Ústav fyzikální chemie J. Heyrovského, ČAV,
Praha 8, Dolejškova 3

Scanning Probe Microscopy I
Basic Techniques

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Odd. elektrochemických materiálů

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Microscopic methods/resolutions

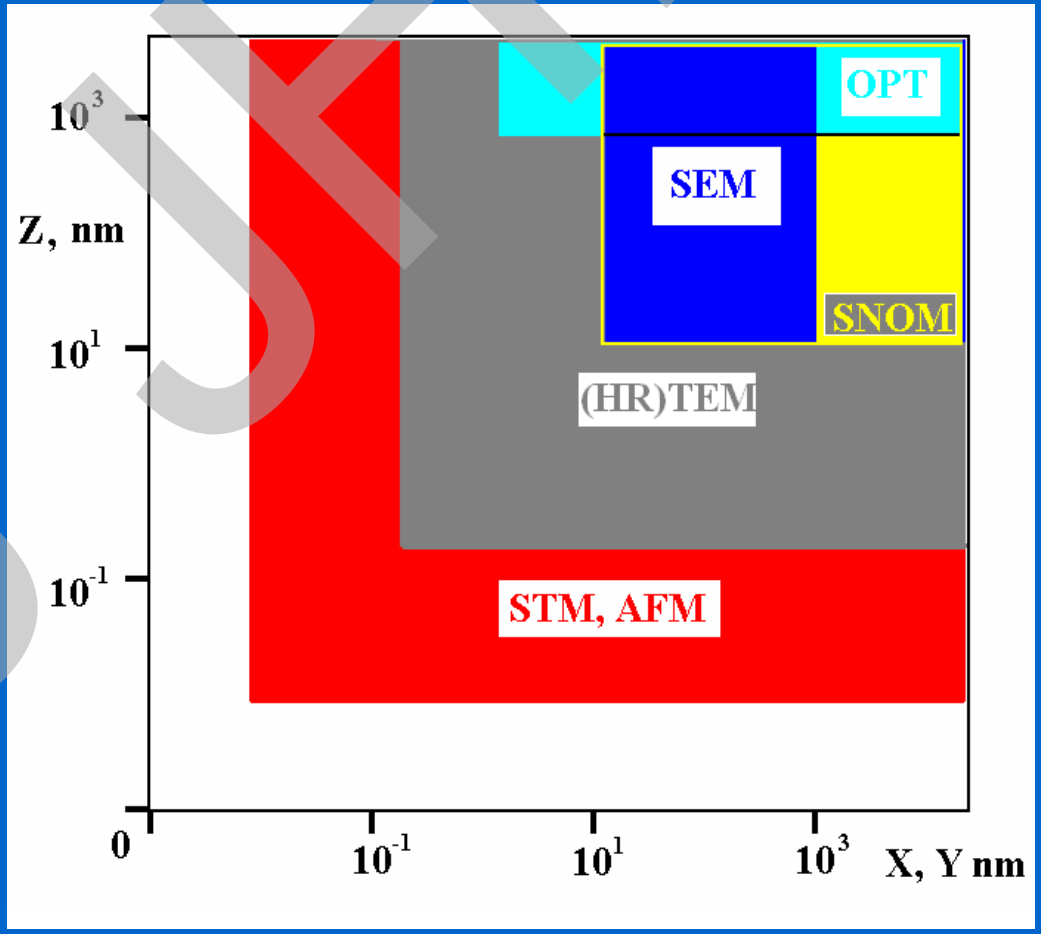
OPT: Optical Microscopy

SNOM: Scanning Near Field Optical Microscopy

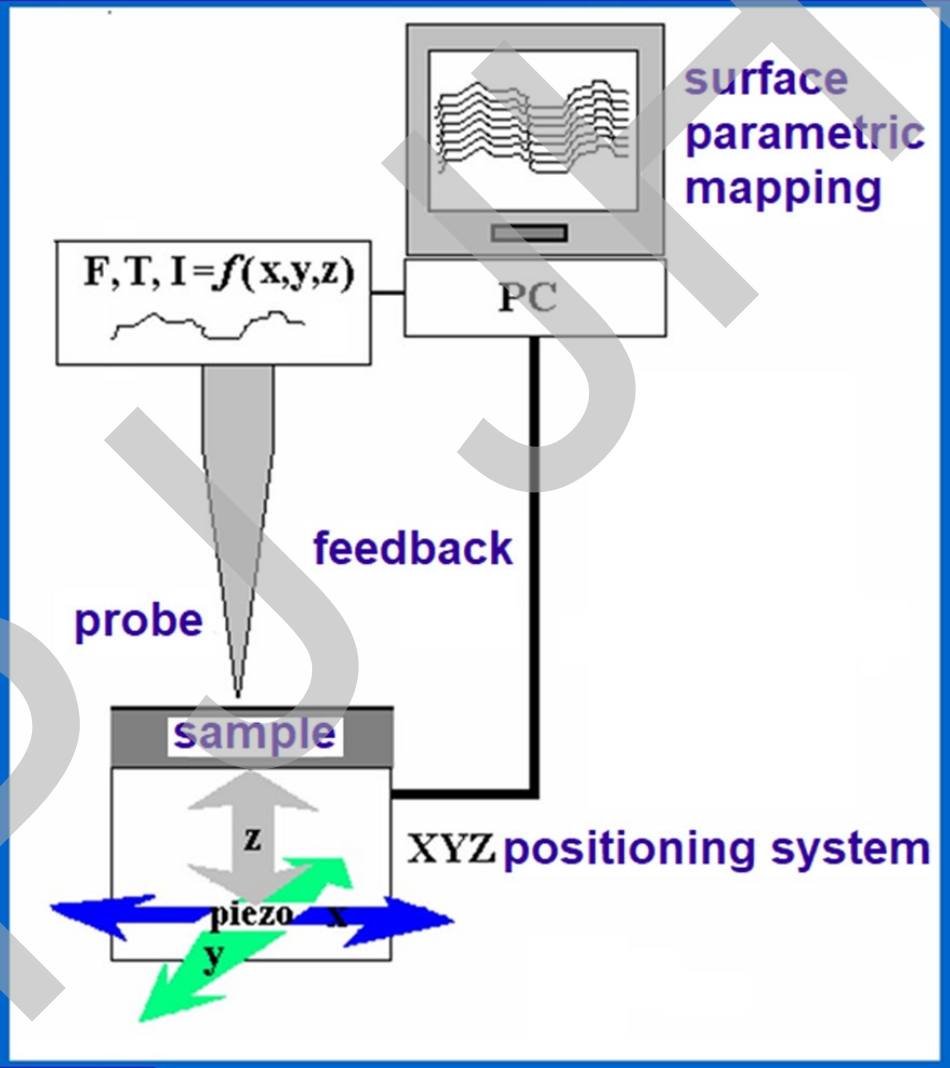
SEM: Scanning Electron Microscopy

HRTEM: High Resolution Transmission Electron Microscopy

STM, AFM:
Scanning Tunneling Microscopy, Atomic Force Microscopy



Scanning Probe Microscopy

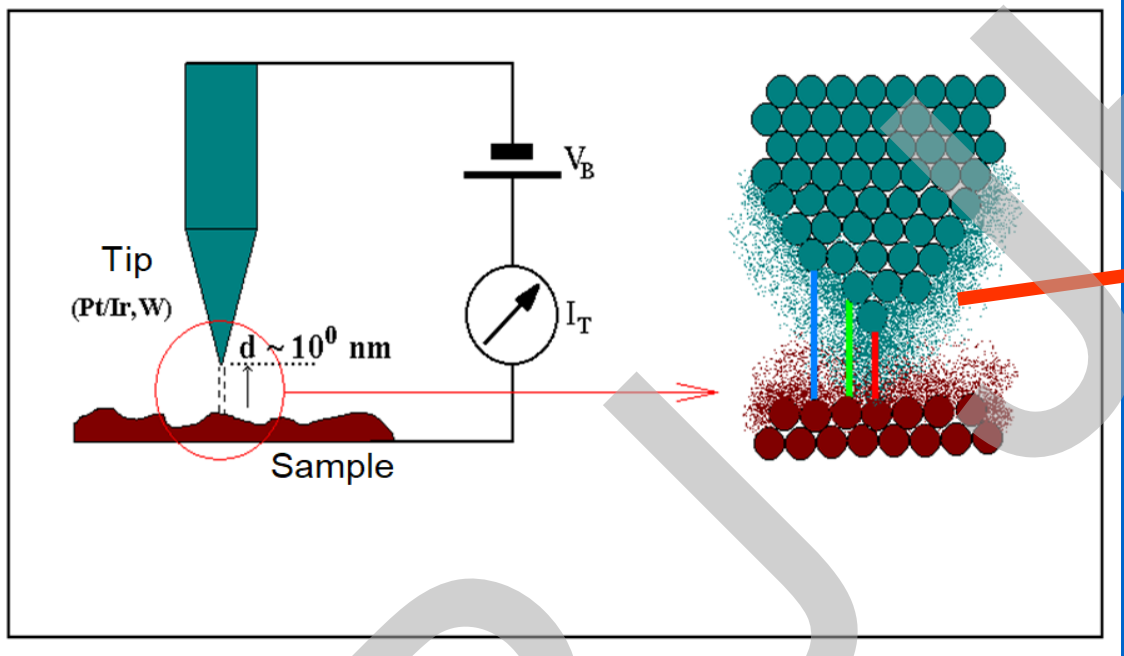


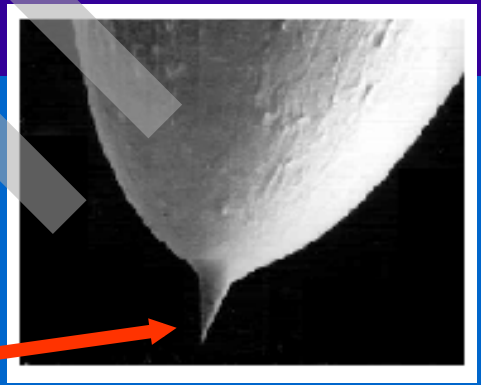
SPMs by information carriers

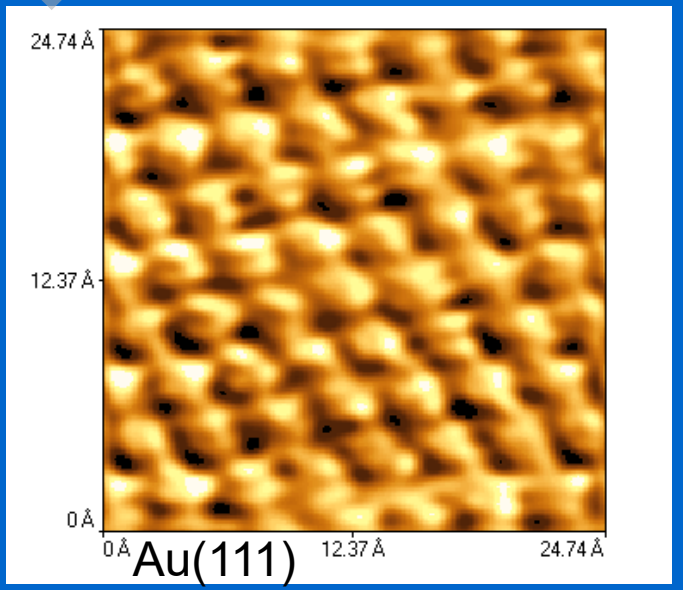
Electron - tunneling microscopy **STM/ECSTM,**
conductive AFM **CAFM (PFTUNA)**
Ion - electrochemical microscopy **EC STM/EC AFM**
Force interactions - atomic force microscopy **AFM/ECAFM**

Tunneling Microscopy

Binning, Rohrer, IBM, 1981, Nobel Prize 1986







Approximation of tunneling current

$$I_T \sim V_B f_{mTS}(V_B) \exp\left[-2z\sqrt{(2m\Phi_{ST}/\hbar^2)}\right]$$

$\hbar = h/2\pi$, $f_{mTS}(V_B)$...reduced Planck.const.

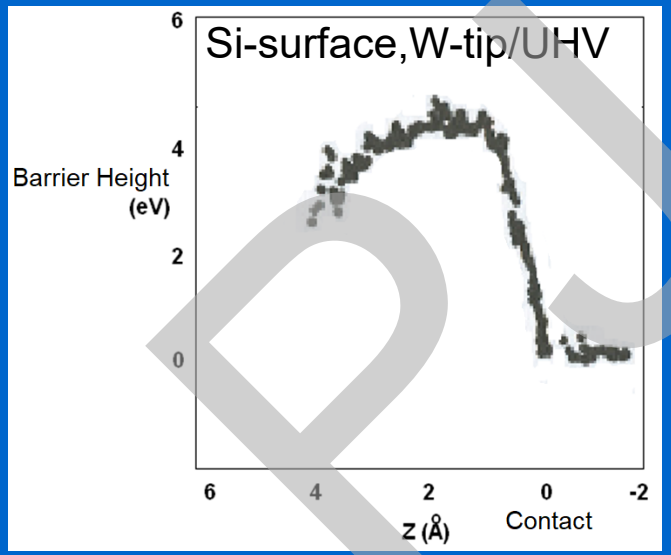
$I_T(V_B)$ given by e-structure tip x sample,
z...distance tip-sample (~ 10^{-1} nm), V_B up to ±1-2 V, I_T ~nA - pA

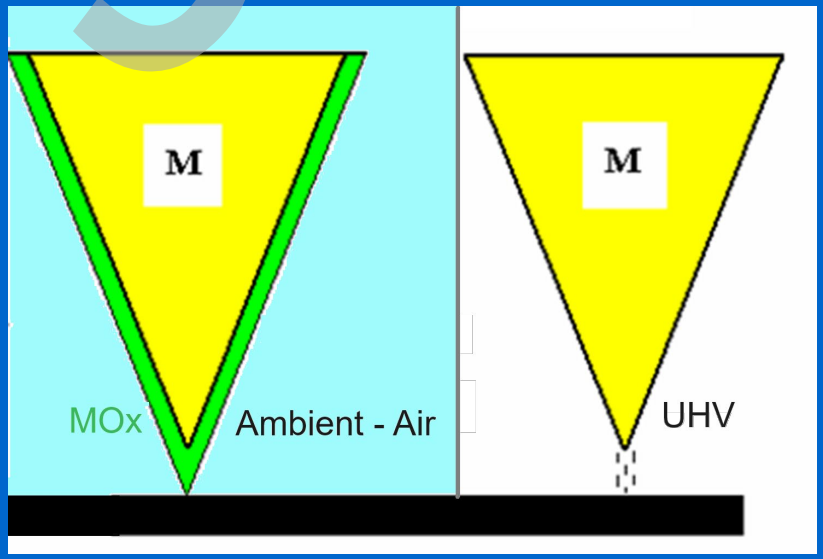
Tunneling barrier (distance) spectroscopy

Low bias V_B = const. : $(dI_T/dZ)/I_T \sim (2\sqrt{2}m_e)/\hbar \sqrt{(\Phi_S + \Phi_T)}$

Φ_{Sample} , Φ_{Tip} local work functions, I_T tunneling current,
Z tip-sample distance, m_e e-mass

Realization:
modulated axial distance (Z-axis) VVVVV, recording dI_T/dZ => $\Phi_{S,T}$
Considering Φ_{Tip} ≈ const. => lateral variation of barrier height ~ local Φ_S





D.A. Bonnel: Scanning Tunneling Microscopy and Spectroscopy VCH 1993

Tunneling voltage spectroscopy

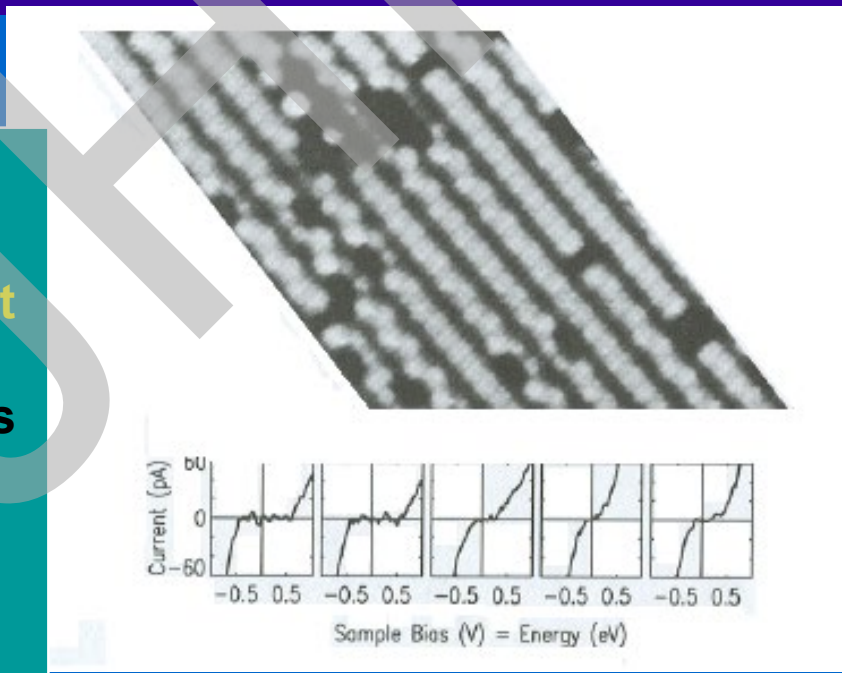
V_B < work function tip-sample (~10 mV)

$dI_T/dV_B \approx$ local surface density of states real or derived from internal band arrangement

Modulation VVVVV V_B, recording I_T-V_B curves

Output: $d(\log I_T)/d(\log V_B)$ vs V_B

Yields: map of surface states (in UHV) shows filling of states, ad-atoms free (*dangling*) bonds...

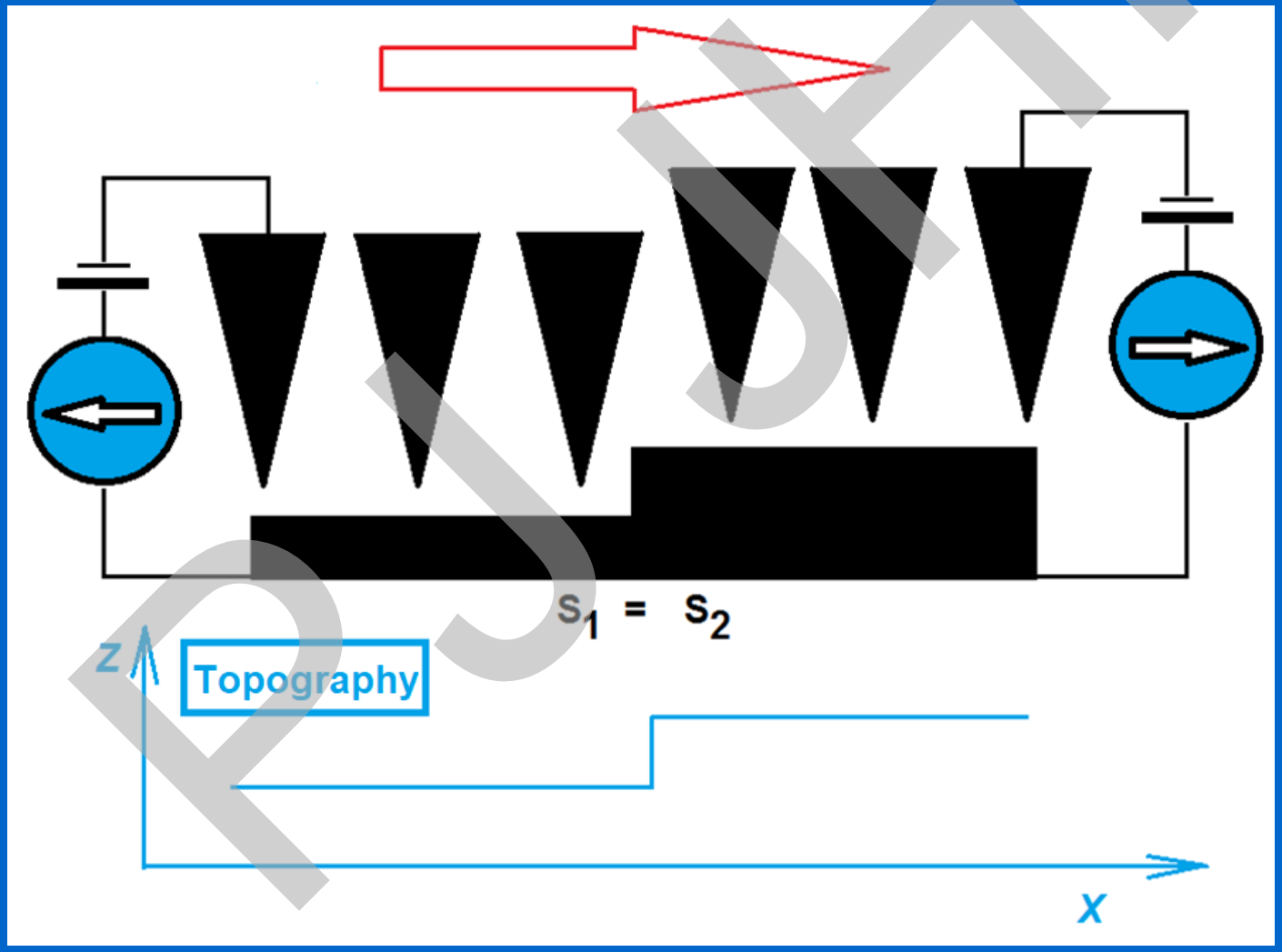


I_T-V_B plots at single cryst. Si (UHV): STM Tip passing over defect

[*B. Persson, A. Baratoff, Phys.Rev.Lett. 59, 339*]

