Advanced scanning probe microscopy

Outline

Scanning Tunneling Microscopy - STM
- How does it work

Atomic Force Microscopy - AFM
- How does it work

Contact mode
- Topography
- Piezoresponse Force Microscopy - PFM
- Conductive Atomic Force Microscopy - CAFM
- Friction mode AFM
- Tomographic Atomic Force Microscopy - TAFM

Non-contact mode
- Topography
- Magnetic Force Microscopy - MFM
- Scanning Capacitance Microscopy - SCM
- Electrostatic Force Microscopy - EFM
- Kelvin Probe Force Microscopy - KPFM

Faculty of Science - Department of Quantum Matter Physics
Celine.Lichtensteiger@unige.ch

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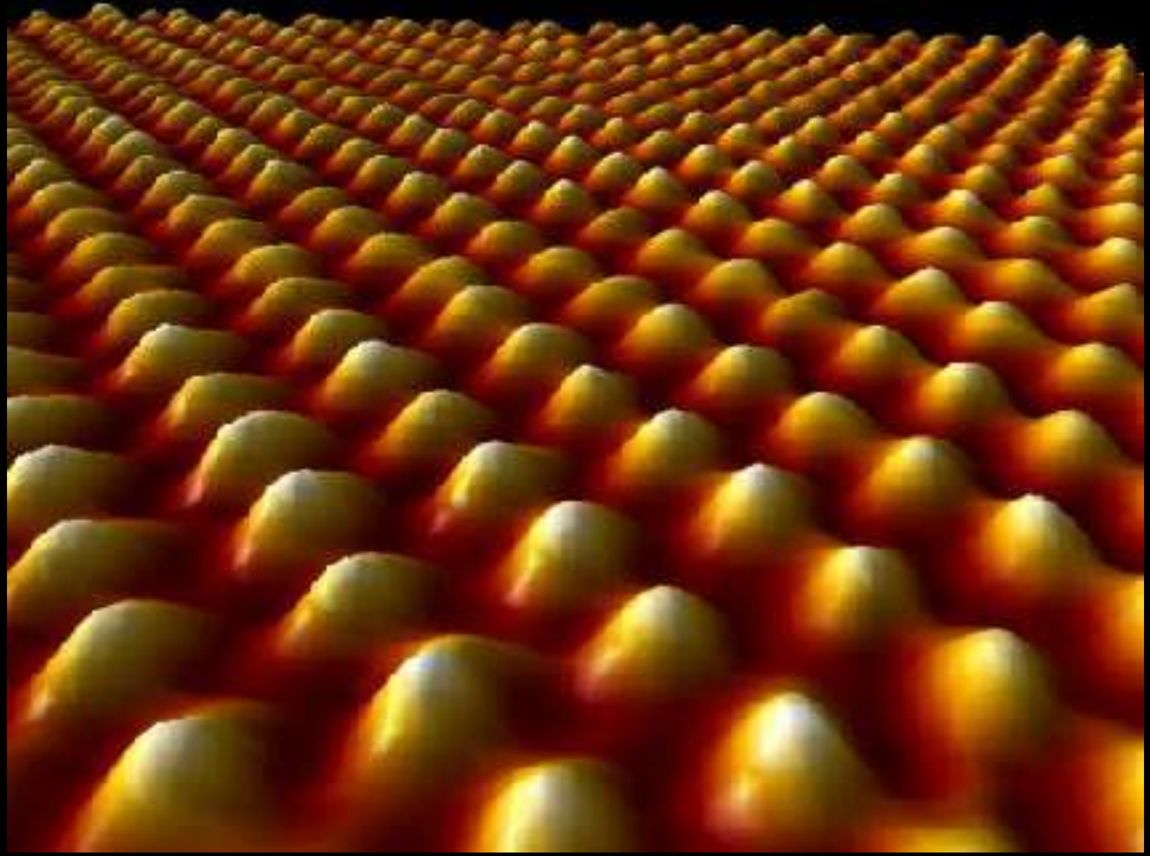
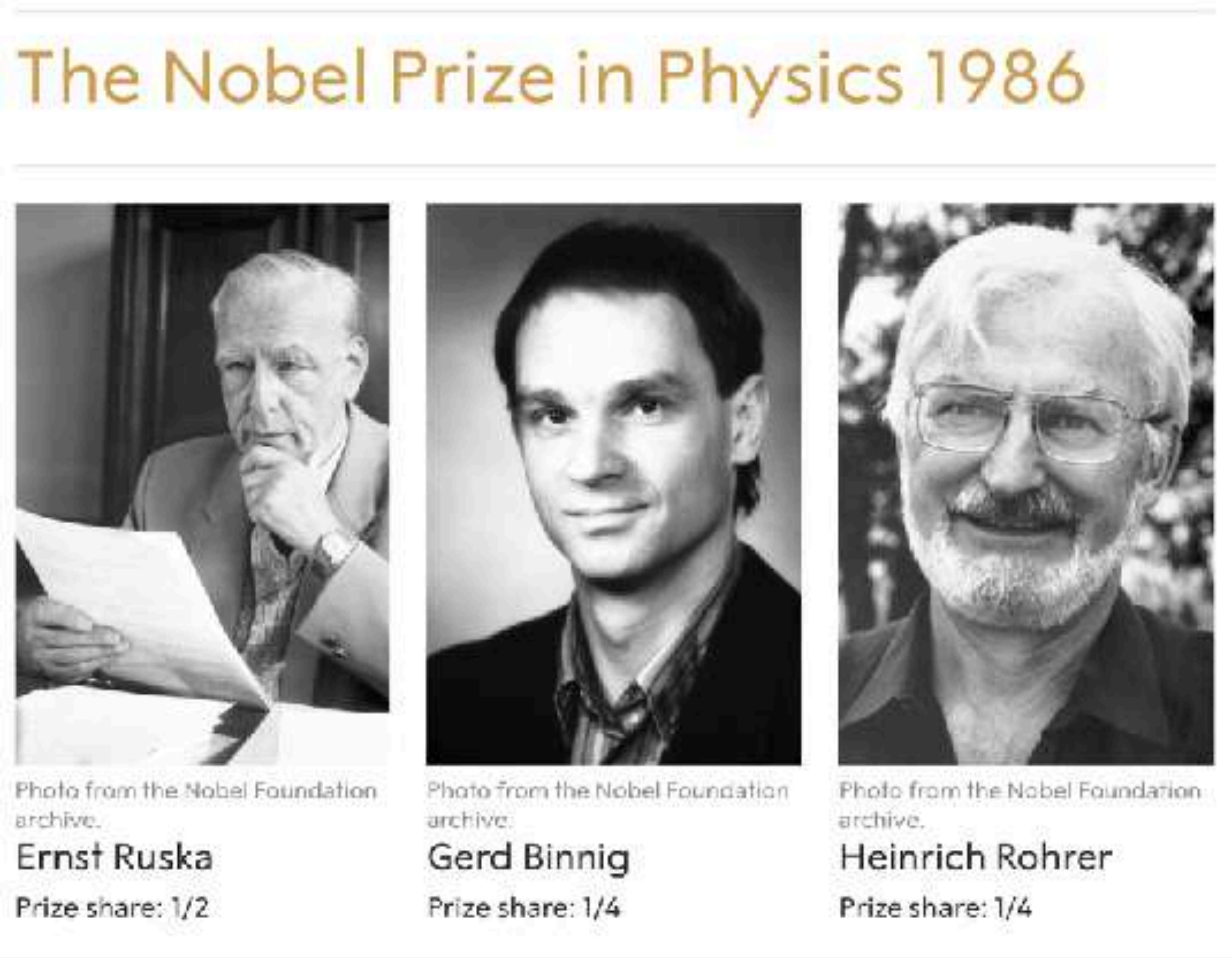
1981: invention of the Scanning Tunneling Microscope (STM)

Heinrich Rohrer and Gerd Binnig (IBM Zürich)





The Nobel Prize in Physics 1986

Photo from the Nobel Foundation archive.
Ernst Ruska
Prize share: 1/2

Photo from the Nobel Foundation archive.
Gerd Binnig
Prize share: 1/4

Photo from the Nobel Foundation archive.
Heinrich Rohrer
Prize share: 1/4

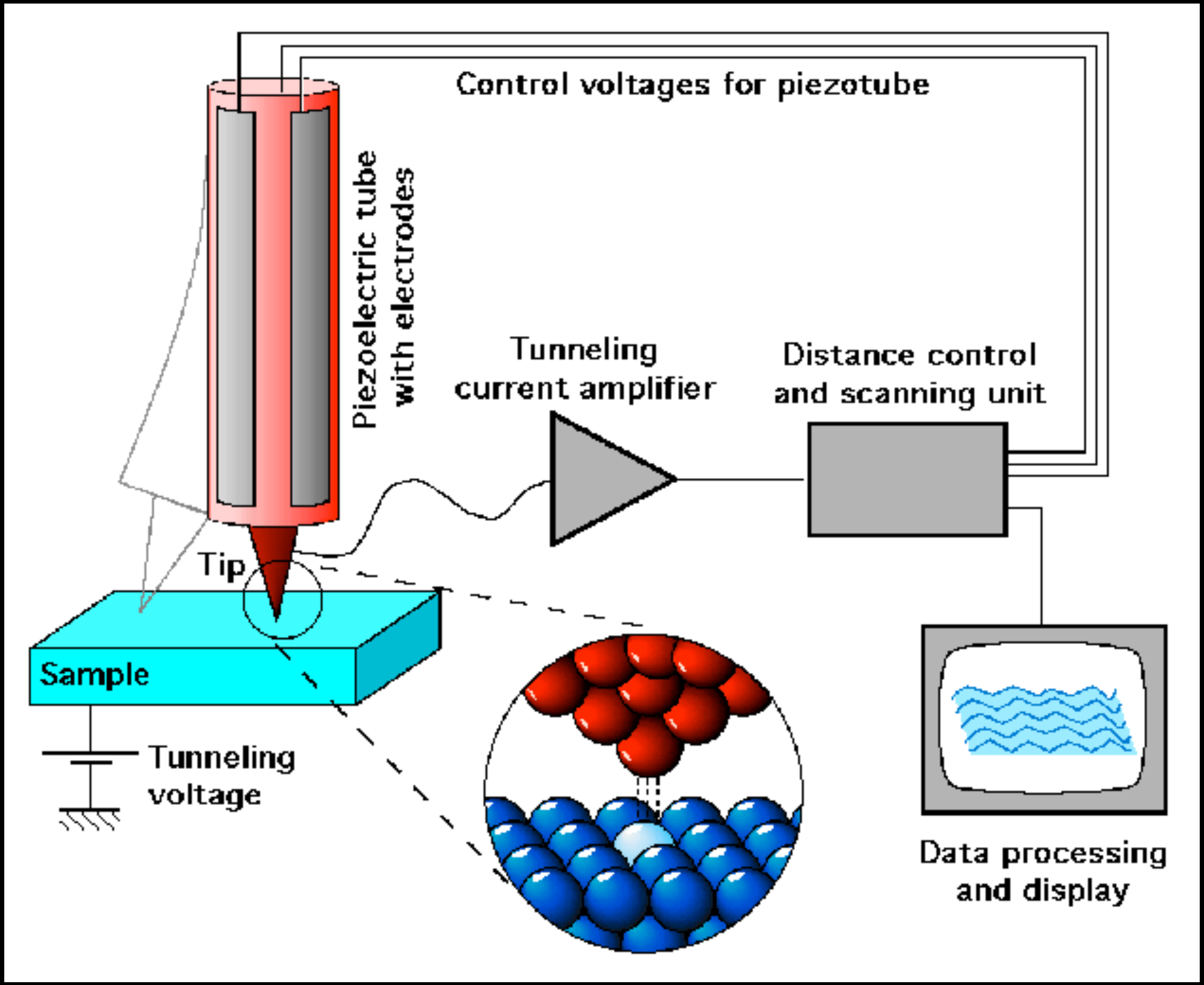
One half awarded to:

Ernst Ruska
"*for his fundamental work in electron optics, and for the design of the first electron microscope*"

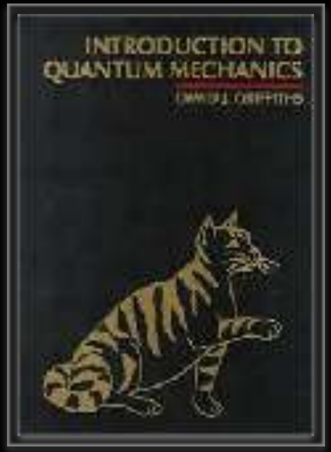
The other half jointly to:

Gerd Binnig and Heinrich Rohrer
"*for their design of the scanning tunneling microscope*"

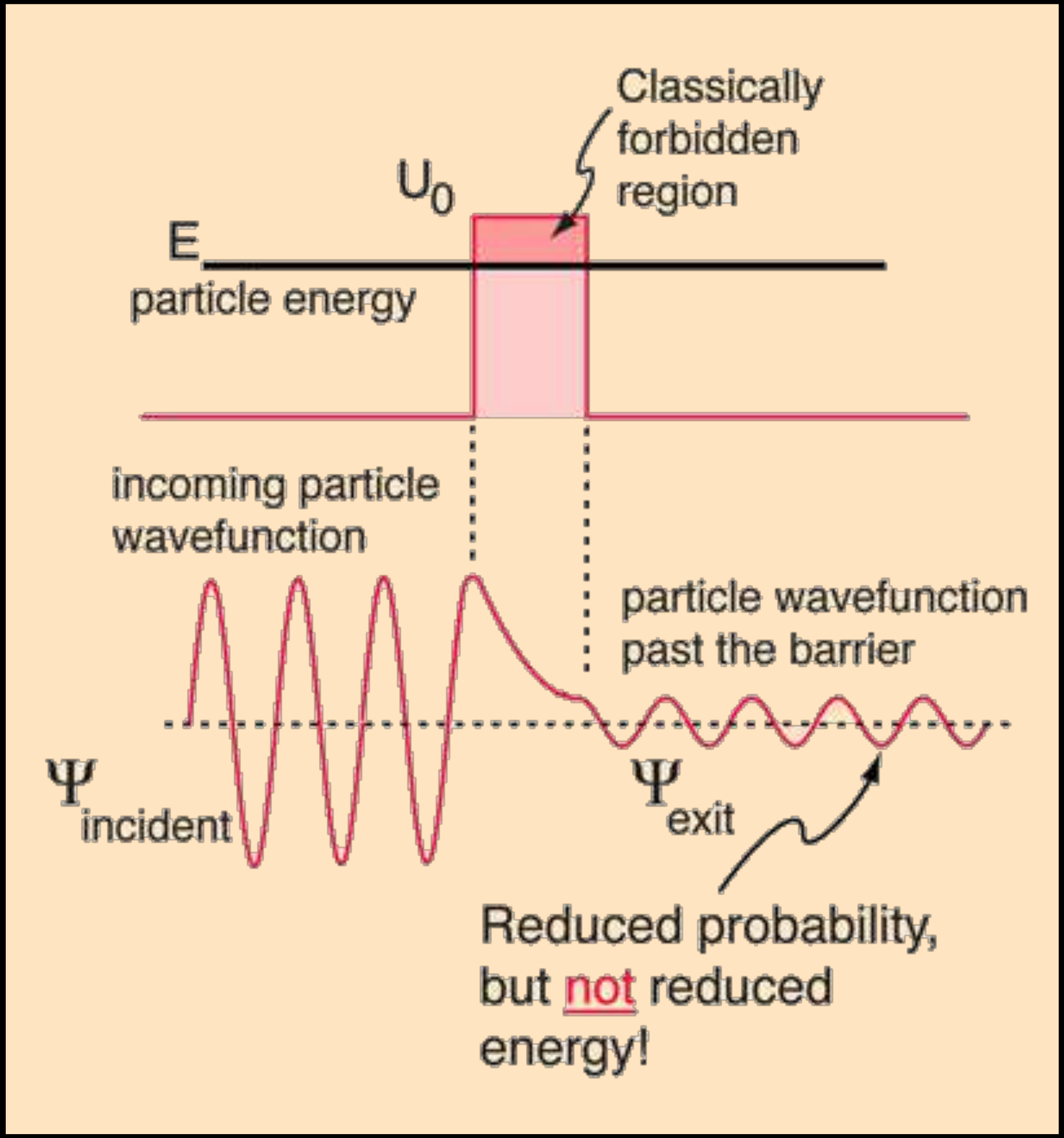
How does STM work?



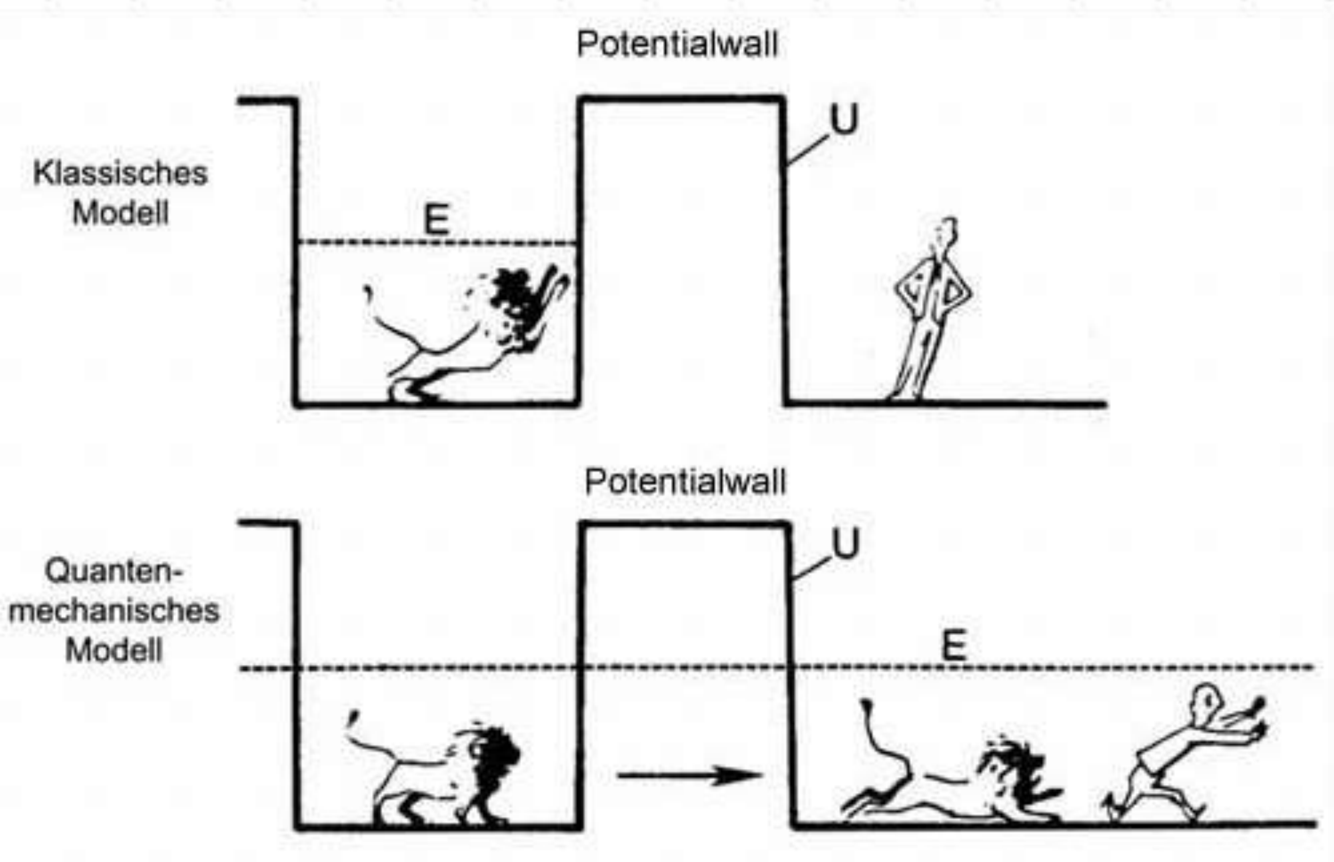
Quantum tunneling



Introduction to quantum mechanics
David J. Griffiths

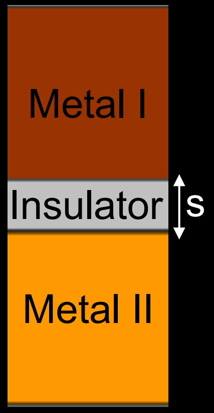


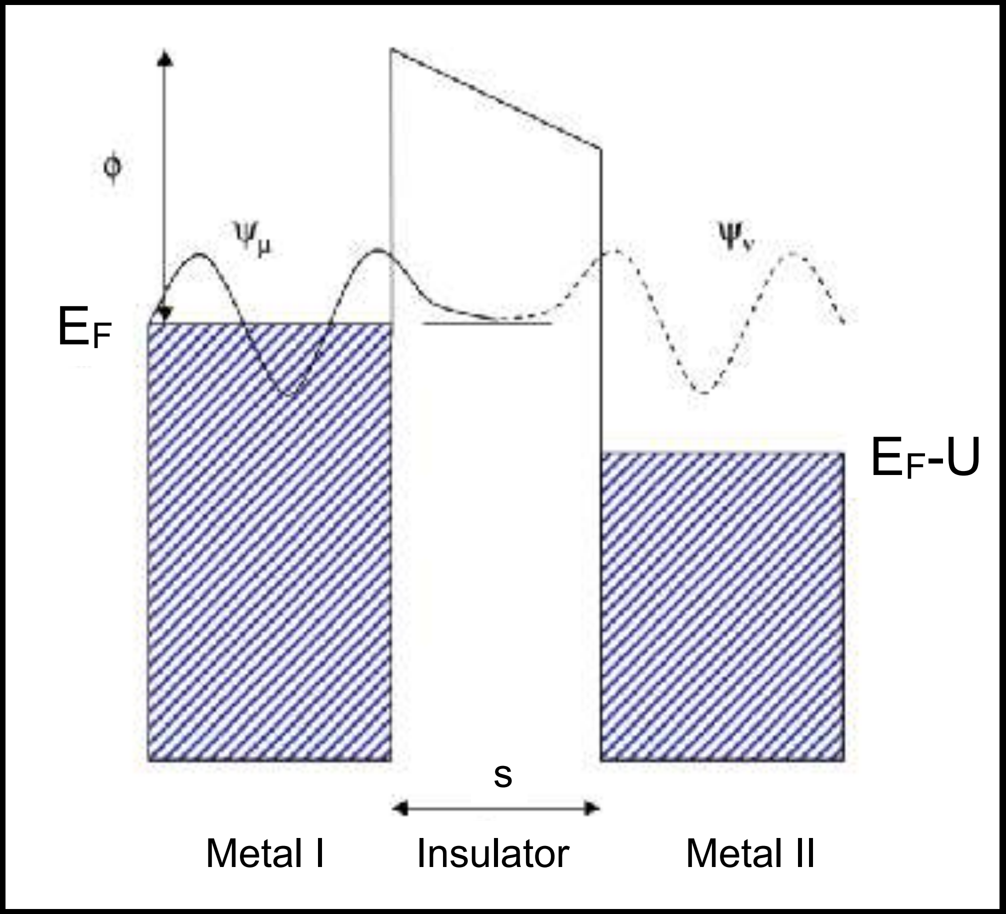
http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/barr.html



How does STM work?

Tunneling current





$$I = f(U)\exp\left(-A\sqrt{\phi}\, s\right)$$

$f(U)$ depends on electronic structure of sample and tip (for free electrons f(U)~U)
U: externally applied voltage

$$A = 2\sqrt{\frac{2m}{\hbar^2}} = 1.025\ \text{Å}^{-1}\text{eV}^{-1/2}$$

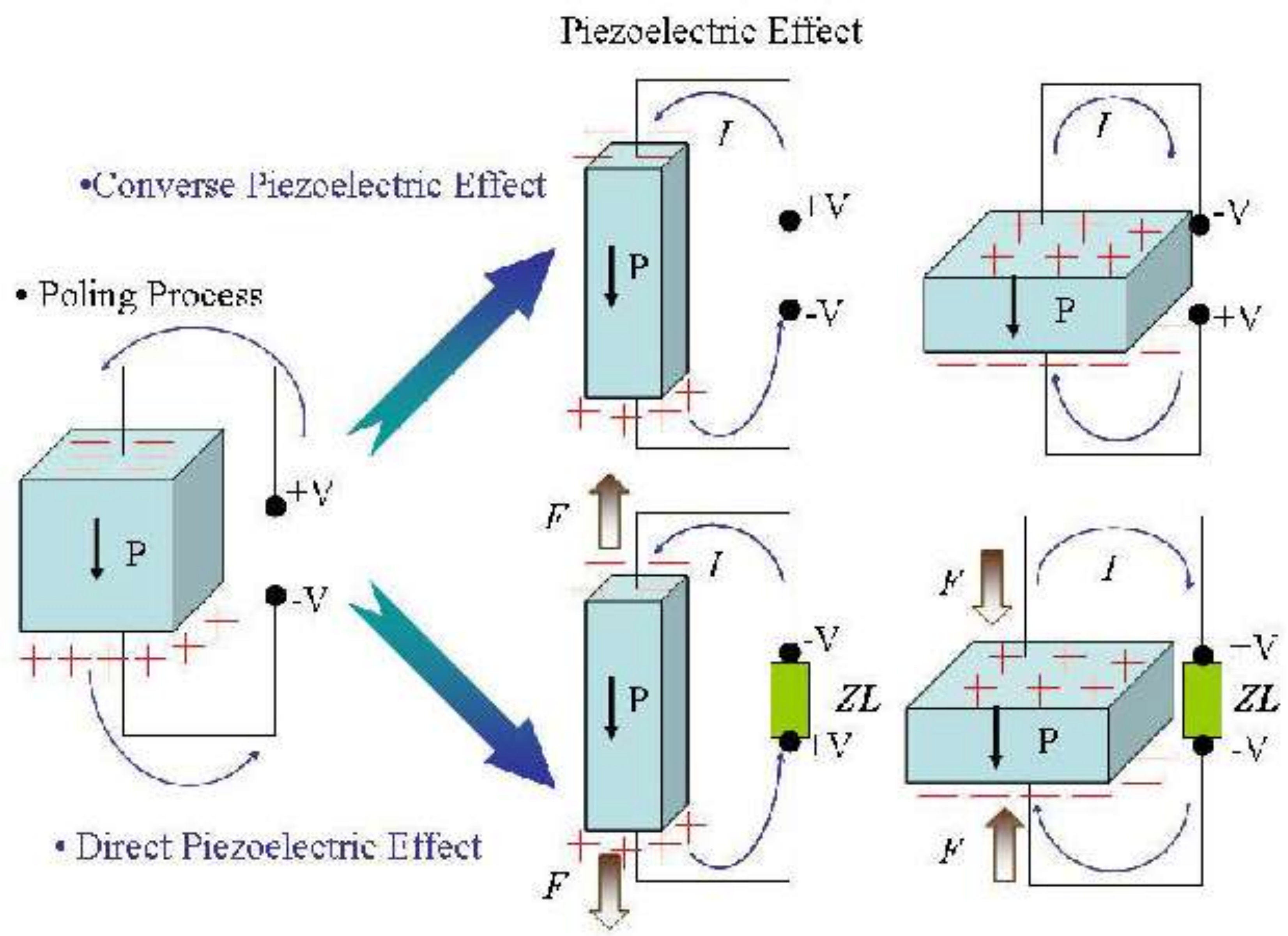
$$\phi \approx \frac{\phi_1 + \phi_2}{2}$$ work functions of metal I and metal II

The tunnel current depends **exponentially** on the distance s.
For typical work functions ϕ=4.5eV, the current changes by ~1 order of magnitude when the distance changes by 1Å.

J. Frenkel, *Phys. Rev.* **B 36**, 1604 (1930)

How does STM work?

Precise motion control by piezoelectric actuators

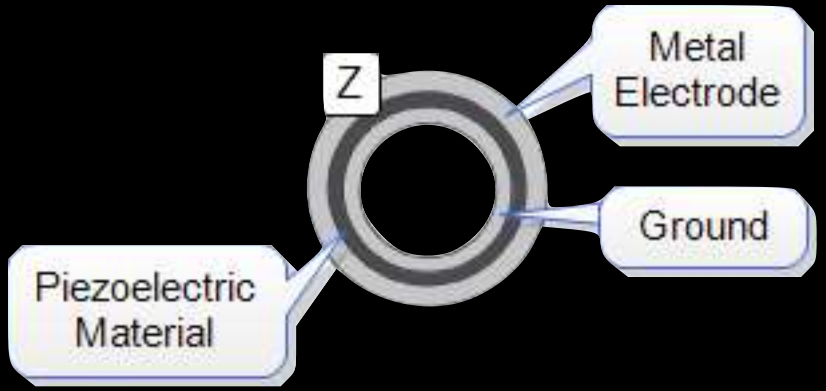


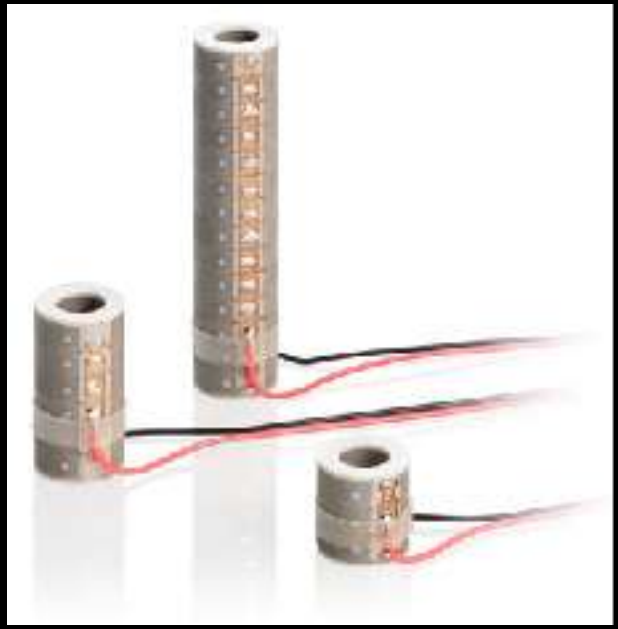
strain $X_j = d_{ij} E_i$ electric field

How does STM work?

Precise motion control by piezoelectric actuators

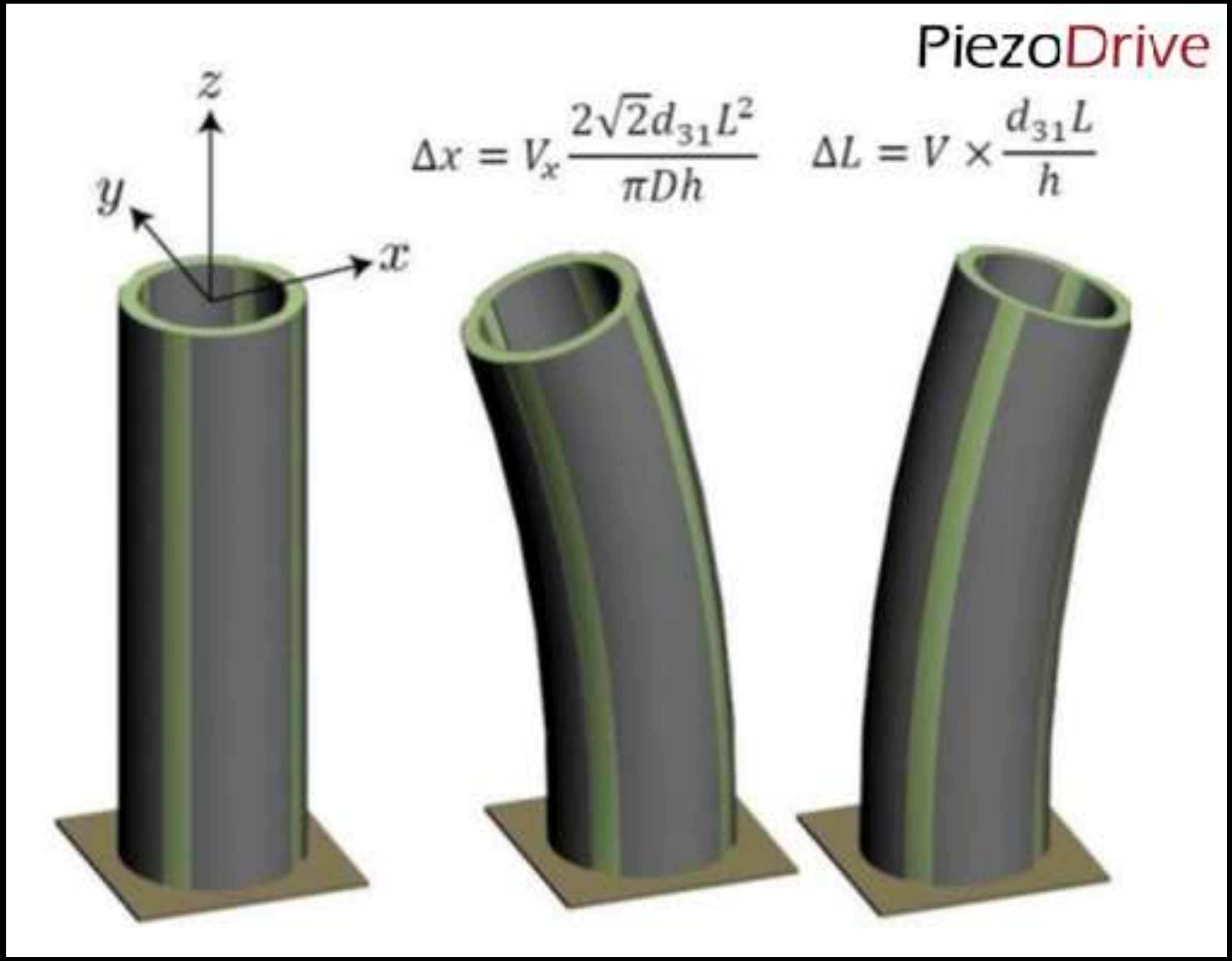
High voltage control of scanner displacement





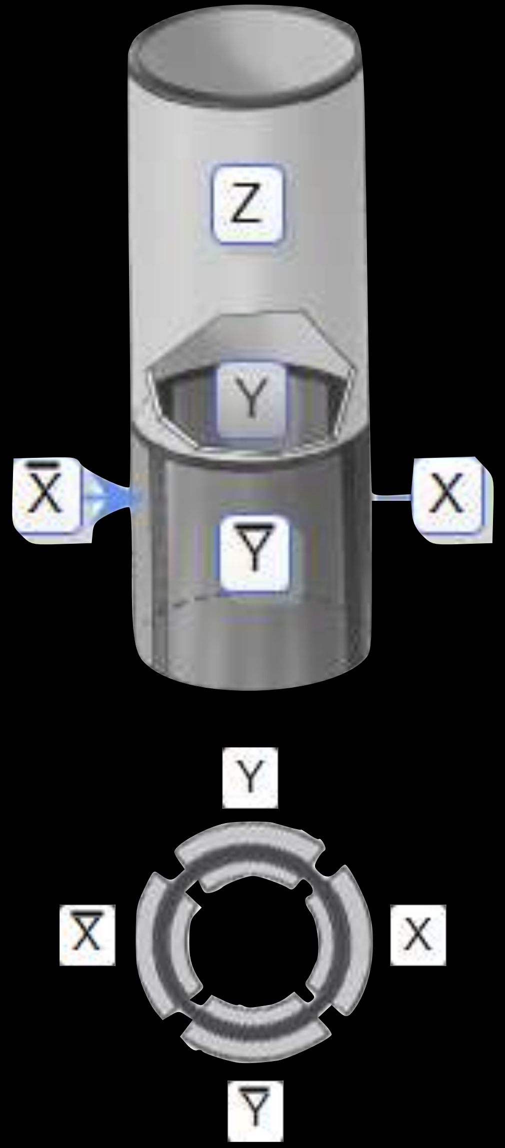
Piezocolumns by Pi-USA

d_{31}: piezoelectric strain constant
L: tube length
D: outside diameter
h: tube thickness



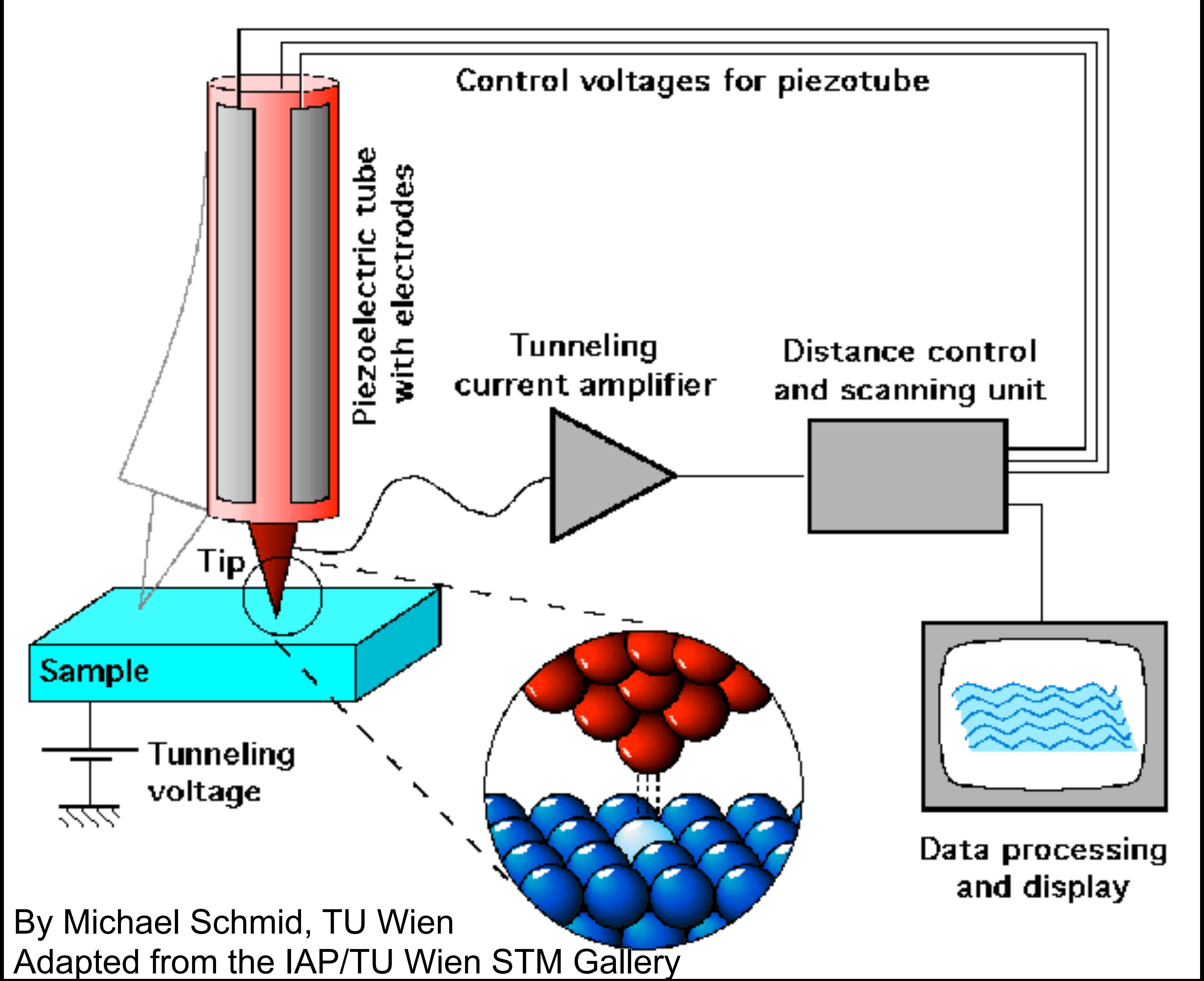
$$\Delta x = V_x \frac{2\sqrt{2}d_{31}L^2}{\pi D h} \qquad \Delta L = V \times \frac{d_{31}L}{h}$$

https://www.piezodrive.com/actuators/piezoelectric-tube-scanners/



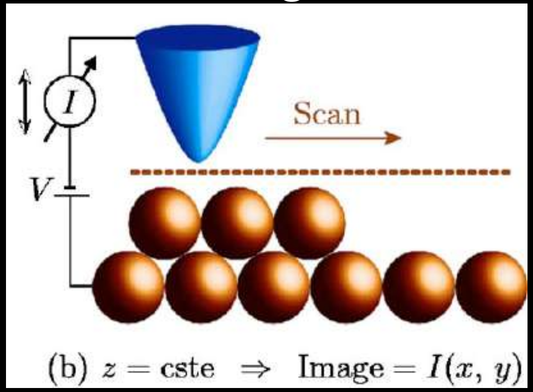
Need to consider scanner nonlinearities, thermal drift, and other sources of image distortion

How does STM work?

