Scanning Probe Microscopies

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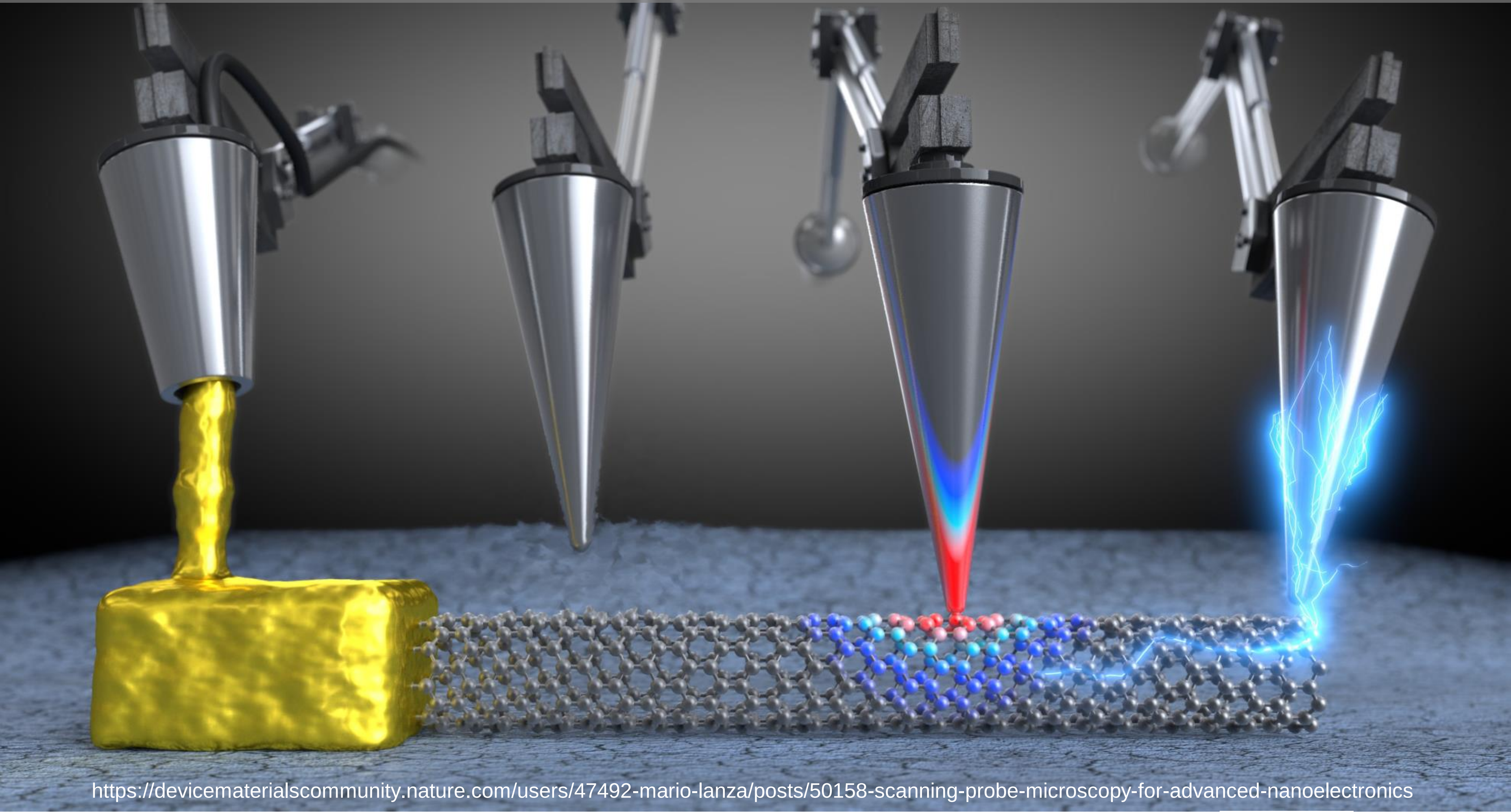

https://devicematerialscommunity.nature.com/users/47492-mario-lanza/posts/50158-scanning-probe-microscopy-for-advanced-nanoelectronics

Outline

UNITE MIXTE DE PHYSIQUE
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1- Basics of Scanning Probe Microscopy

2- Advanced modes : Beyond topography

Scanning Resistance-AFM : Electrical properties

Piezoresponse-AFM : Ferroelectric properties

Scanning NV Magnetometry : Magnetic properties

Scanning Probe Microscopy

No more interaction with electromagnetic waves (light, electron…)

Interaction between a probe and the surface

How to obtain a nanometric resolution ?

Scanning Probe Microscopy
How to obtain nanometric resolution ?

⇨ Positioning the probe with nm precision in the 3 dimensions

⇨ **Piezo-electric materials**

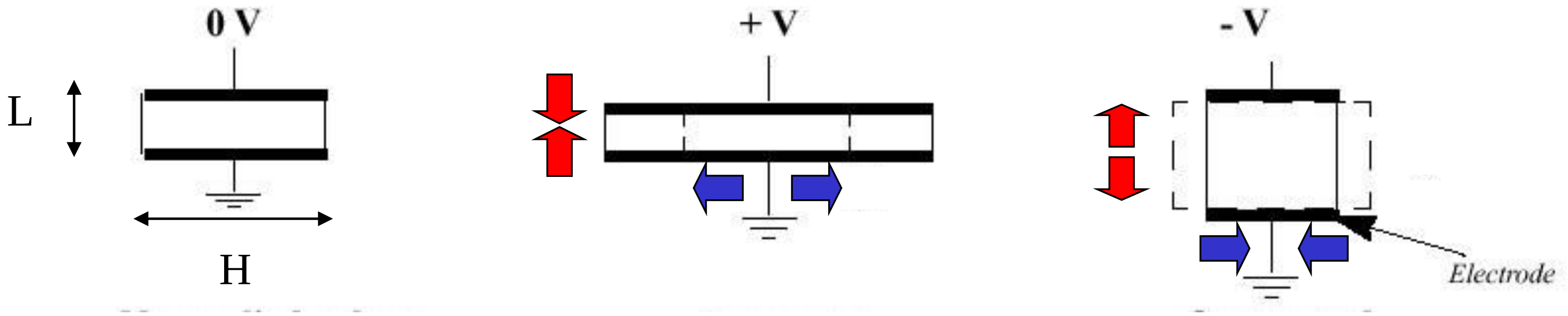
⇨ Probe-sample interaction limited in space

⇨ **Tip geometry** (fabrication technology)

⇨ **Type of interactions** (long or short range)

Piezoelectric material

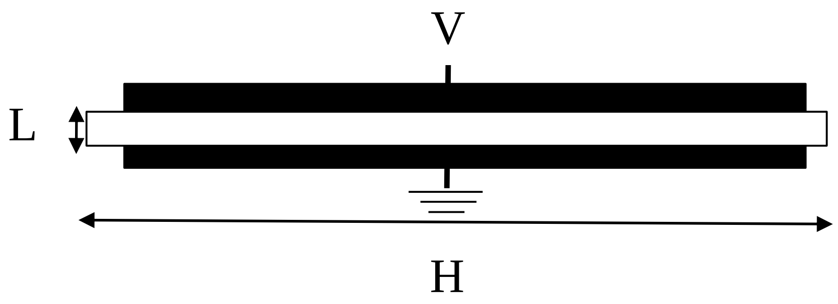
- Electric field ⇨ Elastic deformation of the cristal



$$\Delta L \sim d.E.L \sim d.(V/L).L \sim d.V$$

d : piezoelectric coefficient (m.V^{-1}) E : electric field (V.m^{-1})

$PbZrTiO_3$: d ~ 100 pm.V^{-1}



V = 100V ⇨ $\Delta L \sim 10$ nm
V = 1 mV ⇨ $\Delta L \sim 0.1$ pm

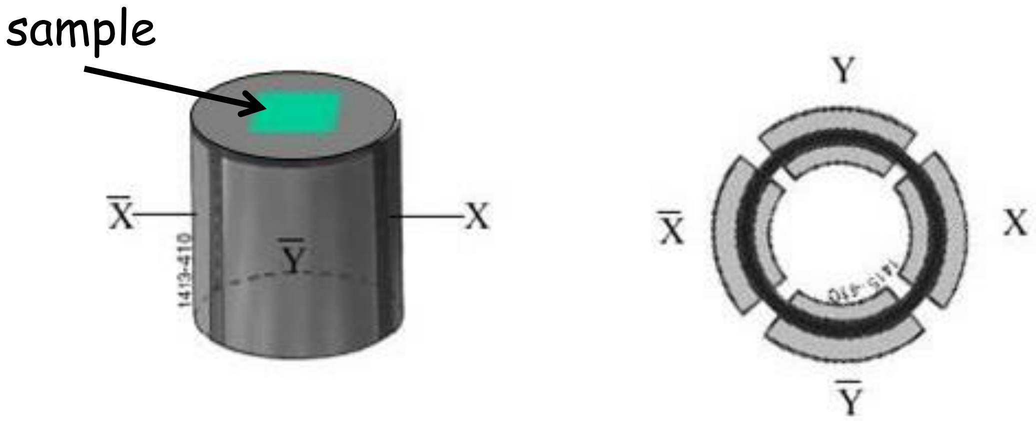
$\Delta H \sim \Delta L * H/L \sim \Delta L$*100mm/1mm

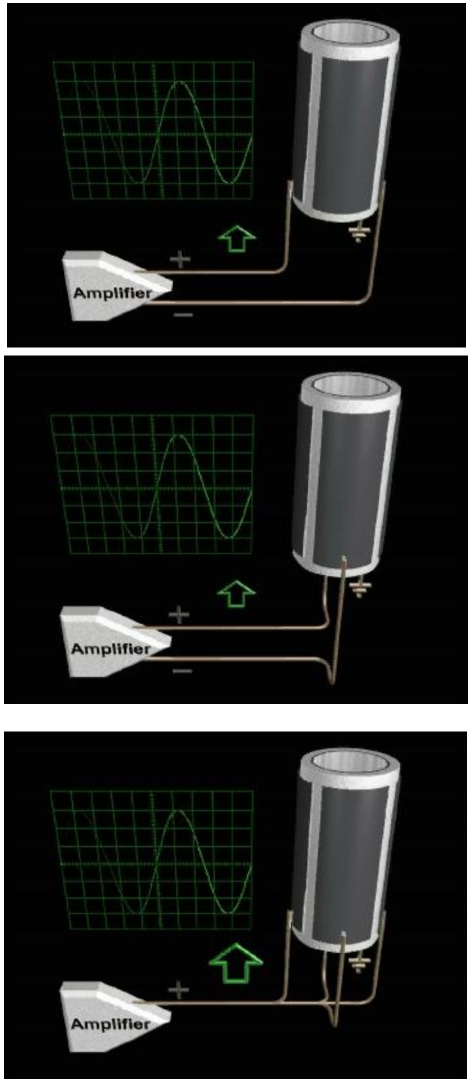
⇨ **$\Delta H \sim$ pm to µm**

Piezoelectric ceramics : nanometric motion

How to obtain nanometric resolution ?
The piezo-scanner

Piezo-tube



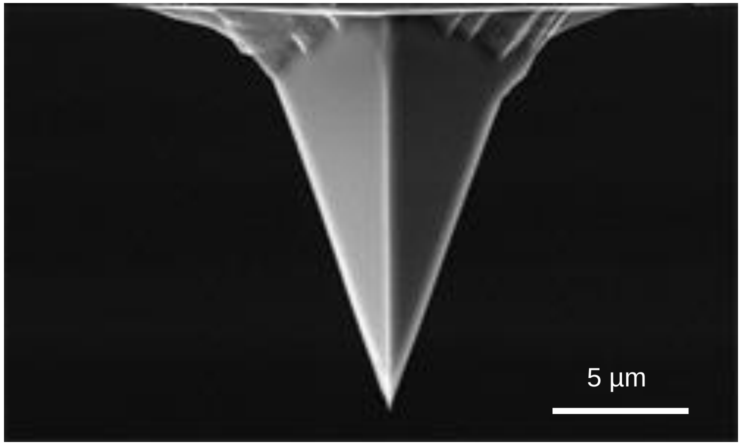


- One position in space = 3 voltages (Vx, Vy, Vz)
- Surface in space = file of voltages (Vxi, Vyi, Vzi)
- Relation $\Delta L = f(V)$ ⇨ Topography (X, Y, Z)

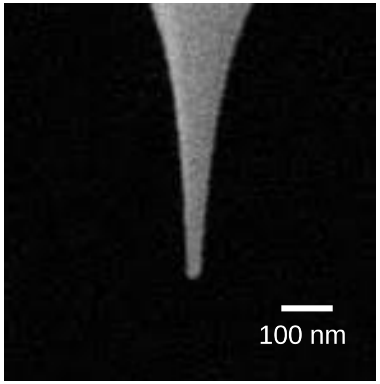
X, Y scan range ~ 100 µm
Z range ~ 10 µm

How to obtain nanometric resolution ?
The probe

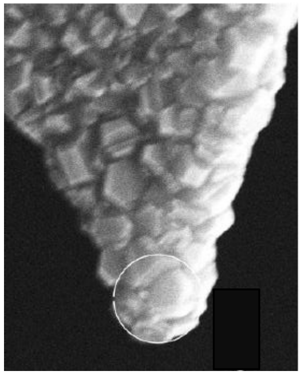
Probe = micro-fabricated tip



Si tip

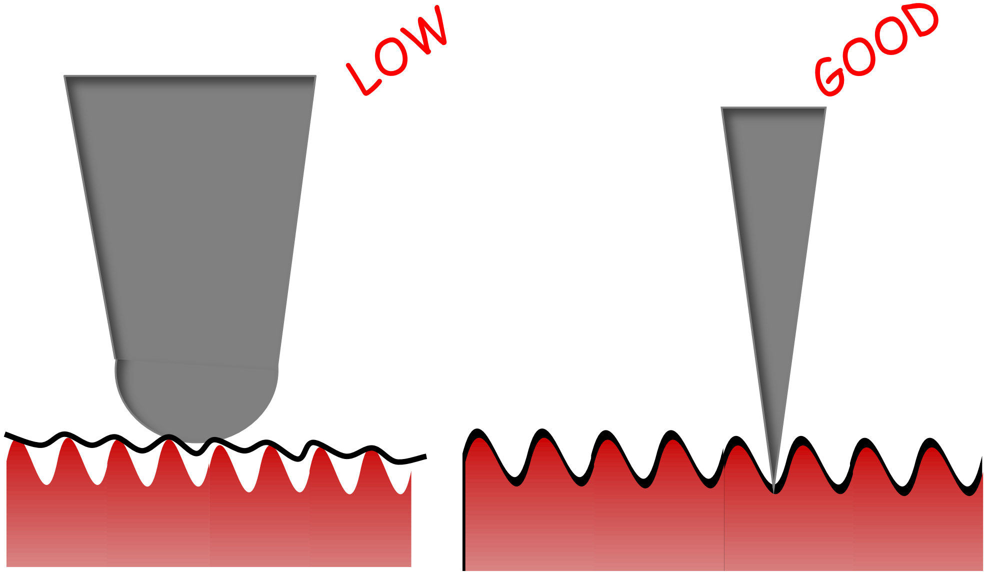


diamond coated Si tip

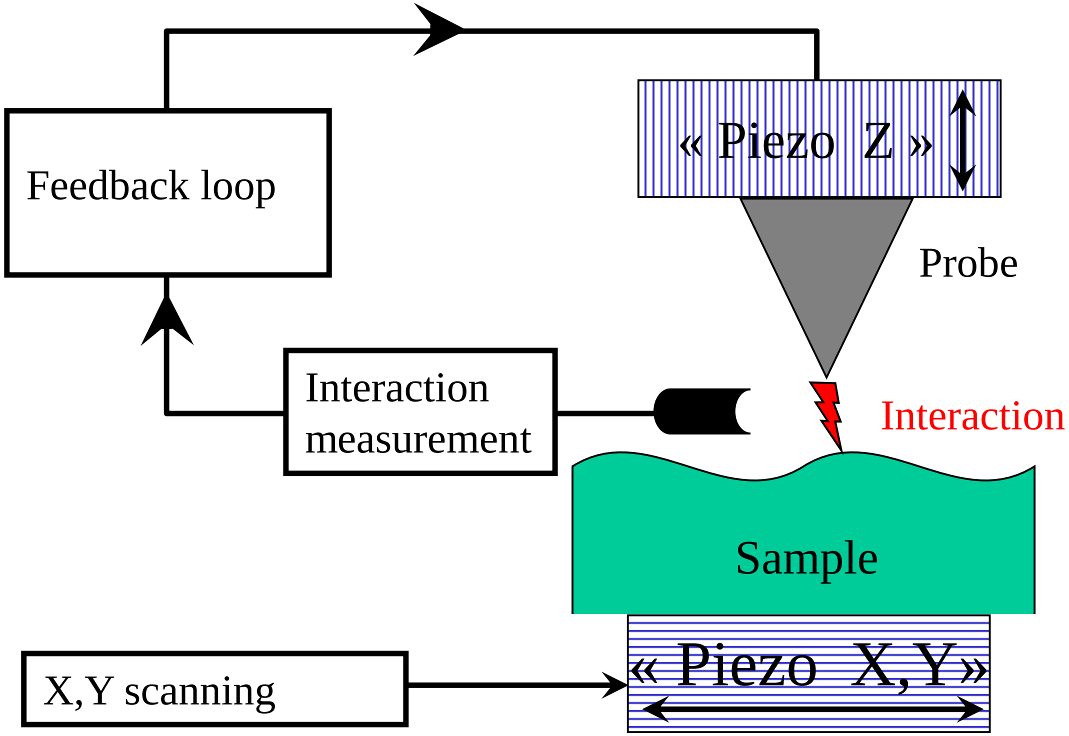


Tip radius ~ 2 to 100nm

- Lateral resolution depends on the tip shape…



General principle of SPM

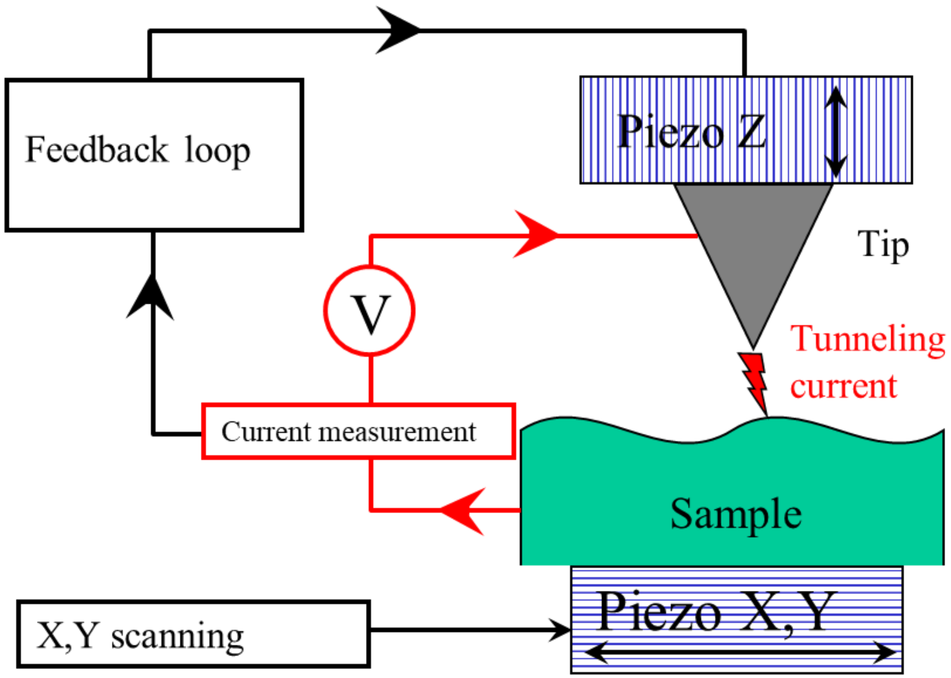


At each point (X_i, Y_i) of the surface, Z_{piezo} has to be distorted of ΔZ to maintain the interaction constant

⇨ Cartography (X,Y, ΔZ (interaction = cst))

Scanning Tunneling Microscopy (STM)

« Interaction » tip-surface = Tunneling current $I \alpha e^{-\kappa d}$


Feedback loop

Piezo Z

Tip

V

Tunneling current

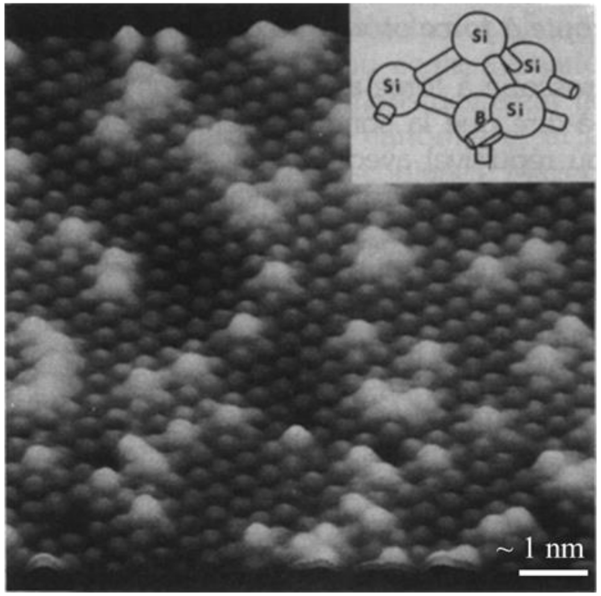
Current measurement

Sample

X,Y scanning

Piezo X,Y

Surface of Boron doped silicon



Bining & Rohrer (1981)
Nobel Prize in physics 1986

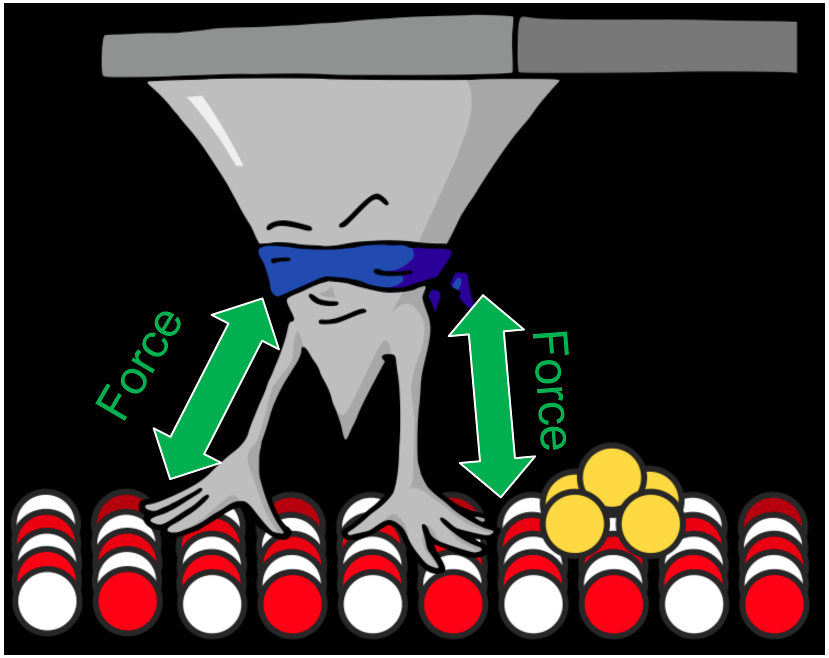
⇨ Cartography (X,Y, Z (I_{tunnel} = cst))

A Revolution but…..

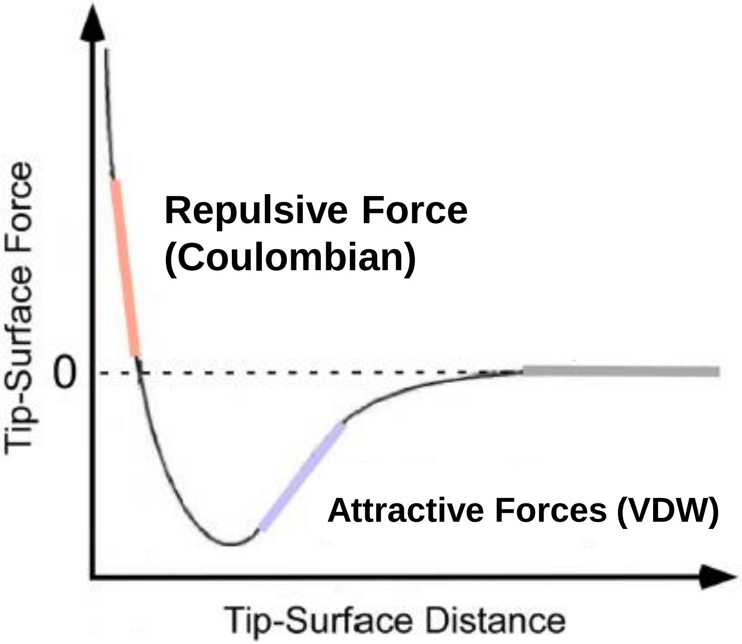
- ⇨ Limited to conducting materials
- ⇨ topo mixed with local DOS
- ⇨ Ultra High Vacuum (surface pollution)

Atomic Force Microscopy : Forces

Interactions between the atoms of a probe and the atoms of the surface



Forces *vs.* distance curve



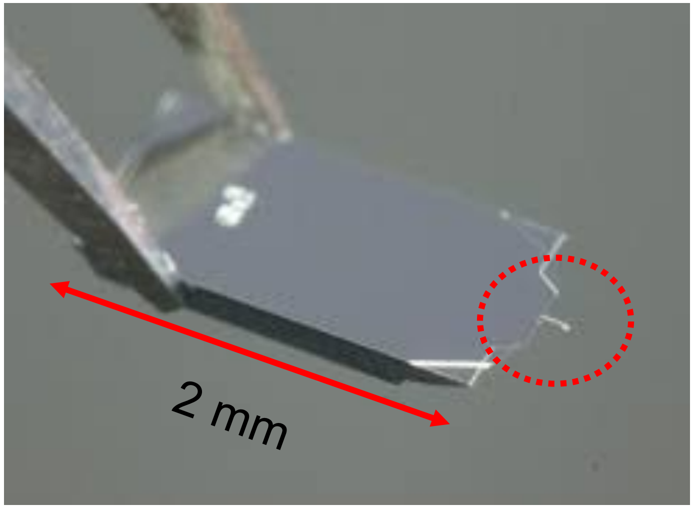
How to measure those forces on the tip ?

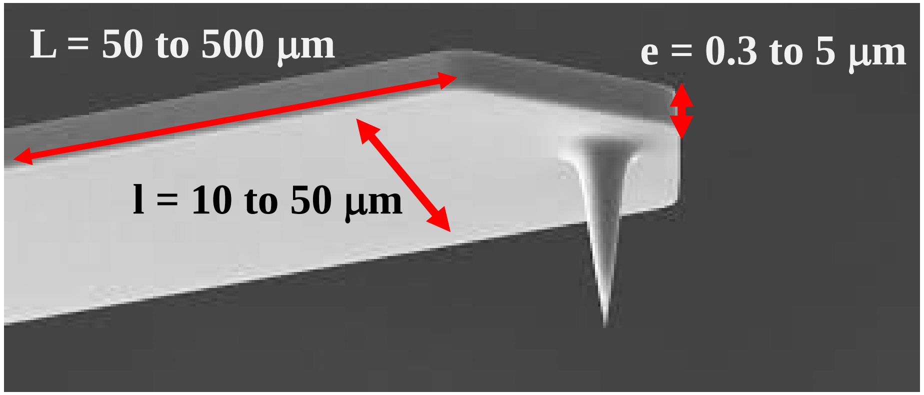
How to measure the forces on the tip ?
The Cantilever

Cantilever = bendable structure holding the tip

⇔ **Spring with stiffness k**

Silicon based micro-fabrication technologies





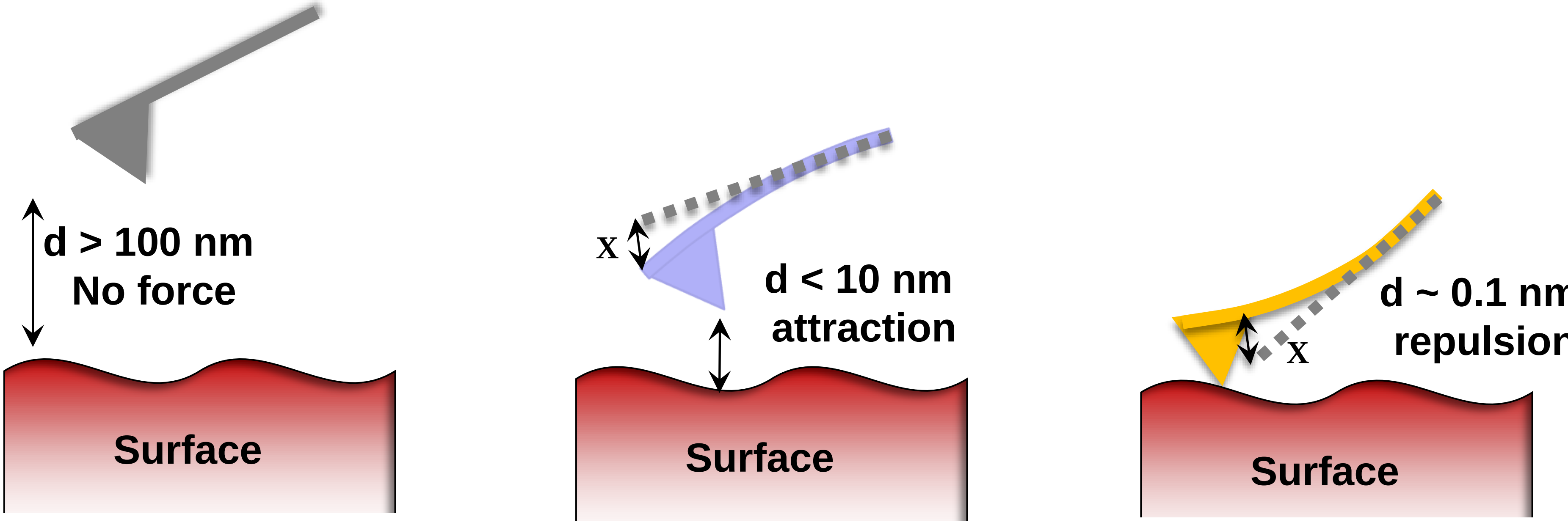
$k \sim 0.01$ to 100 $N.m^{-1}$

depending on geometry and materials

Tip-surface interaction transmitted to the cantilever

Tip on cantilever ⇔ tip attached to a spring

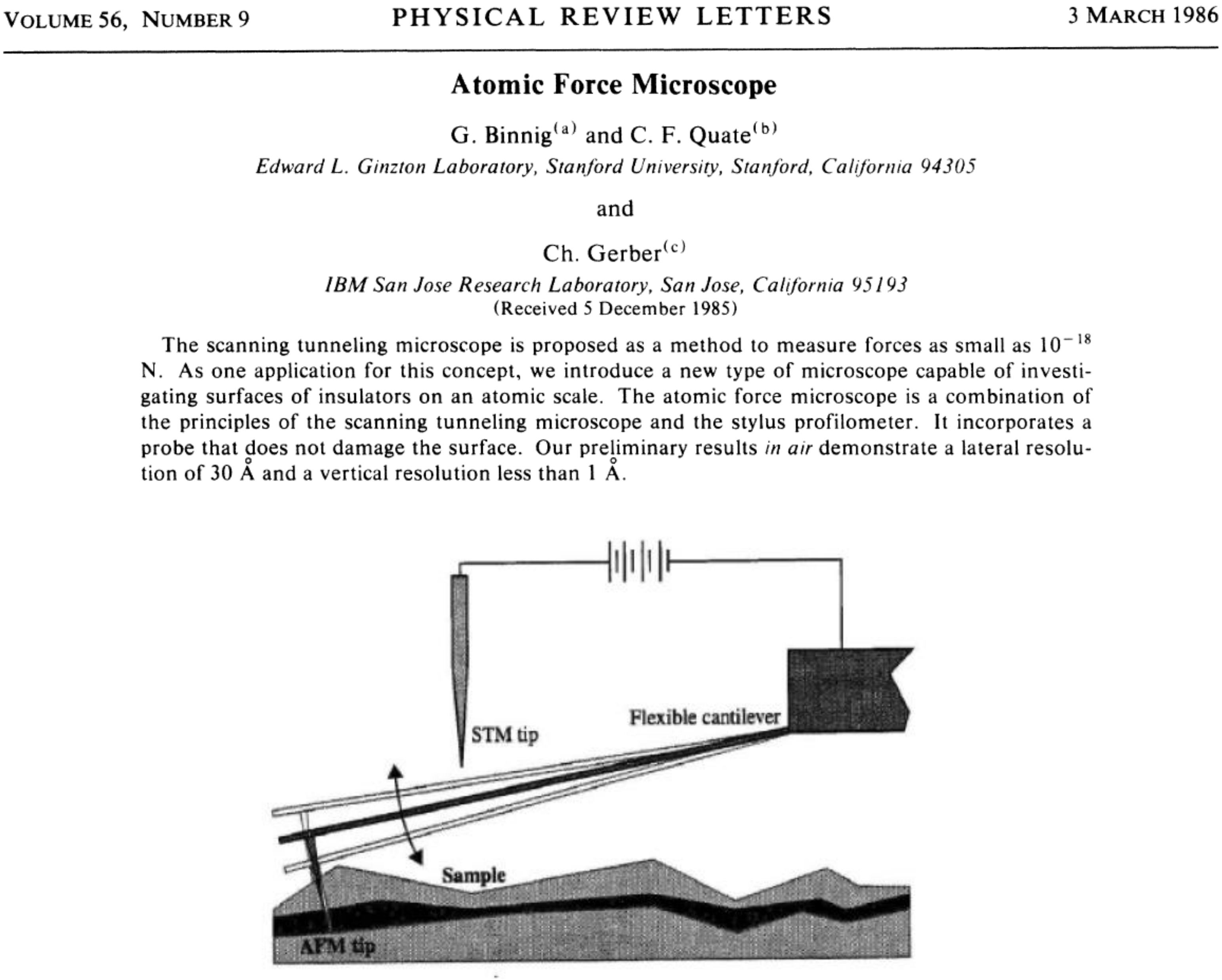
Spring deformation α applied force (on the tip)



$$\boxed{F = - k . x}$$

F : Tip-surface atomic force
k : stiffness
x : cantilever deformation

How to measure the cantilever deformation ?



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Atomic Force Microscope

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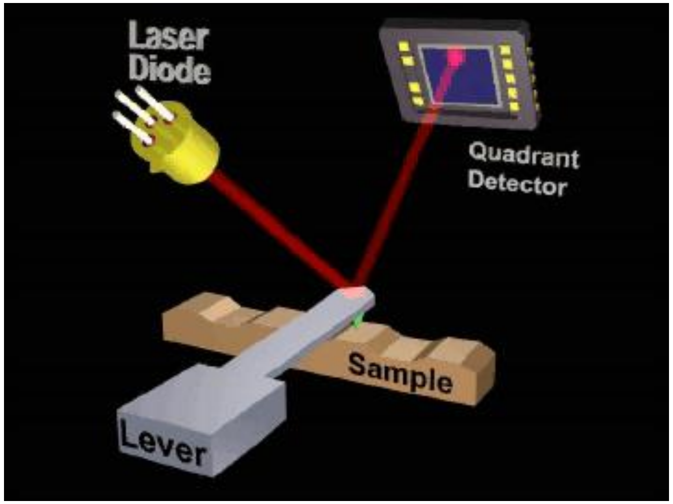
IBM San Jose Research Laboratory, San Jose, California 95193

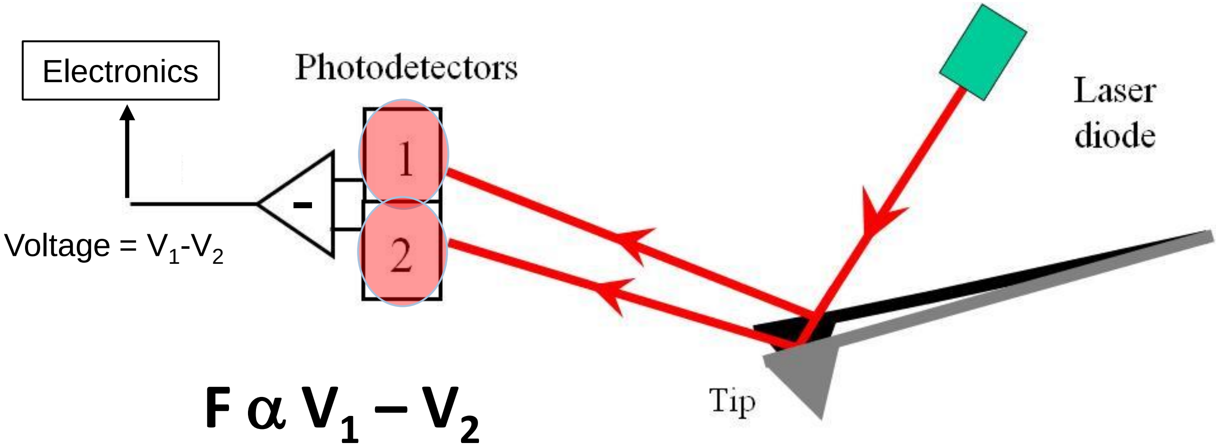
(Received 5 December 1985)

The scanning tunneling microscope is proposed as a method to measure forces as small as 10^{-18} N. As one application for this concept, we introduce a new type of microscope capable of investigating surfaces of insulators on an atomic scale. The atomic force microscope is a combination of the principles of the scanning tunneling microscope and the stylus profilometer. It incorporates a probe that does not damage the surface. Our preliminary results *in air* demonstrate a lateral resolution of 30 Å and a vertical resolution less than 1 Å.

How to measure the cantilever deformation ?



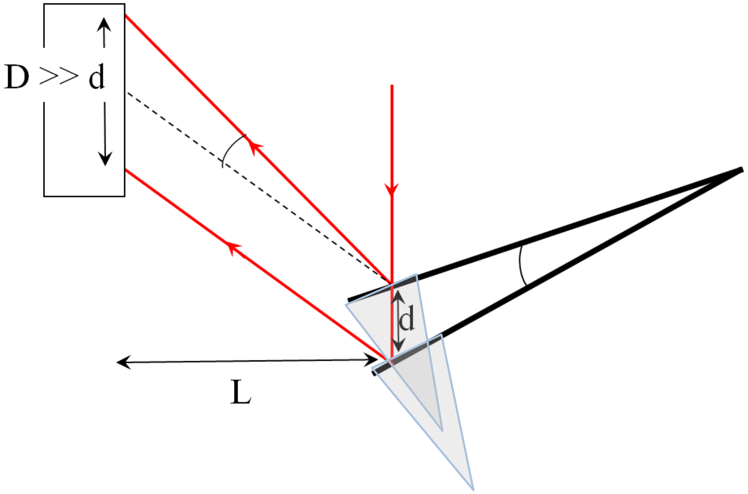
laser deflection on 2 photodetectors



Voltage = V_1-V_2

$$F \alpha V_1 - V_2$$

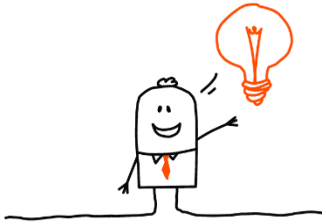
Measure of atomic interactions α a voltage



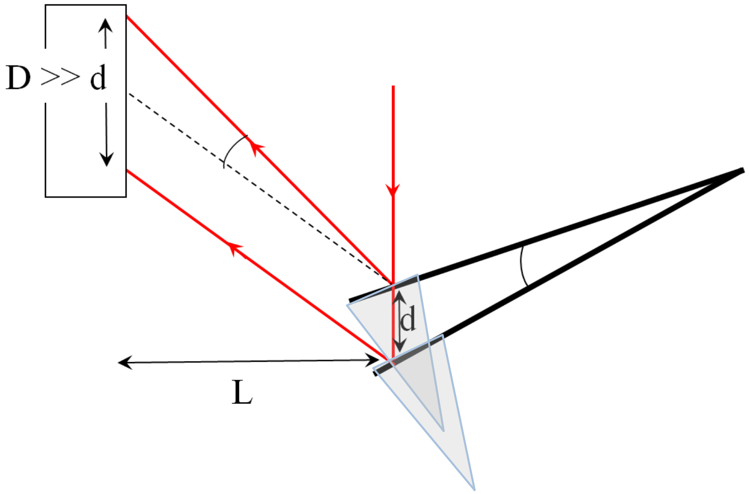
$L \sim 10^{-2}$ m
$d \sim 10^{-9}$ m

Geometrical amplification of the laser deviation ⇨ **vertical resolution < 0.01 nm**

How to measure the cantilever deformation ?



