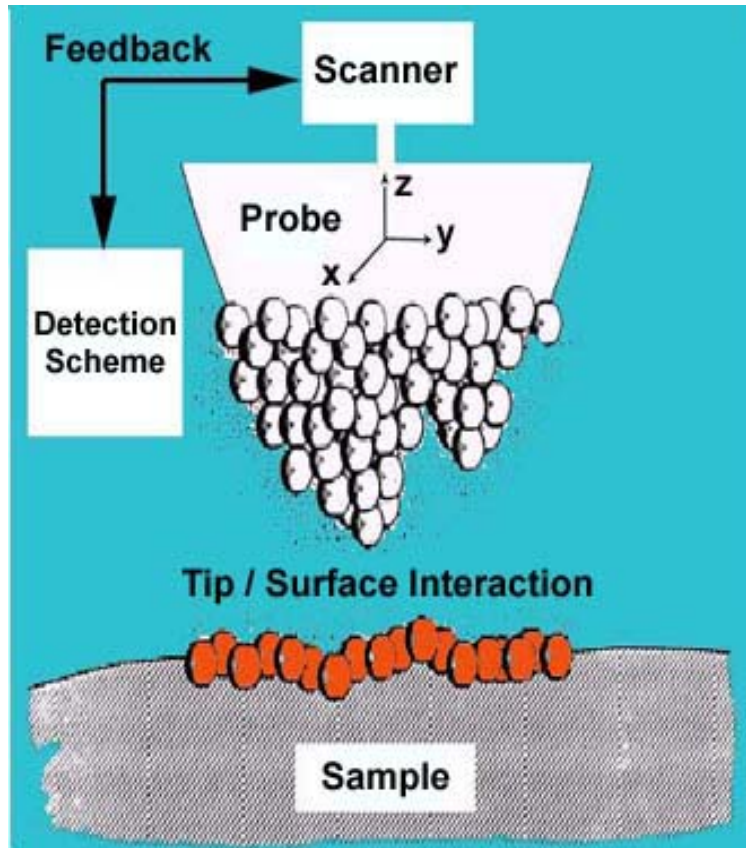# Scanning Probe Microscopy (SPM)

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)

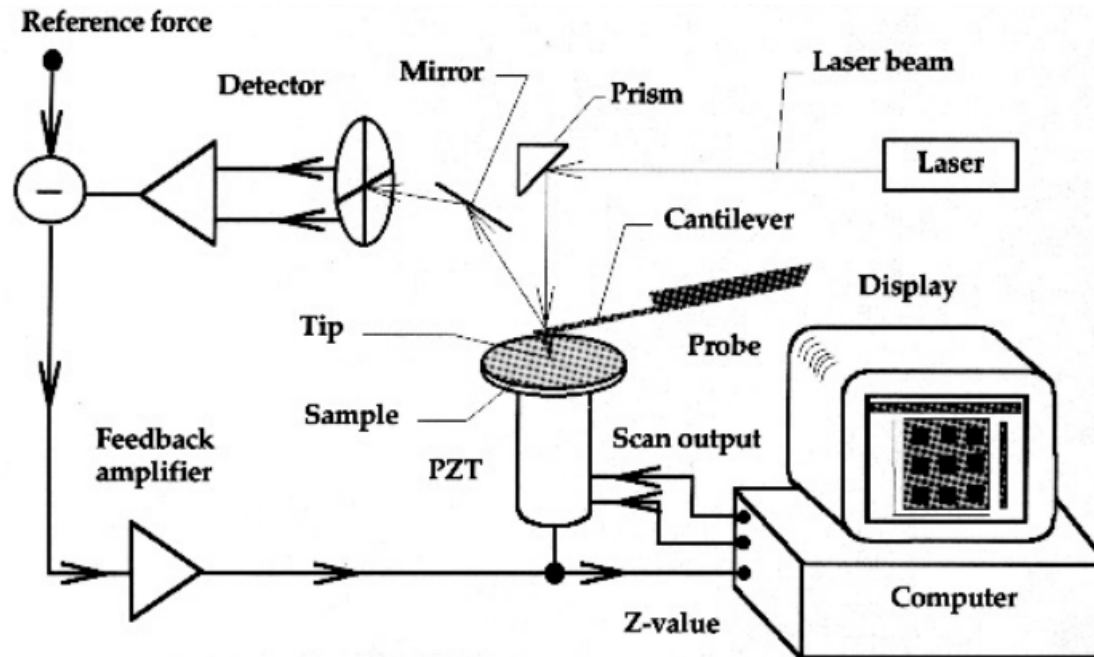--- Y. Martin, D. W. Abraham et al (1988)

Scanning Capacitance Microscopy (SCM)

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

Force Modulation Microscopy (FMM)

--- P. Maivald et al (1991)
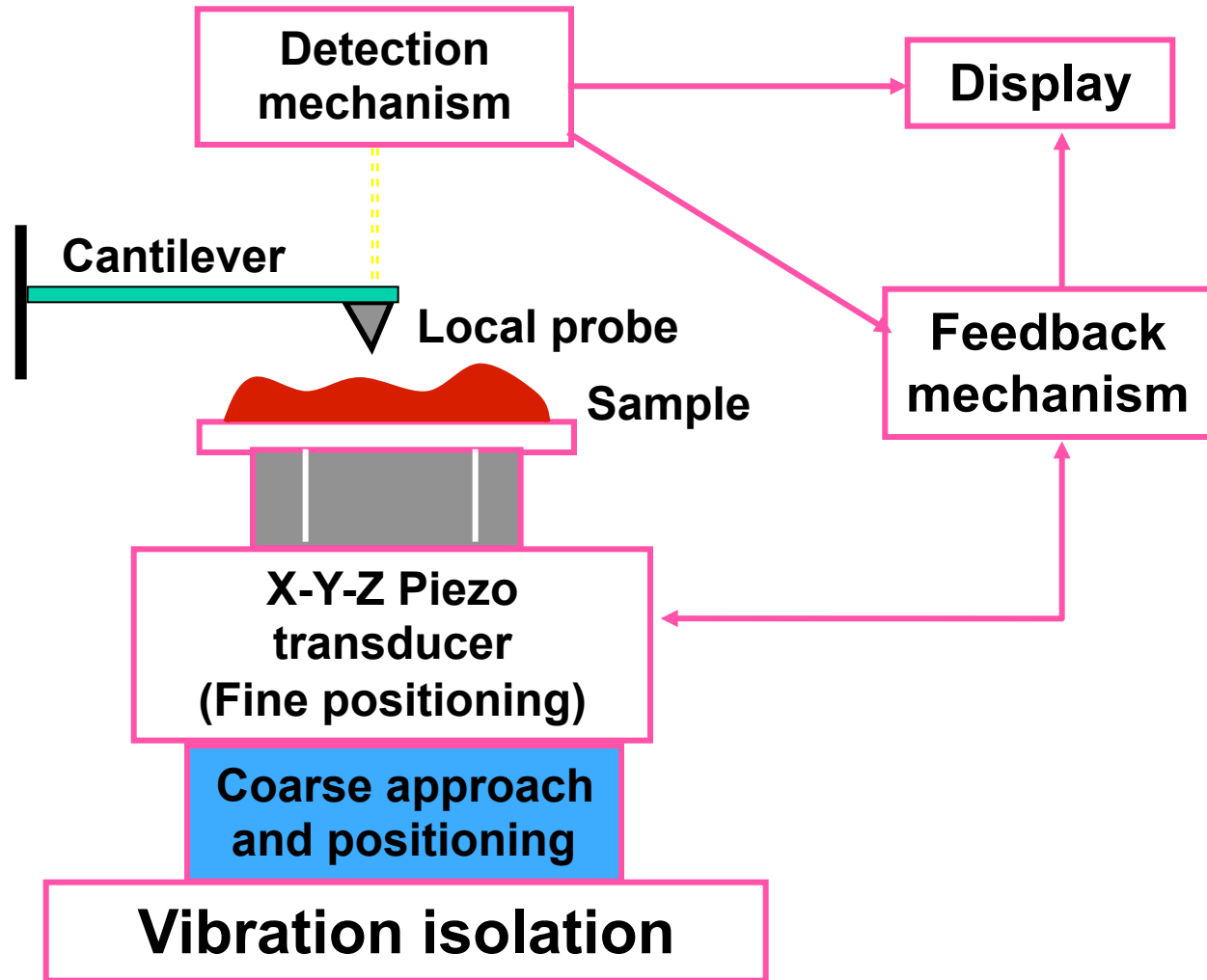
Atomic Force Microscopy (AFM)

$$F = k\Delta z$$

$$F = 10^{-9} - 10^{-6}\ N$$

$$k = 0.1 - 1\ N/m$$

References:

- G. Binnig, C. F. Quate, and C. Gerber, Phys. Rev. Lett. 56, 930 (1986).

- C. Bustamante and D. Keller, Physics Today, 32, December (1995).

- R. Wiesendanger and H.J. Güntherodt, *Scanning Tunneling Microscopy II* , Springer-Verlag, (1992).
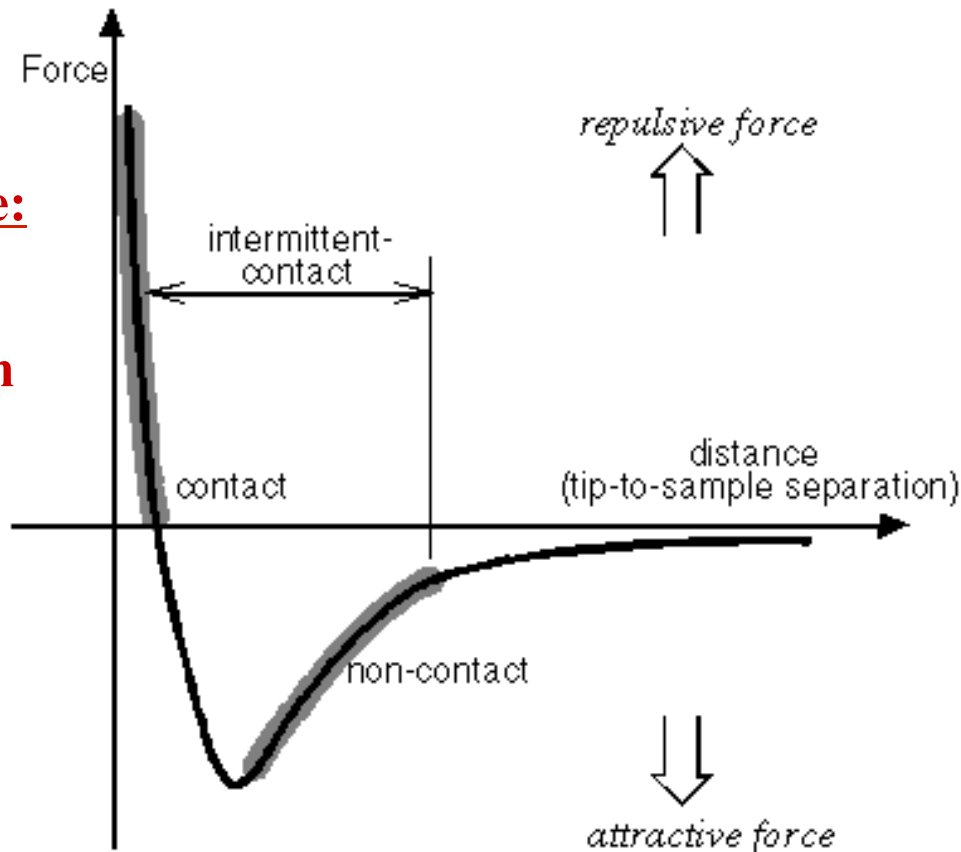
Structure of AFM

Interaction between the probe and sample
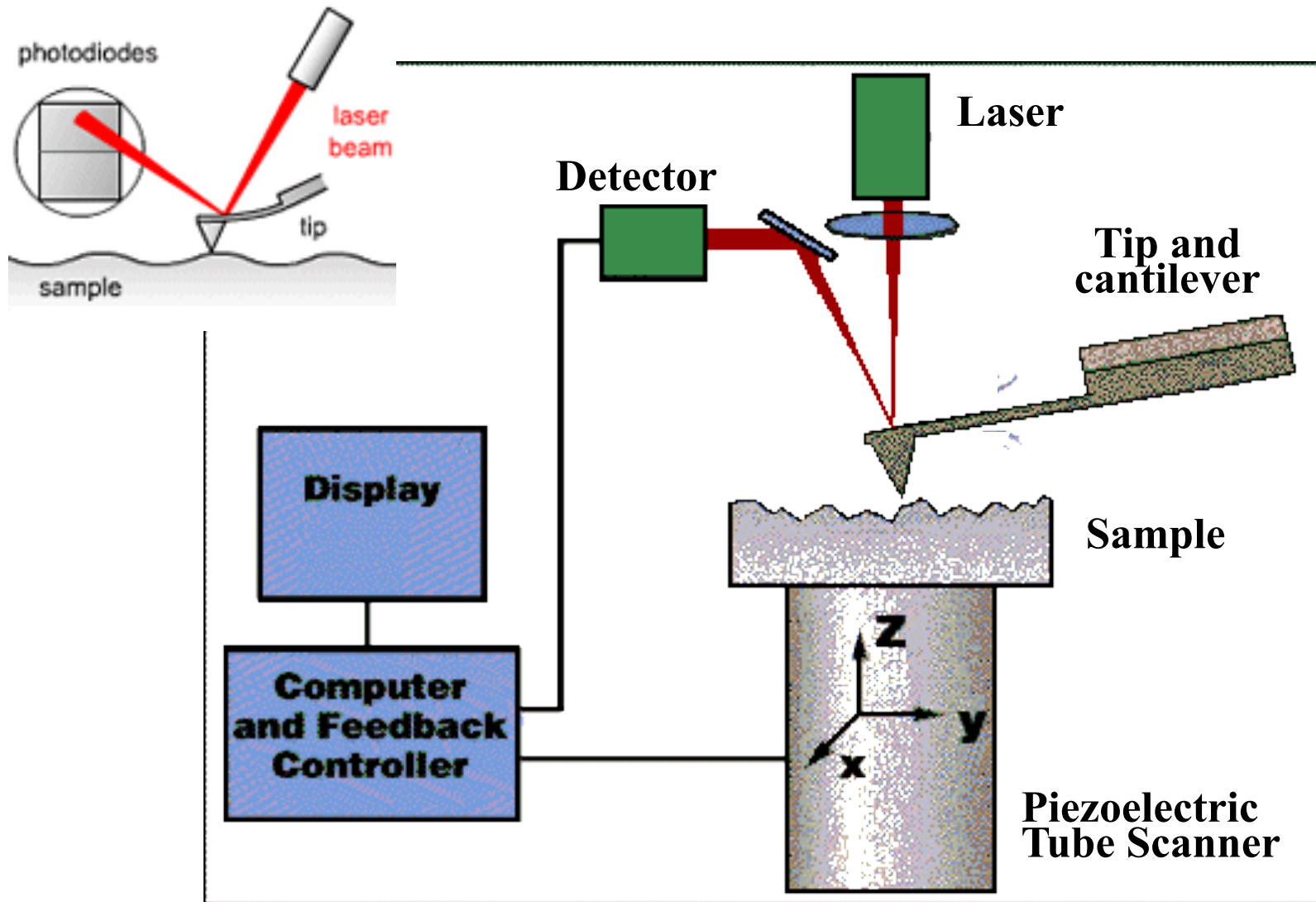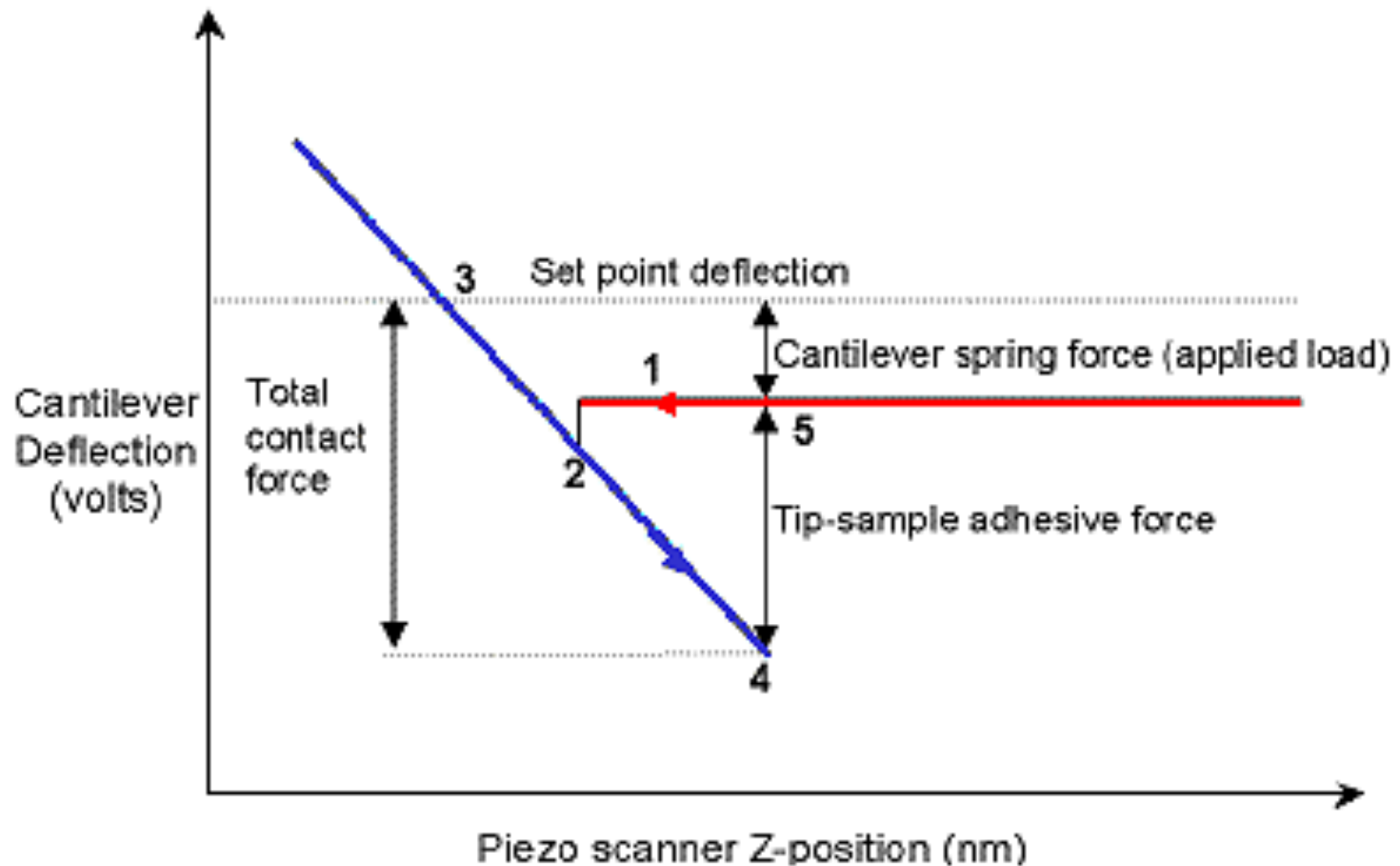

Short-range:

1) Bonding

2) Repulsion

Long-range:

1) Van der Waal

2) Capillary

3) Magnetic

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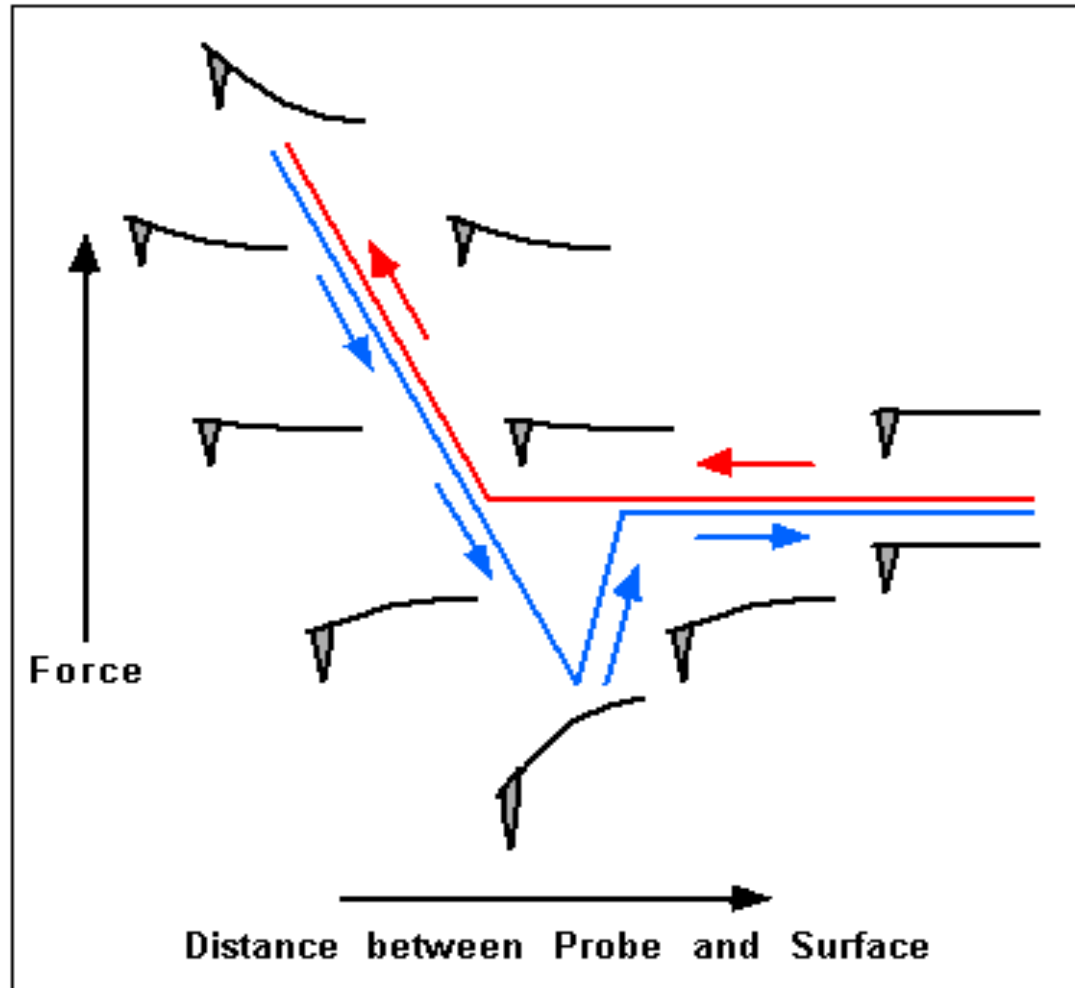
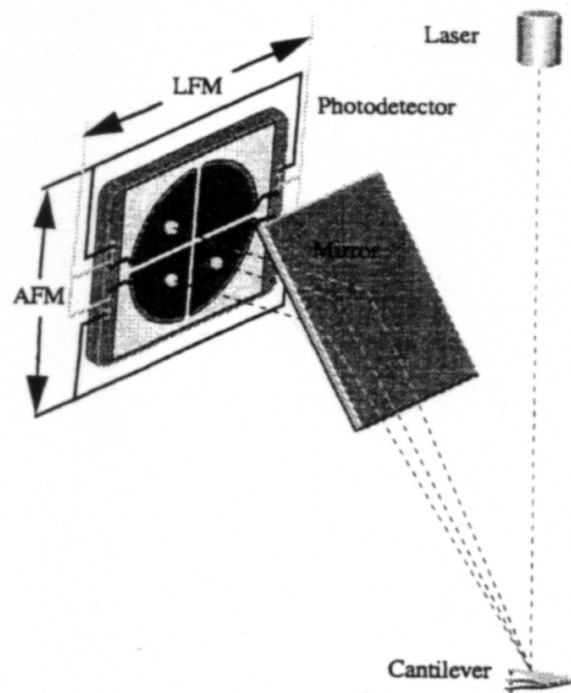Lennard-Jones potential $\phi(r) = -A/r^6 + B/r^{12}$

