Nanofabricação

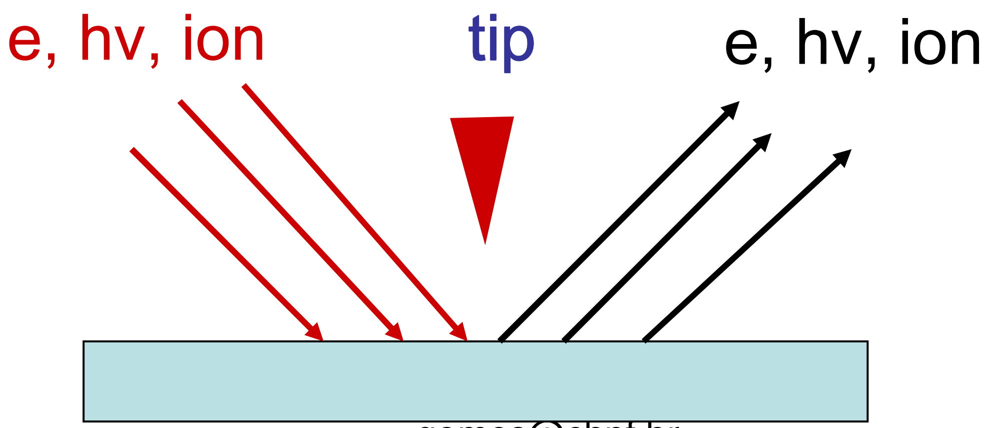
Aula 2 – Prof. Gomes

15 jul 2008

gomes@cbpf.br

Tools for Nanocharacterization

- Structural analysis: SEM, TEM, XRD, SAM, SPM, PEEM, LEEM
- Chemical analysis: AES, XPS, SIMS, EDS, SPM
- Electronic, optical analysis: UV/VIS, UPS, SPM
- Magnetic analysis: SQUID, MOKE, SEMPA, SPM
- Vibrational analysis: IR, HREELS, Raman, SPM
- Local physico-chemical probe: SPM

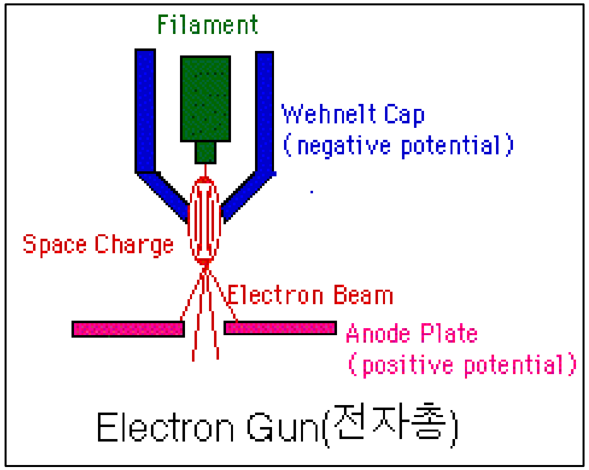


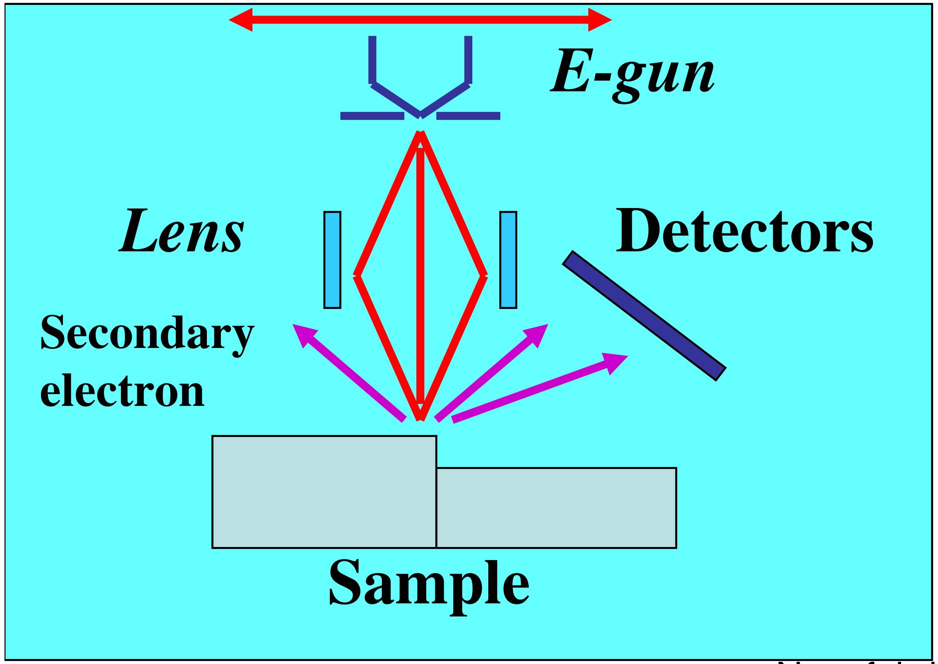
Characteristics of Microscopies

VII Escola do CBPF
Rio de Janeiro, 14 a 25 de julho de 2008

	OM	SEM/TEM	SPM
Operation	air,liquid	vacuum	air,liquid,UHV
Depth of field	small	large	medium
Lateral resolution	1 μm	1-5nm:SEM 0.1nm:TEM	2-10nm: AFM 0.1nm: STM
Vertical resolution	N/A	N/A	0.1nm: AFM 0.01nm: STM
Magnification	1X-2x10^{3}X	10X-10^{6}X	5x10^{2}X- 10^{8}X
Sample	not completely transparent	un-chargeable vacuum compatible thin film: TEM	surface height <10 mm
Contrast	absorption reflection	scattering diffraction	tunneling

Principle: *Scanning Electron Microscopy (SEM)*

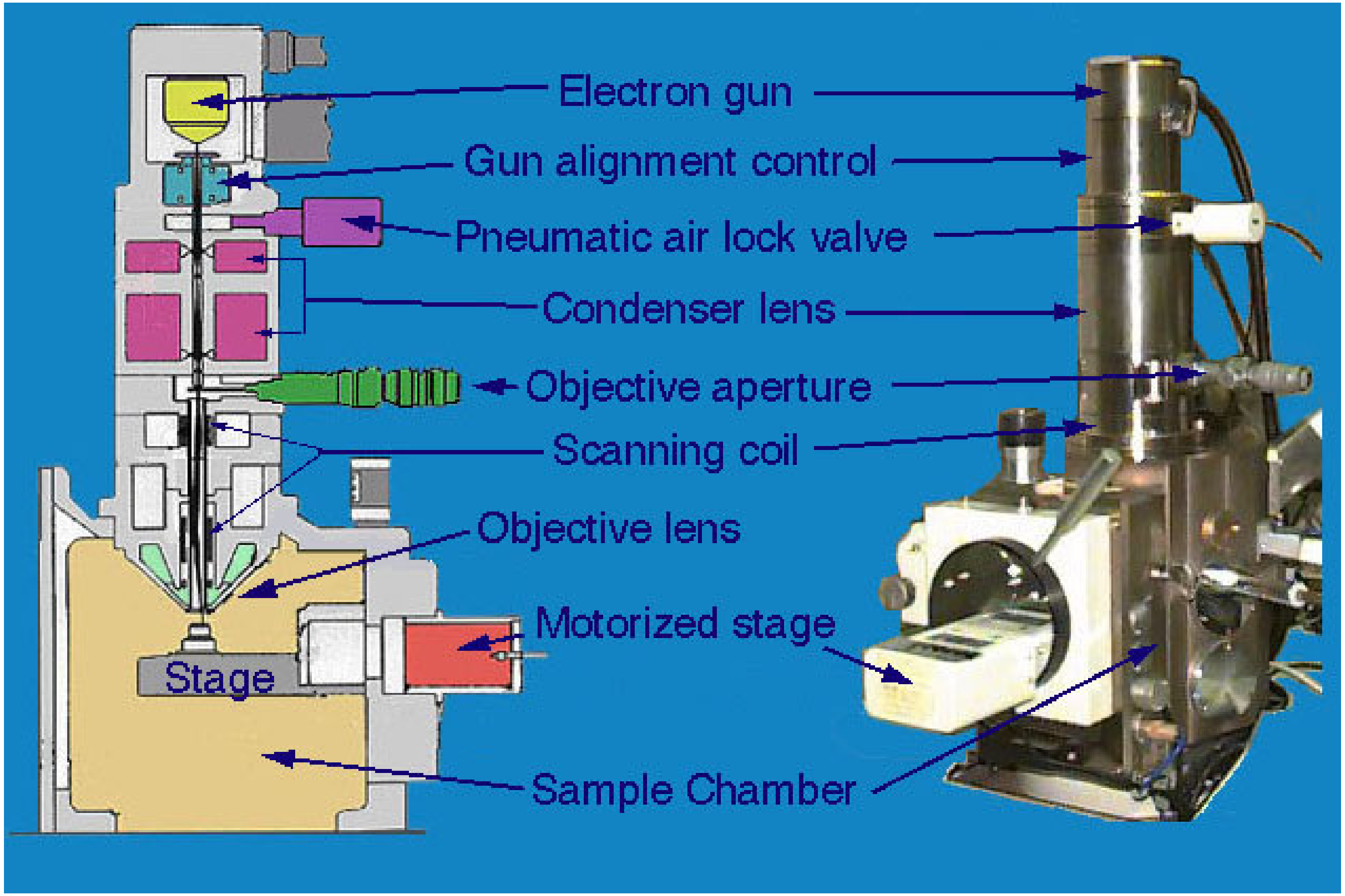




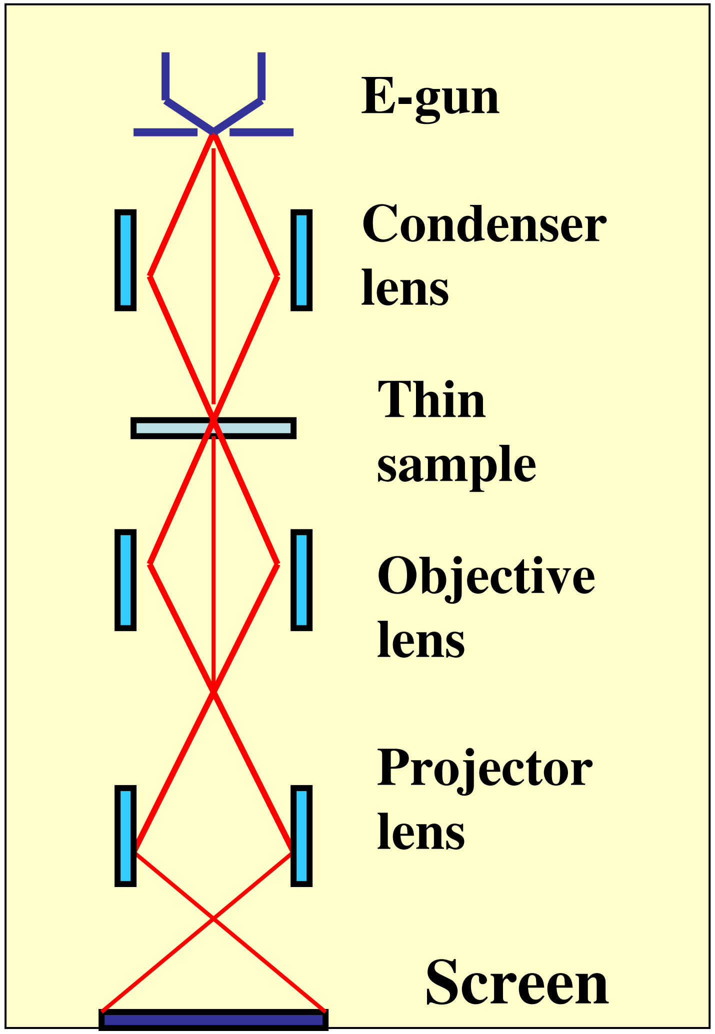
- Beam size: a few – 30 A
- Beam Voltage: 20-40kV
- Resolution: 10-100 A
- Magnification: 20x-650,000x
- Imaging radiations: Secondary electrons, backscattering electrons
- Topographic contrast: Inclination effect, shadowing, edge contrast,
- Composition contrast: backscattering yield ~ bulk composition
- Detections:
  - Secondary electrons: topography
  - Backsactering electrons: atomic # and topography
  - X-ray fluorescence: composition

http://super.gsnu.ac.kr/lecture/microscopy/em.html

Instrumentation: *SEM*



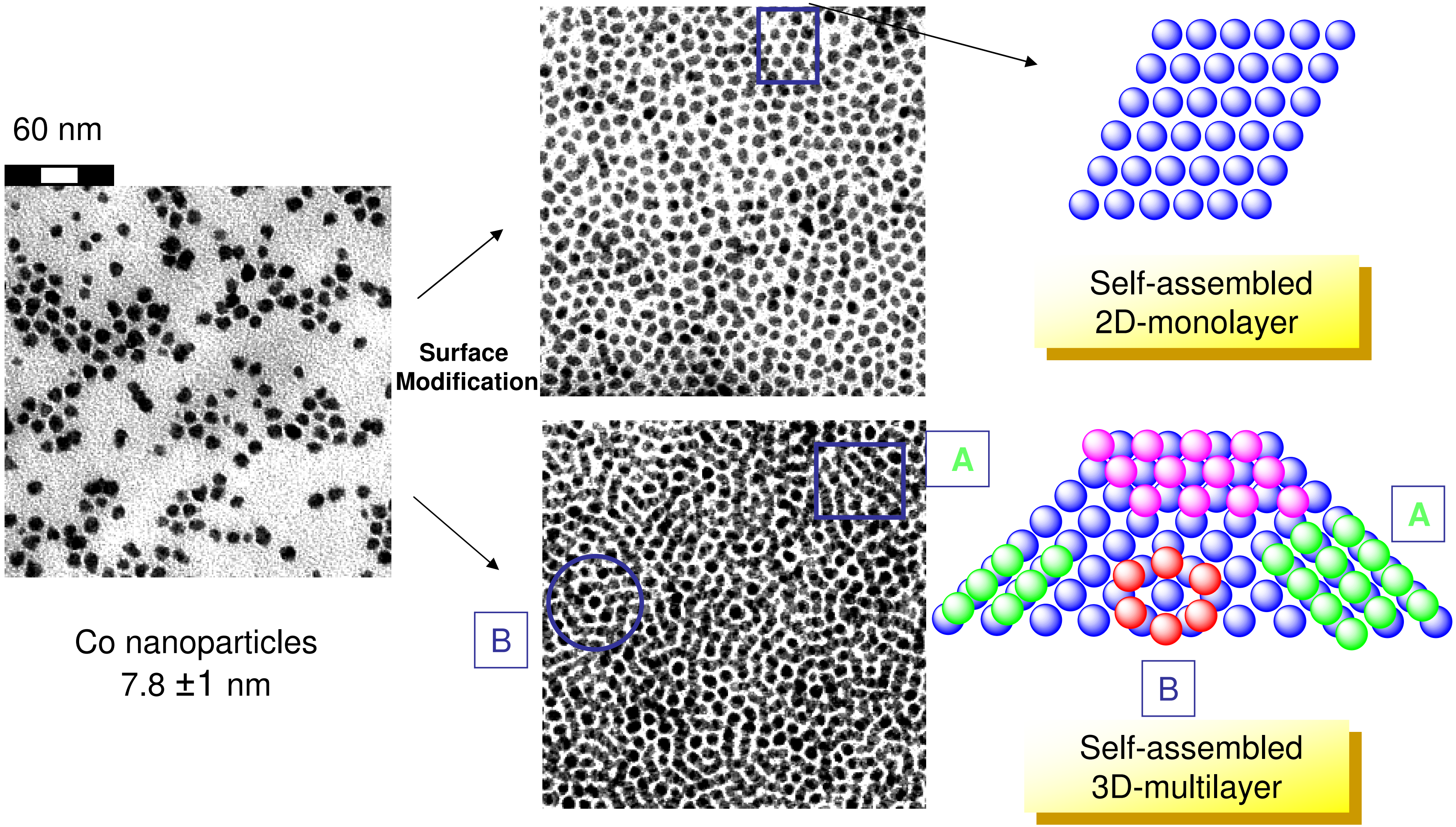
Principle: *Transmission Electron Microscopy (TEM)*



- Beam size: a few – 30 A
- Beam Voltage: 40kV- 1MV
- Resolution: 1-2A
- Imaging radiations: transmitted electrons,
- Imaging contrast: Scattering effect
- Magnification: 60x-15,000,000x
- Image Contrast:

1) Amplitude (scattering) contrast
   - transmitted beam only (bright field image)
   - diffraction beam only (dark field image)
2) Phase (interference) contrast
   - combination of transmitted and diffraction beam
   - multi-beam lattice image: atomic resolution (HRTEM)

Example: TEM images of Co-nanoparticles

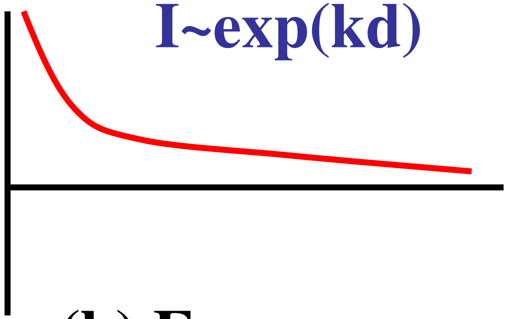


From J.I. Park and J. Cheon

Interactions used for Imaging in SPM

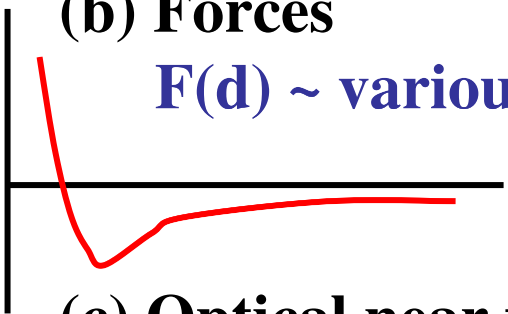
(a) Tunneling

$I \sim \exp(kd)$



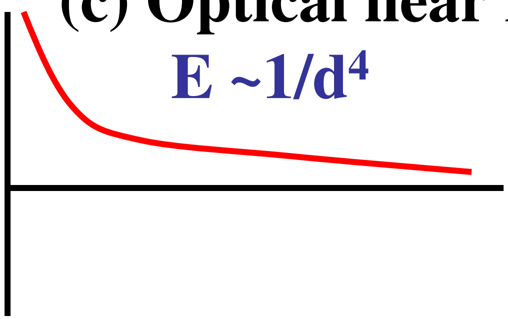
(b) Forces

$F(d) \sim$ various



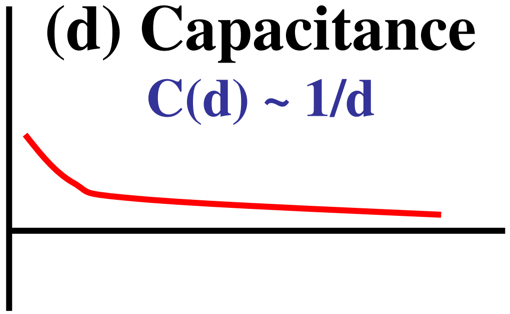
(c) Optical near fields

$E \sim 1/d^4$



(d) Capacitance

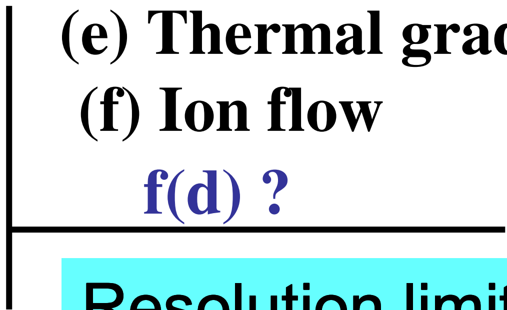
$C(d) \sim 1/d$



(e) Thermal gradient

(f) Ion flow

$f(d)$?

