Surface studies of crystals

Bogdan J. Kowalski

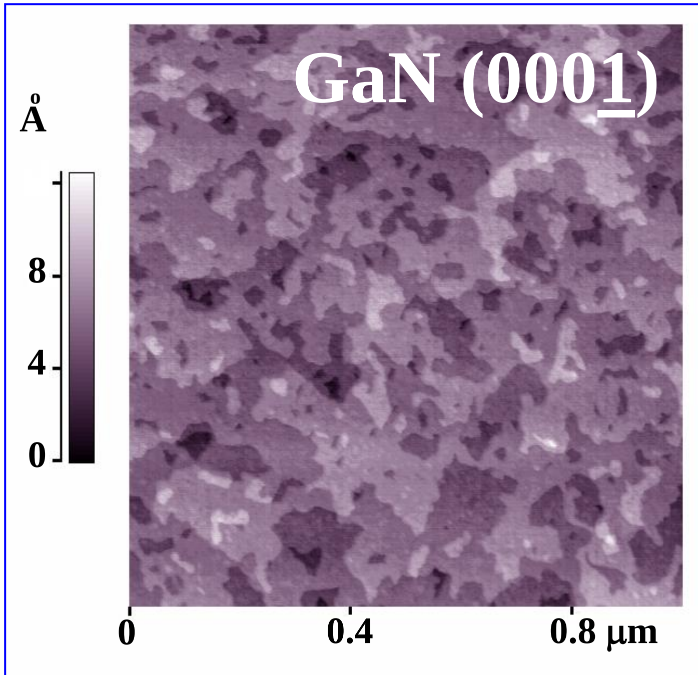
IF PAN

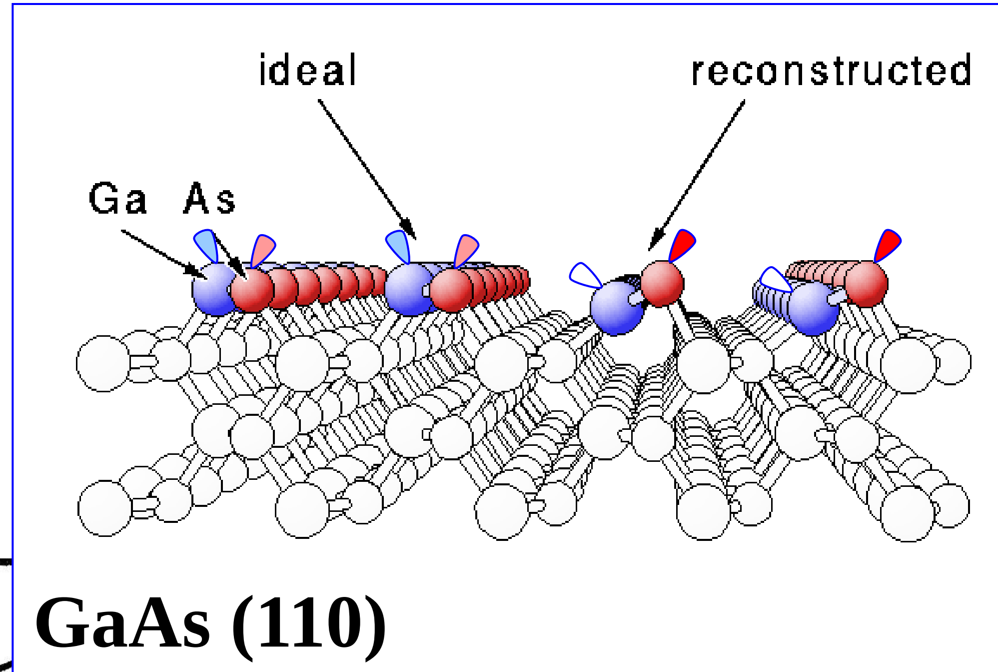
Outline

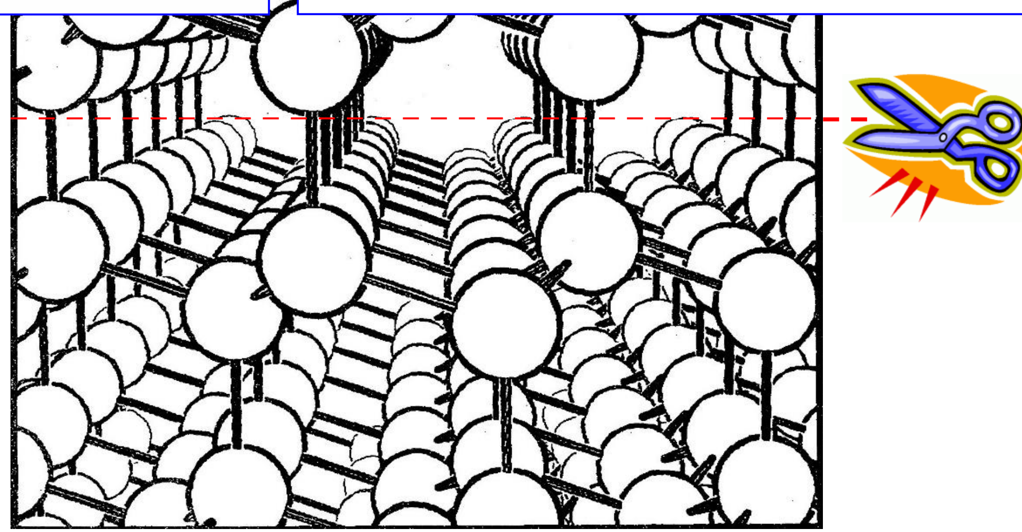
- **Introduction**
- **Methods:**
  - **Electron microscopy**
  - **Scanning probe microscopies**
  - **Electron spectroscopies**
  - **Diffraction methods**
  - **Ion techniques**
  - **Surface-sensitive optical techniques**
- **Summary, literature**

What does it mean *surface?*

Surface


GaN (000$\bar{1}$)
Å
8
4
0
0
0.4
0.8 μm


ideal
reconstructed
Ga As
GaAs (110)



