The Abdus Salam International Centre for Theoretical Physics

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IAEA International Atomic Energy Agency

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Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis

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Complementary techniques II

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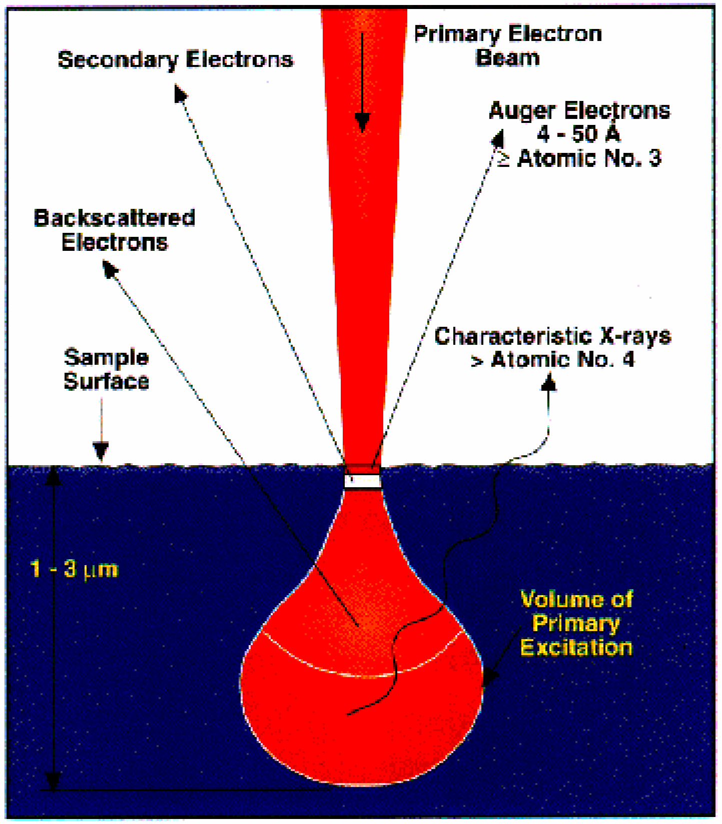
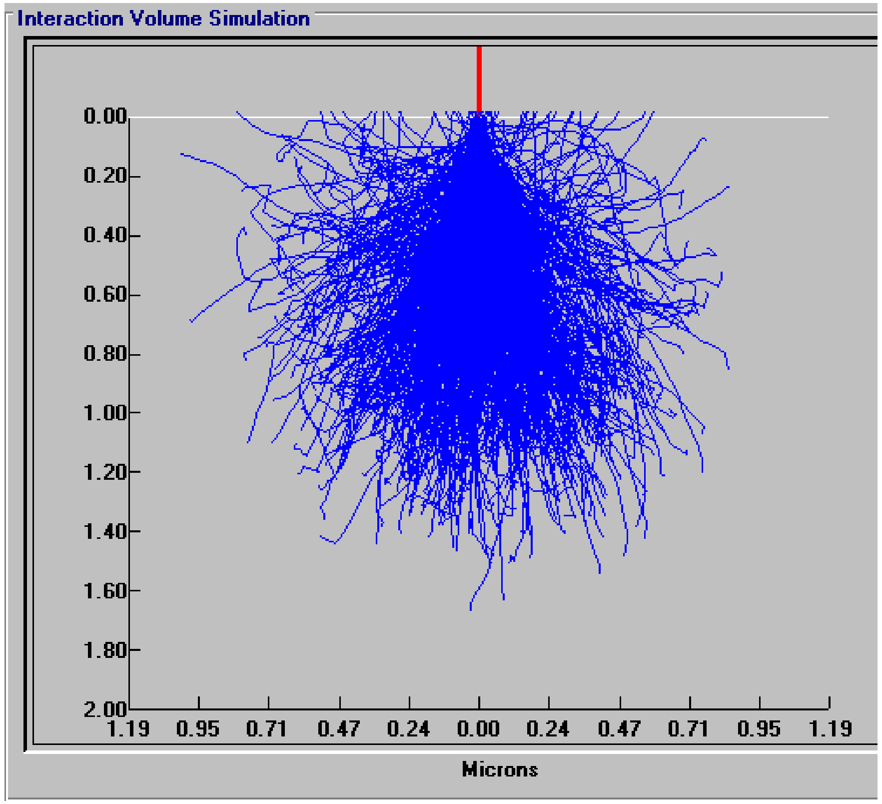
Scanning Electron Microscopy (SEM)

Energy Dispersive X-ray Spectroscopy (EDX)

Focused Ion Beam (FIB)

SEM: Principle

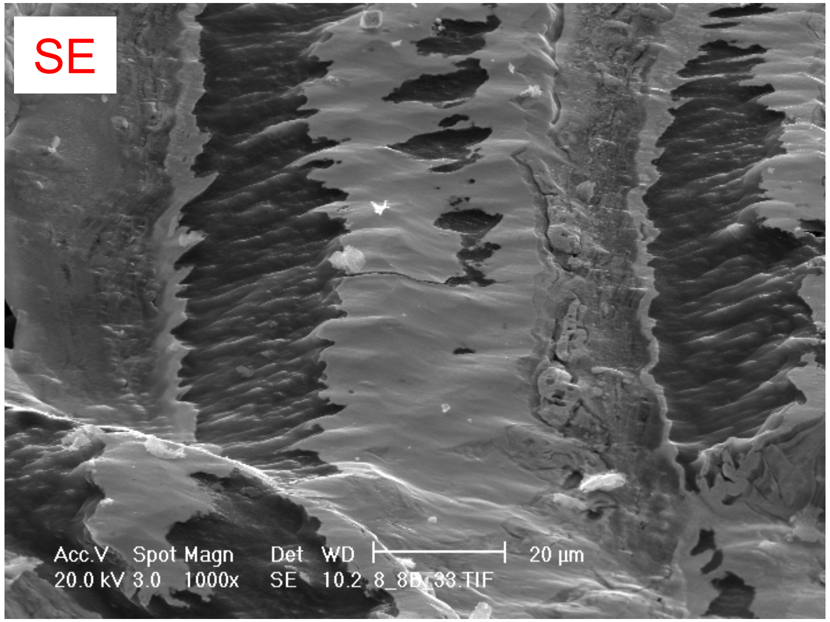


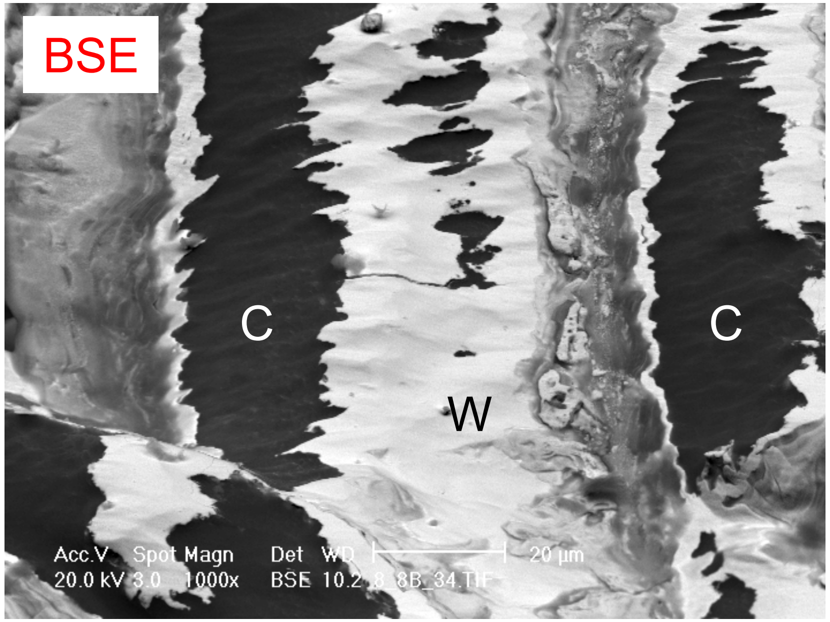


Monte-Carlo-Simulation, 10 keV e^- in C

- **Secondary electrons:**
  Originate few nm to few 10 nm from surface
- **Backscattered electrons:**
  Originate few 10 nm to few µm from surface
- **X-rays:**
  Originate ~µm from surface

