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SURFACE ANALYSIS

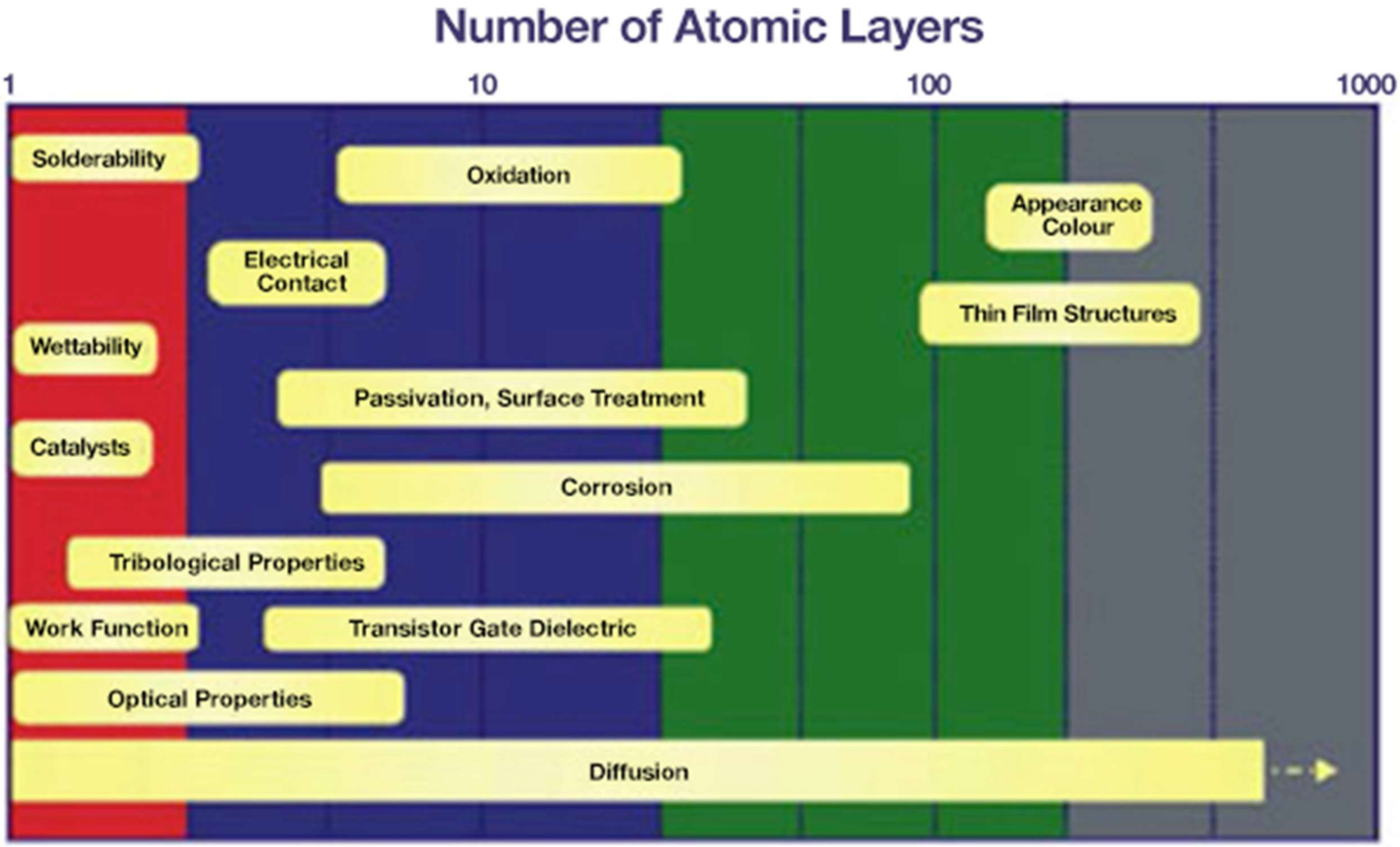
GÁBOR DOBOS

Outline

- Introduction
  - What is the „surface”?
  - Why is it important?
  - Surface sensitive analytical methods
- Secondary Ion Mass Spectroscopy (SIMS)
- Auger Electron Spectroscopy (AES)
- X-ray Photoelectron Spectroscopy (XPS)

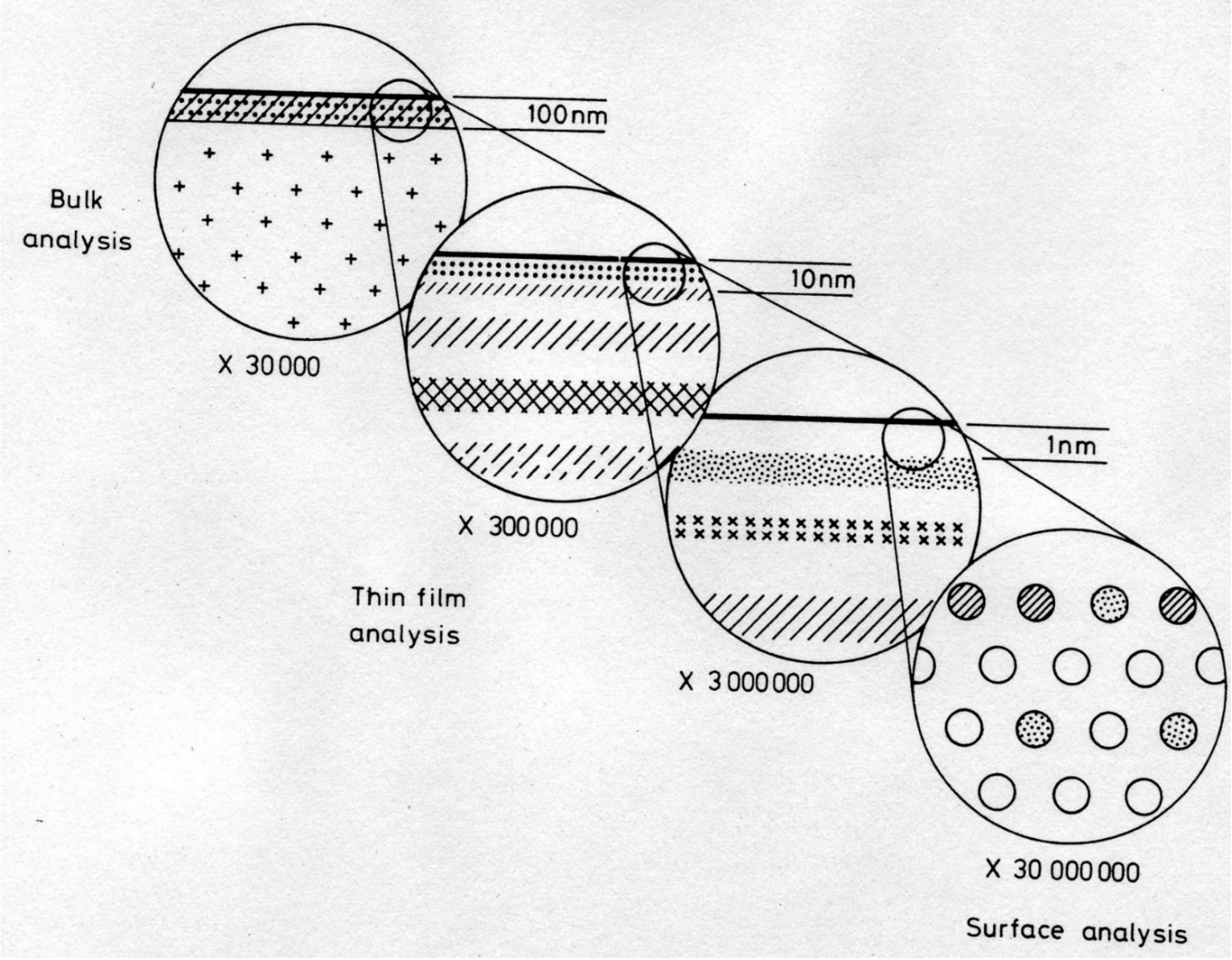
Literature

- Shigemasa Suga, Akira Sekiyama, Christian Tusche: Photoelectron Spectroscopy: Bulk and Surface Electronic Structures, Springer 2021
- M. Kiguchi et. al.:Compendium of Surface and Interface Analysis, Springer 2018
- S. Hofmann: Auger- and X-Ray Photoelectron Spectroscopy in Materials Science, Springer, 2012
- John C. Vickerman, Ian Gilmore, Surface Analysis: The Principal Techniques, Wiley, 2011
- D. Briggs, J.T. Grant: Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, IMPublications, 2003
- J.C. Vickerman, D. Briggs: ToF-SIMS: Surface Analysis by Mass Spectrometry, IMPublications, 2001
- D. Briggs, M.P. Seah: Practical Surface Analysis, Wiley, 1990
- www.nist.gov
- xpssimplified.com
- http://www.xpsfitting.com/

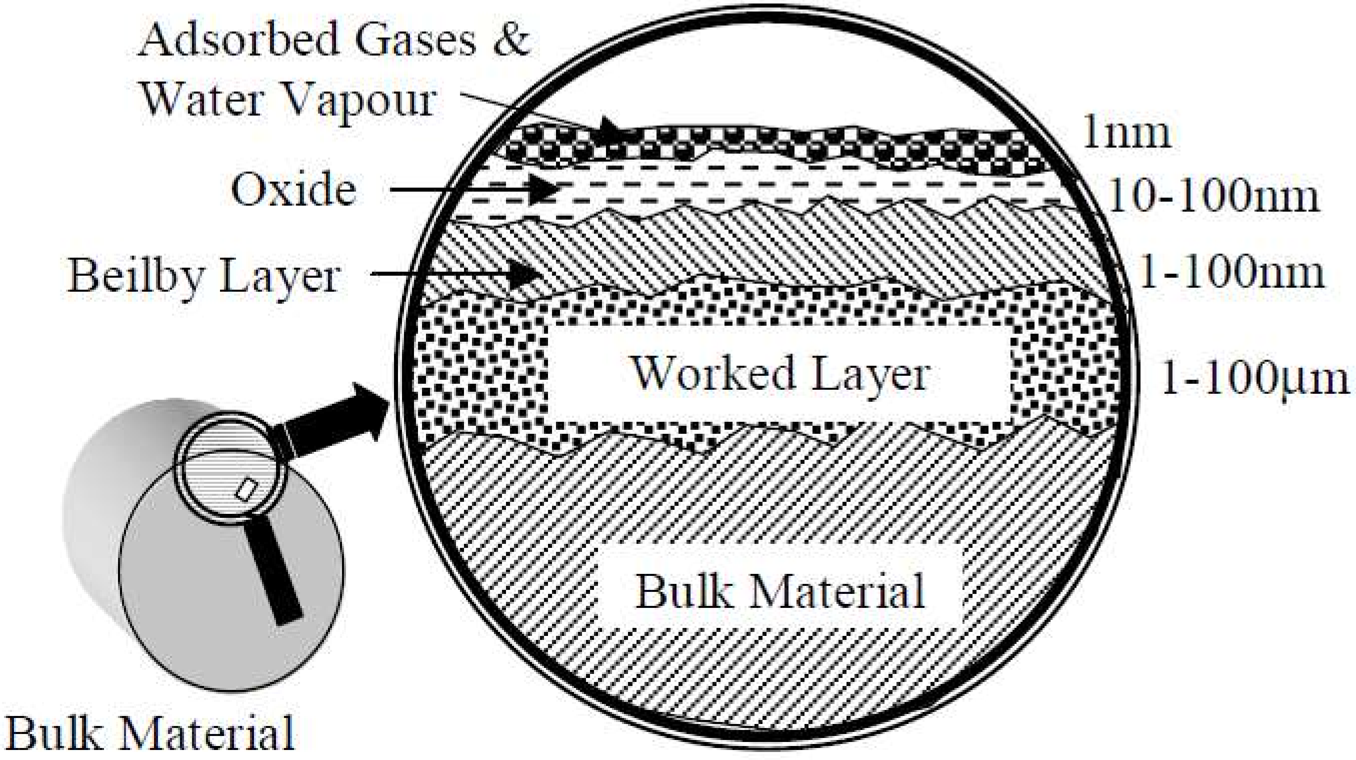


http://xpssimplified.com/whatisxps.php

Surface


100nm
Bulk analysis
X 30000
10nm
X 300000
Thin film analysis
1nm
X 3000000
X 30 000 000
Surface analysis

What is the „surface”?



Source of image: http://webpages.dcu.ie/~stokesjt/ThermalSpraying/Book/Chapter1.pdf

Energetics of solid surfaces

All surfaces are energetically unfavourable in that they have a positive free energy of formation; by cleavage of a solid bonds have to be broken between atoms on either side of the cleavage plane Breaking bonds requires work.

The unfavourable contribution to the total free energy may, however, be minimised in several ways :

1. **By reducing the amount of surface area exposed**
2. **By predominantly exposing surface planes which have a low surface free energy**
3. **By altering the local surface atomic geometry in a way which reduces the surface free energy**

Systems already possessing a high surface energy are thus "metastable".

There is a direct correspondence between the concepts of "surface stability" and "surface free energy" i.e. surfaces of low surface free energy will be more stable and vice versa.

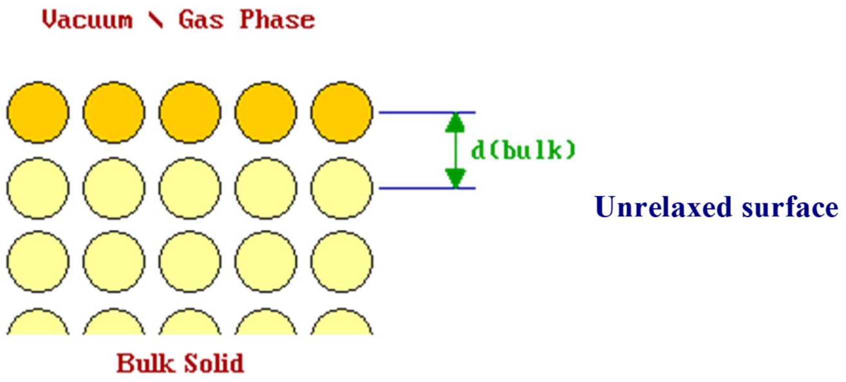
The most stable solid surfaces are those with :

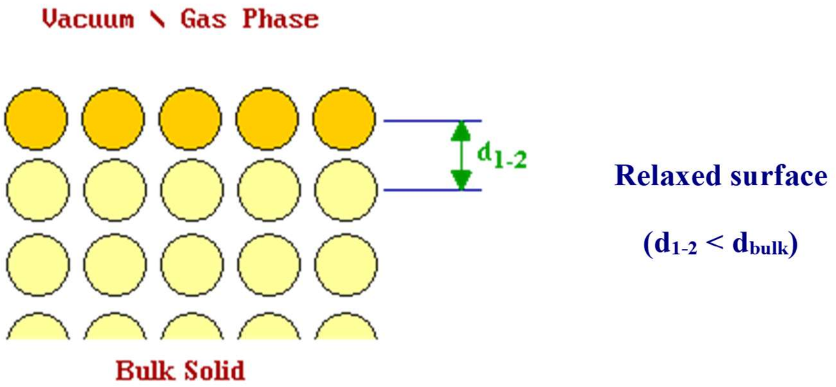
1. a high surface atom density
2. surface atoms of high coordination number

Warning - the above comments strictly only apply when the surfaces are in vacuum. Gas or fluid above the surface can affect (decrease) the surface free energies: possibility of molecular adsorption onto the surface.

