Surface Analysis

Surface: boundary layer between a solid and a vacuum, a gas, or a liquid.
(several or several tens of atomic layers deep)

Surface of a solid in contact with a liquid or gaseous phase:
differs substantially from the interior of the solid
both in chemical composition and physical properties

Characterization of surface properties is of vital importance in many fields.

- Heterogeneous catalysis
- Semiconductor thin-film technology
- Corrosion
- Adhesion mechanism…

Types of Surface Measurement

Physical information

- Optical and electron microscopic images
- Adsorption isotherm
- Surface areas
- Surface roughness
- Pore size

Chemical information

- Composition & quantity

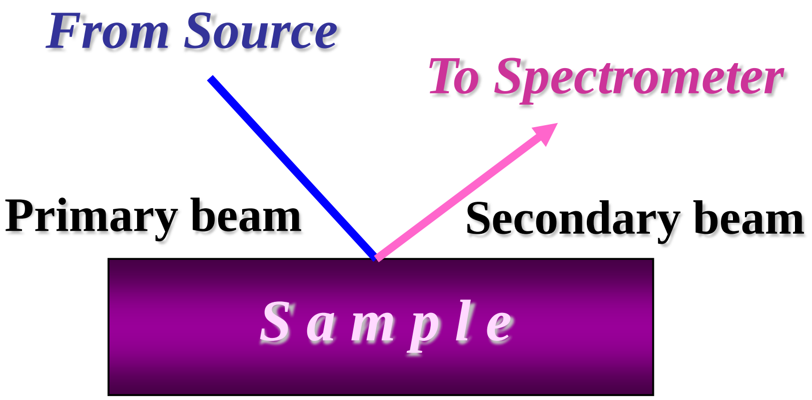
Spectroscopic surface methods

- Qualitative and quantitative chemical information about the composition of a surface layer of a solid
  : ~ Å ~ a few tens of Å in thickness

General Technique in Surface Spectroscopy

Primary beam

Photons, electrons, ions, or neutral molecules



- *Maximum penetration depth of a beam of 1 keV electrons or ions* **≈ 25 Å**
- *The penetration depth of a photon beam of the same energy* **≈ 10^4 Å**

Secondary beam

Photons, electrons, ions from the solid surface

Resulting from scattering, sputtering, or emission

Studied by a variety of spectroscopic methods

Surface Spectroscopic Methods

	Primary	Secondary
X-ray photoelectron spectroscopy (XPS) / ESCA	X-ray	e^-
Auger electron spectroscopy (AES)	e^- / X-ray	e^-
SIMS	ions	ions

Surface Spectroscopic Methods

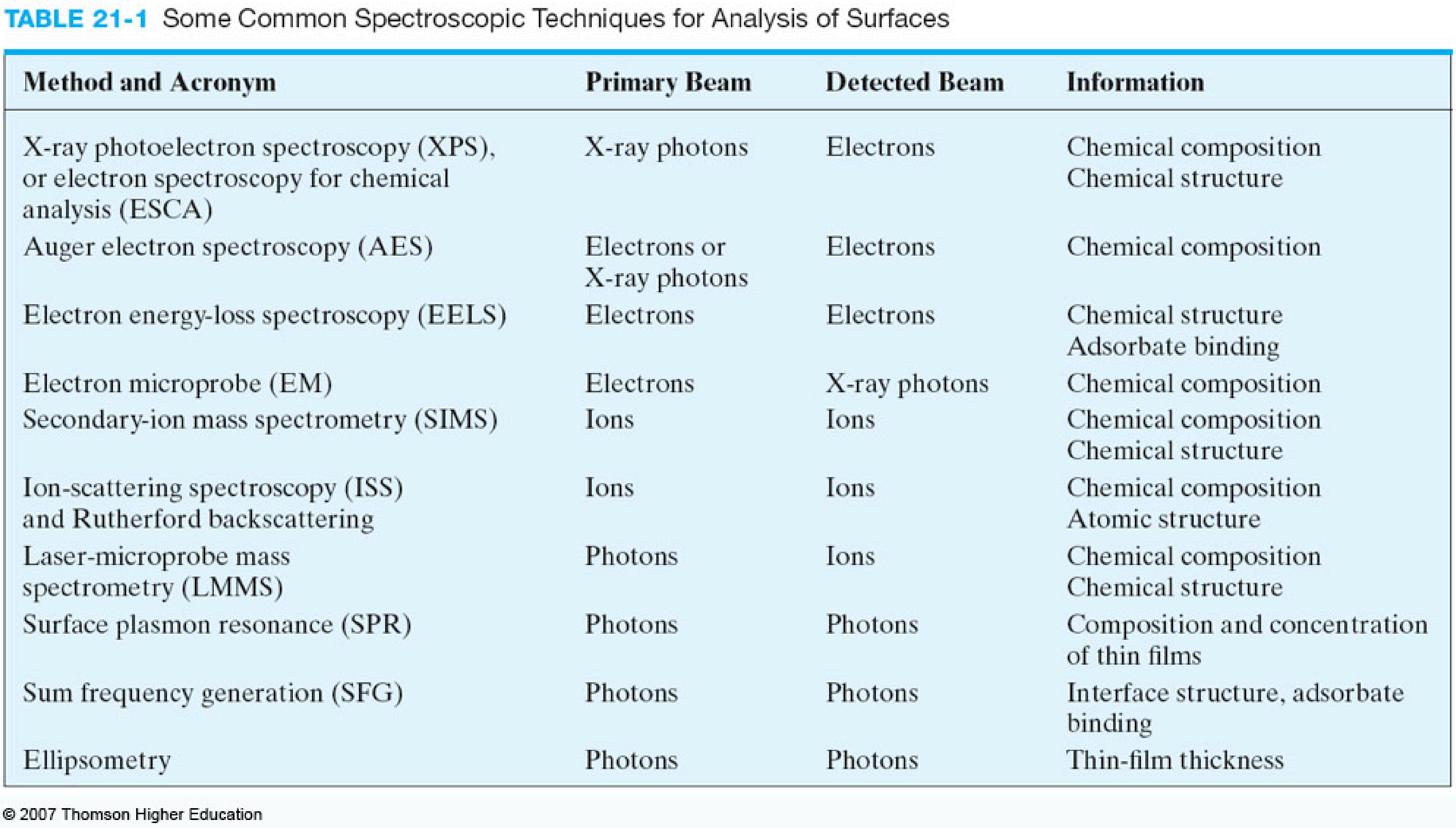


TABLE 21-1 Some Common Spectroscopic Techniques for Analysis of Surfaces

Method and Acronym	Primary Beam	Detected Beam	Information
X-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA)	X-ray photons	Electrons	Chemical composition Chemical structure
Auger electron spectroscopy (AES)	Electrons or X-ray photons	Electrons	Chemical composition
Electron energy-loss spectroscopy (EELS)	Electrons	Electrons	Chemical structure Adsorbate binding
Electron microprobe (EM)	Electrons	X-ray photons	Chemical composition
Secondary-ion mass spectrometry (SIMS)	Ions	Ions	Chemical composition Chemical structure
Ion-scattering spectroscopy (ISS) and Rutherford backscattering	Ions	Ions	Chemical composition Atomic structure
Laser-microprobe mass spectrometry (LMMS)	Photons	Ions	Chemical composition Chemical structure
Surface plasmon resonance (SPR)	Photons	Photons	Composition and concentration of thin films
Sum frequency generation (SFG)	Photons	Photons	Interface structure, adsorbate binding
Ellipsometry	Photons	Photons	Thin-film thickness

General Technique in Surface Spectroscopy

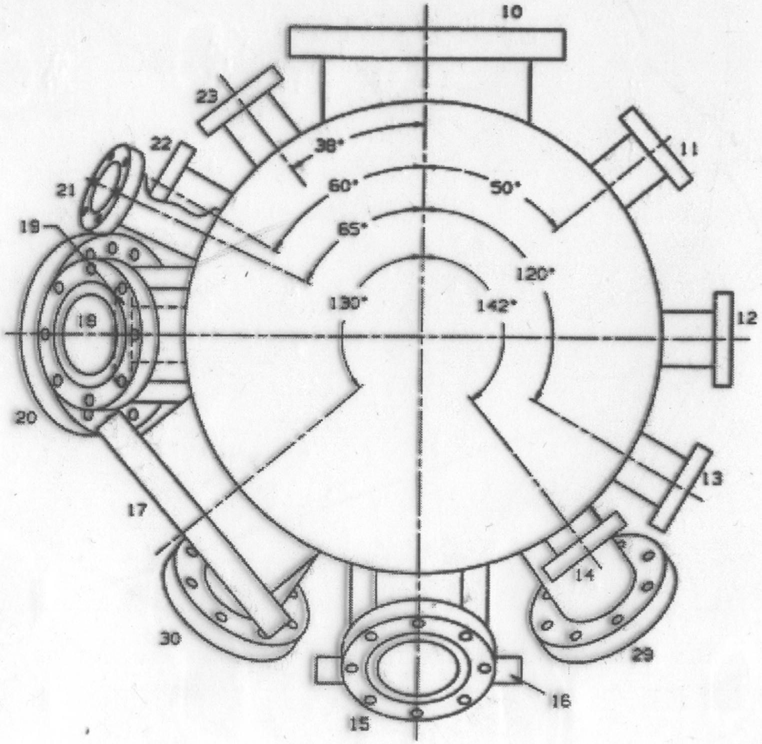
Sampling Surface

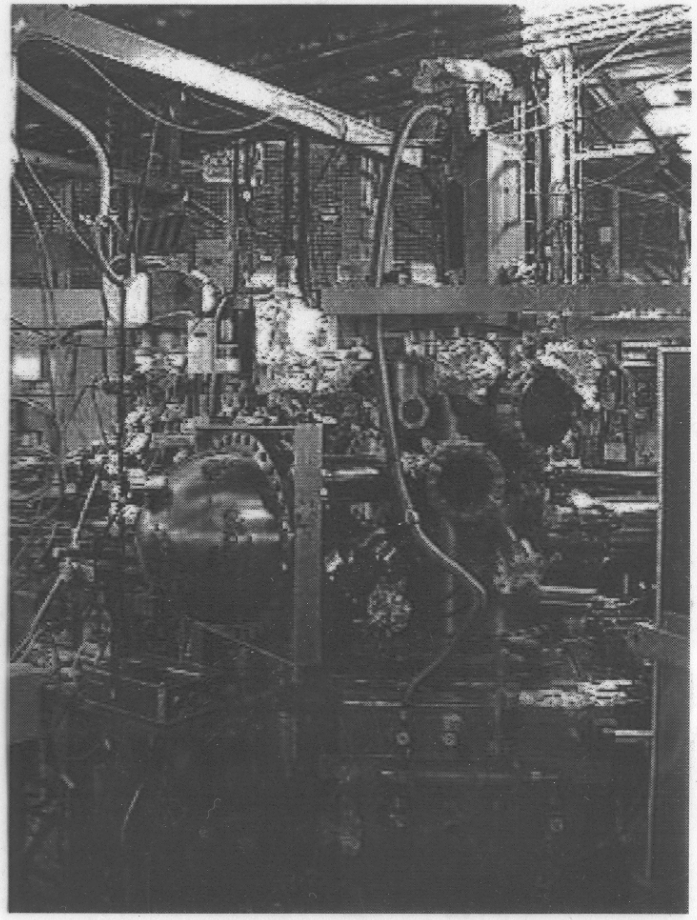
- Focusing the primary beam on a single small area of the sample and observing the secondary beam
- Raster pattern
- Depth profiling (Ar^+ sputtering)

Surface Contamination

- Adsorption of components of the atmosphere : O_2, H_2O, CO_2
- At a pressure of 10^{-6} torr, a clean surface is covered by a monolayer of gas molecules in 3 sec.
- At 10^{-8} torr, ~ 1 hr
  10^{-10} torr, ~ 10 hr
- Need ultra high vacuum chamber (UHV)

Ultra High Vacuum (UHV) Chamber





Electron Spectroscopy : XPS, AES, UPS

- **Based upon analysis of emitted electrons produced by various incident beams**
- **The determination of the power of this electron beam as a function of the <u>energy of the electron</u> (or frequency hν).**

Application

- **Identification of all of the elements in the periodic table except H, He**
- **Oxidation state, chemical structure**

Major Application

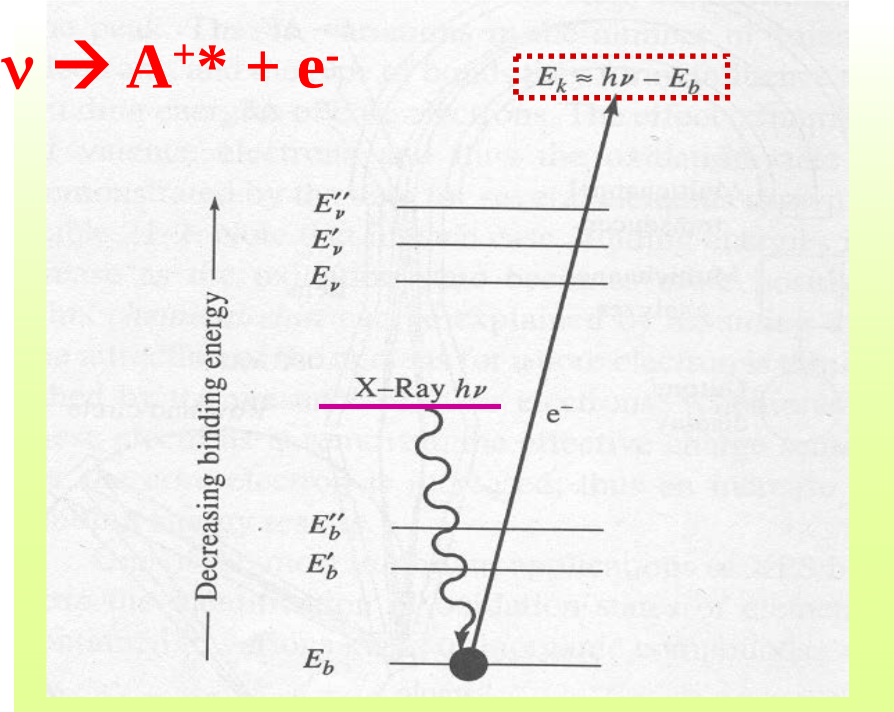
- **Qualitative analysis of the surfaces of solids, such as metals, alloys, semiconductors, and heterogeneous catalysts**
- **Quantitative analysis : limited application**
  RSD – 3~10 %

Electron Spectroscopy : XPS

ESCA (electron spectroscopy for chemical analysis)

K. Sigbahn invented XPS (1981 Nobel Prize Winner)

$A + h\nu \rightarrow A^{+*} + e^{-}$



$$E_k = h\nu - E_b - W$$
$$E_b = h\nu - E_k - W$$

E_b : characteristic of the atom and orbital from which the electron was emitted

***W* : Work function**

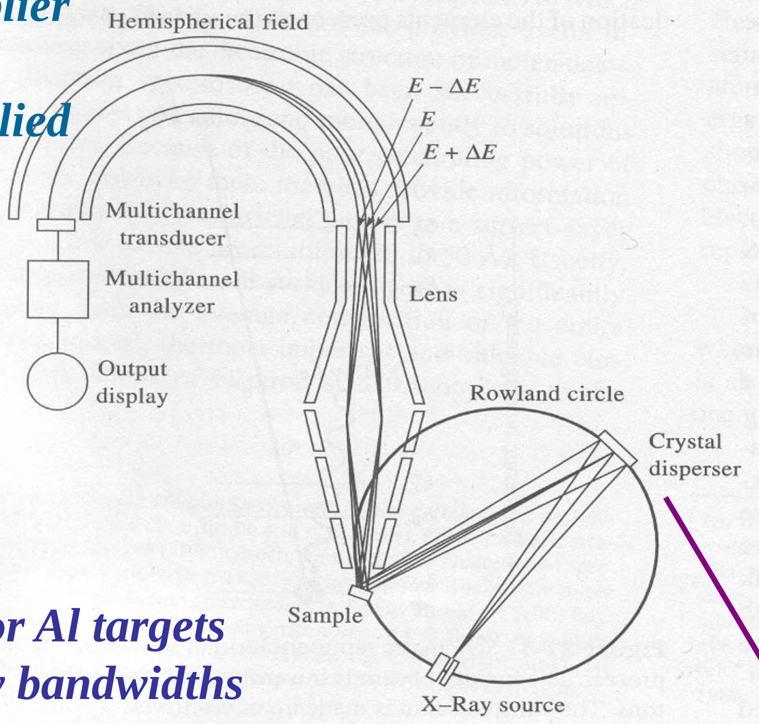
A factor that corrects for the electrostatic environment in which electron is formed and measured.

- **Figure 21.3 Schematic representation of the ESCA process. The incident beam is monoenergetic X-ray photons. The emitted beam is made up of electrons.**

Electron Spectroscopy : XPS

XPS needs UHV system
: 10^{-5}~10^{-10} torr

Detector:
solid-state electron multiplier
:glass doped with Pb or V
:a potential of ~KV is applied to get pulse of 10^{6}~10^{8} e- per one incident e-



Analyzer:
hemispherical field

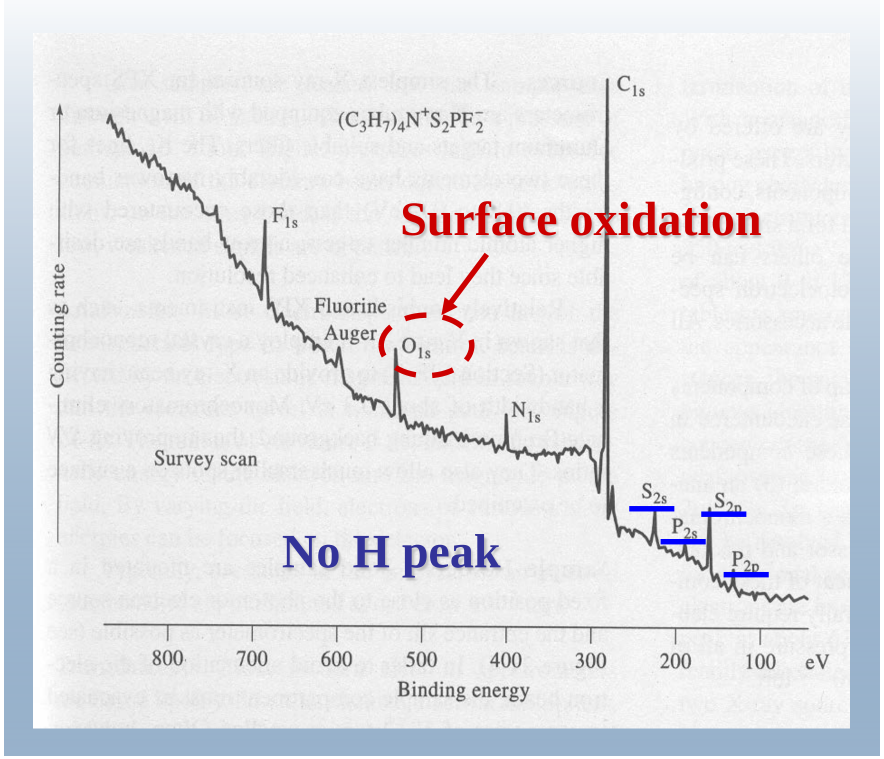
- *Electron beam is deflected by an electrostatic field in a curved path*
- *The radius of curvature is dependent on the kinetic energy of electron and the magnitude of the field*
- *By varing the field, electrons of varius kinetic energies can be focused on the detector*

Source:
X-ray tubes with Mg or Al targets
: K_{α} lines with narrow bandwidths
(0.8~0.9 eV)

- **Figure 21.4 Principle of a modern ESCA instrument (HP5950A) using an X-ray monochromatic source and a hemispherical field spectrometer.**

Monochromator:
Narrower band width
~0.3 eV

Electron Spectroscopy : XPS



- Figure 21.2 X-ray photoelectron spectrum of tetrapropylammonium-difluorodithiophosphate. The peaks are labeled according to the element and orbital from which the emitted electrons originate

Low-resolution or survey XPS

1. Binding energies for 1s electrons increase with atomic number because of the increased positive charge of nucleus

   Order of binding energy:
   $C_{1s} < N_{1s} < O_{1s} < F_{1s}$

2. More than one peak for a given element can be observed; peaks for 2s and 2p for S and P

Electron Spectroscopy : XPS

Application of XPS

- Qualitative analysis (elemental composition)
- Oxidation state

Binding energy increases as the oxidation state becomes more positive (Effective nuclear charge sensed by core electron is increased)

