Scanning probe microscopy

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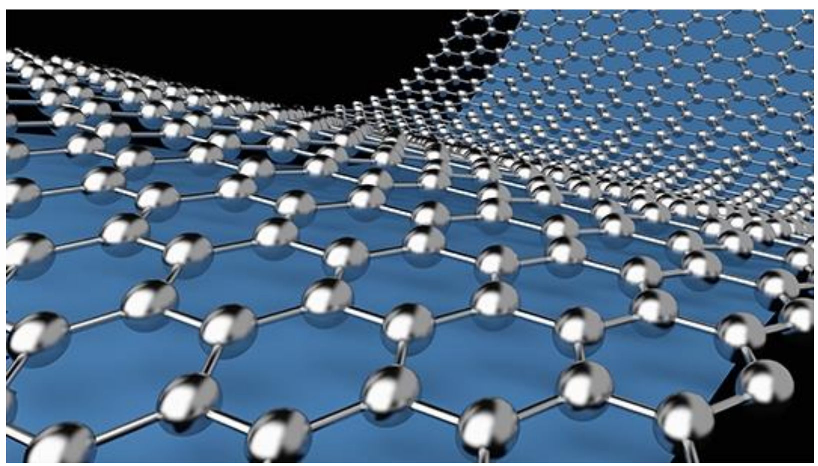
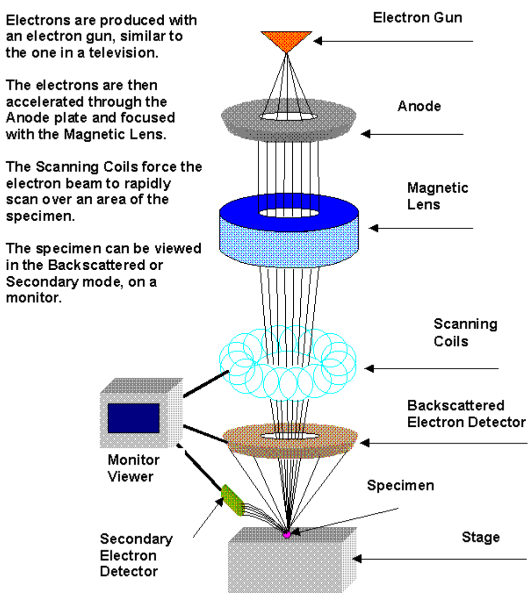
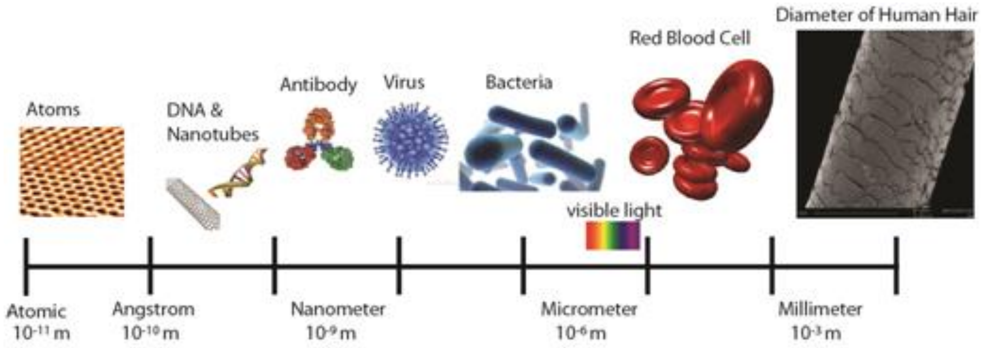


Scanning probe microscopy

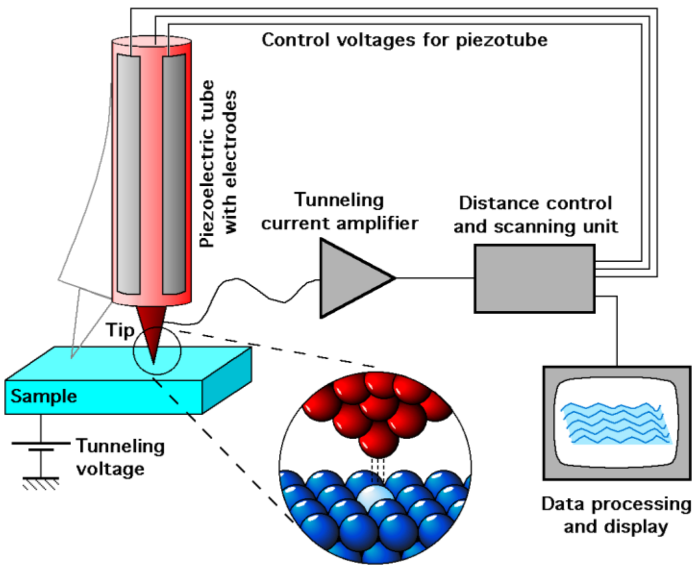
Classical microscope concepts

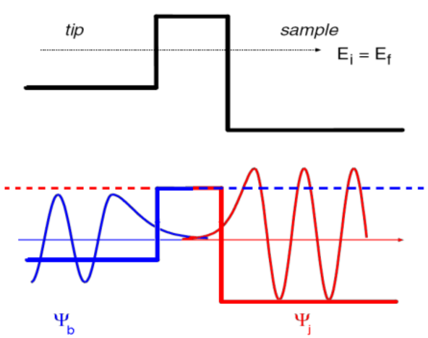


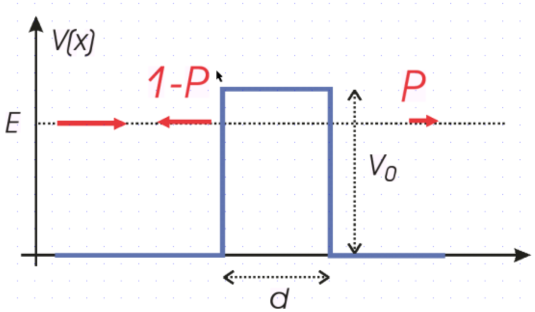


Scanning probe microscopy

Scanning tunneling microscopy







$$P = \frac{16E\,(V_0 - E)}{V_0^2} e^{-2\kappa d},$$

$$\kappa = \sqrt{2m/\hbar^2\,(V_0 - E)}.$$

Scanning probe microscopy

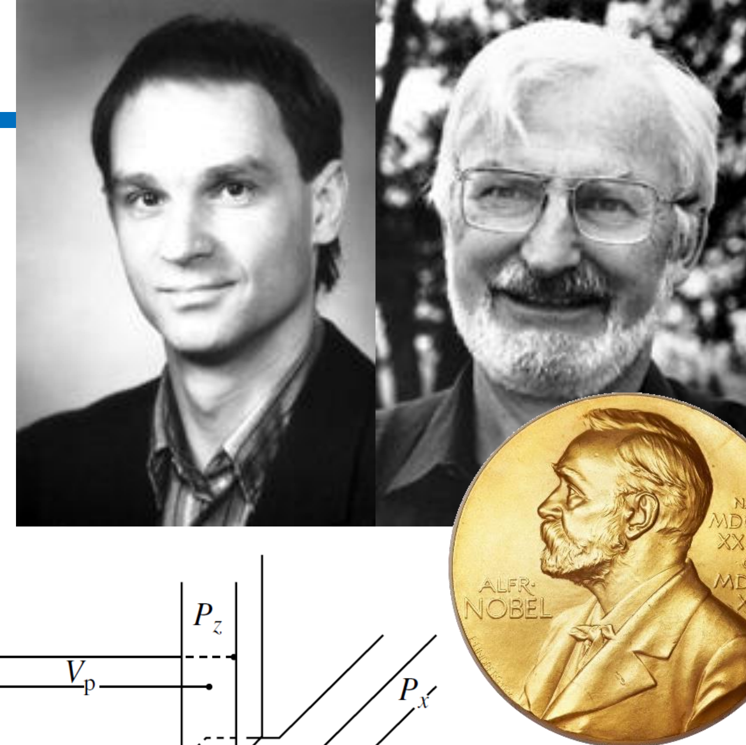
Scanning tunneling microscope (STM)

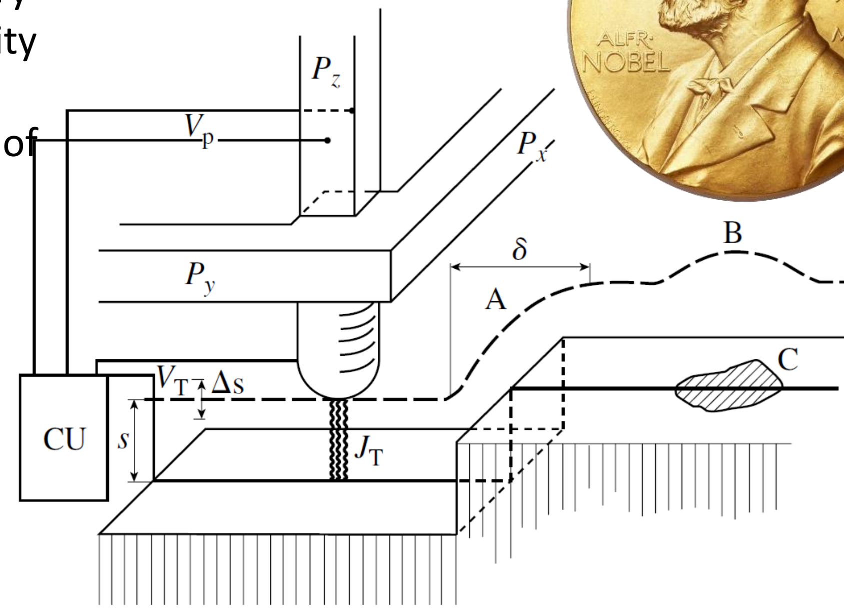
First tool to manipulate single atom, ease of operation and construction of STMs → popularized Nanoscience
Later on followed by AFM (not just for conducting and clean surfaces)

- **1979 Invention of STM** Gerd Binnig and Heine Rohrer at IBM labs.
1986. Nobel prize.
Idea of Binning as grad student: using tunneling to profile surfaces. Try to use very sharp metal whisker. He realized that vibration and stability issues are important. → Make a robust constriction. His expectation that with a tip with 1000A radius due to exponential characteristics of tunneling 45A resolution can be achieved.

1982 First paper about the operation
Basic structure & working principle: metal probe on a tripod consisting of three piezoelectric elements: Px, Py, Pz

- The probe is advanced toward the surface until a preset level of tunnel current is detected.
- *x*−*y* scan of the surface with feedback to control the tunnel current constant.
- Height change → change of the height of the surface (A) or a change of the local work function (B).
- Height vs. x-y is recorded by computer





(Up) G. Binning and H. Rohrer inventors of STM (Down) Basic structure of STM. Tunnel current J_T flows between a metal tio and surface, which exponentially sensitive to the distance. Piezo crystals are used to move the tip up and down (P_z) and above the surface in x-y directions (P_x, P_y).

Wikipedia *Lindsay Section 4.1*

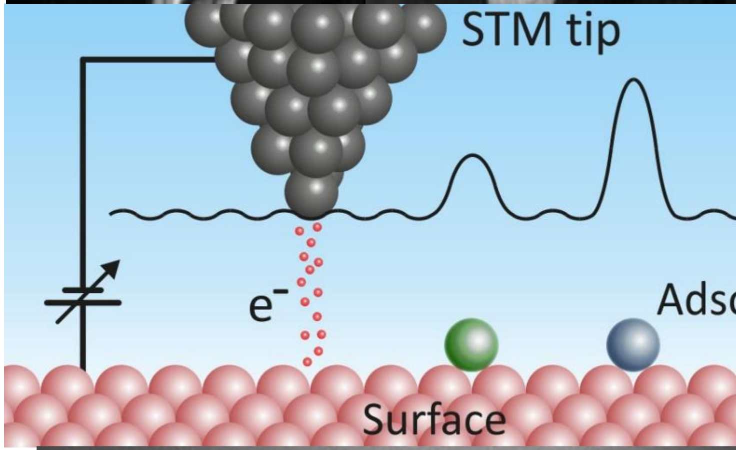
Scanning probe microscopy

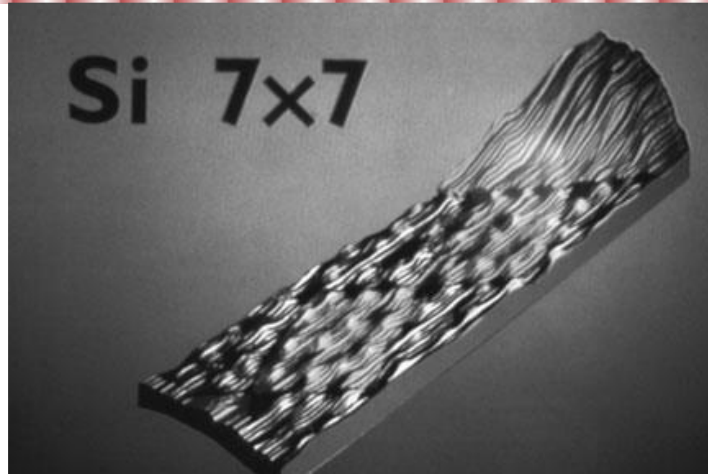
Scanning tunneling microscope (STM)

First test of Au surface was a surprise, atomic terraces were measured (height 3A) → Probe is not a sphere but a single atom dangling from the very tip! → Atomic resolution

- The first image of the silicon 7 × 7 surface reported in the 1983 paper. At this early stage even IBM Corp. had not successfully attached a computer to a scanning probe microscope, so this three-dimensional rendition was made by cutting up copies of traces made on an *x*−*y* chart recorder, stacking them together, and gluing them!

First setup is complicated : magnetic levitation of a superconductor to provide vibration isolation
Few generations later STM mechanism became so small, compact, and rigid that it was easily capable of atomic resolution when operated on a tabletop.
Advantages:
- STM can work without vacuum (not like SEM) and also in water
- Cheap few kEUR
→ widely used, big momentum to Nanotechnology





(Middle) Thee sturcutre of the STM tip contains a single atom at the very end of the tip. Since tunnel current is dominantly coming from this atom, it ensures the atomic resolution. (Down) First image of the surface reconstrction of silicon (111) surface. First direct observation of this structure at the atomic level. IBM.

Wikipedia
Lindsay Section 4.1

Scanning probe microscopy

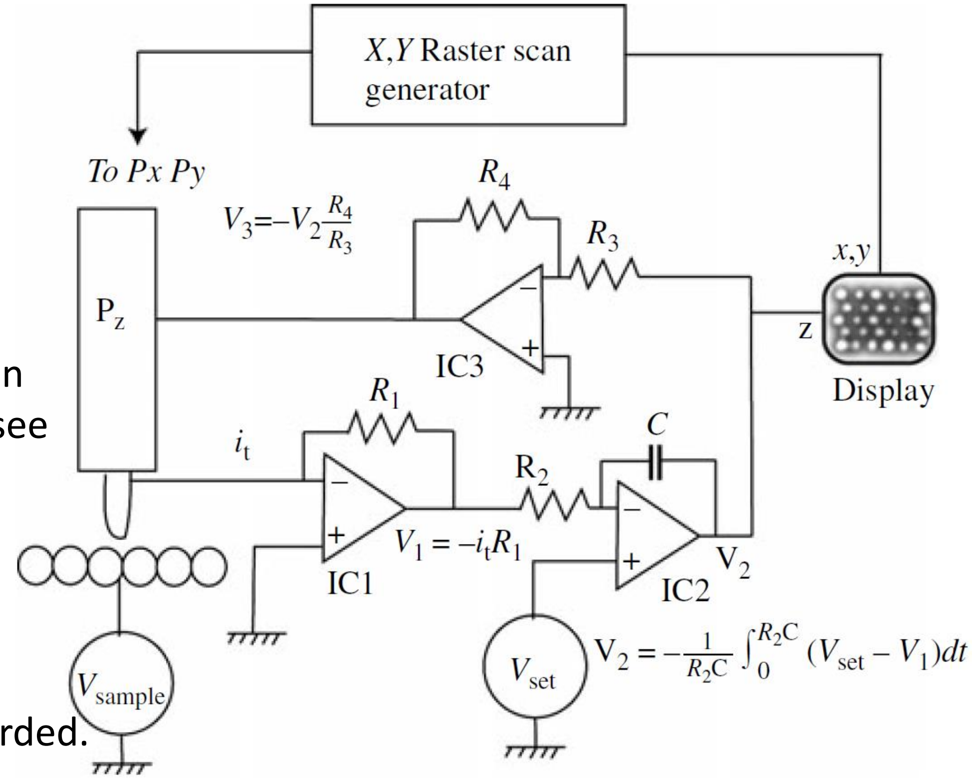
Scanning tunneling microscope (STM)

STM setup - height control circuit

- Tip sample tunnel current (i_T) is converted to voltage (V_1).

$V_1 = -i_1 R_1$ by IC_1&R_1.

- V_{set} sets the targeted tunnel current. IC_2&R_2&C generates an error signal (V_2) between targeted and measured current (see form of V_2).
- Error signal is sent to the piezo actuator Pz after voltage amplification with IC_3&R_3&R_4.
- Overall phase of the feedback is negative: increased i_T → probe is pulled away as long as $V_{set}=V_1$.
- V_2 represents the height of the sample as well. → It is recorded.
- X and y positions are scanned by a scan generator, it is applied to P_x, P_y.



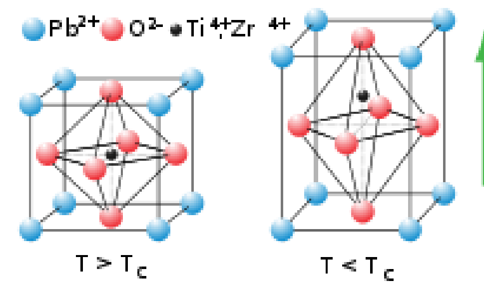
Today entire feedback arrangement is carried out digitally.

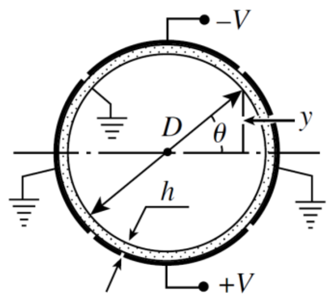
Piezoelectric scanning transducer

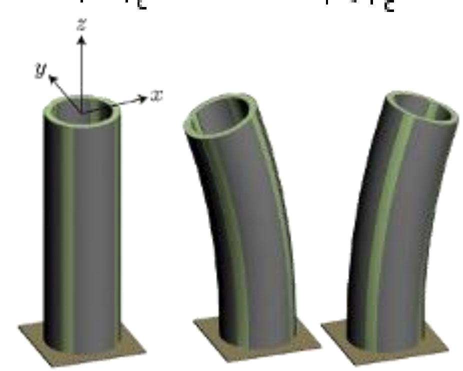
Piezoelectric ceramics e.g. lead zirconium titanate (PZT). V → δz

Scanner tube: metal electrodes both in and outside. Applied voltage across the wall -> changes thickness, increase/decrease depending on direction of P and E. Volume of ceramic ≈ constant → tube length changes. Typical 20A/V.

Driving opposite quardants with different voltage sign → bending of the tube →x, y displacement. Same V on all sides → z displacement.







Wikipedia

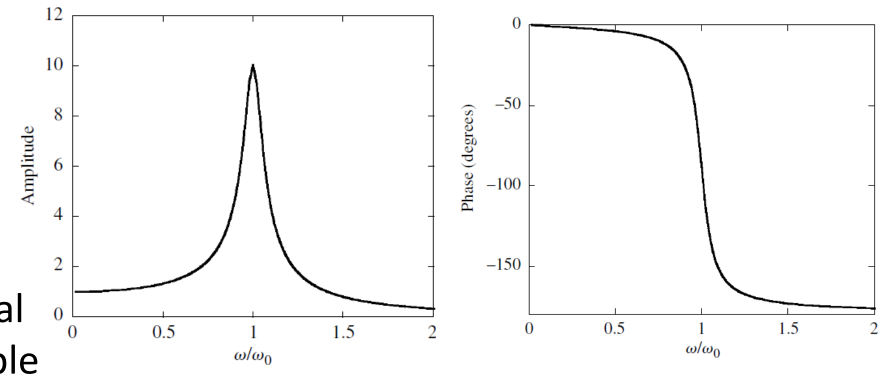
Lindsay Section 4.1

Scanning probe microscopy

Scanning tunneling microscope (STM)

Speed limit of STM response

Typical piezoelectric scanning elements have an intrinsic mechanical resonant frequencies 1 - 50 kHz. → Limitation on the fastest possible response of the microscope. If drive freq > resonance freq. → 180 pahse shift in response → feedback loop gets unstable.
Integrator part has to be sufficiently slow, tuned by R_2 and C values.
→ Shortest time to measure one pixel ~20usec.



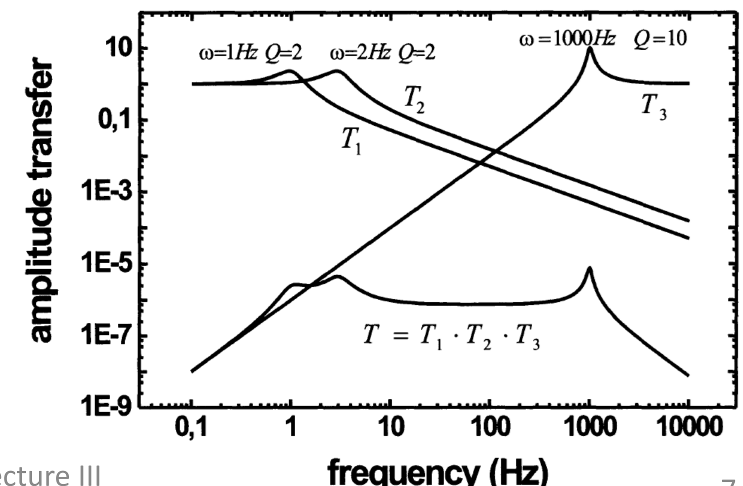
(Up) Amplitude (see also equation bellow) and phase response of a damped harmonic oscillartor when harmonic excited with frequency, ω is applied. For Q=ω_0 τ=10. ω_0 is the resonance frequency, τ is the friction coefficient.

$$x(\omega) = \frac{A_0}{\sqrt{(\omega_0^2 - \omega^2)^2 + \left(\frac{\omega}{\tau}\right)^2}}$$

Mechanical isolation

STM is very sensitive to acoustic noises. → Isolation system.
Mechanical noise transfer chracteristics of STMs (see T3 on the figure) gets suppressed as f → 0Hz. Mid freq. range has to be filtered out.
Solution: Isolation systems with low resonance frequency. As Eq. 1 shows when $\omega >> \omega_0$, the response of the system gets suppressed ~ ω^{-2}.
Various acustic isolation systems: box, mechanical springs, heavy plates with viton rings between, eddy currents, rubber feet, pendulum, silent room etc.

