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Mikroskopie rastrovací sondou I – Základní techniky

Pavel Janda

Laboratoř mikroskopie rastrovací sondou

Odd. elektrochemických materiálů

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Rozdělení mikroskopických metod podle rozlišení

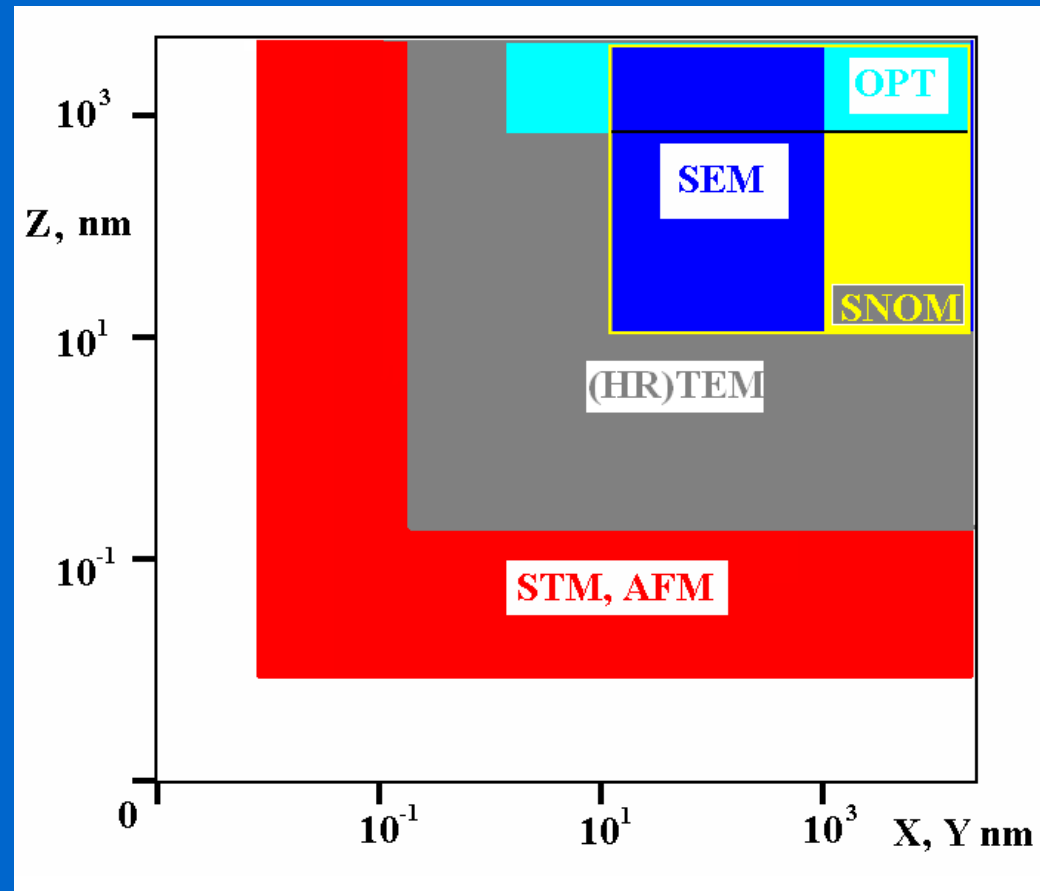
OPT: optická mikroskopie

SNOM: mikroskopie blízkého pole

SEM: elektron.rastr.mikroskopie

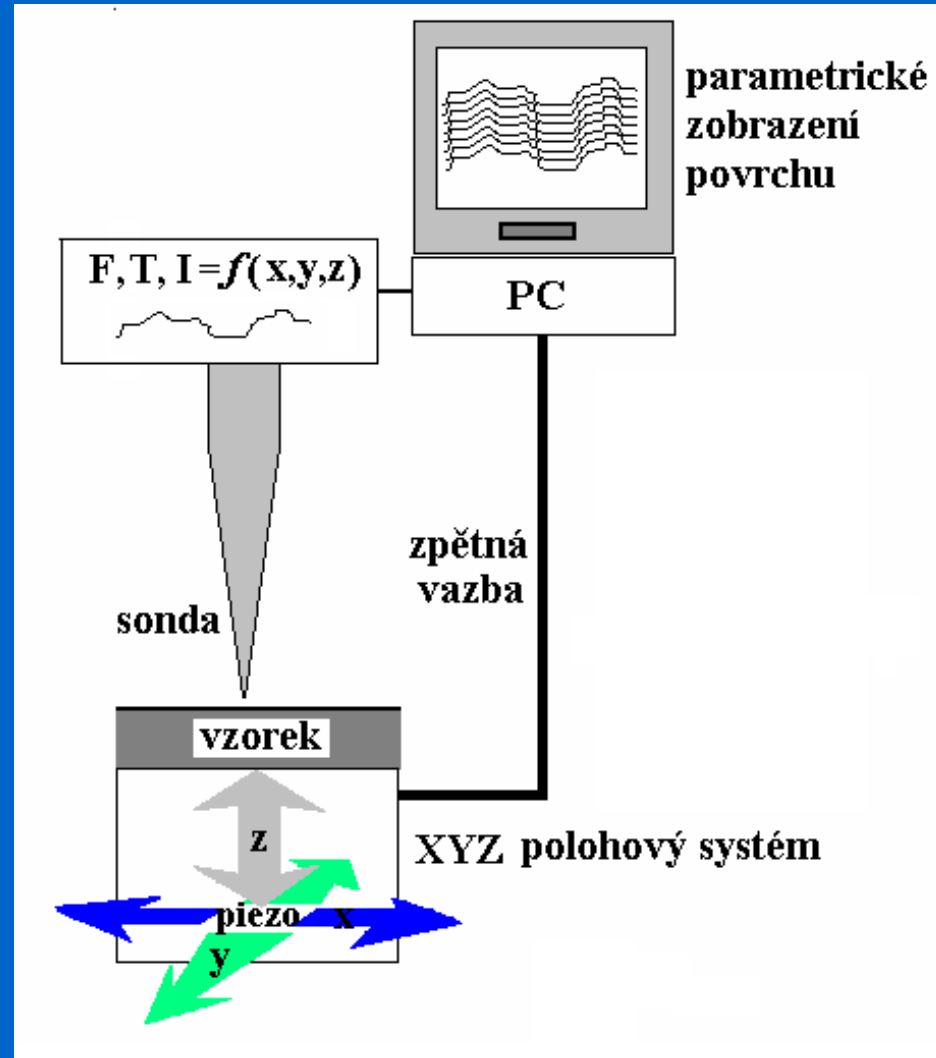
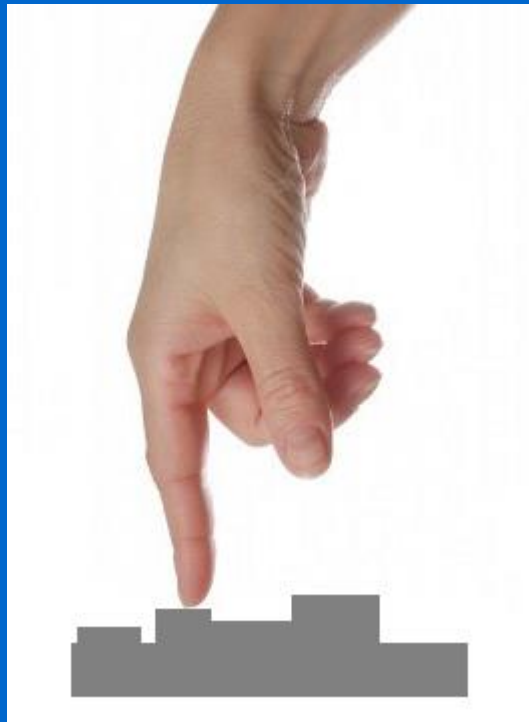
HRTEM: transmisní
el.mikroskopie

STM,AFM:
Tunelová mikroskopie,
mikroskopie atomárních sil



Mikroskopie rastrovací sondou

Scanning Probe Microscopy



Rozdělení SPM podle druhu přenášené informace

Přenos náboje

Elektrony - tunelová mikroskopie **STM/ECSTM**

Ionty - elektrochemická mikroskopie **(S)ECM**

Silové interakce - mikroskopie atomárních sil AFM/ECAFM

Přenos elektromagnetického záření

-IČ - Termální mikroskopie **ThM**

-UV/Vis/IČ - optická mikroskopie/spektr. blízkého pole **SNOM**

- Hrotem zesílená optická mikroskopie/spektr. **TERS/TEFS**

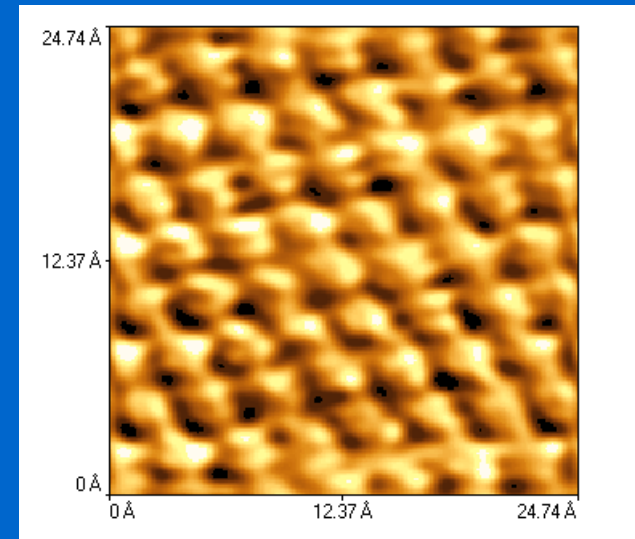
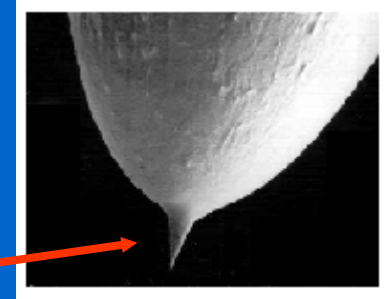
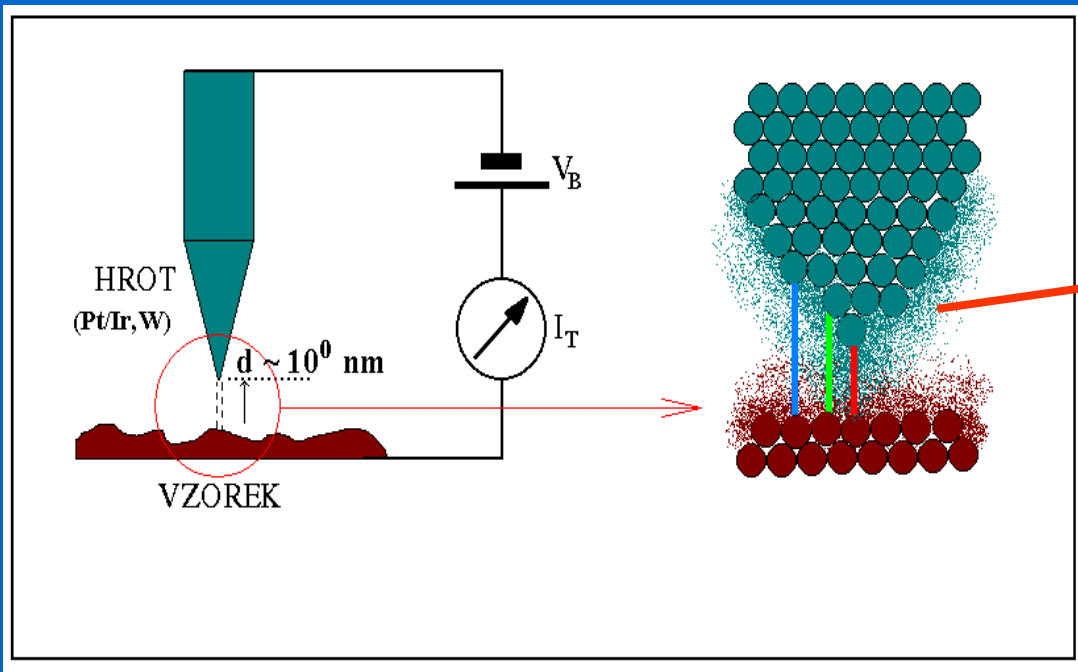
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Tunelová mikroskopie a spektroskopie

Scanning Tunneling Microscopy,
Scanning Tunneling Spectroscopy

Tunelová mikroskopie

Binning, Rohrer, IBM, 1981, Nobelova cena 1986



Aproximace tunelového proudu

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

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

$I_T(V_B)$ daná e-strukturou hrotu a vzorku,
z...vzdálenost hrot-vzorek ($\sim 10^{-1}$ nm), V_B do $\pm 1-2$ V, $I_T \sim nA-pA$

Au(111)

Tunelová spektroskopie barierová (distanční)

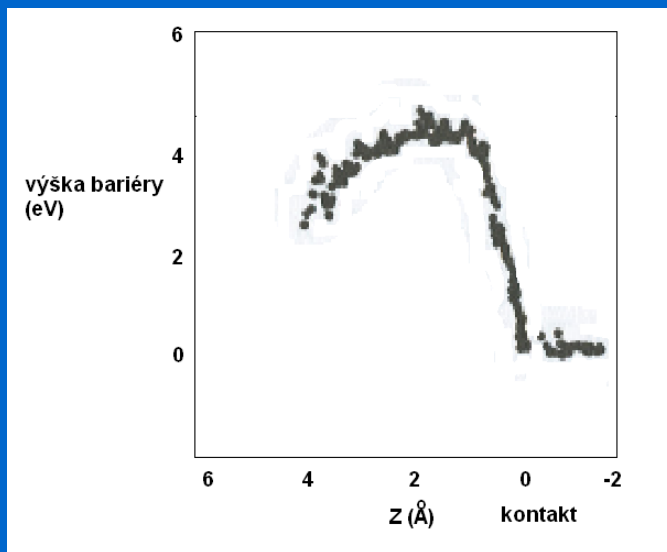
pro nízké $V_B = \text{konst.}$: $(dI_T/dZ)/I_T \sim (2\sqrt{2}m_e)/\hbar \sqrt{(\Phi_S + \Phi_T)}$

Φ_S, Φ_T lokální výstupní práce, I_T tunelový proud,
 Z vzdálenost hrotu od vzorku, m_e hmota e-

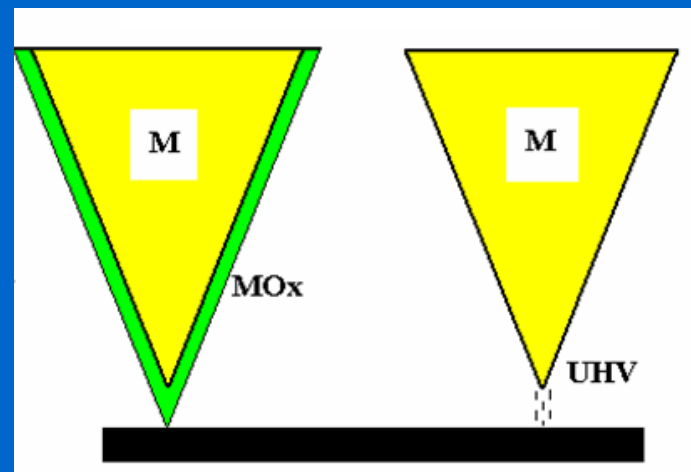
Provedení:

modulace VVVV Z-pieza a záznam $dI_T/dZ \Rightarrow \Phi_{S,T}$

Pro $\Phi_T \approx \text{konst.}$, laterální variace v měřené výšce bariéry \sim lokální Φ_S



Si-povrch, W-hrot/UHV



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

Tunelová spektroskopie napěťová

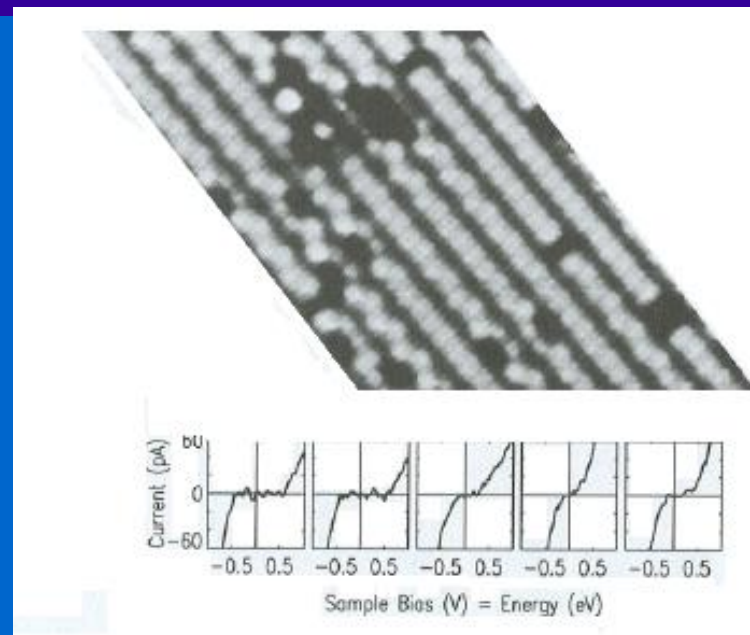
$V_B < \text{výst. práce hrotu a vzorku} (\sim 10 \text{ mV})$,
výraz $dI_T/dV_B \approx \text{lokální povrchová hustota stavů}$ (skutečných nebo pocházejících z uspořádání vnitřní pásové struktury vzorku)

Provedení:

Modulace VVVVV V_B , záznam I_T-V_B křivky,

výstup: obvykle $d(\log I_T)/d(\log V_B)$ vs V_B

Poskytuje: mapu povrchových stavů (v UHV) používá se k zobrazení zaplnění stavů, adatomů a volných vazeb (*dangling bonds*) ...



I_T-V_B křivky na monokryst Si (UHV) při průchodu hrotu nad defektem
[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]

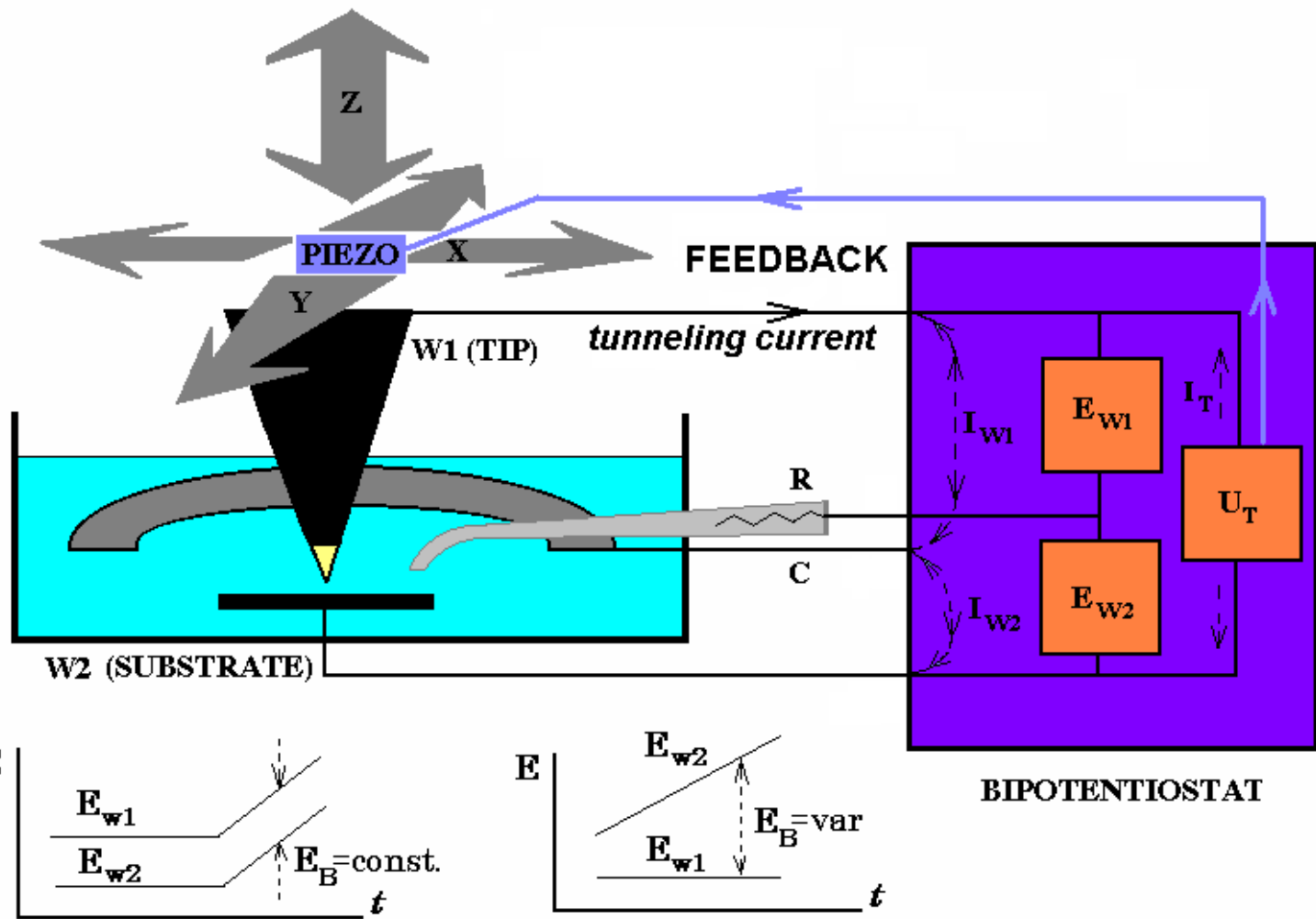
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Elektrochemická tunelová mikroskopie