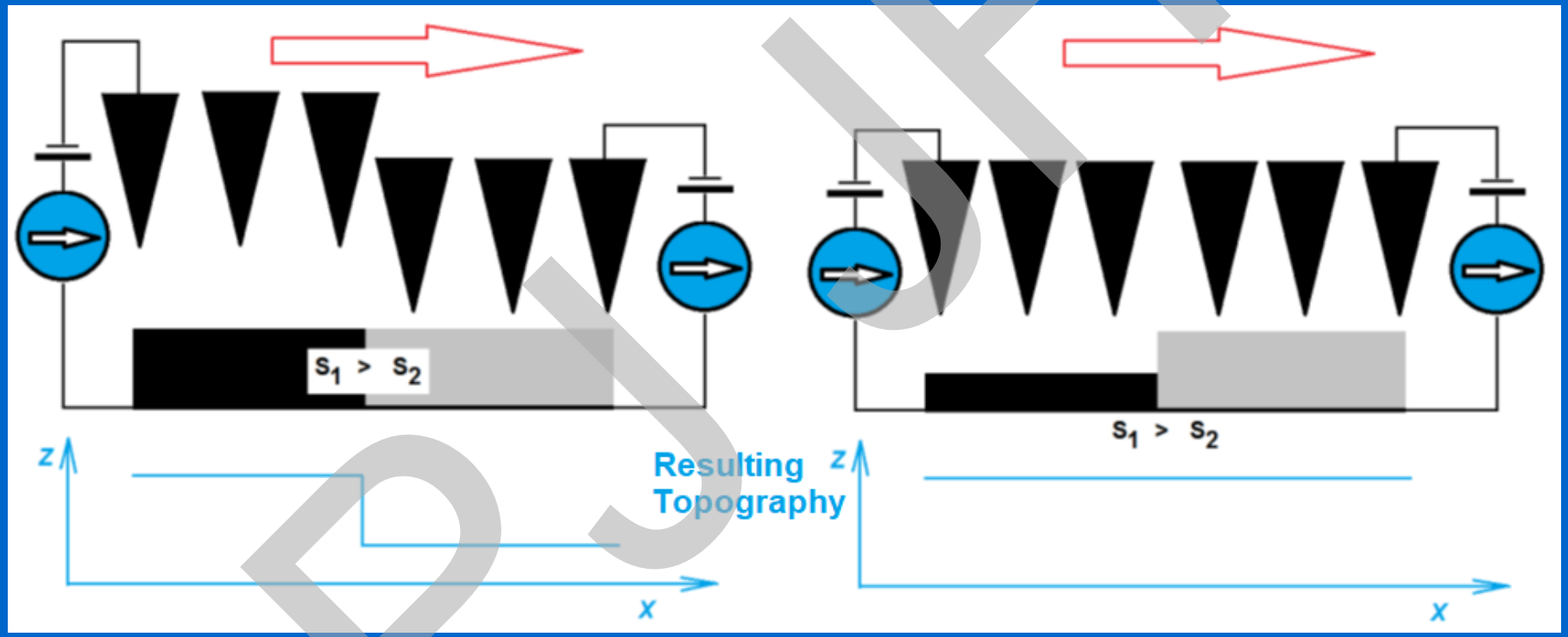
Frank, L. - Král, J., Ed., : Metody analýzy povrchů. Iontové, sondové a speciální metody, Academia, Praha 2002

Tunneling microscopy – topography
uniform surface e-density



Tunneling microscopy – topography

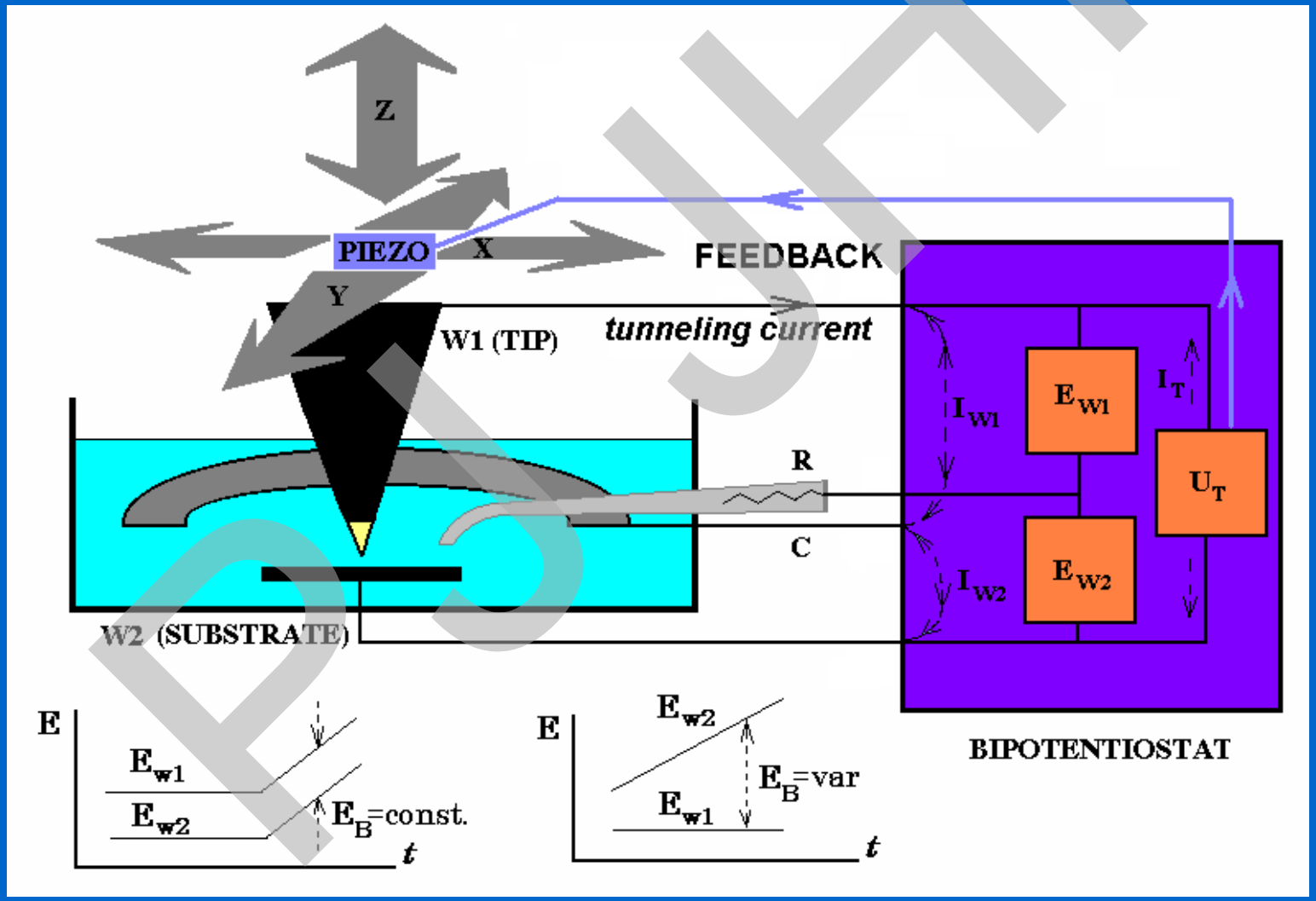
nonuniform surface e-density => artefacts



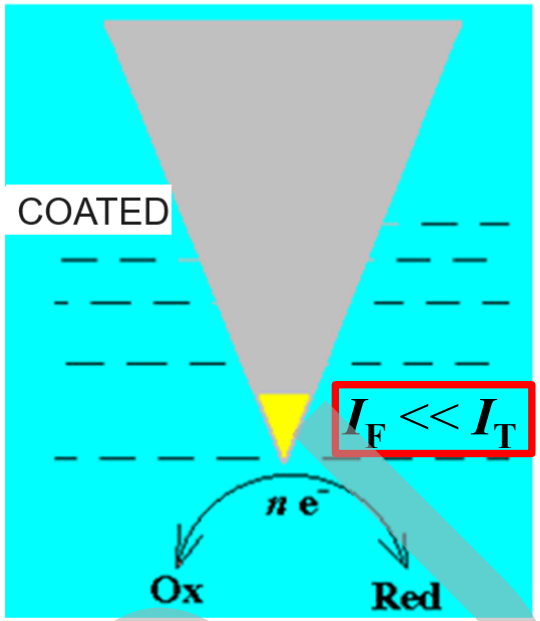
EC STM

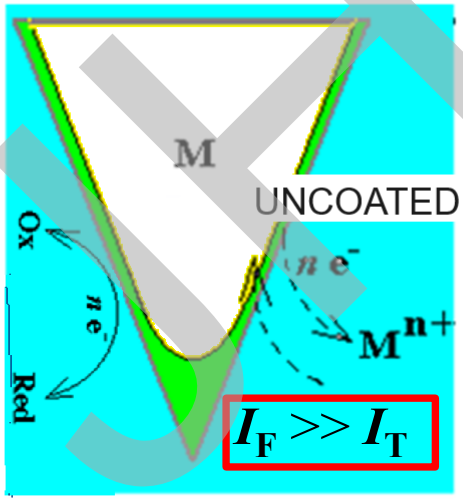
Electrochemical Scanning Tunneling Microscopy

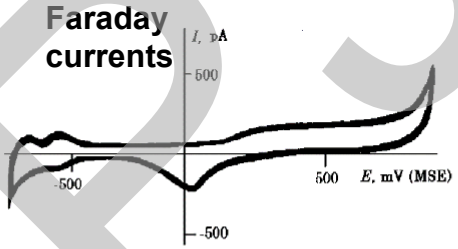
EC STM:
Detection of tunneling currents in EC experimental setting



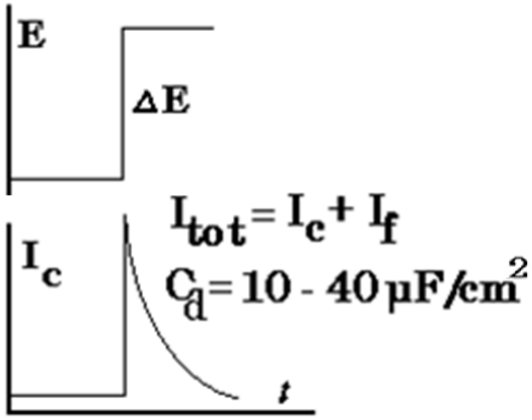
Probe/tip for EC STM







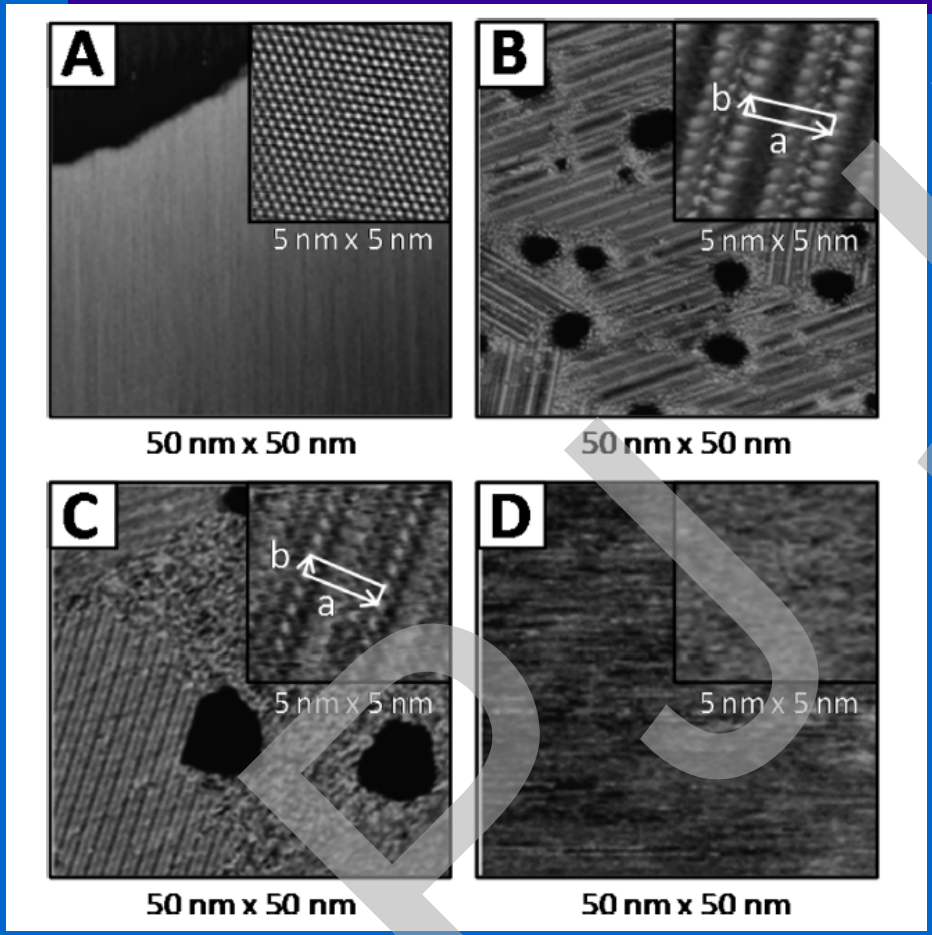
Voltammetry of Pt-Ir STM tip (polymer coated) in 0.1 M H_2SO_4 (deoxygenated) ν=200 mV/sec



$I_{tot} = I_c + I_f$

$C_d = 10 - 40\ \mu F/cm^2$

EC STM: Imaging Self-Assembled Monolayers on immersed surface



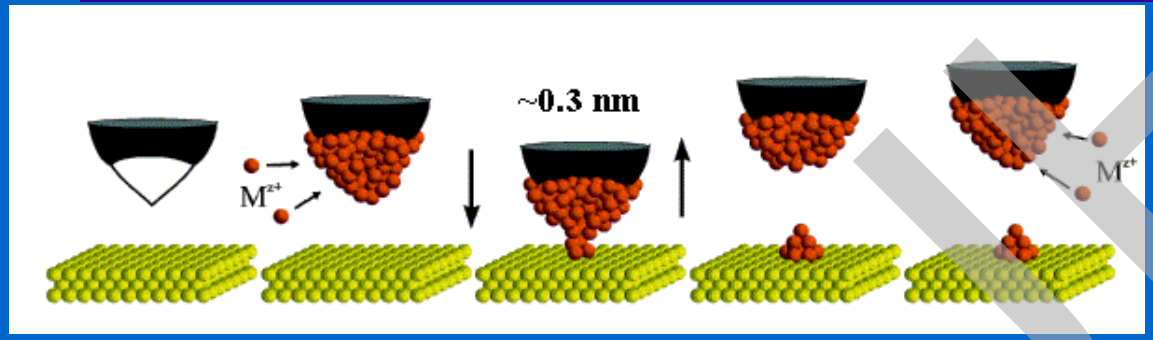
Aq. 0.1M Na_2HPO_4, pH 6

SAM - molecular ad-layer: mercaptopropionic acid (MPA) on Au111,
U_B= 300 mV/I_T = 100 pA

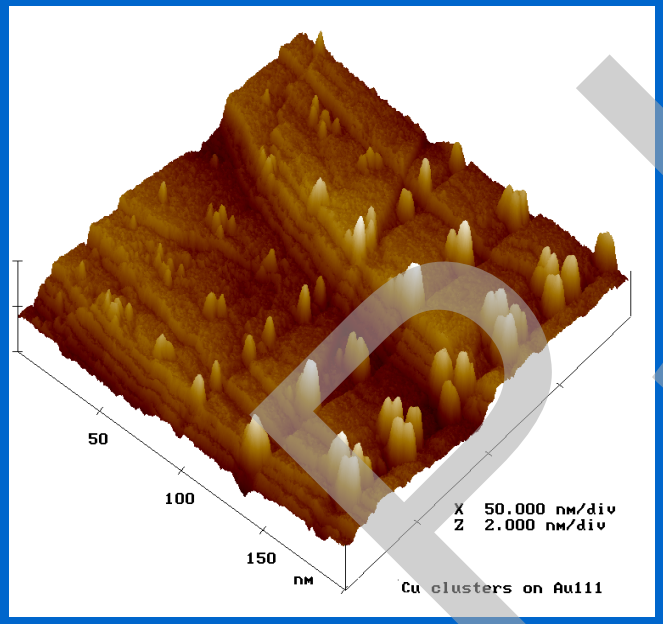
V. Climent et al: J. Phys. Chem. C 2014, 118, 15754−15765

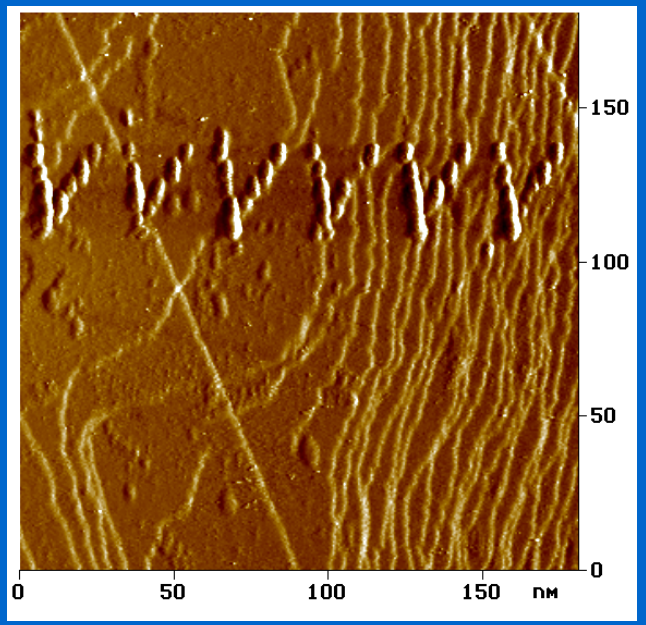
Tip-assisted „nanoprint“

STM tip-deposited nanoparticles Cu $d \geq 8$ nm, $h < 1$ nm



Aqueous 0.1M H_2SO_4 + 10^{-3} $CuSO_4$





Pavel Janda et al: Copper deposition on fullerene nanostructures, Surface Science 597 (2005) 26–31

Atomic Force Microscopy

and force-based techniques

AFM

Force Interactions
Range/mode

Long - magnetic, coulombic - **noncontact**

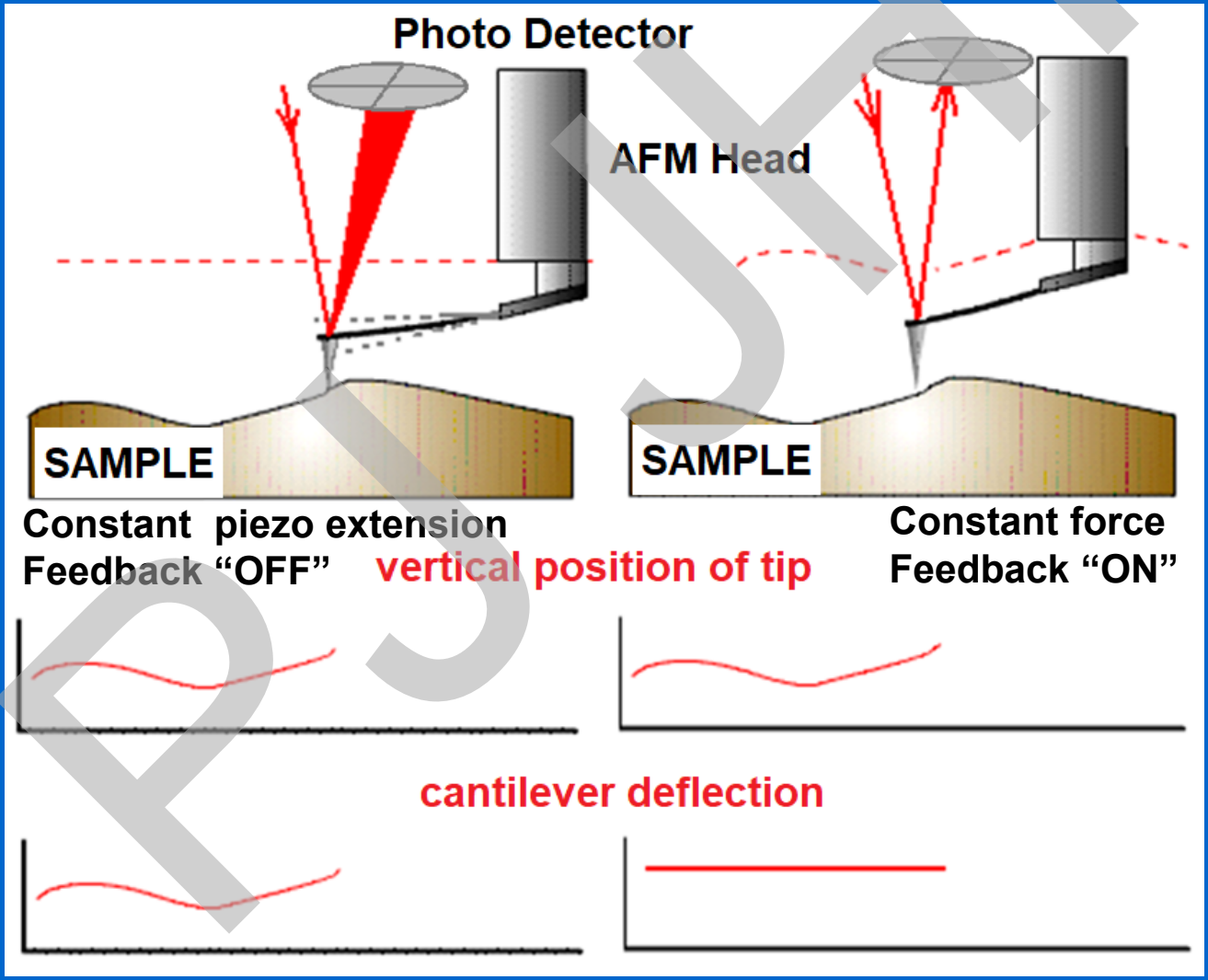
Medium - van der Waals (dipol-dipol, induced - dipol-nonpolar) **semicontact**

Short - binding (attractive) interactions, repulsive (deformation) – **„contact“**

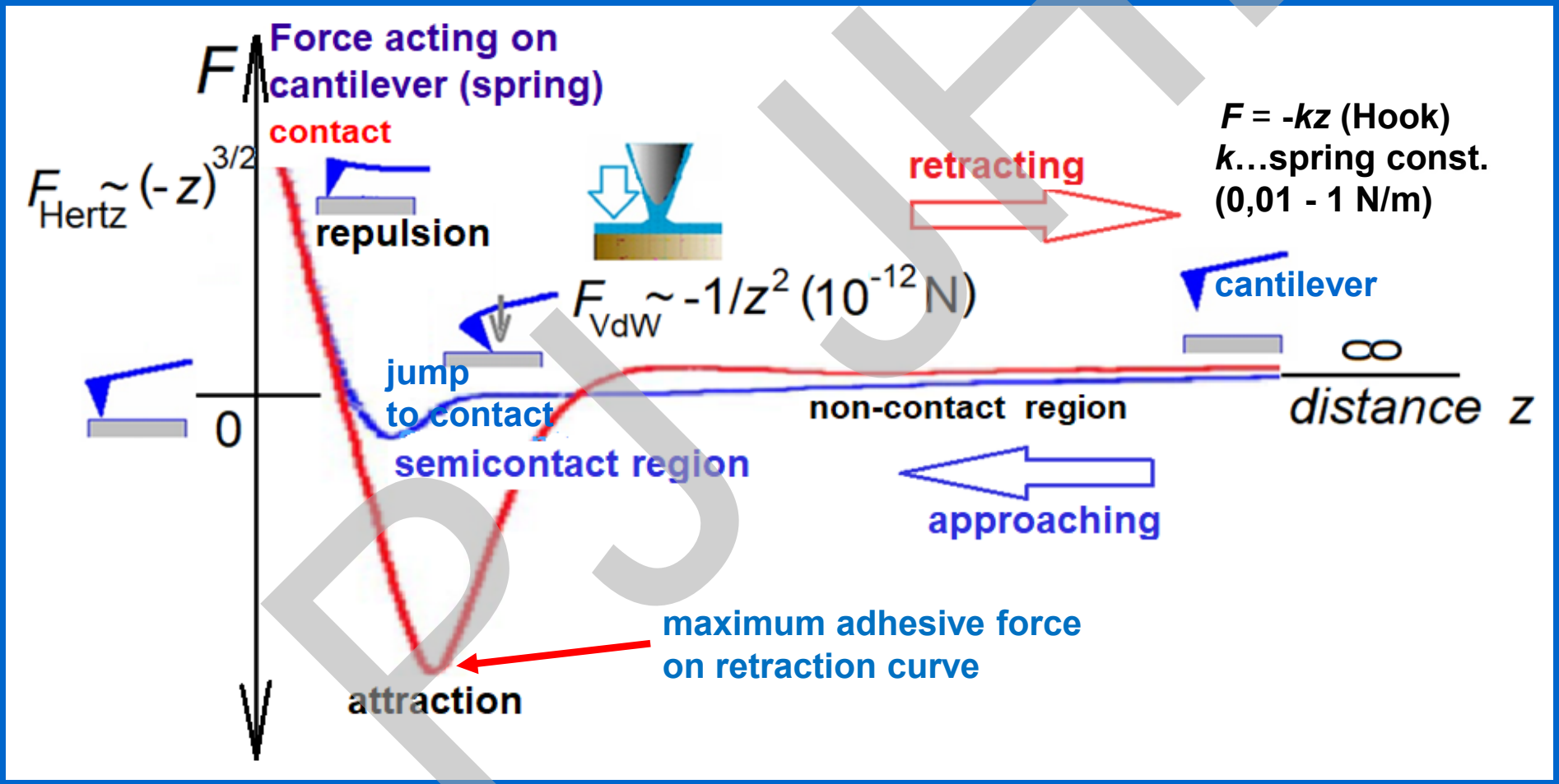
„Derived AFM techniques“ ex-situ / in fluids

