Budapest University of Technology and Economics
Department of Atomic Physics, Surface Physics Laboratory

SURFACE ANALYSIS

GÁBOR DOBOS

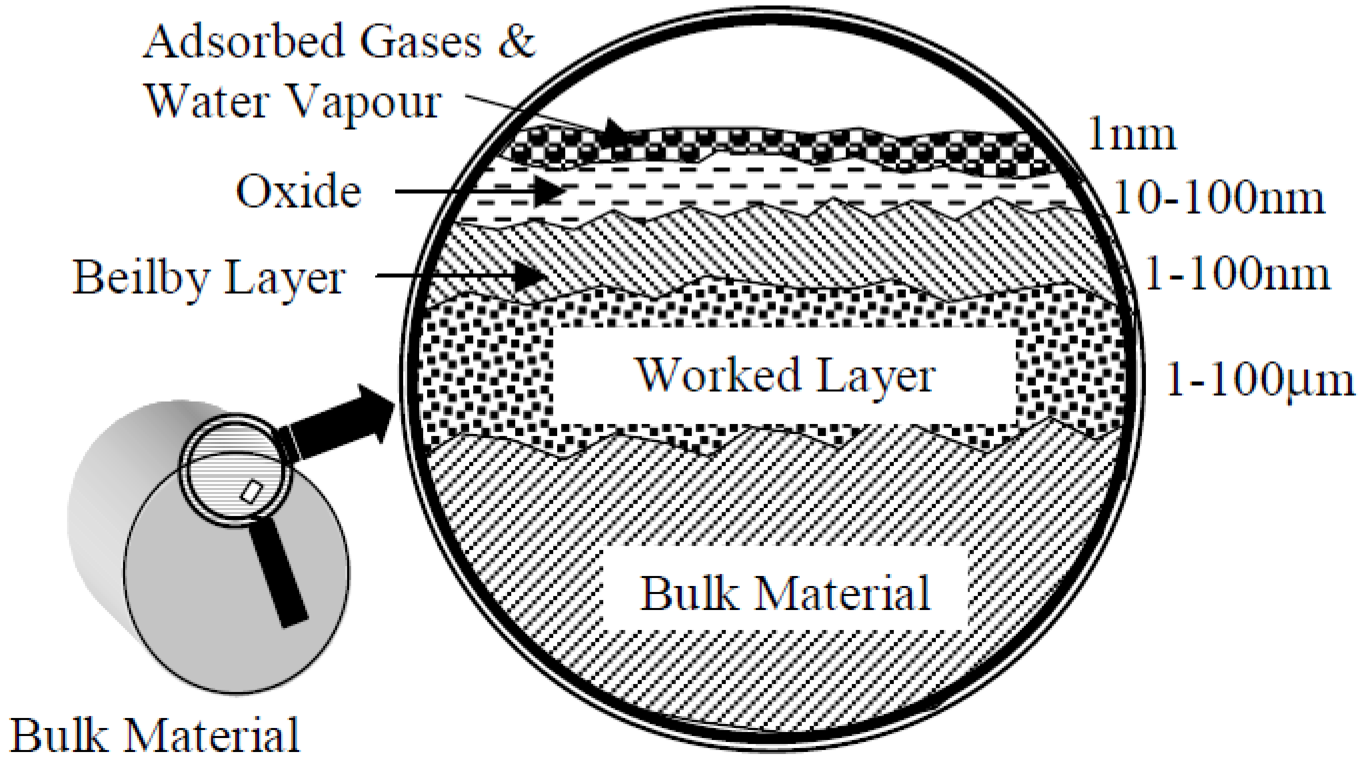
Outline

- Introduction
  - Why is it important?
  - Surface sensitive analytical methods
- Secondary Ion Mass Spectroscopy (SIMS)
  - Principle of operation
  - Properties
  - SIMS spectra
  - Depth profiles
- Auger Electron Spectroscopy (AES)
- X-ray Photoelectron Spectroscopy (XPS)
- Other methods (structure, morphology)

Literature

- 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
- xpssimplified.com
- www.nist.gov

What is the „surface”?



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

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

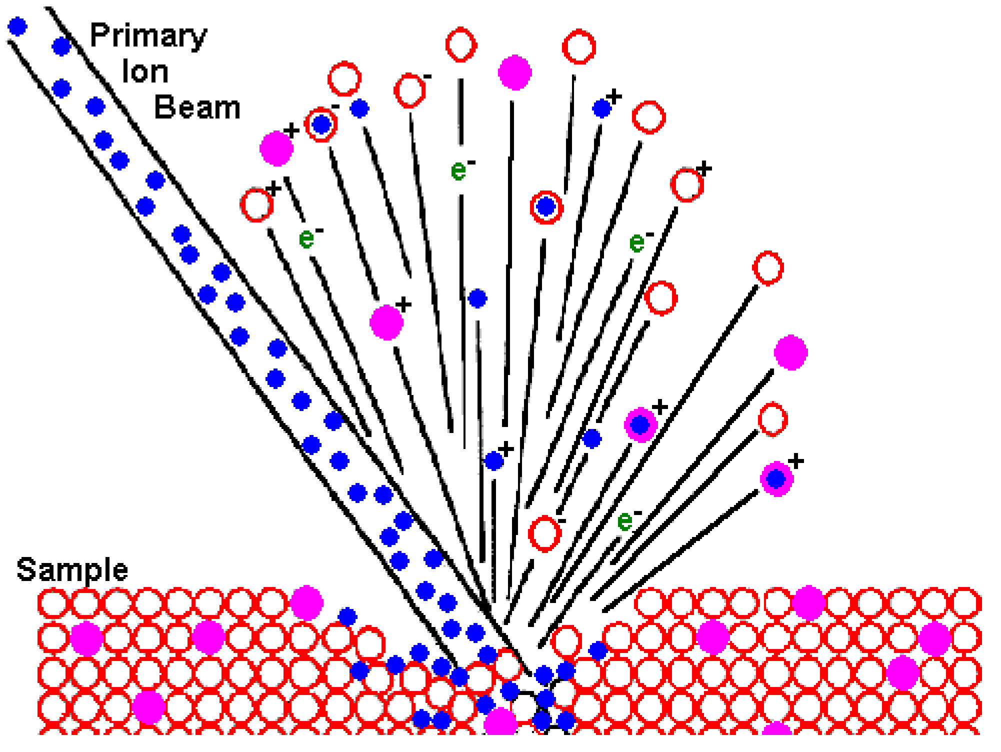
→ Wet chemical methods won't work…

Surface analysis

- Surface sensitive methods are required
- Information depth should be comparable to atomic distances

- The mean free path of charged particles is very short in solids
- Grazing angle incidence
- Comparing measurements with different information depths

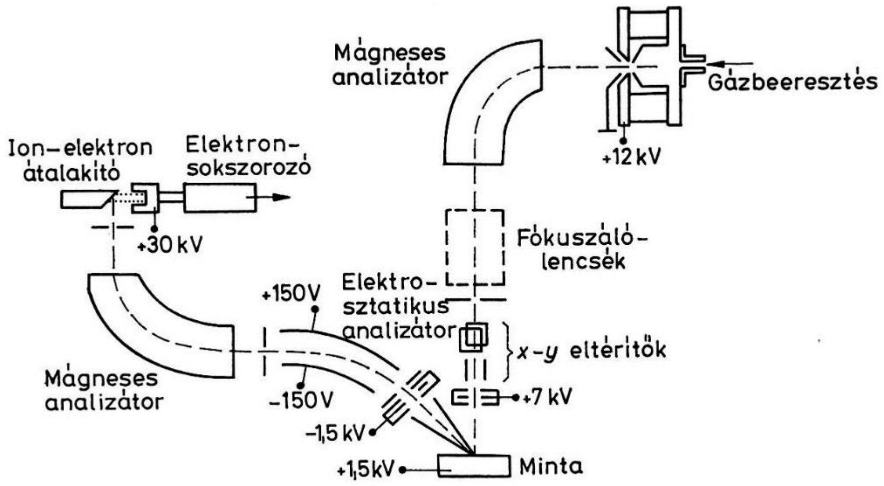
Secondary Ion Mass Spectroscopy (SIMS)



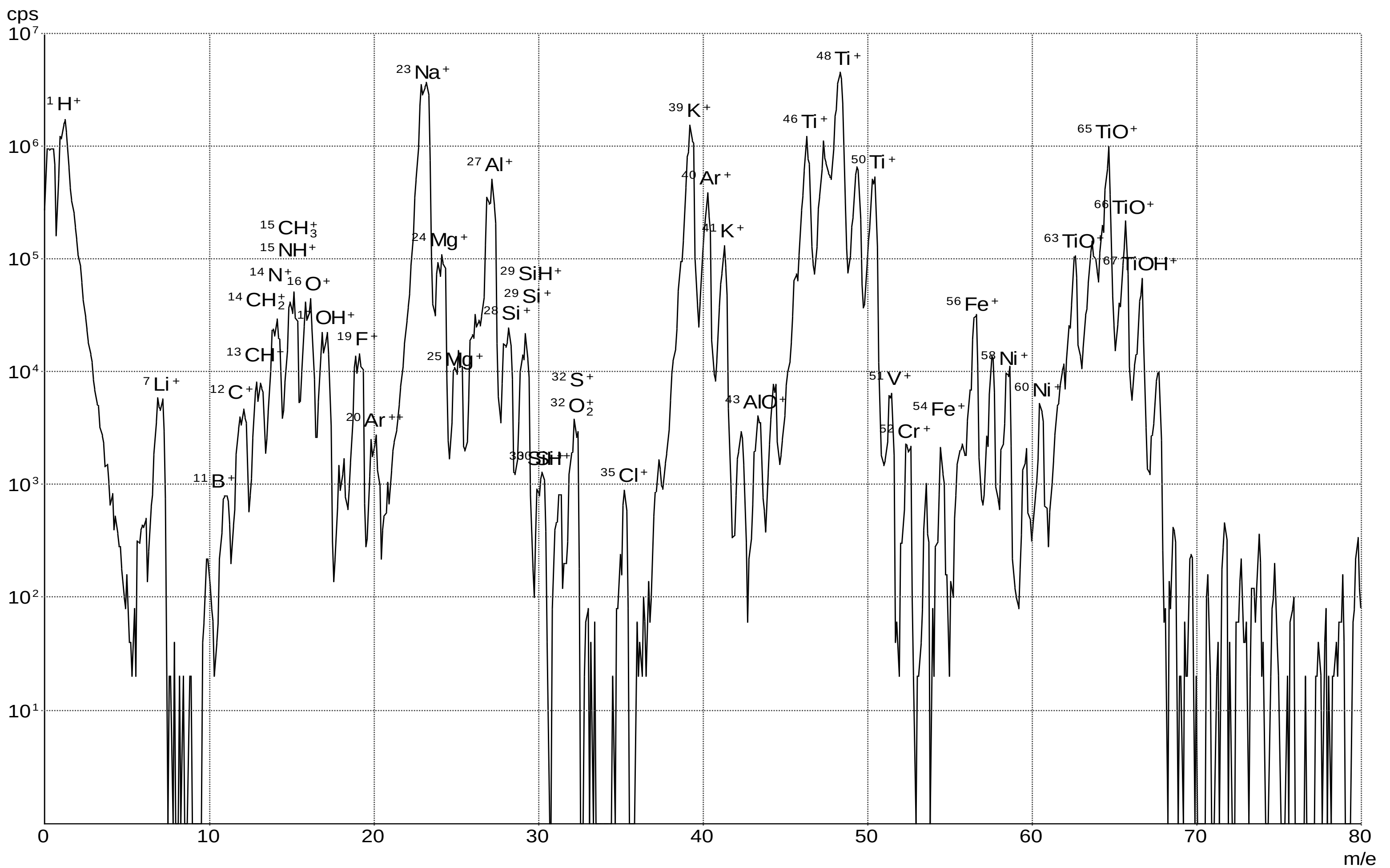
Source of image: http://pprco.tripod.com/SIMS/Theory.htm

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



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


cps
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10^3
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10^1
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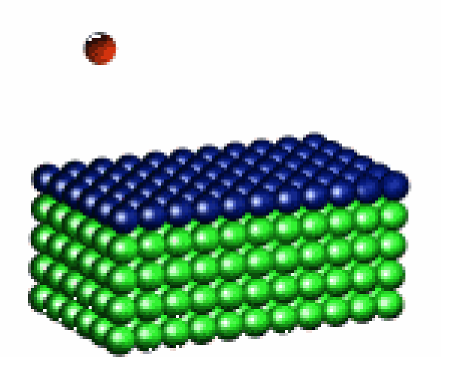
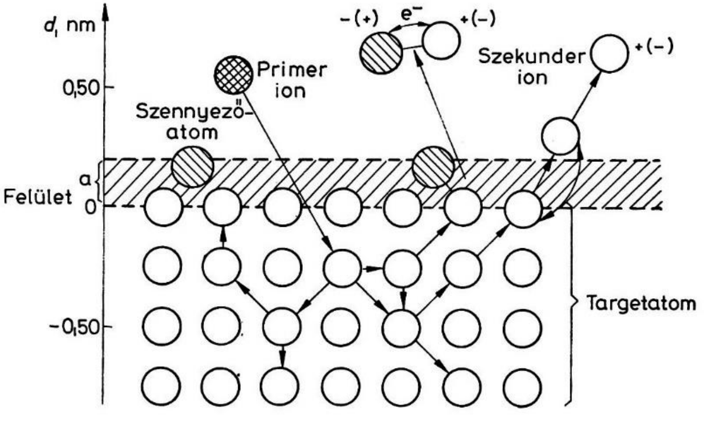
10
20
30
40
50
60
70
80
m/e
$^1H^+$
$^7Li^+$
$^{11}B^+$
$^{12}C^+$
$^{13}CH^+$
$^{14}CH_2^+$
$^{14}N^+$
$^{15}NH^+$
$^{15}CH_3^+$
$^{16}O^+$
$^{17}OH^+$
$^{19}F^+$
$^{20}Ar^{++}$
$^{23}Na^+$
$^{24}Mg^+$
$^{25}Mg^+$
$^{27}Al^+$
$^{28}Si^+$
$^{29}Si^+$
$^{29}SiH^+$
$^{30}SiH^+$
$^{32}S^+$
$^{32}O_2^+$
$^{35}Cl^+$
$^{39}K^+$
$^{40}Ar^+$
$^{41}K^+$
$^{43}AlO^+$
$^{46}Ti^+$
$^{48}Ti^+$
$^{50}Ti^+$
$^{51}V^+$
$^{52}Cr^+$
$^{54}Fe^+$
$^{56}Fe^+$
$^{58}Ni^+$
$^{60}Ni^+$
$^{63}TiO^+$
$^{65}TiO^+$
$^{66}TiO^+$
$^{67}TiOH^+$

