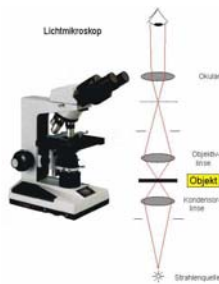


Microscopes

For the visualisation of millimeter to nanometer structures

Light Microscope

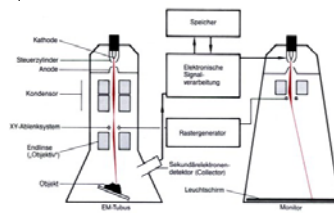
since about 1750



geometric optics
resolution about 500 nm
Light-Intensity contrast

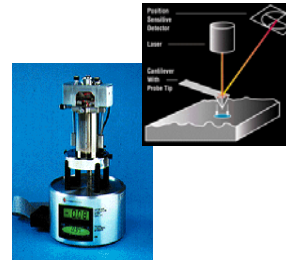
Electron Microscope (SEM) Scanning Probe Microscope

since about 1955



E-beam raster-scan
resolution 5 nm
secondary electron counting
projection image

since about 1981



deflection sensor
piezo-scan
resolution 0.2 nm
3d topographic map

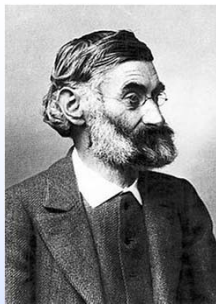
N.B.

Ein Bild sagt mehr als tausend Worte (Daten)

Es wird oft behauptet, es handele sich um ein [chinesisches](#) Sprichwort. Auch [Konfuzius](#) wird oft als Urheber genannt. Der erste gedruckte Nachweis findet sich jedoch im englischen Sprachraum. Am 8. Dezember [1921](#) veröffentlichte Fred R. Barnard in der Zeitschrift "Printers' Ink" eine Anzeige mit dem [Slogan](#) "One Look is Worth A Thousand Words." Es handelte sich um eine [Fachzeitschrift](#) der [Werbebranche](#). Die Anzeige warb für den Gebrauch von Bildern in Werbeaufdrucken auf Autos. Am 10. März [1927](#) erschien eine zweite Anzeige mit der Phrase "One Picture is Worth Ten Thousand Words". Dort wird behauptet, es handele sich um ein chinesisches Sprichwort. Das Buch "The Home Book of Proverbs, Maxims, and Familiar Phrases" zitiert den Autor Barnard, der sagte, er habe den Slogan "als chinesisches Sprichwort betitelt, damit die Leute es ernst nehmen".

**Teil 1:
Sekundär Elektronenmikroskopie
(SEM)**

4



Ernst Karl Abbe
(1840 – 1905)

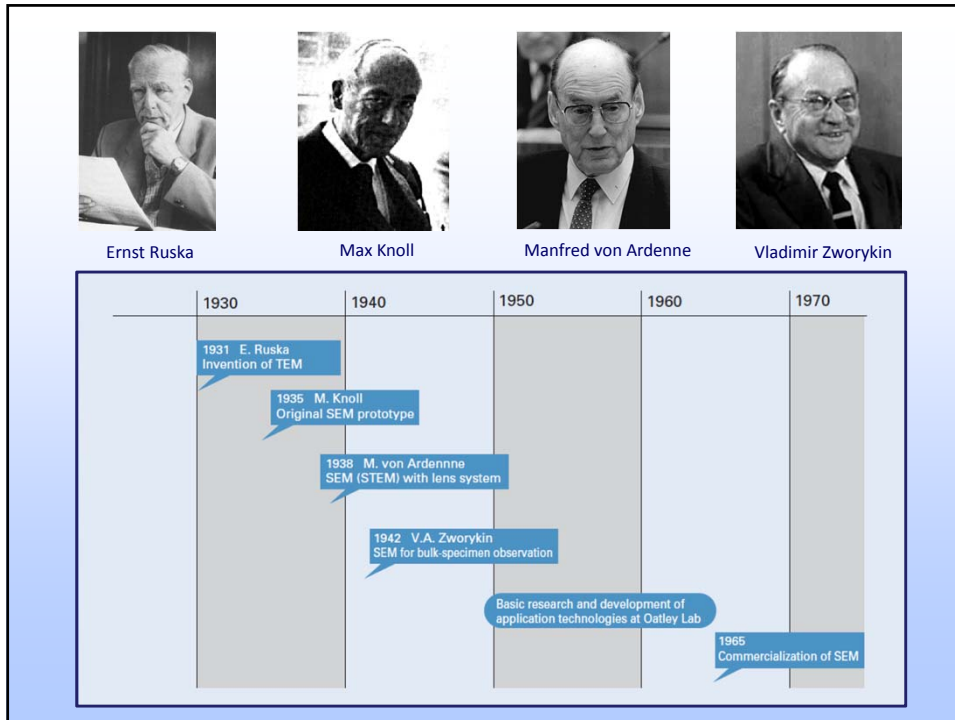
$$d = \frac{\lambda}{2n \sin \theta}$$

$$\lambda = \frac{1.22}{E^{1/2}}$$

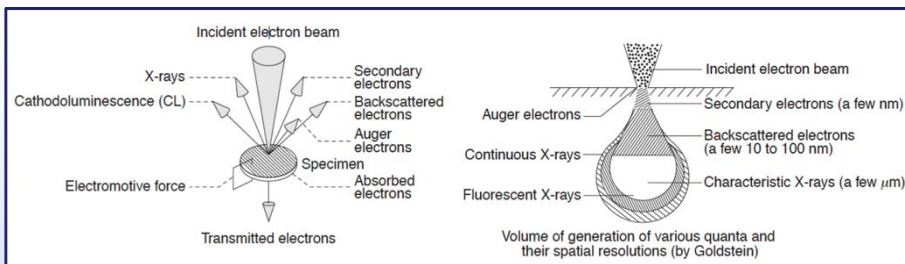


Louis-Victor de Broglie
(1892 – 1987)

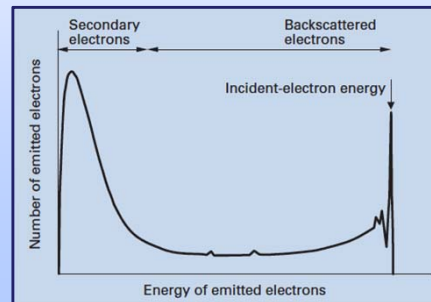
5



Sekundär Elektronenmikroskopie



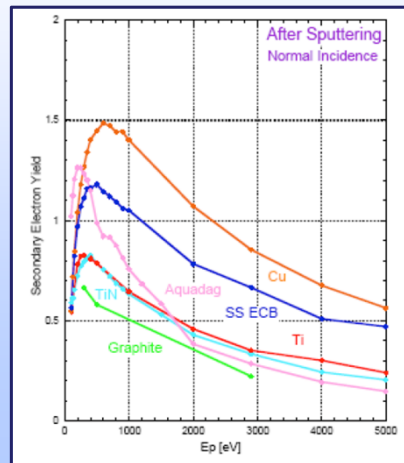
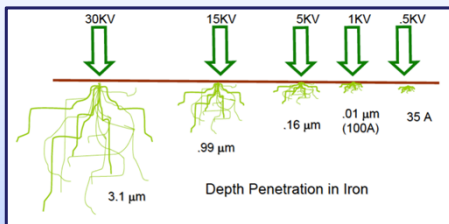
Sekundärelektronen: < 50 eV
Rückstreuelektronen: < 40 keV



Eindringtiefe und Yield

$$R = \frac{0.0276 \times A \times E^{1.67}}{Z^{0.89} \rho} [\mu\text{m}]$$

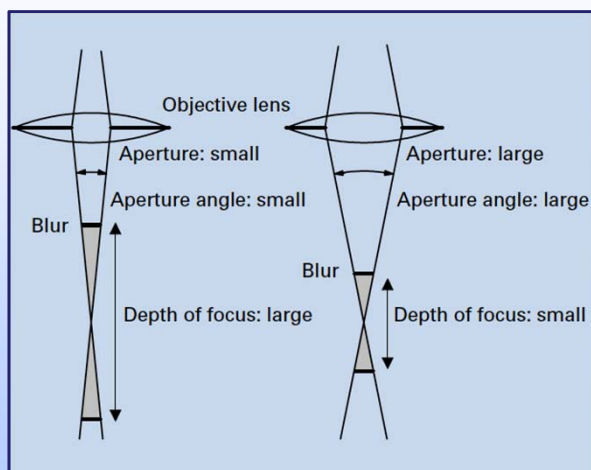
Kanaya-Okayama Formel für Eindringtiefe



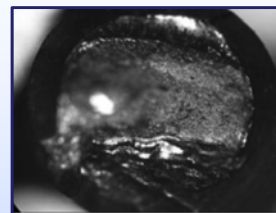
SE Yield

$$\gamma = \frac{SE_{out}}{PE_{in}}$$

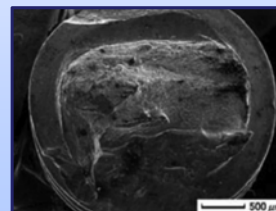
Fokustiefe



Aufnahme mit OM

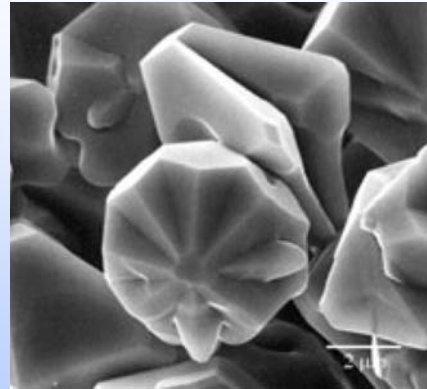
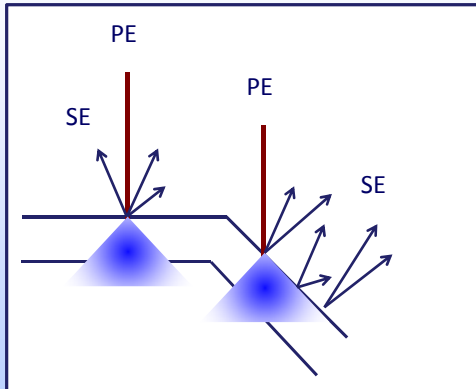


Aufnahme mit SEM



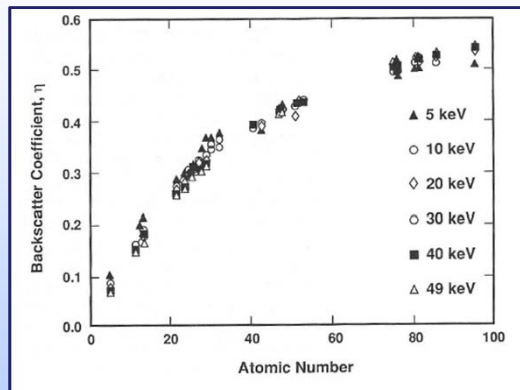
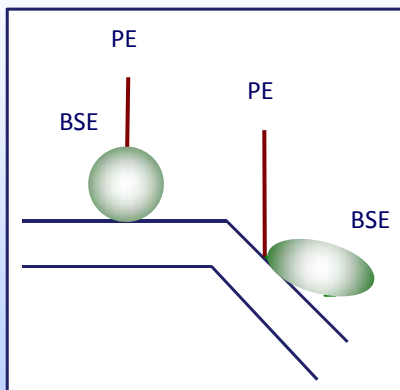
Bilder: JEOL, Scanning Electron Microscopy

Effekt der Topographie: SE



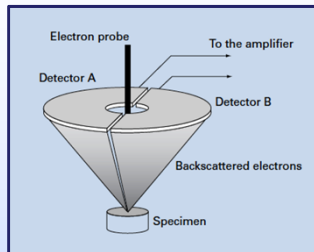
Tungsten Oxide, courtesy of JEOL

Effekt der Topographie und Z-Abhängigkeit: BSE

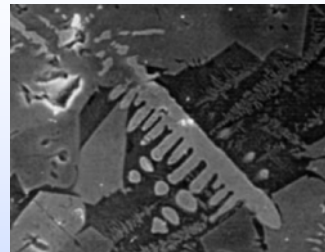


BSE Imaging

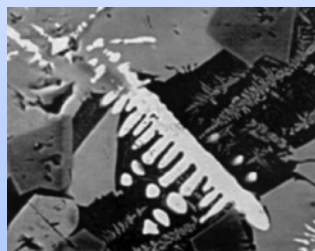
BSE Detektor



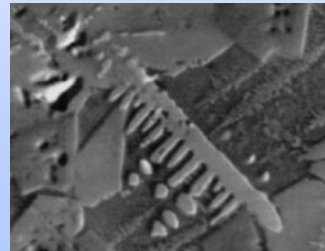
SEM Image



BSE Image (Zusammensetzung)