Relaxation

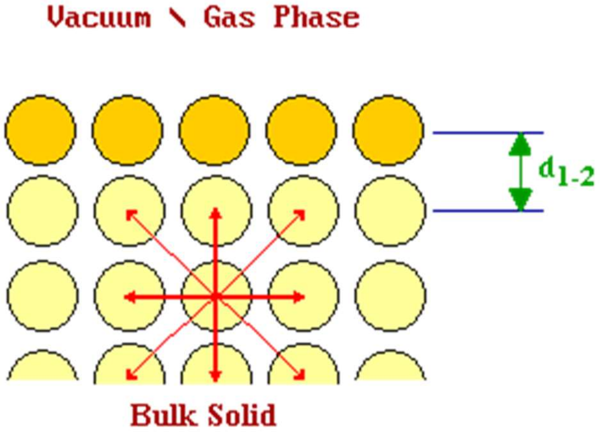
Relaxation involves adjustments in the layer spacings perpendicular to the surface, there is **no** change either in the periodicity parallel to the surface or to the symmetry of the surface.

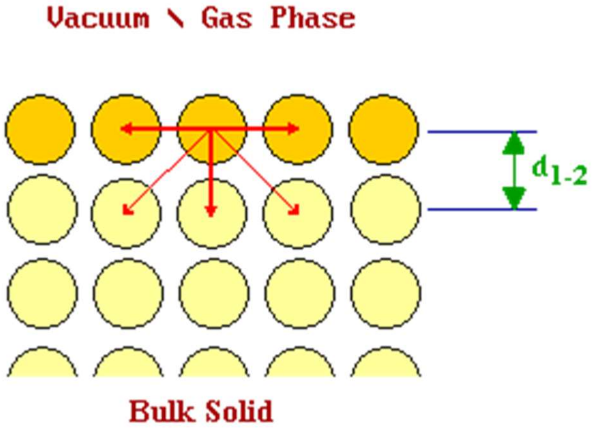




The first layer of atoms is typically drawn in slightly towards the second layer (i.e. $d_{1-2} < d_{bulk}$)

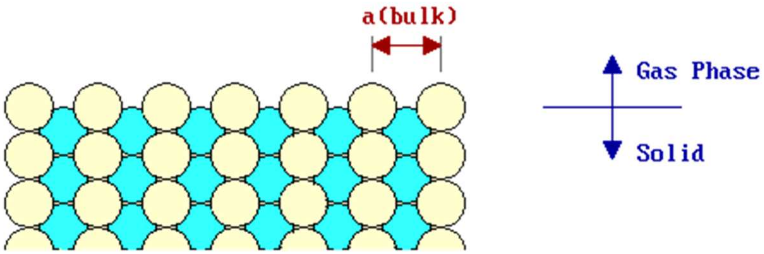
Driving force for this process at the atomic level: An atom in the bulk is acted upon by a balanced, symmetrical set of forces. However, an atom at the unrelaxed surface suffers from an imbalance of forces and the surface layer of atoms may be pulled in towards the second layer. Contraction in the first layer spacing is < 10 %.



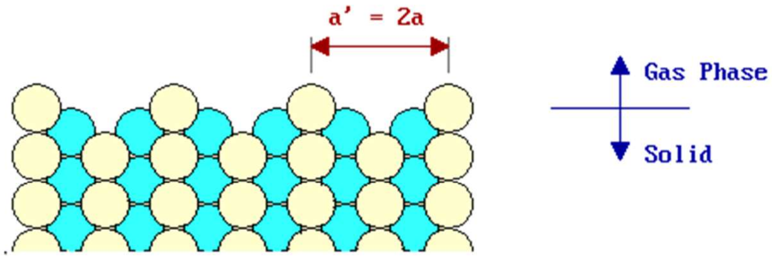


Reconstruction

Involves larger (yet still atomic scale) displacements of the surface atoms, a change in the periodicity of the surface structure.

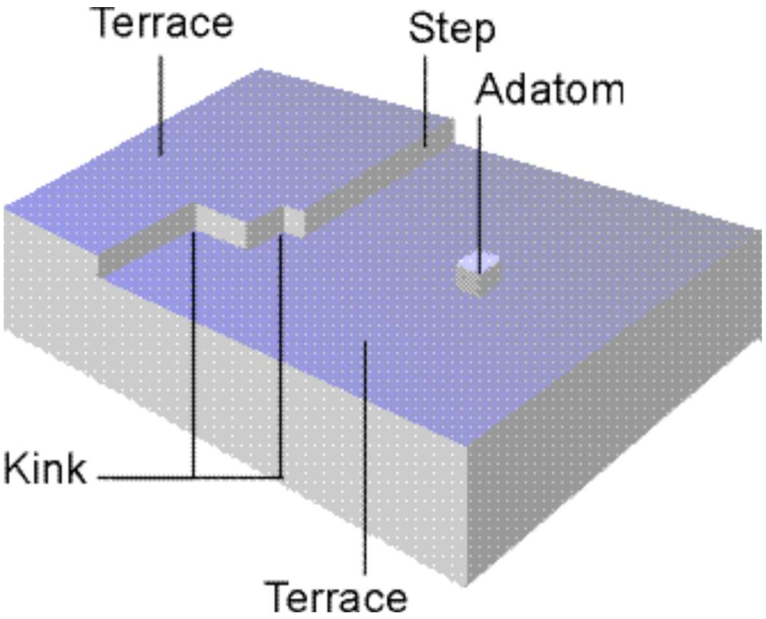


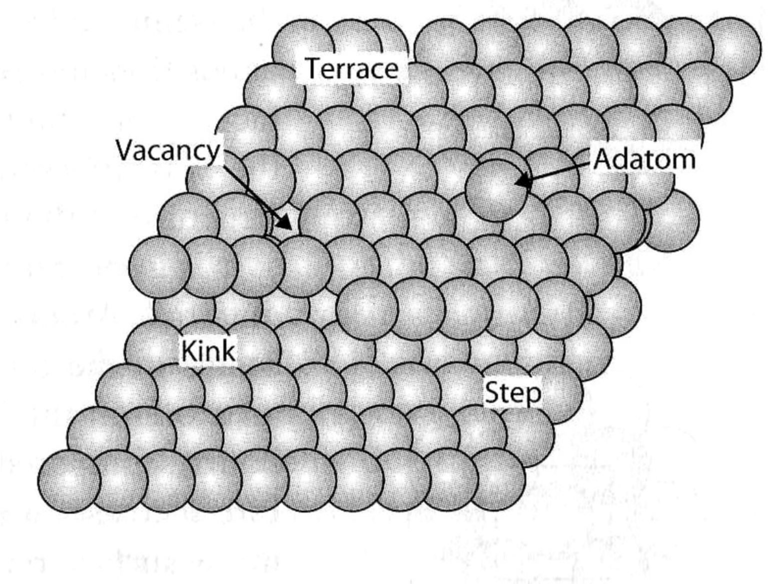
This may be contrasted with the following picture which shows a schematic of a reconstructed surface - this particular example is similar to the "missing row model" proposed for the structure of a number of reconstructed (110) fcc metal surfaces.



The overall driving force for reconstruction is once again the minimization of the surface free energy - at the atomic level, however, it is not always clear why the reconstruction should reduce the surface free energy.

Real surface





Why is it interesting?

- Surface chemistry
  - Corrosion
  - Heterogeneous catalysis
  - Nano materials
  - Molecular sieves
- Contamination
- Adhesion
- Thin layer technology
- Semiconductor industry
- Segregation
- Increased reactivity

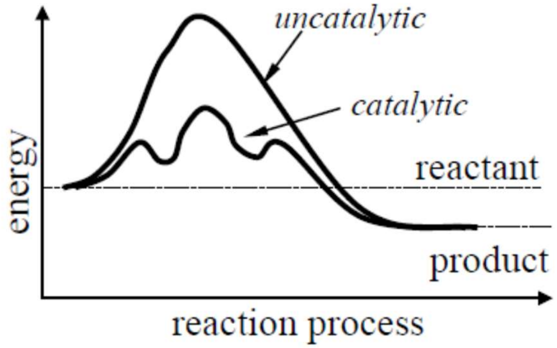
Action of Catalysts

❑ Catalysis action - Reaction kinetics and mechanism

Catalyst action leads to the rate of a reaction to change.

This is realised by changing the course of reaction (compared to non-catalytic reaction)

- Forming complex with reactants/products, controlling the rate of elementary steps in the process. This is evidenced by the facts that
  - The reaction activation energy is altered
  - The intermediates formed are different from those formed in non-catalytic reaction
  - The rates of reactions are altered (both desired and undesired ones)



- Reactions proceed under less demanding conditions
  - Allow reactions occur under a milder conditions, e.g. at lower temperatures for those heat sensitive materials

Why do we need surface analysis?

Example:

Determine the composition of the top 1 nm of a 1 cm^2 Si sample

Density: 2.3 g/cm^3

Mass of the layer: 0.23 µg

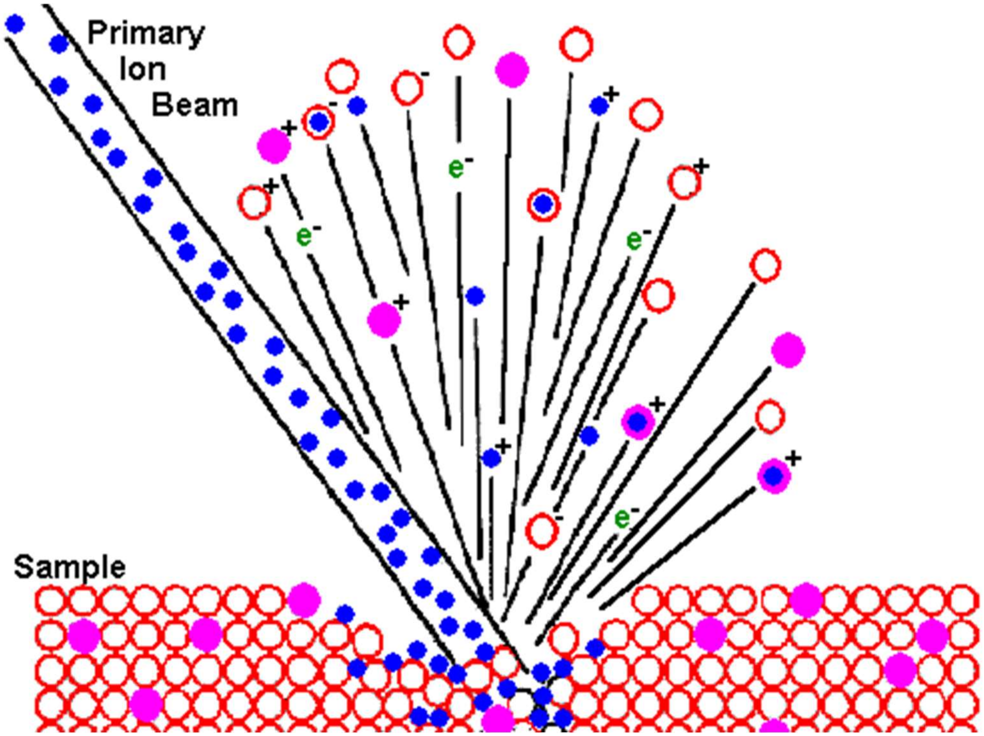
Dissolved in 1 cm^3 → $c_{Si} = 230$ ppb

Concentration of contaminants in Si ~ ppm

Concentration of contaminants in the solution << ppb

→ Wet chemical methods won’t work…

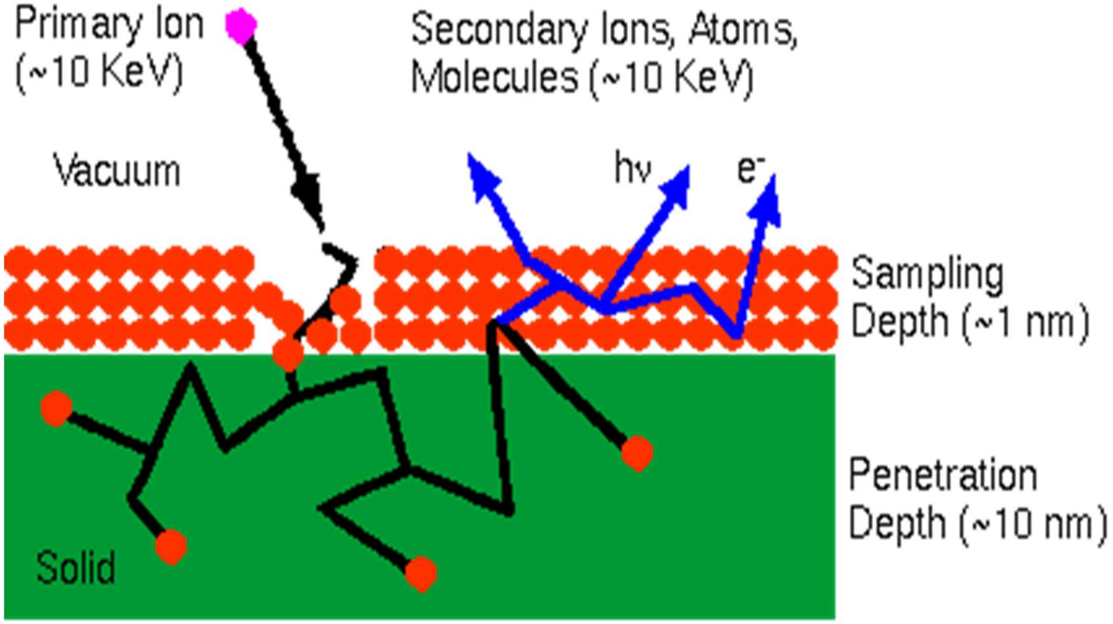
Secondary Ion Mass Spectroscopy (SIMS)



Source of image: http://pprco.tripod.com/SIMS/Theory.htm

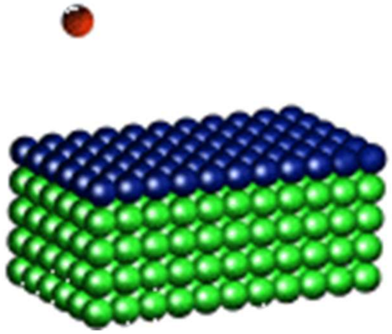
Principle of operation

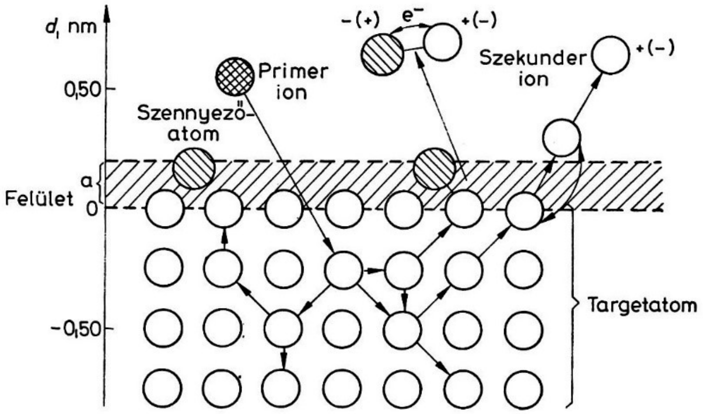
- The sample is irradiated by an ion beam
  - Primer ion: Ar^+, Xe^+, O^-, O_2^+, Cs^+, Au_n^+, Bi_n^+, C_{60}^+
  - Energy: 1-10 keV
- Secondary particles are emitted from the surface:
  - Electrons
  - Photons
  - *Neutral Atoms*
  - **Secondary ions**
- Collection of secondary ions
  - *(Post ionization → SNMS)*
- Mass distribution