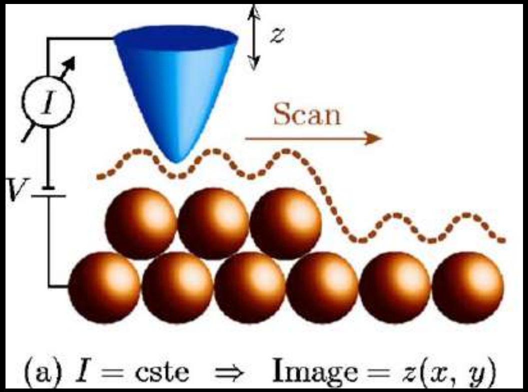


By Michael Schmid, TU Wien
Adapted from the IAP/TU Wien STM Gallery

Constant height:



Constant current:



keywords: tunneling curent piezoelectric tubes feedback loop

Lab equipments

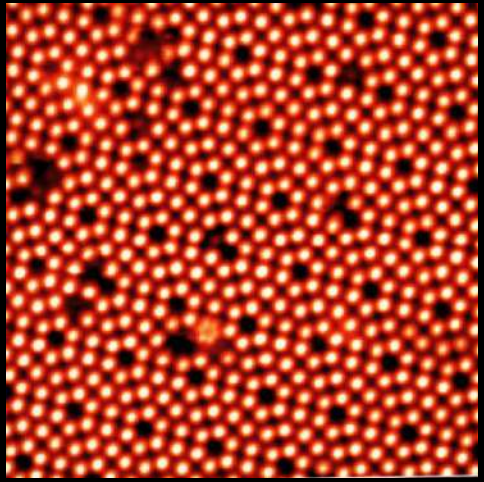
Resolution: 0.1 nm (lateral); 0.01nm (depth)
metallic samples
(UHV environment)
(low temperatures)
small scan range

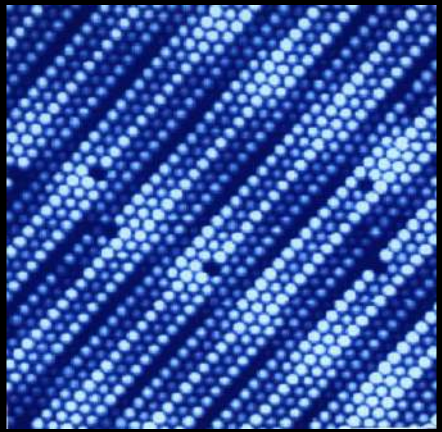
nanosurf

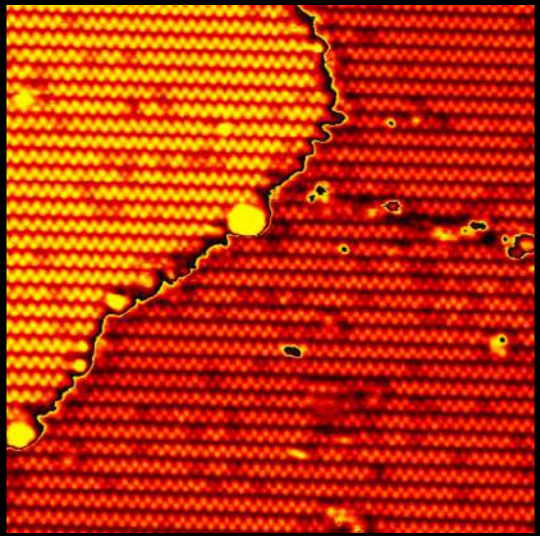
Table top STM

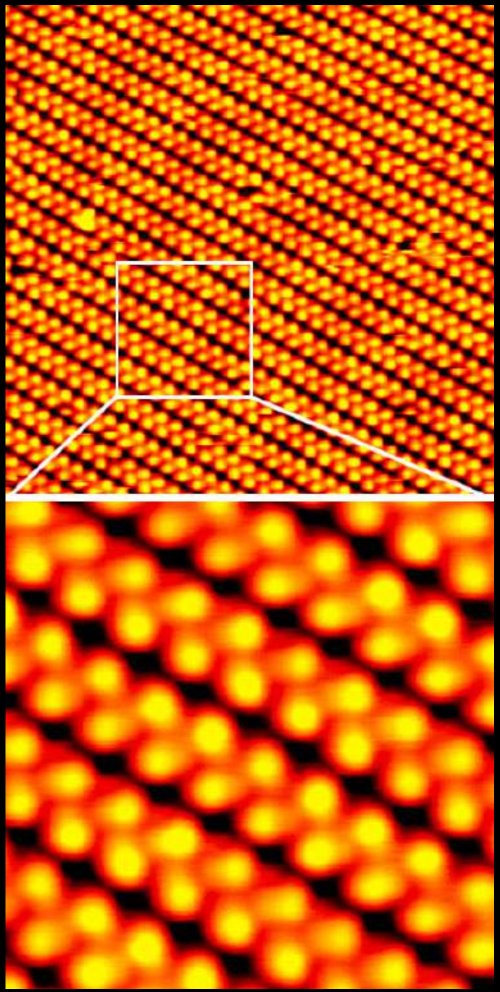
Low temperature Ultra-High vacuum STM
London Centre for Nanotechnology

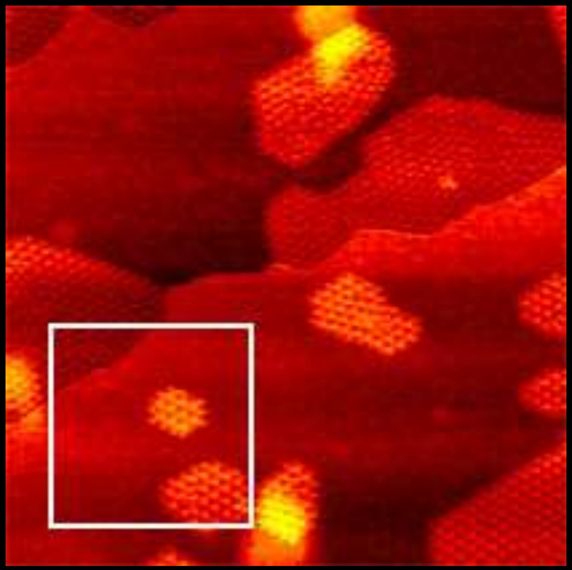
Surface atoms seen by STM


Si(111) 7x7


Pt


Rutile TiO_2 (011)-(2x1)

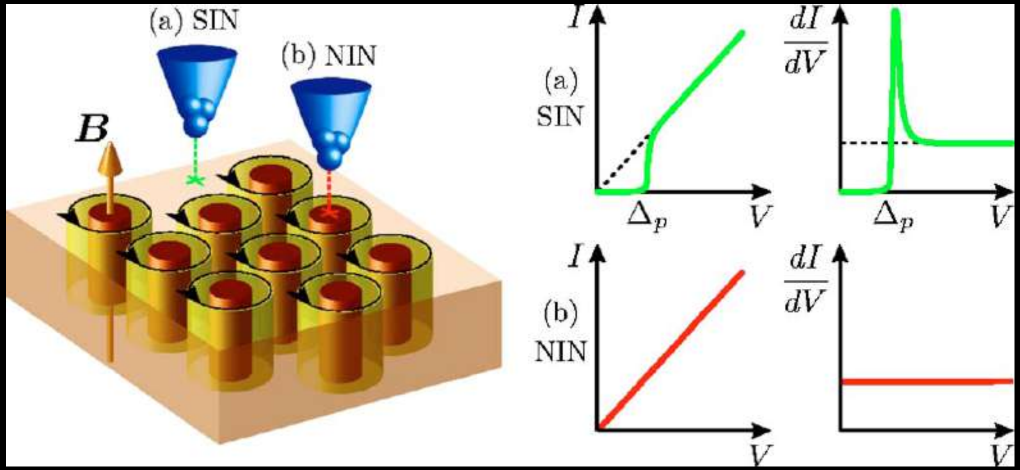

Self-assembly of
Rubrene on Au(111)

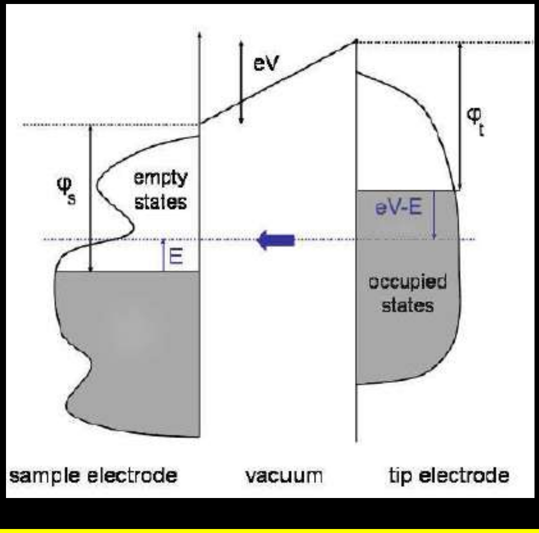

Graphene

Adapted from I. Maggio-Aprile

Scanning Tunneling Spectroscopy - STS

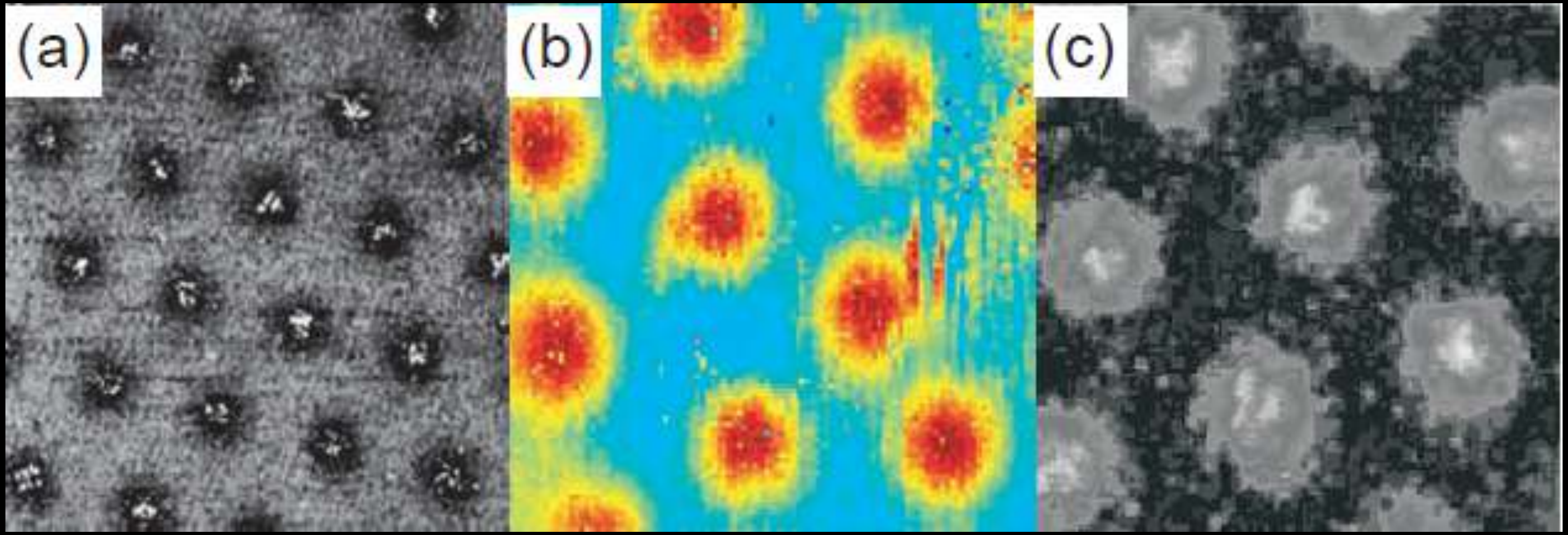
The DOS is a weight factor for the current flow





dI/dV (V) ~ $N_{sample}(eV)$

STS on superconducting material: vortex lattices



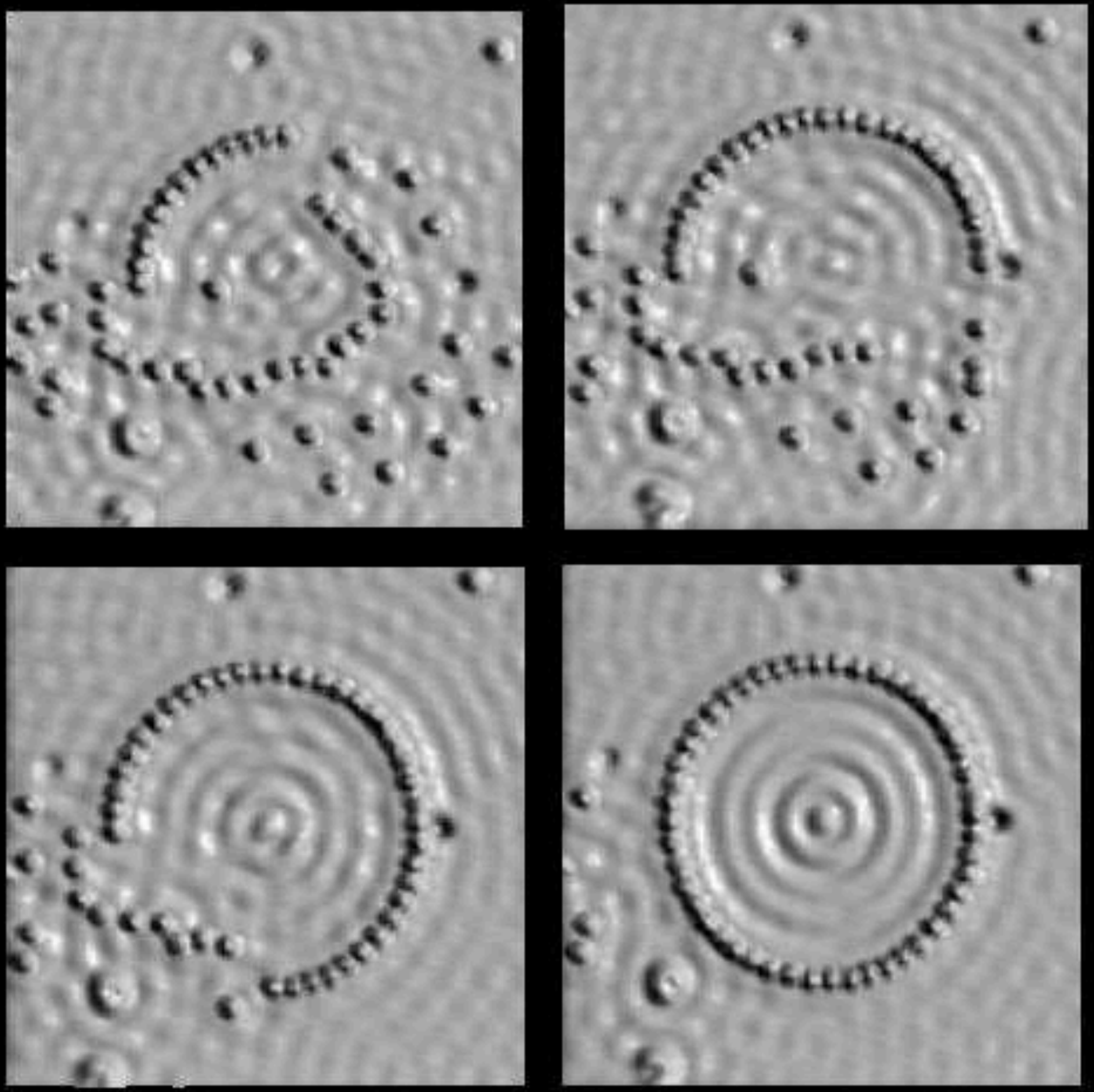
Vortices in YBCO and MgB₂

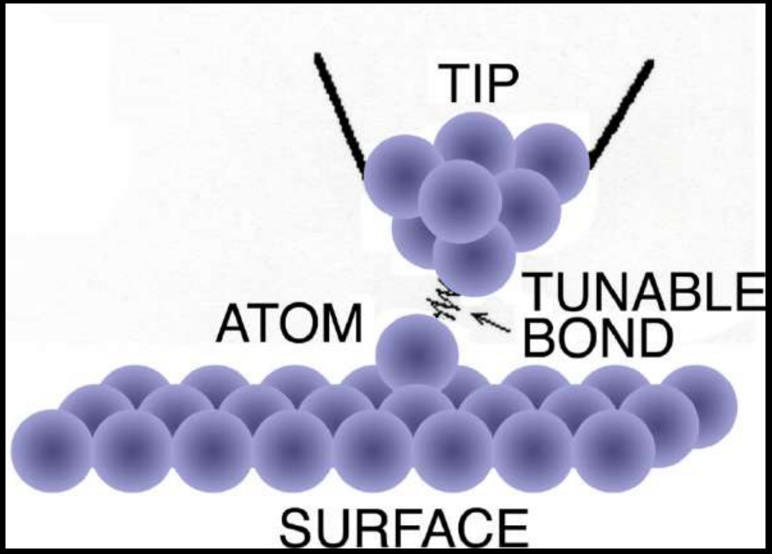
Maggio-Aprile *et al.*, **PRL 1995**, 75

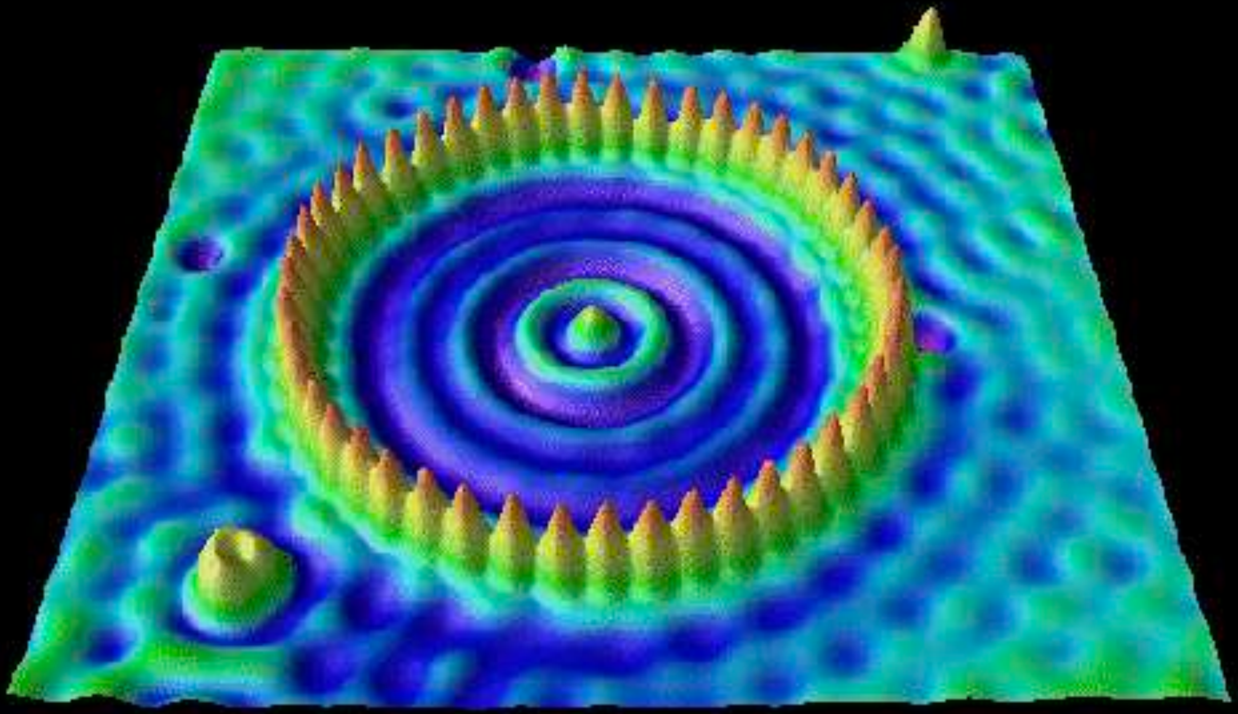
Eskildsen *et al.*, **PRL 2002**, 89

Adapted from I. Maggio-Aprile

Manipulating atoms by STM







Positioning single atoms of Fe on Cu(111)

Eigler et al., **Nature 1990**, 344:524

Imaging standing waves in a two-dimensional electron gas

Crommie, Lutz and Eigler, **Nature 1993**, 363:524

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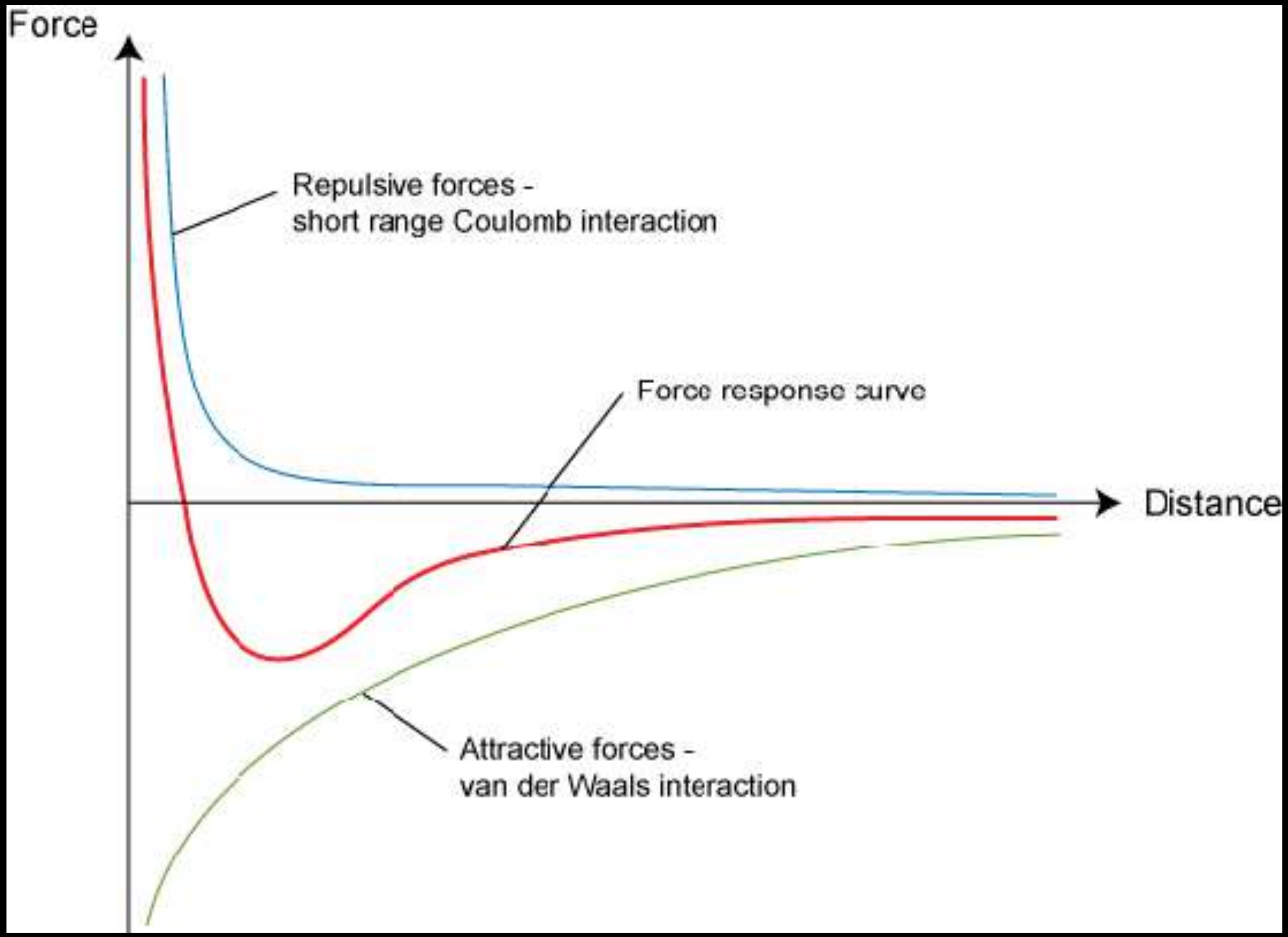
1986: invention of the Atomic Force Microscope (AFM)

Atomic Force Microscope and Method for Imaging Surfaces with Atomic Resolution
G. Binnig, **1986, US Patent** No. 4,724,318

Interaction between a sharp tip and the sample
→ forces

Forces can be measured via displacement of cantilever from its equilibrium position

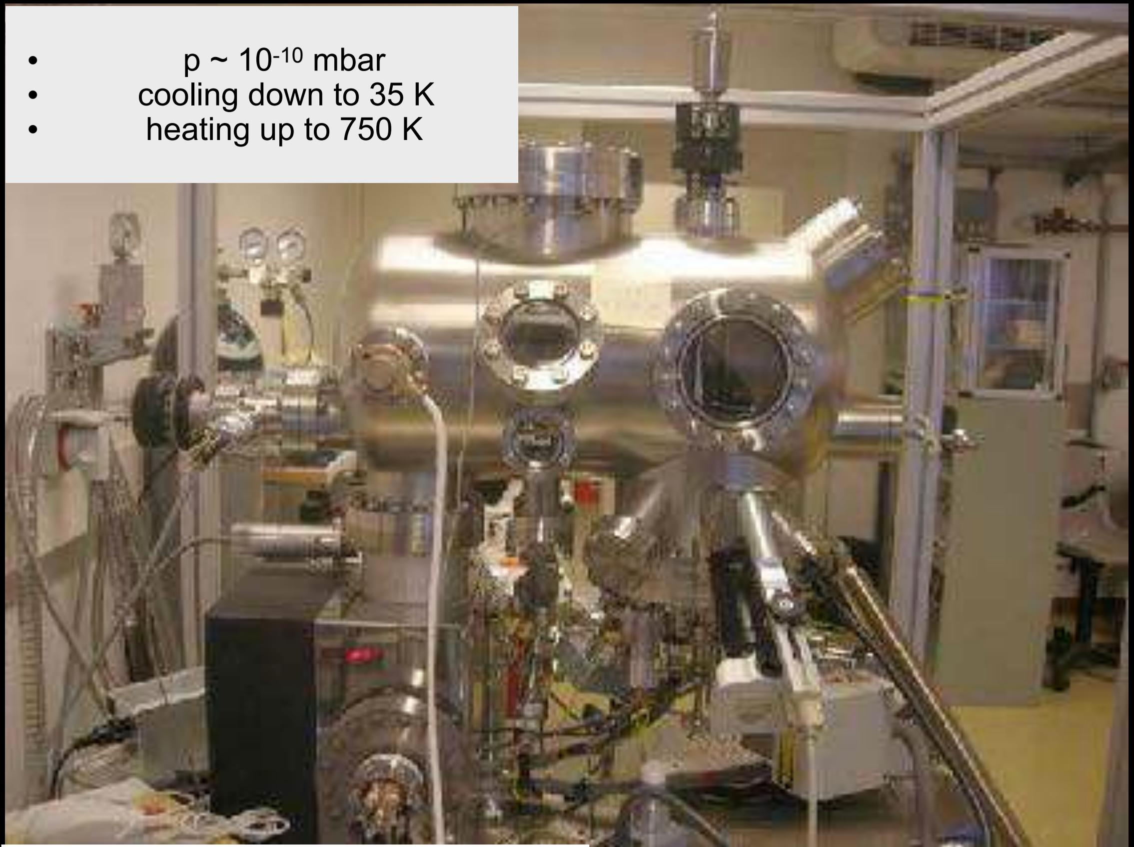


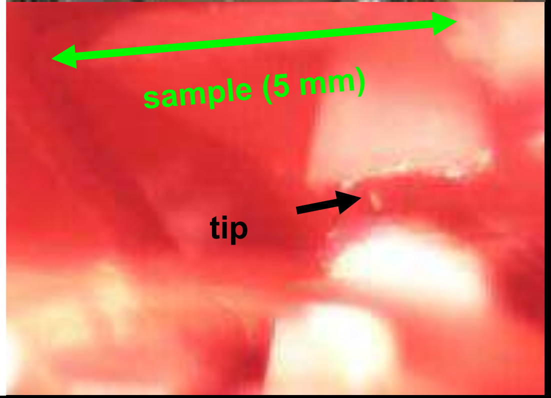
Works for insulating samples as well!

Equipments from Triscone & Paruch labs

Omicron VT AFM/STM Beam Deflection

- p ~ 10^{-10} mbar
- cooling down to 35 K
- heating up to 750 K





Bruker DI3 AFM

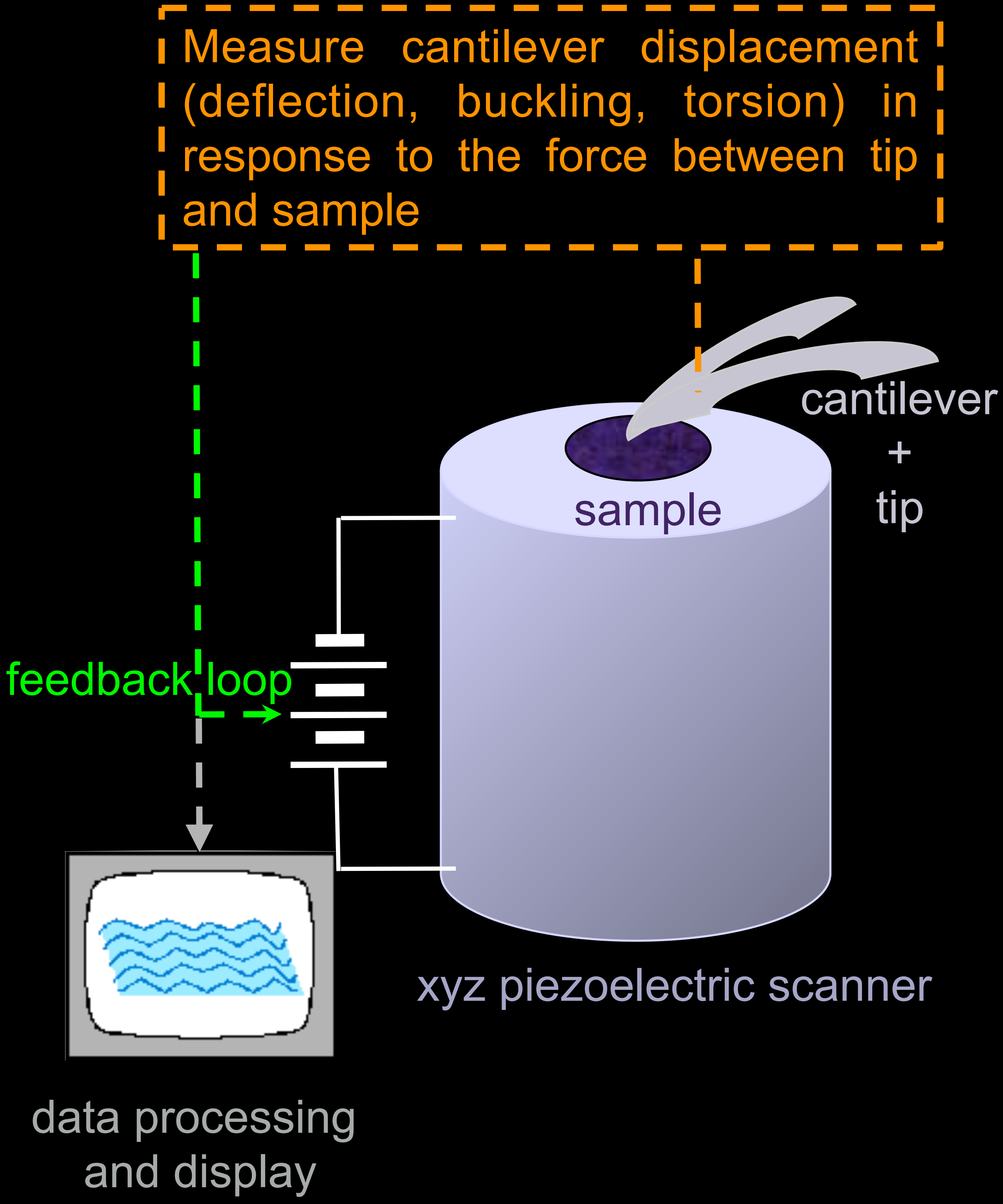
Asylum Cypher AFM

Asylum MFP-3D Infinity AFM

Bruker DI4 AFM

People you might recognise: Jill Guyonnet, Iaroslav Gaponenko, Denver Li, Benedikt Ziegler, Margherita Boselli, Sara Catalano

How does AFM work?



Measure cantilever displacement (deflection, buckling, torsion) in response to the force between tip and sample

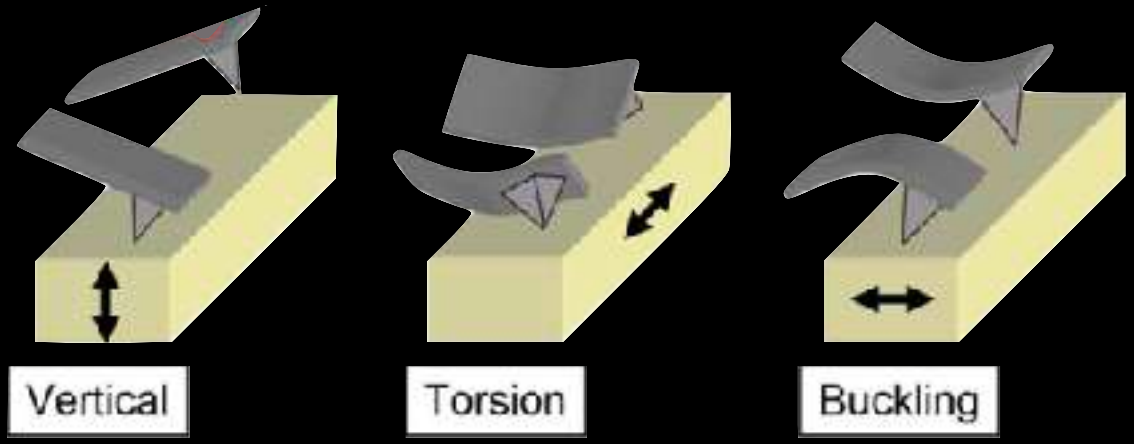
cantilever
+
tip

sample

feedback loop

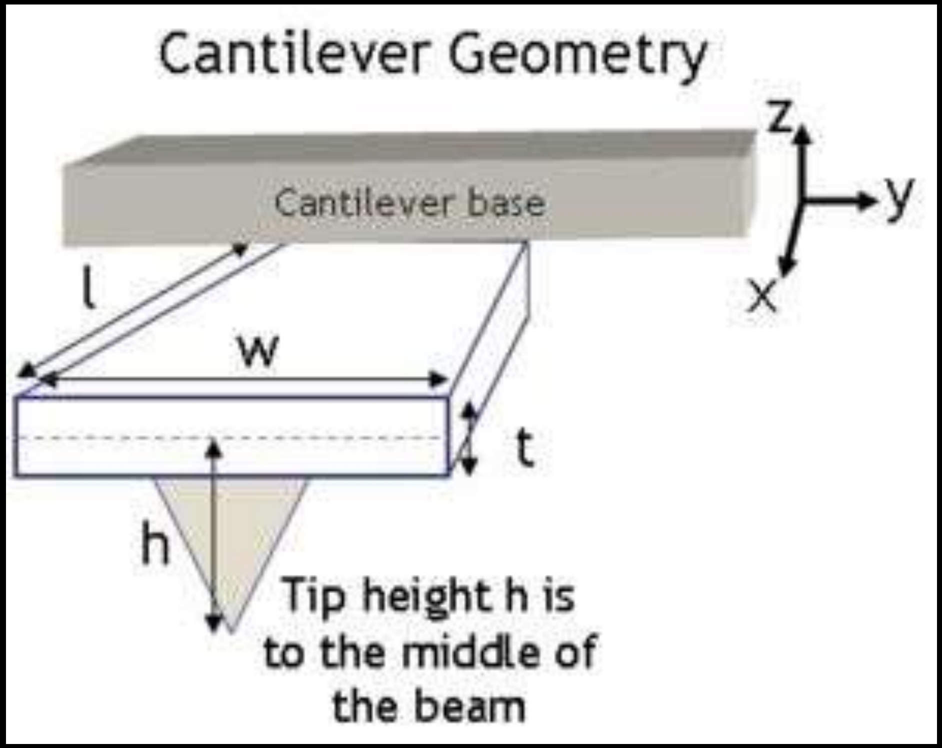
xyz piezoelectric scanner

data processing
and display



Effects of cantilever buckling on vector piezoresponse force microscopy imaging of ferroelectric domains in $BiFeO_3$ nanostructures
Nath, Hong, Klug, Imre, Bedzyk, Katiyar, Auciello, **APL 2010**, 96, 163101

Cantilever response to applied forces



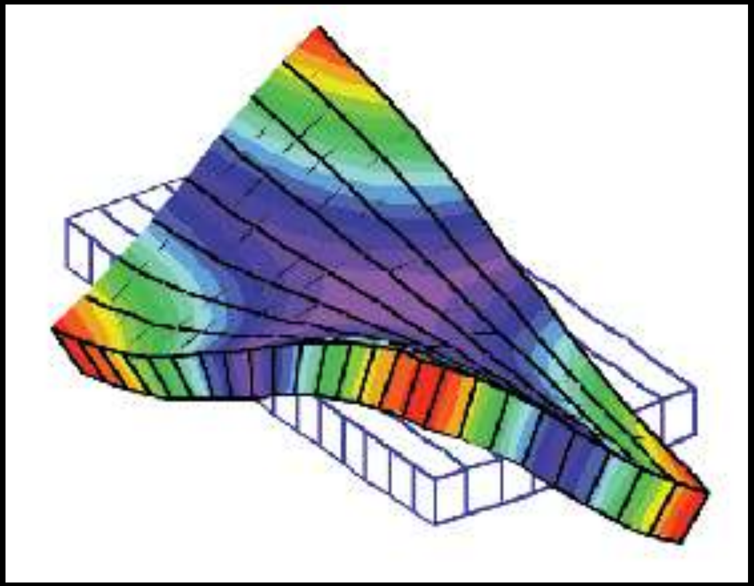
Opensource Textbook of Nanoscience and Nanotechnology

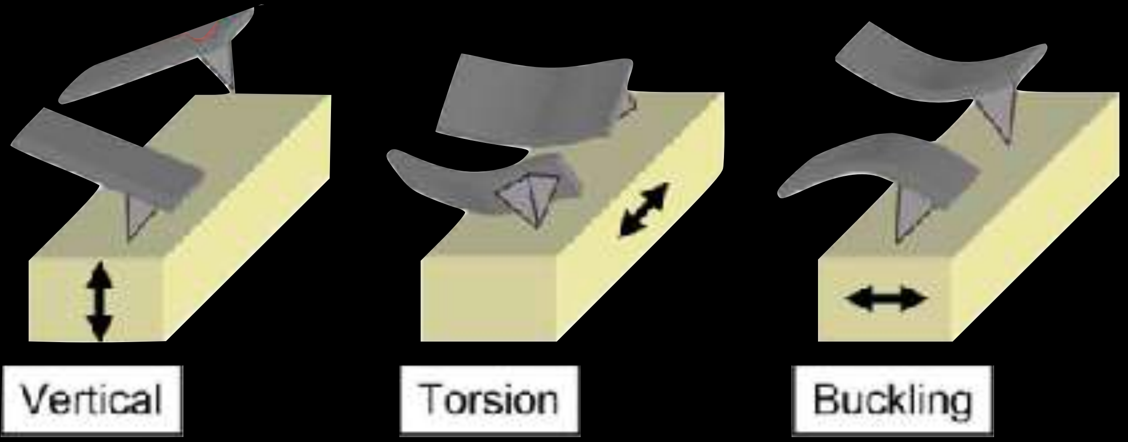
E : Young's modulus
w : cantilever width
l : cantilever length
t : cantilever thickness
G : shear modulus
h: probe height

$$k_N = \frac{E \cdot w}{4}\left(\frac{t}{l}\right)^3$$

$$k_t = \frac{G \cdot w \cdot t^3}{3 \cdot l \cdot h}$$

Jungk *et al.* APL **89,** 043901 (2006)





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Nath, Hong, Klug, Imre, Bedzyk, Katiyar, Auciello, **APL 2010**, 96, 163101

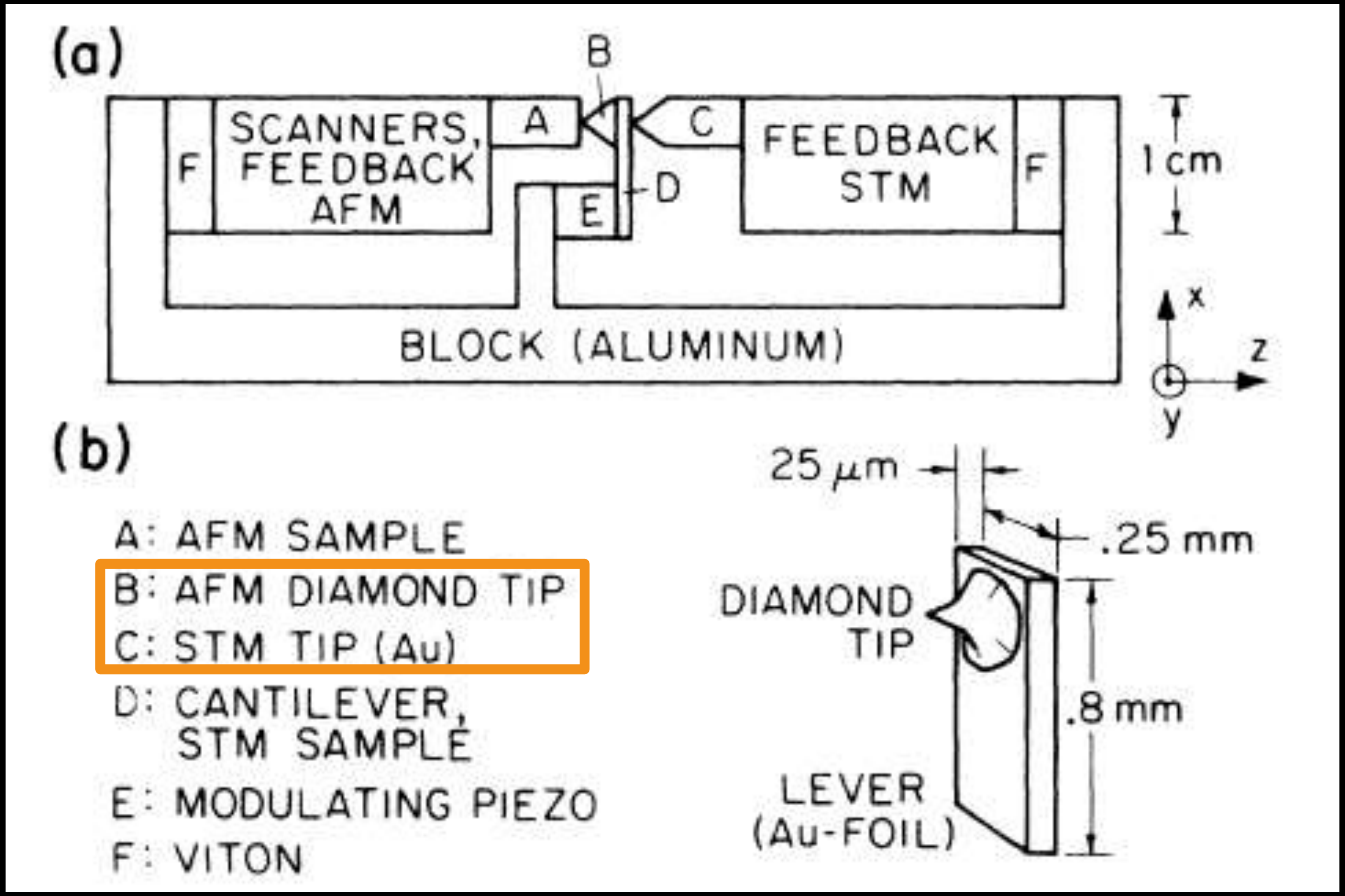
Cantilever responds with vertical deflection, torsion, or buckling

… or some combination thereof

Detecting the cantilever response

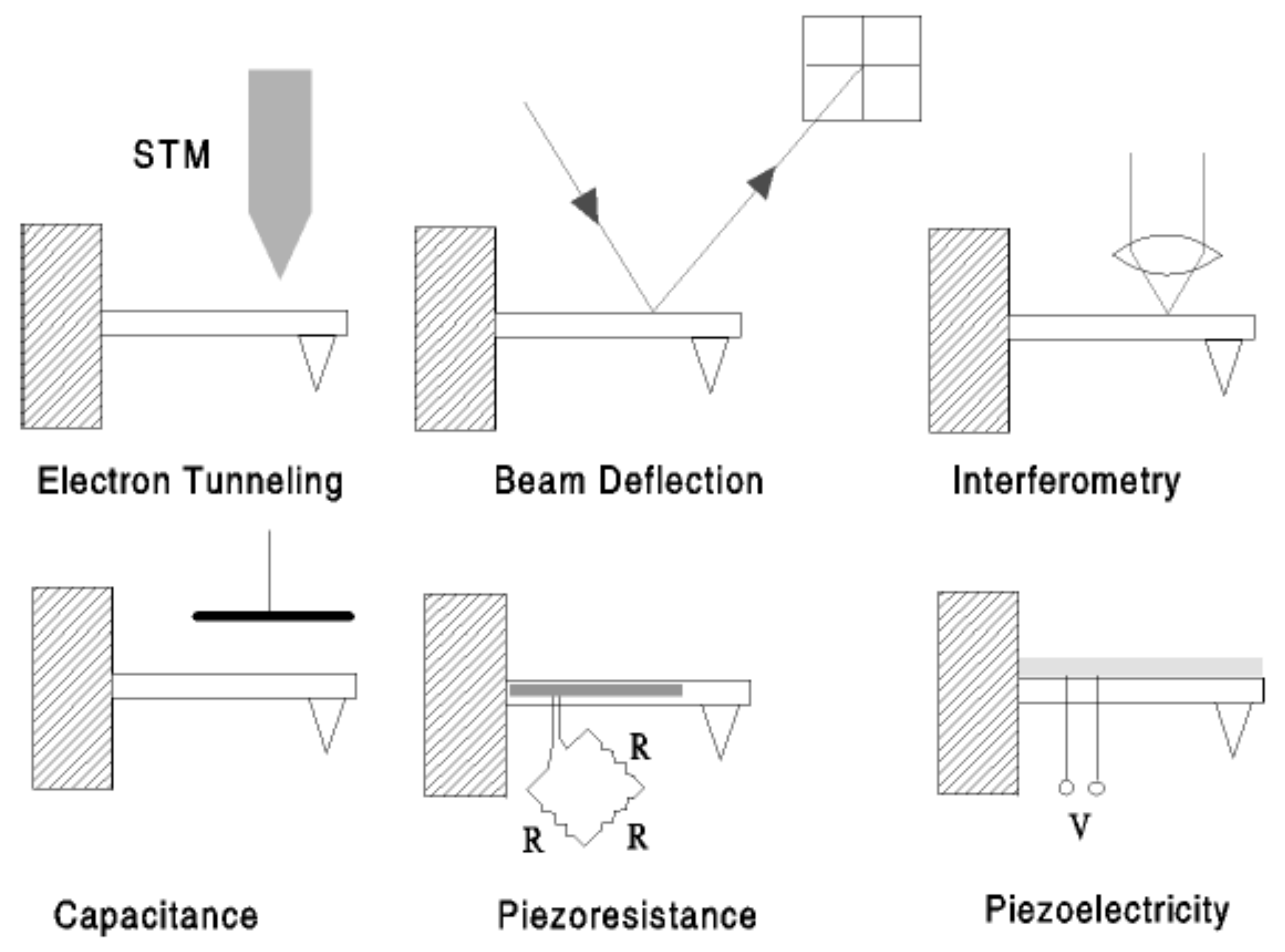
First approach: let’s make things as complicated as possible….

