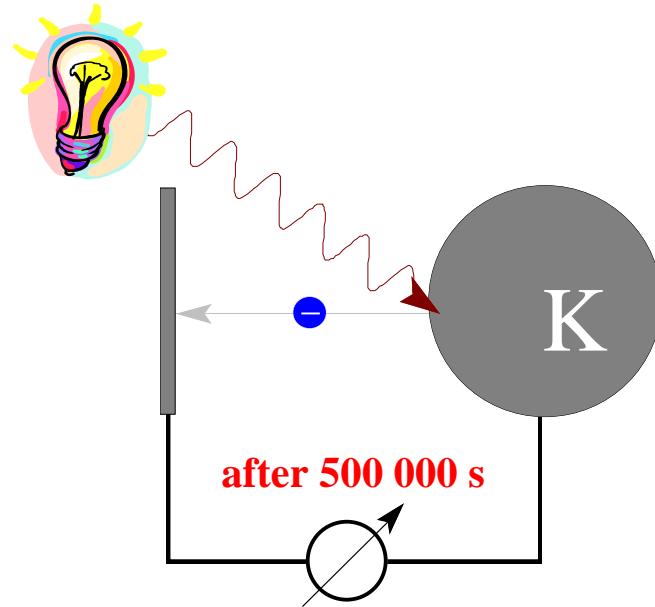


Chemical analysis of surfaces and organic thin films by means of XPS



X-ray photoelectron spectroscopy – The photoelectric effect

– Wilhelm Hallwachs (1886), Albert Einstein (1905) und Ernest Rutherford (1914) –



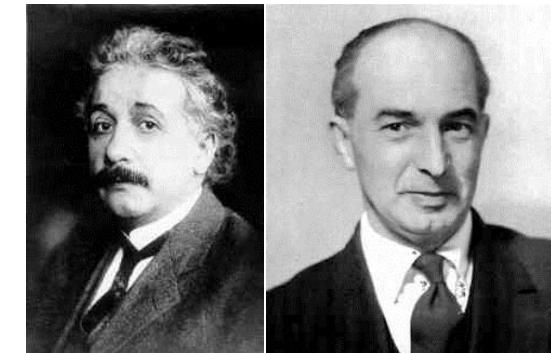
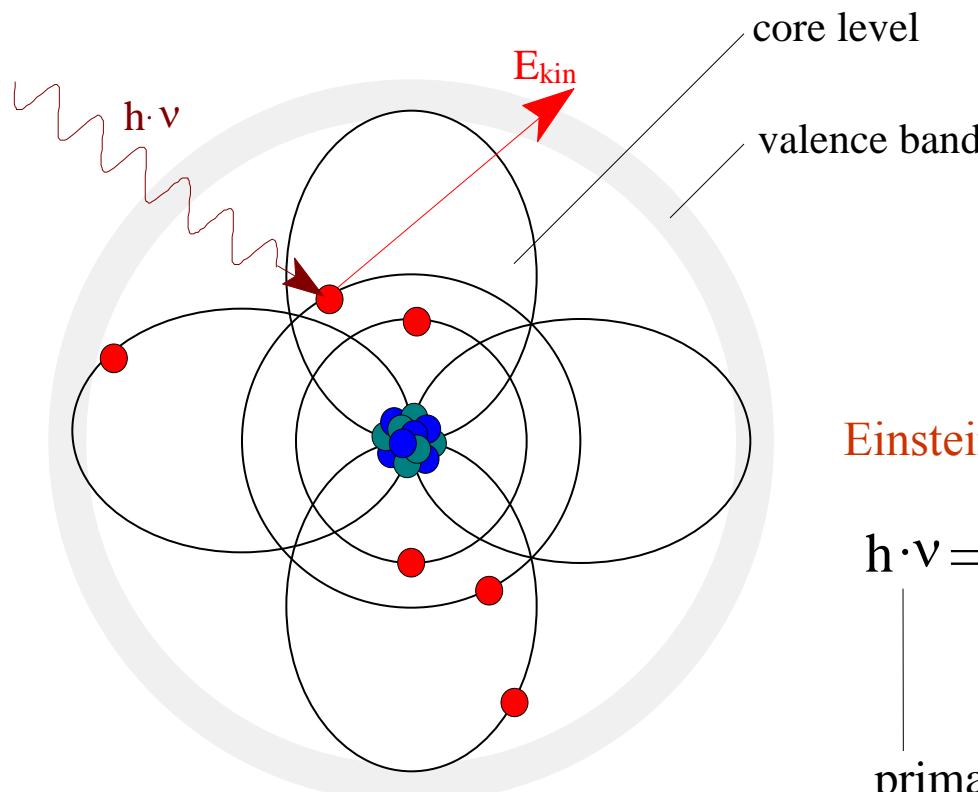
Wilhelm Hallwachs and Philipp Lenard, around 1900:

flux density:	$D = 10^{-5} \text{ W}\cdot\text{m}^{-2}$
flux density per K atom:	$D \cdot A_K = 10^{-5} \text{ W}\cdot\text{m}^{-2} \cdot 8.6 \cdot 10^{-20} \text{ m}^2$ $= 8.6 \cdot 10^{-25} \text{ W}$
energy at 1 s irradiation:	$E_{\text{prim}} = 8.6 \cdot 10^{-25} \text{ W}\cdot\text{s}$
energy to remove one electron:	$E_i = 2.24 \text{ eV} = 3.6 \cdot 10^{-19} \text{ W}\cdot\text{s}$

During irradiation only the $1/2,000,000$ part of energy is supplied which is necessary to remove one electron.

X-ray photoelectron spectroscopy – The photoelectric effect

– Wilhelm Hallwachs (1886), Albert Einstein (1905) und Ernest Rutherford (1914) –



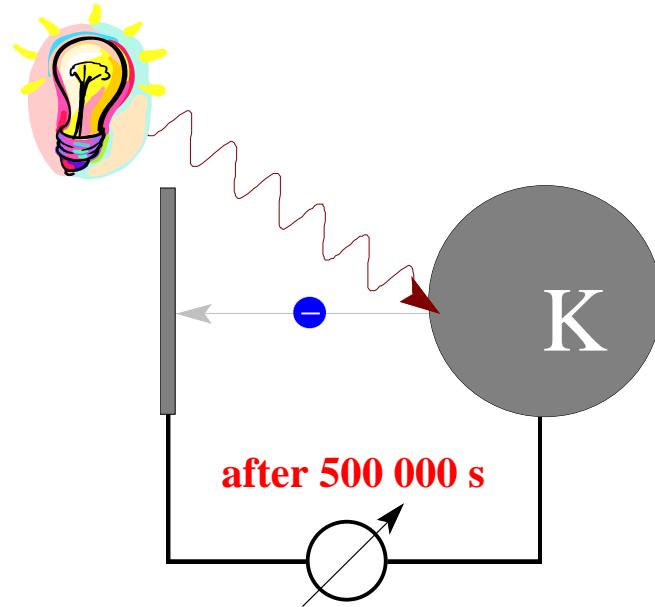
Einstein's Photochemical Equivalence Law (1905)

$$h \cdot v = E_{bind} + E_{kin} \quad [\text{eV}]$$

to determine experimentally
value specific for each element and level
primary energy

X-ray photoelectron spectroscopy – The photoelectric effect

– Wilhelm Hallwachs (1886), Albert Einstein (1905) und Ernest Rutherford (1914) –



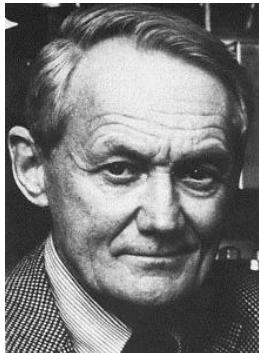
Wilhelm Hallwachs and Philipp Lenard, around 1900:

flux density:	$D = 10^{-5} \text{ W}\cdot\text{m}^{-2}$
flux density per K atom:	$D \cdot A_K = 10^{-5} \text{ W}\cdot\text{m}^{-2} \cdot 8.6 \cdot 10^{-20} \text{ m}^2$ $= 8.6 \cdot 10^{-25} \text{ W}$
energy at 1 s irradiation:	$E_{\text{prim}} = 8.6 \cdot 10^{-25} \text{ W}\cdot\text{s}$
energy to remove one electron:	$E_i = 2.24 \text{ eV} = 3.6 \cdot 10^{-19} \text{ W}\cdot\text{s}$

During irradiation only the $1/2,000,000$ part of energy is supplied which is necessary to remove one electron.

X-ray photoelectron spectrometer

– Kai Manne Börje Siegbahn (1954/1955) – the first spectrum was recorded from common salt –



Born in Lund (Sweden), April 20, 1918
Son of K.M.G. Siegbahn

Studies at the Univ. of Uppsala
1944: PhD (Univ. of Stockholm)
1951: Professor in Stockholm at the
Royal Institute of Technology
since 1954: University of Uppsala

Nobel Prize of Physics 1981

$$h \cdot v = E_{\text{bind}} + E_{\text{kin}}$$

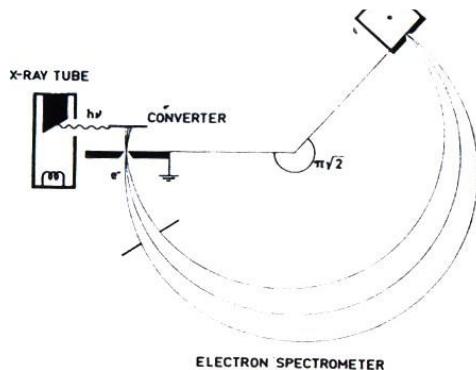


Fig. I:2. Schematic view of an ESCA arrangement for the study of electrons expelled by X-rays.

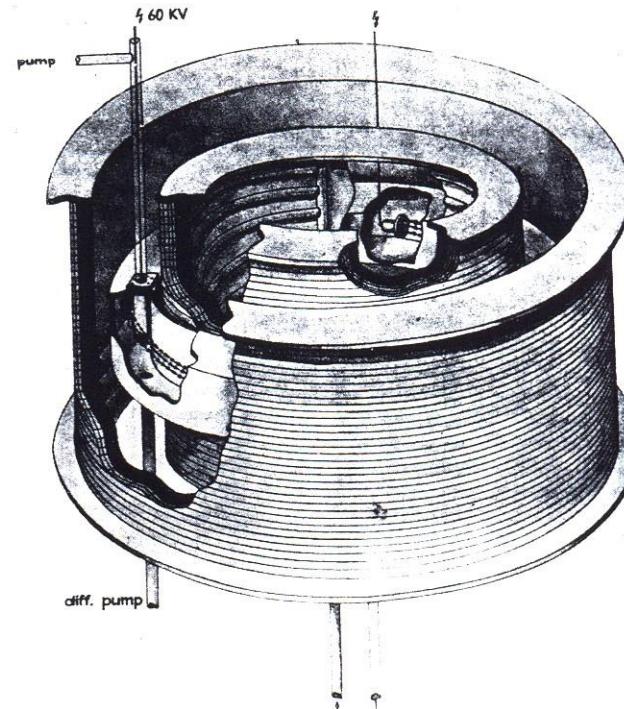


Fig. I:3. First iron-free double focussing spectrometer adapted for ESCA. The magnetic field is obtained from two co-axial coils with radii 24 cm and 36 cm, and height 48 cm.²

Siegbahn, K.: Beta-ray-spectrometer theory and design. High resolution spectroscopy. In: Beta- and gamma-ray spectroscopy. (ed. by K. Siegbahn). Nort-Holland Publ. Co., Amsterdam (1955), S. 52

Modern X-ray photoelectron spectrometer – Axis Ultra (Kratos Analytical, Manchester, United Kingdom) –

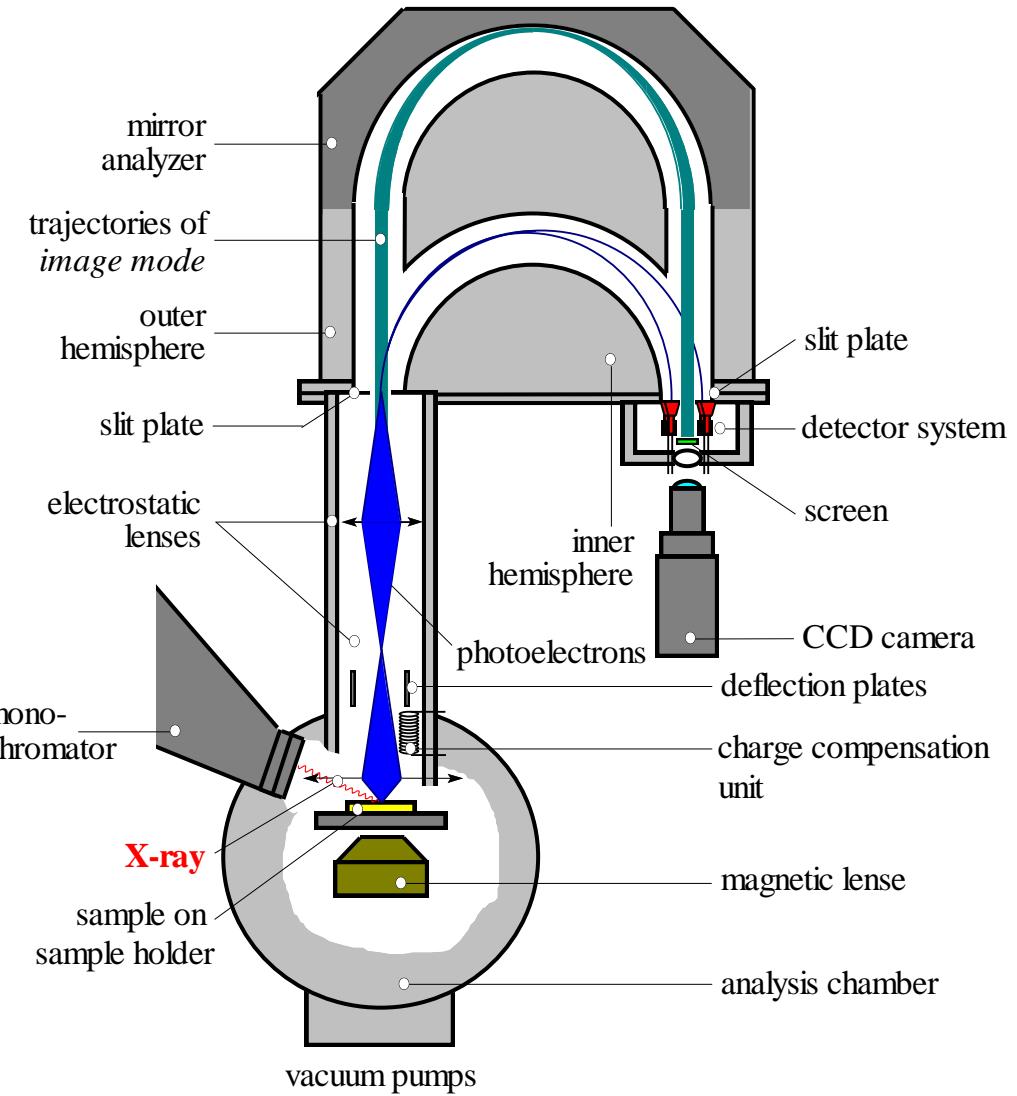
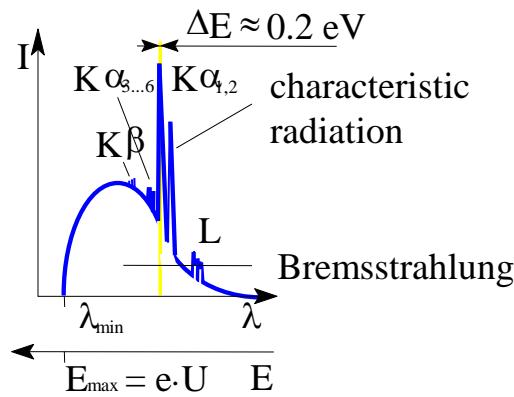
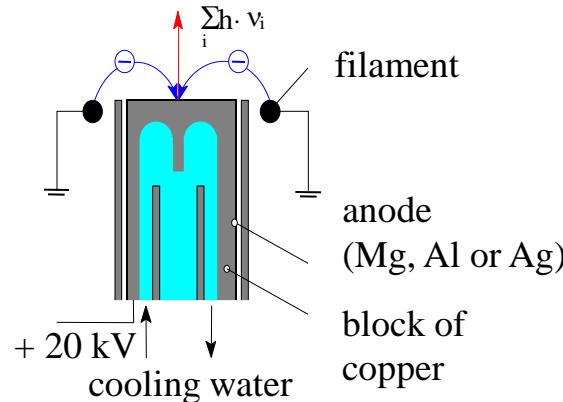


