



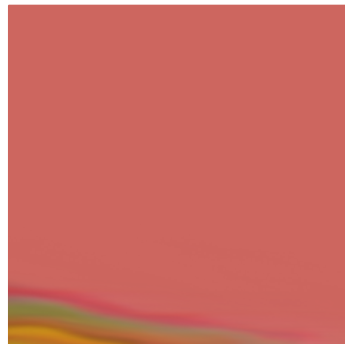
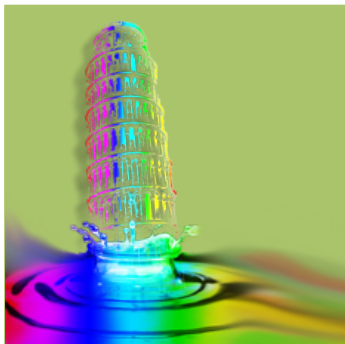
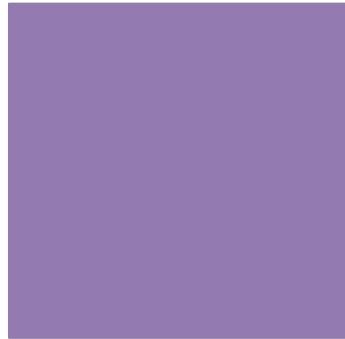
CENTRO E. PIAGGIO

Bioengineering and Robotics Research Center

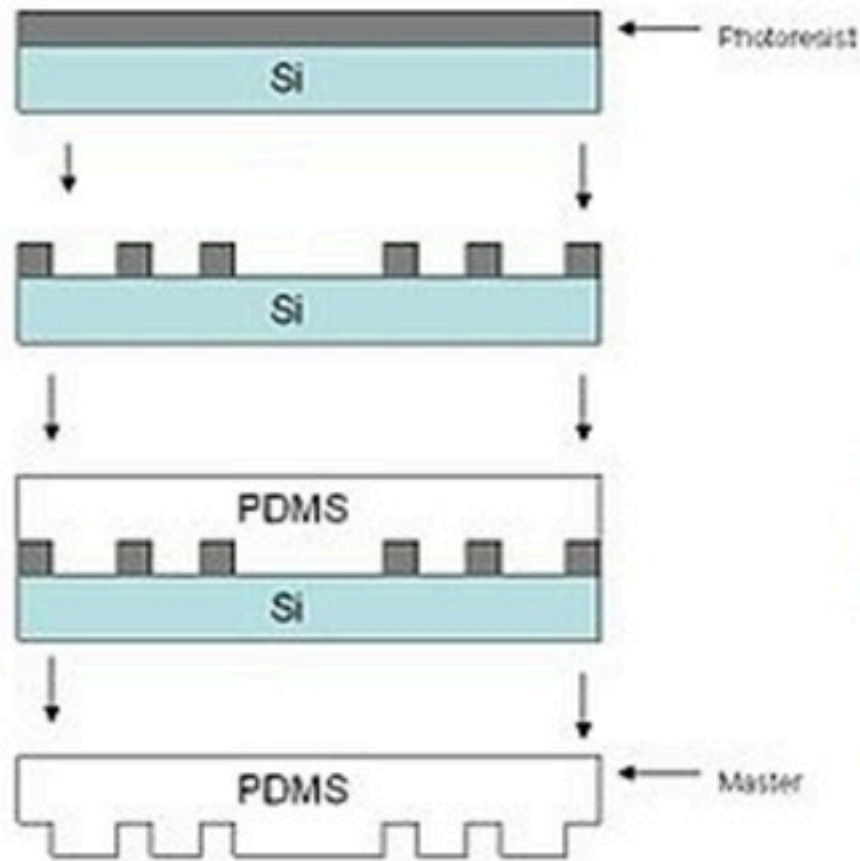
# SOFT-LITHOGRAPHY

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G. Vozzi



# + Soft-lithography



# **Soft-lithography**

**Micro-stamping**

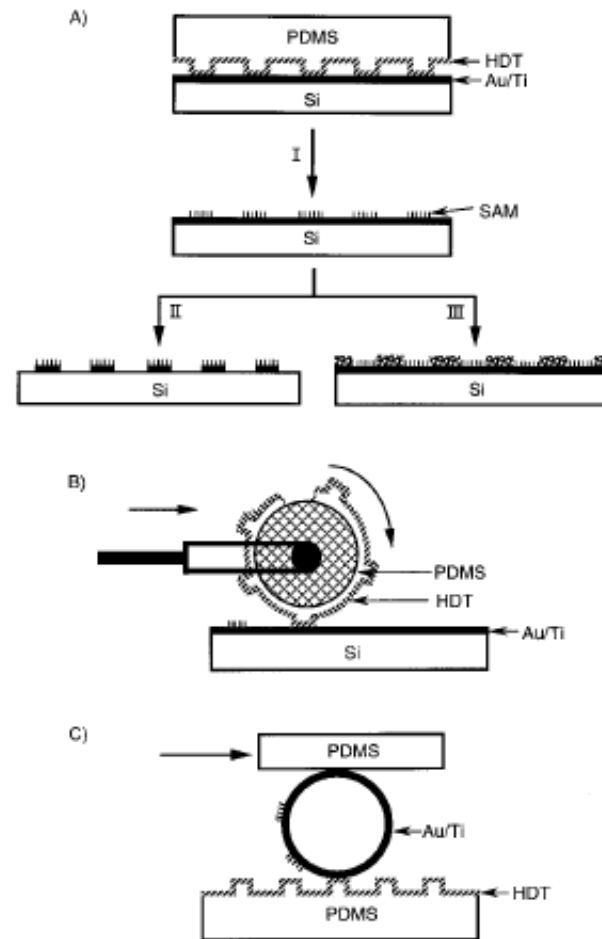
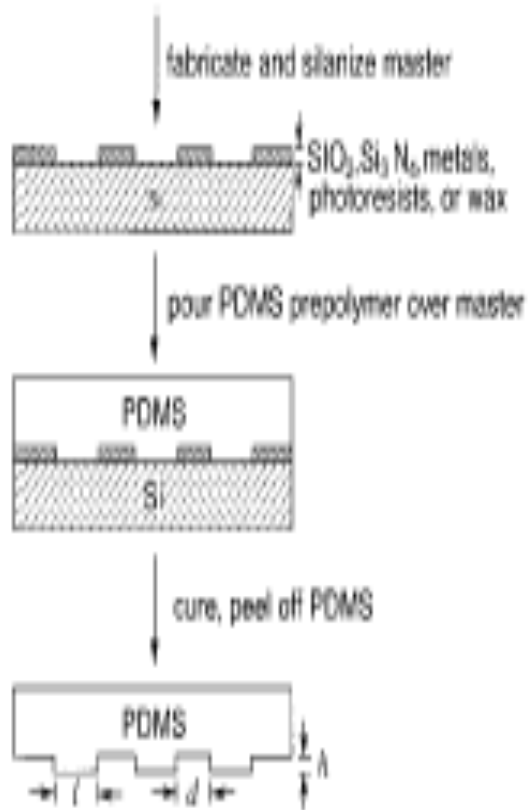
**Micro-molding**

**Micro-fluid dynamics**

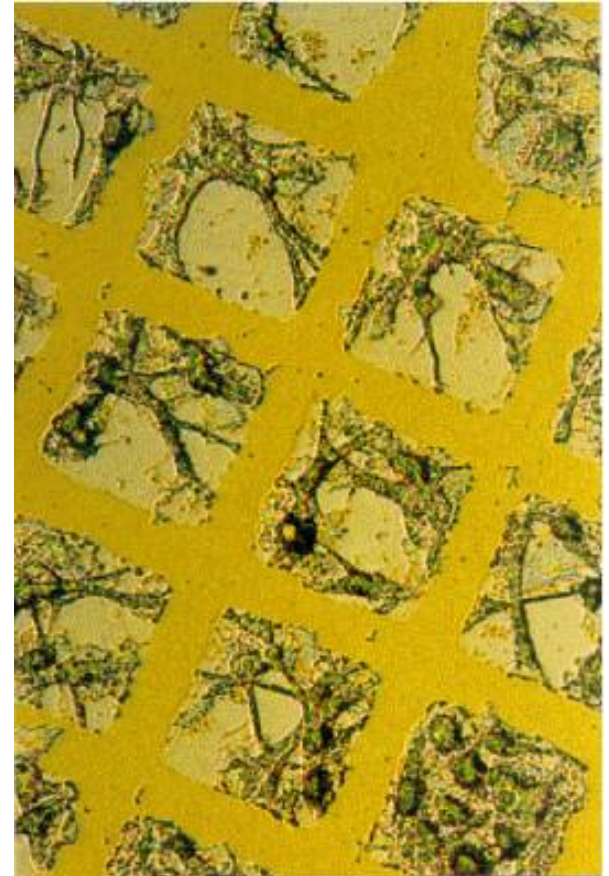
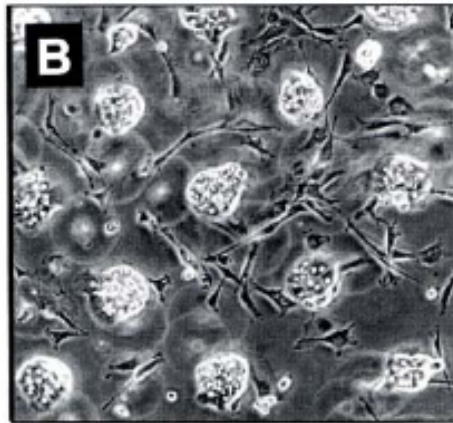
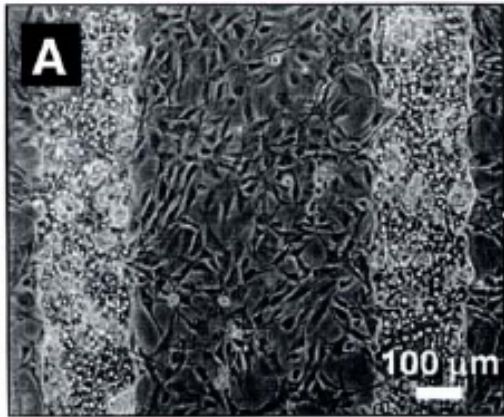
**MEMpat**

**LIFT-OFF**

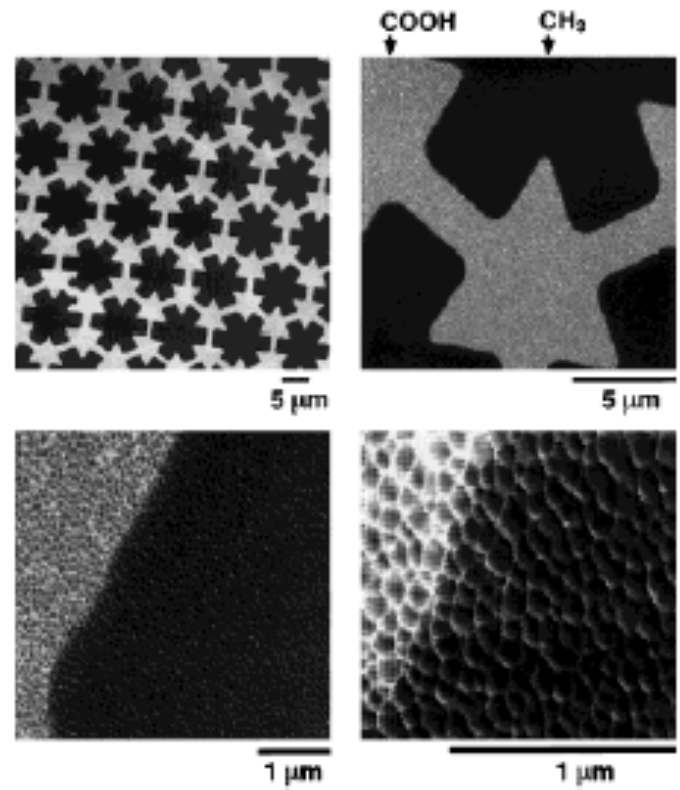
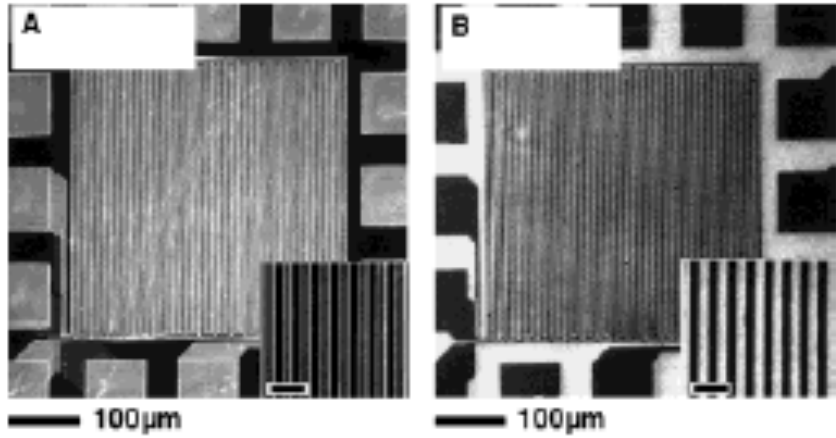
# Micro-Contact Printing