- Primer 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…*

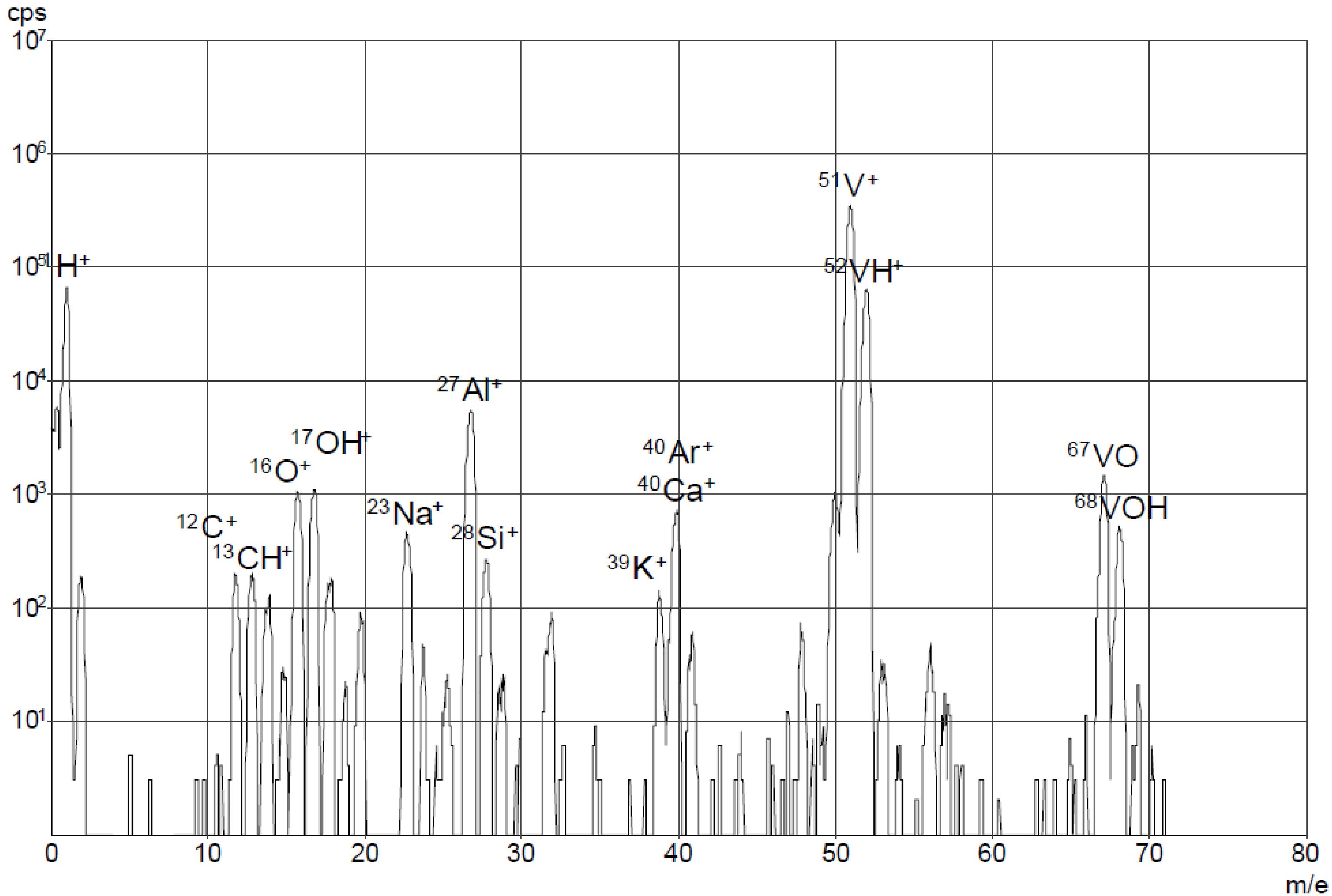




Source of images: http://www.iontof.com/
Brümer et al.: Szilárd Testek Vizsgálata Elektronokkal, Ionokkal és röntgensugarakkal, Műszaki Könyvkiadó, 1984

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
10^7
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10^1
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12C+
13CH+
16O+
17OH+
23Na+
27Al+
28Si+
39K+
40Ar+
40Ca+
51V+
52VH+
67VO
68VOH
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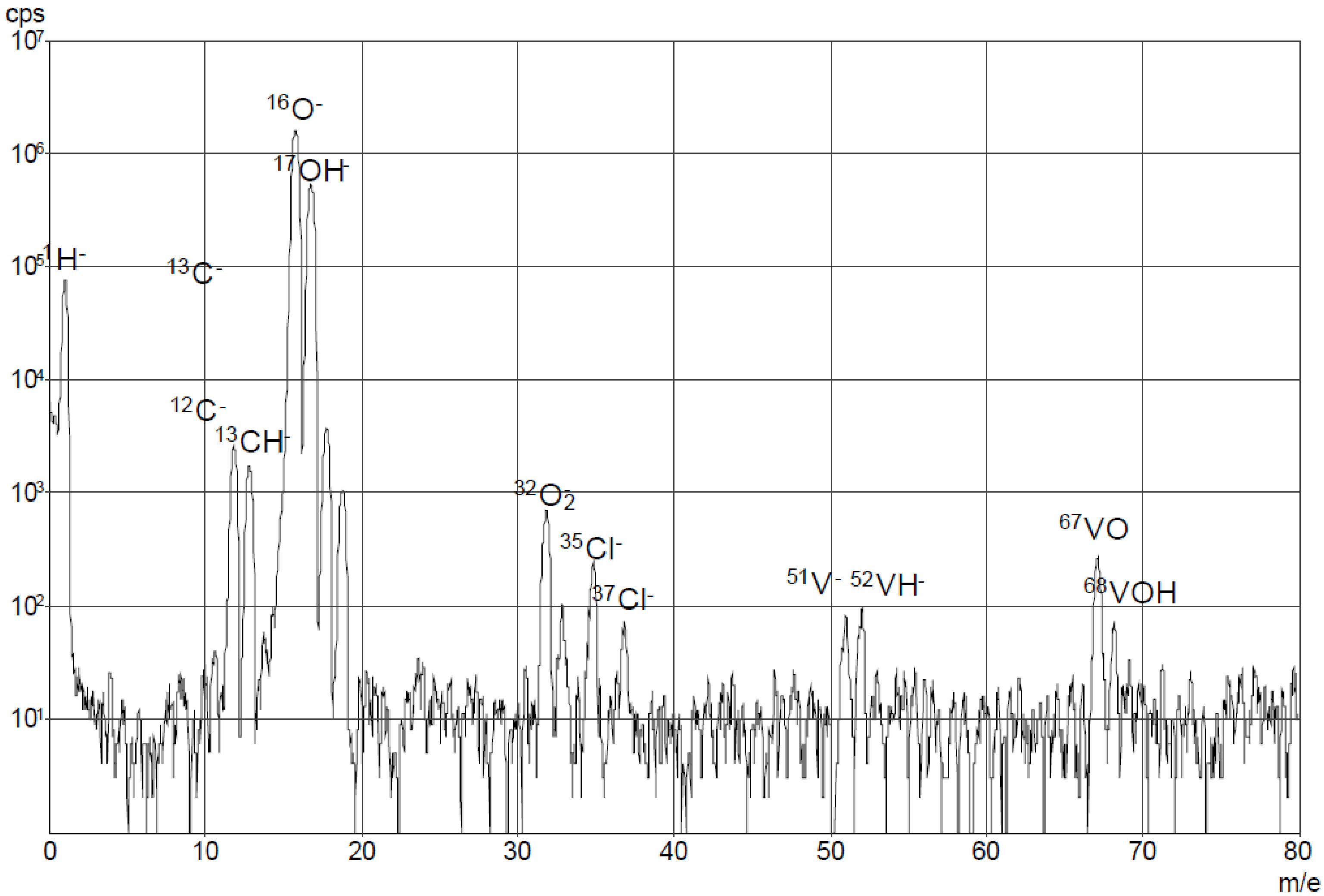
m/e


cps
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17OH-
1H-
13C-
12C-
13CH-
32O2-
35Cl-
37Cl-
51V-
52VH-
67VO
68VOH
0
10
20
30
40
50
60
70
80
m/e

$$I^{\pm}_{s,Z,A/q} = I_p \cdot S \cdot \gamma^{\pm}_{Z,q} \cdot a_{Z,A} \cdot c_Z \cdot \eta_{A/q}$$

I_p – Primer ion current [A]

S – Sputtering yield [atom/ion]

$\gamma^{\pm}_{Z,q}$ – Ionization probability [ion/atom]

$a_{Z,A}$ – Abundance (0-1)

c_Z – Surface concentration (0-1) [atomic%]

$\eta_{A/q}$ – Transmission (0-1)

Main problem

Ionization probability depends on many parameters

- Element
- Matrix effect
  - Local chemical environment
- Measurement conditions
  - Primer ion
  - Energy of primer ions
  - Background pressure

→ No universal sensitivity factors

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

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

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

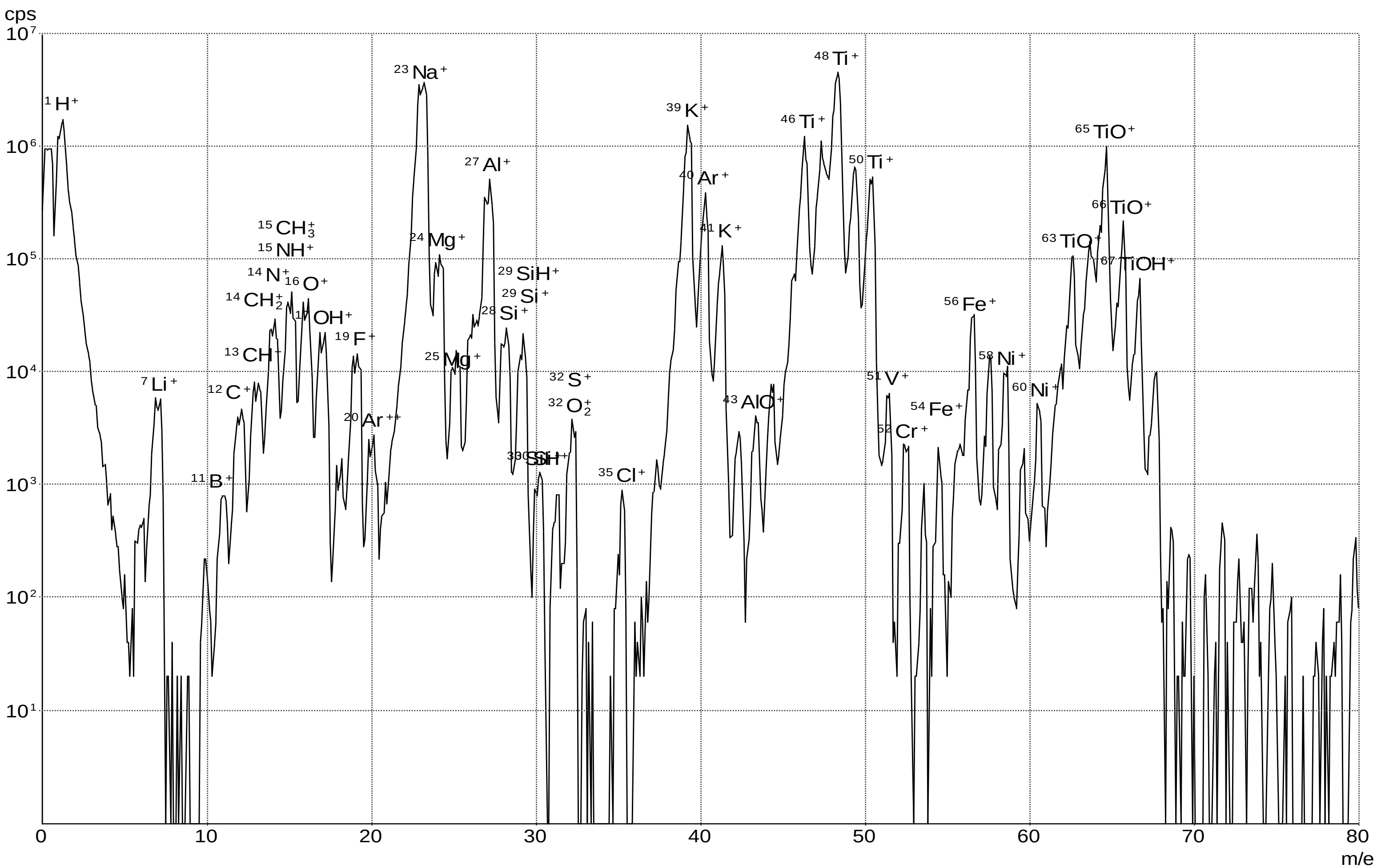
SNMS

- 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)

Spectrum characteristics

- Elements may have multiple isotopes
  - Ratio of isotopes is constant
  - Deviation in isotope ratios indicate the presence of isobars
- Isobars
  - Multiple elements may have isotopes with the same mass
  - Modern spectrometers may be able to separate them
- Cluster ions
- Multiple ionization
- Surface contamination
  - Alkali metals
  - Oxygen, water
  - Organic fragments
  - Primer ions may get implanted in the sample
- Higher background on negative spectra due to electrons


cps
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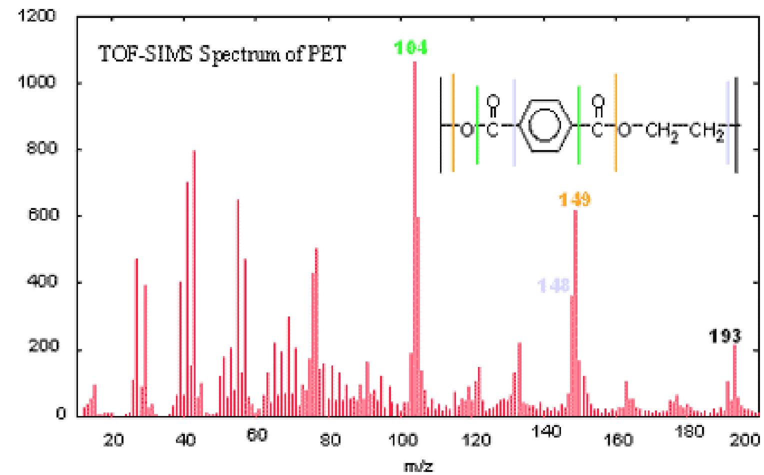
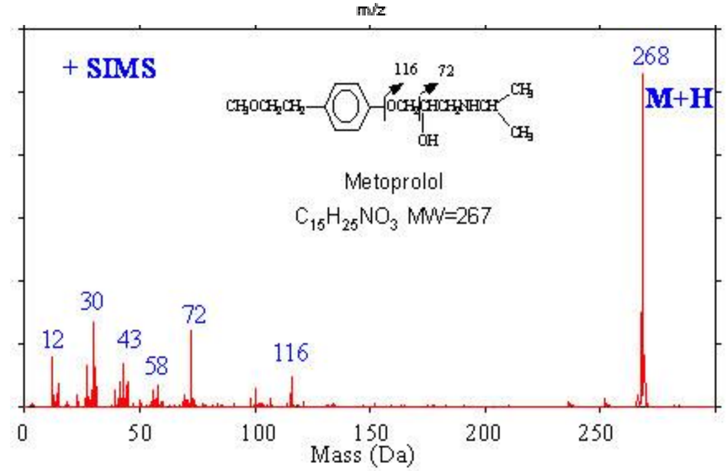
$^{14}N^{+}$
$^{15}NH^{+}$
$^{15}CH_3^{+}$
$^{16}O^{+}$
$^{17}OH^{+}$
$^{19}F^{+}$
$^{20}Ar^{++}$
$^{23}Na^{+}$
$^{24}Mg^{+}$
$^{25}Mg^{+}$
$^{27}Al^{+}$
$^{28}Si^{+}$
$^{29}Si^{+}$
$^{29}SiH^{+}$
$^{32}S^{+}$
$^{32}O_2^{+}$
$^{35}Cl^{+}$
$^{39}K^{+}$
$^{40}Ar^{+}$
$^{41}K^{+}$
$^{43}AlO^{+}$
$^{46}Ti^{+}$
$^{48}Ti^{+}$
$^{50}Ti^{+}$
$^{51}V^{+}$
$^{52}Cr^{+}$
$^{54}Fe^{+}$
$^{56}Fe^{+}$
$^{60}Ni^{+}$
$^{63}TiO^{+}$
$^{65}TiO^{+}$
$^{66}TiO^{+}$
$^{67}TiOH^{+}$

