Lecture 12

Solid Surfaces. Techniques to study surfaces.

Solid Surfaces

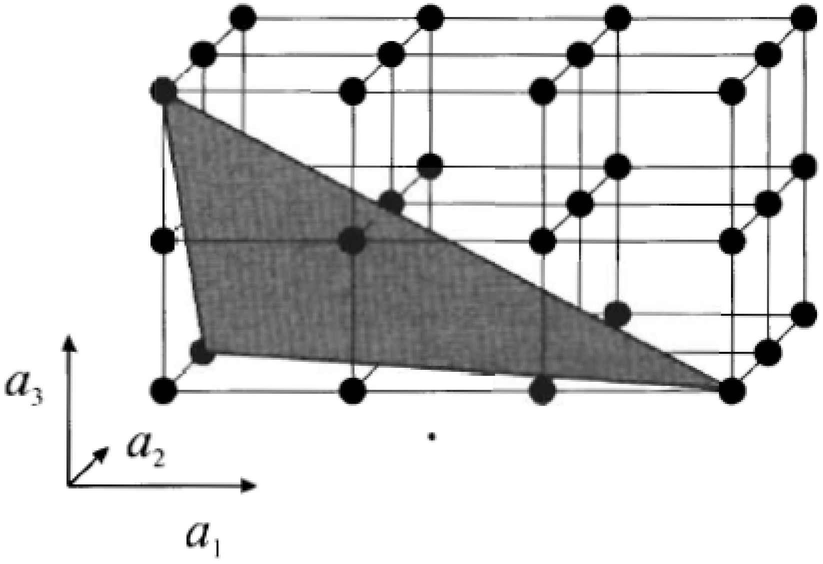
- Molecules on surfaces are not mobile (to large extent)
- Surfaces have a long-range order (crystalline)
- Shape of the surface is not entirely determined by surface tension

Description of crystalline surfaces

- The ideal surface structure corresponding to a certain cut of bulk crystal structure is called the **substrate structure**.

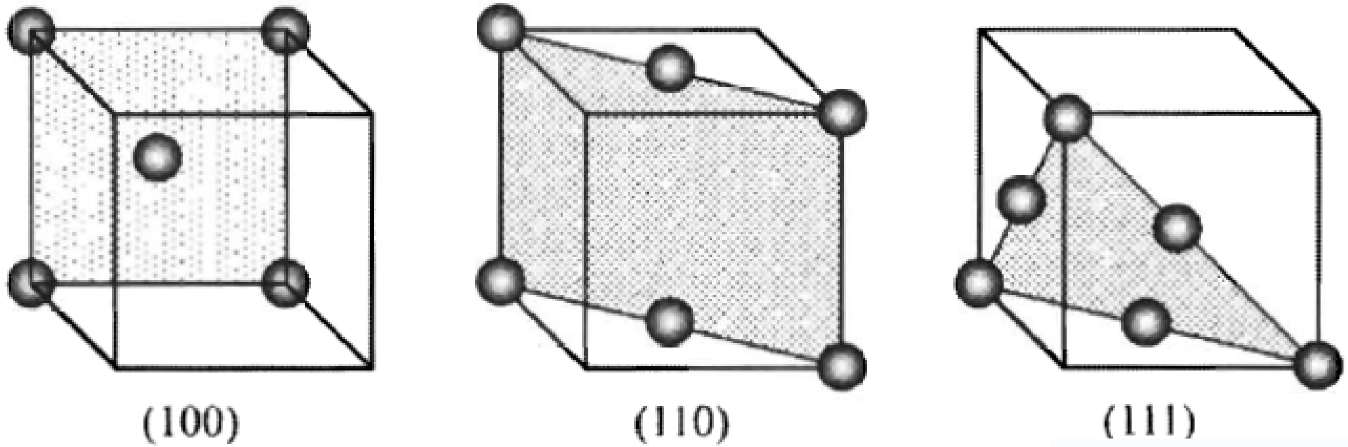
Brief reminder from Solid State Physics

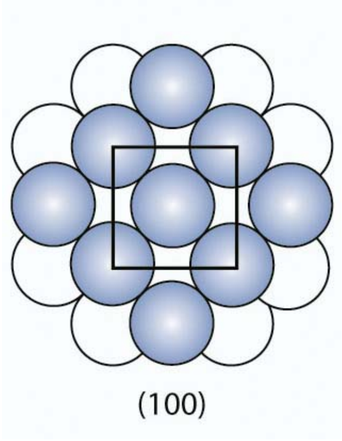
- Crystallographic orientation of a surface is determined by **Miller indices**
- How to detrmine Miller indices:
  1. **find intersection of the surface plane with the crystallographic axes in units of lattice constants**
  2. **take the inverse**
  3. **multiply by a common multiplicator to get them all integer**
  4. **negative numbers are represented as e.g.** $\bar{1}$
  5. **in hexagonal lattice 4 indices are used. The 4th one is not independent:** $(h\,k\,i\,l) \Rightarrow i = -(h+k)$

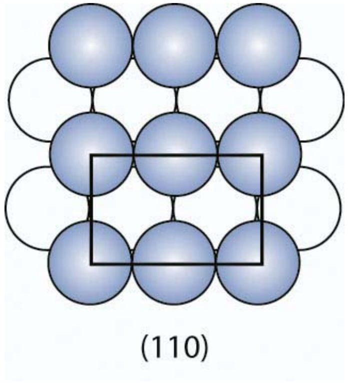


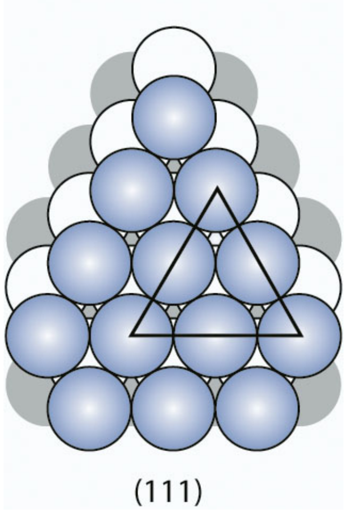
Description of crystalline surfaces

- Example: Major planes in FCC lattice



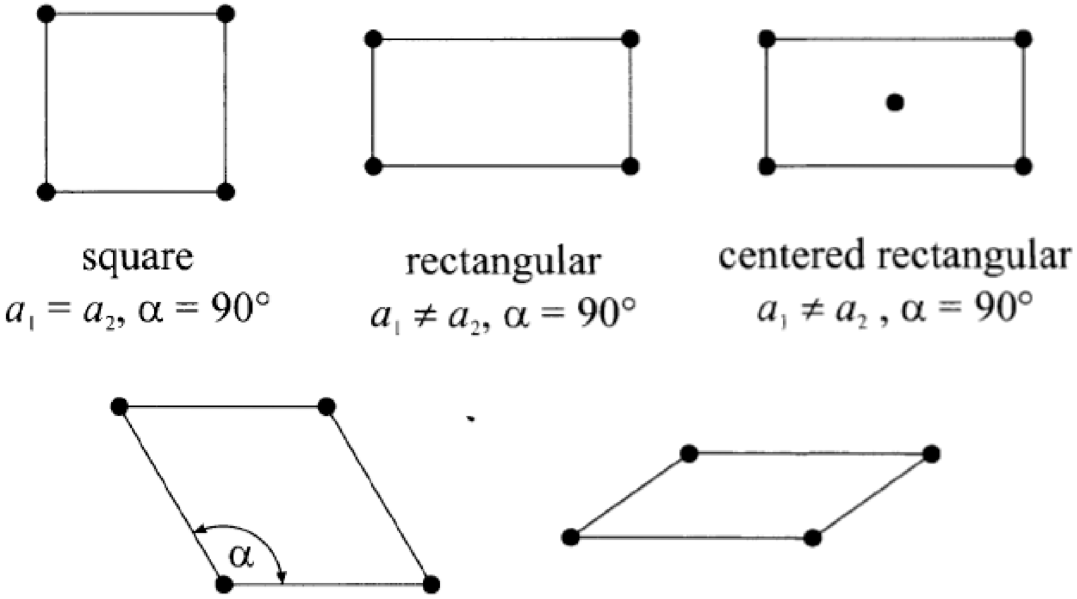






Description of crystalline surfaces

- Crystalline surfaces can be divided into 5 Bravais lattices according to the symmetry



square
$a_1 = a_2, \alpha = 90°$

rectangular
$a_1 \neq a_2, \alpha = 90°$

centered rectangular
$a_1 \neq a_2 , \alpha = 90°$

hexagonal
$a_1 = a_2, \alpha = 120°$

oblique
$a_1 \neq a_2, \alpha \neq 90°$

- Position of individual surface atoms can be indicated as:

$$\vec{r} = n \cdot \vec{a}_1 + m \cdot \vec{a}_2$$

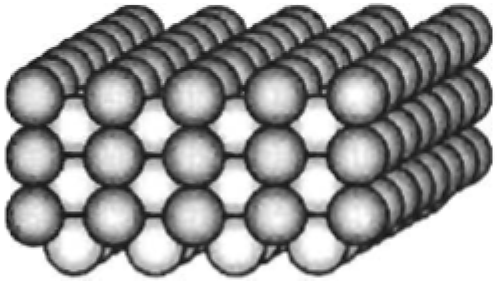
Surface relaxation/reconstruction

- To offset the increase in surface energy, a surface can undergo two types of changes:
  - **Surface relaxation**: distance between the topmost atomic layers is changed (usually 5-6 atomic layers), lateral distances buetween the atoms stay the same as in bulk.
    - usually the distance between the top two layers is reduced due to the presence of dipole layer on the surface

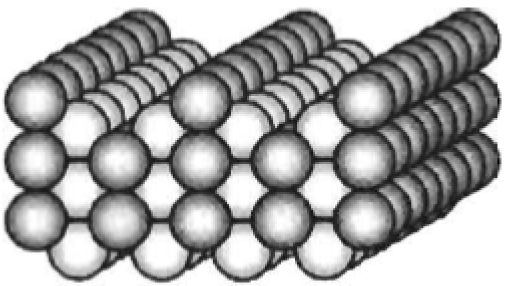
Example: distance reduction for (110) surfaces

Cu	Ni	Au	Pb
0.020 Å	0.156 Å	0.125 Å	0.080 Å

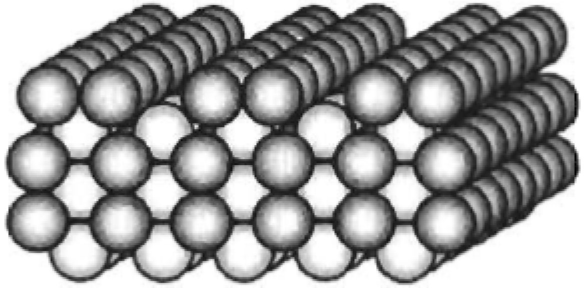
  - **Surface reconstruction** – gross change in surface structure also involving changes in lateral distances



Unreconstructed
fcc(110) surface



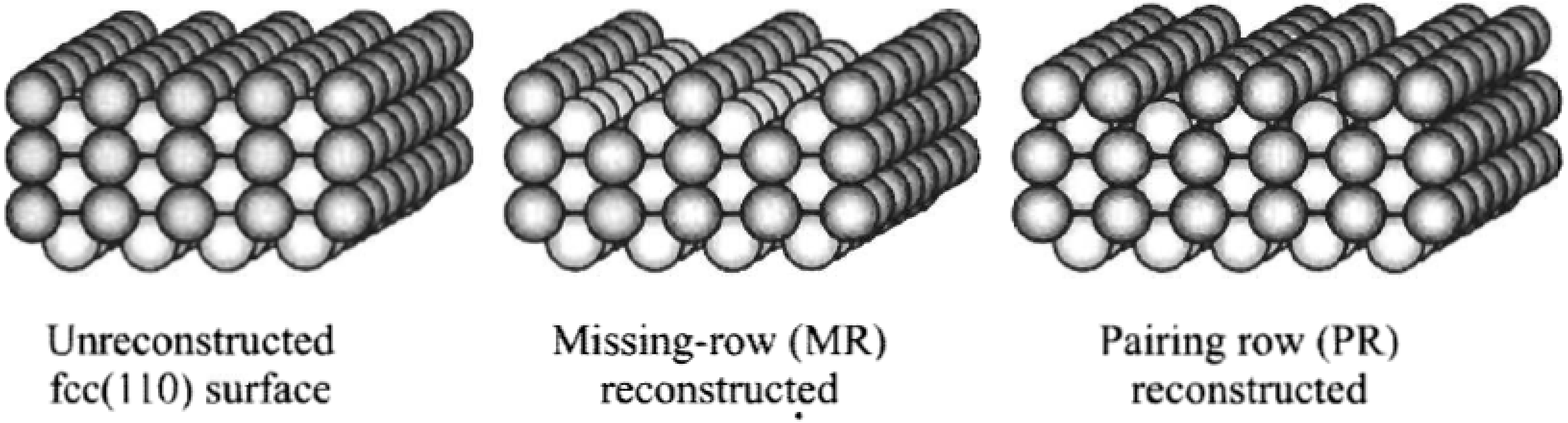
Missing-row (MR)
reconstructed



Pairing row (PR)
reconstructed

Surface relaxation/reconstruction

- **Surface reconstruction** – gross change in surface structure also involving changes in lateral distances
  - common for semiconductor surfaces due to the directional character of dangling bonds
  - also observed on many metals incl. Au, Ir, Pt, W