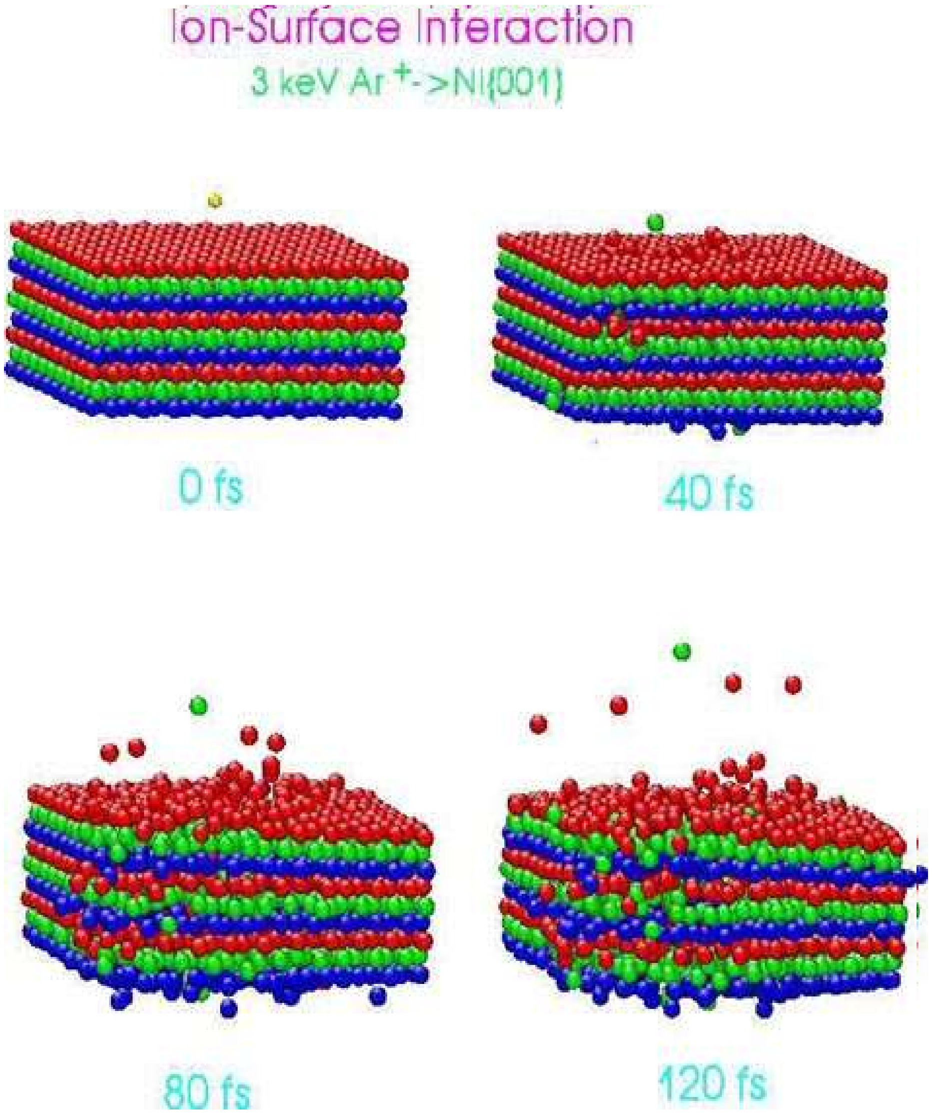
The collision cascade model has the best success at quantitatively explaining how the primary beam interacts with sample atoms. In this model, a fast primary ion passes energy to target atoms in a series of binary collisions. Energetic target atoms (called recoil atoms) collide with more target atoms. Target atoms that recoil back through the sample surface constitute sputtered material. Atoms from the sample's outer monolayer can be driven in about 10 nm, thus producing surface mixing. The term knock-on also applies to surface mixing. Sputtering leads to surface roughness in the sputter craters.

- Primary ion collides with the atoms of the sample
    - It breaks up bonds
    - Its momentum is transferred to the atoms
- Atoms from deeper layers can’t escape
- Secondary ions are emitted from the top 2 atomic layers
- **Information depth < 1 nm**
- *Note: Deeper layers are damaged…*





Source of images: http://www.iontof.com/
Brümer et al.: Szilárd Testek Vizsgálata Elektronokkal, Ionokkal és röntgensugarakkal, Műszaki Könyvkiadó, 1984

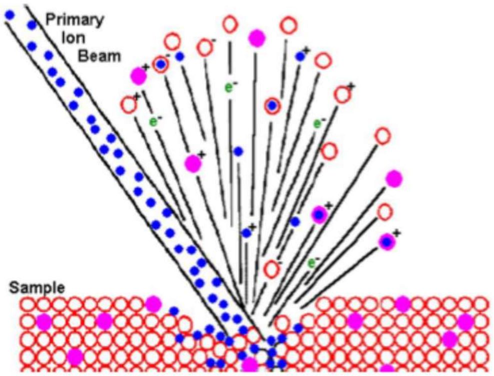


http://galilei.chem.psu.edu/group_pictures/sput.gif

Secondary ion yield

The number of secondary particles (atoms/ions) emitted by the surface for each impinging primary ion is defined as **sputtering yield** and can range between 5 and 15. The fraction of **ionized emitted particles** is called **secondary ion yield** and ranges typically between **10^{-4} to 10^{-6}**.

In SIMS, it is the **secondary ions** that are eventually detected by the mass spectrometer



Secondary ion current of species m

$$\boxed{I_s^m = I_p y_m \alpha^+ \theta_m \eta}$$

I_p = primary particle flux

y_m = sputter yield

α^+ = ionization probability to positive ions

θ_m = fractional concentration of m in the layer

η = transmission of the analysis system

Ion yield is influenced by

- Matrix effects
- Surface coverage of reactive elements
- Background pressure
- Orientation of crystallographic axes with respect to the sample surface
- Angle of emission of detected secondary ions

Secondary ion yields: primary ion beams

Secondary ion yield depends critically on the primary ion beam species. Typically $Cs^+$and O_2^+ ion beams are used in SIMS measurements.

- **O_2^+ ions beam**:
  - Oxygen tends to bind with metal (Me) atoms, if present in the sample.
  - During secondary emission the Me-O bonds break thus generating Me^{n+}
- **Cs^+ ions beam**:
  - The implanted Cs ions lower the sample work function
  - More secondary electrons are excited over the surface potential barrier
  - Increased availability of electrons leads to increased negative ion formation especially for elements with high electron affinity.

Selection of primary ions:

- Inert gas (Ar, Xe, etc.)
  - Minimize chemical modification
- Oxygen
  - Enhance positive ions
- Cesium
  - Enhance negative ions
- Liquid metal (Ga)
  - Small spot for enhanced lateral resolution

Oxygen works as a medium which strips off electrons from the speeding sputtered atoms when they leave surface, while Cesium prefers to load an electron on the sputtered atoms.

Influence of oxygen on the ionization yield

Metal	Elemental state	Oxide
Mg	0,01	0,9
Al	0,007	0,7
Si	0,0084	0,58
Ti	0,0013	0,4
V	0,001	0,3
Cr	0,0012	1,2
Mn	0,0006	0,3
Fe	0,0015	0,35
Ni	0,0006	0,045
Cu	0,0003	0,007
Ge	0,0044	0,02
Sr	0,0002	0,16
Nb	0,0006	0,05
Mo	0,00065	0,4
Ba	0,0002	0,03
Ta	0,00007	0,02
W	0,00009	0,035

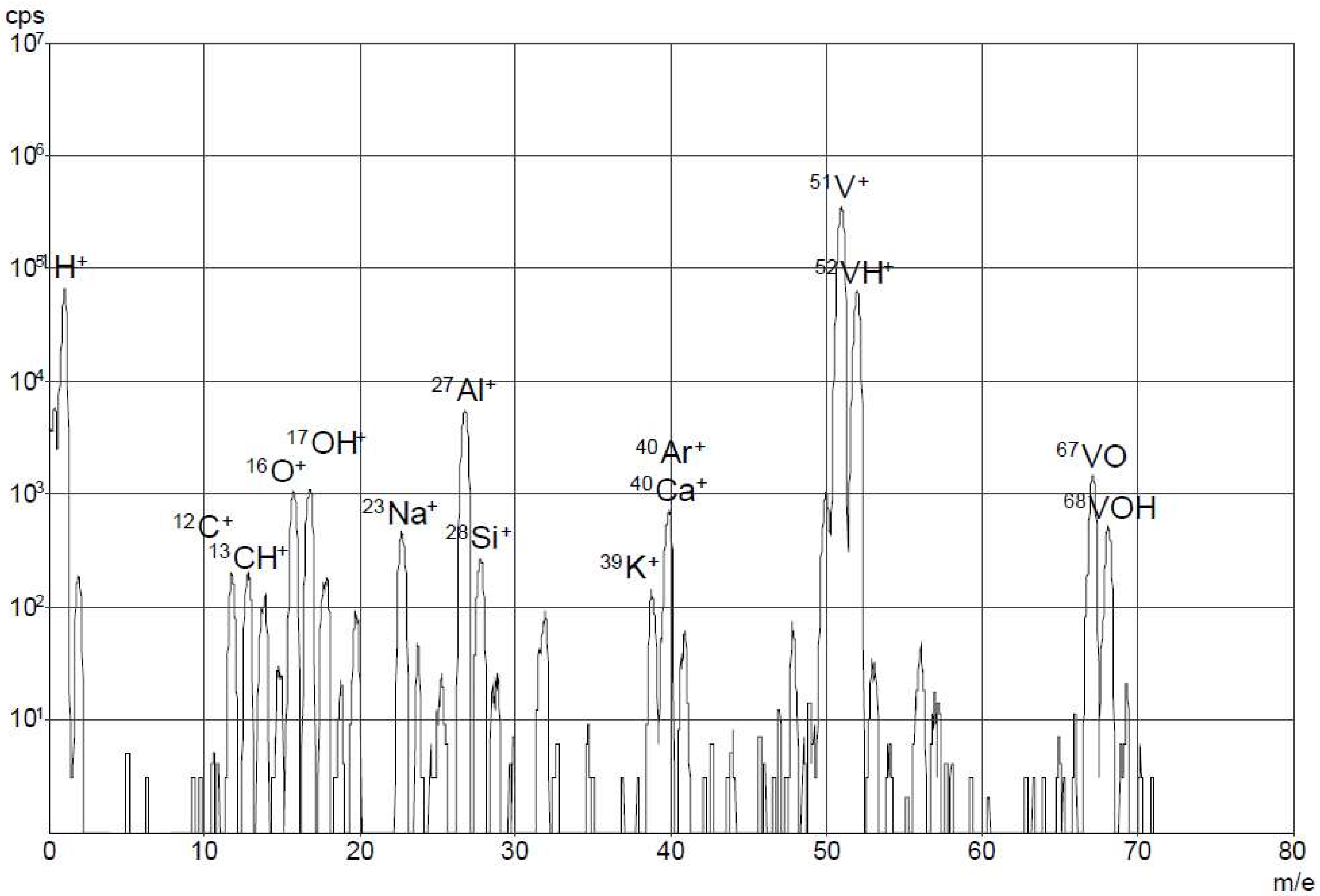
Reactive SIMS

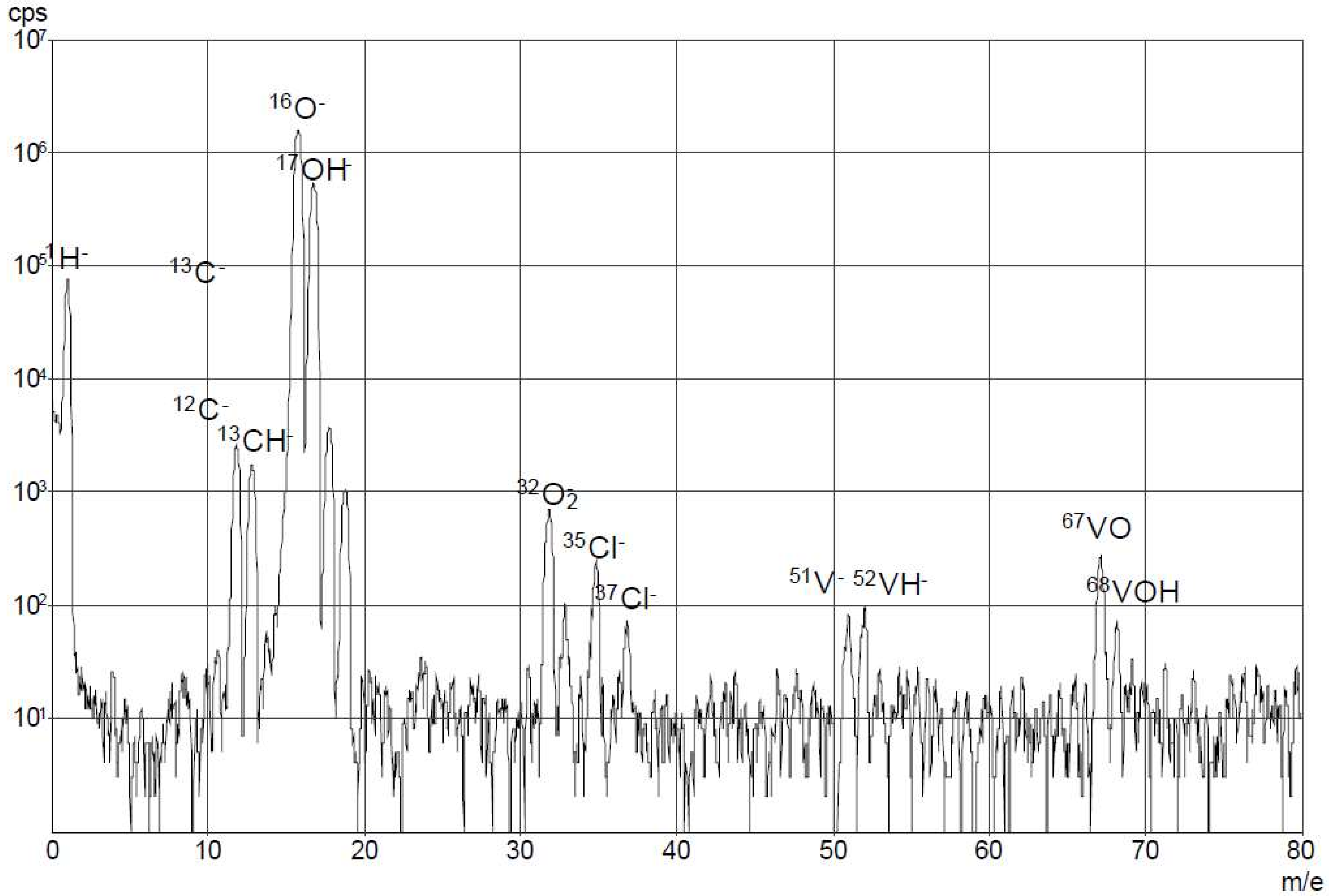
- Introducing oxygen gas to the vacuum system
- Sputtering with O^- or O_2^- ions
- Sputtering with Cs^+ ions

- Increases secondary ion current
- Overrides matrix effect
- Quantitative measurements possible after calibration

Sensitivity

- Highest peaks: 10^6 – 10^7 cps
- Background ~ 0 cps (dark noise?)
  - 1 cps detectable
- Very high dynamic range
  - Ratio of highest and lowest detectable peaks: 6-7 orders of magnitude
- Detection of trace elements

