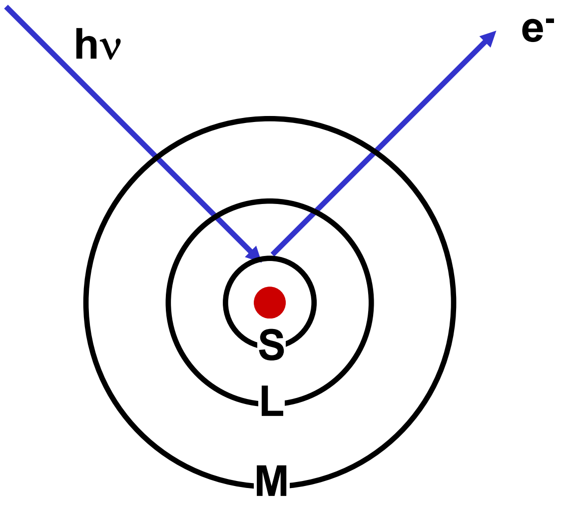
X-Ray Photoelectron Spectroscopy

Dr. Christian Linsmeier
Max-Planck-Institut für Plasmaphysik, Garching
linsmeier@ipp.mpg.de

X-ray Photoelectron Spectroscopy (XPS)

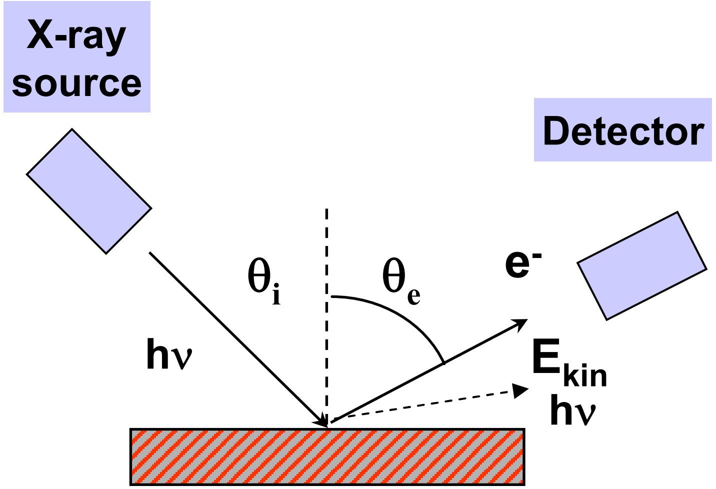
Principle



Photoelectric effect

(Einstein, Nobel prize 1921)

Measurement



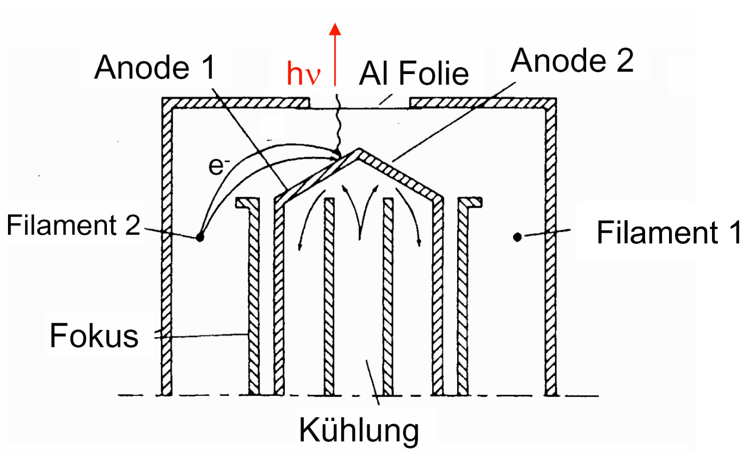
Excitation

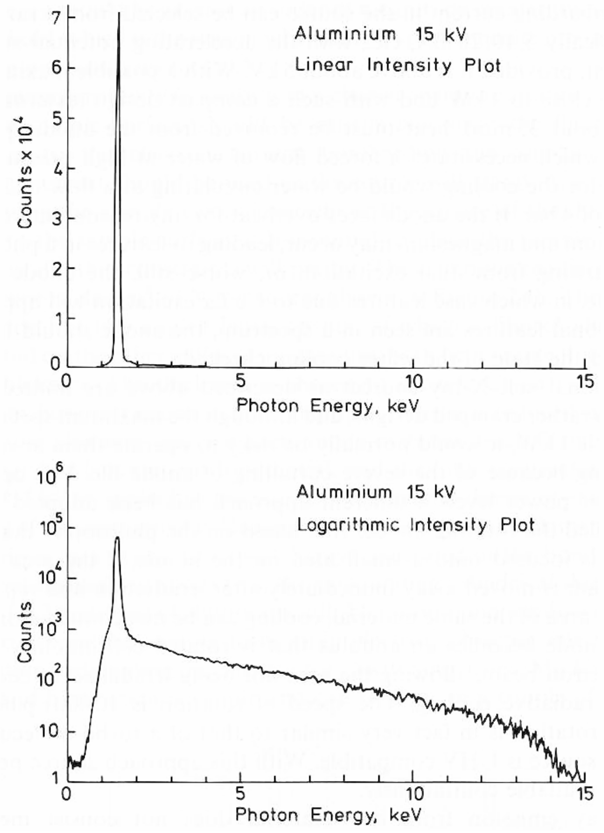
- Mg K_α radiation (1253.4 eV)
- Al K_α radiation (1486.6 eV)
- Synchrotron radiation (~0.1 - several keV)

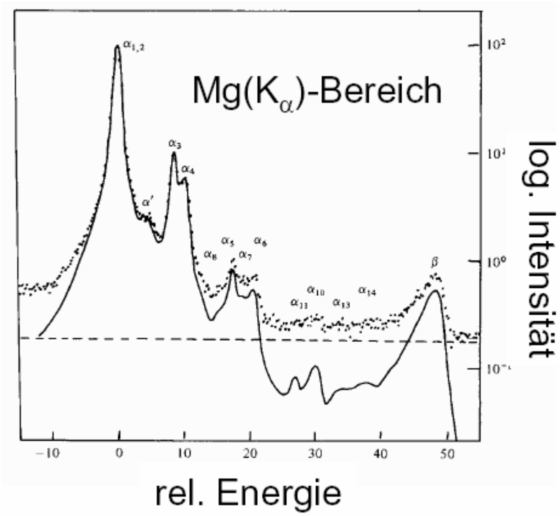
Detector ($N(E_{kin})$)

- Hemispherical analyzer

Laboratory X-ray source



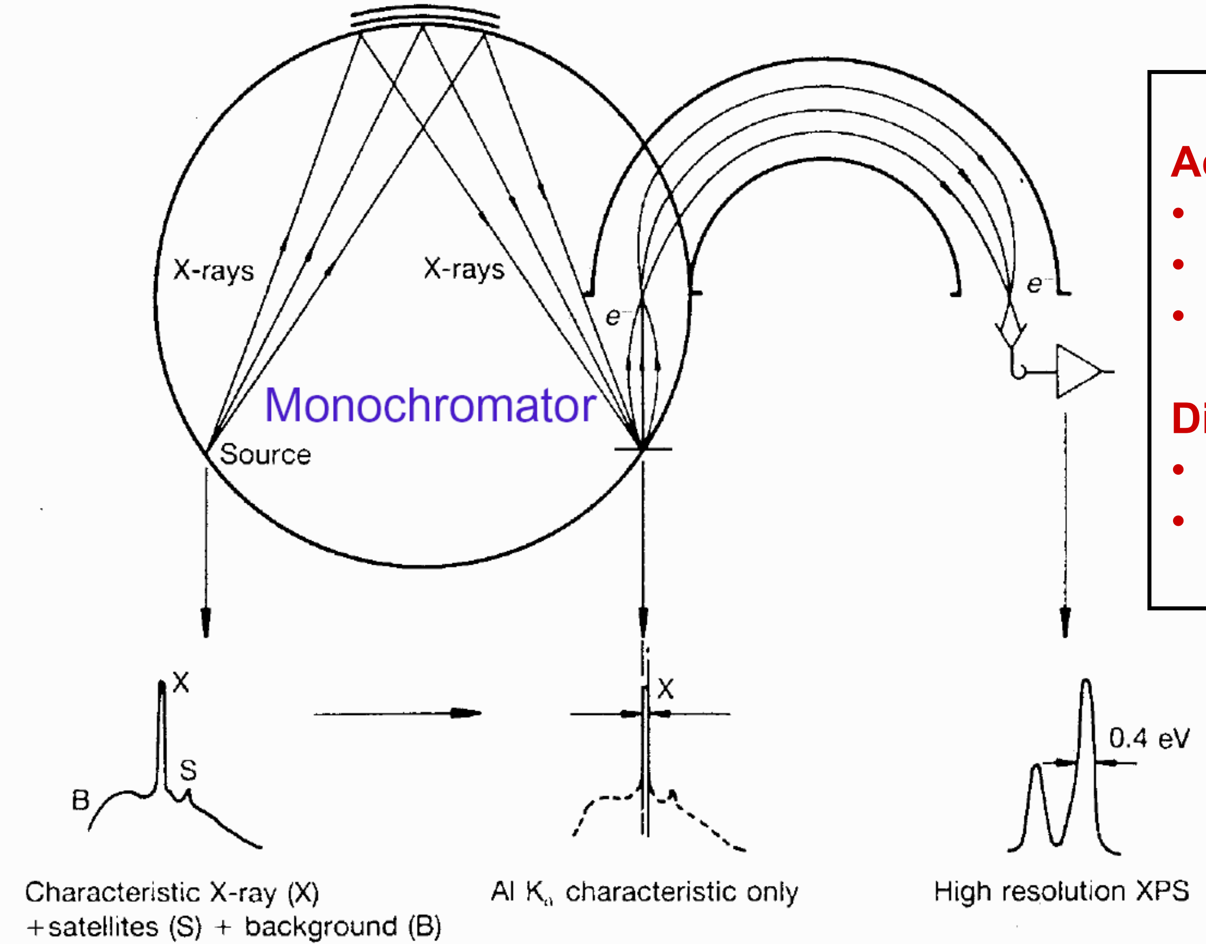




Characteristic X-ray radiation

- **Al K_α (1486.6 eV)**
- **Mg K_α (1253.6 eV)**
- **Bremsstrahlung**

Laboratory X-ray source with monochromator, synchrotron



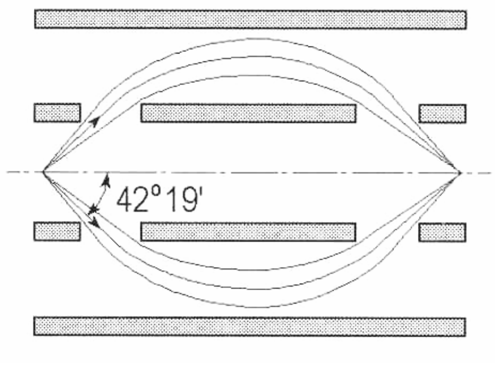
Advantages:
- **no Bremsstrahlung (L,S)**
- **high resolution (L,S)**
- **high intensity (S)**

Disadvantages:
- **low intensity (L)**
- **availability (S)**

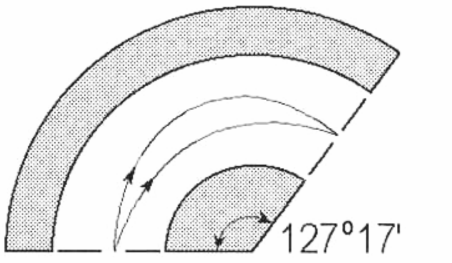
Analyzers

Dispersive analyzers

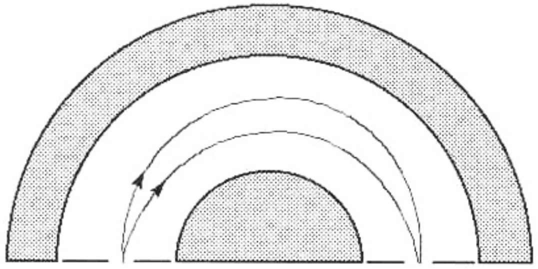
- single or double focusing
- band pass filter
- resolution *E*-dependent (Δ*E*/*E* = const.)