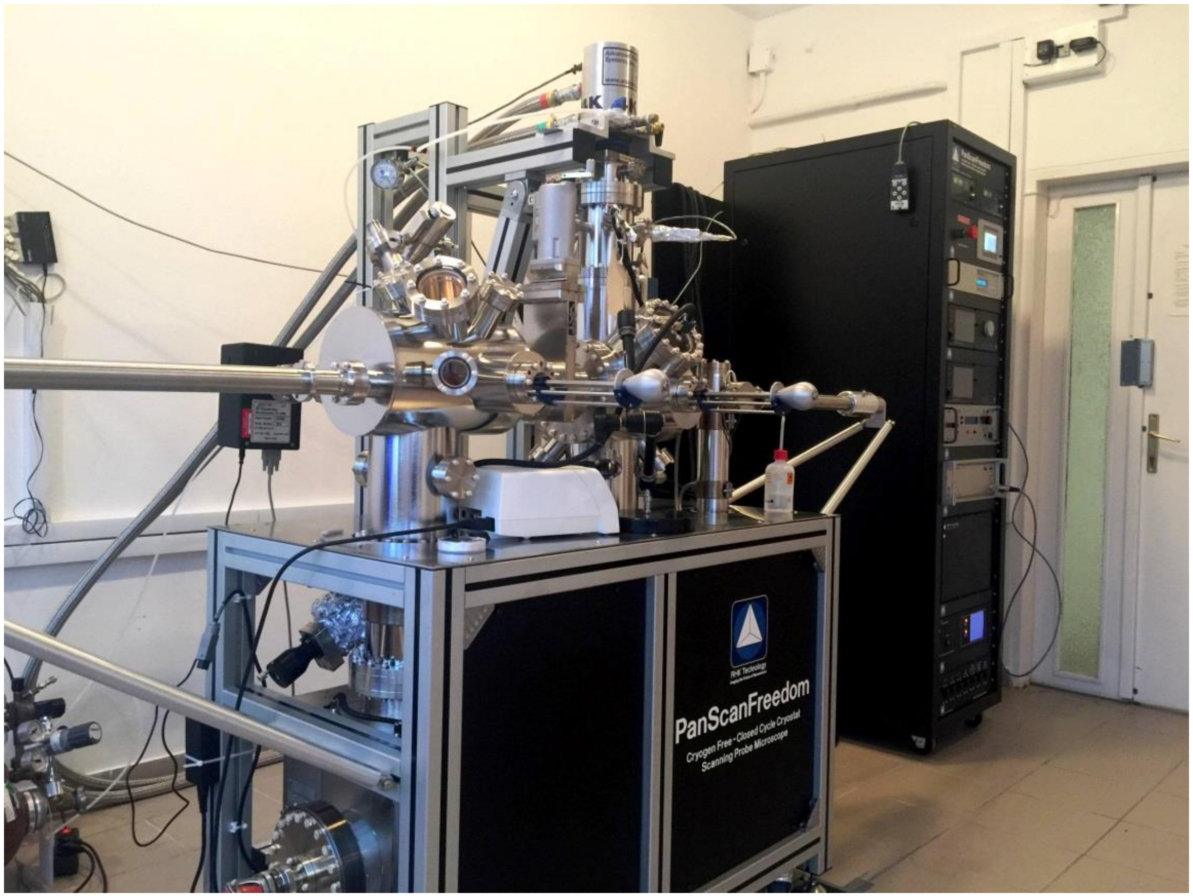
(Down) Mechanical transfer function of an STM system. T3 is the transfer function of STM with resonance frequency of 1kHz, T1 and T2 two damping system e.g. springs, several heavy metal plates with viton rings between, etc., which protect the system from external mechanical noises. Goal is to filter out noises above a few Hz. The total transfer function (T) fulfils this requirement.

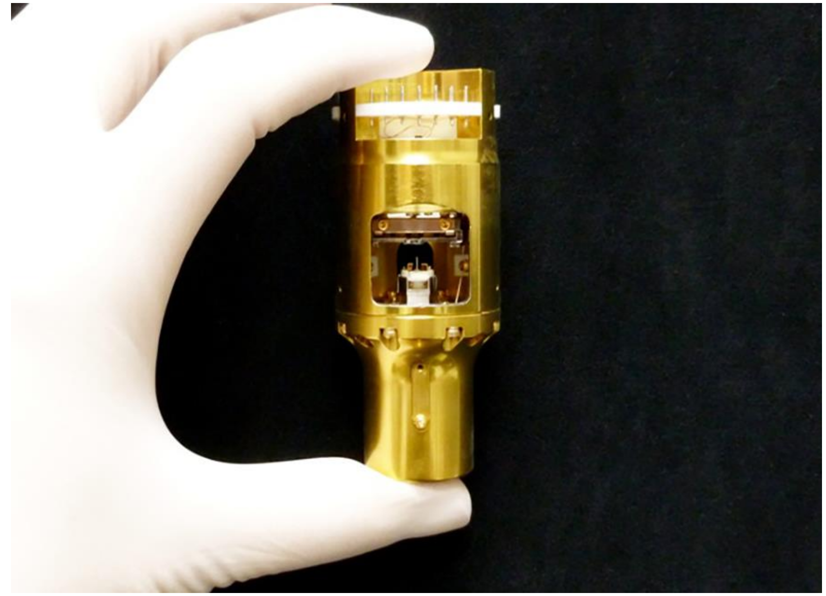


Wikipedia

Lindsay Section 4.1, and Appendix D. also E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 1.2.3

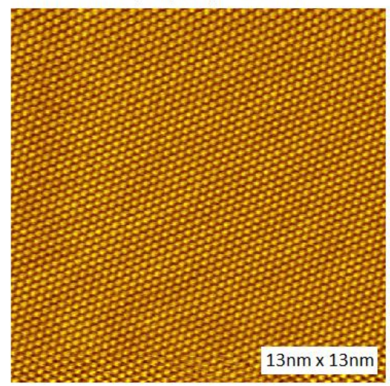
Scanning probe microscopy



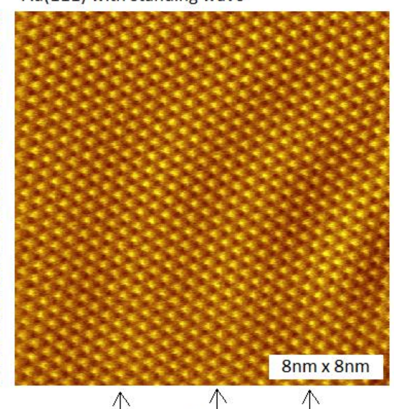


RHK Pan Freedom at 8.5K

Defect free Au(111) image - Raw data



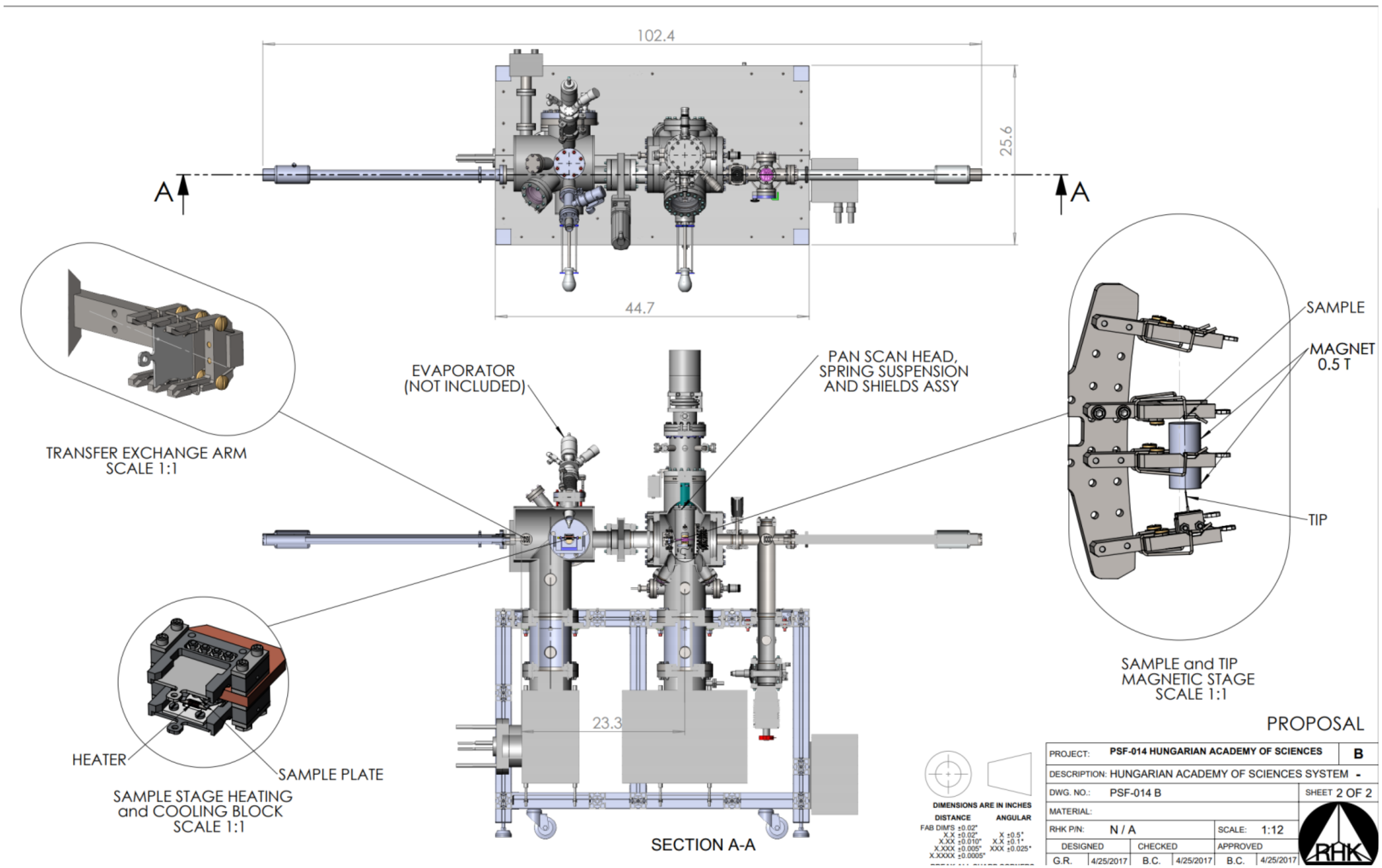
Au(111) with standing wave



standing wave

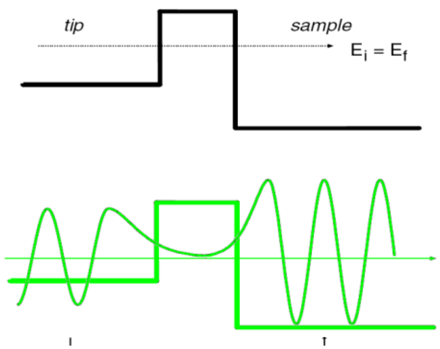
Images courtesy of Tapaszto Lab – Hungarian Academy of Sciences, Centre for Energy Research

Scanning probe microscopy

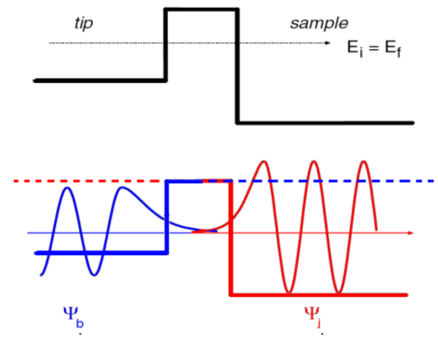


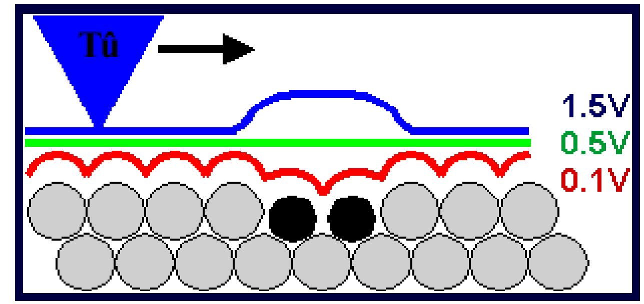
Scanning probe microscopy

exact



perturbative





$$I_t = 2\frac{\pi e}{\hbar}\sum_{f,i}\left|\left\langle f^- \middle| V_{tunel} \middle| i^+\right\rangle\right|^2 \delta\left(E_f - E_i\right)$$ Scattering description

$$I_t = 2\frac{\pi e}{\hbar}\sum_{\mu,\nu}\left|\left\langle \chi_\nu \middle| V_{tunel} \middle| \psi_\mu\right\rangle\right|^2 \delta\left(E_\mu + eV_t - E_\nu\right)$$ Perturbative approx.

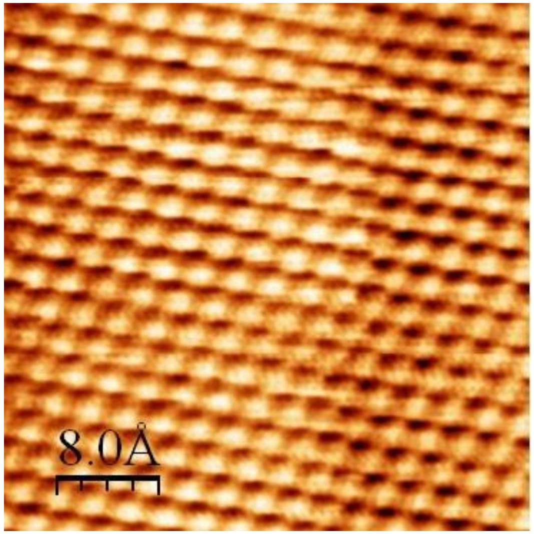
$$M_{\mu,\nu} = \left\langle \chi_\nu \middle| V_{tunel} \middle| \psi_\mu\right\rangle$$ Tunneling matrix element

$$M_{\mu,\nu} = \frac{\hbar^2}{2m_e}\int_S\left(\chi_\nu^*\nabla\psi_\mu - \psi_\mu^*\nabla\chi_\nu\right)$$ Bardeen formula

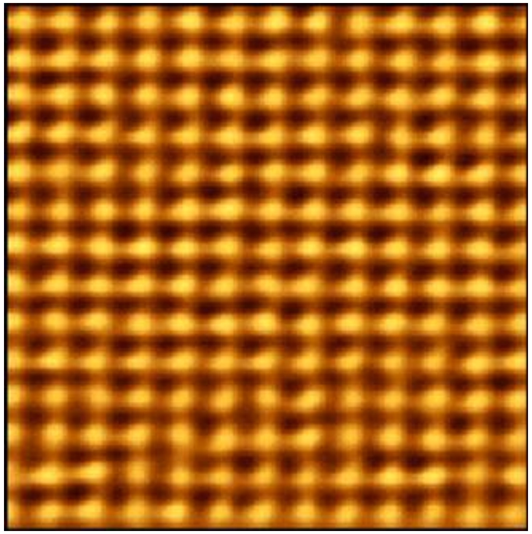
$$I(\vec{r}) \propto \int_{E_F - eU_{bias}}^{E_F}\left|\Psi(\vec{r},E)\right|^2 \qquad I(\vec{r}) \propto \int_{E_F - eU_{bias}}^{E_F}\rho_{LDOS}(\vec{r},E)$$ Tersoff-Hamann approx.

Scanning probe microscopy

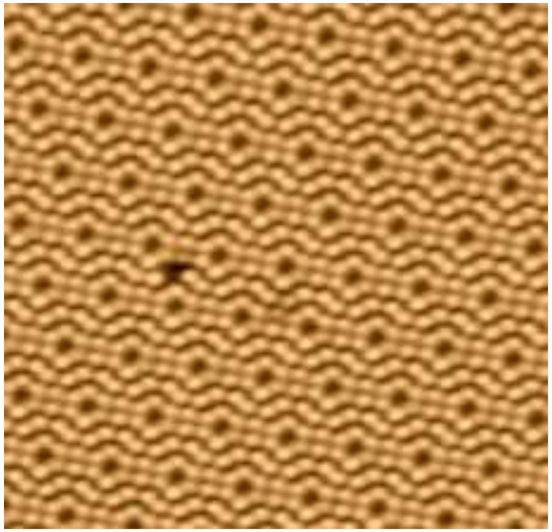
Au (111)



Cu (100)