Focus the laser at the very end of the cantilever for better sensitivity

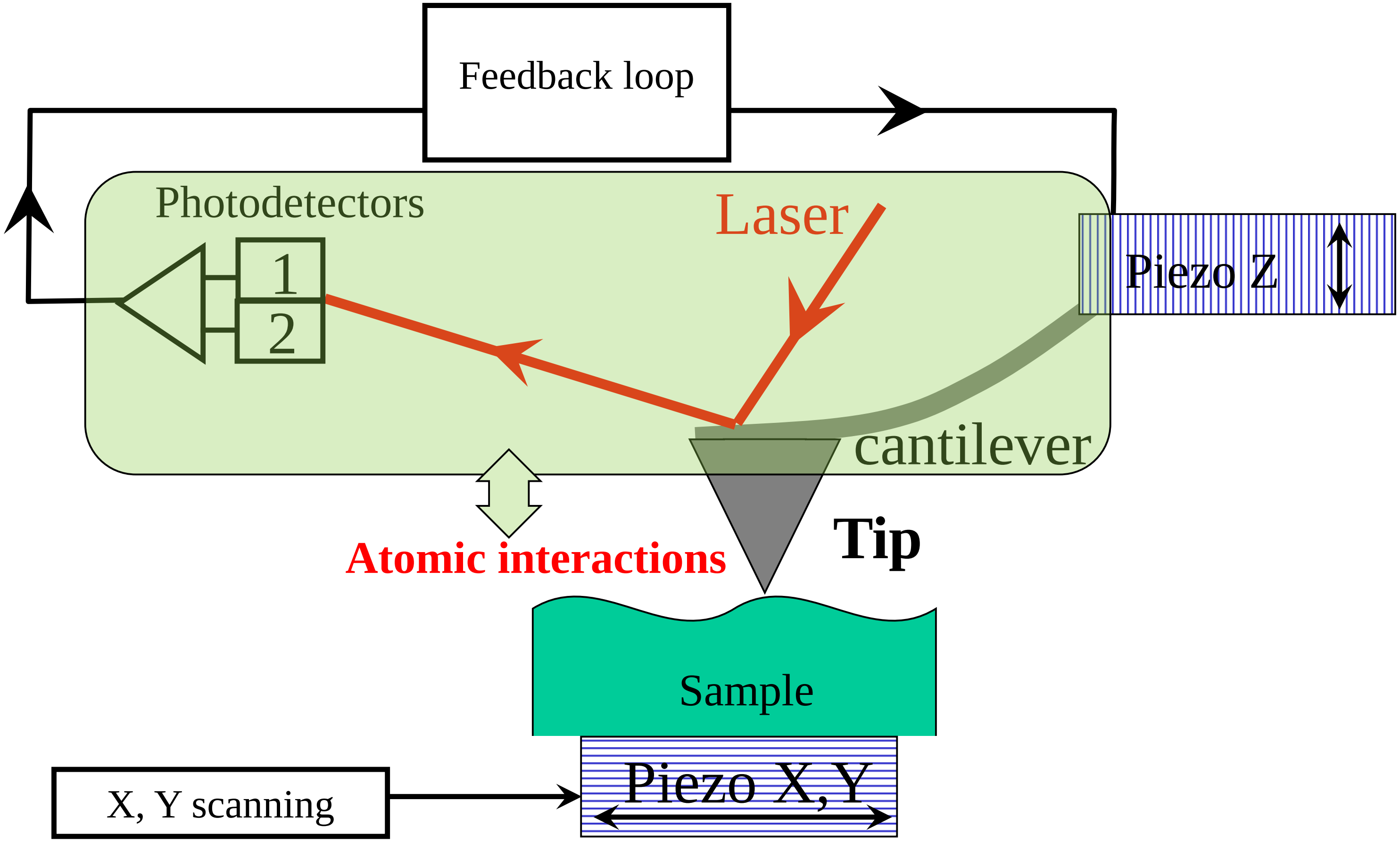


$L \sim 10^{-2}$ m
$d \sim 10^{-9}$ m

Geometrical amplification of the laser deviation ⇨ **vertical resolution < 0.01 nm**

Atomic Force Microscopy

Measure of **atomic interactions** = **voltage** from photodetectors

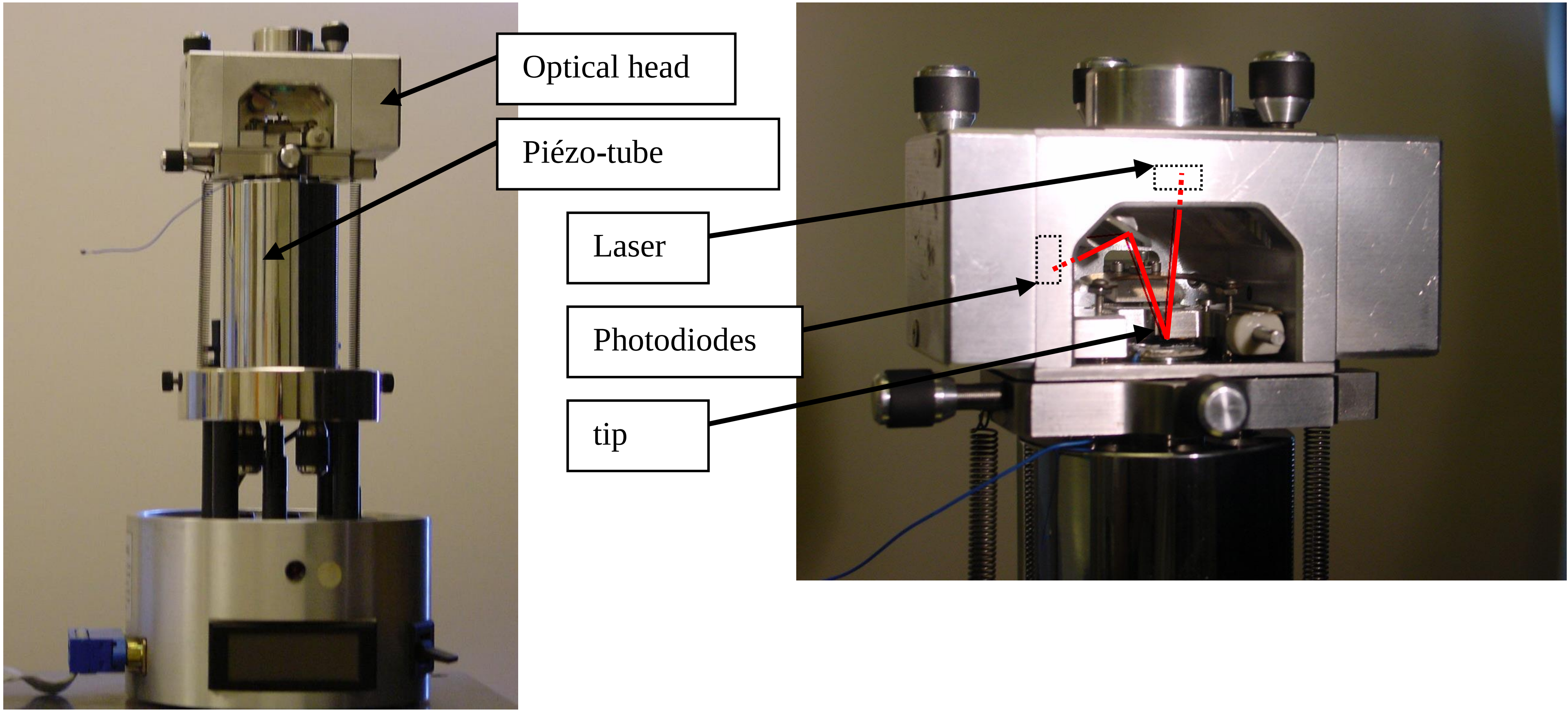


At each point (X_i, Y_i) of the surface, Z_{piezo} has to be distorted of ΔZ to maintain the laser deflection constant

⇨ Cartography (X,Y, Z (**deflection** = cst))

Atomic Force Microscope

Nanoscope II Digital Instruments (~1990)



Optical head

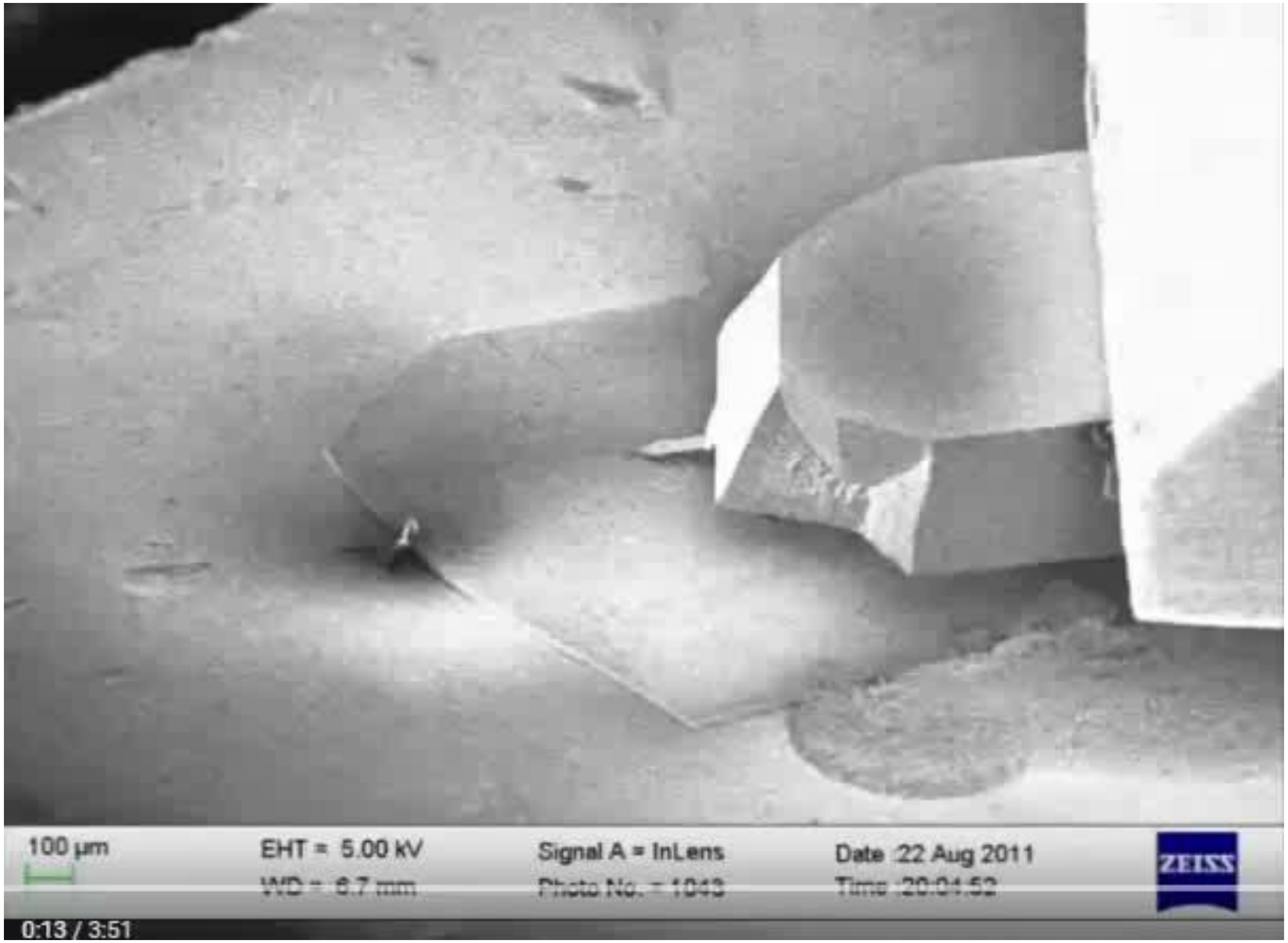
Piézo-tube

Laser

Photodiodes

tip

Atomic Force Microscopy

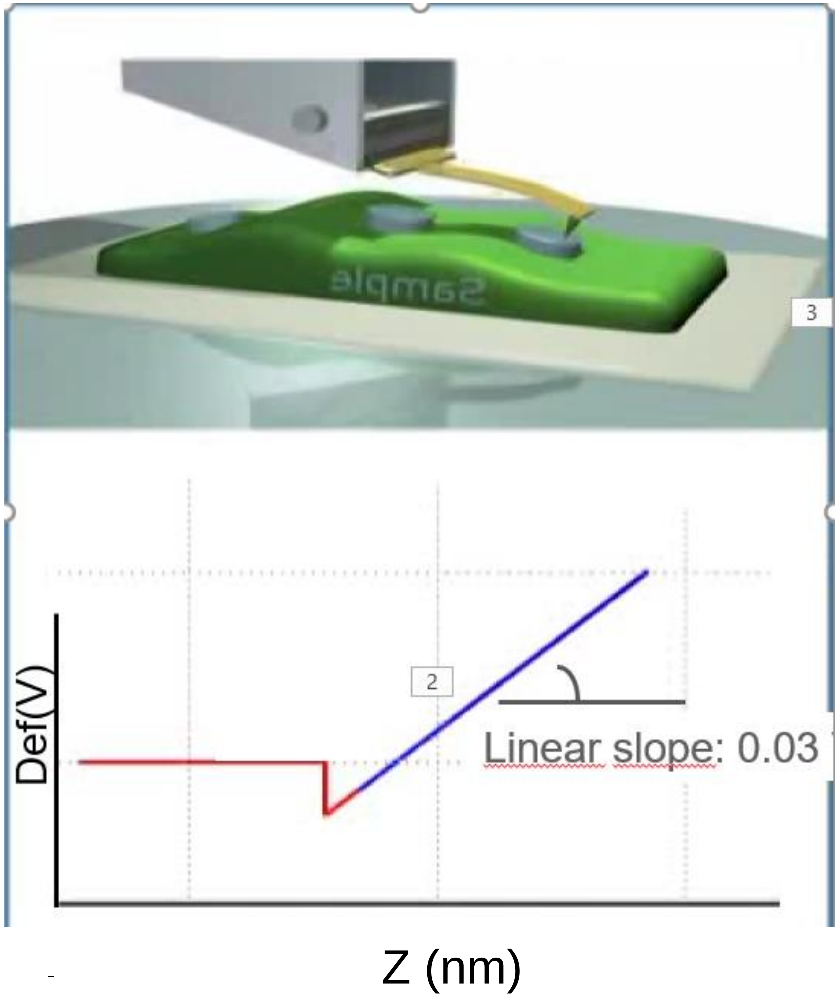


http://www.dme-spm.com/remafm.html

From deflection voltage to actual force

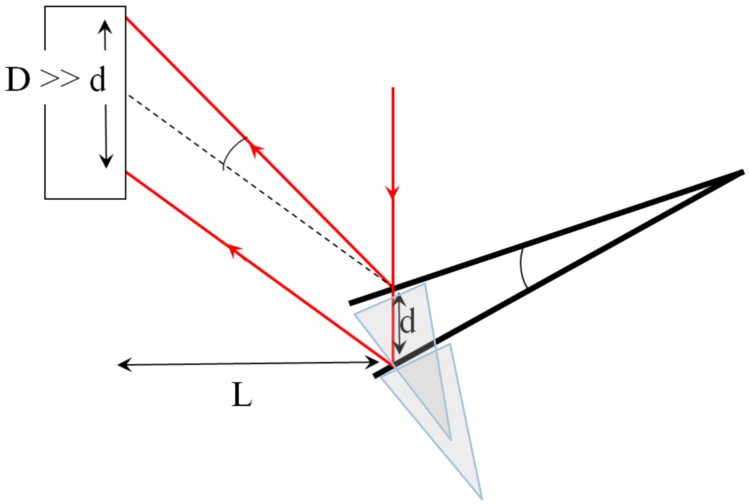
Force curve: Deflection (V) ⇔ cantilever deformation (nm)

No XY scan & extension of the Zpiezo



Sensitivity ~ 33 nm/V

PURELY GEOMETRIC

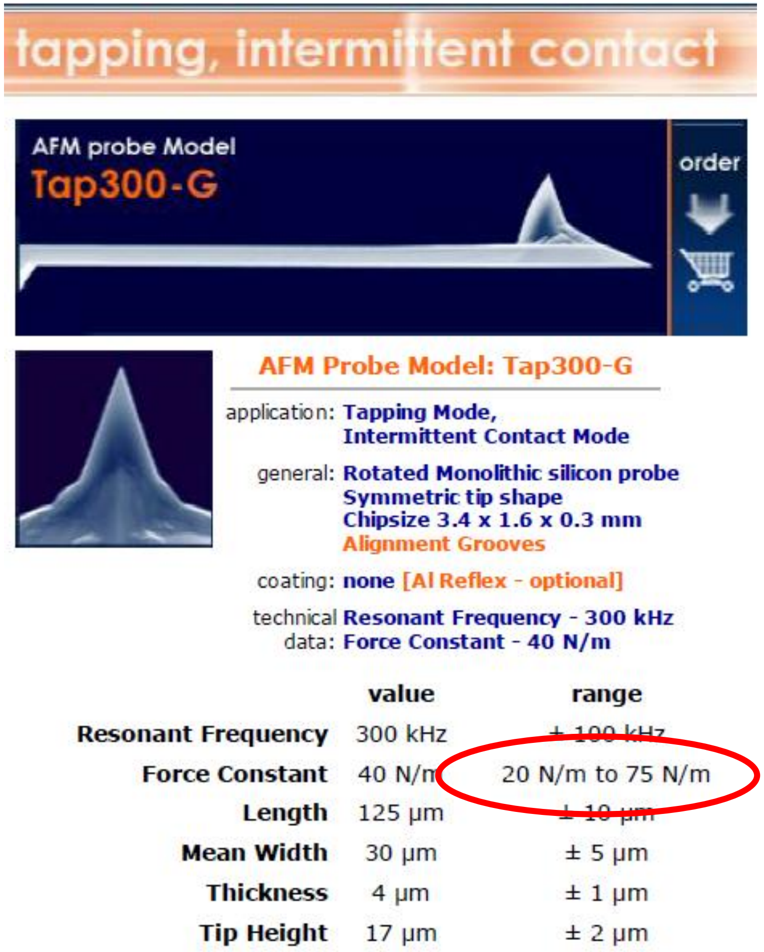


From deflexion voltage to actual force

Hooke's law: cantilever deformation (nm) ⇔ Force (N)

$$F = -k.x$$

Believe manufacturers data sheets



tapping, intermittent contact

AFM probe Model
Tap300-G

AFM Probe Model: Tap300-G

application: Tapping Mode, Intermittent Contact Mode

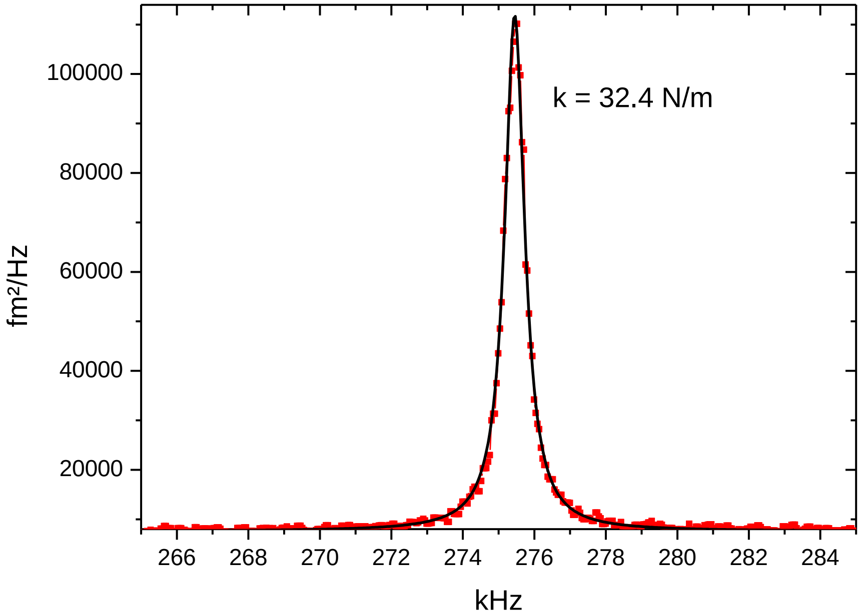
general: Rotated Monolithic silicon probe
Symmetric tip shape
Chipsize 3.4 x 1.6 x 0.3 mm
Alignment Grooves

coating: none [Al Reflex - optional]

technical data: Resonant Frequency - 300 kHz
Force Constant - 40 N/m

	value	range
Resonant Frequency	300 kHz	± 100 kHz
Force Constant	40 N/m	20 N/m to 75 N/m
Length	125 µm	± 10 µm
Mean Width	30 µm	± 5 µm
Thickness	4 µm	± 1 µm
Tip Height	17 µm	± 2 µm

Or measure it
(thermal oscillation of the cantilever + model)



Stiffness: 32.4 N/m (for 40 N/m nominal)

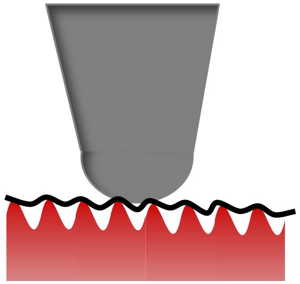
Spatial Resolution

Vertical resolution : ~ 10 pm

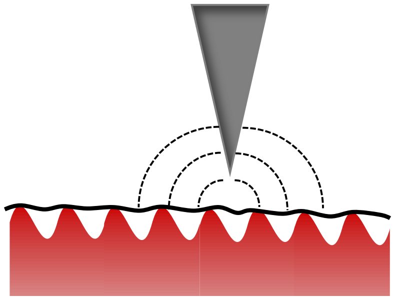
- Ability to measure the smallest cantilever deformation (laser intensity noise, photodiodes noise, thermal noise of cantilever)
- Positioning noise of piezo-ceramic Z….

Lateral resolution : ~ 10 pm to 10’s nm

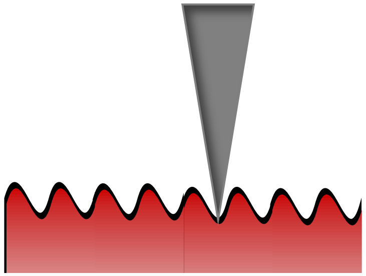
- Positioning noise of piezo-ceramic X/Y….
- Type of interaction (long or short range)
- Tip geometry



- Finite tip radius
- Short range interaction



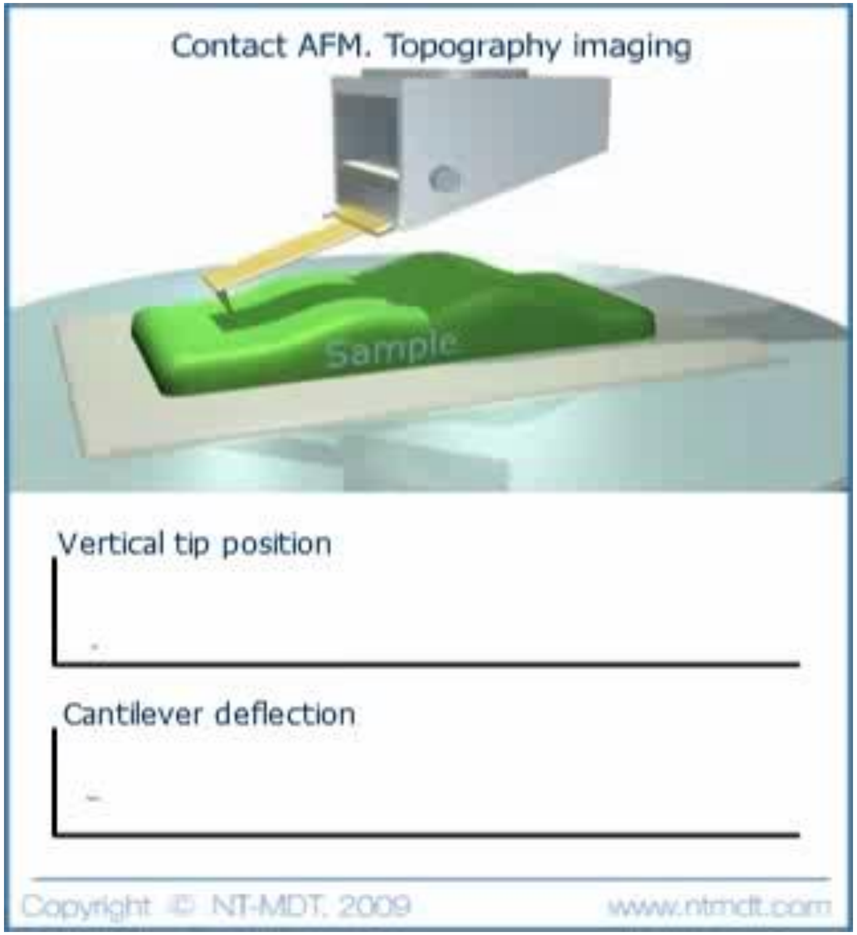
- Infinitely sharp tip
- Long range interaction

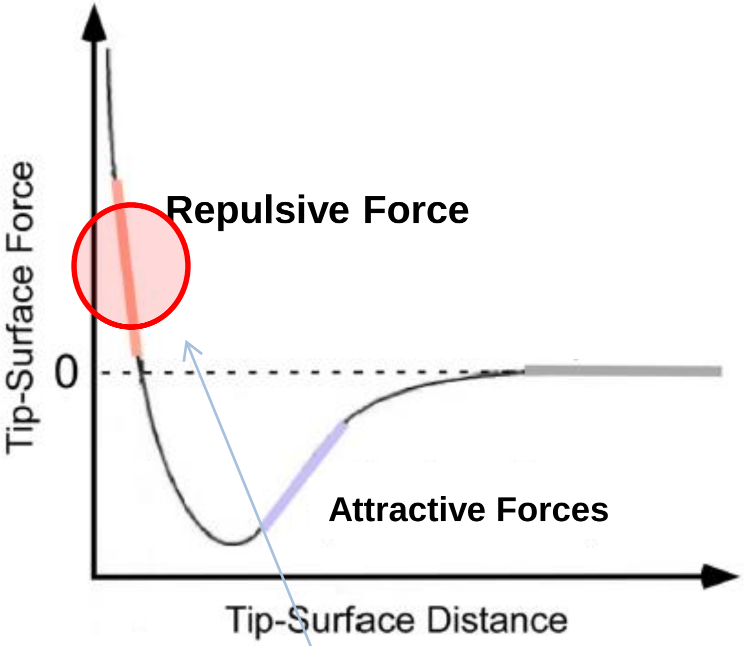


- Infinitely sharp tip
- Short range interaction

Contact mode or "static mode"

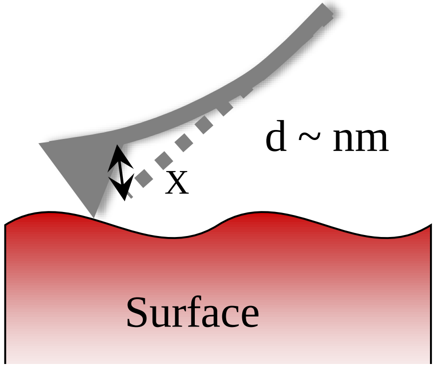
Permanent contact

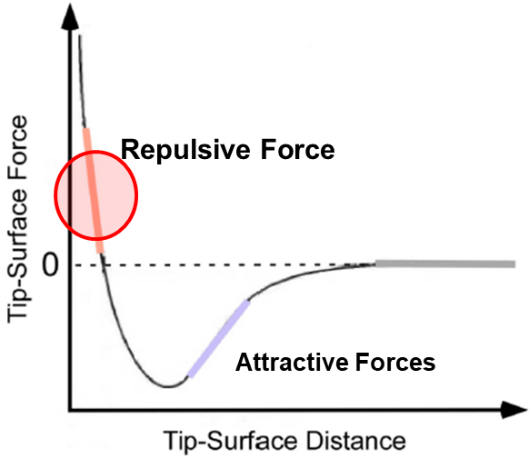




High repulsive force
+
high slope

Contact mode or "static mode"





Advantages

- ❑ High forces (~10^{-8} to 10^{-6} N): surface pollution is swept away
- ⇨ **Work in ambient conditions, liquid…**
- ❑ Images acquisition: "easy" and fast (~mn)
- ❑ **Permanent contact** : Compatible with measurement of some physical parameters (electrical current, thermal properties, mechanical properties…)

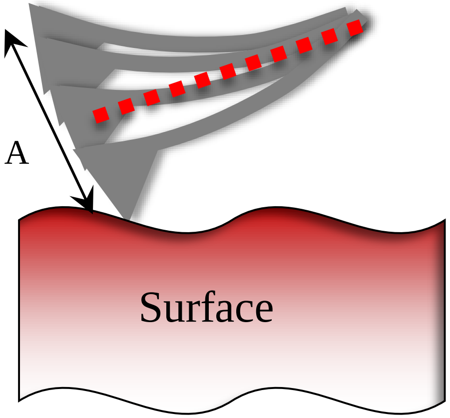
Drawbacks

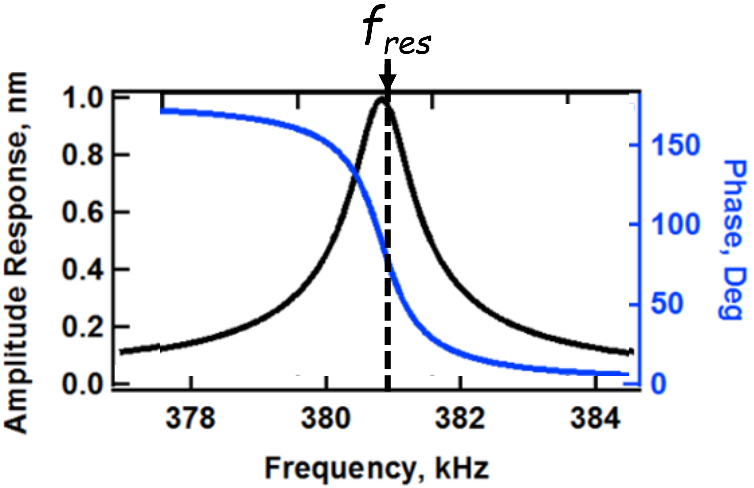
- ❑ High contact pressure (GPa): **sample deformation** or destruction
- ❑ High friction forces
  - ➢ tip wearing and breaking: **tip sharpness is limited** and so is lateral resolution (~10nm)
  - ➢ Sweeping effect : sweep off loosely bonded objects on surface

Dynamic mode

The cantilever is an harmonic oscillator

which has a mechanical resonance





- the cantilever oscillation is modified by the forces acting on the tip
- ⇨ Oscillation parameter is used as the feedback signal : Frequency or Amplitude

Advantages :

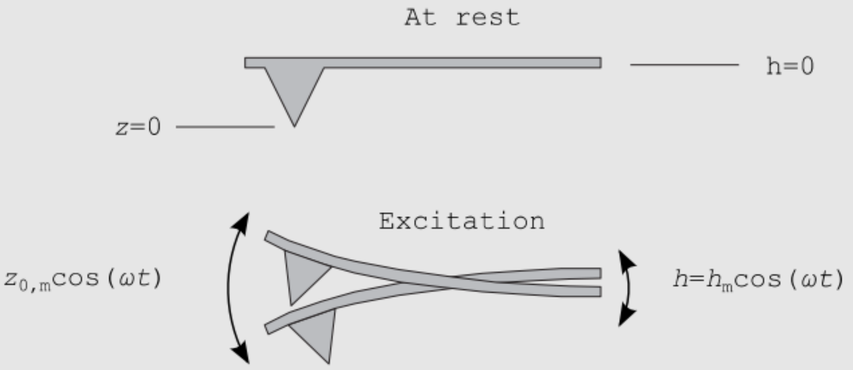
- At resonance, the harmonic oscillator is **very sensitive** to perturbations
- **Frequency measurement or Lock-in amplifier** : small signals

} ⇨ **lower forces**

- **No more friction forces**

Oscillating cantilever : tip sample interaction fundamentals

Excitation méchanique du cantilever + F(z)



$$m\ddot{z}+\Gamma\dot{z}+kz=0$$

m	Inertia
Γ	Damping
k	Spring

Tip-sample interaction treated as a perturbation

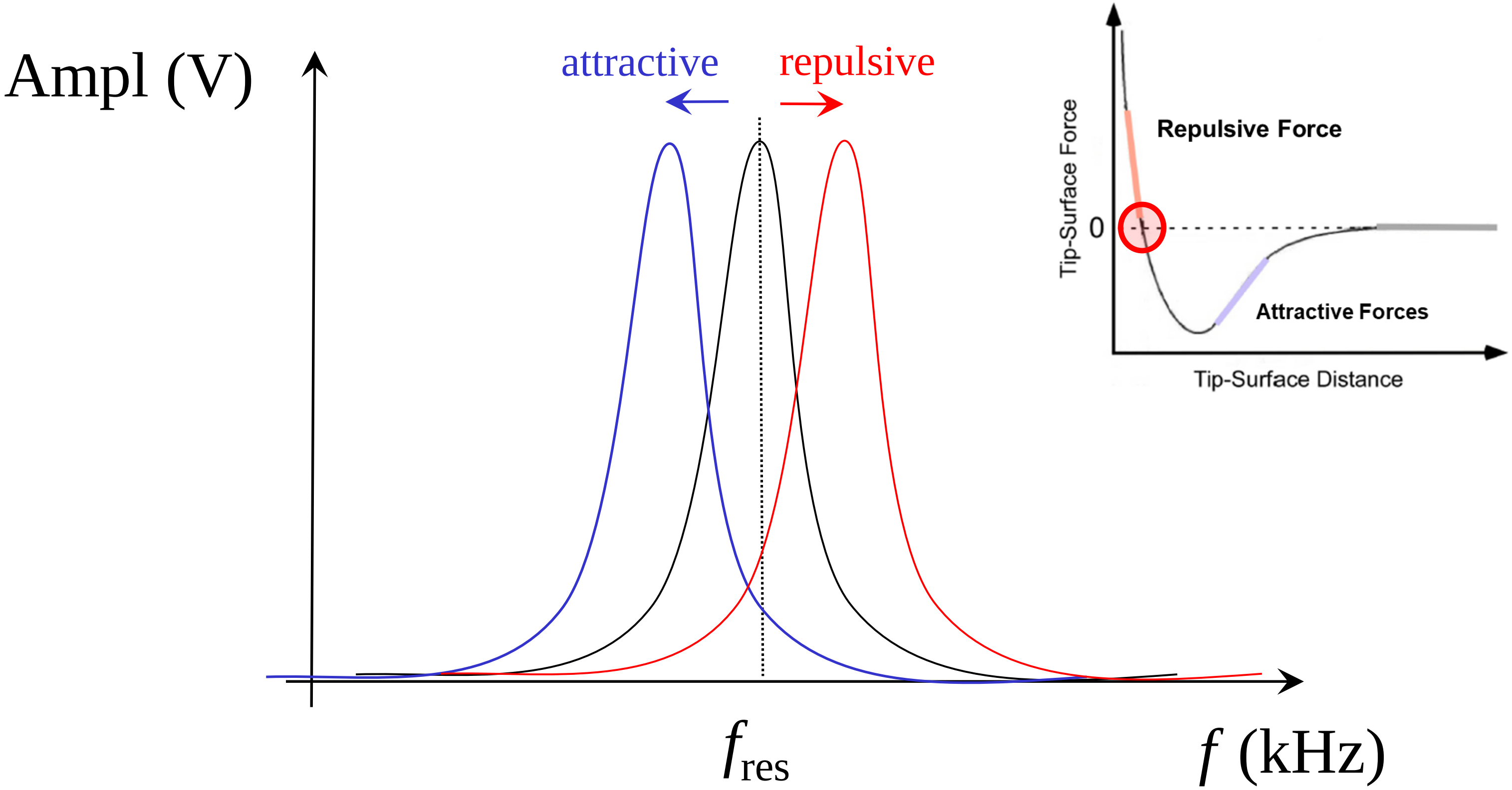
$m\ddot{z}+\Gamma\dot{z}+kz=F(z)$ with $F(z)=F(z_o)+(z-z_o)\partial_z F$

⇨ Mere renormalization : $\omega_{o,eff}=\omega_o\left(1-\frac{1}{2k}\partial_z F\right)$

The resonance frequency is shifted

Oscillating cantilever : tip sample interaction fundamentals

If F(z) is attractive ⇨ f_{res} is reduced
If F(z) is repulsive ⇨ f_{res} is increased

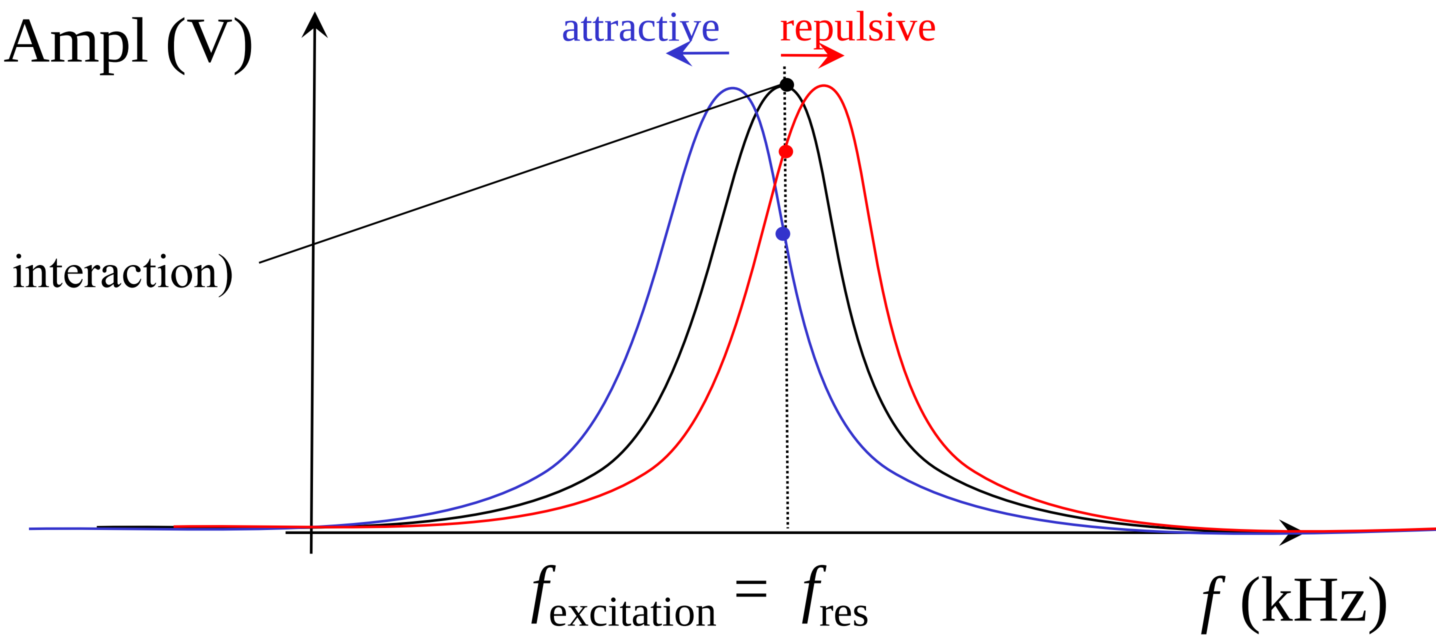


Oscillating cantilever : Forced oscillation

Forced oscillation (Lock-In amplifier) => Amplitude used as feedback signal

Which frequency ?

$f_{excitation} = f_{res}$



“Free” amplitude (no interaction)

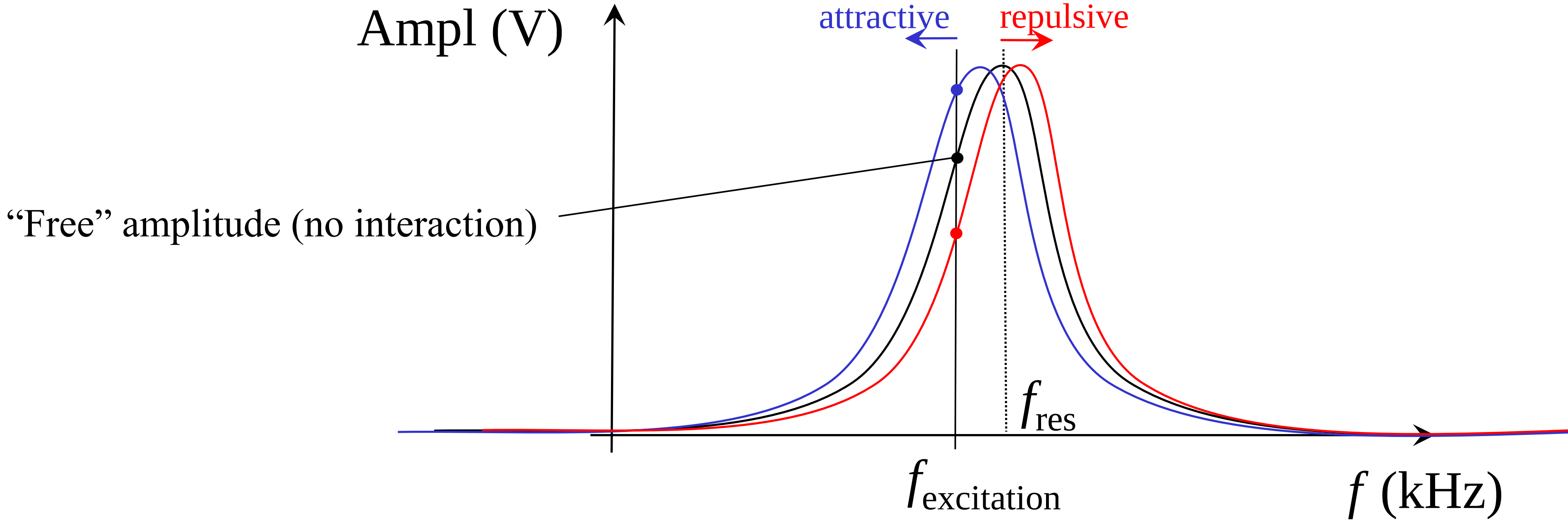
Attractive interaction ⇨ the amplitude decreases
Repulsive interaction ⇨ the amplitude decreases

If the feedback loop detects a drop of the amplitude ⇨ Retract or extend the Zpiezo ?
(is it a bump or a hole on the sample surface ?)

