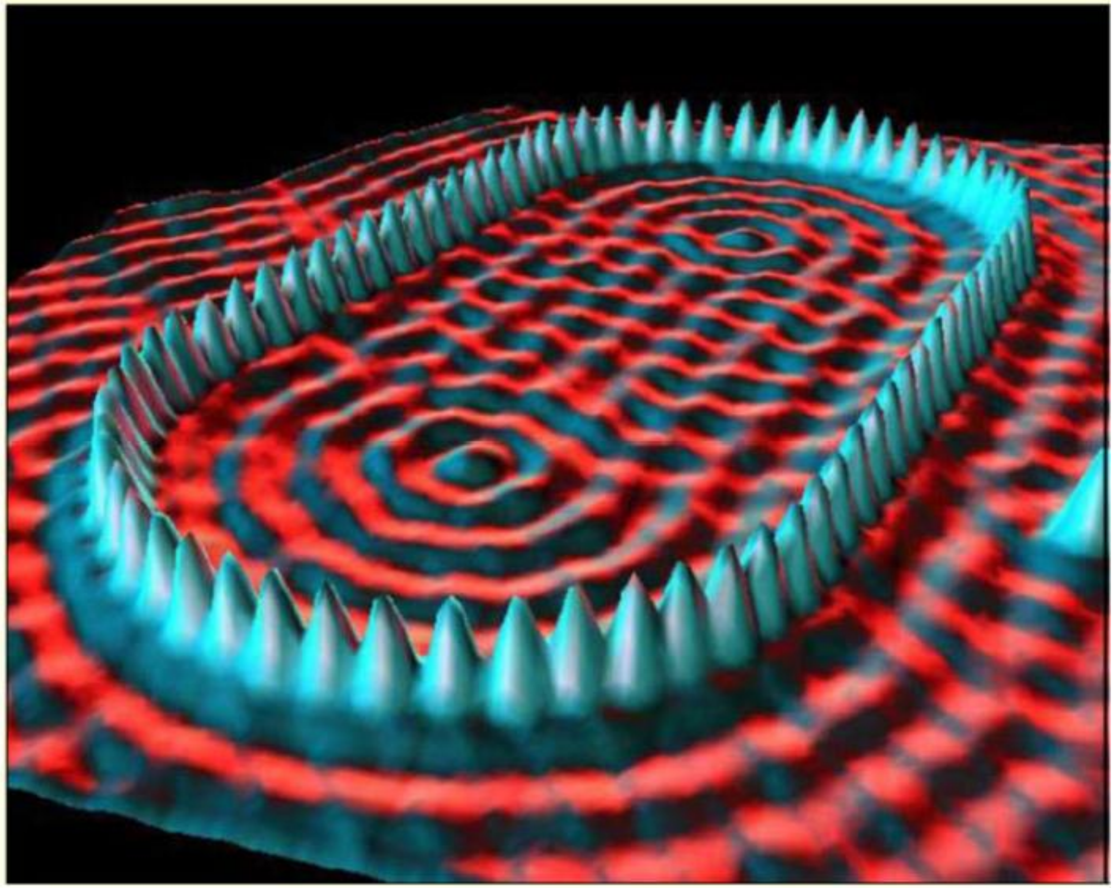
CHAPTER 3: SCANNING PROBE MICROSCOPE (SPM)



STM, AFM, EFM

2002 (Eigleret. al.@IBM)

Microscopes

- 1st generation: Optical Microscope (광학현미경): up to ×2,000
- 2nd generation: Electron microscope (전자현미경):

  SEM (Scanning Electron Microscope) : up to ×1,000,000

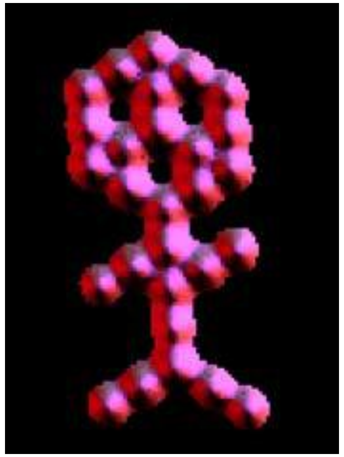
  TEM (Transmission Electron Microscope): up to ×2,000,000

  (주기적인 원자구조 관찰 가능)

- 3rd generation: SPM (Scanning Probe Microscope, 원자현미경)

  Examination on the nanometer scale: up to x 108

  Atoms can be arranged and imaged



Carbon monoxide molecules arranged on a platinum (111) surface.

See also
http://www.youtube.com/watch?v=tDzInhT5zzQ

Characteristics of Microscopies

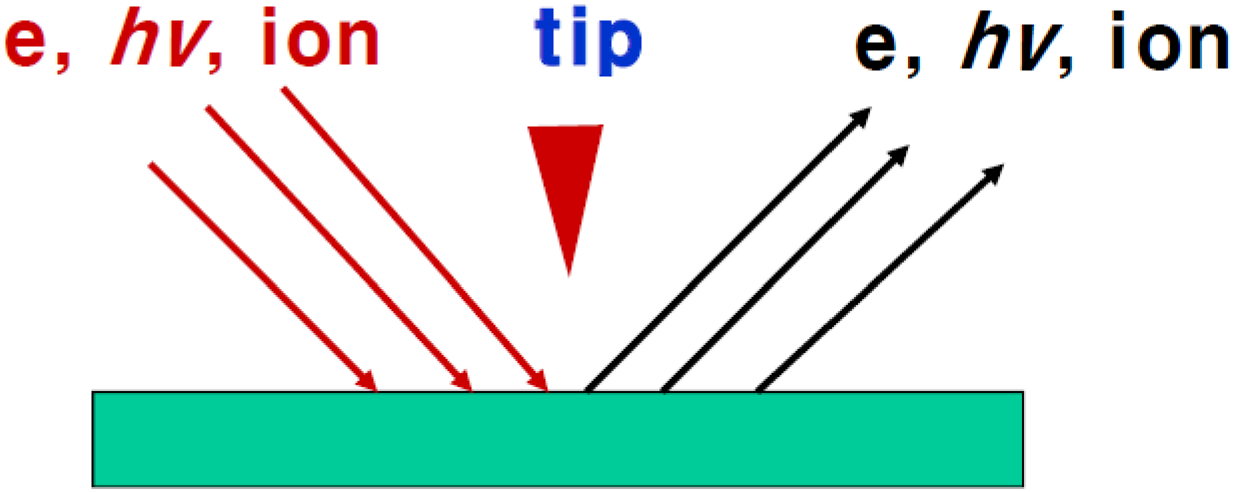
	OM	SEM/TEM	SPM
Operation	Air, Liquid	Vacuum	Air, Liquid, UHV
Depth of Field	Small	Large	Medium
Lateral Resolution	0.1~1 μm	1 nm: SEM 0.1 nm: TEM	2~10 nm: AFM 0.1 nm: STM
Vertical Resolution			0.1 nm: AFM 0.01 nm: STM
Magnification	1~2000 x	$10\sim10^6$ x (SEM) 50×10^6 x (TEM)	$500\sim10^8$ x
Sample	Not completely transparent	Un-chargeable, Vacuum compatible, Thin-film: TEM	Surface height < 10 mm
Contrast	Absorption, Reflection	Scattering, Diffraction	Tunneling Atomic force

SPM (Scanning Probe Microscope)

- Scanning Tunneling Microscopy (STM): topography, local DOS
- Atomic Force Microscopy (AFM): topography, force measurement
- Lateral Force Microscopy (LFM): friction
- Magnetic Force Microscopy (MFM): magnetism
- Electrostatic Force Microscopy (EFM): charge distribution
- Near-field Scanning Optical Microscopy (NSOM): optical properties with spatial resolution (R) smaller than wavelength of light (R ~50 nm)

Tools for Characterization

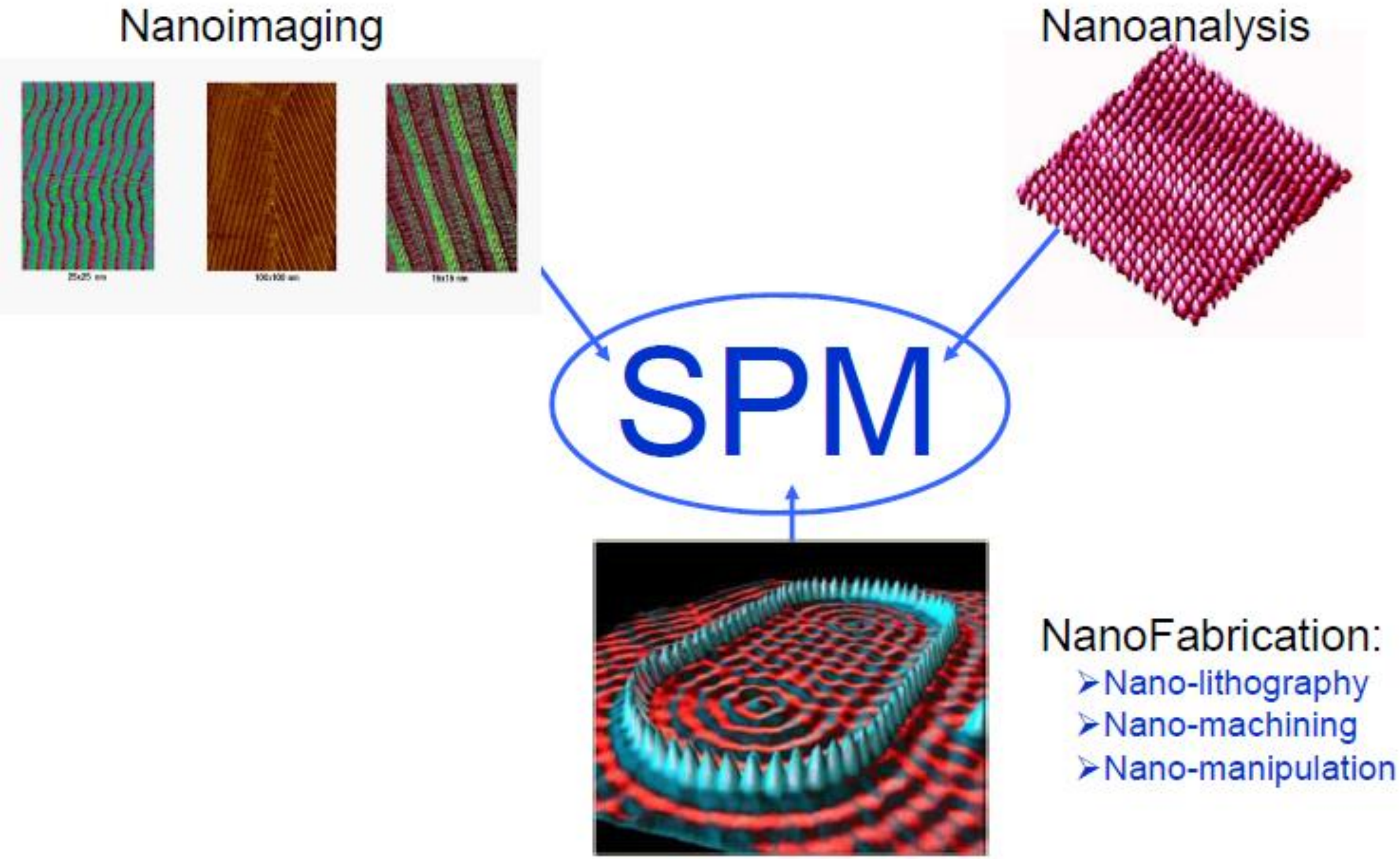
- Structural analysis: SEM, TEM, XRD, SPM
- Chemical analysis: AES, XPS, SIMS, EDS, SPM
- Electronic, optical analysis: UV/VIS spectroscopy, PL, SPM
- Magnetic analysis: *SQUID, SPM



*SQUID: superconducting quantum interference device

조셉슨 접합을 이용하여 매우 작은 자기장을 측정

Applications of SPM



Nanoimaging

Nanoanalysis

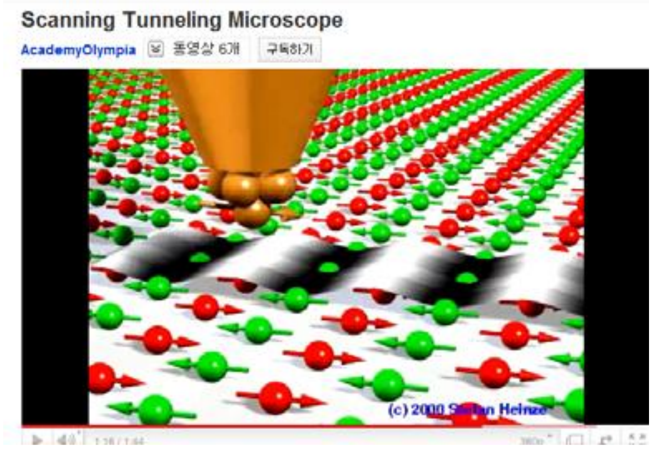
SPM

NanoFabrication:

- ➢Nano-lithography
- ➢Nano-machining
- ➢Nano-manipulation

Scanning Tunneling Microscopy (STM)

STM in YouTube



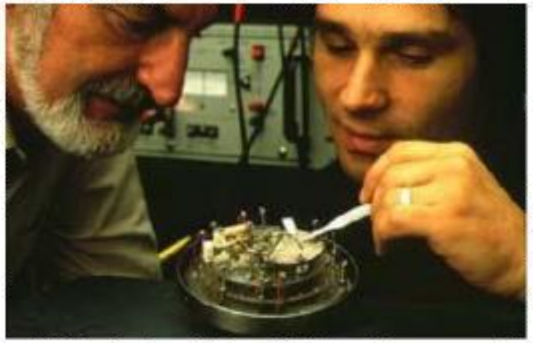
https://www.youtube.com/watch?v=TbWaUODytkw

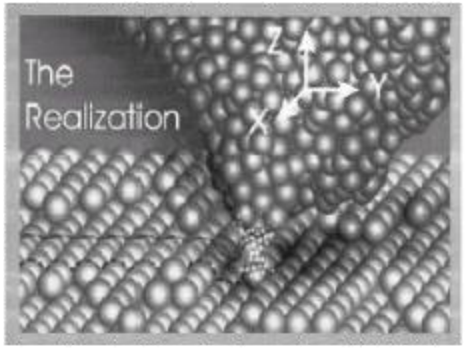
Using SPM for Nano Lithography
https://www.youtube.com/watch?v=thXU23GSByU

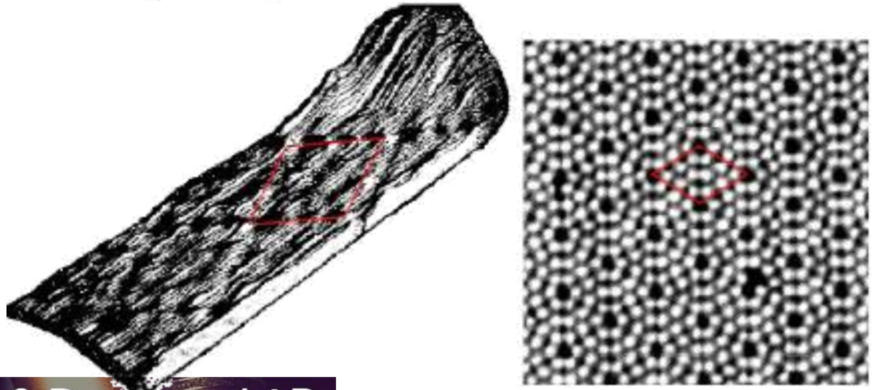
http://www.youtube.com/watch?v=5g43LWUI18Y&feature=related
http://www.youtube.com/watch?v=tDzInhT5zzQ

STM-History

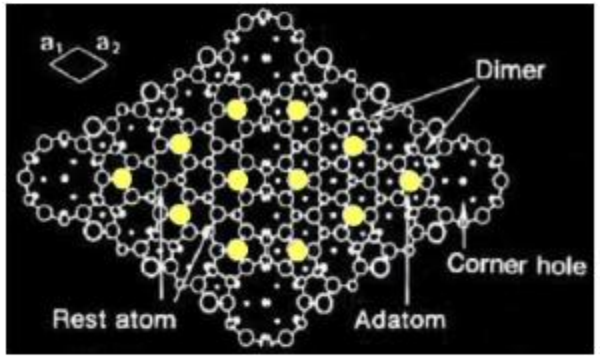
- In March 1981, Gerd Binning, H. Rohrer, Ch. Gerber and E. Weibel observed electrons tunneling in vacuum between W tip and Pt; this in combination with scanning marked the birth of STM.
- The breakthrough: atomic-scale surface imaging in real space
- **1986-Nobel prize to G. Binning and H. Rohrer.**





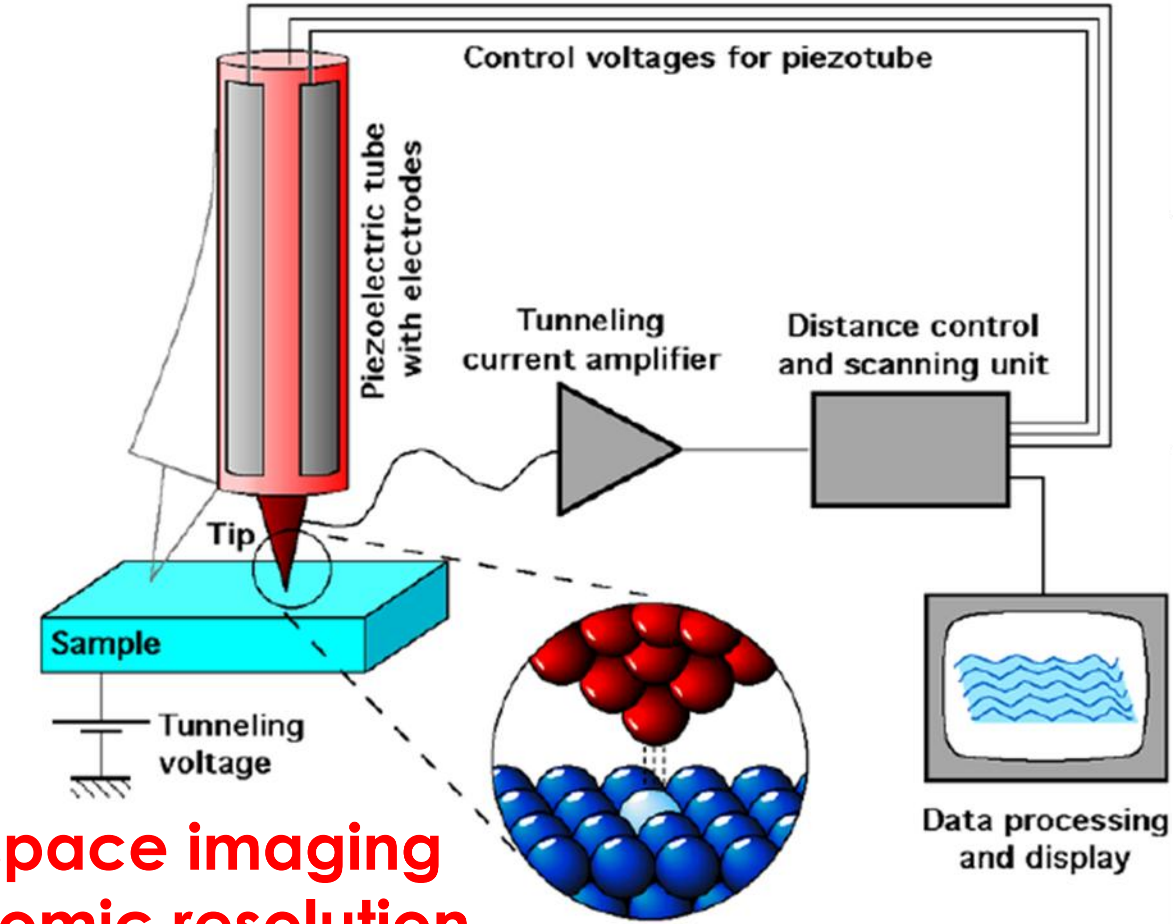


The first STM image of Si(111)-7x7.



Dimer-Adatom-Stacking fault model

STM-Introduction



Real space imaging with atomic resolution

$$I_t \sim e^{-2\kappa d}$$

STM: probing the local geometric and electronic structure of surfaces on a mesoscopic scale down to atomic distances.

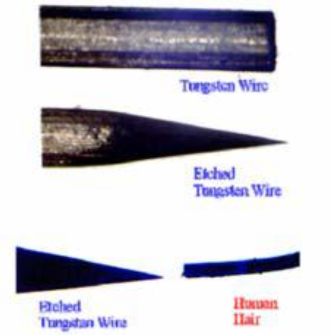
- strong distance dependence of the quantum mechanical tunneling effect.

Scanning Modes:

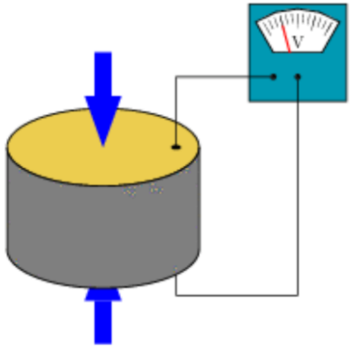
1. Constant current ..
2. Constant height ..
3. Spectroscopic ..

