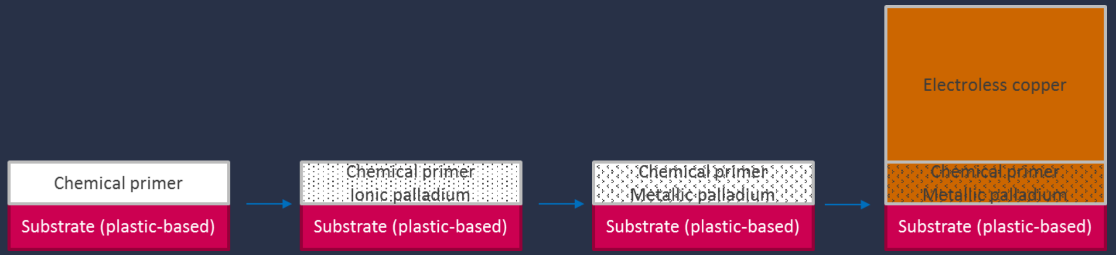


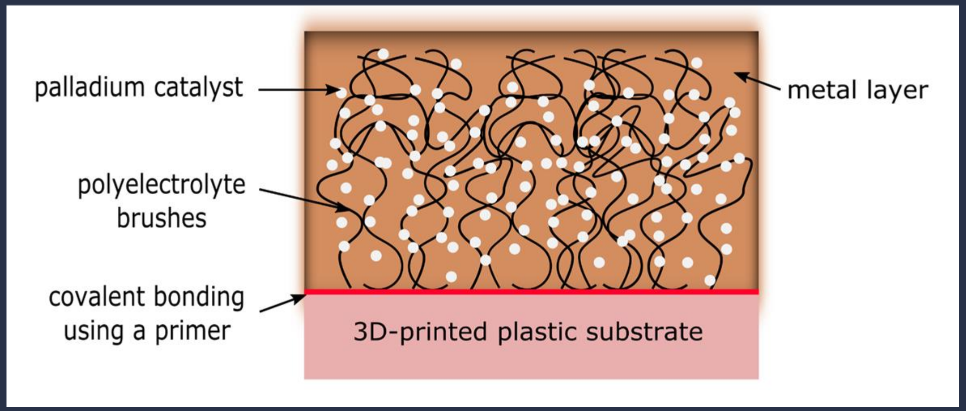
Adhesion improvement strategies

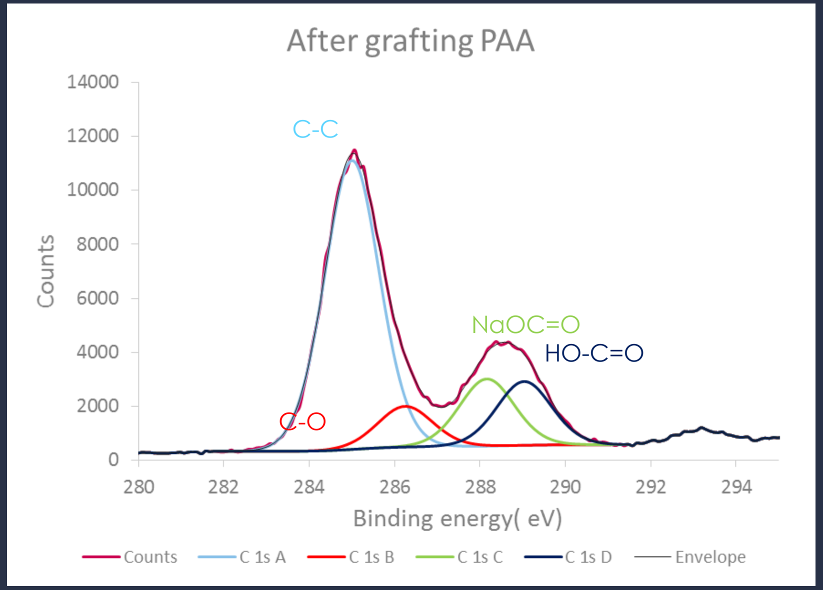


Patented solution

- High molecular weight polyelectrolyte as a chelatant, covalently bonded using a primer (azide-based bonding)
- Chemical interdigitation using intermediate polymeric layer between substrate and metal.
- Surface grafting confirmed by XPS
- Surface density of polyacrylic acid (PAA) obtained from colorimetric data: ≈ 2 to 4 μg/cm







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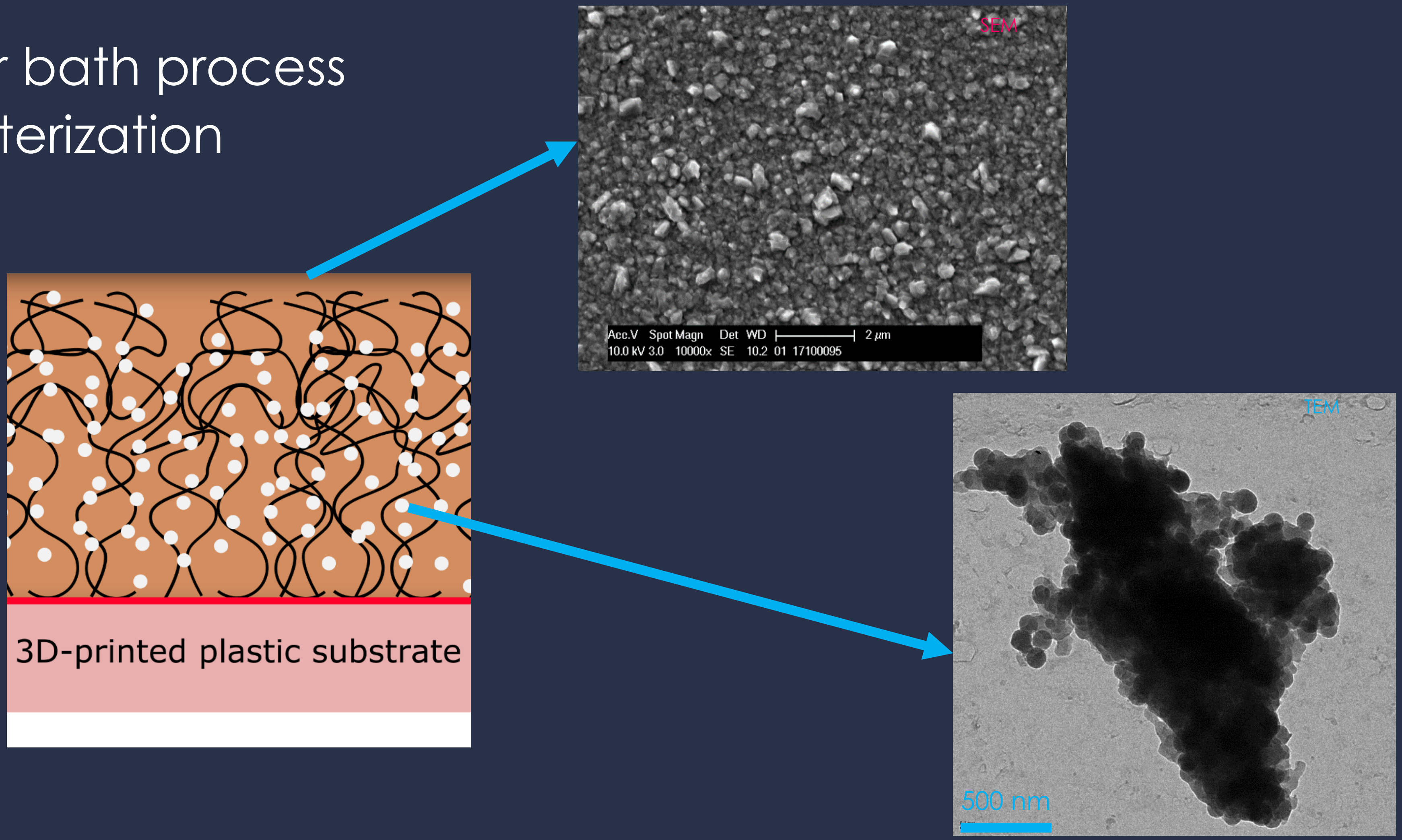
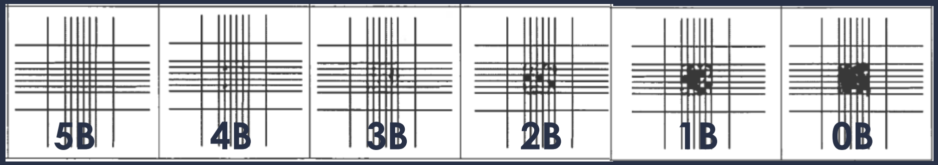
Characterisation of metallization process

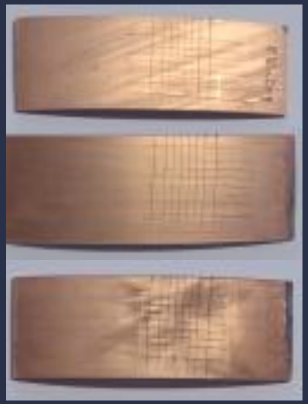
- Copper bath process characterization



Results and perspective

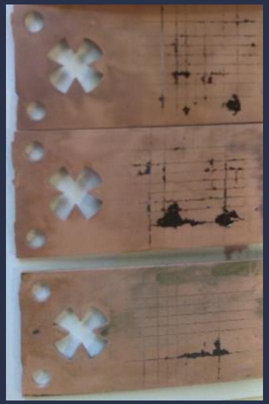
- Adhesion test ASTM D 3359
- Adhesion improved on all tested substrates with up to 3 µm of deposited copper (3B to 4B at the harshest test on substrates with roughness < 5nm)
- Next steps: process upscaling and industrialisation