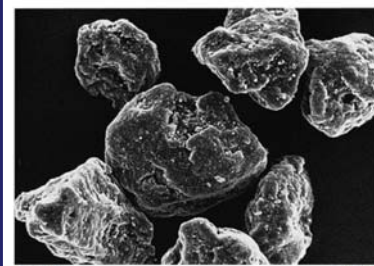
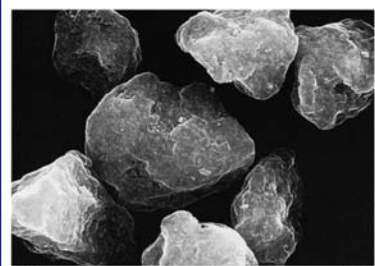
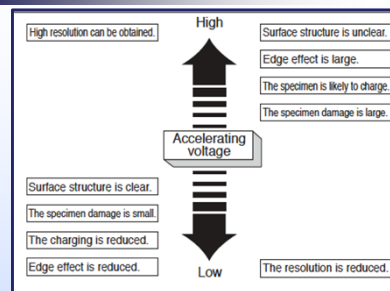
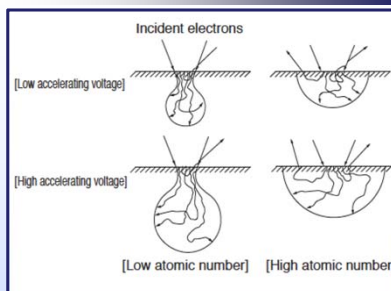


BSE Image (Topographie)



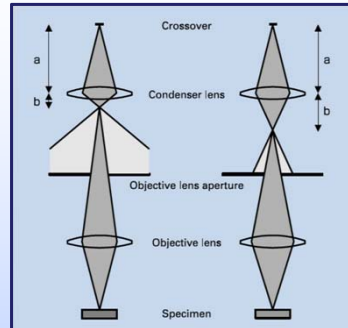
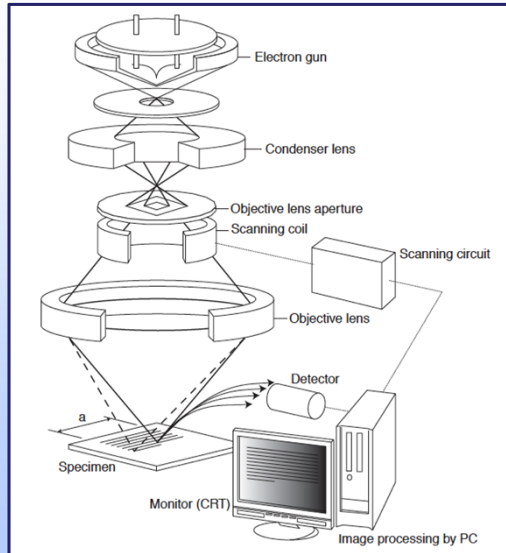
Bilder: JEOL, Scanning Electron Microscopy

Beschleunigungsspannung

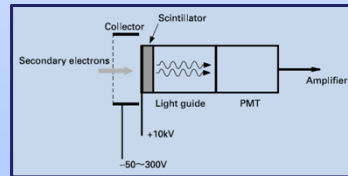


Bilder: JEOL, Scanning Electron Microscopy

SEM Aufbau



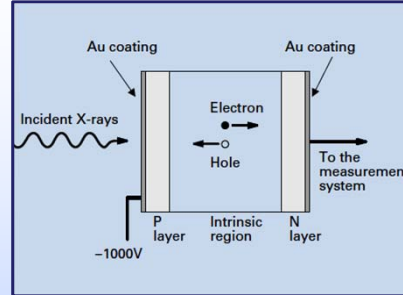
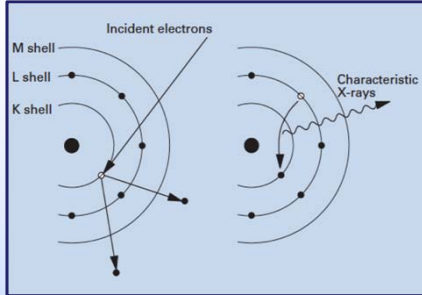
Everhart-Thornley Detektor



SEM Detektoren

Detector	Major Advantage or Uses
Secondary Electron (SED)	General Imaging
Backscattered Electron (BSE)	Difference in atomic number
Immersion Lens (in-lens)	Surface sensitive
X-Ray (EDS)	Elemental information from small area

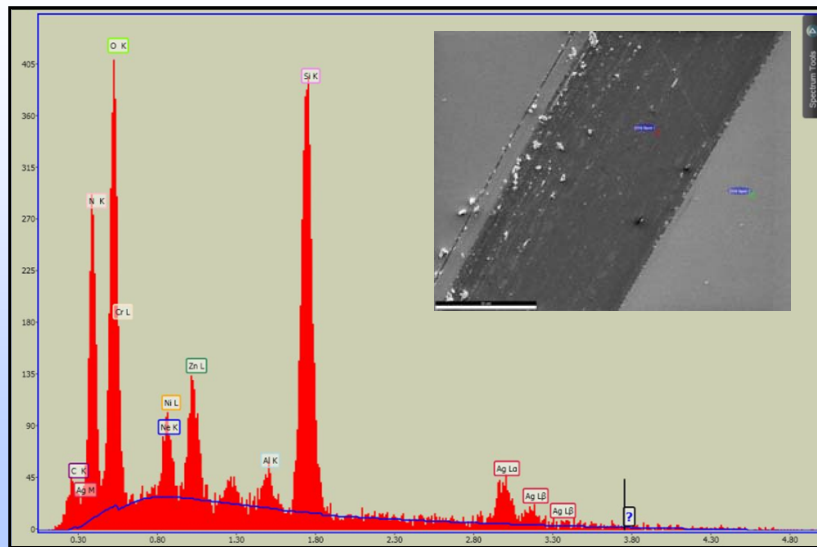
Energy Dispersive X-ray Spectrometry



$$\text{Element A} = \frac{I_{\text{Mess}}^A}{I_{\text{Standard}}^A} \quad \text{Element B} = \frac{I_{\text{Mess}}^B}{I_{\text{Standard}}^B} \times \left[\begin{array}{l} \text{Atomic number correction } Z \\ \text{Absorption correction } A \\ \text{Fluorescence correction } F \end{array} \right]$$

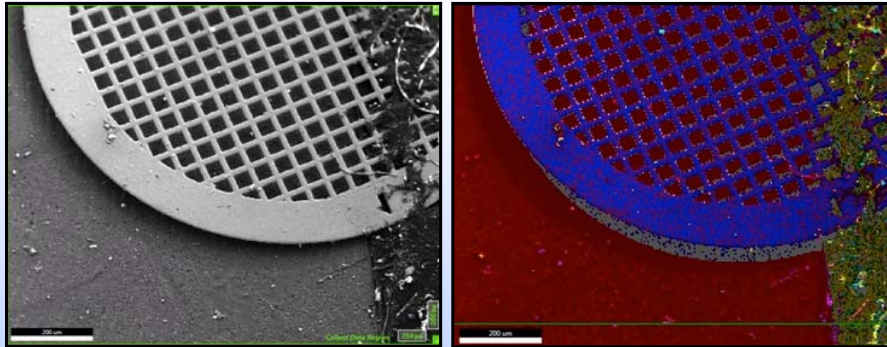
16

Energy Dispersive X-ray Spectrometry



17

EDS Mapping



18

EDS Zusammenfassung

Stärken

- Schnelle Elementanalyse
- Kombination mit SEM => Mapping
- Spotsize < 1 µm (low kV)

Limitierungen

- Quantifizierung
- Spektrale Interferenz
- Empfindlichkeit (1% - 0.1%), schlechter für kleine Z

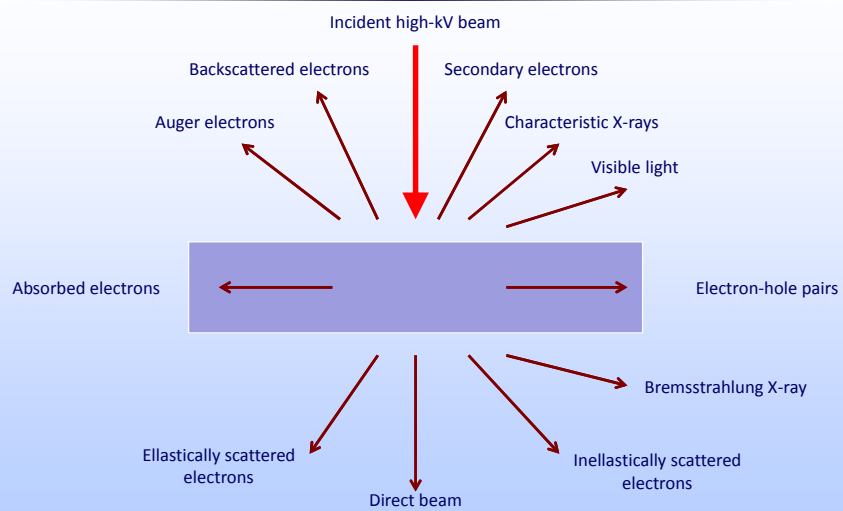
=> schnellere Methode für Elementanalyse

19

Teil 2: Transmissionmikroskopie (TEM)

20

TEM/STEM: Introduction



21

TEM/STEM: Key Anwendungen

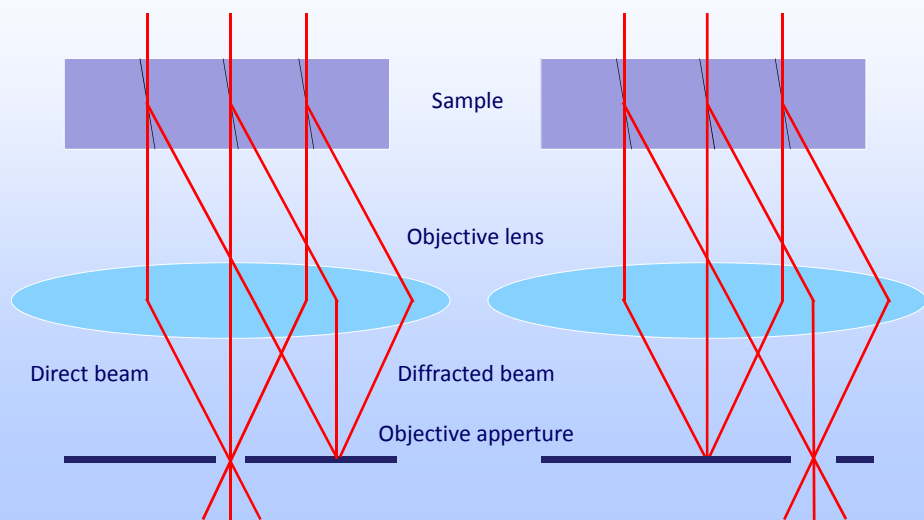
- Dünne Schichten (Dicke, Struktur)
- Failure Analysis
- Reverse Engineering
- Kristallographie (Defekten)
- Nanocluster (Grösser, Struktur)
- Elemental Mapping (EDS, EELS)

22

Imaging Modes

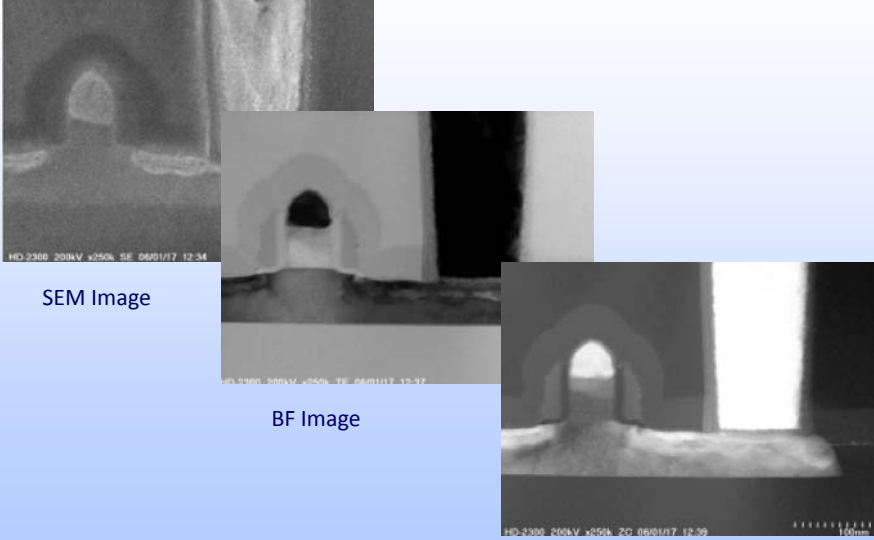
Bright field (un-scattered electrons)

Dark field (diffracted electrons)



23

Imaging Modes: STEM



The figure displays three STEM images of a device structure. The top-left image is an SEM Image showing a bright, rounded feature on a dark background. The middle image is a BF Image showing a similar feature with more detail. The bottom-right image is a DF Image showing a bright, elongated feature. Each image includes technical data at the bottom: 'HD-2300_200kV_x250k_SF_06/01/17_12-34' for the SEM image, 'HD-2300_200kV_x250k_TF_06/01/17_12-37' for the BF image, and 'HD-2300_200kV_x250k_ZC_06/01/17_12-39' for the DF image. A scale bar of 1.00um is visible in the bottom right of the DF image.