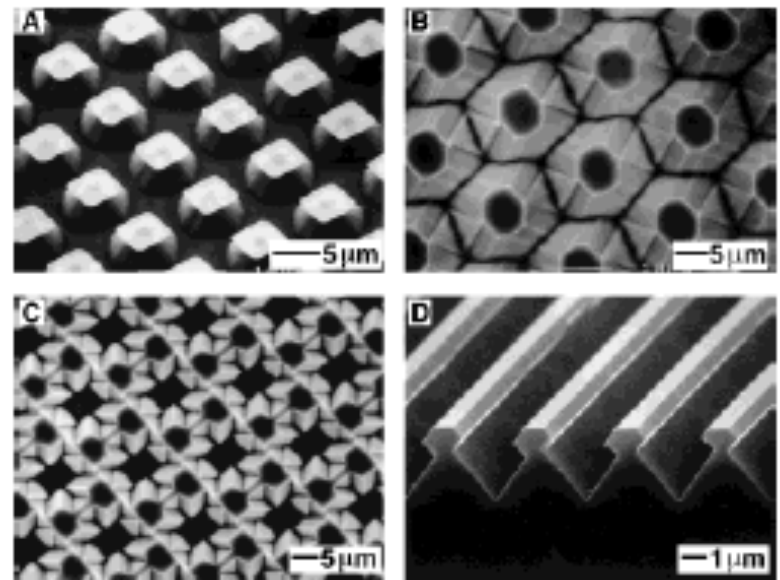
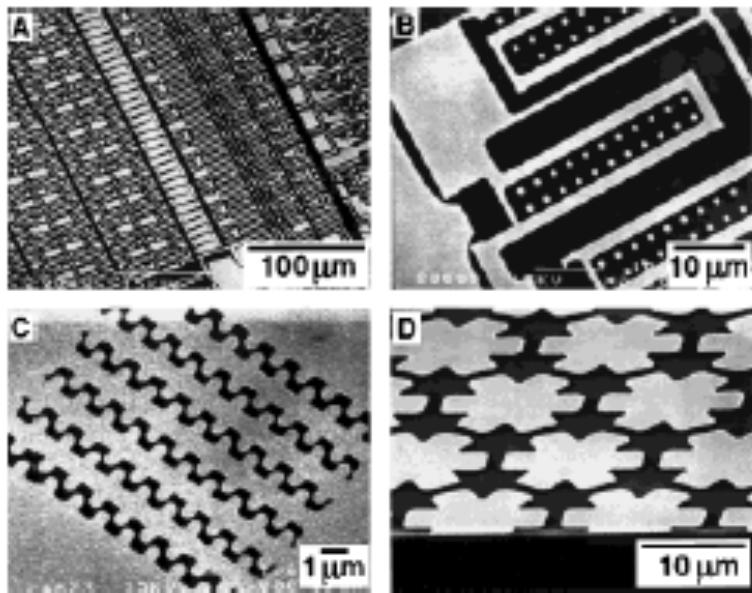
# Results



# Results



# Risultati



# Micromolding

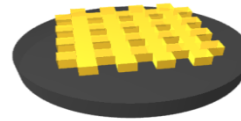
Spin Photoresist



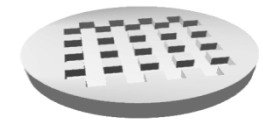
Expose Through Mask



Develop Photoresist

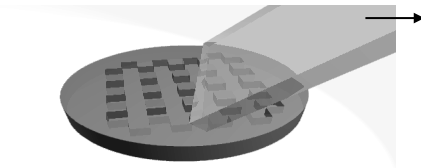


Cast in PDMS  
Use as Mold



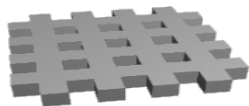
**A**

Micromolding



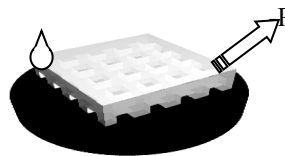
Apply PLGA solution  
Scrape to remove excess

Bake mold+PLGA  
Peel Scaffold from mould



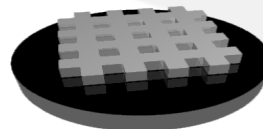
**B**

Microfluidic Molding



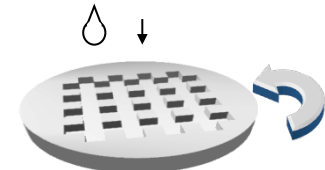
Invert mold, seal to surface  
Perfuse PLGA solution by applying  
negative pressure

Bake mold+PLGA  
Peel PDMS from surface



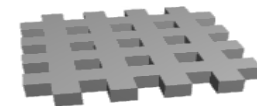
**C**

Spin-coating



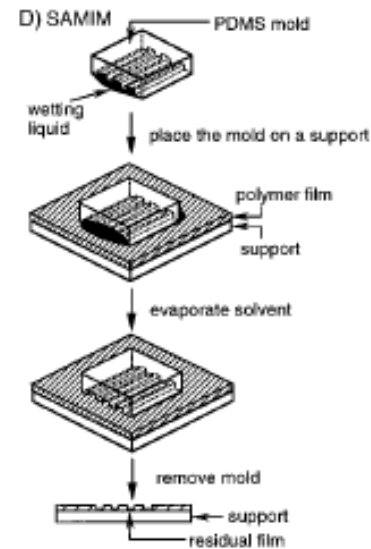
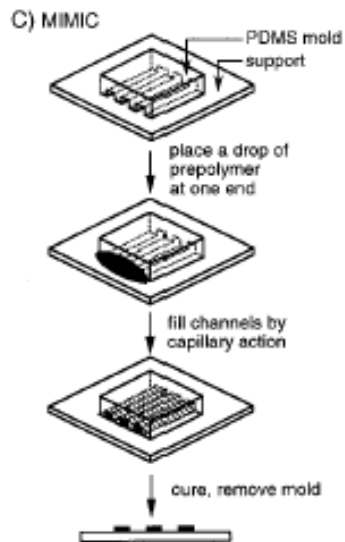
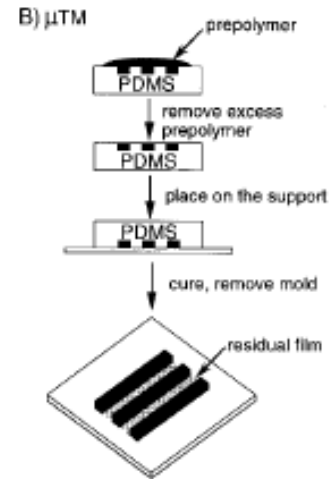
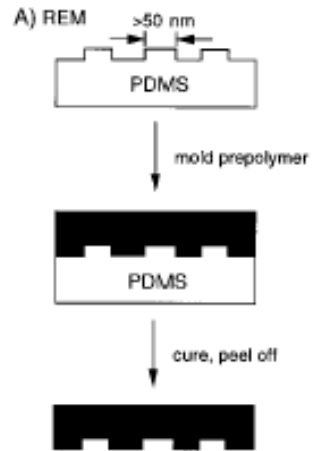
Apply PLGA solution to PDMS mold,  
Spin @ 2000 rpm

Bake mold+PLGA  
Peel Scaffold from mould

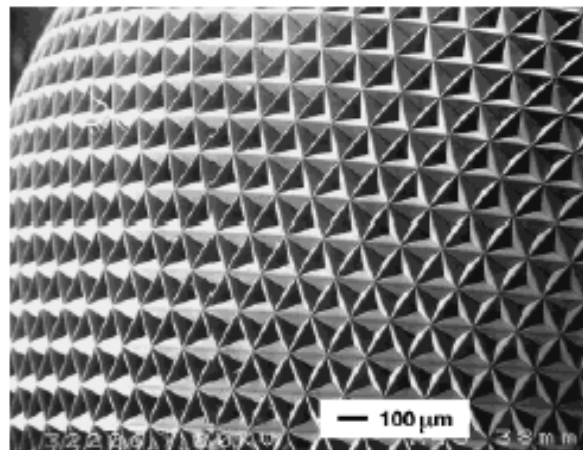
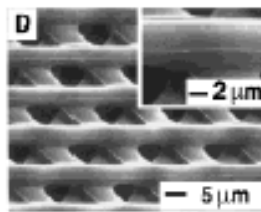
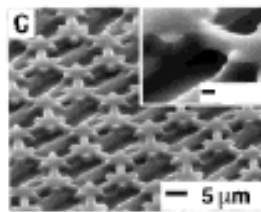
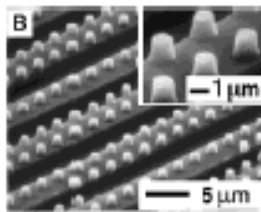
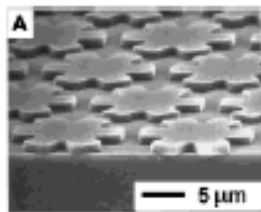
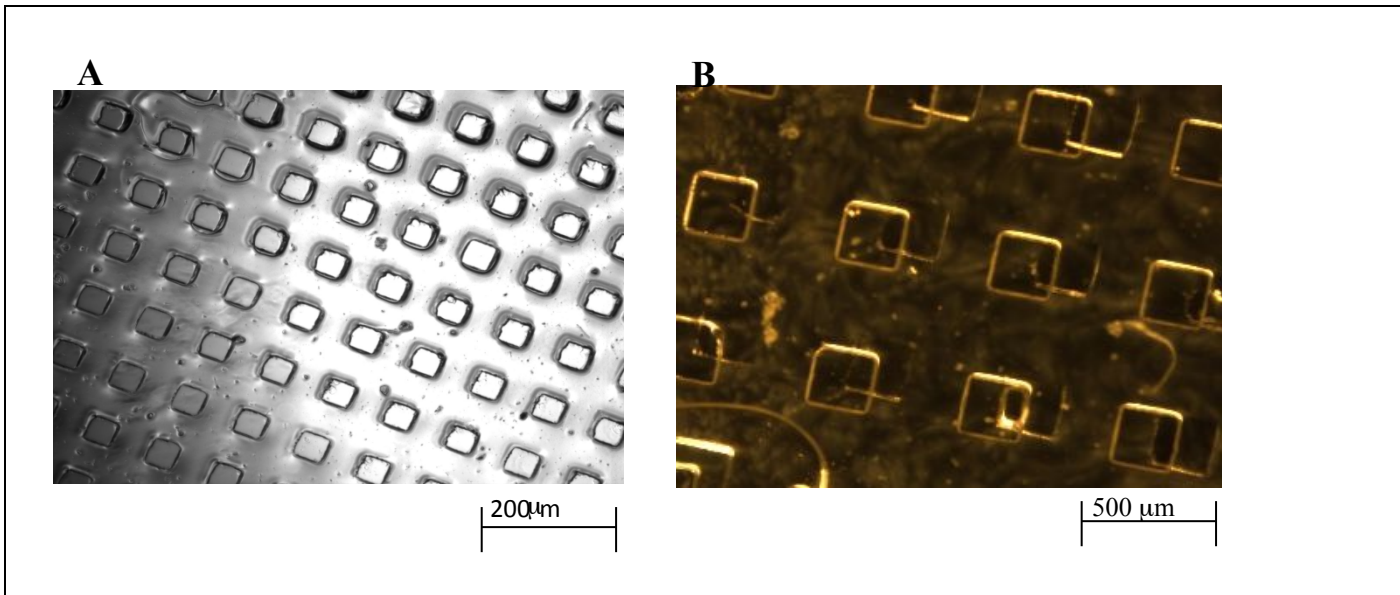