Excellent vacuum: ca. 10^{-12} mbar, at 20°C, one collision each 30 years (at 1000 mbar: ca. 10^9 collisions/s)

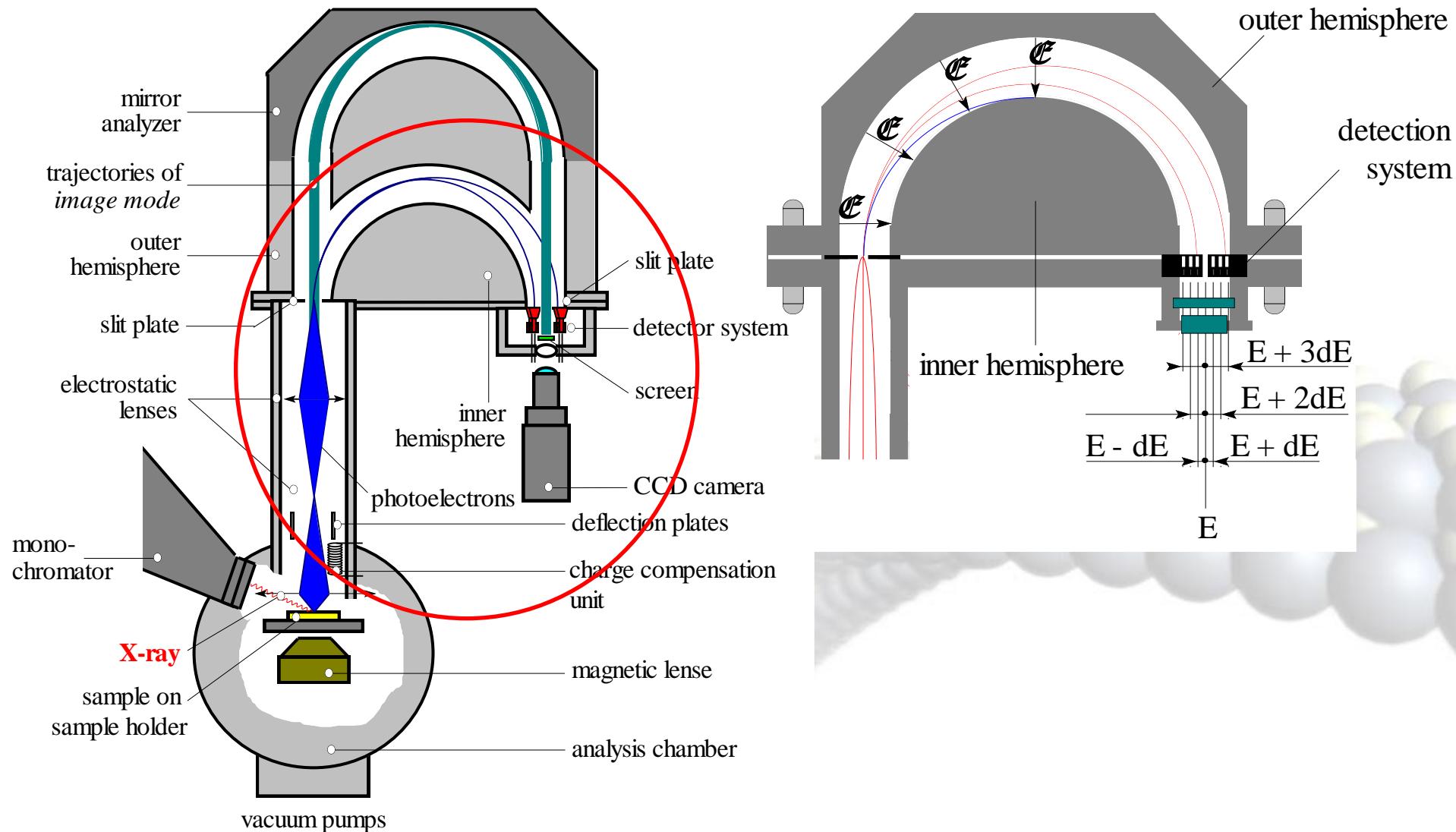
Modern X-ray photoelectron spectrometer

– X-ray source –

$$h \cdot v = E_{\text{bind}} + E_{\text{kin}}$$



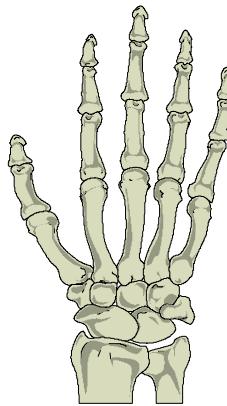
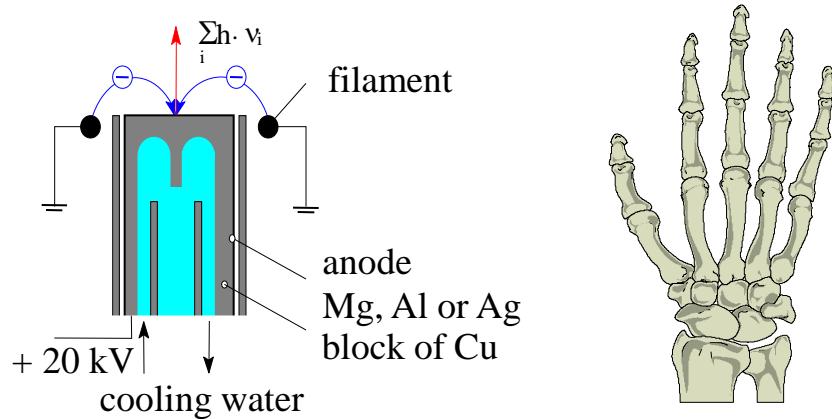
Measuring the kinetic energy of the photoelectrons (E_{kin}) – e.g. 180° hemispheric analyzer –



XPS – A surface sensitive technique

– How depth we do analyze? –

High surface sensitivity vs. X-rays



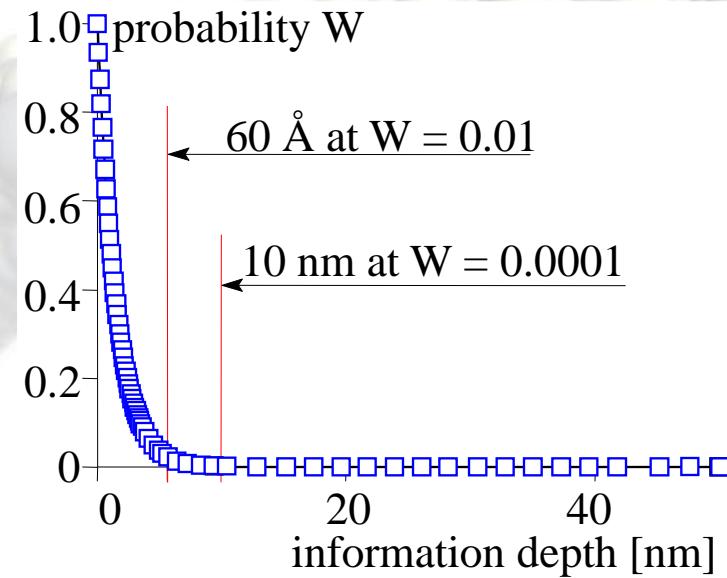
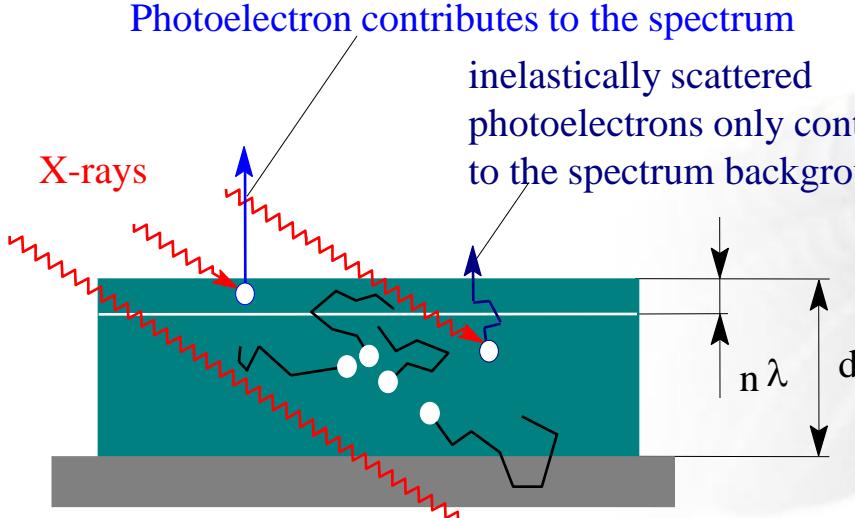
$$dI = A \cdot N \cdot \exp\left[-\frac{x}{\lambda}\right] dx$$

Middle free path of photoelectrons
In the sample material

$$\lambda(C\ 1s, Al\alpha) = 1.2\ nm$$

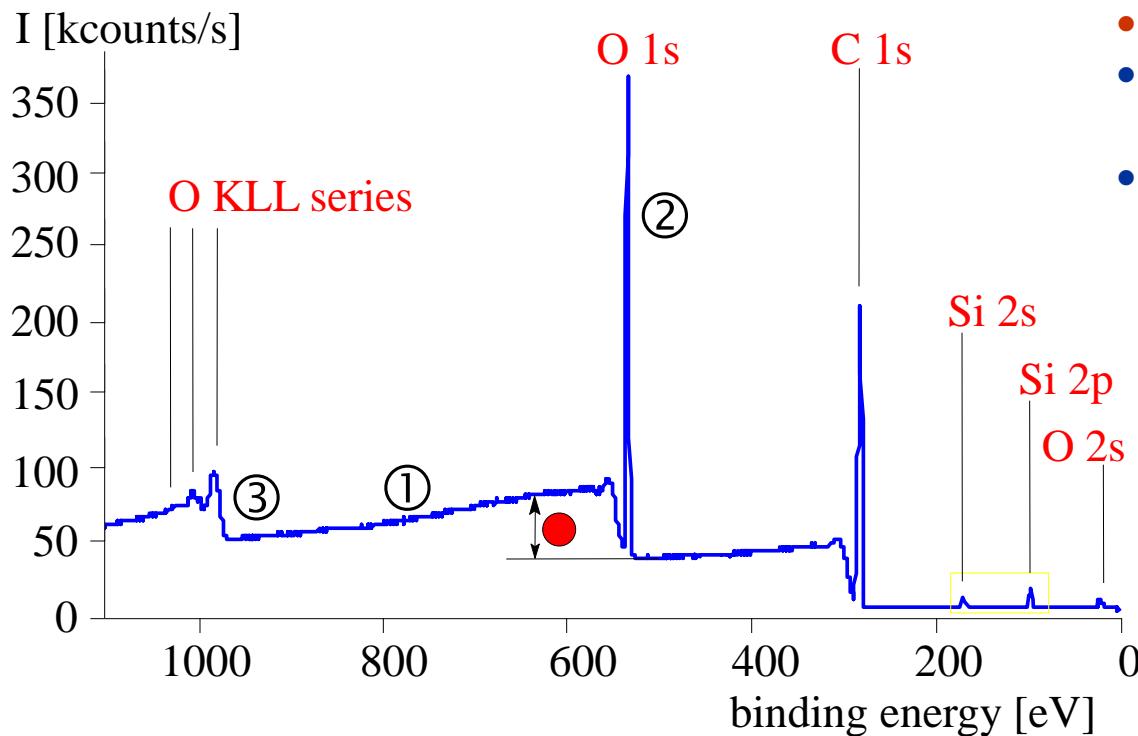
$$I_d = I_\infty \cdot \left(1 - \exp\left[-\frac{d}{\lambda}\right]\right)$$

Photoelectron contributes to the spectrum
inelastically scattered
photoelectrons only contribute
to the spectrum background



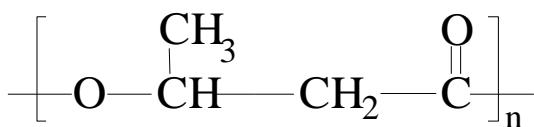
Interpretation of XPS spectra

– Wide-scan spectrum of poly(3-hydroxybutyrate) –



- qualitative surface analysis
- all elements were detected (without hydrogen and helium)
- elements with higher numbers in the periodic table show a couple of peaks.