Oscillating cantilever : Forced oscillation

Amplitude used as feedback signal

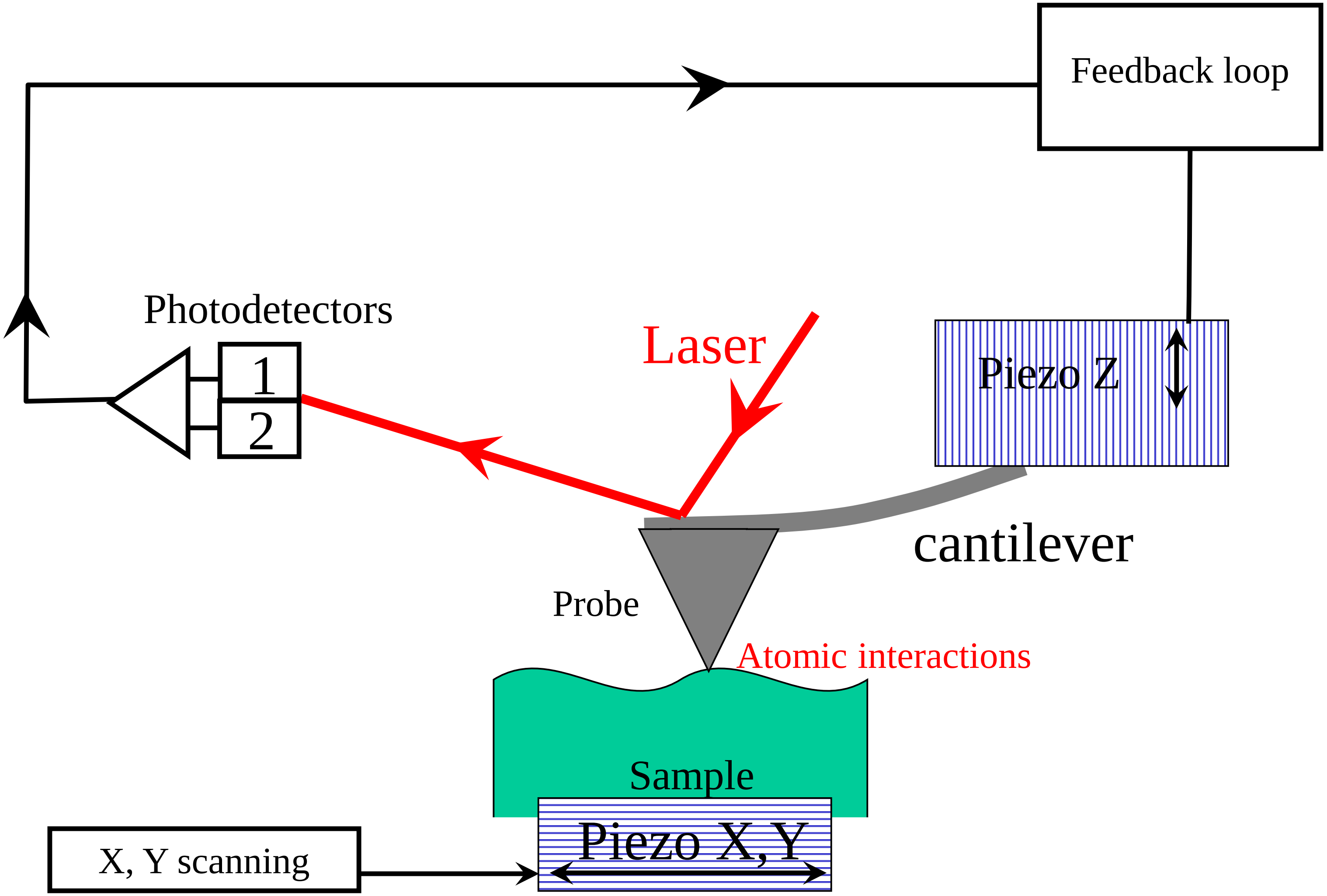
$f_{excitation} < f_{res}$



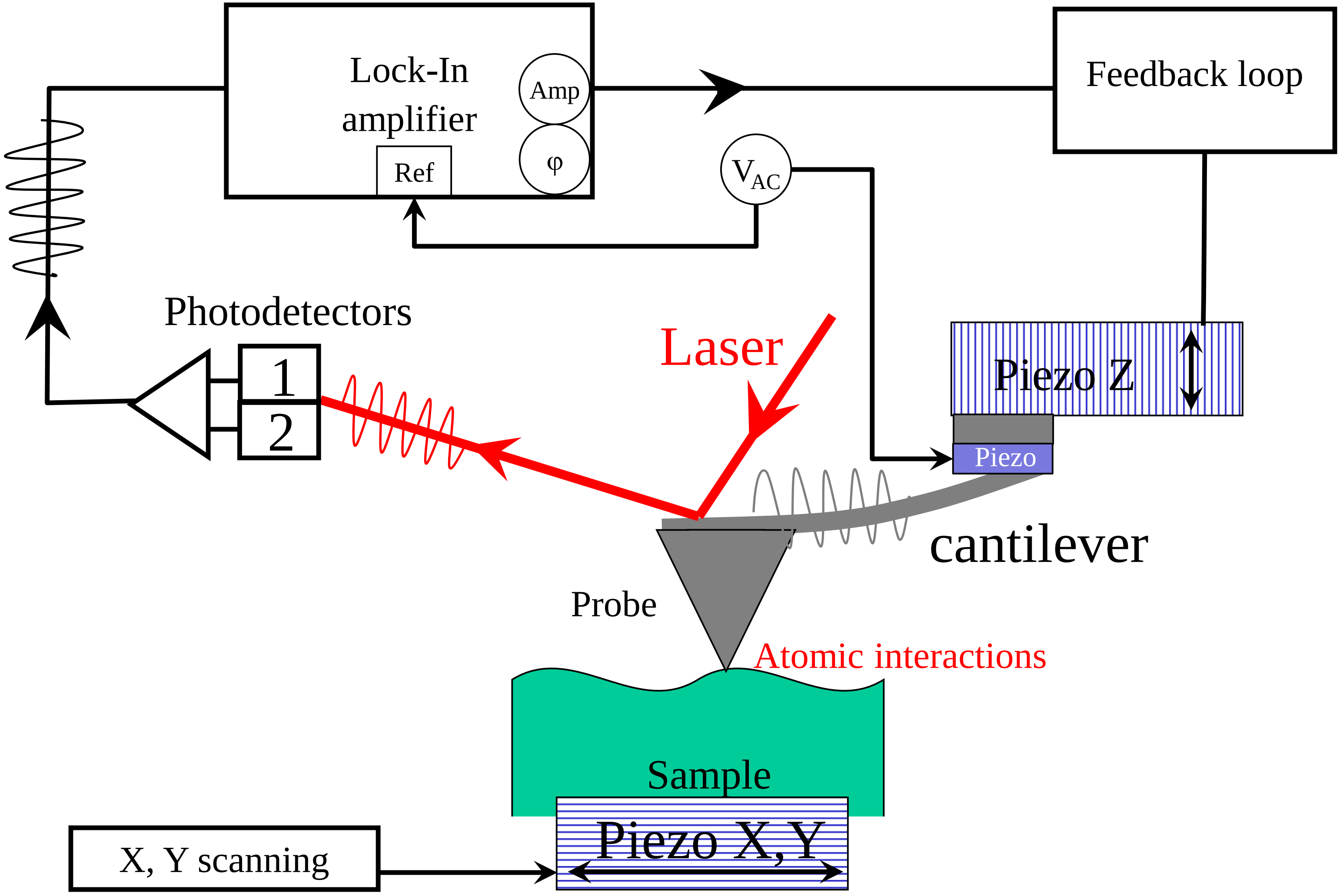
Attractive interaction ⇨ the amplitude increases
Repulsive interaction ⇨ the amplitude decreases

- Amplitude setpoint < free amplitude (repulsive force)
- Increase tip-sample repulsive interaction ⇨ Decrease the amplitude setpoint

Amplitude Modulated mode (« Tapping » mode)



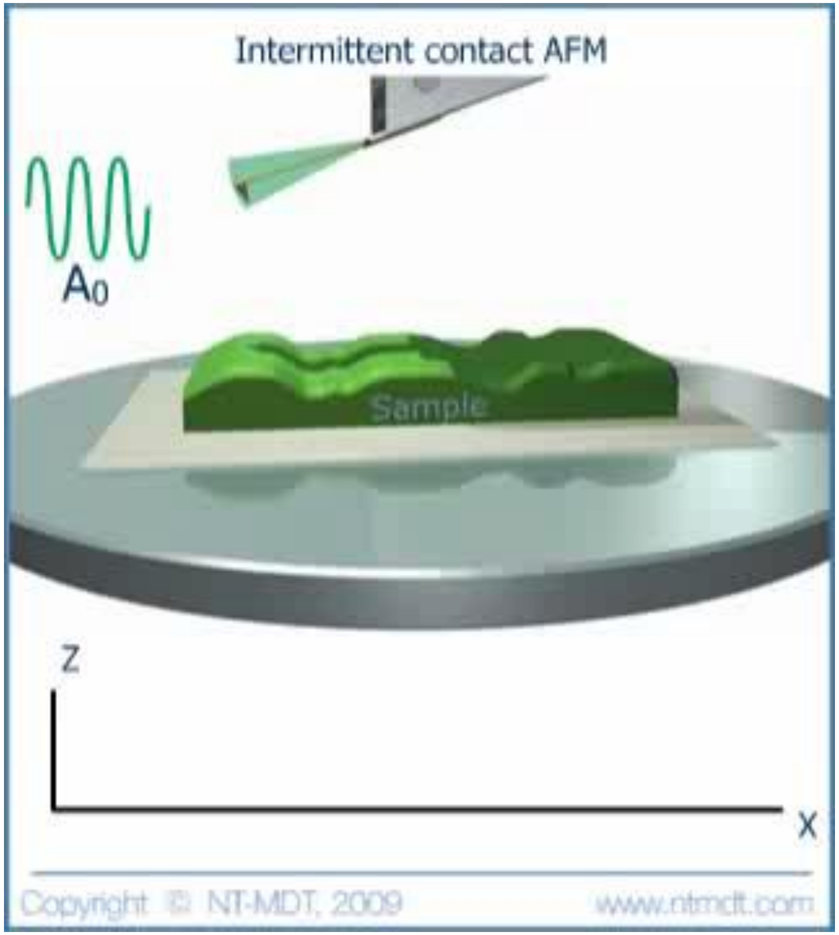
Amplitude Modulated mode (« Tapping » mode)



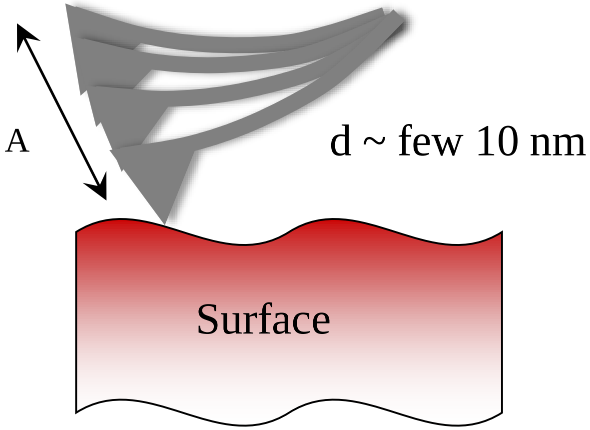
At each point (X_i, Y_j) of the surface, Z_{piezo} has to be distorted of ΔZ to maintain the amplitude constant

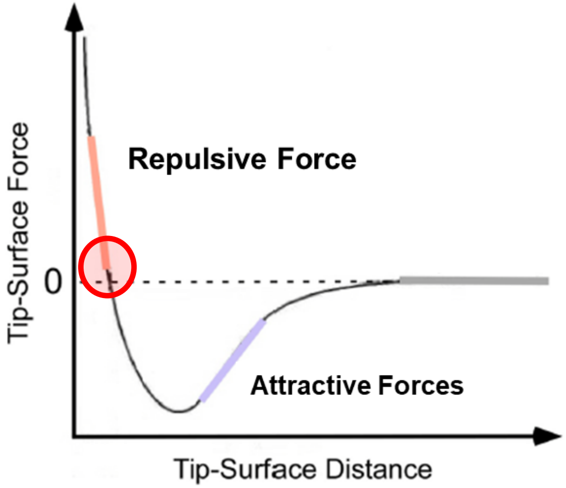
⇨ Cartography (X,Y, Z (**amplitude** = cst))

Amplitude Modulated mode (« Tapping » mode)



Amplitude Modulated mode (« Tapping » mode)





Advantages

- Lower forces ($\sim 10^{-9} – 10^{-10}$ nN) : **soft material preserved**
- Images acquisition: easy
- No friction forces : **sharper tips are preserved** ⇨ better lateral resolution

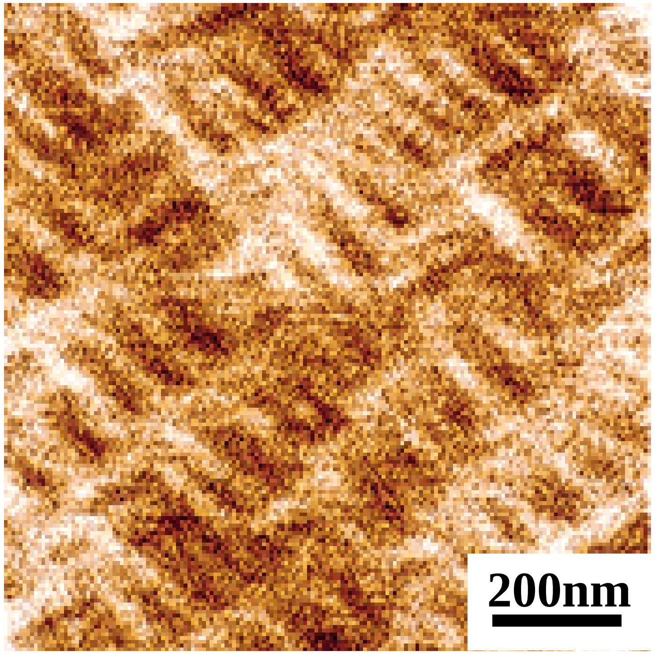
Drawbacks

- Slower feedback than permanent contact: longer acquisition (steady state after $\tau=2Q/\omega_0$)
- Adhesive surfaces catch tips: feedback instabilities
- **No permanent contact** with the surface (~ µsec)

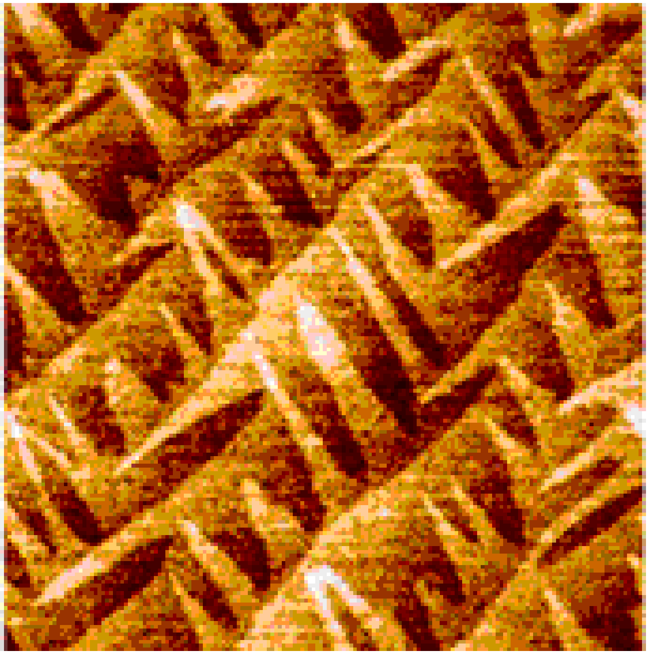
Amplitude Modulated mode (« Tapping » mode)

Epitaxial Silicon

Contact mode

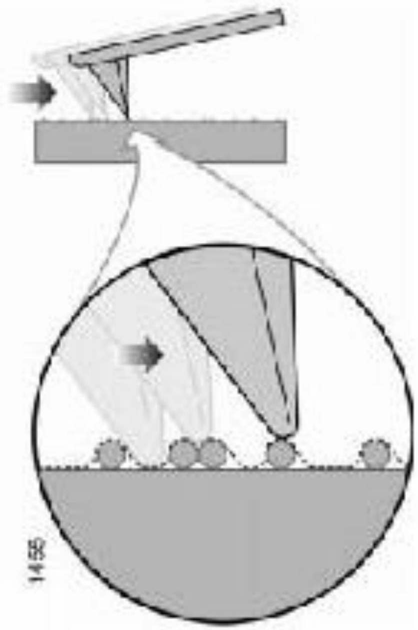


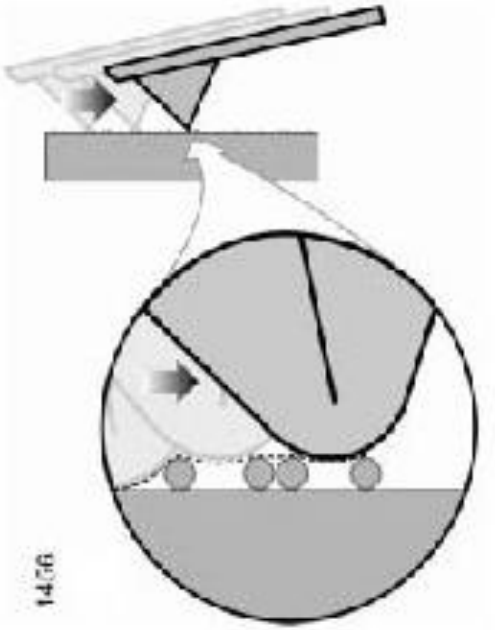
Tapping mode



Images distortion (artefacts) due to the tip

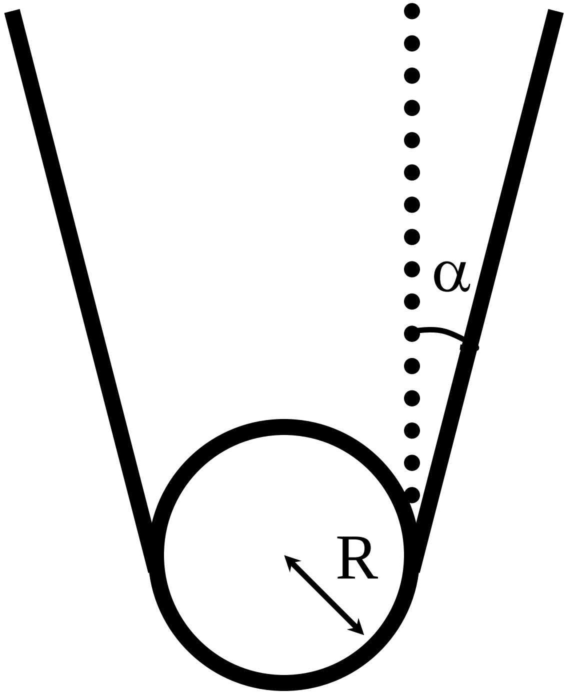
In AFM all what is « seen » is seen by the tip
Many things depend on its shape





Images distortion (artefacts) due to the tip

Tip can be characterized by a tip radius and a cone angle

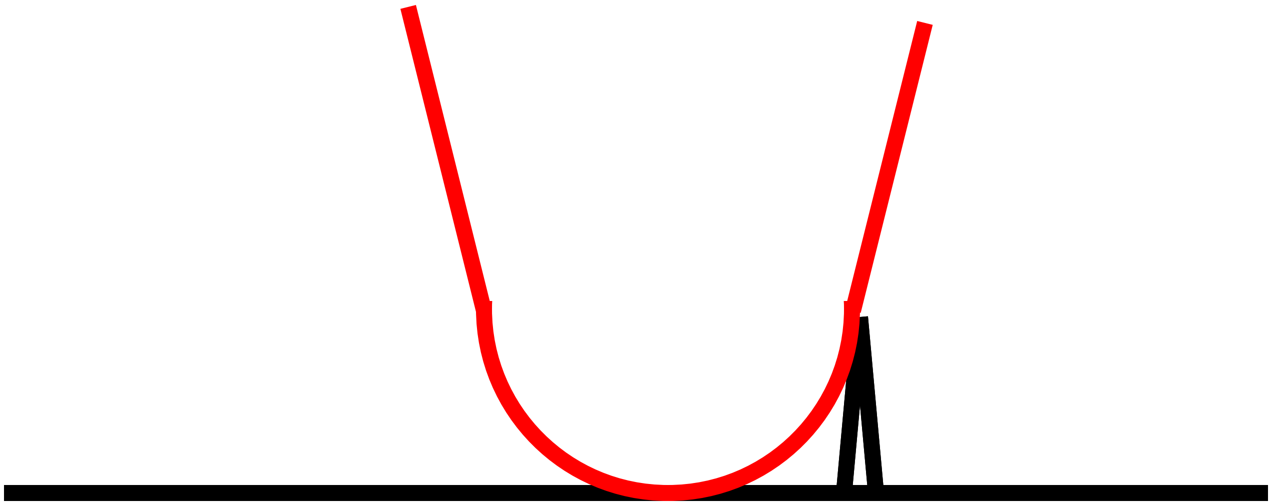


$$2\text{nm} < R < 50\text{nm}$$

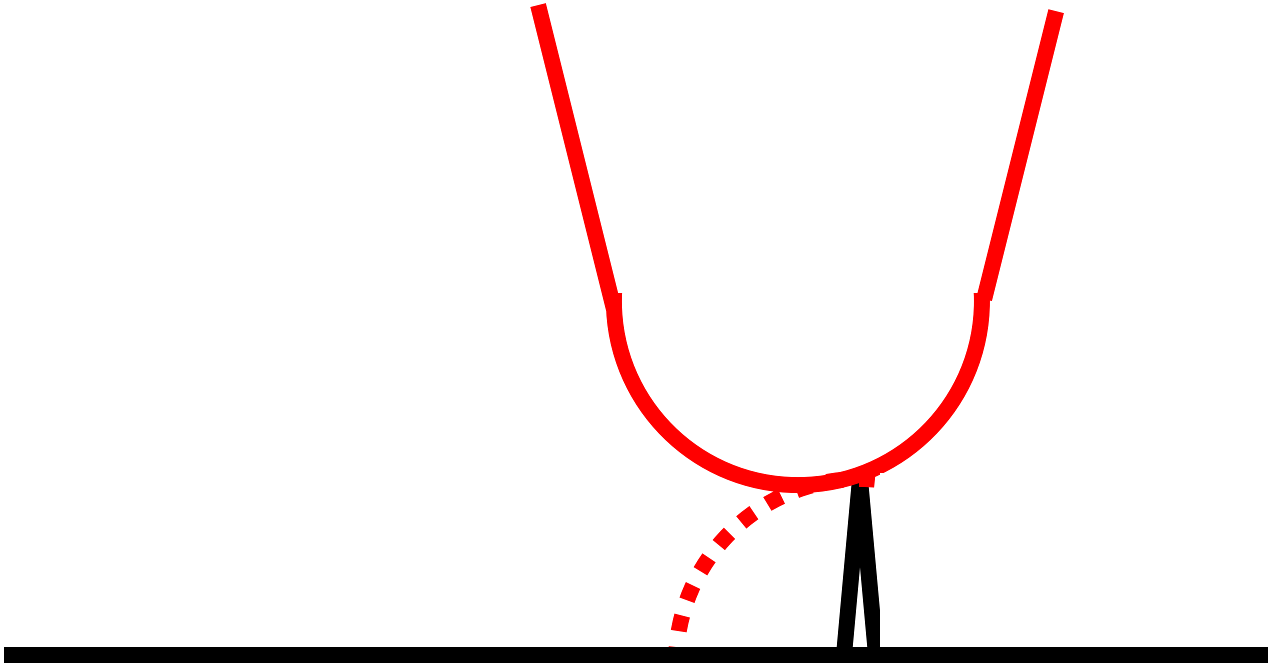
$$2° < \alpha < 35°$$

Artefacts : Tip radius

Artefacts : Tip radius

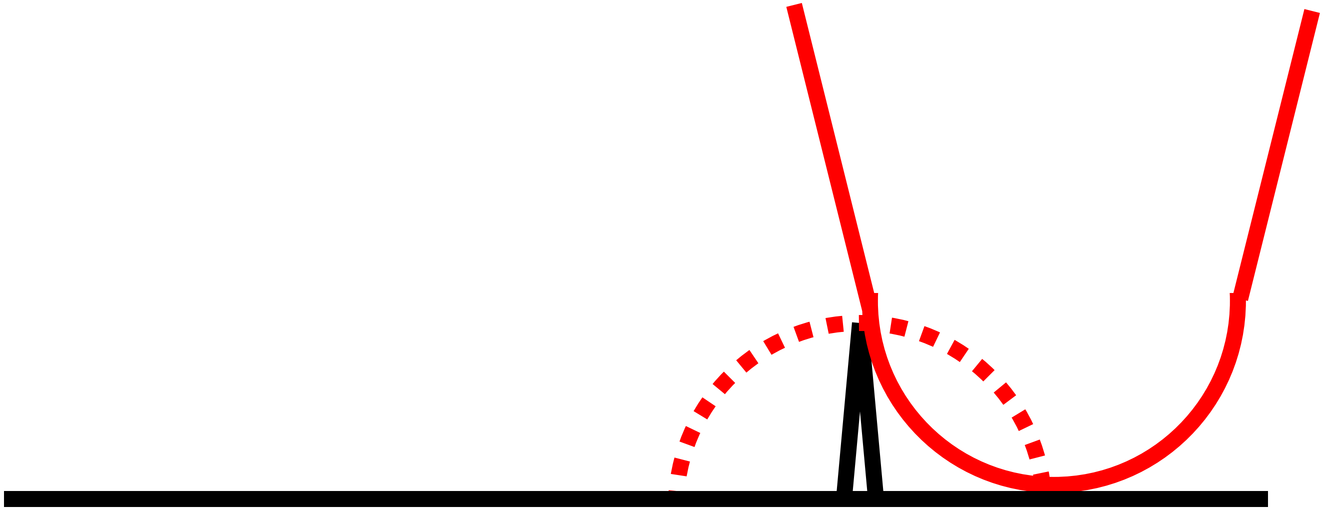


Artefacts : Tip radius

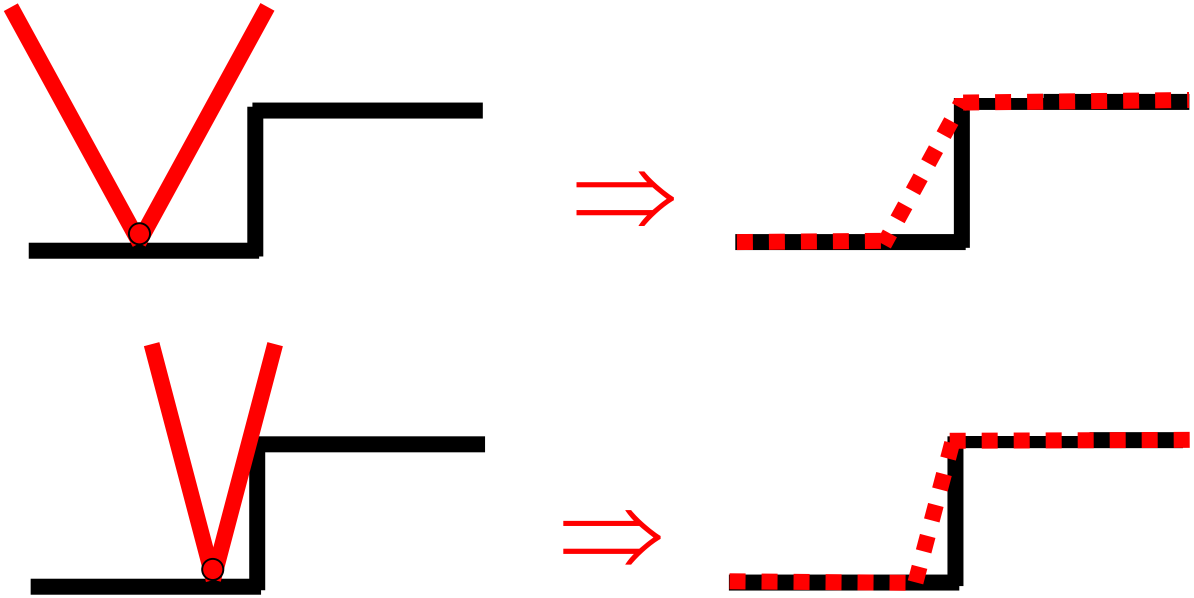


- Tip radius -

$R_{object} << R_{tip}$ => the object images the tip



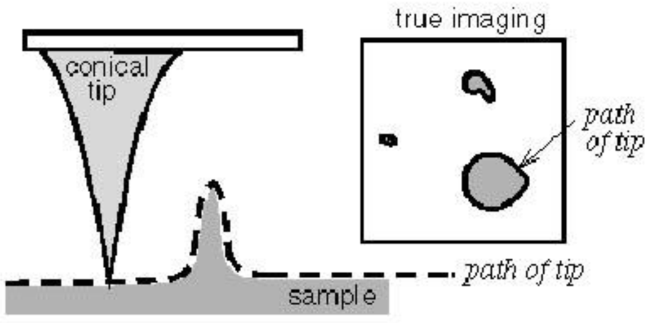
Atefacts : Cone angle



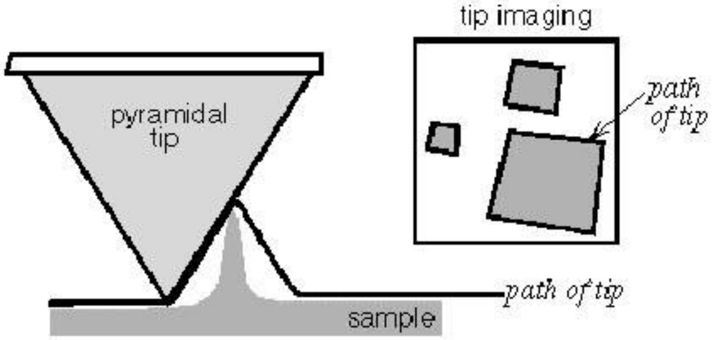
Steep step => image of the tip angle
Easy to detect : tip geometry is known

Atefacts : Think in 3D

OK

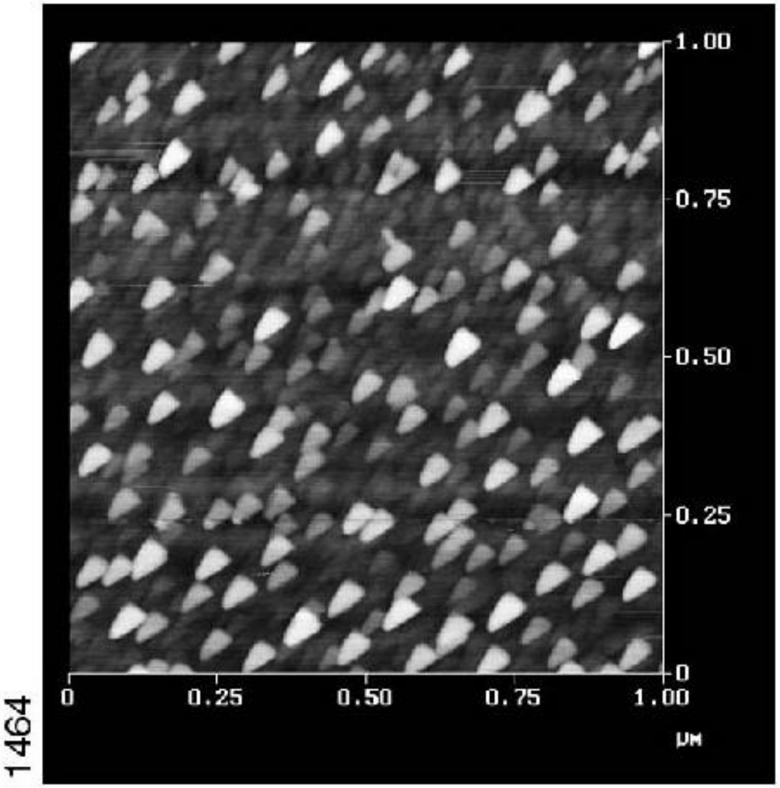


Artefact :
Pyramidal shape of the tip

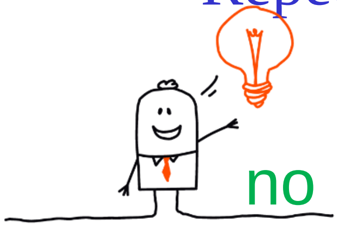


Example of artefacts

Damaged tip



Repetition of the same shape on the sample surface



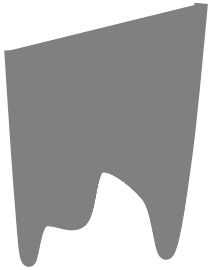
Rotate the sample

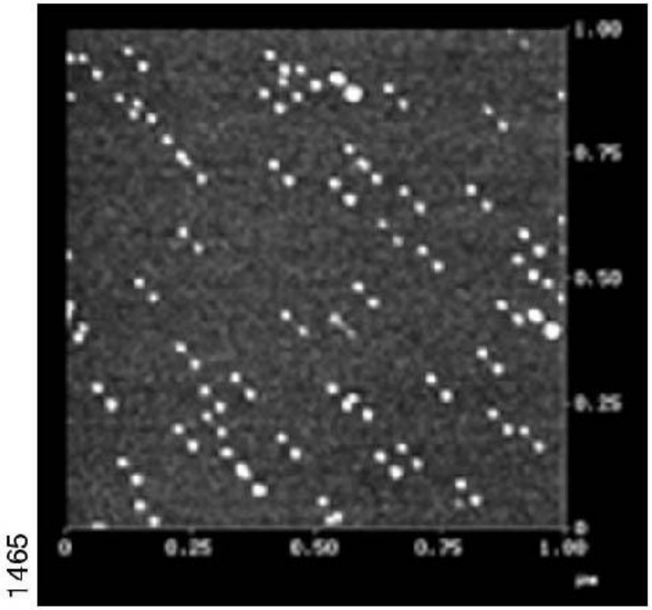
no rotation of the shapes ⇨ the sample images the tip

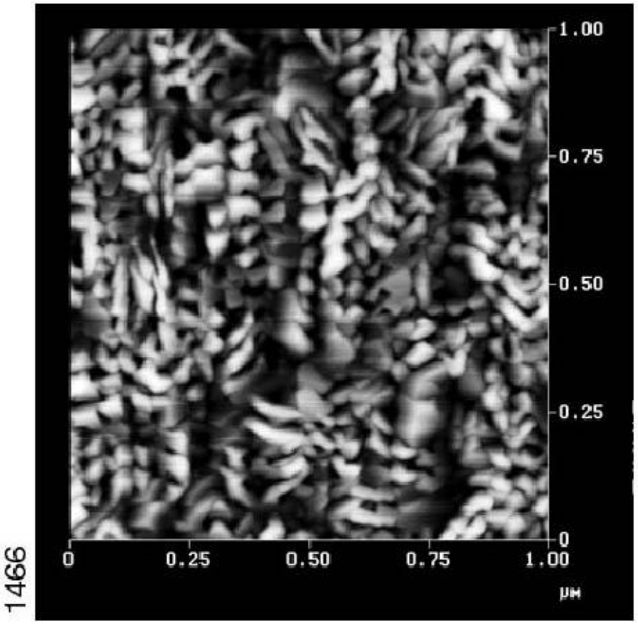
⇨ change the tip

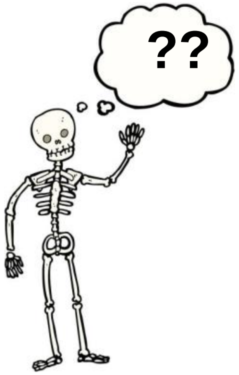
Example of artefacts

Damaged tip : double tip









Any doubt ?

⇨ Change the tip

AFM : Beyond topography

- Electrostatic properties (Electric Force Microscopy, Kelvin Probe Force Microscopy)
- Magnetic properties (Magnetic Force Microscopy)
- Conduction properties (Scanning Resistance AFM)
- Piezo/Ferroelectric properties (Piezoresponse Force Microscopy)
- Thermal properties (Thermal-SPM)
- Mechanical properties (Force Modulation, Quantitative Nanomechanical Microscopy…)
- Dielectric properties (Scanning Microwave Impedance Microscopy)
- Electrochemical properties
- ….

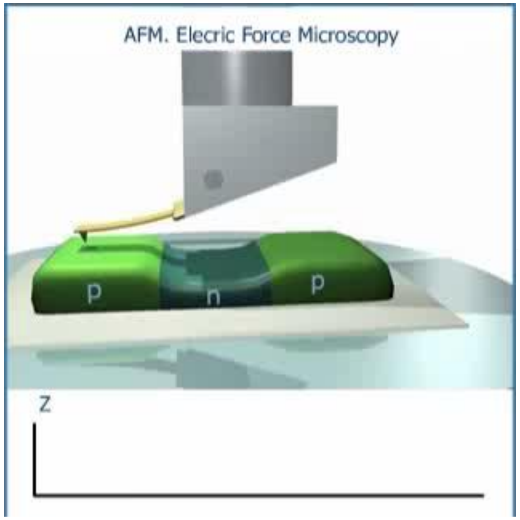
- **Optical properties : Resolution << λ** (IR spectroscopy, RAMAN, Photoluminescence…)
  - Absorption IR spectroscopy
  - Scanning Near Field Optical Microscopy
  - Tip Enhanced Optical Microscopy

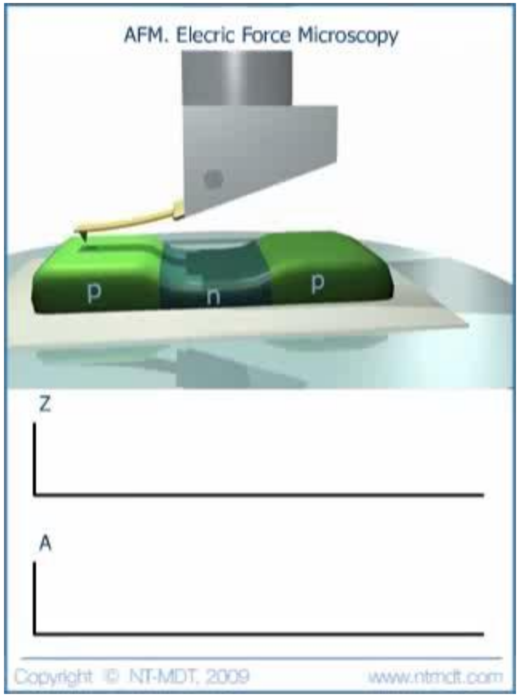
- **Quantum sensors** (Scanning NV Microscopies)

- Atomic and molecular resolution
- Stretching molecules
- Lithography (mechanical, deposition, electrochemistry, electrically…)
- Video rate and beyond
- Life science
- Many more….

