Karlsruhe Institute of Technology

KNMF Karlsruhe Nano Micro Facility

IAM Institute for Applied Materials

Surface Analysis by XPS & ToF-SIMS Basics, Strengths, and Limitations

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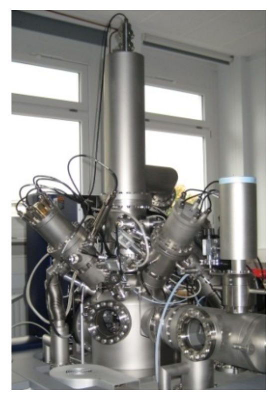
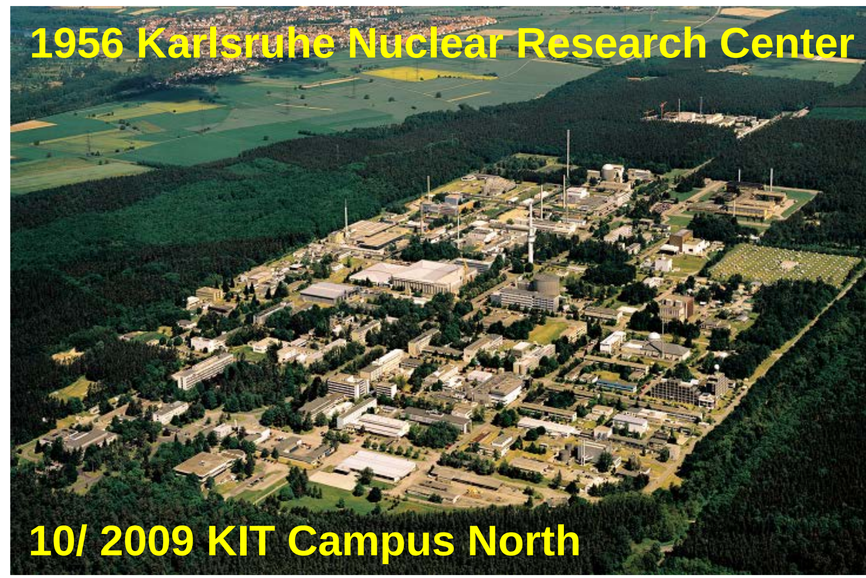
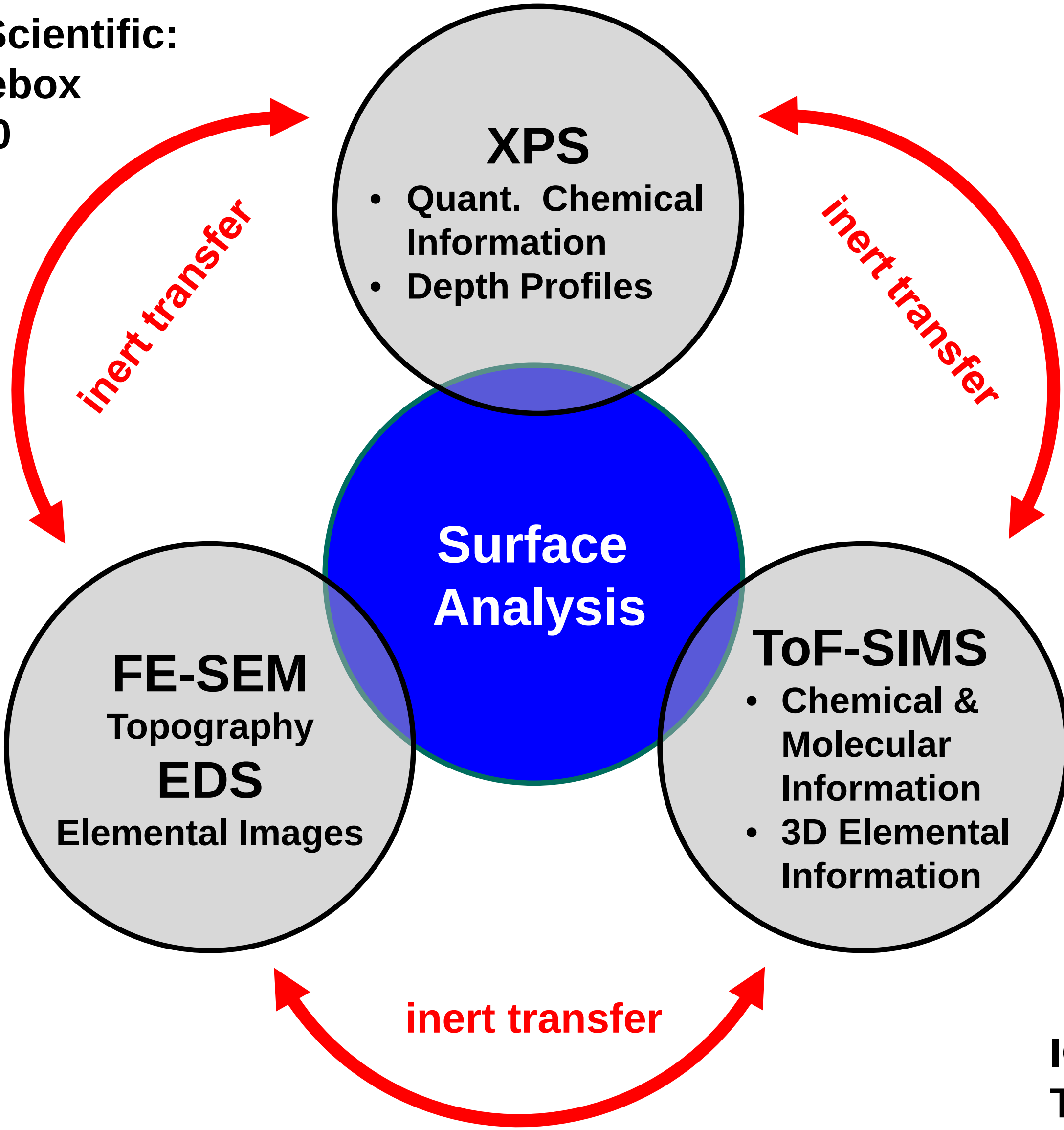


The Merger of Forschungszentrum Karlsruhe and Universität Karlsruhe



Thermo Fisher Scientific:
K-Alpha & Glovebox
ESCA5/Alpha110

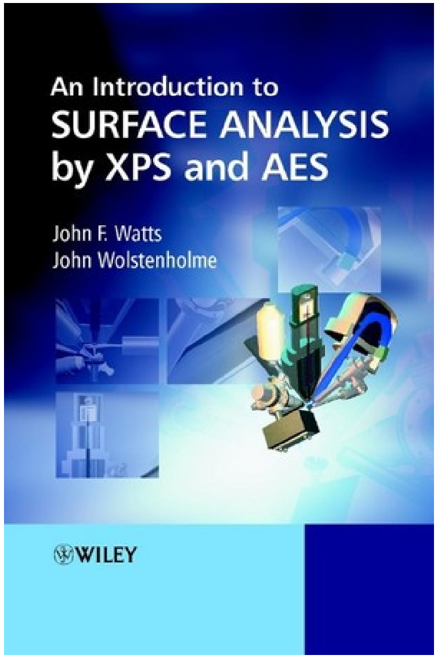


Zeiss GmbH:
Merlin

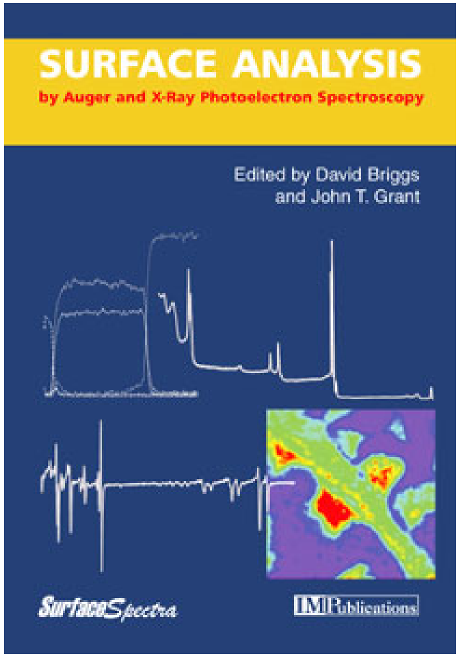
ION-TOF GmbH:
TOF.SIMS 5

Textbooks

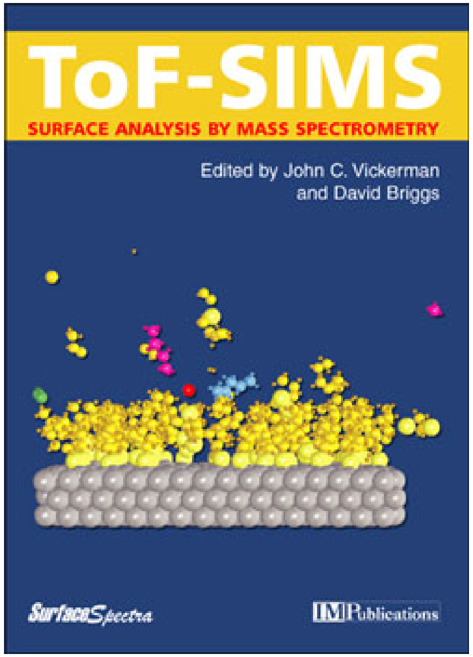
X-ray Photoelectron Spectroscopy — *XPS*
Auger Electron Spectroscopy — *AES*
Time-of-Flight Secondary Ion Mass Spectrometry — *ToF-SIMS*



~ 60



~ 200 €



~ 200 €

➔ **www.xpssimplified.com**

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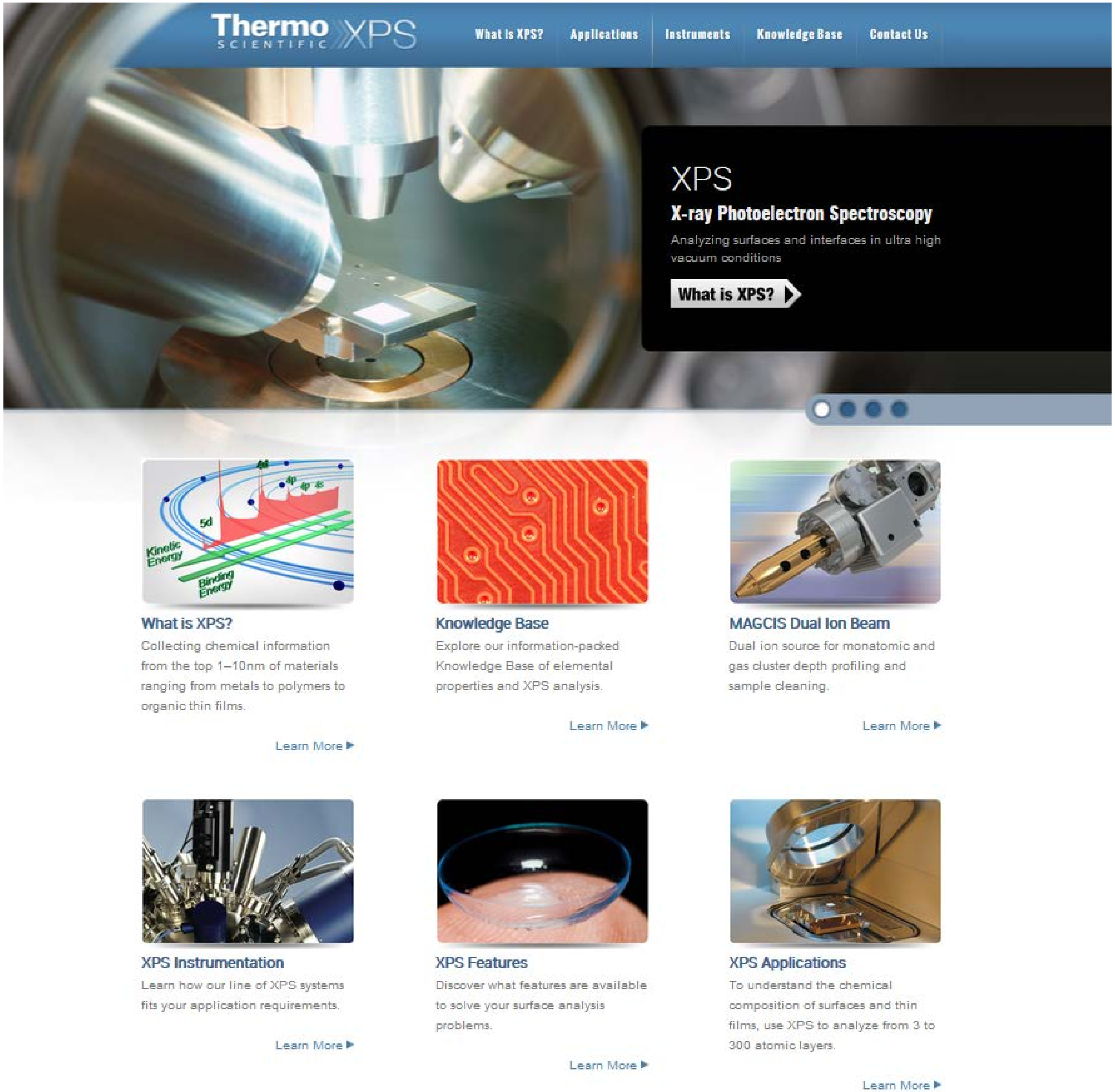
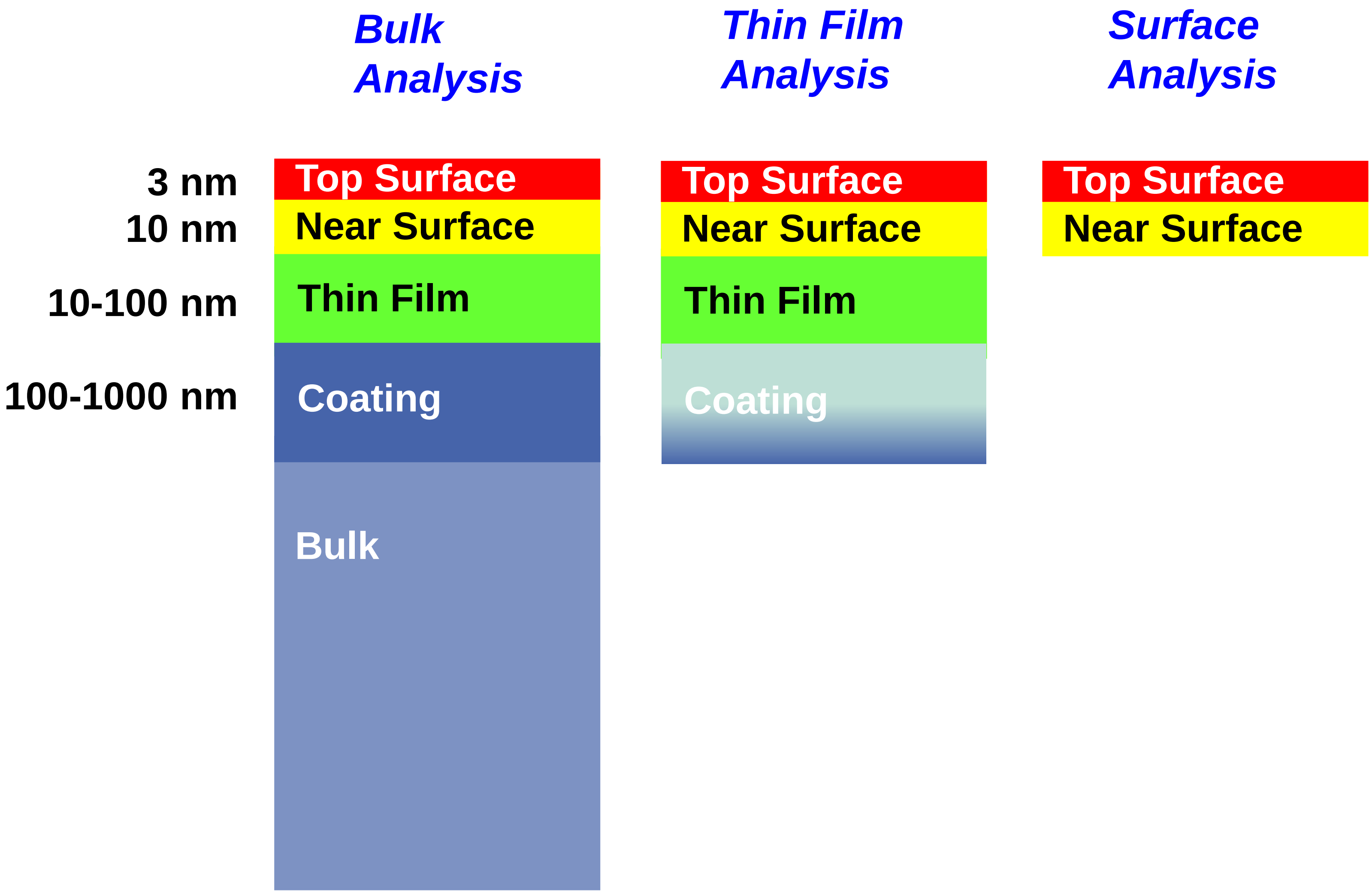