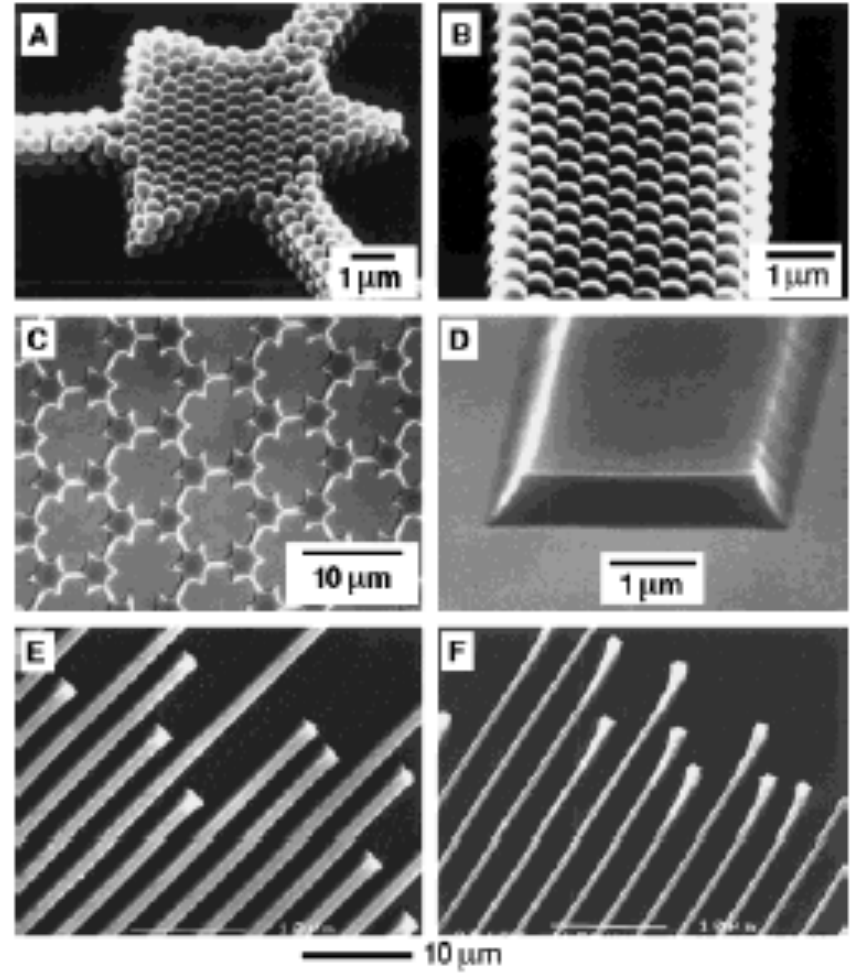
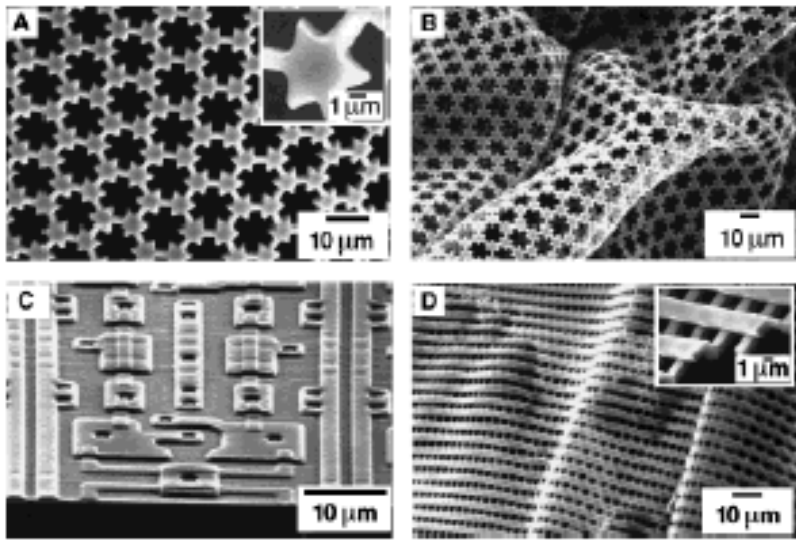
# Micromolding



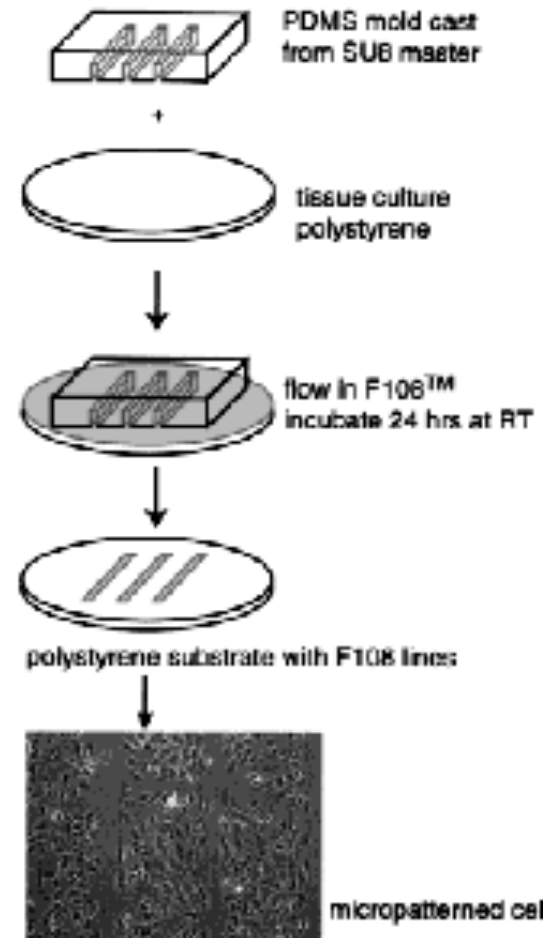
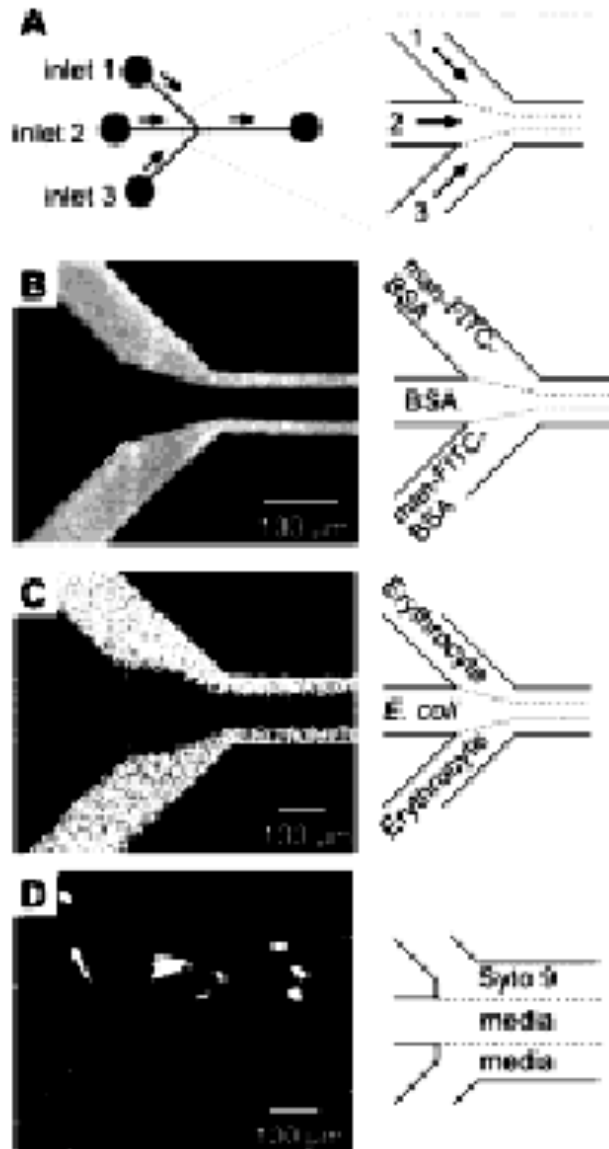
# Risultati