Advanced modes : Long range forces

Long range forces : Two pass modes or lift mode





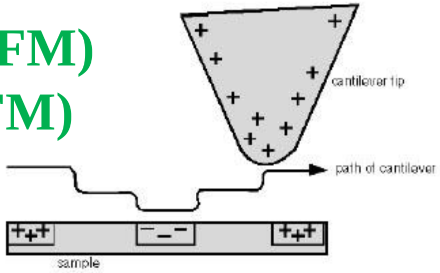
First pass : tapping mode
⇨ Short range repulsive forces dominate
⇨ « atomic » topography is recorded

Second pass : Tip at constant height
⇨ Long range forces (VdW, B, E)
⇨ Constant height => **VdW = Cte**
⇨ Only **B, E** forces are imaged

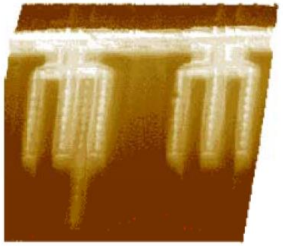
Electric and Magnetic Force Microscopy

- **Conductive tip (Pt coating) ⇨ Electrostatic forces**

Electric Force Microscopy (EFM)
Kelvin Force Microscopy (KFM)



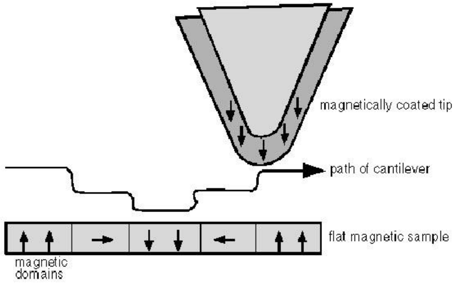
- Trapped charges
- Surface potentials
- Voltage drop in circuits

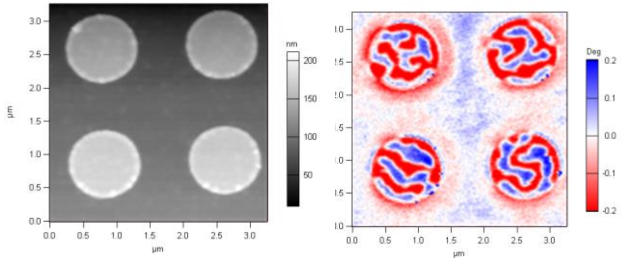


EFM of a failed device
Devices along the region have voltages applied In the 3 pronged arrangement of the right. An extra line feature on the left indicates a saturated transistor

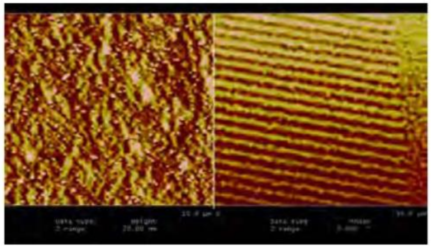
- **Magnetic tip (Co coating) ⇨ Magnetic forces**

Magnetic Force Microscopy (MFM)





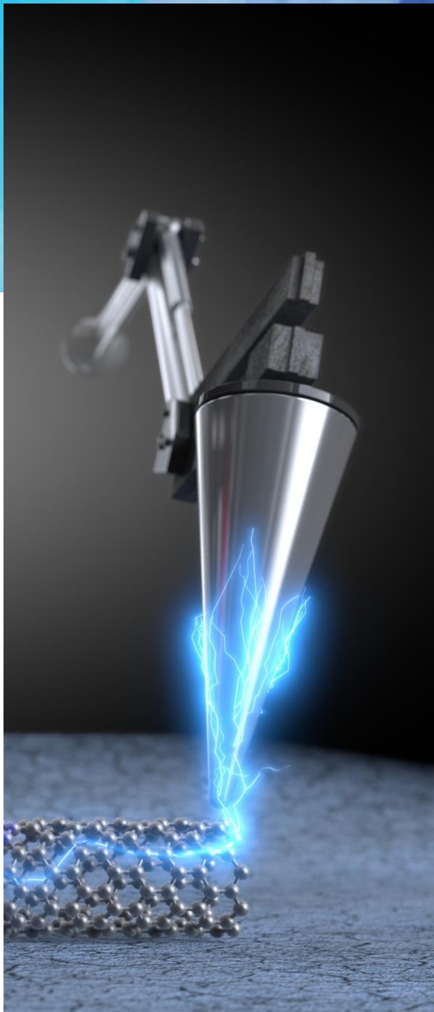
Disk ~ 1µm



1st scan: morphology 2nd scan: MFM phase
Magnetic tape

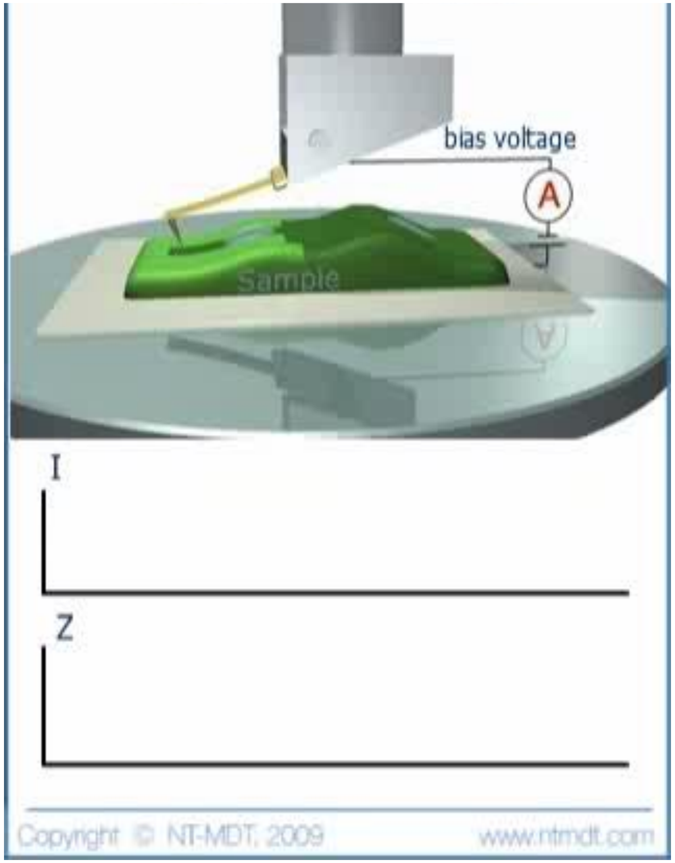
Advanced modes:

Scanning Resistance-AFM

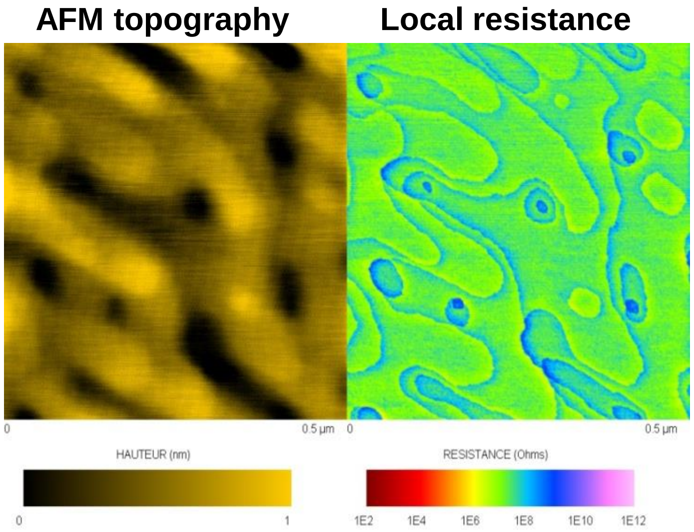


Scanning Resistance-AFM

- Contact mode AFM with a conducting tip
- Voltage bias tip-sample ⇨ Measure of the current

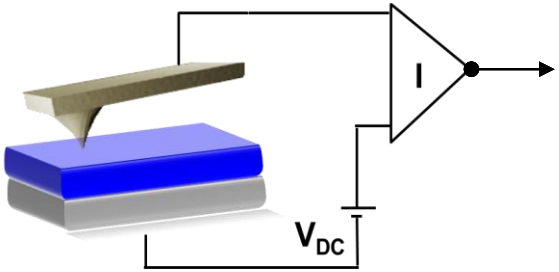


⇨ Simultaneous mapping
topography and local conductivity
at nm-scale



$La_{2/3}Ca_{1/3}MnO_3$ // $SrTiO_3$(001)

Current amplifiers for SR-AFM: need for speed



Voltage to AFM Analog Input (ADC)

- ✓ Resistance mapping: current measurement for each pixel
  - ➢ High bandwidth (>1 kHz)

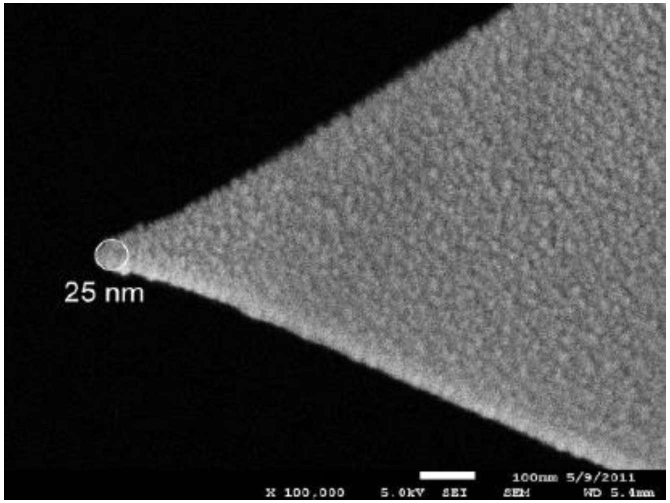
512*512 pixels image
@1ms/pixel ~ 5 min acquisition time
for a single image

- ✓ AFM tip is small ⇨ nanoscale surface contact ⇨ low current
  - ➢ High gain (linear amplifiers)

- ✓ Various samples or properties ⇨ Large current variations
  - ➢ High dynamic (log amplifiers)

Scanning Resistance-AFM : Conducting probes

Pt coated tip

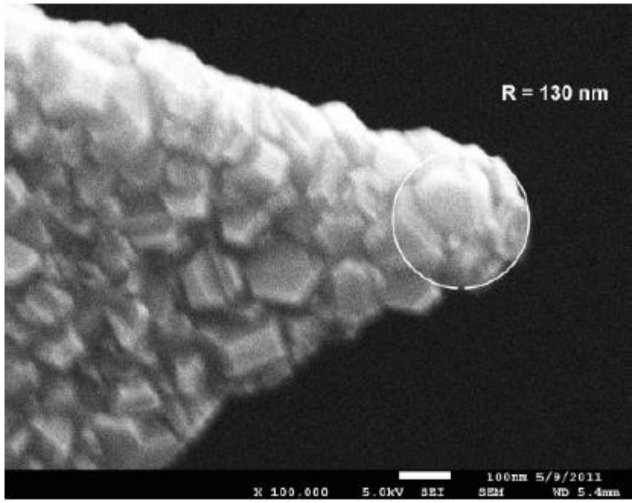


🙂 Small radius

☹ Fast wear out

🙂 Serial resistance (on gold) ~ 100 Ω

Polycristalline B-doped diamond coated tip



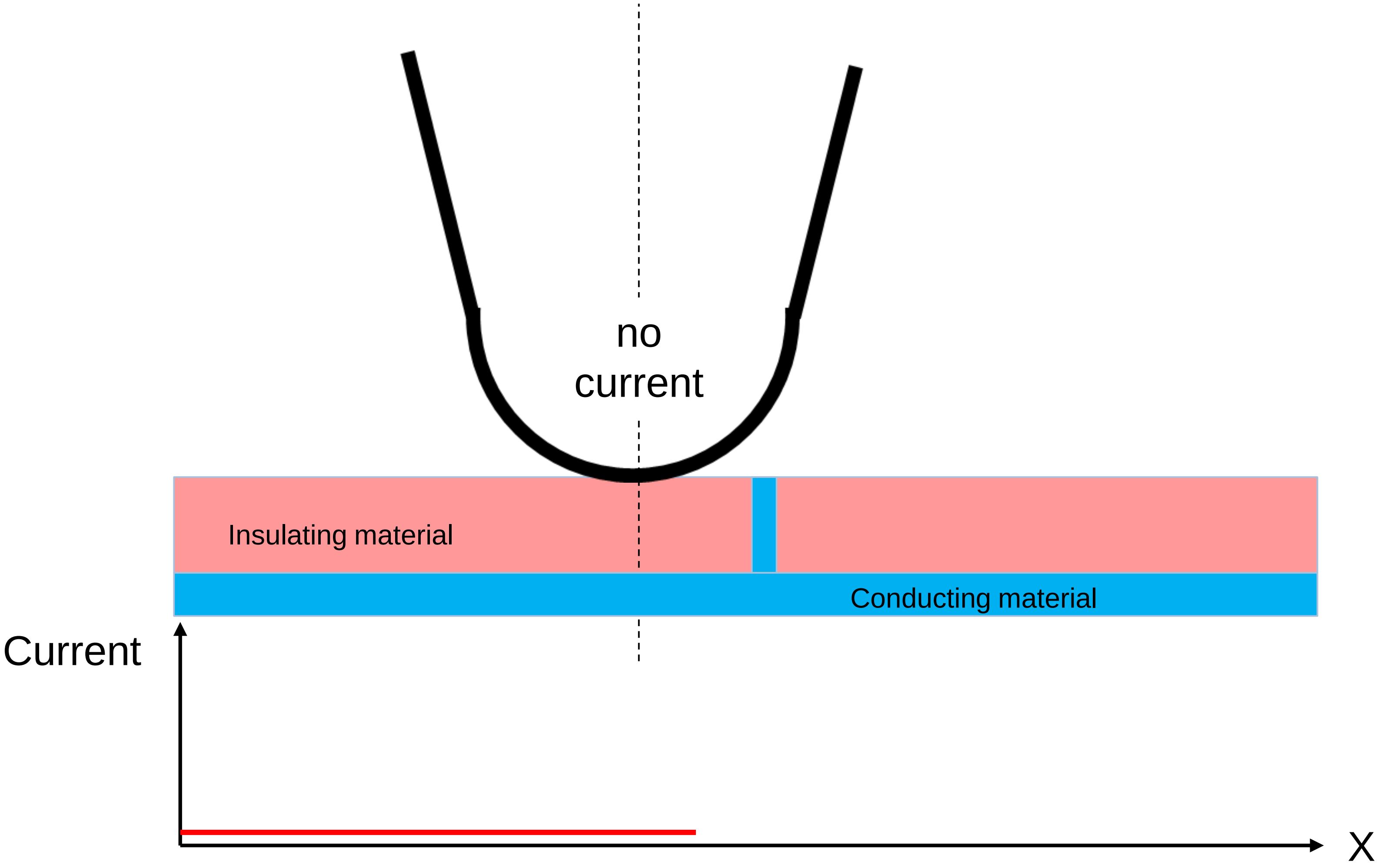
😐 Large radius

🙂 Long lasting

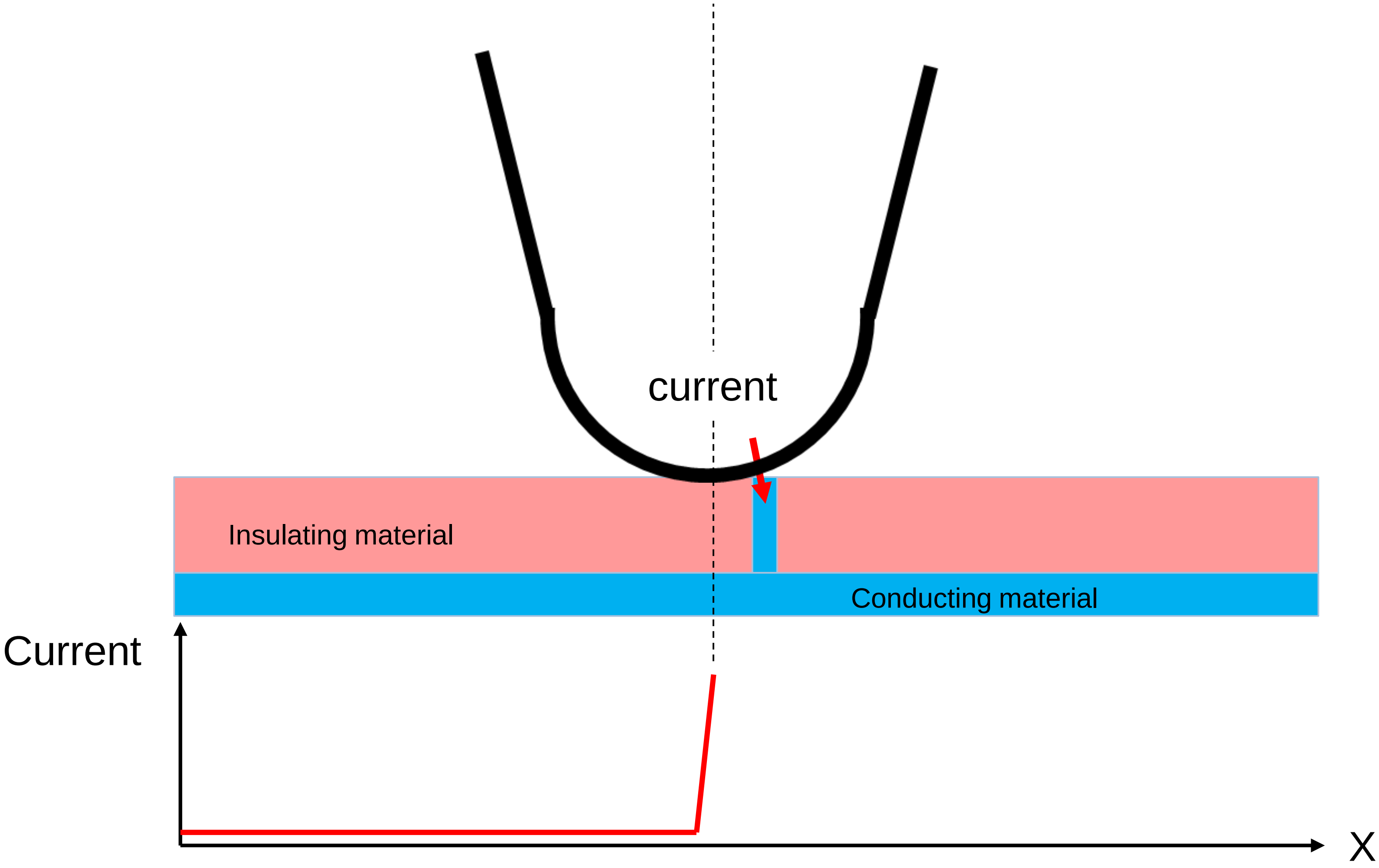
😐 Serial resistance (on gold) ~ 10 kΩ

Also TiN, W, W_2C, Si/Pt, bulk Pt, …

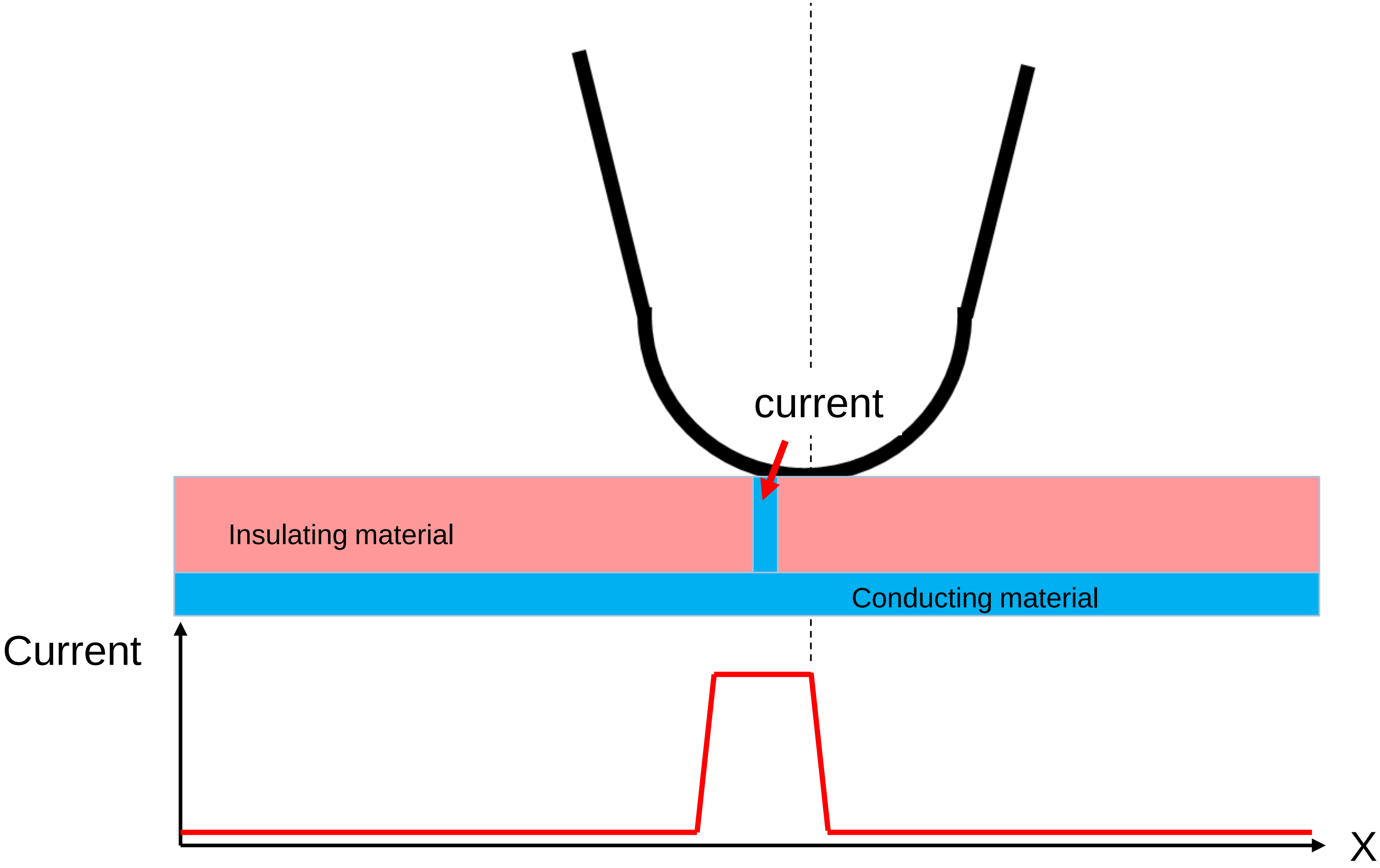
SR-AFM resolution : Tip radius but not only…



SR-AFM resolution : Tip radius but not only…

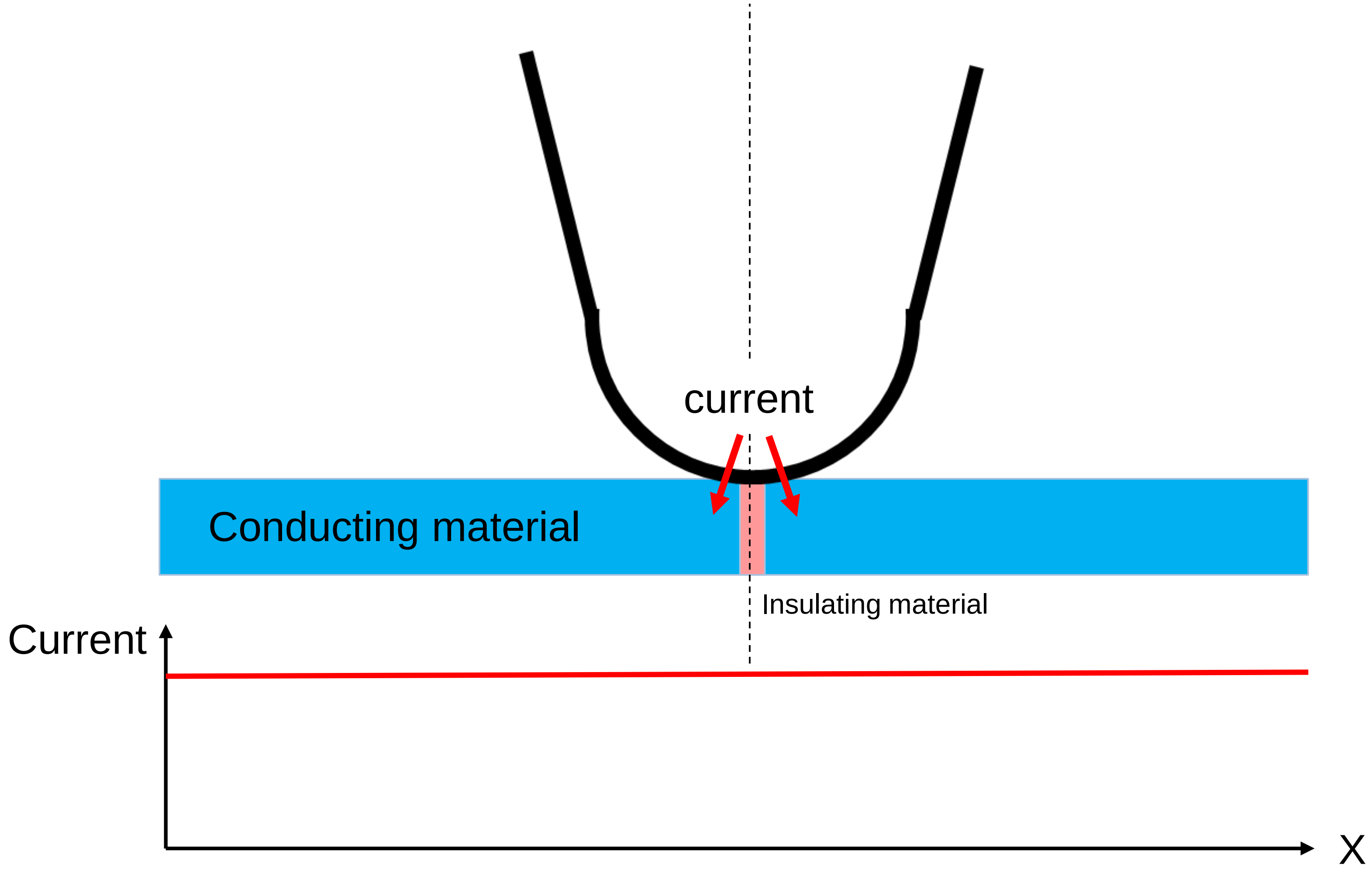


SR-AFM resolution : Tip radius but not only…



⇨ upper limit of the small conductive area size

SR-AFM resolution : Tip radius but not only…

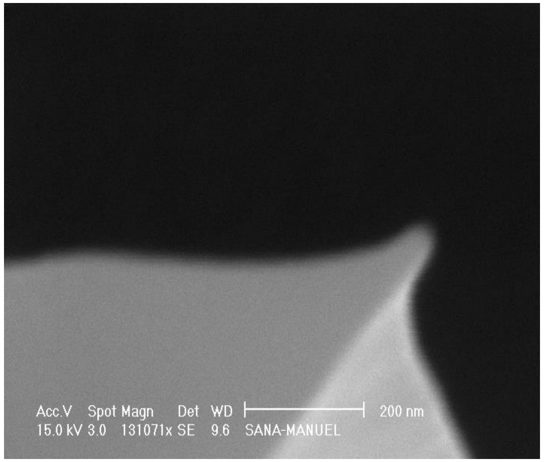


⇨ Small insulating area may not be seen

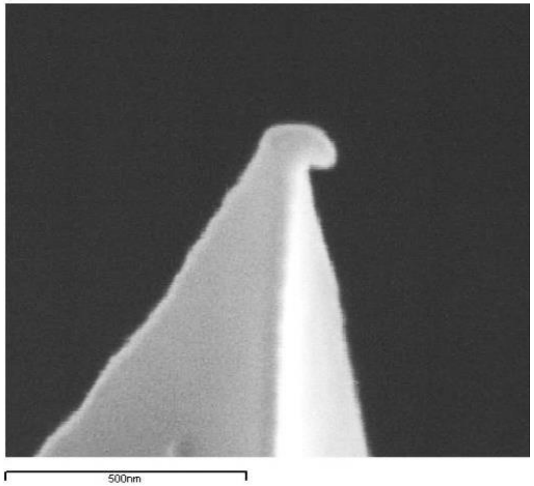
SR-AFM probes: real life of a tip

Pt coated tip

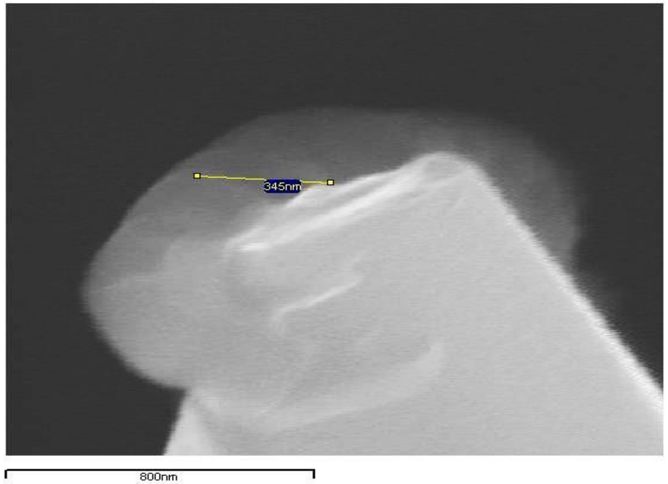
Before



After…



Another after…

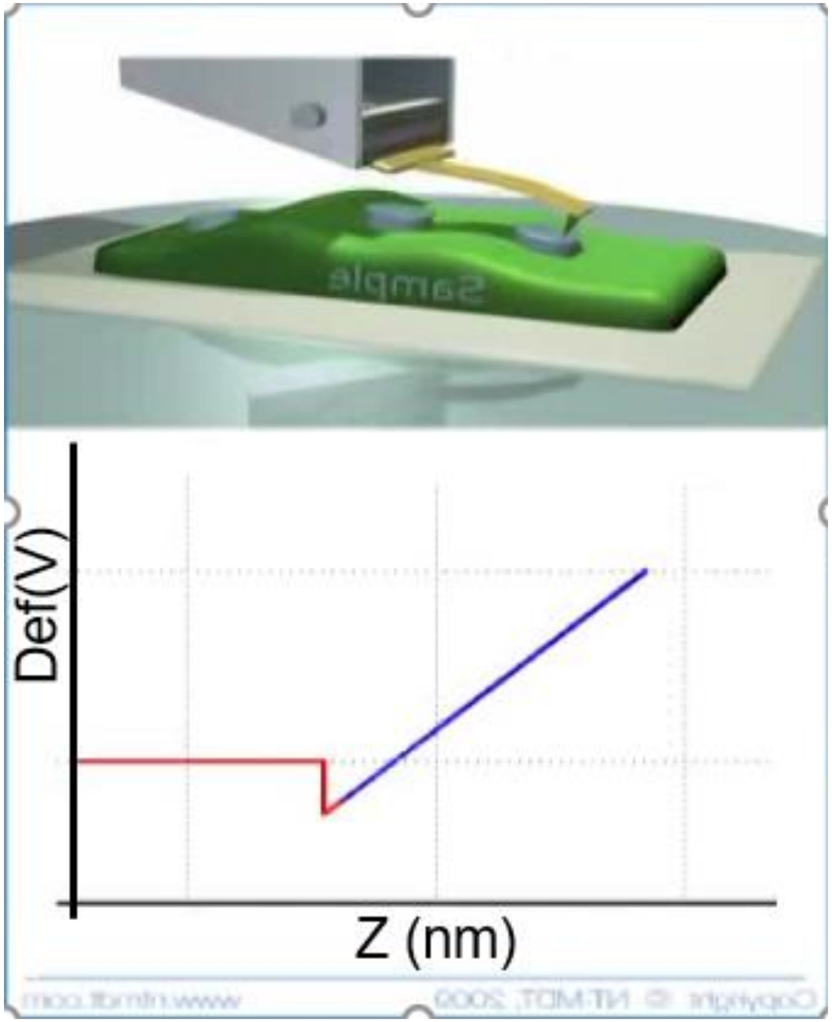


“Patience and a willingness to sacrifice many AFM tips in the name of science are necessary”

S. Fusil, ISOE2015

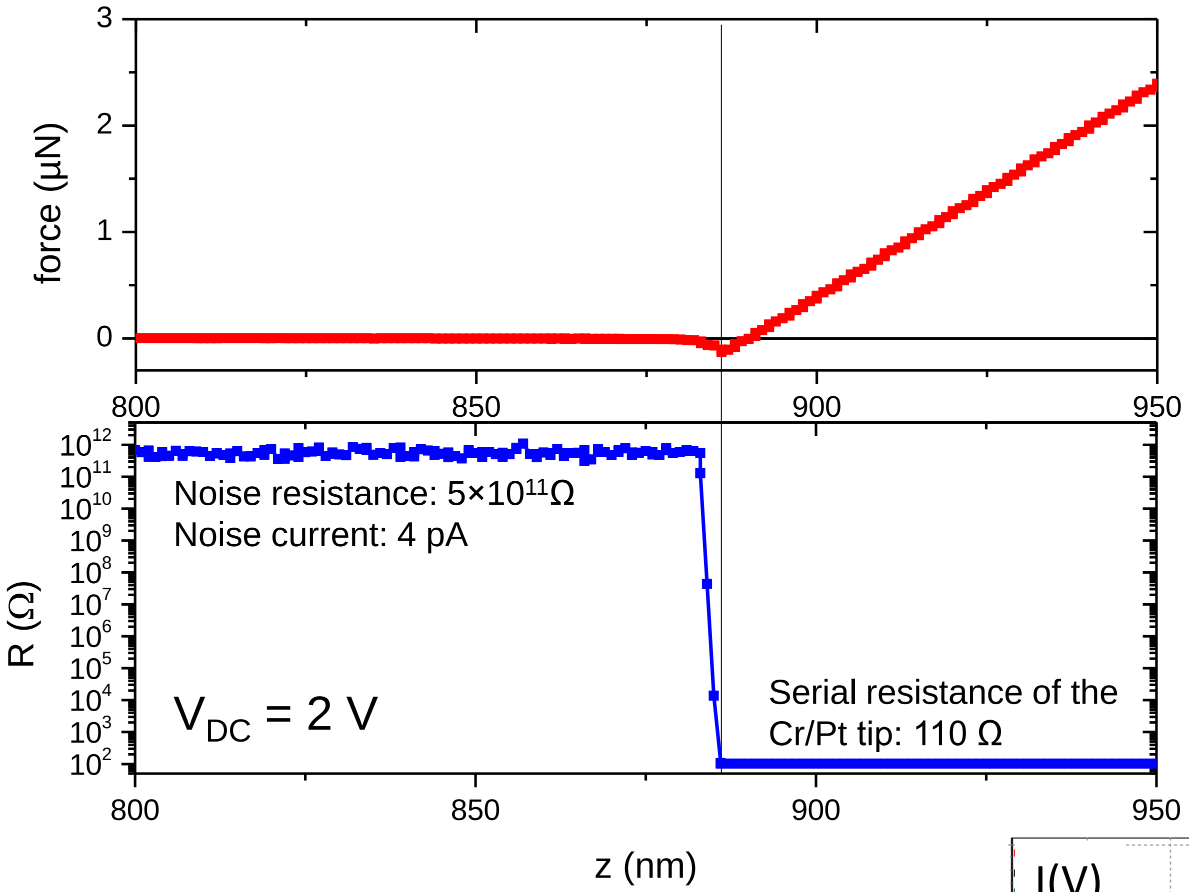
Conducting tip characterization : Force curves on a metallic layer

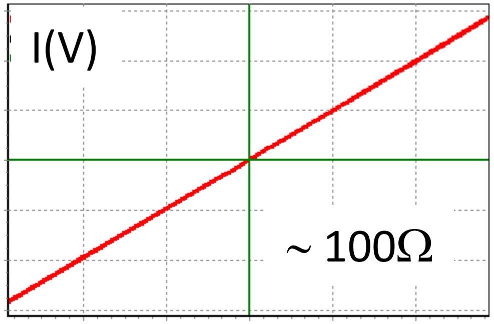
No XY scan - Extend Zpiezo
Record simultaneously laser deflexion & current



Conducting tip characterization : Force and current

The force and the current: metallic Pt tip on Au film





Good Pt tip on Au layer :

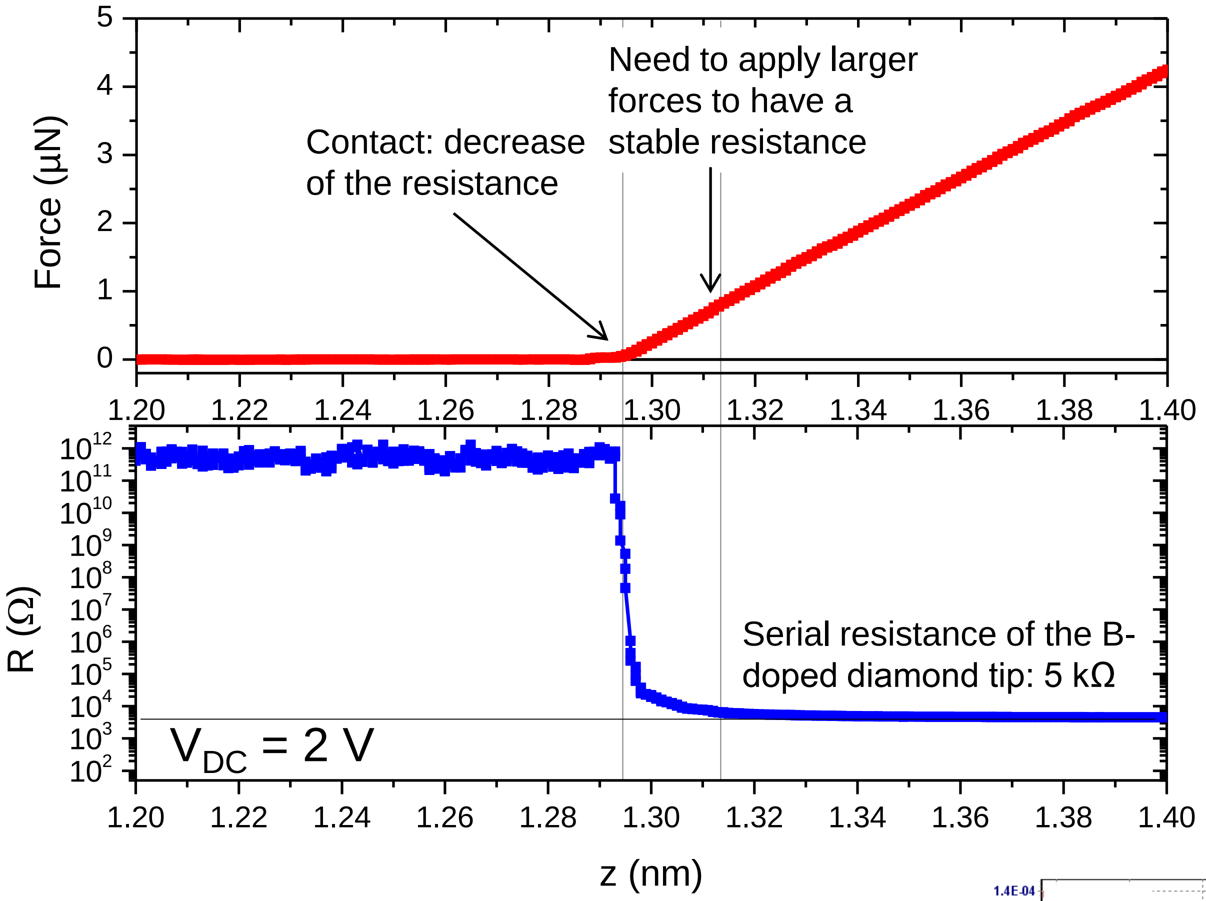
⇨ Simultaneous mechanical and electrical contact

⇨ Serial resistance of about 100Ω

⇨ Linear I(V)

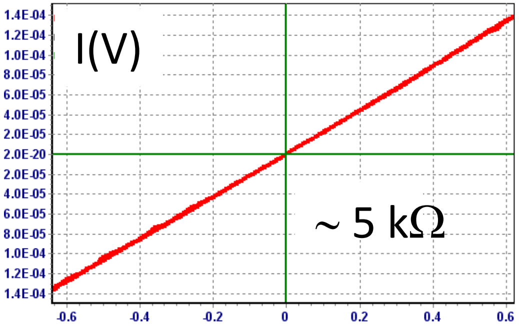
Conducting tip characterization : Force and current

The force and the current: B-doped diamond tip on Au film


Contact: decrease of the resistance

Need to apply larger forces to have a stable resistance

Serial resistance of the B-doped diamond tip: 5 kΩ



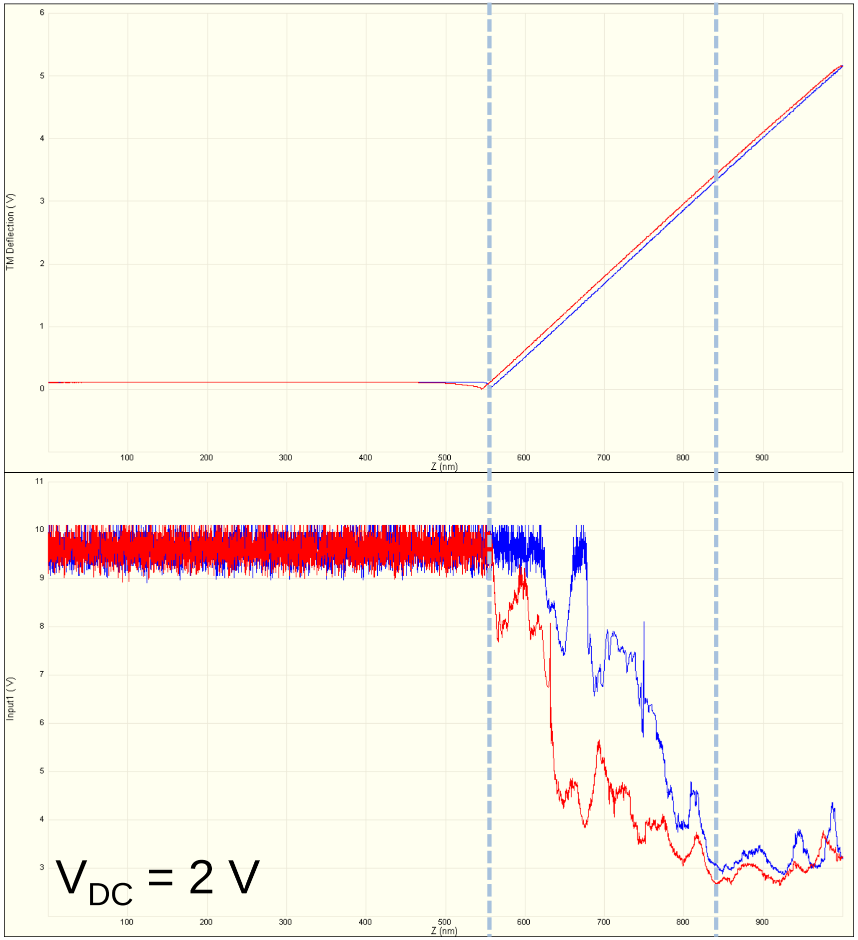
Good B-doped diamond tip on Au layer :

⇨ Force <1µN to achieve a stable electrical contact

⇨ Serial resistance below 10kΩ

⇨ Linear I(V)

Conducting tip characterization : Force curves

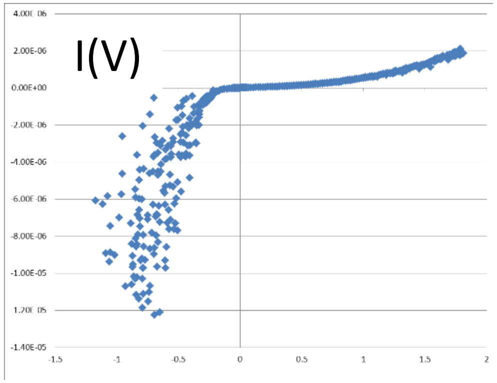


Used B-doped diamond tip on Au layer :

⇨ Force >10µN to reach lowest R

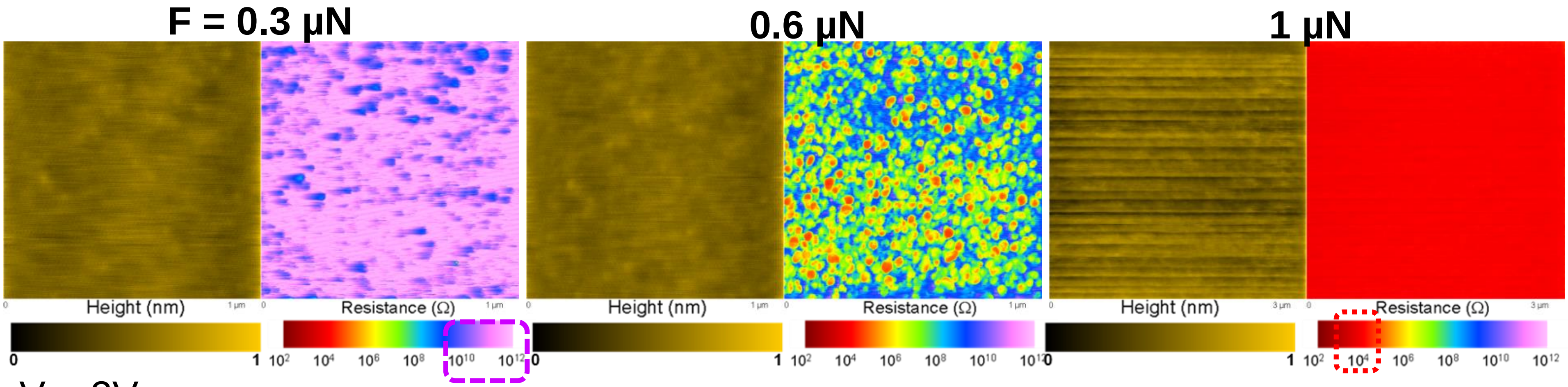
⇨ Unstable electrical contact

⇨ Serial resistance > 100kΩ

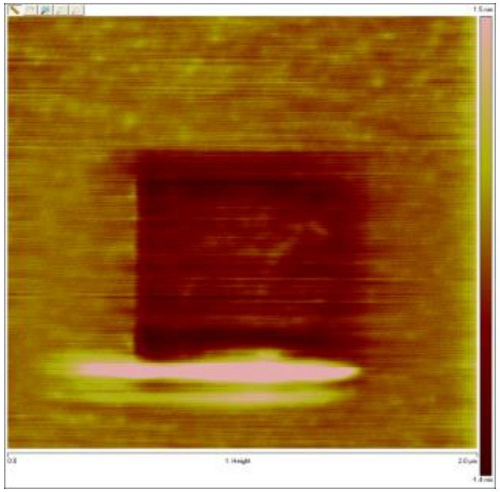


Resistance mapping: gold film

B-doped diamond tip on Au layer



V = 2V



Larger scan on the same area:
Need to dig ~ nm (adsorbates)
to reach gold!!