Core components of AFM

photodiodes

laser beam

tip

sample

Laser

Detector

Tip and cantilever

Sample

Display

Computer and Feedback Controller

Piezoelectric Tube Scanner

Z

y

x

Deflection of Cantilever vs Piezo displacement

Reaction of the probe to the force

Force

Distance between Probe and Surface

Position-sensitive Photo Diode (PSPD)
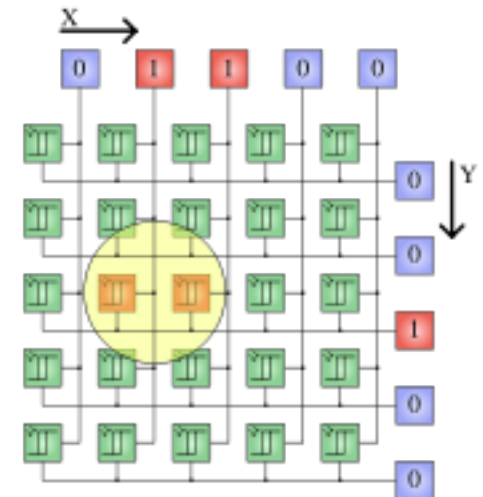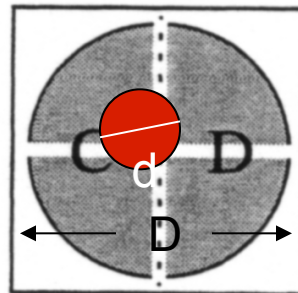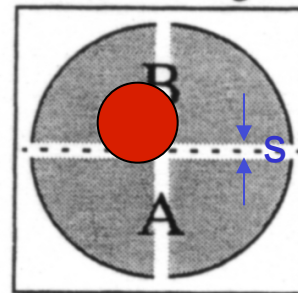
D ~ 10mm   d ~ 1mm   s ~ 0.01mm

Piezo Scanner

Three scanning modes of AFM

SFM contact mode scanned profile

SFM semicontact scanned profile

SFM noncontact mode scanned profile

sample

sample

sample

A ~ 50 - 1000 Å

A ~ 20 - 50 Å

**Contact Mode AFM**

**Semicontact Mode AFM**

Non-contact Mode AFM

(Tapping mode)
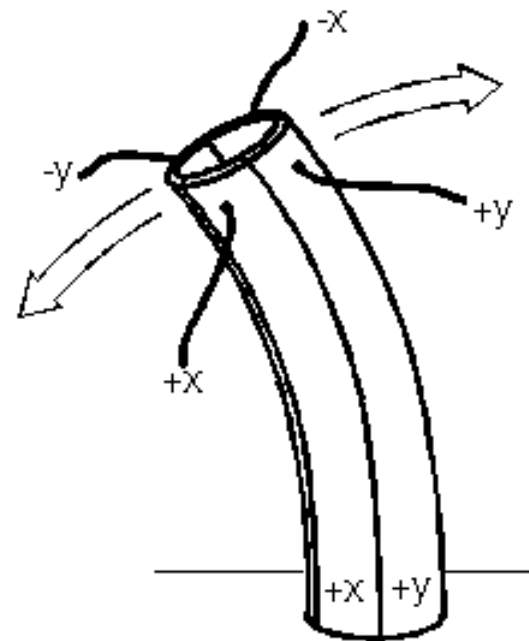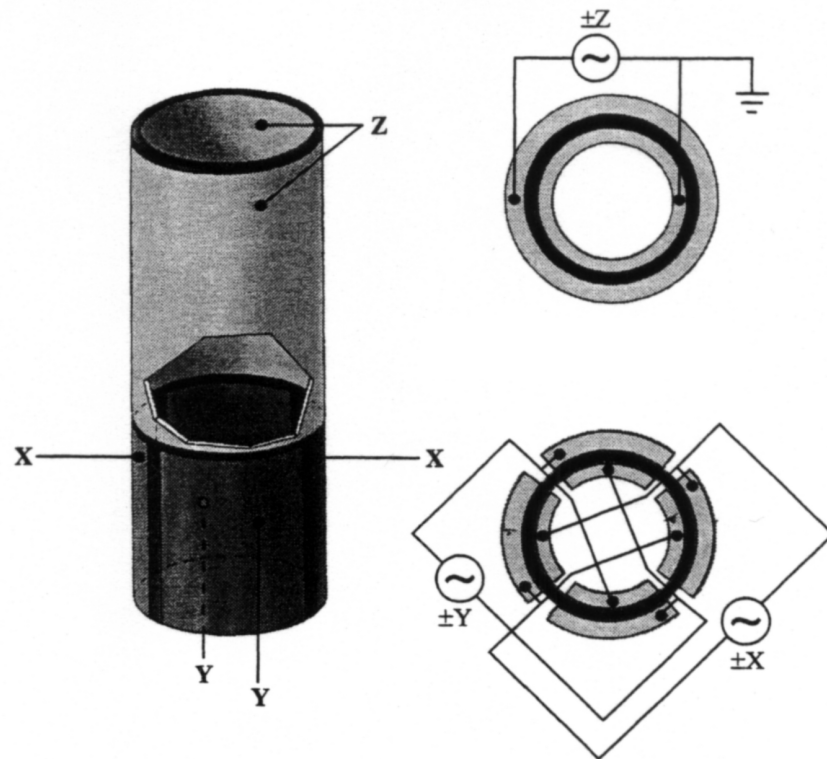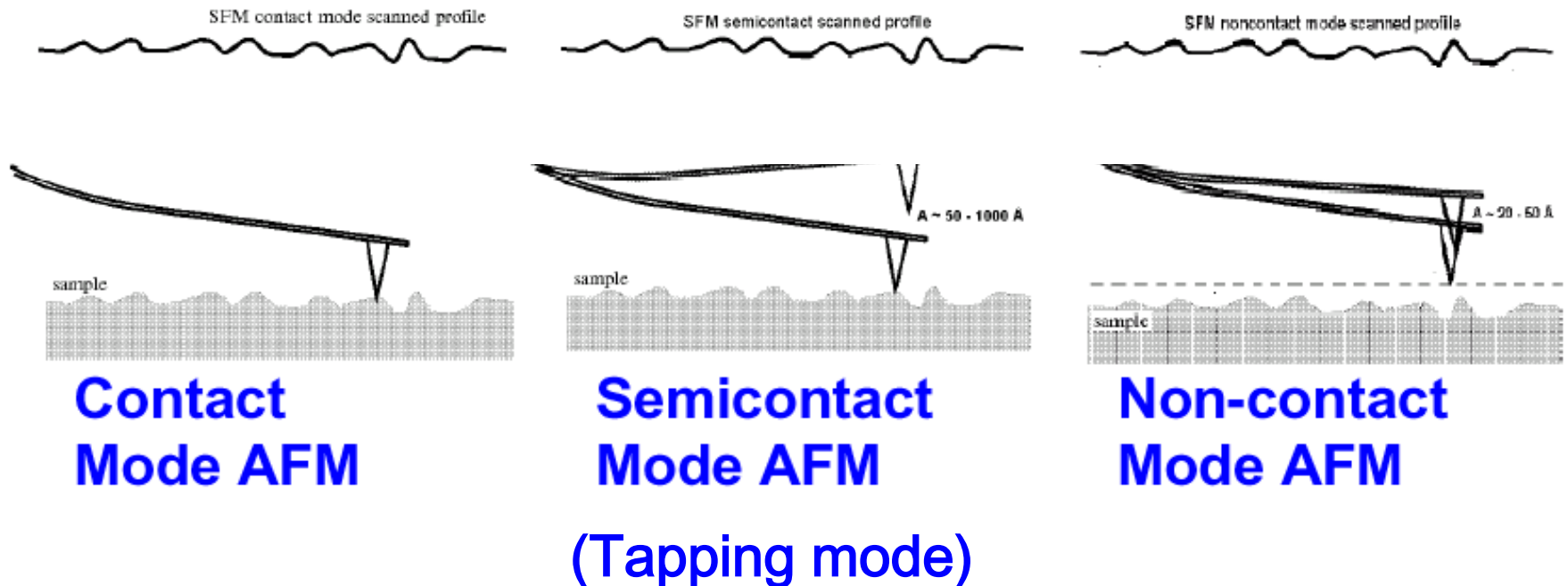
Two imaging methods in contact mode

- 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
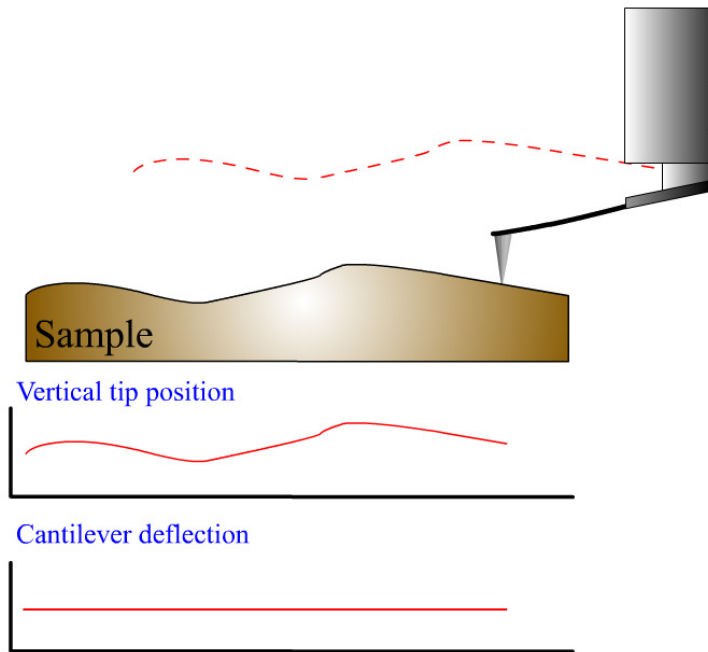
Constant-force mode
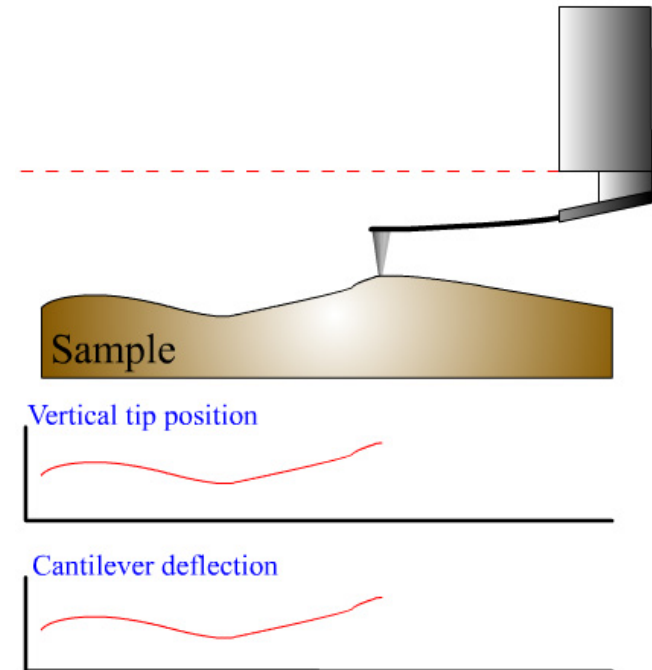
Constant-height mode

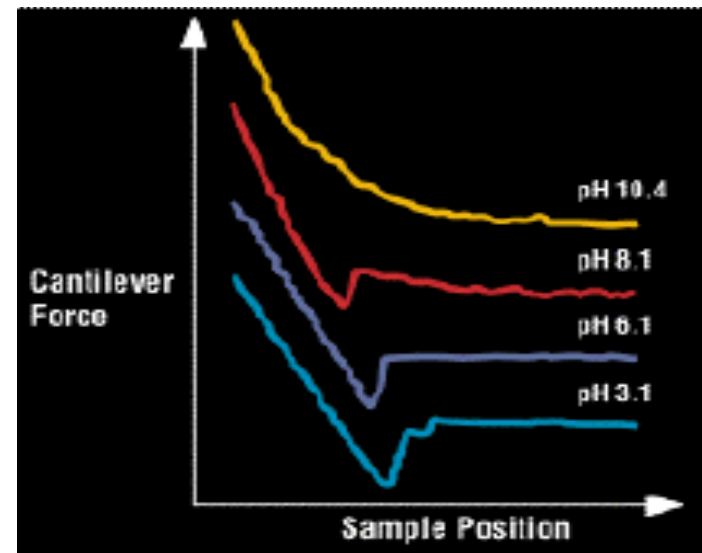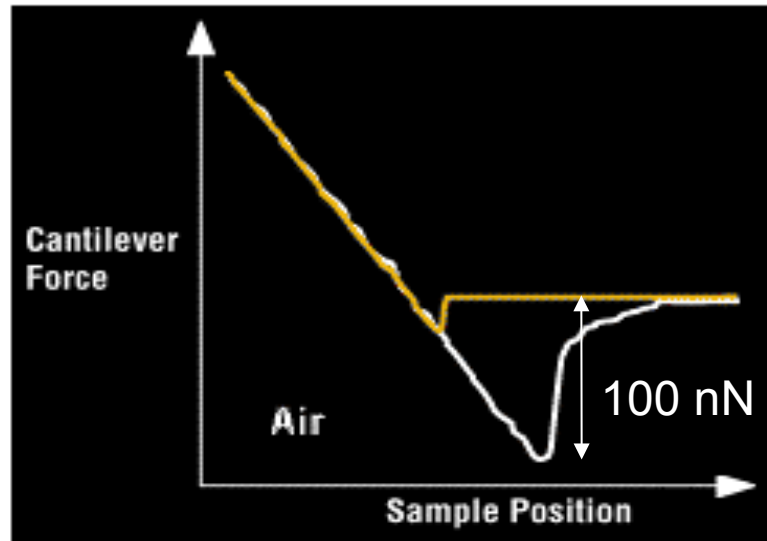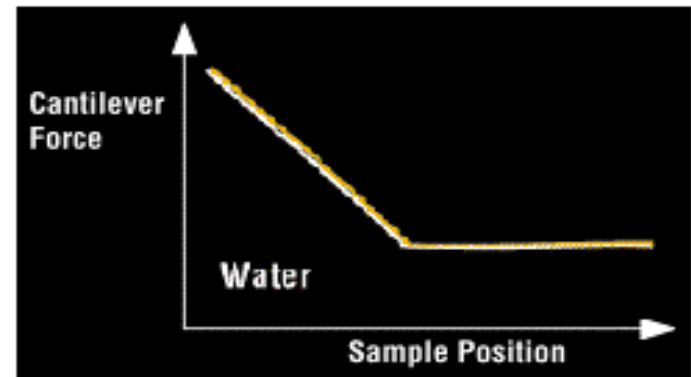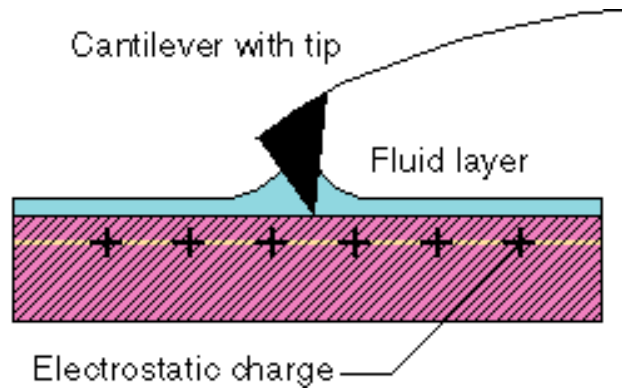# Constant-force scan vs. constant-height scan

Constant-force

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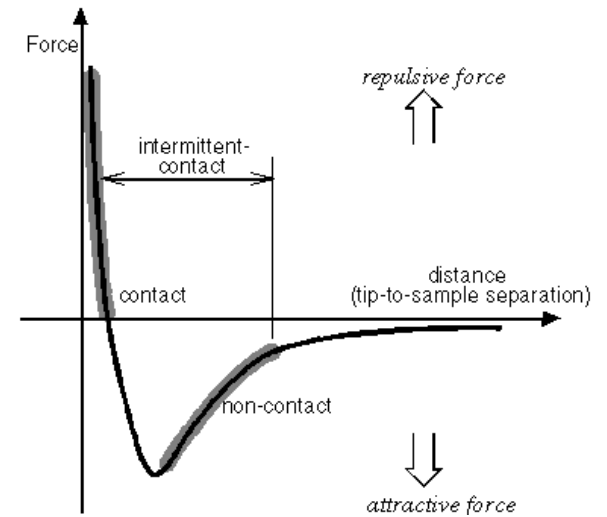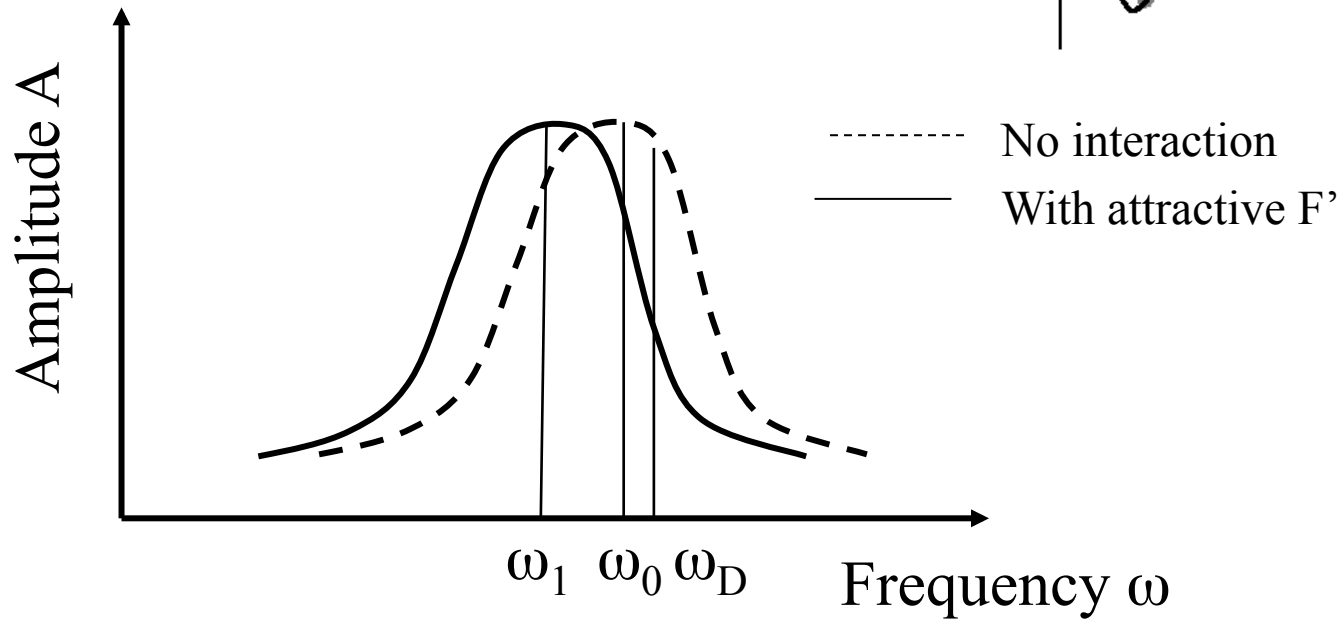 - Slow response

Constant-height

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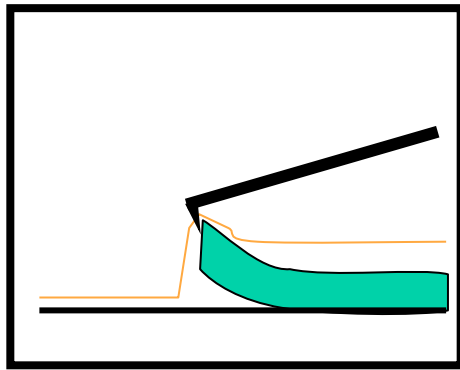 - Varied force

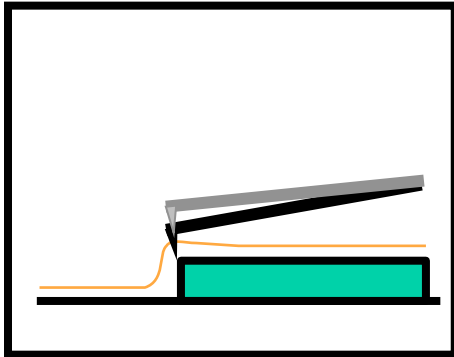# Problems with the contact mode

AC imaging mode

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

Force

repulsive force

intermittent-contact

contact

distance (tip-to-sample separation)

non-contact

attractive force

Amplitude A

- - - - - No interaction

——— With attractive F'