Instrumentation

C.J. Chen, *Introduction to scanning tunneling spectroscpy* (oxford, 1993)



- **Tip**
  - W tip : electrochemically etched
  - Pt-Ir tip: cutting



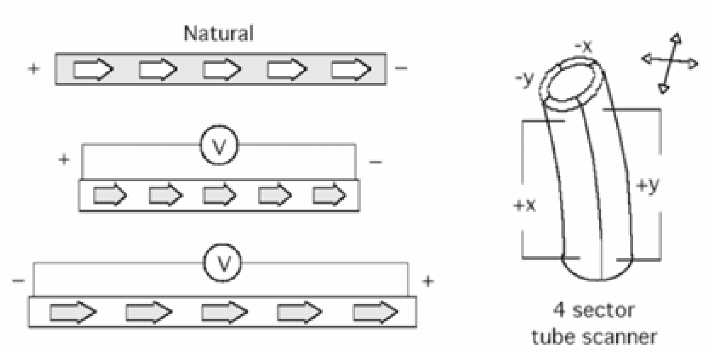
- **Positioning**
  - fine positioning: **piezoelectric ceramic** (Pb(Zr,Ti)O_3)

$$\frac{\Delta L}{L} = d_{ij}E \qquad \Delta L = d_{ij}V$$

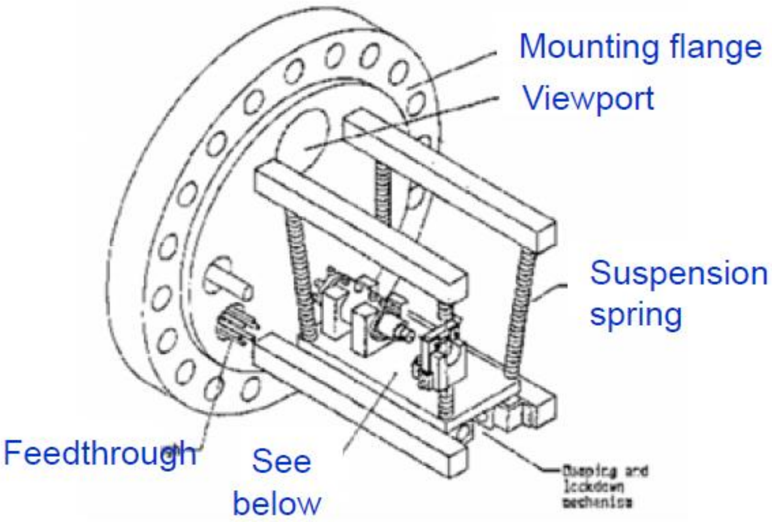
e.g.: PZT5H d_{33}=5.93 Å/V, d_{31} = -2.74 Å/V

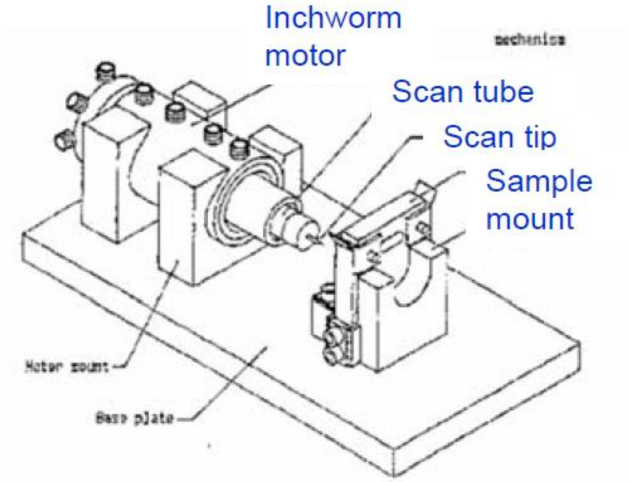
x,y: 0.1 Å z: 0,01 Å resolution

  - coarse positioning : step motor, inch worm
- **Vibration isolation**: -spring, viton O-ring, air table

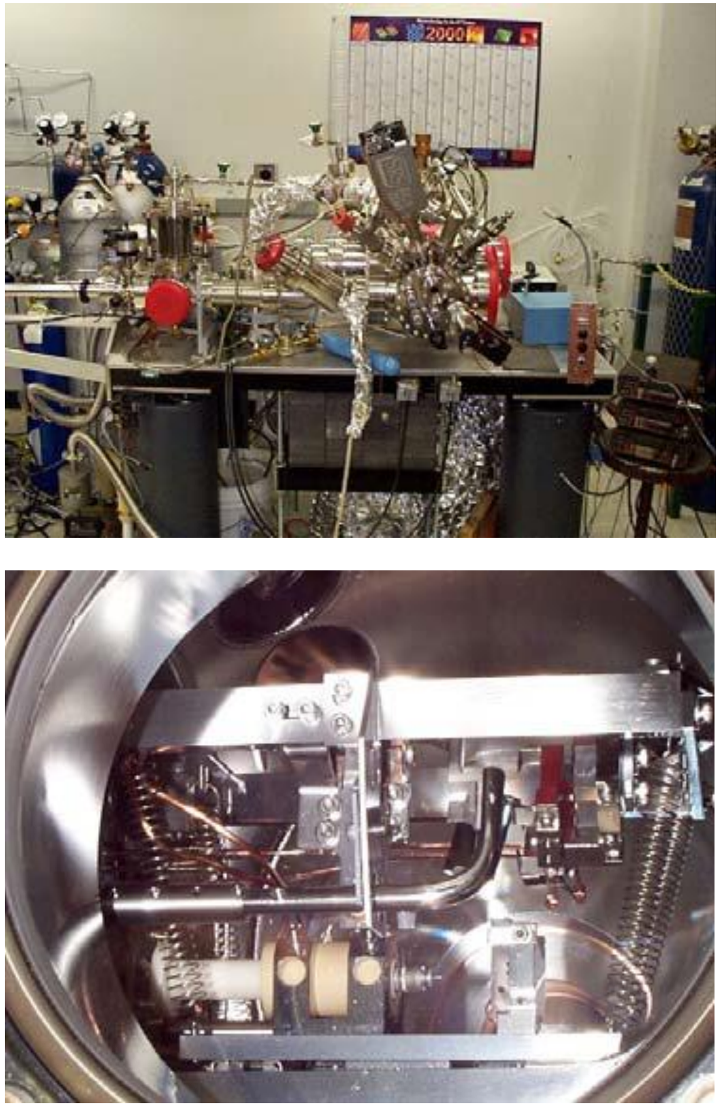


UHV STM





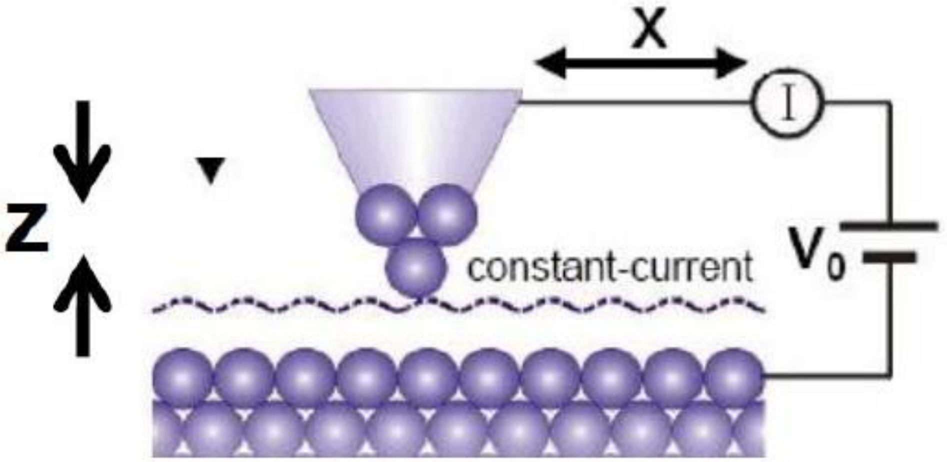
From Burleigh Instrument Inc.



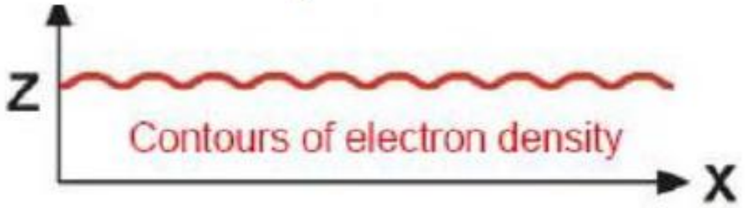
UHV STM System @UNT

What’s Measured in STM ?

STM Junction

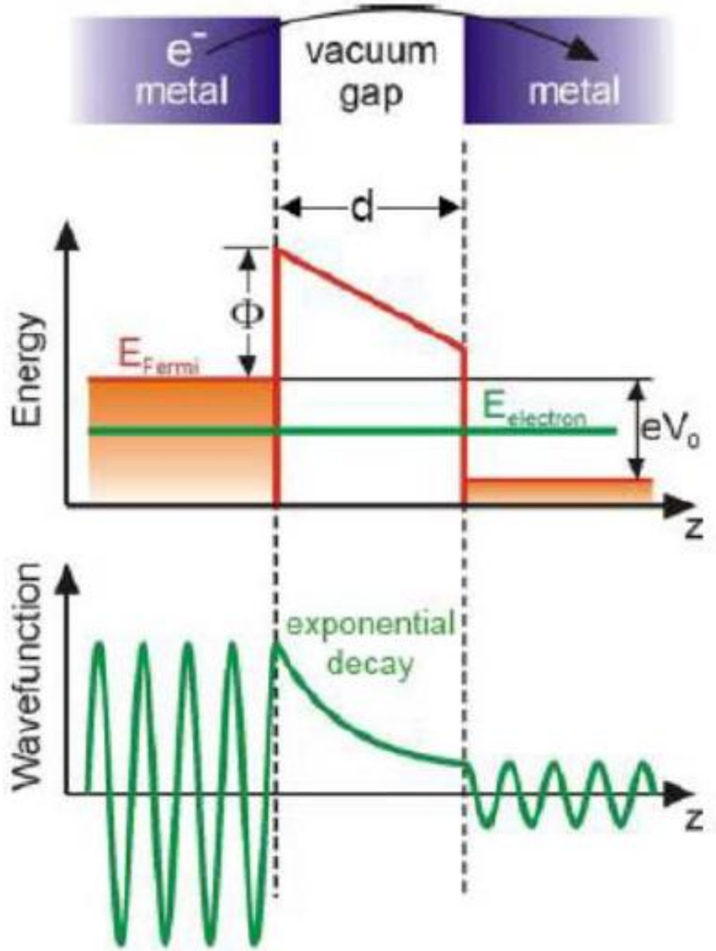


$$I_t \sim e^{-2\kappa d}$$



I_t : tunneling current
d : tip-sample distance
κ : constant depending on the height of the potential barrier (e.g., For metals with typical work functions of 4~5 eV, κ is of the order of 1 $Å^{-1}$)

1D-Tunnel Junction



Theory of SPM: Quantum Mechanics

- Schrodinger's wave equation: describes the space- and time-dependence of quantum mechanical systems

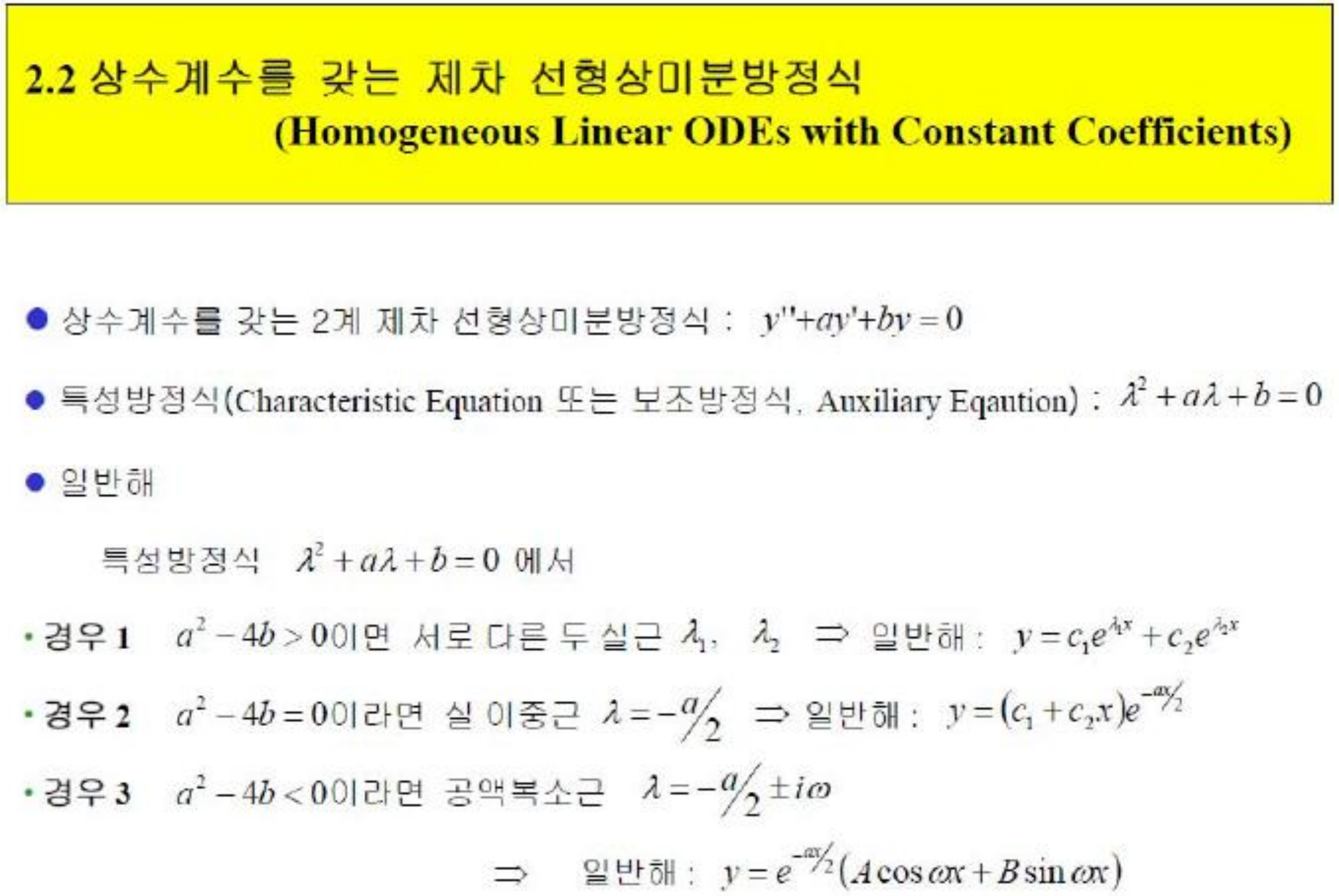
Time-independent Schrodinger equation

$$\boxed{\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x) = 0}$$

- Meaning of Wave function $\psi(x)$: Probability amplitude, ie, the probability to find a particle in x.
- General solutions:
  - In case of $E\text{-}V(x) > 0$: $\psi(x) = Ae^{ikx} + Be^{-ikx}$ $\left(k = \frac{\sqrt{2m(E-V)}}{\hbar}\right)$
  - In case of $E\text{-}V(x) < 0$: $\psi(x) = Ae^{kx} + Be^{-kx}$ $\left(k = \frac{\sqrt{2m(V-E)}}{\hbar}\right)$
  - In case of $V(x) = 0$: $\psi(x) = Ae^{ikx} + Be^{-ikx}$ $\left(k = \frac{\sqrt{2mE}}{\hbar}\right)$

Theory of SPM: Quantum Mechanics

$$ax^2+bx+c=0(a\neq 0) \qquad x=\frac{-b\pm\sqrt{b^2-4ac}}{2a}$$



2.2 상수계수를 갖는 제차 선형상미분방정식
(Homogeneous Linear ODEs with Constant Coefficients)

- 상수계수를 갖는 2계 제차 선형상미분방정식 : $y''+ay'+by=0$
- 특성방정식(Characteristic Equation 또는 보조방정식, Auxiliary Eqaution) : $\lambda^2+a\lambda+b=0$
- 일반해

특성방정식 $\lambda^2+a\lambda+b=0$ 에서

- **경우 1** $a^2-4b>0$이면 서로 다른 두 실근 λ_1, λ_2 ⇒ 일반해 : $y=c_1e^{\lambda_1 x}+c_2e^{\lambda_2 x}$
- **경우 2** $a^2-4b=0$이라면 실 이중근 $\lambda=-a/2$ ⇒ 일반해 : $y=(c_1+c_2x)e^{-ax/2}$
- **경우 3** $a^2-4b<0$이라면 공액복소근 $\lambda=-a/2\pm i\omega$

⇒ 일반해 : $y=e^{-ax/2}(A\cos\omega x+B\sin\omega x)$

Particle (Electron) in Free Space

$$E = \frac{mv^2}{2} = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

$$p = \frac{h}{\lambda} = \hbar k \Leftarrow \left[\hbar = \frac{h}{2\pi}\right], \left[k = \frac{2\pi}{\lambda}\right]$$

$$k = \frac{p}{\hbar} = \frac{\sqrt{2mE}}{\hbar}$$

Theory of SPM: Tunneling Effect

- When the height and thickness are not infinite, tunneling occurs

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0$$

Region I: $\psi_1(x) = A_1 e^{ik_1 x} + B_1 e^{-ik_1 x}$

Region II: $\psi_2(x) = A_2 e^{k_2 x} + B_2 e^{-k_2 x}$ $(E << V_0)$ Tunneling

Region III: $\psi_3(x) = A_3 e^{ik_3 x} + B_3 e^{-ik_3 x}$

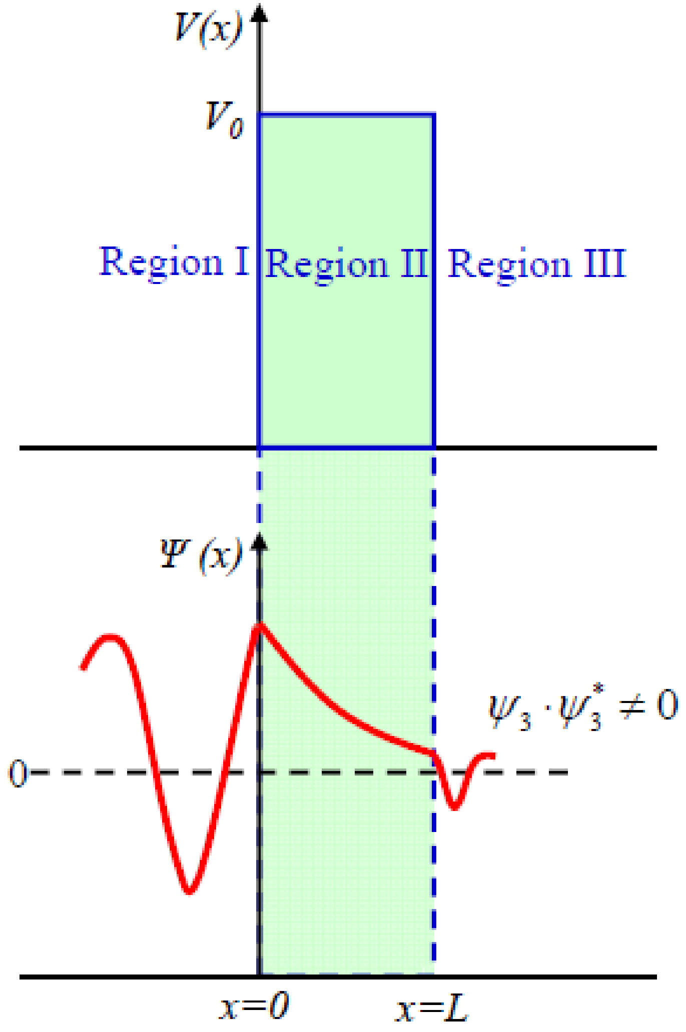
$$k_1 = k_3 = \sqrt{\frac{2mE}{\hbar^2}} \qquad k_2 = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)}$$

- Boundary condition: ψ (not zero) and d ψ/dt are continuous at boundary (@ x=0, L)

$$\psi_1(0) = \psi_2(0)$$
$$\psi_2(L) = \psi_3(L)$$
$$\left.\frac{\partial \psi_1}{\partial x}\right|_{x=0} = \left.\frac{\partial \psi_2}{\partial x}\right|_{x=0}$$
$$\left.\frac{\partial \psi_2}{\partial x}\right|_{x=L} = \left.\frac{\partial \psi_3}{\partial x}\right|_{x=L}$$

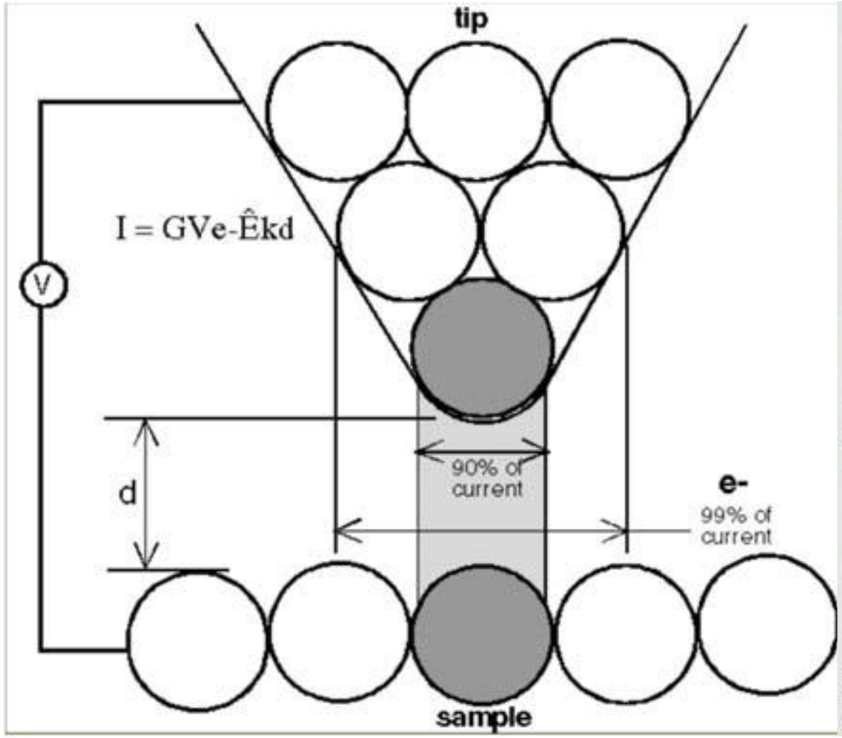
$$\boxed{T = \frac{A_3 \cdot A_3^*}{A_1 \cdot A_1^*} \cong 16\left(\frac{E}{V_0}\right)\left(1 - \frac{E}{V_0}\right)\exp(-2k_2 L)}$$