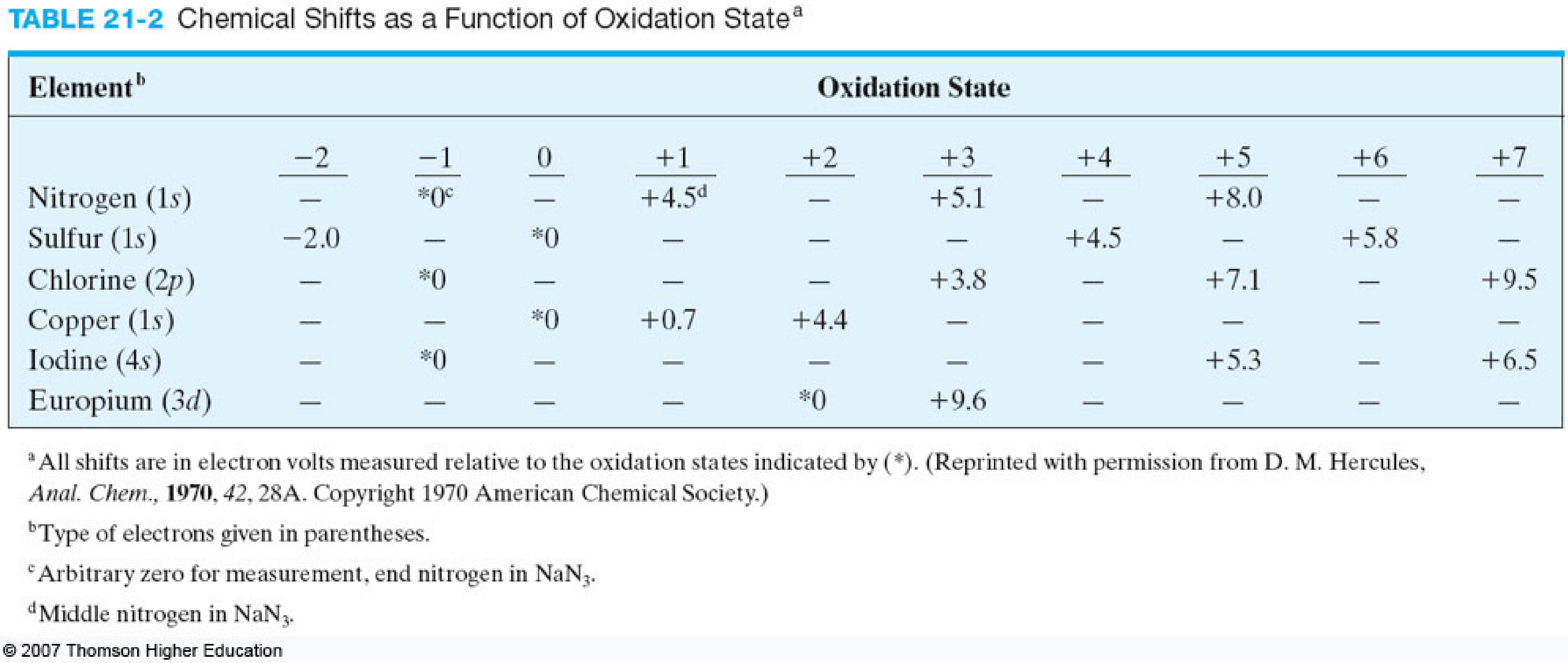


TABLE 21-2 Chemical Shifts as a Function of Oxidation State[a]

Element[b]	Oxidation State −2	−1	0	+1	+2	+3	+4	+5	+6	+7
Nitrogen (1*s*)	—	*0[c]	—	+4.5[d]	—	+5.1	—	+8.0	—	—
Sulfur (1*s*)	−2.0	—	*0	—	—	—	+4.5	—	+5.8	—
Chlorine (2*p*)	—	*0	—	—	—	+3.8	—	+7.1	—	+9.5
Copper (1*s*)	—	—	*0	+0.7	+4.4	—	—	—	—	—
Iodine (4*s*)	—	*0	—	—	—	—	—	+5.3	—	+6.5
Europium (3*d*)	—	—	—	—	*0	+9.6	—	—	—	—

[a] All shifts are in electron volts measured relative to the oxidation states indicated by (*). (Reprinted with permission from D. M. Hercules, *Anal. Chem.*, **1970**, *42*, 28A. Copyright 1970 American Chemical Society.)

[b] Type of electrons given in parentheses.

[c] Arbitrary zero for measurement, end nitrogen in NaN_3.

[d] Middle nitrogen in NaN_3.

Electron Spectroscopy : XPS

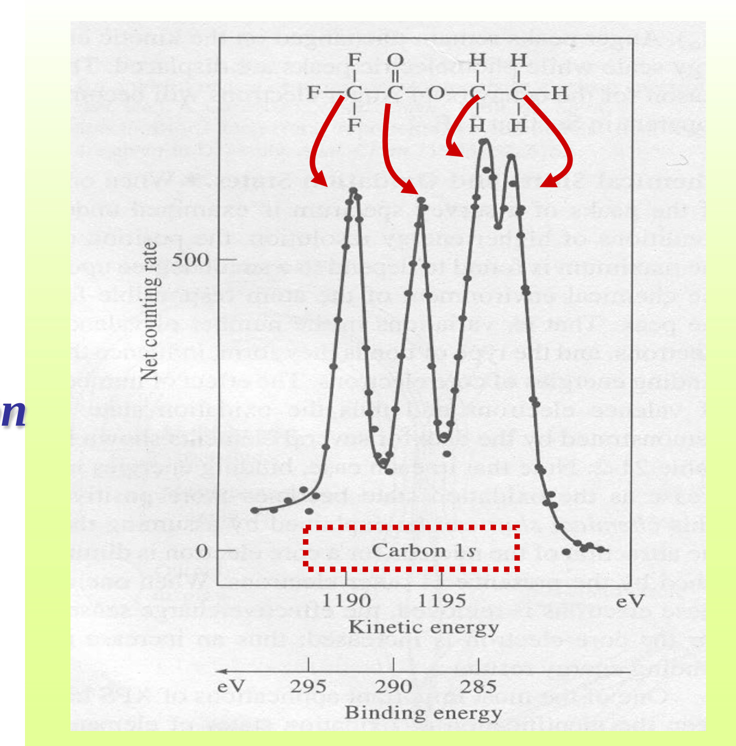
Application of XPS

- **Chemical structure**

C-F_3
F : the greatest ability to withdraw electron density from the carbon atom

Effective nuclear charge felt by the carbon 1s electron is therefore a maximum

Maximum binding energy



- Figure 21.5 Carbon 1s X-ray photoelectron spectrum for ethyl trifluoroacetate.

Binding energy increases as the oxidation state becomes more positive

(Effective nuclear charge sensed by core electron is increased)

Auger Electron Spectroscopy

- **Primary beam : electron or X-ray**

Excited ion

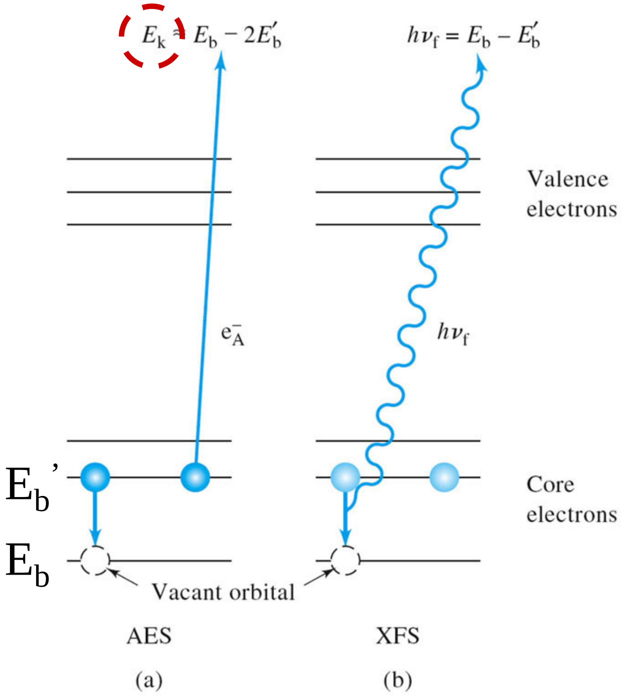
$$A + e_i^- \rightarrow A^{+*} + e_i'^- + e_A^-$$

Incident electron

Incident electron with energy loss

Ejected electron from one of inner orbitals of A

Kinetic energy of Auger electron



© 2007 Thomson Higher Education

$$E_k = (E_b - E_b') - E_b' = E_b - 2E_b'$$

$E_b - E_{b'}$: energy released in relaxation of the excited ions

$E_{b'}$: energy required to remove second electron from $E_{b'}$ orbital

Auger transitions: KLL, LMN, MNN

Auger Electron Spectroscopy

- **The relaxation of the excited ion, A^{+*}**

$$A^{+*} \rightarrow A^{++} + e_A^- \text{ (Auger electron)}$$

or

$$A^{+*} \rightarrow A^{+} + h\nu_f \text{ (x-ray fluorescence)}$$

- The energy of the Auger electron is independent of the energy of the photon or electron that created the vacancy in E_b.

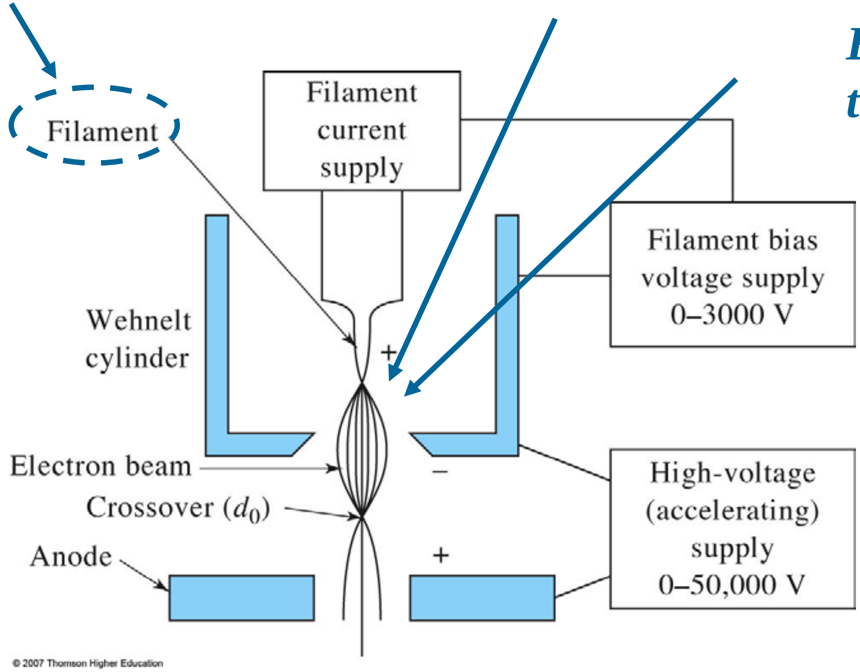
- Because the Auger lines are independent of the input energy, it is possible to differentiate between Auger lines in a spectrum and the XPS peaks.

Auger Electron Spectroscopy

Electron gun

: a beam of electrons with energies of 1~10 KeV

: 500~5 μm diameter of electron beam



Tungsten

0.1 mm in diameter

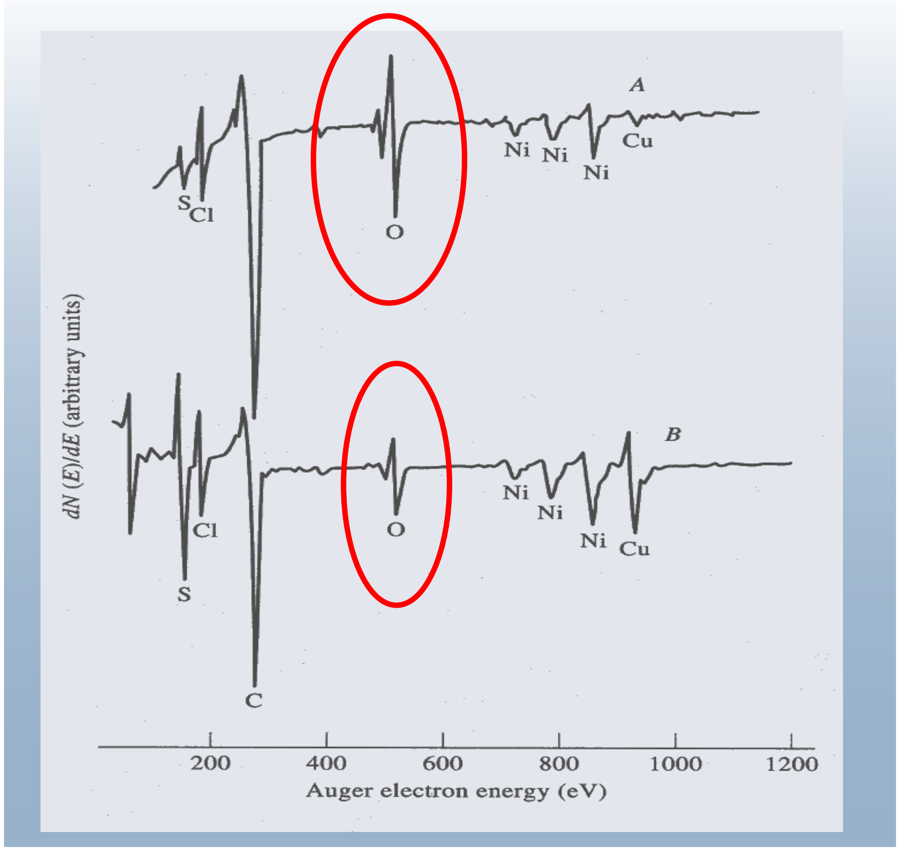
Electric field : cause the emitted electrons to converge on a tiny spot

- *Electron beam can be more tightly focused on a surface than can X-rays*
  ⇒ High spatial resolution

Field emission gun:
10 nm electron beam

- **Figure 21.9 Block diagram of a tungsten filament source.**

Auger Electron Spectroscopy



Passivated

Not passivated

Characteristic peaks in the region of 20 ~ 1000 eV

- Figure 21.8 Auger electron spectra for a 70% Cu/30% Ni alloy. A passivated by anodic oxidation; B, not passivated.

Auger Electron Spectroscopy

- *Derivative spectra are standard for Auger spectroscopy in order to enhance the small peaks and to repress the effect of the large, but slowly changing, scattered electron background radiation.*

- *An advantage of Auger spectroscopy for surface studies is that the low-energy Auger electrons (20 ~ 1000 eV) are able to penetrate only a few atomic layers (3 ~ 20 Å) of solids.*

- *An Auger spectrum is likely to reflect the true surface composition of solids*

  : low matrix effect
  : high spatial resolution

Some comparisons of XPS and AES

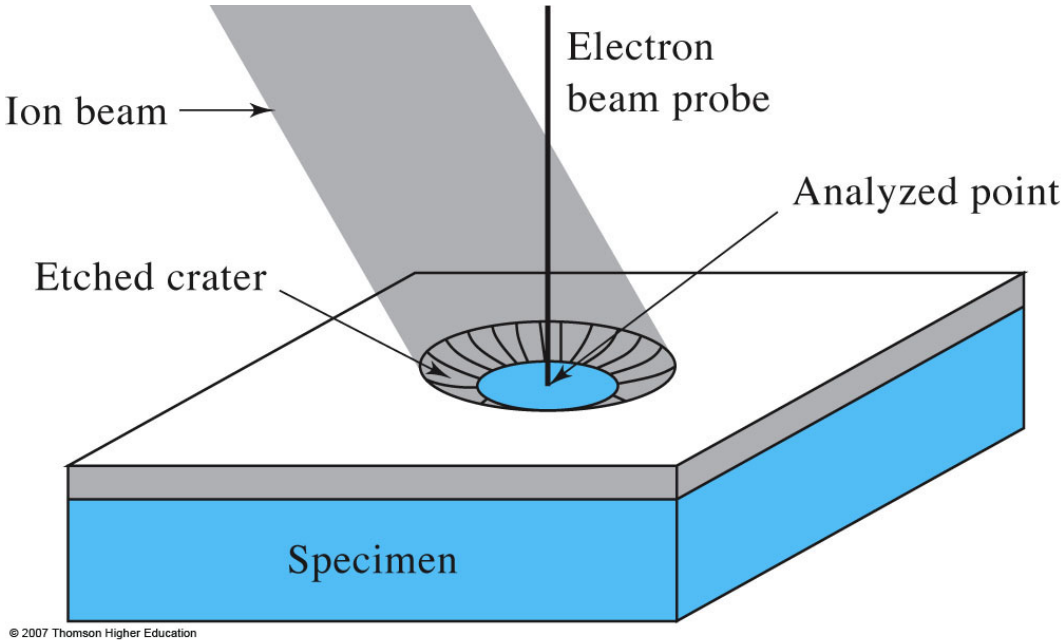
	XPS	AES
Species identification	√	√
Sensitivities	√	√
Speed of analysis	—	√
Spatial resolution-imaging	X	√
Low damage	√	—
Quantification	√	—
Chemical information	√	?

√ : strength, X : weakness, — : neutral

D.P. Woodruff & T.A. Delcher, "*Modern techniques of surface science*", Cambridge solid state science series

Auger Electron Spectroscopy

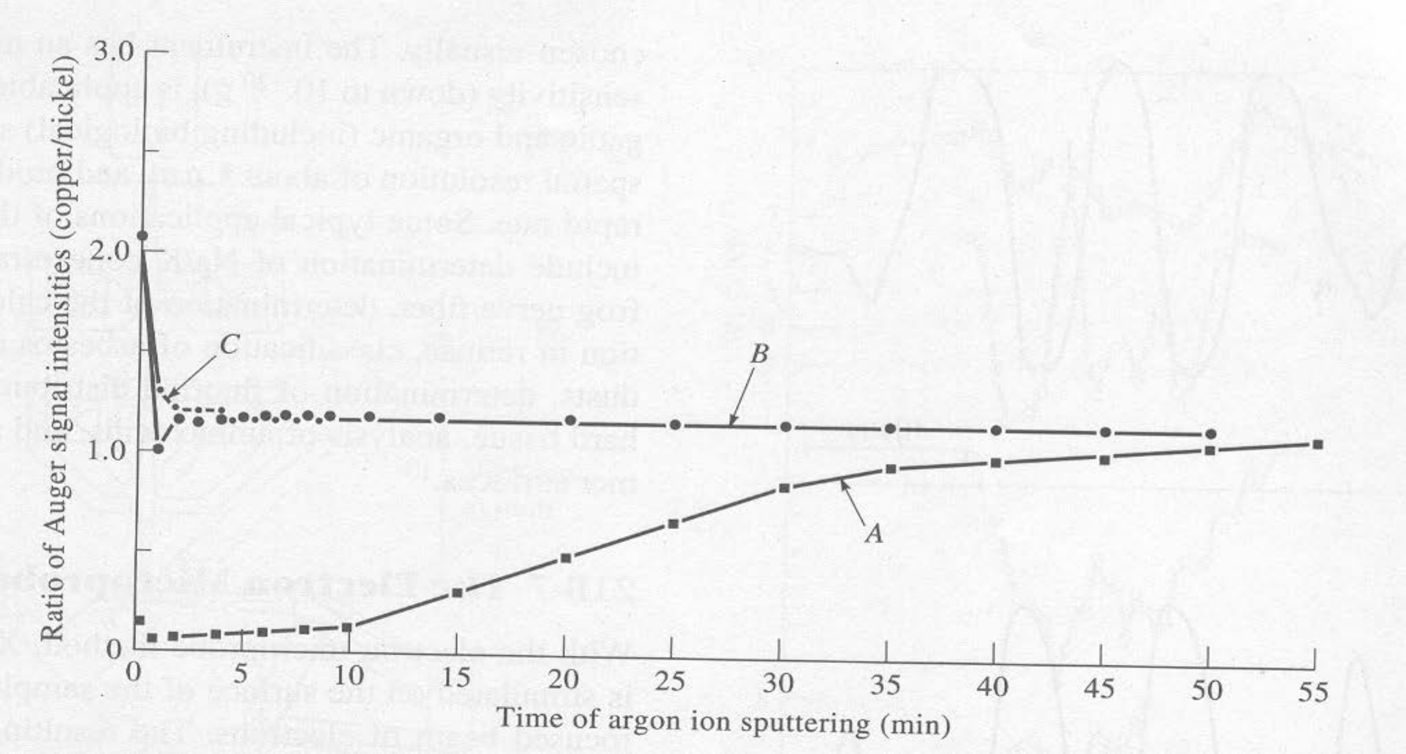
- *Depth profiling of surfaces*
  : Determination of elemental composition of a surface as it being sputtered by a beam of Ar$^+$.