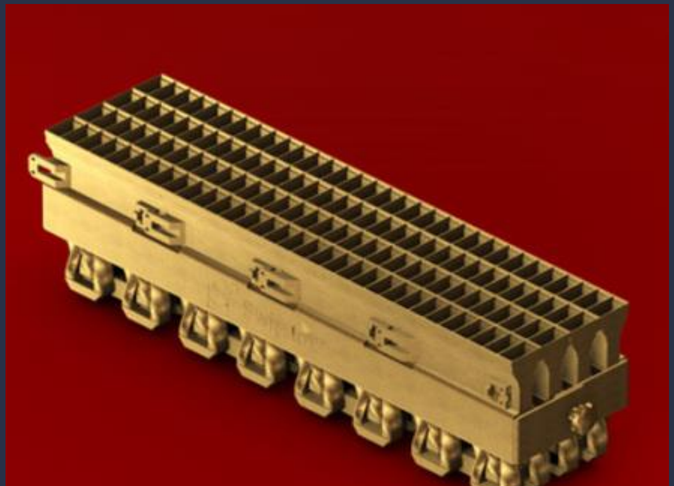
Polyethylene

UV curable resin printed @CSEM



UV curable resin from industrial partner

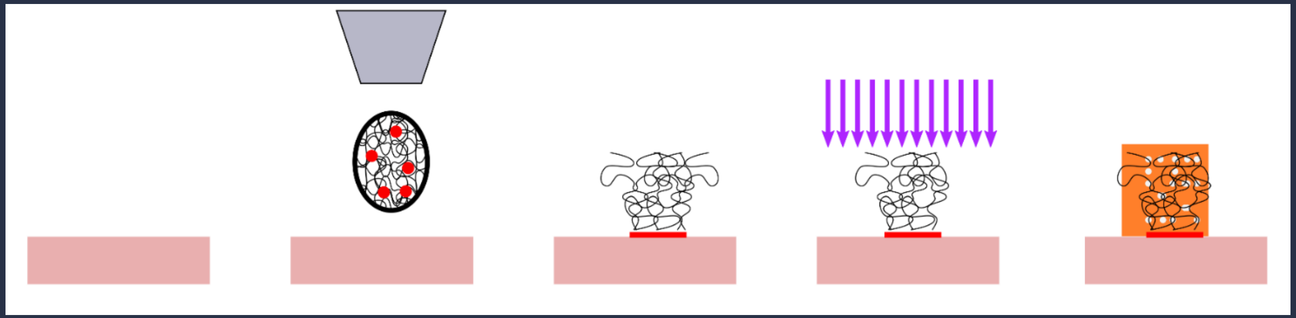
UV curable resin cont. SiO_2 filler



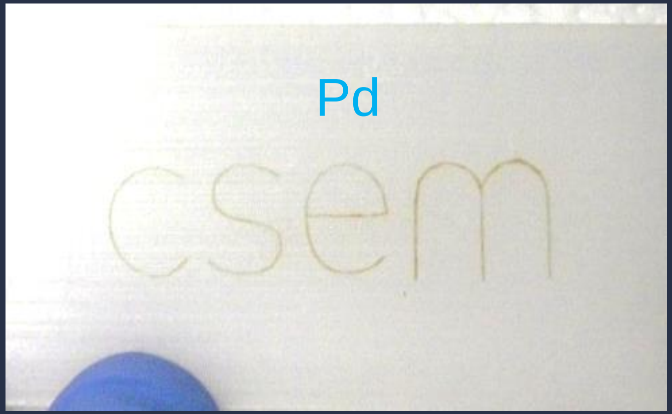
Antenna array to serve satellite connectivity on the move applications

Selective Plating

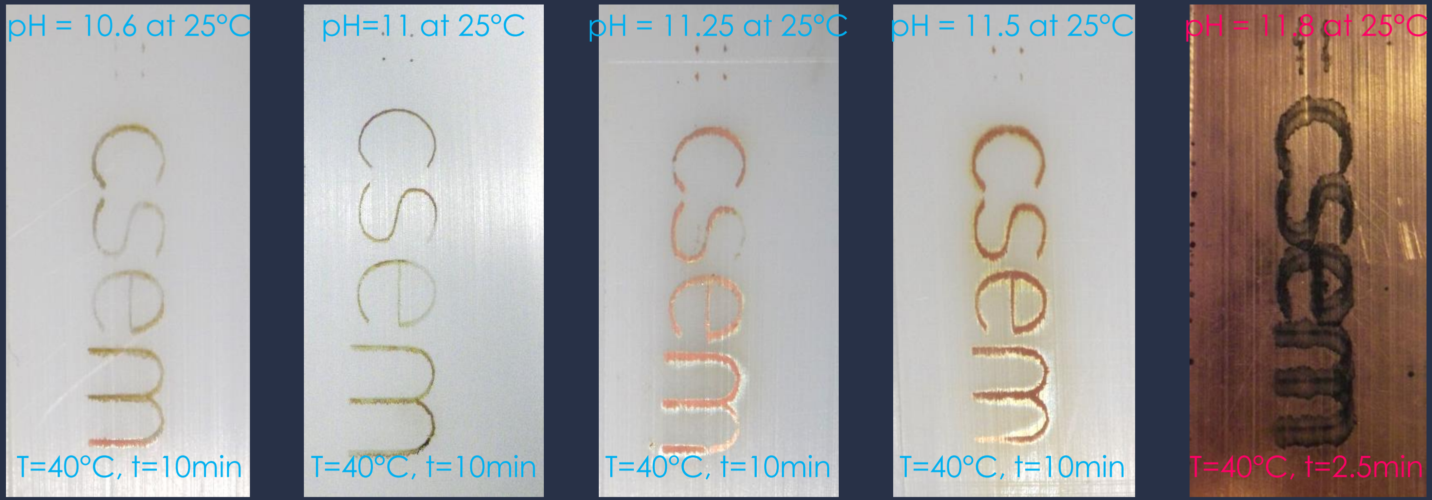
- Pattern by printing with Aerosol Jet Printer



- Palladium seeding is selective

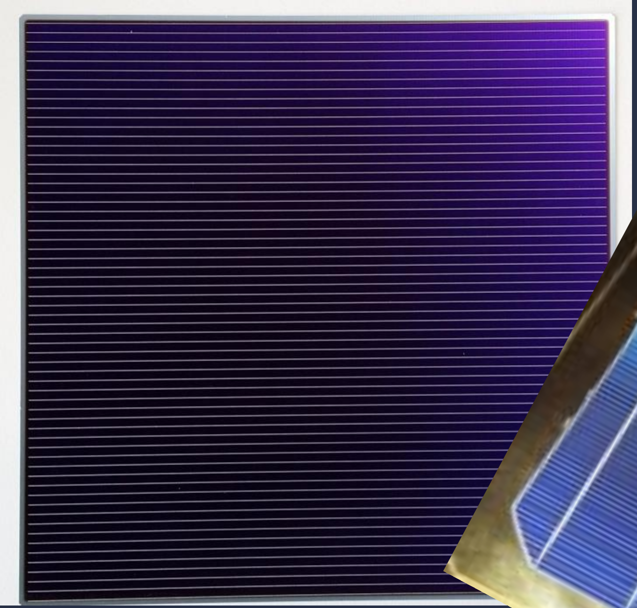


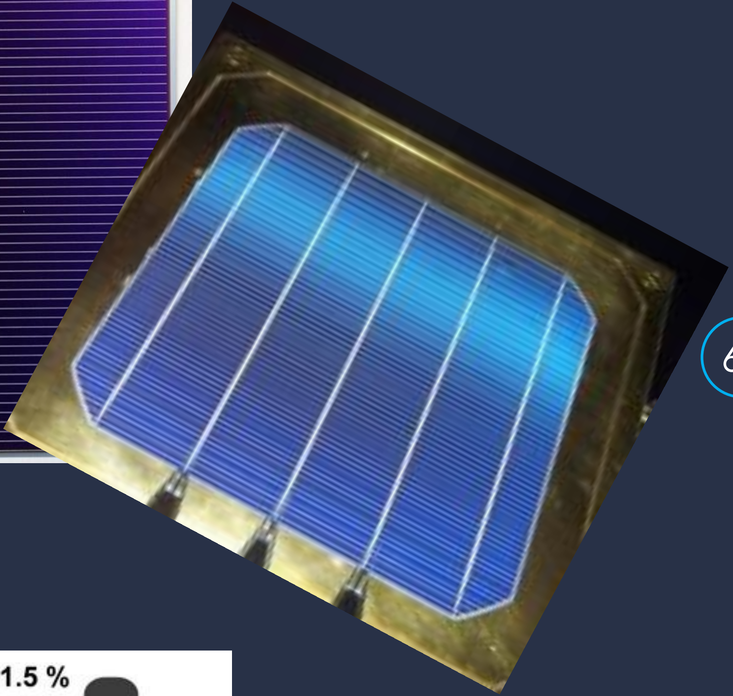
- Effect of pH of electroless copper bath

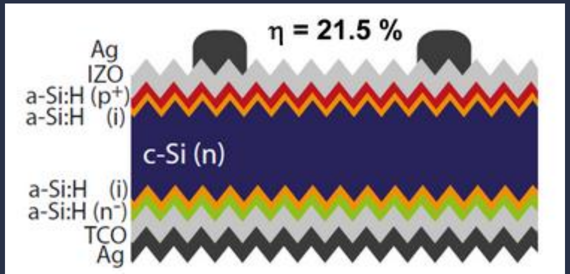


Patterning conductive lines for heterojunction solar cells

- Conductor grids on hetero-junction solar cells are made of screen-printed silver paste
- Screen printed Ag is the most widely used approach to form solar cell electrodes but:
- Limited availability of Ag
- Ag price
- Smearing out of the Ag paste induce additional shadowing of solar cell active area
- **Power loss** is proportional to the **finger line resistance**. In case of low T Ag paste, it is relatively high