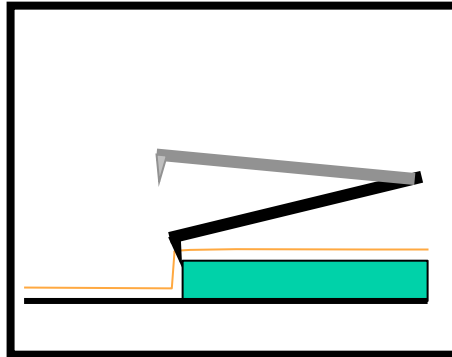ω_1 ω_0 ω_D Frequency ω

Comparison of three scanning modes
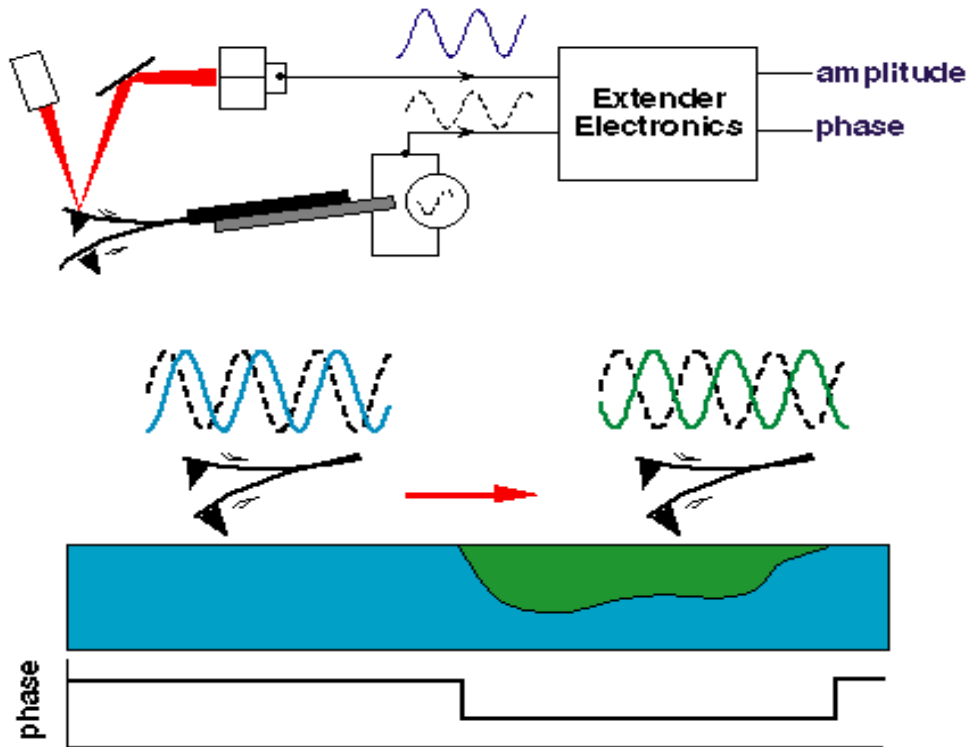

Contact

Non-contact

Intermittent-contact

Tapping mode

Amplitude Detector

High Resolution Oscillator

System Controller

Laser

Photo-detector

Oscillation Piezo (10K – 1MHz)

Silicon Cantilever with Tip

Sample

"Free" amplitude (> 20 nm)

Fluid layer

"Tapping"

Amplitude reduced
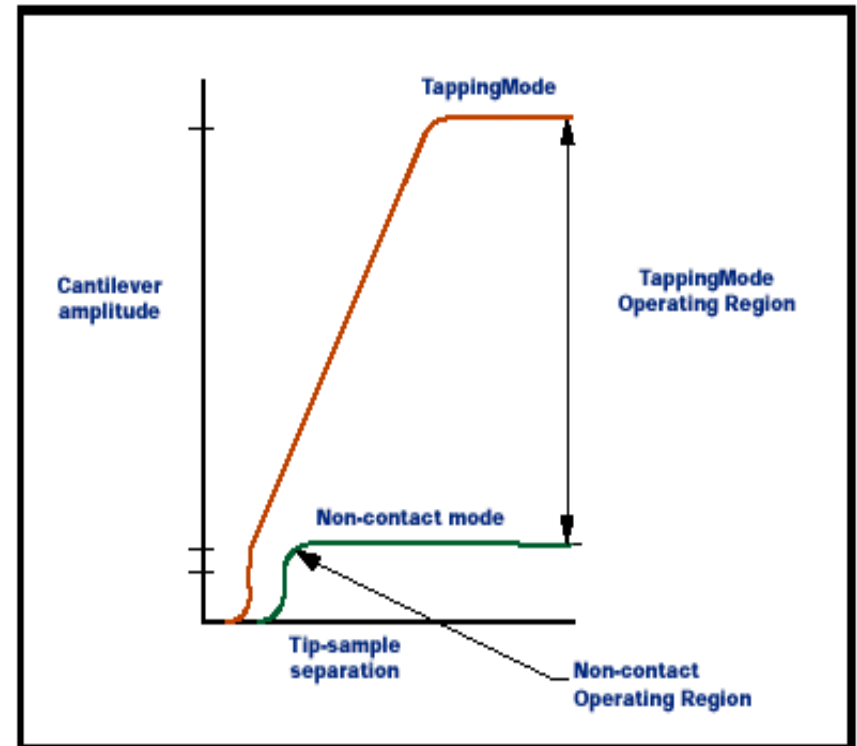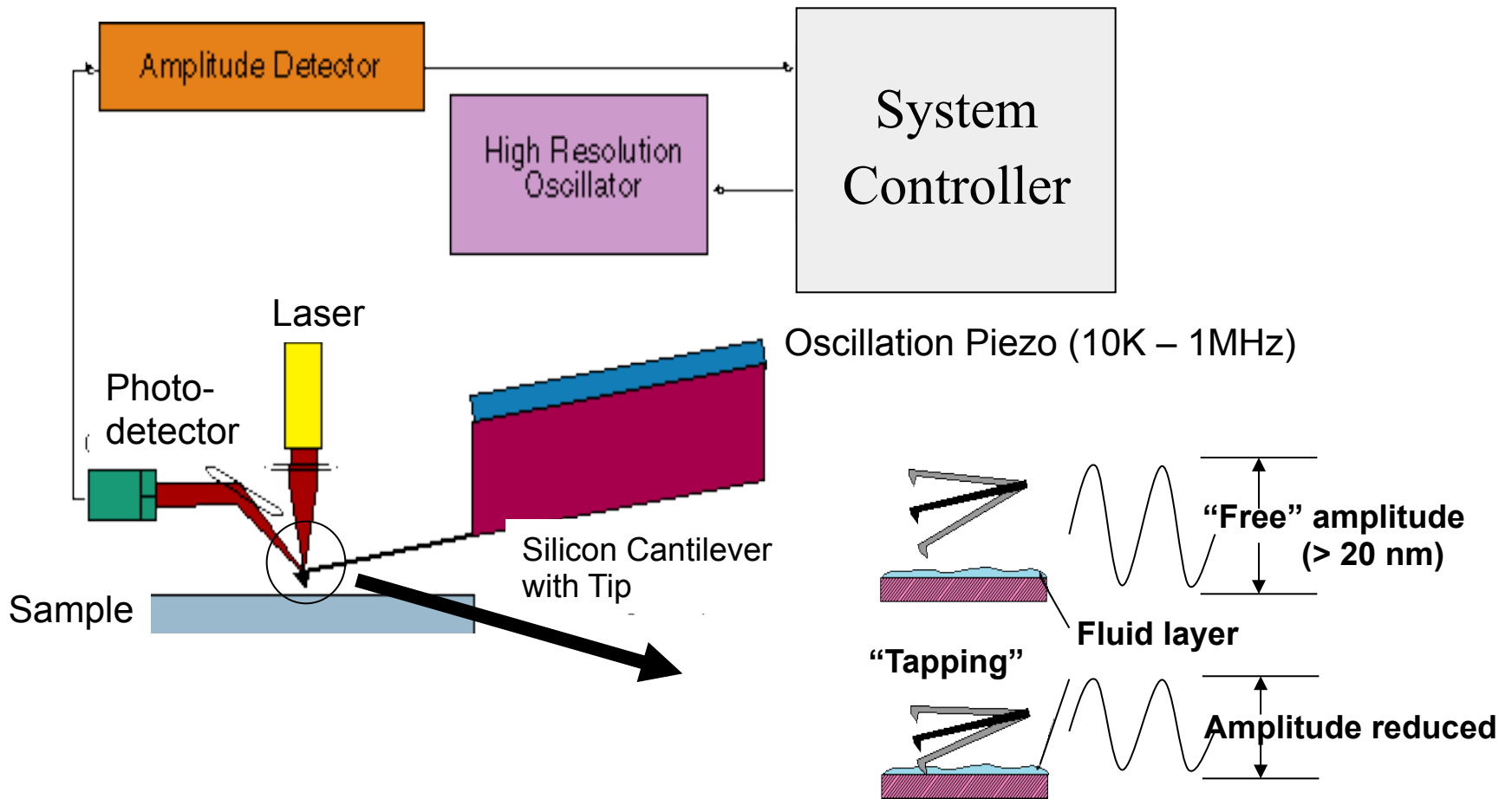
Three Types of Data Collected in Tapping Mode

3) Amplitude Data: output signal measuring RMS value of laser y- axis position on detector

Laser

xyz Scanning Piezo Tube

1) Height Data: z-axis position monitored by input voltage to piezo tube scanner

Four quadrant photo diode detector

Piezo driver vibrates cantilever at resonance frequency

2) Phase Data (ii): phase of feedback signal compared to phase of drive signal

2) Phase Data (i): phase of drive signal compared to phase of output signal from photo diode detector

Silicon Cantilever

Silicon Tip
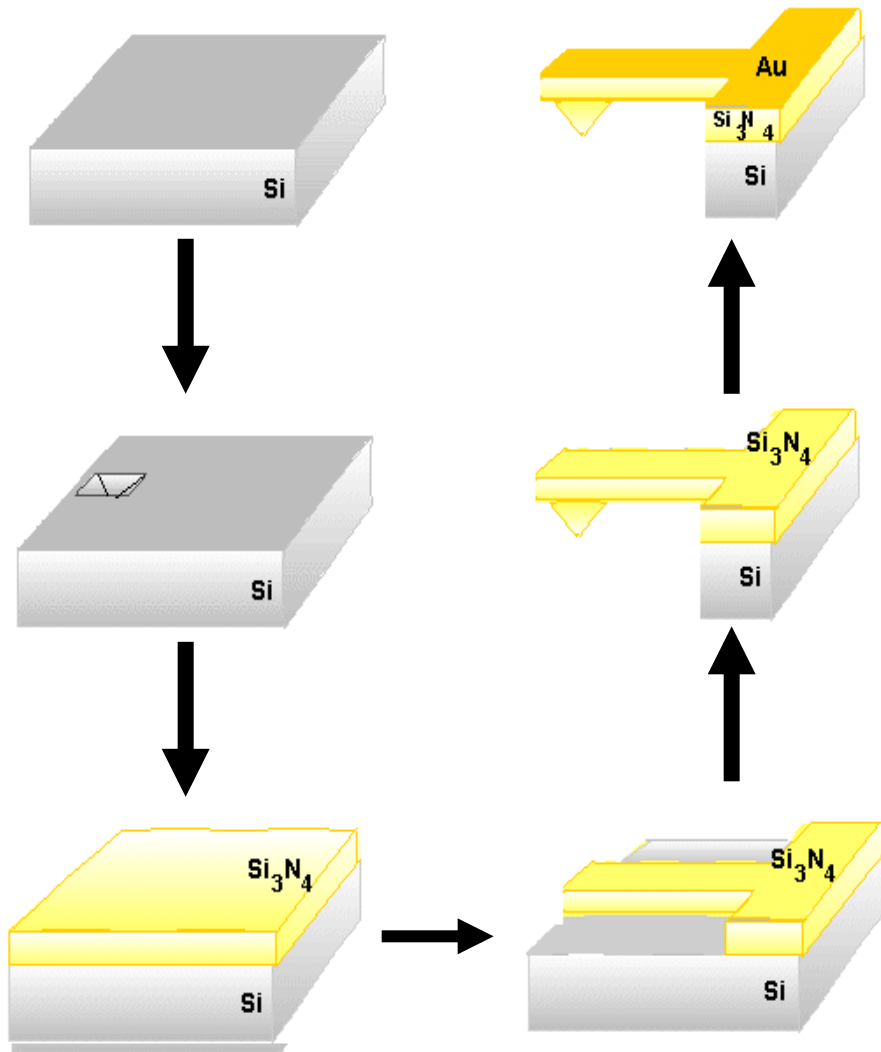
Sample Surface

Images by tapping mode

Topography   Phase
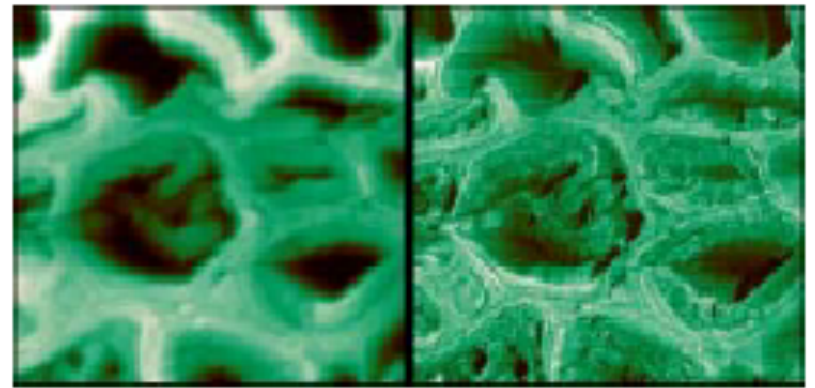
AFM image of a fresh
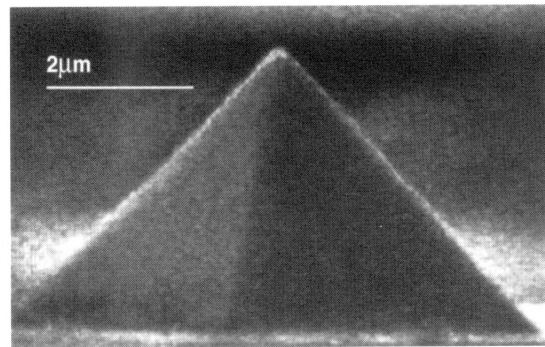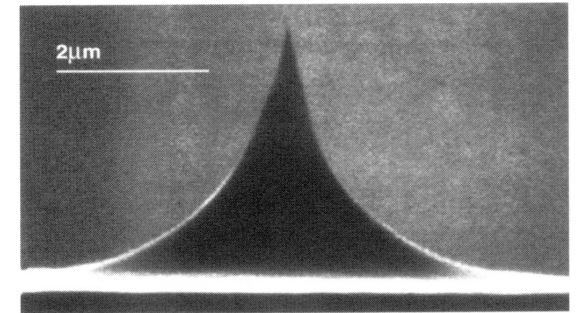Alfalfa root section

Fabrication of AFM probes

Typical Tip Dimension:
$150\mu m \times 30\mu m \times 0.5\mu m$
$k \sim 0.1$ N/m
Materials: Si_3N_4

Typical Tip Dimension:
$150\mu m \times 30\mu m \times 3\mu m$
$f_r \sim 100$ kHz
Materials: Si

V-shaped

100 μm
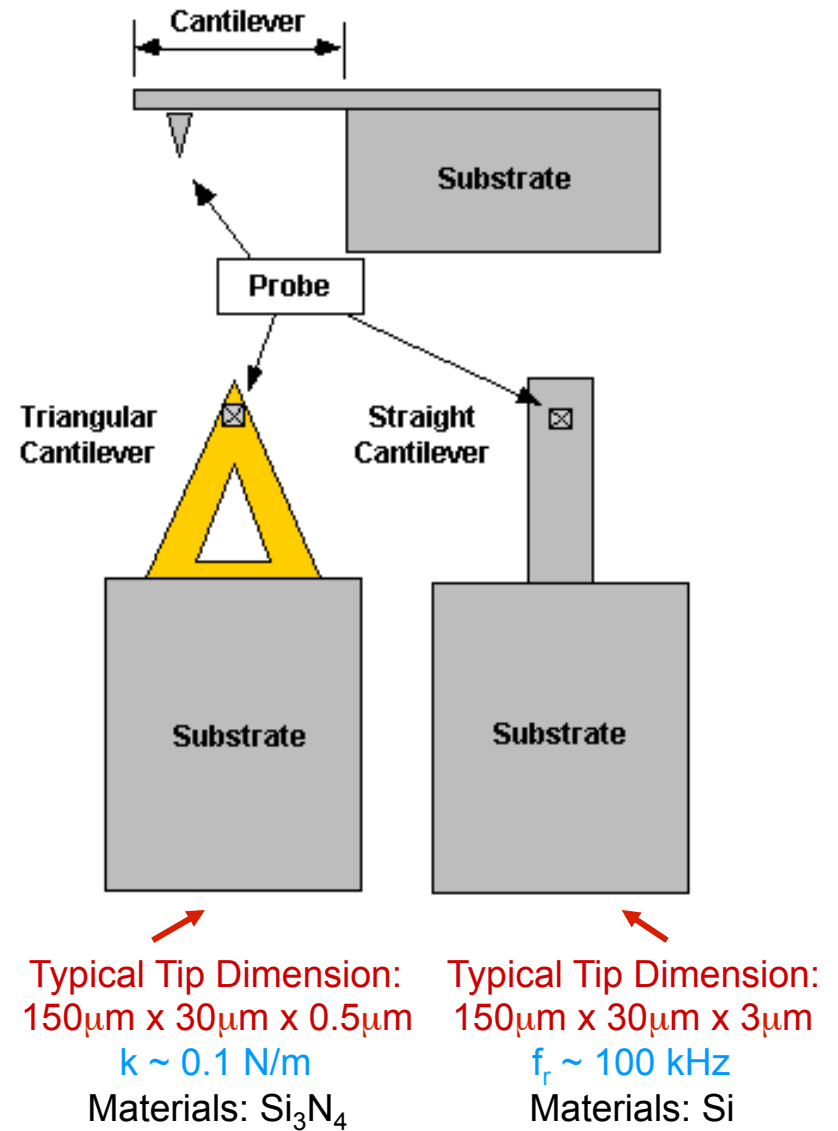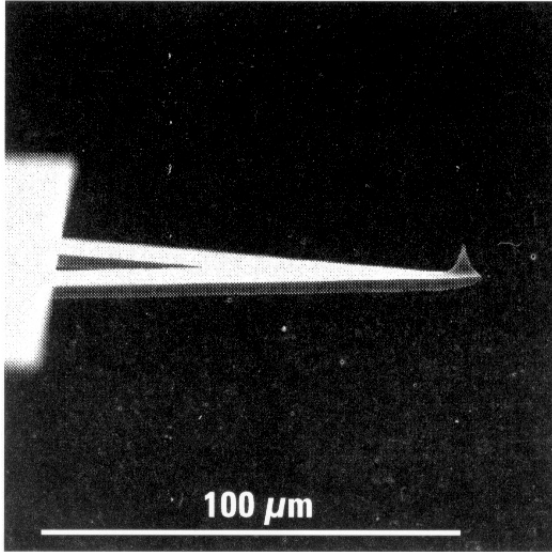
Materials: Si, SiO$_2$, Si$_3$N$_4$
Ideal Tips: hard, small radius of curvature, high aspect ratio

Pyramid Tip

2μm

Ultrasharp Tip

2μm

Rectangular-shaped

100 μm

Diamond-coated Tip

5 μm

2.11kX   25kV WD:21mm   S:00000 P:00015
20μm
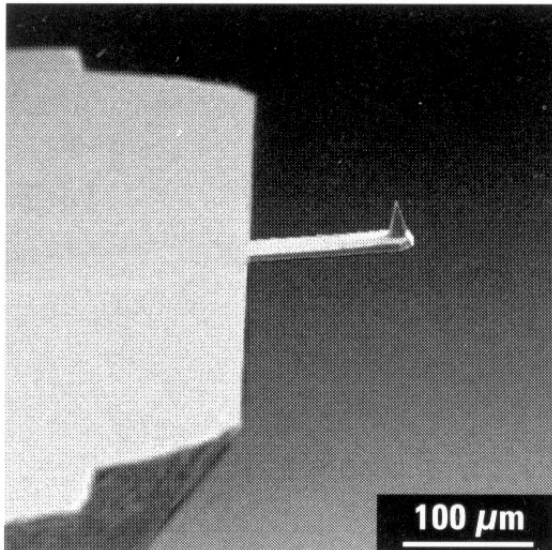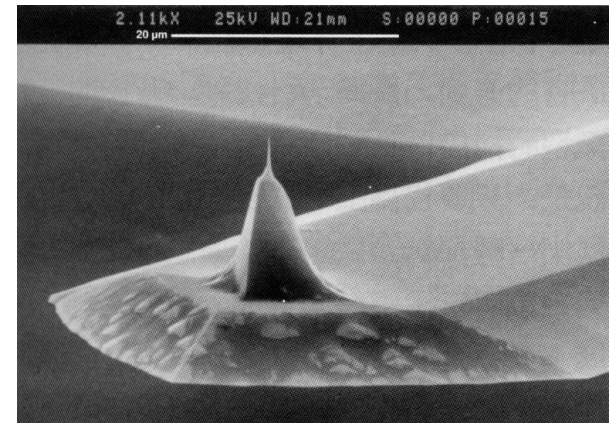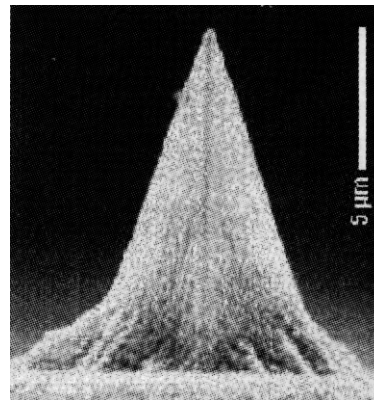
Criteria for AFM probe

1) Small spring constant (k)   F = k Δz

   To detect force of ~ 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 apex
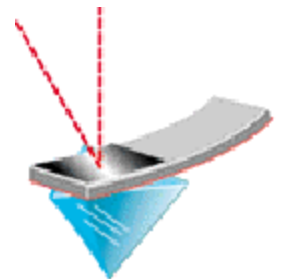
   To better define the tip-sample interaction