Surface relaxation/reconstruction

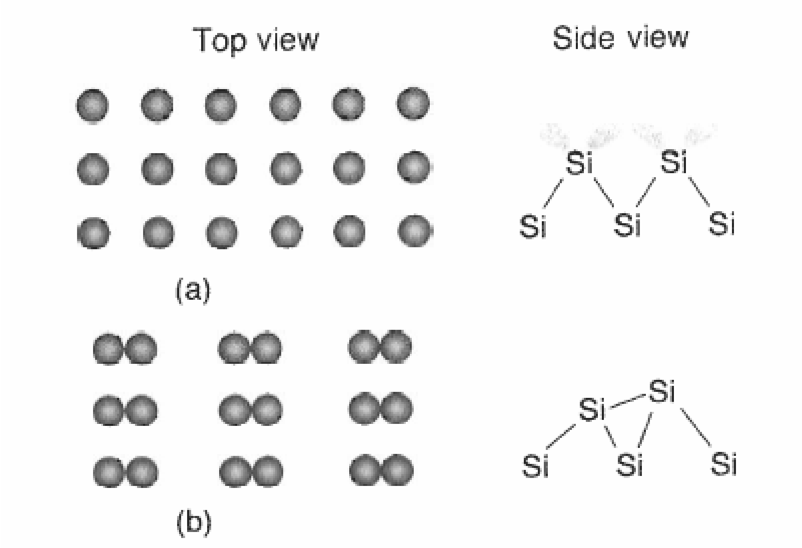
- How to describe reconstructed surfaces:

For reconstructed surface we have new unit cell vectors:

$$\vec{r} = n' \cdot \vec{b}_1 + m' \cdot \vec{b}_2$$

where: $\vec{b}_1 = p \cdot \vec{a}_1;\ \vec{b}_2 = q \cdot \vec{a}_2$

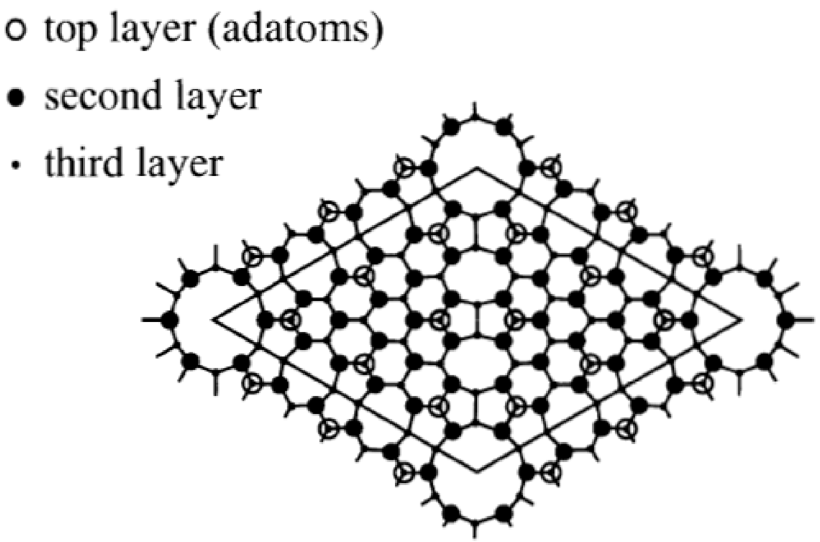
The surface structure is denoted as: $A(hkl)\left(p \times q\right)$

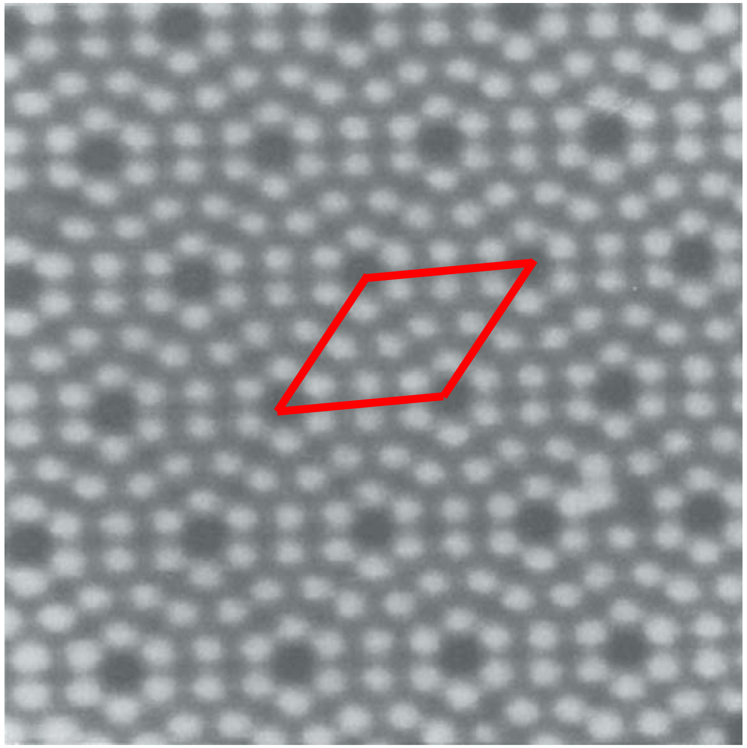


Si (100)-(2x1) reconstruction

Surface relaxation/reconstruction

- Si (111)-(7x7) reconstruction





Description of the adsorbate structure

- When molecules adsorb to a crystalline surface they may form a lattice commensurate with the underlying crystalline lattice

The positions of adsorbate molecules can be written as:

$$\vec{r} = n'' \cdot \vec{c}_1 + m'' \cdot \vec{c}_2$$

and $$p' = c_1 / b_1 \quad q' = c_2 / b_2$$

The surface structure is denoted in so-called Wood notation:

$$A(hkl)c\left(p' \times q'\right)R\beta - B$$

if adsorbate unit cell
is centered

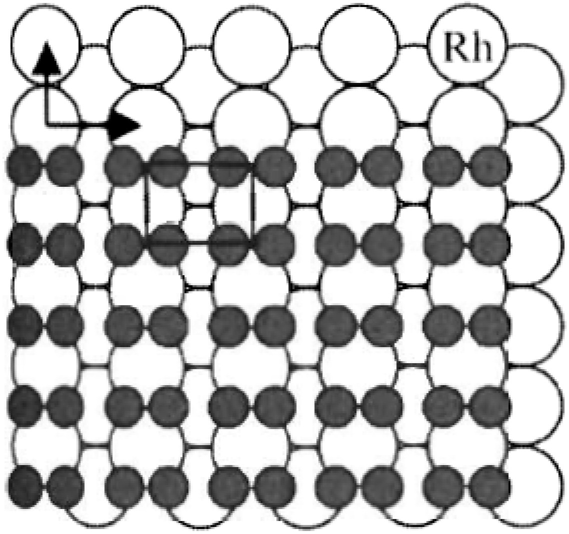
Rotation angle

Examples: Alkanethiols on gold $Au(111)\left(\sqrt{3} \times \sqrt{3}\right)R30^0$

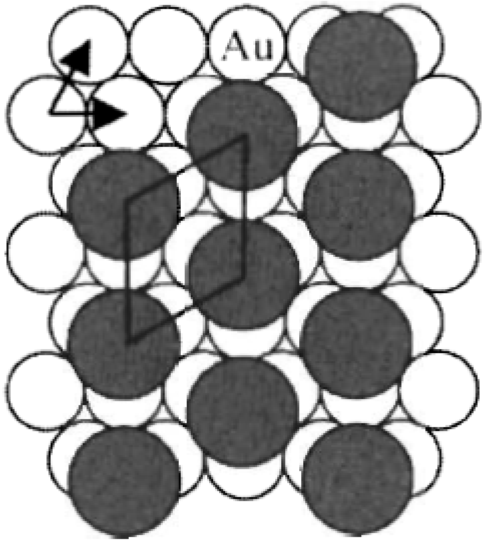
Description of the adsorbate structure

$$A(hkl)c\left(p'\times q'\right)R\beta - B$$

- Examples

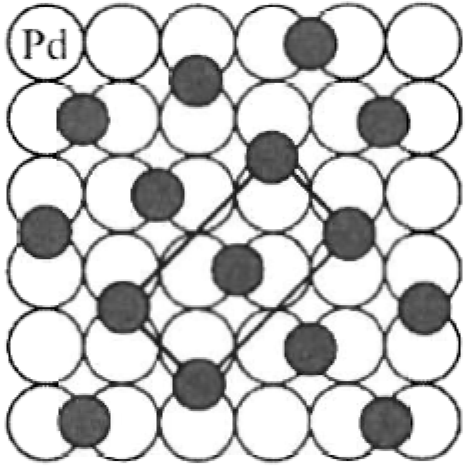


$Rh(110)\left(1\times1\right)-2H$



$Au(111)\left(\sqrt{3}\times\sqrt{3}\right)R30^0 -$

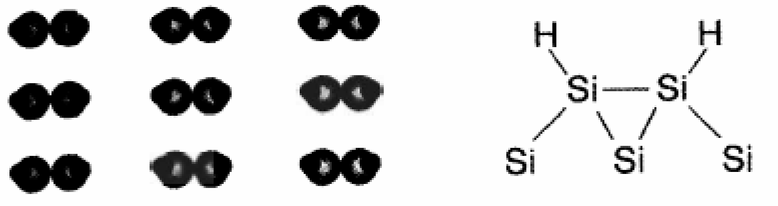
$-CH_3\left(CH_2\right)_n SH$



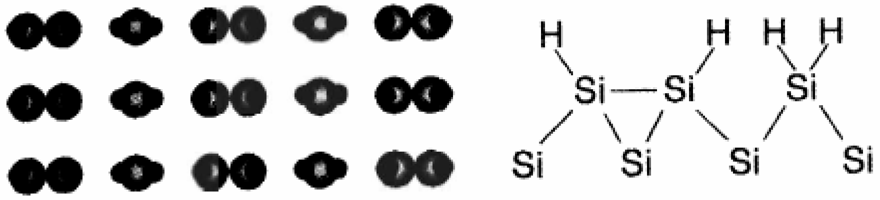
$Pd(100)c\left(2\sqrt{2}\times\sqrt{2}\right)R45^0-CO$

Adsorbate induced reconstruction

- adsorbates can induce reconstruction by reacting with dangling bonds on the surface: assymetric dimers of Si (100)-(2x1) surface are changed into symmetric Si (100)-(2x1):H, Si(111)-(7x7) is changed into Si(111)-(1x1):H and strain is relaxed

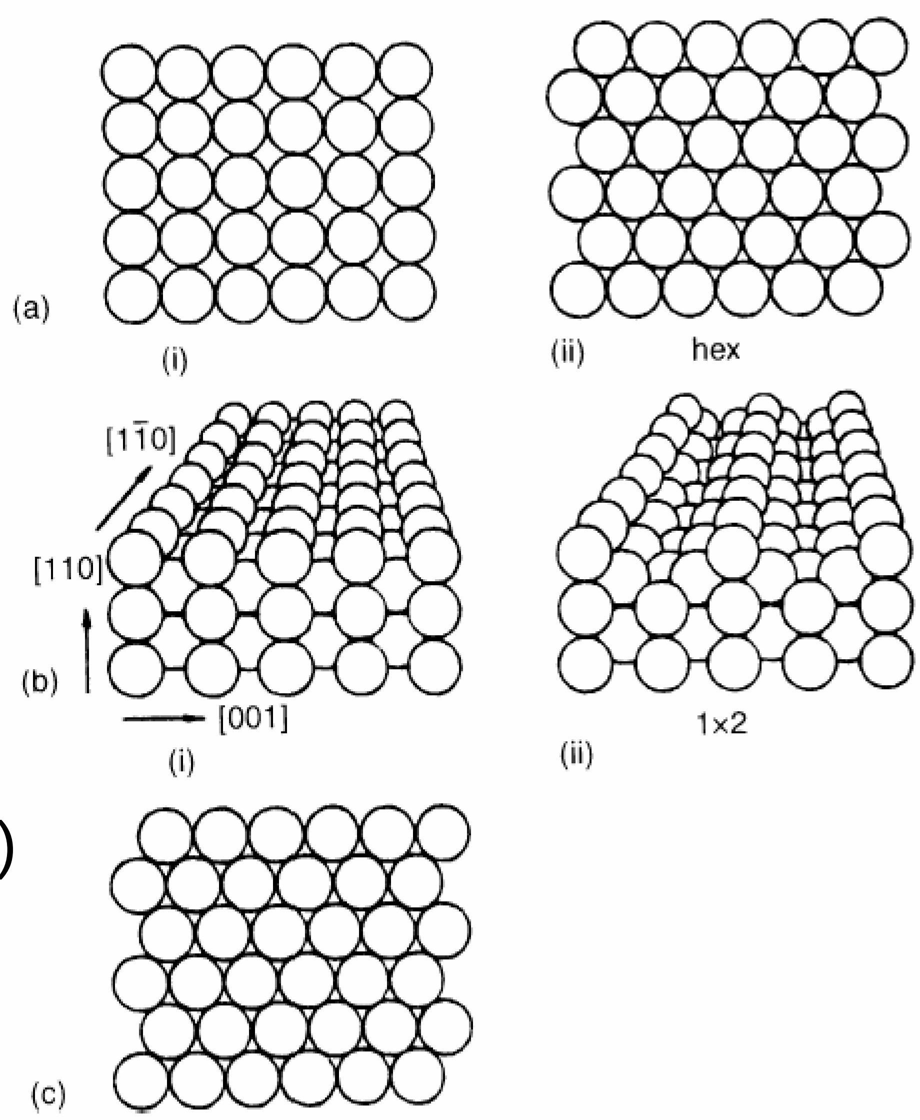


Si (100)-(2x1):H   at 1ML of H



Si (100)-(3x1):H   at 1.33ML of H

Adsorbate induced reconstruction: Pt



- Pt(100)-(1x1)