① background
 ② element peaks
 ③ relaxation phenomena
 (Auger peaks)



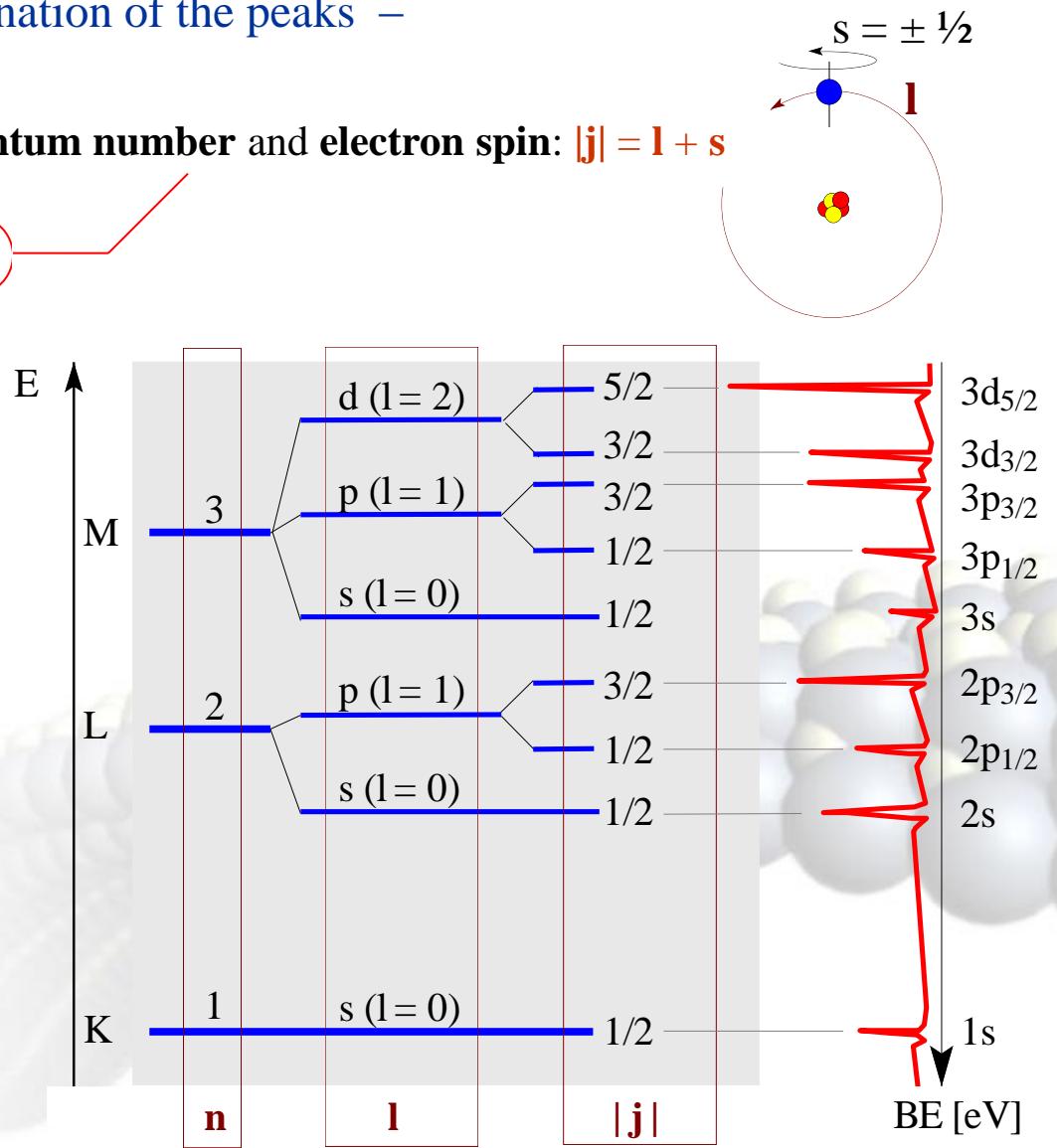
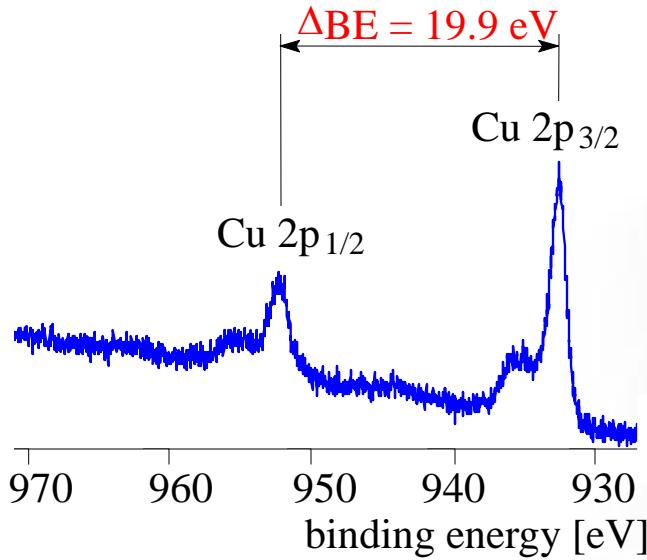
Interpretation of XPS spectra

– Designation of the peaks –

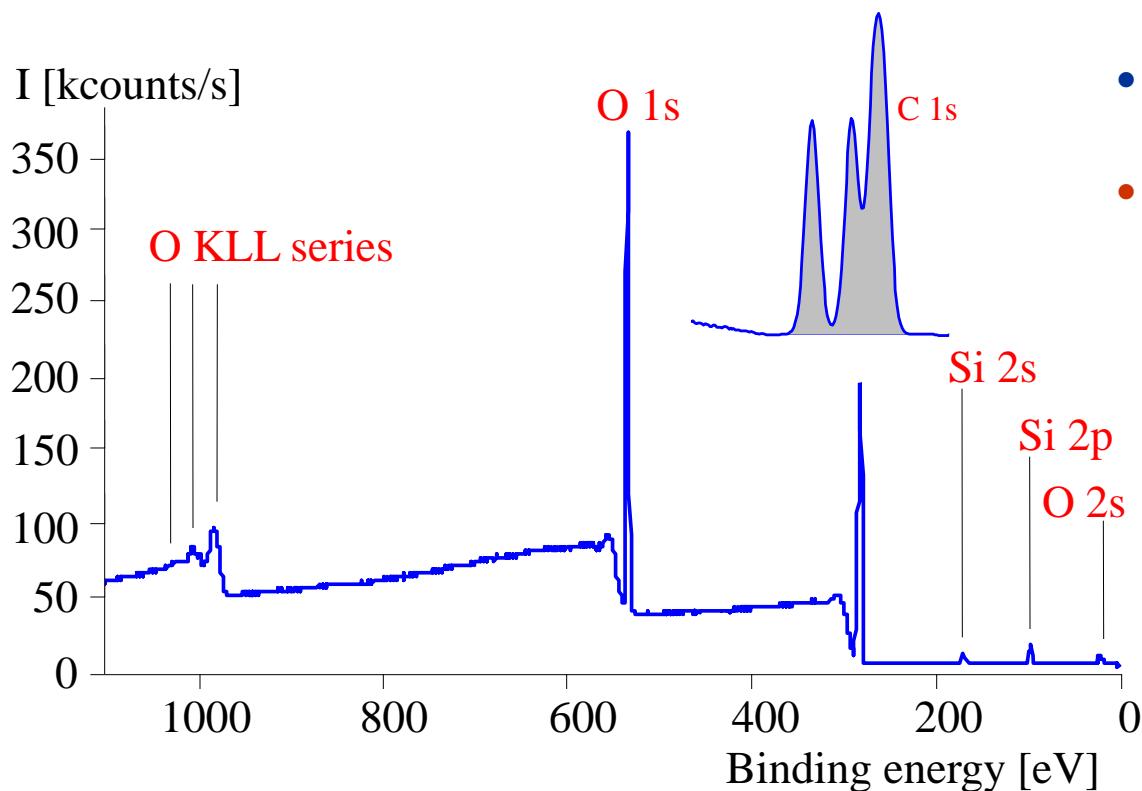
Cu 2p_{3/2}

Coupling of orbit quantum number and electron spin: $|j| = l + s$

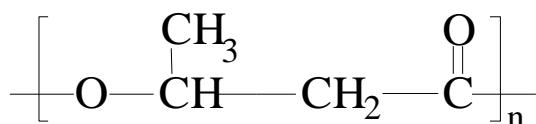
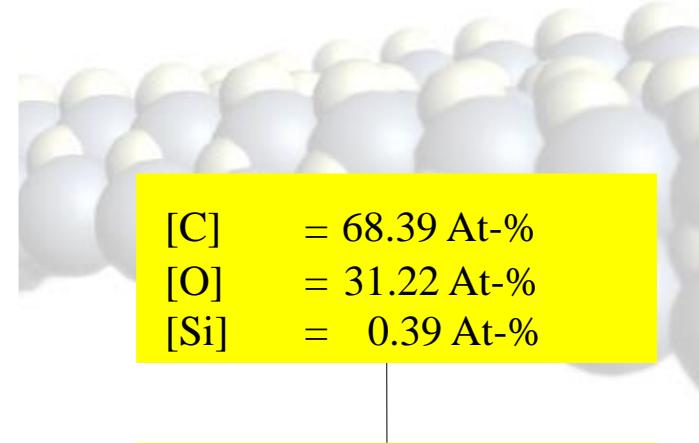
total orbit quantum number **L**
orbit quantum number **l**
main quantum number **s**
chemical symbol



Interpretation of XPS spectra – Quantification –



- qualitative surface analysis (showing all elements),
- quantitative surface analysis



[O]:[C] = 0.456
 [Si]:[C] = 0.005
[O]:[C] should be = 0.5

Interpretation of XPS spectra

– Quantification –

$$I(X) = \mathcal{F} [n(X), \eta_{\text{photon}}, \sigma(X, i, h \cdot v), \lambda(E_{\text{kin}}), \theta, A, T(E_{\text{kin}})]$$

Usually only **relative** values are the matter of interest:
e.g. SiO_2 means an elemental or atomic ratio of $[\text{Si}]:[\text{O}] = 1:2$



Hence, results are given in **atom percents [At-%]**

$$\frac{I(X_1)}{I(X_2)} = \frac{n(X_1)}{n(X_2)} \cdot \frac{\sigma(X_1)}{\sigma(X_2)} \cdot \frac{\lambda(E_{\text{kin}}[X_1])}{\lambda(E_{\text{kin}}[X_2])} \cdot \frac{T(E_{\text{kin}}[X_1])}{T(E_{\text{kin}}[X_2])} = \frac{c(X_1)}{c(X_2)} \cdot \frac{T(E_{\text{kin}}[X_1])}{T(E_{\text{kin}}[X_2])} \cdot \frac{SF(X_1)}{SF(X_2)}$$

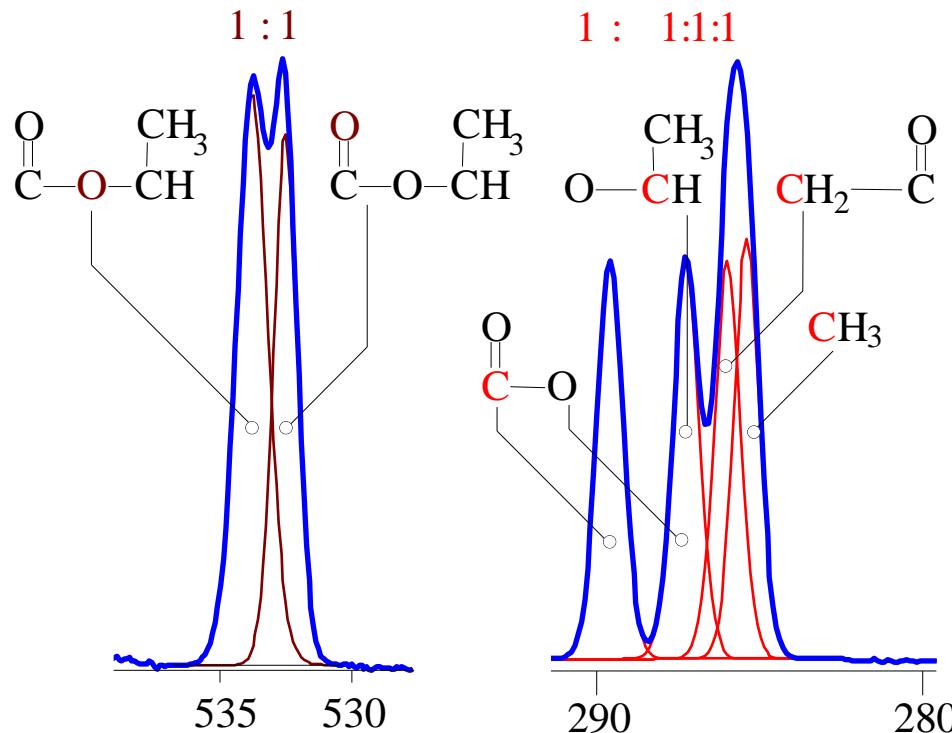
Relative sensitivity factors are
experimentally determined

Peak	SF
C 1s	0.278
F 1s	1.000
O 1s	0.549
O 2s	0.033
Ag 3d _{5/2}	3.592

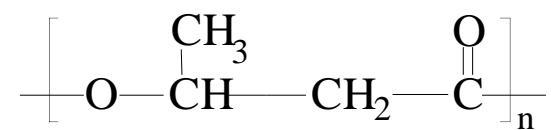
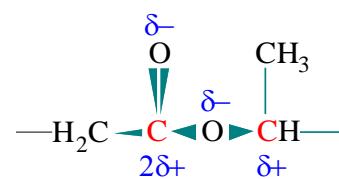
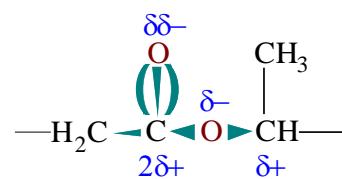
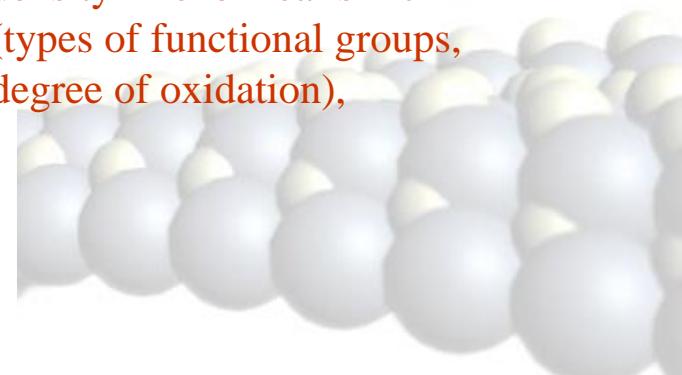
Different elements have a different sensitivity and will be analyzed with **different minimum concentration limits**. However, all elements having a minimum concentration of ca. **0.1 at-%** will be trustworthy analyzed.