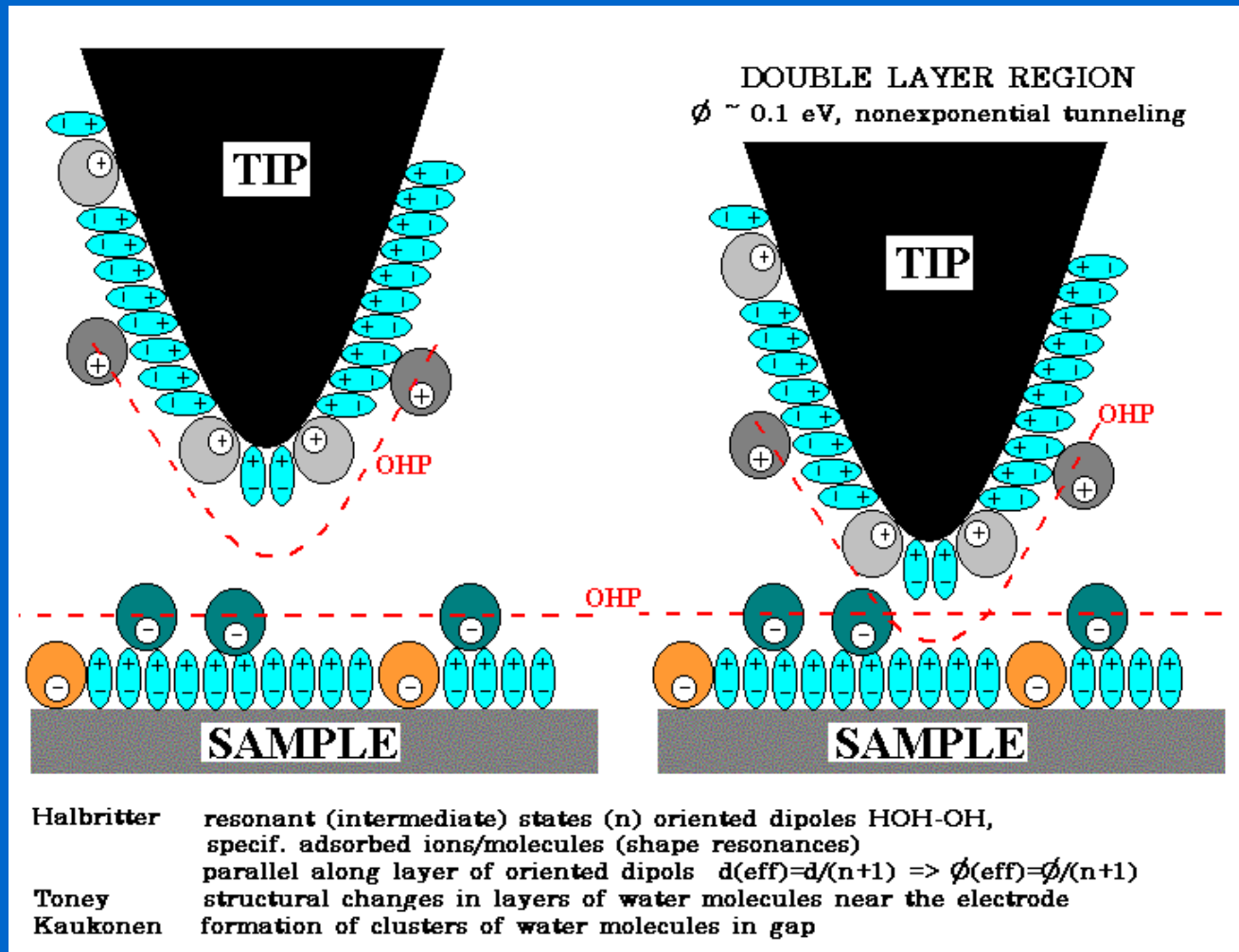
EC STM

Electrochemical Scanning Tunneling Microscopy

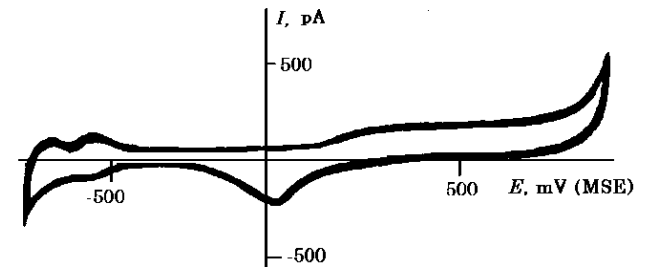
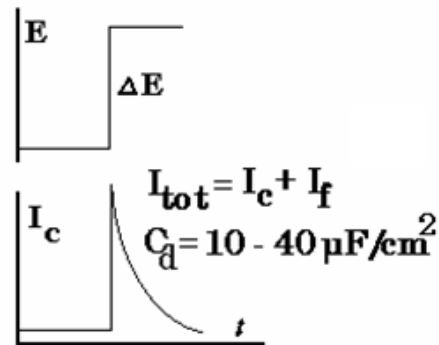
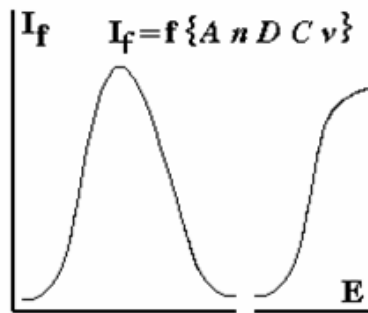
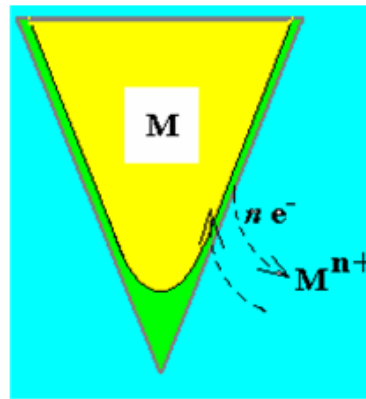
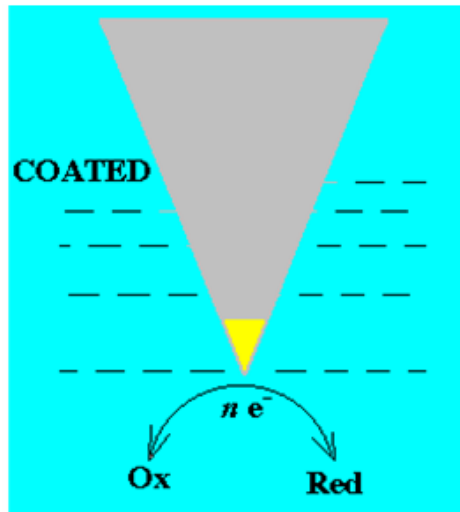
EC STM: Detekce tunelových proudů při EC experimentu



Vodivý hrot SPM v elektrolytu

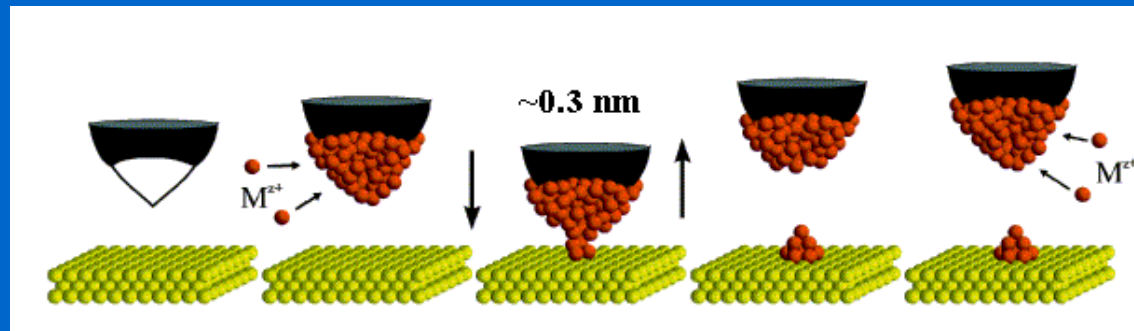
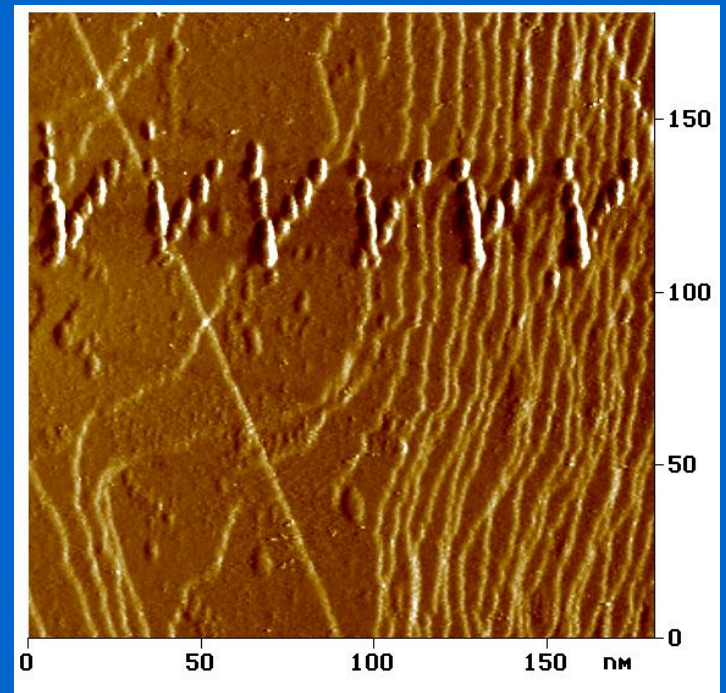
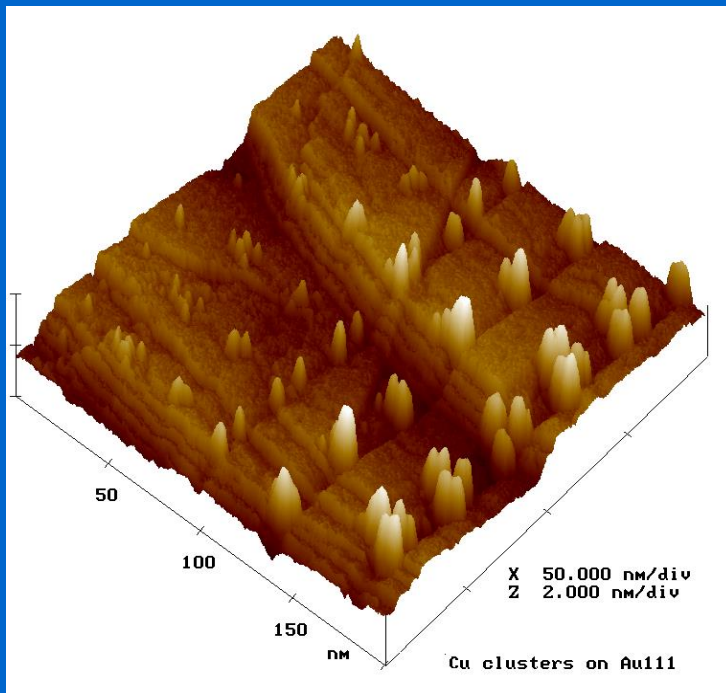


Hrot sondy EC STM

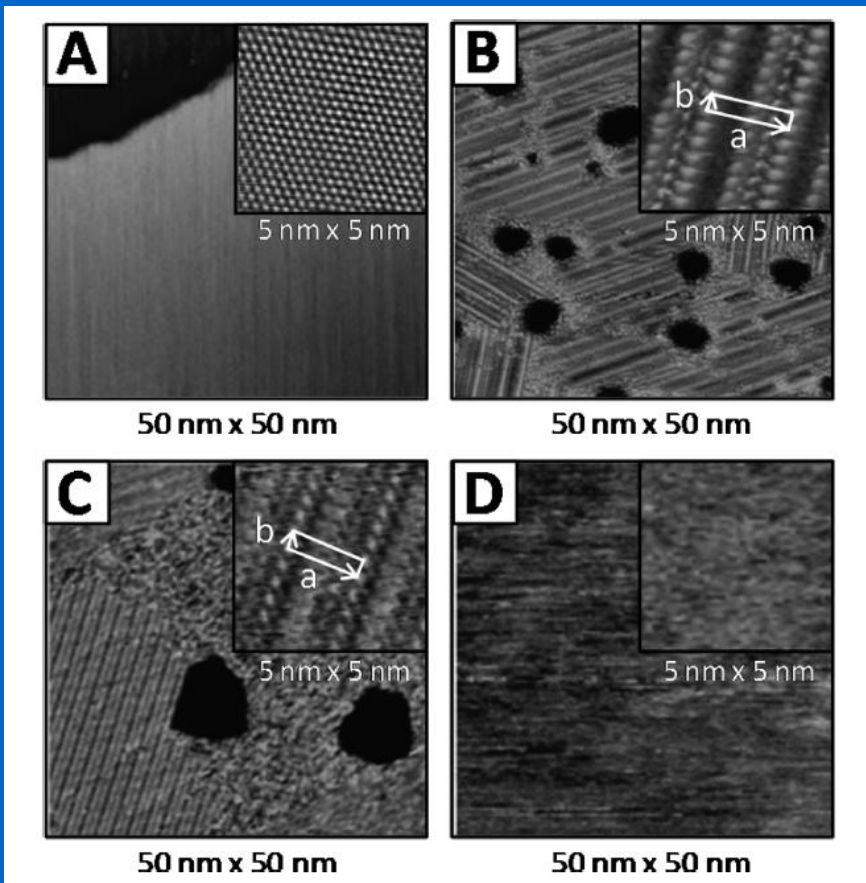


Voltammetry of Pt-Ir STM tip (polymer coated)
in 0.1 M H_2SO_4 (deoxygenated)
 $v = 200$ mV/sec

„Nanoprint“: nanočástice $d \geq 8$ nm, $z < 1$ nm



EC STM: Self-Assembled Monolayers



Aq. 0.1M Na_2HPO_4 , pH 6

SAM molecular adlayer: mercaptopropionic acid (MPA) on Au111, $U_B = 300 \text{ mV} / I_T = 100$

pA

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

-
-
-

Mikroskopie atomárních sil

Atomic Force Microscopy

AFM

Silové interakce

Dlouhého dosahu magnetické, kulombické
nekontaktní režim

Středního dosahu van der Waals (dipol-dipol, indukce dipol-nepolární m.)
semikontaktní režim

Krátkého dosahu vazebné interakce (atraktivní), repulzivní (deformační)
Kontaktní a semikontaktní režim

Vodivostní AFM

+ měření vodivosti, tunelování

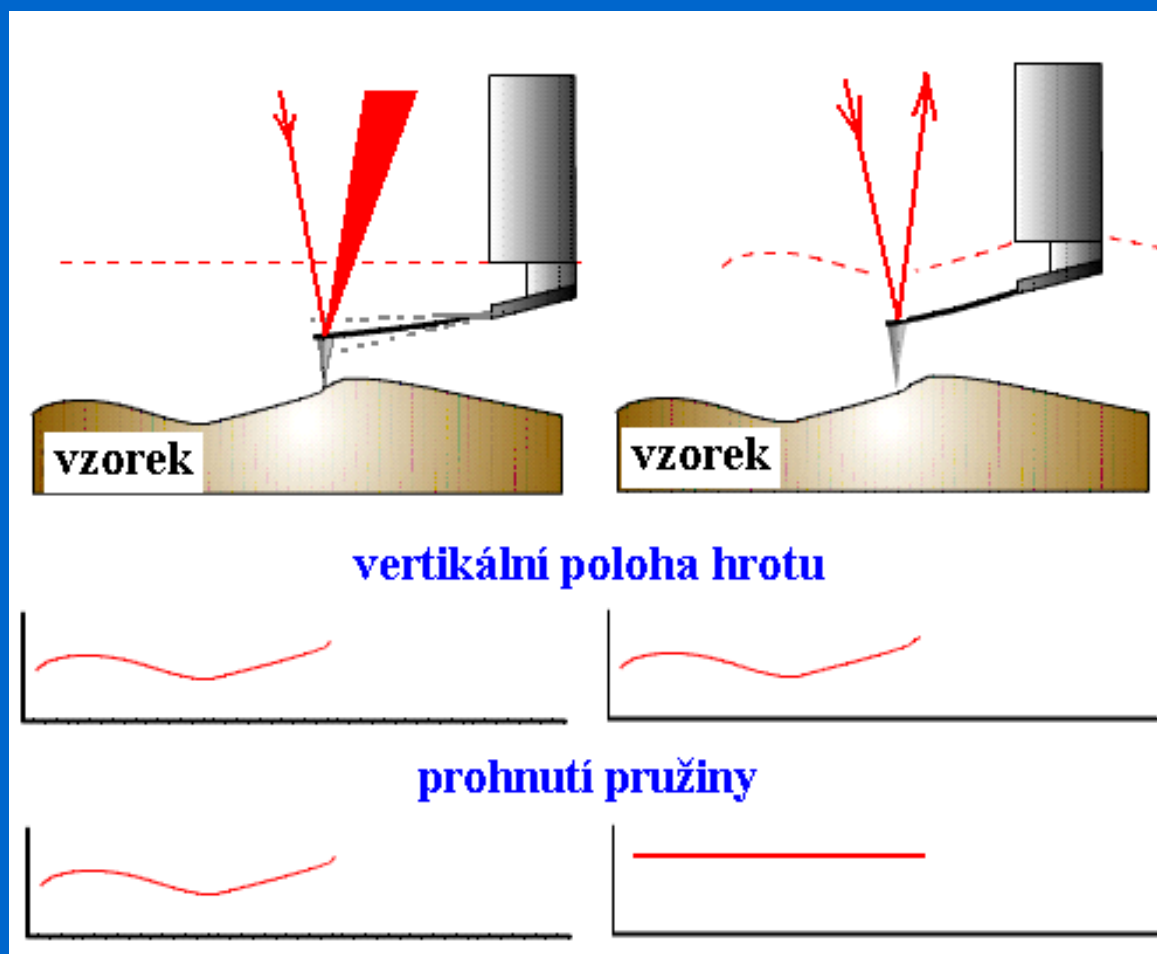
EC AFM

+ reakce přenosu náboje/záznam Farad.proudů,

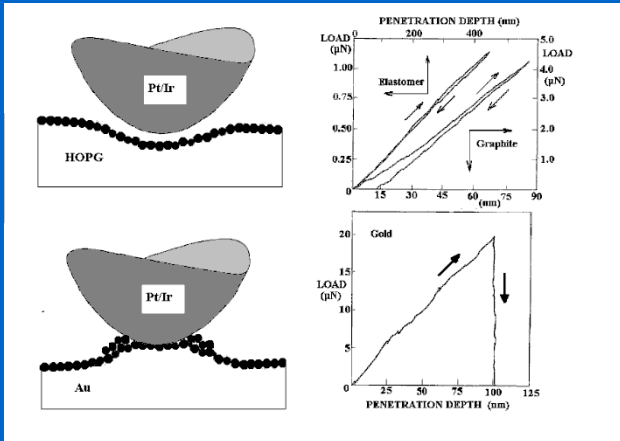
+ tip-assisted „elektro-lithografické“ techniky