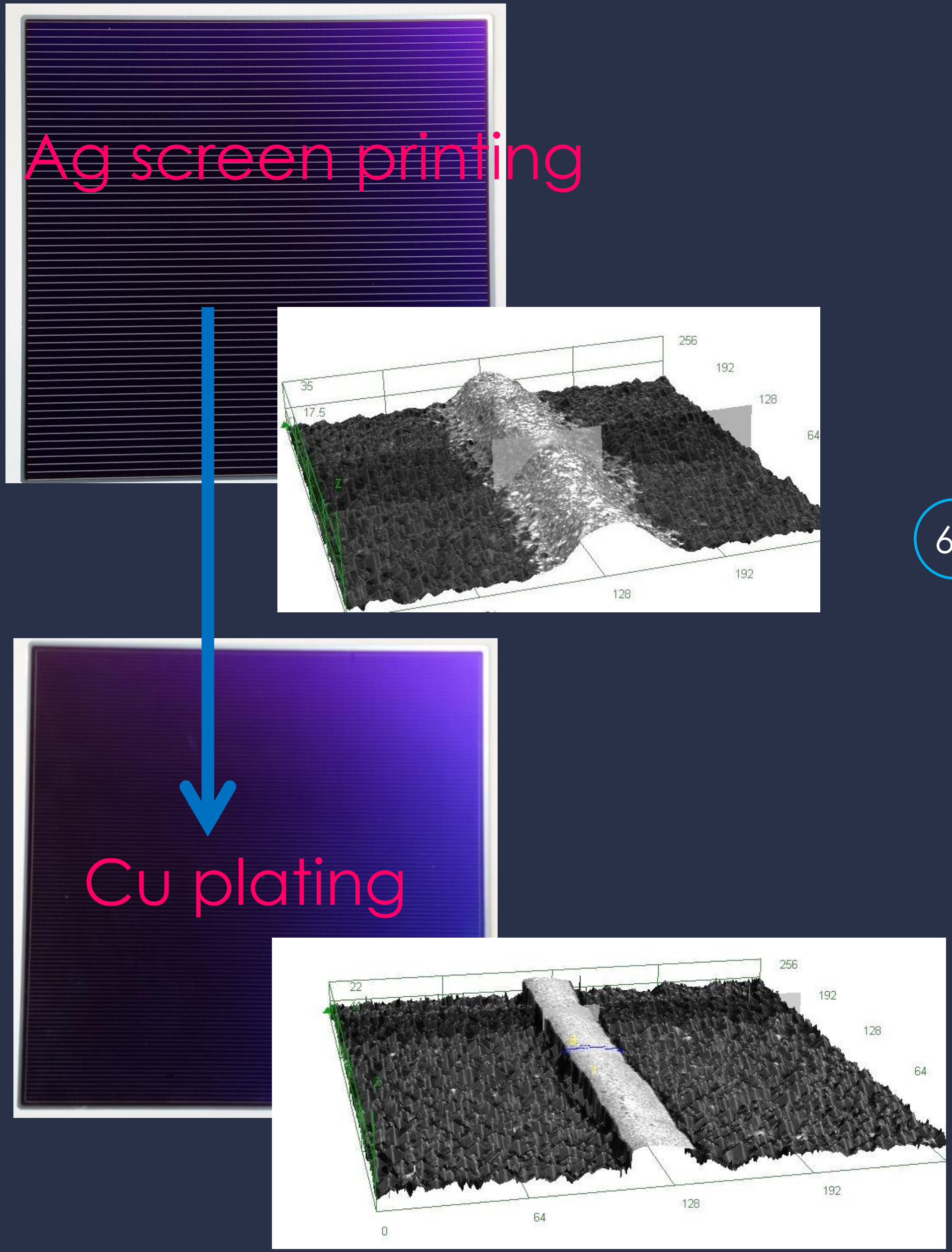






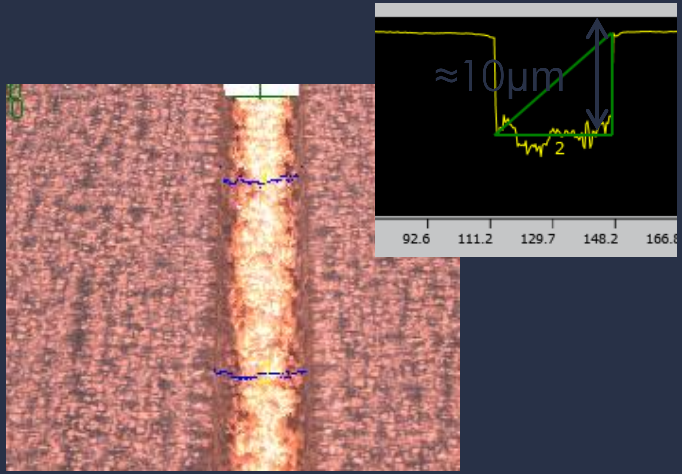
Solar cell electrodes - move to Cu plating

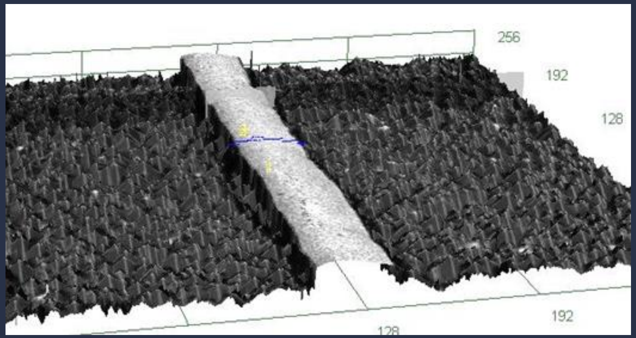
- Copper is a promising candidate to boost solar cell efficiency and reduce the cost of solar energy
  - Highly conductive
  - 100x cheaper than Ag



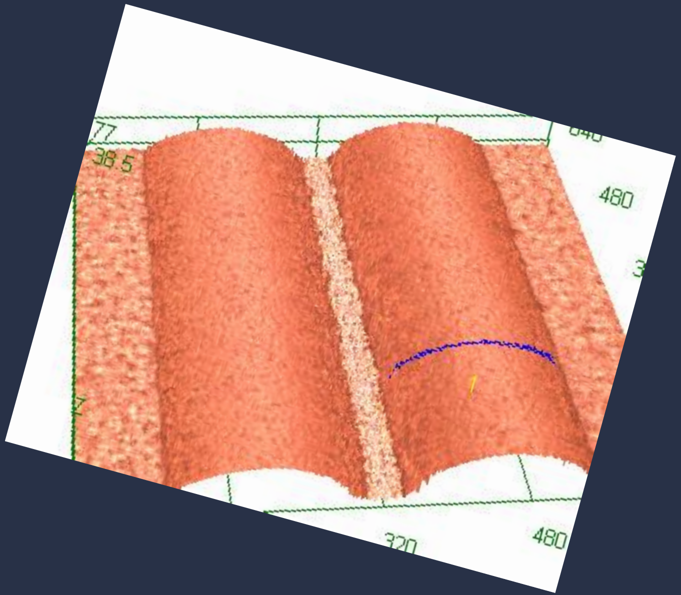
Patterning techniques

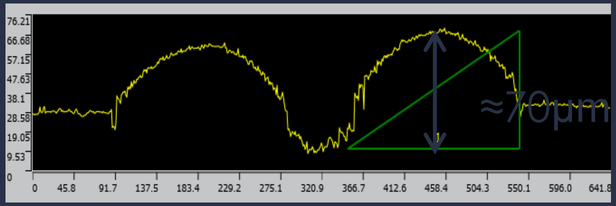
Photolithography



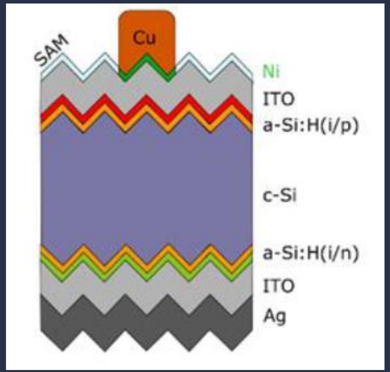


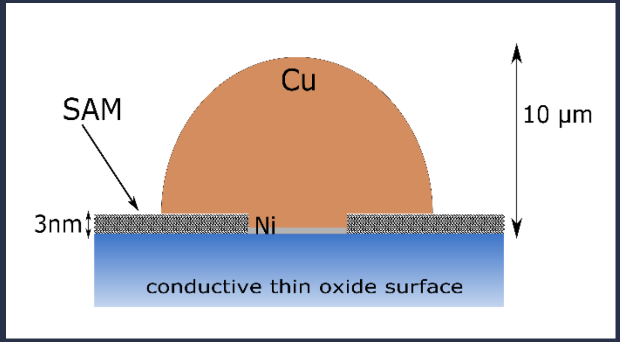
Hot-melt

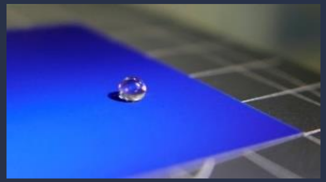




Self Assembled Monolayer (SAM) - Patent filed







Advantages of the SAM approach:

- Process simplification
- Higher throughput
- Cost reduction
- Compatibility with the encapsulation process

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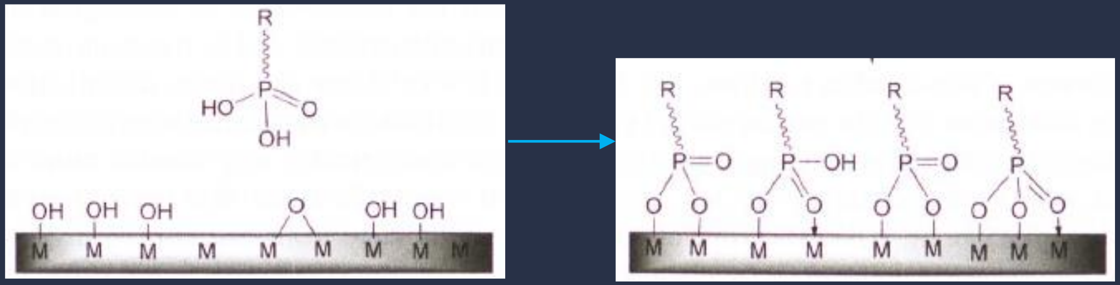
Self Assembly of Phosphonic Acids (PA) on Indium Tin Oxide (ITO)