Surface Analysis



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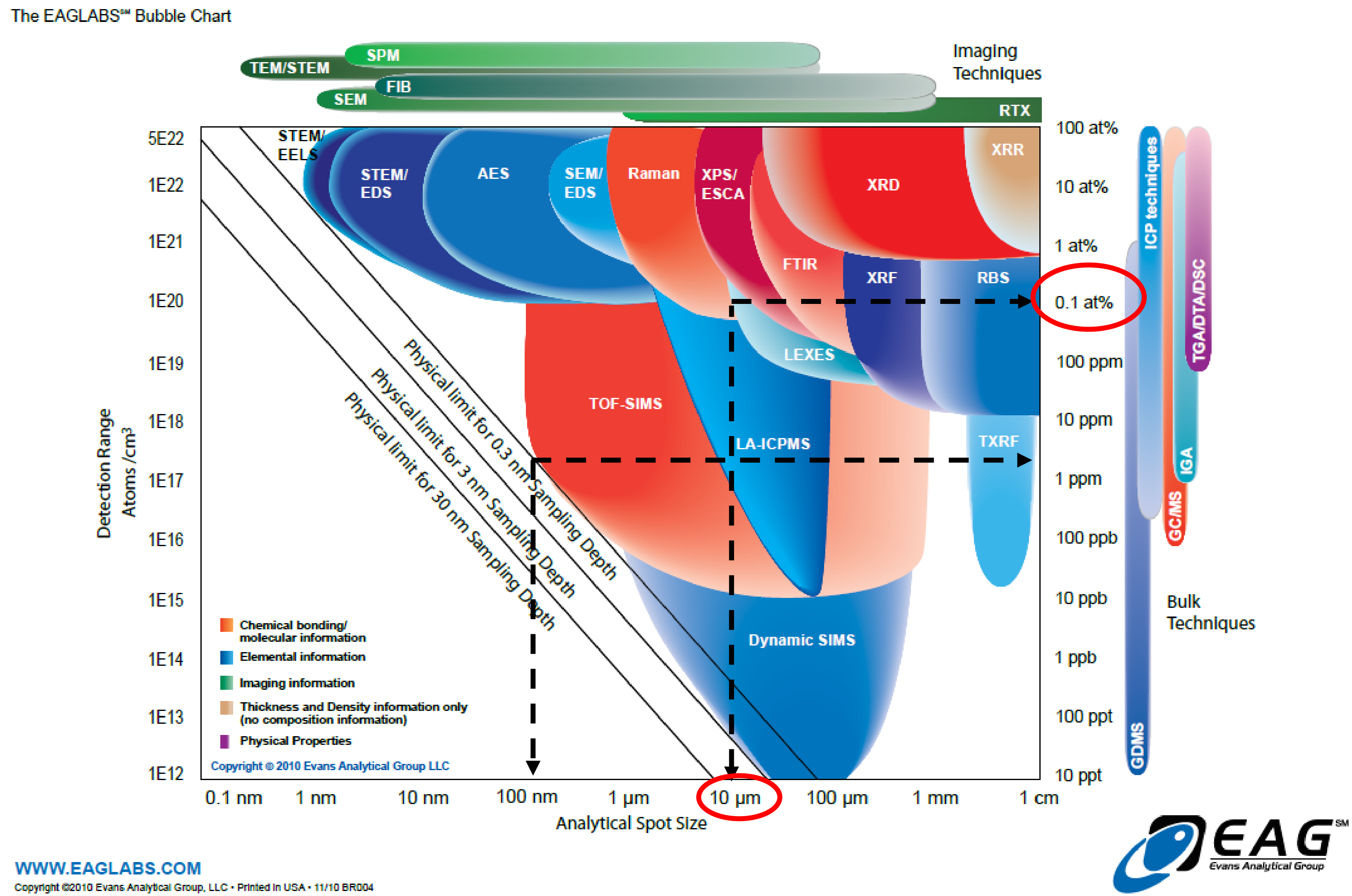
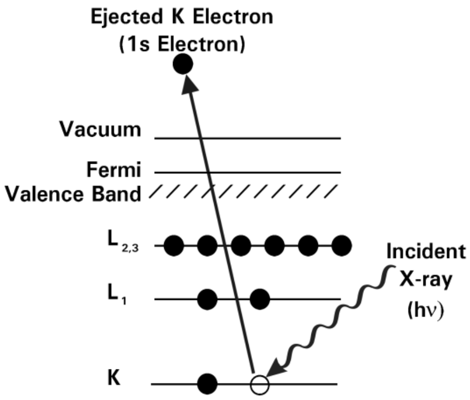
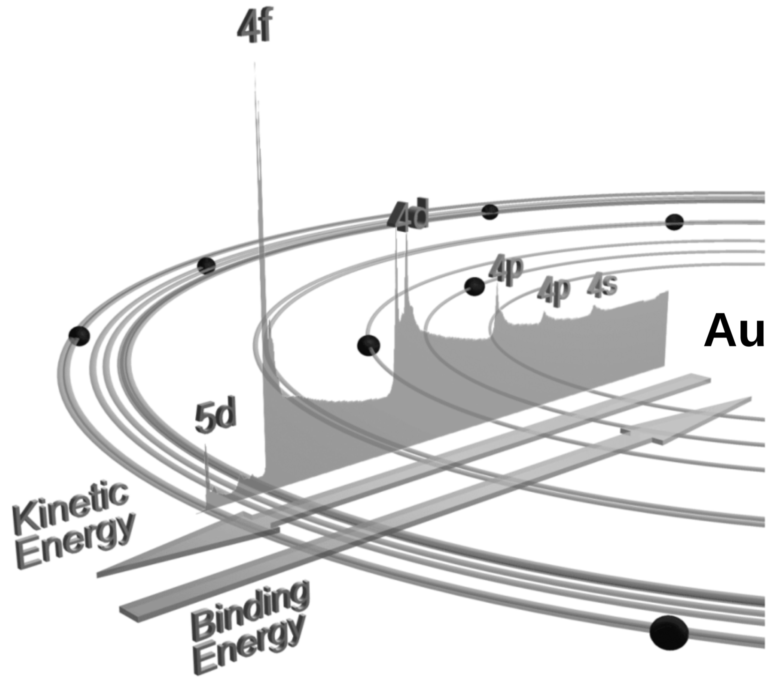
Surface Analysis
Analytical Resolution Versus Detection Limit



X-Ray Photoelectron Spectroscopy (XPS)
Relationship to Electronic Structure





$$E_B = h\nu - E_K - \omega$$

(mono)	Al Kα	1486.6 eV
	Mg Kα	1253.6 eV

s	singlet	
p	doublet	(3/2 & 1/2)
d	doublet	(5/2 & 3/2)
f	doublet	(7/2 & 5/2)

John F. Watts, John Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*, Wiley & Sons, Chichester, UK, 2003

XPS Characteristics

- Depth of analysis 5nm
- All elements except hydrogen
- Readily quantified
- All materials (ultra high vacuum compatible)
- Depth profiling by angle resolved XPS or sputtering
- Analysis area mm^2 to 30 micrometres
- Chemical images

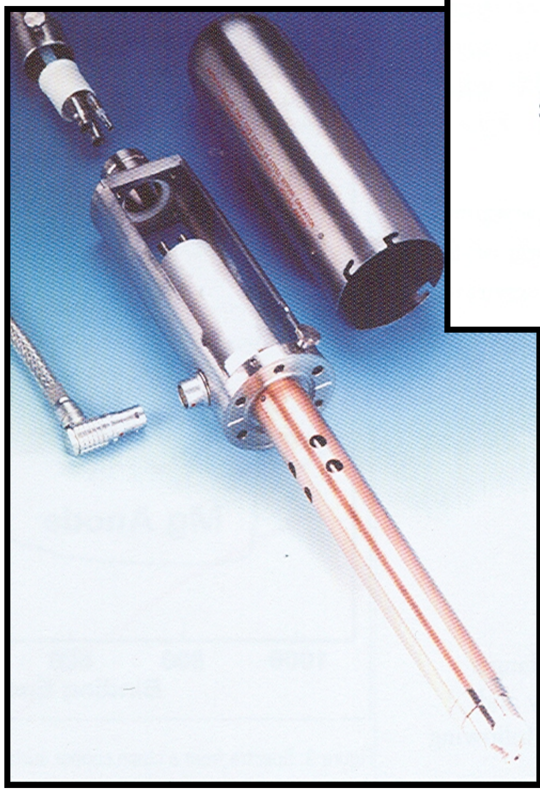
VG ESCA5 & Thermo Fisher Alpha 110 Analyzer

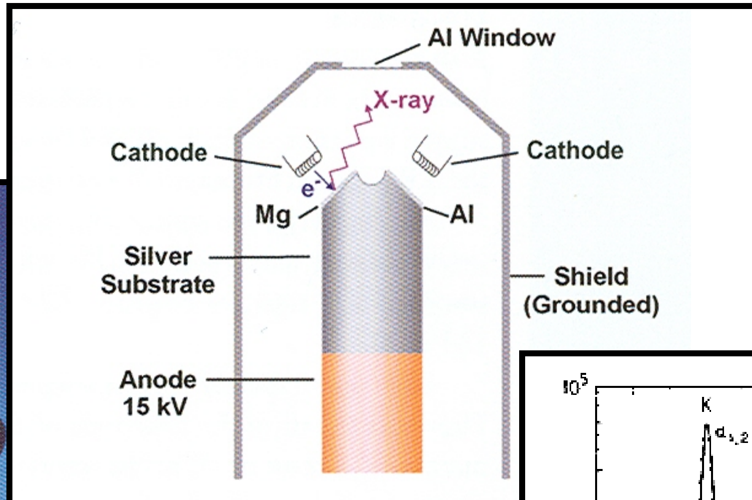
Thermo Fisher K-Alpha

Complementary Methods

- ✓ **ToF-SIMS**
- ✓ LEIS
- ✓ RBS
- ✓ **FE-SEM &EDS**
- ✓ TEM

XPS Instrumentation: X-Rays





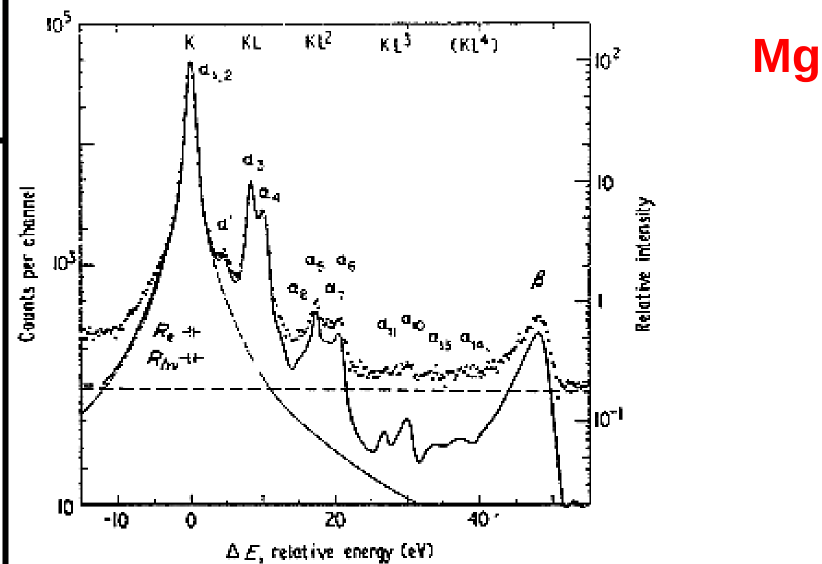
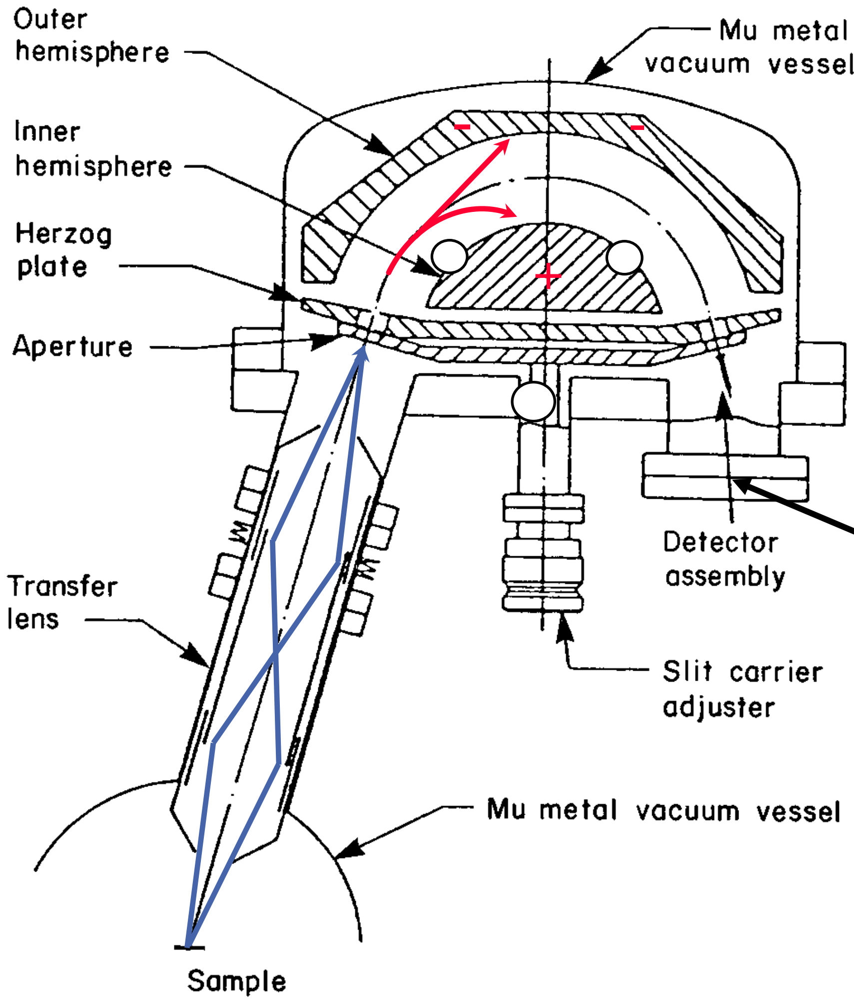
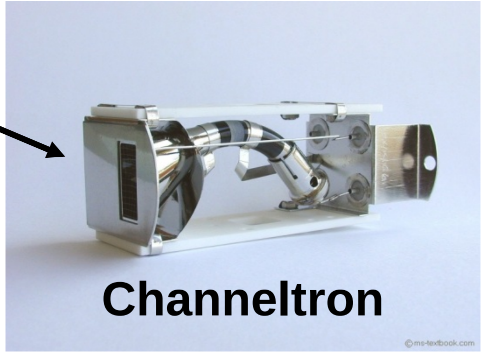


Figure 1. The K emission spectrum of magnesium metal. Dots show raw spectrum, as obtained in a PAX spectrometer: the broken line is the average background and bold full curve the characteristic x-ray spectrum. Also indicated are the shape of the $K\alpha_{1,2}$ line and the window widths for photoelectrons, R_e, and x rays, $R_{h\nu}$. Spectrum was excited by 6 keV electrons; $R_e = 0.15\%$.