# Results

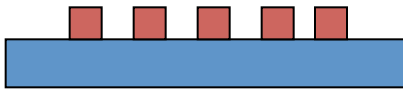


# Micro Fluid Dynamic



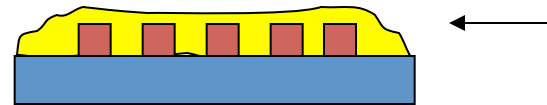
# MEMpat

A

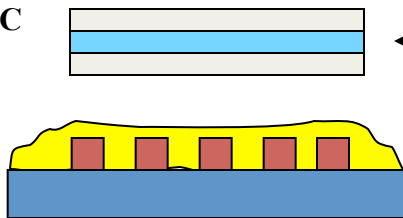


Master di silicio con la geometria desiderata

B

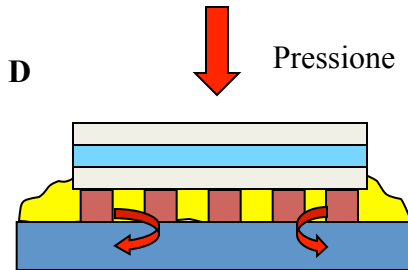


C



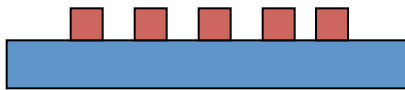
Sandwich di piastre

D



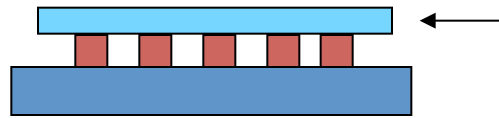
# MEMpat

A

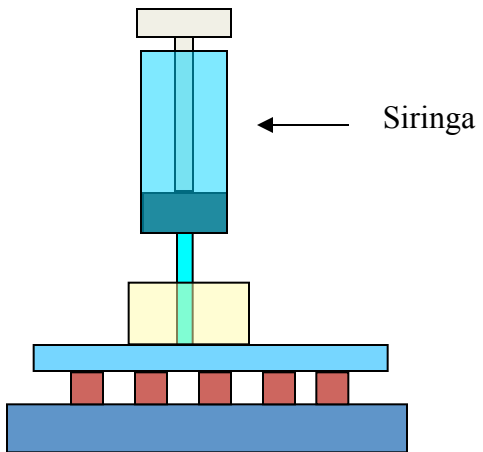


Master di silicio con la geometria desiderata

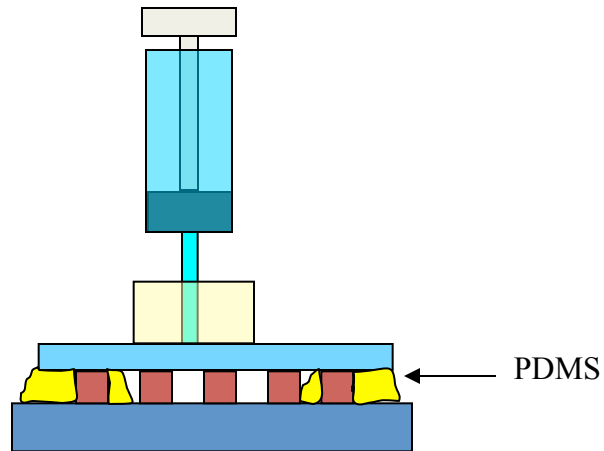
B



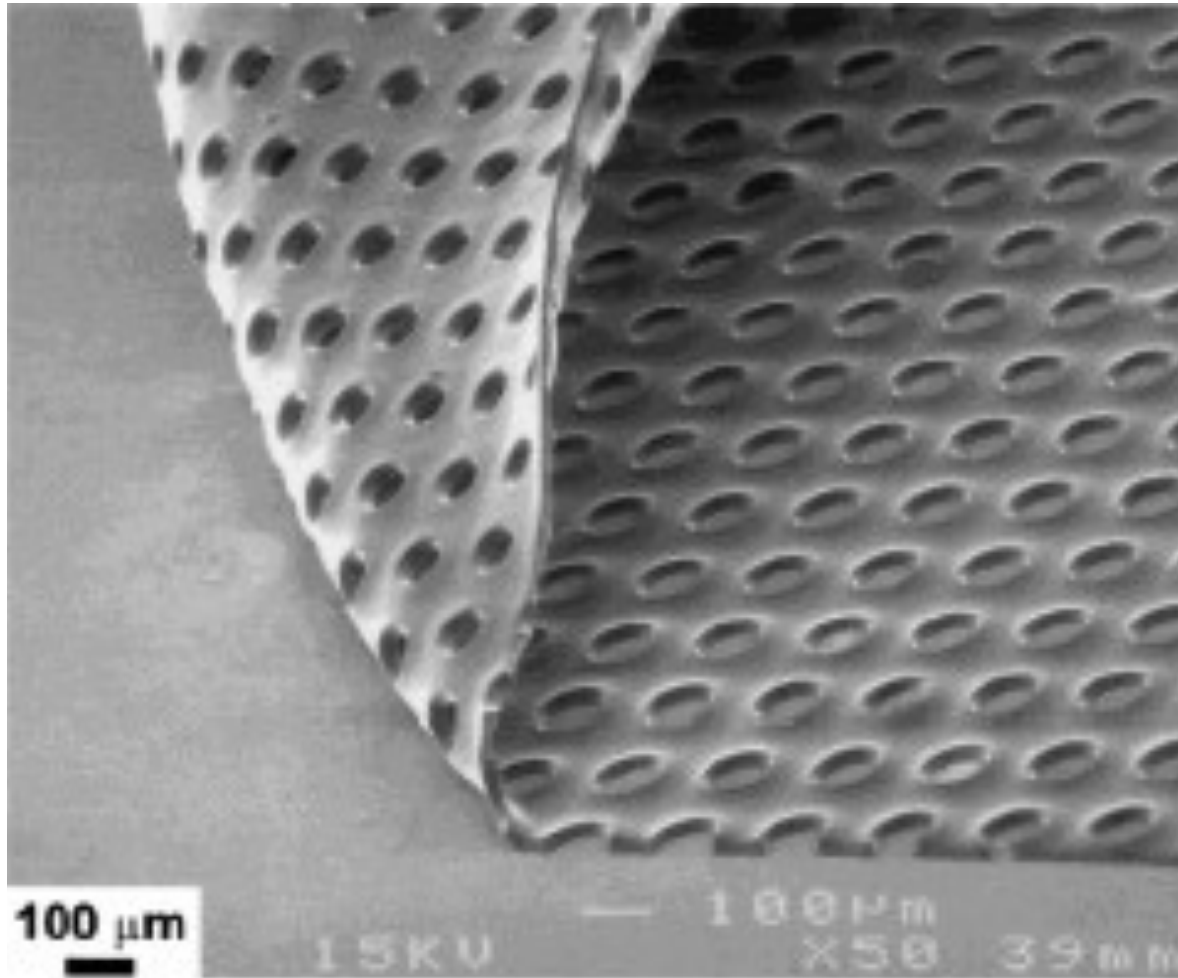
C



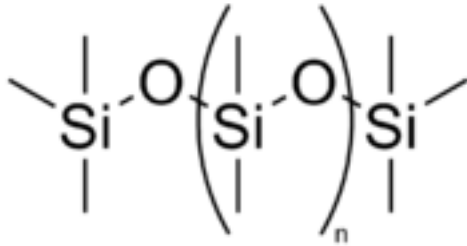
D



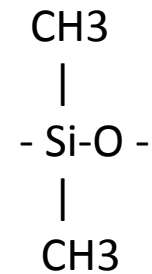
# MEMpat



# Polydimethylsilosane (PDMS)



The polydimethylsiloxane (PDMS) is obtained starting from dimethylchlorosilane  $[(\text{CH}_3)_2\text{SiHCl}]$  which is a chemical compound produced by direct reaction between silicon and methyl chloride ( $\text{CH}_3\text{Cl}$ ). For subsequent hydrolysis of dimethyldichlorosilane cyclic and linear siloxanes are obtained, subsequently they are polymerised in order to produce silicone polymers. The PDMS polymer is formed by the sequence of the following monomer:



It is characterized by a remarkable resistance to temperature, to chemical attack, to oxidation, it is an excellent electrical insulating and resistant to aging; it is optically clean (transparent), it is biocompatible, inert, it is neither toxic nor flammable. This polymer also does not bind to either the glass, neither the metal nor the plastic during solidification, but retains greater grip on smooth surfaces once solidified.



# PDMS

## Features

- colourless
- Boiling temperature > 100°C
- Relative density 1.1
- Dynamic viscosity 3500 Centipoise
- Dielectric Constant at 100 Hz = 2.72
- Dielectric Constant at 100 kHz = 2.68
- Dielectric Strength = 500 volts per mil v/mil
- Heat Cure            10 Minutes @ 150 Deg C
- Heat Cure            20 Minutes @ 125 Deg C
- Heat Cure            35 Minutes @ 100 Deg C
- Hydrophobic
- Mix Ratio            10:1 Base to Catalyst 87-RC
- Room Temperature Cure – Hours = 48 Hours
- Self Leveling
- Shelf Life = 720 Days
- Temperature Range -45 Deg C to 200 Deg C
- Thermal Conductivity = 0.27 Watts per meter K
- Volume Resistivity =  $2.9 \times 10^{14}$  ohm-centimeters
- Water Resistant
- Working Time            > 90 Minutes
- Elastic modulus around MPa



# Methods to modify surface chemistry of PDMS

**PDMS is hydrophobic**

**Chemical and/or Physical treatment to increase its wettability**

## Physical Treatments

1. Exposure to UV ray ( $\lambda = 350 \text{ nm}$ )
2. Argon Plasma

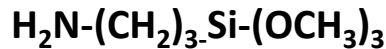
## Chemical Treatments

3. Dipping in Pyranha solution ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  30% m/m = 3:1 v/v)
4. Dipping in  $\text{H}_2\text{O}_2$  30% m/m in deionised water

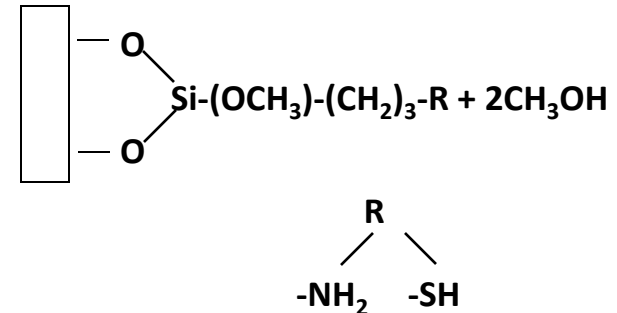
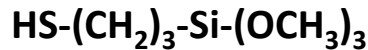
# Functionalisation of PDMS surface

- Derivatisation with polyfunctional silanes in a solution of toluene and deionised water

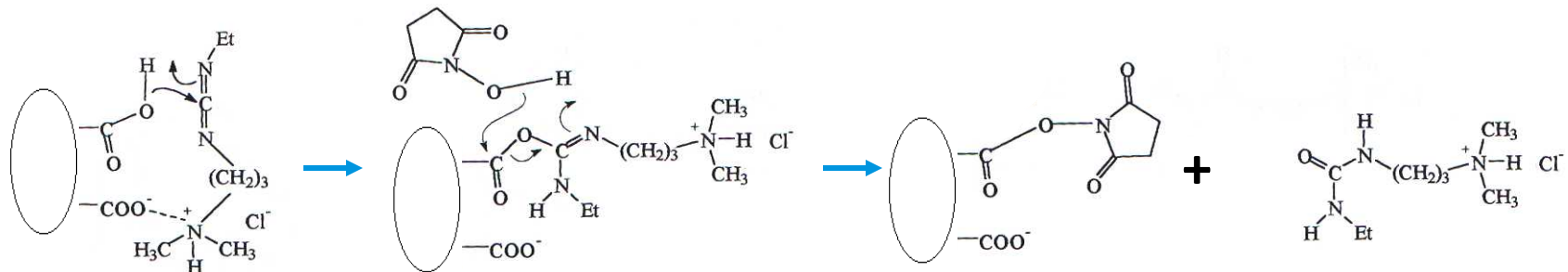
- 3-aminopropyl-trimethoxysilane



- 3-mercaptopropyl-trimethosilane



- Activation of reaction between carboxylic and nucleophilic groups using N-ethyl-N'-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxysuccinimide (NHS) in aqueous solution

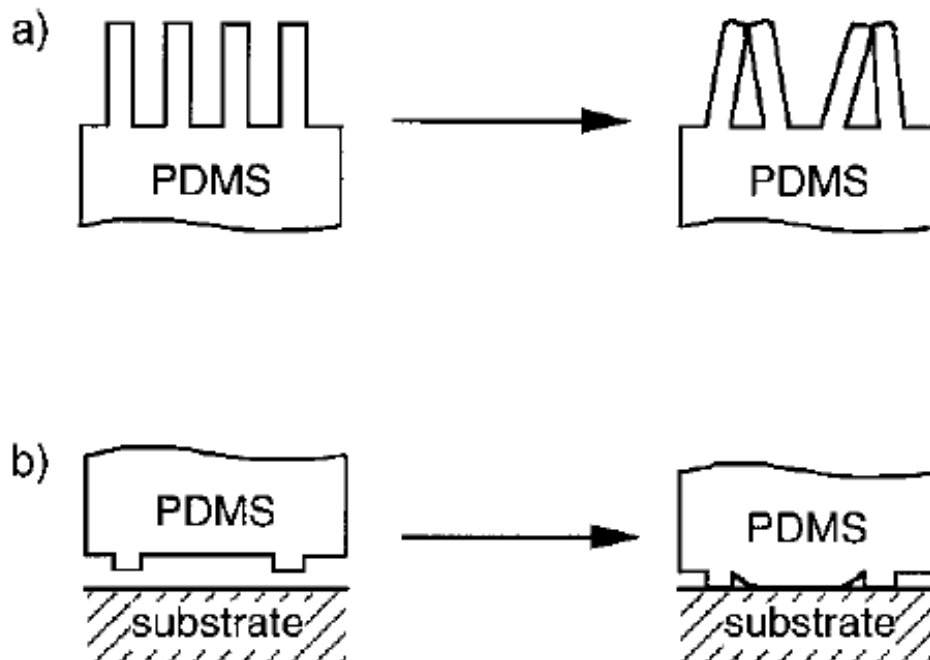


# Stability of Microstructures

When a pressure is applied between the PDMS pattern and a substrate as in microcontact printing and the height of the silicon structures it is lower than the relative distance between the collapse of their structures.

And if the aspect ratio is too high, the structures can be deformed and collapse.

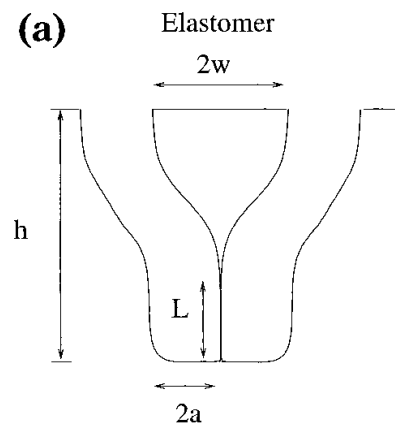
They can adhere to each other if they are too close together.



Delamarche et al. have shown that the 'aspect ratio ( $l / h$ )' of structures made of PDMS must be between 0.2 and 2 to have molds free of defects.

# Stability of Microstructures

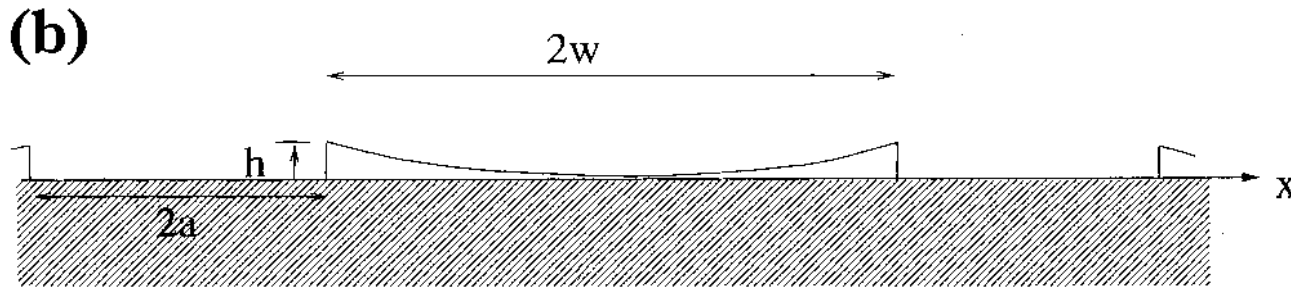
Understanding the mechanisms that make the silicon structure stable and limitations in the design of the pattern is critical in soft-lithographic process. The main limitation is linked to the basal shear modulus that is less than 1 Mpa.



Biebuyck has shown experimentally that if  $h / 2a$  is too large the structures collapse and adhere to each other because of the pressure forces on the mold and of the capillary forces due to the fluid that bathes the surfaces.

# Stability of Microstructures

However if the aspect ratio is too low, all the surfaces can be deformed due to the surface adhesion forces.



