



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

# Mikroskopie rastrovací sondou

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*Laboratoř mikroskopie rastrovací sondou*

**Odd. elektrochemických materiálů**

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# Rozdělení mikroskopických metod podle rozlišení

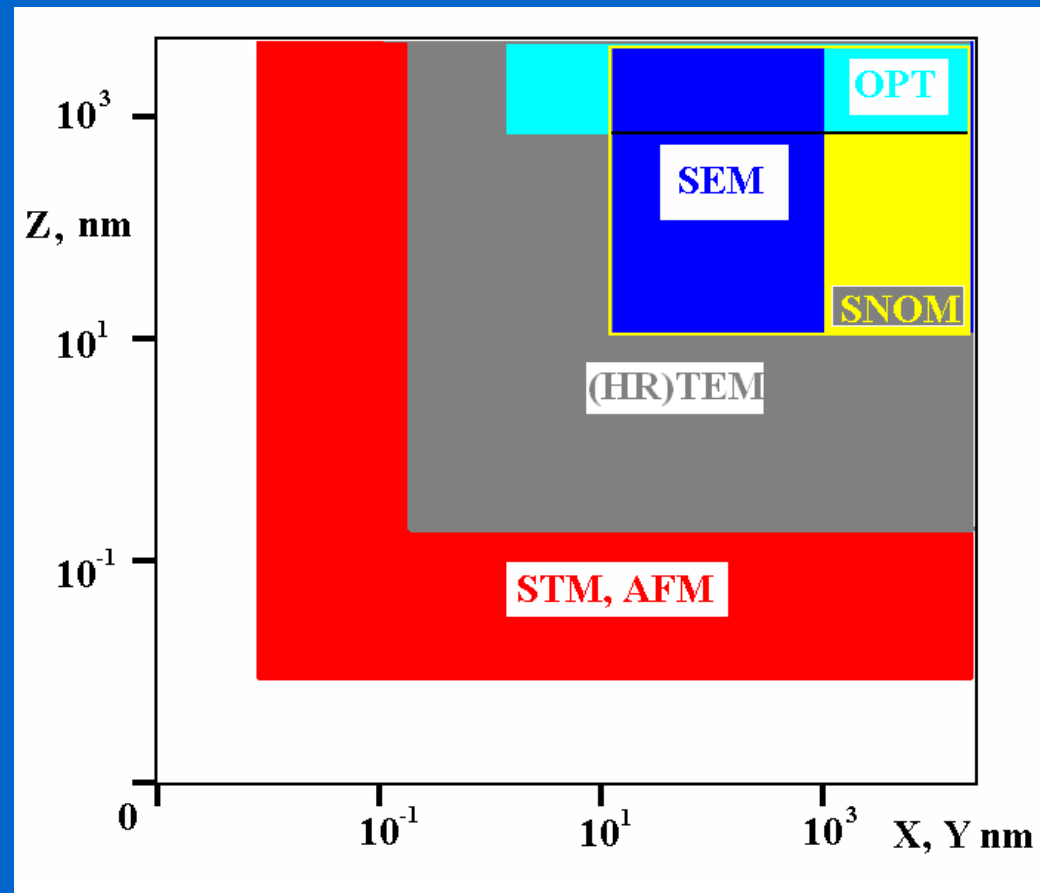
**OPT:** optická mikroskopie

**SNOM:** mikroskopie blízkého pole

**SEM:** elektron.rastr.mikroskopie

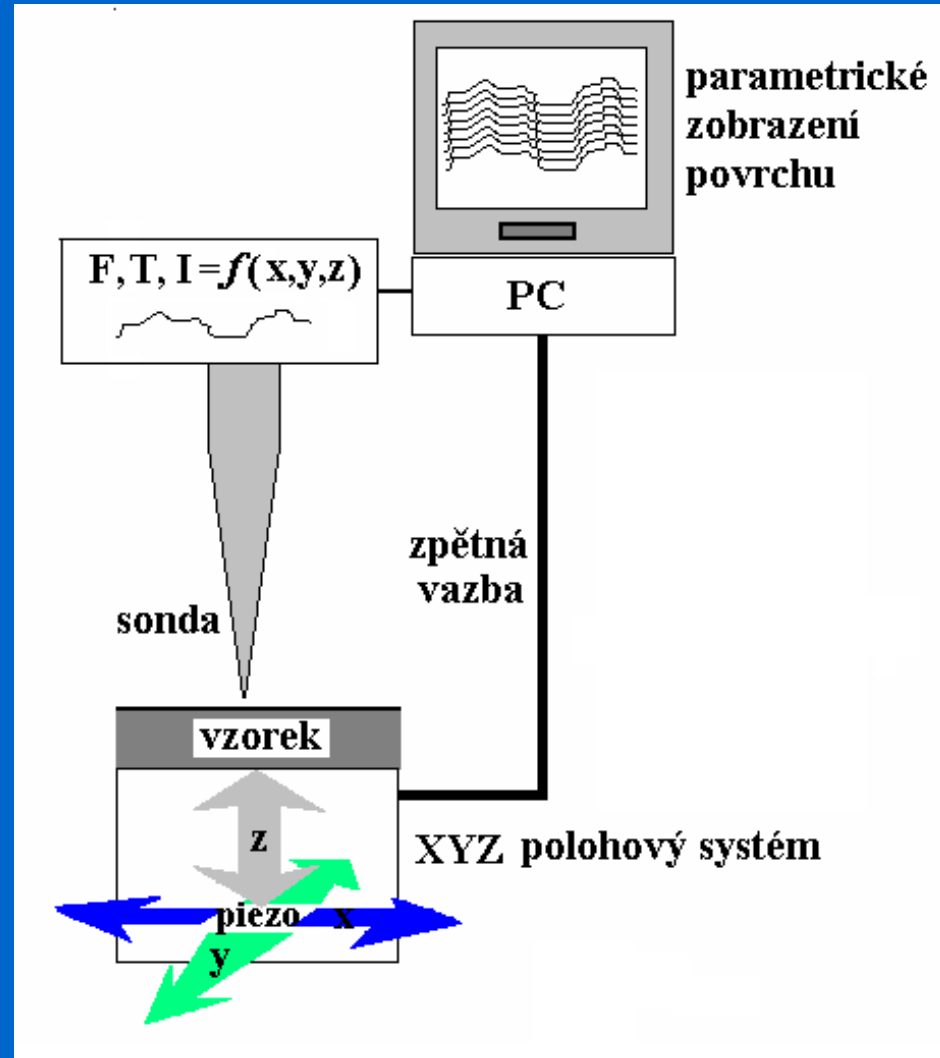
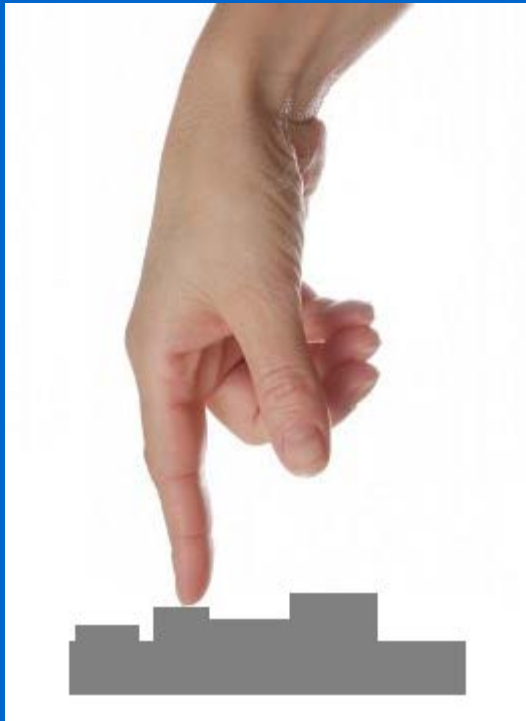
**HRTEM:** transmisní  
el.mikroskopie

**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**

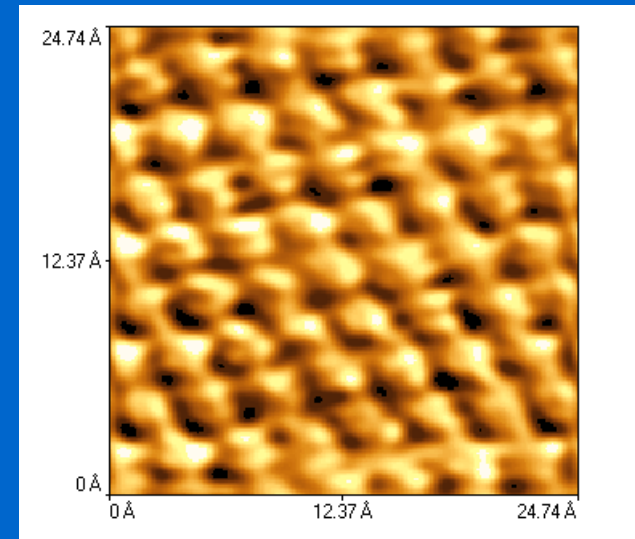
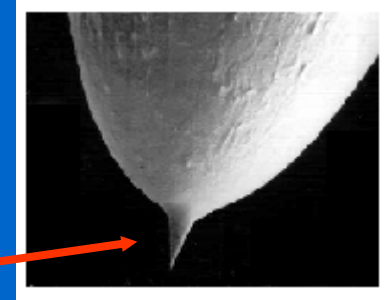
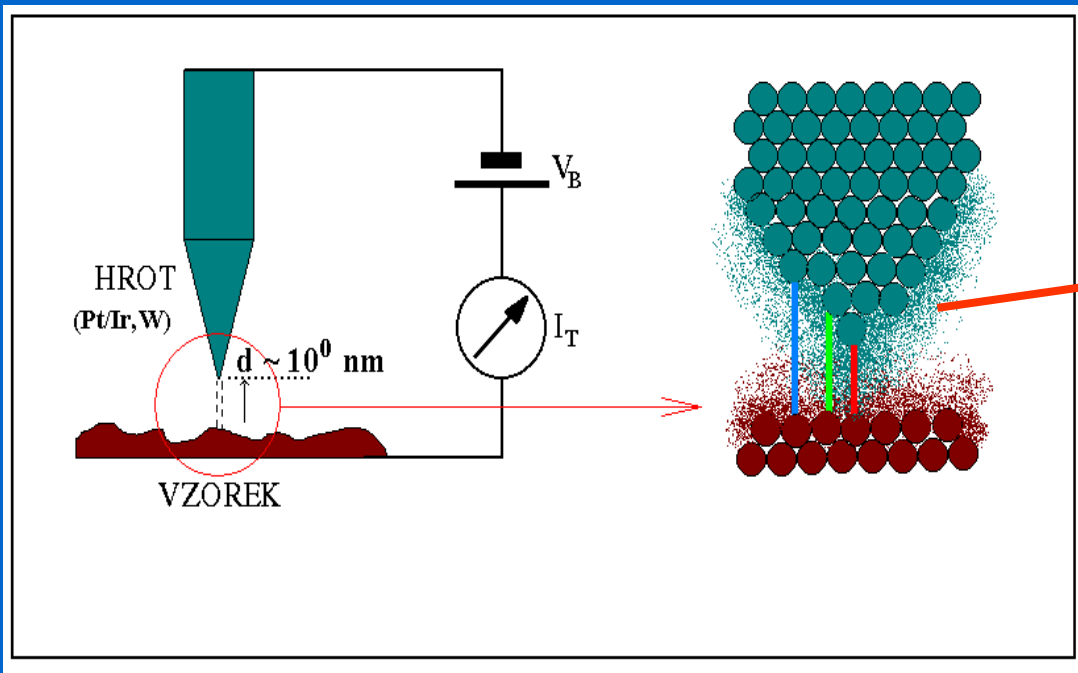
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# Tunelová mikroskopie a spektroskopie

Scanning Tunneling Microscopy,  
Scanning Tunneling Spectroscopy

# Tunelová mikroskopie

Binning, Rohrer, IBM, 1981, Nobelova cena 1986



Au(111)

## 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

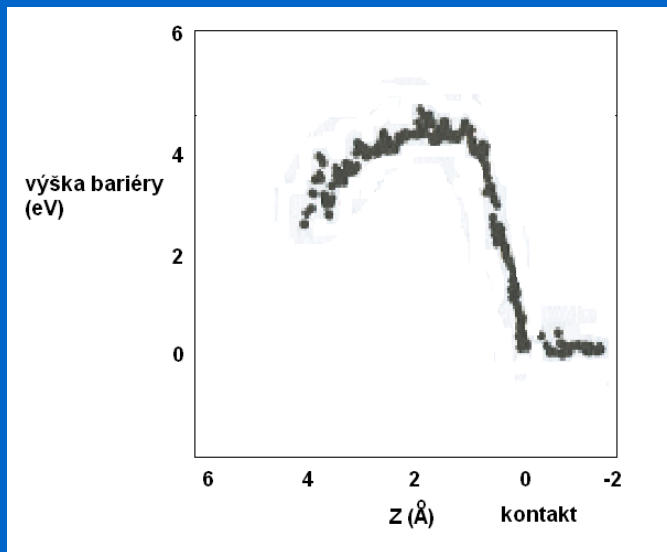
# Tunelová spektroskopie barierová (distanční)

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



Si-povrch, W-hrot/UHV

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

# Tunelová spektroskopie napěťová

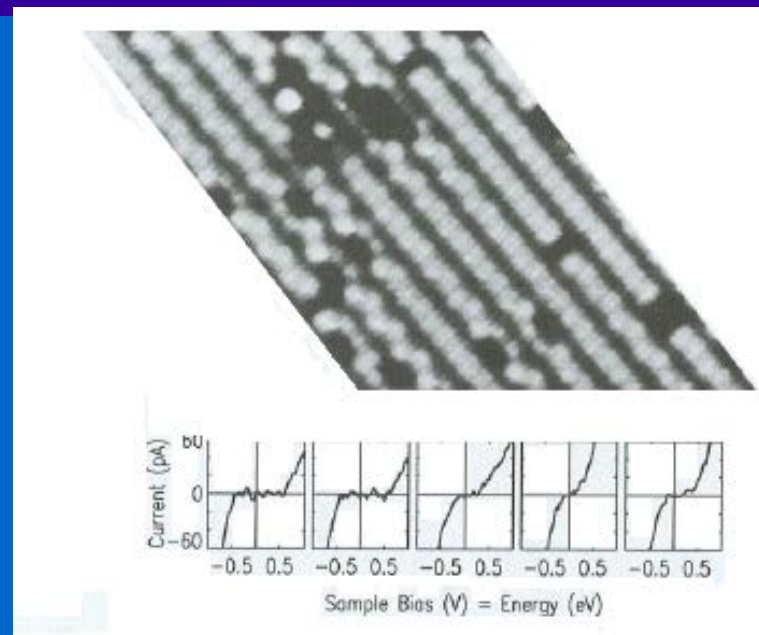
$V_B <$  výst. práce hrotu a vzorku ( $\sim 10$  mV),  
výraz  $dI_T/dV_B \approx$  lokální povrchová hustota stavů (skutečných nebo pocházejících z uspořádání vnitřní pásové struktury vzorku)

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, ad-atomů 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]



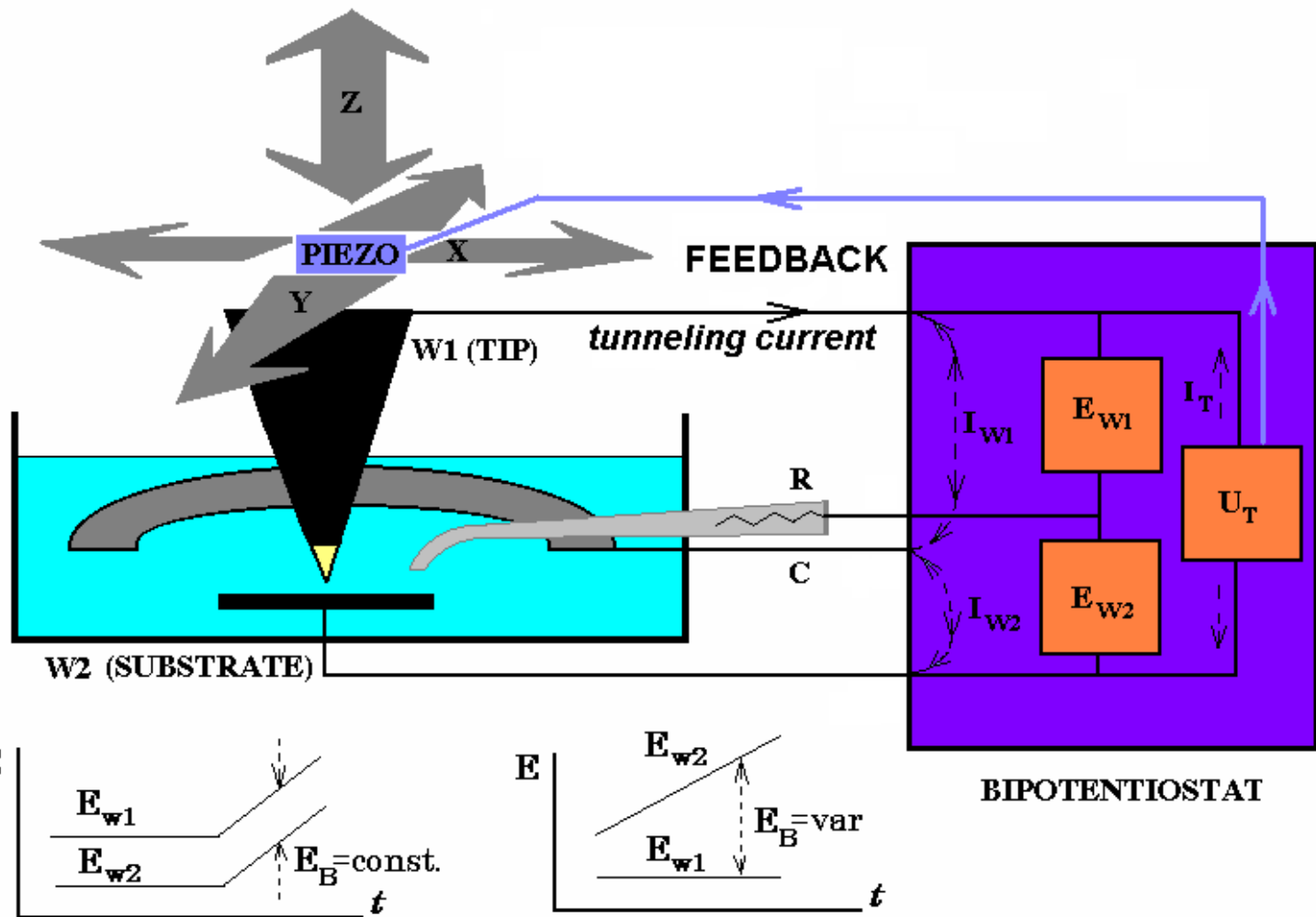
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# Elektrochemická tunelová mikroskopie