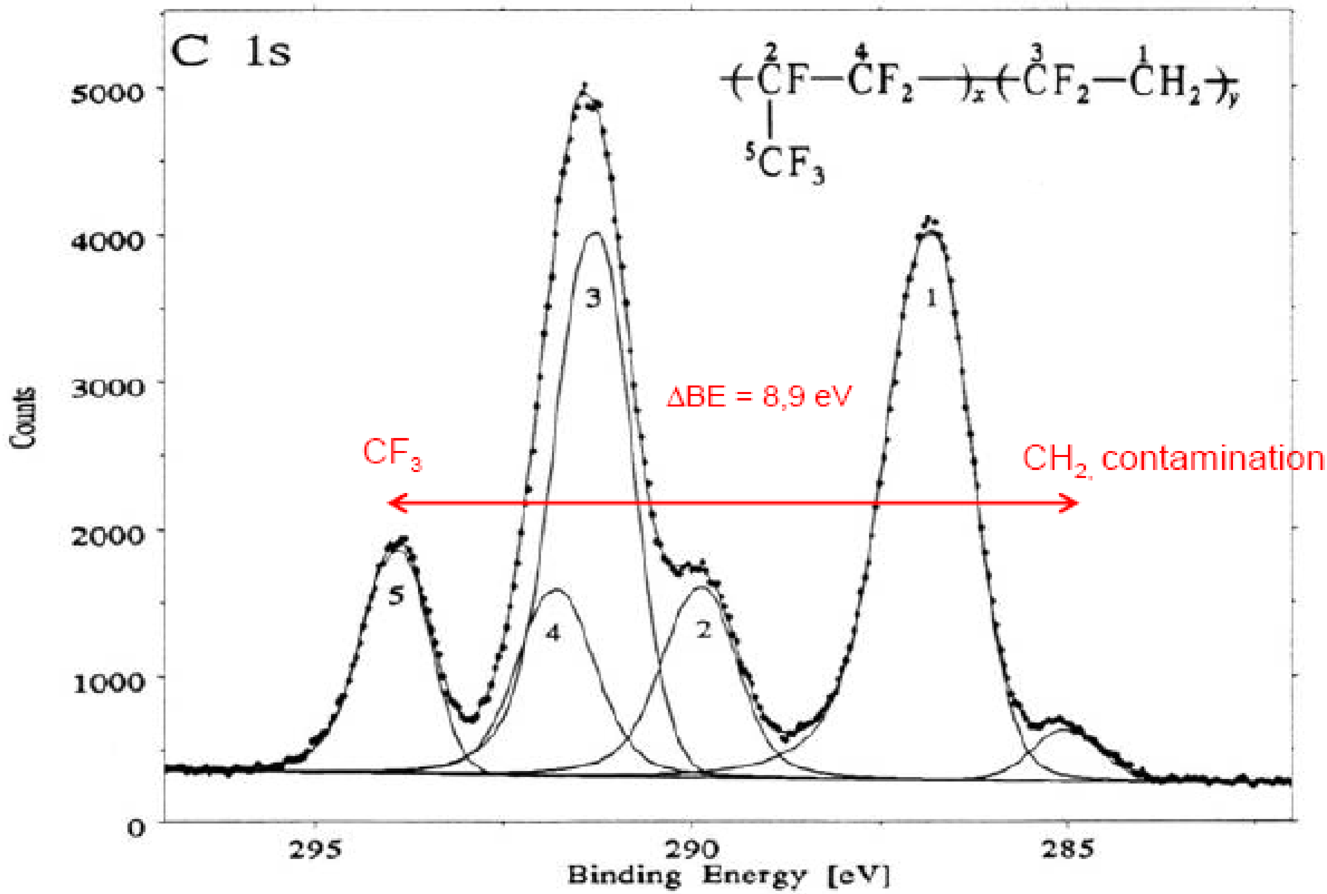
XPS Instrumentation:
Concentric Hemispherical Analyzer





Mu-Metal:
Ni 81/Fe19 - Alloy

Speziation / Chemical Shift



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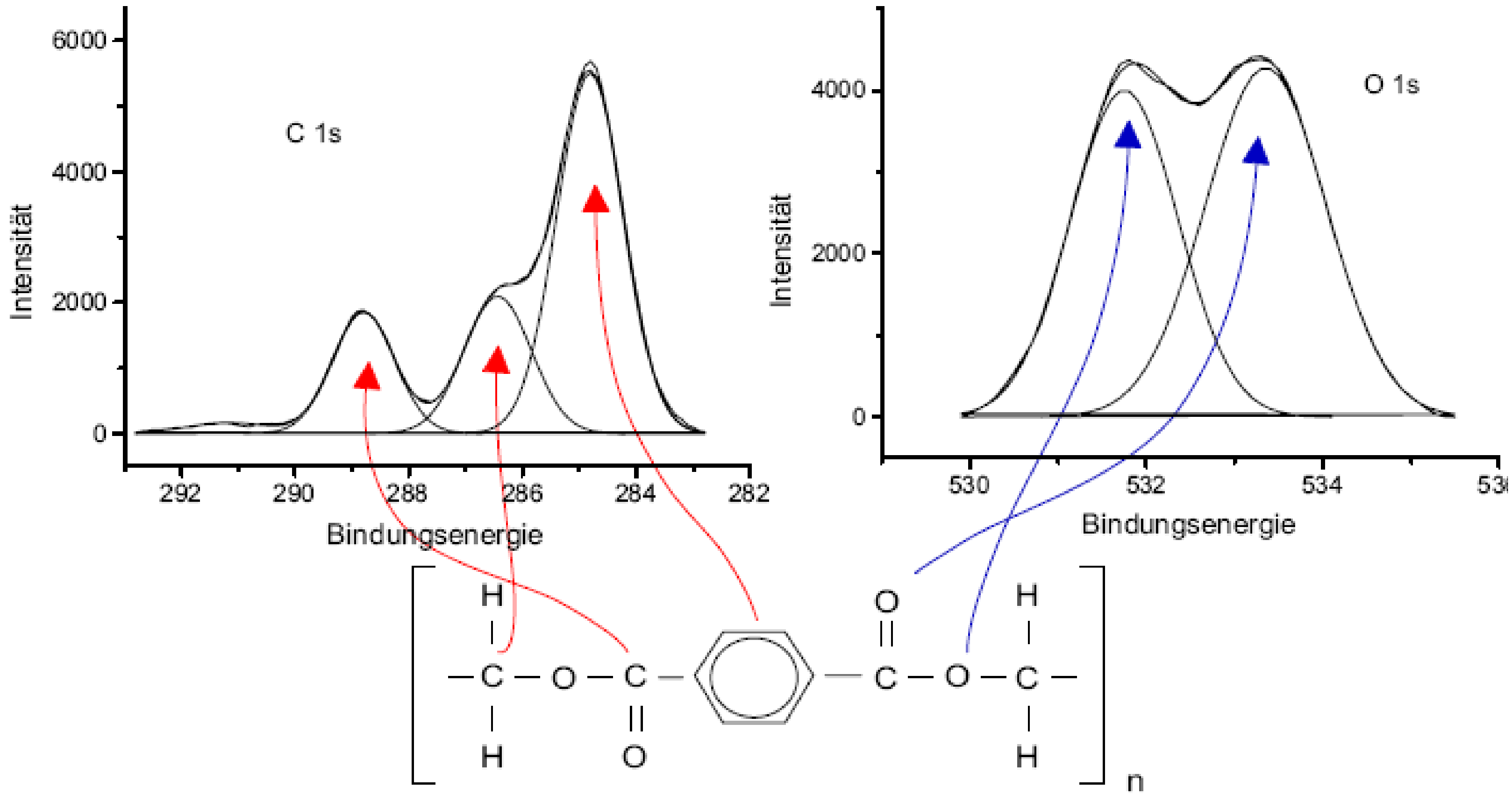
Speziation – Chemical Shift



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XPS: Depth of Analysis

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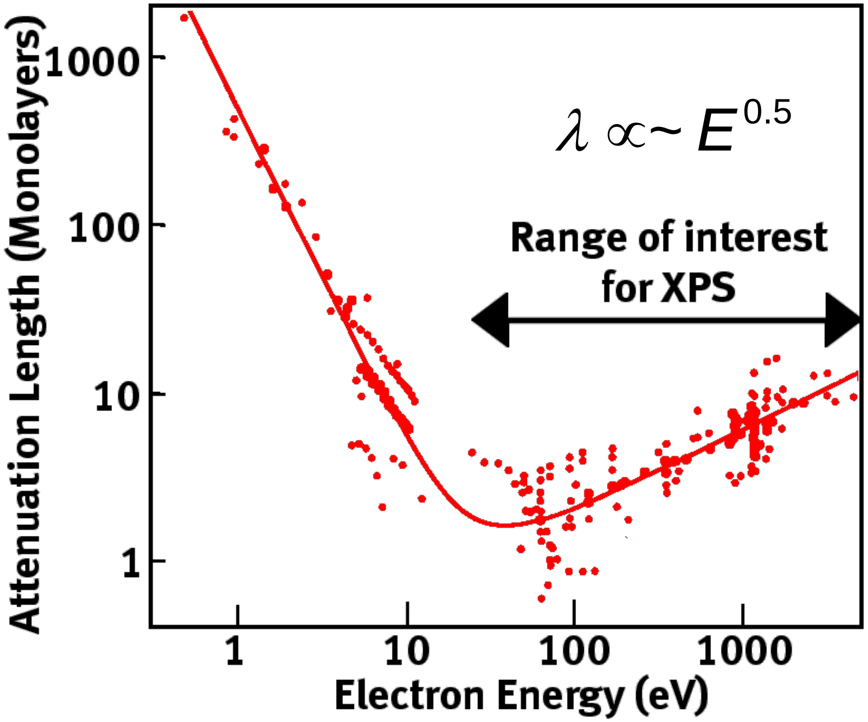
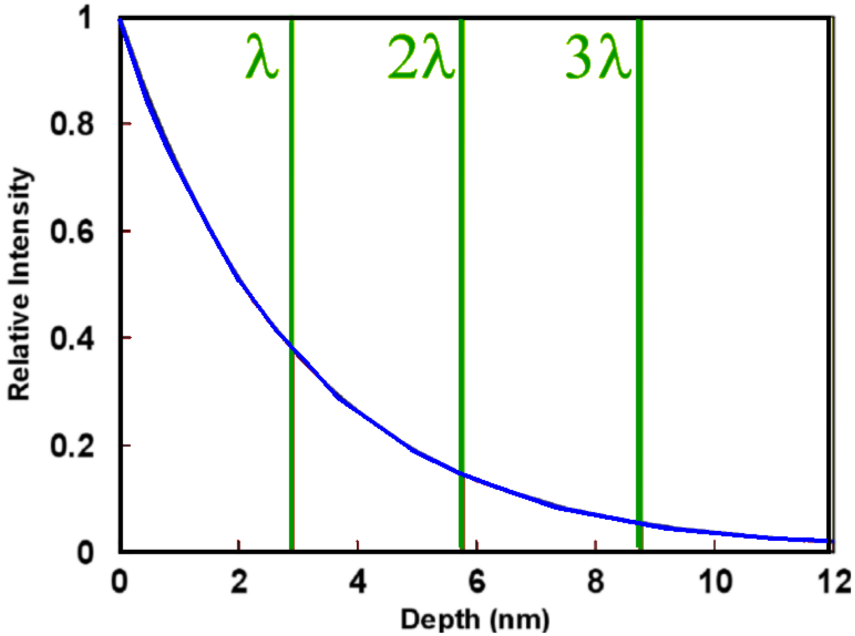


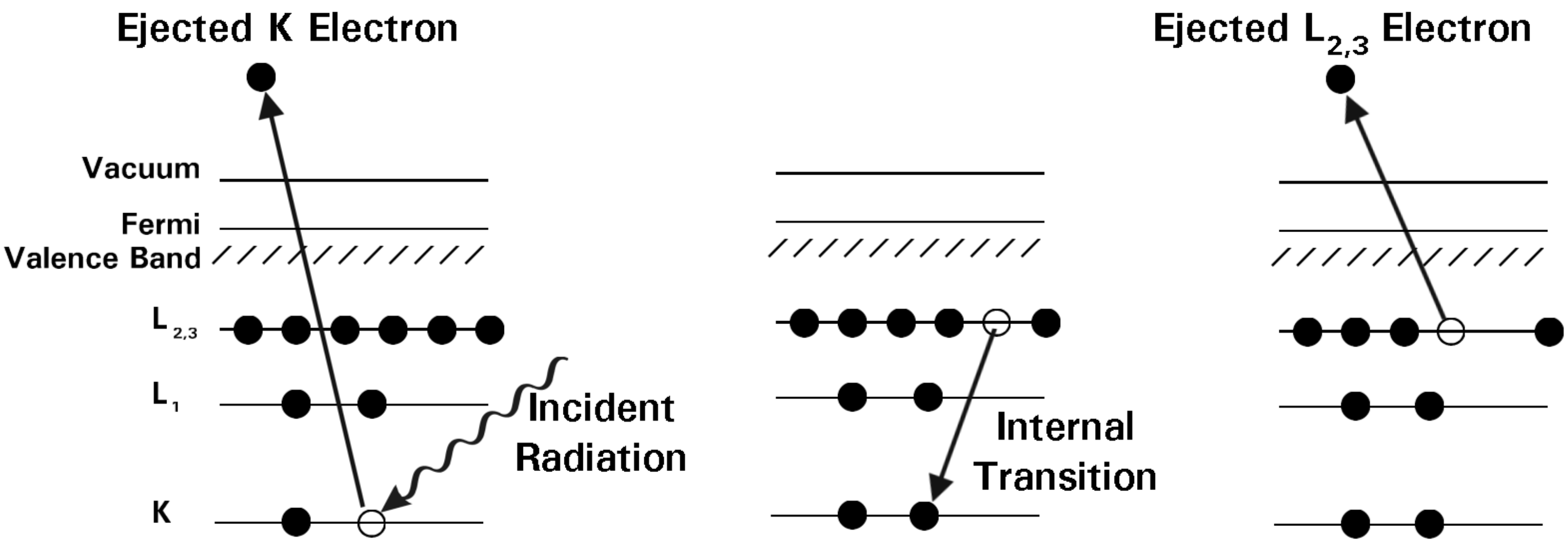


$$\lambda = a_M \left(\frac{2170}{E_{kin}^{\;2}} + 0.55 \sqrt{a_M \; E_{kin}} \right)$$

Intensity as a function of depth

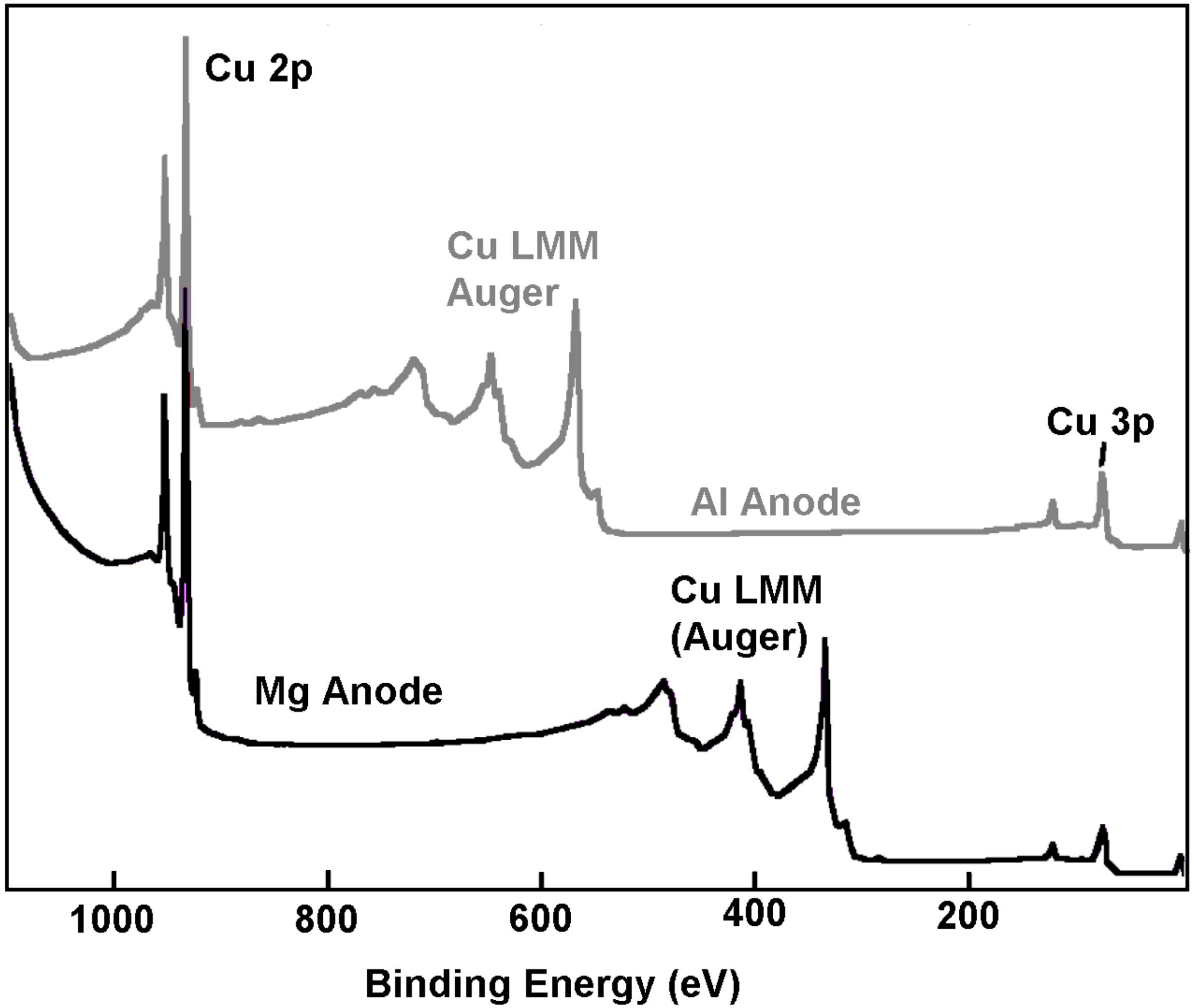
- **65% of the signal from < 1λ**
- **85% from < 2λ**
- **95% from < 3λ**