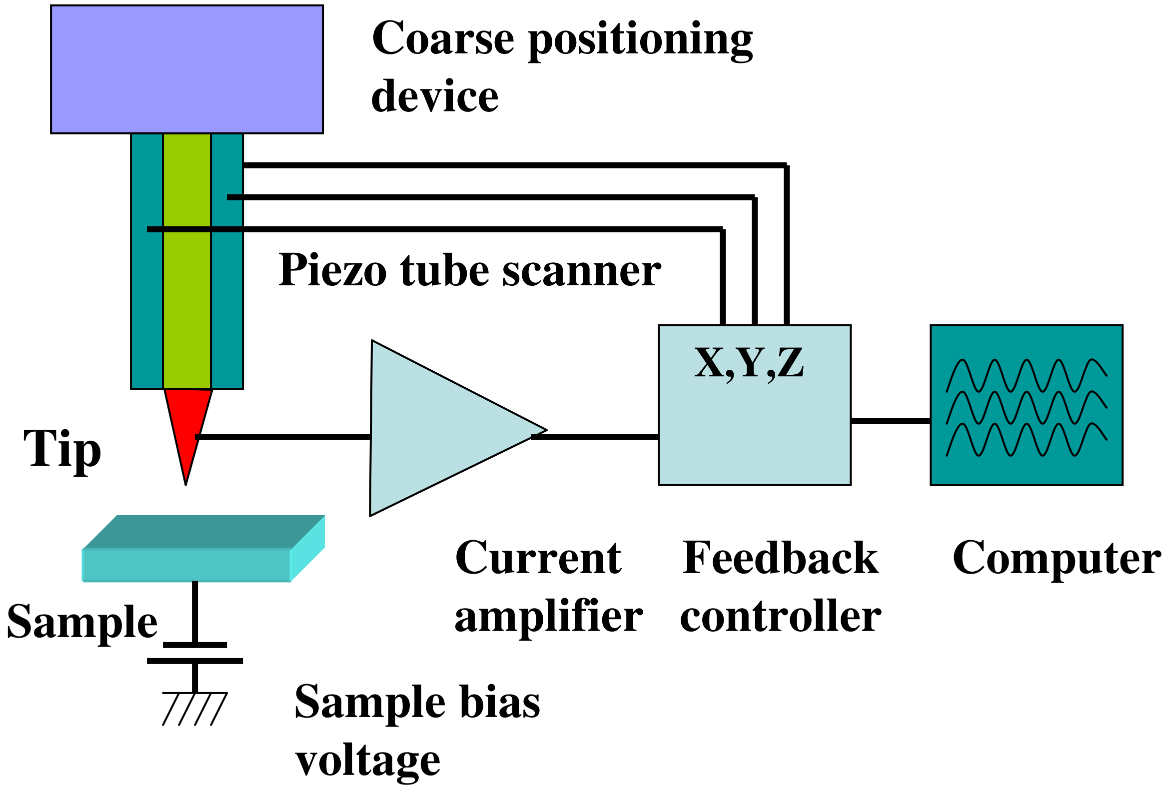


Resolution limits
- The property probed
- The probe size

Scanning Probe Microcopy

- 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
- Nearfield Scanning Optical Microscopy (NSOM): optical properties
- Scanning Capacitance Microscopy (SCM): dielectric constant, doping
- Scanning Thermal Microscopy (SThM): temperature
- Spin-polarized STM (SP-STM): spin structure
- Scanning Electro-chemical Microscopy (SECM): electrochmistry
- Scanning Tunneling Potentiometry (SPM): potential surface
- Photon Emission STM (PESTM): chemical identification

Scanning Tunneling Microscope



Scanning Modes:

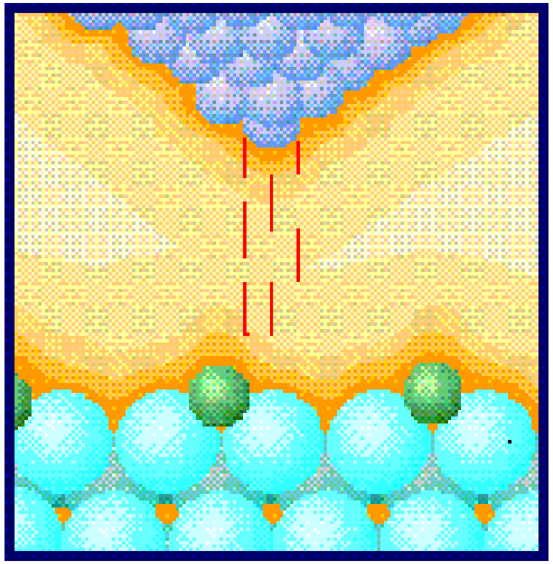
1. Constant current
2. Constant height

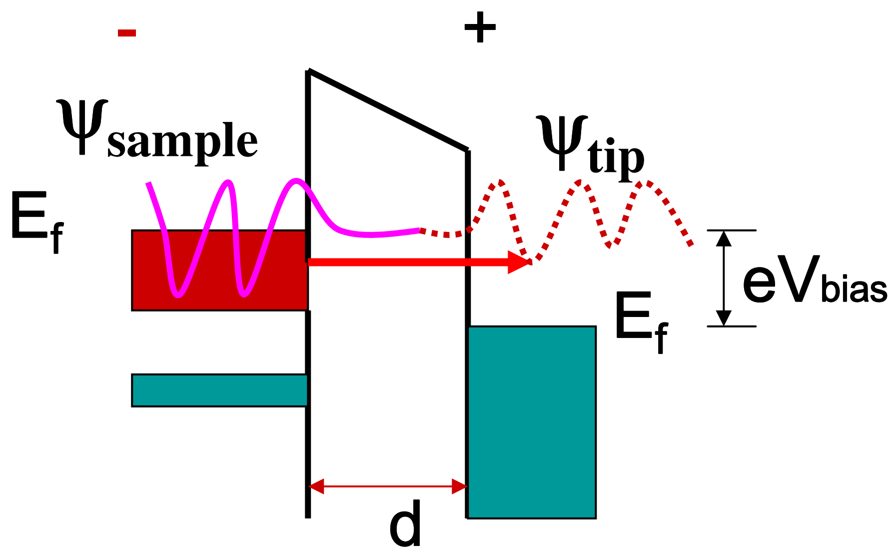
Real space imaging with atomic resolution

Theory of STM

J. Tersoff and D.R. Hamann, *Phys. Rev. lett.* 50, 1988 (1983)

Figure From J. Wintterlin





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

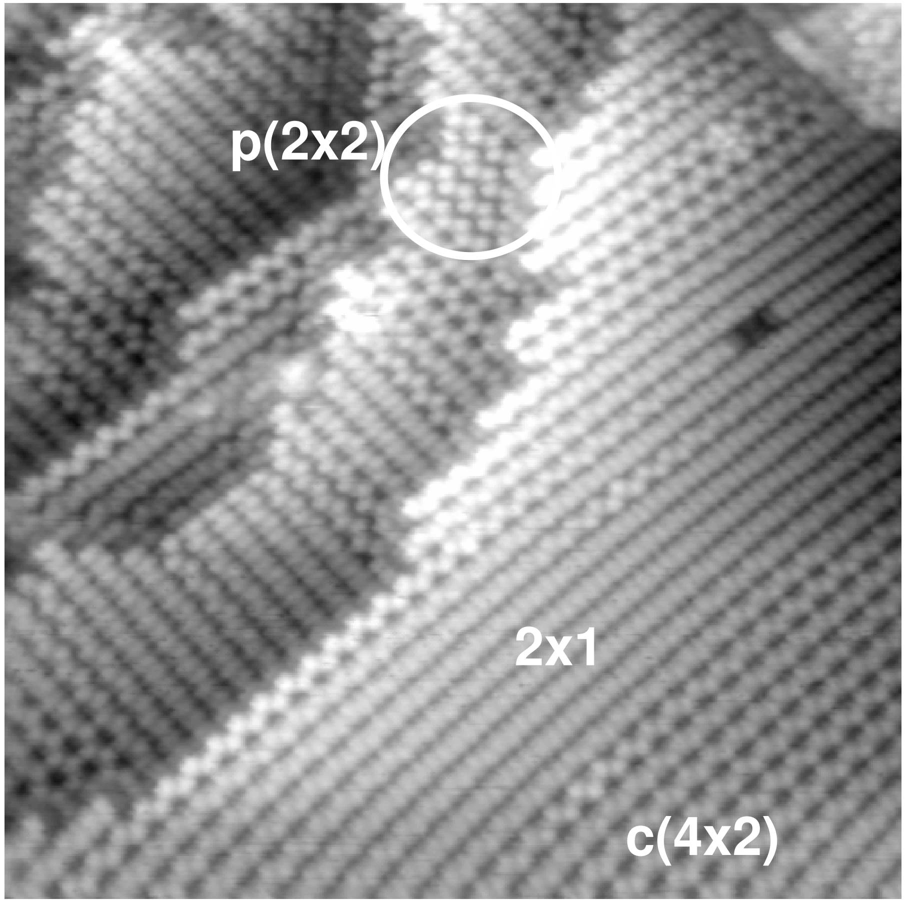
$$\sim \sum |\psi_{sample}|^2 \, \delta(E-E_f)$$ **for low voltage limit; a point tip**

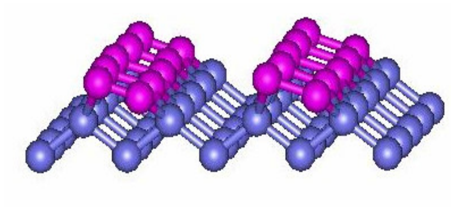
Constant current STM image corresponds to a surface of constant state density.

Applications of STM

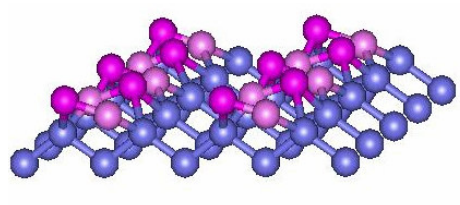
- Surface geometry
- Molecular structure
- Local electronic structure
- Local spin structure
- Single molecular vibration
- Electronic transport
- Nano-fabrication
- Atom manipulation
- Nano-chemical reaction

Atom-resolved Surface Structure

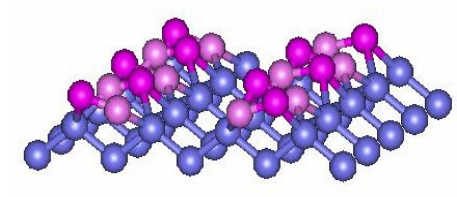




Buckled 2x1



p(2x2)



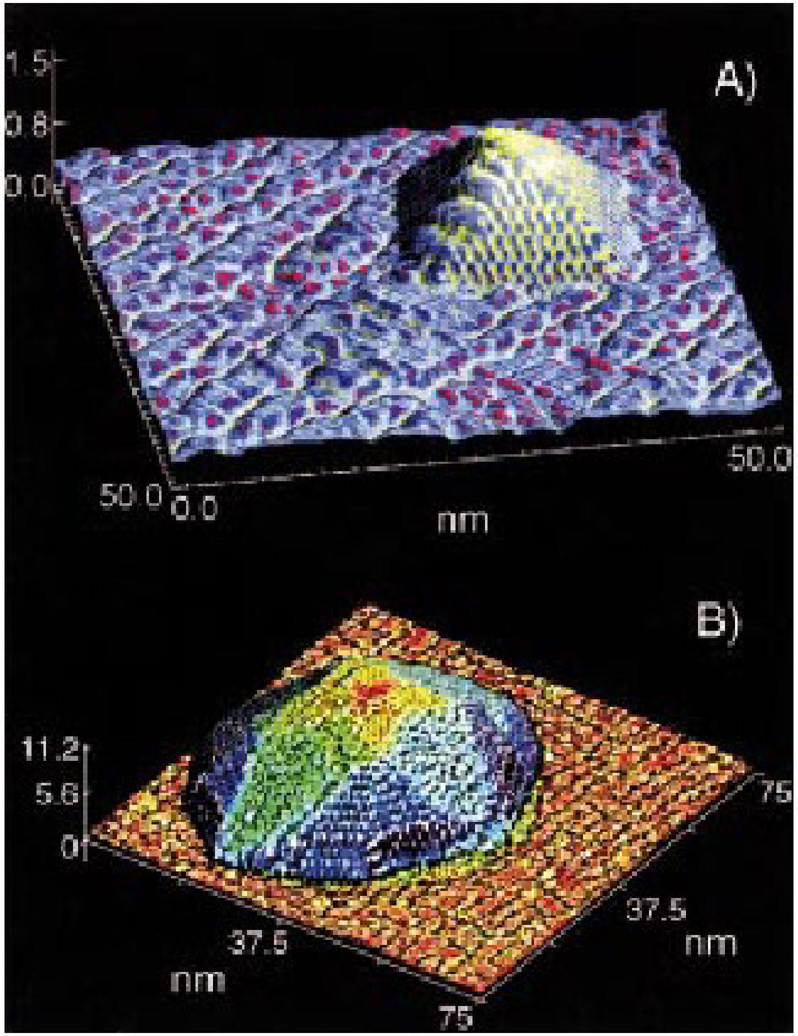
c(4x2)

Various Reconstructions of Ge(100)-2x1

gomes@cbpf.br

J.Y. Maeng et al (2001)

STM Topograph of Quantum Dot

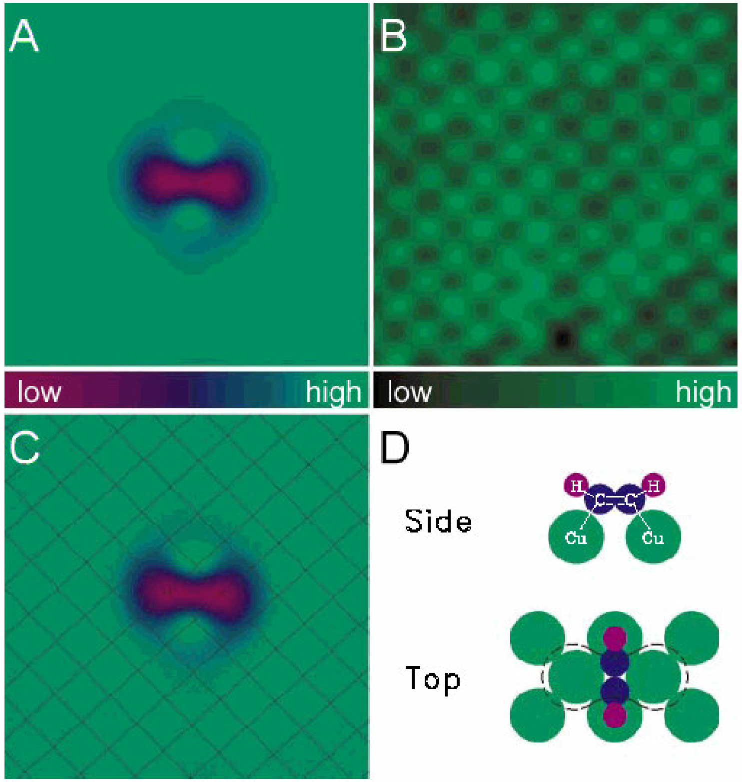


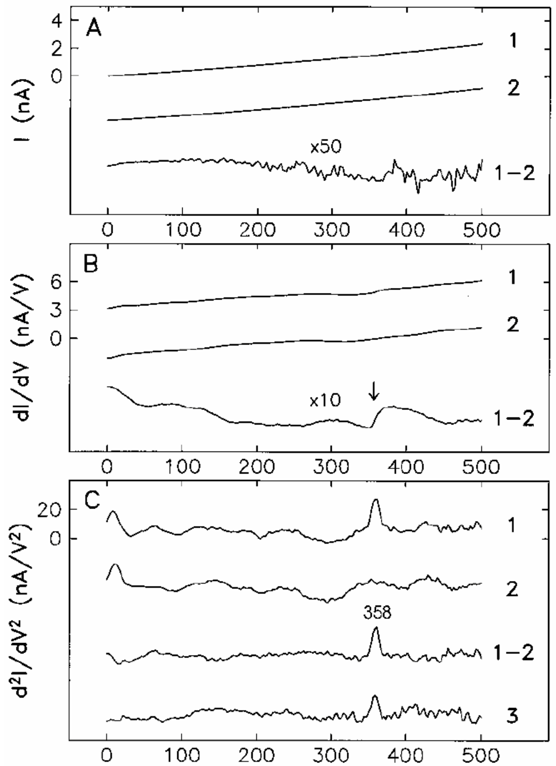
Ge **pyramid** **containing ~2000 Ge atoms on Si(100)**

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

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

Single Molecule Vibrational Spectroscopy



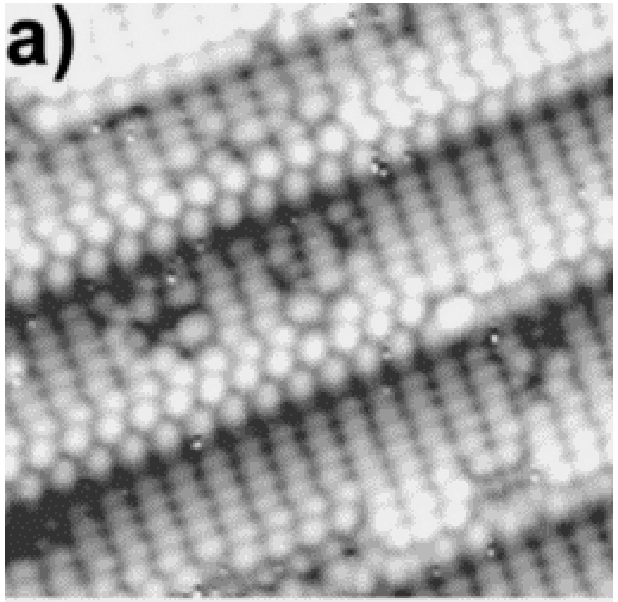


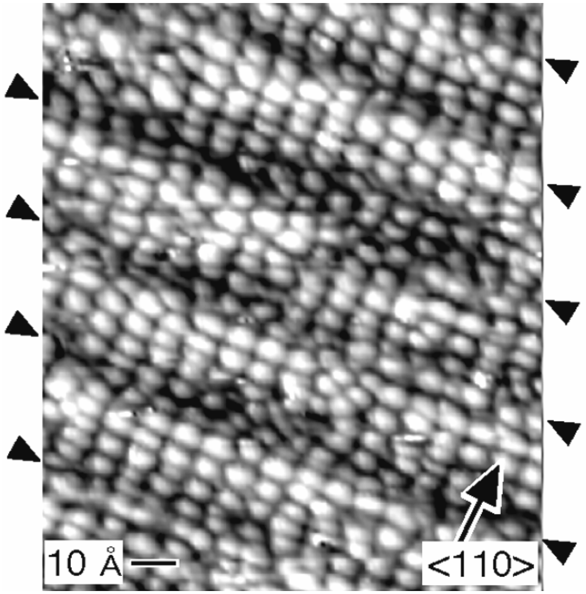
Vibration excitation of the molecule occurs when tunneling electrons have enough energy to excite a quantized vibrational level

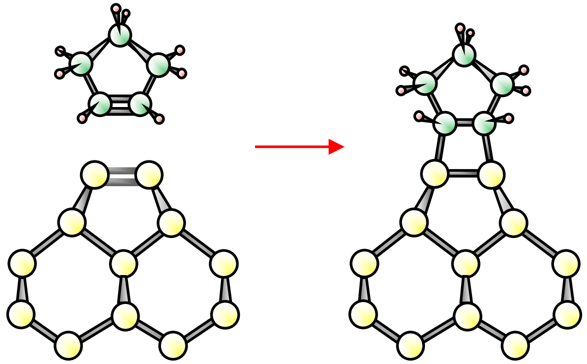
Inelastic tunneling channel

B.C. Stipe. et. al., *Science* 280, 1732 (1998)

Molecular Adsorption: 2+2 cycloaddition reaction



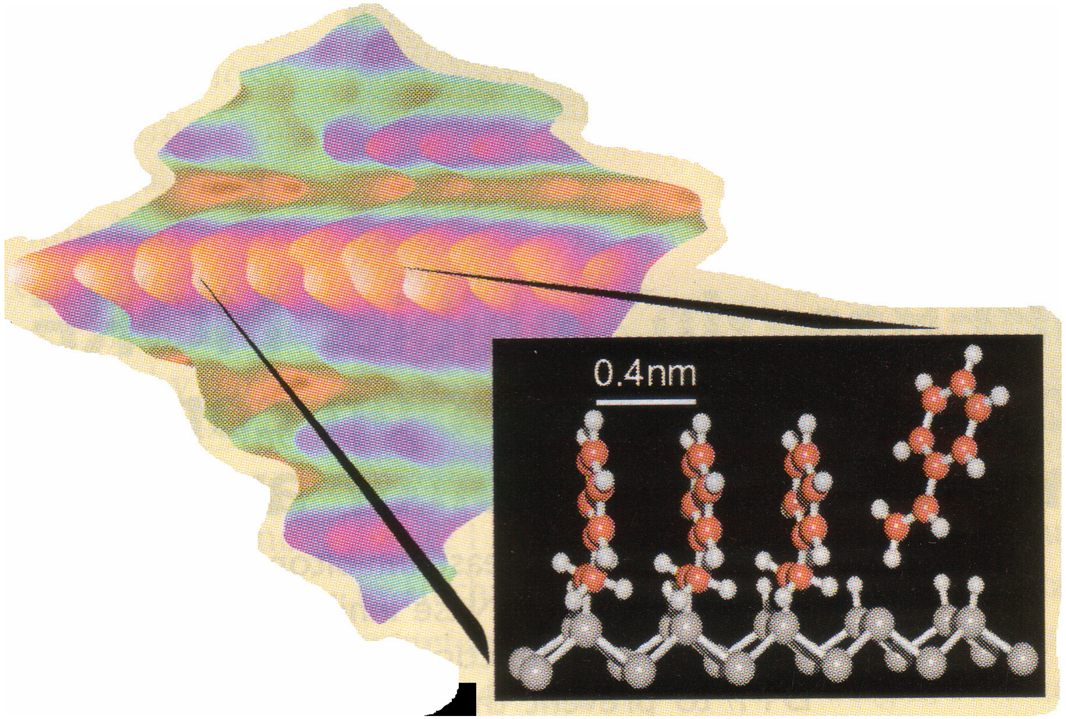


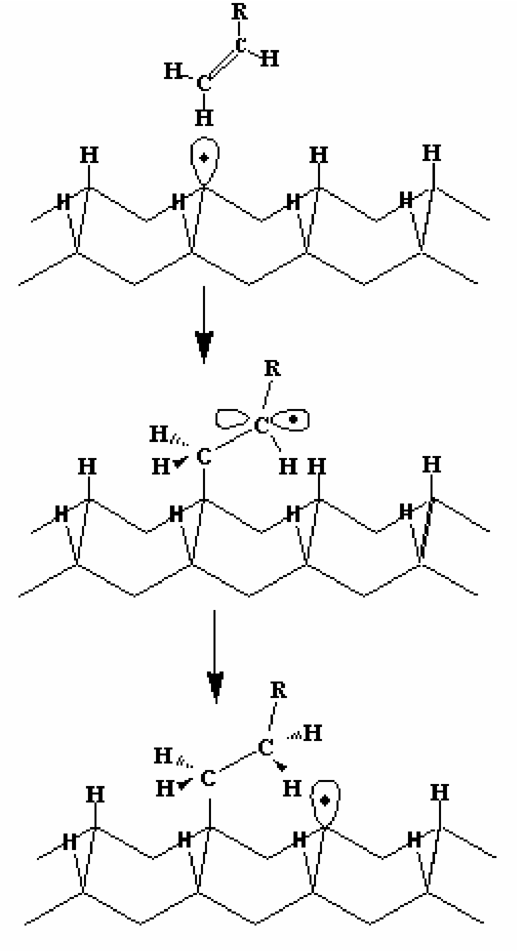


- ✓ **Fabrication of molecularly ordered organic films**
- ✓ **Anisotropic optical and electrical properties**
- ✓ **A Possible way to orient molecular devices**