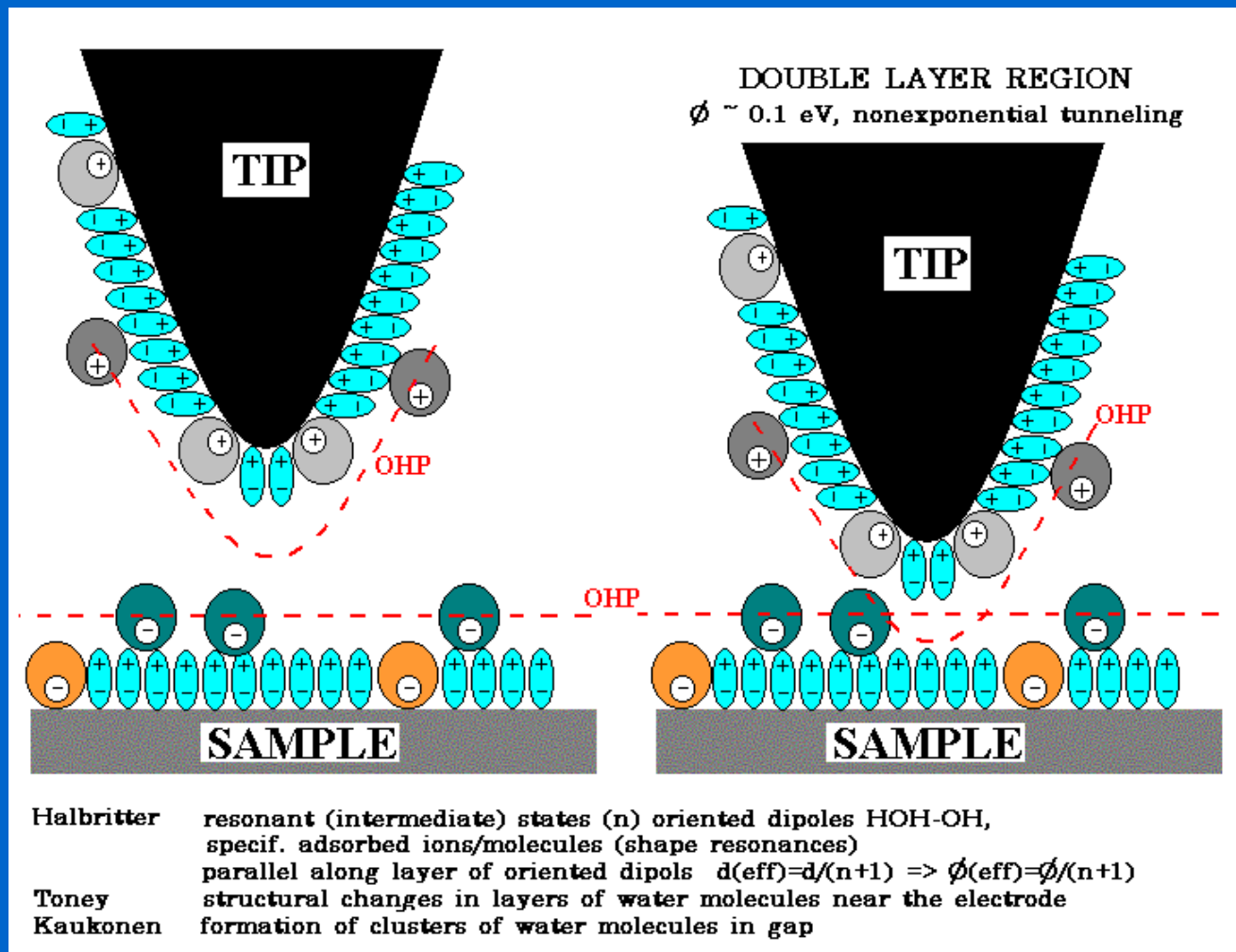
## EC STM

Electrochemical Scanning Tunneling Microscopy

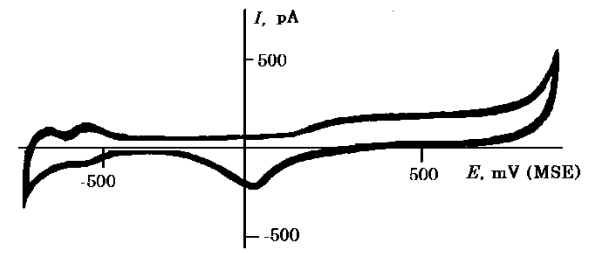
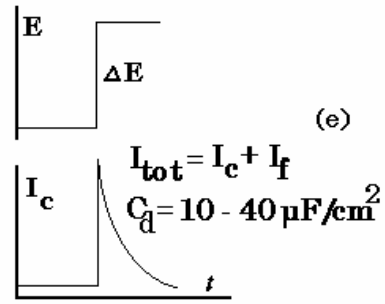
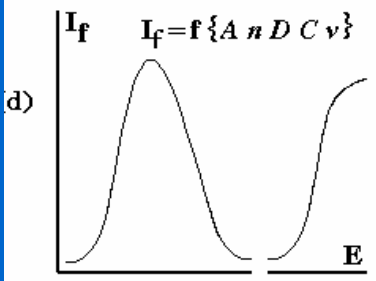
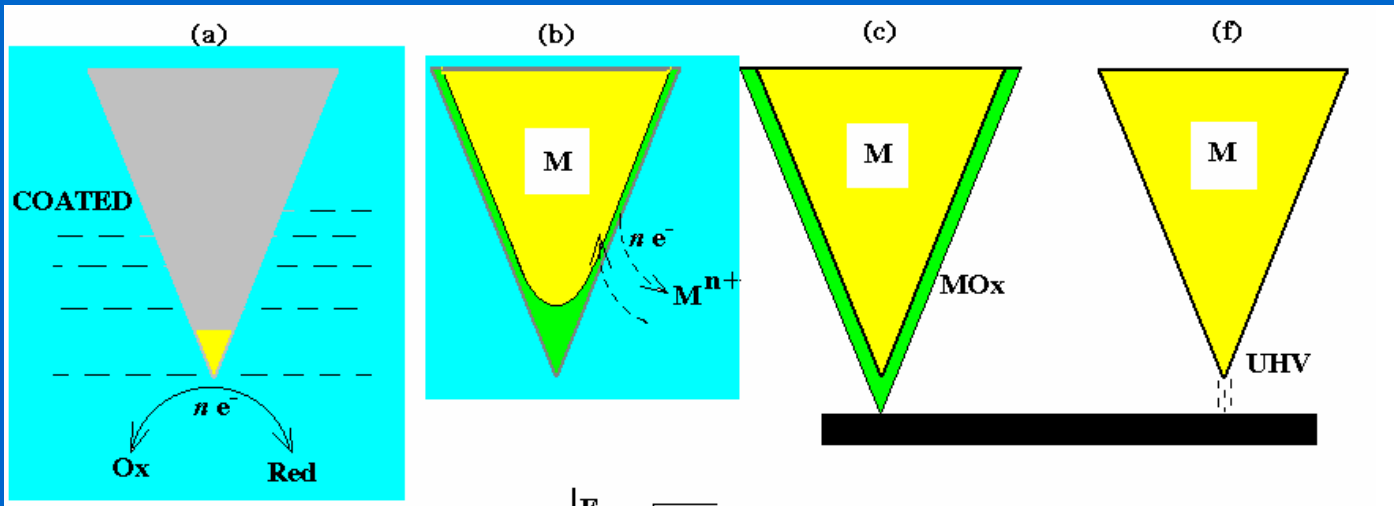
# EC STM: Detekce tunelových proudů při EC experimentu



# Vodivý hrot SPM v elektrolytu

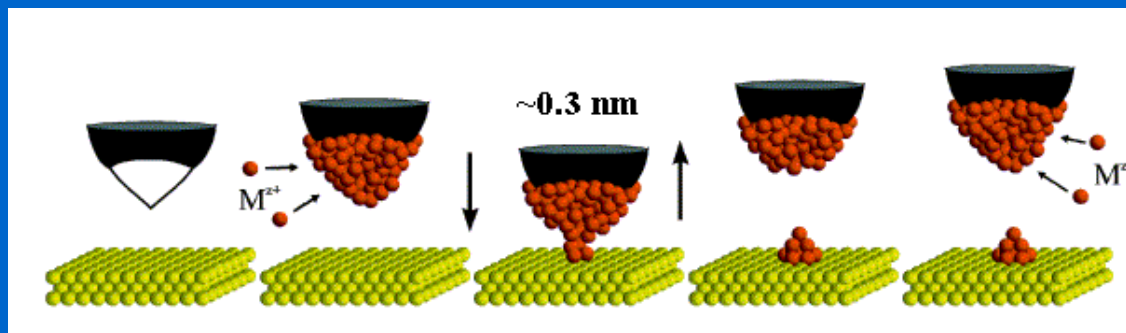
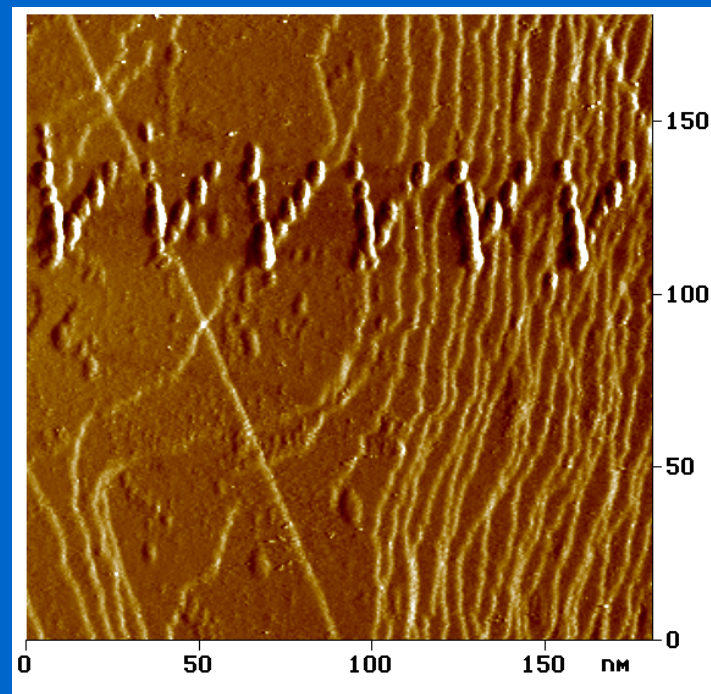
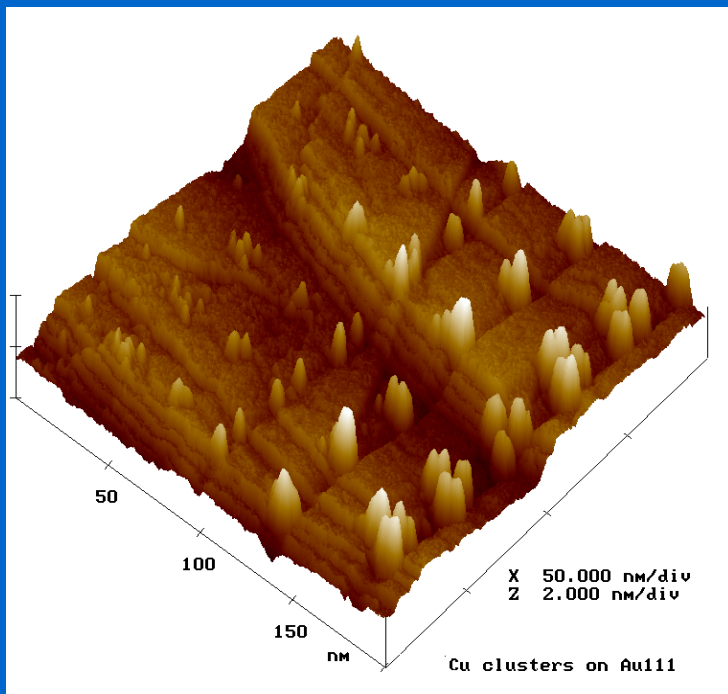


# Sonda EC STM

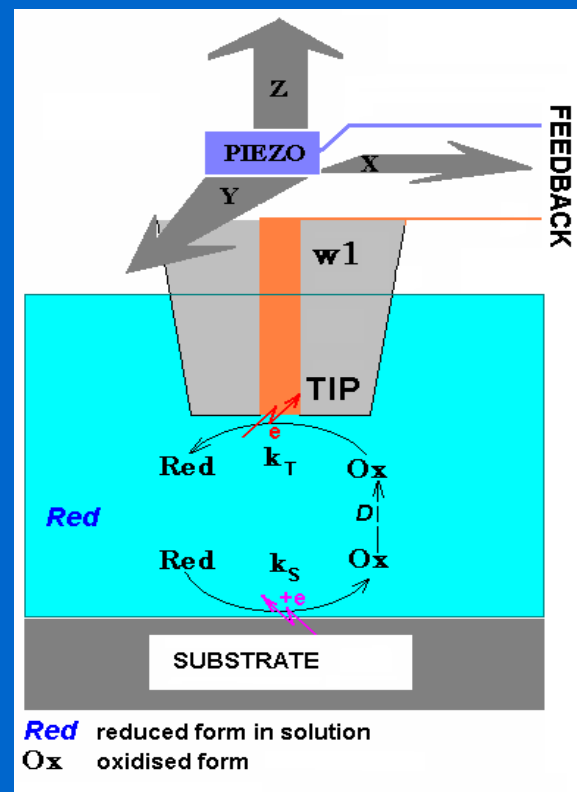
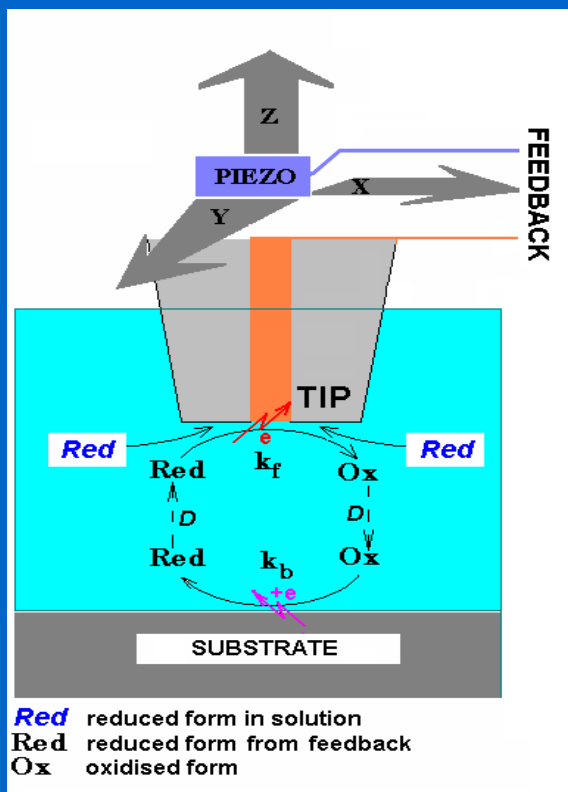


Voltammetry of Pt-Ir STM tip (polymer coated) in 0.1 M  $H_2SO_4$  (deoxygenated)  $v = 200 mV/sec$

# „Nanoprint“: nanočástice $\varnothing \sim 8$ nm, výška $< 1$ nm



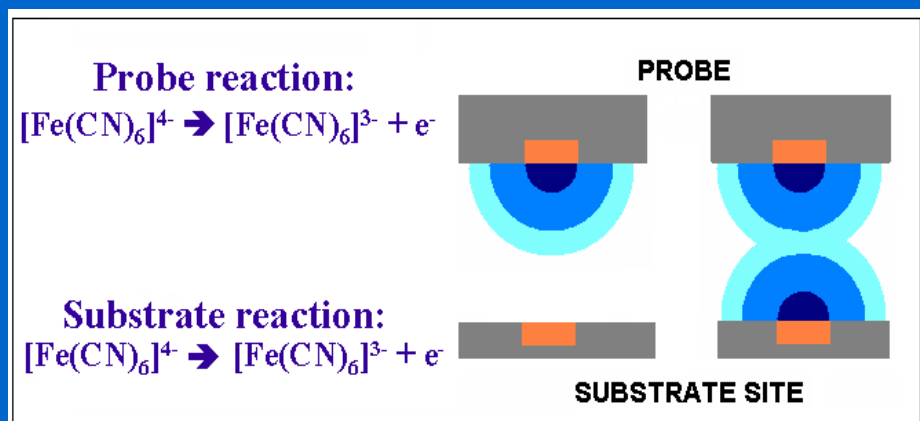
# Režimy SECM - detekce Farad. proudu zpětnovazebný detekční



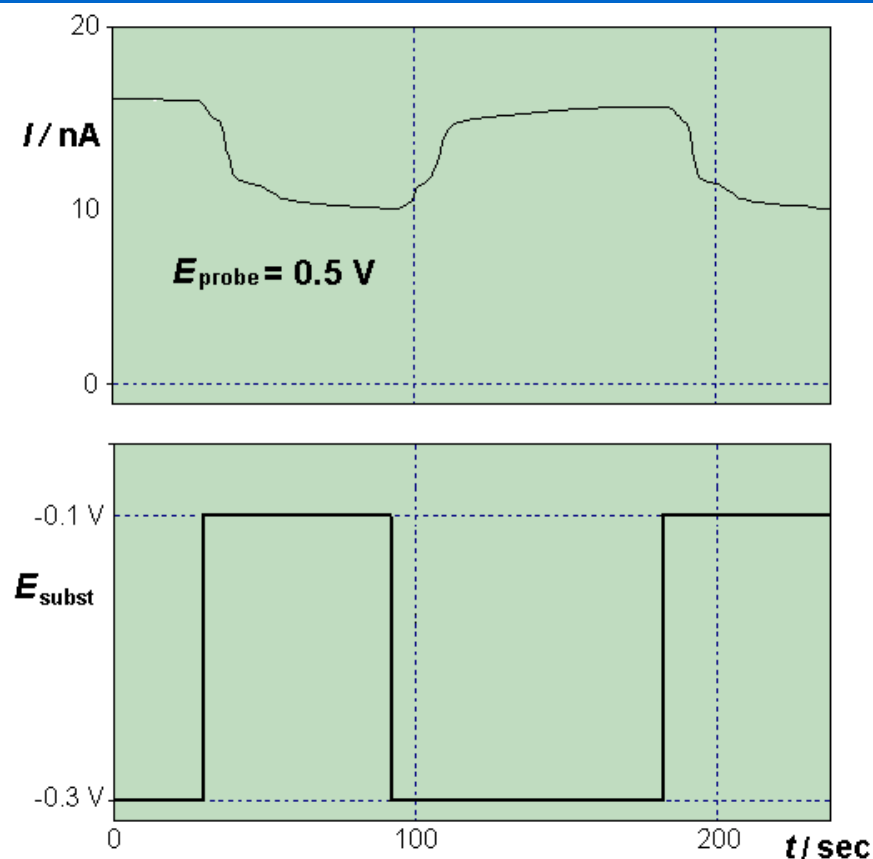
Hrot: generuje  
 Substrát: zpětná reakce  
 Detekce katalytické aktivity substrátu

Substrát: generuje  
 Hrot: detekuje

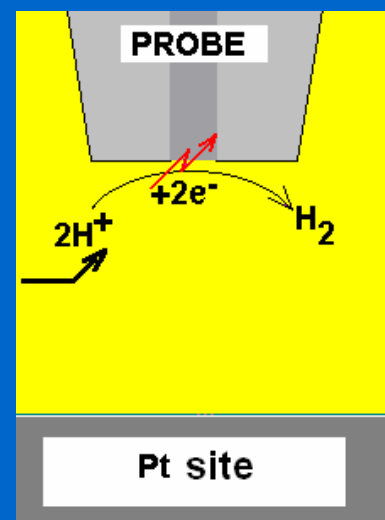
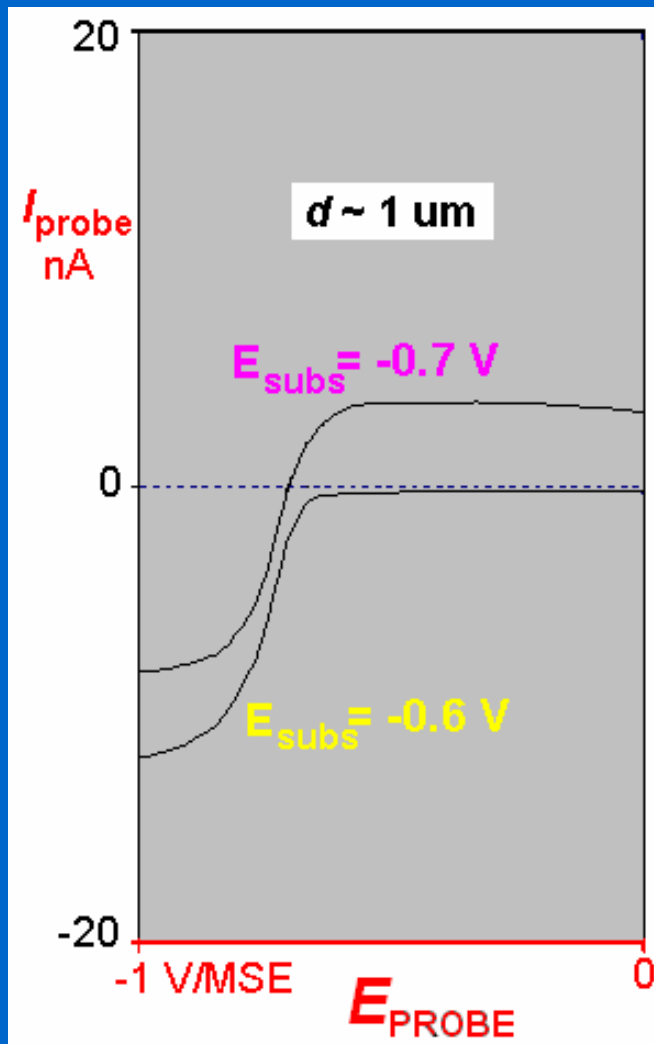
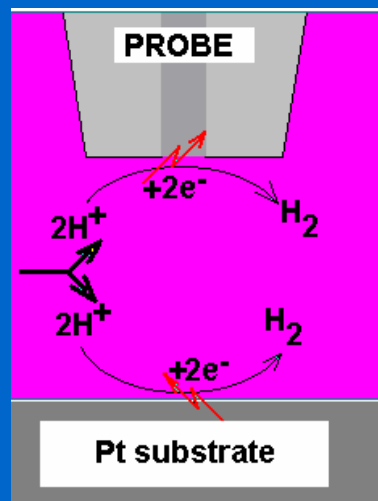
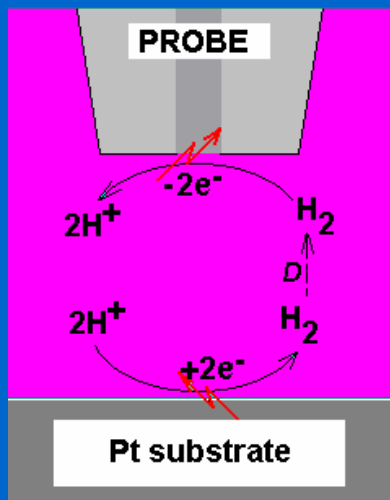
# SECM: Detekce pozice aktivního místa



Konkurenční reakce na aktivním místě.  
Vzdálenost sonda-aktivní místo  
 $d \sim 10^2 \text{ nm}$