SEM: Secondary and backscattered electrons



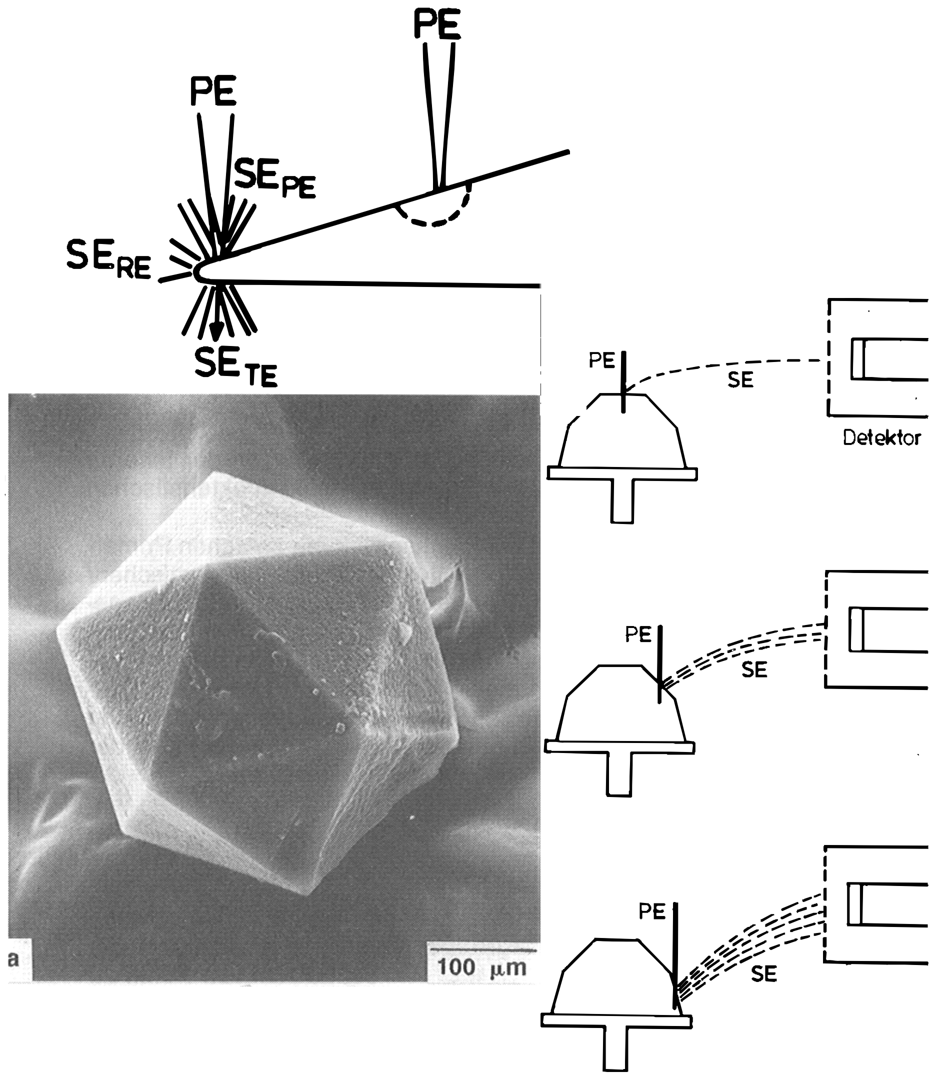


Example: 3 µm W layer on carbon fibre composite (CFC), after plasma exposure

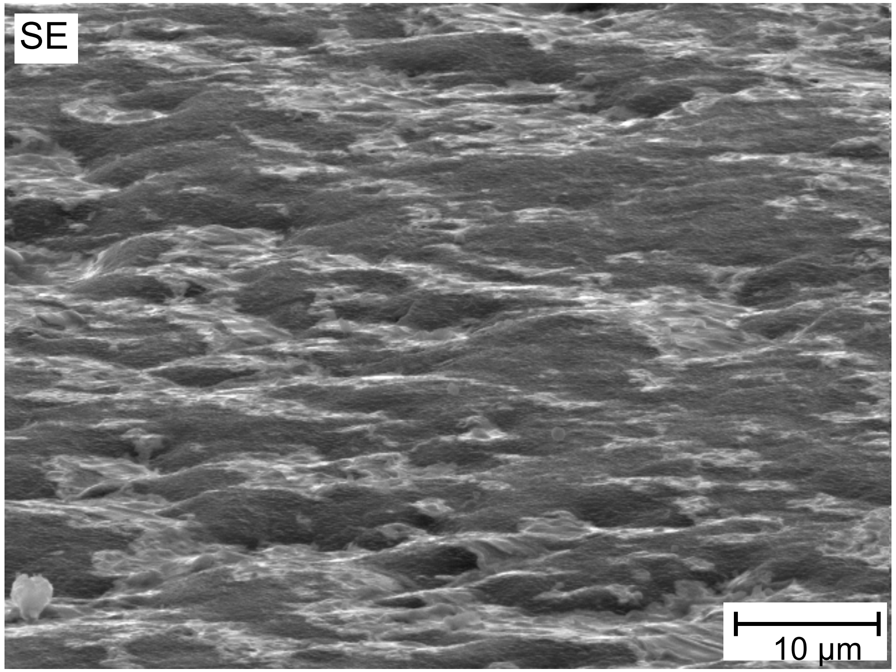
- **Secondary electrons:**
  Provide strong topographic contrast and some elemental contrast
  ⇒ Use to observe topography
- **Backscattered electrons:**
  Provide strong elemental contrast
  ⇒ Use to observe distribution of elements

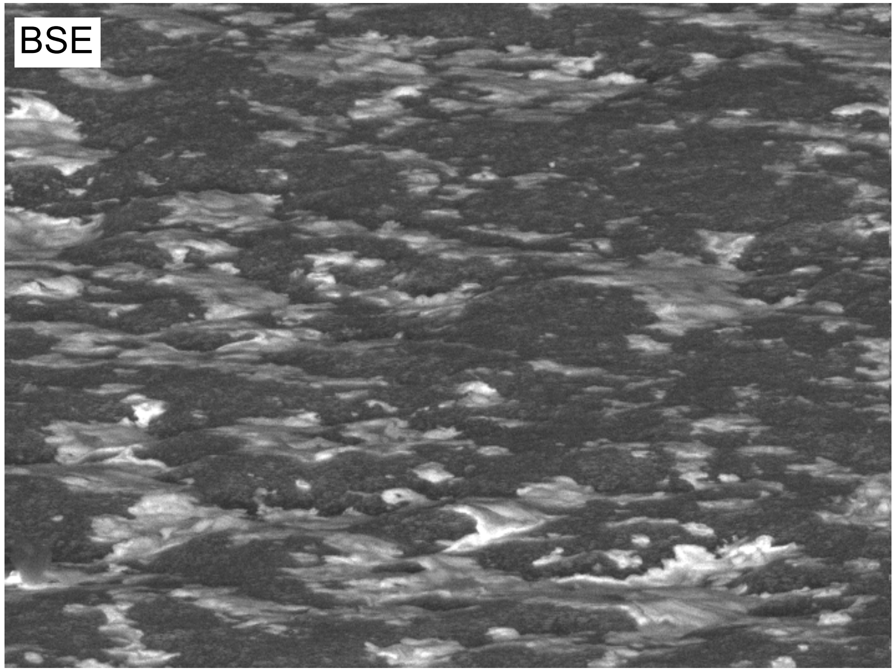
Topographic contrast by secondary electrons due to

- Edge effect
- Tilt angle effect



SEM: Complementary information





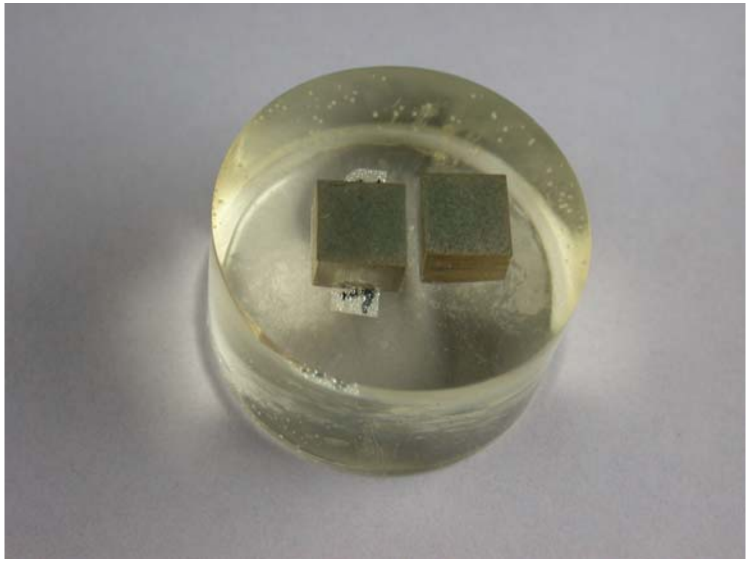
0.5 µm W layer on carbon, after plasma exposure

Complementary information provided by SEM:

- Lateral homogeneity of sample
  ⇒ Depth profiling possible or not?
- Qualitative information about sample roughness

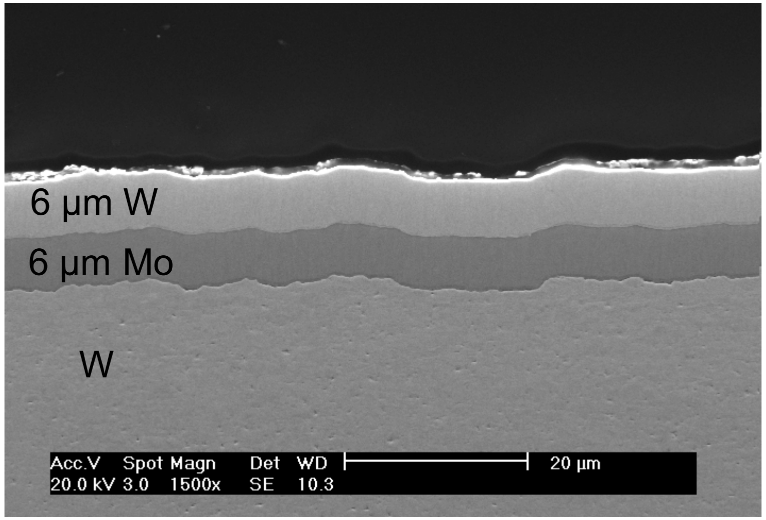
SEM: Metallographic cross-sectioning

- Samples are embedded in resin, cut and polished
- Cross section is observed with SEM
- Applicable for layers in ~µm range
  $\Rightarrow$ Use FIB for thinner layers



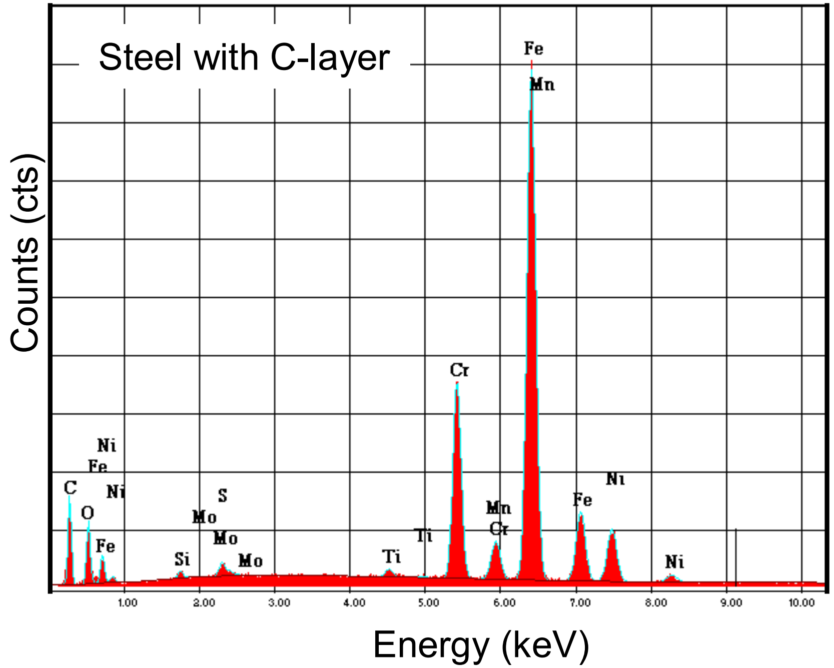
Complementary information provided by cross-sectioning:

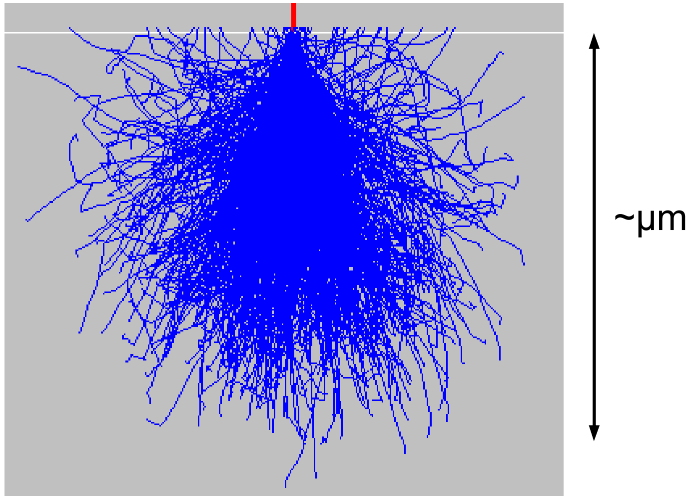
- (Semi-)quantitative information about layer roughness
- (Semi-)quantitative information about porosity
- Lateral homogeneity of sample
- SEM measures thickness in µm, IBA in at/cm^2
  $\Rightarrow$ Combination measures density