Conductive AFM (CAFM) - **conductivity meas., Tunneling AFM (TUNA) (!)**
Electrochemical AFM (EC AFM) – AFM imaging during EC experiments
+ tip-assisted „electro-lithographic“ techniques
Scanning Electrochemical Microscopy (SECM) – imaging based on charge transfer reactions/Faraday currents (feedback)

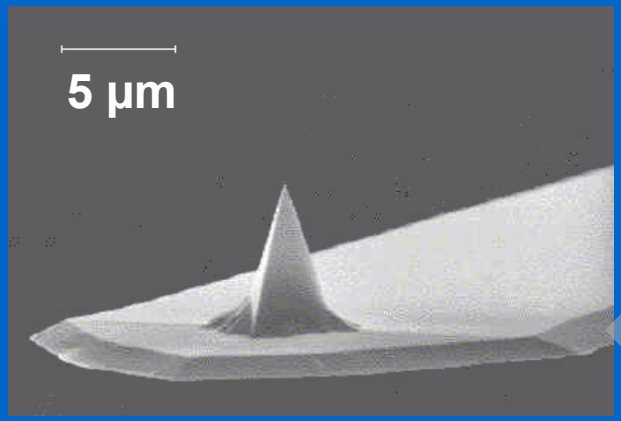
AFM fundamentals

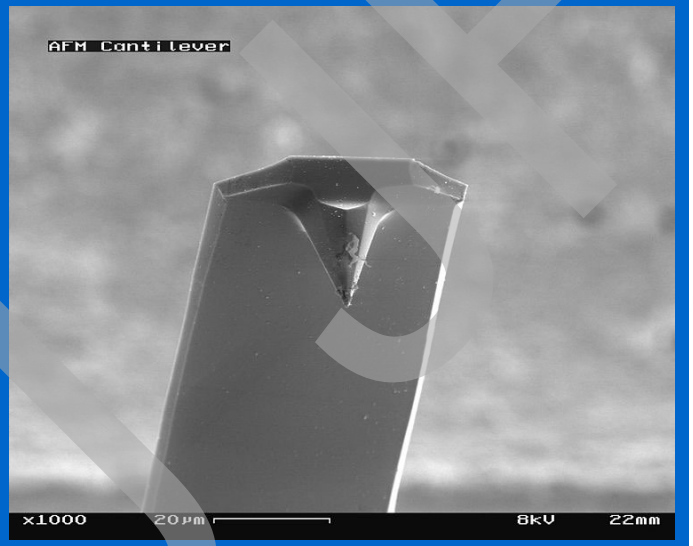


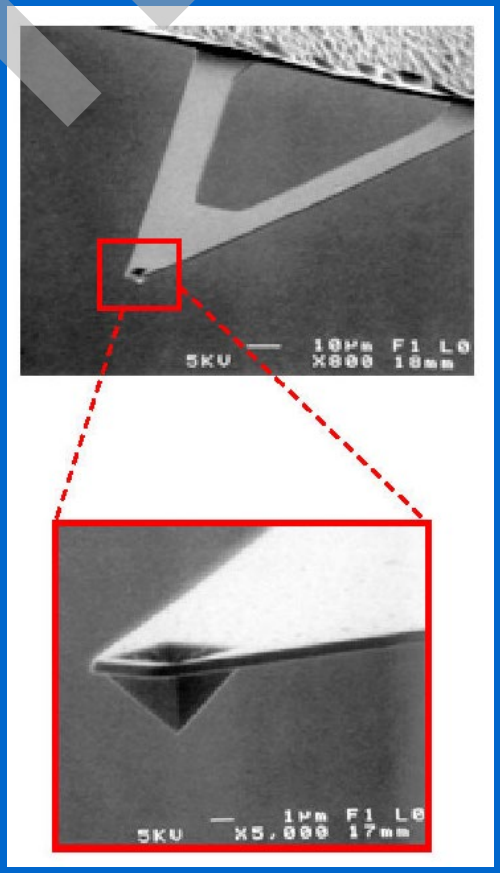
AFM fundamentals – force curve



AFM Probe:
Tip and spring (*cantilever*)







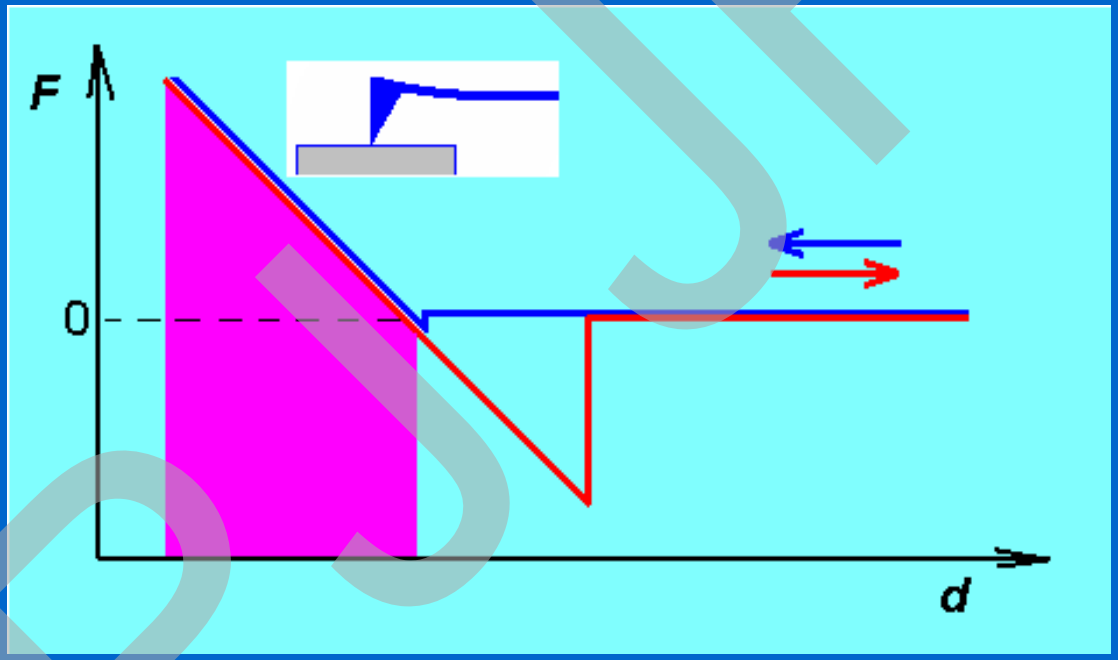
material of tip and cantilever: Si, Si_3N_4

Source: Bruker

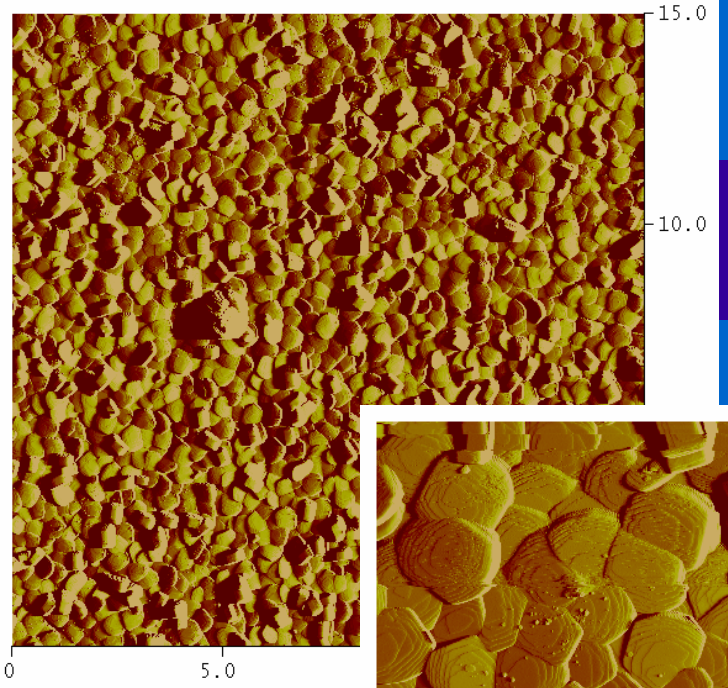
Scanning in selected regions of force curve

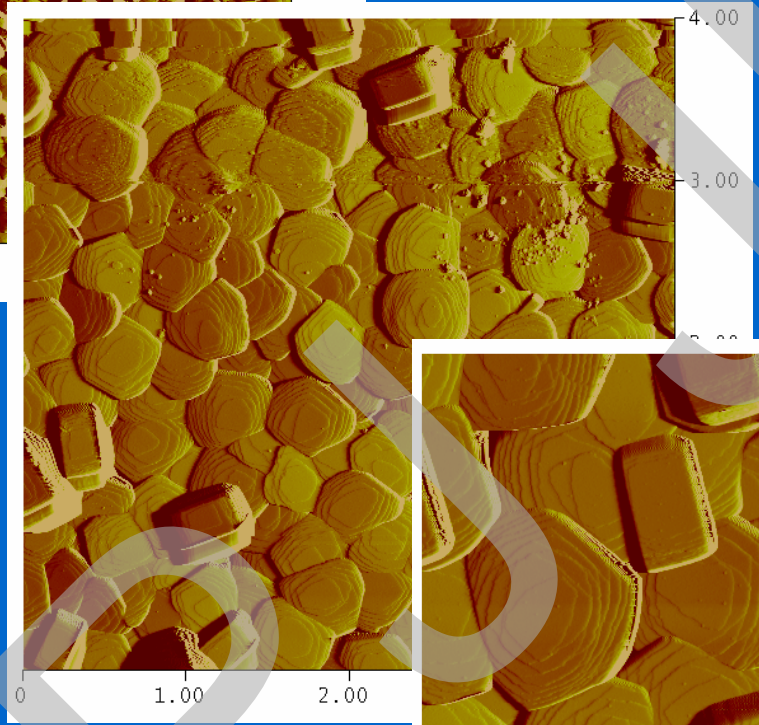
AFM in repulsive forces: Contact Mode

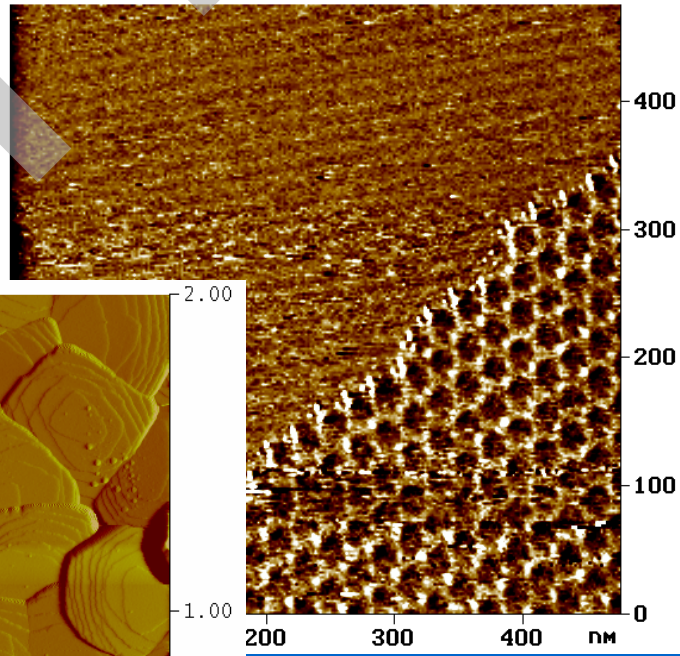
Maximum resolution, but maximum interaction tip-sample

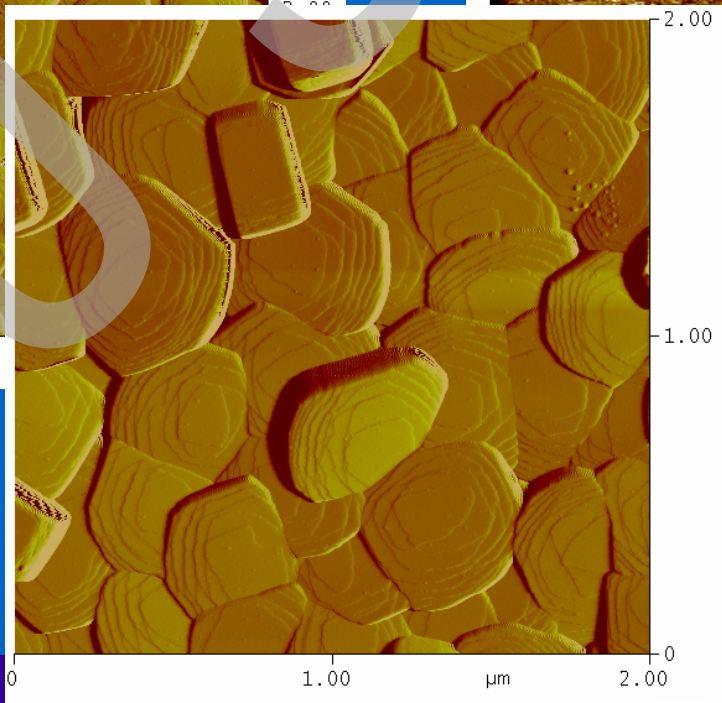


AFM imaging in contact mode





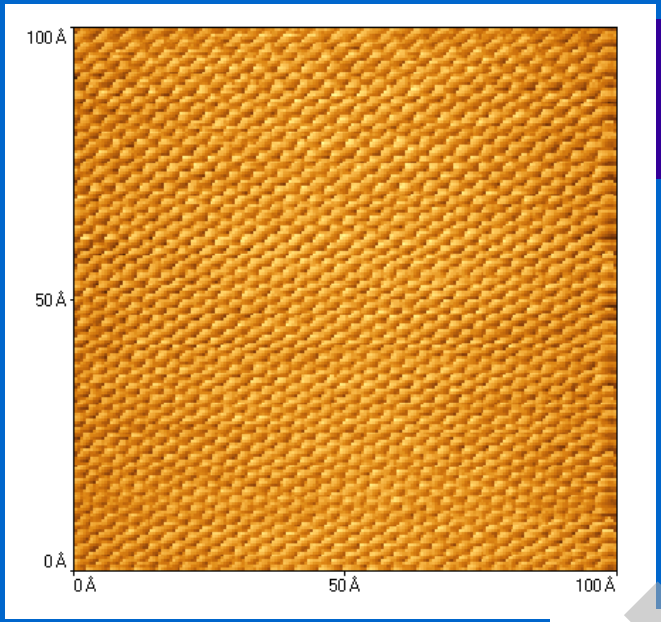




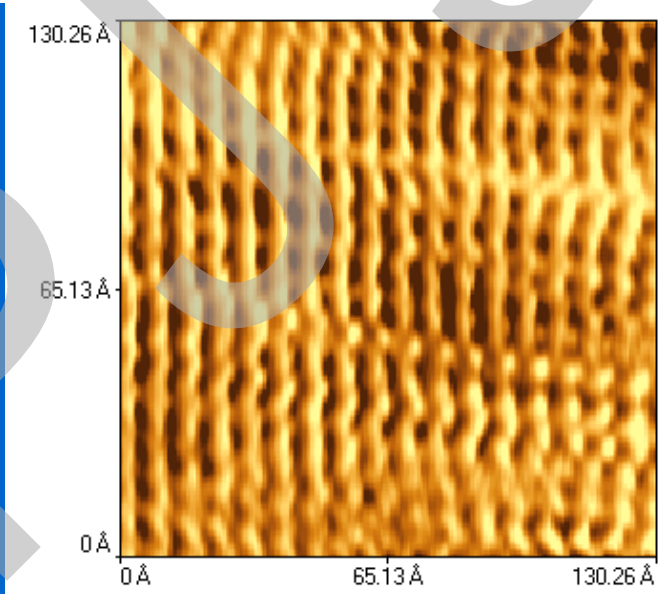
Lateral XY ~20 000x

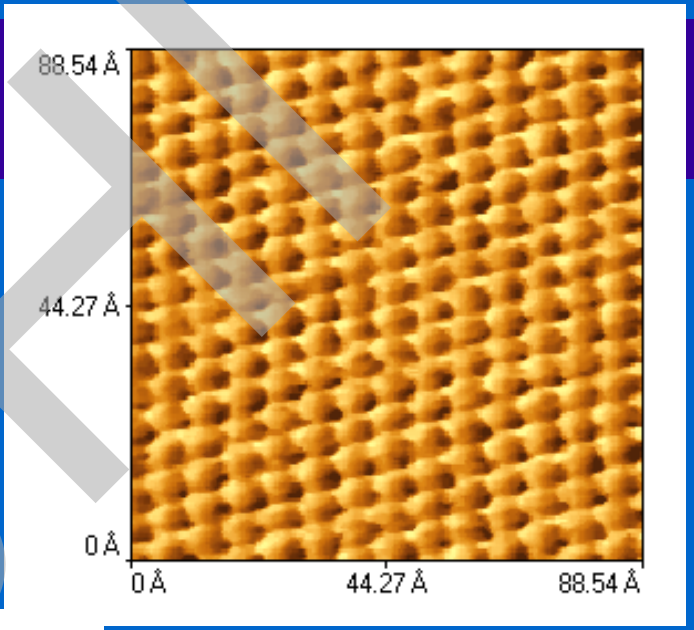
Zeolite crystals

AFM imaging in contact mode



Graphite - HOPG

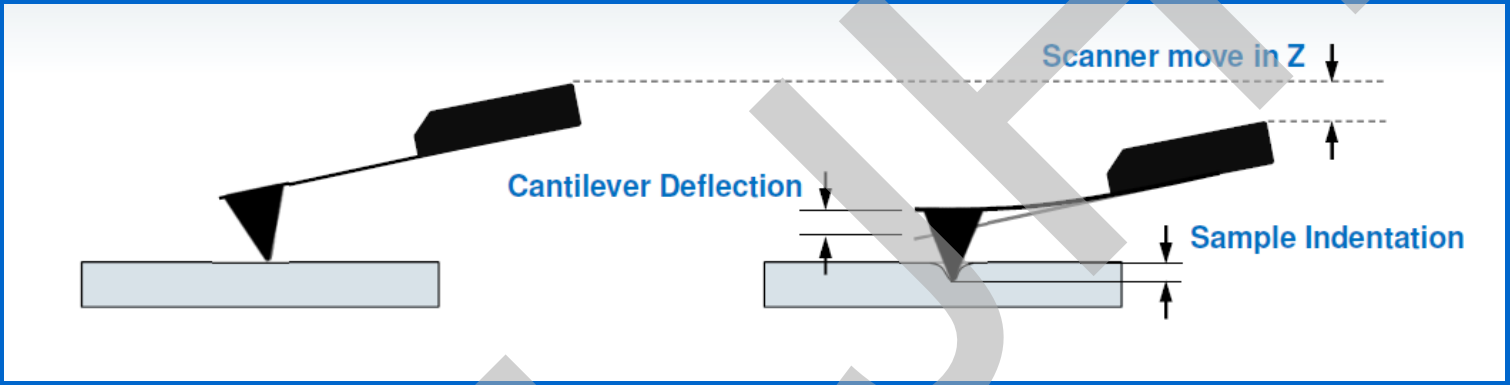


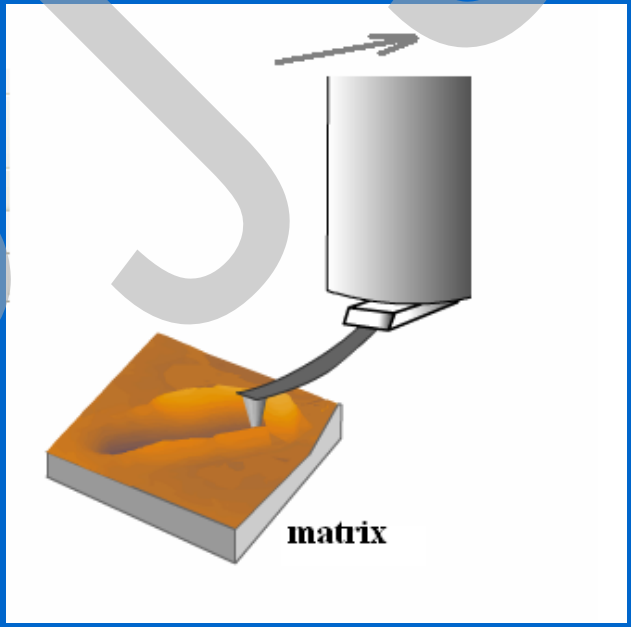


Mica - muscovite

Oriented PTFE molecules on Si wafer

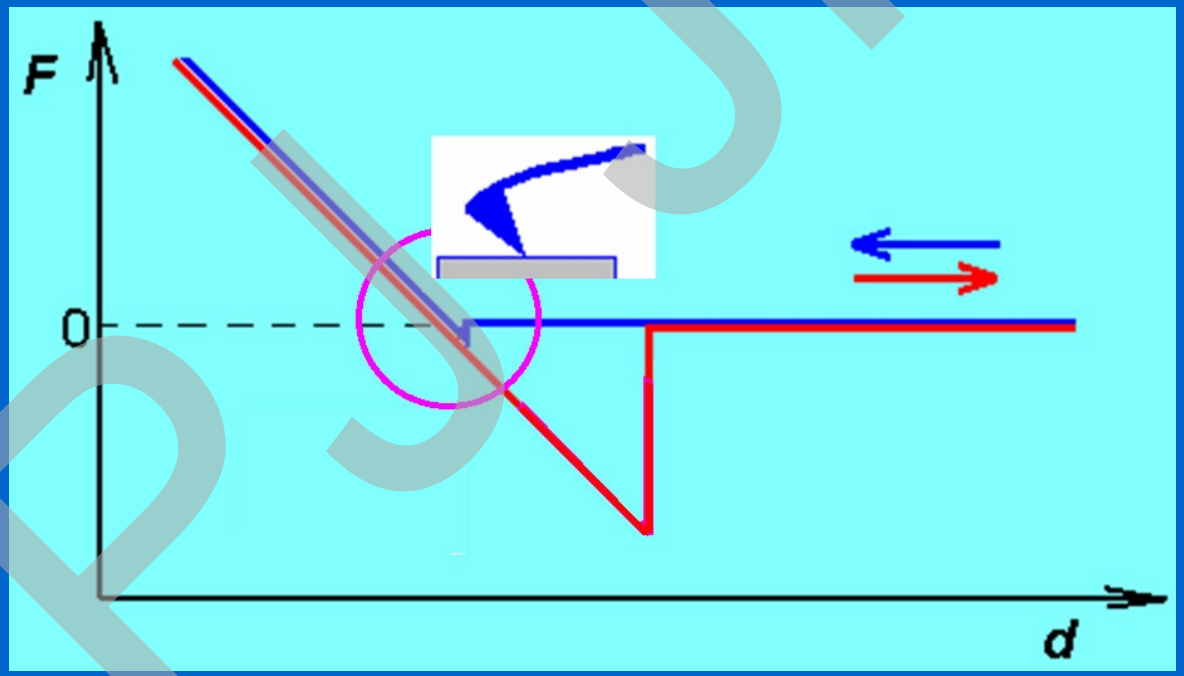
Contact mode AFM - repulsive forces
– indentation, nano-lithography



