# Nanostrukturen-Analysemethoden

## Scanning Probe Microscopy

- **Friction Force Microscopy**
- Force Calibration
- Atomic Stick Slip
- Tomlinson Model
- Nano-manipulation
- **Atomic Force Microscopy**
- Short- and Long-Range Forces
- Kelvin Probe Force Microscopy
- Measurements on Semiconducting Devices
- Molecules on Insulating Surfaces
- Manipulation

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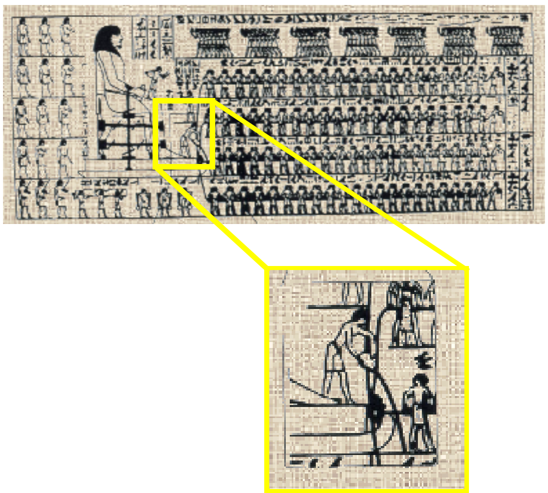
NANOlino Lab

# Importance of Friction

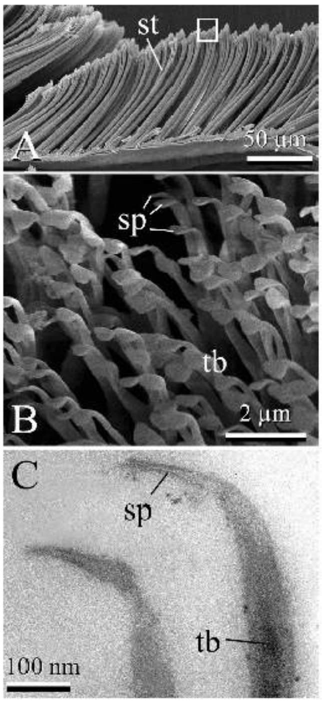
Long time ago...



Nowadays...

In all cases: It is higly desirable to reduce and <u>control</u> friction

## Gecko uses nanometer-sized contacts to climb walls

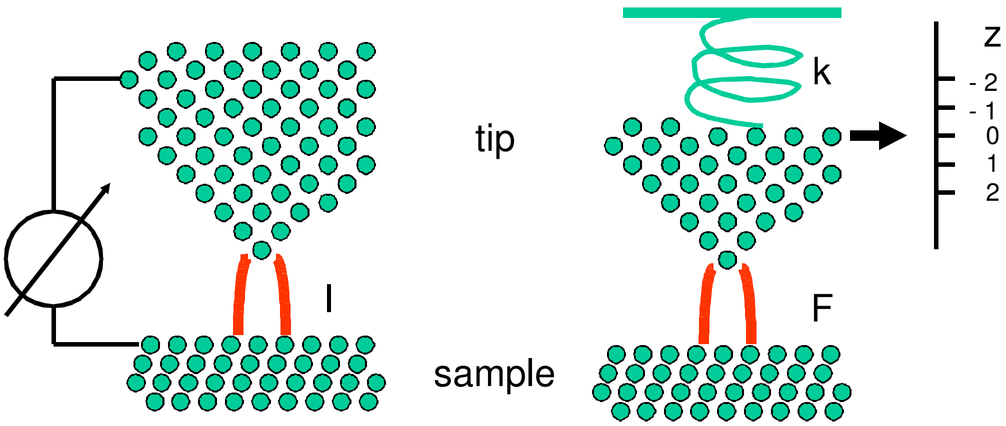



Gecko is able to control the
contact area on all length scales

From B. Persson and S. Gorb
JCP, 119, 11437 (2003)

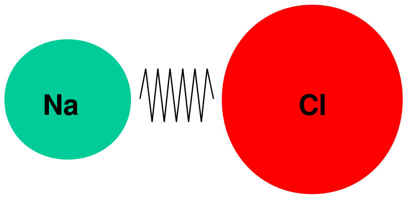
## Scanning X Microscopy

**S** **T**unneling **M** | **S** **F**orce **M**




$$F = -k\,z$$

## Kräfte zwischen zwei Atomen

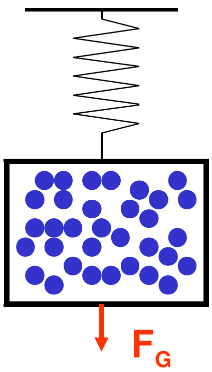



Chemische Bindung

$F_{chem}$ = 1eV/ 0.1 nm

1.6 nN

## „Kräfte Spüren“





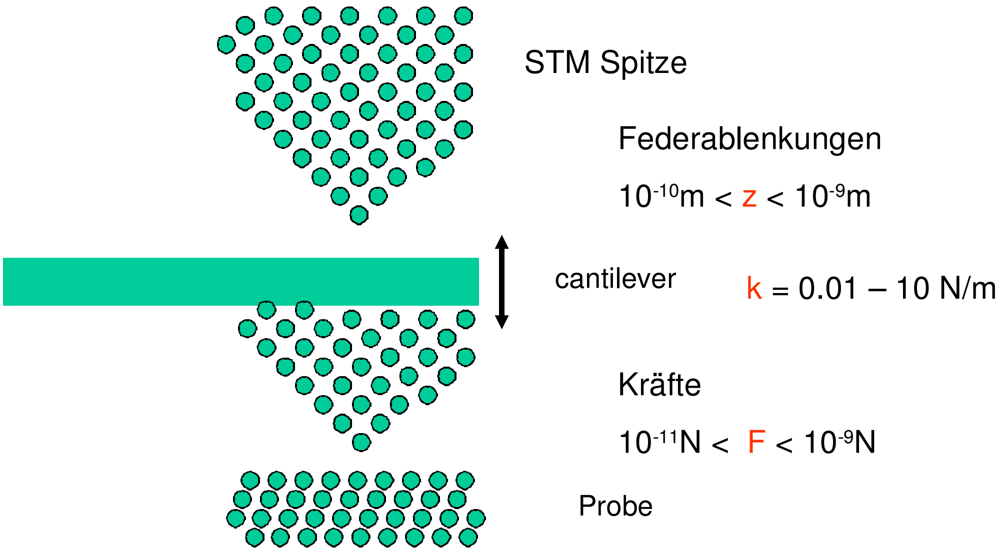
1 nm³ Wasser (33 Moleküle)