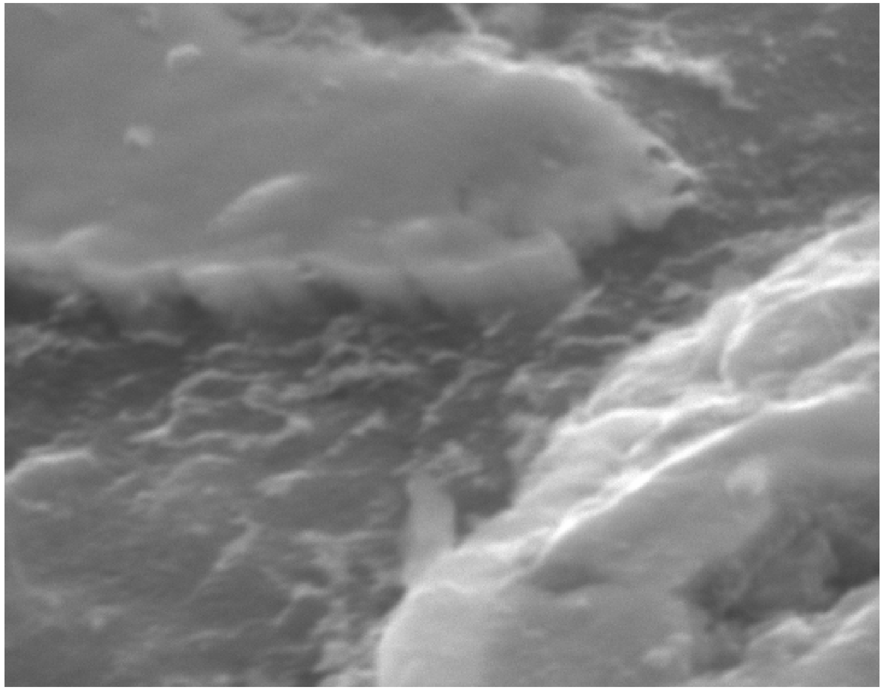
EDX: Principle

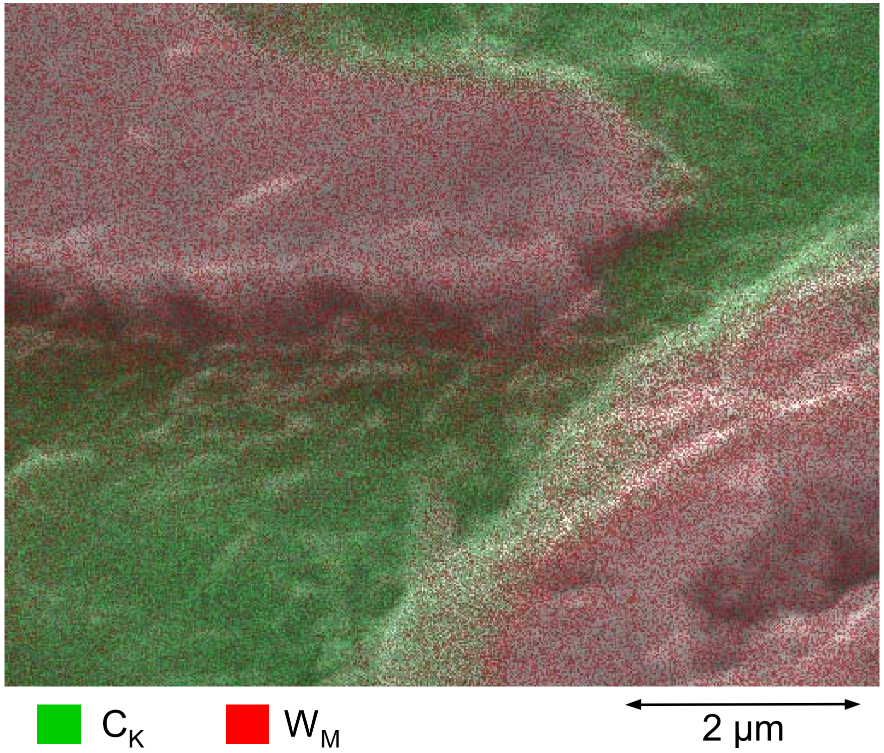
- Characteristic X-ray radiation
  ⇒ Identification of elements
- Qualitative analysis of composition, quantitative analysis difficult
- Low sensitivity for light elements due to absorption
- Large interaction volume of ~ten μm^3
  ⇒ Low depth resolution





EDX mapping



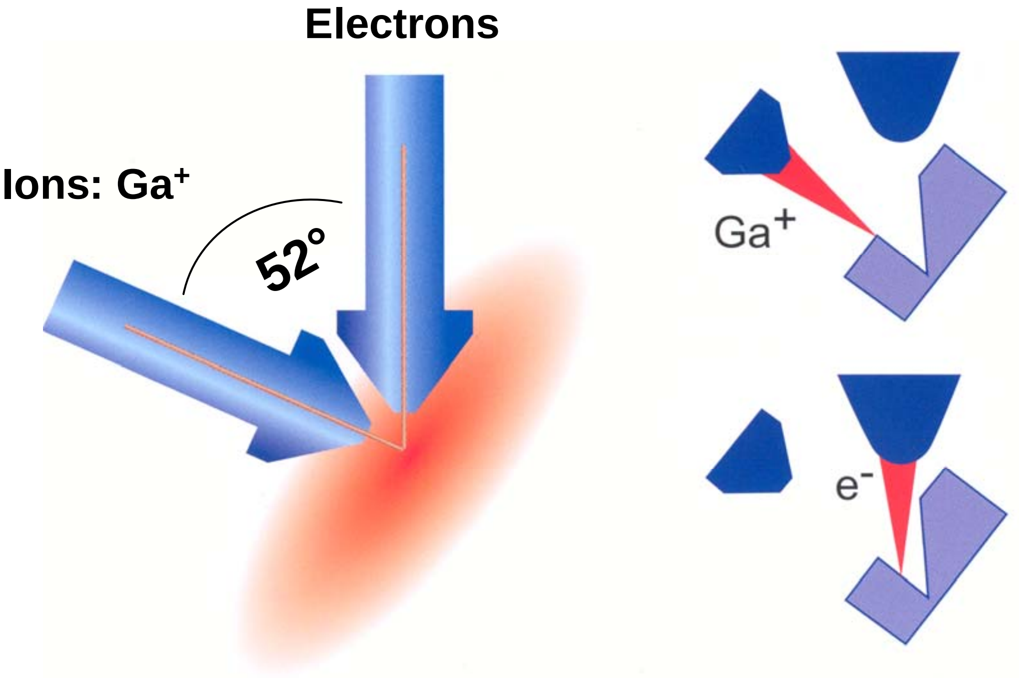


EDX mapping: Simultaneous detection of secondary electrons and X-rays

Complementary information provided by EDX mapping:

- Lateral distribution of elements
  $\Rightarrow$ Homogeneity of sample, clustering

FIB: Principle

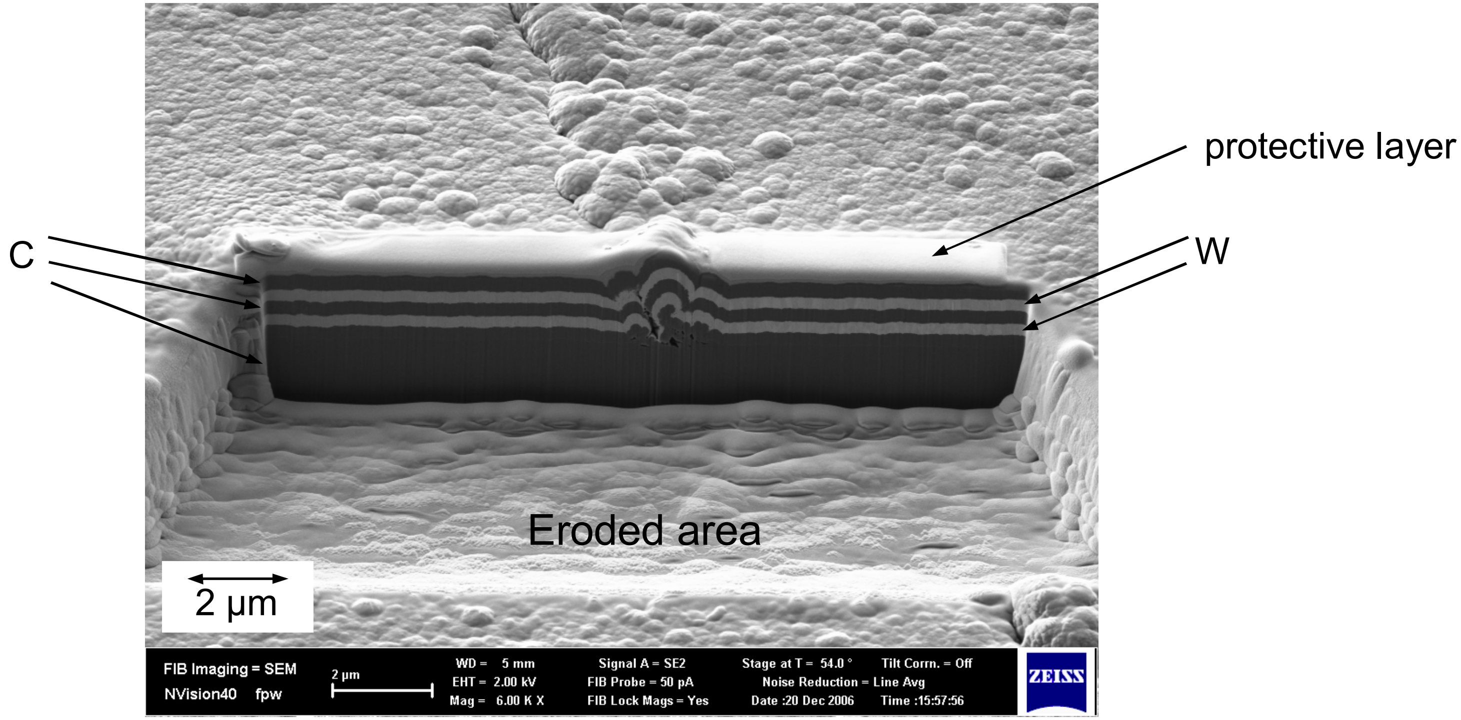


5-30 keV
5 nm
<20 nA

0.2-30 keV
1 nm

- Confocal ion and electron beams
  ⇒ ion beam for material removal by sputtering
  ⇒ electron beam for observation

FIB: Cross sectioning



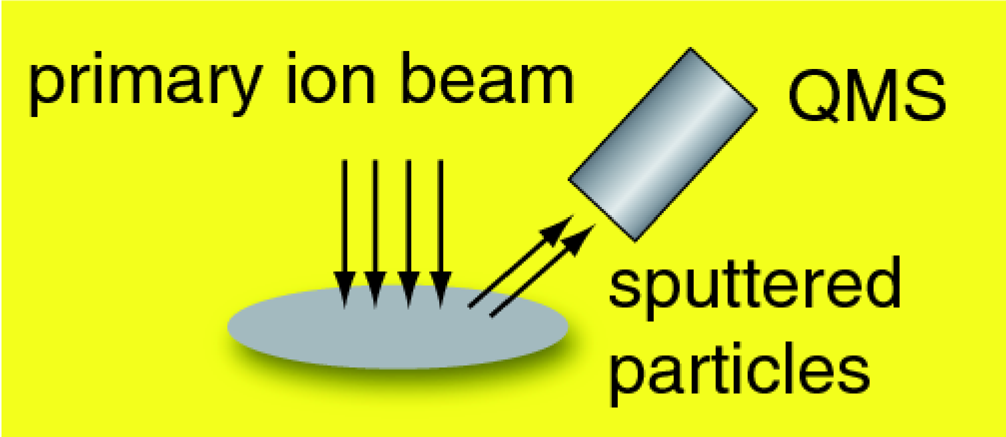
Complementary information provided by FIB:

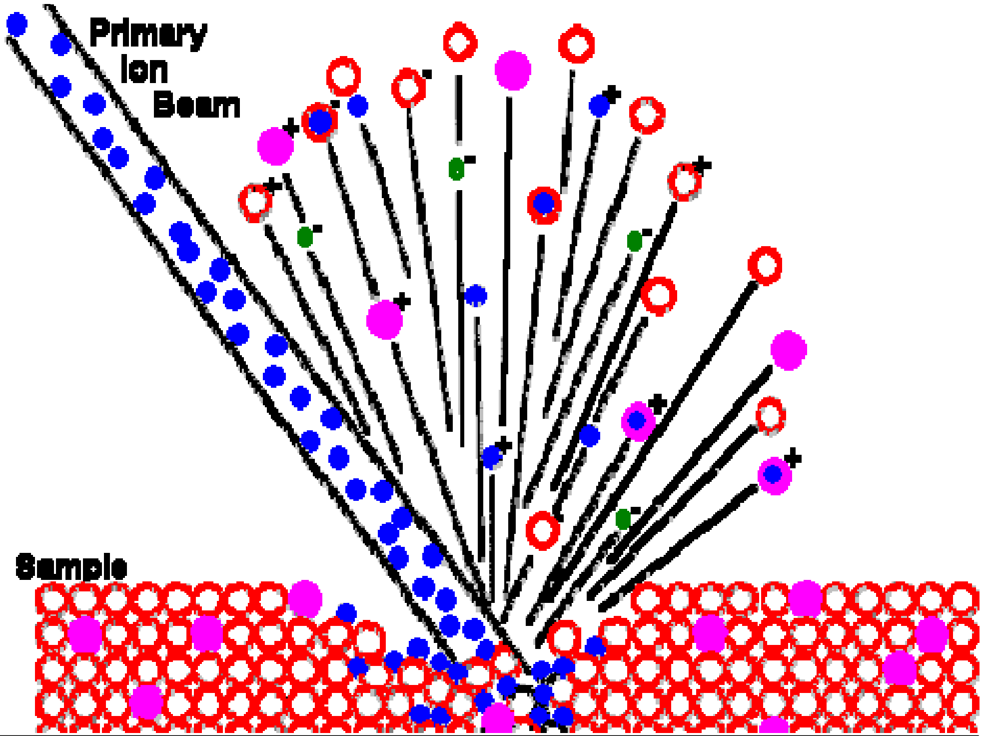
- (Semi-)quantitative information about layer roughness
- (Semi-)quantitative information about porosity
- Lateral homogeneity of sample
- SEM measures thickness in µm, IBA in at/cm^2 $\Rightarrow$ Combination measures density

Secondary Ion Mass Spectrometry (SIMS)

SIMS: Principle

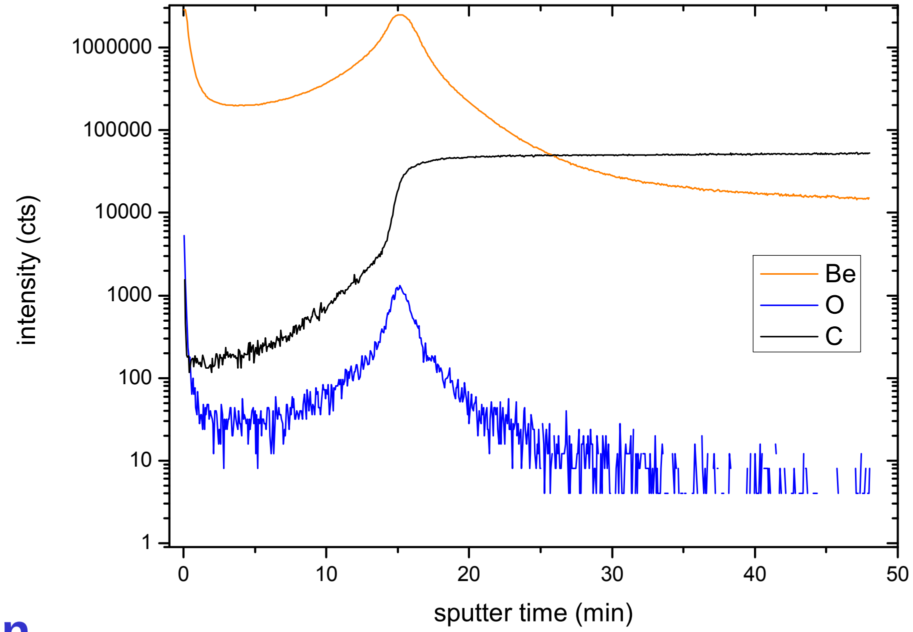
- Sputtering by primary ion beam
  Cs, O, Ar, Ga, 1 – 30 keV
- Detection of secondary ions
  with QMS, other methods possible
- Secondary positive ions are usually detected, neutrals or negative ions possible
- Sputter yields typically 5 – 15
- Sputter rate typically 0.5 – 5 nm/s
- High sensitivity:
  Detection limit 10^{12} – 10^{16} at./cm^3
- Good depth resolution ~ few nm





SIMS: Problems

- **Strong matrix effect on intensity**
  Signal intensity depends on surrounding matrix
  ⇒ Nonlinear dependence Concentration ↔ Intensity
  ⇒ Difficult quantification of concentration
- **Matrix effect on sputter yield**
  ⇒ Nonlinear dependence Sputter time ↔ Depth
  ⇒ Difficult quantification of depth scale for layered samples
- **Recoil implantation**
  ⇒ Tails in profiles, degradation of depth resolution
- **Side-wall effects**
  ⇒ Degradation of depth resolution
  Scanning of primary beam mandatory for reliable results
- **Surface roughness effects**

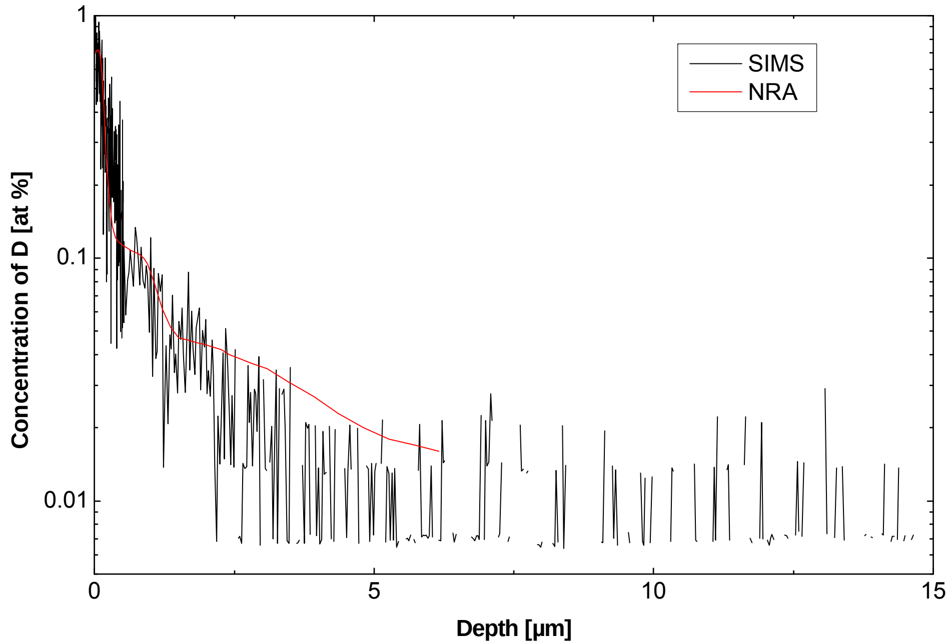


SIMS provides qualitative information

SIMS: Applications

SIMS can be applied successfully for depth profiling of trace elements in a homogeneous matrix

- Calibration of depth scale by measuring crater depth with profiler
- Calibration of concentration by
  - Calibration samples
  - Comparison to ion beam analysis



Example: Implantation and diffusion of D in W
SIMS concentration calibrated by NRA

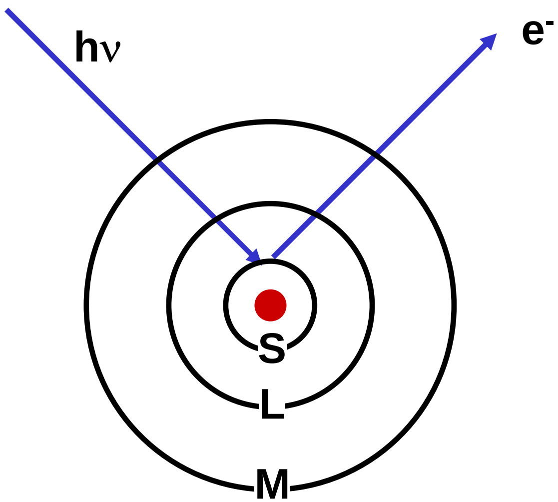
Complementary information provided by SIMS:

- Qualitative information about all elements, including trace elements
- Depth profiling of trace elements with low concentrations below detection limit of IBA
- Depth profiling until large depths (few 10 µm – 200 µm)

X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS)

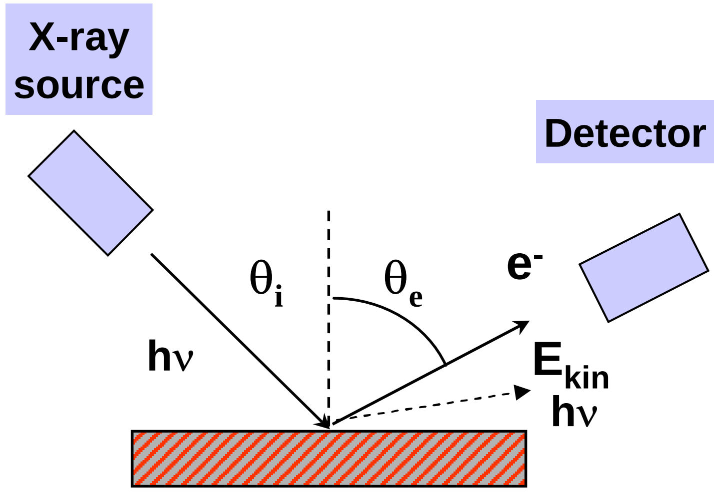
Principle



Photoelectric effect

(Einstein, Nobel prize 1921)