R.J. Hamers et al, J. Phys. Chem., 101, 1489 (1997)

In-situ Monitoring of Self-assembly





Self-directed growth of Nanostructures

Wolkow et al, *Nature*, 406, 48 (2000)

Single-Bond Formation by STM

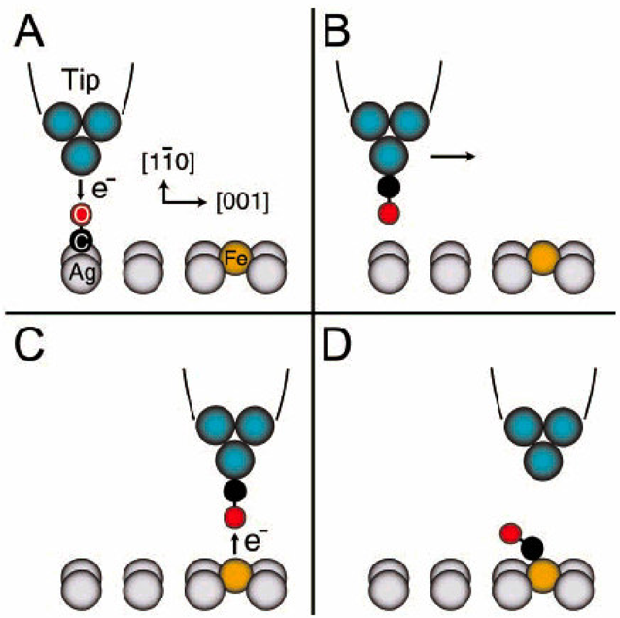


Fig. 1. Schematic diagrams showing the different steps in the formation of a single bond with the STM. The binding sites are determined by imaging the adsorbed species with a CO molecule attached to the tip (Fig. 4). The sizes of the circles are scaled to the atomic covalent radii. The polycrystalline tungsten tip is sputtered and annealed before use; physical contact is made with the Ag surface to further condition the tip. (**A**) The tip is positioned over a single CO molecule to induce the detachment of CO from Ag and its bonding to the tip. Because CO forms a bond predominantly through the carbon, a 180° rotation of the CO occurs in the transfer. (**B**) The tip with the attached single CO molecule is translated (indicted by the arrow) and positioned over an Fe atom. (**C**) The bias voltage and the flow of electrons are reversed, inducing the transfer of CO from the tip to the Fe. (**D**) A single Fe–CO bond is formed. The interaction of the electric field with the dipole moment of CO may also play a role in the transfer of (A) and (C).

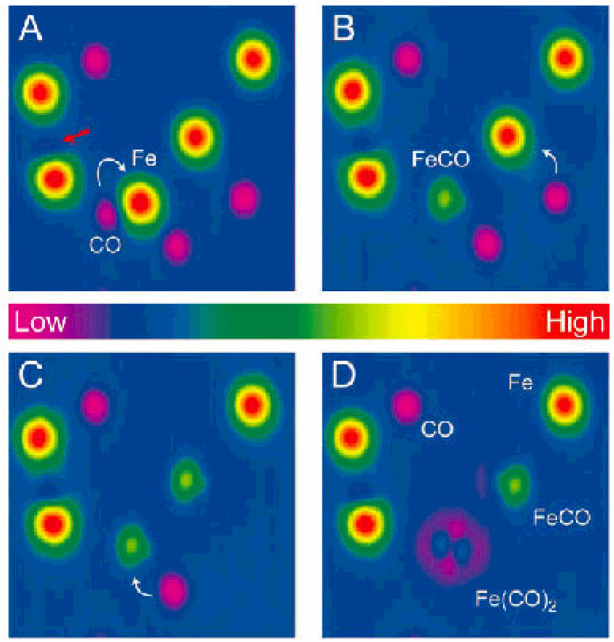
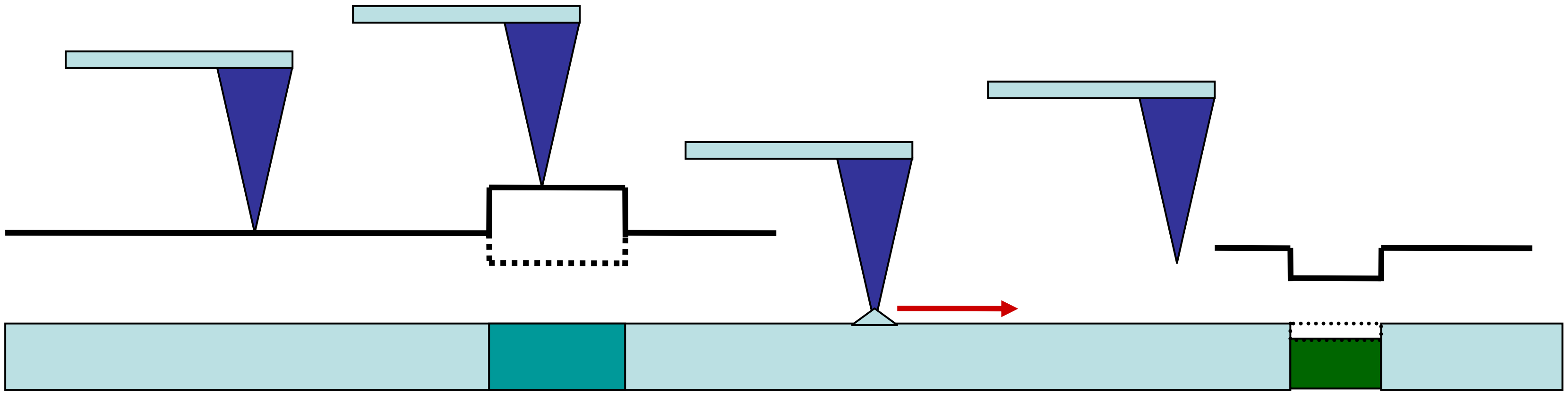


Fig. 2. A sequence of STM topographical images recorded at 70-mV bias, 0.1-nA tunneling current, and 13 K to show the formation of Fe–CO bond with the prescribed method (Fig. 1). The size of each image is 63 Å by 63 Å. Fe atoms image as protrusions and CO molecules as depressions. The white arrows indicate the pair of adsorbed species involved in each bond formation step. (**A**) Five Fe atoms and five CO molecules are adsorbed in this area of the Ag(110) surface. One CO is very close to an Fe atom (indicated by the red arrow). (**B**) A CO molecule has been manipulated and bonded to an Fe atom to form Fe(CO). (**C**) Another Fe(CO) is formed by binding CO to a second Fe atom. (**D**) An additional CO has been bonded to Fe(CO) to form $Fe(CO)_2$. A 180° flip is observed for the remaining Fe(CO).

H.J. Lee and W. Ho, Science, 286, 1719(1999)

Interactions between Sample and Tip in Force Microscopy

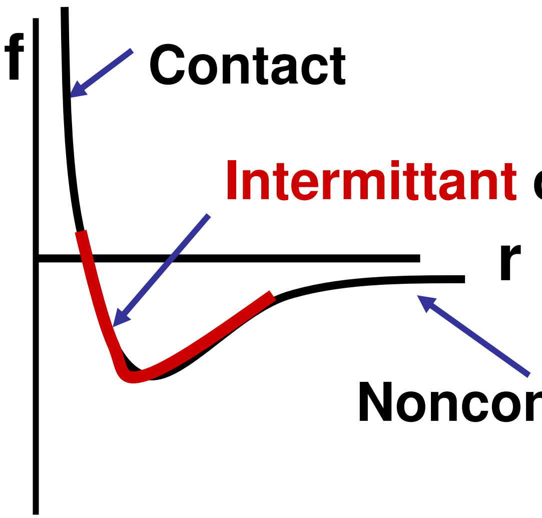


vdW force
attractive
ionic repulsion

magnetic or electrostatic forces

adhesion
bonding
friction forces

elastic and plastic properties

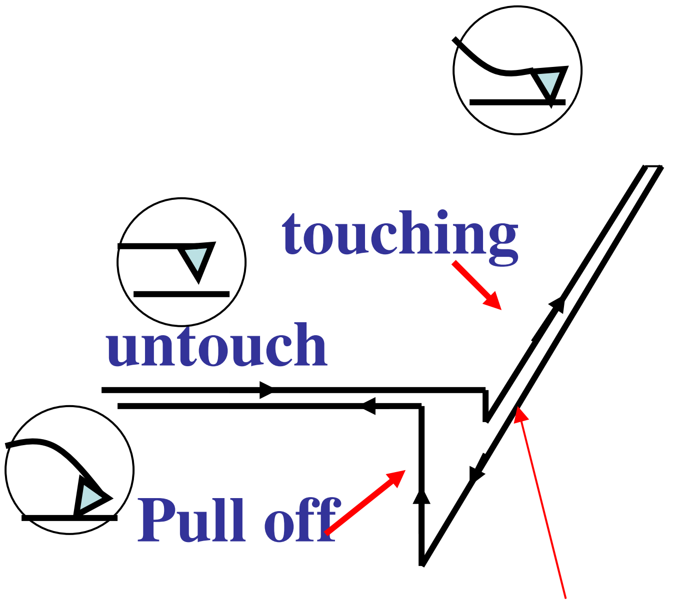


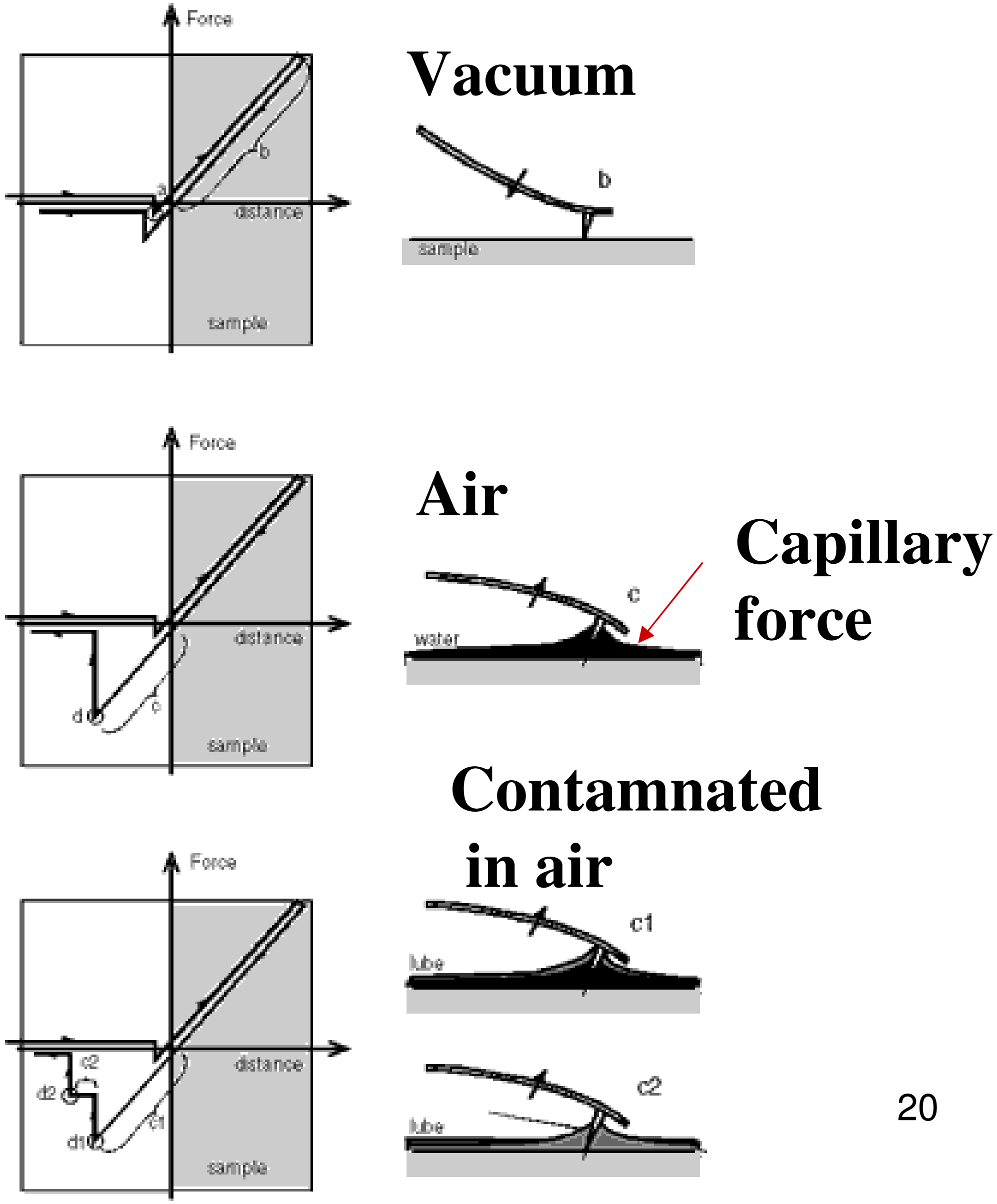
van der Waals force

$$f(r) \sim -1/r^6 + 1/r^{12}$$

$$\sim 10^{-7} \sim 10^{-11}\ \mathrm{N}$$

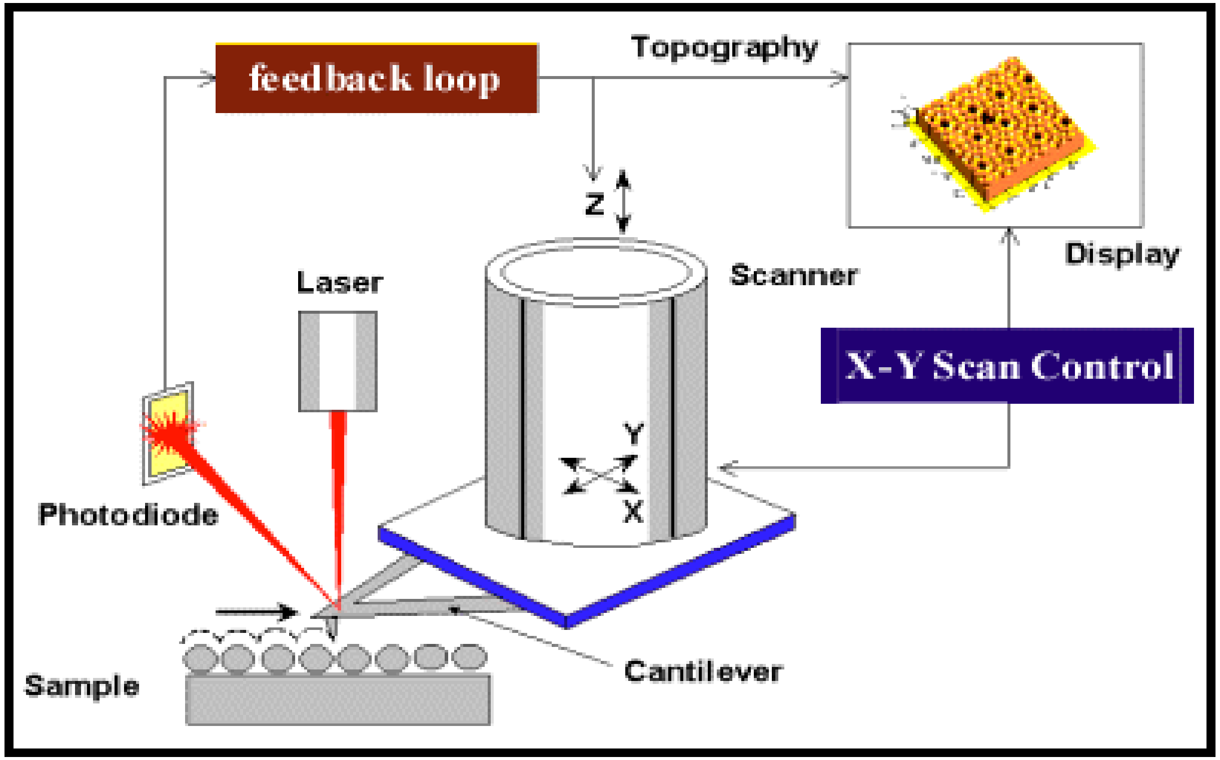
Force vs. Distance





Slope: elastic modulus of soft sample or force constant k of cantilever

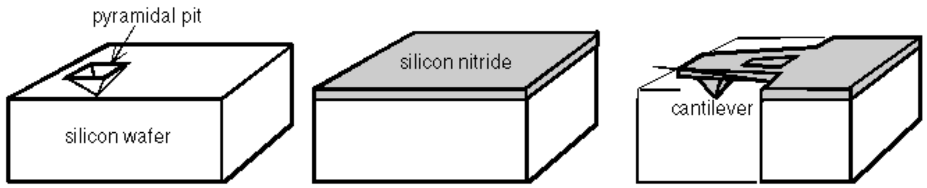
Atomic Force Microscope (AFM)



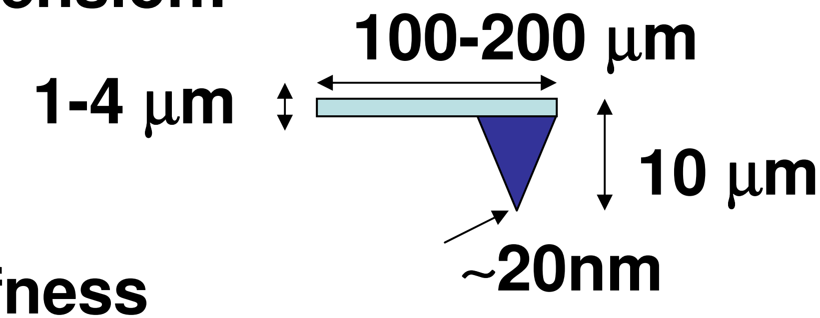
- **Sample: conductor, nonconductor, etc**
- **Force sensor: cantilever**
- **Deflection detection: photodiode interferometry (10^{-4}A)**

Mode of Operation	Force of interaction
Contact	strong (repulsive): constant force or constant distance
Noncontact	weak(attractive): vibrating probe
Intermittent contact	strong(repulsive): vibrating probe
Lateral force	frictional forces exert a torque on the scanning cantilever
Magnetic force	the magnetic field of the surface
Thermal scanning	the distribution of thermal conductivity

Force Sensor: *Cantilever*



- Material: Si , Si_3N_4
- Dimension:



- Stiffness
  - soft: contact mode
  - stiff: vibrating (dynamic force) mode
- Spring constant (k): 0.1-10N/m
- Resonance frequency: 10~100kHz

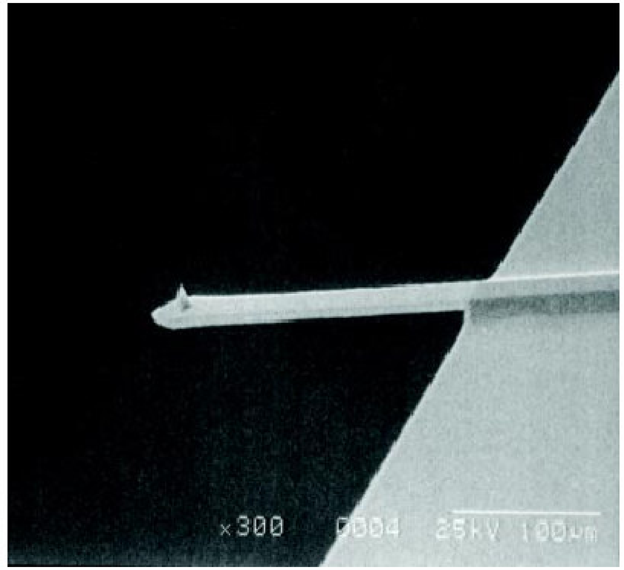
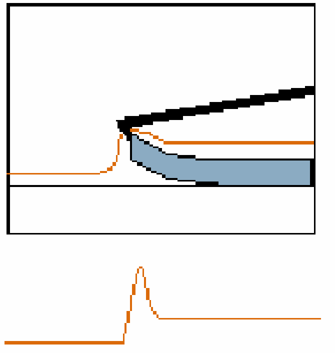
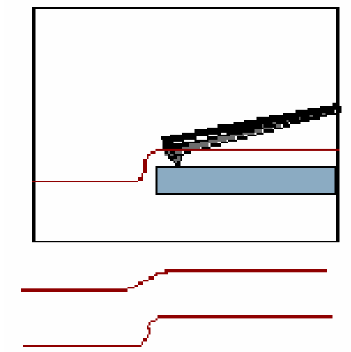
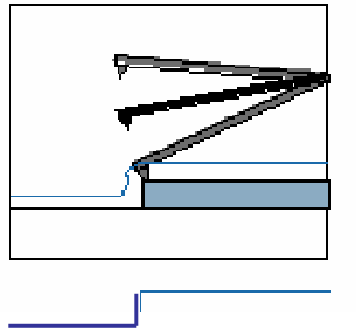


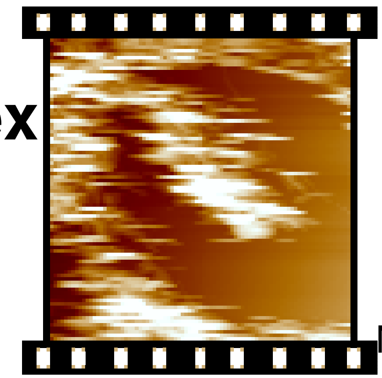
Figure 3. SEM image of an integrated single crystal silicon cantilever and tip which has an end radius of 2 to 10nm. Tips for AFM are typically made of silicon or silicon nitride. Bar=100μm.