- P-O-M bond at the surface



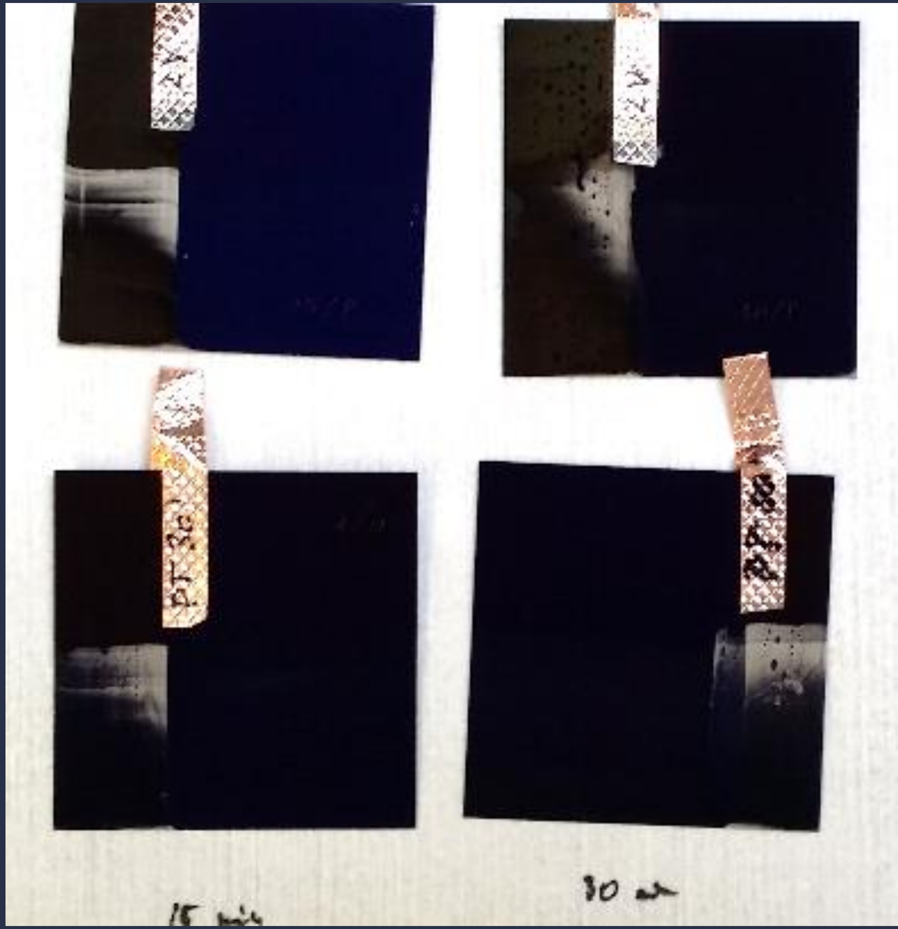
Dalton Trans., 2013, **42**, 12569–12585 | **12571**

- Long chain, fluorinated PA
- First tests with immersion, currently processing 6” wafers with spraying
- On structured wafers

Static water contact angle	Advancing water contact angle	Receding water contact angle
115.2° ± 1°	120.5° ± 0.8°	105.7° ± 1.5°

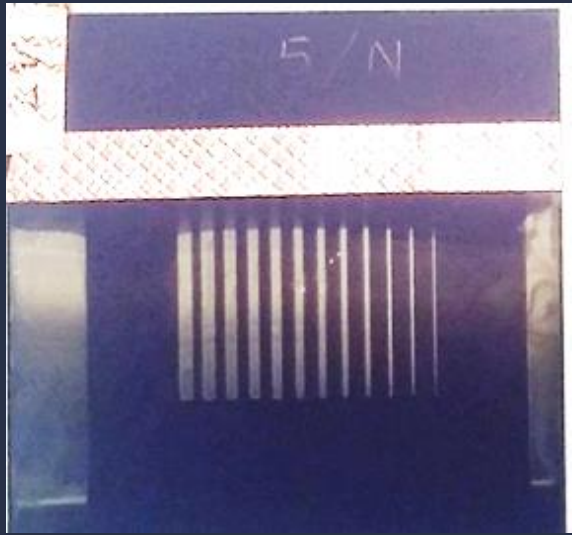
Plating tests

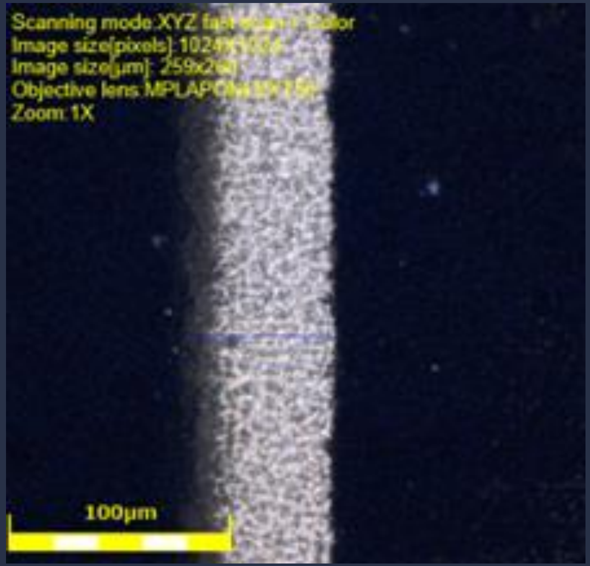
- plating optimization to achieve masking and prevent plating on ITO
  - SAMs removed on one edge with concentrated H_2SO_4
  - Nickel electroplating at pH4.0, T 50°C
  - Optimized to avoid ghost plating
  - SAM is sensitive to handling



Patterning methods

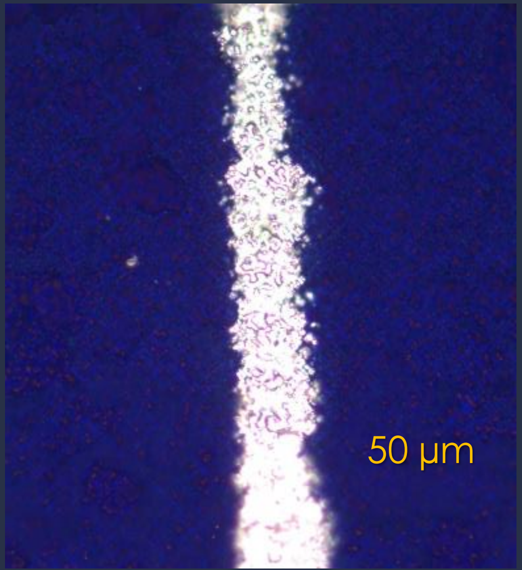
- SAM patterned by O_2 plasma through hard mask





Line width 62 µm
Height 2.5 µm

- SAM patterned by laser etching
- Some ghost plating
- Very fine lines
- Some lines are not continuous

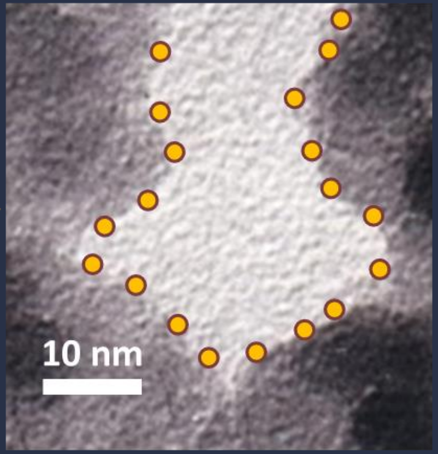


Responsive Surfaces:
Mesoporous sol-gel layer for sensing application

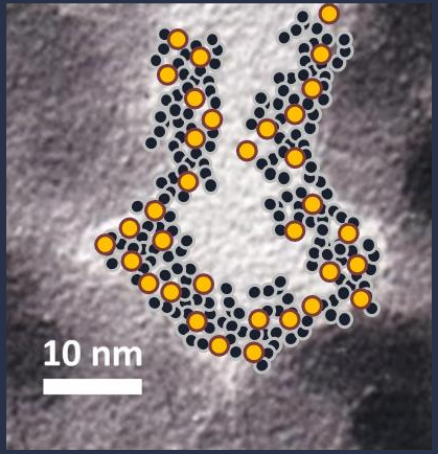
Mesoporous sol-gel layers for sensing

- Porous matrix as a scaffold for dyes encapsulation
- Dyes responsive to gas concentration or pH change

Porous layer based on silica nanoparticles

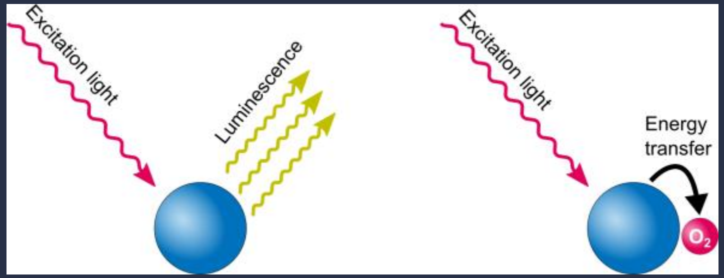


Incorporation of dyes
Single level of porosity



Sol-gel layer + incorporation of dyes
Dual level of porosity

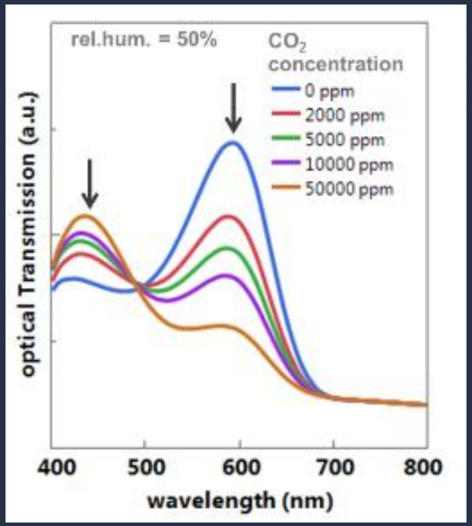
- Different optical monitoring capabilites: fluorescence and absorption monitoring