1. CMA, cylindrical mirror analyzer
   - 2 concentric cylinders
   - resolution < 1%

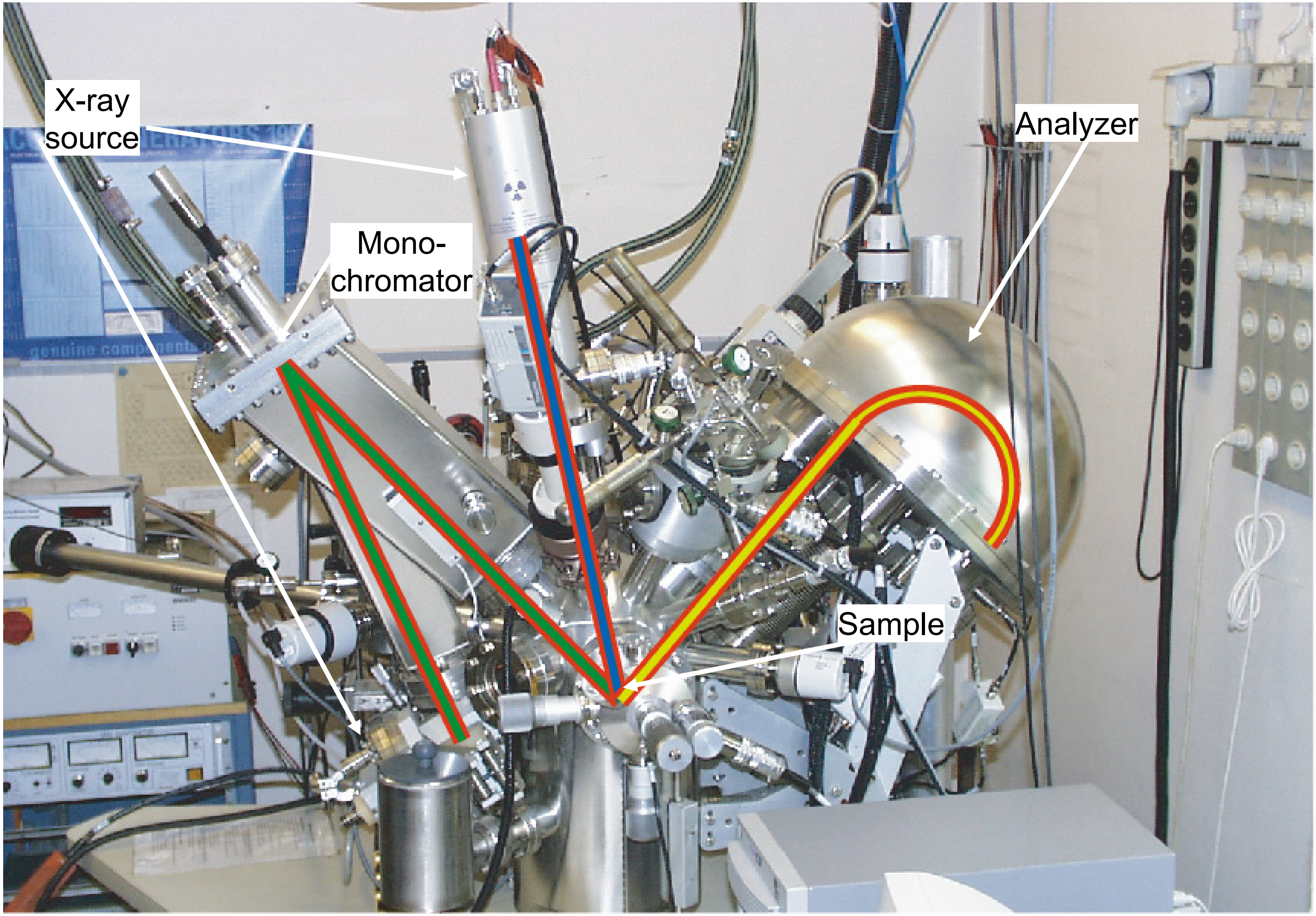


2. 127° sector analyzer
   - small device
   - good resolution (down to 0.1%)

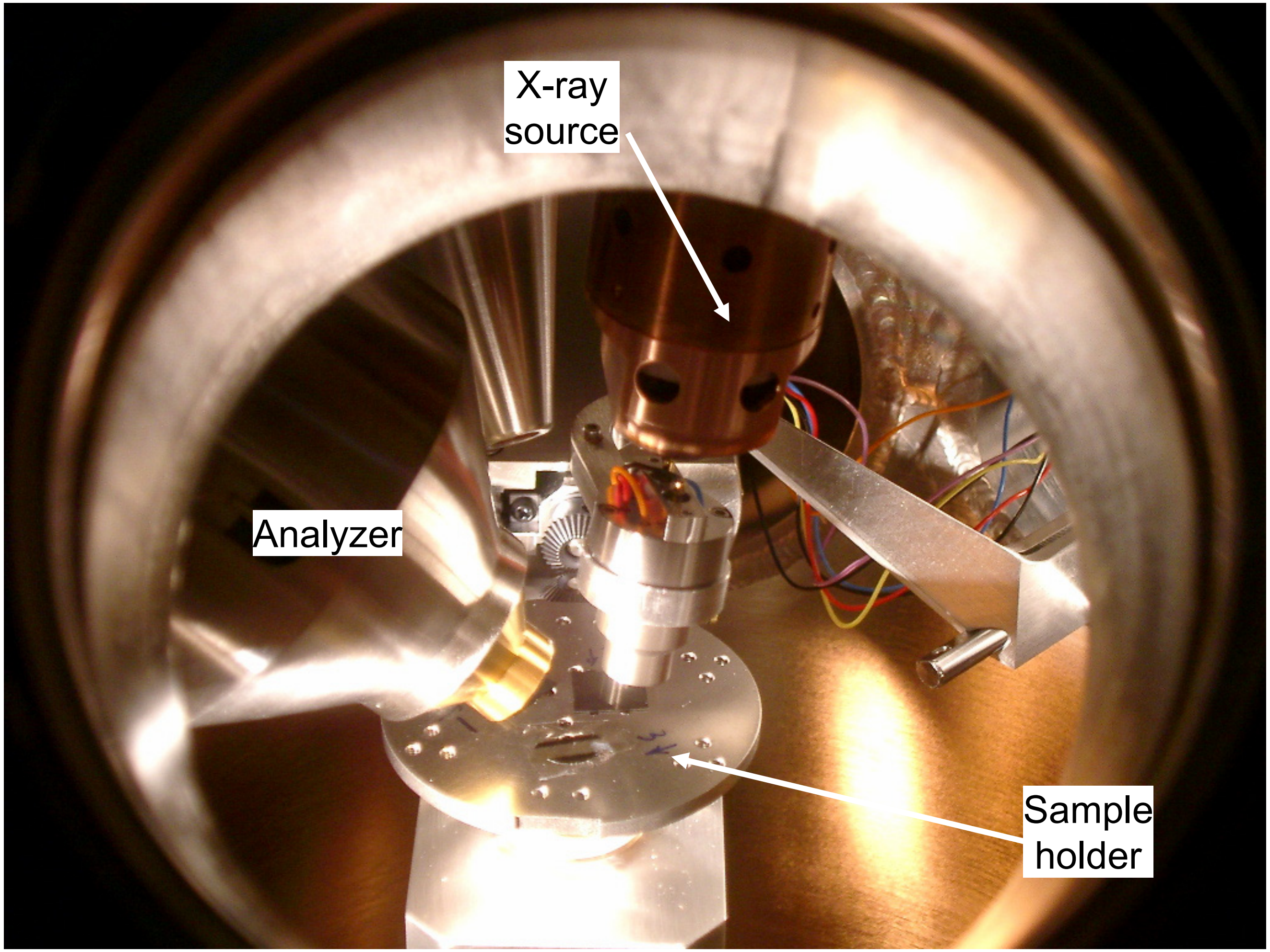


3. CHA, concentric hemispherical analyzer
   - 2 concentric half spheres
   - high transmission
   - resolution depends on radius

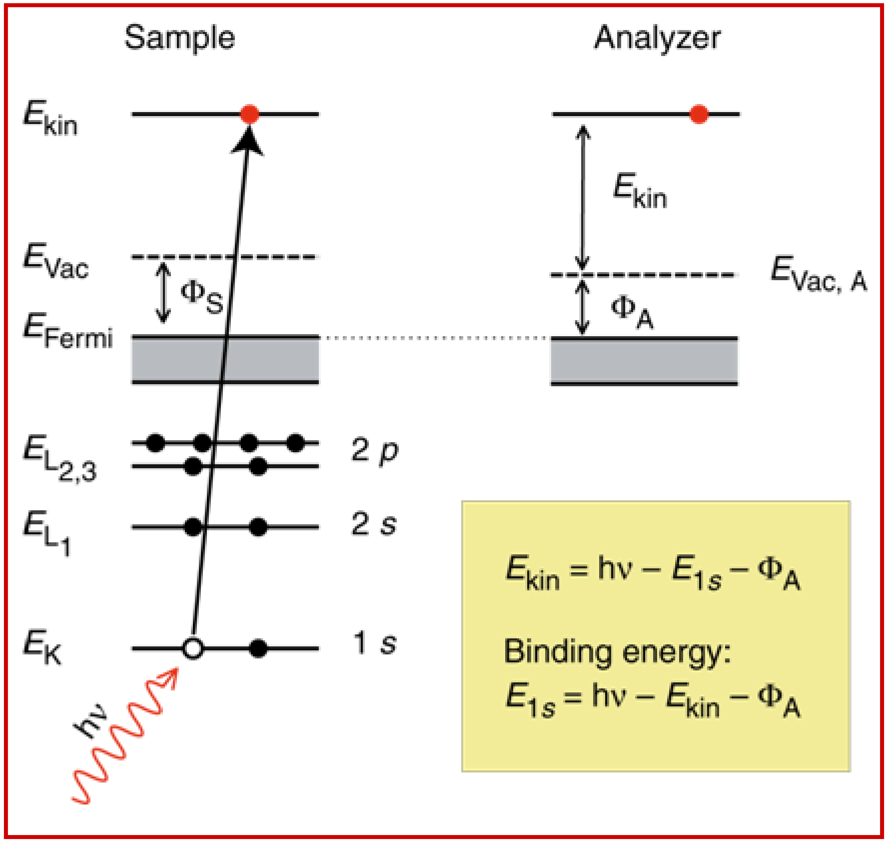
XPS Setup



XPS – Setup: inside view



XPS – Principle and method



Electron Spectroscopy for Chemical Analysis

(K. Siegbahn, Nobel prize 1981)

Binding energy

$$h\nu = E_B + \Phi_A + E_{kin}$$

$$E_B = h\nu - E_{kin} - \Phi_A$$

→ element-specific

Chemical Shift

Shift of E_B by up to several eV due to charge state of the atom

→ chemical state

Intensity

I ∝ Number of atoms × photoionization cross section ($f(E_{ph}, \text{Orbital}, \theta_e)$)

