Přednáška STM, AFM pro EMFKL

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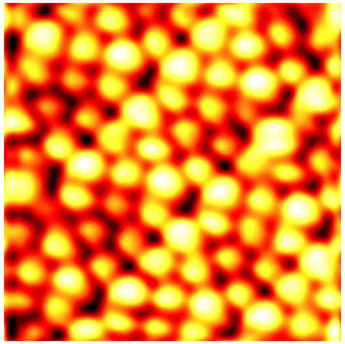
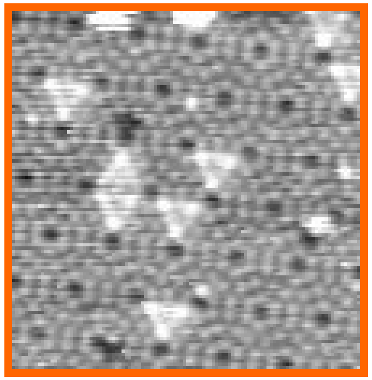
Doc. Ivan Ošťádal, CSc.

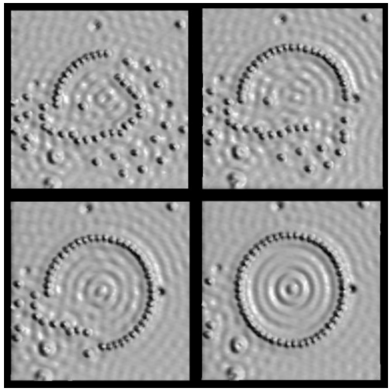
1. scanning tunneling microscope

STM – řádkovací tunelový mikroskop

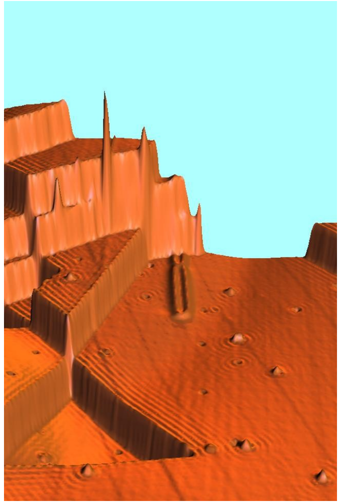
(nebo taky rastrovací tunelový mikroskop…)





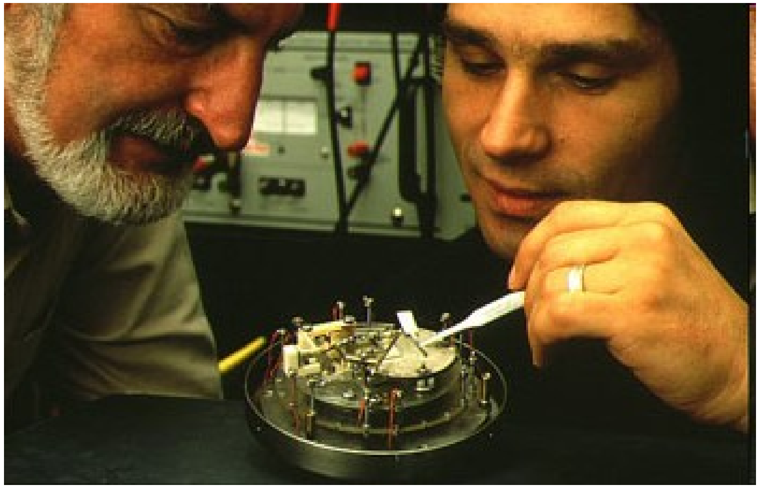


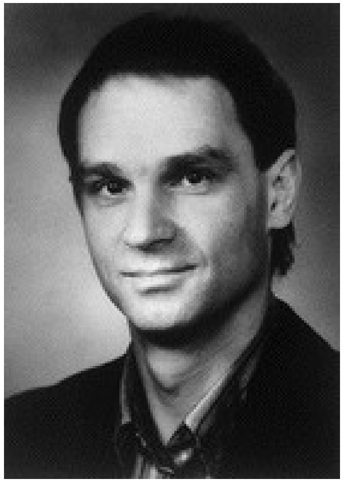
IBM



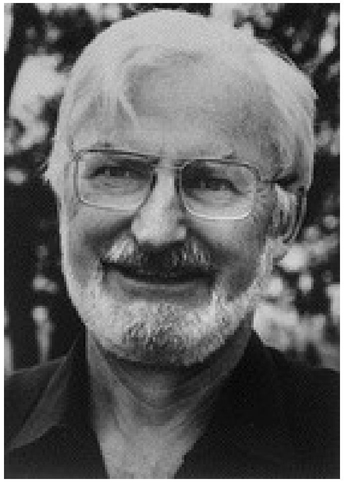
Nature 363, 524-527 (1993)

NC v roce 1986





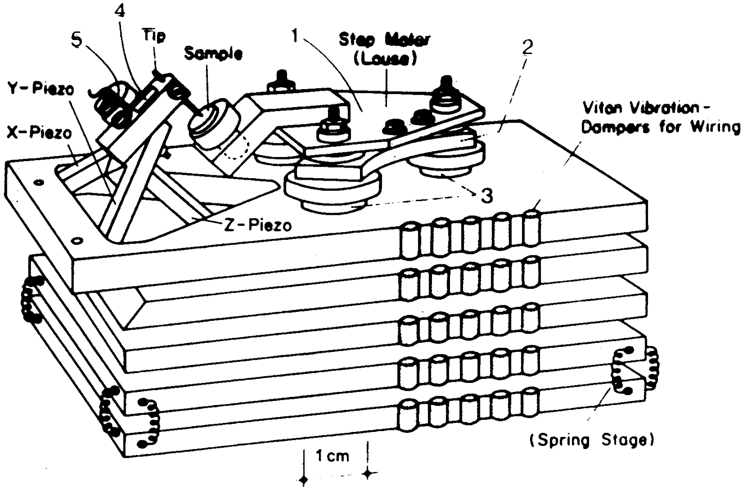
Gerd Binnig



Heinrich Rohrer

Gerd Binnig a **Heinrich Rohrer** (IBM Research Laboratory, Zurich, Švýcarsko) - Nobelova cena roku 1986 **za návrh rastrovacího tunelového mikroskopu**

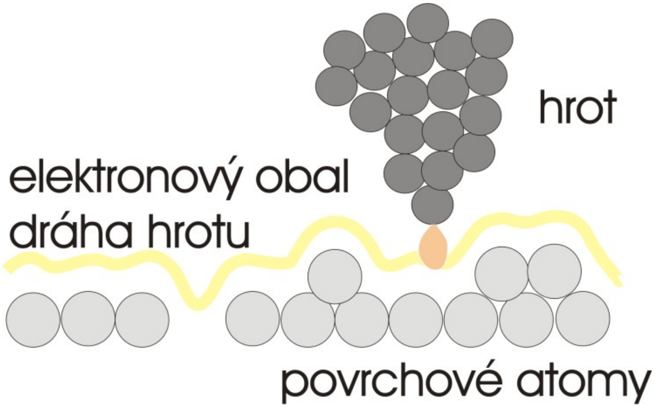
společně s prof. **Ernstem Ruskou** (Fritz-Haber-Institut der Max-Planck-Gesellschaft) za základní práci v elektronové optice a za návrh prvního elektronového mikroskopu



Řádkovací tunelový mikroskop - princip

- Doc. Peksa: “rejpání hřebíkem do kusu plechu”
- sonda – poslední atom ostrého hrotu
- hrot tak blízko povrchu, že teče tunelový proud – tunelový efekt
- udržení konstantní vzdálenosti od povrchu pomocí regulace konstantního tunelového proudu + skenování povrchu =
- výsledek: atomární rozlišení v reálném prostoru

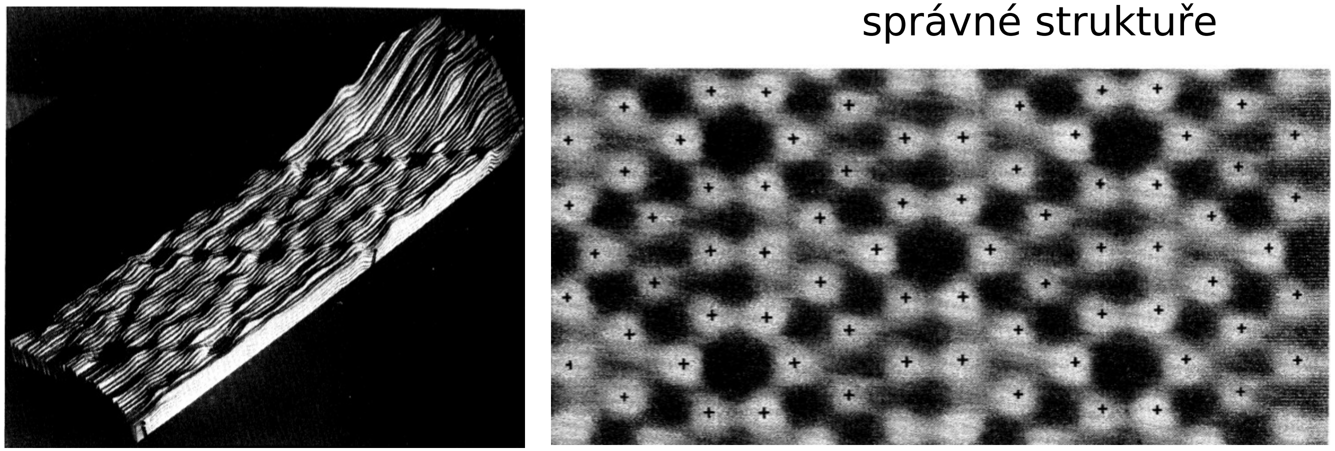
= STM (Scanning Tunneling Microscope)



Zasazení do kontextu

- Povrchové metody
- Integrální metody jsou dlouho známé
  - **Difrakce pomalých elektronů** (LEED) – inv. 1927, populární od 1960
  - **X-ray photoelectron spectroscopy** (XPS) – efekt znám dlouho, první výsledky 1950s
  - **Auger electron spectroscopy** (AES) – inv. 1920s, populární od 1950s.

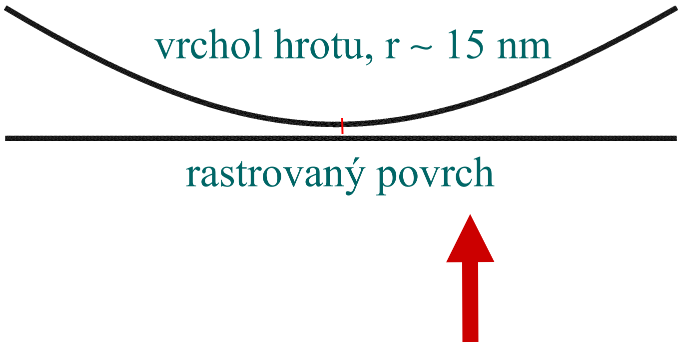
- Chybějící informace: lokální uspořádání na atomární úrovni
- Příklad: Si(111)7x7
  - známa dlouho, množství navržených a zavržených modelů na základě spektroskopických a difrakčních metod
  - po objevu STM a atomárně rozlišených snímcích 7x7 model rychle dokonvergoval ke správné struktuře



G. Binnig et al., Phys. Rev. Lett. 50 (120) 1983

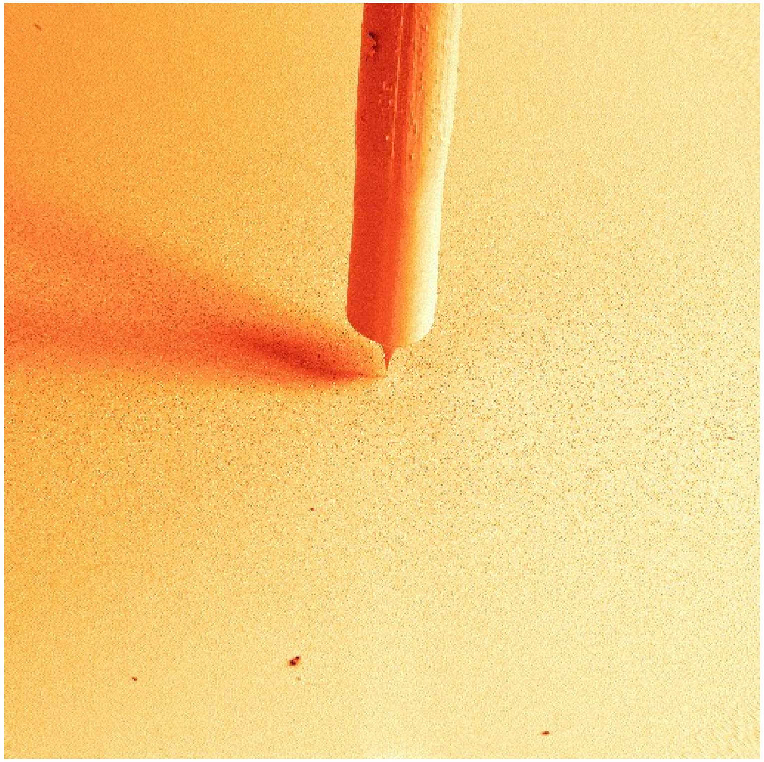
<u>Scanning</u> Tunneling Microscope

wolframový drát, Ø 0.25 mm



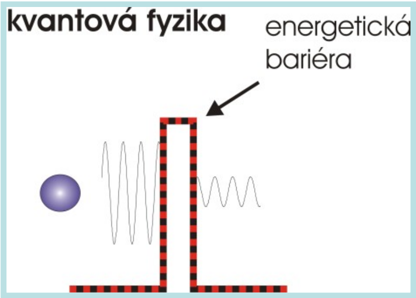
vrchol hrotu, r ~ 15 nm

rastrovaný povrch

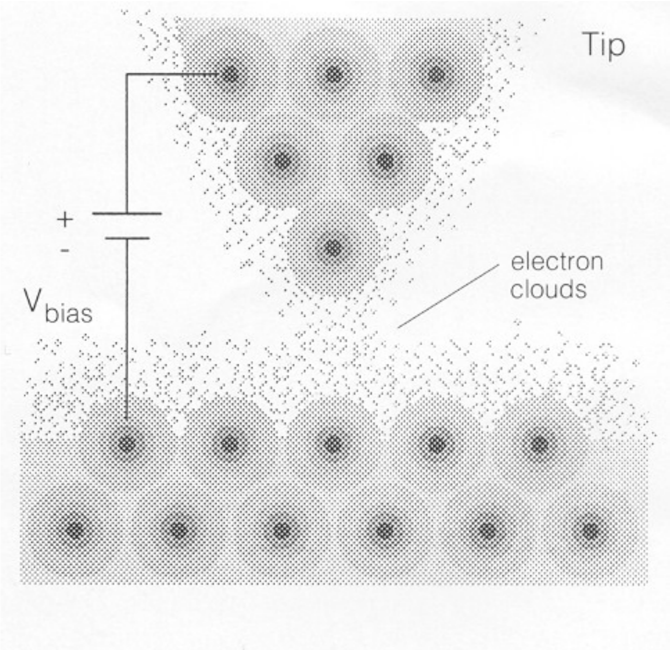


© A. Edmunts & al., IGV KFA Julich, (obrázky z SEM)

Scanning **Tunneling** Microscope

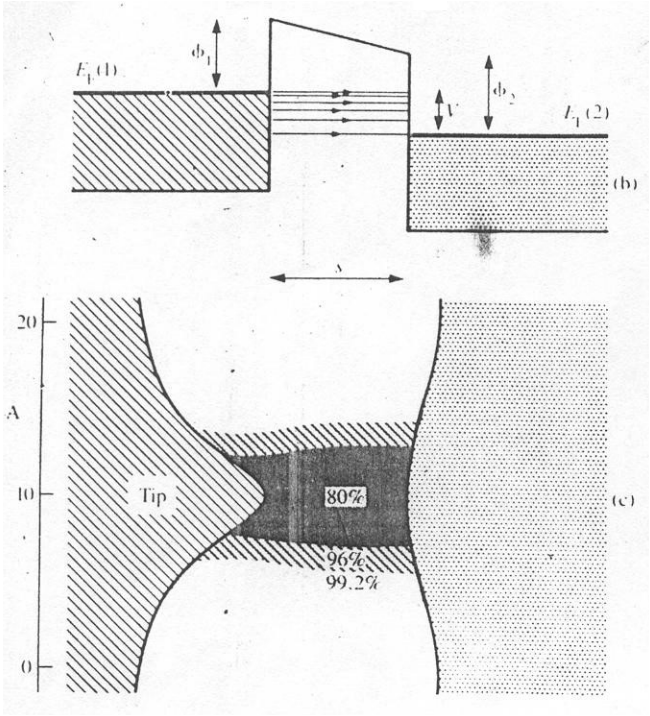


vlnově-částicová dualita - elektron se chová jako částice i jako vlnění

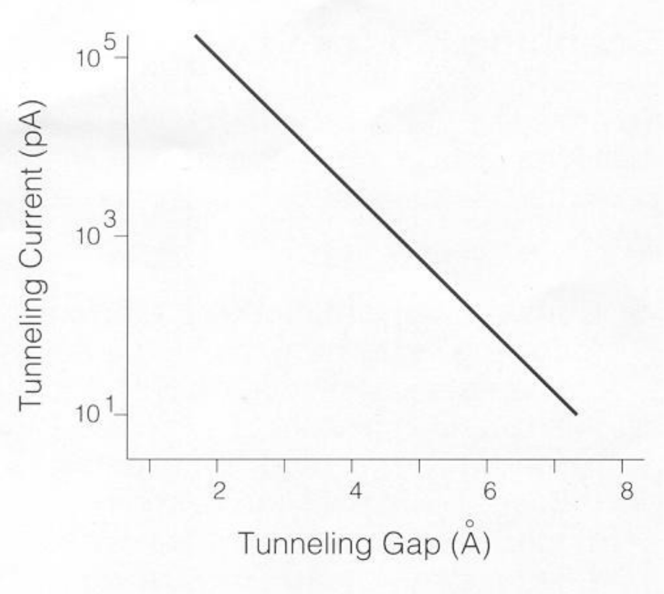


Tip-sample interaction

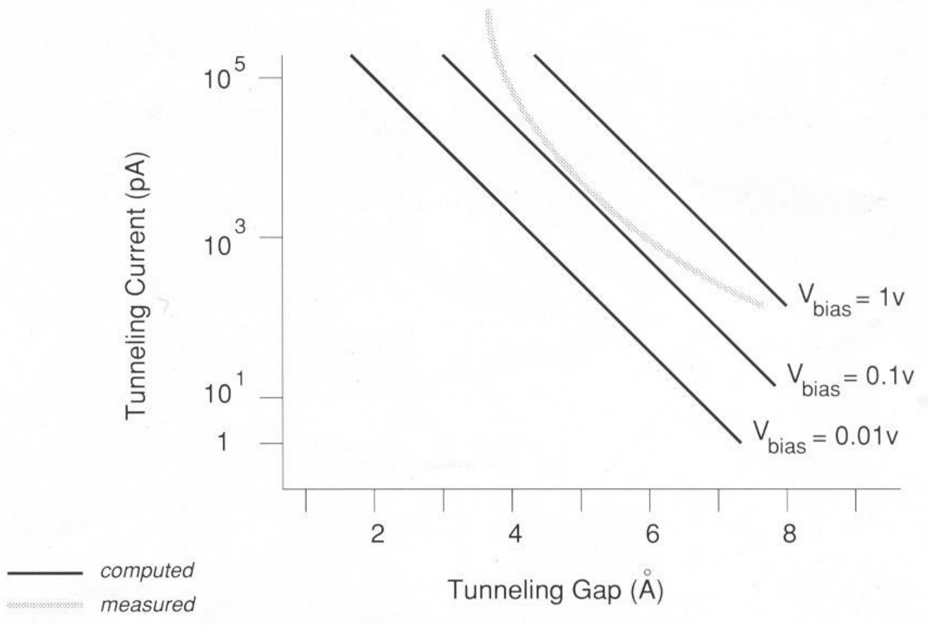
$$I = f(V)\exp(-s\,\phi^{1/2})$$



Závislost tunelového proudu na vzdálenosti elektrod



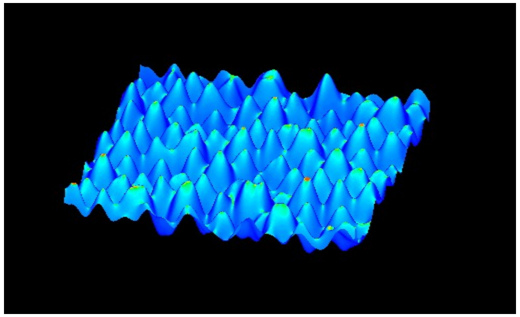
Graph of tunneling current vs. distance

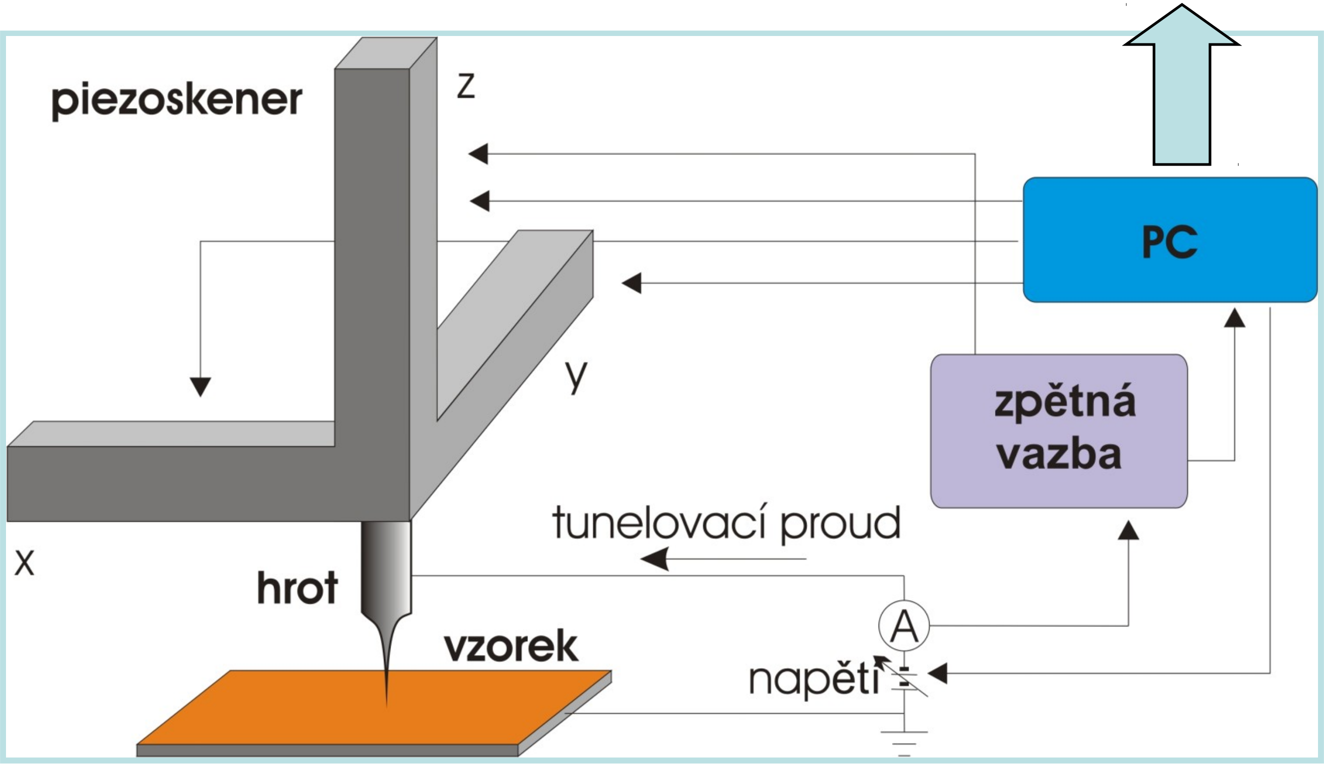


Graph of tunneling current vs. distance (different bias)