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
- Attachment of alkali ion



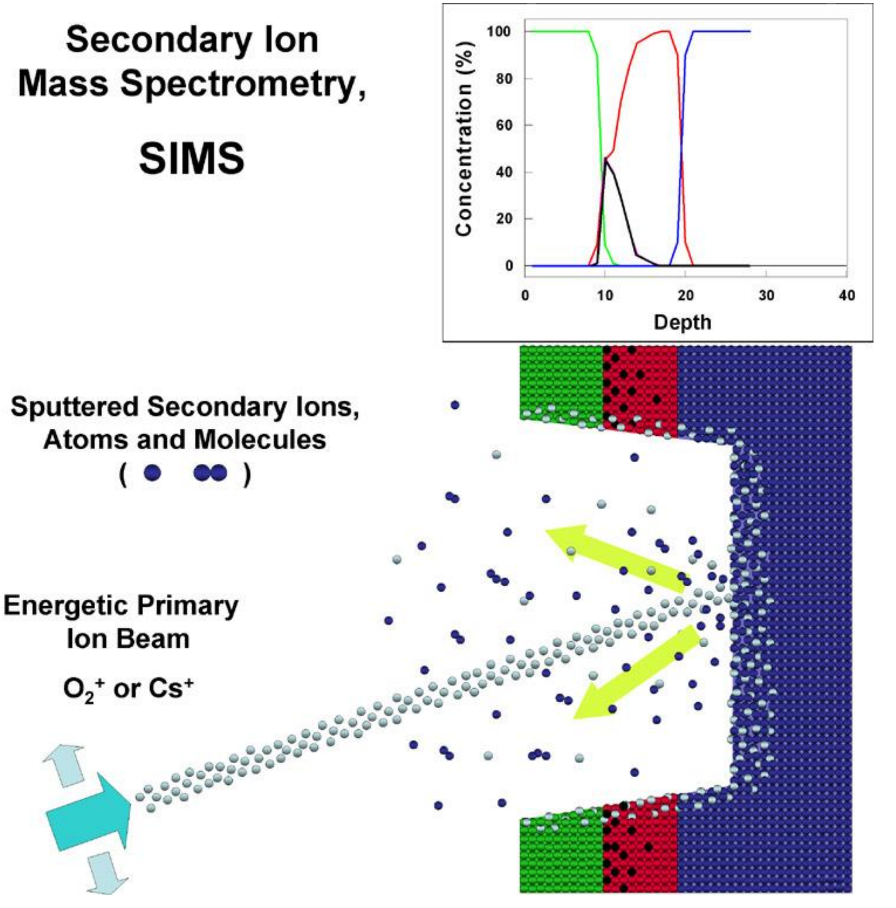


Mass spectrum of Metroprolol showing molecular and fragment peaks

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

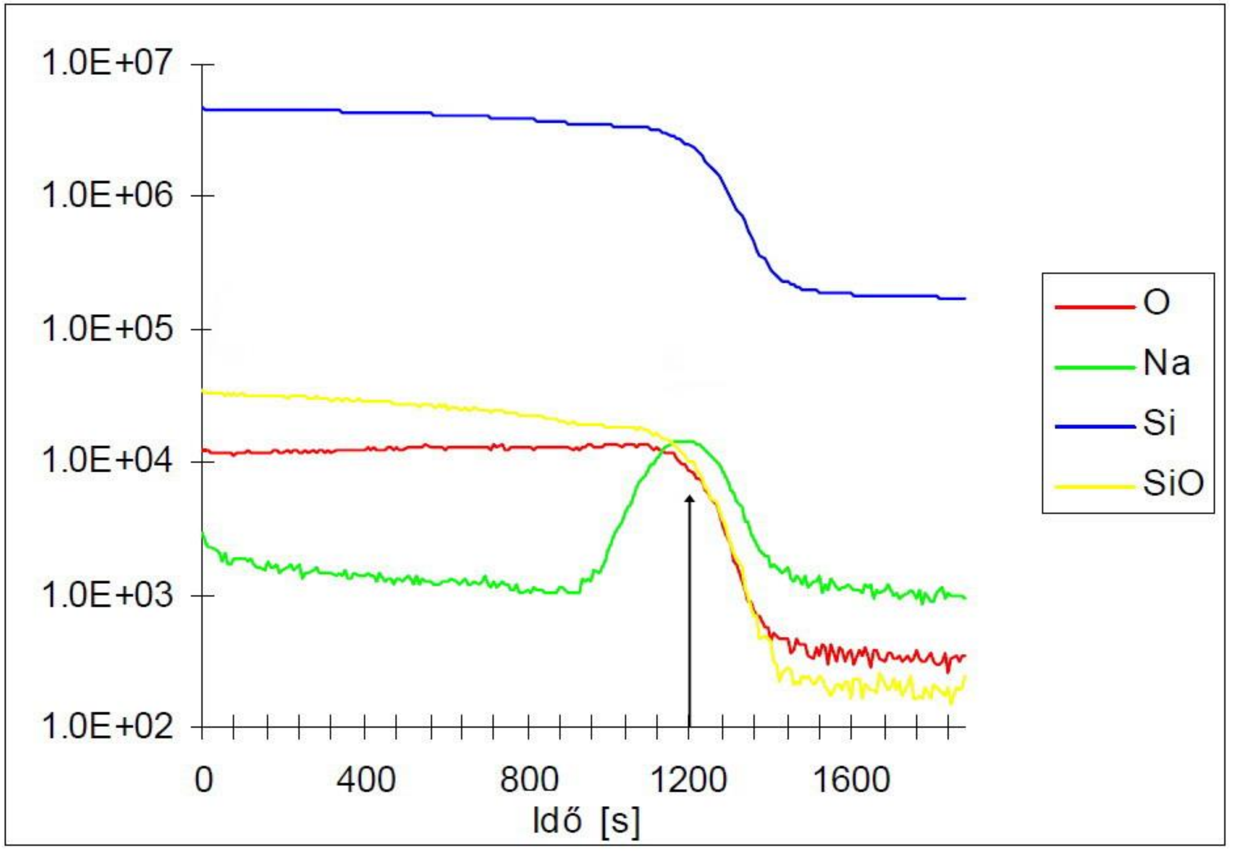
- Continuous ion bombardment
- Record peak intensities as a function of time



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



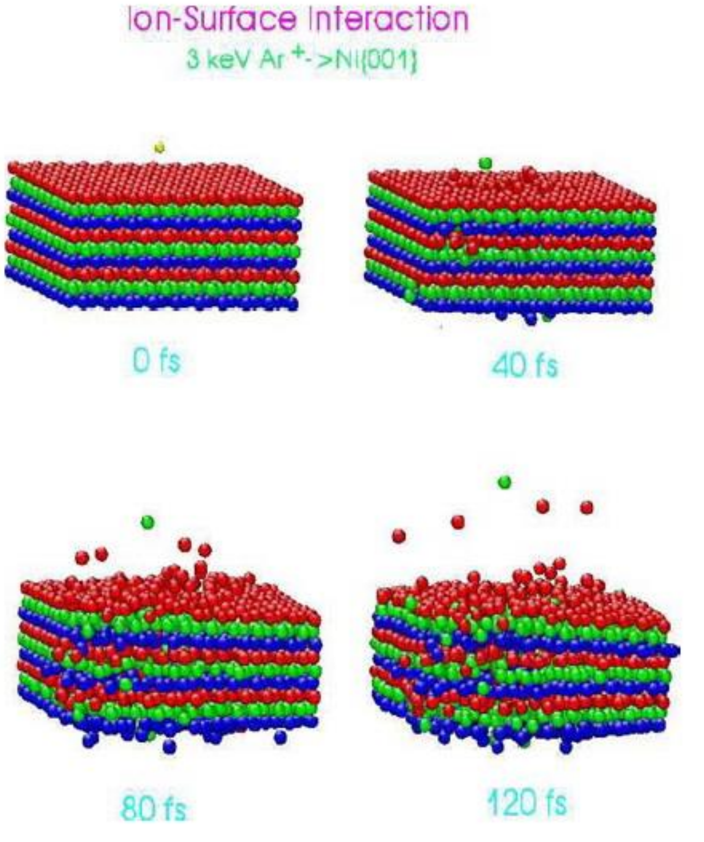
Depth profile

Problems:

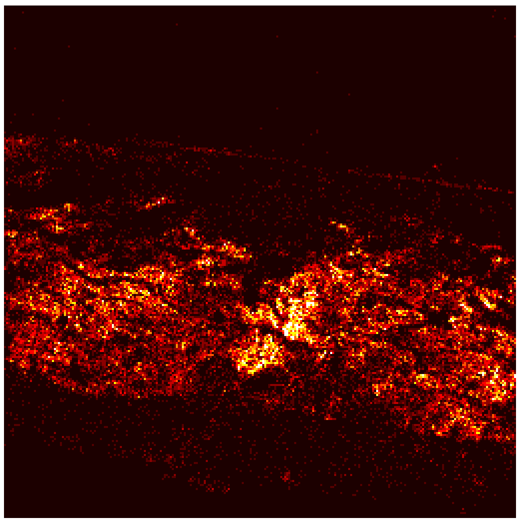
- Mixing due to ion bombardment
- Surface roughness increases
  - Mainly in case of policrystalline samples
  - Rotating the sample elviates the problem
- Bottom of the crater is not flat

→ Resulotion decreases

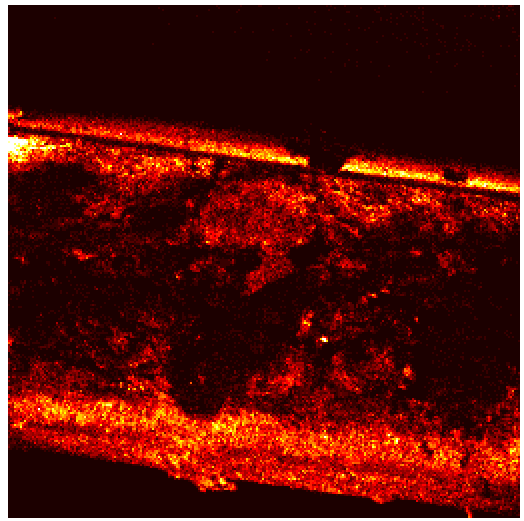
- Preferential sputtering
- Sputtering speed?
  - Depends of the material
  - Requires calibration



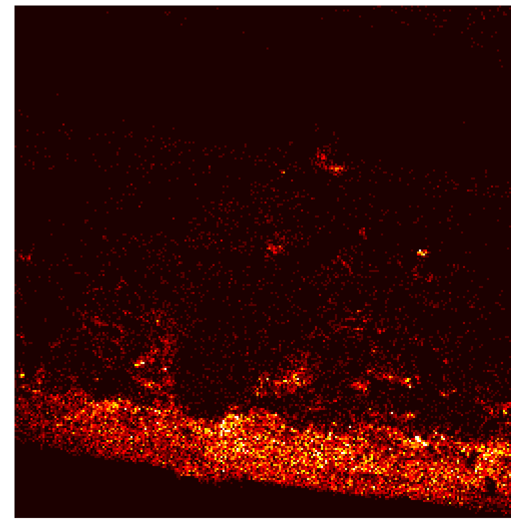
Lateral distribution mapping



$C_3H_7O^+$
(Cellulose fragment)

