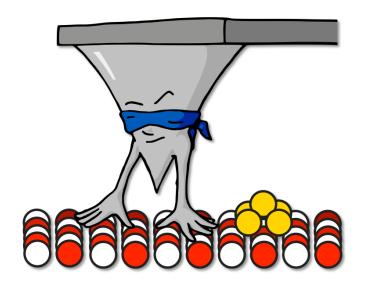
Scanning Probe Microscopy and its Applications



- Scanning-probe-based instrumentation
- AFM-based multi-function modes
- Beyond imaging

Chih-Wen Yang (楊志文)

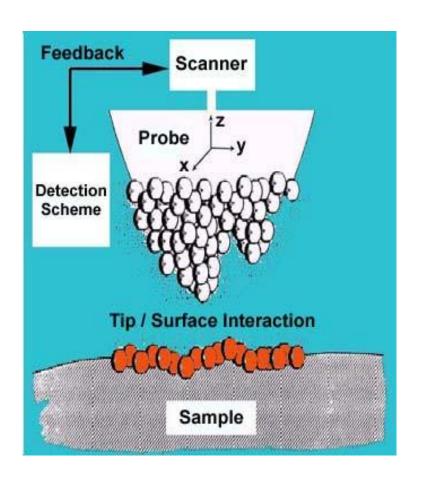
Surface and NanoScience Laboratory
Institute of Physics, Academia Sinica, Taiwan
Mar. 14, 2019







Scanning Probe Microscopy (SPM)



Scanning Tunneling Microscopy (STM)

--- G. Binnig, H. Rohrer et al, (1982)

Near-Field Scanning Optical Microscopy (NSOM)

--- D. W. Pohl (1982)

Atomic Force Microscopy (AFM)

--- G. Binnig, C. F. Quate, C. Gerber (1986)

Scanning Thermal Microscopy (SThM)

--- C. C. Williams, H. Wickramasinghe (1986))

Magnetic Force Microscopy (MFM)

--- Y. Martin, H. K. Wickramasinghe (1987)

Friction Force Microscopy (FFM or LFM)

--- C. M. Mate et al (1987)

Electrostatic Force Microscopy (EFM)

--- Y. Martin, D. W. Abraham et al (1988)

Scanning Capacitance Microscopy (SCM)

--- C. C. Williams, J. Slinkman et al (1989)

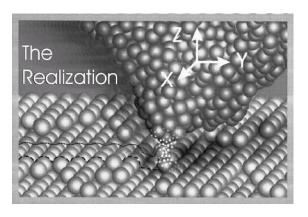
Force Modulation Microscopy (FMM)

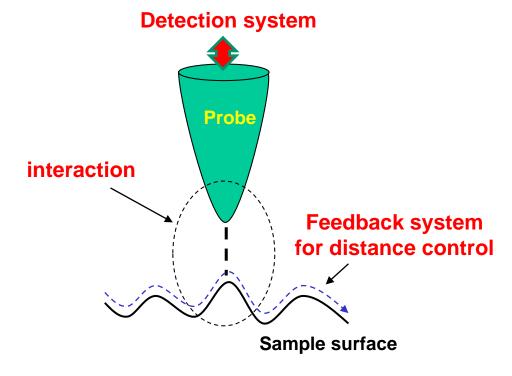
--- P. Maivald et al (1991)

Key elements of SPM



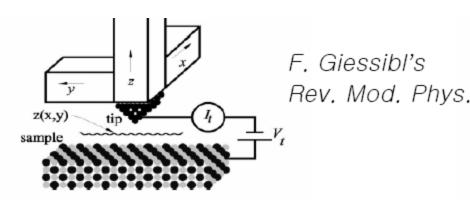
- •Interaction Sensor (figure)
- •Nano-scale Positioner (arm)
- •Computer &. Feedback Controller (brain)





Reviews of Modern Physics, Vol. 71, No. 2

The starting point- STM



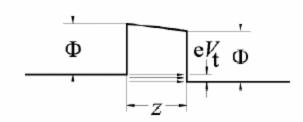


FIG. 3. Energy diagram of an idealized tunneling gap. The image charge effect (see Chen, 1993) is not taken into account here.

IG. 2. A scanning tunneling microscope (schematic).

- Binnig, Gerber, Rohrer, Wiebel (1982)
- Binnig and Rohrer awarded Nobel Prize in Physics in 1986 for STM
- If $|V_t|$ is small compared to workfunction Φ , and tunneling current is given by $I_t(z) = I_0 e^{-2\kappa_t z}$ where z is the gap I_0 is a function of the applied voltage and the density of states in the tip and the sample, and $\kappa_t = \sqrt{2m\Phi/\hbar}$
- For most metals, Φ[~] 4eV, so that κ_t=1Å⁻¹
- Most current carried by "front atom" blunt tips, so atomic resolution possible even with relatively blunt tips
- Only electrically conductive samples, restricting its principal use to metals and semi-conductors

The AFM

G. Binnig, C. F. Quate and Ch. Gerber, PRL 56, 930 (1986)

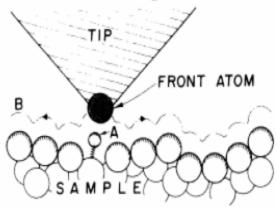


FIG. 1. Description of the principle operation of an STM as well as that of an AFM. The tip follows contour B, in one case to keep the tunneling current constant (STM) and in the other to maintain constant force between tip and sample (AFM, sample, and tip either insulating or conducting). The STM itself may probe forces when a periodic force on the adatom A varies its position in the gap and modulates the tunneling current in the STM. The force can come from an ac voltage on the tip, or from an externally applied magnetic field for adatoms with a magnetic moment.

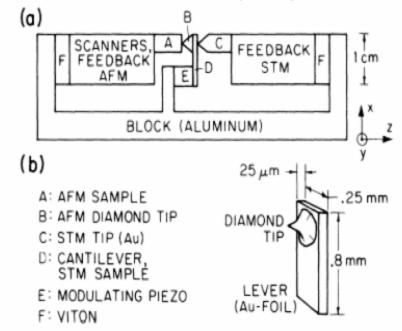
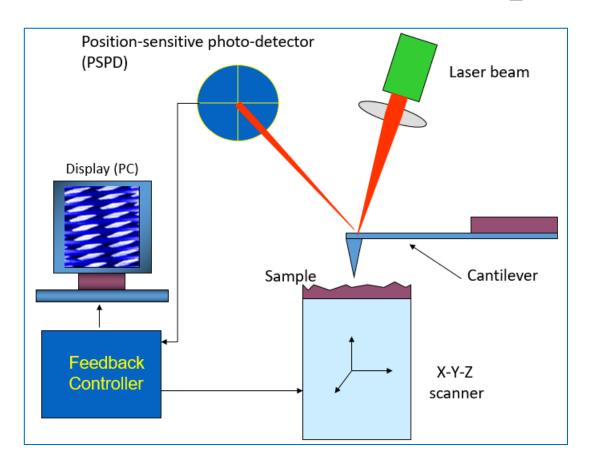


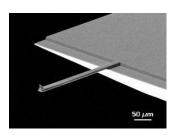
FIG. 2. Experimental setup. The lever is not to scale in (a). Its dimensions are given in (b). The STM and AFM piezoelectric drives are facing each other, sandwiching the diamond tip that is glued to the lever.

 Binnig invented the AFM in 1986, and while Binnig and Gerber were on a Sabbatical in IBM Almaden they collaborated with Cal Quate (Stanford) to produce the first working prototype in 1986

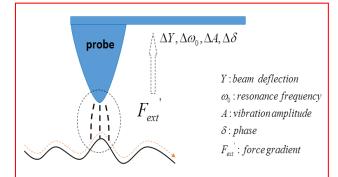
Atomic force microscope (AFM)

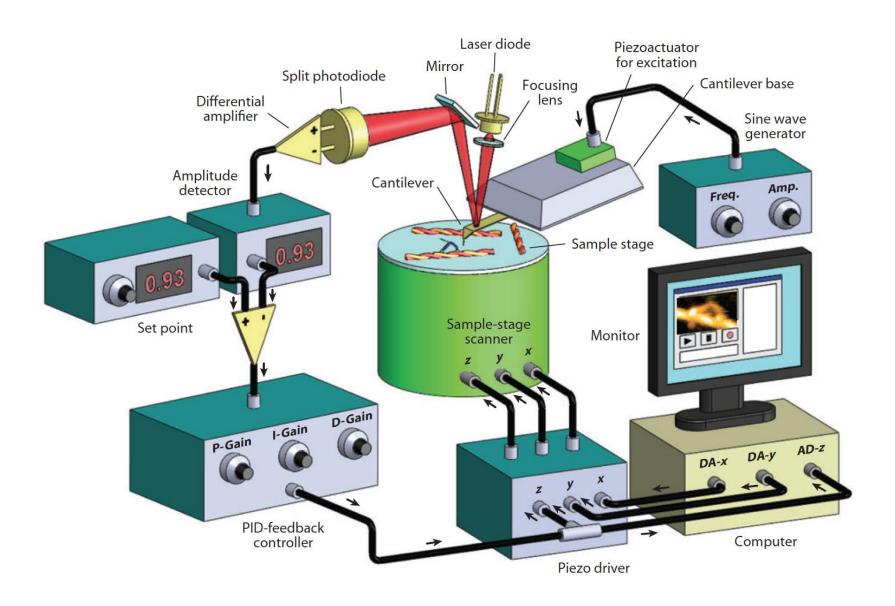


- Cantilever-tip sense the force interaction
- Beam deflection system detect the change of cantilever beam (PSPD)
- Feedback system monitor the PSPD signal to keep constant tip-sample interaction (constant distance)
- By raster scanning, the surface morphology can be obtained