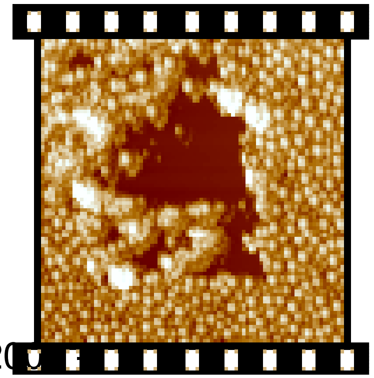
From DI

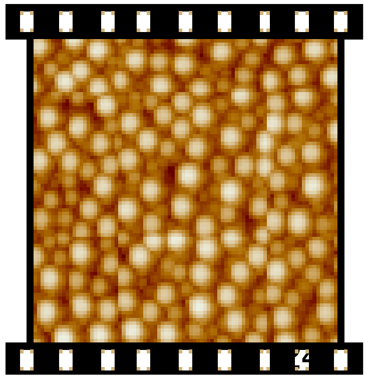
Scanning Modes

	Contact	Noncontact	Vibrating (tapping)
			
Cantilever	soft	hard	hard
Force	1-10nN	0.1-0.01nN	
Friction	large	small	small
Distance	<0.2nm	~ 1nm	>10nm
Damage	large	small	small

Polymer latex particle on mica

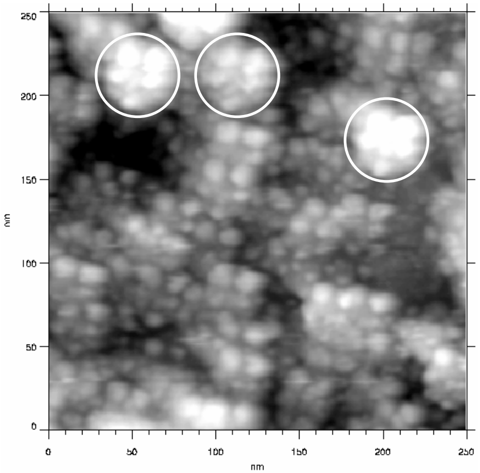




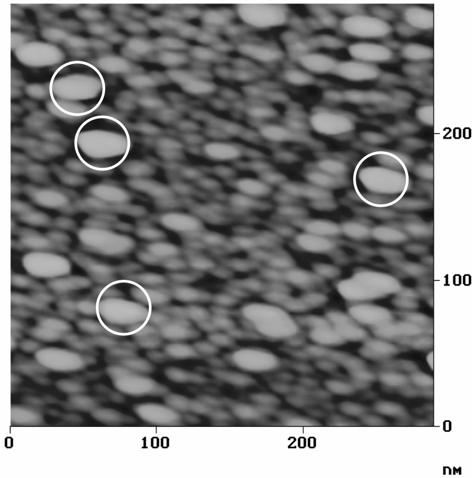


From DI

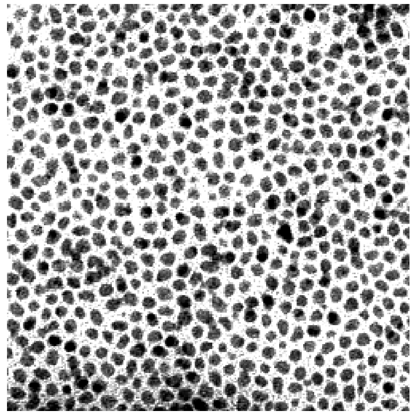
STM and AFM Images of Co-Nanoparticles



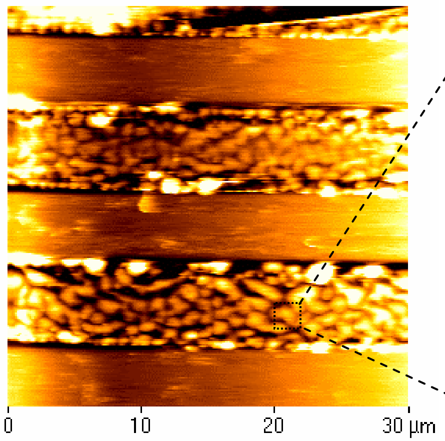
STM: on H/Si(111)



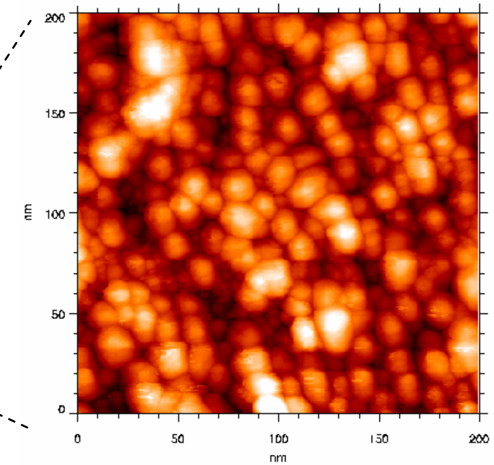
AFM: on HOPG



TEM: on Carbon grid



AFM image



Co-nanoparticle stripes prepared

By Mirco Contact Printing

UHV-STM image (200 nm x 200 nm)
after annealing under 500 °C

S.S.Bae et al (2001)

Manipulation of Nanoparticles by AFM

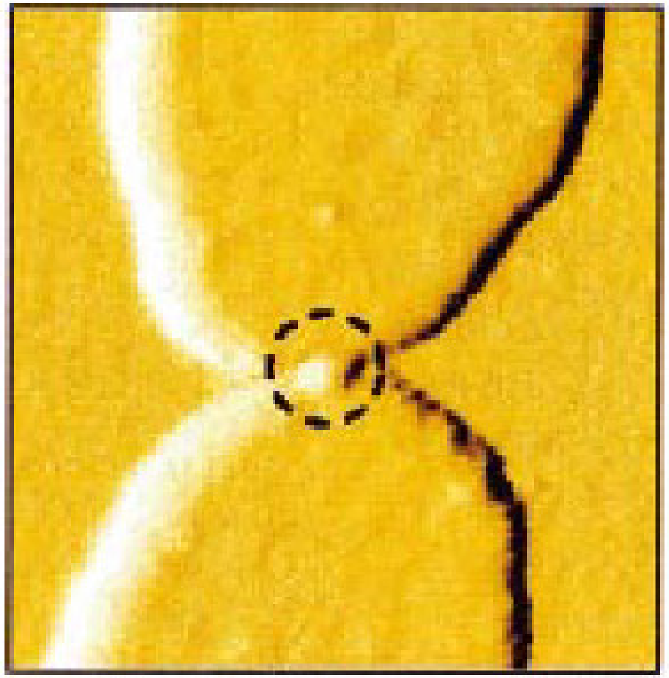
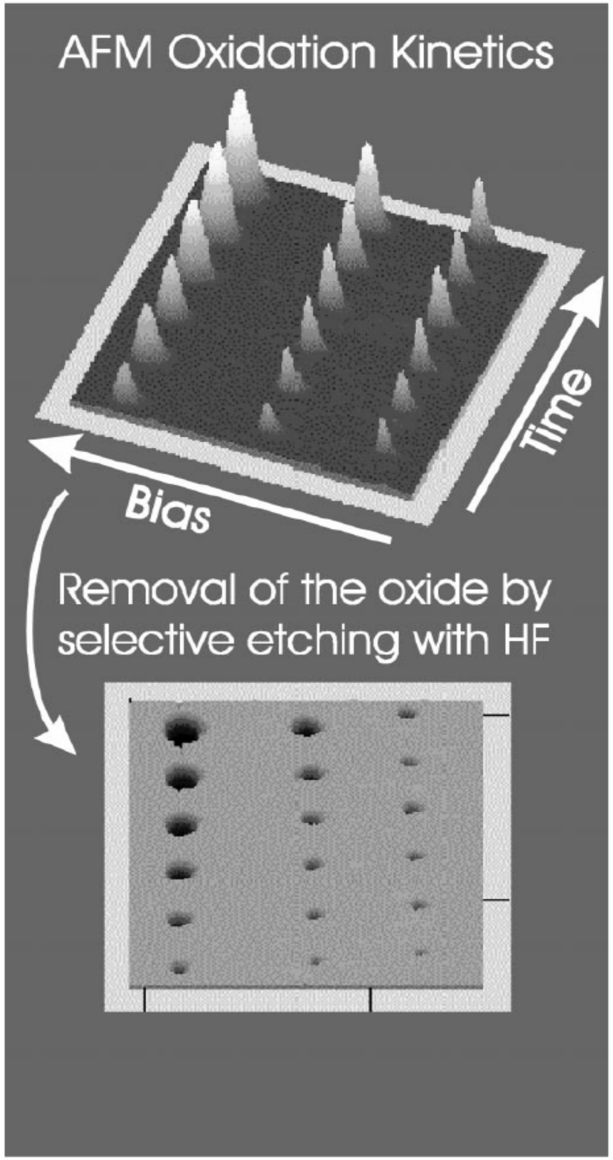


Figure 8. Single-particle device fabricated by AFM-assisted manipulation of a 20 nm sized Au nanoparticle between two metallic leads. Image size: 400 nm × 400 nm (from ref 15).

Ref 15 in G.S. McCarth and P.S. Weiss, *Chem. Rev.* 99, 1983 (1999)

AFM-tip-induced Local Oxidation on Si



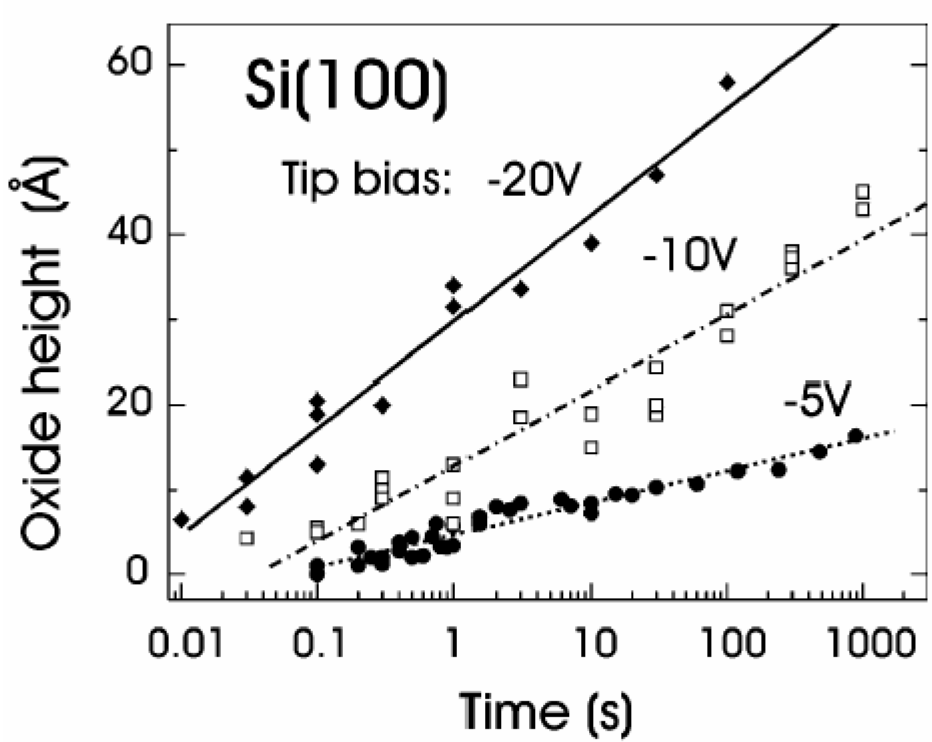
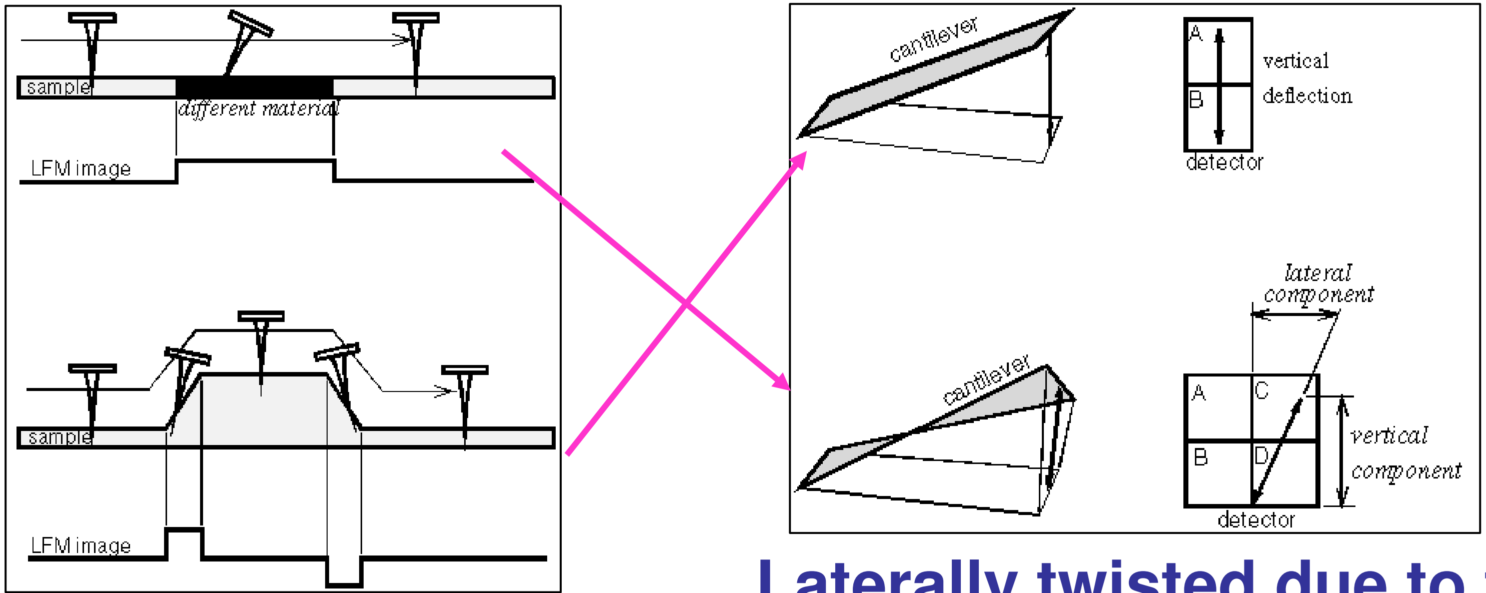


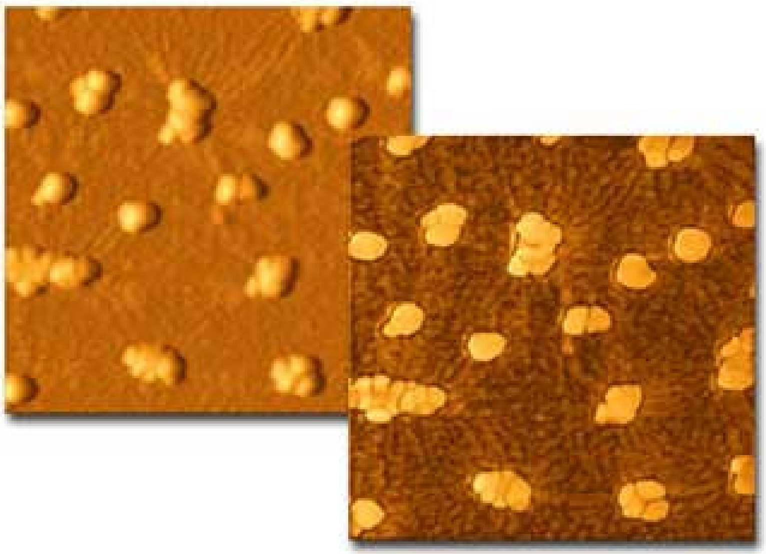
Fig. 3. Kinetics of oxide dot growth for different tip biases at ~ 50% ambient humidity

Ph. Avouris et al, *App. Phys. A* 66, S659 (1998)

Lateral Force Microscopy



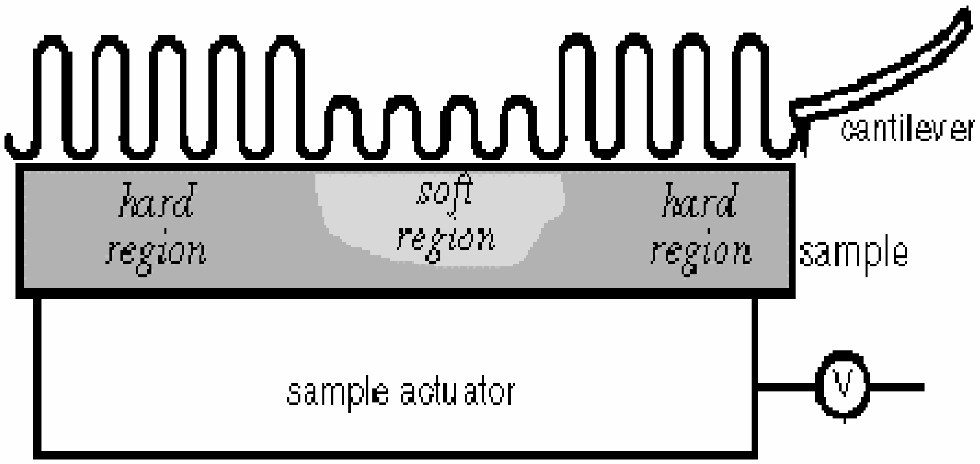
Laterally twisted due to friction

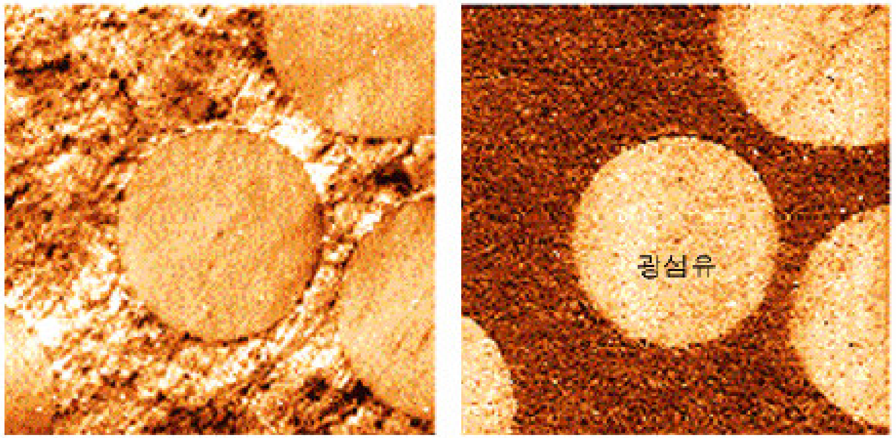


High resolution topography (top) and Lateral Force mode (bottom) images of a commercially avail-able PET film. The silicate fillers show increased friction in the lateral force image.