(a) no oxygen (b) oxygen collision

fluorescence fluorescence quenching

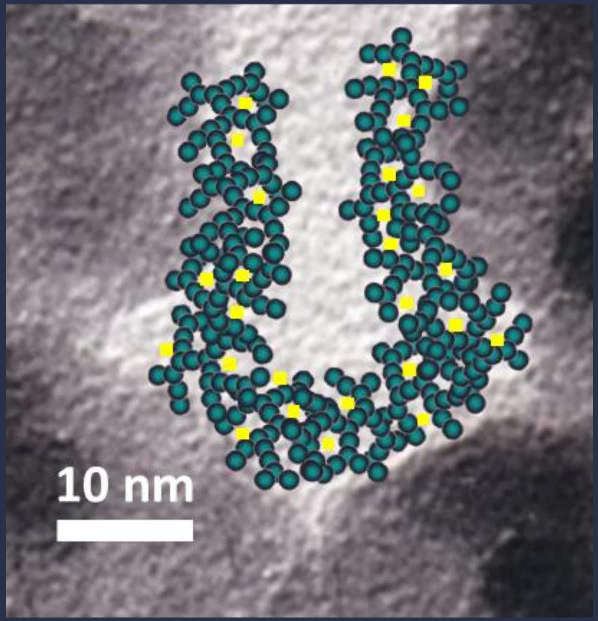
Fluorescence quenching for O_2 detection

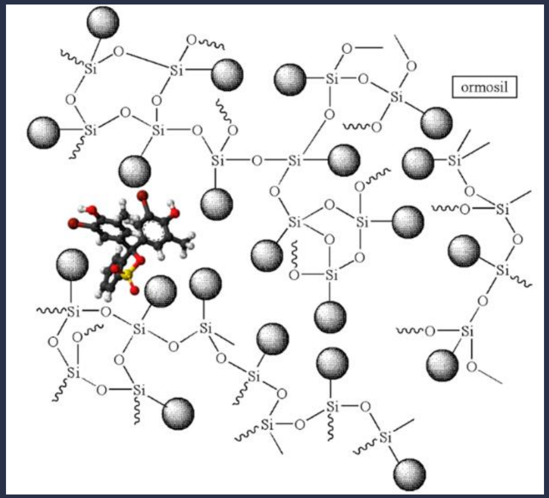


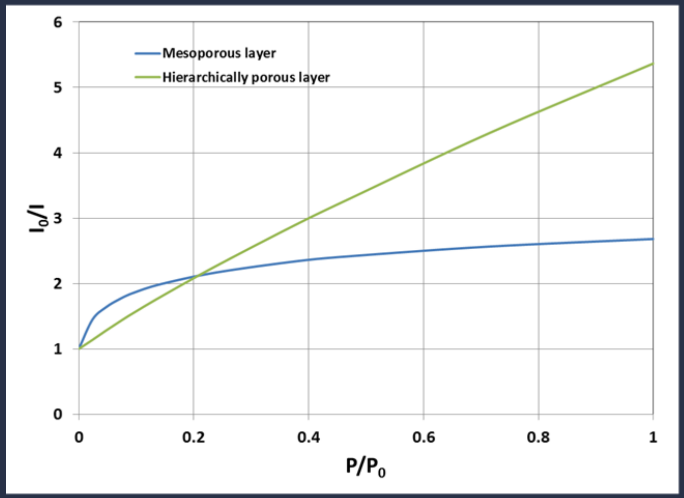
Absortption for CO_2 detection

Hierarchical porosity, CSEM patented technology

- Beyond SoA: Encapsulation of active species into a secondary microporous matrix
- Advantages:
  - dye protection and enhanced lifetime
  - higher emitted intensity
  - enhanced sensitivity (to O_2/CO_2)
  - lower impact of H_2O
  - linear sensitivity curves
  - no drift

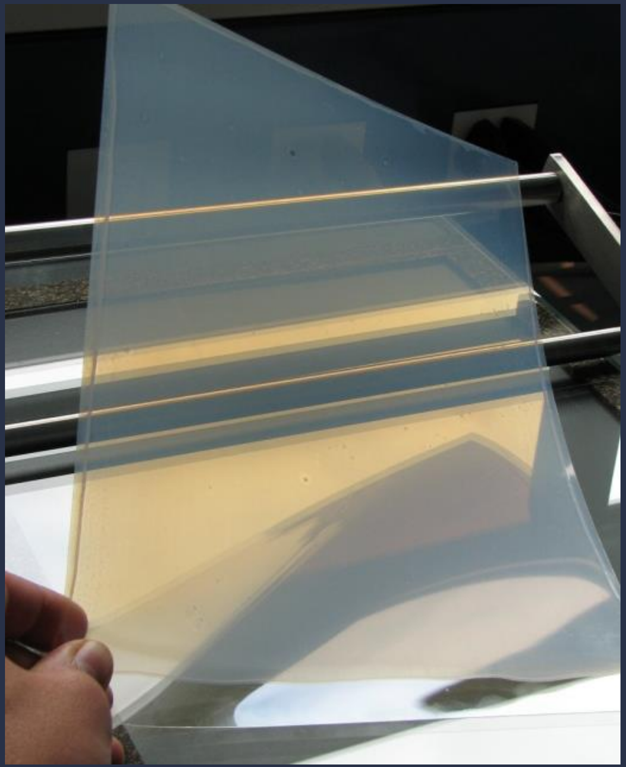


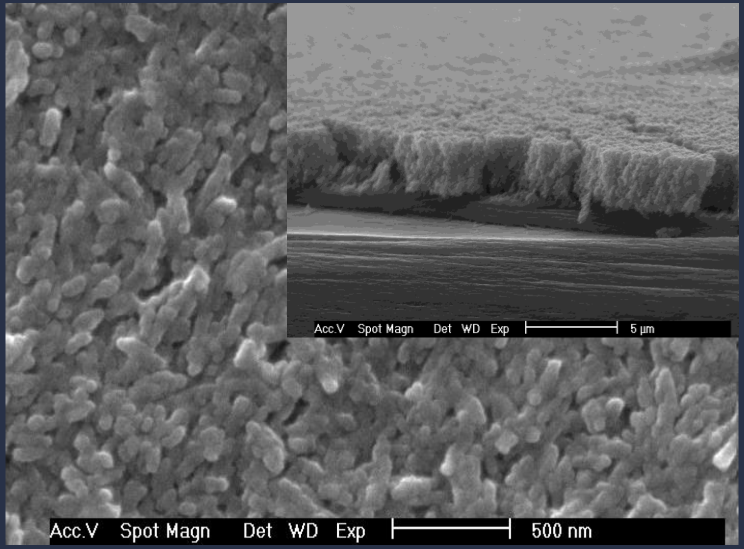




Fabrication of the mesoporous sol-gel layer

- Optimize and upscale sol-gel processes for the manufacturing of mesoporous films with highly controlled
  - Chemical composition (AlOOH, SiO_2, polym. binder, crosslinker, funct. silanes)
  - range of porosity (from few nm up to few 100s of nm)
  - And good adhesion and mechanical stability
  - Processes: dip-, spin-, spray- or bare coating





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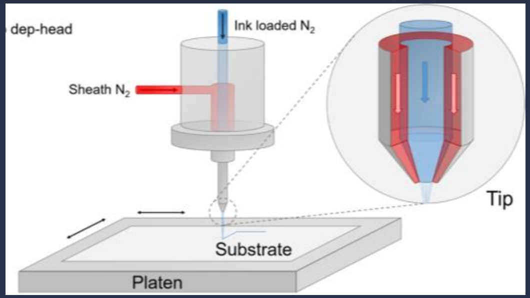
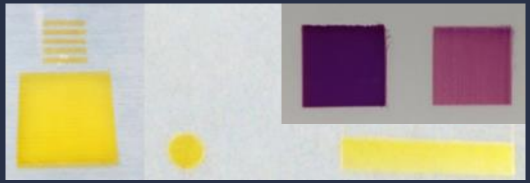
Functionalisation of the mesoporous sol-gel layer with dyes responsive to gas concentration

- Different wet coating and printing techniques available:
  - Automated slot die: homogeneity & upscaling up to A4 size (600 sensors), min. volume : 20-30mL
  - Automated dip- and spray-coating for complex 3D- sensing devices (eg. optical fibers)
  - Inkjet and Aerosoljet printing: different pattern down to 10 microns sizes, on 2- and 3-D substrates, min. volume: few mL





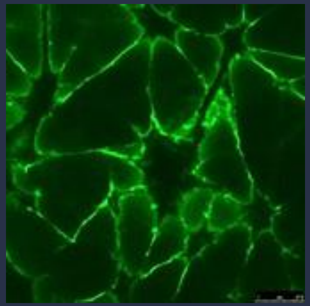
Non-invasive O2 monitoring in cell culture device

- Miniature objective-like reader for non-invasive oxygen concentration measurement in cell culture device (2015)
  - Integrated optics & electronics
  - Advanced data processing, algoritms and software

O_2 sensing in gas phase at 23/37°C and 70/90% humidity	
Accuracy	0.1% at 2% O_2
	0.2% at 21% O_2
Precision - 95% confidence interval	±0.3% at 2% O_2
	±0.3% at 21% O_2

O_2 monitoring in bioreactor and cell incubator

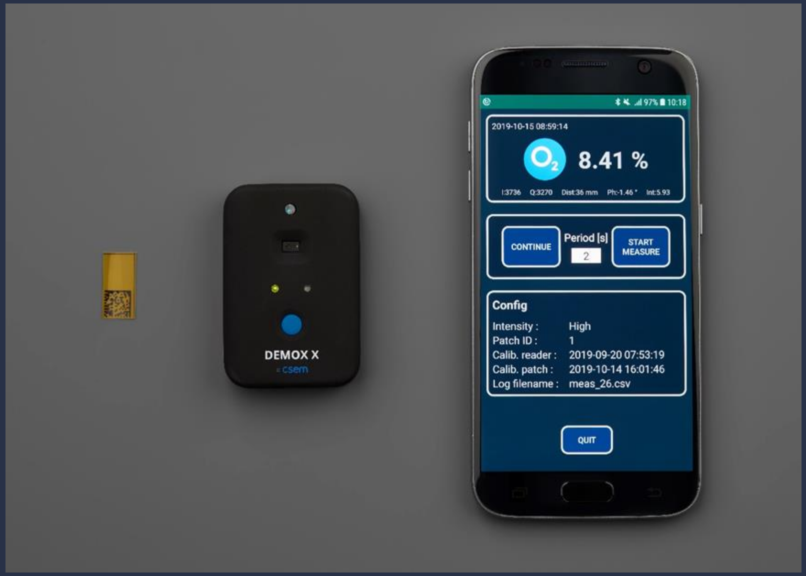
- Evaluation of oxygen concentration of cells in bone regeneration under pressure