Transmission Coefficient



Probability of finding electron is not 0

STM-Tunneling Models



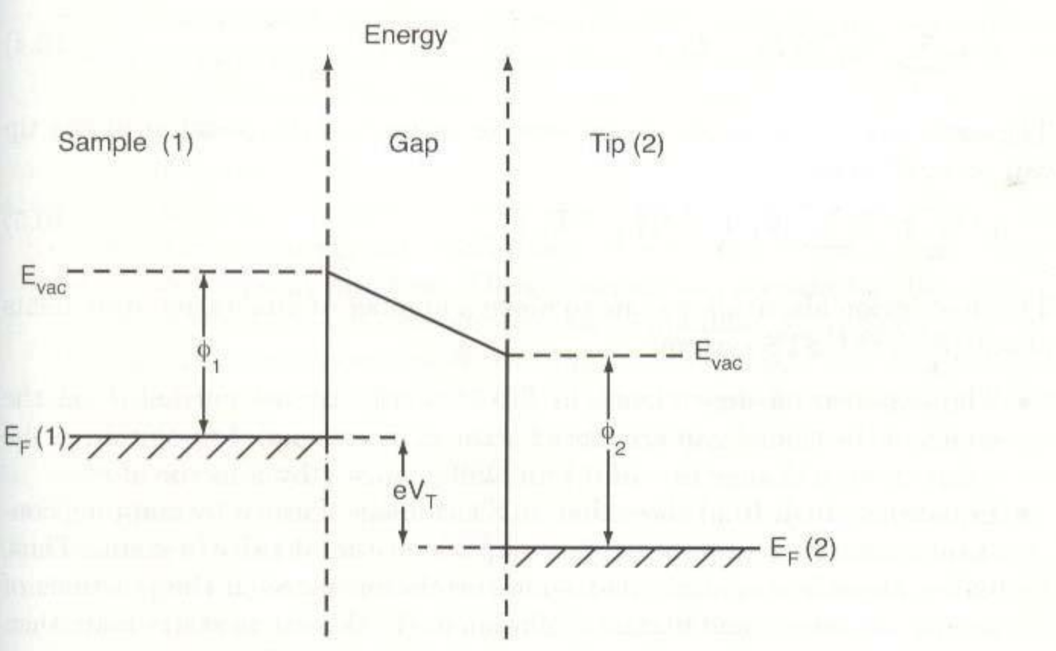


Fig. 10.4. The energy level scheme of a tunnel barrier. Sample and tip are denoted (1) and (2), respectively. Work function is ϕ, and tunnel voltage is V_T

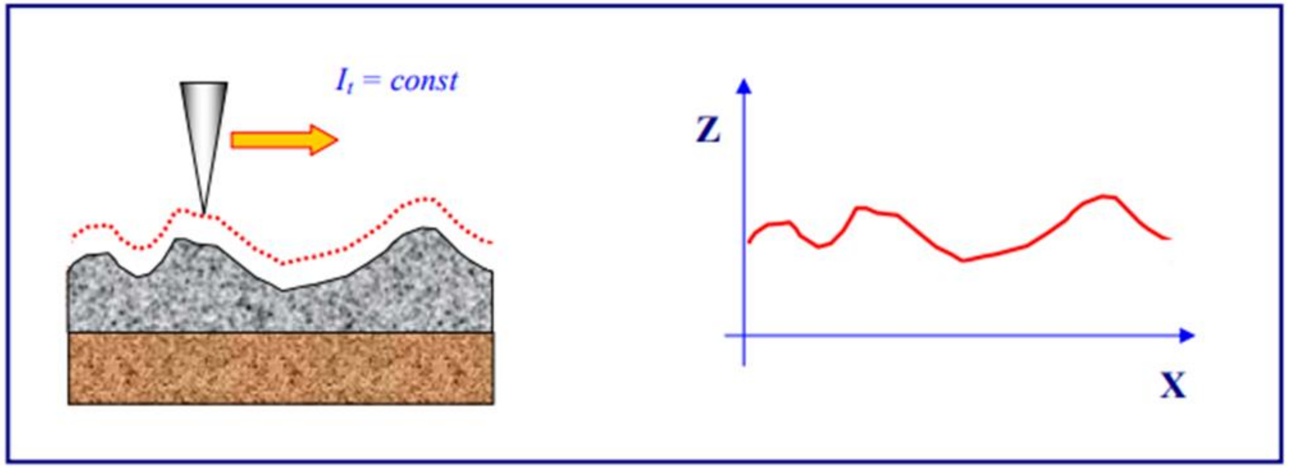
$$T \cong 16\left(\frac{E}{V_0}\right)\left(1-\frac{E}{V_0}\right)\exp(-2kL)$$

$$\left(k = \frac{\sqrt{2m(V-E)}}{\hbar}\right)$$

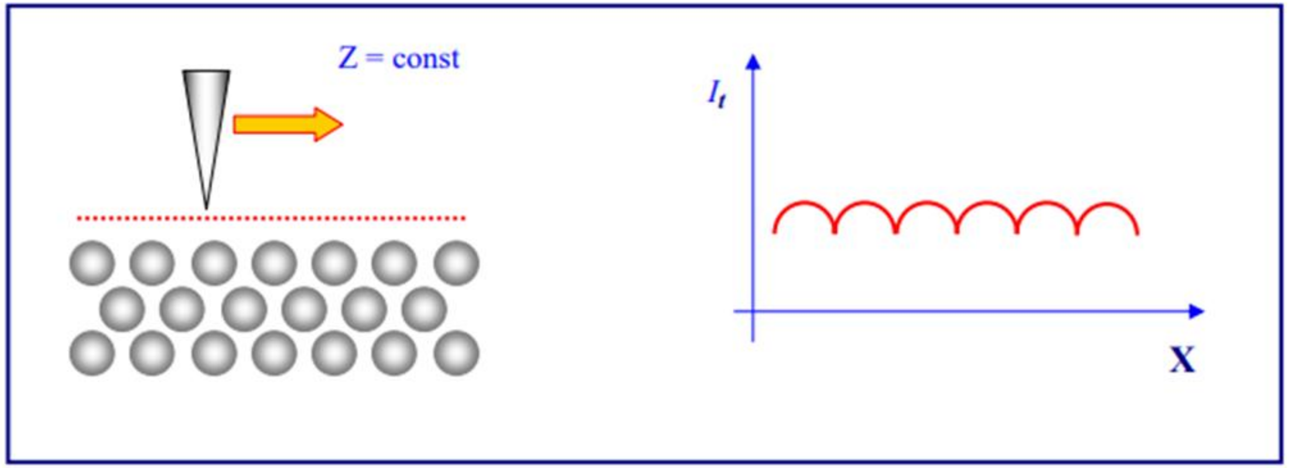
$$I_t \sim e^{-2\kappa d} \qquad \left(k = \frac{\sqrt{2m\phi_1}}{\hbar}\right)$$

Constant current STM image corresponds to a surface of constant state density.

Scanning Mode of STM



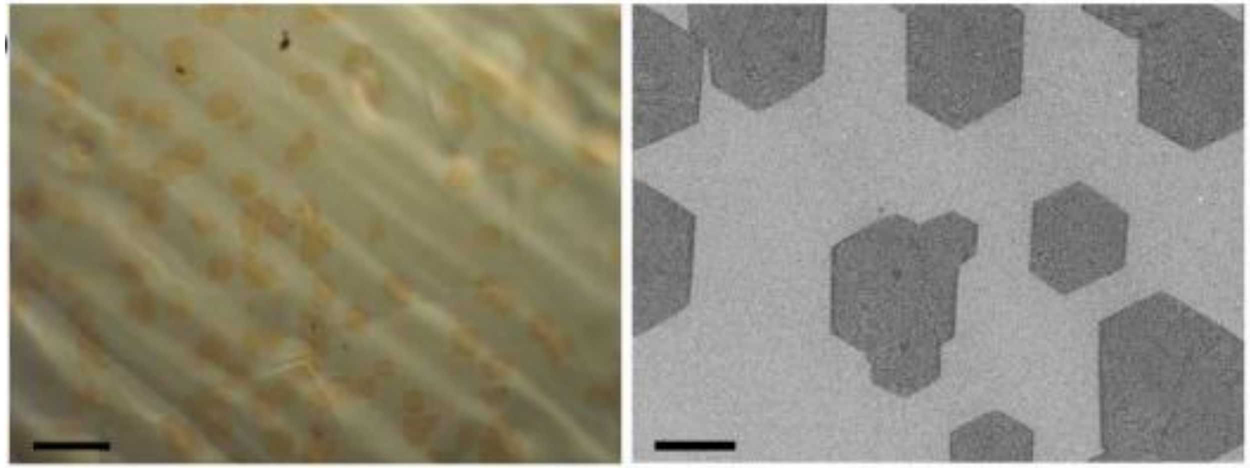
- **Constant current mode**
- Slow scanning mode (z-stage moving)
- Rough surface sample
- Sensitive to tilting
- Minimal drift



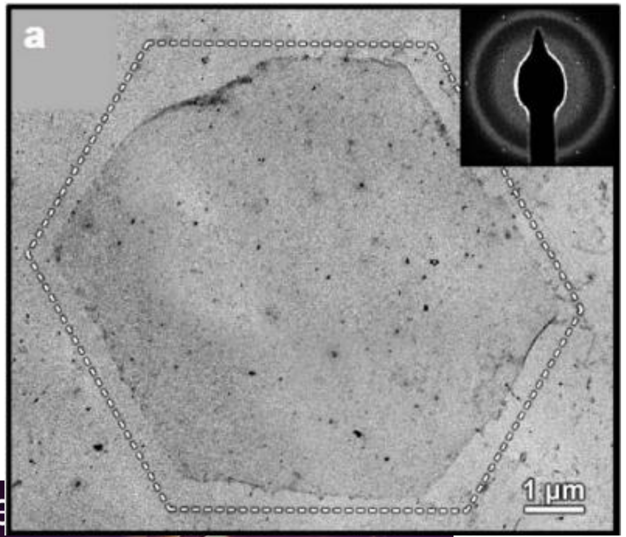
- **Constant height mode**
- Fast scanning mode (z-stage constant)
- Flat surface sample
- Typical mode

Analysis of Graphene Grain

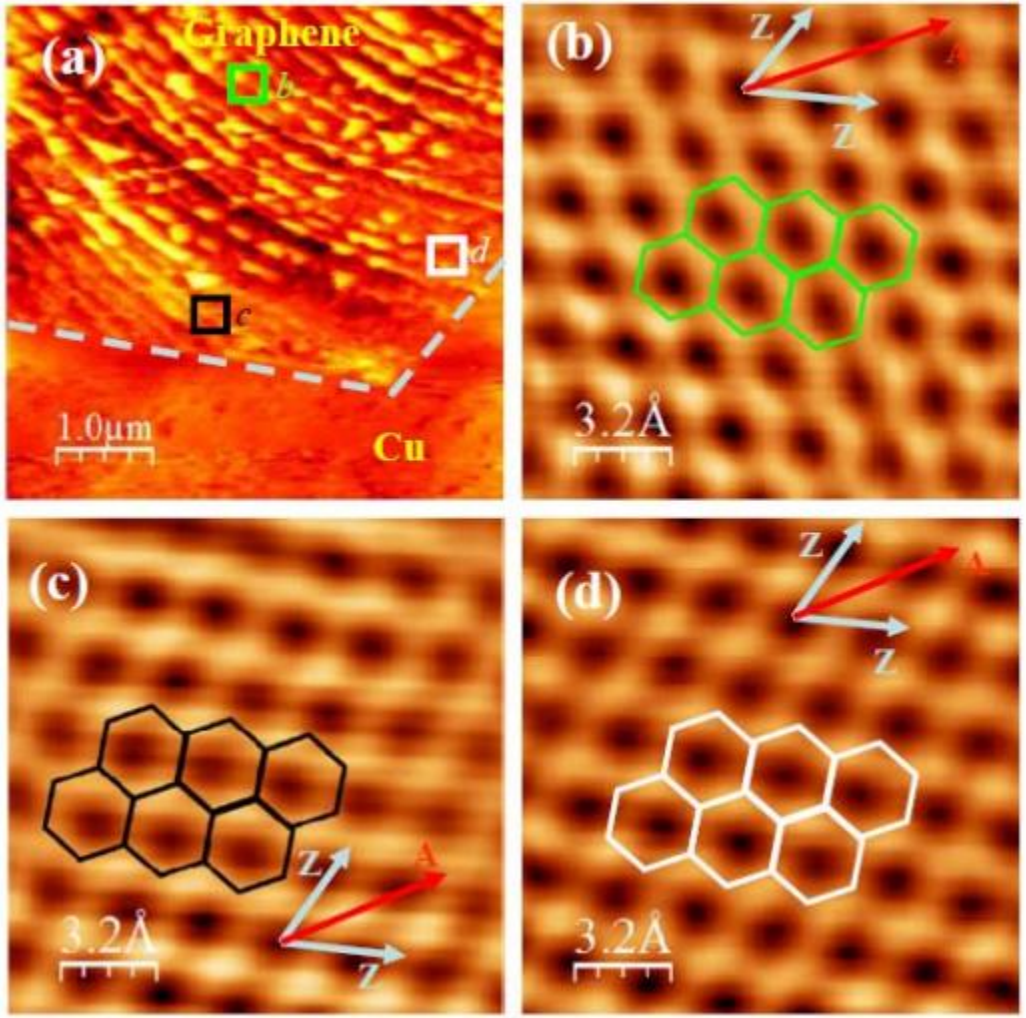
- **Optical image & SEM image of graphene on Cu substrate**



- **TEM image and electron diffraction pattern**



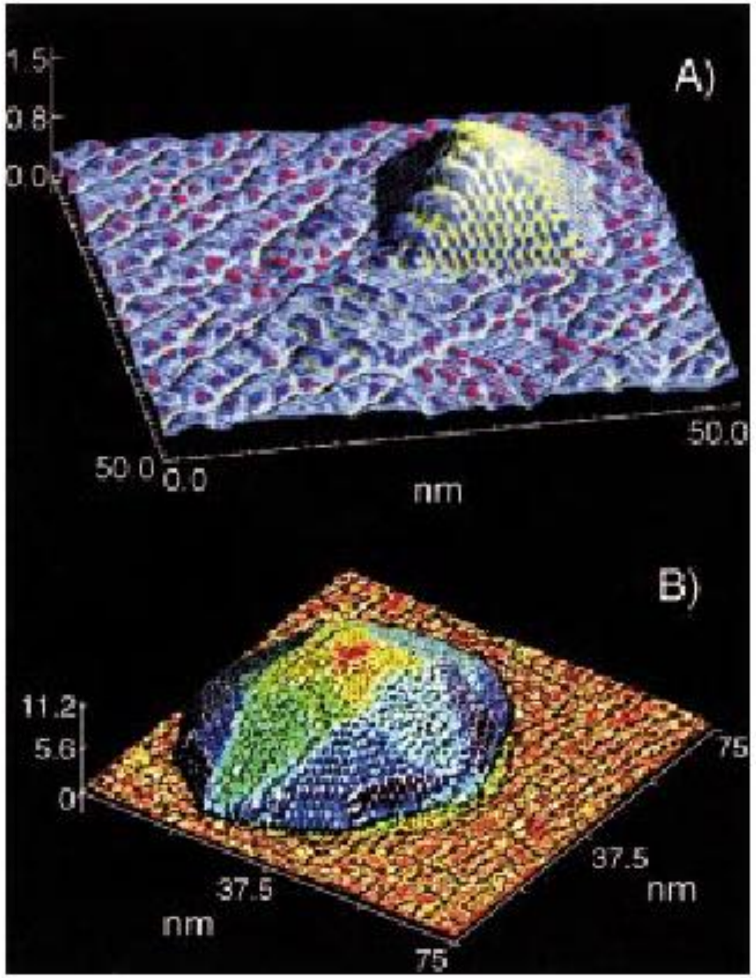
- **STM image of single-crystal graphene on Cu**



Applications of STM

- Surface geometry/atomic structure
- Molecular structure
- Local electronic structure
- Electronic transport
- Atom manipulation
- Nano-chemical reaction

Surface Geometry/Atomic Structure of Quantum Dot

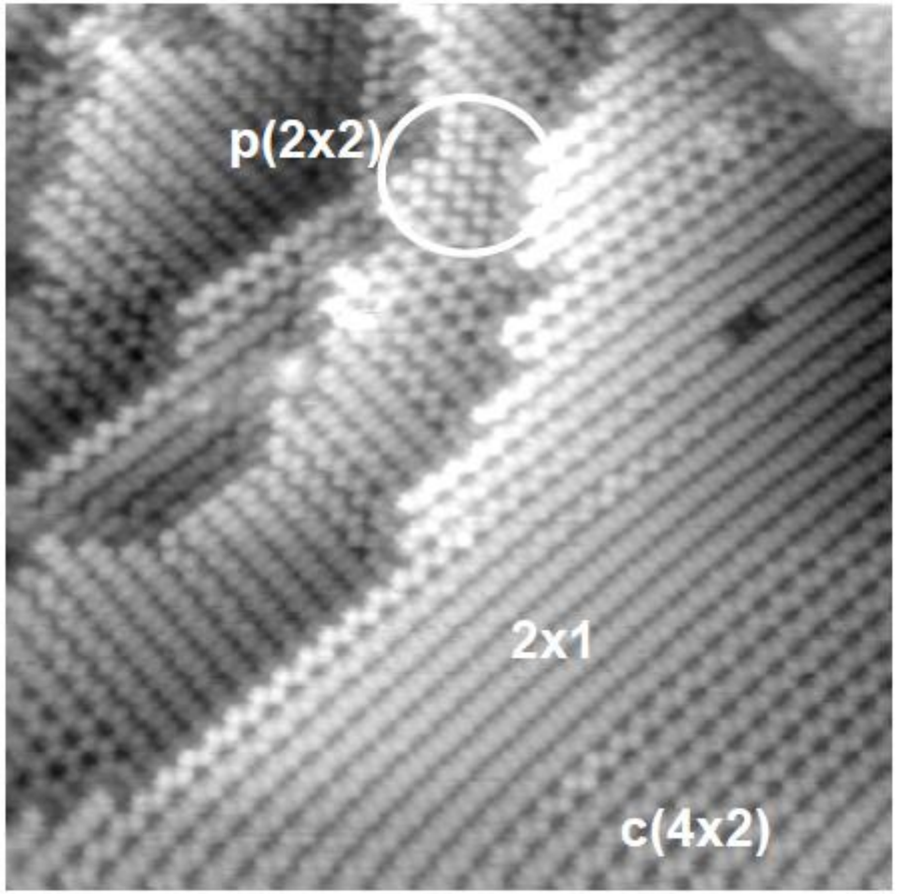


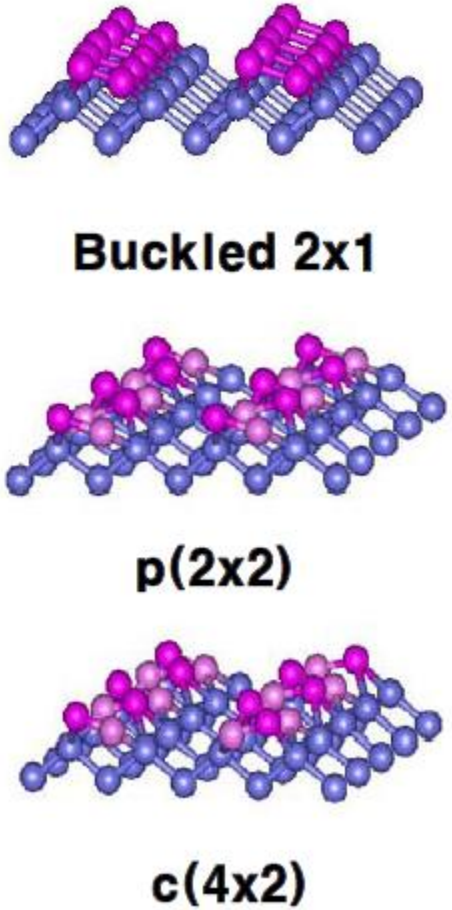
R.S. Williams et al, ***Acc. Chem. Res*. 32,** 425 (1999)

Ge pyramid containing ~2000 Ge atoms on Si(100)

Ge dome grown by PVD on a 600 C Si(100)

