Nanodroplet deposition and manipulation with an AFM tip

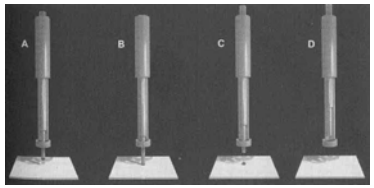
Laure Fabié, Hugo Durou, Thierry Ondarçuhu

Nanosciences Group, CEMES-CNRS Toulouse (France)

Direct deposition methods

Liquid lithography

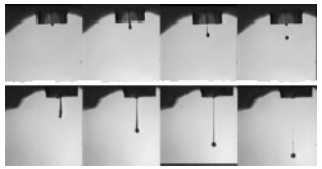
Pin and Ring method (DNA chips)



~ 200 µm

Inck jet

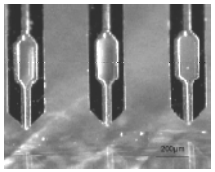
De Gan et al., *Adv Mat* 2004



10 µm

Pins

Belaubre et al., *APL* 2003

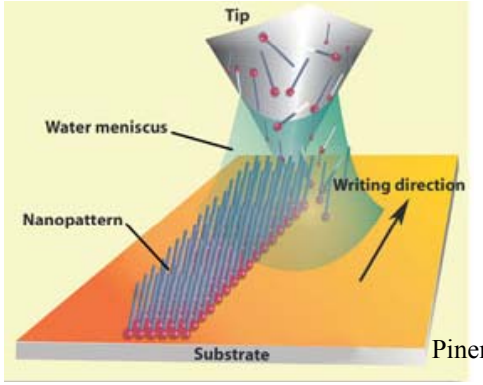


Few µm

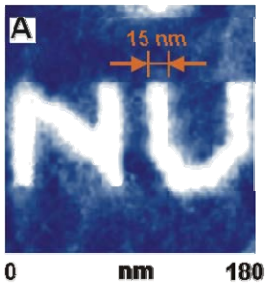
\+ flexibility

-- Ø ~ 5 to 200 µm

Dip pen lithography



Piner et al., *Science* 1999



\+ Ø ~ 10 nm

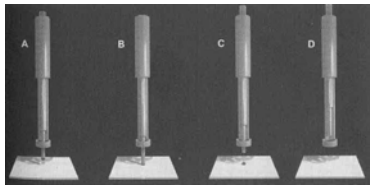
-- limited in terms of transferrable molecules

-- no reservoir

Direct deposition methods

Liquid lithography

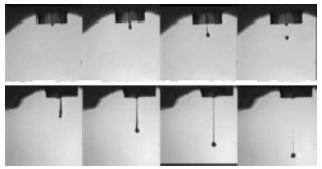
Pin and Ring method (DNA chips)



~ 200 µm

Inck jet

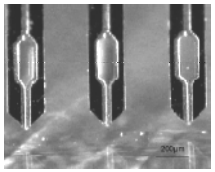
De Gan et al., *Adv Mat* 2004



10 µm

Pins

Belaubre et al., *APL* 2003



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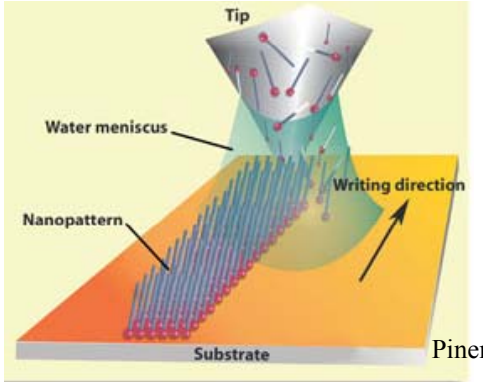

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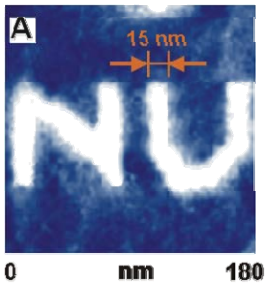
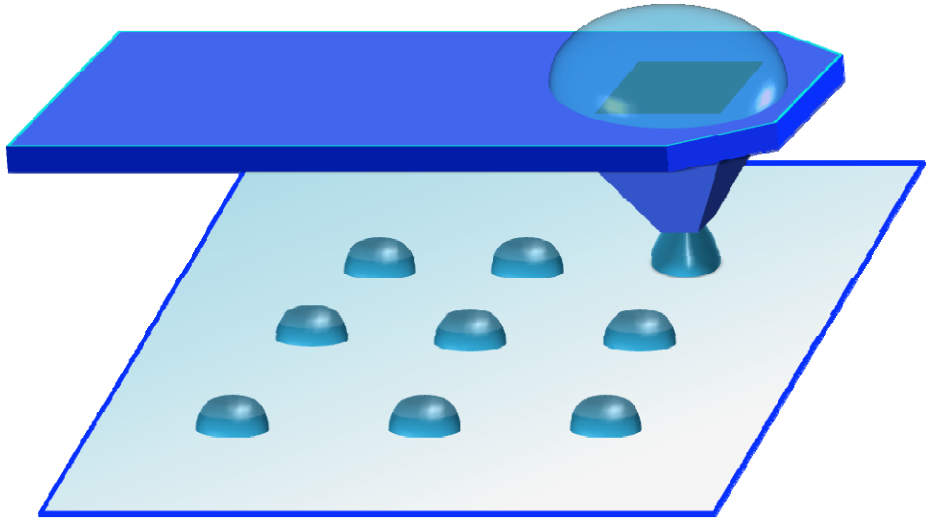


\+ Ø ~ 10 nm

-- limited in terms of transferrable molecules

-- no reservoir

NADIS : Liquid NAnoDISpensing



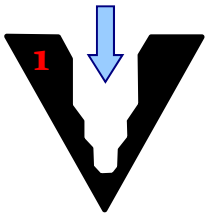
Meister et al, *Appl. Phys. Lett*. 2004
A.Fang, E. Dujardin, T.Ondarçuhu, *NanoLett* 2006