SEM Image

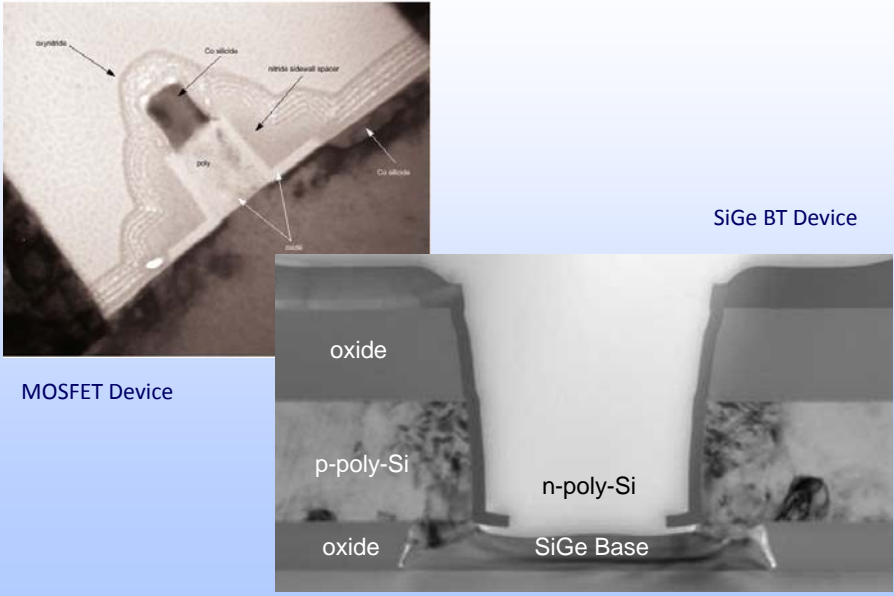
BF Image

DF Image

Bilder: Courtesy of EAG

24

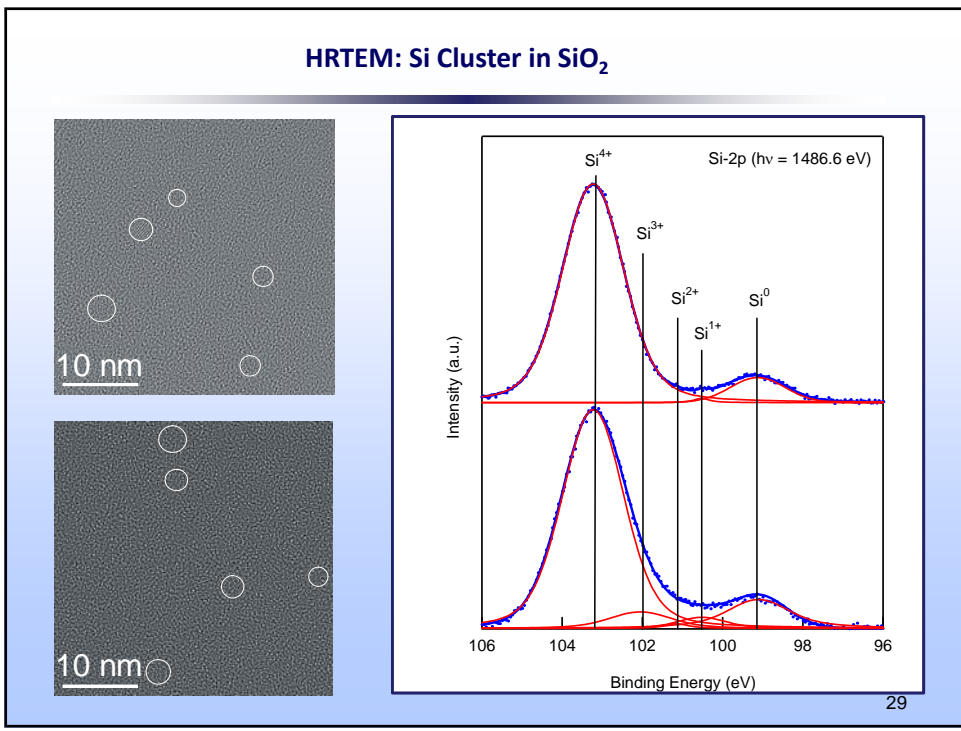
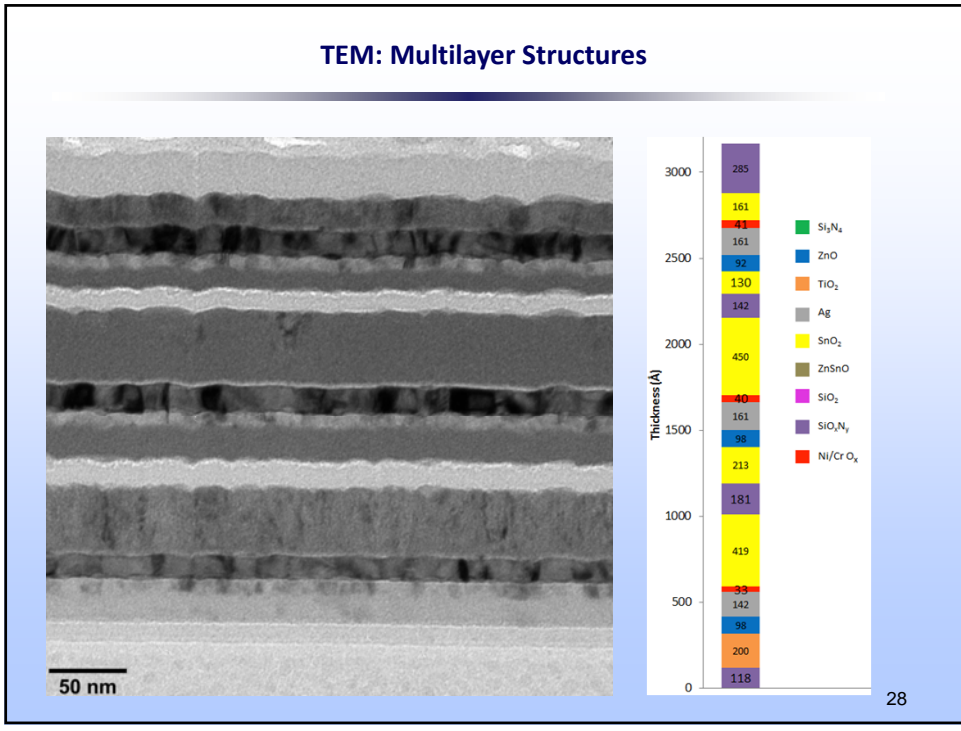
Integrated Circuit Cross-Section



The figure shows two cross-sections of integrated circuit devices. The top-left image is a cross-section of a MOSFET Device with labels: 'oxynitride', 'Cu silicide', 'nitride sidewall spacer', 'poly', and 'oxide'. The bottom-right image is a cross-section of a SiGe BT Device with labels: 'oxide', 'p-poly-Si', 'n-poly-Si', and 'SiGe Base'.

MOSFET Device

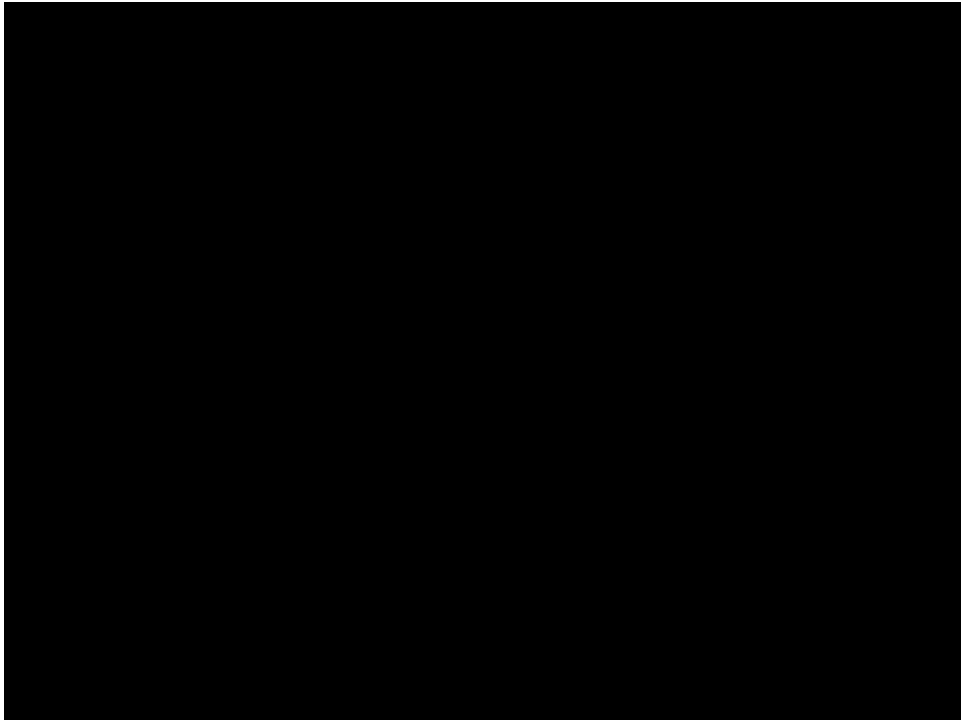
SiGe BT Device



Wie mache ich 100 nm dünne Probe?

Ganz vorsichtig ...

30



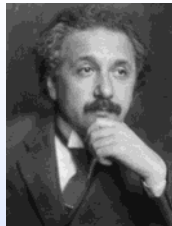
Teil 1: Photoemissionspektroskopie

1

Photoemission



Heinrich Hertz 1857 – 1894



Albert Einstein 1879 – 1955

Prozess der Photoemission
1887 – Heinrich Rudolf Hertz
1905 – Albert Einstein

Ultraviolettes Licht und electriche Entladung. 988

XIV. *Ueber einen Einfluss des ultravioletten Lichtes auf die electriche Entladung;*
von *H. Hertz.*

(Hierzu Taf. VII Fig. 8–11.)

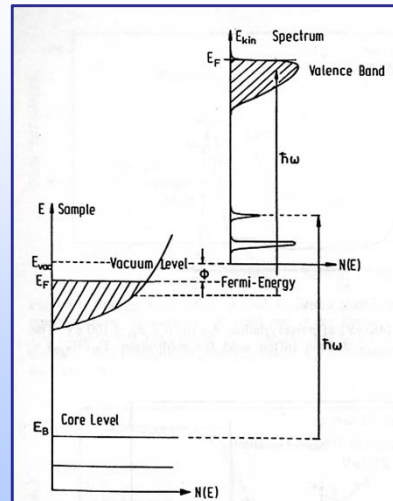
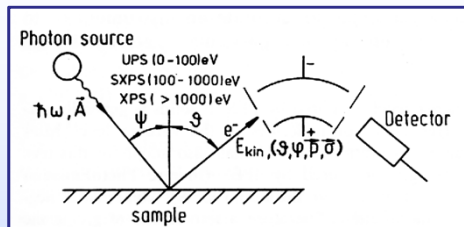
In einer Reihe von Versuchen, welche ich über die Resonanzerscheinungen zwischen sehr schnellen electricen Schwingungen angestellt und kürzlich veröffentlicht habe¹⁾, wurden durch dieselbe Entladung eines Inductoriums, also genau gleichzeitig, zwei electriche Funken erregt. Der eine derselben, der Funke *A*, war der Entladungsfunke des In-

§ 8. *Über die Erzeugung von Kathodenstrahlen durch Belichtung fester Körper.*

Die übliche Auffassung, daß die Energie des Lichtes kontinuierlich über den durchstrahlten Raum verteilt sei, findet bei dem Versuch, die lichtelectricen Erscheinungen zu erklären, besonders große Schwierigkeiten, welche in einer bahnbrechenden Arbeit von Hrn. Lenard dargelegt sind.²⁾

Nach der Auffassung, daß das erregende Licht aus Energiequanten von der Energie $(h\nu)$ bestehe, läßt sich die Erzeugung von Kathodenstrahlen durch Licht folgendermaßen auffassen. In die oberflächliche Schicht des Körpers dringen Energiequanten ein, und deren Energie verwandelt sich wenigstens zum Teil in kinetische Energie von Elektronen. Die einfachste Vorstellung ist die, daß ein Lichtquant seine ganze Energie an ein einziges Elektron abgibt; wir wollen annehmen, daß dies vorkomme. Es soll jedoch nicht ausgeschlossen sein,

Photoemission



$$E_{kin} = \hbar\omega - E_B - \phi$$

$$E_B = \hbar\omega - E_{kin} - \phi$$

Koopman's theorem

The binding energy of an electron is simply the difference between initial (atom with n electrons) and final state (atom with $n-1$ electrons and photoelectron)

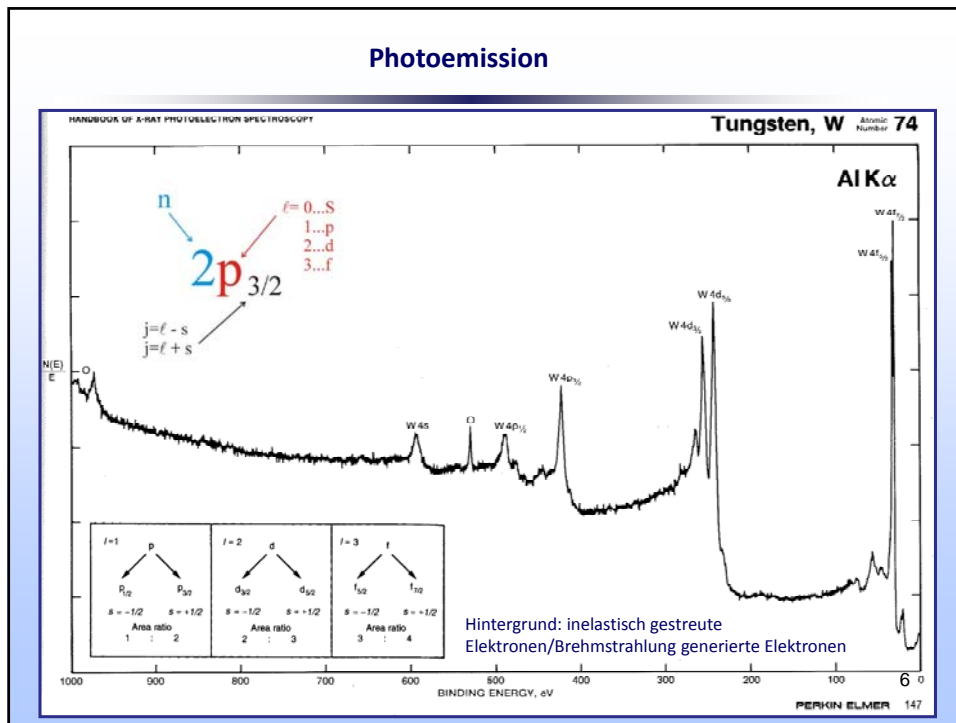
$$E_B = E_{final}(n-1) - E_{initial}(n)$$