STM detection in first AFM



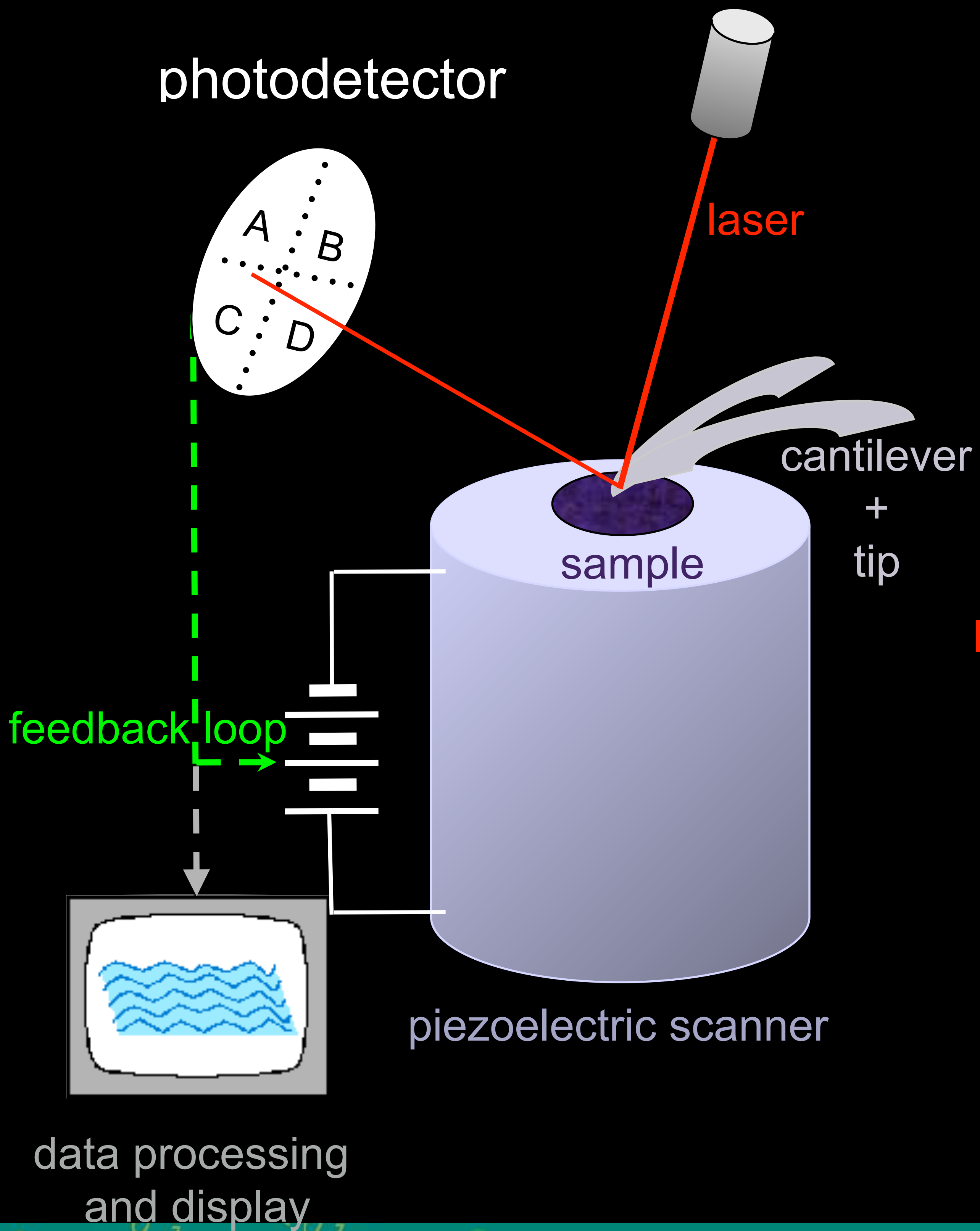
Binning *et al.* PRL **56,** 930 (1986)

Detecting the cantilever response



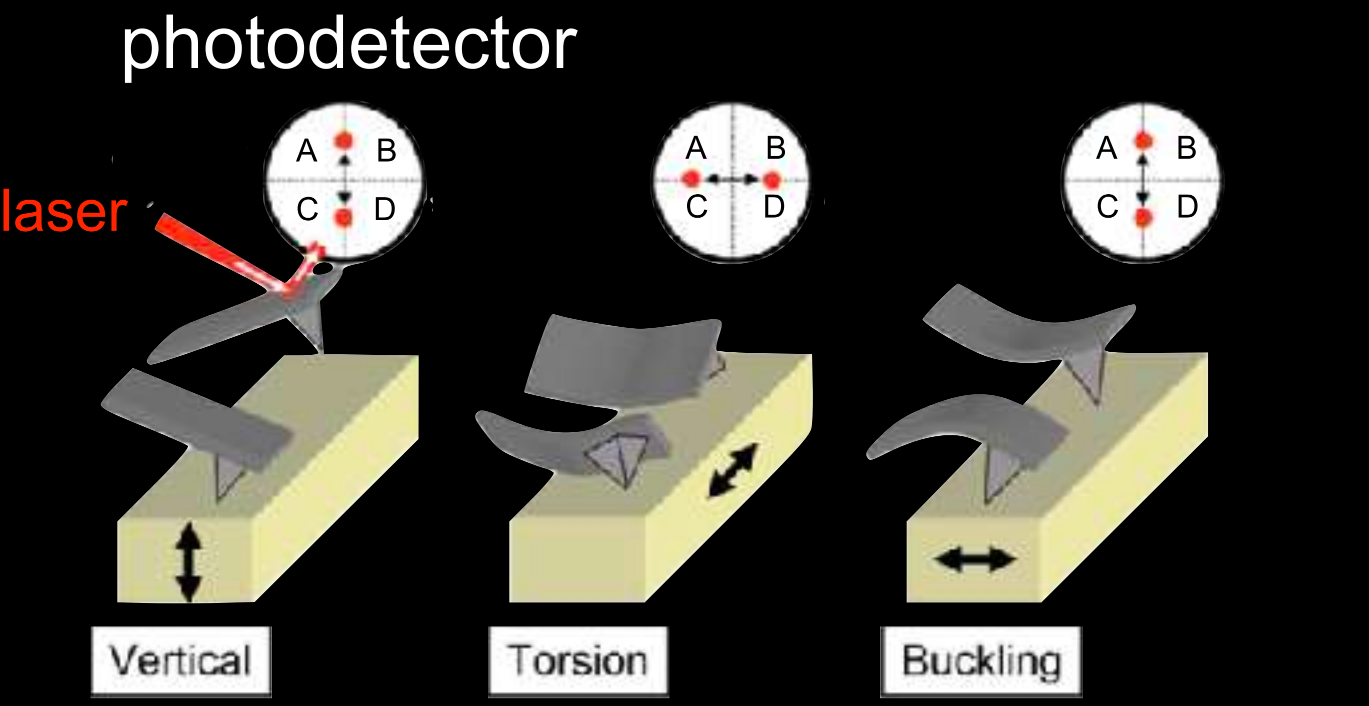
from E. Meyer

Detecting the cantilever response



Vertical deflection/buckling:
vertical signal
= (A+B) - (C+D)

Torsion:
horizontal signal
= (A+C) - (B+D)



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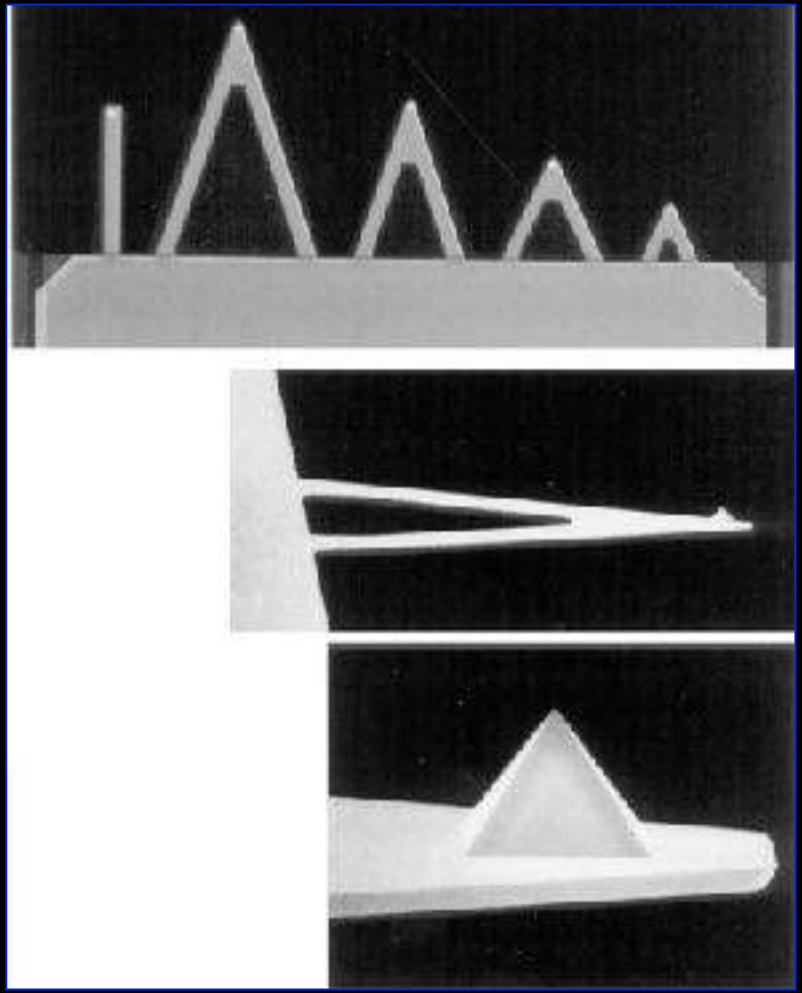
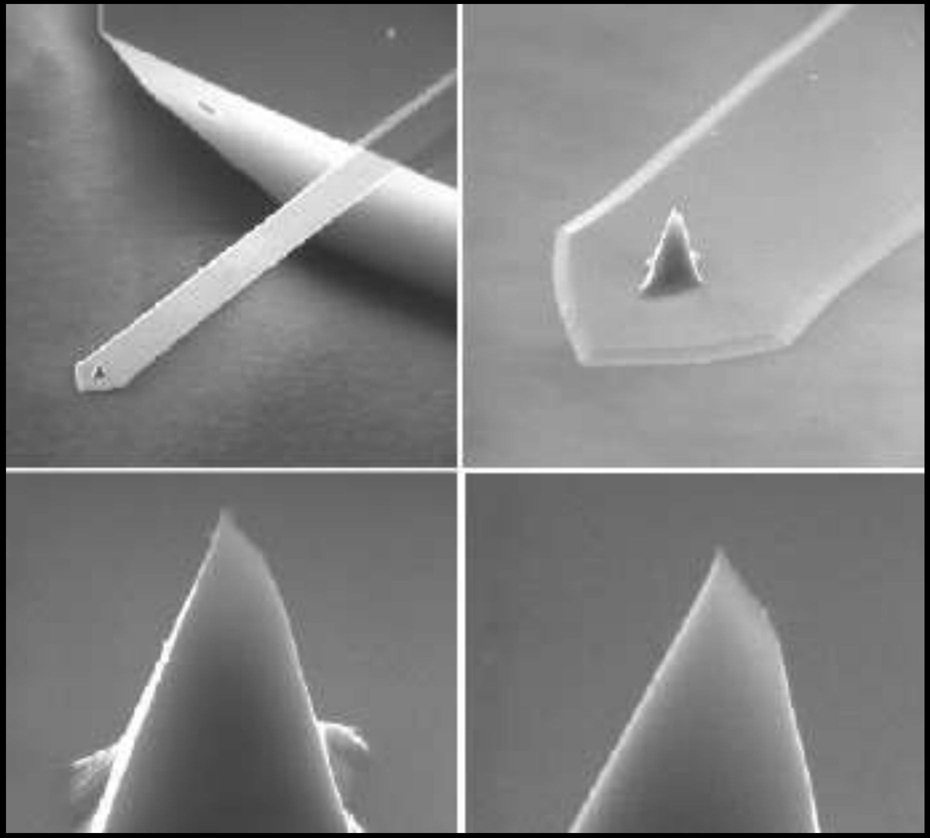
Importance of the cantilever

Tip-sample interaction gives rise to force on cantilever:

- bends in presence of attractive/repulsive forces
- spring system / force sensor: cantilever deflection converted to force using Hooke’s law: $F=k\cdot z$
  - z: deflection
  - k: spring constant





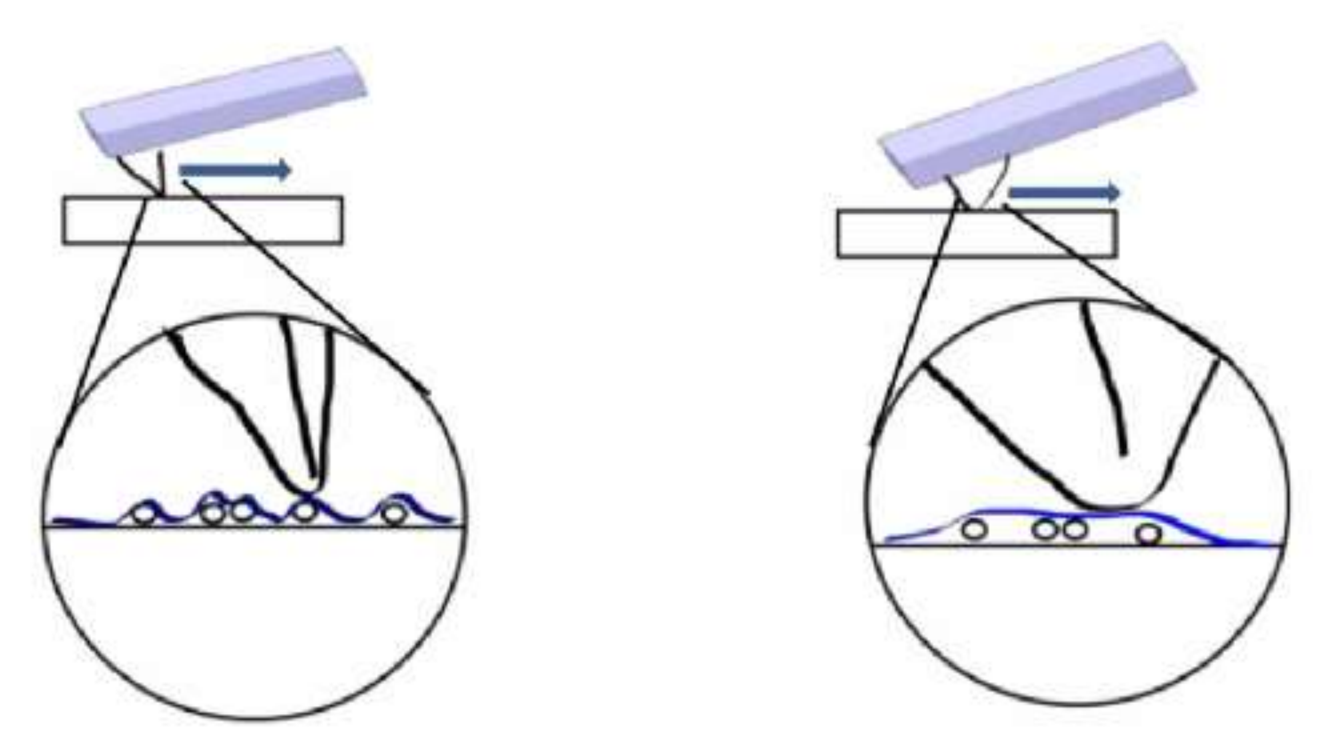
from E. Meyer

length : l = 450 μm
width : w = 45 μm
thickness: t = 1.5 μm

Tip height: 12 μm
Tip radius: 10 nm

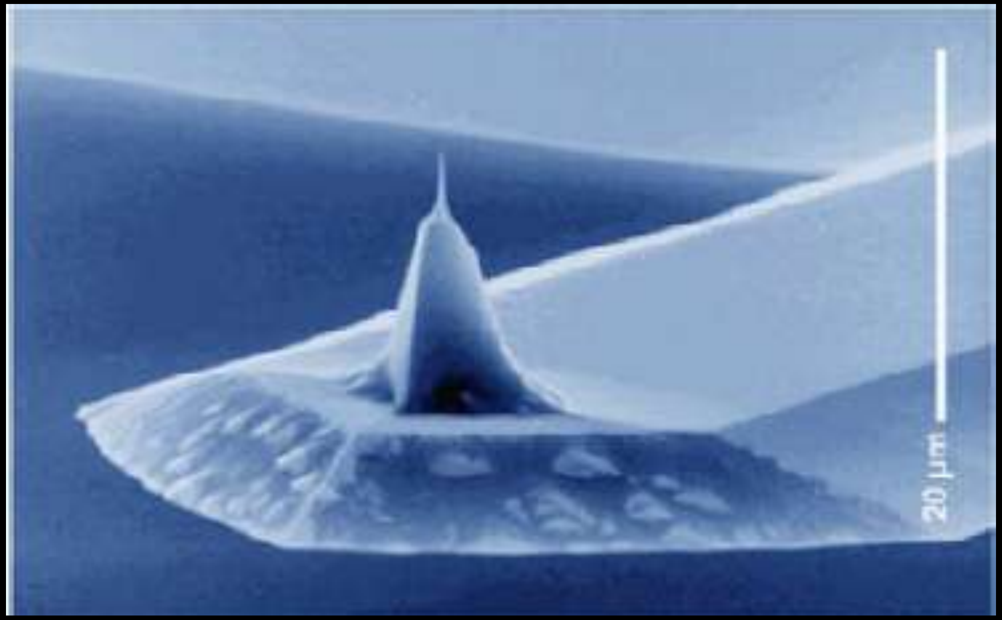
Importance of the tip

Shape is critical: the resolution depends on it

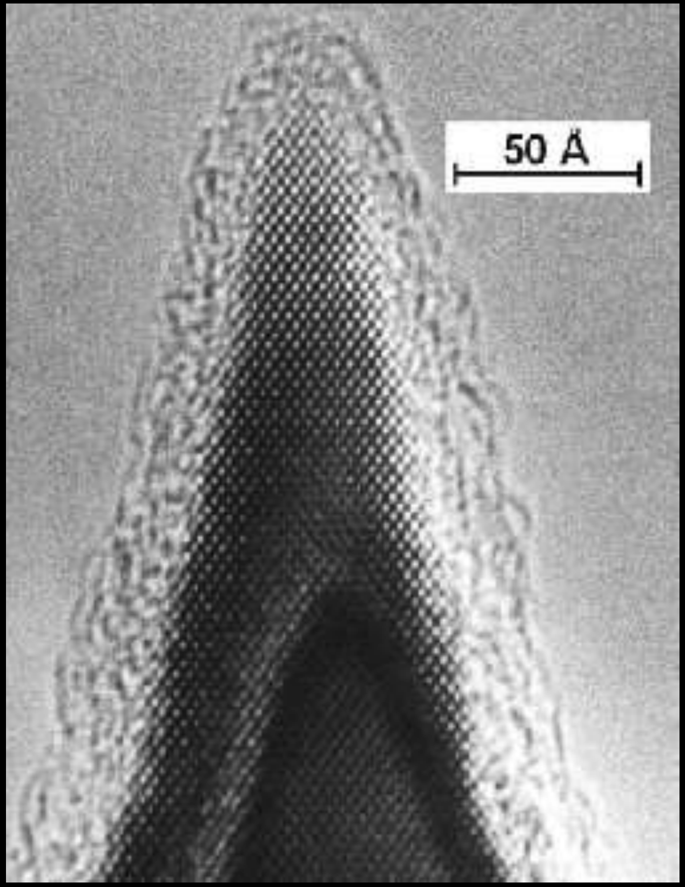


Importance of the tip

Ultrasharp and/or functionalised tips can be engineered to probe specific interactions



Pointprobe by Nanosensors GmbH

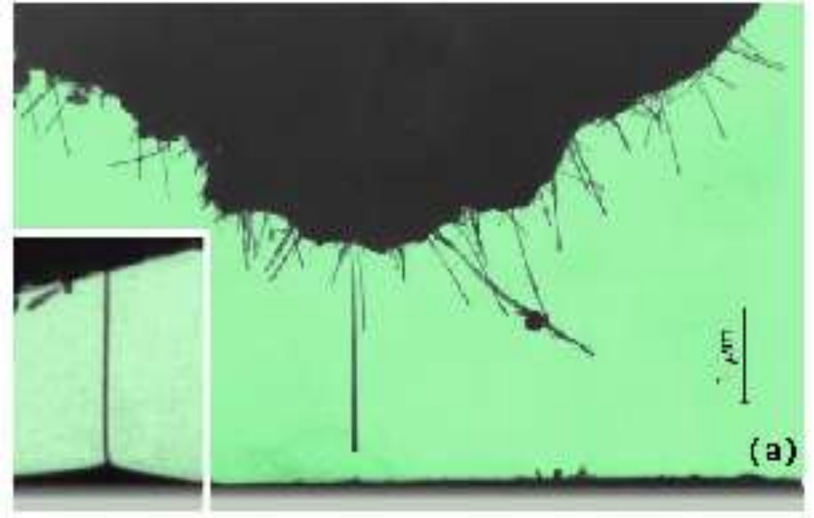


Marcus *et al.* APL **56,** 236 (1990)

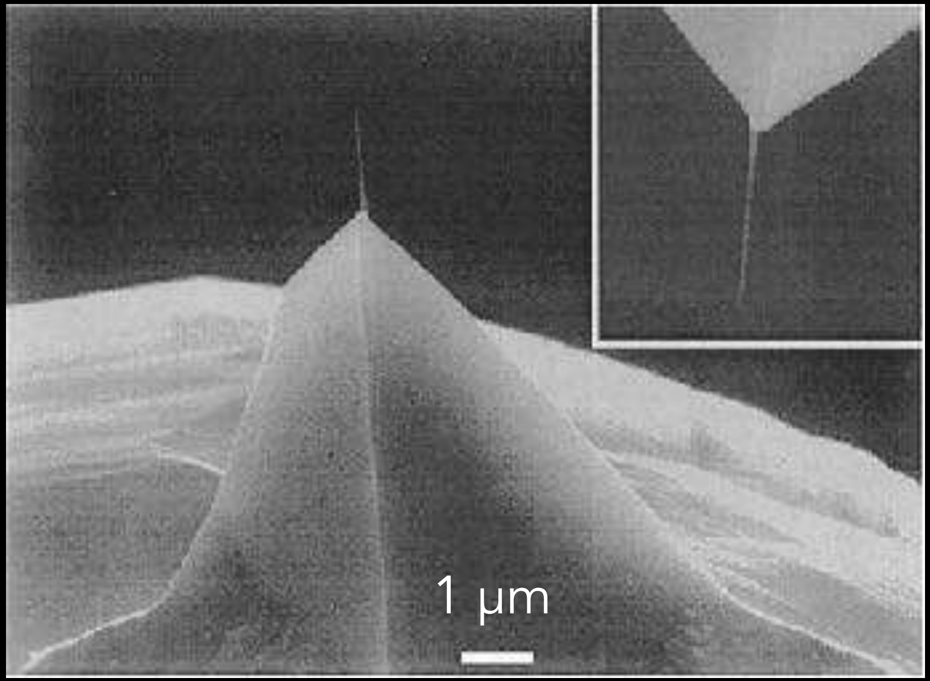
Importance of the tip

Ultrasharp and/or functionalised tips can be engineered to probe specific interactions

Improving tip performance using carbon nano-tubes (CNT)



Poncharal, *et al.* JPCB **106**, 12104 (2002)



Wong *et al.*, JACS **120**, 603 (1998)

- Exceptional mechanical properties
- Ballistic conduction in metallic CNT
- Semiconducting CNT
- Quasi ideal 1D system
- Single molecule electronics
- Nanoscale electric field source

Dai *et al.* APL **73**, 1508 (1998)
Cooper *et al.*, APL **75**, 3566 (1999)
Hafner *et al.* Nat. **398**, 761 (1999)
Nishijima *et al*, APL **74**, 4061 (1999)
Dresselhaus, et al., **Carbon Nanotubes** Springer, Berlin (2001)

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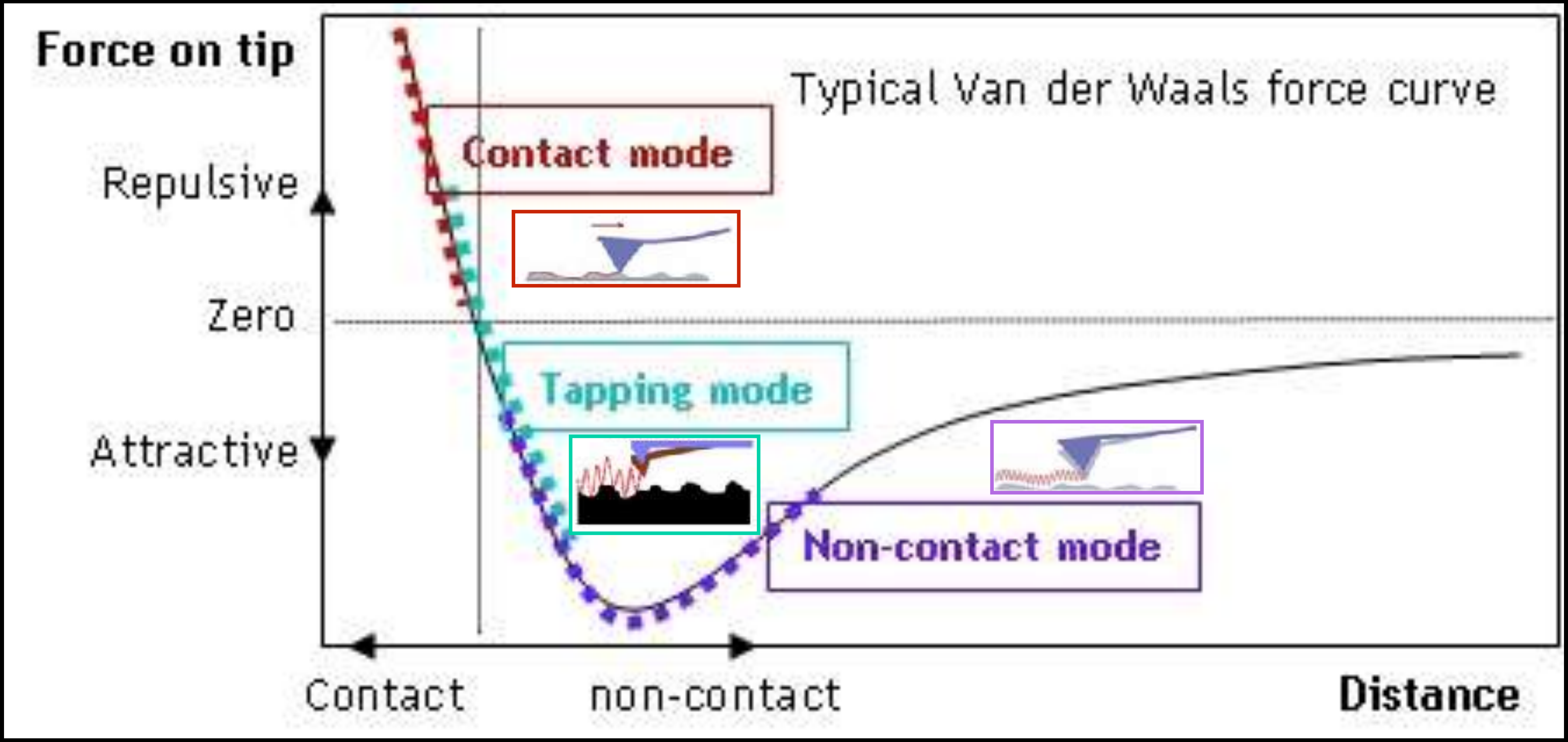
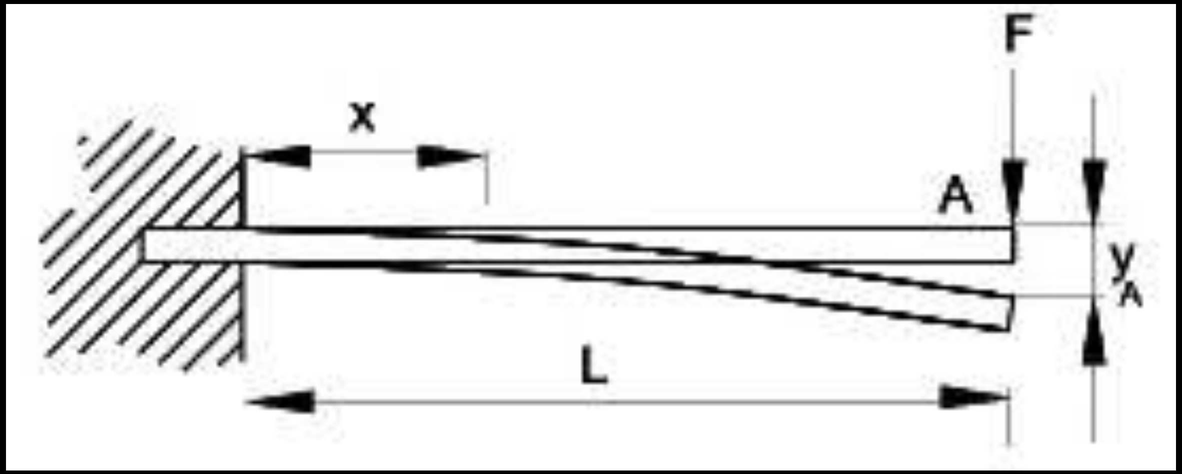
Different modes of operation



Adapted from DHEYAA H. Ibrahim, lecturer at Western Kentucky University

Contact mode

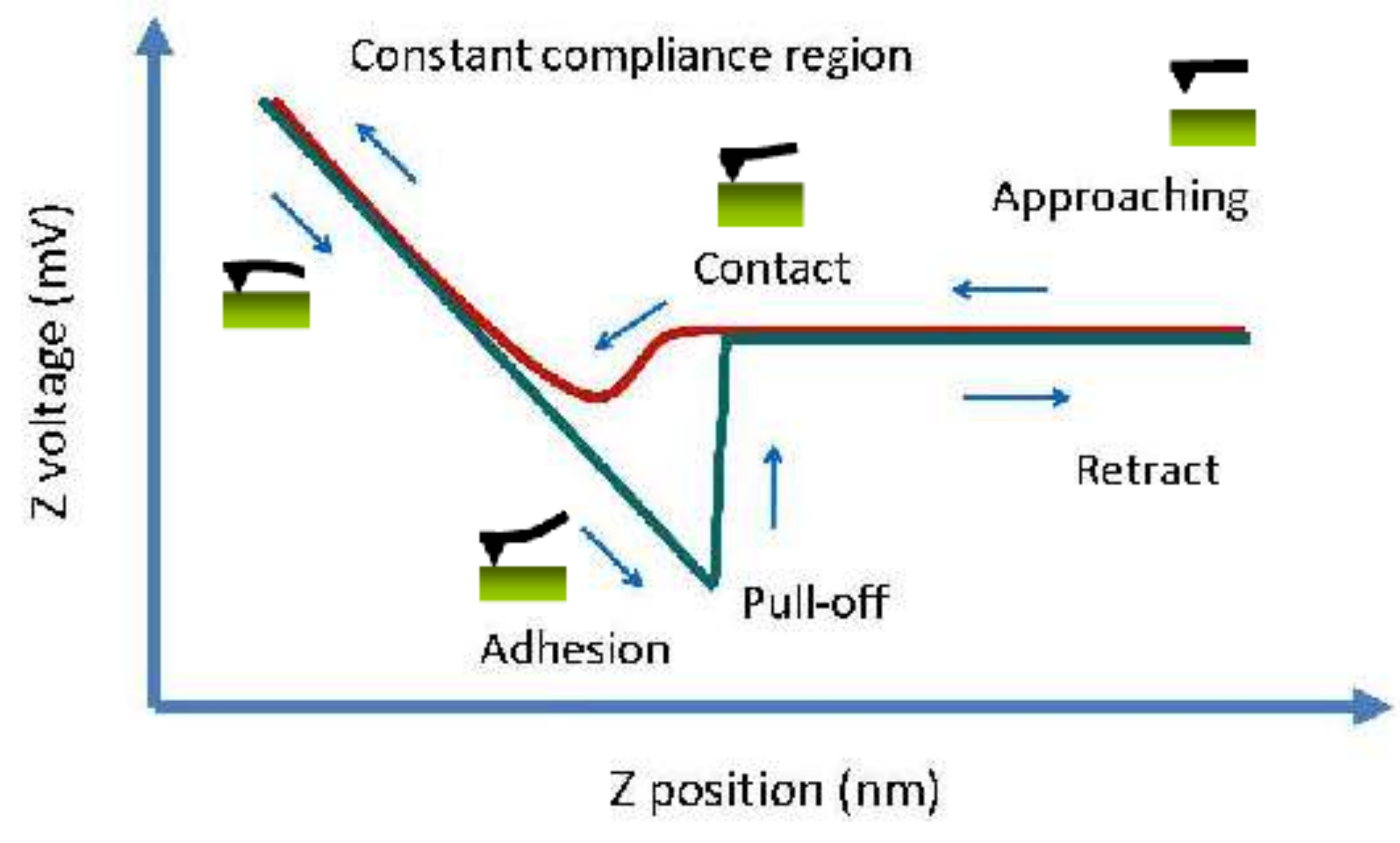
Deflection of cantilever

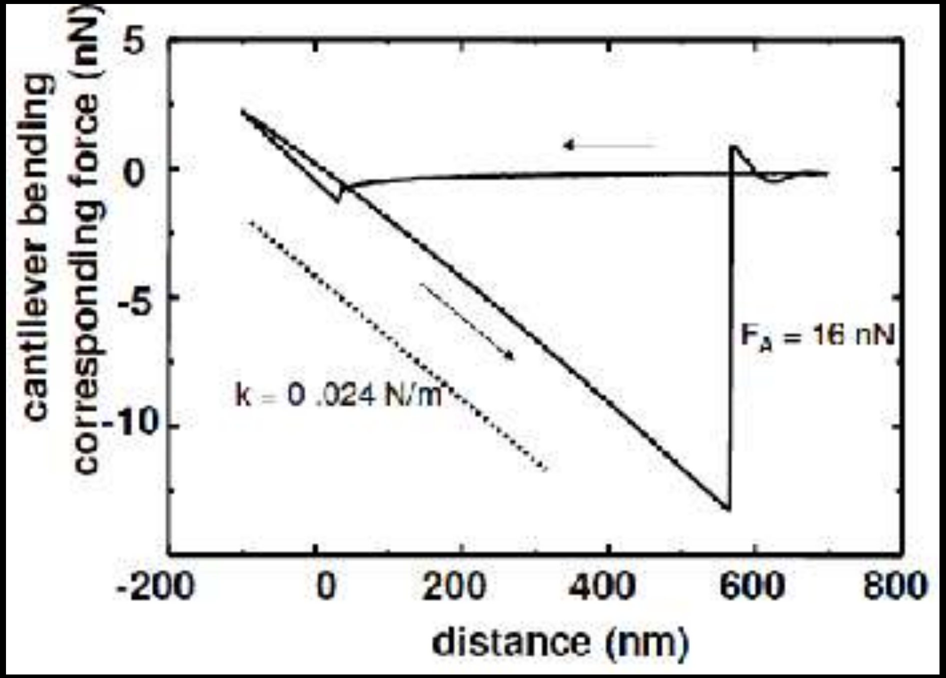


beam bending: one free end, one clamped end

$$y_A = \frac{F}{k} = -\frac{FL^3}{3EI}$$

k : spring constant
E : Young's modulus
I : area moment of inertia



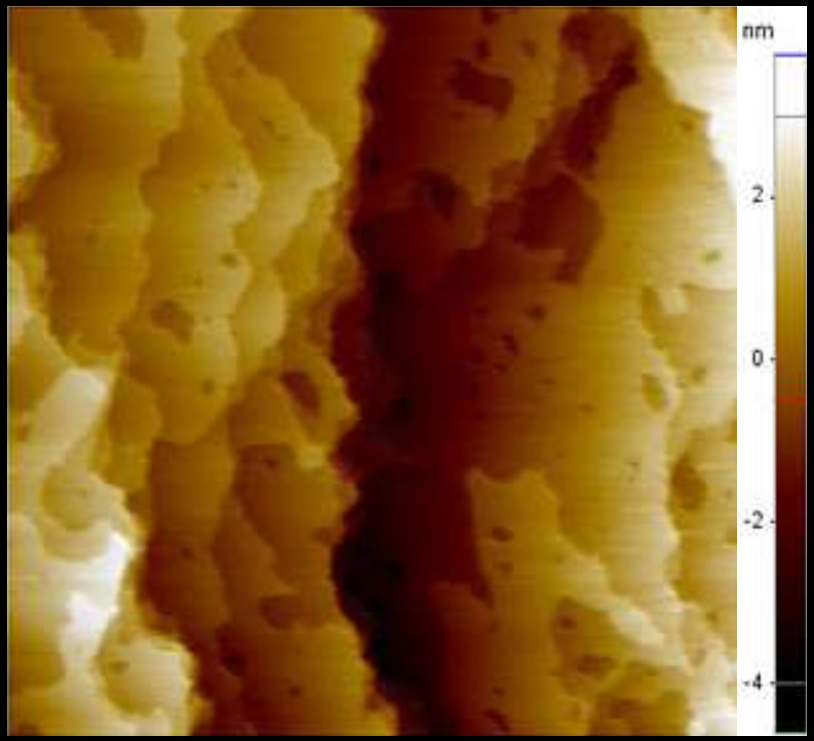


Force distance curve (approach/retract)

Contact mode

The simplest way to acquire the sample topography

The topography signal comes from the Z-scanner position, which maintains the deflection of the cantilever constant on the sample surface.