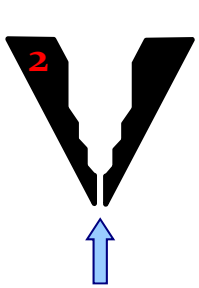
Tip fabrication

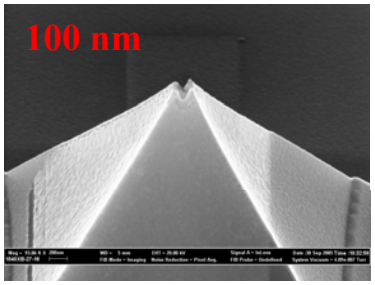
Channel milling by FIB

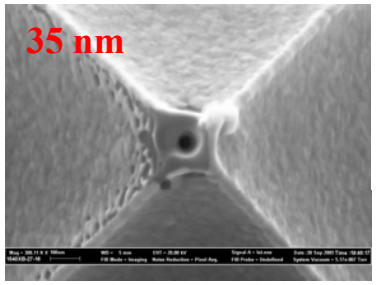
Standard AFM tip: pyramidal and gold coated

2 steps : (i) *thinning of the tip wall from the top* **(ii)** *milling at the tip apex from the tip side*
*(record : **35 nm**)*

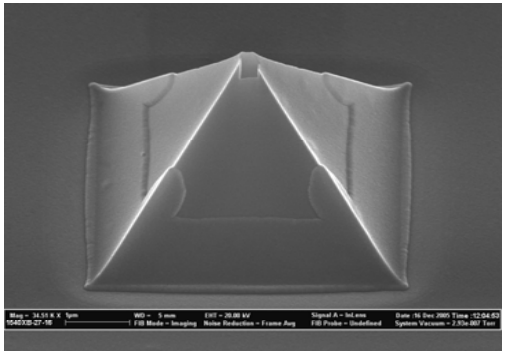




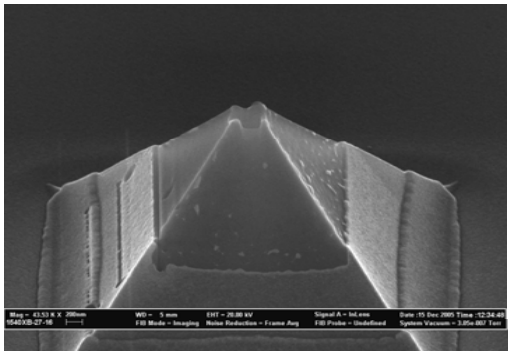




Surface functionnalisation



Intact gold layer
(thiol chemistry)



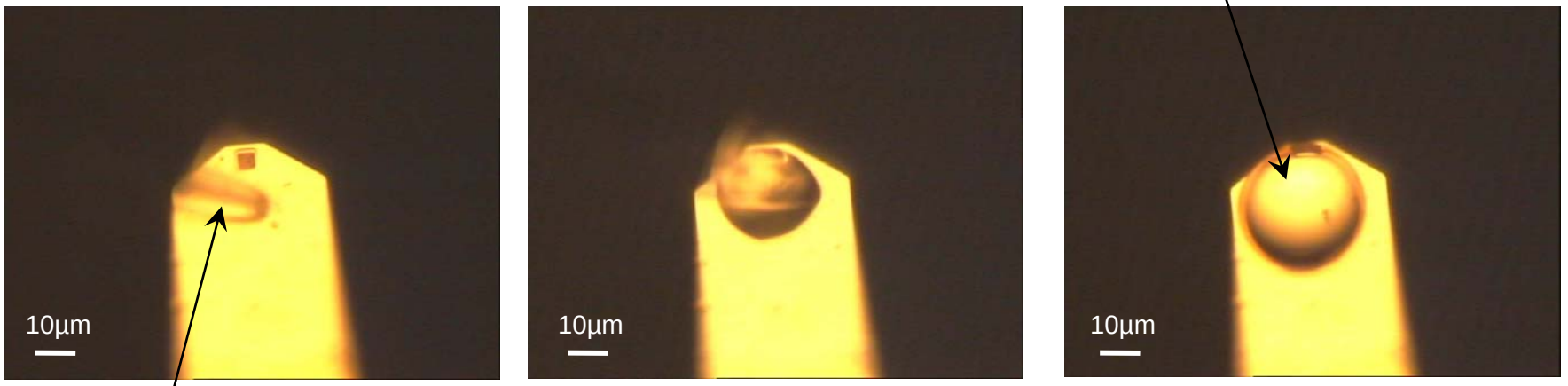
2 distinct areas : Si_3N_4 surface for silane chemistry and gold layer for thiol treatment

Tip loading

Deposited liquid

- Glycerol or glycerol-water mixture (dilution max 6:4)
- Solutions of molecules, proteins, nanoparticles…

Loading of the reservoir



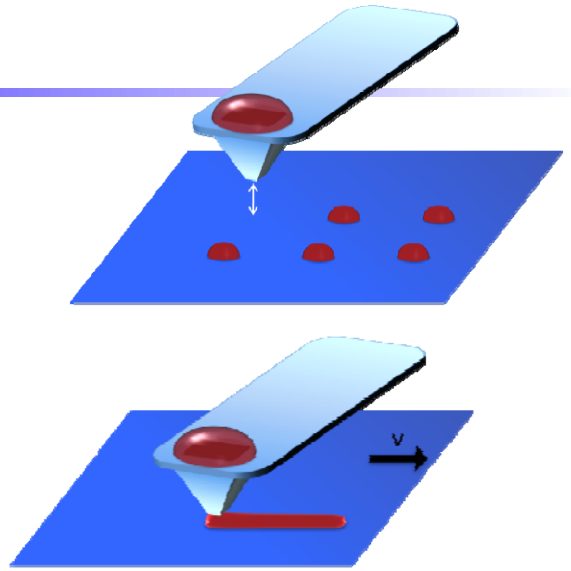
Drop deposited with a micropipette and a micromanipulator