# SECM detekce substrátově-specifické reakce identifikace aktivního místa (Pt nanočástice)





- 
- 
- 

# 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

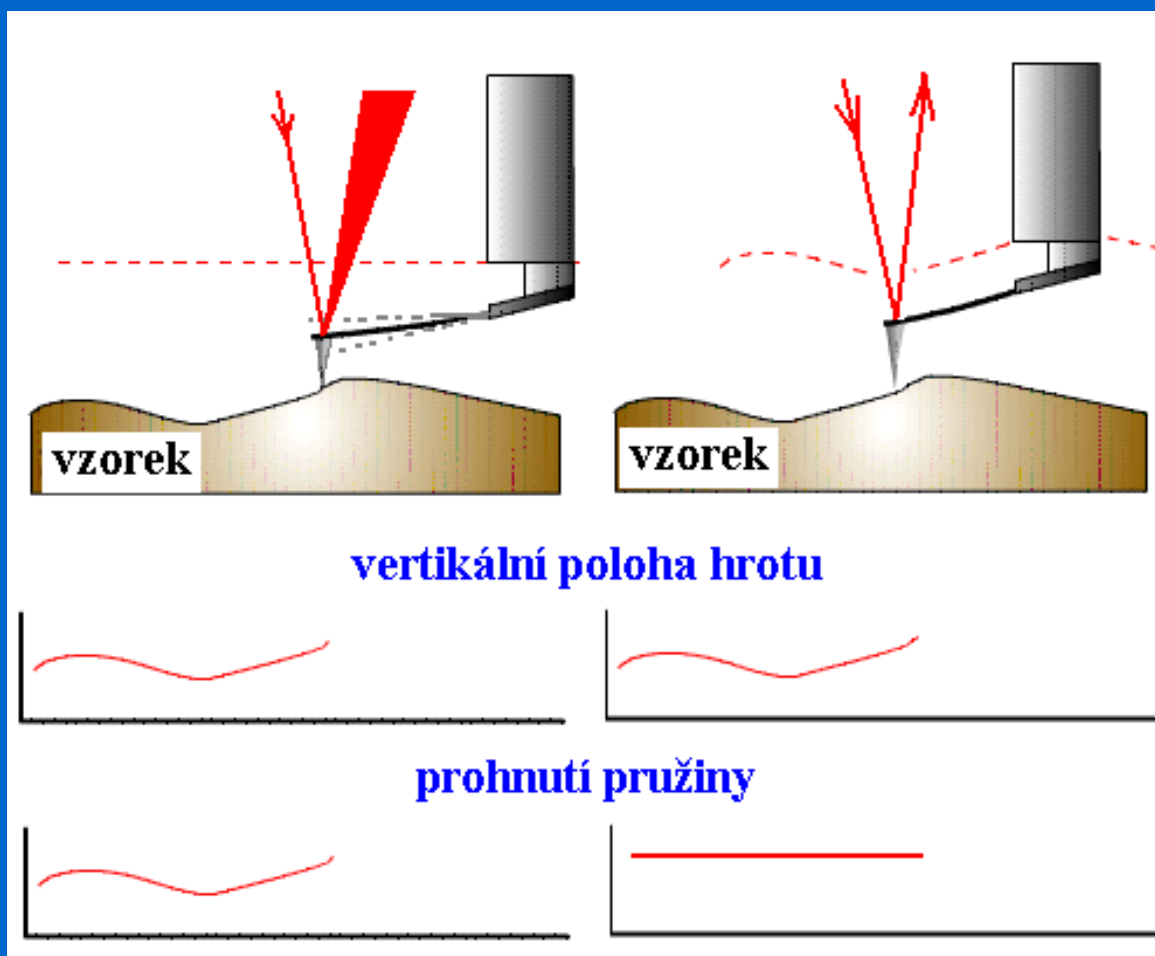
**EC AFM**

+ reakce přenosu náboje/záznam Farad.proudů,

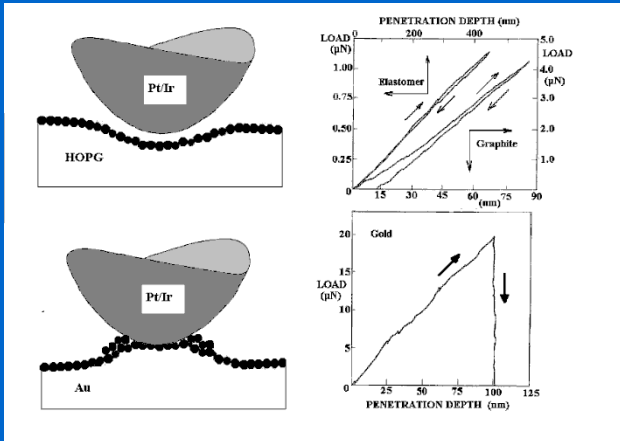
+ tip-assisted „elektro-lithografické“ techniky

+ detekce SECM

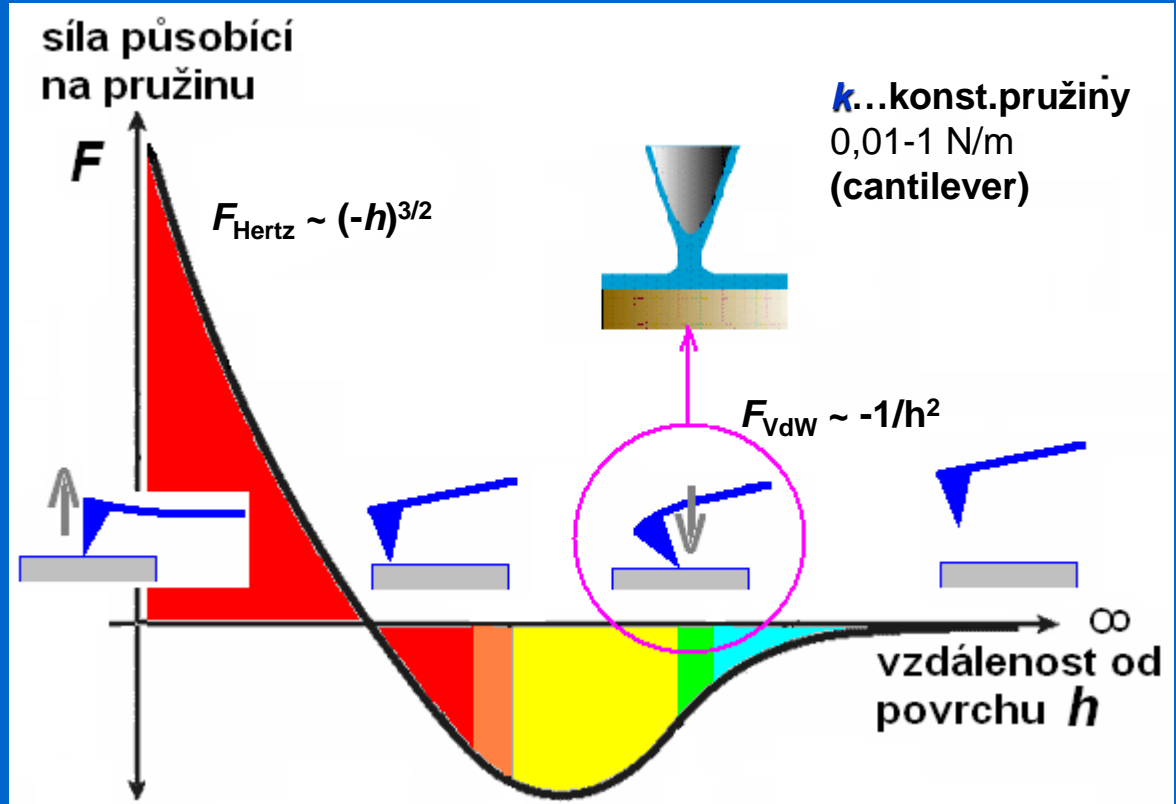
# AFM: Funkce



# AFM – silová křivka

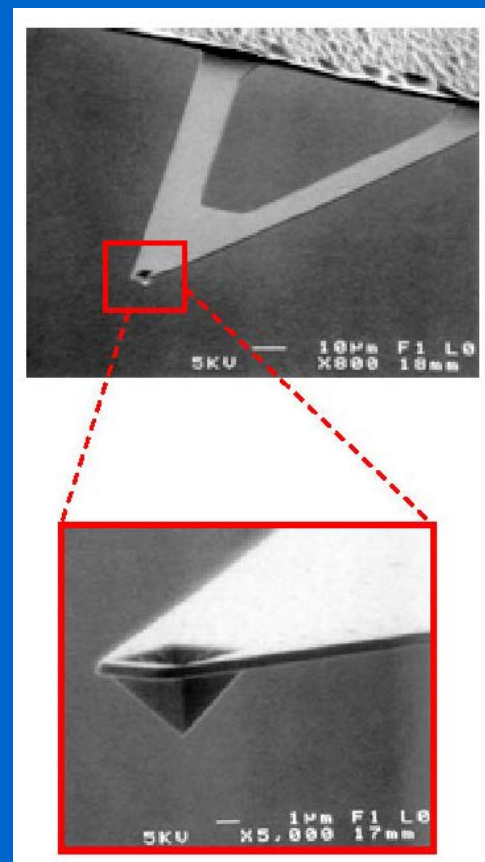
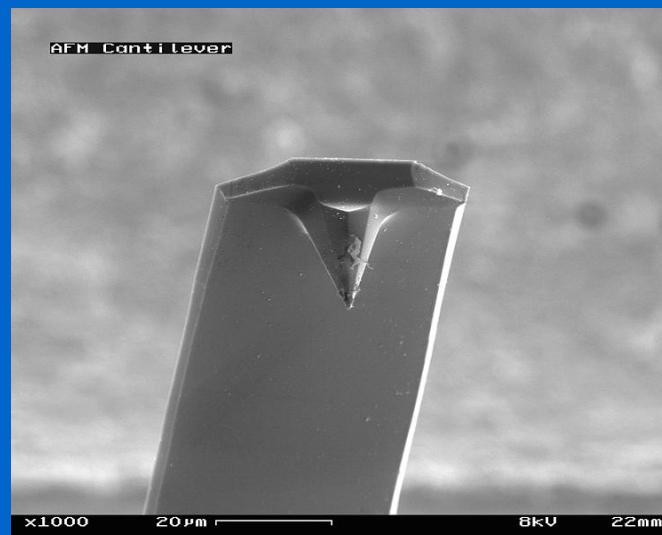
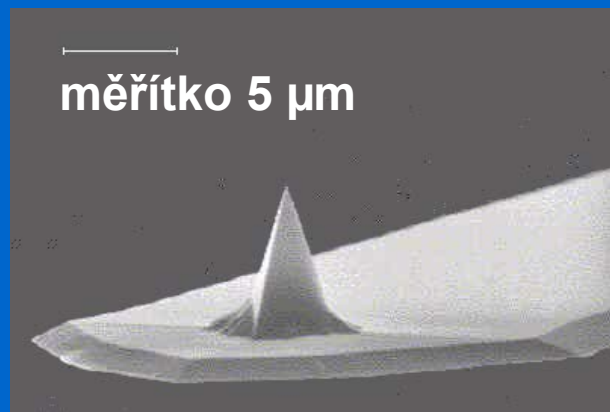


$F = -kz$  Hook



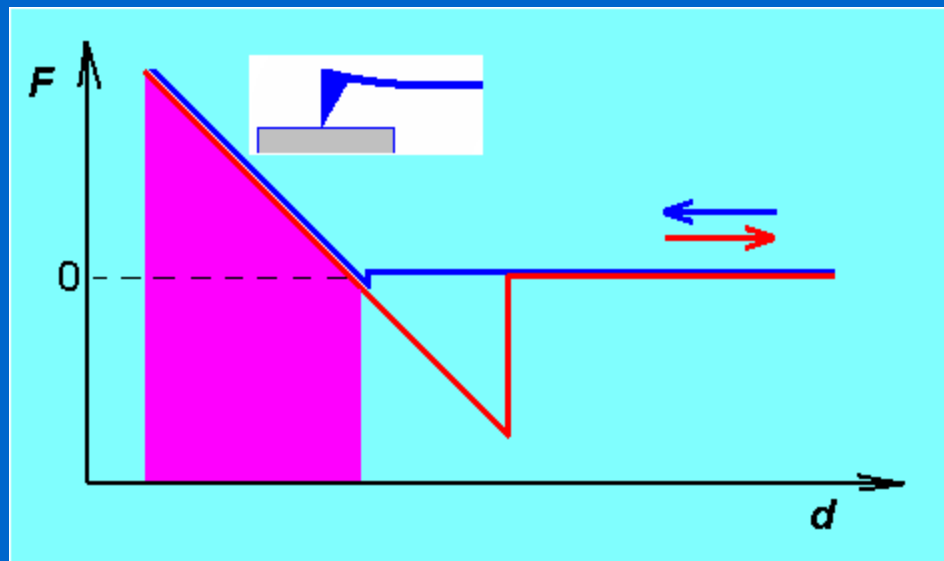
Režim: **kontaktní** **semikontaktní** **nekontaktní**  
 ( $F_{vw} 10^{-12} \text{ N}$ )

# AFM: hrot a pružina (*cantilever*)

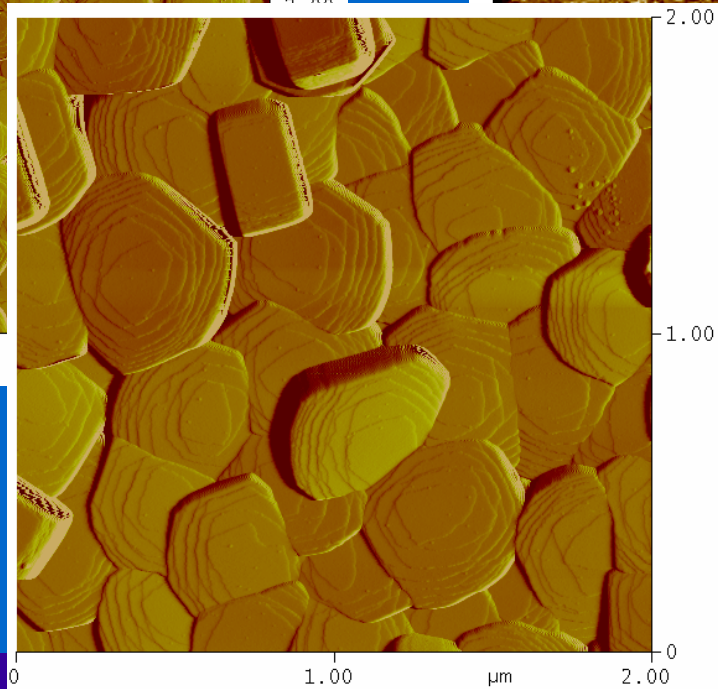
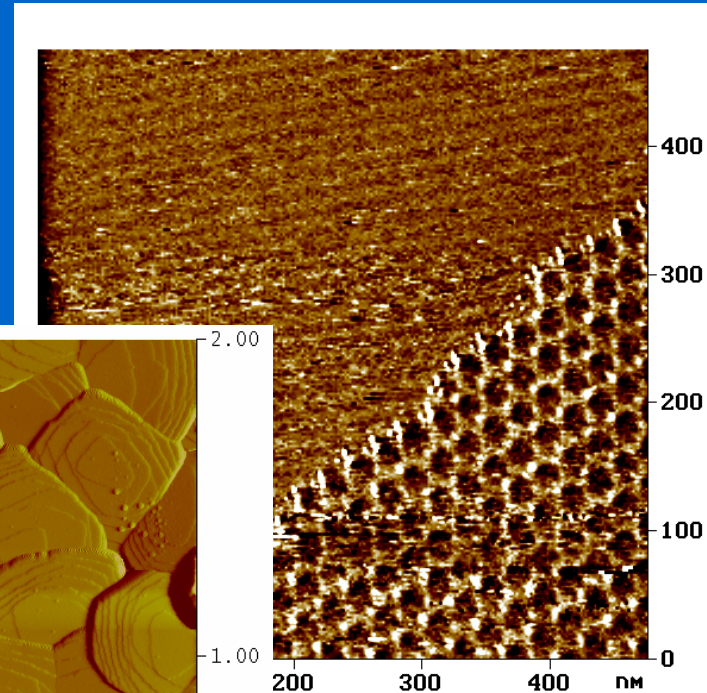
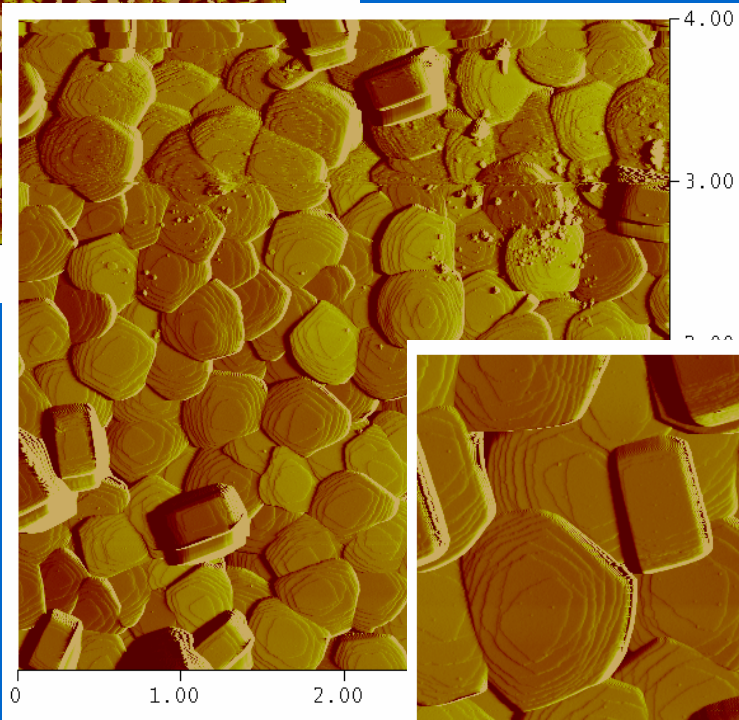
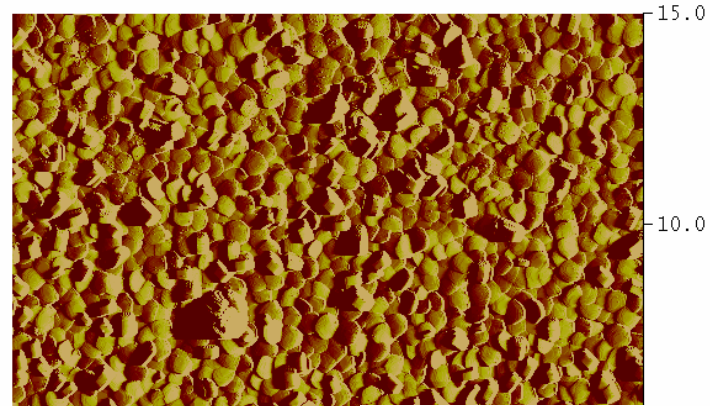