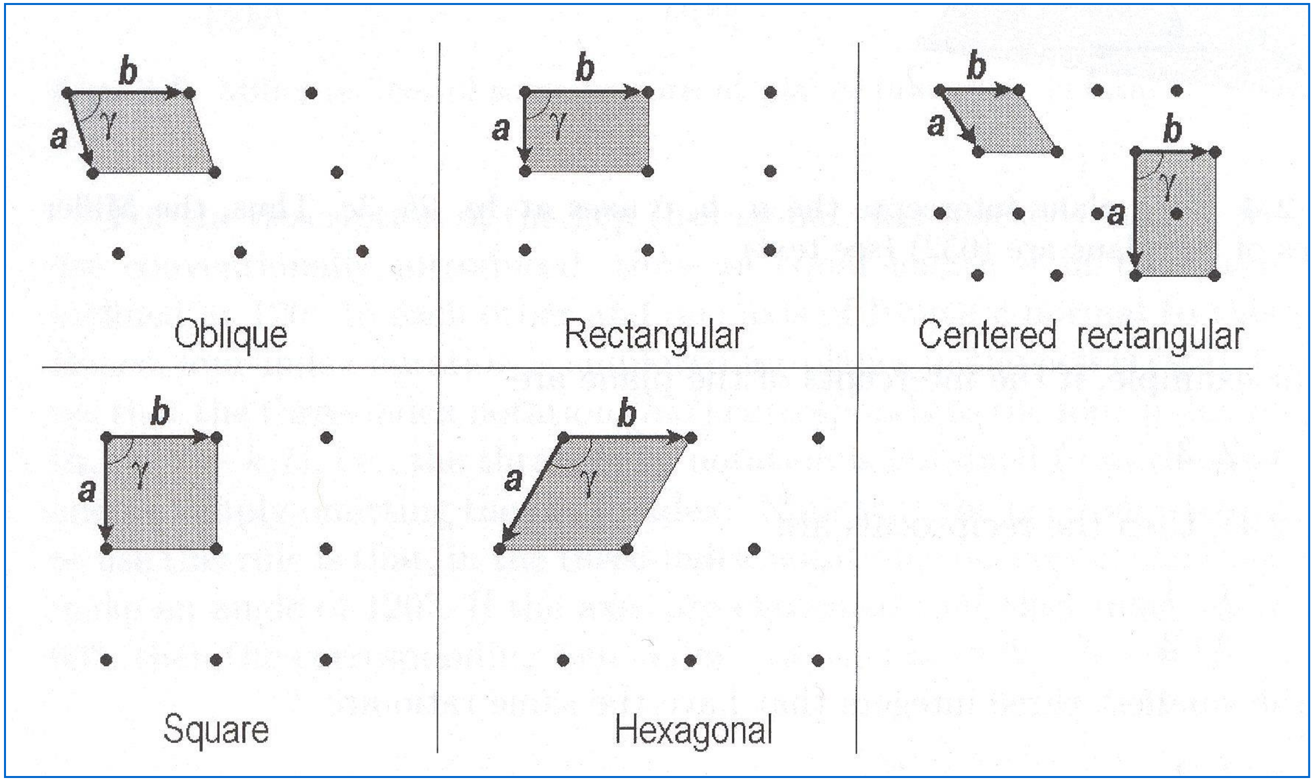
Surface description: Bravais lattices

5 2-dimensional Bravais lattices

(14 3-dimensional Bravais lattices)

|a|≠|b|

|a|=|b|



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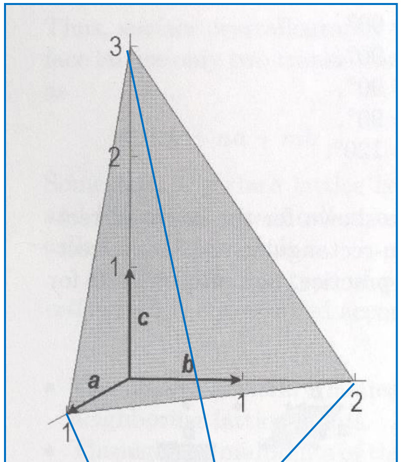
Surface description: Miller indices

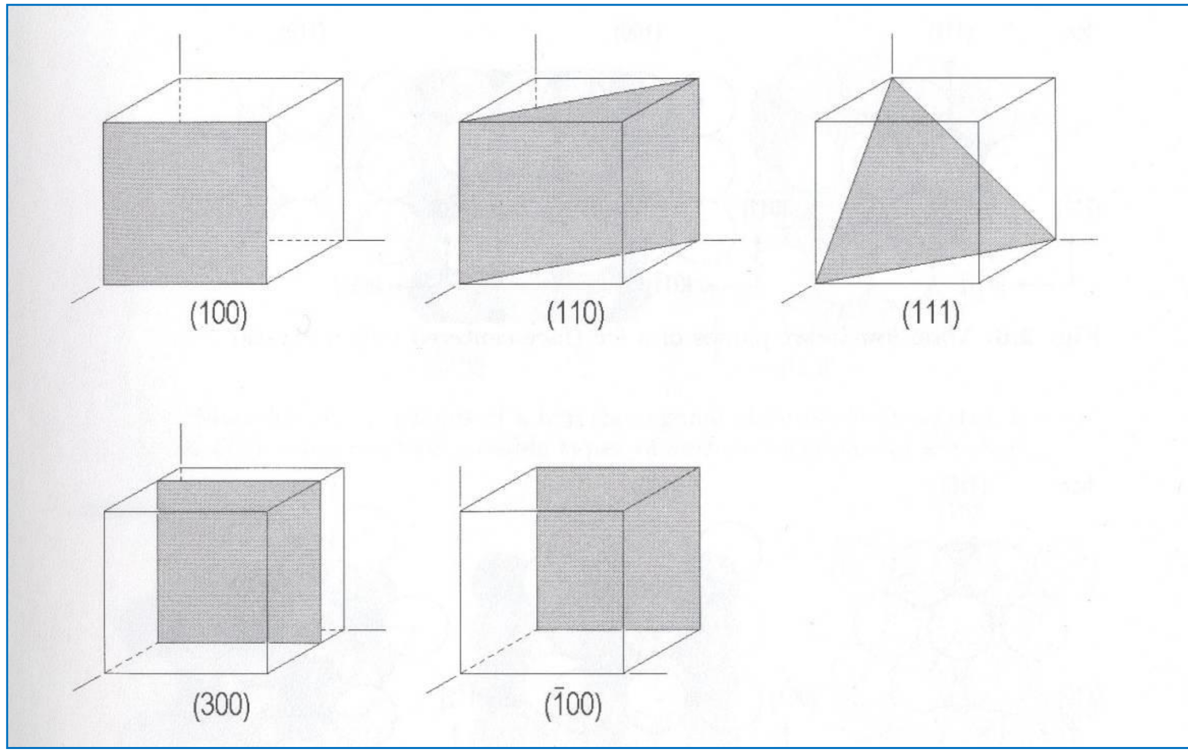


1, 2, 3

1, 1/2, 1/3

(6, 3, 2) - 1 plane
(h, k, l)

{6, 3, 2} - a set of parallel planes



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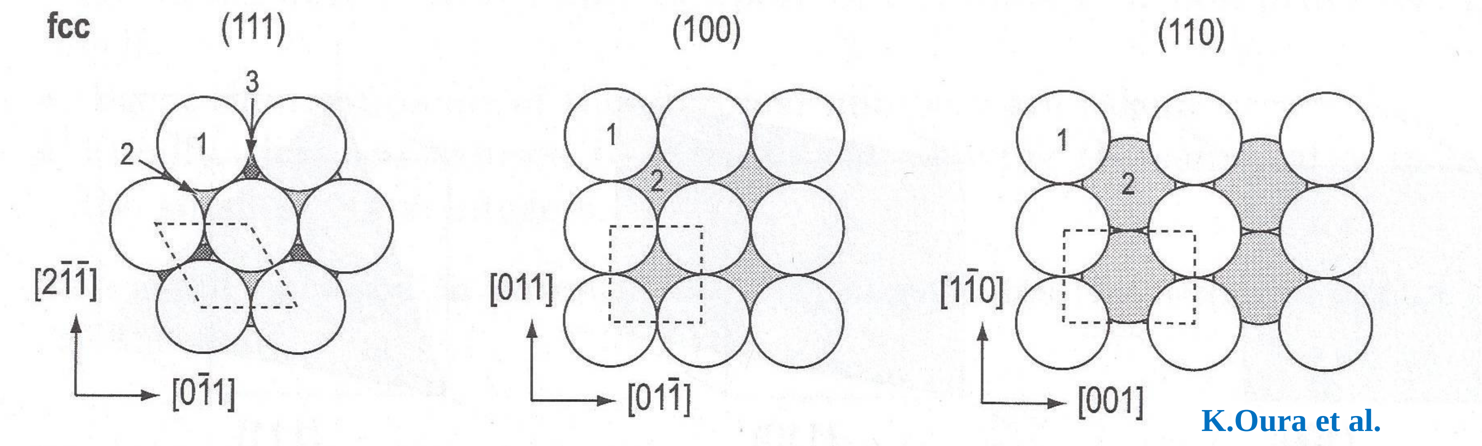
For a hexagonal structure
(h, k, -h-k, l)