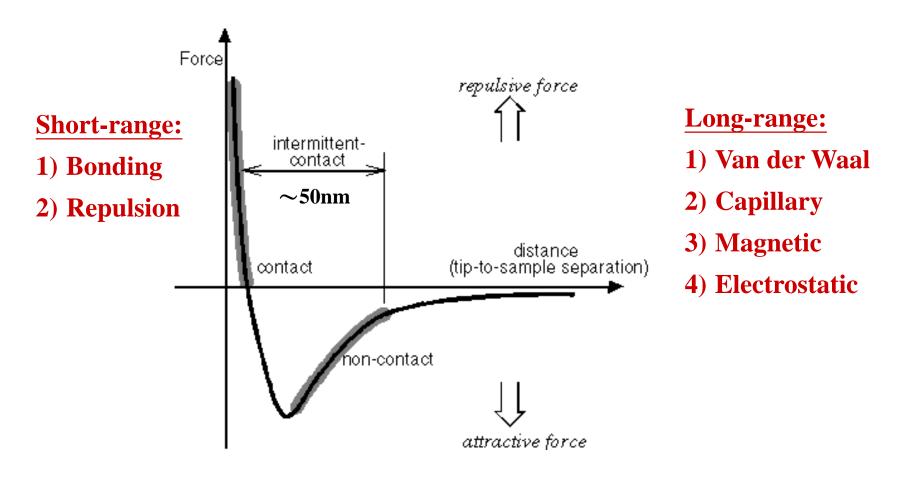


- Force sensitivity
- Tip-shape effect



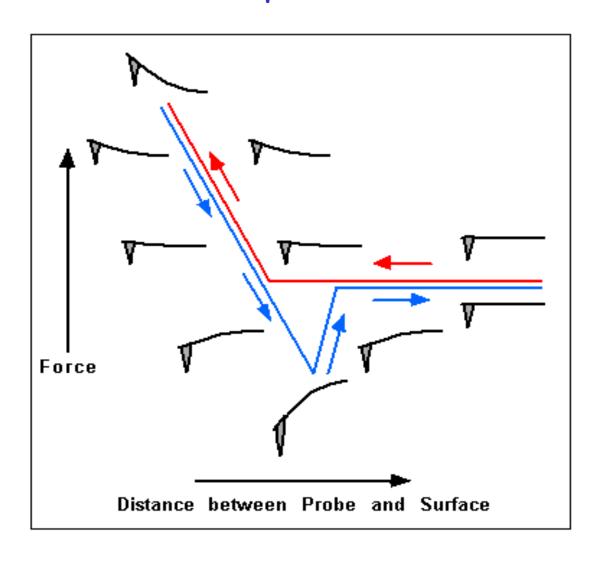


Interaction between the probe and sample

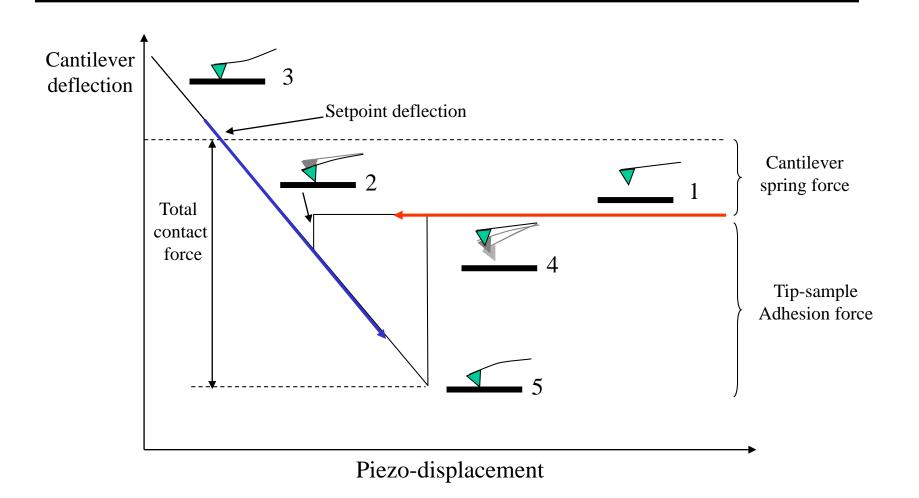


Lennard-Jones potential $\phi(r) = -A/r^6 + B/r^{12}$

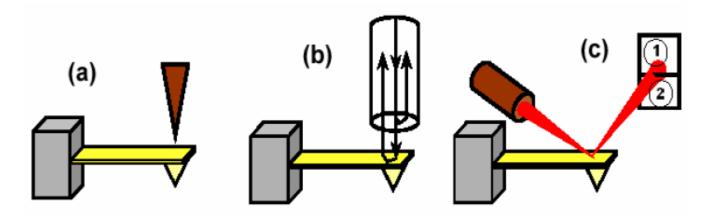
Reaction of the probe to the force



Deflection vs. Distance



Detection mechanism of cantilever deflection

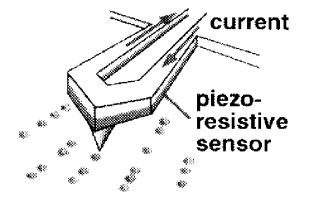


Optical method

- Laser interferometry,
- Beam deflection
- Astigmatism

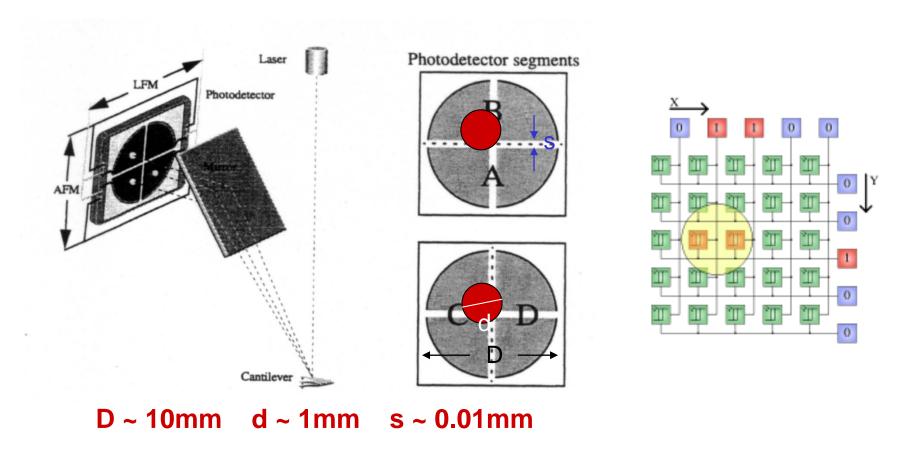
Non-optical method

(STM tip, piezoelectric, piezoresistive...)

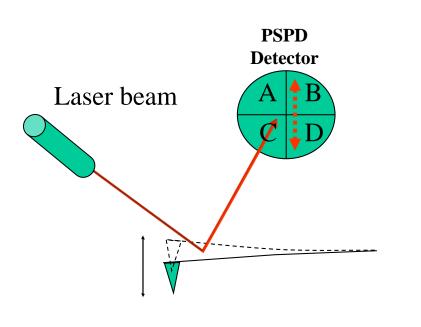


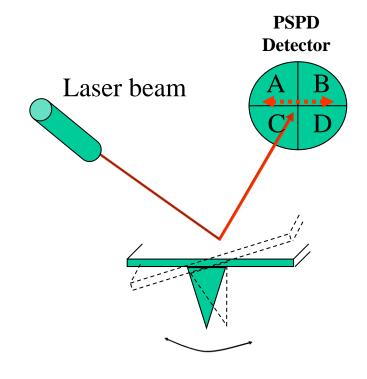


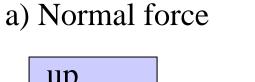
Position-sensitive Photo Diode (PSPD)

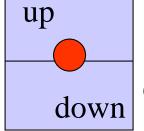


Cantilever beam deflection detection



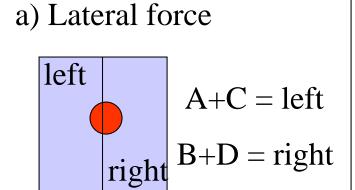




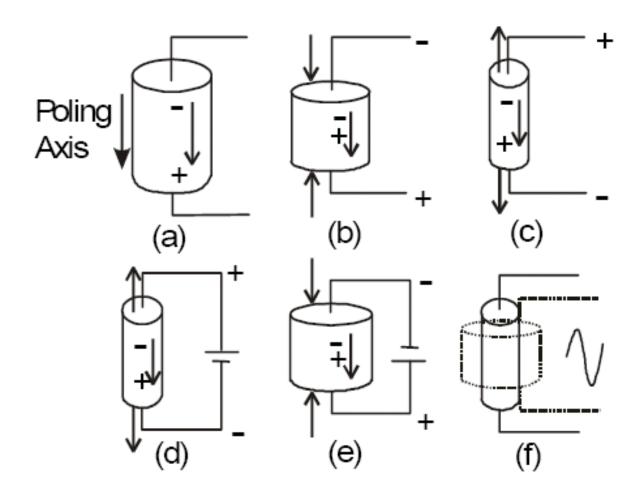


$$A+B = up$$

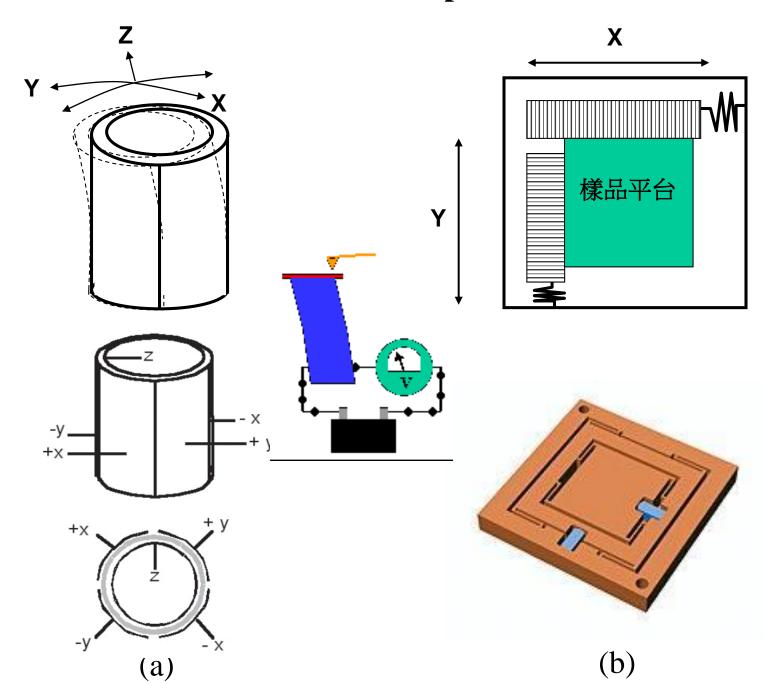
$$C+D = down$$



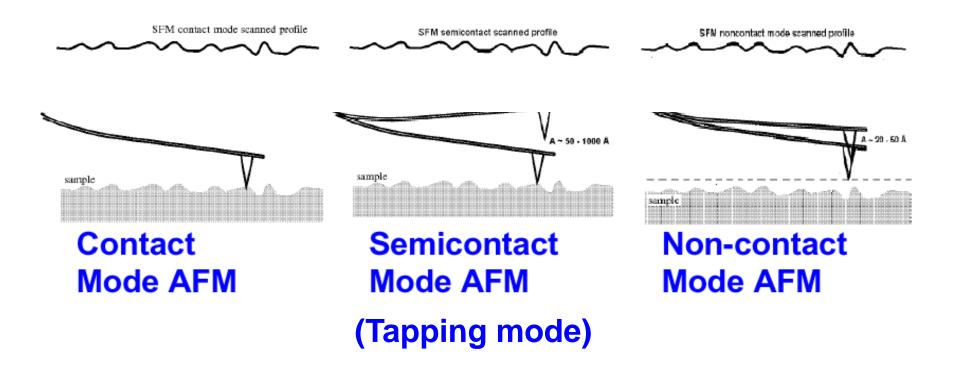
Piezoelectric effect



Piezo-tube scanner for X-Y-Z precision movement



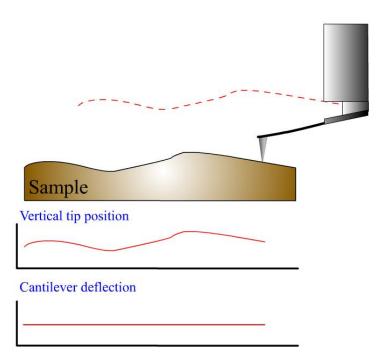
Three scanning modes of AFM



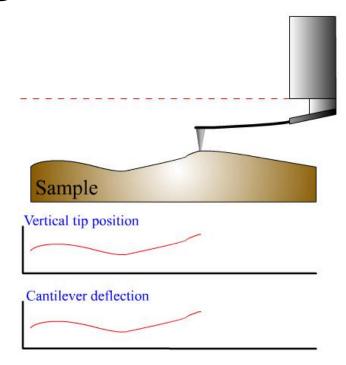
Two imaging methods in contact mode

- Constant force method: By using a feedback loop the tip is vertically adjusted in such a way that the force always stays constant. The tip then follows a contour of a constant contact force during scanning. A kind of a topographic image of the surface is generated by recording the vertical position of the tip.
- Constant height method: In this mode the vertical position of the tip is not changed, equivalent to a slow or disabled feedback. The displacement of the tip is measured directly by the laser beam deflection. One of its advantages is that it can be used at high scanning frequencies.

Constant-force scan vs. constant-height scan



Constant-force mode



Constant-height mode

Constant-force scan vs. constant-height scan

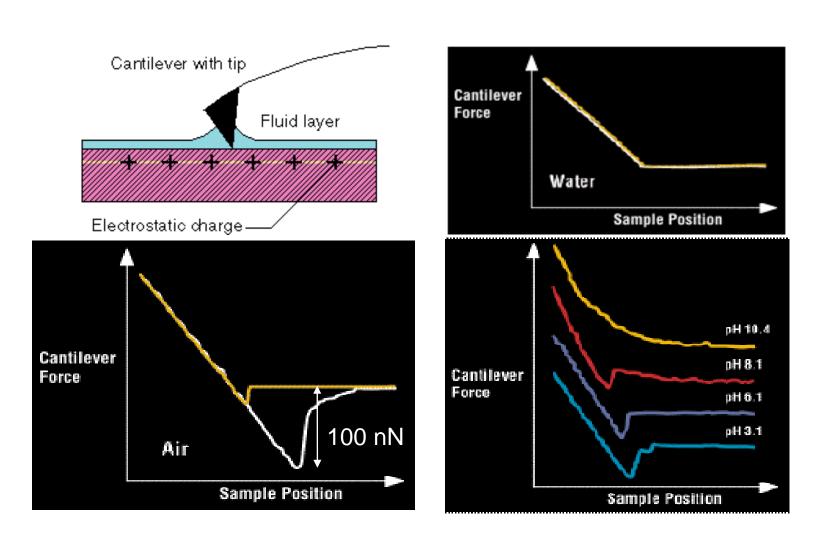
Constant-force

- Advantages:
 - Large vertical range
 - Constant force (can be optimized to the minimum)
- Disadvantages:
 - Requires feedback control
 - Slow response

Constant-height

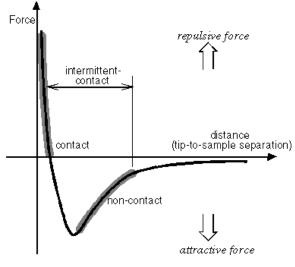
- Advantages:
 - Simple structure (no feedback control)
 - Fast response
- Disadvantages:
 - Limited vertical range (cantilever bending and detector dynamic range)
 - Varied force