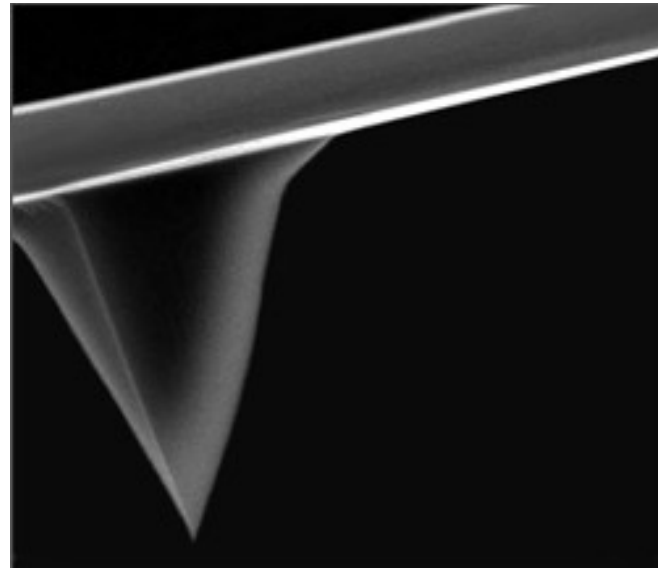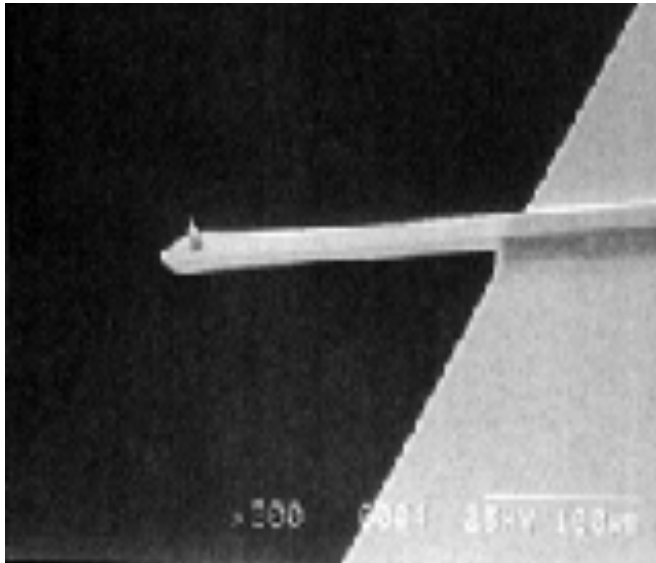# Tip of small shear force

(for Contact mode)

Typical Tip Dimension:
150μm x 30μm x 0.5μm
$k \sim 0.1$ N/m
Materials: Si_3N_4

Tip of high resonant frequency

(for Tapping mode)

Typical Tip Dimension:
150μm x 30μm x 3μm
f_r ~ 100 kHz
Materials: Si

AFM versus STM

1. 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.
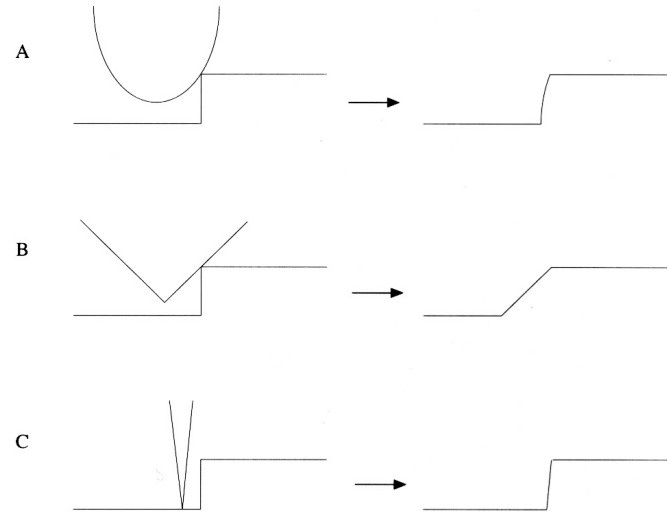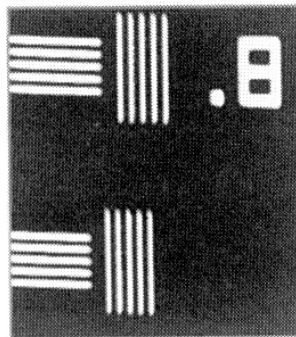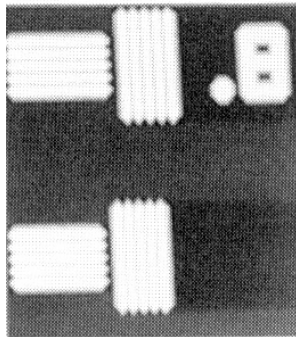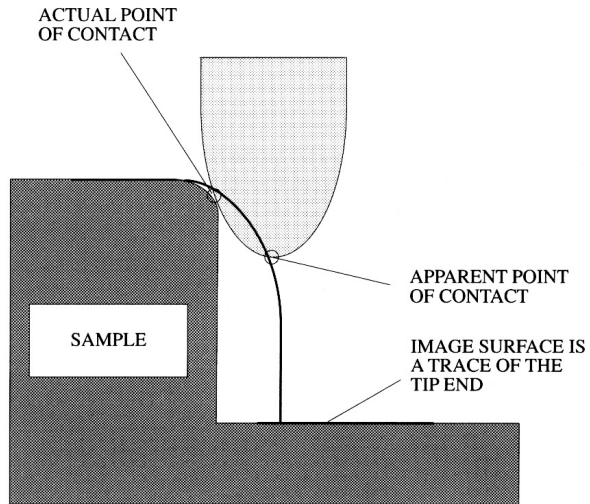
AFM versus EM

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.
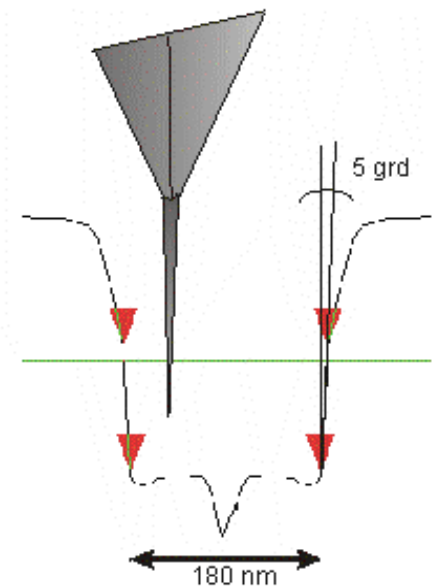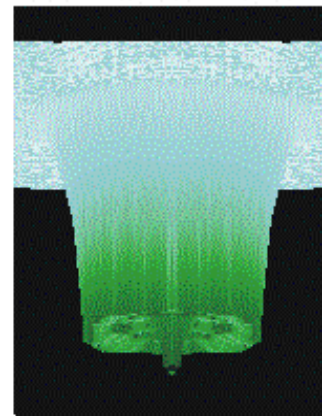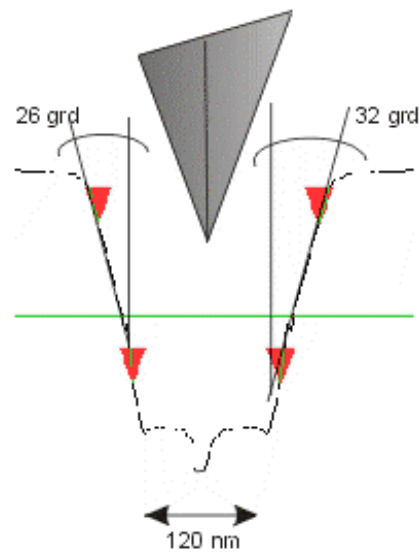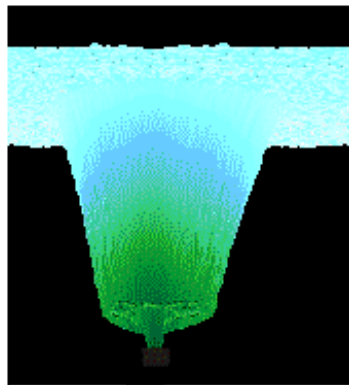
AFM versus Optical Microscope

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.
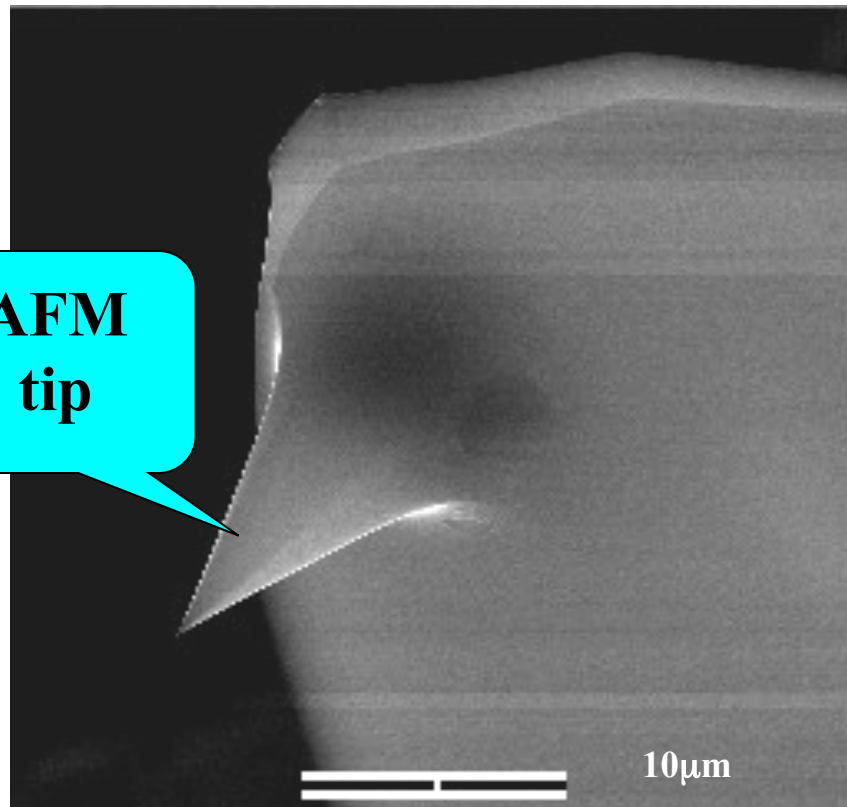
Effects of the Tip Shape

ACTUAL POINT OF CONTACT

APPARENT POINT OF CONTACT

IMAGE SURFACE IS A TRACE OF THE TIP END
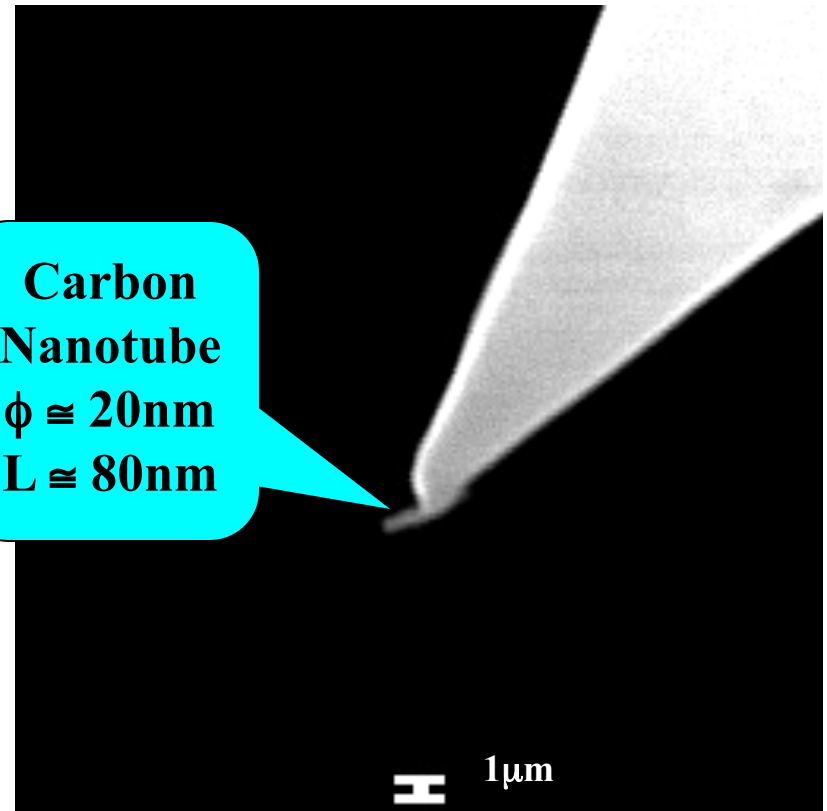
SAMPLE

A

B

C

A

B

A

B
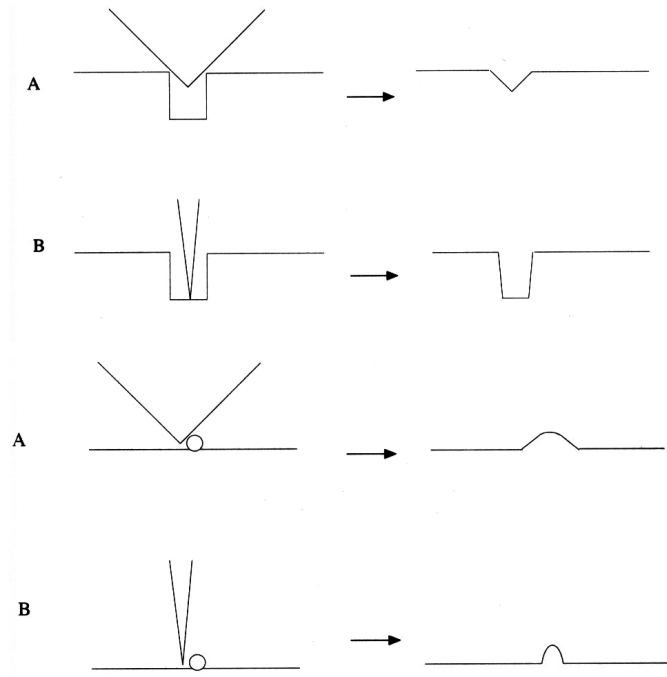
Ultra-sharp tip

AFM Tip + Carbon Nanotube

Image of high aspect ratio

170nm
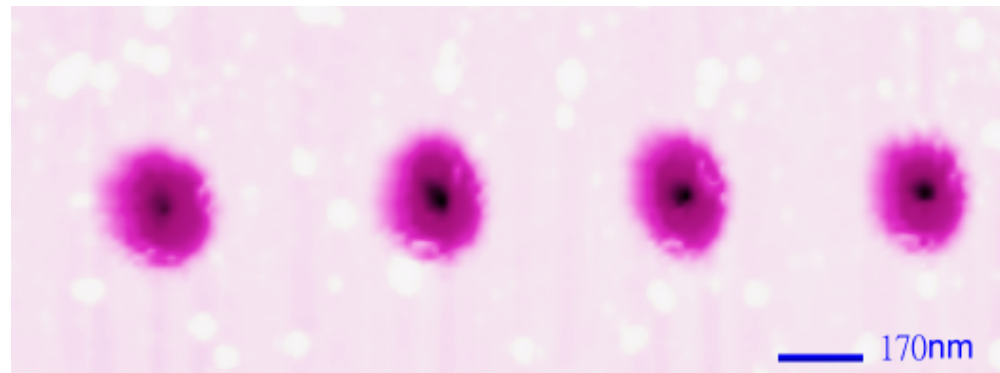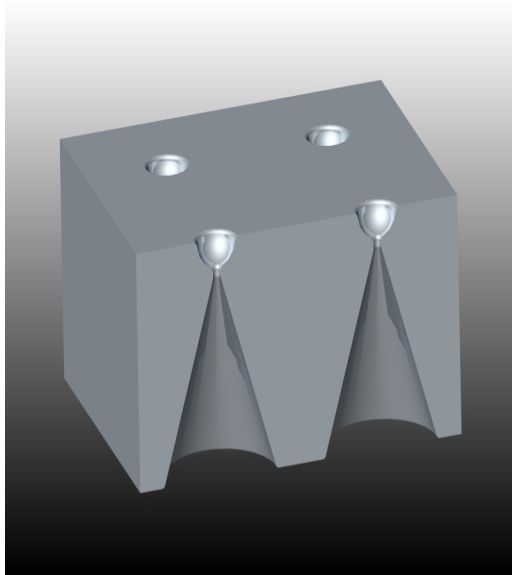
AFM images
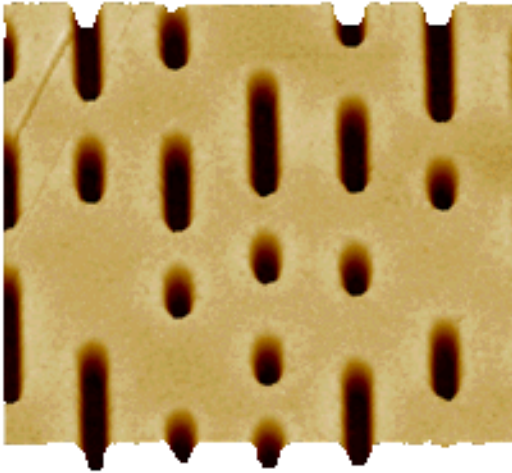
CD pits

Integrated circuit
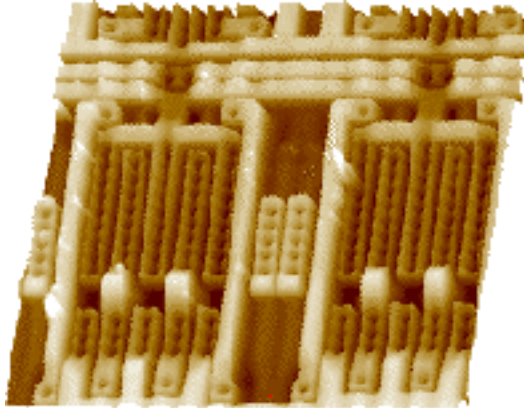
Chromosomes
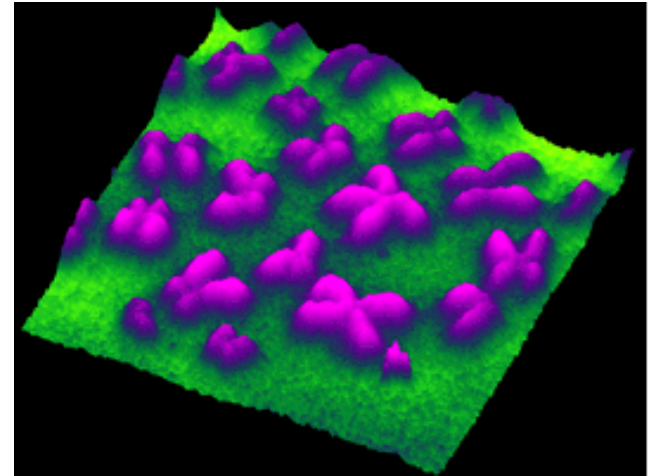
DVD pits
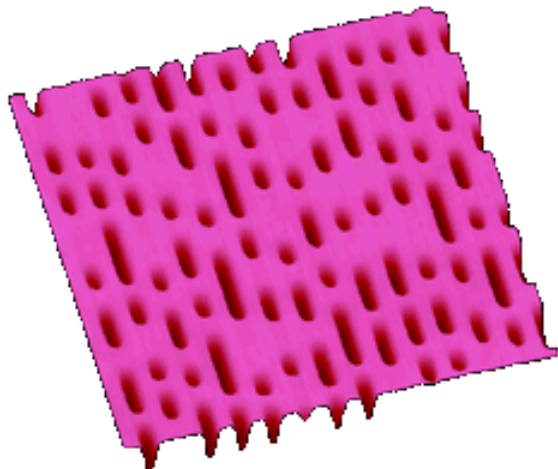
Bacteria
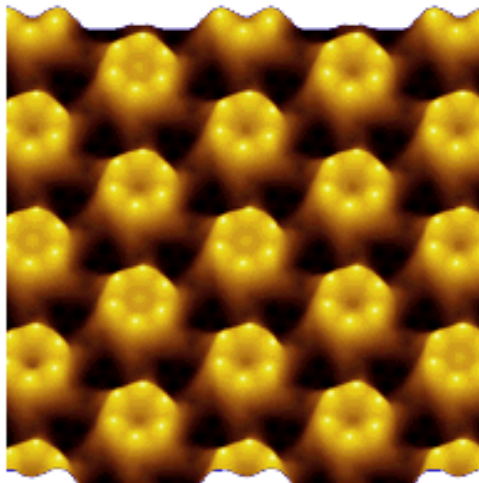
DNA
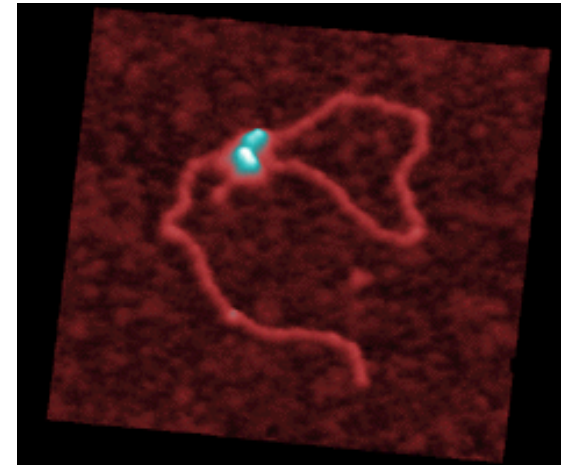
Interaction between the probe and sample
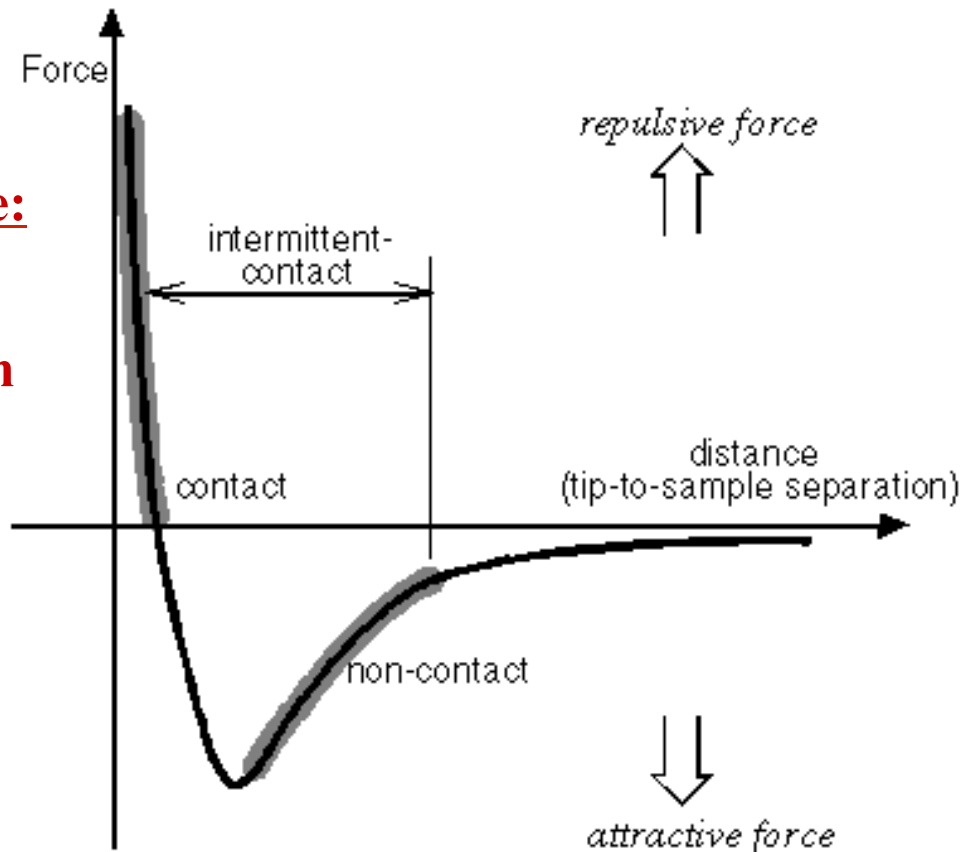
Short-range:

1) **Bonding**

2) **Repulsion**

Long-range:

1) **Van der Waal**

2) **Capillary**

3) **Magnetic**

4) **Electrostatic**

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

Force measurement of an unfolding complex molecule.
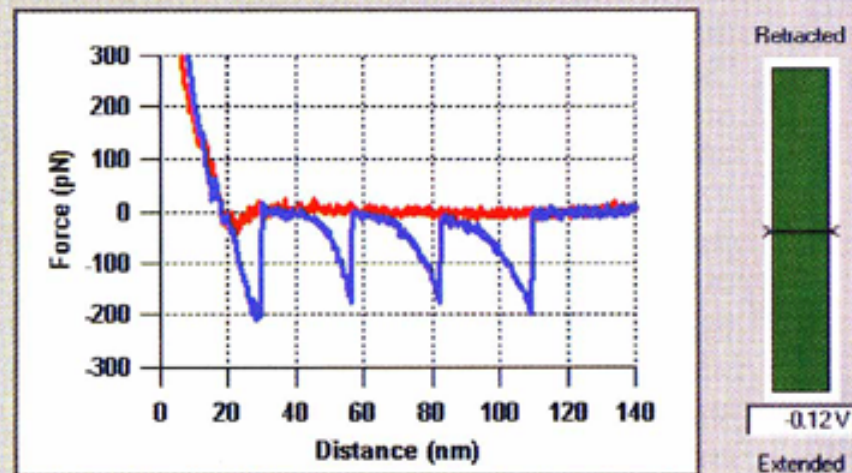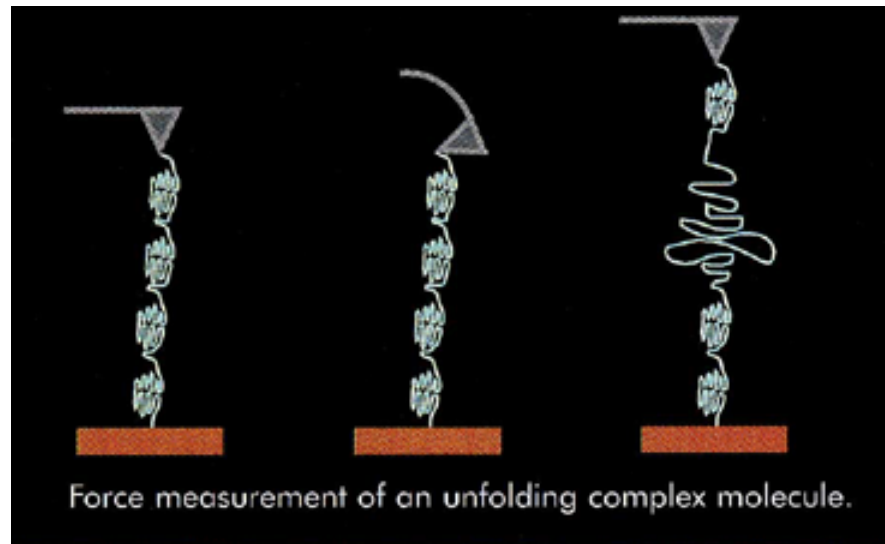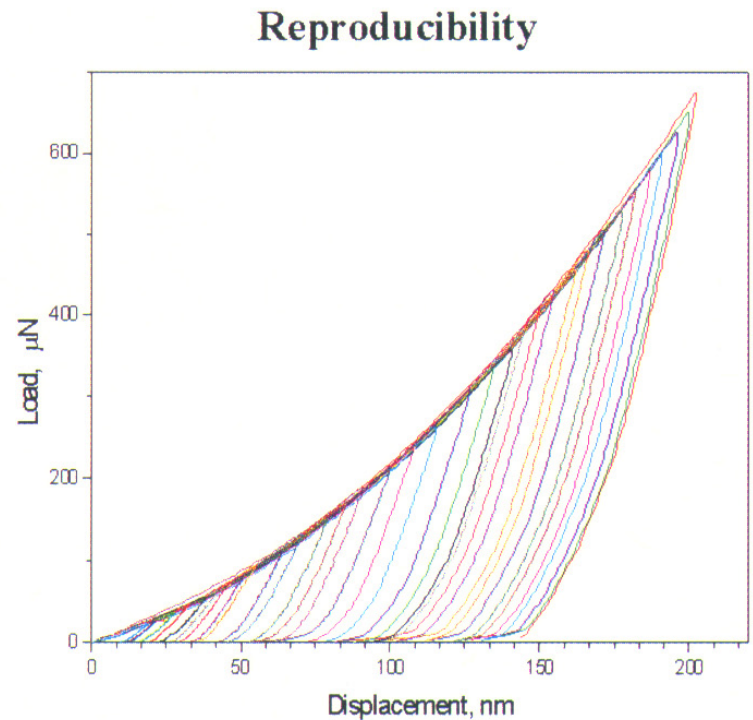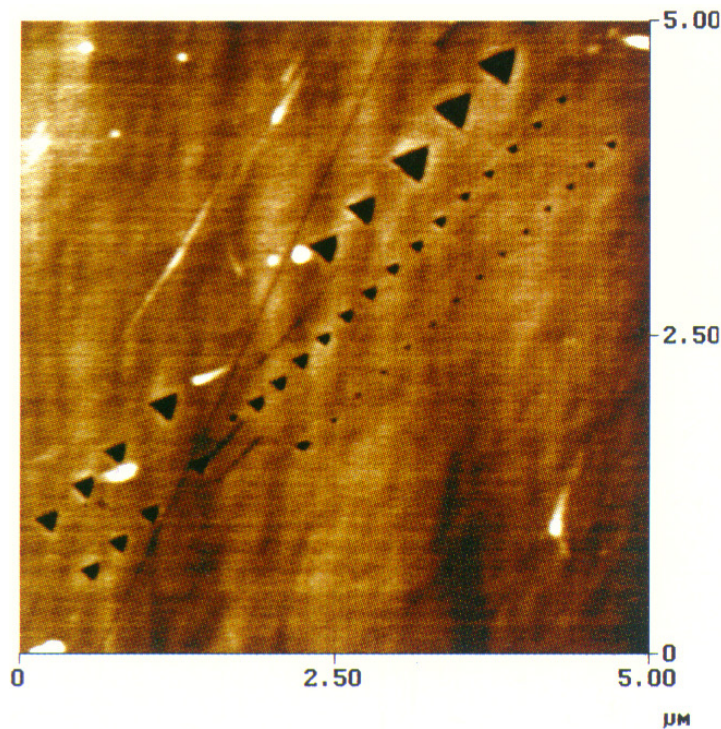
Advanced graphical user interface shows
titin muscle molecule force curve.

Atomic Image of Si(111)-(7×7) Taken with AFM
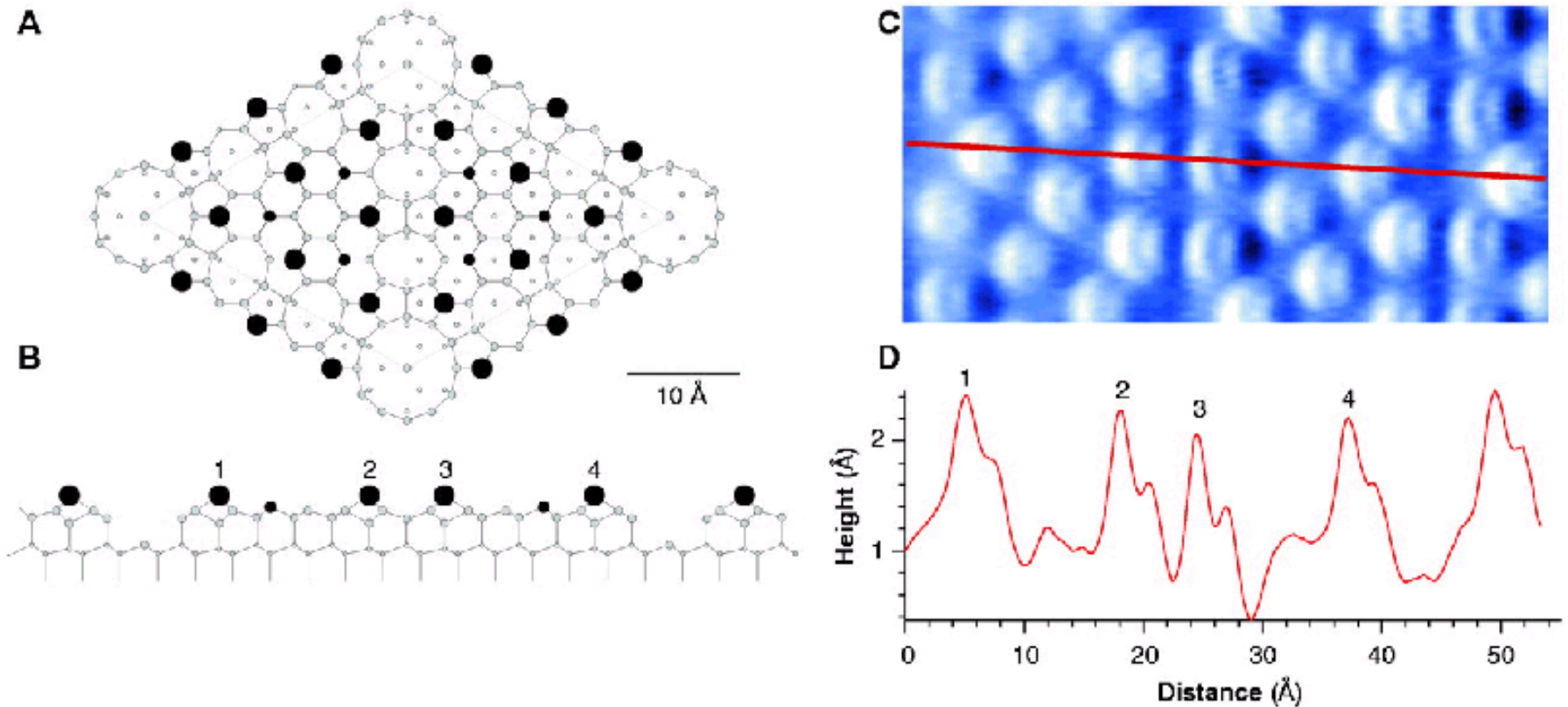
F.J. Giessibl *et al.*, **Science** <u>289</u>, **422 (2000)**

# Measurement of Mechanical Properties

Reproducibility

1. The load-displacement curves provide a "mechanical fingerprint" of material's response to deformation, from which parameters such as hardness and young's modulus of elasticity can be determined.

2. In measuring the mechanical properties of thin coated system, the size of contact impression should be kept small relative to the film thickness.
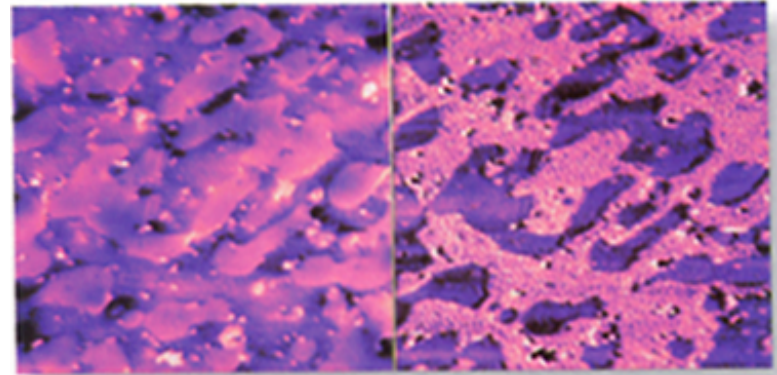
Nanolithography of Tapping-Mode AFM
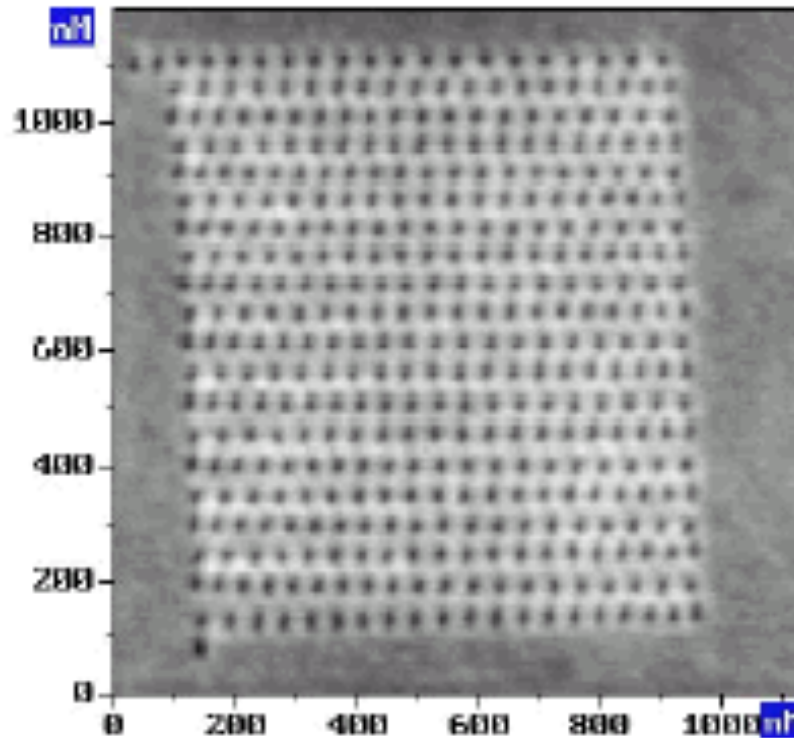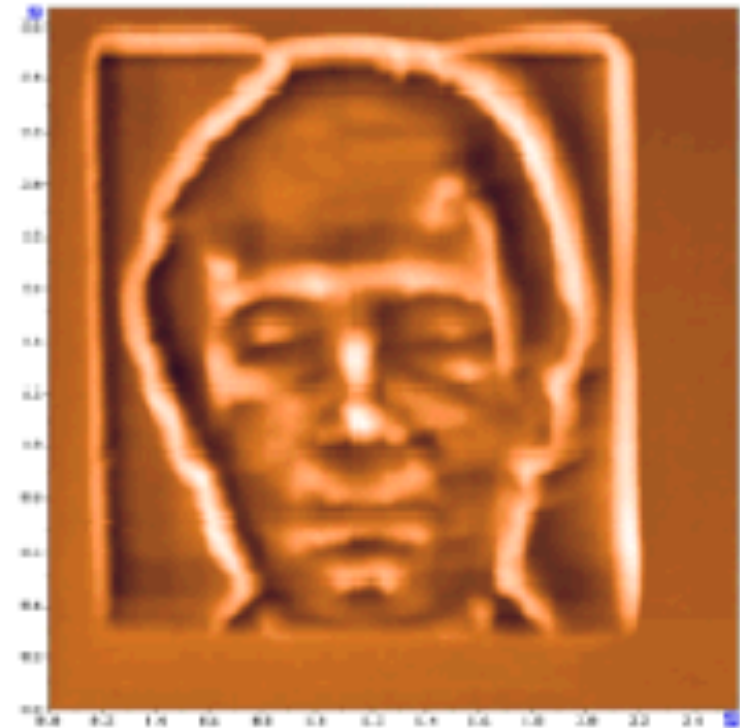
$(1.2\,\mu\mathrm{m} \times 1.2\,\mu\mathrm{m})$ $(2.5\,\mu\mathrm{m} \times 2.5\,\mu\mathrm{m})$

Image of polycarbonate film on silicon surface

Lateral Force Microscopy

Scan Direction

(A+C) – (B+D)
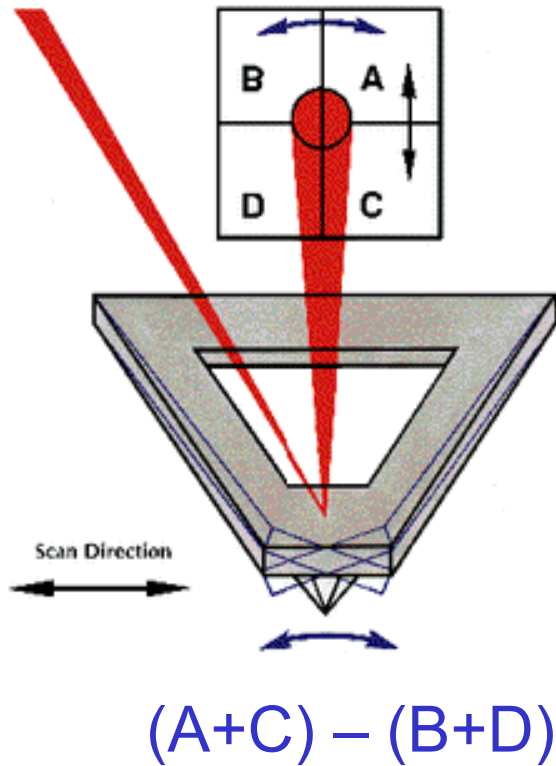
Topography   LFM

Nature rubber/EDPM blend

sample
different material
LFM image

sample
LFM image
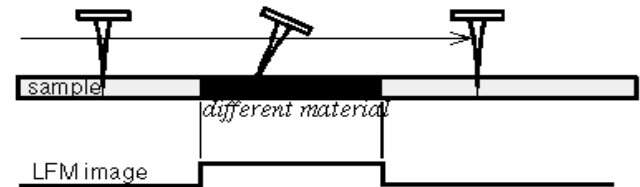
- LFM is sensitive to friction and chemical forces.

- Image contrast depends on the scanning direction.

- Surface roughness will contribute to the contrast.

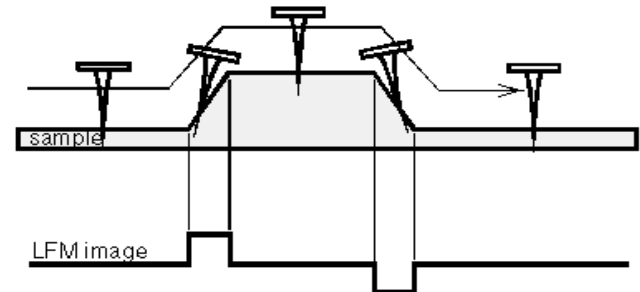# Chemical Force Microscopy

CFM scan of well-defined regions that terminate in either methyl or carboxylic acid groups. When a carboxylic acid-terminated tip is used for imaging (left), the carboxylic acidterminated regions exhibit greater frictional force (lighter color) than the methyl-terminated regions. When a methylterminated tip is used (right), the friction contrast is reversed. No differences are revealed by the topographic AFM scan (not shown) since the functional groups are structurally quite similar. Image courtesy of Dr. C. Lieber, Harvard University.

Magnetic Force Microscopy (MFM)
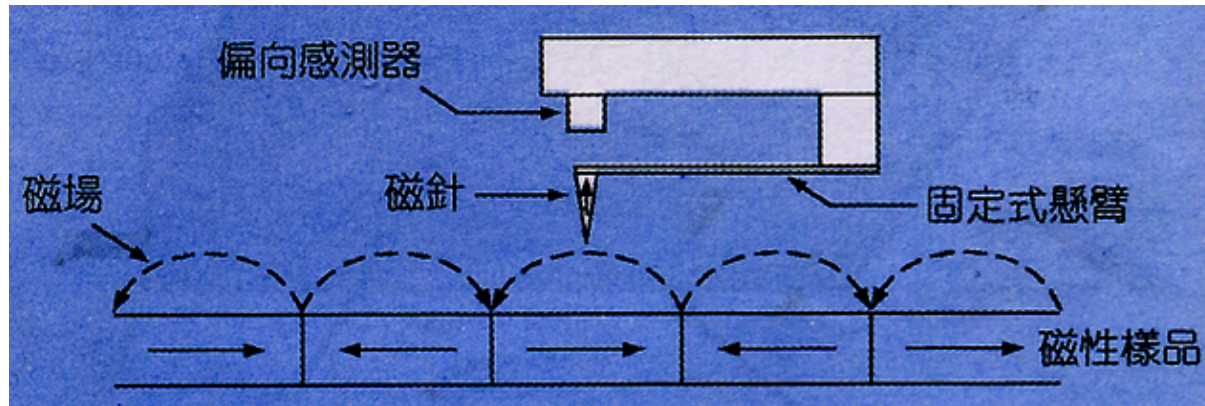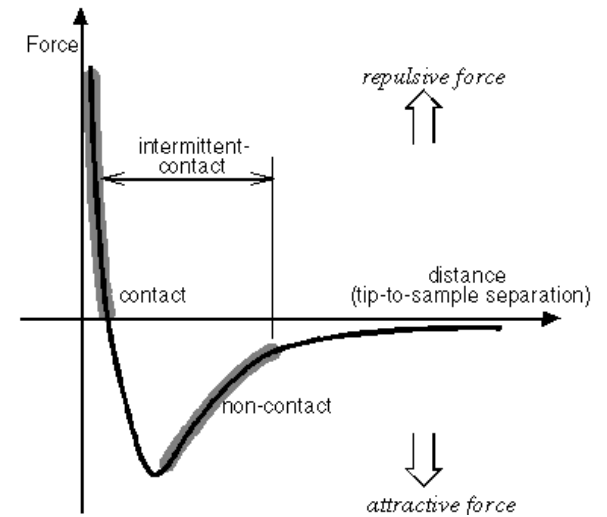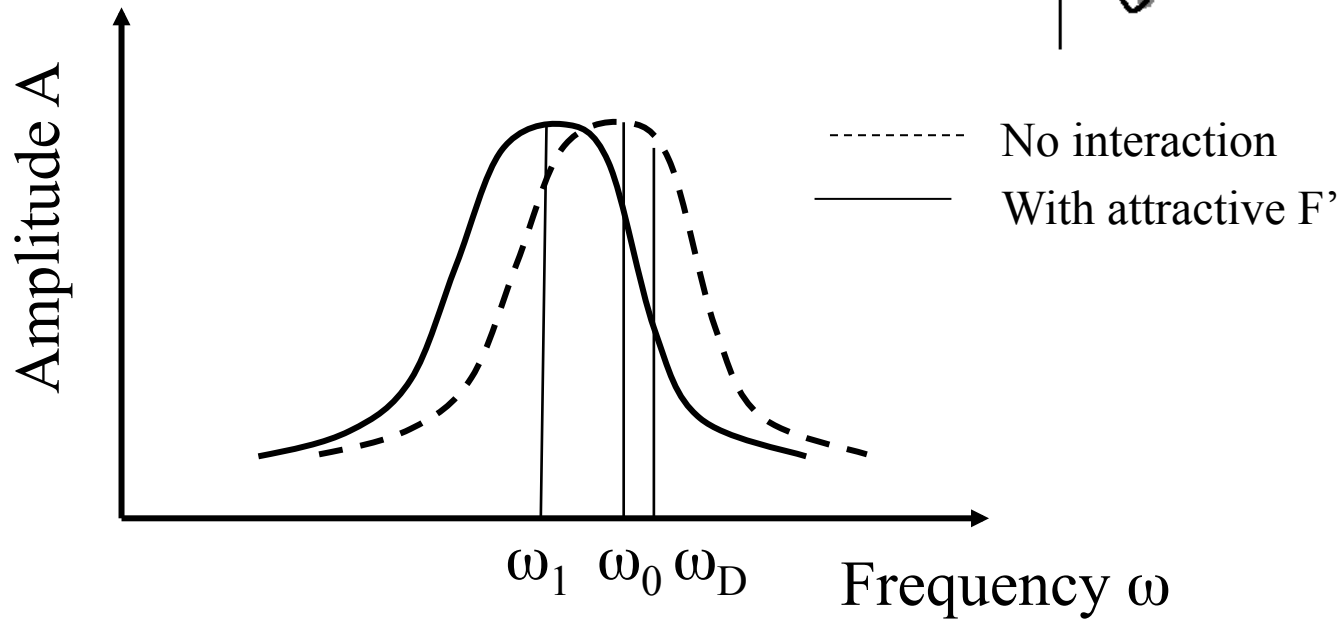

$$F = \nabla(m \cdot H)$$

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

Resolution: 10 ~ 25 nm.