Atomic structure of surfaces - examples

Face-centered cubic crystal



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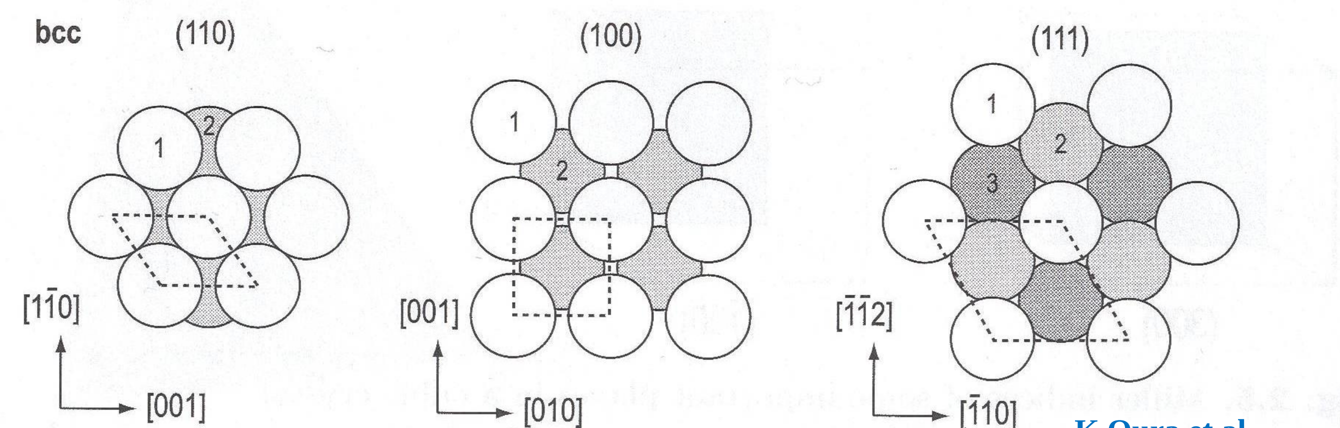
Body-centered cubic crystal



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Surface structure description - notations

Wood's notation

$$|a_s| = m|a|$$

$$|b_s| = n|b|$$

$$\mathrm{S}(hkl) - i(m \times n)R\phi° - N\ Ad$$

$i \downarrow$ $(p \text{ or } c)$

$$\mathrm{Ni}(100) - \left(2\sqrt{2} \times \sqrt{2}\right)R45° - O$$

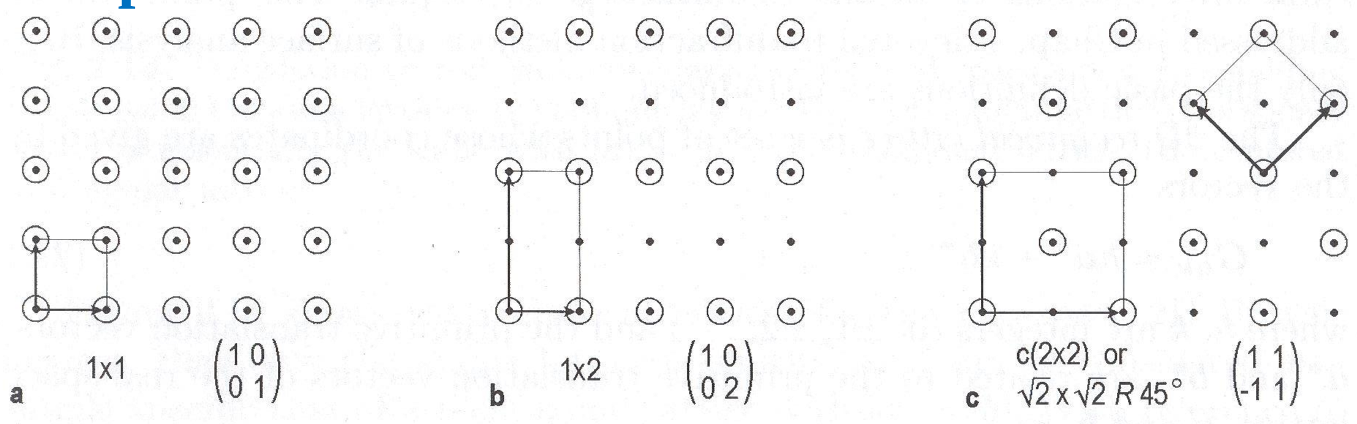
Matrix notation

$$a_s = G_{11}a + G_{12}b$$

$$b_s = G_{21}a + G_{22}b$$

$$G = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$$

Examples:



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Example: Si (111) surface

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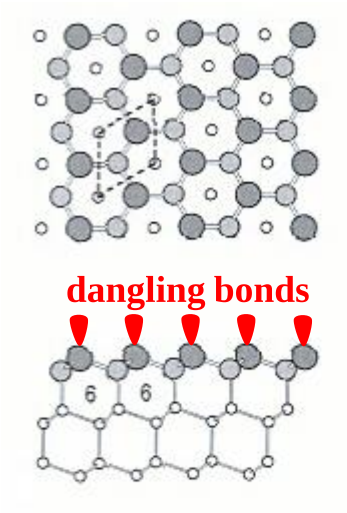
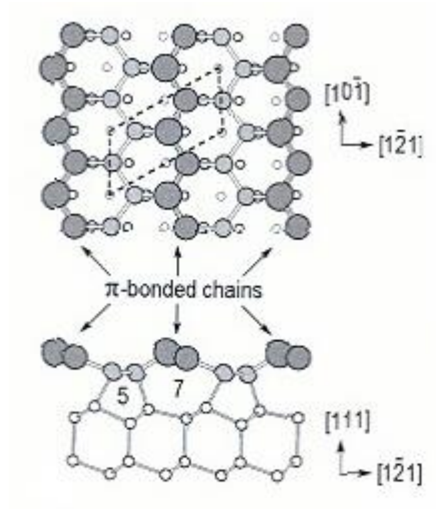
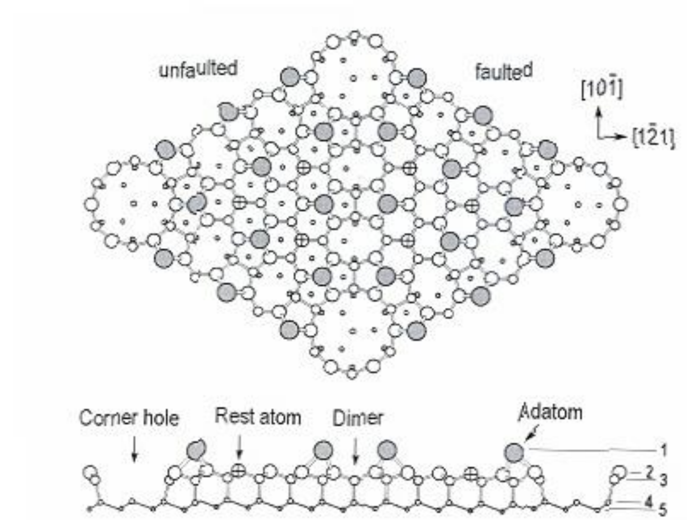






Si(111)- (1x1)

ideal cut

Si(111)- (2x1)

crystal cleaved along (111)