© 2007 Thomson Higher Education

Figure 21.10 Schematic representation of the simultaneous use of ion sputter etching and Auger spectroscopy for determining depth profiles.

Auger Electron Spectroscopy



- Figure 21.11 Auger sputtering profiles for the copper/nickel alloys shown in Figure 21.8. A passivated sample; B, nonpassovated sample; C, chemically etched sample representing the bulk material.

Surface Analysis- Example

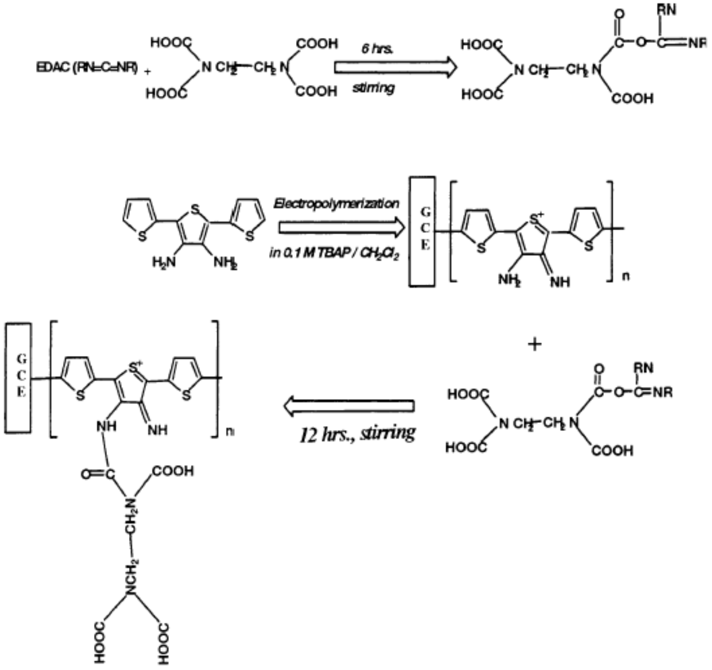
Anal. Chem. **2003,** *75,* 1123–1129

Characterization of an EDTA Bonded Conducting Polymer Modified Electrode: Its Application for the Simultaneous Determination of Heavy Metal Ions

Md. Aminur Rahman,[†] Mi-Sook Won,[‡] and Yoon-Bo Shim*[,†]

Department of Chemistry and Korea Basic Science Institute, Pusan National University, Pusan 609-735, South Korea

Scheme 1



Surface Analysis- Example

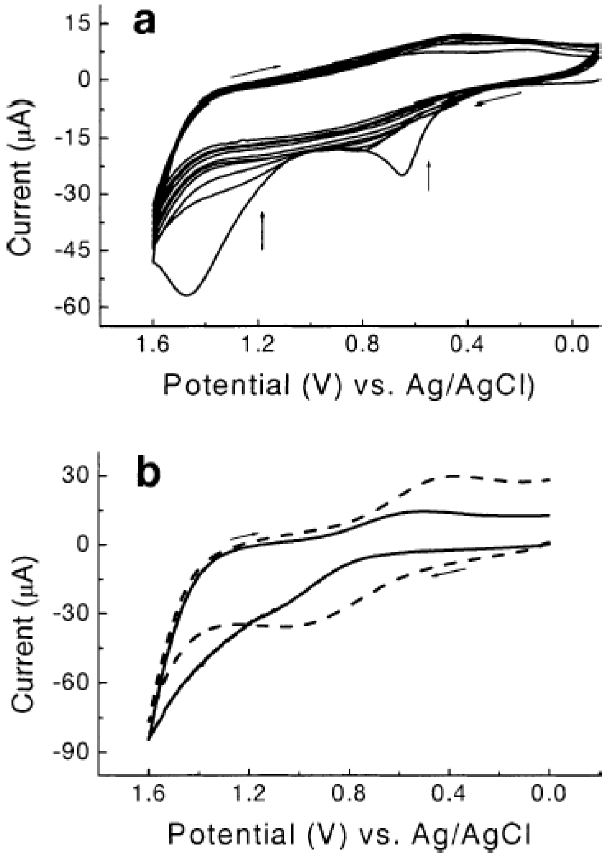


Figure 1. (a) Consecutive CVs (10 cycles) recorded for the oxidation of 1.0×10^{-3} M DATT monomer in 0.1 M TBAP/CH_2Cl_2. (b) CVs recorded for the oxidation of polymer film in pH 4.25 acetate buffer of (solid line) and in 0.1 M TBAP/ CH_2Cl_2. The scan rate was 100 mV/s.

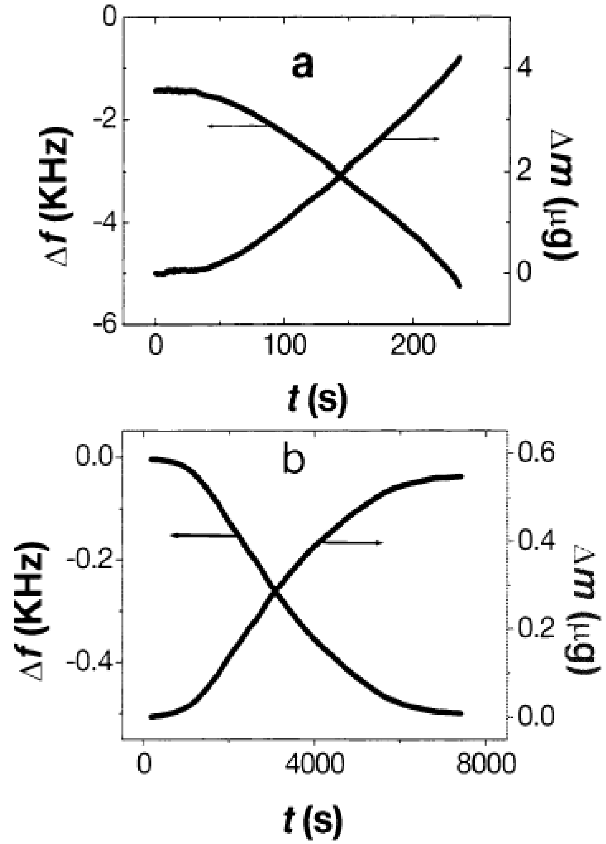


Figure 2. Frequencies and masses changed (a) during polymerization of a 1.0×10^{-3} M DATT monomer in a 0.1 M TBAP/CH_2Cl_2 solution and (b) during EDTA attachment with poly-DATT in CPME.

Surface Analysis- Example

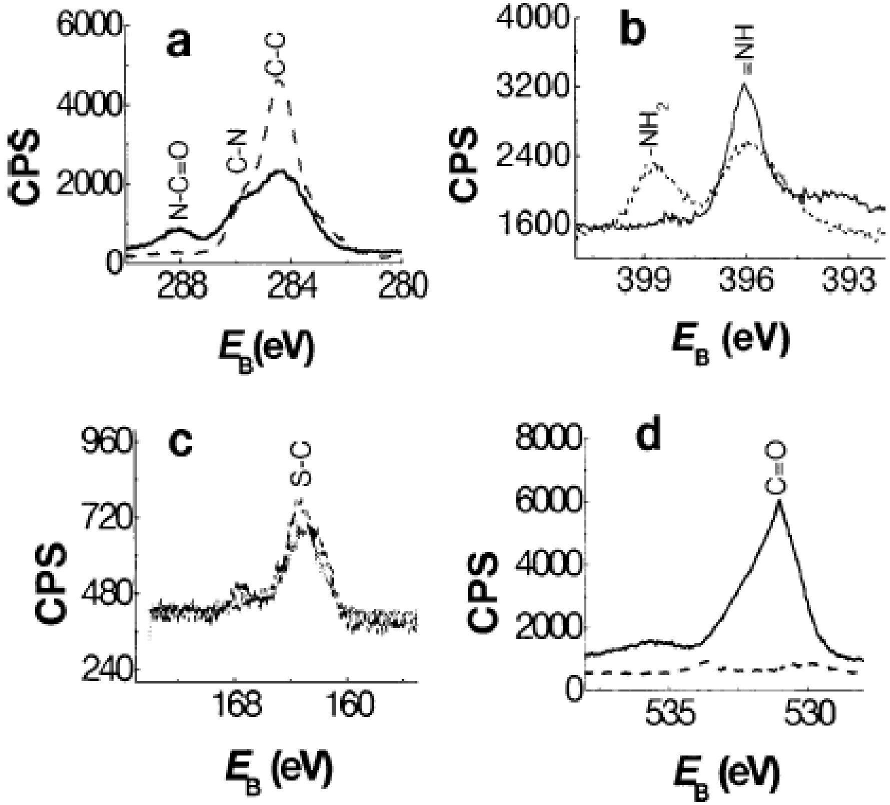


Figure 3. ESCA spectra of (a) C 1s, (b) N 1s, (c) S 2p, and (d) O 1s for (1) poly-DATT in CPME (dash line) and EDTA bonded poly-DATT in EDTA-CPME (solid line).

Surface Analysis- Example

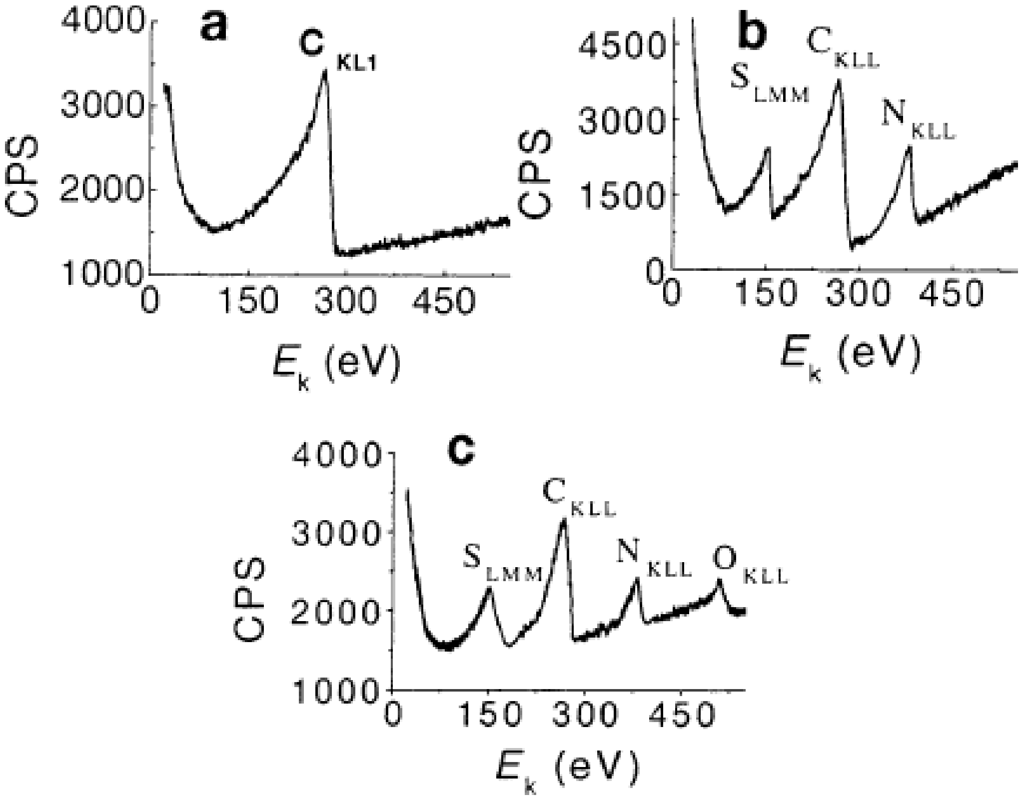
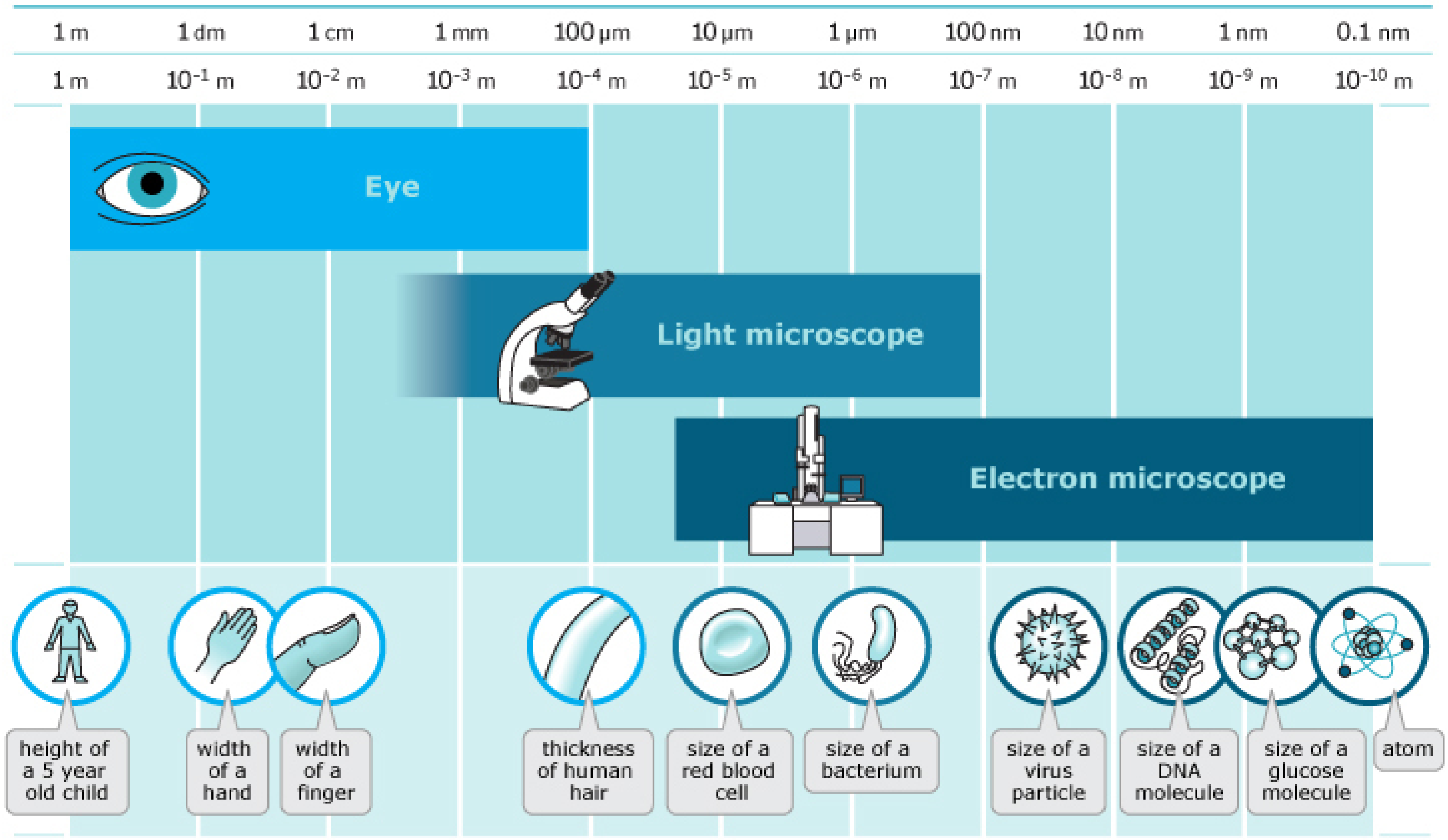


Figure 4. Auger electron spectra of (a) bare GCE, (b) poly-DATT in CPME, and (c) EDTA bonded poly-DATT in EDTA-CPME.

Resolution of Microscopes

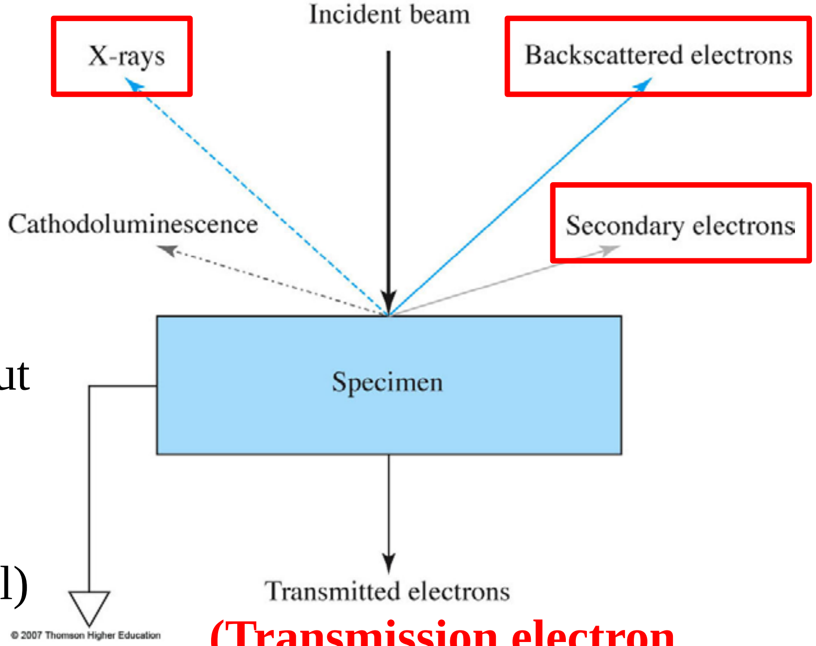


Resolving power of microscopes

Scanning Electron Microscope (SEM)

- **The surface of a solid sample is scanned in a raster pattern with a beam of energetic electrons: several types of signals are produced.**

  Backscattered
  Secondary
  Auger electrons
  X-ray fluorescence photons
  Other photons of various energies



(Transmission electron microscopy: TEM)

Application

Morphologic and topographic information about the surfaces of solid

- SEM: external morphology
- TEM: internal structure (microstructural detail)

Samples

- Conductor is easiest to study
- Non-conductor needs the coating of a thin-metallic film

(to minimize artifacts associated with the charge build-up & to minimize thermal degradation)

Scanning Electron Microscope (SEM)

SEM: Interaction of a solid with an electron beam

Electron beam: 20 keV (wavelength: 0.00859 nm)

Elastic interaction: no energy loss (backscattered electrons: 50 eV – 20 keV)

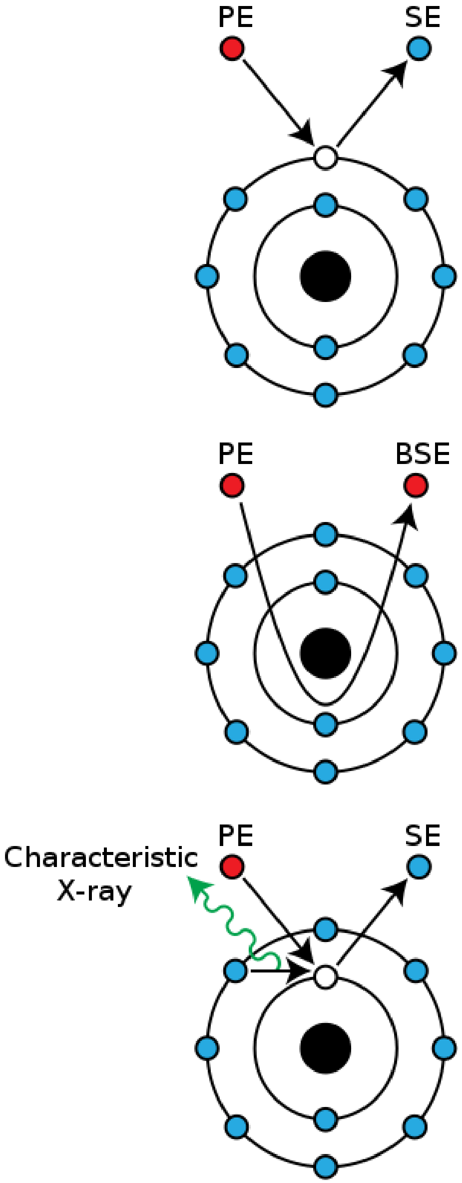
- penetration depth: 1.5 μm or more
- some electrons lose all energy by inelastic interaction and remain in solid,
- majority electrons exit from surface → backscattered electrons