materiál hrotu a pružiny: Si, Si<sub>3</sub>N<sub>4</sub>

# AFM v oblasti repulsivních sil: Kontaktní režim

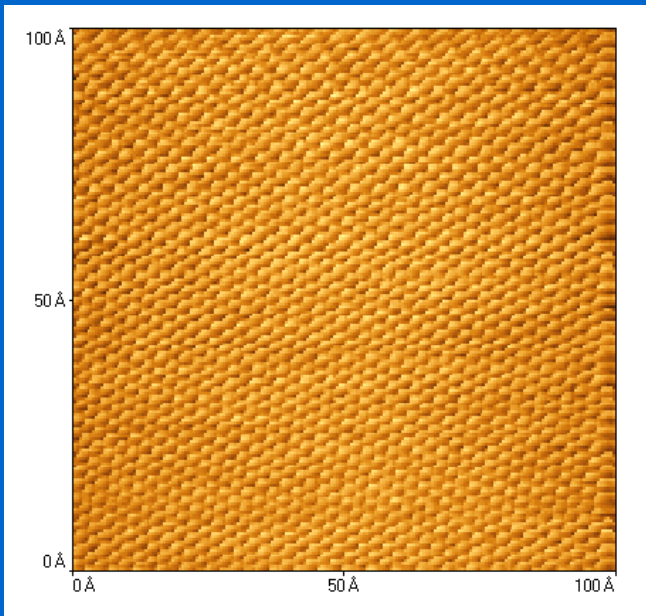


# AFM zobrazení: Kontaktní režim

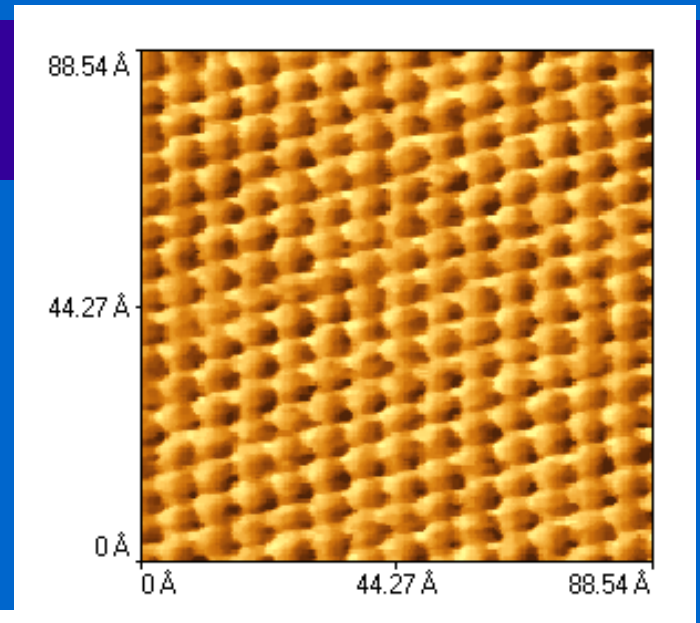


Krystaly zeolitu

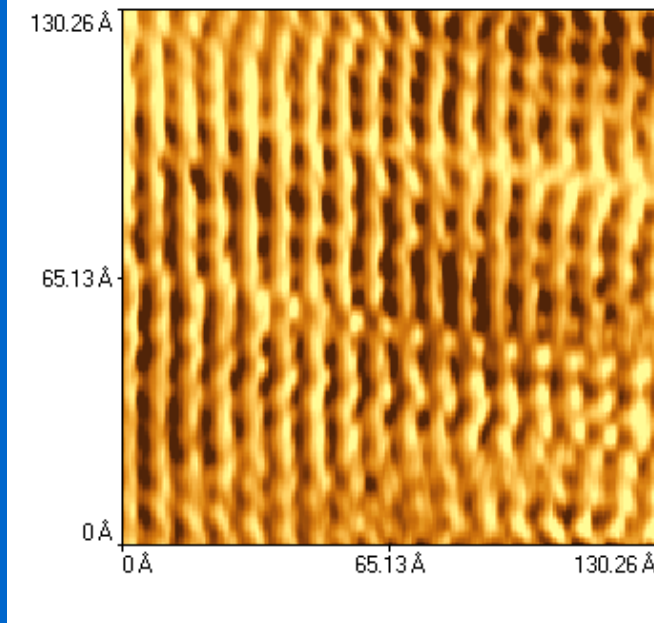
# AFM zobrazení: kontaktní režim



grafit



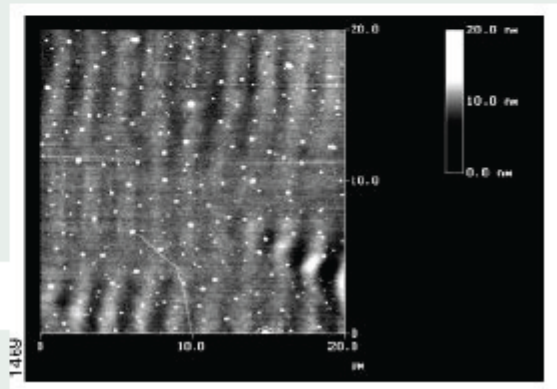
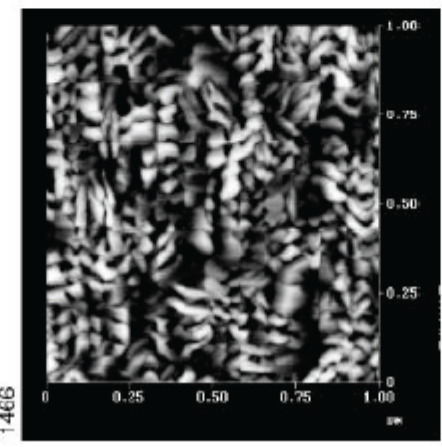
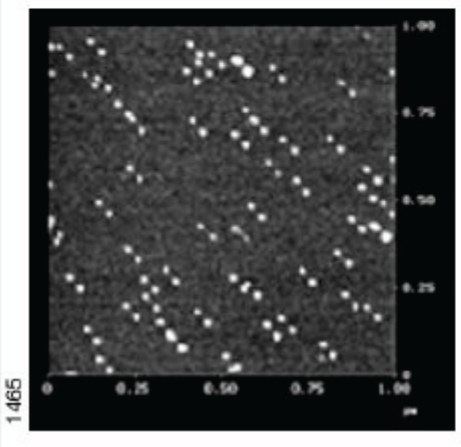
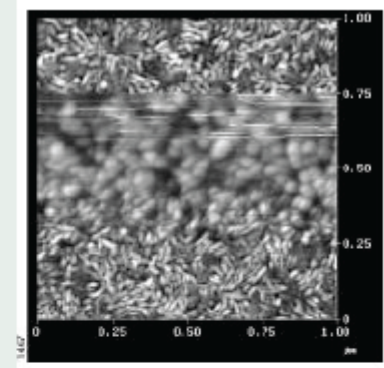
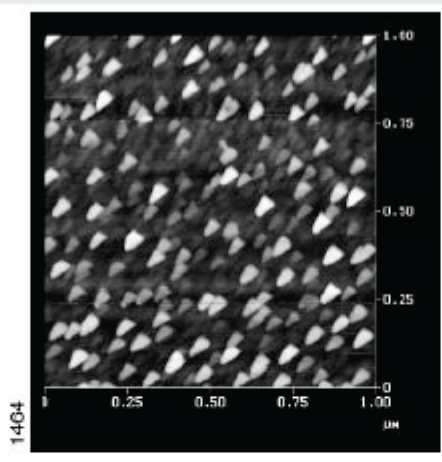
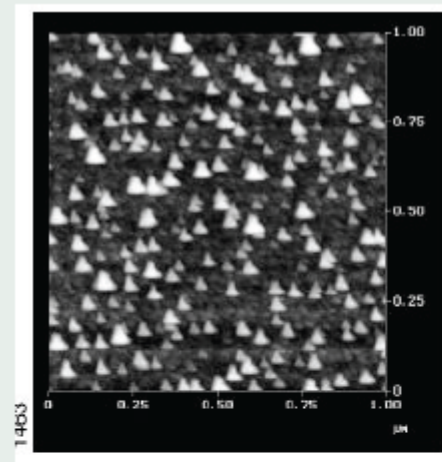
slída



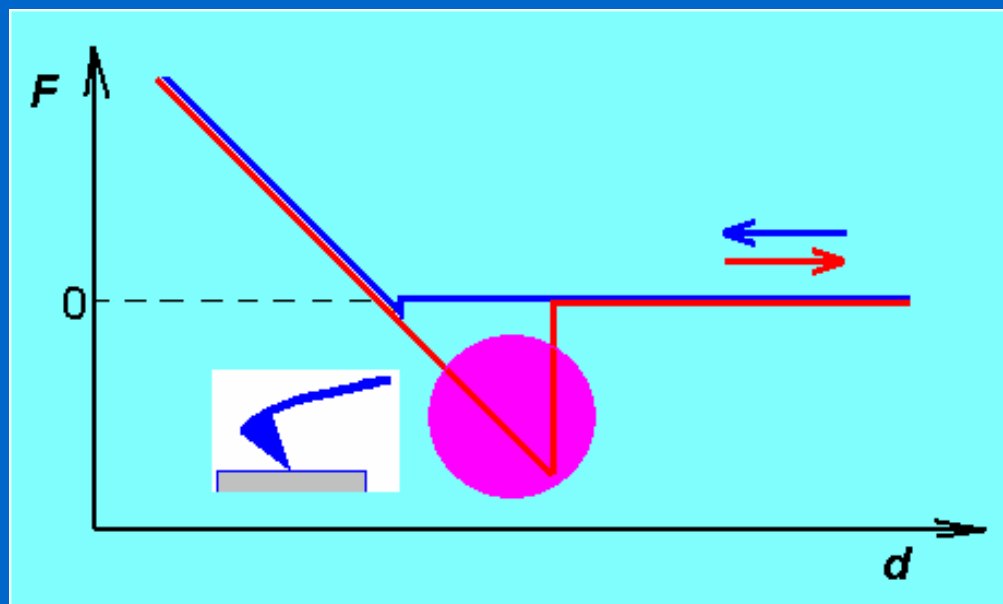
Orientované  
molekuly Teflonu



# AFM: artefakty

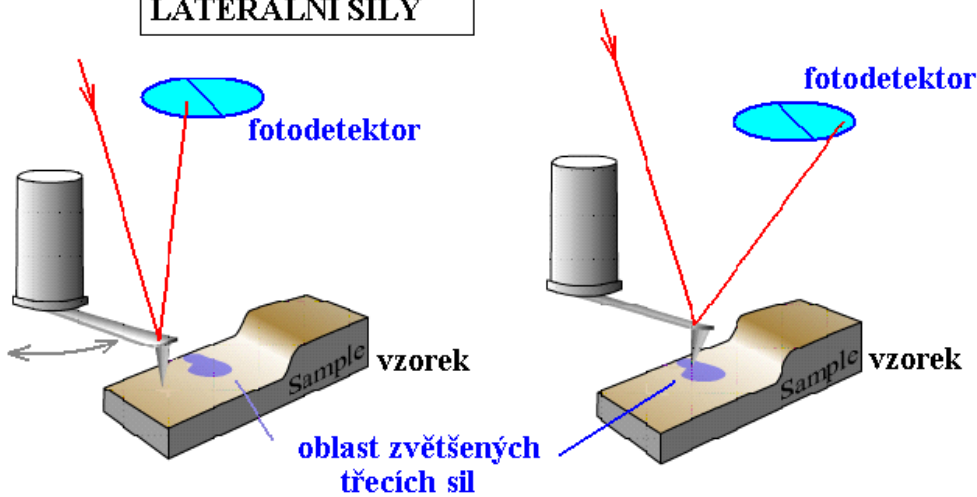


# AFM: Přitažlivé síly- adheze, vazebné interakce

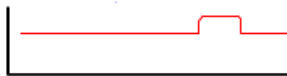


# AFM adhesivních sil: laterální (LFM)

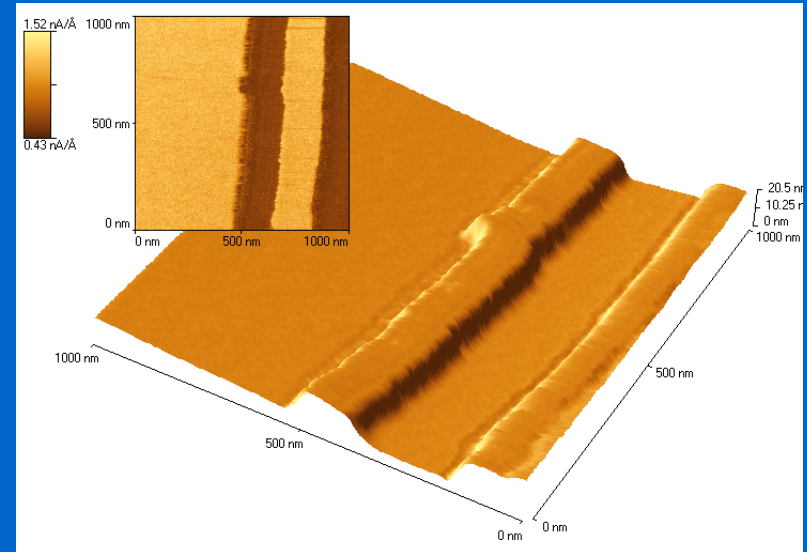
KONTAKTNÍ REŽIM  
LATERÁLNÍ SÍLY



úhel překroučení  
pružiny

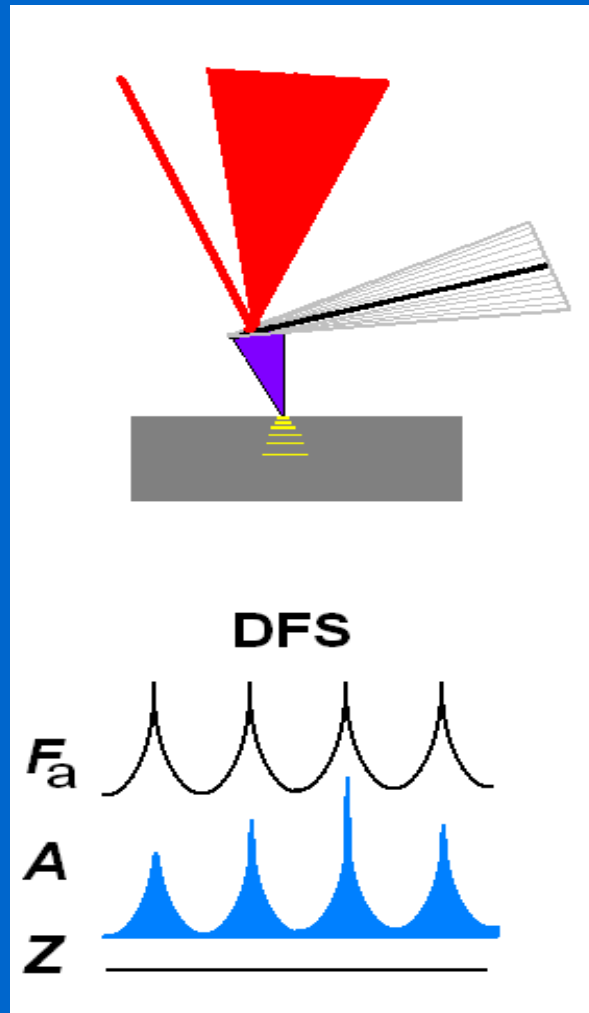


třecí síla



Teflon na skle: AFM  
-topografie  
-rozložení frikčních sil

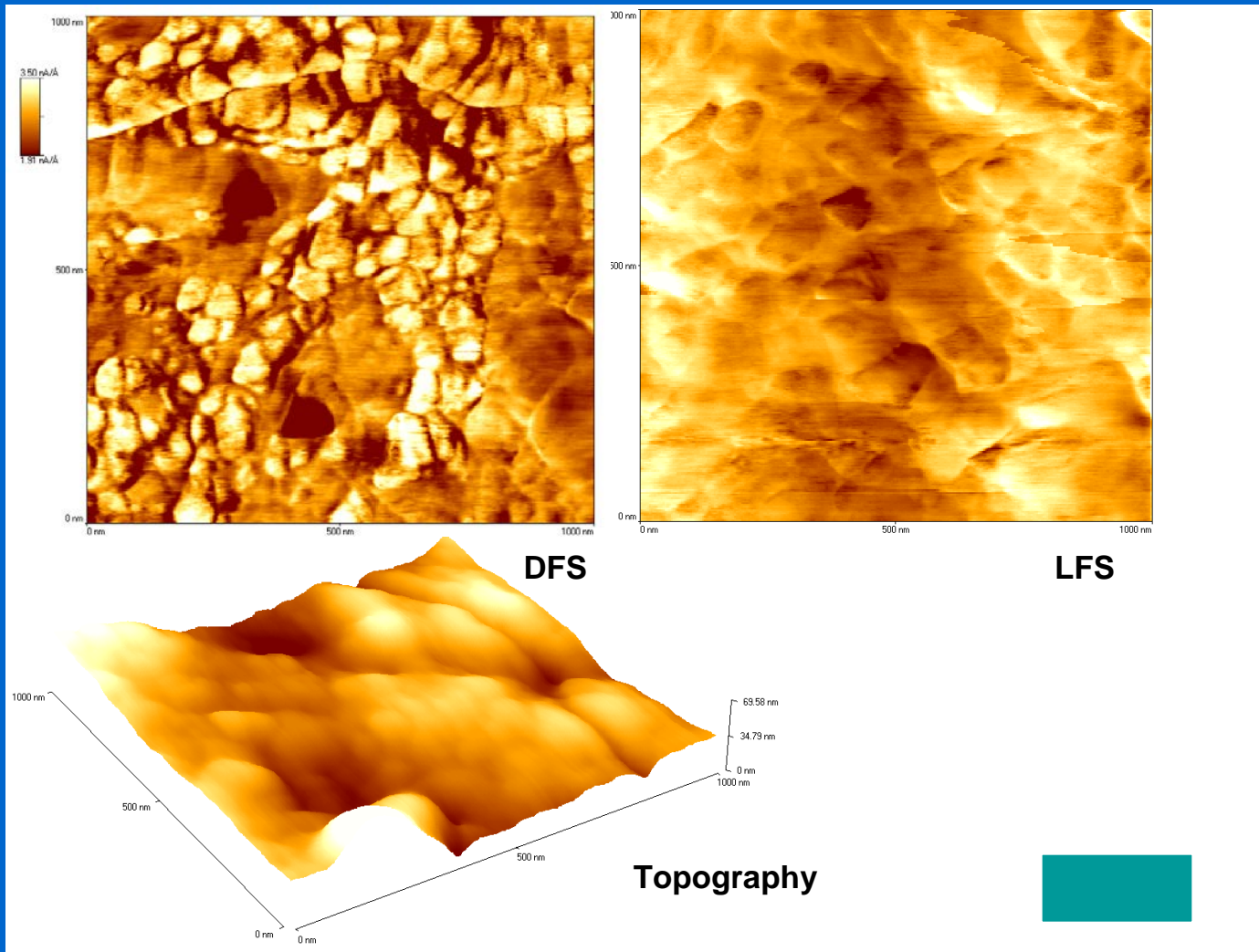
# AFM – Dynamická silová spektroskopie (DFS)



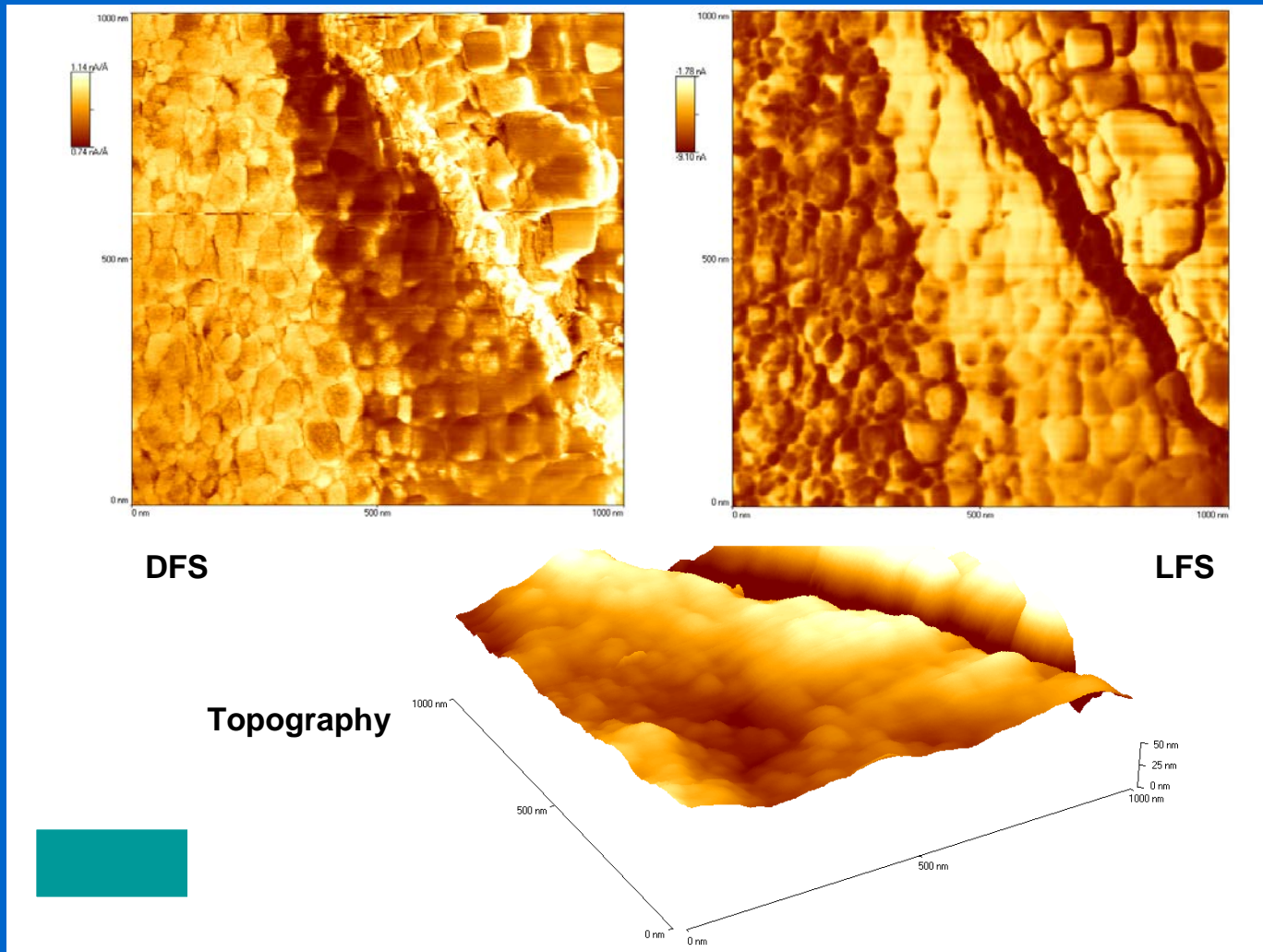
Disipace energie:  
útlum, elasticita, plasticita  
 $Y_M$

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

# AFM materiálová analýza povrchu Zr/ZrO<sub>2</sub>



# AFM materiálová analýza povrchu Zr/Nb/ZrO<sub>2</sub>

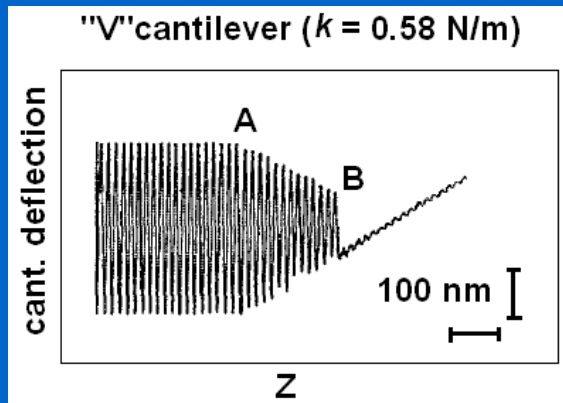
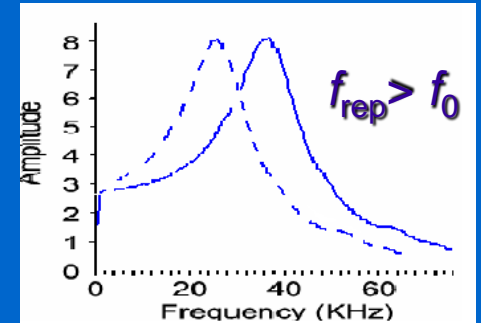
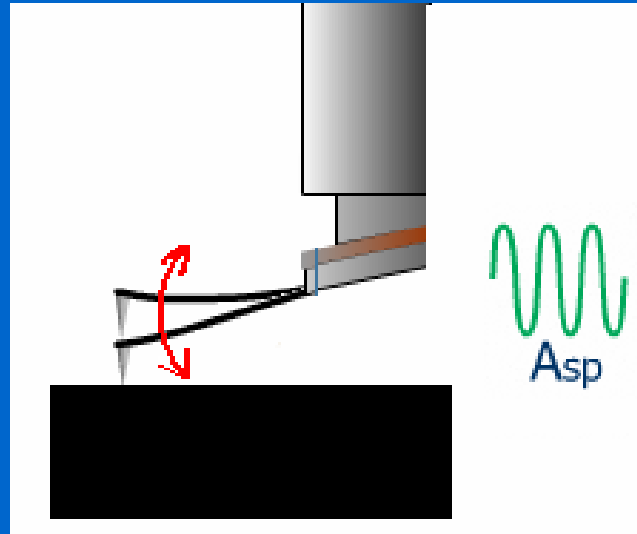


# Semikontaktní režim (tapping)

Akustic./mgt. buzení

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

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



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

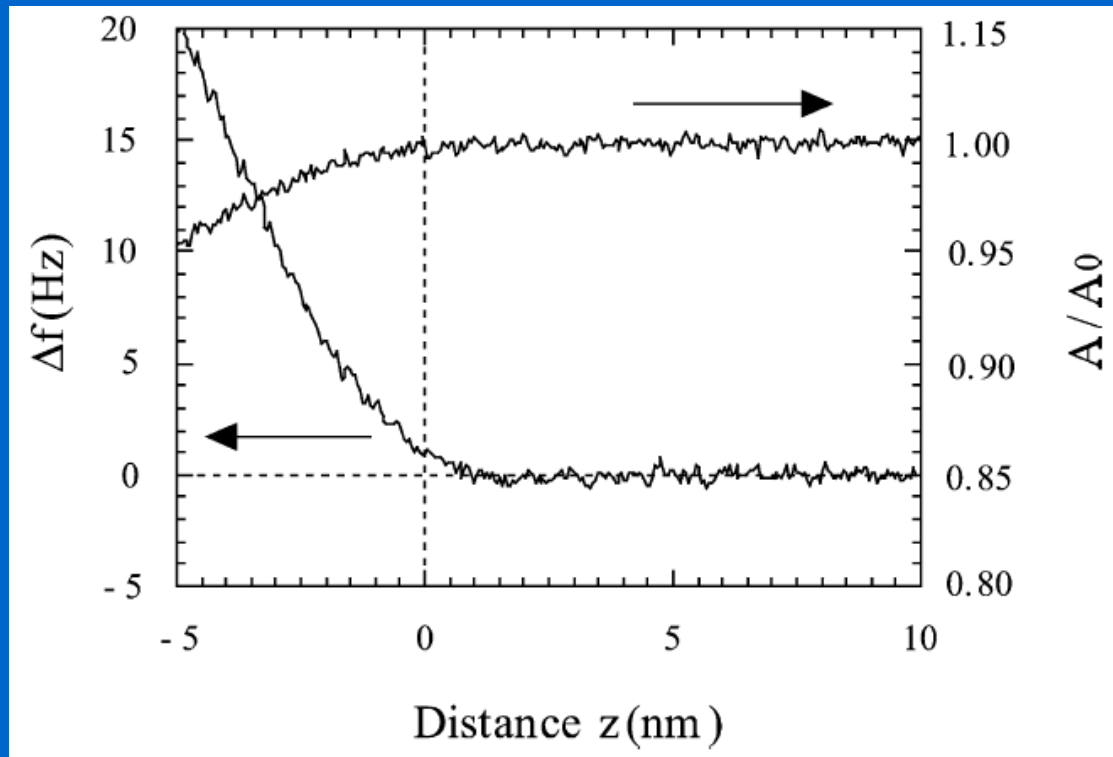
$$\omega_0 = \sqrt{k/m}$$

Hook

disipace e.