X-Ray Induced Auger Emission



$$E_{KL2,3L2,3}(Z) = E_K(Z) - [E_{L2,3}(Z) + E_{L2,3}(Z + 1)]$$

MgKα *vs. AlK*α *X-Rays*
1253.6 eV   1486.6 eV



- **XPS and Auger peaks**

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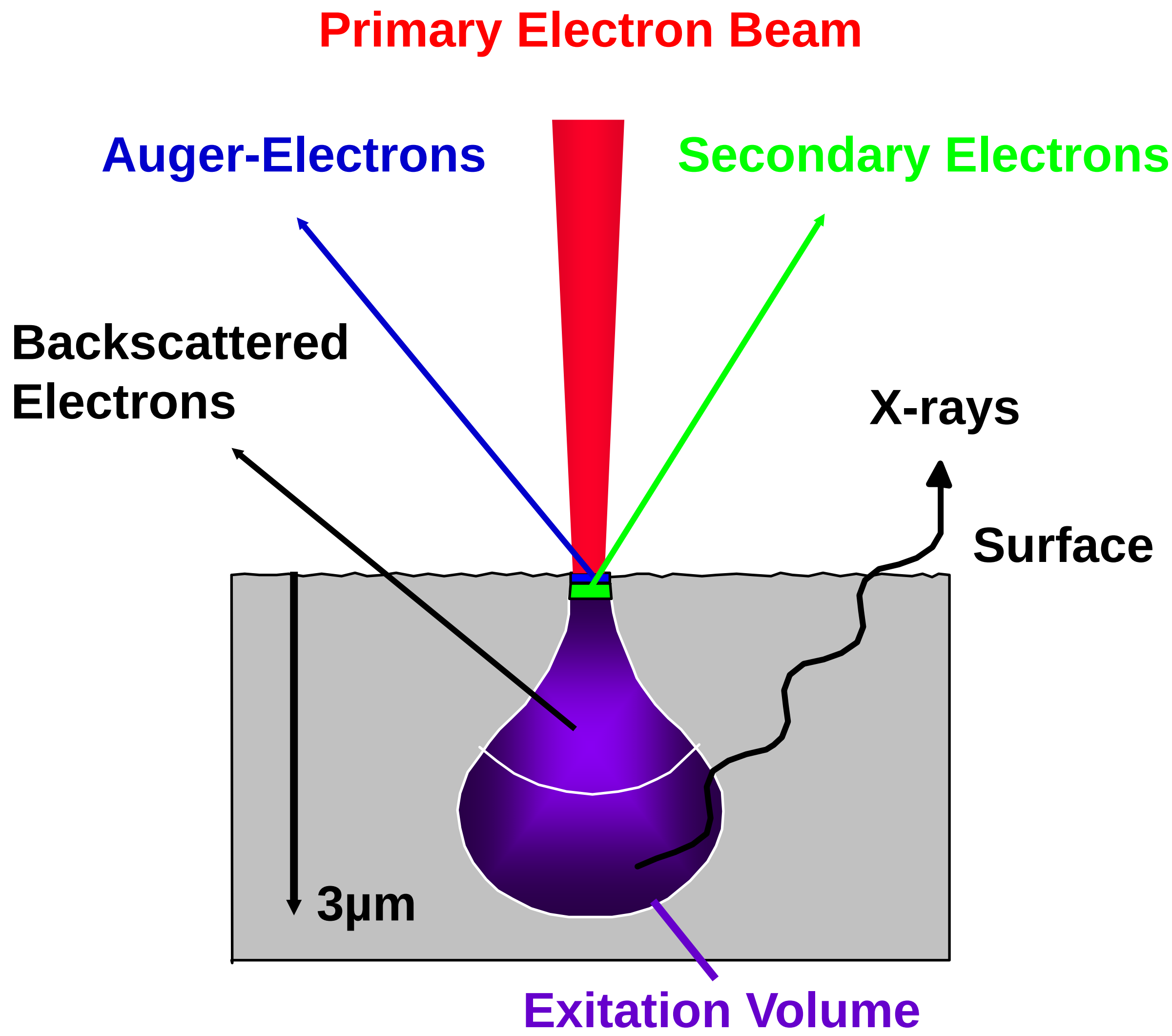
Electron Spectroscopy (AES)
Electron Solid Interactions



- ***All elements Z>2***
- ***Conducting and semi-conducting surfaces***
- ***Spatial resolution <10nm***
- ***Detection limit >0.1at.%***
- ***Quantitative elemental information***

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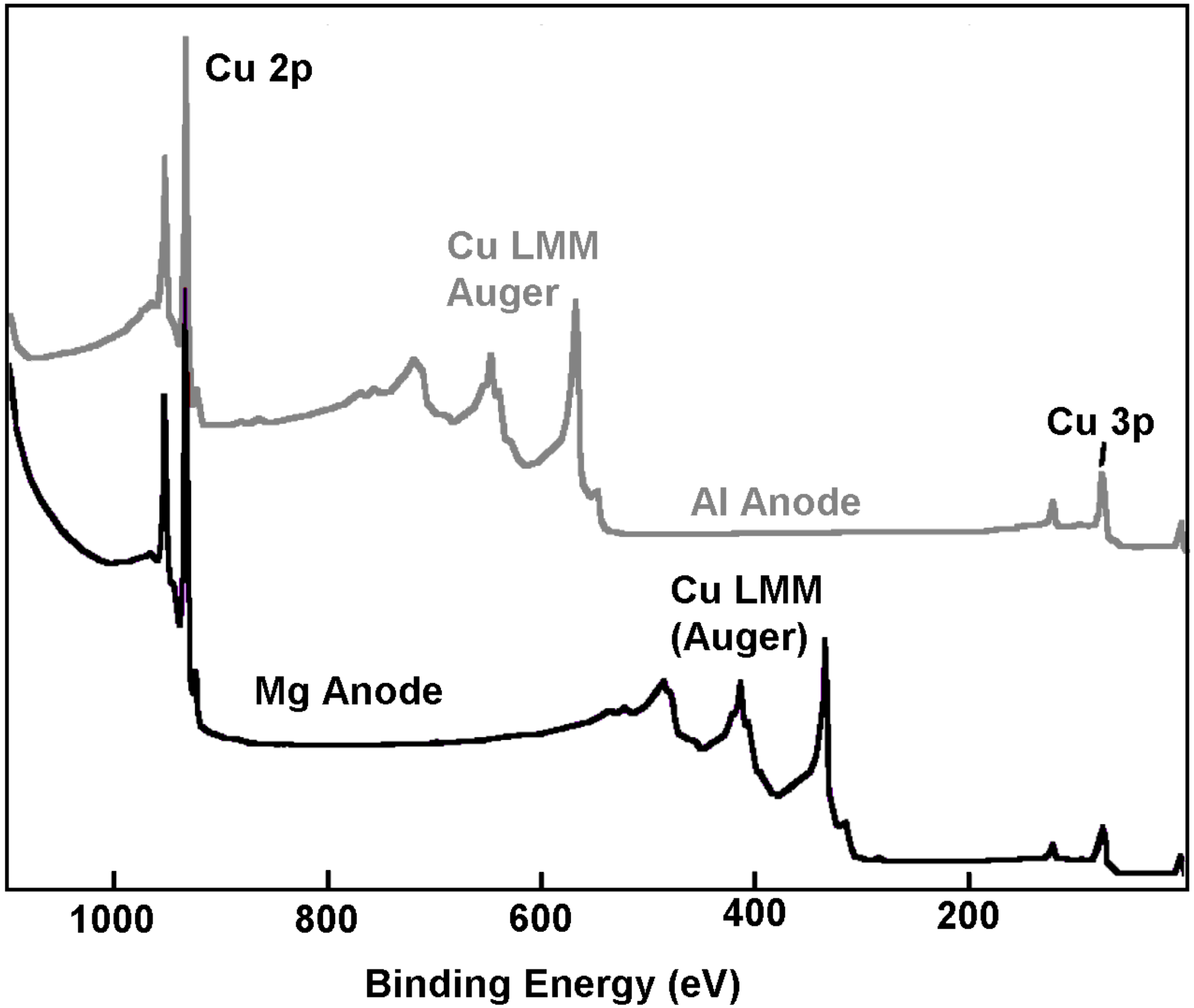
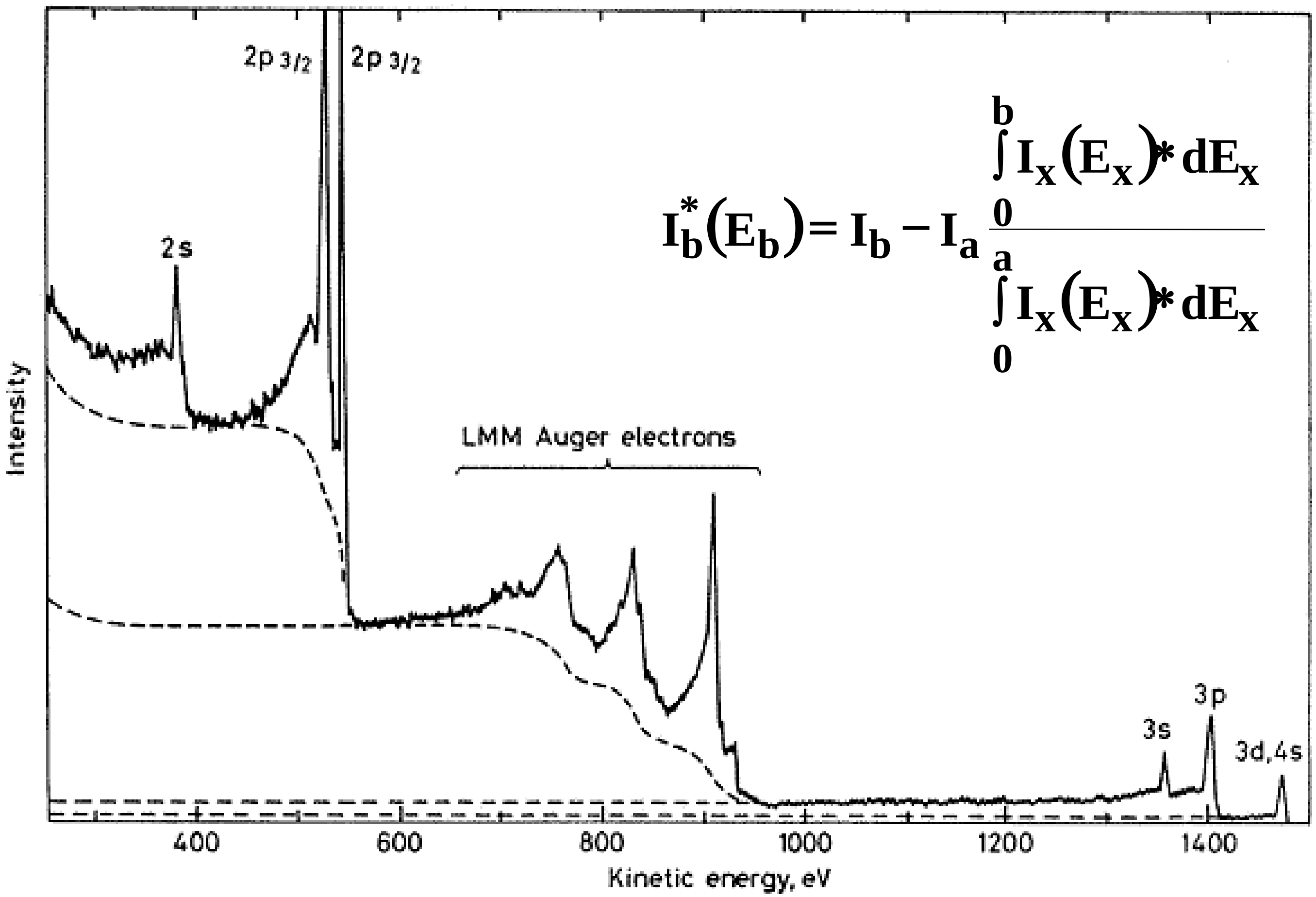
MgKα vs. AlKα X-Rays
1253.6 eV   1486.6 eV



- **XPS and Auger peaks**
- **Shake-up/off satellites**
- **X-ray satellites**
- **Background**
- **Surface charging**

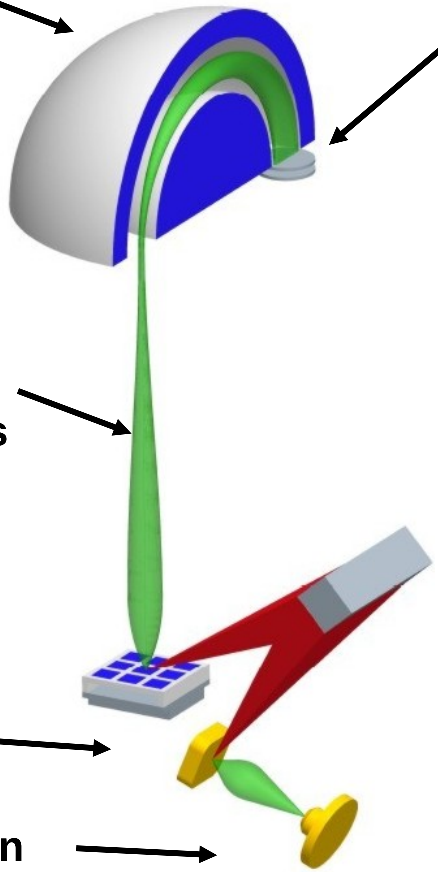
Shirley Type Background



$$I_b^*(E_b) = I_b - I_a \frac{\int_0^b I_x(E_x) * dE_x}{\int_0^a I_x(E_x) * dE_x}$$

Monochromatic AlKα X-Rays

FWHM 0.85 → 0.26 eV



Bragg: $n\lambda = 2d \sin\theta$

$\theta = 78.5°$, AlKα ⇔ Quartz 1010

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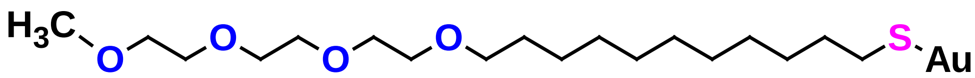
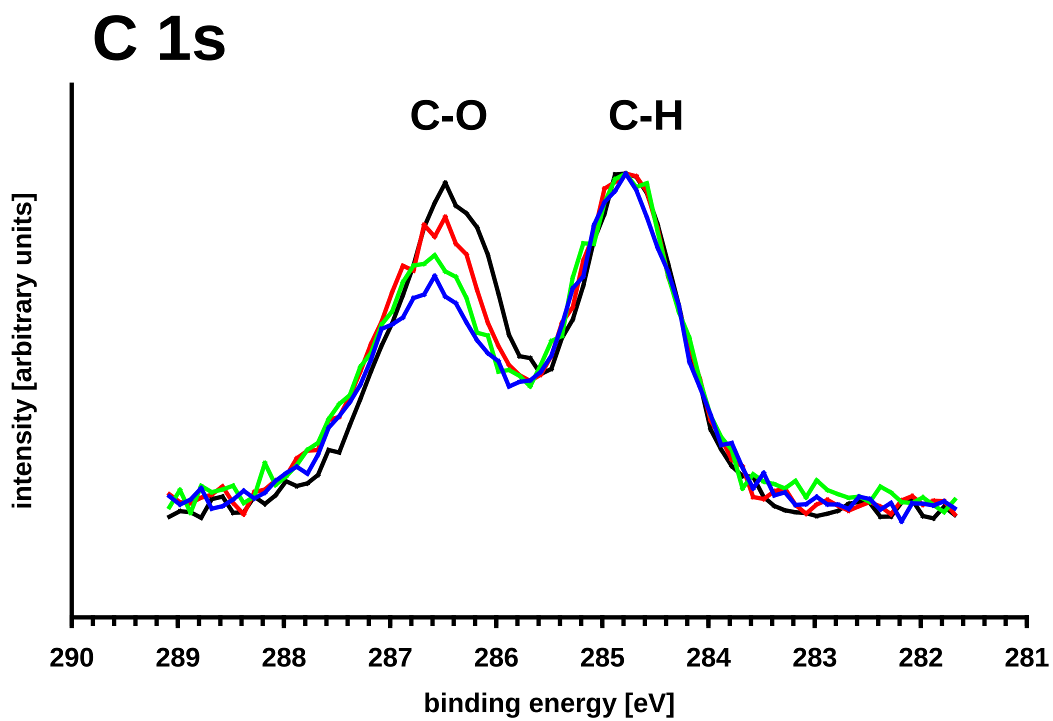
Speciation: SAMs for Biological Applications

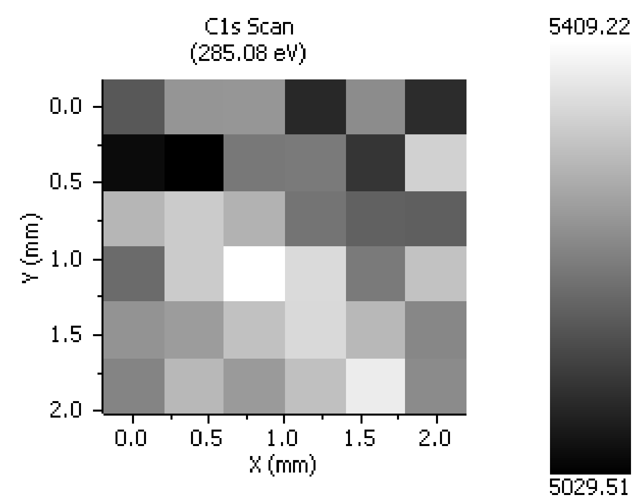
X-Ray Induced Damage





➔ *microfocused X-rays*

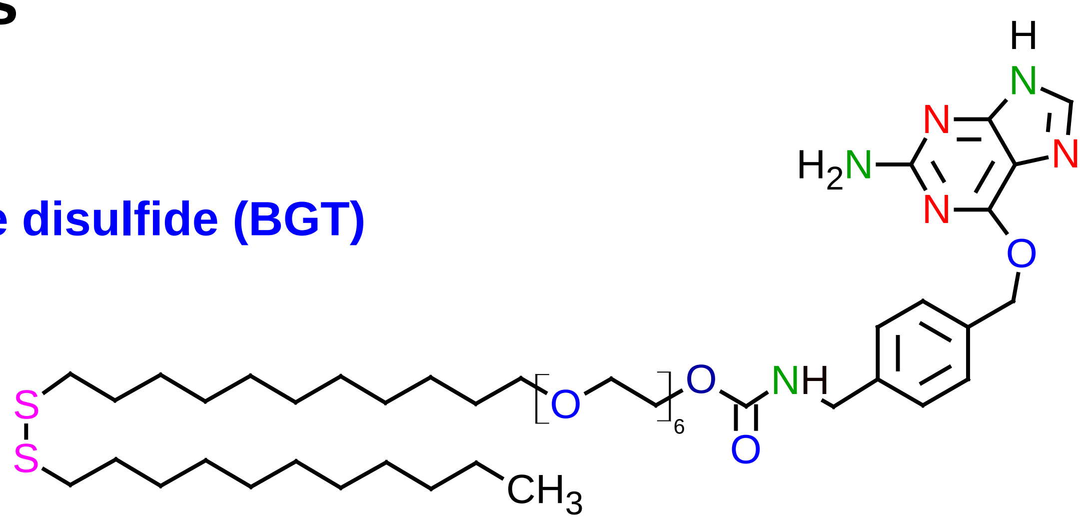
1. **Multi-point analysis with short acquisition time**
2. **Collapse data set to one single spectrum**



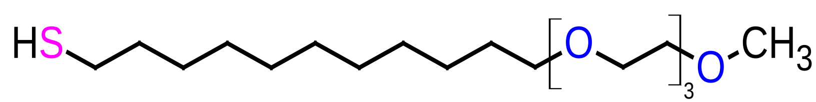
SAM alteration dependant on the X-ray exposure time (-- as received, -- 9 min., -- 21min., -- 27 min.).