+ detekce SECM

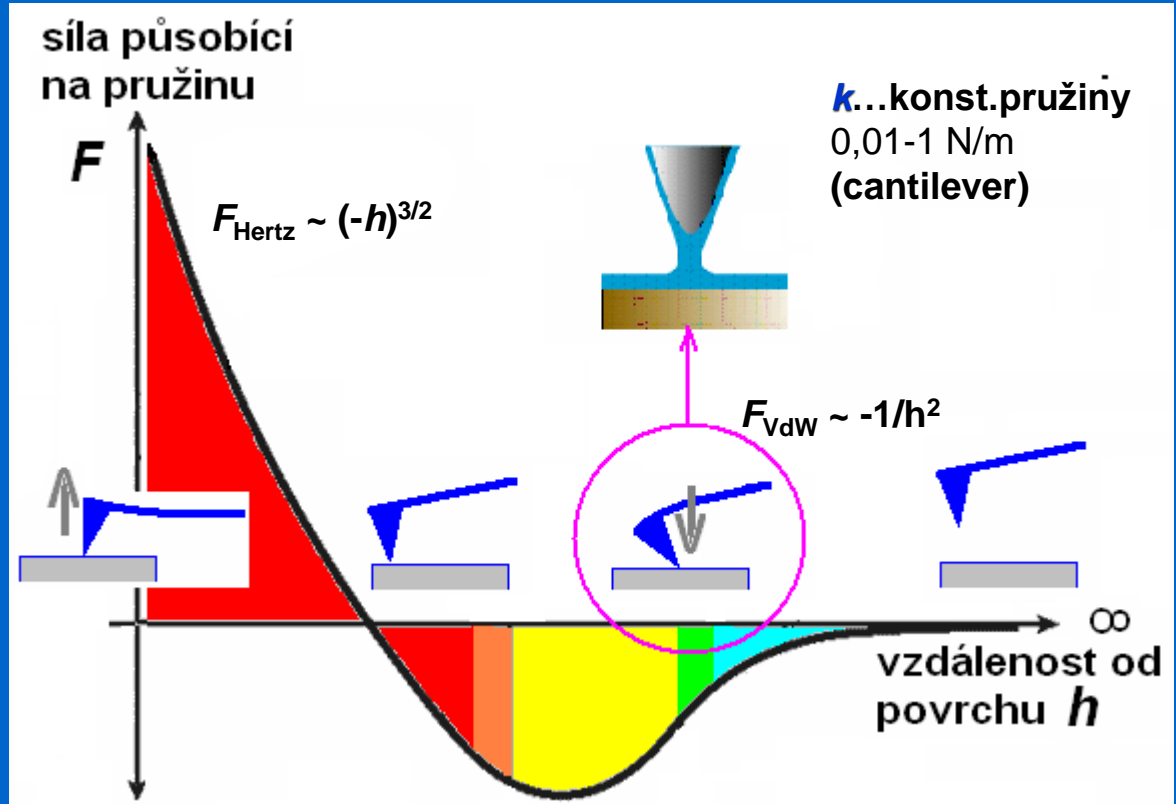
AFM: Funkce



AFM – silová křivka



$F = -kz$ Hook

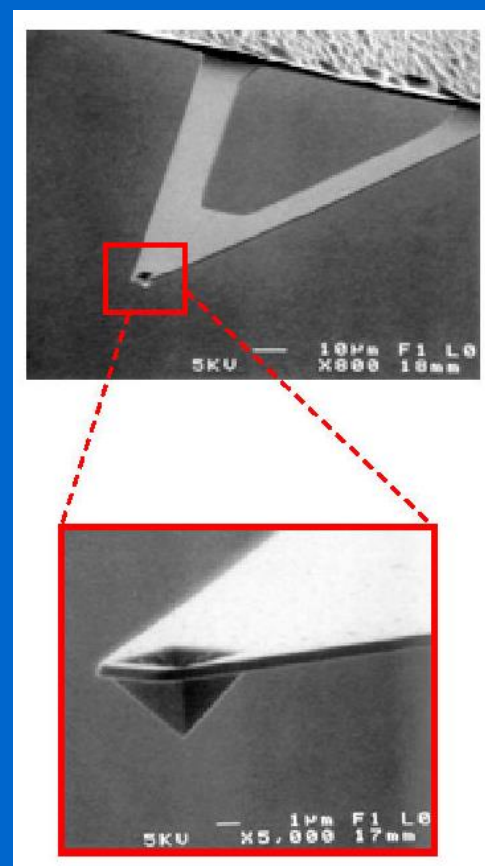
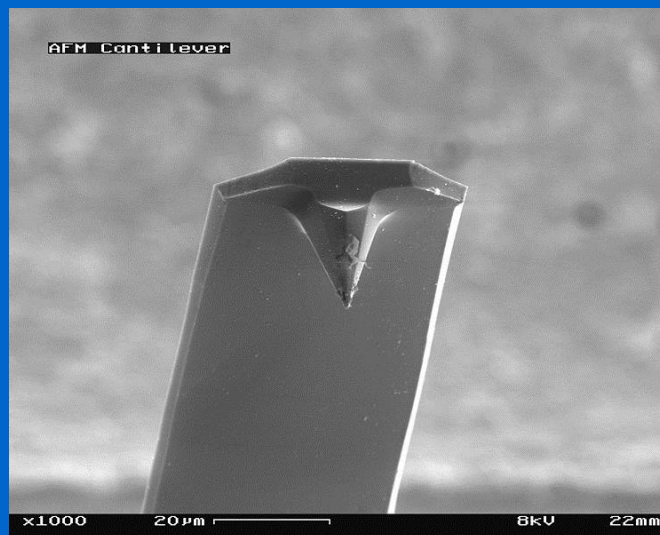
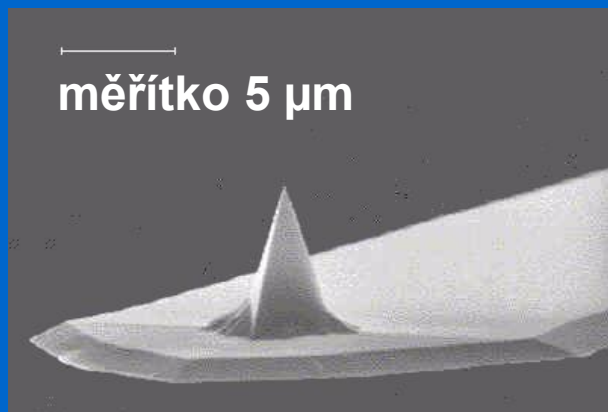


Režim:

kontaktní **semikontaktní** **nekontaktní**

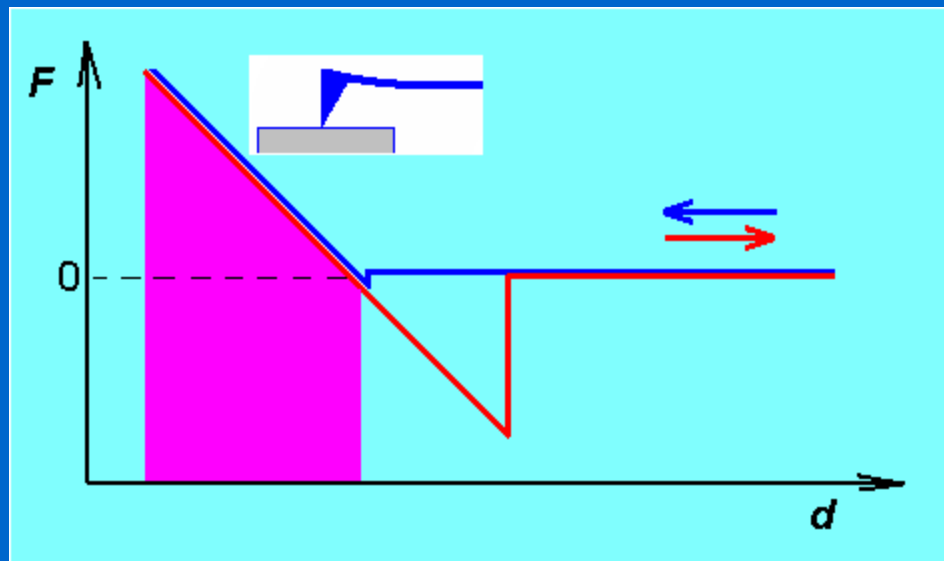
($F_{\text{vw}} 10^{-12}$ N)

AFM: hrot a pružina (*cantilever*)

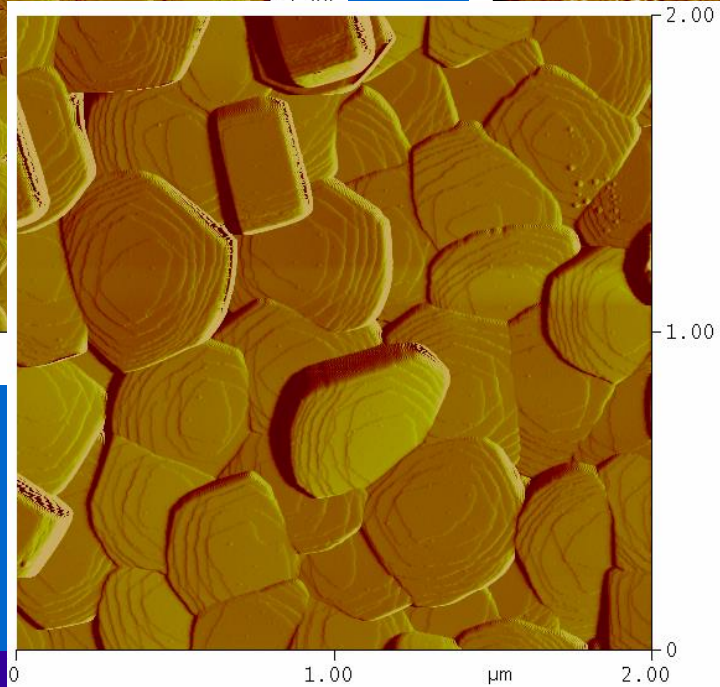
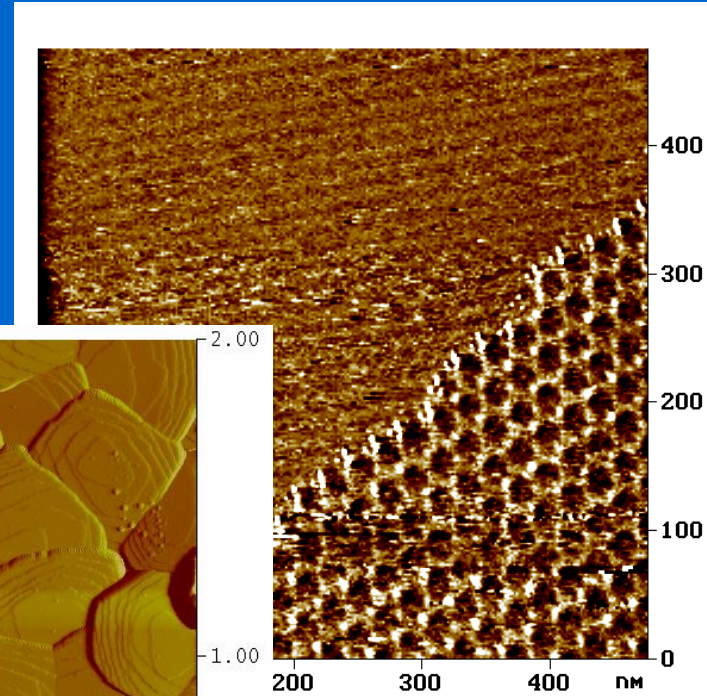
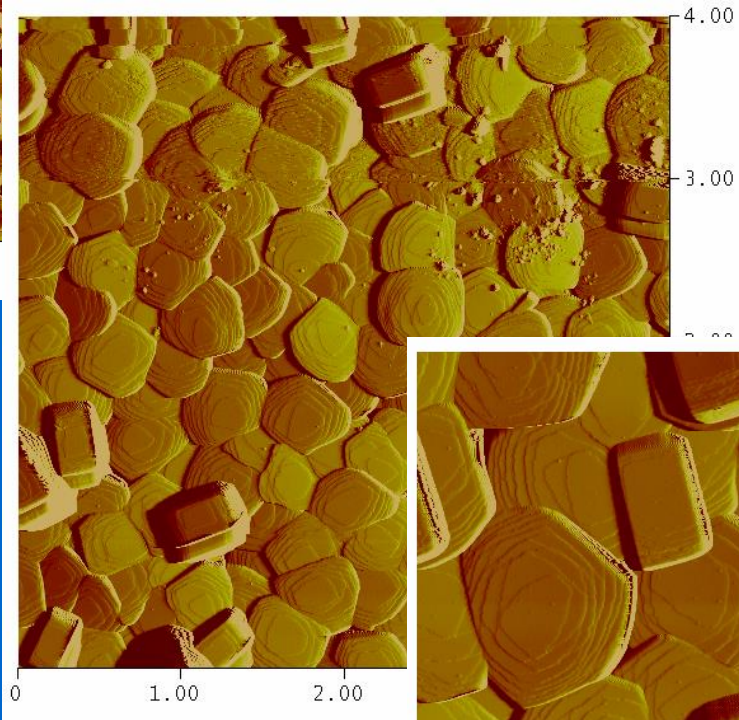
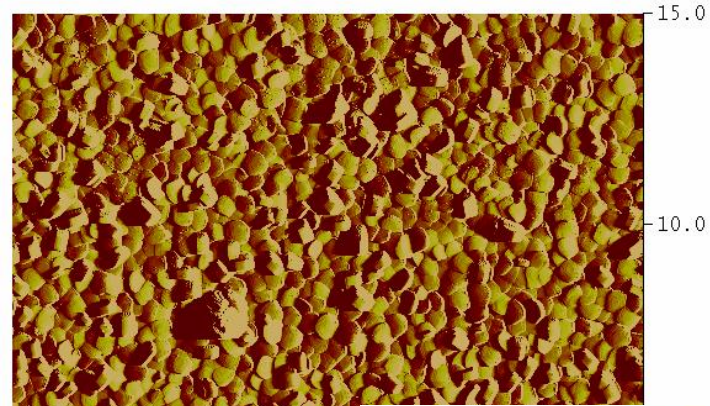


materiál hrotu a pružiny: Si, Si₃N₄

AFM v oblasti repulsivních sil: Kontaktní režim

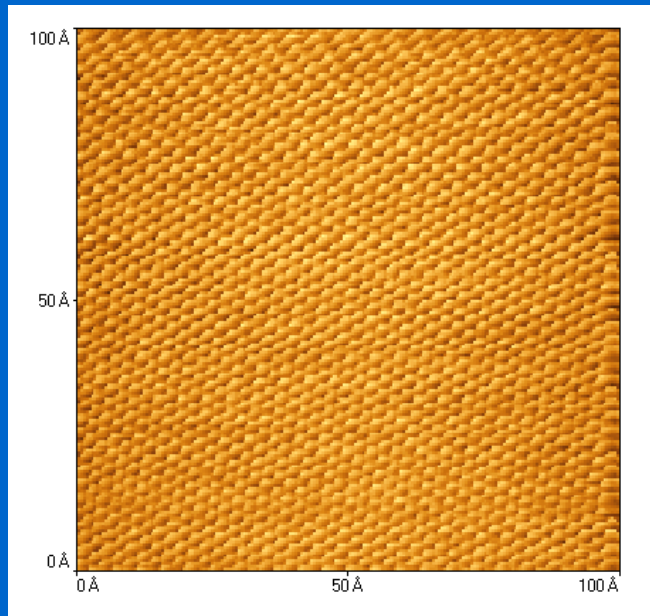


AFM zobrazení: Kontaktní režim

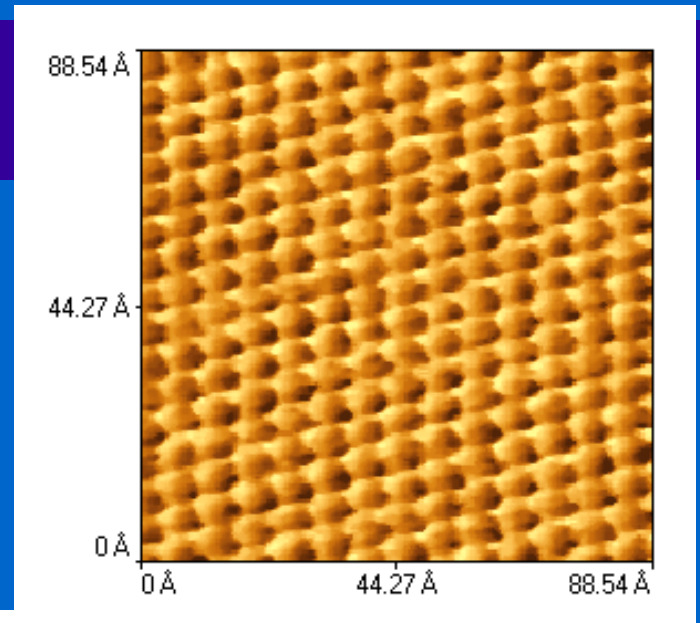


Krystaly zeolitu

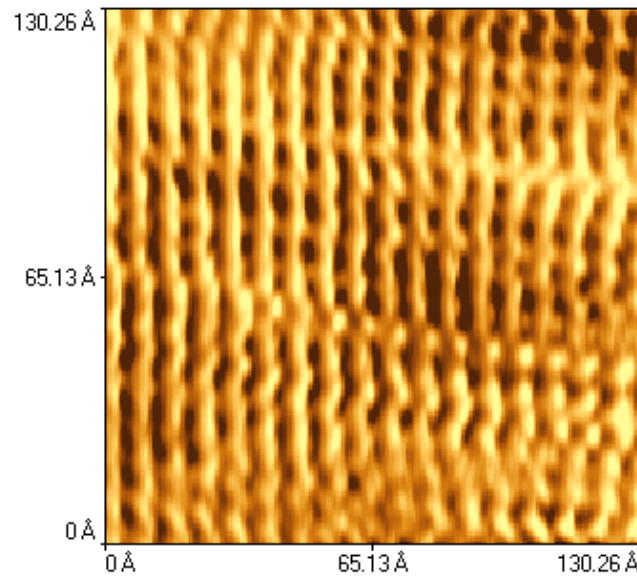
AFM zobrazení: kontaktní režim



grafit



slída

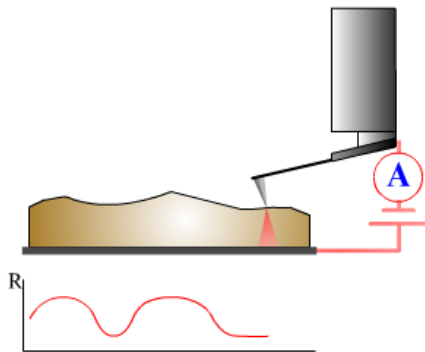


Orientované
molekuly Teflonu

Vodivostní AFM

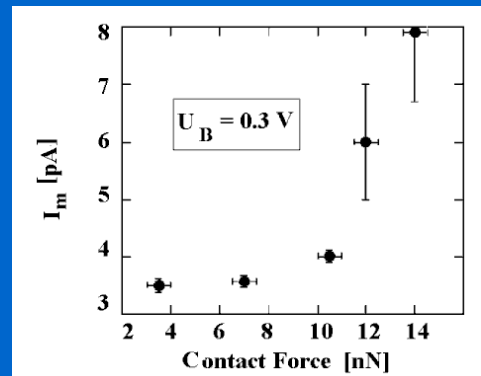
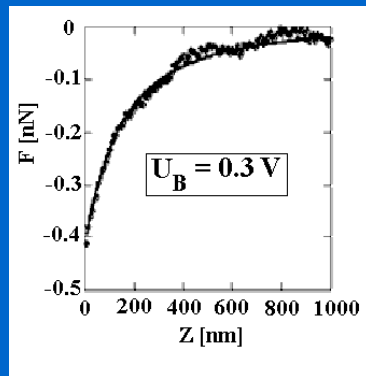
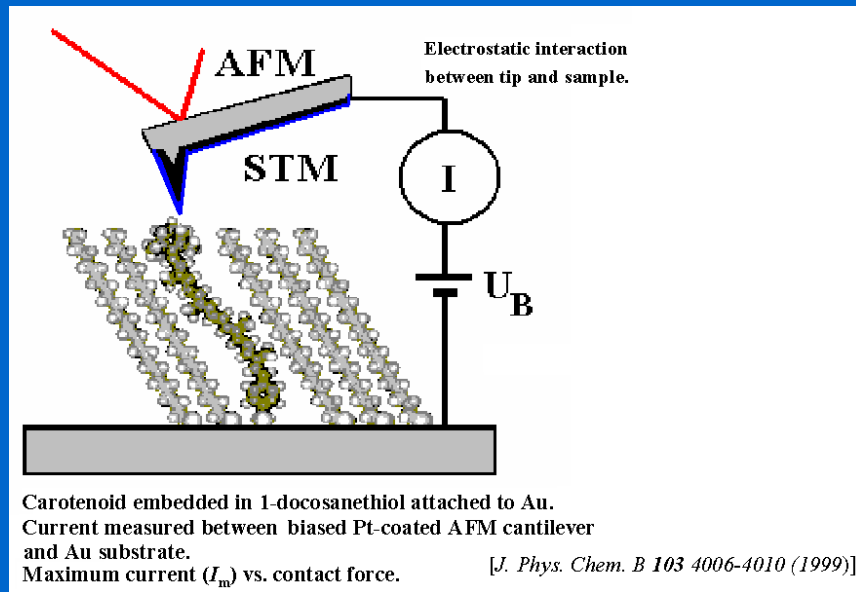
Spreading Resistance imaging

Constant Force mode

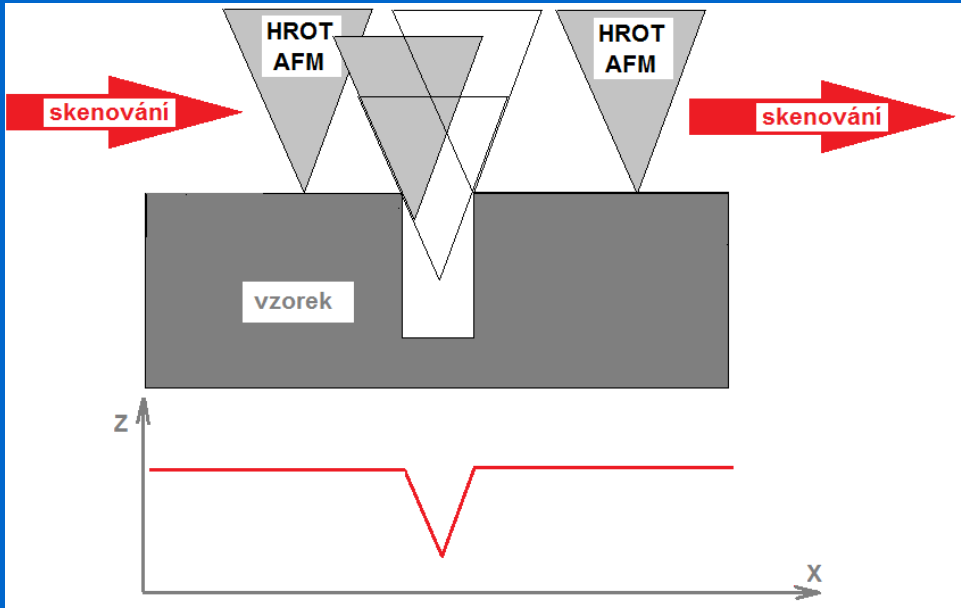
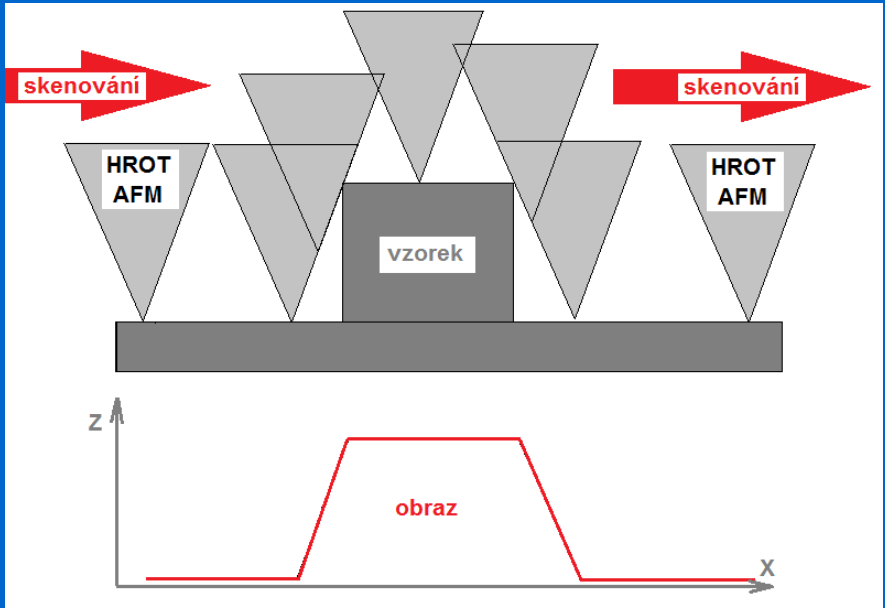


conductive tip
(B-doped diamond, n-doped Si)