Atom-resolved Surface Structure

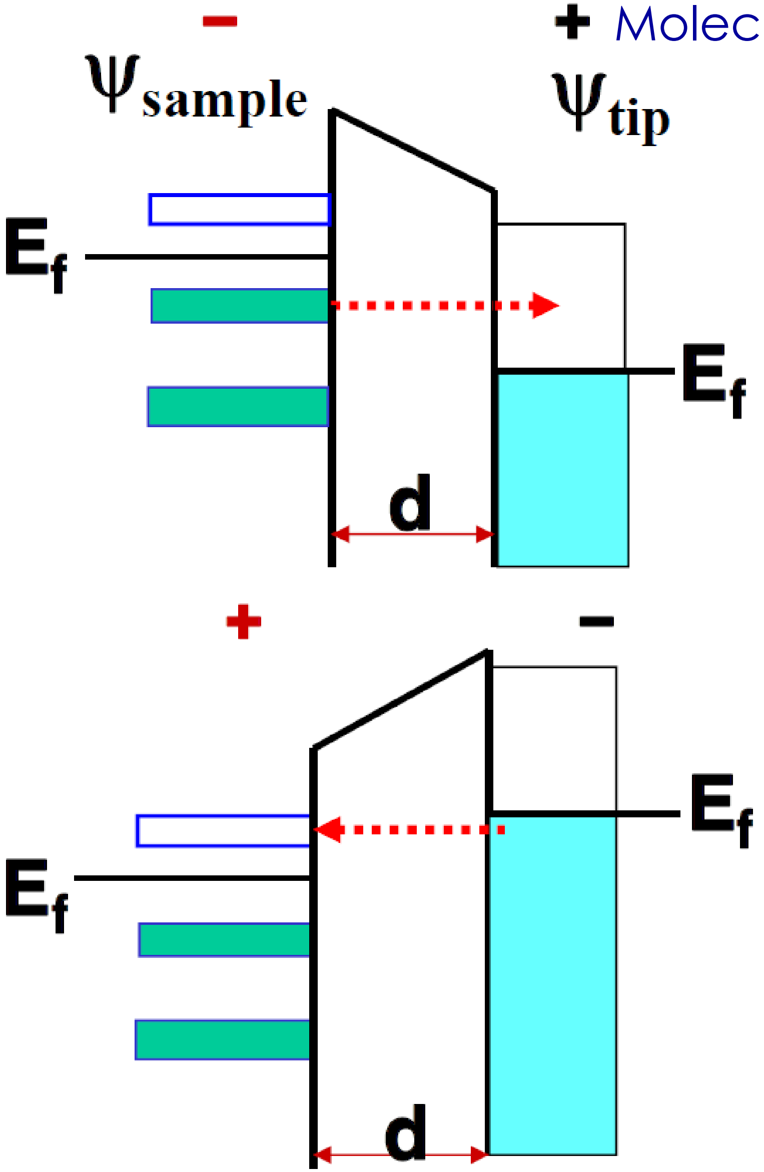




Various Reconstructions of Ge(100)-2x1

Molecular Structure & Local Electronic Structure (Molecular Orbitals):

Molecular Orbitals



Occupied state (HOMO)

Highest
Occupied
Molecular
Orbital

Unoccupied state (LUMO)

Lowest
Unoccupied
Molecular
Orbital

J.J.Boland, *Adv. Phys.* 42, 129(1993)

Molecular Structure & Local Electronic Structure (Molecular Orbitals):

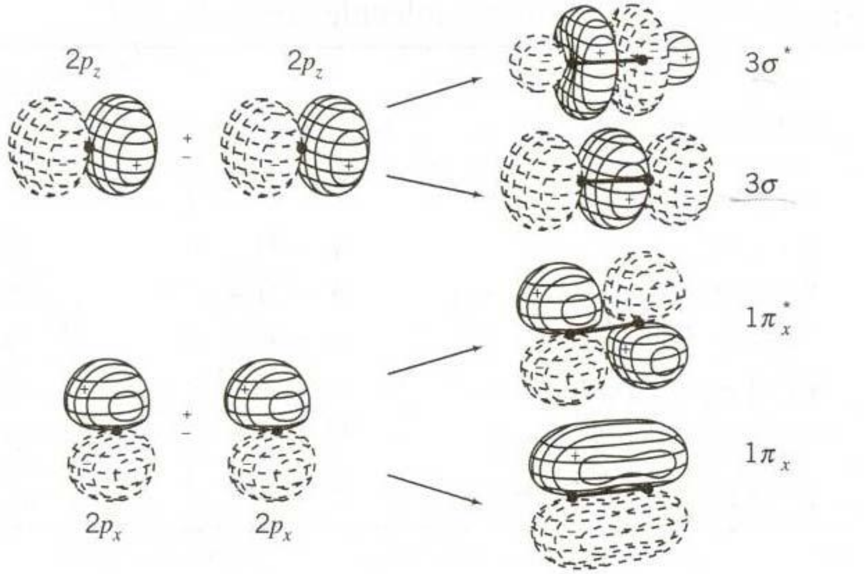
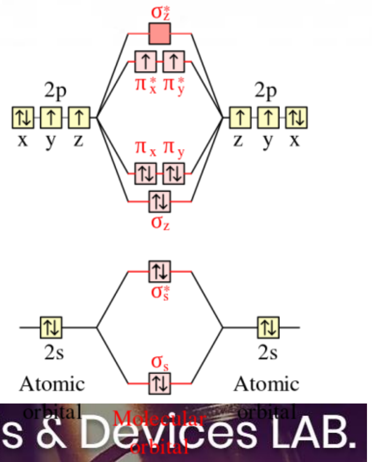


Figure 10.7. Schematic shapes of MOs built from *p* AOs.



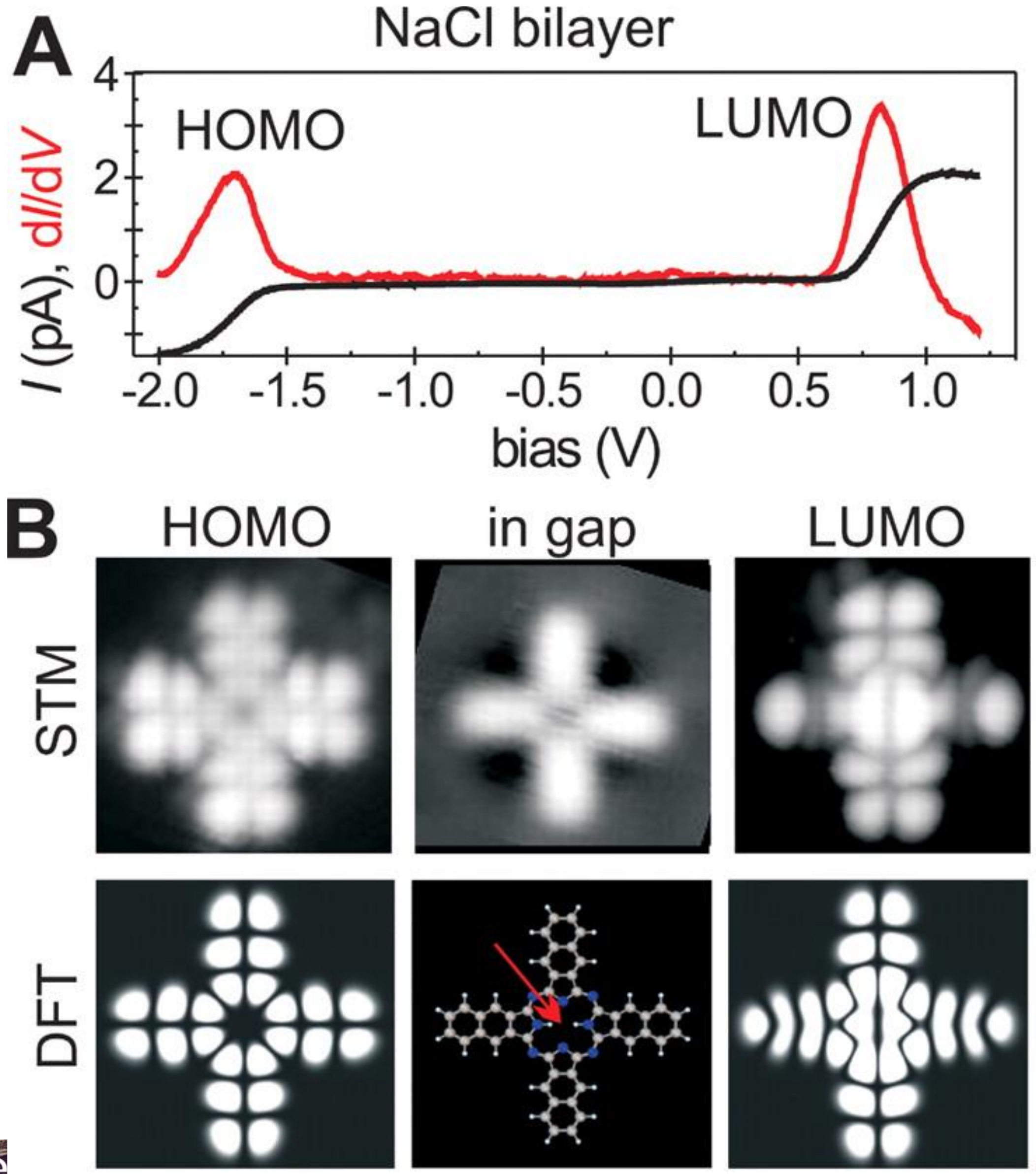
Unoccupied state (LUMO)

π-antibonding*

Occupied state (HOMO)

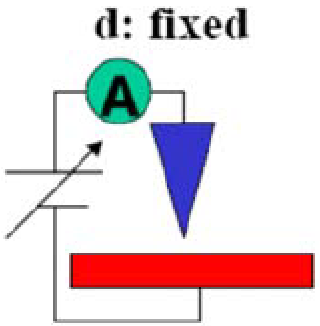
π-bonding

Other example for STM imaging of Molecular Orbitals



Science, 317,1203 (2007)
DOI: 10.1126/science.1144366

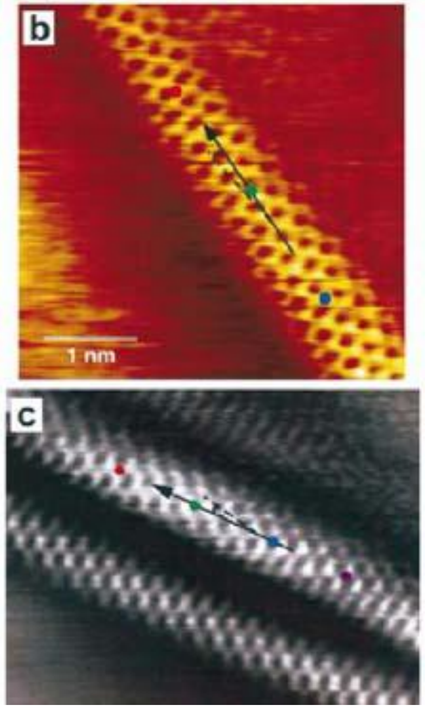
Tunneling spectroscopy of Carbon Nanotubes

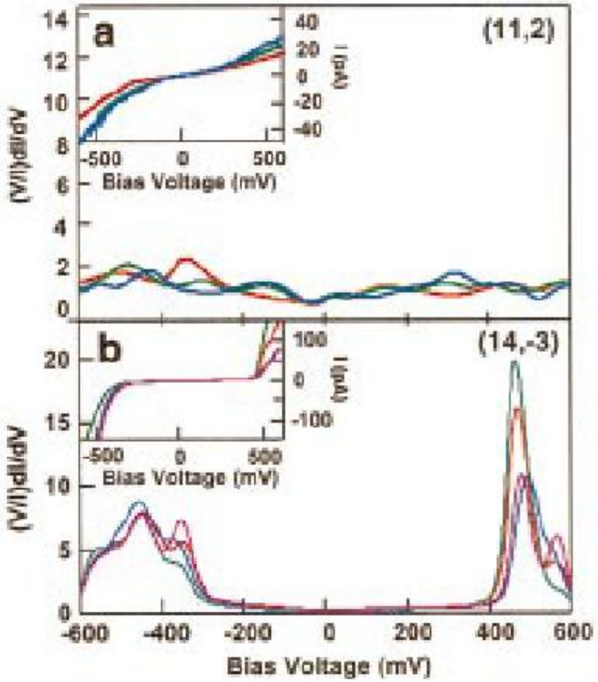


$I_t \sim \Sigma\, |\psi_{tip}|^2\, |\psi_{sample}|^2\, e^{-2\kappa d}$

$(Z)_{I,V}$ - x,y : Topography

dI/dV~ local electronic structure of sample surface
(LDOS: Local Density Of State)





Constant LDOS
Metallic SWNT

Semiconducting
SWNT

"Atomic structure and electronic properties of single-walled carbon nanotubes", Nature 391, 62-64 (1998).

Atomic Manipulation by STM

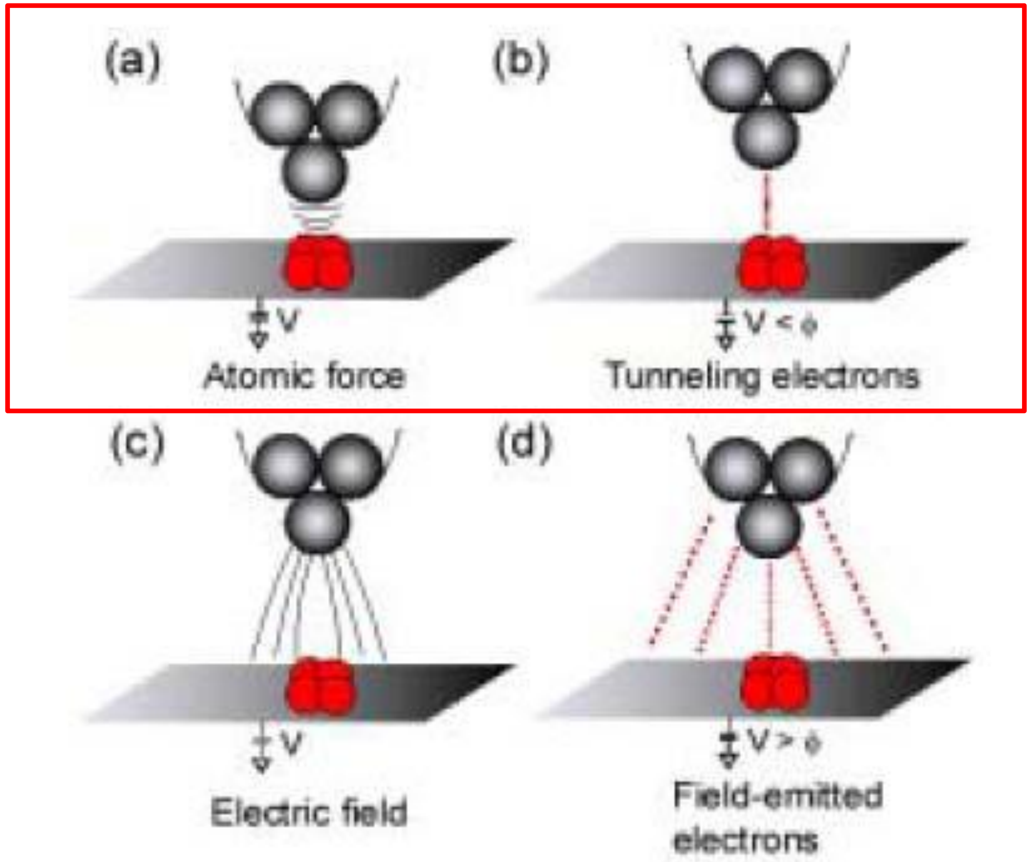
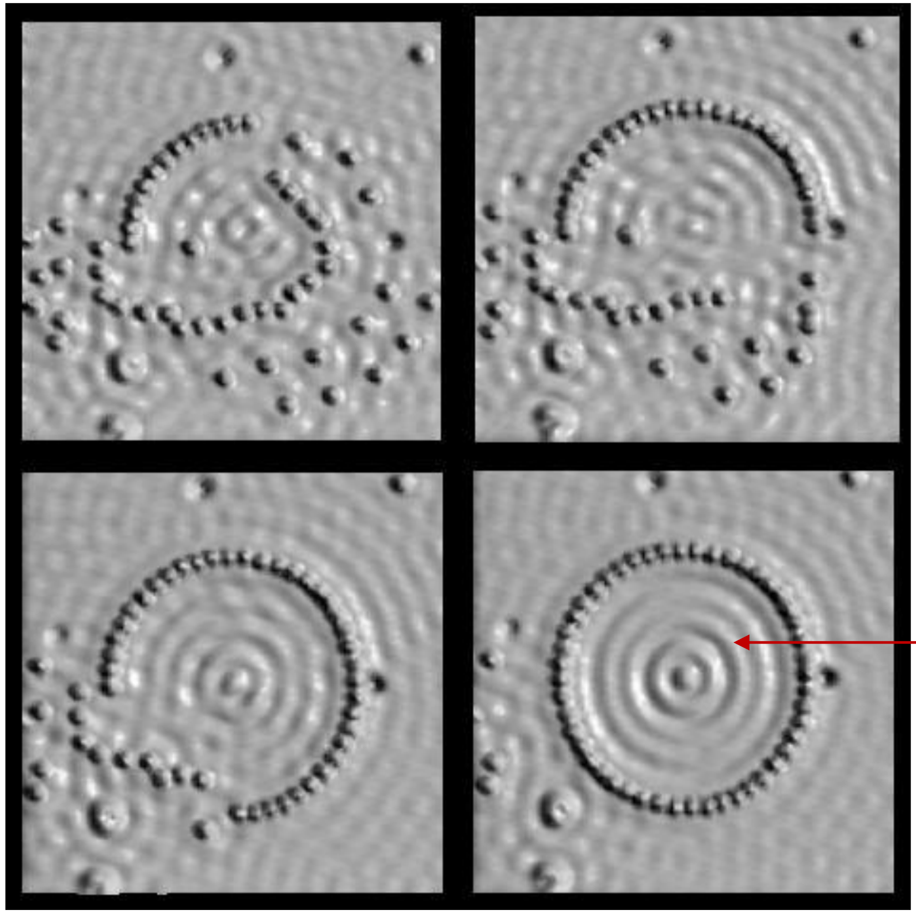


그림 1. STM을 이용한 원자(분자)조작의 주요 원리들. V: 탐침과 표면사이에 가해지는 바이어스 전압, ϕ: 일함수

Atomic Manipulation by STM

Iron on Copper (111):



M.F. Crommie, C.P. Lutz, D.M. Eigler. *Science* 262, 218-220 (1993).