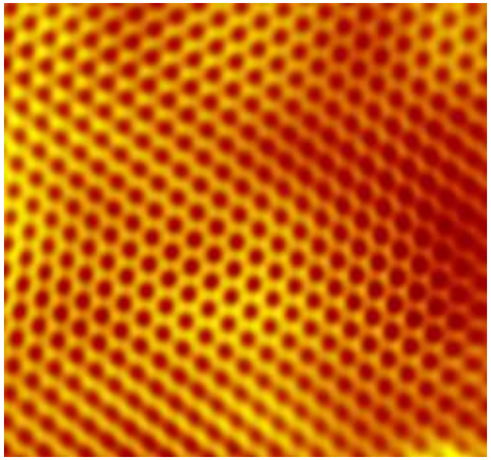


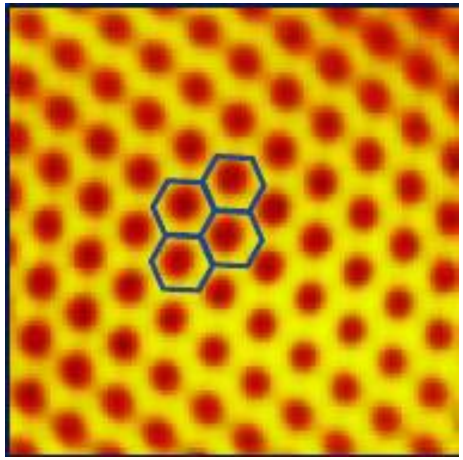
Si (111) 7x7

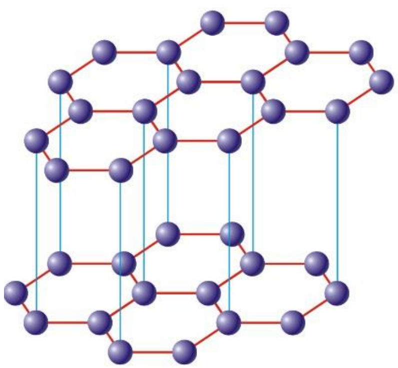


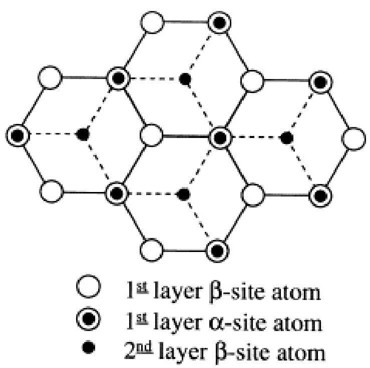
Scanning probe microscopy

Graphene

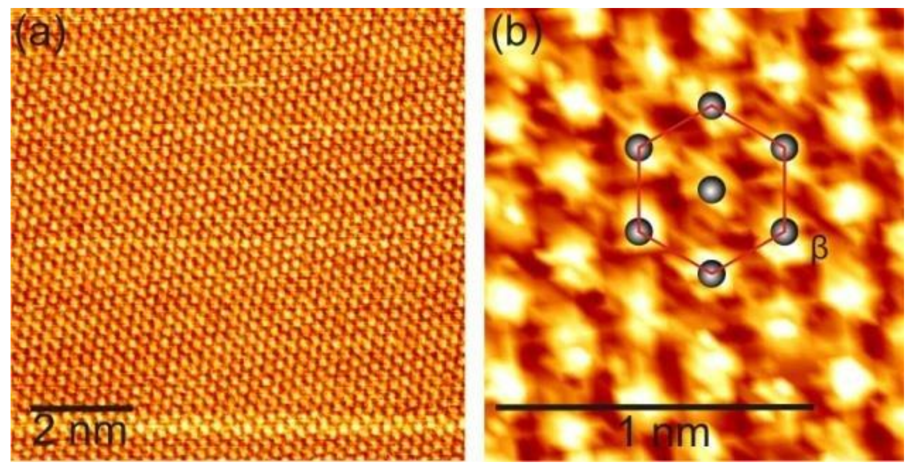






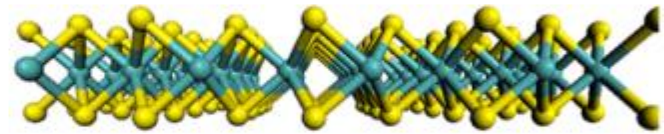


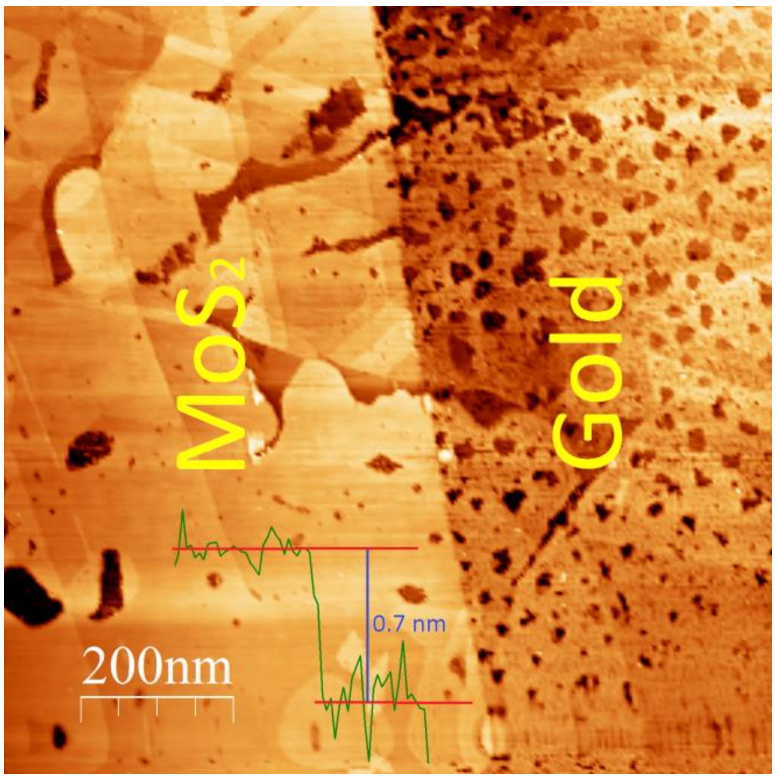
Graphite

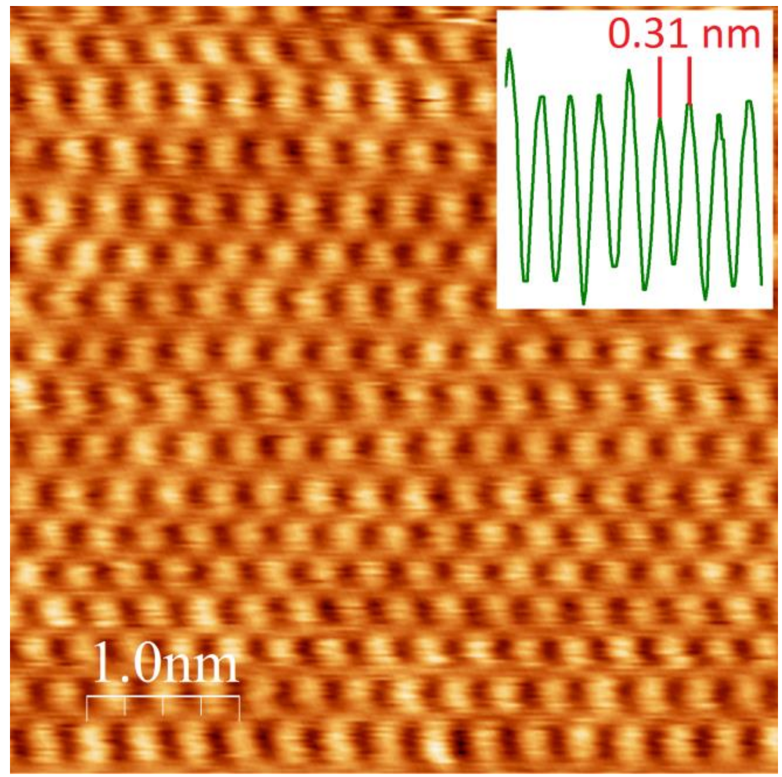


Scanning probe microscopy

MoS_2



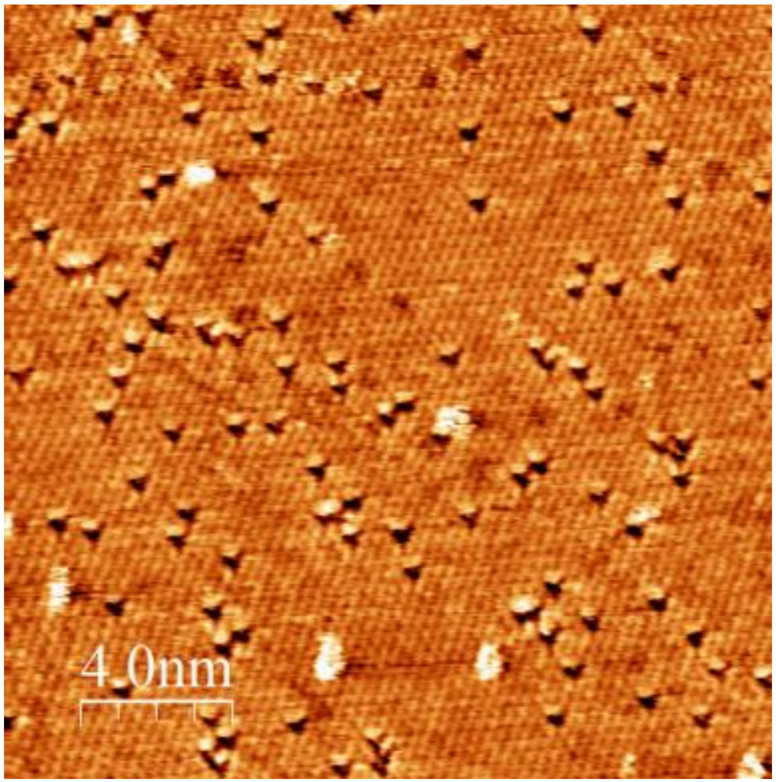


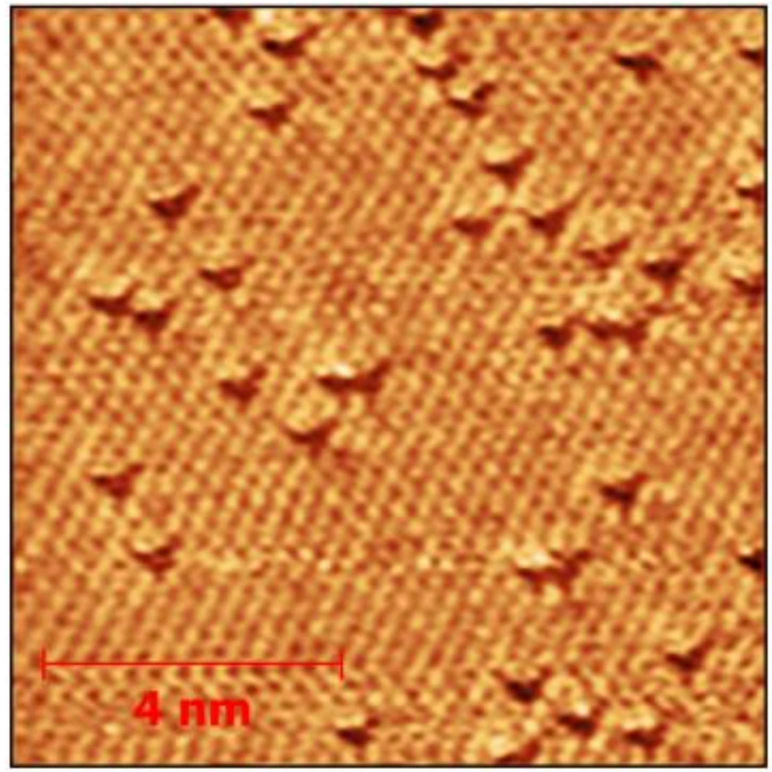


G. Z. Magda,...& L. Tapasztó ***Scientific Reports*** *5, 14714 (2015)*

Scanning probe microscopy

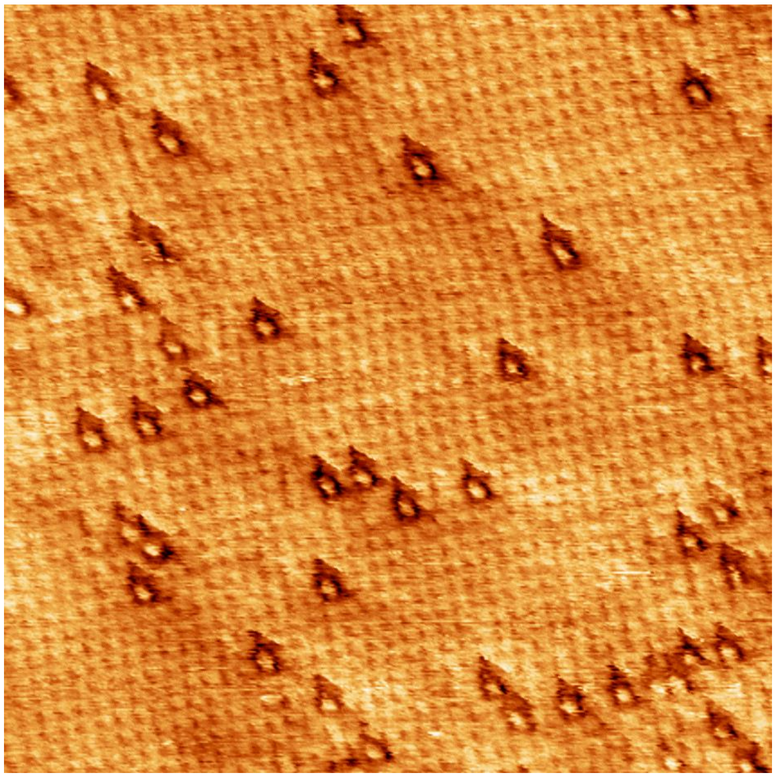
MoS$_2$ - defects

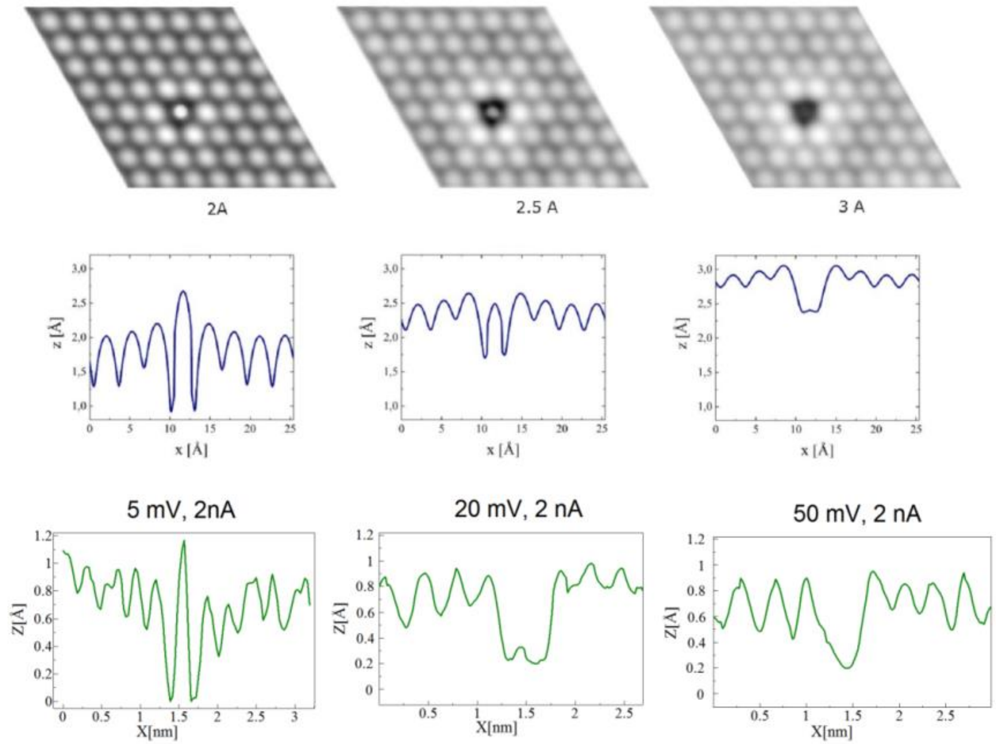




P. Vancsó, … & L.Tapasztó. ***Scientific Reports*** *6, 29726 (2016)*

MoS_2 – defects – O saturation

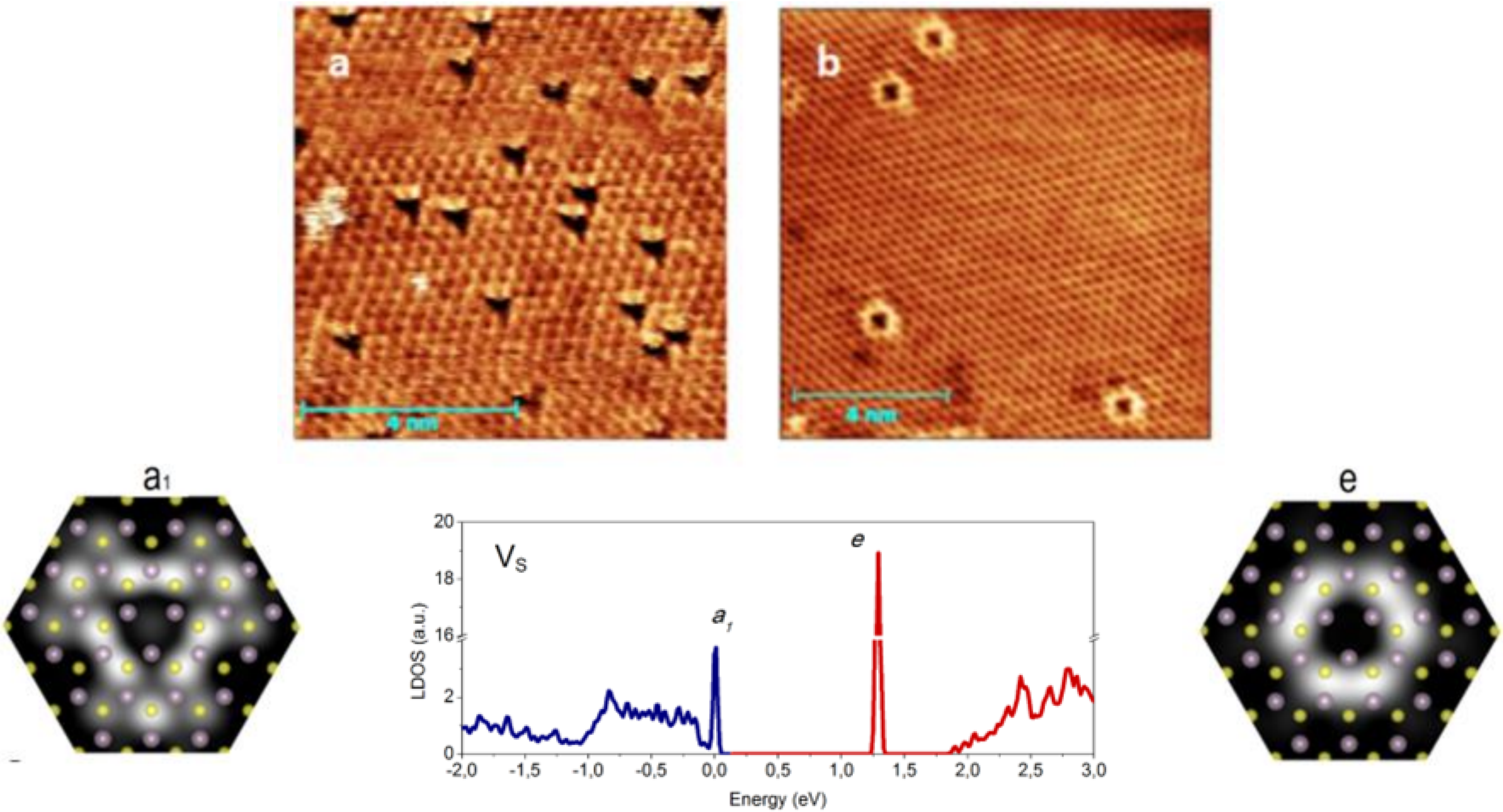




J. Pető, , L.Tapasztó. **Nature Chemistry** *10, 1246 (2018)*

Scanning probe microscopy

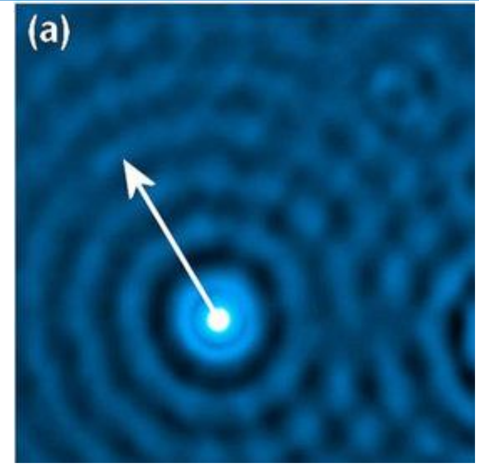
MoS_2 - defects

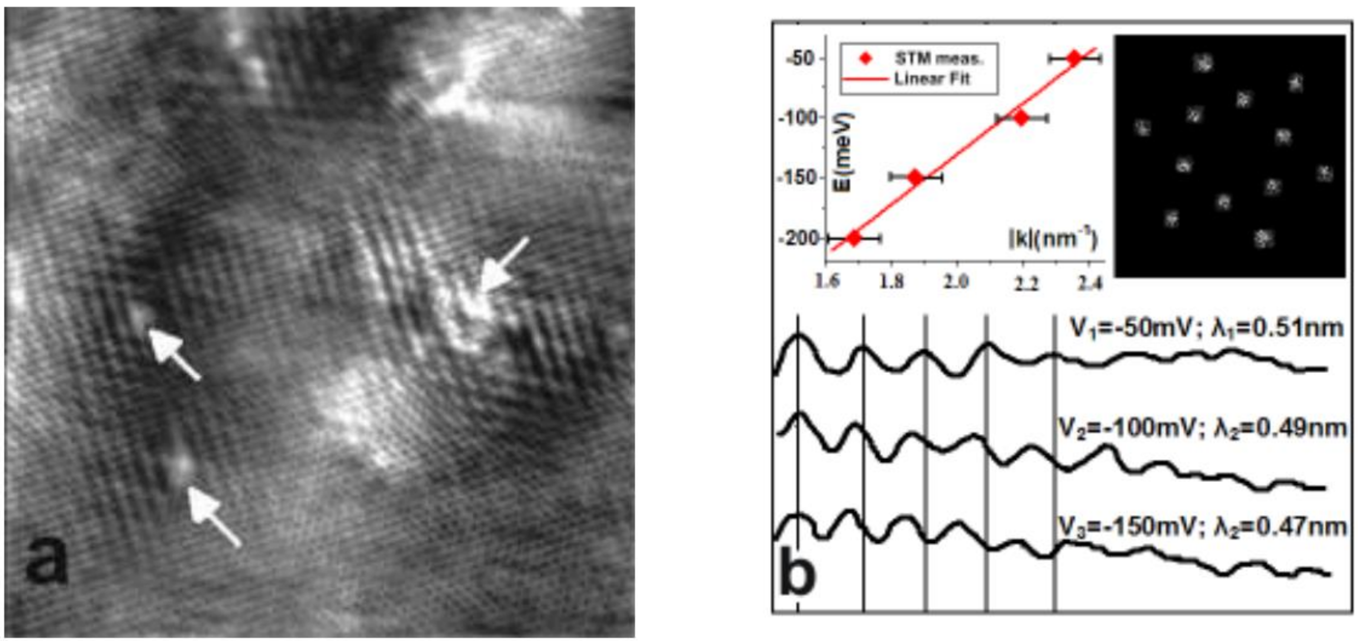


P. Vancsó, … & L.Tapasztó. ***Scientific Reports*** *6, 29726 (2016)*

Scanning probe microscopy

Graphene defects – electron interference

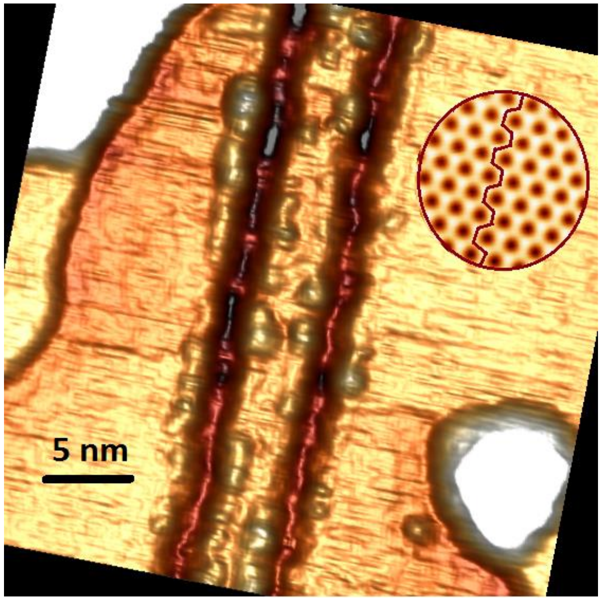


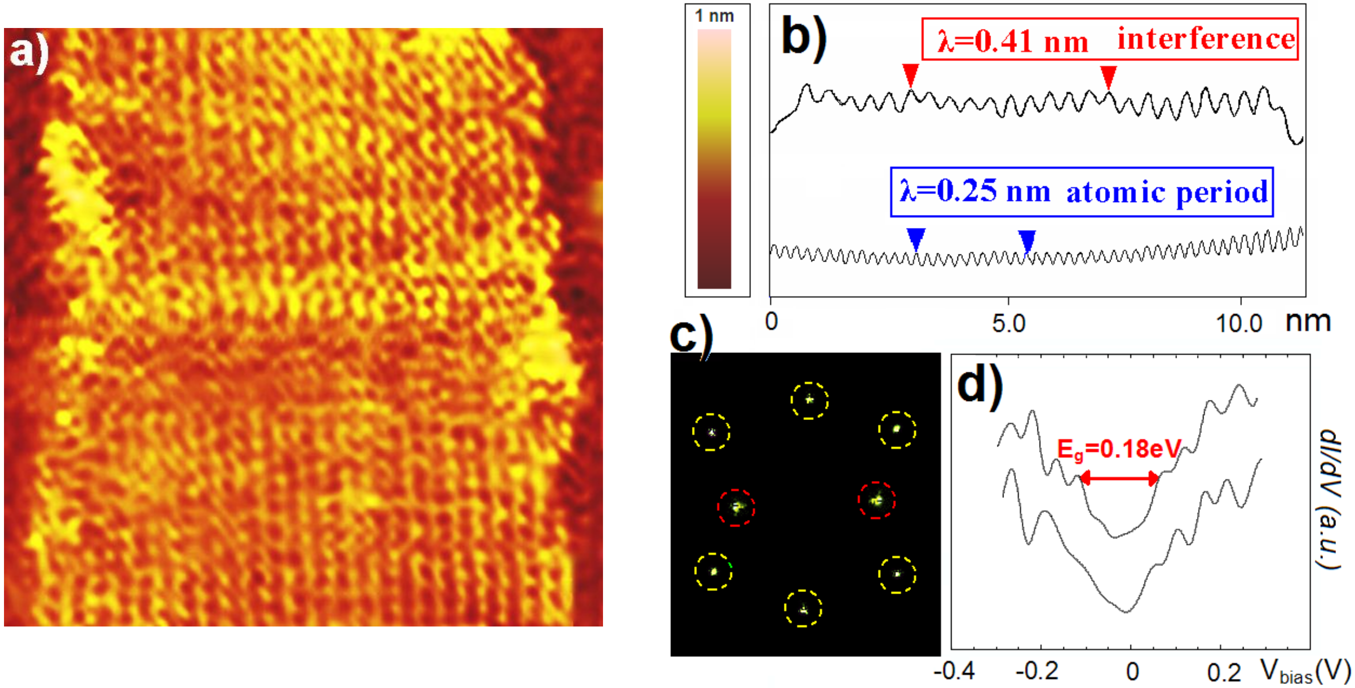


L. Tapasztó et al. ***Phys. Rev. B*** *78, 233407 (2008)*

Scanning probe microscopy

Graphene nanoribbon – electron interference



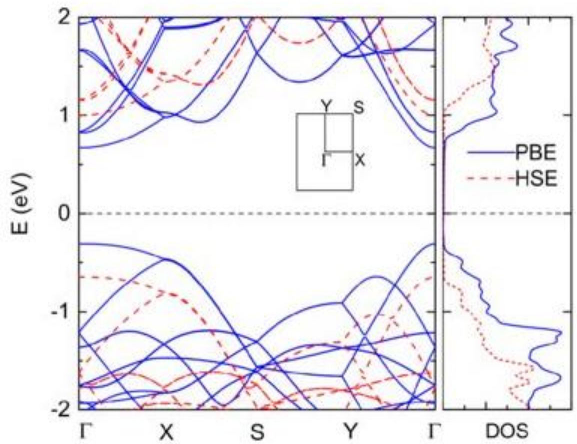


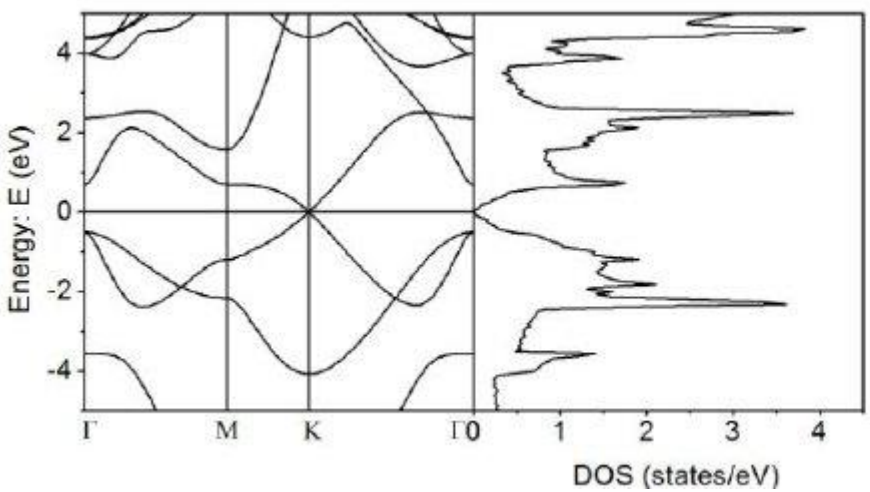
L. Tapasztó et al. **Nature Nanotechnology** 3, 397 (2008)

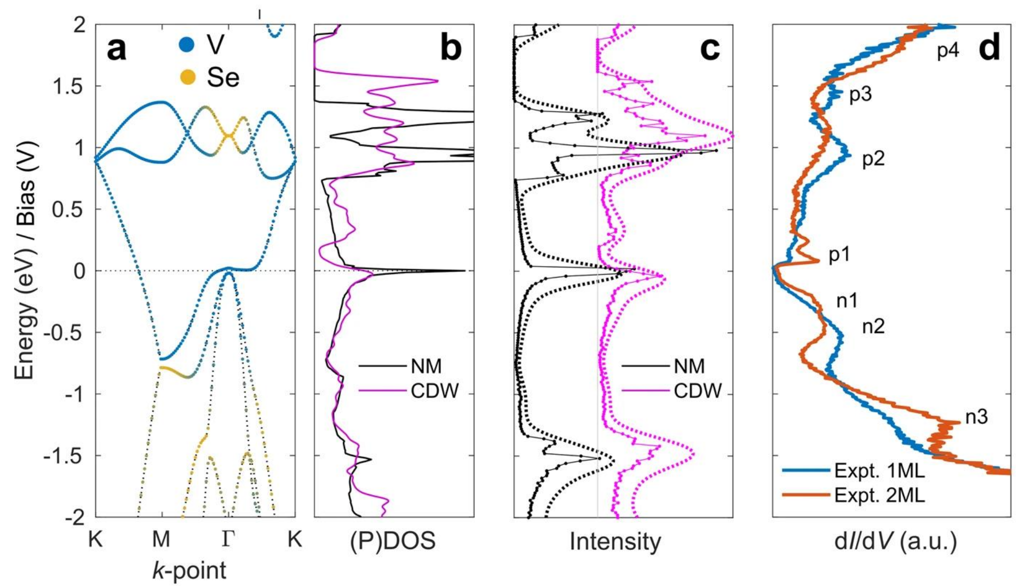
Scanning probe microscopy

Tunneling spectroscopy

$$\frac{dI}{dV} \propto \rho_{\mathrm{S}}(r, E) \equiv \mathrm{DOS}(eV)$$





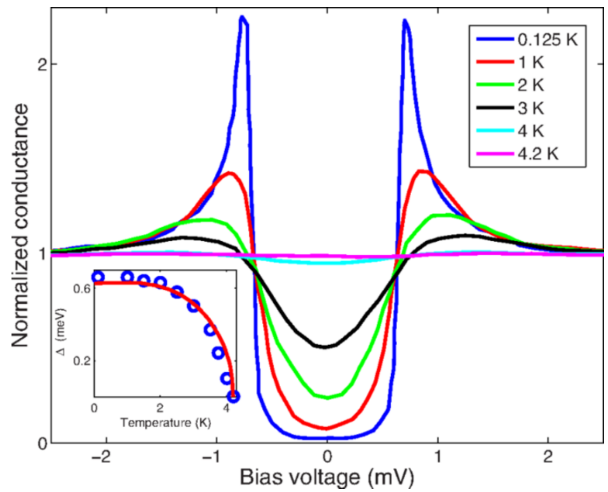


Comm. Phys. 3, 116 (2020)