These phenomena are mainly due to the surface adhesion forces between the substrate adhesion and silicon structures. If we consider a mold PDMS ideal with regular and well straight topologically structures when these adhere to the substrate surface tensions in place because of the low shear modulus of the silicon will begin to deform, by varying the adhesion surface area and therefore the pattern key thing to consider when having structures with submicron resolution.

# Stability of Microstructure

To reduce this problem you can increase the silicone elastic module incorporating particles or increasing the cross-linker but this alters the chemical and physical characteristics of the material that may not adhere as well to master. Furthermore, the increase of the rigidity of the mold leads to less surface area to concentrate stress in the areas that during the manufacturing process may then break or come to a plastic deformation.

We analyze the problem and its possible solutions, using punches to a structure with a rectangular section.

$h$ = Pillar Height

$2a$ = Pillar width

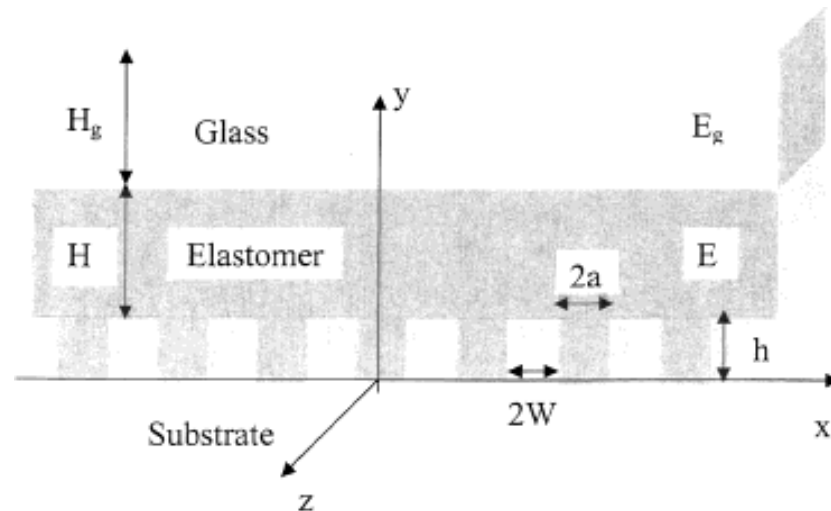
$D$ = Mold lateral size

$H$ = Mold Thickness

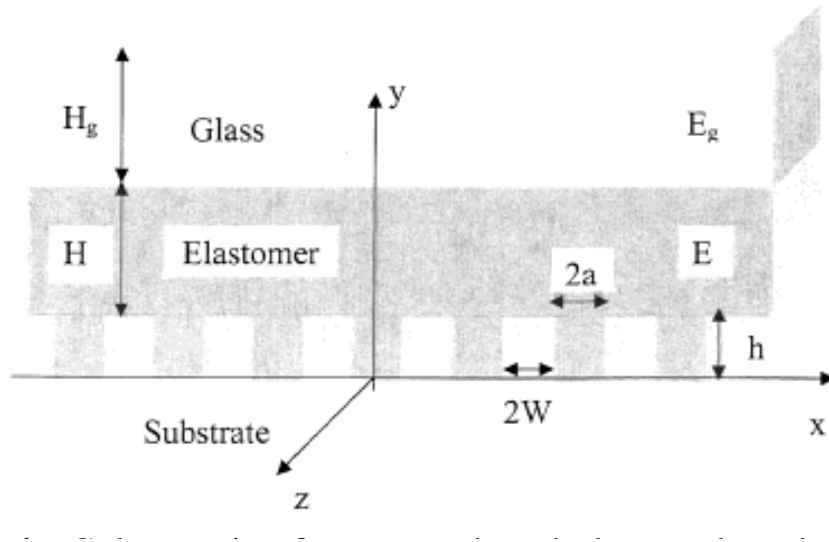
Hypotheses:

$$H/D \ll 1 \quad h/H \ll 1$$

$$a/H \ll 1 \quad w/H \ll 1$$



# Stability of Microstructure



The number of pillars along x axis for length unit is :

$$N = \frac{1}{2(a + w)}$$

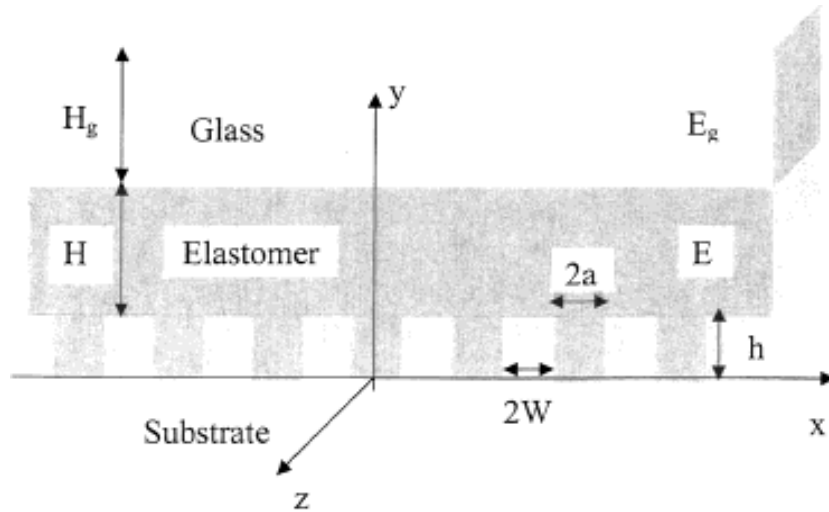
Suppose also that the applied loads do not vary along the z axis.

Often to work using a glass layer above the elastomeric mold which we assume  $H_g$  thickness.

The elastomer is assumed homogeneous and isotropic with Poisson coefficient equal to 0.5 and elastic modulus between 0.1 and 10 MPa



# Stability of Microstructure



Initially, suppose that the pillars are detached from the substrate and then are pressed by a  $\Delta$  tract that induces a compressive load  $\sigma$ , then the agent stress on the single punch is equal to:

$$P = \frac{\sigma}{N} = 2(a + w)\sigma$$

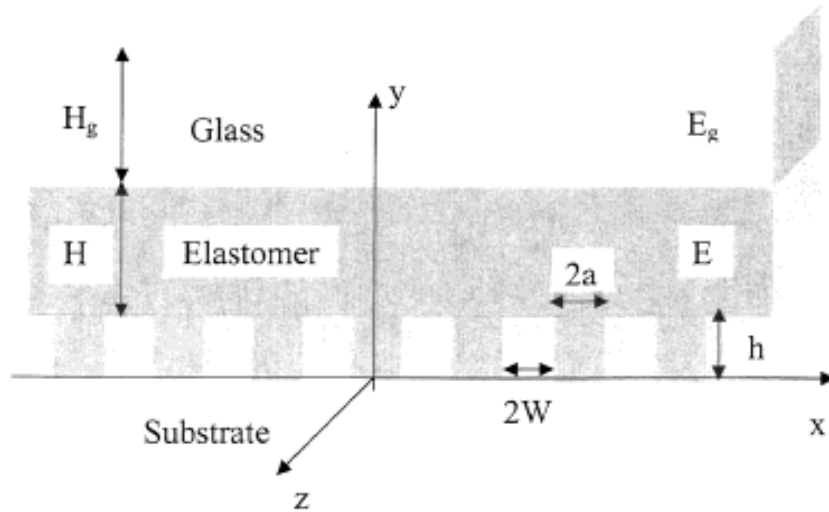
$$\Delta = C\sigma$$

$$C = \frac{(1 + \nu)(1 - 2\nu)H}{E(1 - \nu)}$$

Since glass is stiffer than elastomer can we neglect the glass deformation in the x-y plane that would be equal to:

$$\nu_{\text{vetro}} \frac{\sigma}{E_{\text{vetro}}} < \nu_{\text{vetro}} \frac{E}{E_{\text{vetro}}} \cong 0$$

# Stability of Microstructures



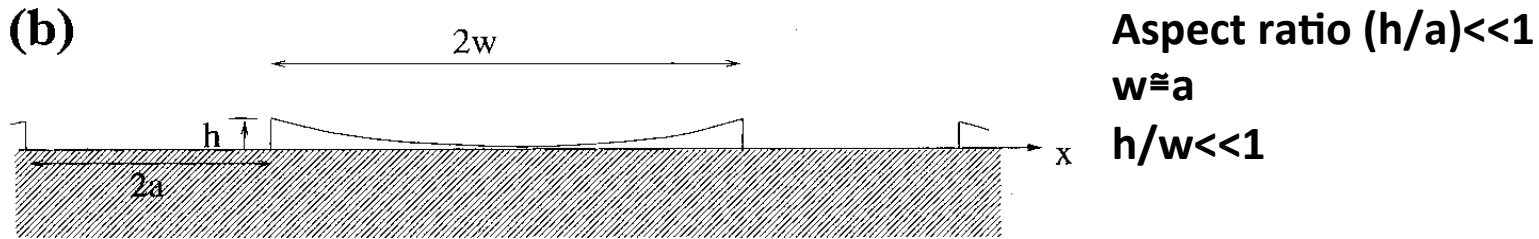
Then the silicone layer in the x-y plane is subjected to a state of biaxial stress

$$\sigma_{xx} = \sigma_{yy} = \frac{\nu\sigma}{(1-\nu)} \cong \sigma$$

So the silicone is subjected to pure compression except the edges that we neglect. On this basis the deformation undergone by the single pillar per unit length is:

$$\varepsilon = \frac{P}{E} = \frac{2(a+w)\sigma}{E}$$

# Stability of Microstructures



When an external load is applied the maximum deformation which can have is equal to  $h$  (the pillar height) in the  $z$  direction but since the material is isotropic and homogeneous we will also have lateral deformation. Therefore it is necessary to determine the contact force that is the upper limit of force before the mold begins to deform. Solving the system of forces the critical pressure is obtained and it is equal to:

$$P_c \approx \frac{1.36\pi^2 E^* a^3}{h^2}$$

From this one it is possible to derive the maximum critical height achievable with  $g$  weight per unit length.

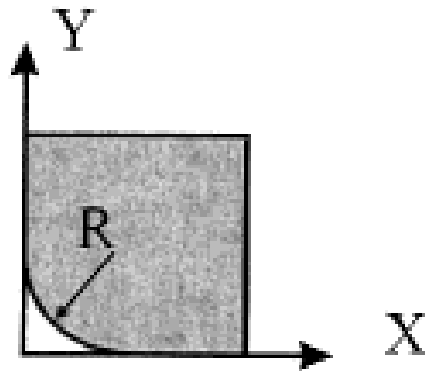
$$h_c = (7.837EI/q)^{1/3}$$

$$I = \frac{\pi d^4}{64}$$

$$q = \rho g \pi \frac{d^2}{4}$$

# Stability of Microstructure

For not having distortions we must have that the pillars are in contact with the substrate but still have not undergone deformations. But when the elastomer is in contact with the substrate the radius of curvature of the pillar varies due to the surface tension  $\gamma$  that so far we have not considered.