If no relaxation followed photoemission, binding energy = - orbital energy

Difference between measurement and calculation due to:

- Electron rearrangement to shield the core hole
- Electron correlation
- Relativistic effects

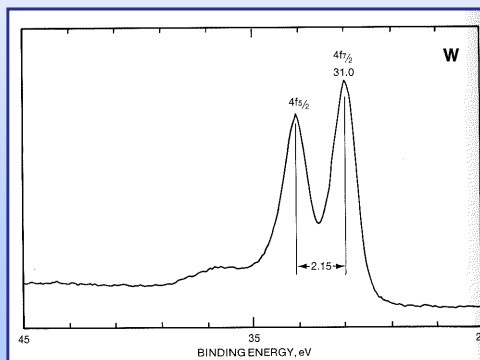
Photoemission



Peakbreite (FWHM)

FWHM: full-width at half-maximum of a peak

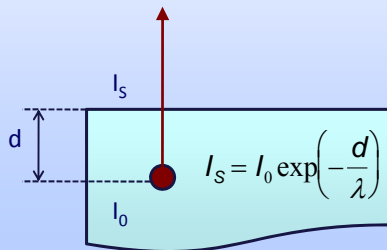
- $$FWHM_{tot} = (FWHM_n^2 + FWHM_x^2 + FWHM_a^2 + FWHM_{ch}^2 + \dots)^{1/2}$$
- $FWHM_n$ Lebensdauer der Photoloch ($4f < 4d < 4p < 4s$)
 - $FWHM_x$ Breite der X-Ray Linie
 - $FWHM_a$ Analysator
 - $FWHM_{ch}$ Aufladungseffekte



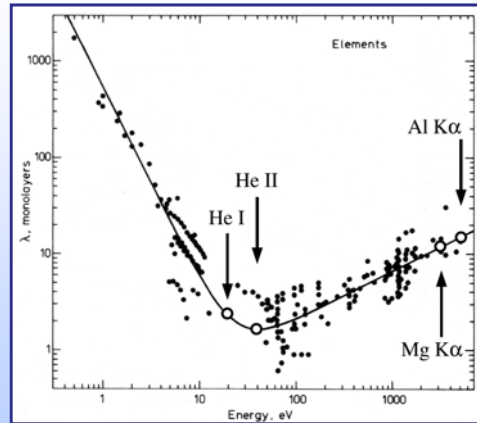
Sampling Depth

λ – Inelastic Mean Free Path of Electrons

$$\lambda^{-1} = \sqrt{3} \frac{a_0 R}{E_{kin}} r_s^{-3/2} \ln \left[\left(\frac{4}{9\pi} \right)^{2/3} \frac{E_{kin} r_s^2}{R} \right]$$



• Information aus ca. 3λ

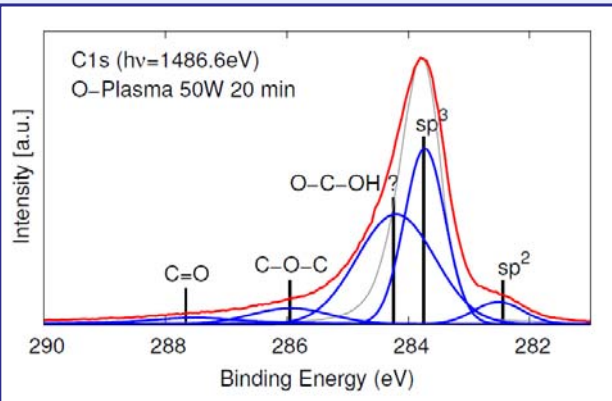
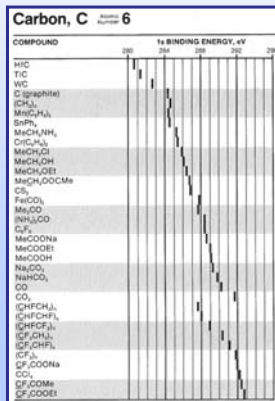


8

Chemical Shift

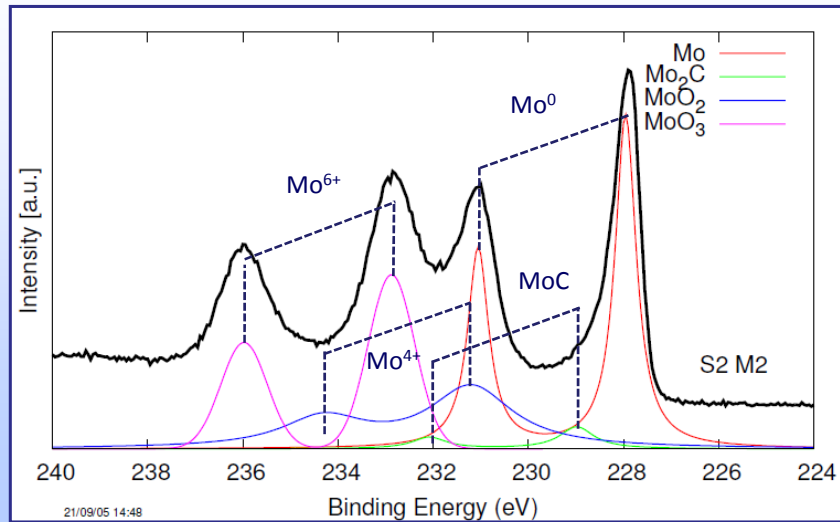
Änderung in Bindungsenergie wegen Änderung in chemischer Umgebung des Atoms

- entnehmen von Valenzelektronen → BE wird höher
- addieren von Valenzelektronen → BE wird kleiner



9

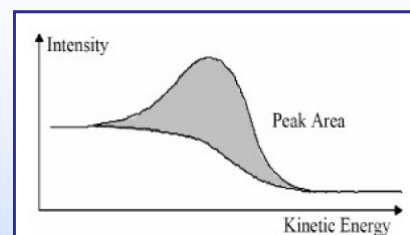
Chemical Shift



10

Quantifizierung

$$I_{ij} = n_i \sigma_{ij} \lambda K \cos(\theta)$$

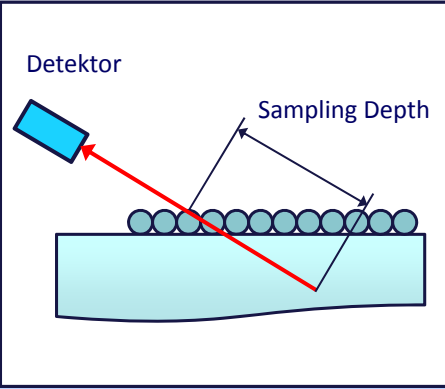


- I Intensität (Fläche unter Spektrum)
- n atomische Konzentration
- σ photoelektronische cross-section (berechnet)
- λ inelastic mean free path of a photoelectron (berechnet)
- K andere Faktoren (konstant während Messungen)

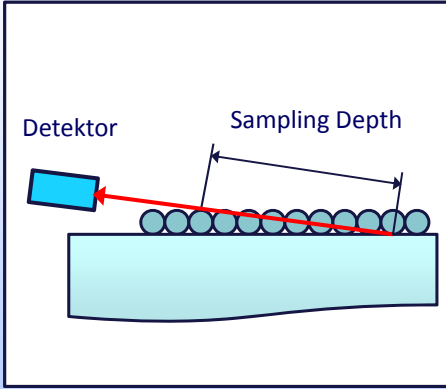
11

Angle-Resolved XPS

Detektionswinkel 50°



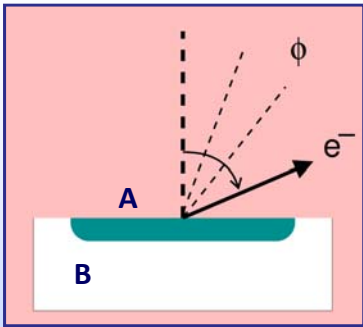
Detektionswinkel 7°



- Erhöhung der Oberflächensensitivität durch Reduktion des Detektionswinkels
- Bandstruktur Mapping in k-Raum

12

Angle-Resolved XPS



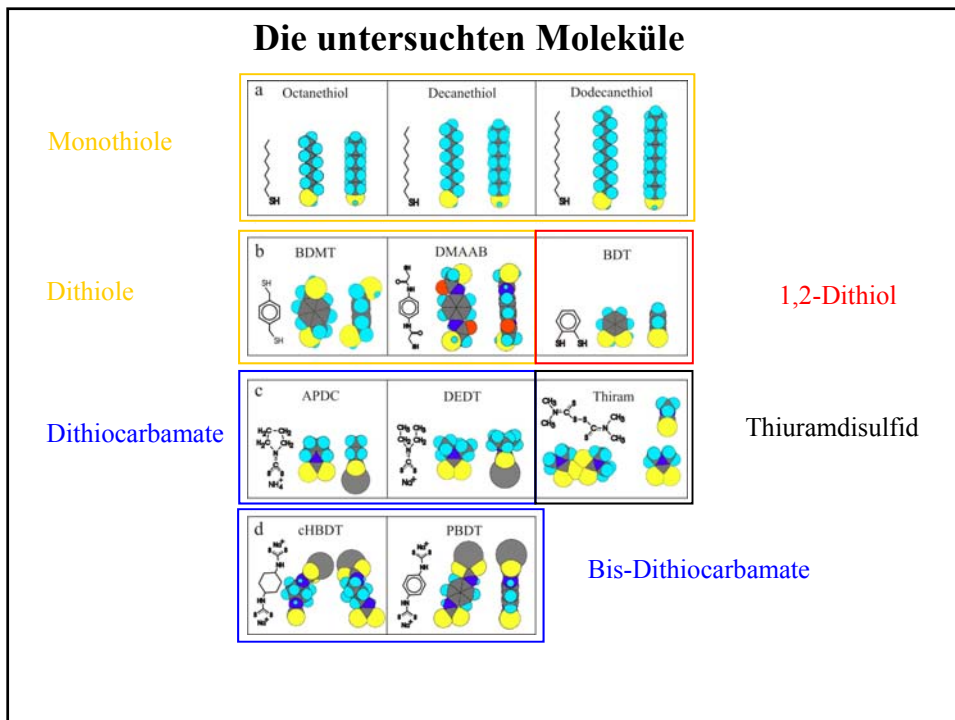
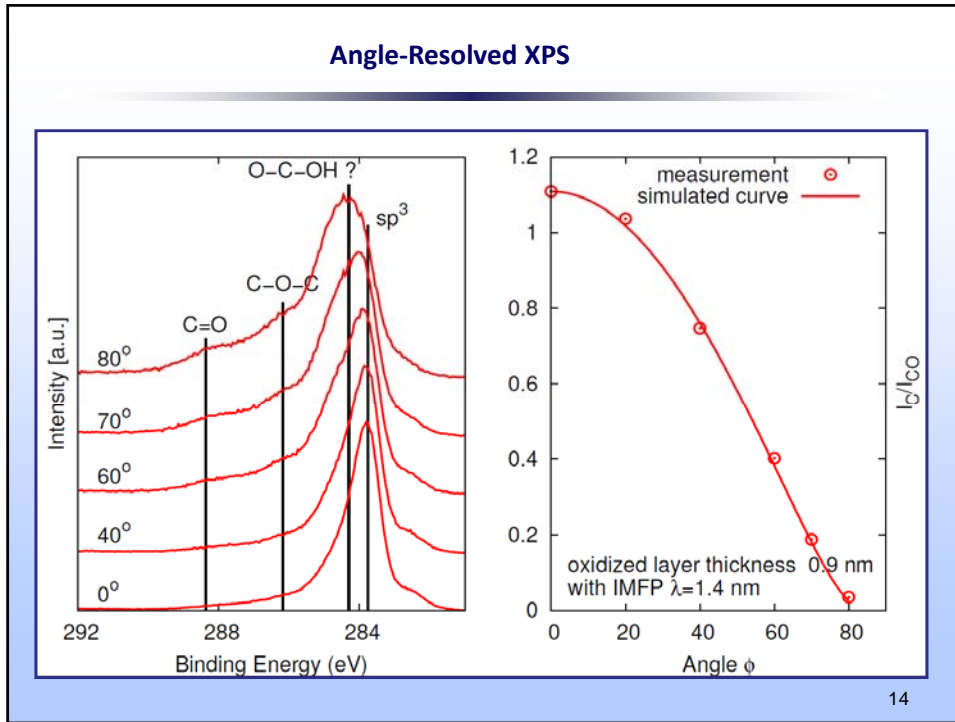
Signal von Substrat B bedeckt mit Schicht A

$$I_B = I_B^\infty (1 - \phi_A + \phi_A \exp[-d_A / \lambda_A \cos \theta])$$

Signal von Schicht A

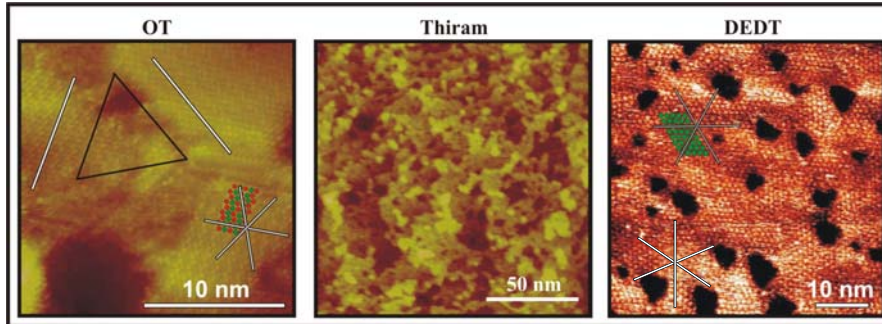
$$I_A = \phi_A I_A^\infty (1 - \exp[-d_A / \lambda_A \cos \theta])$$