- Fiber-based sensors for cell incubation chamber

Oxygen sensing for smartphones

- Disposable sensors
  - Quenching of fluorescent dye in the presence of oxygen
  - Slot die/aerosol jet printing (+ matrix barcodes)
- Reader
  - Non-invasive oxygen measurements
  - Miniaturized optics & electronics
- Smartphone
  - Mobile application (display)



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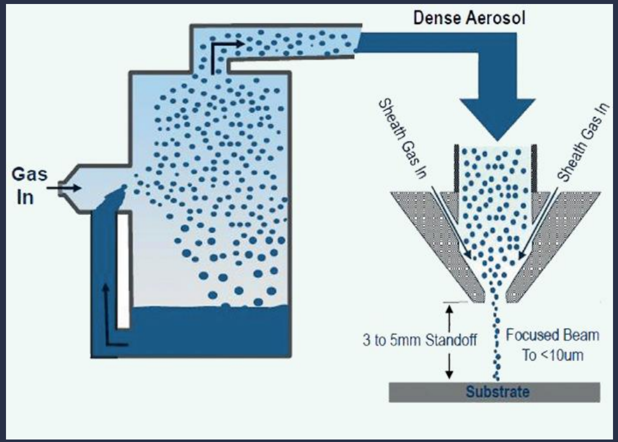
Aerosol Jet Printing - Technique Overview

- Non-contact direct-writing deposition technique
- Pneumatic and ultrasonic atomizers
- Capable of processing particle inks (Ø= 1nm - 1000nm), polymers, biomolecules, etchants, and paste-like fluids
- Printable line widths or critical dimensions = 10µm - 2000µm
- Print speeds = 0.01mm/s - 20mm/s - capable of 200mm/s
- Stage accuracy (X, Y, and Z) = ±6µm
- Stage precision (X, Y, and Z) = ±1µm
- Stage area = 30cm x 30cm with heating to 80°C
- Processing on non-planar substrates
- Solids loading = 0wt.% - 70wt.%
- Viscosity = 1cP - 1000cP, Volume = >1mL



Optomec AJ300 Tool

Functional Materials and Ink Development for AJP

- Current Customized Inks Developed at CSEM for AJP
  - Metal Oxides (SnO_2, SiO_2, WO_3, TiO_2, Al_2O_3, …)
  - Composites (Metal Oxides in Epoxy/Thiol-Ene Matrices)
  - UV-Curable Inorganics (TiO_2 with Sol-Gel Precursors)
  - Carbon Black and Carbon Black Composites (Carbon Black in Epoxy)
  - Polymeric Membranes (Poly(Vinyl Chloride))
- Inks Available from Commerical Suppliers
- Ink Development Directly with End User

Dispersion Equipment for Inks

BANDELIN SONOPULS
Ultrasonic Homogenizer

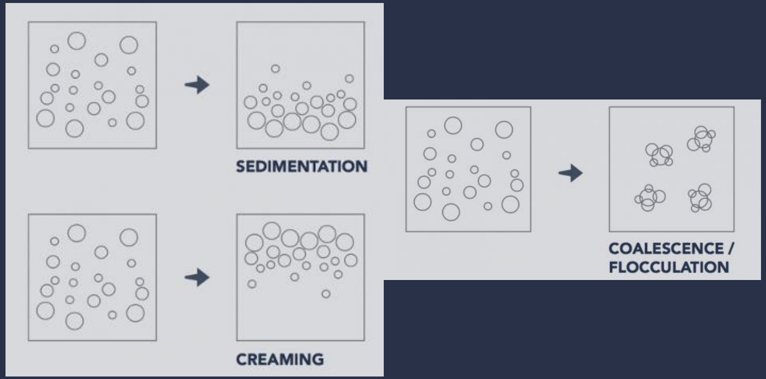
VMA GETZMANN
DISPERMAT LC55
Dissolver

Planetary Ball Mill

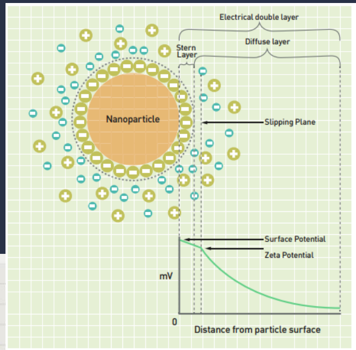
Planetary
Centrifugal Mixer

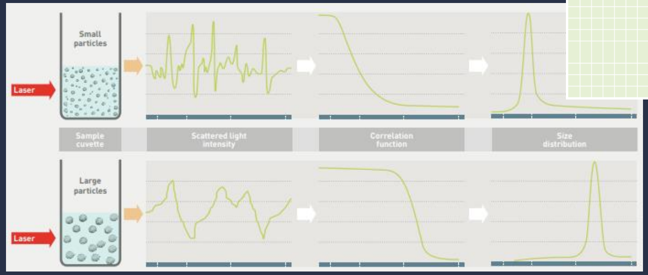
Characterization Equipment for Inks

Formulaction Turbiscan Lab Expert - Size and Stability Analyzer



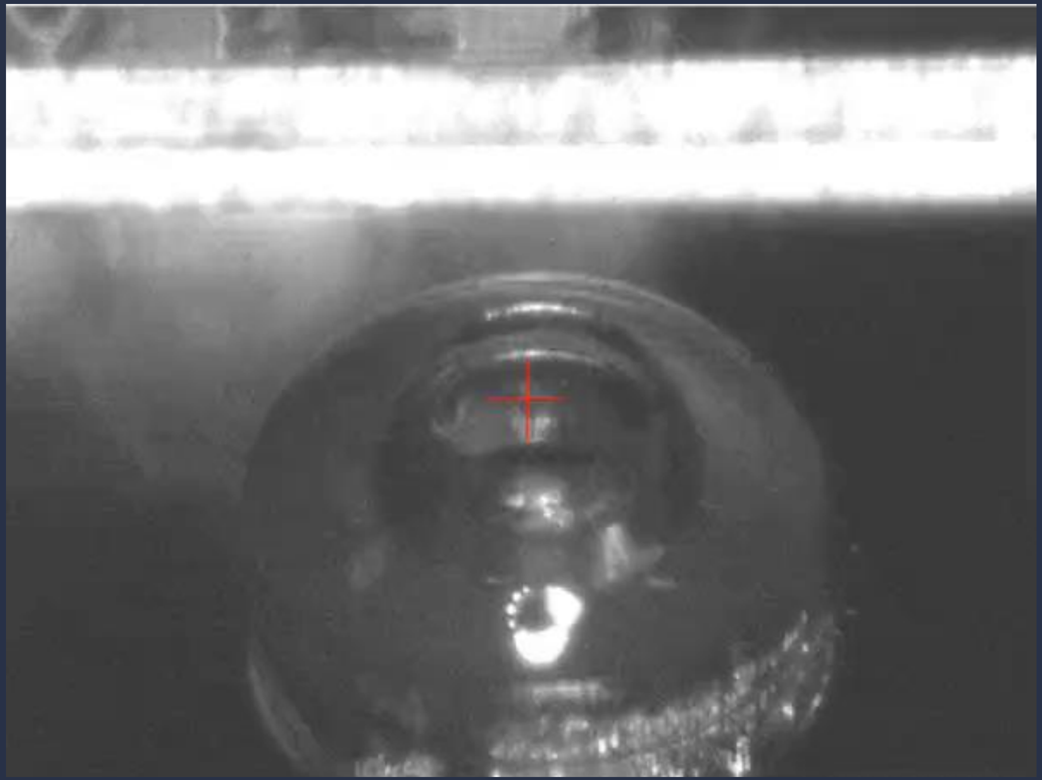
Malvern Zetasizer Nano ZS - Size and Zeta Potential Analyzer

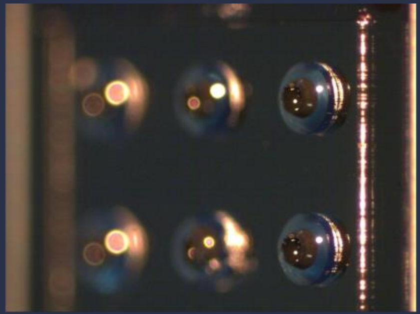




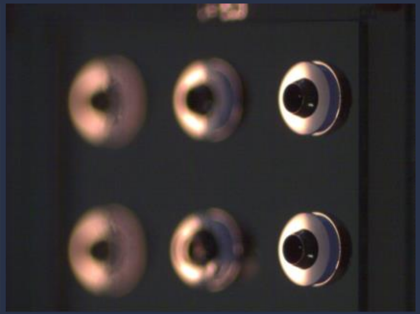
Brookfield DVII+ Pro Viscometer - Viscosity Analyzer