- Pt(100)-hex

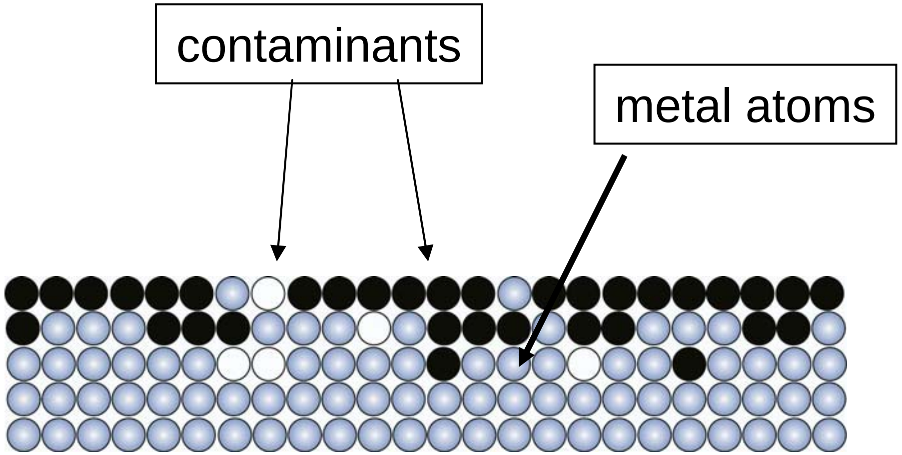
more stable, 40kJ/mol difference;
CO adsorbtion:
155kJ/mol on (1x1)
113kJ/mol on hex

- Pt(110)-(1x1)

- Pt(110)-(1x2)

- Pt(111)-(1x1)

Structure of a surface



contaminants

metal atoms

- Surface is contaminated when exposed to the atmosphere
- Surface has it’s own variety of defects

Structure of a surface

- Flux towards the surface

$$J = \frac{1}{4} n \bar{c}; \; n = \frac{P}{kT}; \; \bar{c} = \sqrt{\frac{8kT}{m\pi}}$$

$$J = \frac{P}{\sqrt{2\pi mkT}}, \text{ molecules/m}^2\text{s}$$

Vacuum	**Pressure (Torr)**	**Density (molecules m^{-3}**	**Mean Free Path (m)**	**ML (s)**
Atmospheric	760	2×10^{25}	7×10^{-8}	10^{-9}
Low	1	3×10^{22}	5×10^{-5}	10^{-6}
Medium	10^{-3}	3×10^{19}	5×10^{-2}	10^{-3}
High	10^{-6}	3×10^{16}	50	1
UltraHigh	10^{-10}	3×10^{12}	5×10^{5}	10^{4}

Preparation of clean surfaces

- Usually proper surfaces are cut from a single crystal (orientation controlled by X-ray),
- hard materials are grounded and polished
- soft materials are chemically/electrochemically cleaned
- additional cleaning in UHV chamber
  - thermal treatment
  - cleavage
  - sputtering
- In-situ preparation: evaporation, molecular beam epitaxy (MBE).

Thermodynamics of solid surfaces

- Surface strain:

$$d\varepsilon_{tot} = \frac{dA}{A} = d\varepsilon_p + d\varepsilon_e$$

increase of area per molecule

insertion of extra molecules, area per molecule constant

$$dW = \gamma^S dA = d\left(E_S N\right) = E_S \frac{\partial N}{\partial A} dA + N \frac{\partial E_S}{\partial A} dA$$

- for plastic deformation:

$$\left(\frac{\partial E_S}{\partial A}\right)_{pla} = \left(\frac{\partial E_S}{\partial\left(N\sigma_A\right)}\right) = \frac{1}{\sigma_A}\left(\frac{\partial E_S}{\partial\left(N\right)}\right) = 0$$

$$\gamma^S{}_{pla} = \left(E_S \frac{\partial N}{\partial A}\right)_{pla} = \frac{E_S}{\sigma_A} \equiv \gamma$$

Thermodynamics of solid surfaces

- Elastic deformation

$$\left(\frac{\partial E_S}{\partial A}\right)_{pla} = \left(\frac{\partial E_S}{\partial \left(N\sigma_A\right)}\right) = \frac{1}{\sigma_A}\left(\frac{\partial E_S}{\partial \left(N\right)}\right) = 0$$

$$\gamma^{S}{}_{ela} = \left(N\frac{\partial E_S}{\partial A}\right)_{ela} = \frac{\partial E_S}{\partial \sigma_A} = \gamma + \sigma_A \frac{\partial \gamma}{\partial \sigma_A}\Bigg|$$

$$\gamma^{S}{}_{ela} \equiv \Upsilon = \gamma + \frac{\partial \gamma}{\partial \varepsilon_e}\Bigg|$$

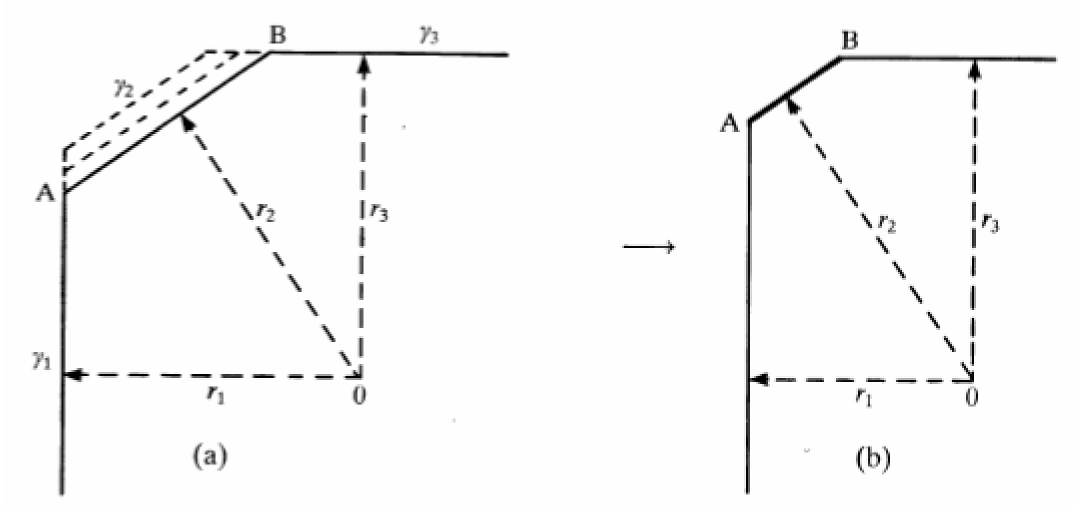
Surface stress

Shape of a crystal

- Crystal faces grow in such a way as to minimize the total surface energy
- Wulff's law:

$$\frac{\gamma_1}{r_1} = \frac{\gamma_2}{r_2} = \frac{\gamma_3}{r_3} = const$$

Adsorption of impurities might steer the crystal away from the equilibrium shape



(a) (b)

Shape of a crystal

- Example: growth of a prismatic crystal at constant volume

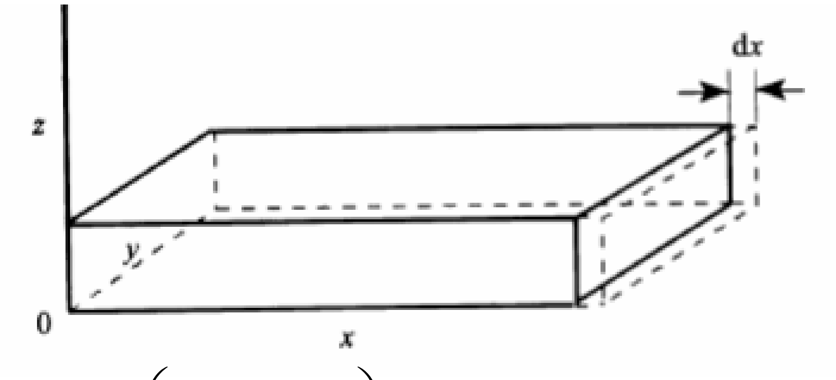
$$dF = -SdT - pdV + \mu dn + \gamma dA$$

$$dT = 0; dV_s = -dV_{liq};\ dn_s = -dn_{liq};\ \mu_s = \mu_{liq}$$

$$dF_s - dF_{liq} = 0 = -(p_s - p_{liq})dV + \sum_i \gamma_i dA_i$$

$$-(p_s - p_{liq})yzdx + 2\gamma_y zdx + 2\gamma_z ydx = 0$$

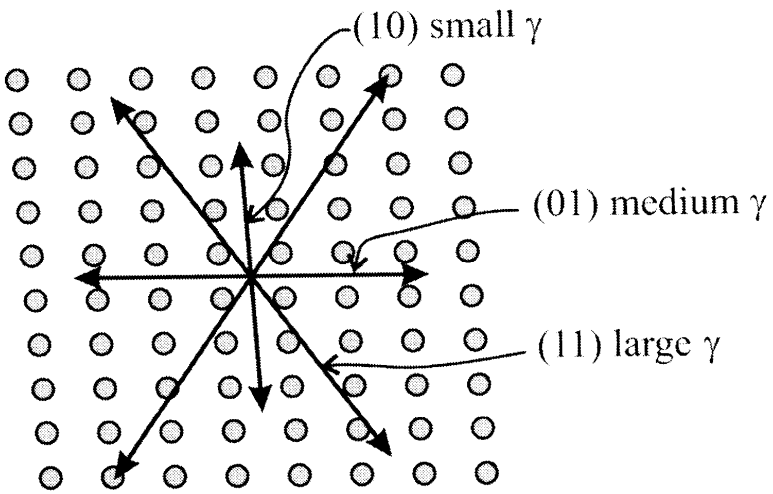
$$\frac{\gamma_y}{y} + \frac{\gamma_z}{z} = \frac{1}{2}(p_s - p_{liq}) = \frac{\gamma_y}{y} + \frac{\gamma_x}{x} = \frac{\gamma_x}{x} + \frac{\gamma_z}{z}$$

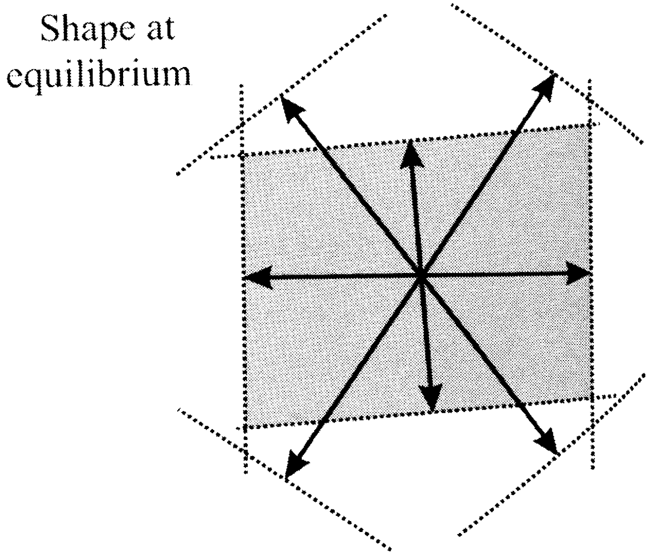


$$\frac{\gamma_x}{x} = \frac{\gamma_y}{y} = \frac{\gamma_z}{z} = const = \frac{1}{4}(p_s - p_{liq}) \qquad \text{compare: } -\Delta p = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Shape of a crystal

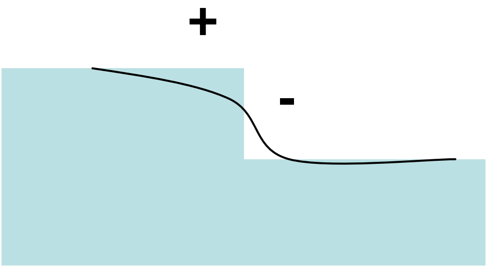
- How to plot the shape of the crystal:



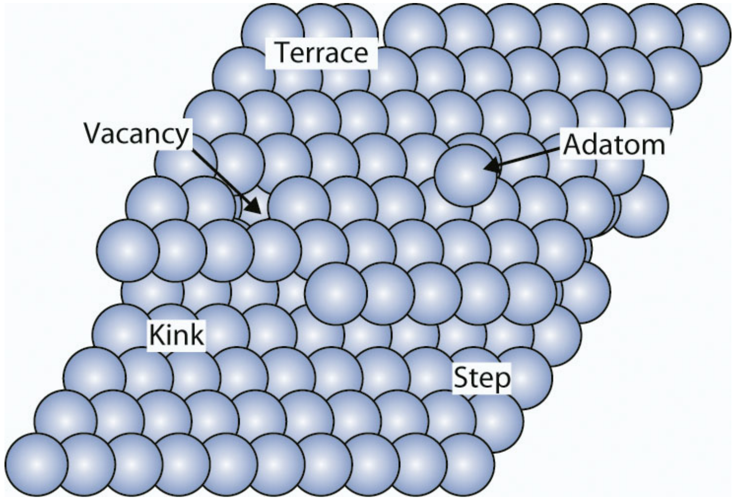


Vicinal surfaces

- vicinal surface – high index plane (hkl) with h, k, l > 1)
- have tendency to stay close to low-index structure by introducing steps or facets
- electronic structure (and reactivity) of steps is different from terraces!
- bimetallic surfaces: as the energy of A-A, B-B, and A-B bonds can be different , the surface will be enriched by low surface energy species