Inelastic interaction: energy loss (secondary electrons: 50 eV or less)

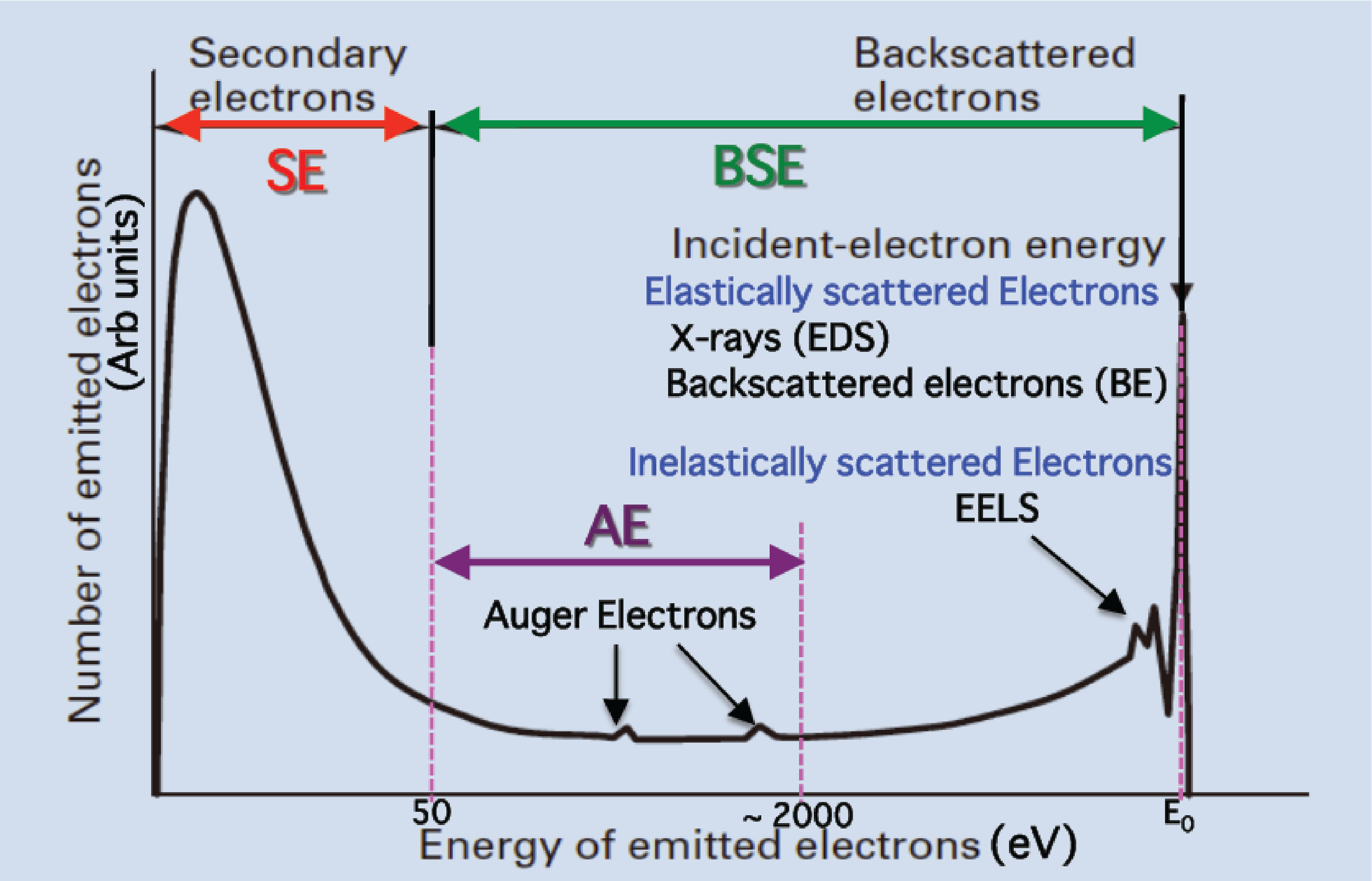
- secondary electrons are produced as a result of *interactions between the energetic electrons and weakly bound conduction electrons in solids*, which leads to ejection of the conduction band electrons with a few electron volts of energy
- The number of secondary electrons is generally one half to one fifth or less the number of the backscattered electrons
- Secondary electrons are produced from a depth of only 5-50 nm and exit in a beam that is slightly larger in diameter than the incident beam

X-ray photons: basis for the electron microprobe for X-ray fluorescence analysis

SEM: Interaction of a solid with an electron beam



SEM: Interaction of a solid with an electron beam

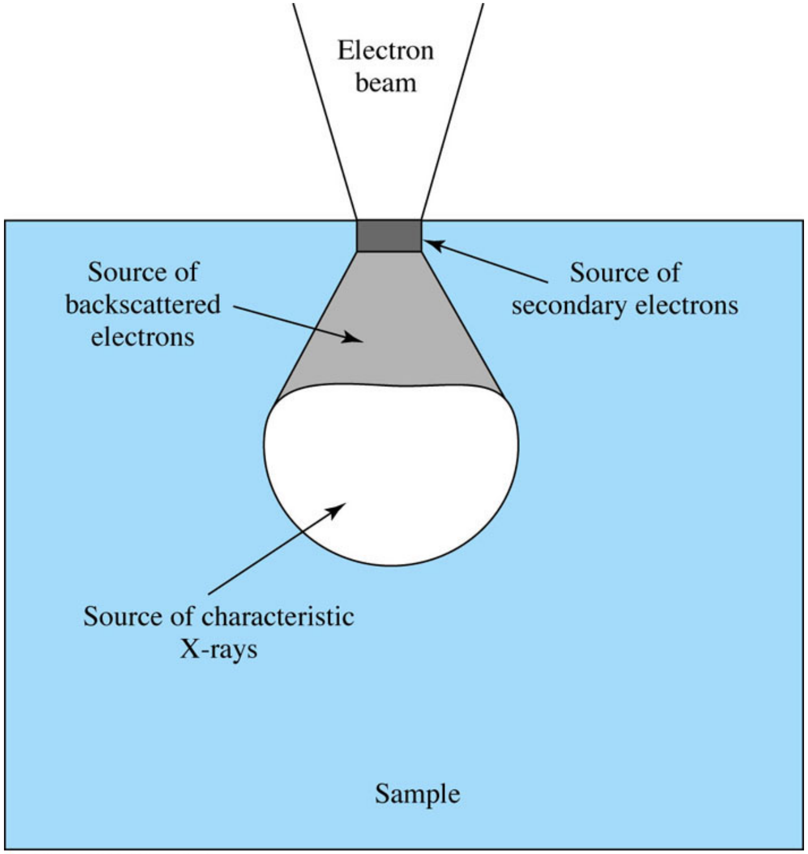


Electron energy spectrum of electrons leaving the sample

Goldstein et al. 1981

Scanning Electron Microscope (SEM)

- X-rays are not easily absorbed so must escape.



Interaction volume:
“the region electrons penetrate”

Scanning Electron Microscope (SEM)

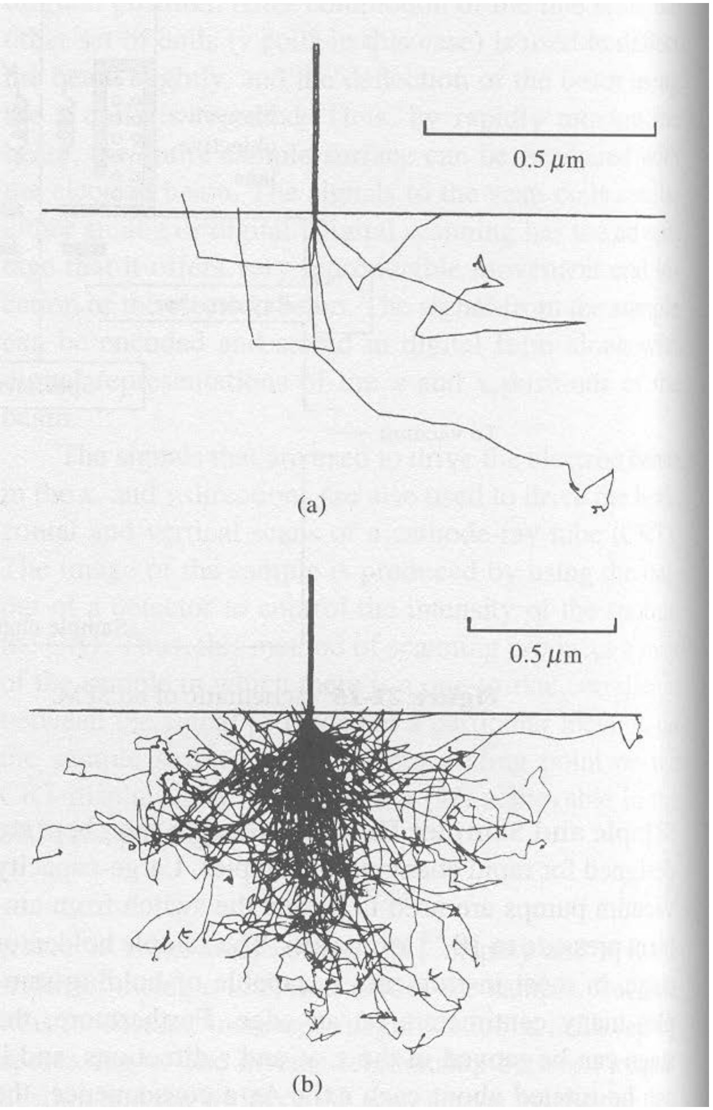
Backscattered electrons:

- The beam of backscattered electrons has a much larger diameter than the incident beam→ limits the resolution of SEM
- The spatial resolution of BSE images is poor (usually ~1 µm; at best ~0.1 µm) however, BSE provide valuable information because of their sensitivity to atomic number variations (atomic contrast).

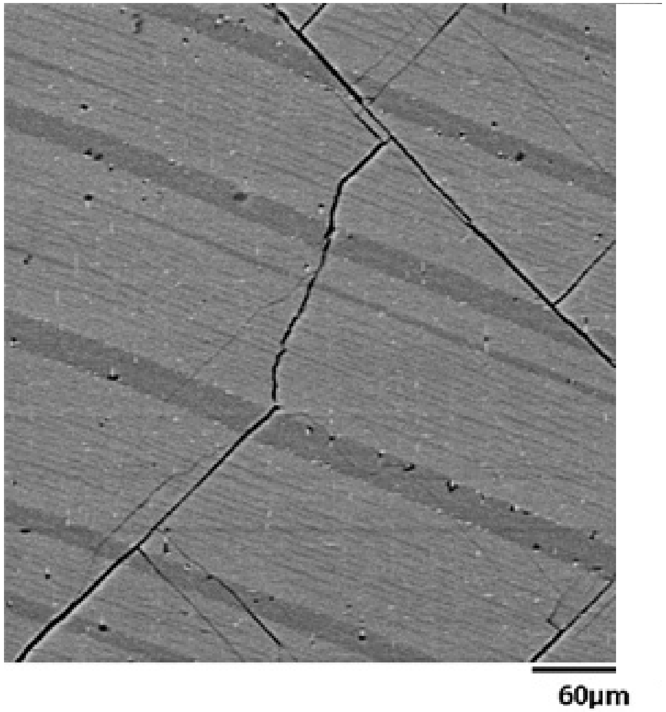
Secondary electrons:

- The secondary electron signal arises from a region that is on the order of diameter of the incident electron beam

→ Thus, secondary electron signals are capable of giving much higher spatial resolution than the other signals, and they are most widely used signals in the SEM system.



Scanning Electron Microscope (SEM): Backscattered electrons



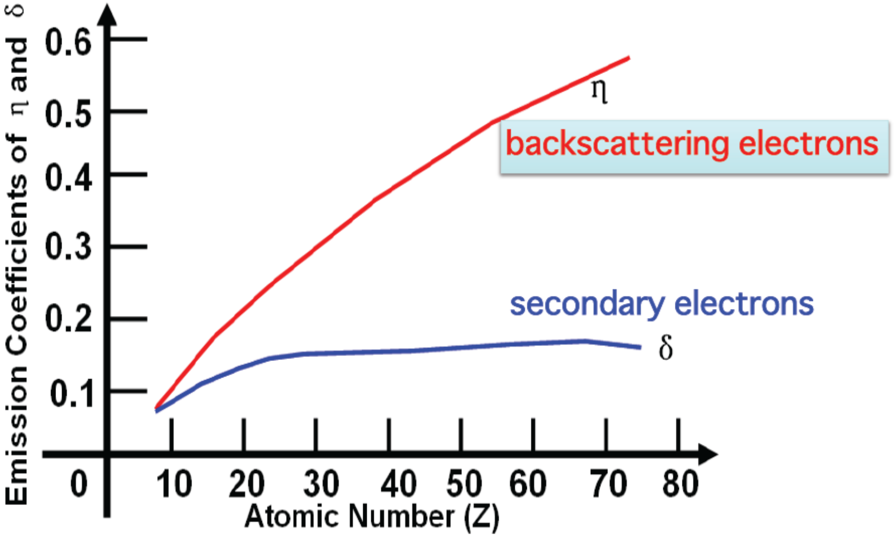


Figure 4801. Schematic shows emission coefficients of backscattering electrons (η) and secondary electrons (δ), depending on atomic number (Z).

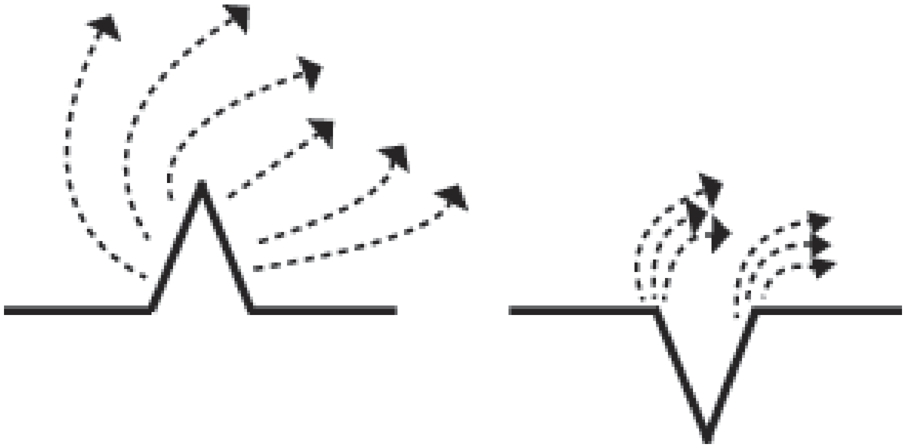
Backscattered electron image of exsolution of orthopyroxene lamellae in large iron-rich meteoritic pigeonitic pyroxene.

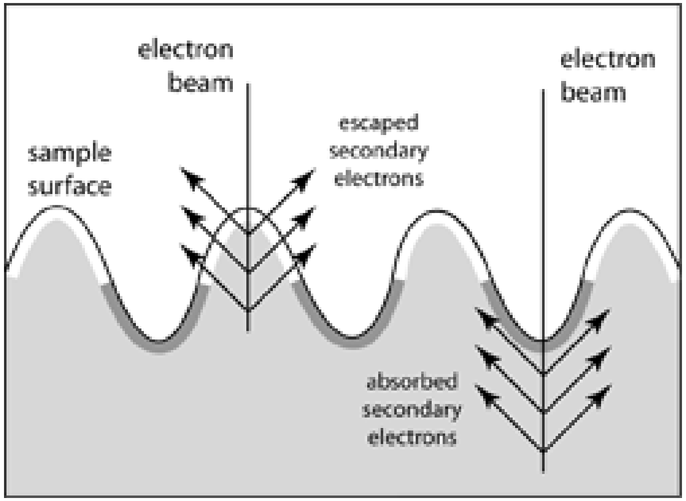
Scanning Electron Microscope (SEM)

- The number of secondary electrons that can be detected depends, among other things, on specimen topography

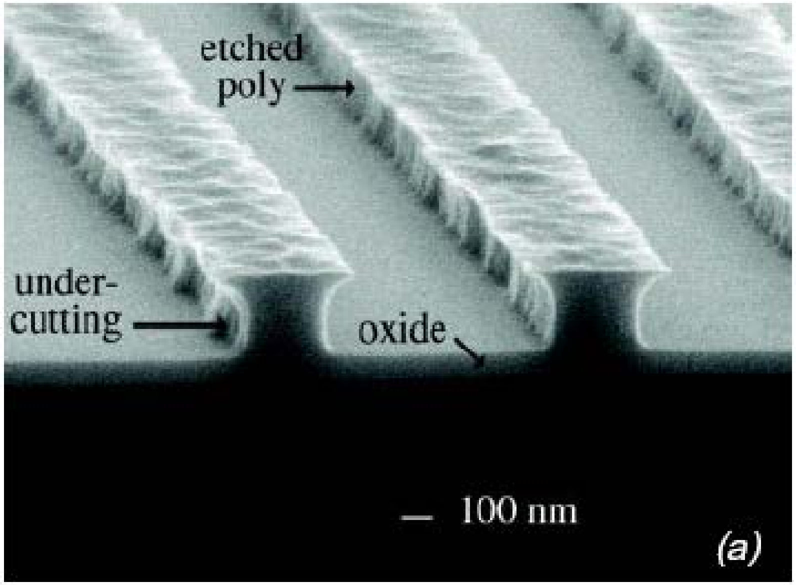
- Edge effect:

- Edges of the specimen provide greater amounts of surface area from which the weak secondary electrons can escape.
- Thus, at the edges of features on the specimen, more secondary electrons are emitted. These areas appear brighter in the image.