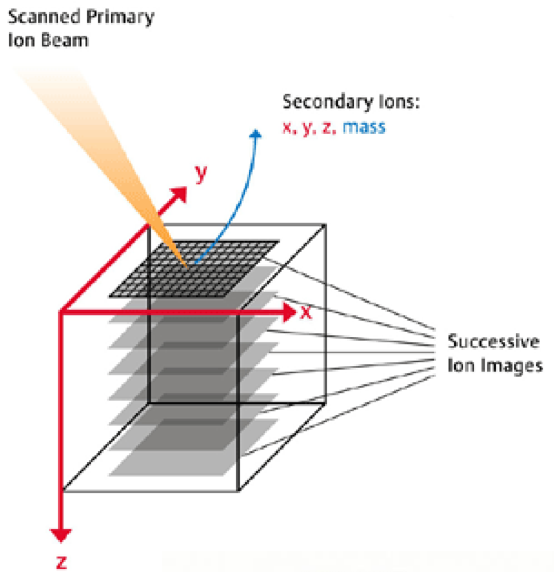


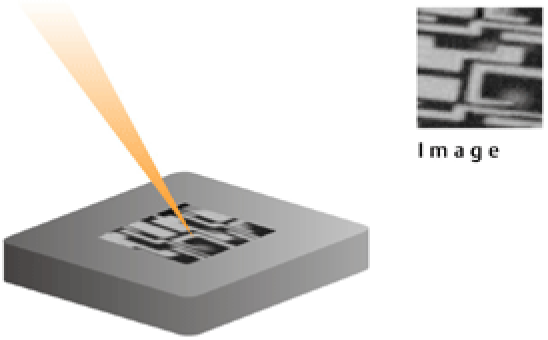
Na^+

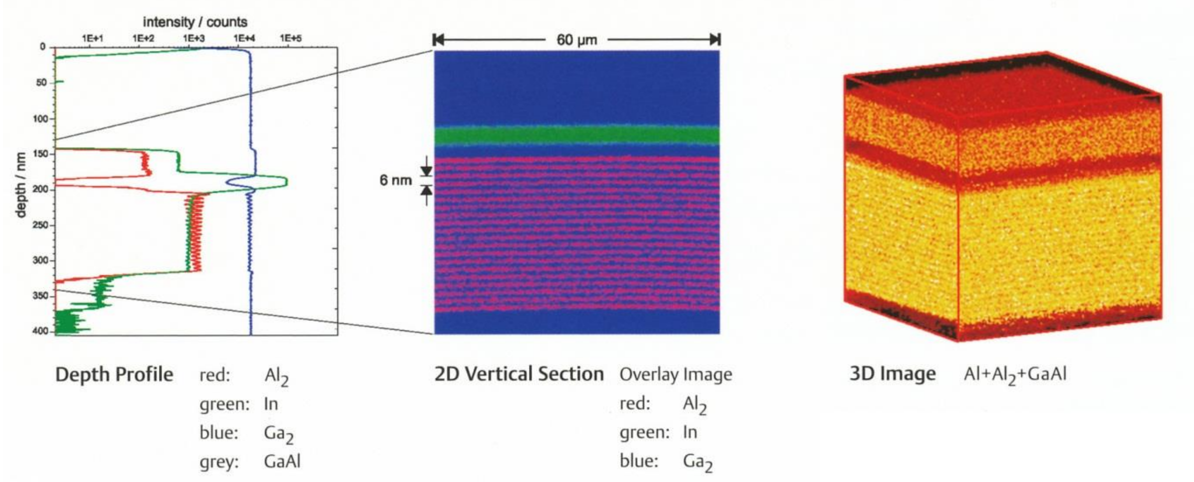


Fe^+

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







Source of images: http://www.iontof.com/

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

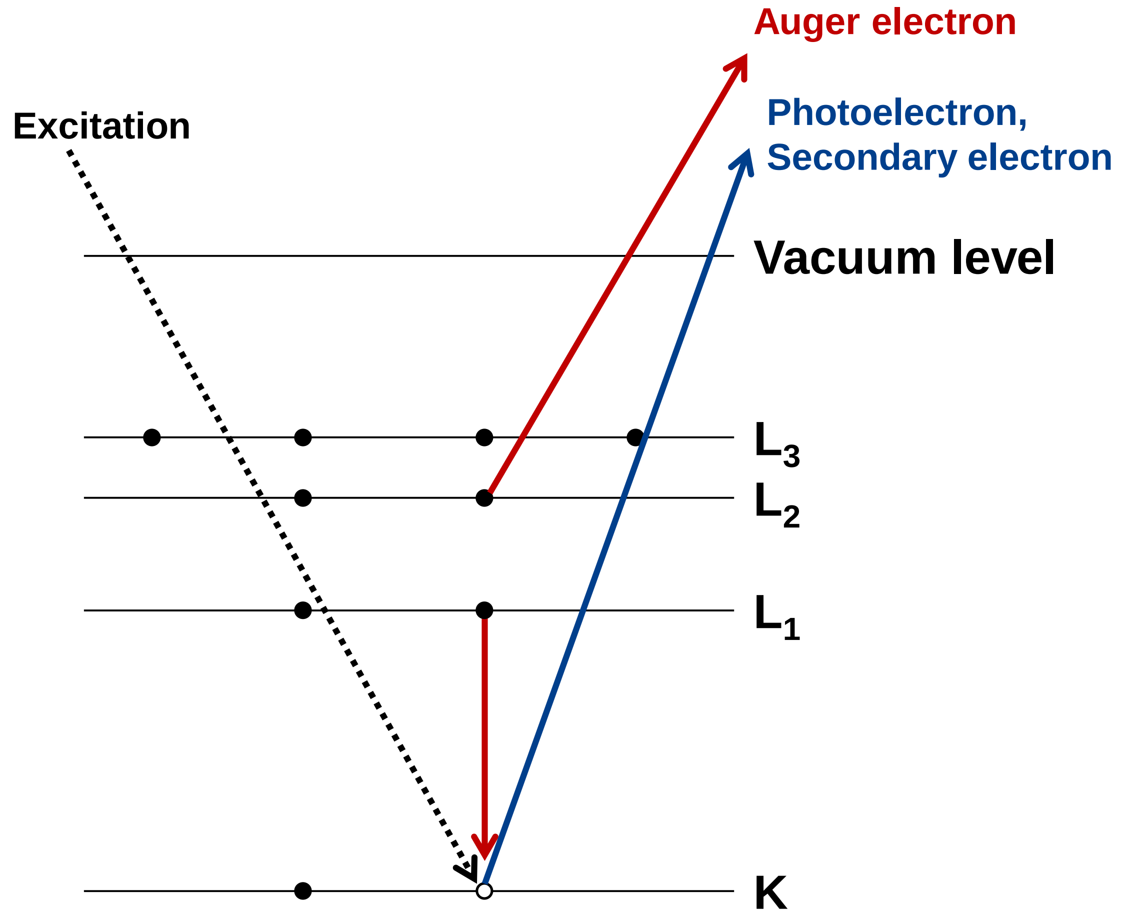
- Advantages
  - Surace sensitive
    - Information depth: 1-2 atomic layers
  - Trace element analysis
  - Depth profiles, lateral distribution, 3D analysis
  - Organic molecule identification
  - Chemical information from claster ions and organic fragments

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

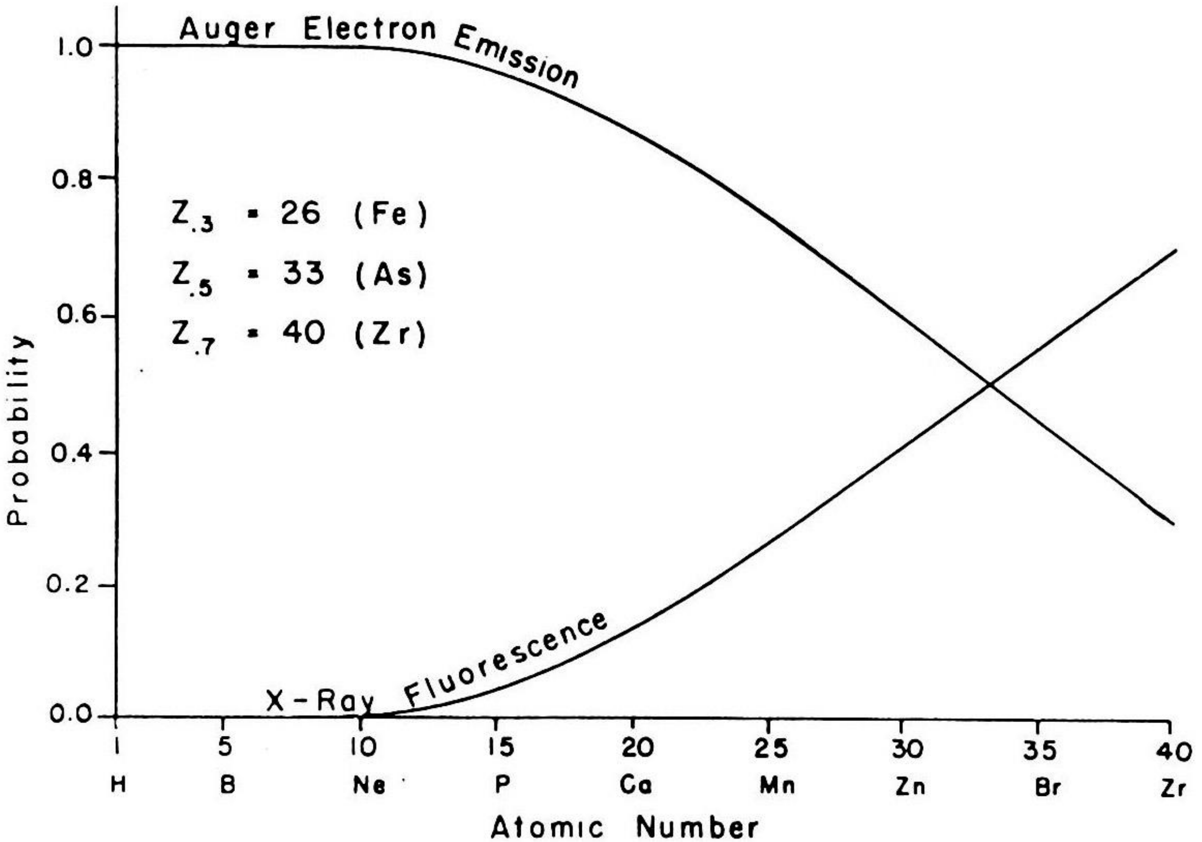
Auger Process

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
. . .			

V: Valence electron
C: Core electron



Likelihood of the Auger process

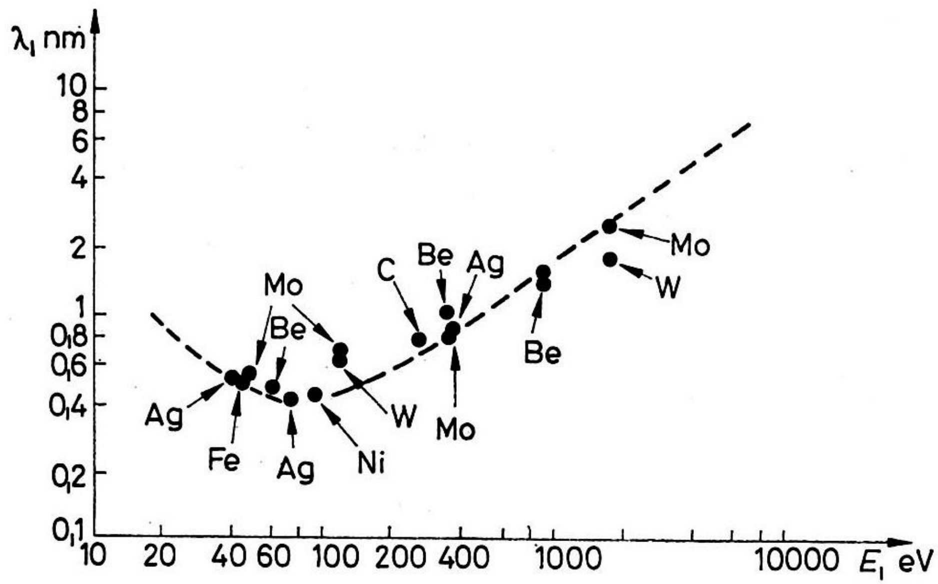


Source of image: D. Briggs, et al.: Practical Surface Analysis, Vol. 2, Wiley, 1990

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:
  - $E_{KLL} = E_K – E_{L1}^* - E_{L2}^*$
- Measurement of secondary electron energy distribution
- Peak positions → Element identification
- Peak intensities → Concentrations

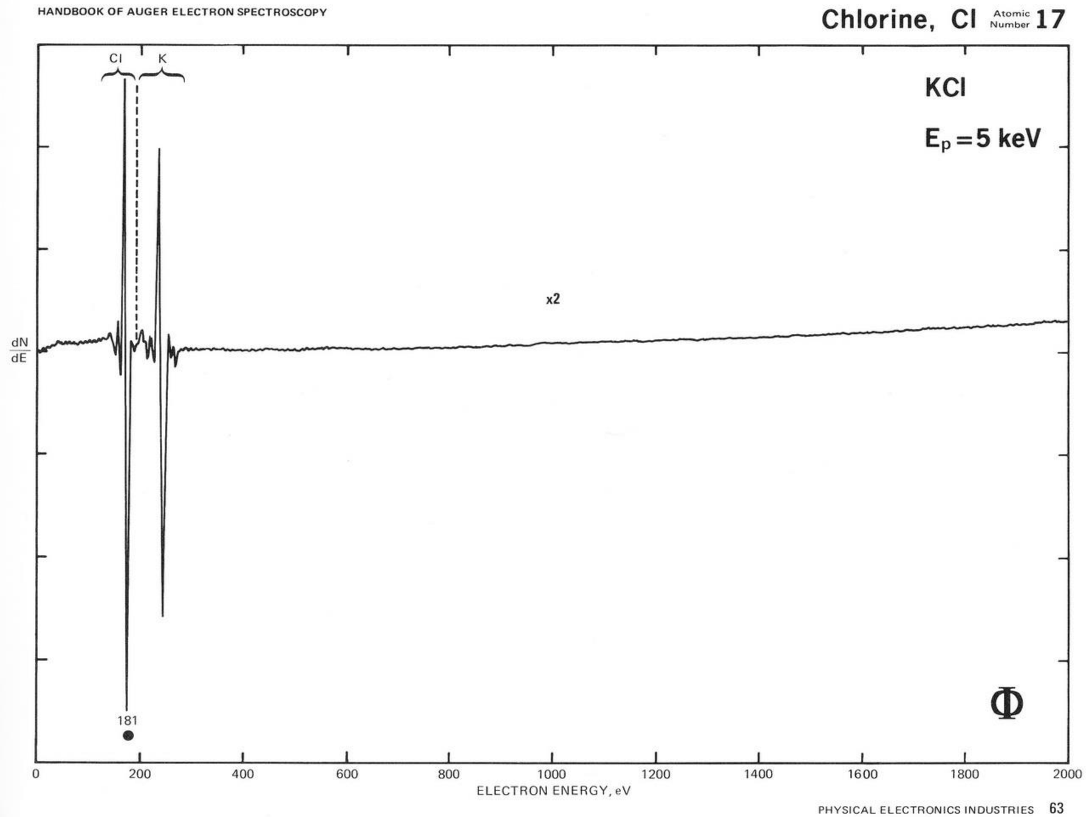
Surface Sensitivity



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

  → Background

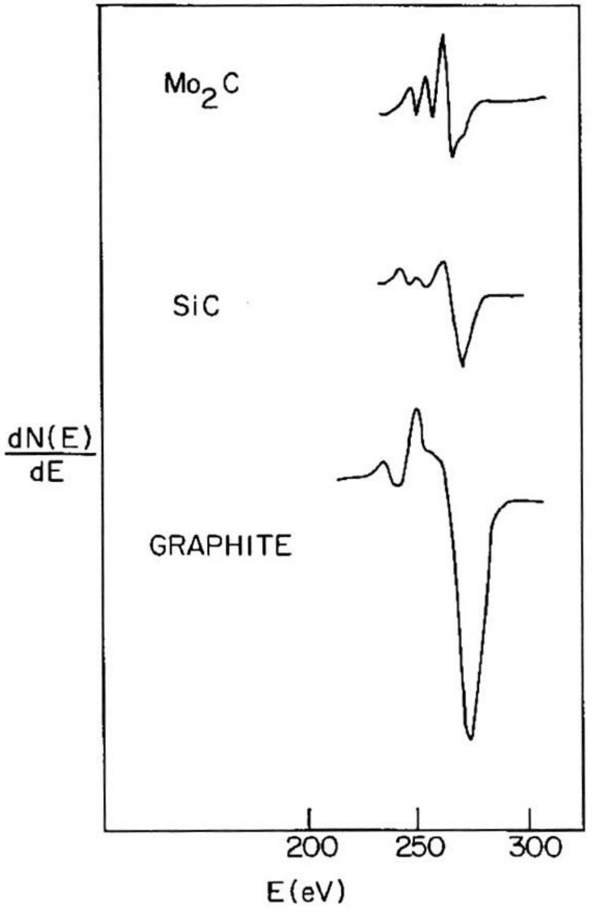
Source of image: Brümer et al.: Szilárd Testek Vizsgálata Elektronokkal, Ionokkal és röntgensugarakkal, Műszaki Könyvkiadó, 1984



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

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

Chemical State Identification



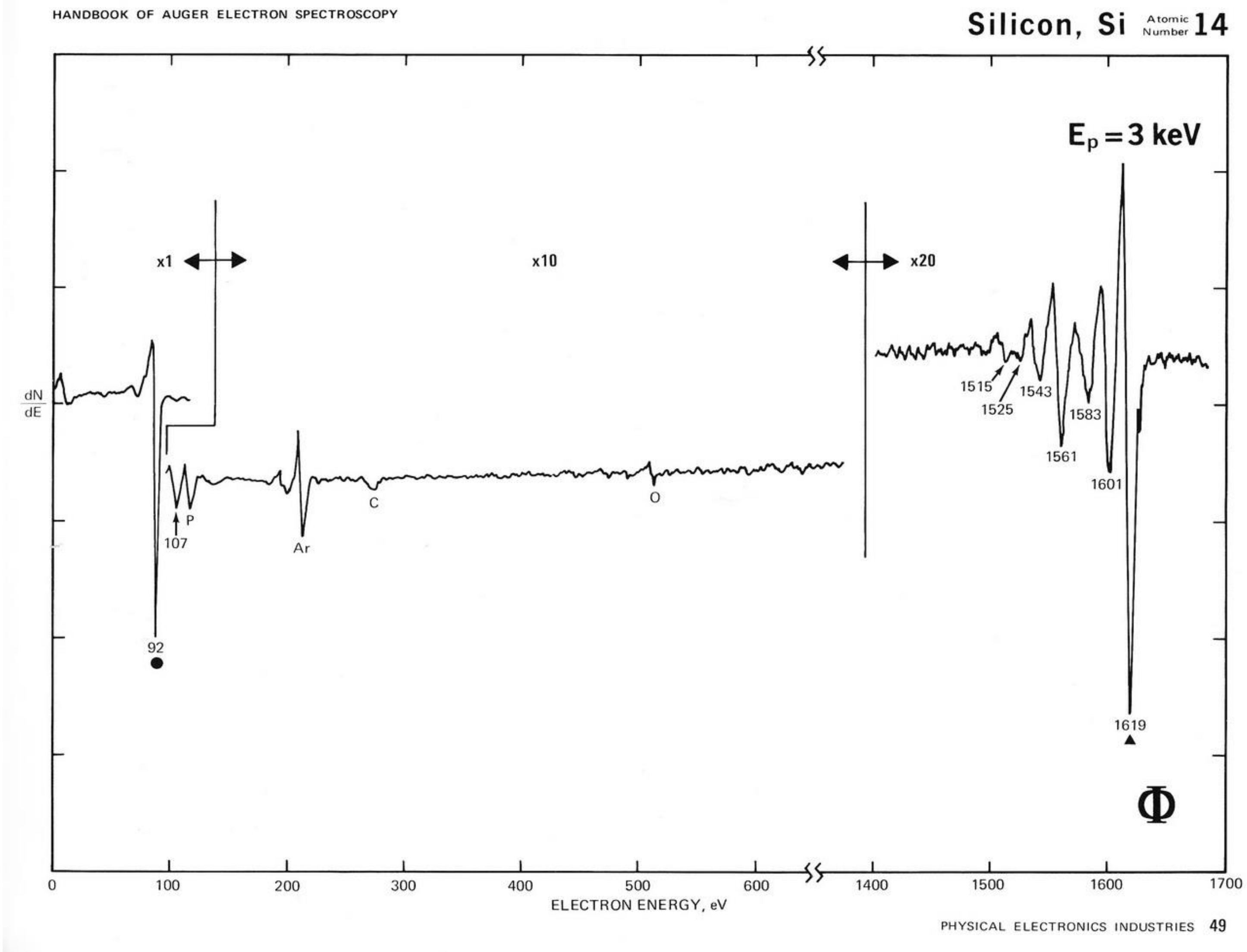
- Auger electron energies are determined by atomic energy levels
- The formation of chemical bonds, changes the electron structure of the atom
- Even the core levels shift