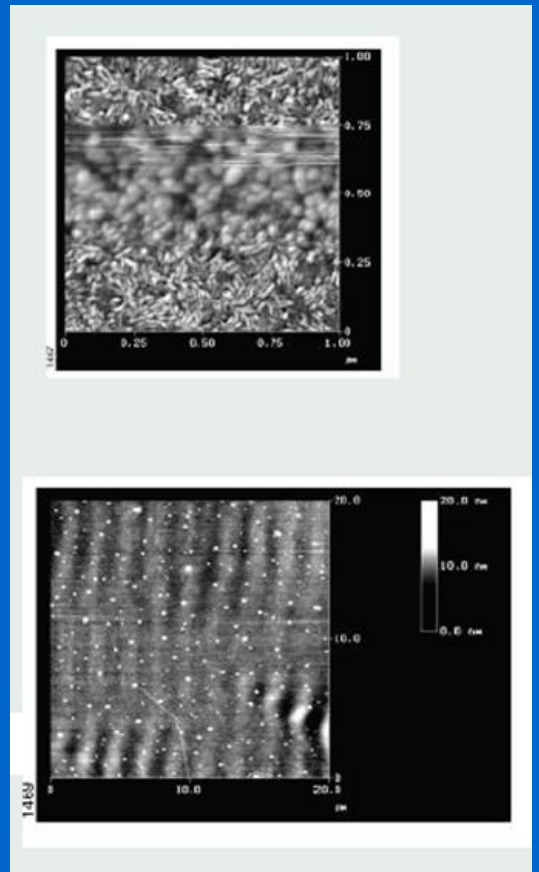
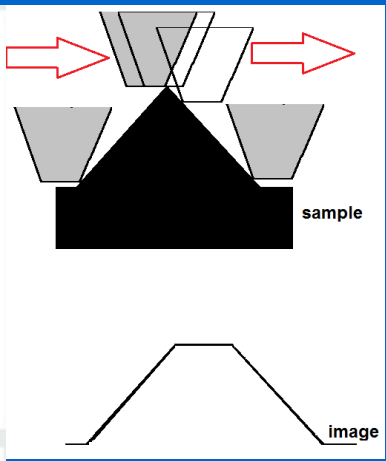
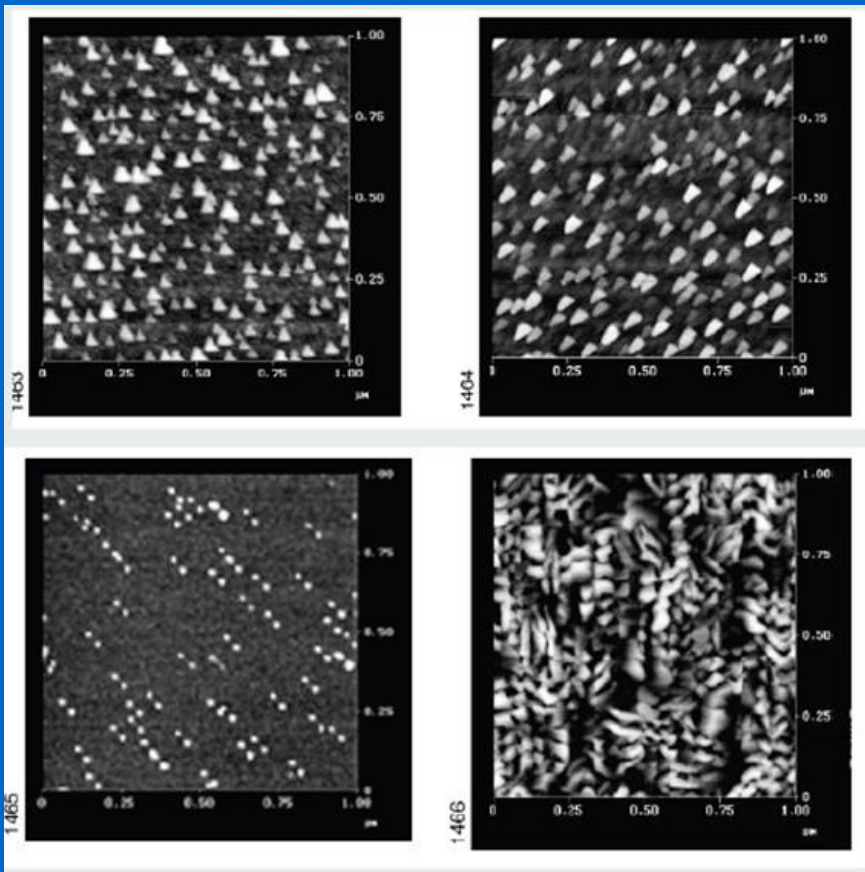
Copyright © NT-MDT, 2002



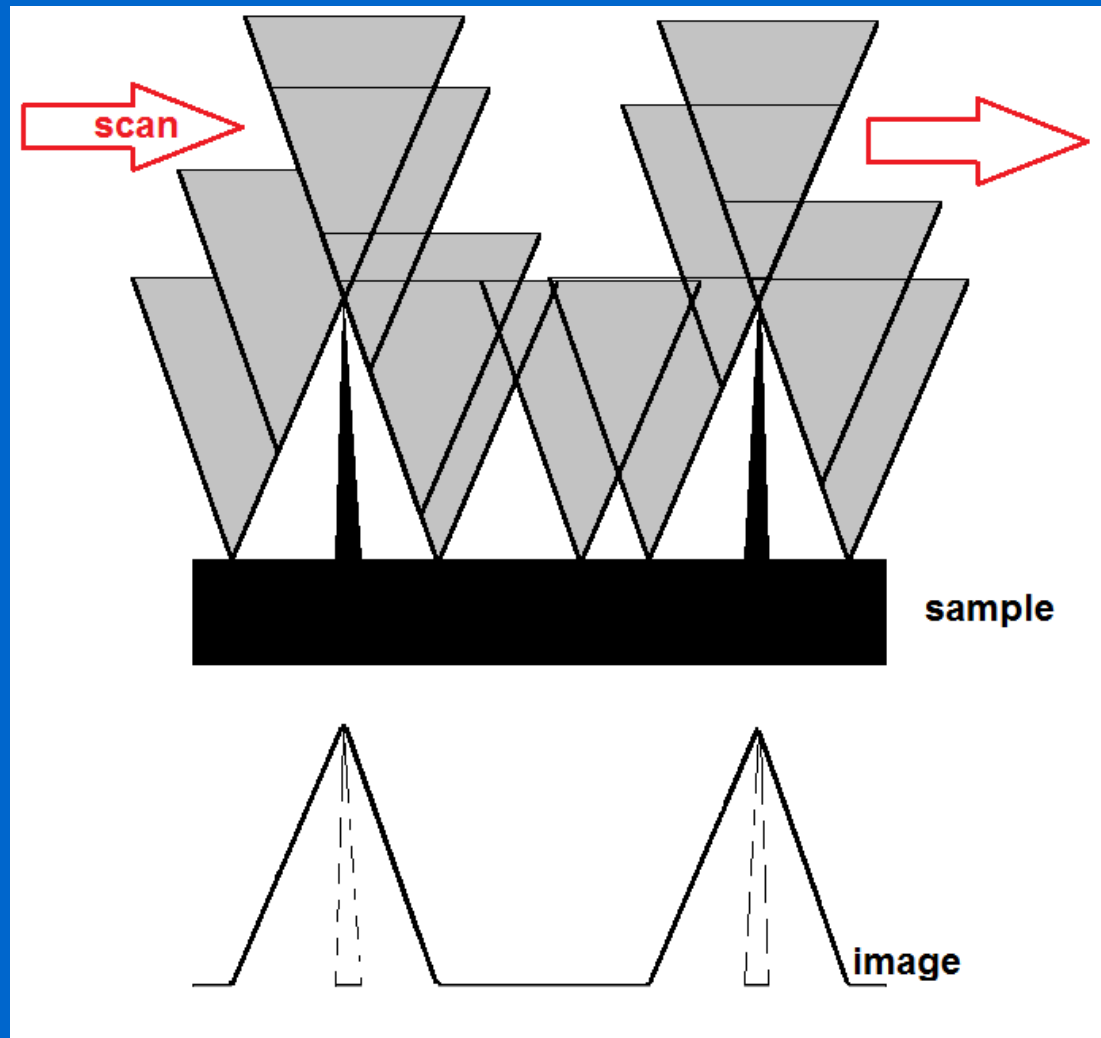
AFM: artefakty



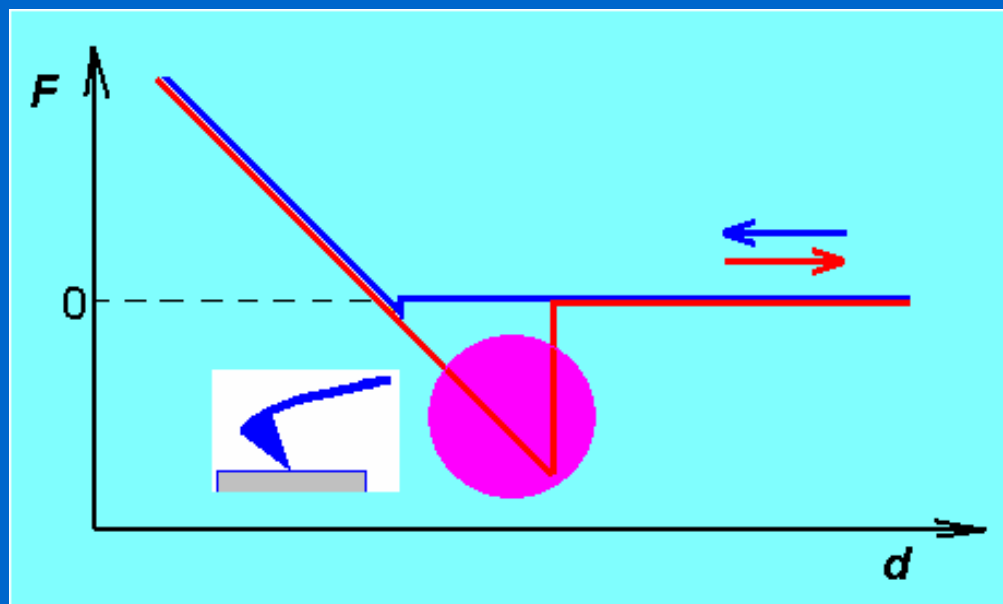
AFM: artefakty



zobrazení hrotu

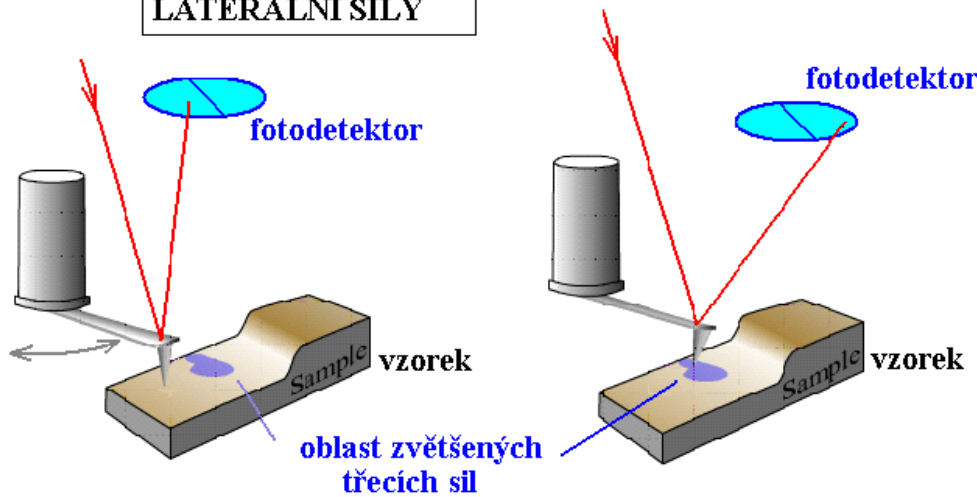


AFM: Přitažlivé síly- adheze, vazebné interakce

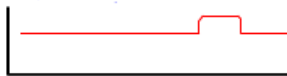


AFM adhesivních sil: laterální (LFM)

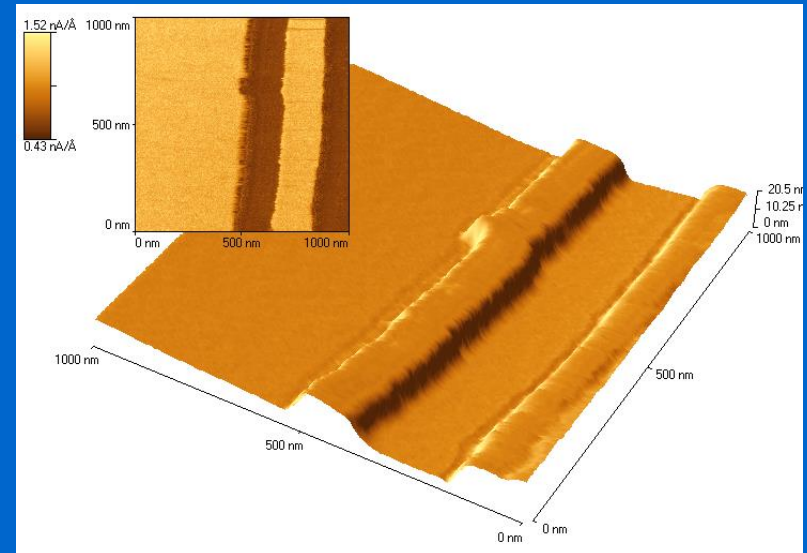
KONTAKTNÍ REŽIM
LATERÁLNÍ SÍLY



úhel překroučení
pružiny

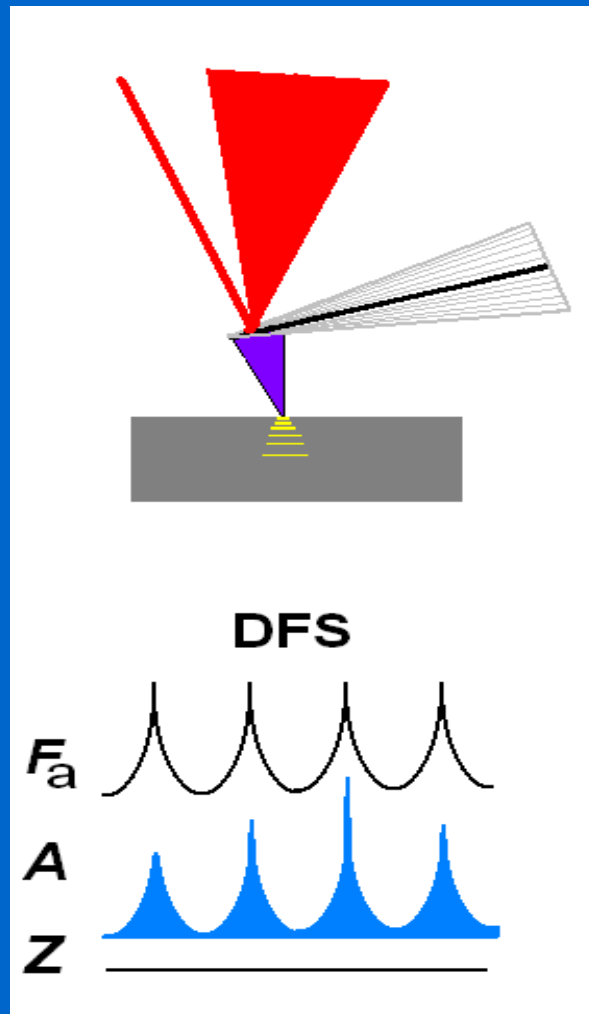


třecí síla



Teflon na skle: AFM
-topografie
-rozložení frikčních sil

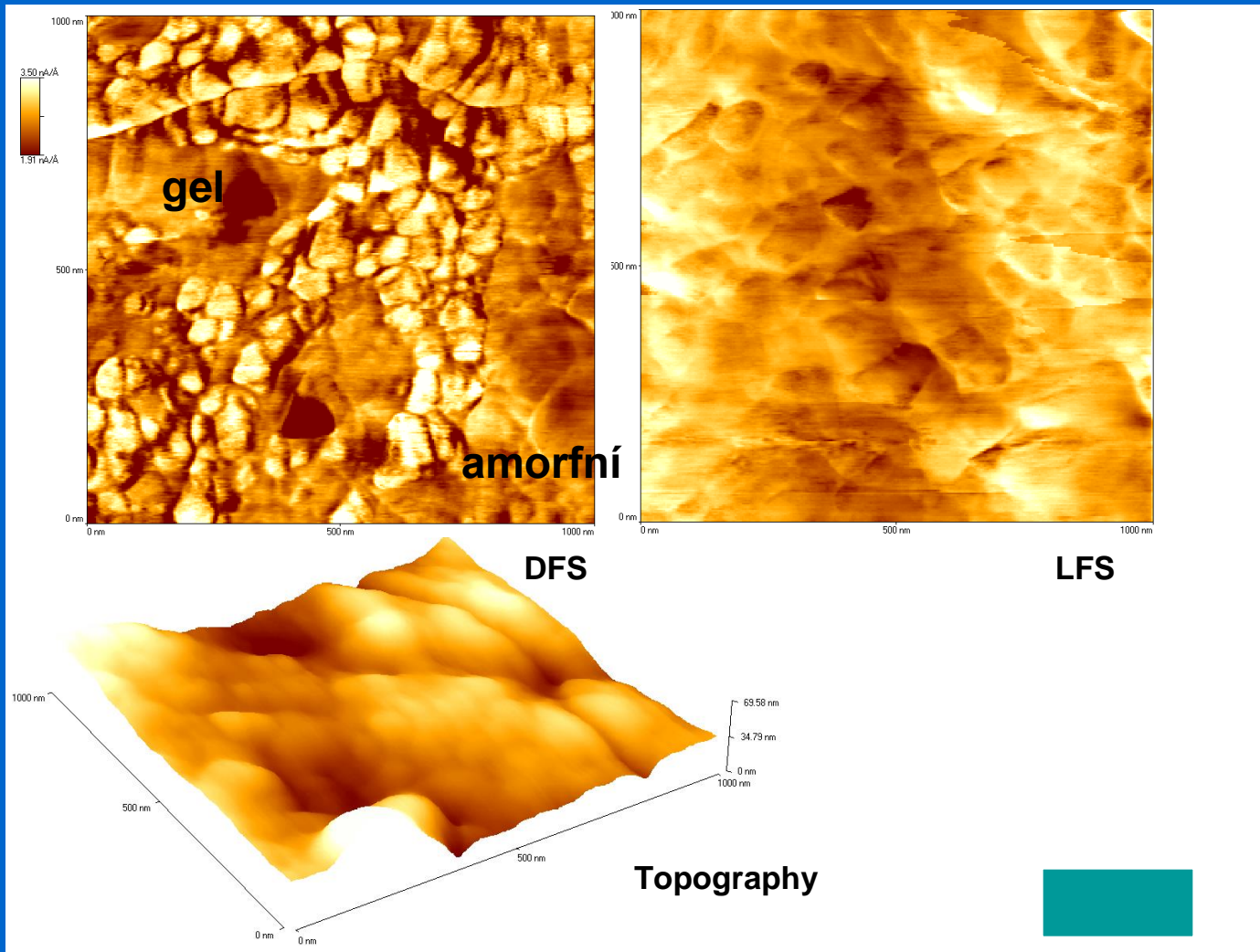
AFM – Dynamická silová spektroskopie (DFS)



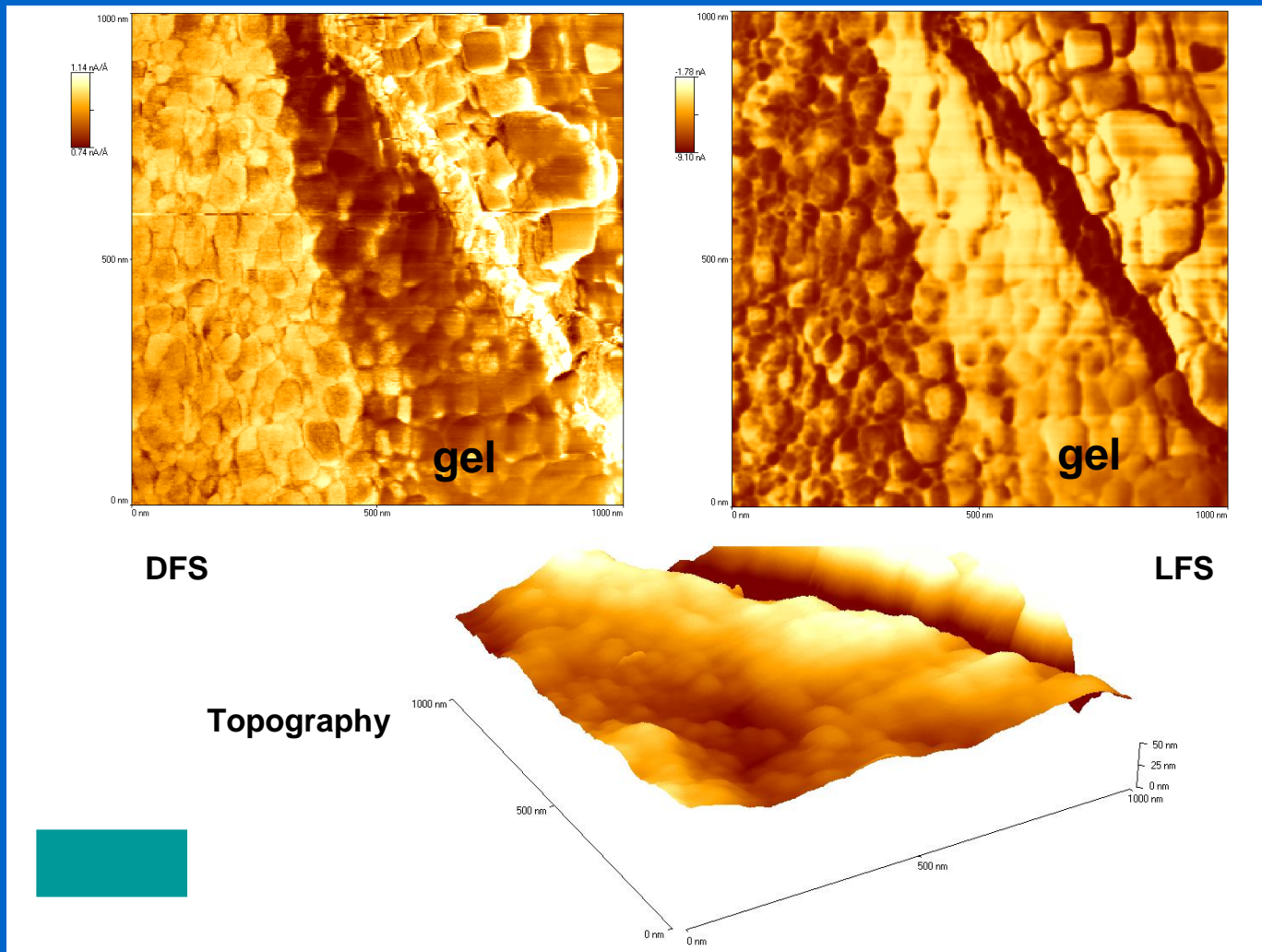
Disipace energie:
útlum, elasticita, plasticita
 Y_M