13



STM 2D Self-assembled Monolayer

- etch pits
- domain boundaries
- $(\sqrt{3} \times \sqrt{3})R30^\circ$
- 0.5 nm dot distance
- jagged step edges
- no molecular resolution
- etch pits
- chiral domains
- $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$
- 0.96 nm dot distance



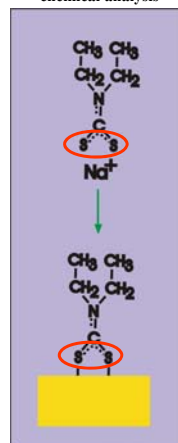
1 Schwefel/Punkt

6 Schwefel/Punkt

Untersuchung der Chemisorption

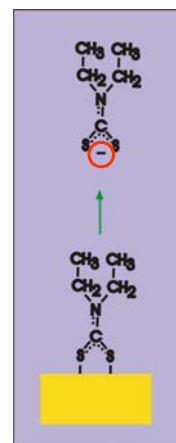
XPS - ESCA

x-Ray photoelectron spectroscopy
Electron spectroscopy for
chemical analysis



CV

Cyclic voltammetry



X-Ray Photoelectron Spectroscopy - XPS

Monochromatic X-Ray
Al K_α 1486.6 eV

Outgoing Elektrons
„lots of background“

Elastic mean free path of electrons

Mean free path [Å]
Electron energy [eV]

PAUL SCHERRER INSTITUT

SONY

XPS signal and chemical Shift

$$E_{\text{kin}} = h\nu - E_b - \Phi \quad (\text{Conservation of energy})$$

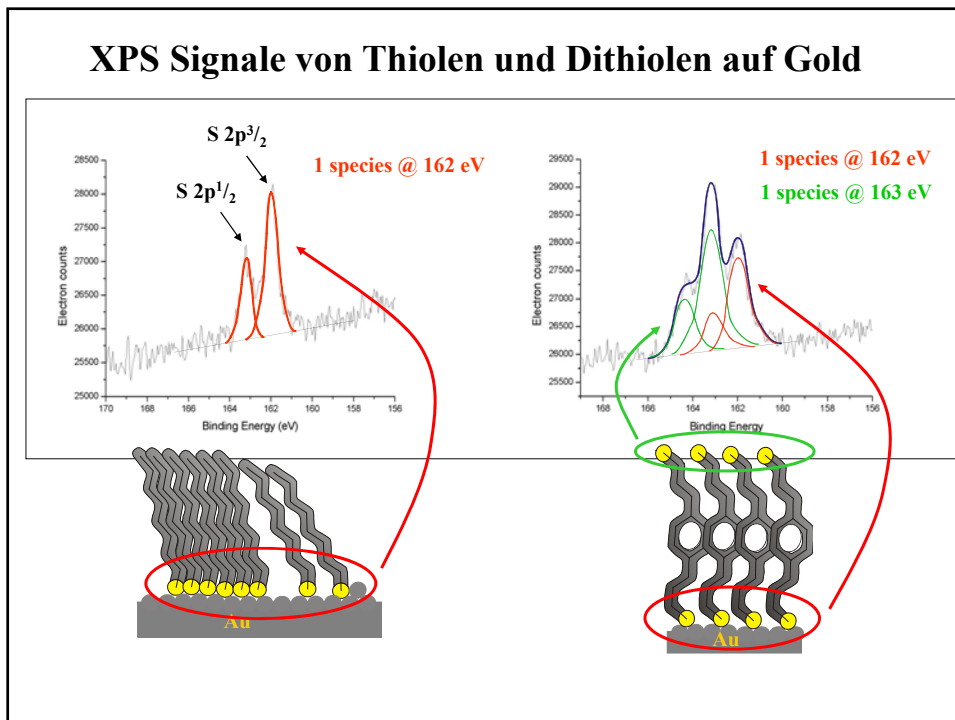
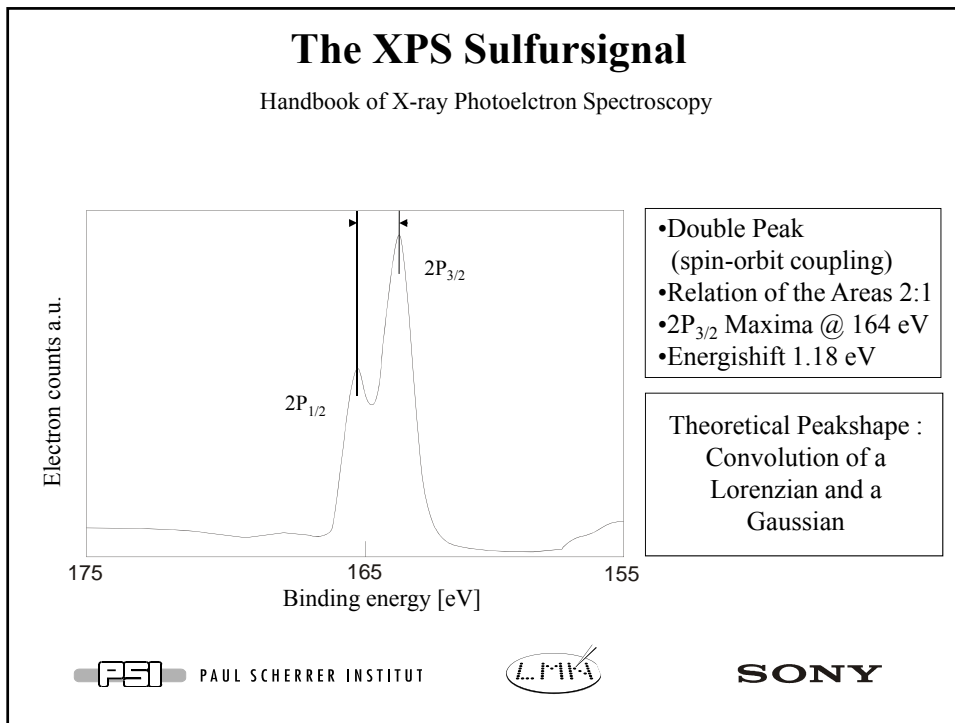
Given by the
X-ray source:
constant

Given by the
Bulk properties:
**small and almost
constant**

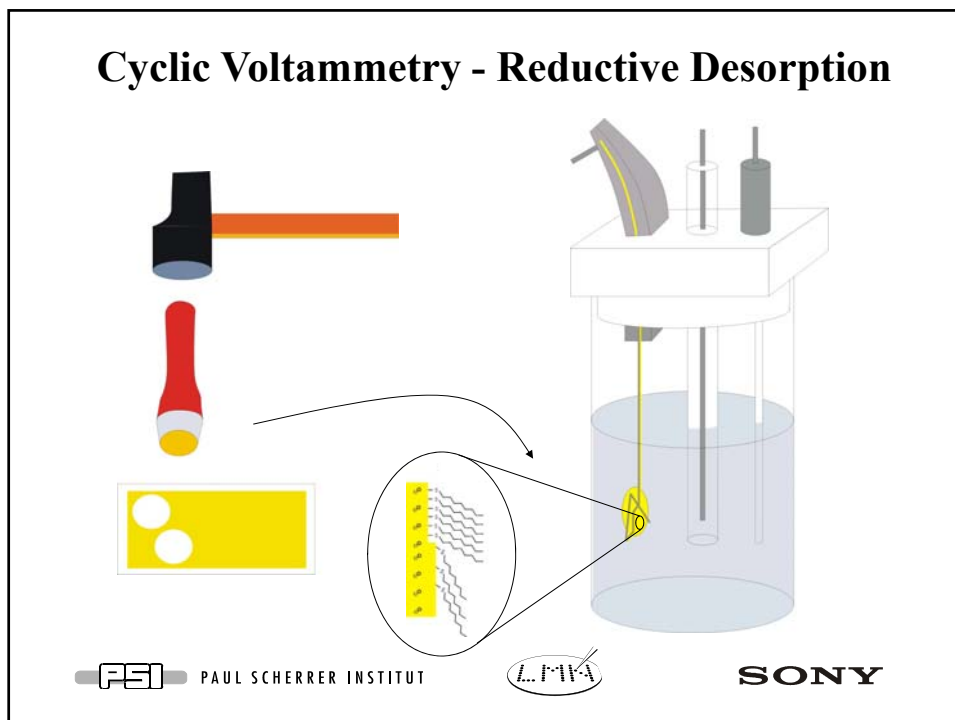
Represents strength of interaction between
ELECTRONS and the NUCLEUS
(Chemistry) (Physics)

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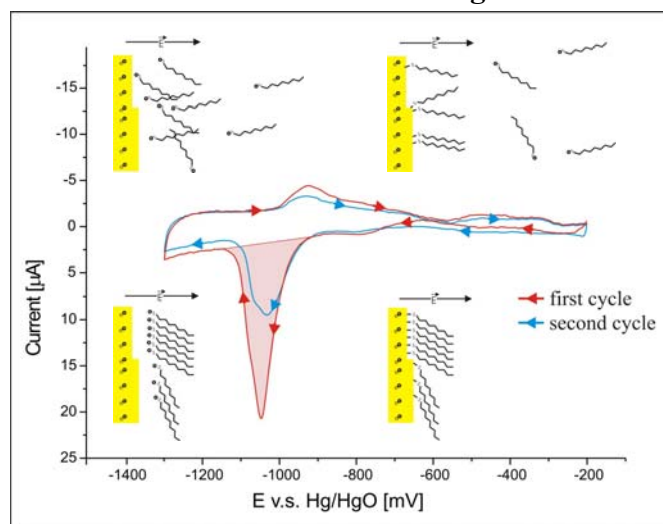
SONY



Cyclic Voltammetry - Reductive Desorption

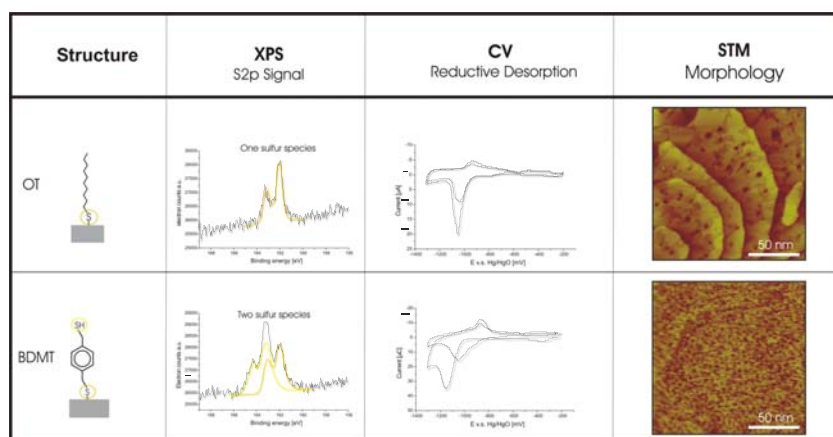


Reductive Desorption of dodecanethiol from gold

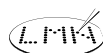


Chemical Interaction at the surface

Thiols and Dithiols



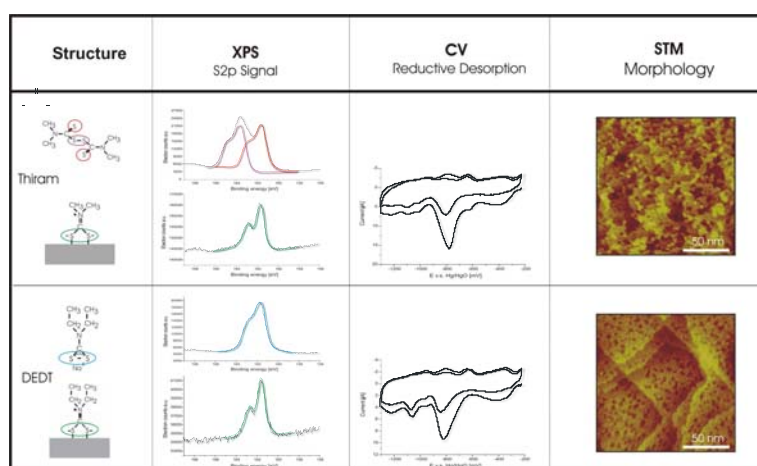
 PAUL SCHERRER INSTITUT



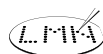
SONY

Chemical Interaction at the surface

Thiurames and Dithiocarbamates

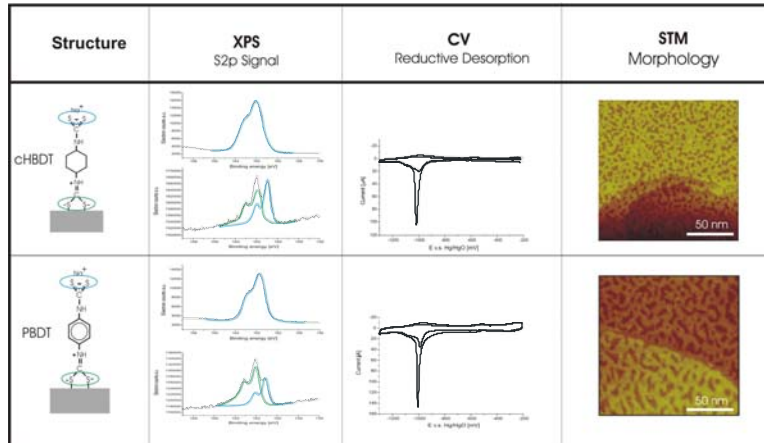


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Chemical Interaction at the surface Bis Dithiocarbamates