Analyzing the chemical structure and binding states

– Chemical shifts in the C 1s and O 1s spectra of poly(3-hydroxybutyrate) –

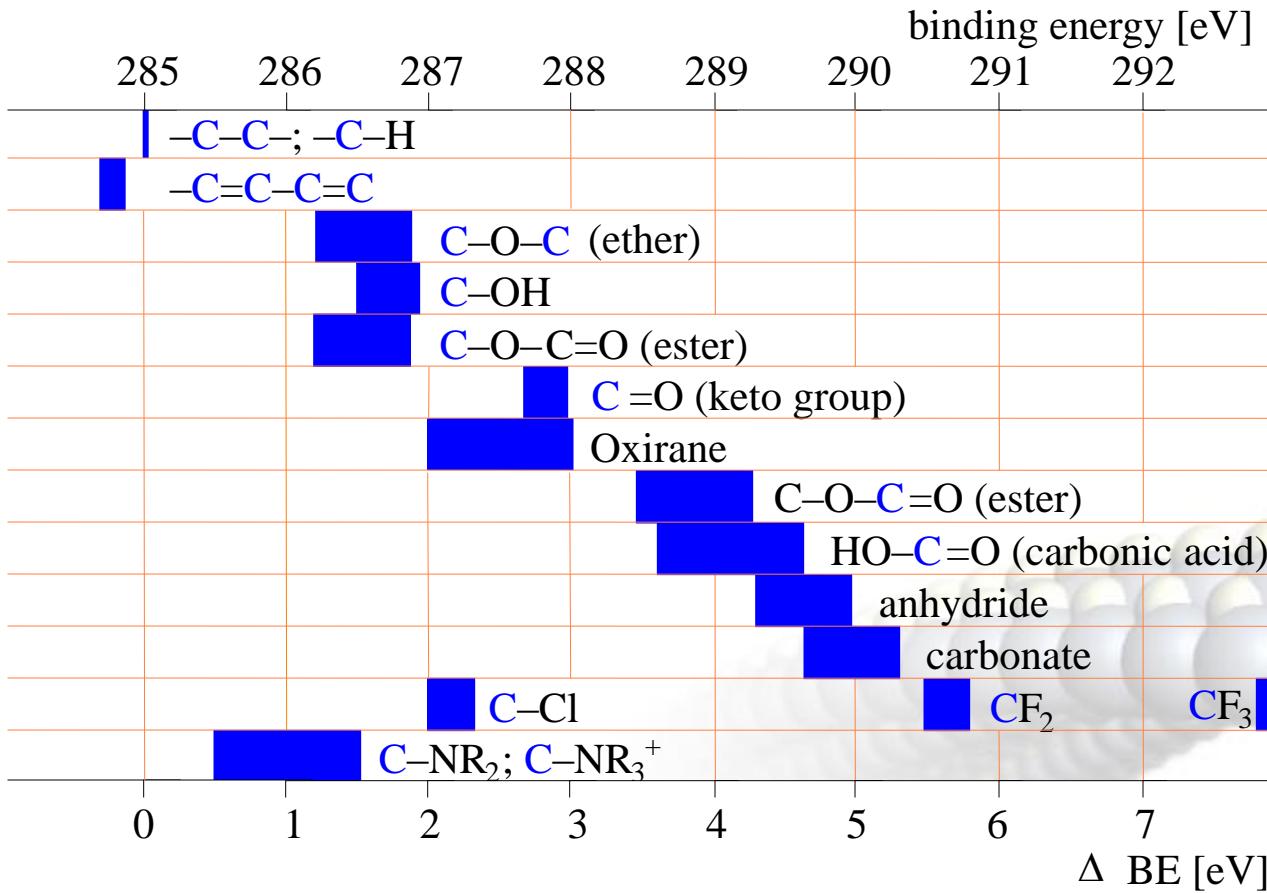


- qualitative surface analysis (showing all elements),
- quantitative surface analysis
- chemistry of the element's neighbourhood controls the electron density \Rightarrow chemical shift (types of functional groups, degree of oxidation),

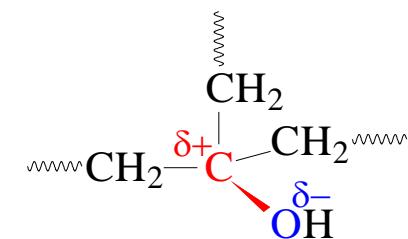


Chemical shifts and binding states

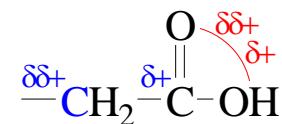
– Qualitative and quantitative detection of functional groups –



primary shift



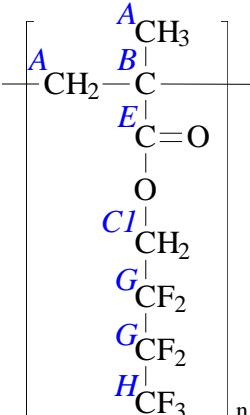
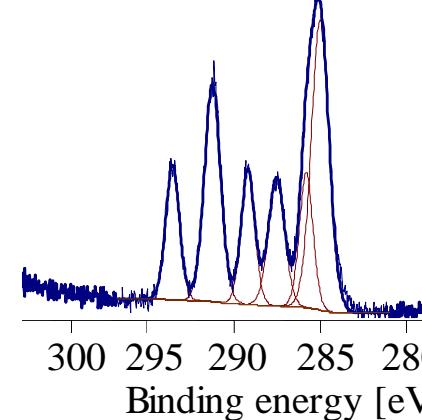
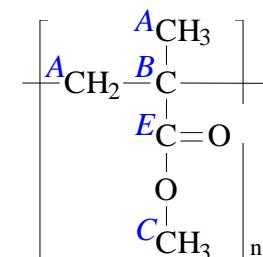
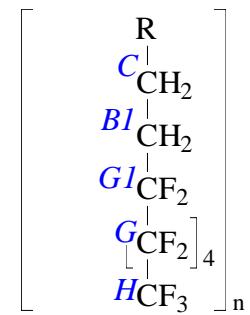
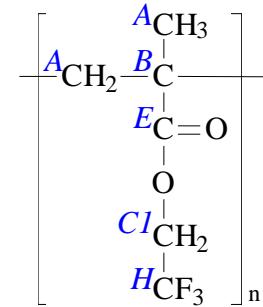
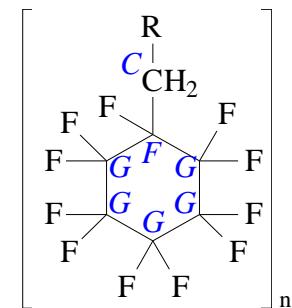
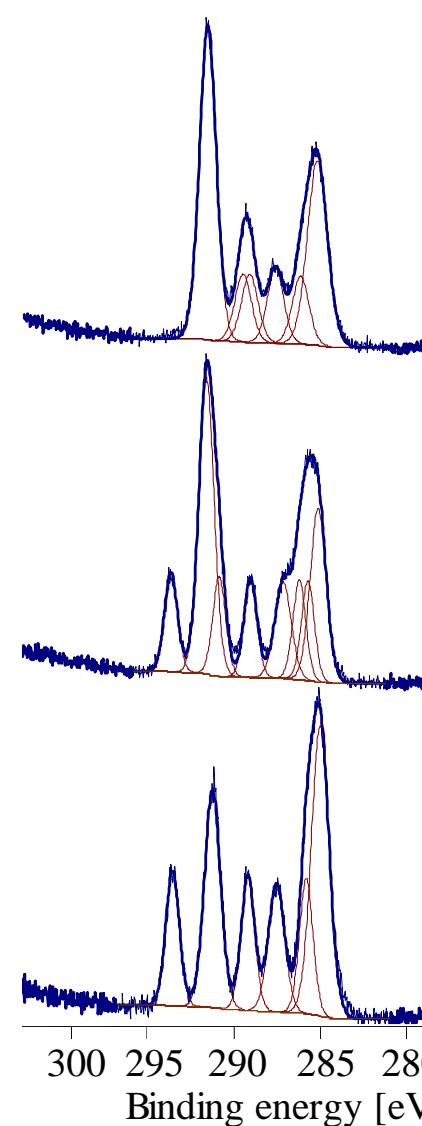
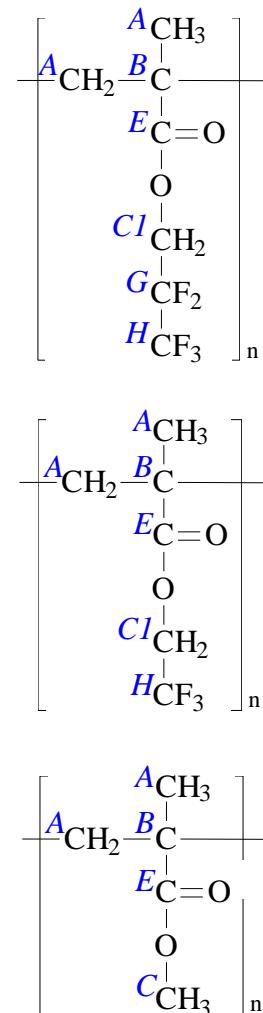
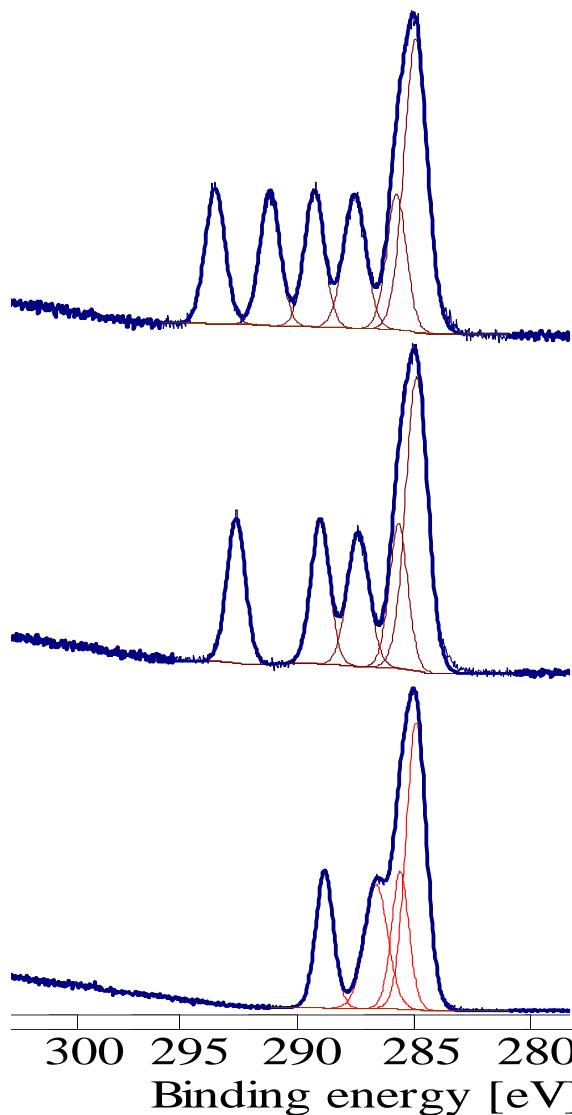
β-shift by strongly electronegative groups



	ΔBE
$\text{HO}-\text{C}-\text{C}-$	0.05...0.2 eV
$\text{O}-\text{C}(\text{O})-\text{C}-$	0.4 ...0.6 eV
$\text{F}-\text{C}-\text{C}-$	0.5...0.7 eV
$\text{Cl}-\text{C}-\text{C}-$	0.4 eV

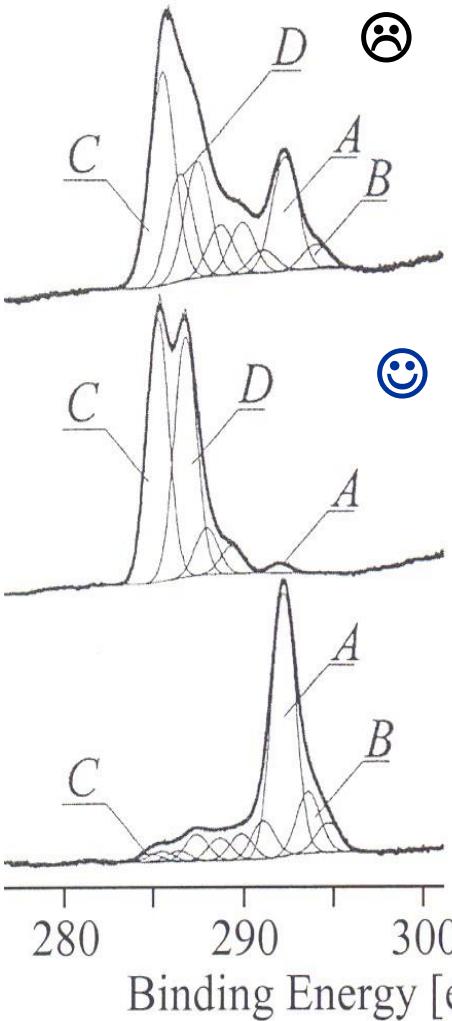
C 1s spectra to analyze chemical structures

– Polymethacrylates with different alcohol rests –



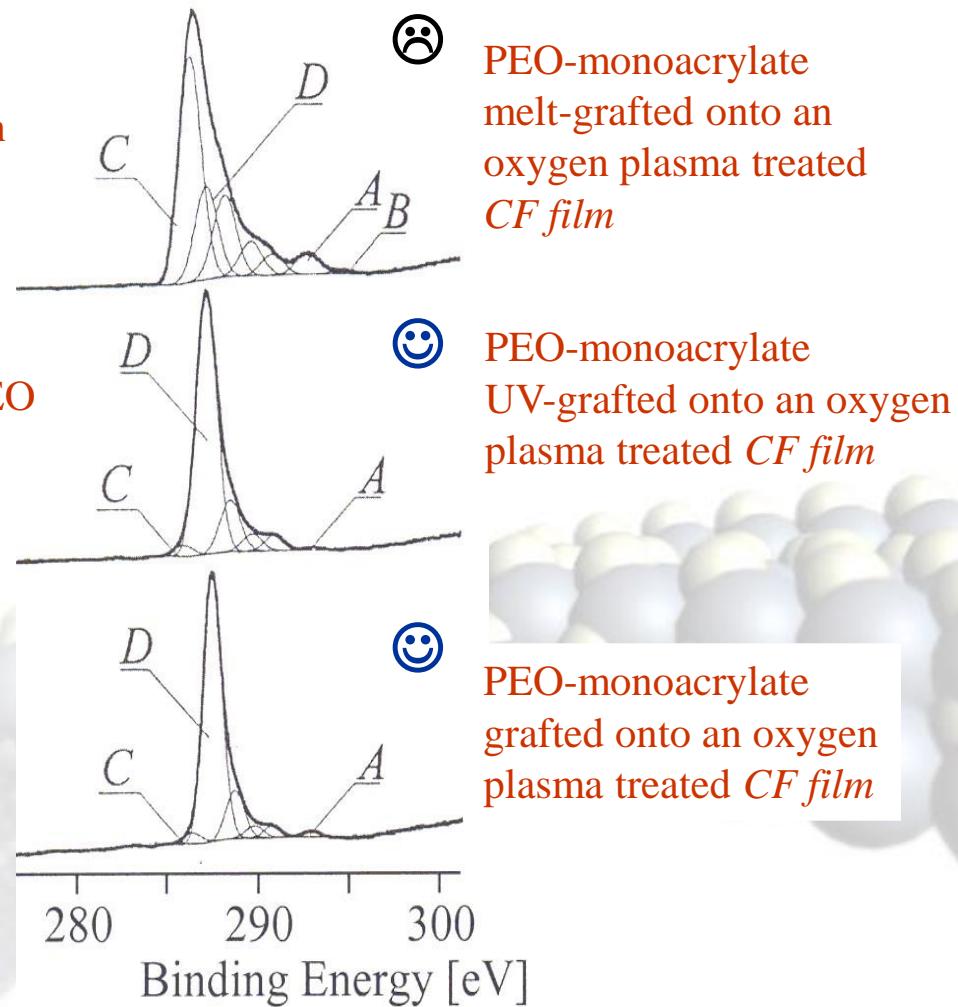
C 1s spectra to analyze surface reactions

– Hydrophobic fluorocarbon films should get hydrophilic properties –



PEO-dimethacrylate
UV-grafted onto an oxygen
plasma treated *CF film*

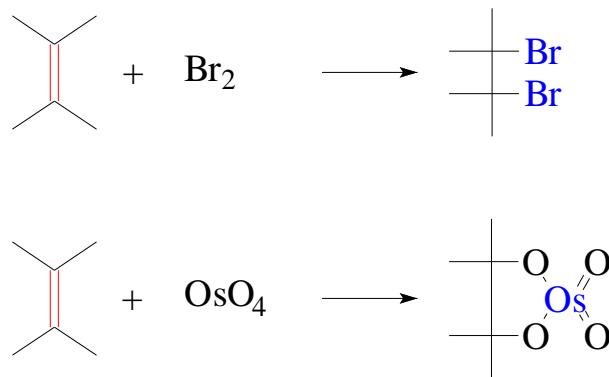
CF film with PEO-PPO-PEO
cross-linked in an argon
plasma