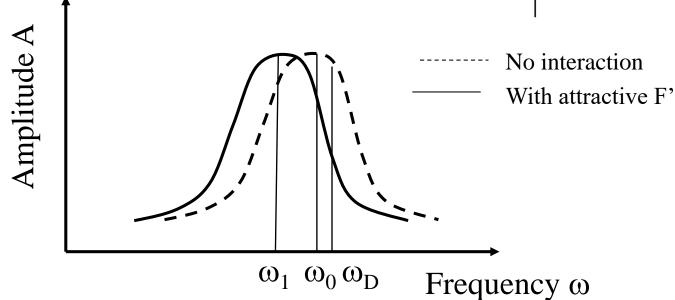
Problems with the contact mode

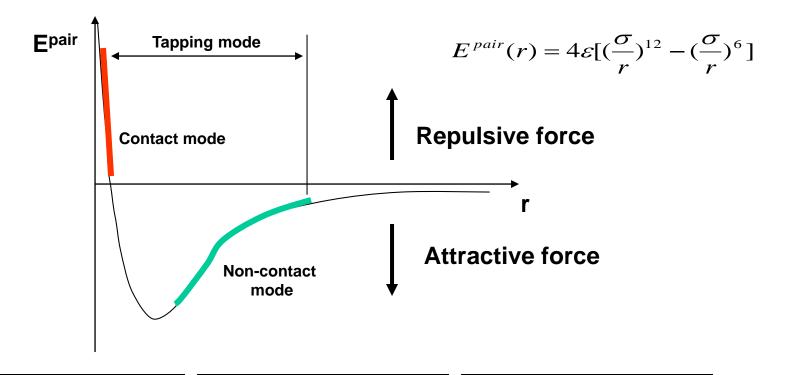


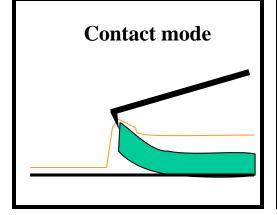
AC imaging mode

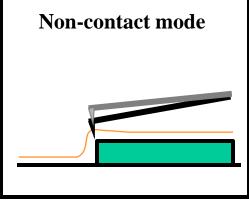
$$\omega_1 = \omega_0 (1 + F'/2c)$$

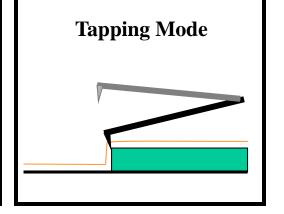




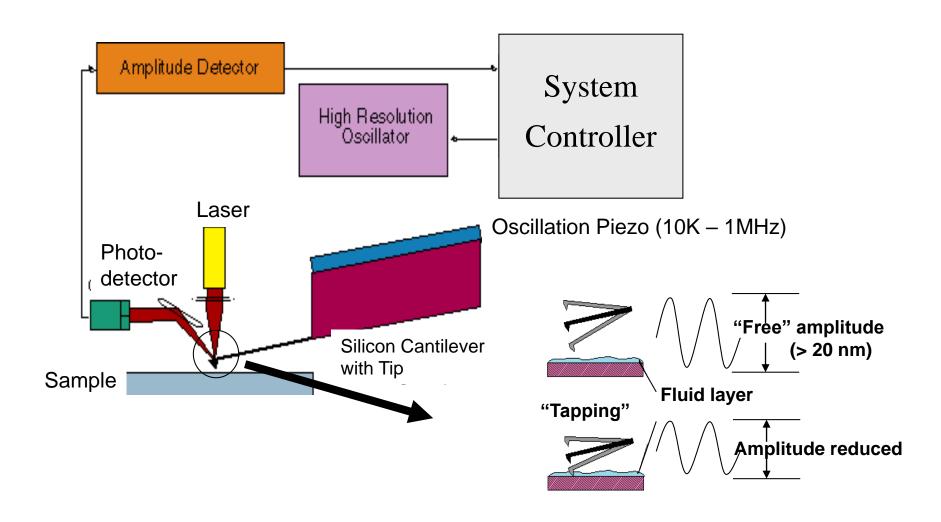




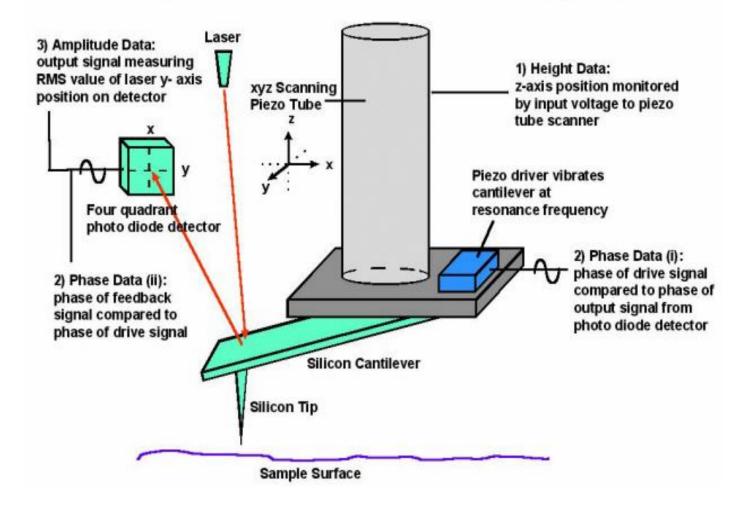




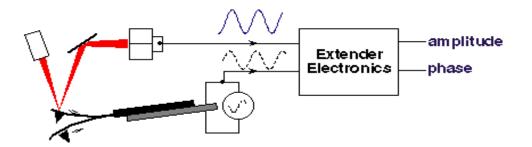
Tapping mode

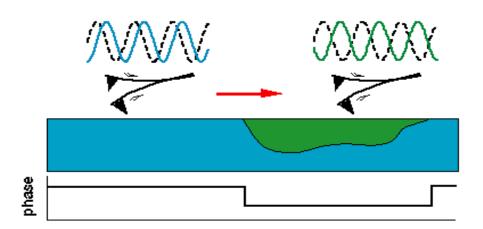


Three Types of Data Collected in Tapping Mode



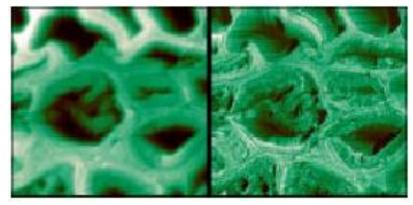
Images by tapping mode



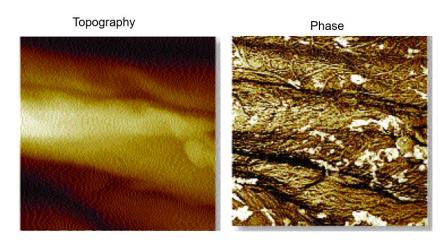


Topography

Phase

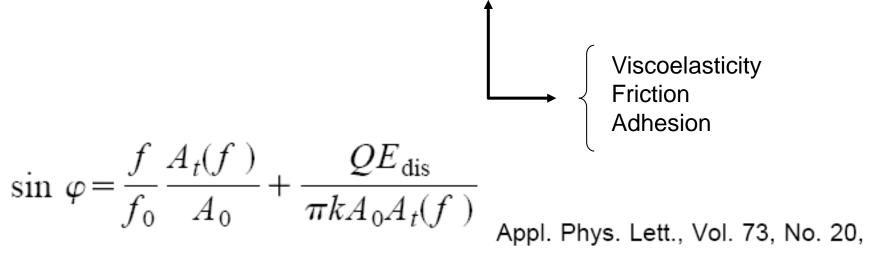


AFM image of a fresh Alfalfa root section



Wood pulp fiber phase image highlights cellulose microfibrils

Phase is related to energy dissipation

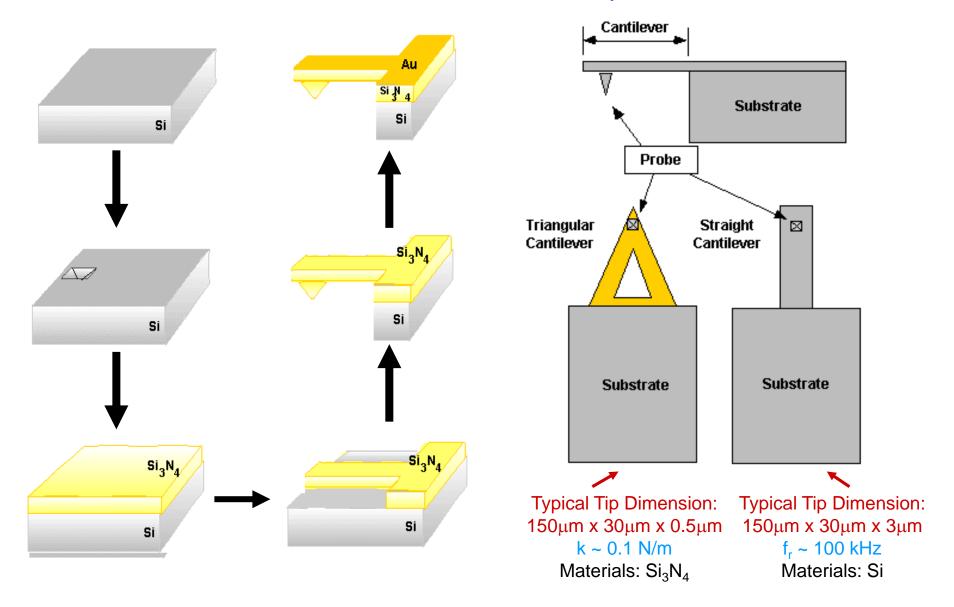


$$\sin \varphi = \frac{f}{f_0} \frac{A_t(f)}{A_0} + \frac{QE_{\text{dis}}}{\pi k A_0 A_t(f)}$$

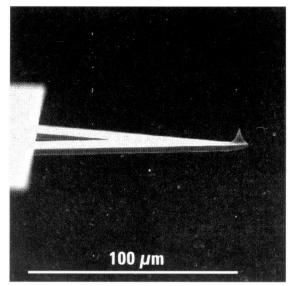
Phase in tapping-mode depends on:

- drive frequency f (vs. f₀)
- drive amplitude A₀
- damping ratio A_{setpoint}/A₀
- surface topography
- material properties
- There is no simple, general relation between phase in tappingmode AFM and material properties

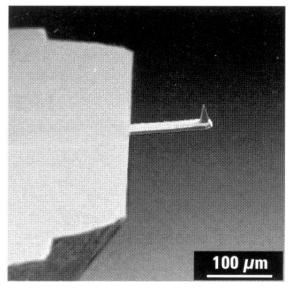
Fabrication of AFM probes



V-shaped



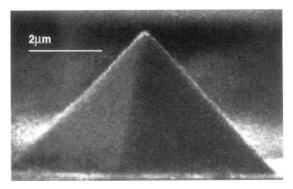
Rectangular-shaped



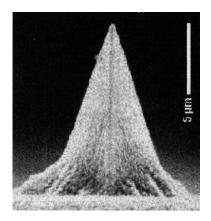
Materials: Si, SiO₂, Si₃N₄

Ideal Tips: hard, small radius of curvature, high aspect ratio

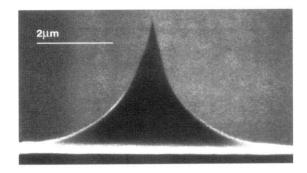
Pyramid Tip

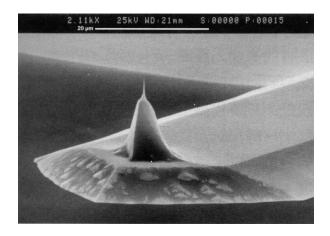


Diamond-coated Tip



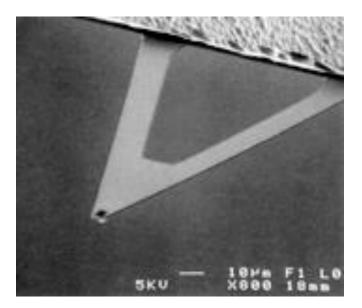
Ultrasharp Tip

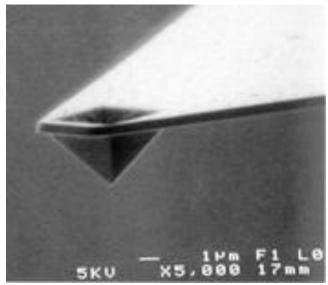




Tip of small shear force

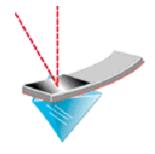
(for Contact mode)