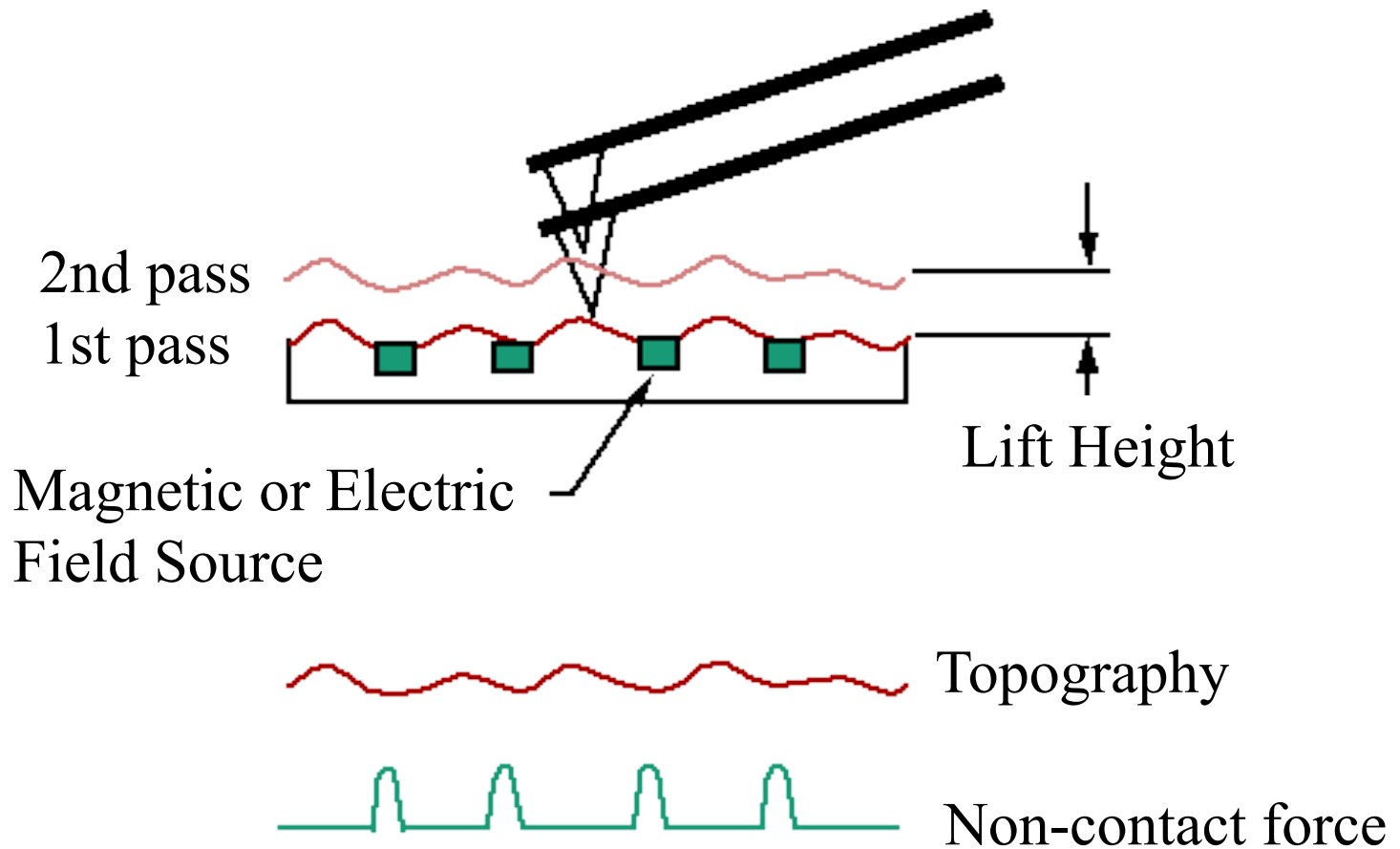Applications: hard disks, magnetic thin film materials,
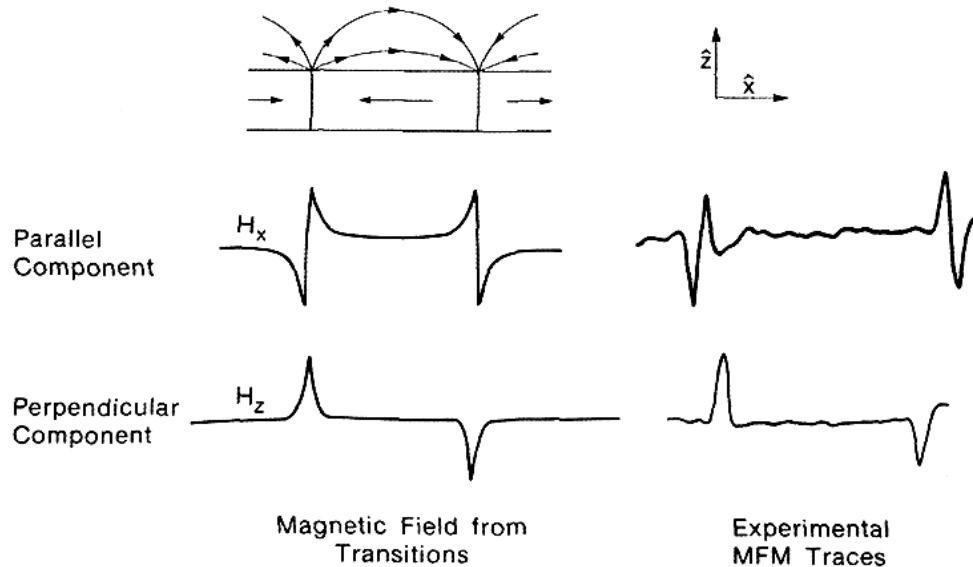   micromagnetism.

AC imaging mode

$$\omega_1 = \omega_0 \left(1 - F'/2k\right)$$

Force

repulsive force

⇑

intermittent-contact

contact

distance
(tip-to-sample separation)

non-contact

⇓

attractive force

Amplitude A

- - - - - - - No interaction
——————— With attractive F'

ω_1 ω_0 ω_D Frequency ω

Lift mode of AFM

2nd pass
1st pass

Magnetic or Electric
Field Source

Lift Height

Topography

Non-contact force

MFM Images

Parallel Component

Perpendicular Component
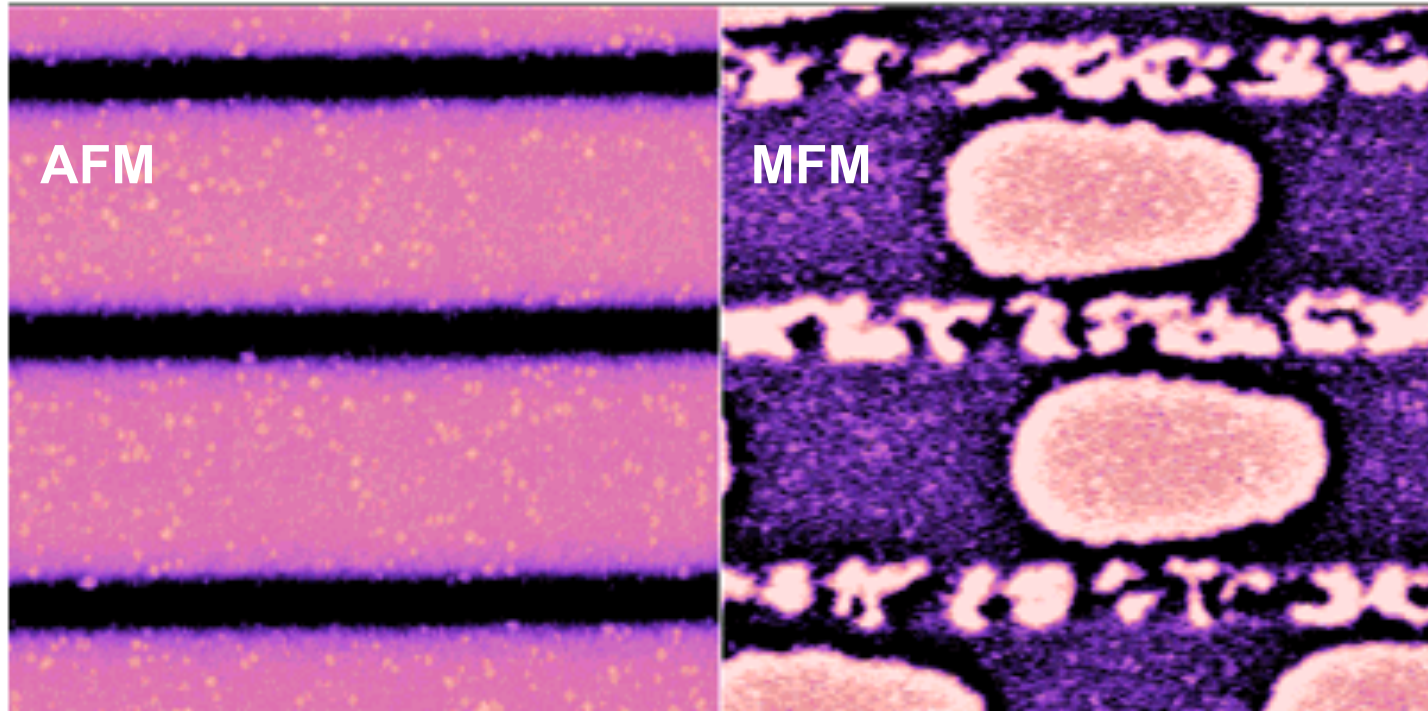
Magnetic Field from Transitions

Experimental MFM Traces
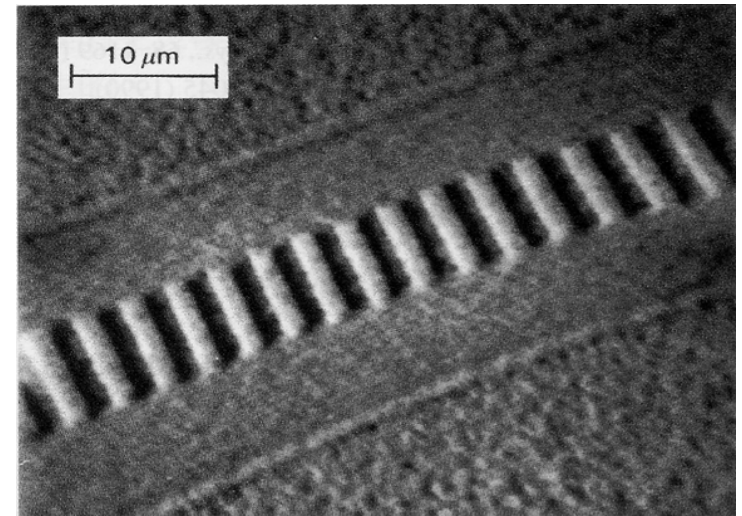
$m^T = m_Z$

Tip as a point dipole

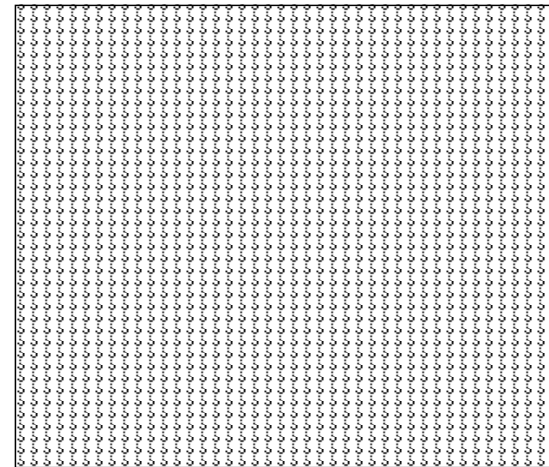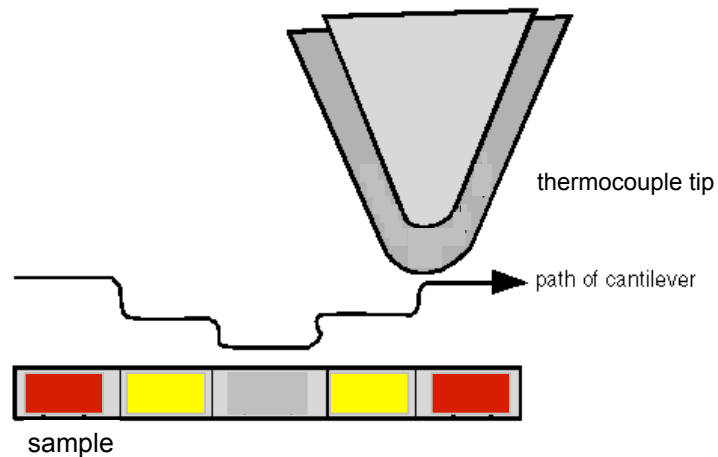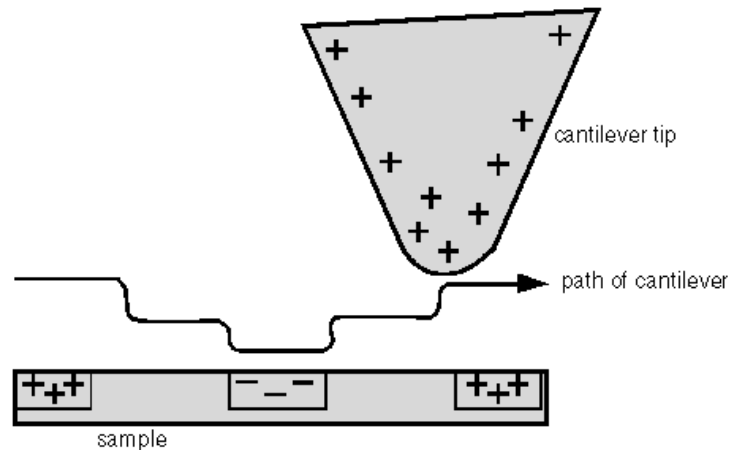$$F_z = \partial(m_x H_x + m_y H_y + m_z H_z)/\partial z$$
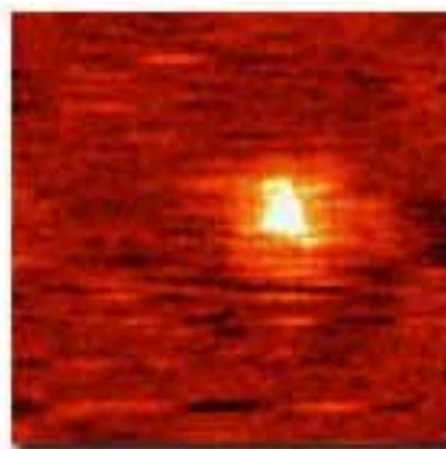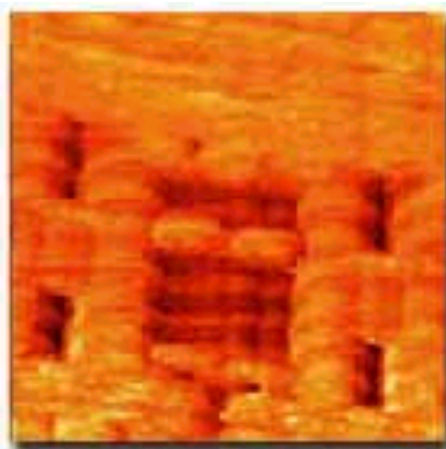
Tip as a long rod

$$F_z = m_z H_z$$

$m^T = m_x + m_z$

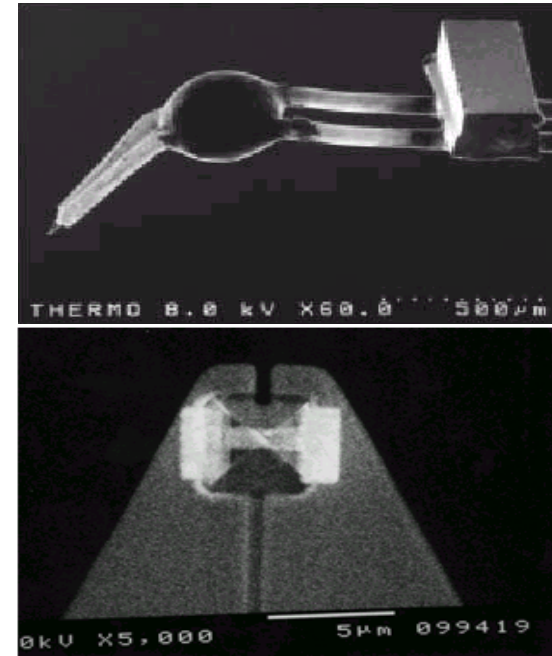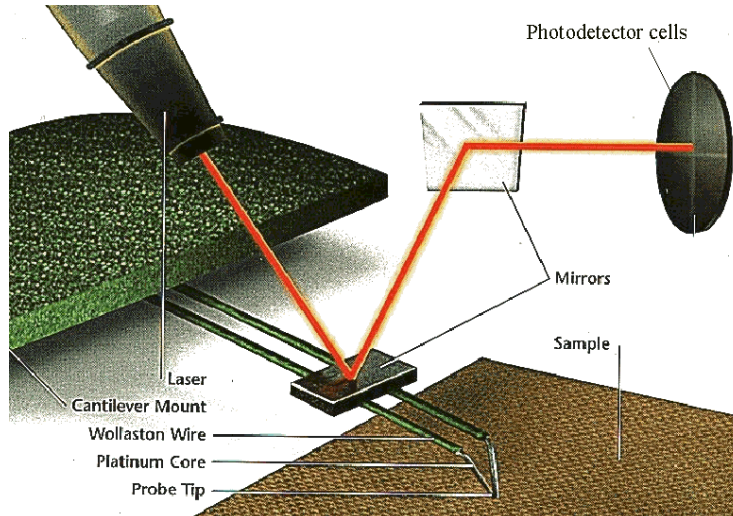**Bits (50 nm) on a magneto-optical disk**

Scan area (5μm× 5μm)

Probes of various functions

Scanning Thermal Microscopy (SThM)

Photodetector cells

Mirrors

Sample

Laser
Cantilever Mount
Wollaston Wire
Platinum Core
Probe Tip

THERMO 8.0 kV X60.0 500µm

0kV X5,000 5µm 099419
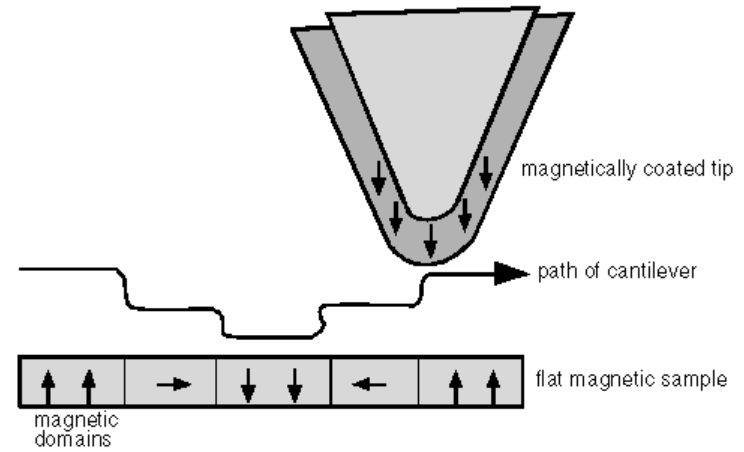
Scanning Capacitance Microscopy (SCM)

Operational principle of the SCM
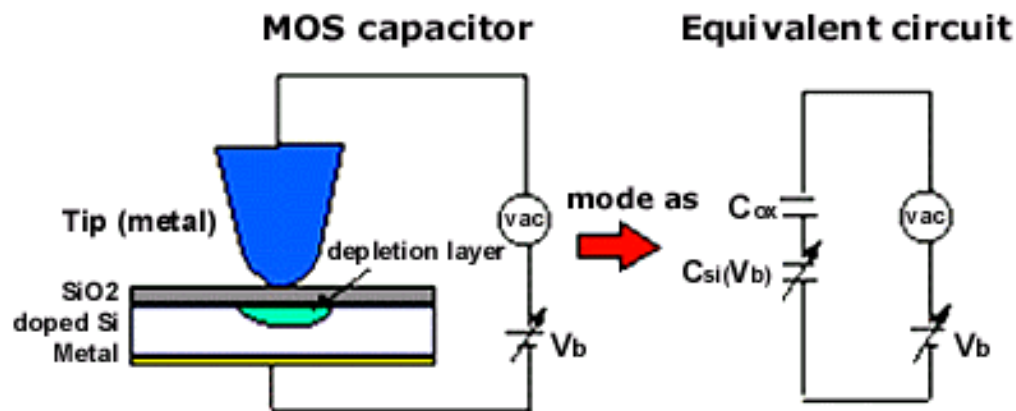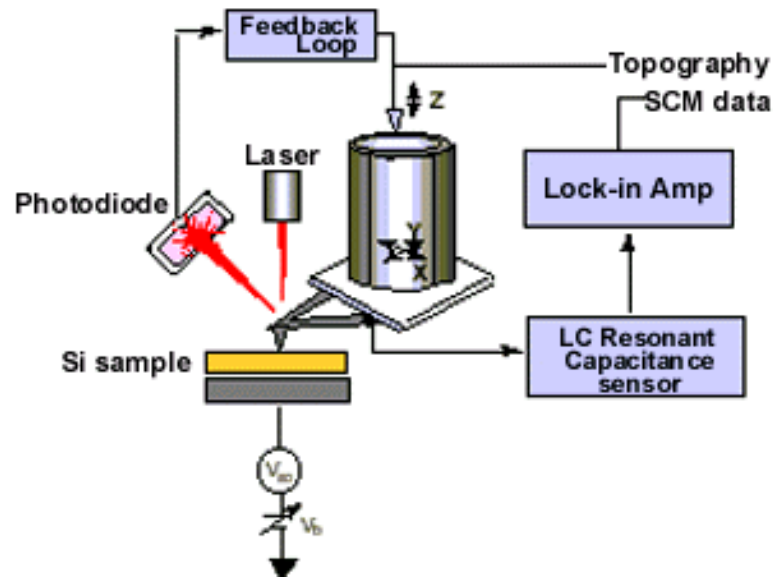
SCM CV Curve