Measurement



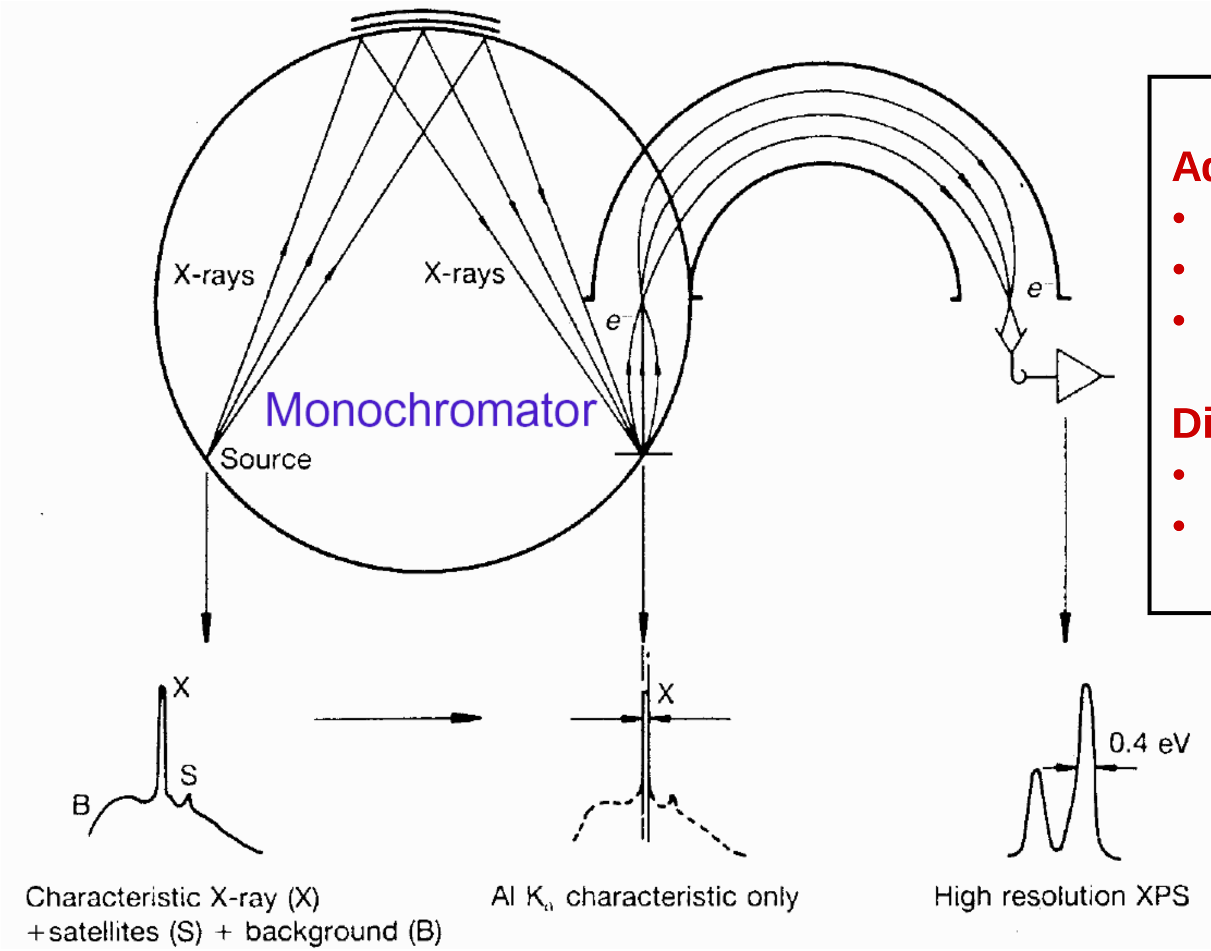
Excitation

- 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

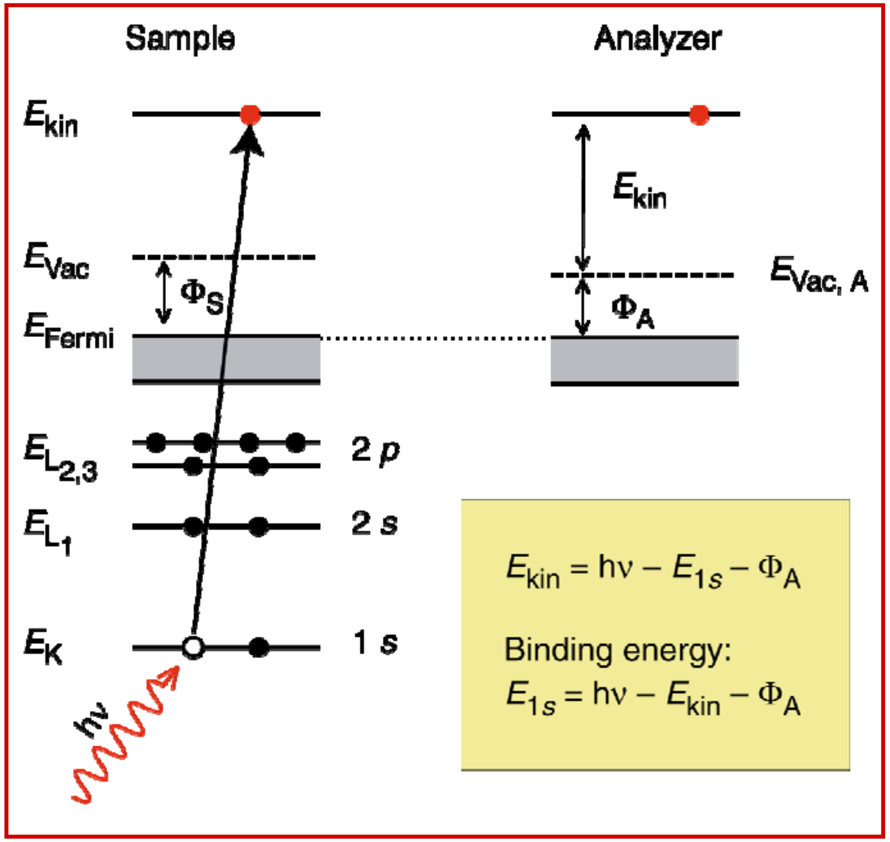
Laboratory X-ray source with monochromator



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

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

XPS – Principle and method



Binding energy

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

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

→ element-specific

Chemical Shift

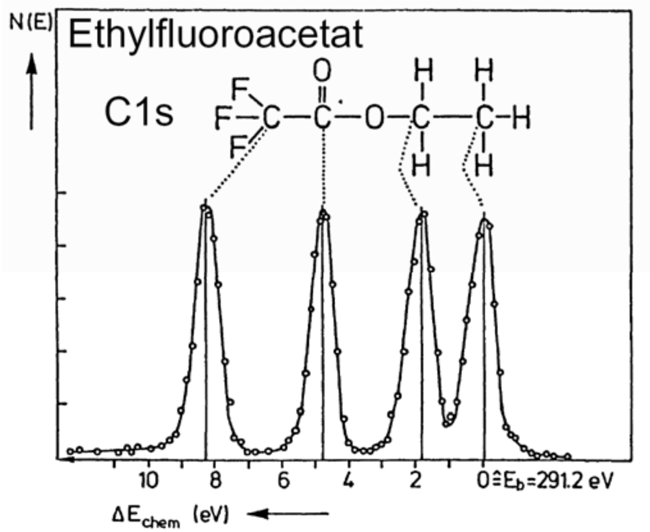
Shift of E_B by up to several eV due to charge state of the atom

→ chemical state

Electron Spectroscopy for Chemical Analysis

(K. Siegbahn, Nobel prize 1981)