0.01 g

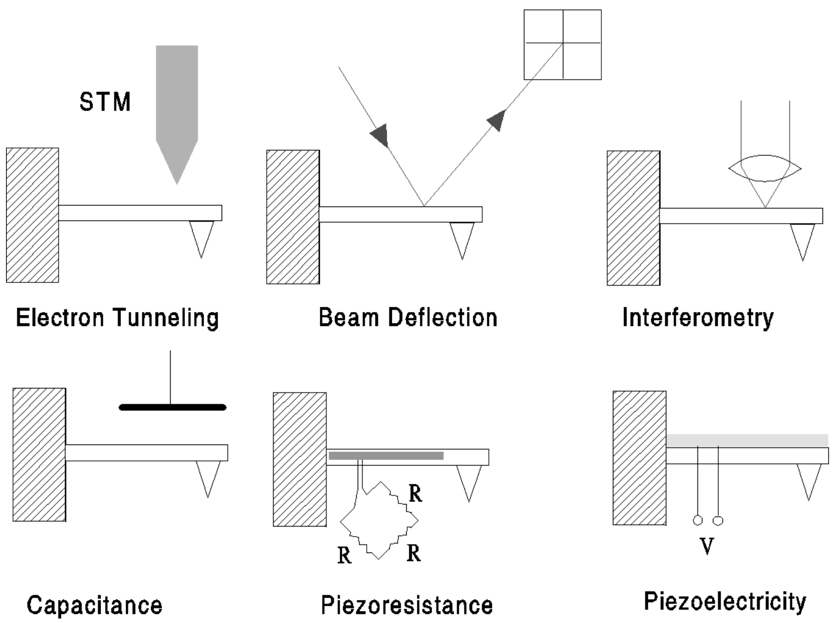
$F_G = 10^{-23}$ N = $10^{-14}$ nN

F= 0.1 mN = $10^5$ nN

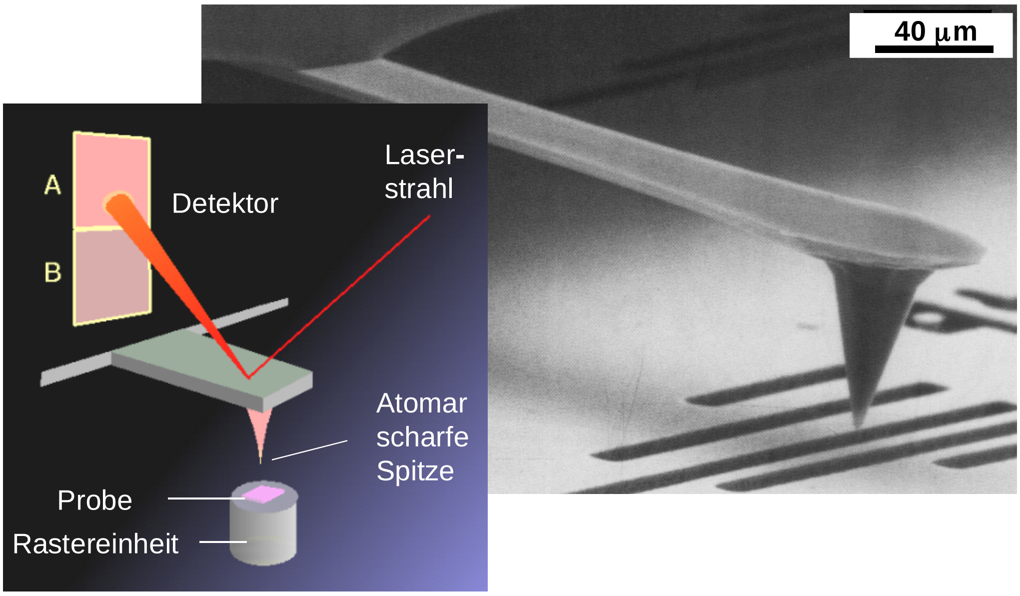
# Prinzip des ersten AFMs



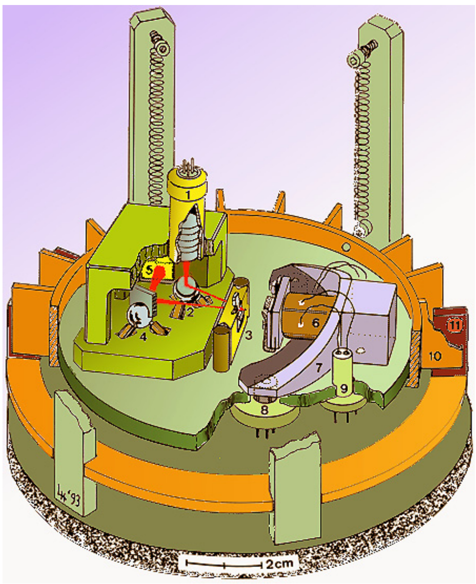

# Ablenkungssensoren



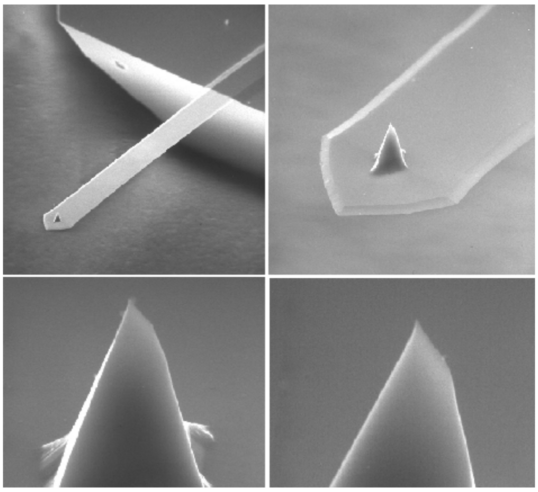
# „Beam deflection“-Methode




# Beispiele



# Microfabrizierte “Cantilever”



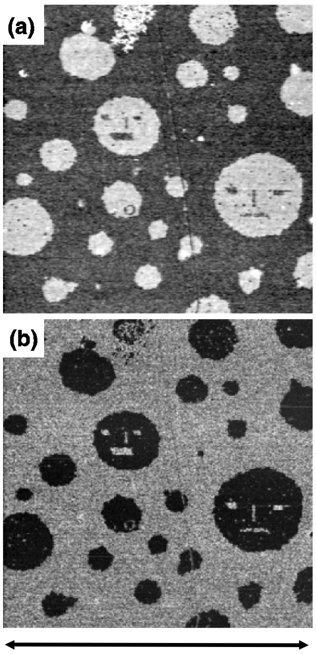
Länge : l = 450 μm
Breite : w = 45 μm
Dicke: t = 1.5 μm
E=1.69 $10^{11}$N/$m^2$

Spitzenhöhe: 12 μm
Spitzenradius: 10 nm

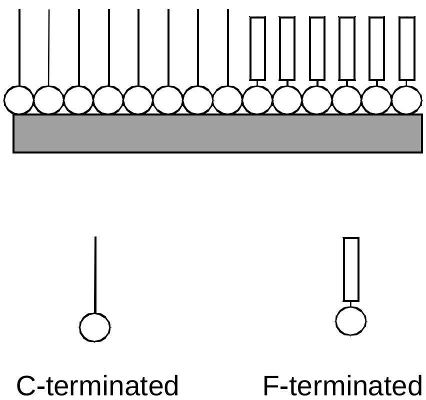
Federkonstante k:

$$k = \frac{Ewt^3}{4l^3} = 0.15 \text{ N/m}$$

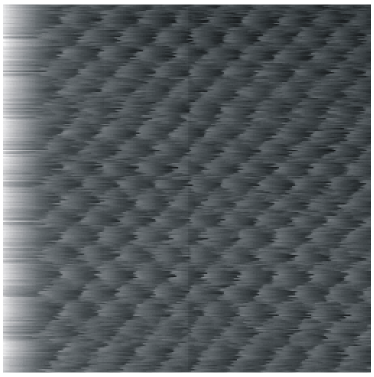
# FFM on Langmuir-Blodgett films

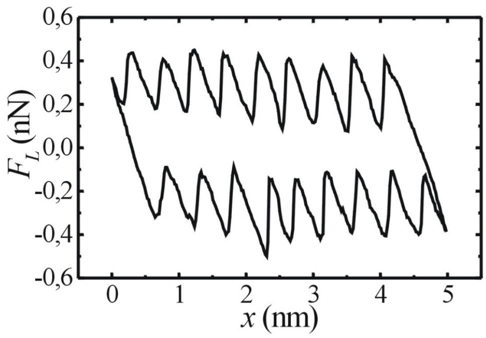



- **Material contrast** on mixed Langmuir-Blodgett films:



# Atomic stick-slip

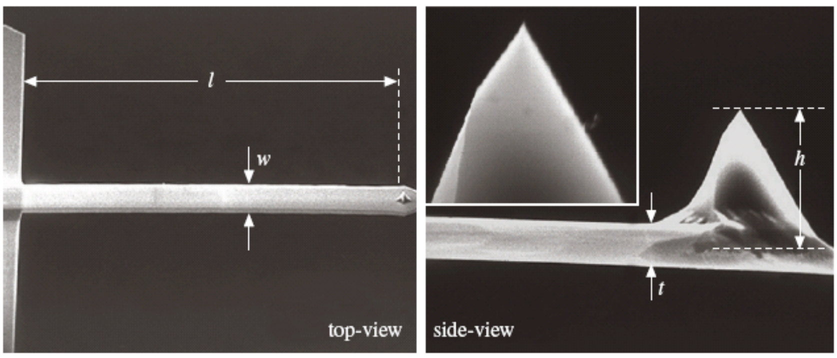





(friction map and friction loop on NaCl(100) in UHV)

# Force Calibration

- Simple if **rectangular** cantilevers are used
- Cantilever width, thickness and length, tip height: from **SEM pictures**



# Force Calibration

- Cantilever **thickness** also **from** the **resonance frequency**:

$$t = \frac{2\sqrt{12}\pi}{1.875^2}\sqrt{\frac{\rho}{E}} f_0 l^2$$

- $\rho$, E: density and Young modulus

(Nonnenmacher et al., JVSTB 1991)

- For pure silicon:

$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

# Force Calibration

- **Normal** and **lateral spring constants** of cantilever:

$$c_N = \frac{Ewt^3}{4l^3} \qquad c_L = \frac{Gwt^3}{3h^2 l}$$

- G: shear modulus
- For pure silicon:

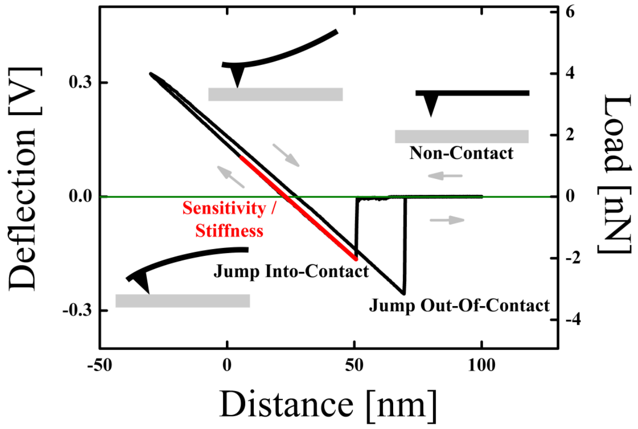
$$\rho = 2.33 \cdot 10^3 \text{ kg/m}^3$$

$$E = 1.69 \cdot 10^{11} \text{ N/m}^2$$

$$G = 0.5 \cdot 10^{11} \text{ N/m}^2$$

# Force Calibration

- Next step: **sensitivity of photodetector**
- Force-distance curves on hard surfaces (e.g. $Al_2O_3$):




- Scanner movement = cantilever deflection
- Slope → sensitivity

# Force Calibration

- **Normal** and **lateral forces**:

$$F_N = c_N S_z V_N \qquad F_L = \frac{3}{2} c_L \frac{h}{l} S_z V_L$$

(if the laser beam is above the probing tip!)