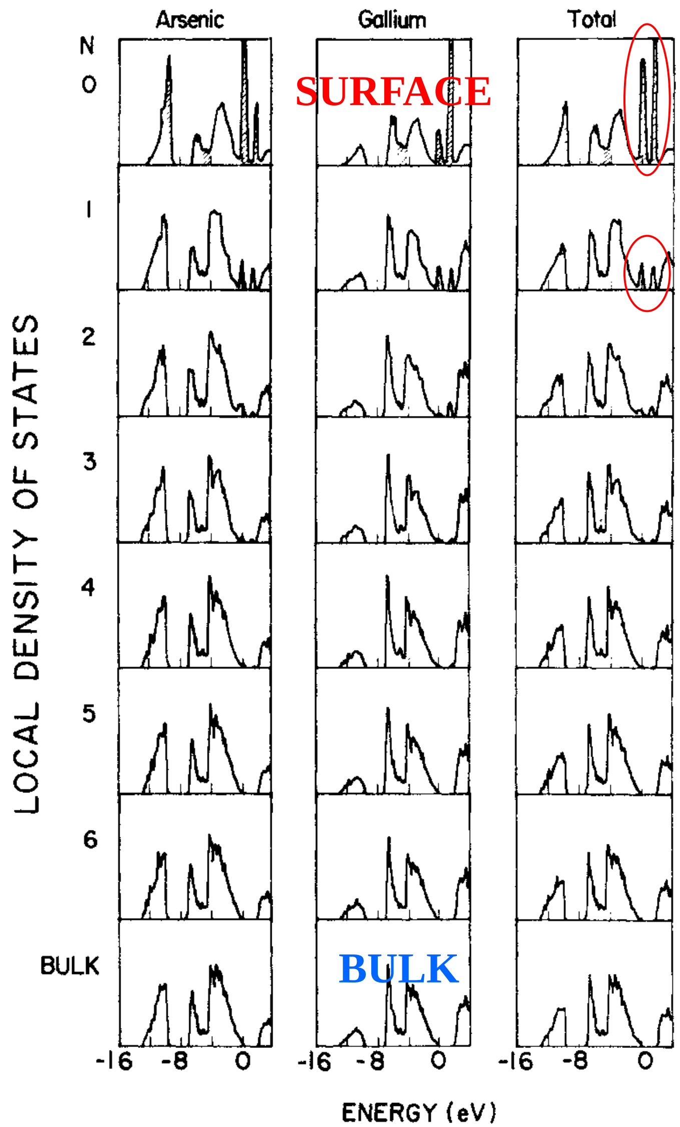
Si(111)- (7x7)

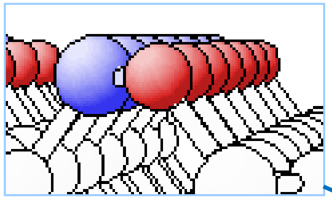
obtained from 2x1 by annealing at 450^{0}C

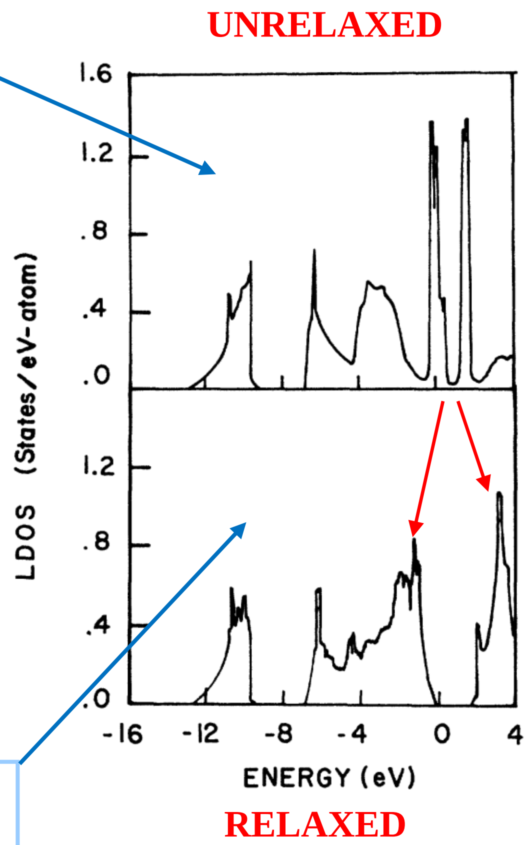
dimer-adatom-stacking fault (DAS) model

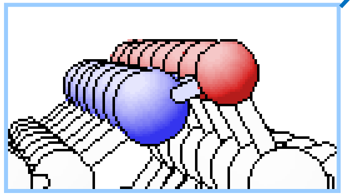
Electronic structure of the surface

unrelaxed GaAs(110)





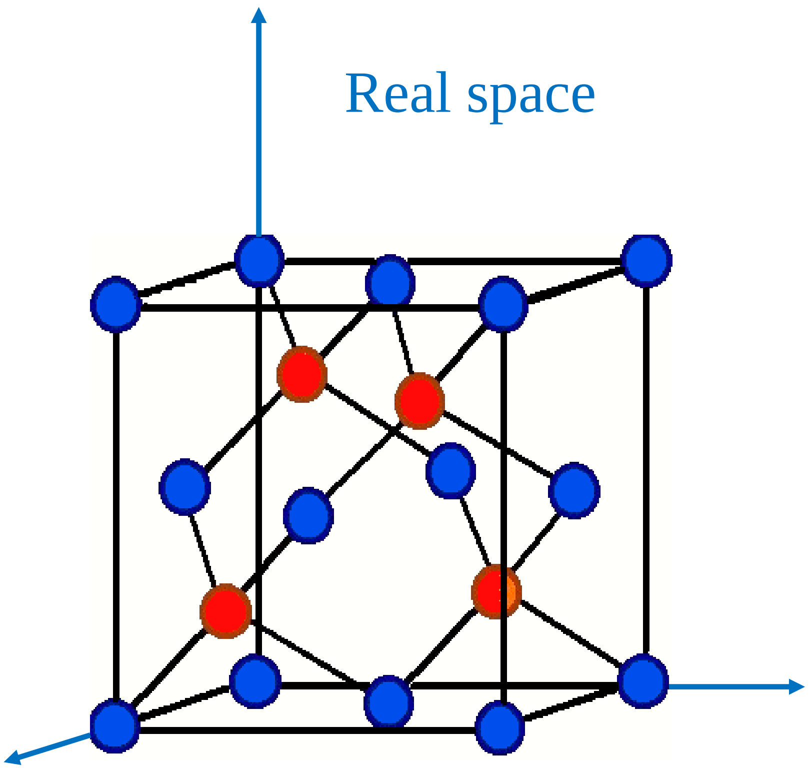


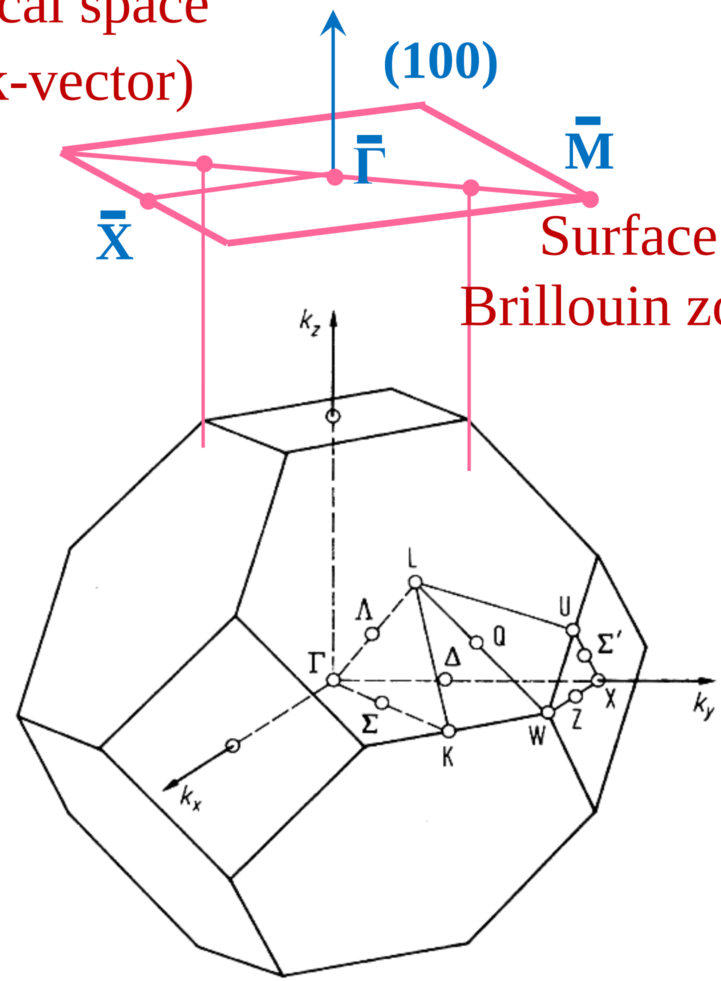


E.J. Mele…, Phys. Rev. B. **17,** 1816 (1978)