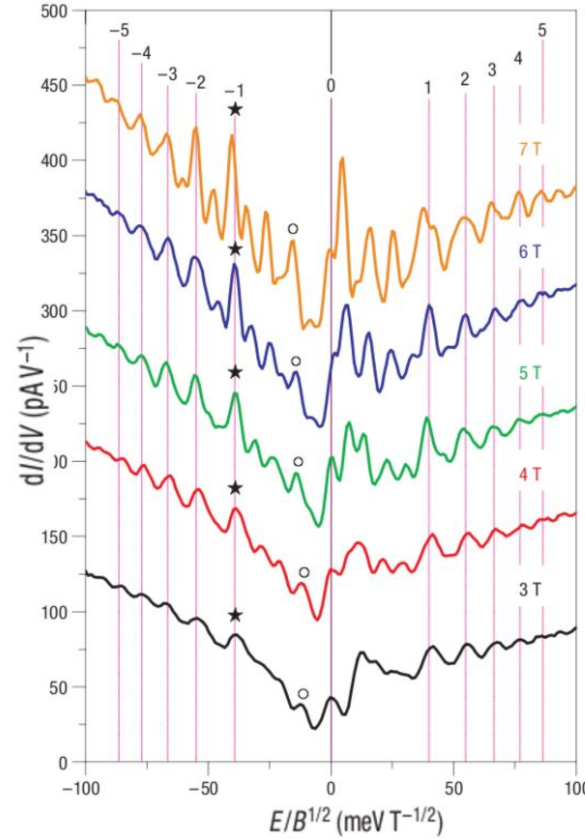
Scanning probe microscopy

Tunneling spectroscopy

BCS band gap in SCs

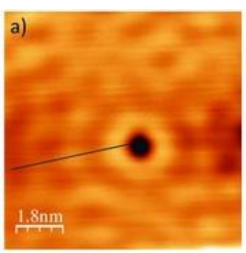


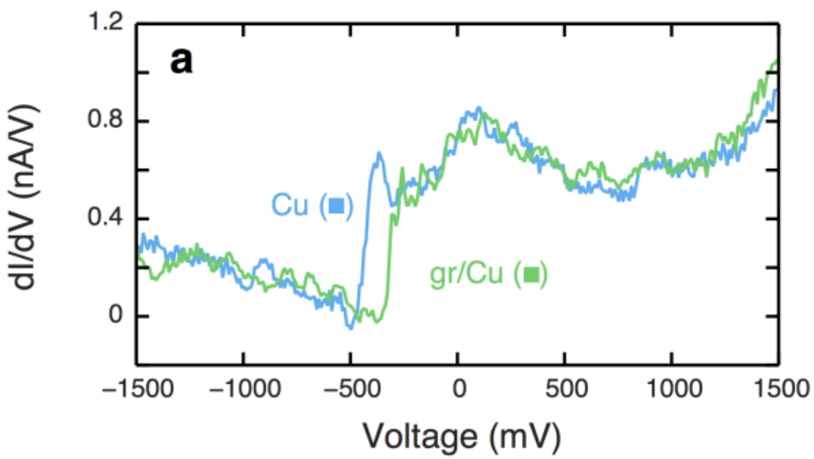
Landau levels in graphene



Nature Physics 3, 623 (2007)

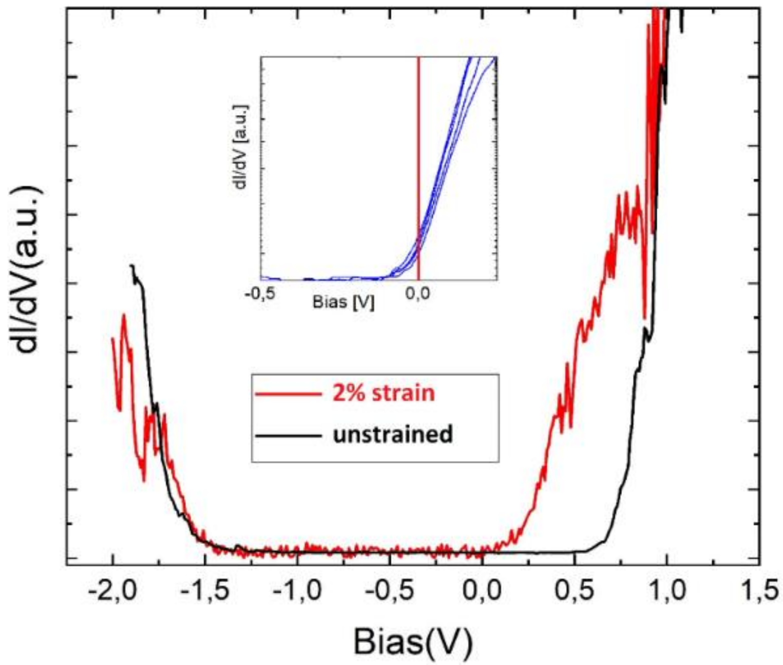
Surface states of Cu 111

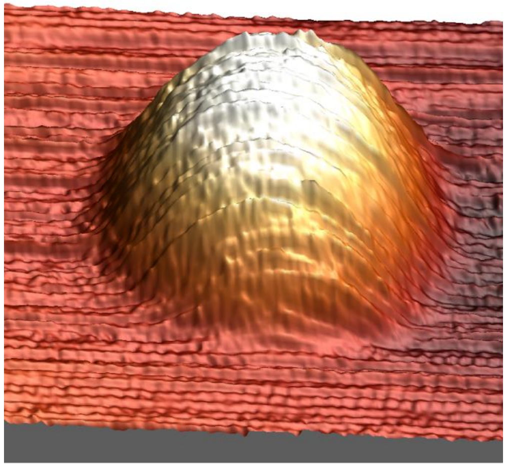


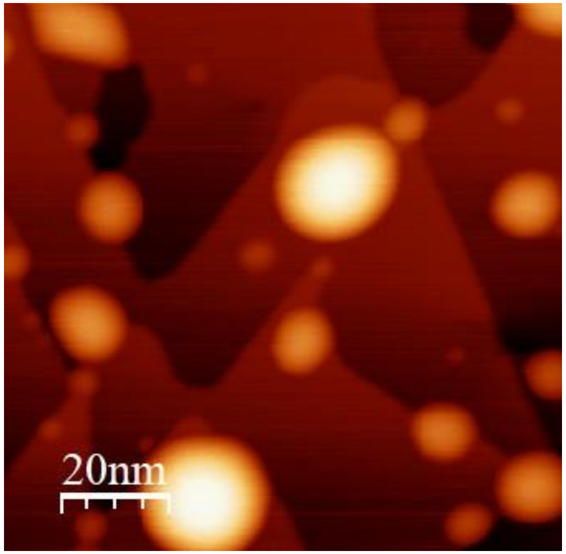


Scanning probe microscopy

MoS$_2$ single layer bandgap –effect of strain



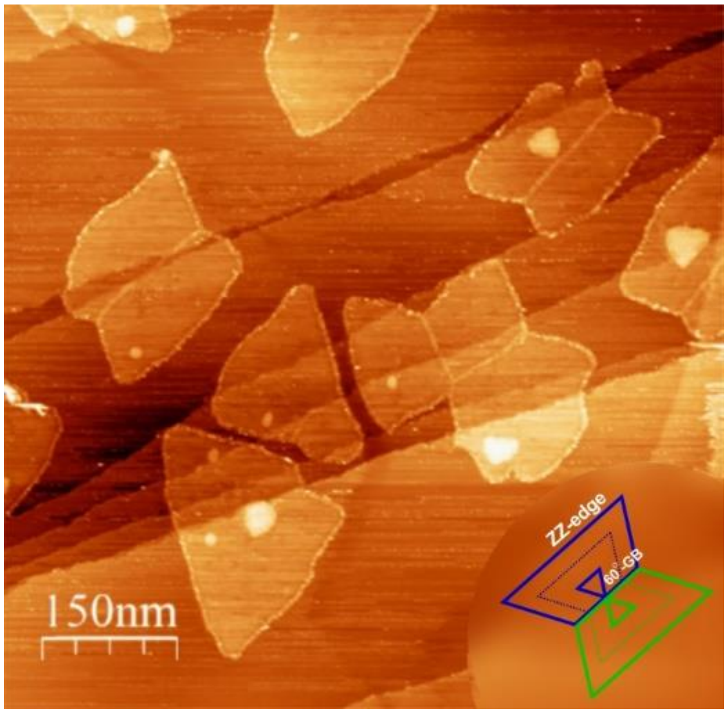


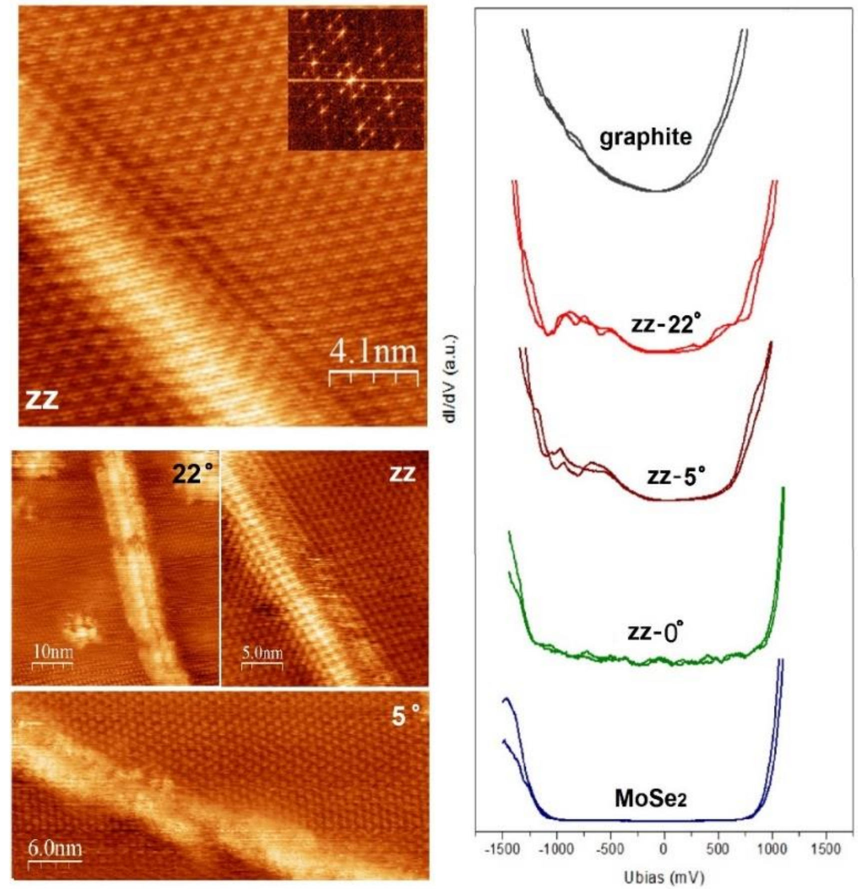


J. Pető, , L.Tapasztó. Npj 2D Mater & Appl. *3, 39 (2019)*

Scanning probe microscopy

MoS$_2$ single layer bandgap –effect of grain boundaries

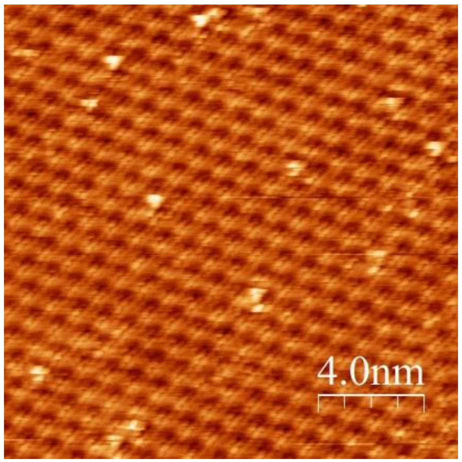


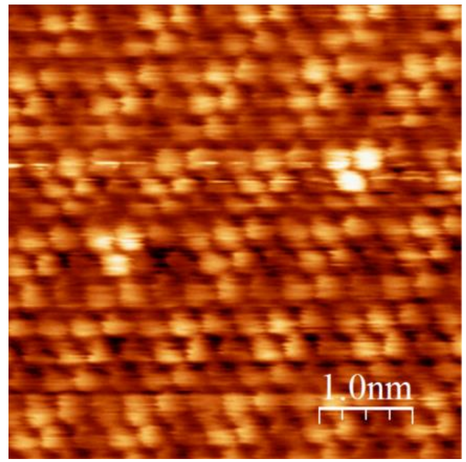


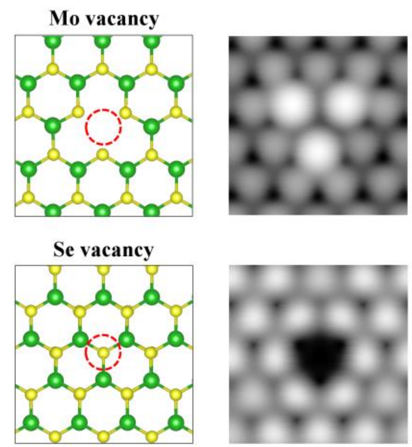
A.A. Koós, , L.Tapasztó. **J. Phys. Chem. C** 123*, 24855 (2019)*

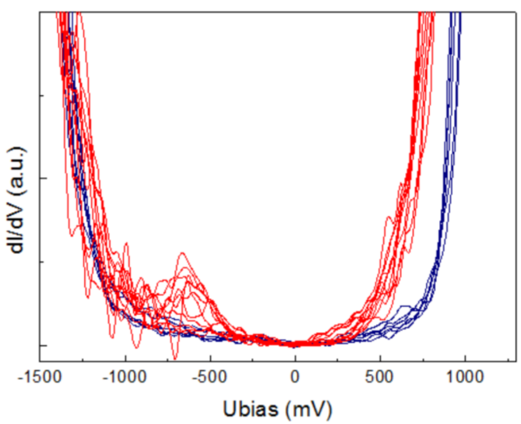
Scanning probe microscopy

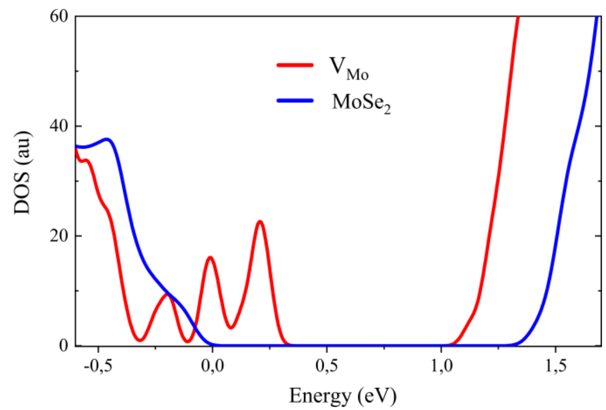
MoS_2 single layer identifying defects







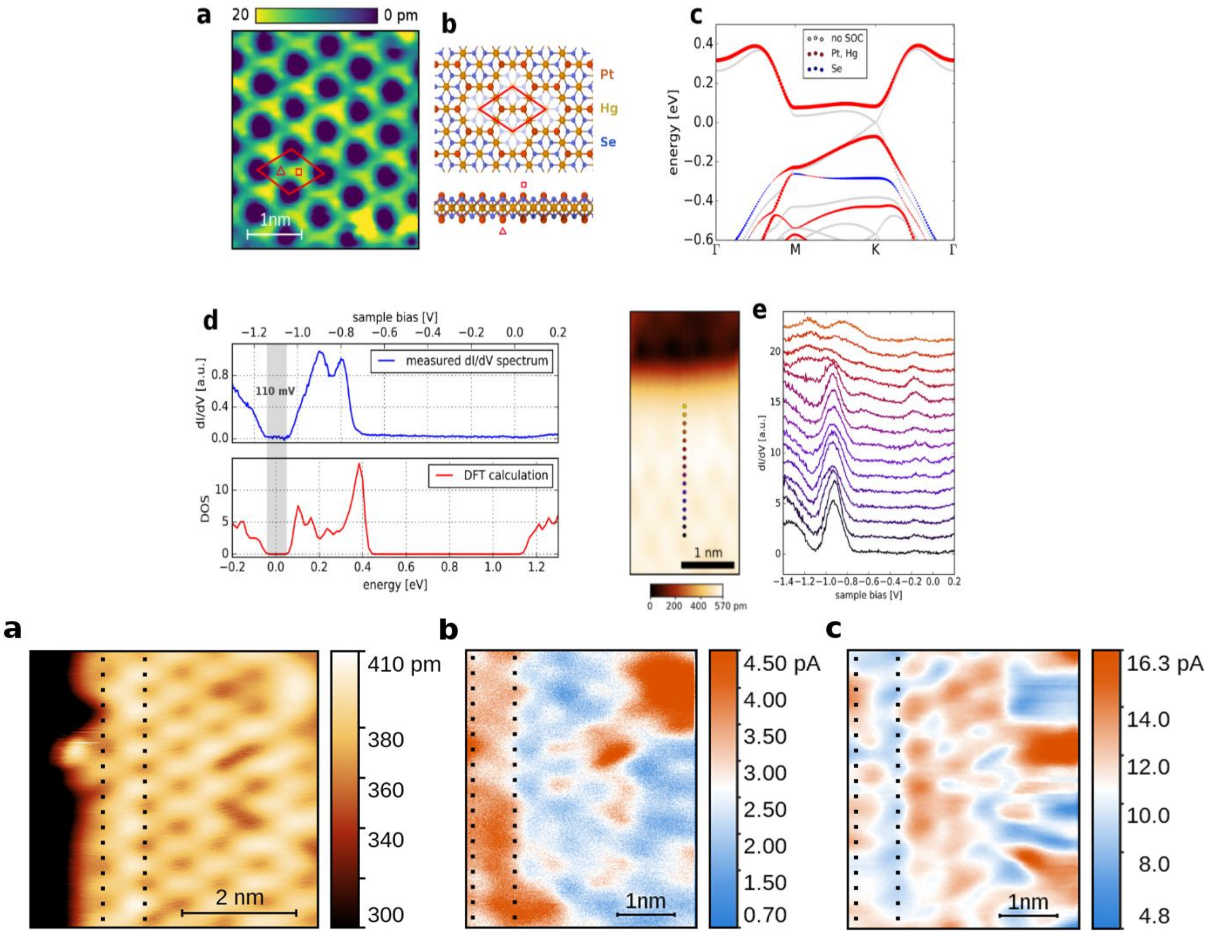




A.A. Koós, , L.Tapasztó. **J. Phys. Chem. C** 1*23, 24855 (2019)*

Scanning probe microscopy

Hunting electronic states



K. Kandrai, et al. **Nano Lett.** 20*, 5207 (2020)*

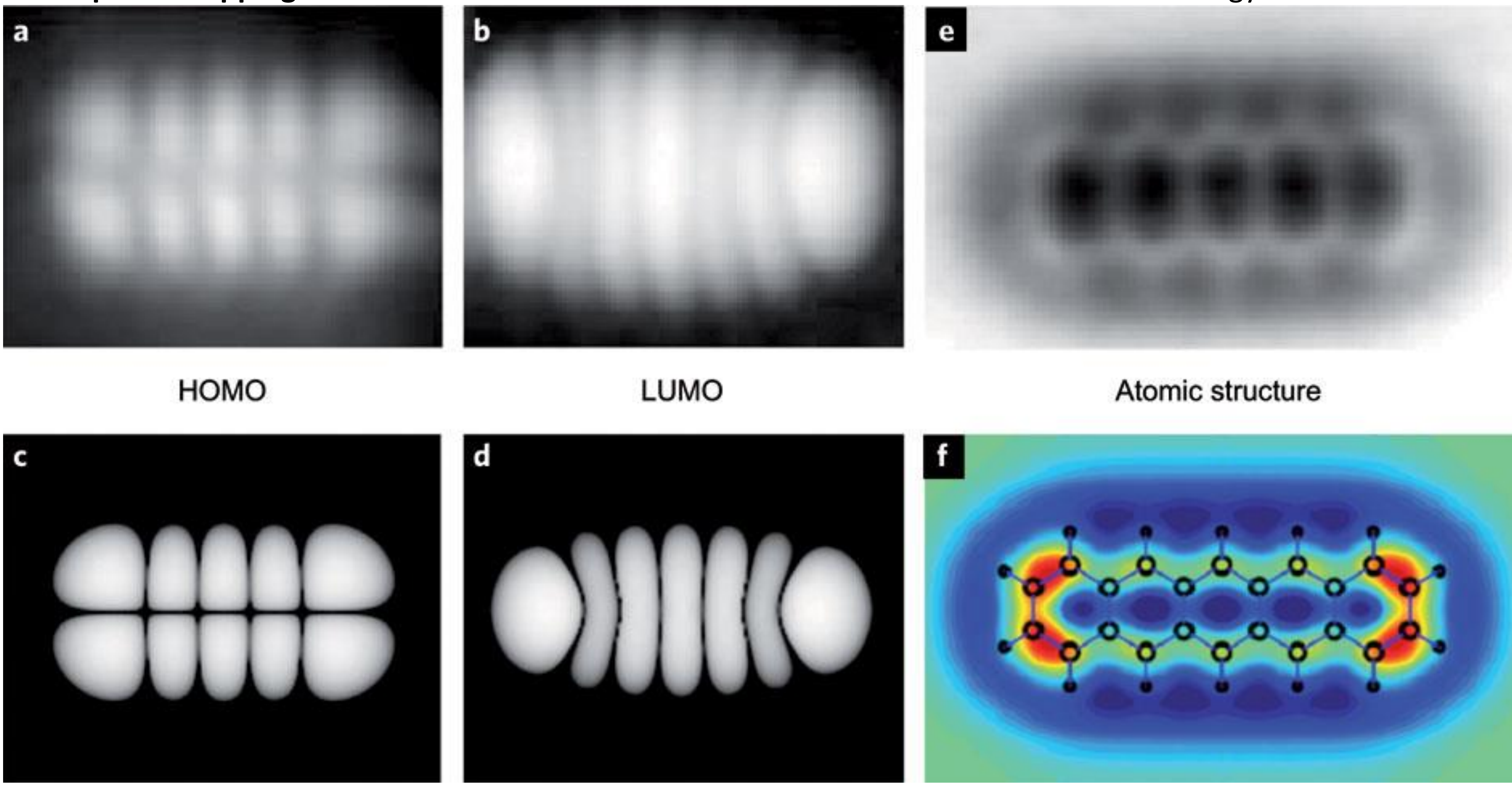
Scanning probe microscopy

Recent advances in submolecular resolution with scanning probe microscopy
Leo Gross, Nature Chemistry 3, 273–278 (2011) doi:10.1038/nchem.1008

Scanning tunneling microscope (STM)
Scanning tunneling spectroscopy (STS)

a and b spatial resolved HOMO and LUMO orbitals and corresponding calculations (c), (d). e and f ar NC-AFM images with CO functionalized tip.

Example 3: Mapping of Homo or Lumo orbital of a molecule when bias reaches their energy



E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.2.

Scanning probe microscopy

Scanning tunneling microscope (STM)

Manipulation mode

Vertical and lateral manipulations

Vertical manipulation

a) transfer of the surface atom to the tip.

b) Tip is moved to the desired position. c) Deposition

Transfer of the adsorbate atom from the surface to the tip, or vice versa, is achieved by bringing the tip close and applying voltage pulse.

E.g. Xe atoms moves same direction as tunneling electrons due to heat assisted electromigration.