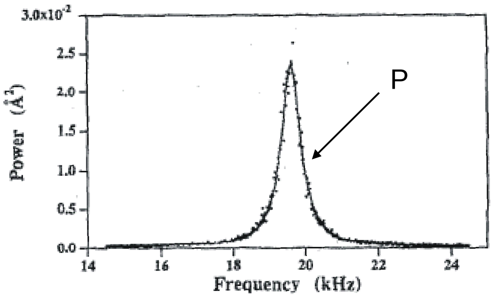
- $V_N$, $V_L$: normal and lateral signals

# Force Calibration

• Alternative method: Spring constant **from thermal power spectrum** (Hutter et al., RSI 1993)

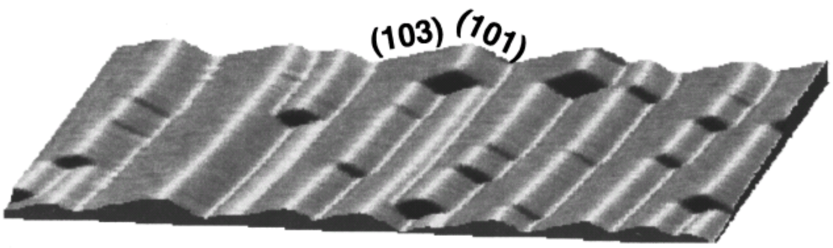
• Correct relation (Butt et al., Nanotech. 1995):

$$c_N = \frac{4k_BT}{3P}$$

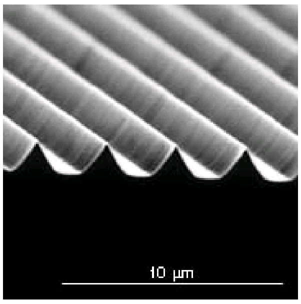



# Force Calibration

• Alternative method: Scanning over profiles with **well-defined slope** (Ogletree et al., RSI 1996)



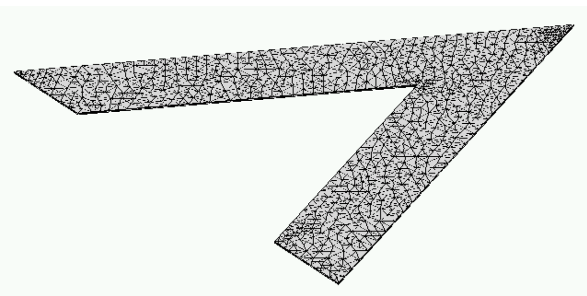

Commercially available grating:

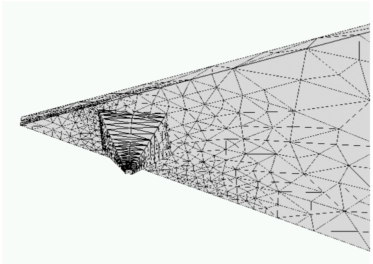


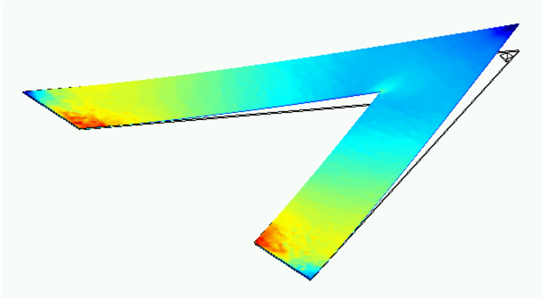

(TGG01, NT-MDT, Moscow)

## Force Calibration

- Different shapes → **Finite elements analysis**



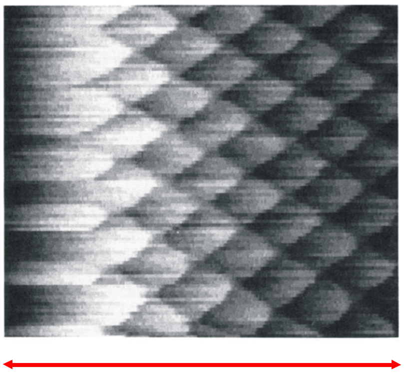




(Femlab™ 3.0)

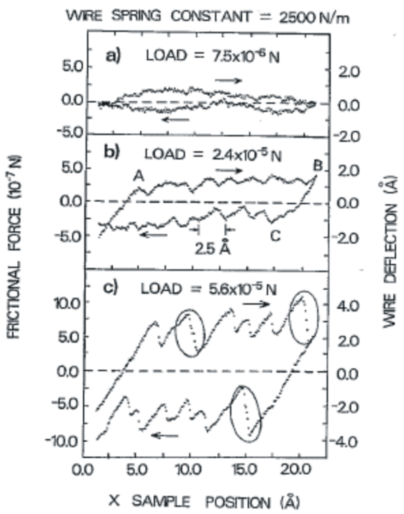
## Atomic-Scale Measurements

- Atomic friction on **graphite**:



2 nm

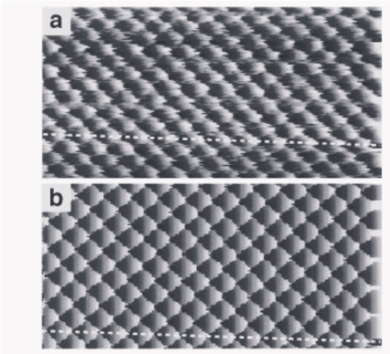
(Mate at al., PRL 1987)



# Atomic-Scale Measurements

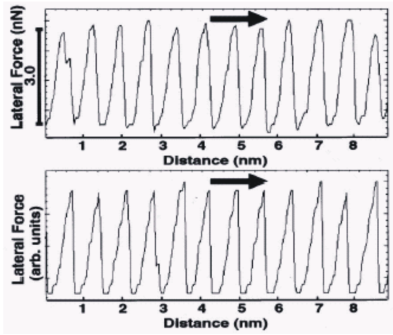
• Friction on **insulating surfaces** (Lüthi et al., JVSTB 1996):

KBr




Exp

Theo

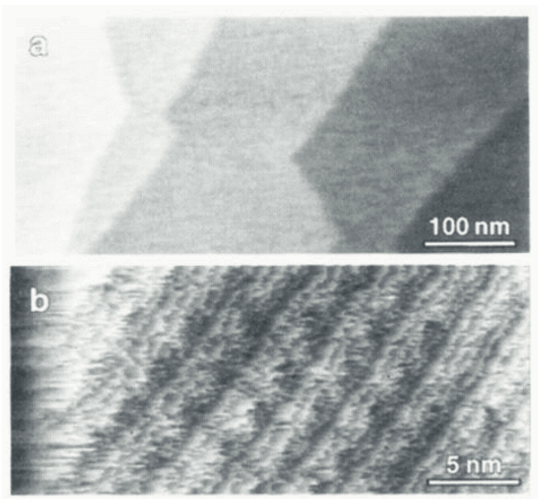



• No individual defects are observed

# Atomic-Scale Measurements

• Friction on **semiconductors** (Howald et al., PRB 1995):

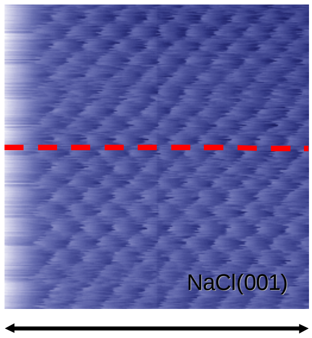
Si(111)7x7

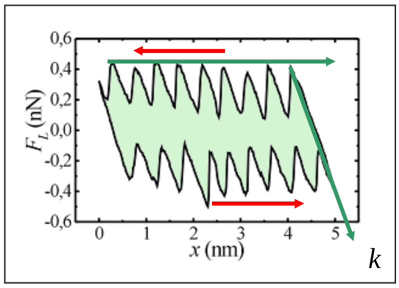



(tip coated with PTFE)

# Atomic friction on crystal surfaces

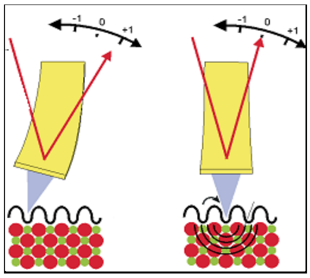
Our model systems: alkali halide surfaces (easy preparation, simple structure)




$$F_L^{max} = \frac{2\pi V_0}{a}$$

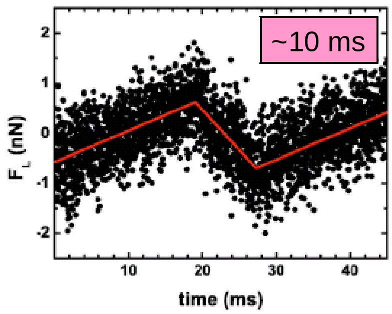
Tomlinson model:
(Phyl. Mag. 1929)

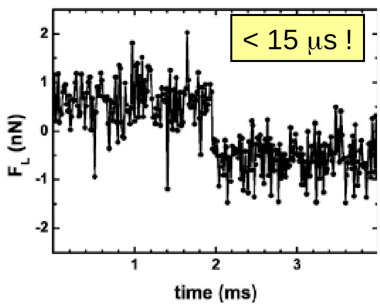


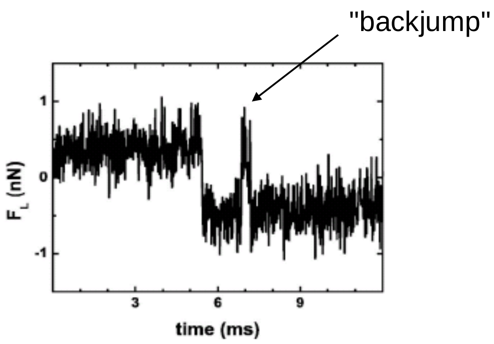

$V_0 \sim 1\,\mathrm{eV}$
$k \sim 1\,\mathrm{N/m}$

# Atomic-Scale Measurements

• Wide distribution of slip durations:



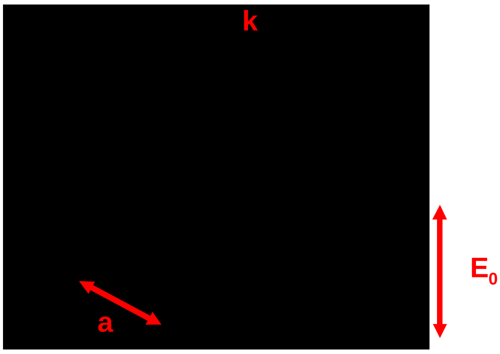

Why?