Smoluchowski smoothing



Techniques for studying solid surface

- Spectroscopic methods give information on identity and chemistry of the surface

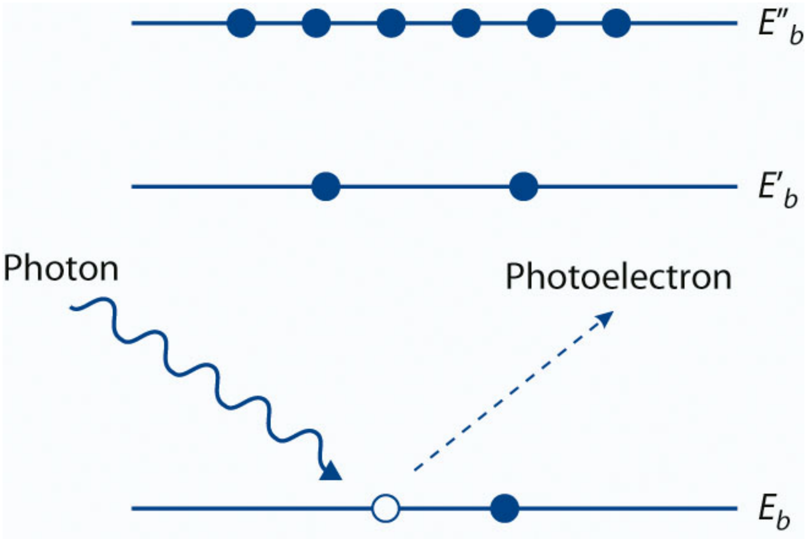
- X-ray photoelectron spectroscopy (XPS)

- developed in 1950s by Kai Siegbahn (Nobel price 1981)
- provides information on binding energy

$$E_k = h\nu - E_b + \phi$$

kinetic energy of a photoelectron

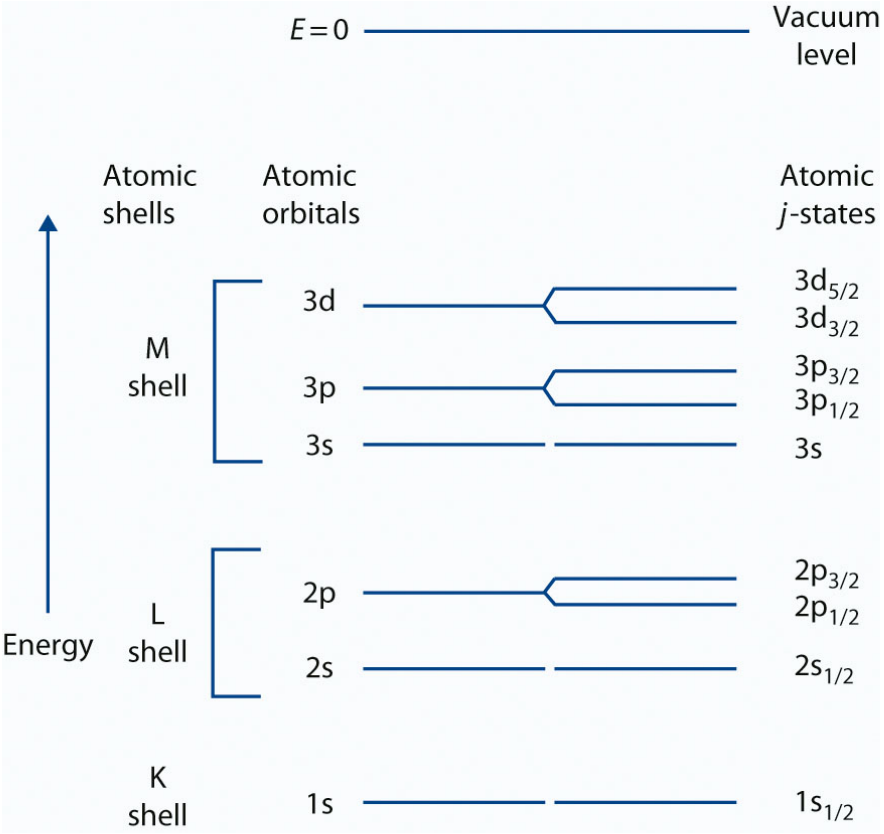
spectrometer work function

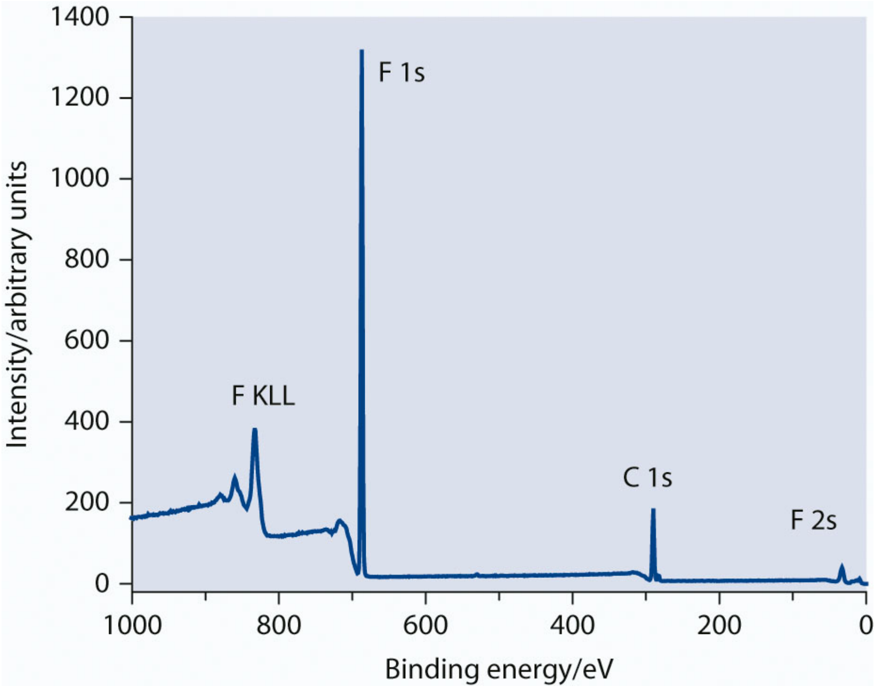


Spectroscopic and diffraction methods

- XPS

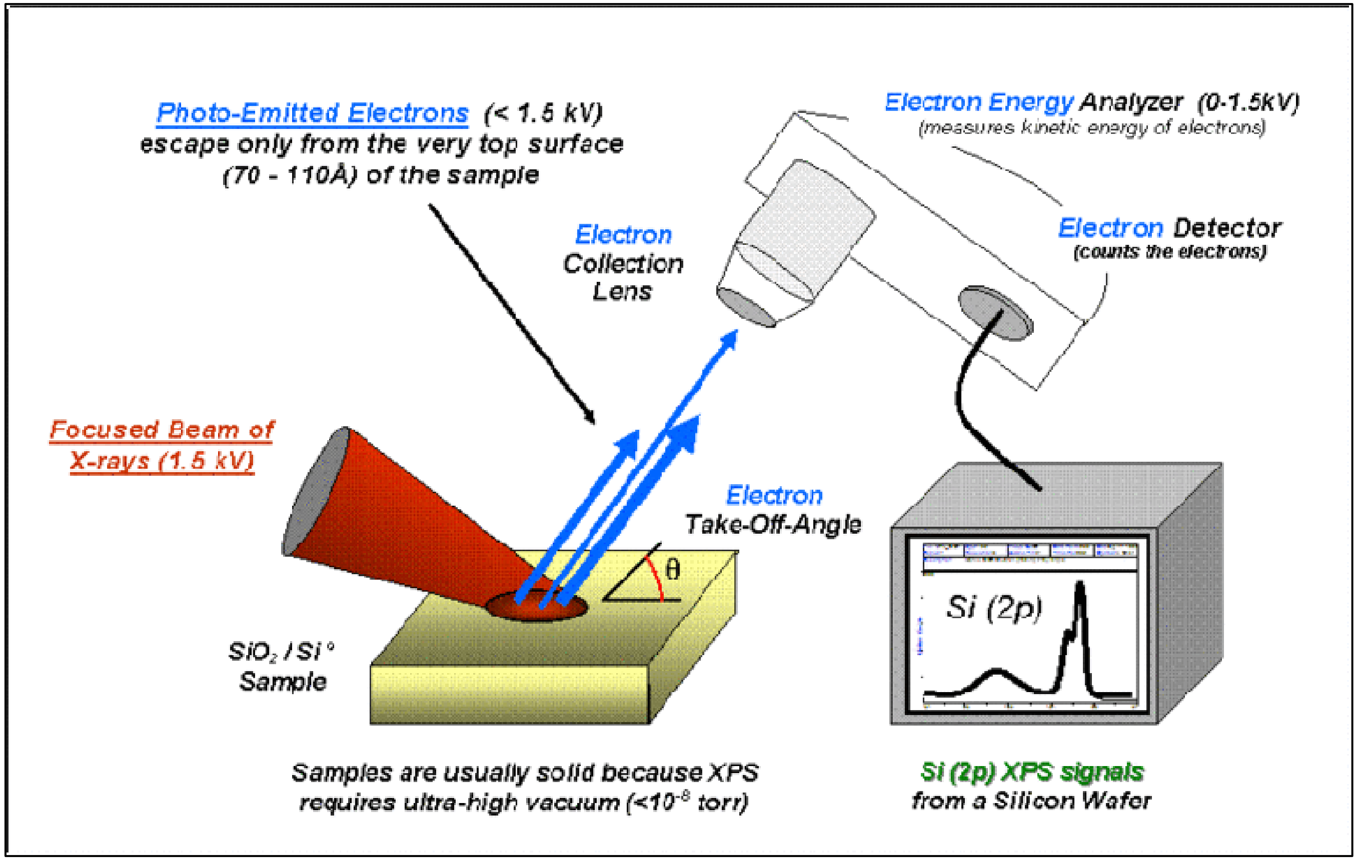
$$E_k = h\nu - E_b + \phi$$





XPS spectrum of FEP
(fluorinated ethylene propylene)

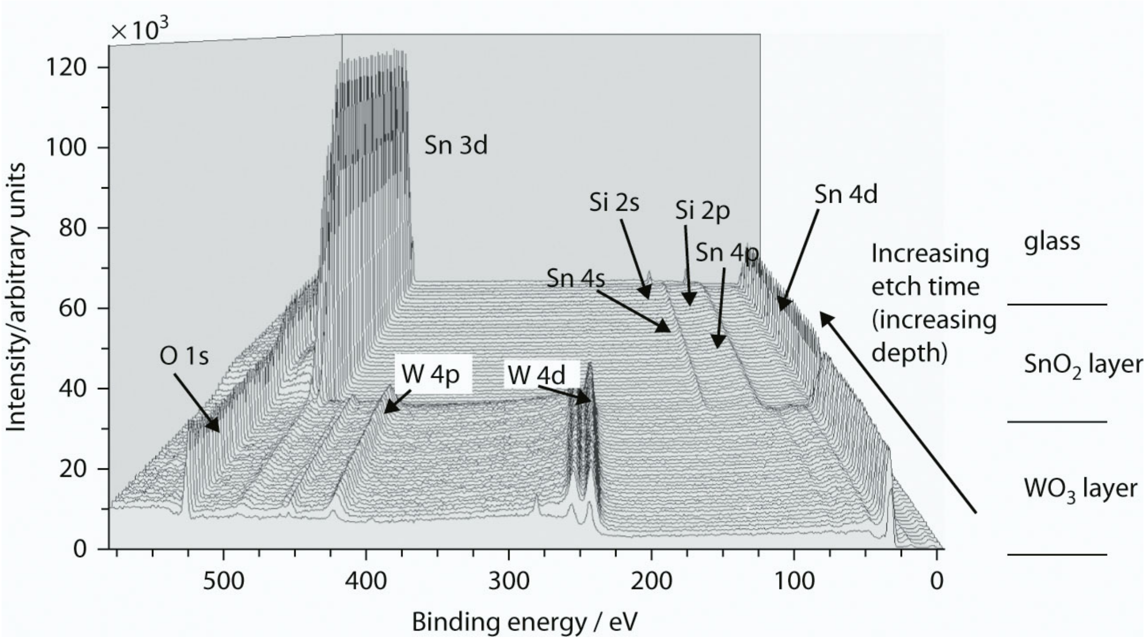
XPS

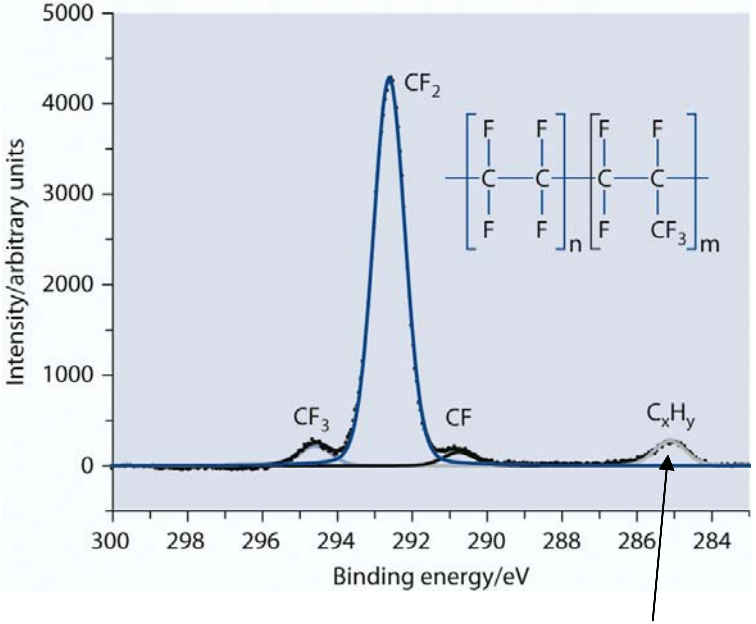


- XPS is also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis.
- XPS detects all elements with an atomic number (Z) between those of lithium (Z=3) and lawrencium (Z=103). This limitation means that it cannot detect hydrogen (Z=1) or helium (Z=2).
- Detection limits for most of the elements are in the parts-per-thousand (PPTh) range.
- XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, etc.