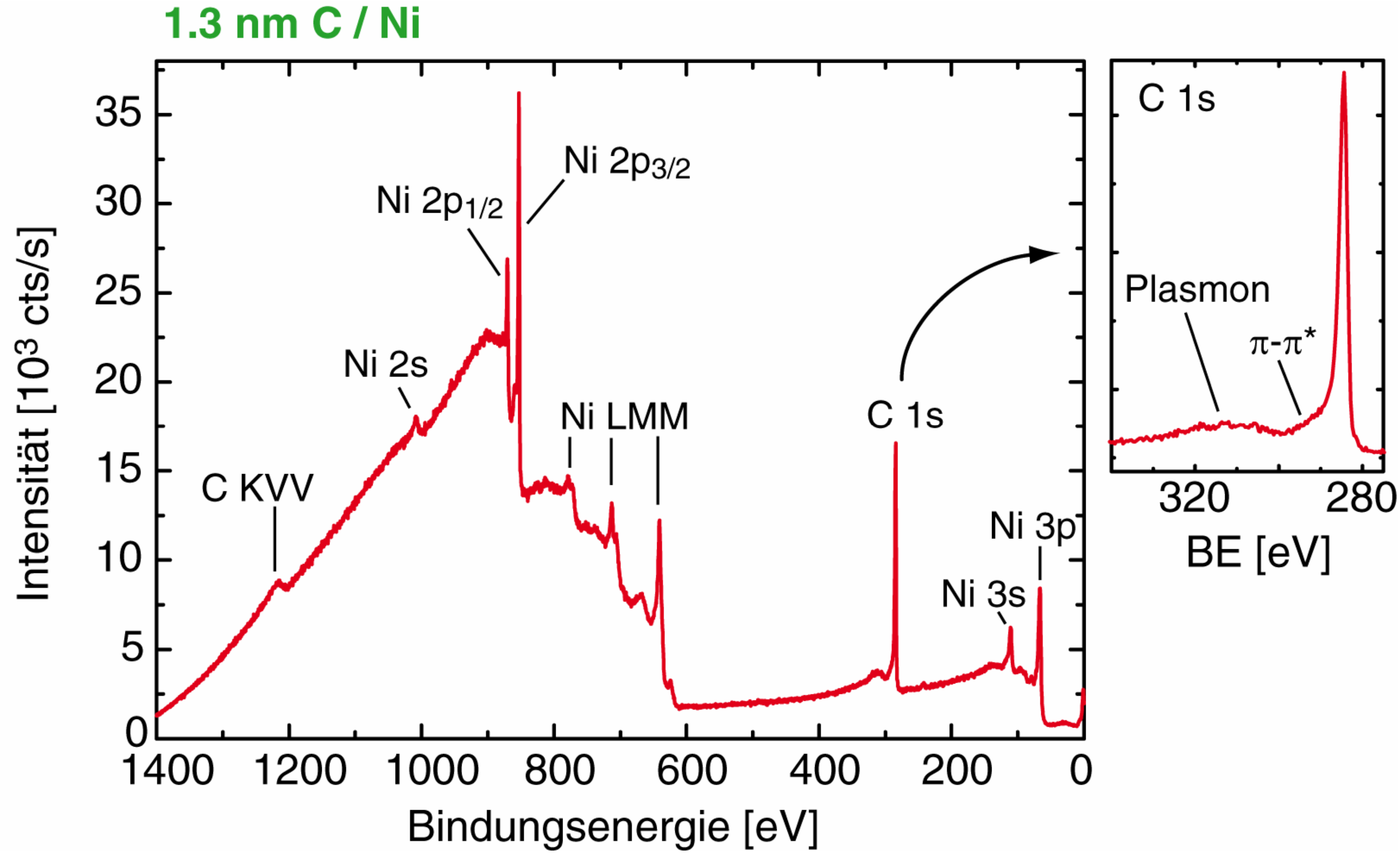
→ quantitative

Depth information

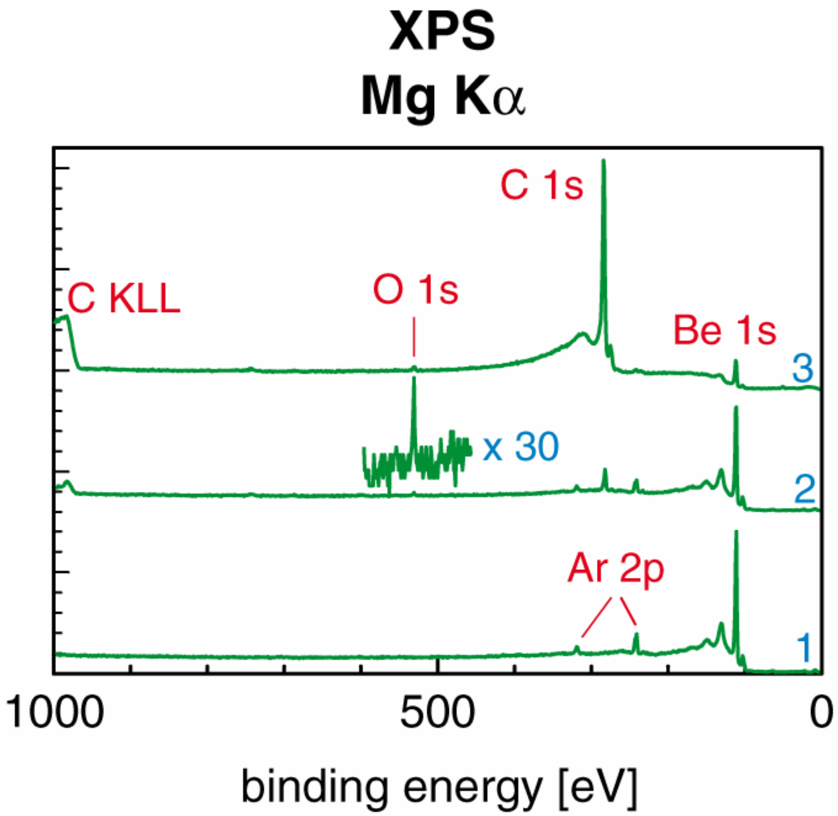
- angle-dependent intensity
- sputter-depth profiling
- variation of X-ray energy
- background analysis

→ depth-resolved

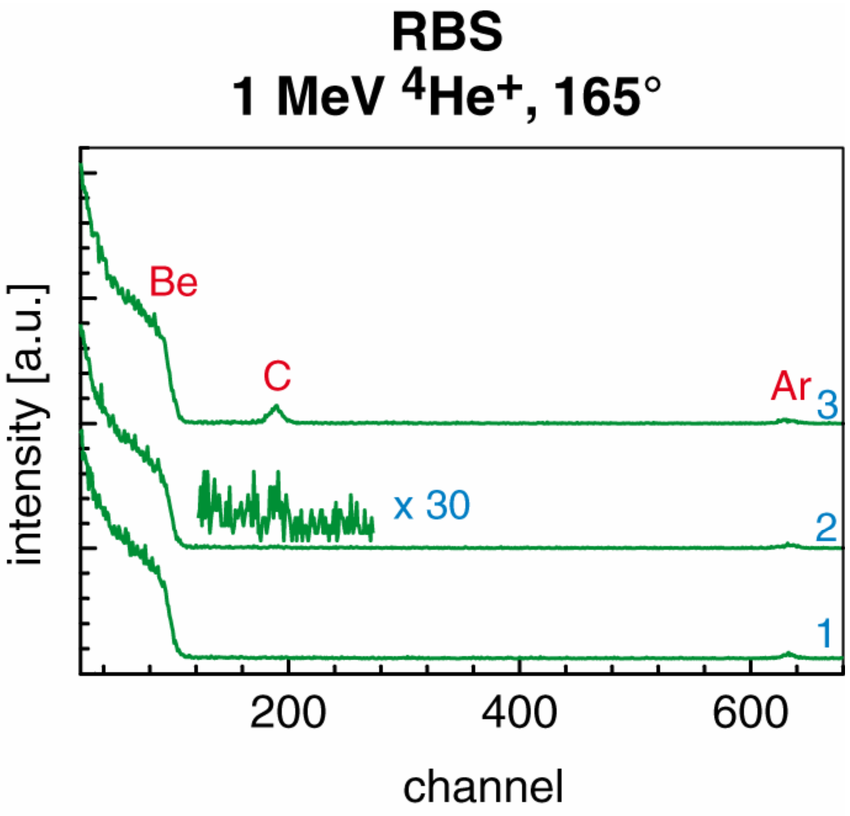
XPS – Survey spectrum



XPS – Element sensitivity



XPS
Mg Kα



RBS
1 MeV $^4He^+$, 165°

C / Be

1: clean

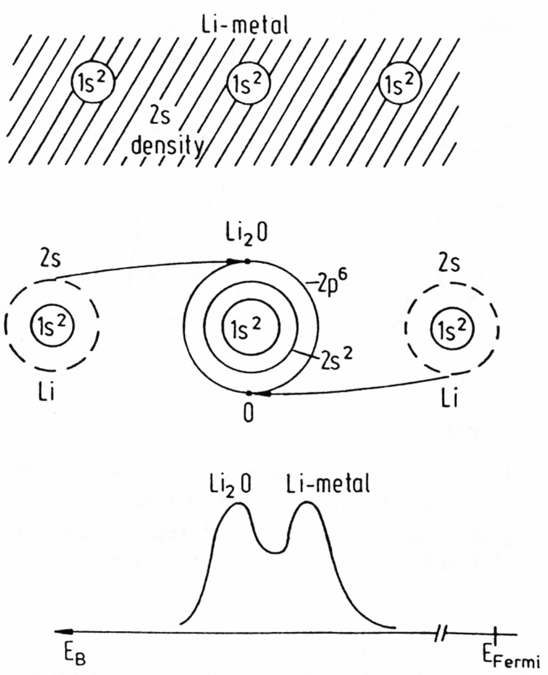
2: 0.20 nm (XPS) *(~1 ML)*

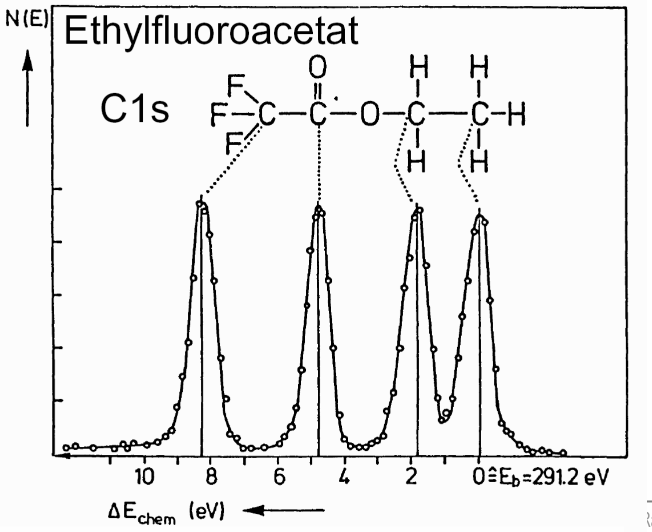
3: 4.86×10^{16} cm^{-2} (RBS) *(~24 ML)*

$\rho_{\mathrm{carbon}} = 1.8$ g cm^{-3}

1 ML = 2.01×10^{15} cm^{-2} = 0.22 nm

XPS – Chemical shift





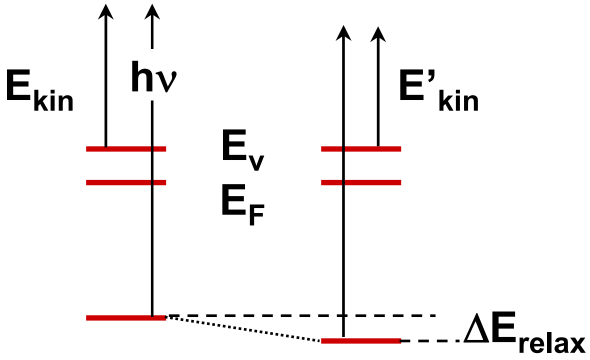
Chemical shift

- Binding energy of core levels depends on electron density at the emitting atom (→ screening of core level electrons), determined by the electronegativity of the neighboring atoms.