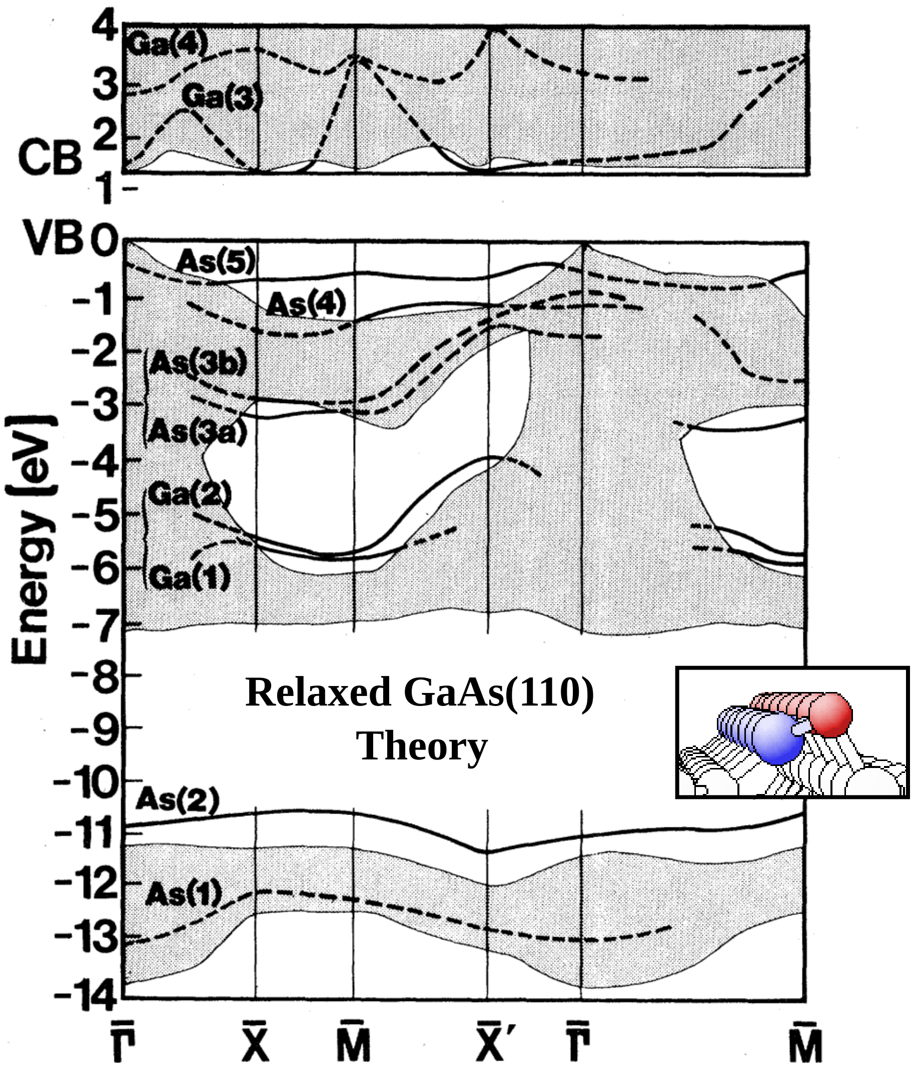
Electronic structure of the surface (cont.)

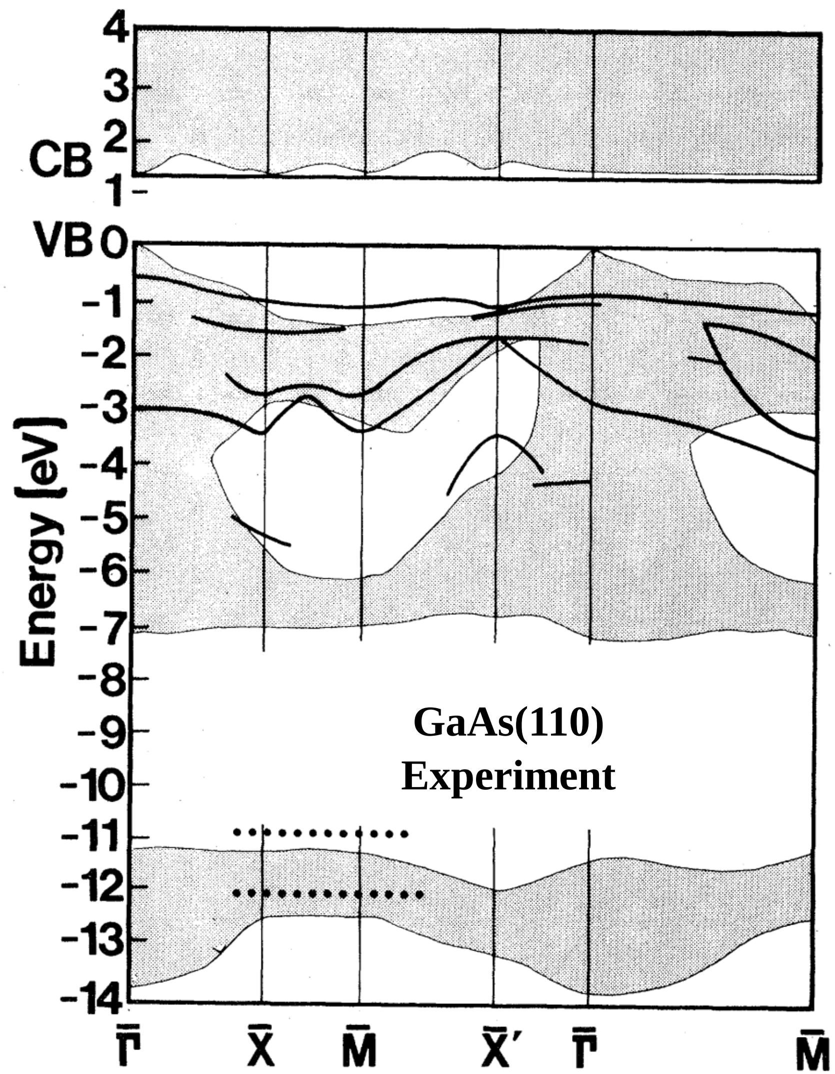
Brillouin zones





Electronic structure of the surface (cont.)



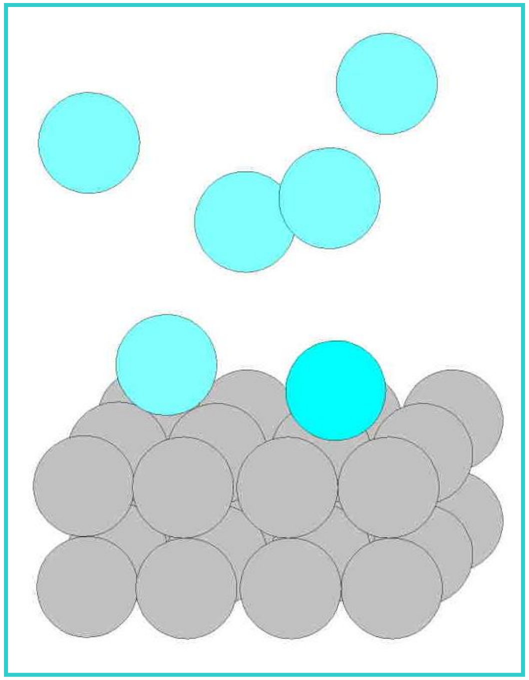


A. Zunger, Phys. Rev. B **22**, 959 (1980)

What do we want to know about surfaces?

- Morphology
- Chemical composition (cleanness, presence of impurities, their surface and depth distribution…)
- Atomic structure
- Electronic structure
- Electronic/electric properties
- Optical properties

Warning! The surface may easily be modified!