XPS – Chemical shift

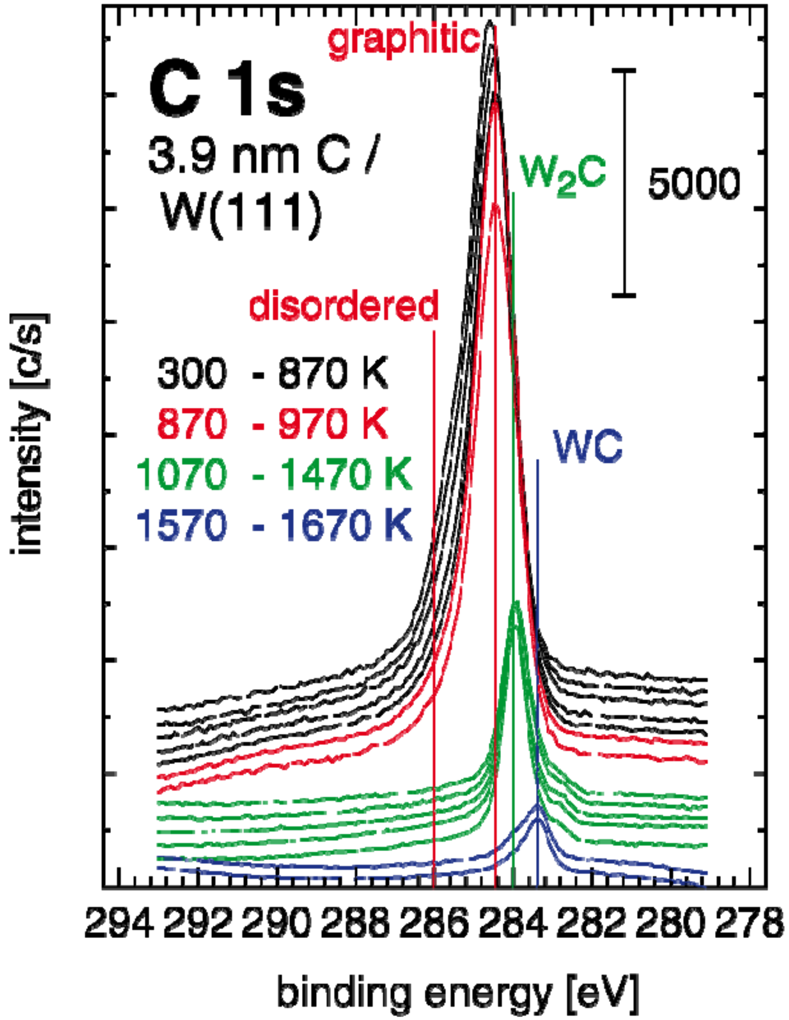


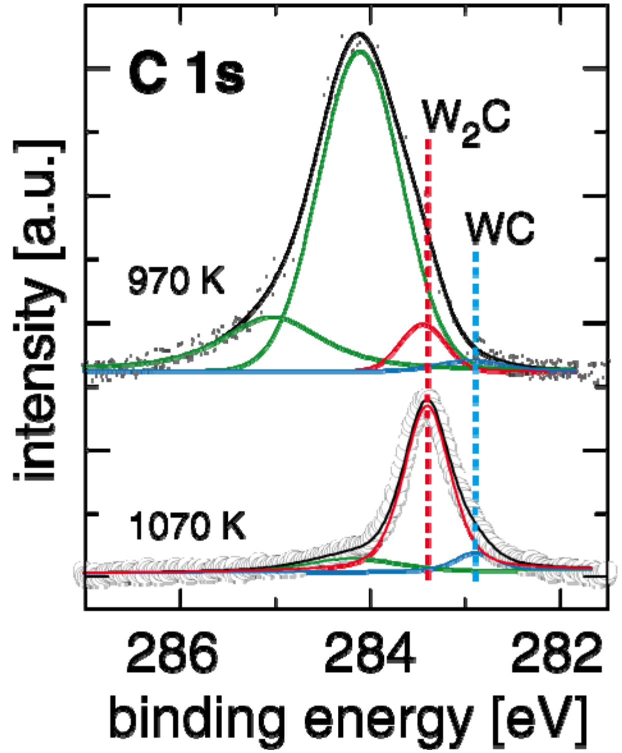
Chemical shift

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

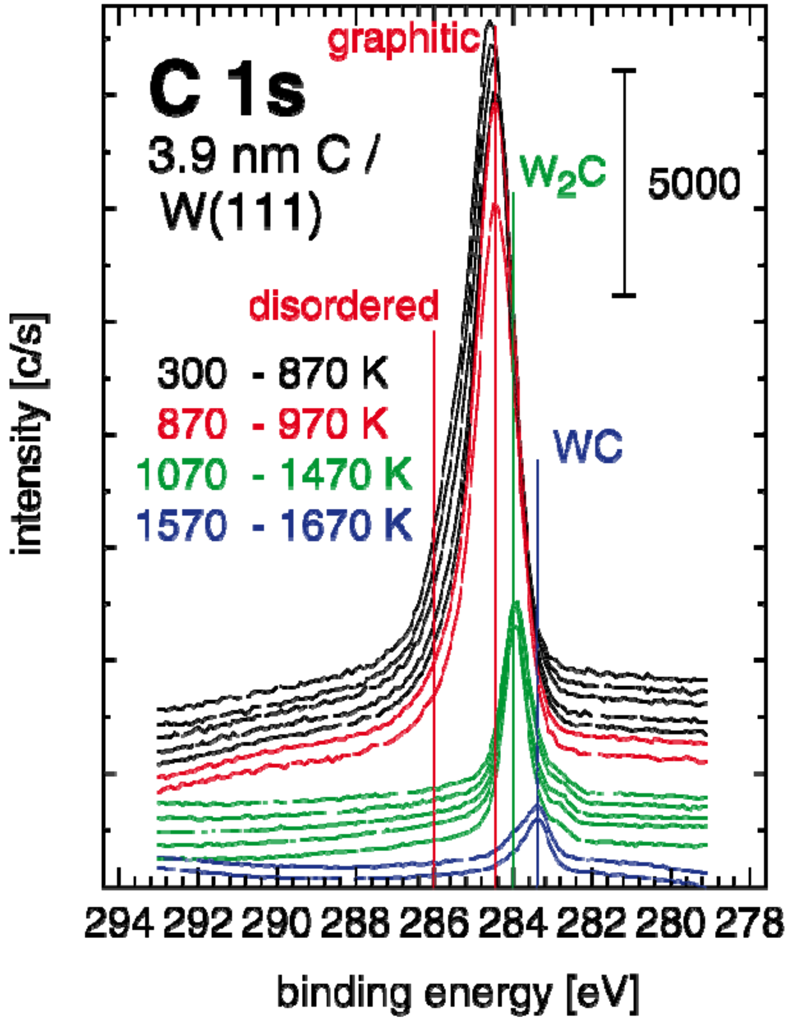
⇒ **Information about chemical binding**

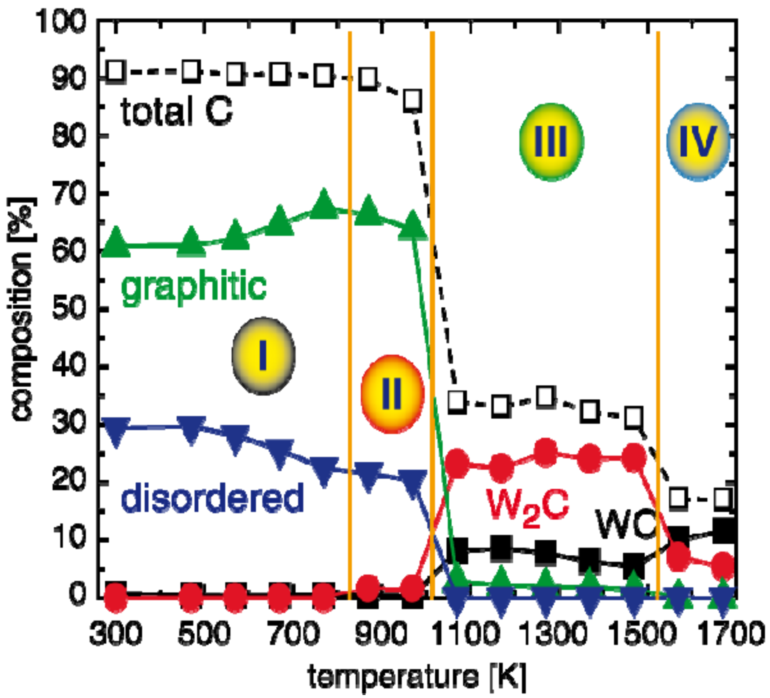
Tungsten carbide phase formation





Tungsten carbide phase formation

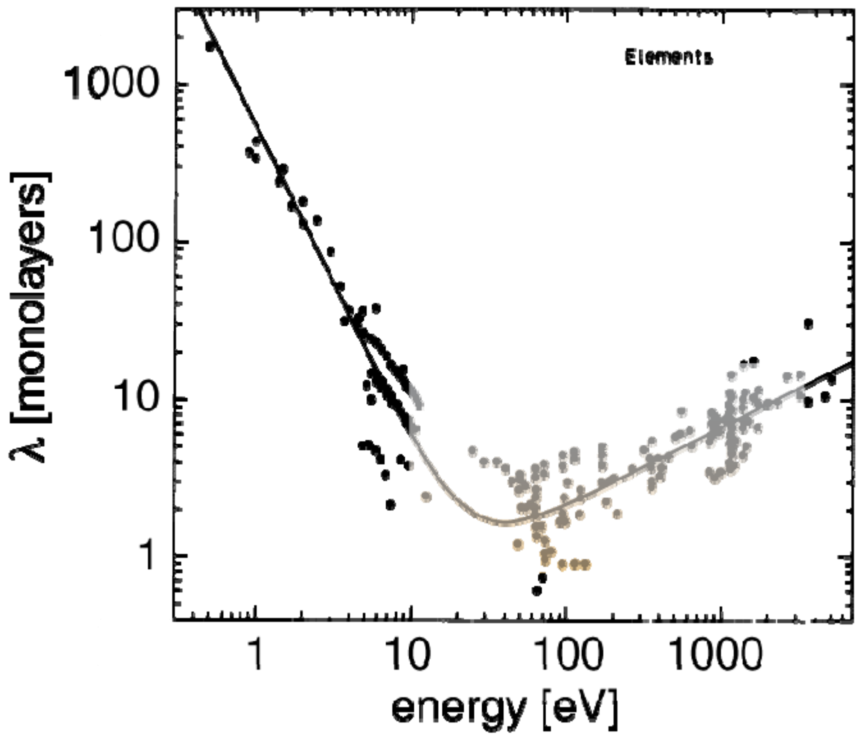




Carbide formation:

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

Information depth in electron spectroscopies

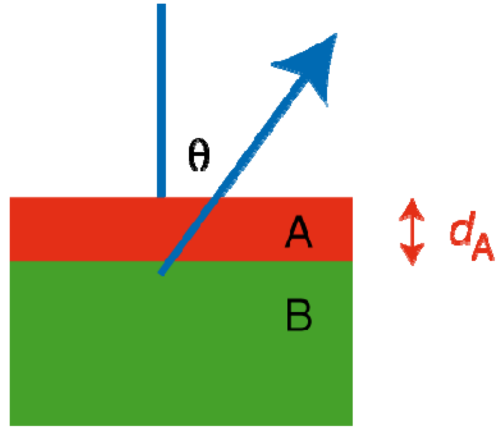


Seah, Dench (1979)

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

a: atom diameter from density (in nm)

E: electron kinetic energy (in eV)



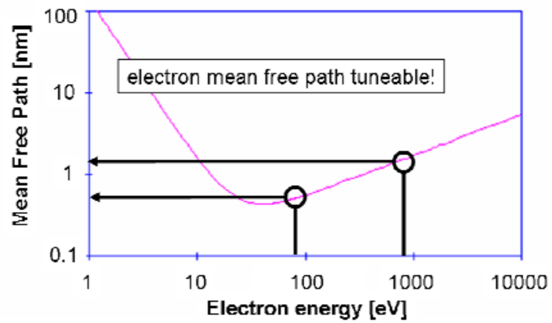
Quantification:

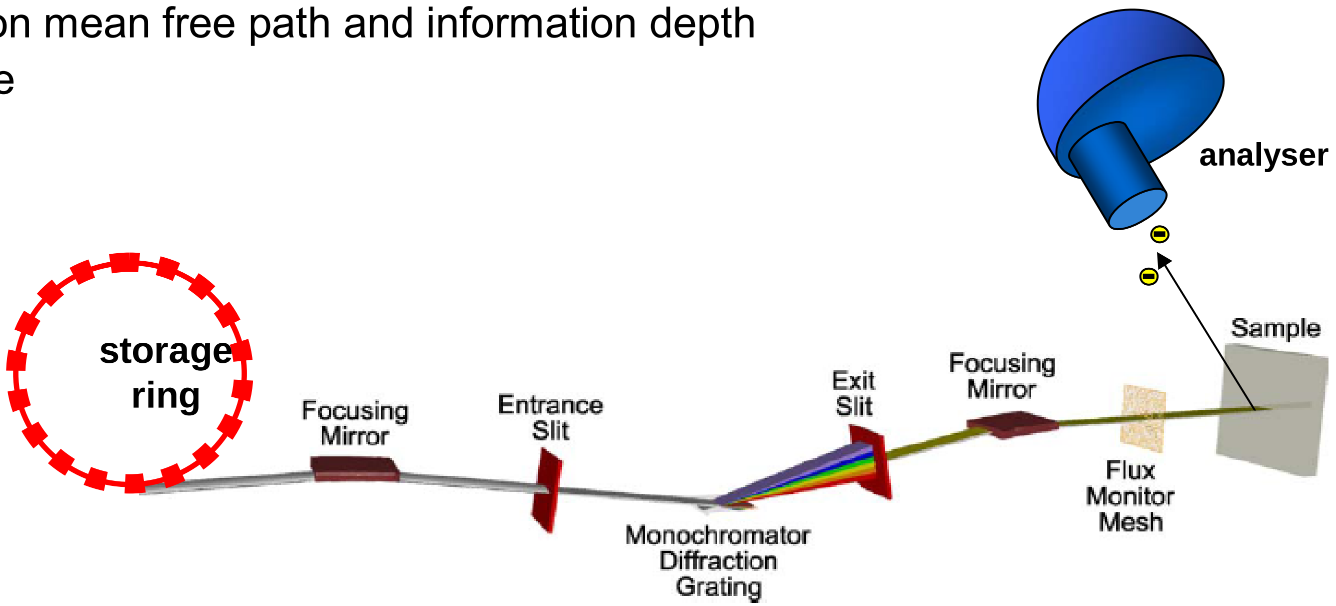
$I_B = I_B^{\infty} \exp(-d_A / \lambda_A \cos\theta)$