XPS

- depth profiling is possible (w. ion gun)
- can be measured with high spatial resolution
- **peak position** depends on chemical environment (**chemical shift**)
- **peak intensity** depends on the concentration (and photoemission cross-section)

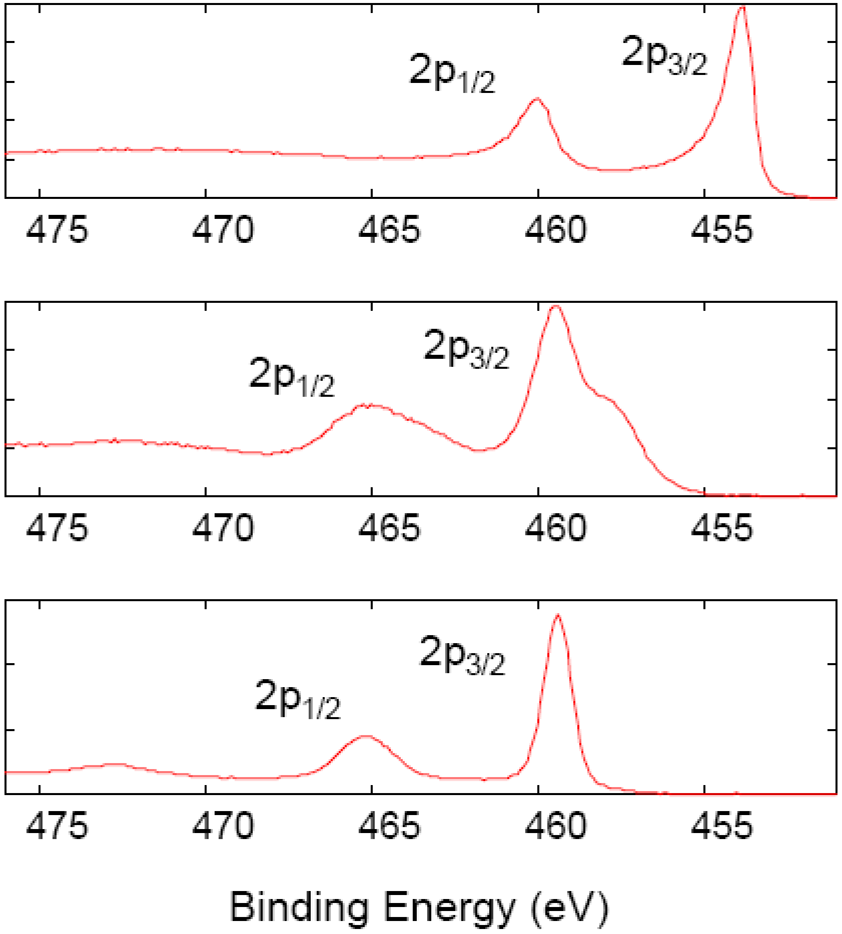




carbon surface contamination

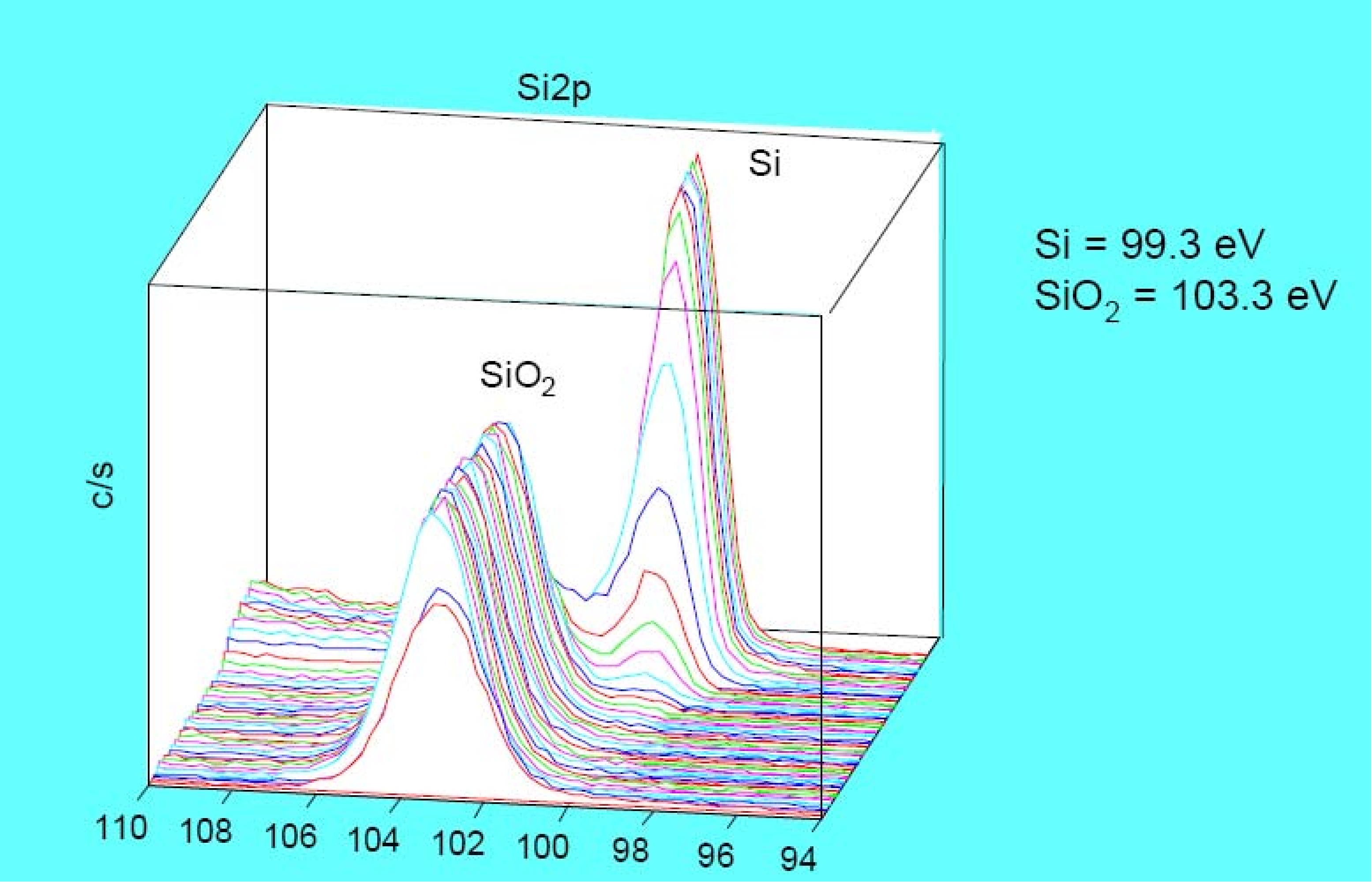
XPS

- Chemical shift: Ti – TiO_2.



XPS

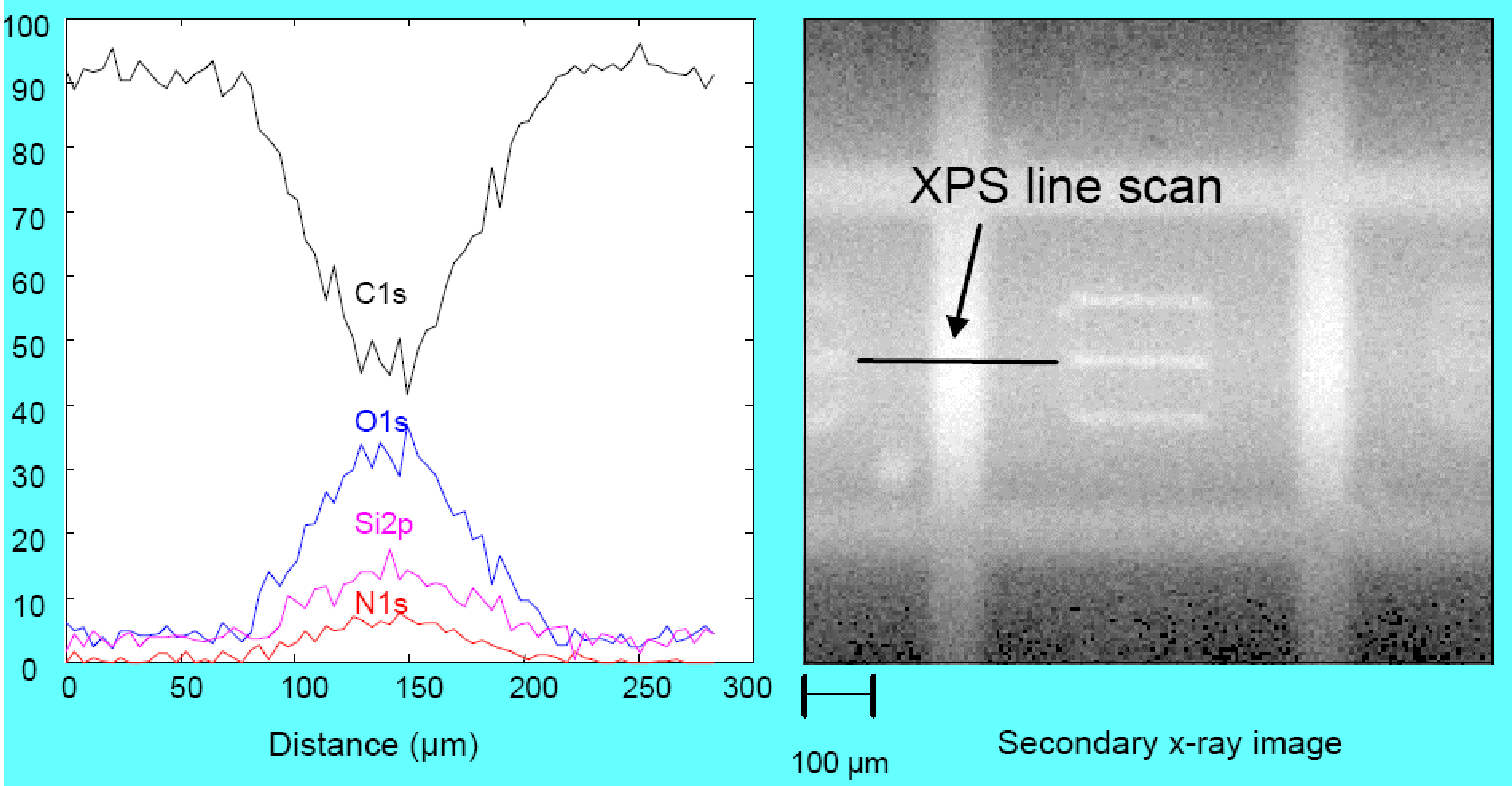
- Depth profiling of a chemical shift in Si/SiO_2.



Si = 99.3 eV
SiO_2 = 103.3 eV

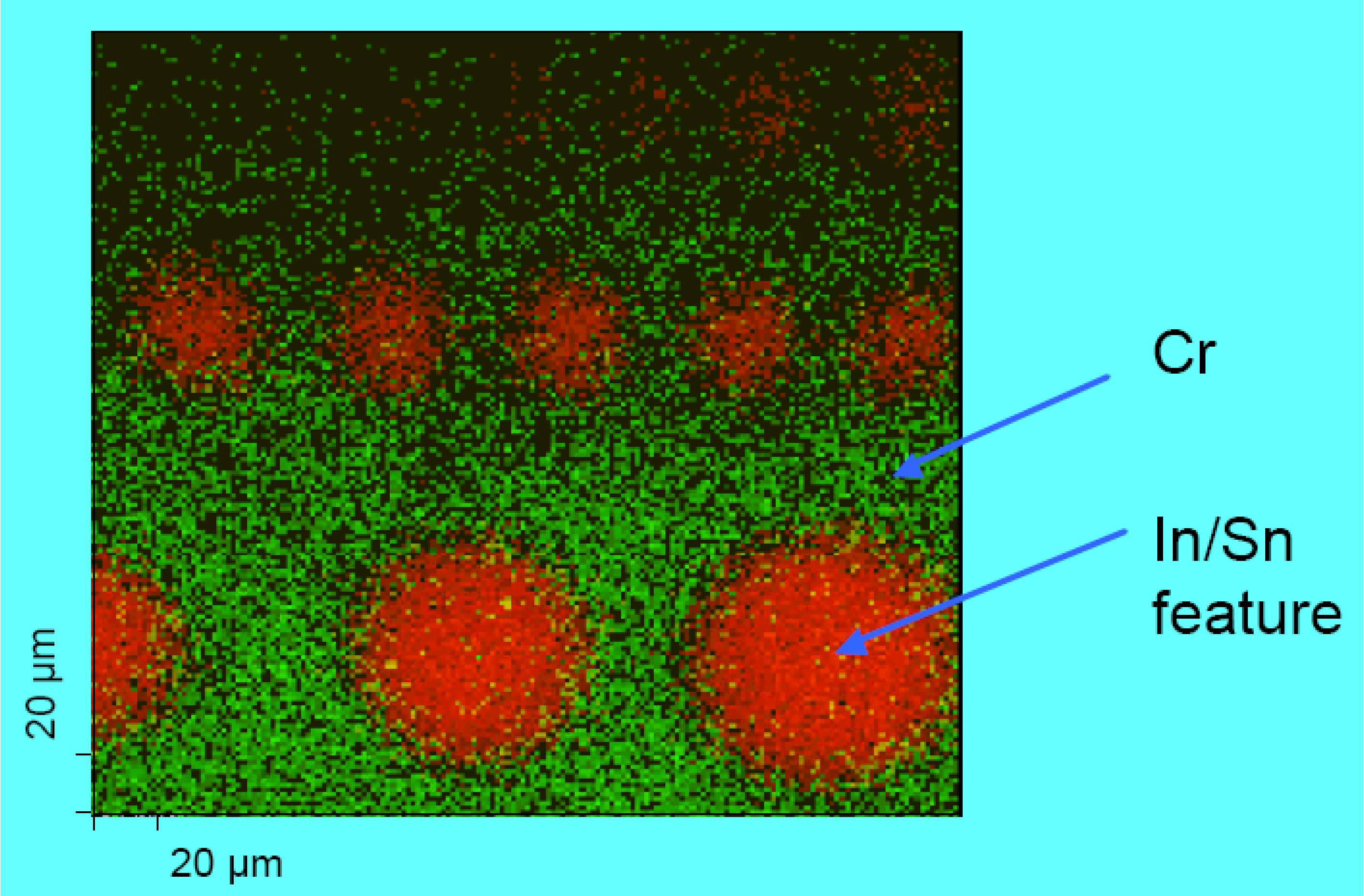
XPS

- Imaging and line profiling: profiling a polymer film with 20um Al Kα X-ray beam