Deposition process

Deposition

Nanodroplet deposition : with an AFM in force spectroscopy mode

Line deposition : with an AFM in contact mode and using a nanopositioning table



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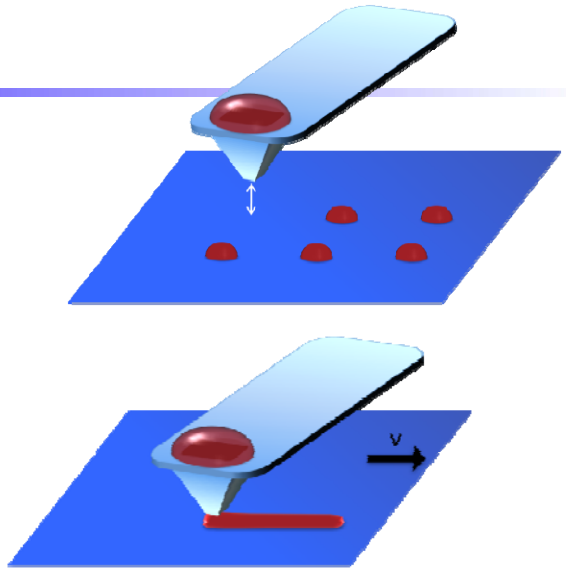
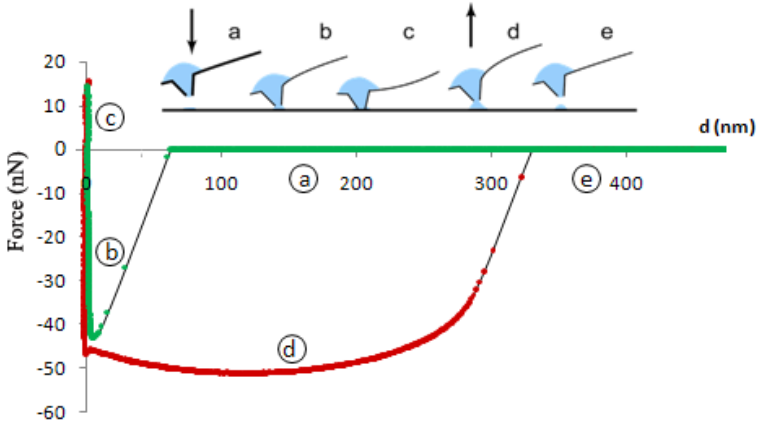


Force curve recorded during liquid transfert



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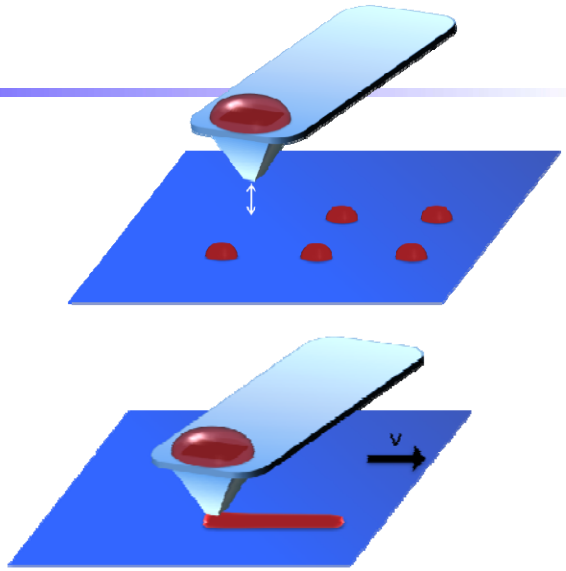

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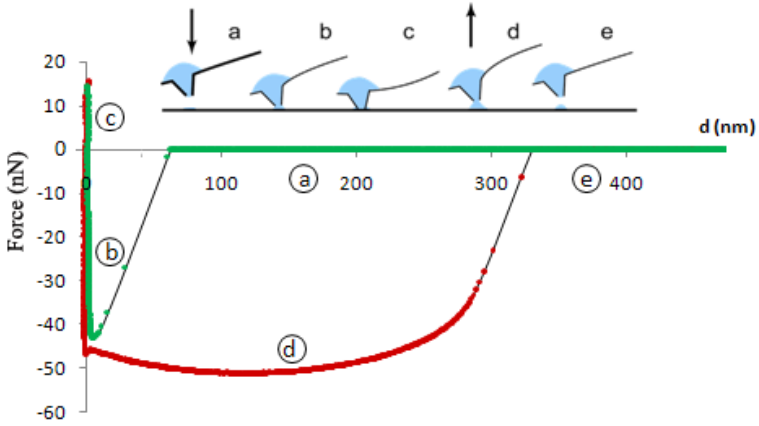
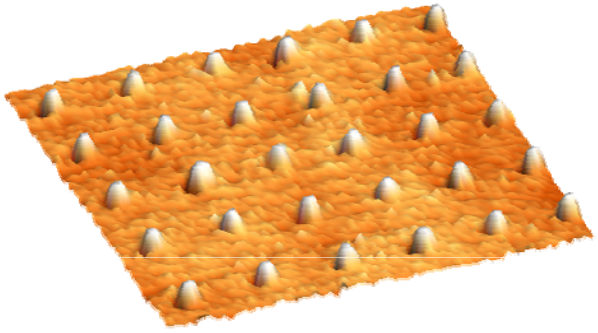
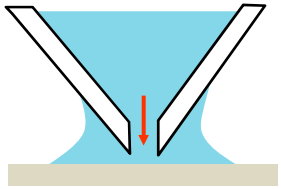


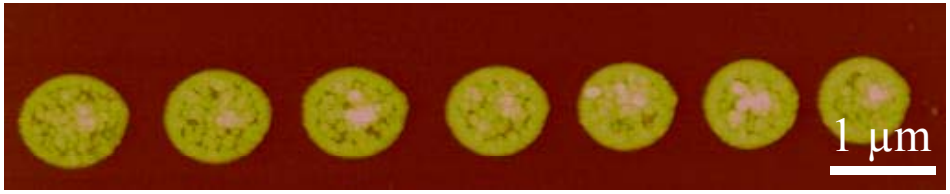
Deposit observation (after solvent evaporation)



Nanodroplet deposition

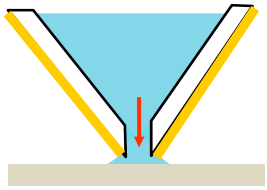
Hydrophilic tip with an aperture of 400nm

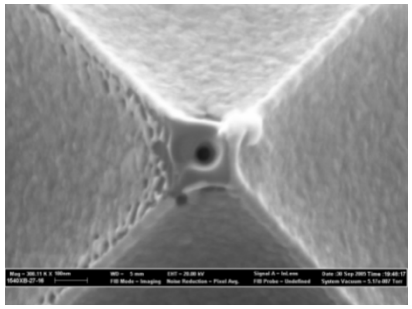


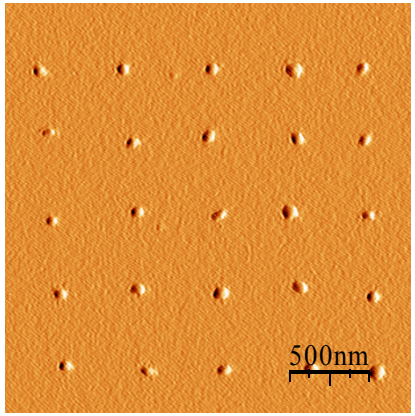


Hydrophobic tip with an aperture of 35nm

(treated with dodecanethiol)