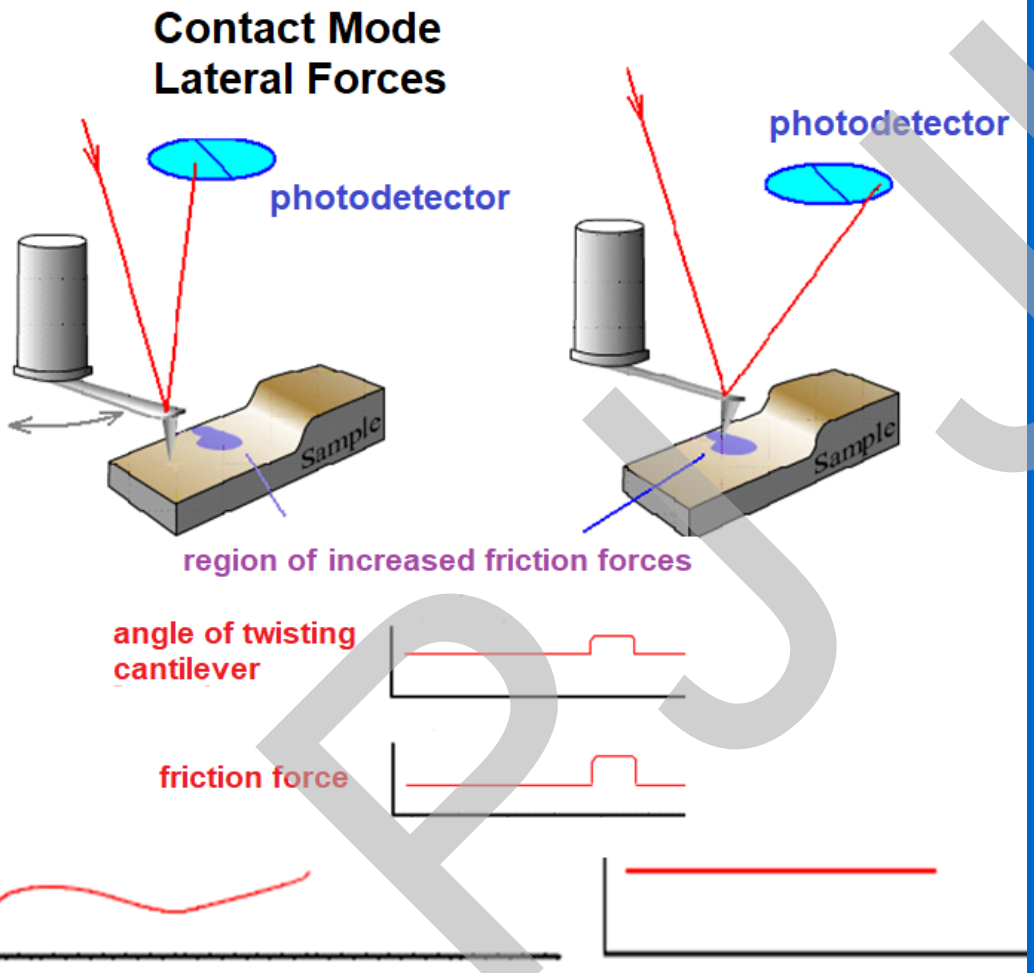


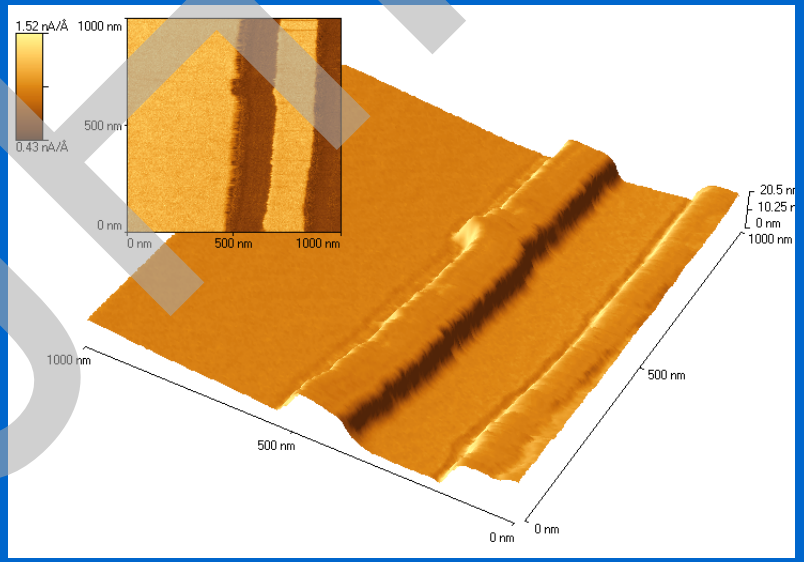
Contact mode AFM – attractive forces:

Adhesion
Friction



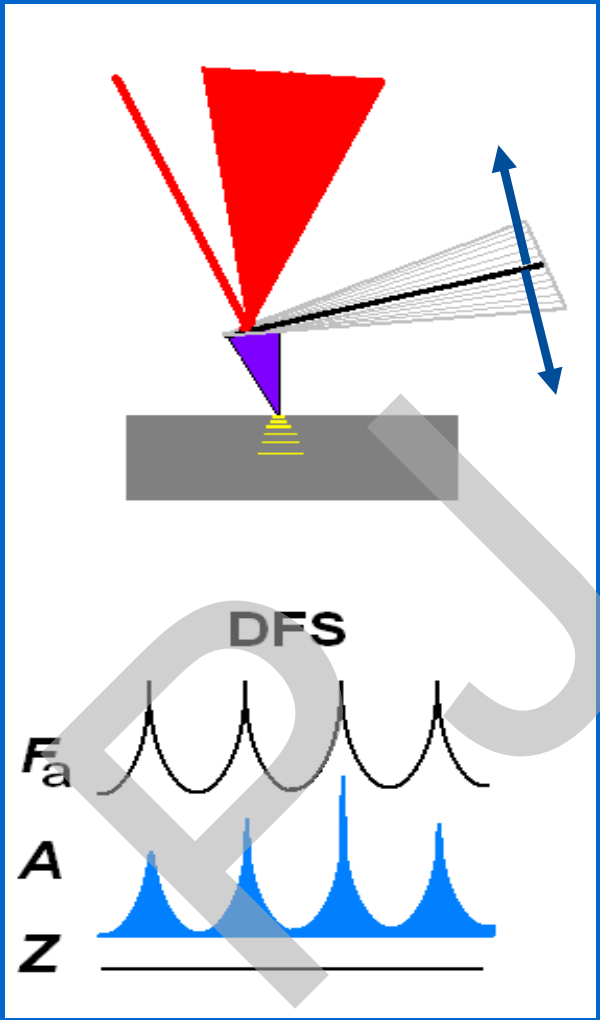
Attractive Lateral Forces (friction) for material analysis (LFM)





PTFE film on glass
-topography
-map of lateral forces (friction)

Contact mode AFM – Dynamic Force Microscopy/Spectroscopy (DFM/S)

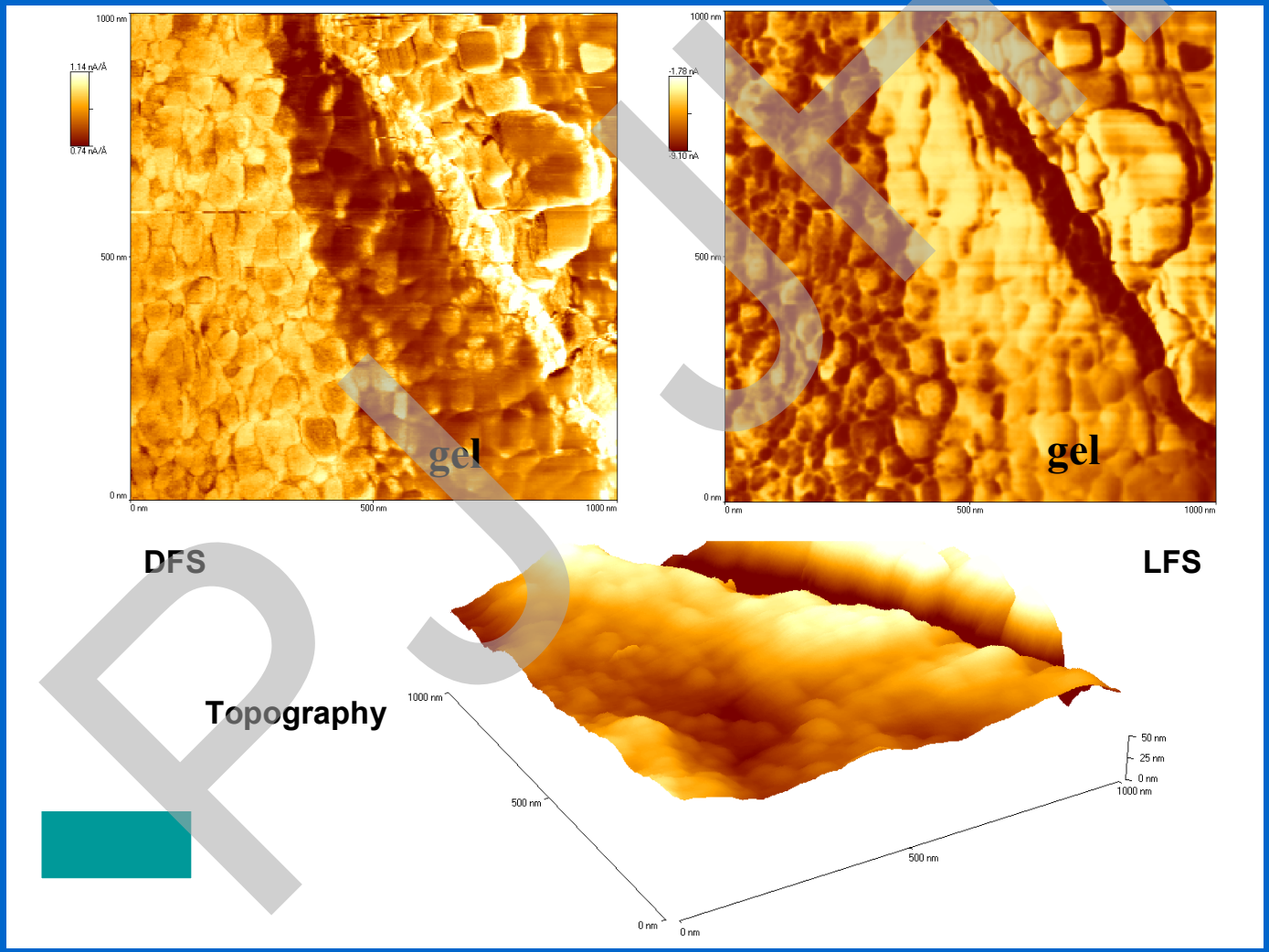


Energy dissipation - "probe defectoscopy": elasticity (Y_M), plasticity

Tip in contact, oscillating cantilever

f_{drive} => $A_{drive}/A_{response}$

AFM DFS material analysis - $Zr/Nb/ZrO_2$

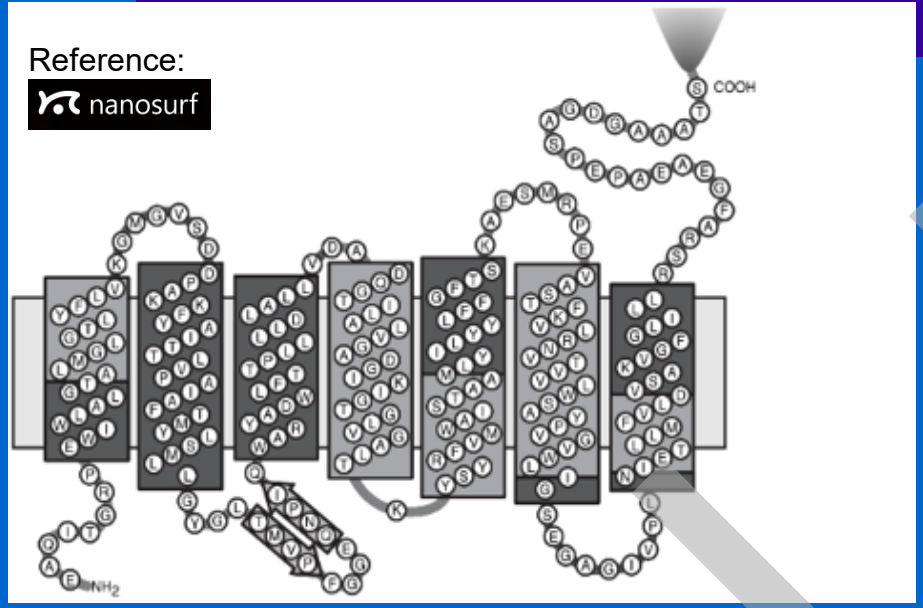


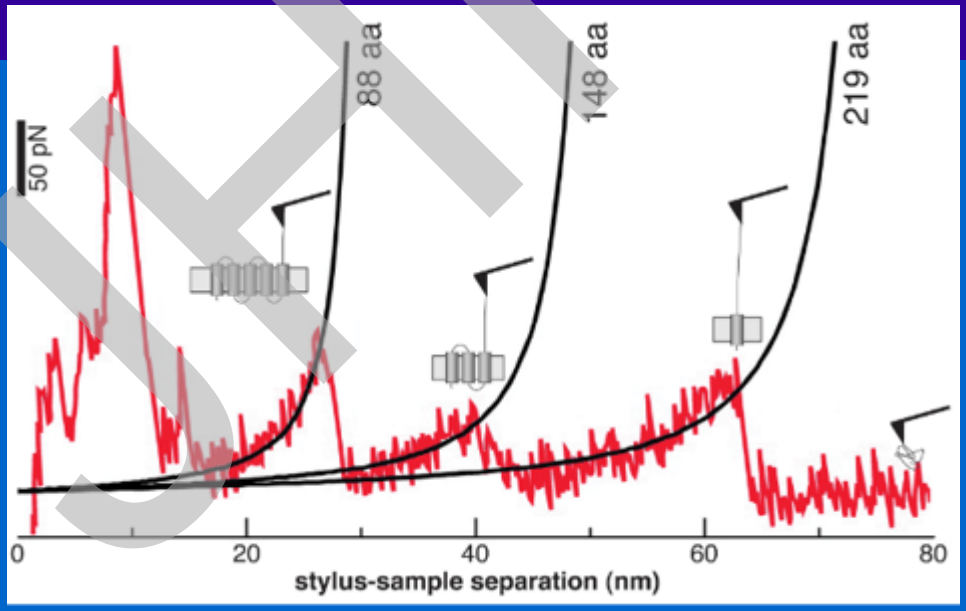
Attractive axial forces for „chemical“ analysis

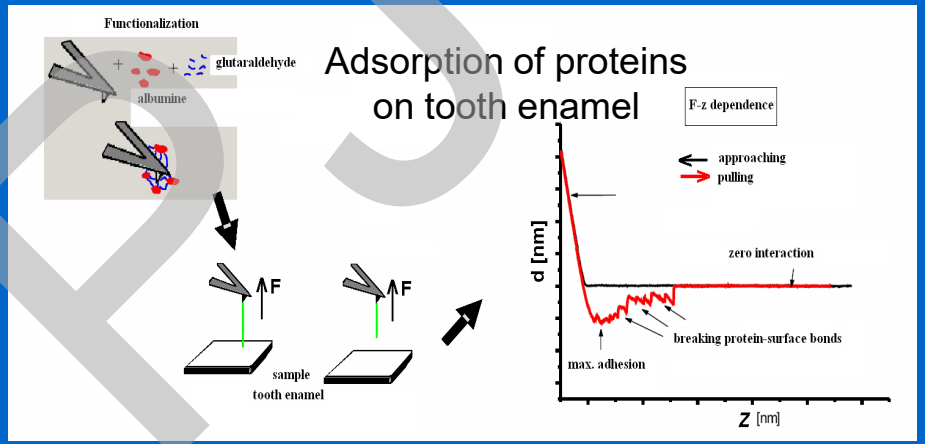
Stretching molecules between cantilever tip and sample

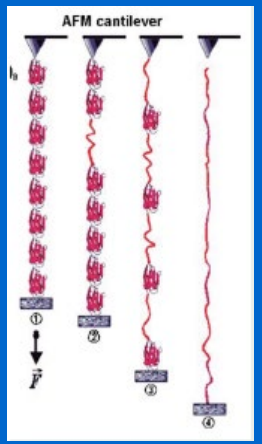
Reference:

nanosurf









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Techniques combining AFM and e-conductivity

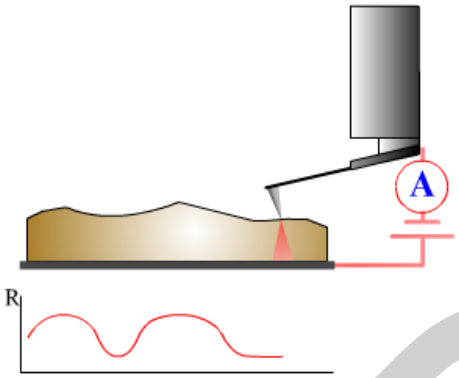
Contact mode:
Conductive Force Microscopy (CFM)

Non-contact mode (!):
Tunneling AFM (TUNA)

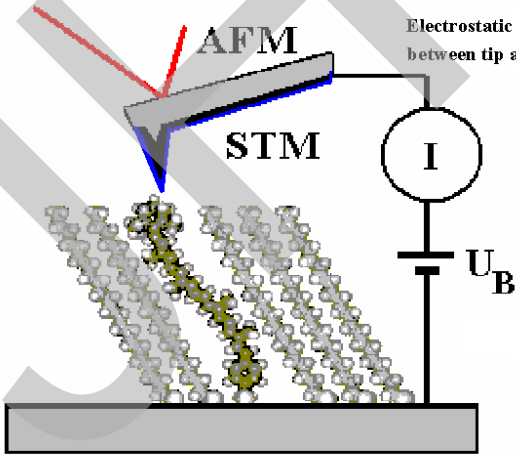
Conductive Force Microscopy (CFM)
Tunneling AFM (TUNA)

Spreading Resistance imaging

Constant Force mode .



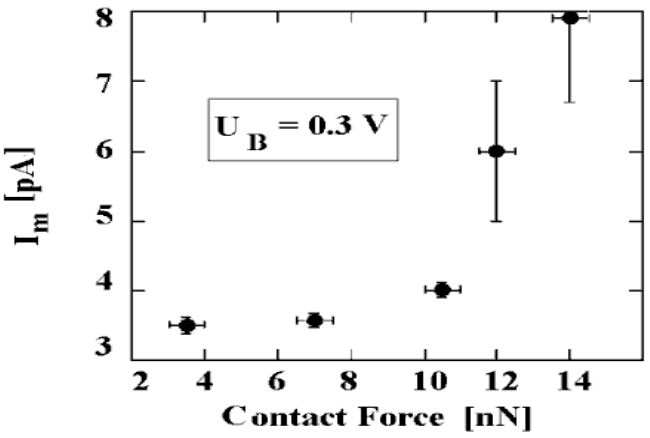
conductive tip
(B-doped diamond, n-doped Si)



Electrostatic interaction between tip and sample.

Carotenoid embedded in 1-docosanethiol attached to Au.
Current measured between biased Pt-coated AFM cantilever and Au substrate.
Maximum current (I_m) vs. contact force.

[*J. Phys. Chem. B* **103** 4006-4010 (1999)]



PeakForce Tapping QNM

Complete force curve is collected at each point of scan

For

- 3D Topography (contact, height) at chosen Peak Force
- Quantitative Nanoscale Mechanical analysis:

Mapping surface nanomechanical properties

adhesion

stiffness/Y_M

deformation

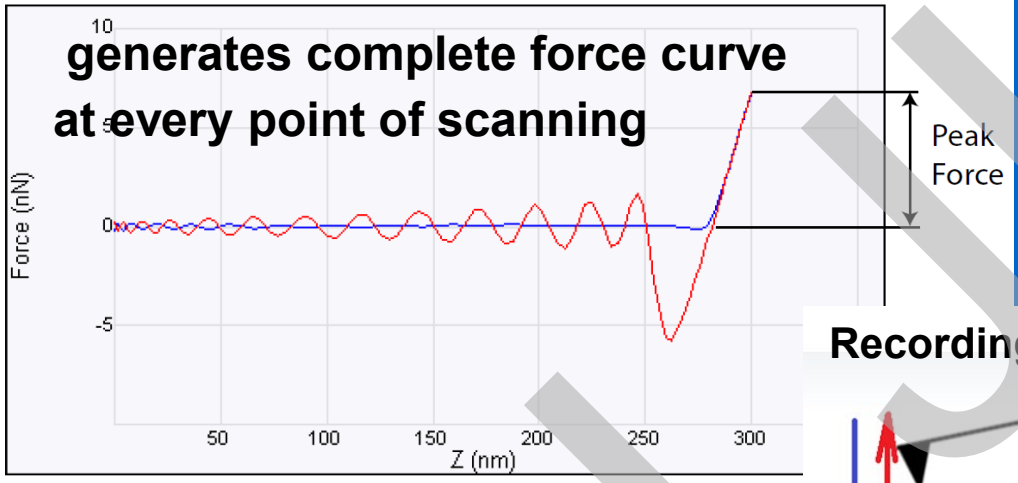
dissipation

extracted simultaneously from various regions of force curve.