Pressure (hPa)	Mean free path	Arrival rate ($cm^{-2}s^{-1}$)	Monolayer arrival time
1000	700 Å	$3x10^{23}$	3 ns
10^{-3}	5 cm	$4x10^{17}$	2 ms
10^{-9}	50 km	$4x10^{11}$	1 hour

1 ML – 10^{15} cm^{-2}, sticking coefficient = 1

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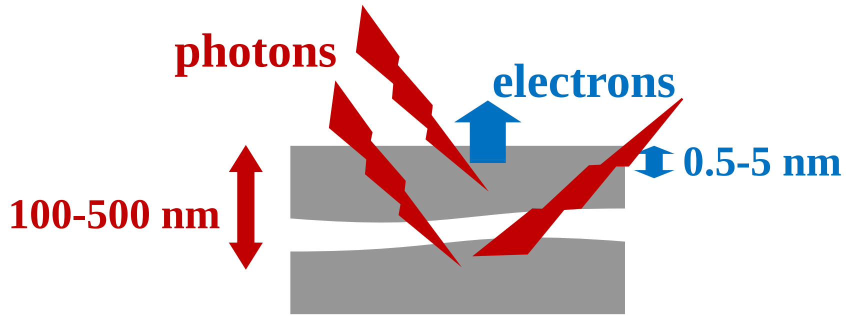
Pressure of the order of 10^{-10} hPa is necessary for studying pristine surfaces!

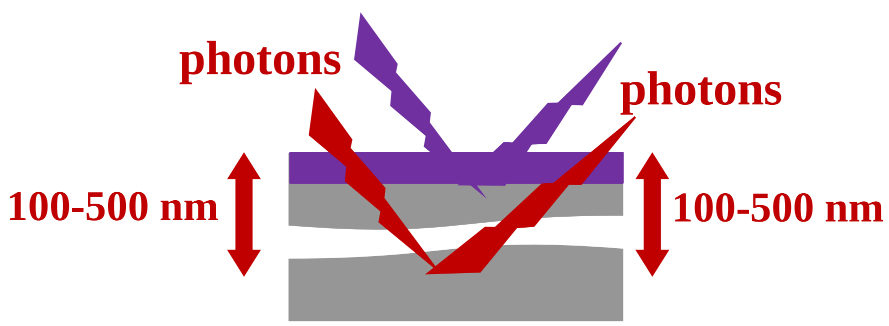
How to extract the signal coming from the surface?

We have to find a proper „probe”



or

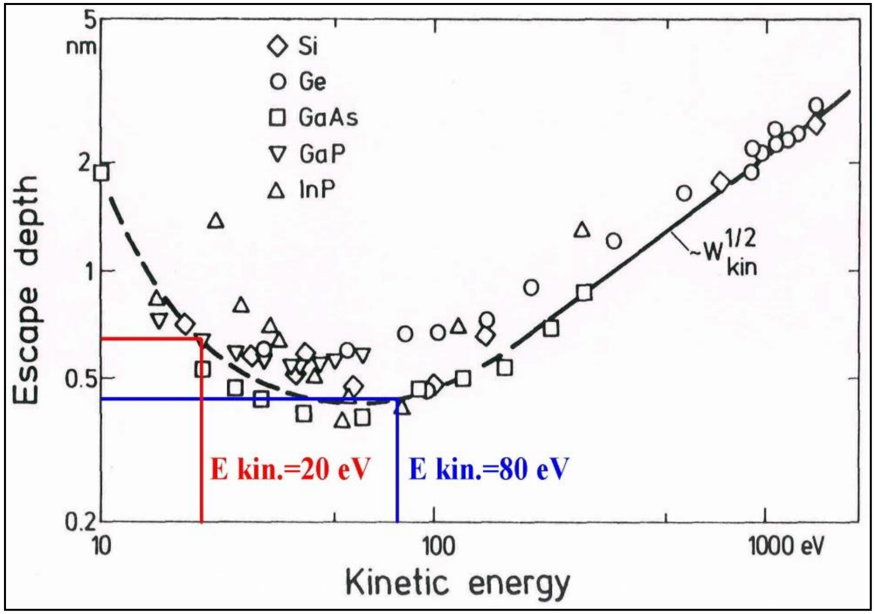
a proper surface-related property



What can be a surface sensitive „probe”?

- **Electrons**

Short escape depth



W. Mönch „Semiconductor surfaces and interfaces” 1993

Available techniques:

•Microscopy

•Diffraction (LEED, RHEED)

•Spectroscopy (photoemission, Auger electron spectroscopy)

What can be a surface sensitive „probe" (cont)?

- **Ions**
  - **Scattering (n.p. RBS)**

  Increased surface sensitivity for selected crystallographic directions (channelling)

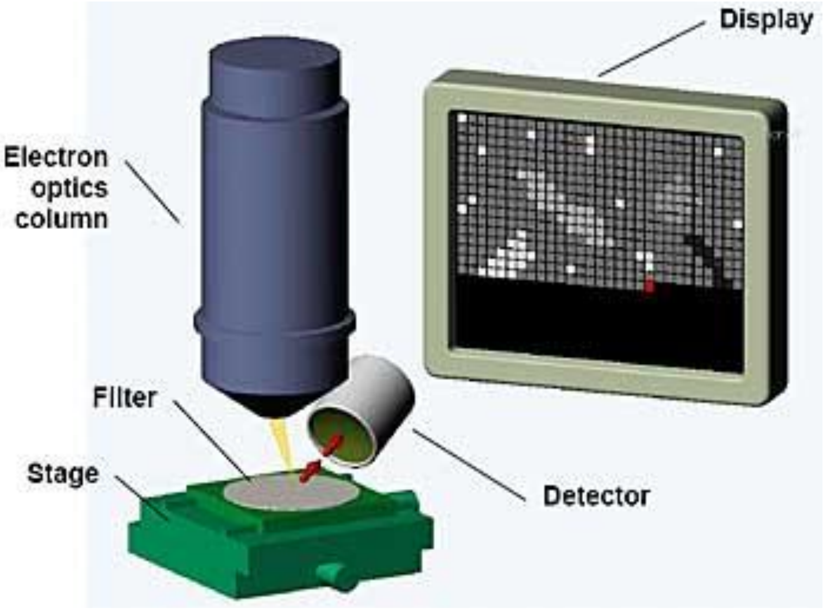
  - **Surface sputtering (SIMS)**

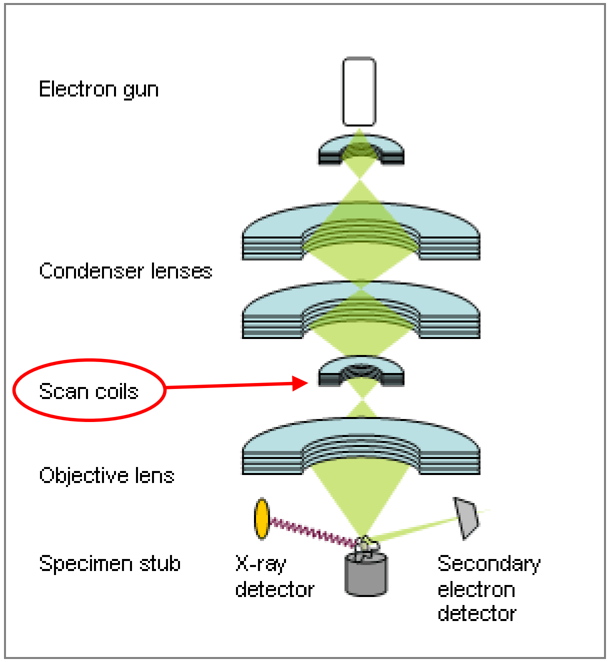
- **Photons**
  - **Surface differential spectroscopy**
  - **X-ray diffraction**