Scanning Electron Microscope (SEM)



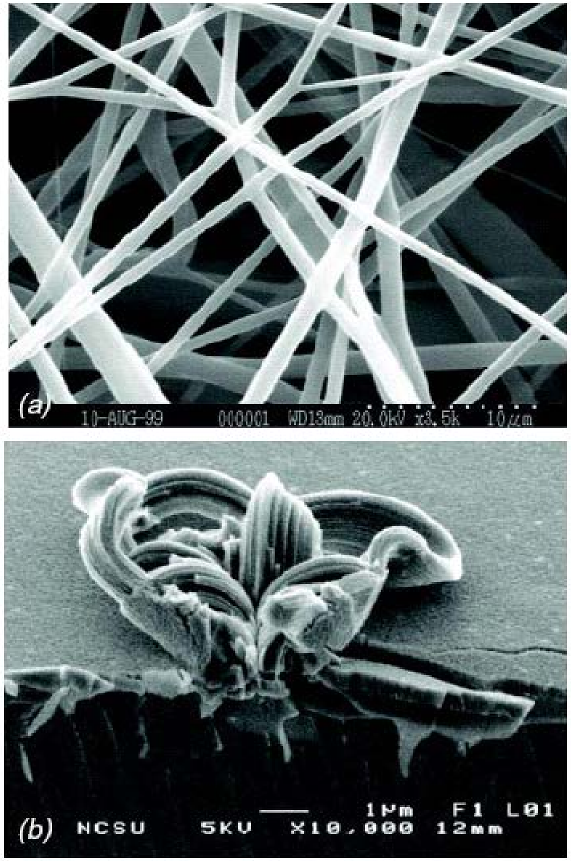
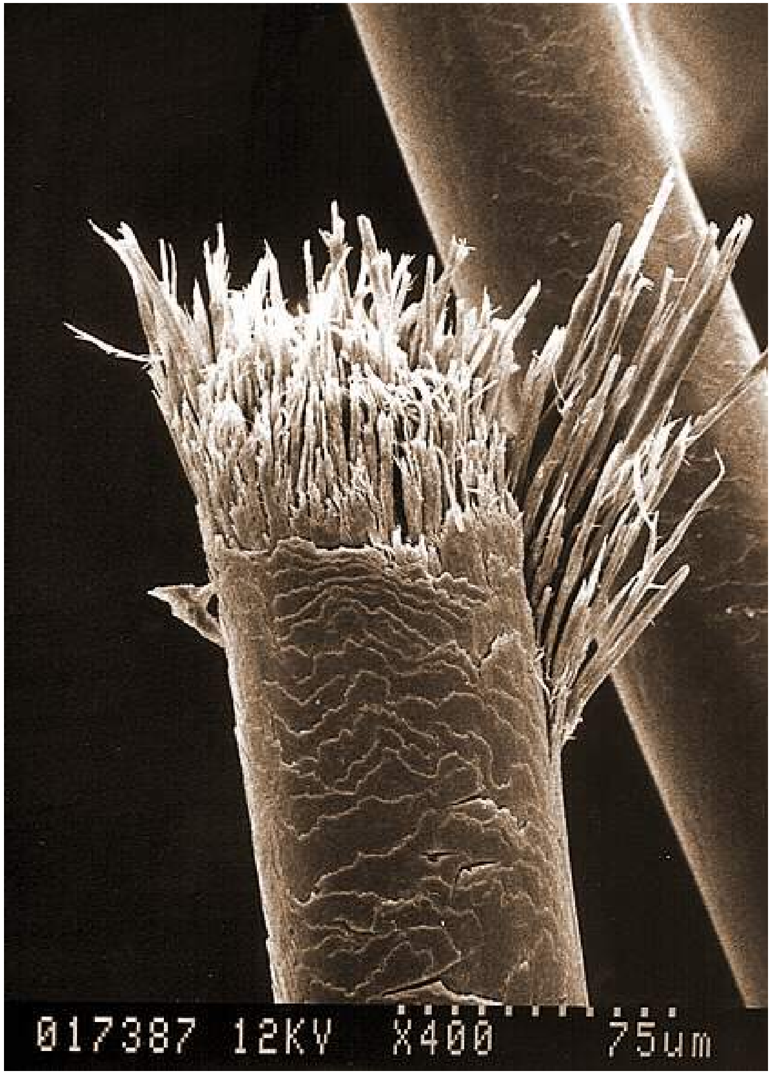
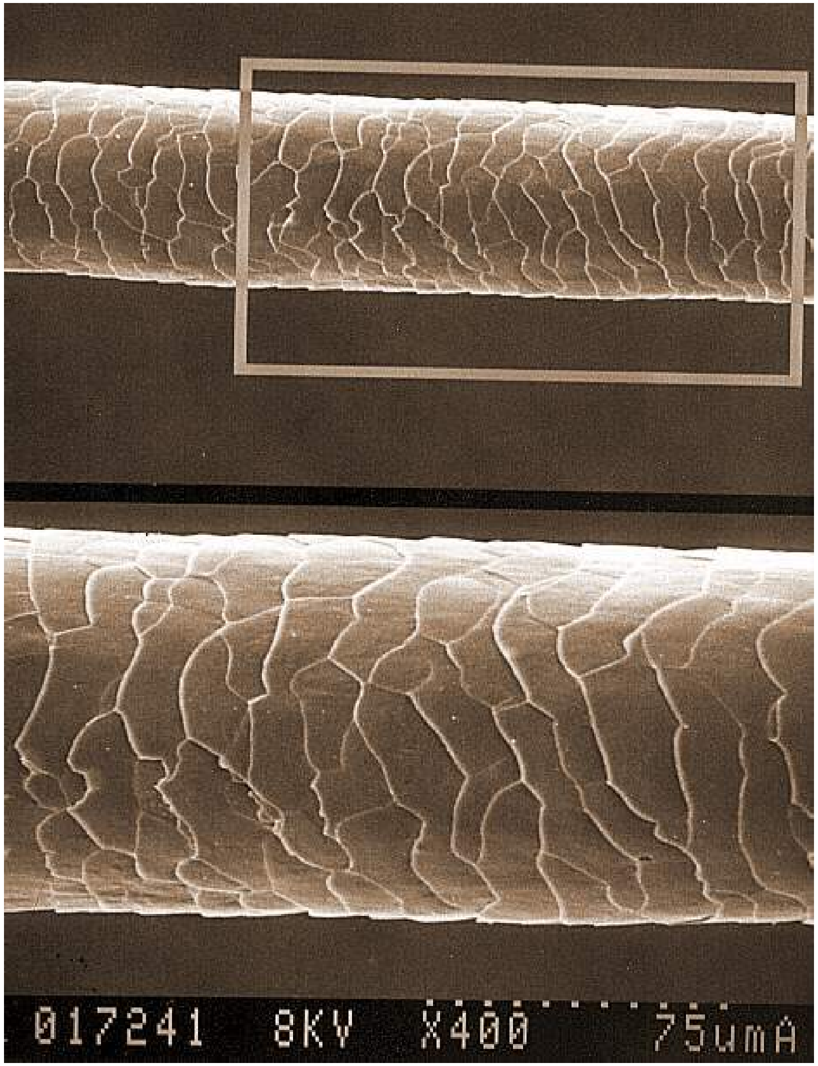


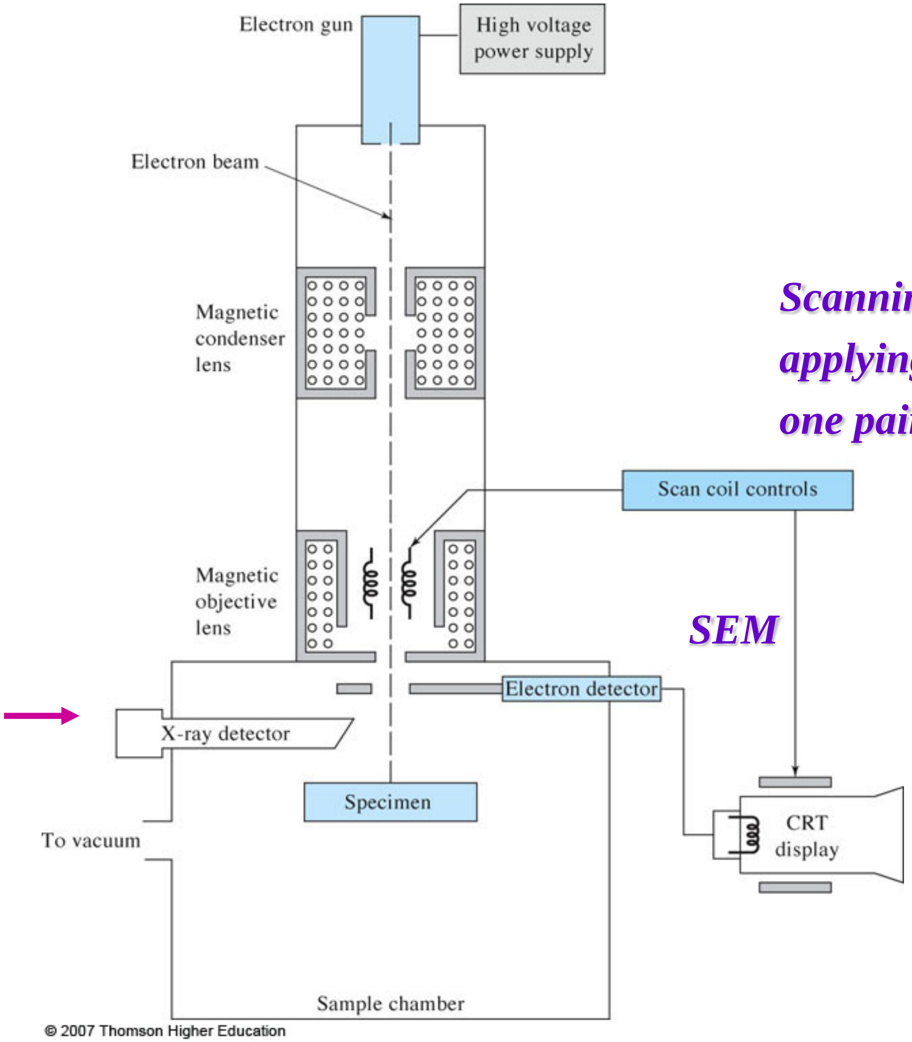
Figure 8. (a) SEM image of a non-woven textile sample of polyethylene oxide fibers. The large depth of field of the SEM makes it possible to image fibers which are 10's of μm's below the upper layer of fibers. Bar=10μm; (b) SEM image of Y_2O_3 crystal. Bar=1μm.

Scanning Electron Microscope (SEM)





Scanning Electron Microscope (SEM)



© 2007 Thomson Higher Education

Scanning is controlled by applying an electric signal to one pair of scan coils

SEM

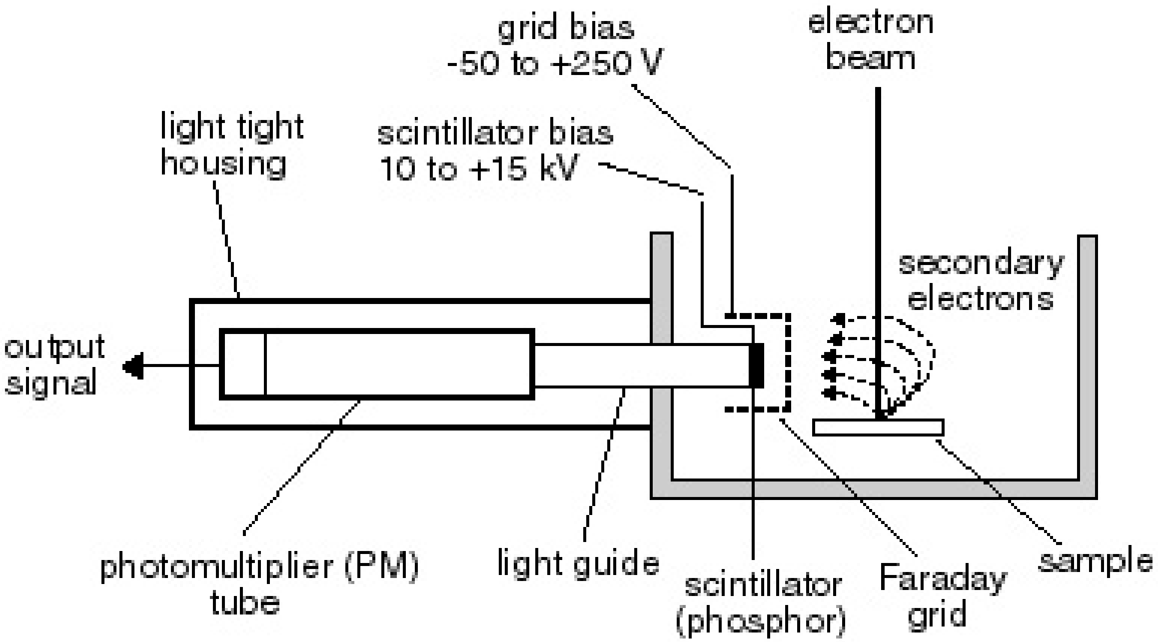
Electron microprobe →

(EDS x-ray, WDS)

- **Figure 21.15 Schematic of an SEM.**

Scanning Electron Microscope (SEM)

Secondary electron detector: Everhart-Thornley detector
Scintillator-PMT system



Secondary Electron Detection. Low-energy secondary electrons (trajectories shown by dashed lines) are collected by applying a suitable bias to the Faraday grid. Tese electrons are further accelerated in order to give them sufficient energy to scintillate the phosphor (after Potts 1987).

Scanning Electron Microscope (SEM)

<EDS (energy disperse spectrometer) X-ray spectrum>

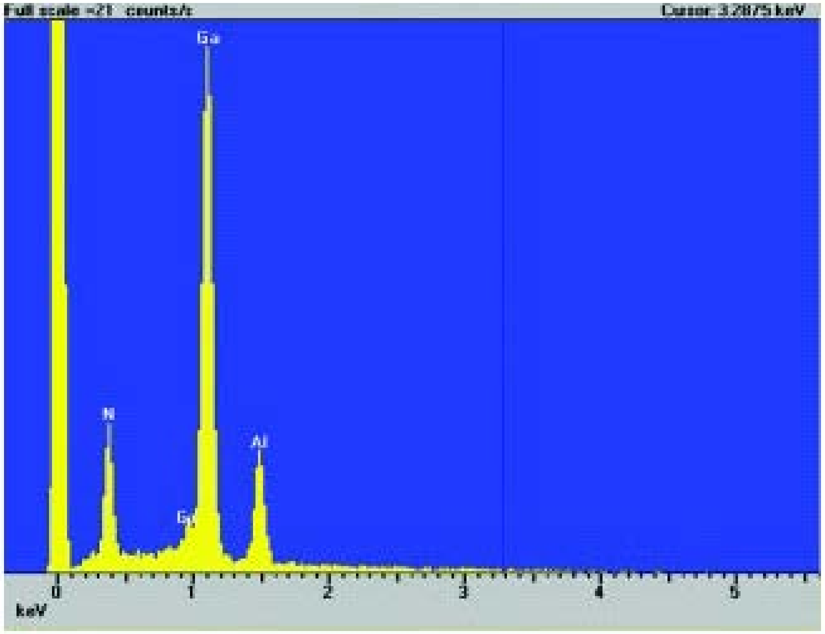


Figure 10. EDS X-ray spectrum of an AlGaN thin film on SiC substrate showing the presence of N, Ga, and Al.

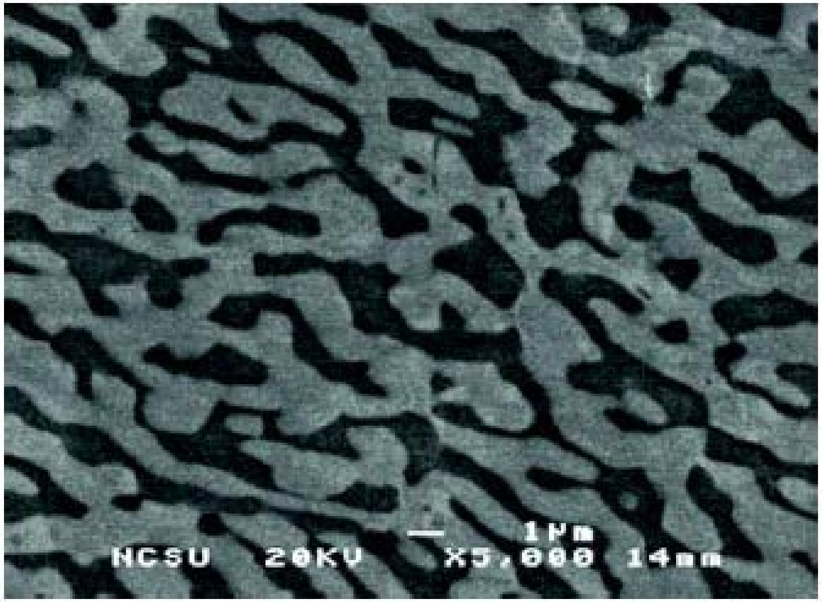


Figure 11. Backscattered SEM image of an PbSn alloy showing contrast based on the atomic number of the two components. The brighter areas are Pb-rich. 5,000x, Scale bar=1μm.

Scanning Electron Microscope (SEM)

Philips XL30-FEG

JEOL JSM-890

https://www.youtube.com/watch?v=GY9lfO-tVfE

Scanning Probe Microscope (SPM)

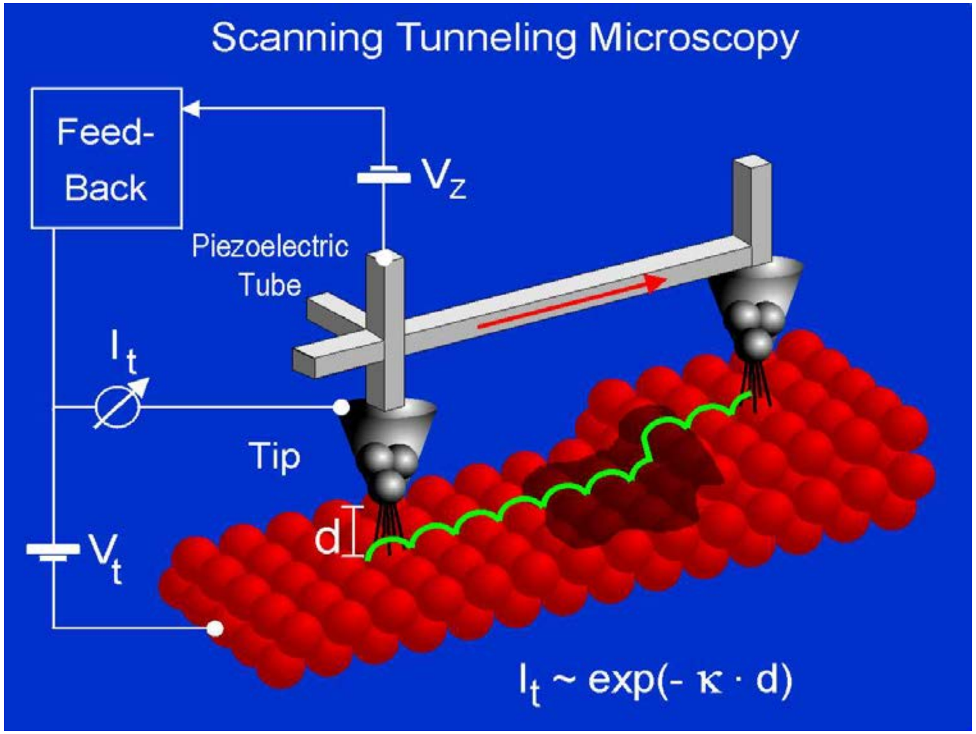
- Scanning tunneling microscopy (STM) and Atomic force microscopy (AFM) are referred collectively as scanning probe microscopy (SPM).
- SPMs are capable of resolving details of surfaces down to the atomic level.
- STMs was invented by G. Binnig & H. Roher in 1982.
  In 1986, Novel Prize in physics.
- The primary use of SPM is for measuring surface topography of samples.

Scanning Probe Microscope (SPM)

- The resolution of SPMs is
  - ♠ 20 Å in the x and y directions with ideal samples & best instrument ⇒ ~ 1 Å
  - ♠ 1 Å in the z dimension
- SPM are based upon scanning the surface of the sample in an x/y raster pattern with a very sharp tip that moves up and down along the z axis as the surface topography changes
- This movement of the tip is measured and translated by a computer into an image of the surface topography.
- This image often shows details on an atomic size scale.

Scanning Tunneling Microscope (STM)

- These are used to obtain information about the topography and the local electronic properties on a surface.