Feedback set by Peak Force (contact)Tapping

AFM PFQNM – Peak Force tapping

Figure 2.5f Force curve, Force vs. distance



Periodic contact with surface
contact 3D (height) images

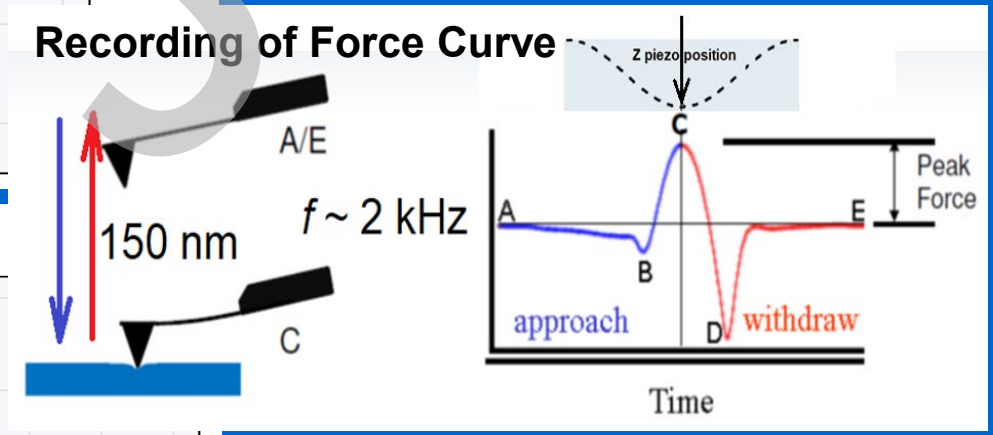
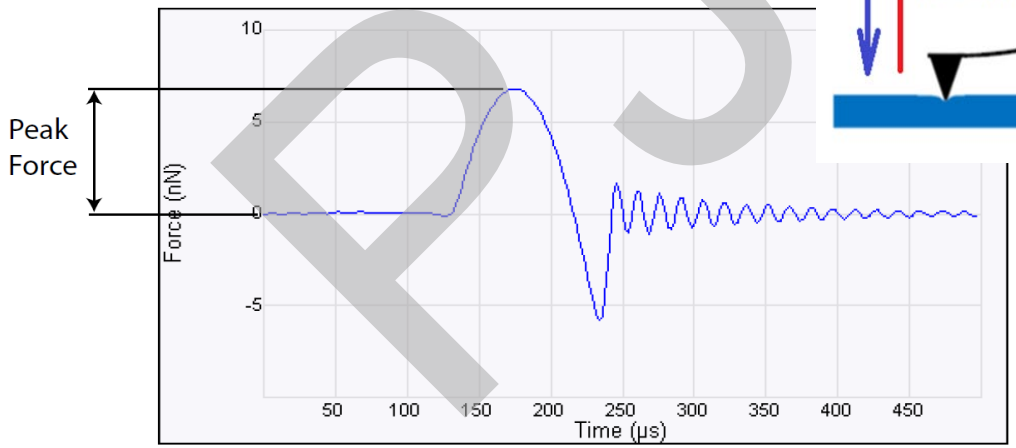


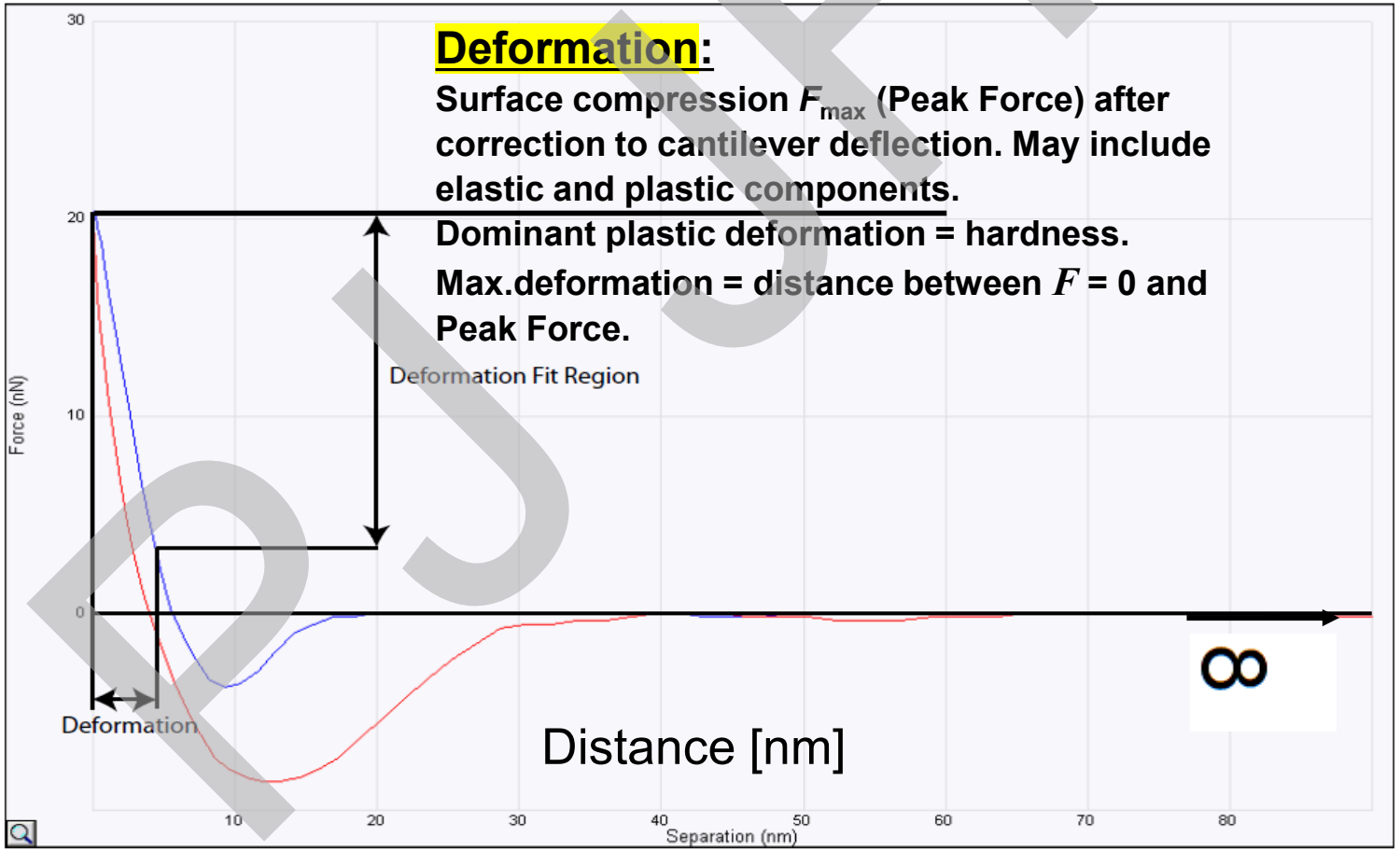
Figure 2.5e The "heartbeat," Force vs. Time



Source: Bruker

AFM PFQNM –interpretation of force curve: Deformation

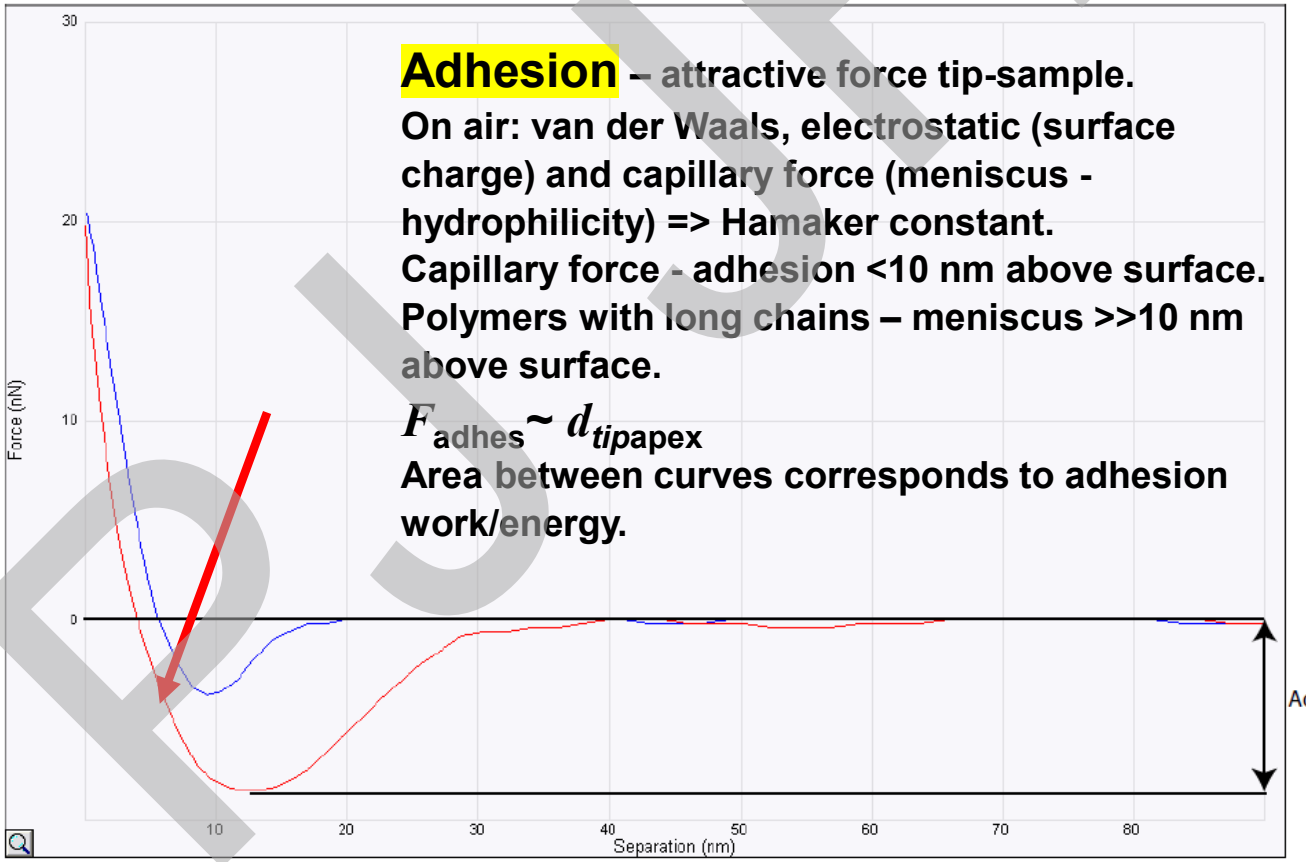
Figure 2.5j Deformation



Source: Bruker

AFM PFQNM –interpretation of force curve: Adhesion

Figure 2.5c Adhesion on a PS+LDPE blend



Adhesion – attractive force tip-sample.

On air: van der Waals, electrostatic (surface charge) and capillary force (meniscus - hydrophilicity) => Hamaker constant.

Capillary force - adhesion <10 nm above surface.

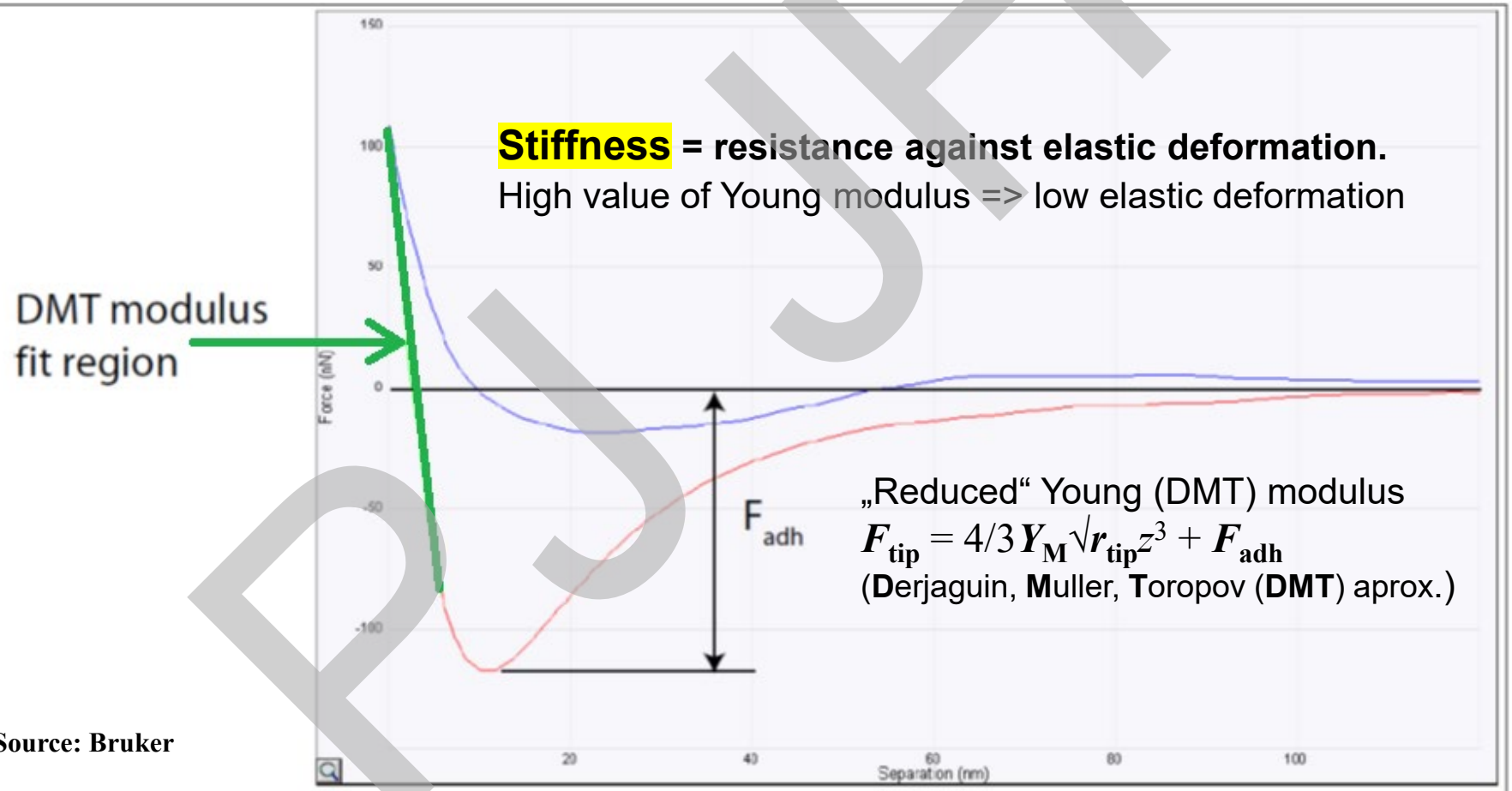
Polymers with long chains – meniscus >>10 nm above surface.

$F_{adhes} \sim d_{tipapex}$

Area between curves corresponds to adhesion work/energy.

Source: Bruker

AFM PFQNM –interpretation of force curve: Stiffness (Y_M/DMT)



Stiffness = **resistance against elastic deformation.**
High value of Young modulus => low elastic deformation

„Reduced“ Young (DMT) modulus

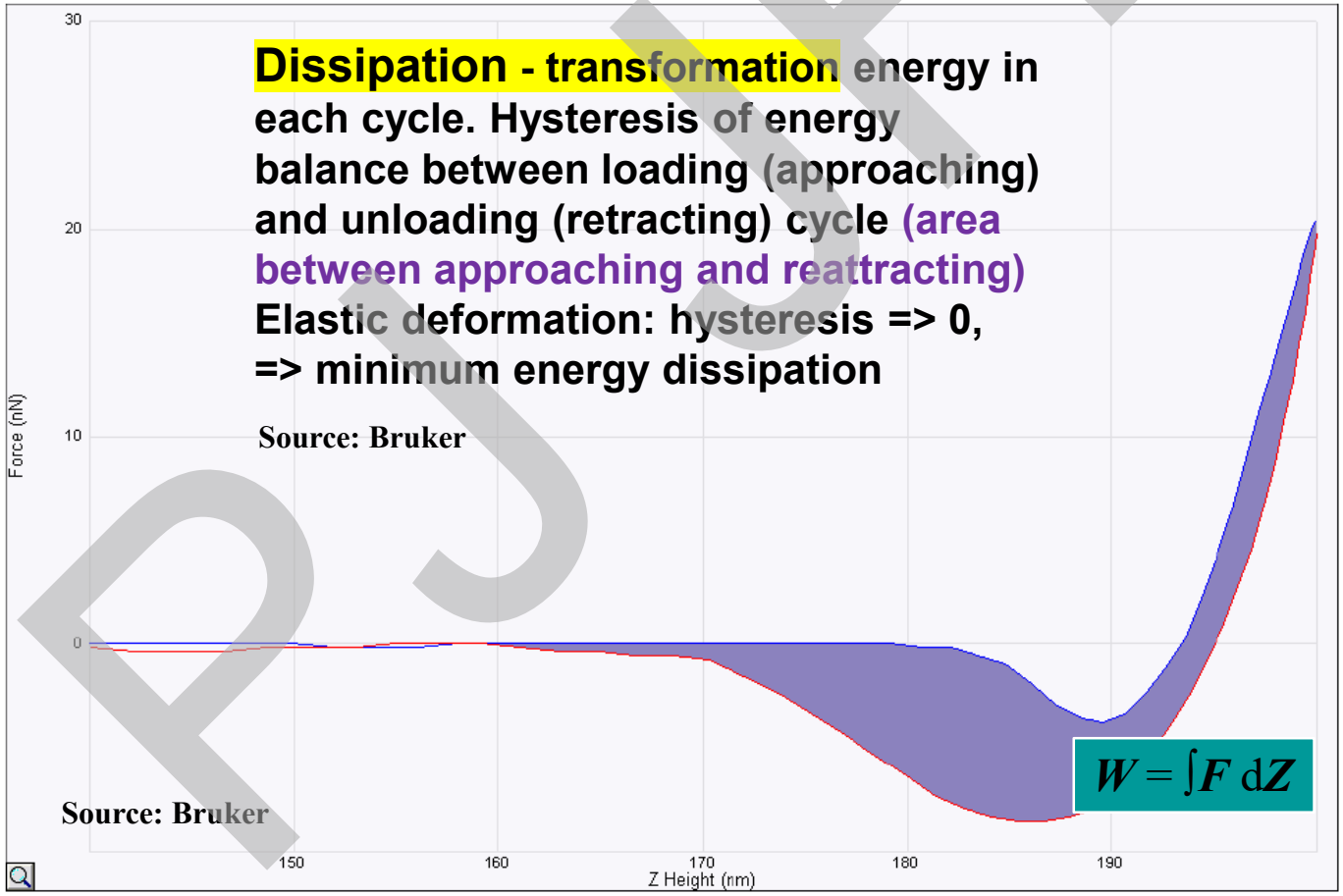
$$F_{tip} = 4/3\, Y_M \sqrt{r_{tip}} z^3 + F_{adh}$$

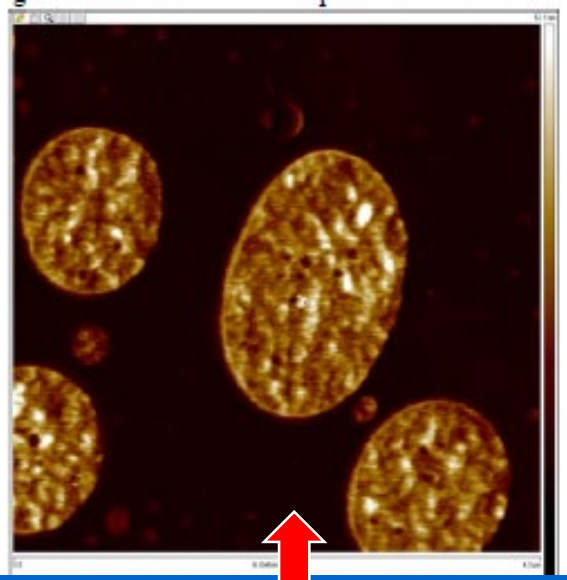
(**D**erjaguin, **M**uller, **T**oropov (**DMT**) aprox.)

Source: Bruker

AFM PFQNM – interpretation of force curve
Dissipation

Figure 2.5h Dissipation (shaded area) in a polystyrene (PS) and Low-density polyethylene (LPDE) blend





Composite **PS/LDPE**
(Y_{PS}~3GPa/Y_{LDPE}~0.3GPa)

AFM PFQNM - interpretation of force curve

Figure 2.5d Adhesion map of a PS+LDPE blend

Deformation

Adhesion

Dissipation

Stiffness (Y_M, DMT-approx.)