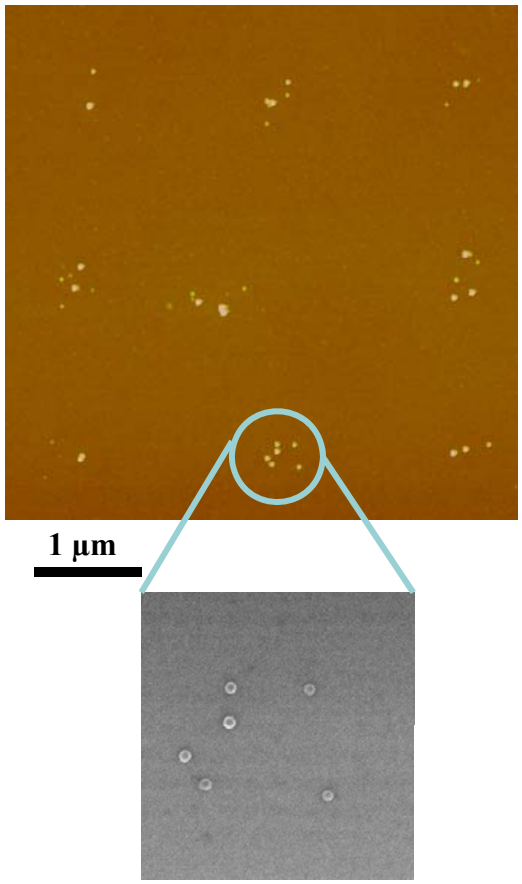




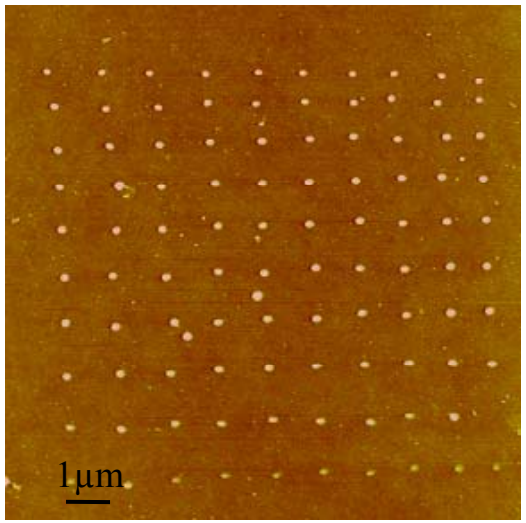
The influence of the different parameters is studed in : A. Fang, E. Dujardin, T.Ondarçuhu. *NanoLett* (2006)