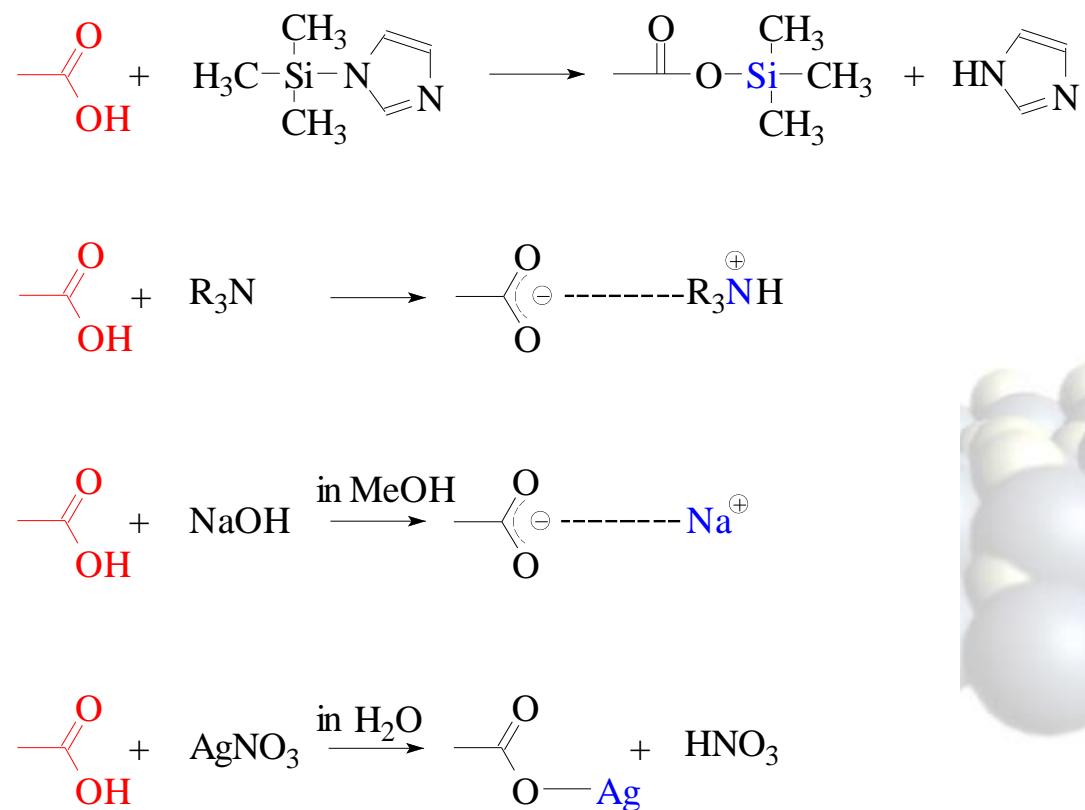
Derivatization to analyze of functional surface groups

– Double bonds and carbonic acids –

Double bonds



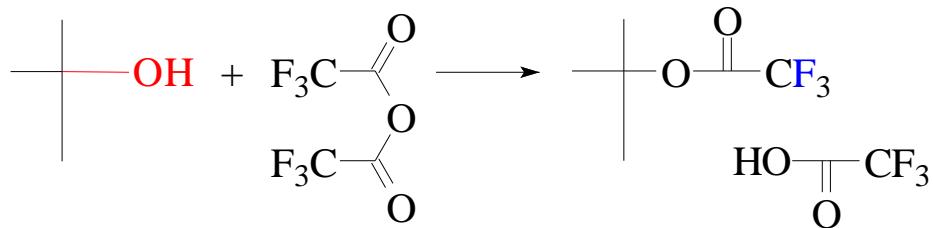
Carbonic acids



Derivatization to analyze of functional surface groups

– Alcohol, oxiran and amino groups –

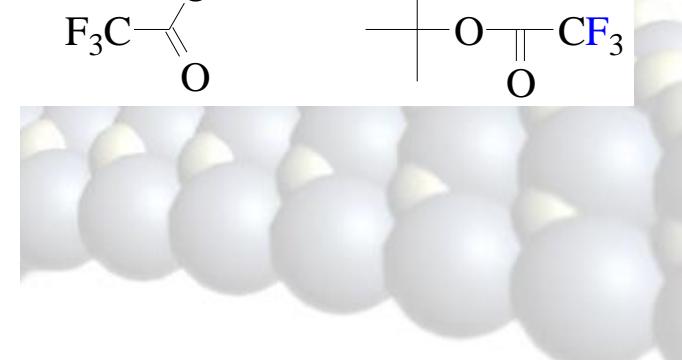
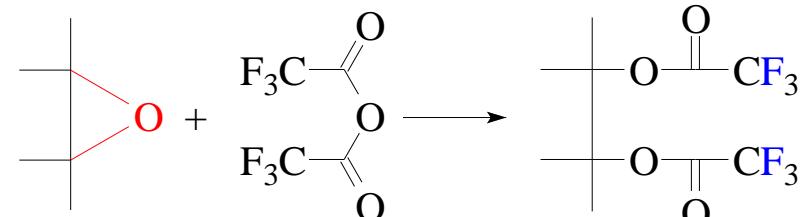
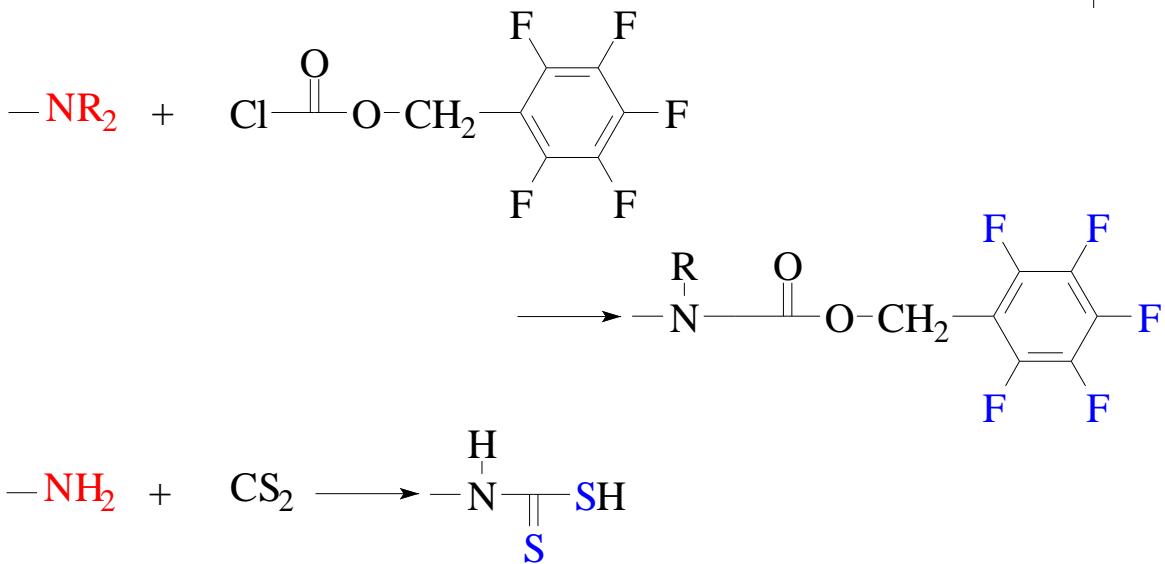
Alcohol groups



Oxiran groups



Amino groups

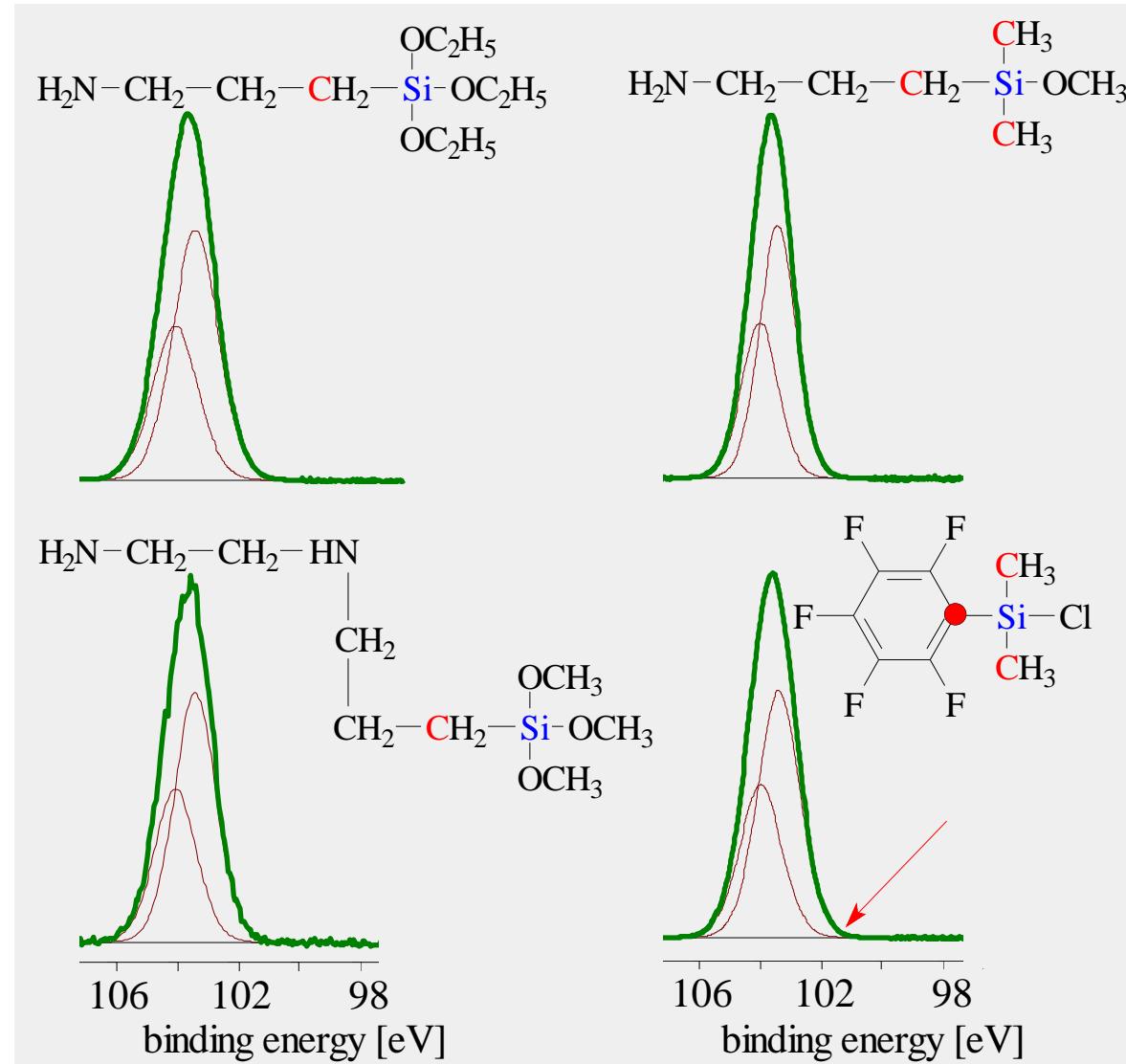
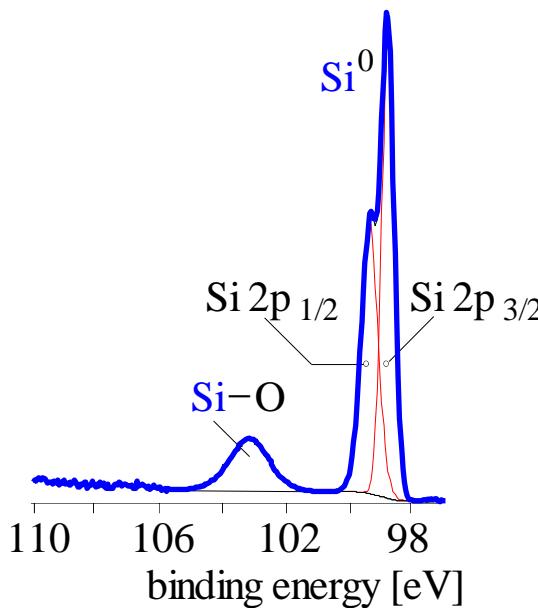


Chemical shift in the Si 2p spectrum

– Detection of silanol groups and the condensation of silanes on glass surfaces –

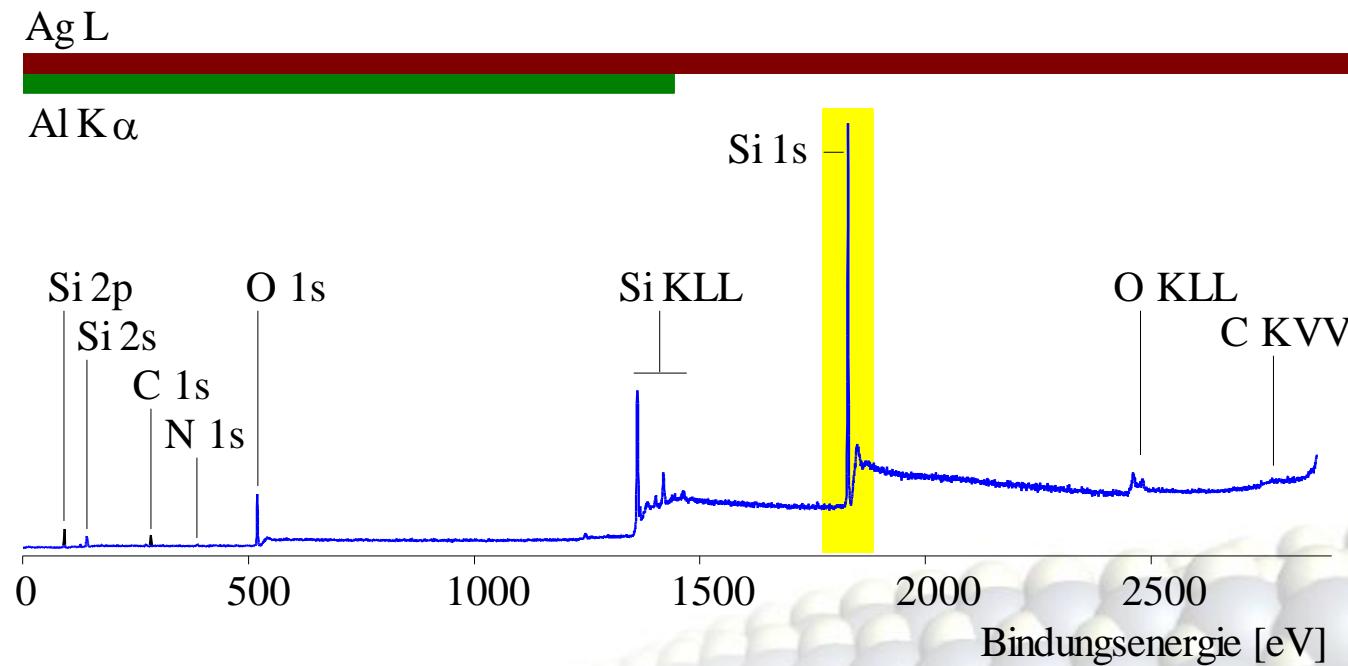
No significant chemical shift at BE ca. 102 eV.

Separation of component peaks of O-Si(-O)₃, Si-OH und Si-C seemed to be impossible.