PMG Crystal in glyphosate solution

Scan size: 2µm

Probe: Biolever mini

Imaged on a Park NX10 using contact mode in liquid

Advanced scanning probe microscopy

Outline

Scanning Tunneling Microscopy - STM
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- Conductive Atomic Force Microscopy - CAFM
- Friction mode AFM
- Tomographic Atomic Force Microscopy - TAFM

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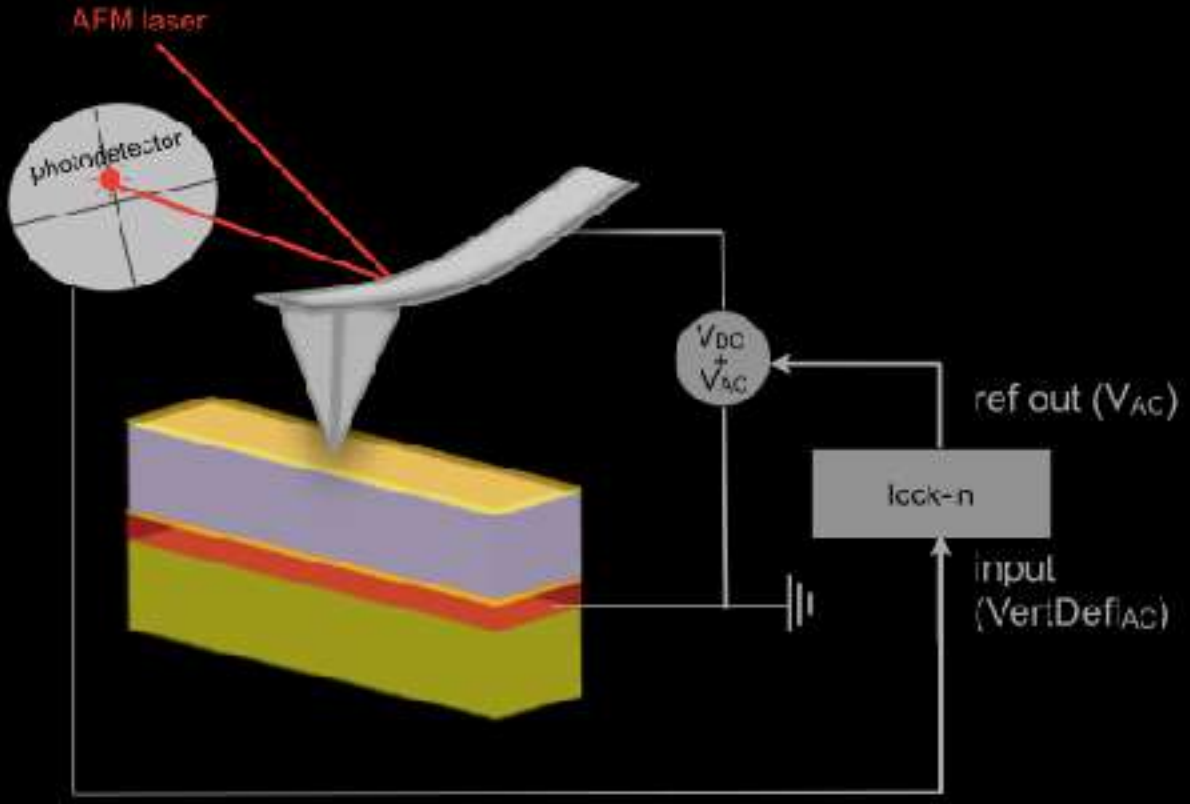
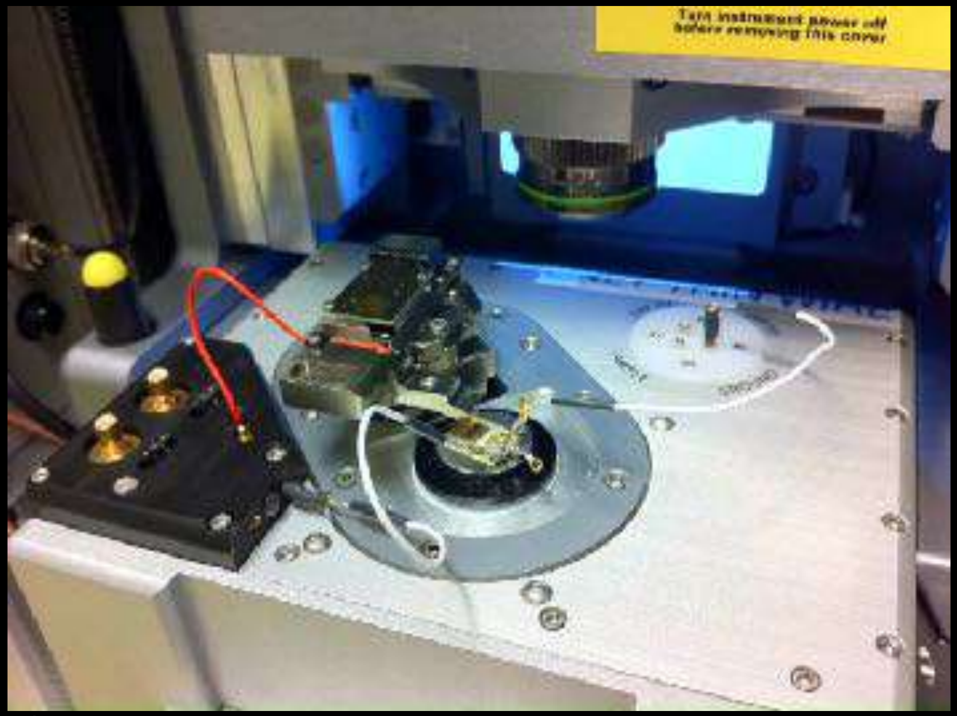
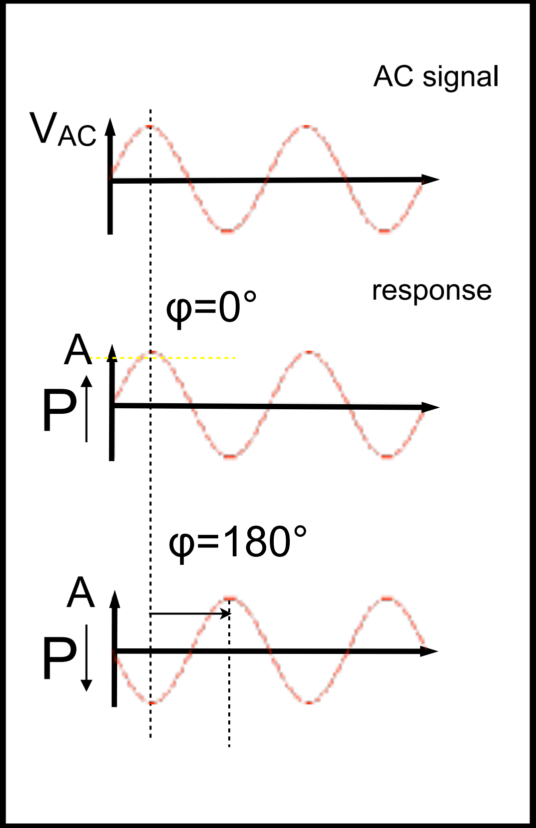
Piezoresponse Force Microscopy - PFM

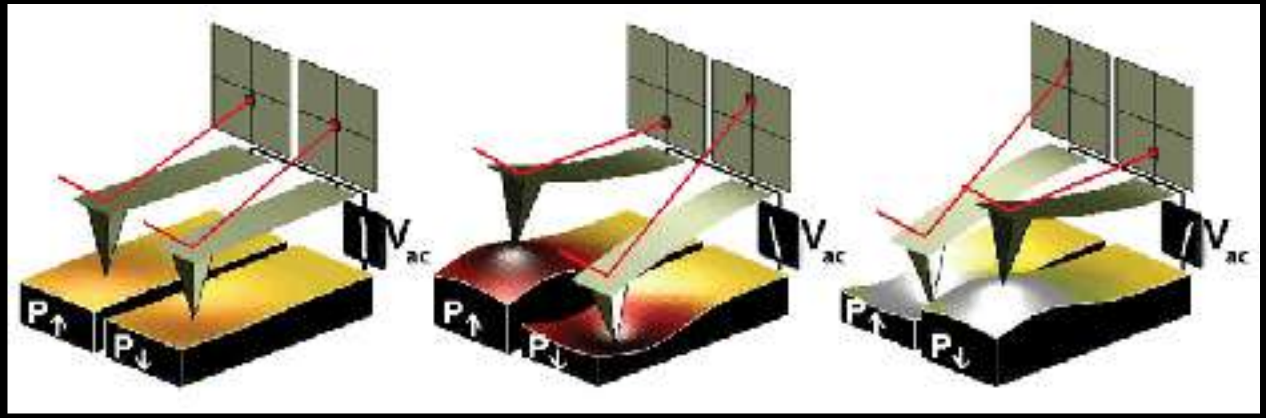
Piezoresponse Force Microscopy - PFM



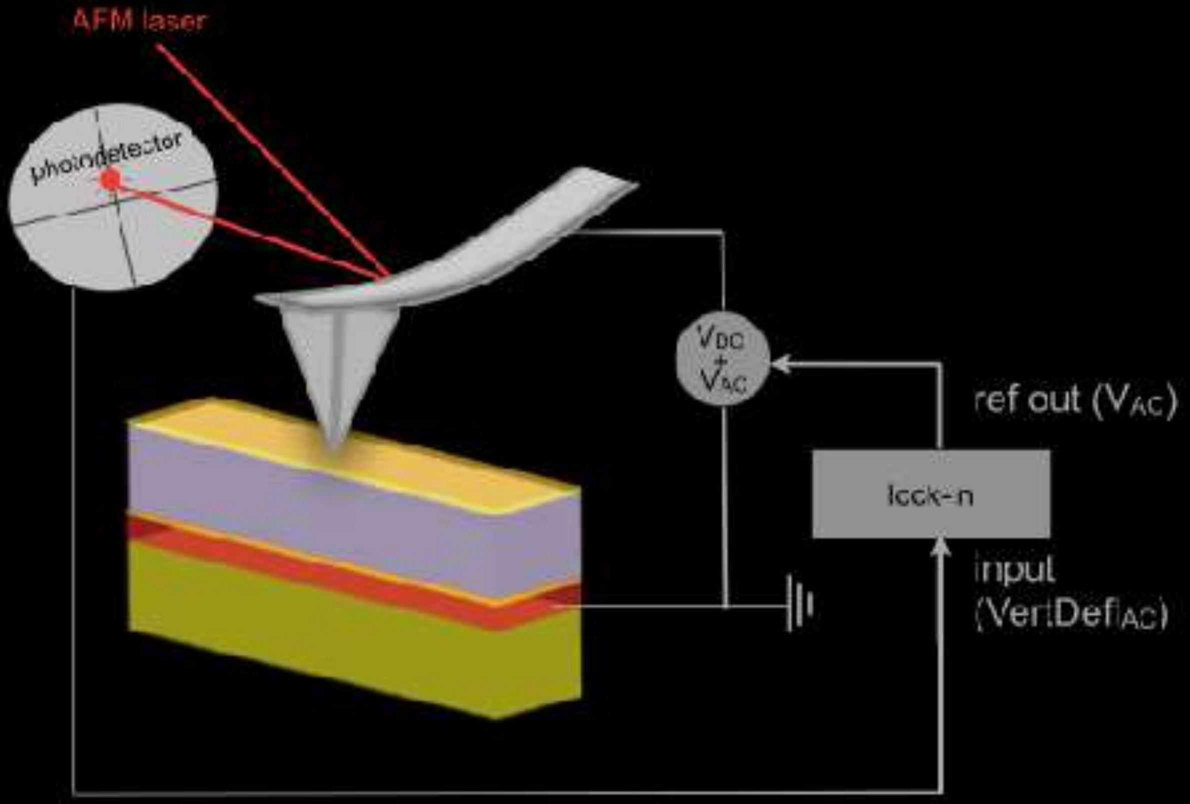


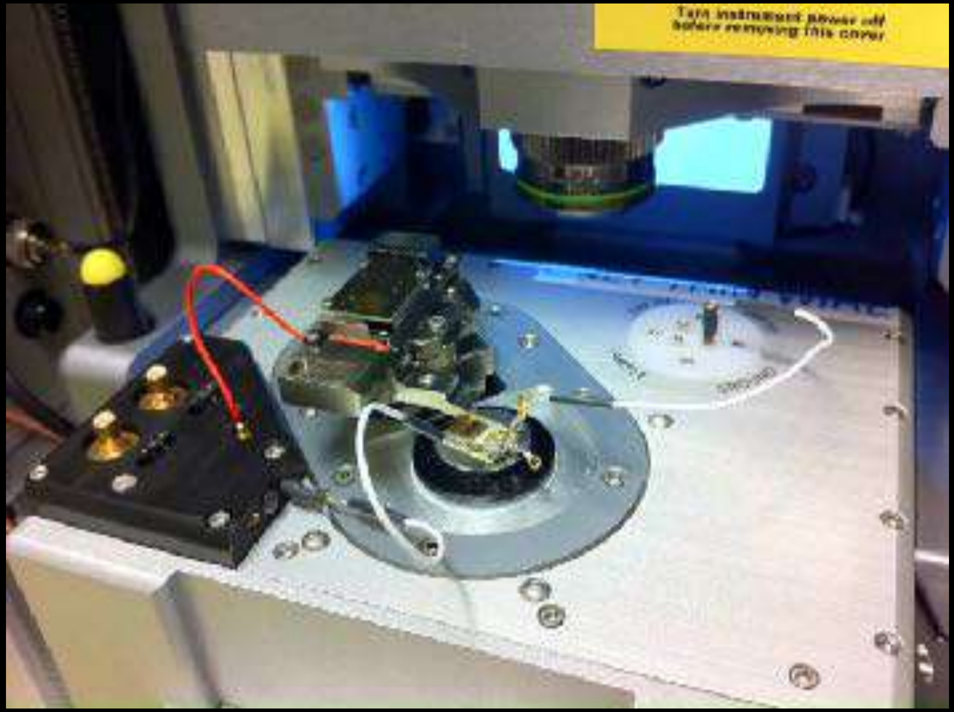
Cypher AFM



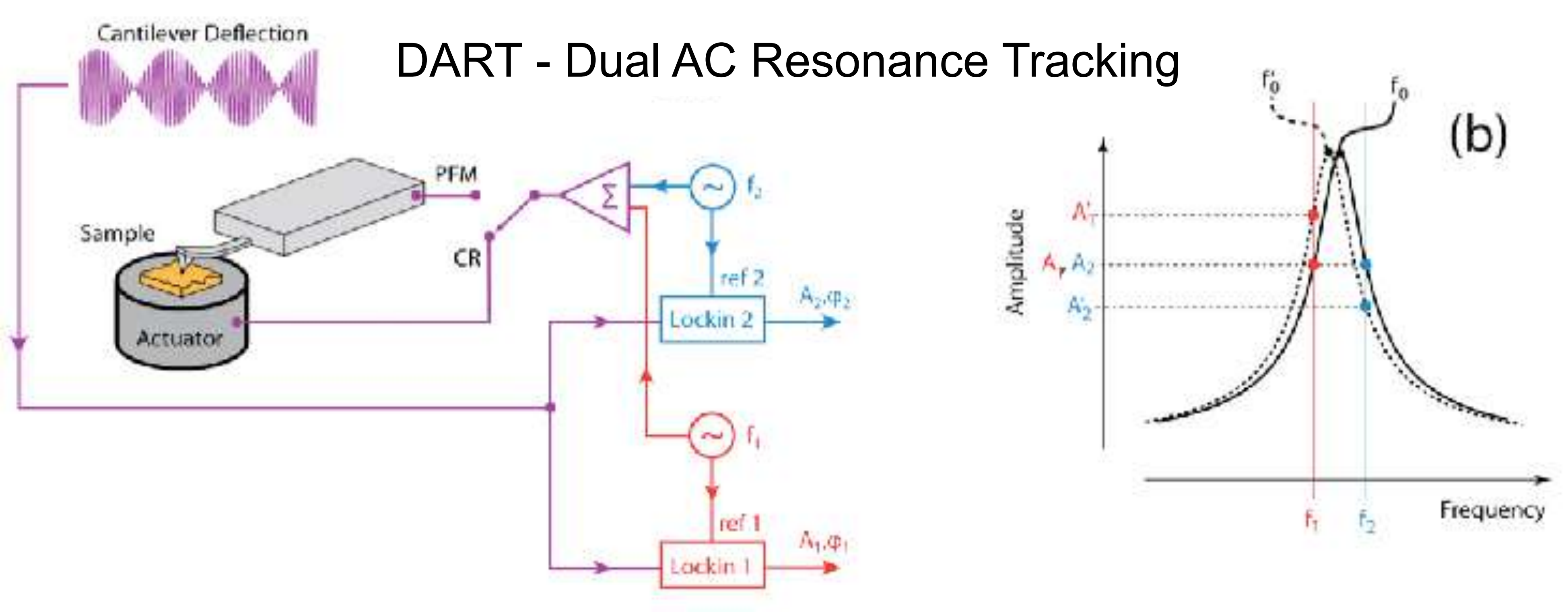


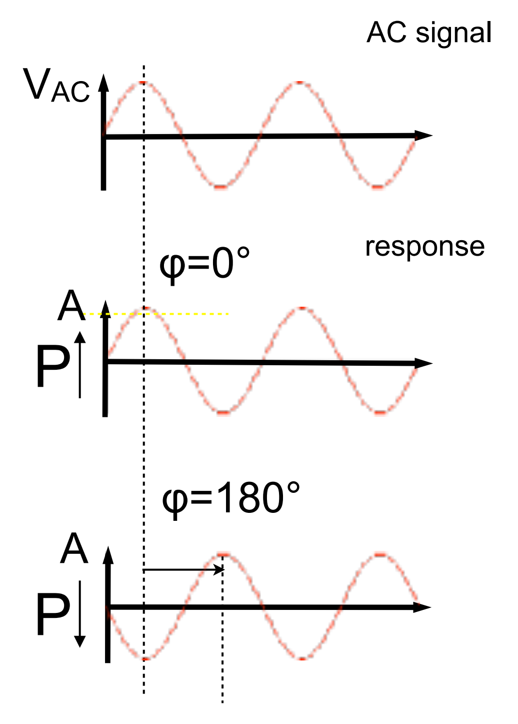
Piezoresponse Force Microscopy - PFM





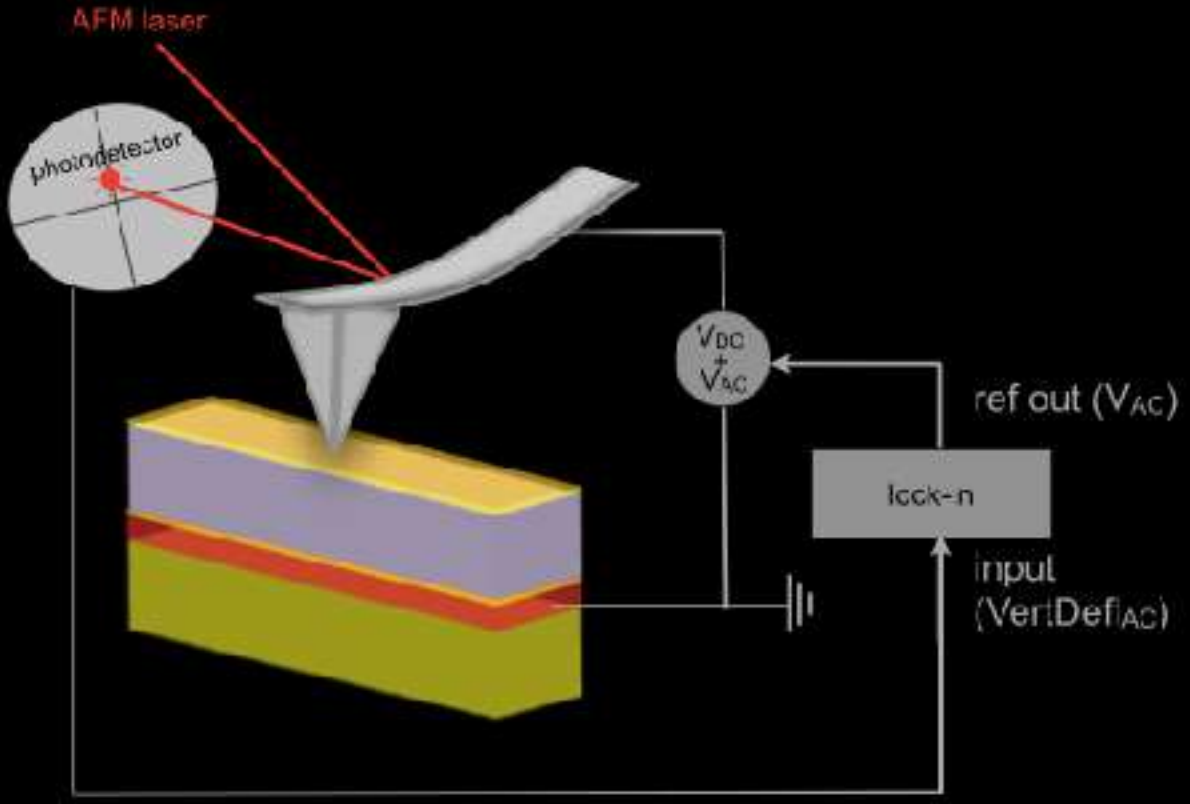
Cypher AFM

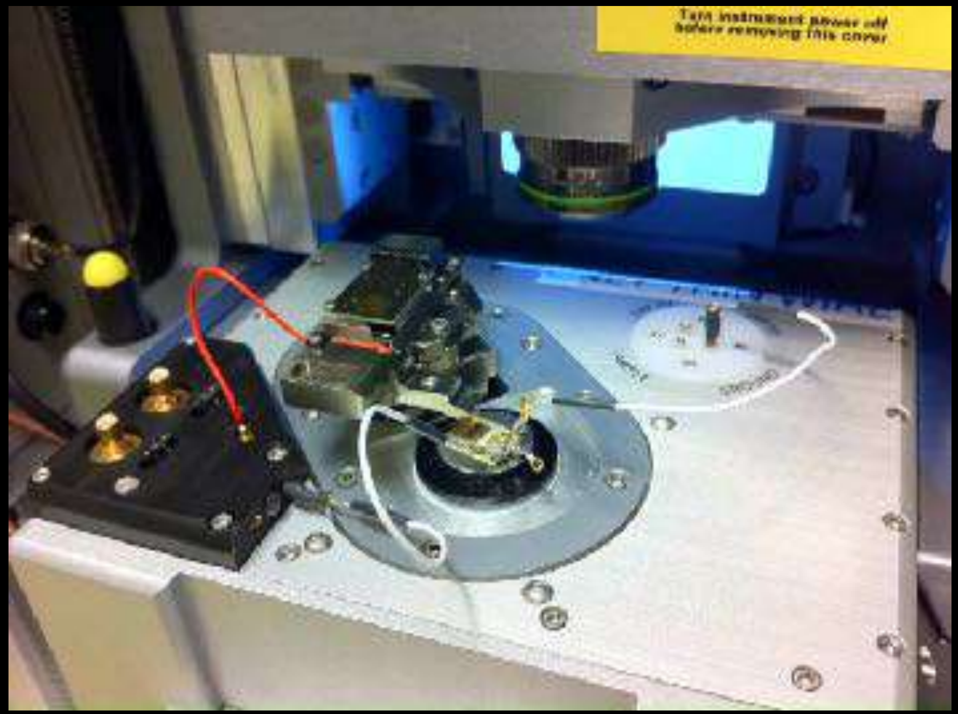




Mapping nanoscale elasticity and dissipation using dual frequency contact resonance AFM
Gannepalli, Yablon, Tsou, Proksch, **Nanotechnology 2011**

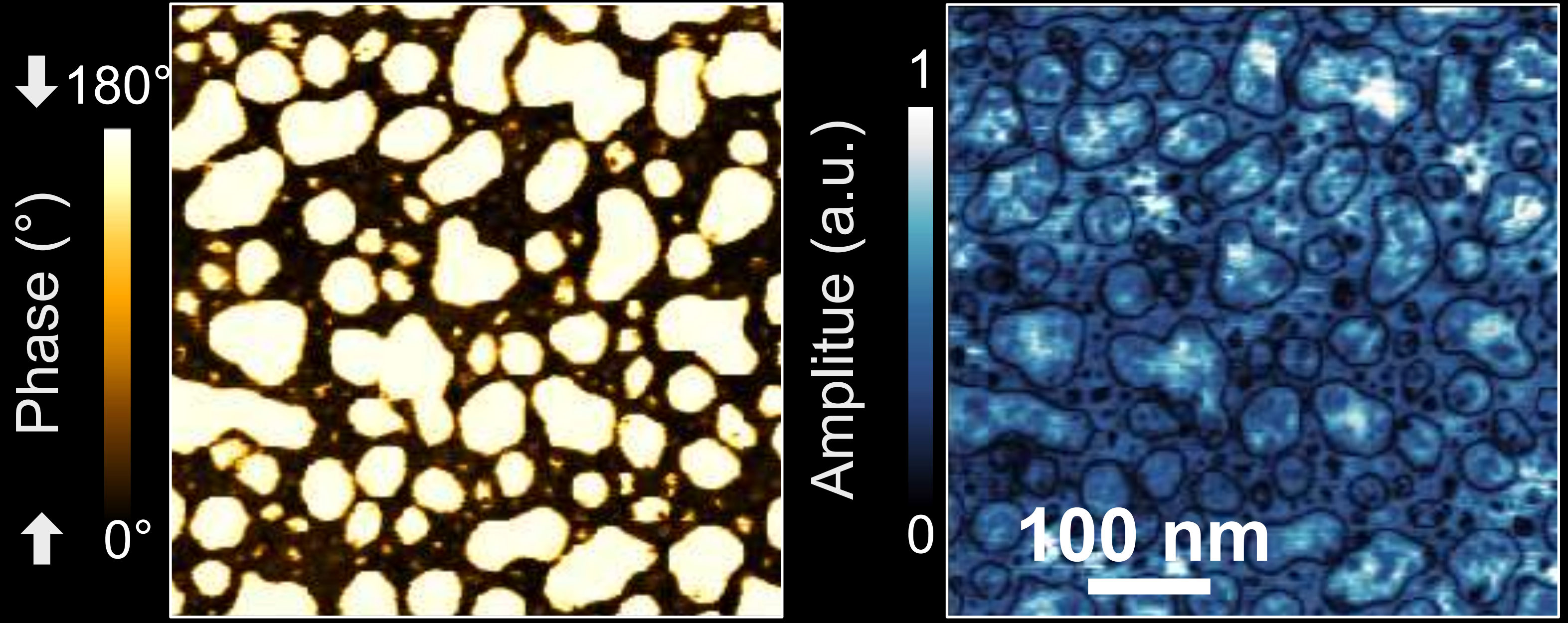
Piezoresponse Force Microscopy - PFM

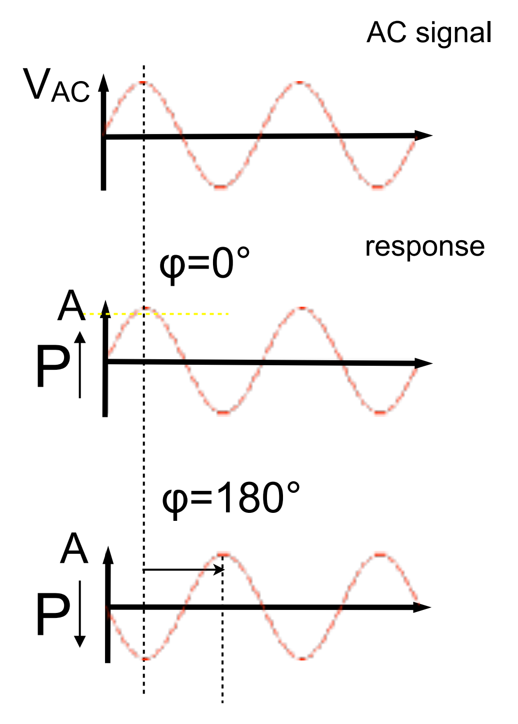




Cypher AFM

PbTiO$_3$ film thickness: 50nm

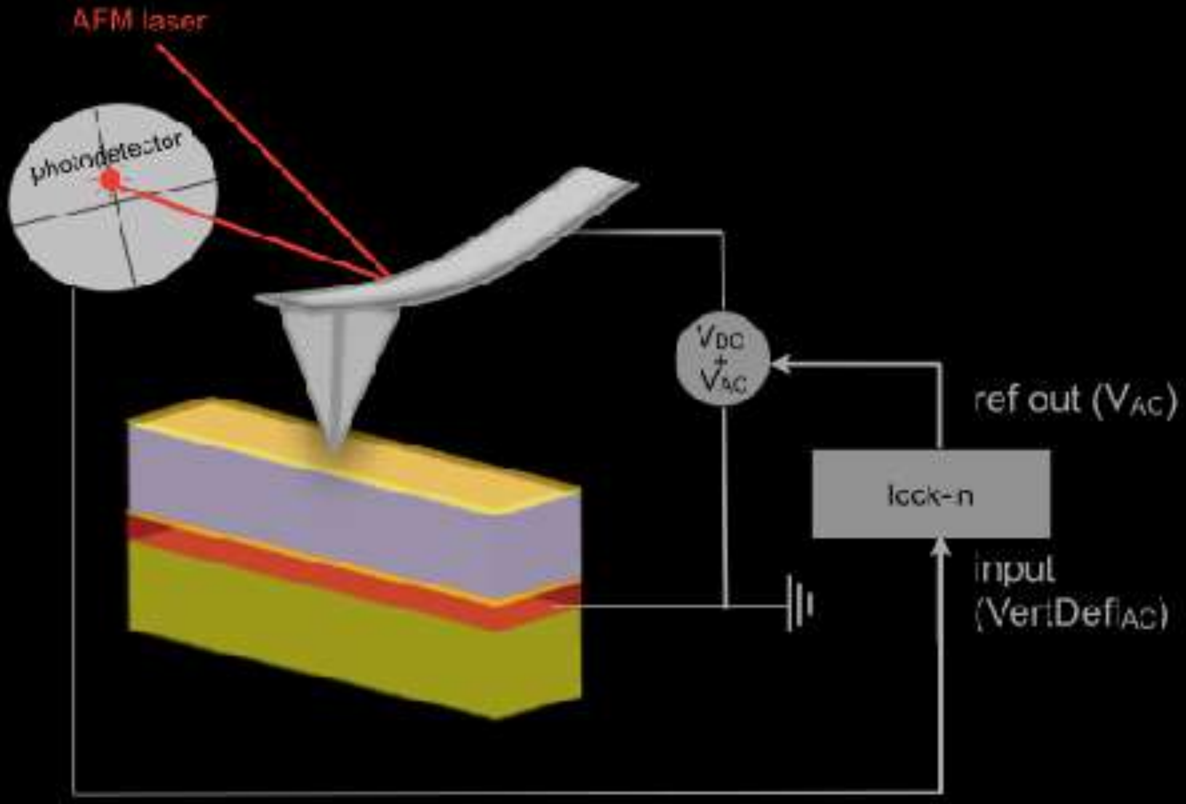


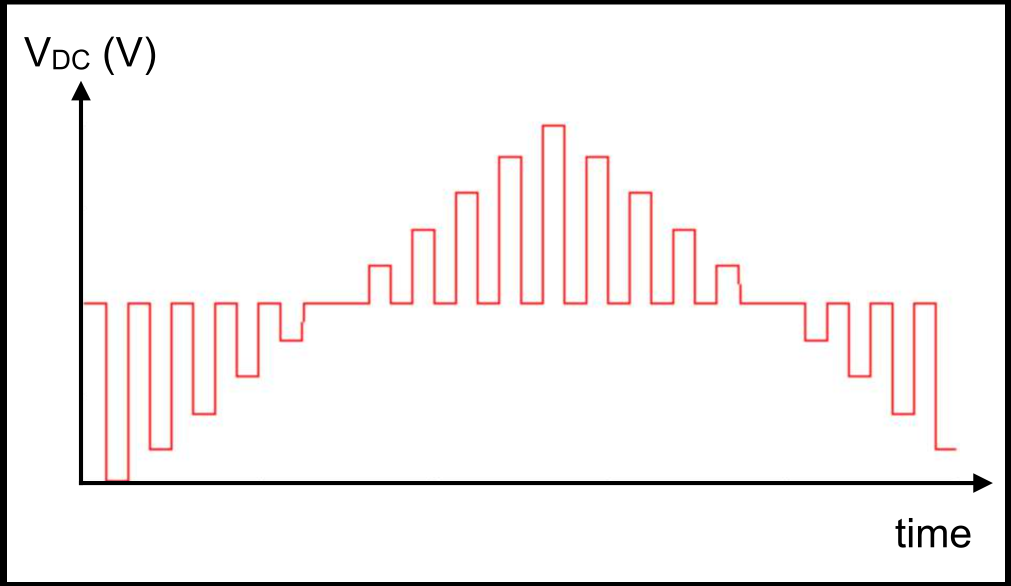


Tuning of the depolarization field and nanodomain structure in ferroelectric thin films

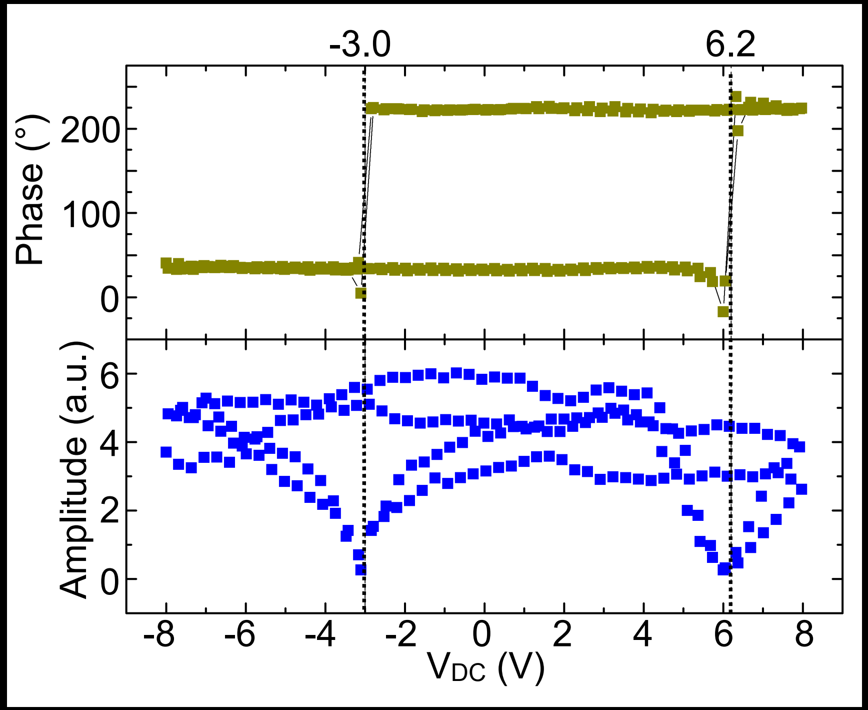
Lichtensteiger, Fernandez-Pena, Weymann, Zubko, Triscone, **Nano Lett. 2014**

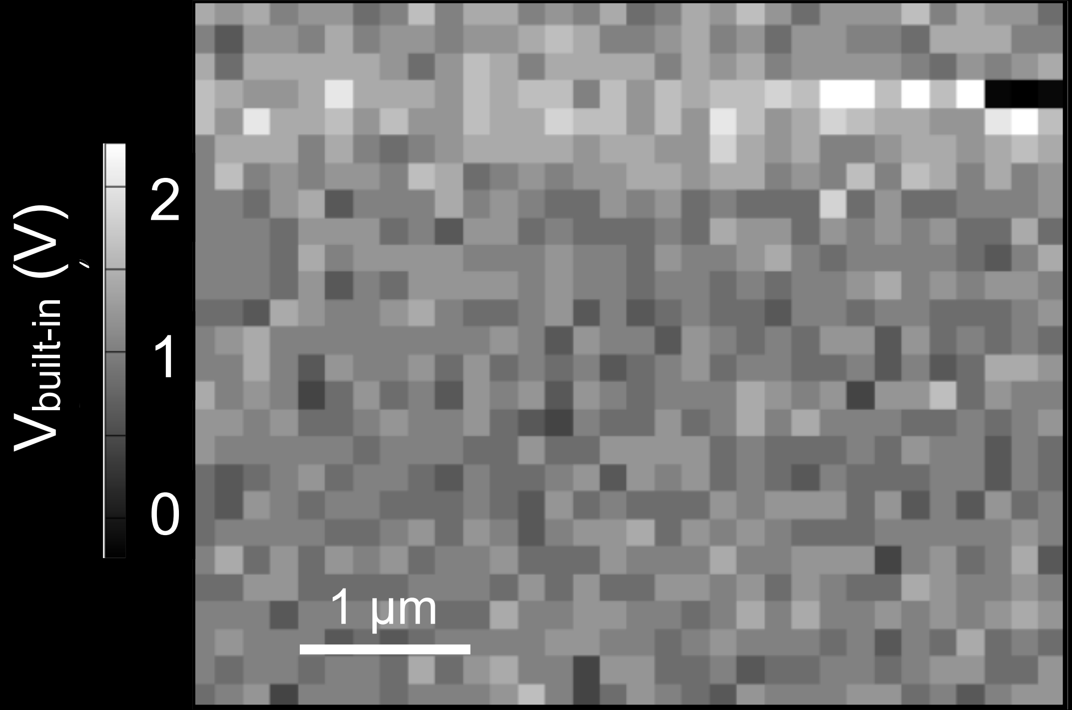
Switching Spectroscopy - SSPFM





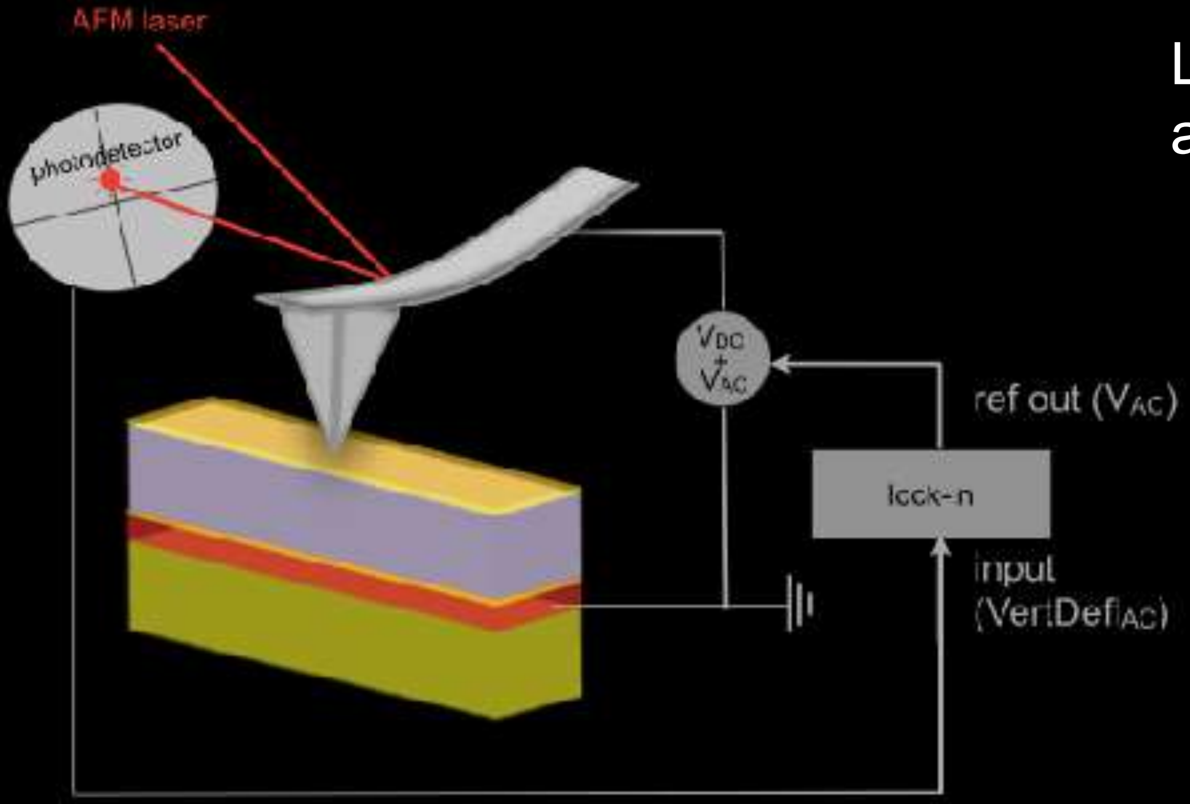
Switching spectroscopy piezoresponse force microscopy of ferroelectric materials Jesse, Baddorf, Kalinin, **APL 2006**



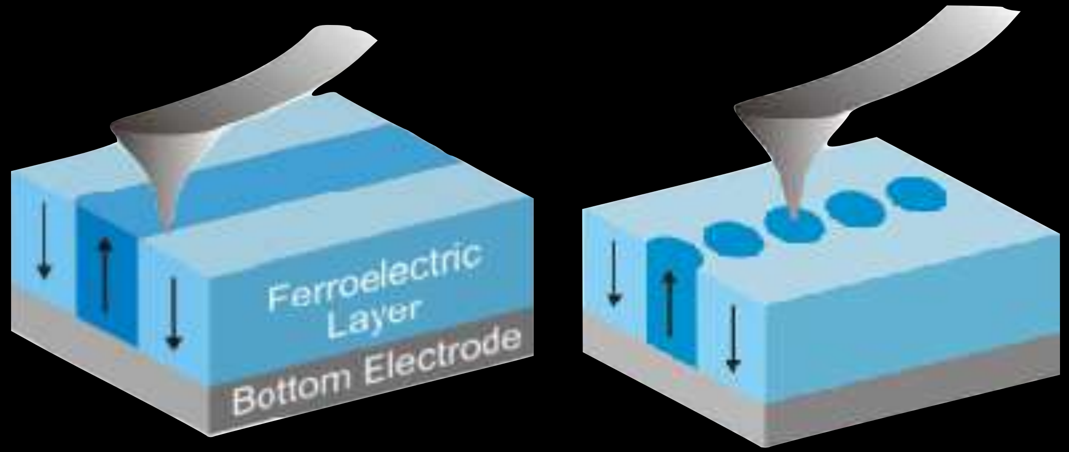


Built-in voltage in thin ferroelectric $PbTiO_3$ films: the effect of electrostatic boundary conditions Lichtensteiger, Weymann, Fernandez-Pena, Paruch, Triscone, **New J. Phys. 2016**

Switching polarization by PFM

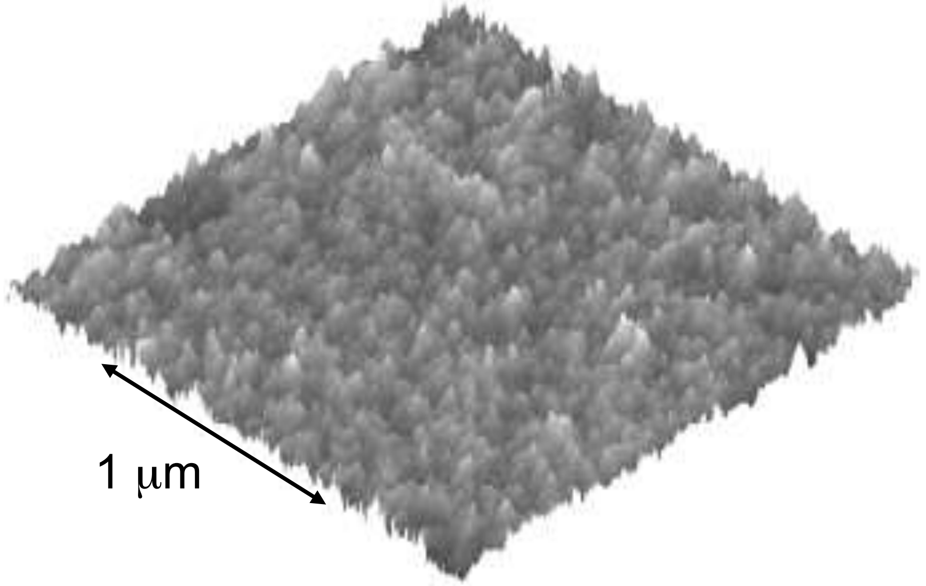


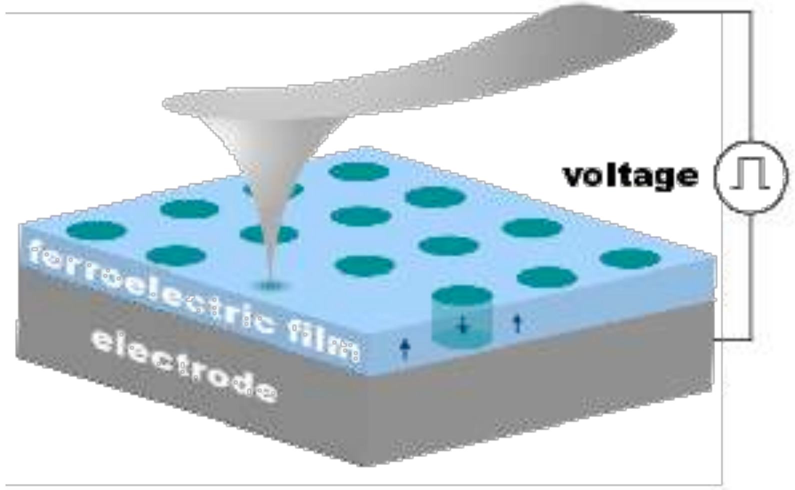
Local electric field application with a metallised probe tip allows the formation of very small domains



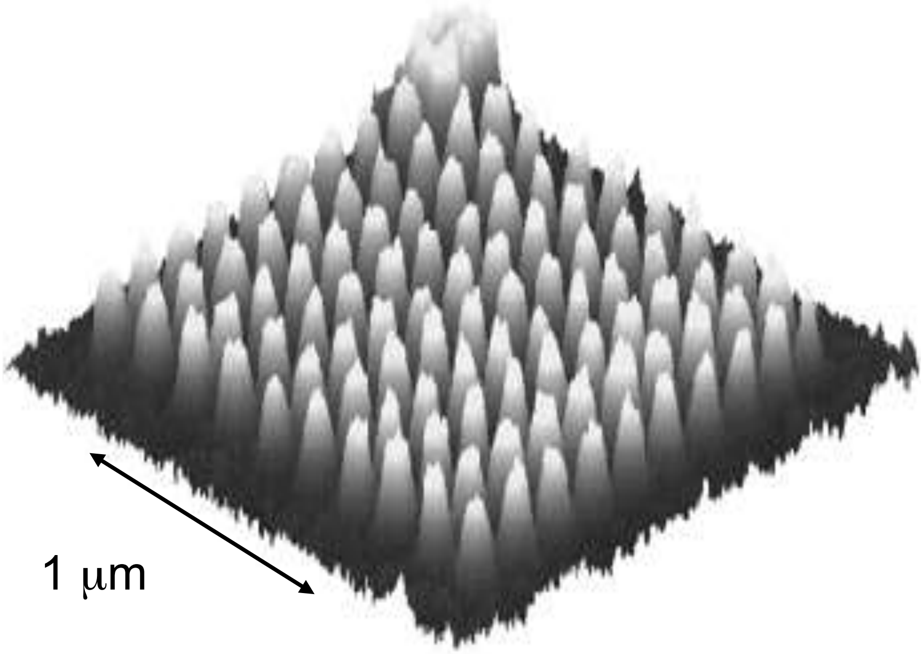
T. Tybell *et al.* APL 72, 1454 (1998).
P. Paruch, *et al.* PRL 94, 197601 (2005).