Thiol-SAMs

Benzylguanine disulfide (BGT)



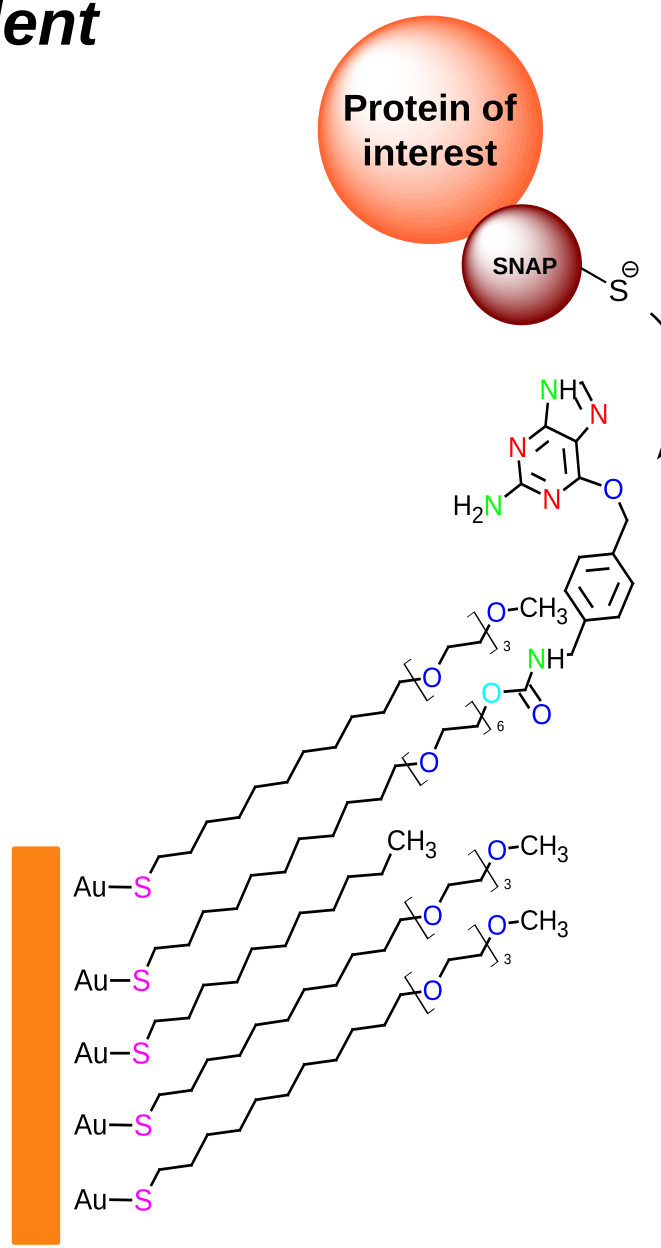
EG3OMe thiol



Methoxy-capped tri(ethylene glycol) undecanthiol

1. **S. Engin, V. Trouillet, C. M. Franz, A. Welle, M. Bruns, and D. Wedlich, Langmuir 26 (2010) 6097-6101.**
2. **M. Bruns, C. Barth, P. Brüner, S. Engin, T. Grehl, C. Howell, P. Koelsch, P. Mack, P. Nagel, V. Trouillet, D. Wedlich, R. G. White, Surf. Interface Anal. 44 (2012) 909–913.**

SNAP-tag system for covalent immobilization of proteins

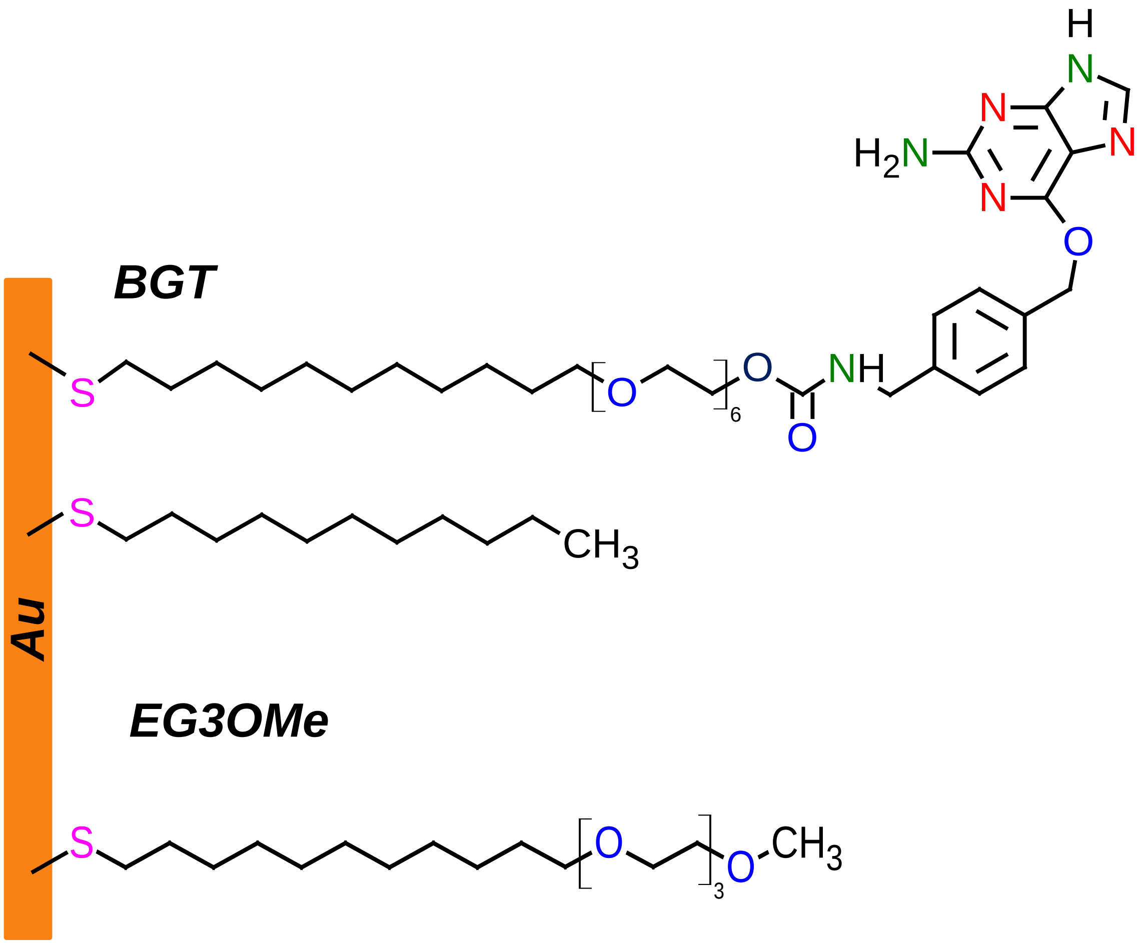


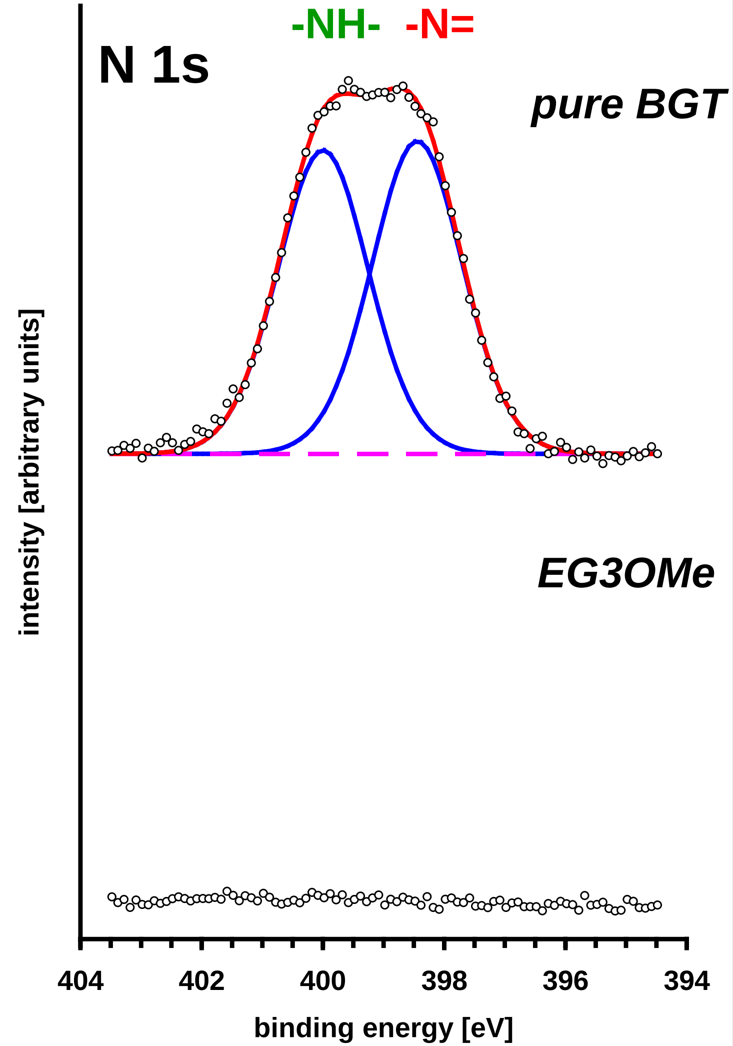
Applications

- **cell culture: cell adhesion, migration, differentiation**
- **biosensors in diagnosis,**
- **lab-on-chip technology,**
- **…..**

SNAP-tag system:
genetically modified
O^6-alkylguanin-DNA alkyltransferase

Thiol – SAMs for Biological Applications





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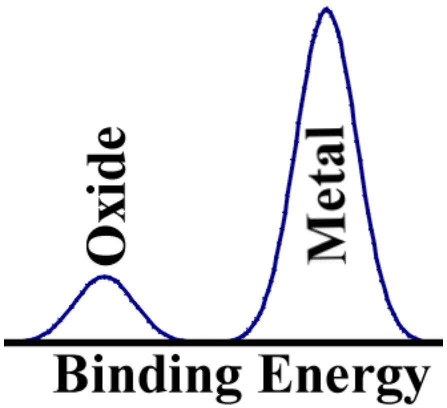
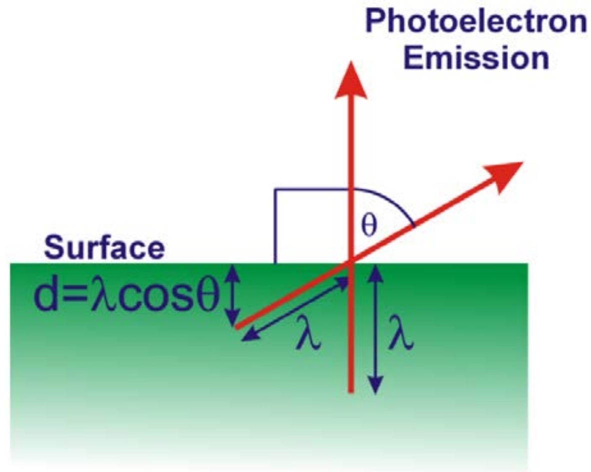
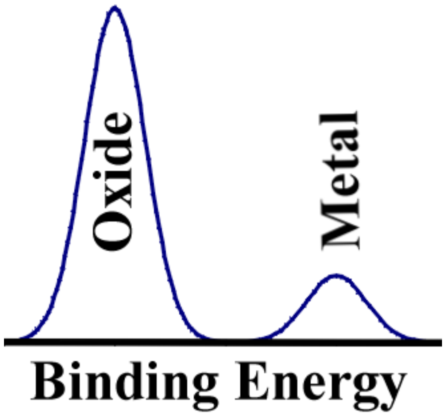
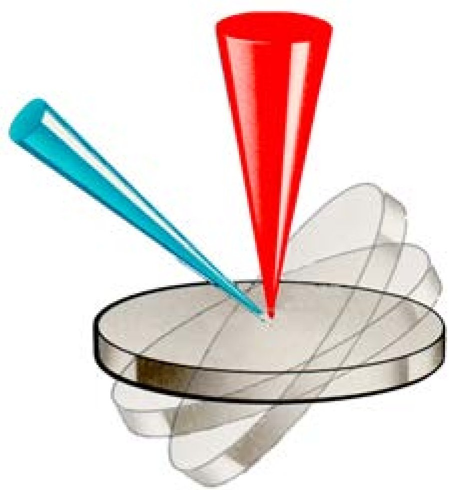
XPS Information Depth