Flexibility of the method

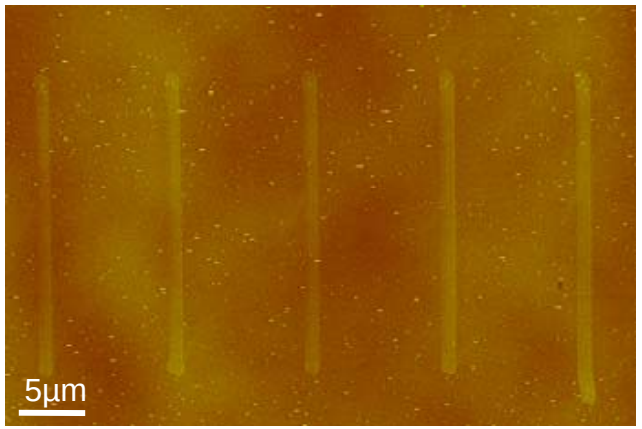
25 nm PS NPs



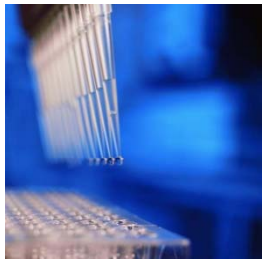
DsRed Proteins

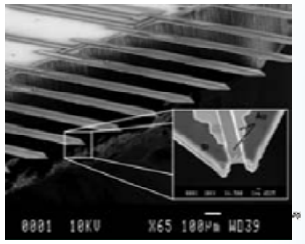


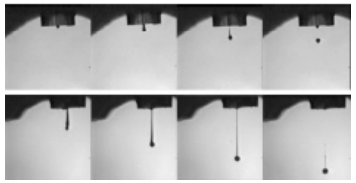
Ruthenium complexes

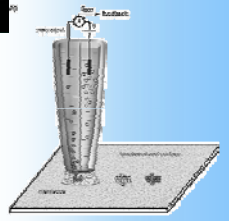


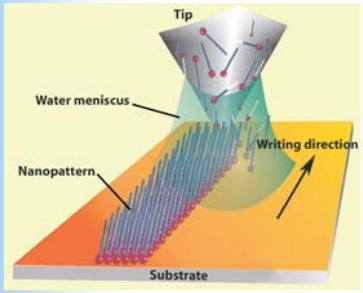
Nanopatterning conclusion

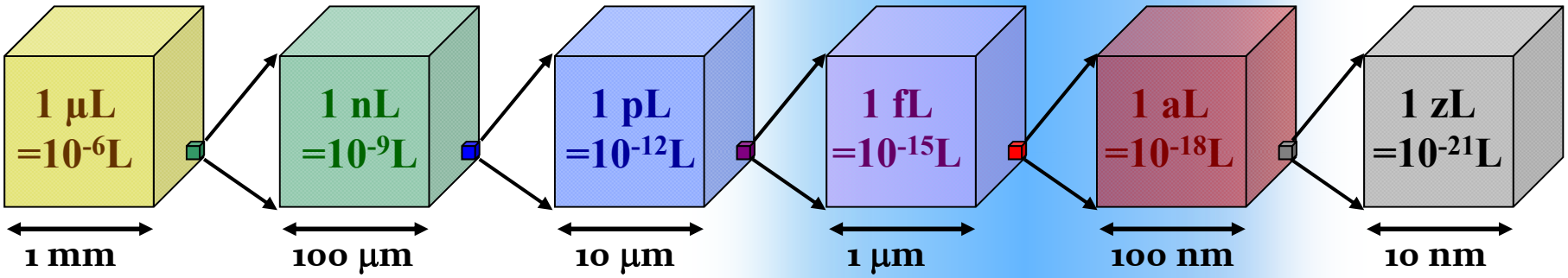






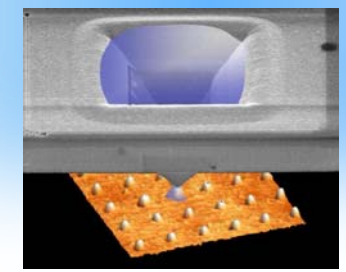






LIQUID LITHOGRAPHY

NADIS

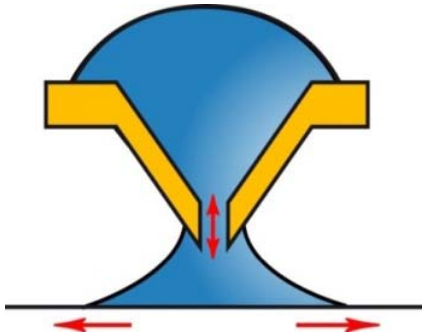


DIP PEN

Study of the deposition mechanisms

Final deposits due to :

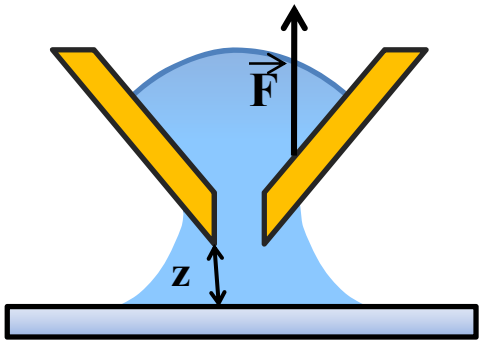
- **flow through the channel**
- **spreading on the substrate surface**

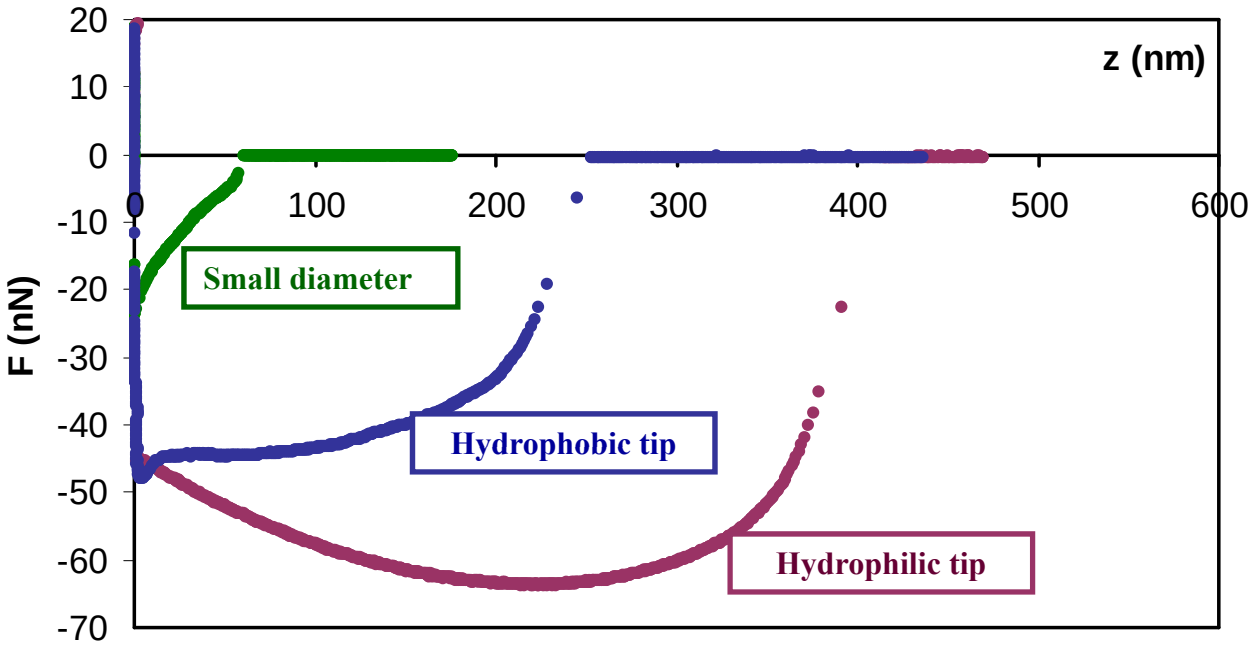


Analyse of the retraction force curves

Force curve study :

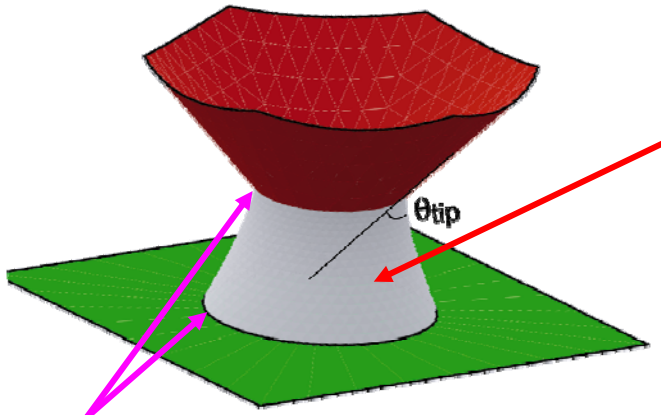
- **understanding the deposition mechanisms**
- **capillary force**





Modeling with Surface Evolver

- **Energy minimization for different boundary conditions and constraints**



Pressure and volume

Contact radii and angles

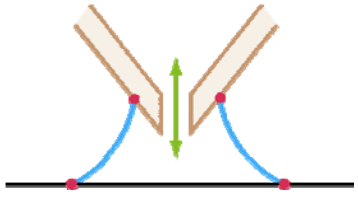
- **surface shape**
- Energy
- Pressure
- Volume
- **Force**