Hrot v kontaktu,
 f_{drive} , $A_{drive}/A_{response}$

AFM-DFS materiálová analýza povrchu Zr/ZrO₂



AFM materiálová analýza povrchu Zr/Nb/ZrO₂

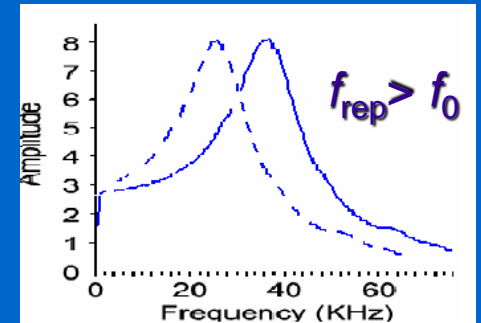
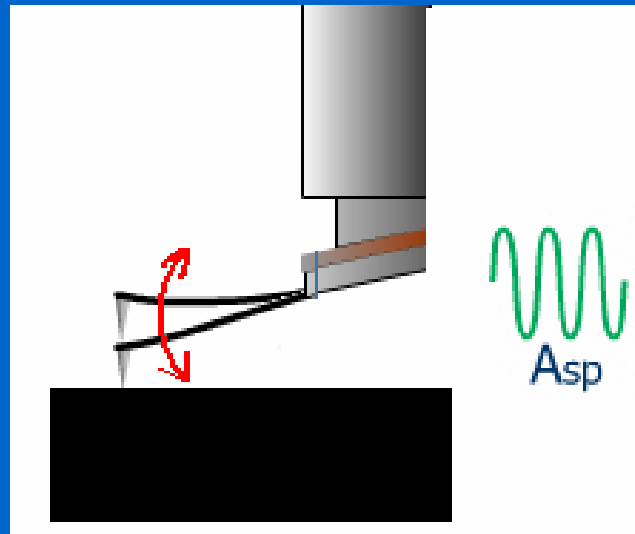


Semikontaktní režim (tapping)

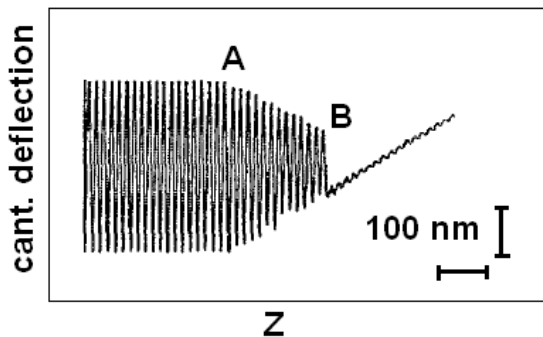
Akustic./mgt. buzení

mechanický oscilátor
kmitající v rezonanci
vstupní parametry:
 f_{rez} A_{sp} (~ 20 nm)

výstupní parametry
 A , Δf , $\Delta\theta$, d (deflexe)



"V" cantilever ($k = 0.58$ N/m)



$$m \frac{d^2 z}{dt^2} = -kz - \left(\frac{m\omega_0}{Q} \right) \frac{dz}{dt} + F_{ts} + F_d \cos \omega t \quad \text{piezo (drive)}$$

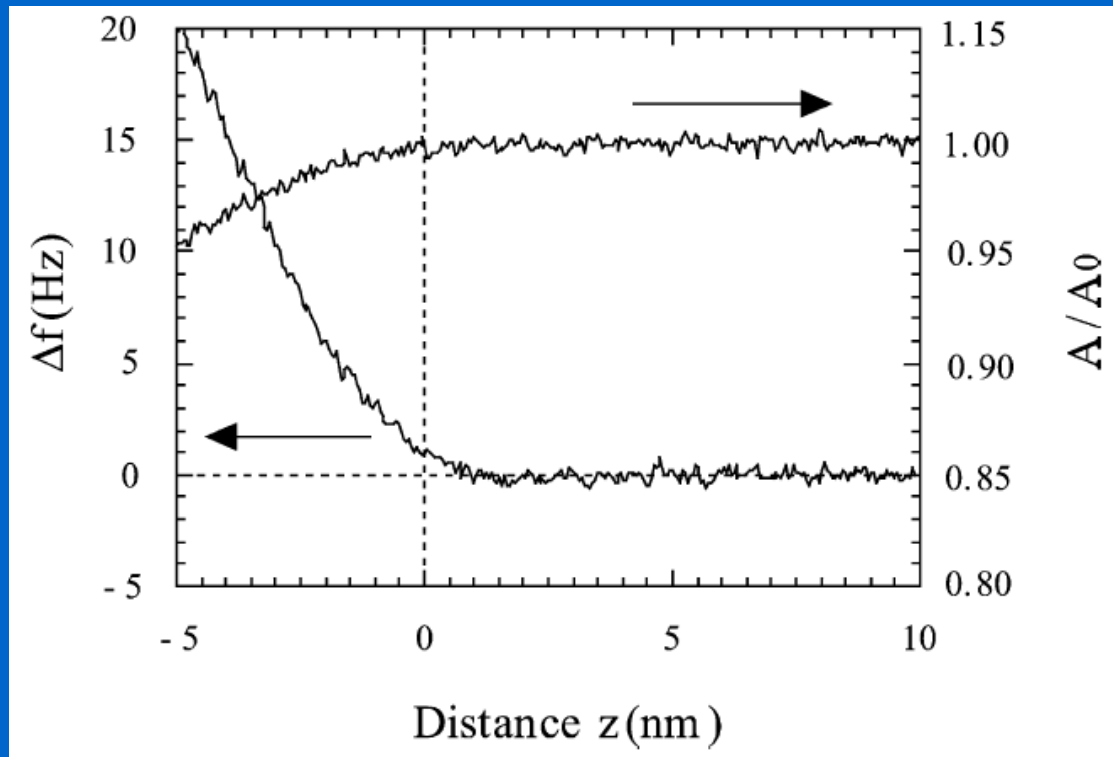
Hook

disipace e.

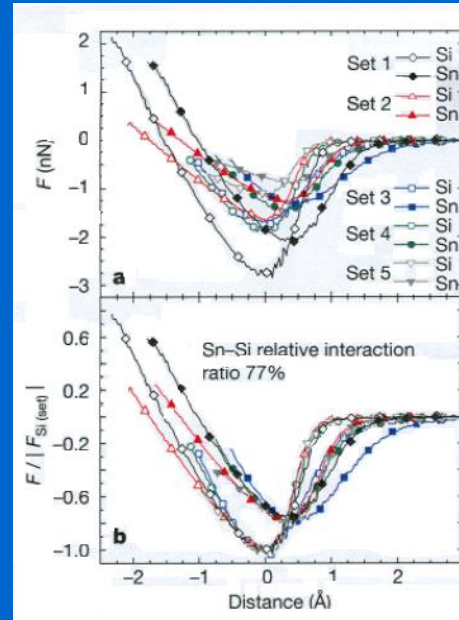
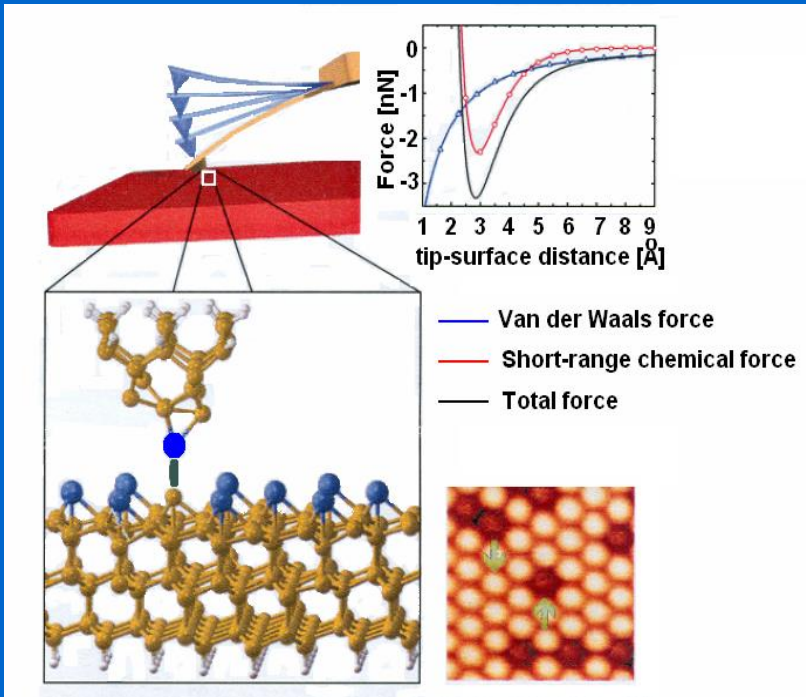
Tip-Surf. interakce

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

Semikontaktní režim (tapping)



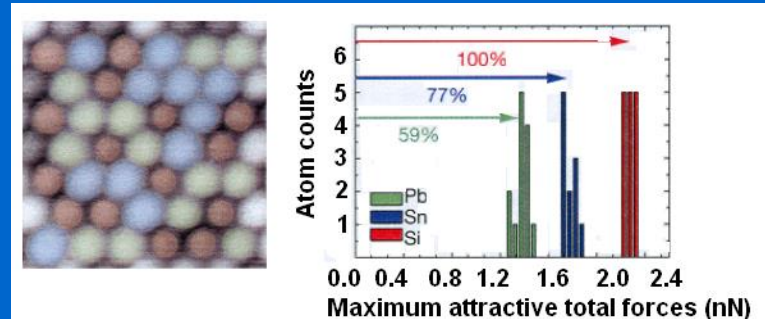
Semikontaktní režim: Chemická identifikace atomů (UHV)



silová křivka
před normalizací

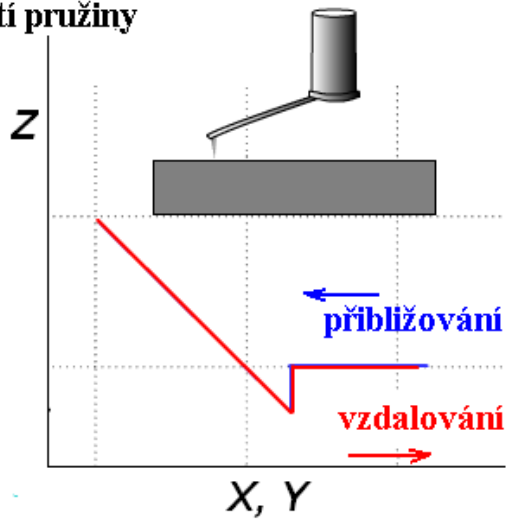
křivka normalizovaná
na maximum interakce
substrát-hrot

Dynamic Force Spectroscopy
silová spektroskopie
sil blízkého dosahu – chemické interakce

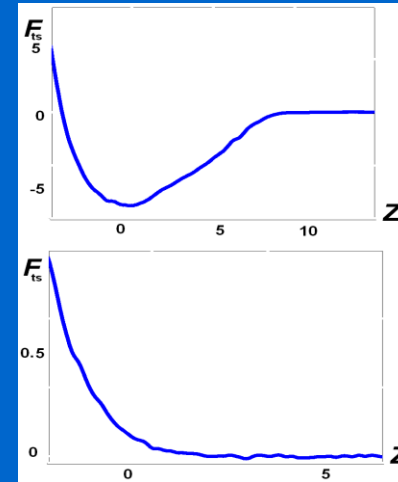
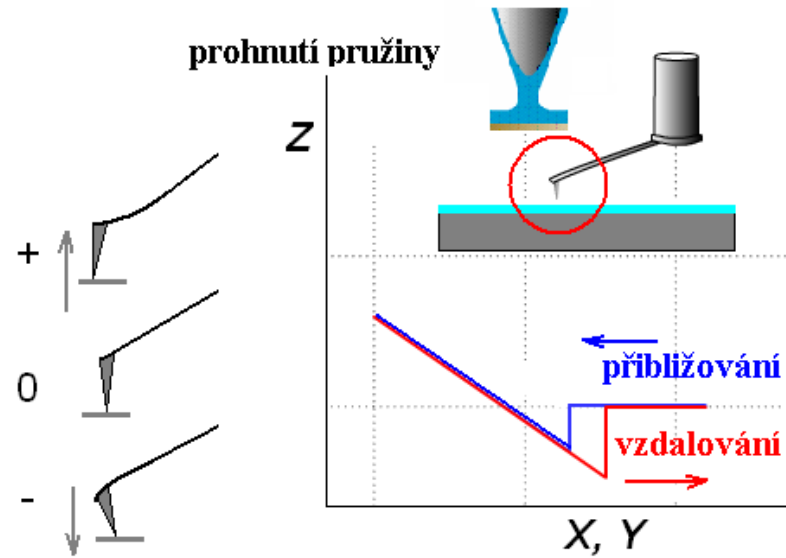


AFM adhesivních sil axiální

prohnutí pružiny



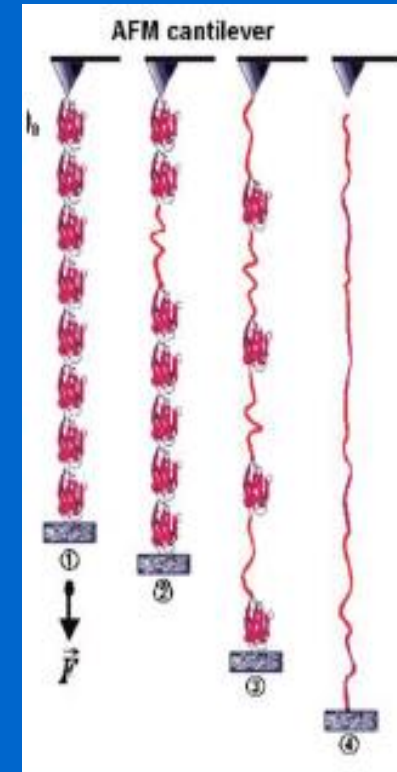
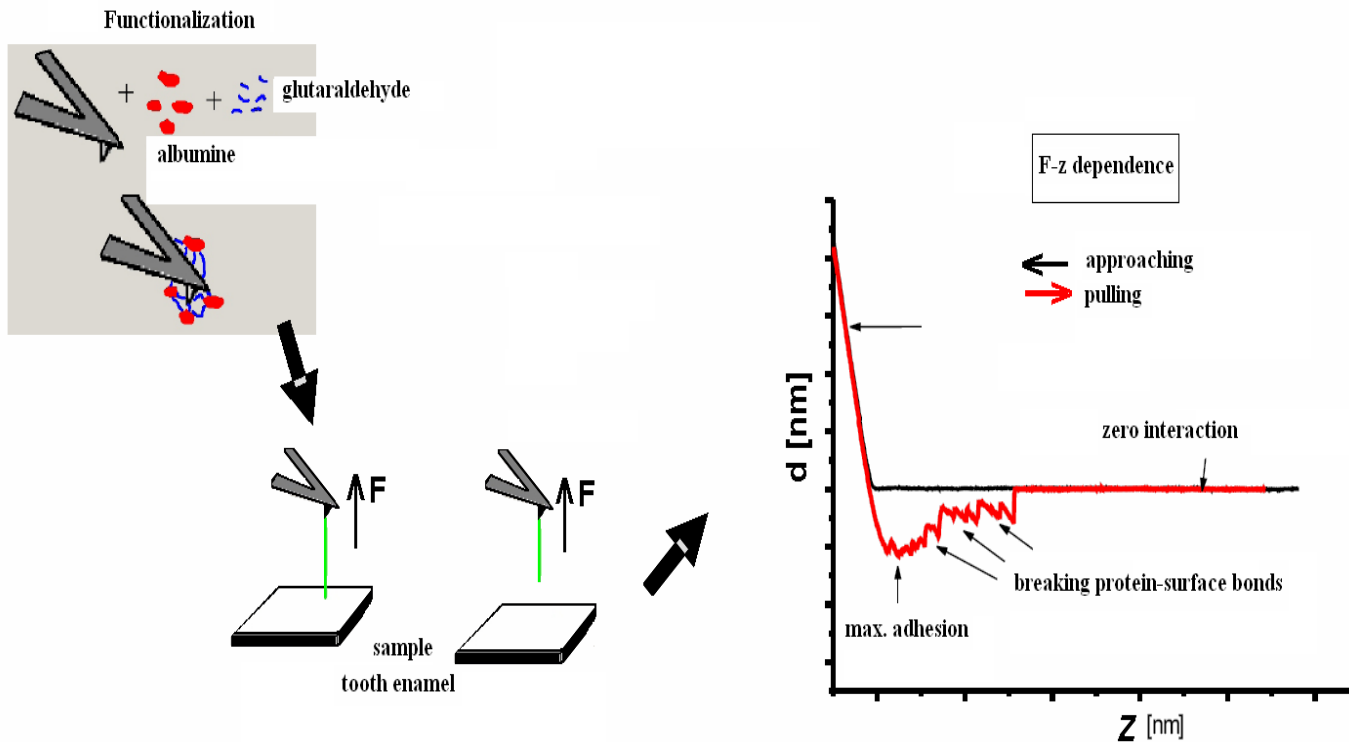
prohnutí pružiny



$F_{ts}(Z)$
(Si/SiO₂)/vzduch

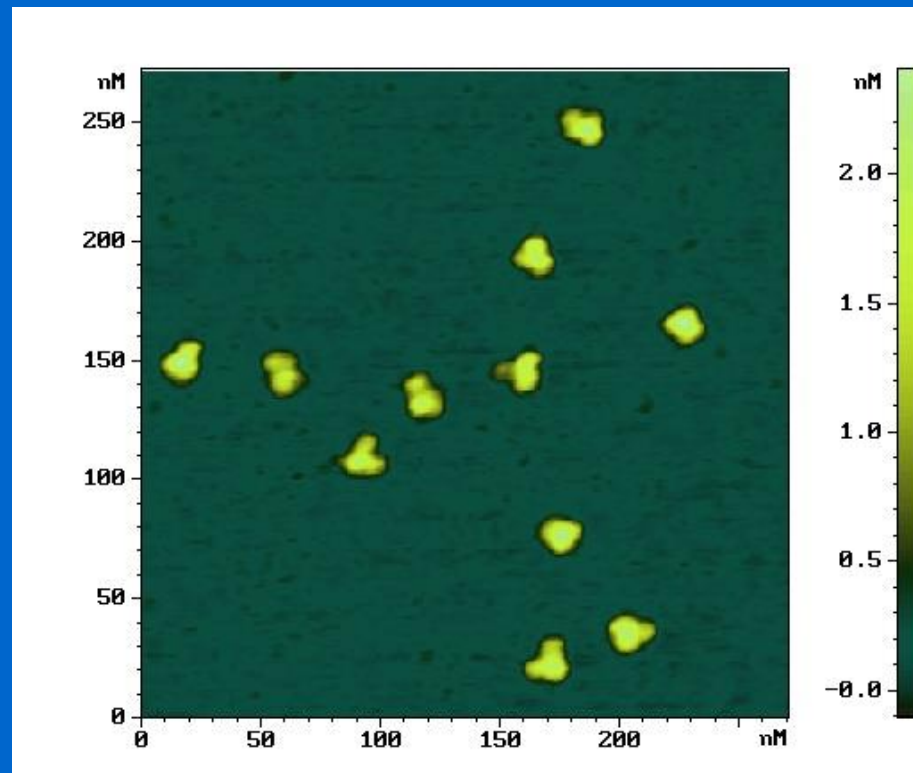
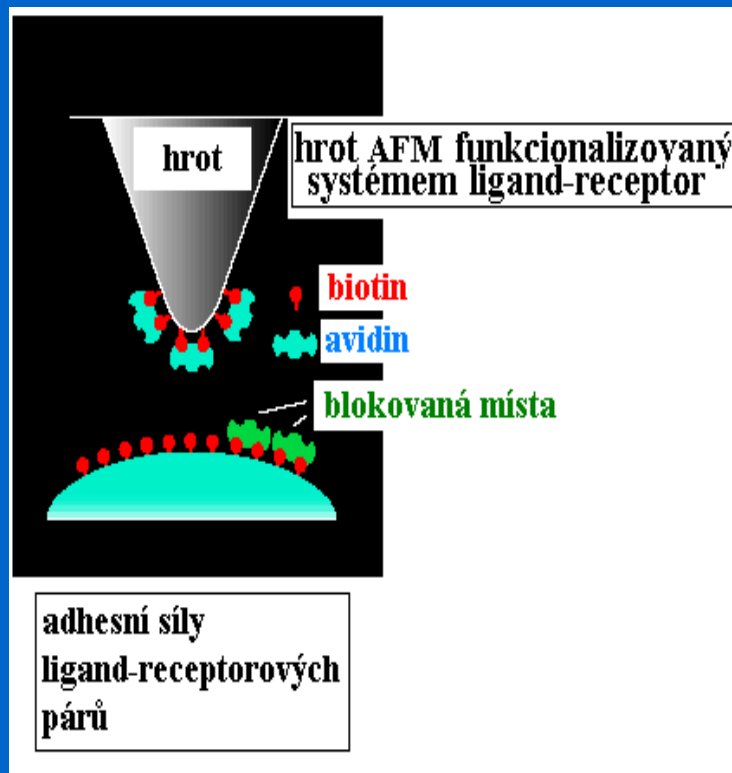
in situ (voda)