→ 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



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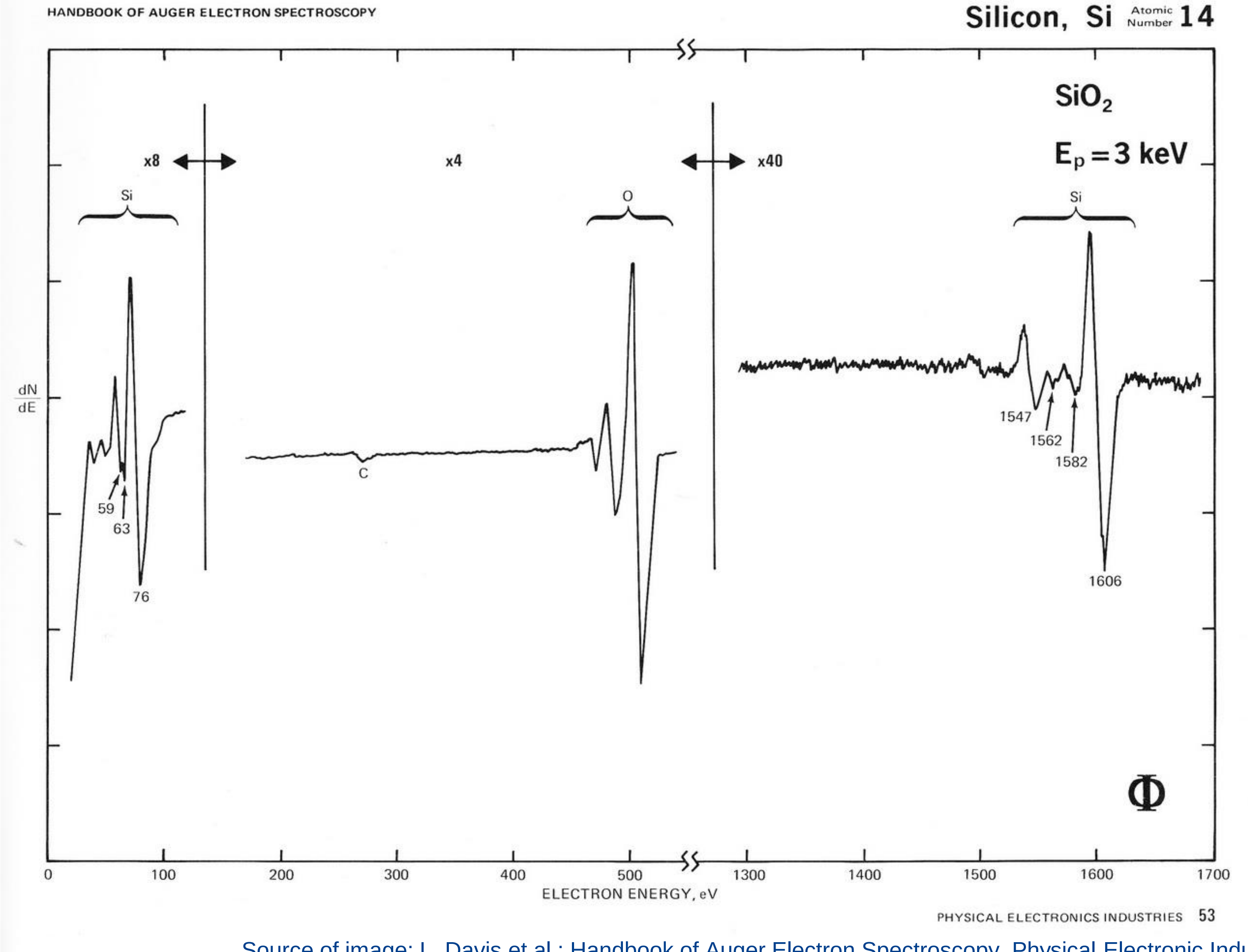


Source of image: L. Davis et al.: Handbook of Auger Electron Spectroscopy, Physical Electronic Industries, 1976

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

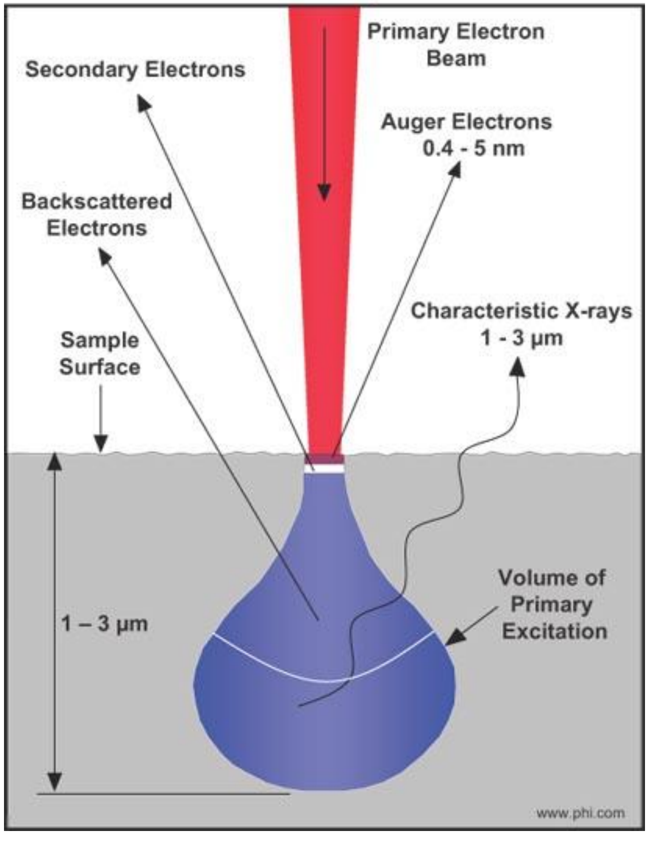
Lateral Resolution

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

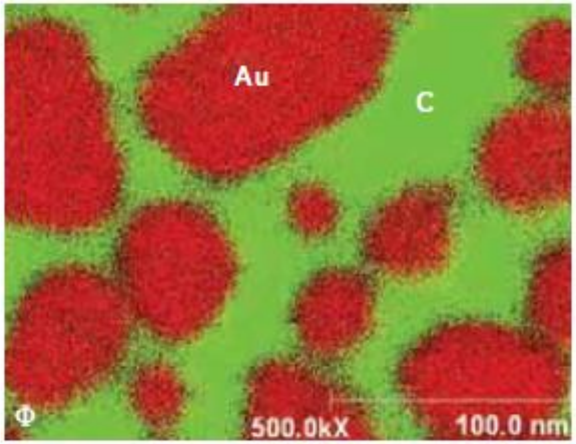
  → Not affected by beam broadening in deeper layers

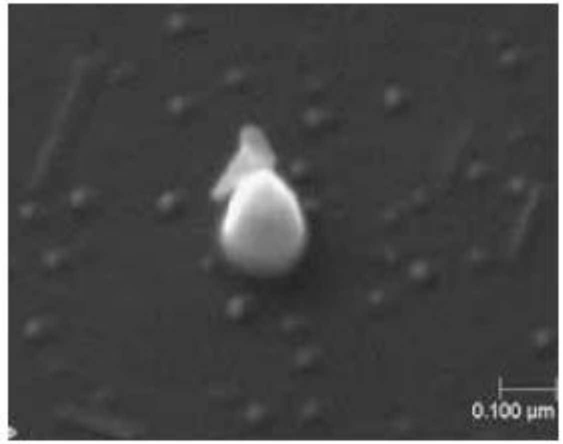
- Lateral resolution can be ~ 8nm

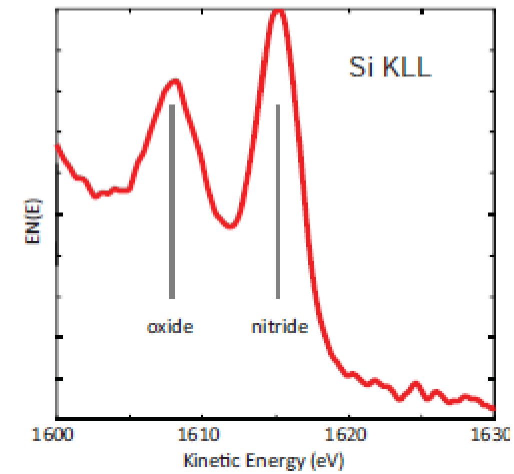
Electron Beam – Sample Interaction

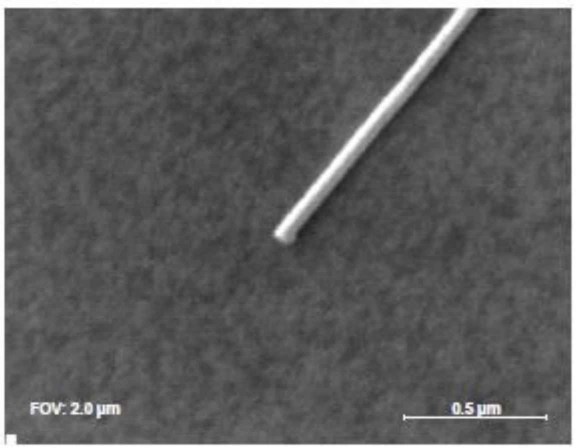


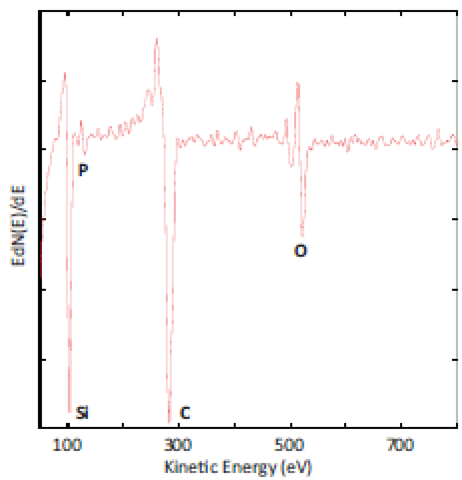
Source of image: http://www.phi.com/surface-analysis-techniques/aes.html

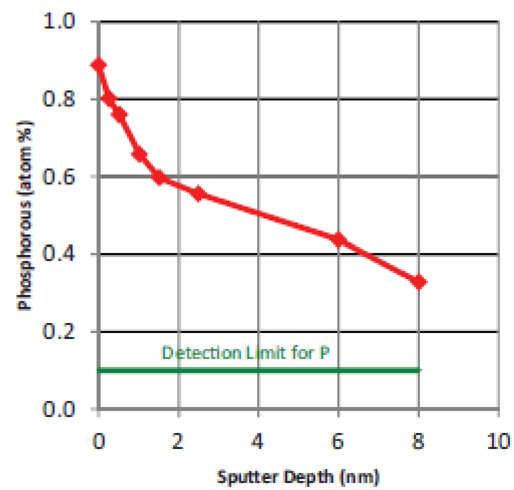








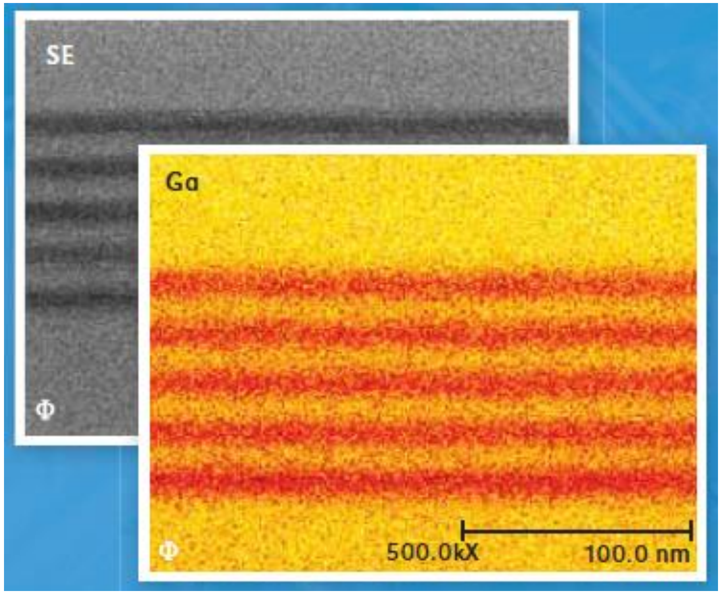




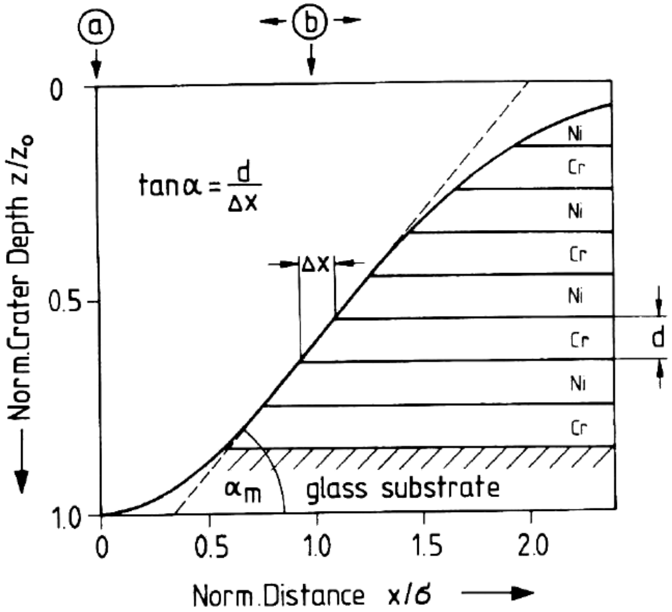
Source of images: http://www.phi.com/surface-analysis-techniques/aes.html

Depth Profile

- By ion beam sputtering (just like in SIMS)
- Based on lateral distribution on a crossection cut or a crater