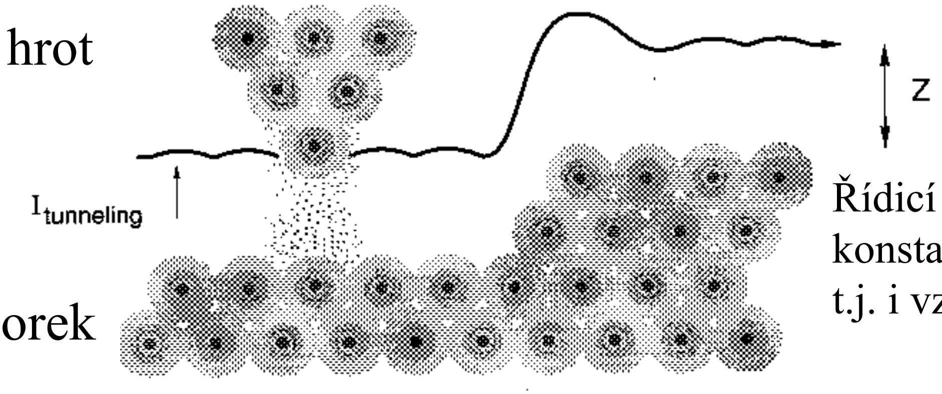
Řádkovací tunelový mikroskop - realizace

1) (polo)vodivý vzorek
2) ostrý hrot
3) jemný pohyb x,y,z – piezokeramika
4) zpětná vazba





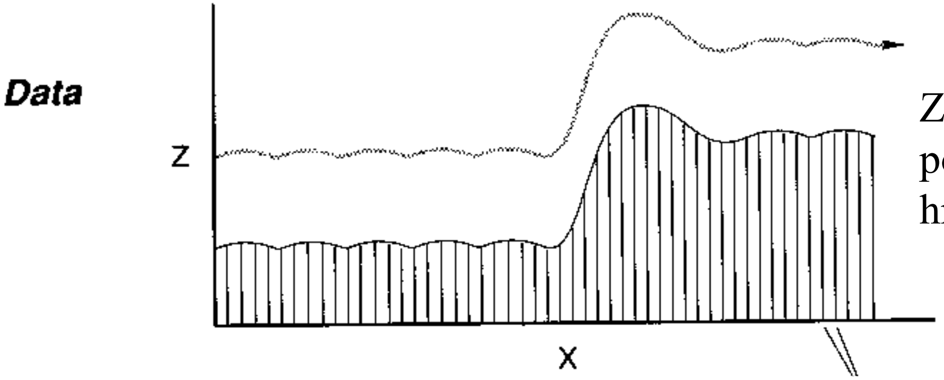
Technika STM – mód konstantního proudu



hrot

vzorek

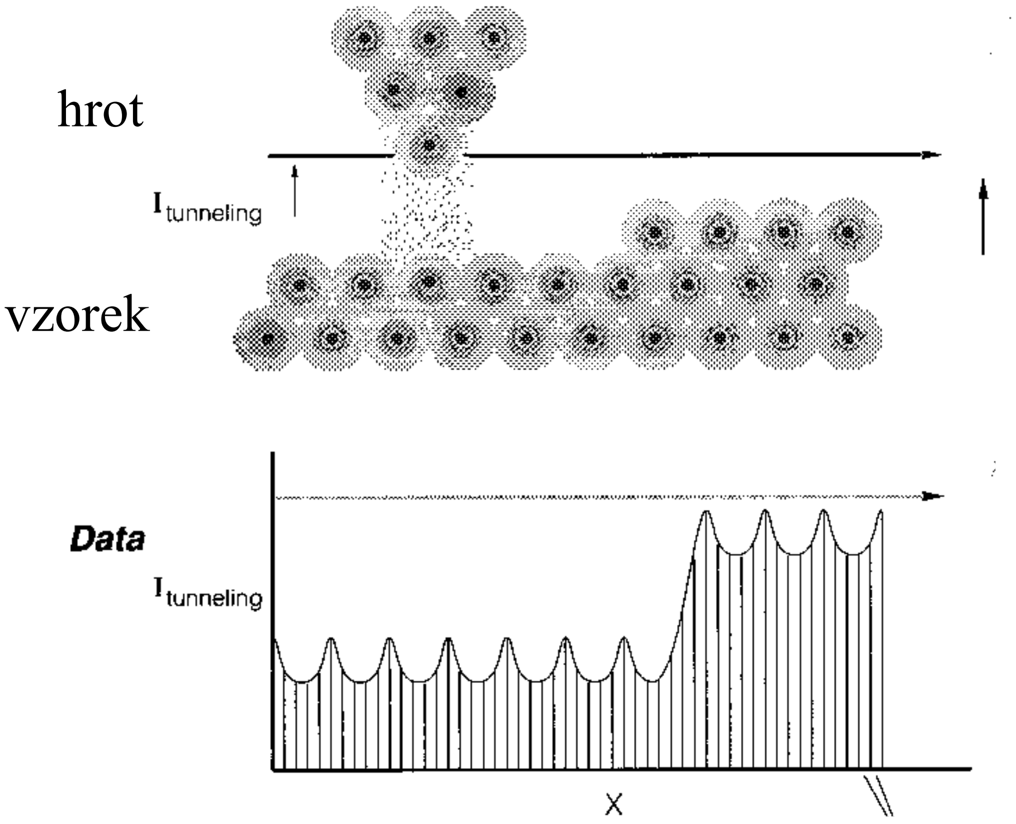
Řídicí systém udržuje
konstantní tunelový proud,
t.j. i vzdálenost hrotu od povrchu



Zaznamenává se úroveň signálu
potřebného pro „opravu“ výšky
hrotu nad povrchem

data čtená v diskrétních
intervalech (pozicích)

Technika STM – mód konstantní výšky



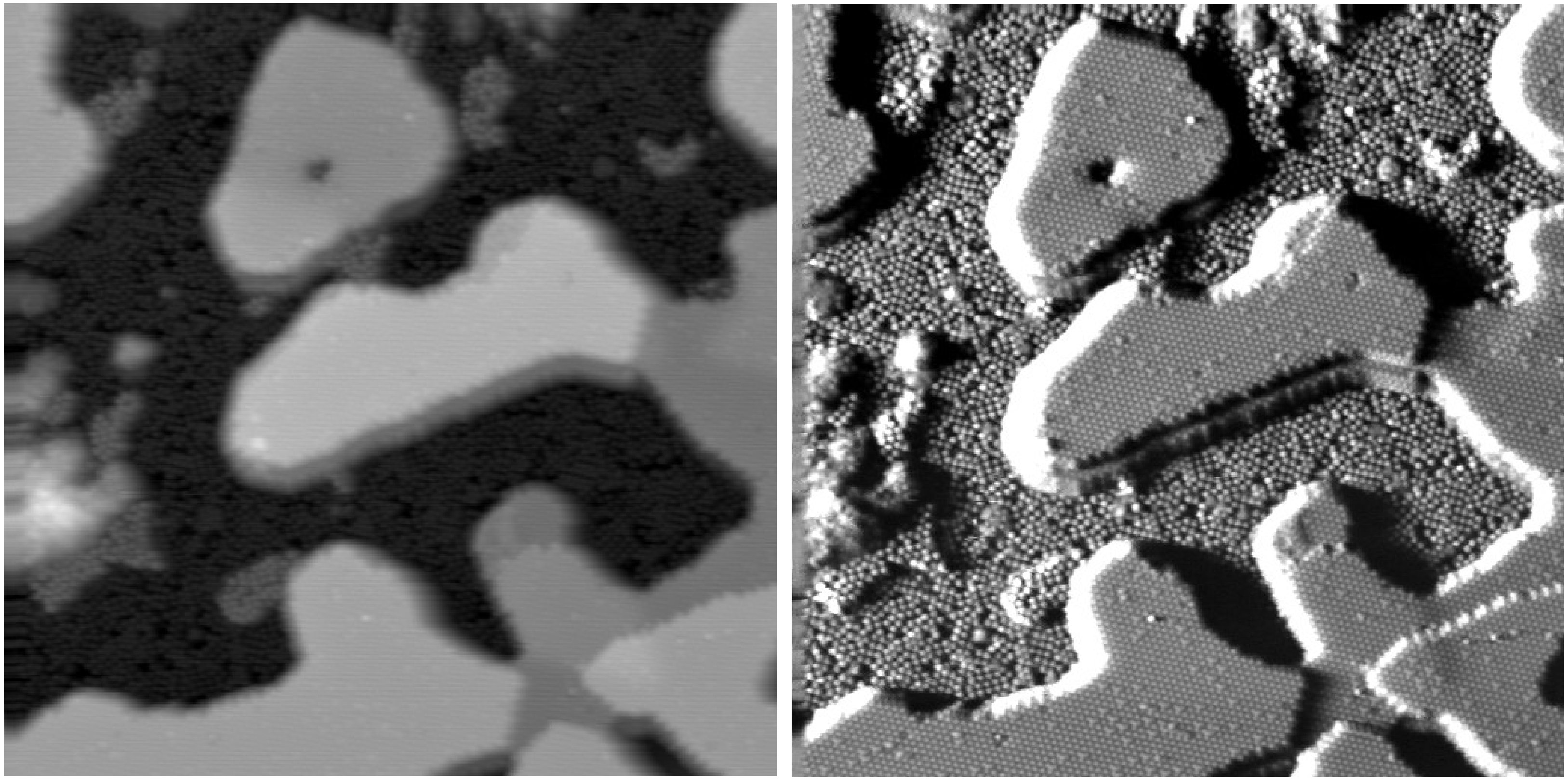
Výška hrotu nad povrchem je konstantní

Data odpovídají hodnotě tunelového proudu

Data jsou čtena v diskrétních intervalech (pozicích)

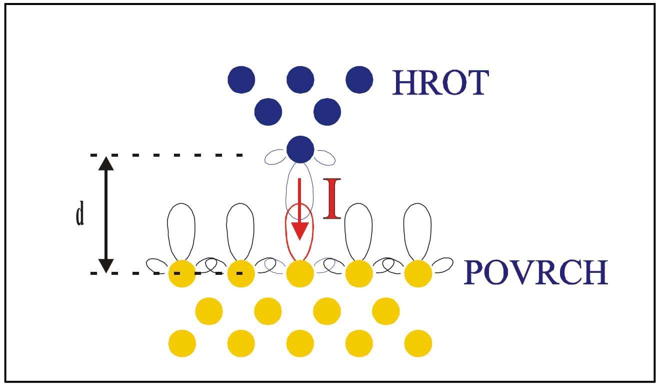
v praxi – zpětná vazba se potlačí pouze částečně – reaguje pouze na „hrubší“ změny, v proudovém obrázku vyniknou detaily

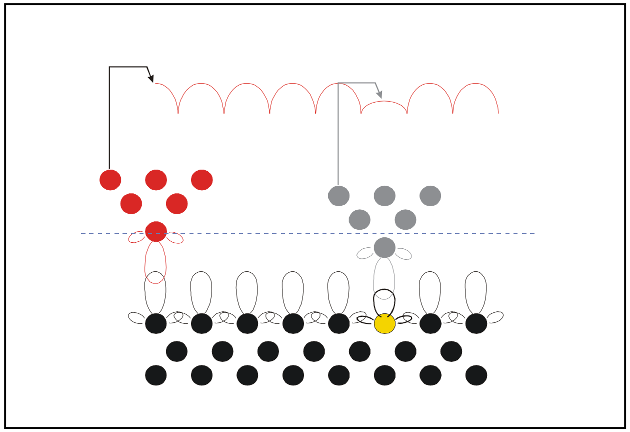
Porovnání z-ového a proudového modu



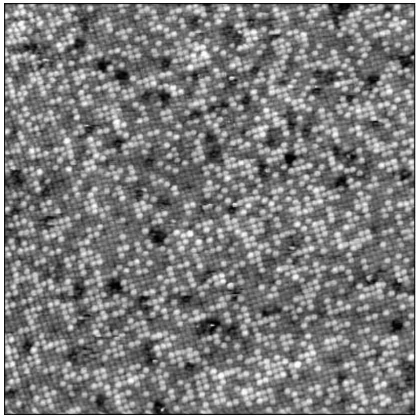
MnSi na Si(7x7)

Princip STM – vliv elektronových stavů





STM zohledňuje lokální hustotu elektronových stavů:



Institut für Allgemeine Physik, TU Wien

$$I=\frac{2\pi|e|}{\hbar}\int_{0}^{eV}\rho_L(E_F-eV+\varepsilon)\,\rho_R(E_F+\varepsilon)\,|M|^2\,d\varepsilon$$

Hrot sleduje plochu konstantní lokální hustoty stavů pro energii odpovídající potenciálu hrotu vůči Fermiho mezi vzorku. Zdánlivá „výška“ atomu viděná hrotem závisí na elektronické konfiguraci atomů zkoumaného povrchu.

◄ Proto se v obrázku monokrystalické slitiny PtRh jeví Pt tmavší.

► STS –Scanning Tunneling Spectroscopy

vliv elektronových stavů – inverzní kontrast

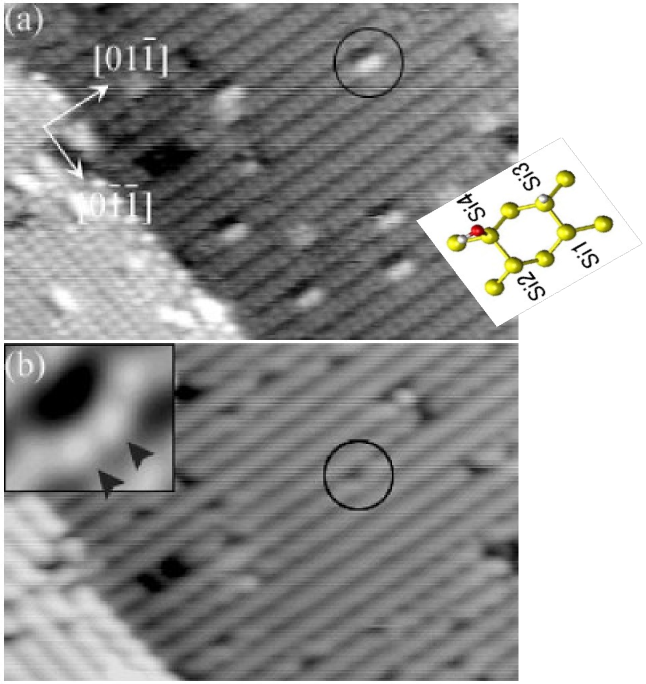
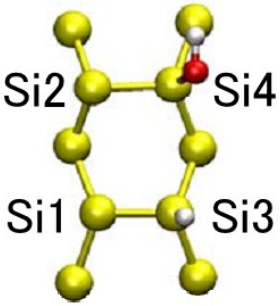


FIG. 1. STM images at the same area of clean Si(100) in (a) the unoccupied and (b) the occupied states at 300 K. Scan area is 15 $\times 10$ nm^2 for both images. For (a), $V_{sample} = 1.4$ V, $I = 0.13$ nA and for (b), $V_{sample} = -1.9$ V, $I = 0.13$ nA. A typical *C* defect is enclosed by the circles. A zoomed-in *C* defect in the occupied state is shown in the inset where two protrusions on two adjacent dimers are clearly seen and the other half of the dimers is depressed.

PRB 67 153307 (2003)



PRB 77 113301 (2008)

tungsten tips used in experiments

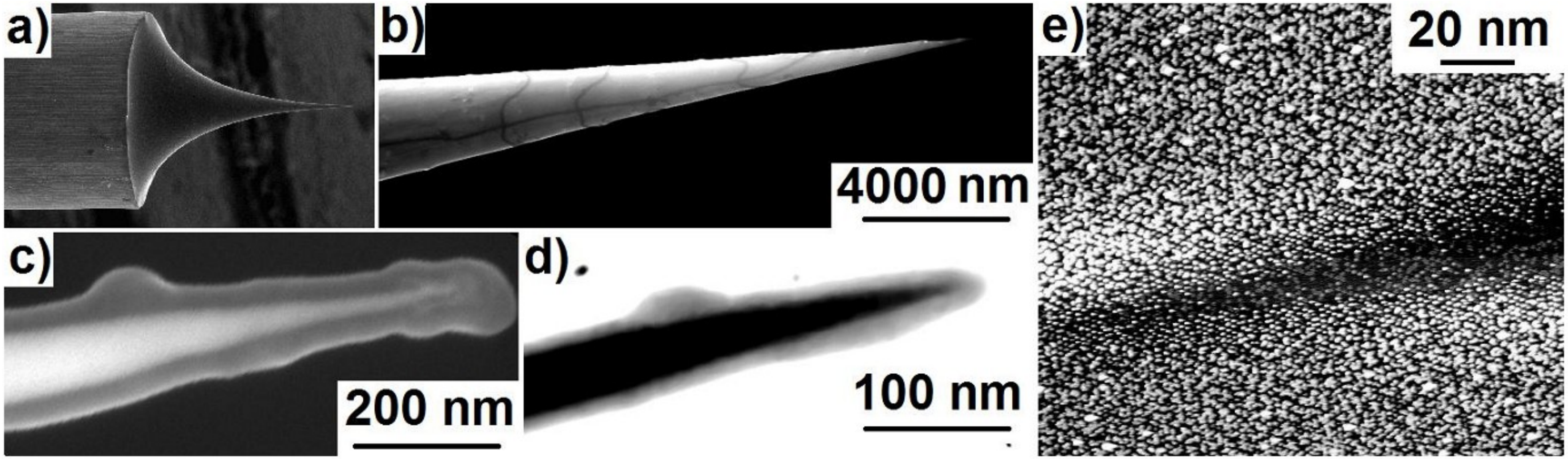
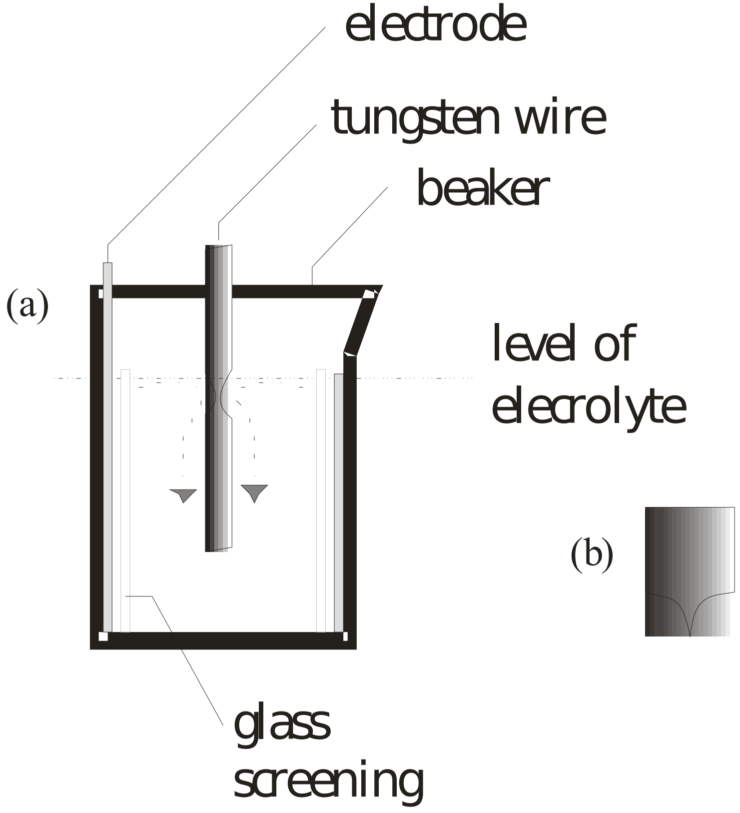


Figure 1: Images of tungsten tips taken few hours after etching. a) Large-scale SEM image, the wire diameter is 0.3 mm; b) SEM image showing microcrystalline structure of the tip; c) and d) SEM and TEM images of tips with curvature radius less than 5 nm. Tungsten core is covered by a thick oxide layer; e) STM image of Ag/Si(111)-(7×7) layer deposited when the tip was in tunneling contact with the surface. The tip 'shadow' is visible in the layer.