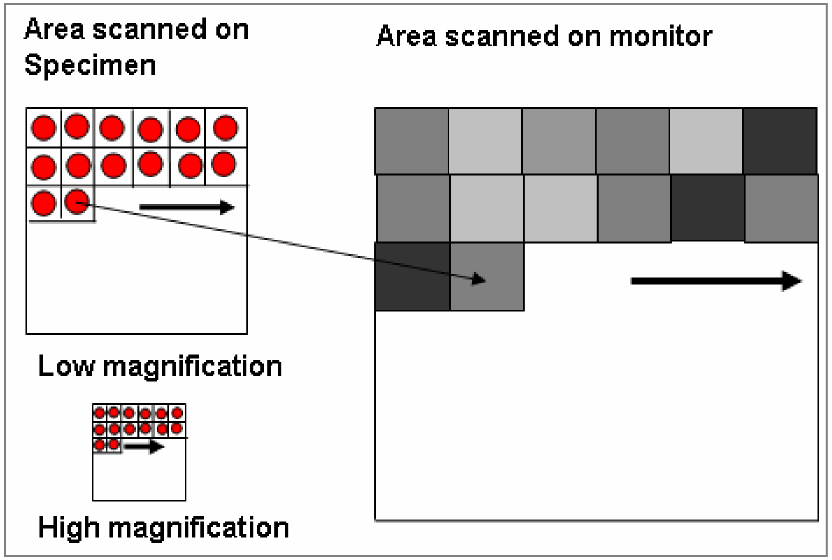
  Increased surface sensitivity for glancing incidence

Microscopies

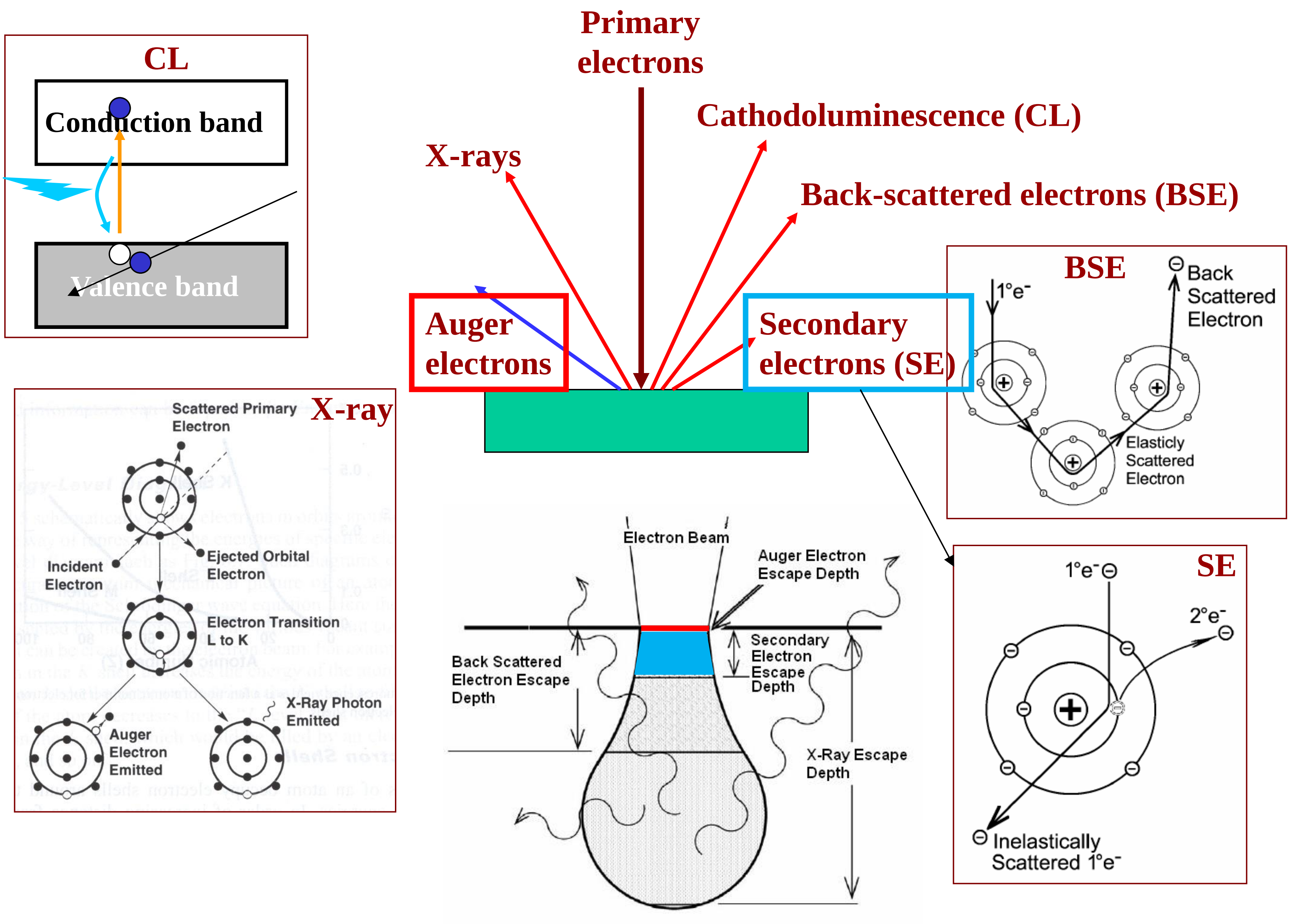
Scanning Electron Microscopy (SEM)