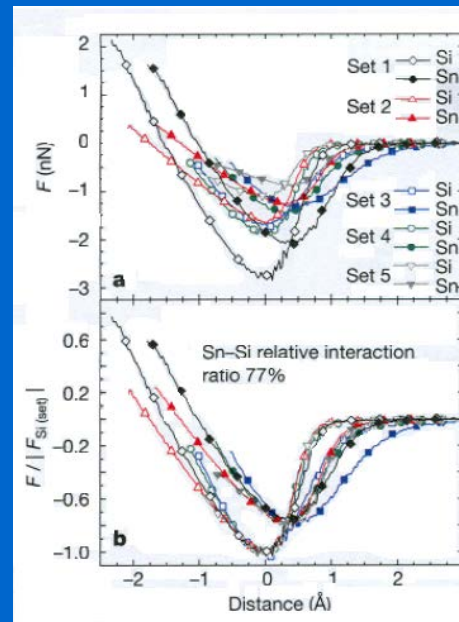
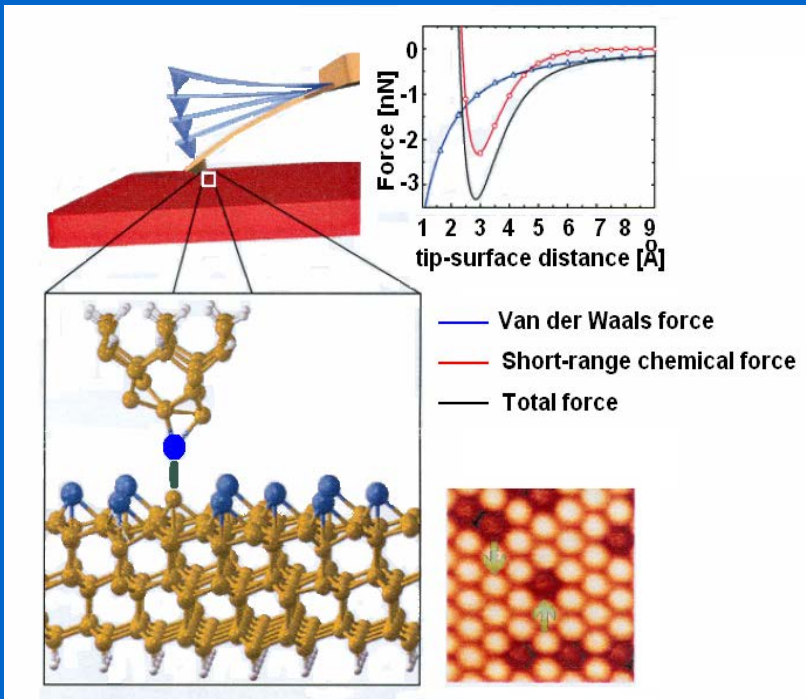
Tip-Surf. interakce

## Semikontaktní režim (tapping)





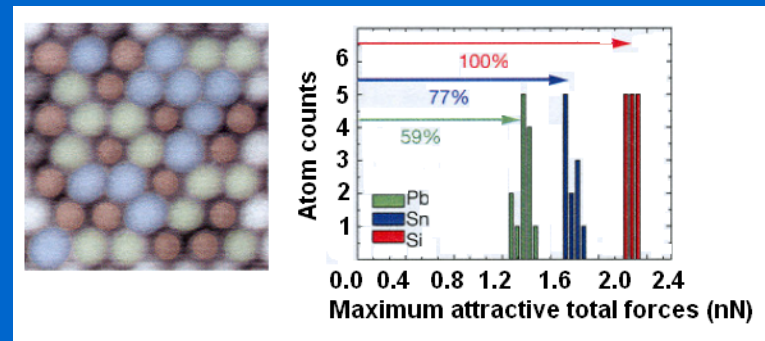
# Semikontaktní režim: Chemická identifikace atomů (UHV)



silová křivka  
před normalizací

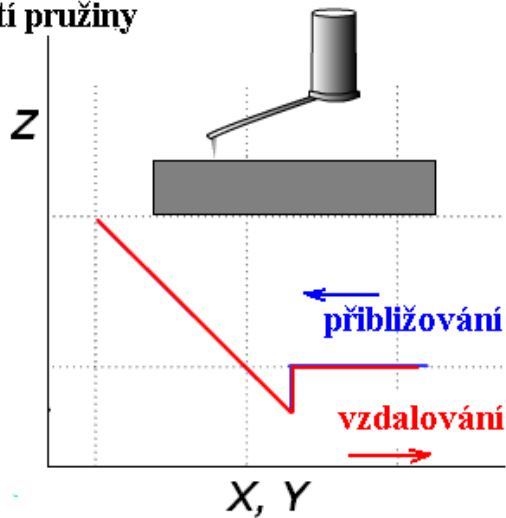
křivka normalizovaná  
na maximum interakce  
substrát-hrot

Dynamic Force Spectroscopy  
silová spektroskopie  
sil blízkého dosahu – chemické interakce

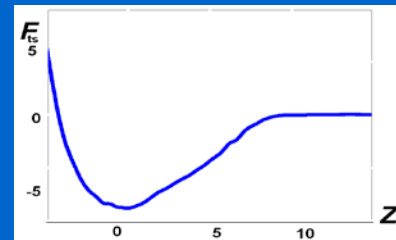
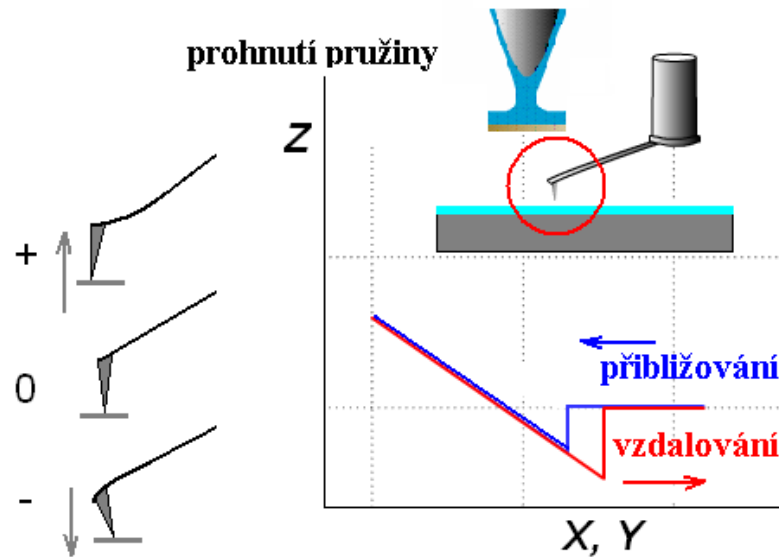


# AFM adhesivních sil axiální

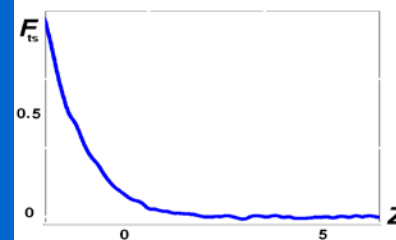
prohnutí pružiny



prohnutí pružiny

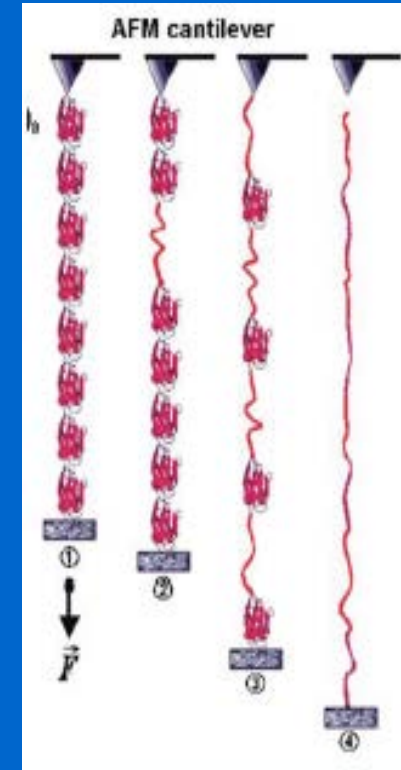
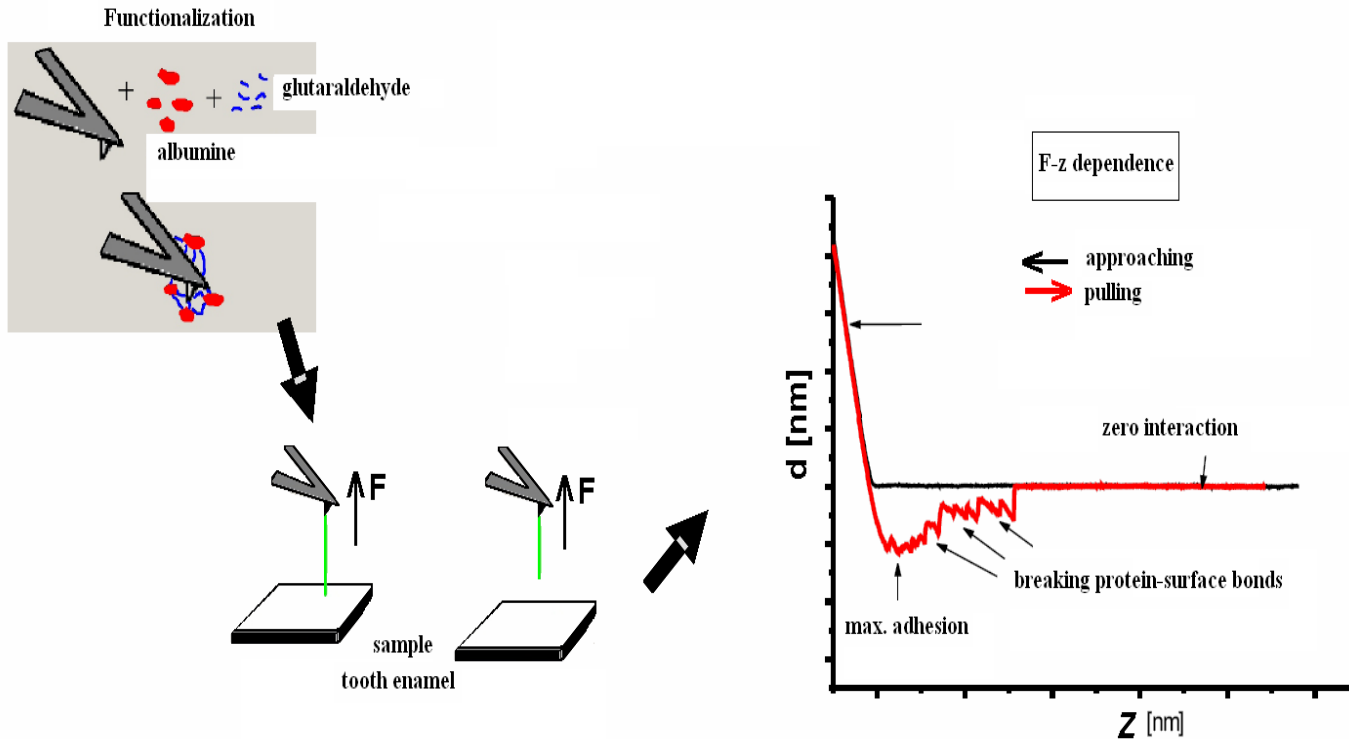


$F_{ts}(Z)$   
(Si/SiO<sub>2</sub>)/vzduch



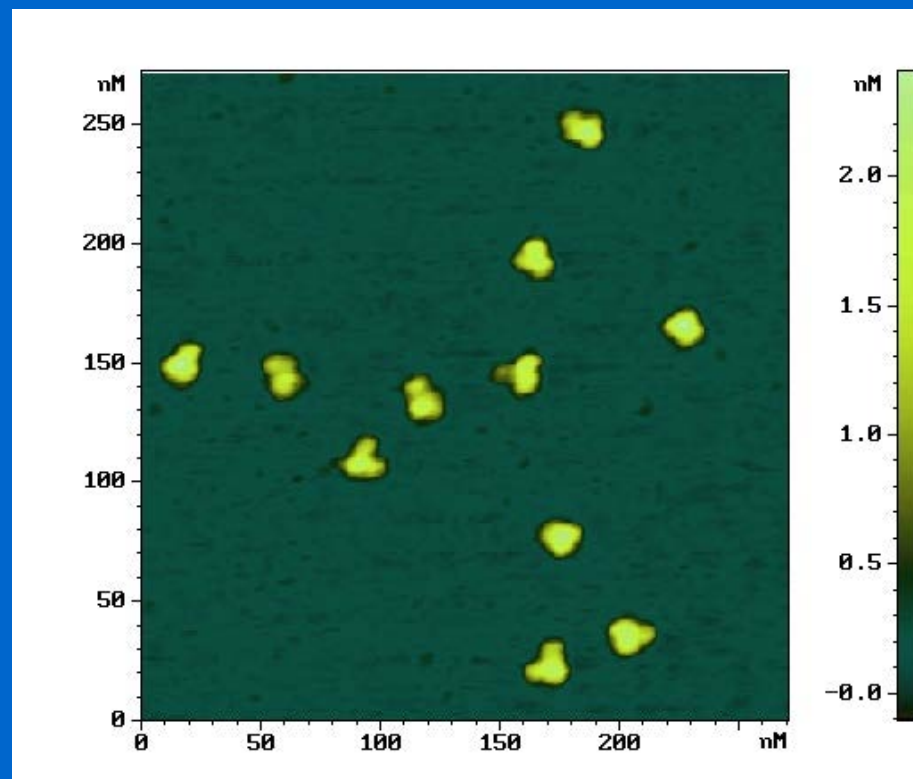
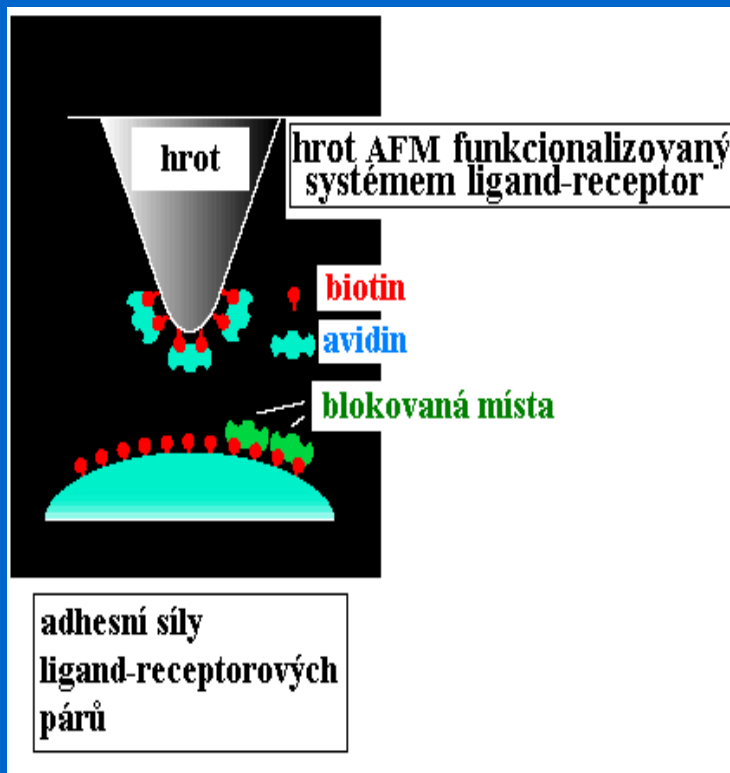
voda

# 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]

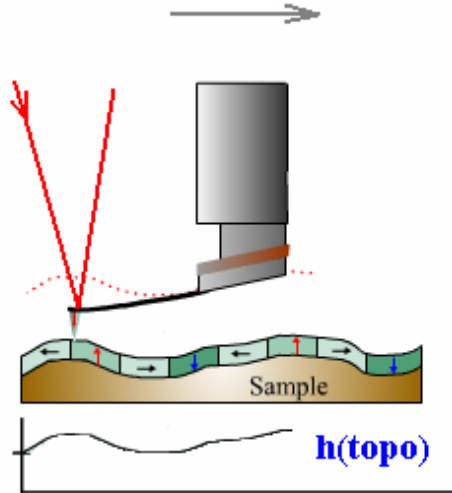
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# AFM: bezkontaktní režim

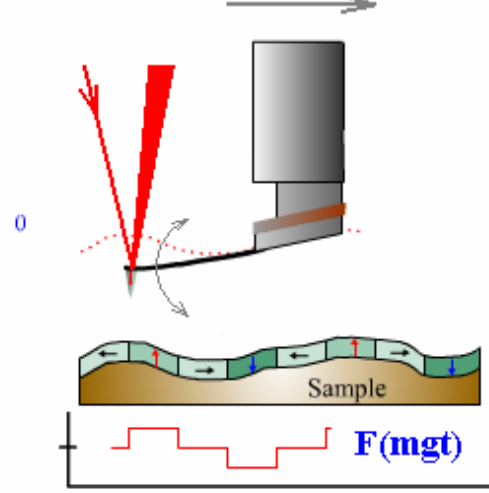
# Bezkontaktní AFM: Mikroskopie magnetických sil Magnetic Force Microscopy