Depth profiling with XPS

- **Sputter-XPS:**
  Sputtering combined with XPS
  Problem: Collision cascades lead
  to mixing and may result in formation of new phases

- **Synchrotron radiation:**
  Electron mean free path and information depth
  tunable





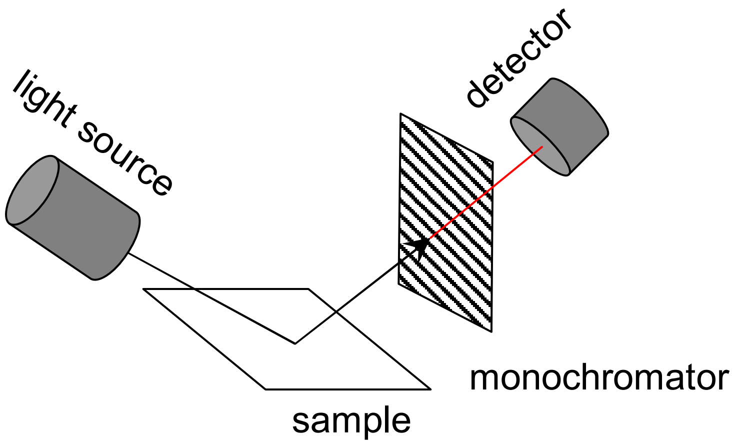
Complementary information provided by XPS:

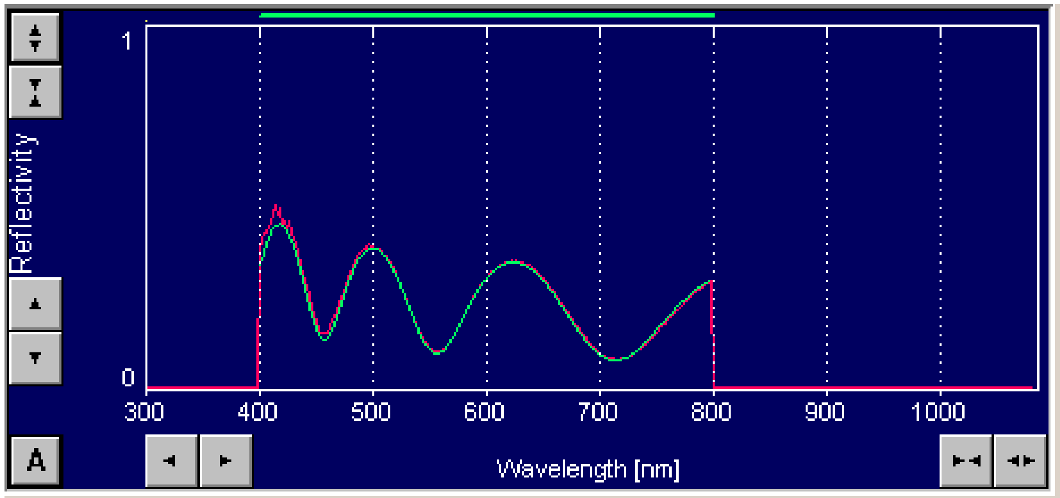
- Chemical binding state of elements

Ellipsometry / Reflectometry

Principle of Reflectometry

detection of the intensity of light as a function of *wavelength*





Example: SiO_2

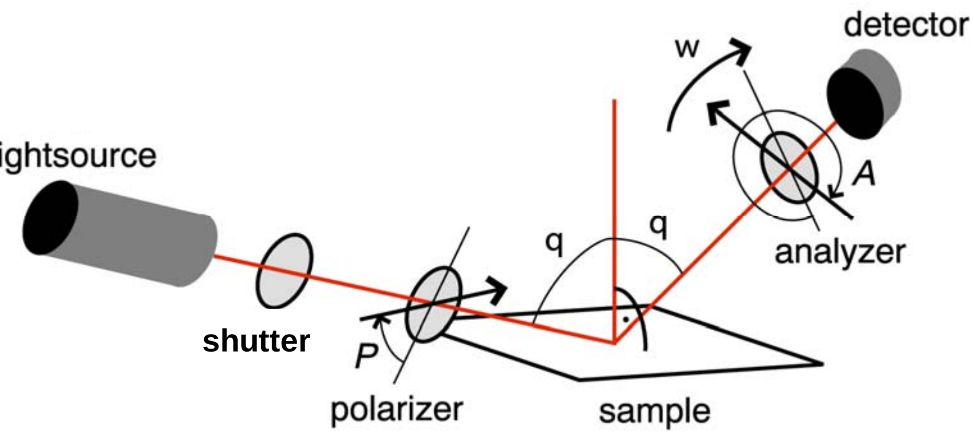
Fitting the measurement with known dispersion relation (Cauchy formula)

⇒ **Film thickness * refractive index**

Complementary information provided by reflectometry:

- Film thickness (in µm) * refractive index

detection of the change of polarization of *linearly polarized light* due to the reflection at the sample surface



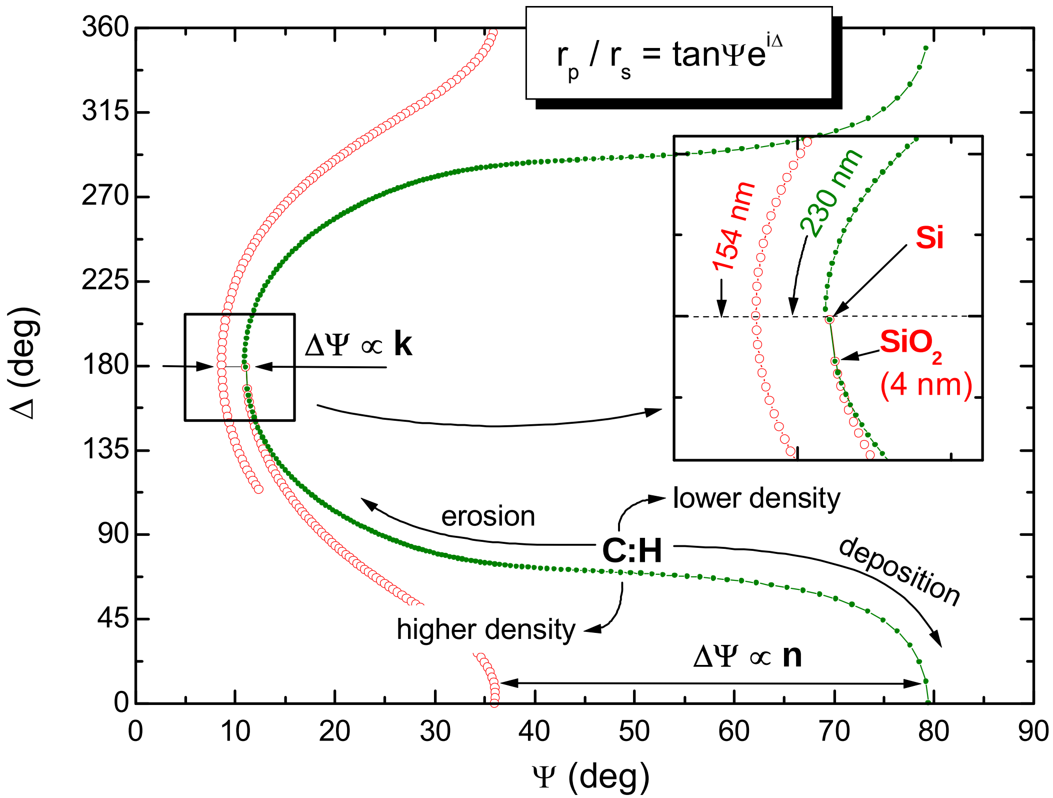
$$\frac{r_p}{r_s} = \tan\Psi \cdot e^{i\Delta}.$$

r_p: Reflection parallel
r_s: Reflection perpendicular

For a single measurement result is ambiguous

Layer growth in ΨΔ plane

- Accuracy 0.01 nm (sub-monolayer)
- Very cheap and simple method



Complementary information provided by ellipsometry:

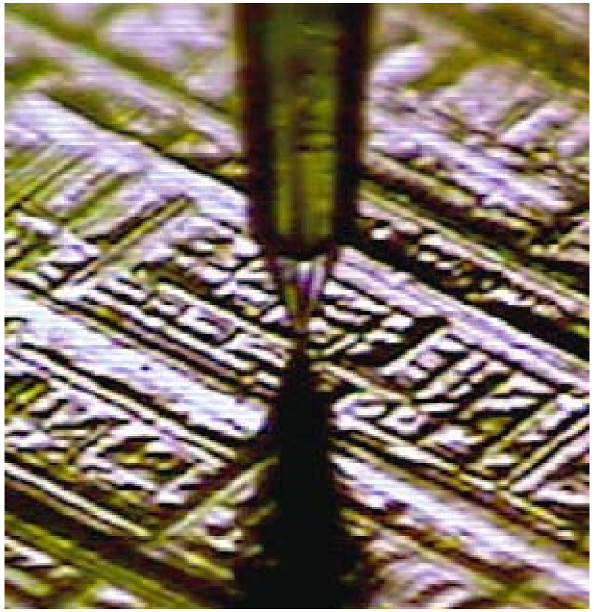
- Film thickness (in μm) * refractive index

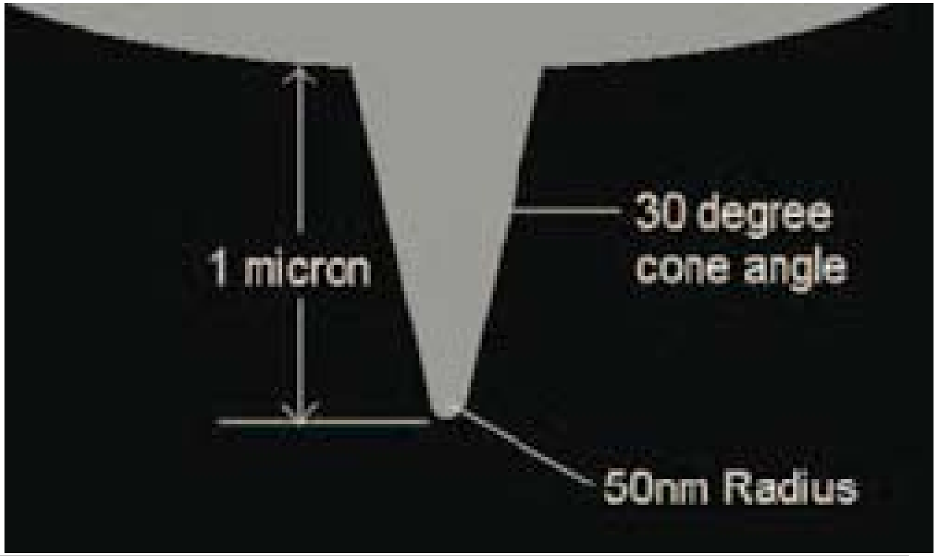
Profilometry

Atomic Force Microscopy (AFM)