# Modelling Atomic Friction

- The tip is subject to

1) periodic interaction with the underlying surface

2) elastic deformation of the cantilever




- In 1D the corresponding potential energies are represented by

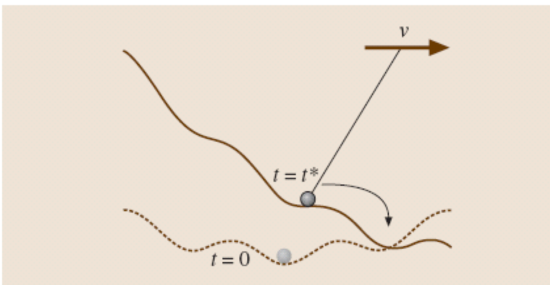
1) a sinusoid

2) a parabola

# Modelling Atomic Friction

- Total energy of the system:

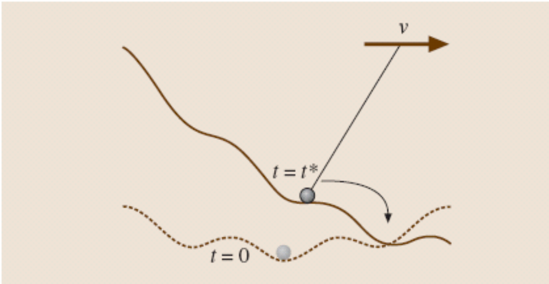
$$U_{\text{tot}}(x,t) = -\frac{E_0}{2}\cos\frac{2\pi x}{a} + \frac{1}{2}k_{eff}(vt - x)^2$$




- The tip can "stick" to the minima of the potential profile

# Modelling Atomic Friction

- Tip position at a given time t: $$\frac{\partial U_{tot}}{\partial x} = \frac{\pi E_0}{a}\sin\frac{2\pi x}{a} - k_{eff}(vt - x) = 0$$

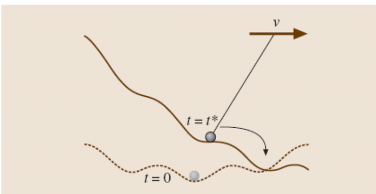


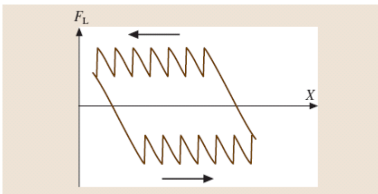

- Critical position (reached at t = t*):

$$x^* = \frac{a}{4}\arccos\left(-\frac{1}{\eta}\right) \qquad \eta = \frac{2\pi^2 E_0}{k_{eff}\,a^2}$$

- **Frictional parameter $\eta$** → tip-surface interaction vs. lateral stiffness

# Modelling Atomic Friction




- Critical lateral force (at t = t*):

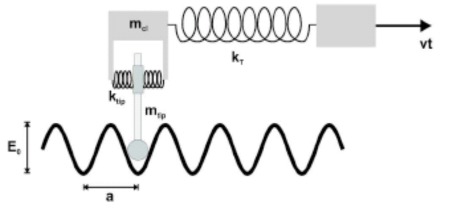
$$F^* = \frac{\pi E_0}{a}\sqrt{1 - \frac{1}{\eta^2}}$$

[redacted]

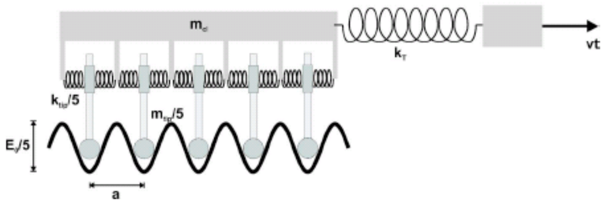
- Note that $F^* < F_{max}$!

$$F_{max} = \frac{\pi E_0}{a}$$

## Modelling Atomic Friction



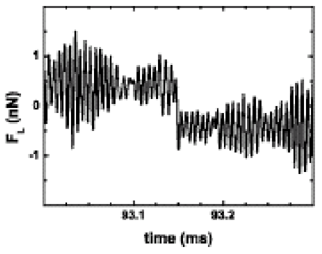

multiple contact



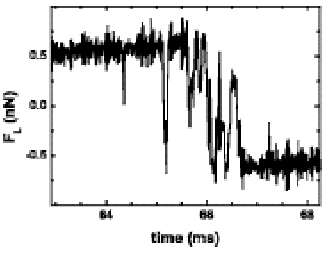

## Modelling Atomic Friction

- Tip → Langevin equation (including thermal noise)
- Cantilever → Newton equation (without thermal noise)

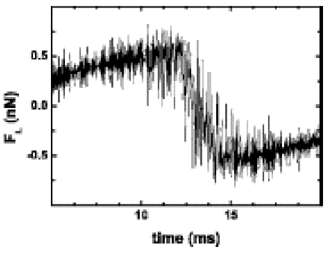
**One tip**




**Three tips**




**Five tips**

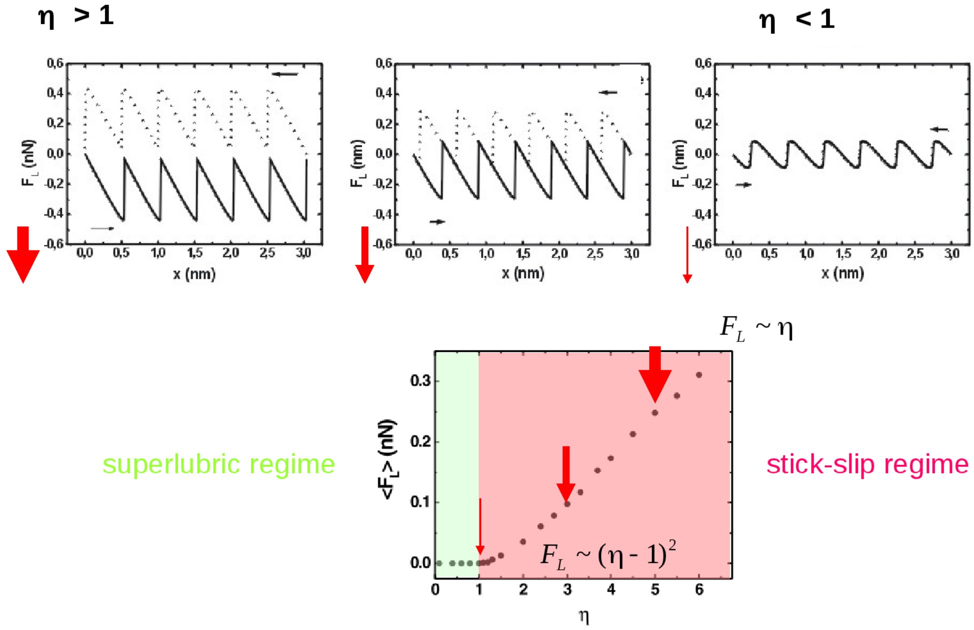



- Long slip times are found with multiple tips only

(Maier et al., PRB 2005)

# Superlubricity

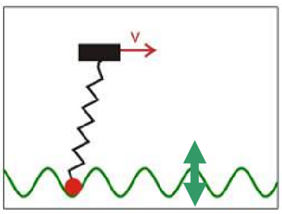
- From the Tomlinson model (without thermal activation):



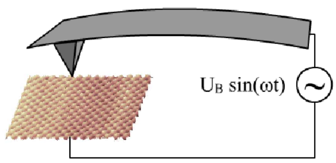

*A. Socoliuc et al., Phys. Rev. Lett. 92 (2004) 134301*

# "Dynamic superlubricity"

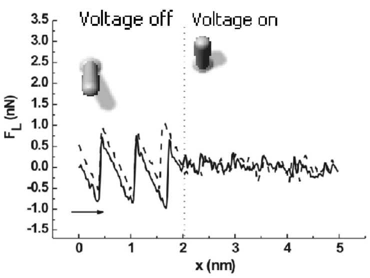
A third way to reduce friction: Tomlinson model with TIME modulation

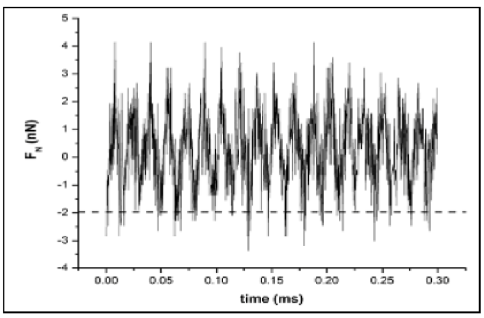



AC actuation
of the nanocontact:




NaCl(001)



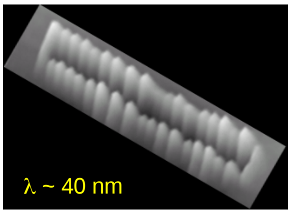




*A. Socoliuc et al., Science 313 (2006) 207*

# Abrasion wear at the nanoscale

Ripples induced by localized abrasion:

Scratching single lines:



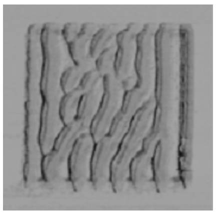

Analogies to waterjet cutting:

- Combined erosion and relaxation

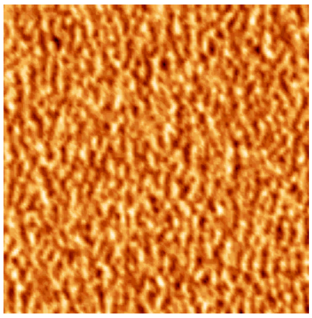
Thermal activation of atomic-scale wear

Numerical analysis in progress

Scratching square areas:



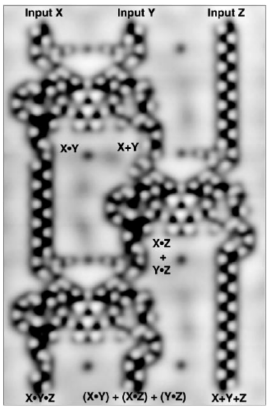
Analogies to sand ripples:



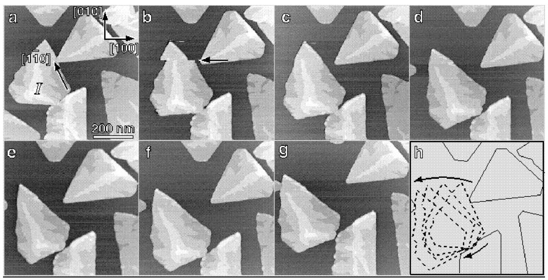
*A. Socoliuc et al.,a Phys. Rev. B 68 (2003) 115416*

# Nanomanipulation Techniques

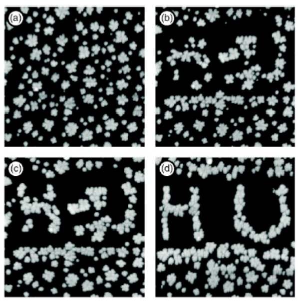
By STM (Heinrich et al. 2002):