Adsorpce proteinů na zubní sklovině



N. Schwender, M. Mondon, K. Huber, M. Hannig, C. Ziegler Department of Physics, University of Kaiserslautern, Department of Operative Dentistry and Periodontology, Saarland University

AFM s modifikovaným hrotem semikontaktní režim (tapping): vazebné interakce



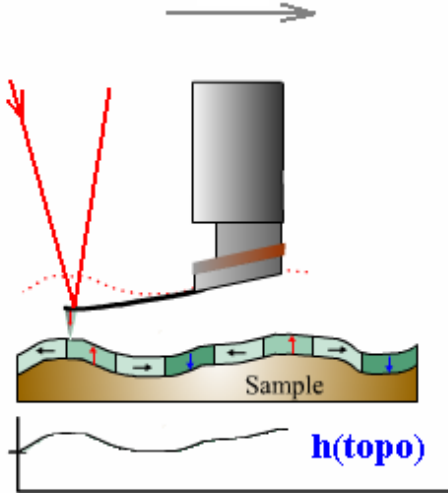
Monoklonální antigen 1RK2 k A-řetězci ricinu (hrot-IgG1).
Viditelná je Y-struktura antigenu.
AFM-semikontaktní režim na vzduchu. [Veeco]

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AFM: bezkontaktní režim

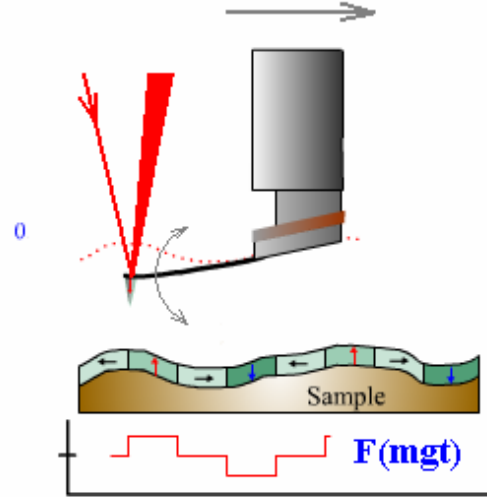
Bezkontaktní AFM: Mikroskopie magnetických sil Magnetic Force Microscopy

1. topography



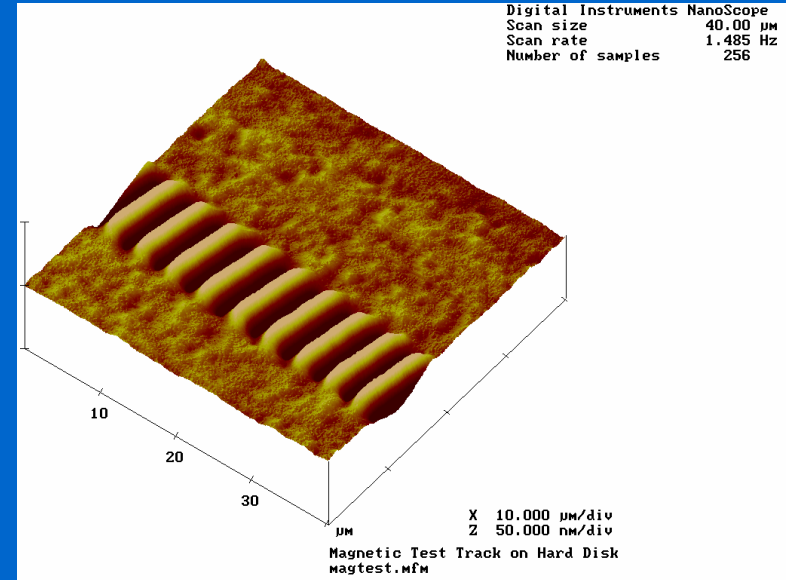
van der Waals. forces
(semicontact)

2. mag. forces



noncontact imaging

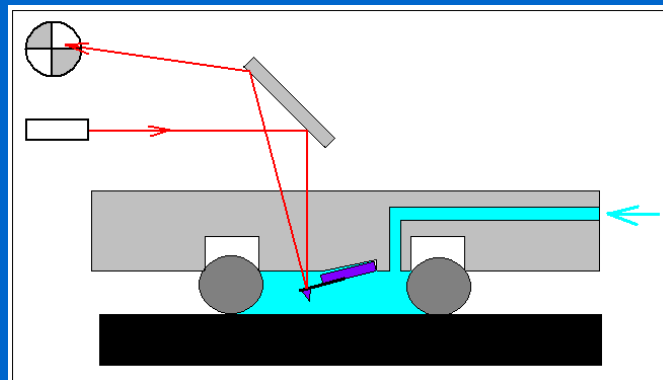
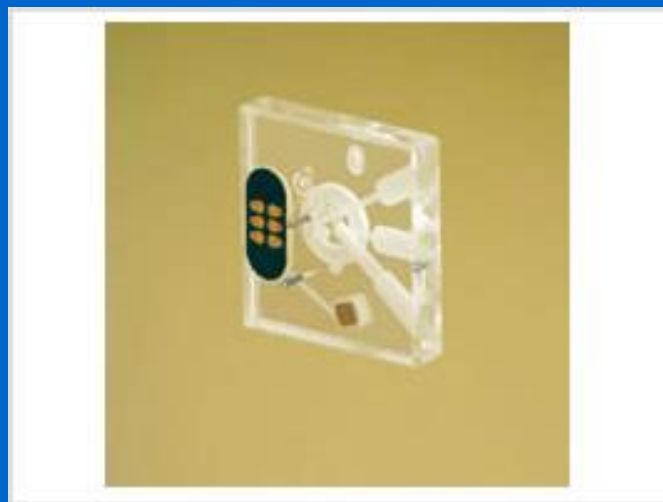
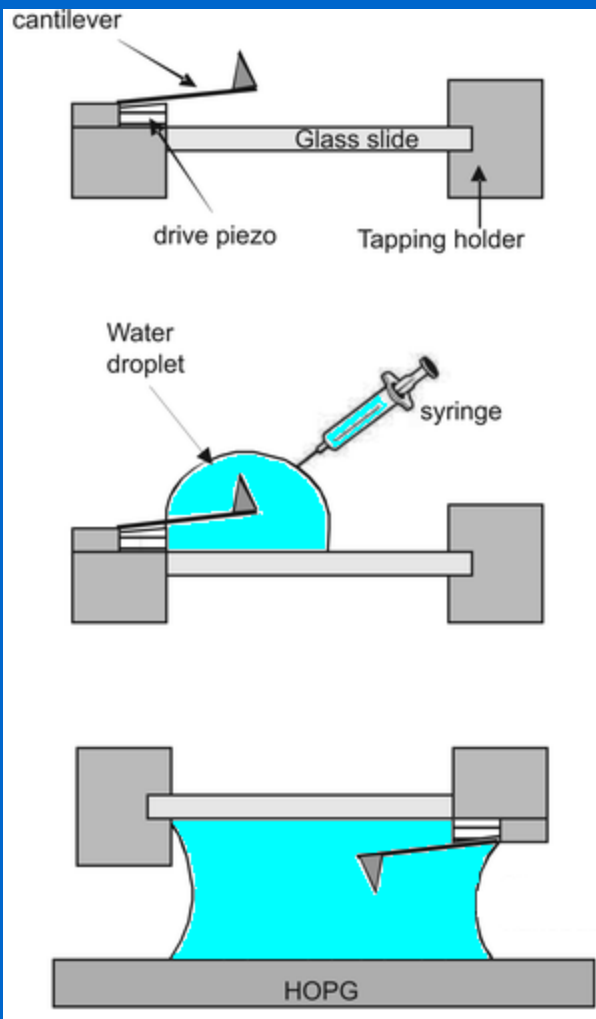
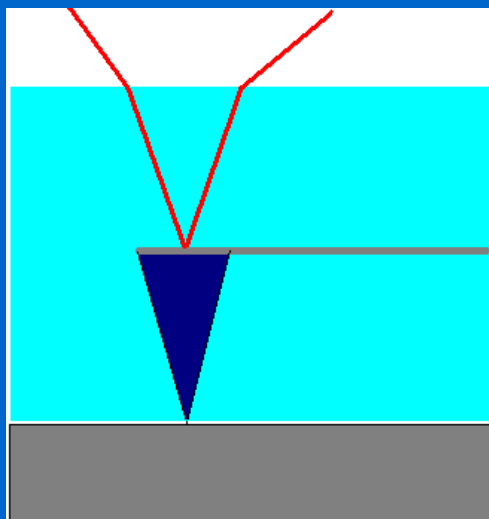
NT-MDT



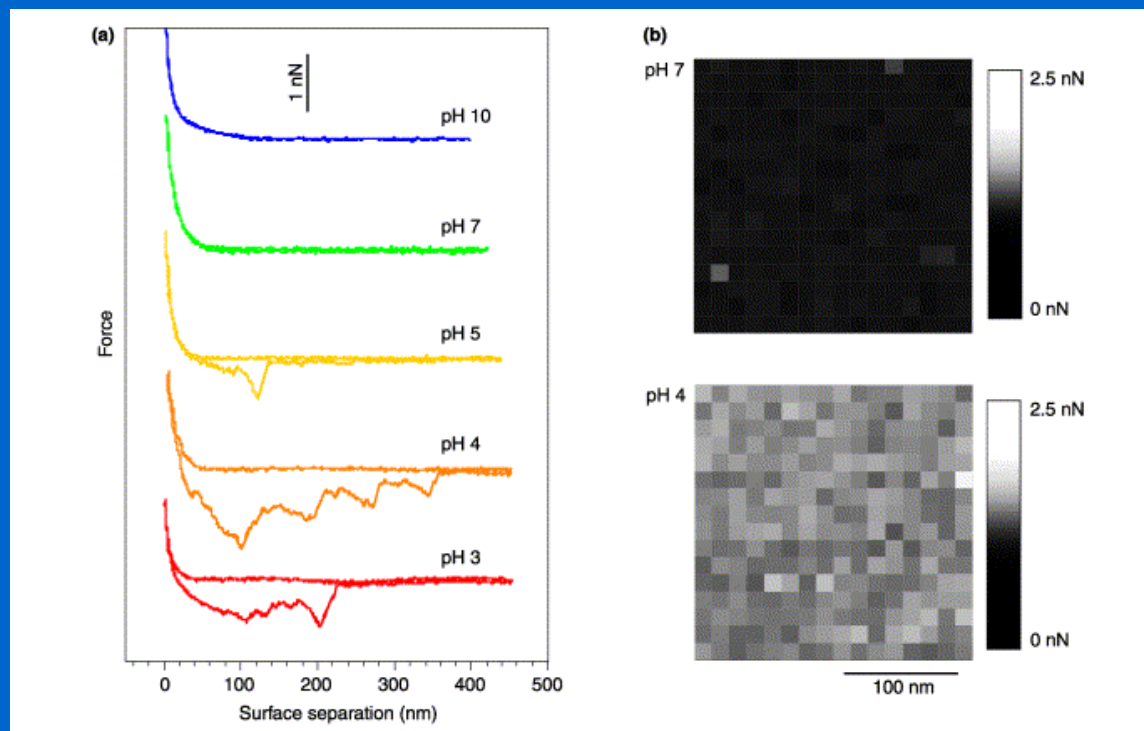
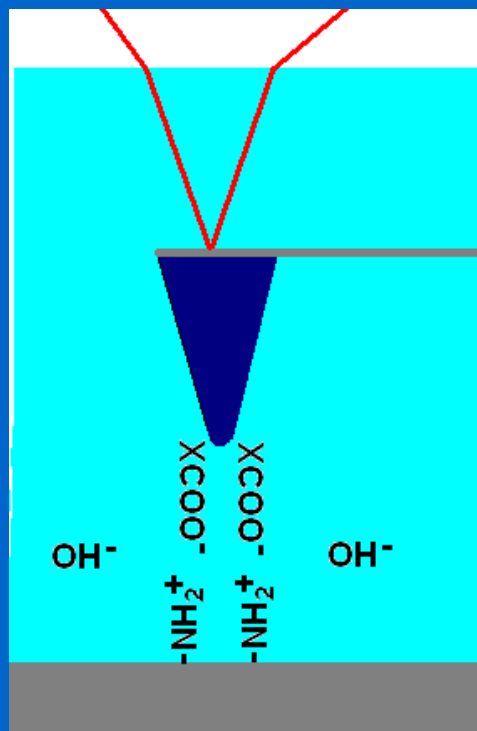
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Mikroskopie atomárních sil (AFM) v kapalinách

AFM v kapalině

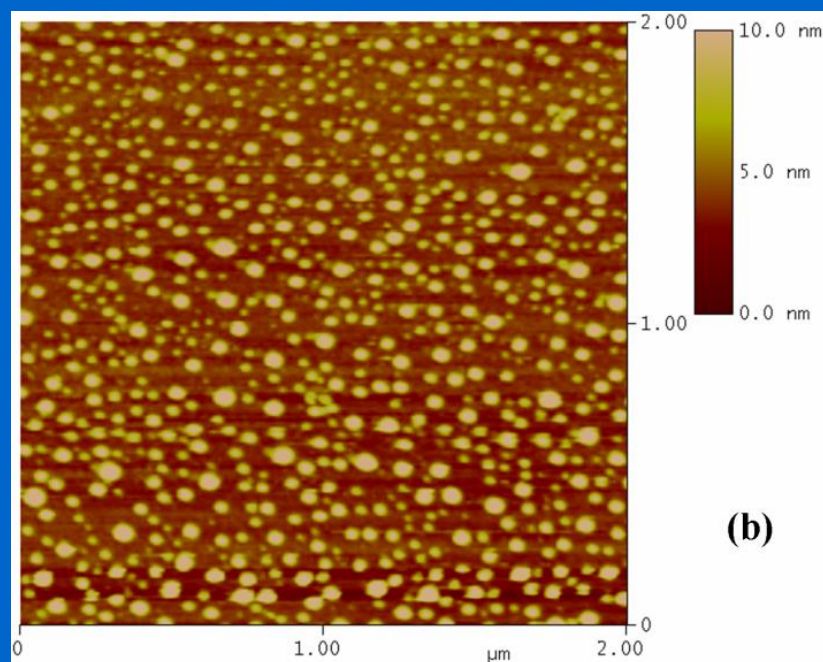
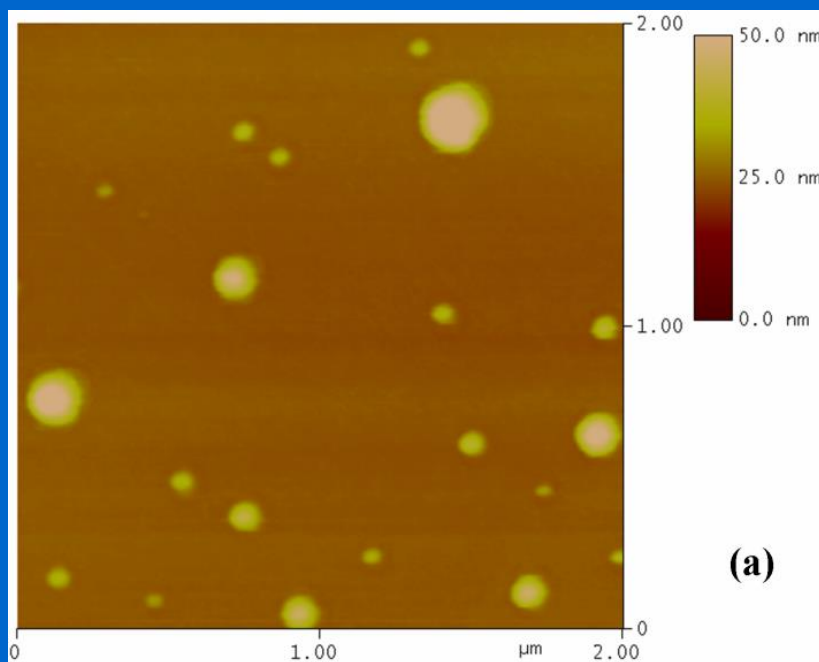


AFM adhesivních sil - axiální (semikontaktní režim *in situ*)



„Break-up“ adhesivní síly na povrchu buněčné membrány
Saccharomyces cerevisiae při změně pH

Nanobubliny na mezifázi kapalina/pevná látka

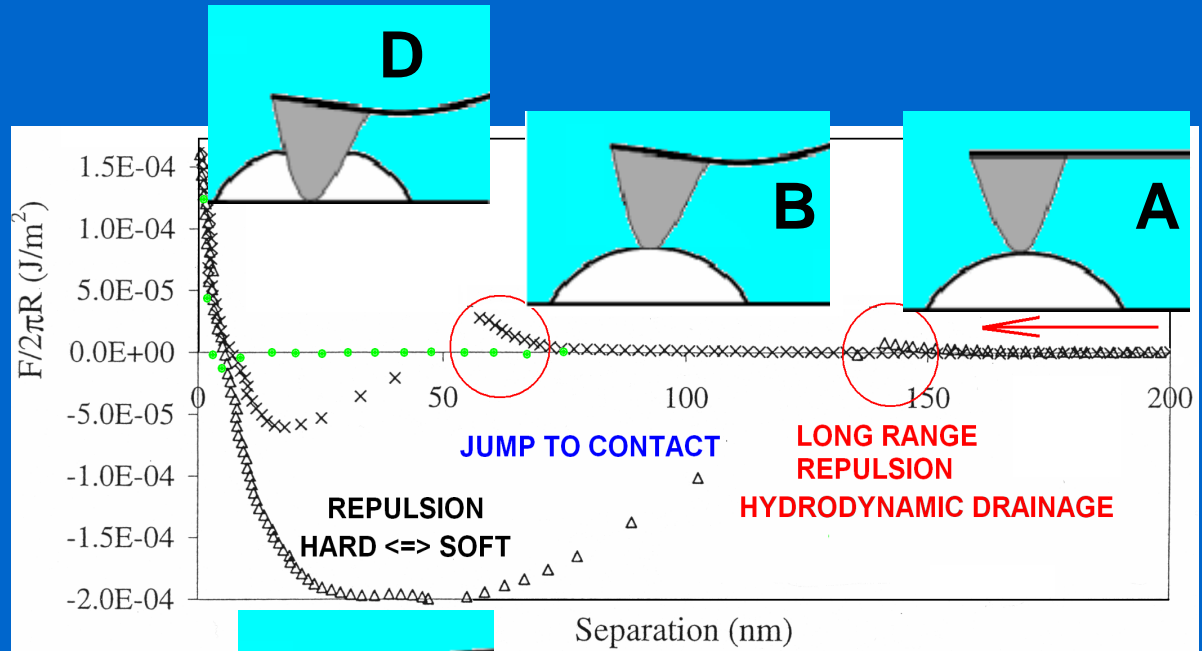
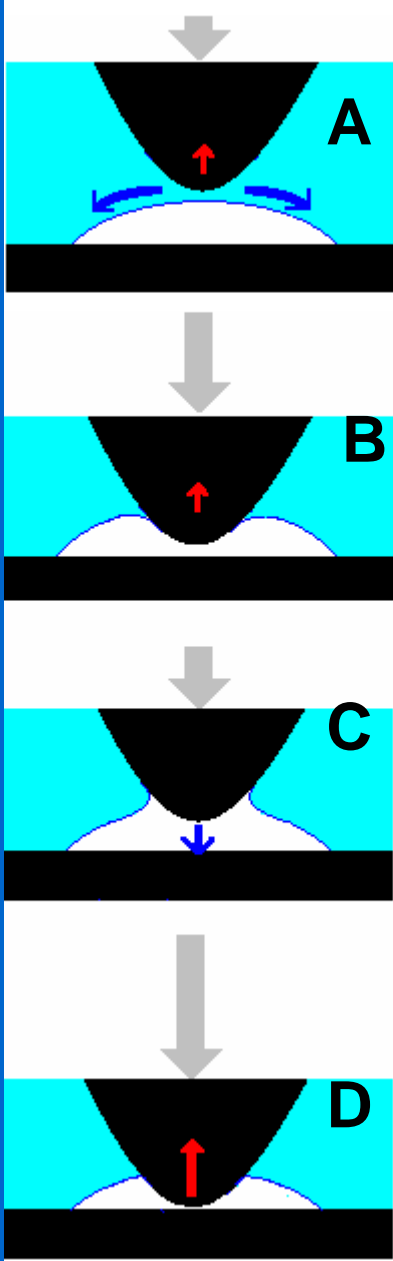