Scanning Capacitance Microscopy

SCM

AFM

InP/InGaAsP
Diode Laser

p (2E17 cm³)

n (2E16 cm³)

0.5 μm

P⁺

(2E18 cm³)

Fe:InP (2E17 cm³)
3.5 μm

InP/InGaAsP Buried
Heterostructure Laser

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, 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.
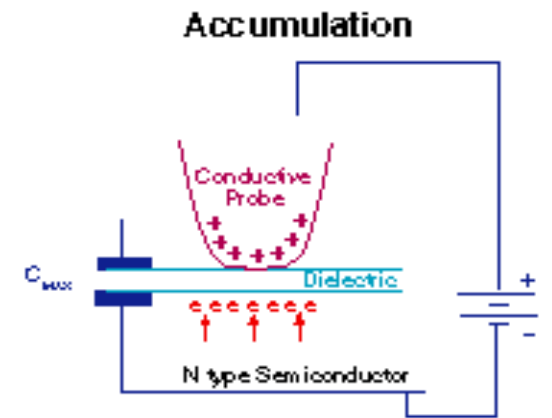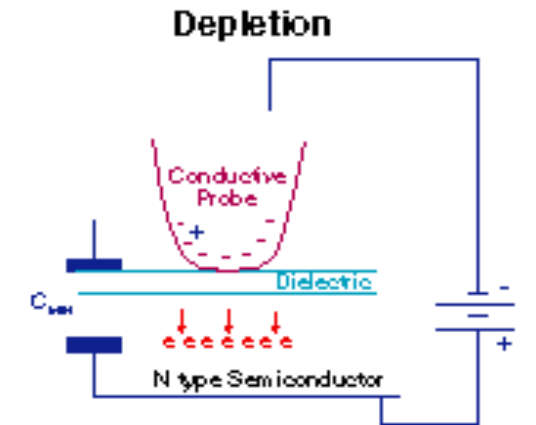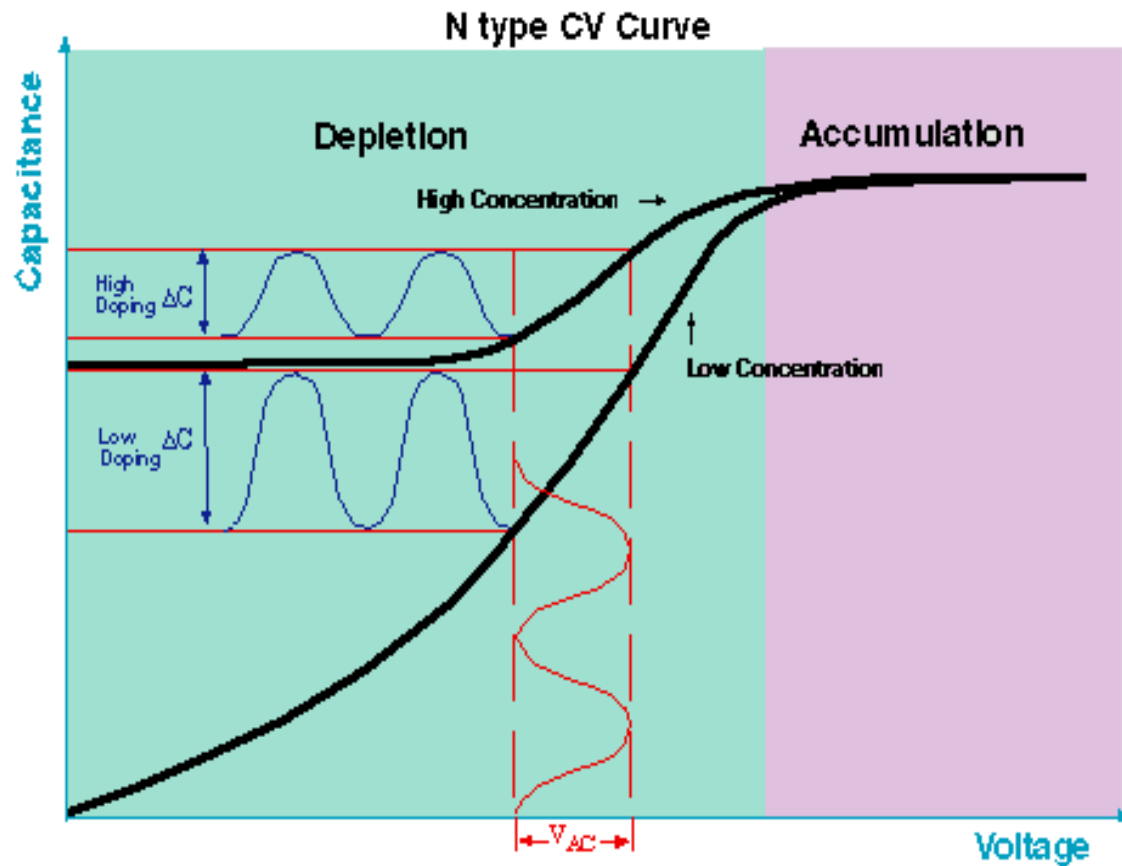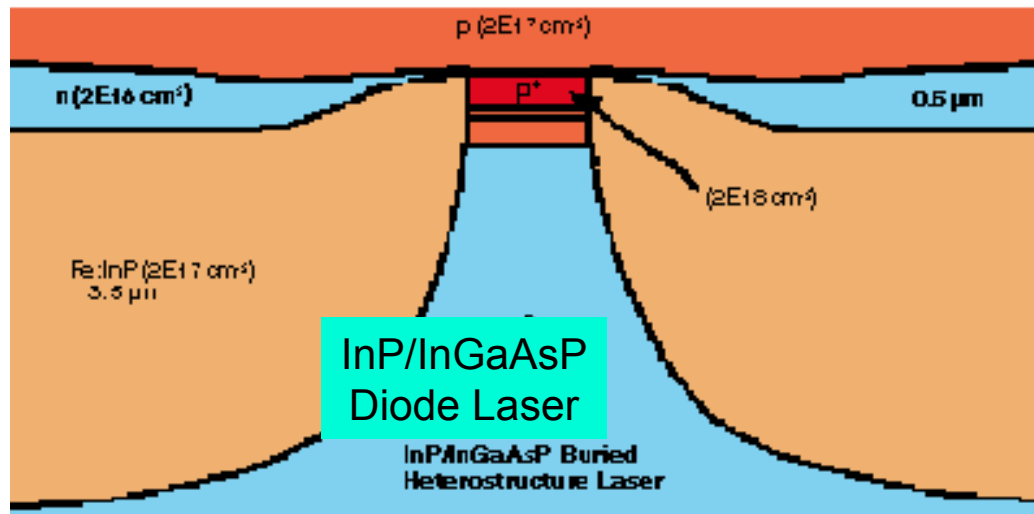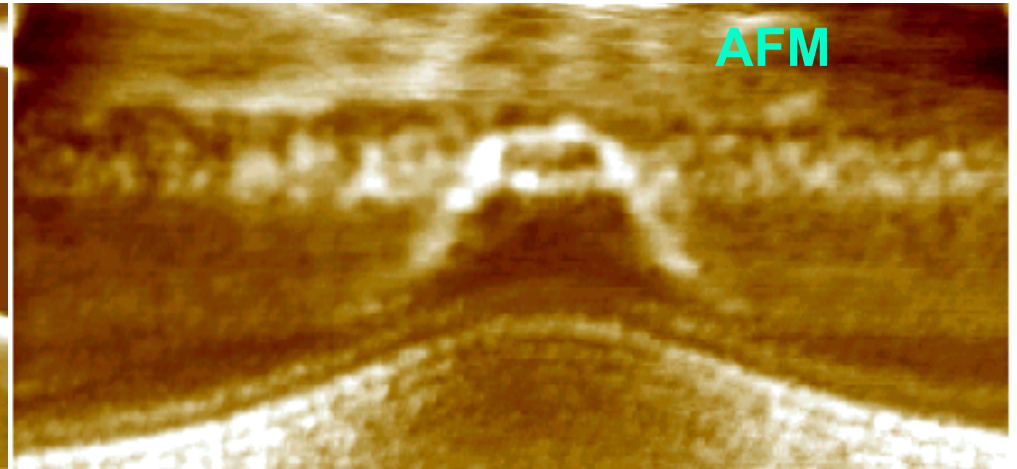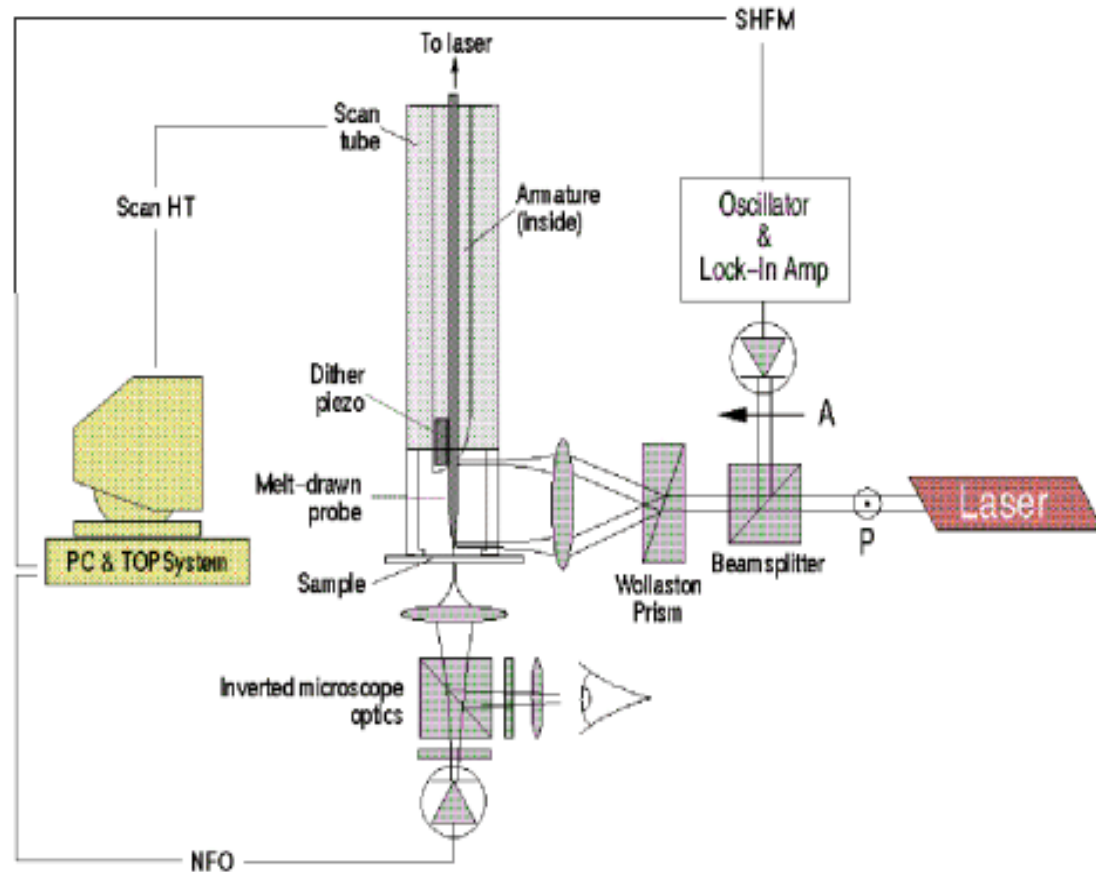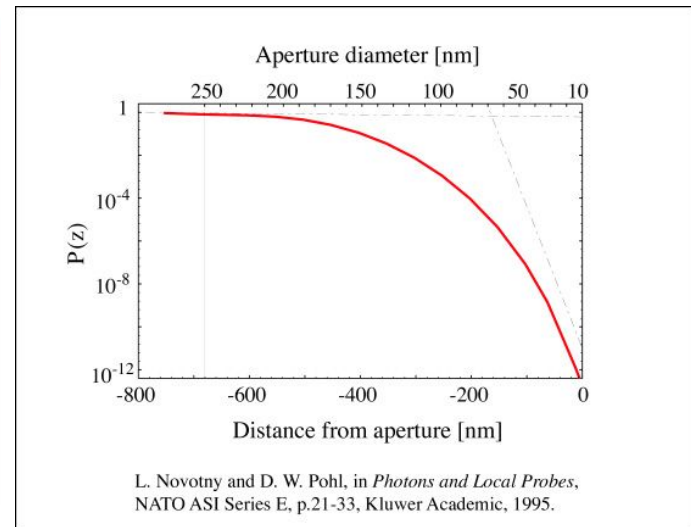
Near-field Scanning Optical Microscopy (NSOM)

Shear force detection is used to regulate
the tip/sample separation

Probes for NSOM

L. Novotny and D. W. Pohl, in *Photons and Local Probes*, NATO ASI Series E, p.21-33, Kluwer Academic, 1995.
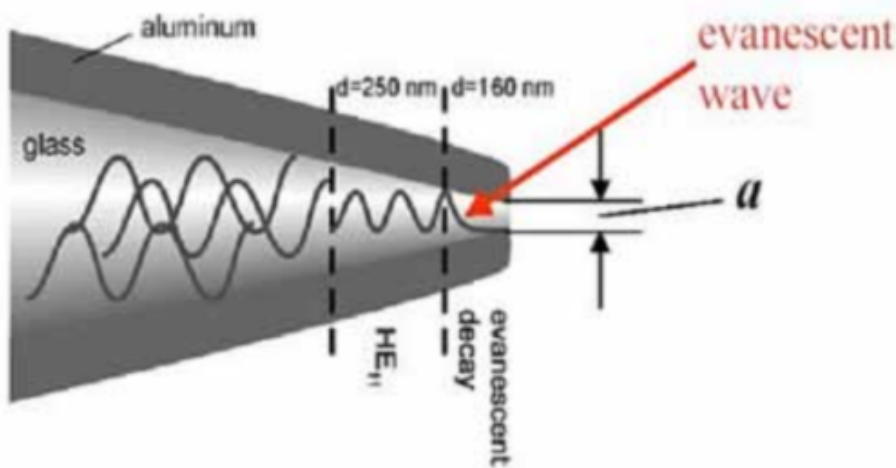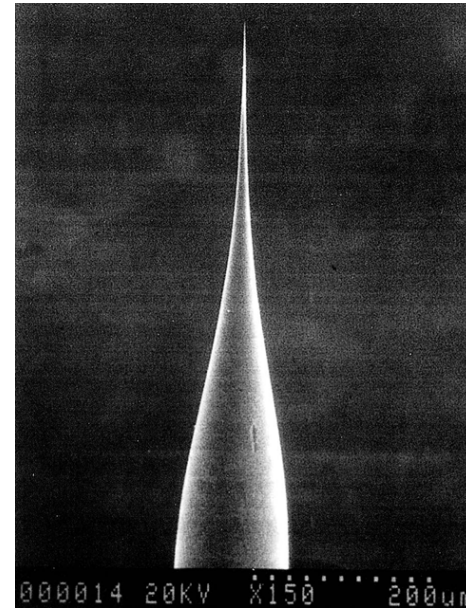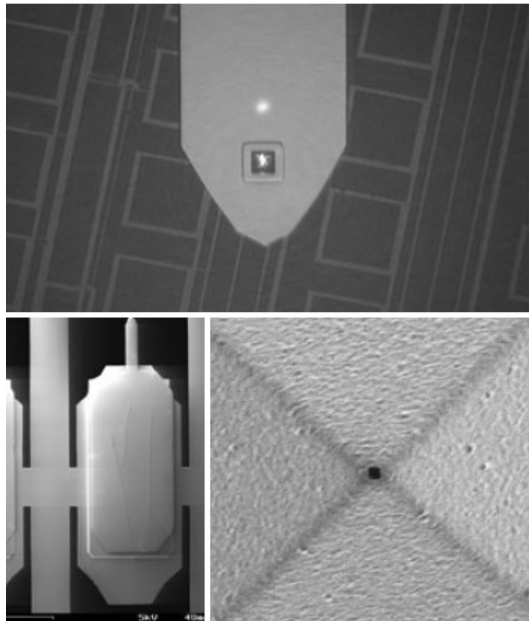
Imaging modes for NSOM
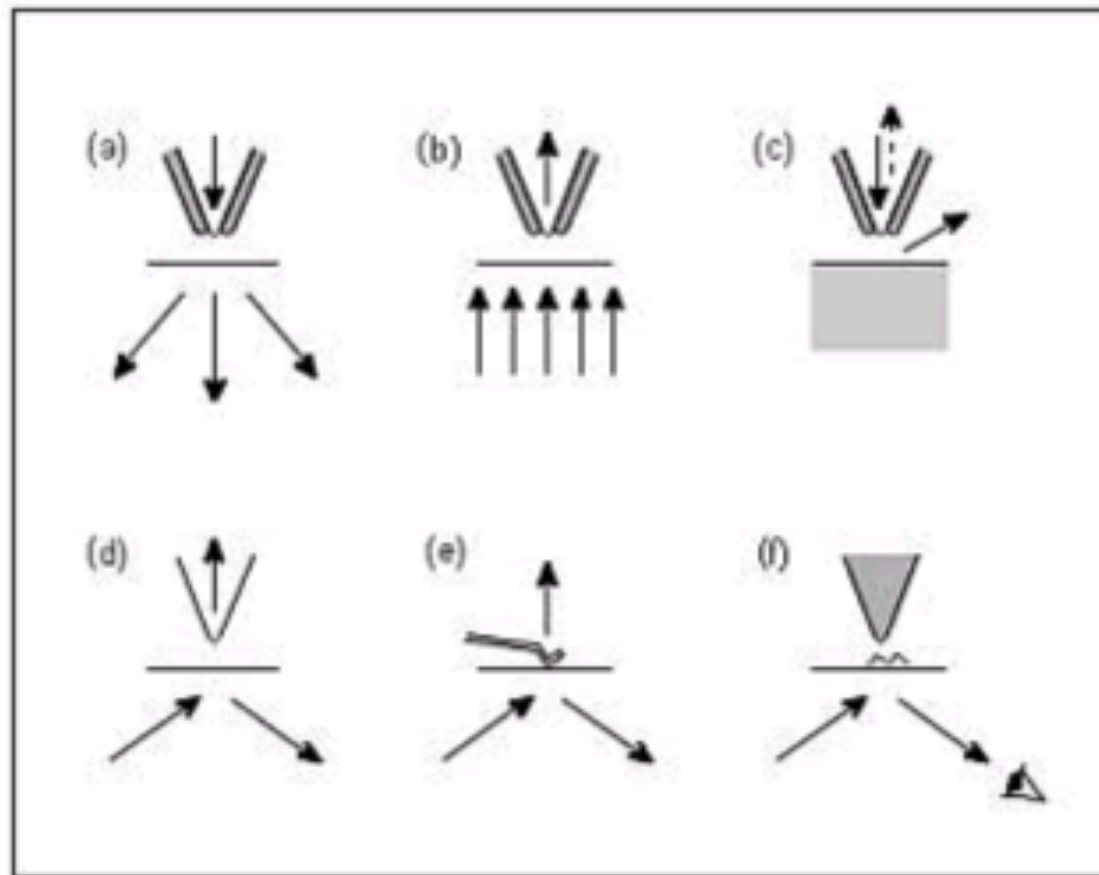
Topography

NSOM Image

Data type	Height
Z range	60.3 nm

Data type	Aux B
Z range	0.0370 V
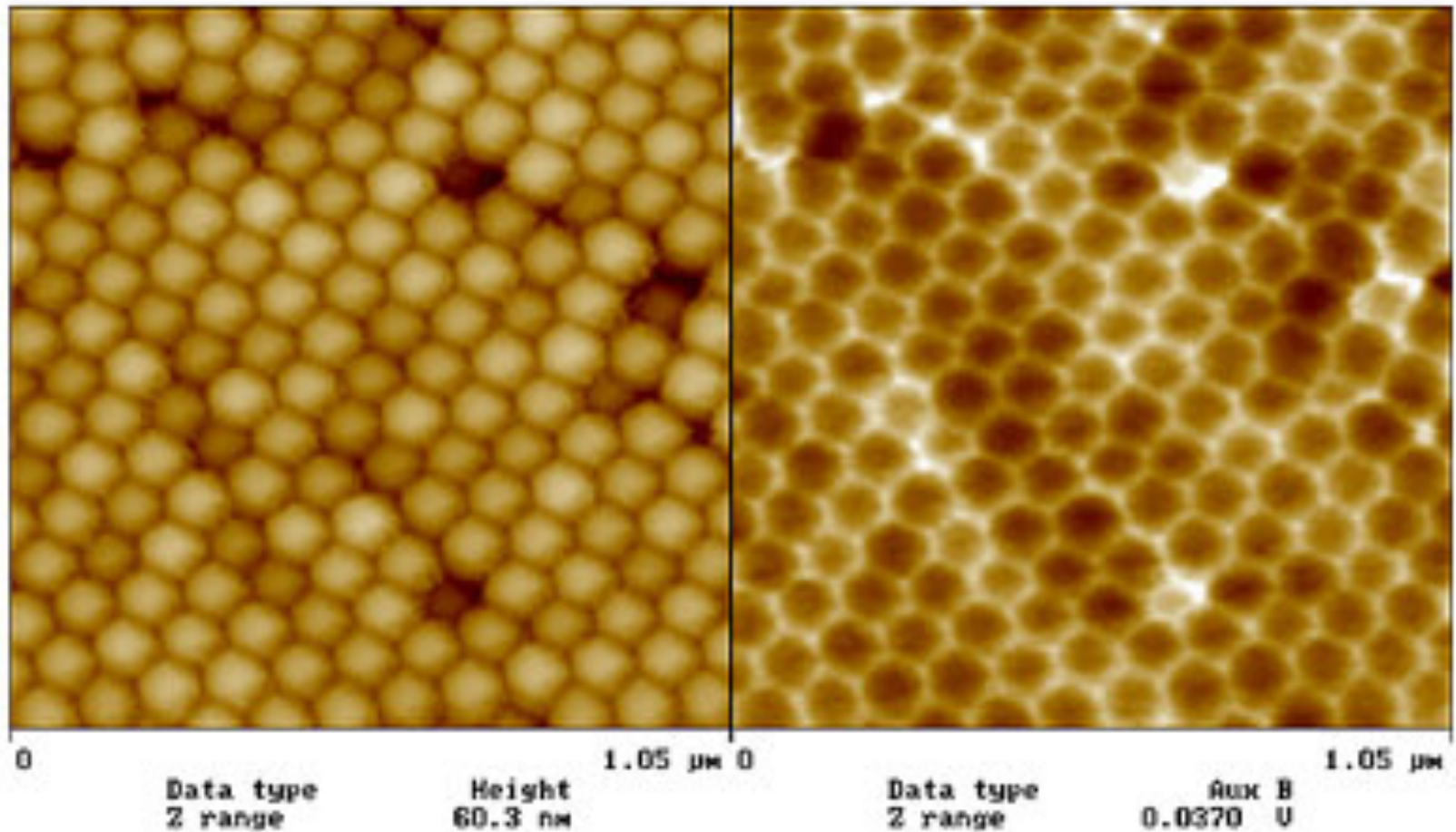
Polystyrenes of 100 nm on glass