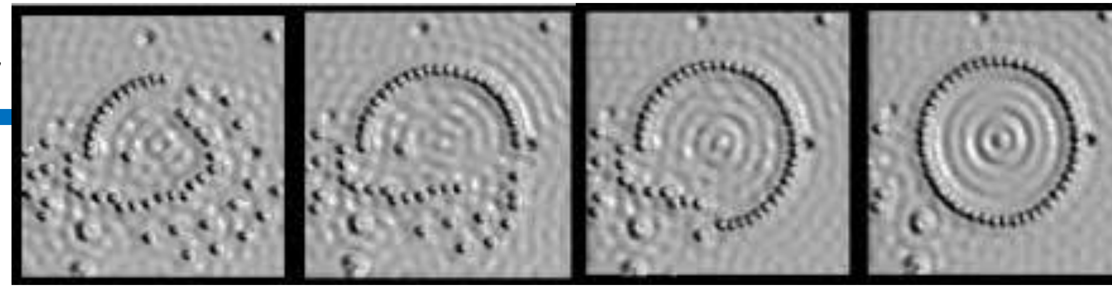
Lateral manipulation

a) Tip is moved down a few Å, set point is increased b) Tip forms a weak bond with the adsorbate atom or molecule. c) Tip is then moved along the line of manipulation. Typical threshold resistances to slide an adsorbate are 5k-20kΩ.

Tip height during manipulation can be recorded, which gives some insight about the manipulation process.

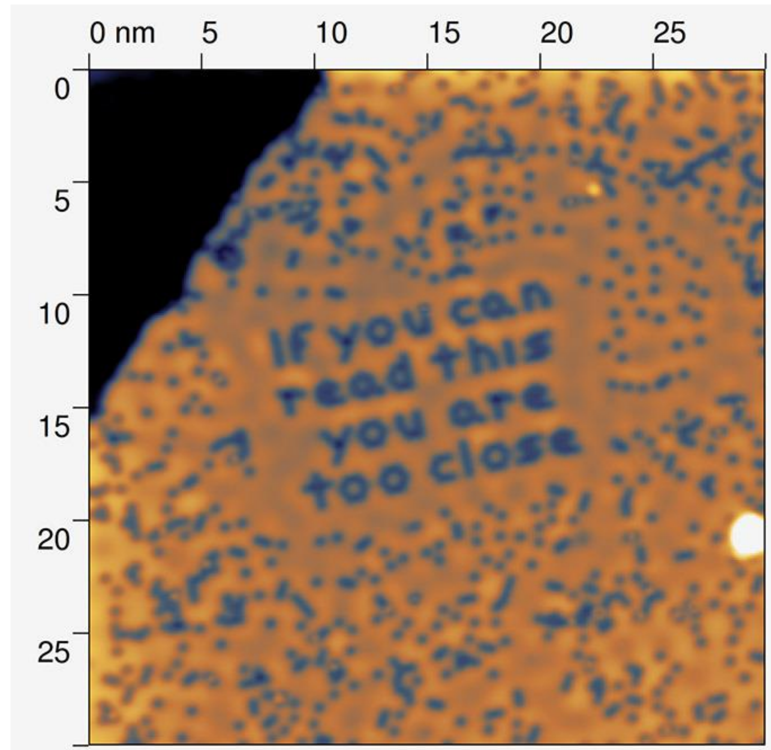
See example: e.g. Cu adatoms are shifted sites by sites (a), Pb dimmer (e-g) can jump several sites, since it is larger object.

Other mechanisms: field assisted direction diffsuion, inelastic tunneling induced movement for H adatoms



(Up) Arranged 48 iron atoms on the surface of a copper substrate. These images show the various stages of the process. Once complete the circular arrangement of the iron atoms it forces the electrons at the surface of the copper to specific quantum states as shown by the rippled appearance of the surface. By Don Eigler IBM.

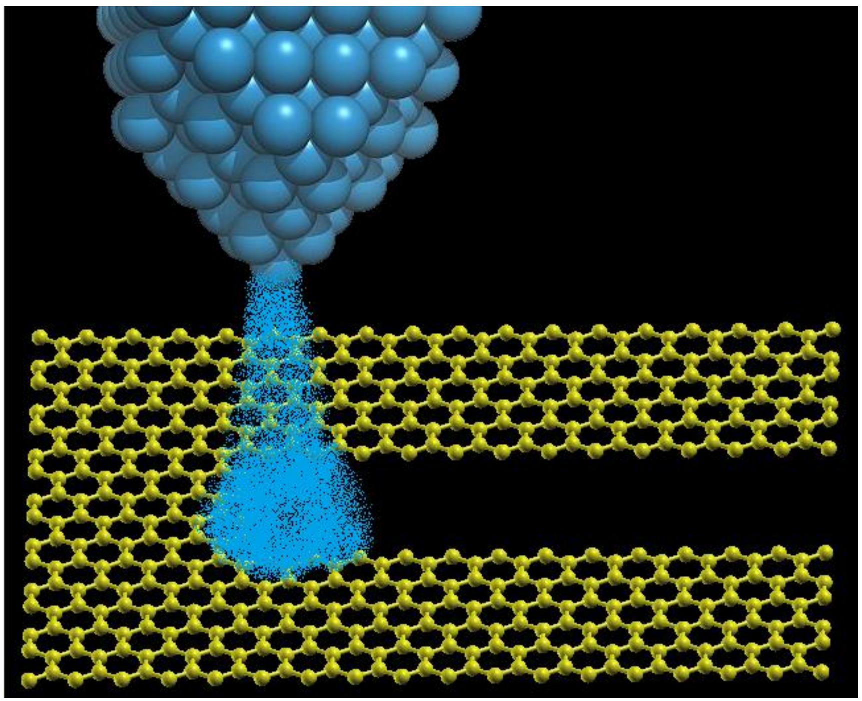
(Down) Tip height curves during lateral manipulation of various atoms on the Cu(211) surface. The tip movement is from left to right, the fixed tunneling resistances are indicated. Vertical dotted lines correspond to fcc sites next to the step edge.

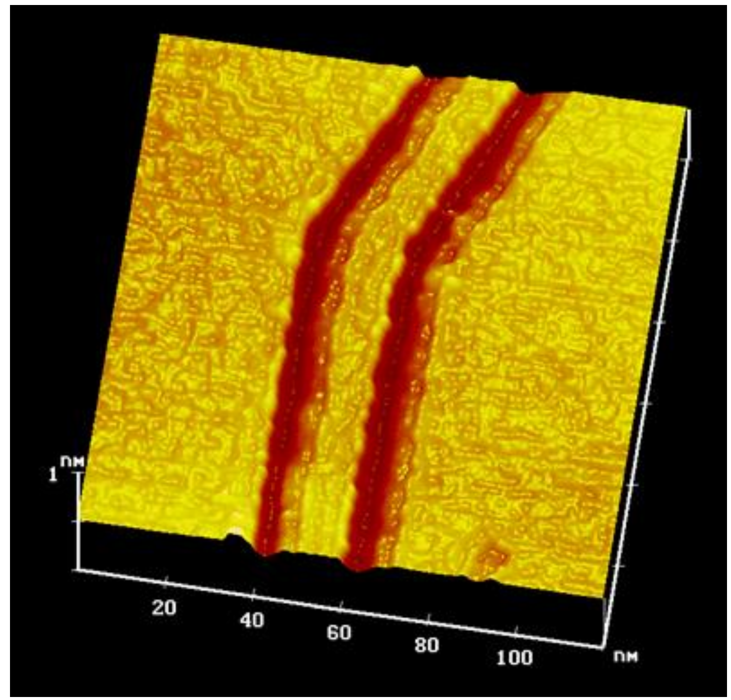


E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 2.2.

Scanning probe microscopy

STM lithography of graphene

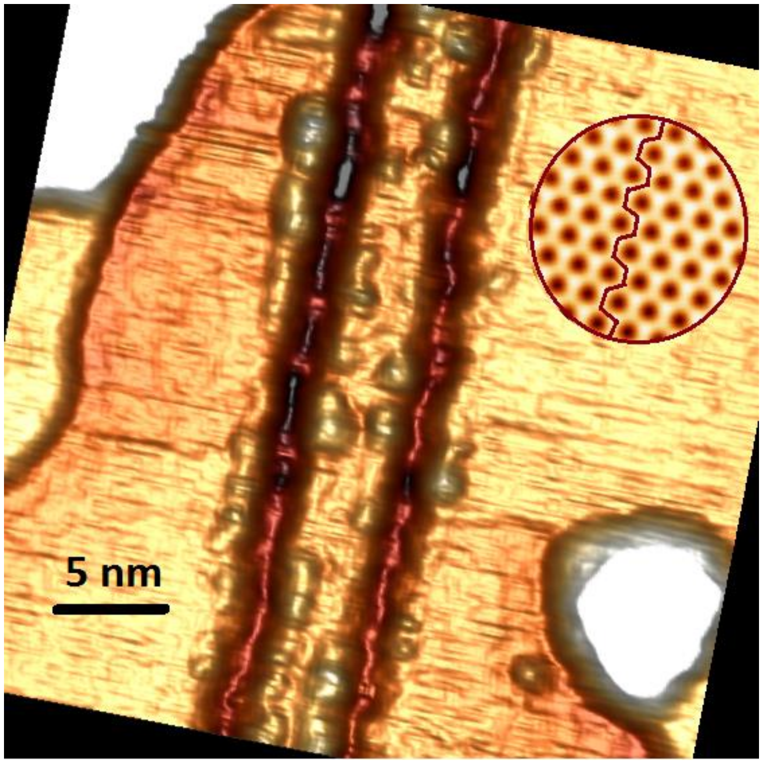


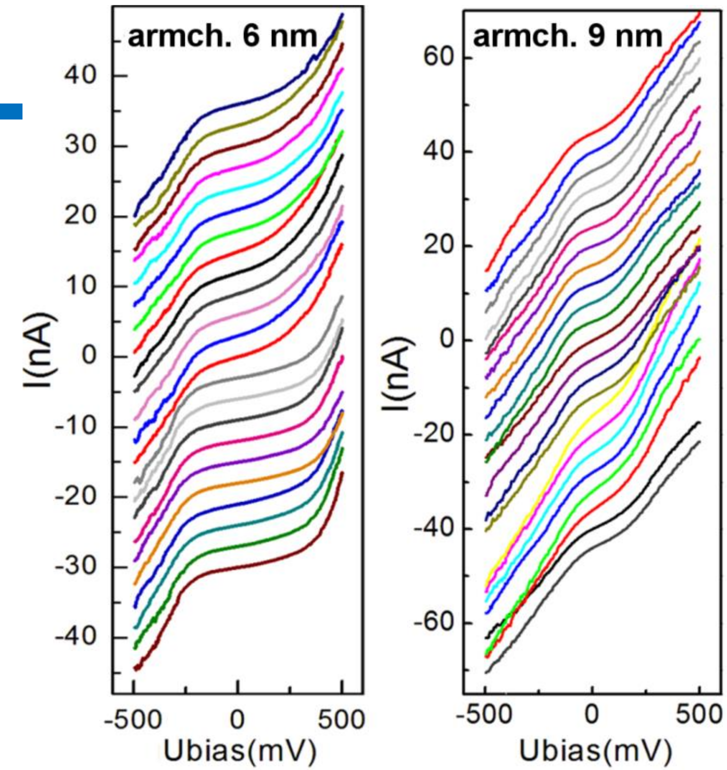


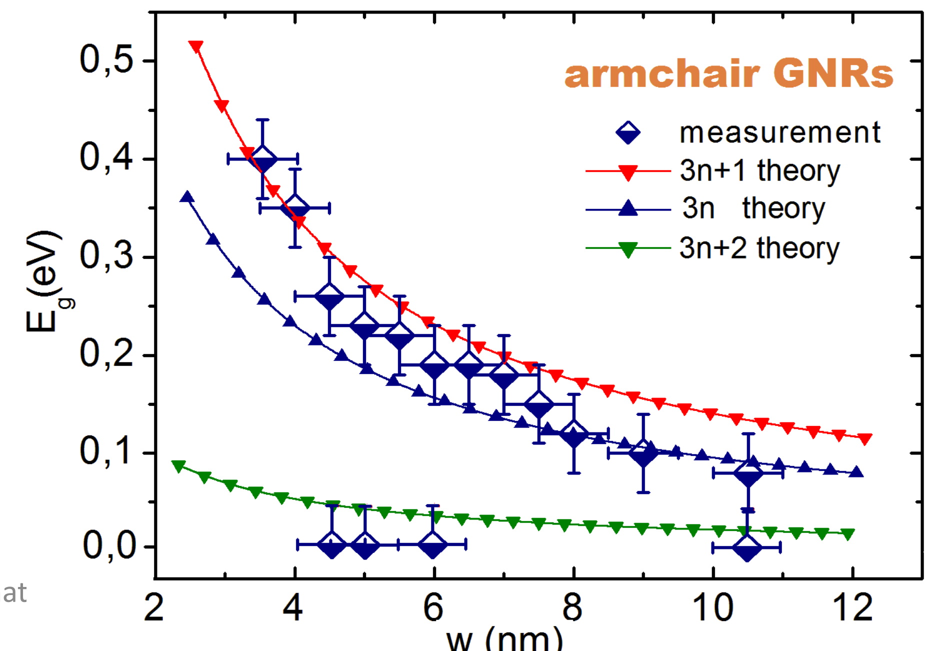
L. Tapasztó et al. **Nature Nanotechnology** 3, 397 (2008)

Scanning probe microscopy

STM lithography of graphene



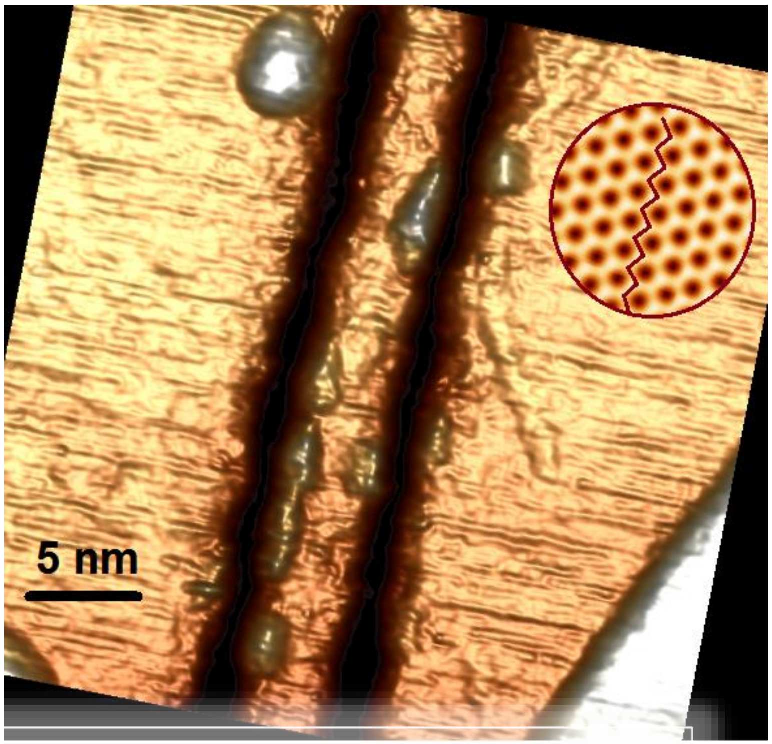


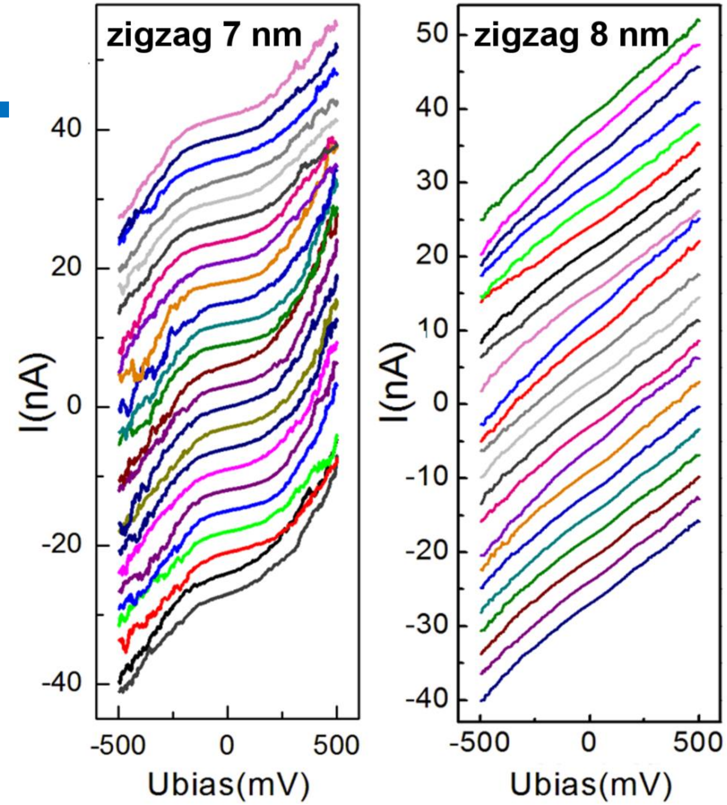


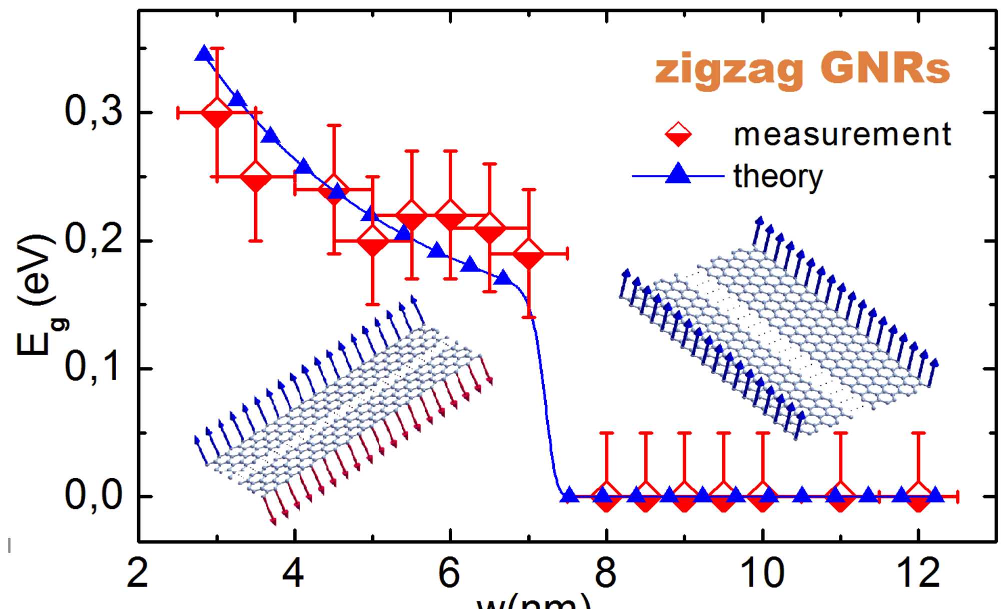
G.Z. Magda et al. ***Nature***, **514**, 608-611 (**2014**)

Scanning probe microscopy

STM lithography of graphene







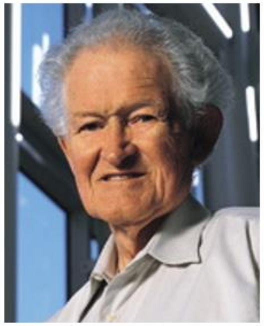
G.Z. Magda et al. ***Nature***, **514**, 608-611 (**2014**)

Atomic Force Microscope (AFM)

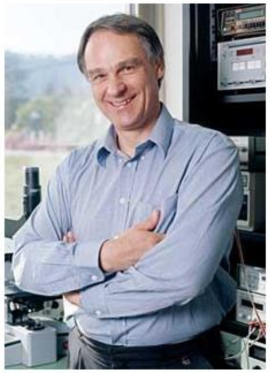
- STM makes use of tunneling current

It can only image conducting or semiconducting surfaces

- Binnig, Quate, and Gerber invented the Atomic Force Microscope in 1985
- It can image almost any type of surface, including polymers, ceramics, composites, glass, and biological samples



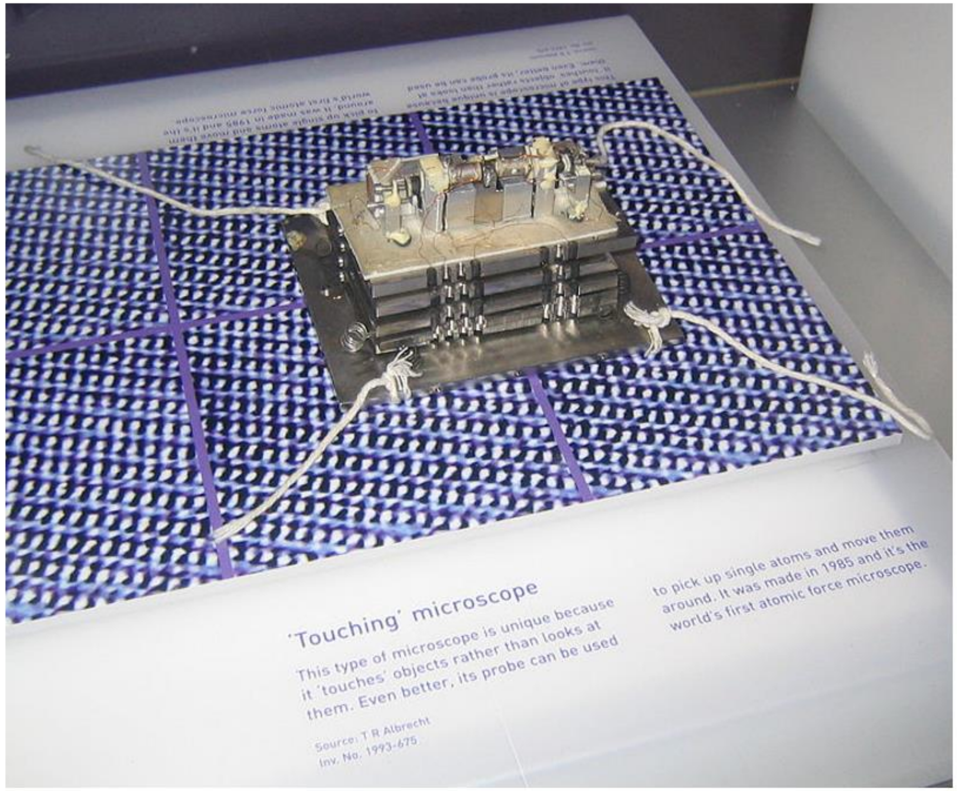
Calvin Quate (1923)



Gerd Binnig (1947)