By contact AFM (Lüthi et al. 1994):

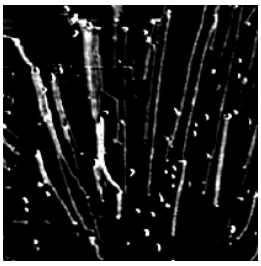


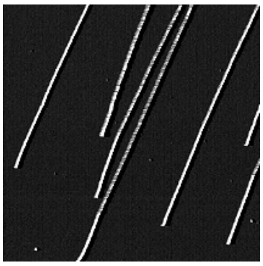

By dynamic AFM (Ritter et al. 1995):



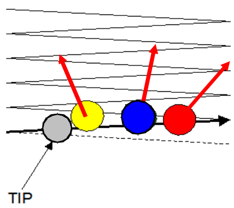
# Manipulation of Nanoparticles

Nanoparticles can be “scattered” by the AFM tip:

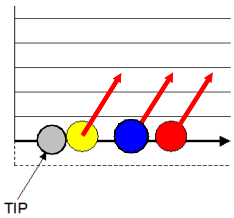


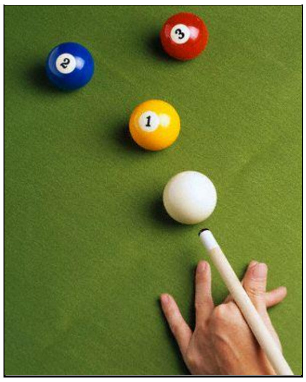


*Zigzag path:*

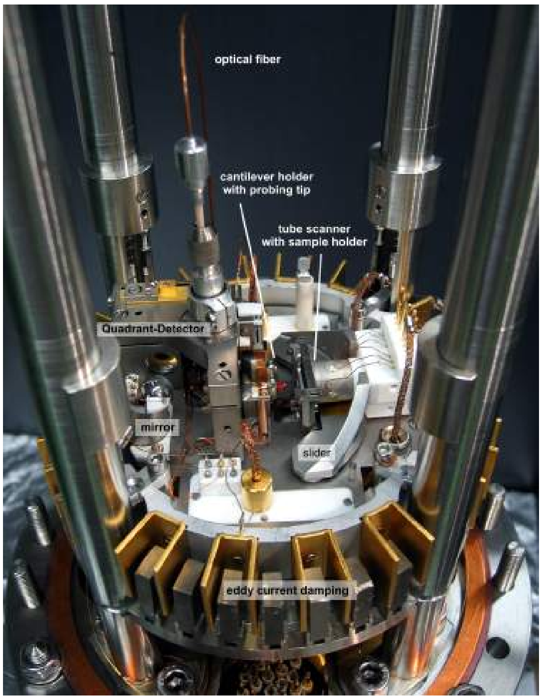



*Raster path:*



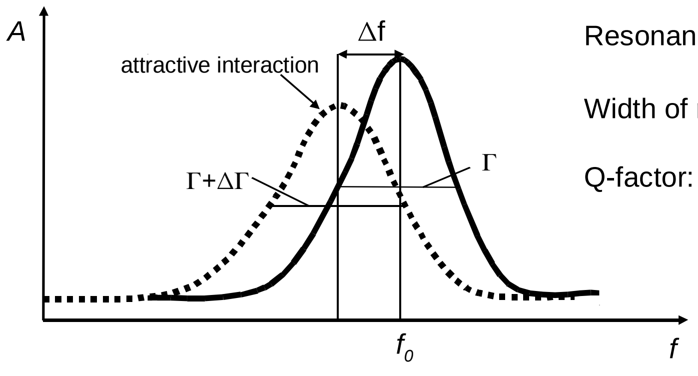



# Noncontact-AFM (nc-AFM)




- UHV: Base pressure below $1x10^{-10}$ mbar
- Operation at room temperature
- Mixed mode: AFM/STM
- Beam deflection method
- Bandwidth of the photodetector: 3MHz
- Evaporation of molecules from a k-cell kept at 165ºC or 170ºC

# Quantitative understanding of nc-AFM




Resonance frequency: $f_0$

Width of resonance curve (FWHM): $\Gamma$

Q-factor: $Q = \frac{2\pi \cdot f_0}{\Gamma}$

Conservative forces ⇒ shift of resonance curve $\Delta f$
Dissipative forces ⇒ broadening of curve $\Delta\Gamma$

# Forces in nc-AFM

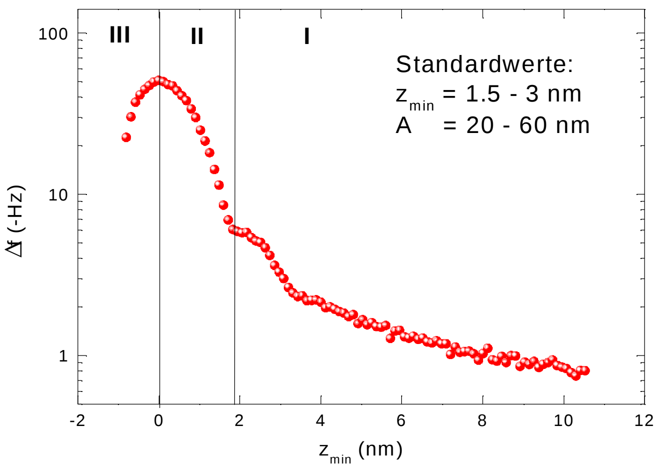
Frequency modulation: $f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$ $\quad \Delta f = -\frac{f_0}{2k}\frac{\partial F_{tot}}{\partial z}$

⇒ measured topography = surface of constant $\frac{\partial F}{\partial z}$

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

- $F_{chem}$: bonding between tip and sample atoms (only for d < 5 Å)
- $F_{mag}$: only for magnetically sensitive tips
- $F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V^2$
- $F_{vdW} = -\frac{HR}{6d^2}$

# Dynamic Mode, non-contact

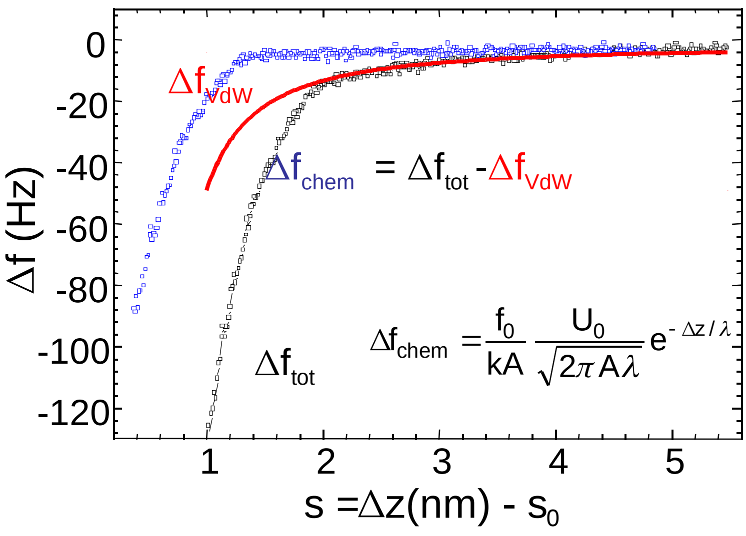



region I:
attractive forces
non-contact mode

region II:
attractive forces
atomic resolution

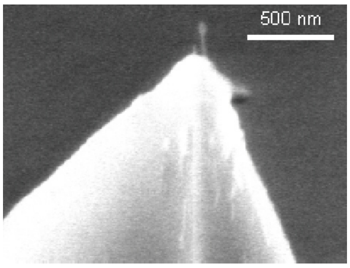
region III:
repulsive forces
tapping mode

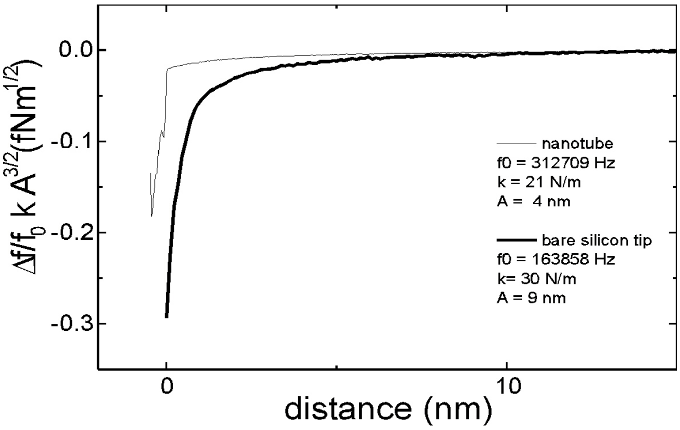
# Short range interaction




$\lambda$ = 0.35 nm
$U_0$ = -4.7 eV
$s_0$ = 0.45 nm

# Carbon nanotubes as probing tips for nc-AFM



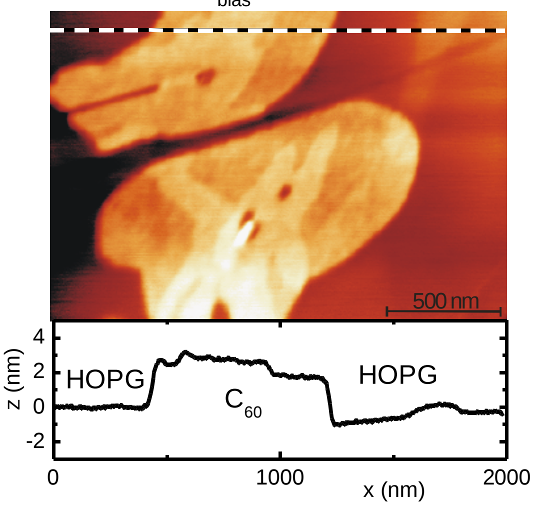




⇒ Long-range forces are reduced

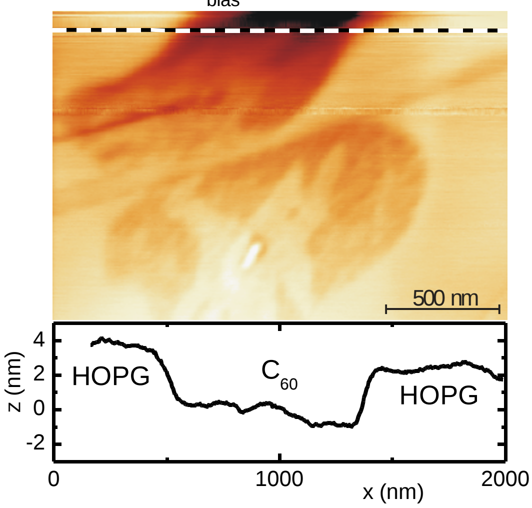
# inhomogeneous sample: HOPG + ½ monolayer C60