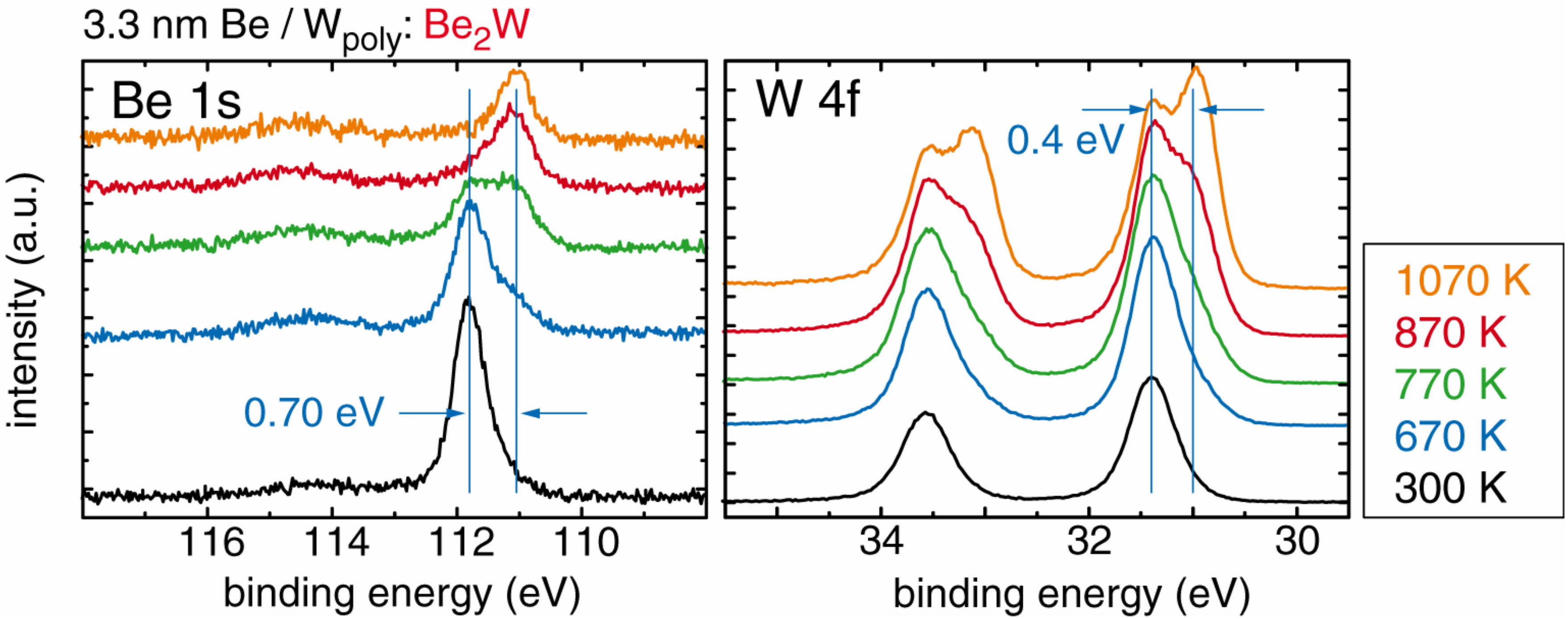
Chemical shift used as a ‚fingerprint‘

Final state effects

- Relaxation of the ion ‚during the photoelectron emission‘



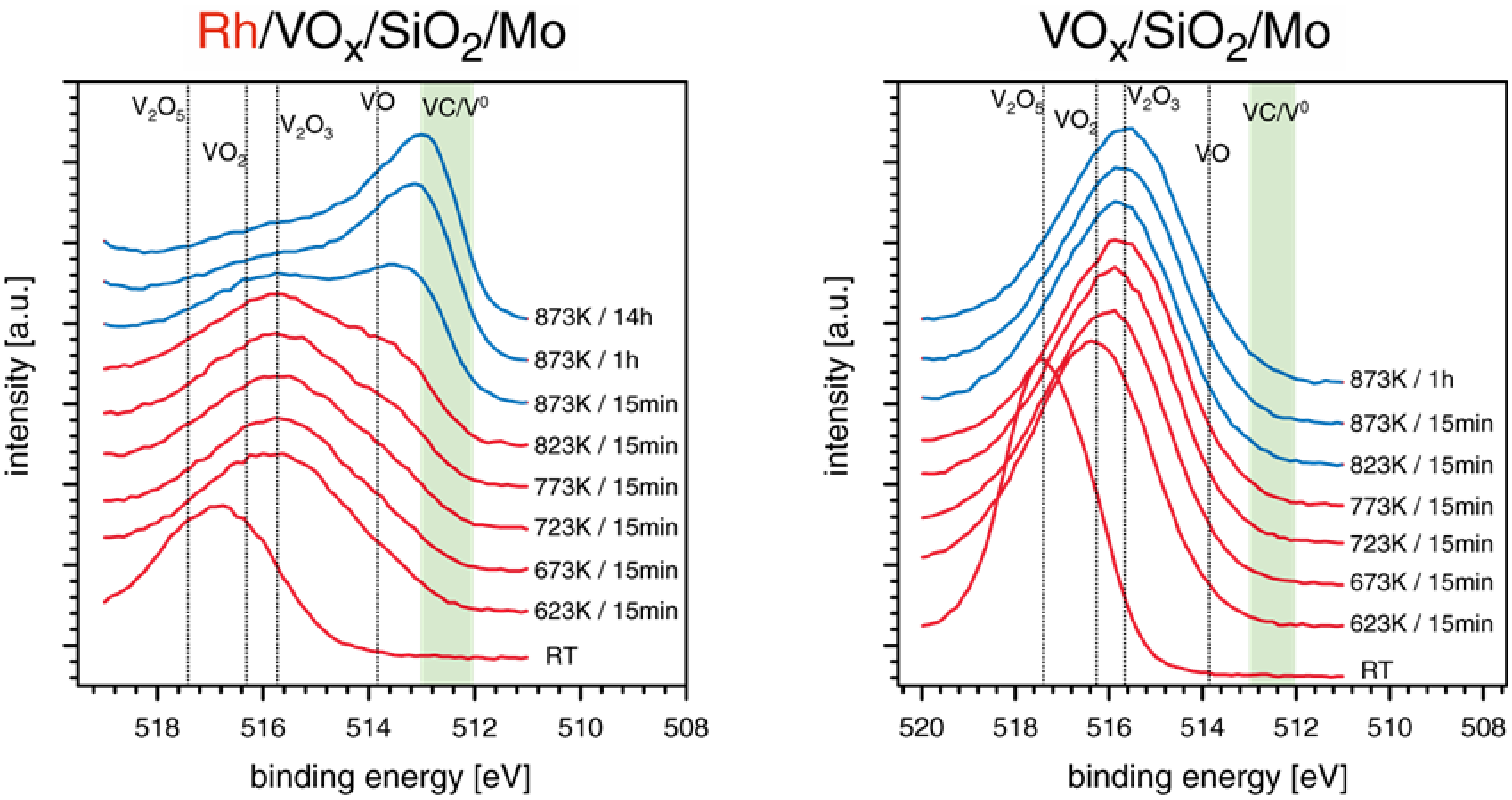
Alloy formation



Alloy formation:

Be is incorporated within the W metal structure
Overlap of W *d* orbitals is reduced
→ Change in binding energy of 4*f* core level electrons

Promotor-metal reaction

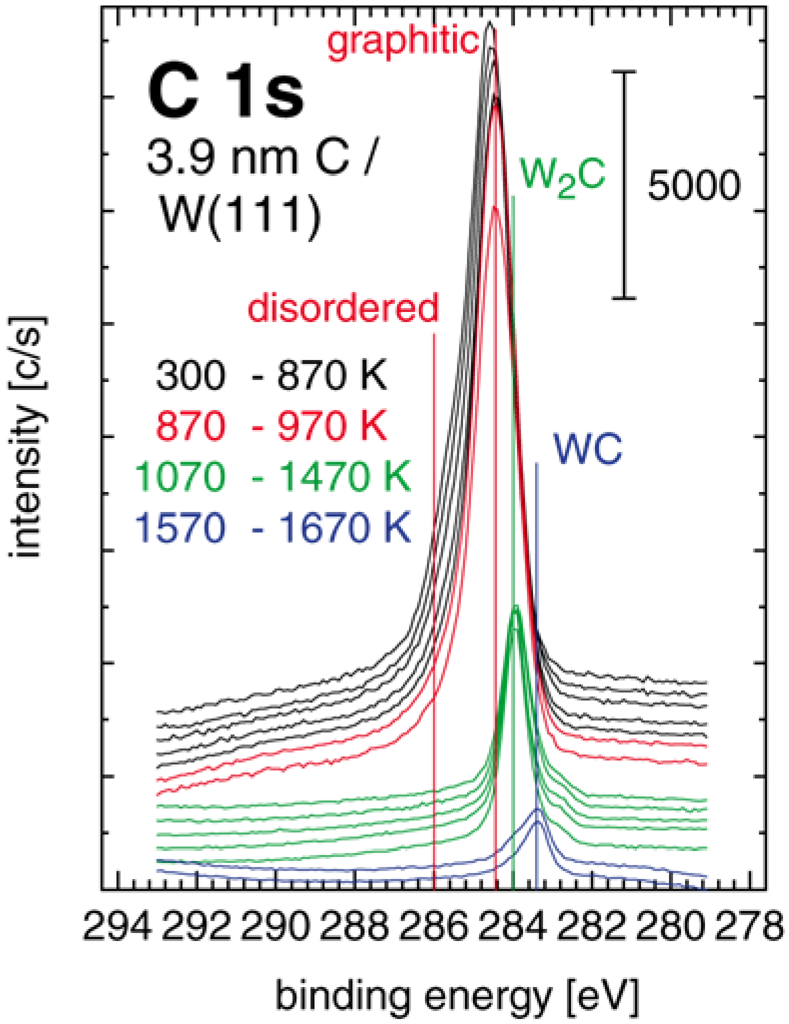


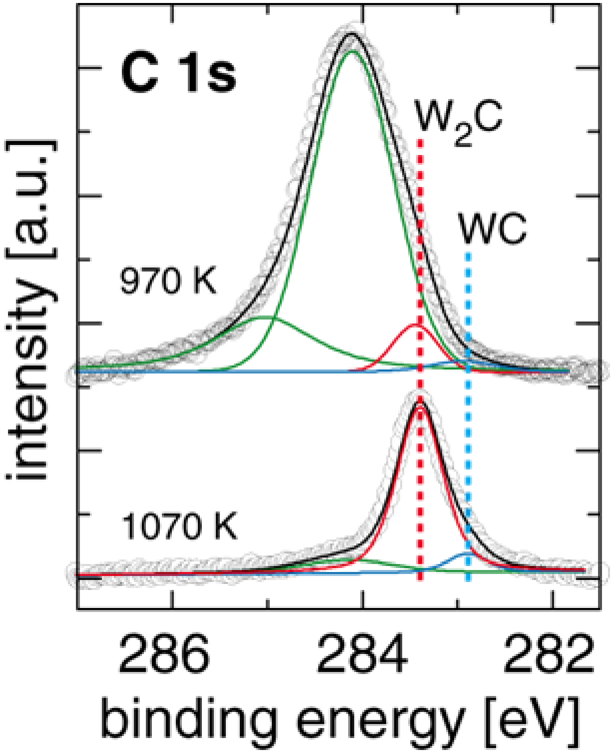
Rhodium monolayer:

→ catalyst metal leads to reduction of the VO$_x$ promotor oxide

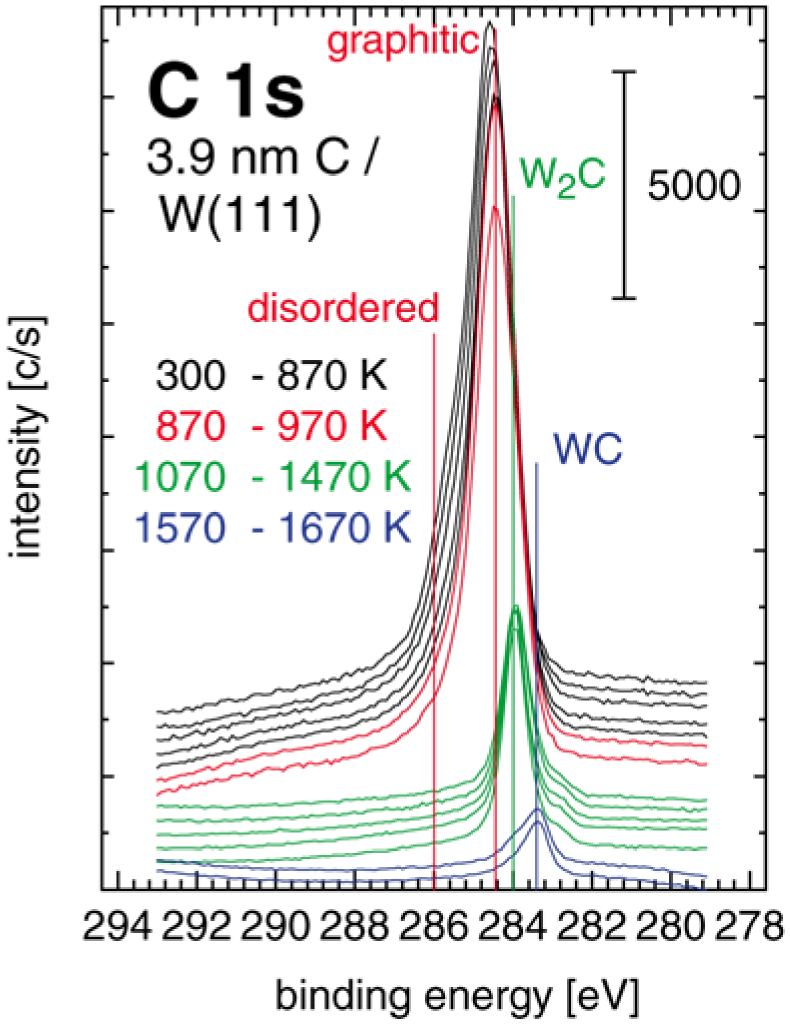
→ vanadium oxidation states identified by chemical shift