Topography

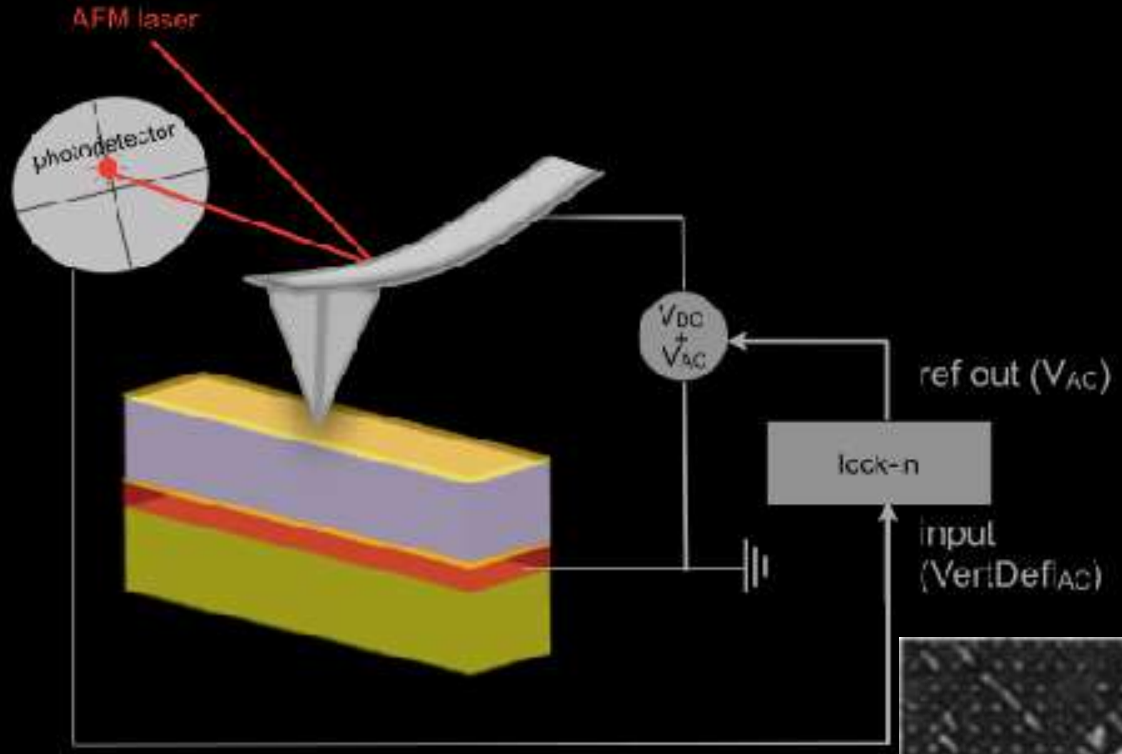




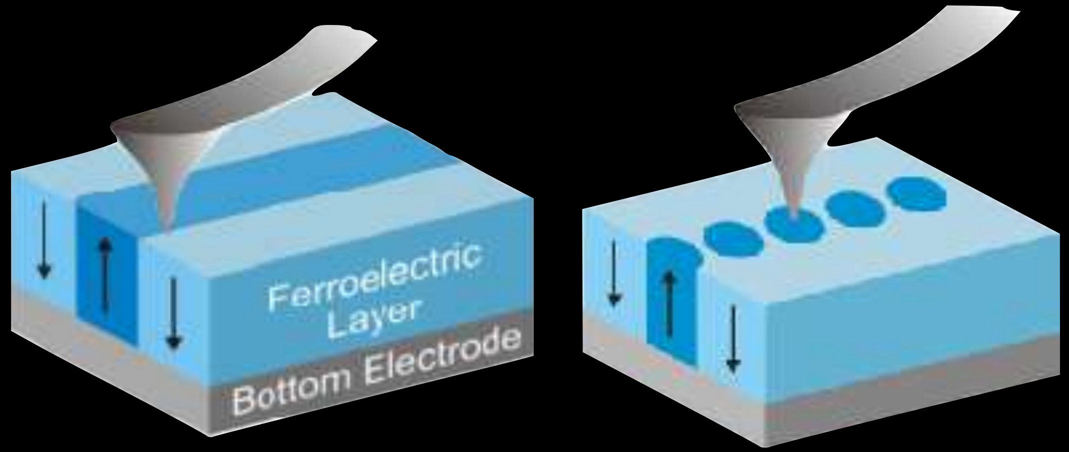
Piezoresponse



Switching polarization by PFM

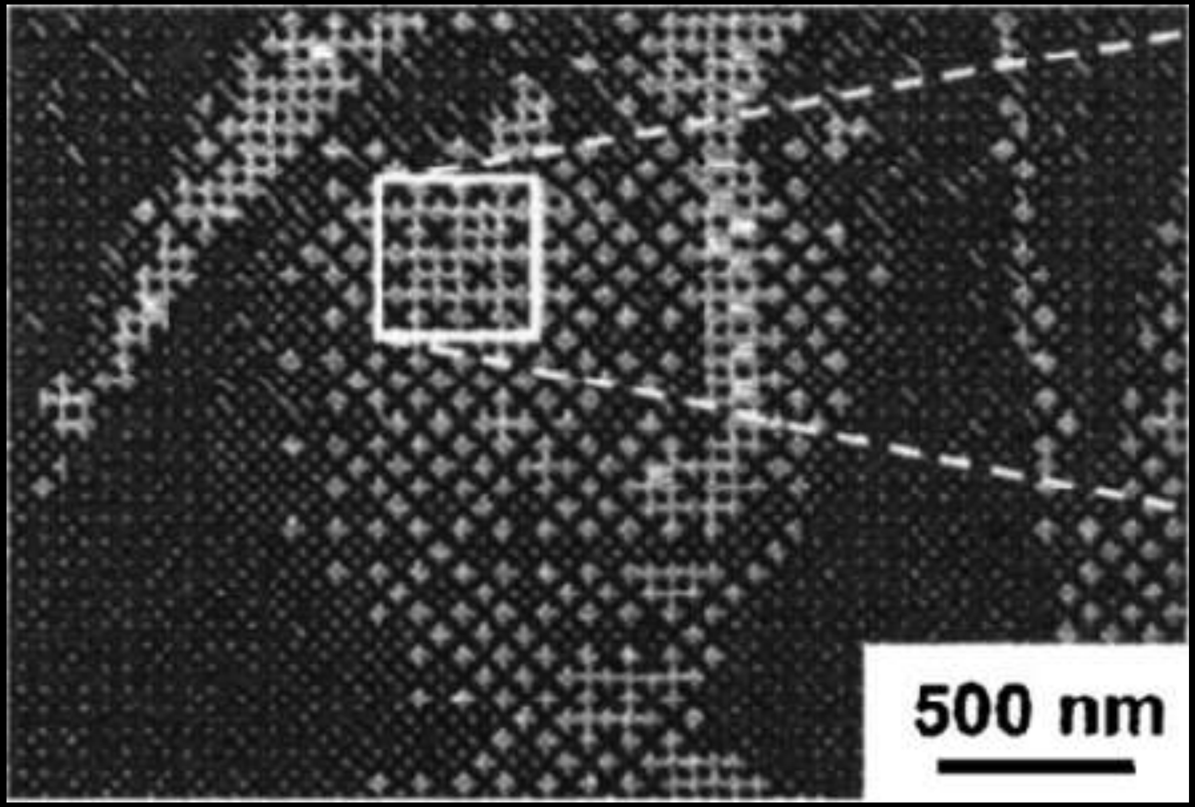


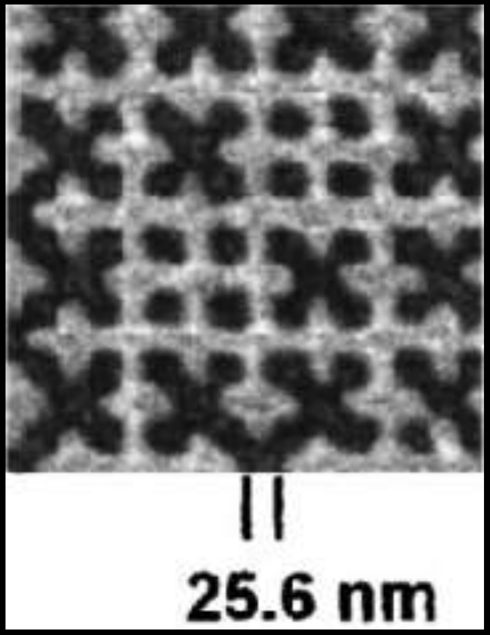
Local electric field application with a metallised probe tip allows the formation of very small domains



<u>Density</u>: no clear theoretical limit. 1nm lateral size would lead to 100Tbit/cm^2, 500 times today's hard disks record (Seagate 2015 1.34Tbit/in^2).

<u>Stability</u>: tests performed at HP suggest that domains are stable for more than 30 years in PZT. (T. Hidaka et al. **Integrated Ferro. 1997,** 17, 319)





LiTaO$_3$ single crystal

Realization of 10Tbit/in.^{2} memory density and subnanosecond domain switching time in ferroelectric data storage

Cho, Hashimoto, Odagawa, Tanak, Hiranaga, **APL 2005**, 87, 232907

Advanced scanning probe microscopy

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Conductive Atomic Force microscopy (C-AFM)

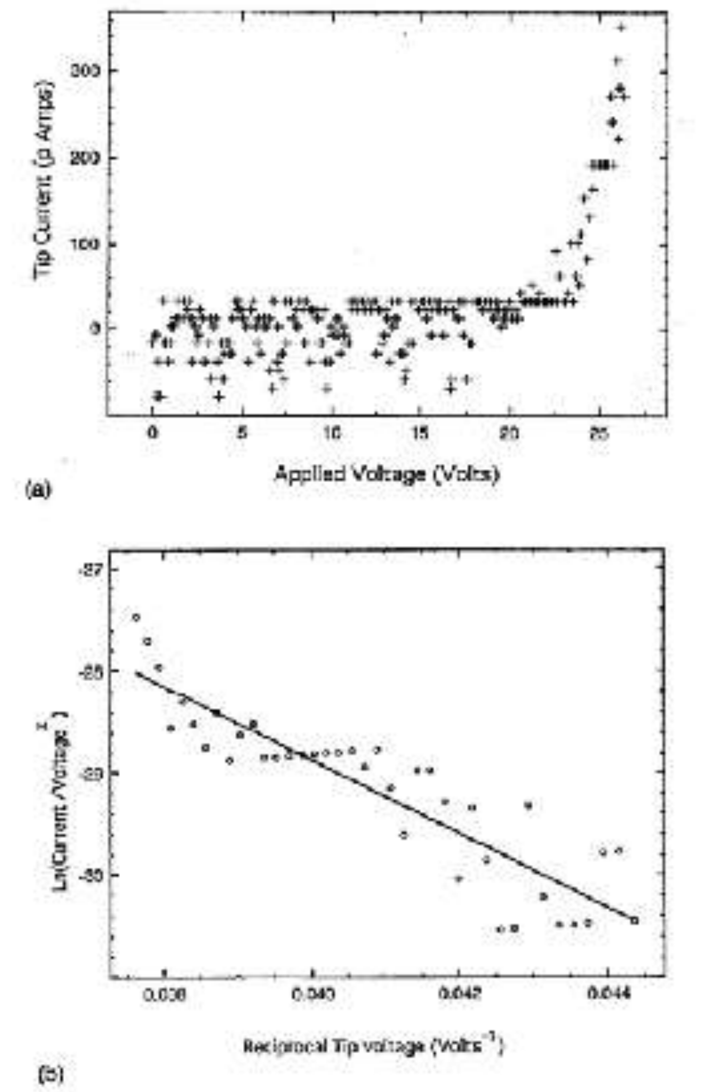


FIG. 1. (a) I/V plot. The sample-tip feedback loop was frozen during the measurement. (b) Data of (a), in the region above 22.5 V, replotted as a Fowler plot so as to determine the work function and effective emission area.

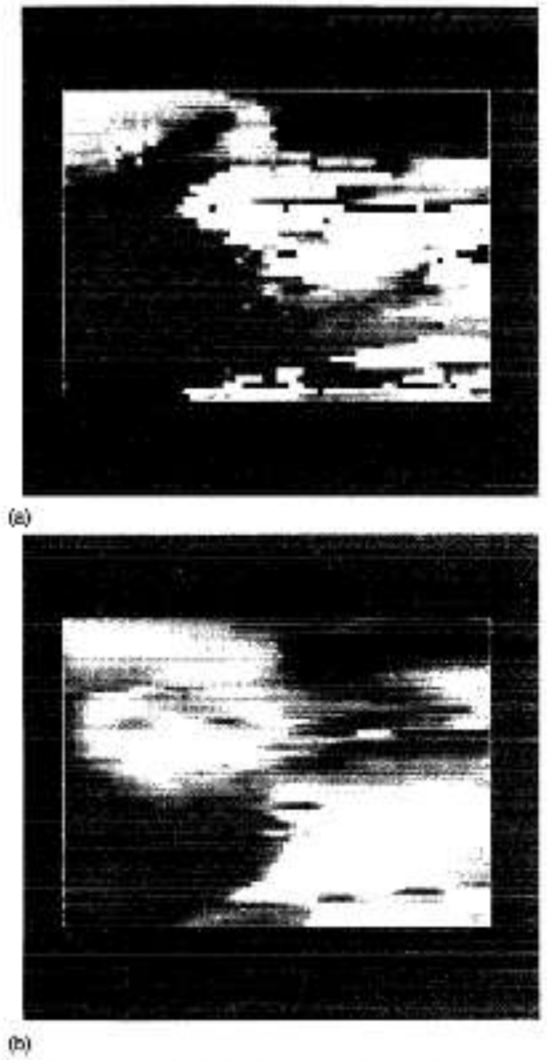
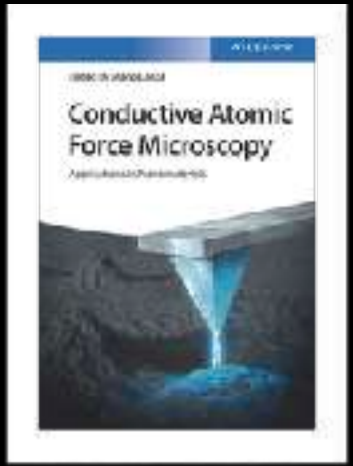


FIG. 2. (a) Tunneling voltage image over an area 450×330 nm. The contrast is proportional to the threshold voltage required at each image point to generate a tunnel current of 50 pA. White to black corresponds to applied voltages of 15.0 and 40.5 V, respectively. (b) AFM topograph of oxide surface recorded in the repulsive mode. Black to white correspond to a total vertical excursion of 90 nm.

In contact mode, add a current-to-voltage amplifier

⇛ Measure the I-V local response

⇛ Map topography + current simultaneously



Also known as local-conductivity AFM (**LC-AFM**), conductive probe AFM (**CP-AFM**), conductive scanning probe microscopy (**C-SPM**), conductive scanning force microscopy (**C-SFM**).

ISBN:978-3-527-34091-0, October 2017

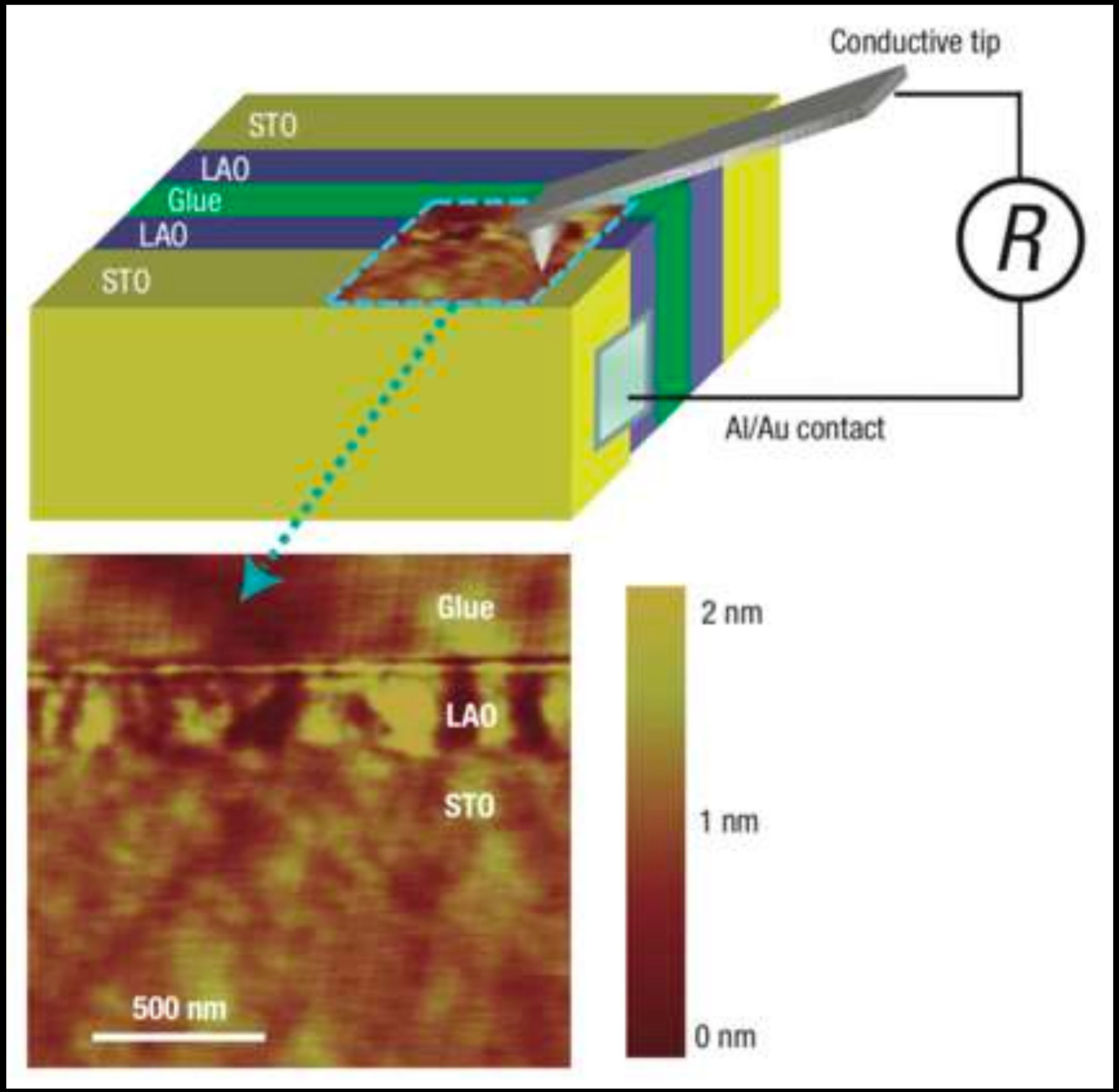
Spatially resolved electrical measurements of SiO_2 gate oxides using atomic force microscopy

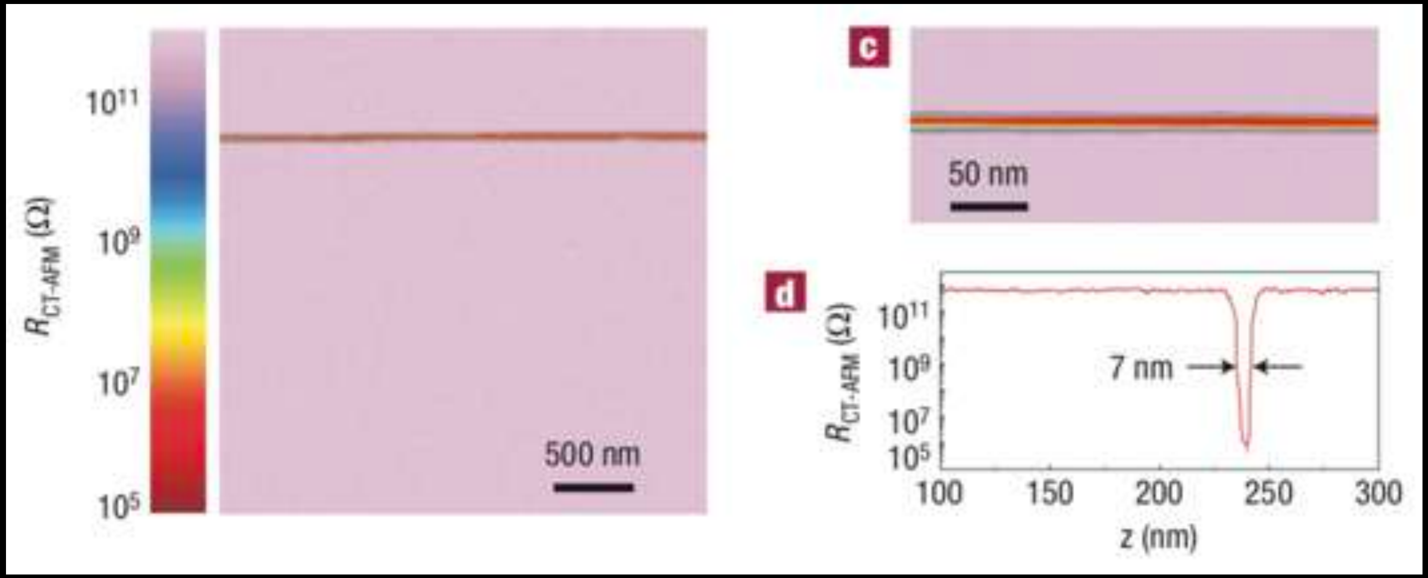
Murrell, Welland, O’Shea, Wong, Barnes, McKinnon, Heyns, Verhaverbeke,

Applied Physics Letters 1993, 62(7):786-788

Conductive Atomic Force Microscopy (C-AFM)

$LaAlO_3/SrTiO_3$ interface

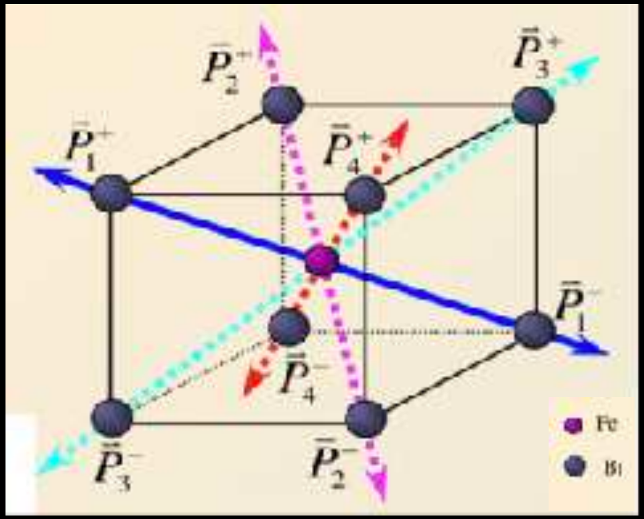


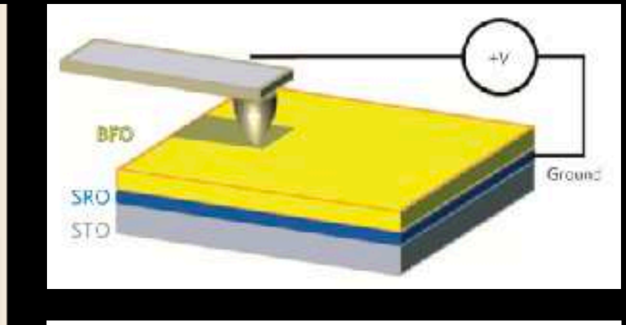


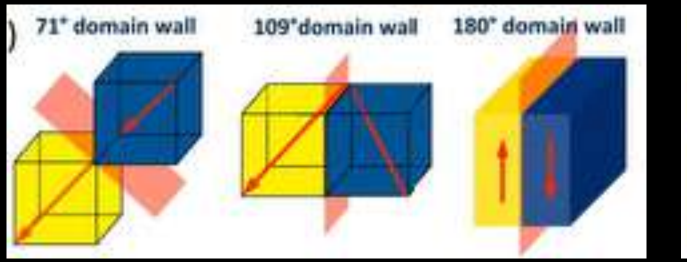
Mapping the spatial distribution of charge carriers in $LaAlO_3/SrTiO_3$ heterostructures
Basletic, Maurice, Carrétéro, Herranz, Copie, Bibes, Jacquet, Bouzehouane, Fusil, Barthélémy,
Nature Mater. 2008, 7:621

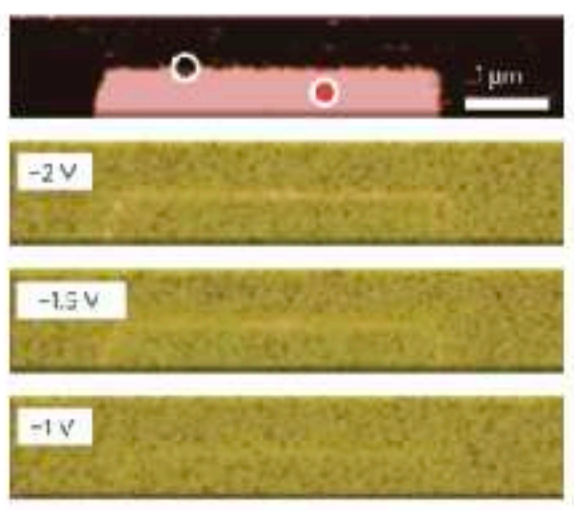
Conductive Atomic Force Microscopy (C-AFM)

BiFeO$_3$

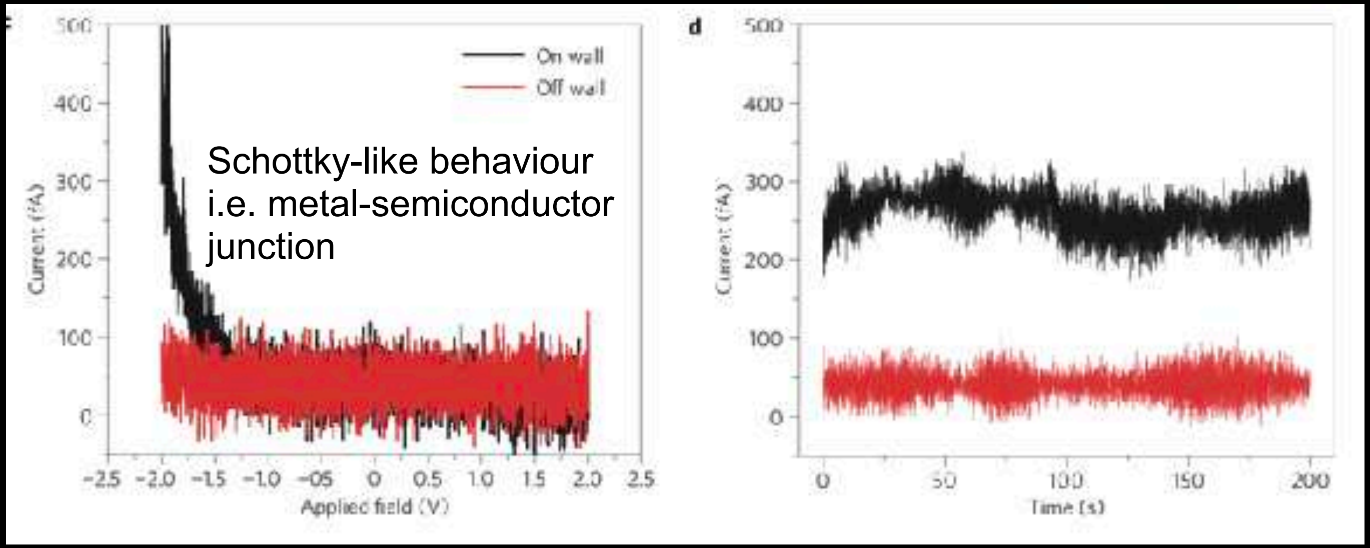




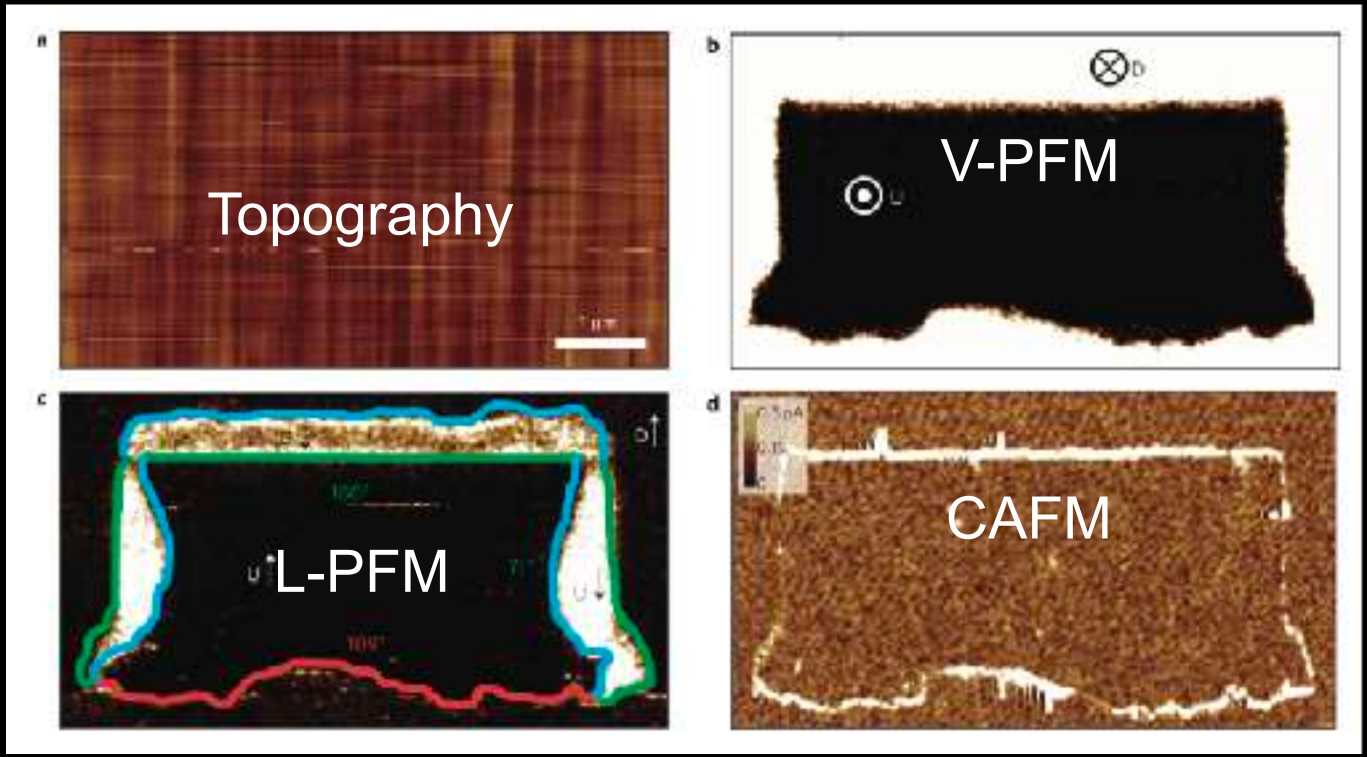




Room-temperature electronic conductivity at ferroelectric domain walls in the insulating multiferroic BiFeO$_3$



Schottky-like behaviour i.e. metal-semiconductor junction



Conduction @109° and 180° domain walls

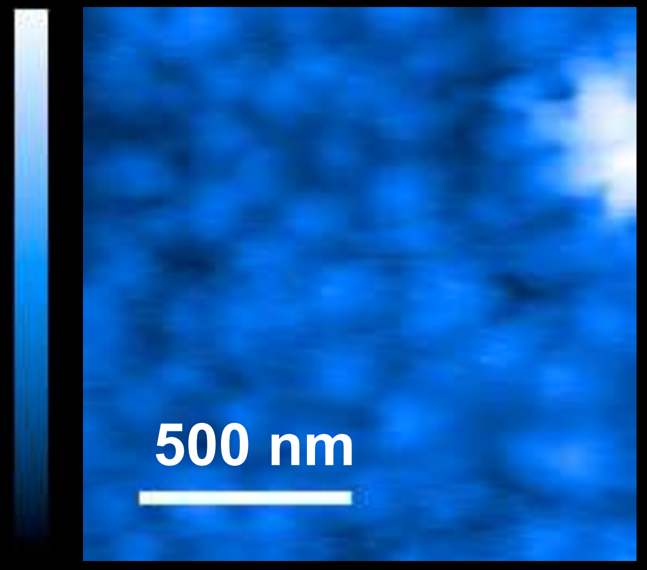
Conduction at domain walls in oxide multiferroics

Seidel, Martin, He, Zhan, Chu, Rother, Hawkridge, Makymovych, Yu, Gajek, Balke, Kalinin, Gemming, Wang, Catalan, Scott, Spaldin, Orenstein, Ramesh, **Nature Materials 2009**, 8:229

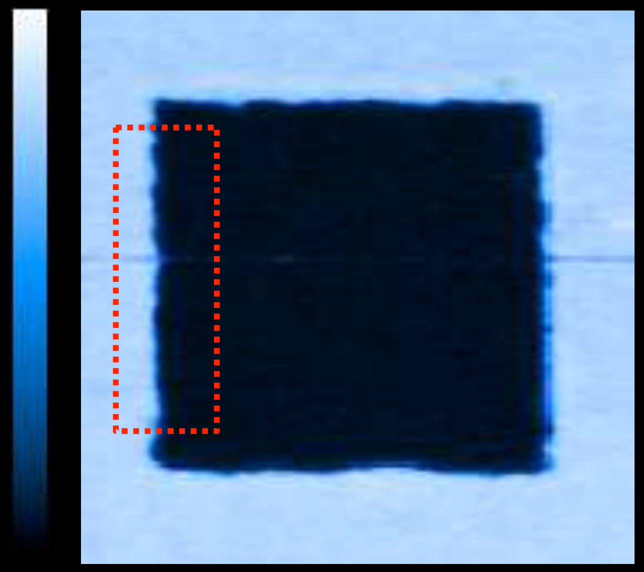
Conductive Atomic Force Microscopy (C-AFM)

$Pb(Zr_{0.2}Ti_{0.8})O_3$

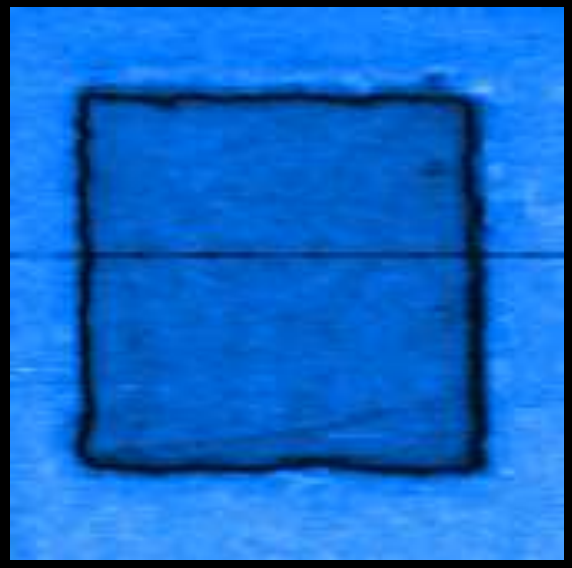
topography



PFM phase

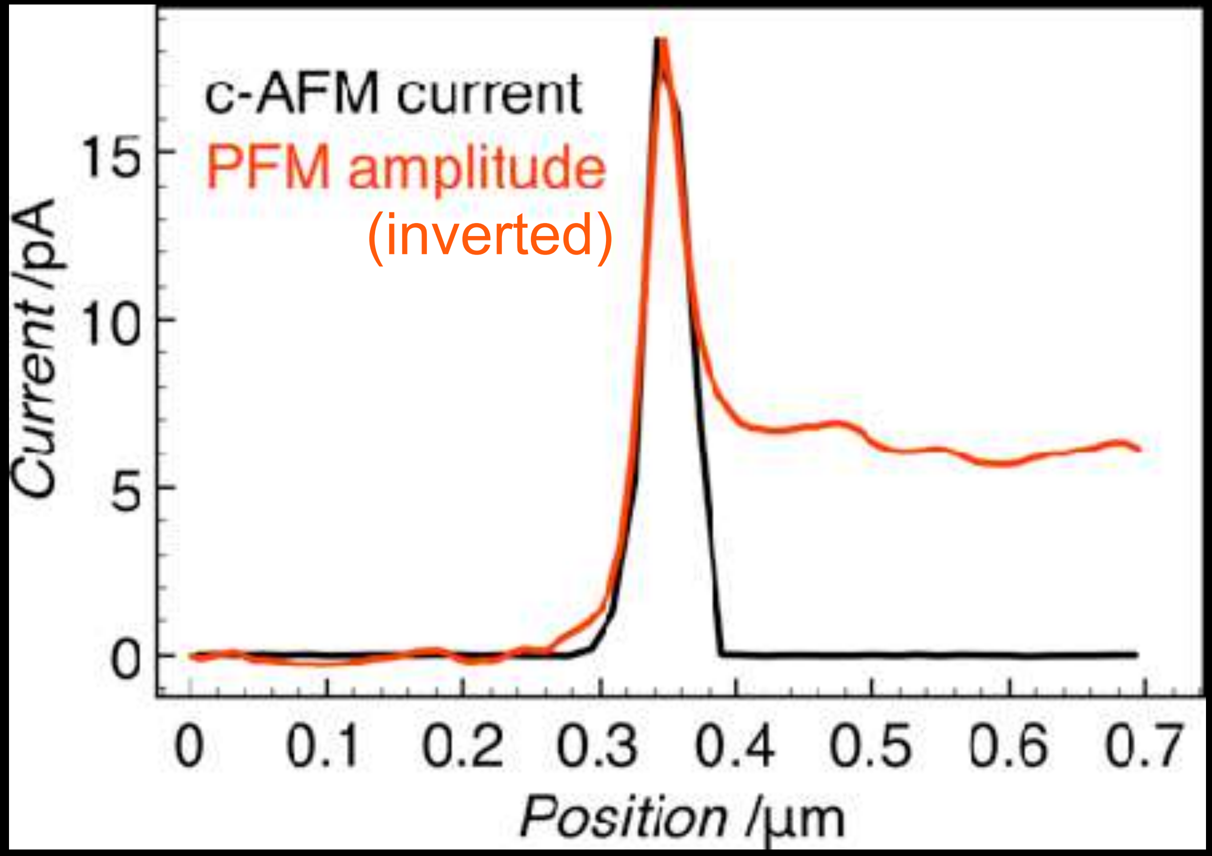


PFM amplitude

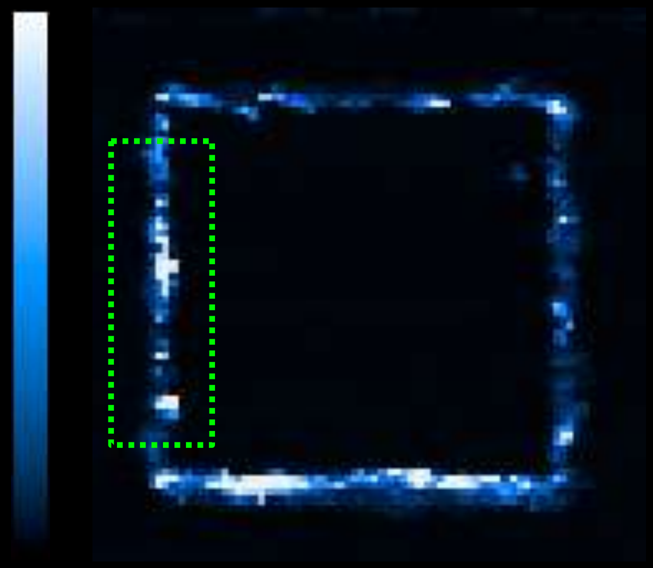


PFM
V_{tip} = 1 V AC
f = 1 kHz

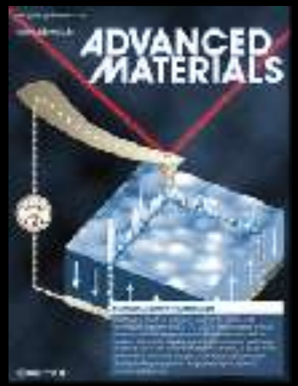
Domain-wall-specific current measured by local probe



current



c-AFM
V_{tip} = -1.5 V DC



Ferroelectric Materials: Conduction at Domain Walls in Insulating $Pb(Zr_{0.2}Ti_{0.8})O_3$ Thin Films
Guyonnet, Gaponenko, Gariglio, Paruch, **Adv. Mater. 2011**, **23**:5376