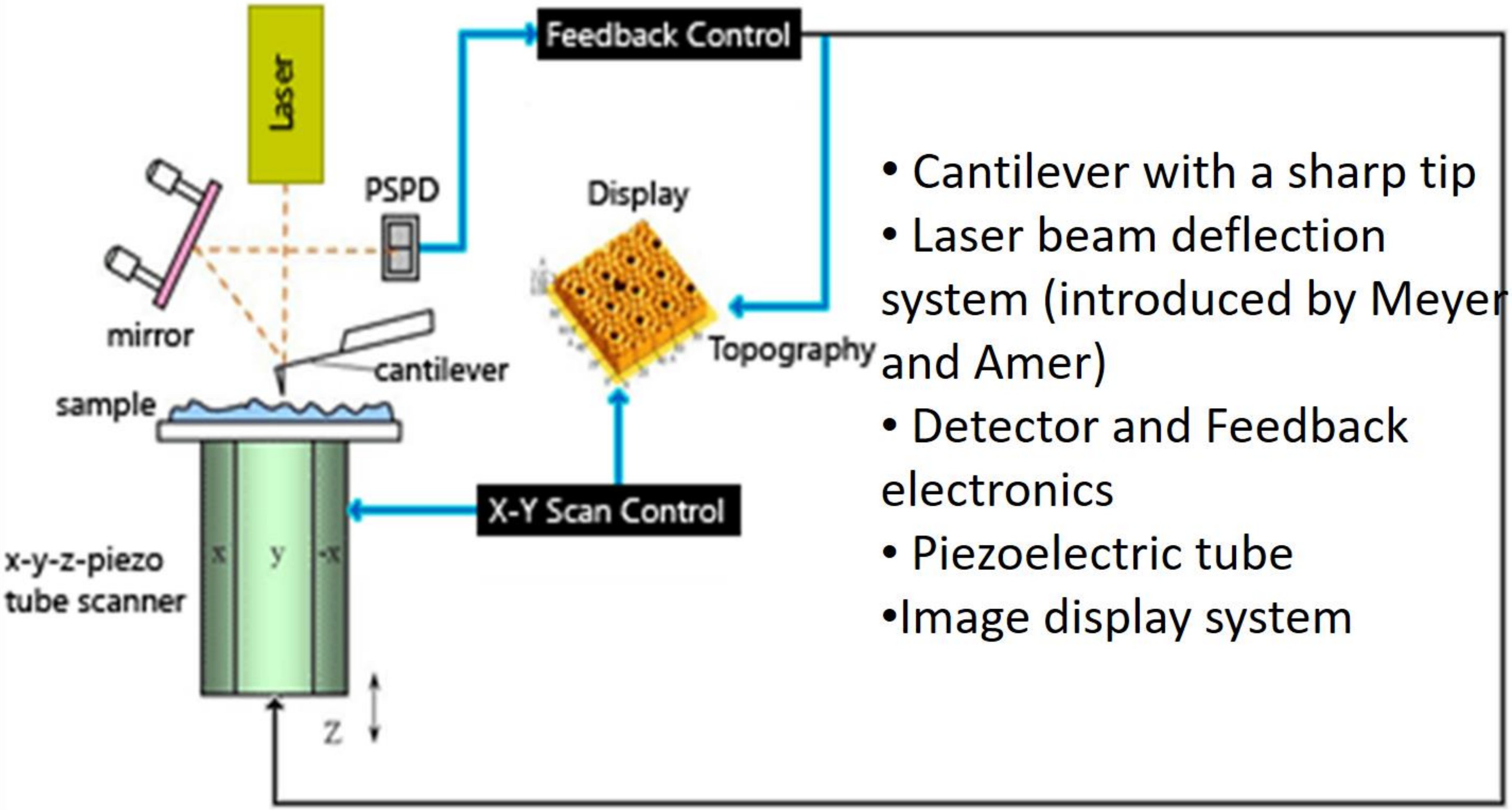
Christoph Gerber (1942)

Scanning probe microscopy



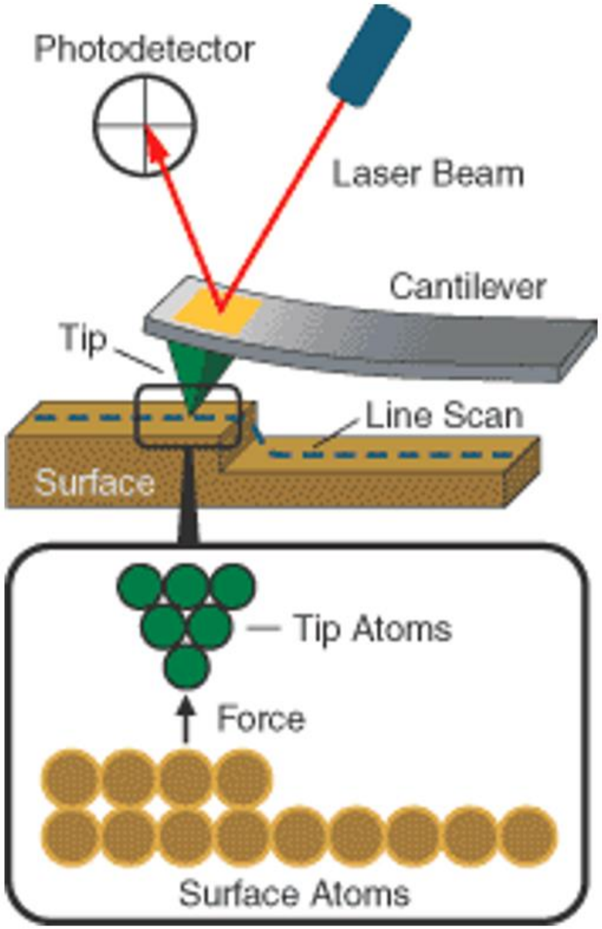
The first Atomic Force Microscope - Science Museum London

Main Components of an AFM



- Cantilever with a sharp tip
- Laser beam deflection system (introduced by Meyer and Amer)
- Detector and Feedback electronics
- Piezoelectric tube
- Image display system

How It Works



http://www.molec.com/what_is_afm.html

- Invented in 1986
- Cantilever
- Tip
- Surface
- Laser
- Multi-segment photodetector

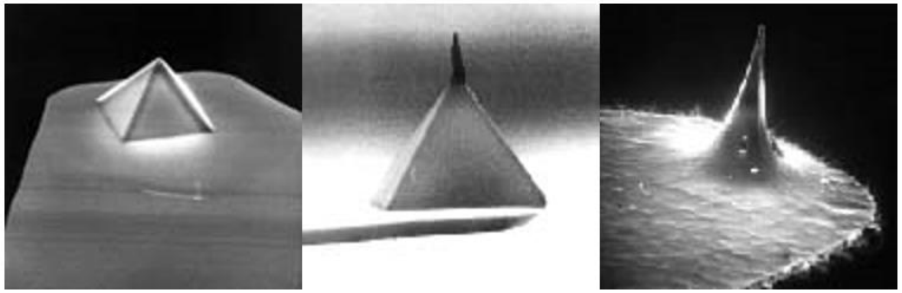
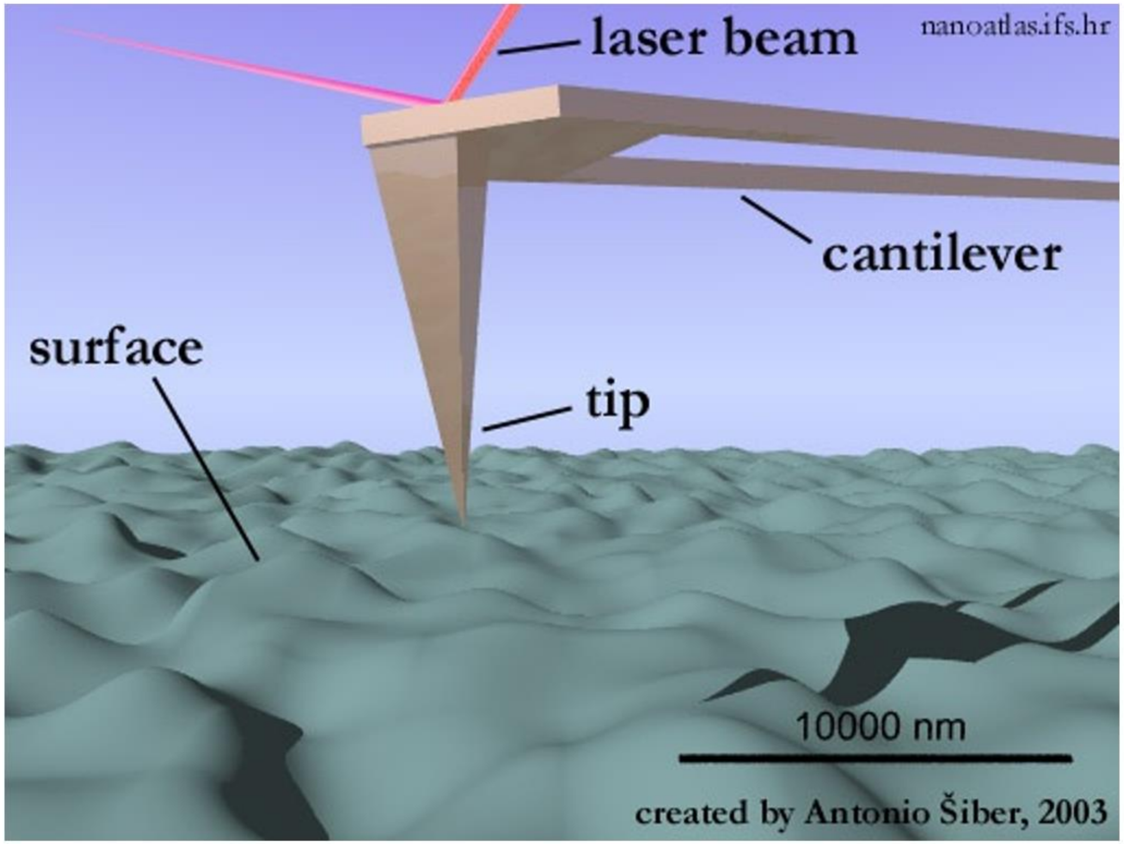


Figure 4. Three common types of AFM tip. (a) normal tip (3 μm tall); (b) supertip; (c) Ultralever (also 3 μm tall). Electron micrographs by Jean-Paul Revel, Caltech. Tips from Park Scientific Instruments; supertip made by Jean-Paul Revel.

http://stm2.nrl.navy.mil/how-afm/how-afm.html#imaging%20modes

Scanning probe microscopy



How does AFM work?

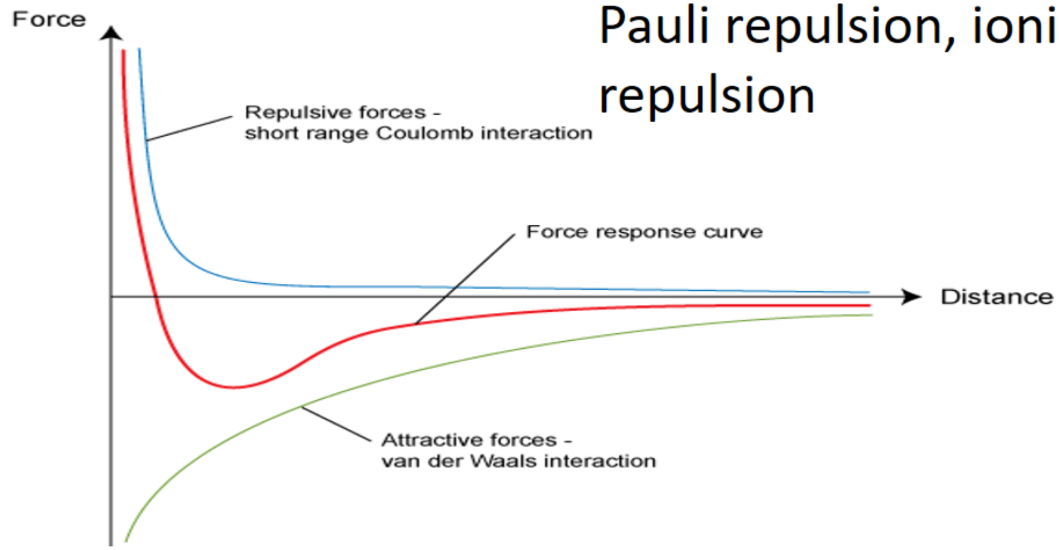
Measure the forces between the sharp tip and sample surface

<u>Long-range forces</u>

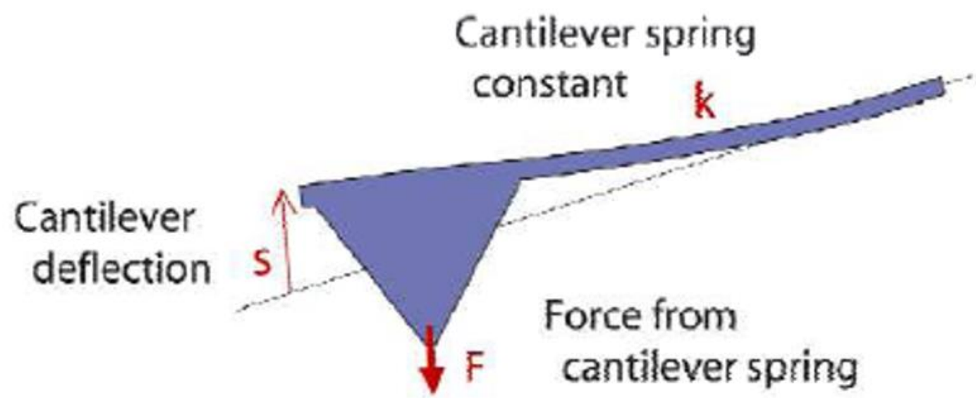
Van der Waals forces
Capillary forces
Magnetic forces
Electrostatic force

<u>Short-range forces</u>

Chemical forces:
ionic bonds, covalent bonds, metallic bonds
Repulsion forces:
Pauli repulsion, ionic repulsion

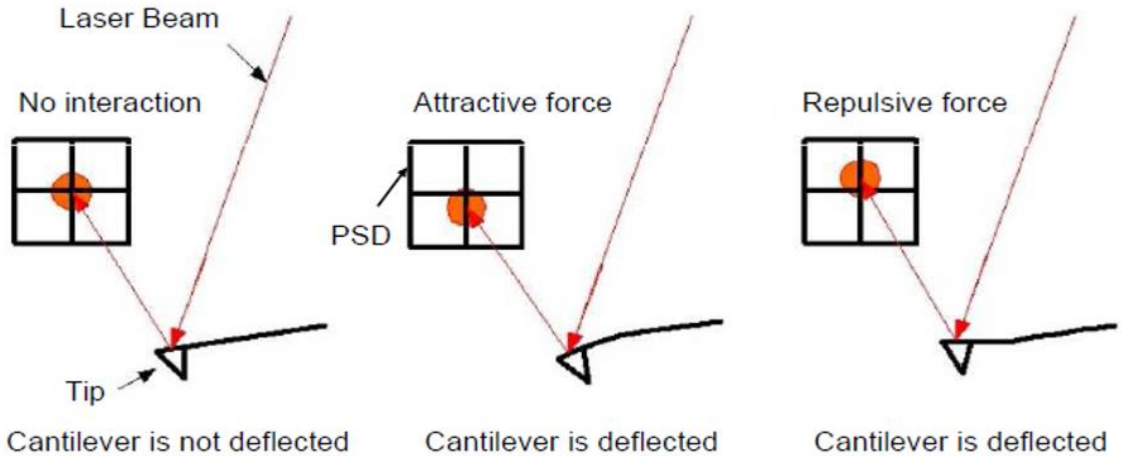


How are forces measured?



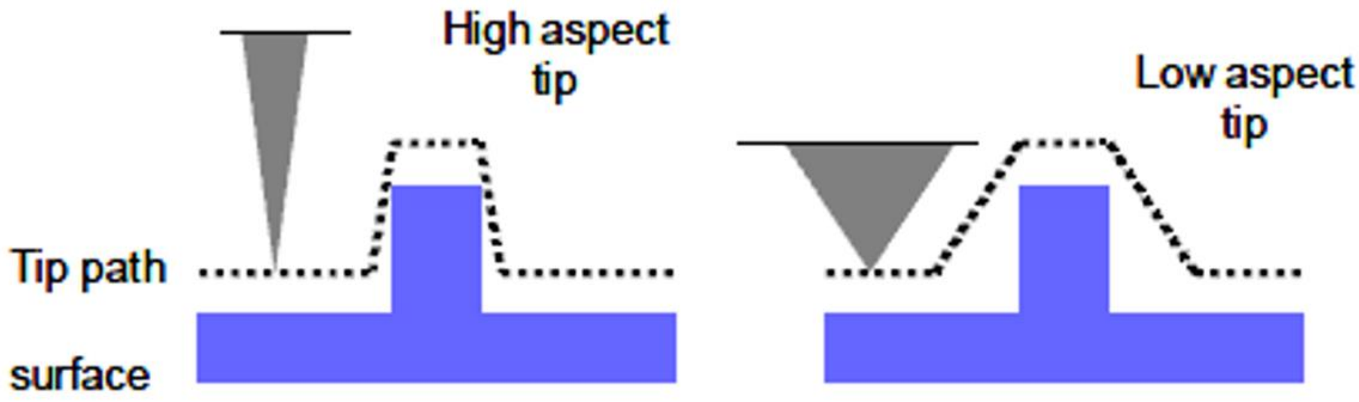
Hooke's law: F= -ks

Laser Beam Deflection Method



Fabrication of Tip

- Made from Si_3N_4 or Si
- As sharp as possible
- The radius of curvature of the tip does not influence the height of a feature but the lateral resolution

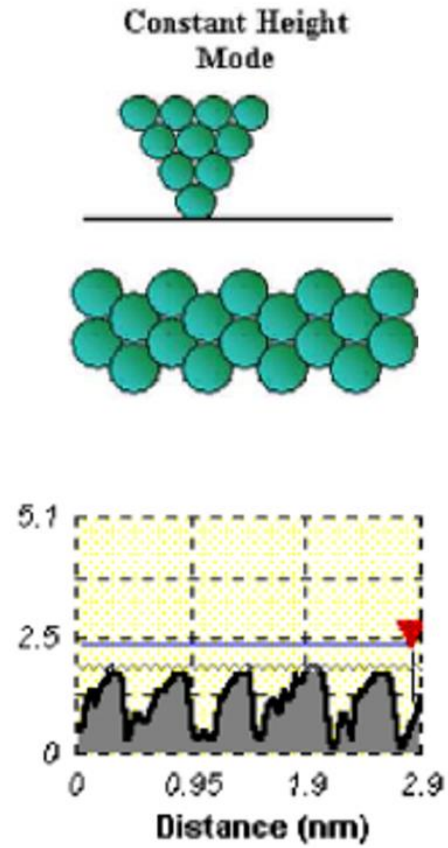


Modes of Imaging

Constant Height

- Cantilever is "dragged" across the surface of the sample
- Tip is free to move up and down
- Force between tip and sample surface is measured directly using the deflection of the cantilever

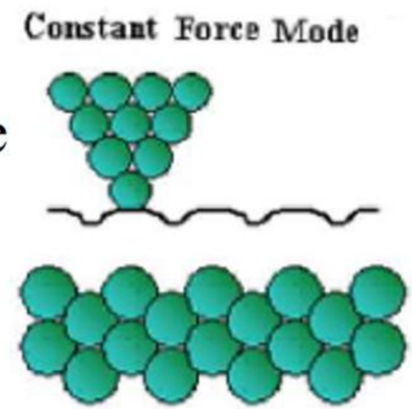
✓No need to wait for the response of feedback system, scan in high speed
✓No signal error
x If surface is rough, can cause damage to tip and surface

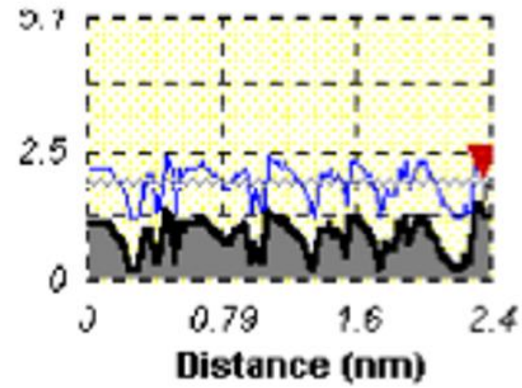


Modes of Imaging

Constant Force

- Move the cantilever up and down using the piezoelectric tube
- so that the position of laser beam is unchanged
- i.e. force between tip and sample surface remain constant

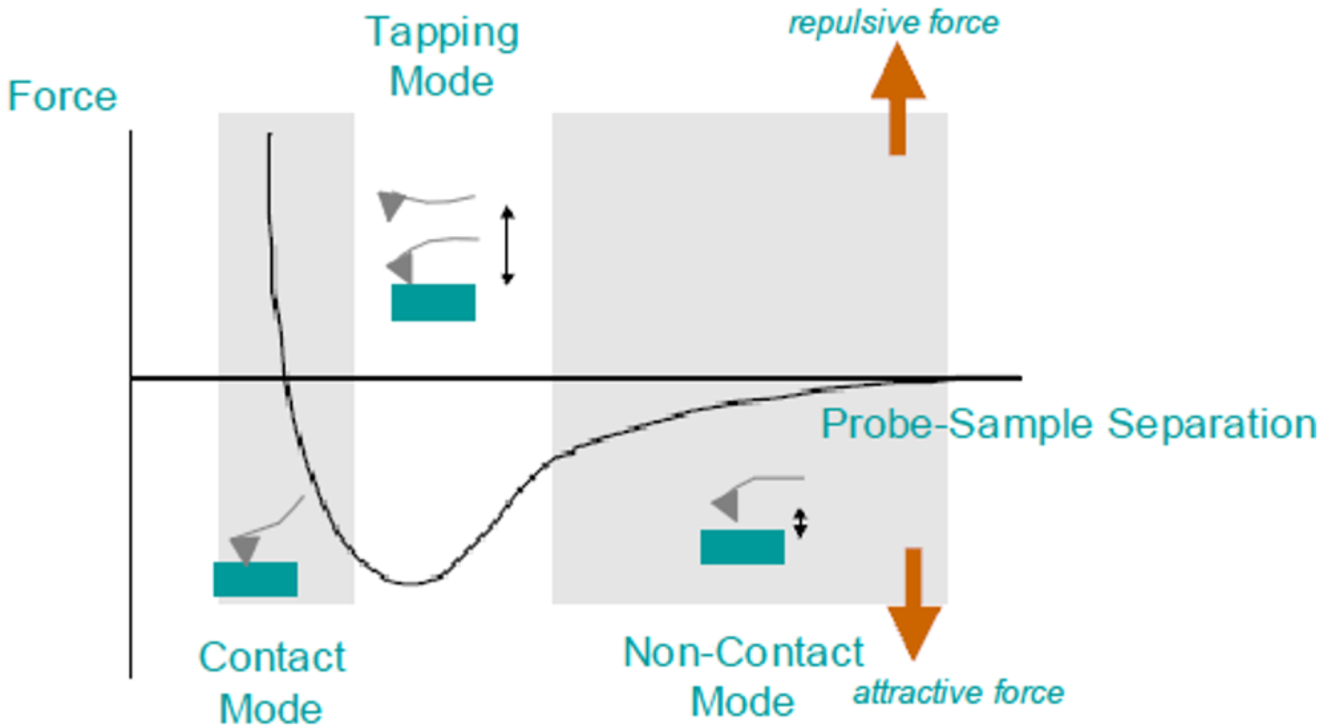




✓Suited for almost every surface
x Scan slowly, need to wait for the response of feedback system
x Sensitive to random noise, has signal error

Constant Force Modes

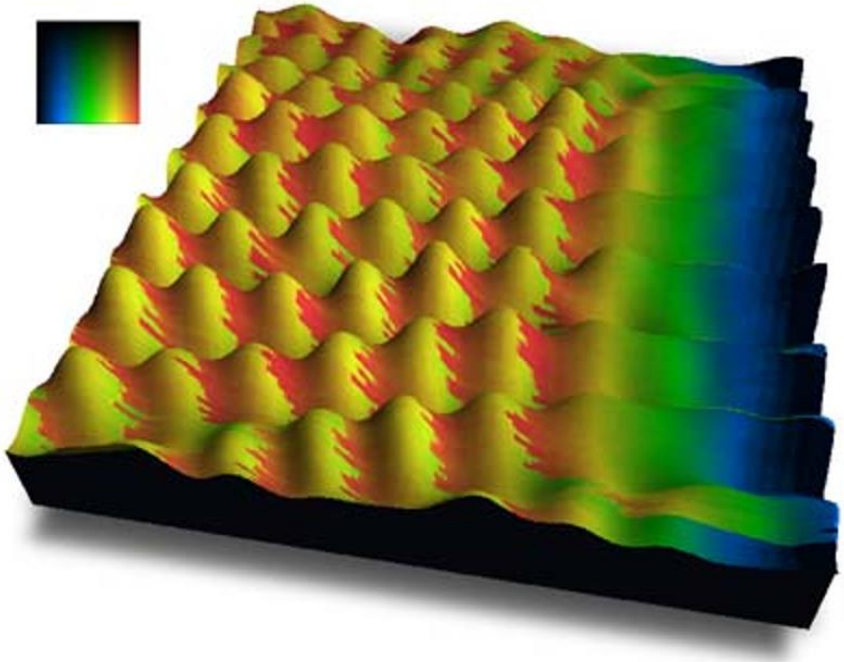
- Contact Mode (<0.5nm tip-surface separation)
- Tapping Mode (0.5-2nm tip-surface separation)
- Non-contact Mode (0.1-10nm tip-surface separation)