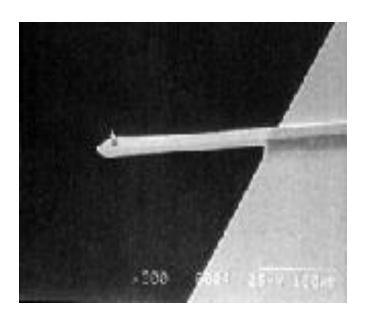
Typical Tip Dimension: 150μm x 30μm x 0.5μm $k \sim 0.1$ N/m

Materials: Si₃N₄



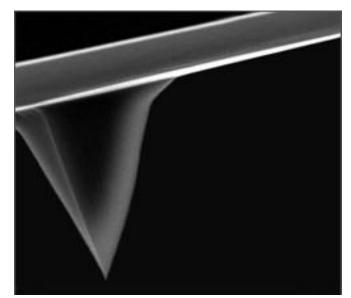
Tip of high resonant frequency

(for Tapping mode)





Materials: Si

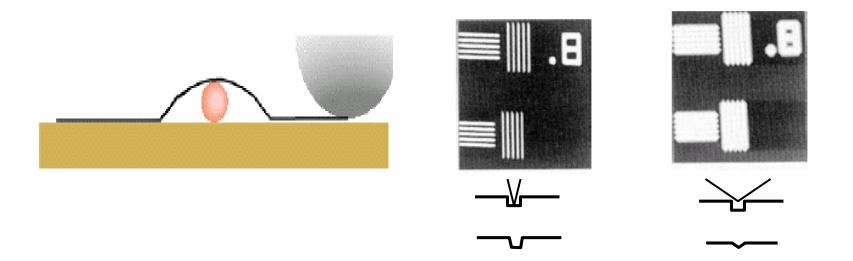


Criteria for AFM probe

- 1) Small spring constant (k) $F = k \Delta z$ To detect force of $\sim nN$
- 2) High resonant frequency (f_r) $f_r \propto (k/m)^{1/2}$ To enable scanning and other operations
- 3) Highly anisotropic stiffness

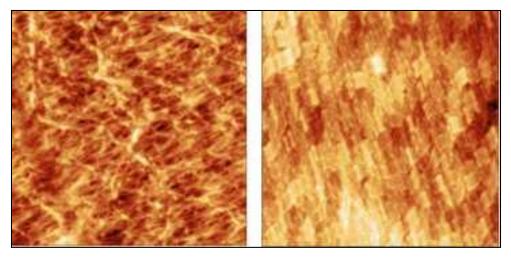
 Easy to bent and difficult to twist
- 4) Sharp protrusion at the apexTo better define the tip-sample interaction

Convolution Effect

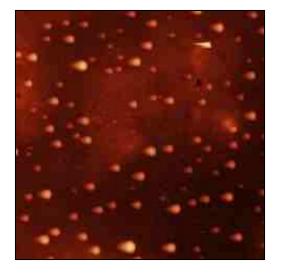


- •AFM image is a convolution of the surface features and the tip geometry.
- •The spatial resolution is limited by the sharpness of the probe tip.
- •When the tip is much sharper than the surface features, it will collect an image reflecting the "true" surface features.
- •When the tip is much larger than the surface features, using such a tip to scan the surface will result in an image that is merely a reflection of the geometry of the tip apex itself.

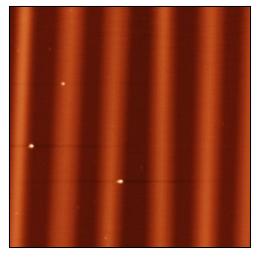
AFM artifact



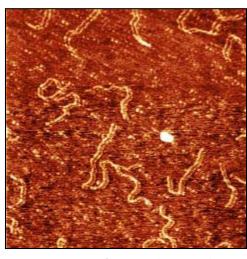
Dirty or Contaminated Tips



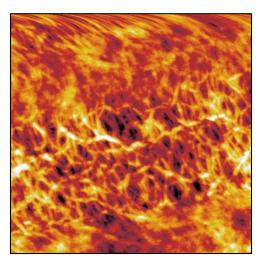
Flying Tip



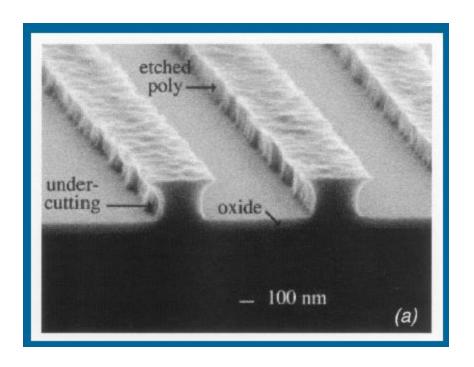
Laser interference

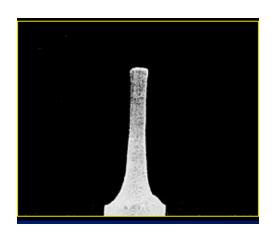


Double/multiple tips

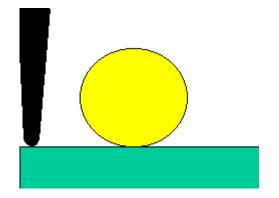


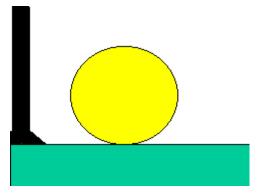
Piezo drift



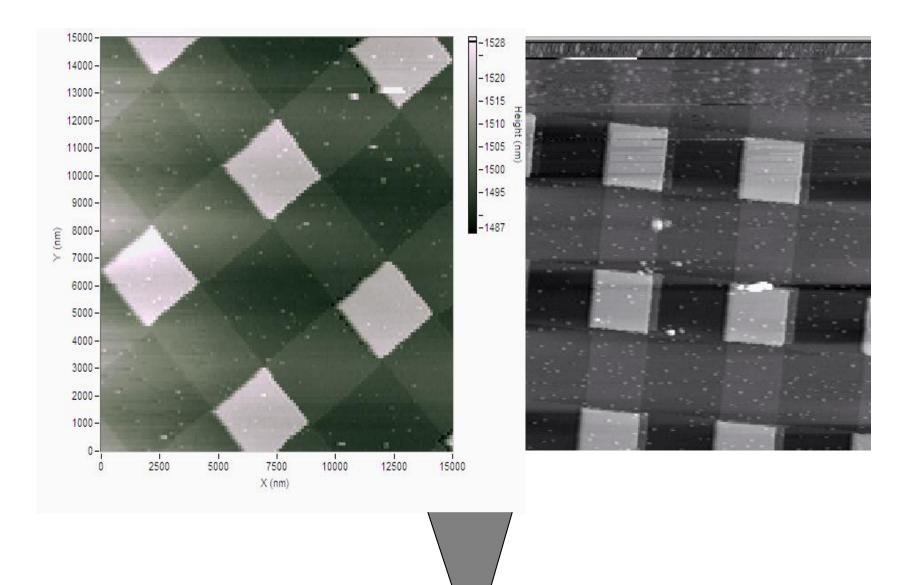


Boot-shaped tip





AFM artifact



Double tip

Optical interference artifacts

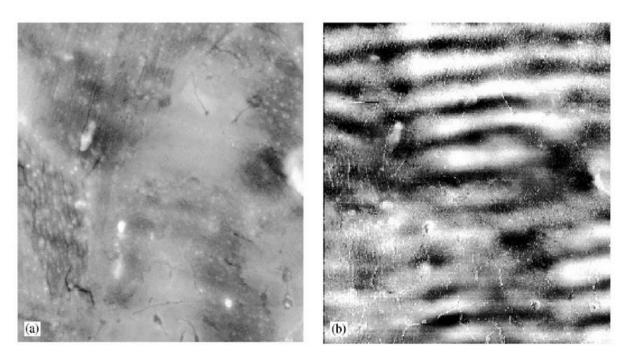
Quadrant detector

A

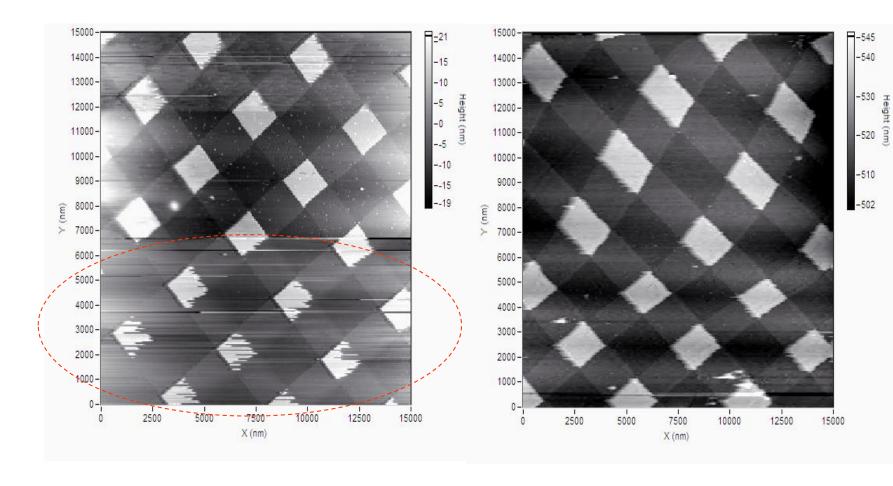
Laser light

Cantilever

Sample surface



A. Méndez-Vilas et al. | Ultramicroscopy 92 (2002) 243-250



Scan rate over feedback

Piezo-Scanner drift

AFM versus STM

- 1. Generally, STM has "better" resolution than AFM.
- 2. The force-distance dependence in AFM is much more complex when characteristics such as tip shape and contact force are considered.
- 3. STM is generally applicable only to conducting samples while AFM is applied to both conductors and insulators.
- 4. AFM offers the advantage that the writing voltage and tip-to-substrate spacing can be controlled independently, whereas with STM the two parameters are integrally linked.

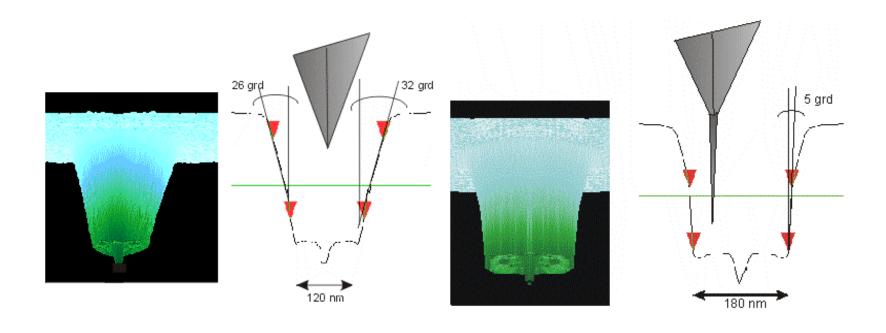
AFM versus EM

- 1. AFM only reveal the surface and EM can probe the interior structure of the sample with higher resolution.
- 2. AFM provides direct topographic measurements and EM provides only 2D projection of the sample structure.
- 3. No charging effect occurs in AFM. So, for insulating samples, no metallic coating is necessary.

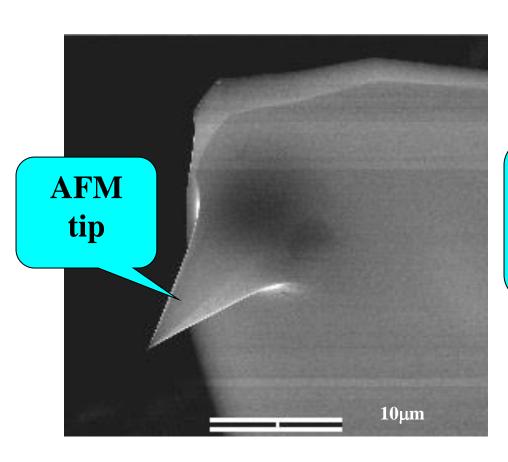
AFM versus Optical Microscope

- 1. AFM has much better resolution than Optical Microscope (OM).
- 2. AFM provides unambiguous measurement of step heights, independent of reflectivity differences between materials.
- 3. OM can be applied to much faster dynamic studies with the pump-probe method.