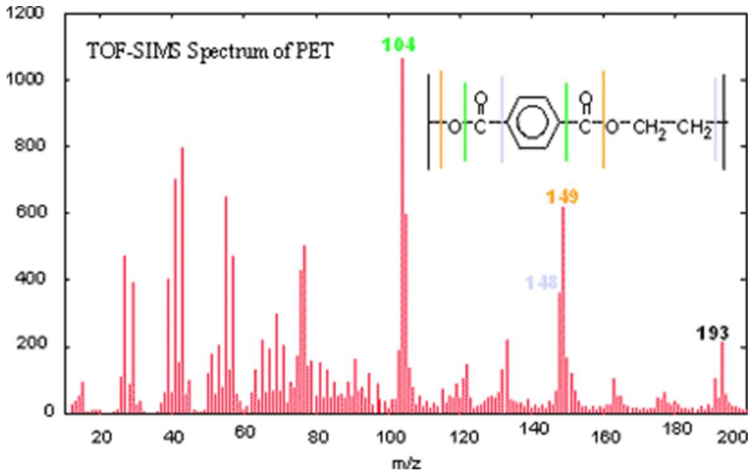

cps
10⁷
10⁶
10⁵
10⁴
10³
10²
10¹
0
10
20
30
40
50
60
70
80
m/e
¹H⁺
¹²C⁺
¹³CH⁺
¹⁶O⁺
¹⁷OH⁺
²³Na⁺
²⁷Al⁺
²⁸Si⁺
³⁹K⁺
⁴⁰Ar⁺
⁴⁰Ca⁺
⁵¹V⁺
⁵²VH⁺
⁶⁷VO
⁶⁸VOH

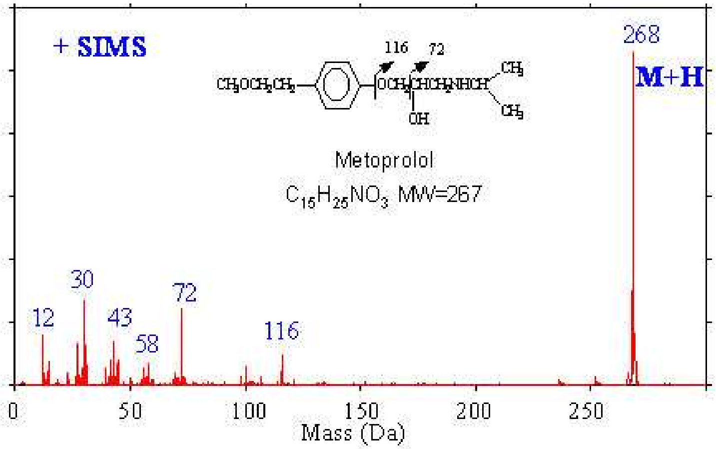

cps
10^7
10^6
10^5
10^4
10^3
10^2
10^1
1H-
13C-
16O-
17OH-
12C-
13CH-
32O2
35Cl-
37Cl-
51V-
52VH-
67VO
68VOH
0
10
20
30
40
50
60
70
80
m/e

Identification of organic molecules

- Organic molecules may get fragmented due to ion bombardment
- Each molecule has a set of characteristic fragments
- Fingerprint database

- Measurement conditions may influence the process
- Background pressure
- Energy and type of ion beam
- Proton transfer reaction



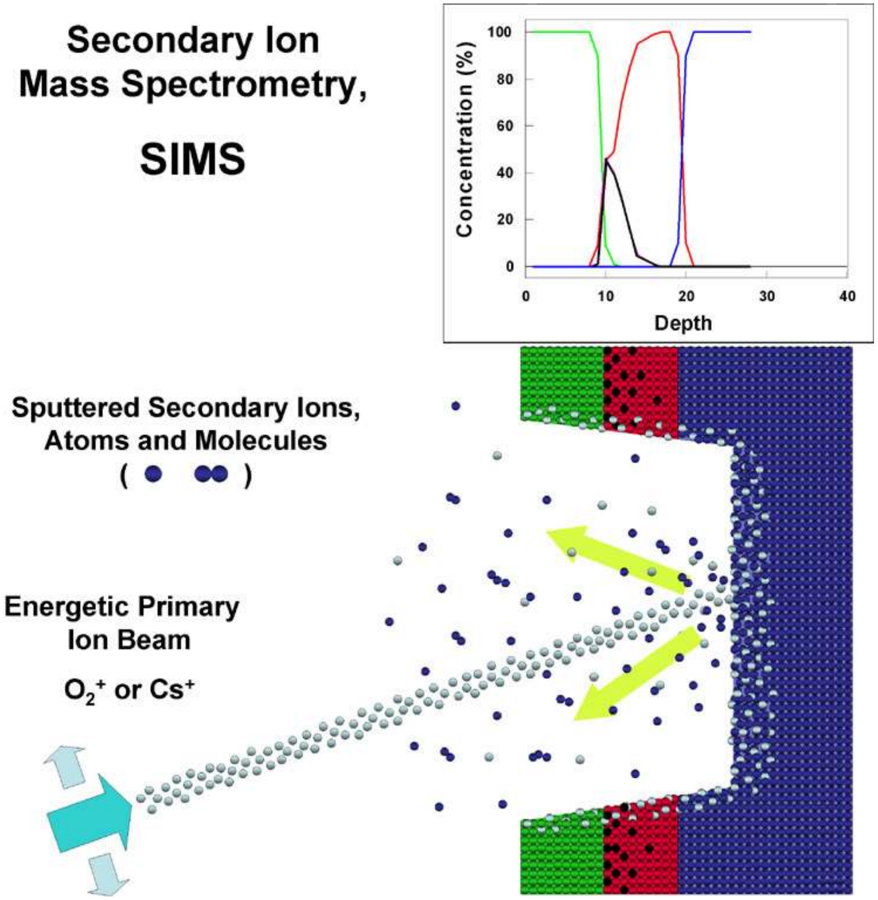


Mass spectrum of Metroprolol showing molecular and fragment peaks

Source of images:http://www.phi.com/surface-analysis-techniques/tof-sims.html
http://www.stinstruments.com/products/126/126-122-73-/surface-analysis-techniques-tof-sims

Depth profile

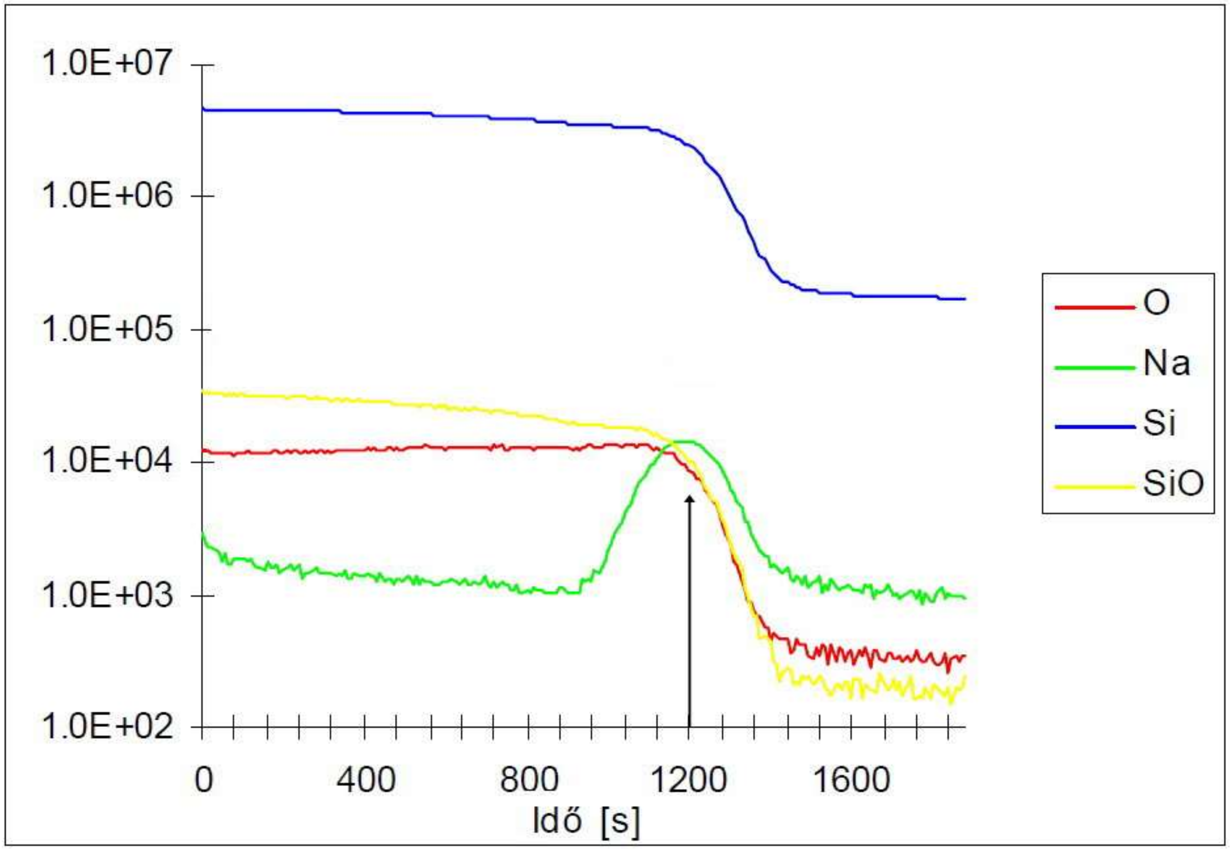
- Continuous ion bombardment
- Record peak intensities as a function of time



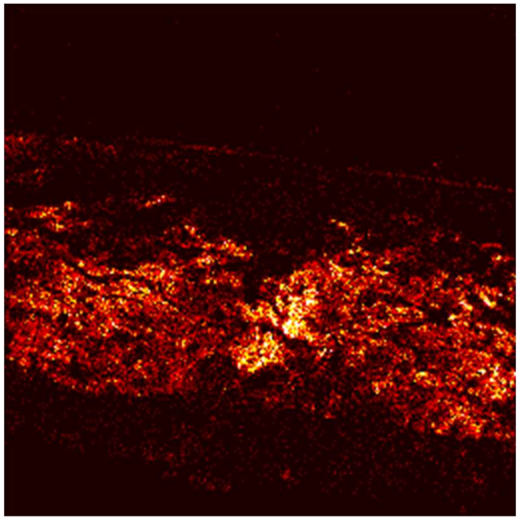
Source of image: http://www.almaden.ibm.com/st/scientific_services/materials_analysis/sims/

Depth profile

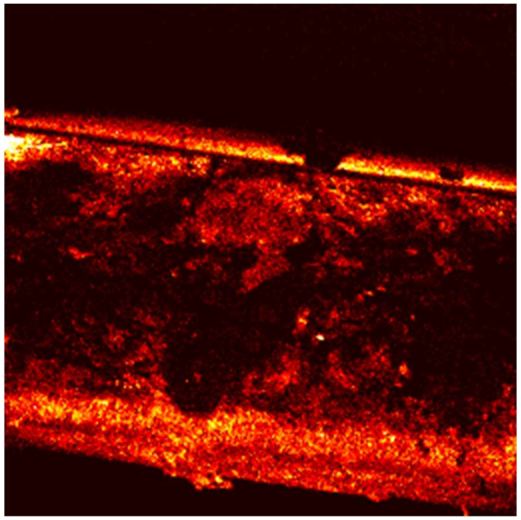
Si egkristályon termikusan növesztett 50 nm vastag SiO_2 réteg



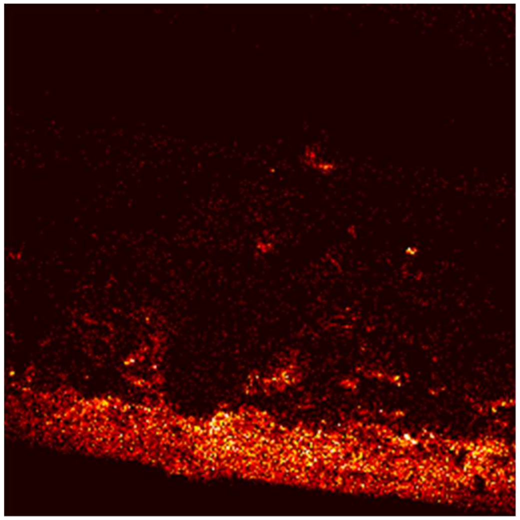
Lateral distribution mapping



$C_3H_7O^+$
(Cellulose fragment)



Na^+



Fe^+

Source of images: http://www.phi.com/surface-analysis-techniques/tof-sims.html

Main problem

Ionization probability depends on many parameters

- Element
- Matrix effect
  - Local chemical environment
- Measurement conditions
  - Primary ion
  - Energy of primary ions
  - Background pressure

→ No universal sensitivity factors

SNMS

- Most of the atoms are not ionized
- Post ionization increases the number of detectable ions
- Matrix effect less important
- Quantitative after calibration

- Usual setup:
  - RF plasma above the sample
  - Atoms from the surface are ionized in the plasma
  - Measure the mass distribution of the ions in the plasma
  - Problems with insulator samples
  - No lateral resolution
  - No cluster ions or organic fragments
- SIMS instruments may have a post ionization upgrade (using an electron or laser beam)

Summary

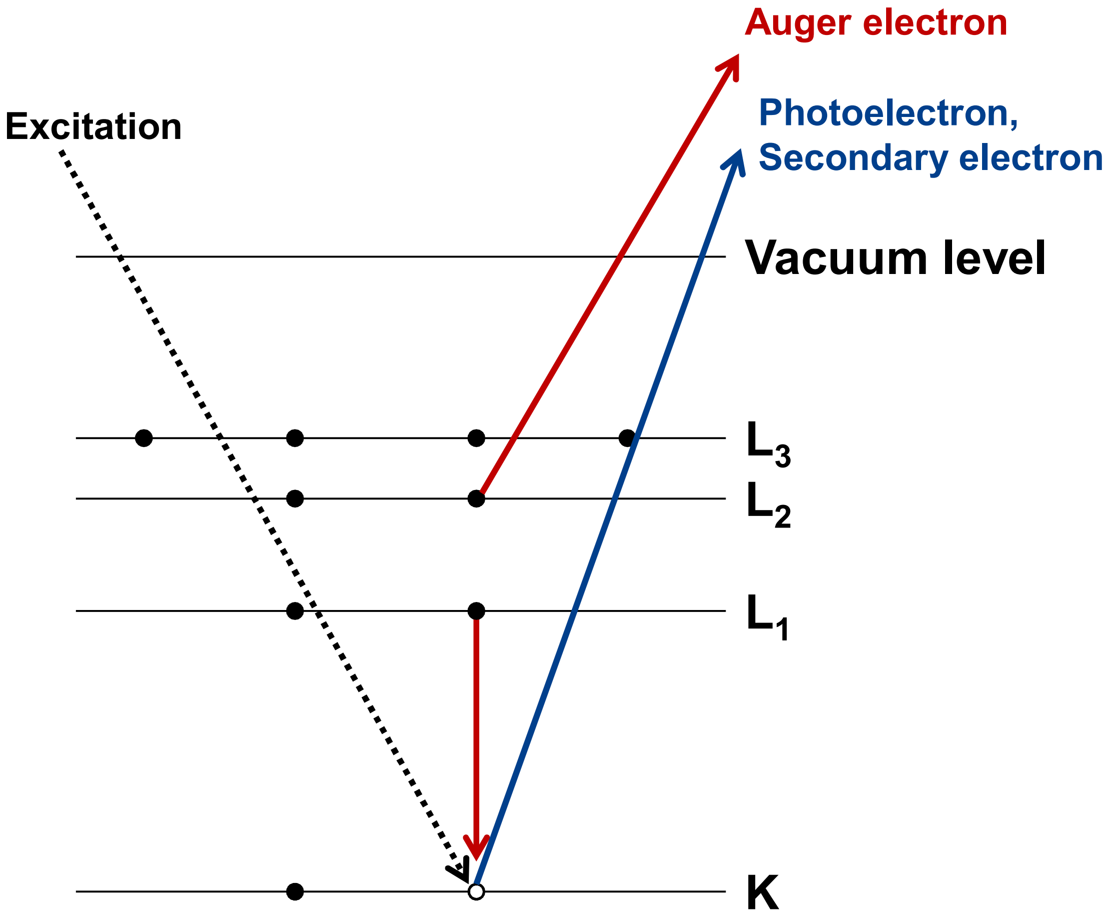
- Sputtering of the surface by an ion beam
- Collection of secondary ions
- Mass spectrum
- High dynamic range
- Trace element analysis
- Especially sensitive to alkali metals and halogens
- Matrix effect makes quantitative measurements difficult
- Reactive SIMS