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

Force Modulation Microscopy

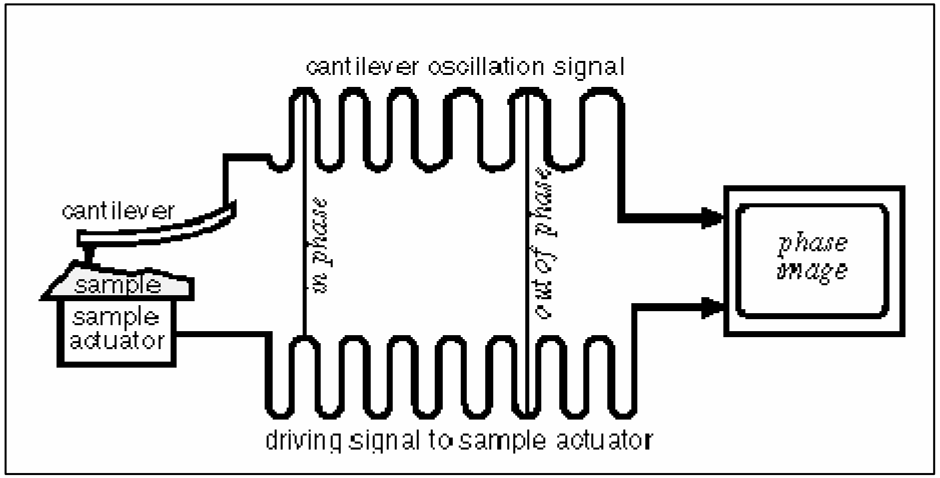




- Contact AFM mode
- Periodic signal is applied to either to tip or sample
- Simultaneous imaging of topography and material properties
- Amplitude change due to elastic properties of the sample

PSIA, ***www.psia.co.kr/appnotes/apps.htm***

Phase Detection Microscopy



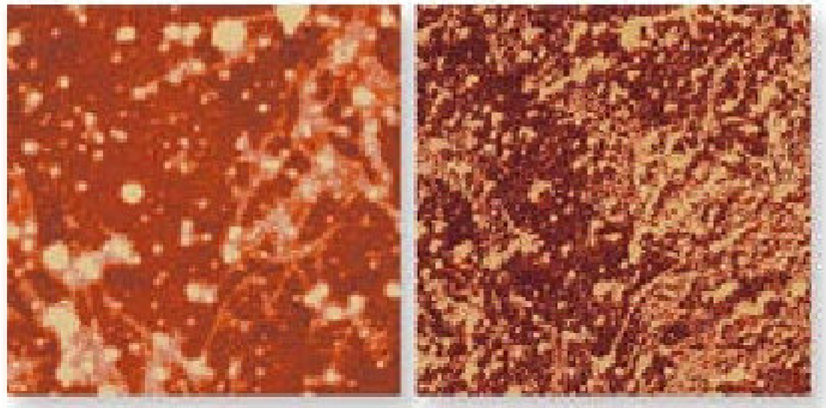
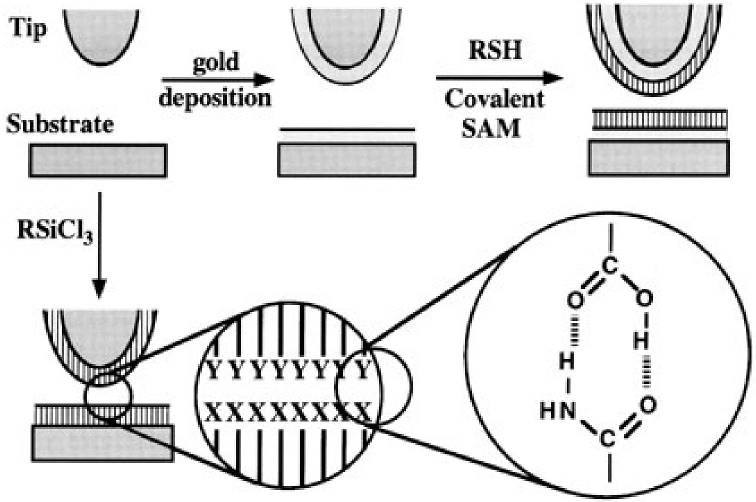
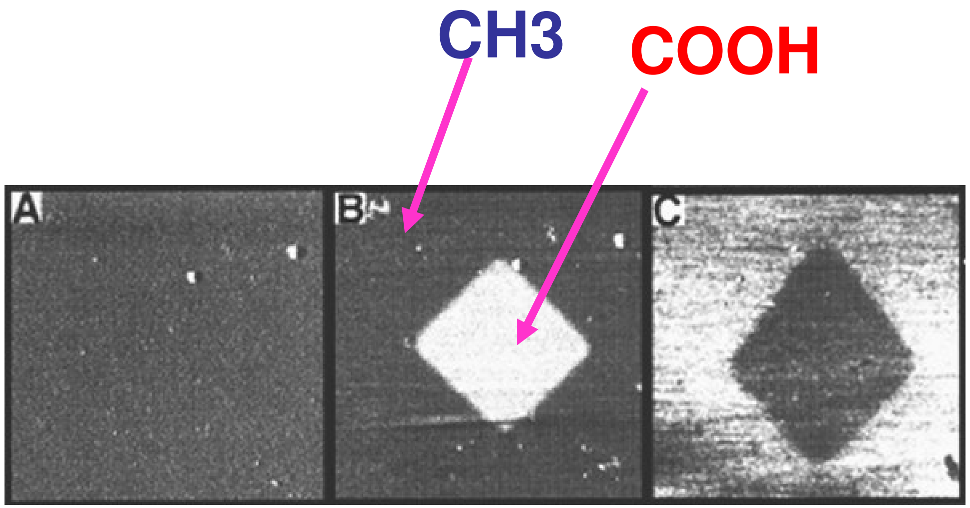


그림 14. 폴리머 코팅한 것을 원자현미경으로 찍은 사진. 오른쪽 사진은 단순한 시료의 표면을 형상화한 것이고 왼쪽 사진은 같은 시료의 표면을PDM 을 이용하여 찍은 사진.

- **Intermittant-contact AFM mode**
- **Monitoring of phase lag between the signal drives the cantilever and the catilever oscillation signal**
- **Simultaneous imaging of topography and material properties**
- **Change in mechanical properties of sample surface**

Chemical Force Microscopy

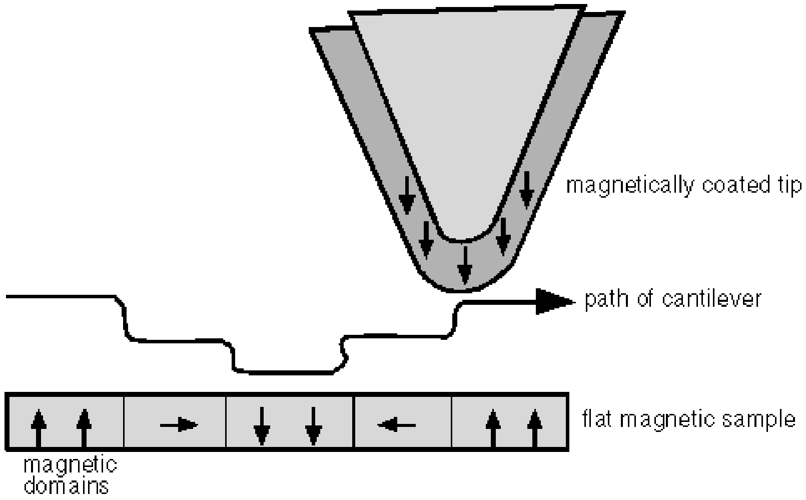




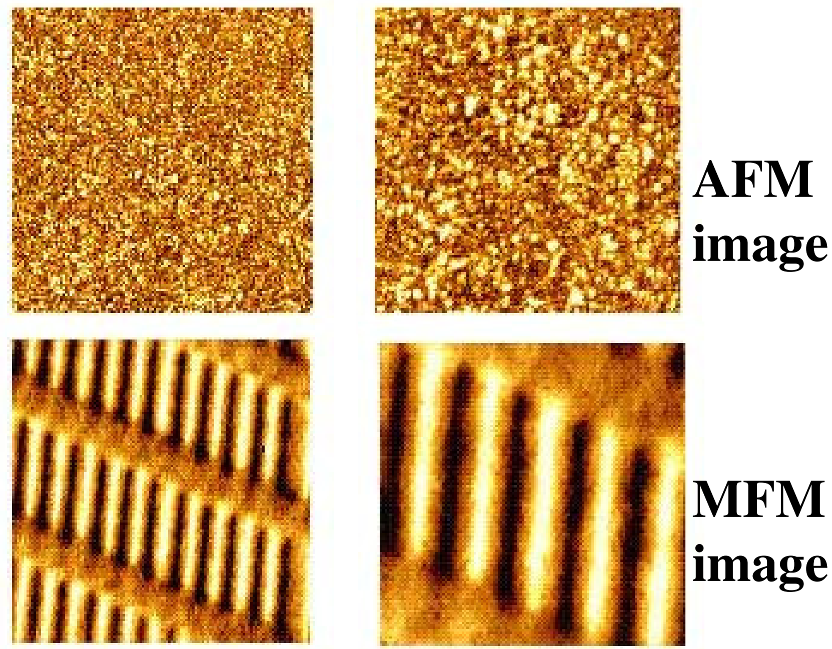
(A) topography
(B) friction force using a tip modified with a COOH-terminated SAM,
(C) friction force using a tip modified with a methyl-terminated SAM.
Light regions in (B) and (C) indicate high friction; dark regions indicate low friction.

A. Noy et al, *Ann. Rev. Mater. Sci.* 27, 381 (1997)

Magnetic Force Microscopy



Glass Hard Disk Sample



- **Ferromagnetic tip: Co, Cr**
- **Noncontact mode**
- **vdW force: short range force**
- **Magnetic force: long range force; small force gradient**
- **Close imaging: topography**
- **Distant imaging: magnetic properties**

http://www.tmmicro.com/tech/index.htm

Electrostatic Force Microscopy(EFM)

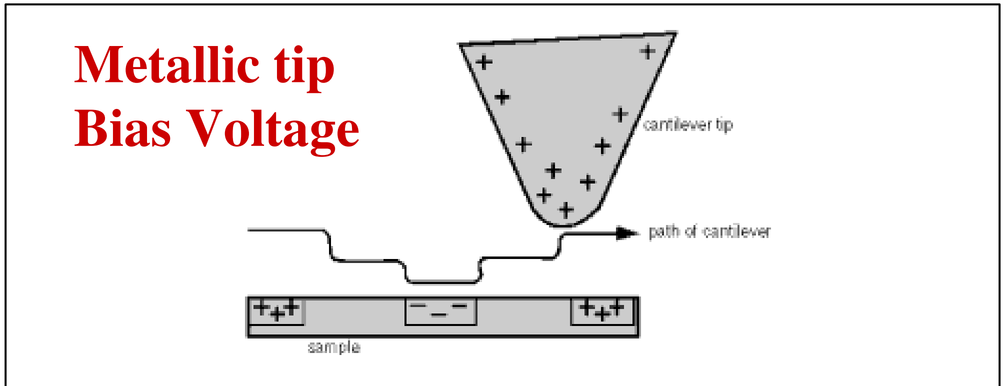
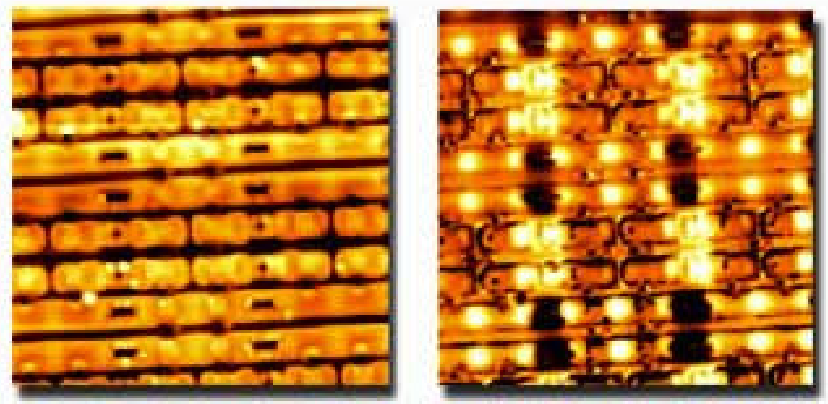


Figure 1-15. EFM maps locally charged domains on the sample surface.

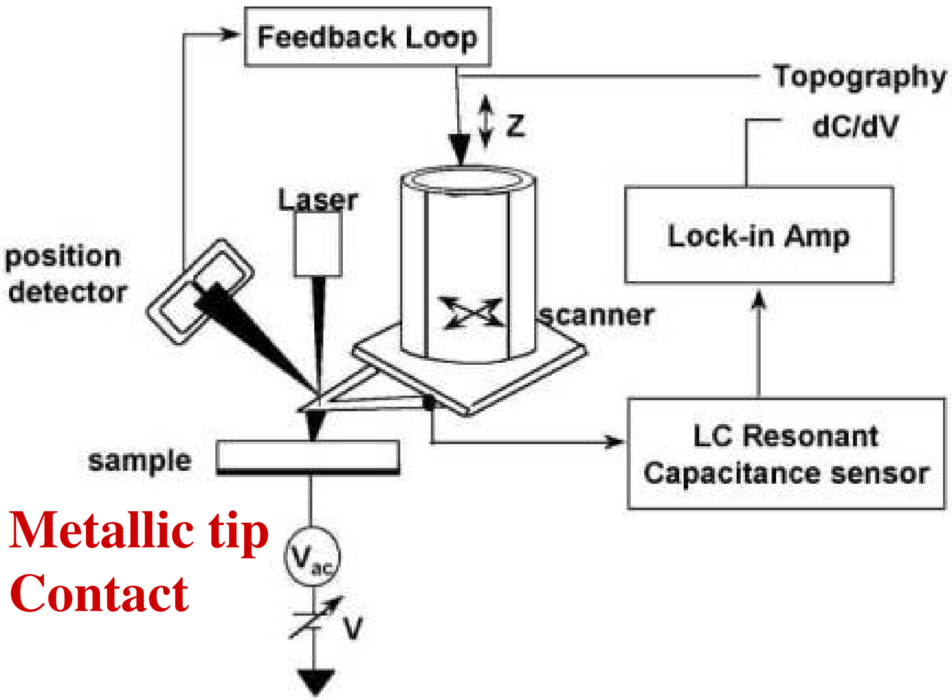


The subsurface structure of electrical contacts and doping trenchesin this SRAM sample can be revealed using electrostatic force microscopy (EFM)

- **Ferroelectric materials**
- **Charge distribution on surfaces**
- **Failure analysis on the device**

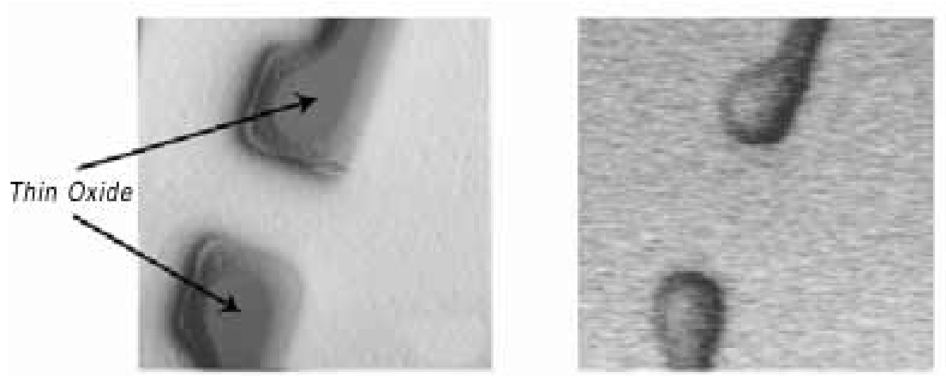
http://www.tmmicro.com/tech/index.htm

Scanning Capacitance Microscopy (SCM)



Metallic tip Contact

Transistor Oxide Thickness

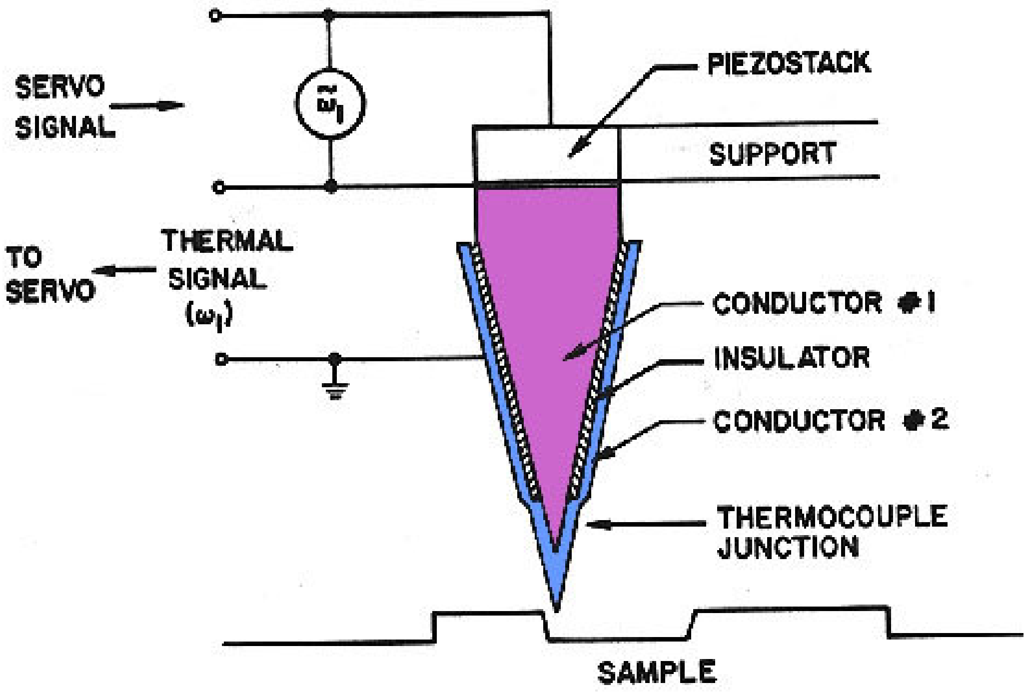


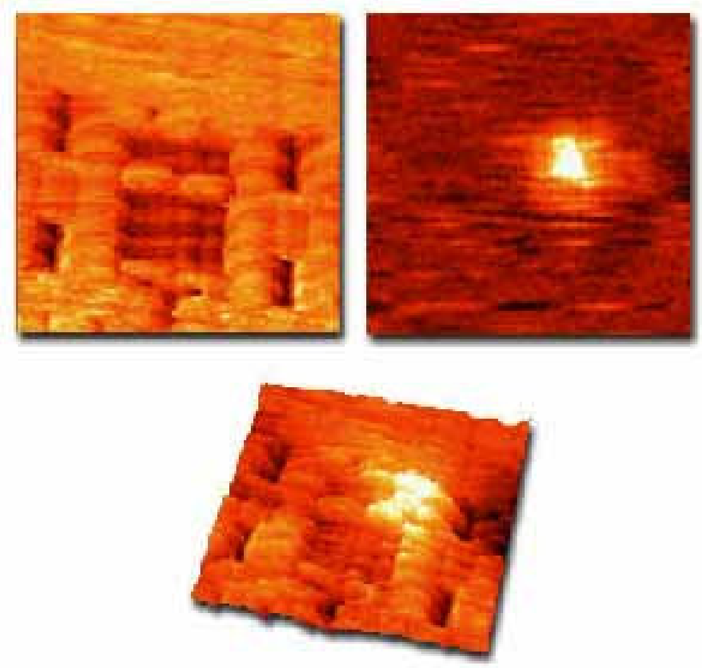
Topograph SCM

- LC capacitance circuit
- Doping concentration
- Local dielectric constant

http://www.psia.co.kr/appnotes/apps.htm

Scanning Thermal Microscopy



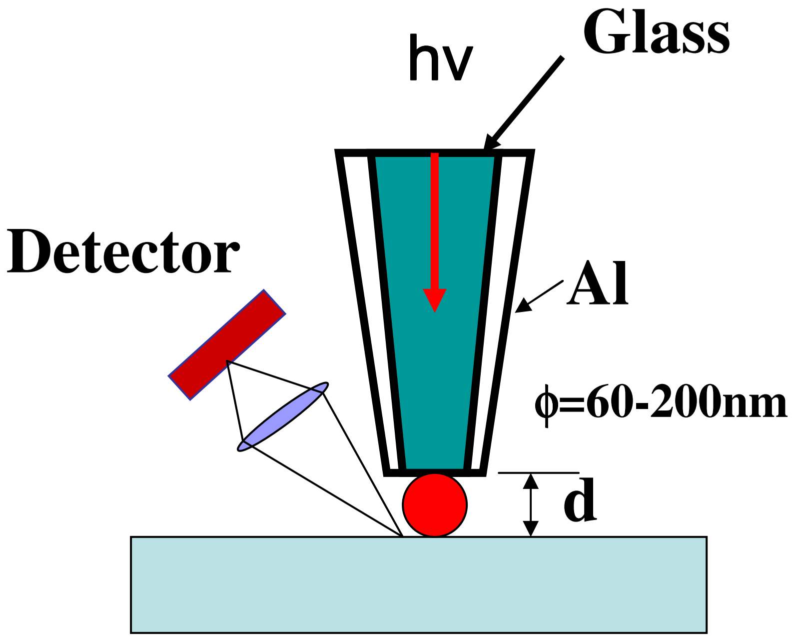


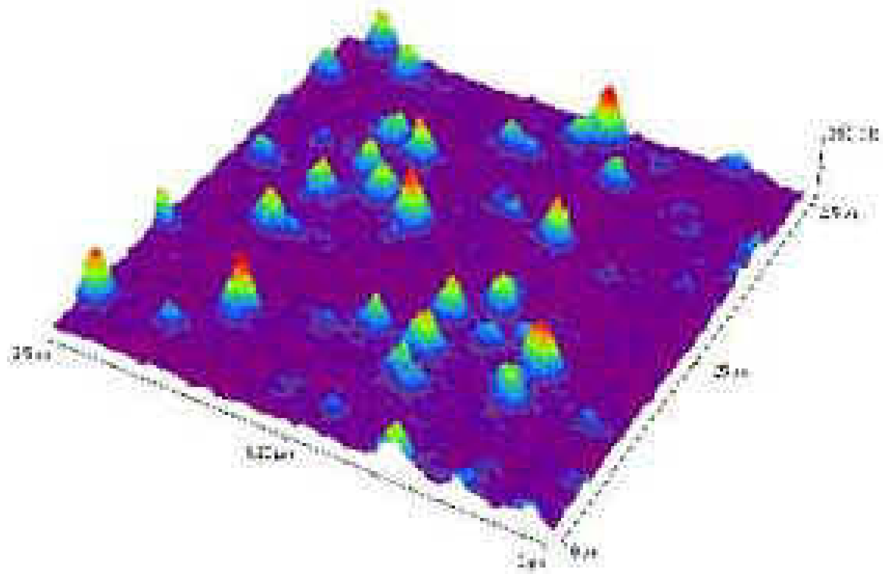
Topographic (upper left) and Thermal (upper right) images of a "hot spot" in a powered IC. The images were added together to get a composite image (bottom)which indicates the location of the failed region.