Ultra-sharp tip



AFM Tip + Carbon Nanotube



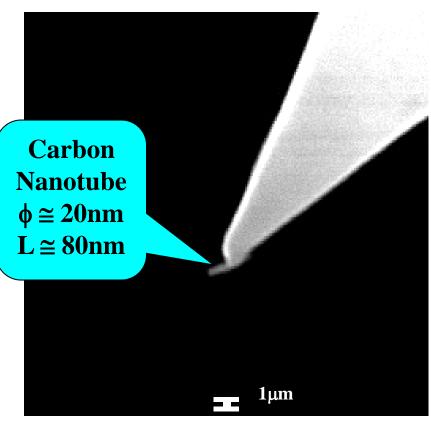
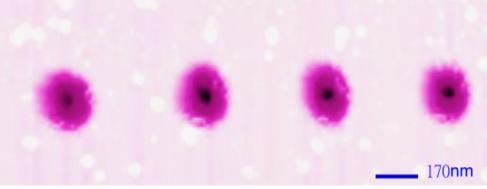


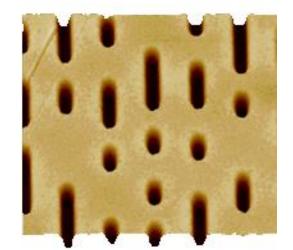
Image of high aspect ratio



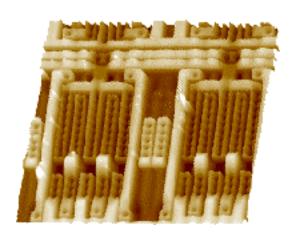


AFM images

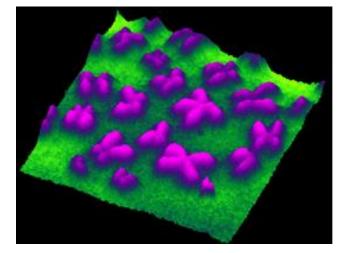
CD pits



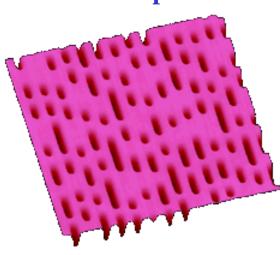
Integrated circuit



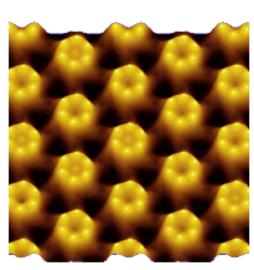
Chromosomes



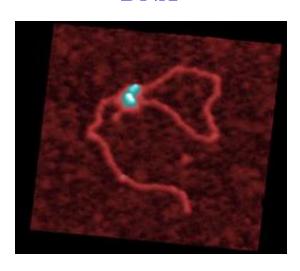
DVD pits



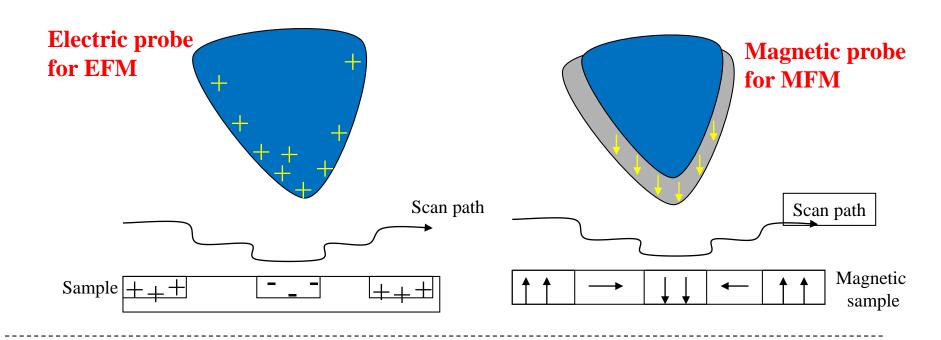
Bacteria



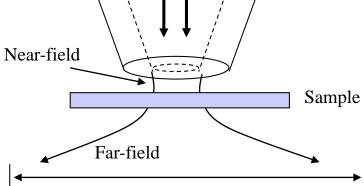
DNA



AFM-based multi-function modes

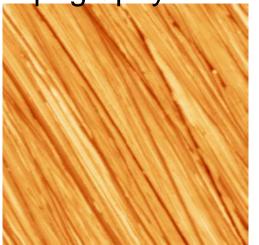


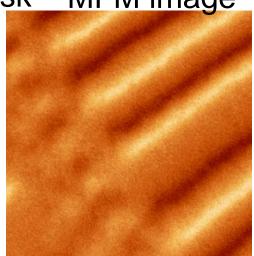
Excitation | Fiber probe or aperture probe for SNOM



Magnetic Force Microscope, MFM

Topography of hard disk MFM image





Scan mode: AC lift-mode

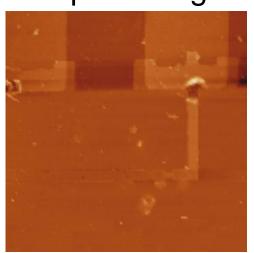
Sample: hard disk surface

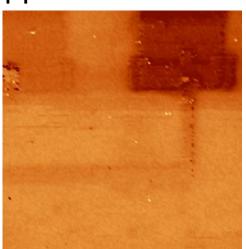
•Scan area: 10μm× 10μm



Electrical Force Microscope, EFM

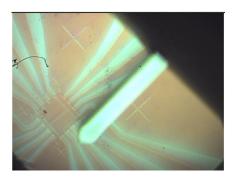
Sample voltage bias applied on one circuit electrode





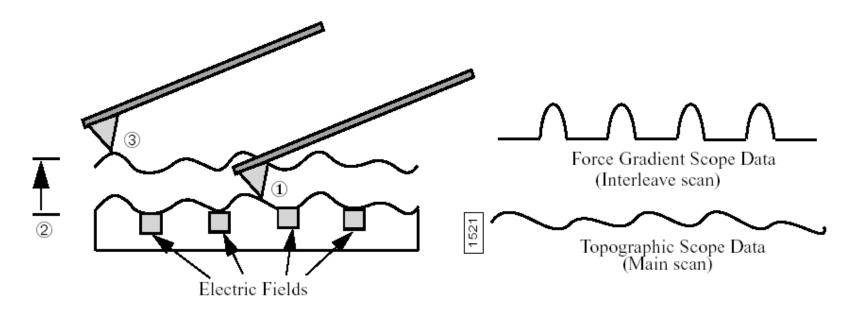
•Scan mode: AC lift-mode

•Size: 21µmx21µm



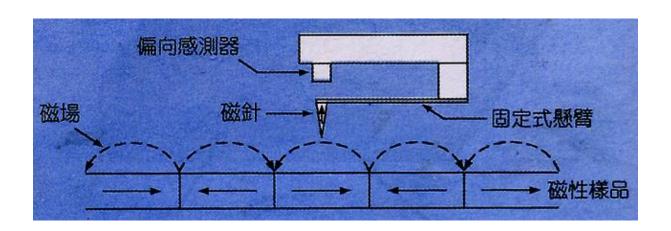
Lift Mode (MFM & EFM)

Since magnetic (electrostatic) forces can be either attractive or repulsive, problems with feedback loop stability in the non-contact imaging mode are likely to occur.



- 1. Cantilever measures surface topography on first (main) scan.
- 2. Cantilever ascends to lift scan height.
- 3. Cantilever follows stored surface topography at the lift height above sample while responding to magnetic (electric) influences on second scan (measured by amplitude, phase or frequency detection).

Magnetic Force Microscopy (MFM)

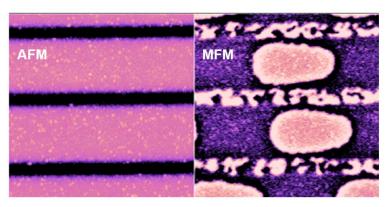


$\mathbf{F} = \nabla(\mathbf{m} \cdot \mathbf{H})$

Tips: silicon probes are magnetically sensitized by sputter coating with a ferromagnetic material.

Resolution: 10 ~ 25 nm.

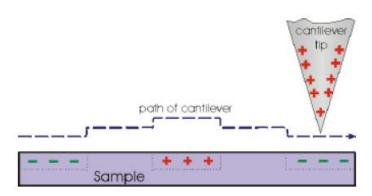
Applications: hard disks, magnetic thin film materials, micromagnetism.

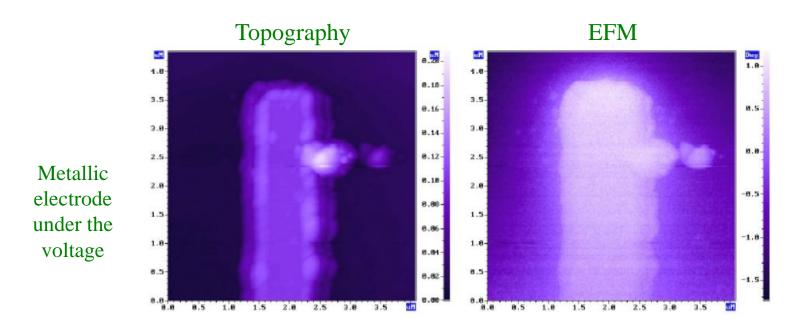


Bits (50 nm) on a magneto-optical disk Scan area (5μm× 5μm)

Electrostatic Force Microscopy (EFM)

- Tip: Si cantilevers with conductive coating.
- The grounded tip first acquires the surface topography using the tapping mode.
- A voltage between the tip and the sample is applied in the second scan (Lift-Mode 50 to 100 nm) to collect electrostatic data. EFM measures electric field gradient and distribution above the sample surface.
- EFM is used to monitor continuity and electric field patterns on samples such as semiconductor devices and composite conductors, as well as for basic research on electric fields on the microscopic scale.





Scanning Surface Potential Microscopy (SSPM) Kelvin Probe Microscopy(KPM)

As in EFM, this technique is usually implemented in the non-contact mode. In the second scan, the piezo is disenganged and oscillating is applied to the tip.

$$F(z) = \frac{1}{2} \frac{\partial C(z)}{\partial z} \left[(V_{dc} - V_{surf})^2 + \frac{1}{2} V_{ac}^2 [1 - \cos(2\omega t)] + 2(V_{dc} - V_{surf}) V_{ac} \sin(\omega t) \right]$$

$$F_{dc}(z) = \frac{1}{2} \frac{\partial C(z)}{\partial z} \left[(V_{dc} - V_{surf})^2 + \frac{1}{2} V_{ac}^2 \right] \qquad V_{tip} = V_{dc} + V_{ac} \sin(\omega t)$$

$$F_{1\omega}(z) = \frac{\partial C(z)}{\partial z} (V_{dc} - V_{surf}) V_{ac} \sin(\omega t)$$

$$F_{2\omega}(z) = \frac{1}{4} \frac{\partial C(z)}{\partial z} V_{ac}^2 \cos(2\omega t)$$

- 1. The lock-in technique allows extraction of the first harmonic signal, $F_{1\omega}$. A feedback loop is employed to keep it equal to zero (nulling force approach) by adjusting V_{dc} on the tip. When $V_{dc} = V_{surf}$, $F_{1\omega} = 0$. Thus the surface potential is measured.
- 2. The high spatial and voltage resolution (~ mV) make KPM a prominent tool for the characterization of current devices, especially intergated circuit analysis..
- 3. This technique is also sensitive to local charge on the surface.

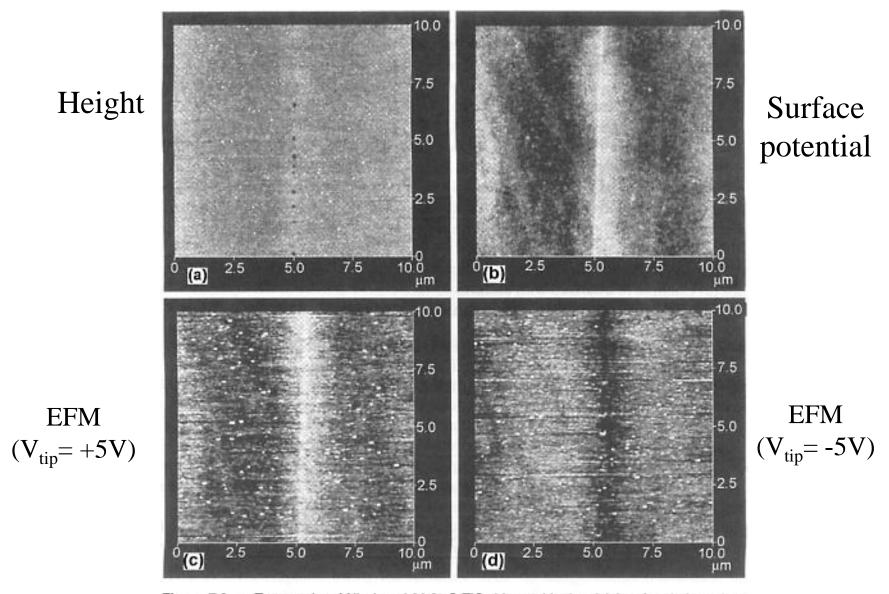
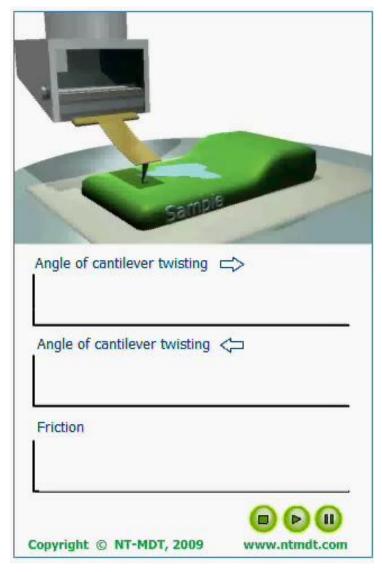
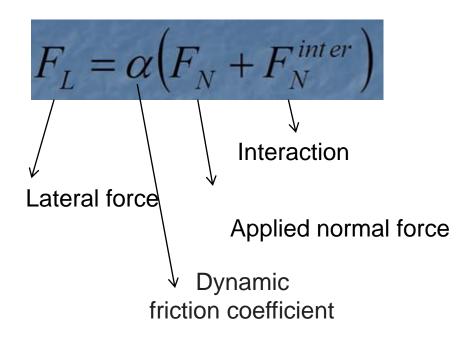


Figure 7.2. a, Topography of Nb-doped 36.8° SrTiO₃ bicrystal in the vicinity of grain boundary (a). b, Surface potential (SSPM) image of the same region. c, EFM (force gradient) images at tip bias $V_{\rm tip} = 5V$ and (d) $V_{\rm tip} = -5V$. The range is (a) 5 nm, (b) 20 mV and (c, d) 2 Hz.