GaAs/AlAs layer structure
Layer thickness =10 nm



Source of images: 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

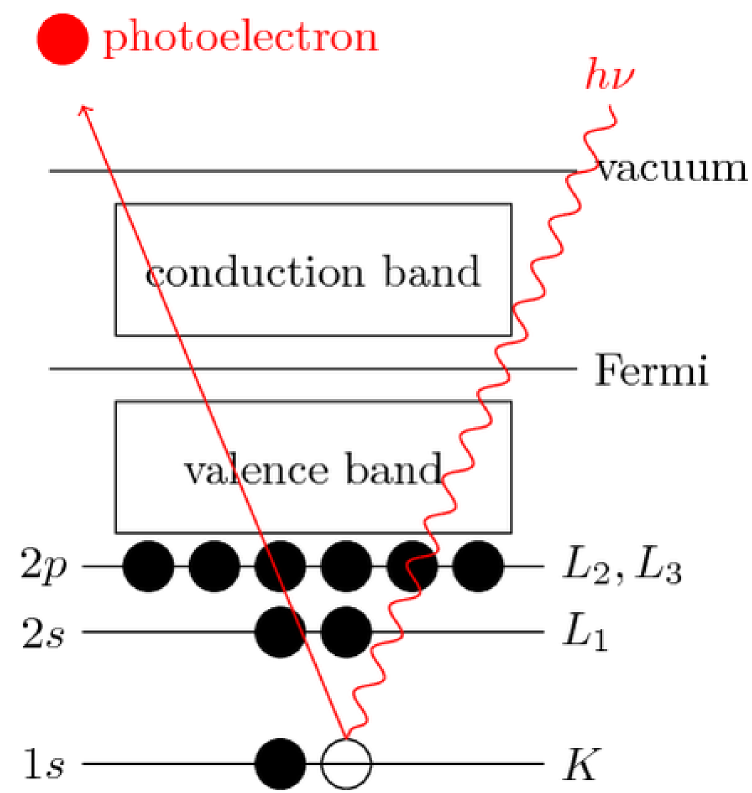
  → Information depth 0,5 – 5 nm
- Differential specrta
- Quantitative elemental compositions
  - Simple in case of alloys
  - Otherwise, calibration may be required
- Sensitivity ~ 1 atomic percent

Summary

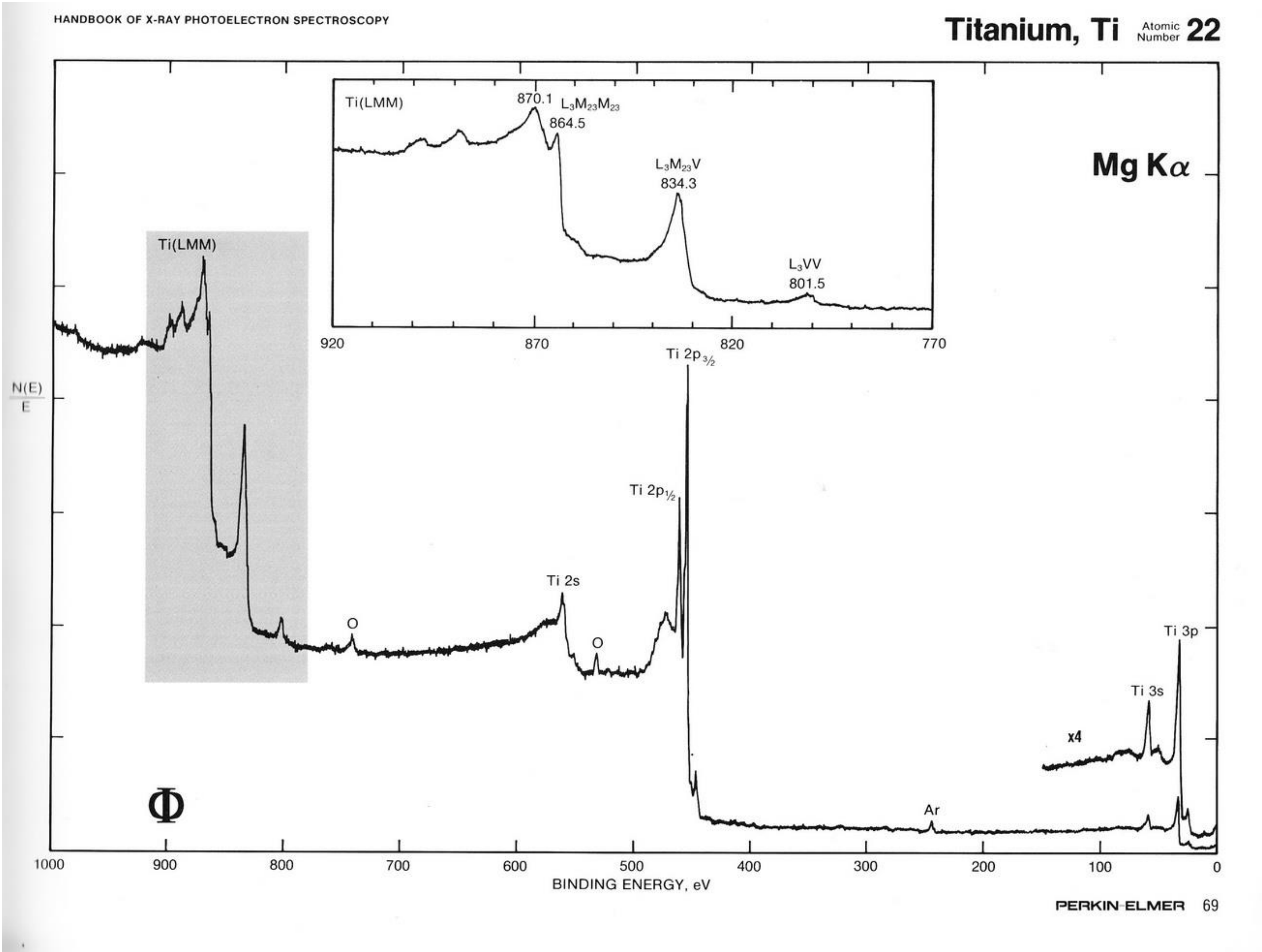
- Chemical state identification based on peak position and peak shape
- Lateral resolution ~10nm
- Depth profile
  - By ion beam sputtering
  - From lateral distribution
- (Usually) Nondestructive
  - There may be damage due to local heating
  - Organic samples may degrade due to electron bombardment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

X-ray Photoelectron Spectroscopy (XPS)

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

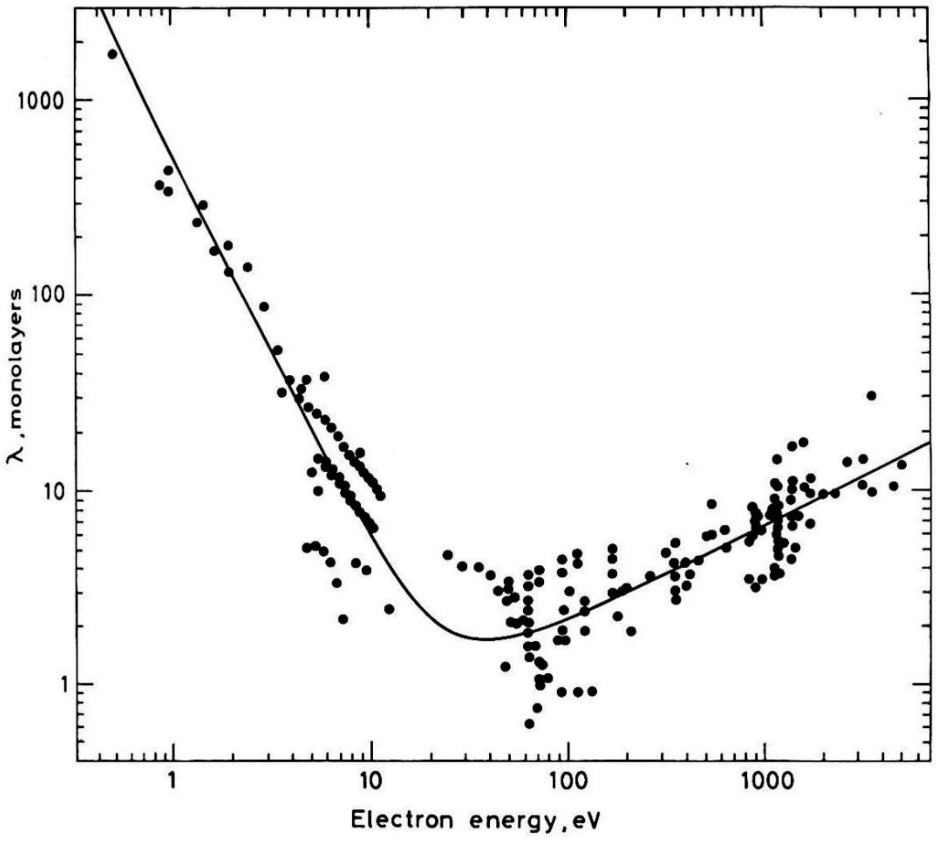


Source of image: http://www.texample.net/tikz/examples/principle-of-x-ray-photoelectron-spectroscopy-xps/

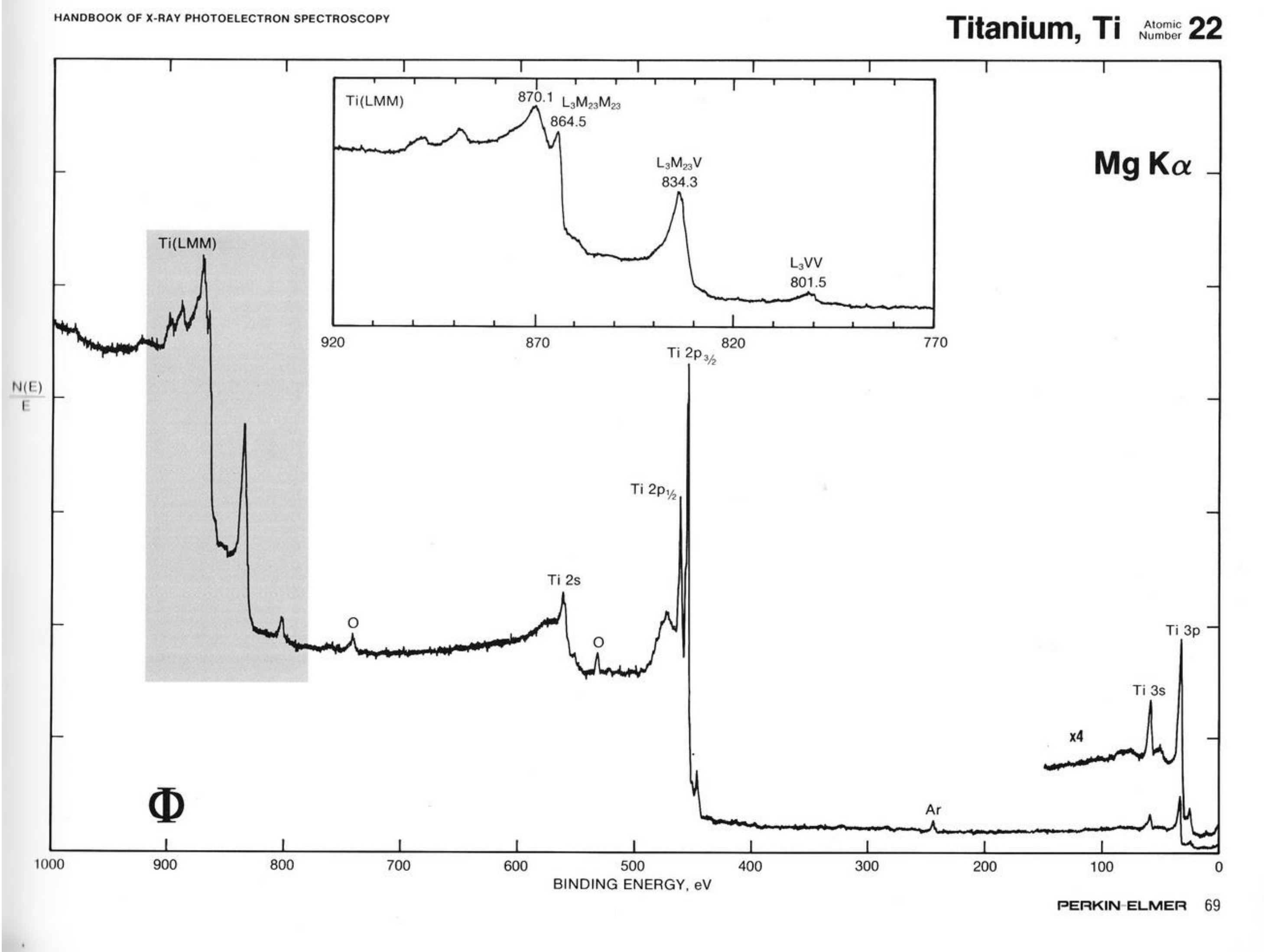


Source of image: C.D. Wagner, et al.: Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, 1978