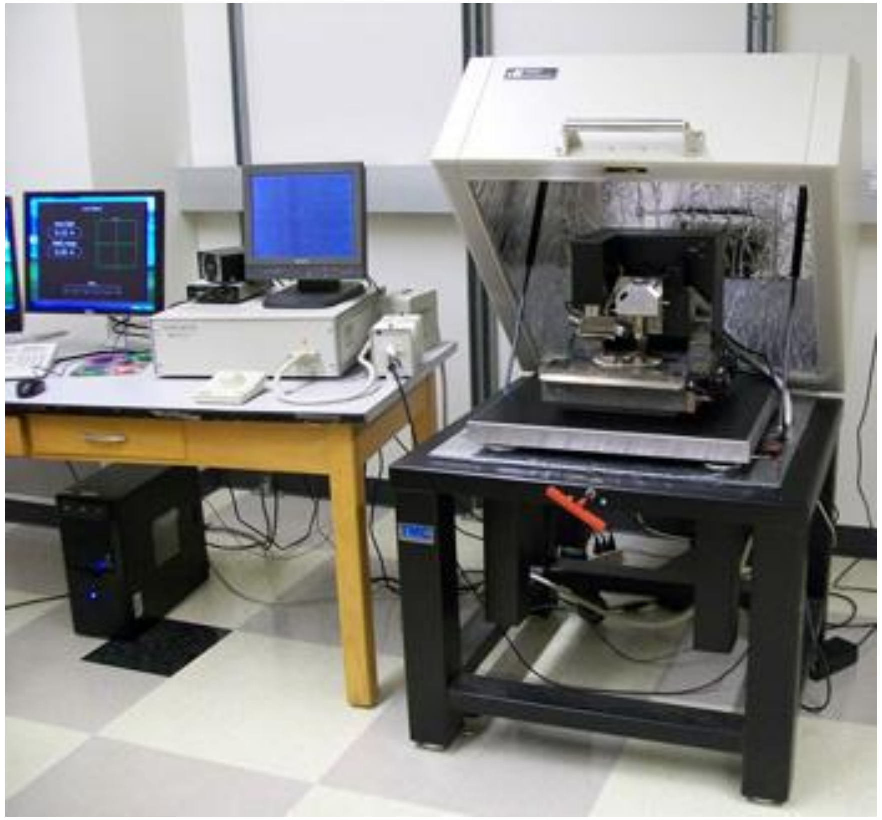
Circular corral
radius= 71.3 A
48 Fe atoms

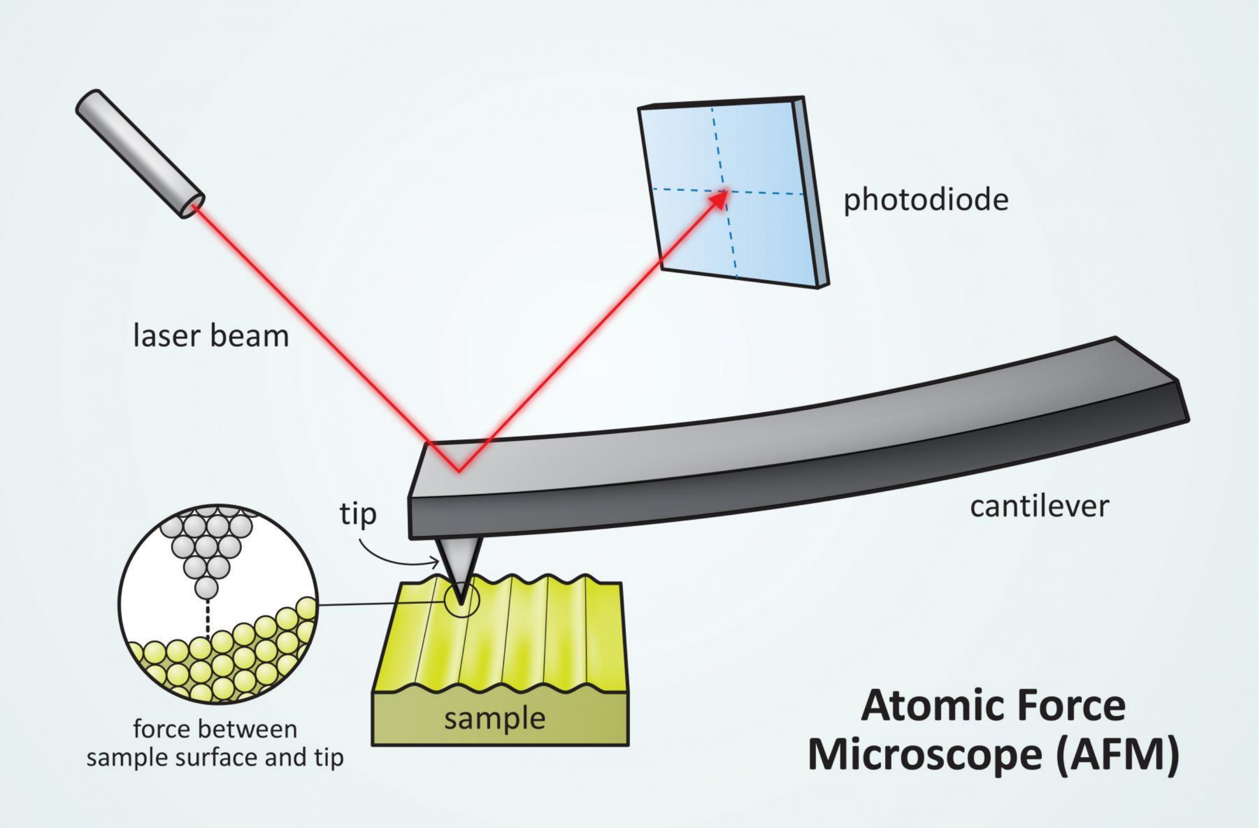
Quantum-mechanical interference patterns

Atomic Force Microscopy (AFM)

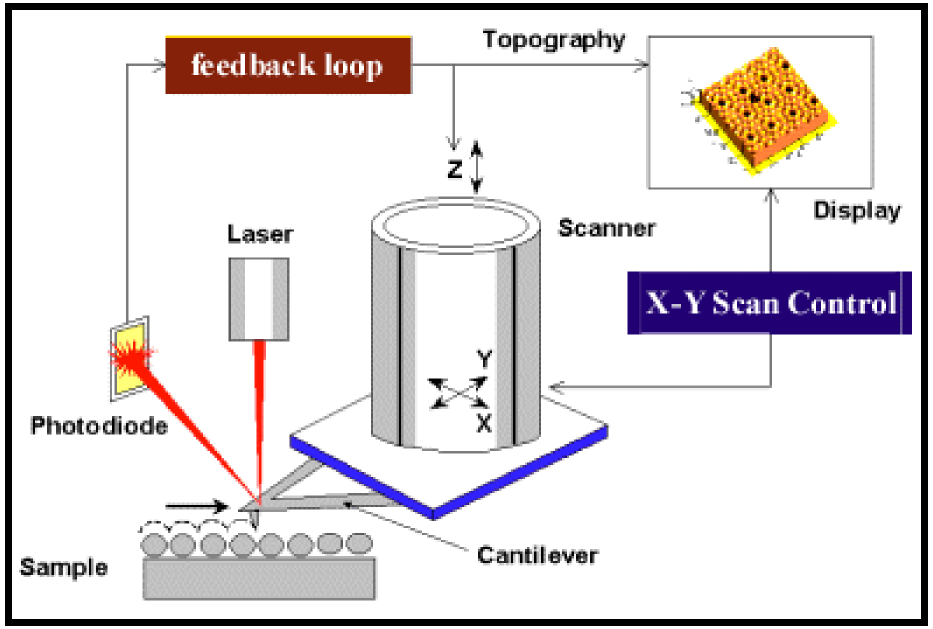
AFM: measuring the sample topography or mechanical properties.

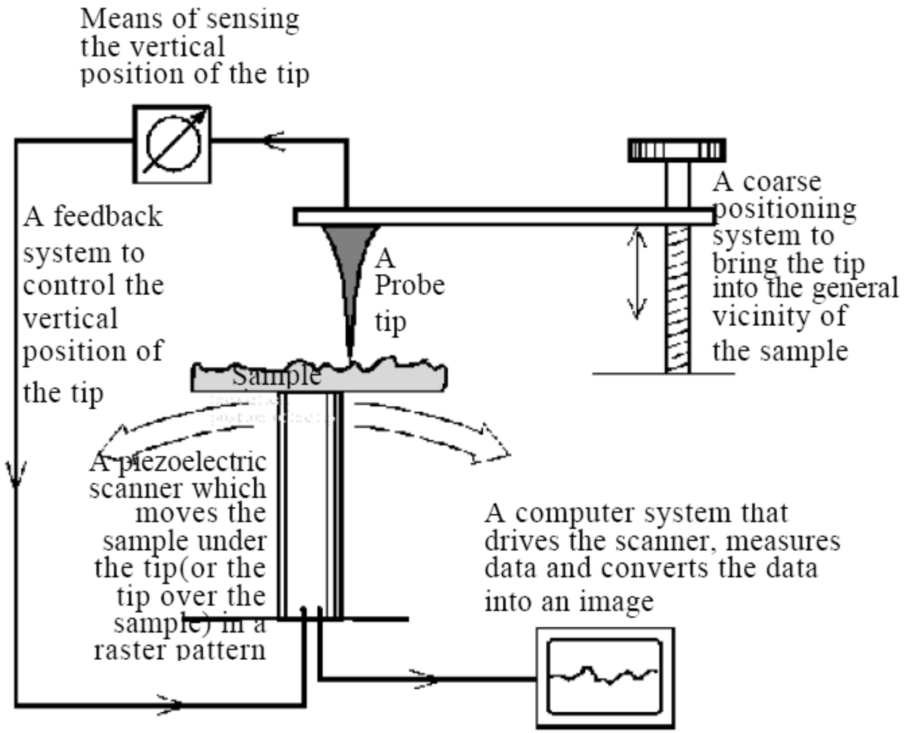
- van der Waals molecular forces or contact forces between a tip and the sample
- Able to analyze polymers, ceramics, composites, glass, and biological samples (STM: conducting or semiconducting surfaces)





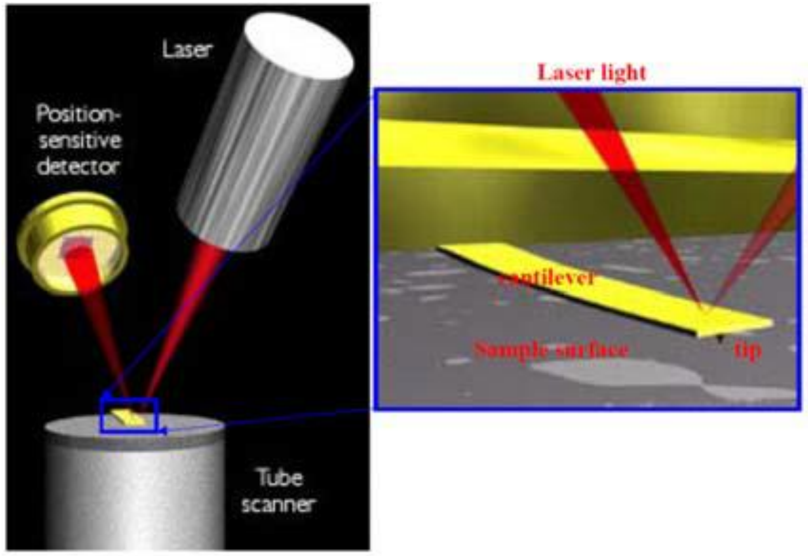
Instrumentation: Operation





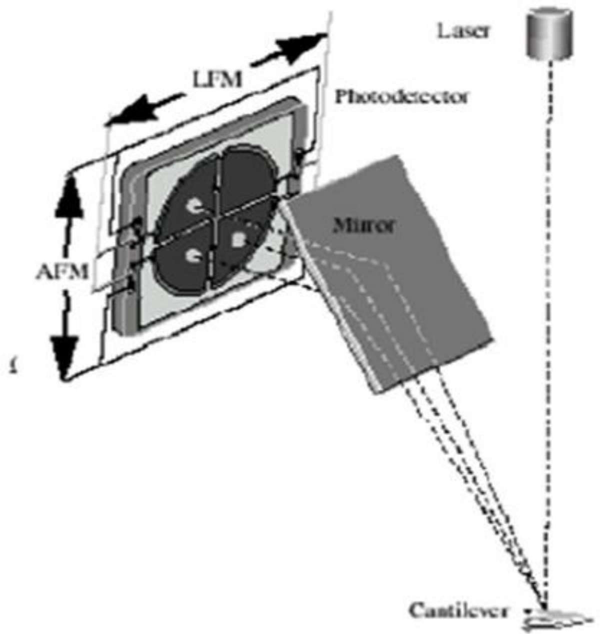
- Atomically sharp tips scan over surface + piezoelectric scanner to maintain the tip at constant force + optical detection system
- **constant force mode**: height variation is recorded
- **constant height mode**: deflection force is recorded
- sensitivity: ~2–10 nm in lateral, 0.1 nm in vertical

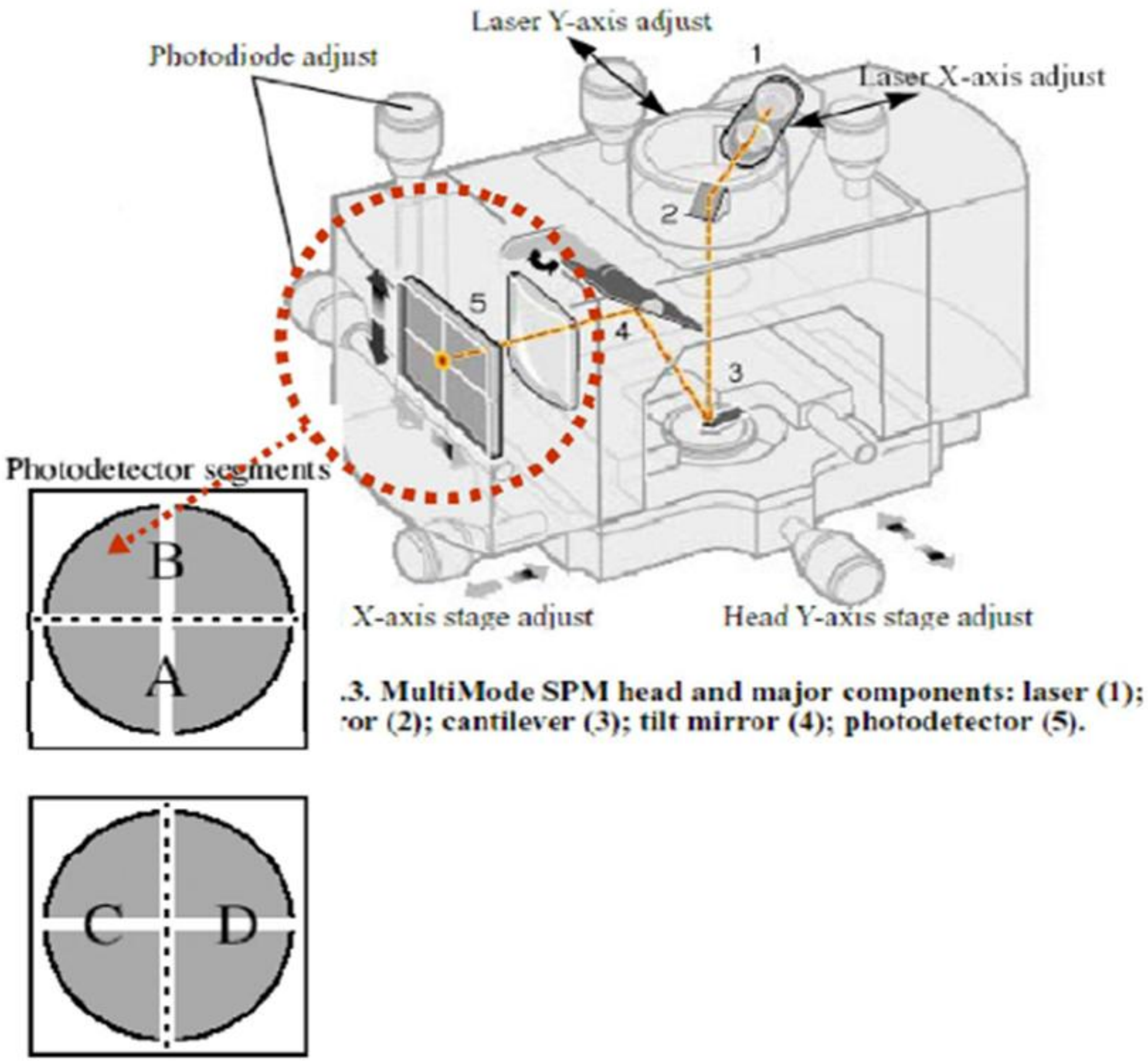
Operating Principles



- Relies on measuring forces between a sharp tip and surface at very short distances (1-100 Å tip-surface separation)
- Concept of AFM and the optical lever: (left) a cantilever touching a sample; (right) the optical lever.
- Force sensor: cantilever
- Fine positioning: piezoelectric scanner
- Deflection detection (optical detection system): photodiode interferometry

AFM Layout

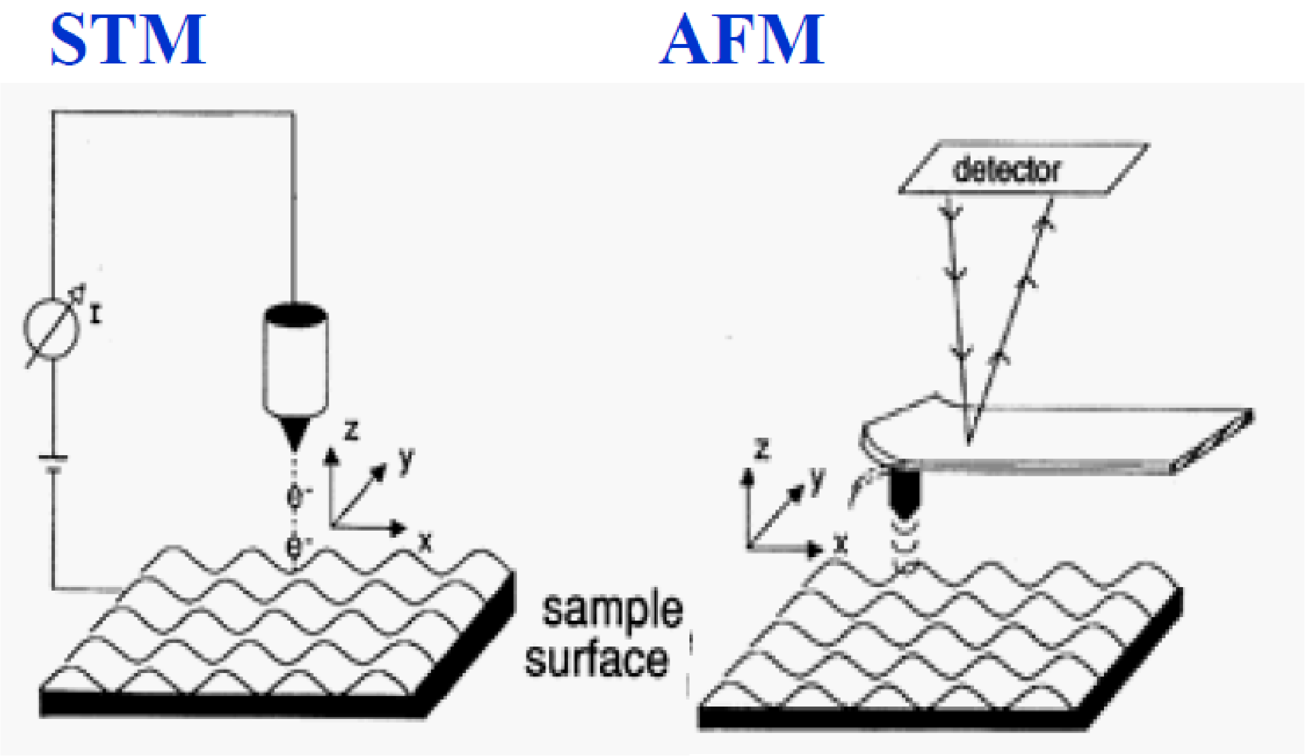




.3. MultiMode SPM head and major components: laser (1); ror (2); cantilever (3); tilt mirror (4); photodetector (5).

http://www.youtube.com/watch?v=DwB6I5cCf8E&feature=related

STM vs AFM



- **AFM (atomic force microscopy) vs. STM**
  - resolution in z axis: STM is better.
  - dependence of tip geometry in AFM
  - STM only applicable to conducting material under UHV

Instrumentation: Cantilever & Tip

- Material: Si , Si_3N_4

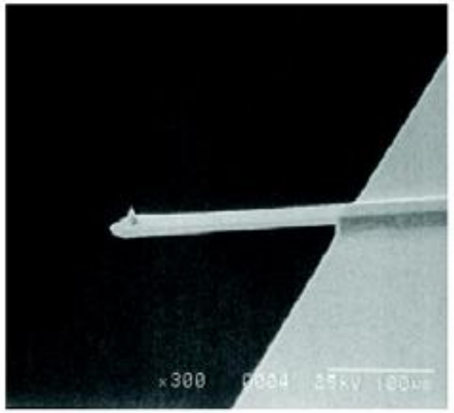
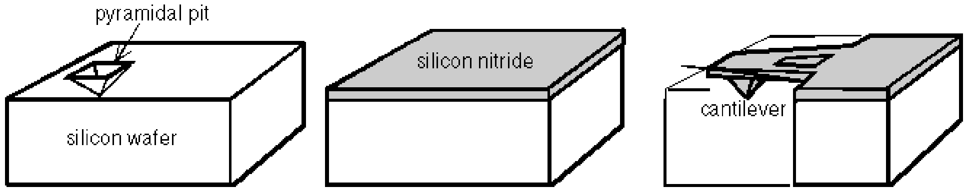
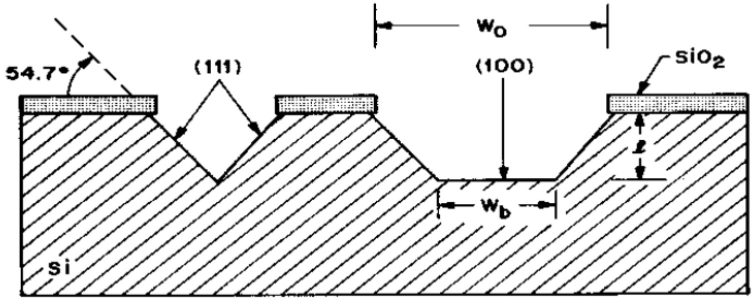


Figure 3. SEM image of an integrated single crystal silicon cantilever and tip which has an end radius of 2 to 10nm. Tips for AFM are typically made of silicon or silicon nitride. Bar=100µm.