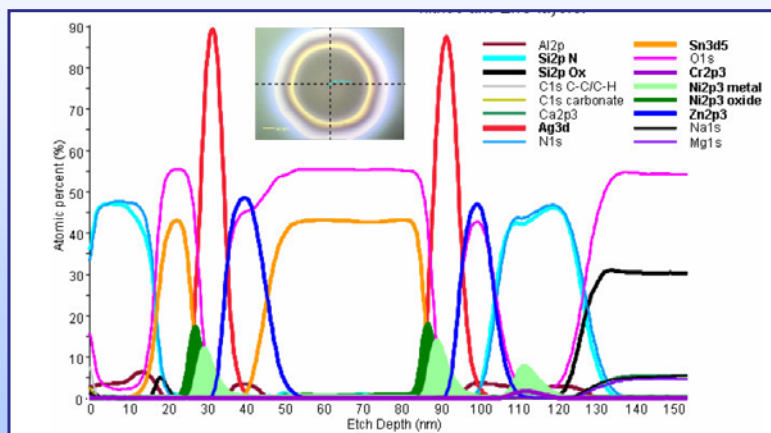
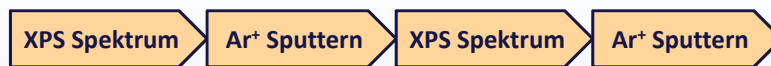


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XPS Tiefenprofil

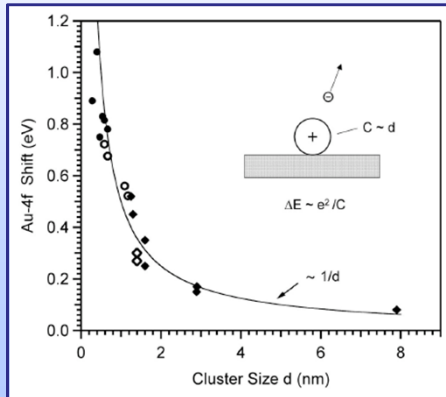


48

Untersuchung von Size-Effects mittels XPS

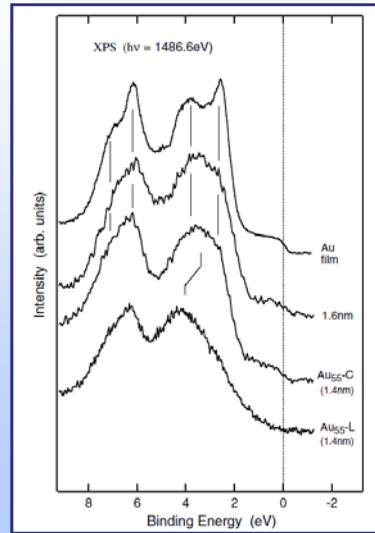
Änderung in Bindungsenergie wegen Aufladung

$$\Delta E = \frac{\alpha e^2}{4\pi\epsilon_0 r}$$



H.-G. Boyen et al in Phys. Rev. Lett. (2005) 016804.

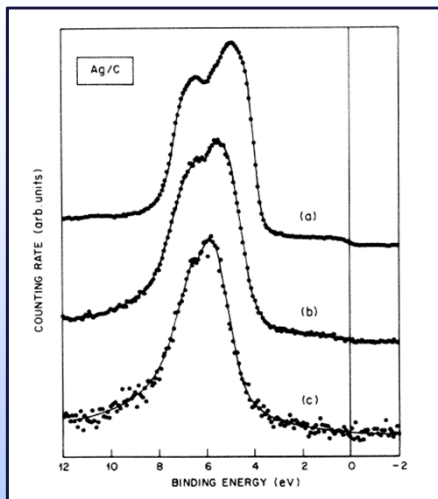
Metal-Insulator Übergang



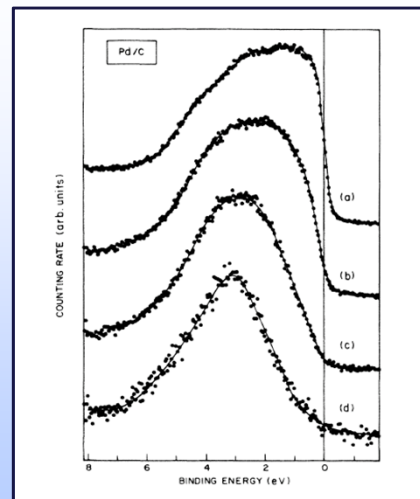
H.-G. Boyen et al in Phys. Rev. Lett. (2001) 276401.

49

Untersuchung von Size-Effects mittels XPS



Bedeckung: a) bulk b) 1×10^{15} c) 2.5×10^{14} atoms/cm²



Bedeckung: a) bulk b) 4×10^{15} c) 1×10^{15} d) 3×10^{14} atoms/cm²

G.K. Wertheim et al in Phys. Rev. B 33 (1986) 5384.

50

Ultraviolett Photoelektronenspektroskopie

Ionisationsquellen:

- Ne I (16.6 eV) und Ne II (26.8 eV)
- He I (21.2 eV) und He II (40.8 eV)
 - I – Emission neutrale Atomen
 - II – Emission ionisierte Atomen

Hauptanwendungsgebiete:

- Elektronische Struktur der Festkörper
- Absorbierte Moleküle

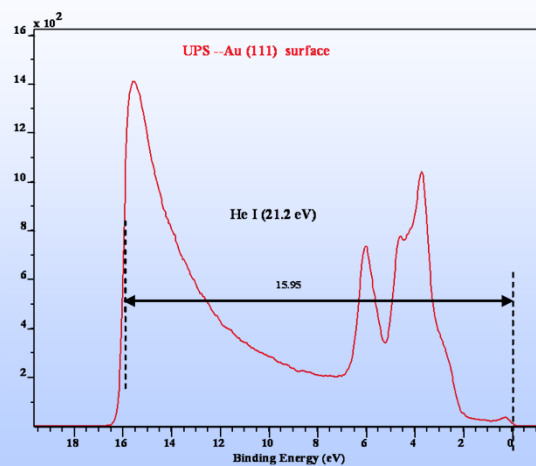
Spezifische Beispiele:

- Determinierung der Arbeitsfunktion von Festkörper
- Messung der orbitalen Energien der Molekülen
- Bandstruktur Mapping in k-Raum (mit AR-UPS)

51

Determinierung der Arbeitfunktion von Au

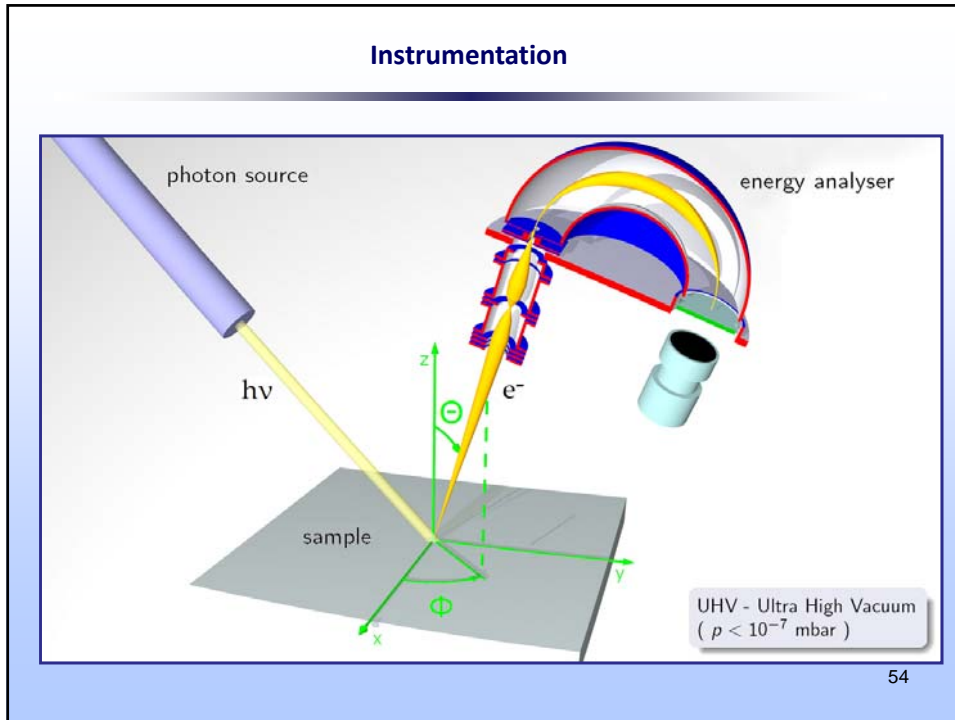
Beispiel: Au (111) single crystal



$W = 15.95 \text{ eV}$, Photonenenergie $h\nu = 21.2 \text{ eV}$

$\phi = 21.2 \text{ eV} - 15.95 \text{ eV} = 5.25 \text{ eV}$

52



X-Ray Quelle

(b) Anode face 1 Al window Anode face 2

X-ray lines		
Line	Energy, eV	Width, eV
Y <i>M</i> ζ	132.3	0.47
Zr <i>M</i> ζ	151.4	0.77
Nb <i>M</i> ζ	171.4	1.21
Mo <i>M</i> ζ	192.3	1.53
Ti <i>L</i> α	395.3	3.0
Cr <i>L</i> α	572.8	3.0
Ni <i>L</i> α	851.5	2.5
Cu <i>L</i> α	929.7	3.8
Mg <i>K</i> α	1253.6	0.7
Al <i>K</i> α	1486.6	0.85
Si <i>K</i> α	1739.5	1.0
Y <i>L</i> α	1922.6	1.5
Zr <i>L</i> α	2042.4	1.7
Ti <i>K</i> α	4510.0	2.0
Cr <i>K</i> α	5417.0	2.1
Cu <i>K</i> α	8048.0	2.6

Häufig im Einsatz

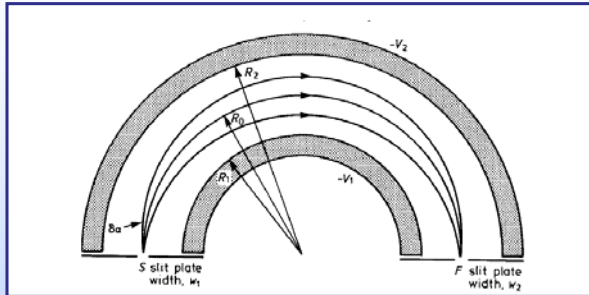
INTEGRATED INTENSITY (COUNTS PER SECOND PER UNIT ENERGY INTERVAL)

BINDING ENERGY, eV

Energy Analyzer
Quartz Crystal Disperser
Sample
Rowland Circle
X-ray Anode

55

Concentric Hemispherical Analyzer (CHA)



$$V_0 = \frac{V_1 R_1 + V_2 R_2}{2R_0}$$

$$R = \frac{\Delta E}{E} = \frac{w}{R_0} + \frac{\alpha}{4}$$

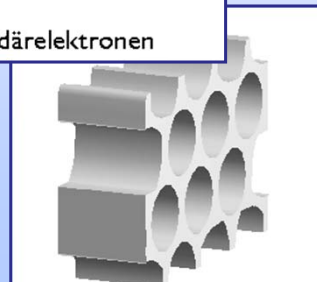
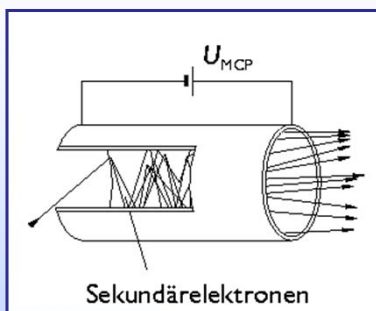
Beim 10 eV $R = 0.5/10 = 0.05$ eV
 Beim 1000 eV $R = 0.5/1000 = 0.0005$ eV

$$R = \frac{\Delta E}{E_0} = \frac{w}{2R_0}$$

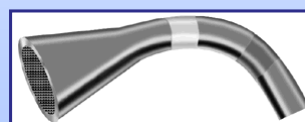
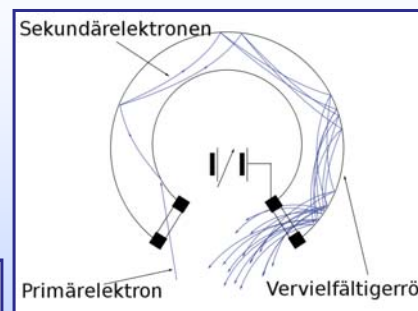
56