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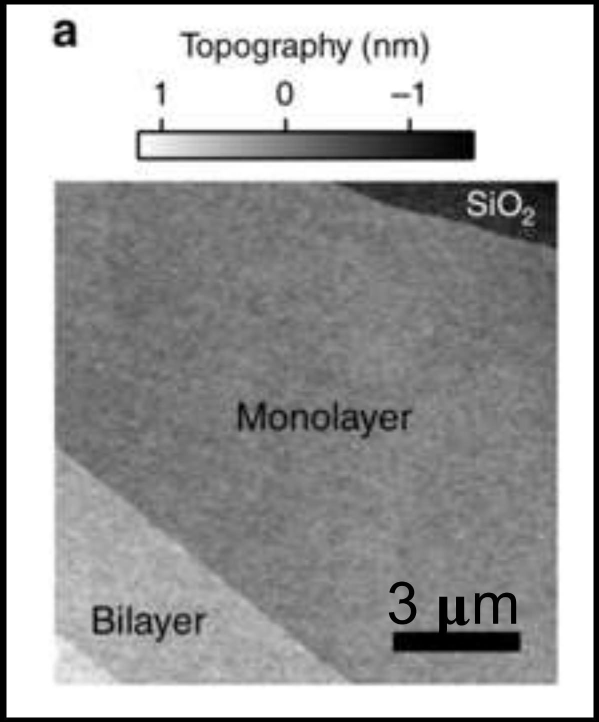
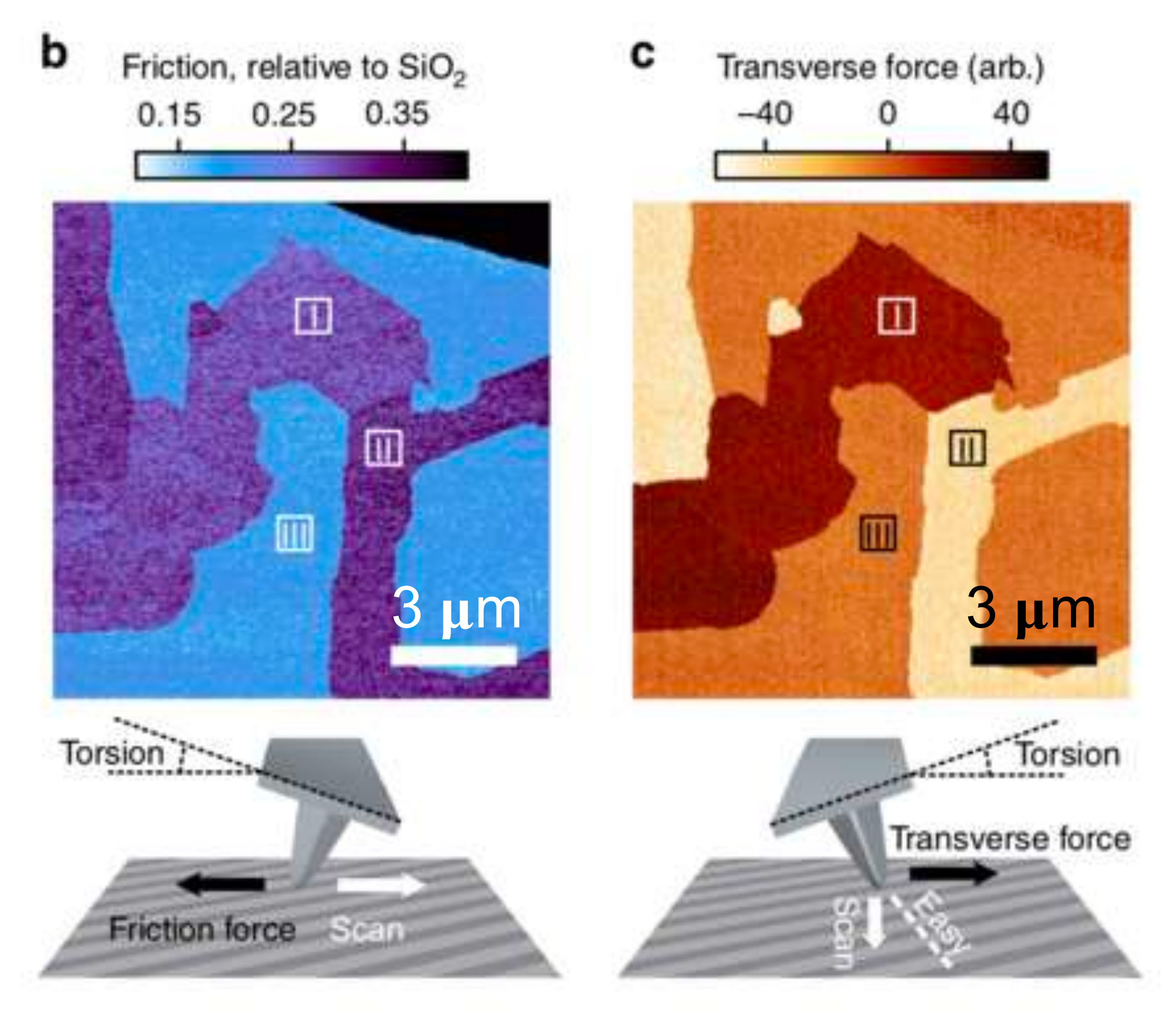
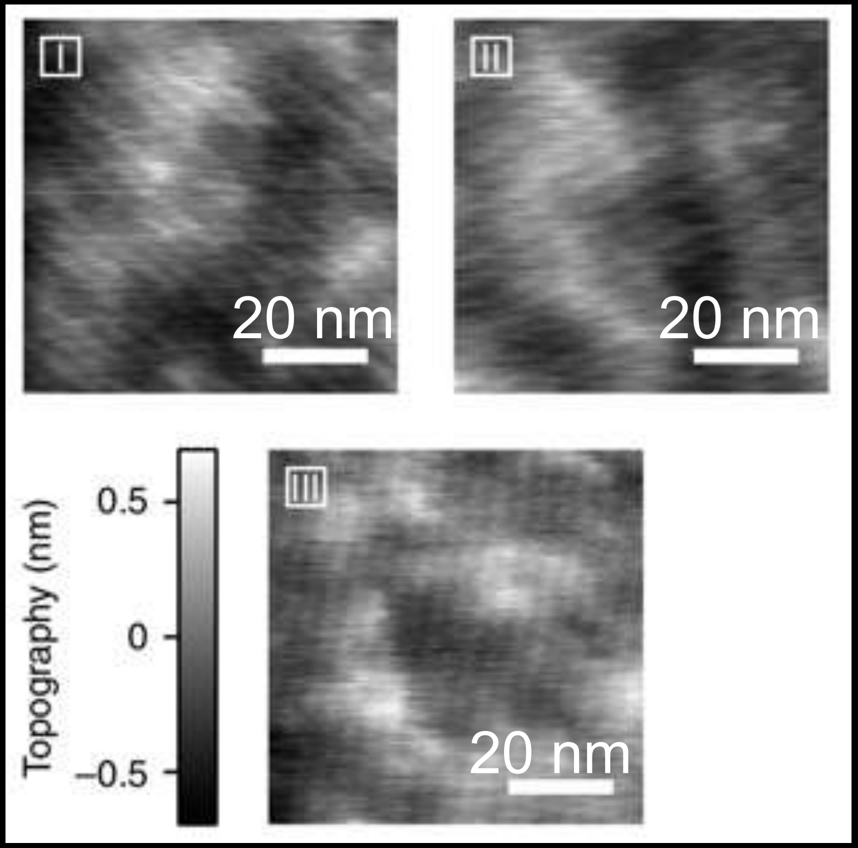
Friction mode AFM

Friction measurements using either lateral force (torsion) or transverse force (buckling)
⇛ access the friction between the tip and the sample



Graphene on
SiO2 substate





⇛ Self-assembly of environmental adsorbates into a highly regular superlattice of stripes
⇛ Friction response depends on stripes orientation

Switchable friction enabled by nanoscale self-assembly on graphene
Gallagher, Lee, Amet, Maksymovych, Wang, Wang, Lu, Zhang, Watanabe, Taniguchi, Goldhaber-Gordon,
Nature Com. 2016, 7: 10745

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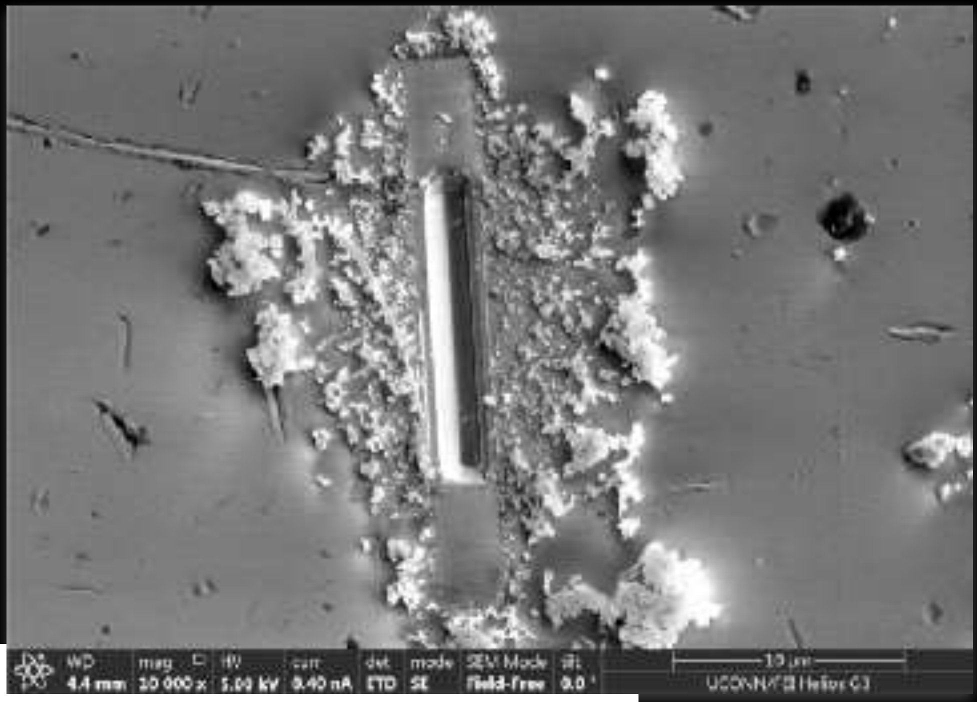
Tomographic Atomic Force Microscopy (TAFM)

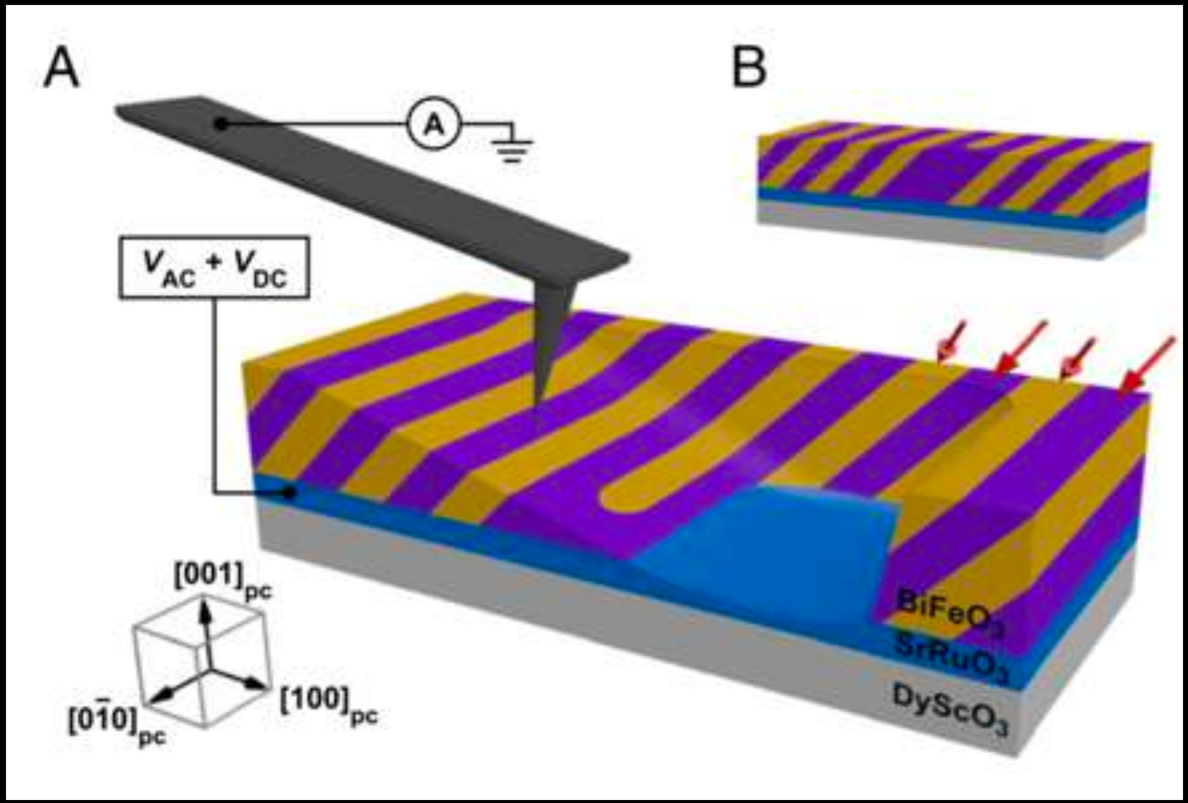
120nm $BiFeO_3(001)_{pc}/SrRuO_3(001)_{pc}/DyScO_3(110)_o$

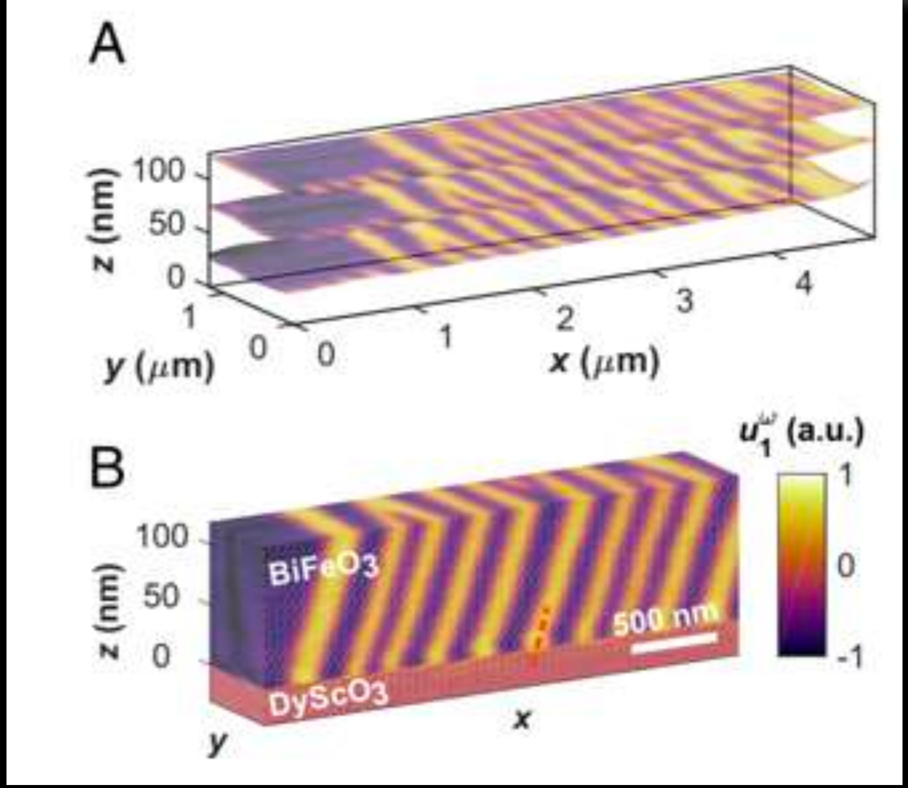
11.4μN mean probe downforce

⇛ mean vertical removal rate of 0.97nm per frame

⇛ 3D imaging of domains and domain walls







Thickness scaling of ferroelectricity in $BiFeO_3$ by tomographic atomic force microscopy
Steffes, Ristau, Ramesh, Huey, **PNAS 2019**, 116(7)2413-2418

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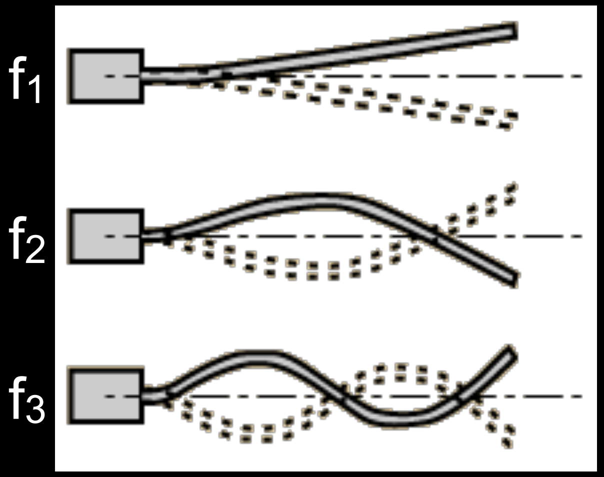
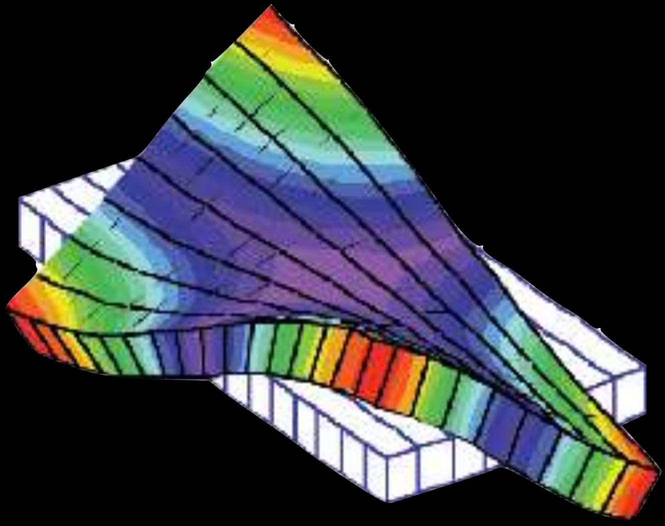
Non-contact mode

Different modes of vibration of the cantilever are possible:
vertical deflection, torsion, buckling…

Oscillation of cantilever (resonant mode)

Clamped bar



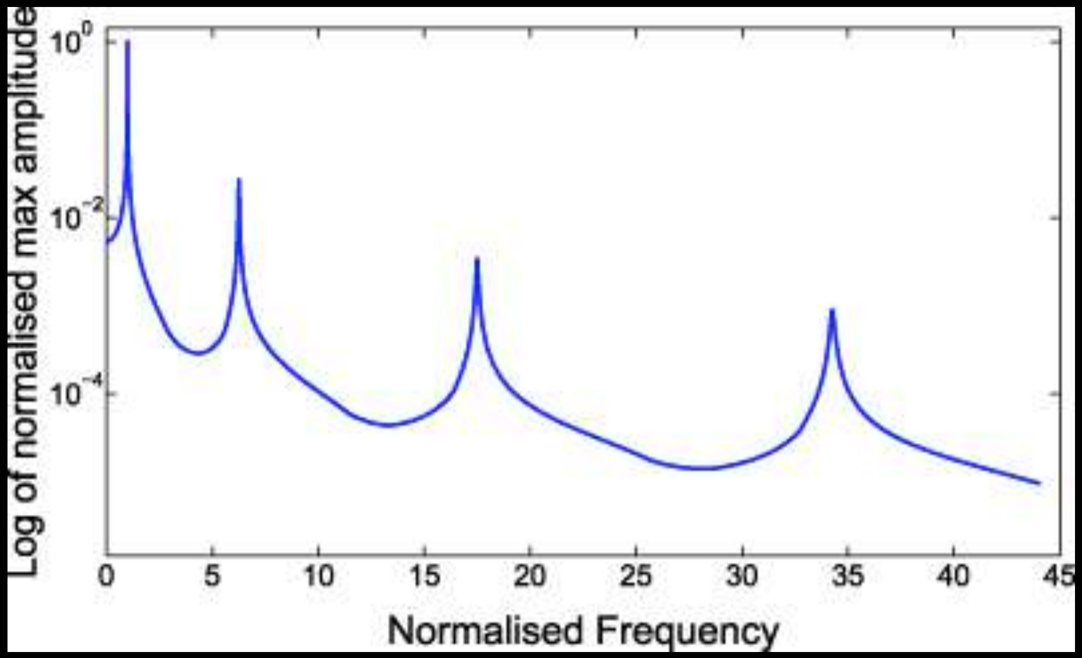


For thin bars:

$$f_1 \simeq 0.162\frac{a}{L^2}\sqrt{\frac{Y}{d}}$$

$$f_n \simeq 2.81\left(n-\frac{1}{2}\right)^2 f_1$$

a: thickness; L: length; Y: Young's modulus; d: density



Non-contact mode

Oscillation of cantilever (resonant mode)

Harmonic oscillator approximation

damping drive

$$m\ddot{z} + kz + \frac{m\omega_0}{Q}\dot{z} = F_{\mathrm{ts}} + F_0\cos(\omega t)$$

elastic response tip-surface interaction

Driving force:
- amplitude F_0
- angular frequency ω

Free cantilever:
- quality factor Q
- angular resonance ω_0
- spring constant k

Tip-surface intaraction forces:
- amplitude F_{ts}

- With no interaction ($F_{ts}=0$): forced harmonic oscillator with damping

Solution = sinusoidal function of amplitude A with a phase lag ϕ with respect to the excitation force and a modified resonance frequency ω_r

$$A(\omega) = \frac{F_0/m}{\left[(\omega_0^2 - \omega^2)^2 + (\omega\omega_0/Q)^2\right]^{1/2}}$$

$$\tan\phi = \frac{\omega\omega_0/Q}{\omega_0^2 - \omega^2}$$

$$\omega_{\mathrm{r}} = \omega_0\left(1 - \frac{1}{2Q^2}\right)^{1/2}$$

The damping modifies the resonance frequency of the cantilever

- With tip-surface interaction: for small displacements, consider the Taylor expansion:

$$F = F_0 + \left(\frac{\mathrm{d}F}{\mathrm{d}z}\right)_{z_0}(z - z_0)$$

Results in an effective spring constant k_e

$$k_{\mathrm{e}} = -\frac{\mathrm{d}F}{\mathrm{d}z} = \left(k - \frac{\mathrm{d}F_{\mathrm{ts}}}{\mathrm{d}z}\right)_{z_0}$$

with a new effective resonance frequency ω_e

$$\omega_{\mathrm{e}} = \left(\frac{k - (\mathrm{d}F_{\mathrm{ts}}/\mathrm{d}z)}{m}\right)^{1/2}$$

Dynamic atomic force microscopy methods

García, Pérez, **Surface Science Reports 2002**, 47:197

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Oscillation of cantilever (resonant mode)

Harmonic oscillator approximation

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Harmonic oscillator approximation

damping | drive

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elastic response | tip-surface interaction

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Tip-surface intaraction forces:

- amplitude F_{ts}

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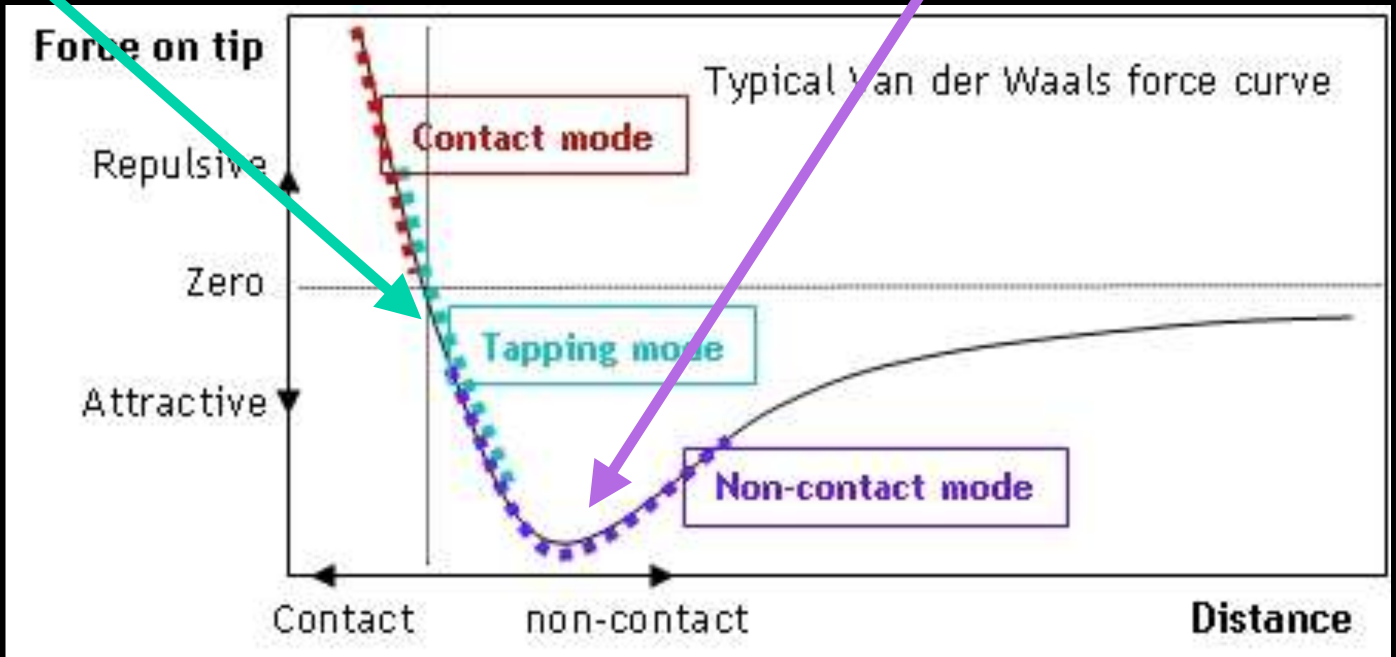
$$F = F_0 + \left(\frac{dF}{dz}\right)_{z_0}(z - z_0)$$

Amplitude modulation AFM
(AM-AFM)
= tapping mode

$$\omega_e = \left(\frac{k - (dF_{ts}/dz)}{m}\right)^{1/2}$$

Frequency modulation AFM
(FM-AFM)



Dynamic atomic force microscopy methods
García, Pérez, **Surface Science Reports 2002**, 47:197

Non-contact mode

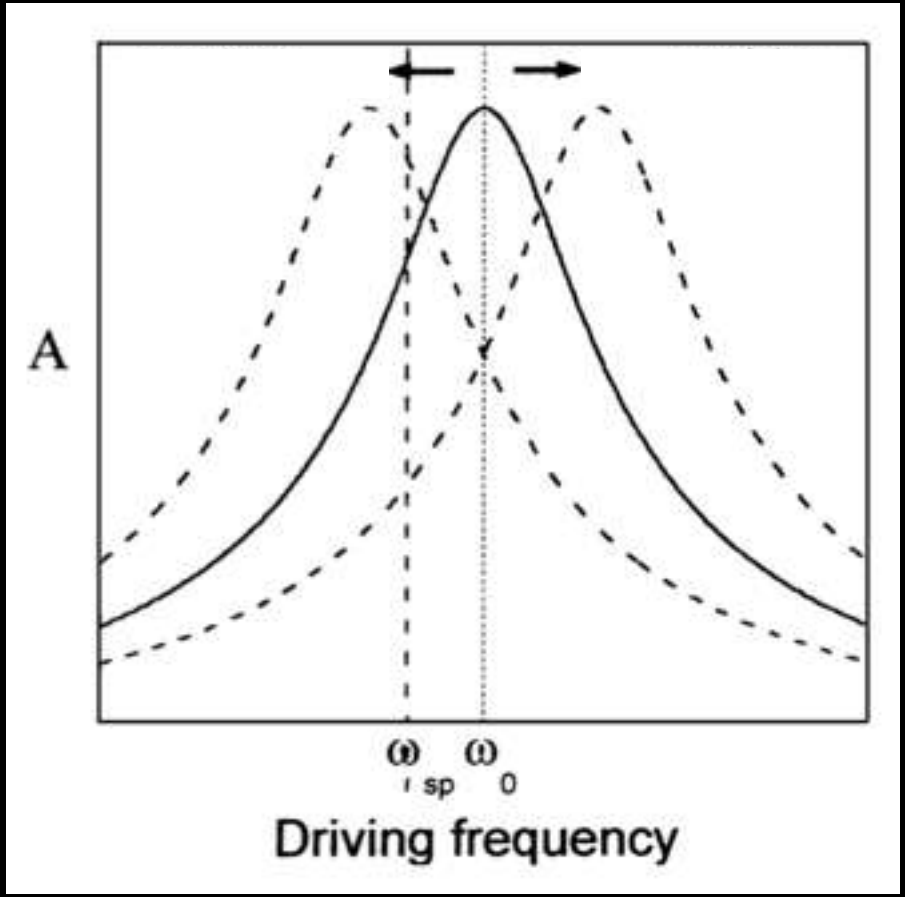
Oscillation of cantilever (resonant mode)

Harmonic oscillator approximation

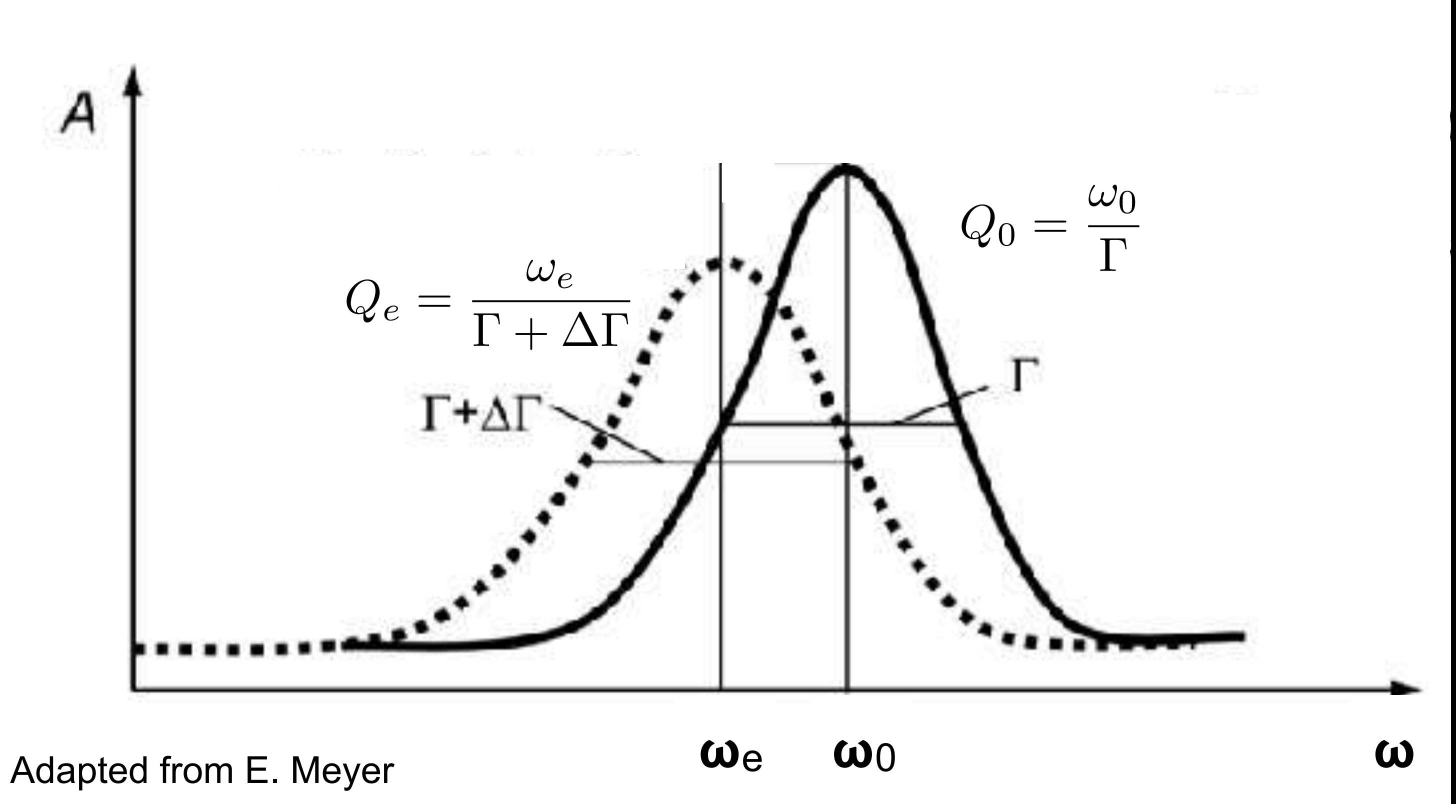
$$\omega_e = \left(\frac{k - (\mathrm{d}F_{ts}/\mathrm{d}z)}{m}\right)^{1/2}$$

Frequency modulation AFM (FM-AFM)

Conservative forces
⇛ shift of resonance curve



Dissipative forces
⇛ additional broadening of resonance curve

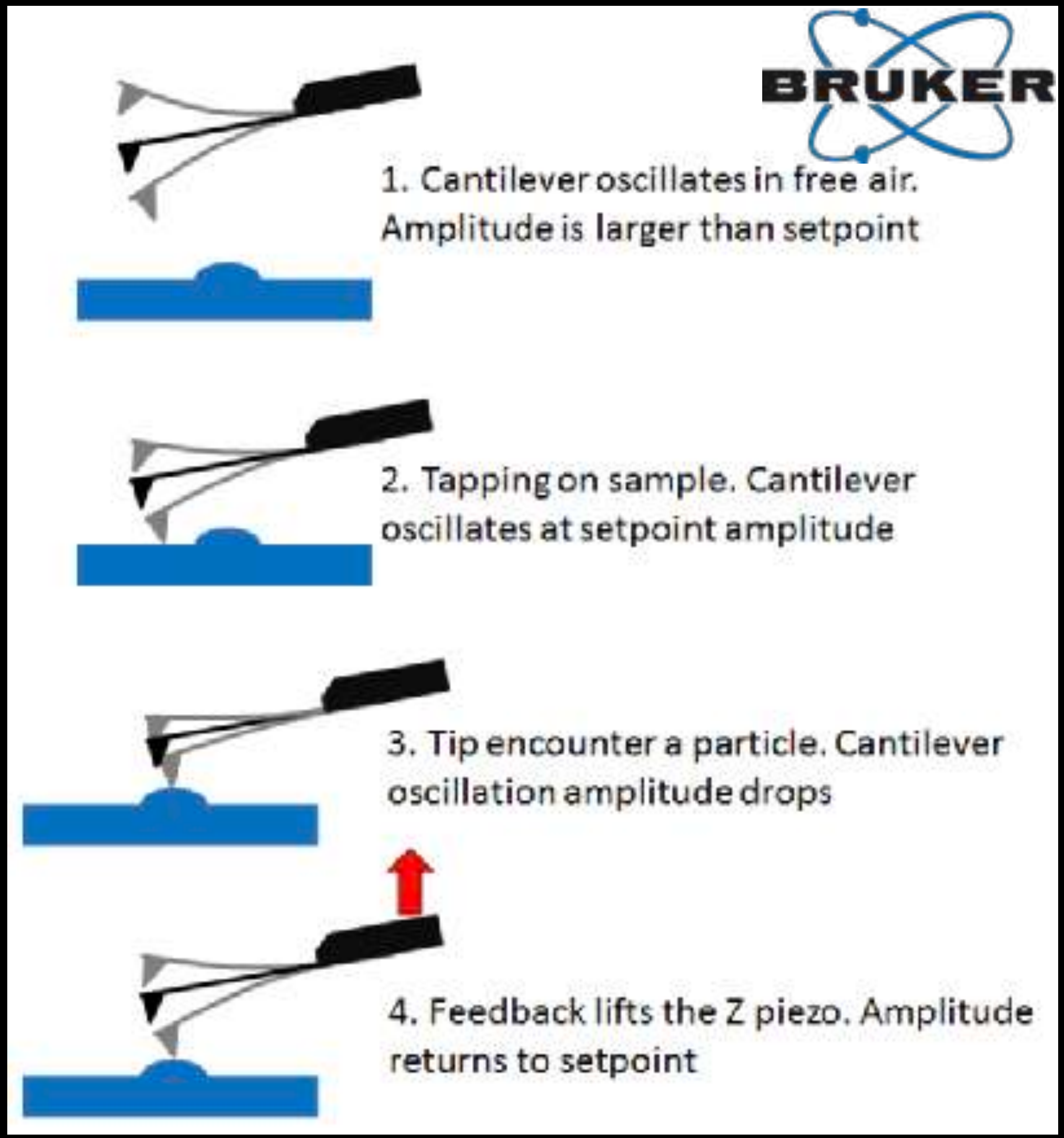


Adapted from E. Meyer

Dynamic atomic force microscopy methods
García, Pérez, **Surface Science Reports 2002**, 47:197

Tapping mode

Oscillation of cantilever (resonant mode)



1. Cantilever oscillates in free air. Amplitude is larger than setpoint
2. Tapping on sample. Cantilever oscillates at setpoint amplitude
3. Tip encounter a particle. Cantilever oscillation amplitude drops
4. Feedback lifts the Z piezo. Amplitude returns to setpoint

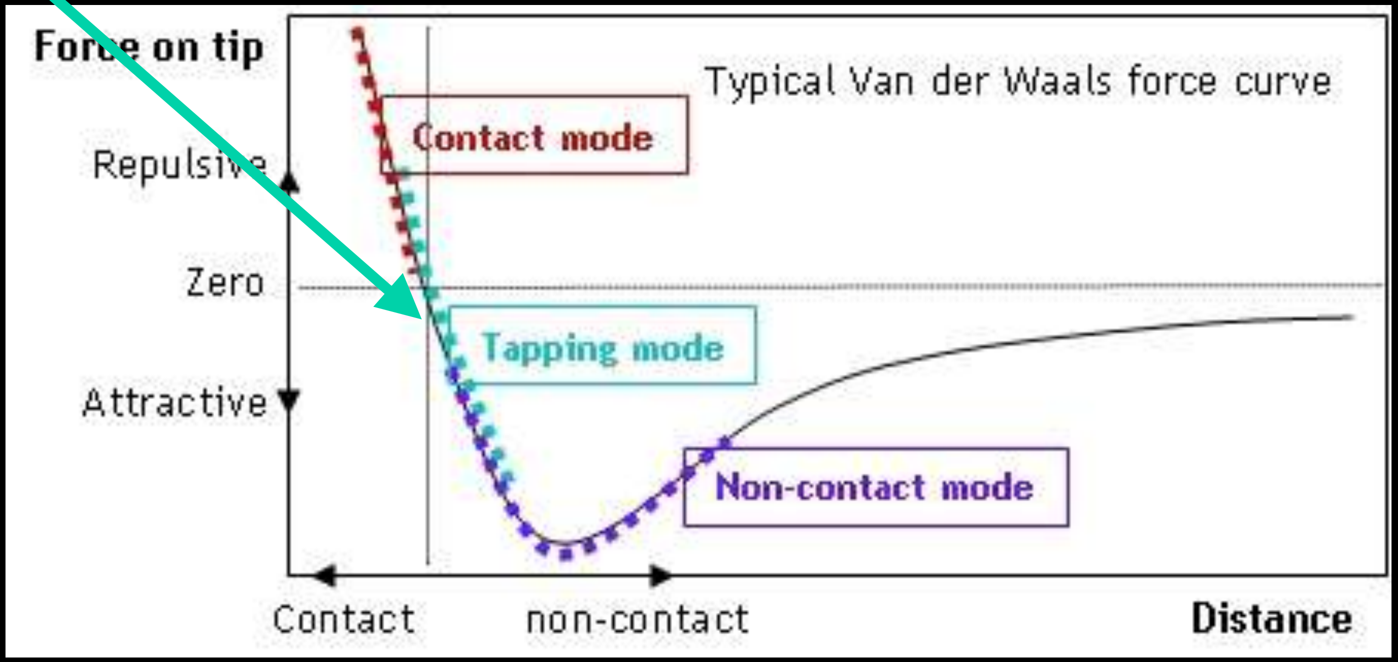
http://www.nanophys.kth.se/nanophys/facilities/nfl/afm/fast-scan/bruker-help/Content/TappingMode%20AFM/TappingMode%20AFM.htm

$$A(\omega) = \frac{F_0/m}{\left[(\omega_0^2 - \omega^2)^2 + (\omega\omega_0/Q)^2\right]^{1/2}}$$

$$F = F_0 + \left(\frac{\mathrm{d}F}{\mathrm{d}z}\right)_{z_0} (z - z_0)$$

Amplitude modulation AFM
(AM-AFM)
= tapping mode

Measured topography
=
surface of constant dF/dz

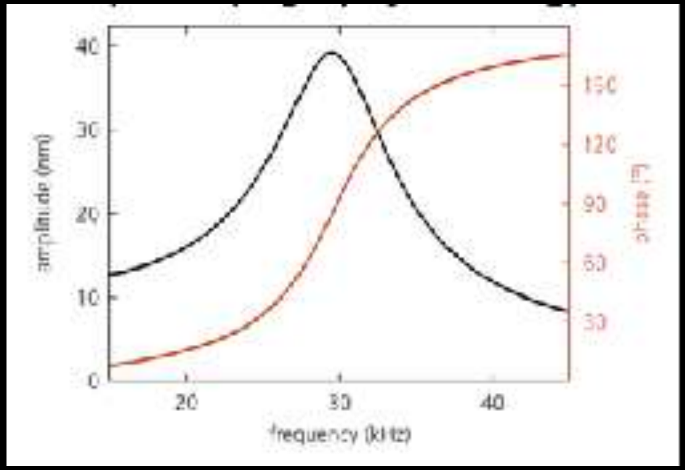


Dynamic atomic force microscopy methods
García, Pérez, **Surface Science Reports 2002**, 47:197

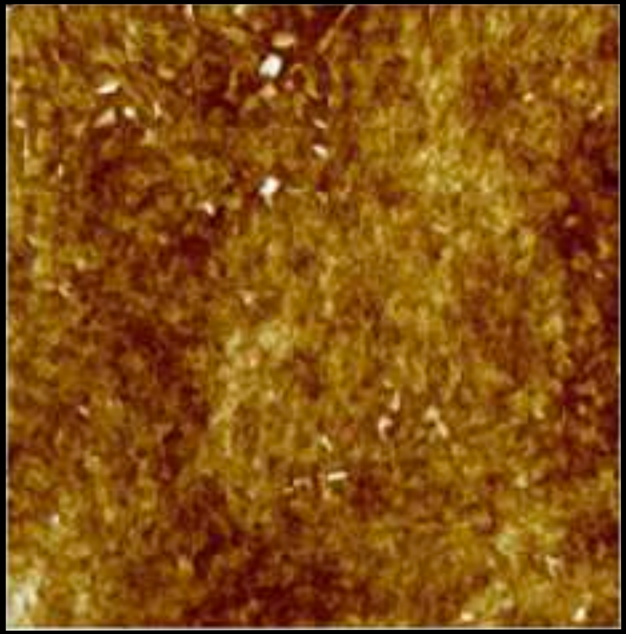
Tapping mode

- eliminates lateral forces that can distort or damage samples in contact mode
- information on the material properties: adhesion
- can be used on delicate and soft sample, or samples that are weakly attached to a substrate
- can be performed in both air and fluid
- might damage the tip and the sample

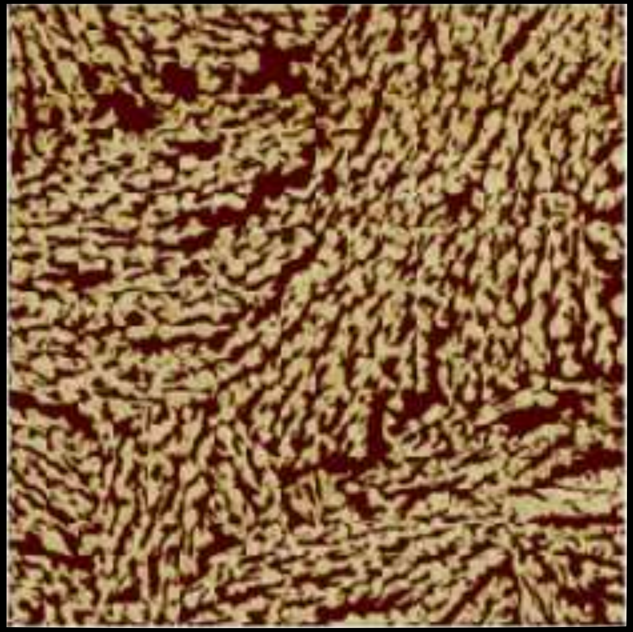
$$\tan\phi = \frac{\omega\omega_0/Q}{\omega_0^2 - \omega^2}$$



Topography



Phase



Topography: obtained by recording z adjusted by feedback control to maintain fixed cantilever oscillation amplitude setpoint

Phase: obtained by recording the phase difference between the cantilever oscillation and tapping piezo drive signal
⇛image contrast caused by differences in surface adhesion and viscoelasticity
⇛qualitative information on surface mechanical properties.