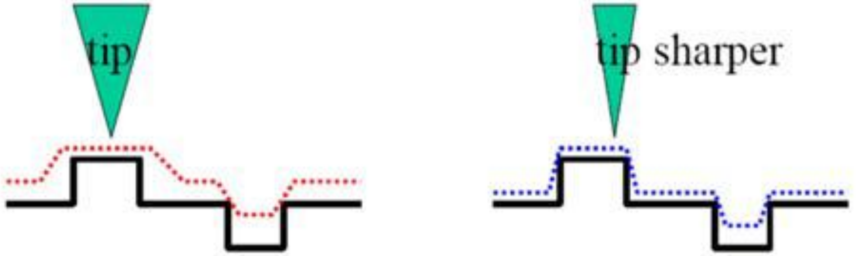


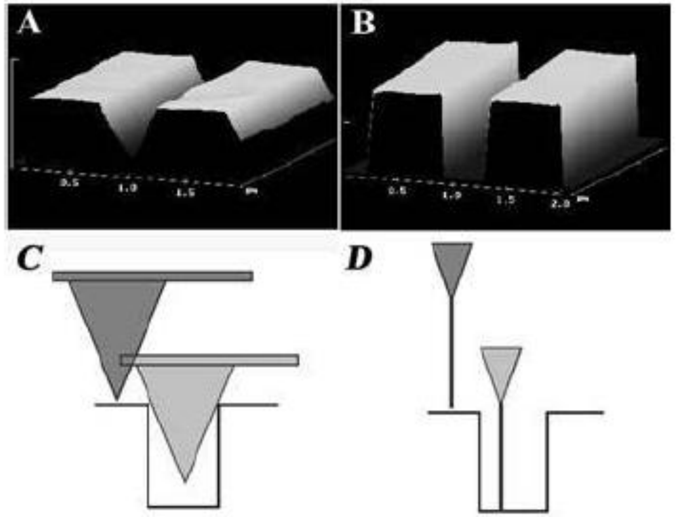


Orientation-dependent (Anisotropic) etching

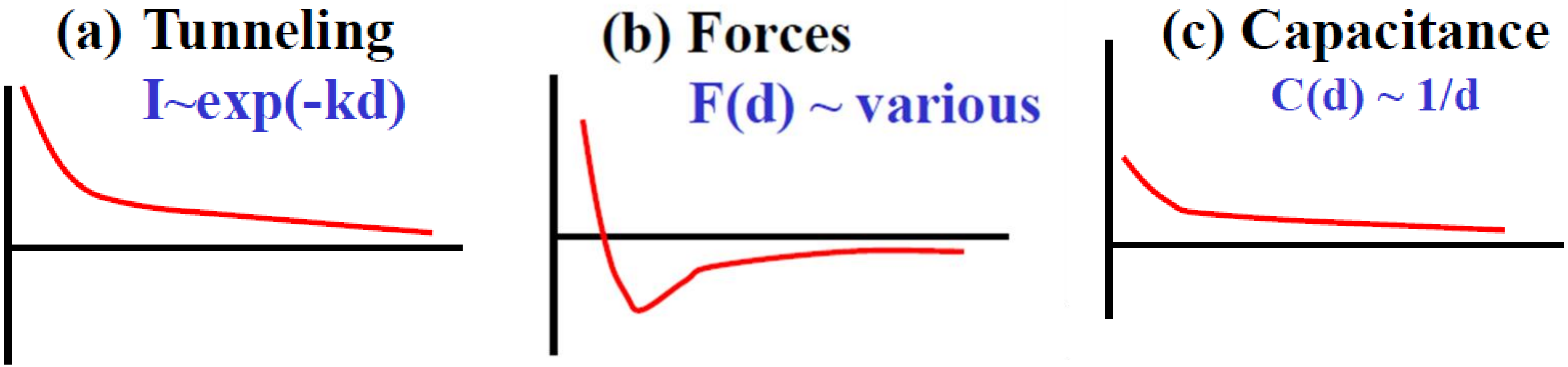
- The etching rate depends on the atomic packing density of crystal plane: (111) < (110) < (100)
- Etchant: KOH + IPA (isopropyl alcohol) + H_2O

- AFM Tip (image artifacts)



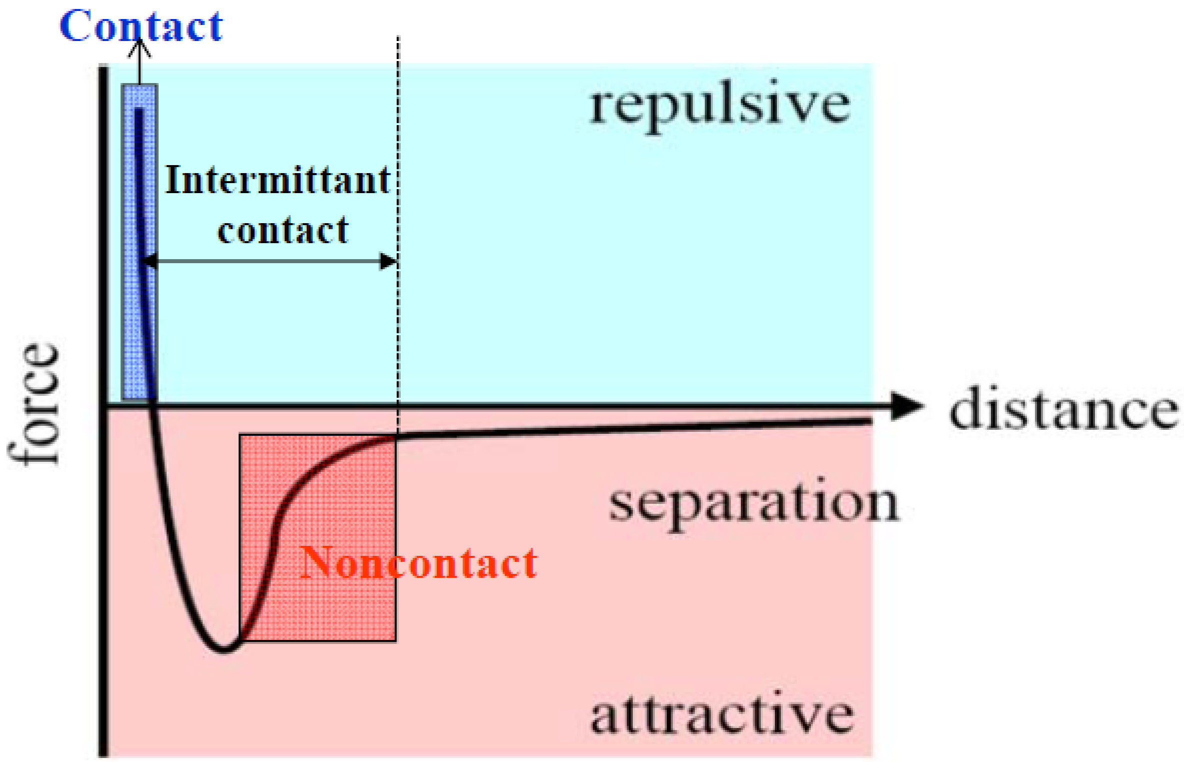


Interactions Used for Imaging in SPM



- **Resolution limits**
- **The property probed**
- **The probe size**

Theory of AFM: Atomic Force vs Distance



Near Field Force

$$f(r) = f_A(r) + f_R(r)$$

$$\cdots\cdots = -\frac{A}{r^2} + \frac{B}{r^n}$$

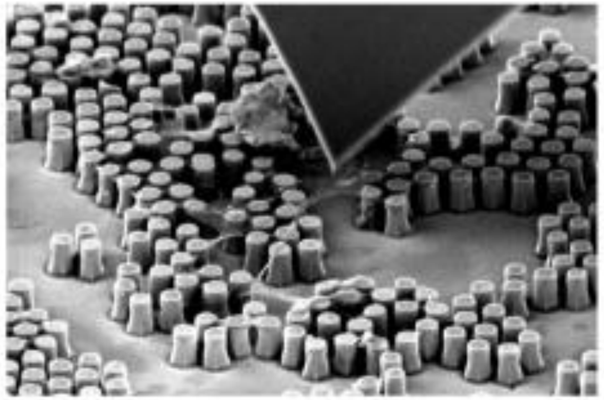
- Contact AFM: repulsion < 5Å tip-surface separation.
- Non-contact AFM: Van der Waals attraction 10-100Å tip-surface separation.

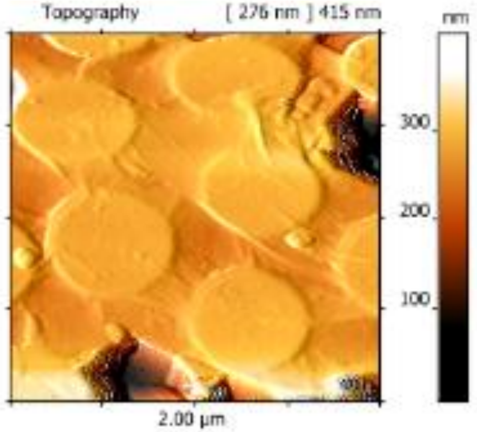
[Intermittent contact AFM (tapping mode AFM): 5-20Å Tip-surface separation]

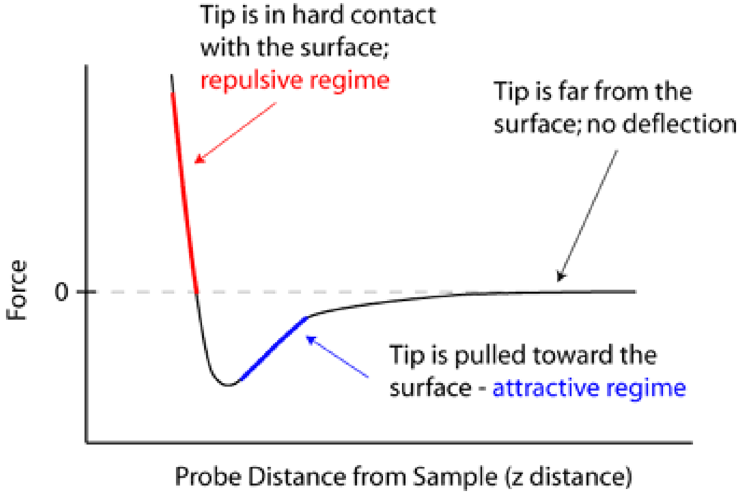
Scanning Modes

AFM	Contact	Strong (repulsive): constant force or constant distance
	Non-contact	Weak (attractive): vibrating probe
	Intermittent contact	Strong (attractive): vibrating probe
LFM	Lateral force	Frictional forces exert a torque on the scanning cantilever
MFM	Magnetic force	The magnetic field of the surface
EFM	Electrostatic force	Charge distribution on surfaces

Scanning by AFM



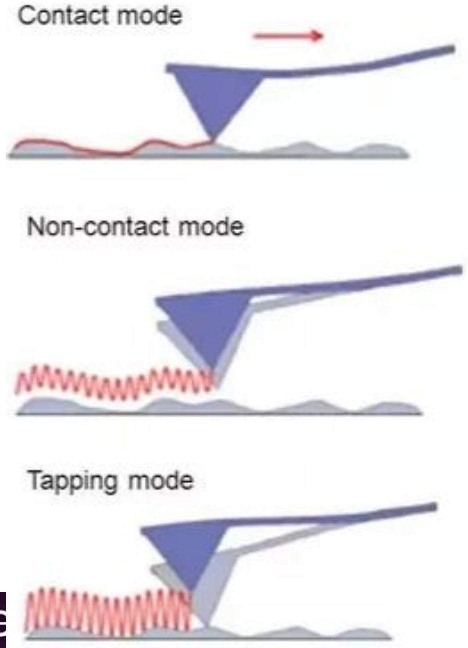




Hooke's law

F = -kz

F : force
k : stiffness of the lever
z : lever bending distance



AFM Modes of Operation	Working Principle	Advantage	Disadvantage
Contact Mode	• Physical contact between the tip and the surface	• High scan speeds • High resolution	• Damage to soft sample • Later forces may produce image artefacts
Non-contact Mode	• No contact between the tip and the sample	• Low resolution • No damage to sample	• Slower scan speed if compared with both contact and tapping mode
Tapping Mode	• Intermittent and short contact between the sample and the tip	• High resolution • Minimal damage to sample	• Slower scan speed if compared with contact mode

Scanning by AFM

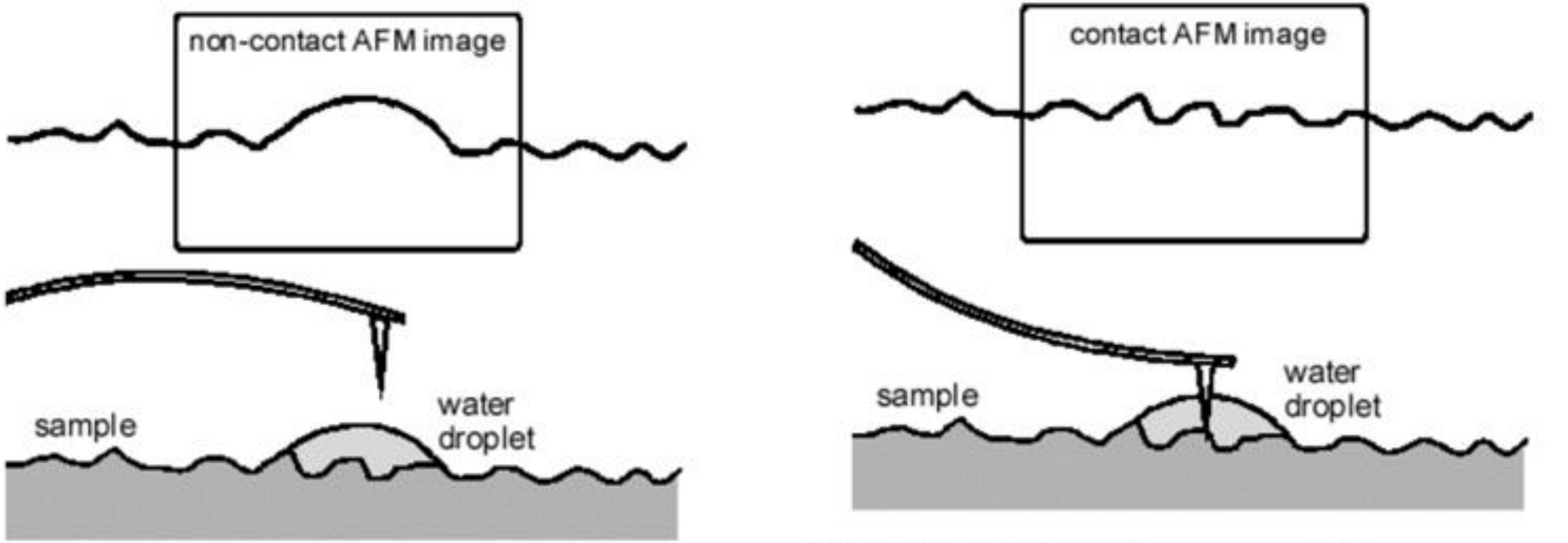


그림 7. 액체표면위에서의 *contact mode* 와 *non-contact mode*

AFM Operation Modes

- **(Static) Contact Mode**
  - **contact** between tip and surface: < 5Å tip-surface separation
  - force on the tip is **repulsive**. (a few nN scale)
  - **deflection** of cantilever is sensed.
  - if the measured deflection is different than desired value, applied voltage to piezo is adjusted to the cantilever to restore the desired value of deflection.
  - this feedback voltage → height information on surface

- **(Dynamic) Non-Contact Mode / Tapping Mode**
  - high resolution topographic image can easily be damaged.
  - Non-contact/tapping mode can overcome problems associated with friction, adhesion and electrostatic force → suitable technique for the samples loosely bound or easily damaged.
  - **no contact** between tip and surface: 10-100 Å above surface
  - **attractive van der Waals force** acting between tip and surface
  - **attractive force is much weaker** than repulsive force in contact mode
  - small forces between tip and surface are detected by measuring the change in **amplitude**, **phase** or **frequency** (related to force gradient)

See also https://www.youtube.com/watch?v=s6KqJS1GZNE

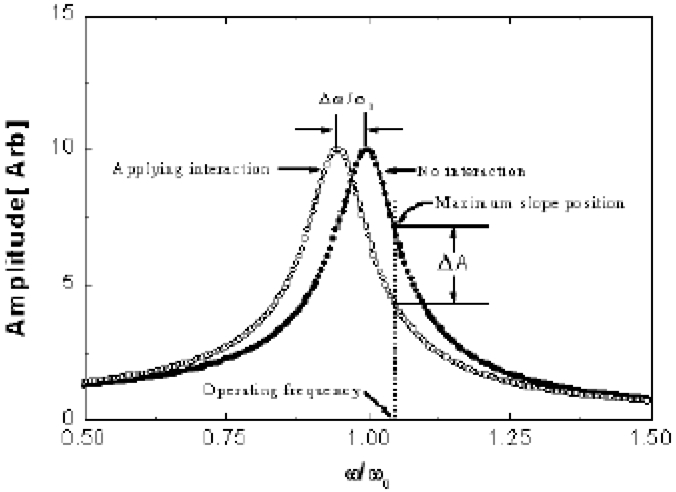
Vibrating Cantilever: Non-Contact & Tapping Modes

- Vibration of cantilever around its resonance frequency
- Change of frequency (ω_o) due to interaction between sample and cantilever

Resonance Frequency

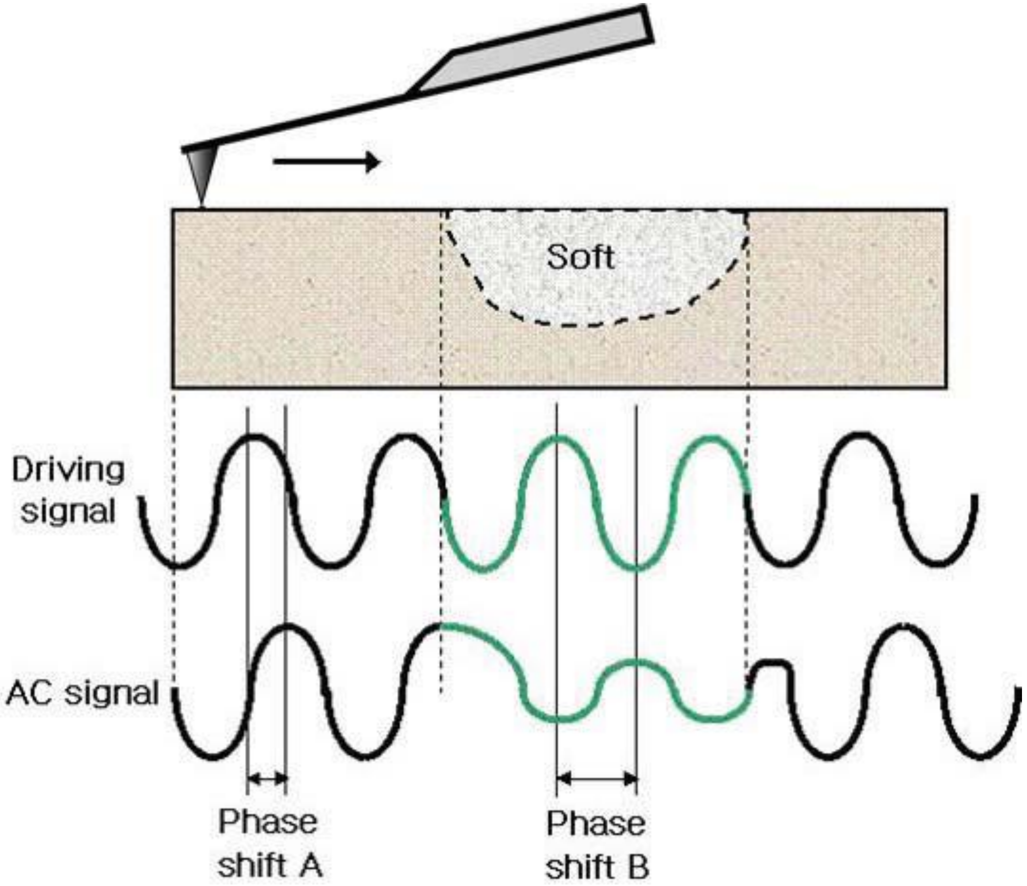
$$k_{eff} = k_o - \frac{dF}{dz}$$

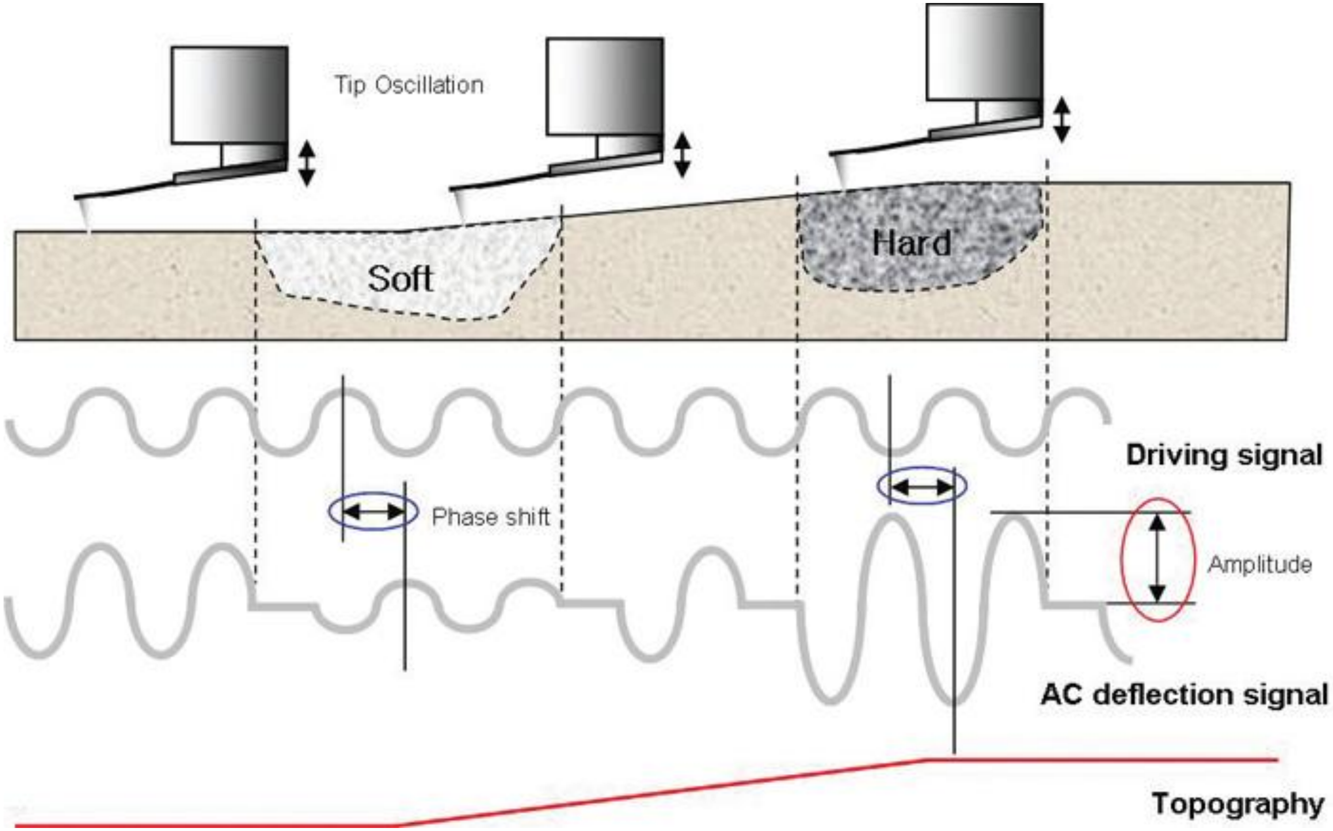
$$\omega_{eff} = \sqrt{\frac{k_{eff}}{m}}$$