AFM-IR system

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

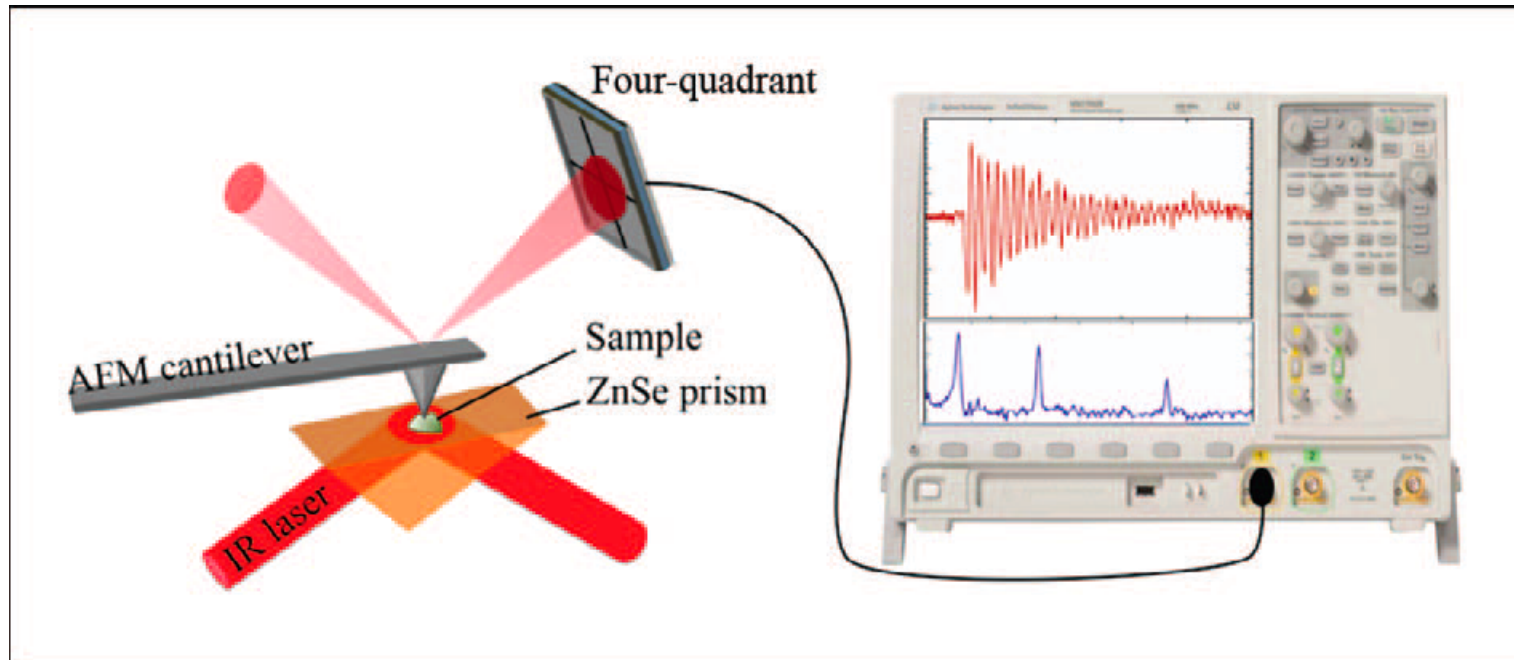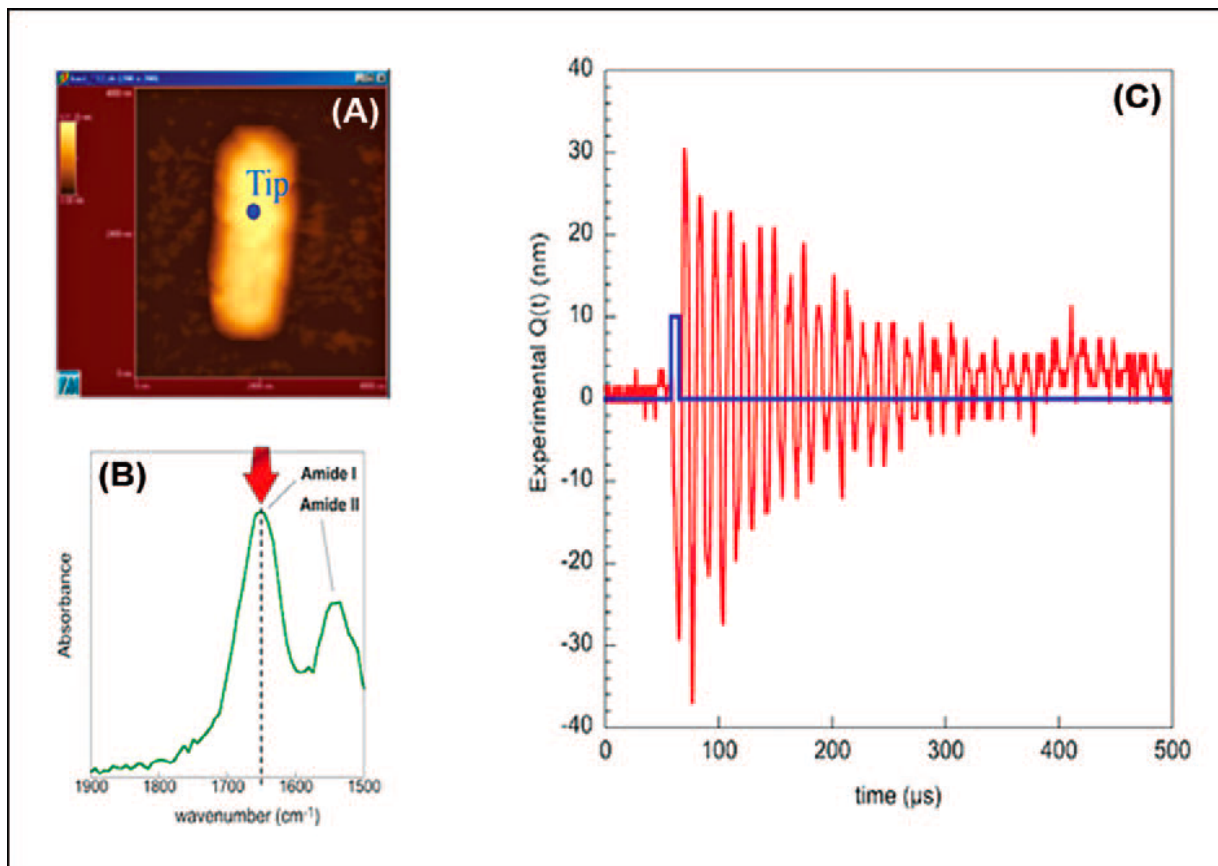(a) AFM topography picture of the bacterium; the position of the tip is indicated in blue. (b) FT–IR spectrum; the bacterium absorption spectrum is drawn in green, and the wavenumber of the CLIO laser is indicated by the red arrow. (c) Oscillations recorded by the four-quadrant detector (in red) as function of time superposed on the CLIO pulse laser (blue).

Alexandre Dazzi et al., APPLIED SPECTROSCOPY OA 66, 1365 (2012)

Chemical Structure of a Molecule
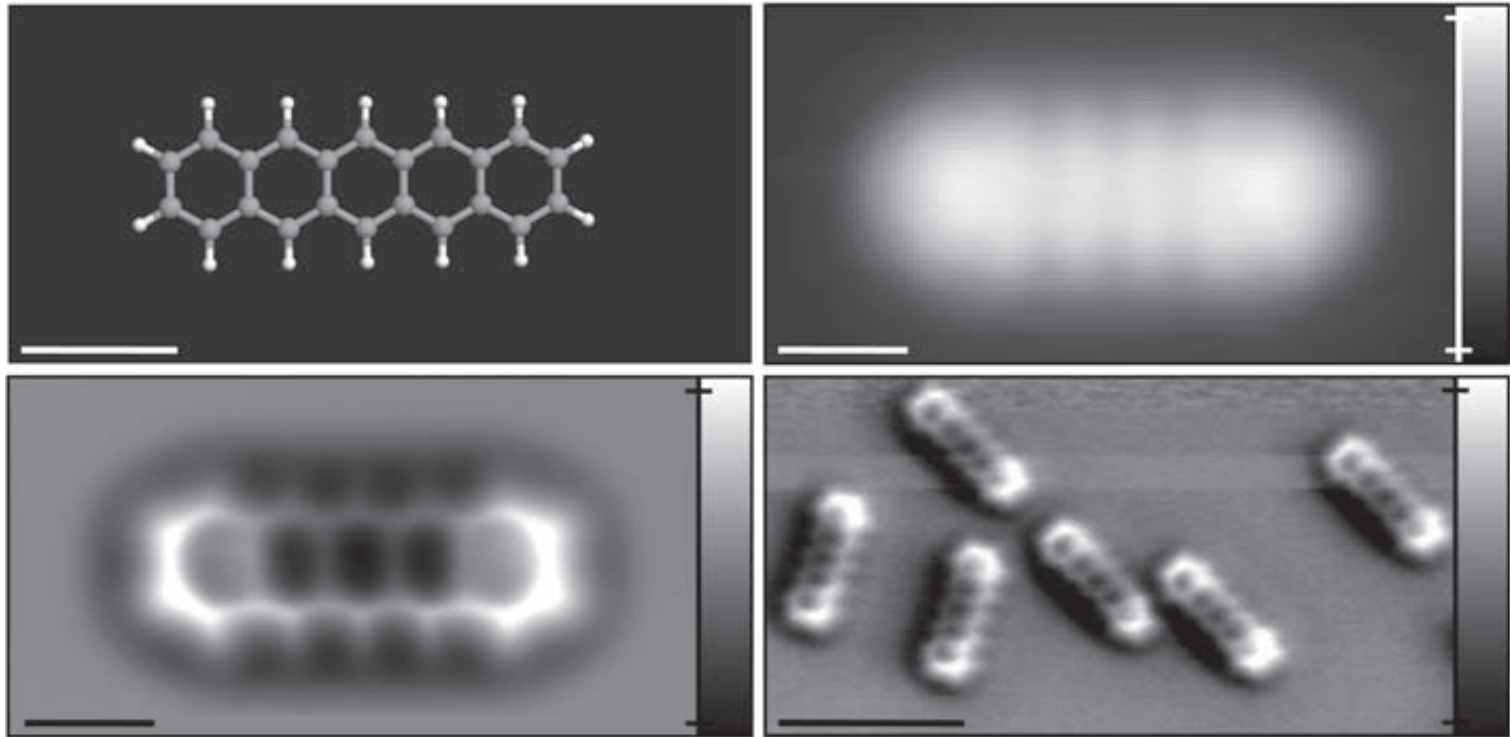
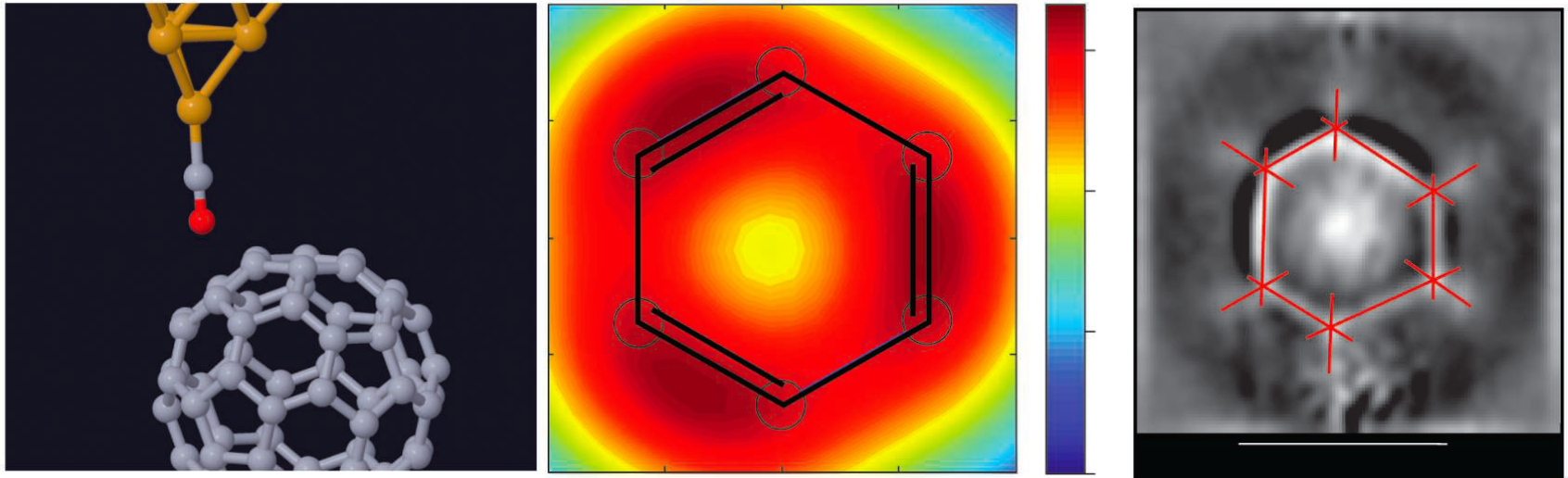STM and AFM imaging of pentacene on Cu(111). (A) Ball-and-stick model of the pentacene molecule. (B) Constant-current STM and (C and D) constant-height AFM images of pentacene acquired with a CO-modified tip

L. Gross et al., Science 325, 1110 (2009)

Discriminating Chemical Bonds

Forceful discrimination. Gross et al. used AFM with a CO-functionalized tip (A) to map the subtle differences in charge density (B) and bond length (C) associated with nonequivalent C-C bonds in a fullerene (C60) molecule and to correlate them with their bond order.

L. Gross et al., Science 337, 1326 (2012)

Why High Speed AFM?

- Most dynamic biological processes occur within milliseconds time scale or less.

Example:

1. Photocycle of Bacteriorhodopsin (*Nature Nanotechnology* **5**, 208-212 (2010))

   WT: ~10 ms   D96N bR mutant: ~10 s

2. F_1-ATPase's rotary rate: 0.5 r.p.s (*Nature* 386, 299-302(1997))

Ando's High-Speed AFM

- Small cantilever of small spring constant (150-280 pN/nm) to reduce tip forces

- Small cantilever of high resonance frequency (450-650 kHz) to decrease response time

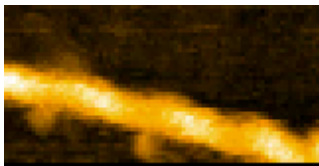- Effective dynamic PID control

- Low-noise sensor amplifier
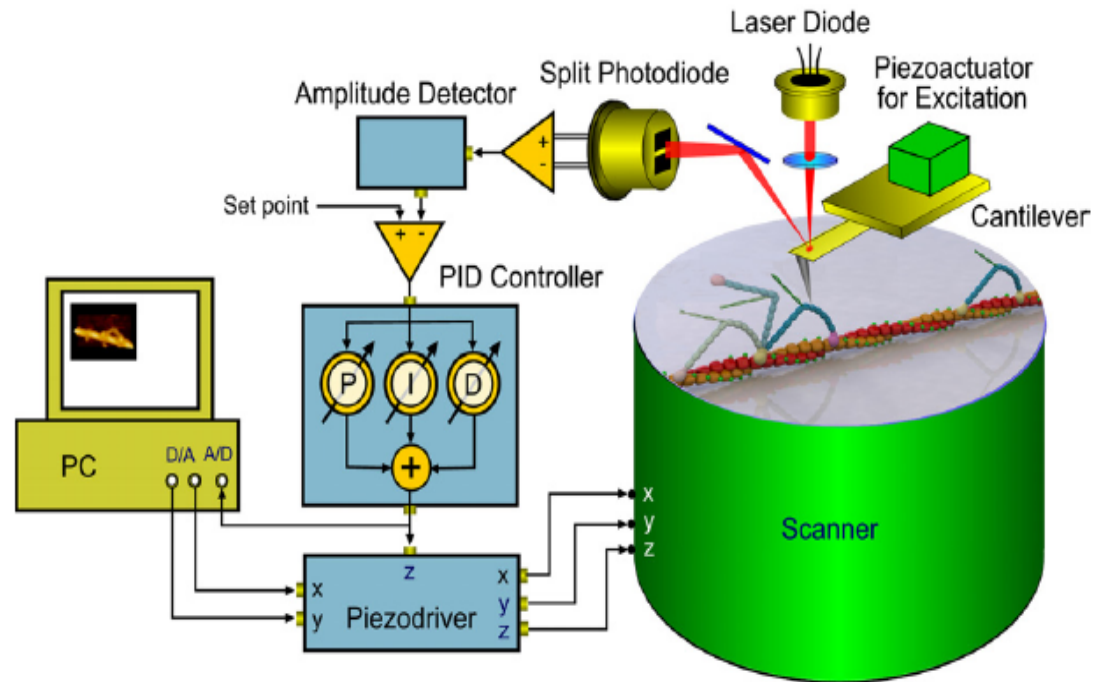
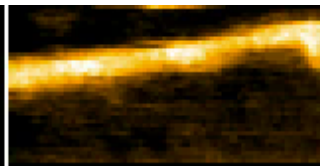**Obtain consecutive images of a 240 x 240 nm^2 area in as little as 80 ms**

Hand-Over-Hand Movement
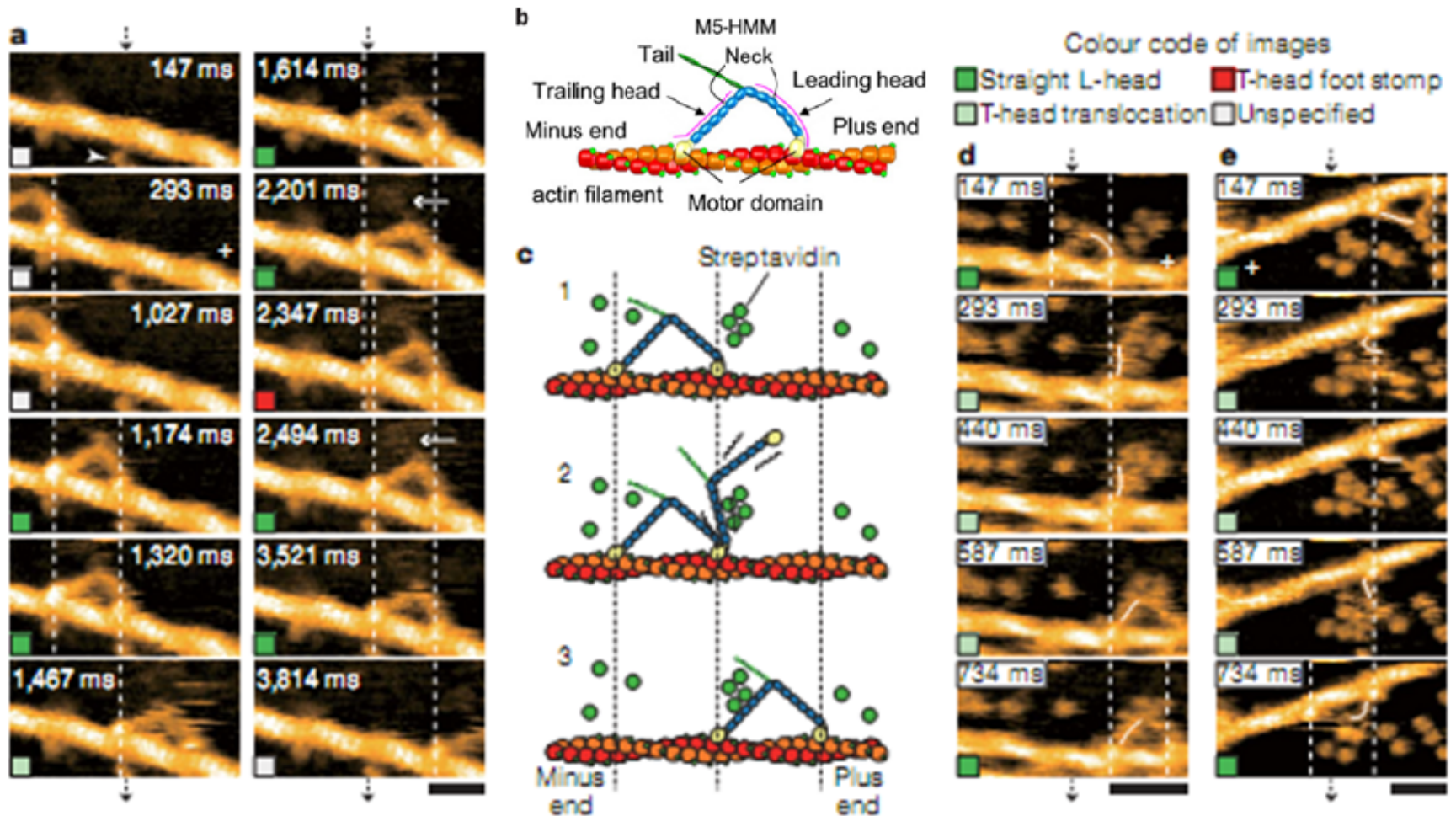
Noriyuki Kodera, Daisuke Yamamoto, Ryoki Ishikawa & Toshio Ando, Nature 468, 72 (2010)

a
b
c
d

Myosin V motor
Erin M.Craig and Heiner Linke,
Mechanochemical model for myosin V, PNAS 2009

Basic model; no fine-tuning of parameters