The pressure at the corners is therefore proportional to the surface tension

$$P \approx \gamma / r$$

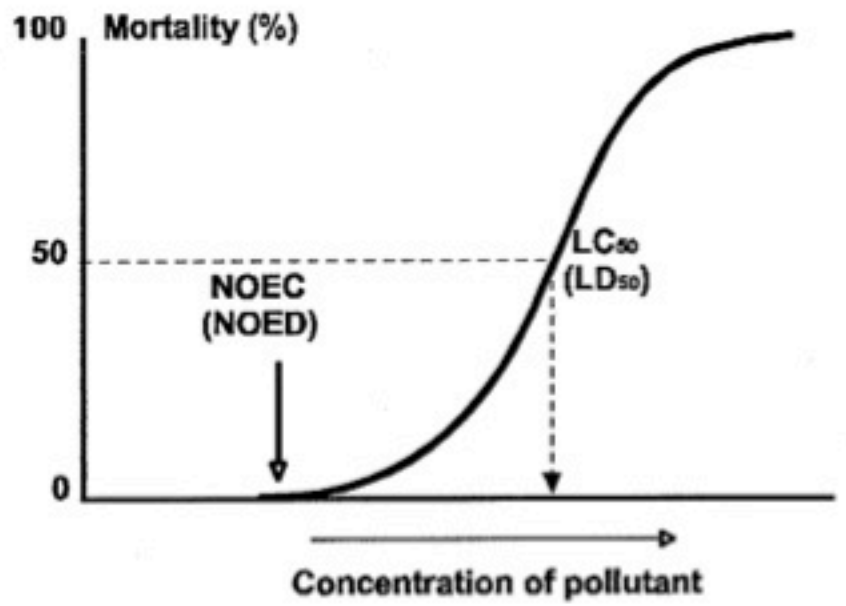
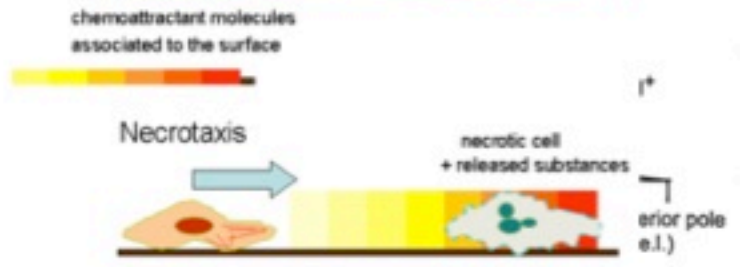
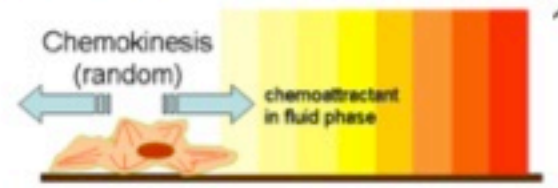
and

$$r \approx \gamma /$$

and generally it is seen that for the  $\gamma$  / And silicon is about 0.05 micrometers



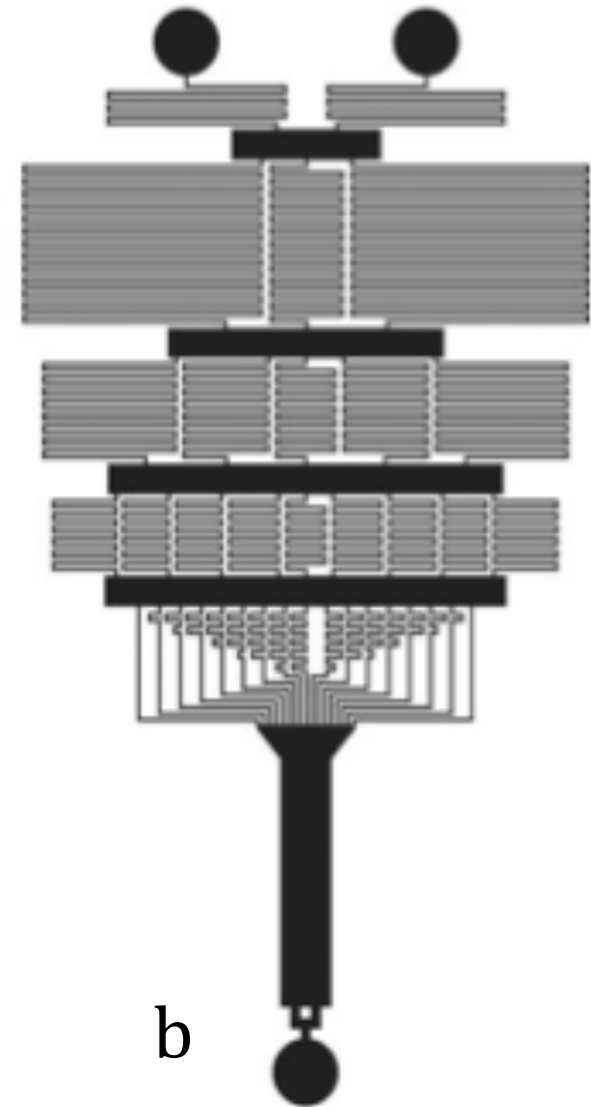
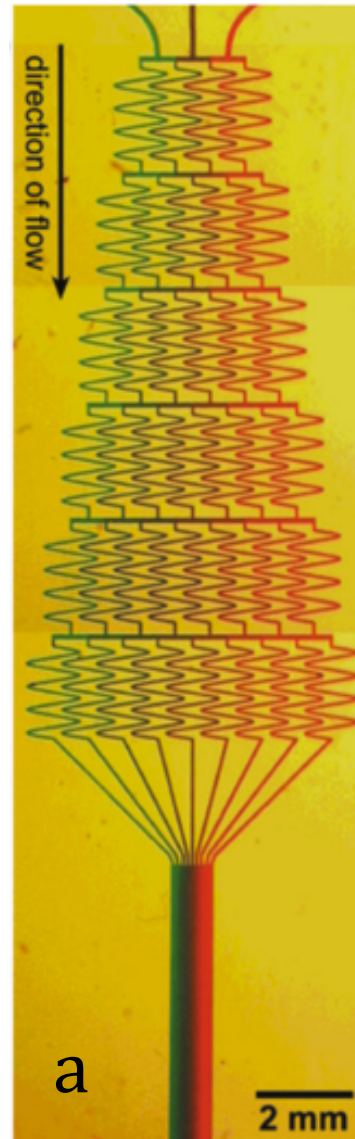
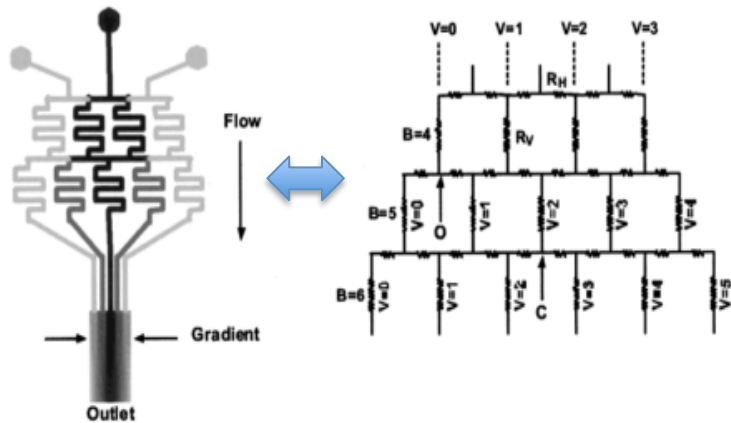
# Importance of nonlinear concentration gradients



# Gradient maker

Necessary  
condition:  
 $Re \ll 1$

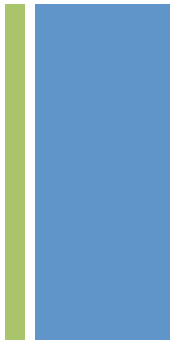
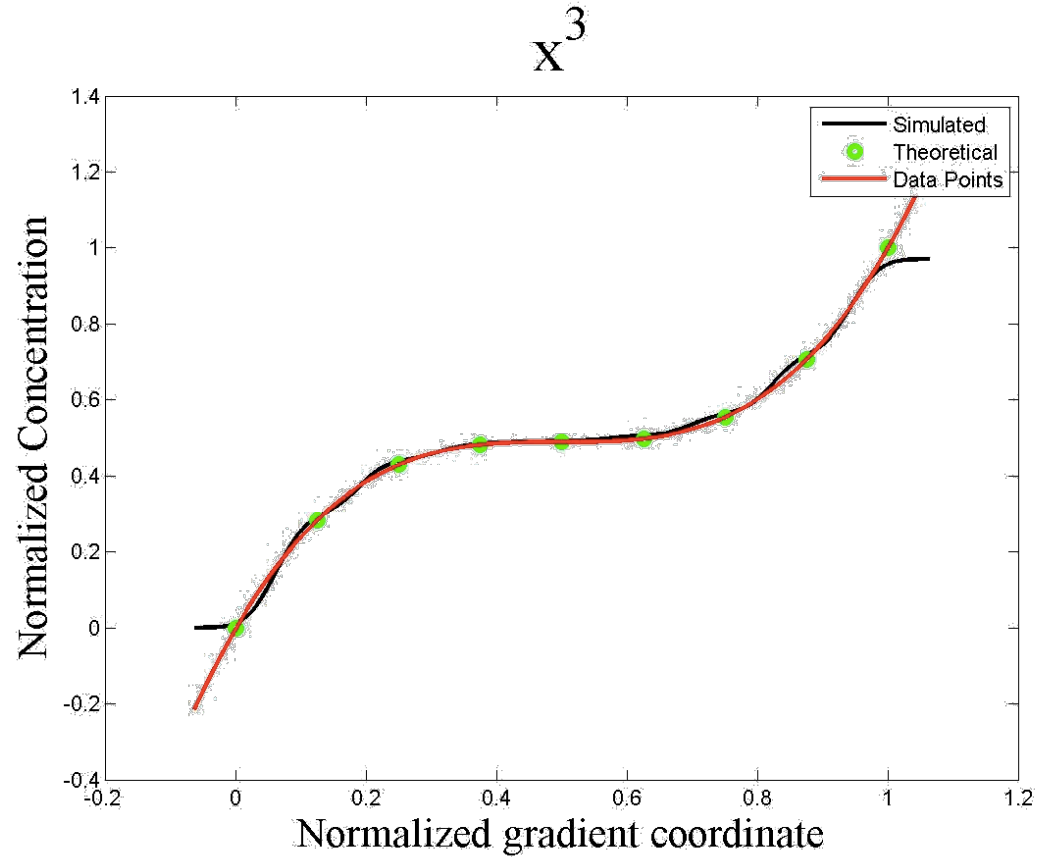
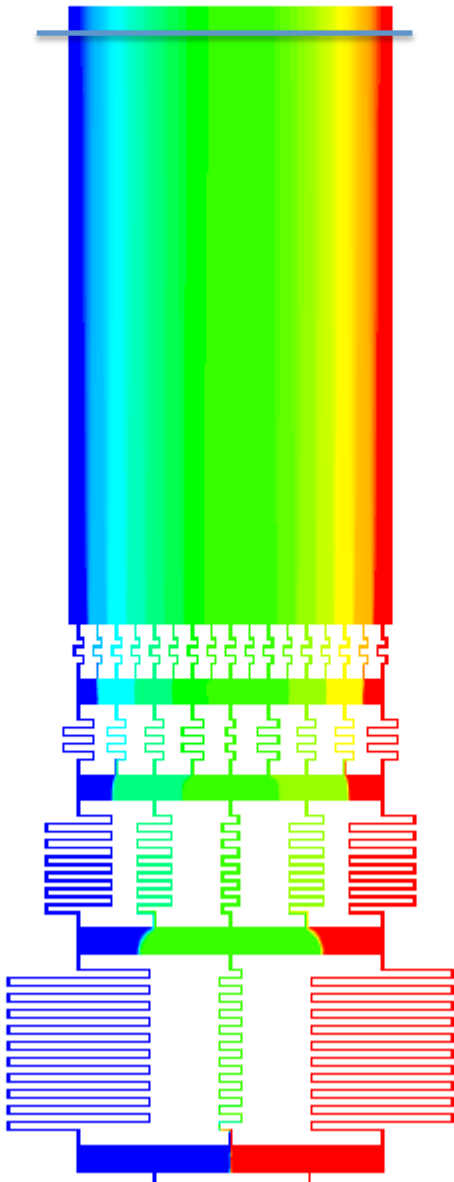
The hydraulic circuit  
can be reduced in an  
electrical equivalent.



- a) S. K. W. Dertinger et al. *Analytical Chemistry*, 2001.
- b) K. Campbell et al., *Lab on a Chip*, 2007.