**Topography**

$V_{bias}$ = 0 V



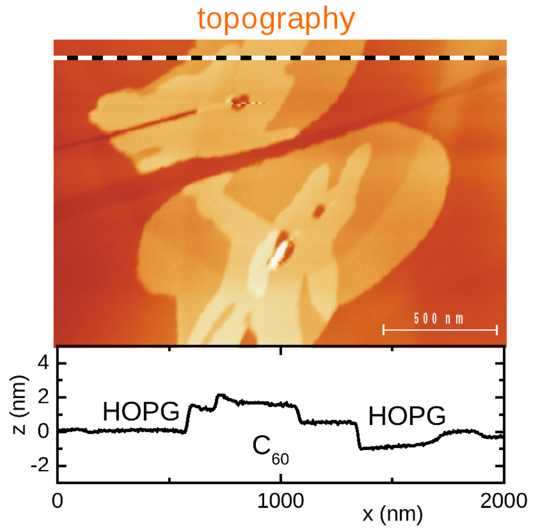

$V_{bias}$ = 1.34 V

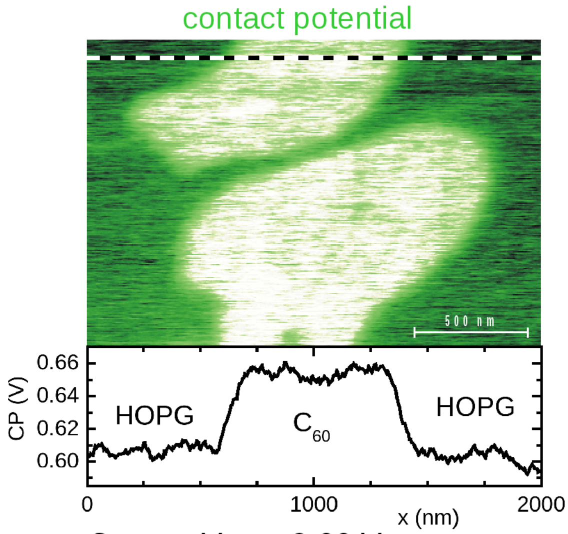



**→ contrast inversal: HOPG ↔ $C_{60}$**

S. Sadewasser et al., PRL 91 266101 (2003)

## inhomogeneous sample: HOPG + ½ monolayer C60



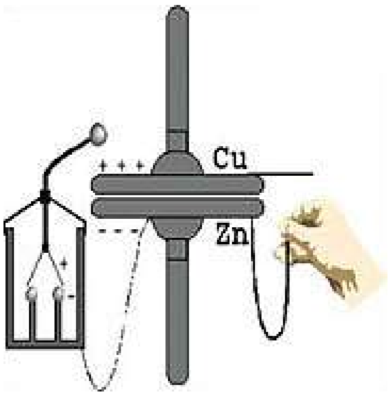

HOPG: $V_{CP} \cong 0.61$ V

$C_{60}$: $V_{CP} \cong 0.66$ V

⇒ NC-AFM: residual electrostatic force for fixed $V_{bias}$

## Makroskopische Kelvin-Sonde

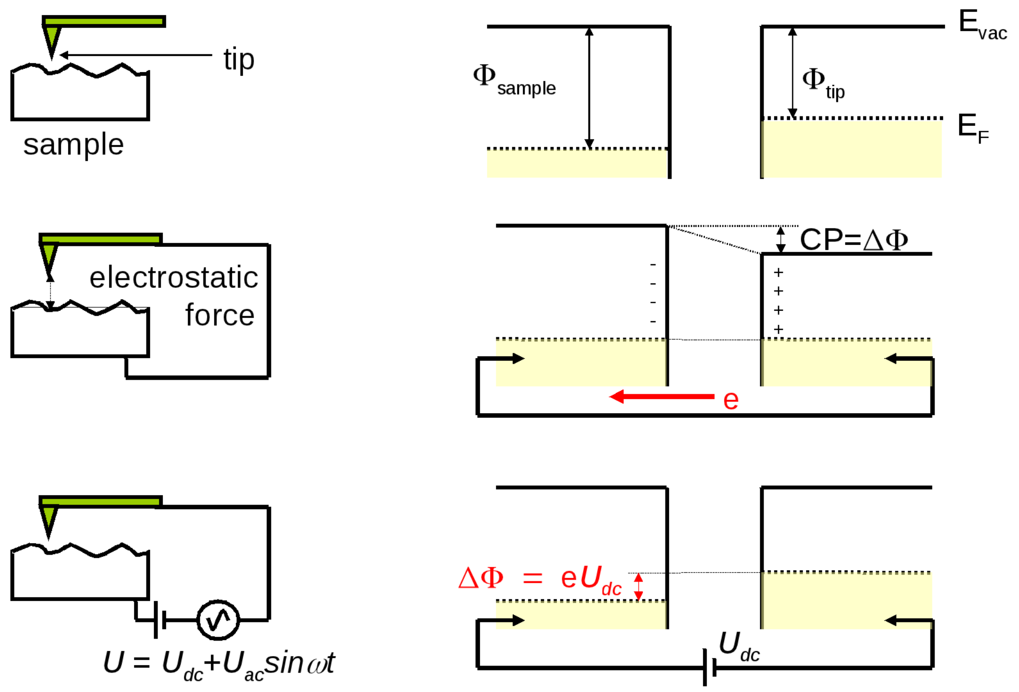
Lord Kelvin 1861




**Verschiebestrom**

$$I(t) = (U_{dc} - U_{CPD})\, f\ \ \Delta C \cos \omega t.$$

## Kelvin Principle




# Electrostatic Forces in nc-AFM

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V_{eff}^2 \quad \Rightarrow \quad F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}(V_{bias} - V_{CP})^2$$

$$V_{CP} = 1/e \cdot (\Phi_{tip} - \Phi_{sample})$$

contact potential

Φ - work function

apply bias: $V_{bias} = V_{dc} + V_{ac} \cdot \sin(\omega t)$

# Kelvin Probe Force Microscopy

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V_{eff}^2 = F_{dc} + F_{\omega} + F_{2\omega}$$

$$F_{dc} = -\frac{\partial C}{\partial z}\left[\frac{1}{2}(V_{dc} - V_{CP})^2 + \frac{V_{ac}^2}{4}\right]$$

$$F_{\omega} = -\frac{\partial C}{\partial z}(V_{dc} - V_{CP})V_{ac}\sin(\omega t)$$

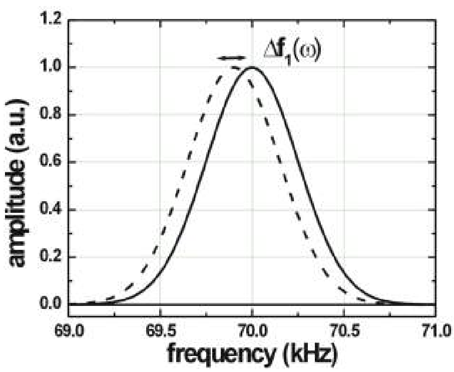
$$F_{2\omega} = \frac{\partial C}{\partial z}\frac{V_{ac}^2}{4}\cos(2\omega t)$$

**AM-KPFM**
**Amplitude Modulation**

**FM-KPFM**
**Frequency Modulation**

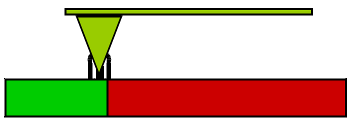
# FM – KPFM
# Frequency Modulation Detection

$$\Delta f(\omega) \propto \frac{\partial F_{el}}{\partial z} \propto \frac{\partial^2 C}{\partial z^2}(V_{dc} - V_{CP})V_{ac}\sin(\omega t)$$



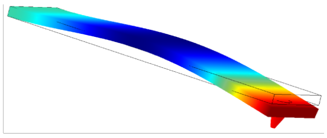

- frequency $\omega$ of $V_{ac}$ between 1-3 kHz
- detection of the oscillation of $A(\Delta f_1)$ with a lock-in
- limiting factor: bandwidth of the FM-demodulator / PLL

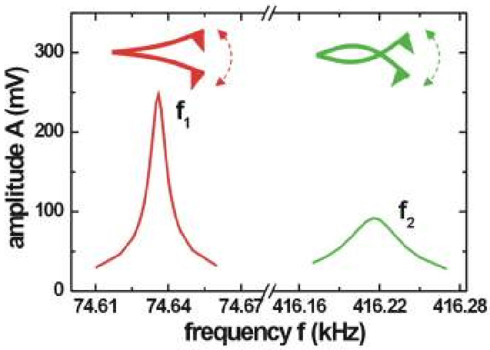
$$A(\Delta f_1) \propto \partial F_{el}/\partial z$$



# AM – KPFM
# Amplitude Modulation Detection

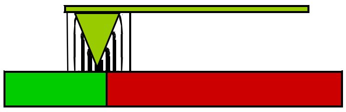
$$F_{\omega} = - \frac{\partial C}{\partial z} (V_{dc} - V_{CP}) V_{ac} \sin(\omega t)$$