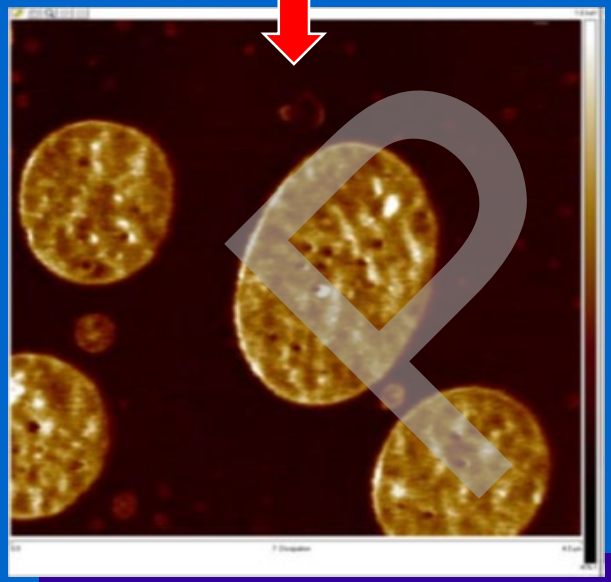
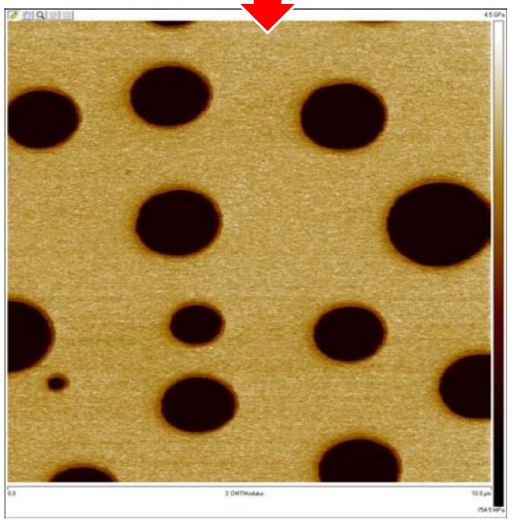
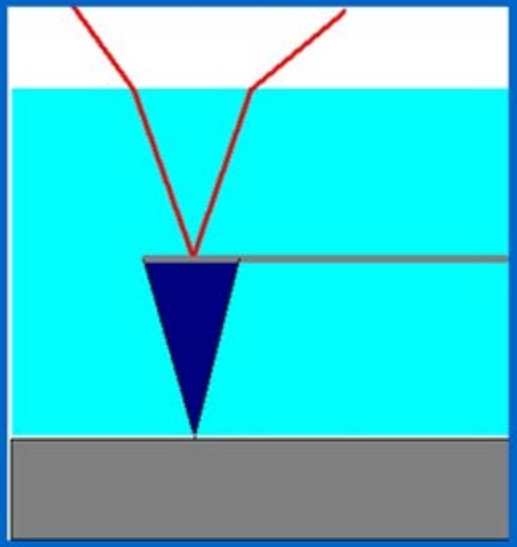


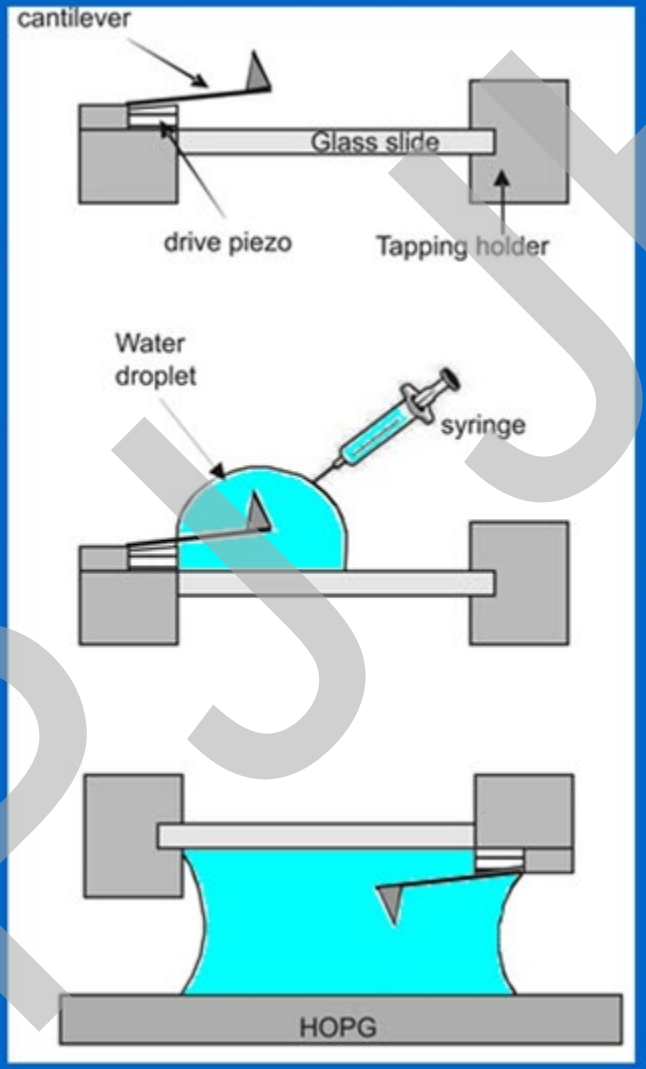
Figure 2.5b DMT Modulu ap of a PS+LDPE blend

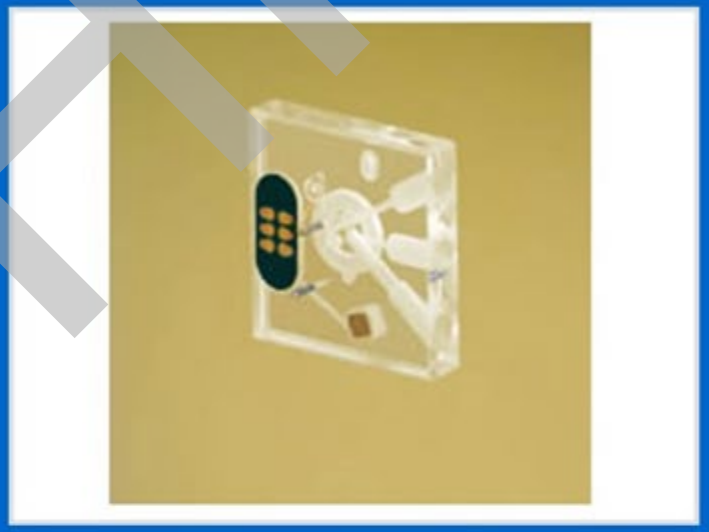


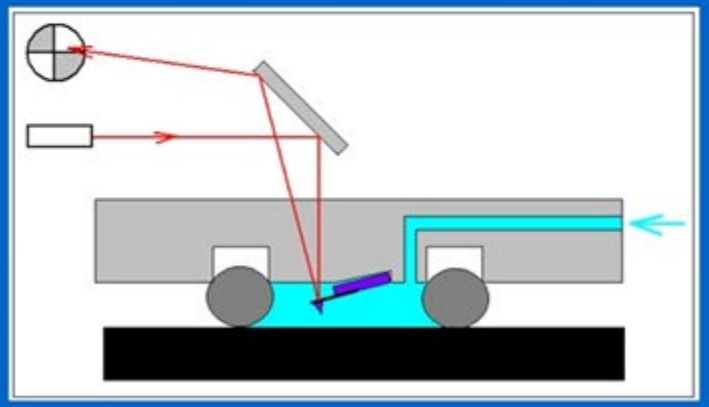
Source: Bruker

AFM in liquids

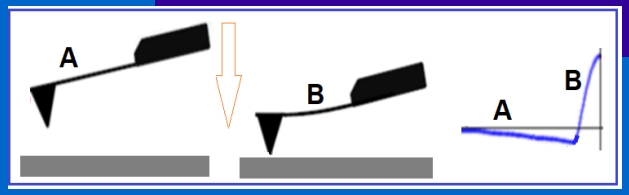


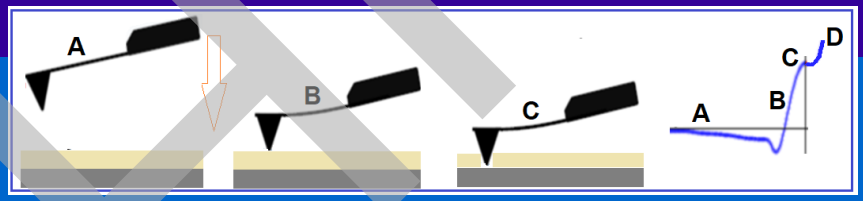


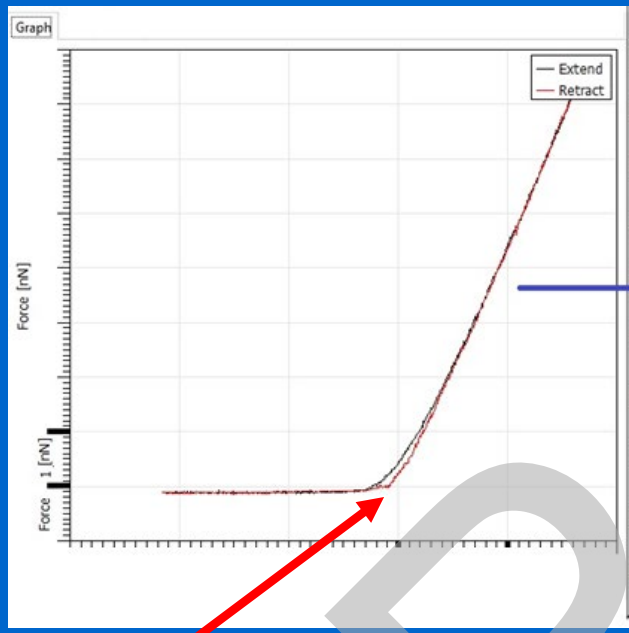


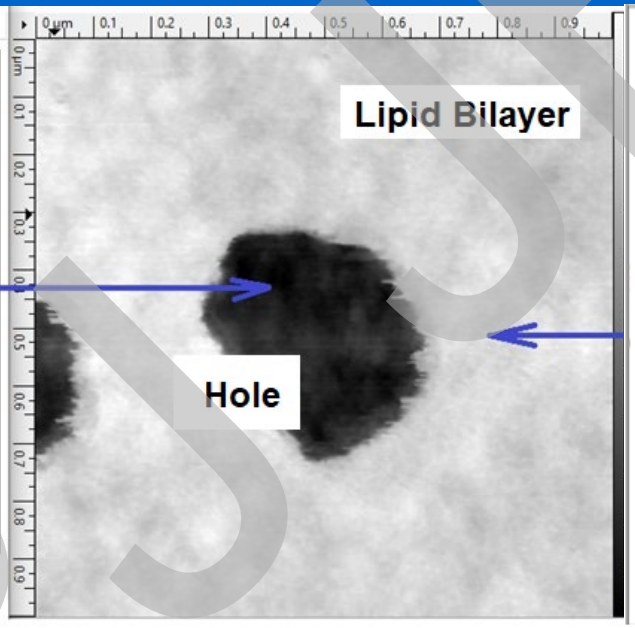


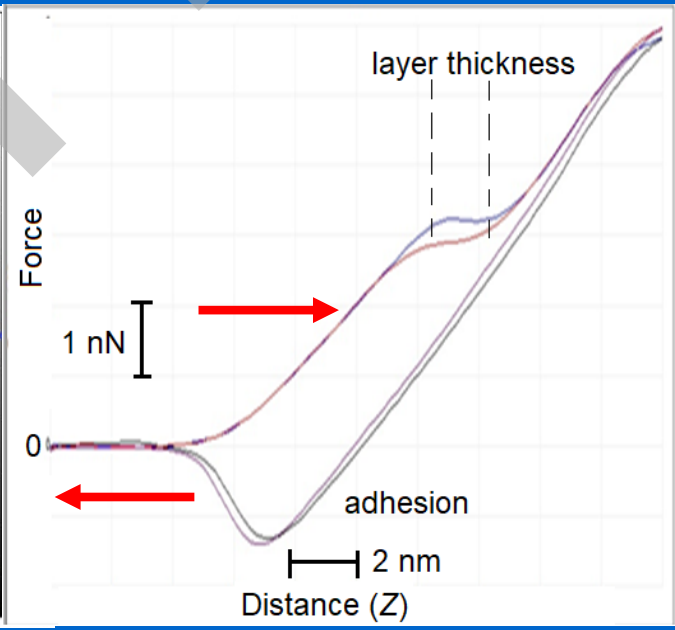
PFQNM on soft layers - interpretation of force curve









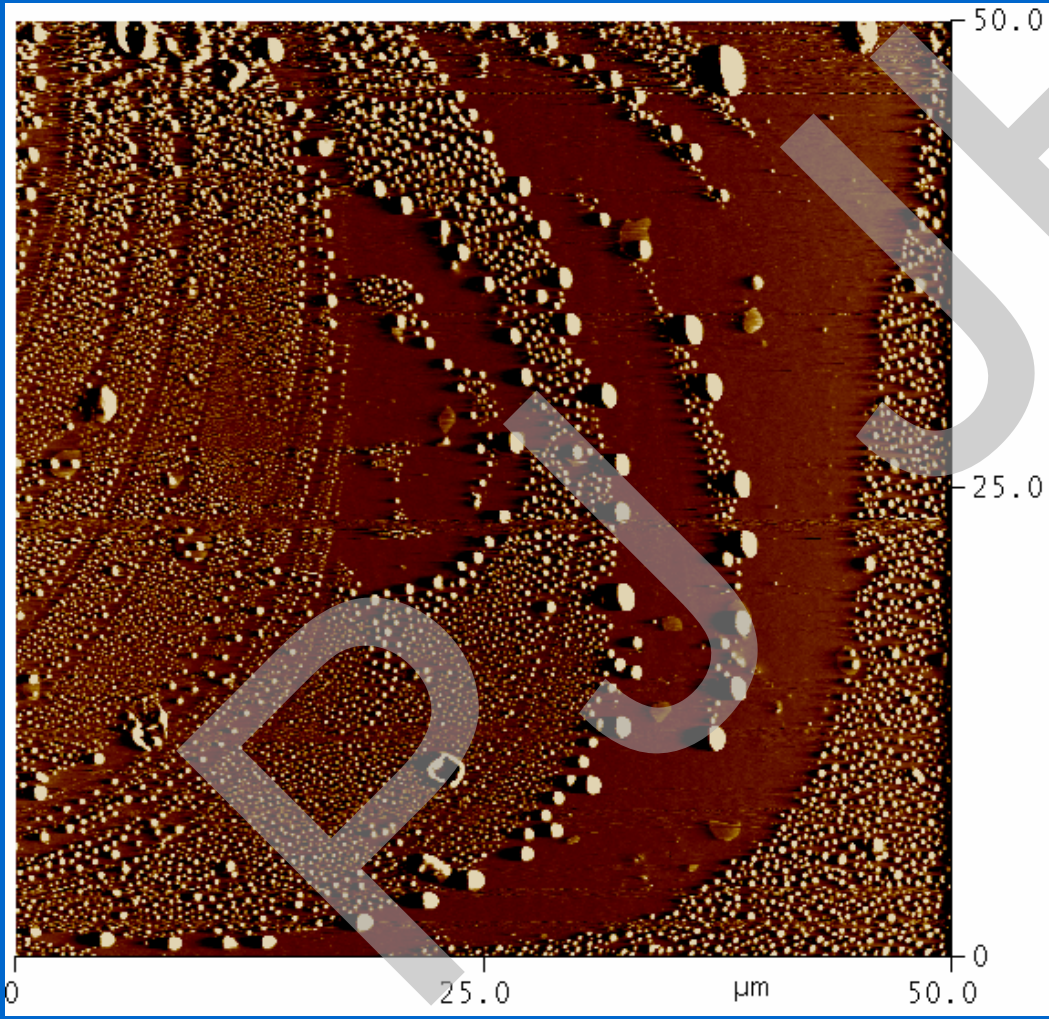


No adhesion to clean Si-wafer (water-immersed)

Source: Lopez Mora et al - study on LBL films

Lipid bilayer on Si-wafer immersed in aqueous media – delay on rising part of force curve: compression, penetration resistance (PFQNM)

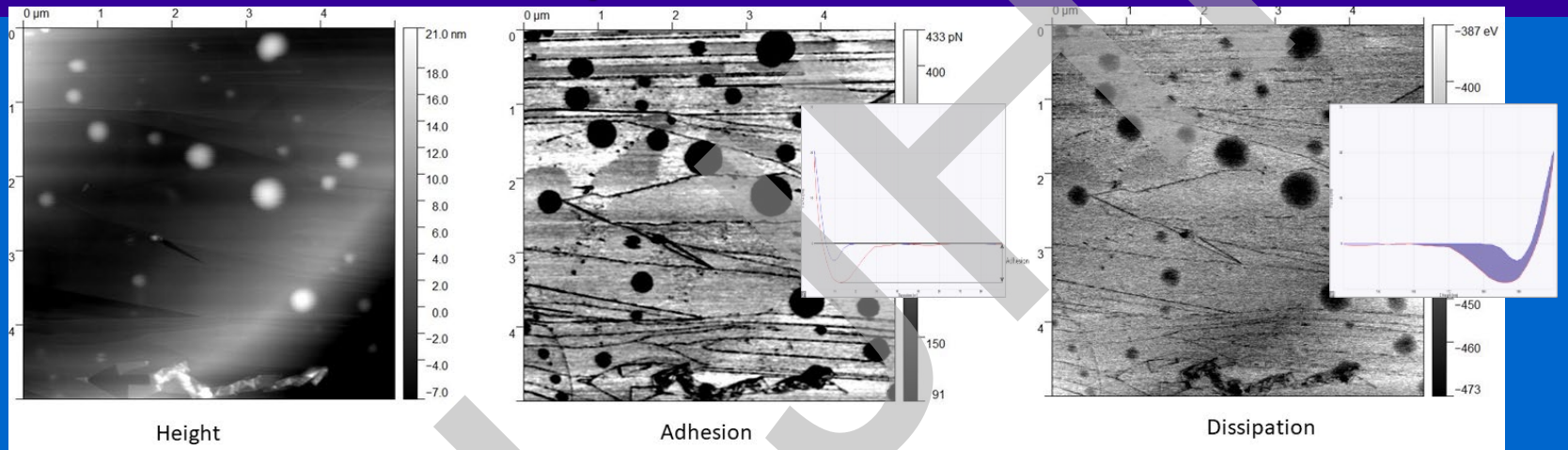
AFM imaging of “zero-mass” nano-objects:
Gaseous nanobubbles on immersed surfaces



In-situ AFM *tapping*, amplitude image of surface nanobubbles on water-immersed HOPG.
Hydrophilized tip and cantilever

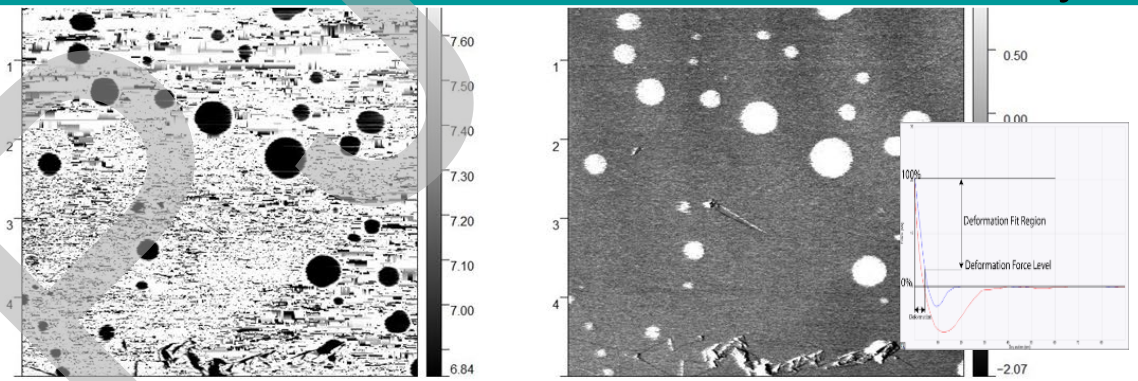
AFM-PFQNM of gaseous nanodomains

- interpretation of force curve



Height Adhesion Dissipation

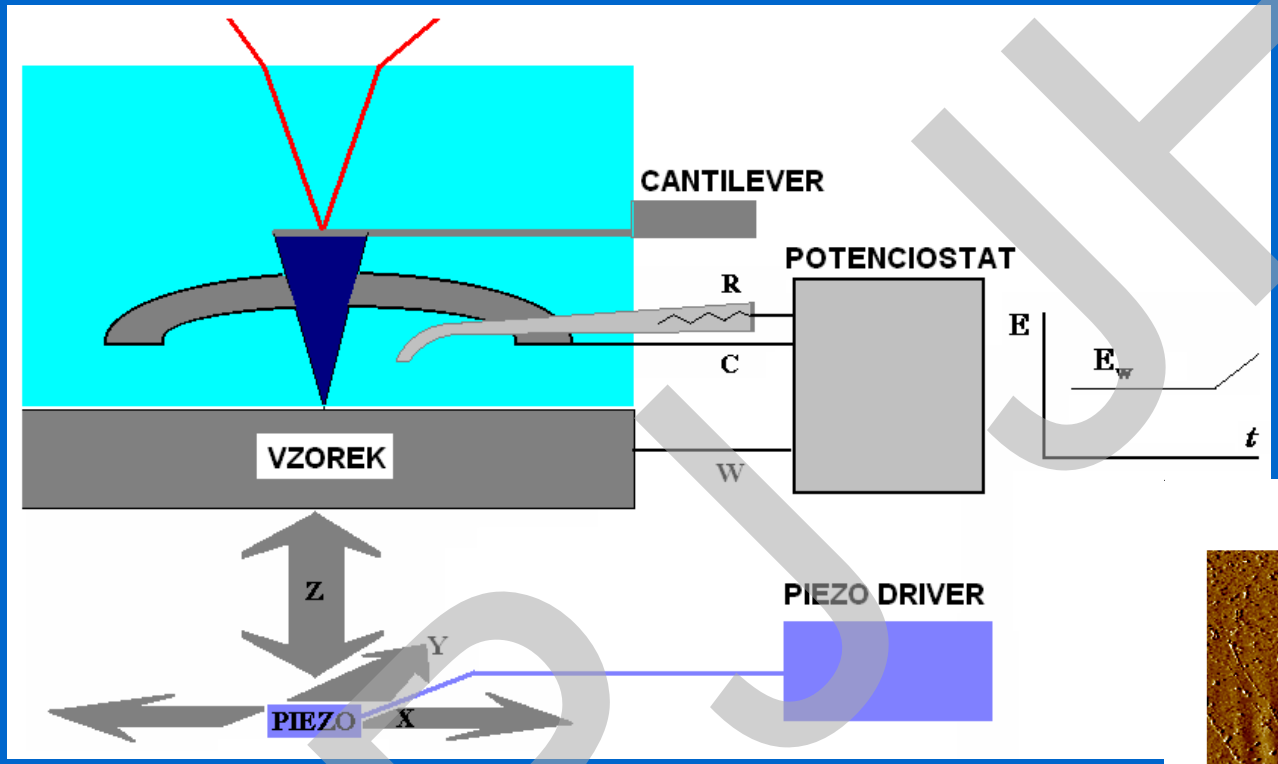
Gaseous nanodomains on water-immersed surface – hydrophilized tip

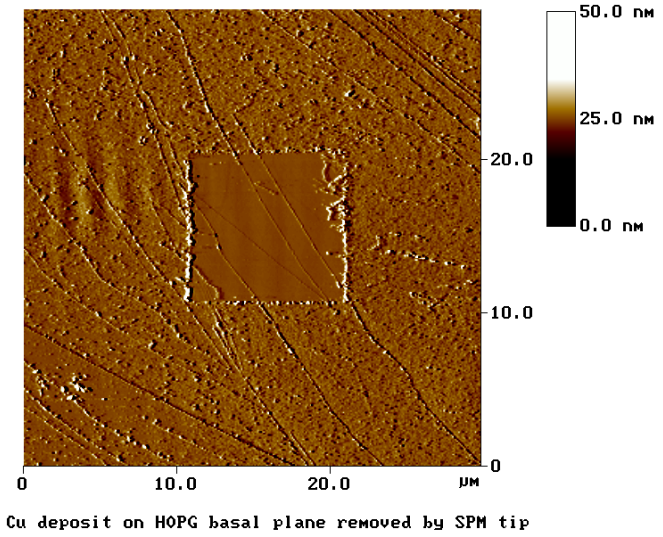


LogStiffness Deformation

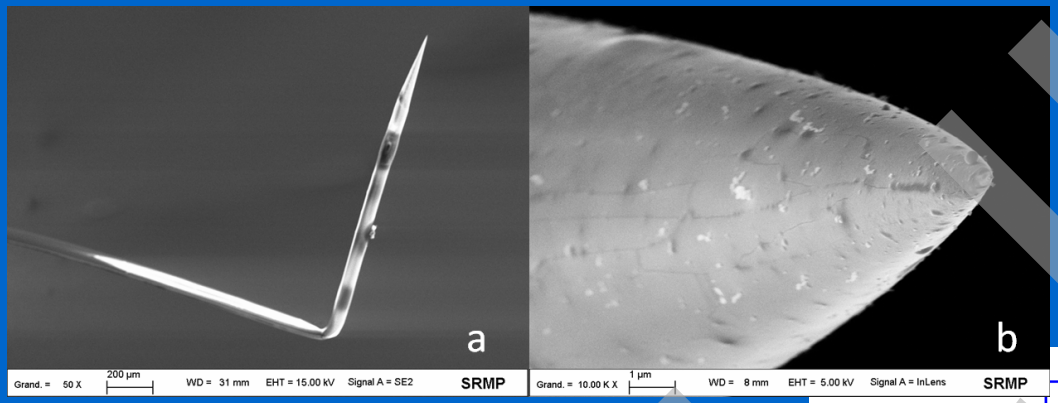
Hana Tarabkova and Pavel Janda: Effect of Graphite Aging on Its Wetting Properties and Surface Blocking by Gaseous Nanodomains, Langmuir 2023, 39, 14154−14161