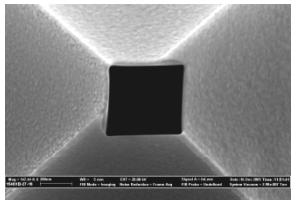
Hydrophilic NADIS tips

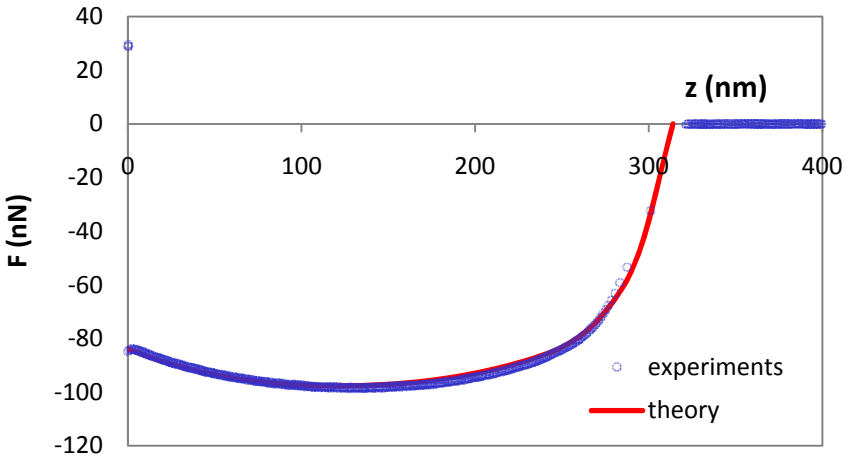
Boundary conditions : fixed radii on the tip and on the substrate

Channel of 280nm

Constant pressure defined by the reservoir : Laplace pressure of a spheric drop with a 20µm radius



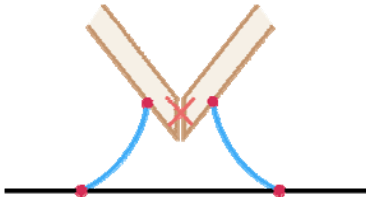


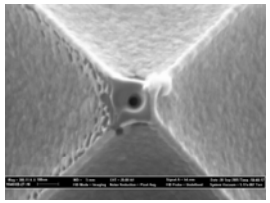


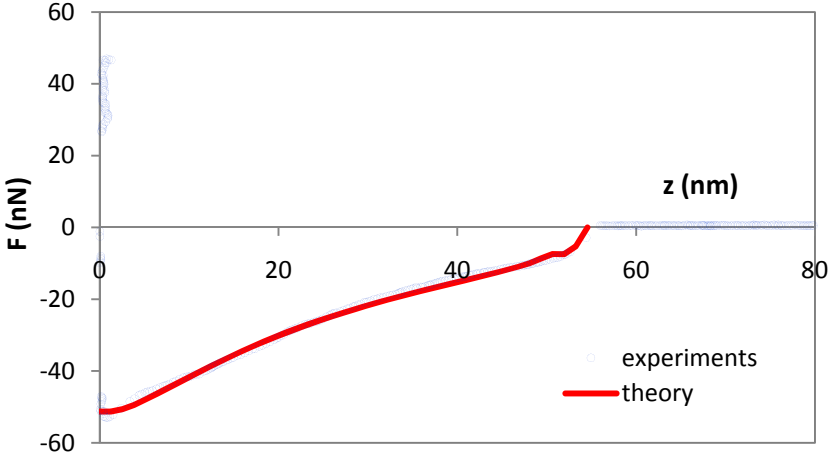
Rsurf = 400 nm, **Rtip** = 250 nm
P = 6.4 10^3 Pa

Channel of 35nm

Constant volume : No liquid flow





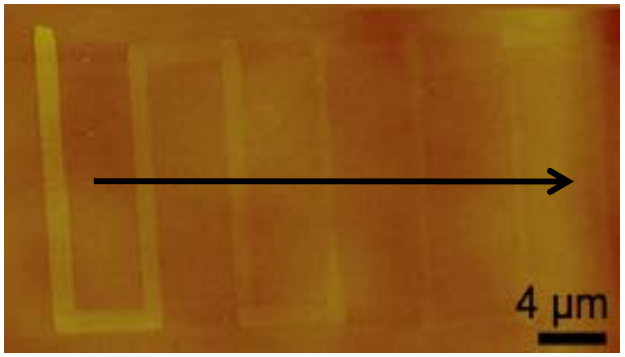


Rsurf = 97 nm **Rtip** = 65 nm
V = 0.4 aL

More details on the influence of the different parameters on the force curve in :
L. Fabie, H. Durou, T.Ondarçuhu. *Langmuir* (2010)

Lines deposition

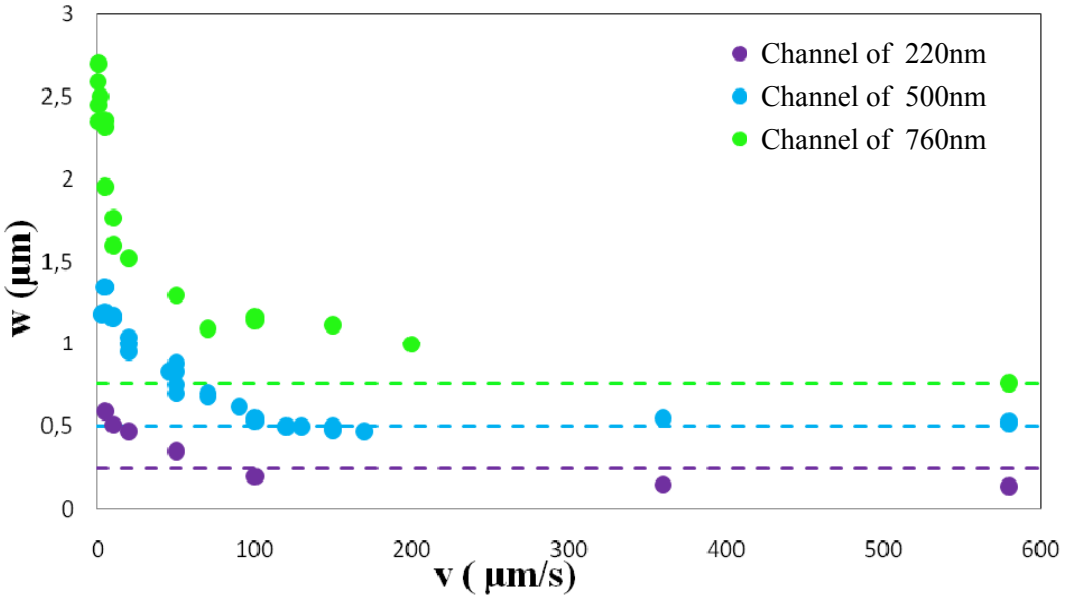
NADIS tip is moved at constant velocity while maintaining contact onto the surface thanks to a nanopositioning table incorporated to the AFM