Chemical shift in the Si 2p spectrum

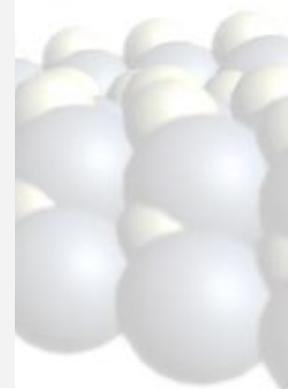
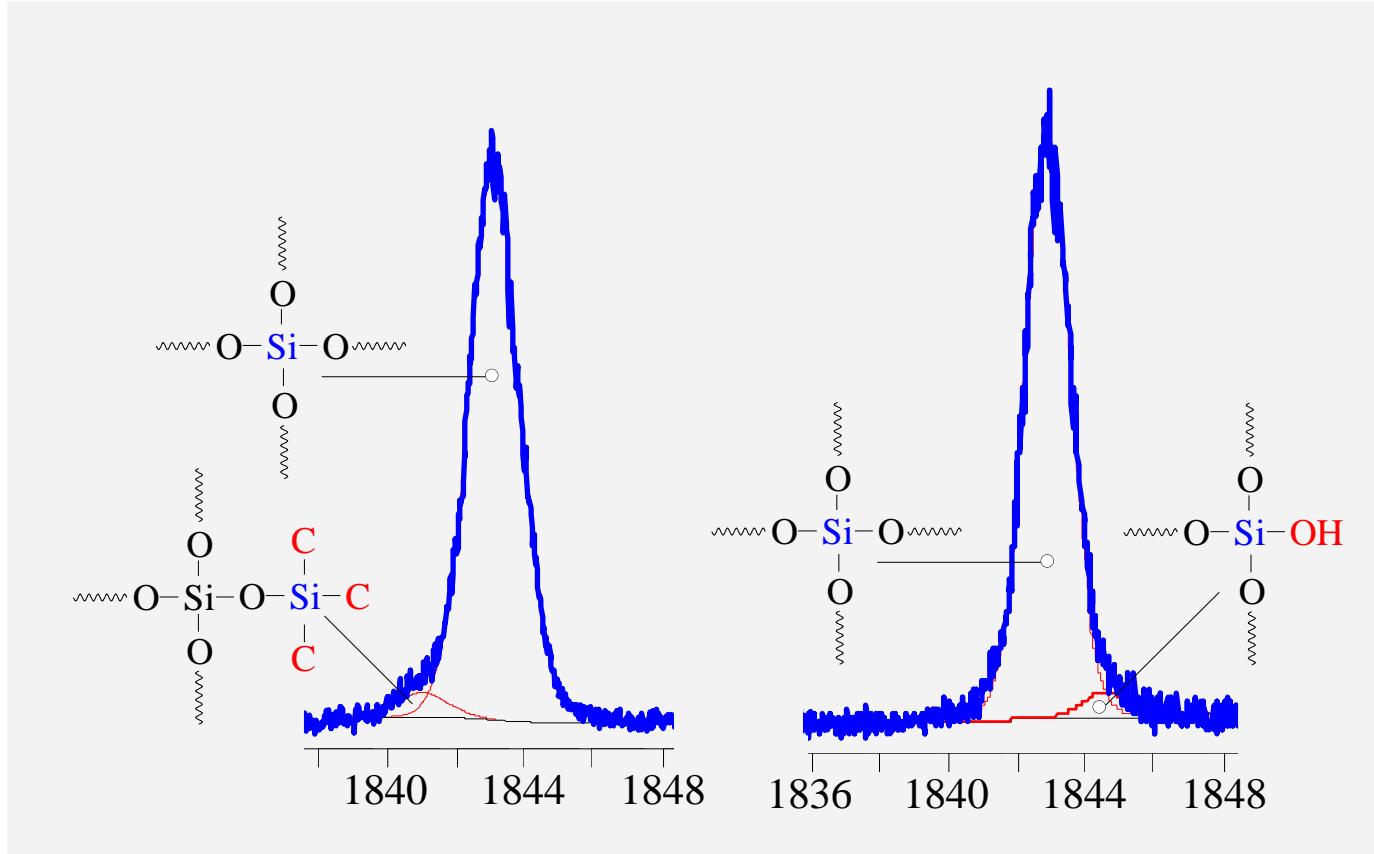
– Detection of silanol groups and the condensation of silanes on glass surfaces –



Pleul, D.; Frenzel, R.; Eschner, M.; Simon, F.:
X-ray photoelectron spectroscopy for the detection of different Si–O bonding states of silicon.
Analytical and Bioanalytical Chemistry, 375 (2003) 1276-1281.

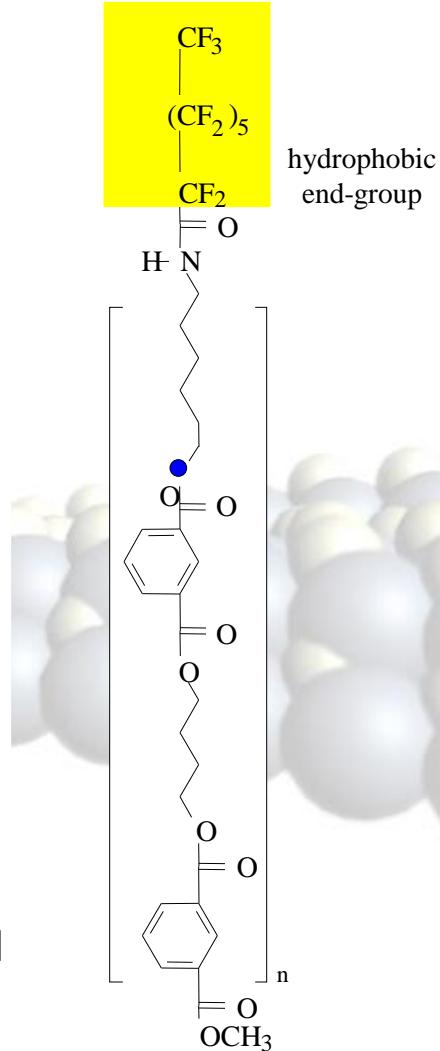
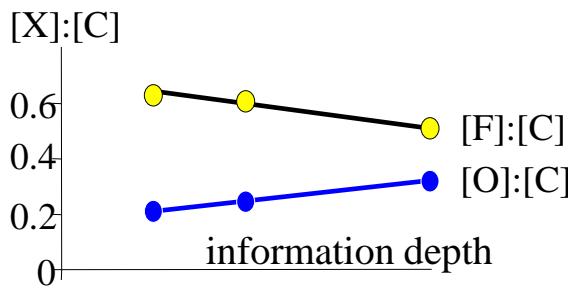
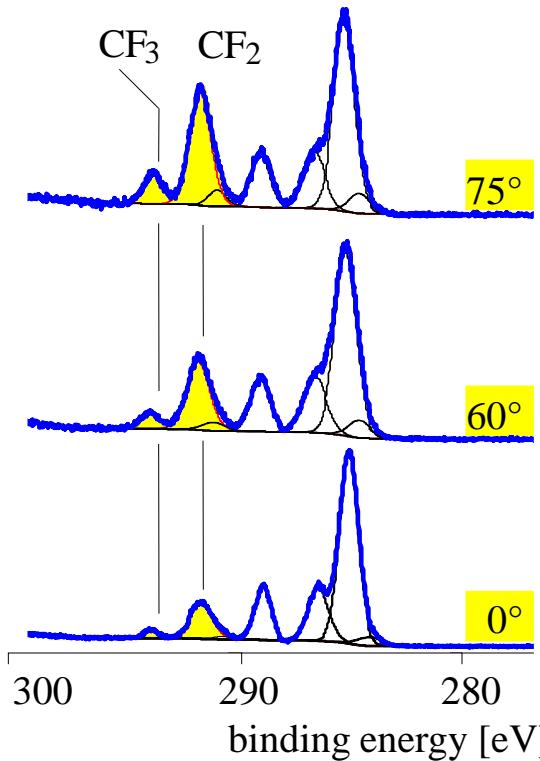
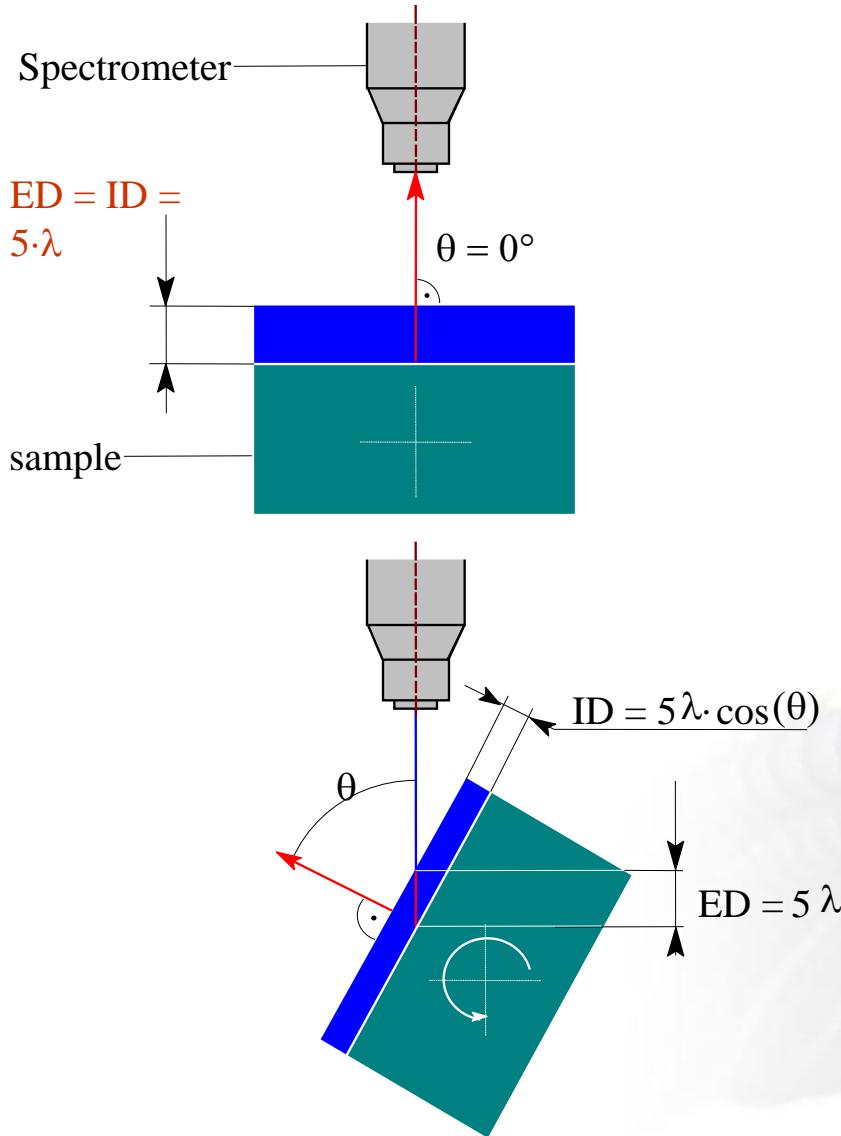
Chemical shift in the Si 2p spectrum

– Detection of silanol groups and the condensation of silanes on glass surfaces –



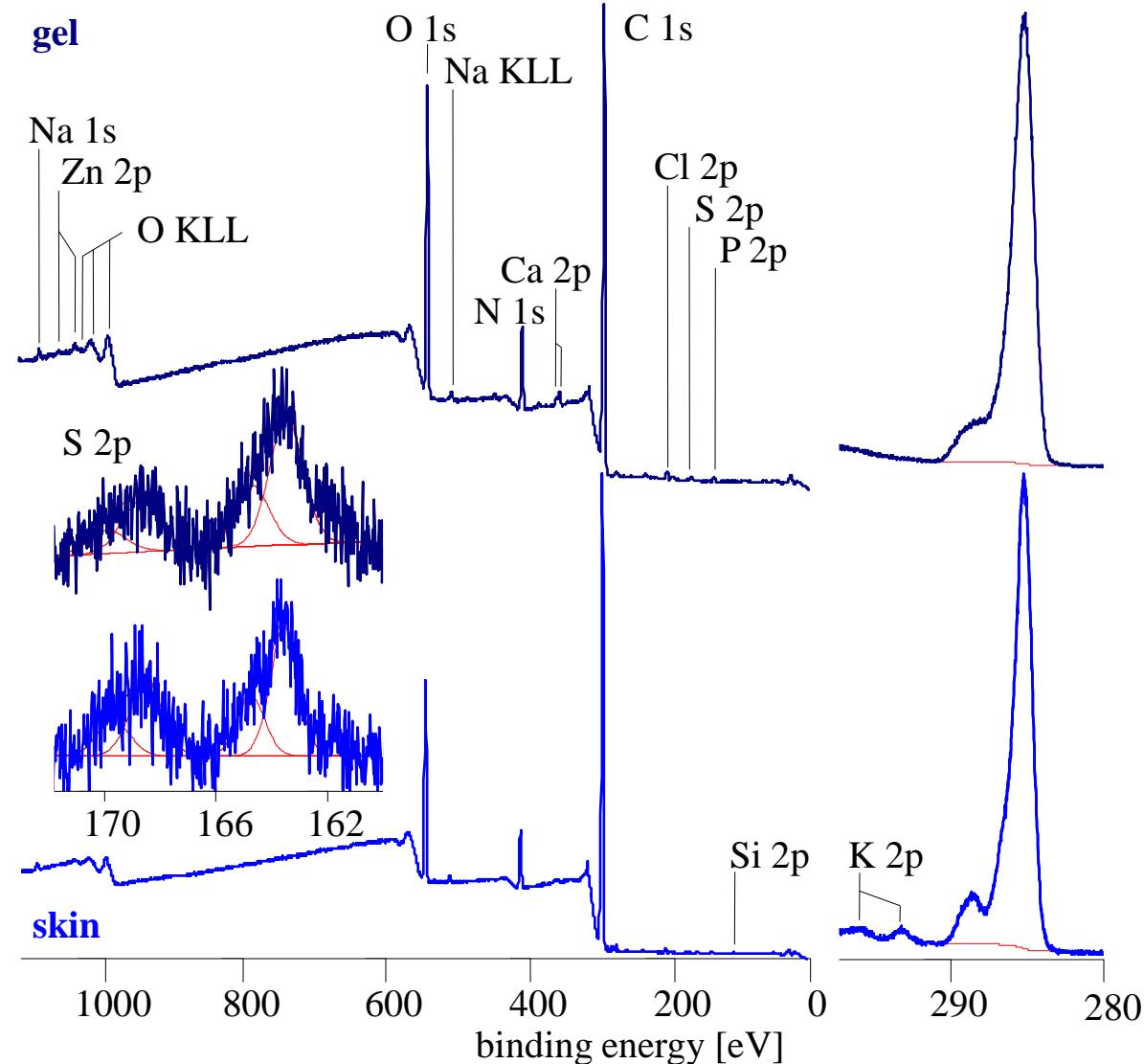
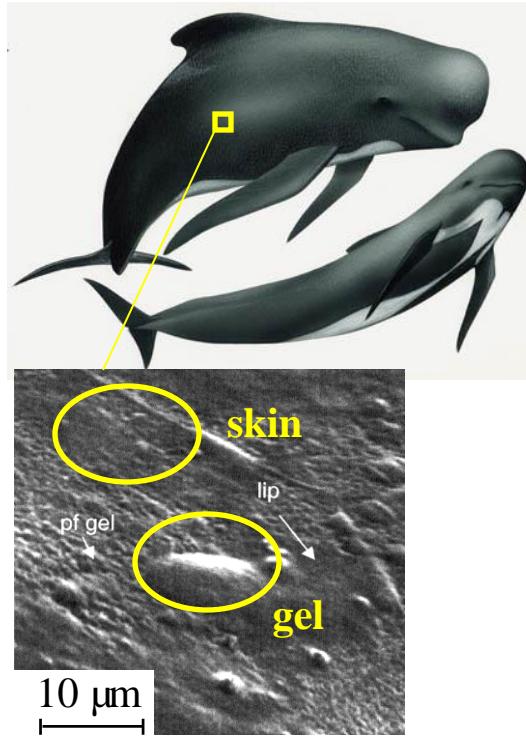
Angle-resolved X-ray photoelectron spectroscopy (ARXPS)