Scanning probe microscopy

Topography

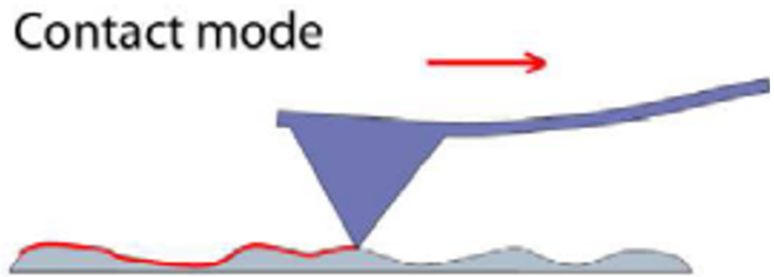
- Contact Mode
  - High resolution
  - Damage to sample
  - Can measure frictional forces
- Non-Contact Mode
  - Lower resolution
  - No damage to sample
- Tapping Mode
  - Better resolution
  - Minimal damage to sample



2.5 x 2.5 nm simultaneous topographic and friction image of highly oriented pyrolytic graphic (HOPG). The bumps represent the topographic atomic corrugation, while the coloring reflects the lateral forces on the tip. The scan direction was right to left

http://stm2.nrl.navy.mil/how-afm/how-afm.html#imaging%20modes

Contact Mode



- Tip almost touches the surface
- Force on the tip is repulsive
- Force between the tip and the surface is kept constant during scanning by maintaining a constant deflection

<u>Advantages:</u>

✓ Better resolution than tapping mode and non-contact mode

✓ Fast scanning

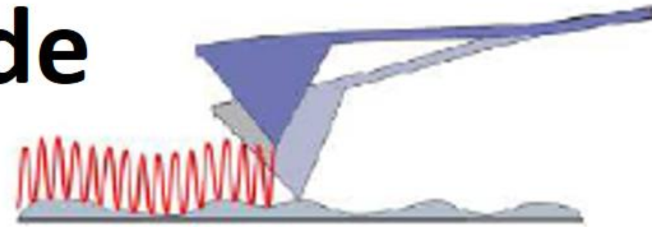
✓ Good for rough surface

<u>Disadvantages:</u>

x Force can damage or deform soft samples

Scanning probe microscopy

Tapping Mode



- Cantilever is driven to oscillated up and down at its resonant frequency
- Probe slightly taps on the surface during scanning, contacting the surface at the bottom of its swing
- Adjust the height of cantilever by the piezoelectric tube to maintain a constant oscillation amplitude

i.e. constant force between tip and surface is maintained

<u>Advantages:</u>

✓High resolution for the samples that are easily damaged (biological sample)

<u>Disadvantages:</u>

x Slower scanning speed needed

Non-contact Mode

- Tip does not contact the surface
- Similar to tapping mode, cantilever is oscillated at its resonant frequency
- Adjust height of cantilever to keep constant oscillation amplitude, constant force between tip and surface

<u>Advantages:</u>

✓ Prevent tip from sticking to the surface *(Note: all samples unless in a controlled UHV or environmental chamber have some liquid adsorbed on the surface).*

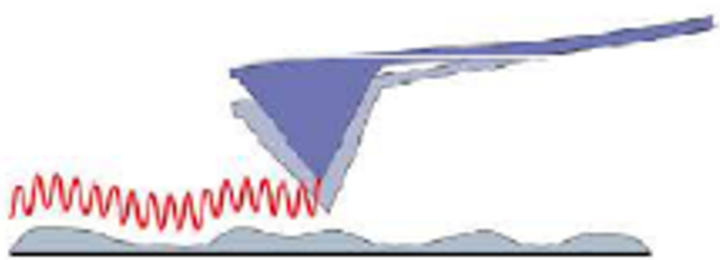
✓ Low force exerted on surface

✓ No damage to tip and surface

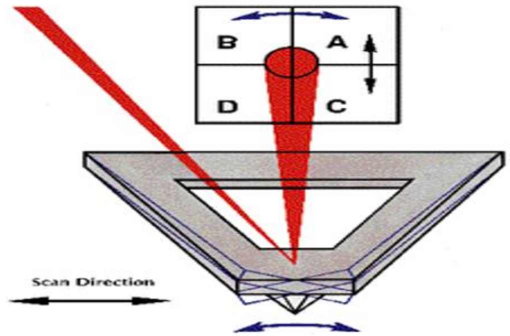
<u>Disadvantages:</u>

x Lower resolution

x Slower speed



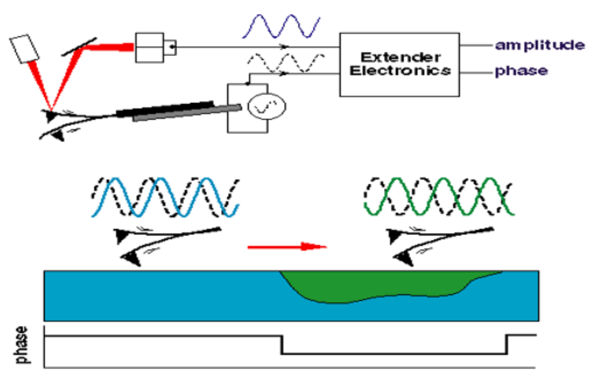
Lateral Force Microscopy



- The probe is scanned sideways. The degree of torsion of the cantilever is used as a relative measure of surface friction caused by the lateral force exerted on the probe.
- Identify transitions between different components in a polymer blend, in composites or other mixtures
- This mode can also be used to reveal fine structural details in the sample.

Phase Imaging

- Accessible via TappingMode
- Oscillate the cantilever at its resonant frequency. The amplitude is used as a feedback signal. The phase lag is dependent on several things, including composition, adhesion, friction and viscoelastic properties.

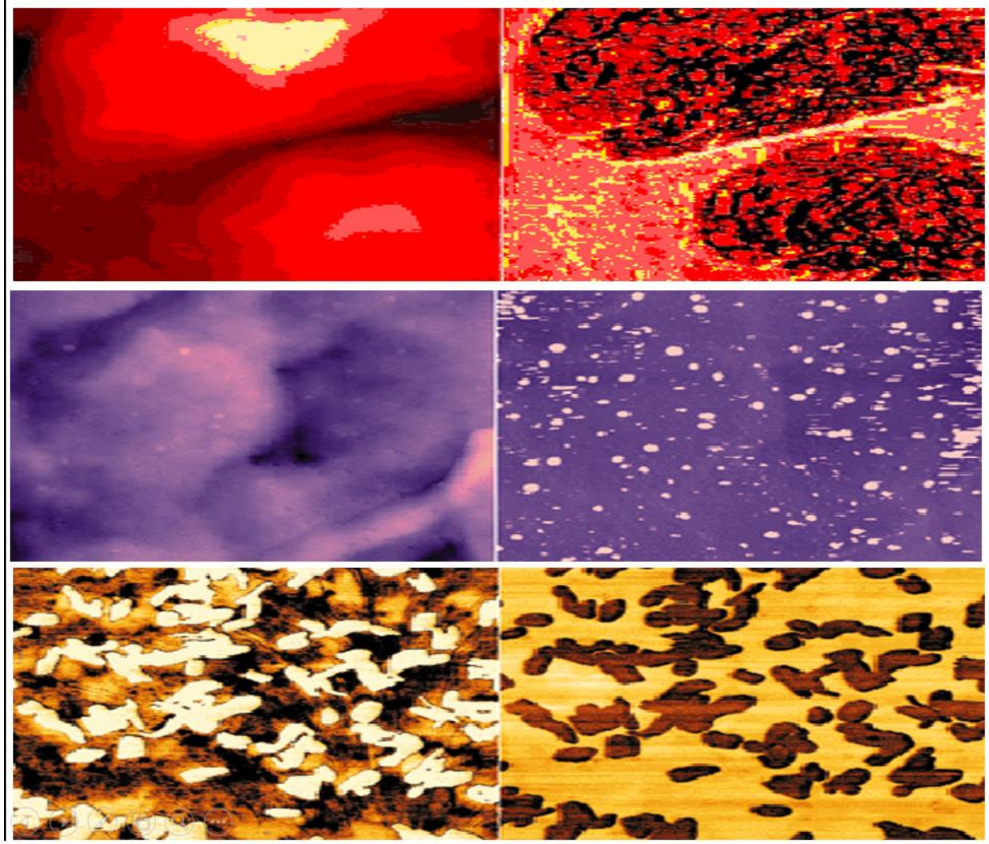


- Identify two-phase structure of polymer blends
- Identify surface contaminants that are not seen in height images
- Less damaging to soft samples than lateral force microscopy

Scanning probe microscopy

Phase Imaging

Image/photo taken with NanoScope® SPM, courtesy Digital Instruments, Santa Barbara ,CA



Compositepolymer
imbedded in a matrix

1 micron scan

Bond pad on an
integrated circuit

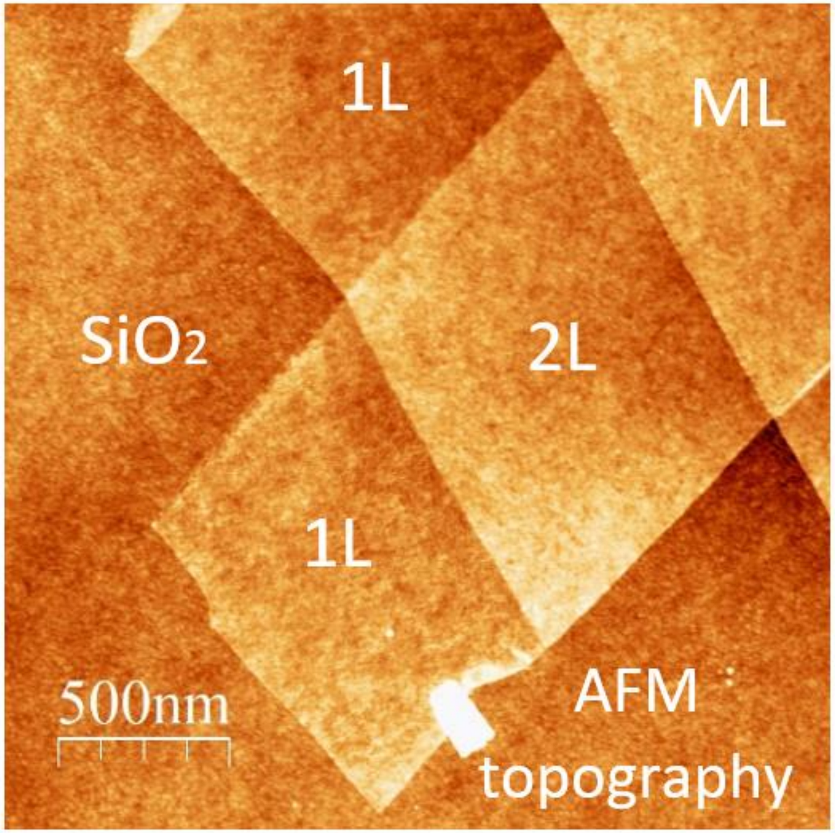
Contamination

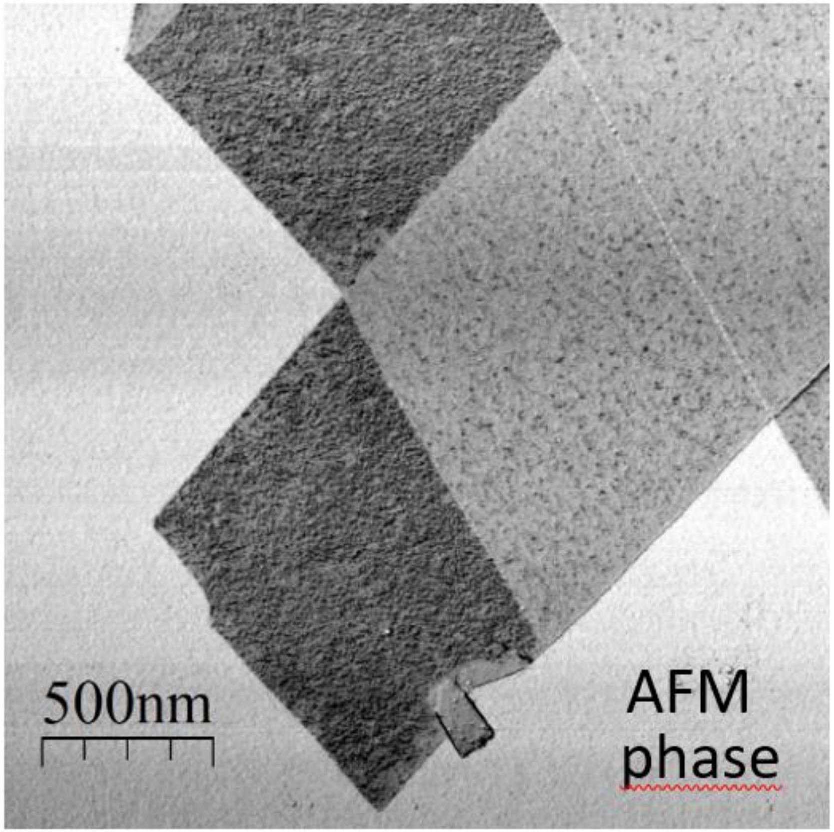
1.5 micron scan

MoO_3 crystallites
on a MoS_2 substrate

6 micron scan

Phase imaging

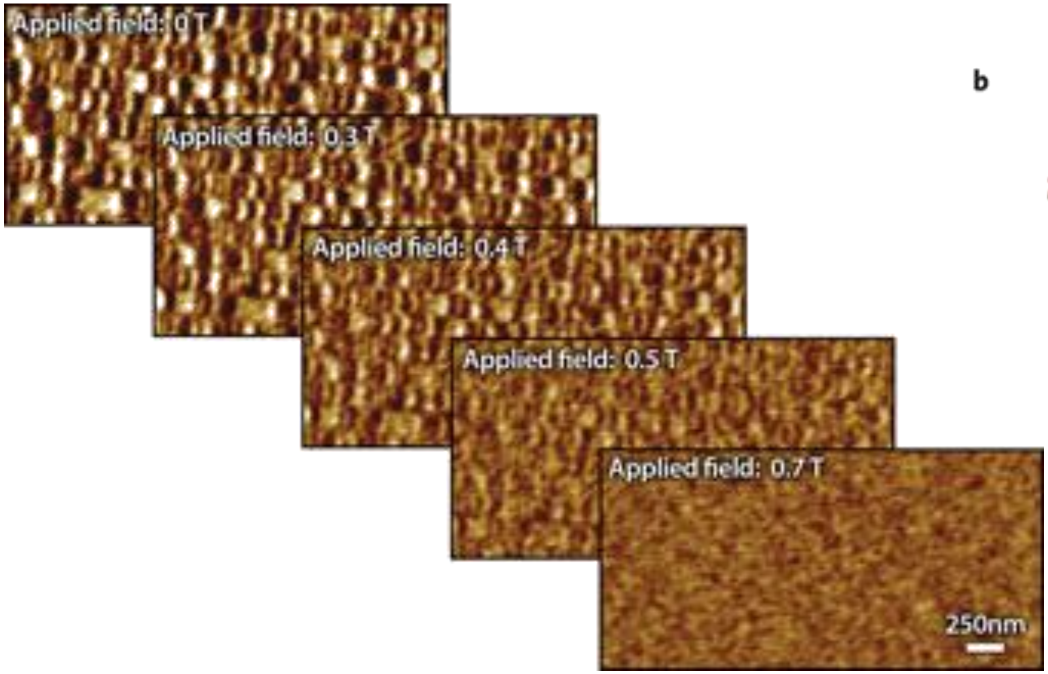




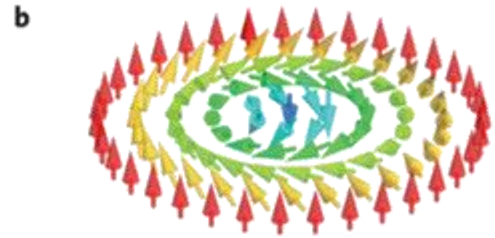
Magnetic Force Microscopy

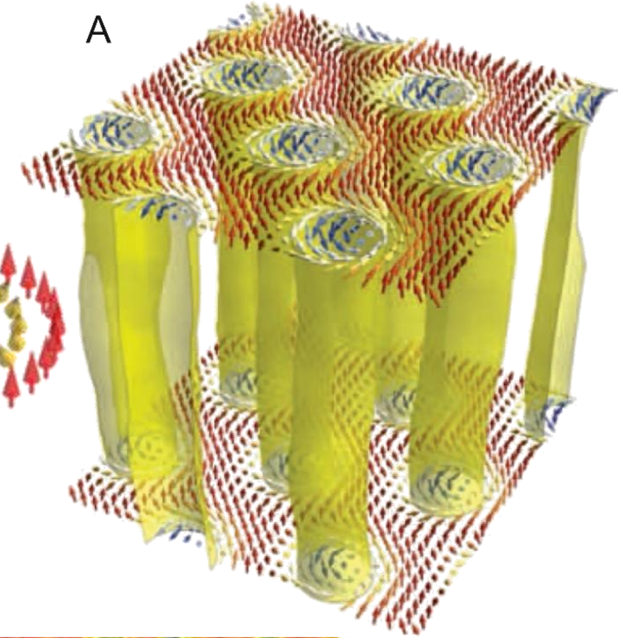
- Special probes are used for MFM. These are magnetically sensitized by sputter coating with a ferromagnetic material.
- The cantilever is oscillated near its resonant frequency (around 100 kHz).
- The tip is oscillated 10's to 100's of nm above the surface
- Gradients in the magnetic forces on the tip shift the resonant frequency of the cantilever .
- Monitoring this shift, or related changes in oscillation amplitude or phase, produces a magnetic force image.
- Many applications for data storage technology

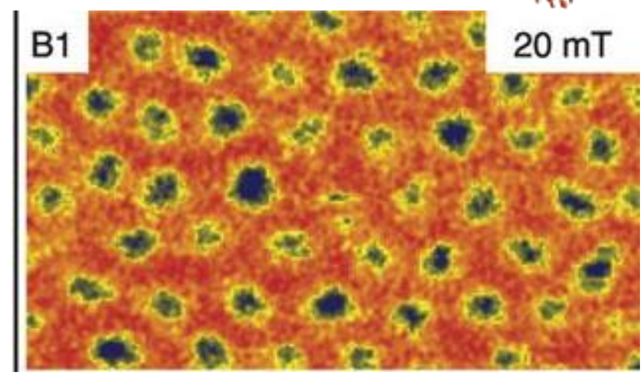
Scanning probe microscopy



MFM image of a hard disk in different external B field. As applied field saturates the magnetization of the surface the contrast disappears. (Oxford Instruments)





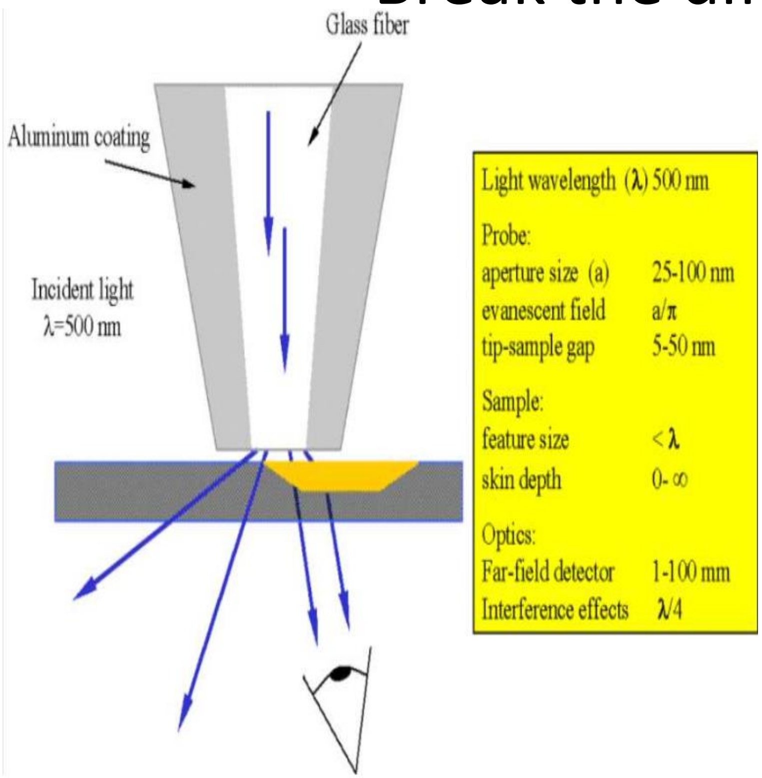


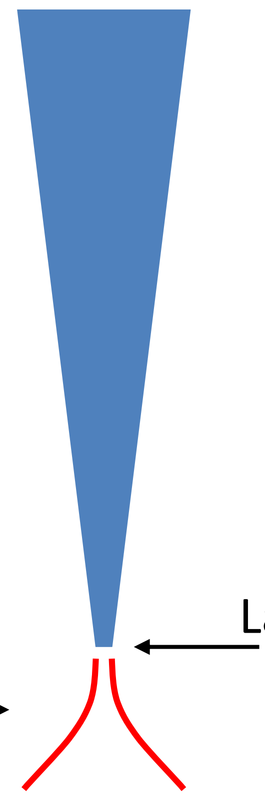
E. Meyer: Scanning Probe Microscopy Springer (2004) Sec. 4..