Crystal facetts

Scan size: 10µm

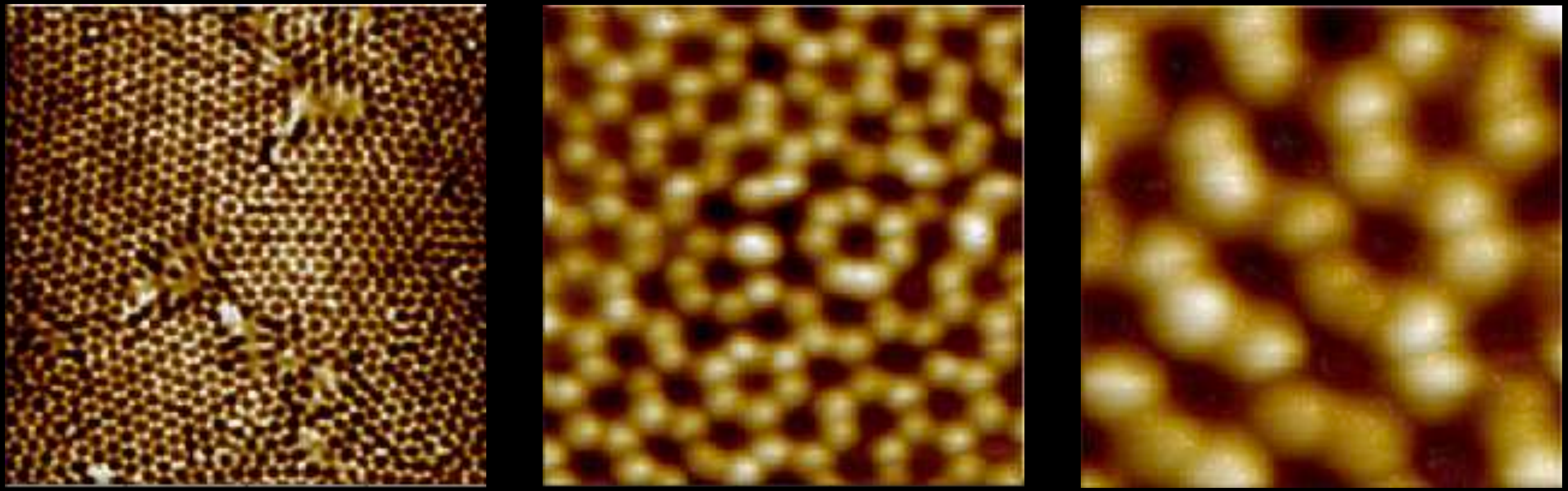
Probe: AC160TS

Imaged on a Park NX10 using tapping mode

Non-contact mode

Preserves tip sharpness and sample surface

Tip-sample distance: 10-100Å



Nano-arrayed particles

Scan size: 1μm, 250nm, 120nm

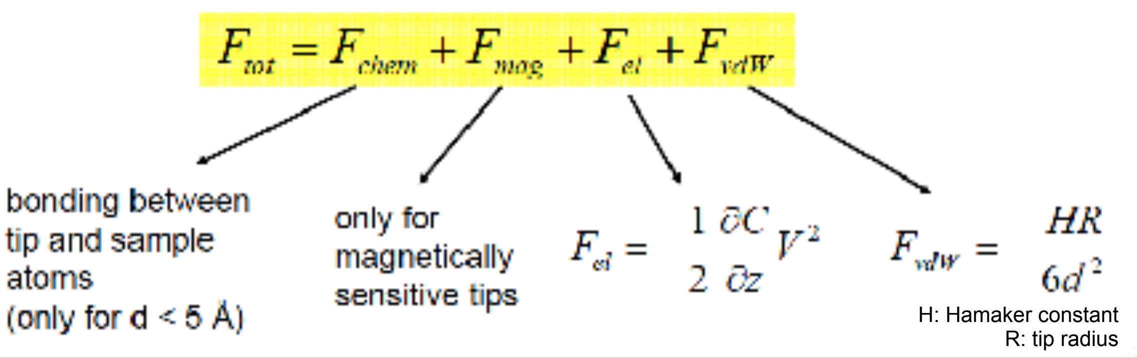
Probe: AR5T-NCHR

Imaged on a Park NX10 using non-contact mode in liquid

Non-contact mode

Oscillation of cantilever (resonant mode)

Harmonic oscillator approximation



$$F_{tot} = F_{chem} + F_{mag} + F_{el} + F_{vdW}$$

bonding between tip and sample atoms (only for d < 5 Å)

only for magnetically sensitive tips

$$F_{el} = \frac{1}{2}\frac{\partial C}{\partial z}V^2$$

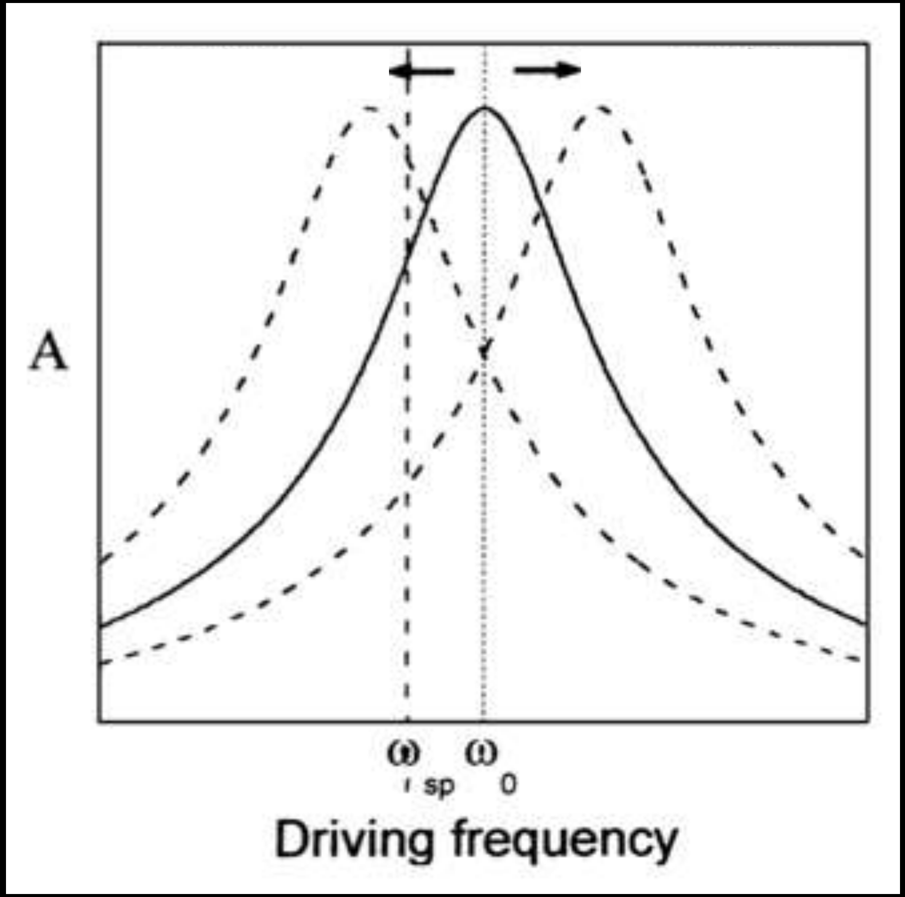
$$F_{vdW} = \frac{HR}{6d^2}$$

H: Hamaker constant
R: tip radius

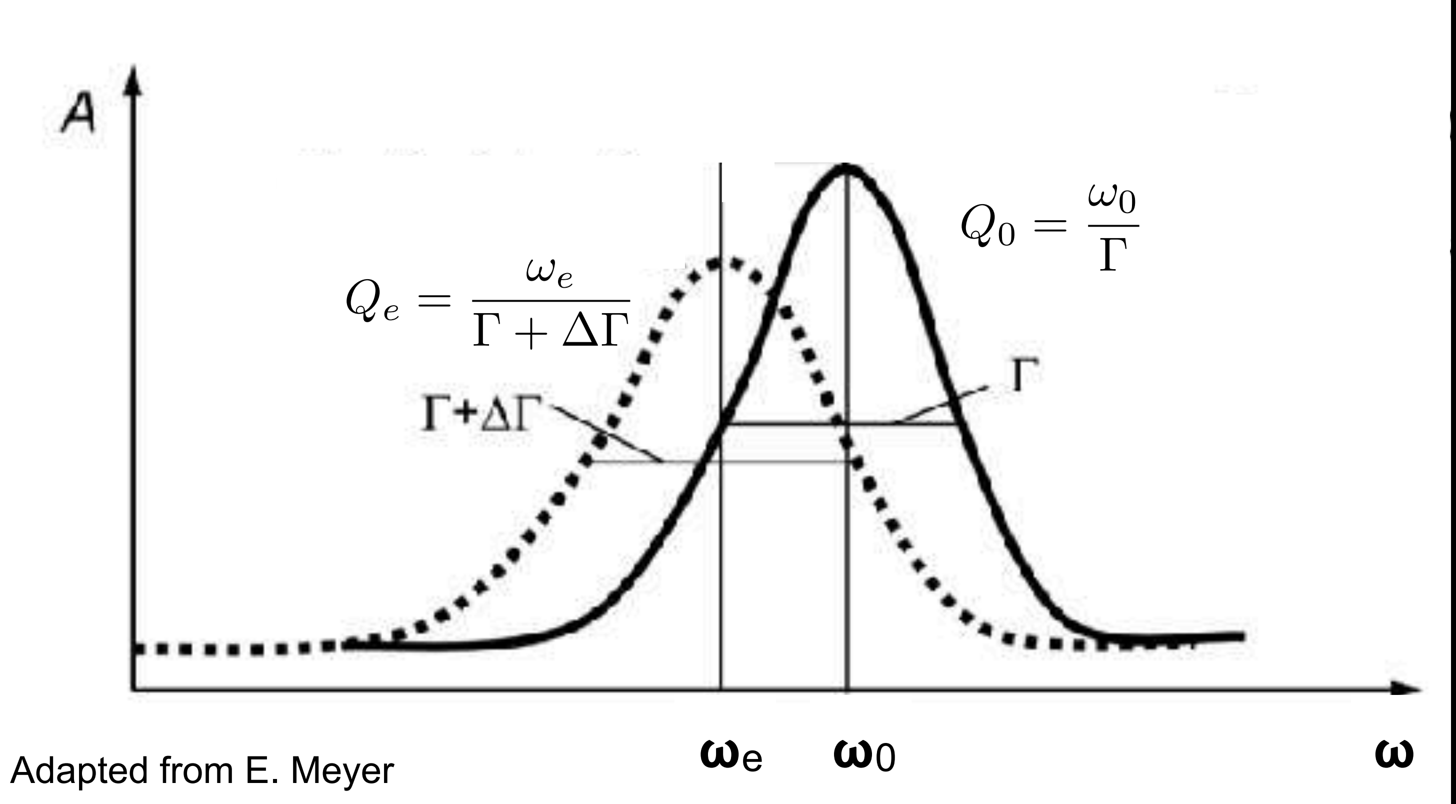
$$\omega_e = \left(\frac{k - (dF_{ts}/dz)}{m}\right)^{1/2}$$

Frequency modulation AFM (FM-AFM)

Conservative forces
⇛ shift of resonance curve



Dissipative forces
⇛ additional broadening of resonance curve



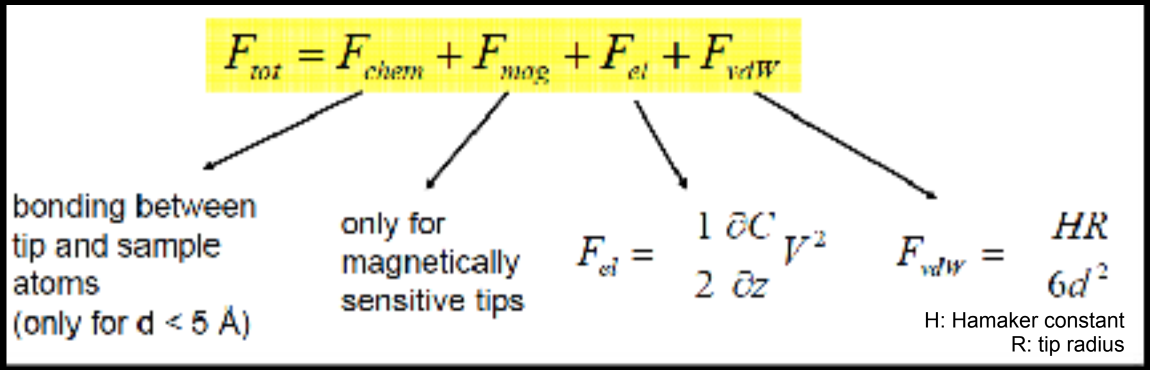
Adapted from E. Meyer

Dynamic atomic force microscopy methods
García, Pérez, **Surface Science Reports 2002**, 47:197

Non-contact mode

Oscillation of cantilever (resonant mode)

Harmonic oscillator approximation



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R: tip radius

$$\omega_e = \left(\frac{k - (dF_{ts}/dz)}{m}\right)^{1/2}$$

Frequency modulation AFM (FM-AFM)

Relevant forces

- Short-range repulsive forces (Pauli exclusion) or ionic repulsion forces
- Short-range chemical binding forces
- van der Waals forces (always present, retarded beyond 100 nm)
- electrostatic forces (long-ranged)
- magnetic forces
- interaction in liquids: hydrophobic/ hydrophilic forces; steric forces; solvation forces

Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems
Israelachvili**, Academic Press (1985)**

Gases, liquids and solids
Tabor**, Cambridge University Press (1979)**

Dynamic atomic force microscopy methods
García, Pérez, **Surface Science Reports 2002**, 47:197

Advanced scanning probe microscopy

Outline

Scanning Tunneling Microscopy - STM
- How does it work

Atomic Force Microscopy - AFM
- How does it work

Contact mode
- Topography
- Piezoresponse Force Microscopy - PFM
- Conductive Atomic Force Microscopy - CAFM
- Friction mode AFM
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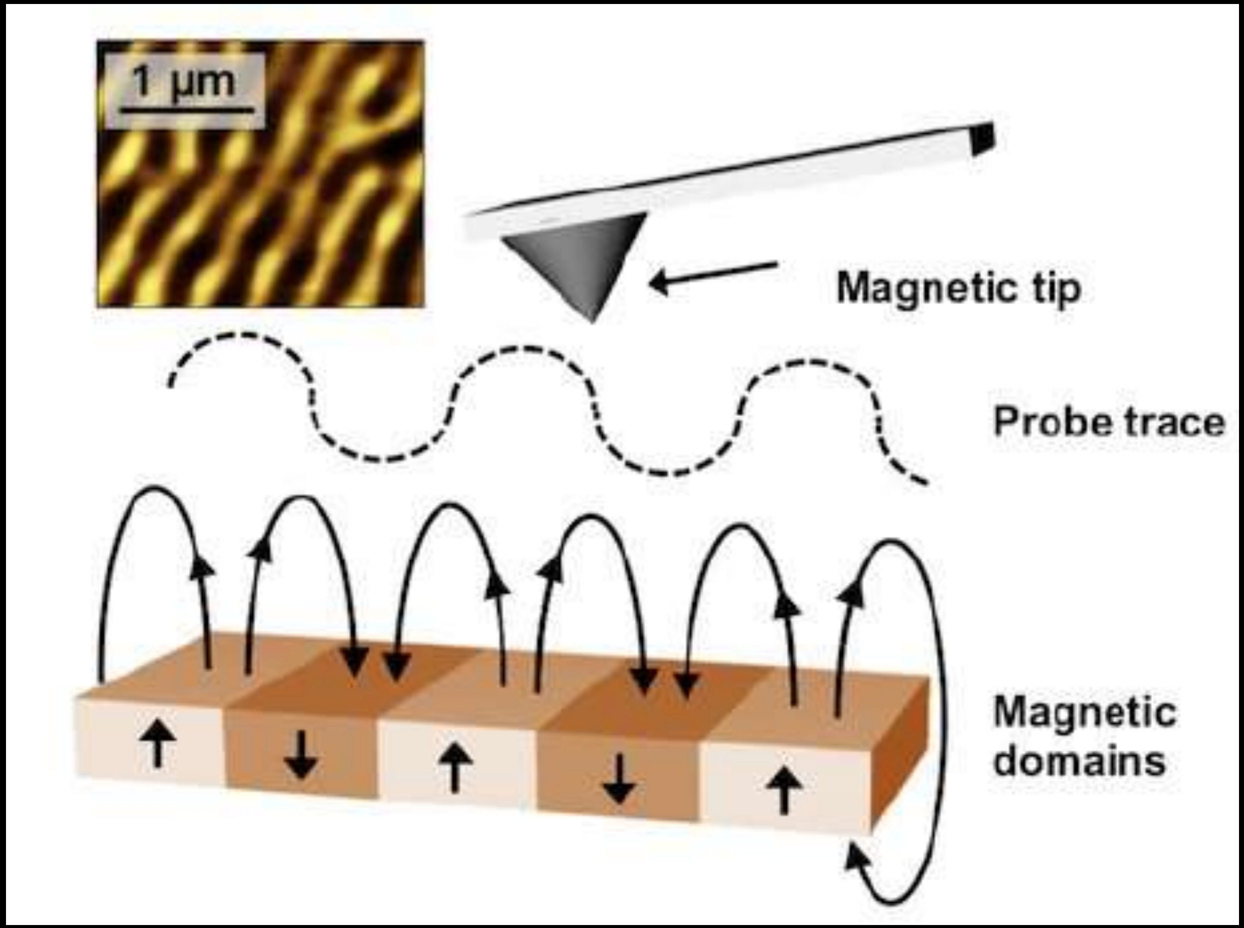
Magnetic Force Microscopy (MFM)

Imaging of Magnetic Properties

Force = magnetic interaction between magnetized tip and magnetic sample

$$\vec{F} = \mu_0 (\vec{m} \cdot \nabla) \vec{H}$$



μ_0 magnetic permeability of free space

$\vec{m}$ magnetic moment of the tip (approximated as a point dipole)

$\vec{H}$ magnetic stray field from the sample surface

In non-contact mode, use a tip coated with a ferromagnetic layer

⇛ information on magnetic domain distributions on the sample surface

200 nm thick sputtered Co film exhibiting a perpendicular strip domain structure

FEBID fabrication and magnetic characterization of individual nano-scale and micro-scale Co structures
Idigoras, Nikulina, Porro, Vavassori, Chuvilin, Berger, **Nanofabrication 2014**, 1:23

Magnetic Force Microscopy (MFM)

Imaging of Magnetic Properties

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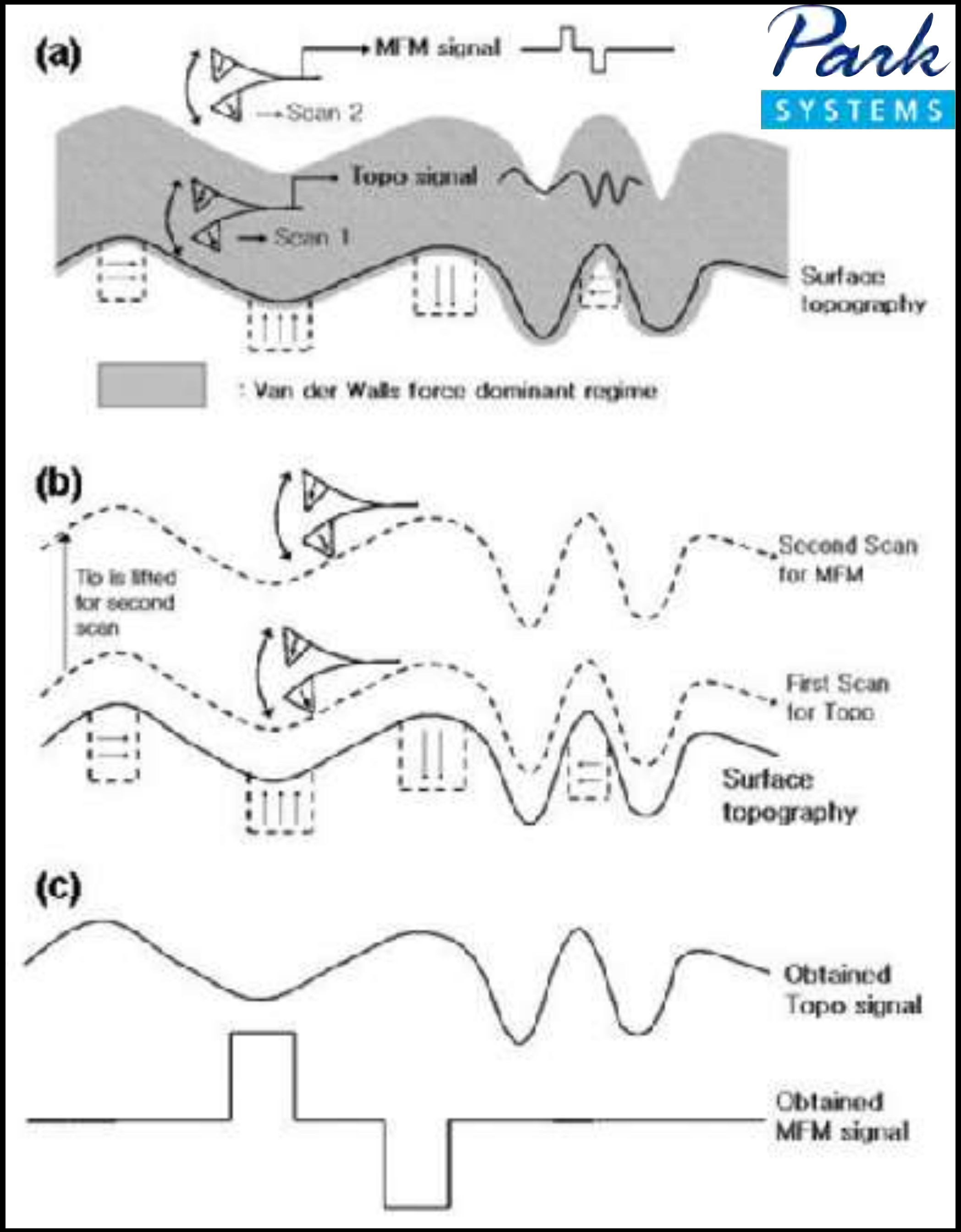
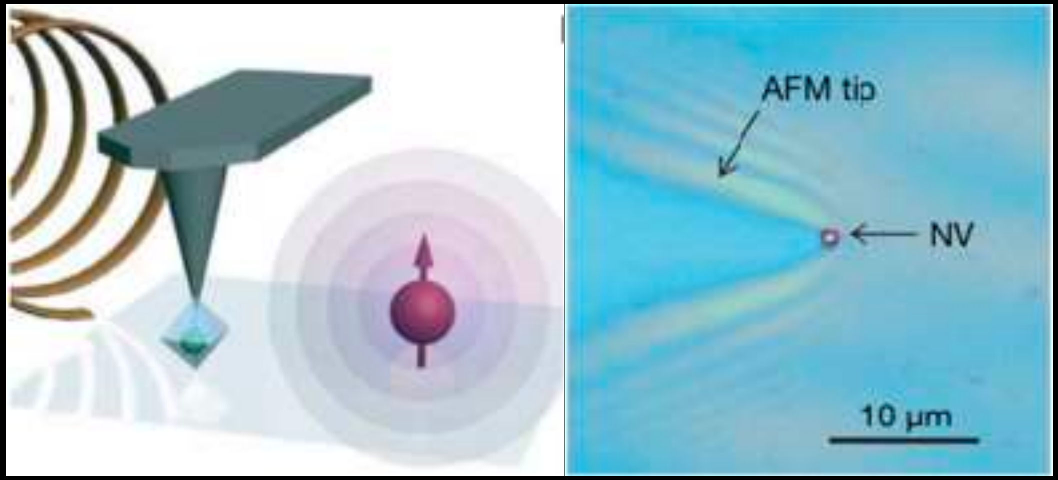


Force Range technique

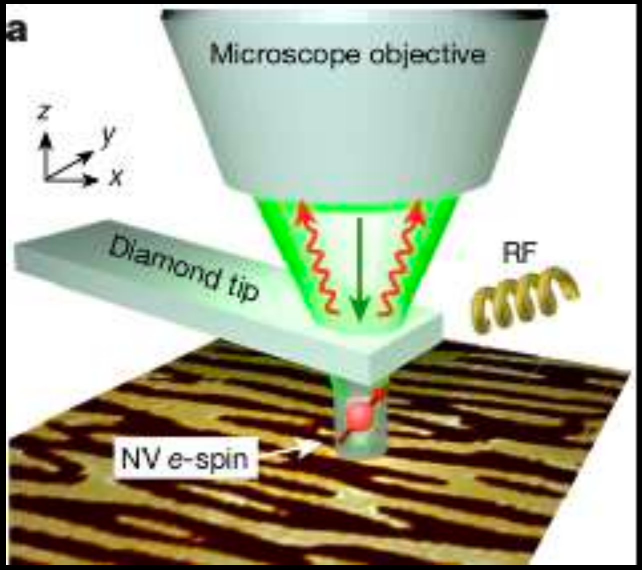
"Two Pass technique" or "Lift Mode" (better)

Scanning probe magnetometry: single spin magnetometer

A single nitrogen-vacancy defect (NV) fixed at the scanning probe tip



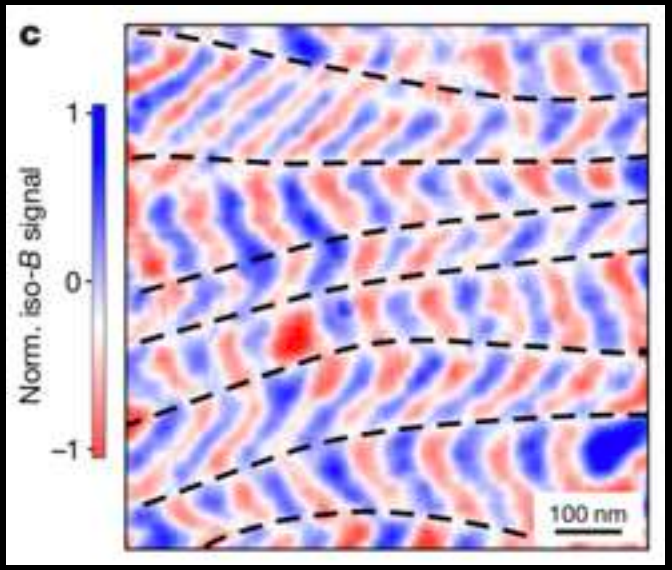
Nanoscale imaging magnetometry with diamond spins under ambient conditions
Balasubramanian, Chan, Kolesov, Al-Hmoud, Tisler, Shin, Kim, Wojcik. Hemmer, Krueger, Hanke, Leitenstorfer, Bratschitsch, Jelesko, Wrachtrup, **Nature 2008**, 455:648



Microscope objective: excite and collect spin-dependent photoluminescence of the NV defect

Radiofrequency (RF) source: manipulate the NV defect electronic spin state

Spin cycloid in $BiFeO_3$ with abrupt rotations of the antiferromagnetic order at ferroelectric domain walls



Real-space imaging of non-collinear antiferromagnetic order with a single-spin magnetometer
Gross, Akhtar, Garcia, Martinez, Chouaieb, Garcia, Carrétéro, Barthélémy, Appel, Malentinsky, Kim, Chauleau, Jaouen, Viret, Bibes, Fusil, Jacques, **Nature 2017**, 549:252

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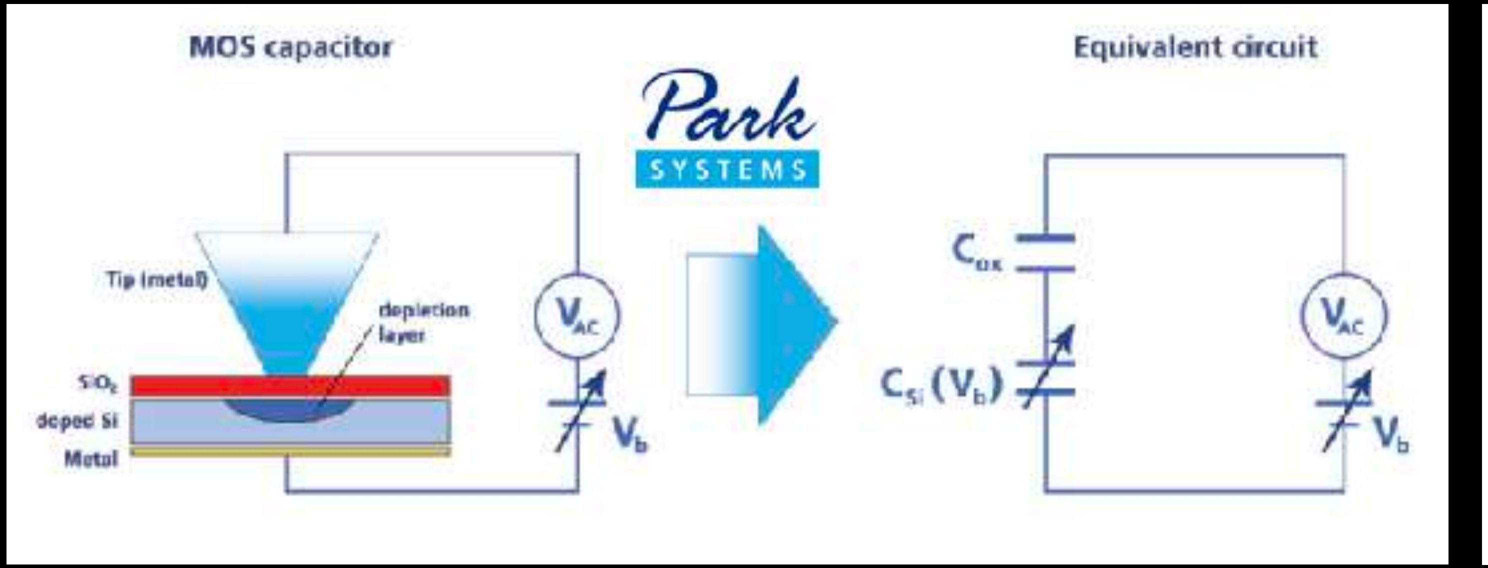
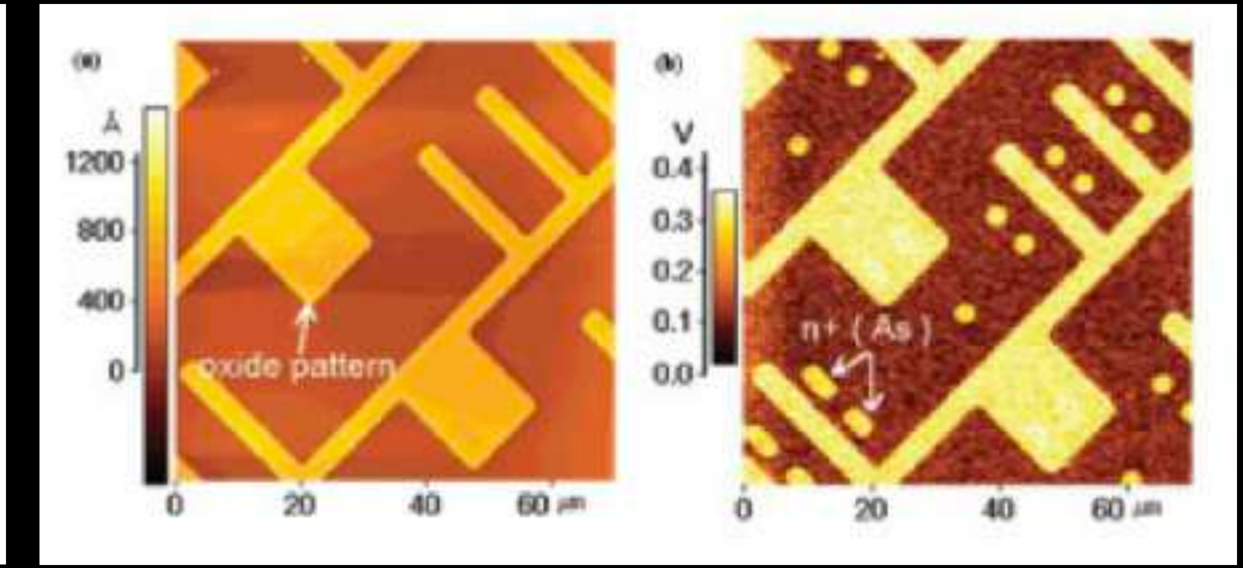
Scanning Capacitance Microscopy (SCM)

$$C = \frac{q}{V}$$





Use a conducting probe
Work close to the surface (tapping mode)
Apply an alternating bias voltage: generates an alternating capacitance
⇛ induces carriers accumulation or depletion within the semiconductor's surface layer
⇛ changes the tip-sample capacitance
⇛ magnitude of this change: information on carriers concentration
⇛ phase shift: sign of the charge carriers

Topography (a) and SCM (b) image of a semiconductor surface showing thermally grown silicon dioxide pattern with 70 nm height. The bright regions in the SCM image are heavily doped by As^+

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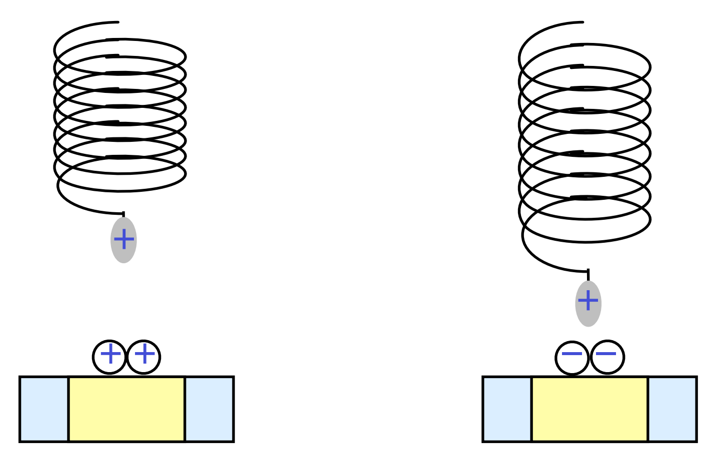
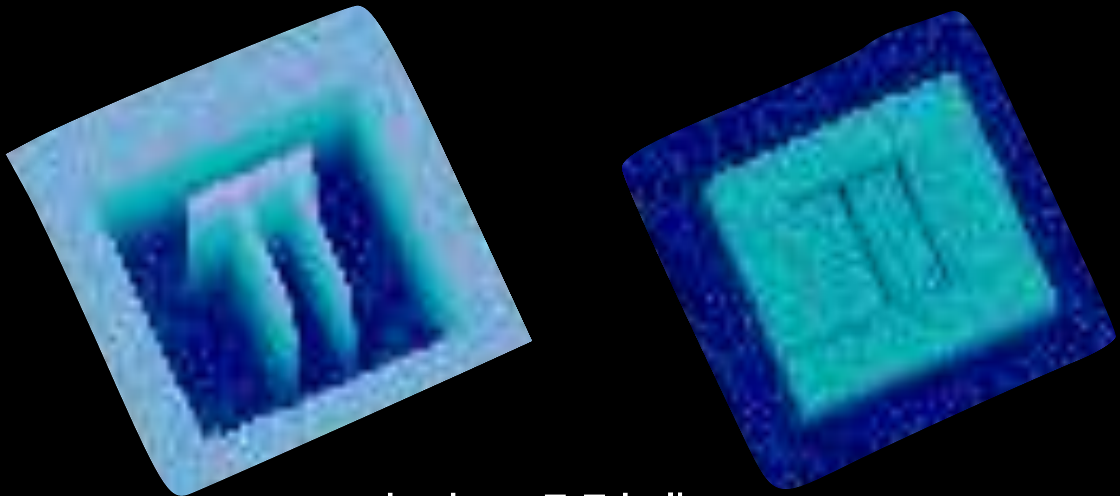
Electrostatic Force Microscopy (EFM)

Need functionalised tip (metallic/charged)



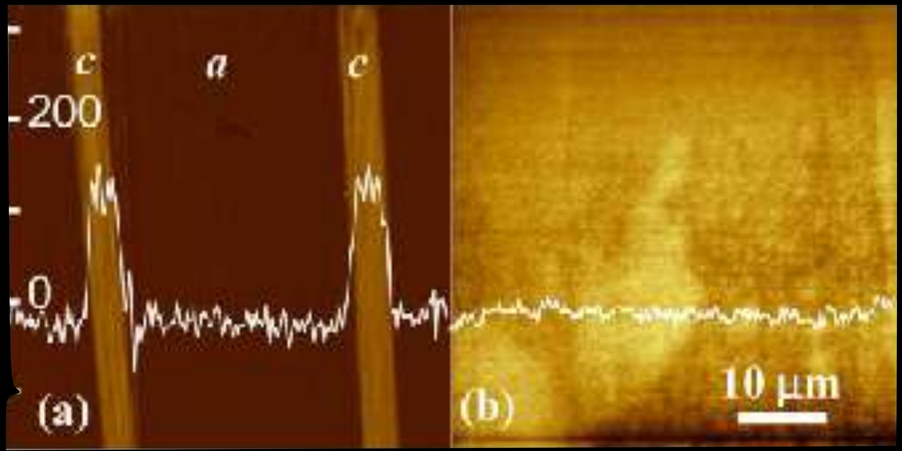


thanks to T. Tybell

Screening charges on ferroelectric domains

Similar to MFM: 2-pass technique, acquiring first topography, then EFM signal at a specific height above the sample to avoid topographical crosstalk.

Very sensitive to relative humidity at ambient conditions.



He *et al.* APL **98,** 062905 (2011)

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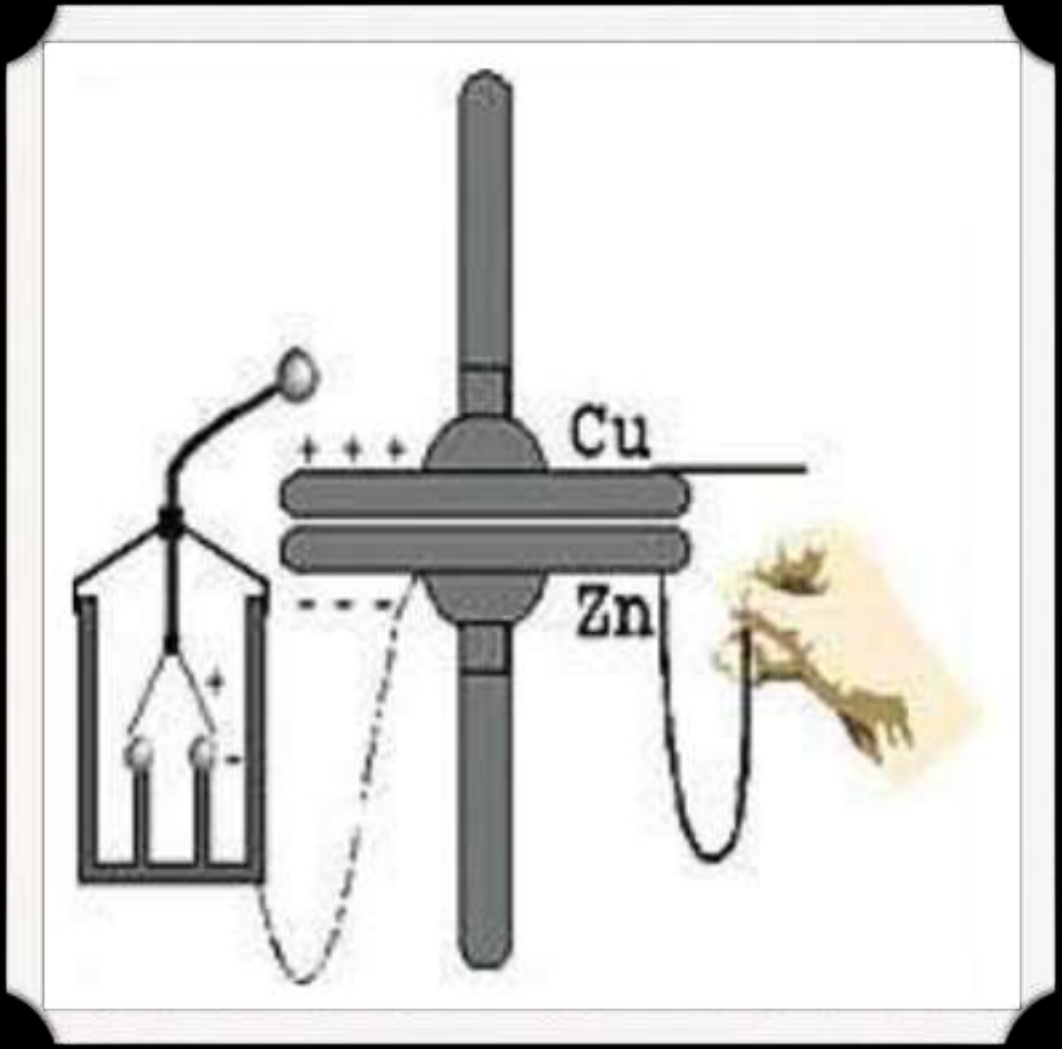
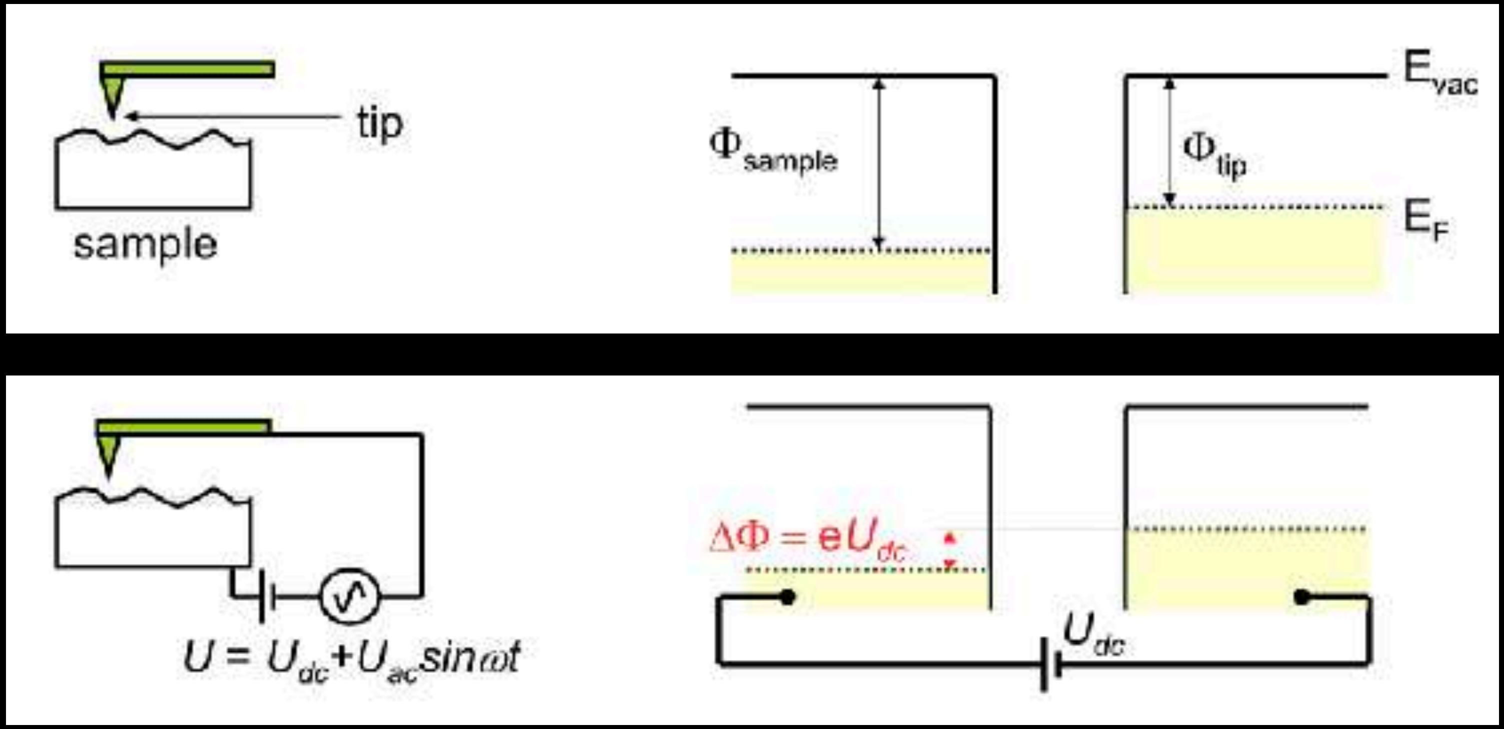
Kelvin Probe Force Microscopy (KPFM)

Imaging of surface potential



1861 Lord Kelvin



Contact potential difference V_{CPD}

$$V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{e^-} = \frac{\Delta\phi}{e^-}$$

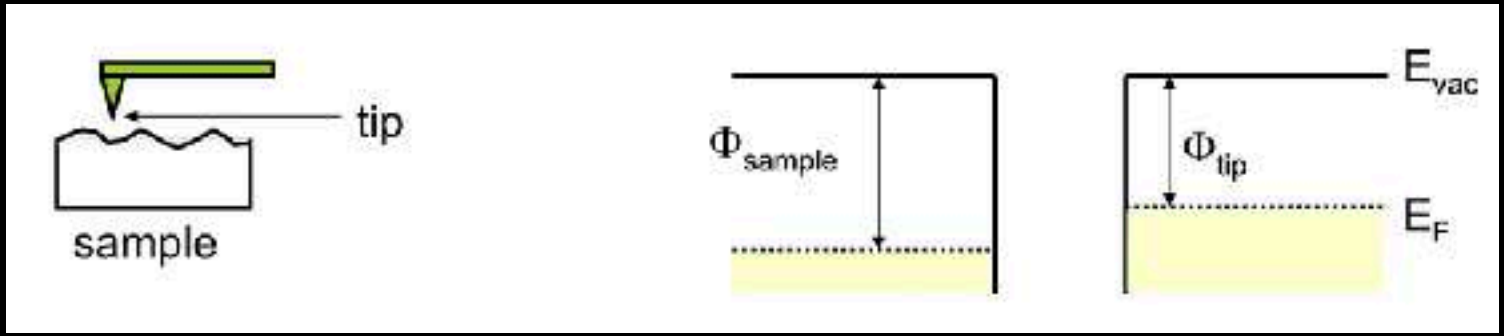
Information on the electronic state of the local structures on the surface of a solid.