Aerosol Jet Printing - Patterning on Non-Planar Substrates

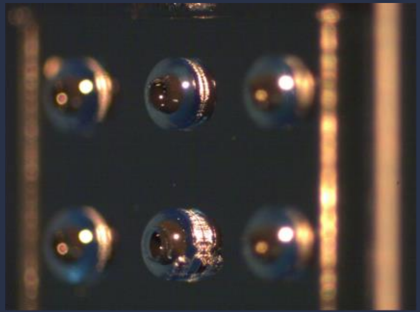




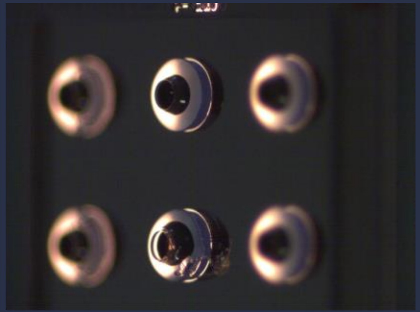
Reflection (2.5x) - Tilted



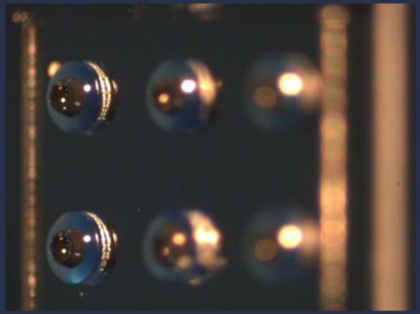
Transmission (2.5x) - Tilted



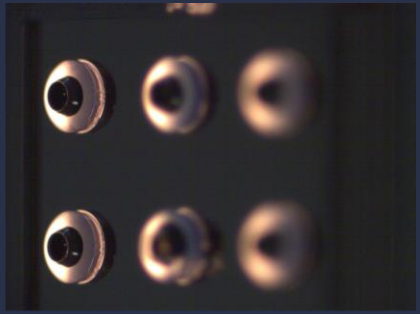
Reflection (2.5x) - Tilted



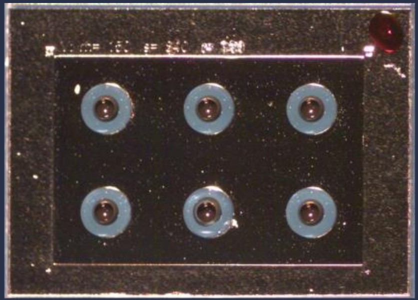
Transmission (2.5x) - Tilted



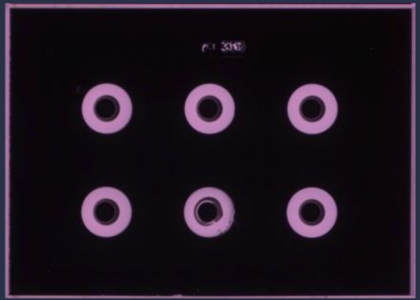
Reflection (2.5x) - Tilted



Transmission (2.5x) - Tilted

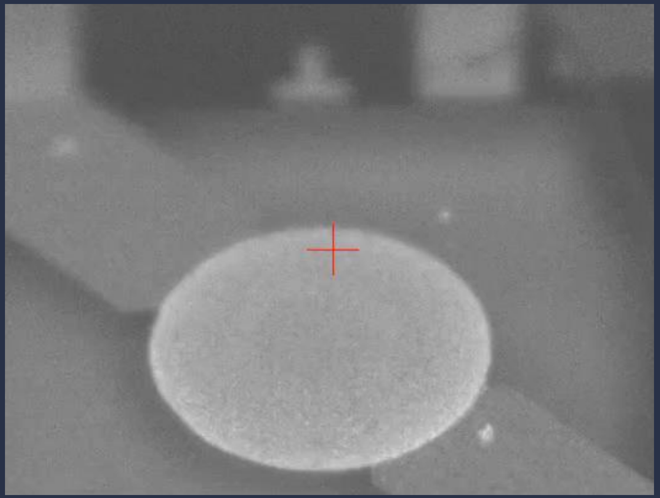


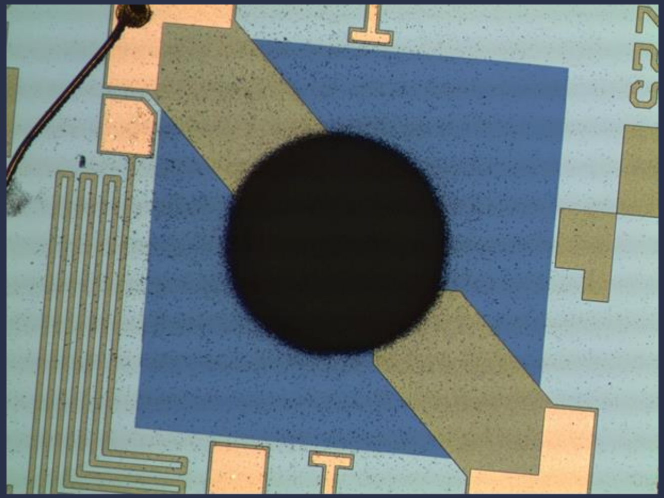
Reflection (1.25x)



Transmission (1.25x)

Aerosol Jet Printing on fragile freestanding membranes





Reflection (5x)

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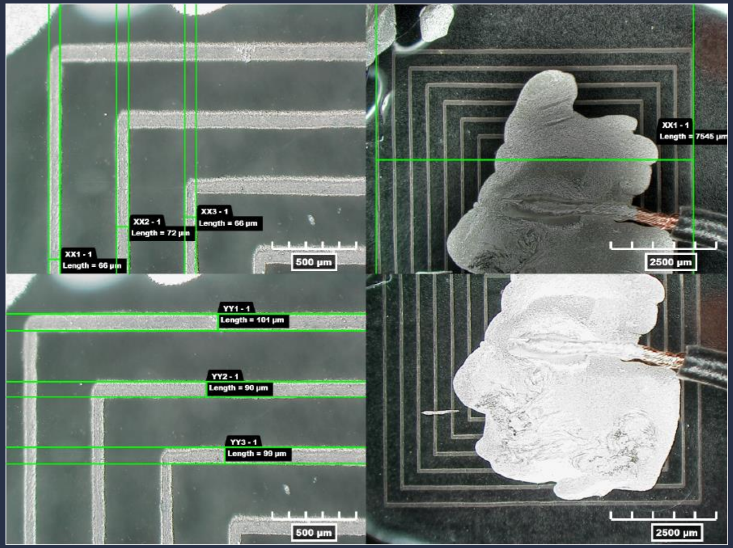
Aerosol Jet Printing - Metals

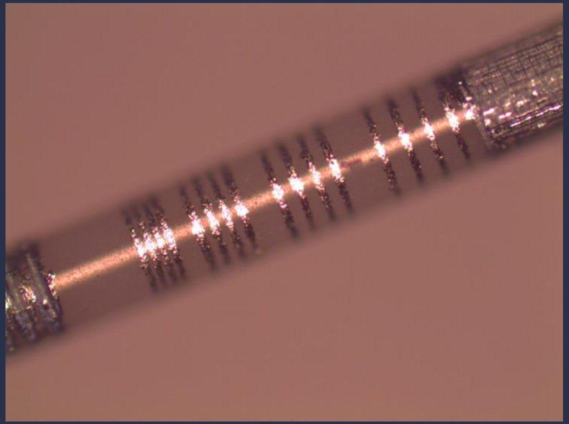


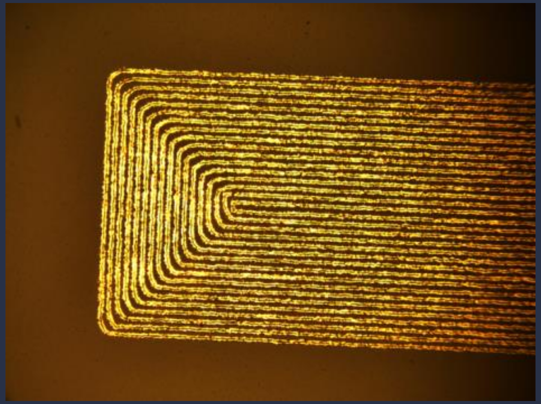
Capacitive Sensor Based on Ag


Strain Gauges Based on Ag

Decoration with Au
CSEM patented technology

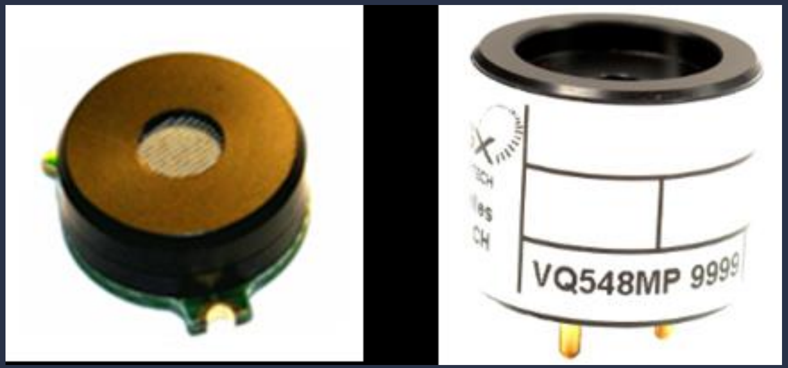
Complex Patterning with Au


Non-Planar Patterning of Au


High-Resolution Patterning of Au (15µm Liens)

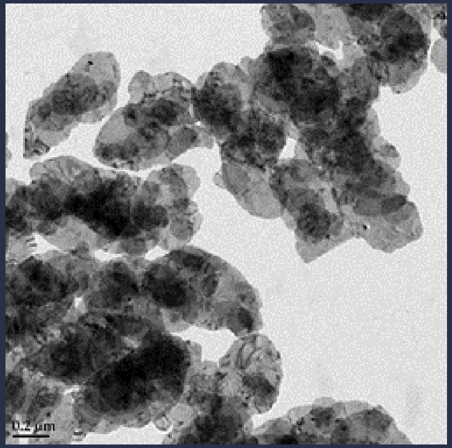
Aerosol Jet Printed gas sensors (CO, NOx, VOCs)

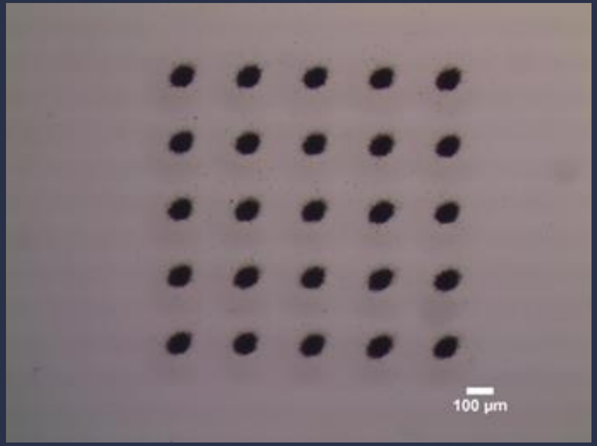
- Objective: develop new high resolution printing process for the continuous miniaturisation of gas sensors.
    - New ink formulation
    - Optimisation of printing parameters
    - Printing the functional element on chip
    - Performance evaluation (sensitivity, selectivity, stability)