Significant force is usually needed to achieve good electrical contact
in ambient atmosphere

- **Make force curves on reference sample** (Au layer) to check your tip before **AND** after your measurements

- **Check I(V) on your sample :**
  - Have different type of conductive coatings (sometime Schottky, ….)
  - Try positive and negative voltages (sometime Schottky, ….)

- **Check the topography after conduction imaging** at larger scale & lower force (electrochemistry, tip digging…)

- If during experiments suddenly you don't understand what's going on

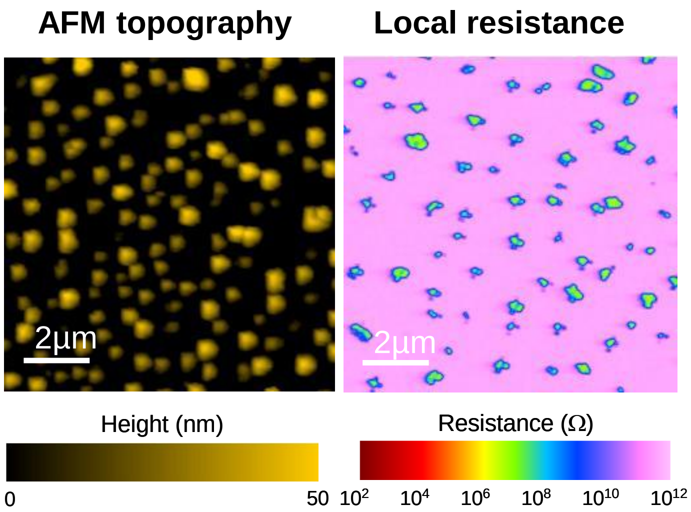
  ⇨ **Change the tip**
  ⇨ then think…

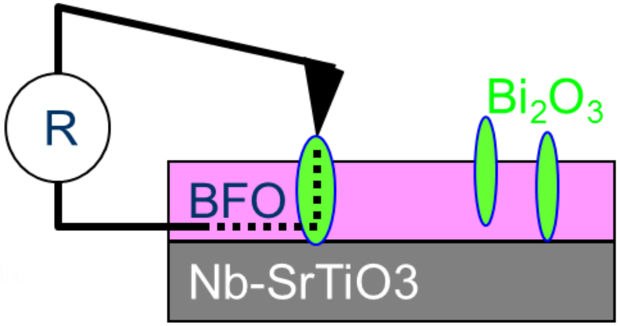
Examples of applications of SR-AFM for oxides

Material studies : Thin films characterization

A multiferroïc oxide (Ferroelectric & Antiferromagnetic) : $BiFeO_3$

70 nm $BiFeO_3$ on Nb-doped $SrTiO_3$





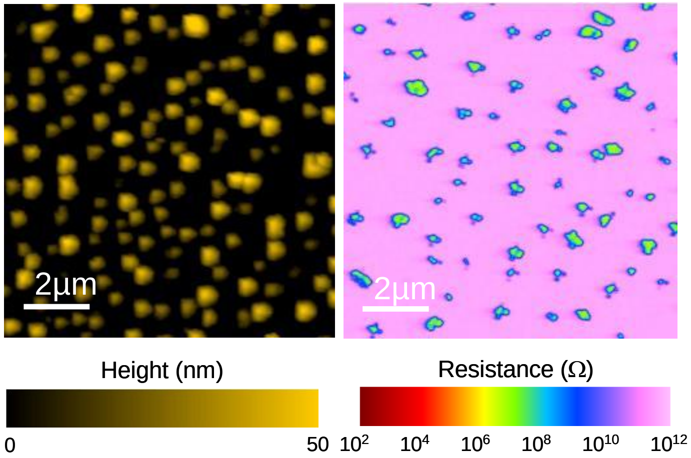
Béa et al APL (2005)

⇨ Conductive parasitic phase prevents macroscopic measurement of ferroelectric properties

Material studies : Thin films characterization

A multiferroïc oxide (Ferroelectric & Antiferromagnetic) : $BiFeO_3$

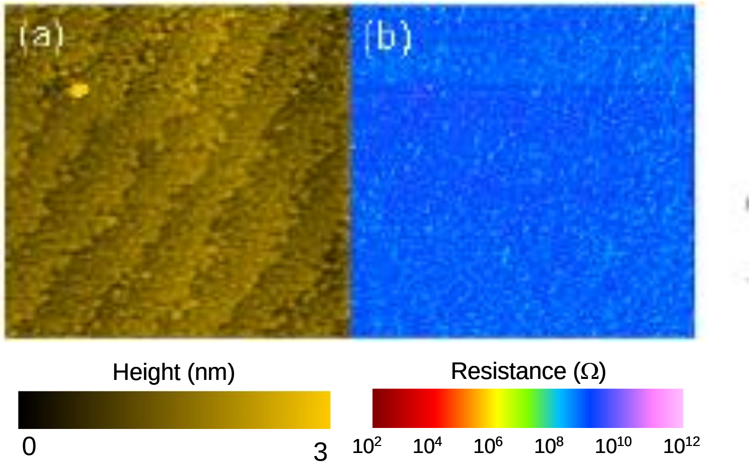
70 nm $BiFeO_3$ on Nb-doped $SrTiO_3$



AFM topography **Local resistance**

Béa et al APL (2005)

5 nm $BiFeO_3$ on LSMO electrode

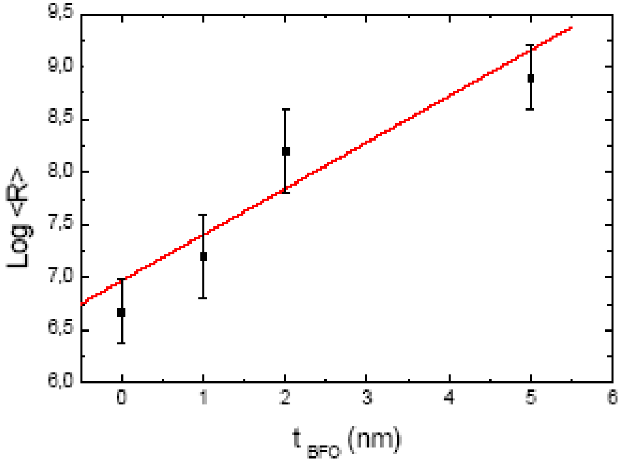


AFM topography **Local resistance**

Béa et al APL (2006)

⇨ Conductive parasitic phase prevents macroscopic measurement of ferroelectric properties

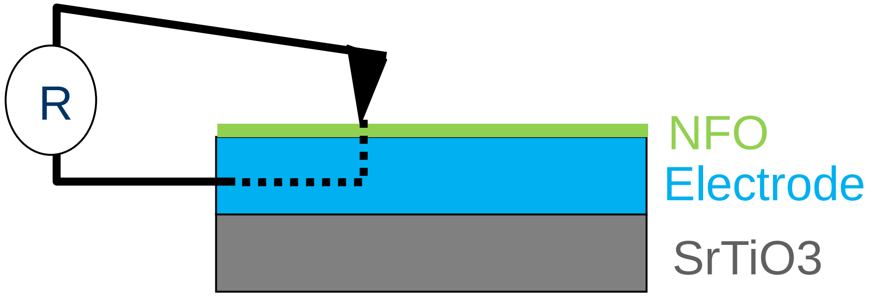
⇨ Optimized BFO ultrathin films are homogeneous and show tunneling conduction

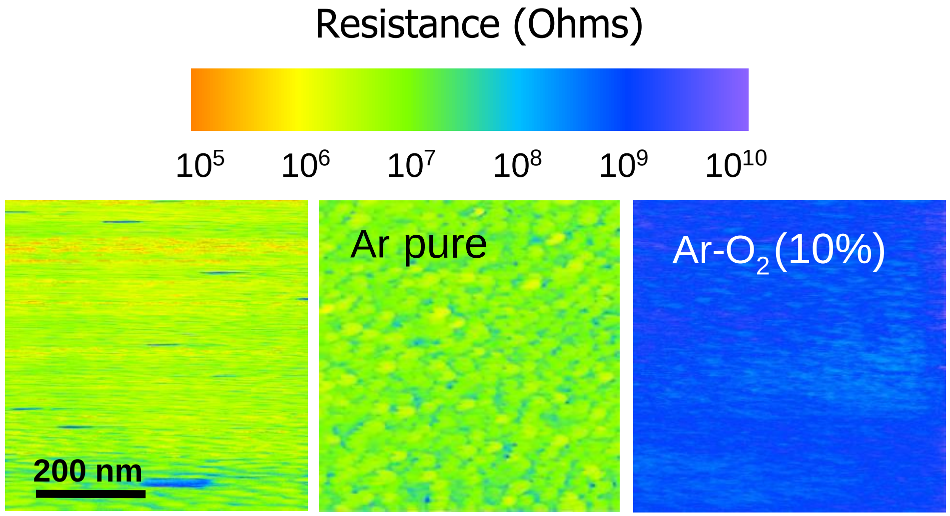


Material studies : Tunnel barrier of $NiFe_2O_4$

$NiFe_2O_4$: Ferrimagnetic insulator (Tc~850K)

Ultra thin films of NFO grown by sputtering

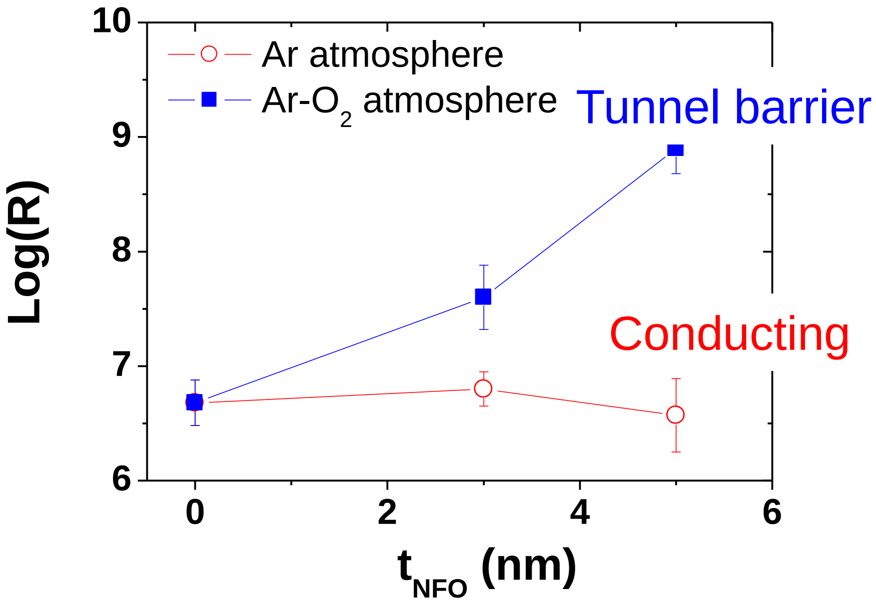




Electrode

+ 5 nm NFO

+ 5 nm NFO

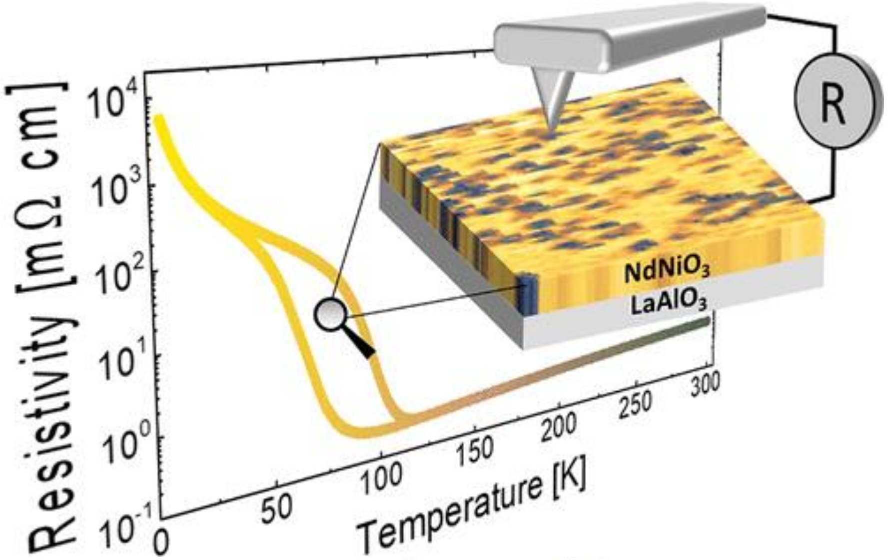


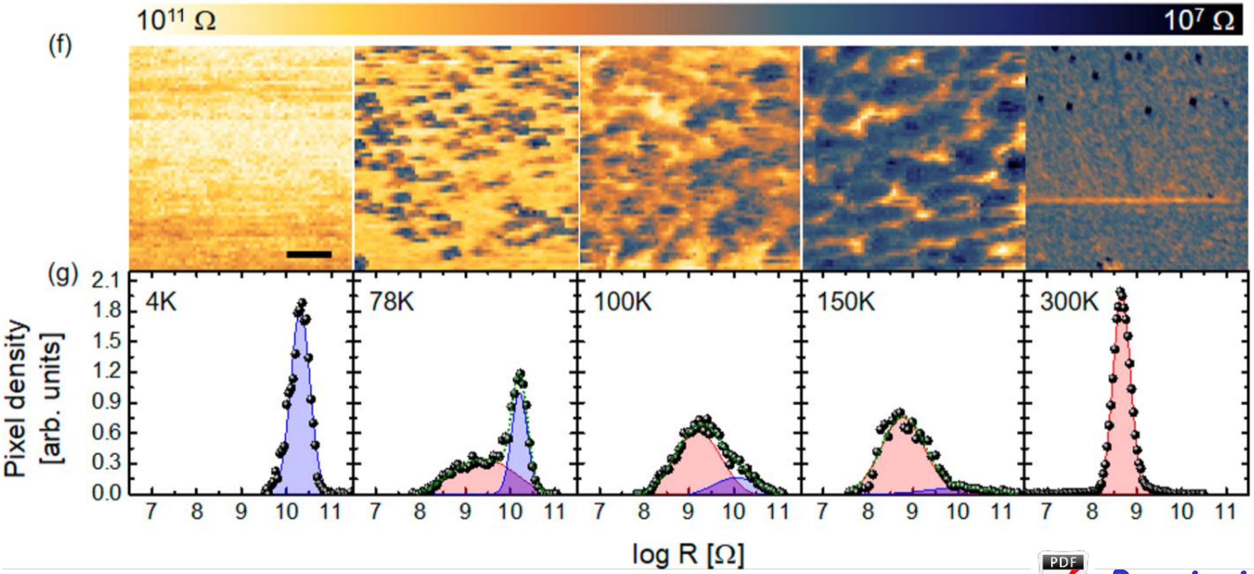
⇨ Optimization of NFO growth without complex micro-fabrication of tunnel junction

Lüders et al, Adv. Mater. (2006), APL (2006)

Metal–Insulator transition in oxides : SR-AFM at low T

Direct Mapping of Phase Separation across the Metal−Insulator transition



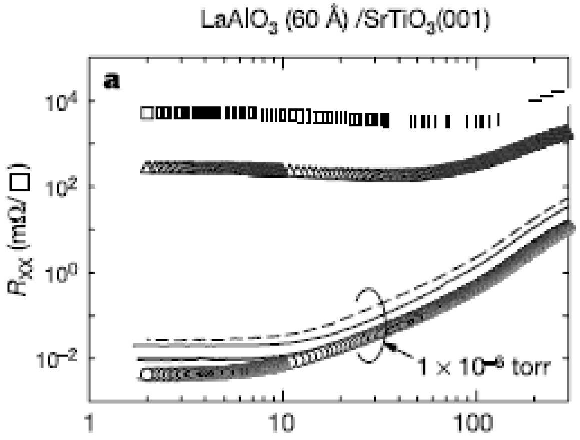


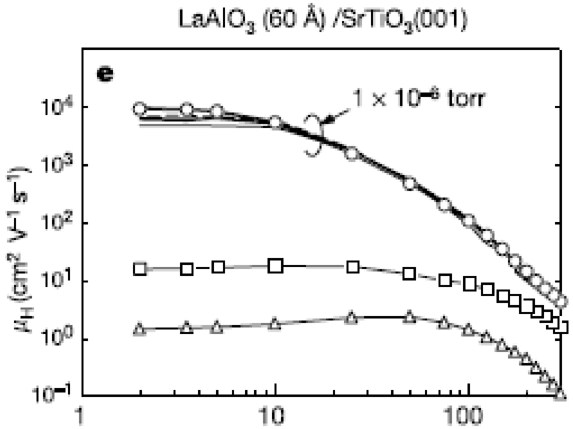
Preciosi Nanoletters 2018

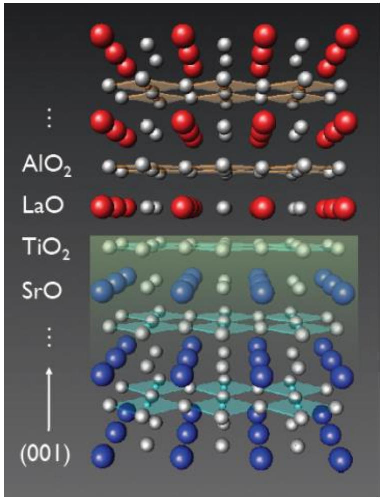
Material studies : Interfaces in oxides

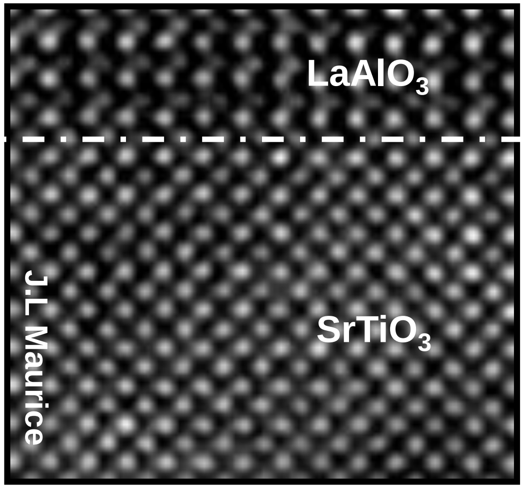
A high-mobility electron gas at the $LaAlO_3/SrTiO_3$ heterointerface

A. Ohtomo[1,2,3] & H. Y. Hwang[1,3,4]   Nature 2004







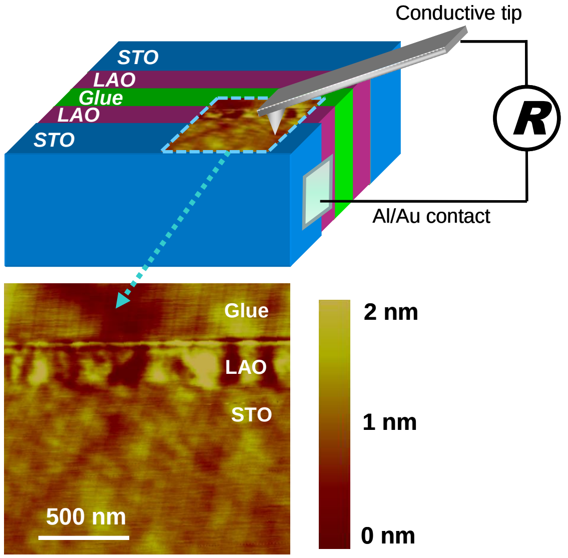


Opened questions :

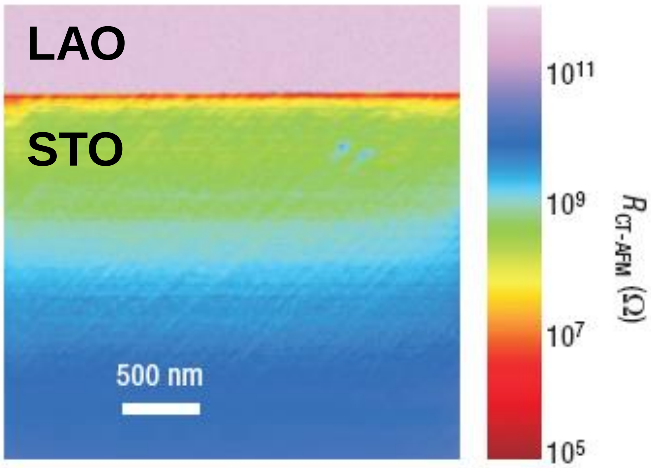
- Are the carriers really confined or is it bulk STO properties (oxygen vacancies) ?

- If confined, what is the thickness of the electronic gas ?

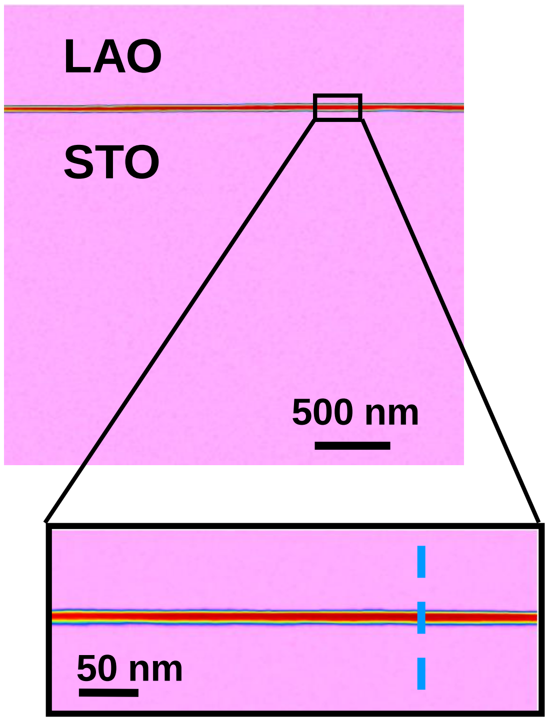
Interfaces in oxides : Cross section SR-AFM



Low O_2 pressure deposition



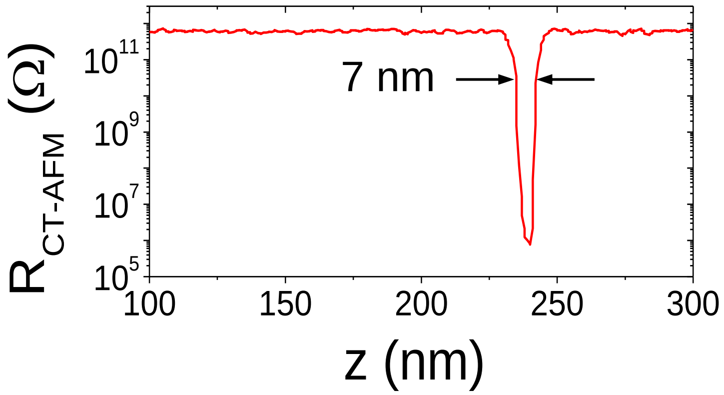
Additional Oxygenation step



STO substrate is doped by oxygen vacancies

- ⇨ Electrons are confined (300K)
- ⇨ Gas thickness < 7nm

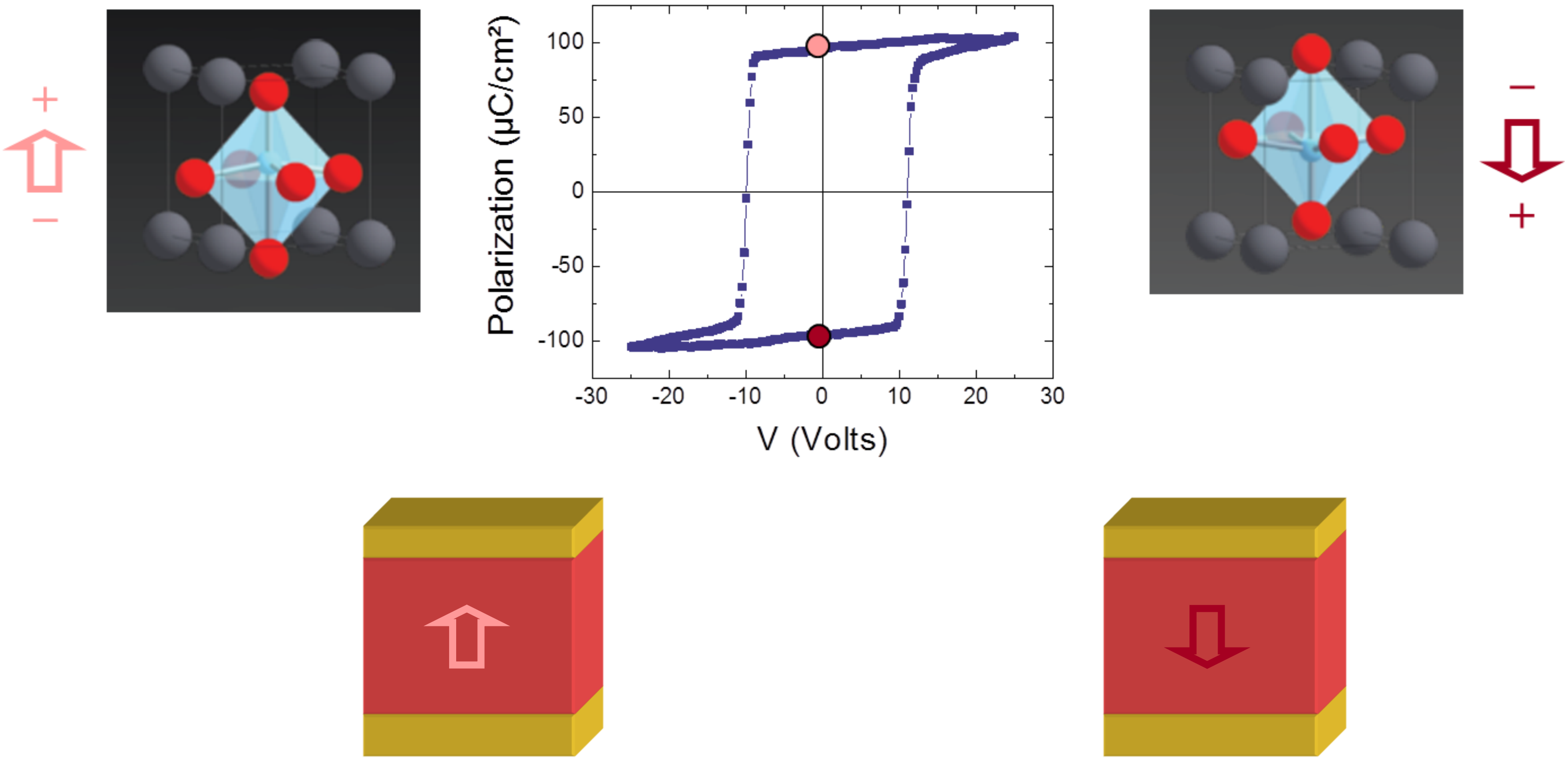
Basletic, Nature Materials 7 (2008)



Advanced modes :

Piezoresponse Force Microscopy

Ferroelectric materials

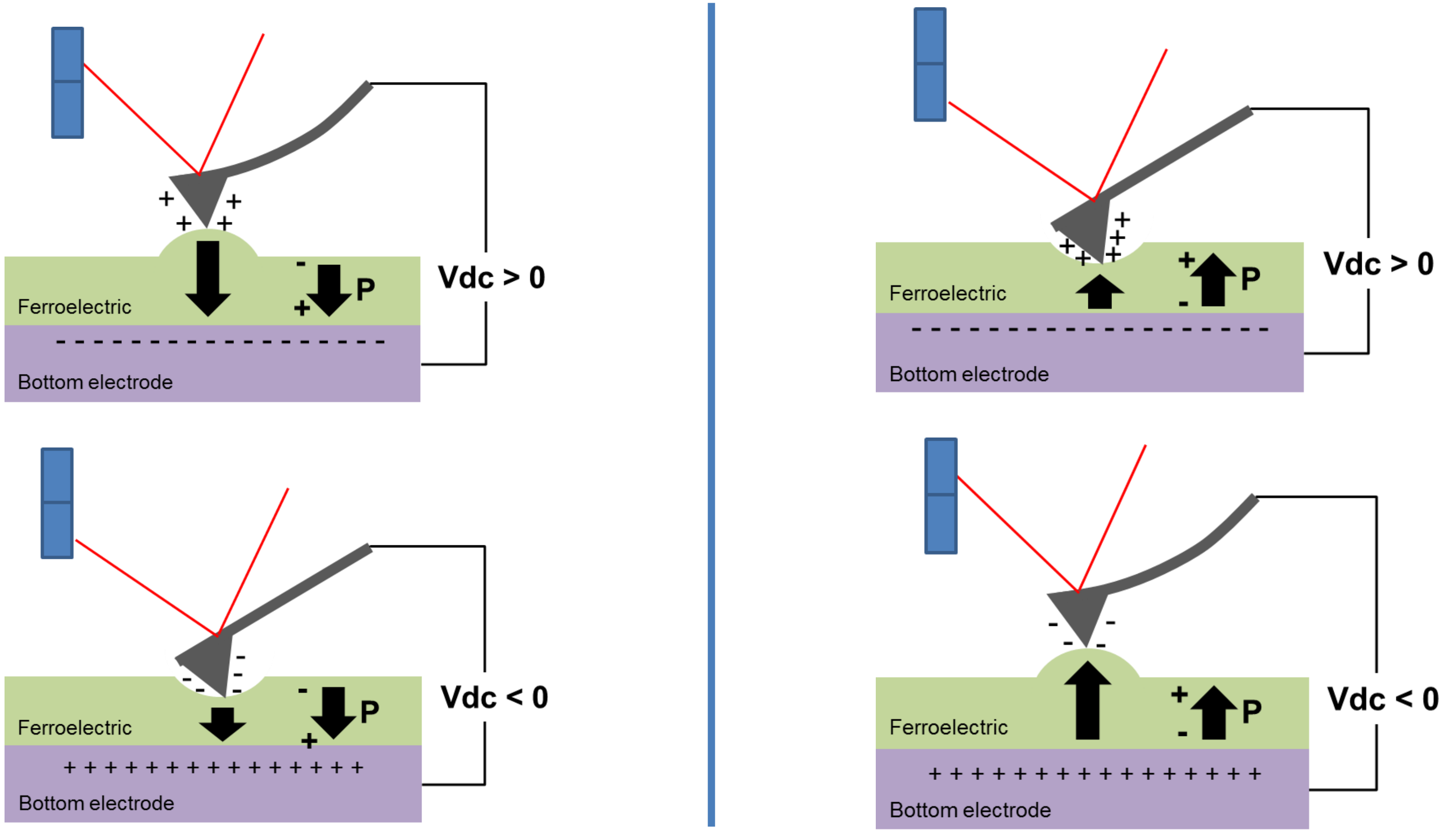


- ✓ In ferroelectrics, spontaneous electric polarization switchable by an electric field
- ✓ **Ferroelectrics are always piezoelectric**

Piezoresponse - AFM : Ferroelectric is piezoelectric

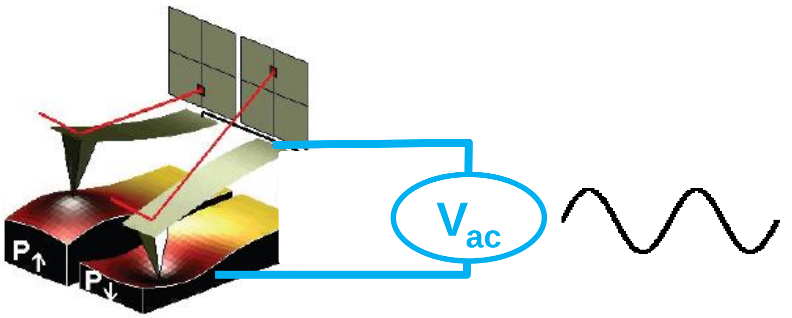
Contact mode AFM with a conducting tip

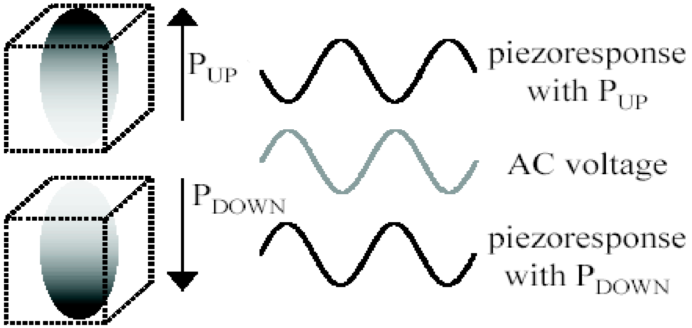
Electric field ⇨ elastic deformation



Static deformation ~ 10-100 pm

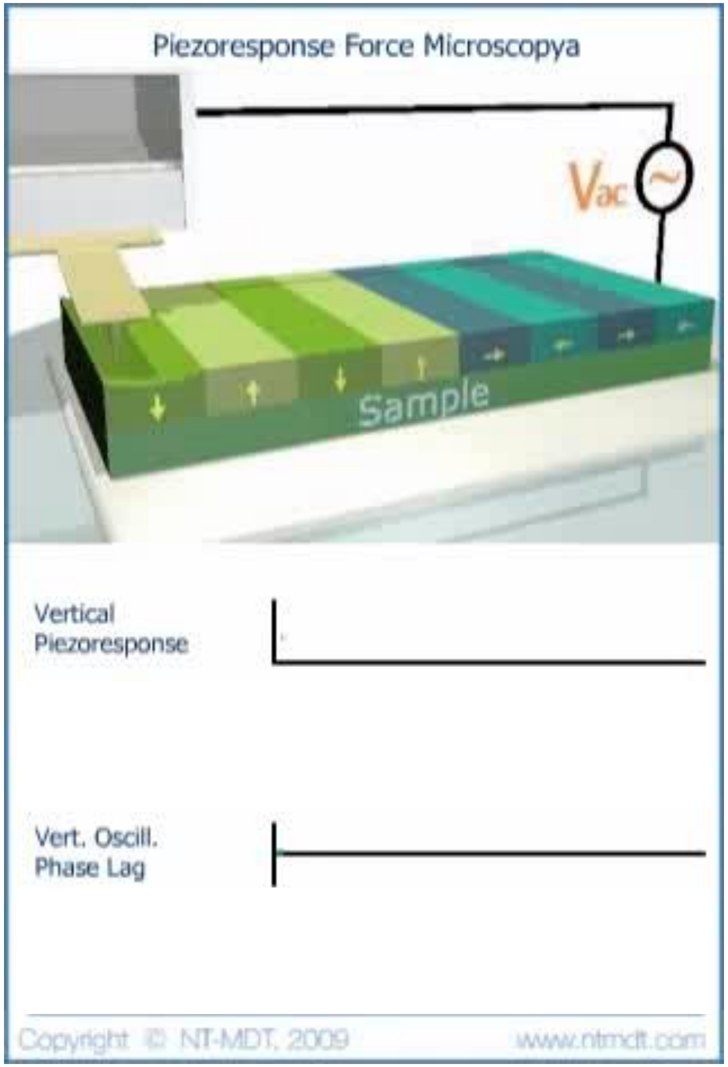
Piezoresponse - AFM



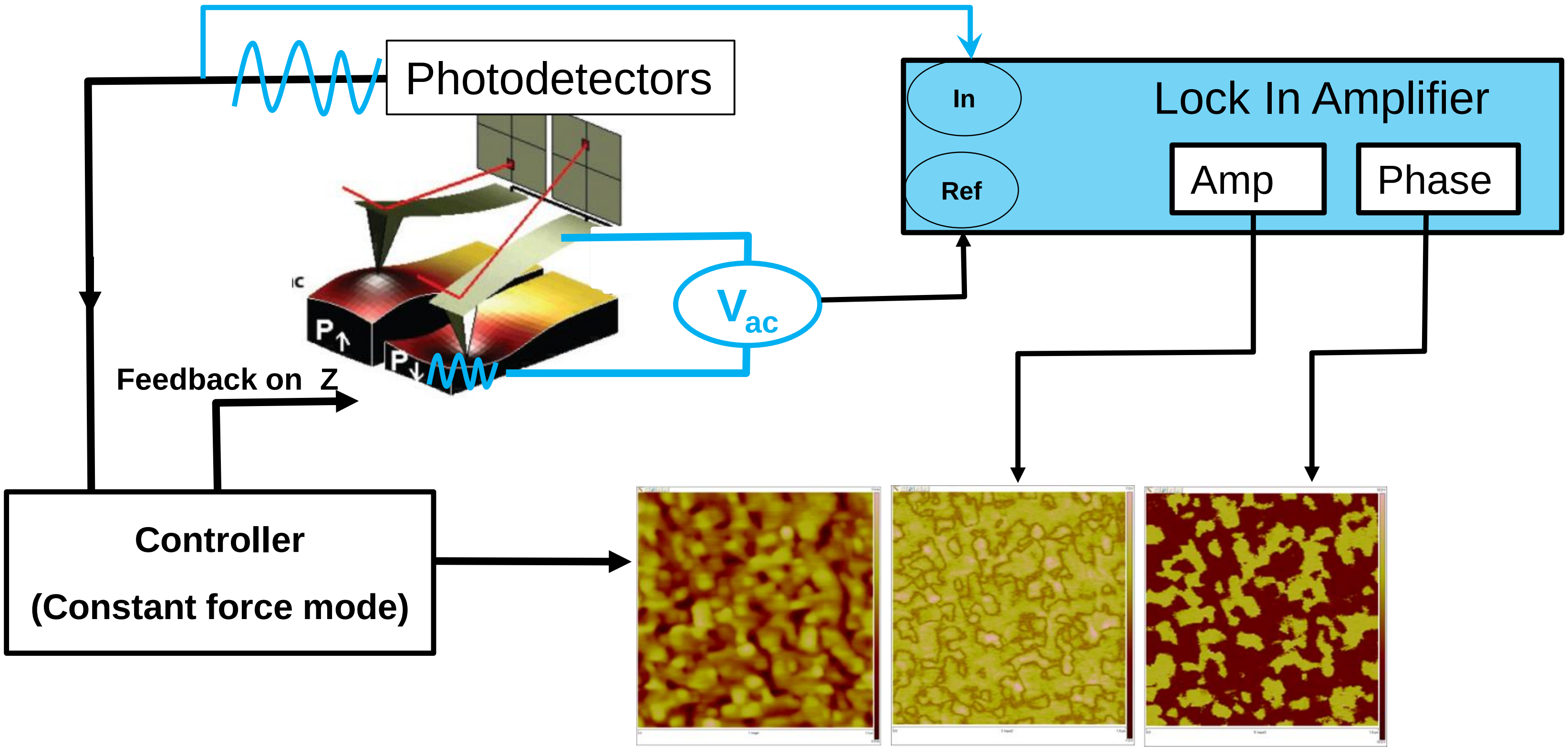


P_{DOWN} domains:
in phase
with AC voltage

P_{UP} domains :
180° out of phase
with AC voltage



Piezoresponse - AFM


Photodetectors

Lock In Amplifier

In

Ref

Amp

Phase

V_{ac}

P↑

P↓

Feedback on Z

Controller

(Constant force mode)

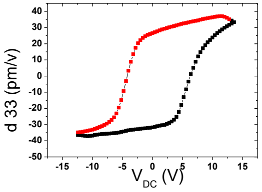
Topo

Amplitude

Phase

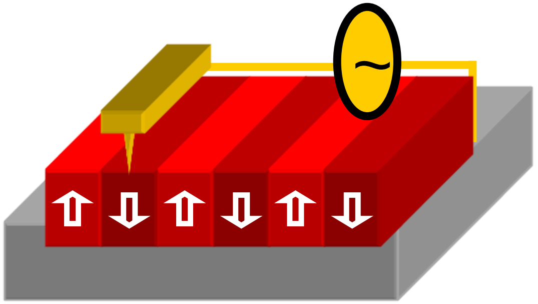
- **Simultaneous imaging** of the topography and ferroelectric domains
- $|V_{DC}| > |V_{coercives}|$: Write artificial domains

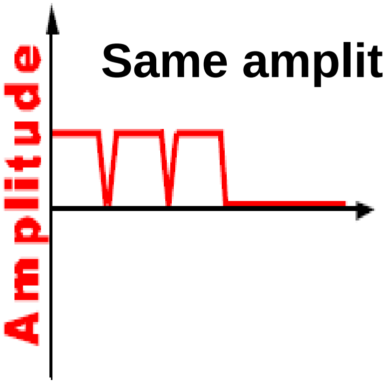
- Cycle of local piezoresponse : Stop scan + (V_{AC} + sweep V_{DC})