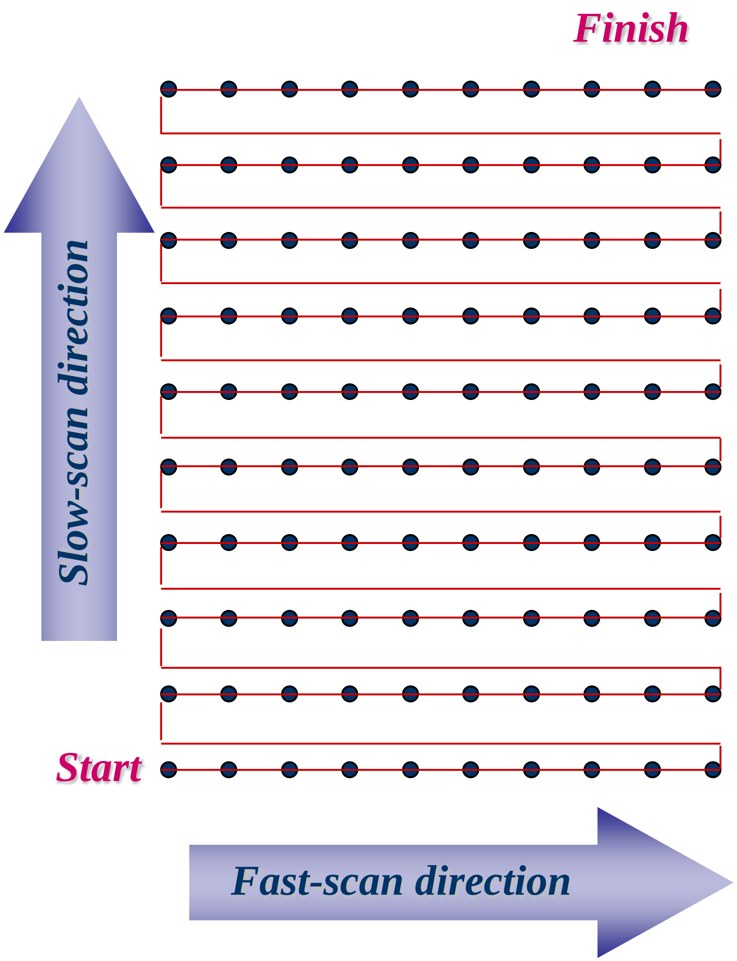
Basic set-up

Scanner: piezoelectric tube for x,y,z-position scan

Probe: electron tunneling force

Controller: feedback and processing electronics

Scanning Tunneling Microscope (STM)

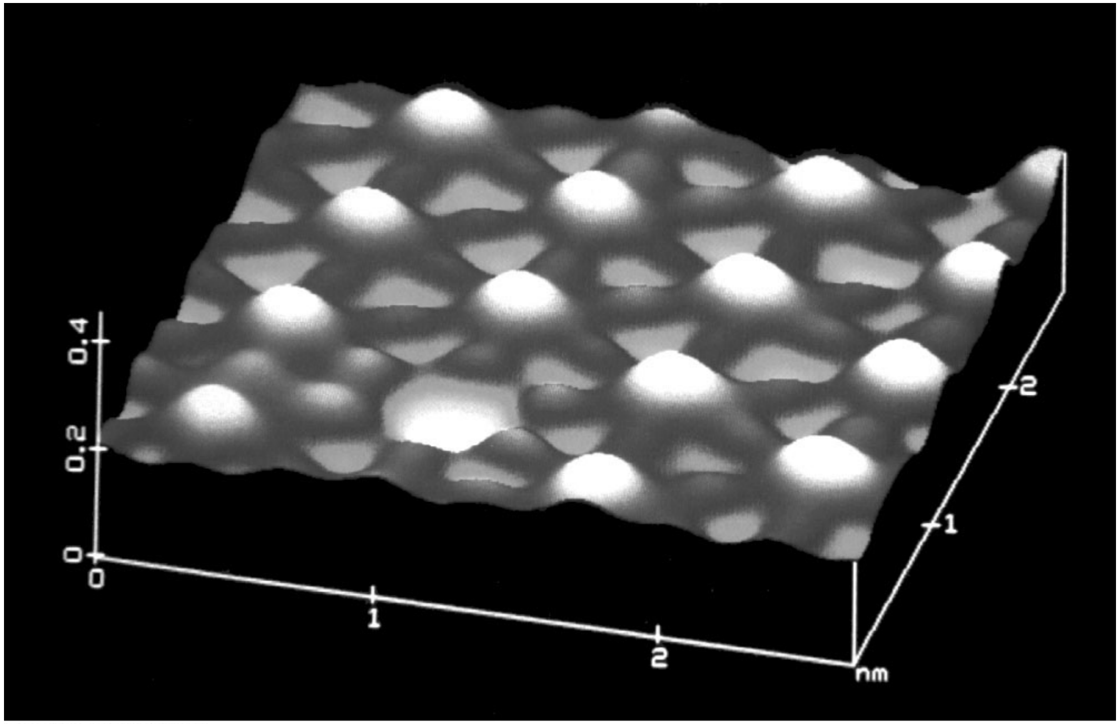


Finish

Slow-scan direction

Start

Fast-scan direction



- **Fig. 21.23** STM scan of iodine atoms in a 3-nm x 3nm array adsorbed on platinum. Note the missing iodine atom in the bottom center of the image.

Modes: Constant height and Constant current

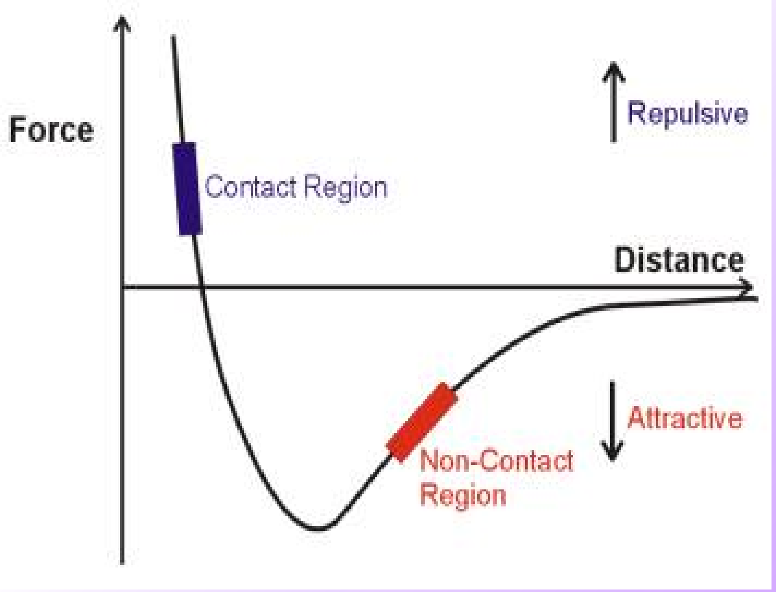
Atomic Force Microscope (AFM)

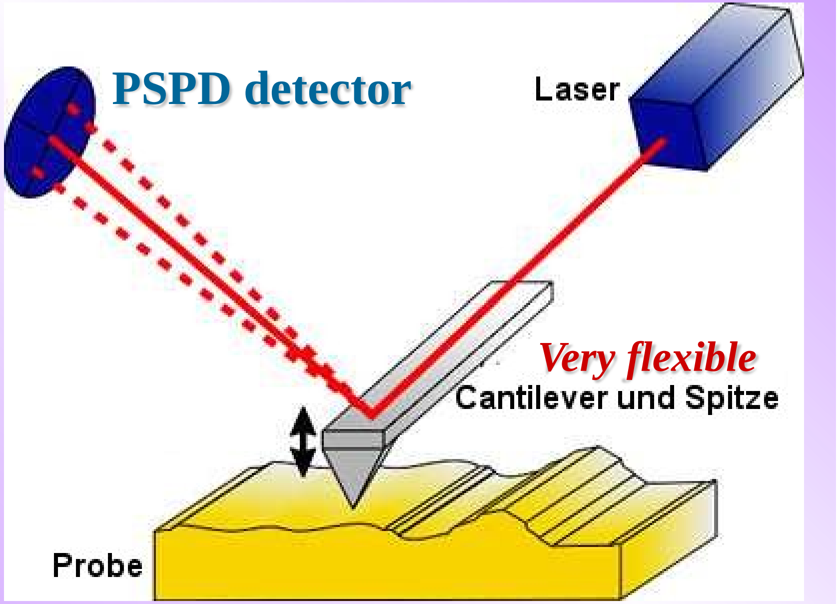
- AFM was invented in 1986
- Resolution of individual atoms on both conducting and insulating surfaces.
- A flexible force-sensing cantilever stylus is scanned in a raster pattern over the surface of the sample.
- The force acting between the cantilever and the sample surface causes minute deflections of the cantilever, which are detected by optical means.
- The optical signal from the laser beam detector is feed back into the sample piezoelectric transducer, which causes the sample to move up and down to maintain a constant force between the tip and the sample.

Atomic Force Microscope (AFM)

Lennard-Jones potential

$u = A/r^{12} - B/r^{6}$

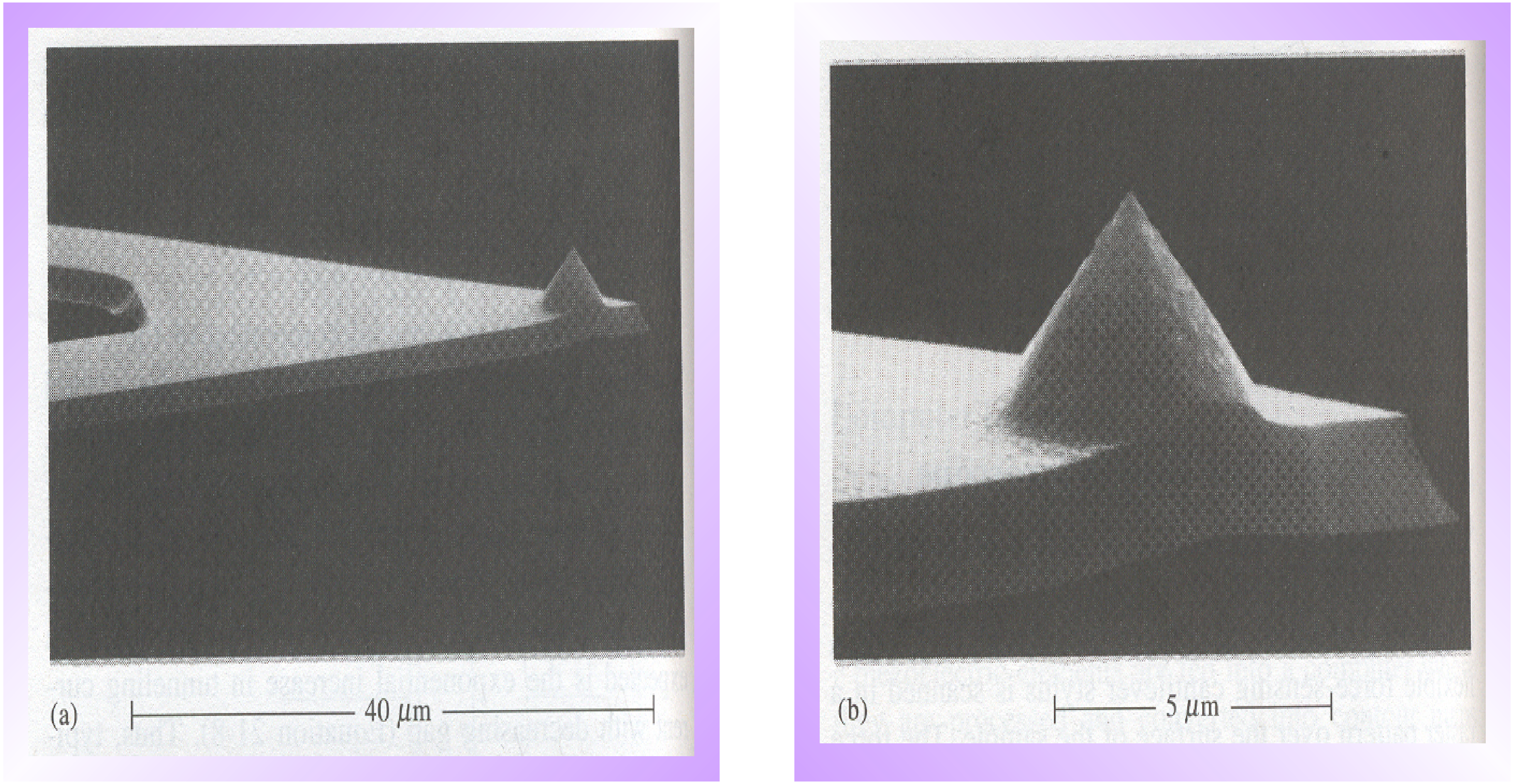




Force detection via cantilever deflection

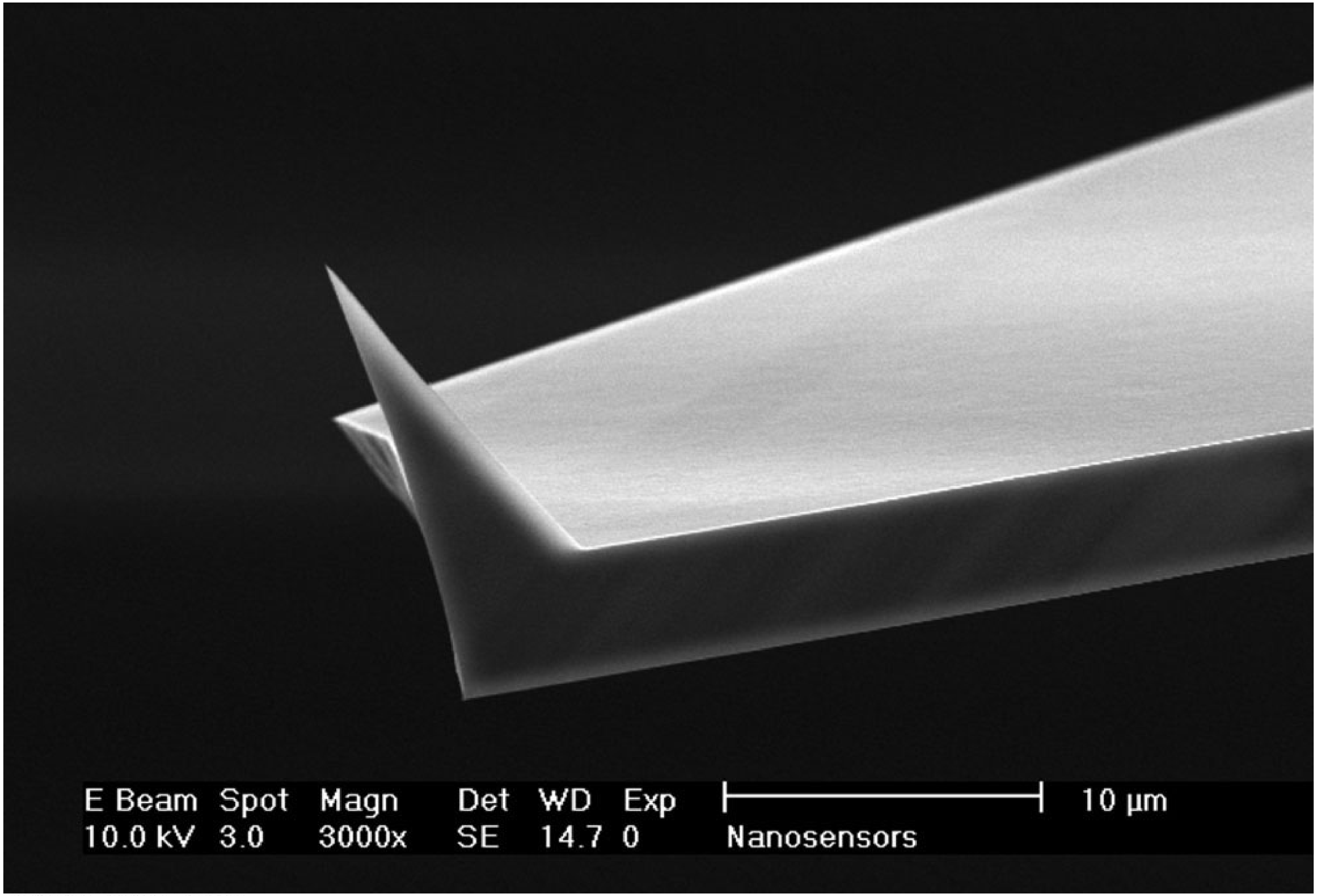
- Figure 1.2.Van der Waals force versus tip-to-sample separation. Atomic force microscopes can be designed to operate in either of the two regimes indicated by heavy lines.
- Figure Schematic of optical-deflection technique for detecting cantilever deflection. This method is also called beam-bounce detection.

Atomic Force Microscope (AFM)



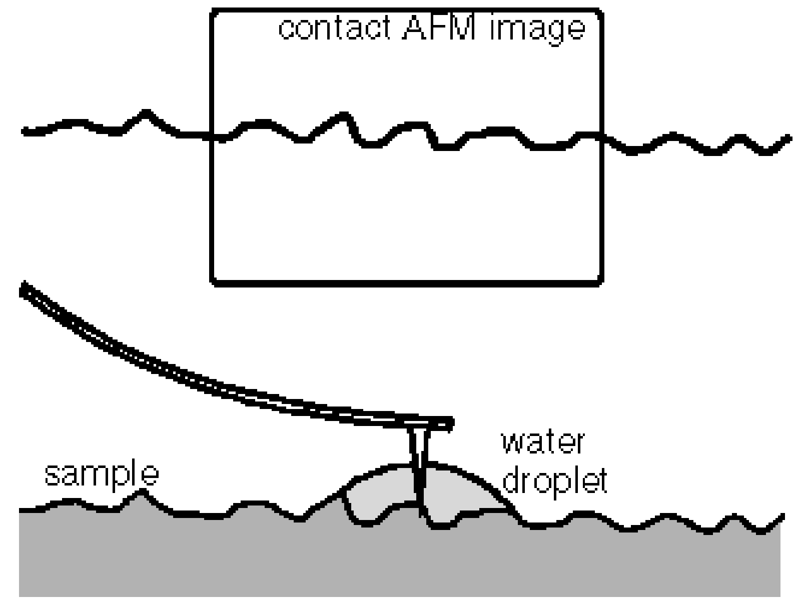
- **Figure 21.22. Micrograph of (a) an SiO_2 cantilever and tip and (b) a SiO_2 tip.**

Atomic Force Microscope (AFM)



Operational modes of AFM

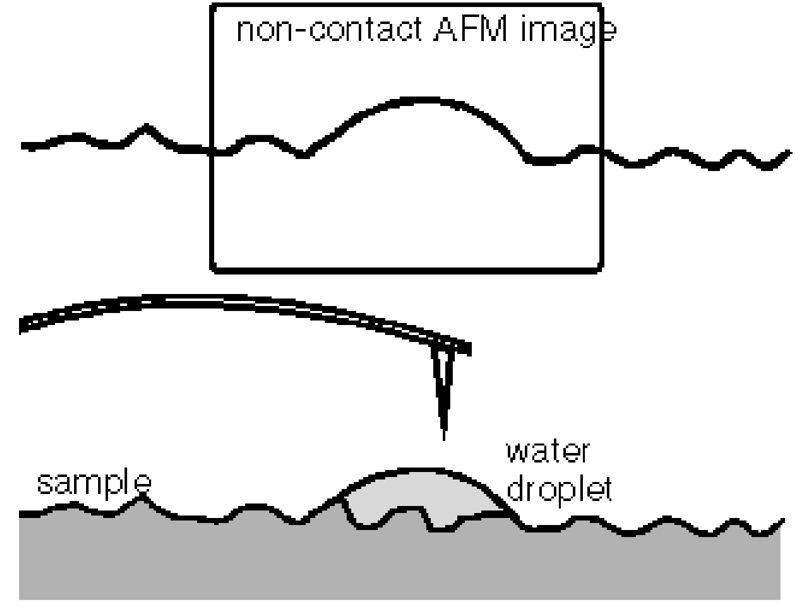
Contact Mode Repulsive force



http://www.topometrix.com

Resolution in contact AFM is determined by the area contact between the tip and sample
≈ 25 Å^2

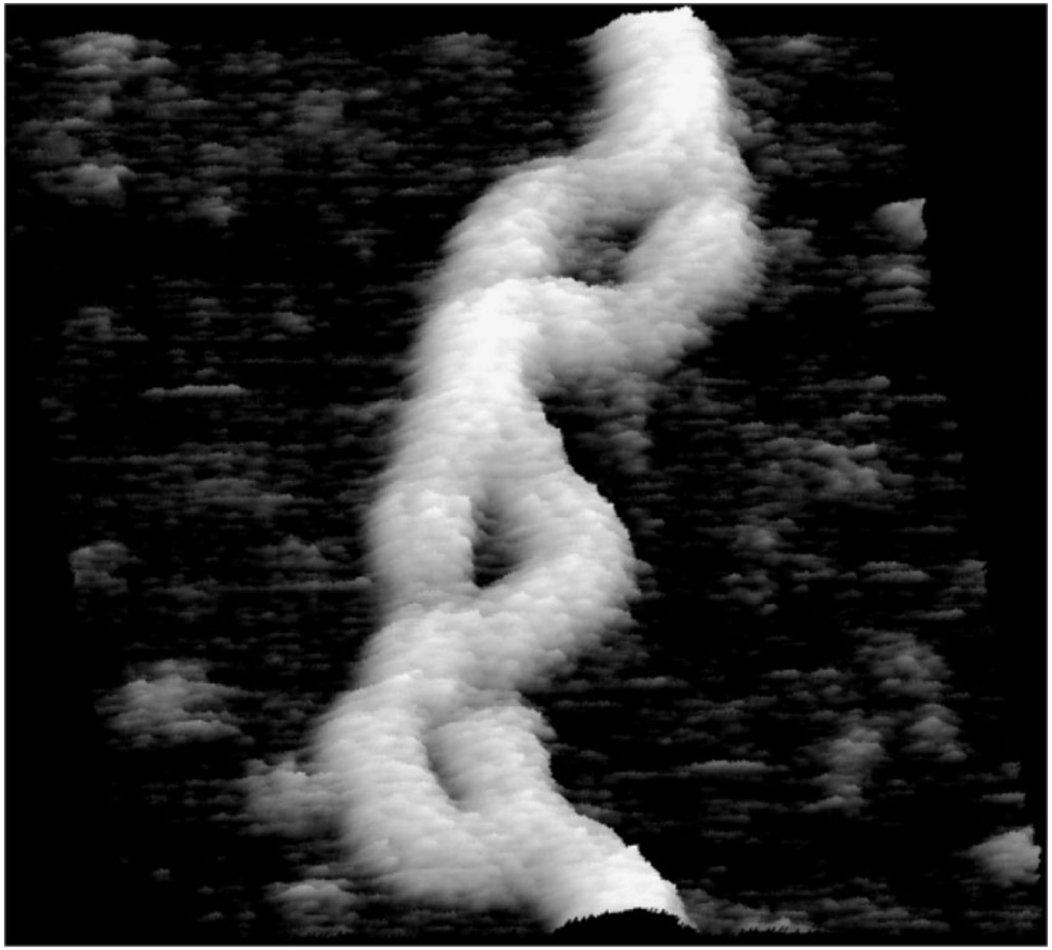
Non-contact Mode attractive force



Biological materials and soft polymers are damaged by contact AFM.
Disadvantage : loss of resolution

Operational Modes of AFM

Tapping Mode


© 2007 Thomson Higher Education

Hybrid of noncontact and contact AFM

Vibrating cantilever near the surface at hundred kHz.