– Depth profiles in the range of a few nanometers –



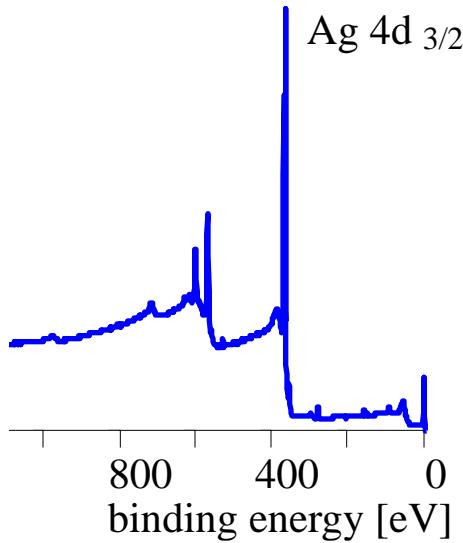
XPS employed to study biological surfaces

– XPS spectra recorded at low temperature (Cryo-XPS) –

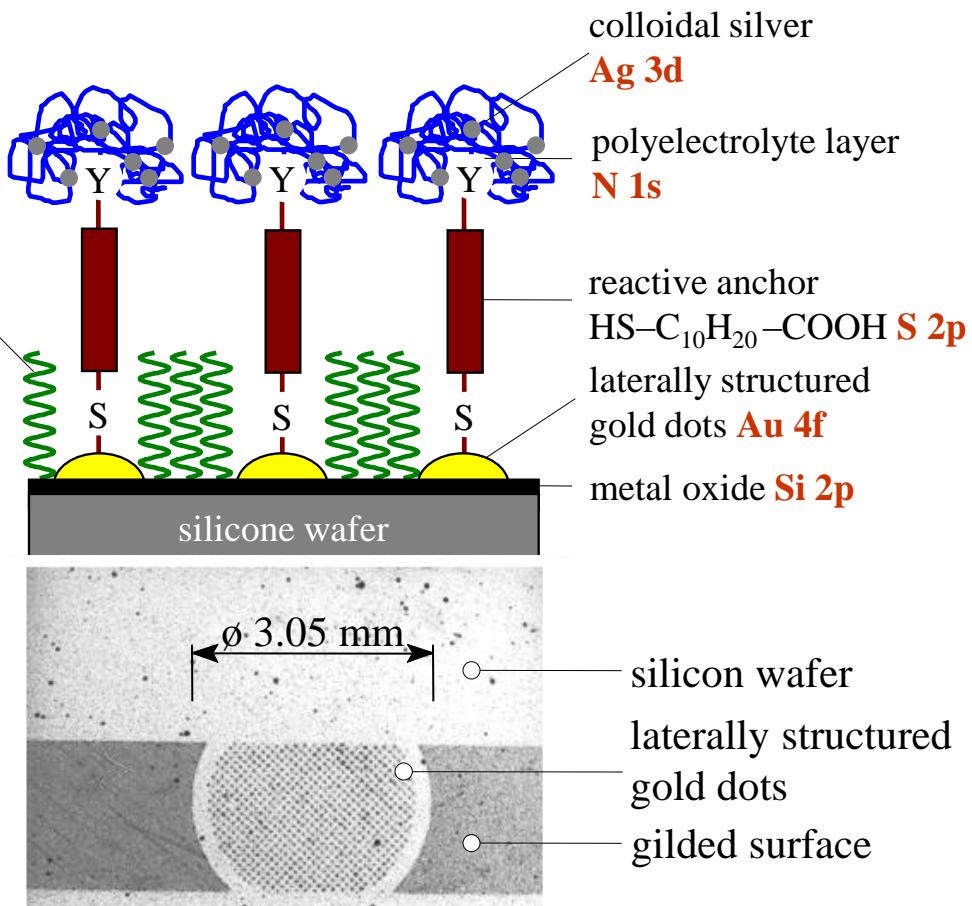
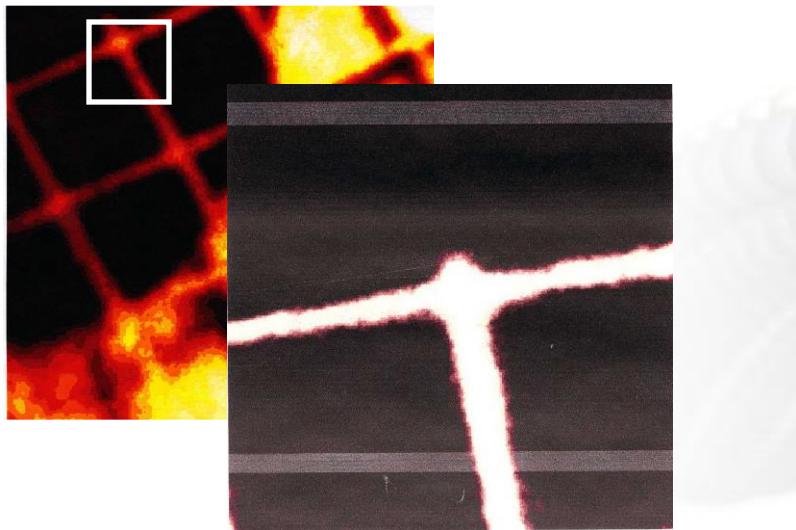


Baum, C.; Simon, F.; Meyer, W.;
Fleischer, L.G.; Siebers, D.:
Surface properties of the skin of
Delphinids. Biofouling 19 (2003)
181-186

Imaging XPS

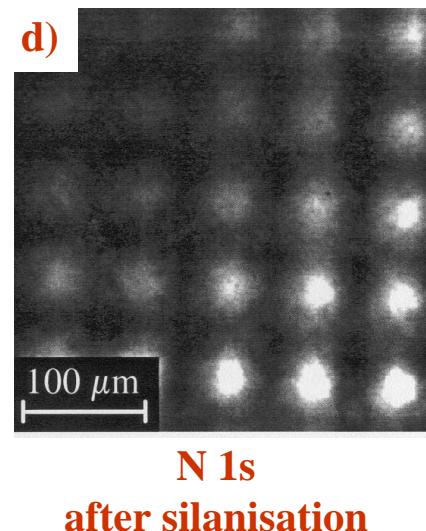
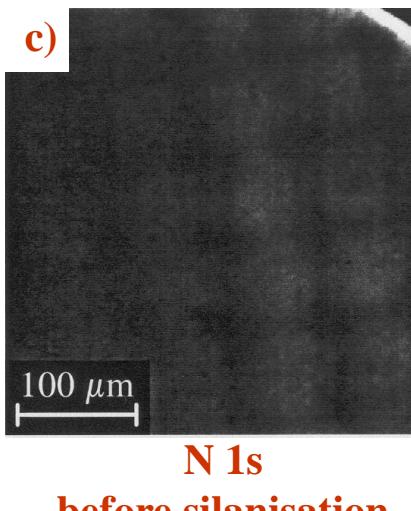
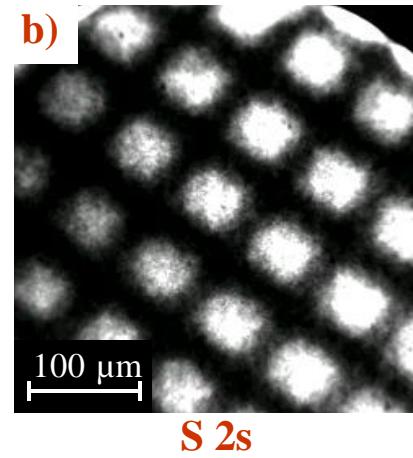
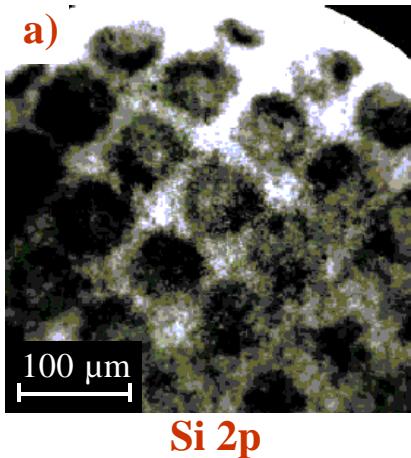


semi-fluorinated silane **F 1s**

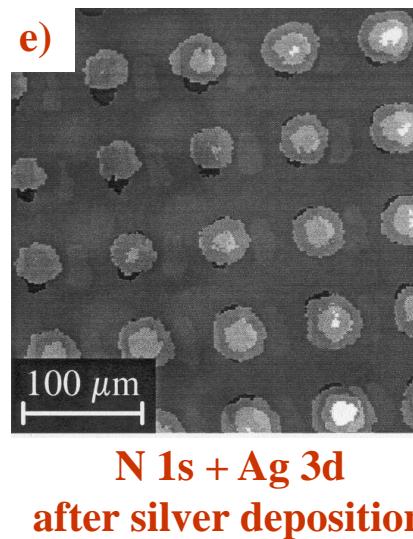


Imaging XPS

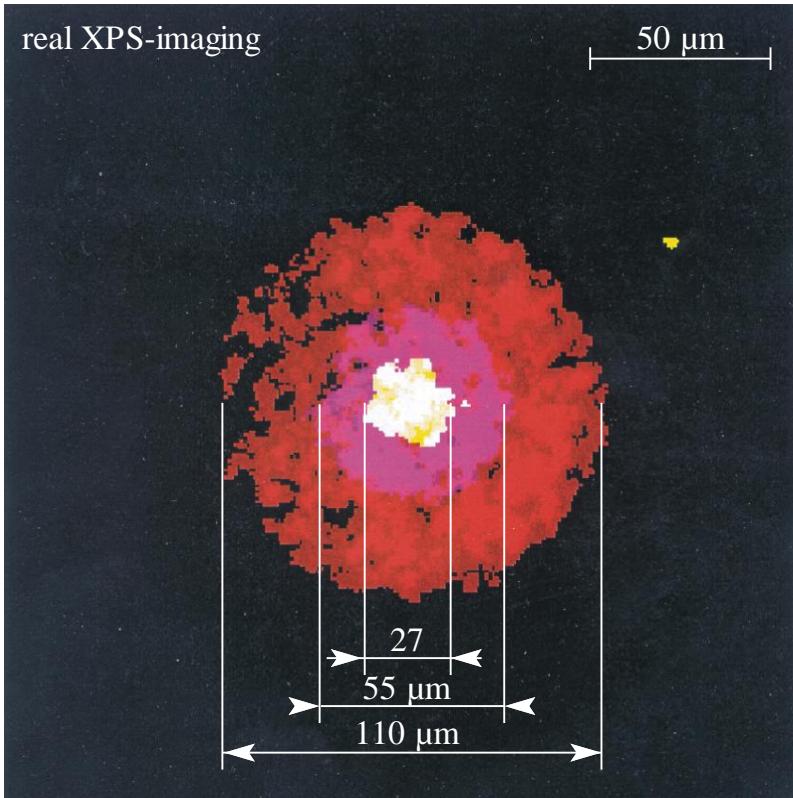
– Laterally structured samples –



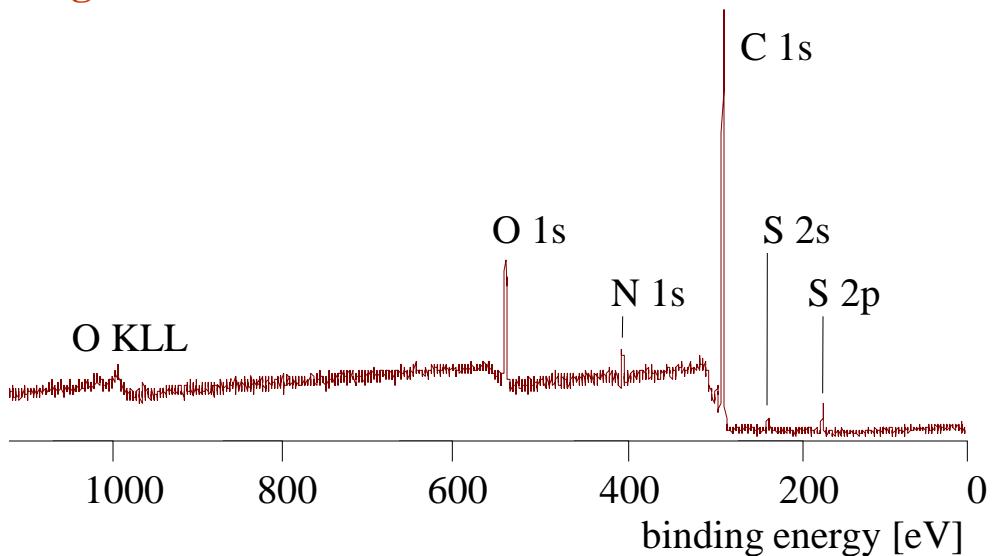
Eschner, M.; Simon, F.; Pleul, D.; Spange, S.: In: "Dresdener Beiträge zur Sensorik", Band 16, w.e.b. Universitätsverlag, Dresden (2002) 149-153, ISBN 3-935712-71-5



Small spot XPS



hollow fibre of an artificial kidney cut along its length axis



Summary

XPS

XPS is a method oriented to detect elements in the surface region of samples

- qualitative surface analysis: identification of all elements (H and He are excluded),
- quantitative surface analysis \Rightarrow relative amounts of the elements, e.g. [X]:[Y],
- peak deconvolution allows to analyze (qualitatively and quantitatively) functional surface groups or the oxidation states, labelling can be helpful to identify the species,
- depth profile analysis on molecular scale without destroying the sample, sputtering is also able,
- special features: cryo-XPS, thermo- XPS, imaging XPS, small spot XPS