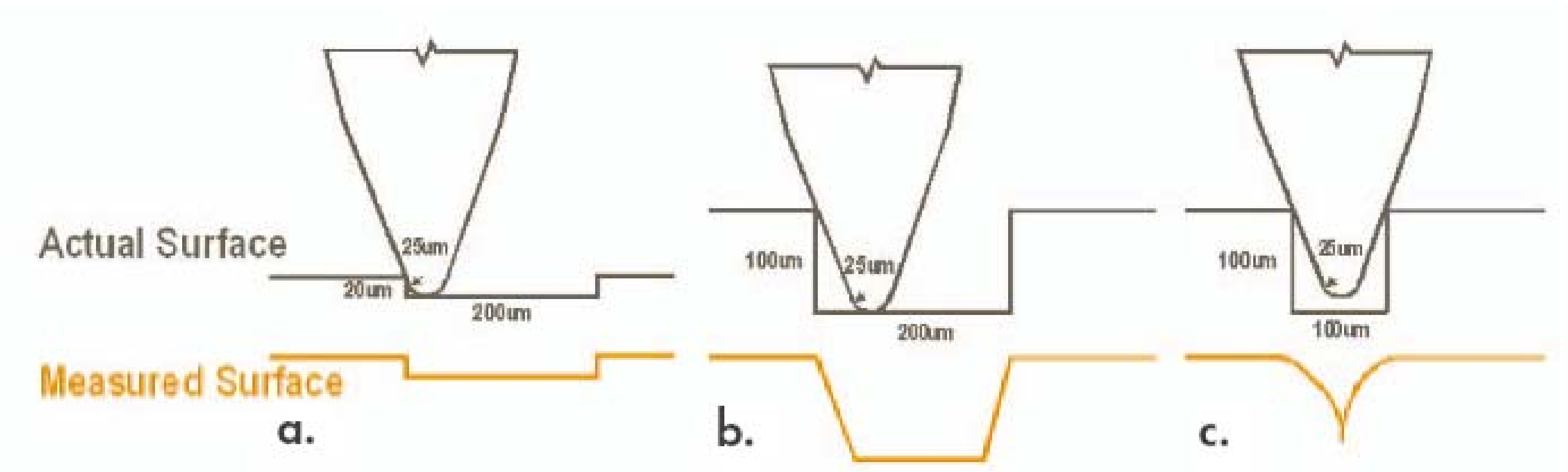
Profilometry: Principle

- Stylus moves with constant stylus force along the surface
- Deflection of stylus gives an image of the surface
- Optical (non-contact) profilers also available
- Vertical resolution:
  Profiler ≤ 5 nm
  AFM 0.01 nm



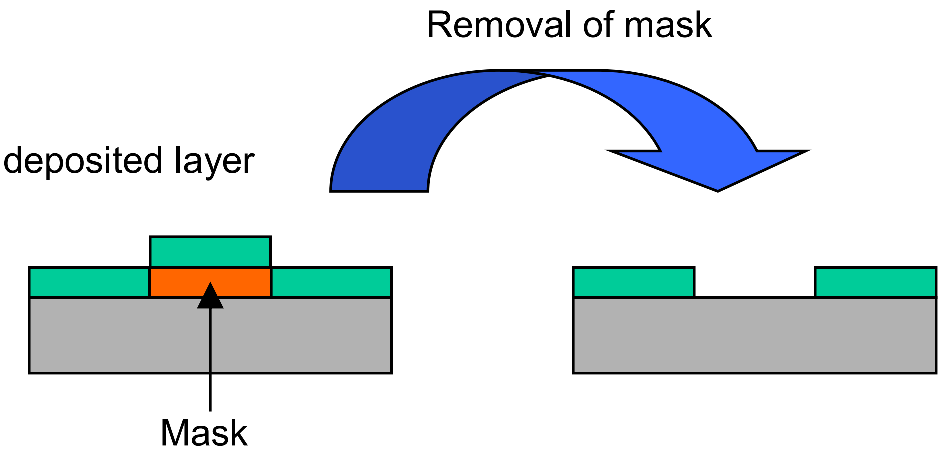


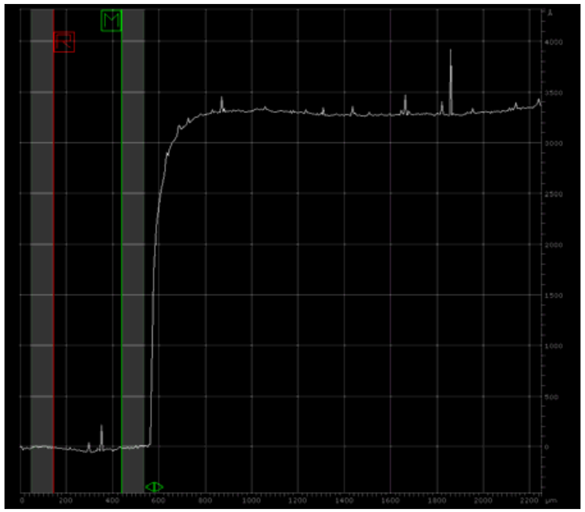
Profilometry: Influence of stylus



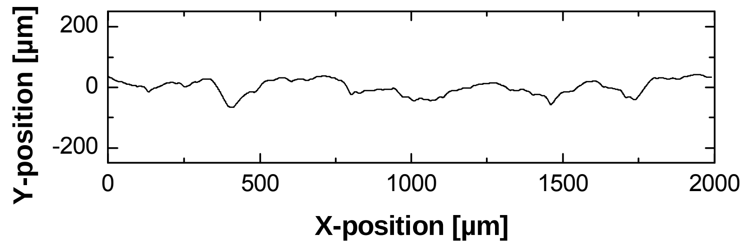
Available stylus radii: 50 nm - 25 µm

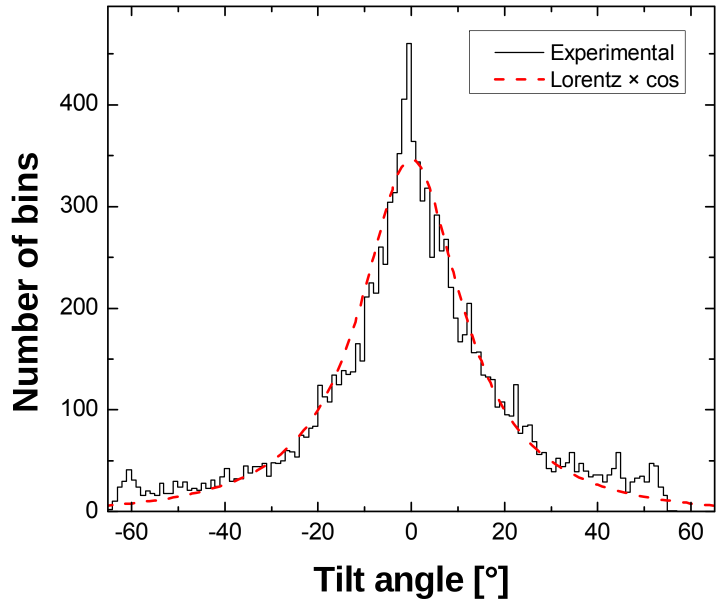
Layer thickness and roughness measurement





Example: Step height measurement

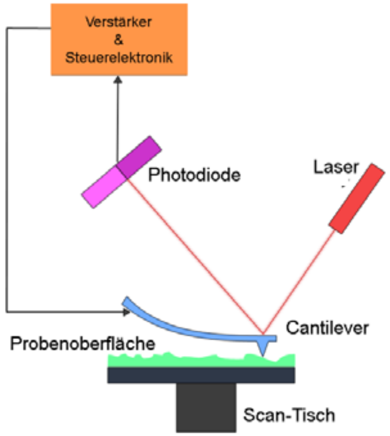


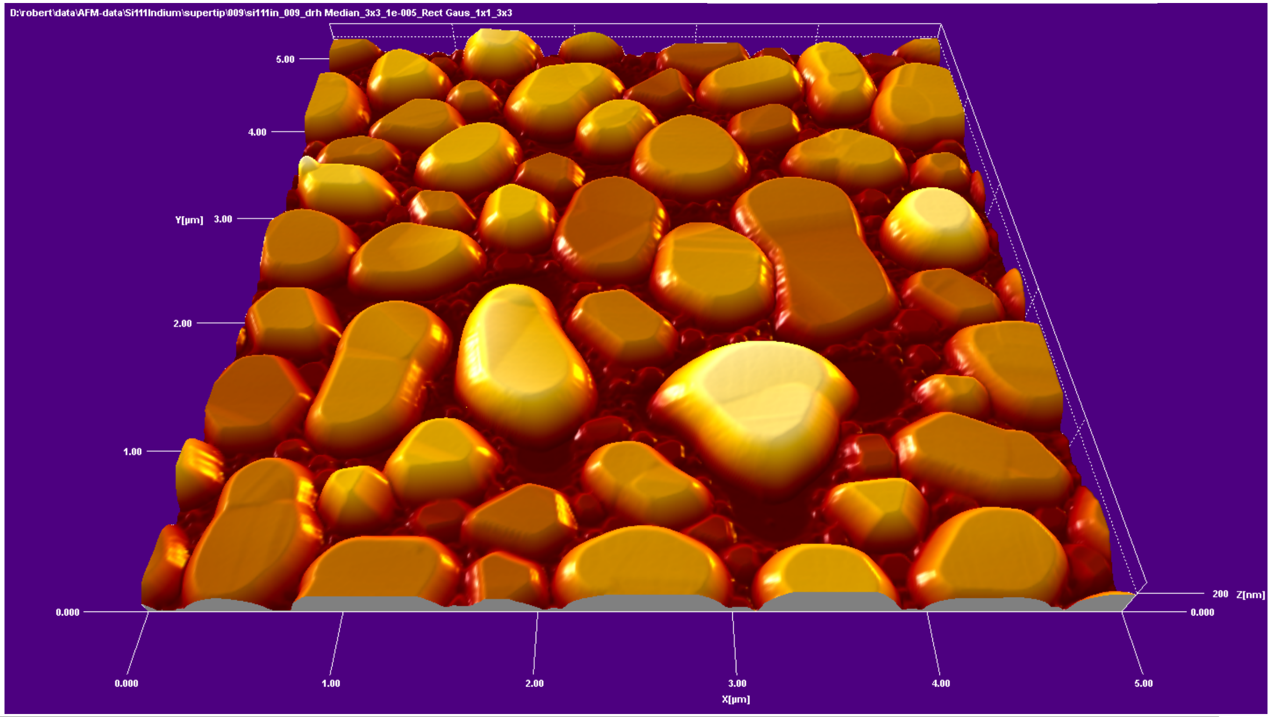


AFM

Complementary information provided by Profilometry / AFM:

- Layer thickness (in µm) ⇒ Density in combination with IBA
- Quantitative measurement of surface roughness





Example: In on Si

Summary

Technique	Complementary information
SEM, EDX	Lateral distribution of elements Roughness (qualitative)
SEM + Cross-sectioning **FIB**	Layer thickness (µm) Layer roughness Porosity Lateral distribution of elements
SIMS	Depth profile of trace elements (qualitative) Depth profile until large depths
XPS	Chemical binding
Ellipsometry **Reflectometry**	Layer thickness (µm)* refractive index
Profilometry **AFM**	Layer thickness (µm) Roughness