Příprava hrotů pro STM – leptání W hrotu v roztoku NaOh



Úprava hrotu v UHV

- ohřev
  - přímým kontaktem
  - elektronovým bombardem
  - autoemisním proudem

- vyboření hrotu o povrch

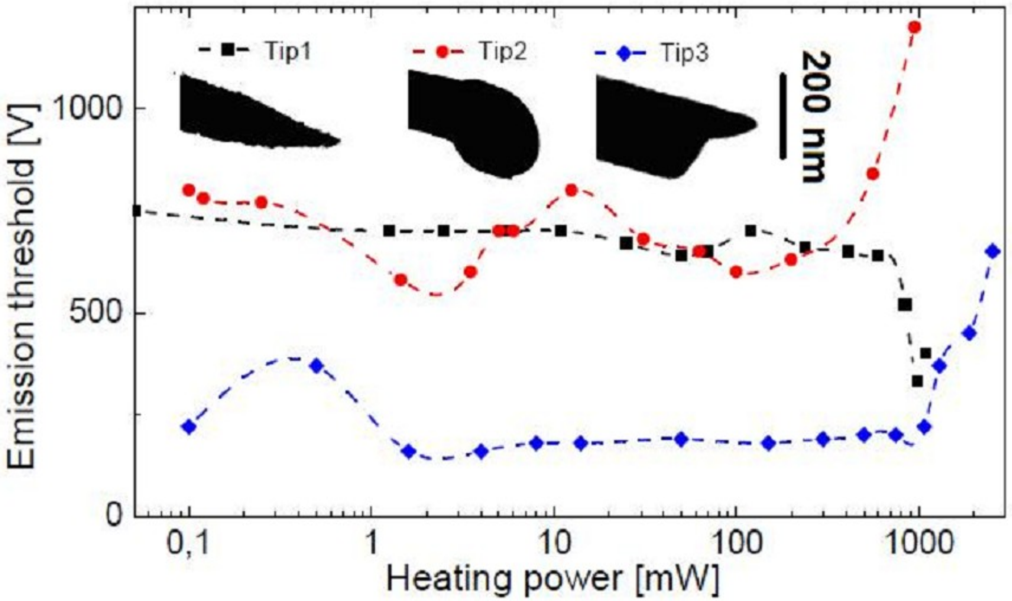
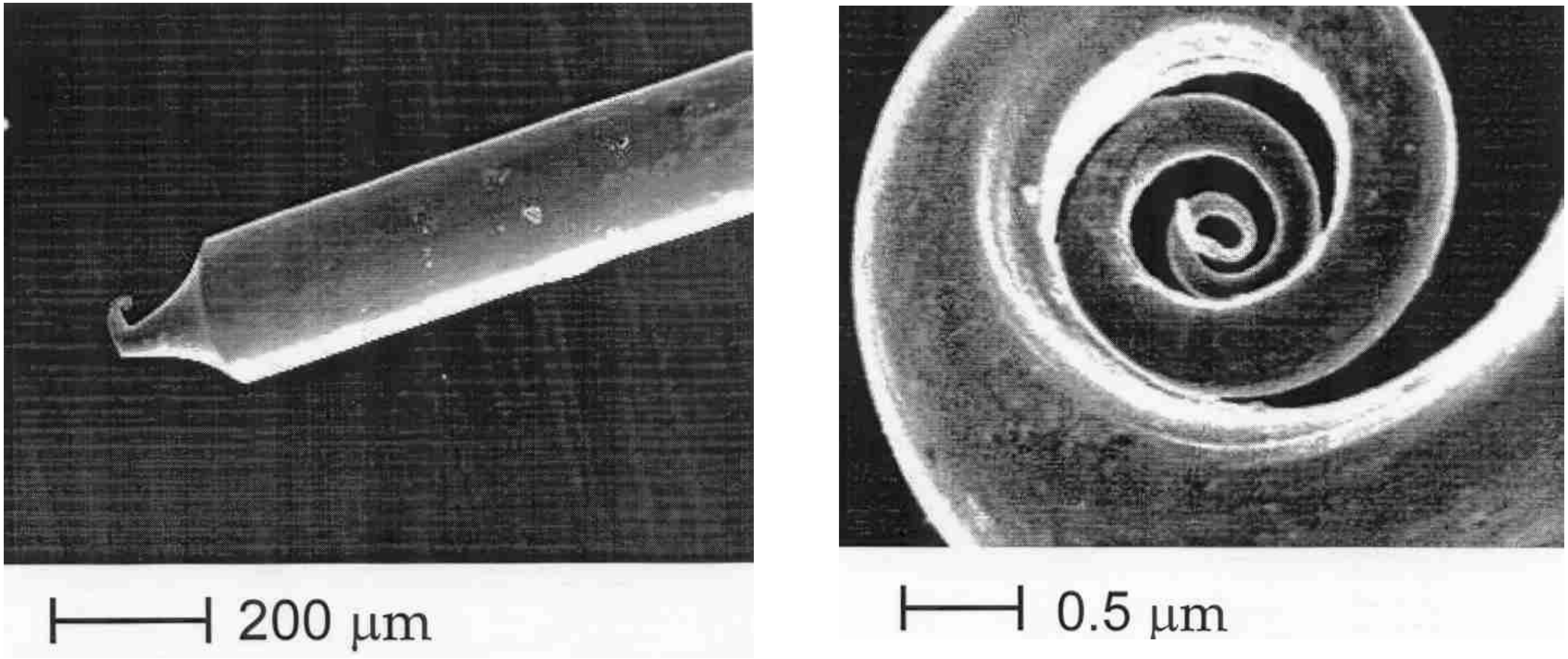
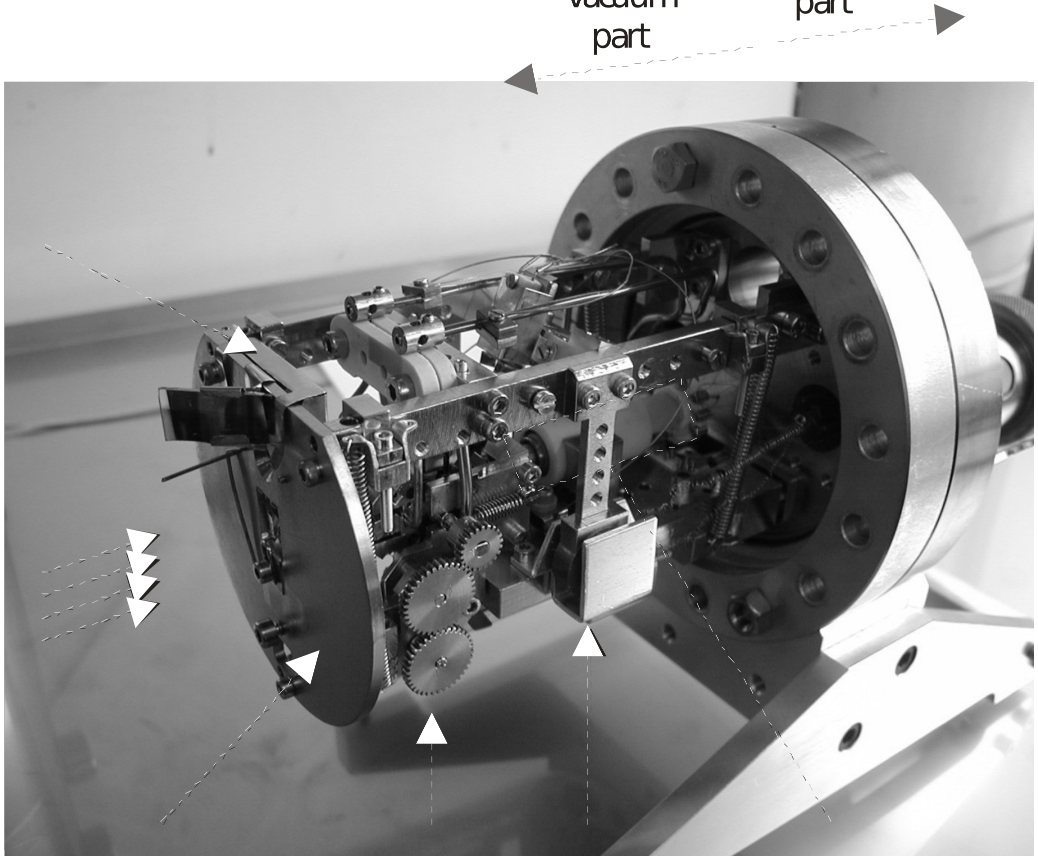


Figure 5: Cleaning the tips by electron bombardment. Evolution of autoemission threshold with increasing heating power. Dashed lines are to guide the eye. Profiles of the tips after the treatment are included (imaged by TEM).



Pt-Ir hrot po kolizi s povrchem vorku
KFPP, snímek ze SEM (J. Macl)

Realizace STM na KFPP



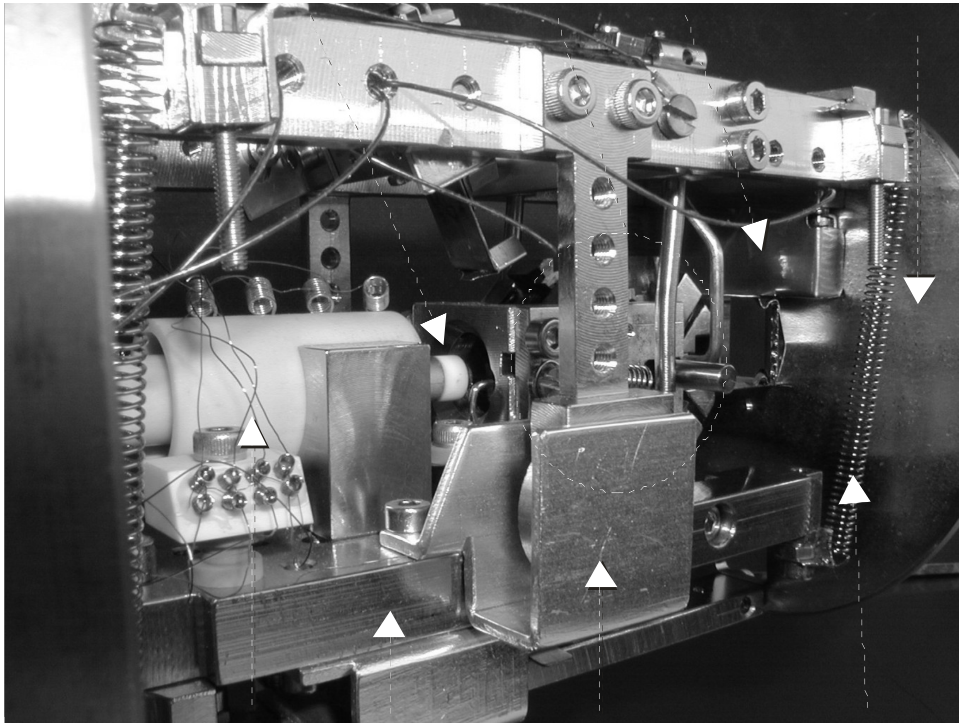
Realizace STM na KFPP

PZT tube with STM tip

rotating carrousel

pozition of the quartz monitor

back plate



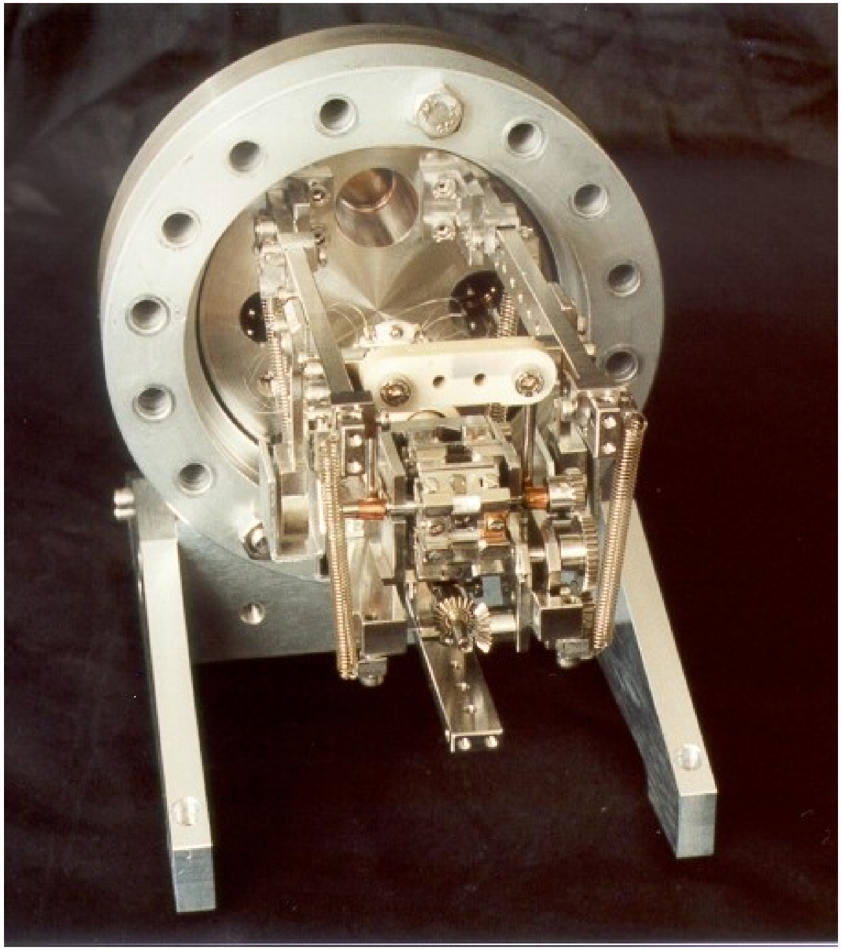
linear inchworm® motor

STM baseplate

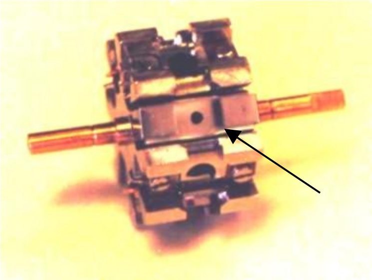
magnetic damping

antivibration spring

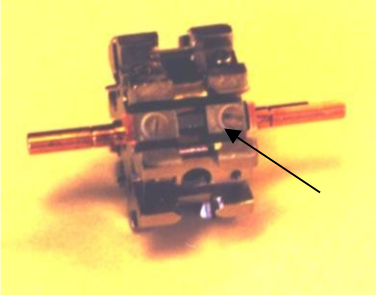
UHV STM head ASCAN



Carrousel

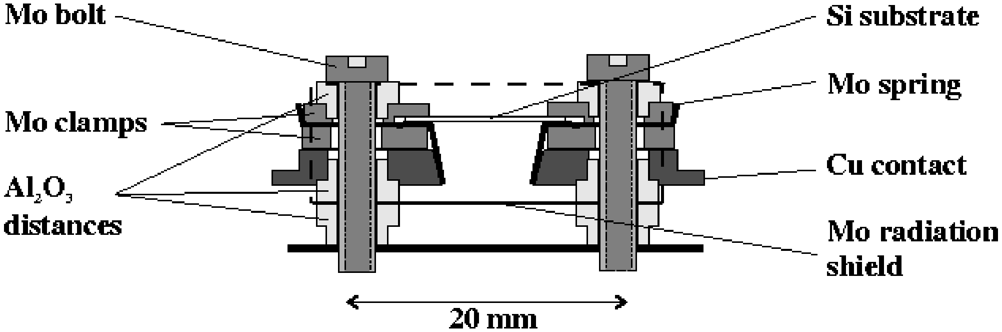


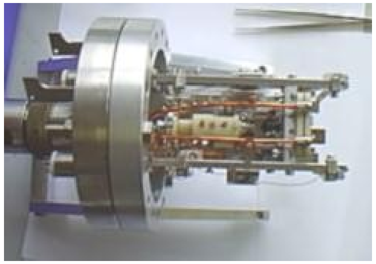
the cell for cleaning a tip by electron bombardment



sample position

sample holder



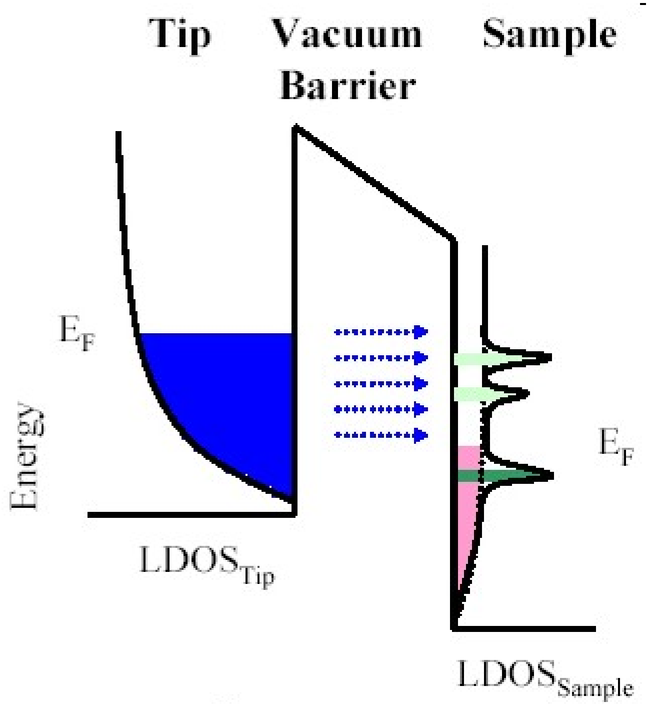


Top view

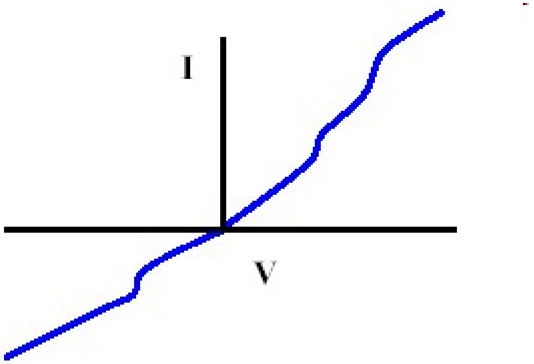
Řádkovací tunelová spektroskopie

scanning tunneling spectroscopy - STS

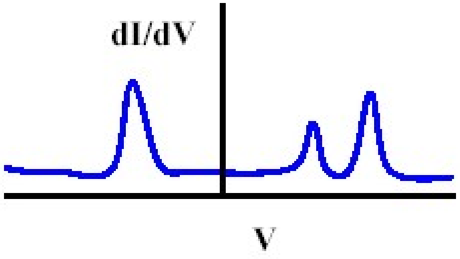
Řádkovací tunelová spektroskopie - princip



$$I \sim e^{-\kappa z} \int_0^{eV} dE \cdot LDOS_{Sample}(E_F + E)$$

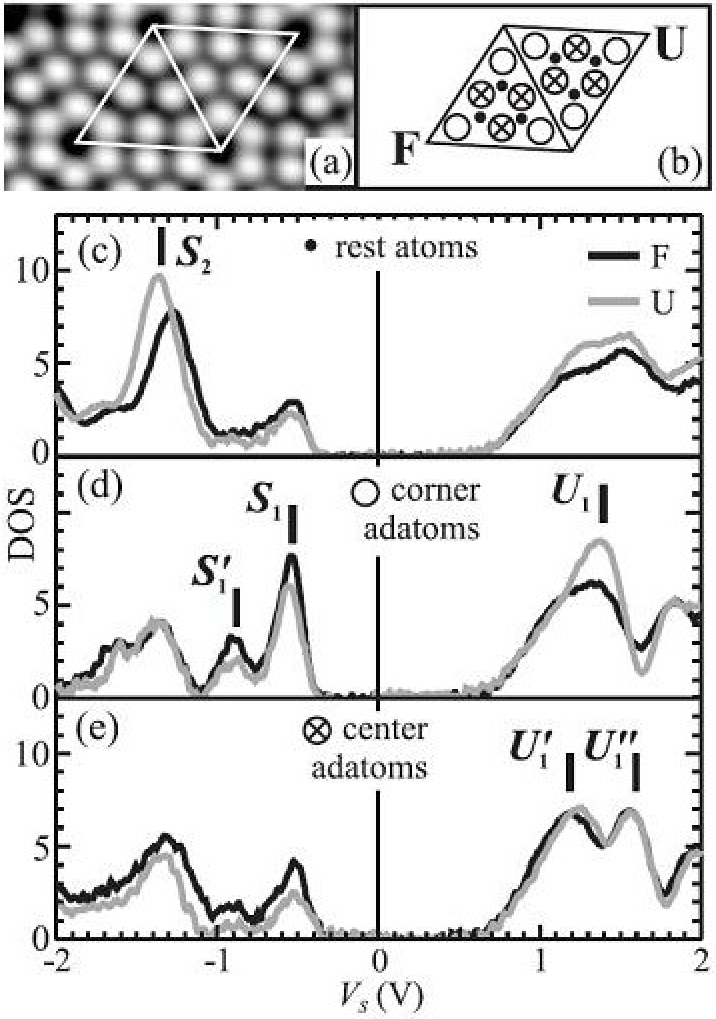


$$I \sim e^{-\kappa z} \int_0^{eV} dE \cdot LDOS_{Sample}(E_F + E)$$

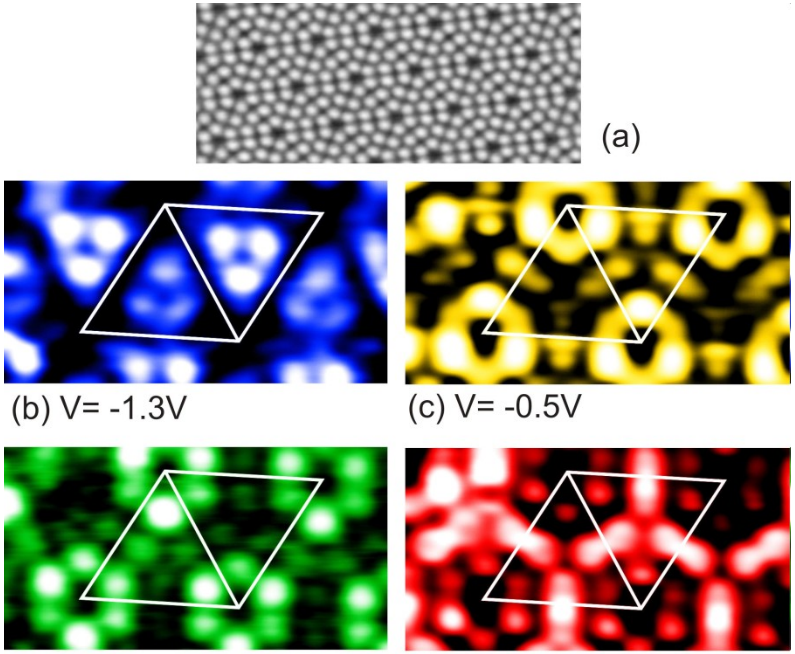


$$\left.\frac{dI}{dV}\right|_V \sim LDOS_{Sample}(E_F + eV)$$

Řádkovací tunelová spektroskopie - příklad



Spectroscopic imaging



(b) V= -1.3V

(c) V= -0.5V

(d) V= 1.4V

(e) V= 1.6V

Phys. Rev. B 73, 161302(R) (2006)

STM – co lze pozorovat - příklady

Co lze pozorovat…

… atomární strukturu

… pohyb atomů po povrchu

… reakce atomů

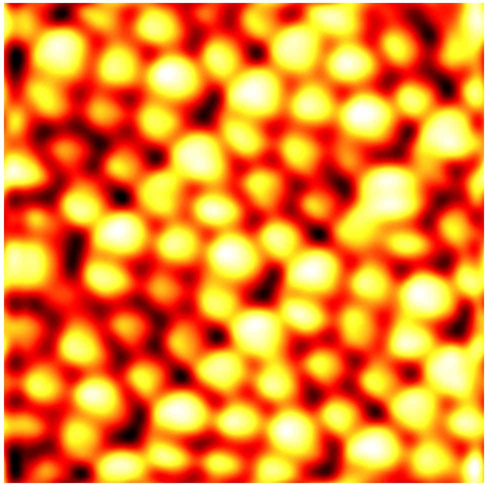
… růst objektů s malou dimenzí (kvantové tečky, dráty a spol.)