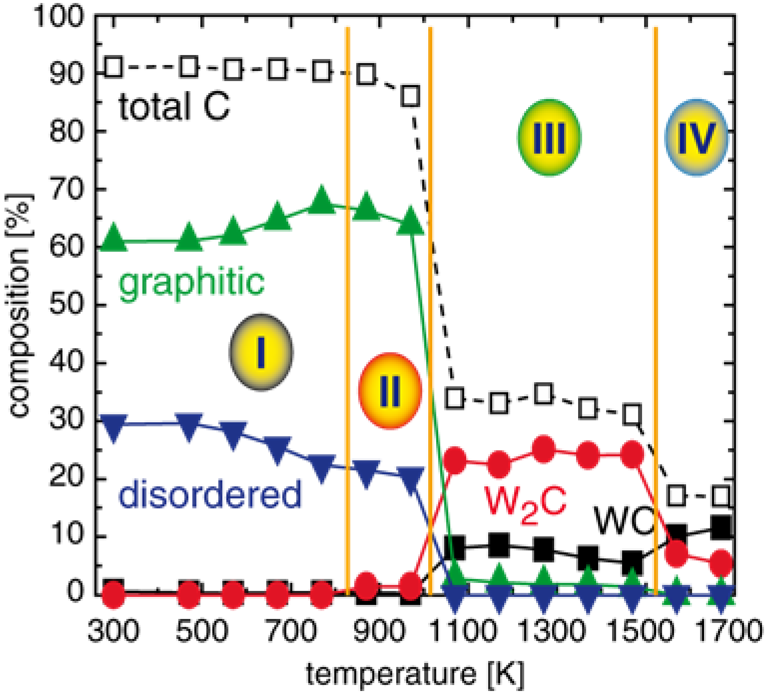
Tungsten carbide phase formation





Tungsten carbide phase formation

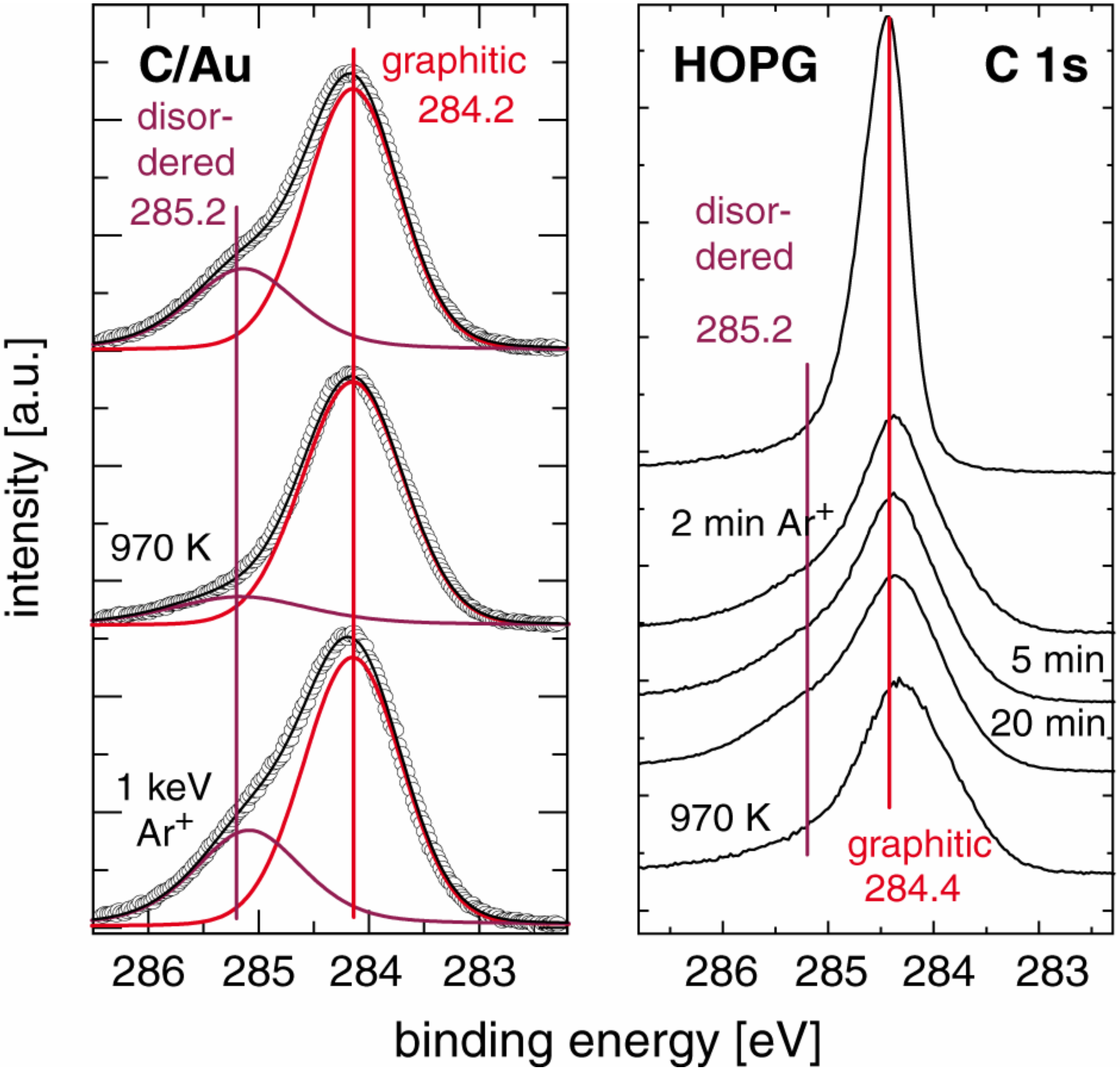


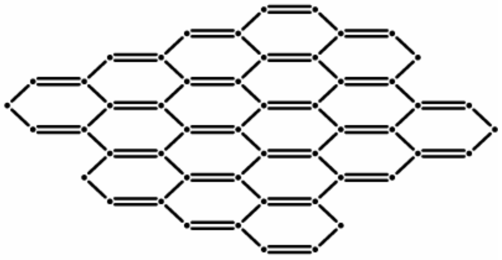


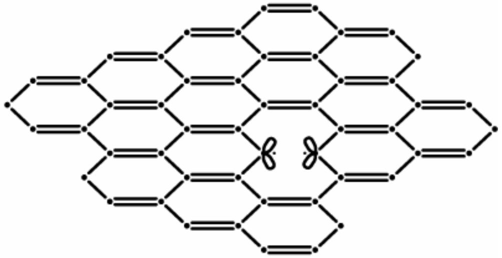
Carbide formation:

- → analysis of peaks by fitting
- → identification of chemical and structural phases
- → WC, W_2C formed
- → C loss into bulk by diffusion

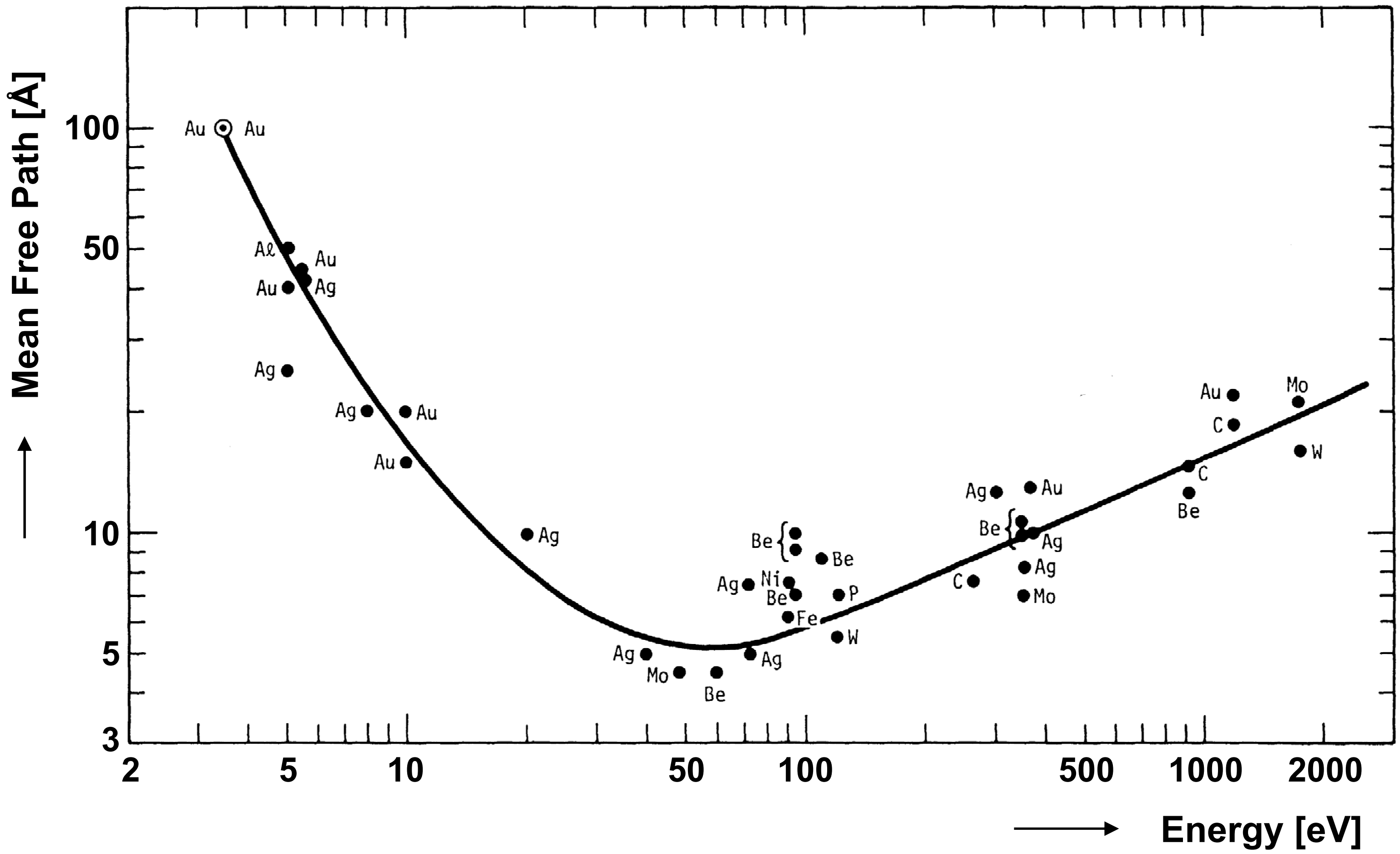
Sensitivity to structural changes





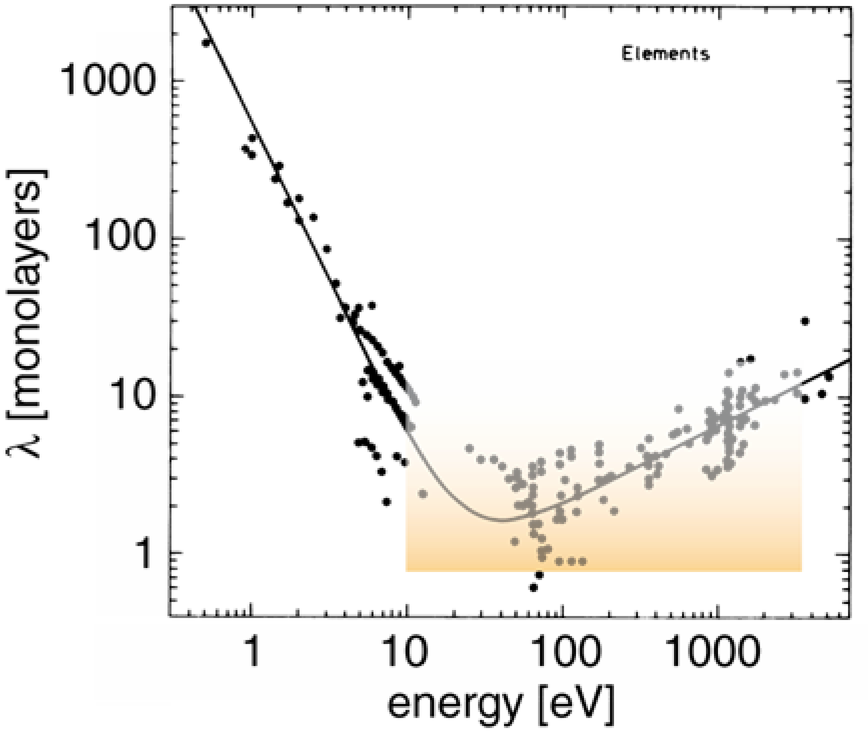


Electron mean free path



G.A. Somorjai, “Introduction to Surface Chemistry and Catalysis” (Wiley, New York, 1994), p.383