10 %

pokrytí

70 %

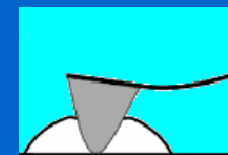
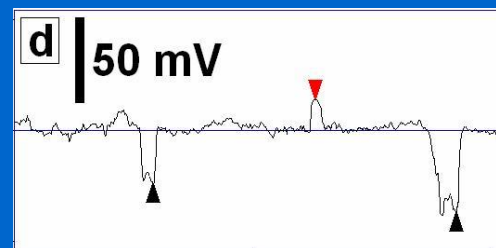
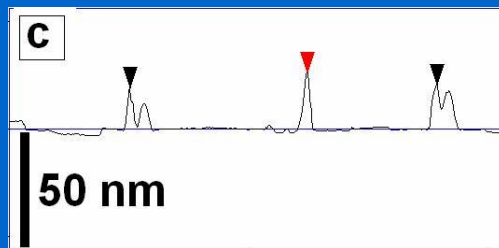
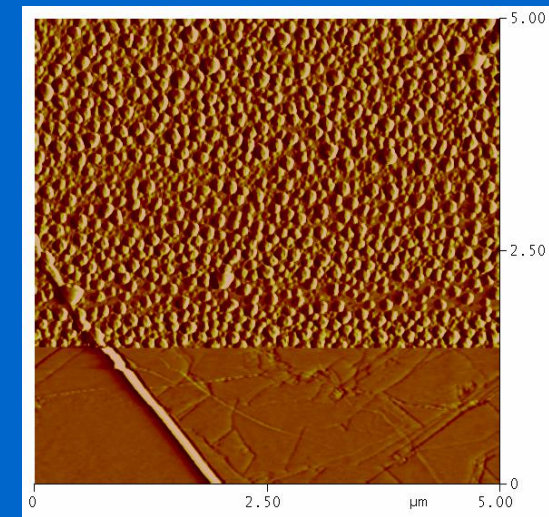
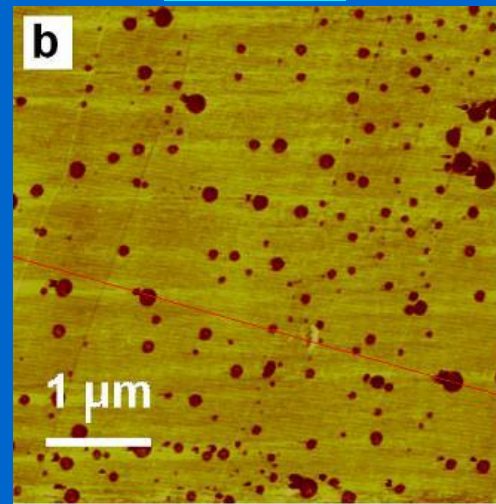
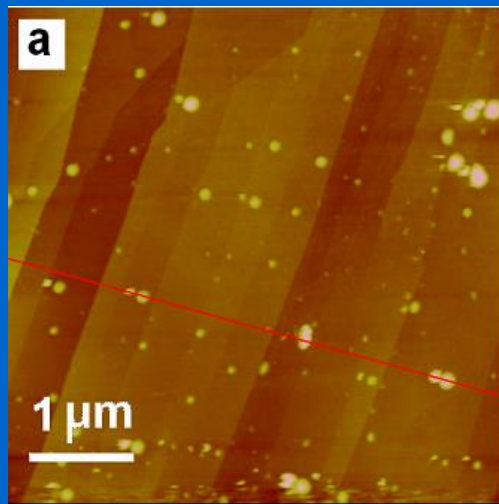
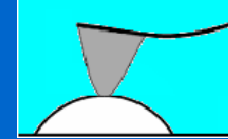
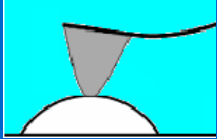
Nanobubliny na mezifázi kapalina/pevná látka



AFM silová křivka

[A. Carambassis, L. C. Jonker, P. Attard, and M. W. Rutland, *Phys. Rev. Lett.* 80, 5357-5360 (1998)]
 [Holmberg et al.: *Langmuir*, Vol. 19, No. 25, 2003]

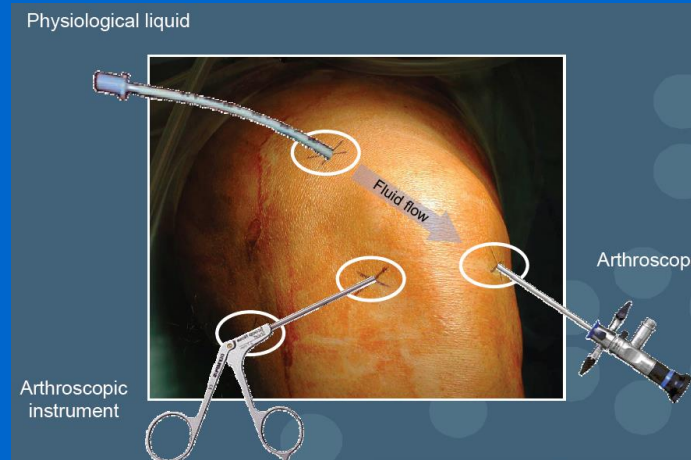
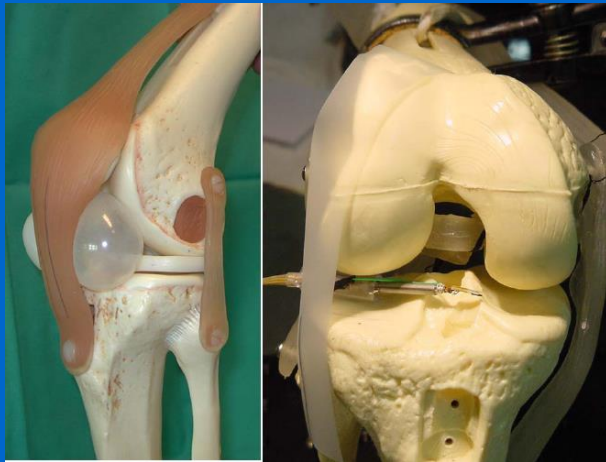
Nanobubliny na mezifází kapalina/pevná látka



Topografie

Prohnutí cantileveru

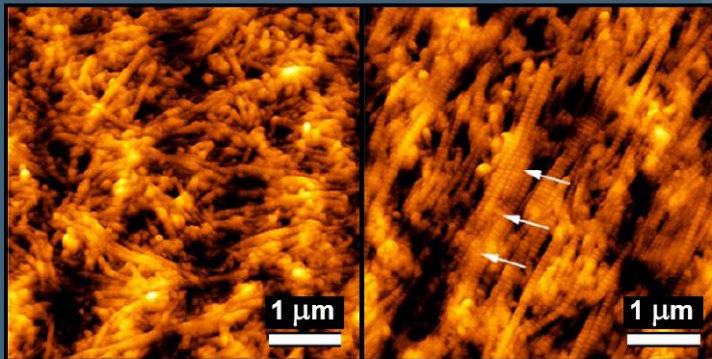
AFM *in vivo*: Scanning Force Endoscope



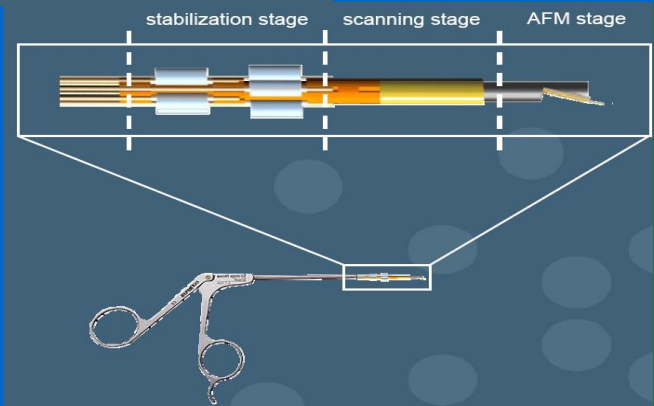
Diagnosing cartilage diseases at an early stage

healthy

osteoarthritic



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



Institute of Microtechnology
University of Neuchâtel

R. Imer
T. Akiyama
N.F. de Rooij
U. Staufer

M.E. Müller Institute (MSB)
University of Basel

M. Stolz
U. Aebi

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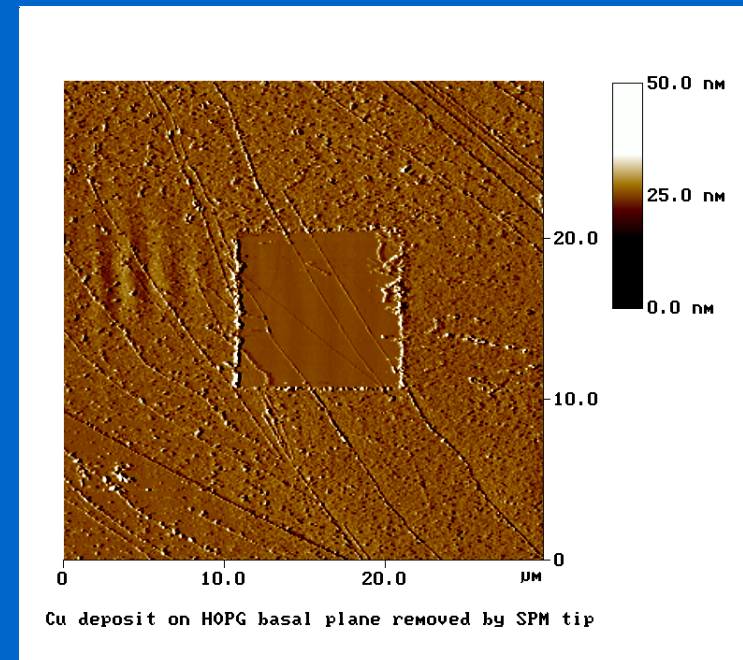
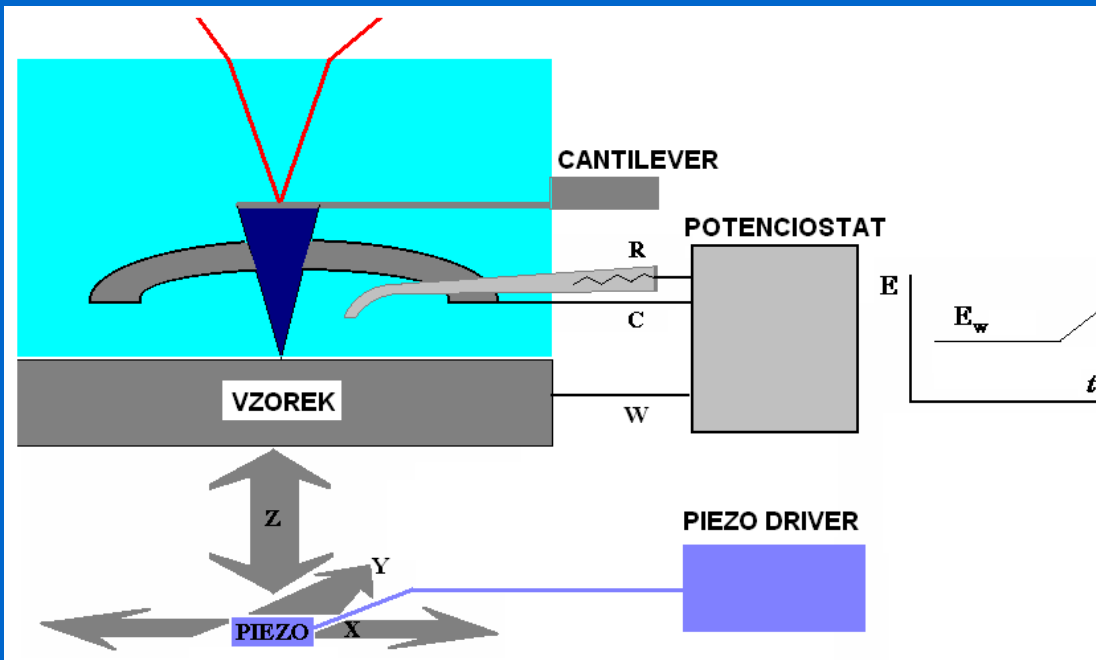


AFM v elektrochemických aplikacích

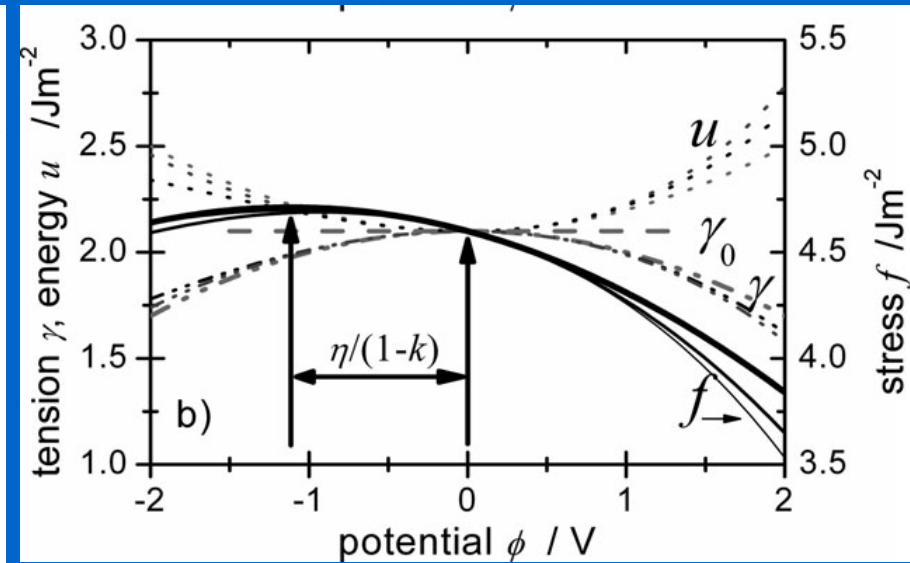
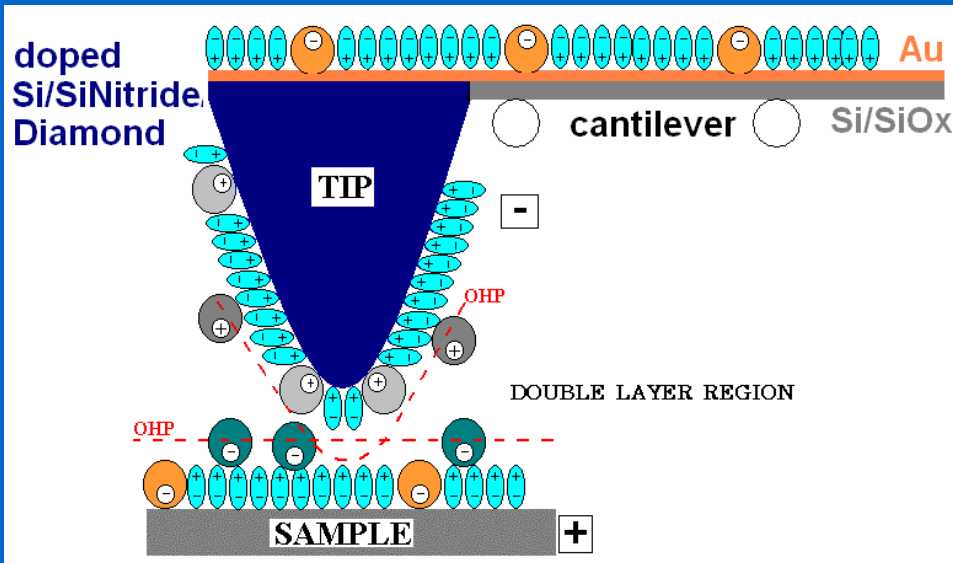


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AFM v průběhu EC experimentu: zobrazení *in situ*



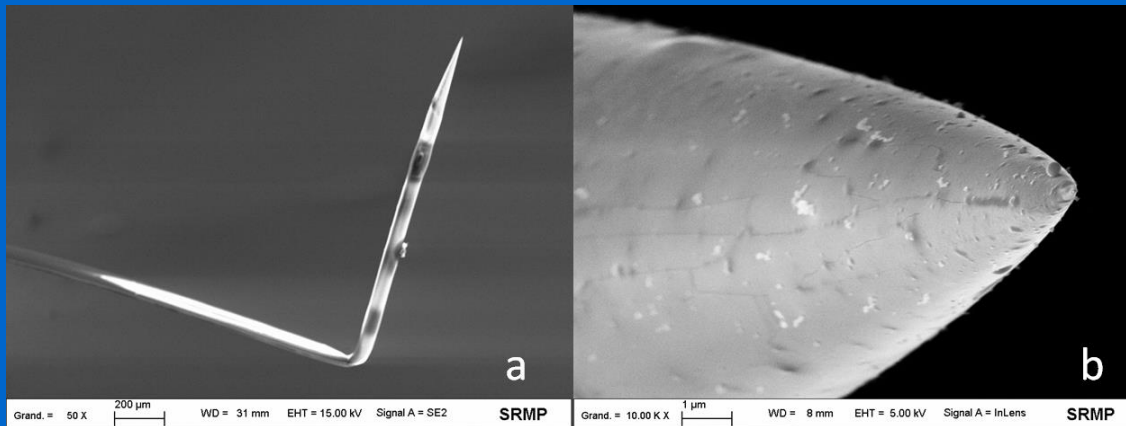
Hrot-cantilever v režimu SECM



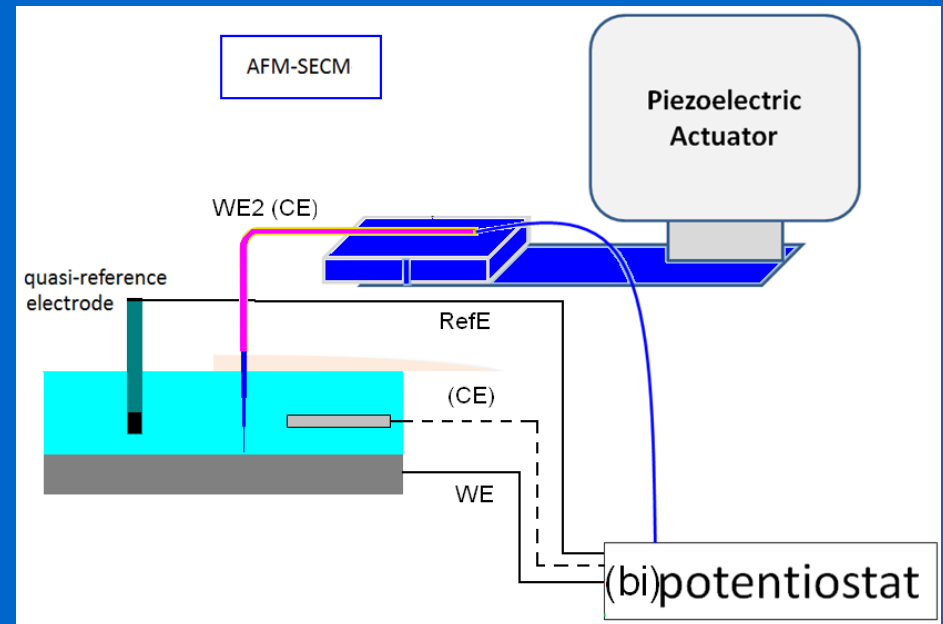
Dependence of surface tension γ , surface stress f and surface energy u on the electrode potential ϕ ($\phi = E - E_0$ (zero charge)), calculated for different double layer capacities.

Lippmann: $d\gamma/dE = -q$, $q = C_0(E - E_0)$,
 $\gamma - \gamma_0 = 0.5q^2/C_0$ ($E_0 \dots \text{pzc}$)

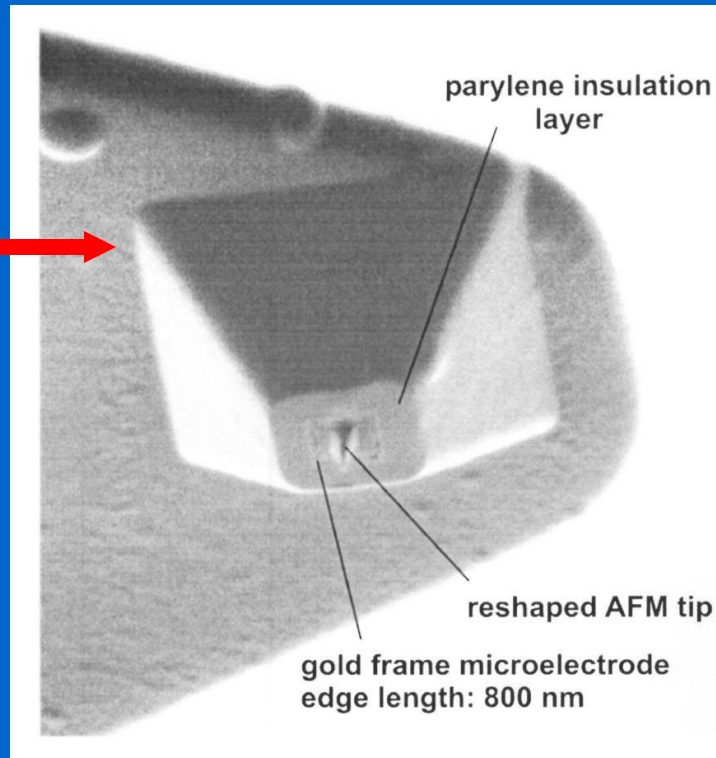
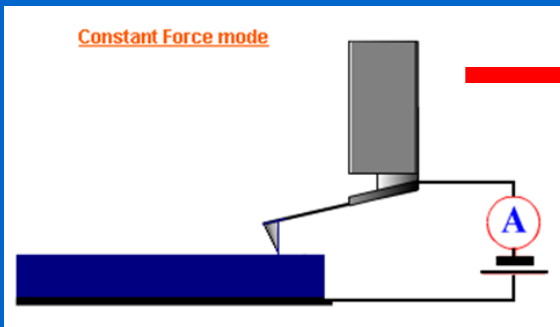
AFM-SECM v objemu



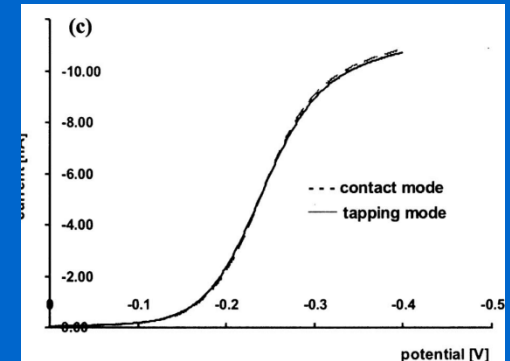
AFM-SECM-elektroda
izolovaná elektroforetickým
lakem, hrot R ~130 nm