- **Subsurface defect review**
- **Semiconductor failure analysis**
- **Measure conductivity differences in copolymers, surface coatings etc**

Nearfield Scanning Optical Microscopy

Topography and Optical properties



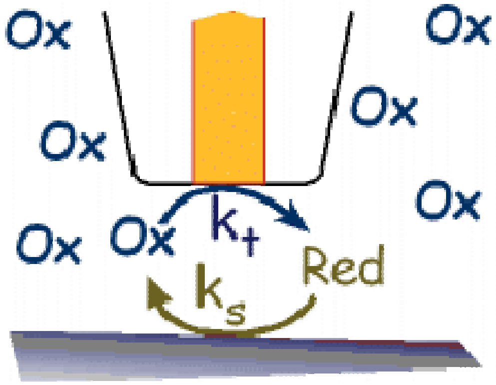


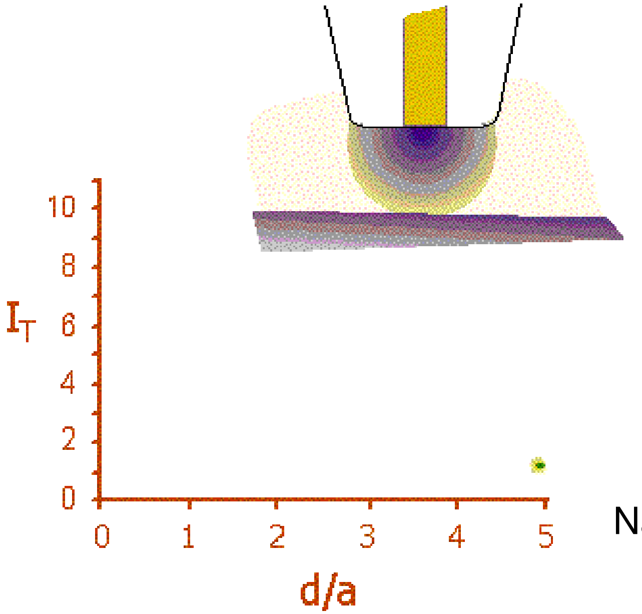
- Near field: $d \ll \lambda$
- Resolution ~ d and ϕ
- Approach: shear force

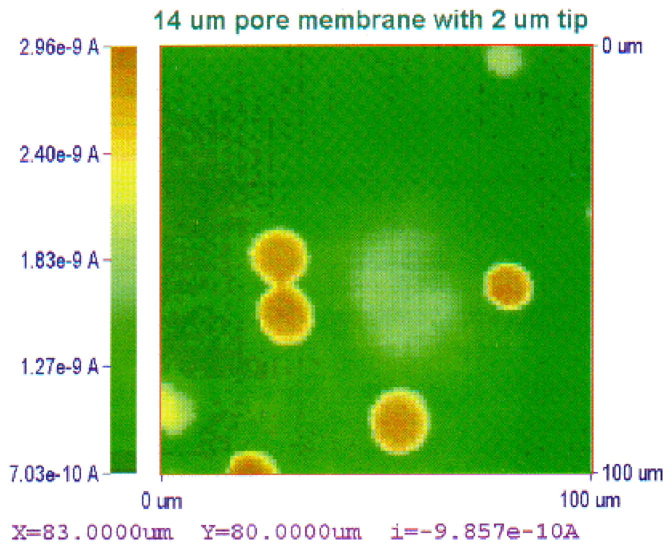
Fluorescence image of a single DilC molecule. Image courtesy of P. Barabara/Dan Higgins

http://www.psia.co.kr/data/nsom.htm

Scanning Electrochemical Microscopy



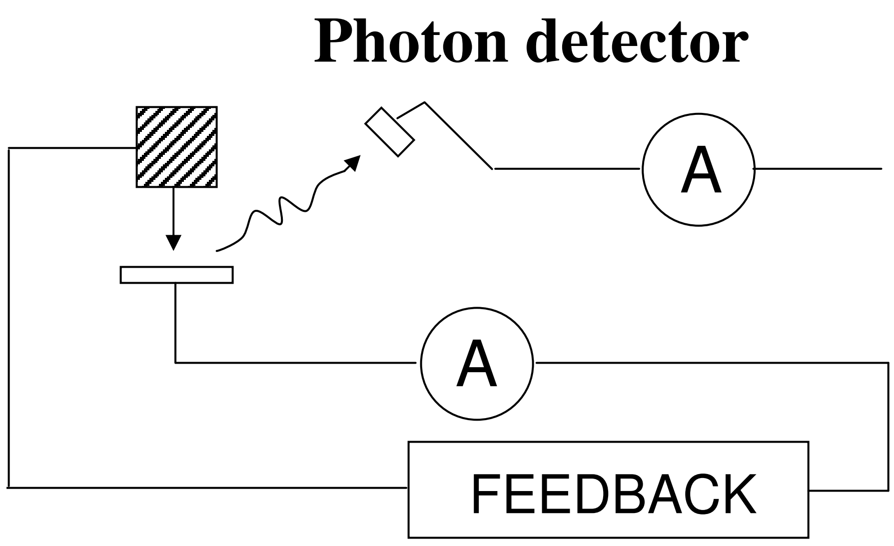




Electrochemistry
Surface structure
Electrochemical deposition
Corrosion

From J. Kwak

Photon Emission STM



Local chemical environment

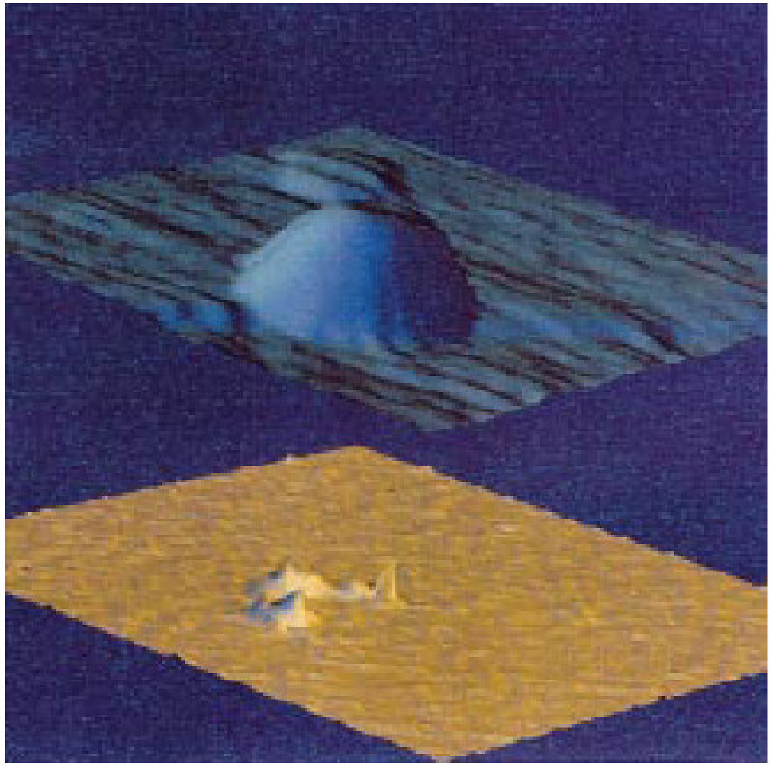


Figure 3. Photon emission comes exclusively from an asperity on a gold nanoparticle adsorbed on a mercapto-ethylamine-functionalized Au{111} terrace. Topography acquired by STM (top) and simultaneously acquired photon emission map (bottom). Image size 180 Å × 180 Å, V_{sample} = −2.0 V, I_{tunnel} = 5.0nA.

G.S. McCarty and P.S. Weiss, *Chem. Rev.* 99, 1983 (1999)

Summary

• **SPM has *eyes* to see the geometry and properties of nanostructures and *fingers* to manipulate and build nanostructures**

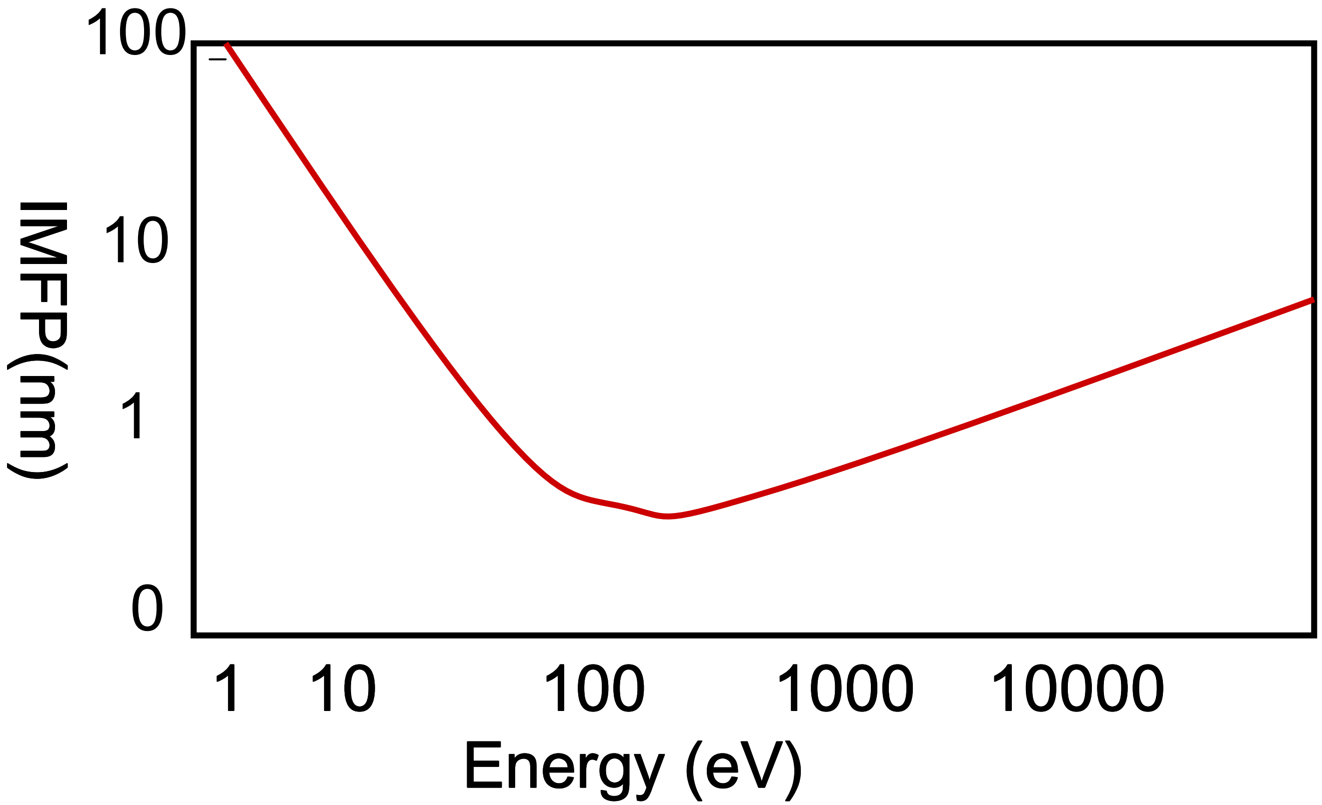
Raman spectroscopy

- **Raman spectroscopy** is a spectroscopic technique used in condensed matter physics and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary information.
- Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector.

Acronyms

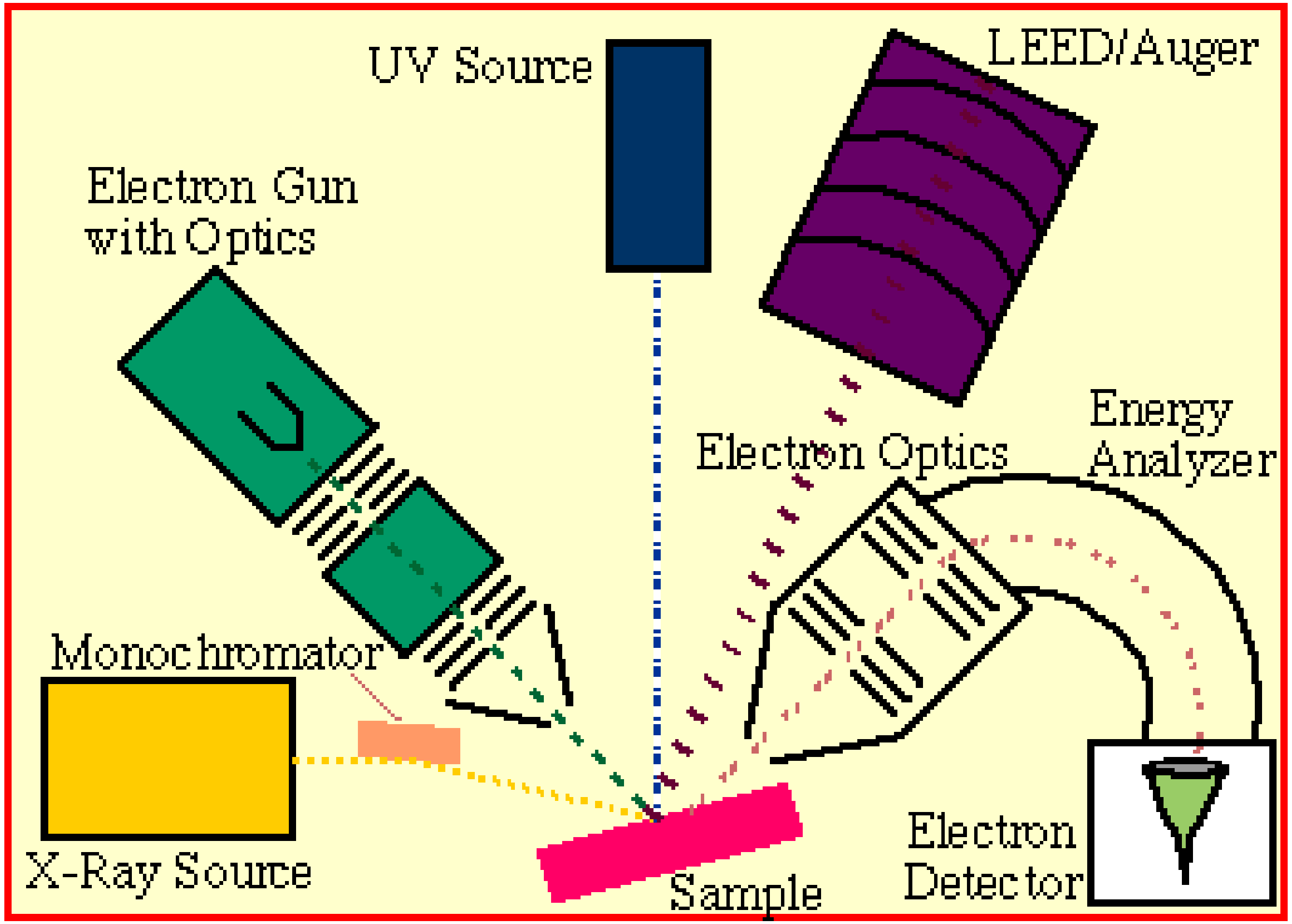
- *Electron Spectroscopies*
  - **Auger Electron Spectroscopy (AES)**
  - **X-ray Photoelectron Spectroscopy (XPS)**
  - **Ultraviolet Photoelectron Spectroscopy (UPS)**
  - **Electron Energy Loss Spectroscopy (EELS)**
  - **High Resolution EELS**
- *Electron Microscopies*
  - **Scanning Auger Microscopy (SAM)**
  - **Photoemission Electron Microscopy (PEEM)**
  - **Low Energy Electron Microscopy (LEEM)**
  - **Scanning X-ray Photoelectron Microscopy (SXPEM)**
  - **Secondary Electron Microscopy with Polarization Analysis (SEMPA)**

Why are electron spectroscopies surface sensitive ?

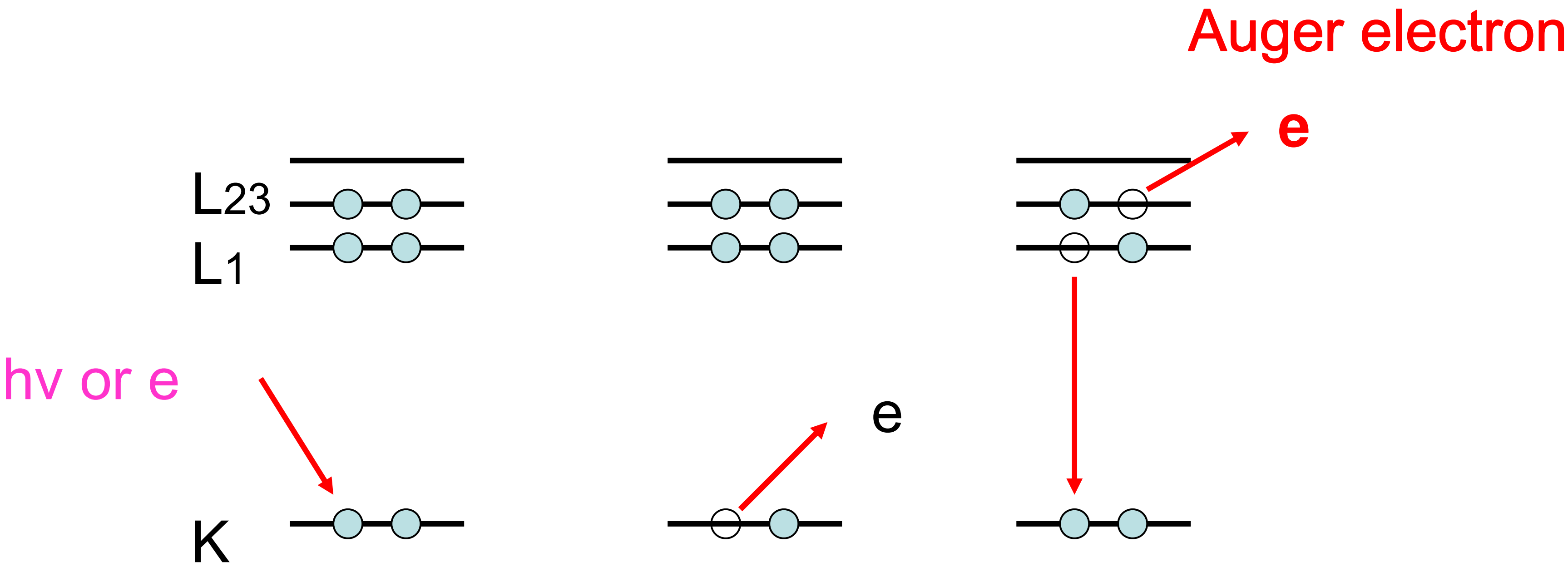


The inelastic mean free path (IMFP) of electrons is *less than 1 nm* for electron energies with 10~1000 eV.