… Depends on Electron Emission Angle

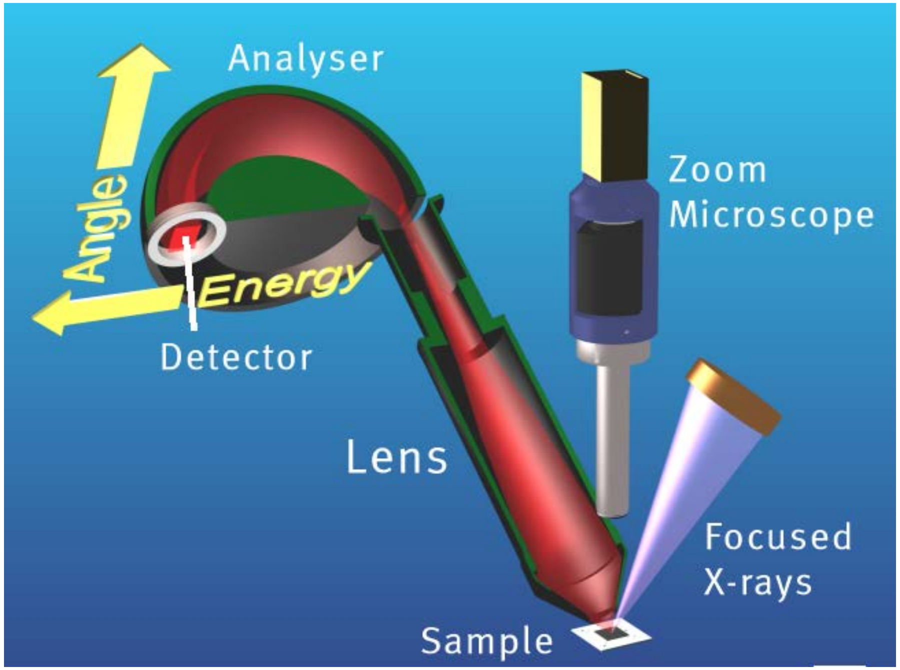


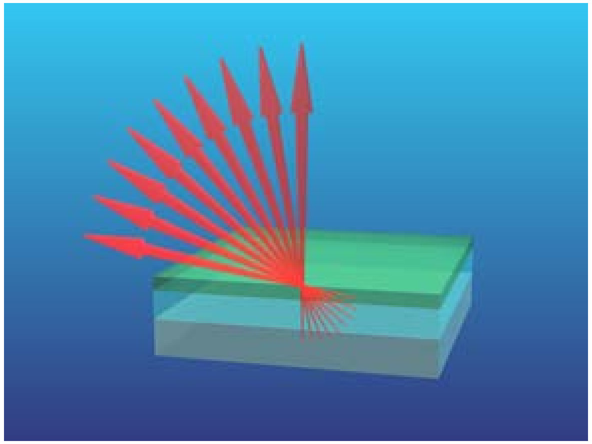






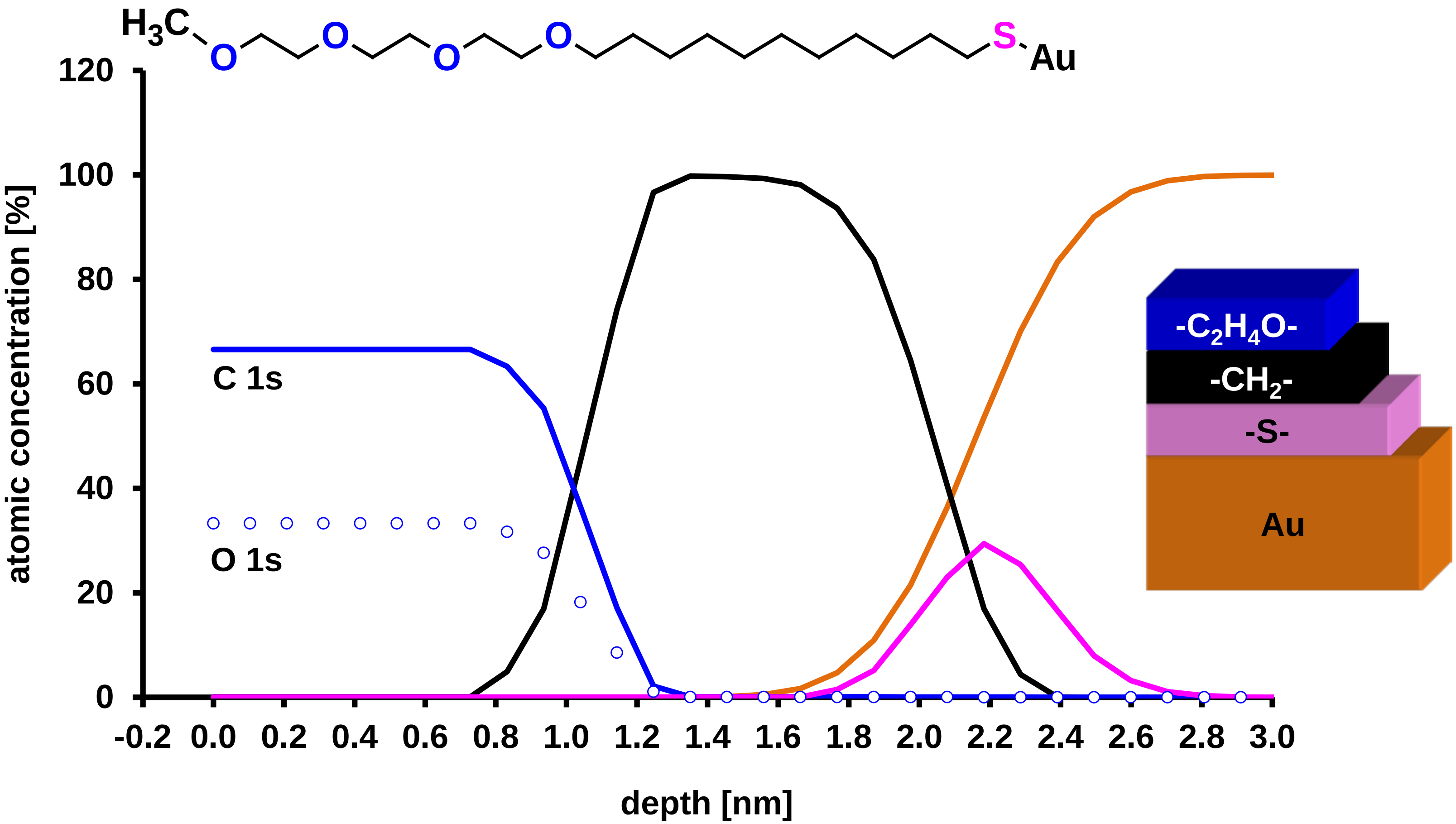
Parallel ARXPS: non-Destructive Depth Profile



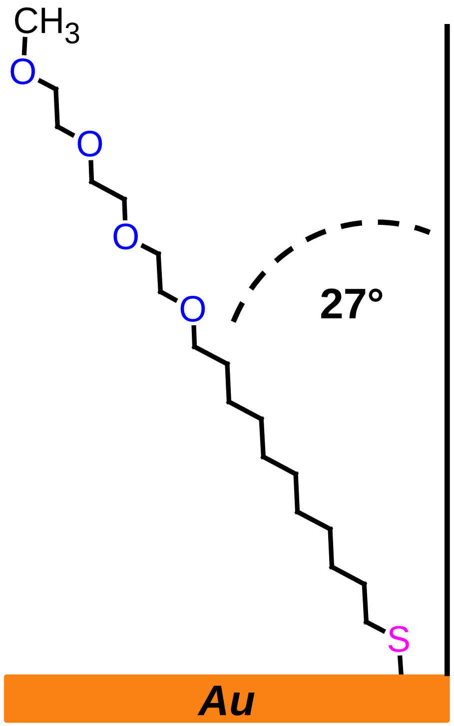


Parallel ARXPS: EG3OMe SAM

non-Destructive Depth Profile



High-sensitive Low Energy Ion Scattering SAM Thickness



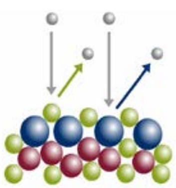
Projectile: 3 keV $^{3}He^{+}$

Au peak onset energy shift:

✓ **EG3OMe = 200 eV ➔ 2.2 nm SAM thickness**

➔ well-ordered SAM

Reliable estimation of the SAM thickness is prerequisite for the reconstruction of non-destructive elemental depth profiles from parallel ARXPS data.



Qtac 100

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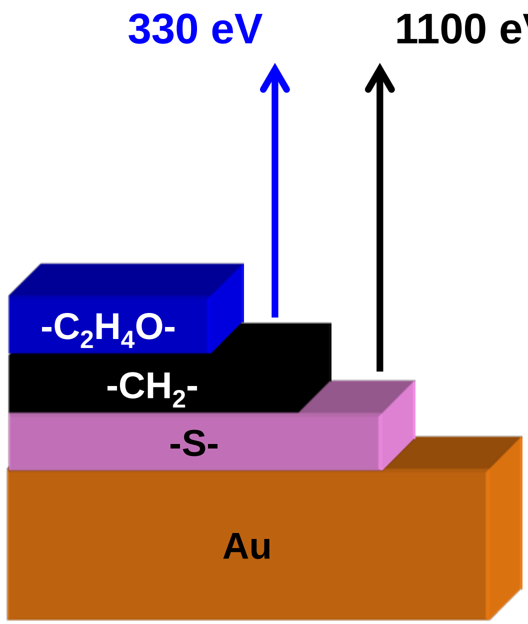
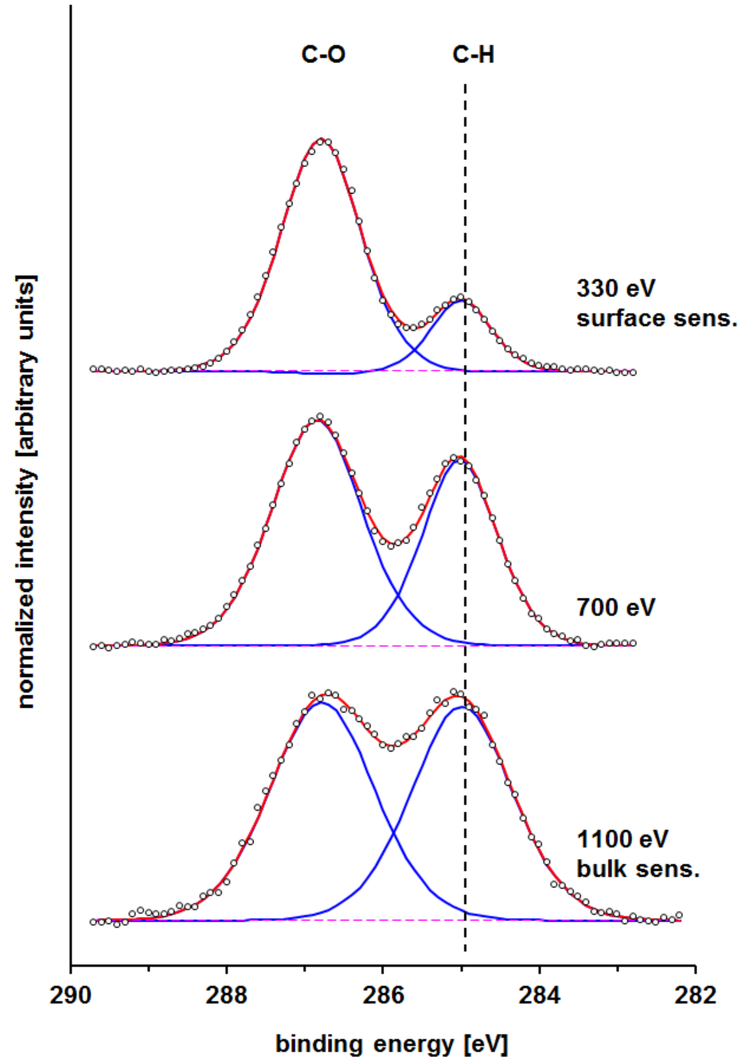
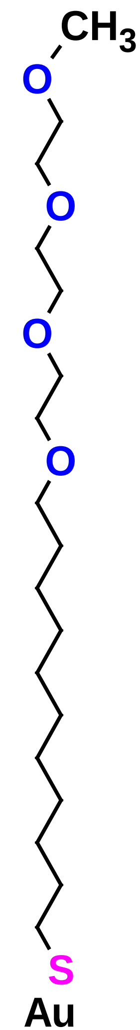
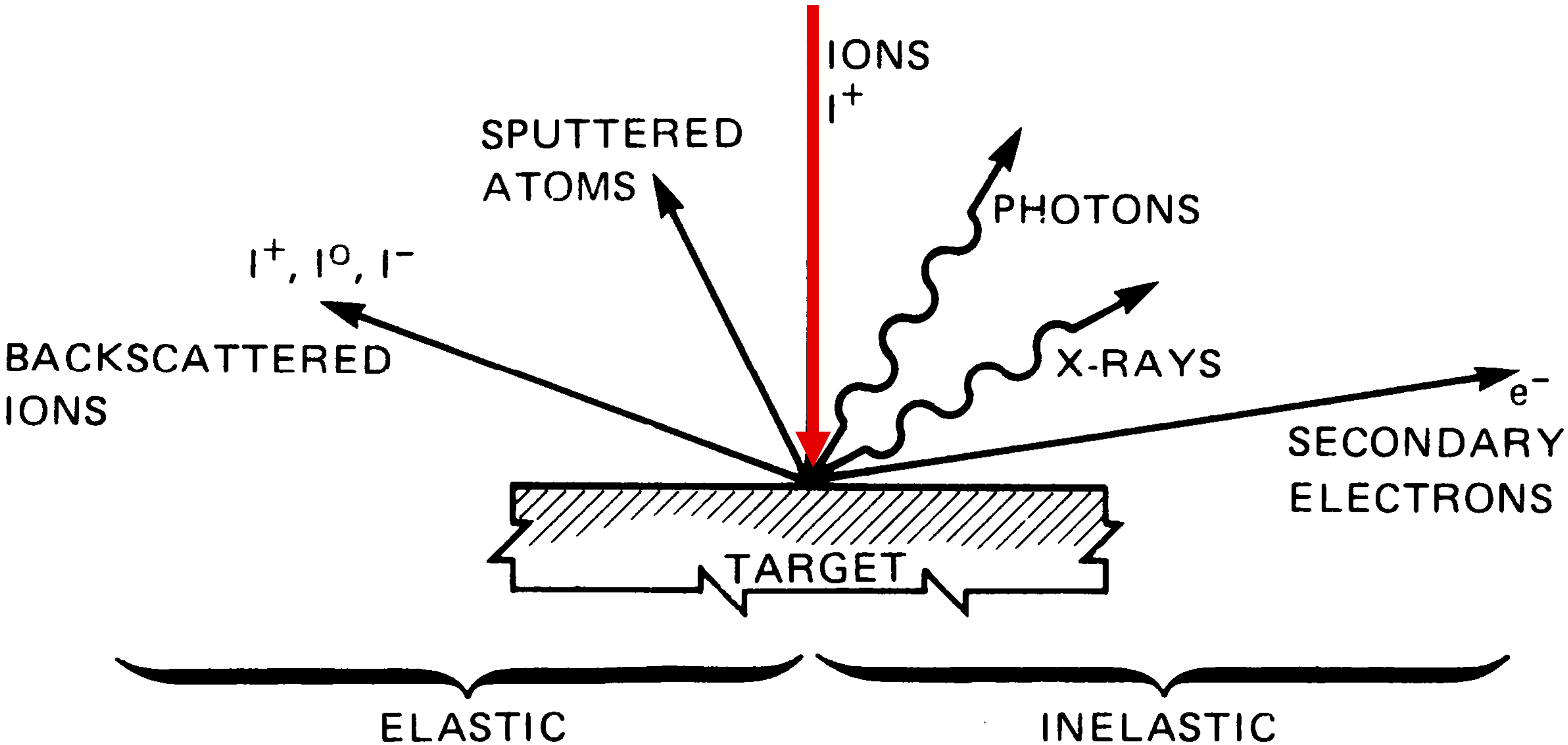
ER PES: EG3OMe SAM
non-Destructive Depth Information







Sputtering
Ion Solid Interaction



Implantation

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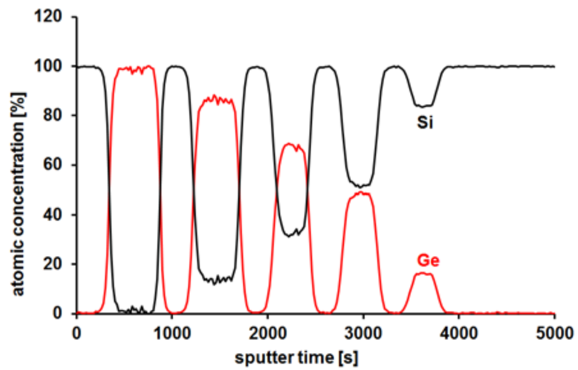
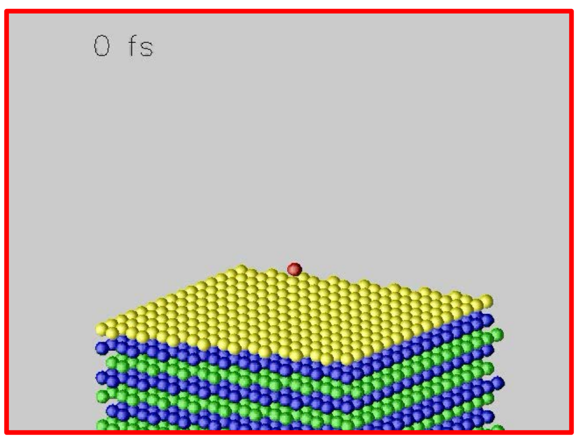
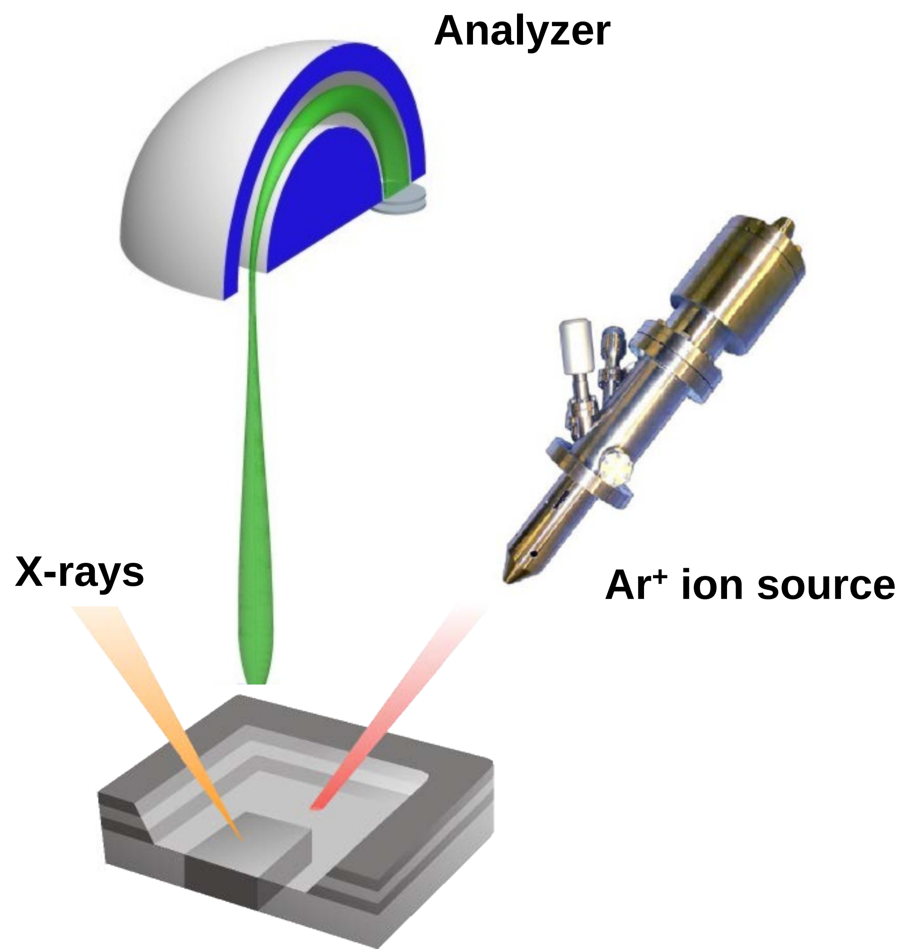
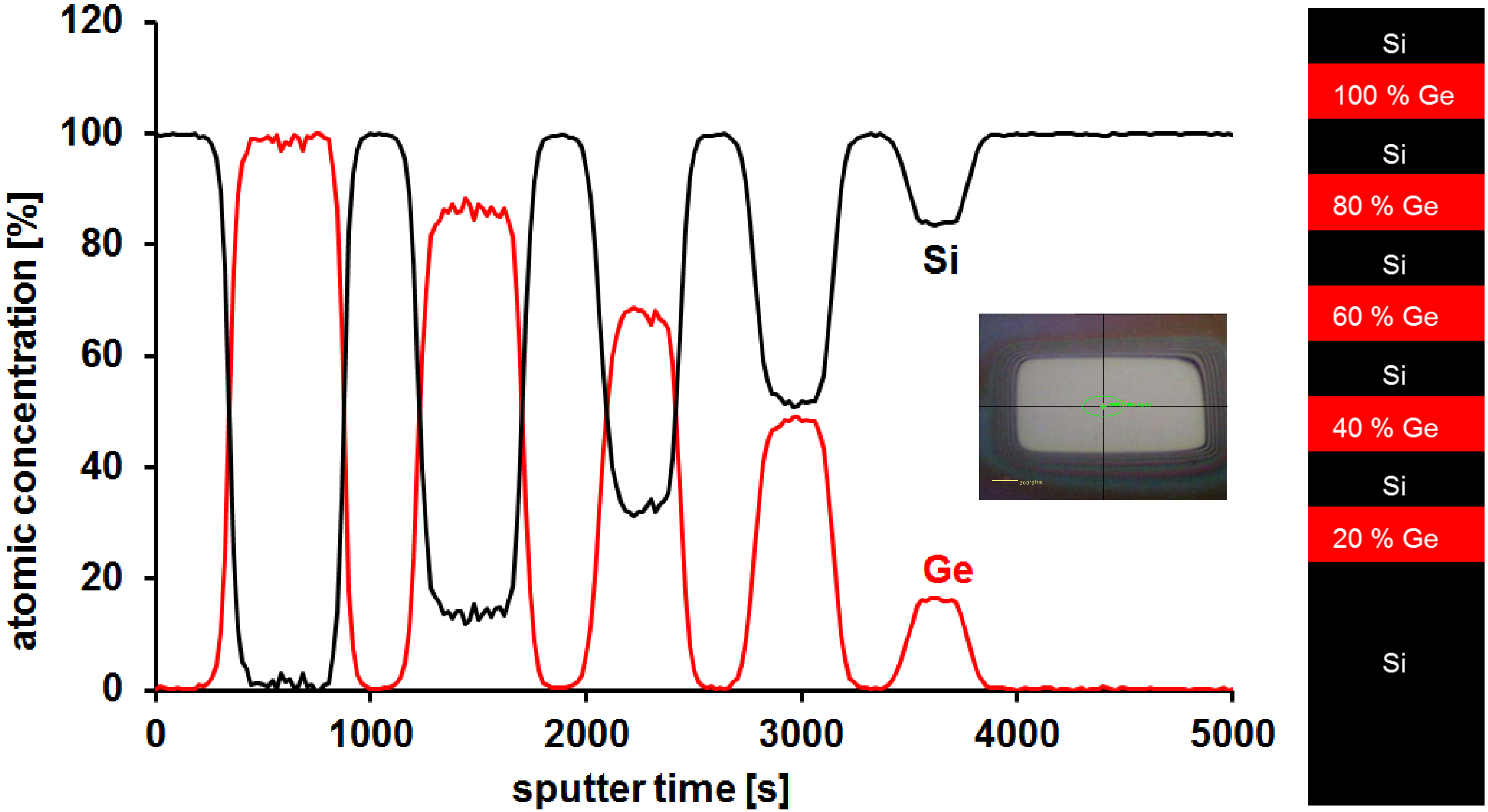
Depth Information via Sputter Depth Profiles