In-situ AFM imaging of electrochemical experiment

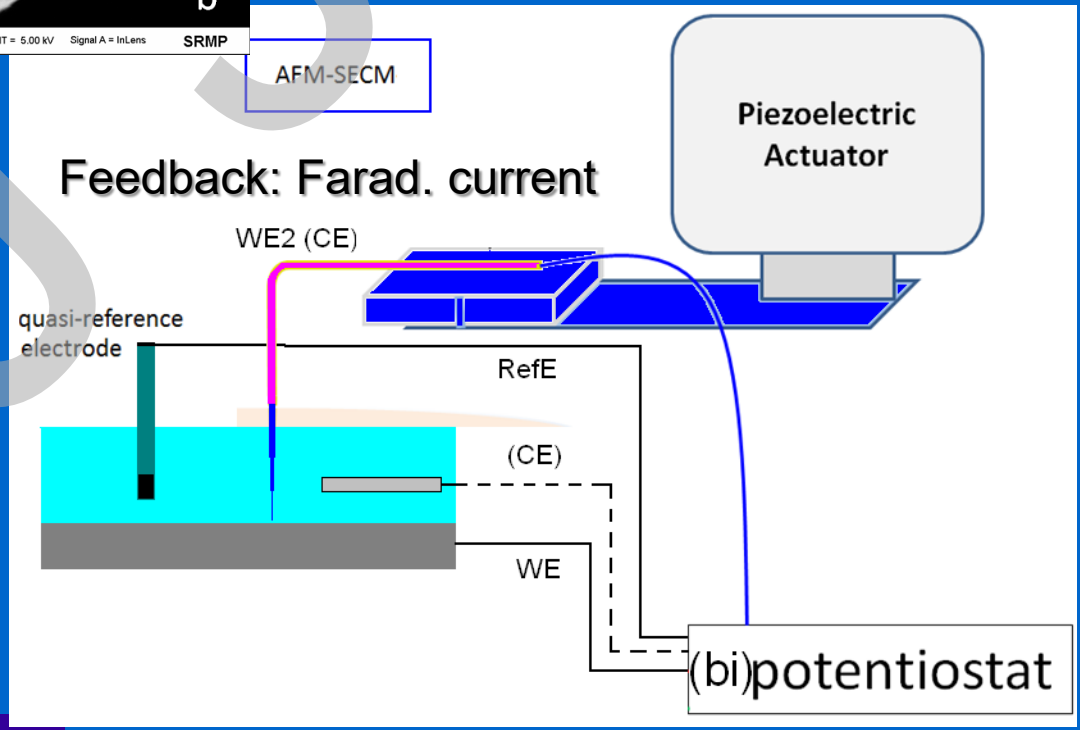




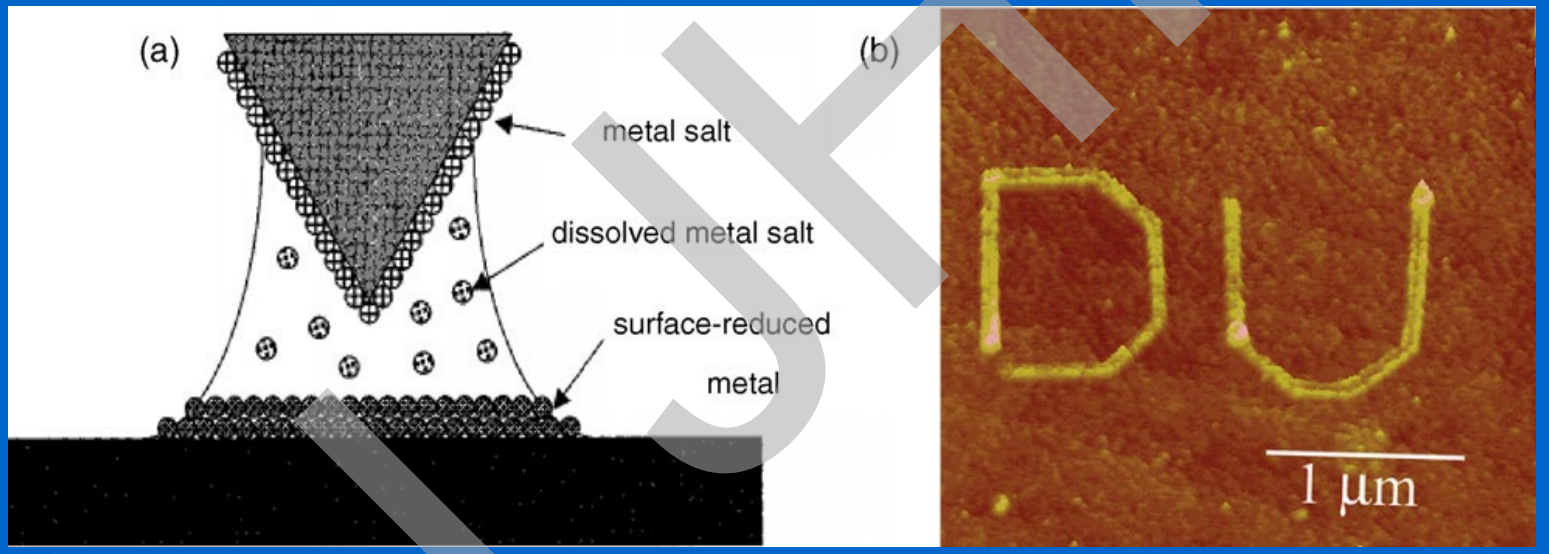
AFM in Scanning Electrochemical Microscopy (SECM)



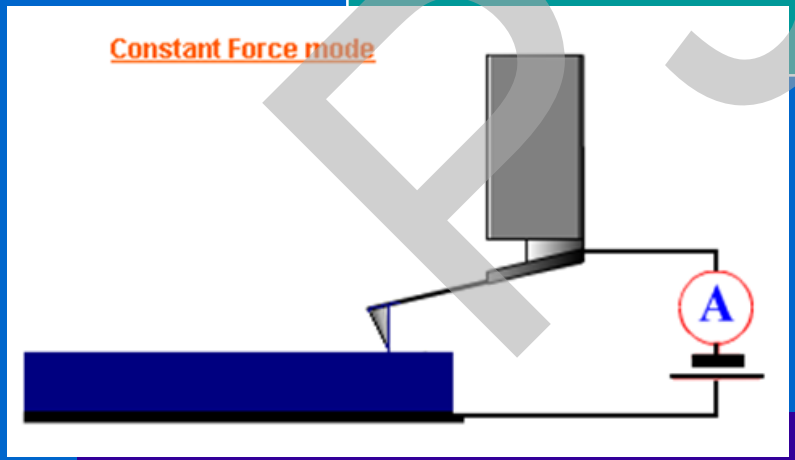
AFM-SECM tip/electrode insulated by electrophoretic coating, tip *r* ~130 nm



AFM in EC: ECAFM/lithography
tip-assisted electrodeposition of metal in droplet

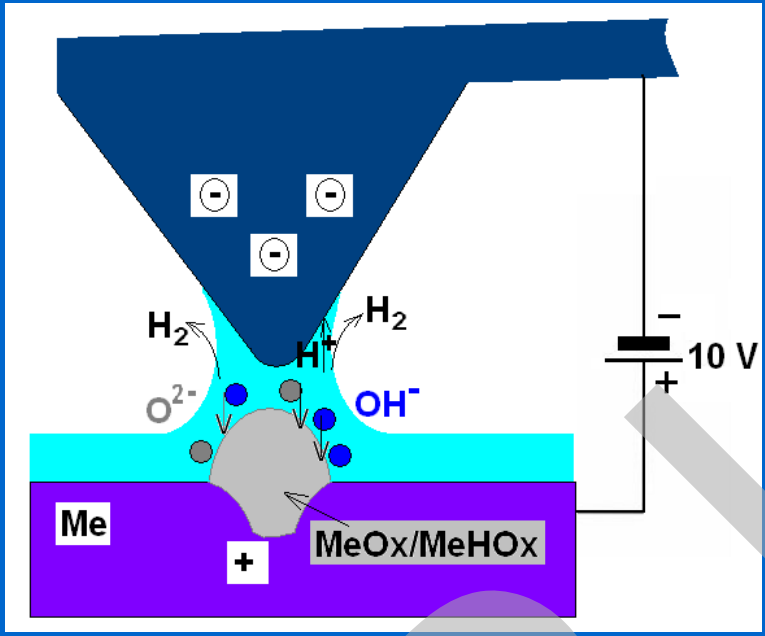


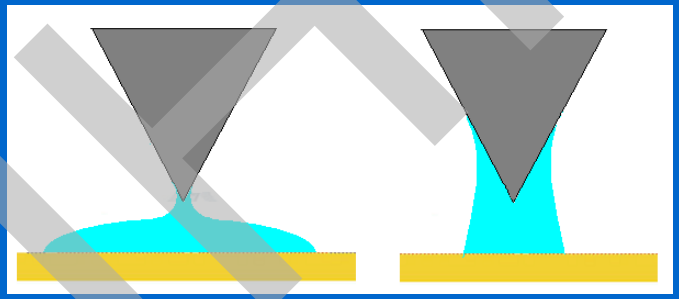
Au electro-deposition: conversion Au(III) (ink) => Au(0)
2-electrode system



TSENG, Ampere A. Tip-Based Nanofabrication Fundamentals and Applications. Springer New York Dordrecht Heidelberg London 2011. ISBN 978-1-4419-9898-9.

ECAFM/lithography: tip-assisted local electrochemical deposition/dissolution of oxide

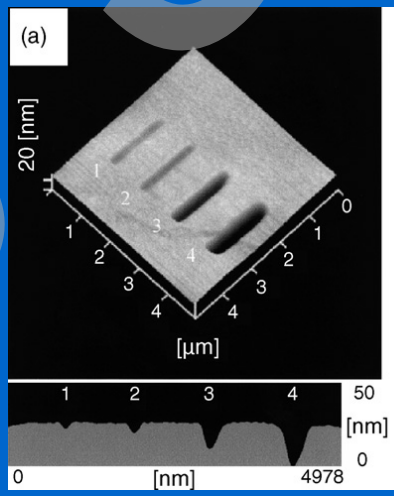


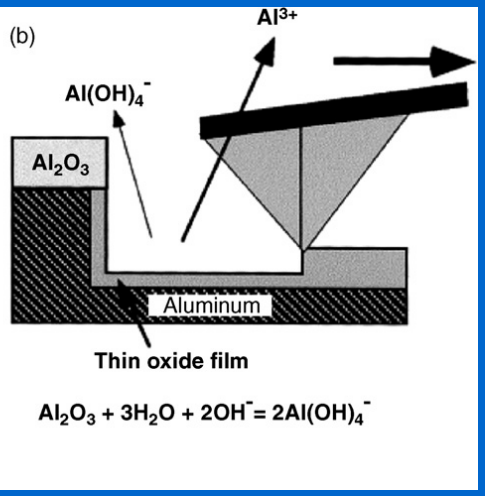


Water meniscus on hydrophilic and hydrophobic substrate

Field intensity 10^7 V/cm => water dissociates H_2O => OH^- + H^+

2-electrode system





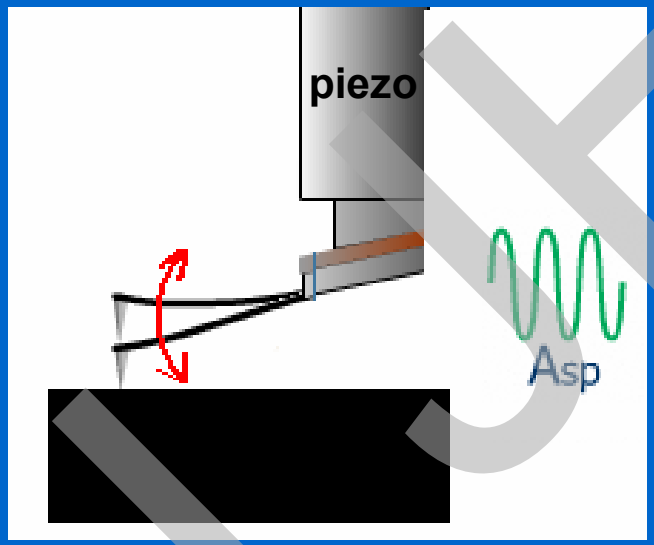
TSENG, Ampere A. Tip-Based Nanofabrication Fundamentals and Applications. Springer New York Dordrecht Heidelberg London 2011. ISBN 978-1-4419-9898-9.

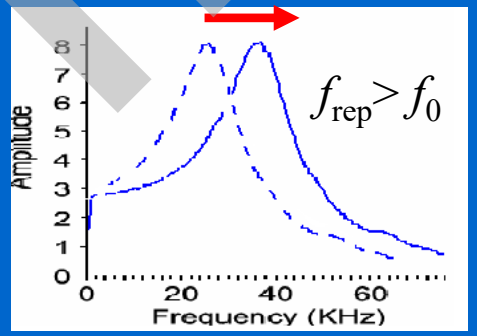
Semi(contact) mode - tapping

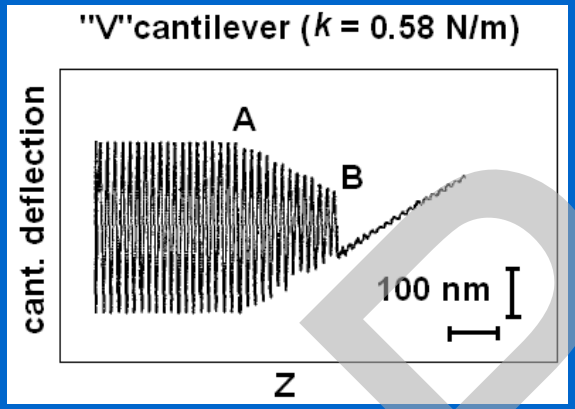
Acoustic/mgt. drive

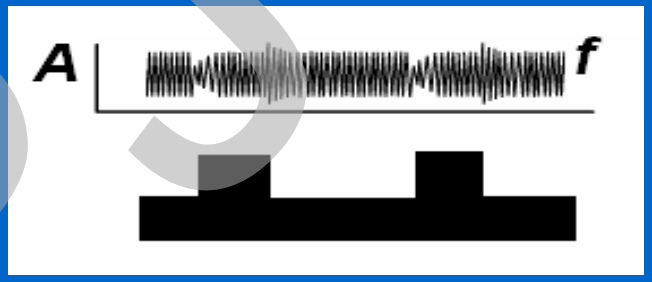
Mechanical oscillator
oscillation in resonance
input parameters:
f_{rez} A_{sp} (~ 20 nm)

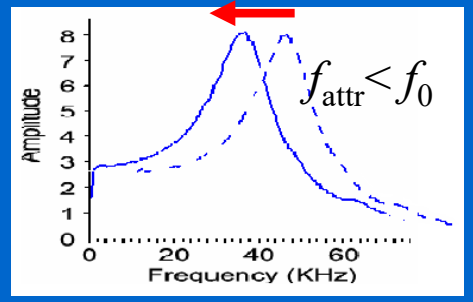
output parameters
A, Δf, $\Delta\theta$, d *(deflect.)*











$$md^2z/dt^2 = -kz - (m\omega_0/Q)dz/dt + F_{tip\text{-}sample} + F_{drive}\cos\omega t$$

Hook

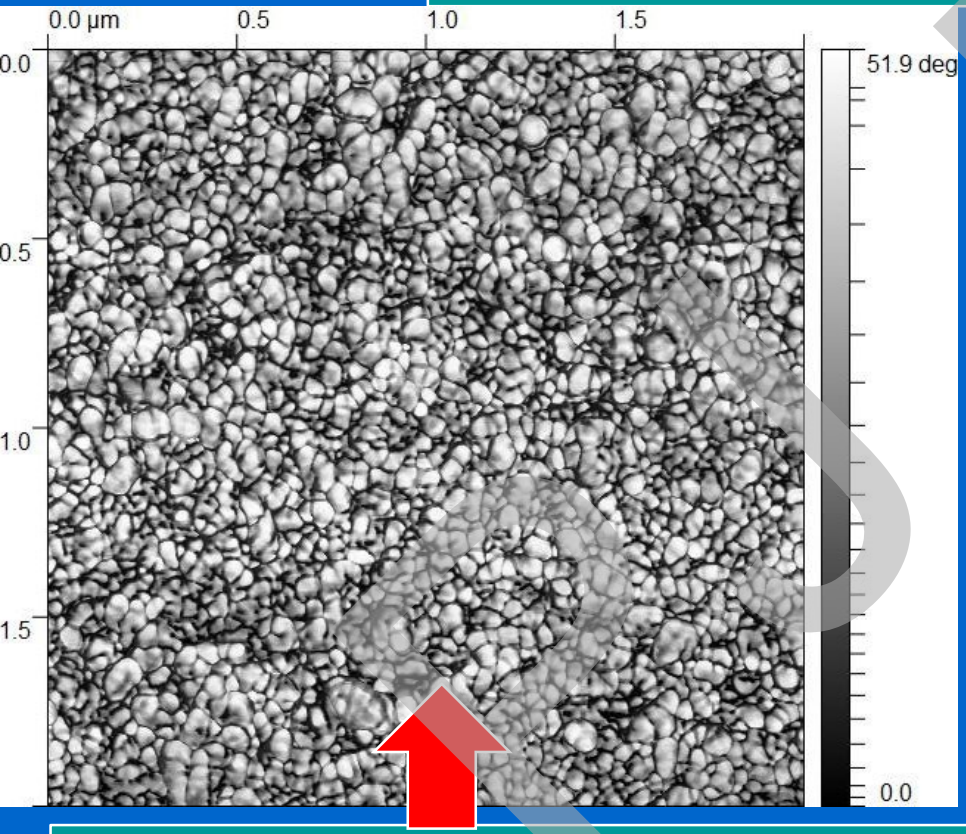
Dissipation (dumping)

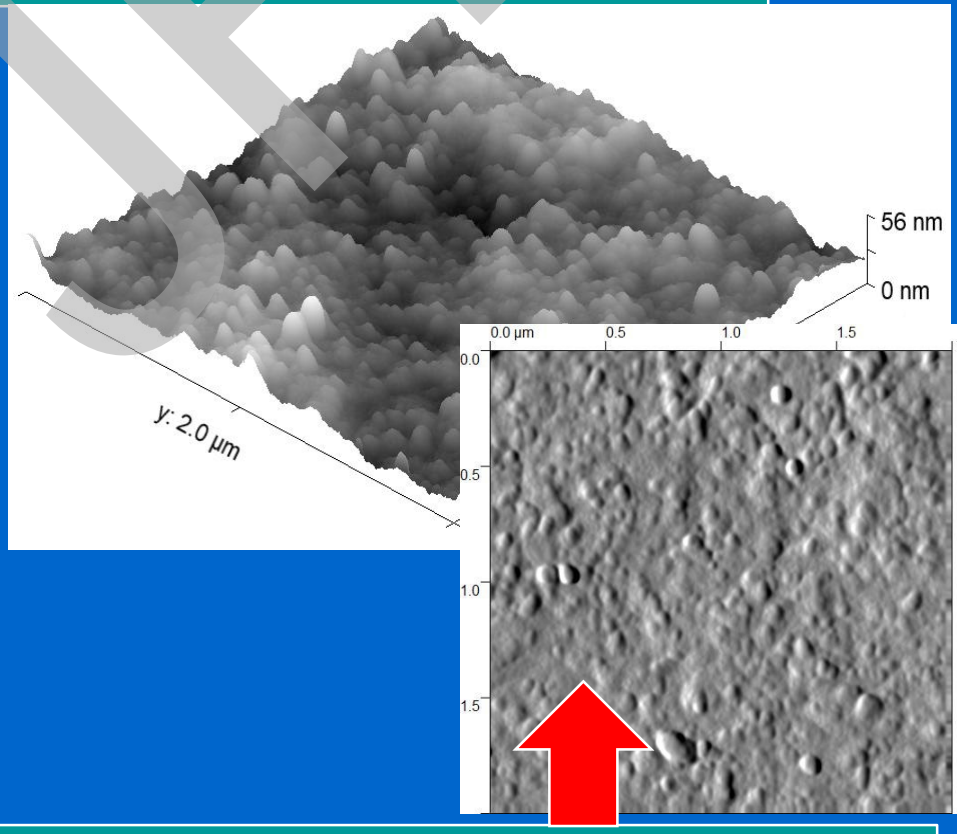
Interaction tip-sample

$$\omega_0 = \sqrt{k/m}$$

Semicontact mode (tapping) phase imaging

Enhances edges of (nano)structure boundaries.
Less affected by height fluctuation