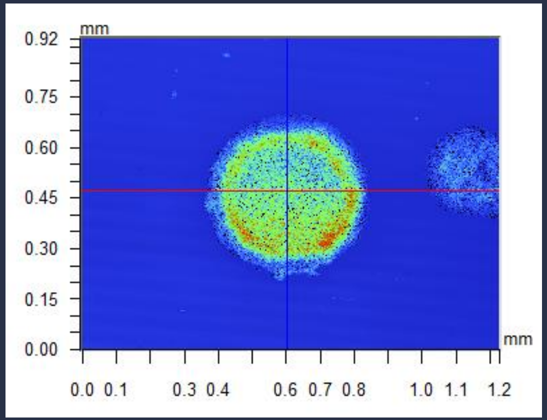


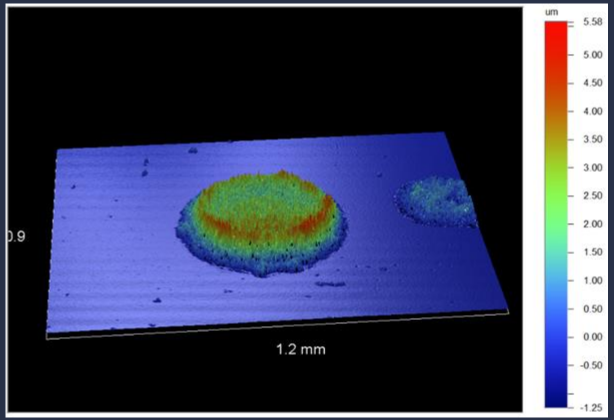
Ink formulation and optimisation of printing parameters

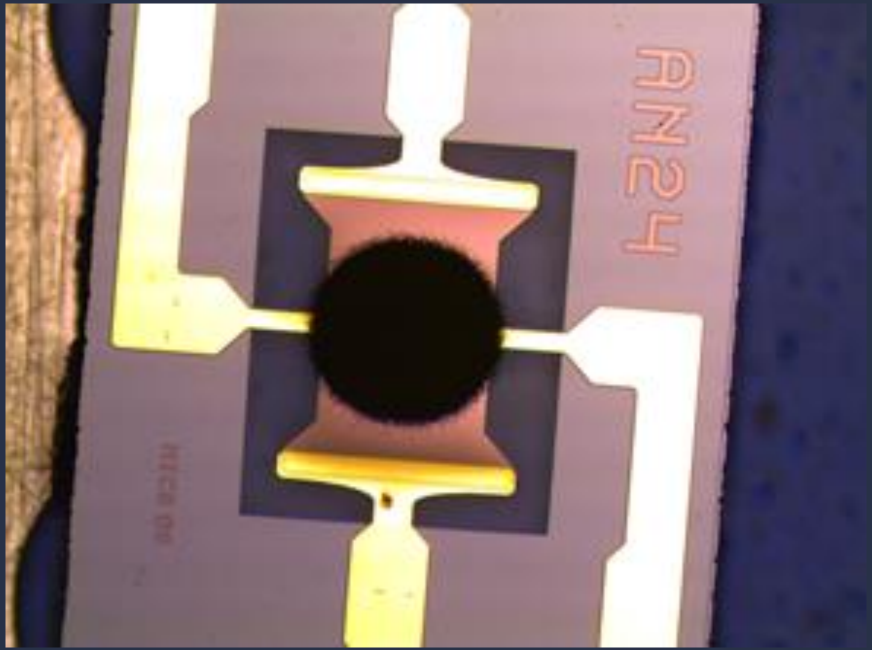
- Good ink stability
- Spot size down to 50 microns
- Controlled thickness
- Good adhesion of printed sensitive ink
- No satellites











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Sensor performances, CO sensing (red. Gas)

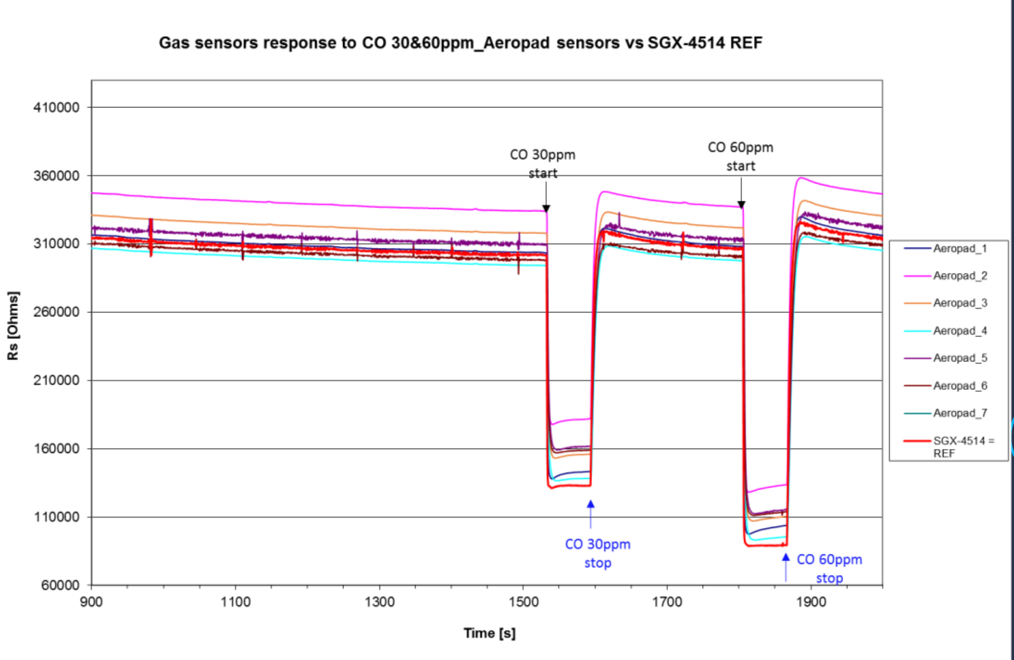
- AJP printed sensors have been evaluated and compared to screen printed sensors:
  - comparable sensitivity under CO

  Sensitivity=(RCO-R0)/R0 (with R0: electr. resist. in air)

  - comparable selectivity under CO

  Selectivity coeff: K=SA/SB with SA and SB are the sensitivities of sensor in "target gas" (A) and (B)

  - good stability
  - comparable base line



	CO Sensitivity									selectivity of the CO sensor under NO2		
	30ppm CO			60ppm CO			Base Line [KΩ]					
	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max
Aeropad sensors * (Aerosol Jet Printed)	-50%	-53%	-46%	-65%	-68%	-61%	310	294	334	2.7	2.1	3.4
SGX-4514 reference ** (Screen-printed)	-56%	n/a	n/a	-71%	n/a	n/a	302	n/a	n/a	2.6	n/a	n/a

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Sensor performances, NO_2 sensing (ox. Gas)

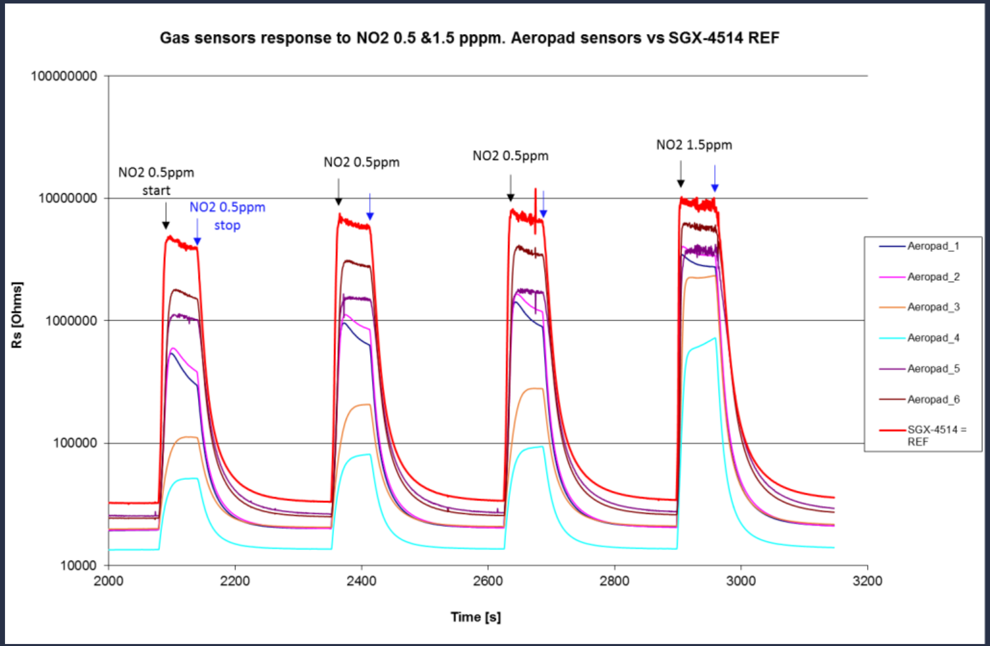
- AJP printed sensors have been evaluated and compared to screen printed sensors:
  - comparable or lower sensitivity under NO_2, but still very high. Values dispersion should be reduced.

  Sensitivity=(RNO_2-R0)/R0 (with R0: electr. resist. in air)

  - comparable or higher selectivity under NO_2

  Selectivity coeff: K=SA/SB with SA and SB are the sensitivities of sensor in "target gas" (A) and (B)

  - good stability, comparable base line



	NO2 Sensitivity									selectivity of the NO2 sensor under CO		
	0.5ppm NO2			1.5ppm NO2			Base Line [KΩ]					
	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max
Aeropad sensors * (Aerosol Jet Printed)	7262%	587%	18865%	15986%	5167%	29406%	22	14	30	154	62	288
SGX-4514 reference ** (Screen-printed)	19668%	n/a	n/a	29396%	n/a	n/a	34	n/a	n/a	74	n/a	n/a

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Conclusion

- Self-Assembly, a powerful techniques for surface nanostructuring and surface functionalization
- Nanosphere lithography could be hybrized with photolitho and micro/nanoreplication processes. Many applications demonstrated in MEMS, Energy, Security and Life Sciences.
- Self-assembled nanolayers have been used for improving metal adhesion on 3D printed plastic parts. Process currently industrialized for the fabrication of antenna for space, also for PV
- Responsive Surfaces: Functional mesoporous sol-gel layer have been developd for O_2 (also pH & CO_2) sensing application. Integration of these smart films in fully integrated systems successfully achieved. Application in Bio-, Med-tech and aeronautics
- AJP: a new and unique printing technique with high potential for electronic and sensor applications

Thank you for your attention. We look forward to working with you.

Raphael.pugin@csem.ch

T: +41 32 720 50 42