Information depth in electron spectroscopies

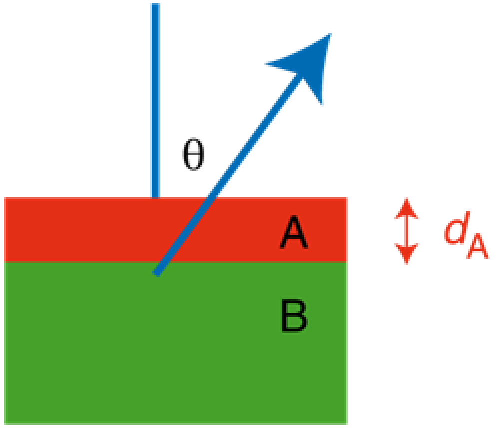


Seah, Dench (1979)

$\lambda_M = 538 / E^2 + 0.41\,(a\,E)^{1/2}$ [ML]

a: atom diameter from density (in nm)

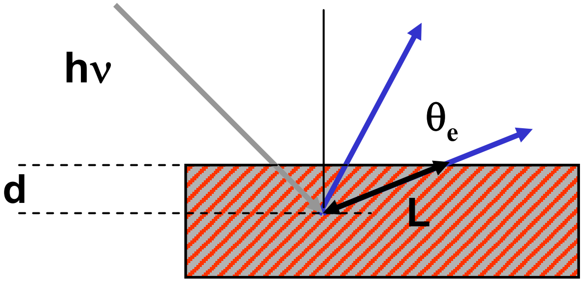
E: electron kinetic energy (in eV)

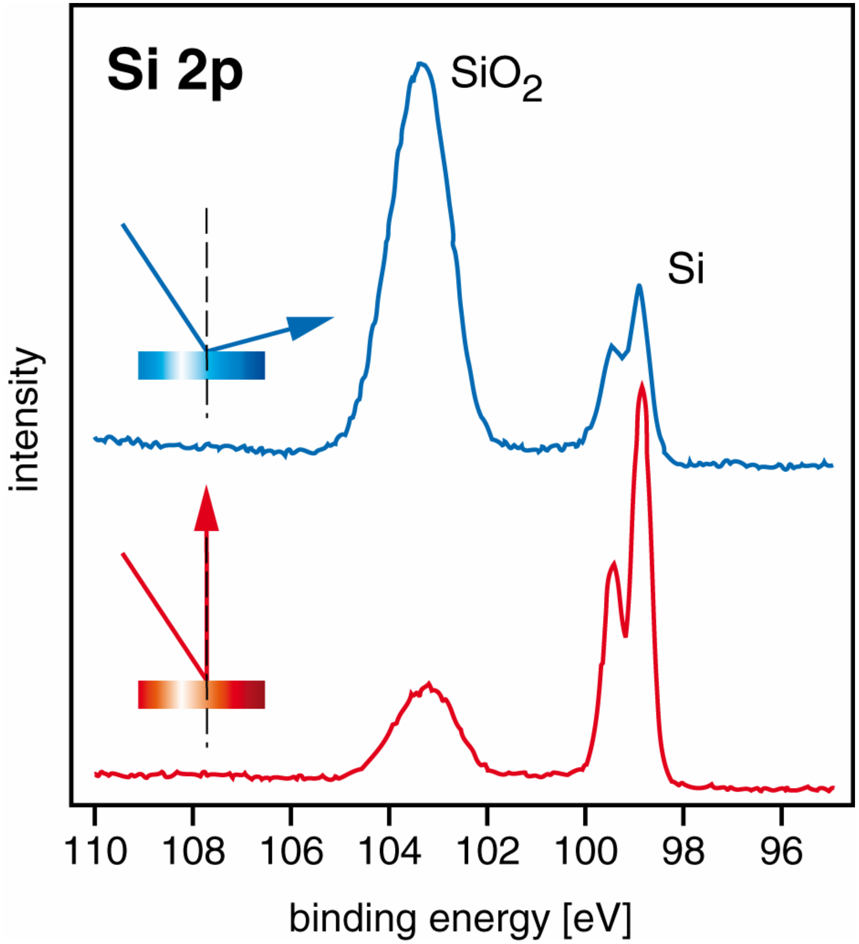


Quantification:

$I_B = I_B^{\infty} \exp(-d_A / \lambda_A \cos\theta)$

Depth information – variation of electron exit angle





Angular dependence of electron emission

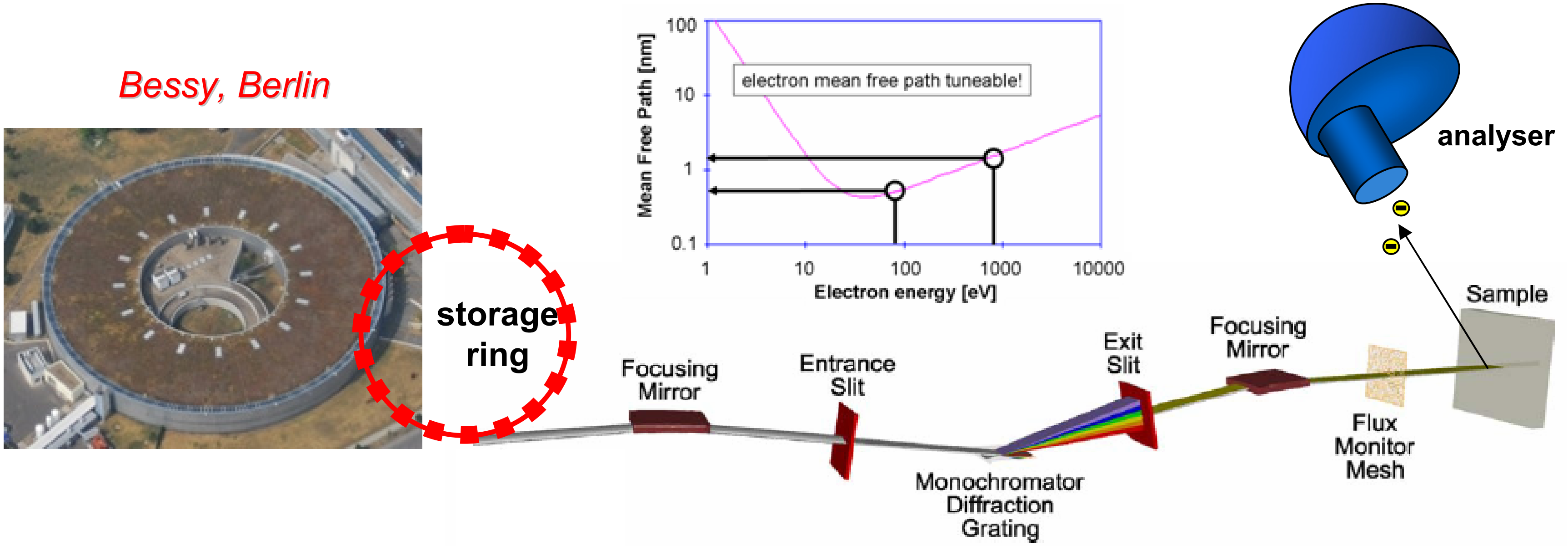
Intensity depends on mean free path λ and depth distribution of the detected elements.

$$I = I_0 \cdot \exp\left(-\frac{L}{\lambda}\right)$$

$$I = I_0 \cdot \exp\left(-\frac{d}{\lambda \cdot \cos\theta_e}\right)$$

Synchrotron light source

Bessy, Berlin



$$E_{kin} = h\nu - E_B - \Phi_A$$

$$I(E_{kin}) = J(h\nu) \cdot N \cdot \sigma(h\nu,\theta) \cdot \lambda(E_{kin}) \cdot T(E_{kin})$$