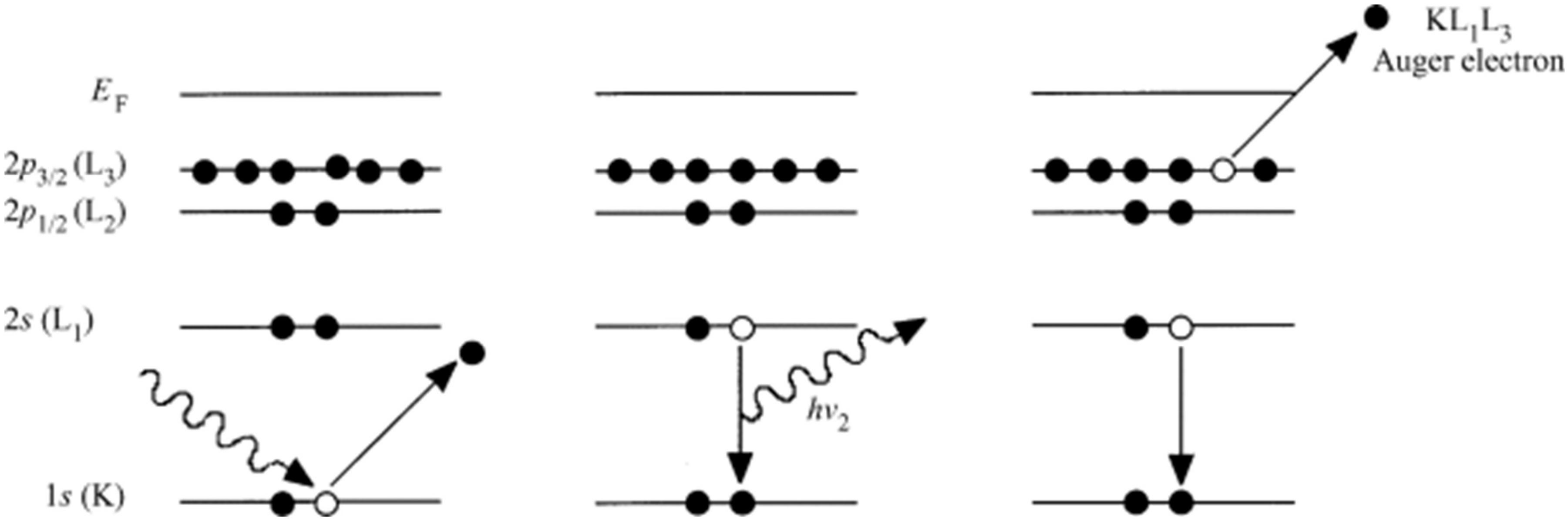
- Advantages
  - Surface sensitive
    - Information depth: 1-2 atomic layers
  - Trace element analysis
  - Depth profiles, lateral distribution, 3D analysis
  - Organic molecule identification
  - Chemical information from cluster ions and organic fragments

- Disadvantages
  - Usually not quantitative
  - Usually provides only elemental composition
  - Problems with insulators
    - FAB gun
    - Flood gun
  - Expensive

Auger Process

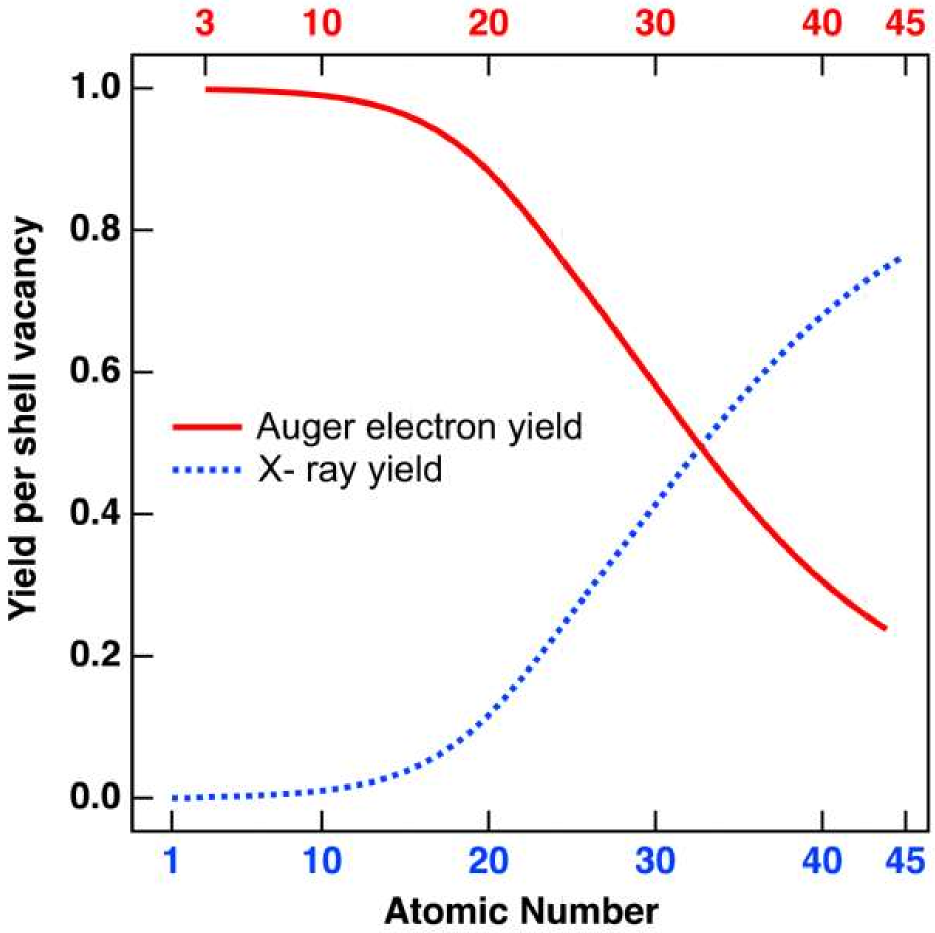
n	l	j	AES
1 (K)	0 (s)	1/2	K
2 (L)	0 (s)	1/2	L_1
2 (L)	1 (p)	1/2	L_2
2 (L)	1 (p)	3/2	L_3
3 (M)	0 (s)	1/2	M_1
3 (M)	1 (p)	1/2	M_2
3 (M)	1 (p)	3/2	M_3
3 (M)	2 (d)	3/2	M_4
3 (M)	2 (d)	5/2	M_5
. . .			





Photoemission **X-ray fluorescence** **Auger effect**

Likelihood of the Auger process

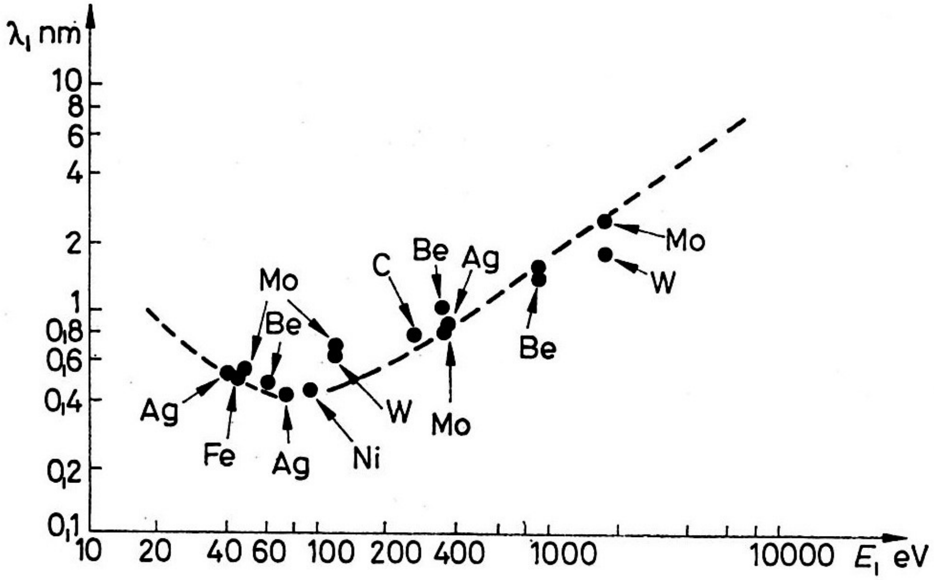


Auger Electron Spectroscopy

- Excitation of the sample by
  - Electrons
  - X-ray photons
  - Ions
- Auger electron energy is determined by the energy levels in the atom:

  $E_{KLL} = E_K - E_{L1}^* - E_{L2}^*$ (exited atom!)
- Measurement of secondary electron energy distribution
- Peak positions → Element identification
- Peak intensities → Concentrations

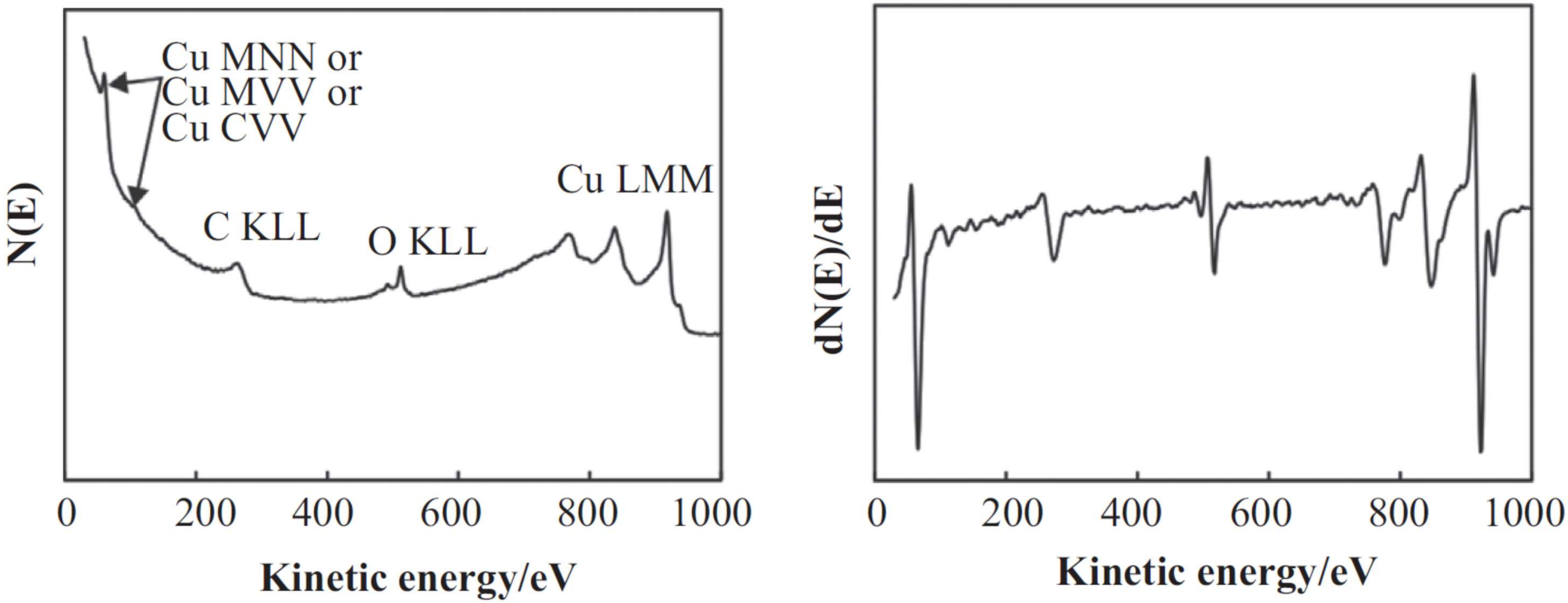
Surface Sensitivity



- Inelastic Mean Free Path (IMFP) of 50 – 2000eV electrons is very short
- Electrons from deeper layers loose energy

→ Background

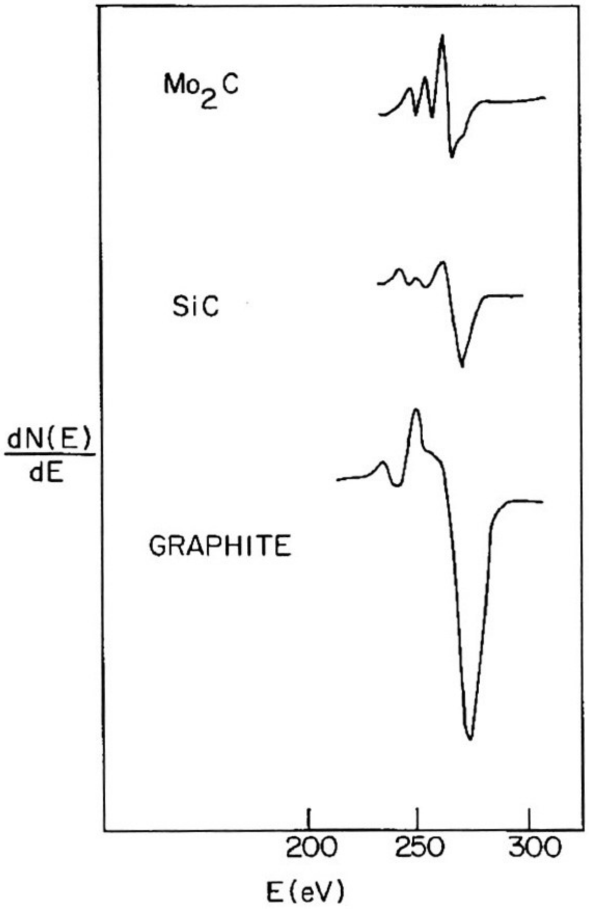
Source of image: Brümer et al.: Szilárd Testek Vizsgálata Elektronokkal, Ionokkal és röntgensugarakkal, Műszaki Könyvkiadó, 1984



- Problem: small, flat peaks
- Solution: differential spectrum
  - Background disappears
  - Peaks are enhanced

Source of image: J. Wolstenholme: Auger electron spectroscopy: practical application to materials analysis and characterization of surfaces, interfaces, and thin films, Momentum Press, 2015