1. topography

2. mag. forces

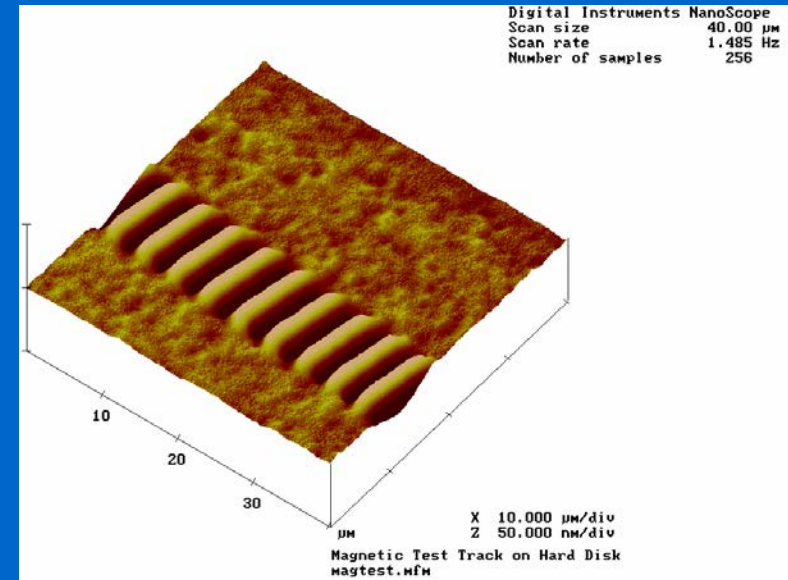


van der Waals. forces  
(semicontact)



noncontact imaging

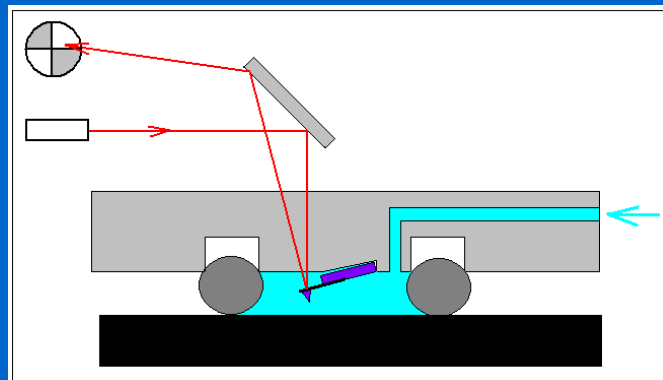
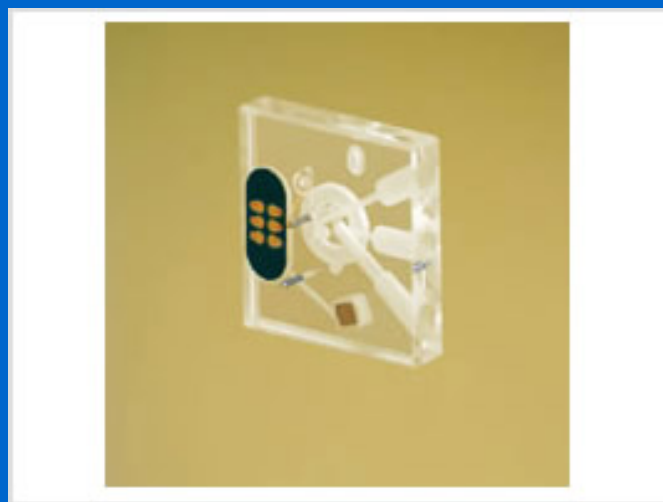
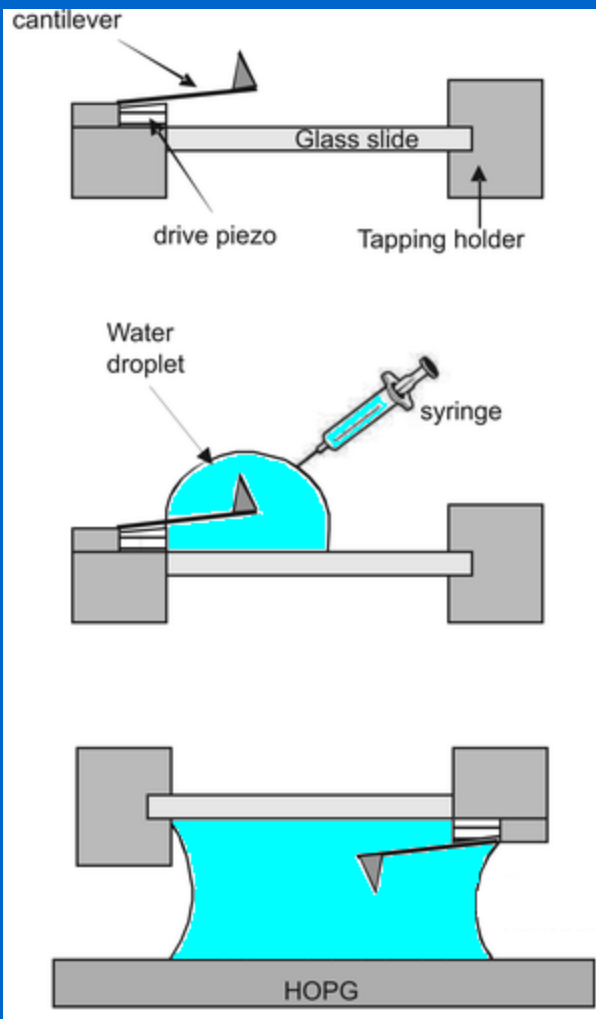
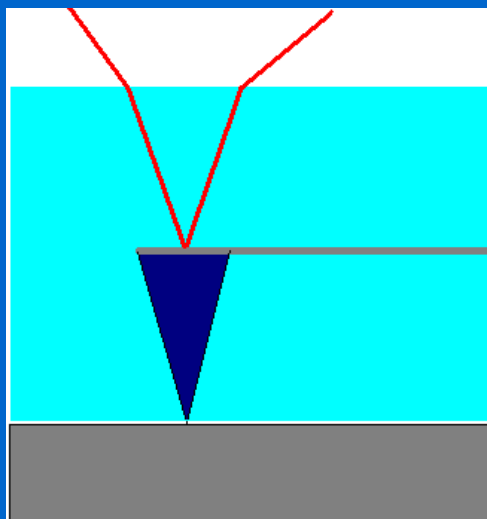
NT-MDT



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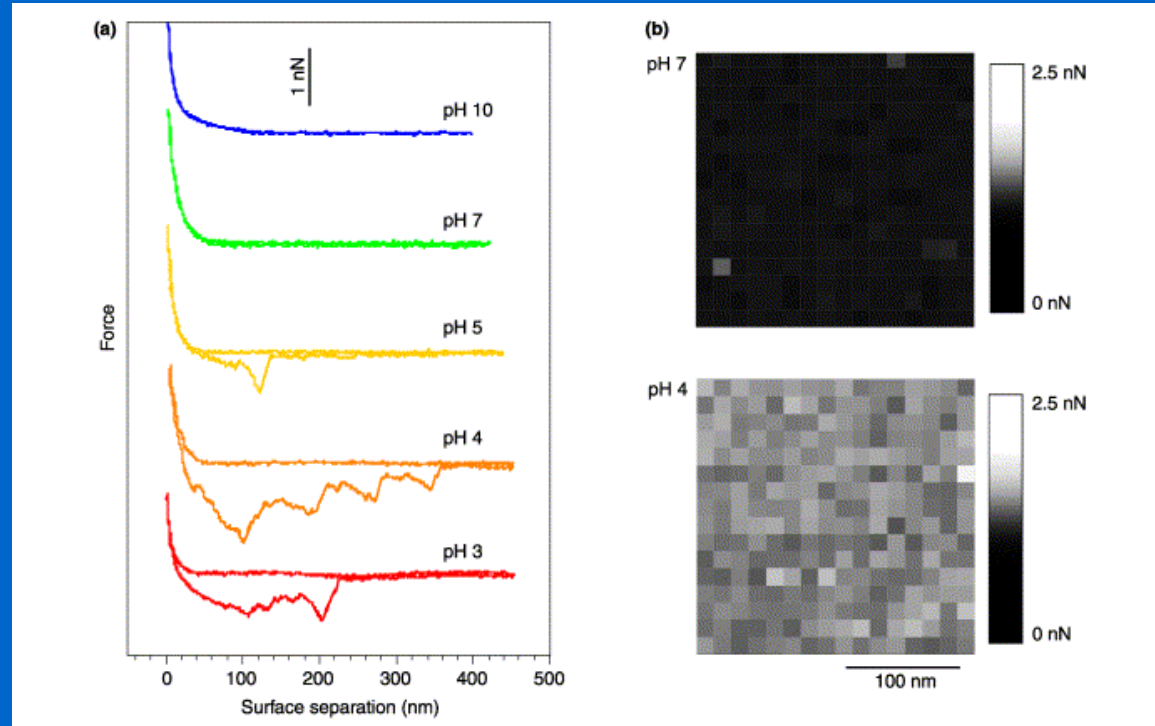
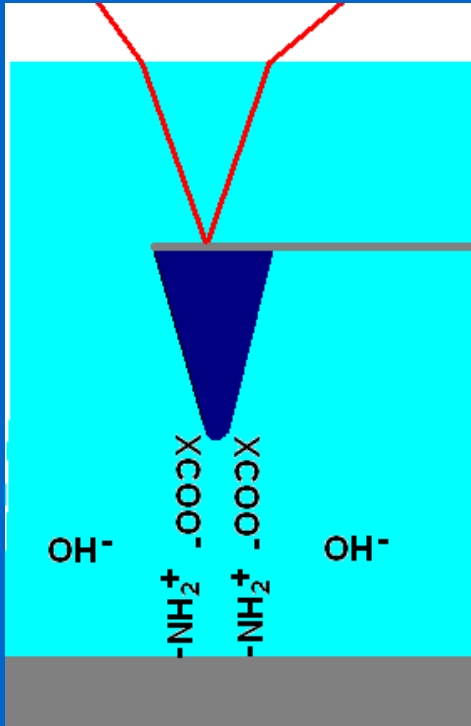
# Mikroskopie atomárních sil (AFM) v kapalinách

# AFM v kapalině



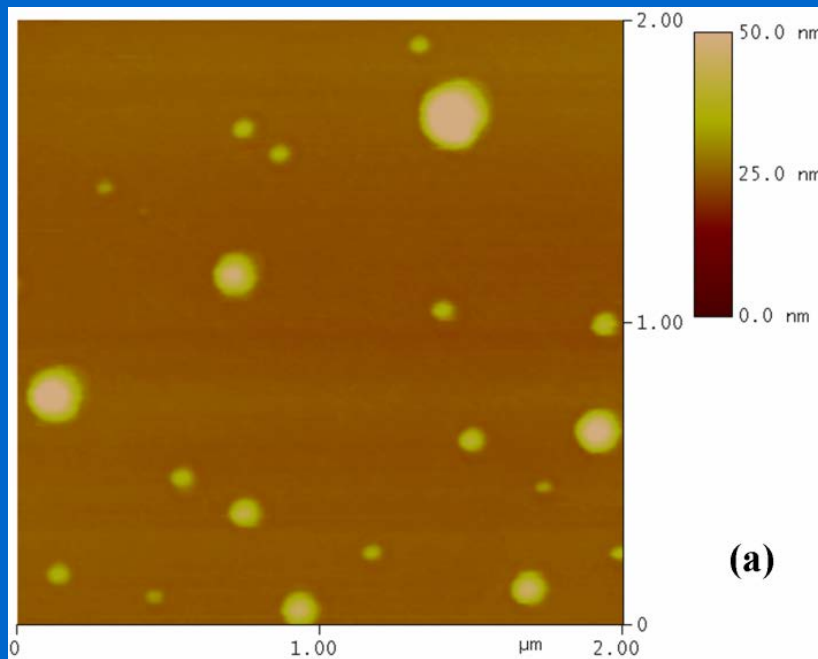


# AFM adhesivních sil - axiální (semikontaktní režim *in situ*)



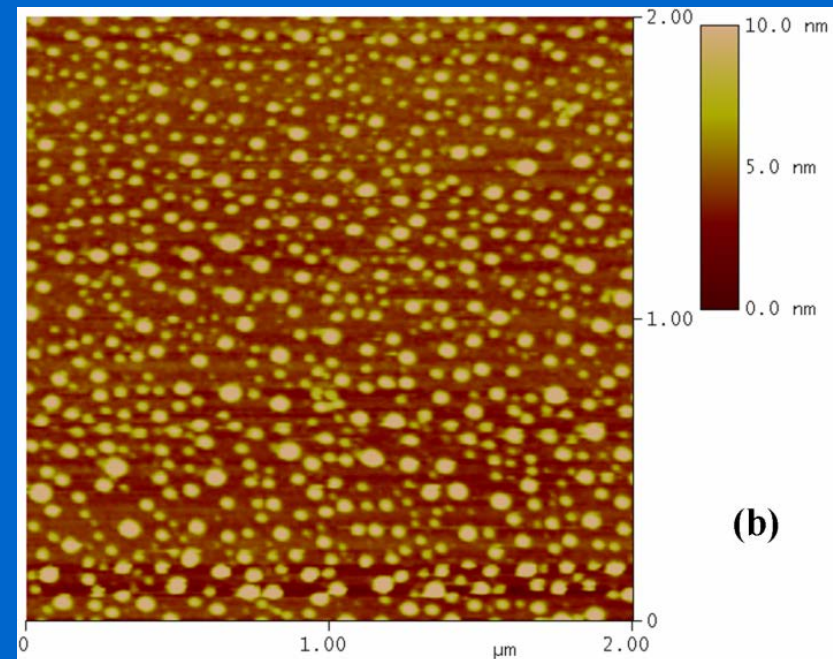
„Break-up“ adhesivní síly na povrchu buněčné membrány  
*Saccharomyces cerevisiae* při změně pH

# Nanobubliny na mezifázi kapalina/pevná látka



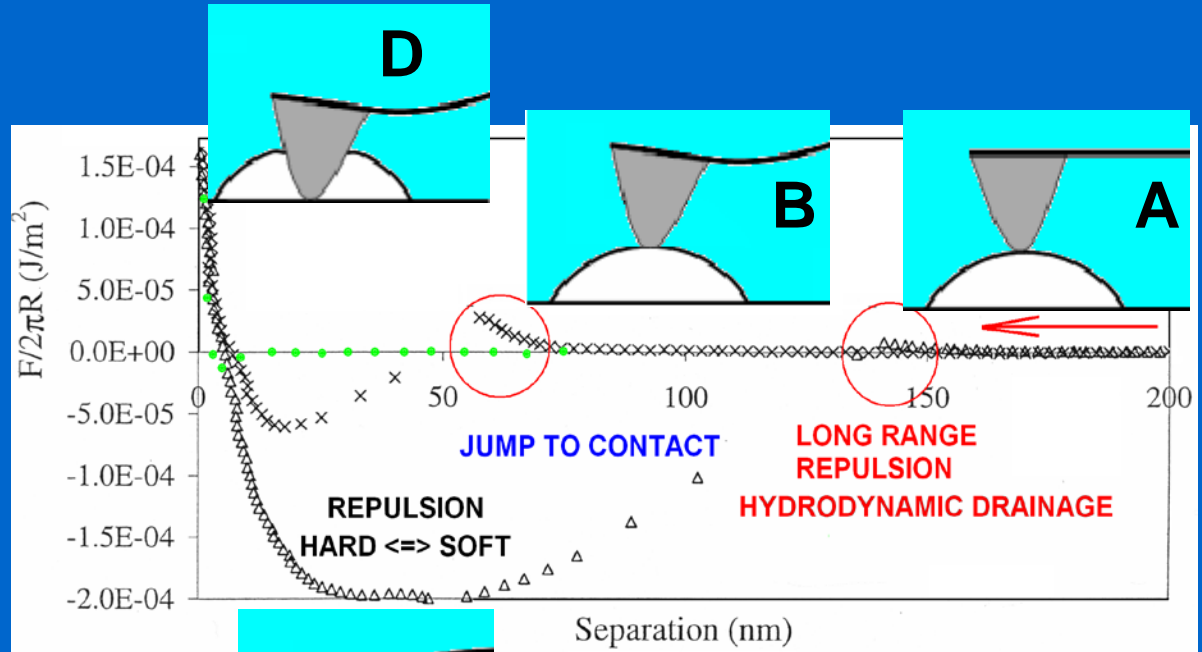
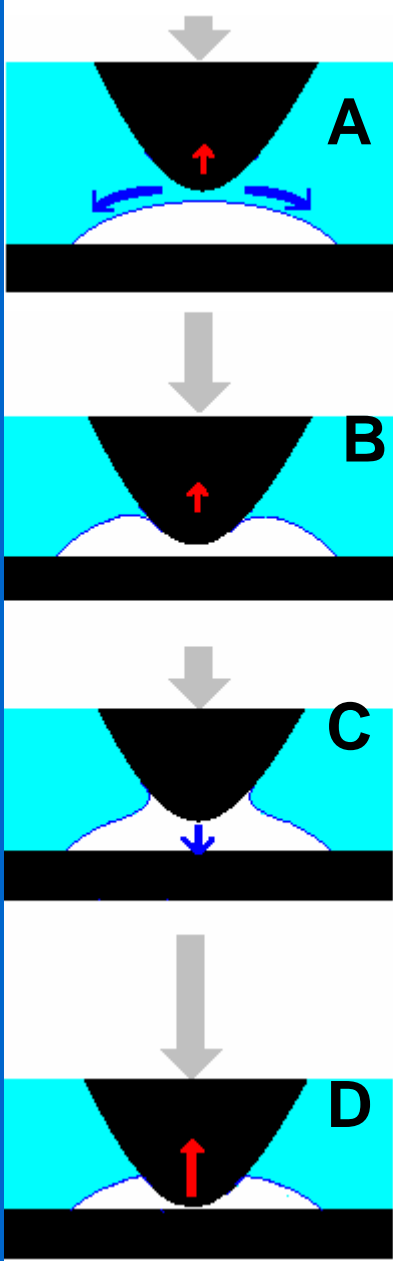
10 %

pokrytí



90 %

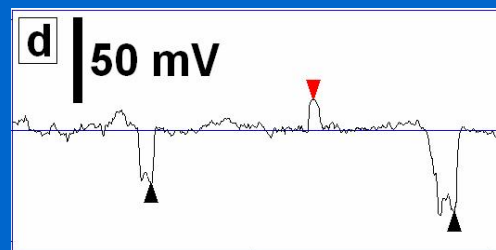
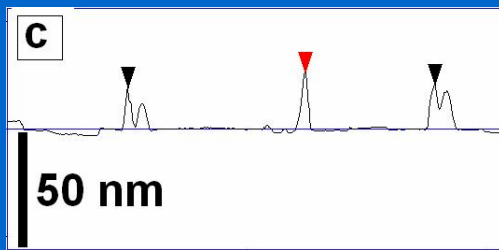
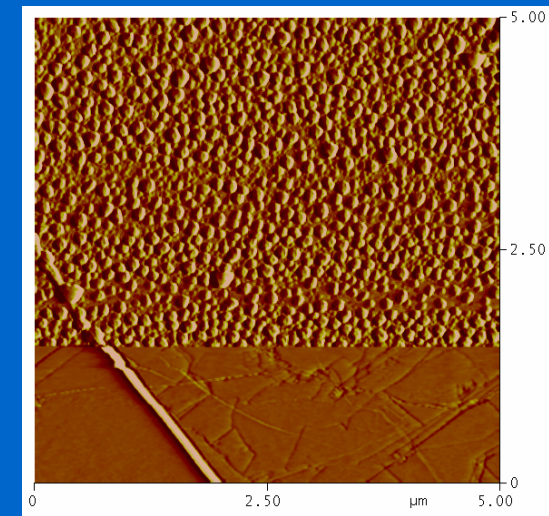
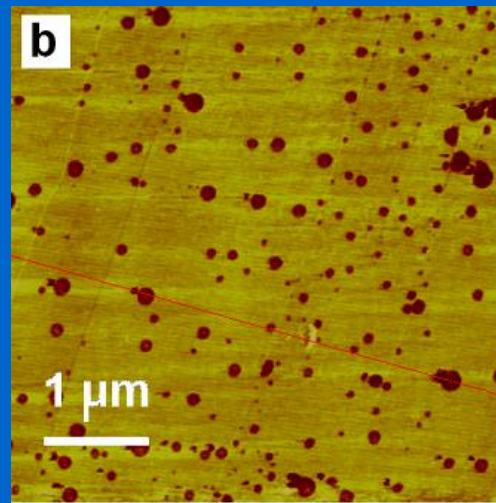
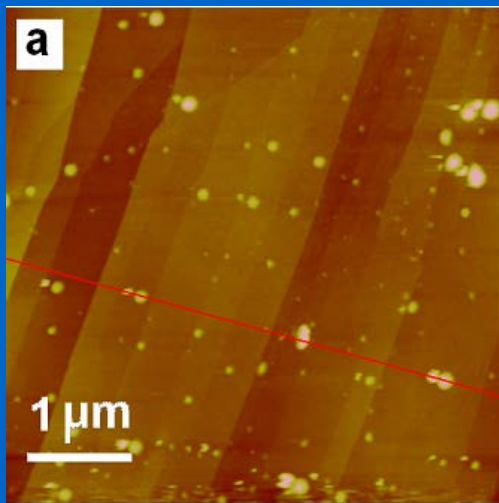
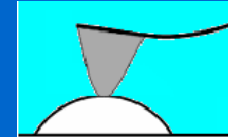
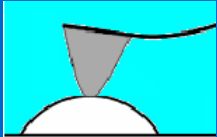
# Nanobubliny na mezifází kapalina/pevná látka



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]

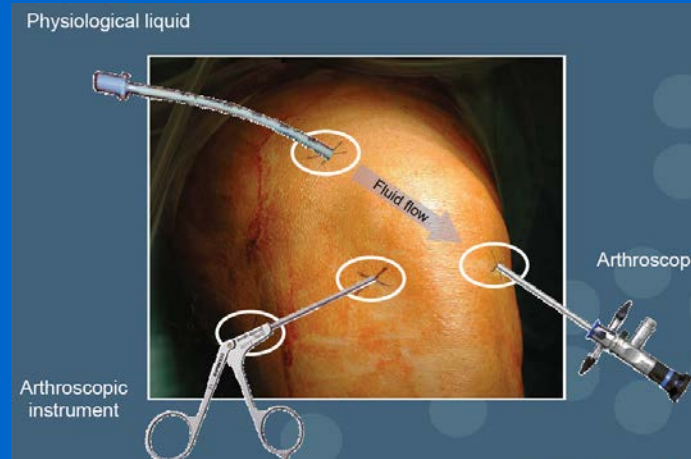
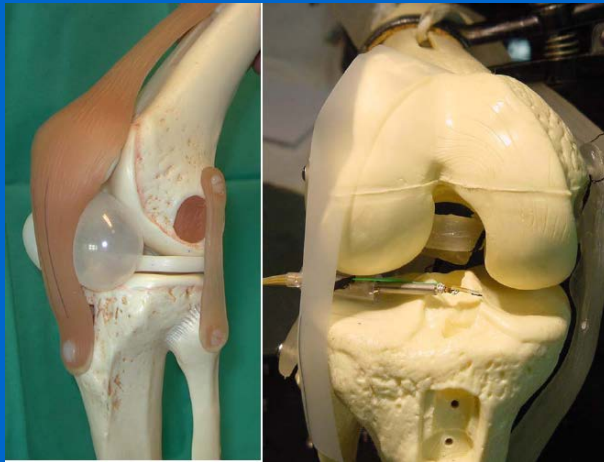
# Nanobubliny na mezifází kapalina/pevná látka