… fázové přechody

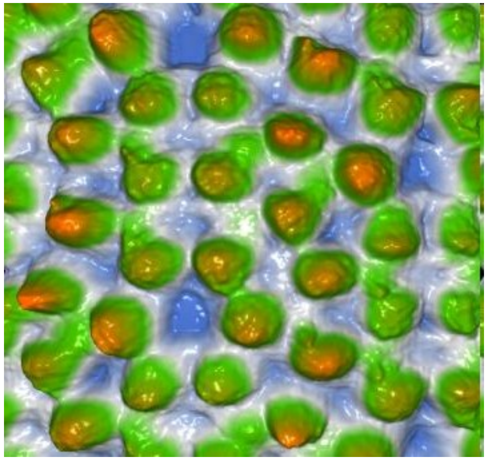
… kvantové jevy

Povrch Si (111)7x7

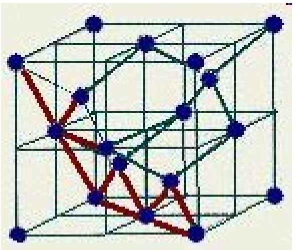
STM

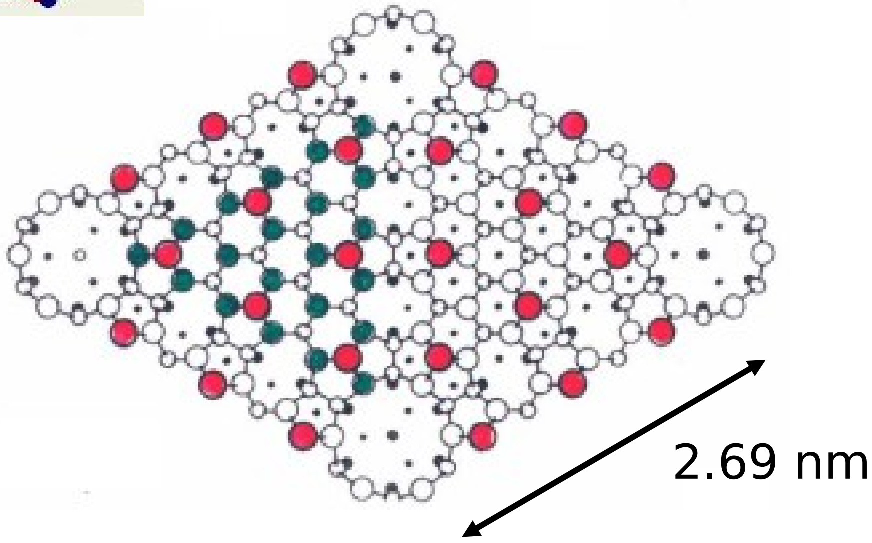


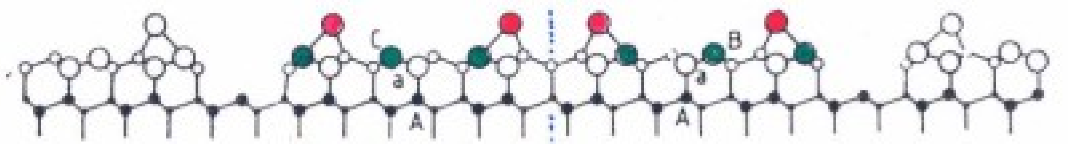
AFM



Phys. Rev. Lett.. 84 2642

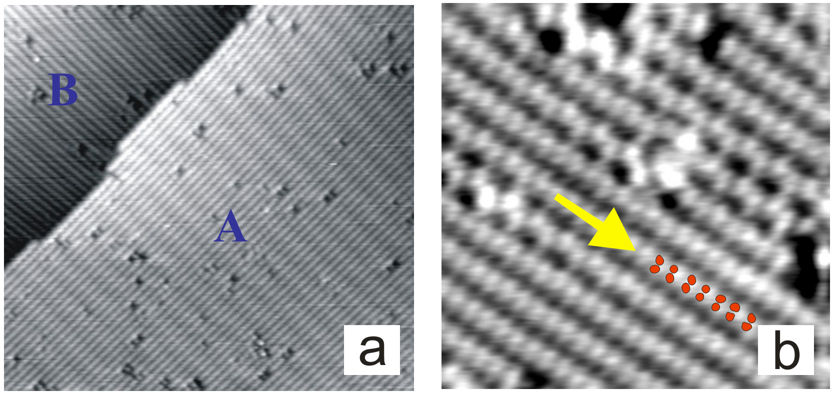


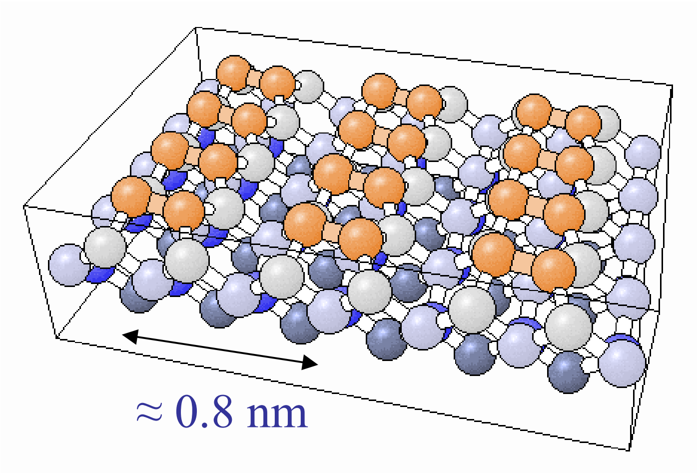




Surface Si(100) 2x1

STM imaging

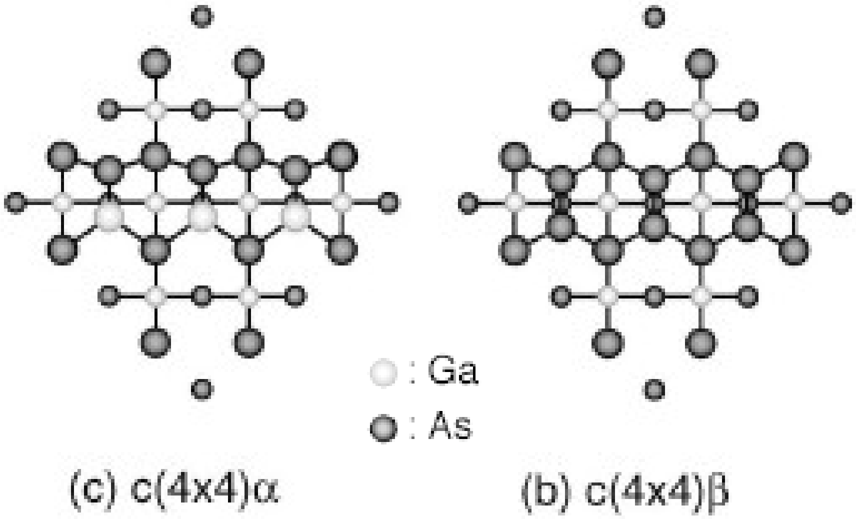




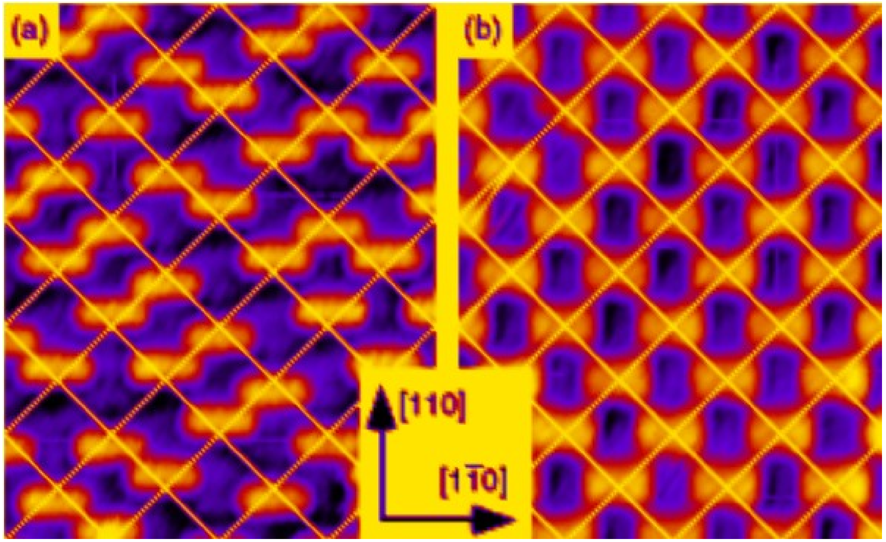
a) empty state image
b) filled state image (defects of various types visible)

GaAs (100)

GaAs – polovodič budoucnosti :)



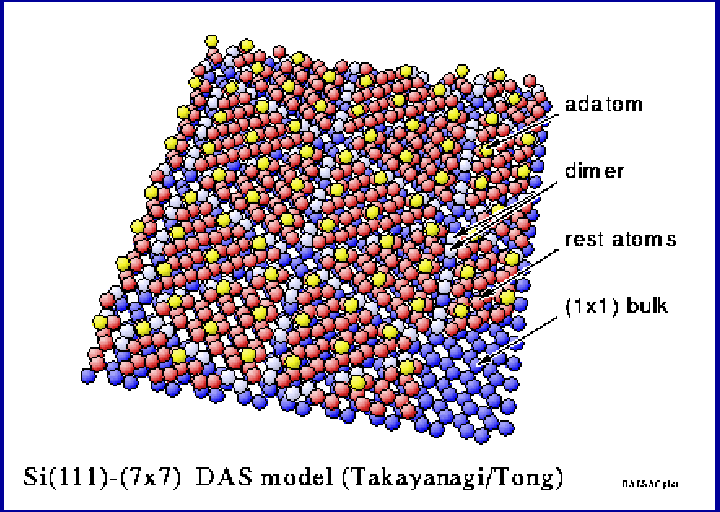
(c) c(4x4)α (b) c(4x4)β



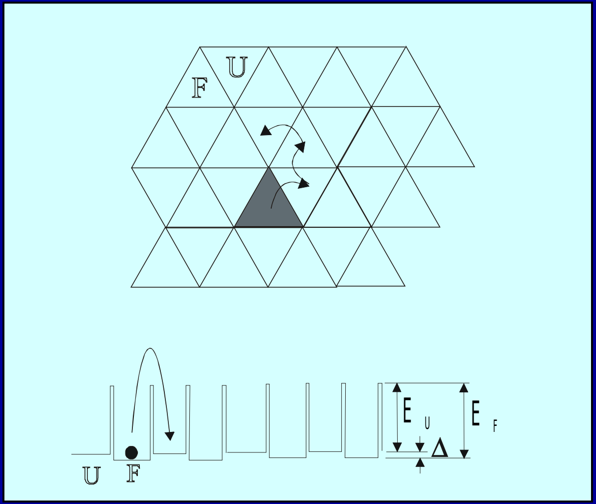
6,4 nm x 8,0 nm **napětí na hrotu ~ 3V**
- zobrazuje As atomy

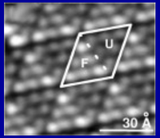
Adsorpce kovů na Si površích
povrchová rekonstrukce - předloha pro růst nanostruktur

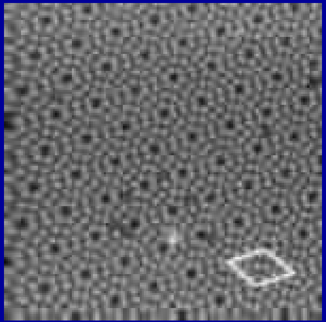
Si(111)-(7×7)



Si(111)-(7x7) DAS model (Takayanagi/Tong)







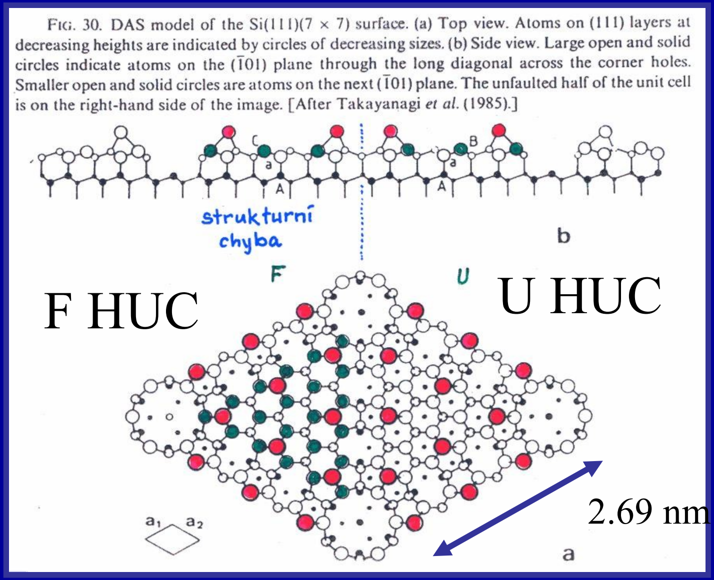
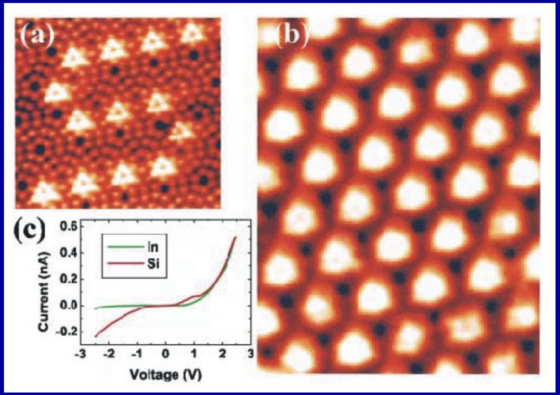


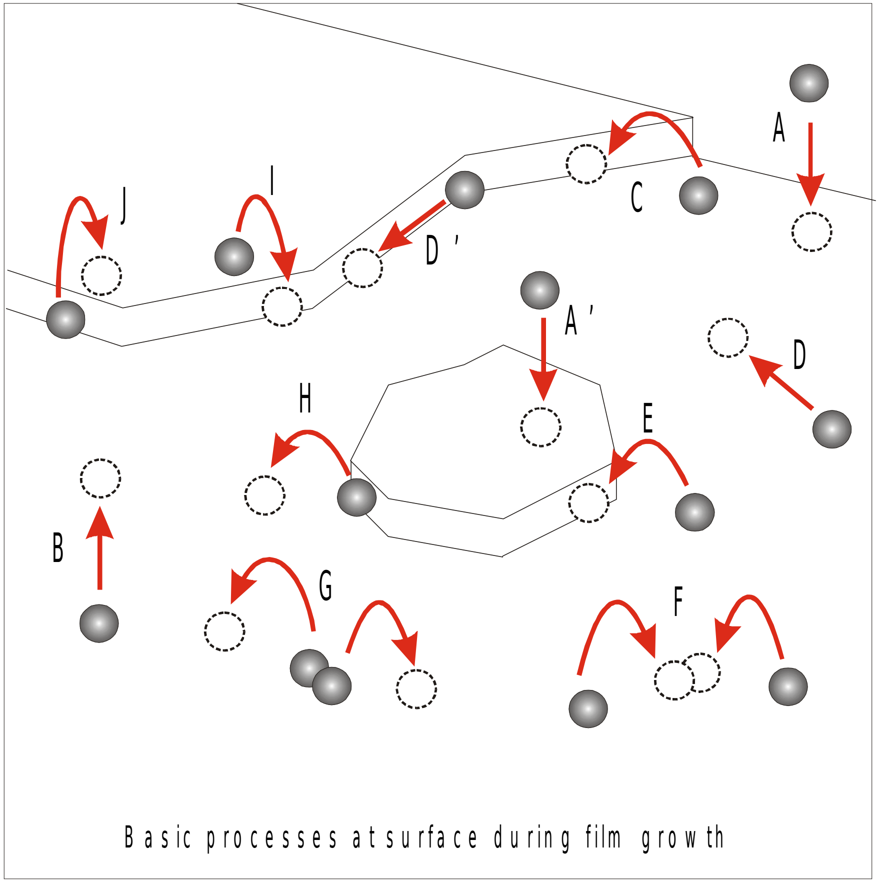
FIG. 30. DAS model of the Si(111)(7 × 7) surface. (a) Top view. Atoms on (111) layers at decreasing heights are indicated by circles of decreasing sizes. (b) Side view. Large open and solid circles indicate atoms on the ($\bar{1}01$) plane through the long diagonal across the corner holes. Smaller open and solid circles are atoms on the next ($\bar{1}01$) plane. The unfaulted half of the unit cell is on the right-hand side of the image. [After Takayanagi *et al.* (1985).]

In na Si(111)-(7×7)



Jian-Long Li et al., PRL 88 (2002),66101

Povrchové procesy



Basic processes at surface during film growth

A, A'- depozice

B - desorpce

C – připojení ke schodu

D - difuse

D'- difuse podél schodu

E – připojení k ostrůvku

F – vznik nového zárodku

G – rozpad nestabilního zárodku

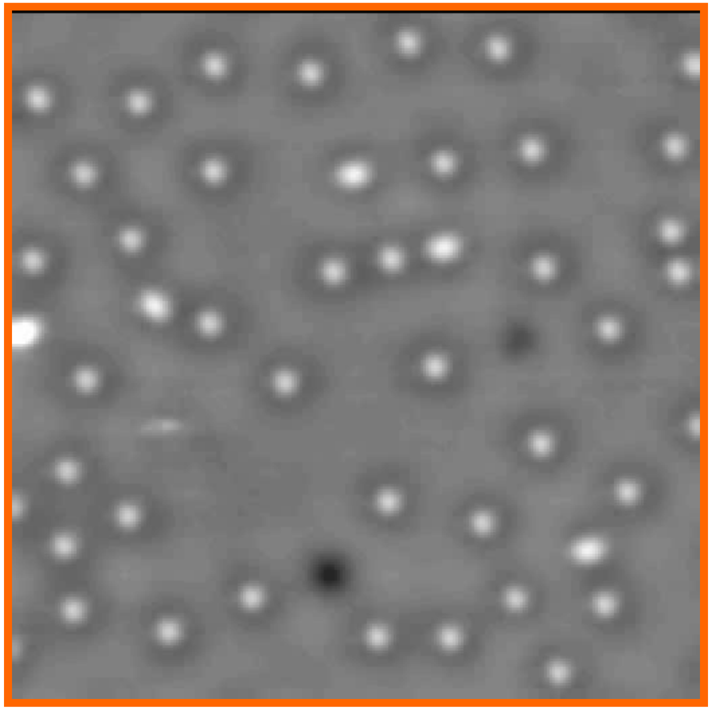
H – odpojení atomu od ostrůvku

I – přeskok atomu ze schodu dolu

J – skok atomu nahoru na schod

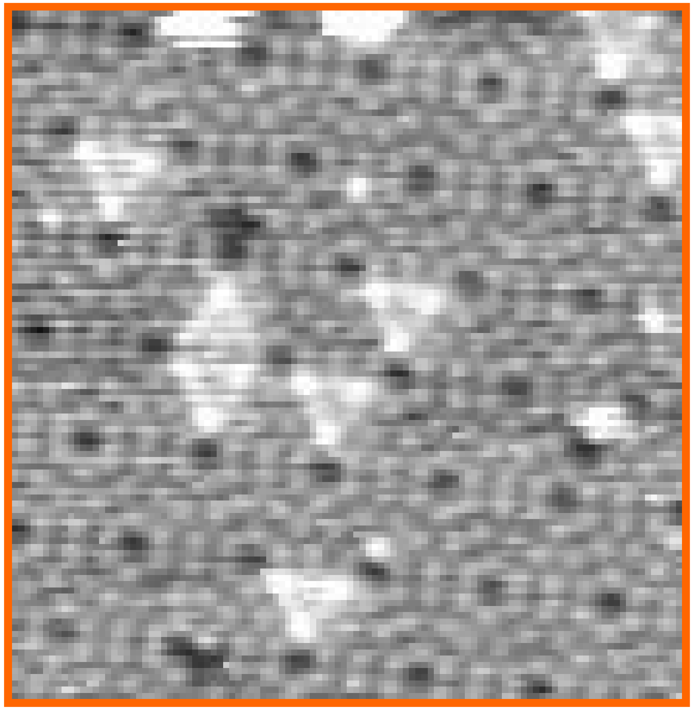
…atomární difuse

Atomy a páry atomů Cu
na Ag(111), T = 16 K

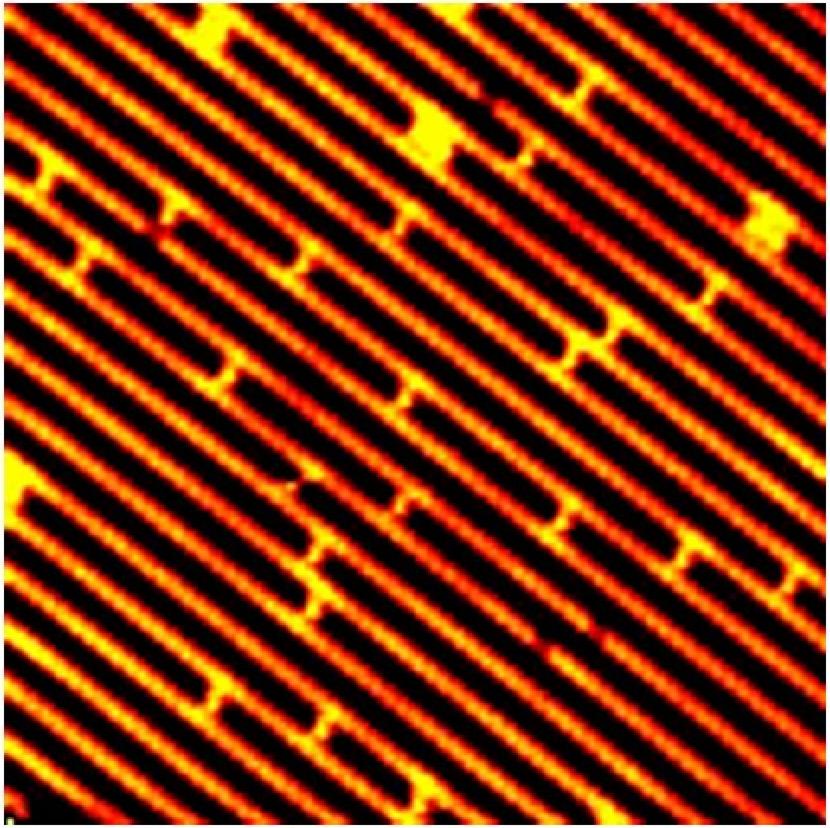


Phys. Rev. Lett.. 93 (2004) 056102

Atomy Ag na Si(111)
T = 40 ºC

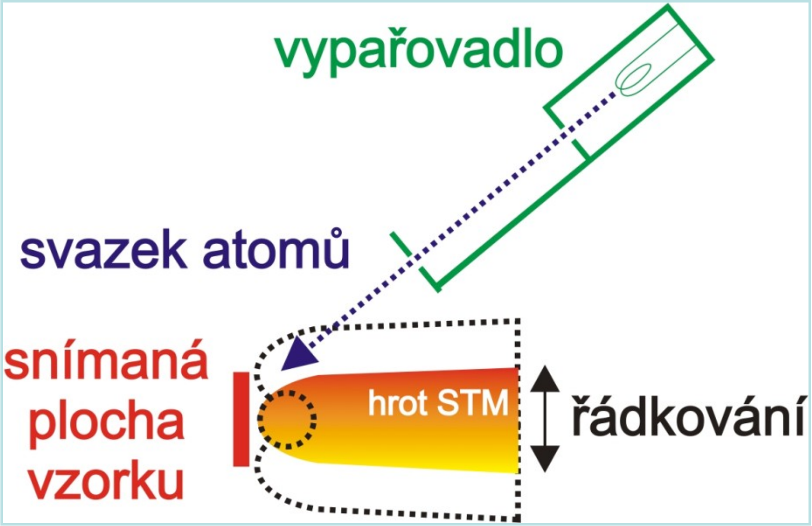


Pt atomy na Pt(110)