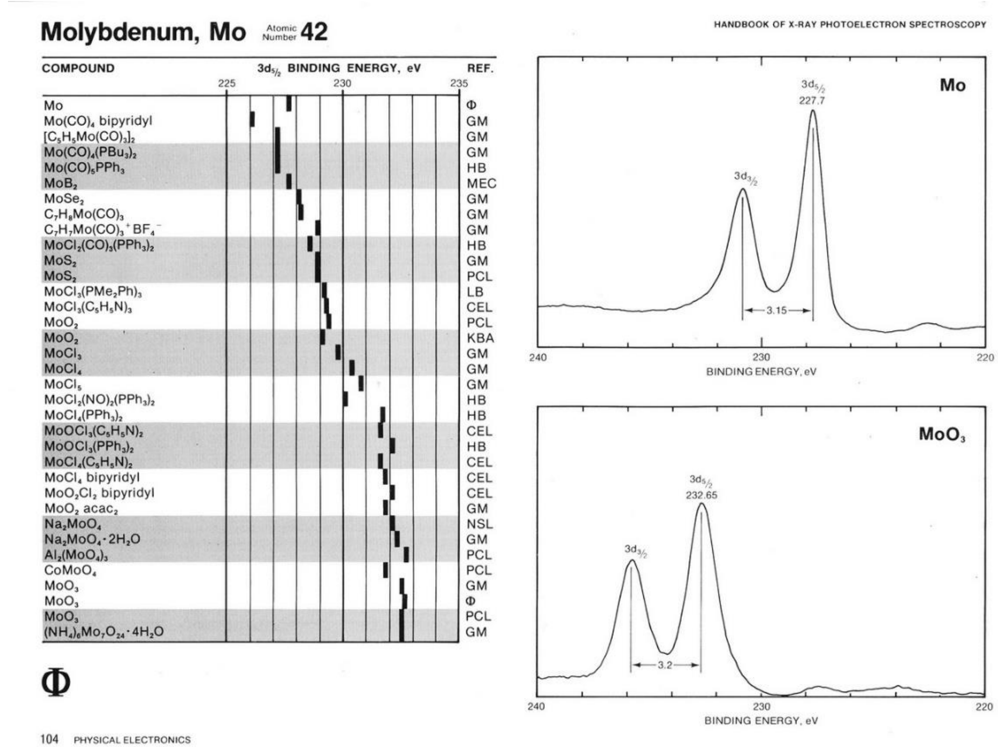
Surface sensitivity



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

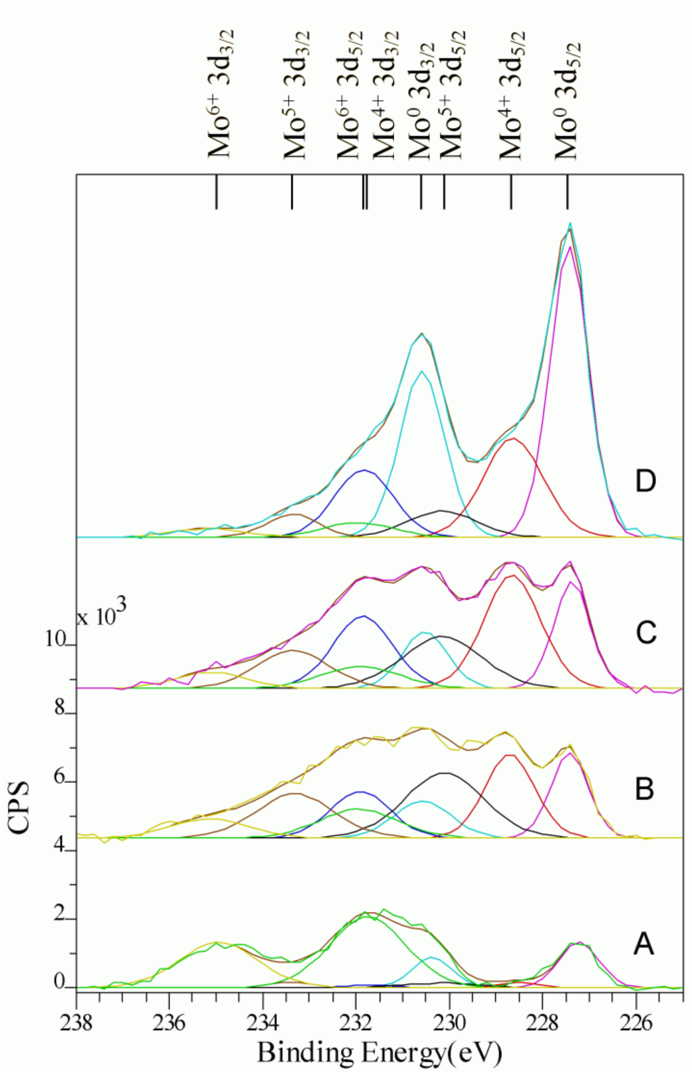


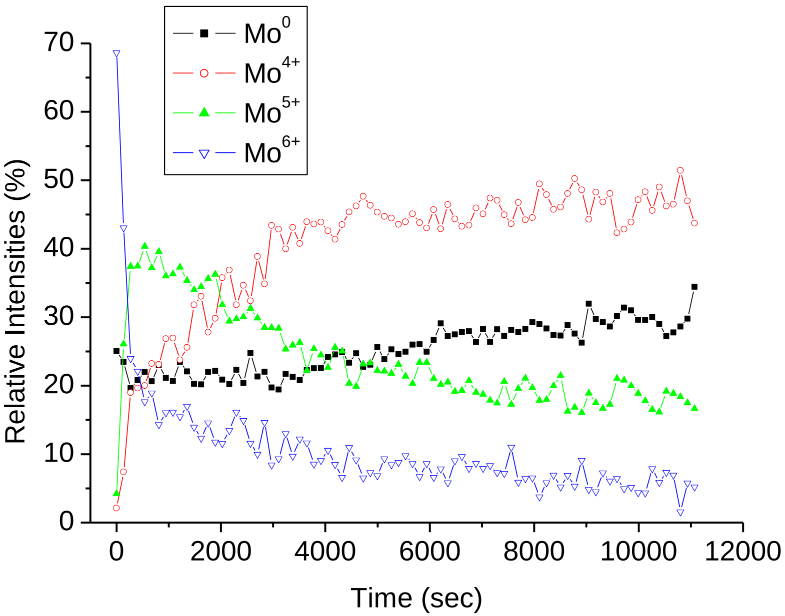
Source of image: C.D. Wagner, et al.: Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, 1978



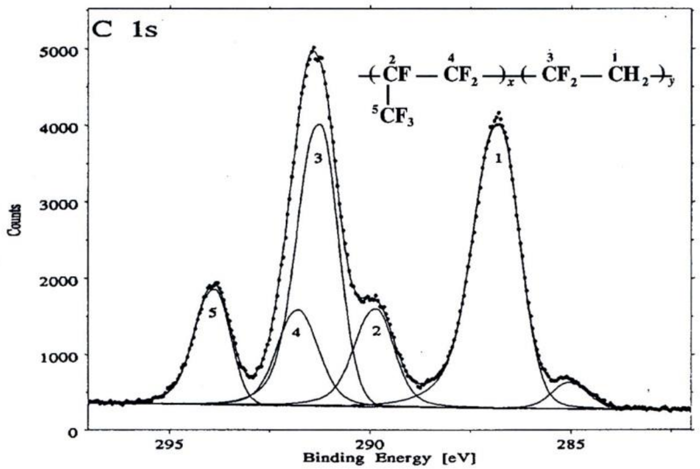
- Chemical bonds influence electron structure
- Core levels shift
- XPS peaks shift
- Higher oxidation state results in higher binding energy

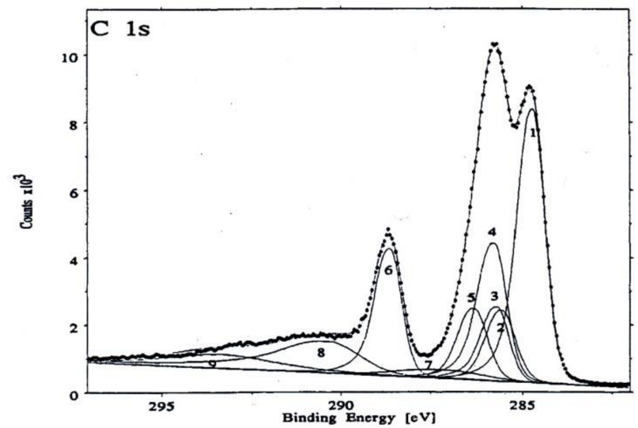
Source of image: C.D. Wagner, et al.: Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, 1978

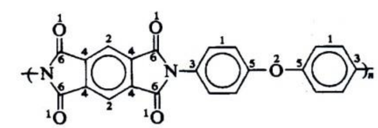


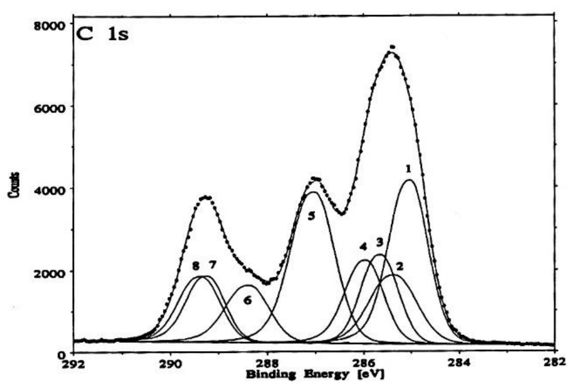


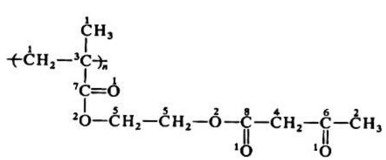
- XPS peaks may be decomposed to multiple synthetic components
- Ratio of atoms in different chemical states can be determined by peak fitting

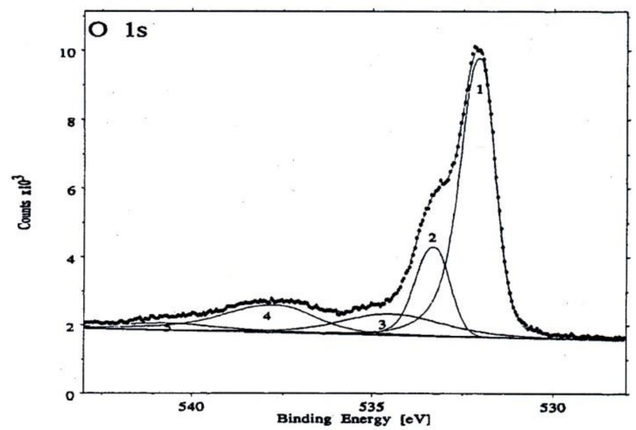












Source of images:D.Briggs, J.T. Grant: Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, IM Publications, 2003
D.Briggs: Surface Analysis of Polymers by XPS and Static SIMS, Cambridge University Press, 1998

Functional group	Chemical shift Min.	Chemical shift Max.	Chemical shift Mean	Number of examples
C—O—C	1.13	1.75	1.45	18
C—OH	1.47	1.73	1.55	5
*C—O—C(=O) [a]	1.12	1.98	1.64	21
C—C bridged by O (epoxide, C—O—C ring)	–	–	2.02	1
C=O [b]	2.81	2.97	2.90	3
O—C—O	2.83	3.06	2.93	5
O—C—C*(=O) [c]	3.64	4.23	3.99	21
HO—C(=O)—	4.18	4.33	4.26	2
O—C(—O)—O	4.30	4.34	4.32	2
—C(=O)—O—C(=O)—	4.36	4.46	4.41	3
—O—C(=O)—O—	5.35	5.44	5.40	2

[a] Neglecting aromatic carboxylic esters, mean of 18 is 1.72, min. 1.48.

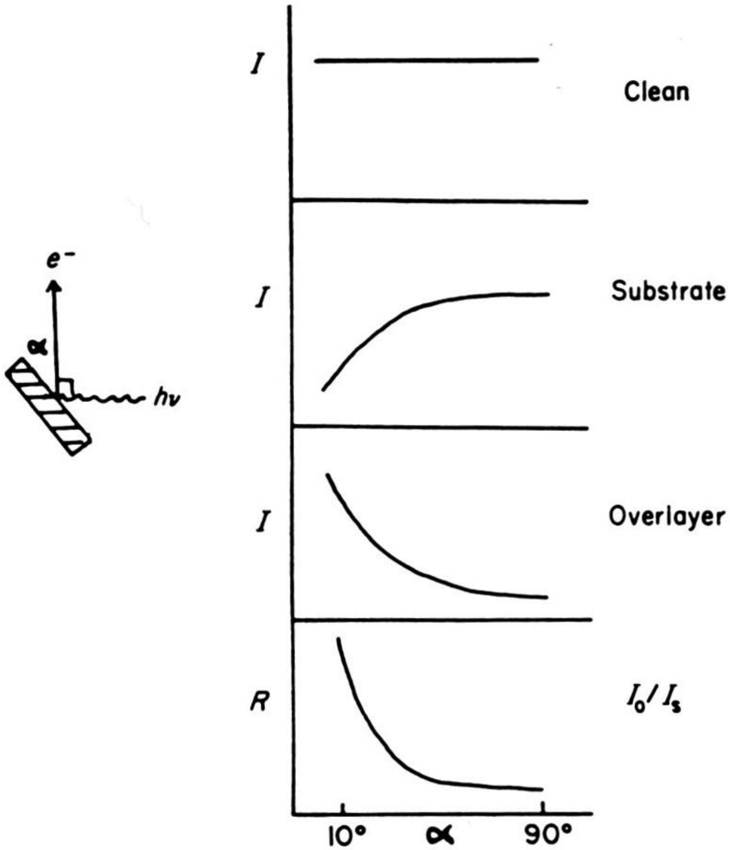
[b] PEEK significantly lower: shift=2.10 (binding energy) referenced to aromatic CH C 1s=284.70 eV).

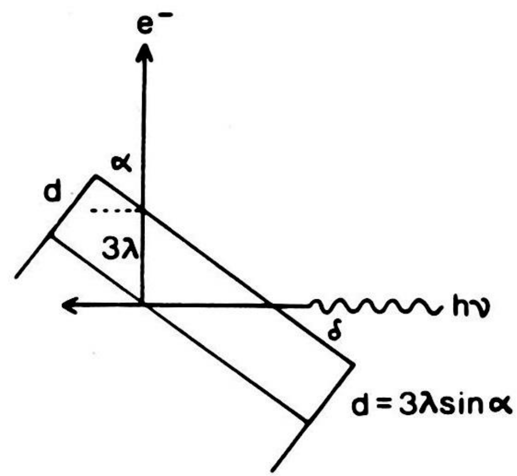
[c] Neglecting aromatic carboxylic esters, mean of 18 is 4.05, min. 3.84.

Source of image: D.Briggs, Surface Analysis of Polymers by XPS and Static SIMS, Cambridge University Press, 1998

Budapest University of Technology and Economics
Department of Atomic Physics, Surface Physics Laboratory

Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS)





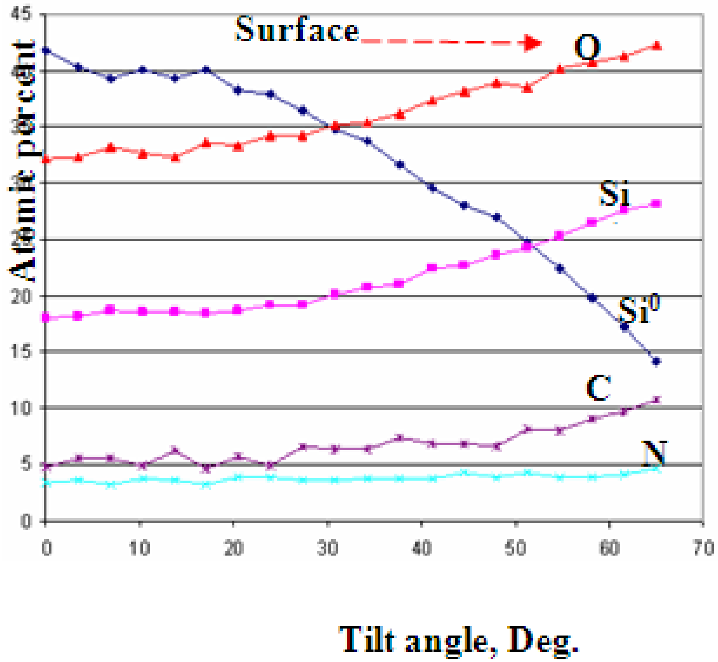
$$I_s^d = I_s e^{-d/\lambda \cdot sin\alpha}$$

$$I_o^d = I_o\left(1 - e^{-d/\lambda \cdot sin\alpha}\right)$$

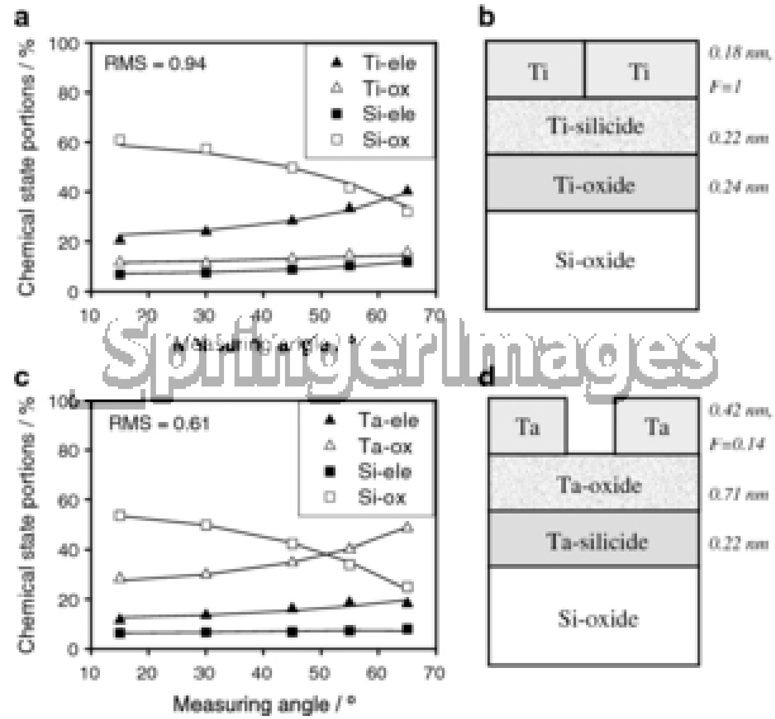
Information depth changes with the angle