XPS Sputter Depth Profiles



Collaboration: Tascon GmbH, Heisenbergstr. 15, D-48149 Münster, Germany

XPS Sputter Depth Profiles

Time-to-Depth Conversion

$$z(t) = \frac{j_P \cdot Y_i \cdot M_i \cdot t}{N_A \cdot e_0 \cdot \rho_i}$$

j_P = Ion beam density

N_A = Avogadro constant

e_0 = Elementary charge

t = Sputter time

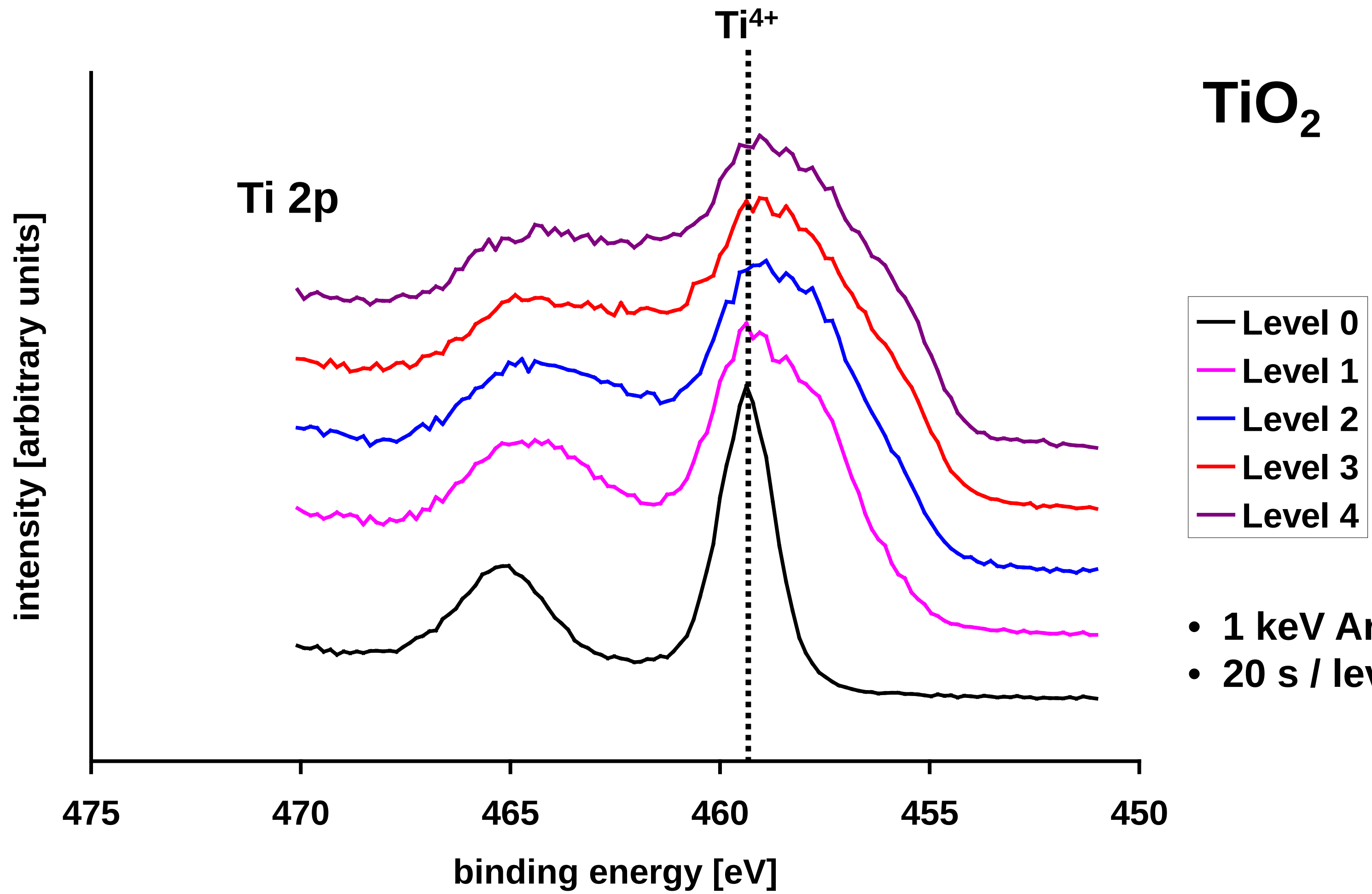
Y_i = Sputter yield

M = Molecular weight

ρ_i = Density

XPS Sputter Depth Profiles

Loss of Chemical Information



TiO_2

- 1 keV Ar^+ ions
- 20 s / level

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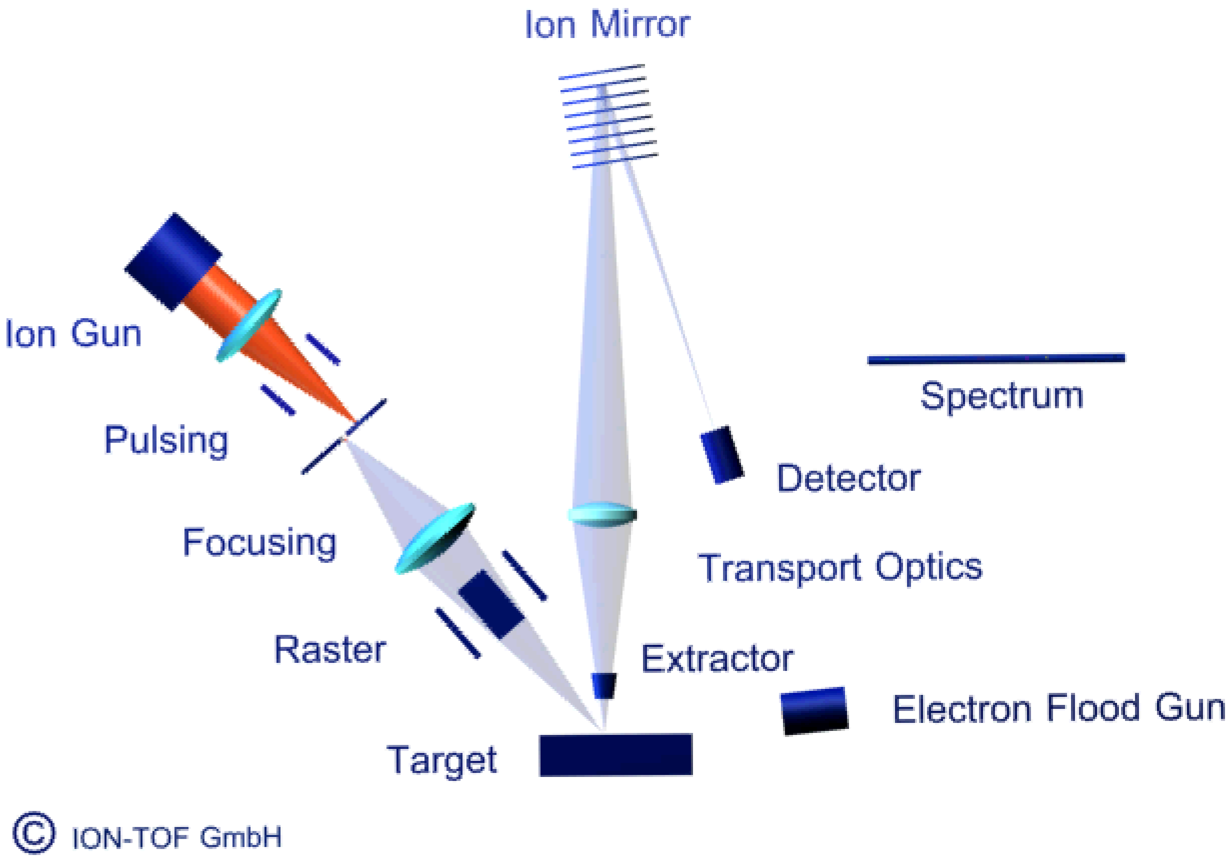
ToF-SIMS

Time-of-Flight SIMS Principle



- **A short-pulsed ion beam defines the starting point of the time-of-flight measurement.**
- **All secondary ions are accelerated to the same kinetic energy: the time-of-flight for a given drift path varies as the square root of mass.**
- **Time focusing devices (i.e. electrostatic fields) for good mass resolution.**

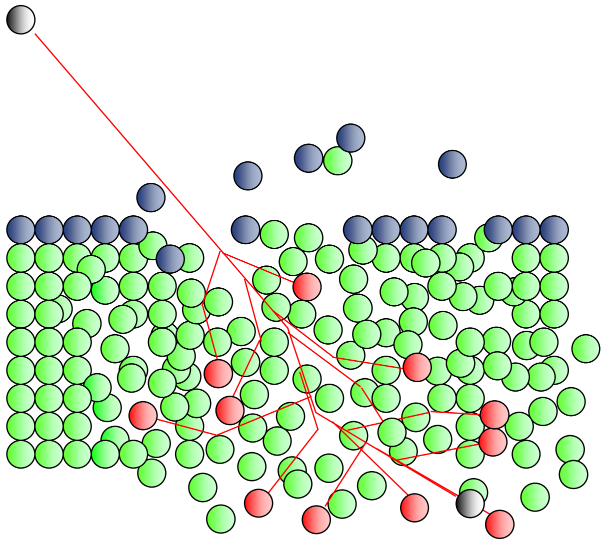
ToF-SIMS
Ion Solid Interaction

Excitation

Bombardment with primary ions, energy: 5-25 keV

(Ga^{+}, Au^{n+}, Bi^{n+}, O^{2+}, Cs^{+}, Ar^{+}, Xe^{+}, ...)

➔ Collision cascade in solid



Results

Desorption of neutrals (95%), electrons,

and **secondary ions** (+/-).

- ❖ area 5-10 nm diameter
- ❖ depth of origin 1-2 monolayers

- ➢ Implantation of primary ions
- ➢ Atoms relocation (mixing)
- ➢ Damaging of organic molecules

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ToF-SIMS
Characteristics

+	detection of all elements	
+	isotope sensitivity	
+	chemical information	molecules, clusters
+	low detection limit	ppm - ppb
+	small information depth	first 1-3 monolayers
+	high depth resolution	<1 nm
+	high lateral resolution	<100 nm
+	high mass resolution	> 16000
+	high mass range	up to 10000 u
+	parallel mass detection	
-	quantification limited (requires standards)	typical ion yield 10^{-1} - 10^{-5} strong influence of chemical environment
-/+	destructive	

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ToFSIMS

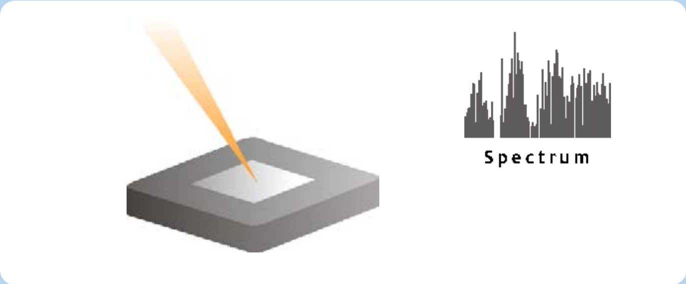
Modes of Operation

Surface Spectroscopy

Surface Imaging

Depth Profiling

3D Analysis



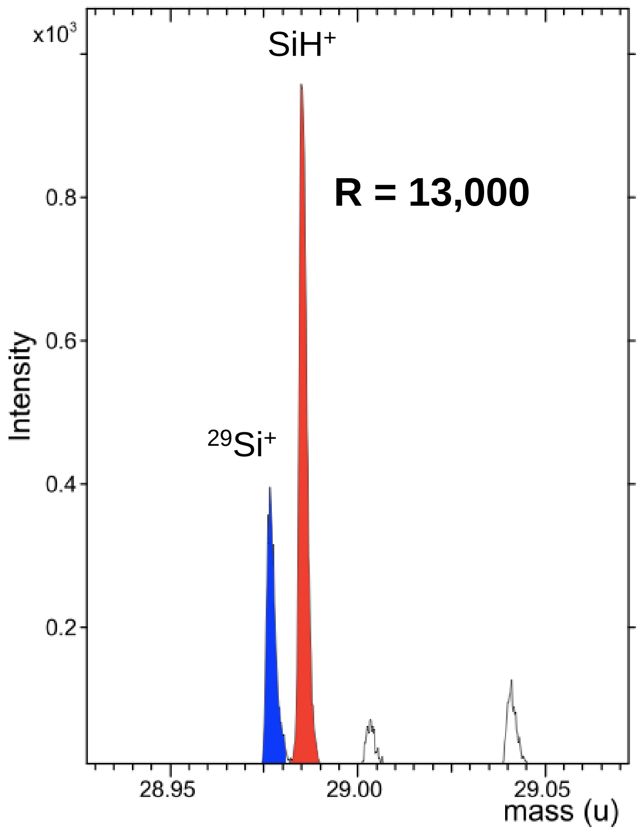
Quasi non-destructive surface analysis of the outer monolayers

Features:

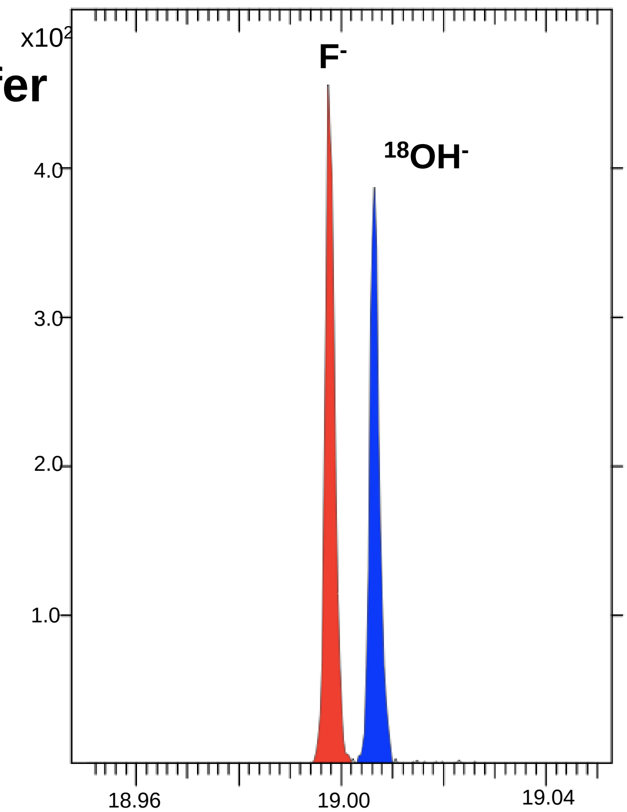
- **elemental and molecular information**
- **ppm/ppb sensitivity**
- **suited for insulators**