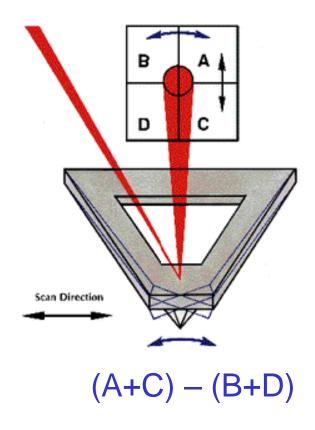
Friction force microscopy (FFM)

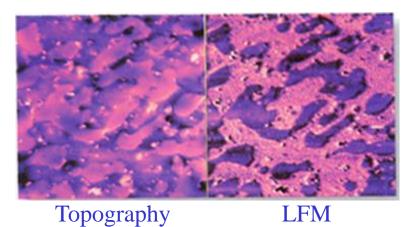




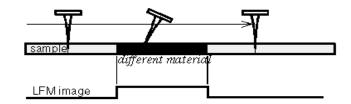


Lateral Force Microscopy

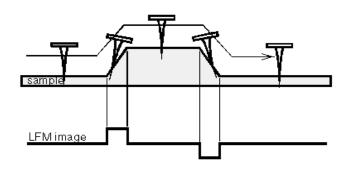




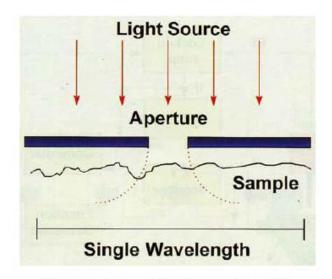
Nature rubber/EDPM blend

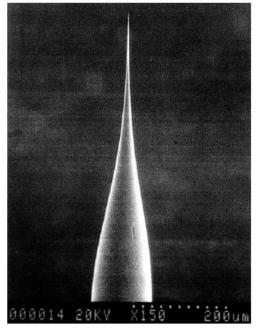


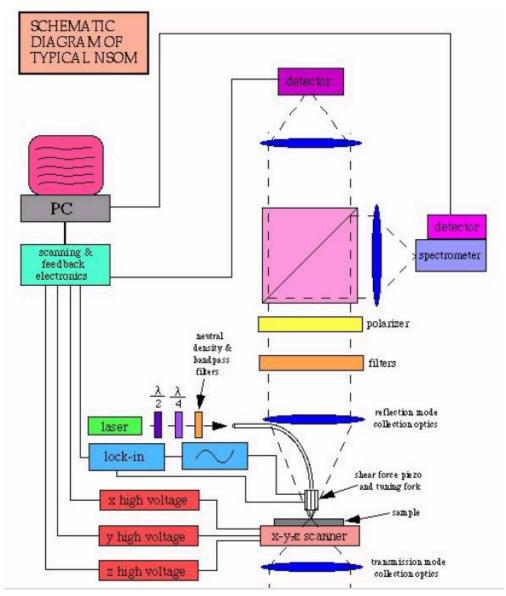
- LFM is sensitive to friction and chemical forces.
- Image contrast depends on the scanning direction.
- Surface roughness will contribute to the contrast.



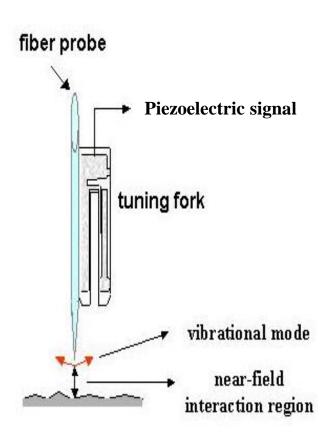
Scanning Near-field Optical Microscopy, SNOM



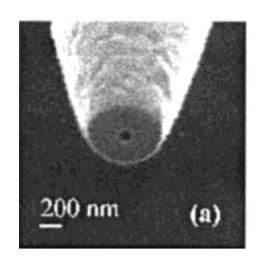


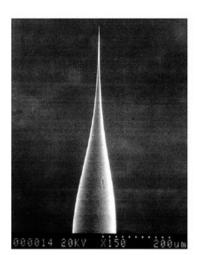


SNOM Probe

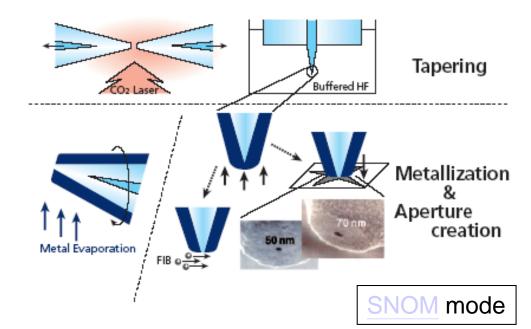


- •No diffraction limit
- •Resolution depends on aperture size
- •Shear force detection is used to regulate the tip/sample separation

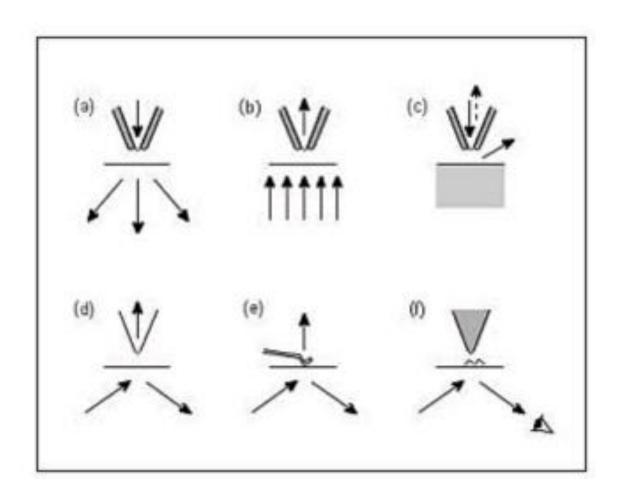




横回刀乙剖面圖

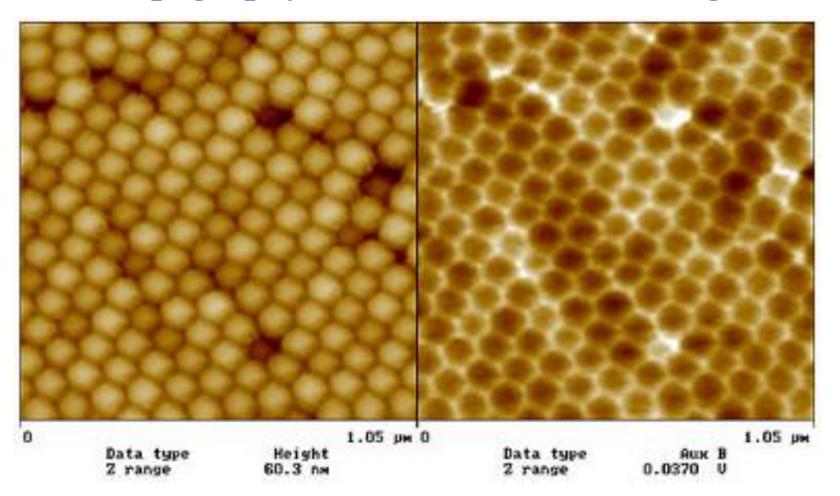


Imaging modes for NSOM



Topography

NSOM Image

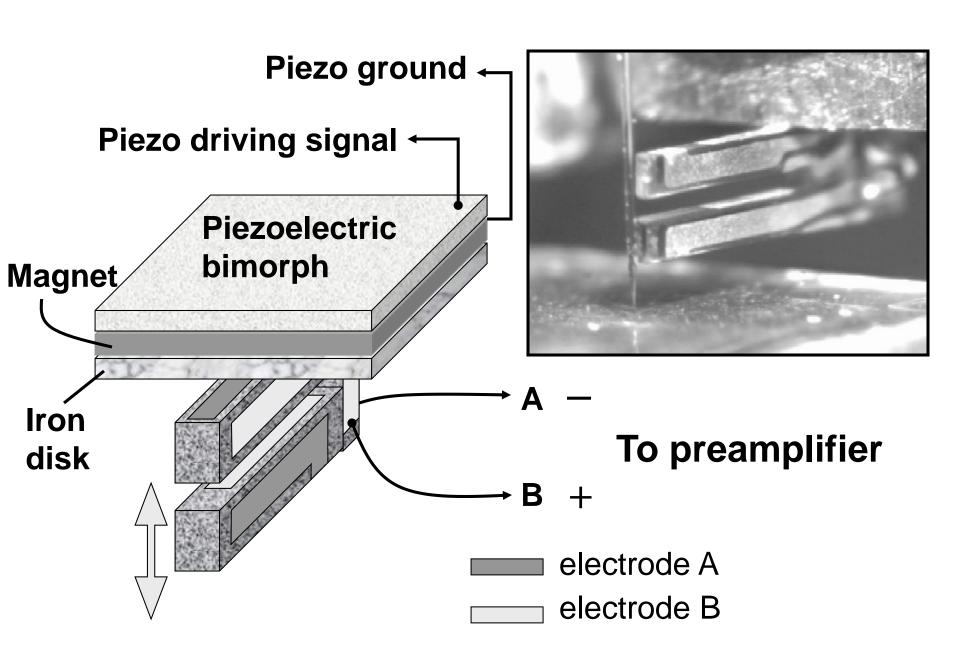


Polystyrenes of 100 nm on glass

Quartz Tuning fork (piezoelectric material)



 $f_0 = 32.768 kHz$ L=3.0mm T=330 μ m W=120 μ m

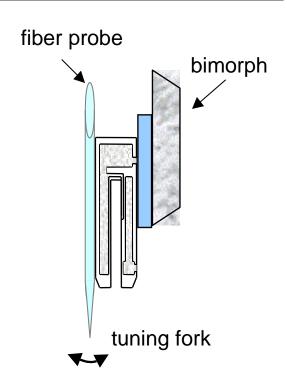


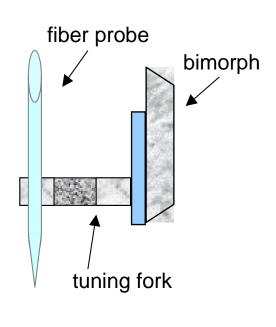
Vibration modes of Tuning Fork

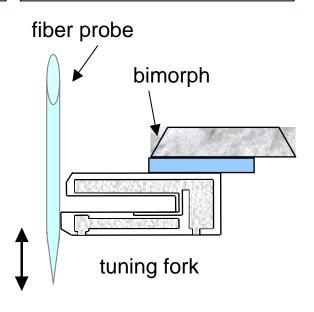
Shear force mode (I)

Shear force mode (II)