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

ARXPS

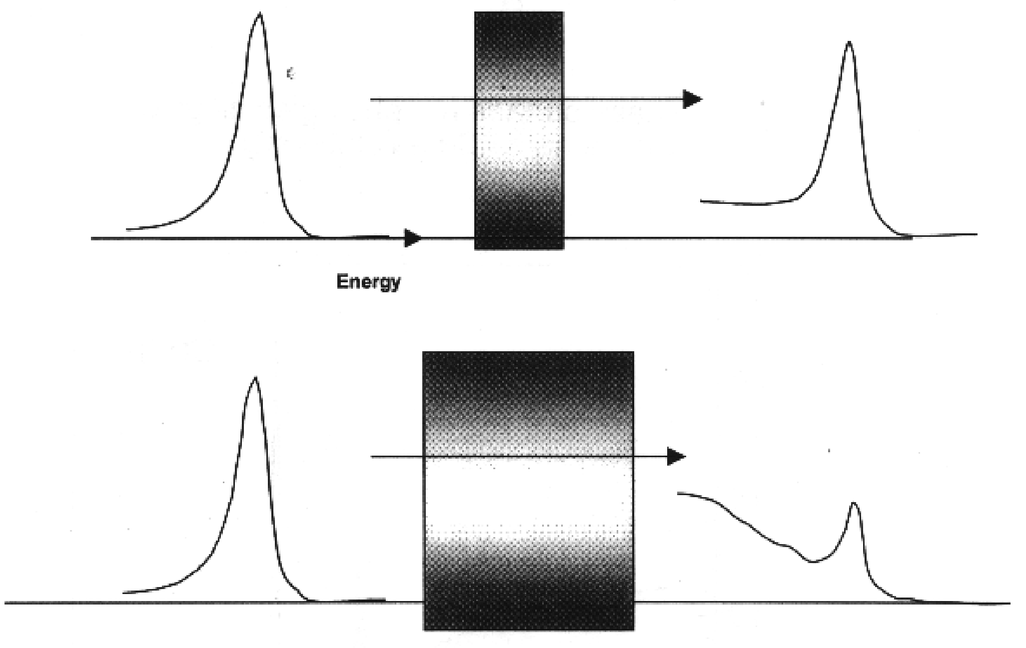


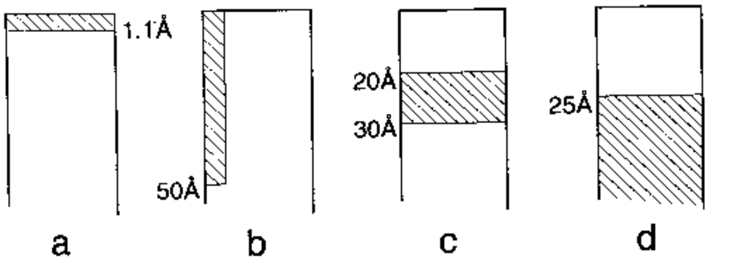
18A vastag SiON réteg Si hordozón



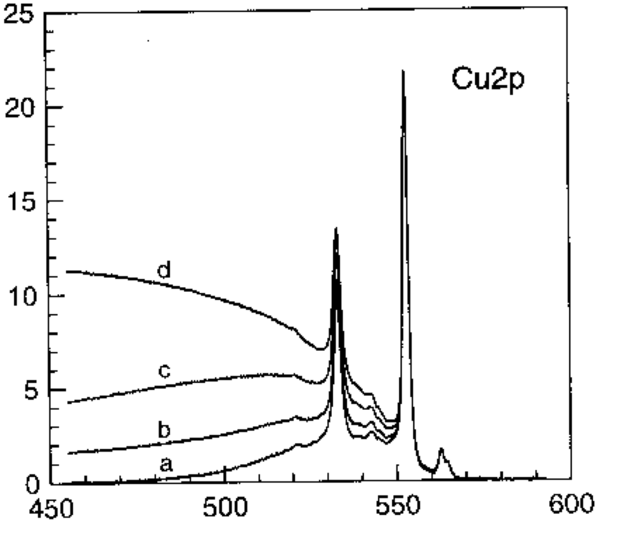
Layer thicknesses may be determined by fitting a model to the measurement data

Source of images: http://web.bgu.ac.il/Eng/Centers/nano/labs/XPS_AES.htm
http://www.springerimages.com/Images/Chemistry/1-10.1007_s00216-009-3282-y-4

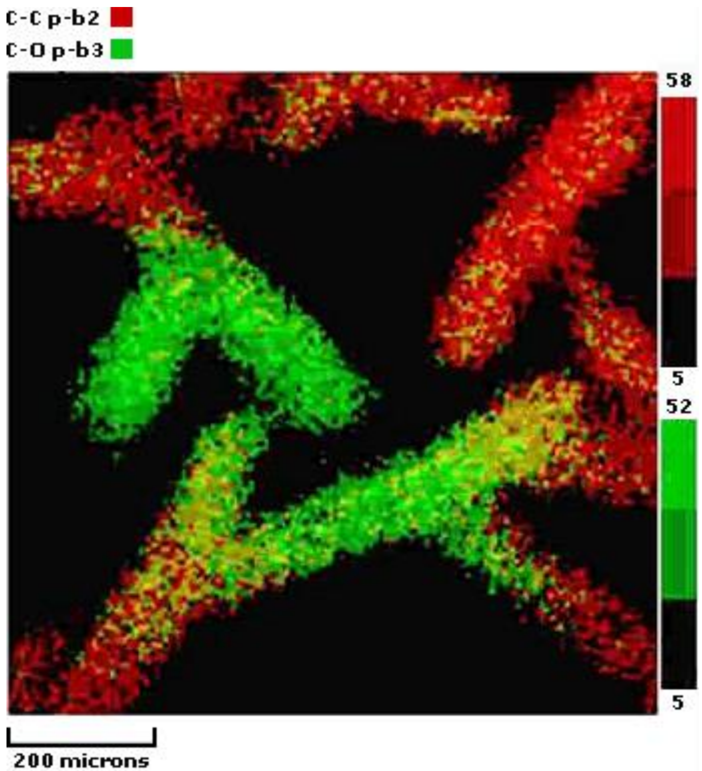


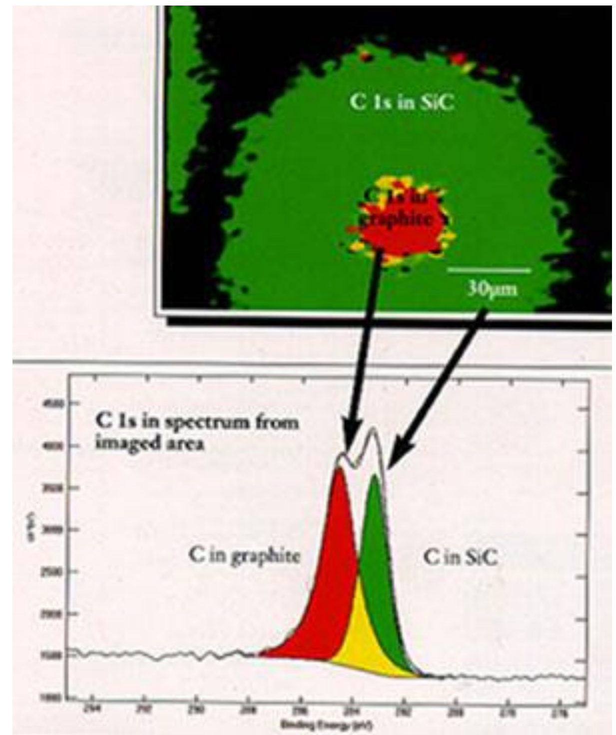


These surface morphologies all give the same XPS-peak intensity



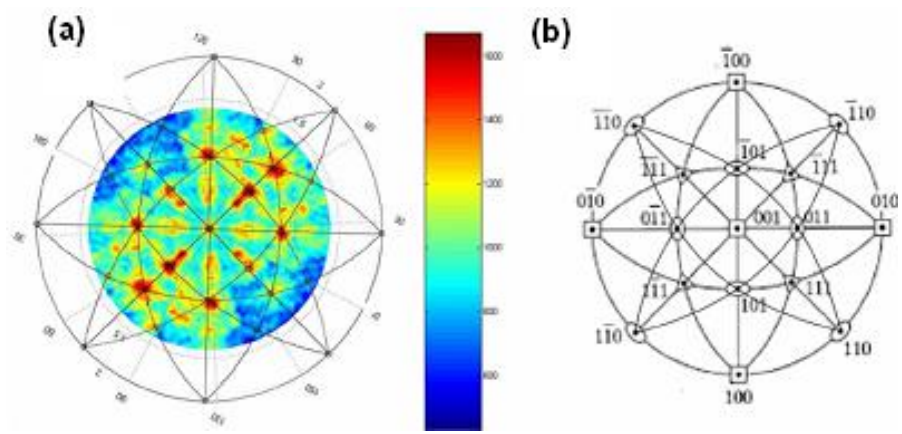
Source of images: http://www.quases.com/





Source of images: http://www.csma.ltd.uk/techniques/xps-imaging.htm
http://www.udel.edu/chem/beebe/surface.htm

X-Ray Photoelectron Diffraction (XPD)

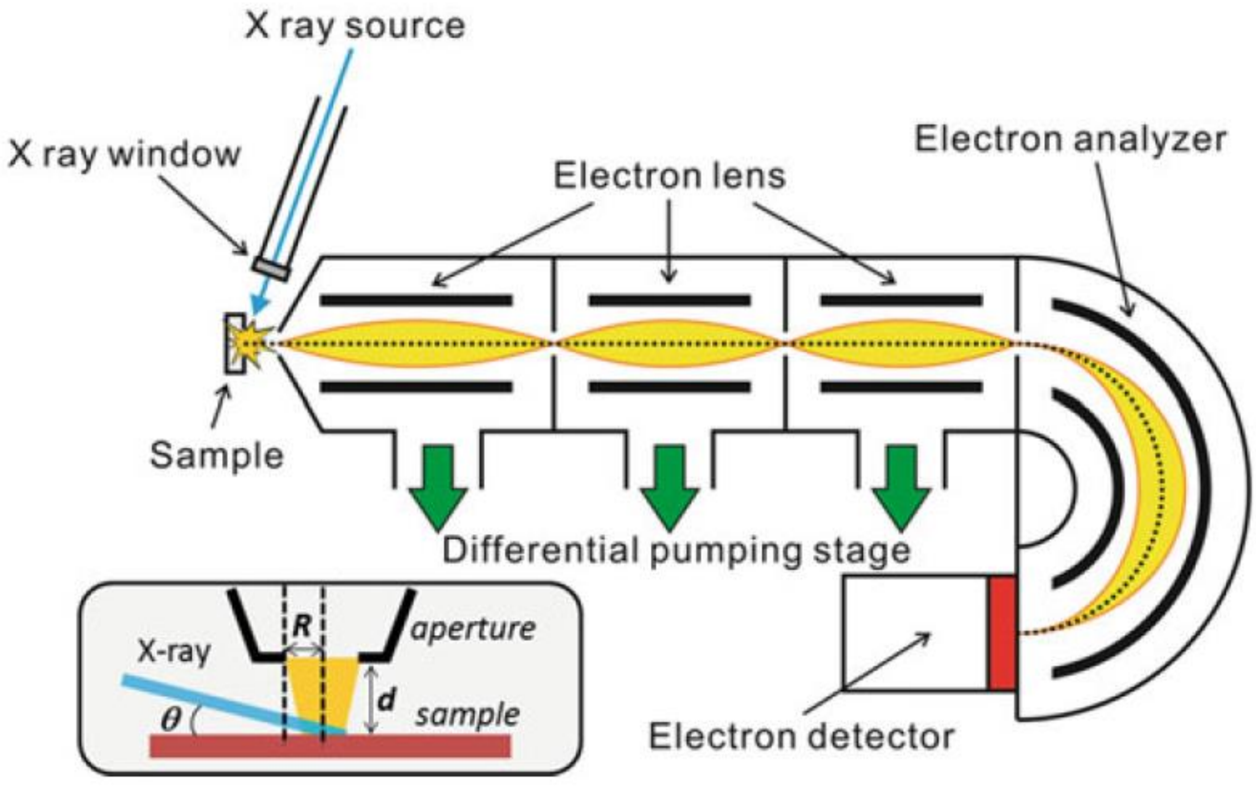


Sr 3d5/2 XPD ábra SrTiO3 felületéről

- Photoelectrons are scattered on the atoms in the sample
- Photoelectron wavelengths are comparable to atomic distances → Diffraction
- AED: Similar with Auger electrons

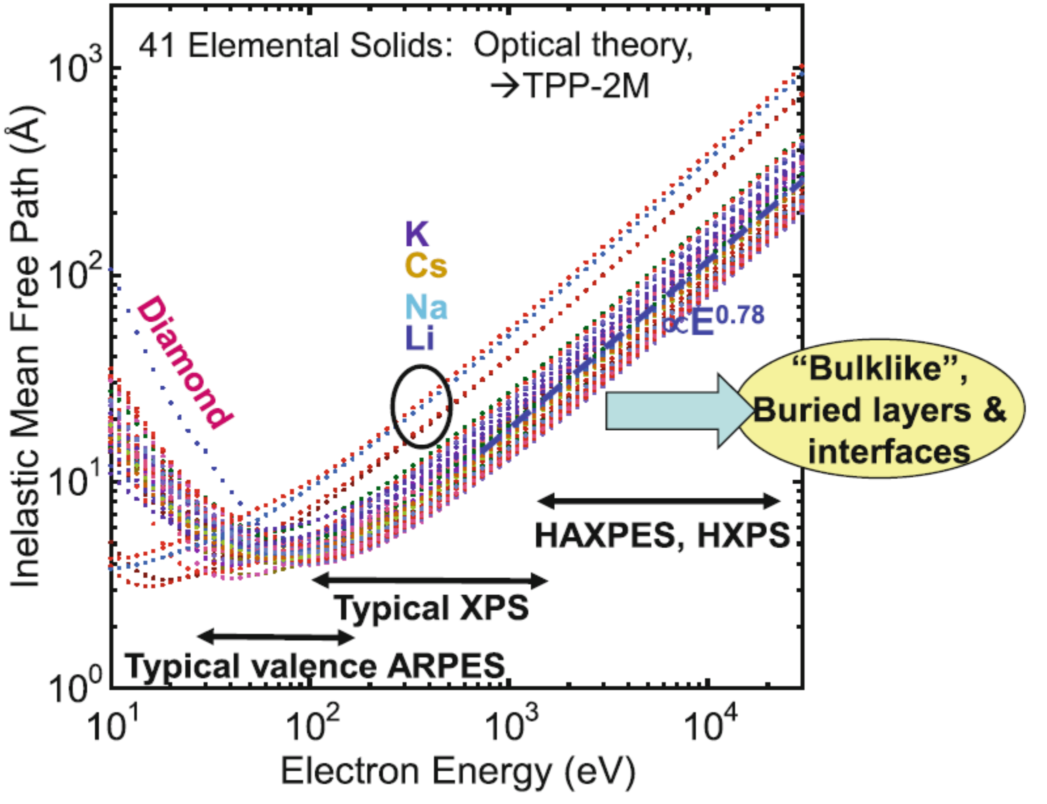
Source of image:http://iramis.cea.fr/Phocea/Vie_des_labos/Ast/ast_visu.php?id_ast=1483

Ambient Pressure XPS



Source of image:M. Kiguchi et. al.:Compendium of Surface and Interface Analysis, Springer 2018

Hard X-Ray Photoelectron Spectroscopy



Source of image:J.C. Woicik: Hard X-ray Photoelectron Spectroscopy (HAXPES), Springer, 2016

XPS Characteristics

- Accurate elemental composition (~0.1 atomic percent)
- Chemical state identification
- Information depth: 3-5 nm
- Lateral resolution ~30μm
- Depth profile
  - By ion by sputtering
  - ARXPS
  - (From the background)
- XPD, AED → Atomic structure

- 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