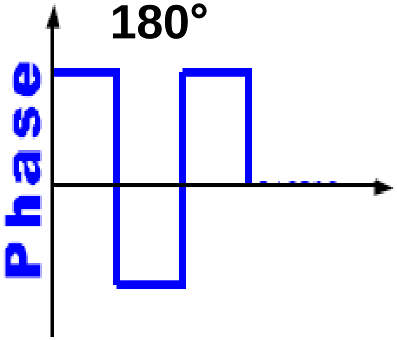


Piezoresponse - AFM : Imaging example

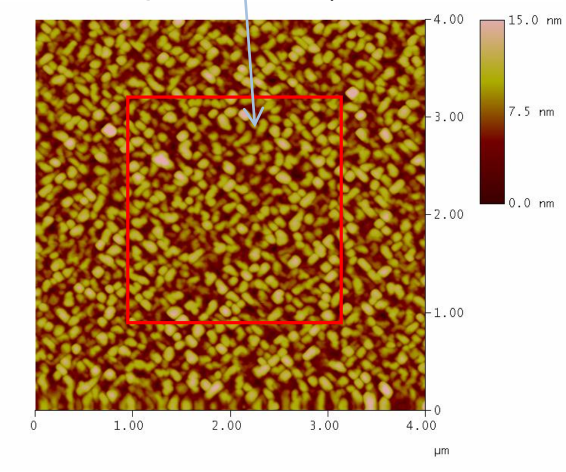
$BiFeO_3$ / $La_{0.7}Sr_{0.3}MnO_3$ // $SrTiO_3$



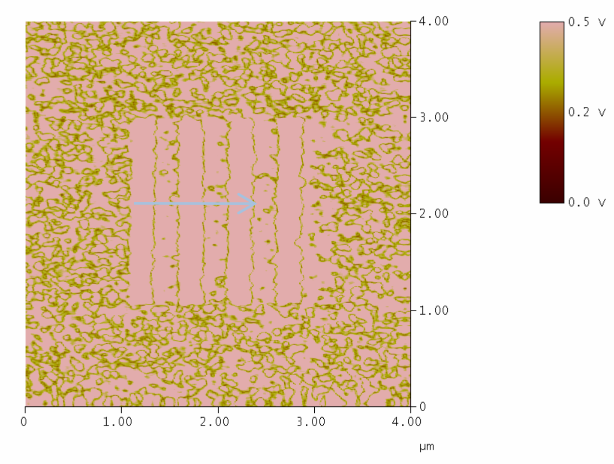




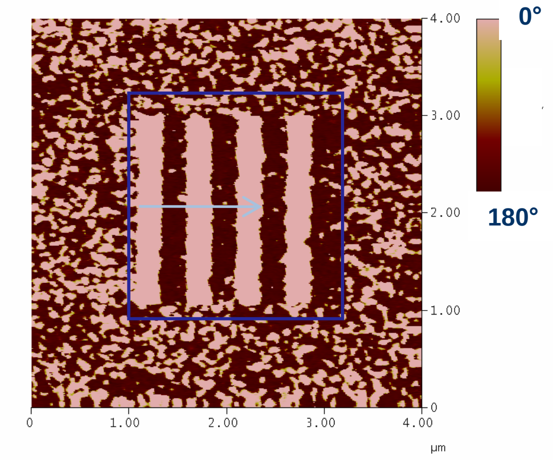
Topography 4x4 µm



Amplitude

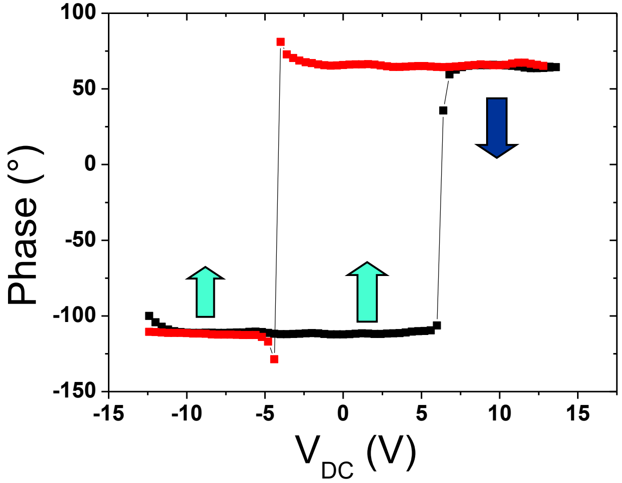


Phase

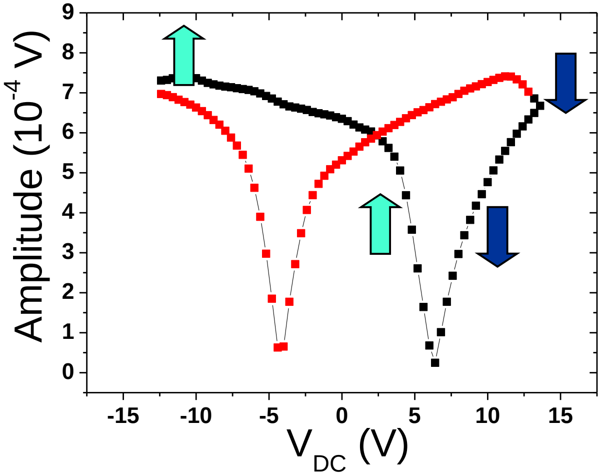


Piezoresponse – AFM : Switching spectroscopy

Hysteretic piezoresponse cycle : $V = V_{DC} + V_{AC}\cos(\omega t)$

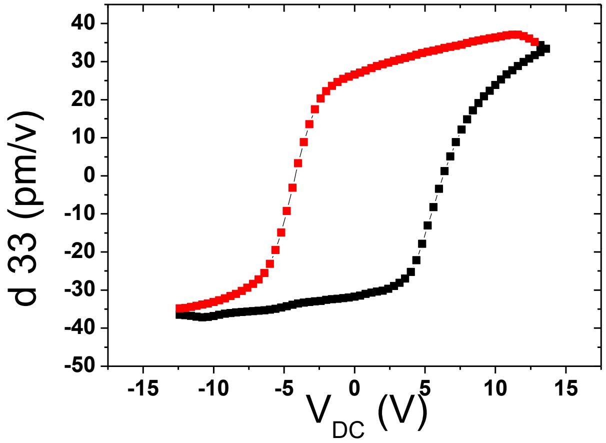


+

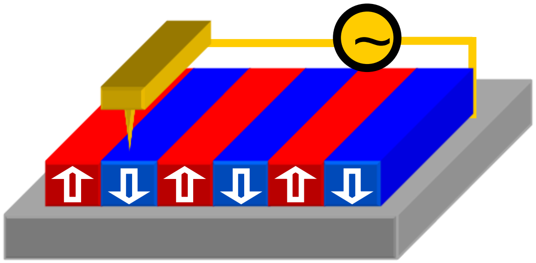


Coercive voltage ≈ +6V /-4 V

Piezoelectric coefficient d_{33} ≈ 35 pm/V



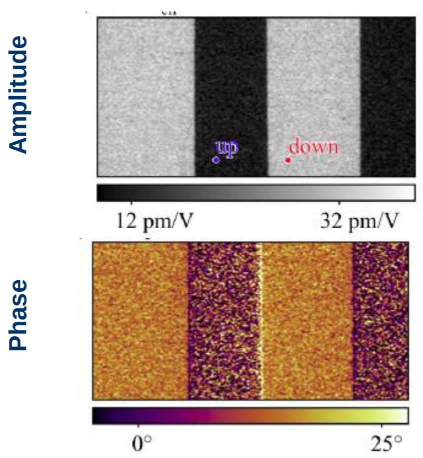
PFM : AC excitation, but which frequency?



LiNbO$_3$

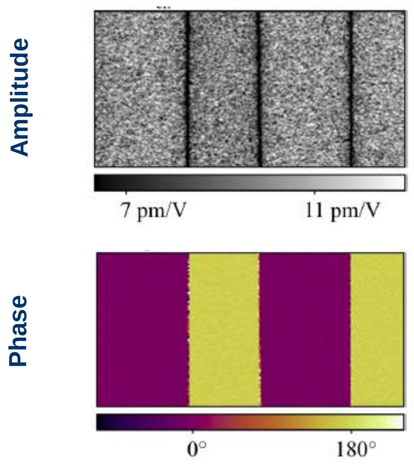
expected piezoresponse = 8 pm/V

5x10 µm scan



Non optimized frequency

- Amp(P$_{up}$) < Amp(P$_{down}$)
- Phase contrast ~ 20°

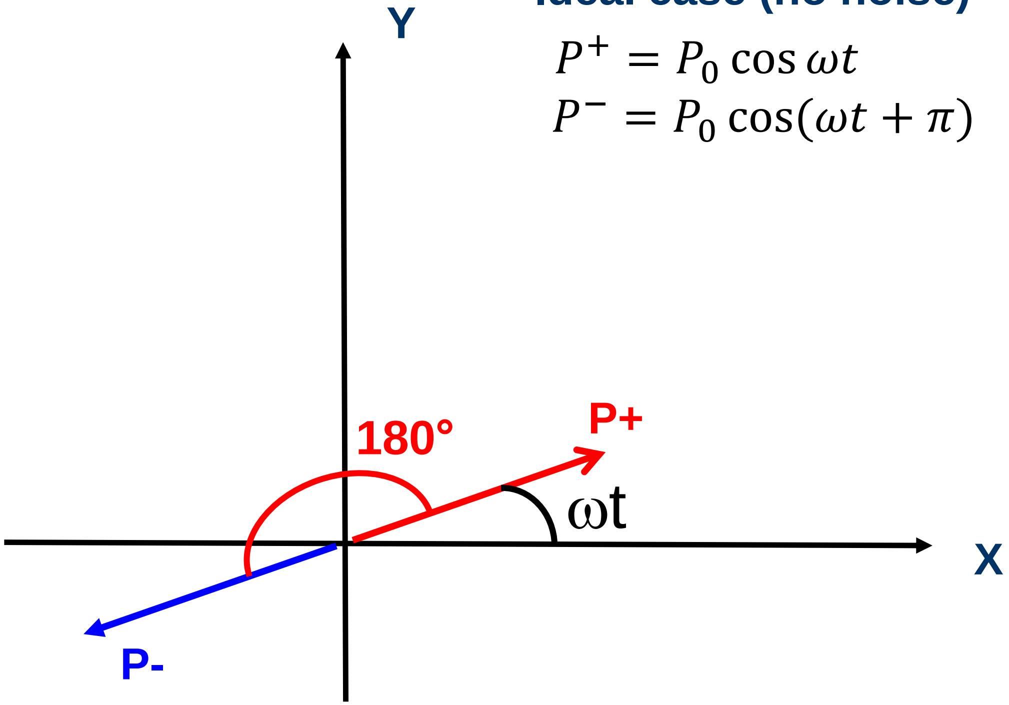


Optimized frequency

- Amp(P$_{up}$) = Amp(P$_{down}$)
- Phase contrast = 180°

Proksch R. et Al., cond-mat > arXiv:1505.05562

PFM : AC excitation, but which frequency?



Ideal case (no noise)

$$P^{+} = P_0 \cos \omega t$$

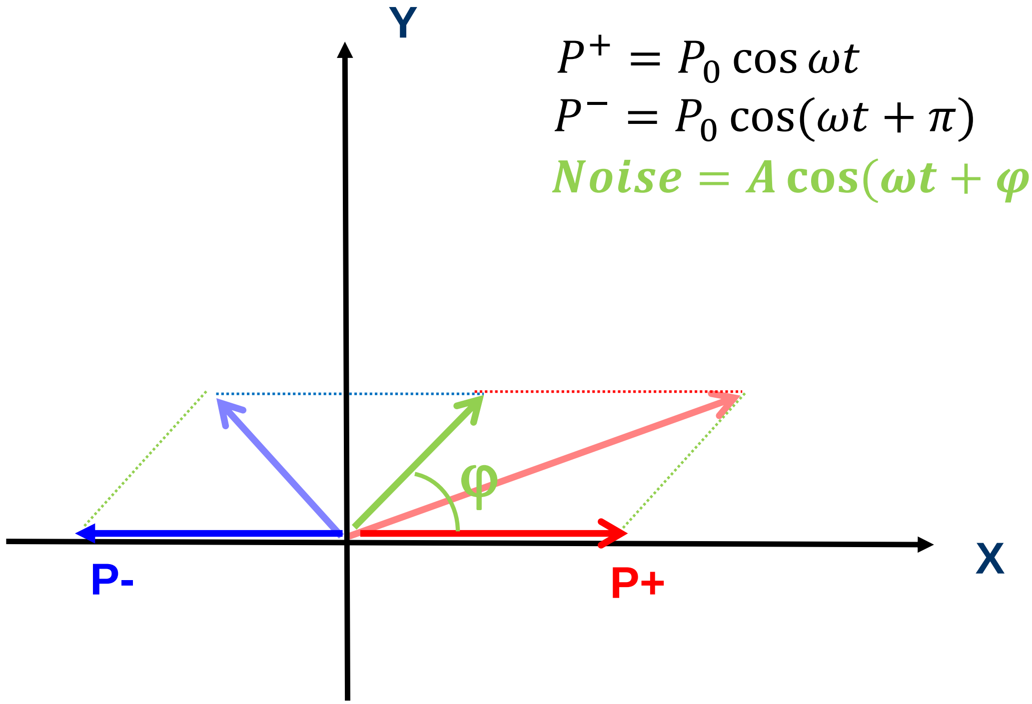
$$P^{-} = P_0 \cos(\omega t + \pi)$$

PFM : AC excitation, question of noise…

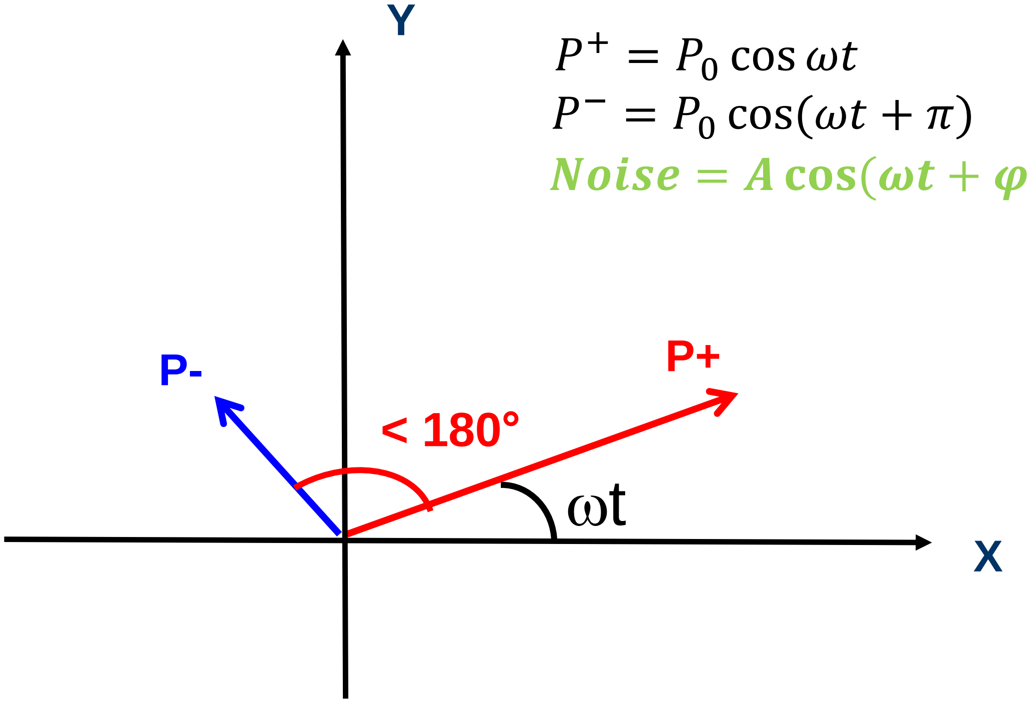
$$P^{+} = P_0 \cos \omega t$$

$$P^{-} = P_0 \cos(\omega t + \pi)$$

$$\boldsymbol{Noise = A\cos(\omega t + \varphi)}$$



PFM : AC excitation, question of noise…



$$P^{+} = P_0 \cos \omega t$$
$$P^{-} = P_0 \cos(\omega t + \pi)$$
$$\boldsymbol{Noise = A\cos(\omega t + \varphi)}$$

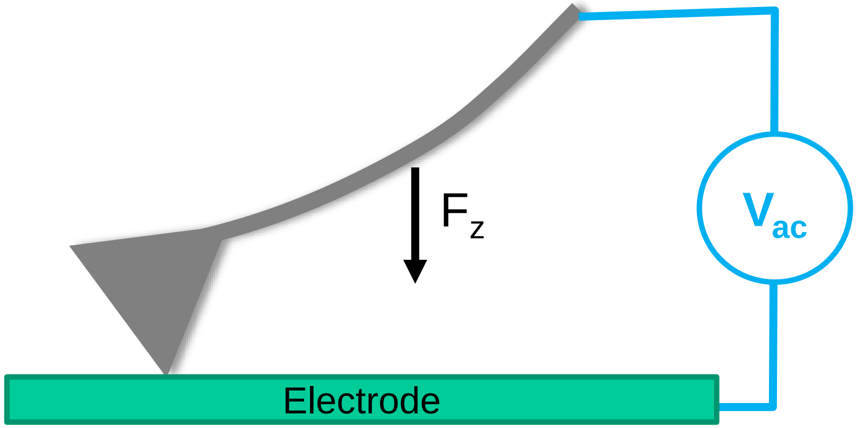
- ⇨ **Dissymmetric amplitudes**
- ⇨ **Phase contrast is reduced below 180°**

Soergel E, J. Phys. D: Appl. Phys. 44 (2011) 464003

Piezoresponse – AFM : Noise

Main source of « noise » at excitation frequency :
Attractive force between capacitor plates (cantilever/sample)

⇨ **Vertical cantilever oscillation**

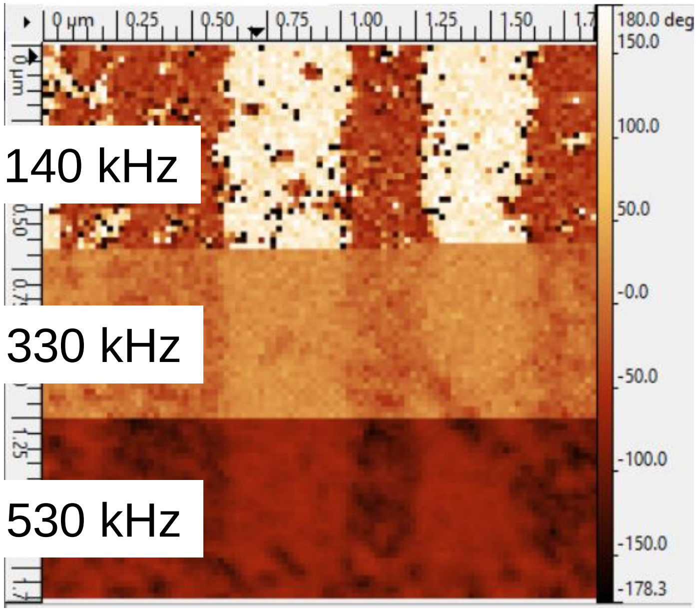


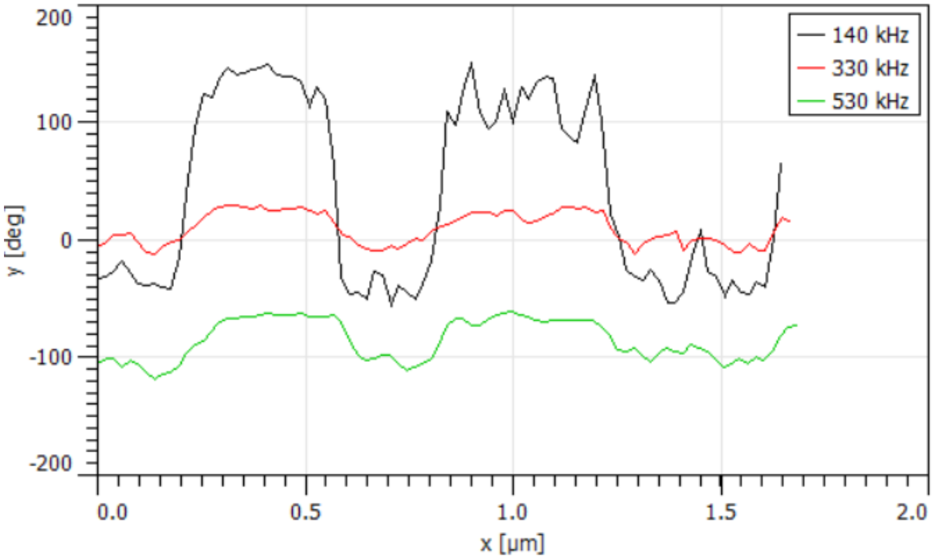
- **For PFM (Out-of-Plane) prefer stiff cantilever (~ 40N/m)**
- **Use excitation frequency far from cantilever resonance**

Piezoresponse – AFM : Noise

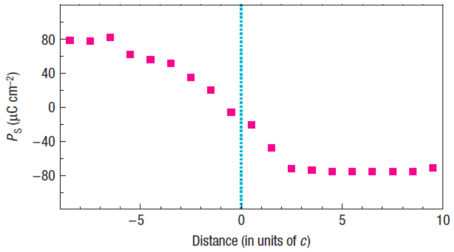
- It also **REALLY** depends on your AFM
- Optimize with a reference sample ⇨ Phase contrast ~ 180°

PFM Phase



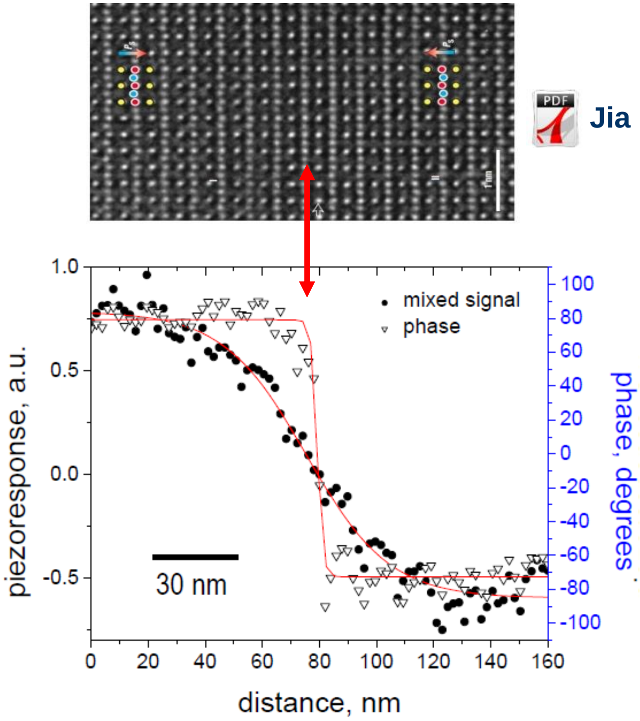


Piezoresponse – AFM : Resolution



$PbTiO_3$

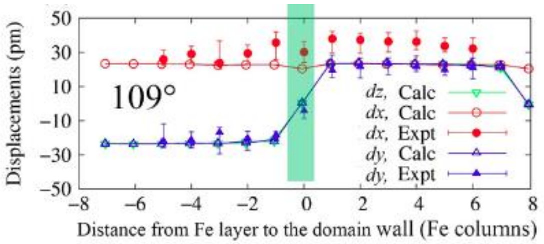
Jia C.L., Nat. Mat.7 57 (2008)



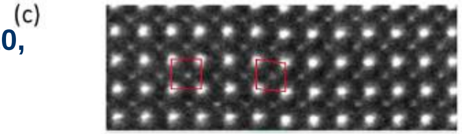
Phase resolution ~3 nm

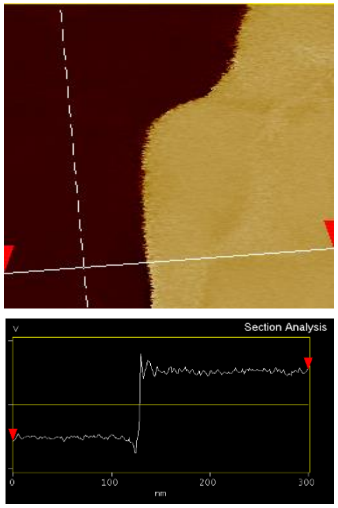
Amplitude resolution ~30nm

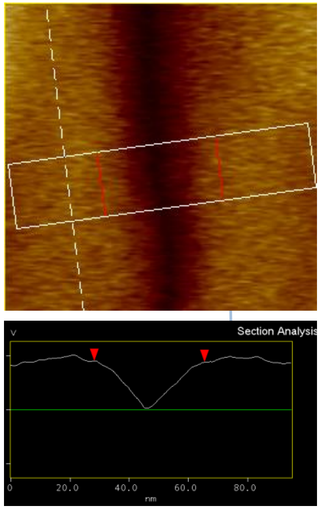
$BiFeO_3$



Wang Y.,PRL 110, 267601 (2013)







Phase resolution

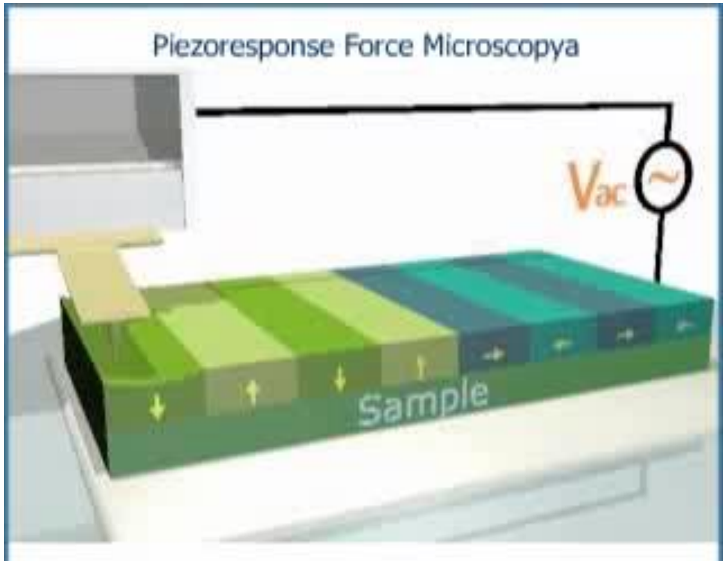
~ 5 nm (0→180°)

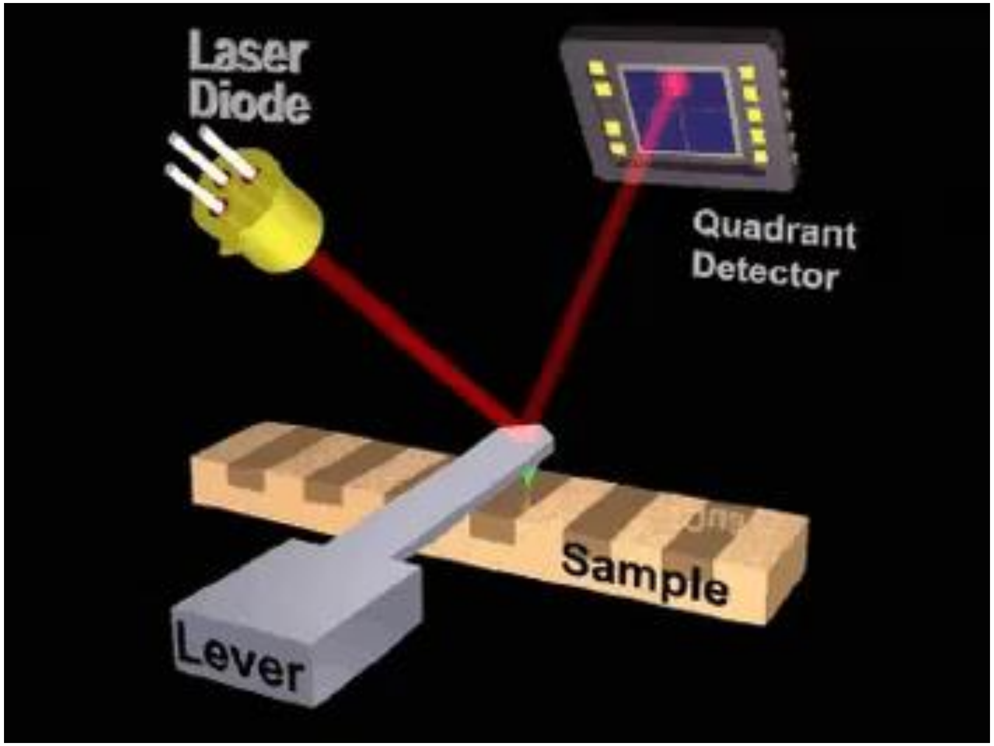
Amplitude resolution

~ 30nm

Lateral or “in plane” PFM

In-plane component of the polarization

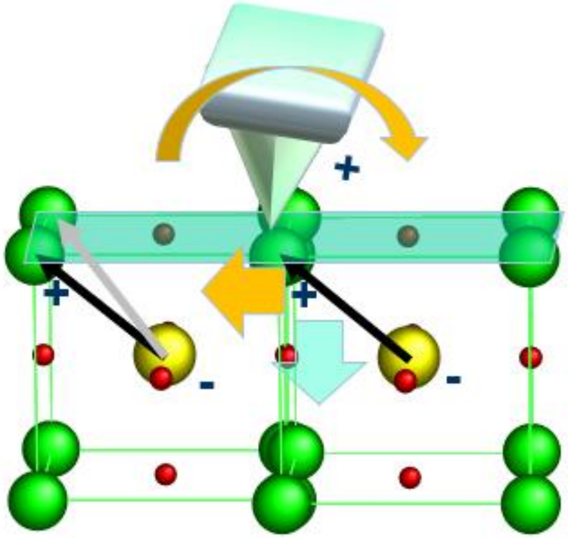




Lateral or “in plane” PFM

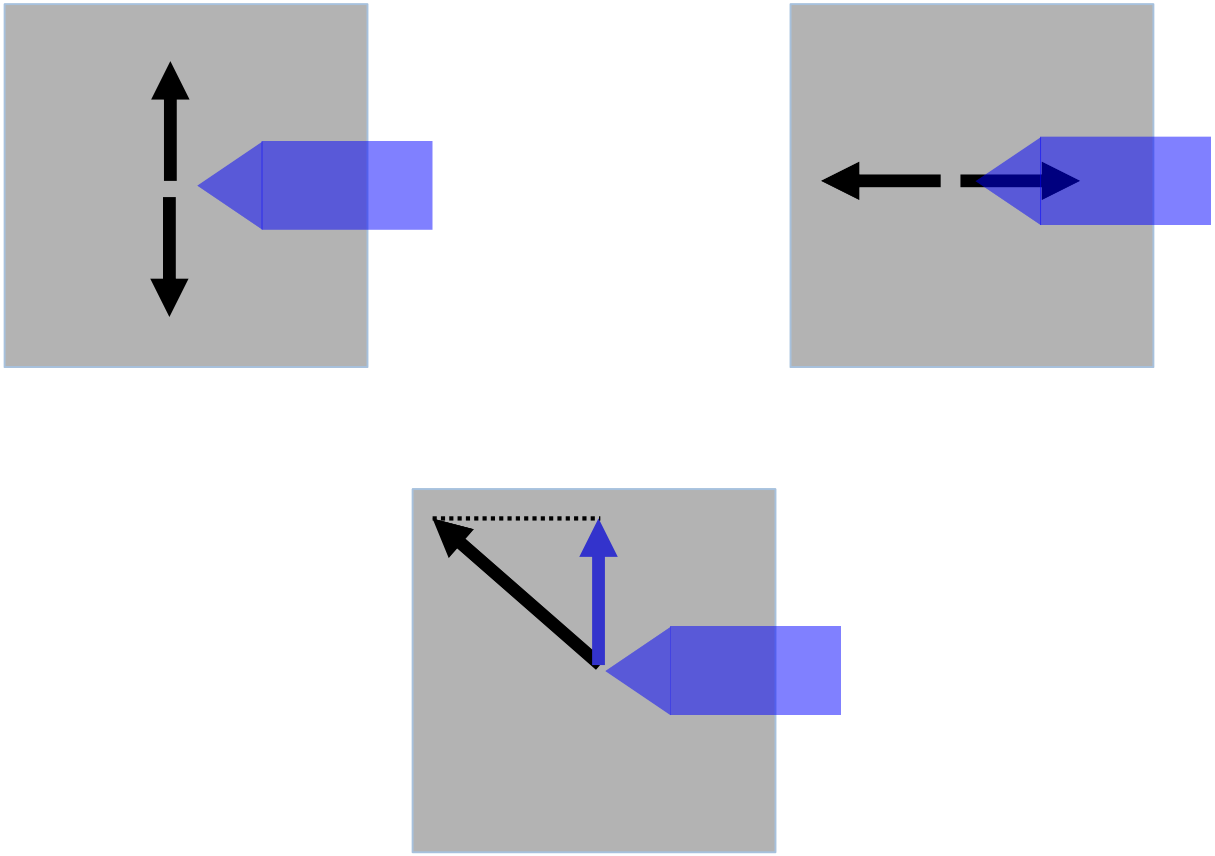
If the cantilever torsion stiffness is too high, tip will « slide » on the surface

⇨ **Reduced signal**



For In-Plane PFM, prefer soft cantilever (~1N/m)

Lateral or “in plane” PFM



Component of the polarisation vector perpendicular to cantilever axis

⇨ Rotation of the sample

⇨ Full determination of in-plane polarisation vector

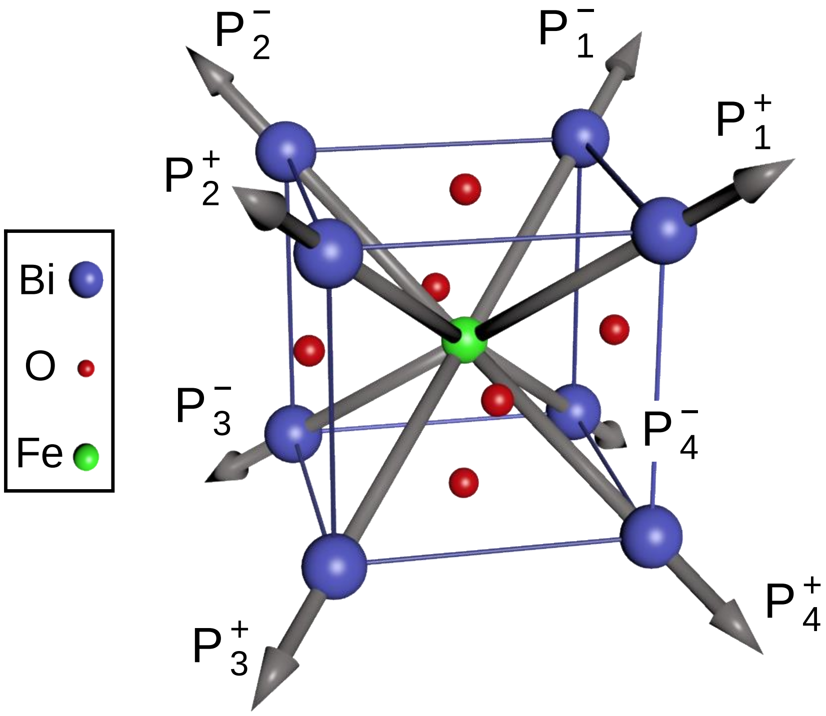
⇨ « Vertical » PFM : Out of plane component of the polarisation

Vectorial PFM

Vectorial PFM

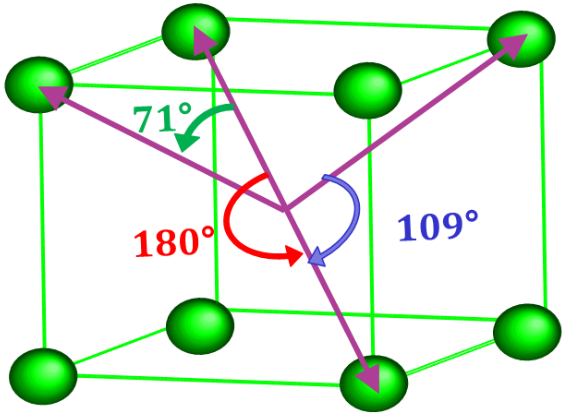
$BiFeO_3$

Polarization along <111> directions



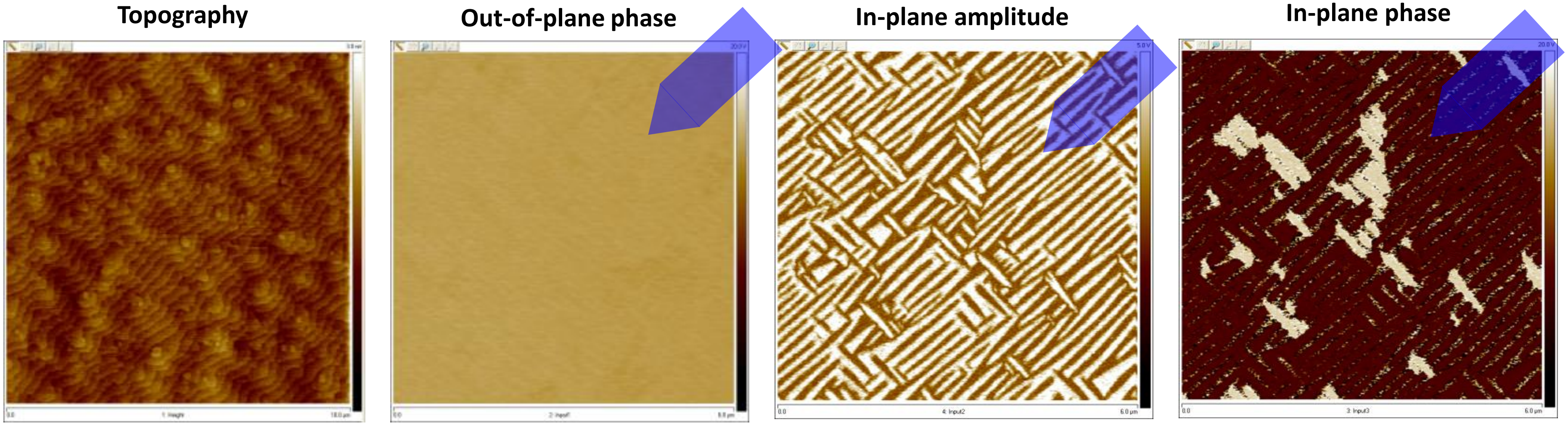
8 possible $P_i^\pm$

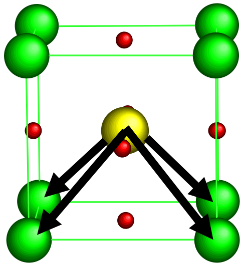
3 types of DWs

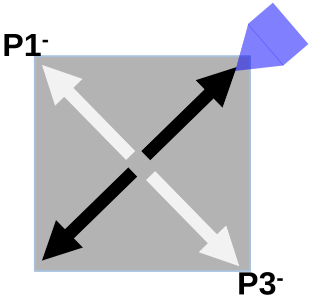


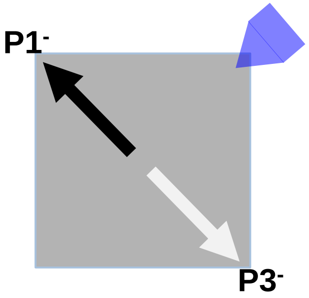
Vectorial PFM

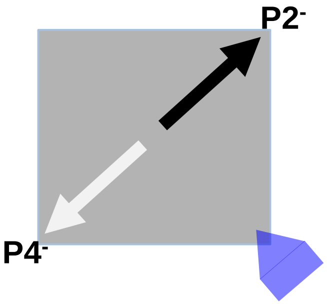
$BiFeO_3$ / $SrRuO_3$ // $DyScO_3$ (001)









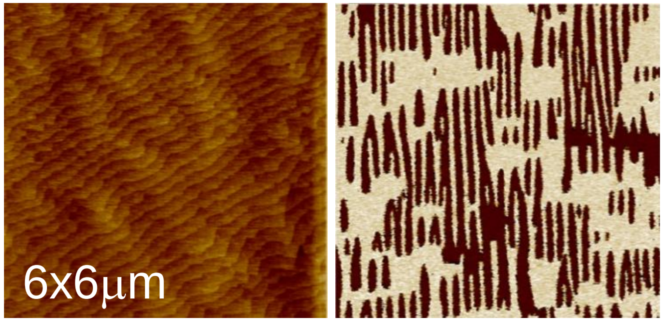


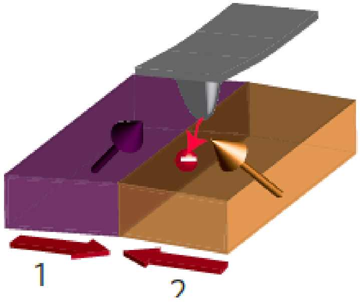
⇨ full picture of domains and domain walls

In-plane writing

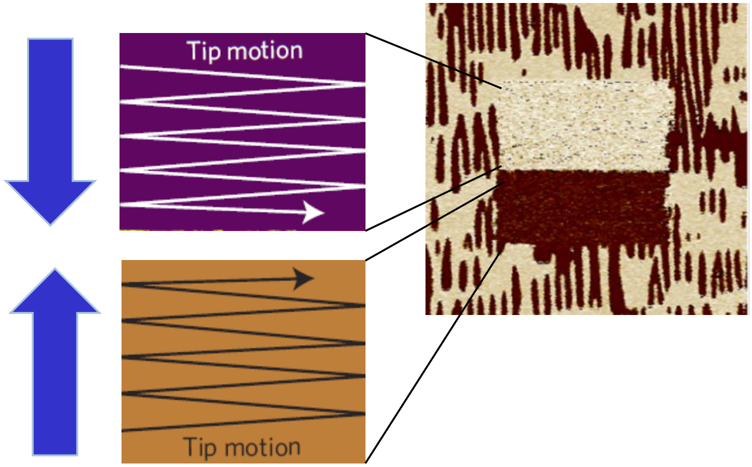
Tip “Trailing Field” ⇨ In-plane polarization variant can be selected/written