Normal force mode



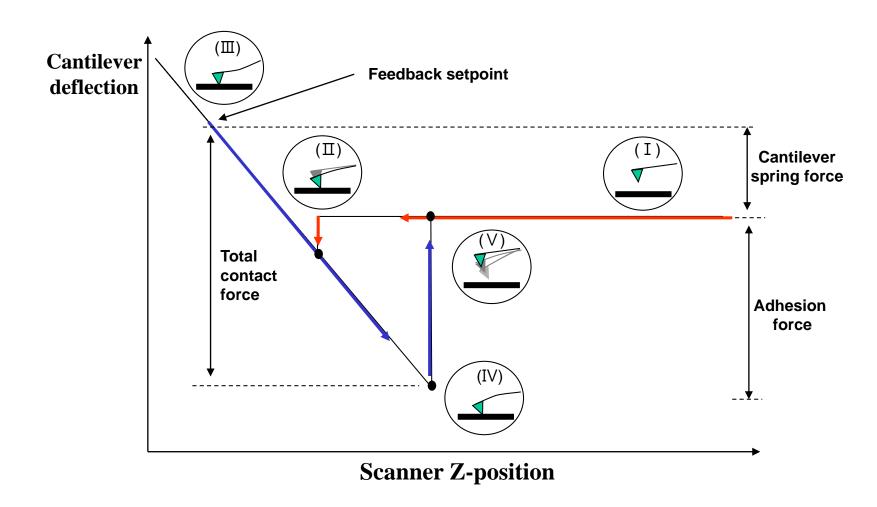




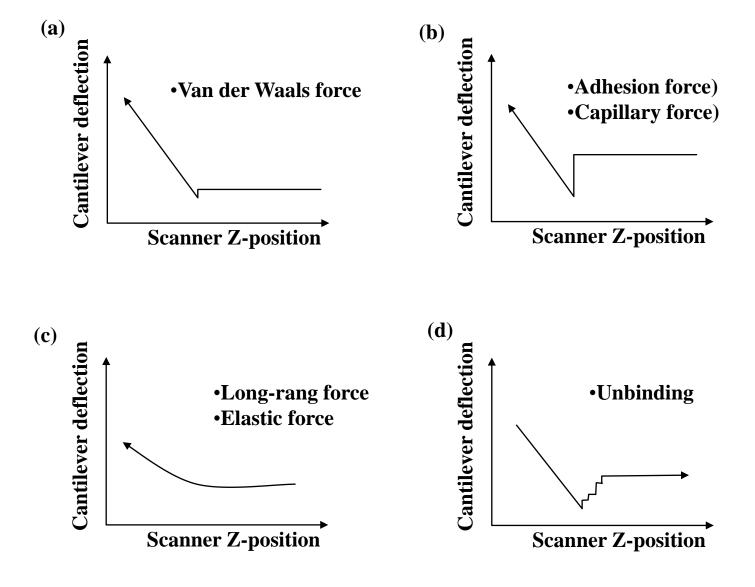
Beyond imaging

- Force spectroscopy
- Dynamic observation
- Chemical mapping
- Nano-manipulation
- Nano-lithography

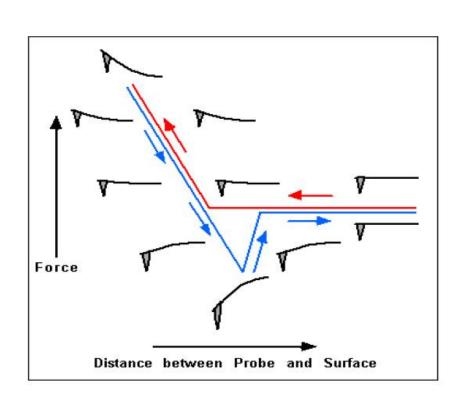
Cantilever deflection vs. Distance

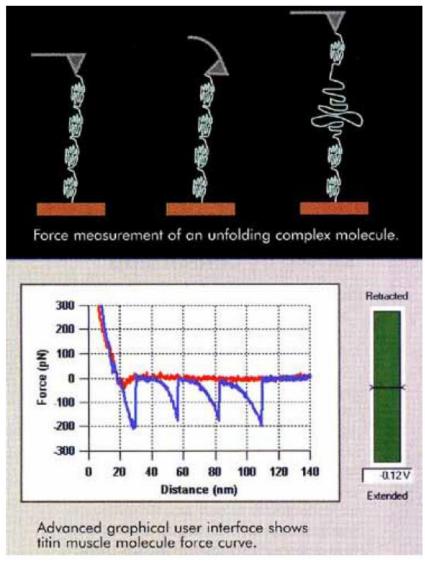


Force curves vs. different surface interaction

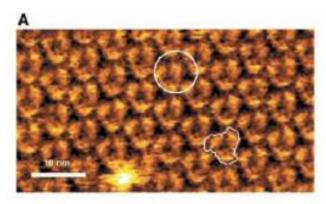


Single Molecule Force Spectroscopy

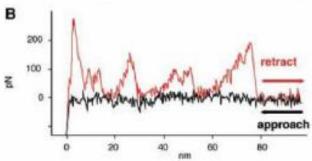


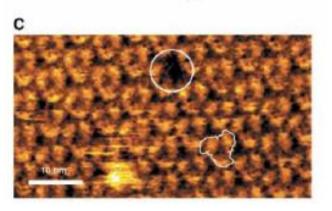


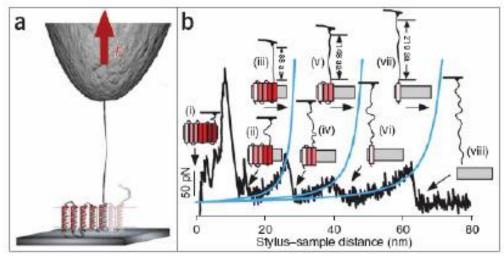
Interaction measurement by AFM tip



Individual bacteriorhodopsin molecules in water

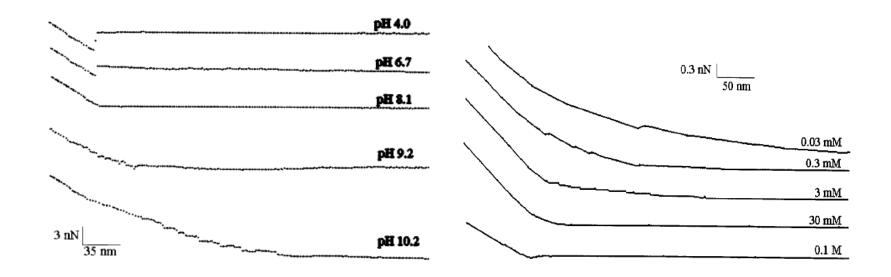






Science 288, 143(2000)

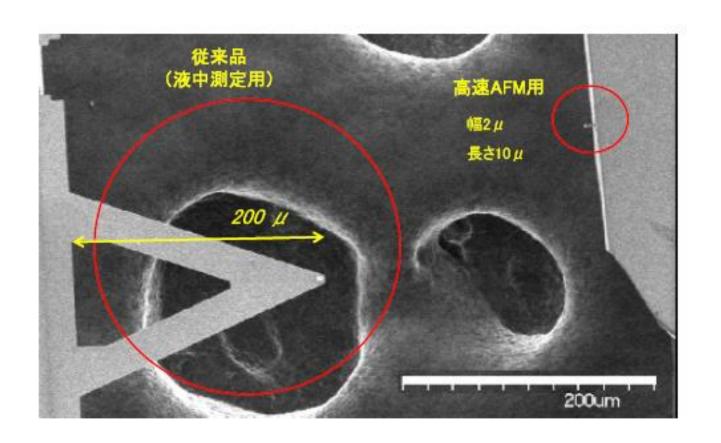
Force curve vs. pH and solution Concentration



Dependence of double-layer force on the surface charge of a stearic acid sample. Curves are acquired at different pH with a silicon nitride tip (tip radius between 50 and 100 nm). On the x-axis, the sample position in nm. On the y-axis, the force in nN.

Force~lisplacement approach curves associated with double-layer force between a silicon nitride tip and mica in KC1 solutions of different concentration. The tip radius is estimated between 50 and 100 nm. On the x-axis, the sample position in nm. On the y-axis, the force in nN

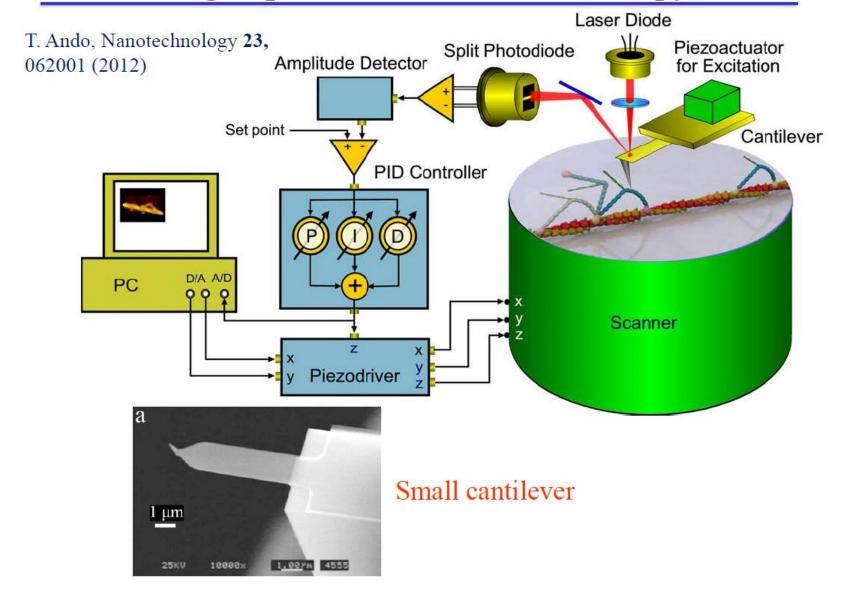
AFM probe for high speed imaging



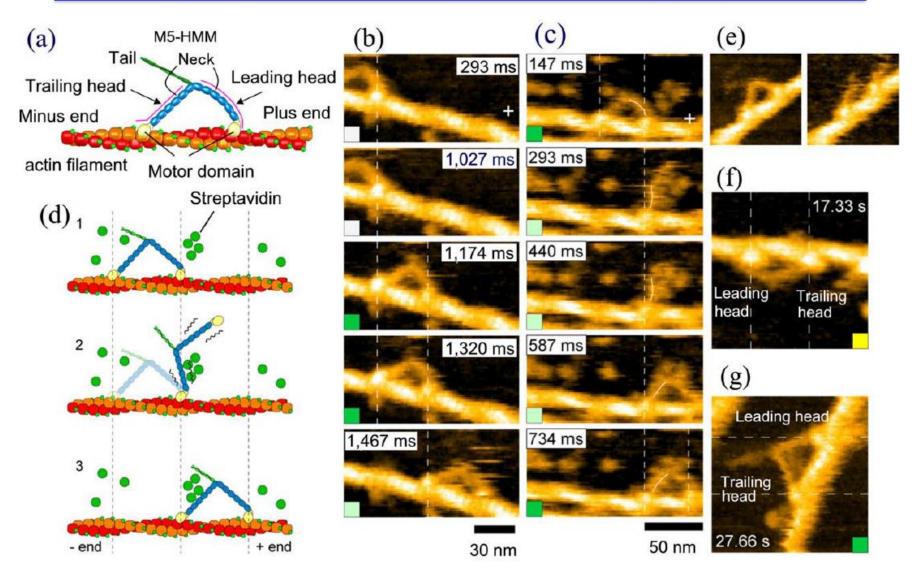
株式会社 生体分子計測研究所

RIBM (Research Institute of Biomolecule Metrology)

High-Speed Atomic Force Microscopy

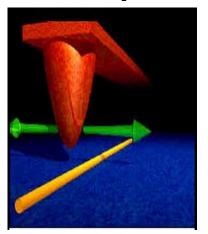


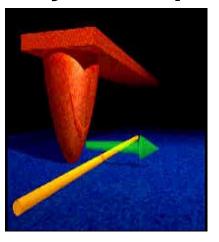
High-Speed AFM Images of Walking Myosin V

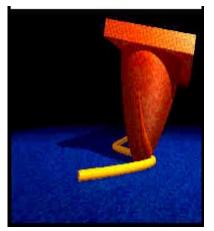


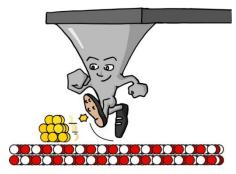
T. Ando, Nanotechnology 23, 062001 (2012)