Surface Spectroscopy

High Mass Resolution in Positive and Negative Polarity



Si-Wafer



Mass Calibration

$$E = \frac{m}{2} v^2 \quad \Rightarrow \quad t \propto \sqrt{m}$$

Mass Resolution

$$\frac{\Delta m}{m} = \frac{\Delta E}{E} + \frac{2(\Delta t_p + \Delta t_R)}{t}$$

ToF-SIMS

Detection Limits

Element	detection limits (atoms / cm^2)		detection limits (atoms / cm^2)
^{7}Li	1E7 = 0.4 ppt	^{52}Cr	1E8
^{11}B	5E7	^{55}Mn	1E9
Na	1E7	^{56}Fe	2E8
^{24}Mg	2E7	^{58}Ni	1E9
Al	2E7	Co	2E8
^{39}K	1E7	^{63}Cu	3E8
^{40}Ca	3E7	^{69}Ga	1E9
^{48}Ti	2E8	$^{*}As$	3E9
^{51}V	2E8	^{98}Mo	6E9

1 Monolayer = 1.5E^{15} atoms/cm^2), the error is estimated to be within a factor of 2-3.

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- 3D Analysis

Chemical Mapping of the surface

Features:

- ➢ lateral distribution of elements and molecules
- ➢ lateral resolution down to 60 nm
- ➢ parallel acquisition of all images

iONTOF

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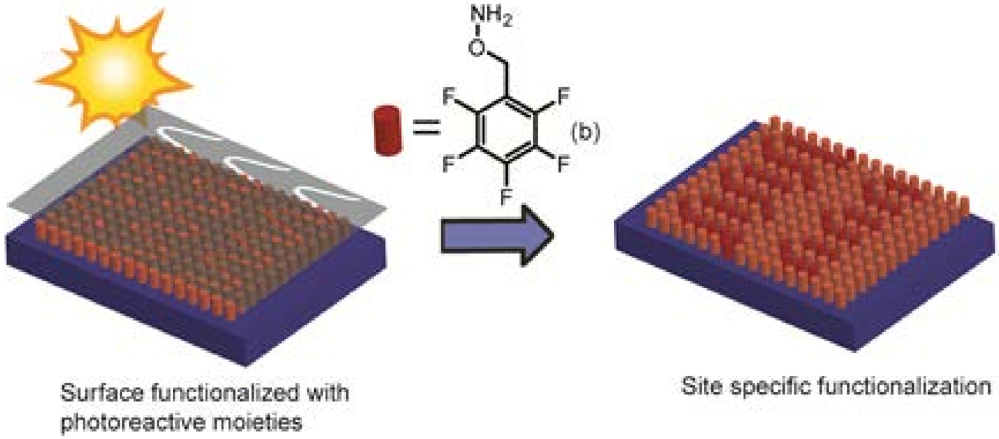
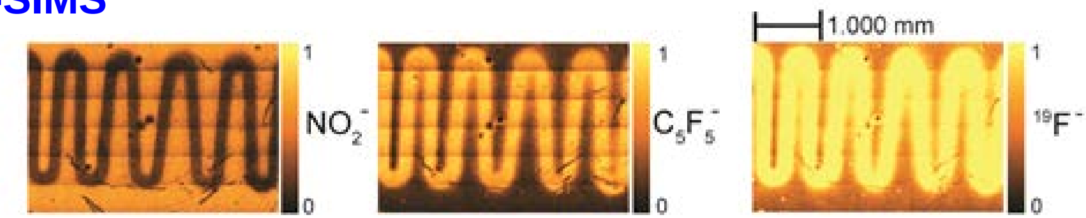
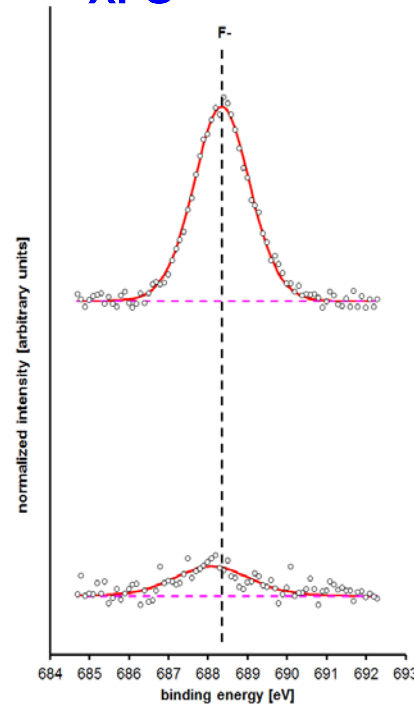
(Bio)Molecular Surface Patterning by Phototriggered Oxime Ligation via shadow-mask techniques



ToF-SIMS



XPS

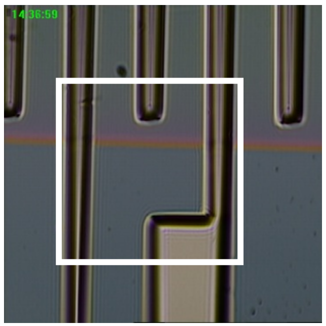


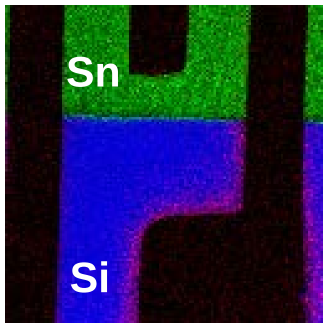
T. Pauloehrl, G. Delaittre, M. Bruns, M. Meiβler, H. G. Börner, M Bastmeyer, and C. Barner-Kowollik, ***Angew. Chem. Int. Ed.***, 51 (2012) 9181 –9184.

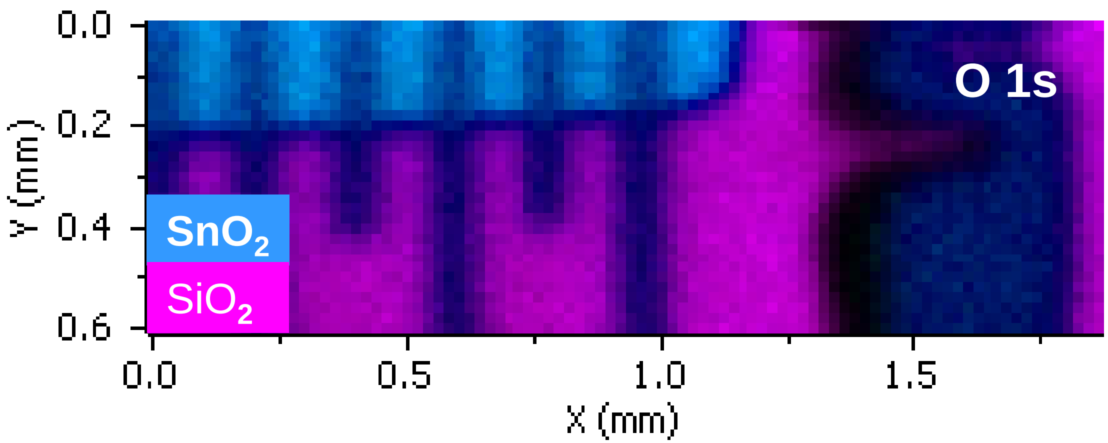
ToFSIMS vs. XPS
Chemical Image

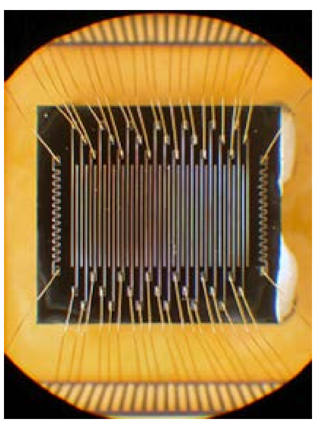
ToFSIMS (1 min acquisition time)

XPS (> 3000 min acquisition time)









500x500 µm²

XPS chemical images are very time consuming
➔ Parallel imaging using Thermo Scientific ESCALAB 250 Xi

! Different positions !

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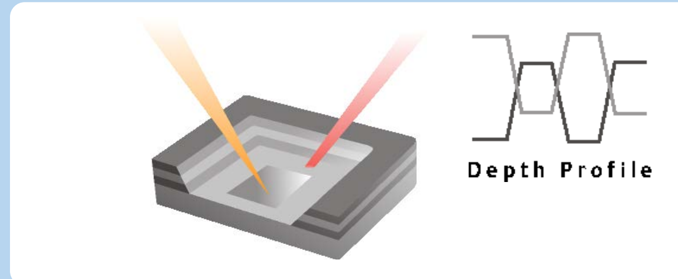

Analysis of the in-depth distribution of elements and molecules

Features:

- elemental and cluster information
- depth resolution < 1 nm
- thin layers from 1 nm to > 10 µm

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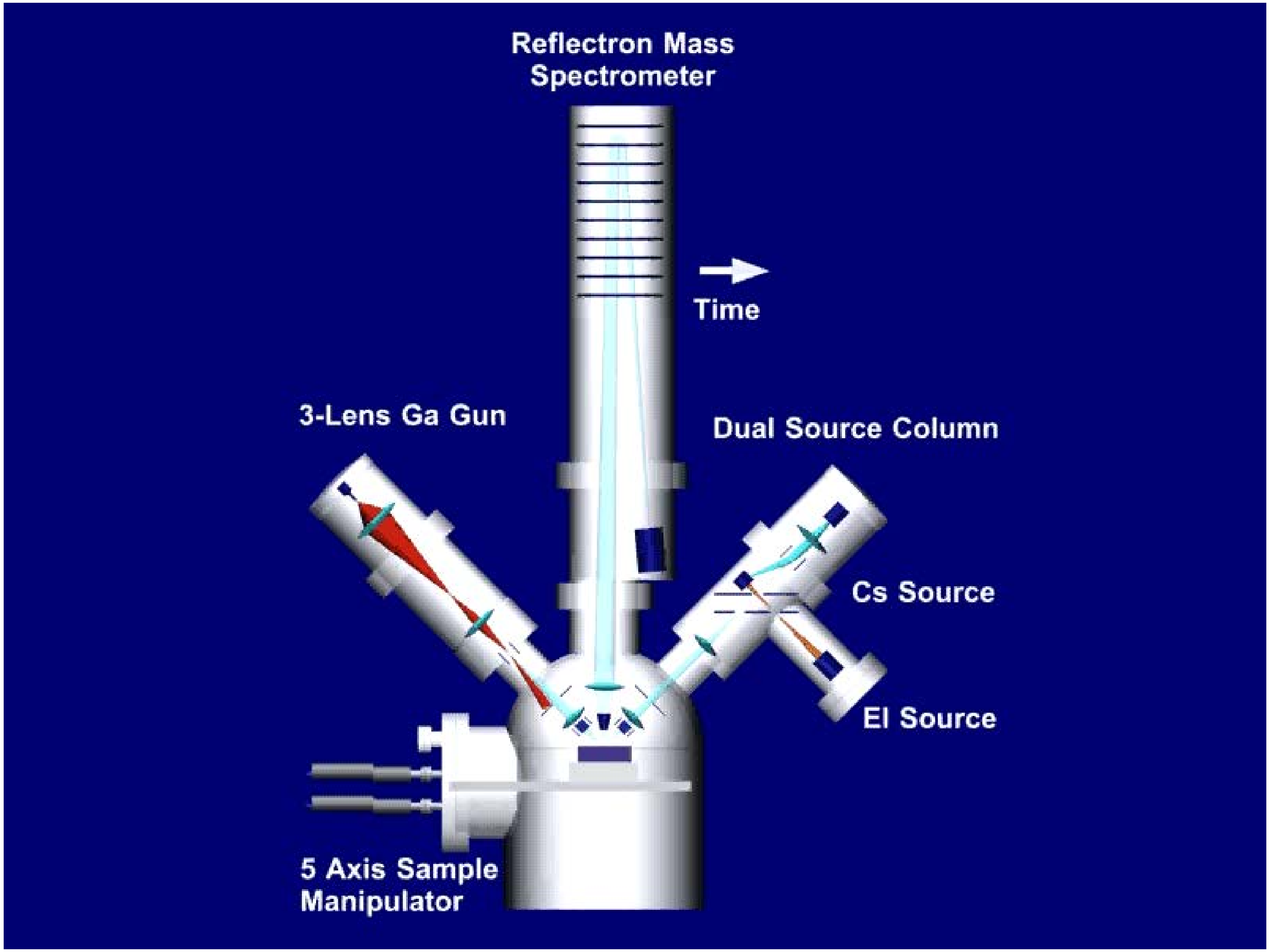
ToFSIMS Sputter Depth Profiling

Dual Beam Mode



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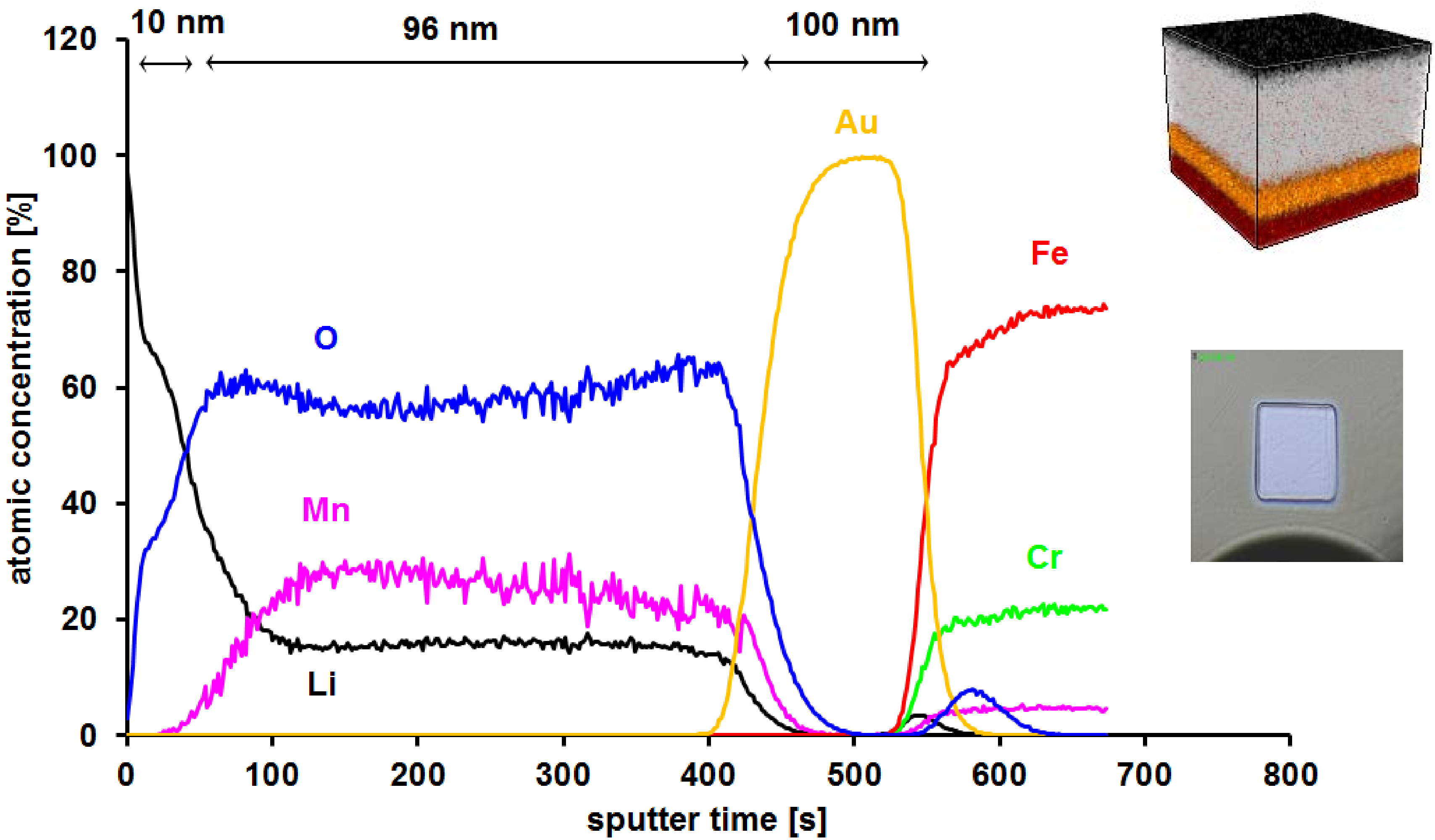
ToF-SIMS Sputter Depth Profile of a R.F. Magnetron Sputtered Li-Mn-O Thin Film calibrated by XPS

Karlsruhe Institute of Technology



ECASIA 2013, Cagliari, Italy

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Thank you!


Florian Stemme
Vanessa Trouillet
Volker Winkler
Vanessa Oberst
Udo Geckle