In plane phase





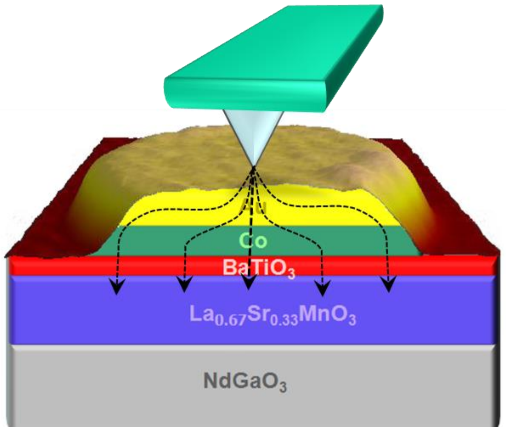
Tip « trailing field »



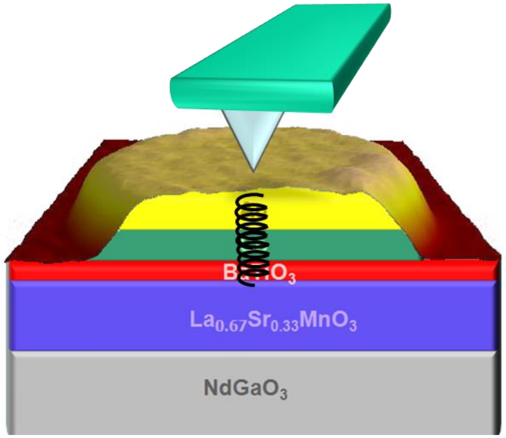
⇨ Domains with various polarization orientations can be created
⇨ Various domains walls can be created

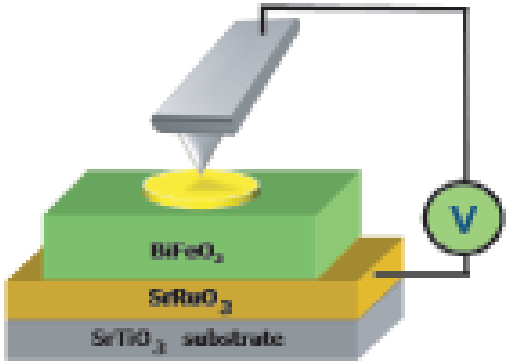
PFM imaging through a top electrode

Global excitation of the FE layer

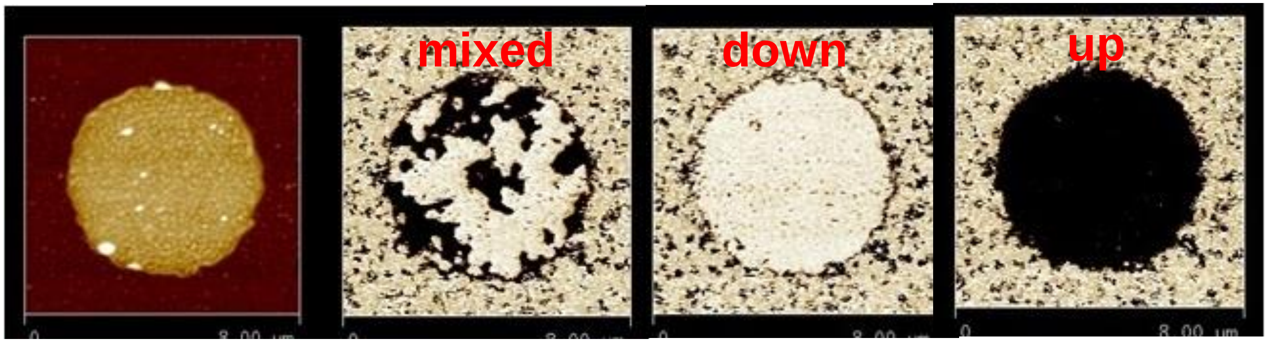


Local piezoresponse



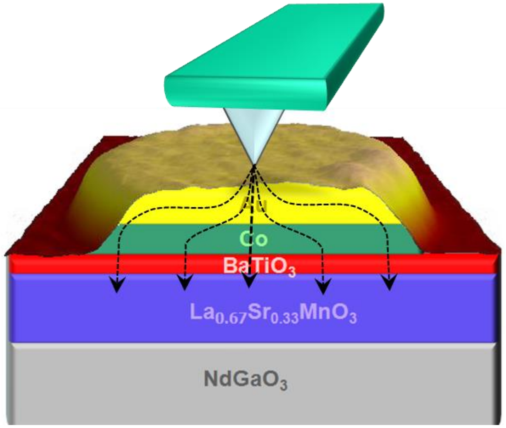


topography **OP phase**

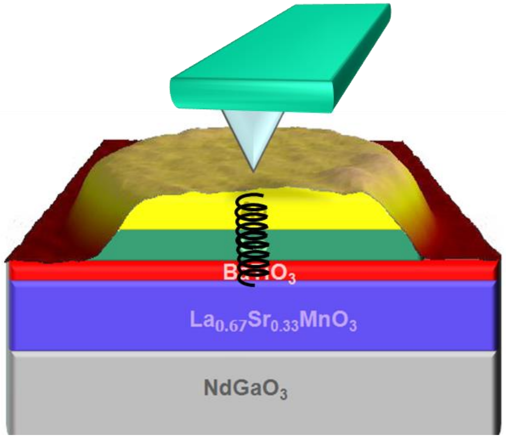


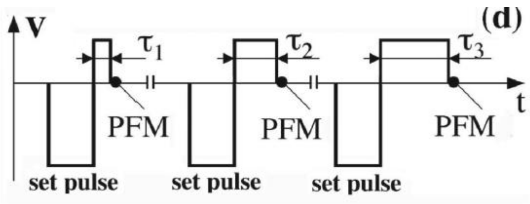
PFM imaging through a top electrode

Global excitation of the FE layer

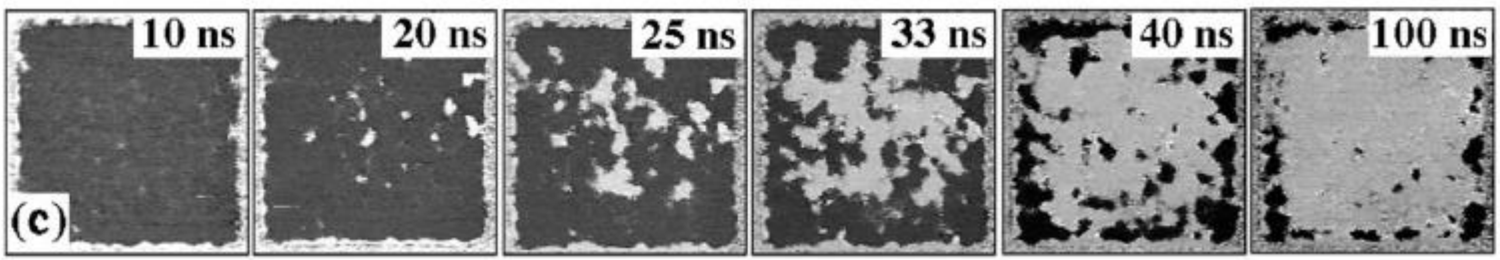


Local piezoresponse





Switching dynamics



Switching kinetics of PbZrTiO3 (PZT) capacitors

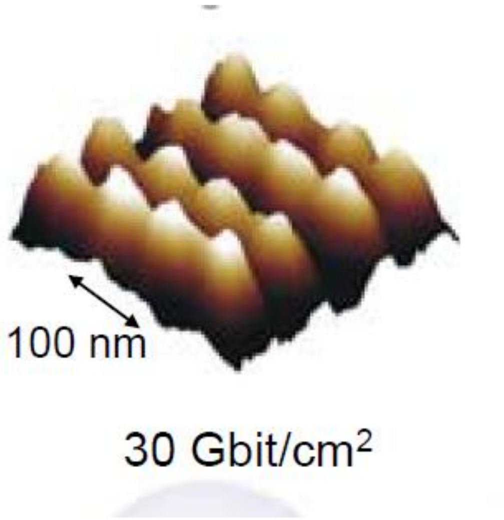
Gruverman A., PRL 100, 097601 (2008)

Piezoresponse – AFM

Vectorial PFM ⇨ All polarization variant can be determined

Tip DC bias ⇨ Out-of-plane polarization variant can be selected/written
⇨ In-plane polarization variant can be selected/written

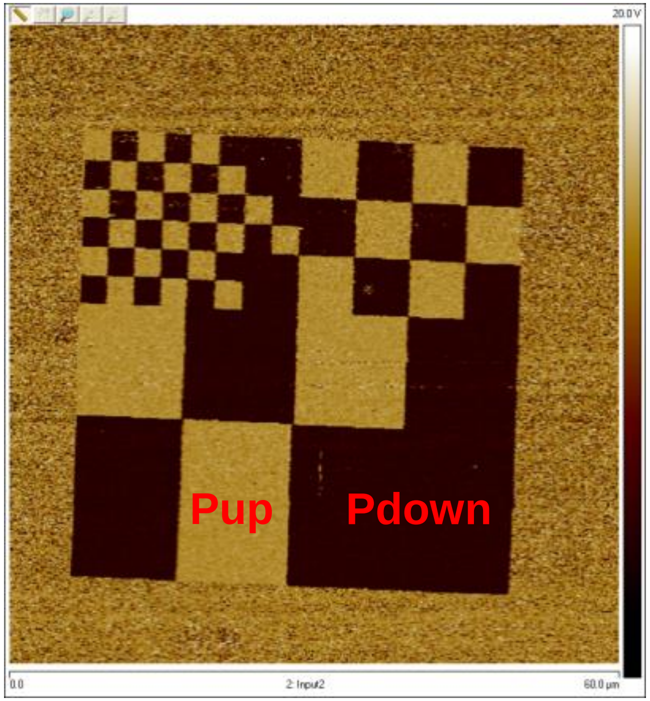
All polarization configurations can be determined and potentially written



Paruch, *APL 79, 530 (2001).*

BFO 60x60 μm

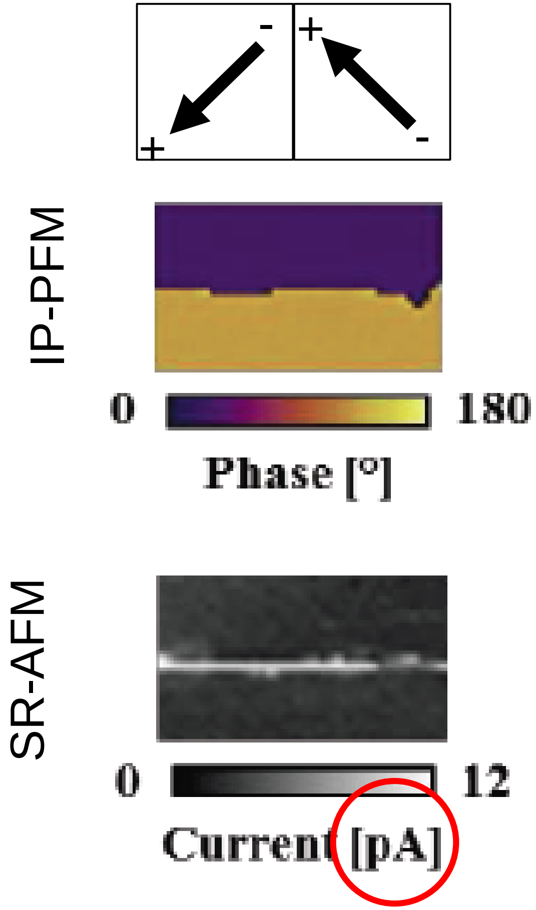
PFM phase images



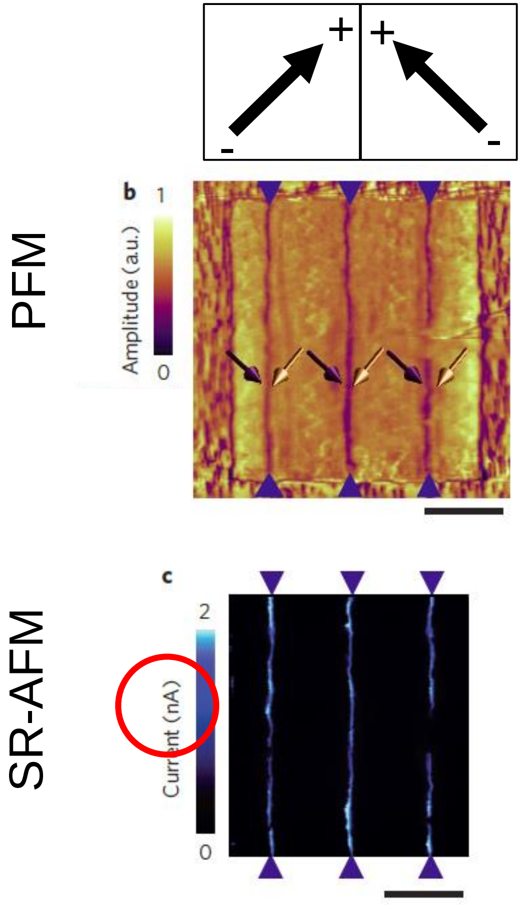
DW conduction in... BiFeO$_3$

Creation of peculiar charged domain walls (« head to head » or « tail to tail »)

neutral domain walls



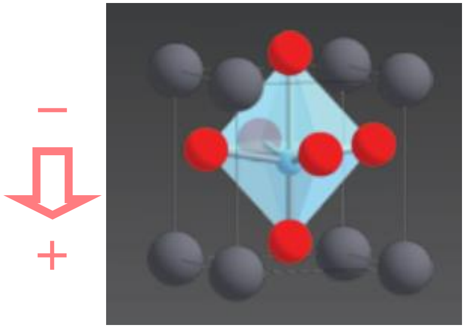
charged domain walls



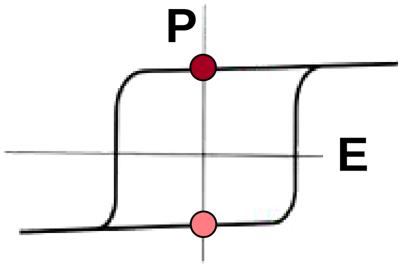
Charged DW are highly conductive

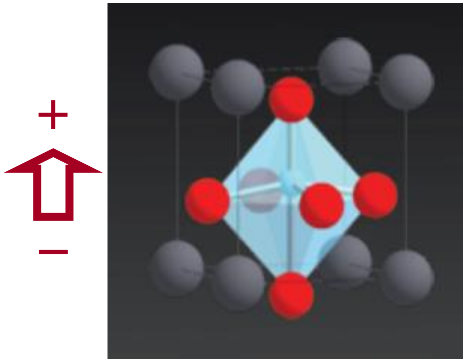
Crassous, Nat. Nano 2015

Ferroelectric tunnel junctions ?

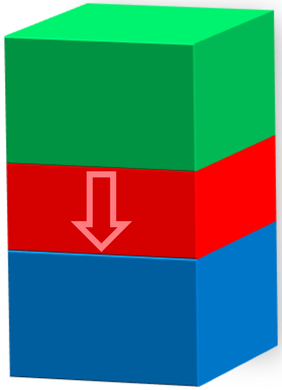


Ferroelectrics

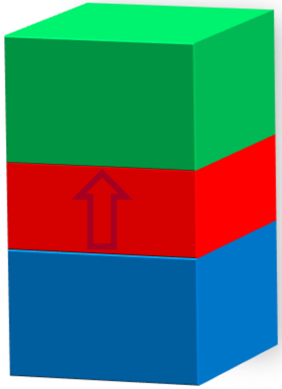


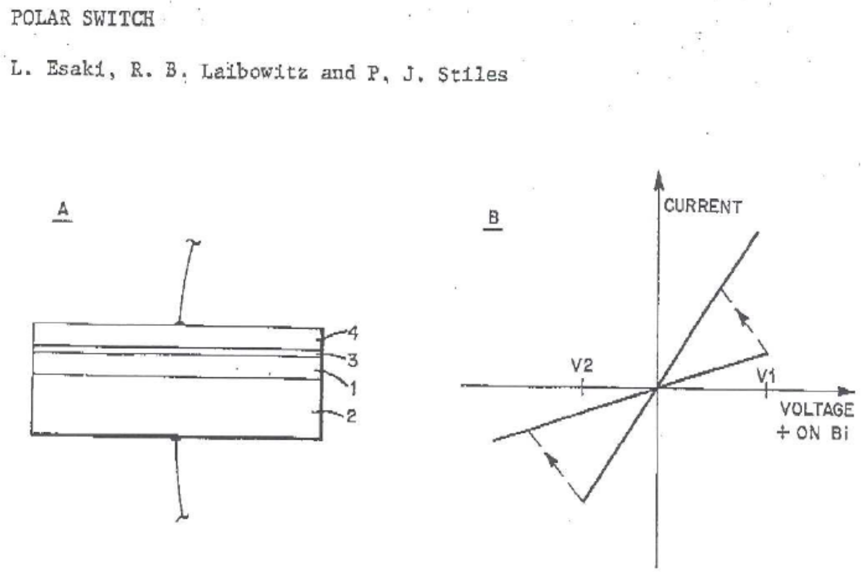


Ferroelectric as a tunnel barrier



$R_{\Downarrow} \neq R_{\Uparrow}$





POLAR SWITCH

L. Esaki, R. B. Laibowitz and P. J. Stiles

Non volatile memory

Esaki *et al.*, IBM Discl. Bull. **13**, 2161 (1971)

Ferroelectric as tunnel barriers : $BaTiO_3$

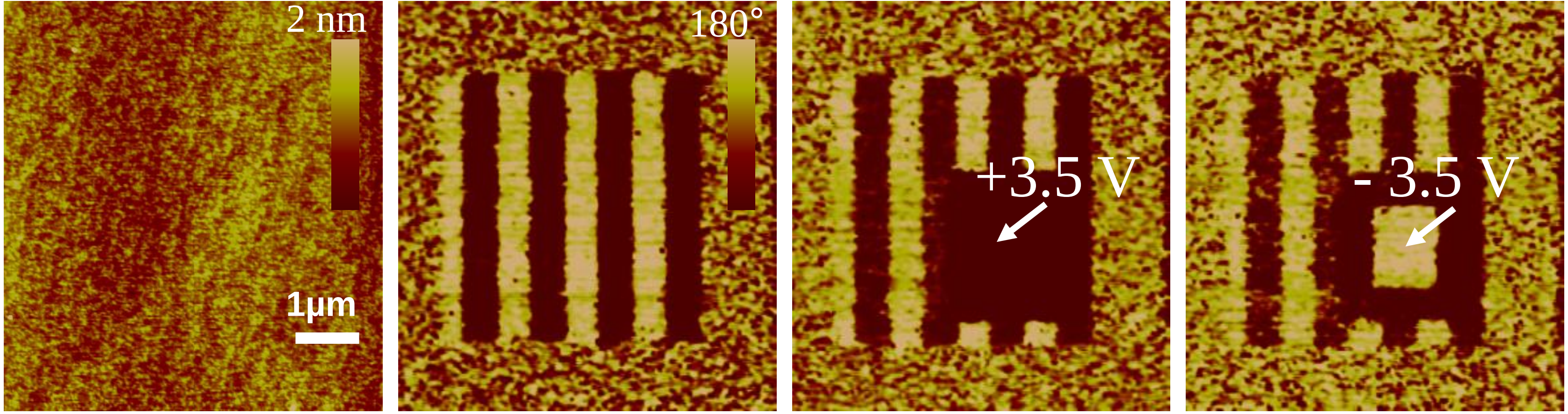
$BaTiO_3$ (1-4 nm)

Electrode ($La_{2/3}Sr_{1/3}MnO_3$)

Question 1 : Are the ultra thin films of BTO still ferroelectric ?

Piezoresponse force microscopy

BTO (1 nm) / $La_{2/3}Sr_{1/3}MnO_3//DyScO_3$



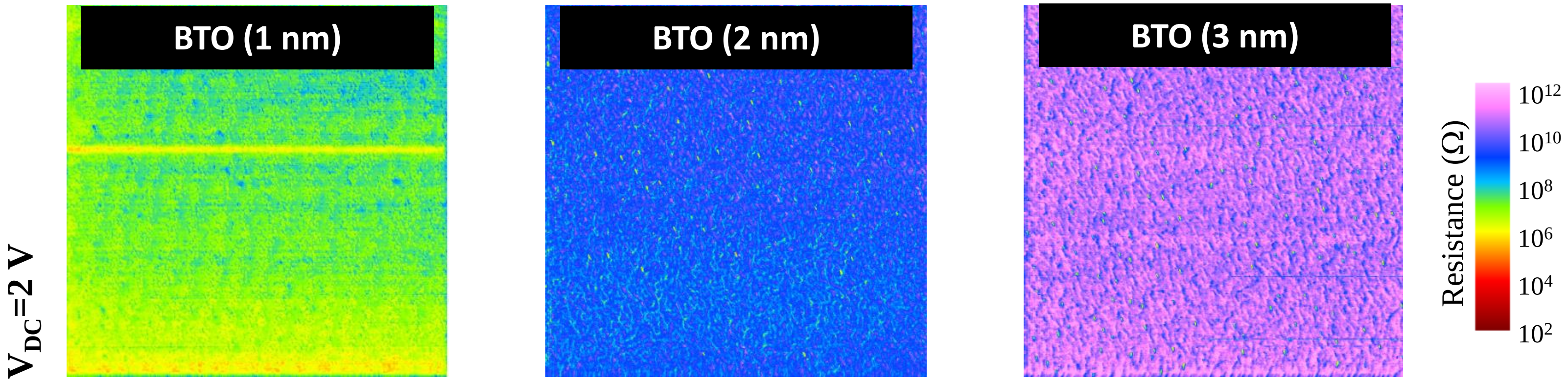
✓The written domains are reversible and stable for at least 72 hours

Strained $BaTiO_3$ is ferroelectric down to 1 nm

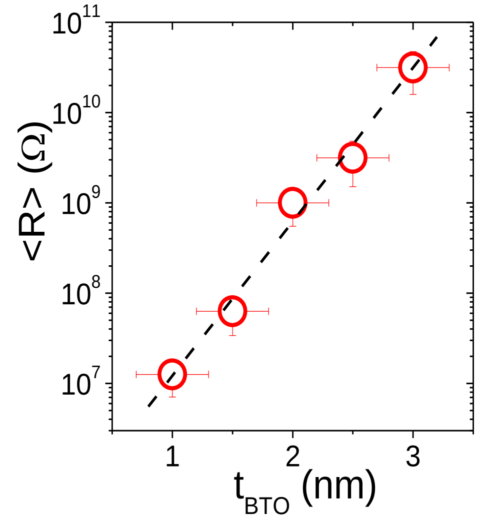
Ferroelectric as tunnel barriers : $BaTiO_3$

Question 2 : Are the ultra thin films of BTO good tunneling barriers ?

Scanning Resistance -AFM



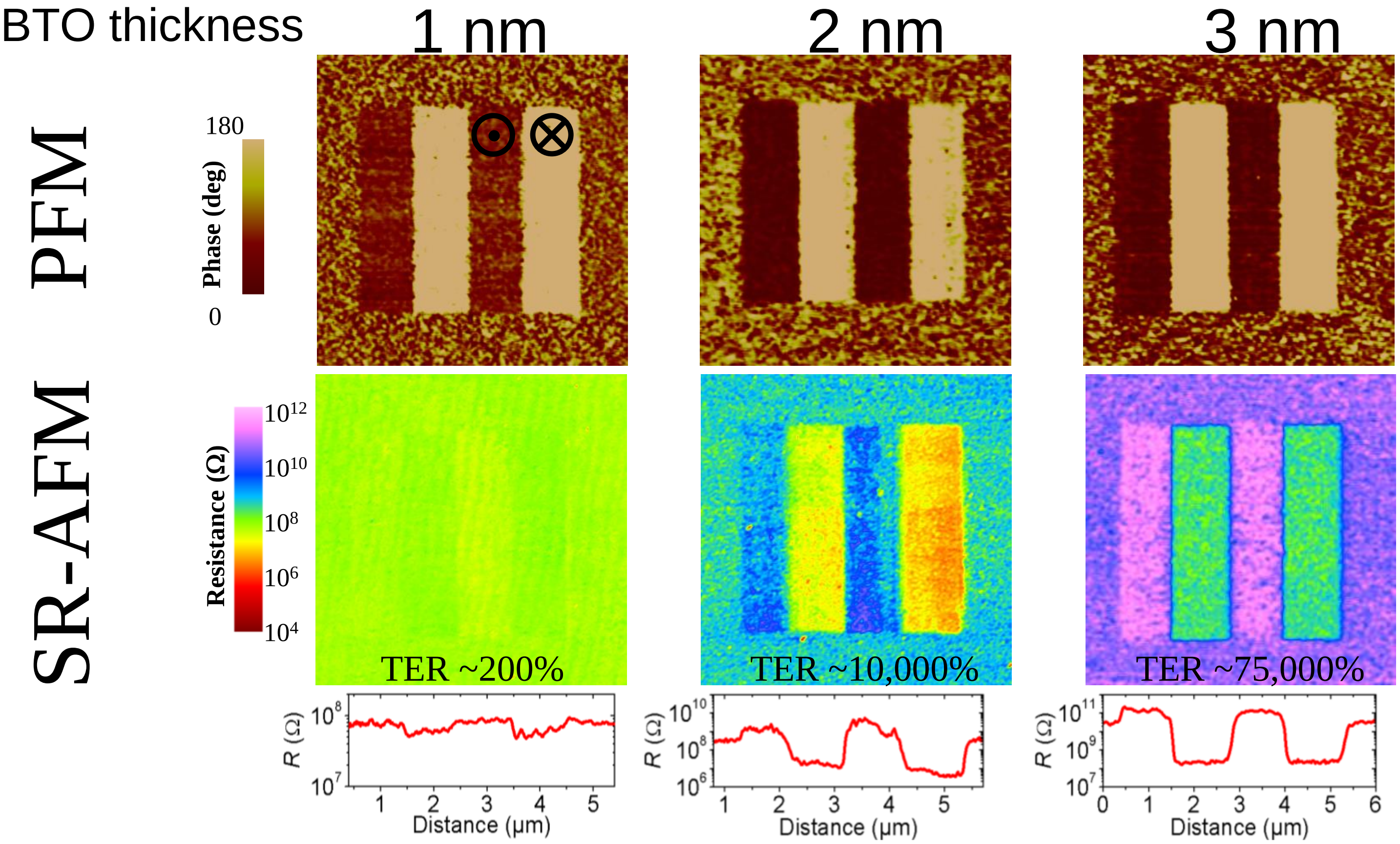
$< \log R > = 7.1 \pm 0.25$ $< \log R > = 9.0 \pm 0.26$ $< \log R > = 10.5 \pm 0.30$



Tunnel transport throught $BaTiO_3$ barriers

Ferroelectric as tunnel barriers : $BaTiO_3$

Question 3 : Is the tunneling conductance related to polarization orientation ?

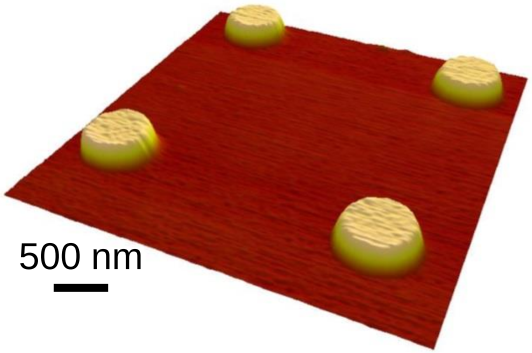


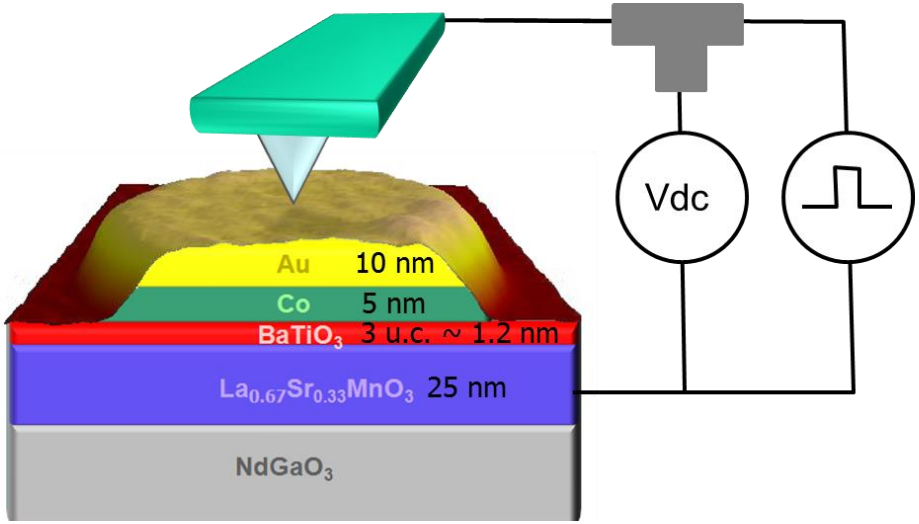
First demonstration of ferroelectricity-related Tunneling Electro Resistance (TER)

Garcia et al, Nature 460 (2009)

From multilayers to devices : Solid-state ferroelectric tunnel junctions

✓ Nanoscale ferroelectric tunnel junctions defined by e-beam lithography (Φ~0,2 to 1µm)

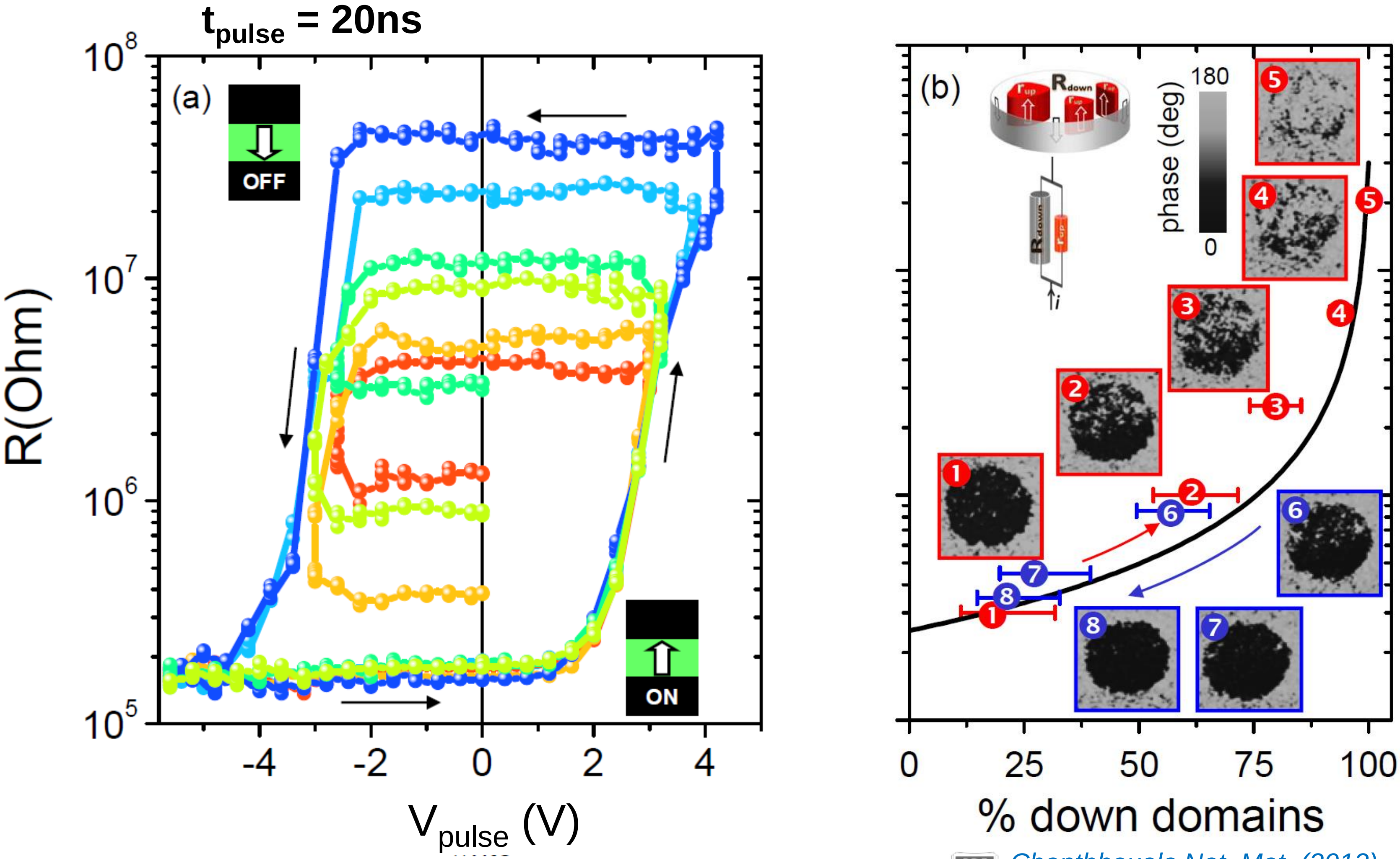




✓ Each device can be electrically connected by the AFM tip for :

- ⇨ DC measurement of its resistance state
- ⇨ Voltage pulses to manipulate its ferroelectric state
- ⇨ Imaging of its ferroelectric state

Solid-state ferroelectric tunnel junctions



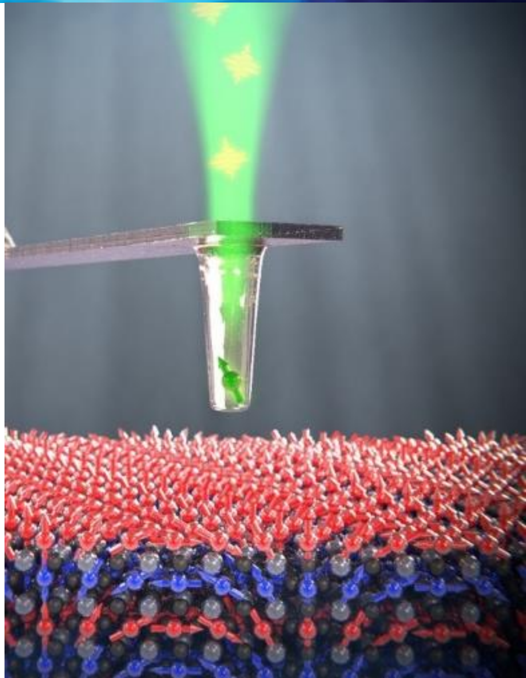
Chanthbouala Nat. Mat. (2012)
Chanthbouala Nat. Nano. (2012)

Ferroelectric tunnel junction ⇨ non volatile memory and memristor

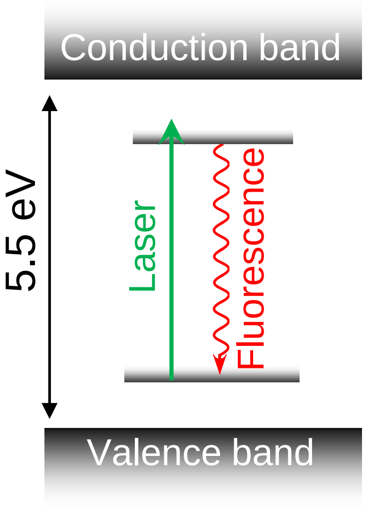
Advanced modes :

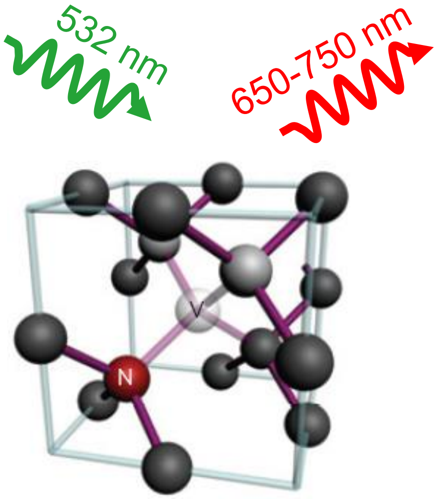
Scanning NV Magnetometry

Seminal proposal: Chernobrod and Berman 2005 (JAP)
First papers : 2008
Commercially available : 2020



The Nitrogen-Vacancy (NV) defect in diamond

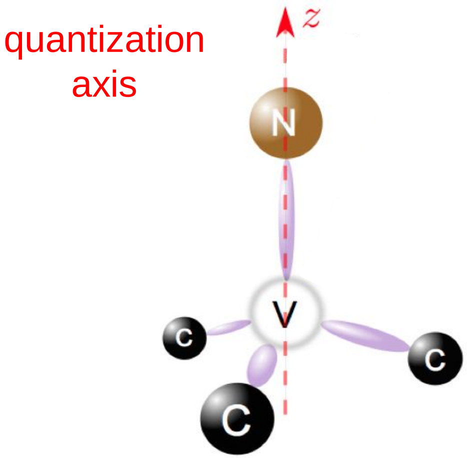




NV defect in the diamond C-lattice

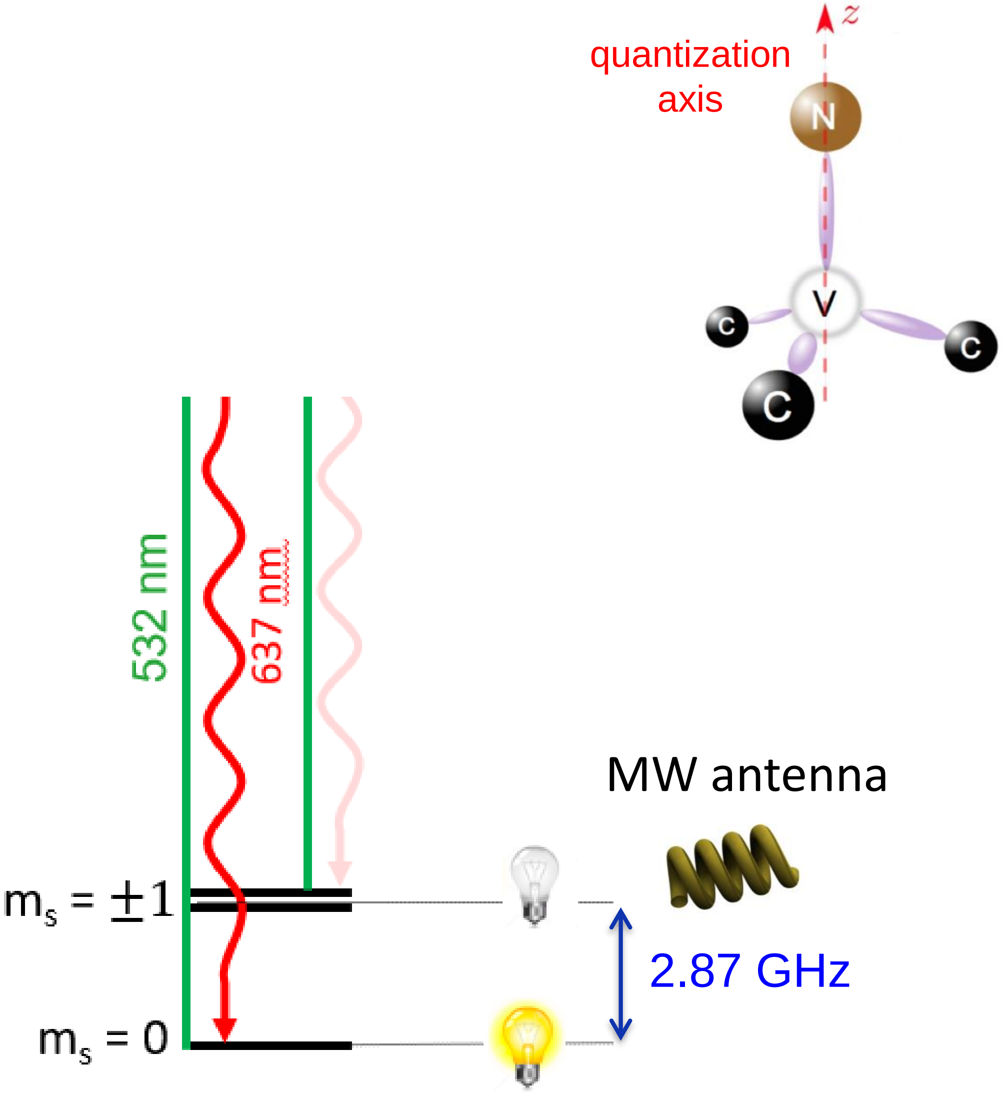
"Hortensia" diamond
(Louvre, Paris)

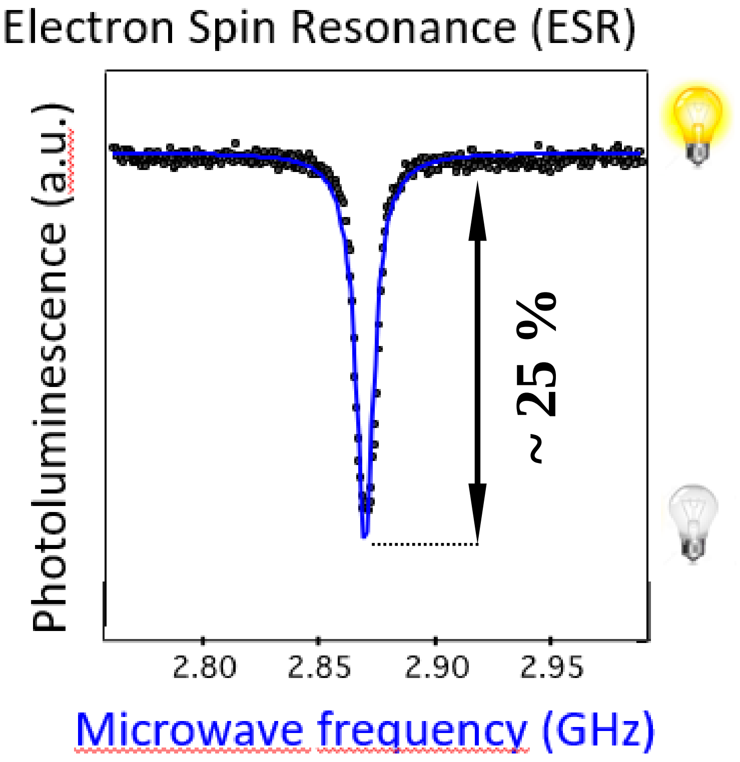
- An artificial atom *"embeded"* in the diamond lattice