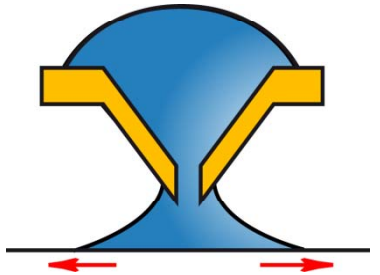


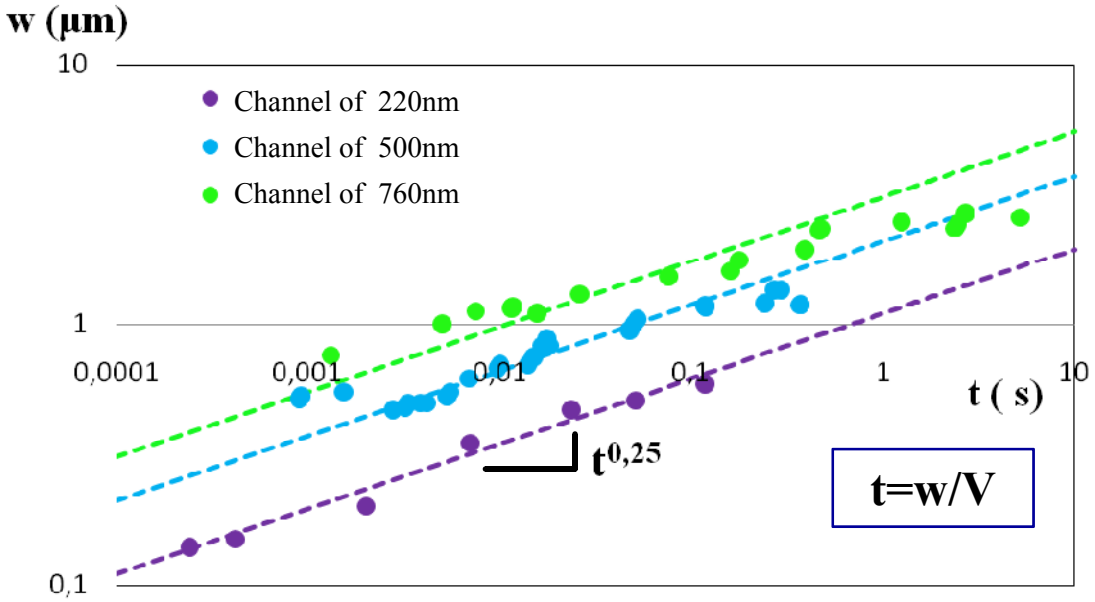
Velocity increasing

Phase image for a better contrast

Spreading dynamics







Different from diffusive law (Dip pen) in $t^{1/2}$

J. Jang et al. *J. Chem. Phys.* (2001)

Spreading dynamics

Cox-Voinov equation : $\theta^3 - \theta_m^3 = 9\frac{\eta v}{\gamma}\ln\left(\frac{L}{l}\right)$

O.V. Voinov, *Fluid Dyn.* (1976)
R.G. Cox, *J. Fluid. Mech.* (1986)

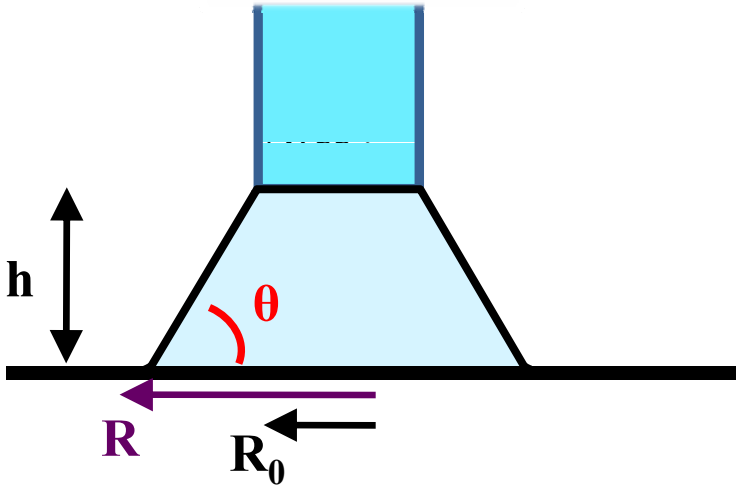
Classical case

$\theta \propto \frac{1}{R^3}$ **Spreading at constant volume**

$R \propto t^{1/10}$

L. Tanner, J. *Phys. D* (1979)

NADIS case



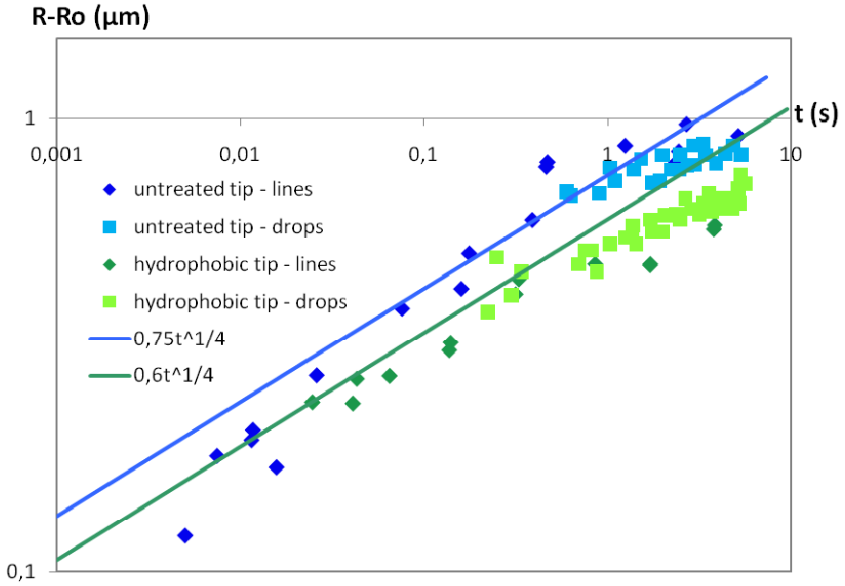
$\tan\theta \approx \theta \approx \frac{h}{R - R_0}$ **Spreading at constant pressure**