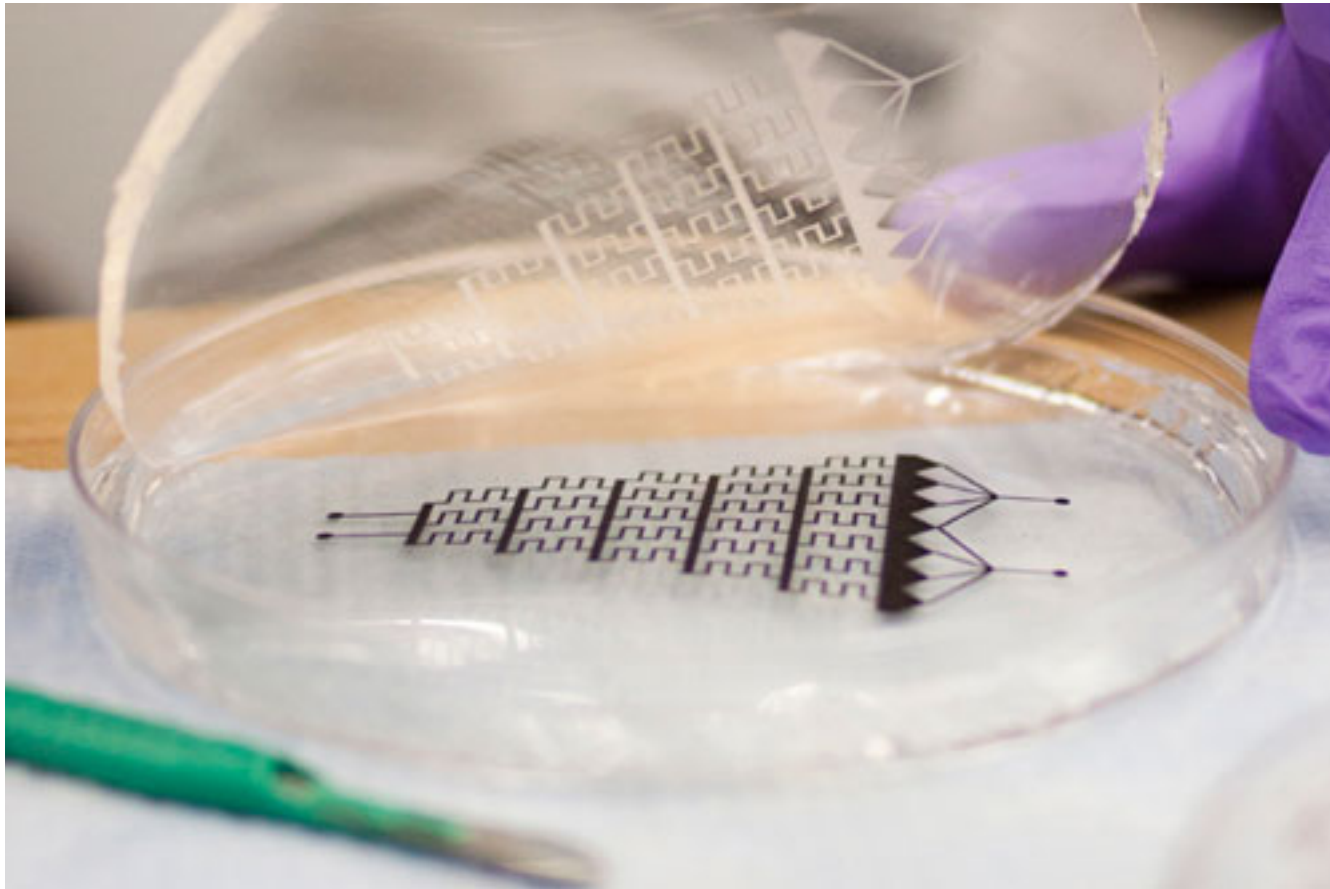
# Simulated concentration pattern

+



+

# Realisation of the device

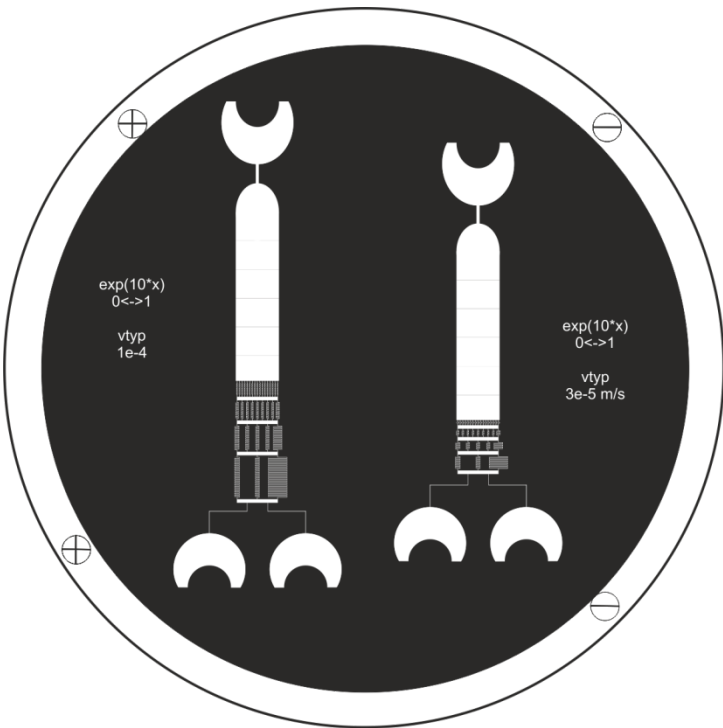




# + Realisation of the device

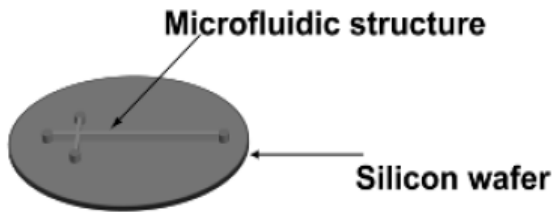


Silicon Wafer with SU-8 structure

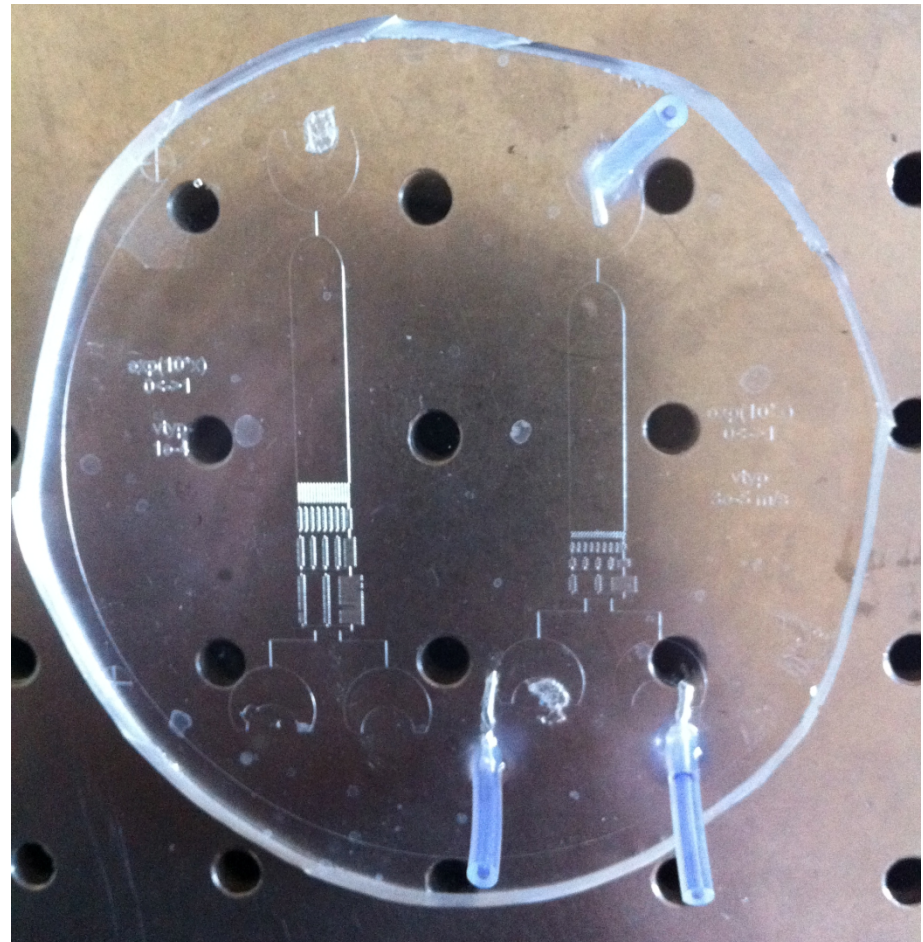
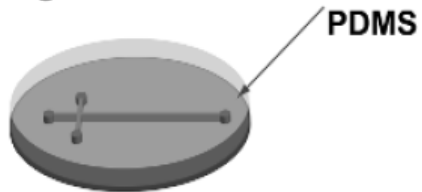


# + Realisation of the device

Master mold with microfluidic in resist

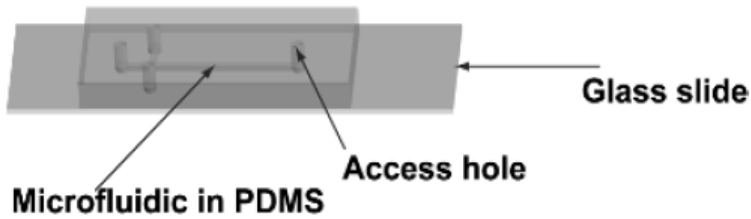


Molding with elastomer



# + Gluing of the device

Peel elastomer, cut out, punch access hole and bond



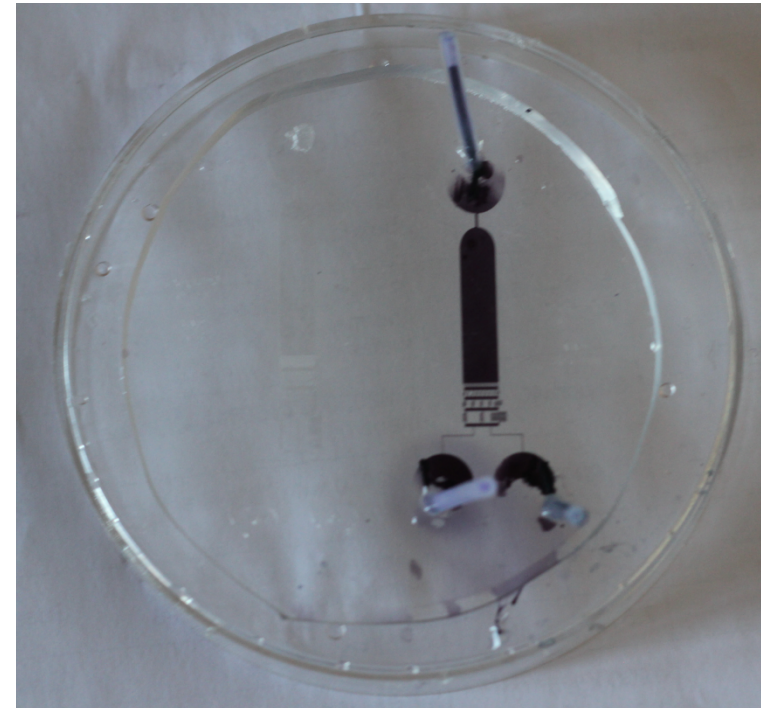
Hydrophobic bond:

Coat the glass slide with a thin layer ( $\sim 10 \mu\text{m}$  thickness) of PDMS mixture (preferably by spin coater).

Heat it at  $70^\circ\text{C}$  for 15 mins (this makes the PDMS hardened but still sticky)

Place the PDMS mould on the sticky PDMS surface. In order to avoid wrinkles and air gaps, lay the mould down from one end to the other.

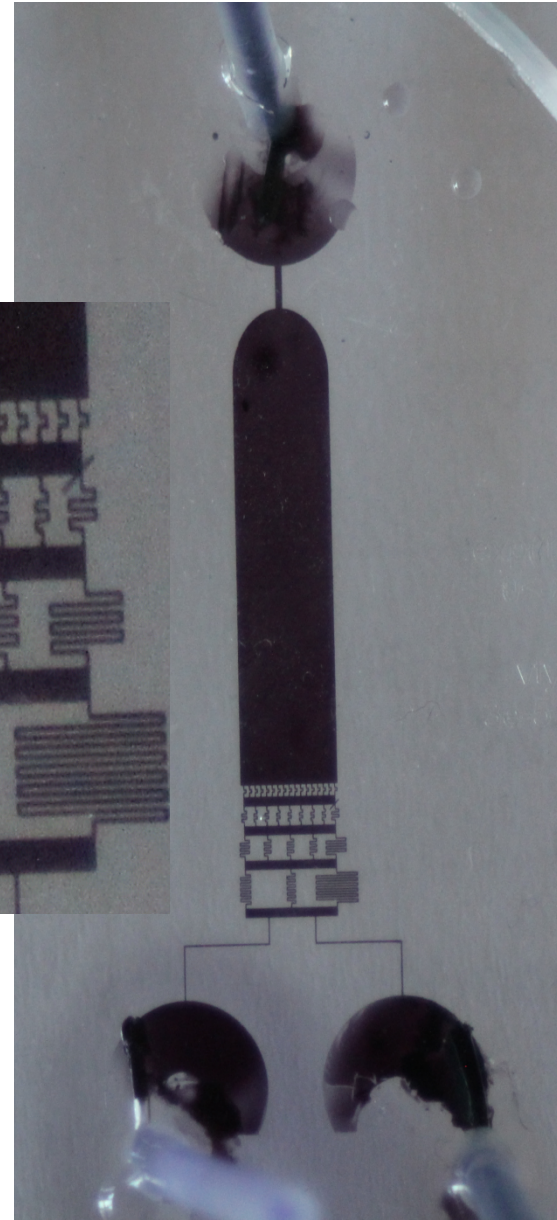
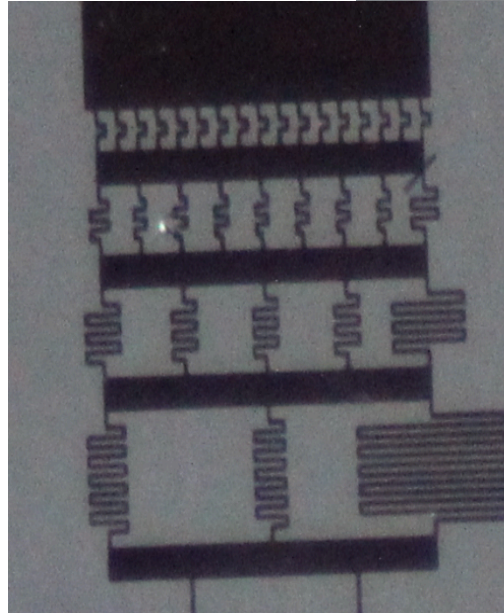
Heat it for at least 1 h at  $70^\circ\text{C}$ .