NV defect optical properties

- Artificial atom with a spin triplet (S=1) ground state

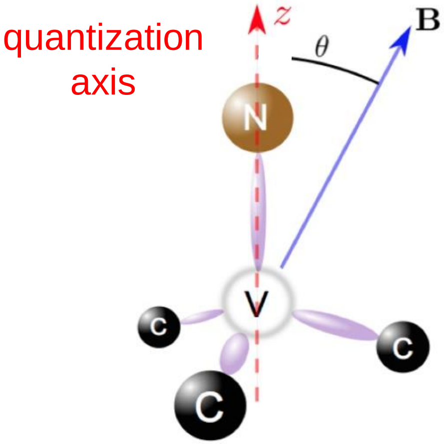


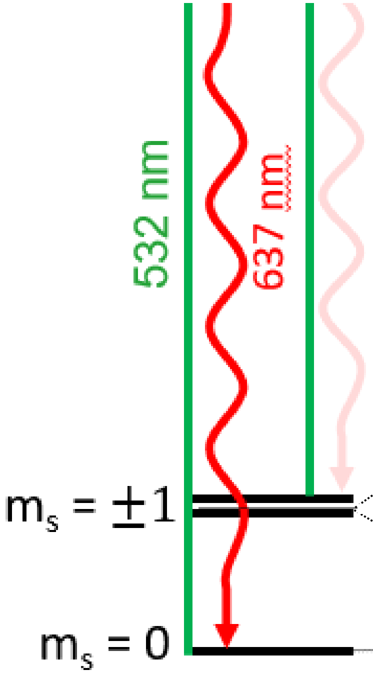


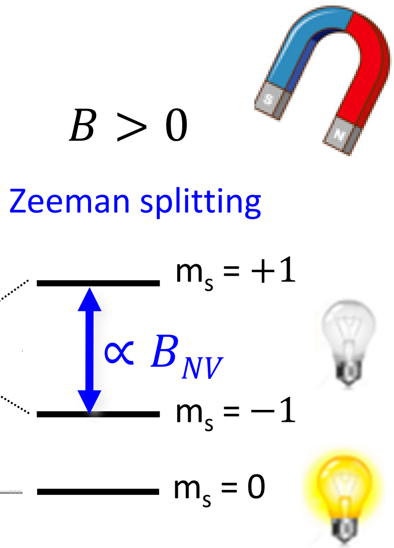
→ Spin-dependent photoluminescence signal

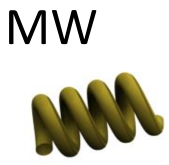
The Nitrogen-Vacancy (NV) optical properties

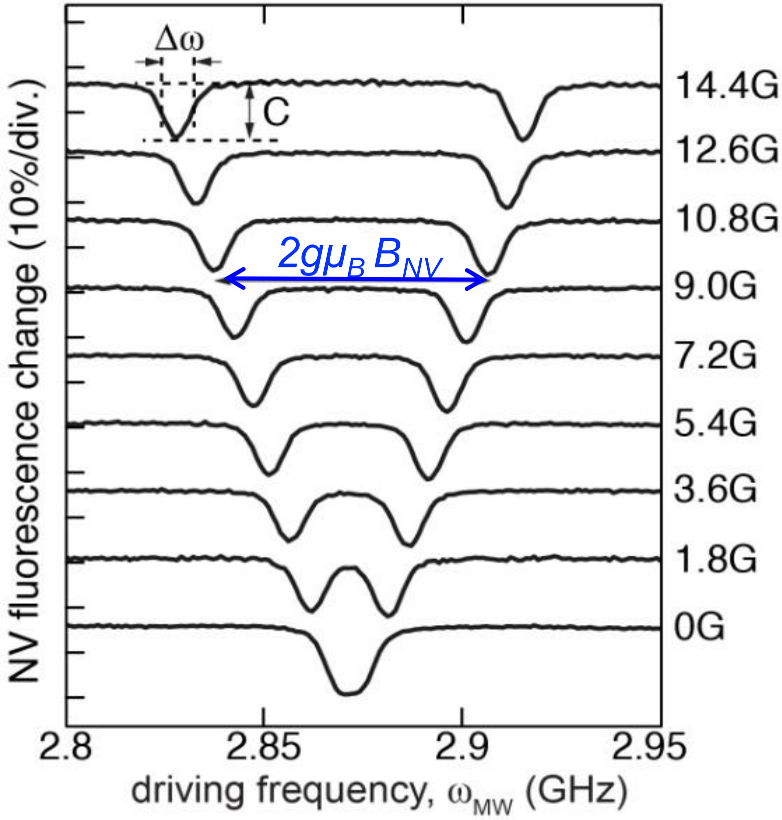
- Artificial atom with a spin triplet (S=1) ground state







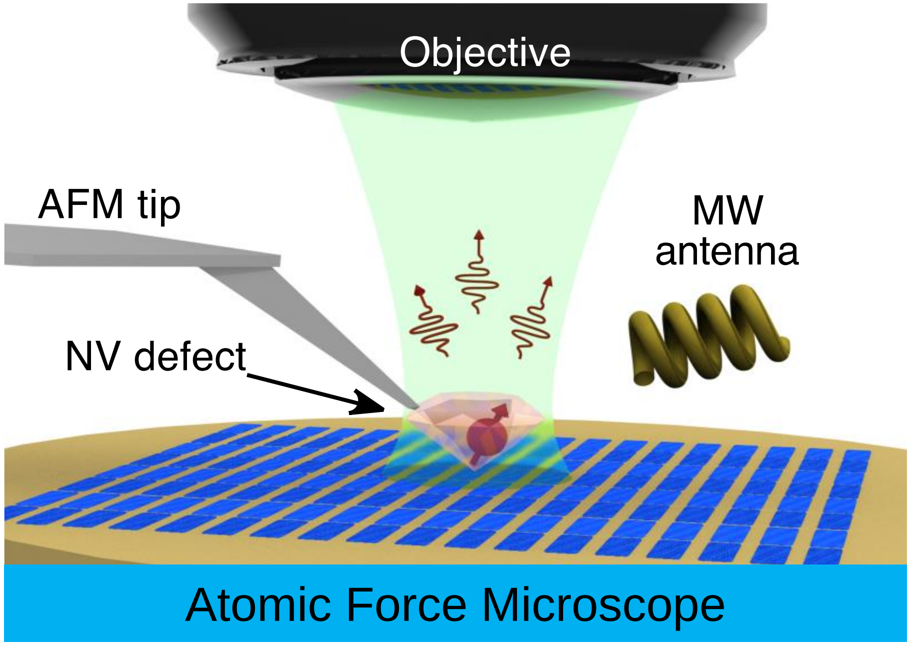




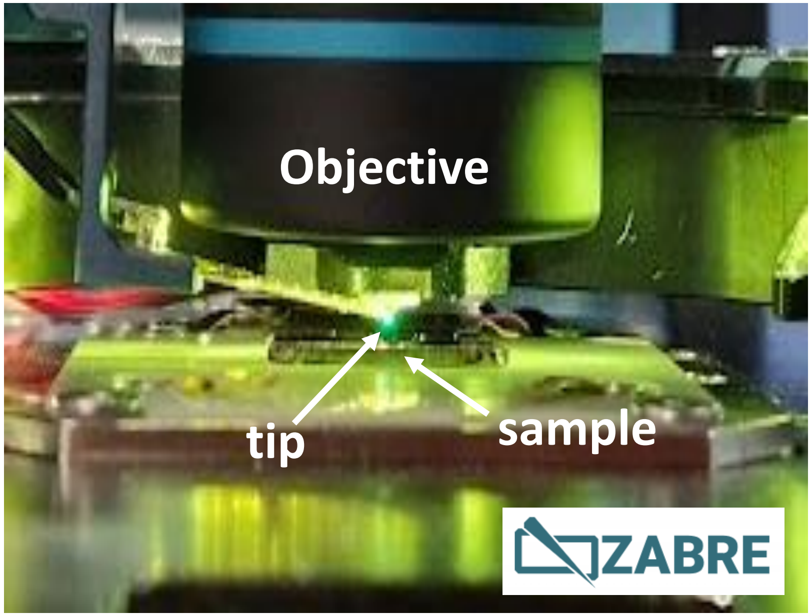
NV = absolute magnetometer

Magnetic imaging with a single NV defect

Scanning-NV magnetometry



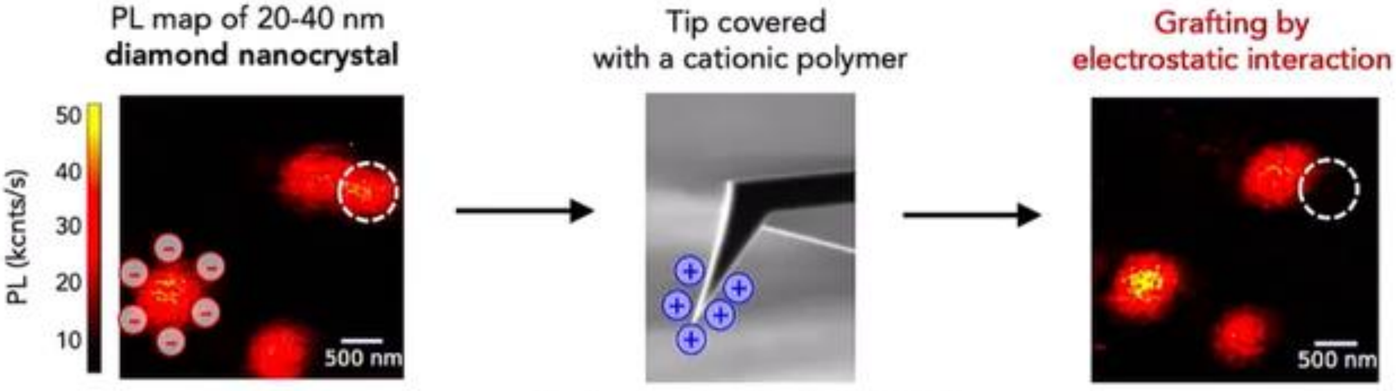
Experimental setup



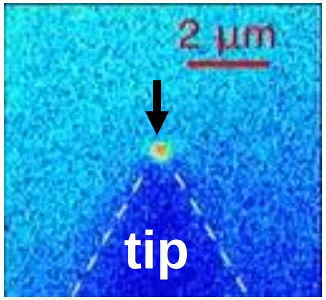
- ★ Quantitative/vectorial (sensitivity - **1 μT/Hz$^{-1/2}$**)
- ★ No magnetic back-action (unlike MFM)
- ★ Atomic-size detection volume
- ★ Spatial resolution depends on NV distance to the sample surface

The NV-based sensor: The Dark Age

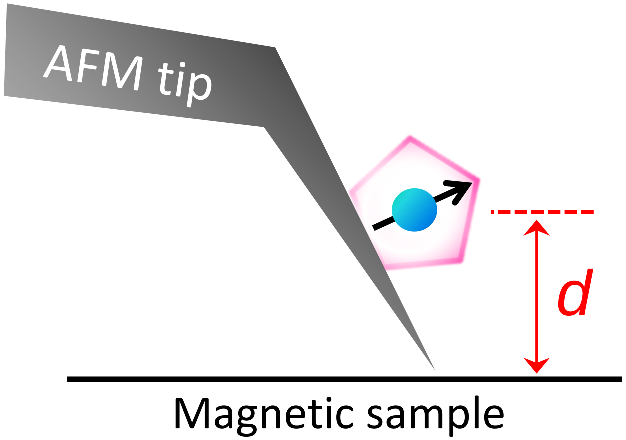
The Dark Age : Diamond nanocrystal fishing



Cuche, *Opt. Exp.* 17, 19969 (2009)



Rondin, APL (2012)



- Time and student consuming
- d ~ 100 - 200 nm (limiting spatial resolution)
- random orientation of the NV axis
- Regular AFM probes are fragile

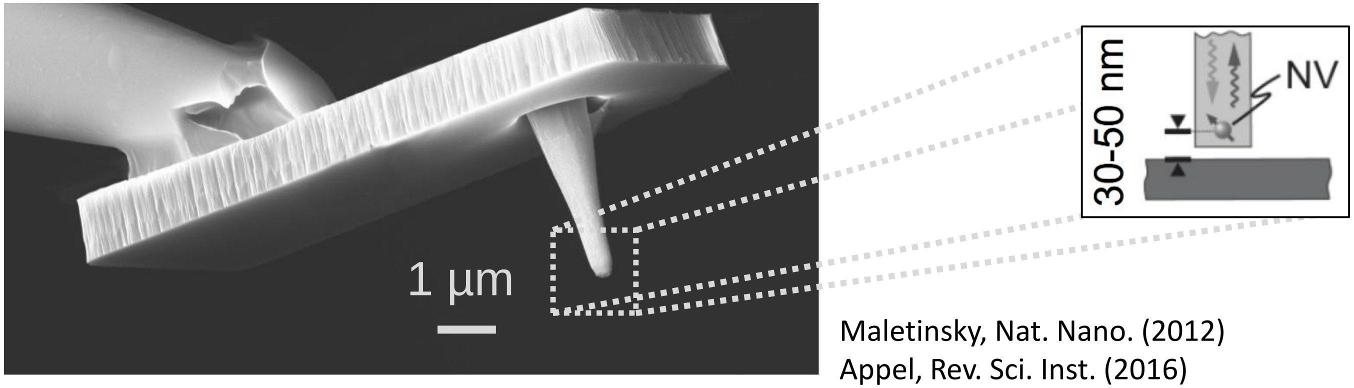
The NV-based sensor: The Swiss Age

The Swiss Age : All-diamond probe hosting a single NV defect

(commercially available since 2018)

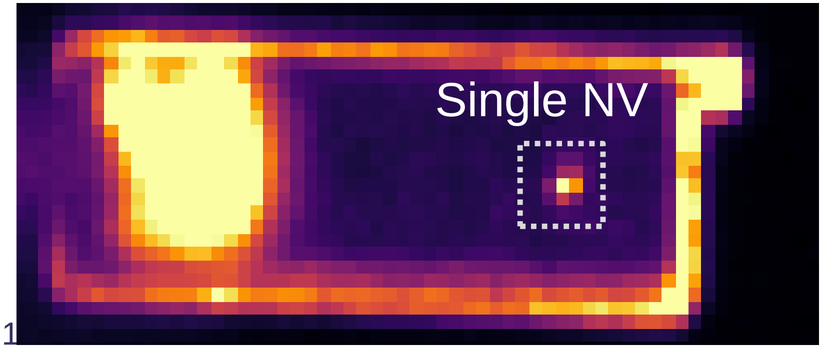
QZabre-LLC ZABRE

nami



Maletinsky, Nat. Nano. (2012)
Appel, Rev. Sci. Inst. (2016)

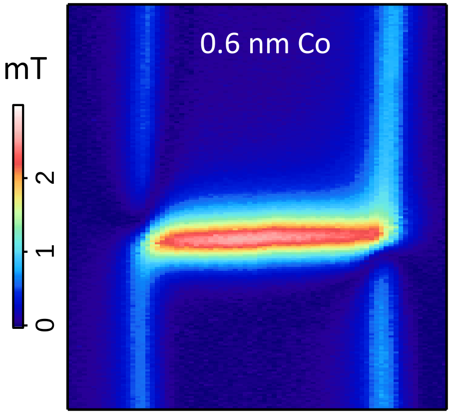
PL map of the diamond probe (top view)



- d ~ 30-50 nm
- Control of the NV axis orientation

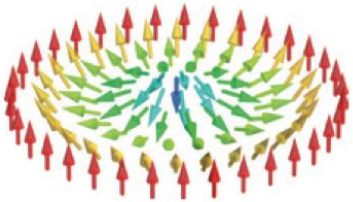
A broad diversity of applications in condensed matter physics

Chiral domain walls in thin ferromagnets

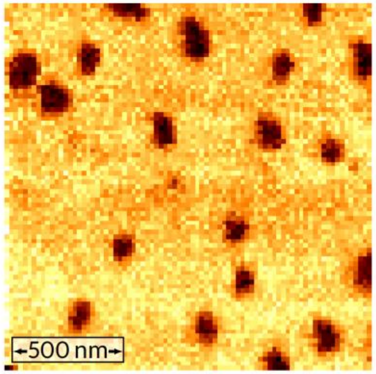


Tetienne *et al.*, *Science* (2014)
Tetienne *et al.*, *Nat. Commun.* (2015)

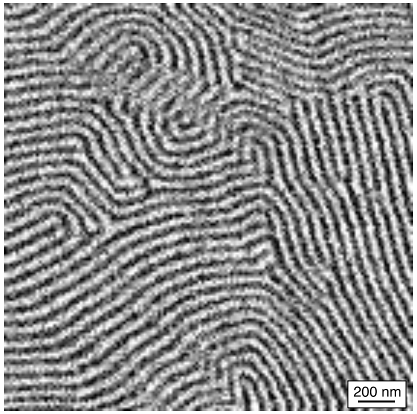
Magnetic skyrmions



Akhtar *et al.*, *Phys. Rev. Appl.* (2019)
Rana *et al.*, *Phys. Rev. Appl.* (2020)

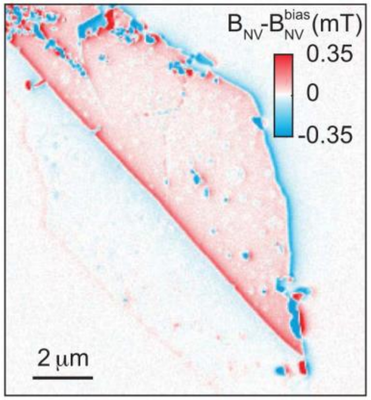


Antiferromagnets



Gross *et al.*, *Nature* (2017)
Finco *et al.*, *PRL.* (2022)

Magnetism in 2D-materials

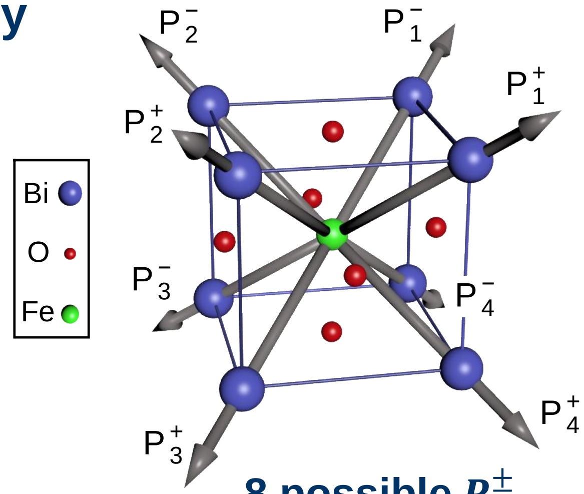


Thiel *et al.*, *Science* (2019) - Basel

Room temperature multiferroic: $BiFeO_3$

Ferroelectricity

(T_C = 1100 K)



8 possible $P_i^{\pm}$

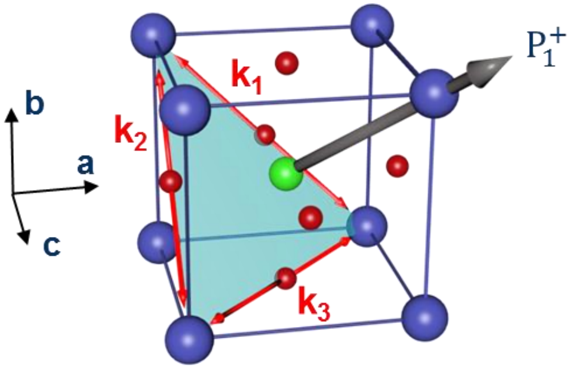
- Rhombohedral R_{3C}
- Large P (100 µC/cm²) ∥ [111]

Wang *et al.*, Science **299**, 1719 (2003)
Lebeugle *et al.*, Appl. Phys. Lett. **91**, 022907 (2007)

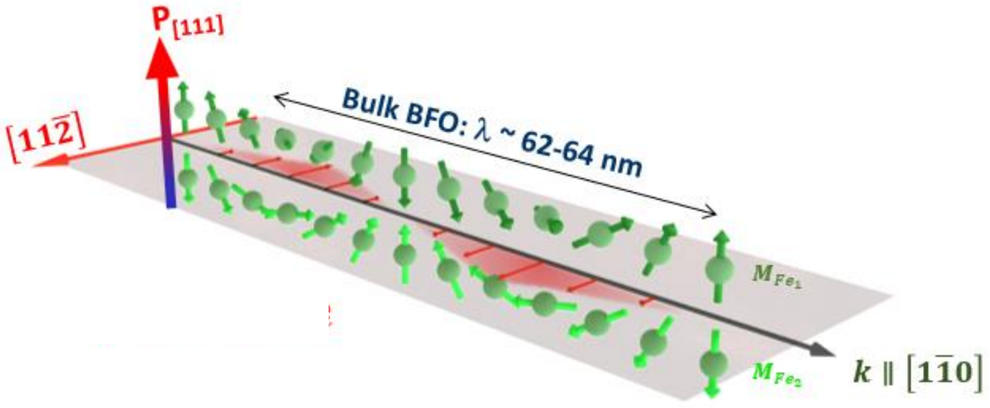
Antiferromagnetism

(T_N = 640 K)

- G-type antiferromagnet (T_N = 640 K)
- Spin cycloid along k_i (λ ~ 62-64 nm)

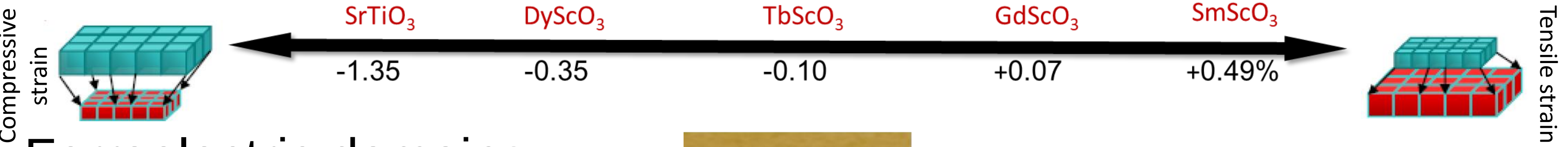


Each $P_i^{\pm}$:
3 propagation directions (k_1, k_2, k_3)



Sosnowska *et al.*, J. Phys. C: Solid State Phys. **15**, 4835 (1982)
Lebeugle *et al.*, Phys. Rev. Lett. **100**, 227602 (2008)

Let's play with strain: Epitaxial BiFeO3/SrRuO3//Substrates



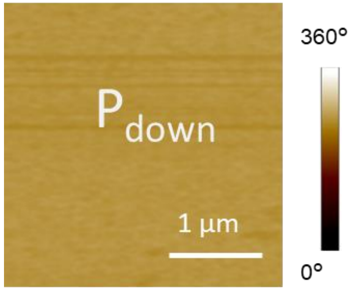
Compressive strain

$SrTiO_3$	$DyScO_3$	$TbScO_3$	$GdScO_3$	$SmScO_3$
-1.35	-0.35	-0.10	+0.07	+0.49%

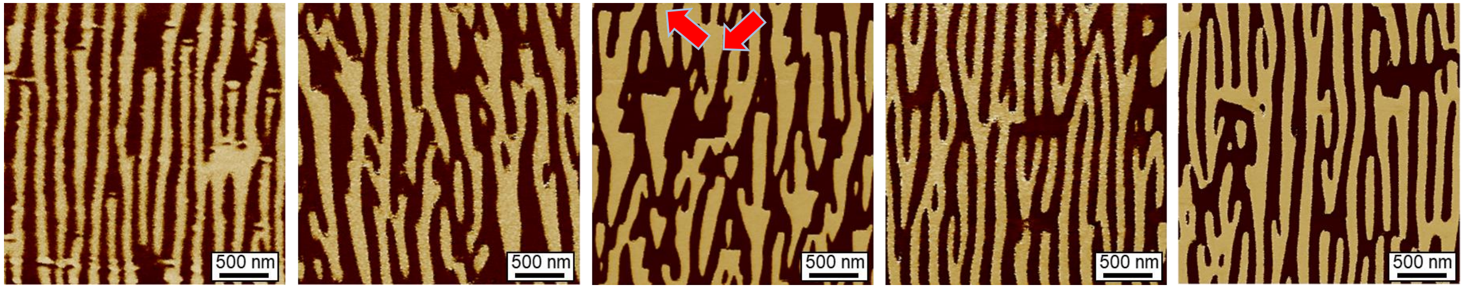
Tensile strain

Ferroelectric domains

Out of Plane PFM



In Plane PFM

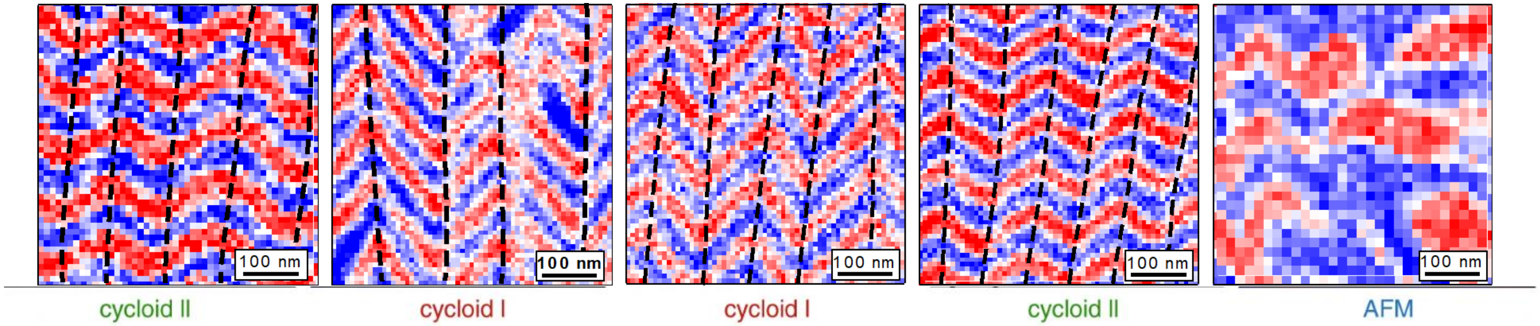


Only two ferroelectric domains in all samples (71° domain walls)

Antiferromagnetic domains

Haykal Nat. Com. 2020

SNVM

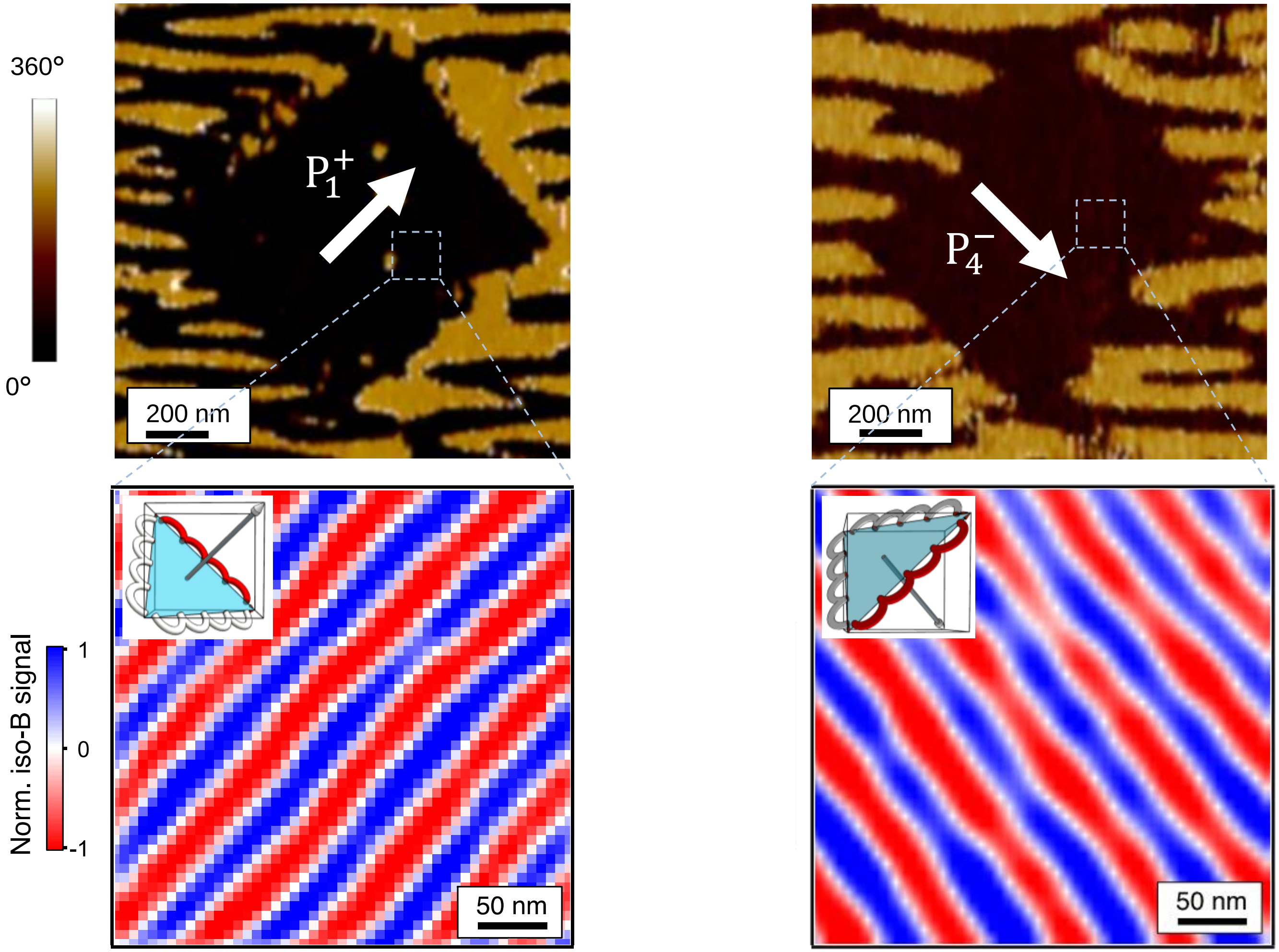


cycloid II · cycloid I · cycloid I · cycloid II · AFM

One Ferroelectric domain ⇔ A single Antiferromagnetic domain

Ferroelectric manipulation of the antiferromagnetic order

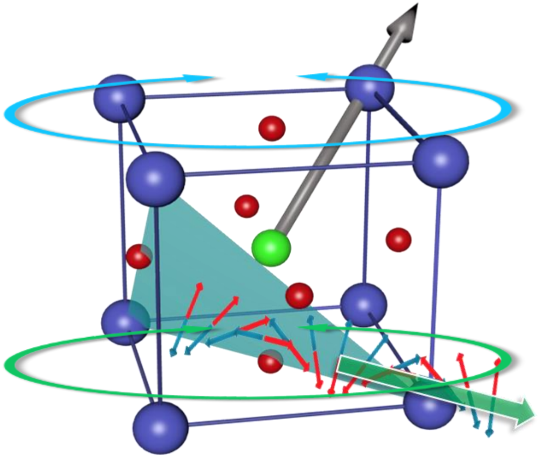
$BiFeO_3/SrRuO_3//DyScO_3$

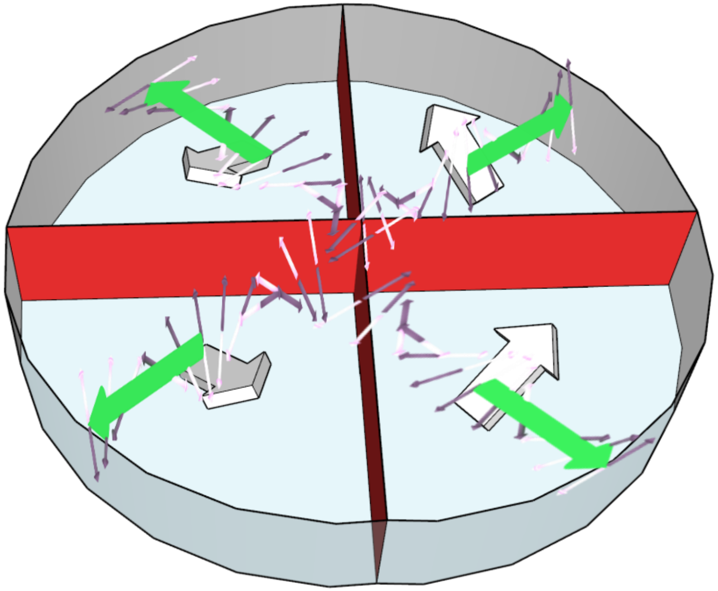


Gross *et al.*, *Nature* (2017)

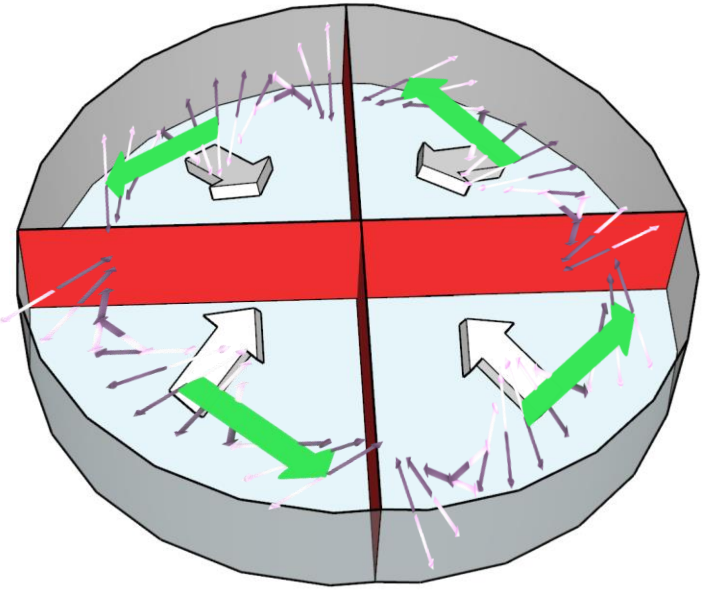
Manipulation of the ferroelectric state ⇨ manipulation of the AF state

Manipulation of the AF order: crafting new AF configurations ?





Polar vortices



Center domains

Antiferromagnetic skyrmions ?

AFM : Beyond topography

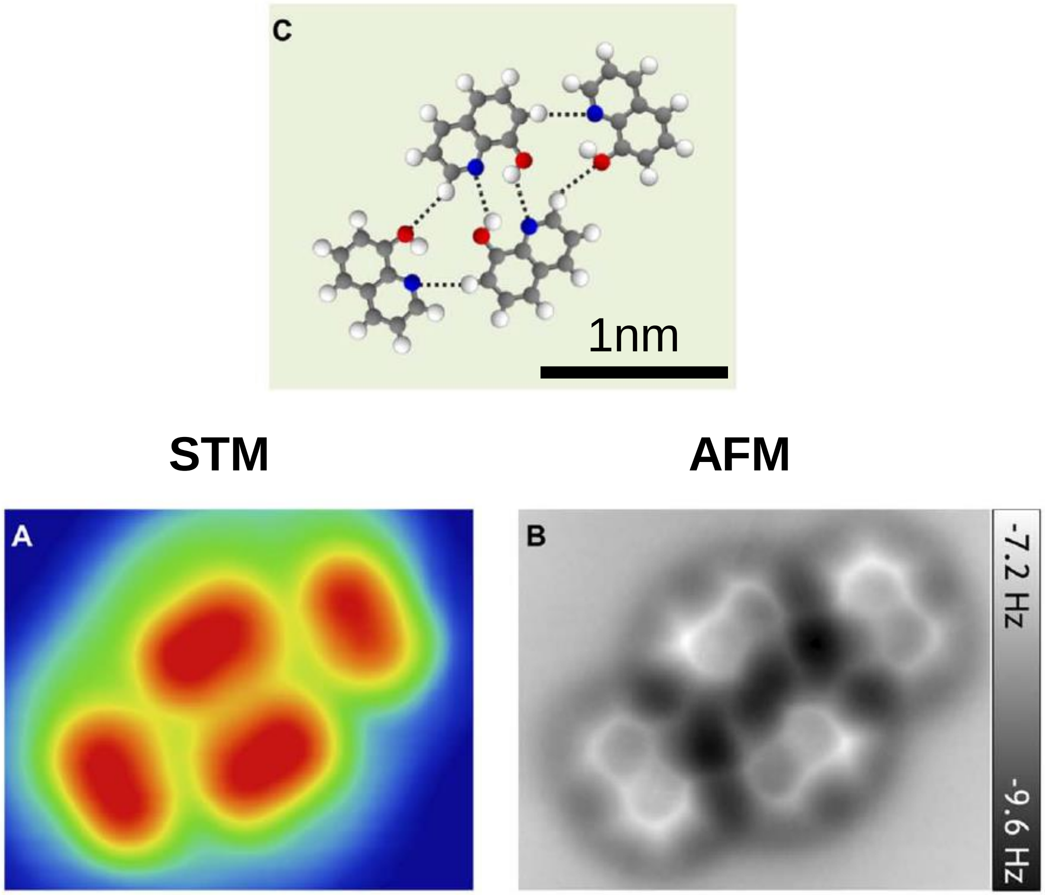
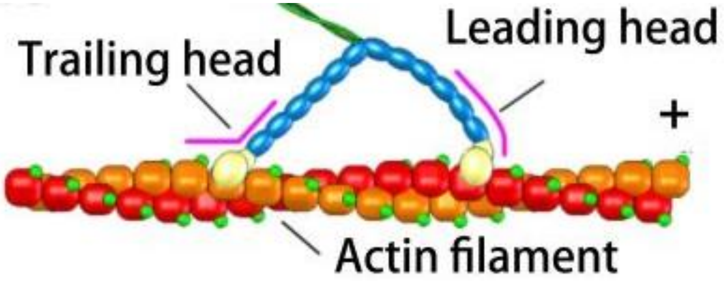


FIG. 52. STM and AFM measurements of 8-hydroxyquinoline (8-hq) assembled clusters on Cu(111).[269] (a) Constant-current STM image (2.5×2 nm^2, $V = -100$ mV, $I = 100$ pA). (b) Constant-height frequency shift image (2.5×2 nm^2, $V = 0$ V, $A = 100$ pm, $f_0 = 27.0$ kHz, $k = 1800$ N/m). (c) The corresponding structure model. The dashed lines refer to the intermolecular H-bonds. Reprinted with permission from X. Qiu. Copyright Xiaohui Qiu, Beijing.

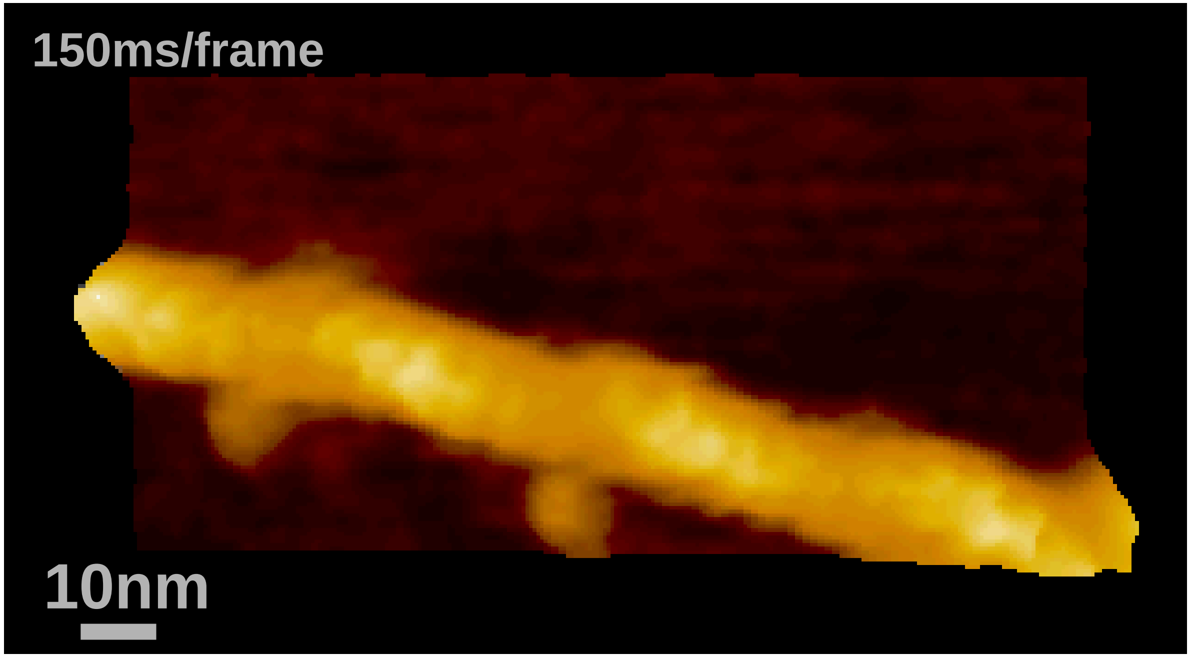
J. Zhang *et al.* “Real-space identification of intermolecular bonding with atomic force microscopy,” Science **342**, 611 (2013).

Franz J. Giessibl, Rev. Sci. Instrum. **90**, 011101 (2019)

AFM : Beyond topography



Myosin V (M5): M5 is one of motor proteins that function as cargo transporters in the cell. Single molecules of M5 move along actin filaments over a long distance.



Kodera *et al, Nature* 2010

International School of Oxide Electronics 2023 – Cargèse, Corsica

Thank you