Vertical resolution : 0.5 Å
Lateral resolution : 5 Å

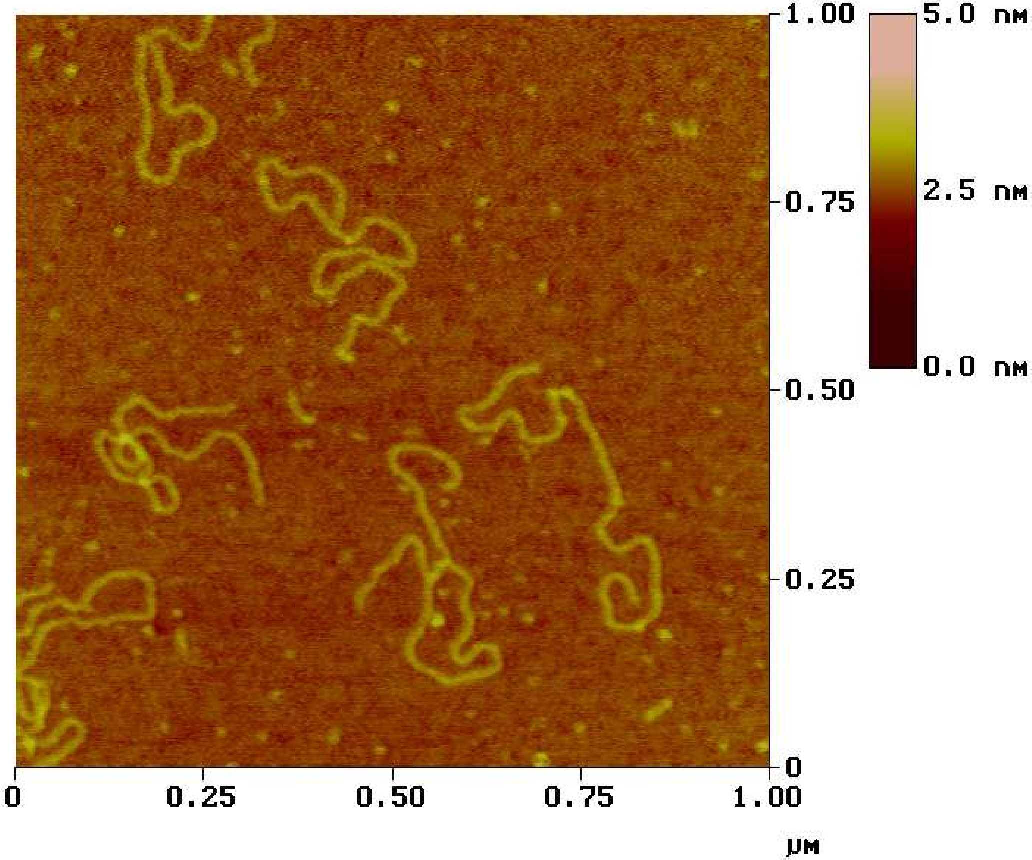
- **Figure 21.24. Two double-stramded DNA molecules imaged on mica, showing tha ability of tapping mode AFM to resolve overlapping molecules.**

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

Operational modes of AFM

Tapping Mode

Tapping Mode Imaging of Linearized DNA



Chemical Force Microscope (CFM)

MFM (Magnetic Force Microscopy)

- ***Tip made of magnetic materials***
  sample : magnetic materials
- ***Non-contact AFM***

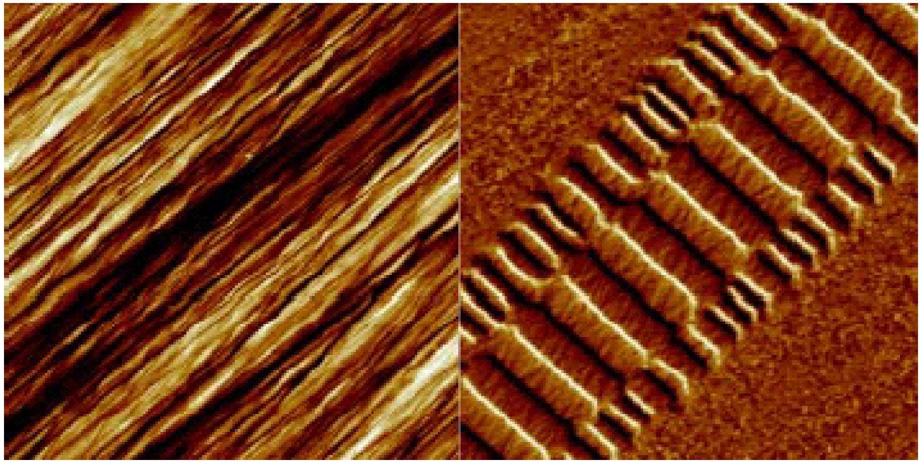
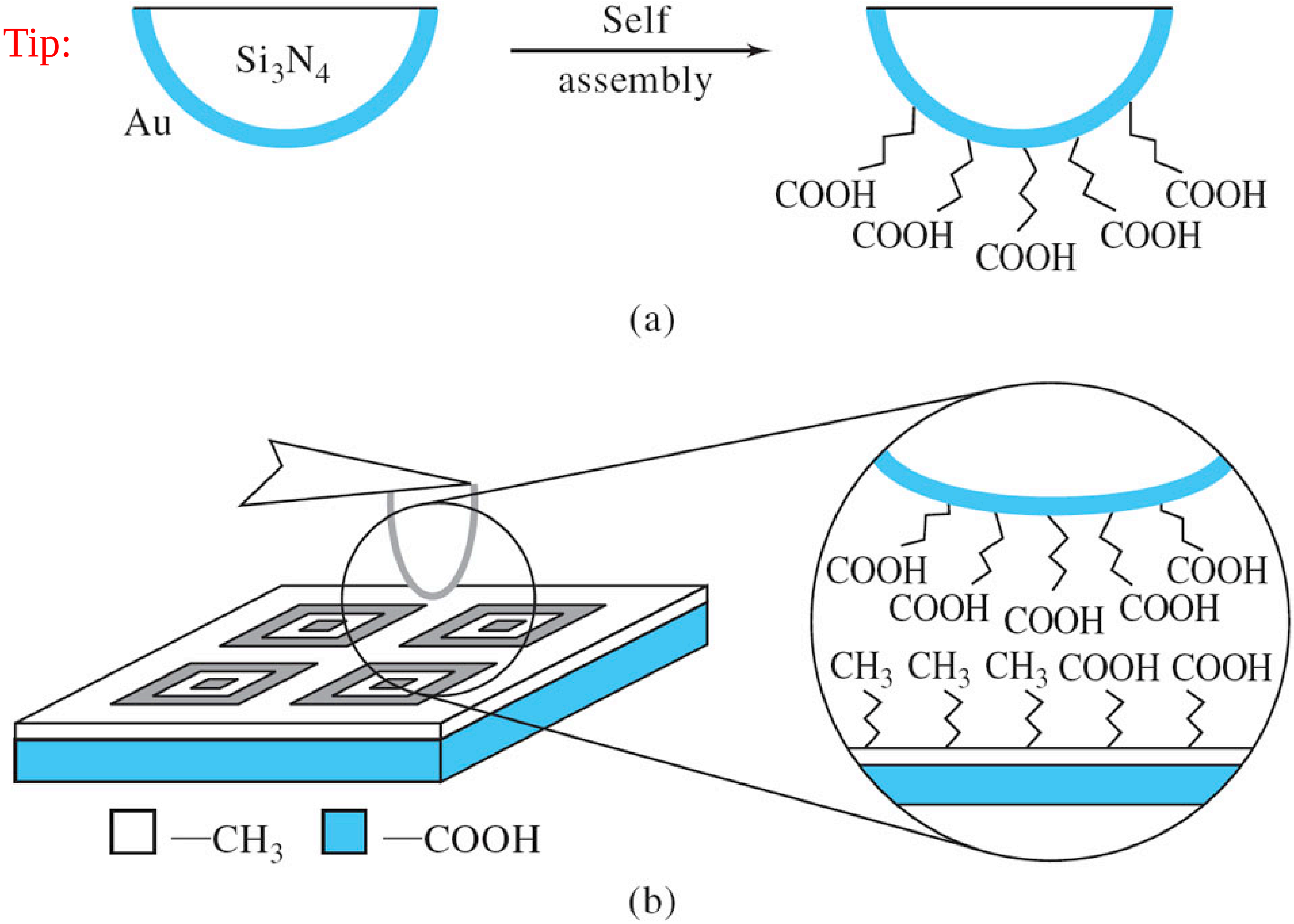


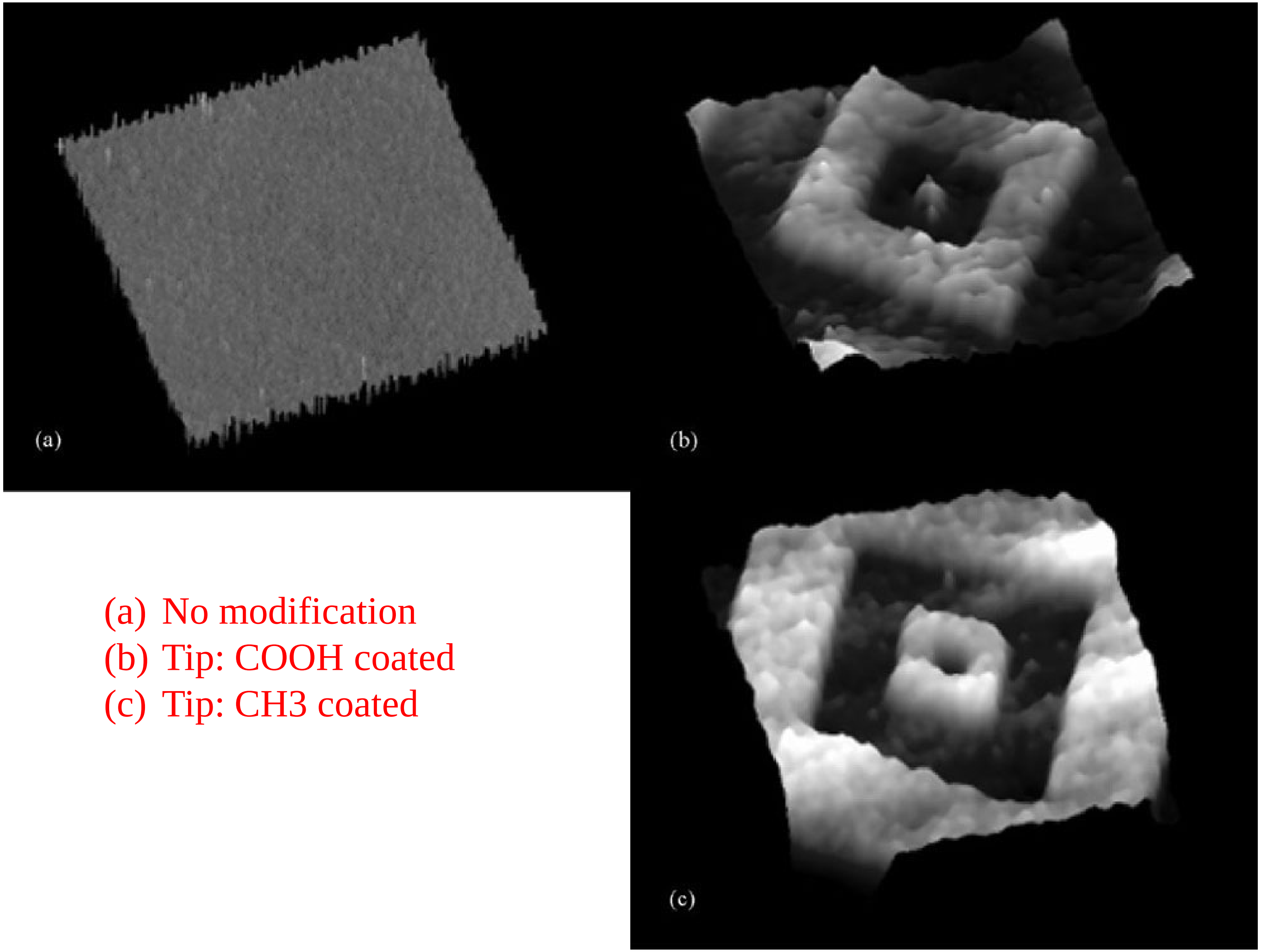
Figure 13. Magnetic Force Microscopy (MFM) image of overwritten tracks on a textured hard disk. The topography (left) was imaged using TappingMode; the magnetic force image of the same area (right) was captured with LiftMode (lift height 35 nm) by mapping shifts in cantilever resonant frequency. 25μm scan. (17)

Chemical Force Microscopy (CFM)

AFM Tip:



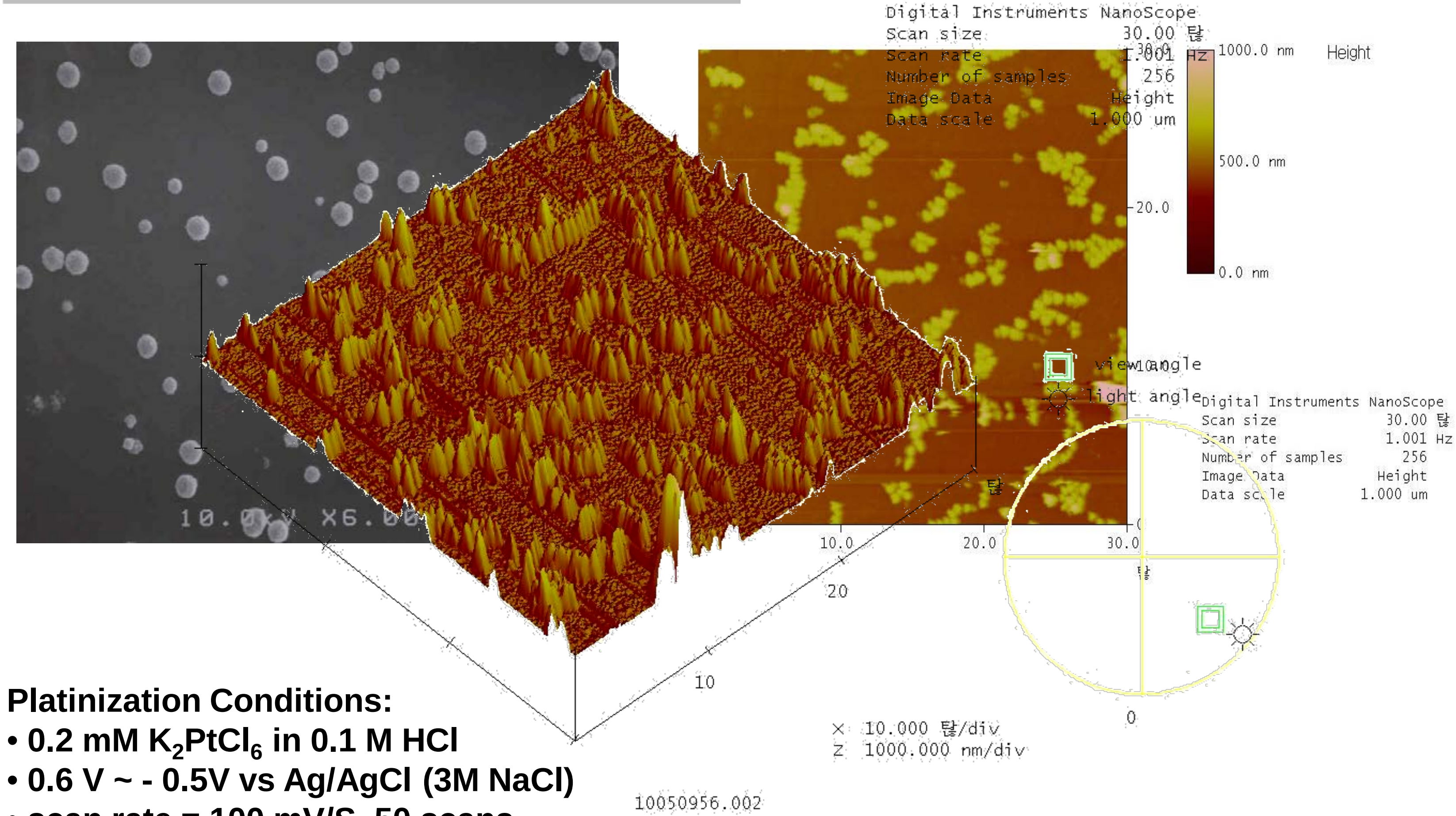
Chemical Force Microscope (CFM)



(a) No modification
(b) Tip: COOH coated
(c) Tip: CH3 coated

Platinized Glassy Carbon Electrode

Plantization under cyclic voltammetric scan



Platinization Conditions:

- **0.2 mM K_2PtCl_6 in 0.1 M HCl**
- **0.6 V ~ - 0.5V vs Ag/AgCl (3M NaCl)**
- **scan rate = 100 mV/S, 50 scans**

Figure 11. **Surface images (a) SEM image, (b) 2D AFM image, (c) 3D AFM image .**

SPM for Biomolecules

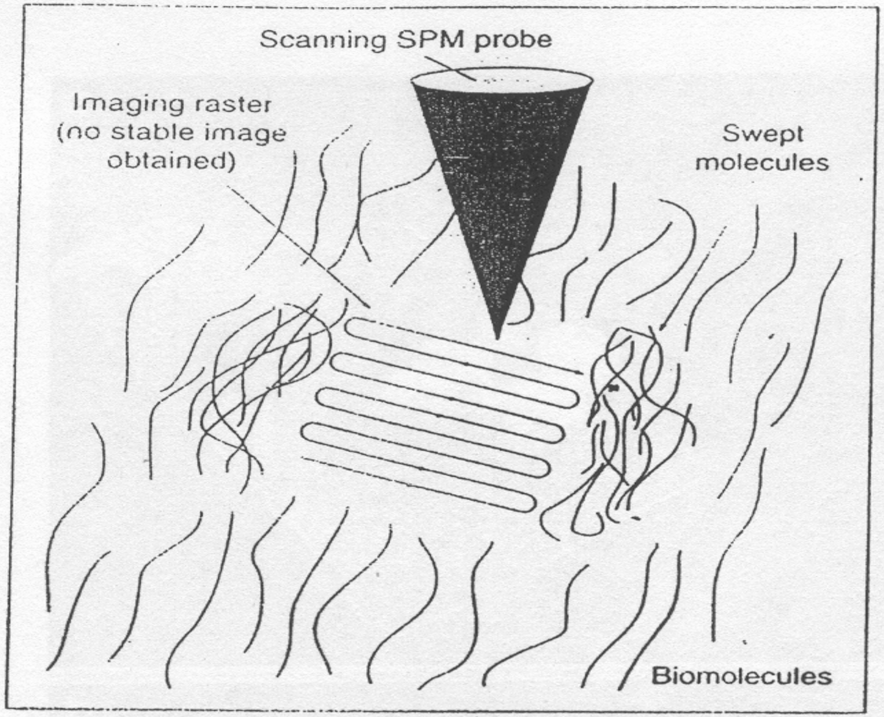


Figure 2

A schematic diagram displaying the result of sweeping biomolecules by the probe of a scanning probe microscope (SPM). Since the sample material is removed from the surface, or severely distorted by the image probe, no reliable image data from the biomolecules are obtained.