Vodivý hrot AFM-ECM pro práci v tenké vrstvě kapalin

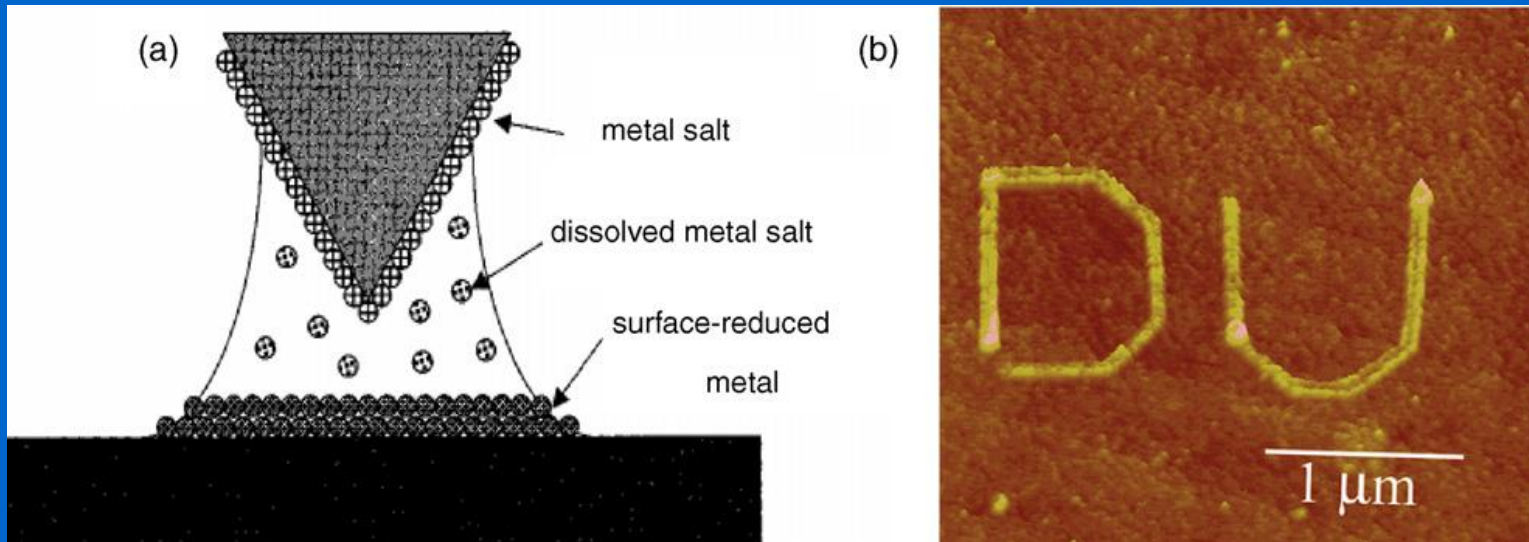


integrovaná sub-mikroelektroda
 $h = 300 \text{ nm}$



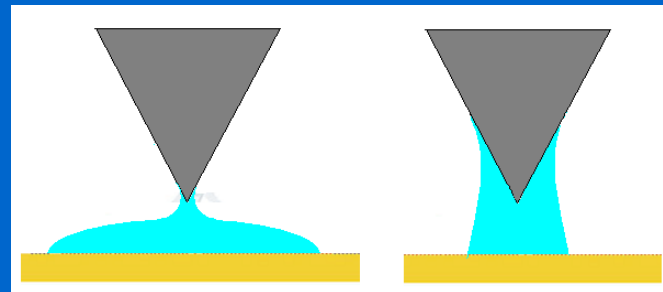
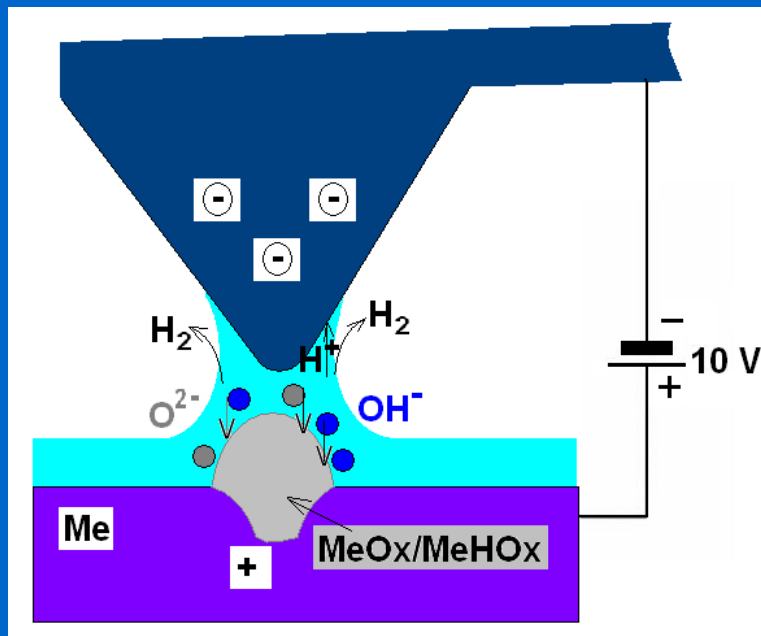
Cantilever with 100 nm Au insulated with 700 nm Parylene.
LSV: SECM-AFM tip in 10 mM Ru(NH₃)/0.5 M KCl soln; 100 mV/s.
---LSV at contact mode
— LSV at tapping

ECAF_M: hrotem zprostředkovaná elektrodepozice kovu (nano-vrstva) v kapce



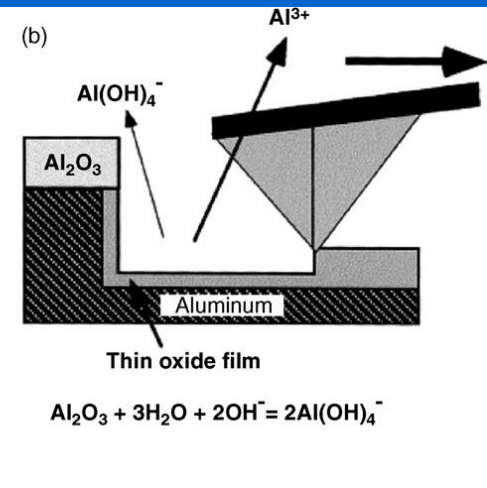
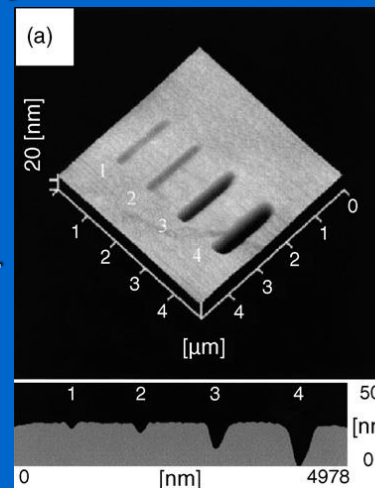
Au elektrodepozice konverzí Au(III) (inkoust) \Rightarrow Au(0)
2-elektrodový systém

ECAFM: hrotem indukované elektrochemické vytváření/rozpuštění oxidu (nano-vrstvy)



Formování vodního menisku na hydrofilním a hydrofobním substrátu

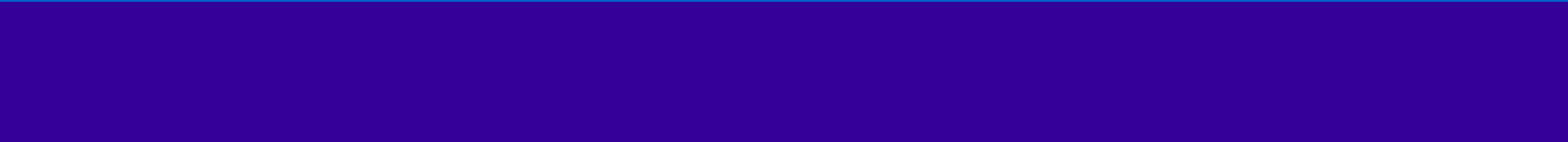
Pole 10^7 V/cm \Rightarrow disociace $H_2O \Rightarrow OH^- + H^+$



2-elektrodový systém

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

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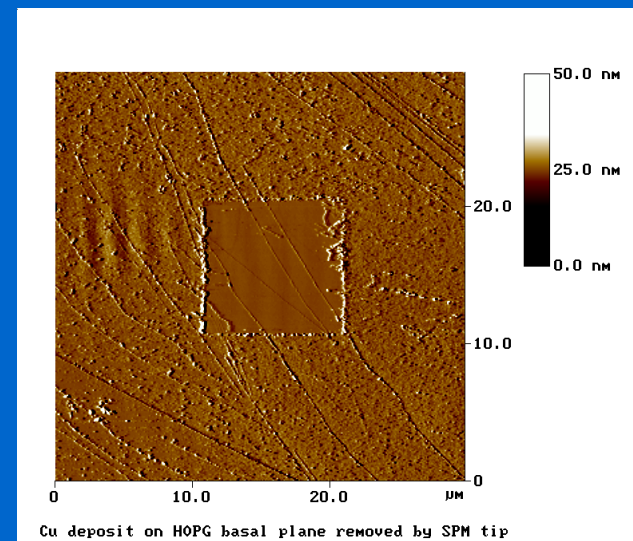
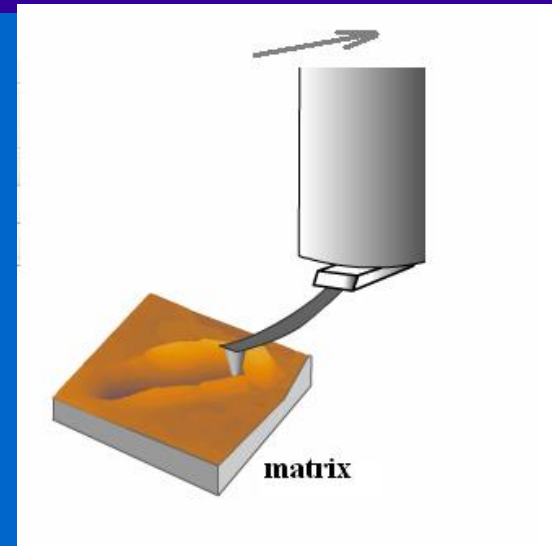
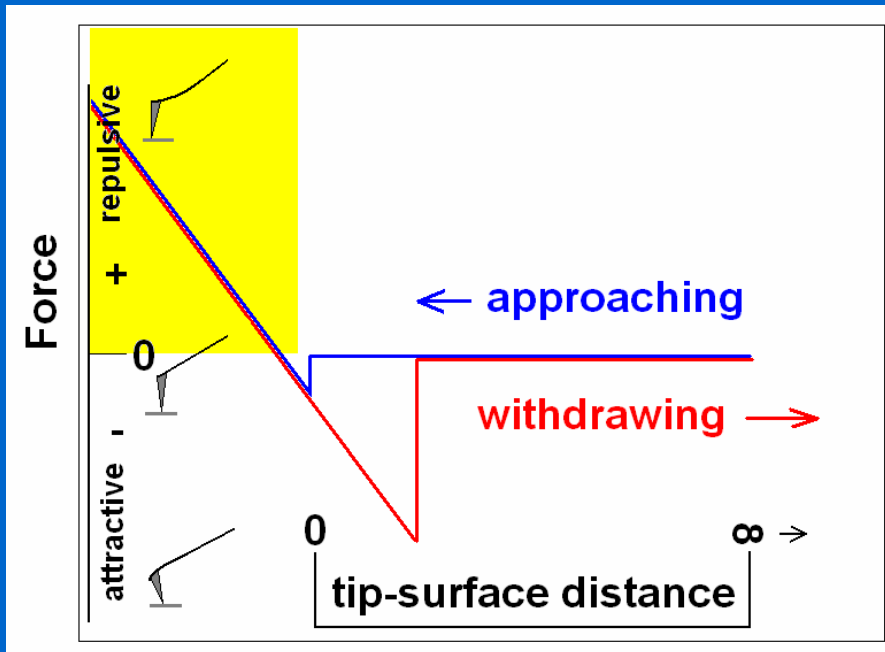


SPM nanomanipulace & nanolithografie



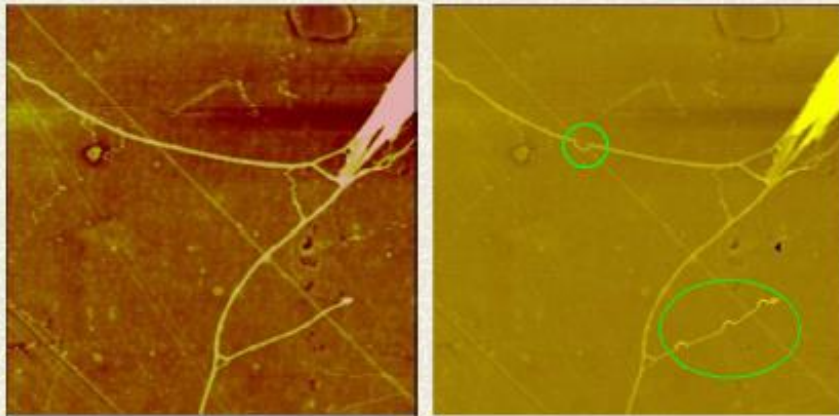
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Interakce sonda-povrch vzorku



Manipulace na molekulární úrovni

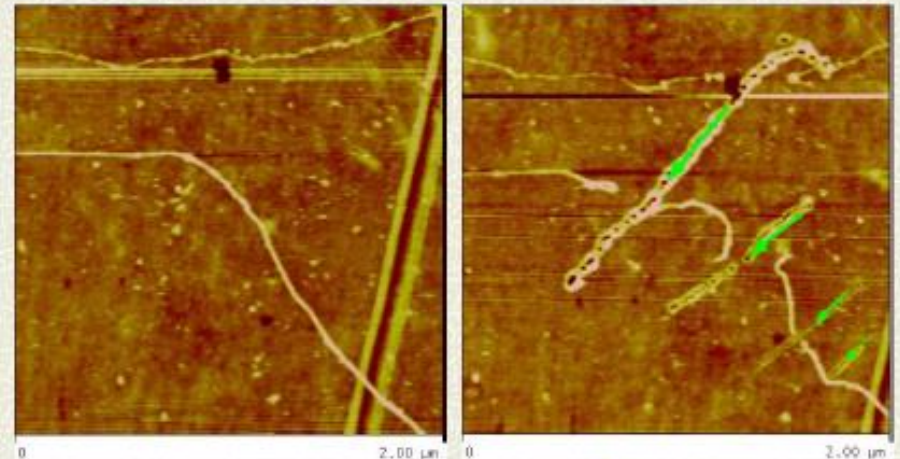
DNA Manipulation: Pushing



Before pushing

After pushing

DNA Manipulation: Cutting



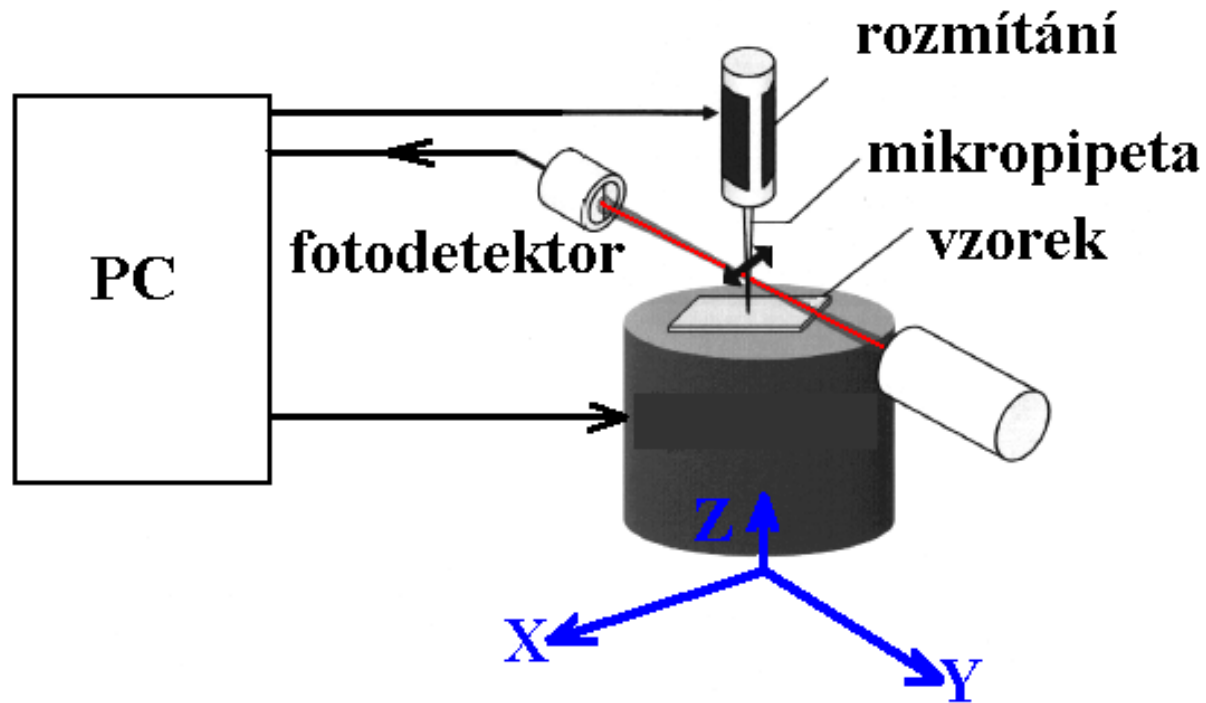
Before cutting

After cutting

Ning Xi

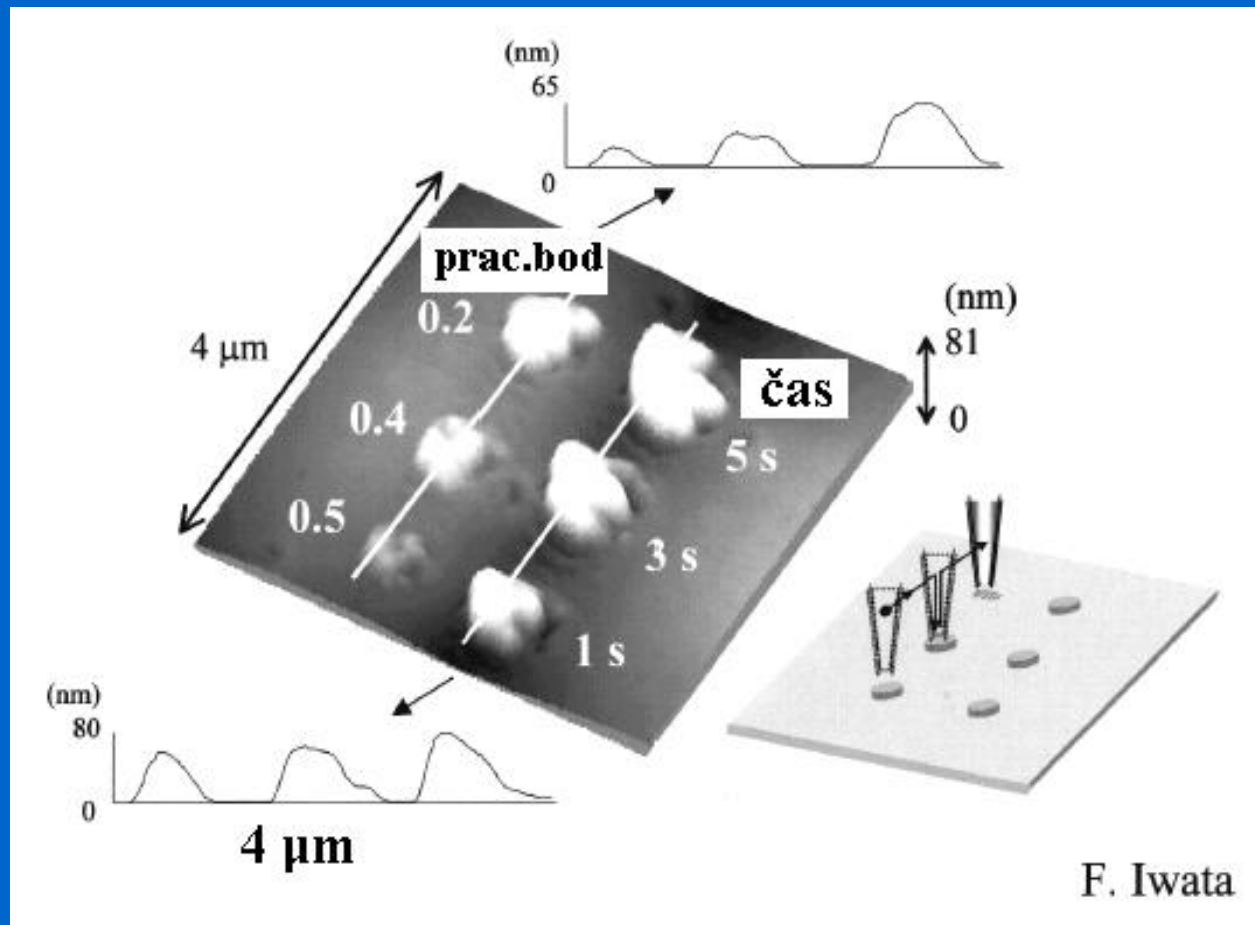
Department of Electrical and Computer Engineering
Michigan State University

Mikroskop s rastrovací mikropipetou



F. Iwata

Nanolithografie AFM s rastrovací mikropipetou





Ústav fyzikální chemie Jaroslava Heyrovského, AVČR v.v.i.
Dolejškova 3, 182 23 Praha 8

Laboratoř mikroskopie rastrovací sondou

AFM/STM Nanoscope IIIa Multimode (Bruker)

Pro práci v kapalinách a plynech
Rozlišení ~ 0,1 nm

AFM/STM TopoMetrix TMX 2010

Pro práci v kapalinách a plynech
Rozlišení ~ 0,1 nm

AFM Dimension Icon (Bruker)

pro práci v kapalinách a plynech



<http://www.jh-inst.cas.cz/~janda>
pavel.janda@jh-inst.cas.cz