Detektor

Channelplate



Channeltron



57

System



58

**Teil 2:
Auger Spektroskopie**

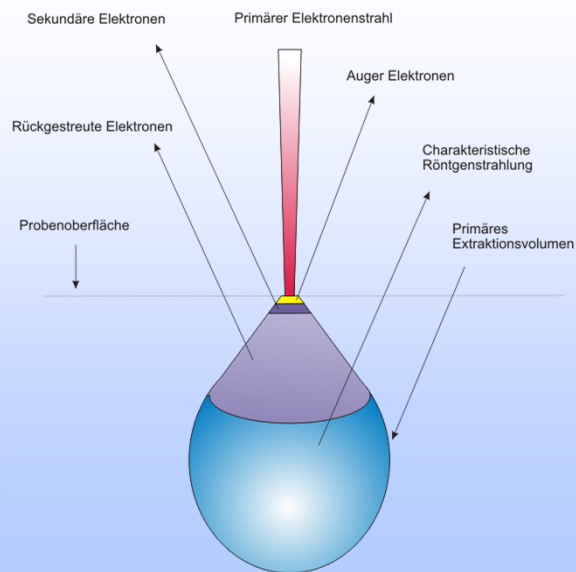
59

X-Ray Bezeichnungen

Quantum numbers			X-ray suffix	X-ray level	Spectroscopic level
n	l	j			
1	0	$\frac{1}{2}$	1	K	$1s_{1/2}$
2	0	$\frac{1}{2}$	1	L_1	$2s_{1/2}$
2	1	$\frac{3}{2}$	2	L_2	$2p_{1/2}$
2	1	$\frac{5}{2}$	3	L_3	$2p_{3/2}$
3	0	$\frac{1}{2}$	1	M_1	$3s_{1/2}$
3	1	$\frac{1}{2}$	2	M_2	$3p_{1/2}$
3	1	$\frac{3}{2}$	3	M_3	$3p_{3/2}$
3	2	$\frac{3}{2}$	4	M_4	$3d_{3/2}$
3	2	$\frac{5}{2}$	5	M_5	$3d_{5/2}$
	etc.	etc.	etc.	etc.	etc.

60

Wechselwirkung primär Strahl – Probe



61

Auger-Meitner Effekt

• Auger-Meitner Effekt ist ein strahlungsloser Übergang eines Elektrons, in der Elektronenhülle eines Atoms

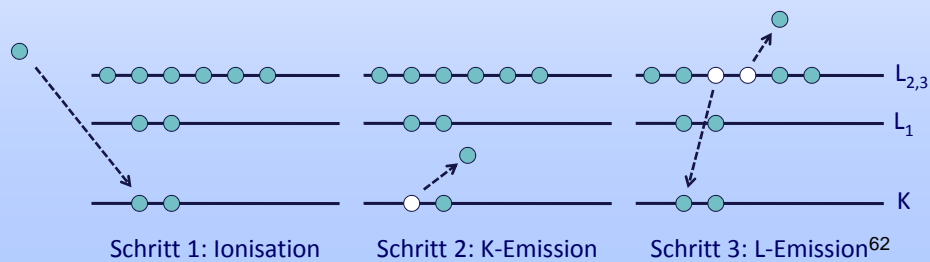
• Entdeckt durch P. Auger (1926) und L. Meitner (1922)



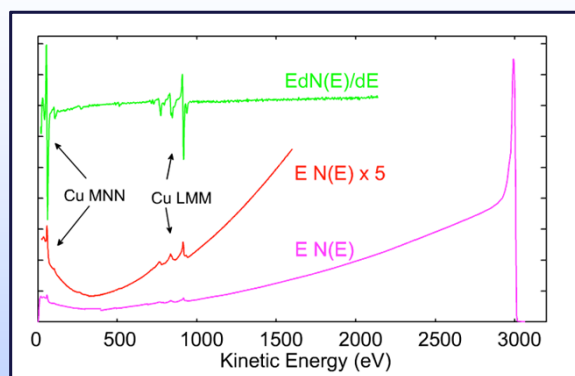
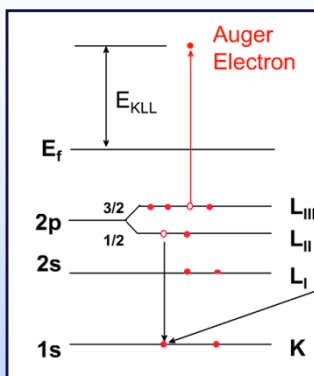
Pierre Auger 1889 – 1993



Lisa Meitner 1878 – 1968

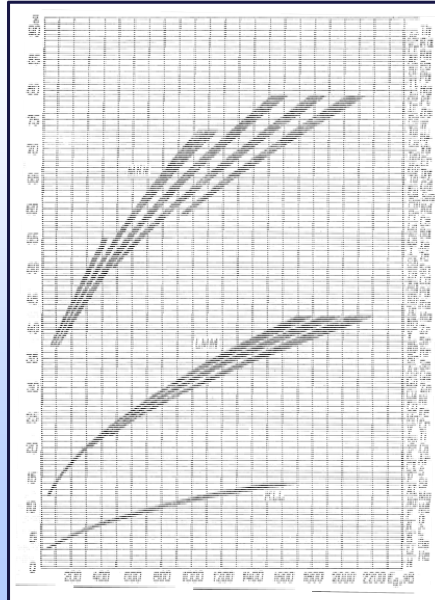


Energie des Auger Elektrones



$$E_{KLL} = E_K - E_{L_{II}} - E_{L_{III}} - \phi - \chi(L_{II} L_{III} : x) + R_x^n + R_x^{ex}$$

Z-Abhängigkeit



NOO

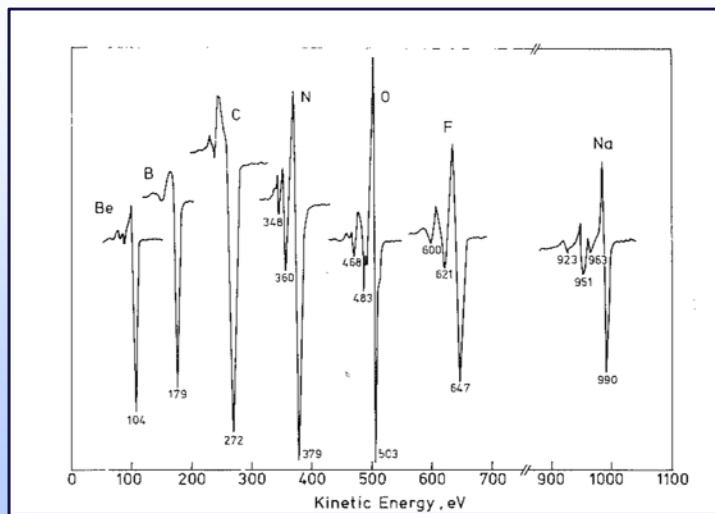
MNN: $40 < Z \leq 79$

LMM: $14 < Z \leq 40$

KLL: $3 \leq Z \leq 14$

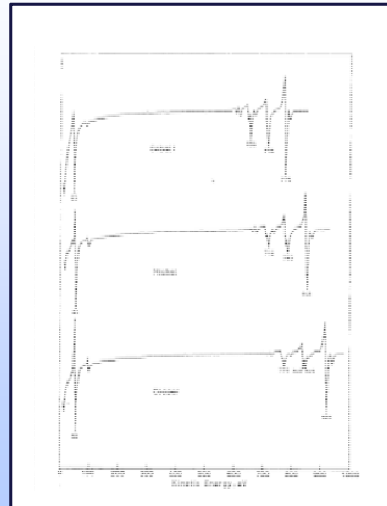
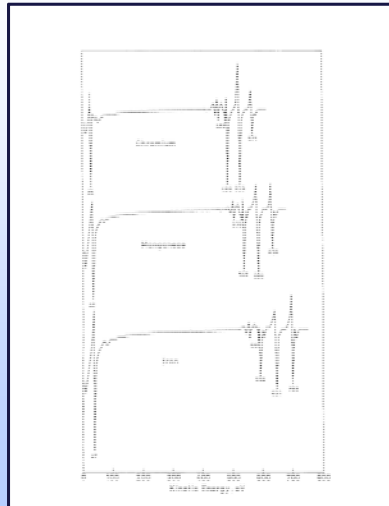
64

Auger Series



65

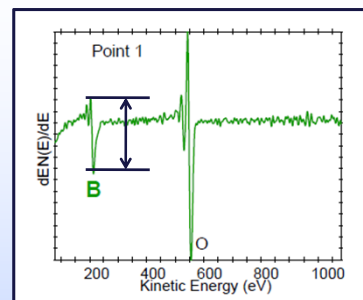
Auger Series



66

Quantifizierung

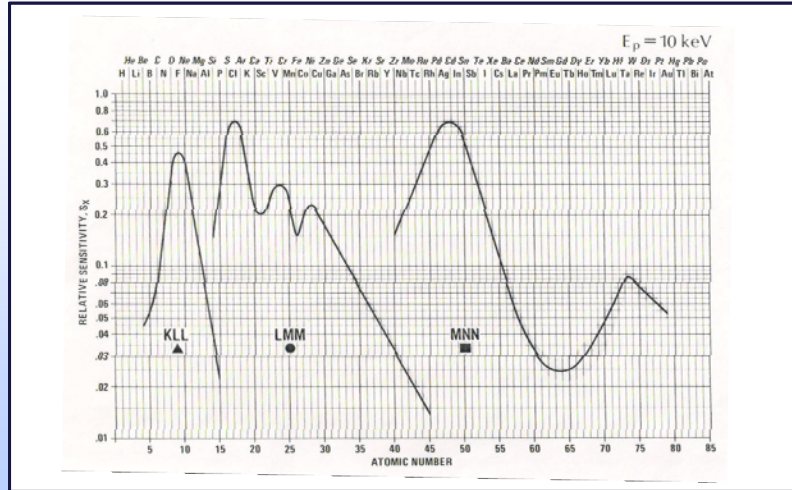
$$I_A \propto n_A \sigma_A \lambda P_A R K \cos(\theta)$$



- I Intensität (Maximum-to-Maximum)
- n atomische Konzentration
- σ Ionisierung cross-section
- λ inelastic mean free path of an electron
- P_A Wahrscheinlichkeit des Auges Emissions
- R Rückstreufaktor
- K andere Faktoren (konstant während Messungen)