**Topografie**

**Prohnutí cantileveru**

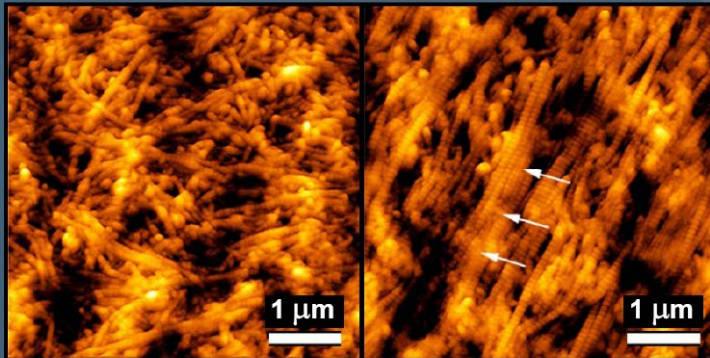
# AFM *in vivo*: Scanning Force Endoscope



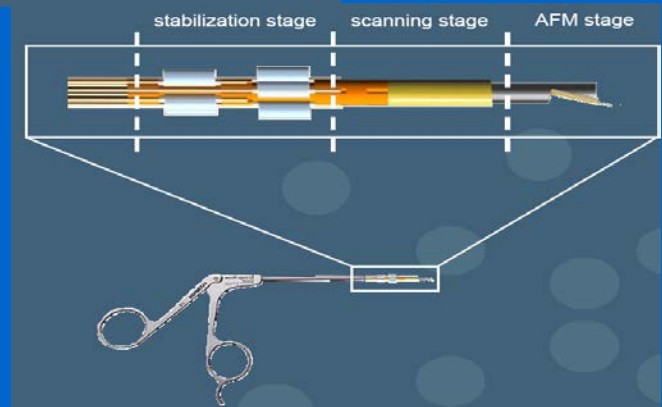
Diagnosing cartilage diseases at an early stage

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

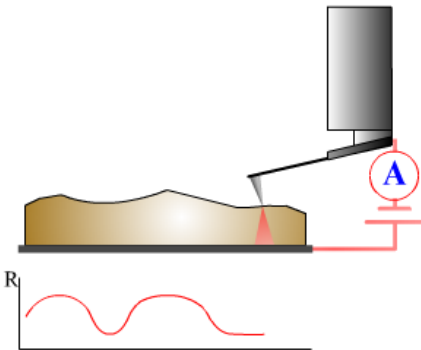
M.E. Müller Institute (MSB)  
University of Basel

M. Stolz  
U. Aebi

# Vodivostní AFM

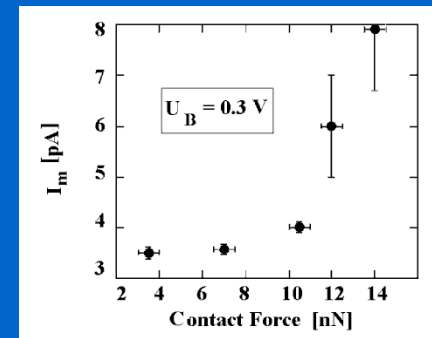
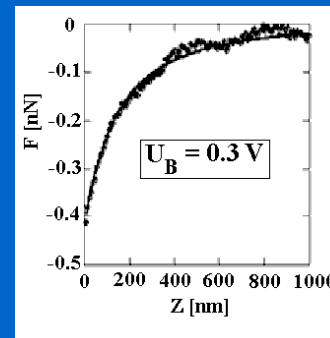
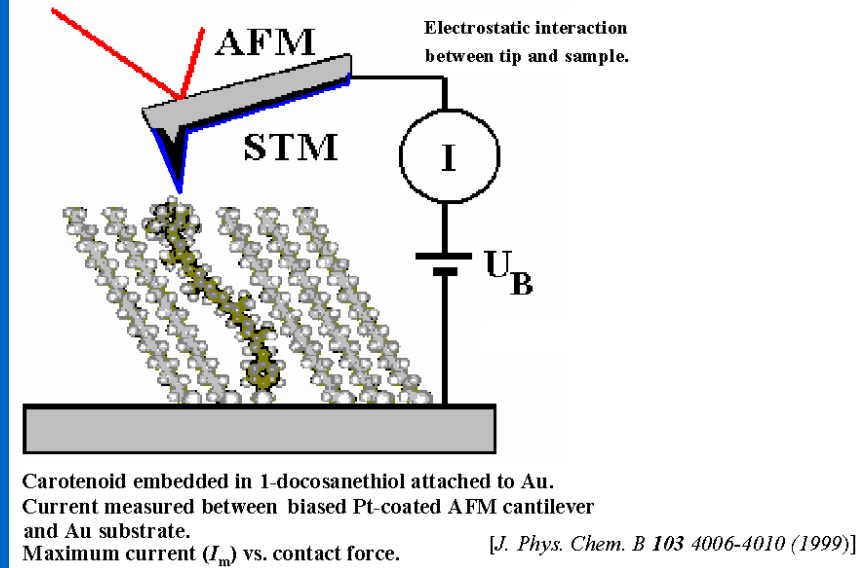
Spreading Resistance imaging

Constant Force mode



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

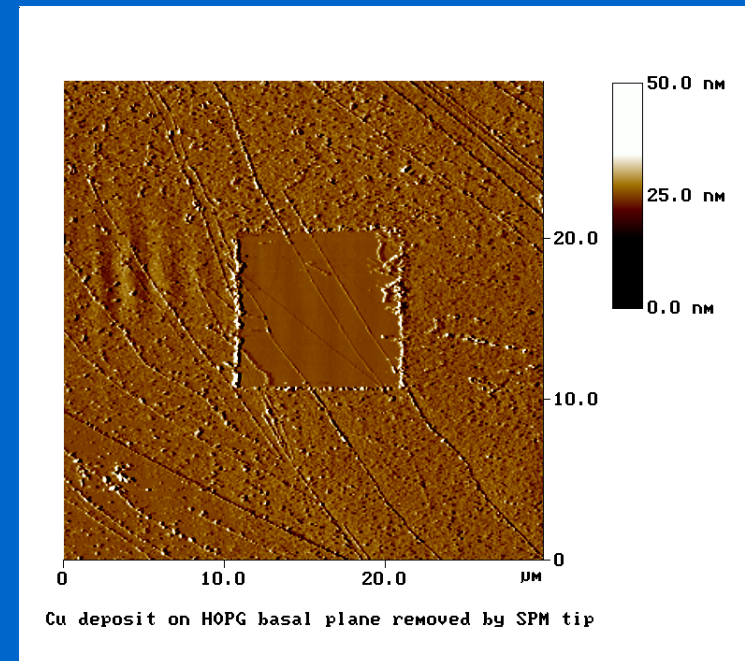
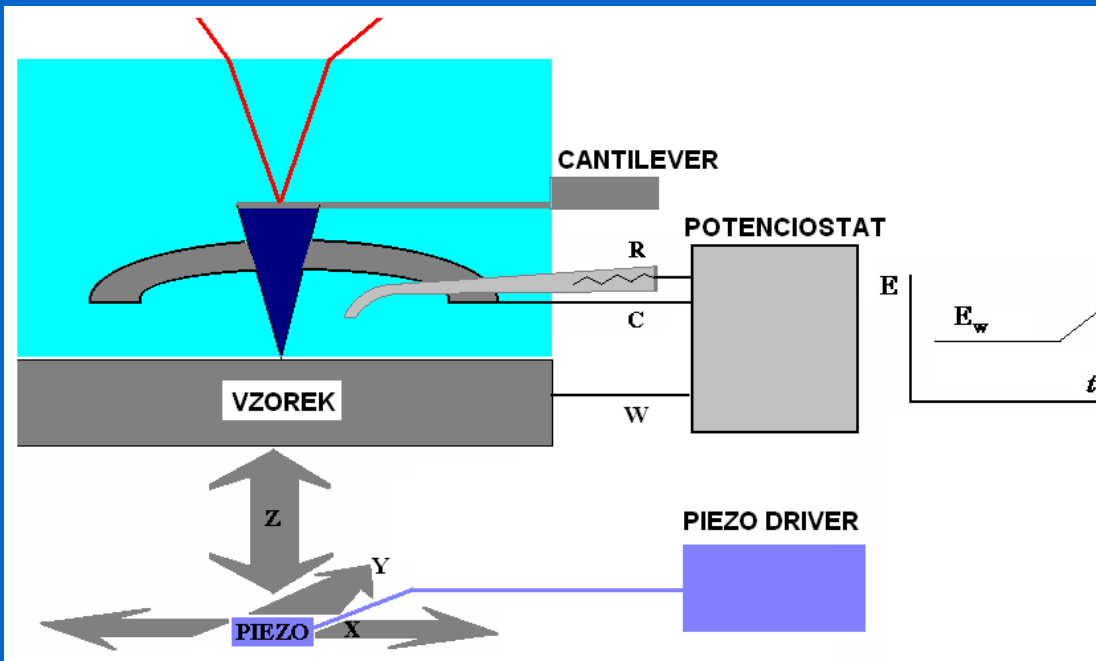
Copyright © NT-MDT, 2002



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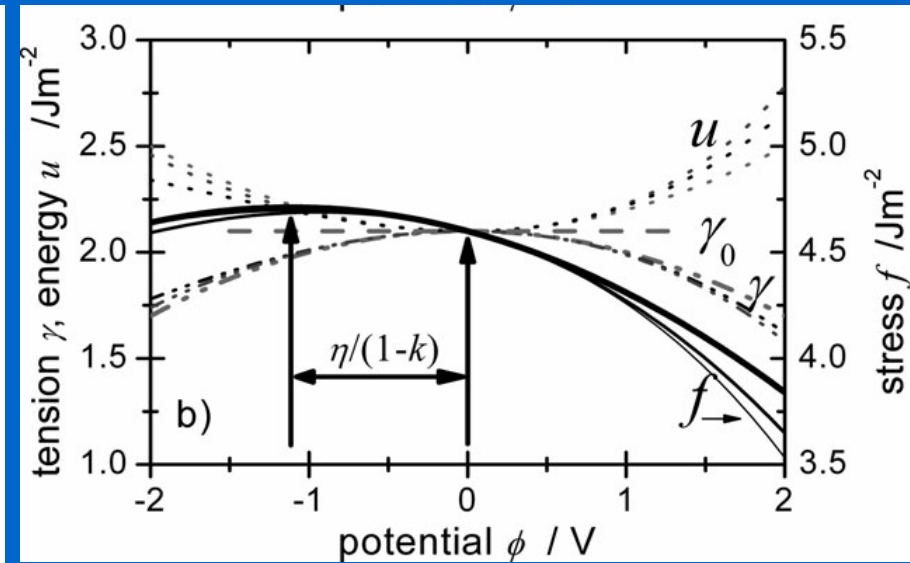
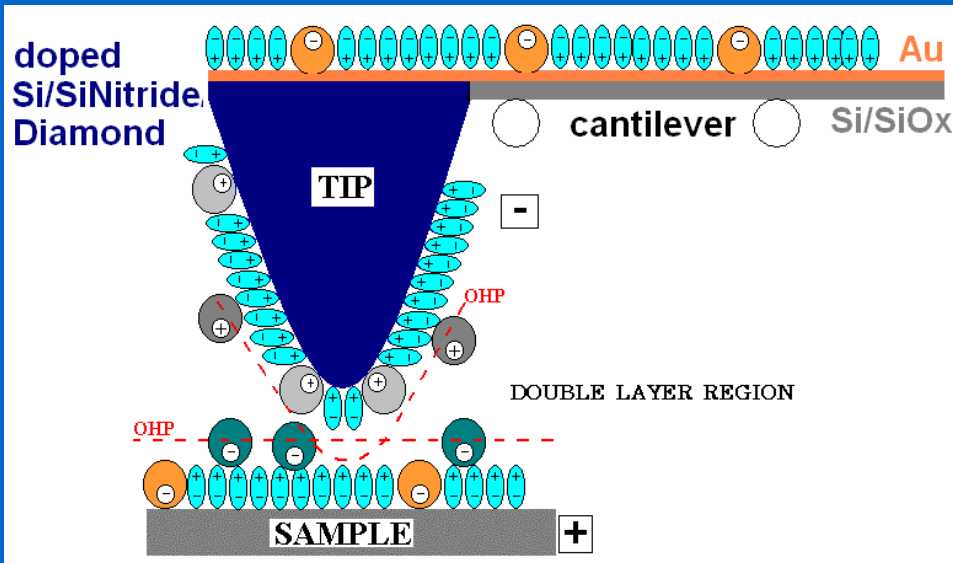
# AFM v elektrochemických aplikacích

# AFM v průběhu EC experimentu: zobrazení *in situ*





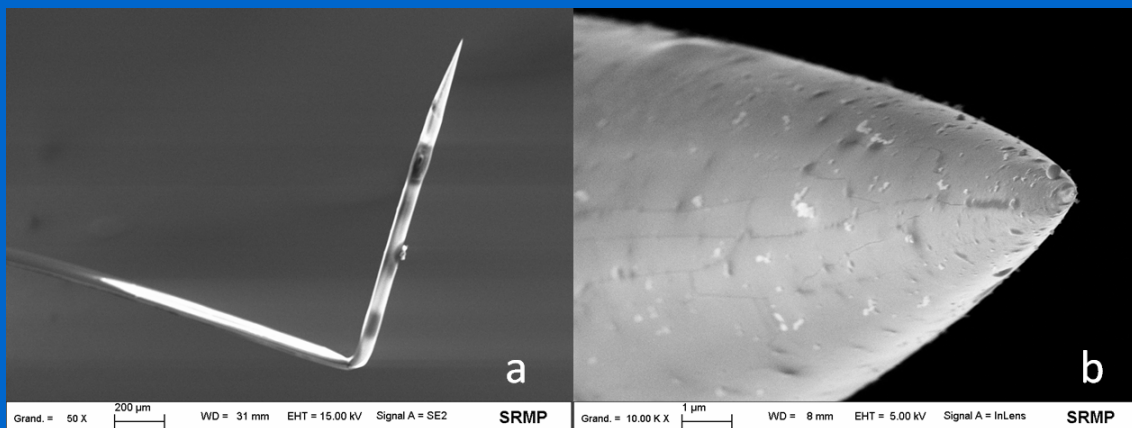
# Hrot-cantilever v režimu SECM



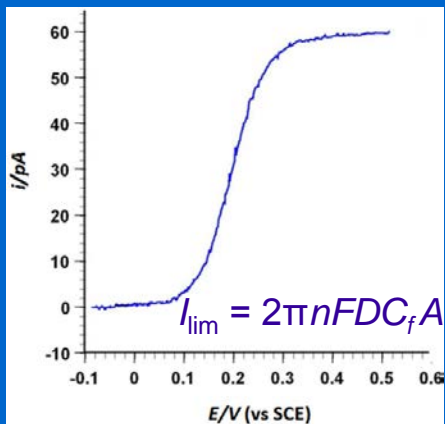
Dependence of surface tension  $\gamma$ , surface stress  $f$  and surface energy  $u$  on the electrode potential  $\phi$  ( $\phi = E - E_0$  (zero charge)), calculated for different double layer capacities.

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

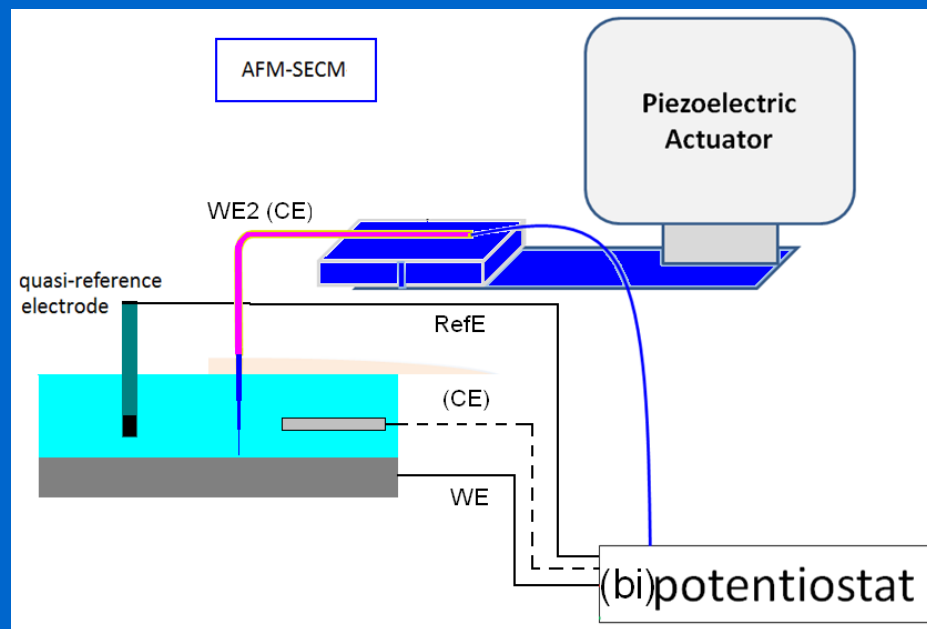
# AFM-SECM v objemu



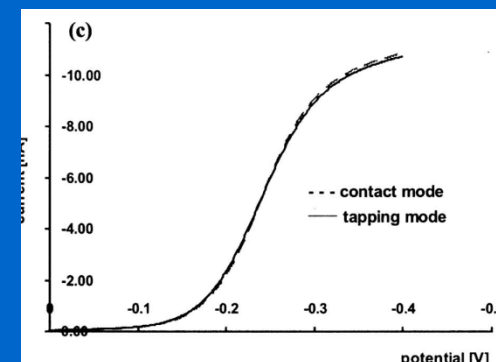
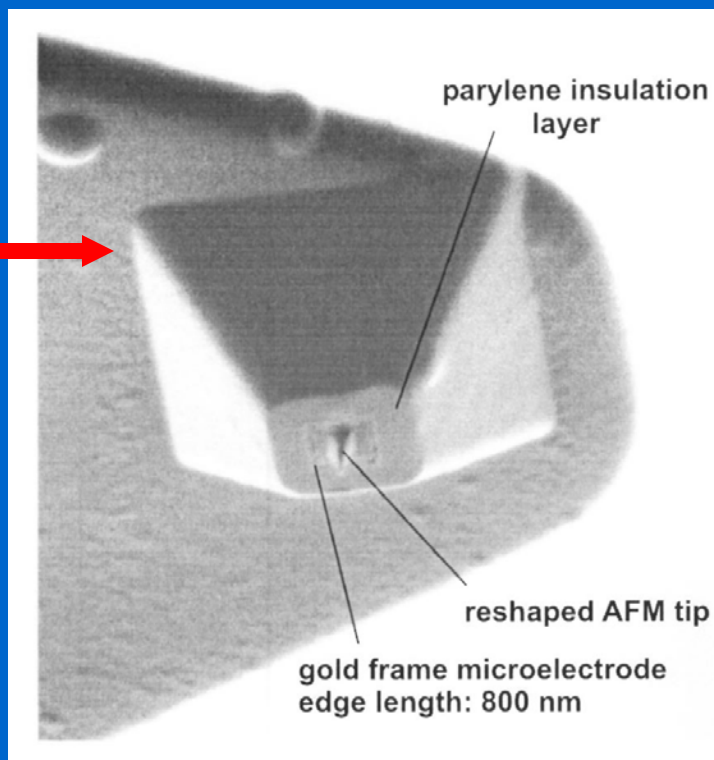
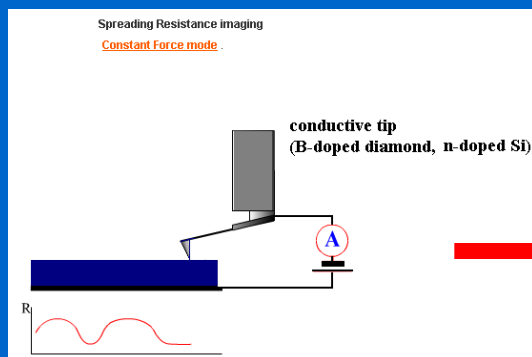
AFM-SECM-elektroda  
izolovaná elektroforetickým  
lakem, hrot  $R \sim 130 \text{ nm}$



CV in 1 mM ferrocene  
0.1 M  $\text{KH}_2\text{PO}_4$   
 $V = 50 \text{ mV s}^{-1}$



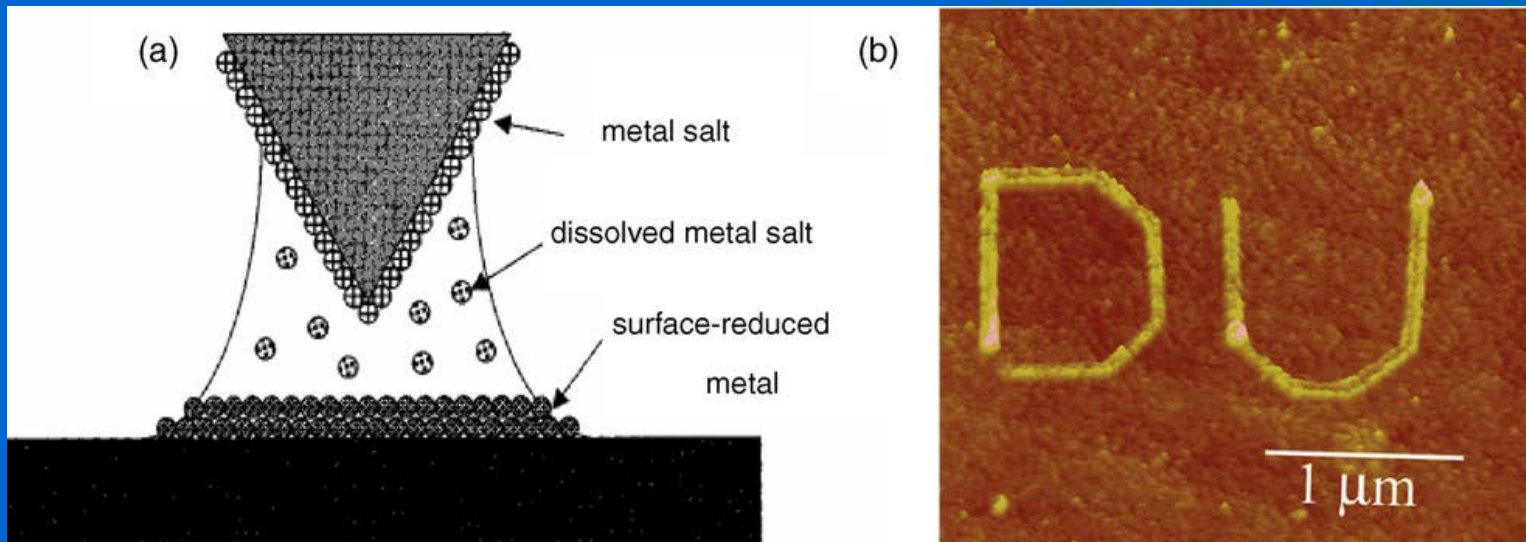
# Vodivý hrot pro AFM-ECM pro práci v kapalinách