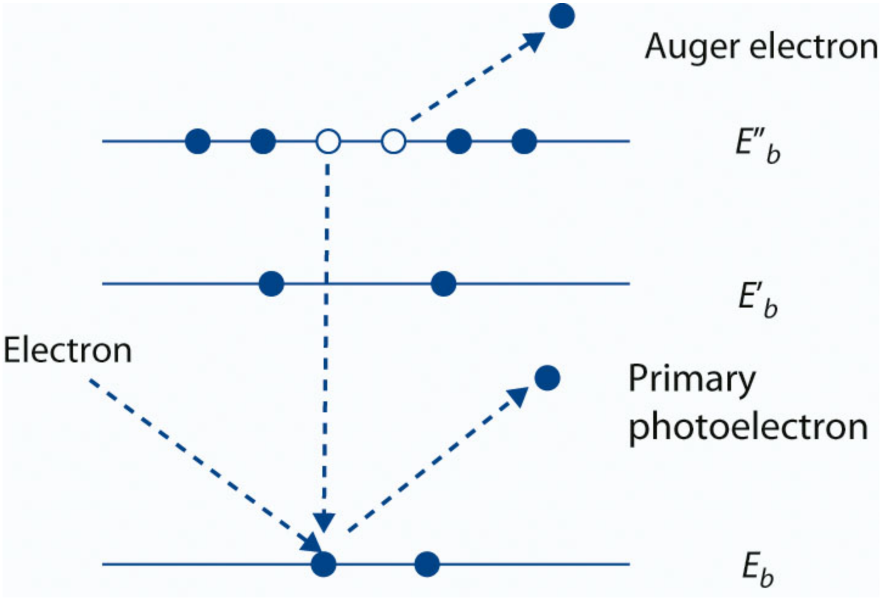
XPS

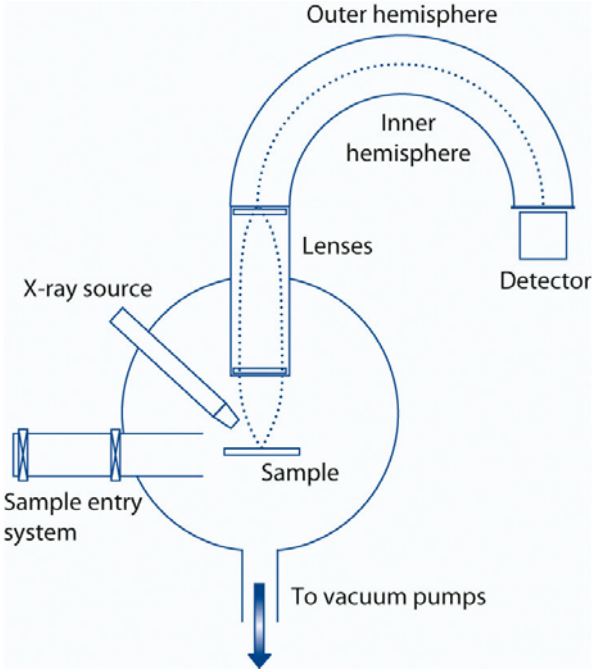
- XPS elemental map



Auger electron spectroscopy

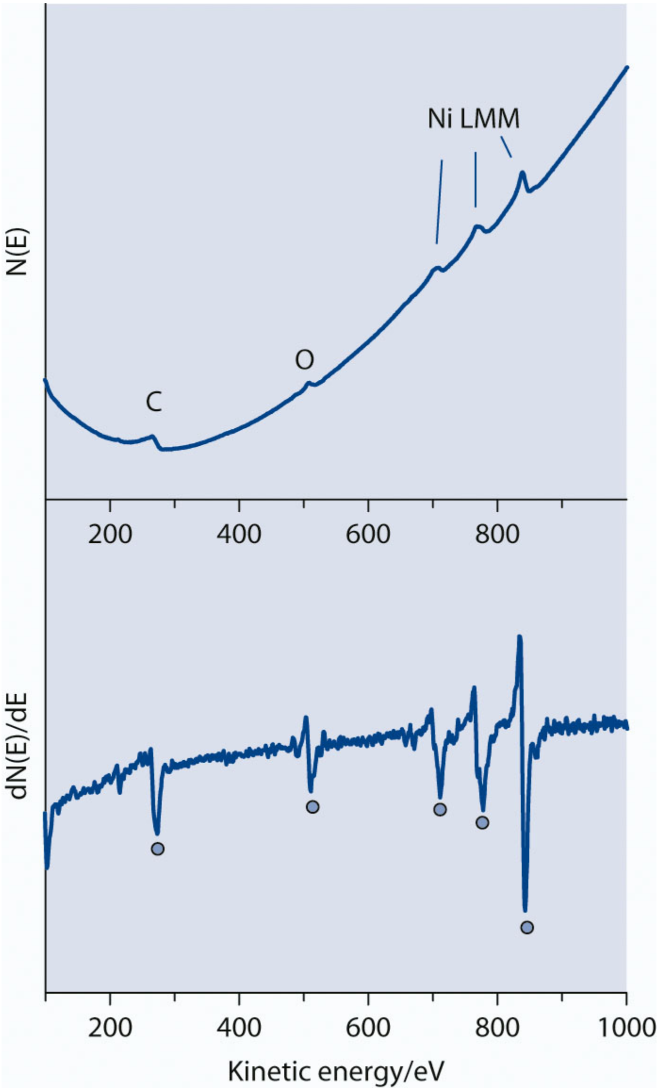
- Auger process:
  1. incident photon (electron) causes ejection of of a primary photoelectron
  2. excited ion relaxes either by X-ray fluorescence or by Auger process (ejection of an Auger electron)





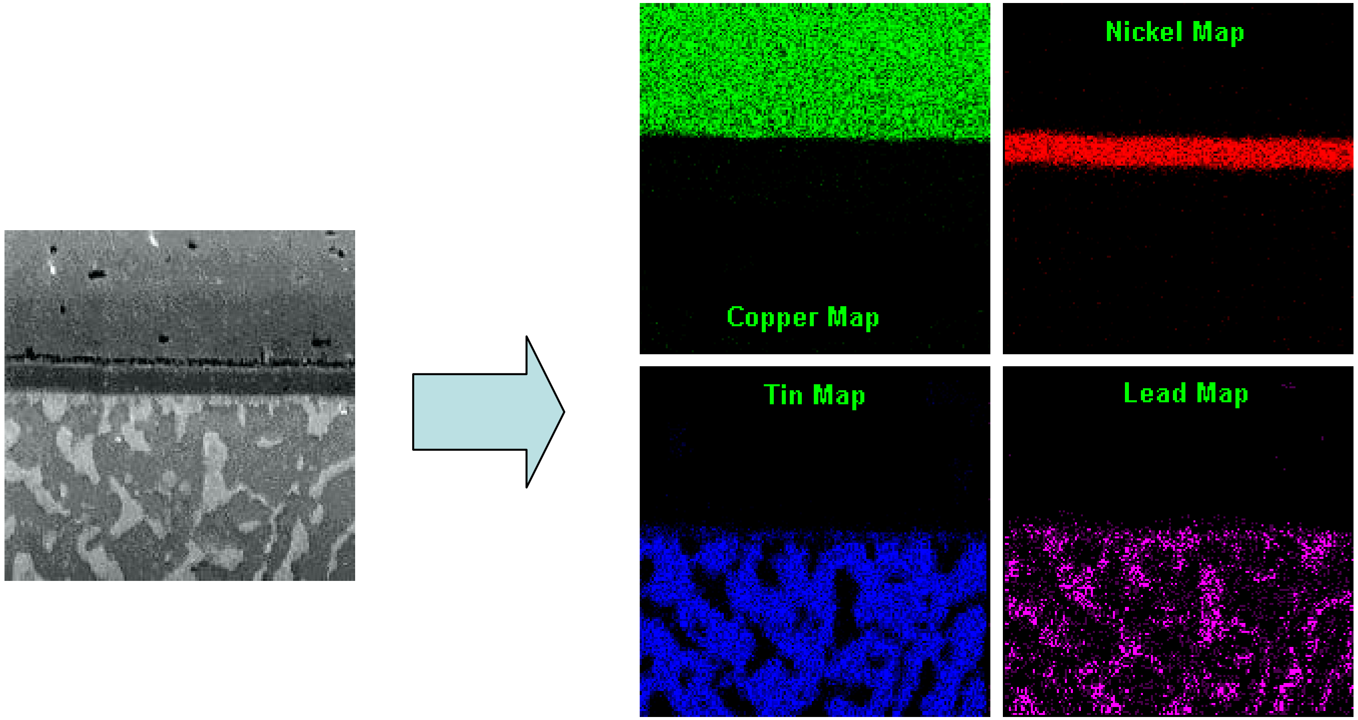
Auger spectroscopy

- in Auger spectroscopy position of peaks is determined by binding energy, doesn't depend on the incident energy
- peaks are marked as e.g. KL_2L_3 where:
  - first letter: initial ionization shell;
  - second: shell where electron dropped from:
  - third: shell where electron is ejected from



Energy Dispersive X-ray Analysis (EDX)

- Not really a surface technique (generated from up to 10um in depth)



Secondary ion mass spectroscopy (SIMS)

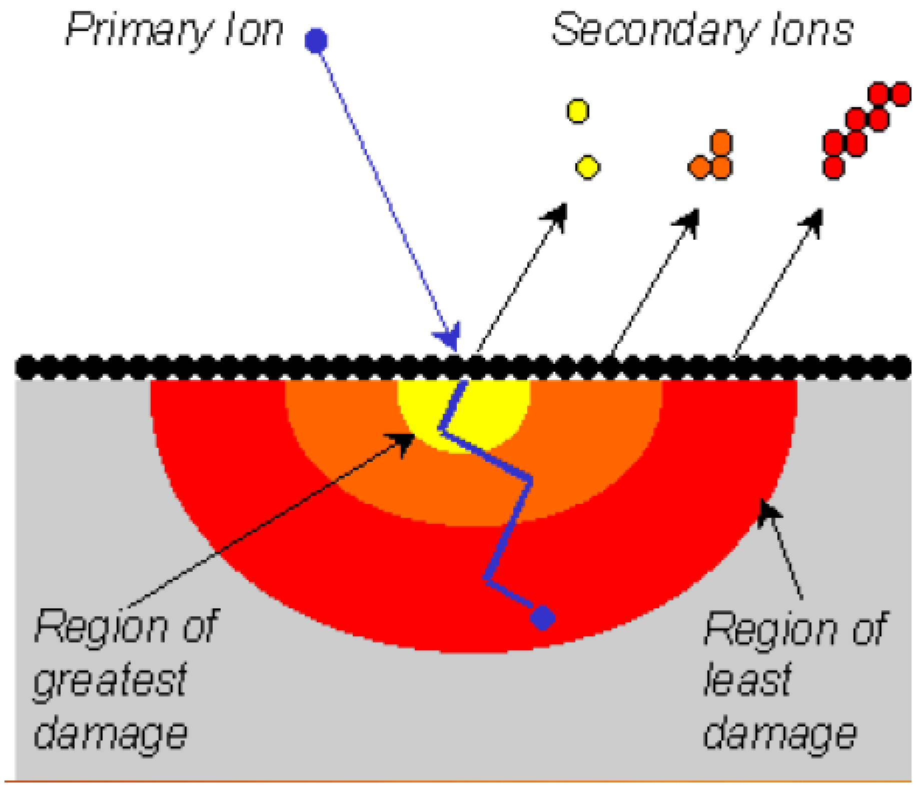
- surface is bombarded by ions of high energy, removed ions analyzed for their masses

Advantages:

- excellent sensitivity for various surfaces incl. organic films, polymers, semiconductors etc.
- can detect all elements and isotopes including H;
- depth profile possible

Weaknesses:

- Destructive
- No chemical information

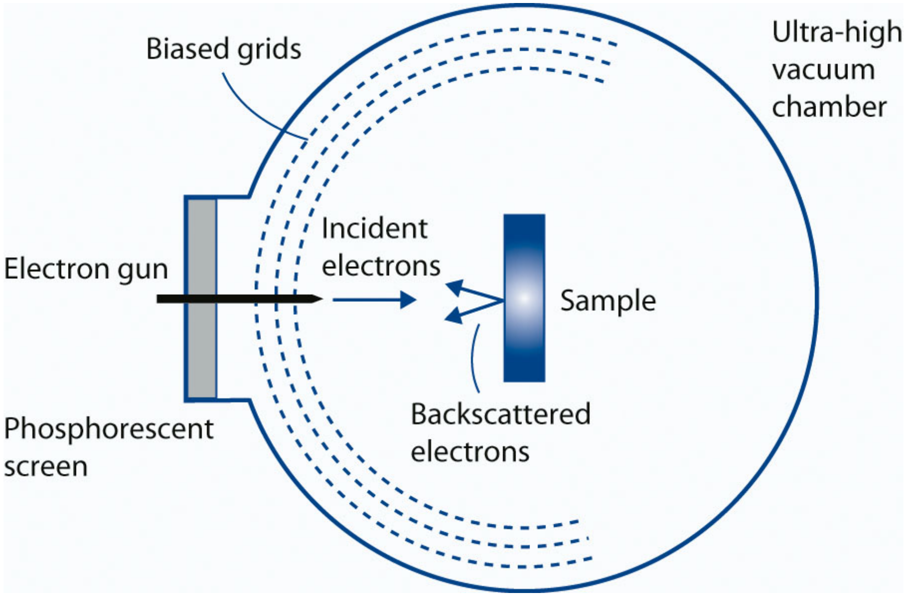


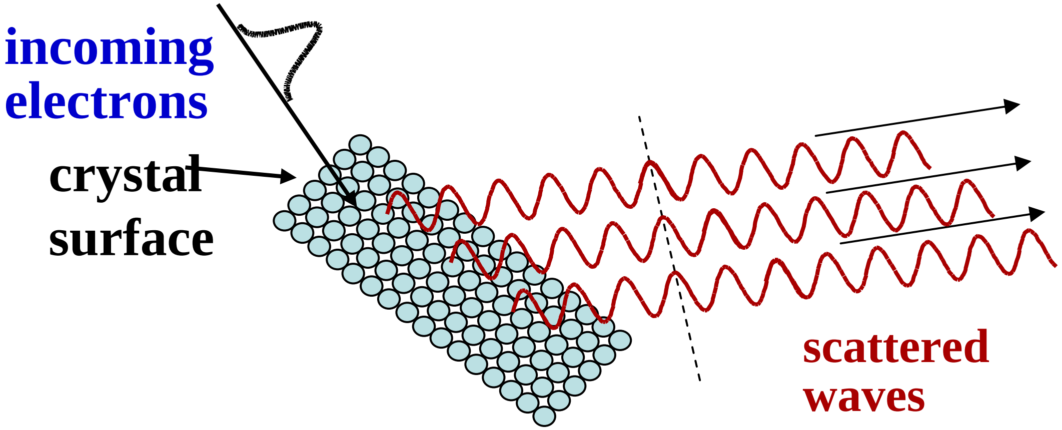
Diffraction-based techniques

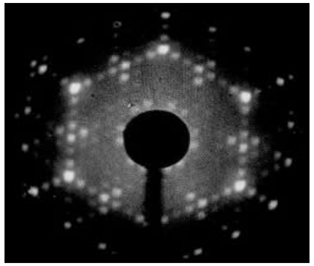
- Low-energy electron diffraction LEED
- Grazing incidence X-ray diffraction GIXD
- Atomic beam diffraction

Low energy electron diffraction (LEED)

- electrons of low energy (20eV-1keV) are elastically scattered from sample)
- due to low penetration depth (0.5-1.5nm) information about few top layers is obtained
- produces information on crystal structure of surface layer and the coordinates of atom within the unit cell
- usually other measurements (or assumptions) are required as multiple scattering complicates the situation







LEED diffraction pattern

Imaging techniques

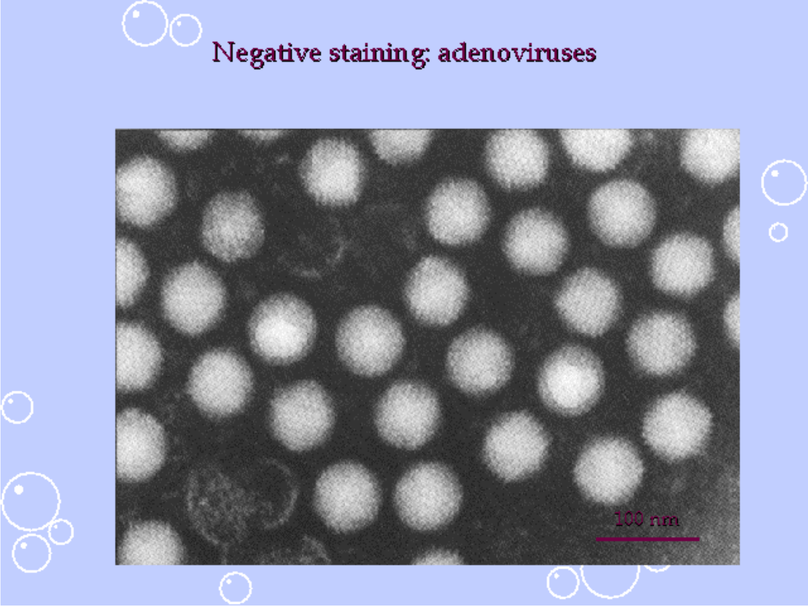
- Scanning Electron Microscopy (SEM)
- Transmission Electron microscopy (TEM)
- Scanning Probe Microscopy (STM, AFM etc.)

TEM

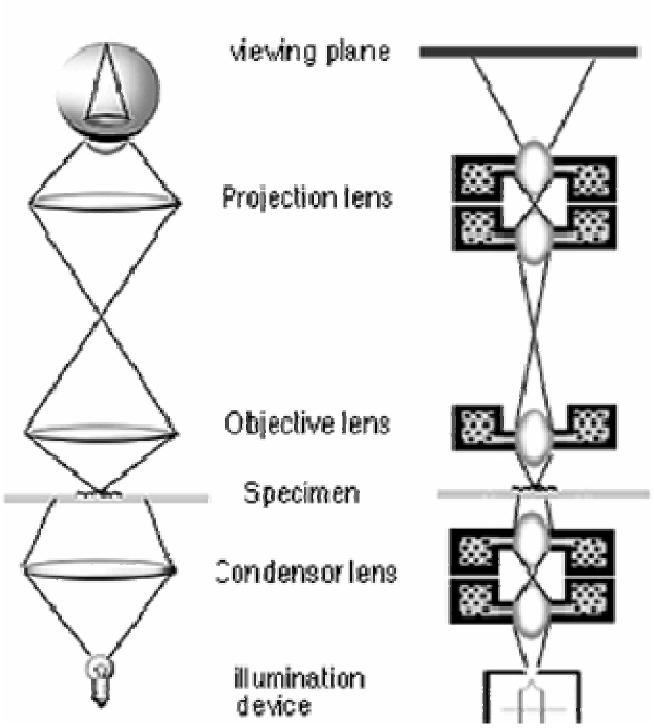
- Imaging electrons transmitted through thin (100nm and below) sections of a sample
- typical energies 1-400 keV

$$\lambda = h / p = h / \sqrt{2mE}$$

- wavelength: 0.4-0.02 Å

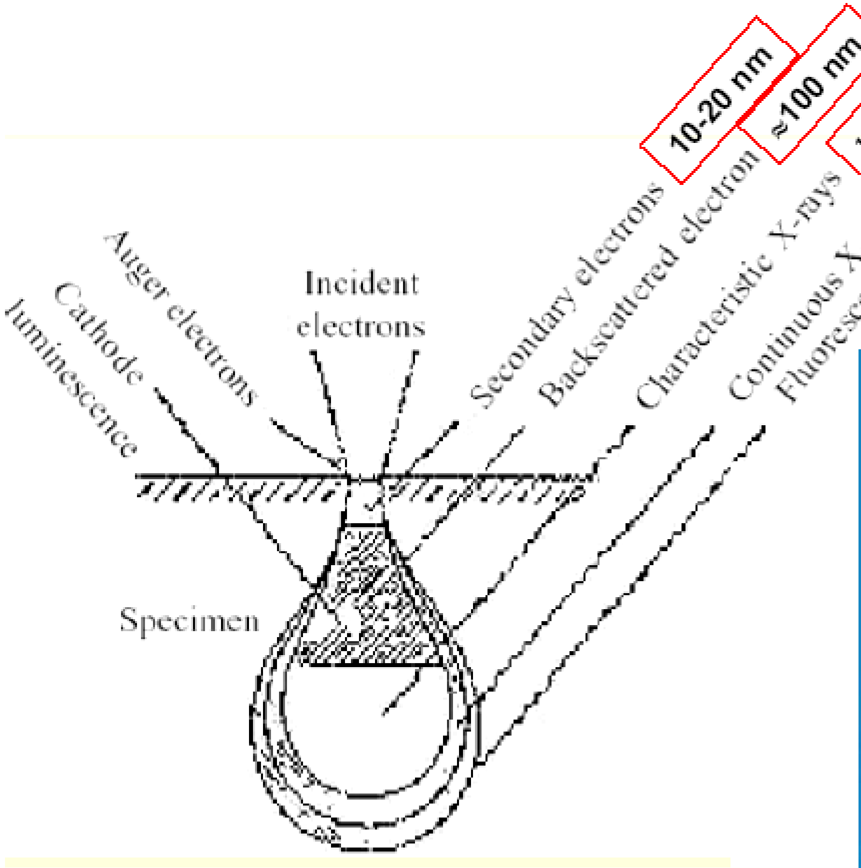


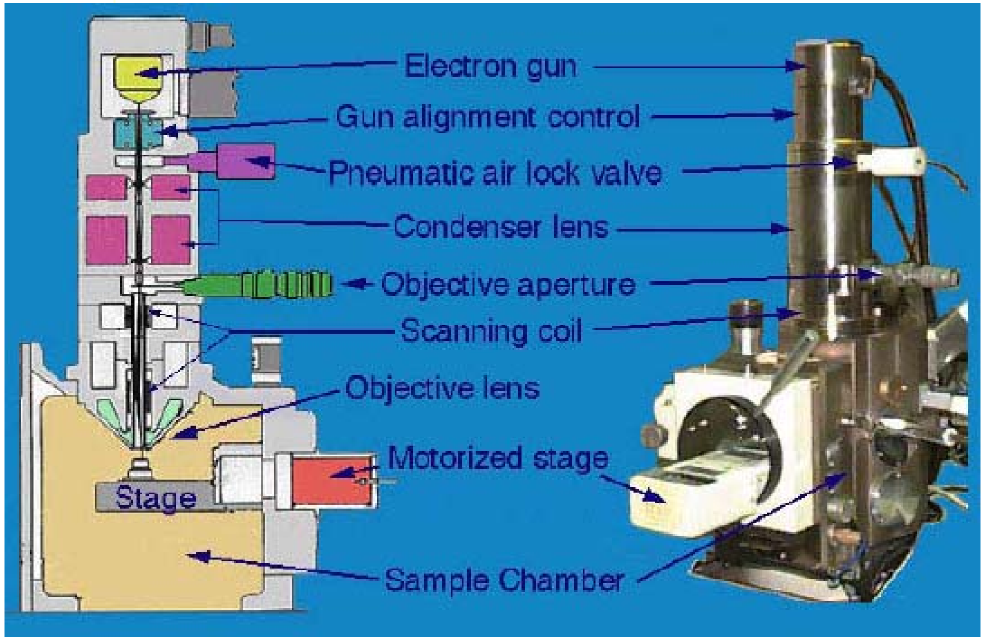
Negative staining: adenoviruses



SEM

- Backscattered electron imaging
- Secondary electron imaging
- EDX

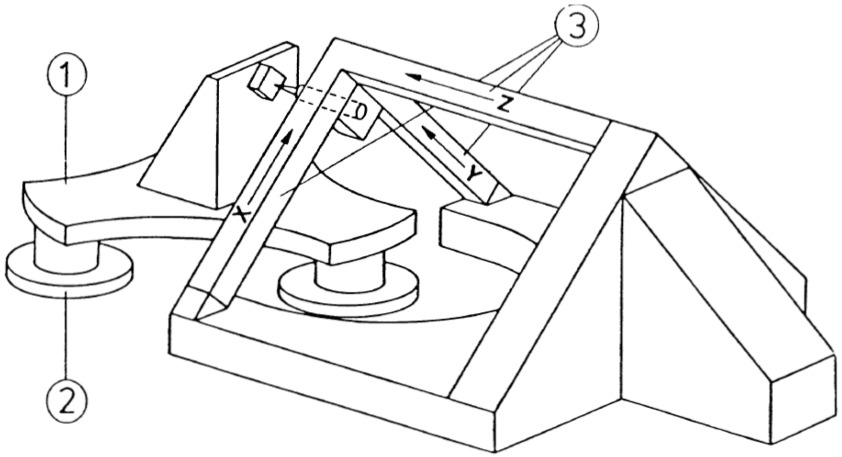


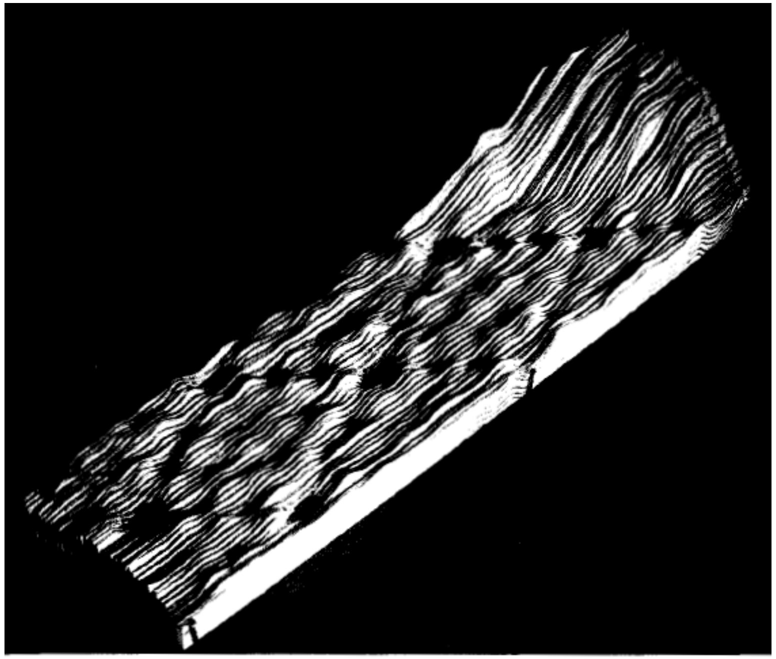


Scanning probe techniques

- Binning and Rohrer 1982 (Nobel prize 1985)