Experimental Set Up



Auger Electron Spectroscopy

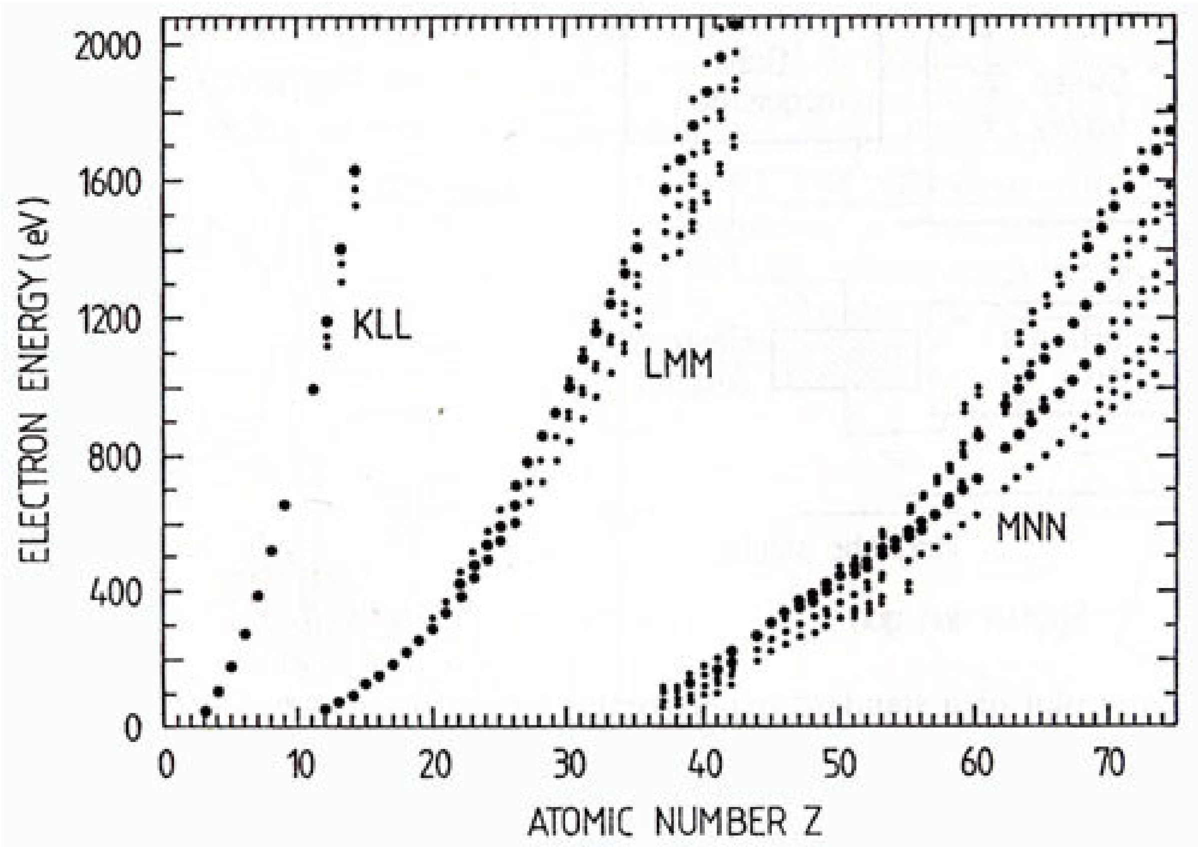


Kinetic Energy of Auger Electrons for KLL Transition

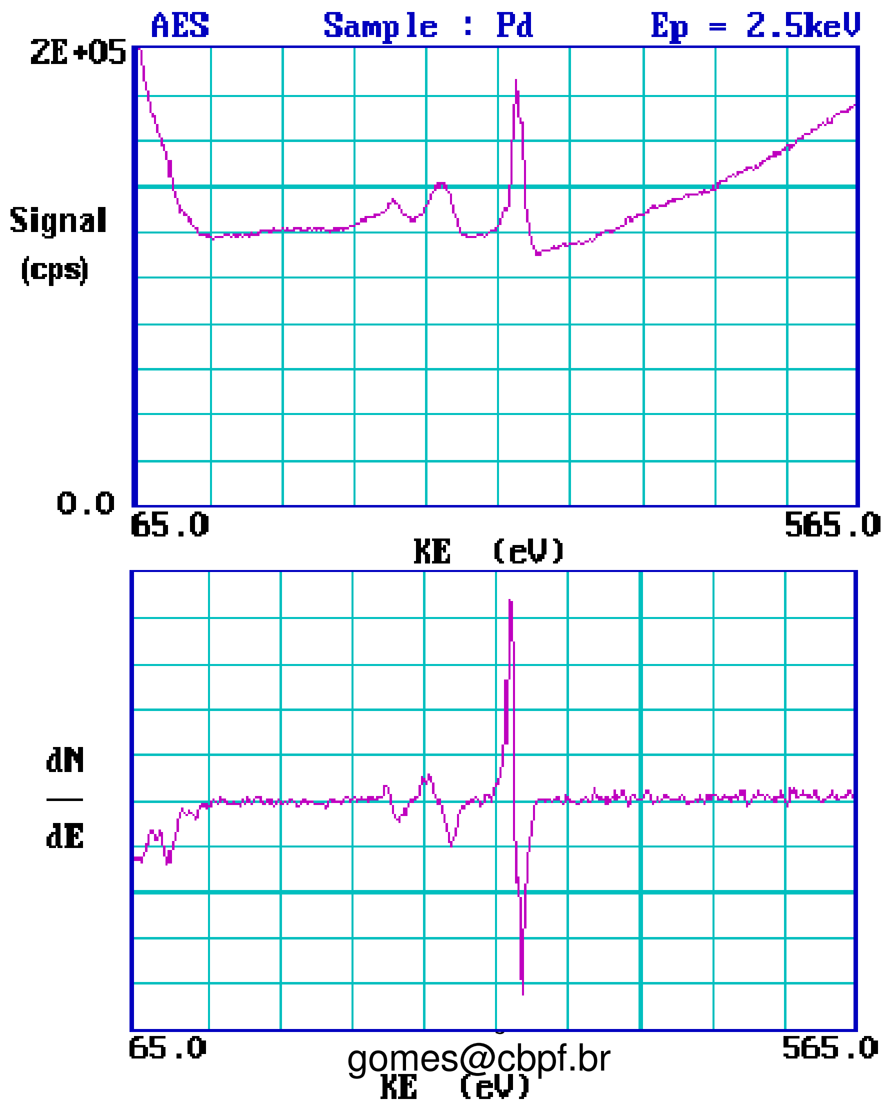
$$KE = E_K - E_{L1} - E_{L23}$$

Element Specific

Auger Electron Energies



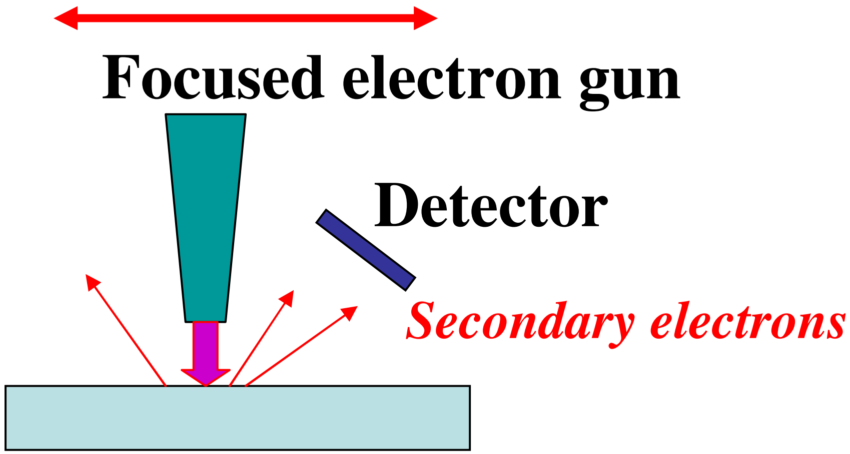
Auger Spectra

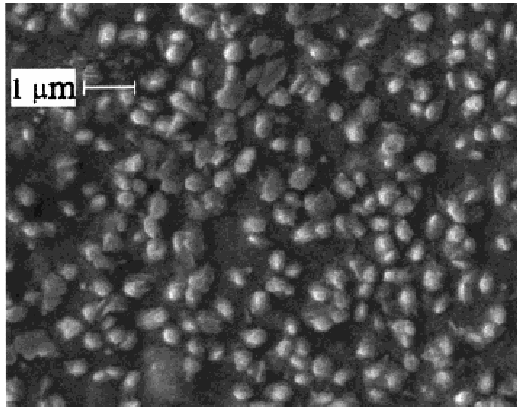


Applicatons

- Chemical identification: 1% monolayer
- Quantitative analysis
- Auger depth profiling
- Scanning Auger Microscopy (SAM)
  - Spatially-resolved compositional information

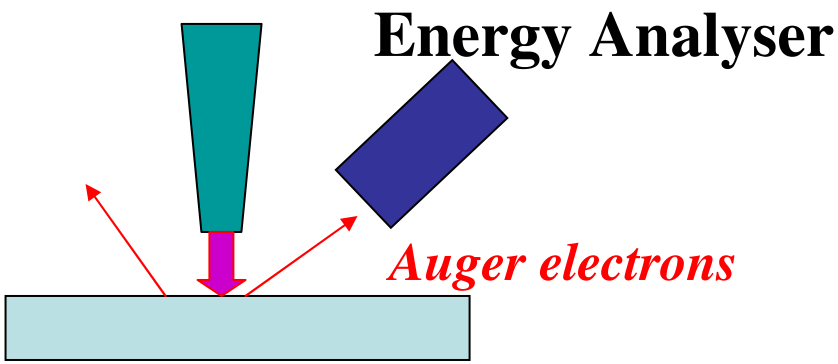
SEM and SAM

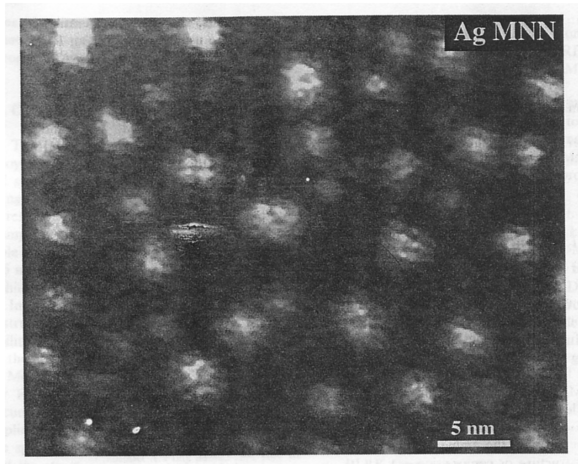




SiC grain size = 0.04 µm

SEM topograph of Au-SiC codeposits

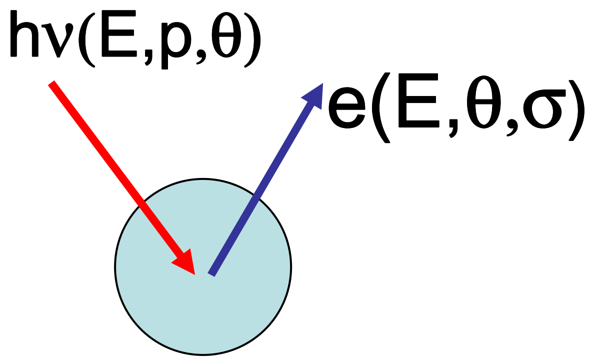


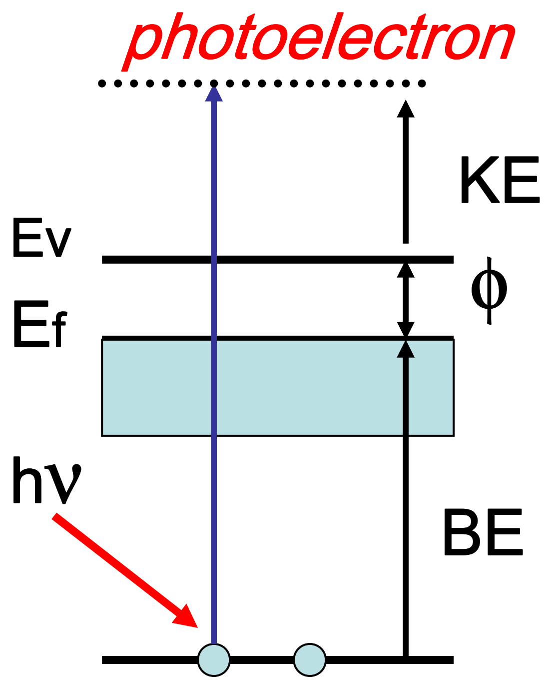


SAM image of Ag particles (d=1nm)

Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS): hν=200~2000 eV
Ultraviolet Photoelectron Spectroscopy (UPS): hν =10~50 eV





KE: kinetic energy
BE: binding energy
Φ: work function

$$KE = h\nu - BE - \phi$$

Photoemission peak intensity

$$I(E, h\nu) \sim N_v(E)\, N_c(E)\, \sigma(E,h\nu)\text{: UPS limit}$$

$$\sim N_v(E)\sigma(E,h\nu)\text{: XPS limit,}$$

where $N_v(E)$: densities of initial states(i)

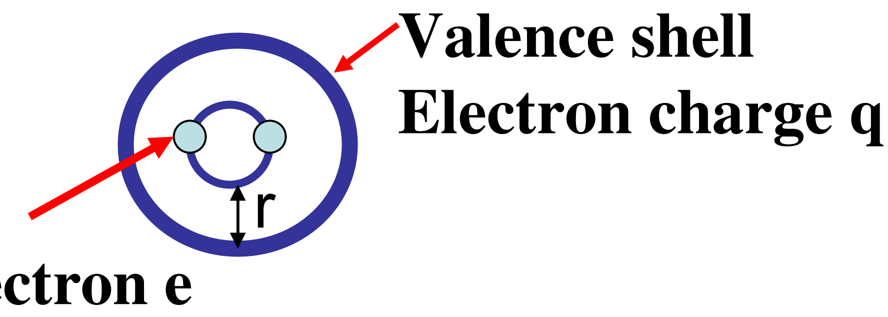
$N_c(E)$: densities of final states(f)

$\sigma(E,h\nu)$: photoionization cross section

$\sigma \sim |\langle f|AP|i\rangle|^2$

The XPS spectra represent the total density-of-states modulated by the cross-section for photoemission

Chemical Shift of Binding Energy

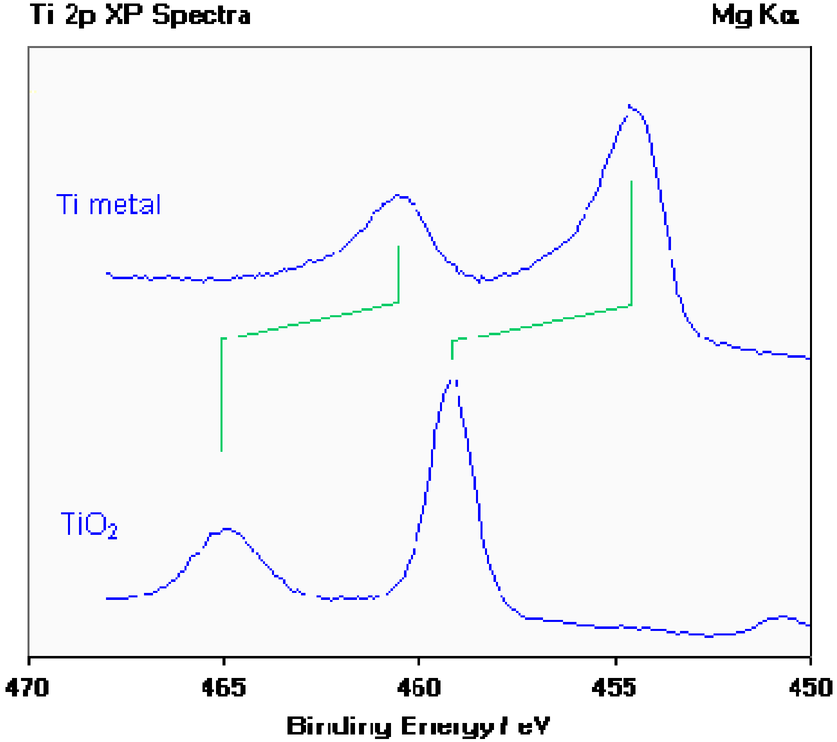


The core electron feels an alteration in the chemical environment when a change in the charge of the valence shell occurs.

A change in q, δq, gives a potential change $\delta E = e\,\delta q/r$

- **the oxidation state of the atom**
- **the chemical environment**

Example of Chemical Shift



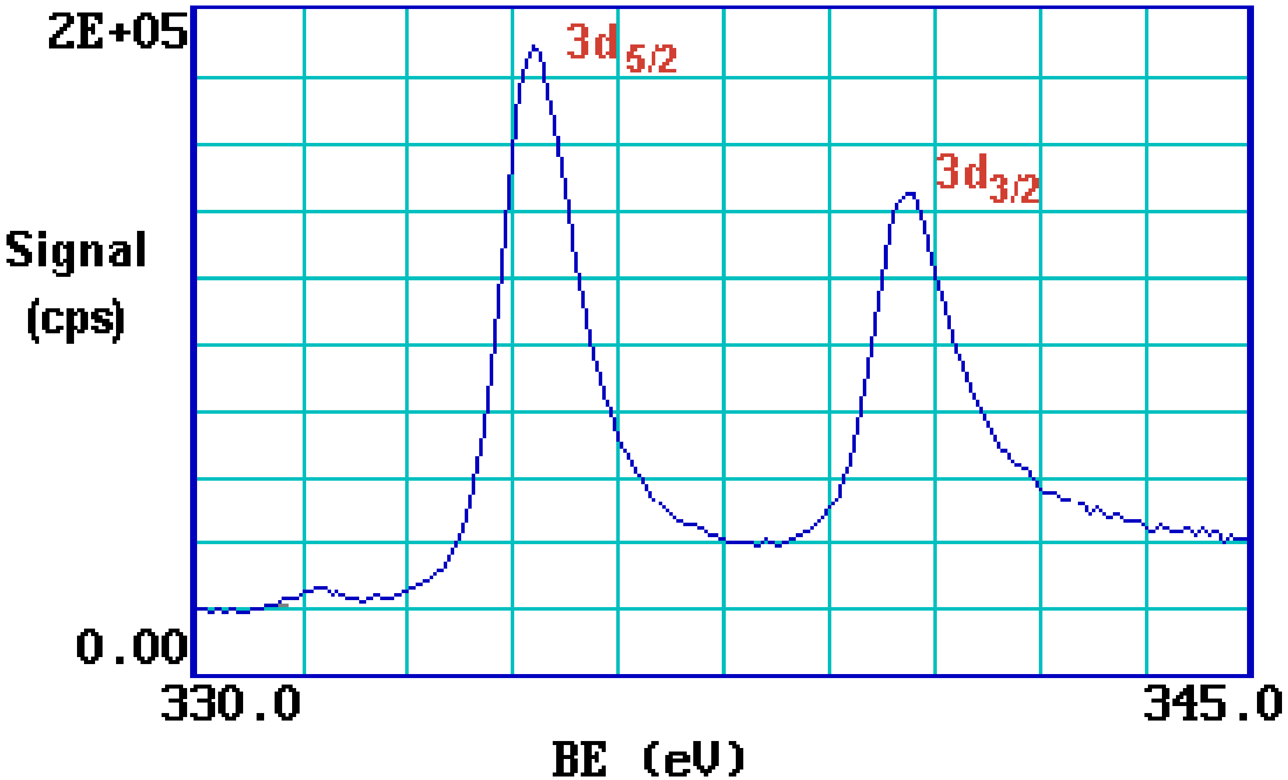
- The chemical shift: ~4.6 eV
- Metals: an asymmetric line shape (Doniach-Sunjic)
- Insulating oxides: more symmetric peak

Photoemission features

- **Spin-orbit splitting**
- **Shake-up and shake off**
- **Multiplet splitting**
- **Plasmon losses**

Ref: ***Electron spectroscopy I-IV*** **edited by C.R. Brundle and A.D. baker**
Photoelectron spectroscopy **by S. Hufner**

Spin-orbit Coupling



Pd: $(3d)^{10} + h\nu \rightarrow (3d)^{9} + e$

Shake up and shake off: Final state effect

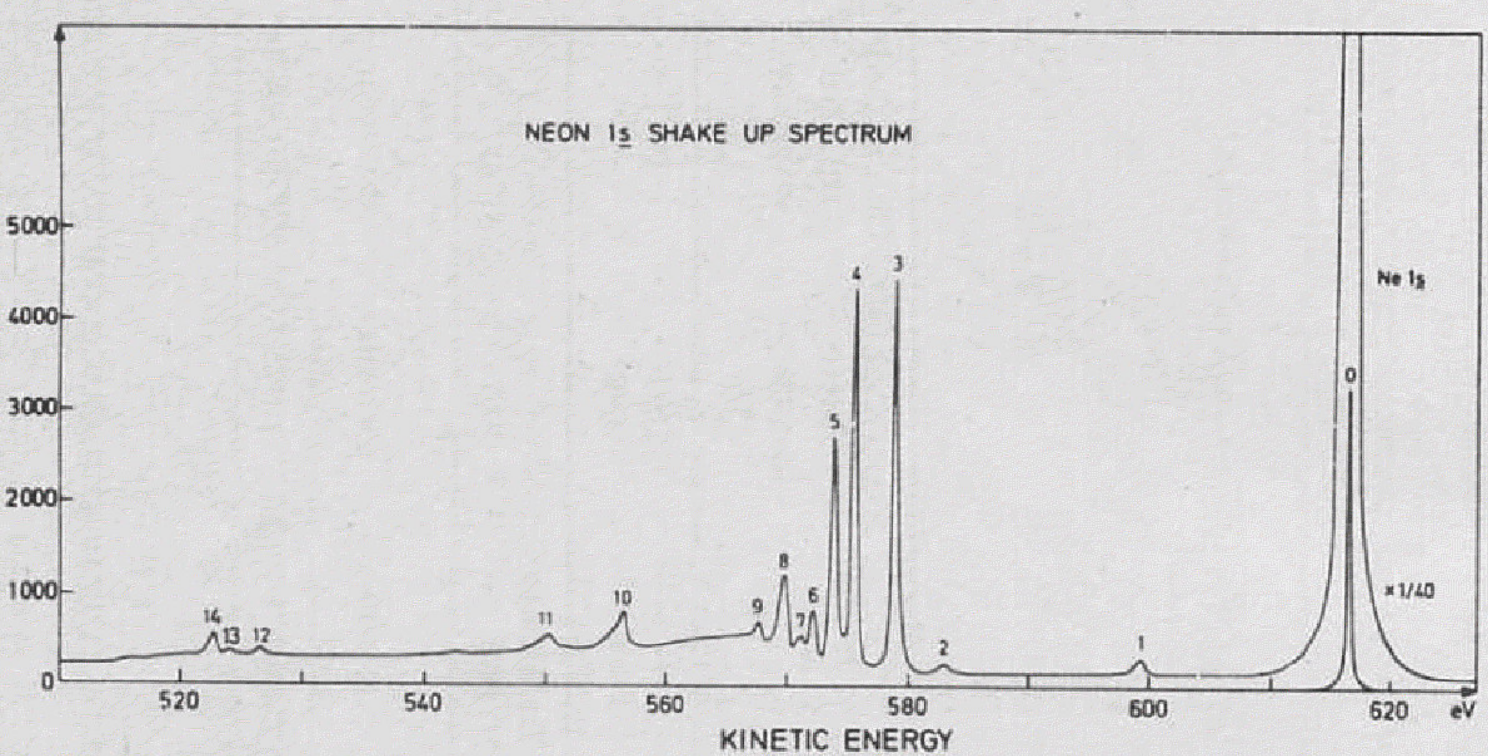
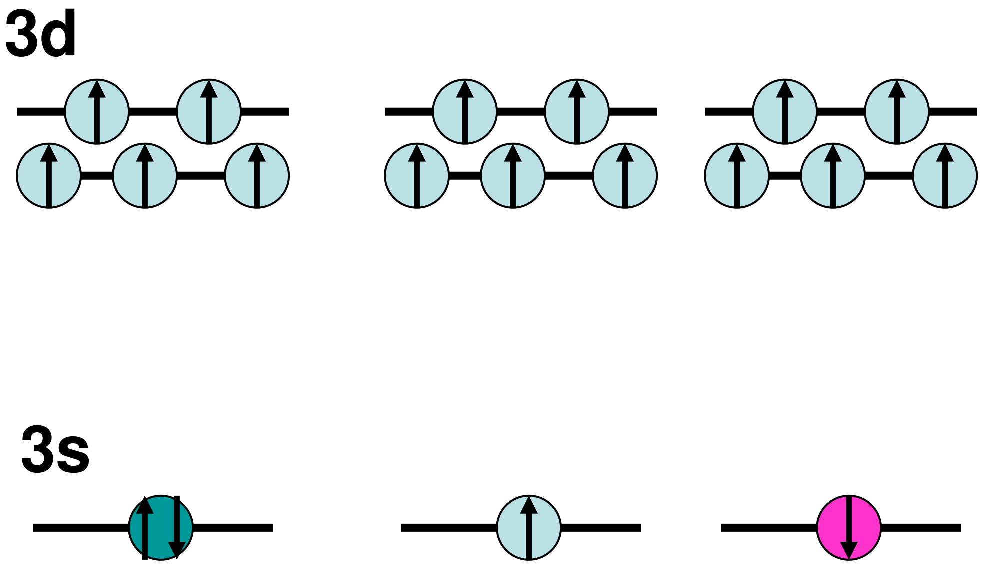


Fig. 36. High-resolution shake-up spectrum associated with excitation from Ne1s in gaseous neon. Table II lists the origins of the various satellite peaks labelled 1–14. The Ne1s FWHM was reduced to 0·4 eV in these measurements by using a monochromatized AlKα source. (From Gelius, ref. 270.)