Chemical State Identification



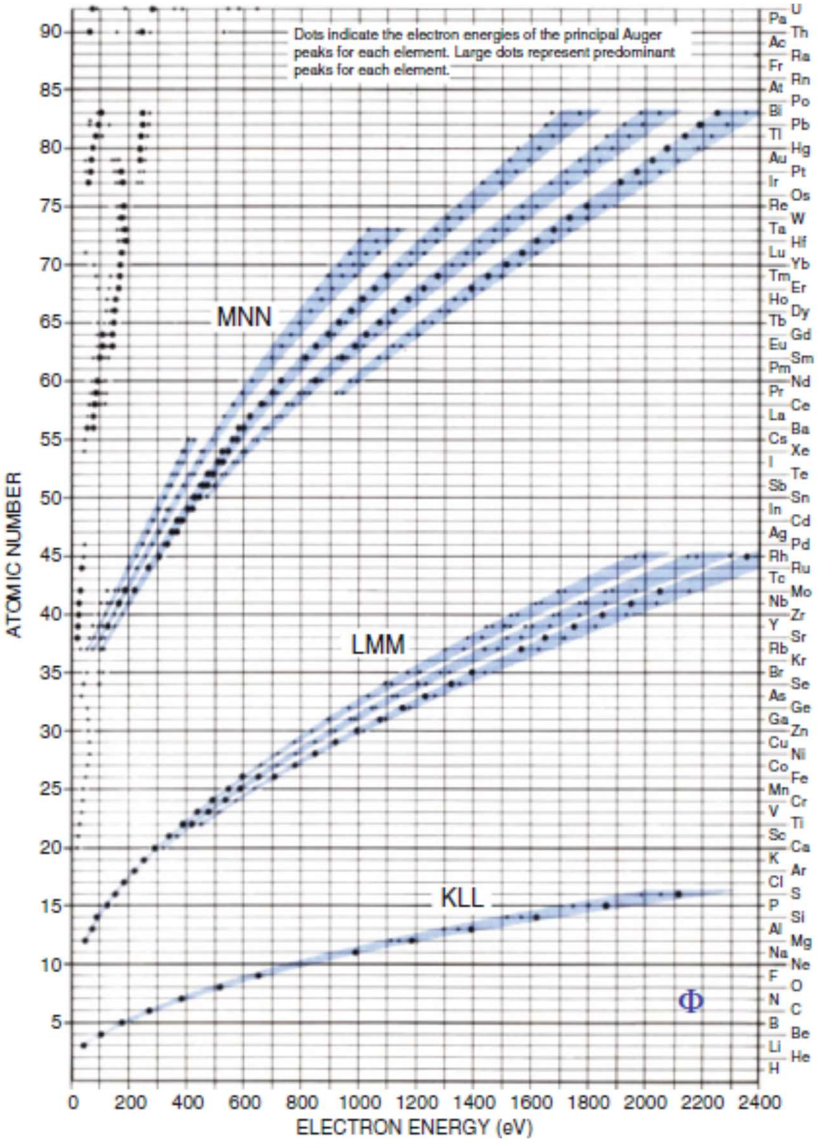
- Auger electron energies are determined by atomic energy levels
- The formation of chemical bonds changes the electron structure of the atom
- Even the core levels shift

→ Auger peak positions and relative intensities change

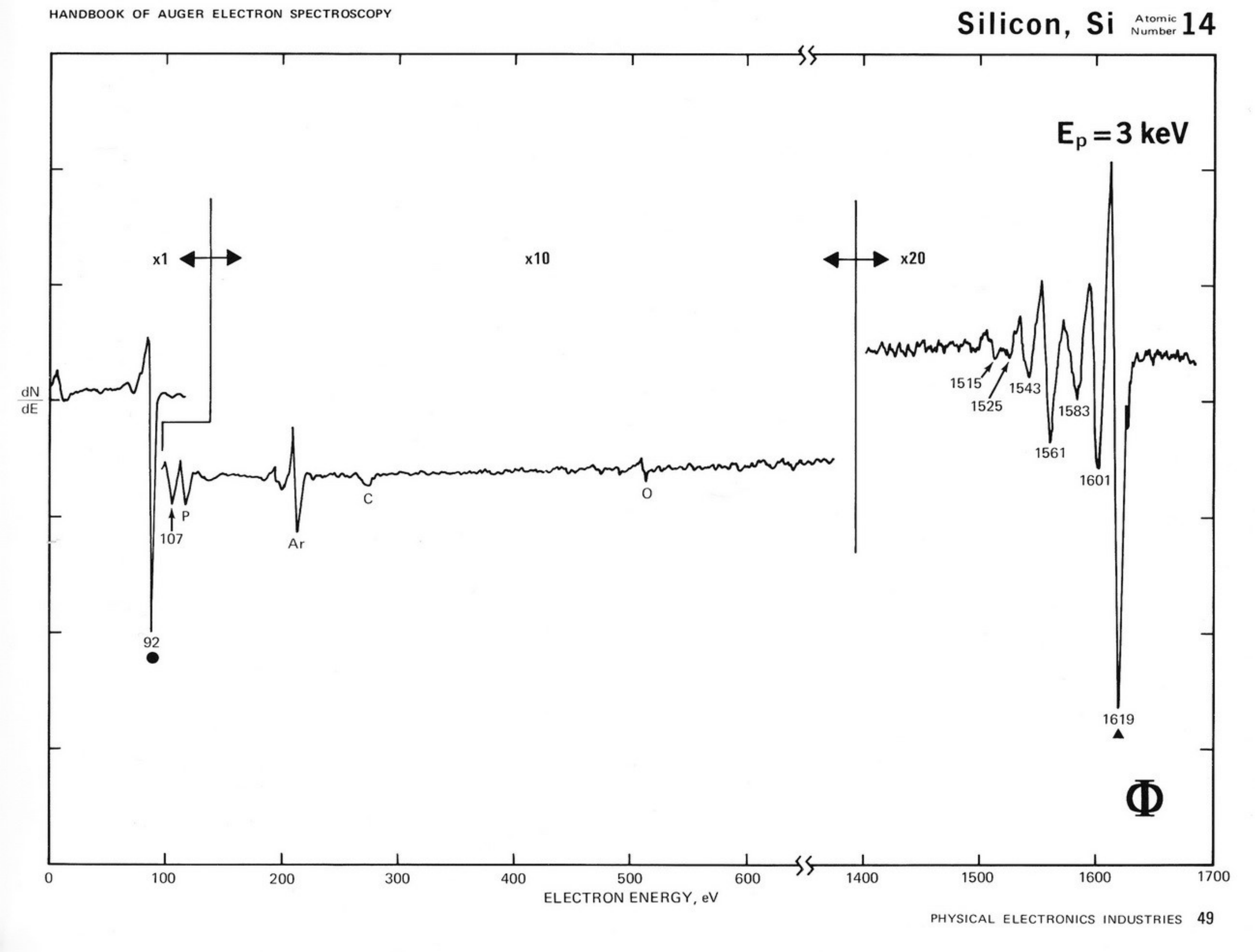
- Visible peaks are often multiple peaks merged together

→ Peak shapes may also change

Source of image: Brümer et al.: Szilárd Testek Vizsgálata Elektronokkal, Ionokkal és röntgensugarakkal, Műszaki Könyvkiadó, 1984


Dots indicate the electron energies of the principal Auger peaks for each element. Large dots represent predominant peaks for each element.

Principal Auger electron energies for each element. The larger dots correspond to prominent Auger peaks

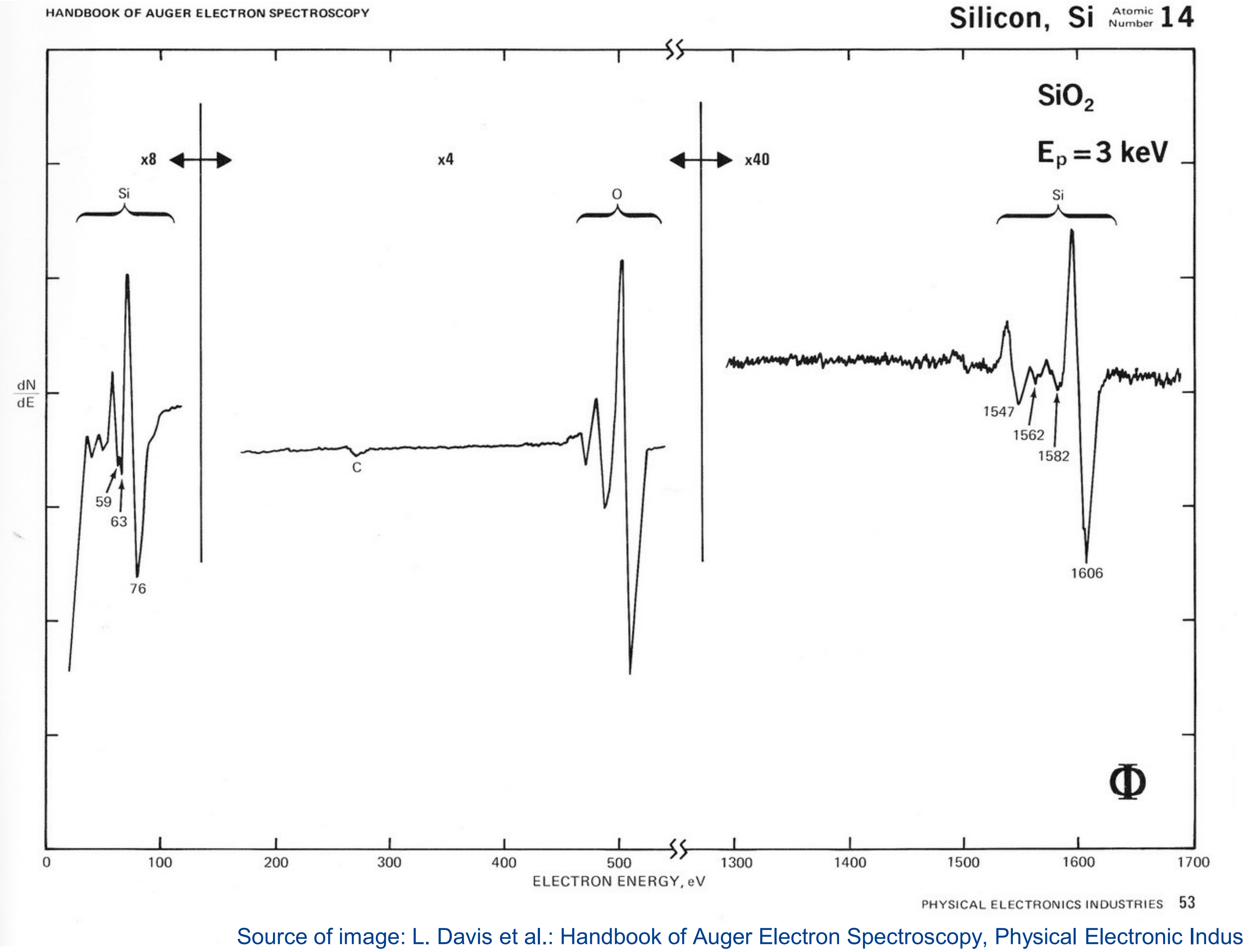


HANDBOOK OF AUGER ELECTRON SPECTROSCOPY

Silicon, Si Atomic Number **14**

PHYSICAL ELECTRONICS INDUSTRIES 49

Source of image: L. Davis et al.: Handbook of Auger Electron Spectroscopy, Physical Electronic Industries, 1976


HANDBOOK OF AUGER ELECTRON SPECTROSCOPY

Silicon, Si Atomic Number **14**

PHYSICAL ELECTRONICS INDUSTRIES 53

Source of image: L. Davis et al.: Handbook of Auger Electron Spectroscopy, Physical Electronic Industries, 1976

Problem

- Peak shapes change due to chemical state
- This affects the gradient of the curve

→ It affects intensities on the differential spectrum

→ Sensitivity factors are influenced by chemical states

  - In case of compounds, calibration may be required
  - Alloys are usually OK

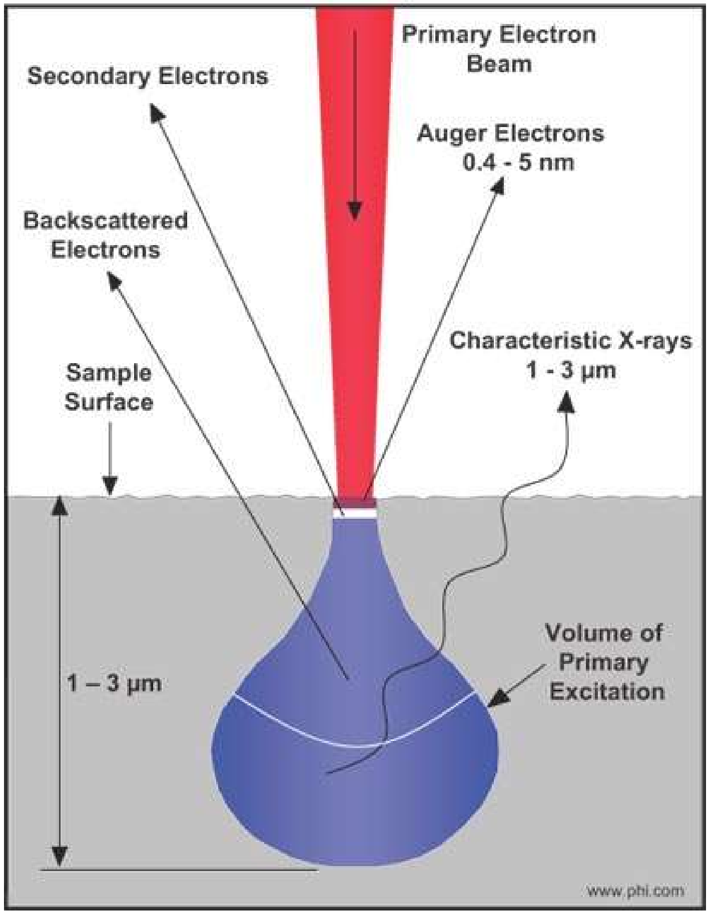
Lateral Resolution

- Excitation by electrons
- Similar to SEM
- Beam diameter ~nm
- Auger electrons come from the surface

  → Not affected by beam broadening in deeper layers

- Lateral resolution can be ~ 8nm

Electron Beam – Sample Interaction



Source of image: http://www.phi.com/surface-analysis-techniques/aes.html

Summary

- Excitation by electrons, ions, X-rays
- Energy spectrum of secondary electrons
- Electrons from deeper layers loose energy

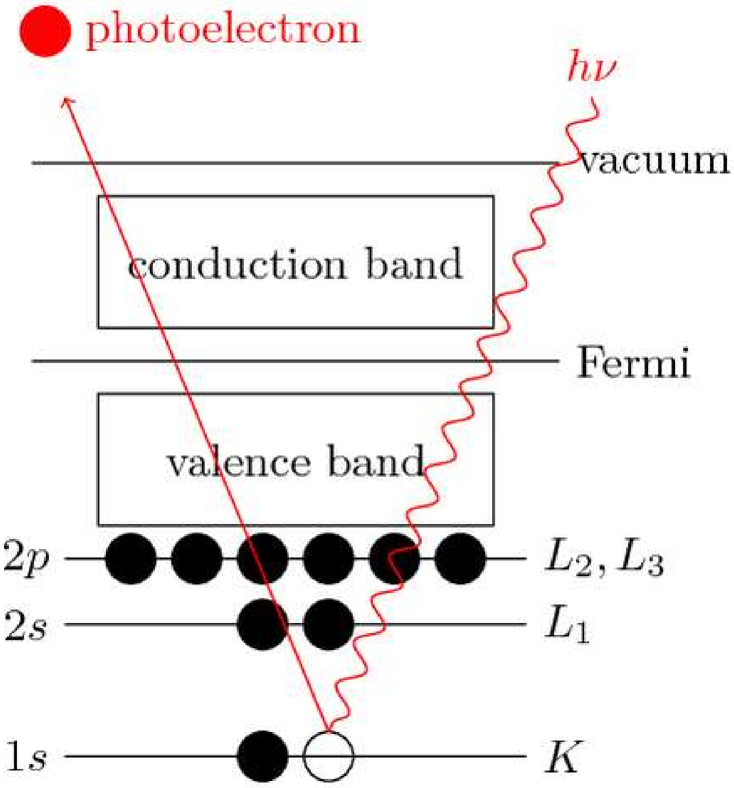
  → Information depth 0,5 – 5 nm
- Differential spectra
- Quantitative elemental compositions
  - Simple in case of alloys
  - Otherwise, calibration may be required
- Sensitivity ~ 1 atomic percent