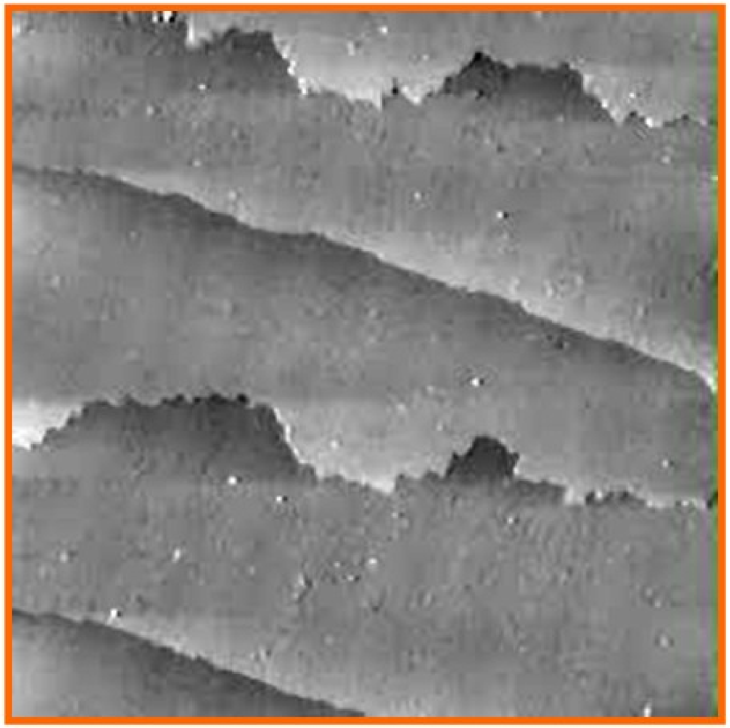


Aarhus Universitet

Růst objektů s malou dimenzí – růst krystalu

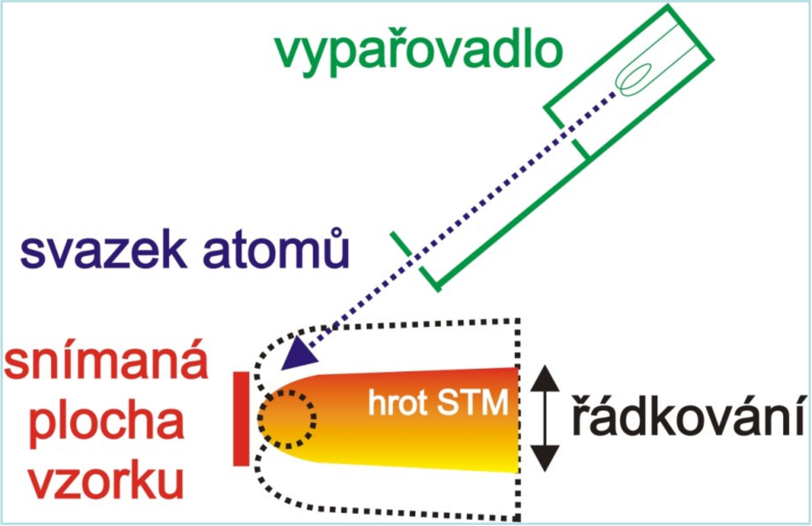


růst Si(100) krystalu

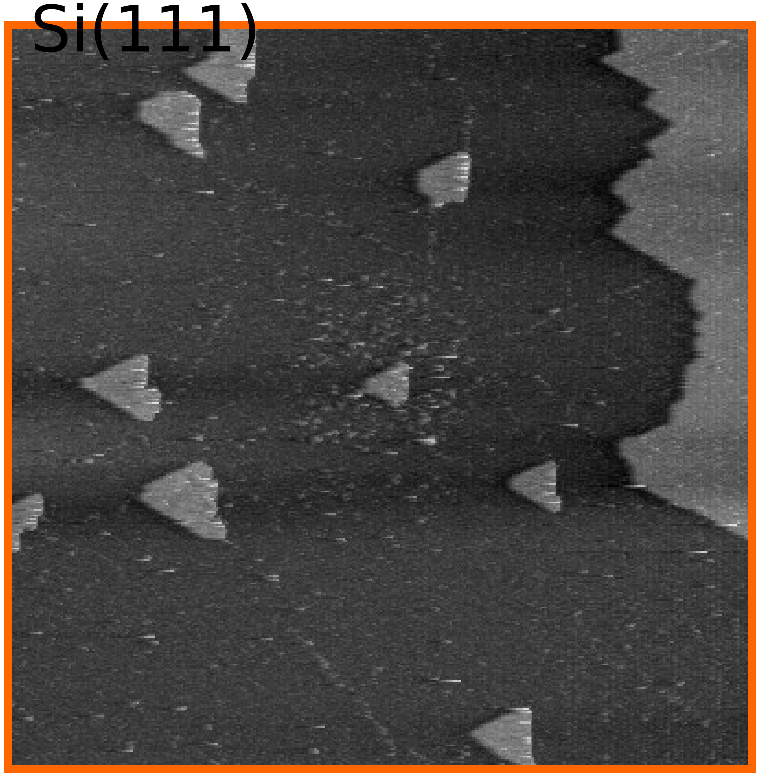


Bert Voigtländer, Jülich

Růst objektů s malou dimenzí – růst krystalu



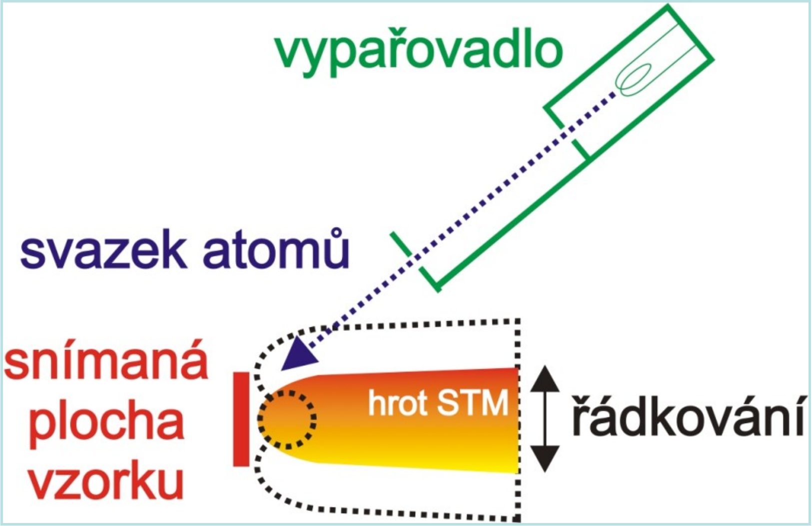
růst Ge vrstvy na Si(111)

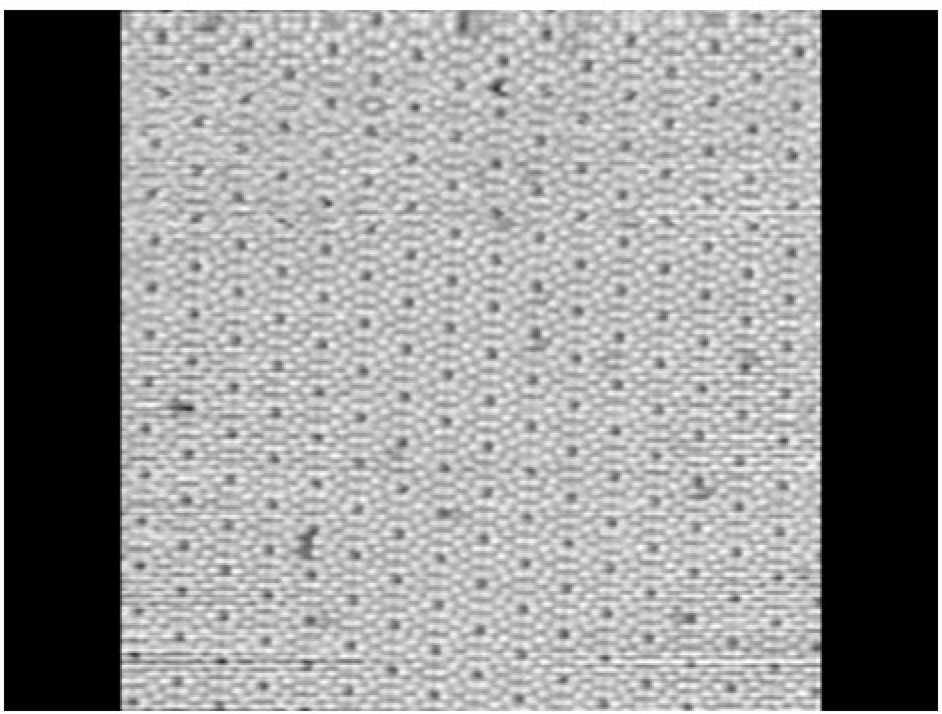


University of Rome

Růst objektů s malou dimenzí – růst krystalu

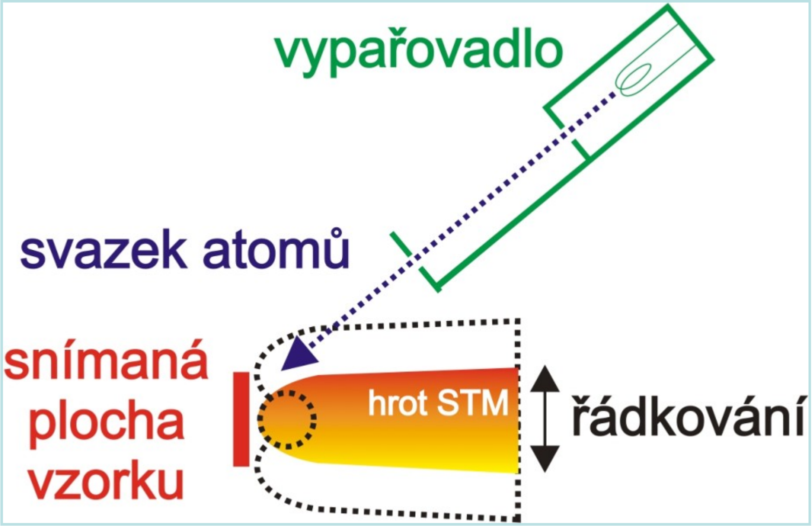
růst Ag kvantových teček na Si(111) - vznik umělého 2D krystal

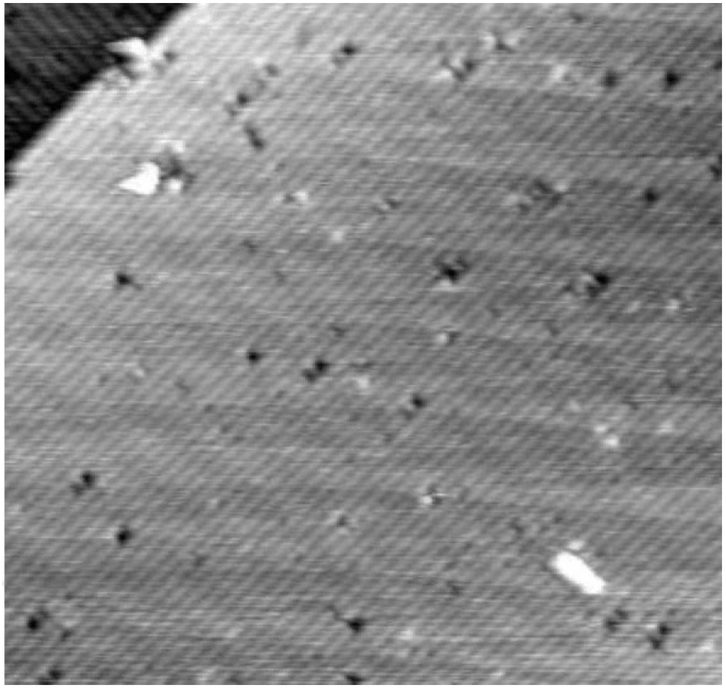




Růst objektů s malou dimenzí – růst kvantových drátů

růst In kvantových drátů na Si(10





jsme omezeni na povrch?

STM omezeně „vidí“ i pod povrch
příklad: Mn dopanty v GaAs

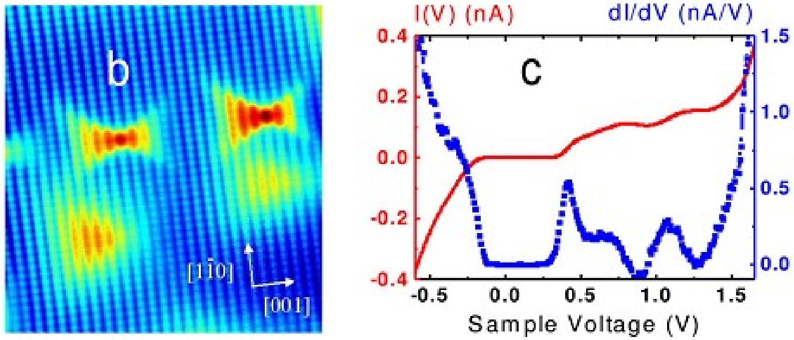


FIG. 1 (color online). (a) Mosaic of three overlapping topographical images measured at $T = 77$ K, on a (110) surface, with sample-to-tip voltage $V_{st} = +1.7$ V, current $I_t = 100$ pA. The Be-doped and Mn-doped GaAs layers are clearly identified. The triangular-shaped and butterflylike images correspond to Be and Mn dopants, respectively. (b) Atomic-resolution image ($V_{st} = 1$ V, $I_t = 100$ pA) showing a few impurity states. (c) Typical $I_t(V_{st})$ and dI_t/dV_{st} curves measured at fixed height in the center of a Mn impurity image.

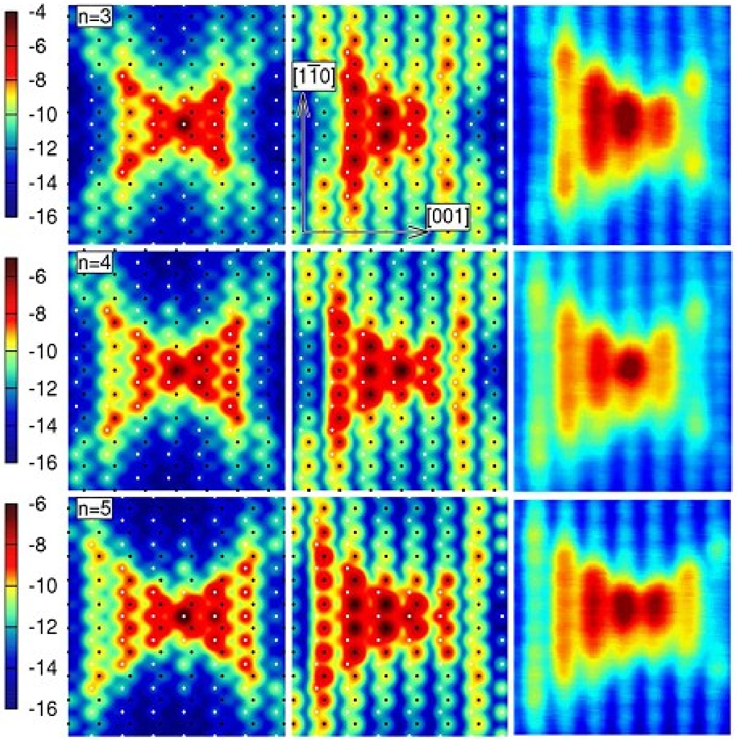
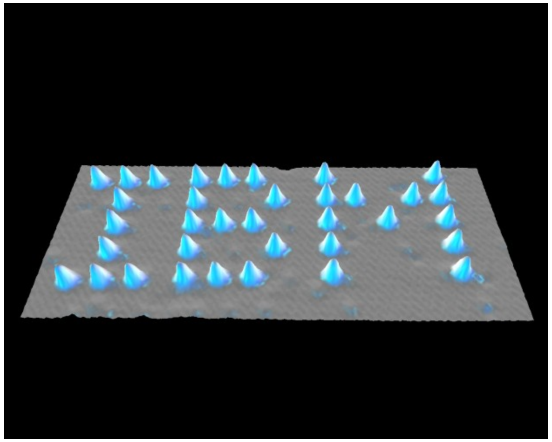


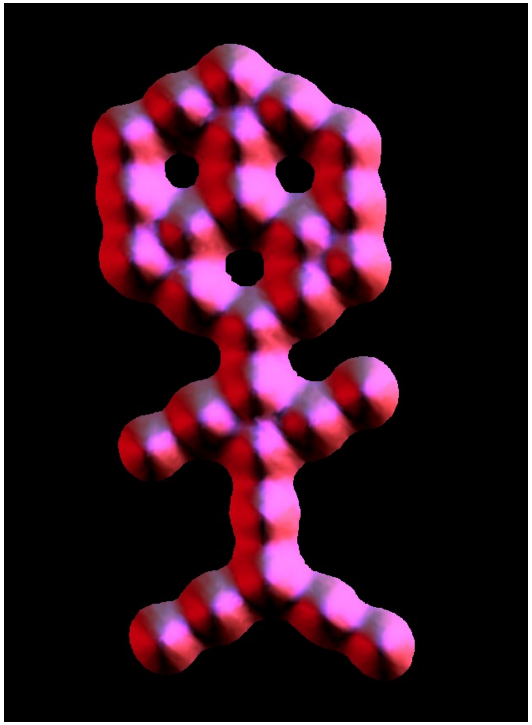
FIG. 4 (color online). Bulk impurity cross section (BICS) (left), simulated STM images (SSTM) (center), and experimental STM images (right) of a Mn neutral acceptor located n monolayers ($n = 3$ to 5) below the (110) surface. BICS is calculated in a (110) plane, n atomic planes away from the impurity, and SSTM 2 Å above the surface. SSTM LDOS is multiplied by 10^4 with respect to BICS. As (white) and Ga (black) positions on the surface are indicated.

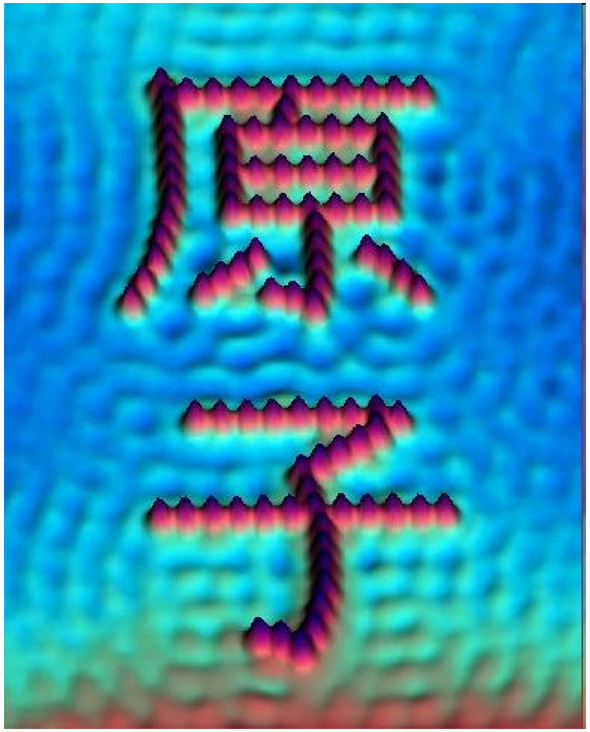
PRL 101, 196801 (2008)