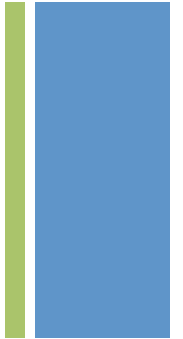
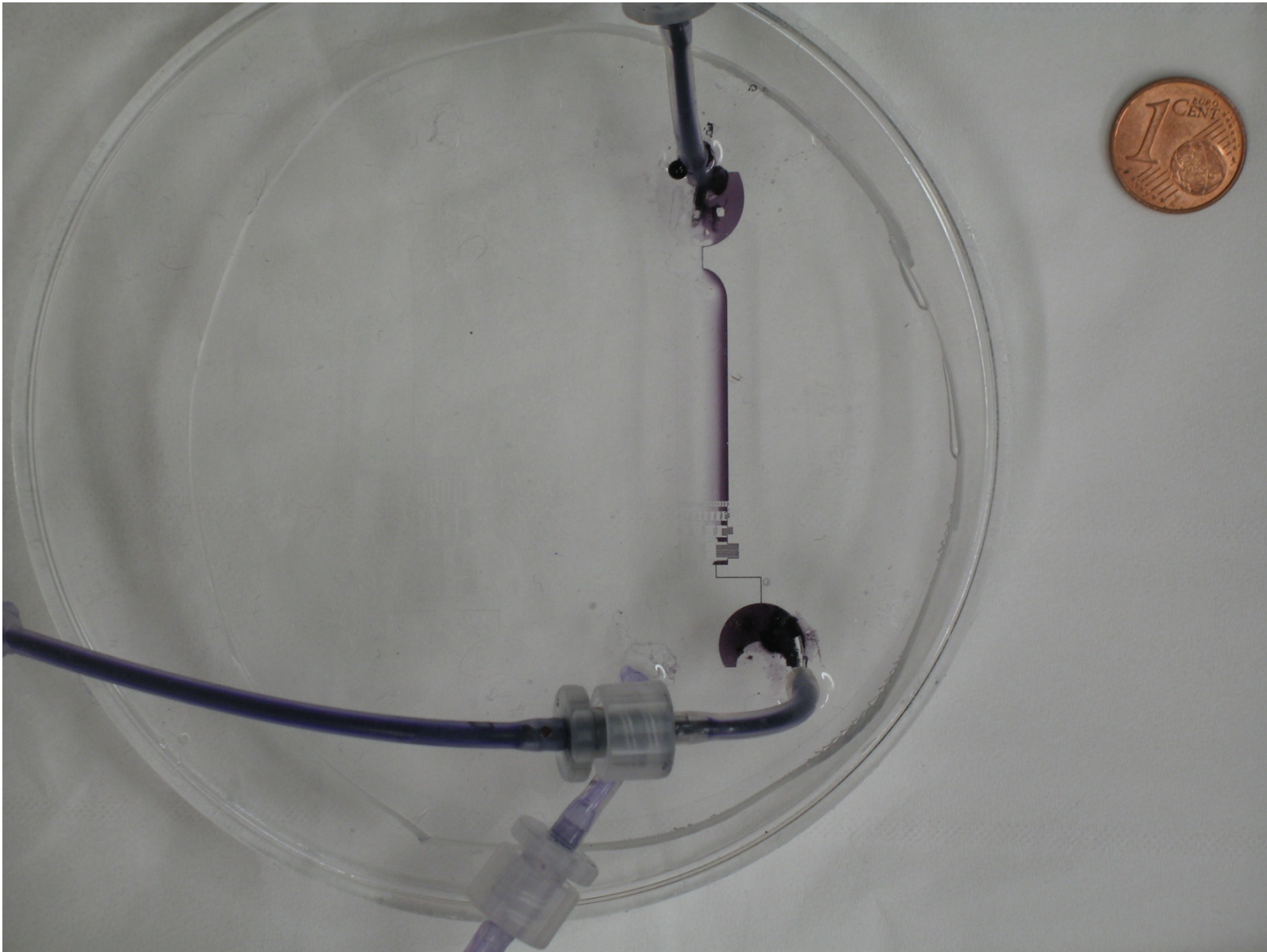
+

# The device

Syringe  
-  
Pump

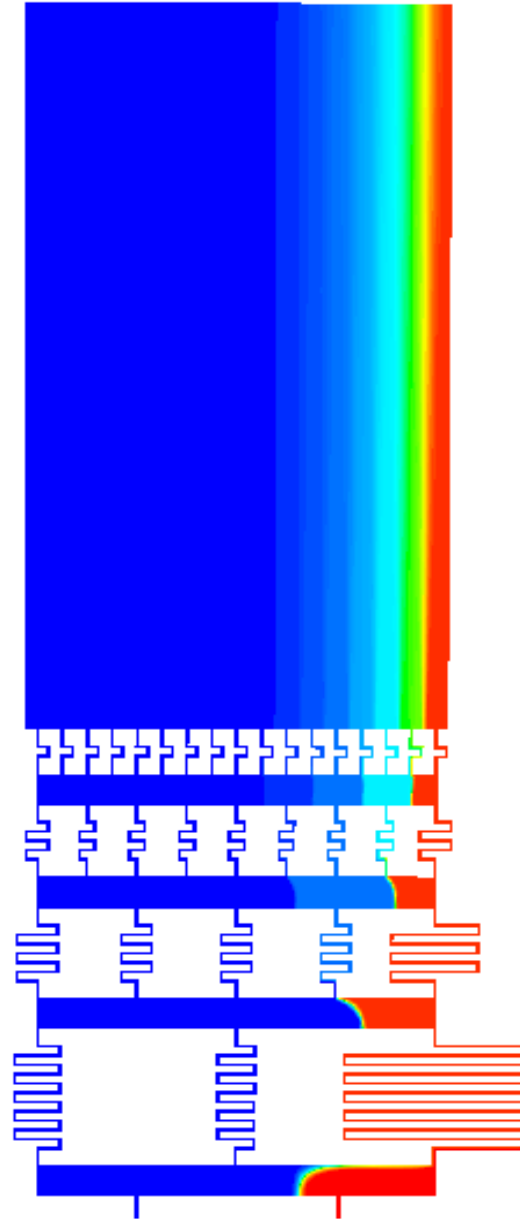


+ The device

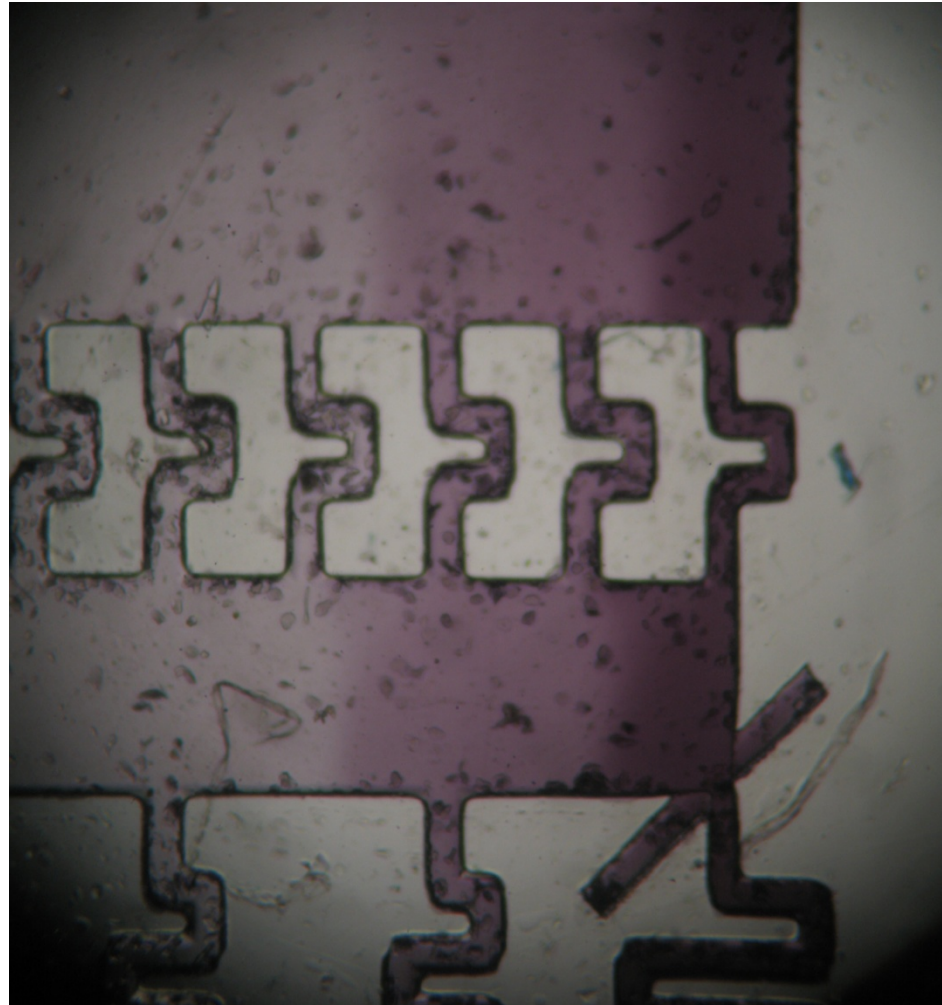
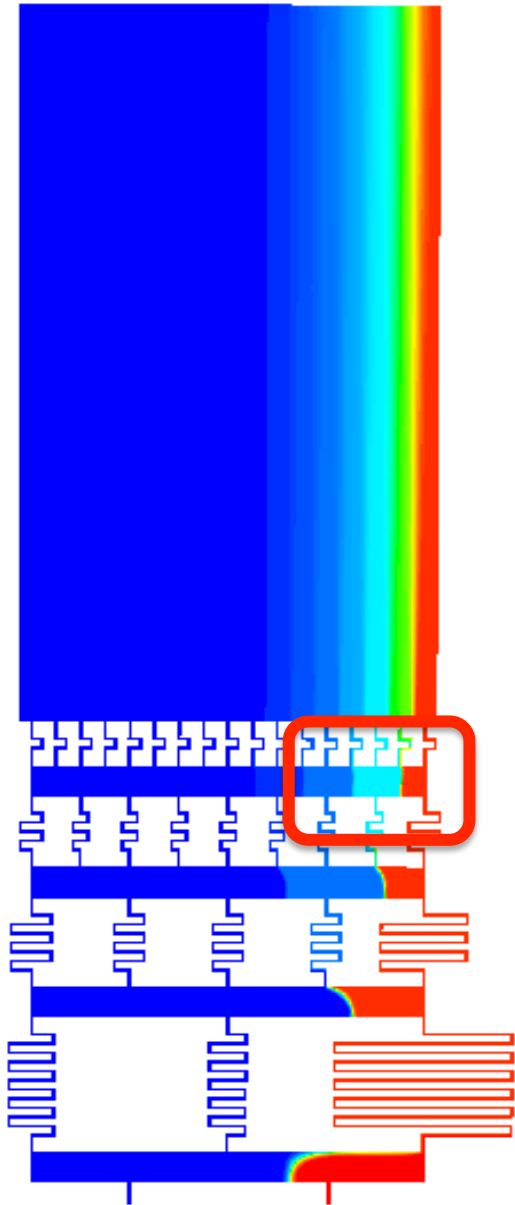


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# Simulation vs Experimental results



# + Simulation vs Experimental results





# Simulation vs Experimental results