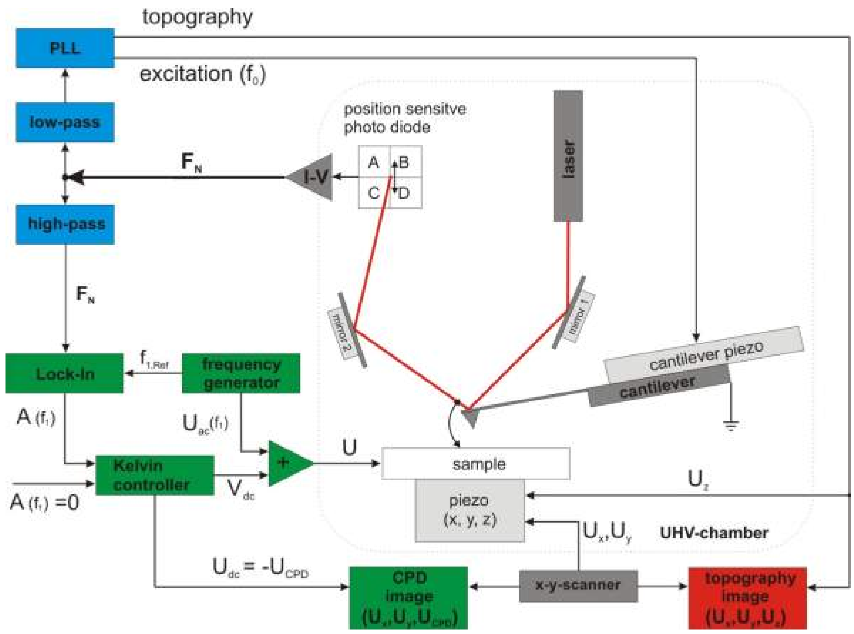



- tune $\omega$ to the second resonance $f_2$
- detection of the oscillation amplitude $A_{\omega}$ with a lock-in
- limiting factor: bandwidth of the photodiode

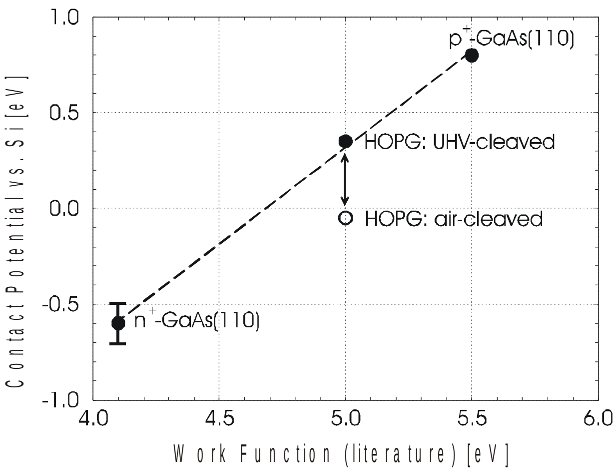
$A_{\omega} \propto F_{\omega}$



# Experimental Setup
# nc-AFM & AM-KPFM



## KPFM calibration and absolute work function




Φ-Si-Cantilever = 4.70 (±0.1) eV

**$U_{ac}$ = 100 mV**

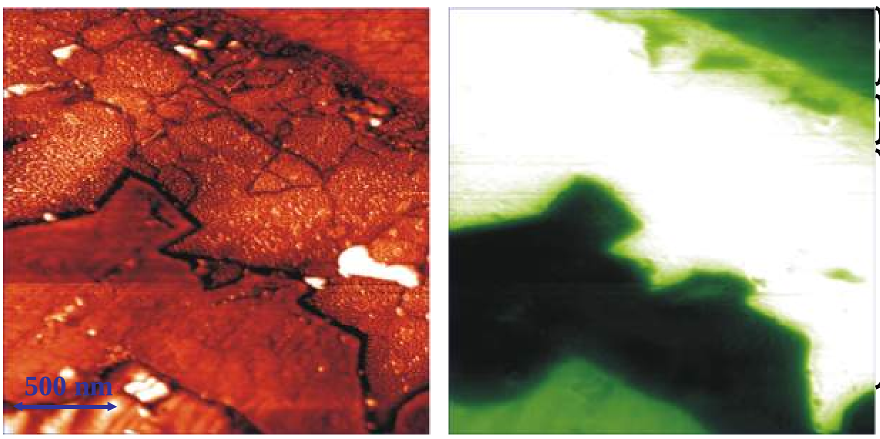
→ absolute and quantitative work function determination

## Polished Cross Section of a $CuGaSe_2$ Solar Cell

$CuGaSe_2$ solar cell device: $V_{oc}$ = 820 mV, η = 4.6 %

polished and Ar-ion sputtered cross section

topography work function




Mo, Φ=4.20eV

$MoSe_2$, Φ=4.40eV

$CuGaSe_2$, Φ=4.80eV

Δz = 65 nm

n-ZnO:Ga, Φ=4.0eV

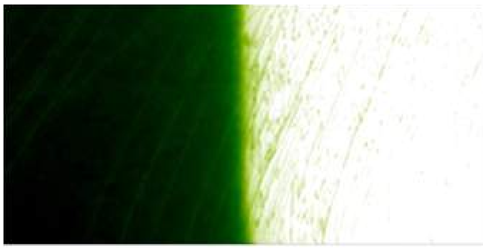
Glatzel *et al*., APL **81**, 2017 (2002)

# AM-KPFM measurement on GaP pn-junction

n-type GaP wafer with p-type GaP layer, ~$10^{18}$ $cm^{-3}$, UHV cleavage along (110) surface

topography

work function



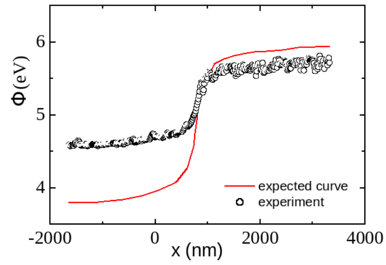
$\Delta z$ = 4.5 nm　　2.5 × 5 $\mu m^2$　　$\Phi$ = 4.56 - 5.77 eV

most III-V semiconductors:

no surface states on the (110) surface

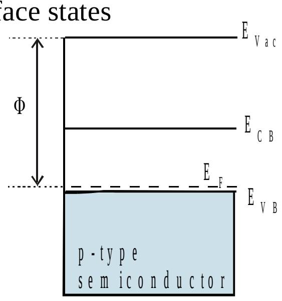
☜ GaP does show surface states

⇒ discrepancy of $\Phi_{exp}$ to $\Phi_{theo}$ due to surface states!

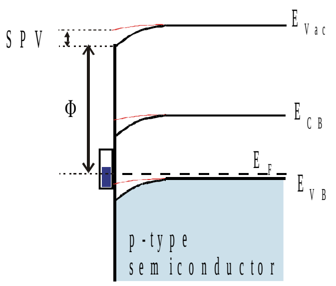


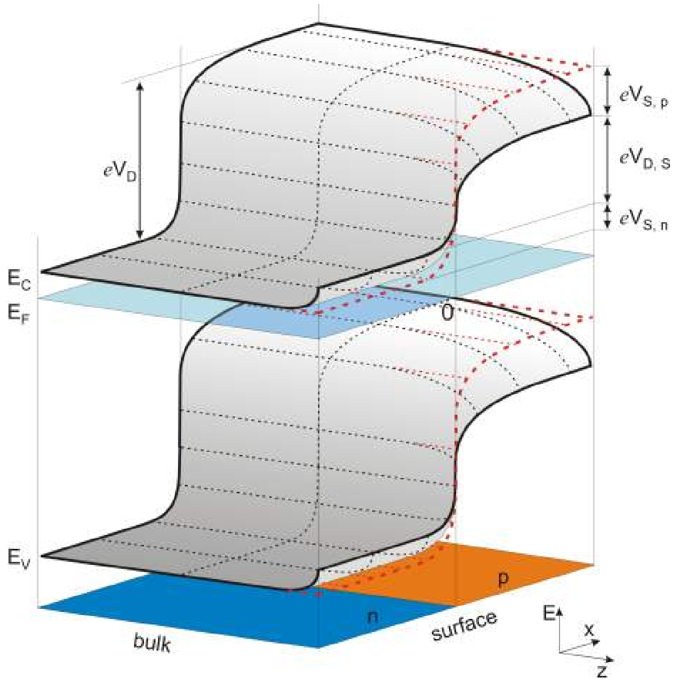

# Surface Effects

no surface states



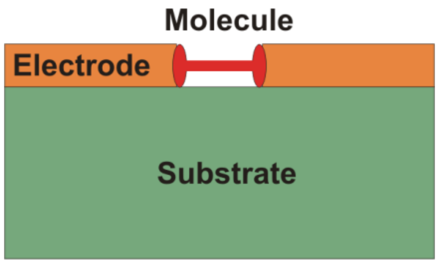

surface states

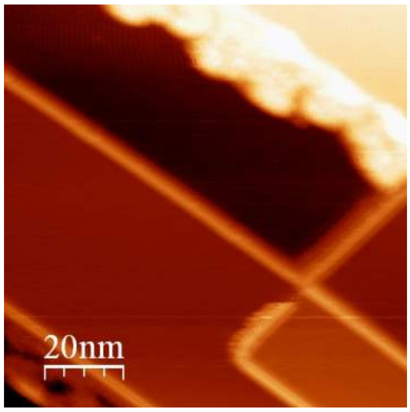


# Motivation

## Molecular electronics



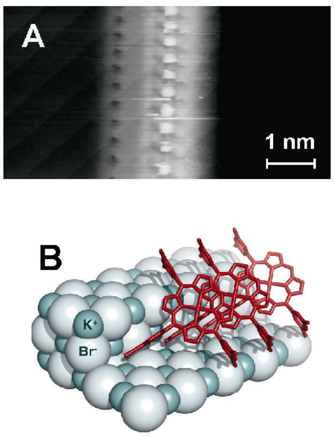




Molecules on Insulators:

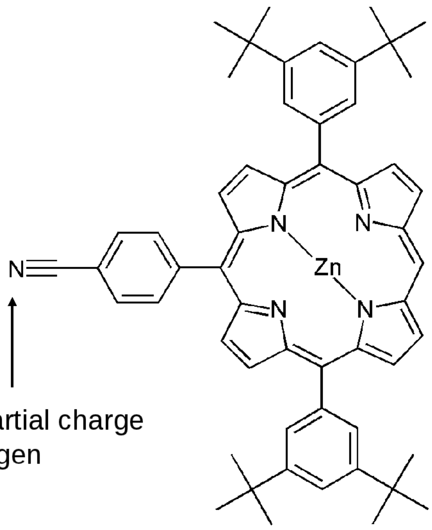
- No STM possible – nc-AFM mandatory
- Low diffusion barrier but high intermolecular interaction
- Low temperatures – easier to “fix” molecules but not so easy to find applications

# Asymmetric Cyano-Porphyrins

## Natural light harvesting complexes




S. Meier et al., Small, 2008, 4, 1115



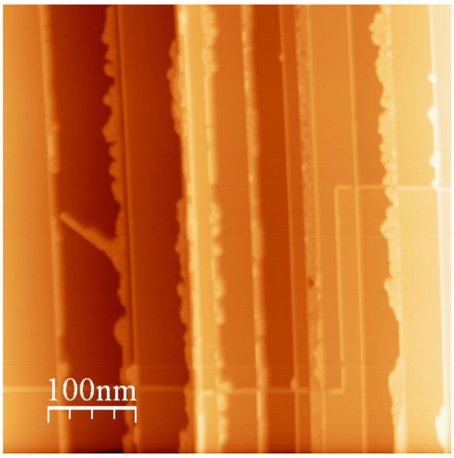

Negative partial charge on the nitrogen

Balaban et al., *Acc. Chem. Res.* **2005**, 38, 612 – 623

# Wire Formation

Decoration of step edges on KBr(100)

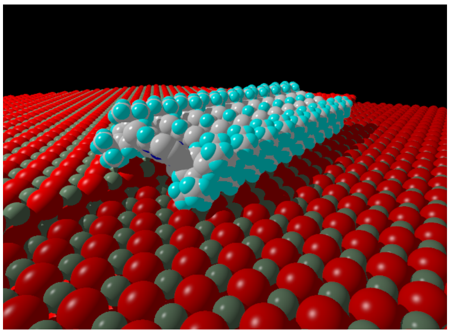
- In situ cleaved KBr with 0.5 ML of molecules
- Steps (< 1nm) are decorated with monowires
- Higher steps act as nucleation sites for structure growth across terraces

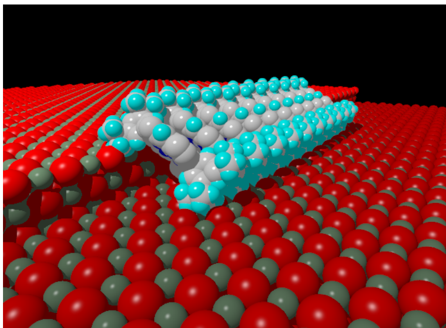



L. Zimmerli et al., J. Phys.: Conf. Ser., 2007, 61, 1357

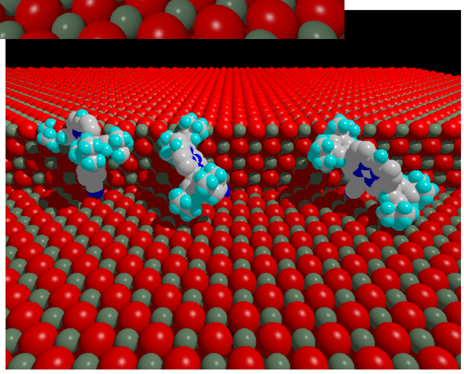
# Wire Formation

Structural model



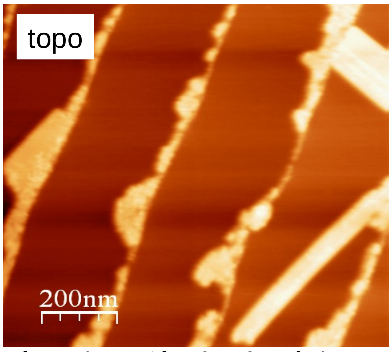


- The tilt angle of the molecules is determined by the side groups, the π-π stacking and the step height.
- Steps higher than 3 ML prevent a π-π stacking.

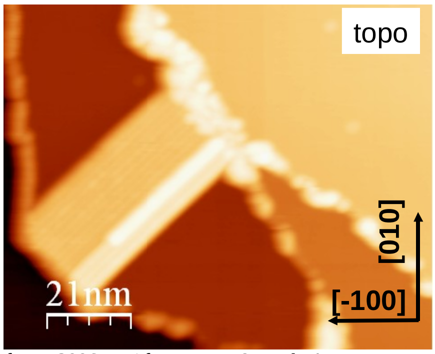


# Molecular Assemblies

## Multiwires on KBr




$f_0 \approx 174054 Hz, \Delta f = -8 Hz, Q = 15k, A = 5nm$



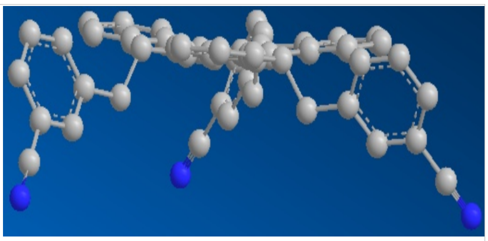

$f_0 \approx 173886 Hz, \Delta f = -52 Hz, Q = 15k, A = 5nm$

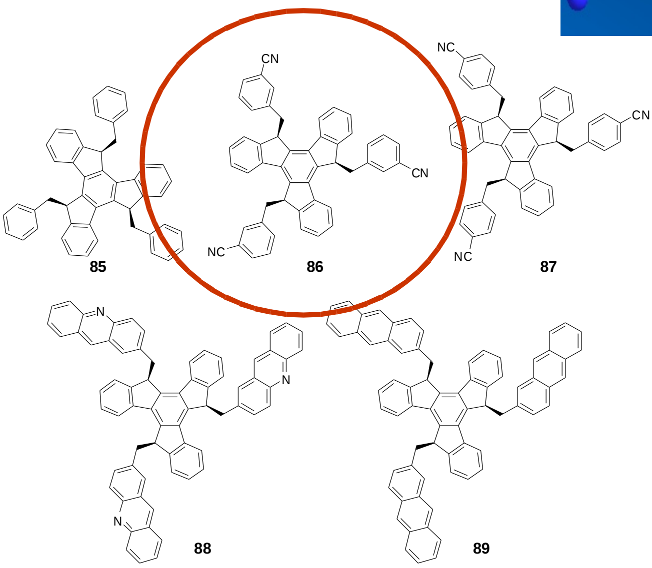
- Multiwire growth across terraces
- The <110> directions are clearly preferred
- Different heights are visible

S. Meier et al., Small, 2008, 4, 1115

# Functionalized Truxenes

## Structure

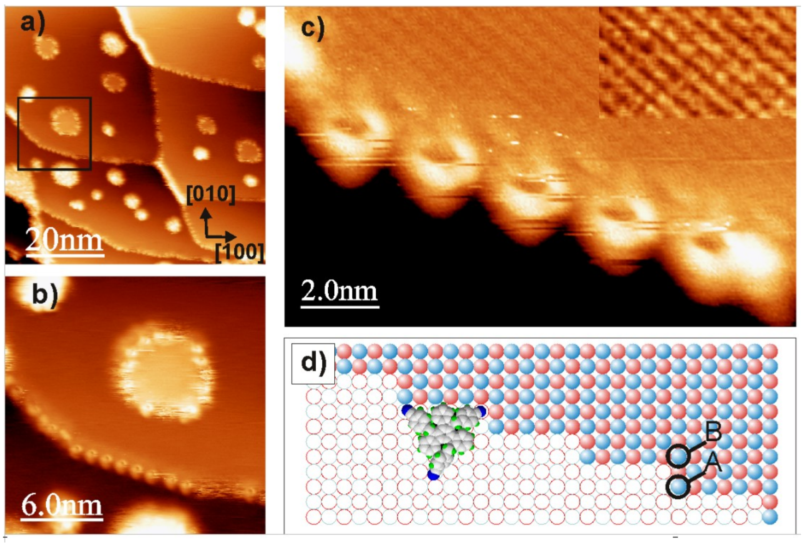





O. de Frutos et al., Chem. Eur. J. 8(13), 2879 (2002)

# Imaging a Single Molecule

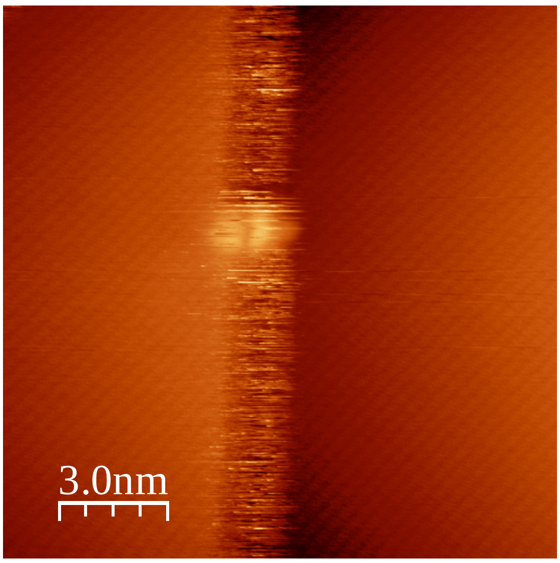
Measurements at RT



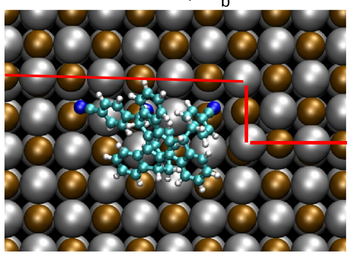

- Re-arrangement of the substrate, edges are running in the [-3 1 0] direction
- no chemical interaction with the surface
- adsorbed on K or Br terminated double atomic kink

# Imaging a Single Molecule

Measurements at RT




Br terminated, $E_b$=1.33eV



K terminated, $E_b$=1.17eV