67

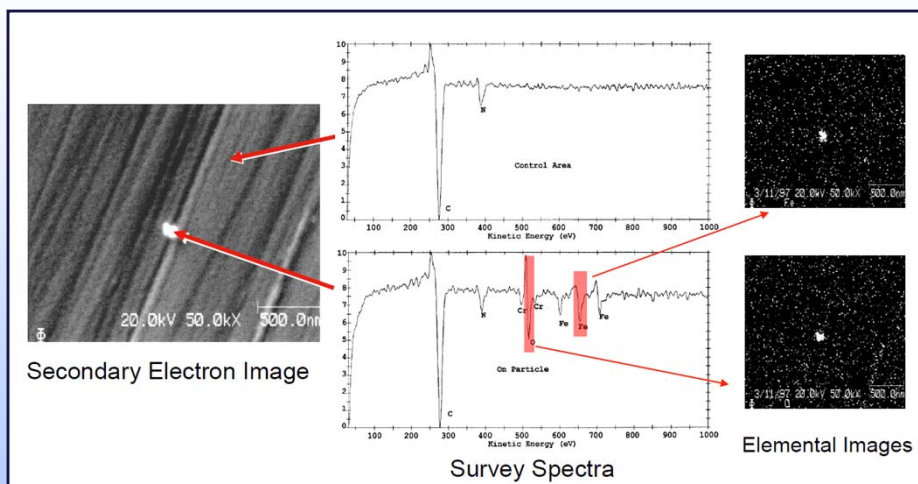
Quantifizierung: Sensitivity Factor



$$n_A = \frac{I_A / S_A}{\sum I_i / S_i}$$

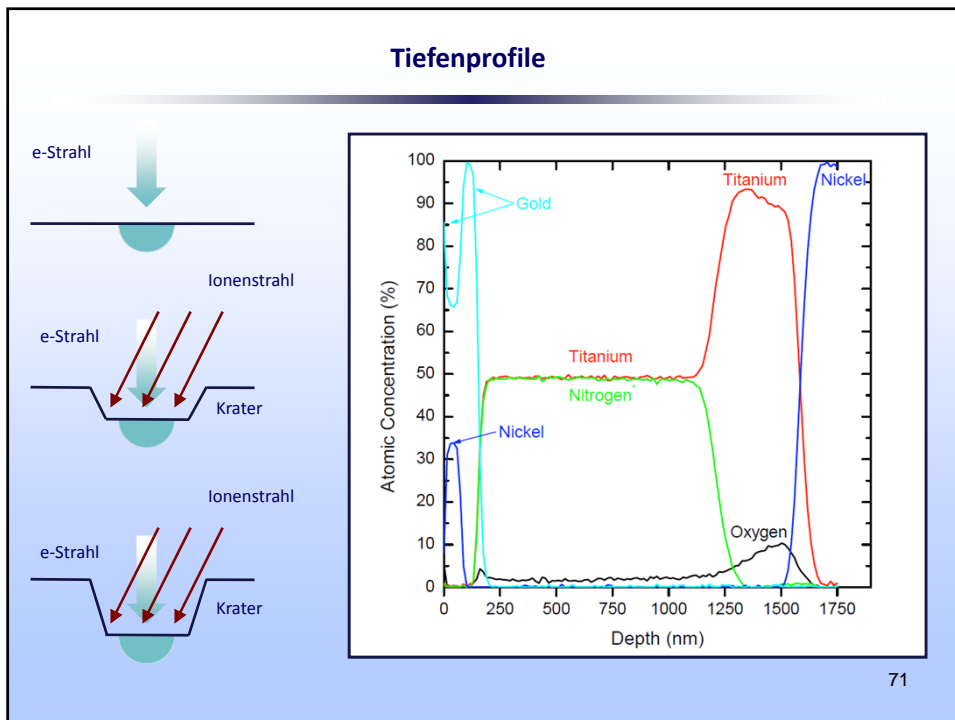
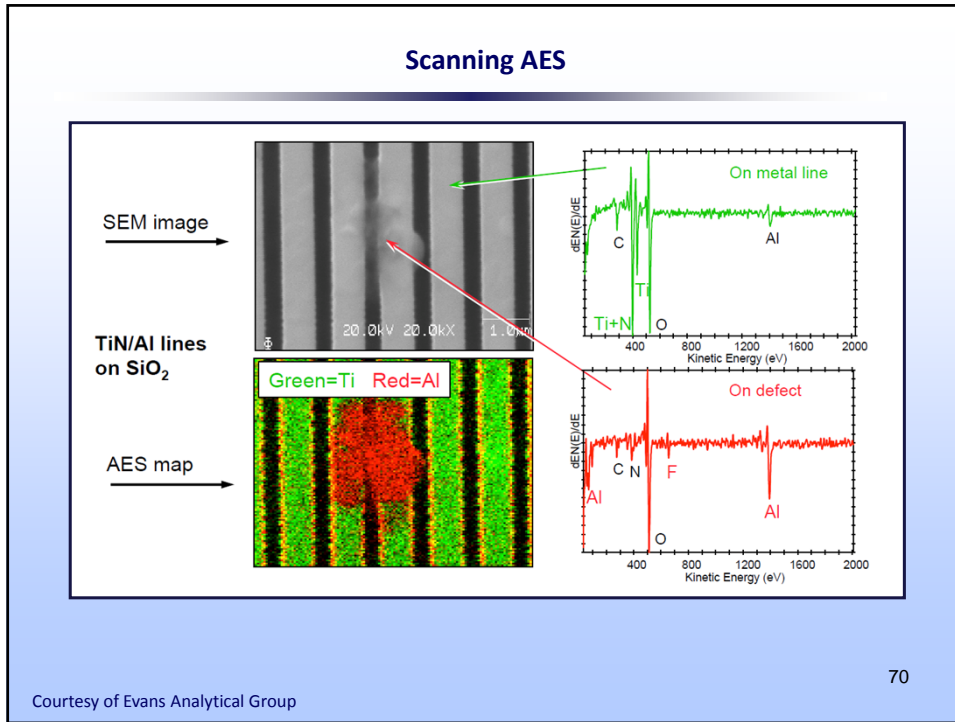
68

Scanning AES



Courtesy of Evans Analytical Group

69



Elektronenquellen

Thermoinonische Quellen:
(Richardson Gleichung)

$$J = A(1 - r)T^2 \exp(-\phi / kT)$$

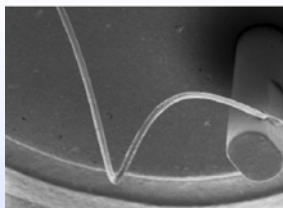
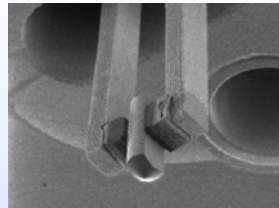
Feldemissionsquellen:
(Fowler-Nordheim Gleichung)

$$J = (1.55 \times 10^{-6} E^2 / \phi) \exp\left[-6.86 \times 10^7 \phi^{3/2} \theta(x) / E\right]$$

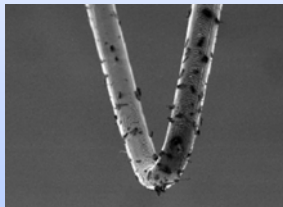
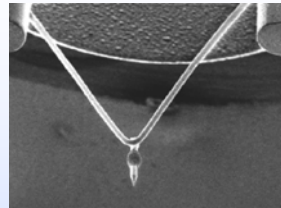
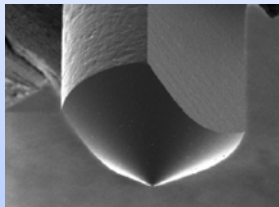
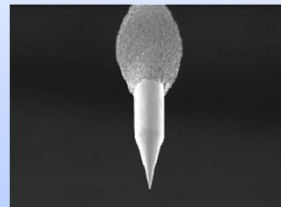
72

e-Emitter

W Thermal

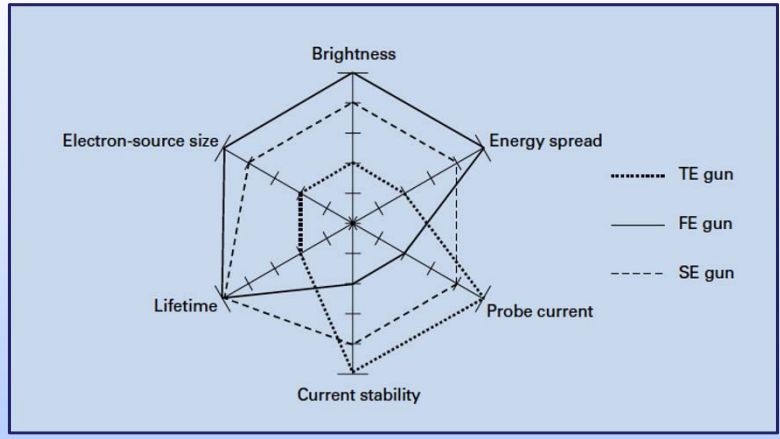
LaB₆ Thermal

W Field Emitter

Crossover
90 μm – 100 μmCrossover
5 μm – 10 μmCrossover
2 nm – 10 nm

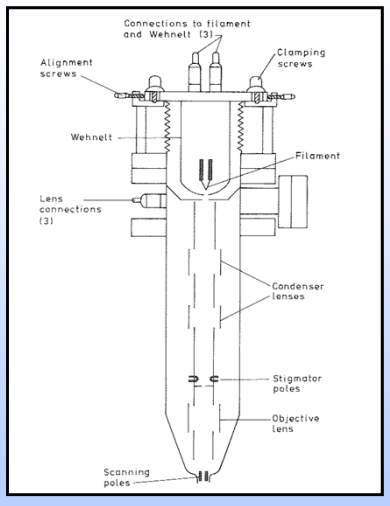
73

e-Emitter

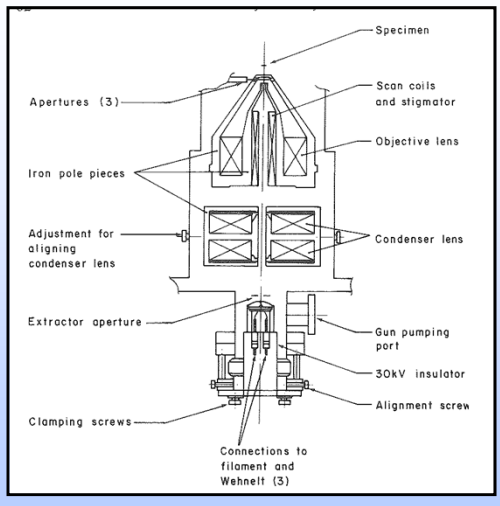


74

Elektronenkanonen



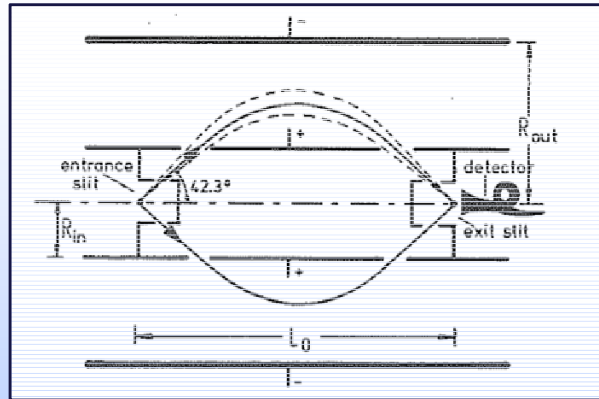
Elektrostatisch: Spotsize 0.5 μm



Elektromagnetisch: Spotsize 50 nm

75

Cilindrical Mirror Analyser (CMA)



Bedienung für Elektronendurchlass:

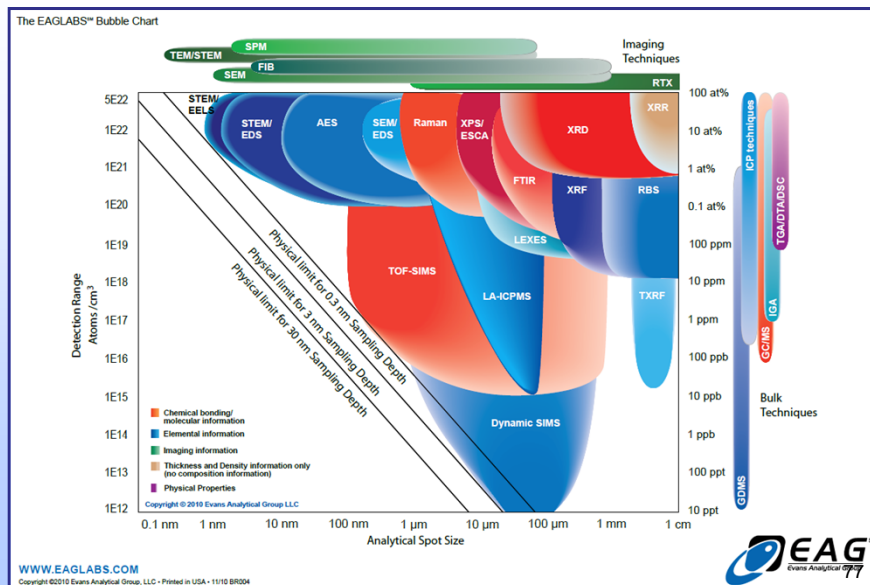
$$\frac{E_0}{eV} = \frac{K}{\ln(R_2/R_1)}$$

Auflösung:

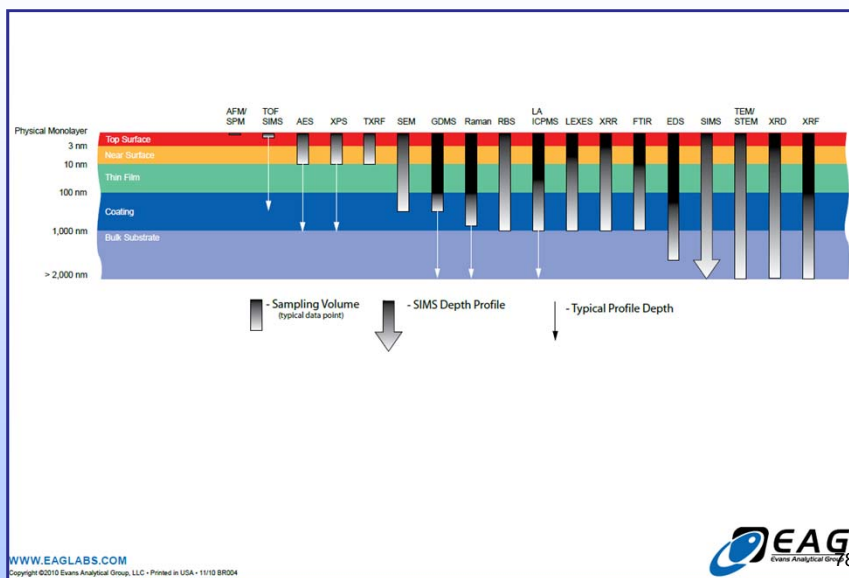
$$\frac{\Delta E}{E} = \frac{0.18w}{R_1} + 1.39(\Delta\alpha)^3$$

76

Detektionslimite: Vergleich



Detektionslimite: Vergleich



Literatur

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D. Briggs and M.P. Seah, John Wiley, 1983.

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A. W. Childs and others, Physical Electronics Publishing, 1995.

Methods of Surface Analysis
A. W. Czandera and S. P. Wolsky, Elsevier 1988.

Principles of Ultraviolet Photoelectron Spectroscopy
J. W. Rabalais, Wiley 1977.

Surface Characterization
G. E. McGuire and others, Analytical Chemistry 65 (1993) 199R.