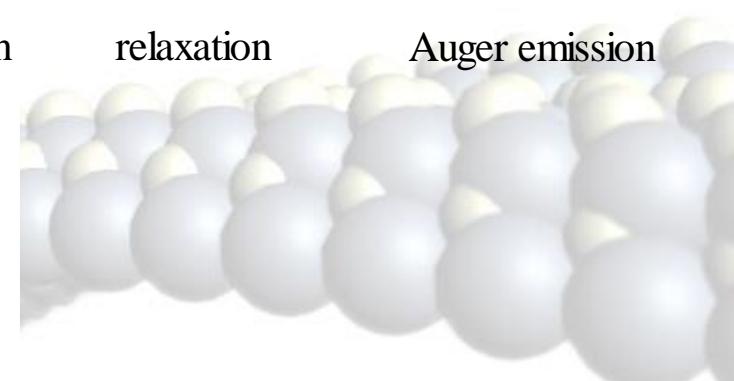
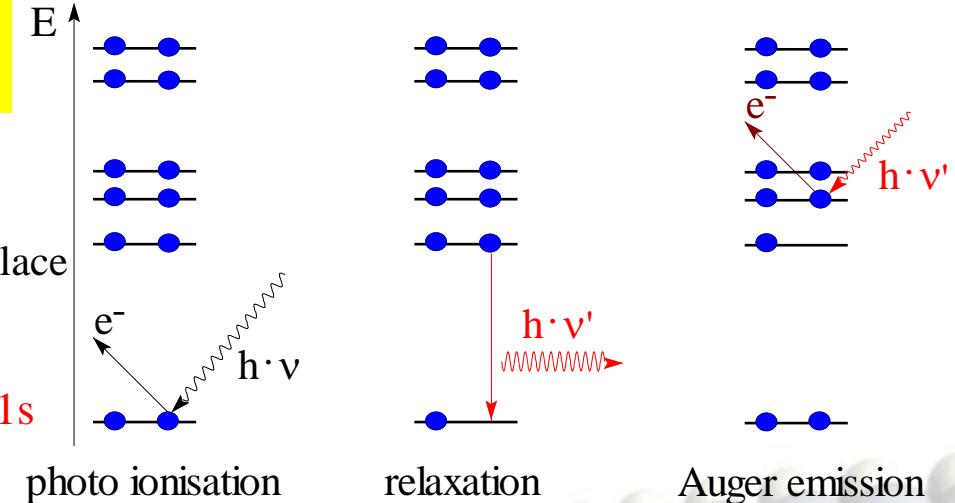
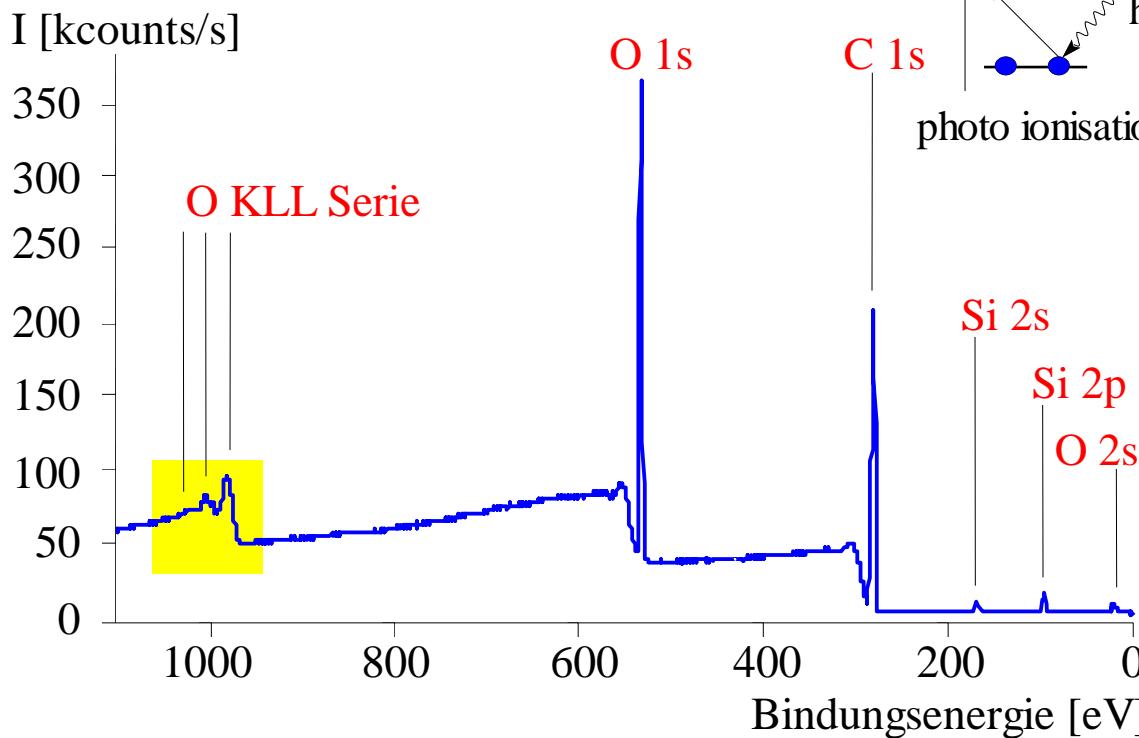
Auger electron spectroscopy (AES)

– Relaxation: Competition between Auger process and X-ray fluorescence –

$$E_{\text{Auger}} = h \cdot v' - E_{\text{kin}}$$

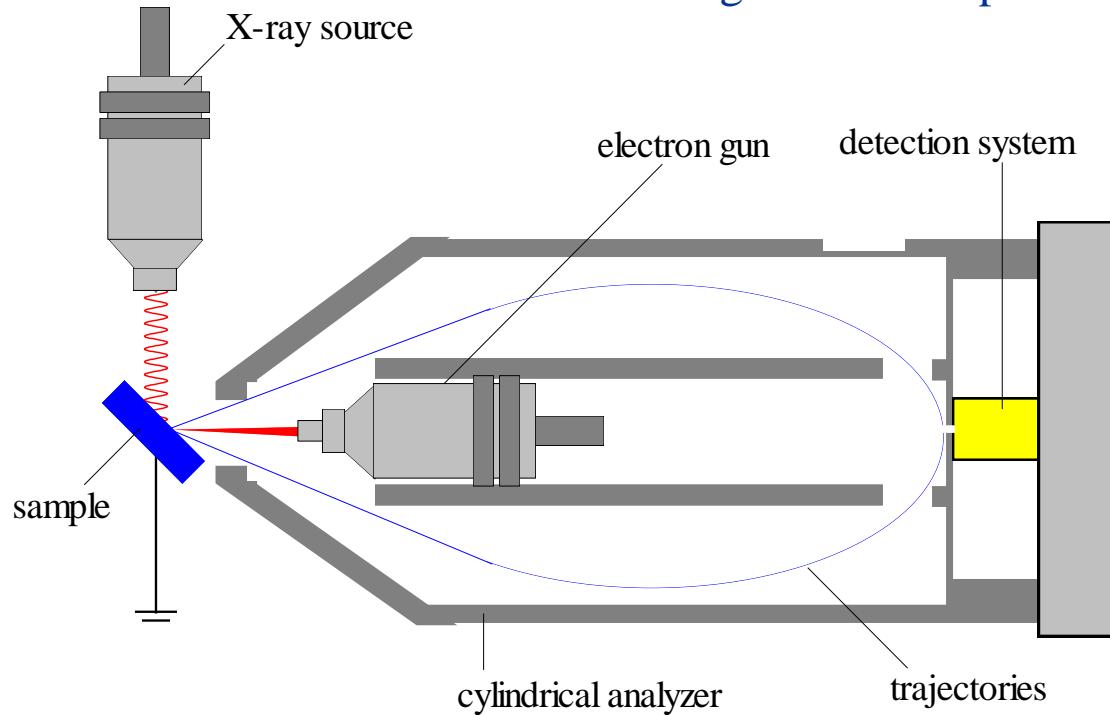
Small atomic number: Auger process is preferred

High atomic number: X-ray fluorescence takes place

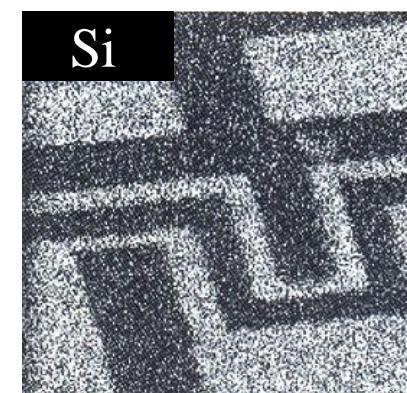
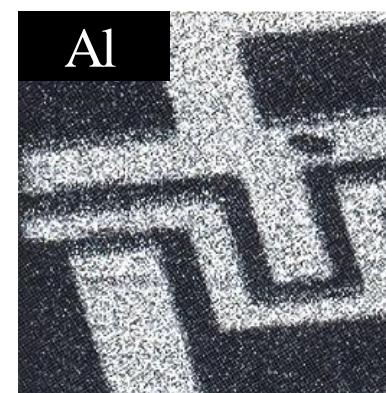
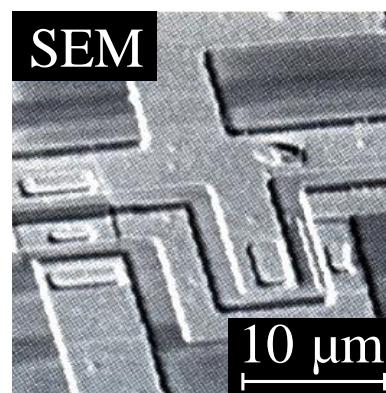


Auger electron spectroscopy (AES)

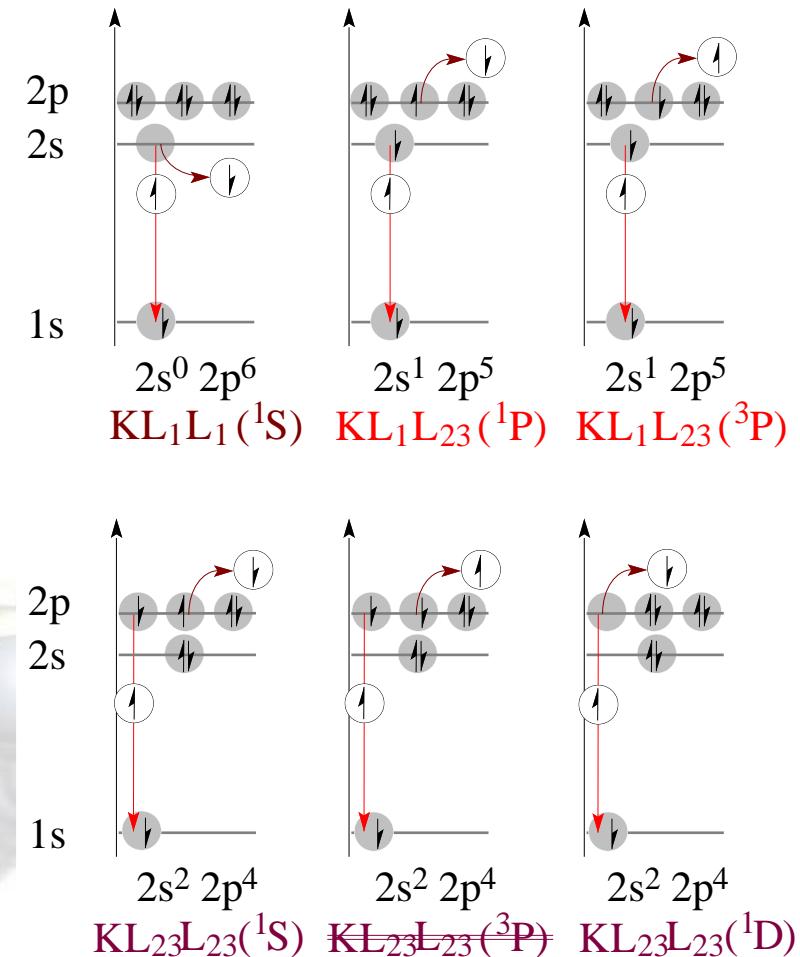
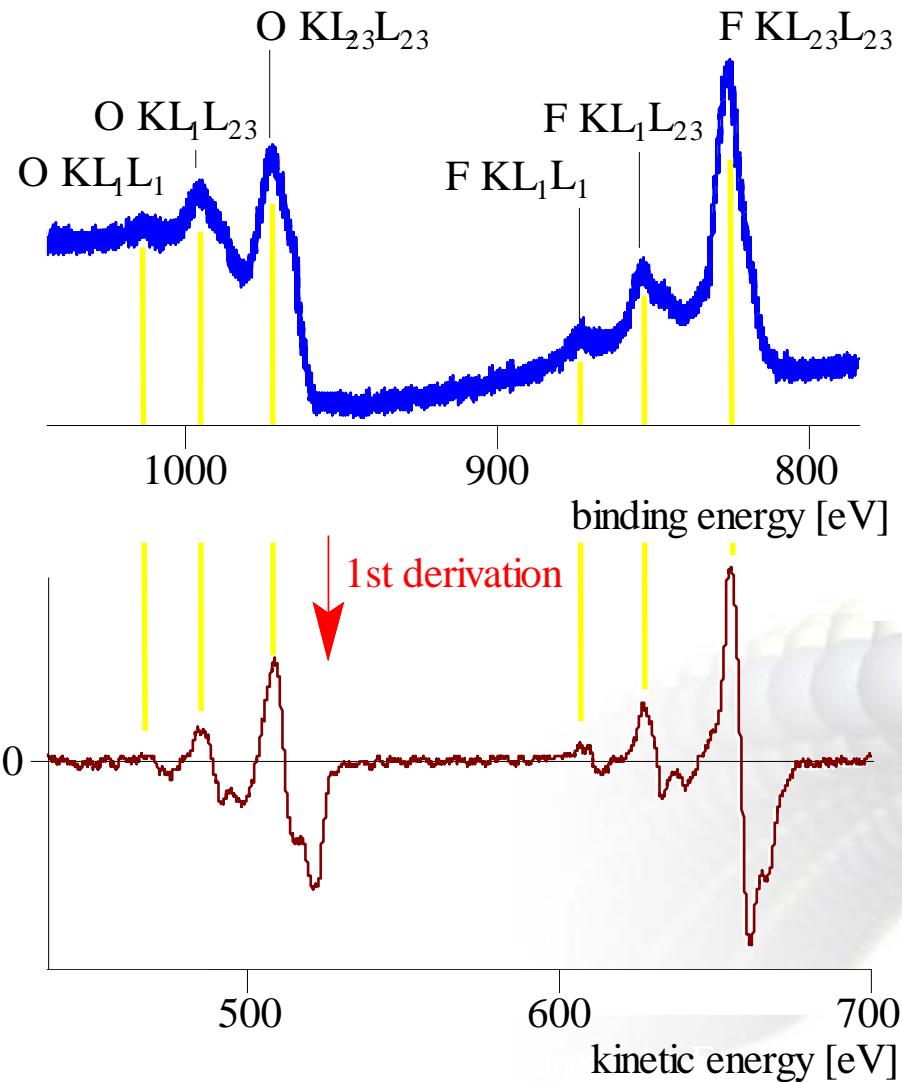
– Auger electron spectrometer –



- qualitative surface analysis
- quantitative surface analysis
- chemistry of the element's neighbourhood controls the electron density \Rightarrow chemical shift (types of functional groups, degree of oxidation)
- depth profiling combined with sputtering
- imaging AES in nanometer resolution



Auger electron spectroscopy (AES) – Spectral information –



Summary

AES

AES is also a method oriented to detect elements in the surface region of samples

- qualitative surface analysis: identification of all elements (H and He are excluded),
- quantitative surface analysis \Rightarrow relative amounts of the elements, e.g. [X]:[Y],
- peak deconvolution allows to analyze (qualitatively and quantitatively) functional surface groups or the oxidation states, labelling can be helpful to identify the species,
- depth profile analysis by sputtering techniques
- **imaging of the lateral distribution of elements in nanometer resolution**