$\left(\frac{h}{R - R_0}\right)^3 = \theta_m^3 + 9\alpha\frac{dR}{dt}$

$\alpha = \frac{\eta}{\gamma}\ln\left(\frac{L}{l}\right)$

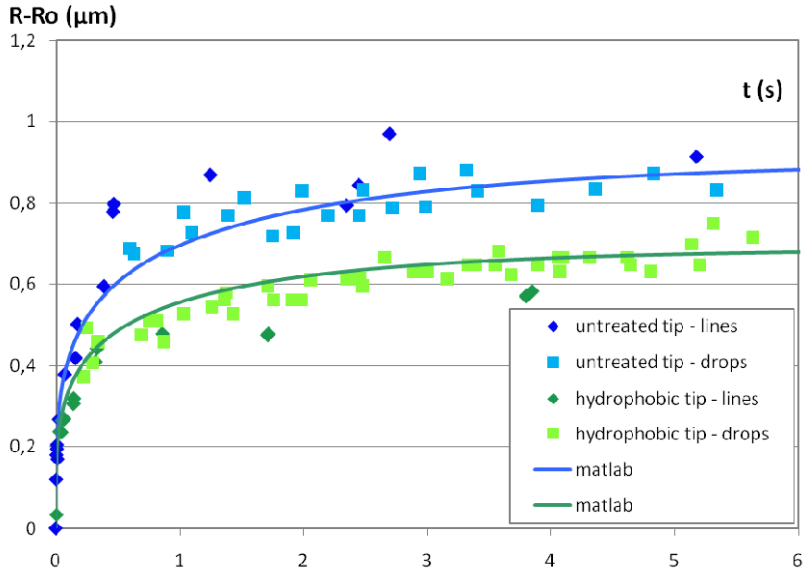
Results of the model

For $\theta_m = 0$, analytical solution :
$$R - R_0 = At^{1/4}$$



For $\theta_m \neq 0$, numerical solution

$$\left(\frac{h}{R - R_0}\right)^3 = \theta_m^3 + 9\alpha\frac{dR}{dt}$$



θ_m=3.5°
R_0=380nm
ln(L/l)=10
α=238s/m
untreated tip: h=56nm
Hydrophobic tip : h=42.5nm

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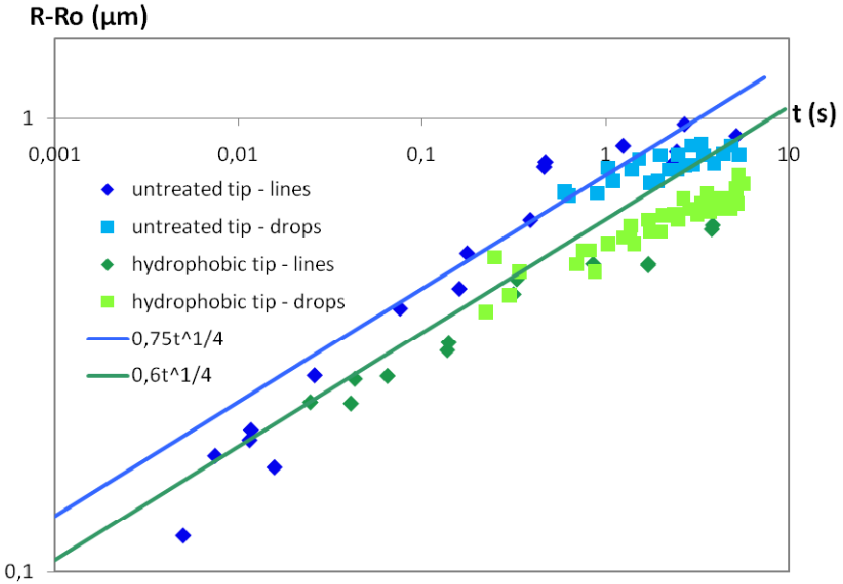

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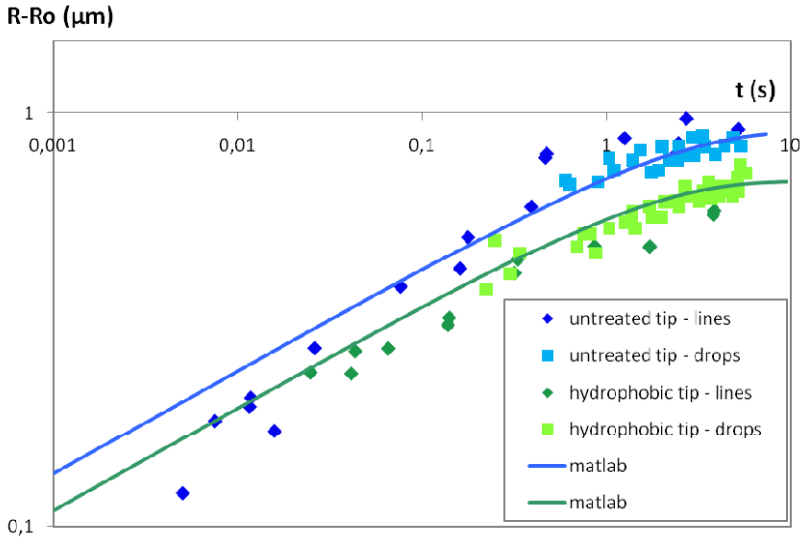

θ_m=3.5°
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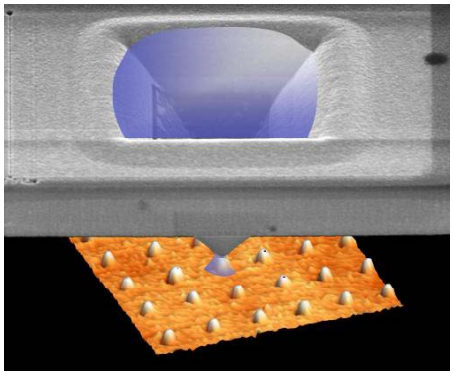
Conclusion

Efficient method for nanopatterning



Fundamental studies

- ***Study of the capillary force at the nanoscale***

  useful for AFM imaging

- ***Spreading dynamics at constant pressure***

  interesting for printing techniques