Manipulation by AFM tip

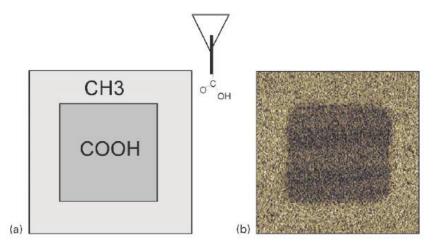






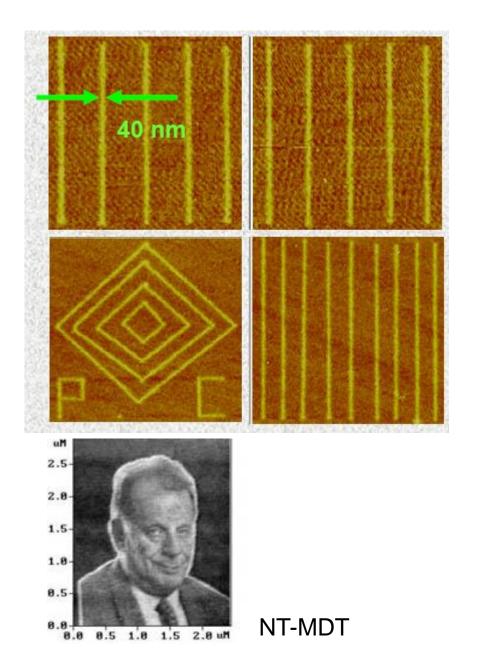


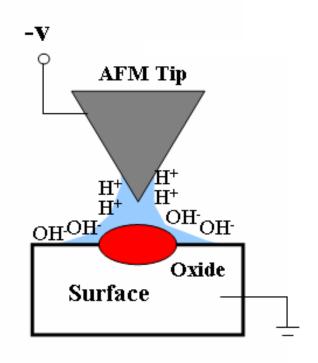
Chemical Characterization



Tip functionialization

AFM oxidation lithography



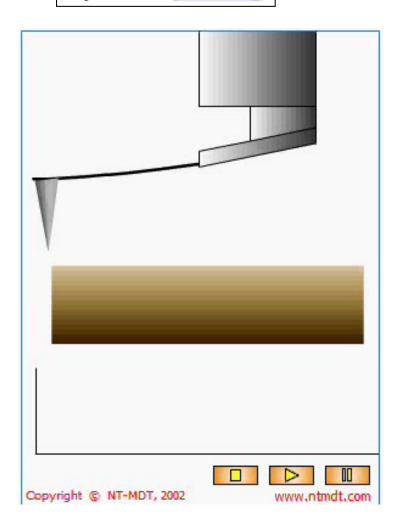


$$H_2O \xrightarrow{E-field} H^+ + OH^-$$

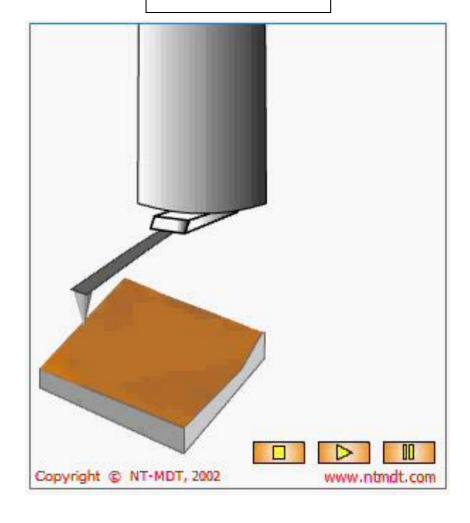
Oxidation

Nanolithography with force control

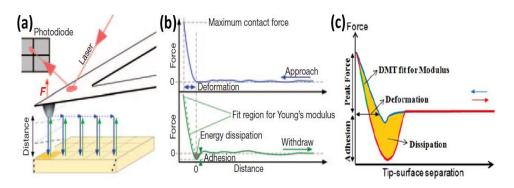
Dynamic plowing



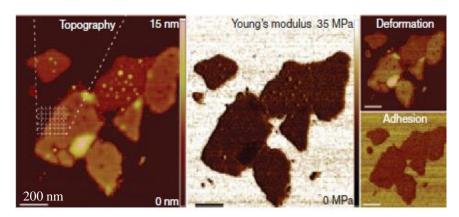
Scratching



Force-Distance (FD) Curve-based AFM



Multiparametric maps of native purple membrane with PFT mode

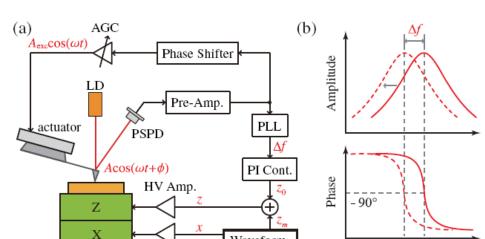


Y. F. Dufrene et al. Nature Methods 10, 847 (2013)

- In 3D force mapping, a tip was scanned in Z as well as in XY to cover the whole 3D interfacial space.
- The sample is modulated in the vertical Z direction with an amplitude of tens to hundreds of nanometers with a sine or triangle wave faster than the bandwidth of the Z distance regulation.
- The vertical Z-movement results in cycles of approaching and retracting traces that lead to force—distance curves
- Topography information is obtained from the height correction performed by the feedback loop to keep a constant 'peak' of force (constant deflection feedback)
- Force—distance curves can determinate surface mechanical information (stiffness, adhesion, deformation or dissipation)
- Soft cantilever (k~ 1 N/m) used for this mode.

(a) 1D-SFM tip tip trajectory sample

3D-SFM mapping

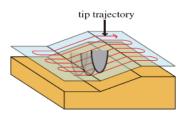


Waveform

Generator

PRL 104, 016101 (2010) Fukuma lab, Kanazawa university

(b) 2D-SFM



scanner

Typical imaging condition:

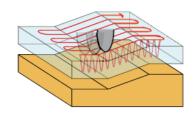
➤ Constant height feedback
➤ Z-Modulation amplitude < 2 nm

➤Z-Modulation frequency < 200 Hz

➤ Line scan rate = 12.2 nm/s

>64 * 64 * 256 pixels for XYZ imaging

(c) 3D-SFM



- For the scan in Z, a small vertical vibration (< 2 nm) was modulated with a sine wave faster than the bandwidth of the Z distance regulation.

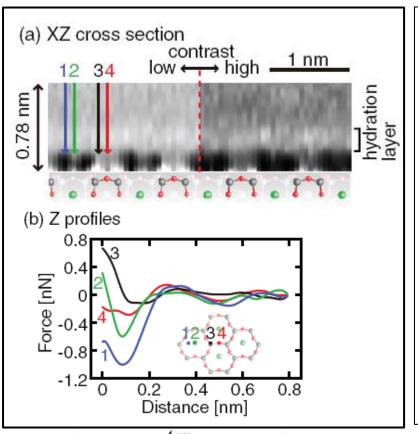
 $f_0 f_0$

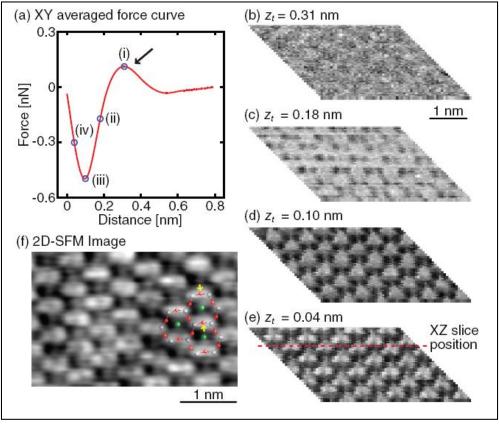
Frequency

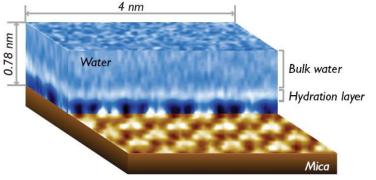
- The 3D △f image was constructed from either approaching or retracting Z profiles at each XY positions and the 2D height image (constant △f feedback) could be obtained simultaneously.
- Stiff cantilever ($k \sim 40 \text{ N/m}$) used for this mode.

Atomic-Scale Distribution of Water Molecules at Mica-Water Interface Visualized with 3D-SFM

PRL 104, 016101 (2010), Fukuma et al.



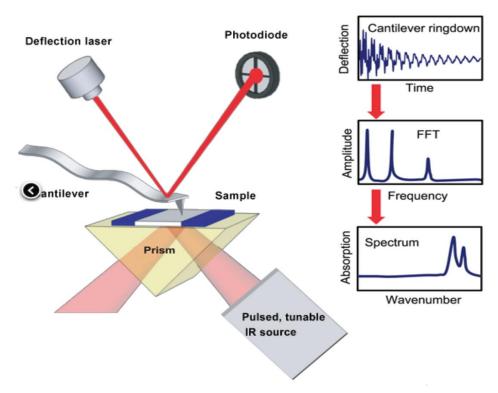




- **➤1D** profiles of hydration force
- **≻2D** images of hydration layers
- ►3D distribution of water molecules

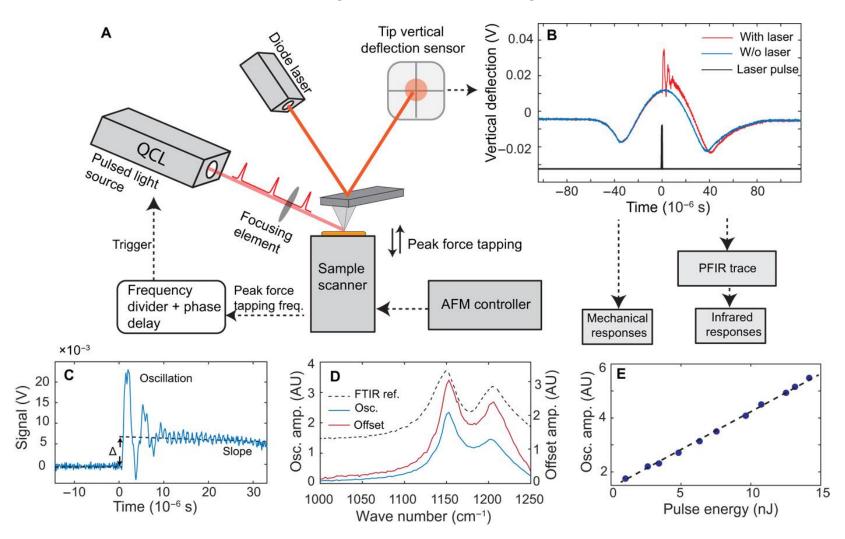
Recent development: AFM-IR system

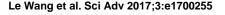
AFM-IR can perform IR spectroscopic chemical identification with sub-100 nm spatial resolution



Scheme of the AFM–IR setup. The AFM cantilever ring-down amplitude plotted as a function of laser excitation wavelength produces the IR spectrum.

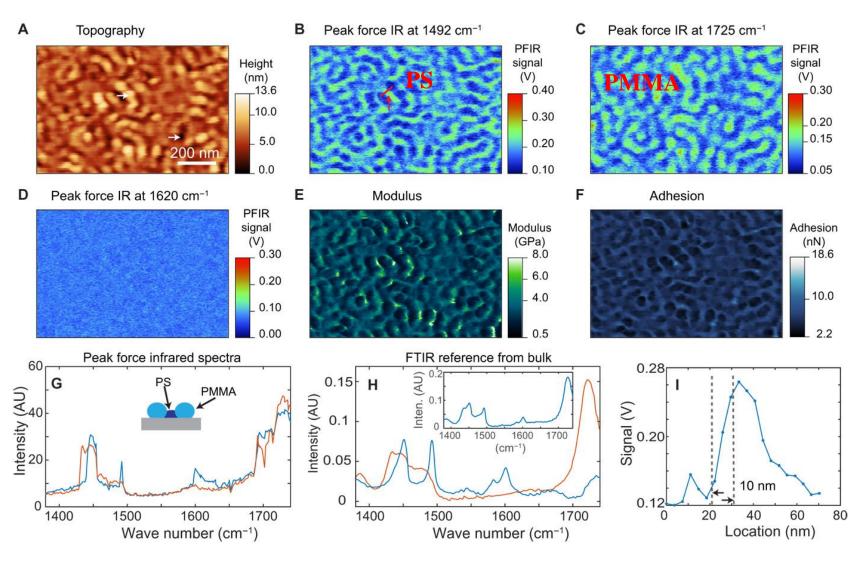
Operational scheme of PFIR microscopy (PeakForce-IR)







PFIR imaging of nanophase separation of a PS-b-PMMA block copolymer.



Le Wang et al. Sci Adv 2017;3:e1700255



- 1. All SPMs are based on the ability to position various types of probes in very close proximity with extremely high precision to the sample under investigation.
- 2. These probes can detect electrical current, atomic and molecular forces, electrostatic forces, or other types of interactions with the sample.
- 3. By scanning the probe laterally over the sample surface and performing measurements at different locations, detailed maps of surface topography, mechanical and electronic properties, magnetic or electrostatic forces, optical characteristics, thermal properties, or other properties can be obtained.
- 4. The spatial resolution is limited by the sharpness of the probe tip, the accuracy with which the probe can be positioned, the condition of the surface under study, and the nature of the force being detected.
- 5. Multi-parameters mapping based on force-distance curve-based AFM mode can obtain rich and useful information for surface mechanical characterization.