- Multi-electronic transitions after creation of Ne 1s core hole
  - Excitation of electron to higher bound state: shake up
  - Excitation to continuum state: shake off

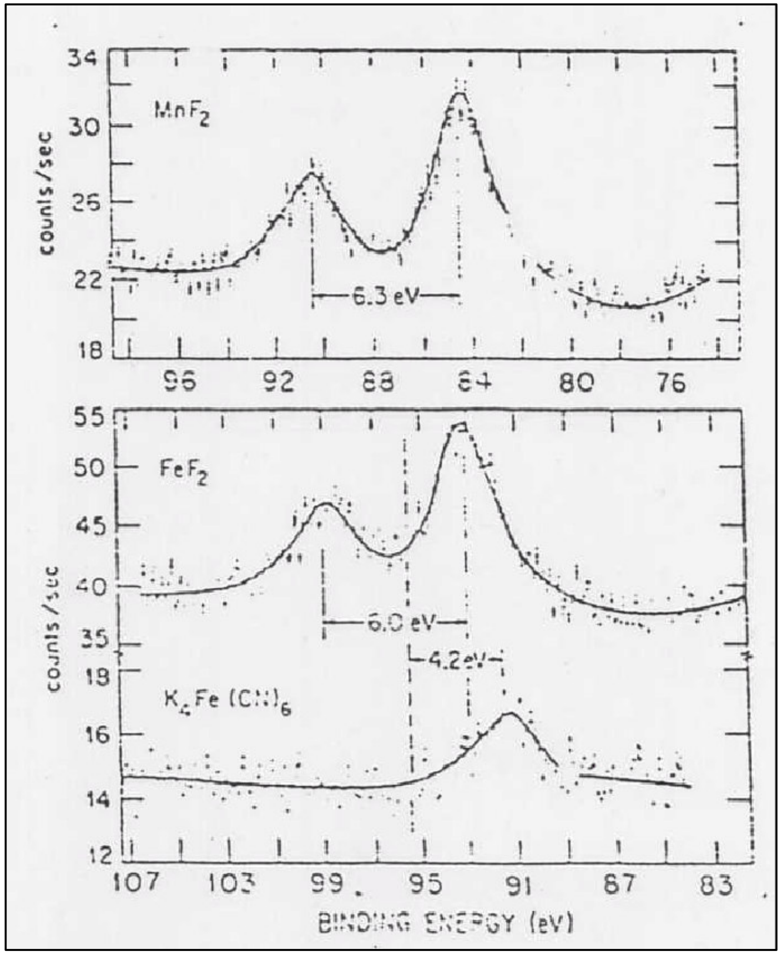
Multiplet Splitting

$Fe\ 3^{+}(3s^{2}3d^{5}) + h\nu \longrightarrow Fe\ 4^{+}(3s^{1}3d^{5}) + e$



Initial state **Final state**

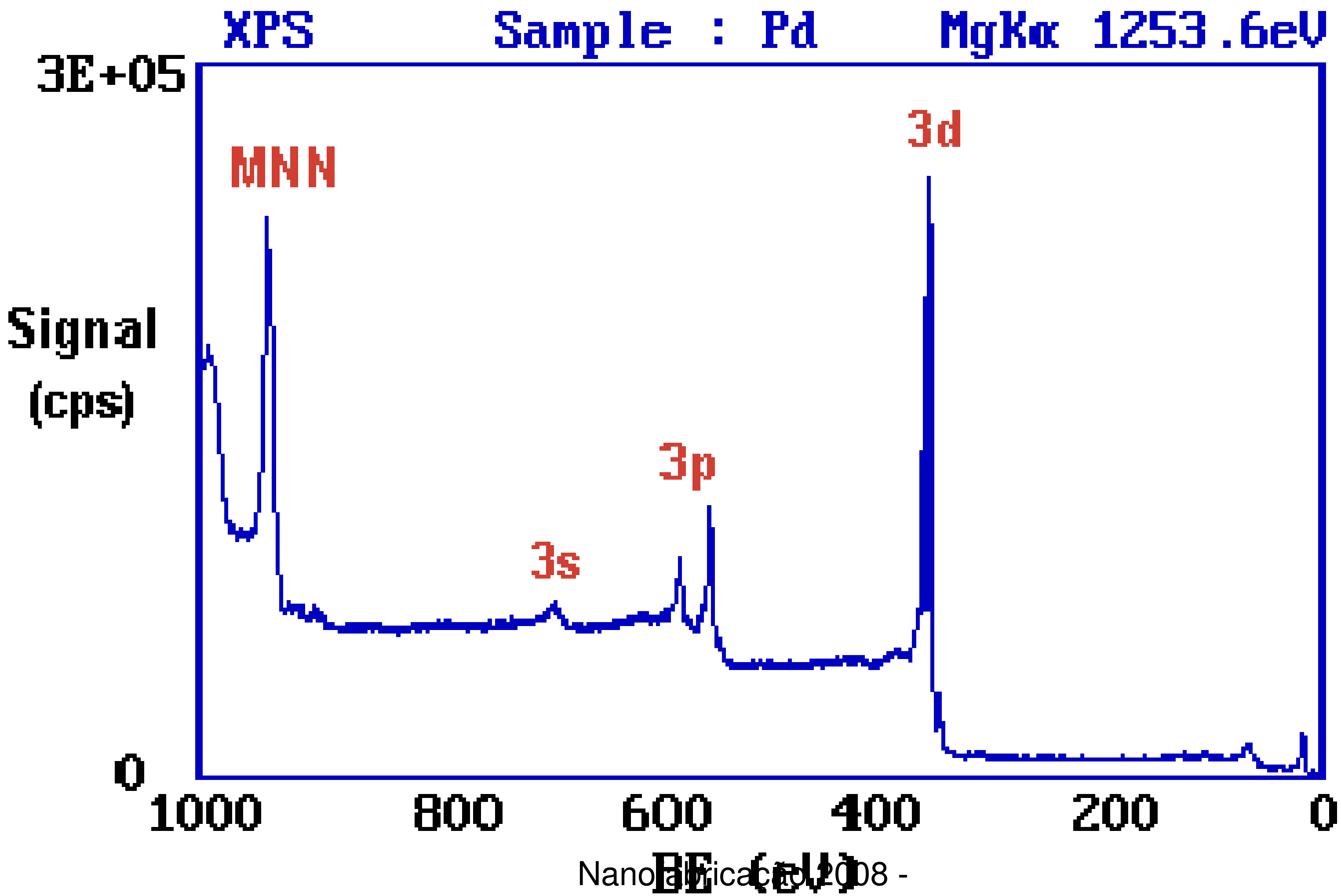
Terms: ^{6}S ^{7}S ^{5}S



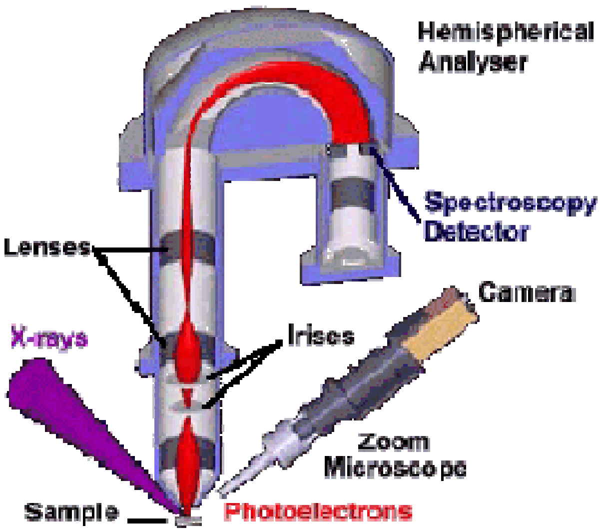
Applications

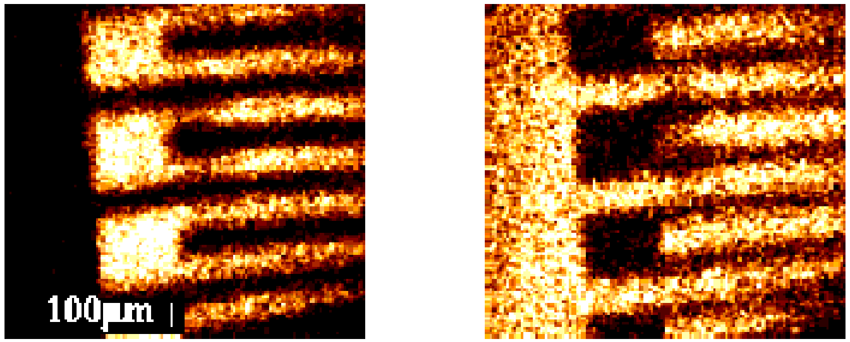
- Determination of energy levels
- Chemical bonding
- Oxidation states
- Density-of-states of valence bands
- Energy bands
- Quantum well states
- Quantitative analysis

XPS spectra


XPS
Sample : Pd
MgKα 1253.6eV
3E+05
Signal
(cps)
0
MNN
3d
3p
3s
1000
800
600
400
200
0
BE (eV)

Imaging XPS



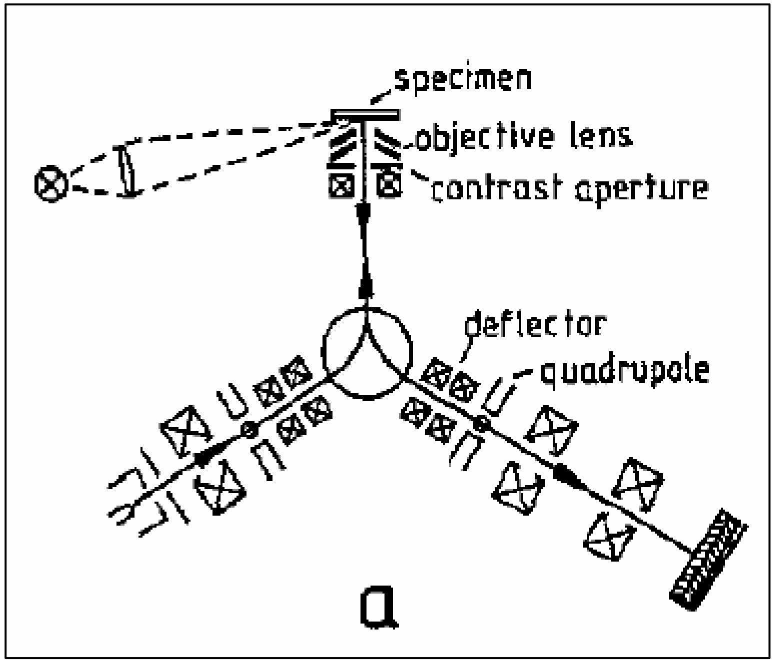


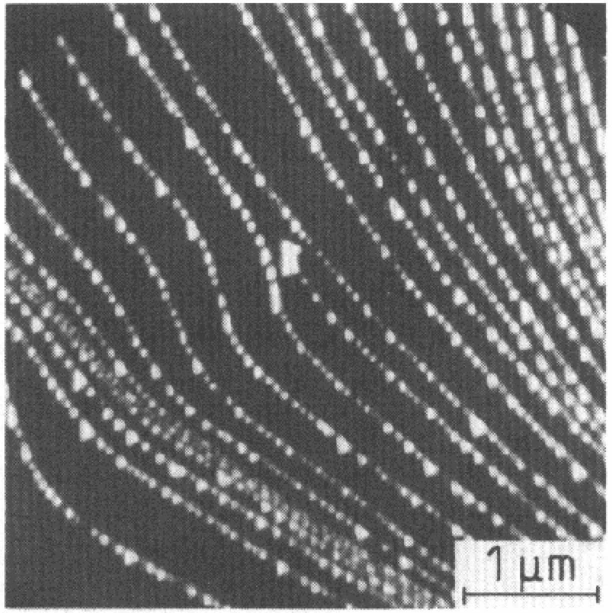
Si SiOx

- Scan Analyzer
- Parallel Direct Imaging
- X-ray microprobe/Zone plate

Present: Submicron resolution

Low Energy Electron Microscopies



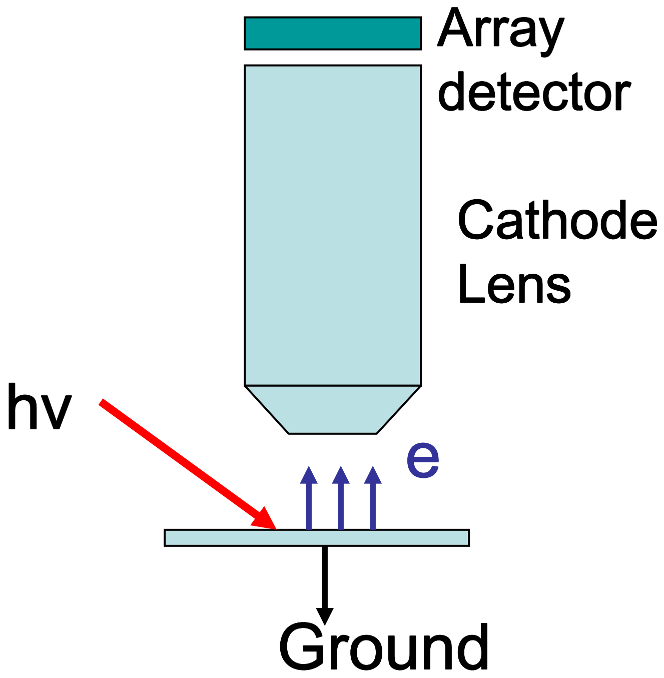


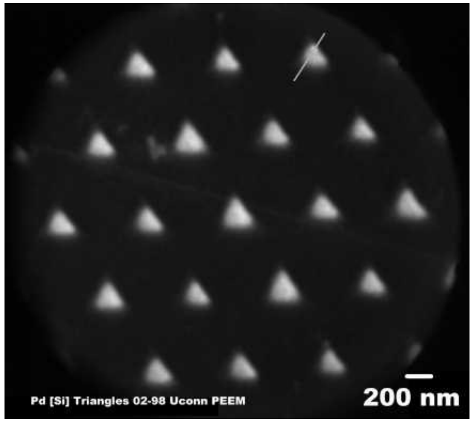
Step decoration of Si(111)

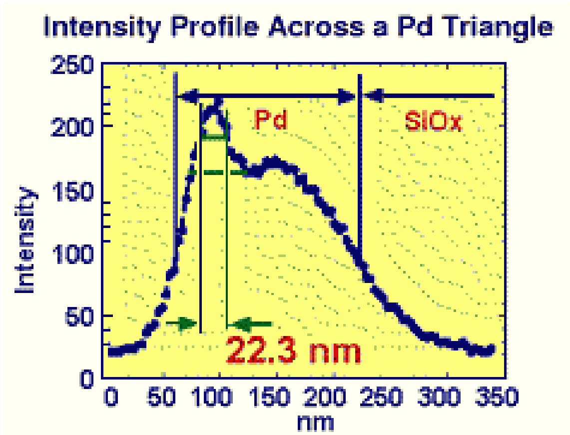
- **Strong elastic backward scattering of slow electrons (10~100eV)**
- **Several monolayer sensitivity**
- **Resolution: ~ 20 nm**

LEEM: E Bauer, Rep. Prog. Phys. 57, 895 (1994)

Photoelectron Emission Microscopy



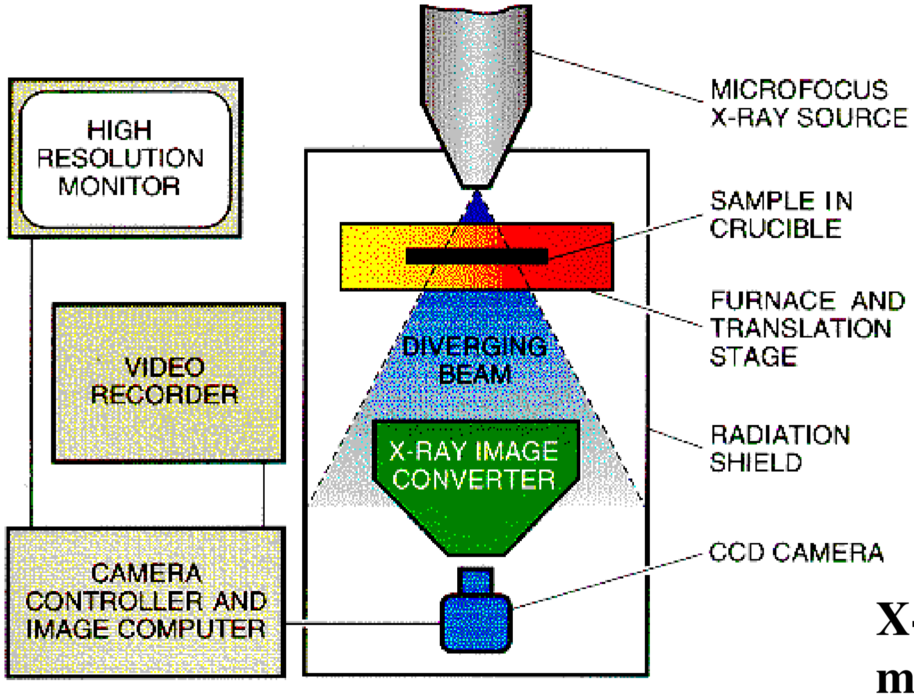


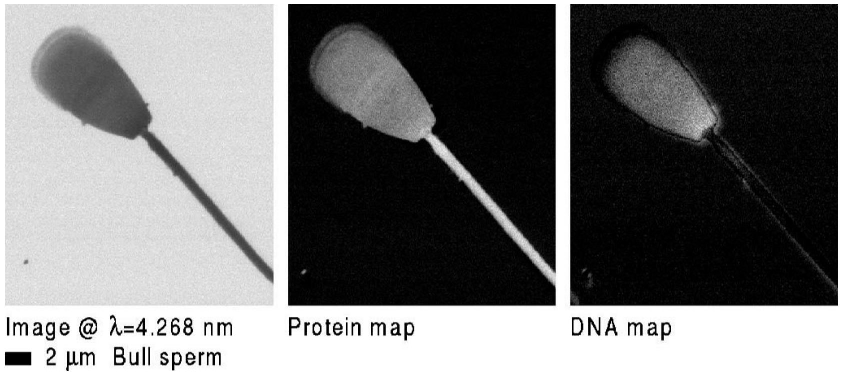


Resolution : 20~100nm

A threshold excitation lamp. g-Arc lamp, operating at 4.9 eV
Due to the presence of oxide at the silicon surface,
Si appears DARK (W >> 4.9 eV) and
Pd appears BRIGHT (W = 5.12 eV ~ 4.9 eV)

Scanning Transmission X-ray Microscopy





hν =10-1000 eV

λ = 0.1-10 nm

X-ray microscope image, and protein and DNA map, of air-dried bull sperm. Images were taken at six x-ray absorption resonance wavelengths, and were used to derive the quantitative maps.
Zhang *et al.*, *J. Struct. Biol.* 116, 335 (1996).

Future Directions for Characterization of Nanosystems

- **Instrument for analysis of biomolecules, and polymers**
- **3-D structure determination**
- **Nanostructure chemical determination**
- **Functional parallel probe arrays**
- **Standardization and metrology**
- **New nano-manipulator**
- **Non-SPM probes that use ions or electrons**
- ***In-situ* nondestructive monitoring techniques**