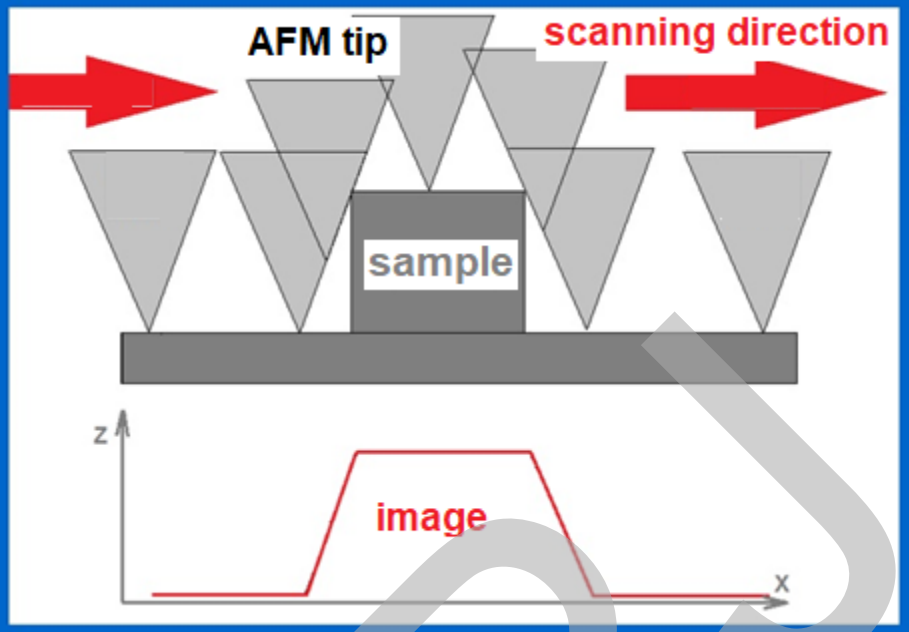


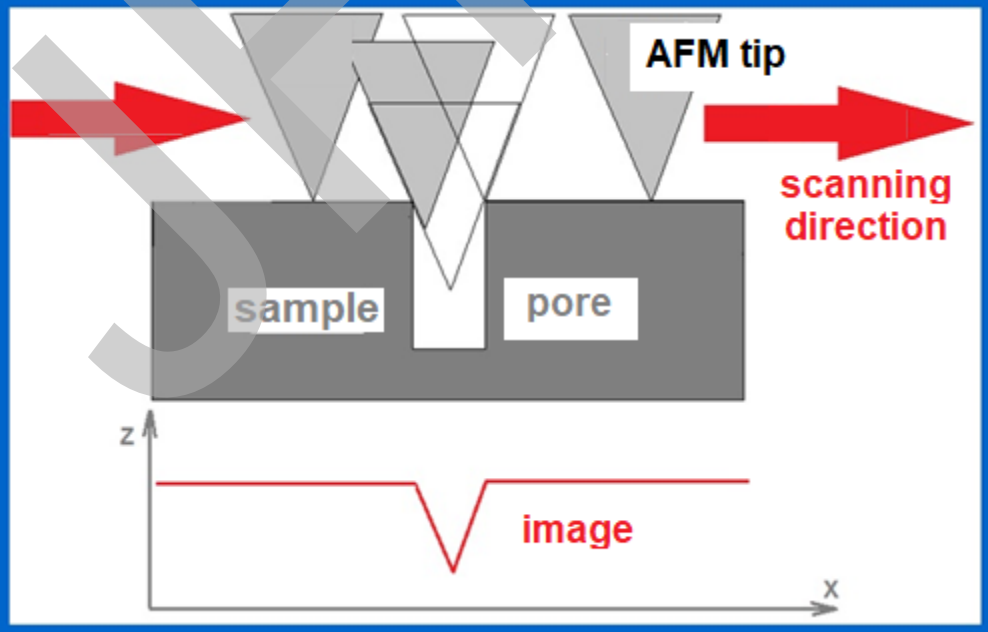


Nanograins ZrO_2 imaged by AFM tapping phase mode (top-view)

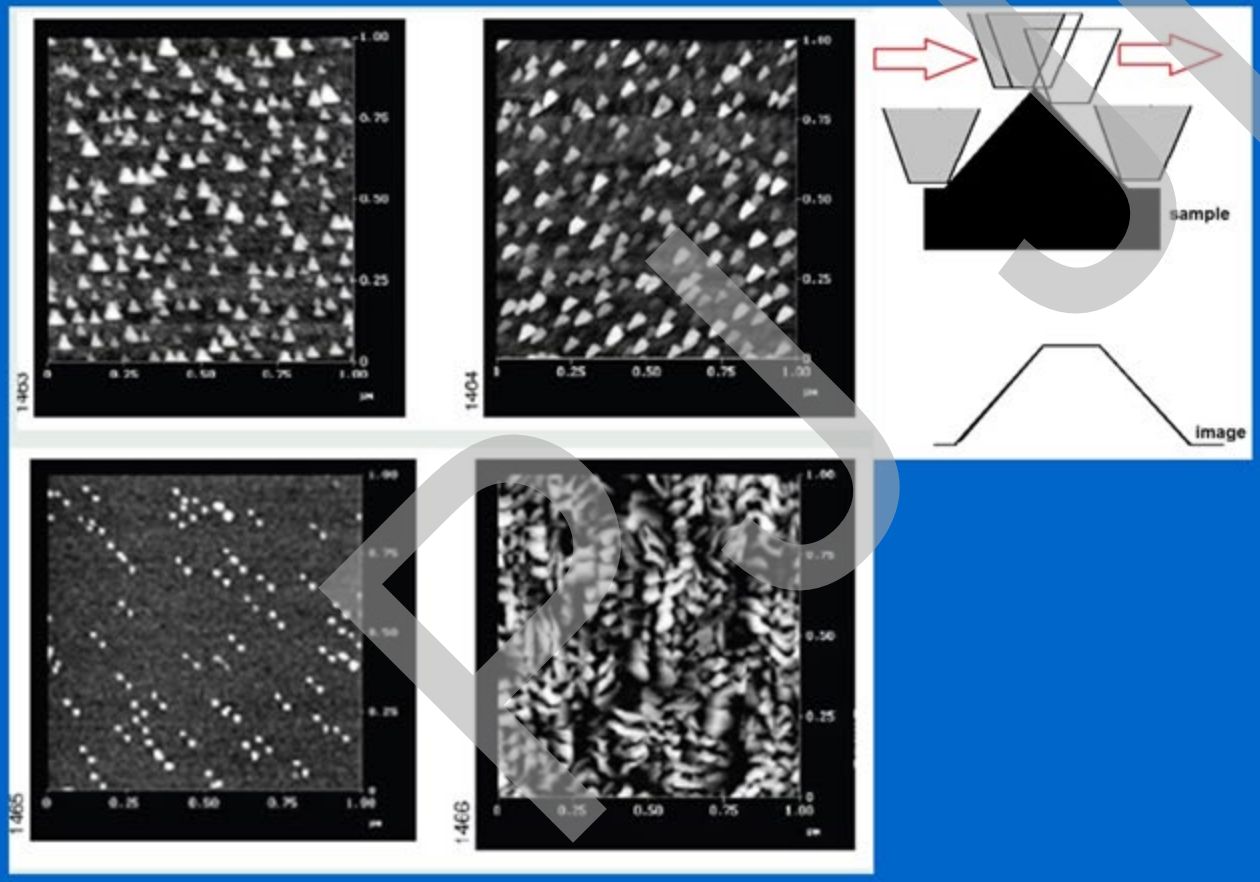
Identical location imaged by 3D topography and amplitude mode (top-view)

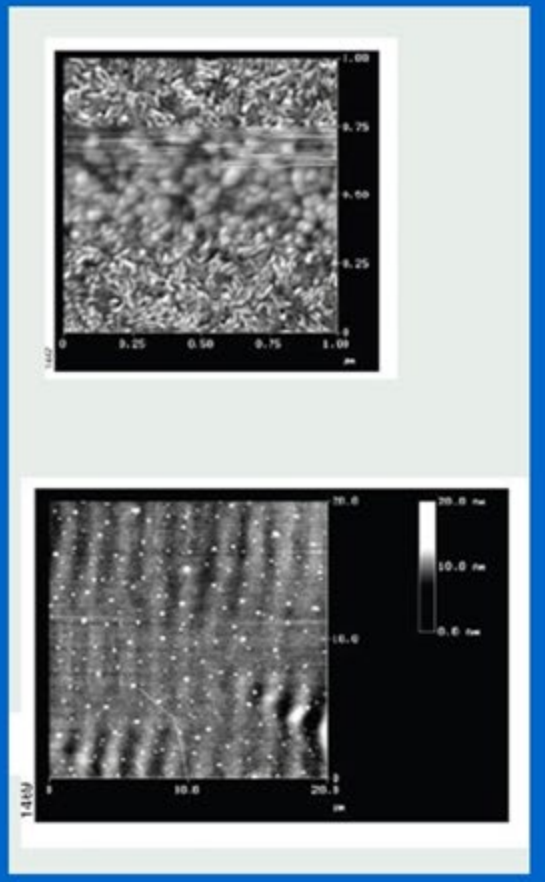
AFM artefacts



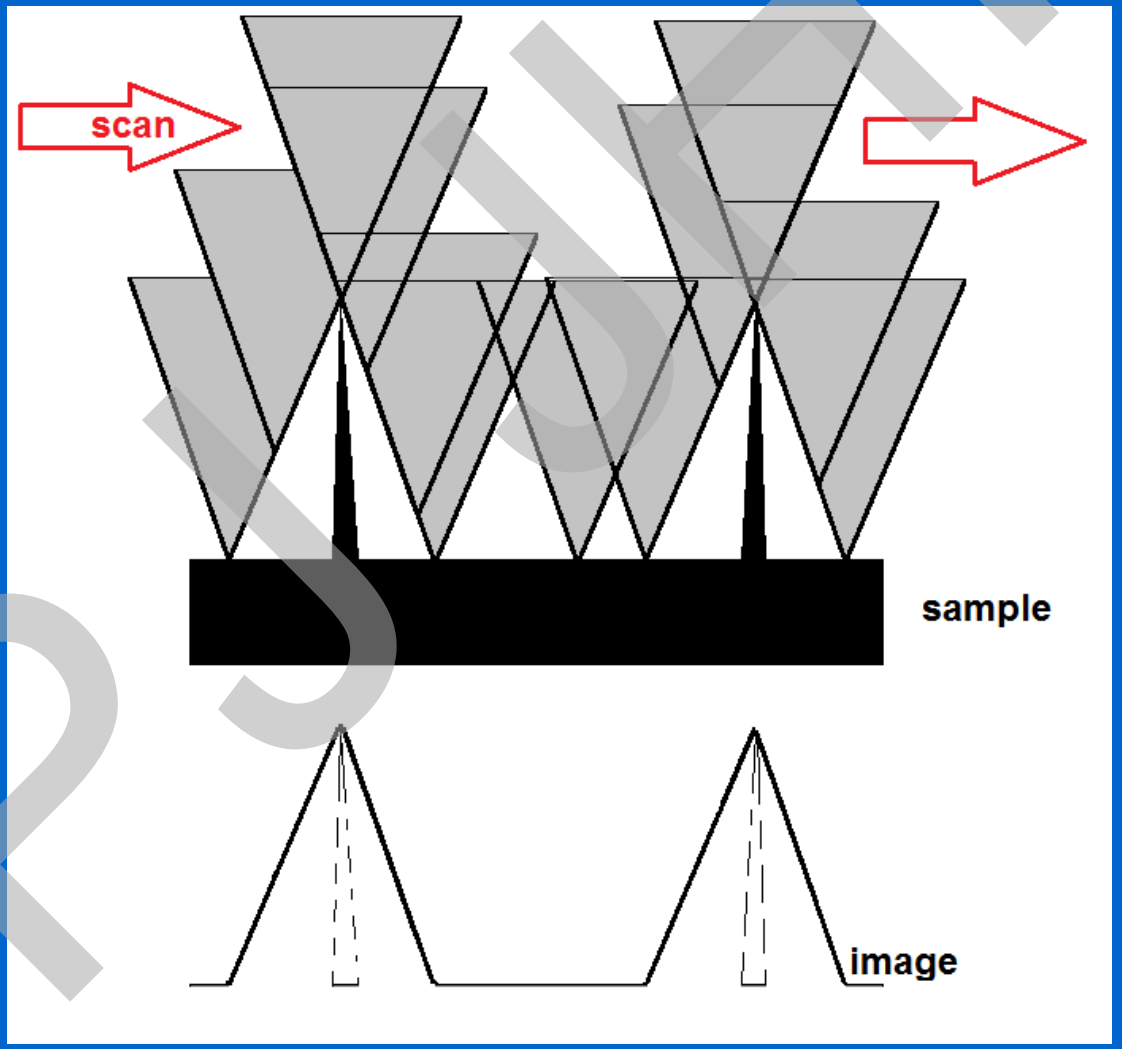


AFM artefacts

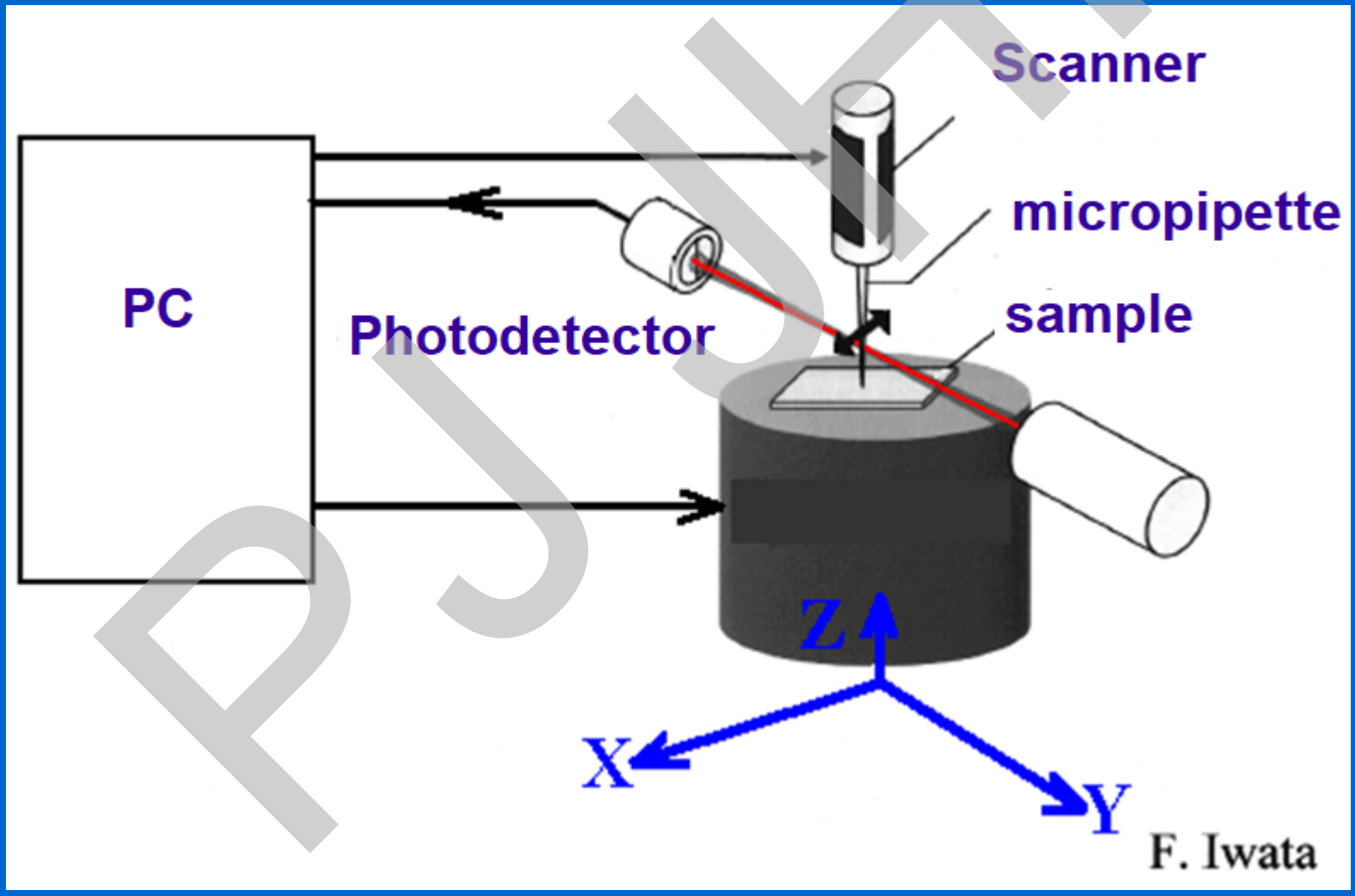




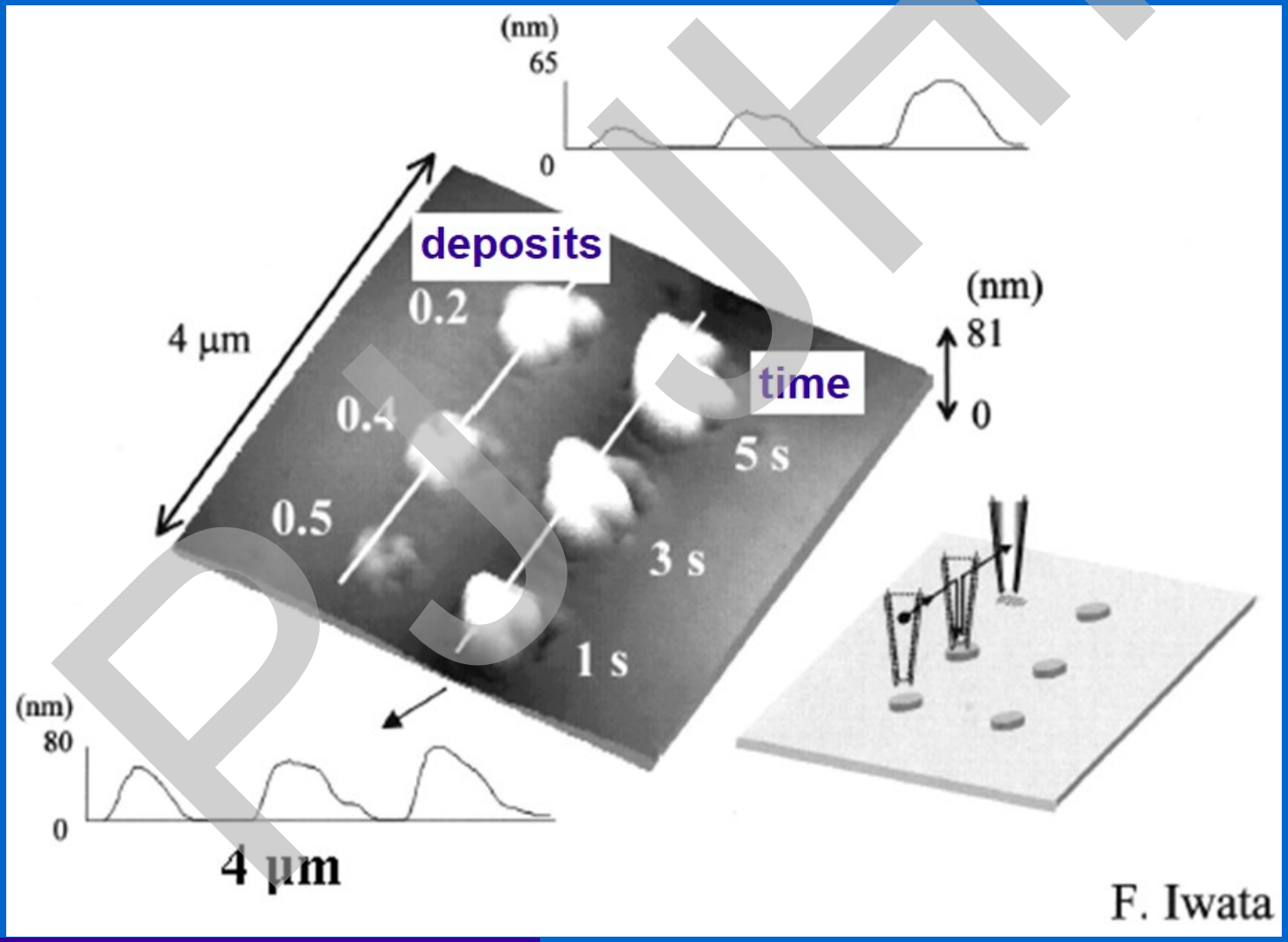
AFM artefacts: Self-image of AFM tip



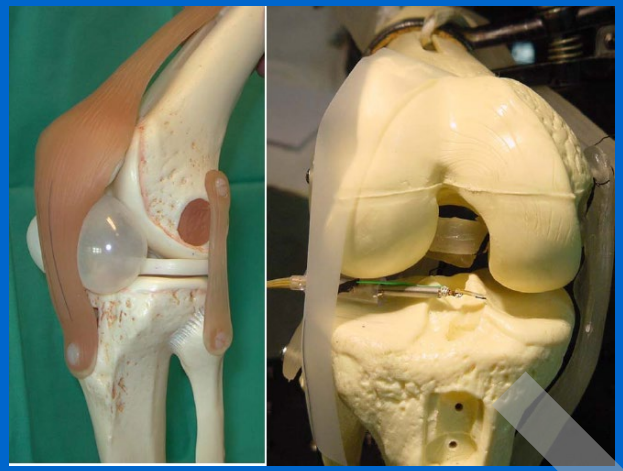
Special: Dual function of micropipette: AFM scanning tip and micro-dispenser

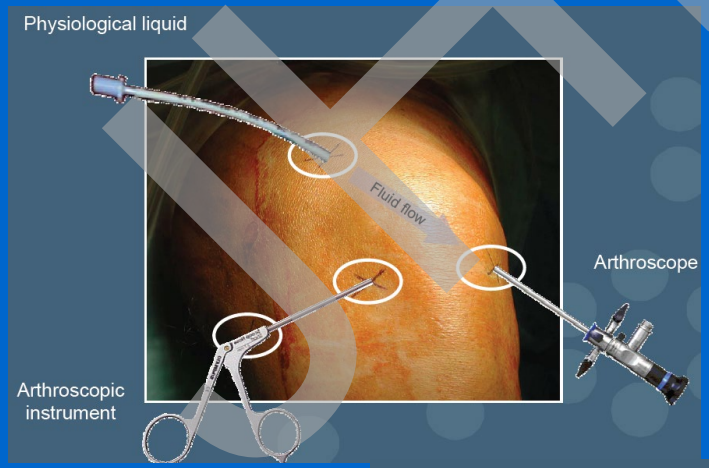


Nano-lithographic AFM with scanning micropipette

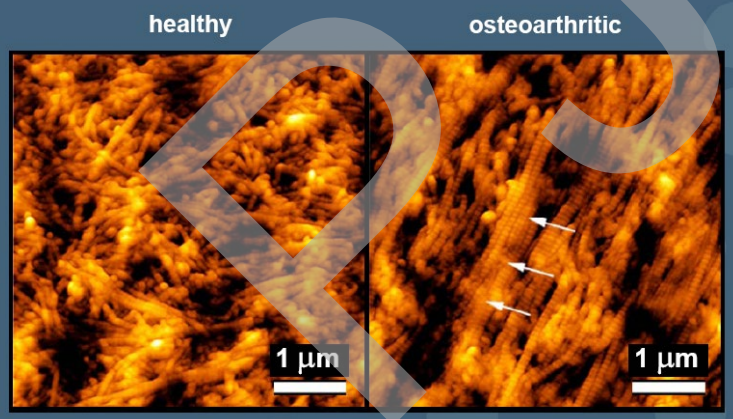


Special: AFM *in vivo* - Scanning Force Endoscope

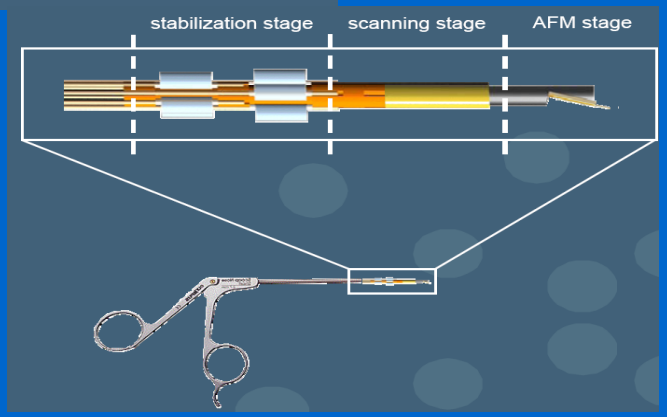




Diagnosing cartilage diseases at an early stage



M. Stolz *et al.*, Biophys. J. 2004; 86 3269-3283



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