Scanning probe microscopy

Near-Field Scanning Optical Microscopy (NSOM)

Break the diffraction limit by working in the near-field





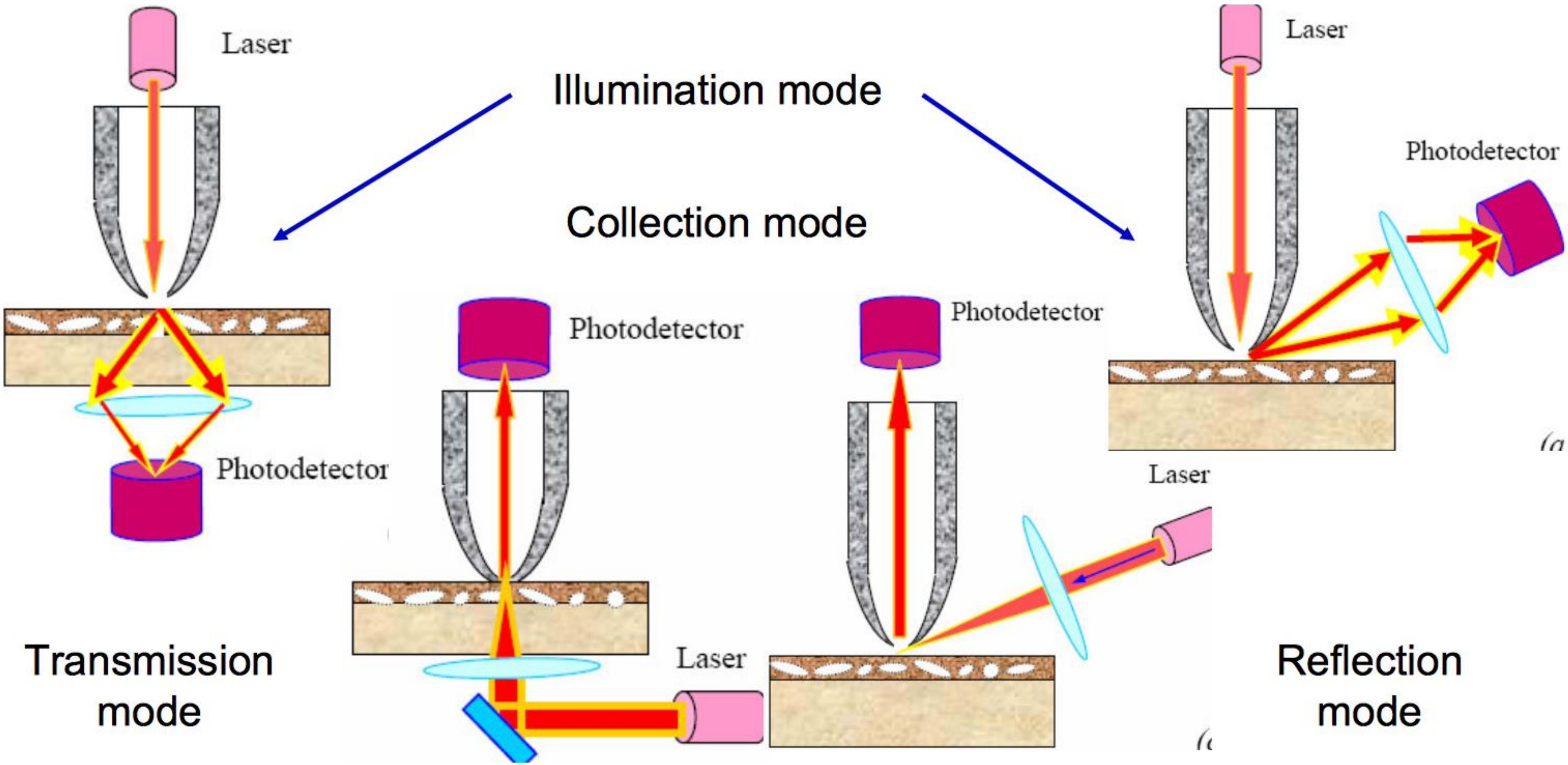
Launch light through small aperture

Illuminated "spot" is smaller than diffraction limit (about the size of the tip for a distance equivalent to tip diameter)

Near-field = distance of a couple of tip diameters

Scanning probe microscopy

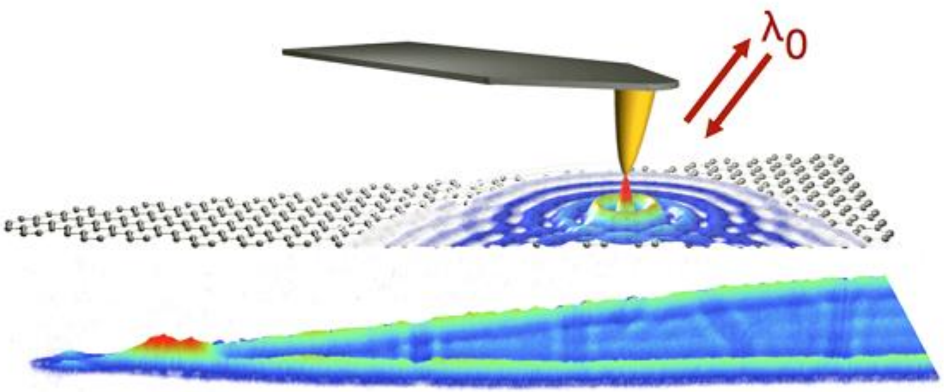
How to move the tip? Steal from AFM



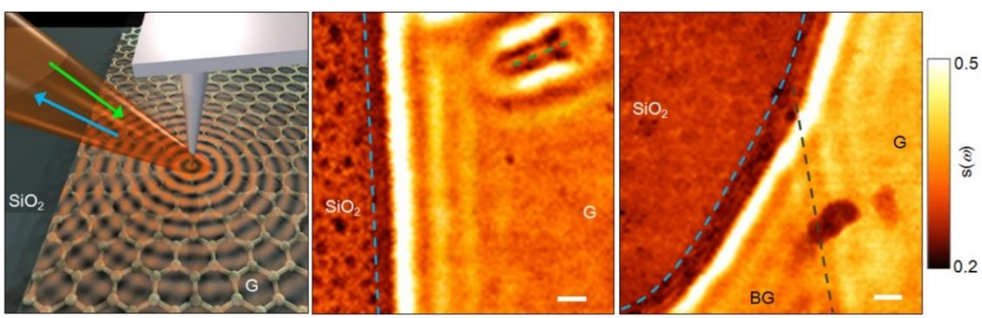
Scanning probe microscopy

SNOM at work: detecting graphene plasmons

IR

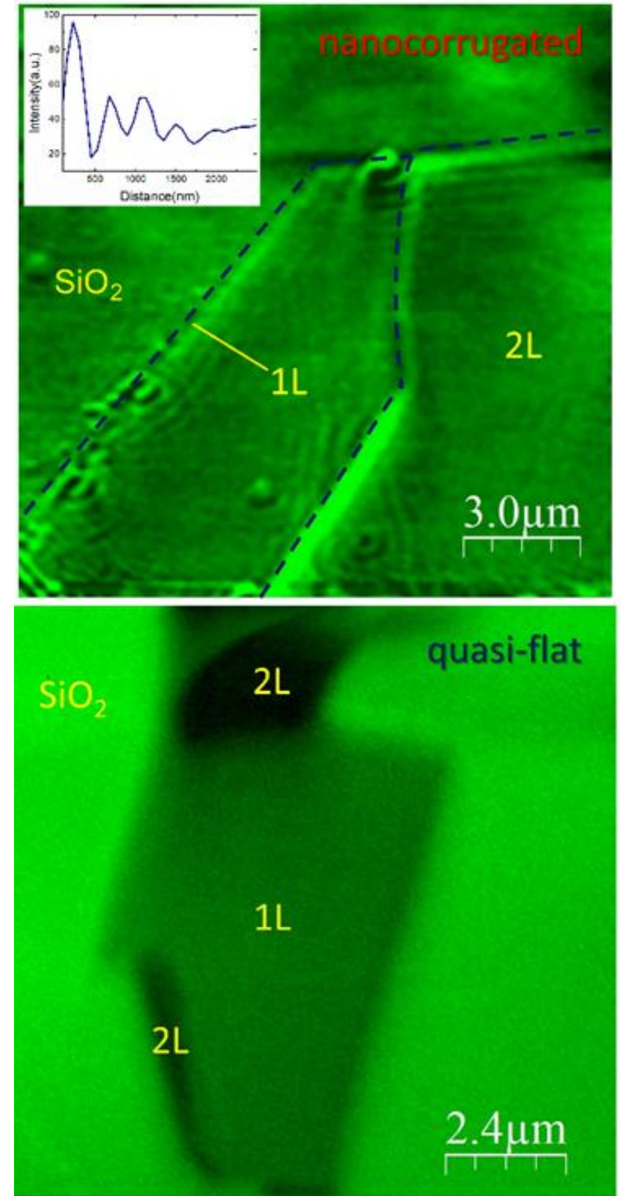


Nature **487,** 77–81 (2012)

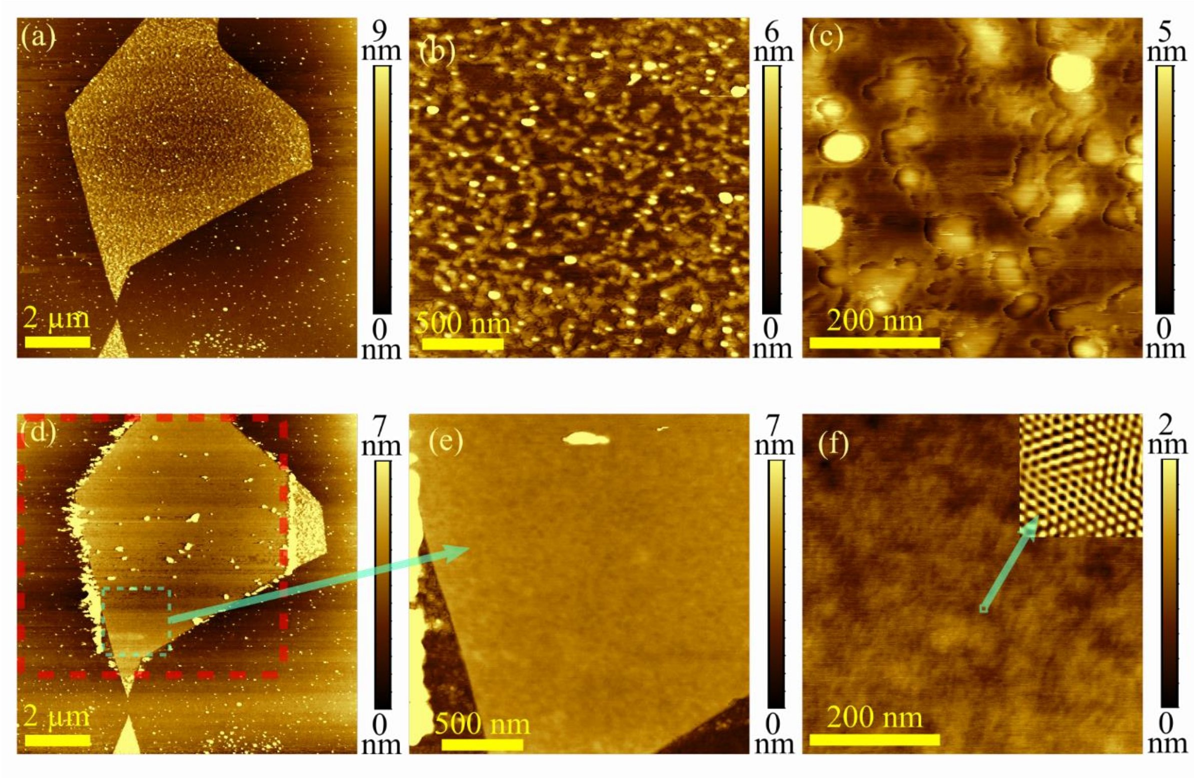


Nature **487,** 82–85 (2012)

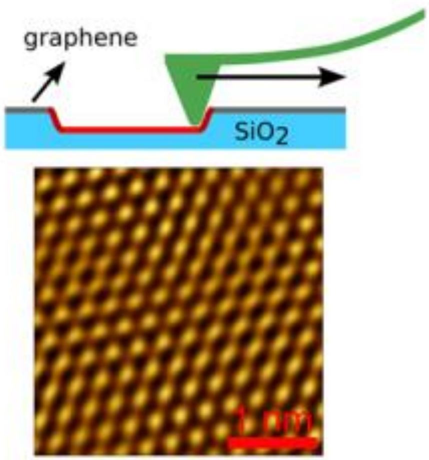
Visible

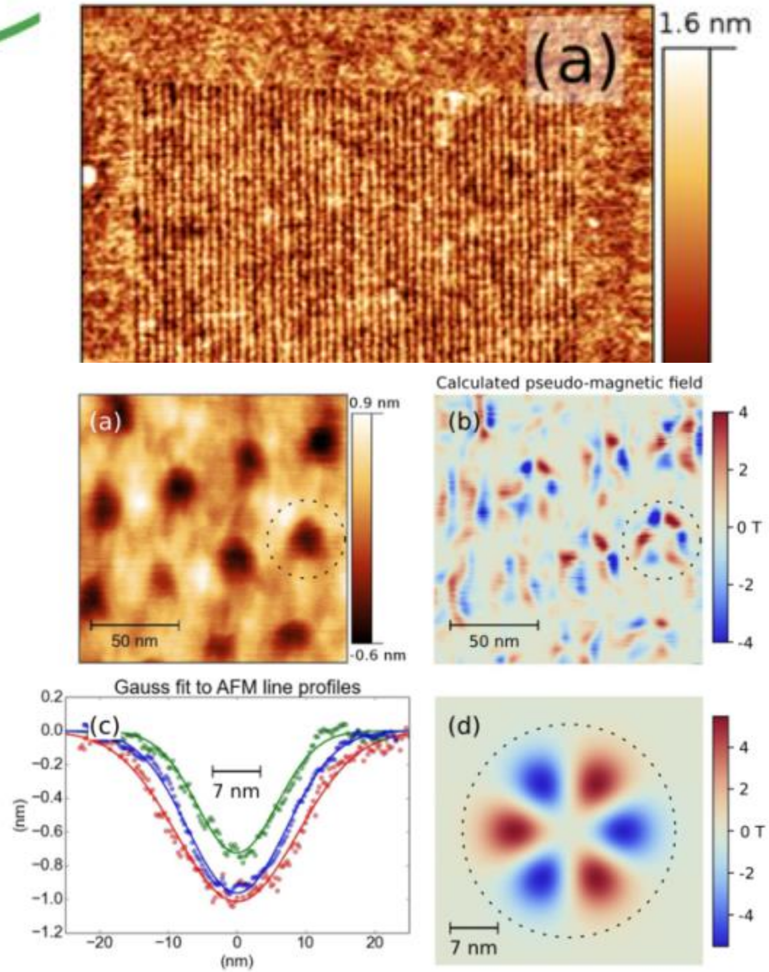


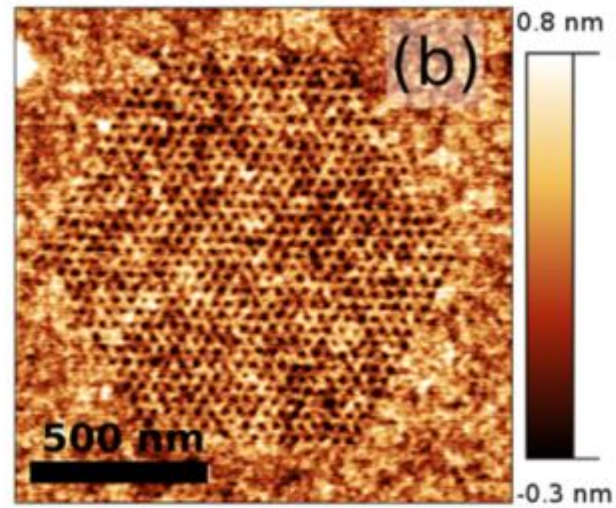
AFM Nano manipulation – nanoscale sweeping



AFM Lithography – nanoscale strain pattern engineering



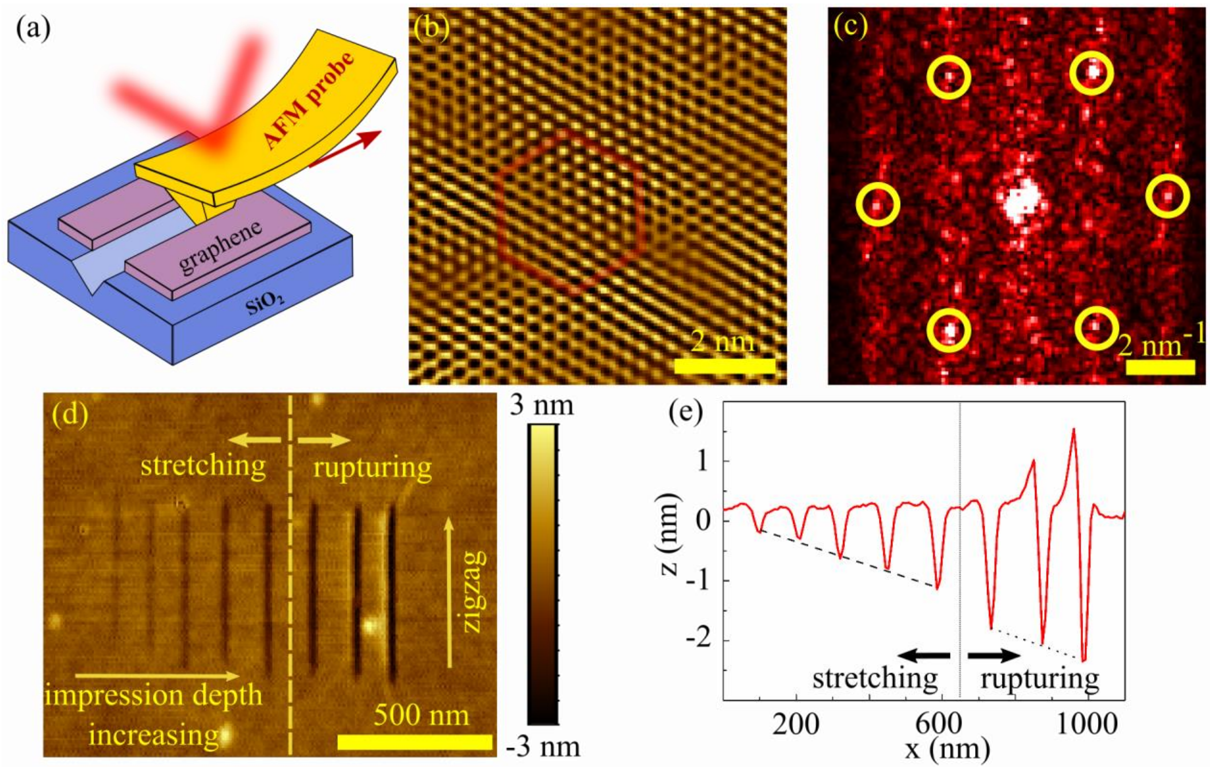




Sci. Rep. **7,** 3035 (2017)

Scanning probe microscopy

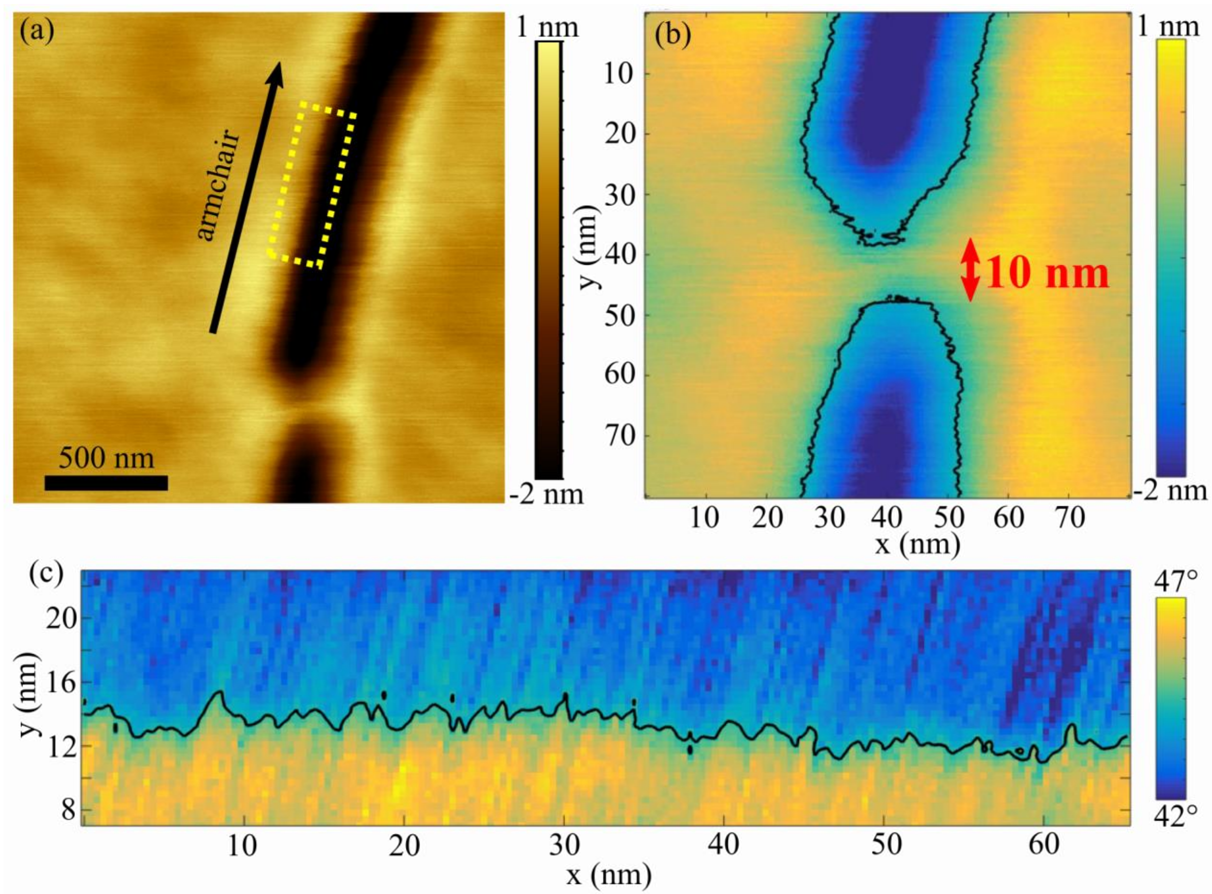
AFM Lithography – defining edges



Npj 2D Maer & Appl. **4,** 43 (2020)

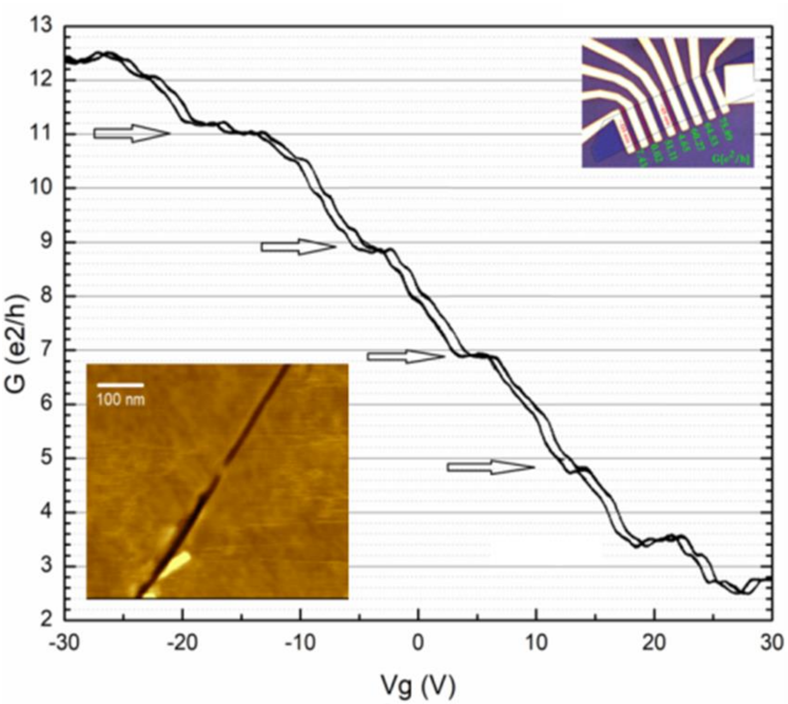
Scanning probe microscopy

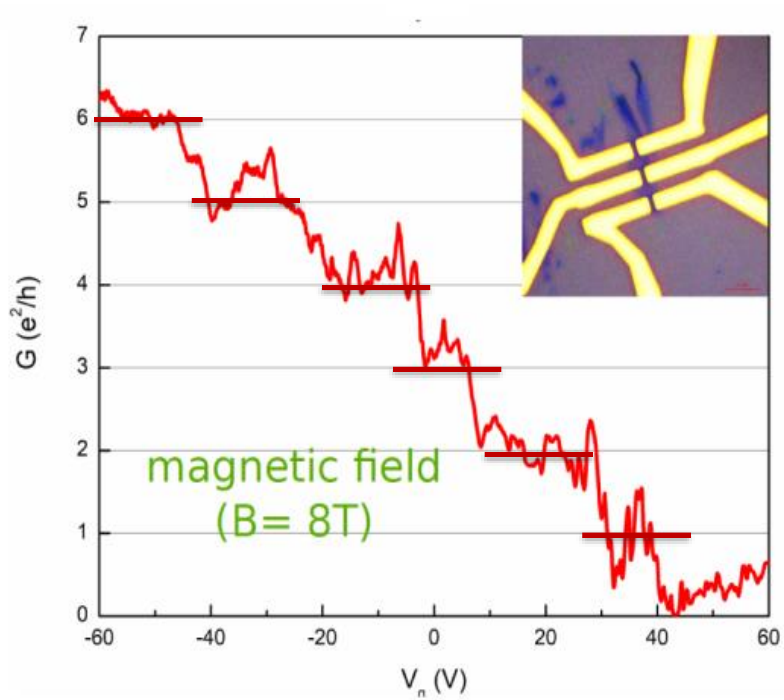
AFM Lithography – graphene nanoconstrictions



Npj 2D Maer & Appl. **4,** 43 (2020)

AFM Lithography – Graphene Quantum Point Contacts





Npj 2D Maer & Appl. **4,** 43 (2020)

Contact

If you

- have questions related to the presentation
- are interested in more details in scanning probe microscopy
- are interested in the atomic scale imaging and modification of 2D materials

contact me at: tapaszto@gmail.com