Cantilever with 100 nm Au insulated with 700 nm Parylene.  
LSV: SECM-AFM tip in 10 mM Ru(NH<sub>3</sub>)/0.5 M KCl soln; 100 mV/s.  
--LSV at contact mode  
\_\_LSV at tapping

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

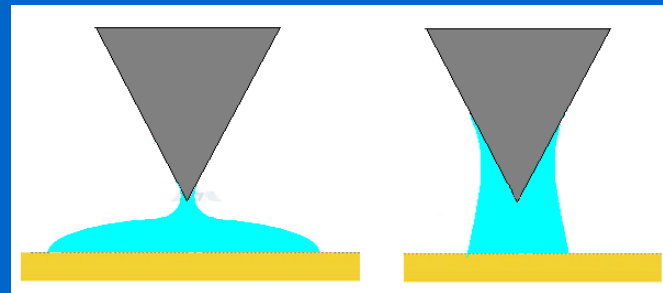
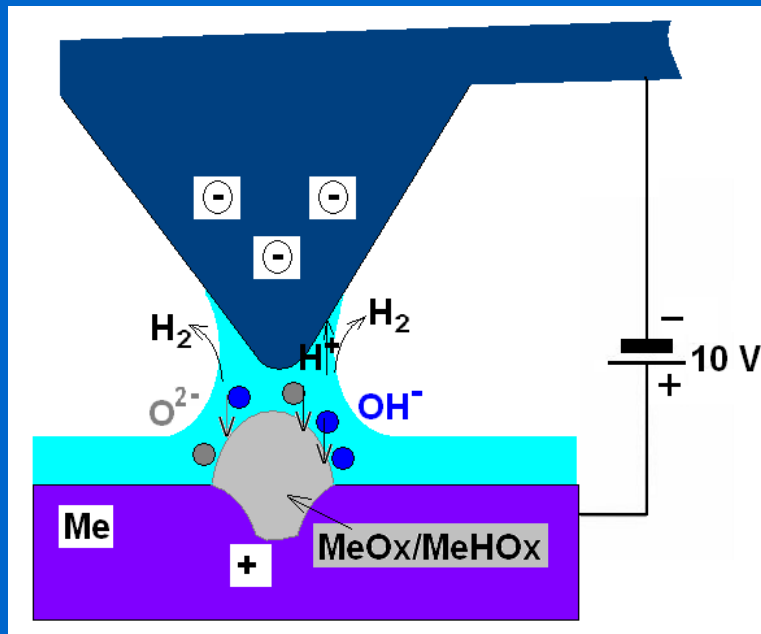
# ECAFM: hrotem zprostředkovaná elektrodepozice kovu (nano-vrstva) v kapce



Au elektrodepozice konverzí Au(III) (inkoust)  $\Rightarrow$  Au(0)

2-elektrodový systém

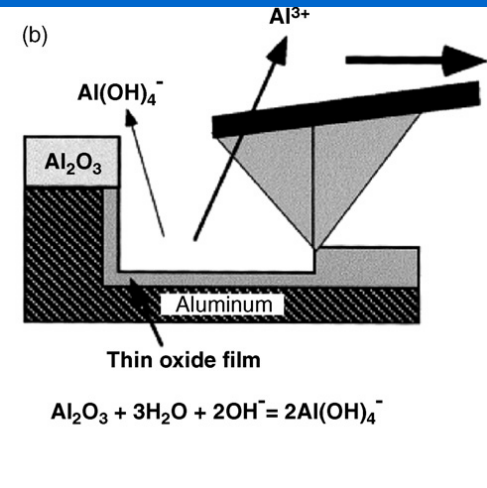
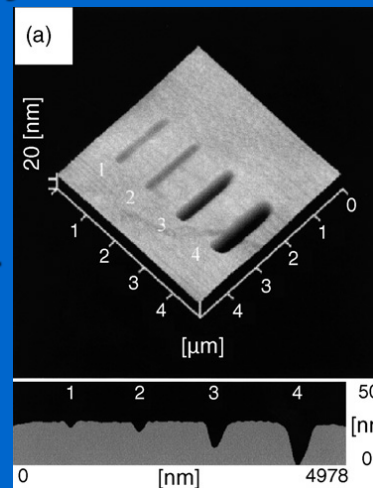
# ECAFM: hrotem indukované elektrochemické vytváření/rozpuštění oxidu (nano-vrstvy)



Formování vodního menisku na hydrofilním a hydrofobním substrátu

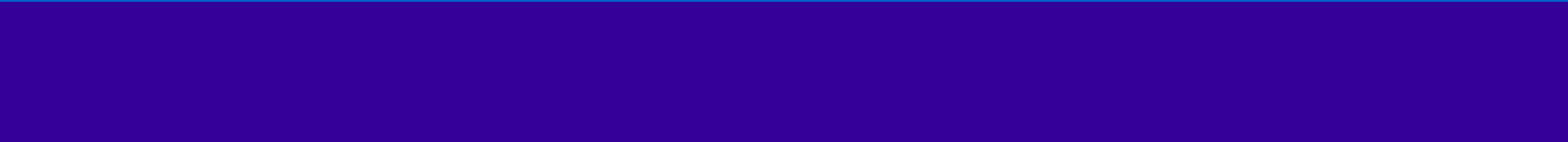
Pole  $10^7$  V/cm  $\Rightarrow$  disociace  $H_2O \Rightarrow OH^- + H^+$

2-elektrodivý 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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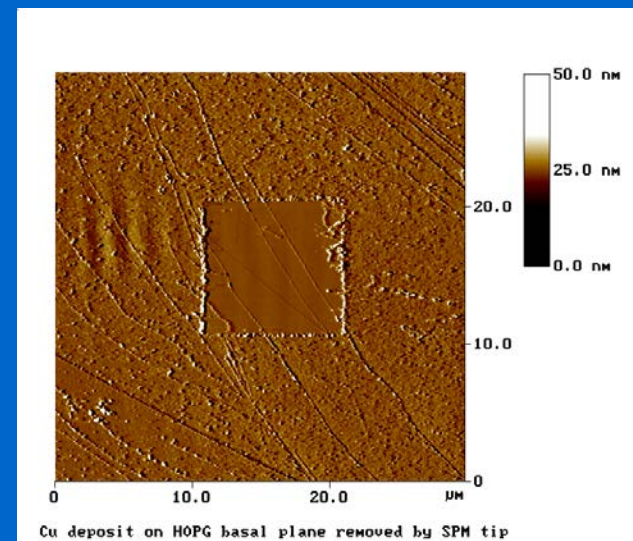
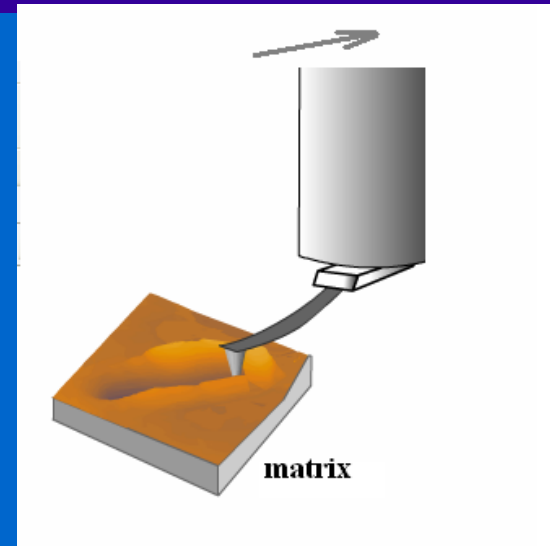
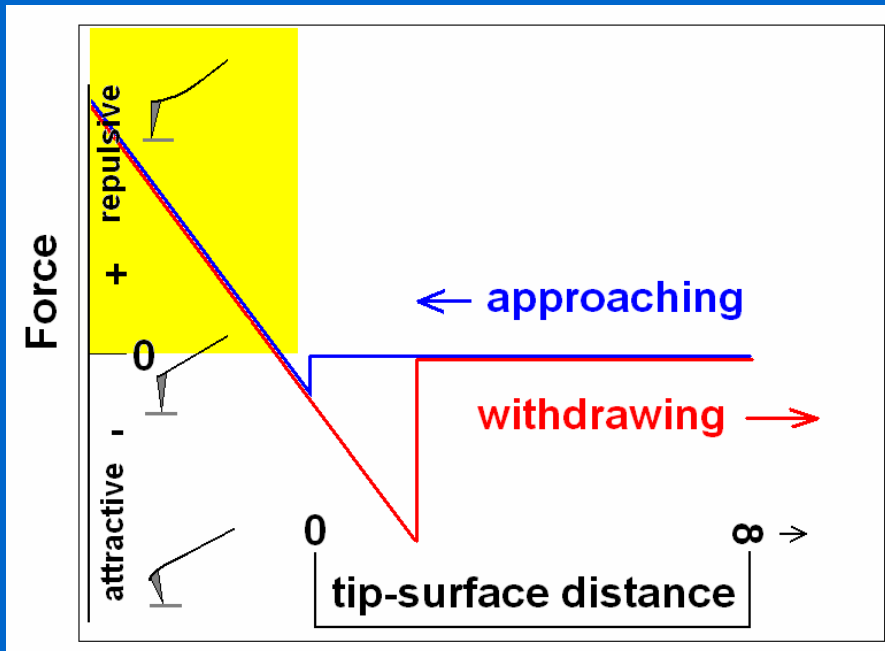


# SPM nanomanipulace & nanolithografie



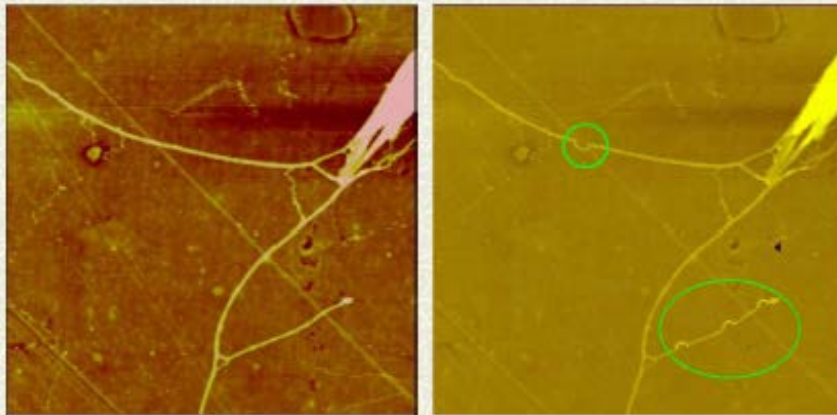
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# Interakce sonda-povrch vzorku



# Manipulace na molekulární úrovni

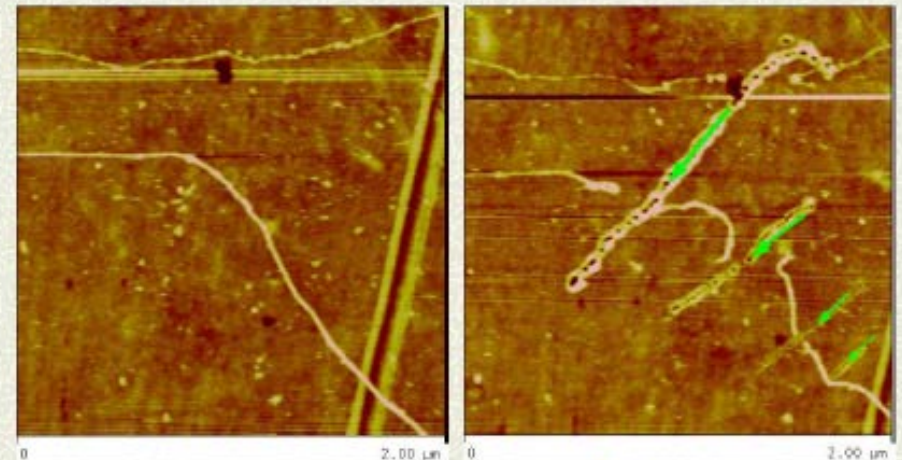
## DNA Manipulation: Pushing



Before pushing

After pushing

## DNA Manipulation: Cutting



Before cutting

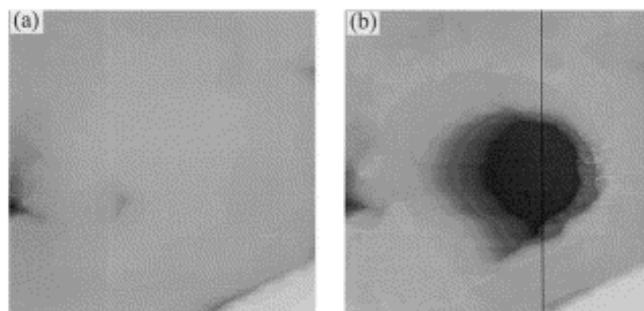
After cutting

**Ning Xi**

Department of Electrical and Computer Engineering  
Michigan State University

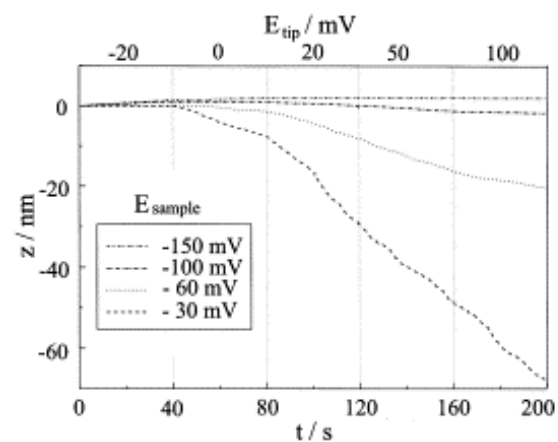
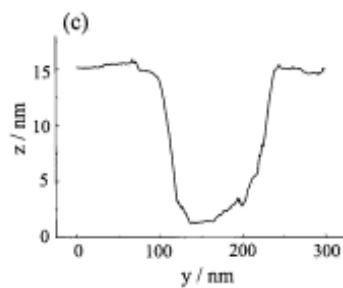


# Hrotem indukované rozpouštění



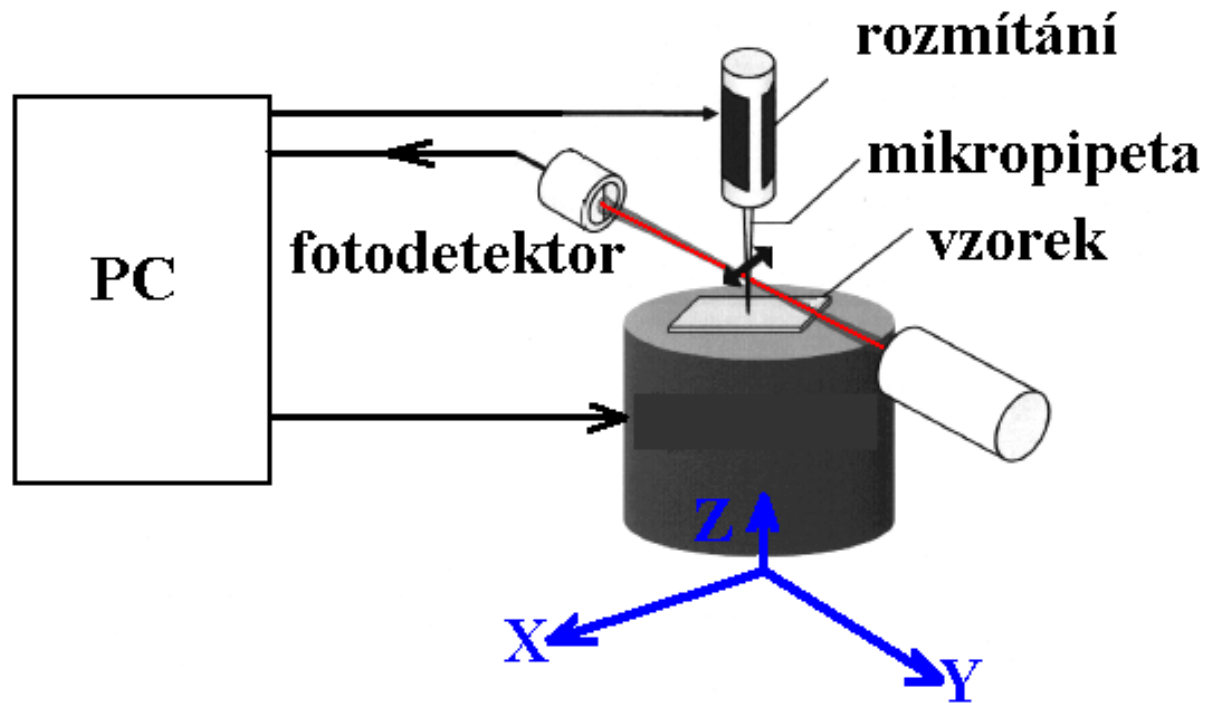
300 nm x 300 nm

300 nm x 300 nm



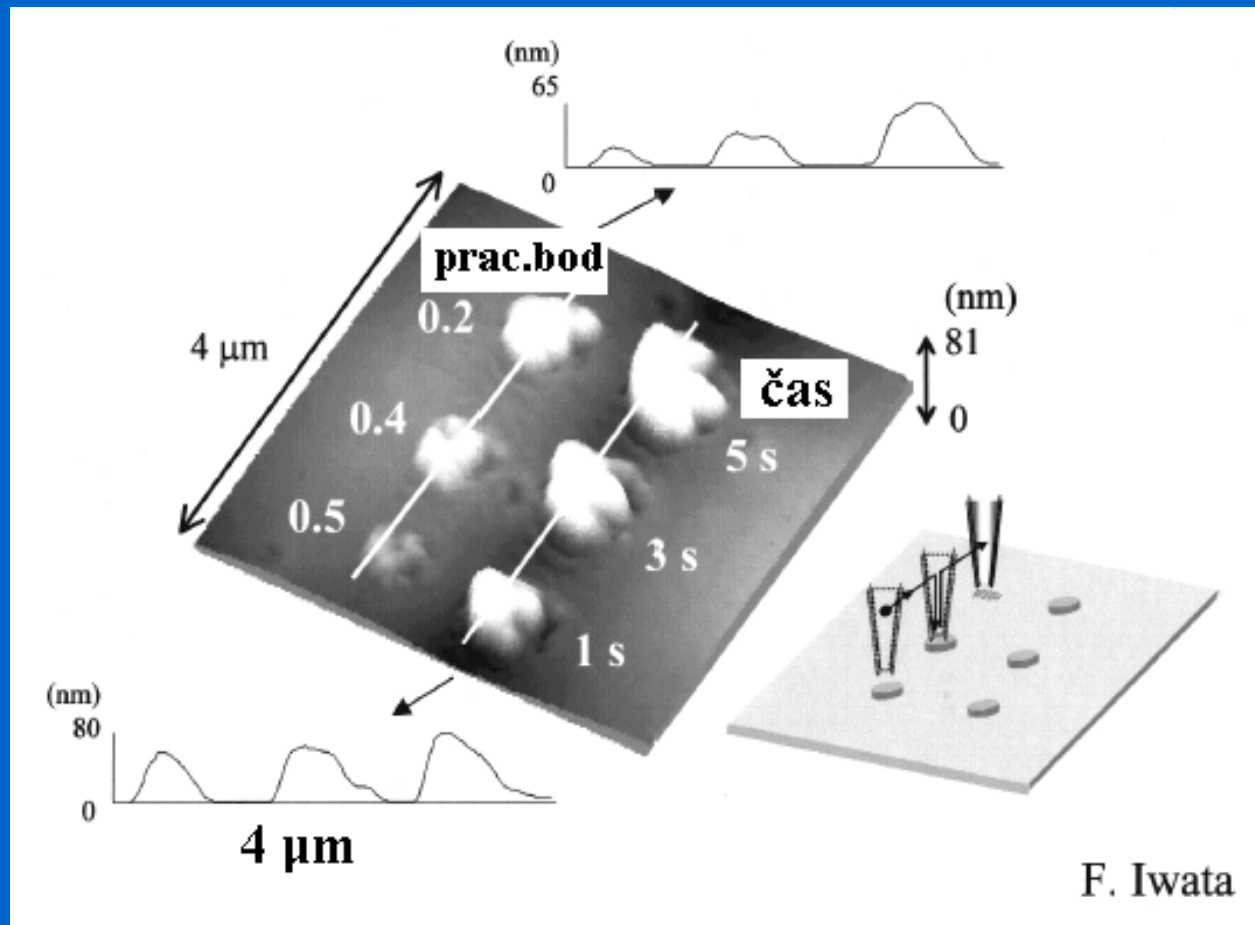
Z. X. Xie, D. M. Kolb: *J. Electroanal. Chem.* 481 (2000), 177.

# 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 (Bruker)

pro práci v kapalinách a plynech



<http://www.jh-inst.cas.cz/~janda>  
[pavel.janda@jh-inst.cas.cz](mailto:pavel.janda@jh-inst.cas.cz)

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