- Attraction force: dF/dz > 0→ k_{eff} (ω_{eff}) decreases
- Amplitude imaging
- Phase imaging
- Removal of lateral force contribution

Non-Contact & Tapping Modes: Amplitude/Phase Imaging

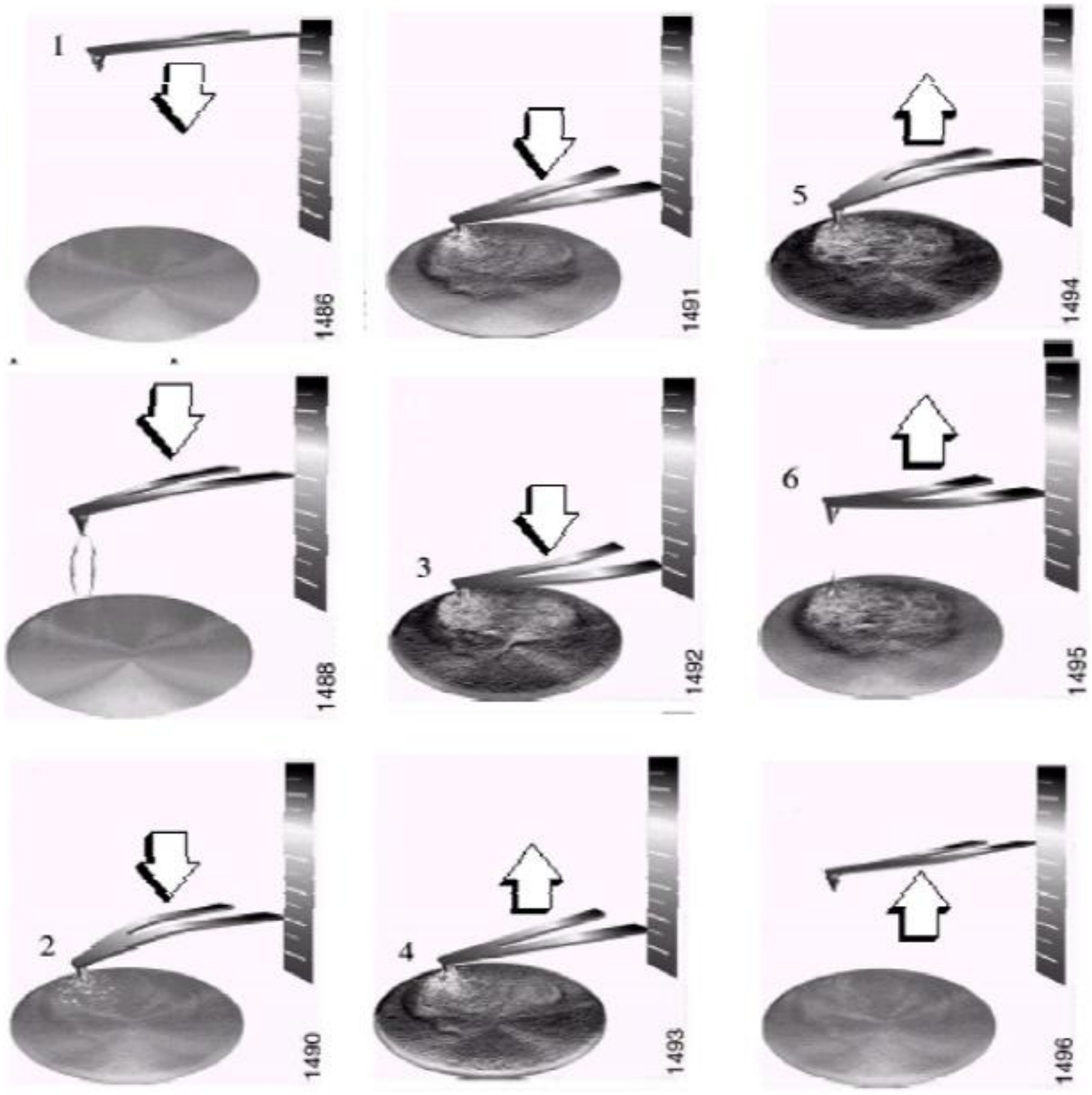


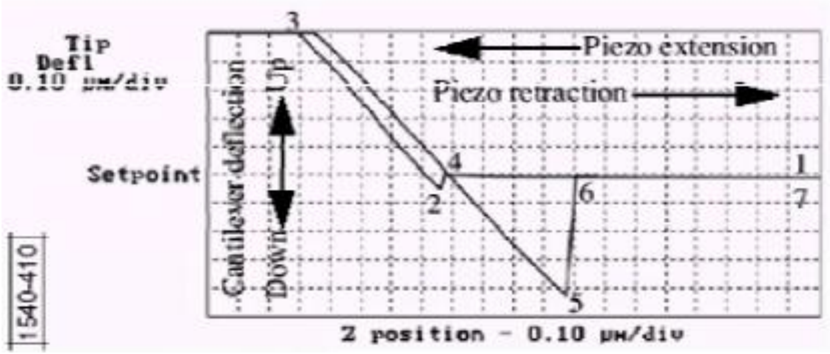


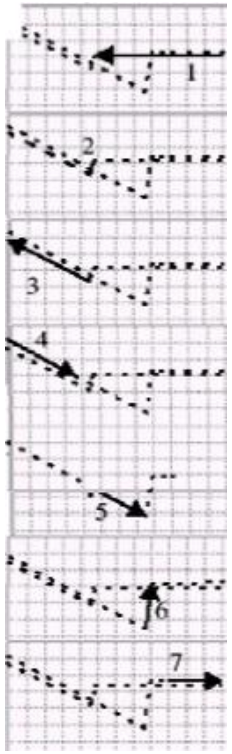
Applications of AFM

- Nanoimaging
- Nanoanalysis
  - Force Measurement (ex: DNA strands)
  - Electrical characterization (Current sensing)
- Nanofabrication
  - Manipulation of Nanoparticles
  - Nano-Lithography:
    - AFM/STM lithography
    - Dip pen lithography

[Advanced Study] Force Measurement



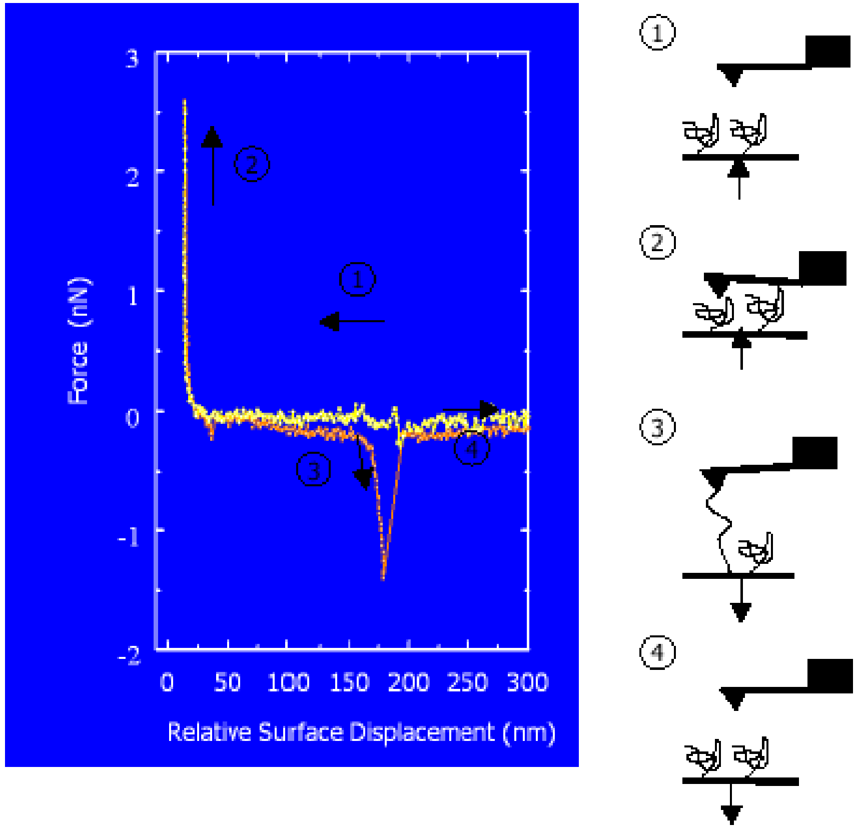




1. Piezo extends; tip descends. No contact with surface yet.
2. Tip is pulled down by attractive forces near surface.
3. As tip presses into the surface, cantilever bends upward.
4. Piezo retracts. Cantilever relaxes downward until tip forces are in equilibrium with surface forces.
5. Piezo continues retraction. Cantilever bends downward as surface attraction holds onto the tip.
6. As piezo continues retracting, tip finally breaks free of surface attraction. Cantilever rebounds sharply upward.
7. As piezo continues retracting. Tip continues its ascent. No further contact with surface during this cycle.

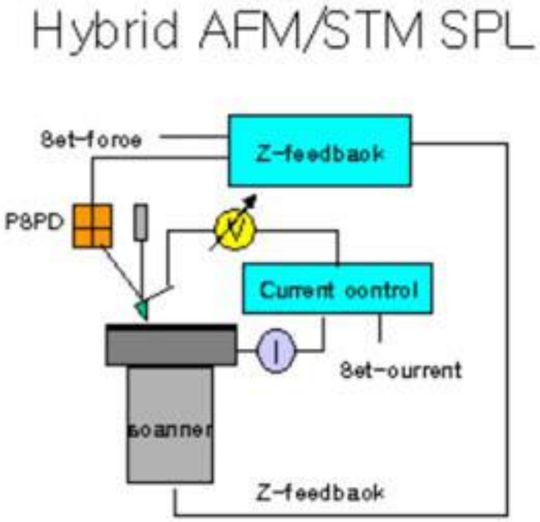
[Advanced study] Force Measurement of DNA Strands

PolyInosine stretching between two dC_{20} surfaces



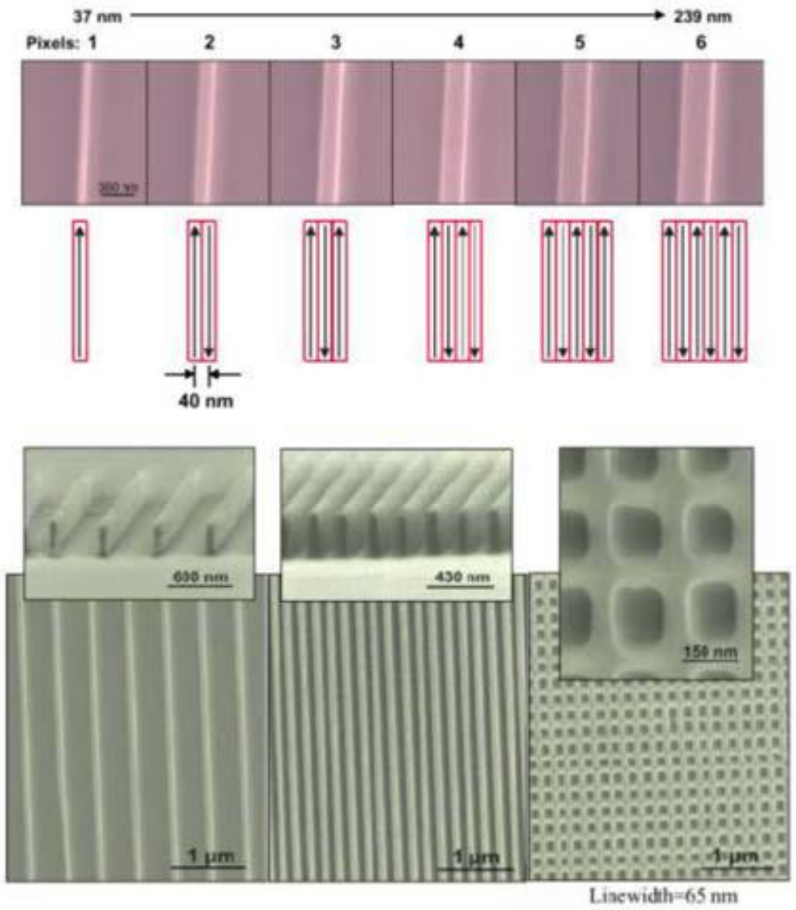
Baselt et al, J. Vac. Sci. Tech. B14, 789 (1996)

[Advanced study] AFM/STM lithography



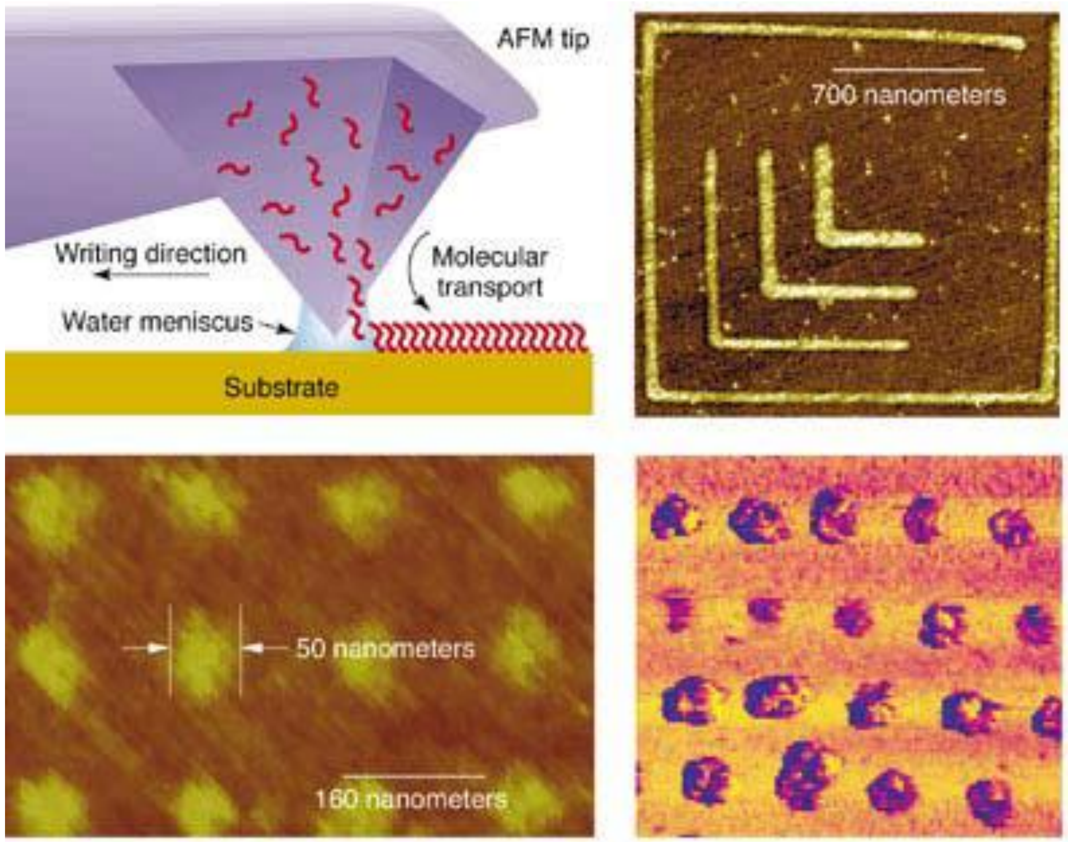
- AFM+STM
- AFM: constant height
- STM: tunneled electrons for lithography

→ constant electron dose (C/cm^2)



From http://www.psia.co.kr/

[Advanced study] Dip Pen Lithography



http://www.youtube.com/watch?v=IlszD5CneQQ&feature=related

http://www.youtube.com/watch?v=2ISOxsxsrAg&feature=related

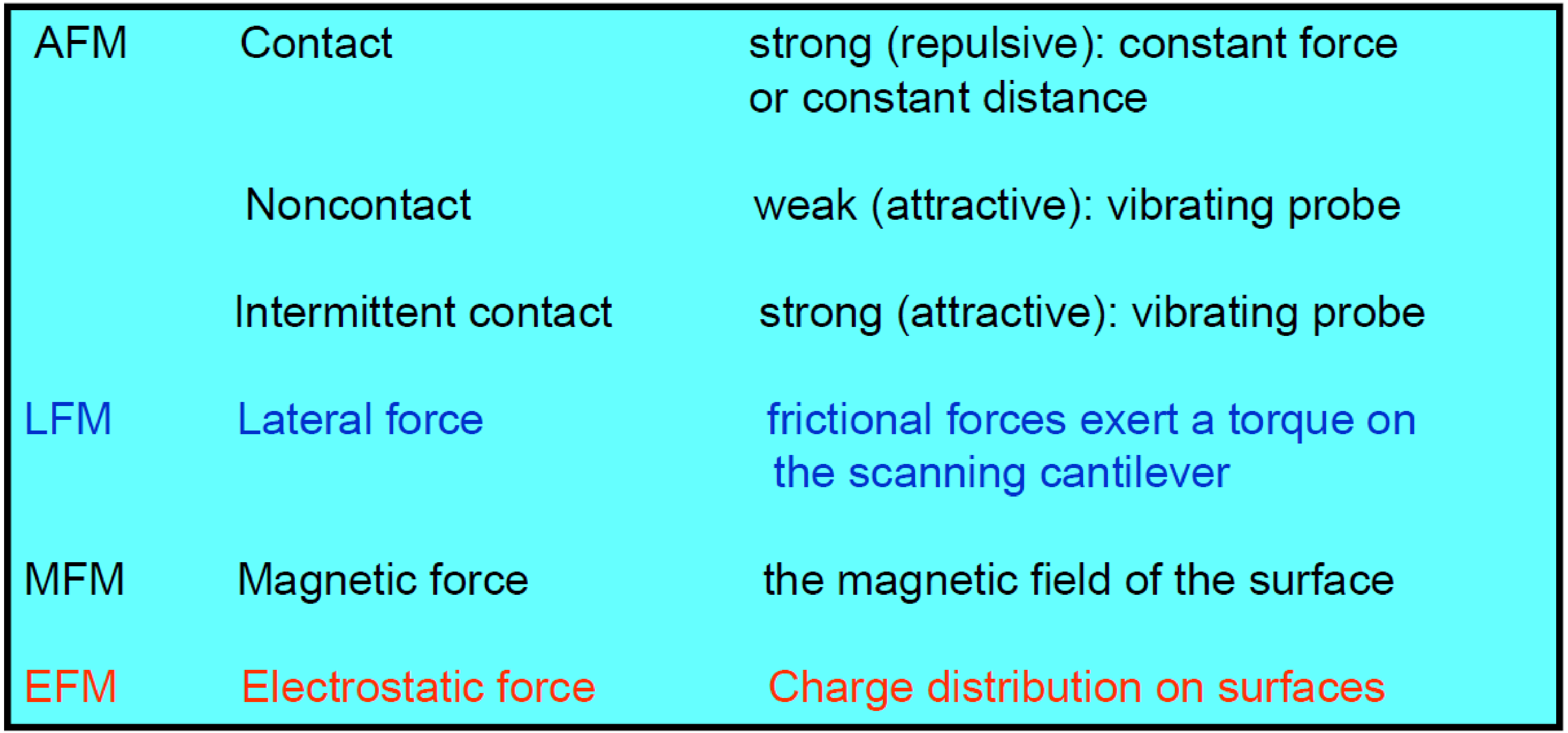
Lateral Force Microscopy (LFM)

Magnetic Force Microscopy (MFM)

Electrostatic Force Microscopy (EFM)

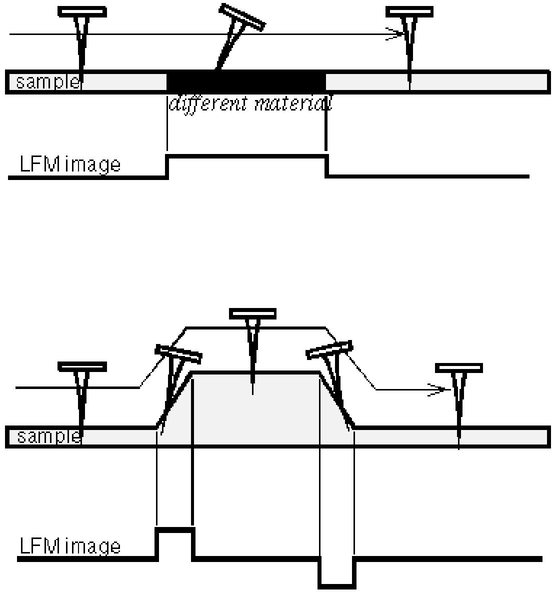
Nearfield Scanning Optical Microscopy (NSOM