Summary

- Chemical state identification based on peak position and peak shape
- Lateral resolution ~10nm
- Depth profile
  - By ion beam sputtering
- (Usually) Nondestructive
  - There may be damage due to local heating
  - Organic samples may degrade due to electron bombardment
- Problems with insulators

X-ray Photoelectron Spectroscopy (XPS)

- Excitation by photons
- If photon energy is high enough
  → Photoeffect
- $h\nu = E_{kin} + E_{binding}$
- UPS (Ultraviolet Photoelectron Spectroscopy)
  - Valence band
- XPS (X-ray Photoelectron Spectroscopy)
  - Core levels



Source of image: http://www.texample.net/tikz/examples/principle-of-x-ray-photoelectron-spectroscopy-xps/

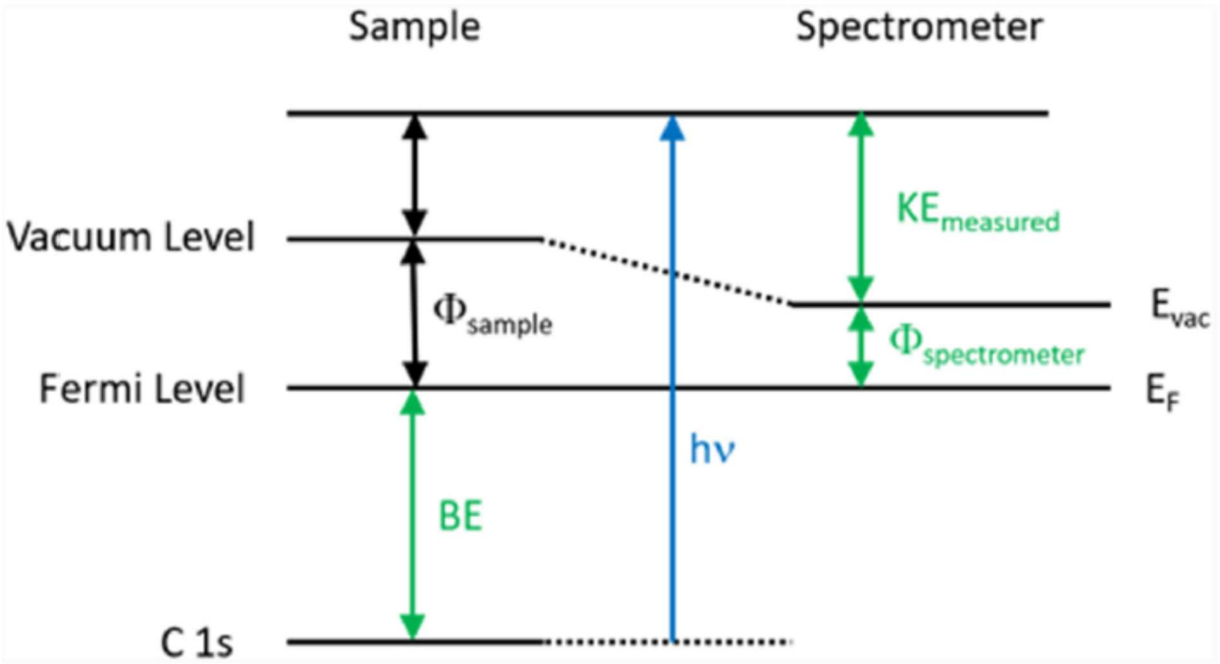


FIG. 2. Energy level diagram illustrates schematically the basic XPS equation, including the x-ray source energy ($h\upsilon$), the binding energy of the electron (BE), the measured kinetic energy of the electron ($KE_{measured}$), and the work function of the spectrometer ($\Phi_{spectrometer}$).

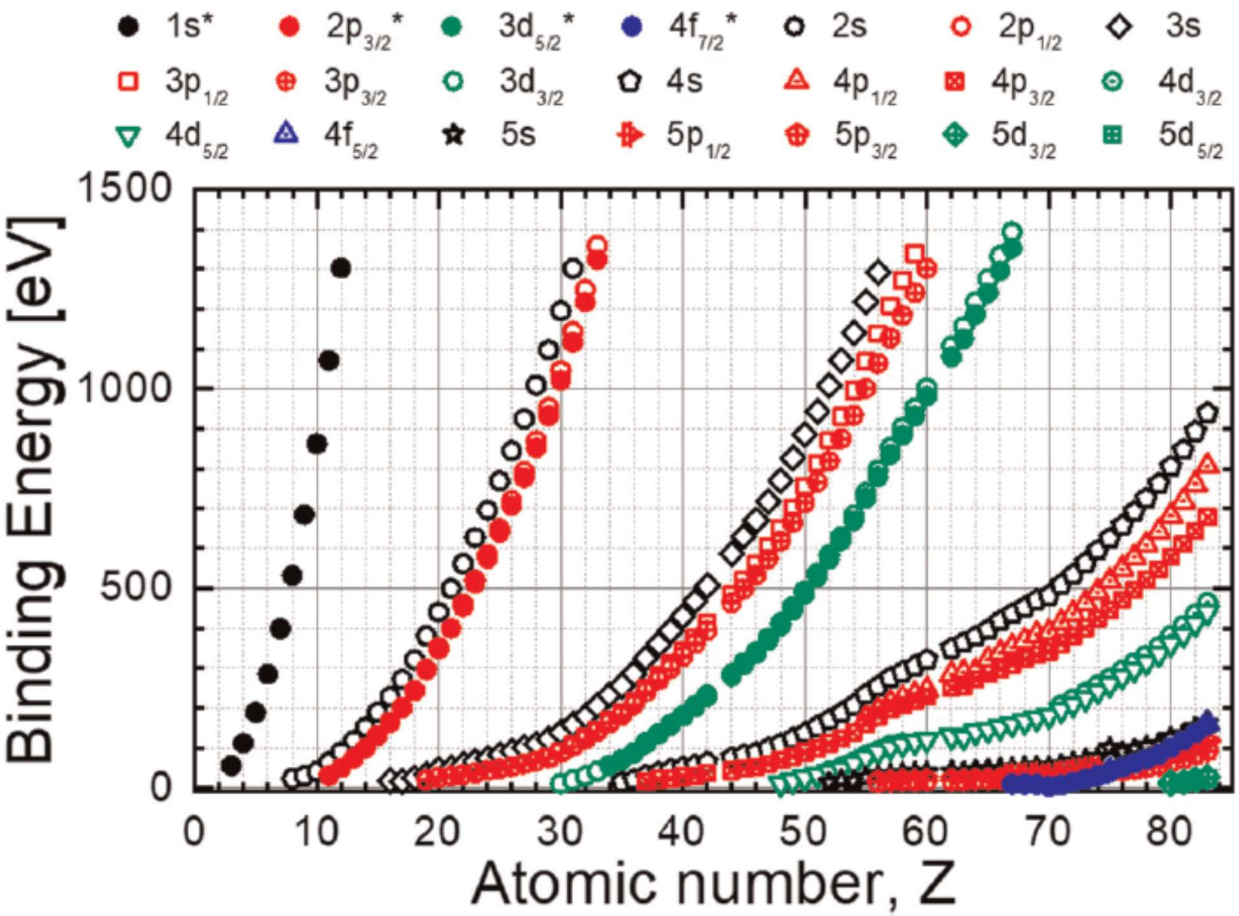
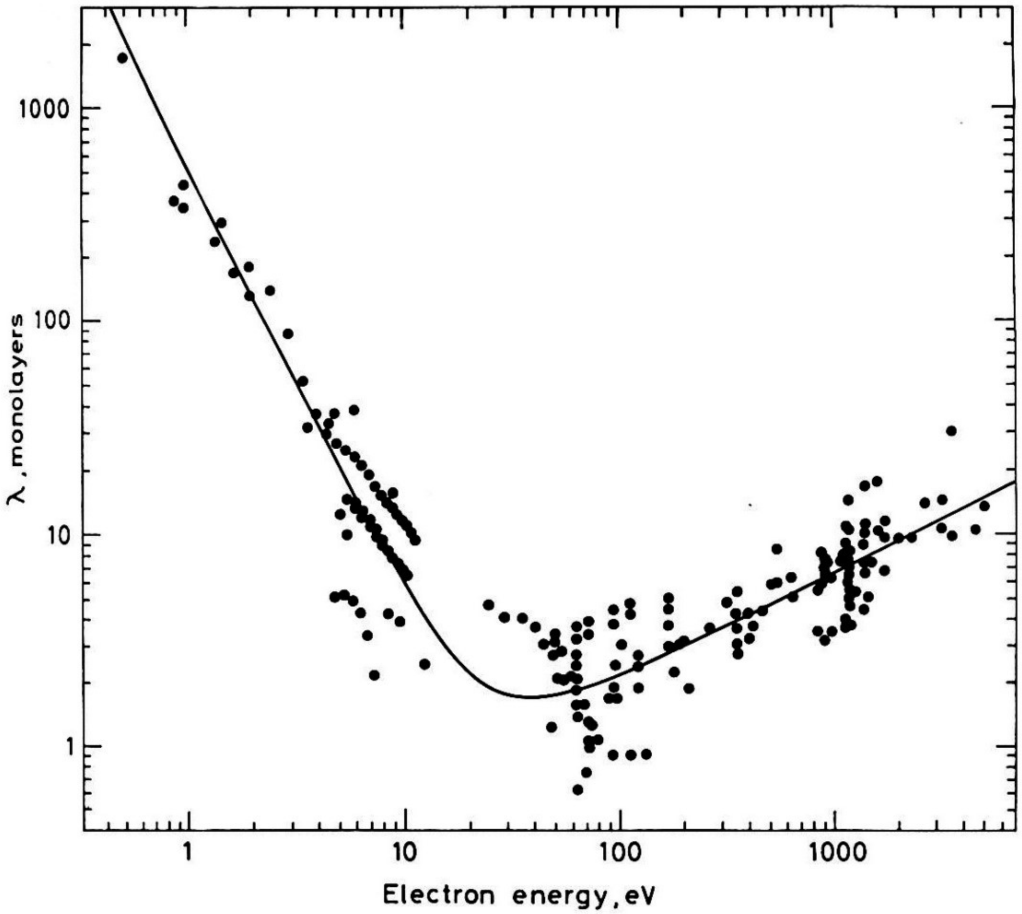
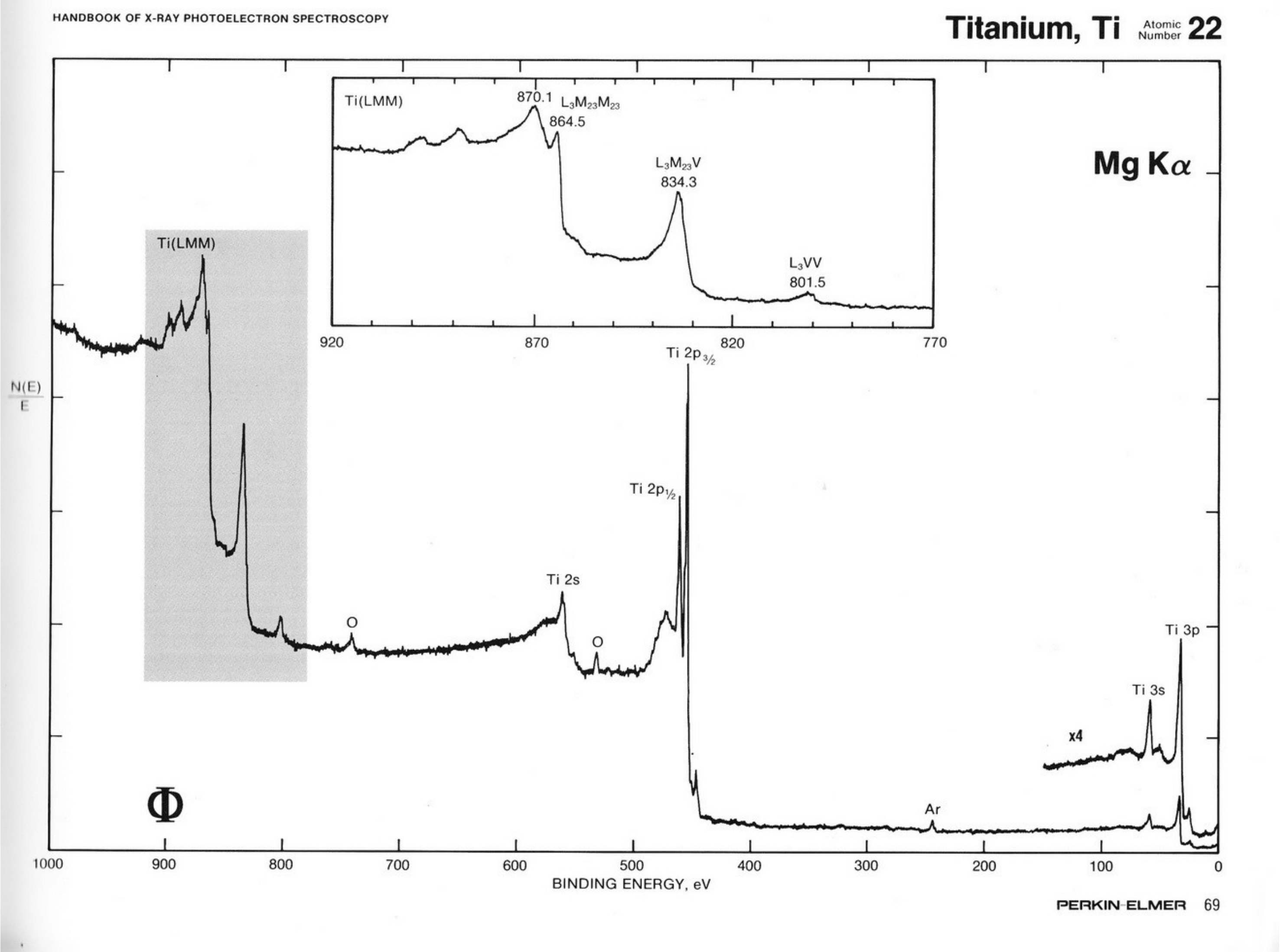


FIG. 5. Variation in core-level binding energies as a function of atomic number Z.