Binning and Rohrer, Helv.Phys.Acta 55, 726 (1982)



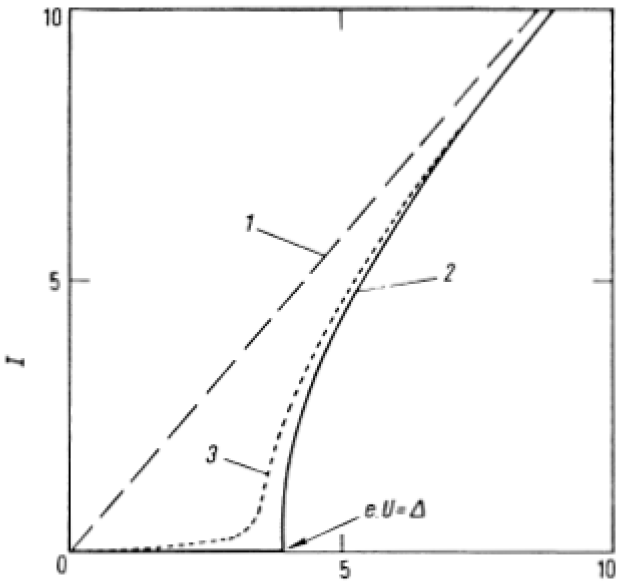


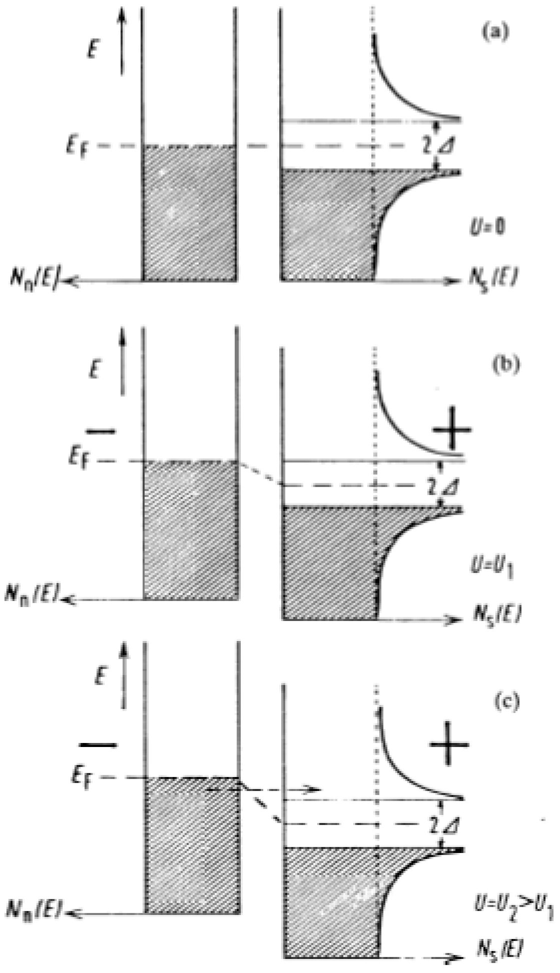
Provides:

- topographical information (electron density vs. coordinate)
- spectroscopic information: electron density of states vs. energy)

Tunneling

- Tunneling and band structure:
  - Metal-Superconductor





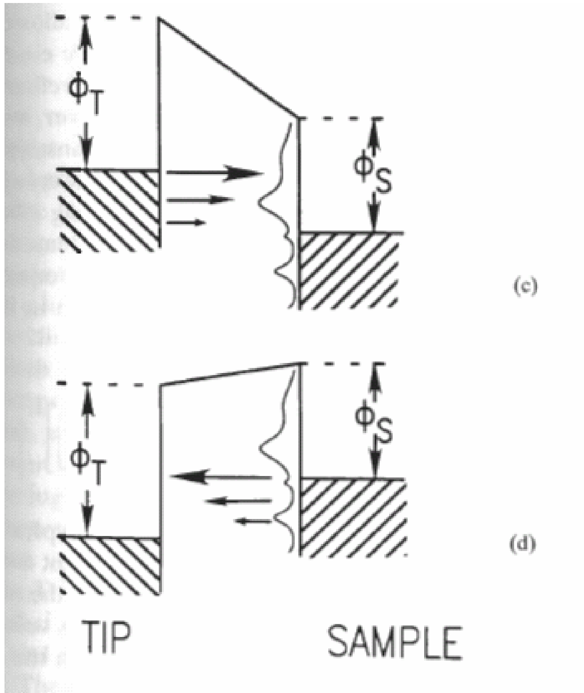
STM spectroscopy

- In constant current STM we are imaging LDOS at fixed energy E_F+eV
- If we scan a tip/sample voltage at a point we will profile LDOS vs E_F+eV at a given point

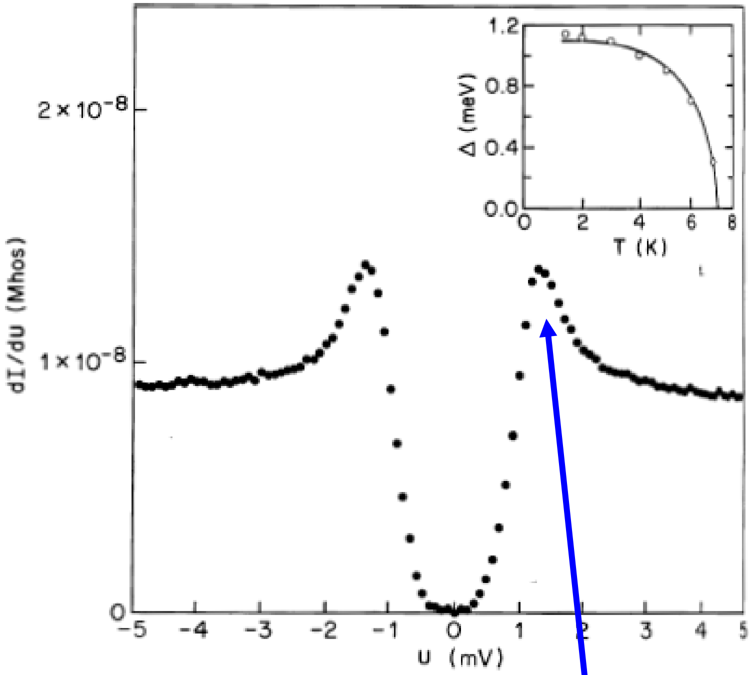
dI/dV ~ density of states

Positive bias applied, electrons tunnel from the tip

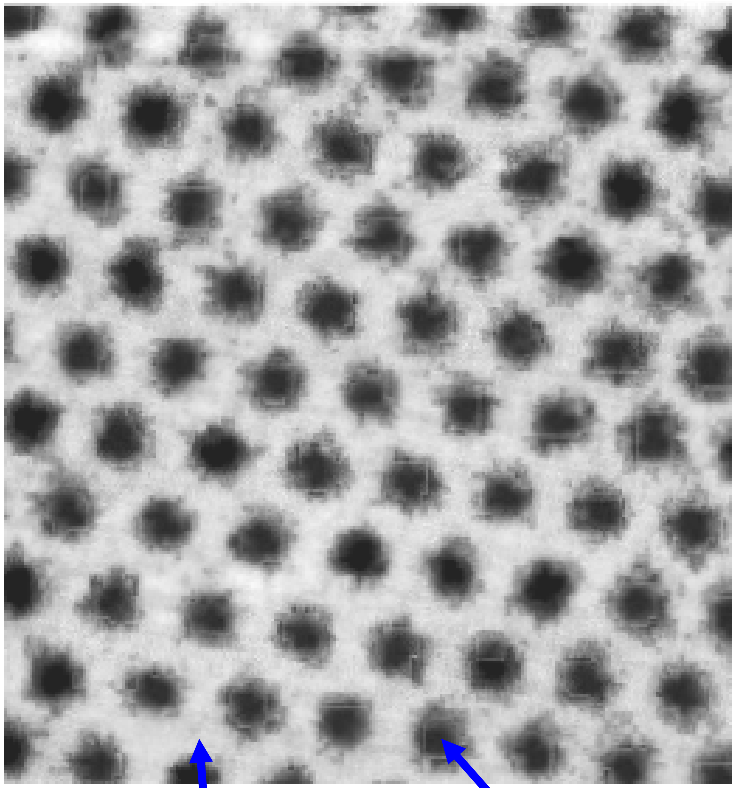
Negative bias applied, electrons tunnel from the sample



STM imaging vortices in a superconductor



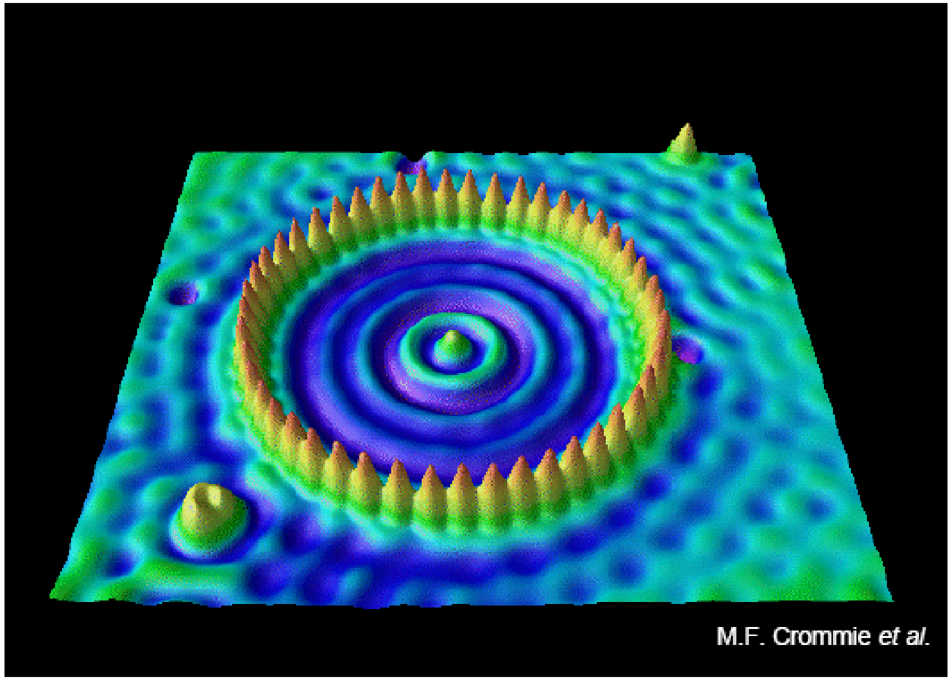
Imaging set point



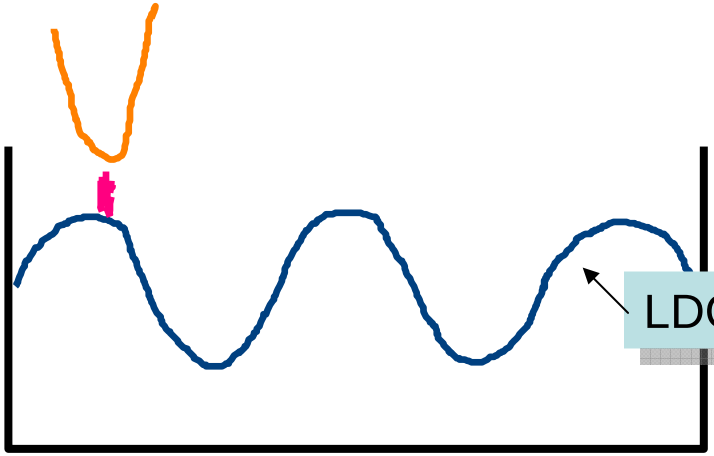
Superconductor (bright, high LDOS at set point)

Vortex (normal core), dark - low LDOS at set point)

Electron in a box



M.F. Crommie *et al.*



LDOS for electron in a box

Scanning probe techniques

- AFM and related techniques:
    - Lateral force microscopy (LFM)
    - Magnetic force microscopy (MFM)
    - Electrostatic force microscopy (EFM) etc…