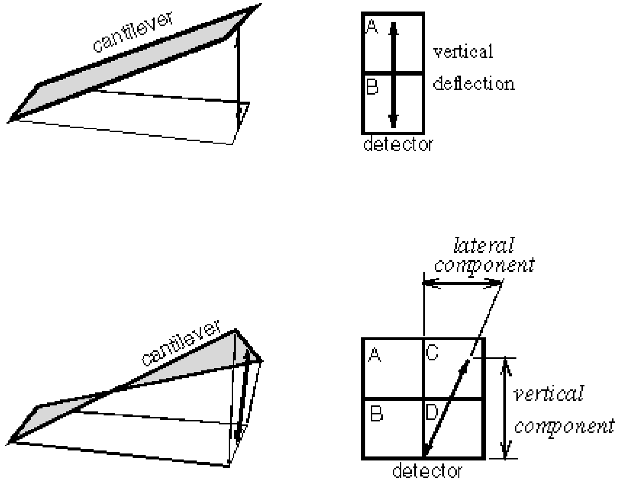
Modes of Operations: Forces of Interactions



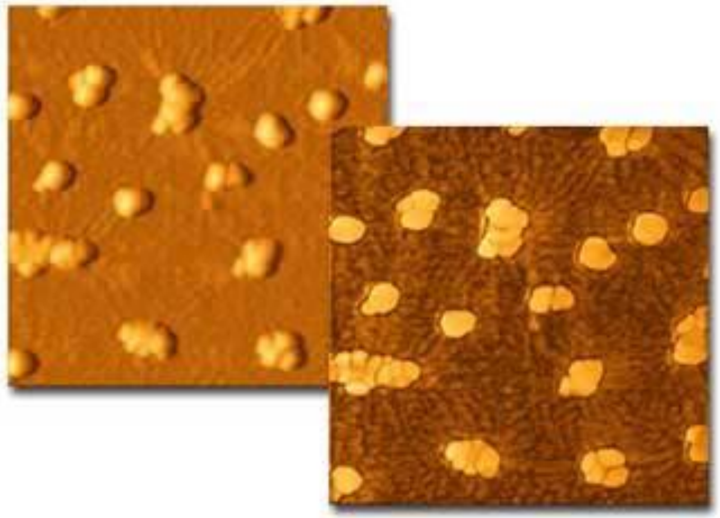
AFM	Contact	strong (repulsive): constant force or constant distance
	Noncontact	weak (attractive): vibrating probe
	Intermittent contact	strong (attractive): vibrating probe
LFM	Lateral force	frictional forces exert a torque on the scanning cantilever
MFM	Magnetic force	the magnetic field of the surface
EFM	Electrostatic force	Charge distribution on surfaces

Lateral Force Microscopy





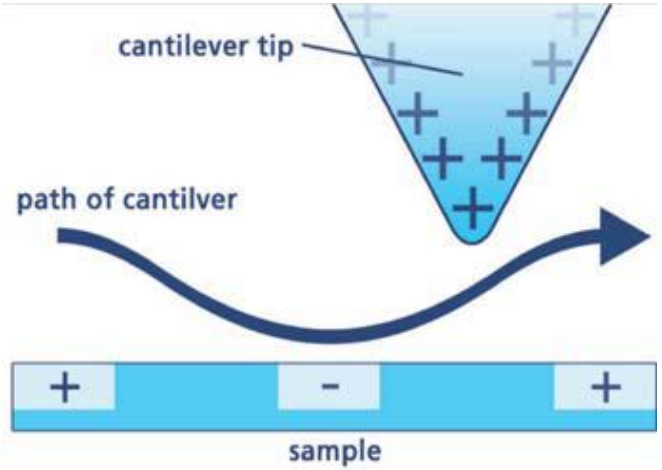
Laterally twisted due to friction



High resolution topography (top) and Lateral Force mode (bottom) images of a commercially avail-able PET film. The silicate fillers show increased friction in then lateral force image.

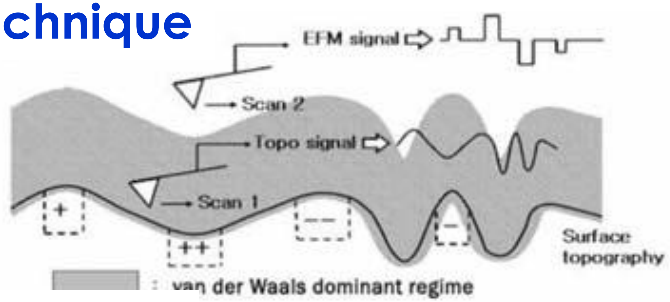
www.tmmicro.com/tech/modes/lfm.htm

Electrostatic Force Microscopy (EFM)

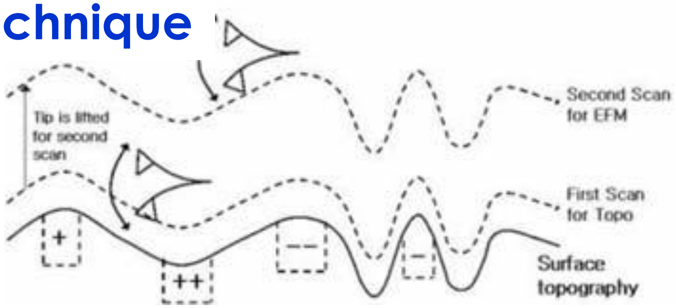


EFM maps locally charged domains on the sample surface.

Force Range Technique



Two pass Technique



- van der Waals (VDW) forces are proportional to $1/r^6$, while electrostatic forces are proportional to $1/r^2$.
- when the tip is close to the sample, VDW forces are dominant.
- As the tip is moved away from the sample, the VDW forces rapidly decrease and the electrostatic forces become dominant.

- **Force Range technique**: the first scan is performed by scanning the tip in the region where the van der Waals force is dominant for topography image. Then, the tip-sample distance is varied to place the tip in the region where the electrostatic force is dominant and scanned for EFM image.
- **Two Pass technique**: the first scan is performed to obtain the topography by scanning the tip near the surface as it is done in NC-AFM, in the region where the VDW forces are dominant. In the second scan, system lifts the tip and increases the tip-sample distance in order to place the tip in the region where electrostatic forces are dominant. The tip is then biased and scanned **without feedback**, parallel to the topography line obtained from the first scan, therefore maintaining constant tip-sample distance.

EFM image

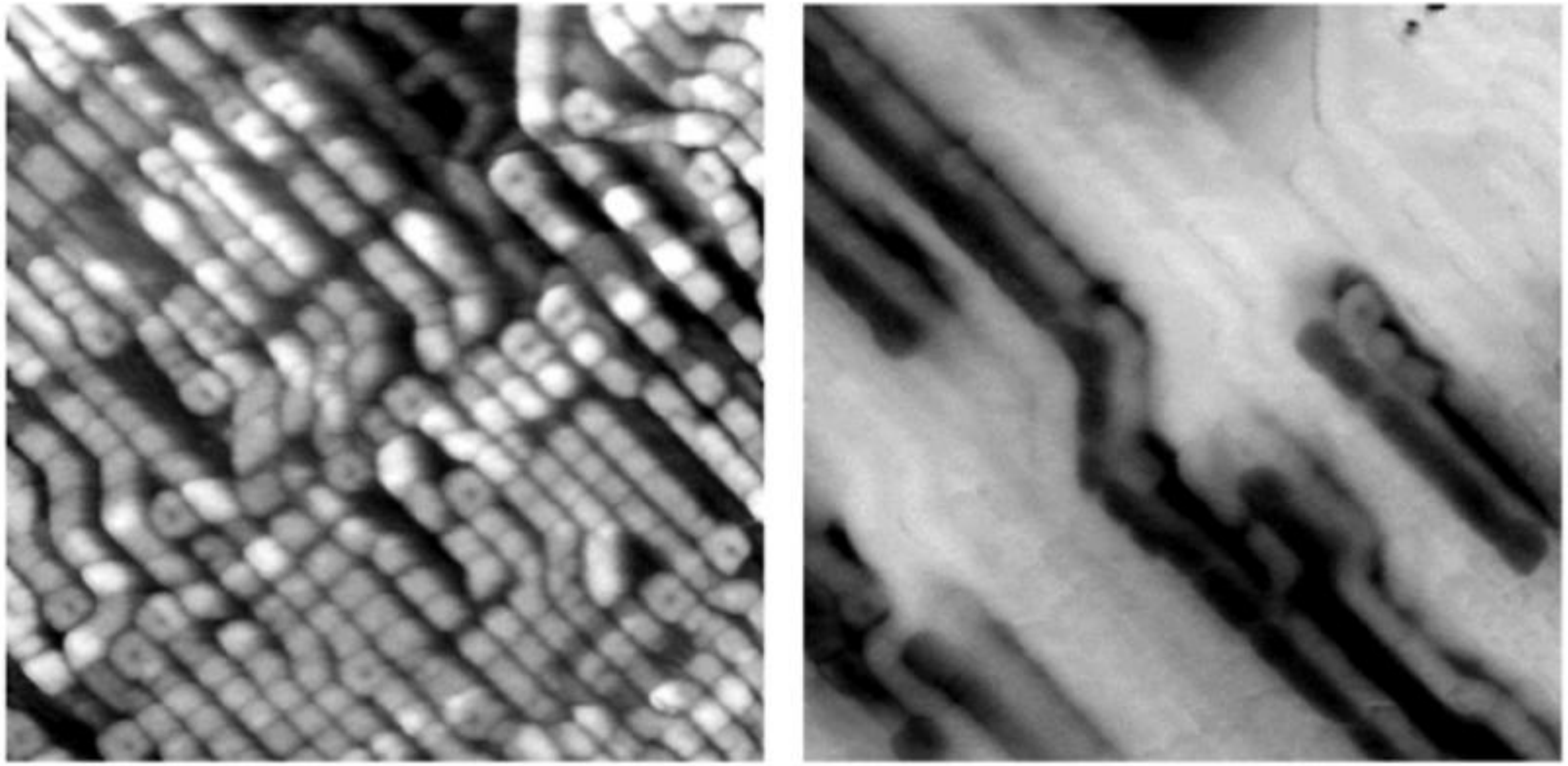
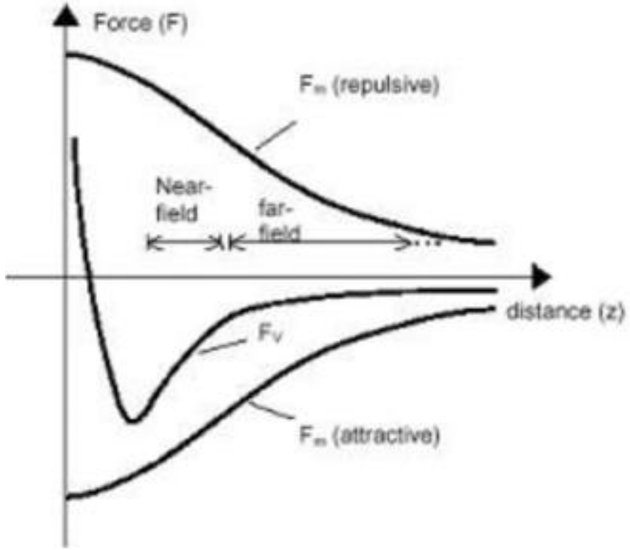
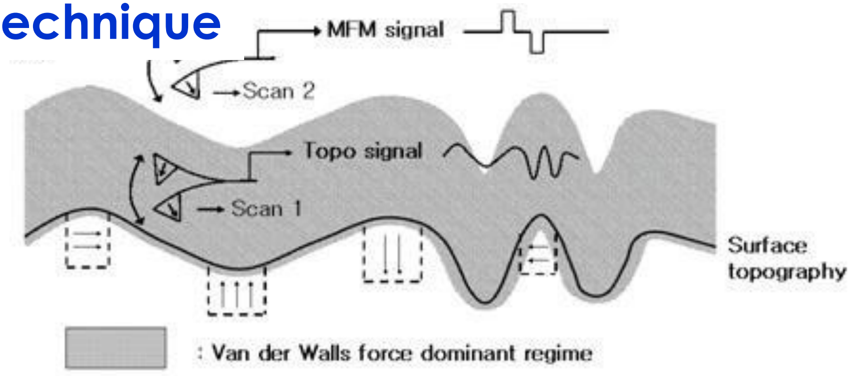


그림 18. *ASIC* 소자를 원자 현미경으로 찍은 사진. 왼쪽이 표면의 형상을 나타내는 *AFM* 사진이고 오른쪽이 표면의 전위 분포를 나타내는 *EFM* 사진이다. 정전기력은 *dielectric* 박막을 투과하므로 이와 같이 표면의 보호막을 제거하지 않고도 각 회로의 로직(*logic*)이 *0* 인지 *1* 인지를 쉽게 알 수 있다.

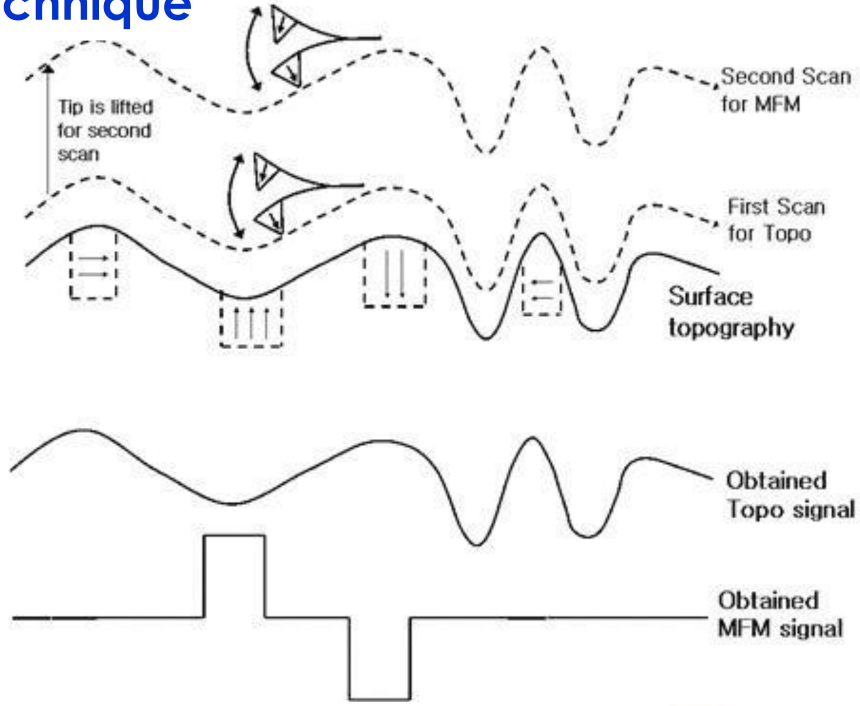
Magnetic Force Microscopy (MFM)



Force Range Technique



Two pass Technique

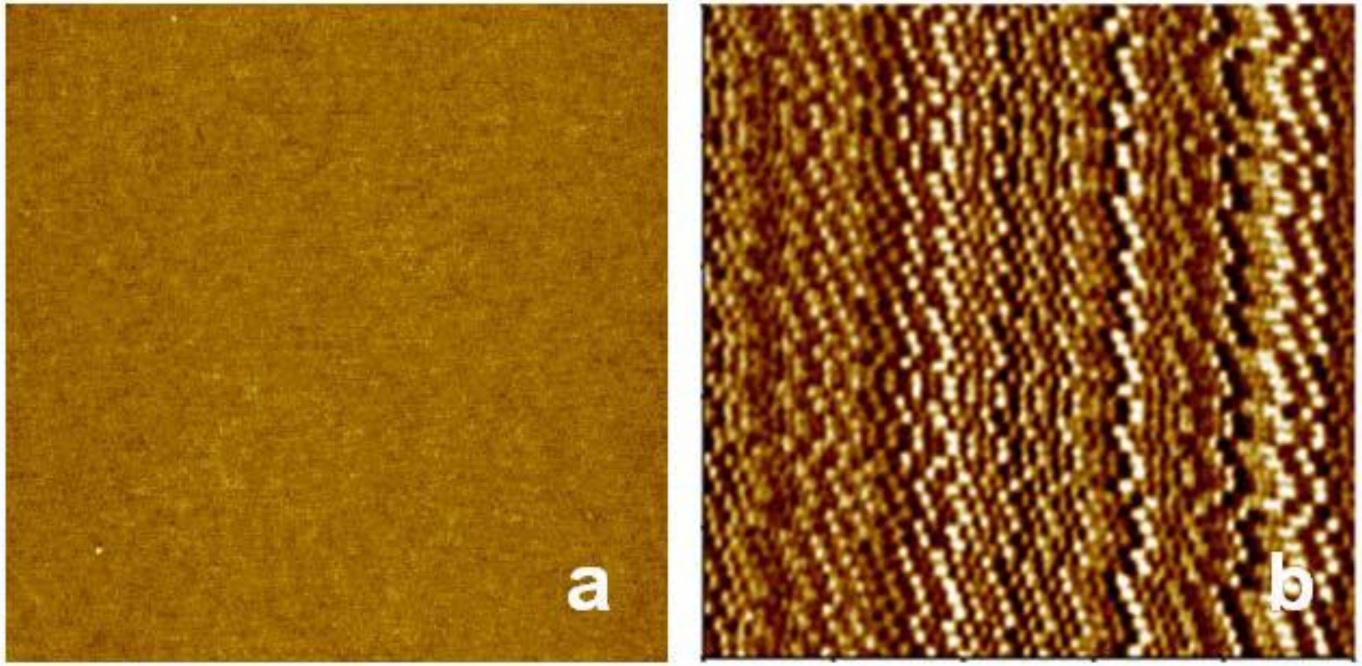


- Ferromagnetic tip: Co, Cr
- Noncontact mode
- Close imaging: topography (vdW force: short range force)
- Distant imaging: magnetic properties

(Magnetic force: long range force; small force gradient)

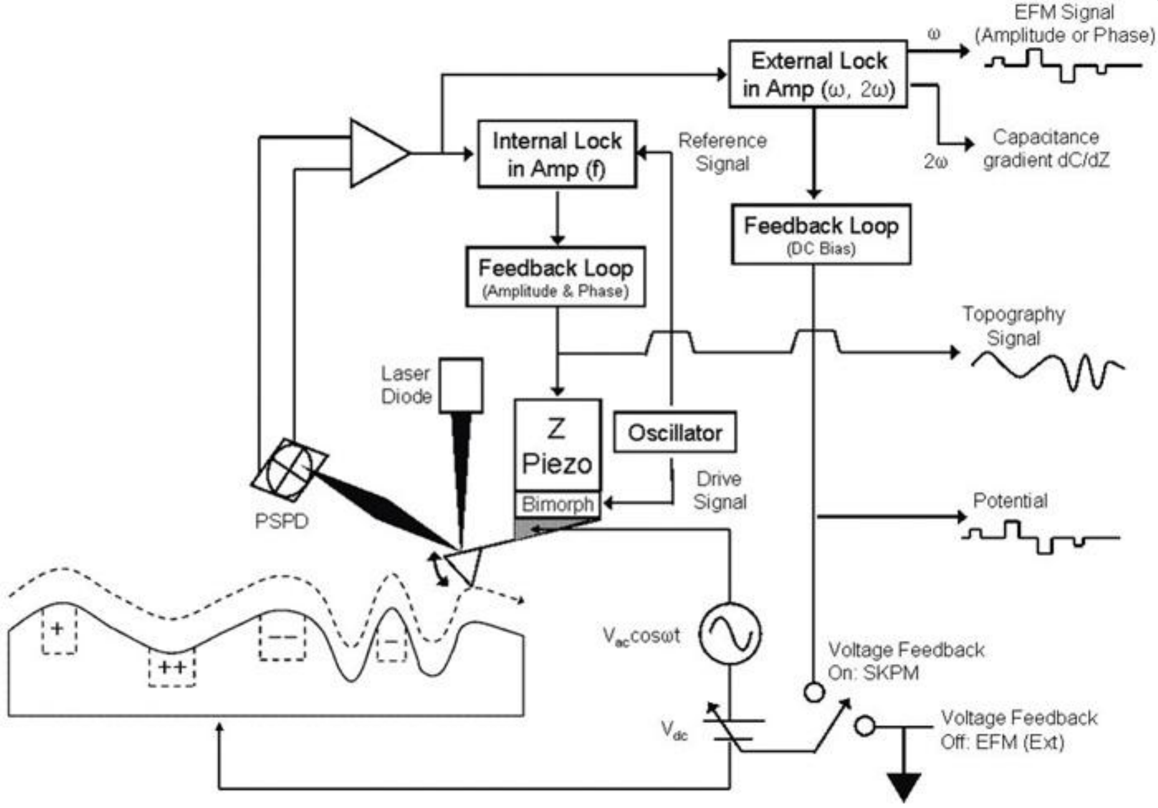
Magnetic Force Microscopy (MFM)

Hard Disk Sample



(a) Topography (b) MFM Phase

Enhanced EFM



$$V(t) = V_{\mathrm{DC}} - V_{\mathrm{S}} + V_{\mathrm{AC}} \sin \omega t \qquad (1)$$

$$F = q \times E = q \times V/d = C \times V^2/d \qquad (2)$$

$$F(t) = (C/d) \times V(t)^2$$

$$= (C/d) \times [(V_{\mathrm{DC}} - V_{\mathrm{S}})^2 + \frac{1}{2} V_{\mathrm{AC}}{}^2] \qquad (a)$$

$$+ 2 \times (C/d) \times (V_{\mathrm{DC}} - V_{\mathrm{S}}) \times V_{\mathrm{AC}} \sin \omega t \qquad (b)$$

$$- \frac{1}{2} (C/d) \times V_{\mathrm{AC}}{}^2 \cos 2\omega t \qquad (c)$$

Cantilever deflection

- DC term: VDW interaction
- ω term: V_S (surface potential) & C/d (capacitance if d = constant)
- 2ω component: C/d (capacitance, i.e. surface charge)

Surface potential, surface charge, doping concentration