Also known as Surface Potential Microscopy.

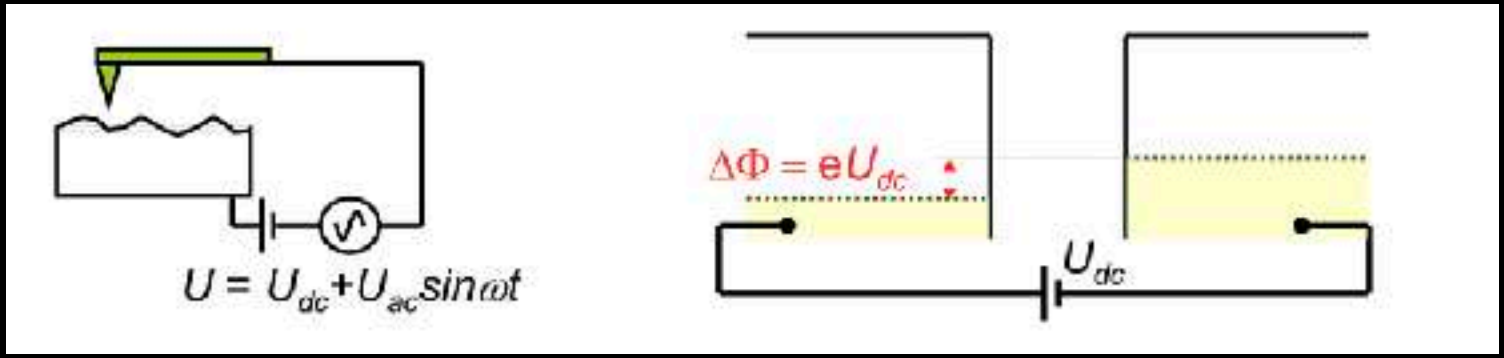
Kelvin Probe Force Microscopy (KPFM)

Imaging of surface potential

Cantilever=reference electrode that forms a capacitor with the surface - scanned at a constant separation.



Not piezoelectrically driven at its mechanical resonance frequency **ω_0** BUT an AC voltage is applied at this frequency.



Energy of the capacitor:

$$E = \frac{1}{2}C[V_{DC} + V_{AC}\sin(\omega_0 t)]^2 = \boxed{\frac{1}{2}C[2V_{DC}V_{AC}\sin(\omega_0 t)}- \frac{1}{2}V_{AC}^2\cos(2\omega_0 t)]$$ +DC terms

only cross-term is at resonance frequency induces mechanical vibration of the cantilever

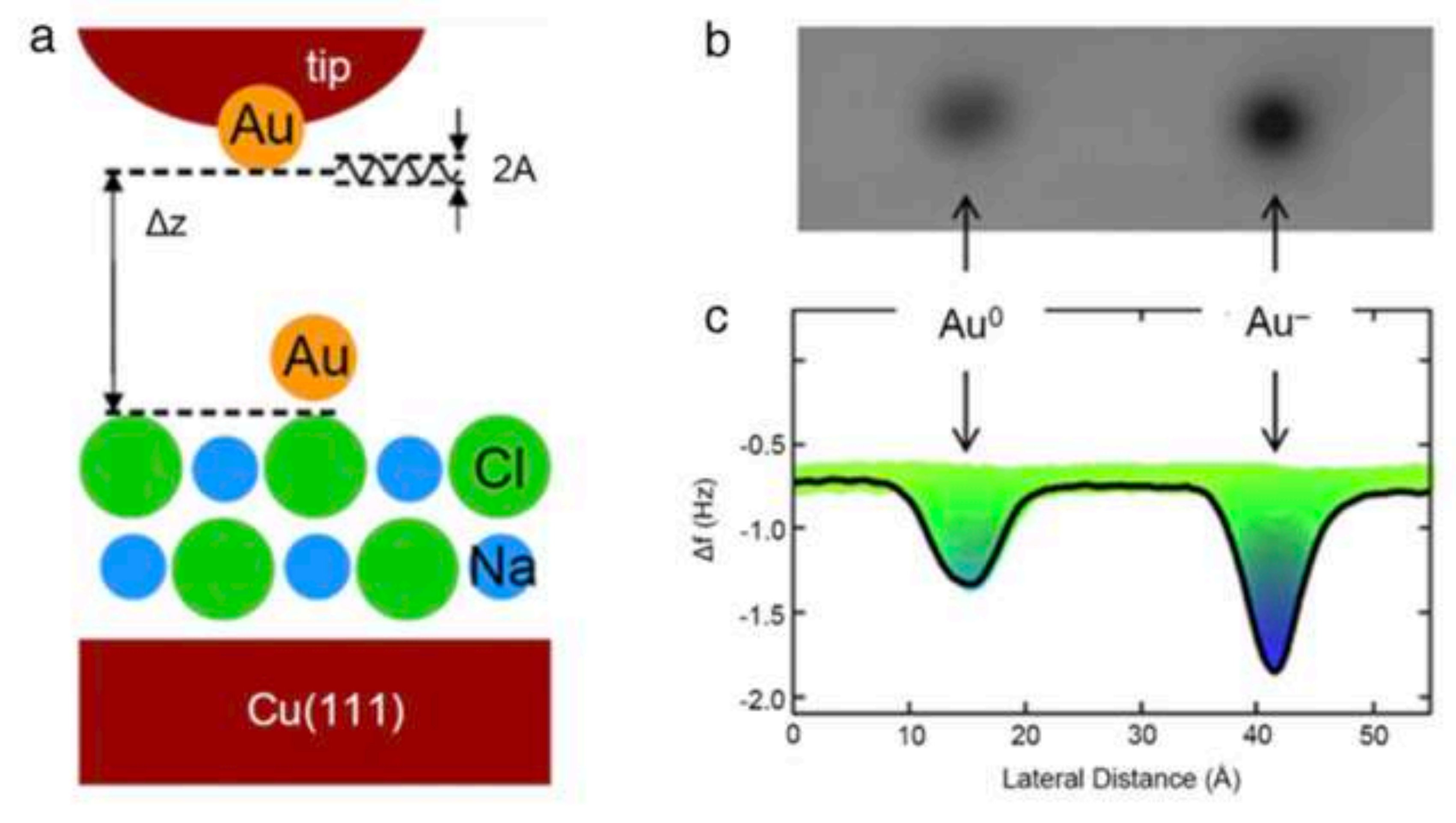
$$V_{DC} = V_{bias} - V_{CPD}$$

The bias voltage V_{bias} is adjusted until the vibration is minimized ⇛ $V_{bias}=V_{CPD}$
The value is recorded as a function of position.

Kelvin Probe Force Microscopy (KPFM)

Imaging of surface potential

Kelvin probe force microscopy and its application
Melitz, Shen, Kummel, Lee, **Surface Science Reports 2011**, 66, 1-27



Measuring the charge state of an adatom with noncontact atomic force microscopy
L. Gross, F. Mohn, P. Liljeroth, J. Repp, F.J. Giessibl, G. Meyer, **Science 2009**, 324:1428.

Future challenges

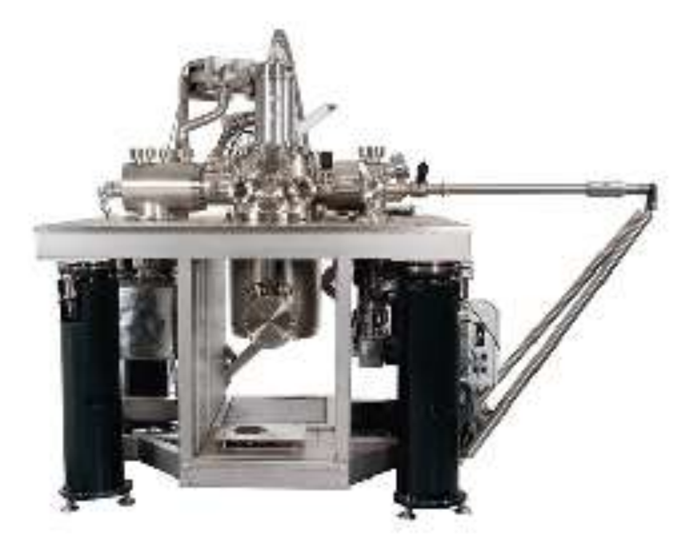
Future challenges for SPM-based techniques

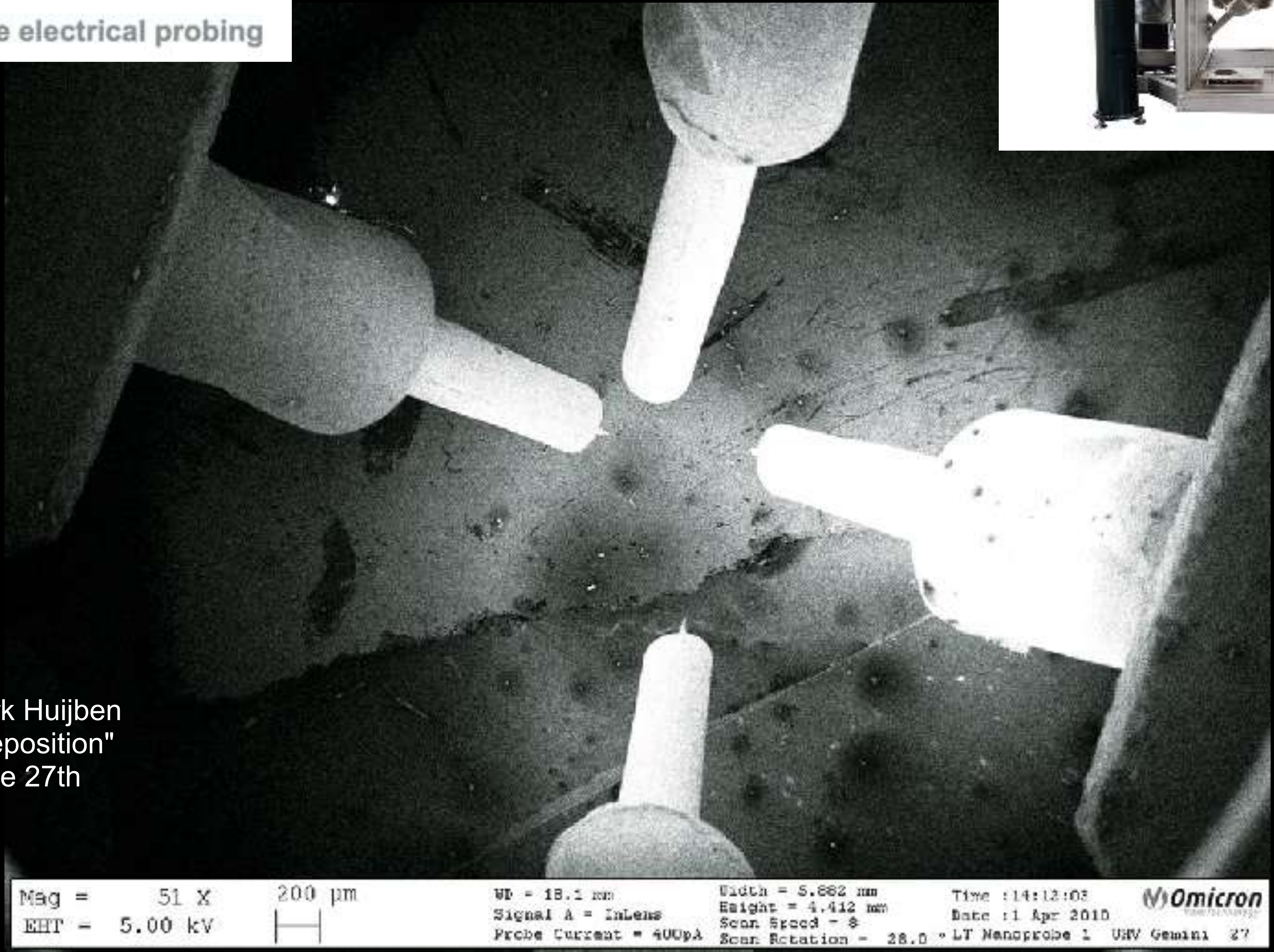
scientaomicron

LT NANOPROBE

Atomically precise electrical probing

Combining several SPM probes

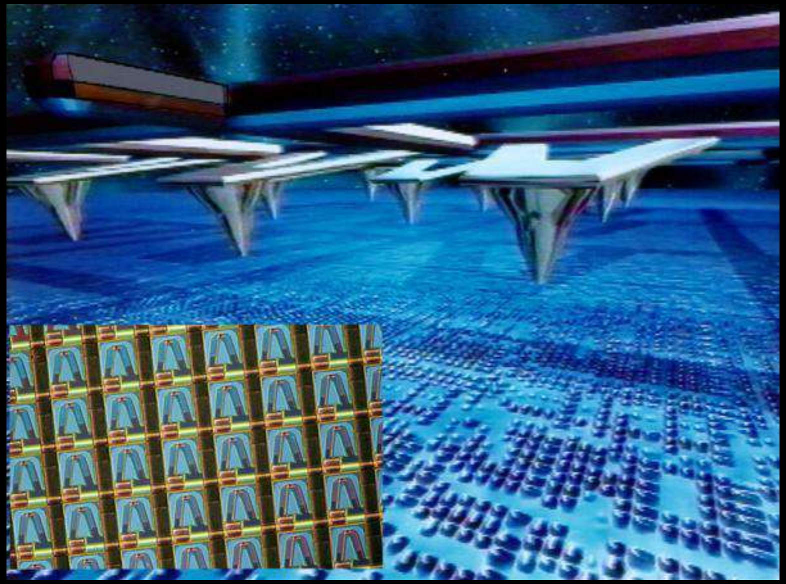




cf lecture by Mark Huijben
"Pulsed laser deposition"
Thursday June 27th

Future challenges for SPM-based techniques

Combining SPM with different techniques

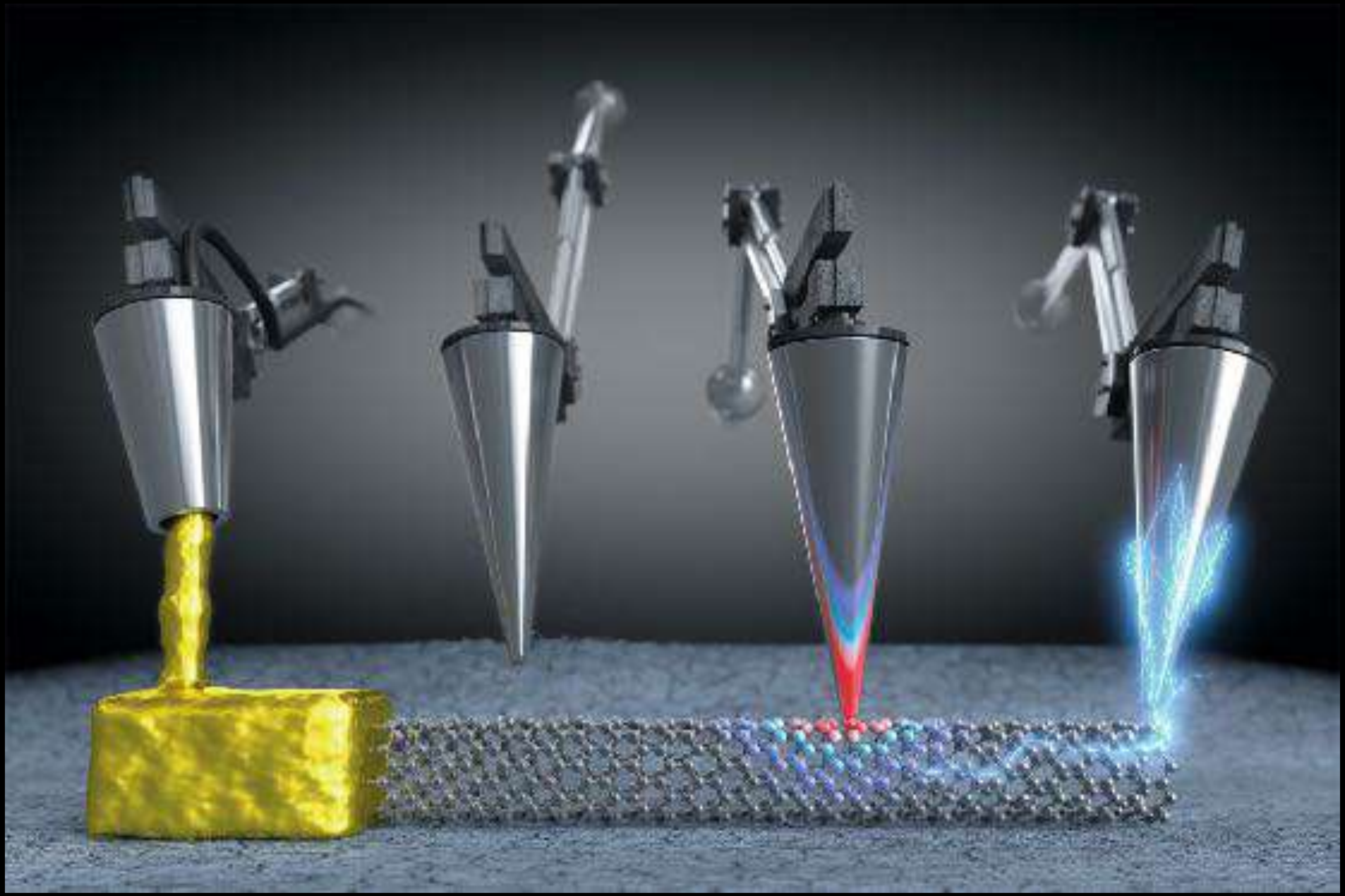


Data storage

IBM Millipede: combining micro-electro-mechanical systems (MEMs) techniques with an AFM
Write by indentation/Erase by heating on a plastic surface
2002: prototype with 1’024 tips

Future challenges for SPM-based techniques

Combining different SPM-based techniques

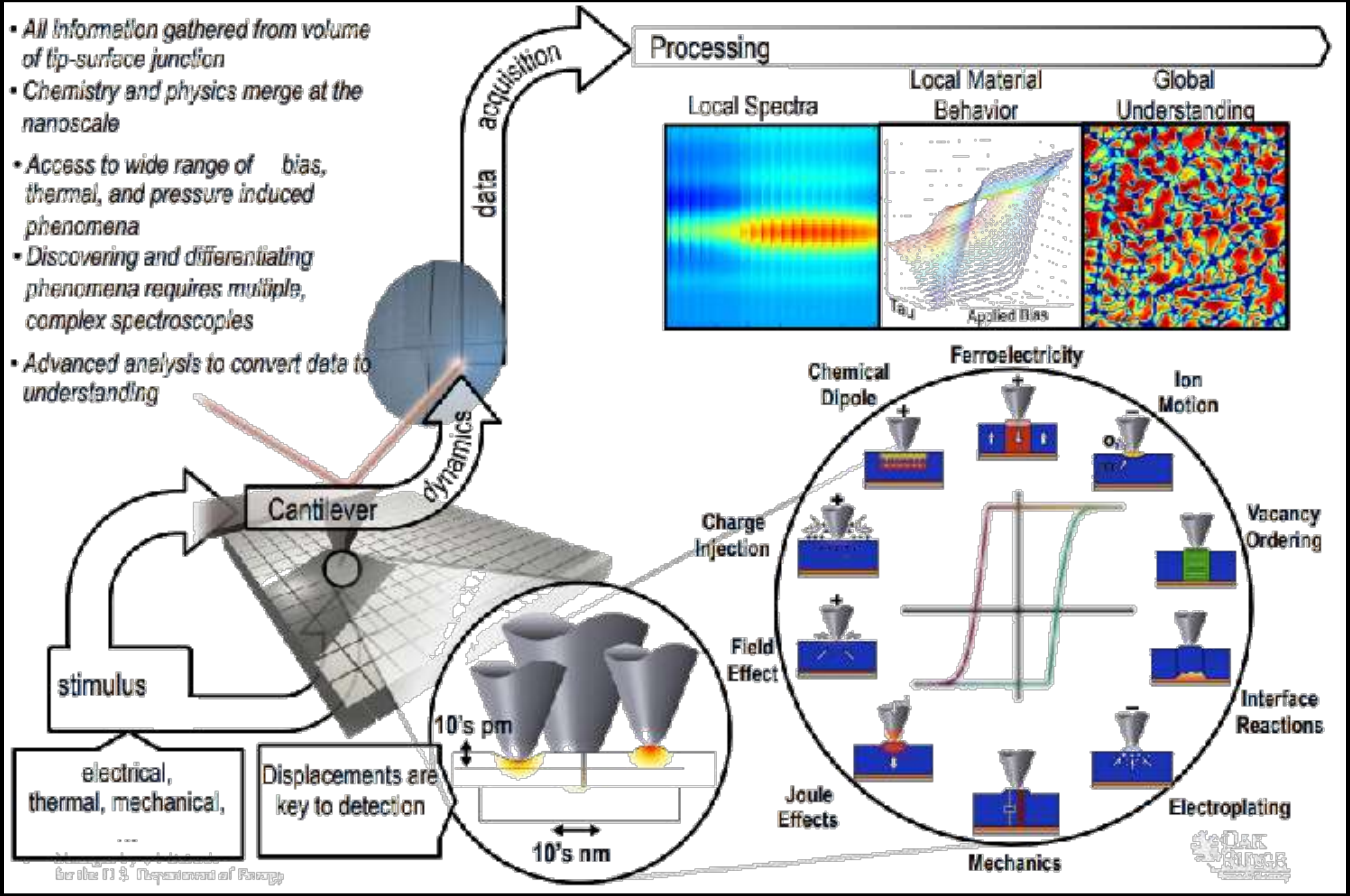


Multiprobe combined scanning probe microscopy

Scanning probe microscopy for advanced nanoelectronics
Hui & Lanza **Nature Electronics 2019**

Future challenges for SPM-based techniques

Information flow in Scanning Probe Microscopy



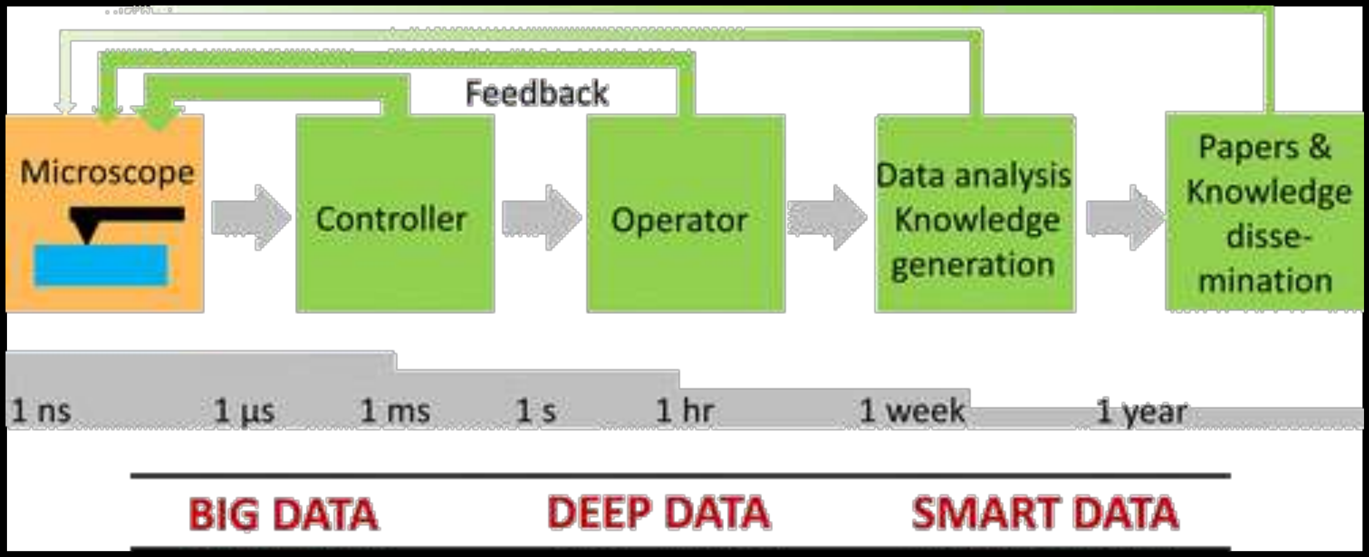
- All information gathered from volume of tip-surface junction
- Chemistry and physics merge at the nanoscale
- Access to wide range of bias, thermal, and pressure induced phenomena
- Discovering and differentiating phenomena requires multiple, complex spectroscopies
- Advanced analysis to convert data to understanding

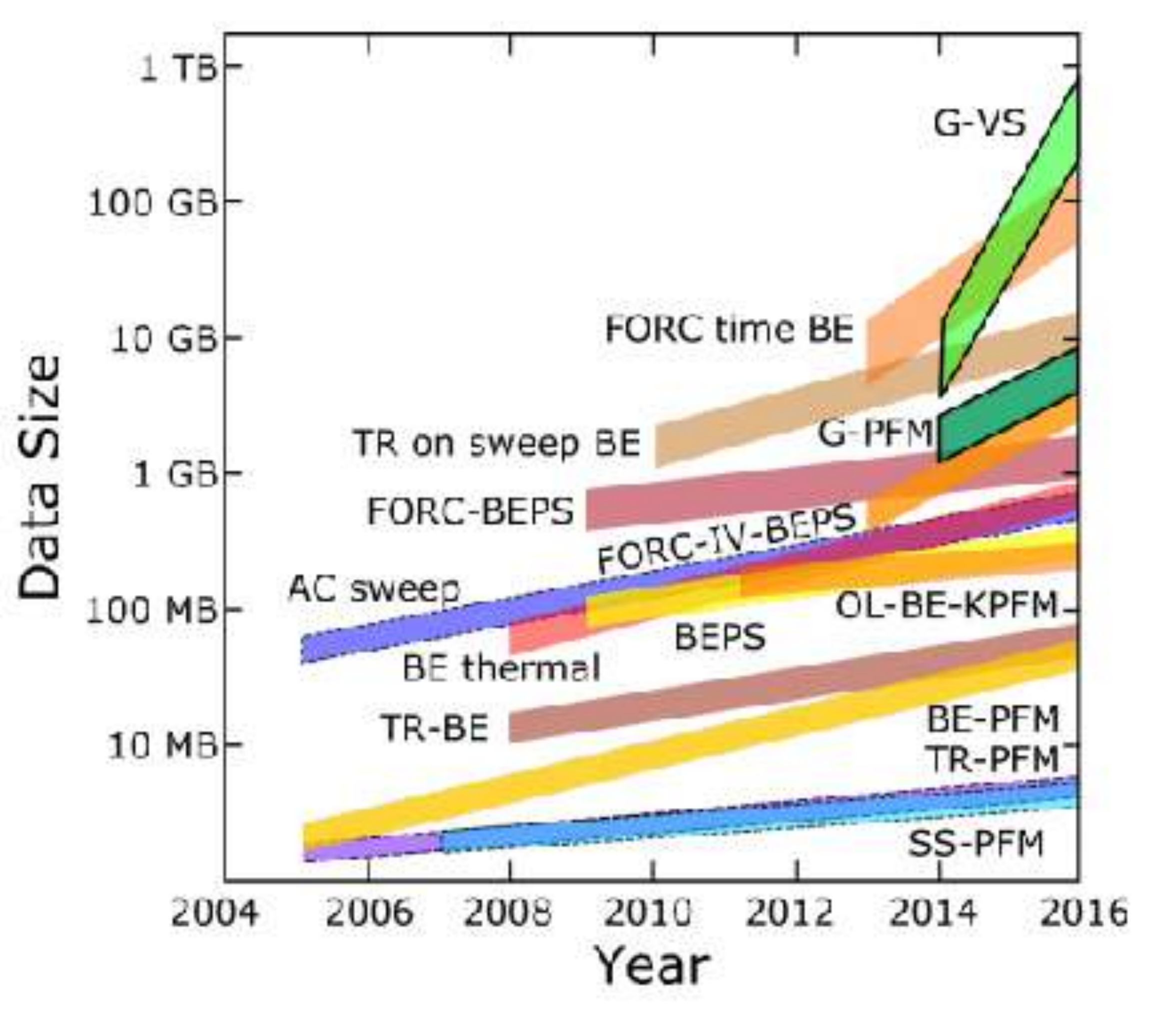
After R. Vasudevan, https://computing.ornl.gov/workshops/SMC16/docs/session2/vasudevan.pdf

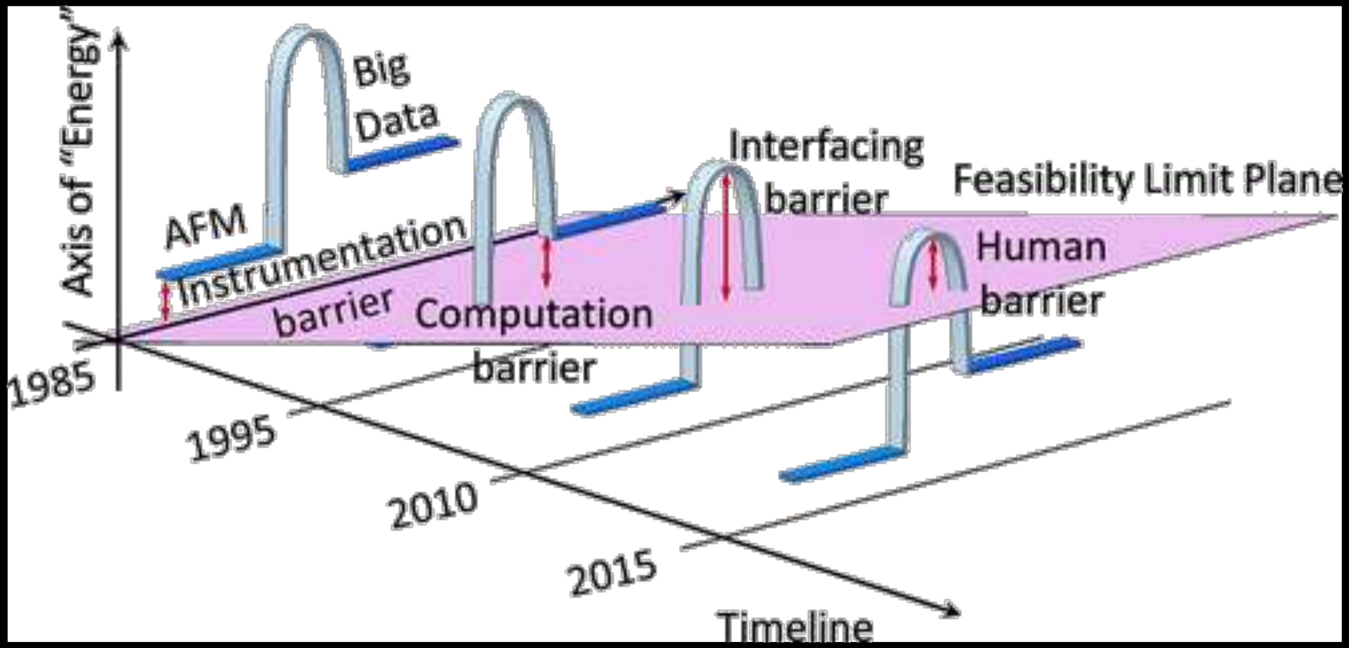
Future challenges for SPM-based techniques

Developing new analysing tools: Big Data

The limit is just human comprehension… … if you have a good enough computer and storage.







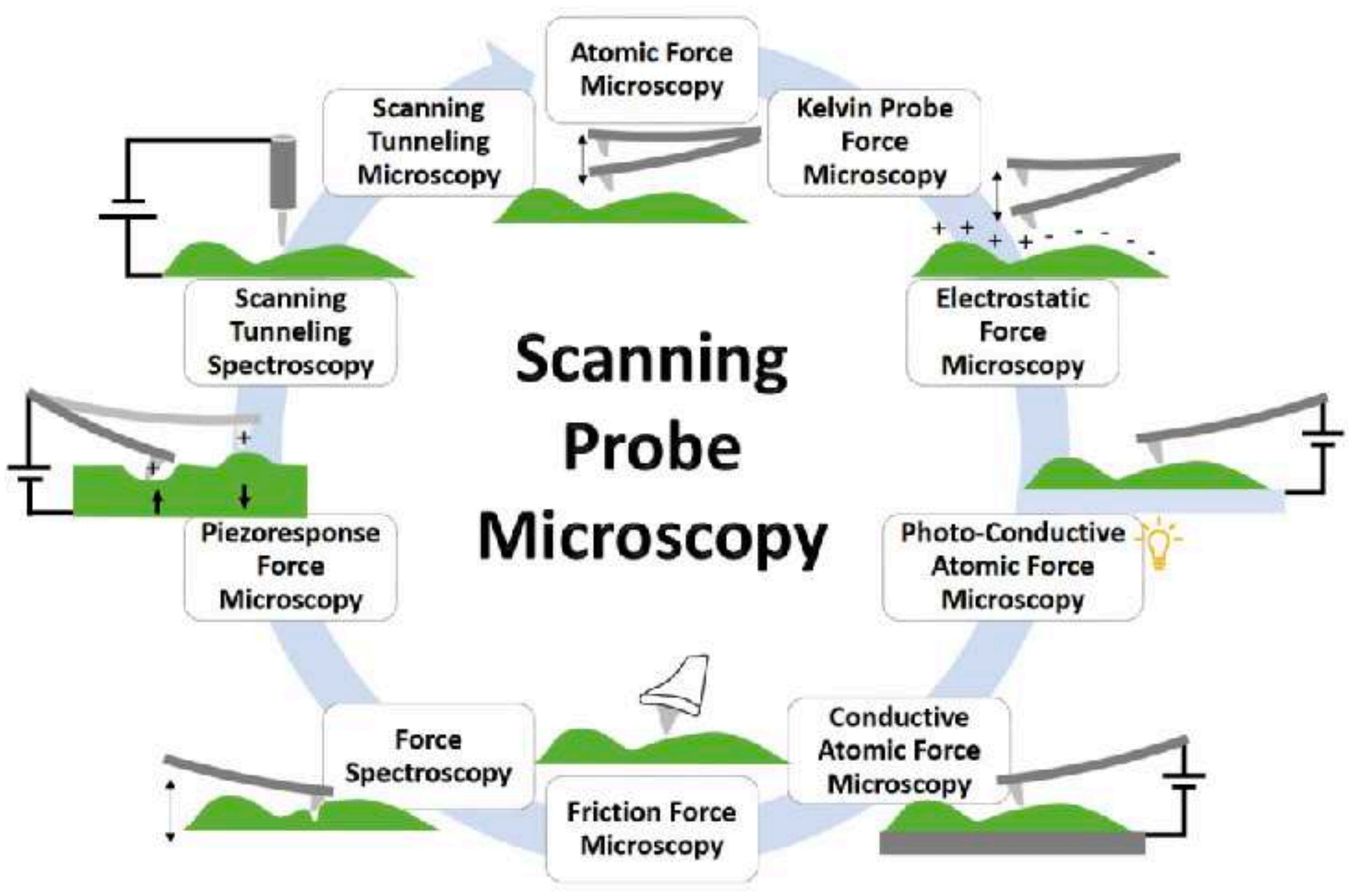
- Data size increases
- Growing dimensionality: cannot use desktop computers for analysis

S. V. Kalinin, ACS Nano 10, 9068 (2016)

After R. Vasudevan, https://computing.ornl.gov/workshops/SMC16/docs/session2/vasudevan.pdf

Conclusions

AFM allows an incredible diversity of physical interactions to be locally probed with nanoscale resolution



Advanced Scanning Probe Microscopy of Graphene and Other 2D Materials
Chiara Musumeci, **Crystals 2017**, vol. 7(7) p.216-219

Conclusions

AFM allows an incredible diversity of physical interactions to be locally probed with nanoscale resolution

M*N: Microscopy, Machine Learning, Materials

Sergei V. Kalinin

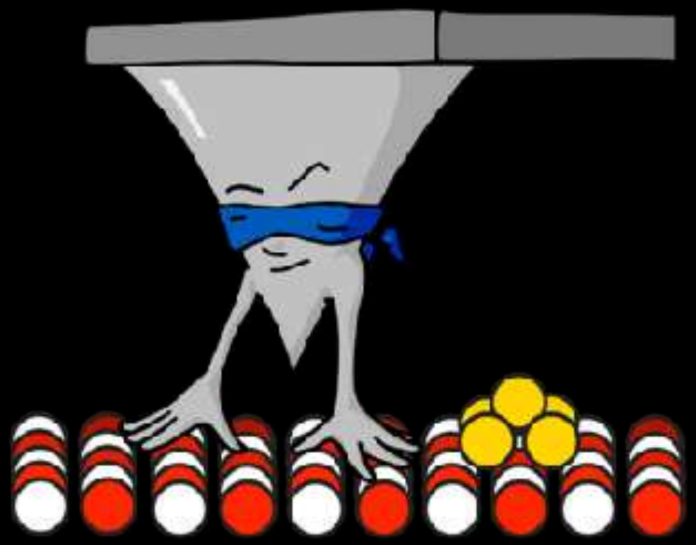
Stephen Jesse

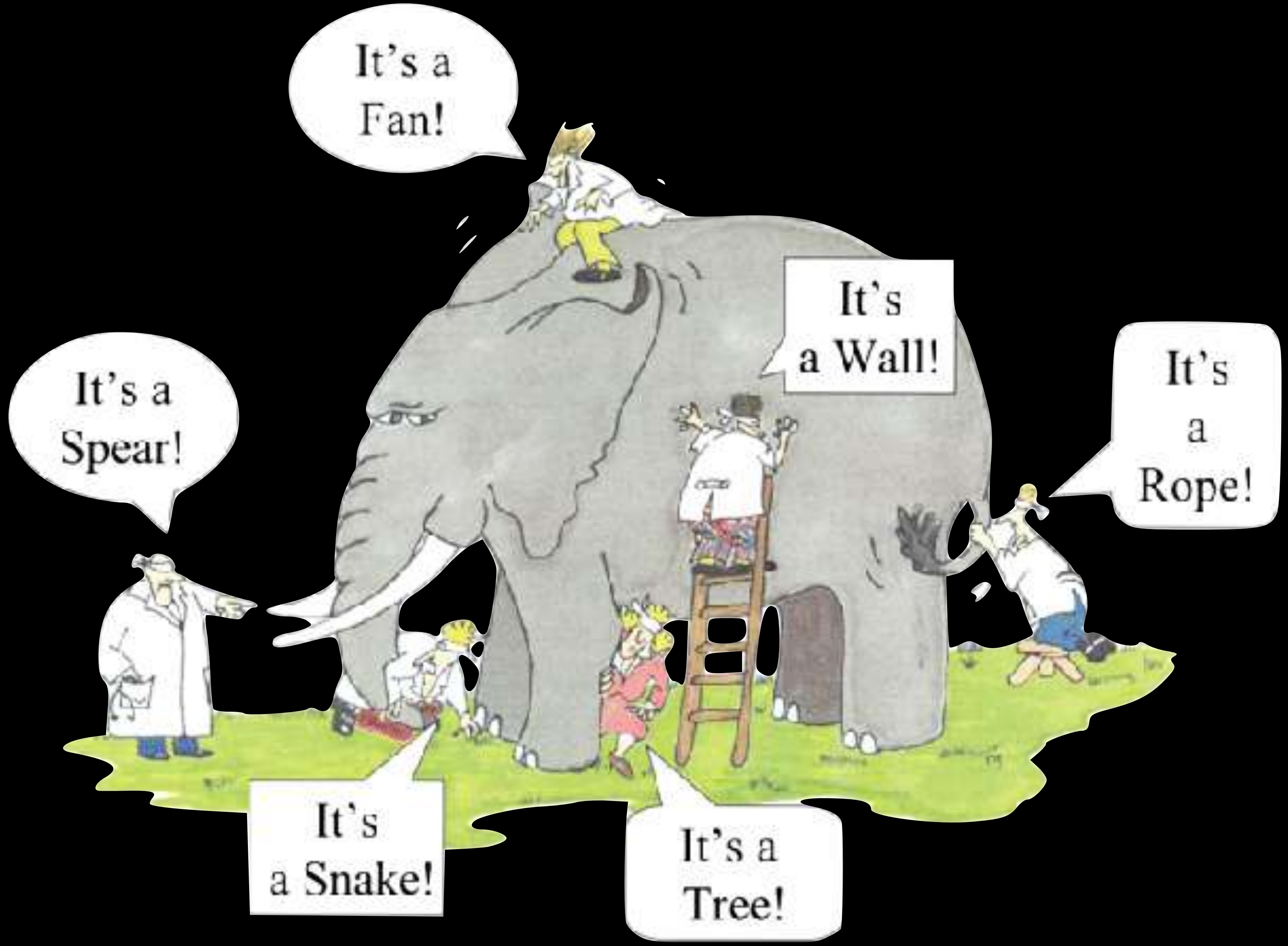
Lectures on Scanning Probe Microscopy, Piezoresponse Force Microscopy, Electrochemical Strain Microscopy and Kelvin Probe Force Microscopy

https://www.youtube.com/channel/UCyh-7XIL-BuymJD7vdoNOvw/about

Conclusions

AFM allows an incredible diversity of physical interactions to be locally probed with nanoscale resolution





BUT *you* need to know what you are searching for and what you are measuring AND expect many potential artefacts.