Manipulace s atomy

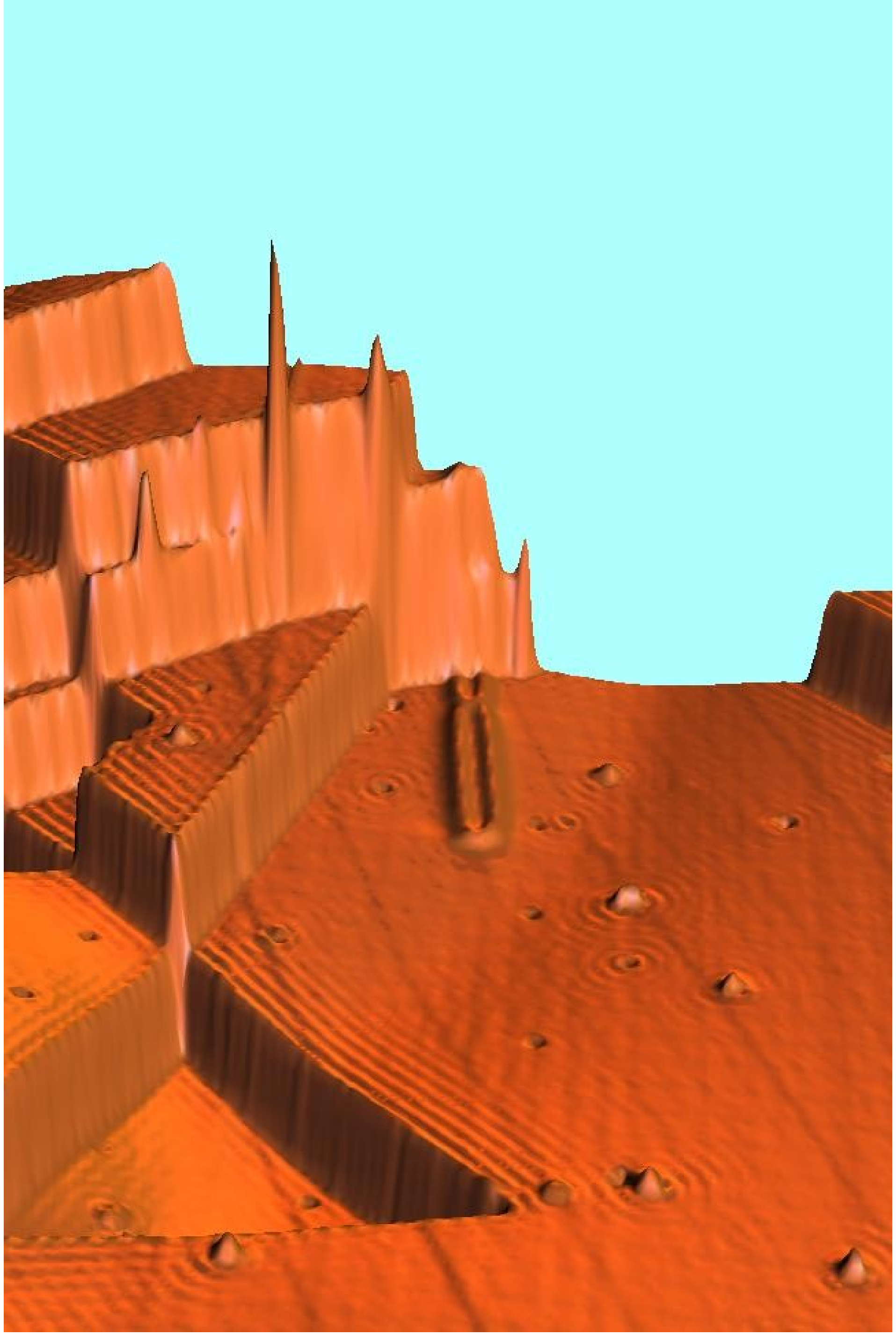
Manipulace s atomy







IBM



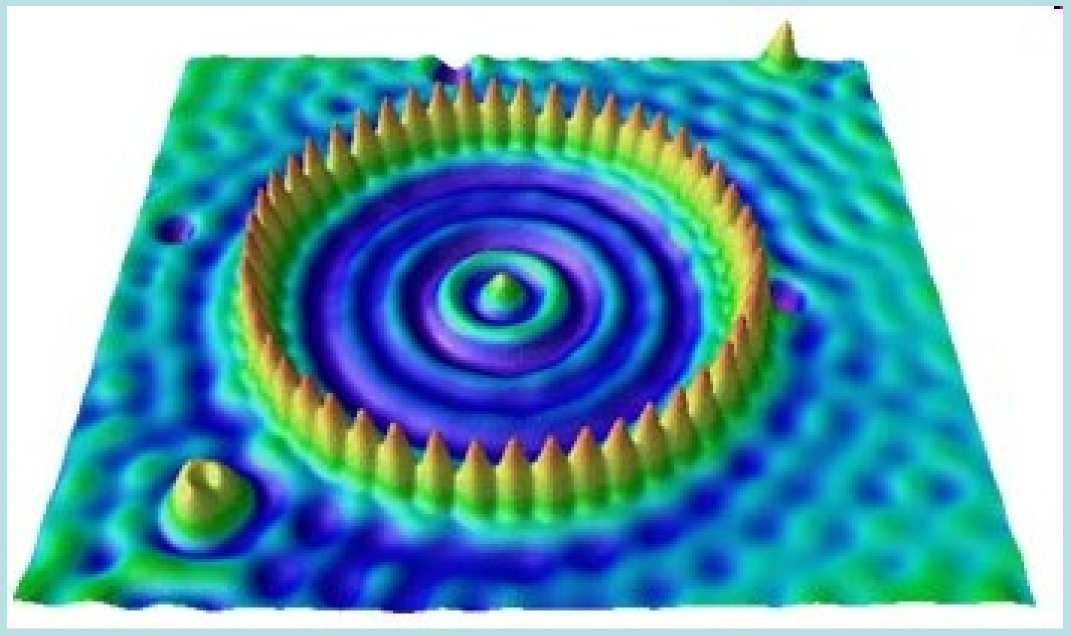
Povrch Cu(111)

Stojaté vlny ve dvourozměrném (2D) „elektronovém plynu“

λ≈1.5 nm (≈10 atoms),
amplituda na hraně schodu ≈0.004 nm
T ≈ 4K

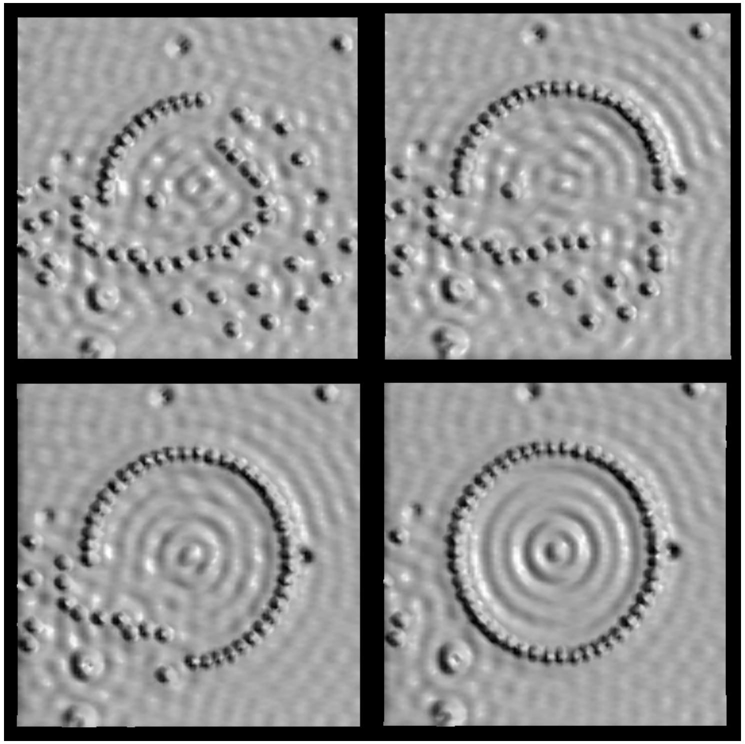
© M.F. Crommie, C.P. Lutz, D.M. Eigler,
Nature 363, 524-527 (1993)

kvantová ohrádka

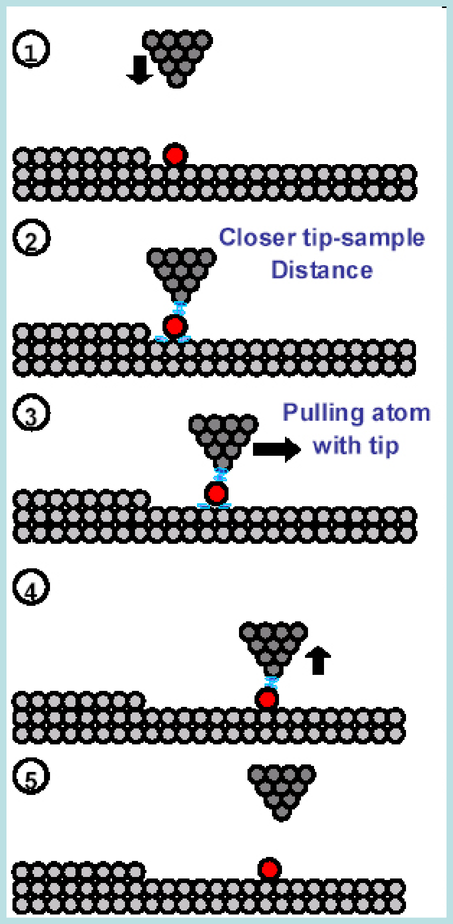


IBM

Vytvořeno atom
po atomu!

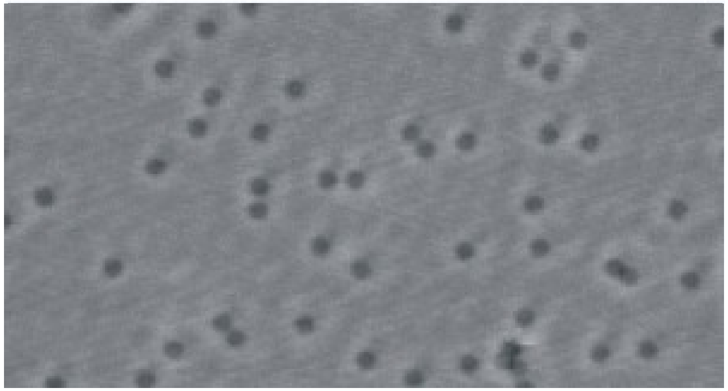


Manipulace s atomy

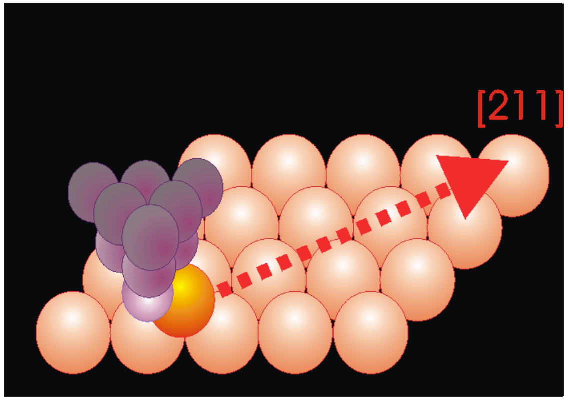


Univ. of California

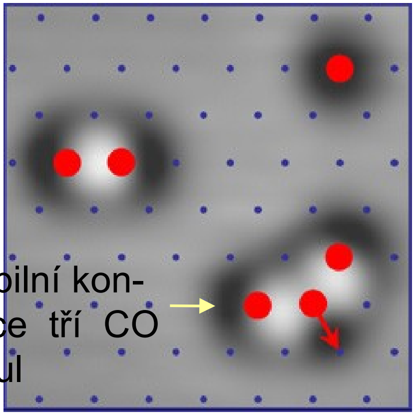
- hrot se přiblíží k atomu tak blízko, aby došlo k interakci
- hrot táhne atom za sebou („pull mode“) nebo tlačí před sebou („push mode“)
- obvykle – nízké teploty (L He)



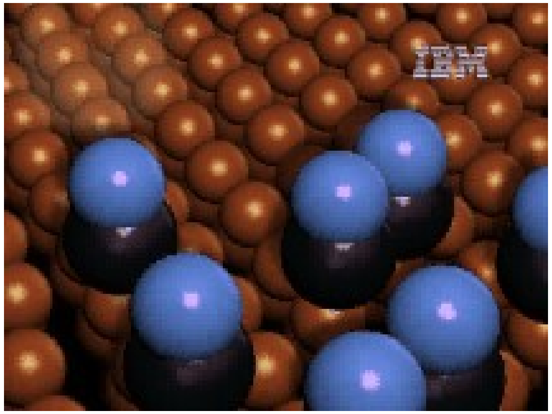
Manipulace s jednotlivými atomy a molekulami



Molekulární kaskády – nejmenší aktivní prvky

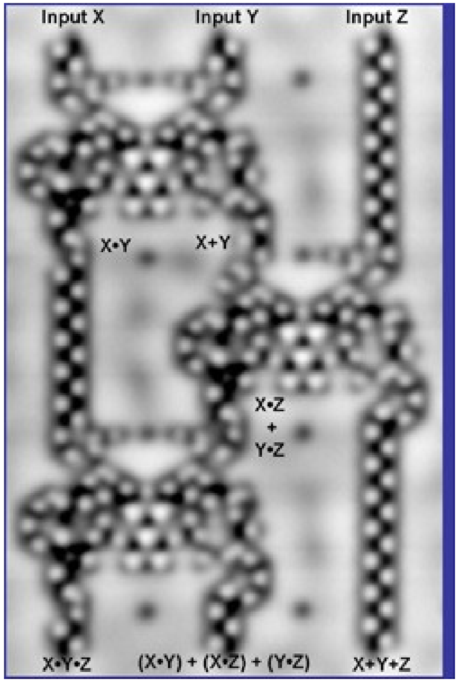


Nestabilní konfigurace tří CO molekul



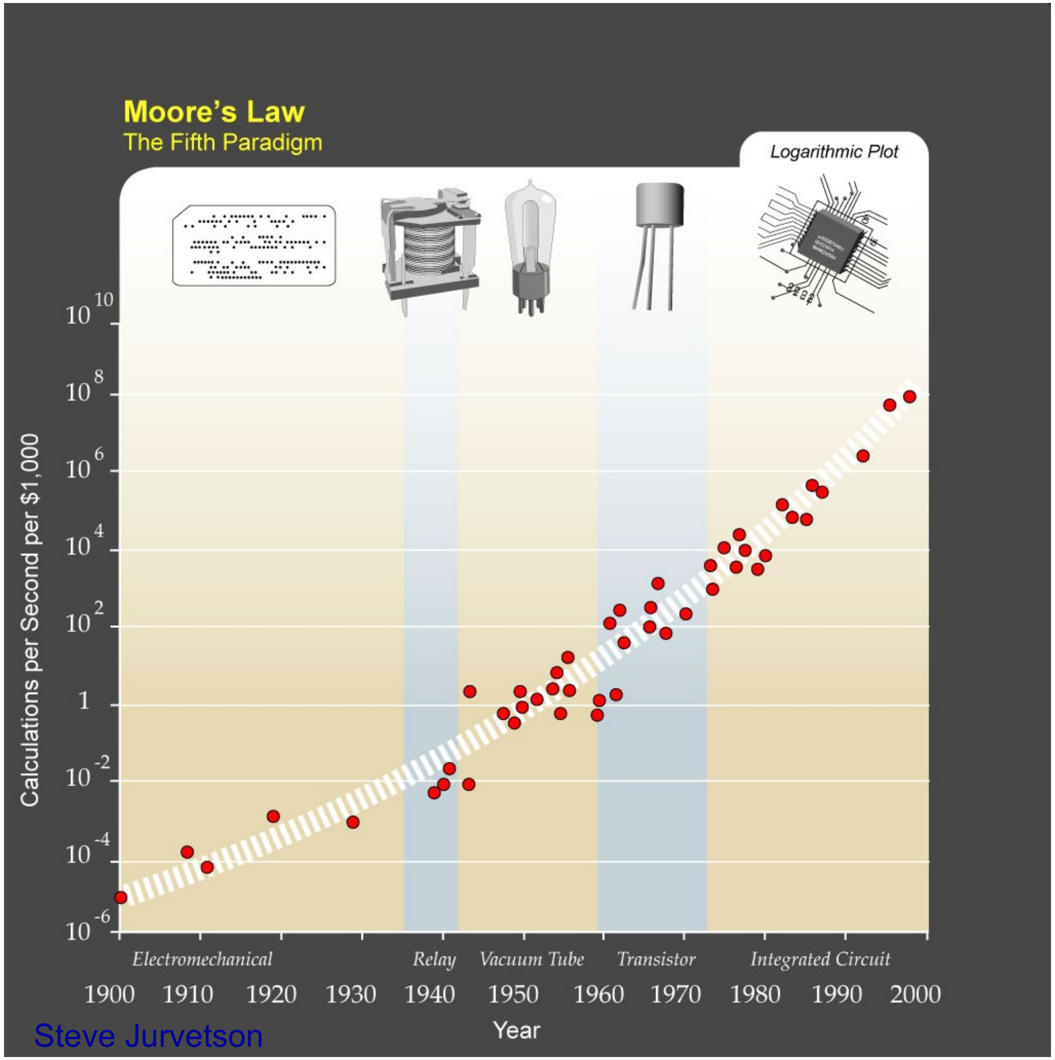
Díky slabé odpudivé interakci mezi molekulami CO na povrchu Cu(111) lze tři molekuly uspořádat do metastabilní konfigurace. Tato nestabilita uměle vyvolaná na konci molekulární kaskády se může šířit na „velké“ vzdálenosti.

Realizace 12×17 nm



Odbočka – Mooreův zákon

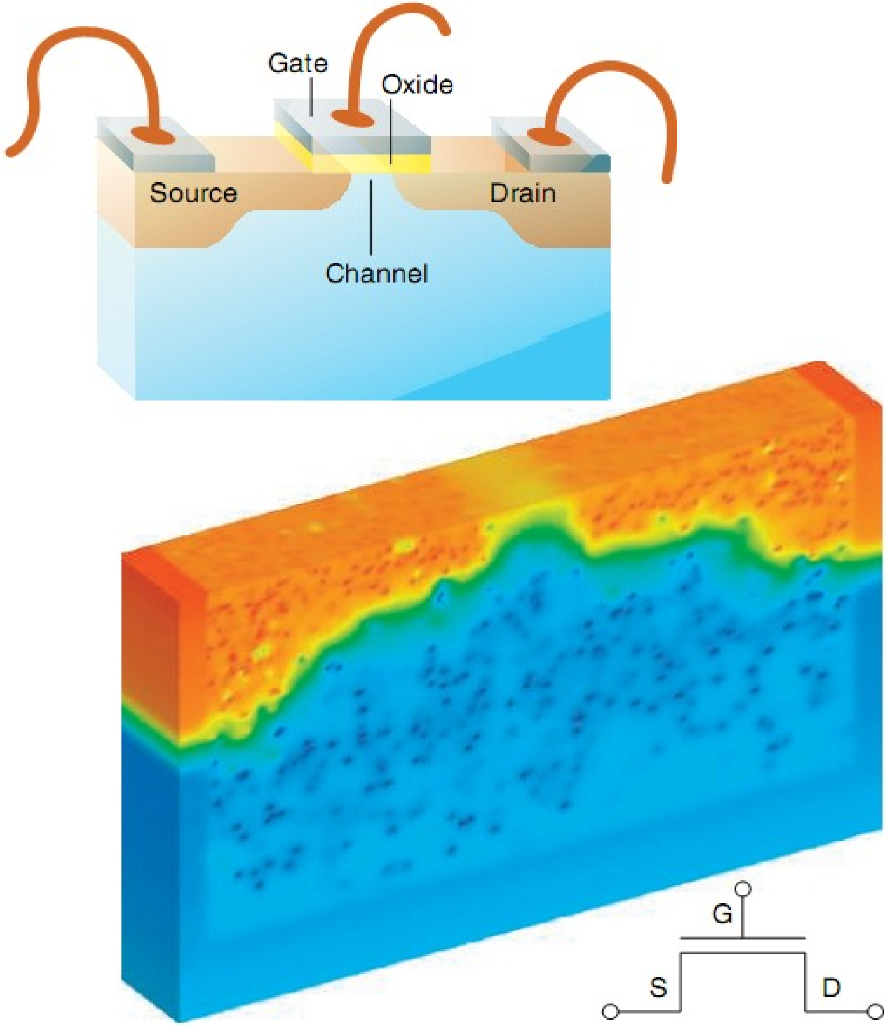
Mooreův zákon (1965!) - „složitost součástek roste s časem exponencielně při zachování stejné ceny.“
(Gordon Moore – spoluzakladatel firmy Intel)



Steve Jurvetson

Jak dlouho bude Mooreův zákon platit?

Význam dopantů

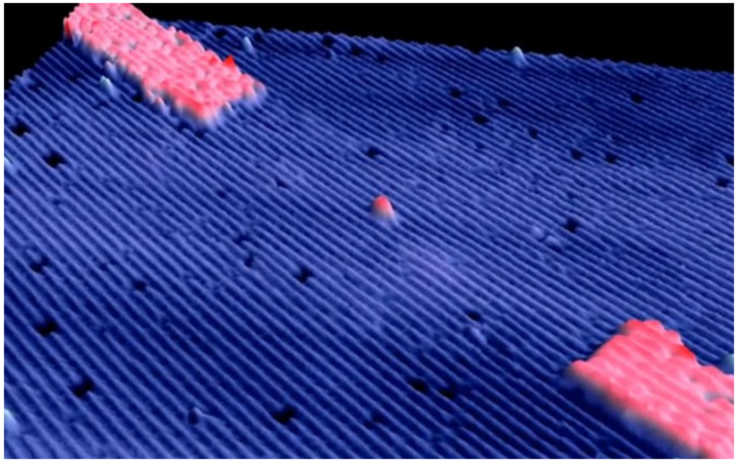


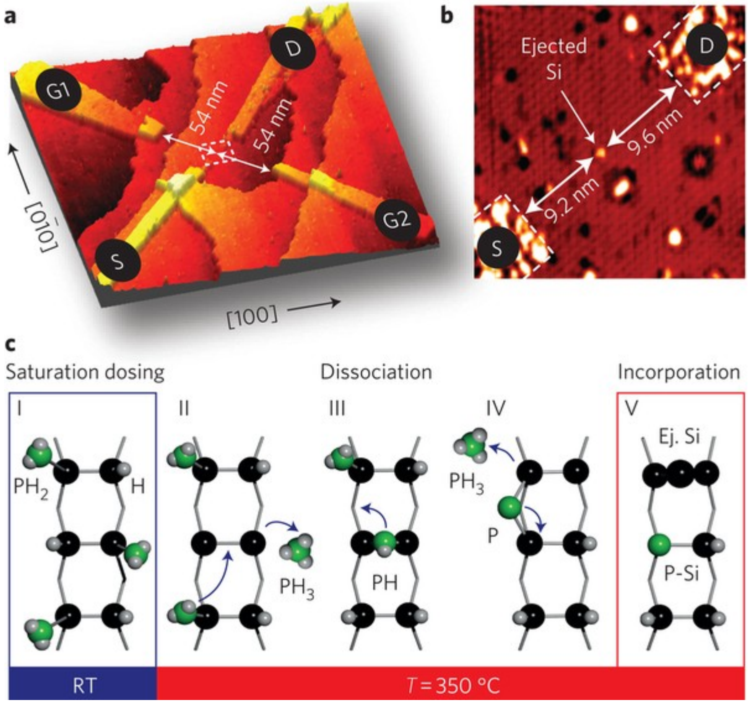
3D simulace FETu (field effect transistor) 30x30nm s náhodně rozmístěnými dopanty, barva odpovídá elstat. potenciálů (červená 1 V, modrá 0 V). Fluktuace vlivem dopantů ovlivňují funkci FETu

se zmenšováním polovodičových součástek začíná být každý jednotlivý dopant důležitý!