SPM for Biomolecules

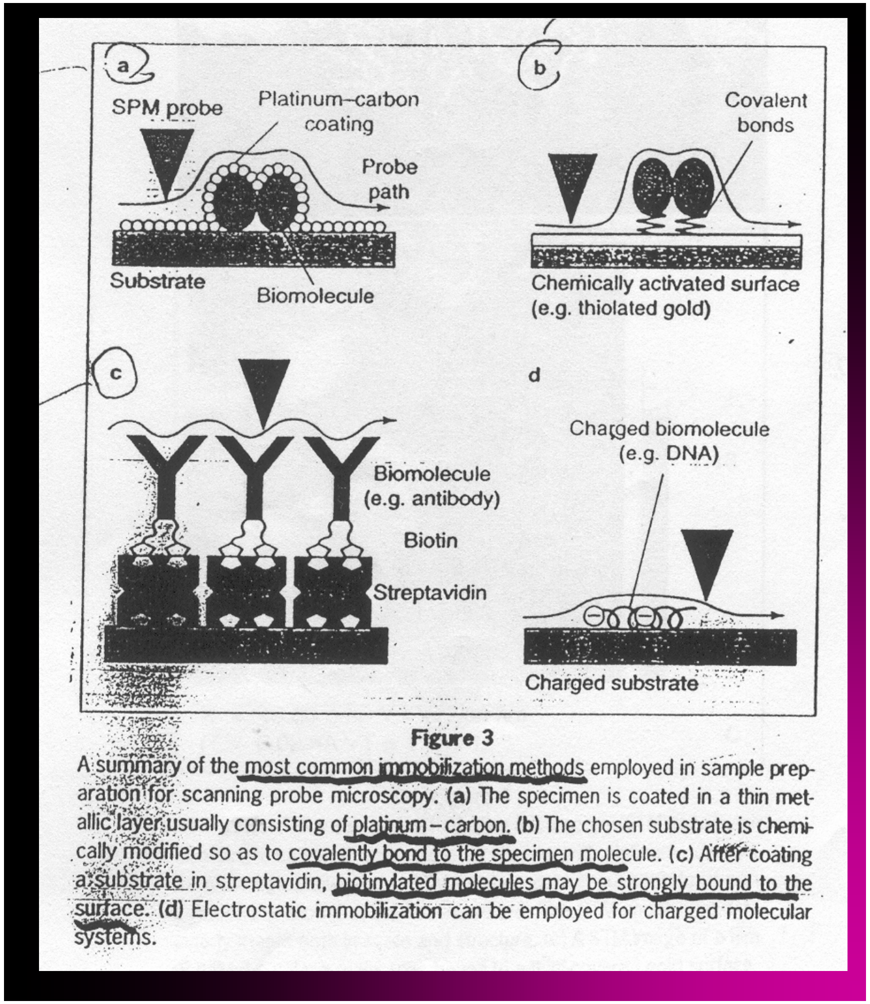


Figure 3

A summary of the most common immobilization methods employed in sample preparation for scanning probe microscopy. **(a)** The specimen is coated in a thin metallic layer usually consisting of platinum–carbon. **(b)** The chosen substrate is chemically modified so as to covalently bond to the specimen molecule. **(c)** After coating a substrate in streptavidin, biotinylated molecules may be strongly bound to the surface. **(d)** Electrostatic immobilization can be employed for charged molecular systems.

Surfactant, BAC (benzyl dimethyl alkyl ammonium chloride) improve surface coverage on gold
(단점 : increase molecular dimension of DNA)

SPM in Liquid Environment

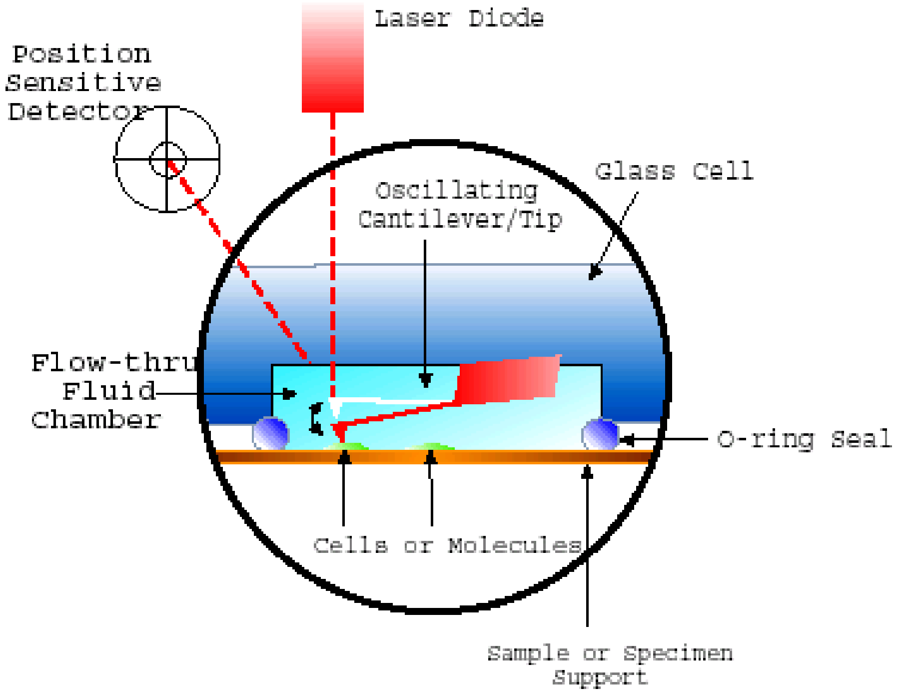


Figure 16. Fluid cell for an AFM which allows imaging in an enclosed, liquid environment.

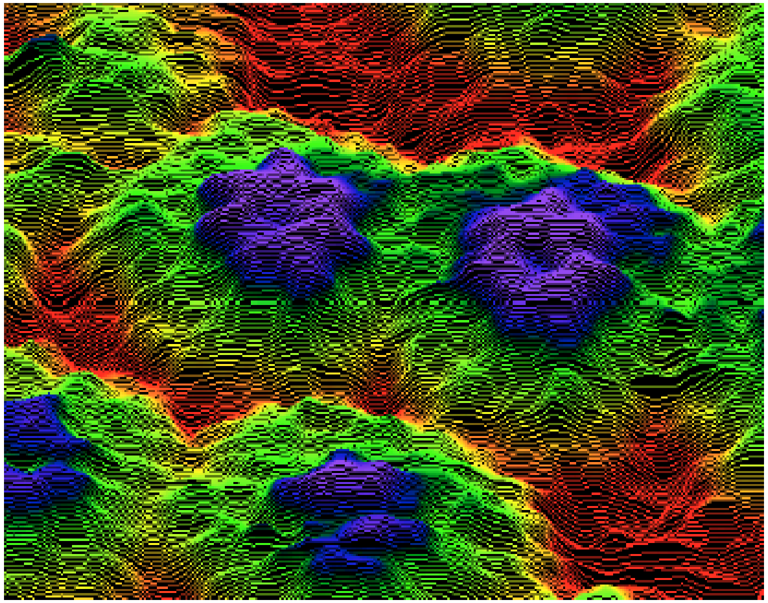
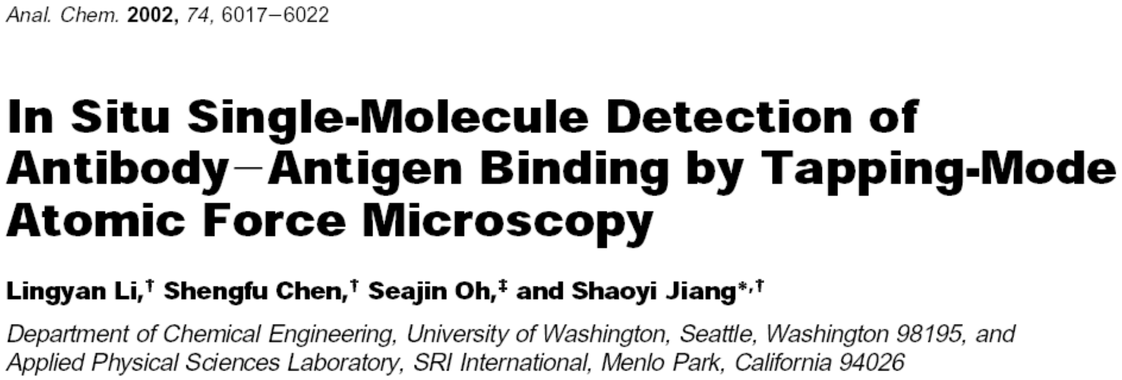


Figure 17. Image of two GroES molecules positioned side-by-side in physiologic fluid, demonstrating 10Å lateral resolution and 1Å vertical resolution. The entire molecule measures 84Å across, and a distinct 45Å heptameric "crown" structure protrudes 8Å above the remaining GroES surface and surrounds a central depression. 18nm scan. Image courtesy of Z. Shao, University of Virginia. (18)

SPM in Liquid Environment

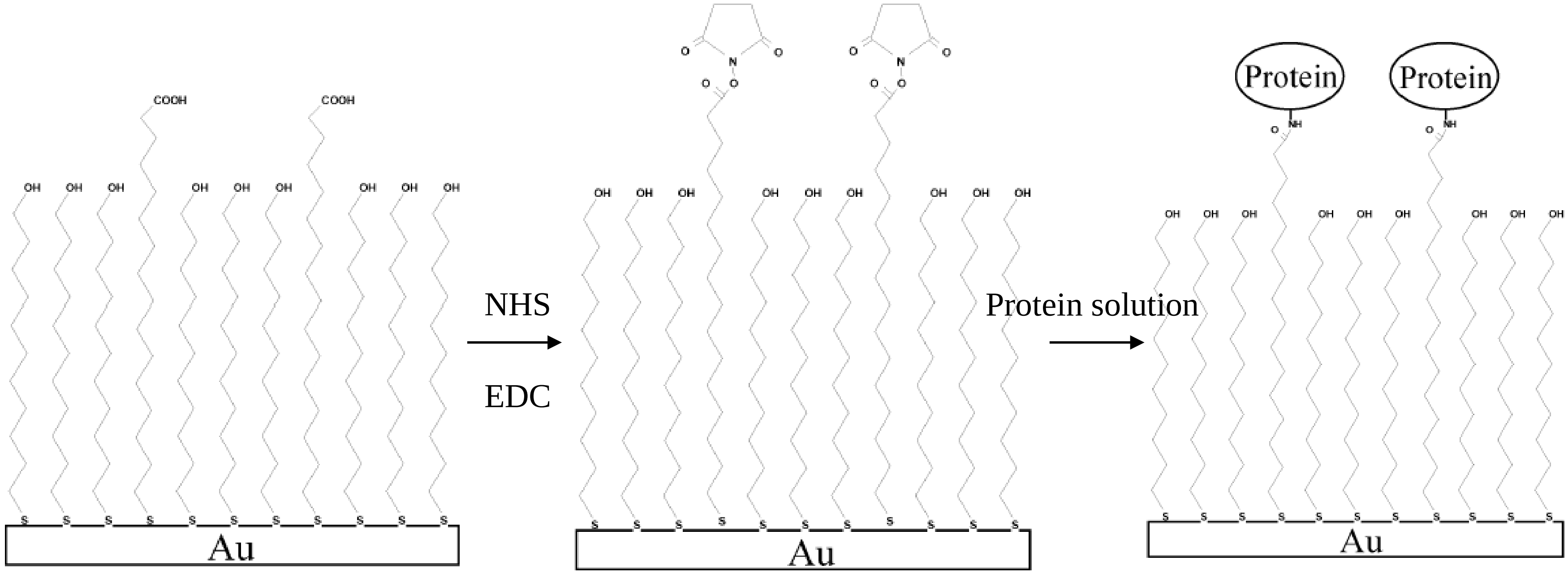


Anal. Chem. **2002,** *74,* 6017–6022

In Situ Single-Molecule Detection of Antibody–Antigen Binding by Tapping-Mode Atomic Force Microscopy

Lingyan Li,[†] Shengfu Chen,[†] Seajin Oh,[‡] and Shaoyi Jiang*[,†]

Department of Chemical Engineering, University of Washington, Seattle, Washington 98195, and Applied Physical Sciences Laboratory, SRI International, Menlo Park, California 94026



SPM in Liquid Environment

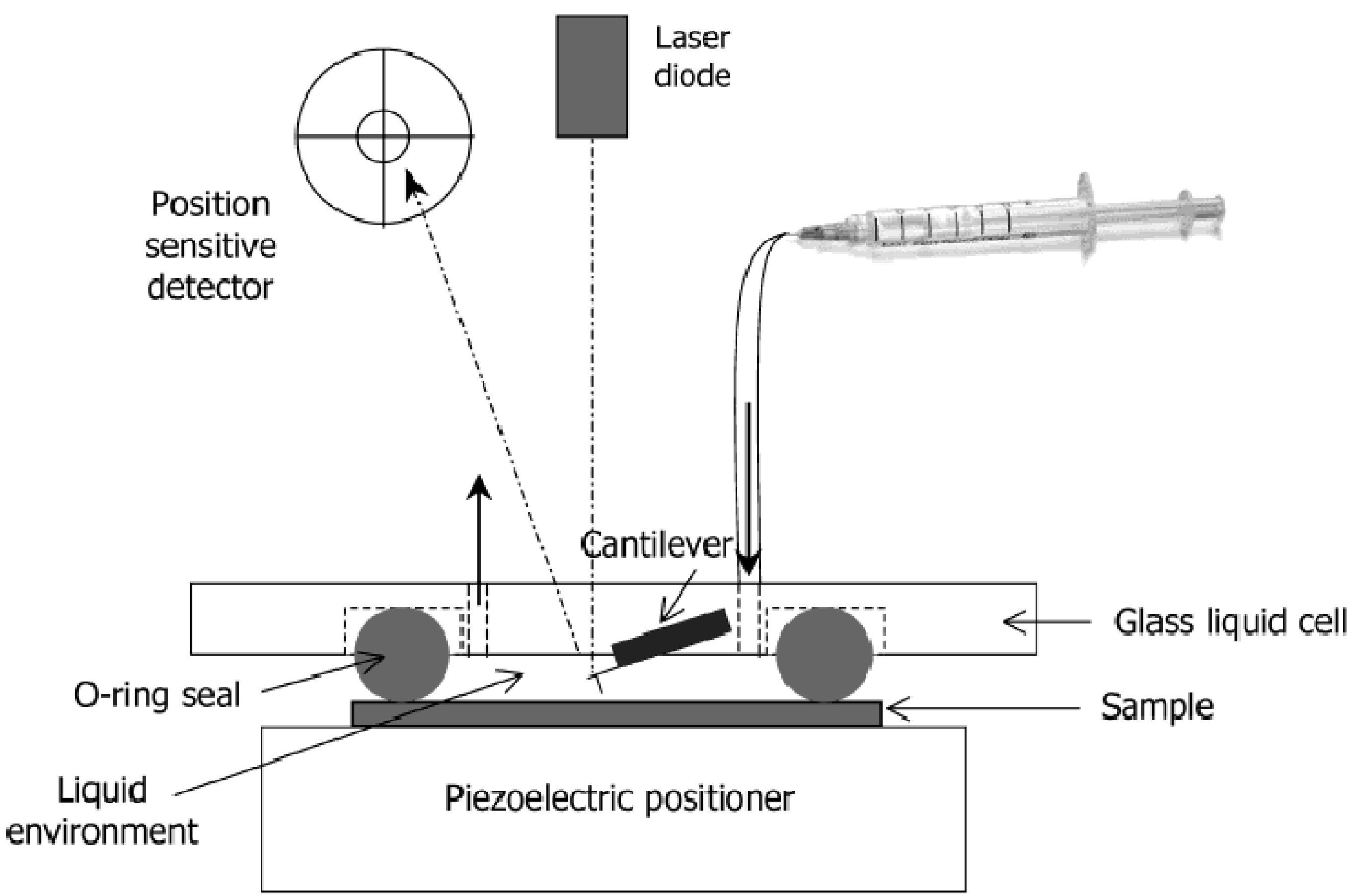
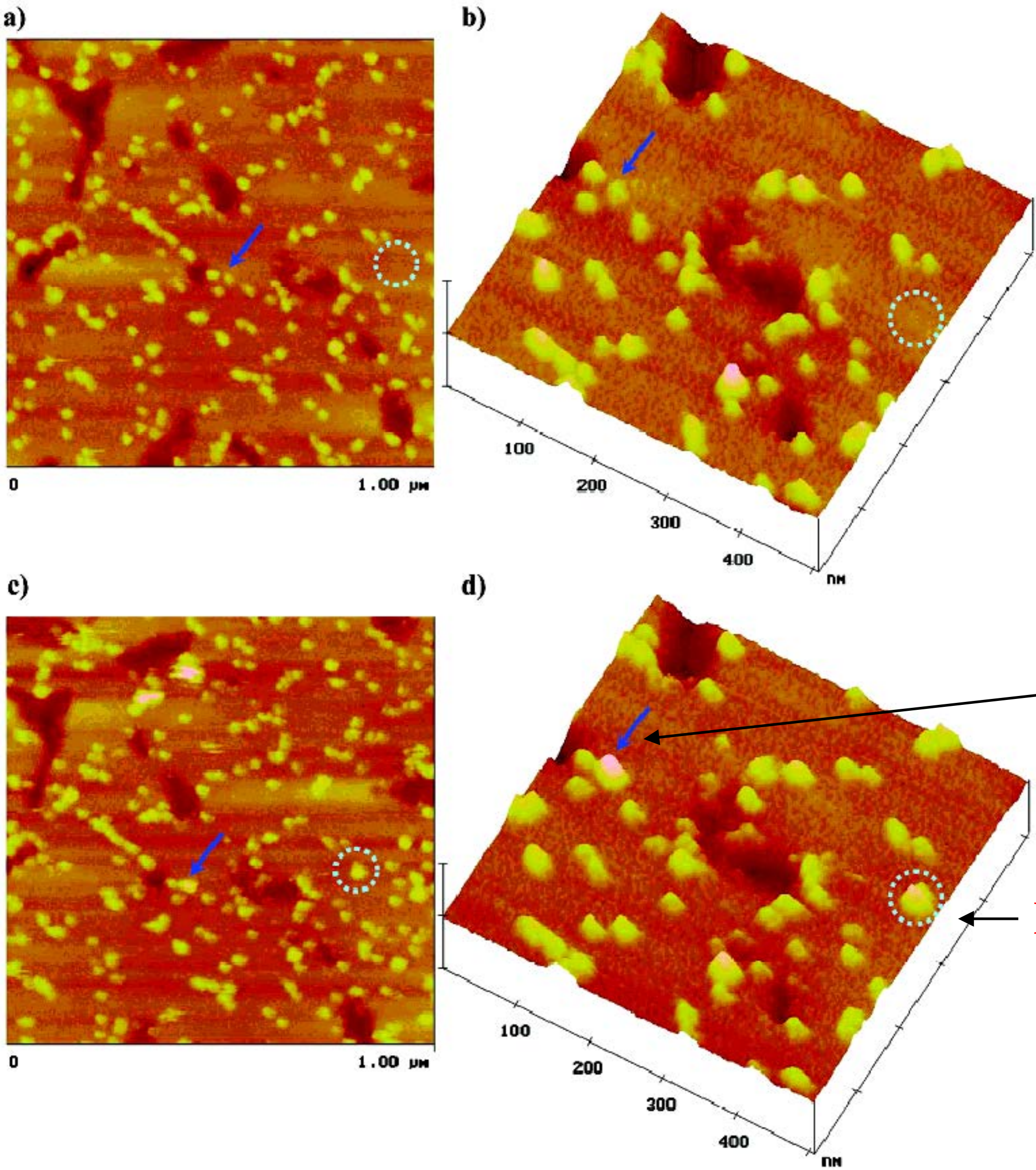


Figure 2. Schematic diagram of the experimental setup used for in situ TM-AFM imaging in liquid environment. With this setup, liquid can be injected into or removed from the liquid cell without significant perturbation to the system.



Specific binding

Non specific binding

Figure 4. In situ tapping-mode AFM images of immobilized anti-goat IgG on mixed C15COOH/C11OH SAMs (1% in solution) before (a, b) and after (c, d) exposure to goat IgG. Images were taken in PBS buffer solution at the same location. Images b and d are corresponding (off-line) zoomed-in three-dimensional images of (a) and (c), respectively. The arrow refers to the specific binding location while the dashed circle refers to the nonspecific binding location. Dark features represent Au defects. *Z* bar is 20 nm.