photon flux

density of atoms

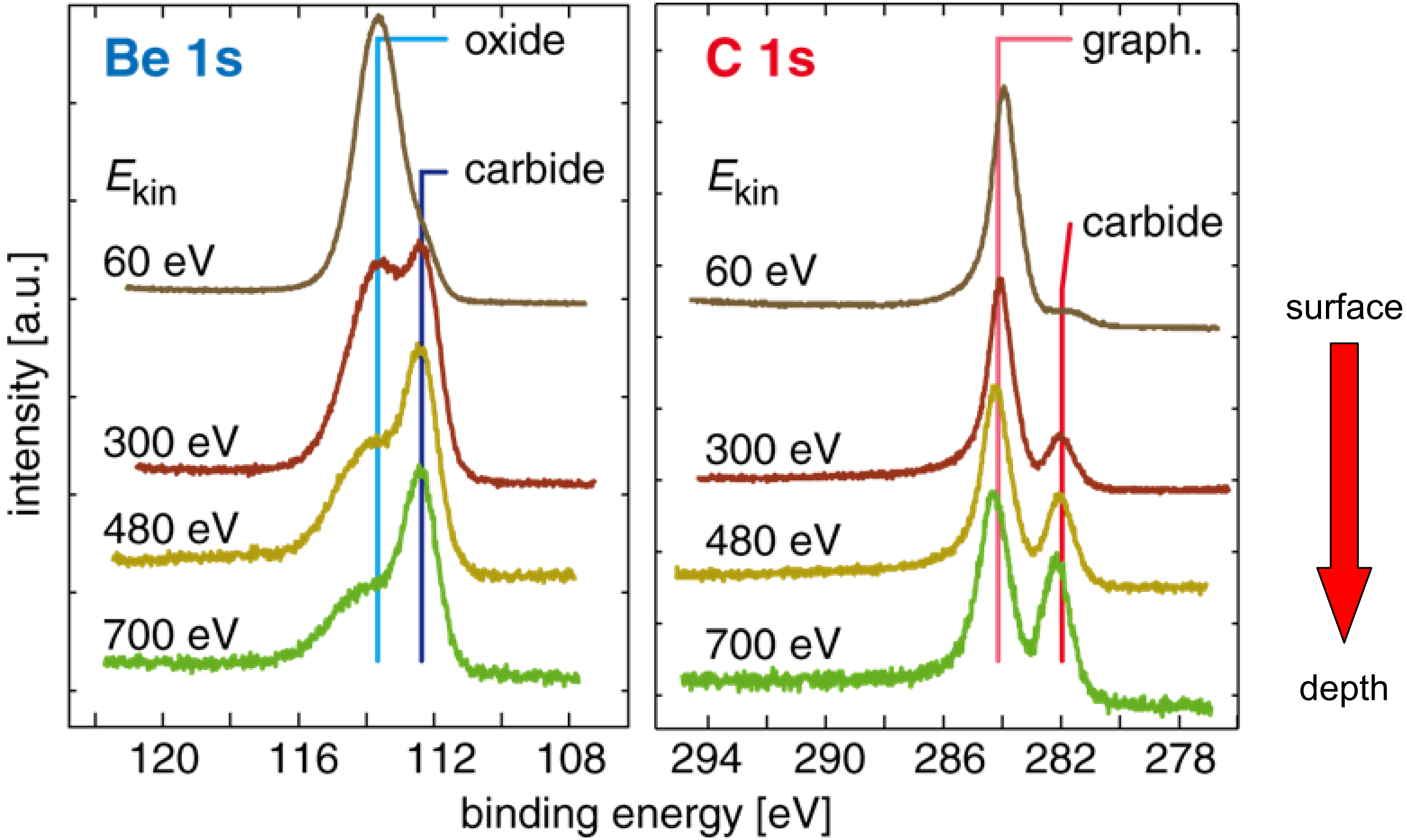
photoelectron cross section

photoelectron mean free path

analyzer transmission

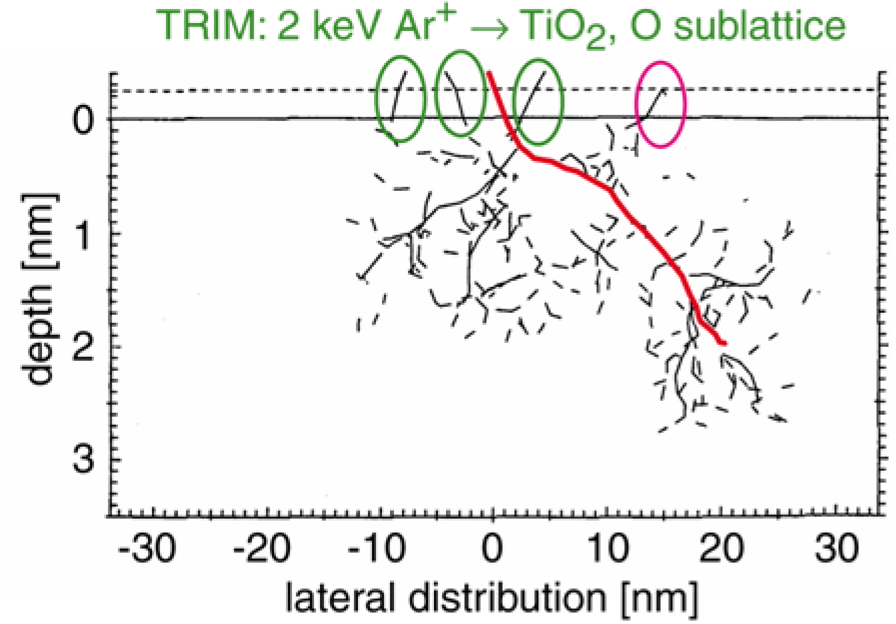
Depth information – variation of photon energy

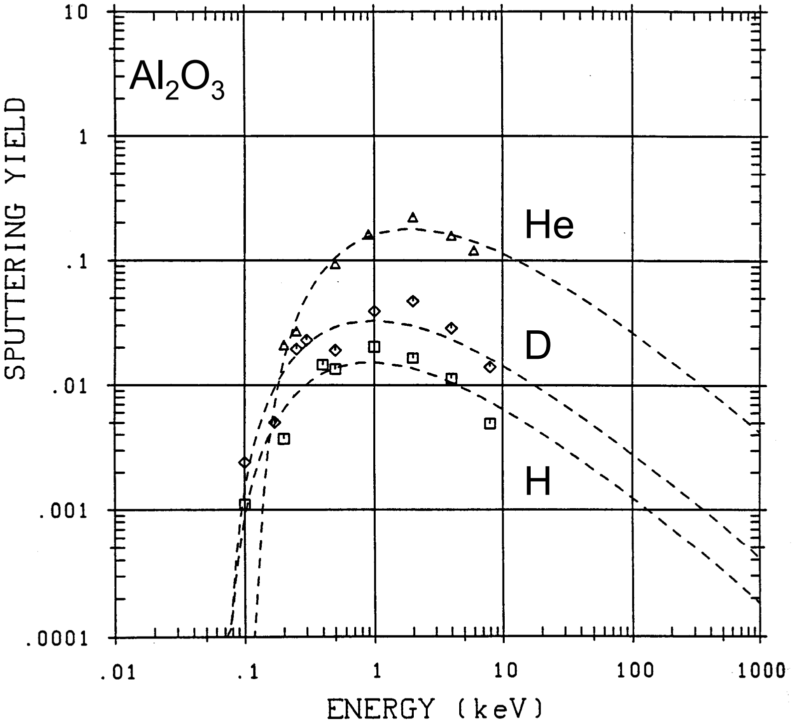
C / Be / W layer system: chemical reactions after 1050 K annealing



Sputtering

Collision cascade in near-surface zone, removal of atoms





Sputtering yield:

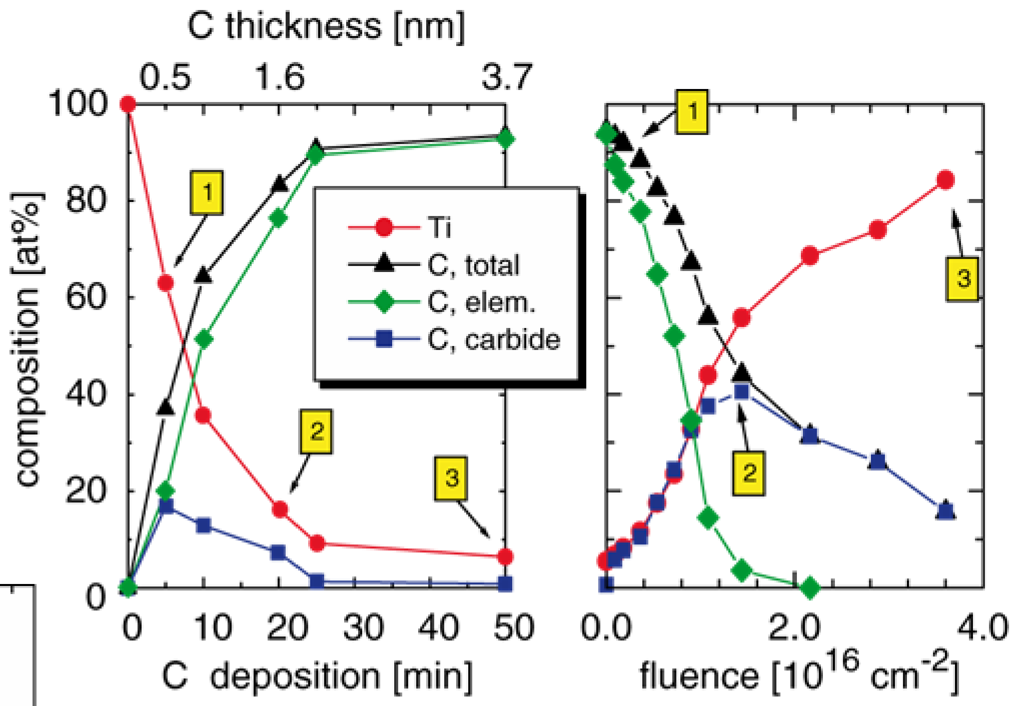
$$Y = \frac{\text{number of sputtered atoms}}{\text{number of incoming projectiles}}$$

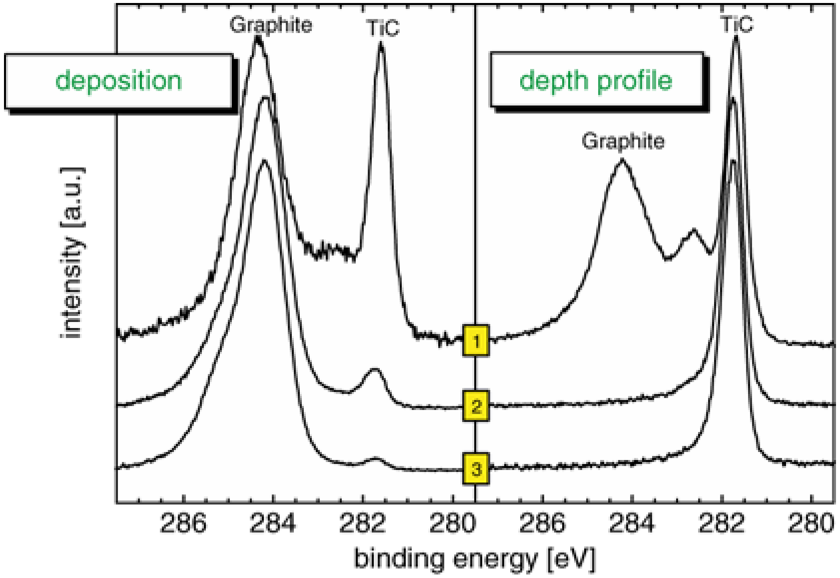
Chemical influence of Ar sputtering

3.7 nm C / Ti:

1. C deposition
2. sputtering by 4 keV Ar

continuous XPS measurements



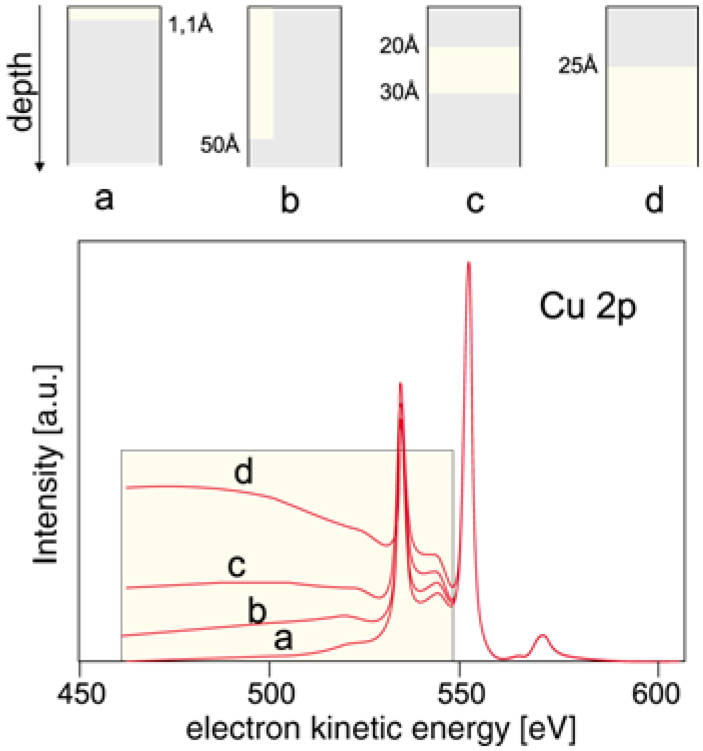


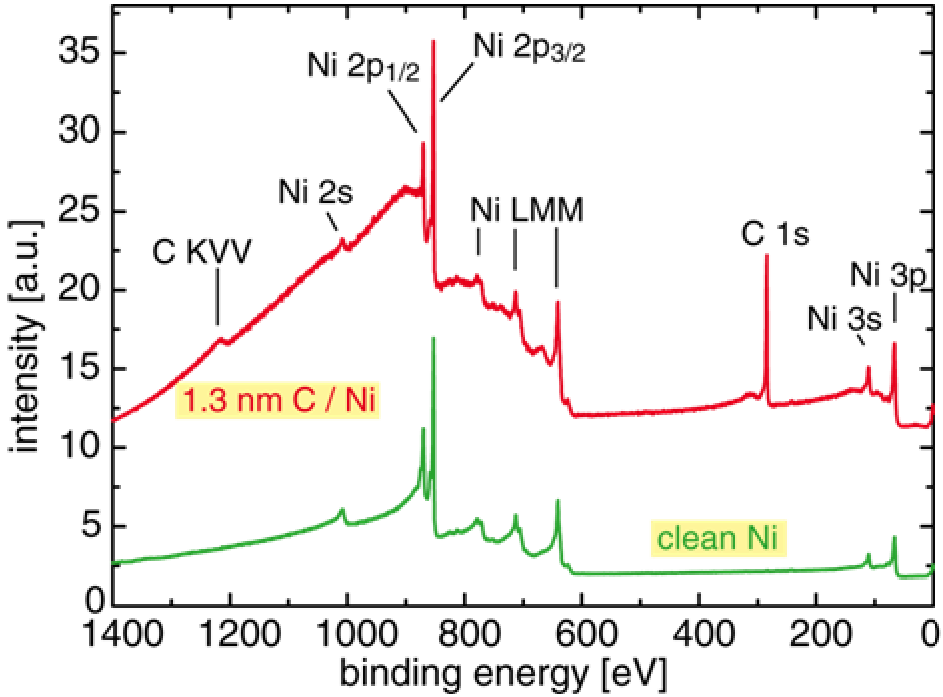
→ ion beam collision cascade leads to mixing and carbide formation!