Roy:**Where Do the Dopants Go?**, Science 309, 388 (2005)

Single atom transistor





M. Fuechsle et al., Nature Nanotechnology 2012, DOI: 10.1038/NNANO.2012.21

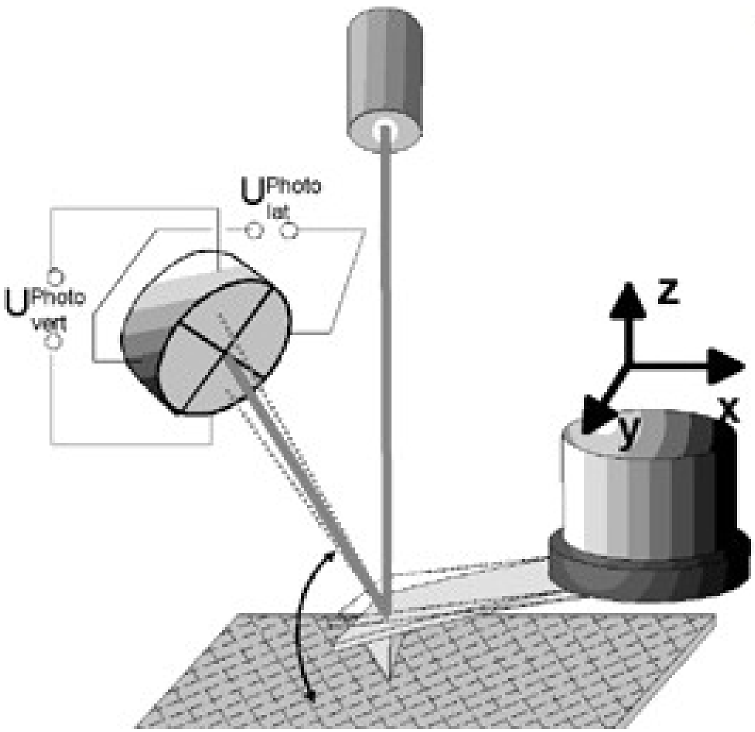
Mikroskopie atomárních sil

atomic force microscopy - AFM

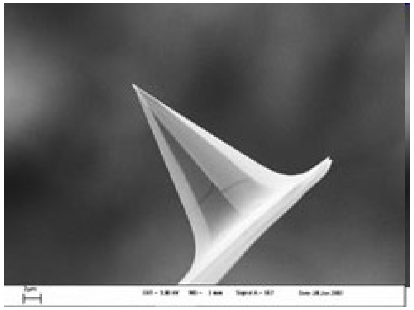
Mikroskopie atomárních sil

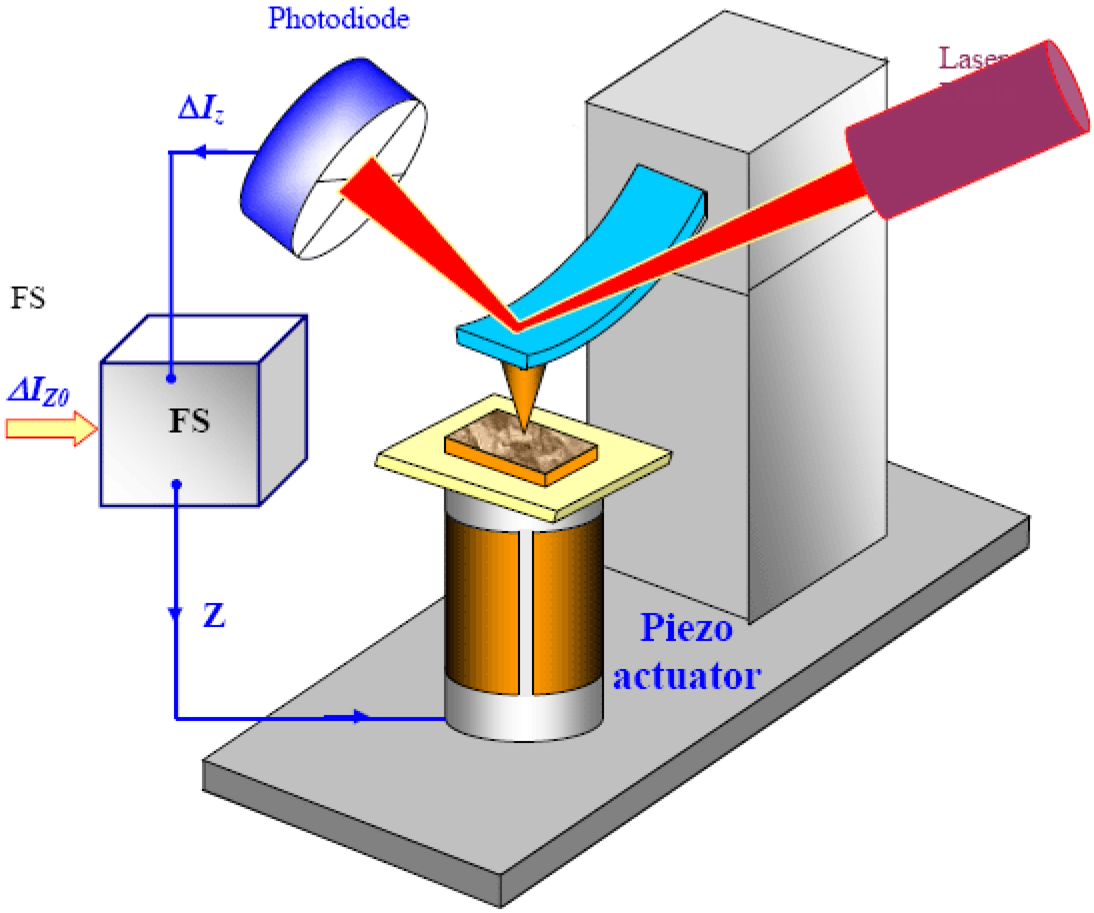
= AFM (Atomic Force Microscope)

- princip podobný jako u STM
- místo tunelového proudu se využívá atomárních sil
- např. pomocí laserového paprsku se měří náklon raménka s hrotem



http://www.nanocraft.de

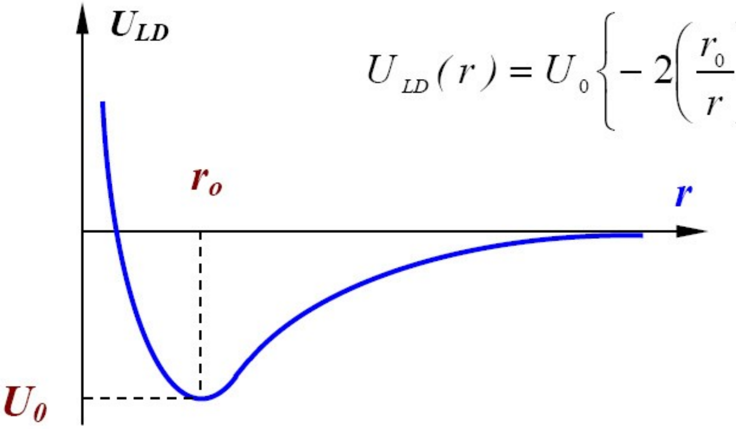




Princip AFM

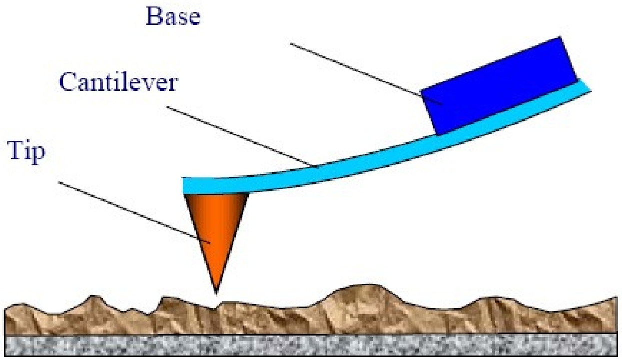
➢ Atomic force microscopy (AFM)

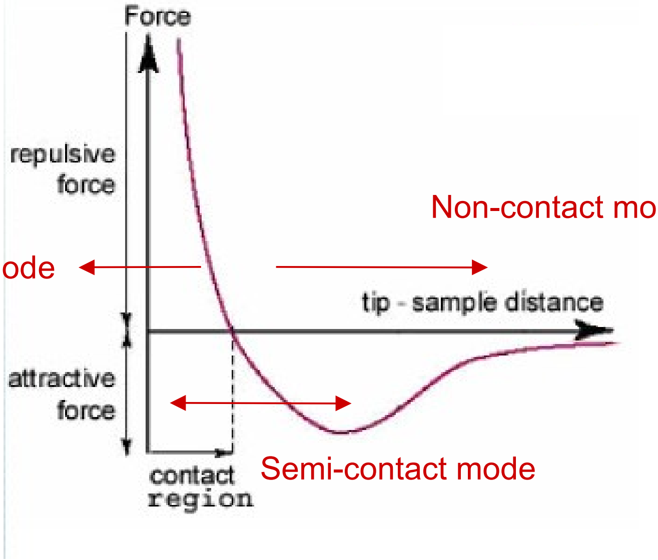
Physical principles:



$$U_{LD}(r) = U_0\left\{-2\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12}\right\}.$$

Lennard-Jones potential qualitative form





Contact mode

Non-contact mode

Semi-contact mode

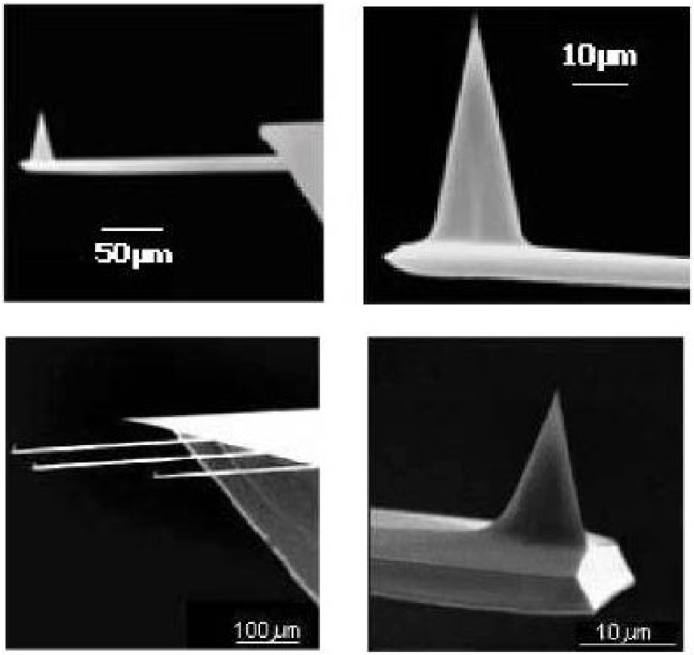


Fig. 68. SEM images of AFM tips on rectangular cantilevers [54]

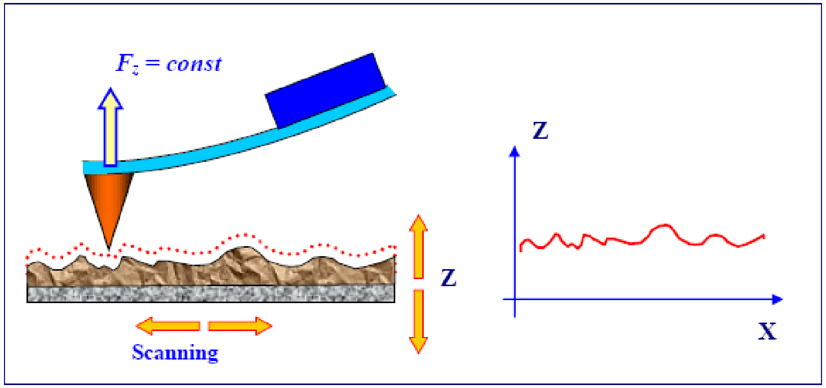


Fig. 72. AFM image acquisition at constant force

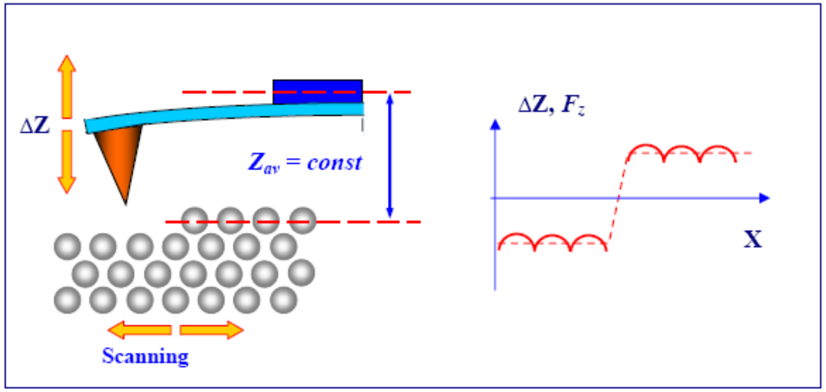
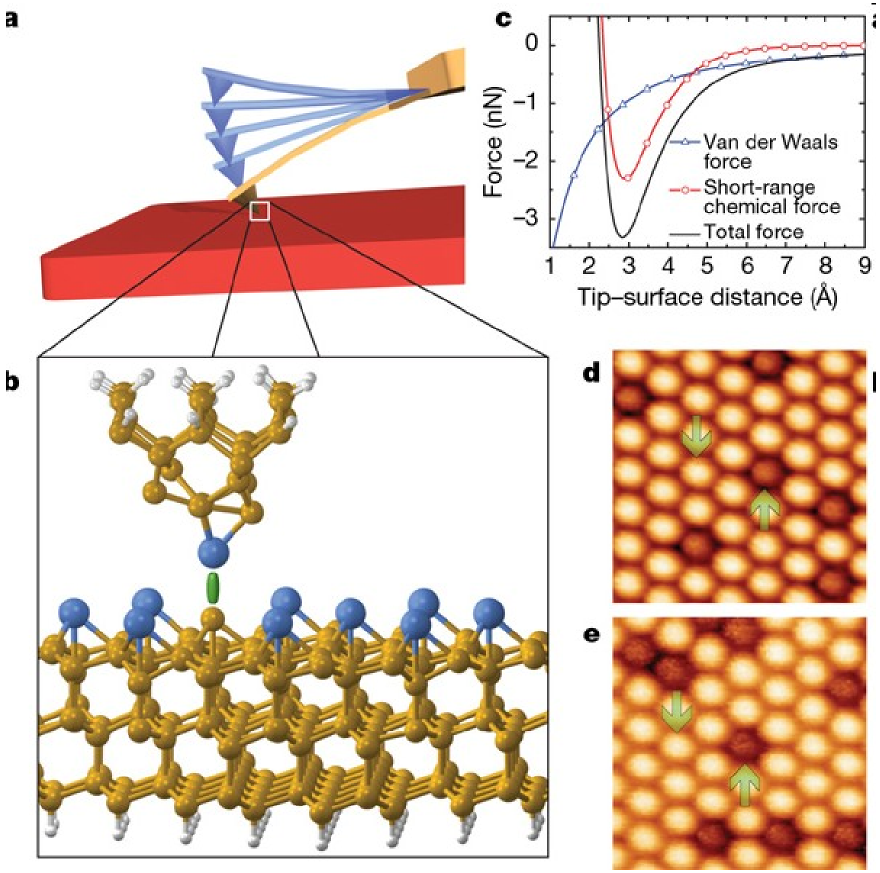


Fig. 73. AFM image acquisition at constant average distance (constant height)

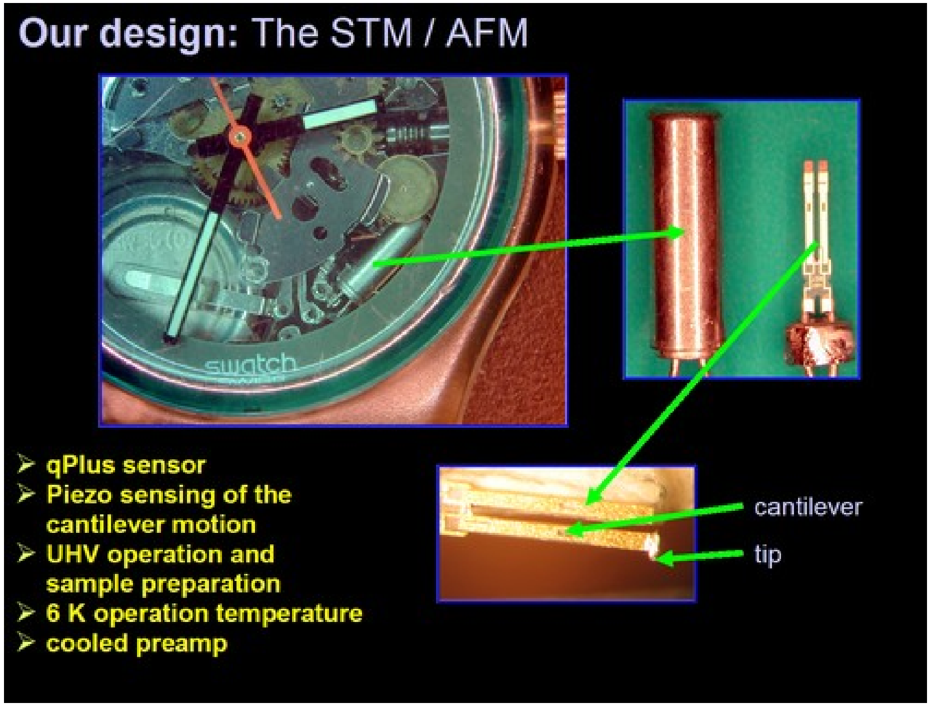
AFM v dynamickém modu

Schematic illustration of AFM operation in dynamic mode (a), and of the onset of the chemical bonding between the outermost tip atom and a surface atom (highlighted by the green stick) that gives rise to the atomic contrast14, 15 (b). However, the tip experiences not only the short-range force associated with this chemical interaction, but also long-range force contributions that arise from van der Waals and electrostatic interactions between tip and surface (though the effect of the latter is usually minimized through appropriate choice of the experimental set-up). c, Curves obtained with analytical expressions for the van der Waals force, the short-range chemical interaction force, and the total force to illustrate their dependence on the absolute tip–surface distance. d–e, Dynamic force microscopy topographic images of a single-atomic layer of Sn (d) and Pb (e) grown, respectively, over a Si(111) substrate. At these surfaces, a small concentration of substitutional Si defects, characterized by a diminished topographic contrast20, is usually found.



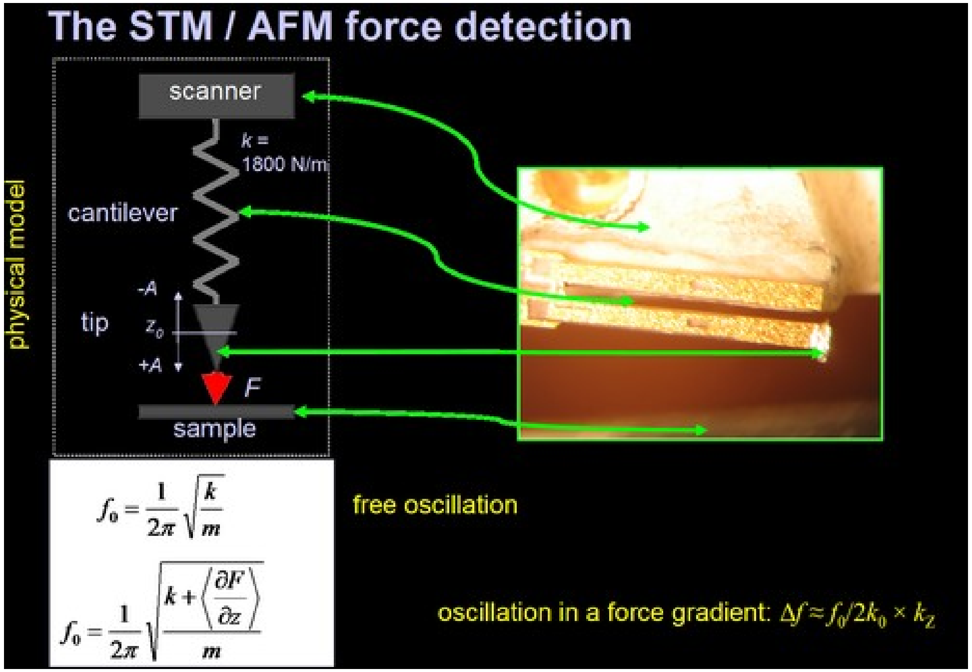
Nature 446, 64-67 (2007)

tuning fork AFM



Our design: The STM / AFM

- **qPlus sensor**
- **Piezo sensing of the cantilever motion**
- **UHV operation and sample preparation**
- **6 K operation temperature**
- **cooled preamp**



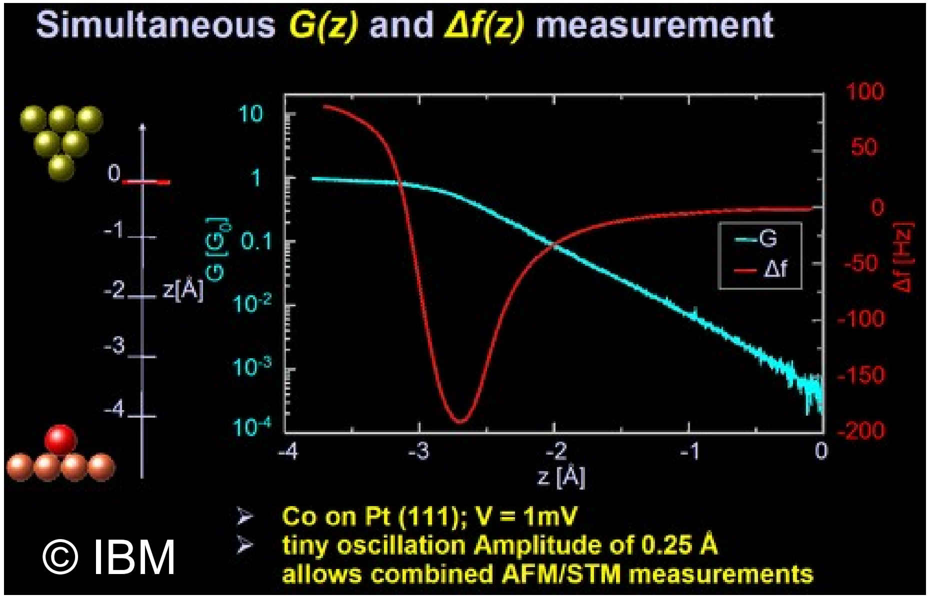
The STM / AFM force detection

$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

free oscillation

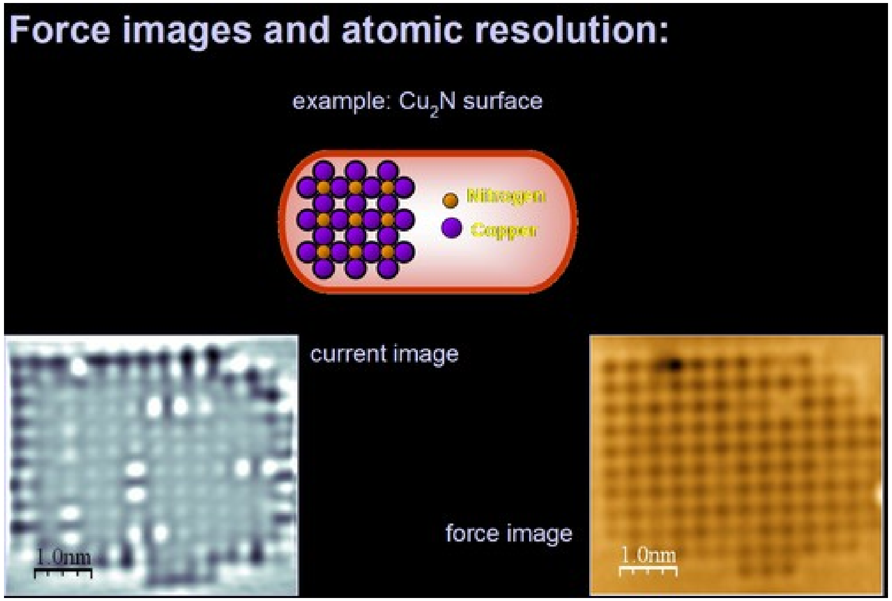
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{k + \left\langle \frac{\partial F}{\partial z} \right\rangle}{m}}$$

oscillation in a force gradient: $\Delta f \approx f_0/2k_0 \times k_z$



Simultaneous *G(z)* and *Δf(z)* measurement

- **Co on Pt (111); V = 1mV**
- **tiny oscillation Amplitude of 0.25 Å allows combined AFM/STM measurements**



Force images and atomic resolution:

example: Cu_2N surface

current image

force image

Příklad MEFM (magnetic exchange force microscopy)

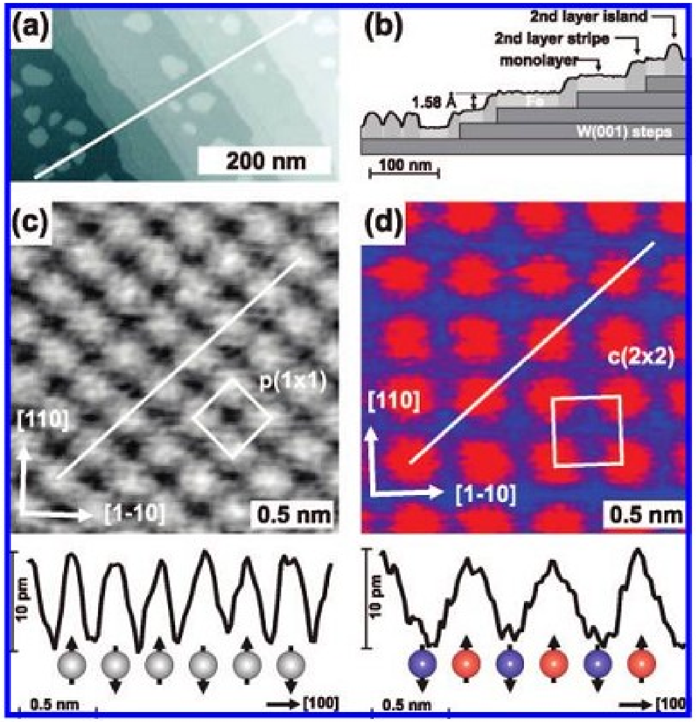


Figure 1. (a) Atomic force microscopy topography image of about 1.3 atomic layers of Fe deposited on W(001). (b) Line section showing substrate steps and areas covered by one and two atomic layers of Fe. (c) Atomic resolution on the Fe monolayer displaying the p (1×1) structural and chemical surface unit cell ($\Delta f = -28.5$ Hz). Protrusions represent the positions of Fe atoms. The corrugation amplitude is about 10 pm; cf. line section. (d) Magnetic exchange force microscopy image of the c (2×2) antiferromagnetic surface unit cell on the Fe ML ($\Delta f = -14.8$ Hz). Only every second Fe atom appears as a protrusion. The magnetic corrugation amplitude is about 10 pm; cf. line section. Parameters for (c) and (d): $c_z = 32.5$ N/m, $A_0 = 5$ nm, $f_0 = 156$ kHz, $Q = 24410$.