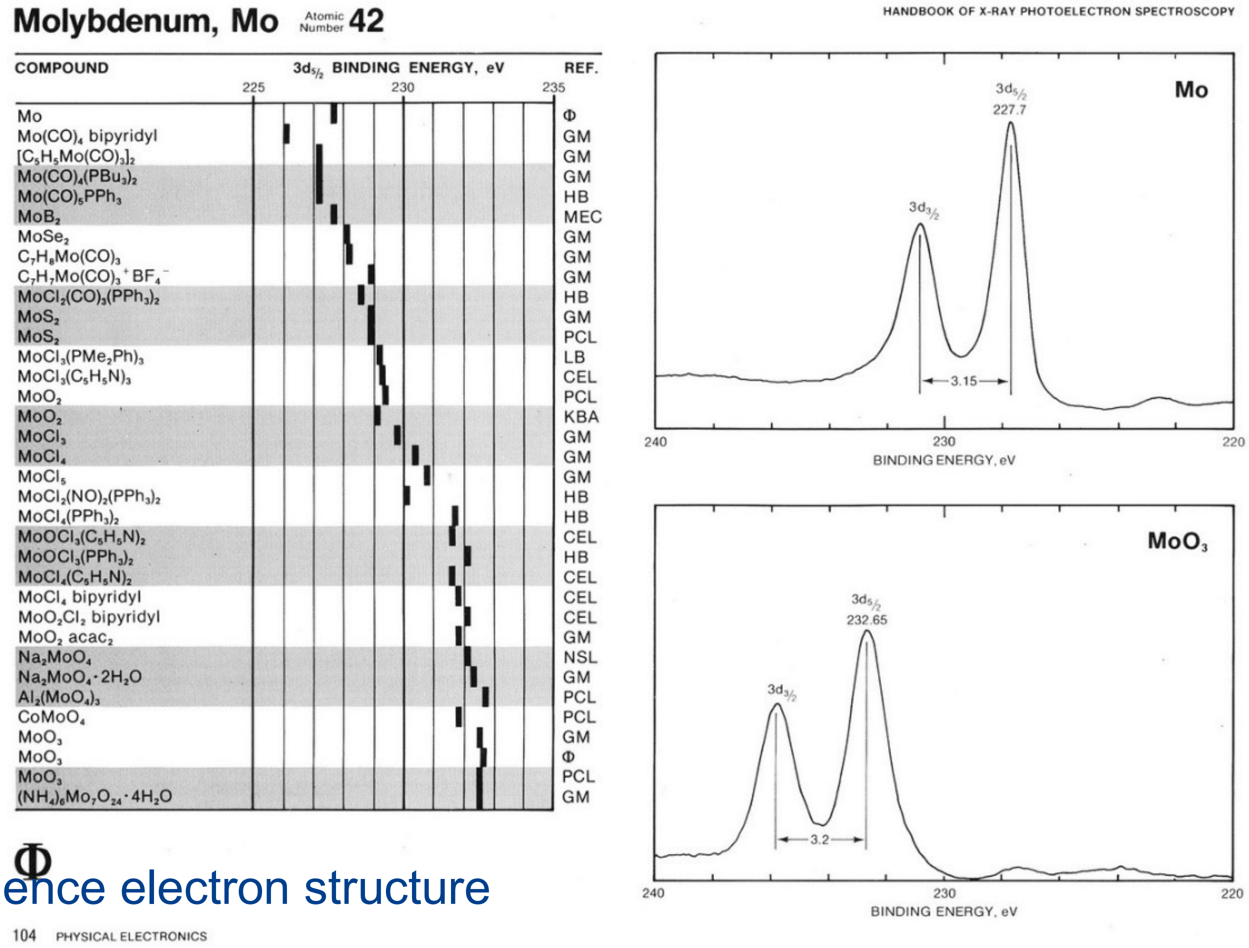
Surface sensitivity



Source of image: D. Briggs, et al.: Practical Surface Analysis, Vol. 2, Wiley, 1990



Source of image: C.D. Wagner, et al.: Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, 1978



Molybdenum, Mo

Atomic Number 42

HANDBOOK OF X-RAY PHOTOELECTRON SPECTROSCOPY

COMPOUND	REF.
Mo	Φ
$Mo(CO)_4$ bipyridyl	GM
$[C_5H_5Mo(CO)_3]_2$	GM
$Mo(CO)_4(PBu_3)_2$	GM
$Mo(CO)_5PPh_3$	HB
MoB_2	MEC
$MoSe_2$	GM
$C_7H_8Mo(CO)_3$	GM
$C_7H_7Mo(CO)_3{}^+BF_4{}^-$	GM
$MoCl_2(CO)_3(PPh_3)_2$	HB
MoS_2	GM
MoS_2	PCL
$MoCl_3(PMe_2Ph)_3$	LB
$MoCl_3(C_5H_5N)_3$	CEL
MoO_2	PCL
MoO_2	KBA
$MoCl_3$	GM
$MoCl_4$	GM
$MoCl_5$	GM
$MoCl_2(NO)_2(PPh_3)_2$	HB
$MoCl_4(PPh_3)_2$	HB
$MoOCl_3(C_5H_5N)_2$	CEL
$MoOCl_3(PPh_3)_2$	HB
$MoCl_4(C_5H_5N)_2$	CEL
$MoCl_4$ bipyridyl	CEL
MoO_2Cl_2 bipyridyl	CEL
MoO_2 $acac_2$	GM
Na_2MoO_4	NSL
$Na_2MoO_4 \cdot 2H_2O$	GM
$Al_2(MoO_4)_3$	PCL
$CoMoO_4$	PCL
MoO_3	GM
MoO_3	Φ
MoO_3	PCL
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	GM

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- Chemical bonds influence electron structure
- Core levels shift
- XPS peaks shift
- Higher oxidation state results in higher binding energy

Source of image: C.D. Wagner, et al.: Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, 1978

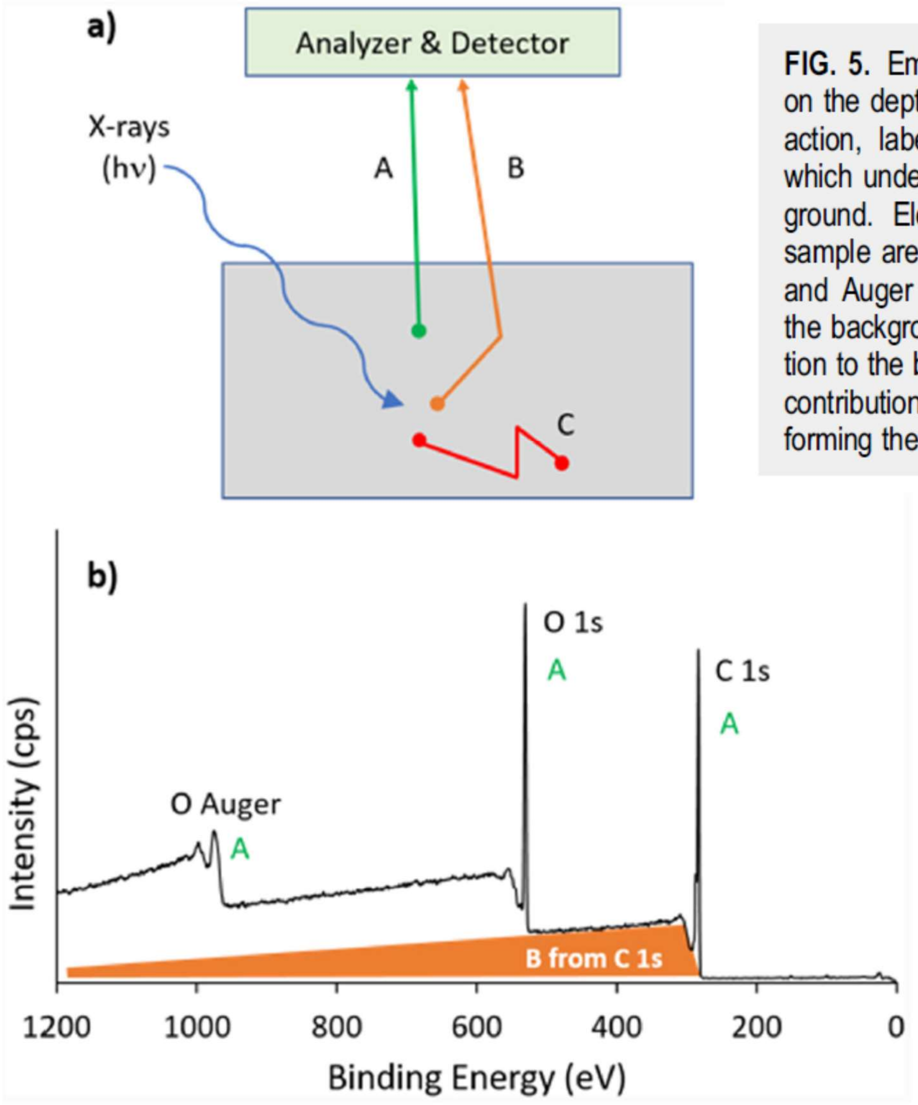


FIG. 5. Emitted electrons interact with the sample in different ways depending on the depth at which they are generated. In (a), electrons emitted without interaction, labeled A, produce XPS photoelectron and Auger peaks. Electrons which undergo at least one inelastic collision, labeled B, contribute to the background. Electrons that undergo multiple collisions and do not escape the sample are labeled C. (b) shows the XPS spectrum for PET with photoelectron and Auger peaks labeled. The orange shaded area shows the contribution to the background signal that results from C 1s electrons. While only the contribution to the background from C 1s electrons is illustrated here, similar background contributions are made by electrons from O 1s and O Auger transitions as well, forming the vertical "steps" in the baseline observed for every major peak.

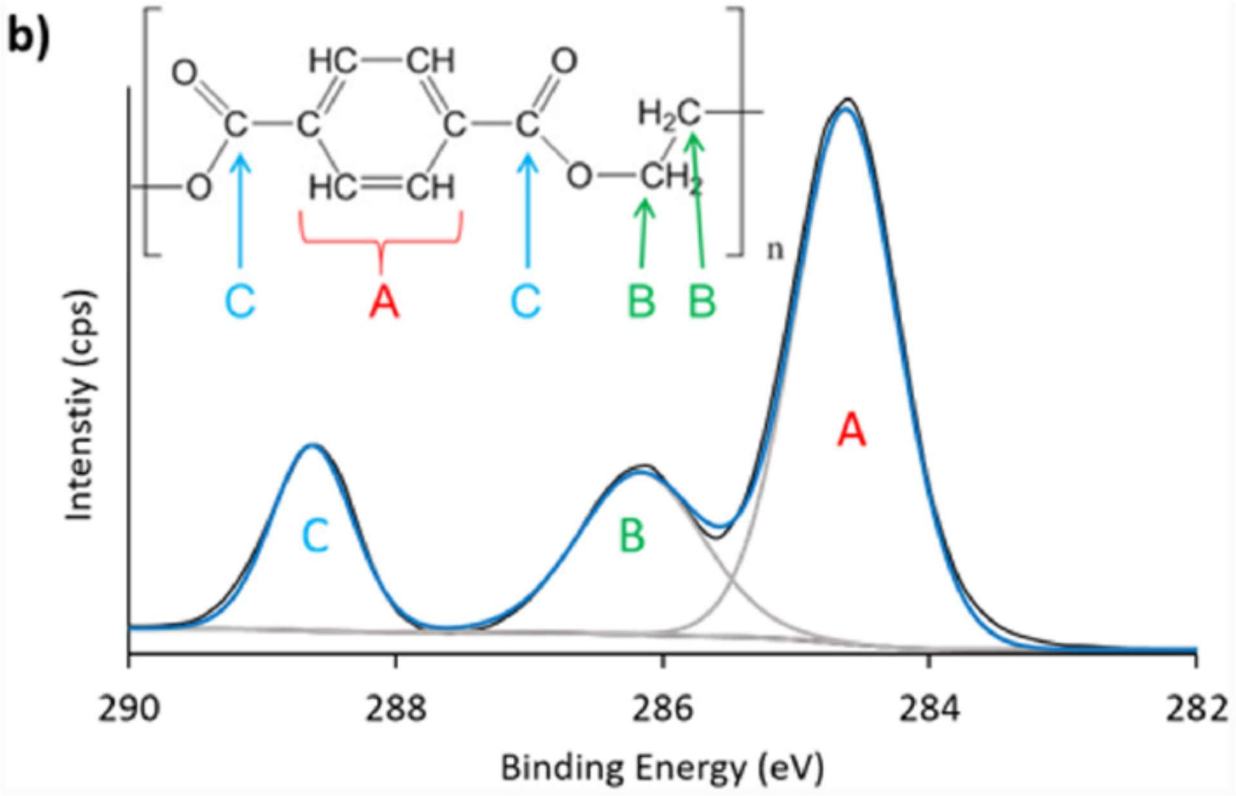


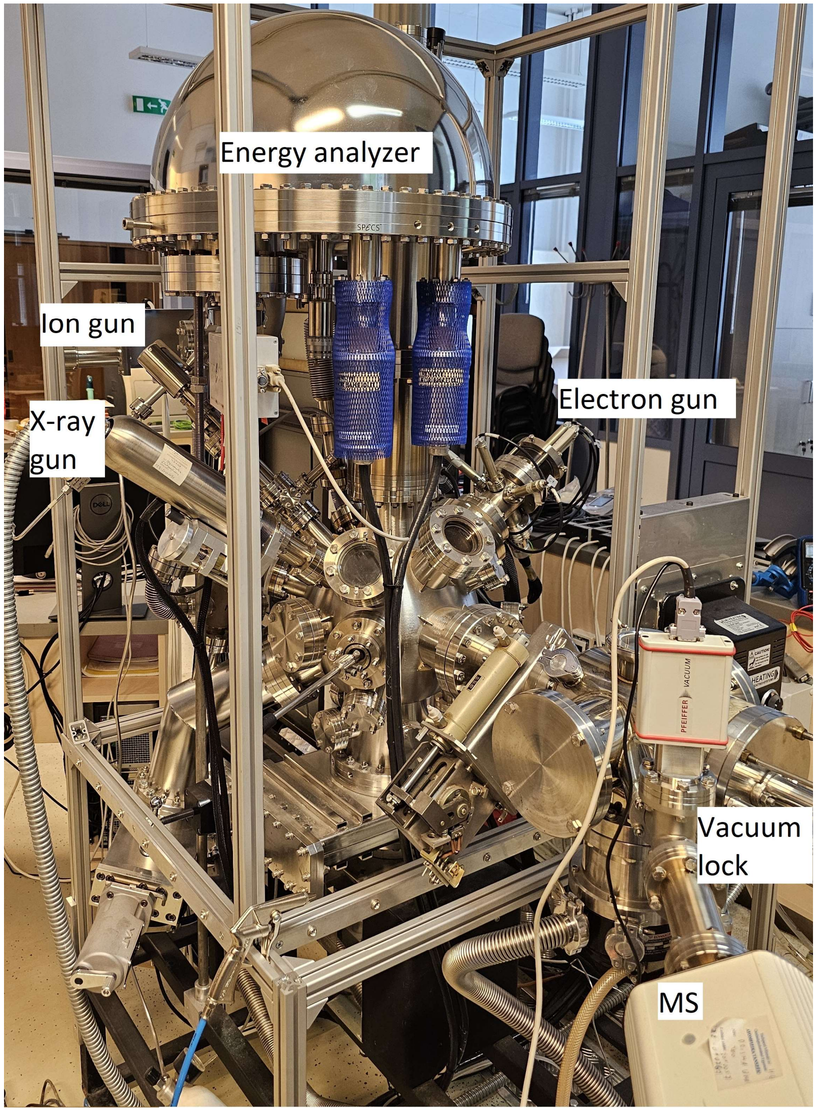
FIG. 4. XPS survey spectrum (a) and high-resolution C 1s spectrum (b) of PET. The inset of (b) shows the chemical structure of PET and the assignments of the three peaks in the C 1s spectrum.

XPS Characteristics

- Accurate elemental composition (~0.1 atomic percent)
- Chemical state identification
- Information depth: 3-5 nm
- Bad lateral resolution ~30μm
- Depth profiling
  - By ion by sputtering

Comparison

- SIMS
  - Trace element analysis (~ppm)
  - Organic compound identification
  - Information depth < 1nm
  - Usually not quantitative
- AES
  - Excellent lateral resolution (~10 nm)
  - Elemental composition
  - Chemical state identification
  - Low sensitivity
- XPS
  - Precise elemental composition (~0.1 atomic percent)
  - Chemical state identification
  - Low lateral resolution


Energy analyzer
Ion gun
X-ray gun
Electron gun
Vacuum lock
MS