Background analysis

Inelastic energy loss: electrons contribute to background

→ Information on surface morphology!

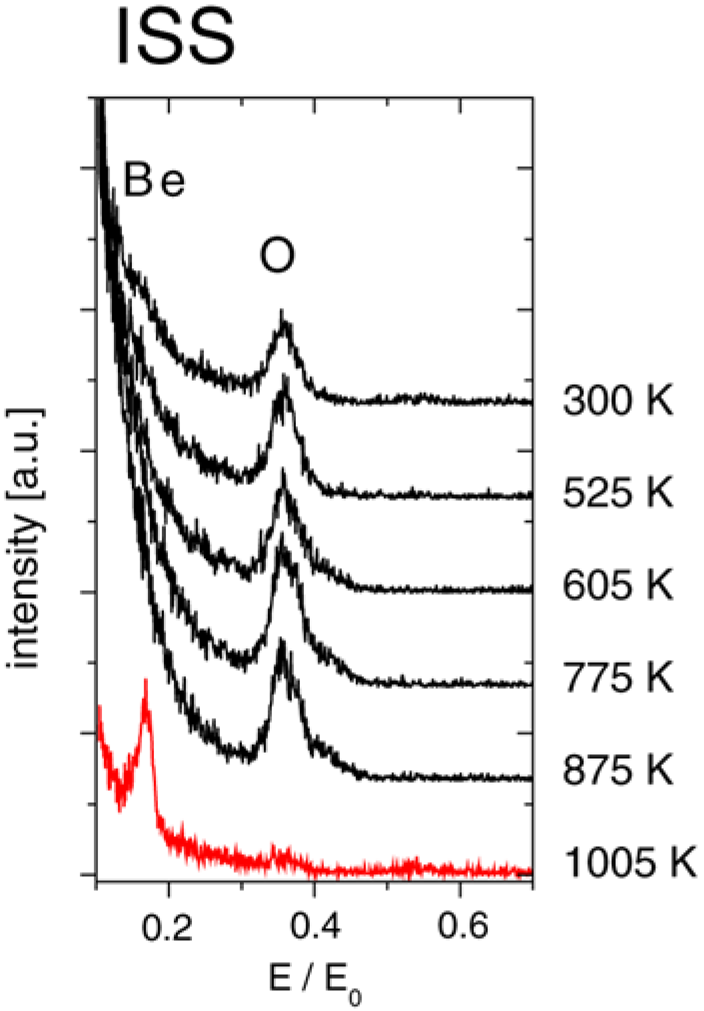




S. Tougaard, Odense

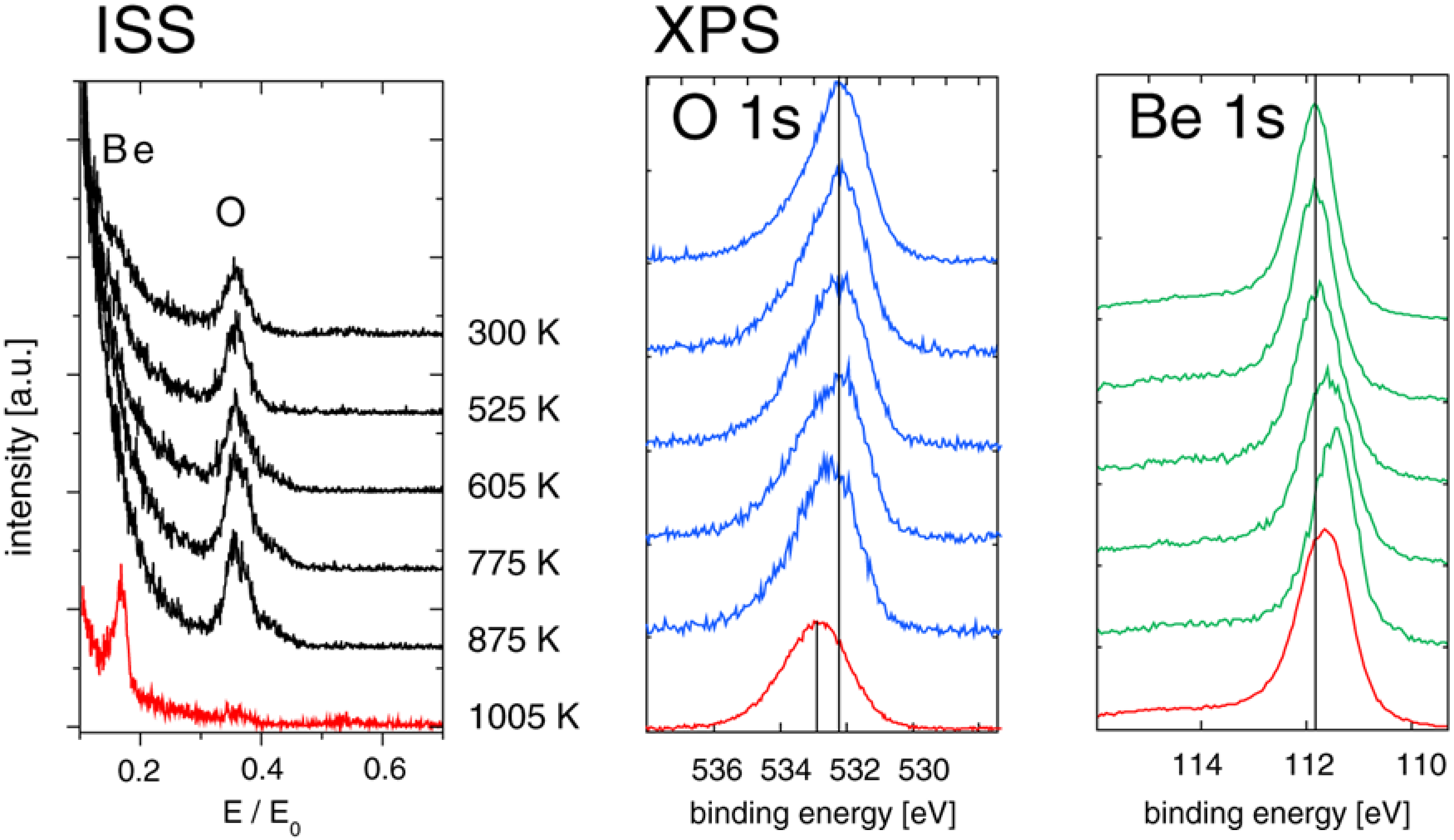
Comparison XPS – Ion Scattering Spectroscopy (ISS)

ISS: 480 eV He, θ=135° → sensitive to 1st monolayer only



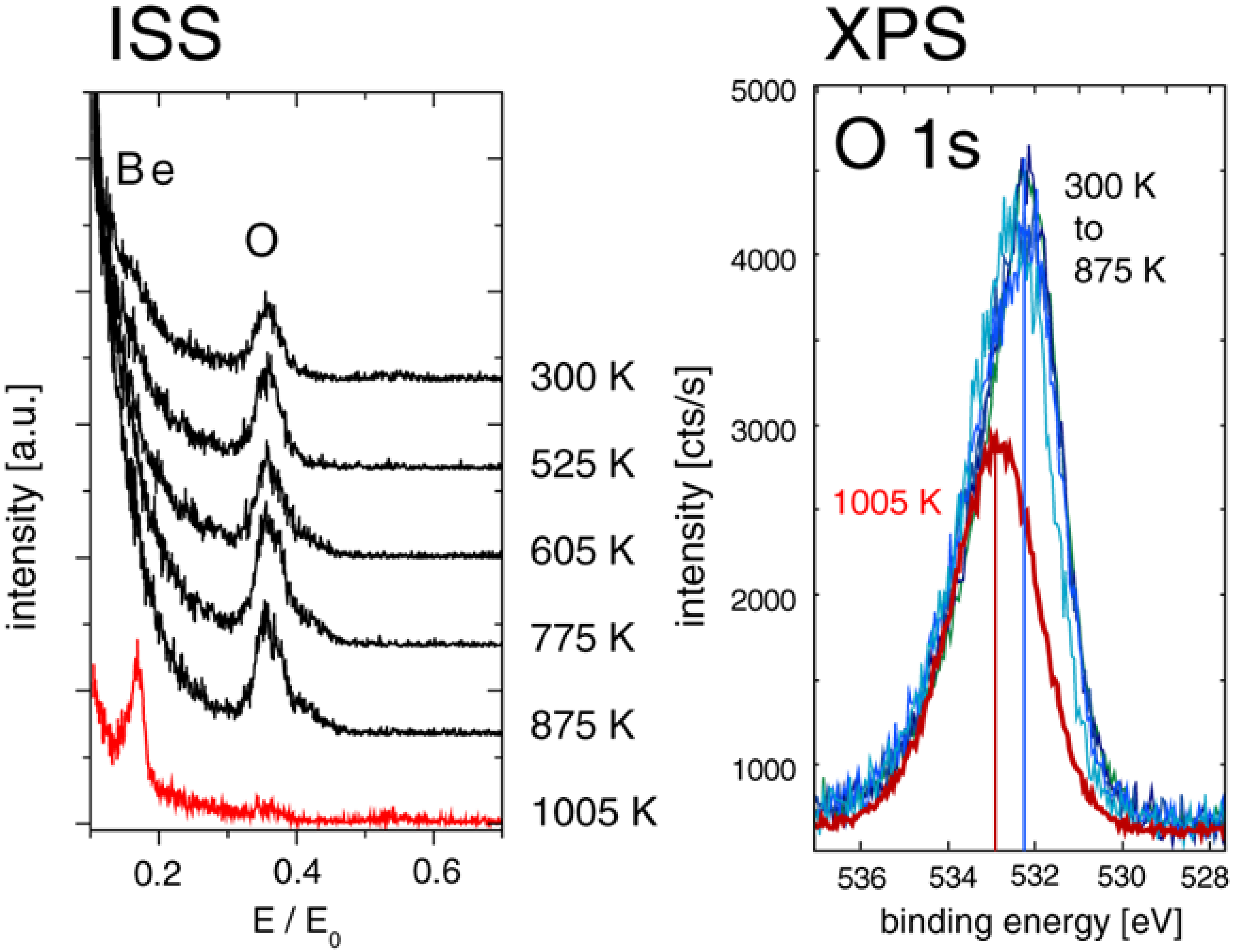
Comparison XPS – Ion Scattering Spectroscopy (ISS)

ISS: 480 eV He, θ=135° → sensitive to 1st monolayer only



Comparison XPS – Ion Scattering Spectroscopy (ISS)

ISS: 480 eV He, θ=135° → sensitive to 1st monolayer only



ISS: first layer composition

XPS: chemical sensitivity

→ complementary information!

→ always use several techniques for complex systems

Summary

- Physical background
- Instrumentation
- Elemental analysis
- Chemical state analysis
- Quantification
- Depth profiling
- Comparison with ISS

Literature

Text and Reference Books:

1. Eds. D. Briggs and M.P. Seah, *Practical Surface Analysis, Vol. 1 – Auger and X-Ray Photoelectron Spectroscopy*, 2nd ed., Wiley (1992).
2. S. Hüfner, *Photoelectron Spectroscopy*, Springer (1995)
3. J.F. Moulder, W.F. Stickle, P.E. Sobol, K.E. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy*, Ed. J. Chastain, Perkin-Elmer Corp., Eden Prairie (1992).
4. Eds. D. Briggs and J.T Grant, *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Chichester (2003)
5. G. Ertl and J. Küppers, *Low Energy Electrons and Surface Chemistry*, Weinheim (1985)