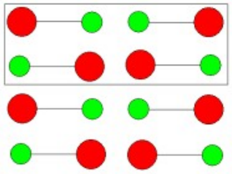
kombinace STM s jinými technikami

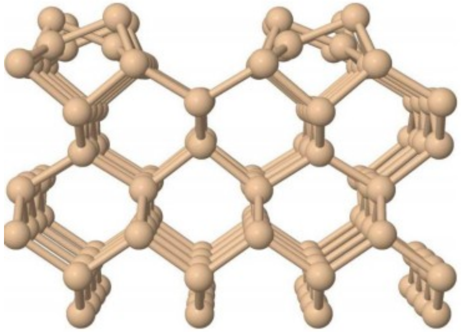
- STM + ab initio výpočty

STM mapy rekonstrukce c(4×2) – porovnání s experimentem

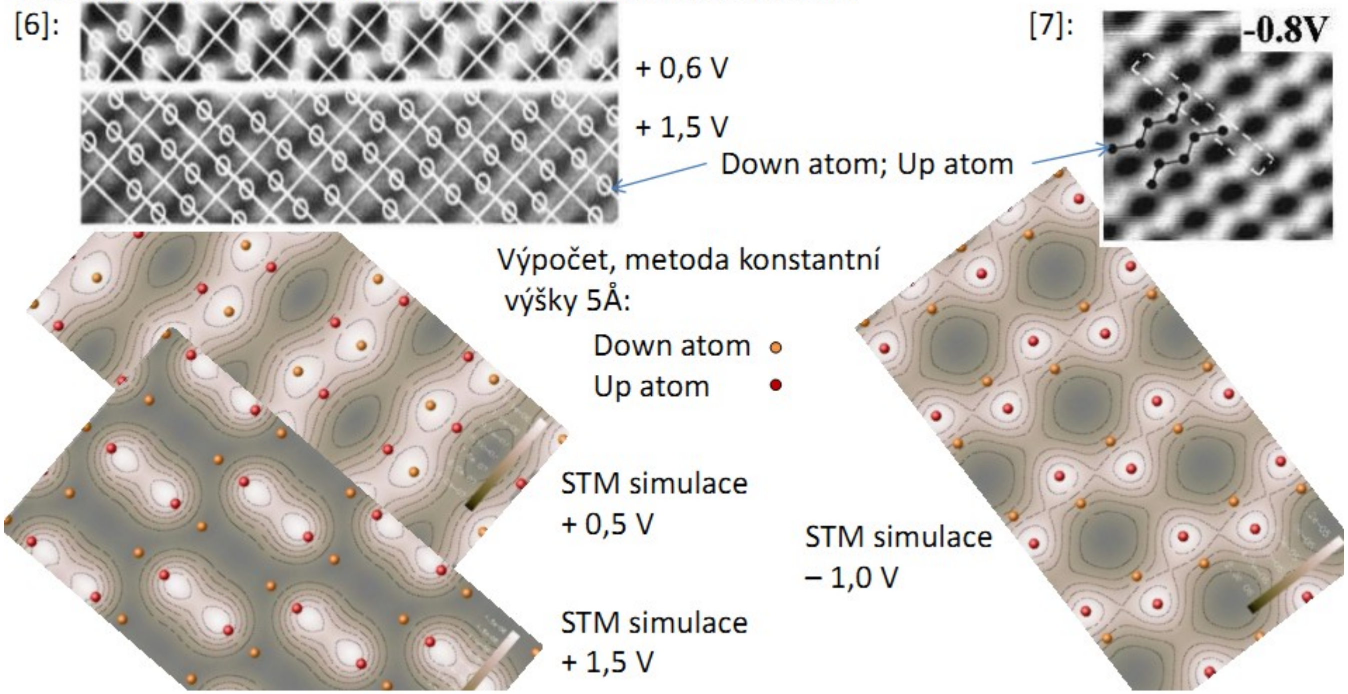
c(4x2)

Schematický horní pohled





Boční pohled



Experiment, K. Hata et al., 80 K, metoda konstantního proudu,

[6]:

+ 0,6 V

+ 1,5 V

Down atom; Up atom

[7]:

Výpočet, metoda konstantní výšky 5Å:

Down atom ●

Up atom ●

STM simulace
+ 0,5 V

STM simulace
+ 1,5 V

STM simulace
– 1,0 V

[6] **K. Hata et al.,** Phys. Rev. B. 64 (2001) 235310.; [7] **K. Hata et al.**, Phys. Rev. B. 60 (1999) 8164.

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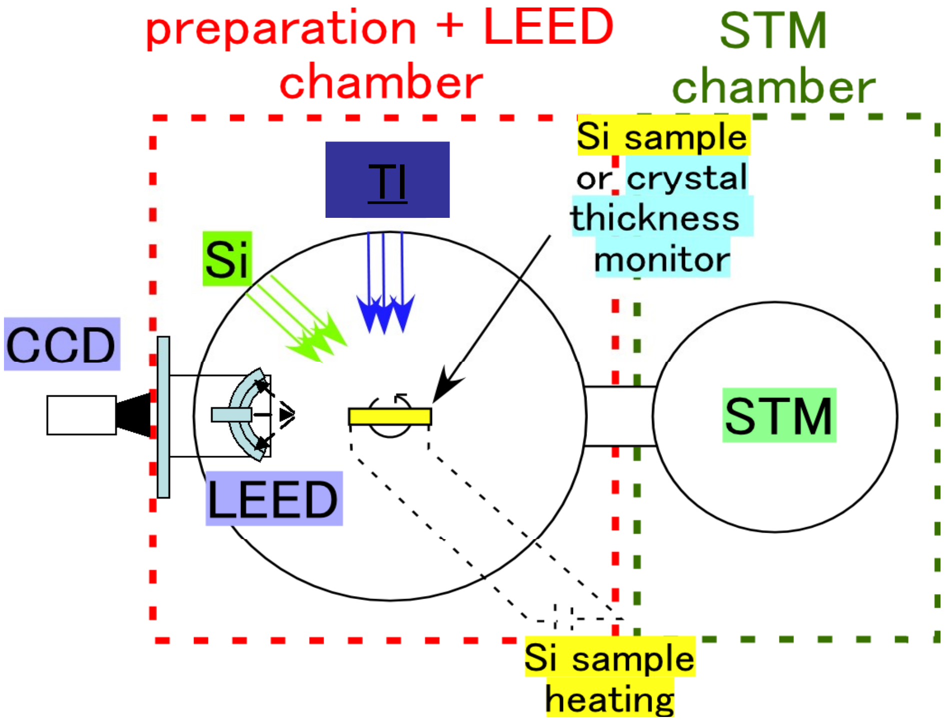
kombinace STM s jinými technikami

- STM + LEED (low energy electron diffraction)



Structural changes observed by LEED

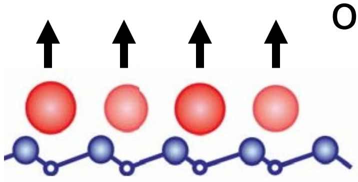
LEED – 70 eV
(5×5) – 60 eV

thallium | clean silicon surface

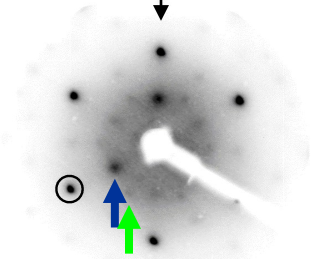
T[⁰ C] 300 350 400 450 500 550 600 650

(1×1)-Tl

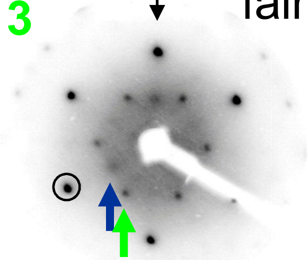
Desorption of Tl



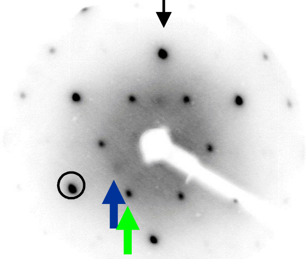
(1,0)



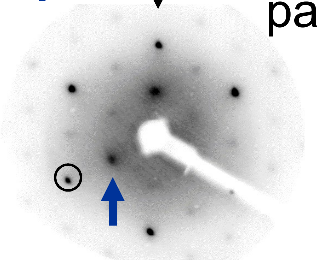
2×1 with faint **√3×√3**



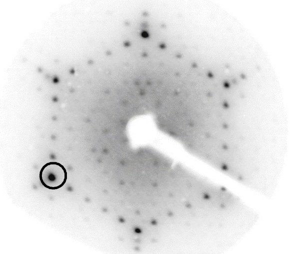
2×1 fading, **√3×√3** becoming brighter



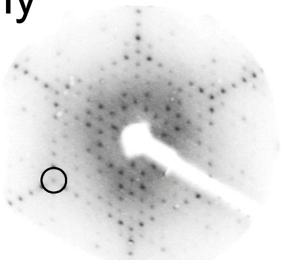
√3×√3 with faint **2×1**



2×1 only

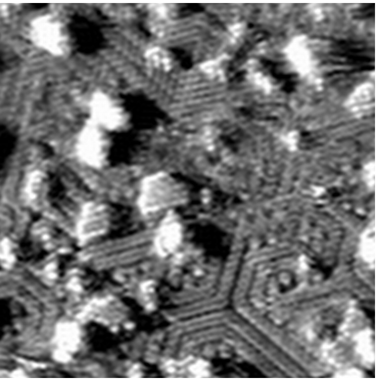


5×5 DAS pattern



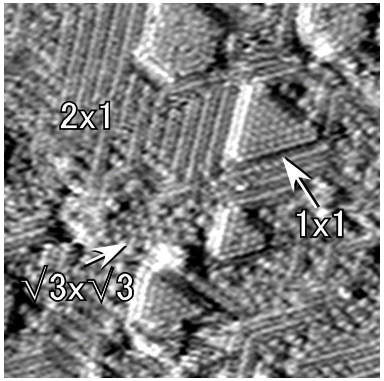
7×7 DAS pattern

Structural changes observed by STM



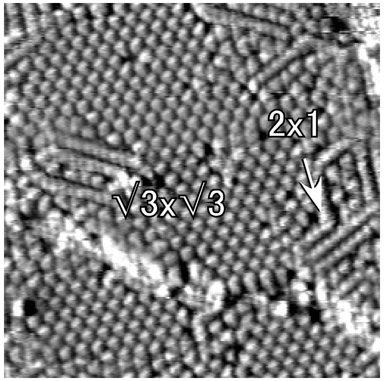
400ºC 15 nm

2×1 reconstruction with bright shapeless clusters



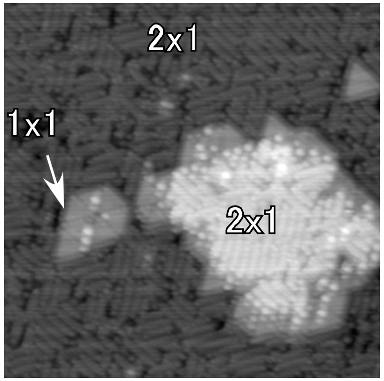
450ºC 15 nm

2×1 coexisting with √3×√3 and 1×1 islands



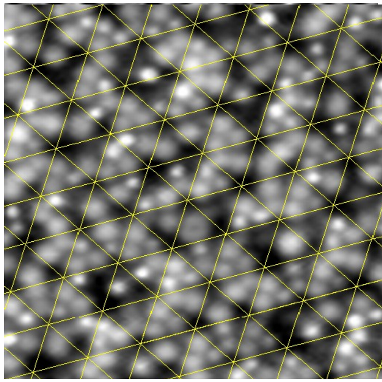
500ºC 15 nm

Mostly √3×√3 with some 2×1 stripes



600ºC 25 nm

Mostly 2×1 stripes



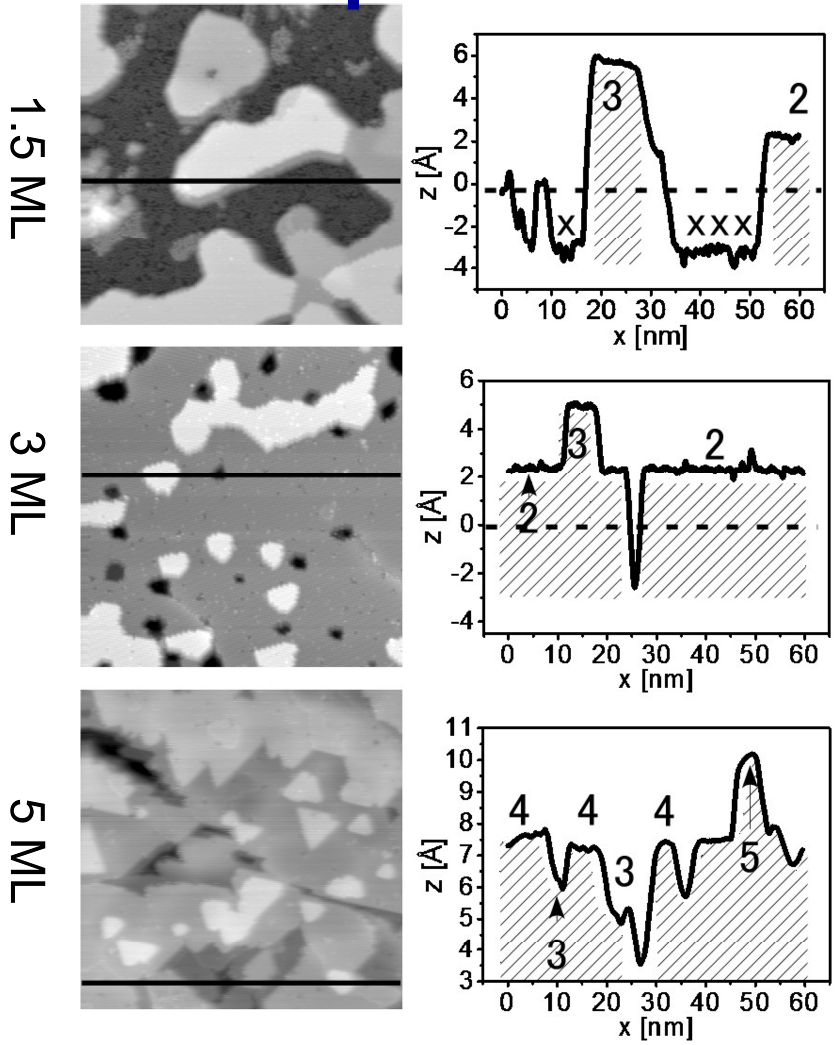
650ºC 10 nm

5×5 with missing adatoms

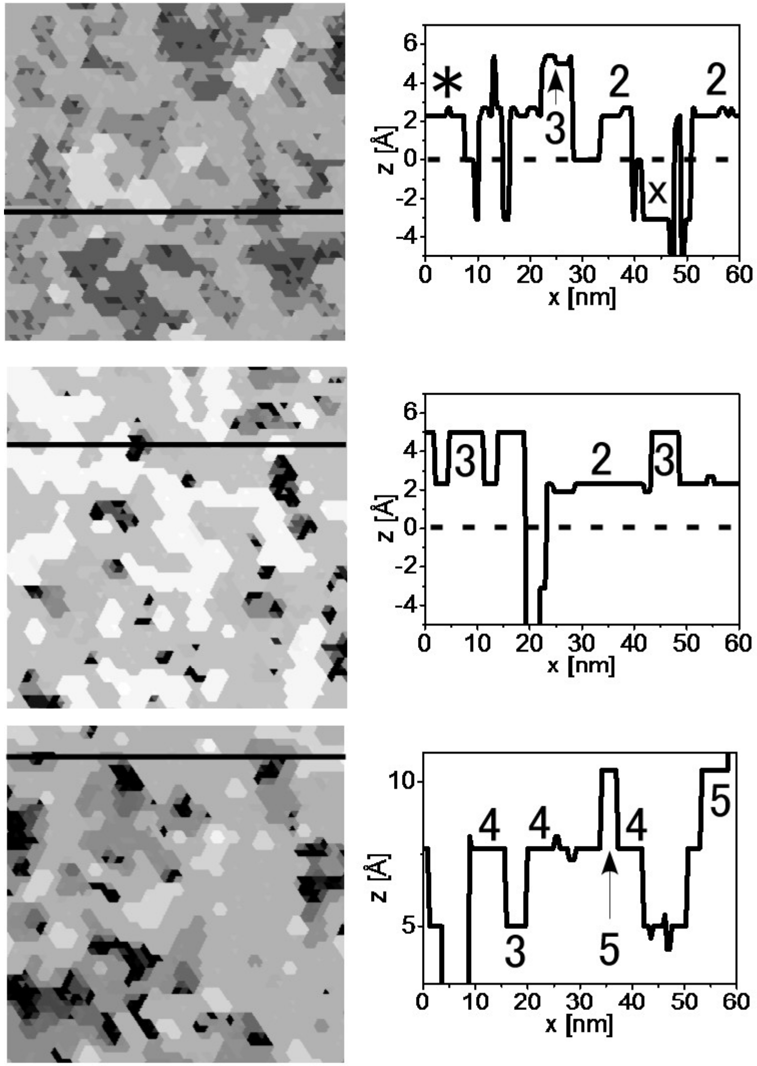
kombinace STM s jinými technikami

- STM + KMC (kinetic Monte Carlo)

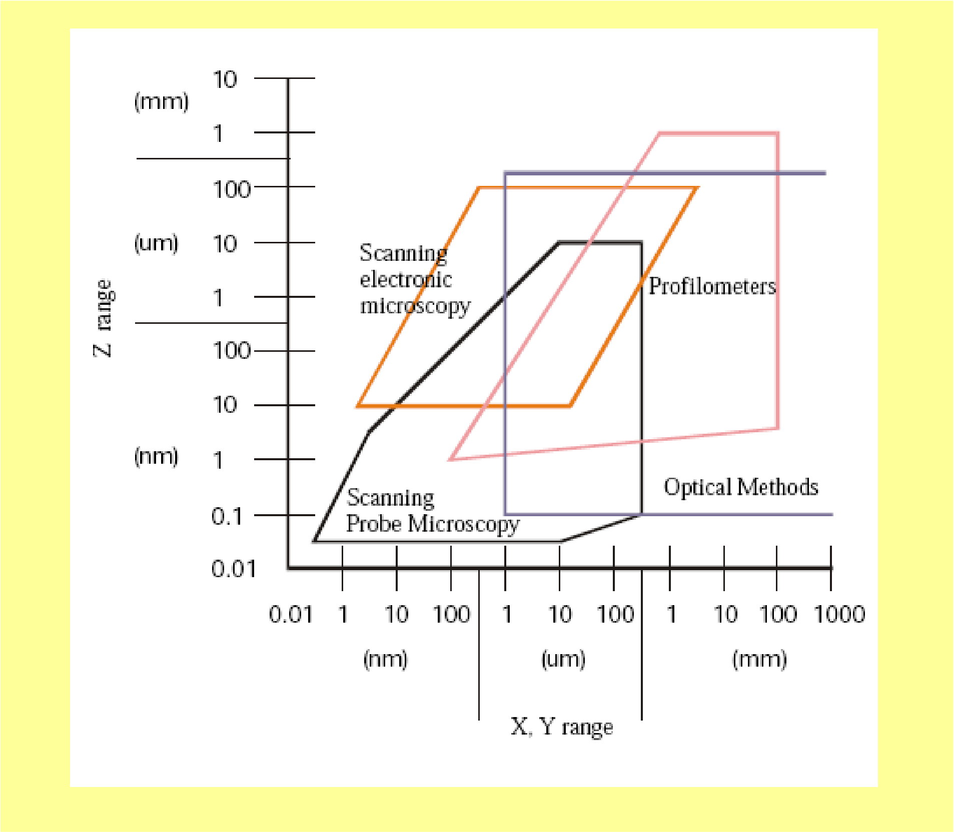
experiment



teorie



➢Comparison with other methods



STM, AFM

- real space imaging

- local, atomic resolution

- local spectroscopy
  STM: tunneling electrons – LDOS, CITS;
  AFM: force – chemical information

- Non destructive methods

- Manipulation with surface atoms (STM, AFM) and simultaneous surface imaging

- exclusively surface sensitive

- experimentally difficult

- **HRTEM** – atomic resolution in phase space
- **LEEM** – atomic step resolution
- **FIM** – atomic resolution, sample in a shape of a tip

Lattice parameters, long range arrangement of atoms:
STM, AFM cannot be comparable with diffraction methods !