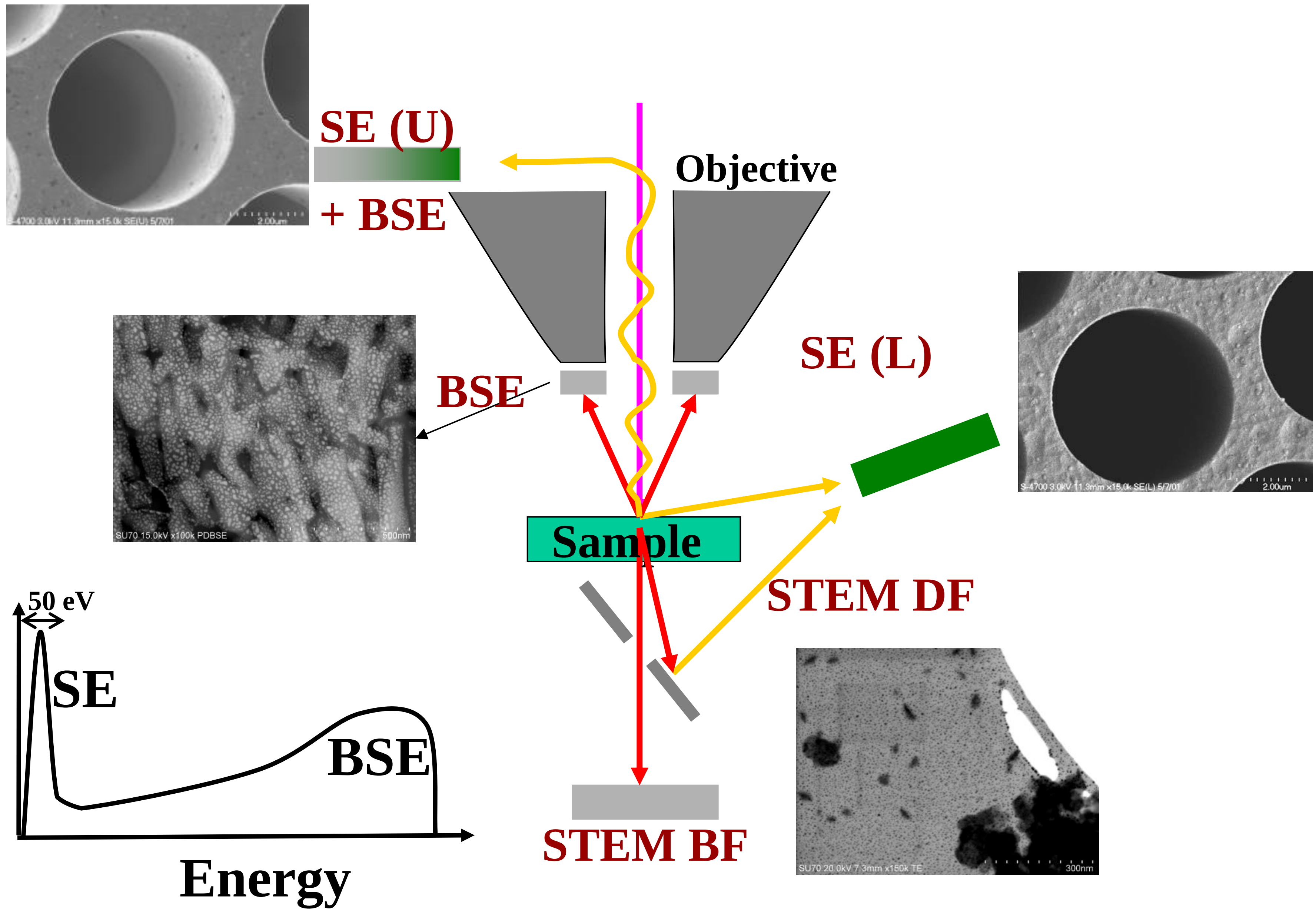


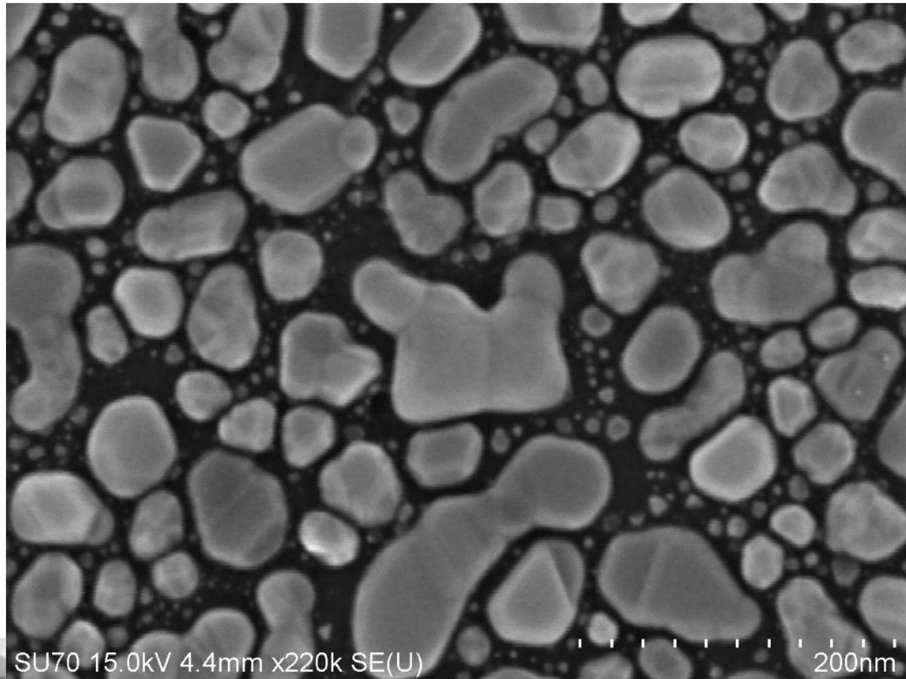
- opaque samples
- $R \approx 1$ nm
- $U_{acc} \leq 30$ kV



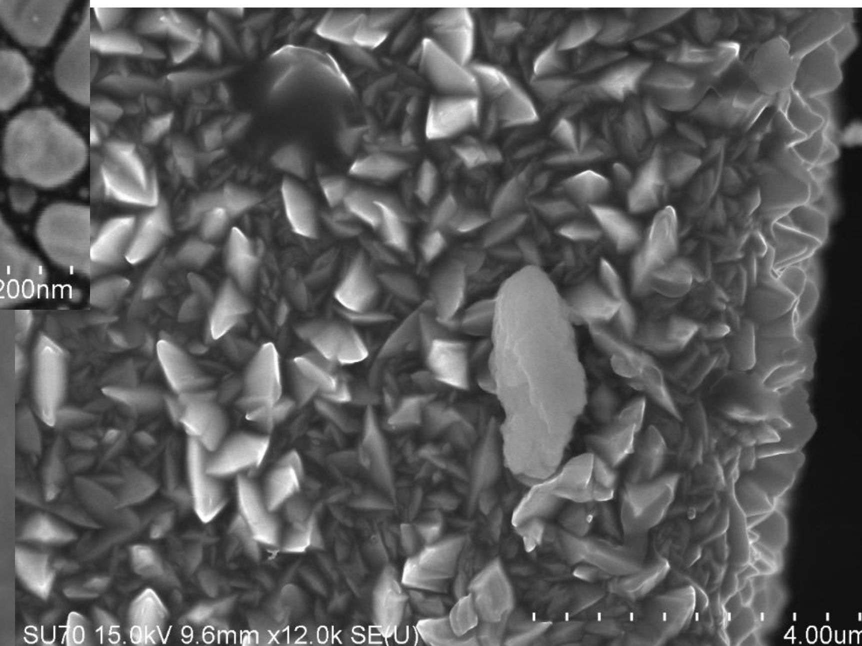
Primary electrons
X-rays
Cathodoluminescence (CL)
Back-scattered electrons (BSE)
Auger electrons
Secondary electrons (SE)
CL
Conduction band
Valence band
X-ray
Scattered Primary Electron
Incident Electron
Ejected Orbital Electron
Electron Transition L to K
Auger Electron Emitted
X-Ray Photon Emitted
BSE
1°e⁻
Back Scattered Electron
Elasticly Scattered Electron
SE
1°e⁻
2°e⁻
Inelastically Scattered 1°e⁻
Electron Beam
Auger Electron Escape Depth
Back Scattered Electron Escape Depth
Secondary Electron Escape Depth
X-Ray Escape Depth

Electron detection in SEM

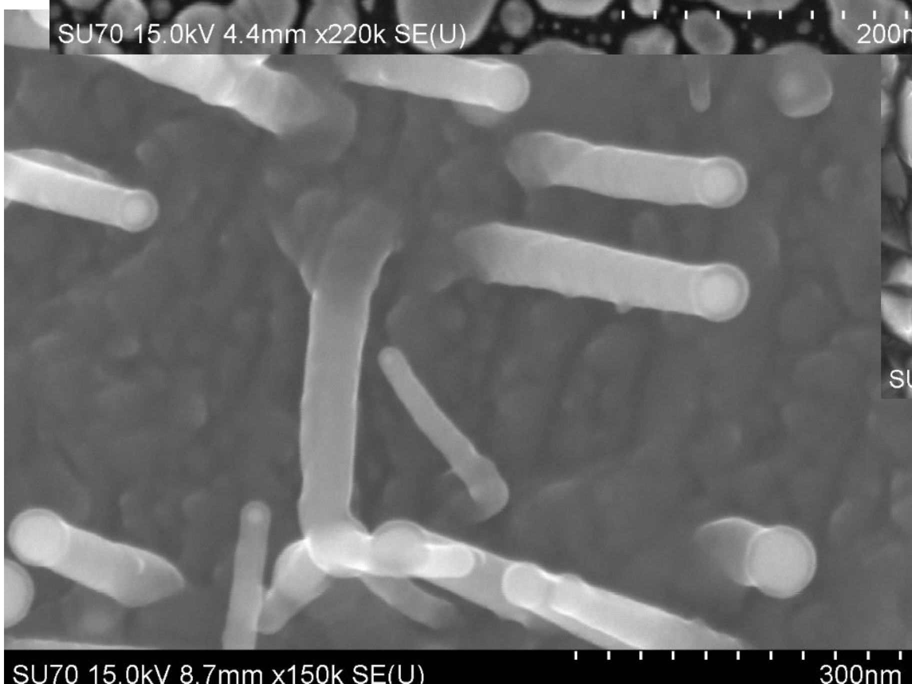




Au islands on C

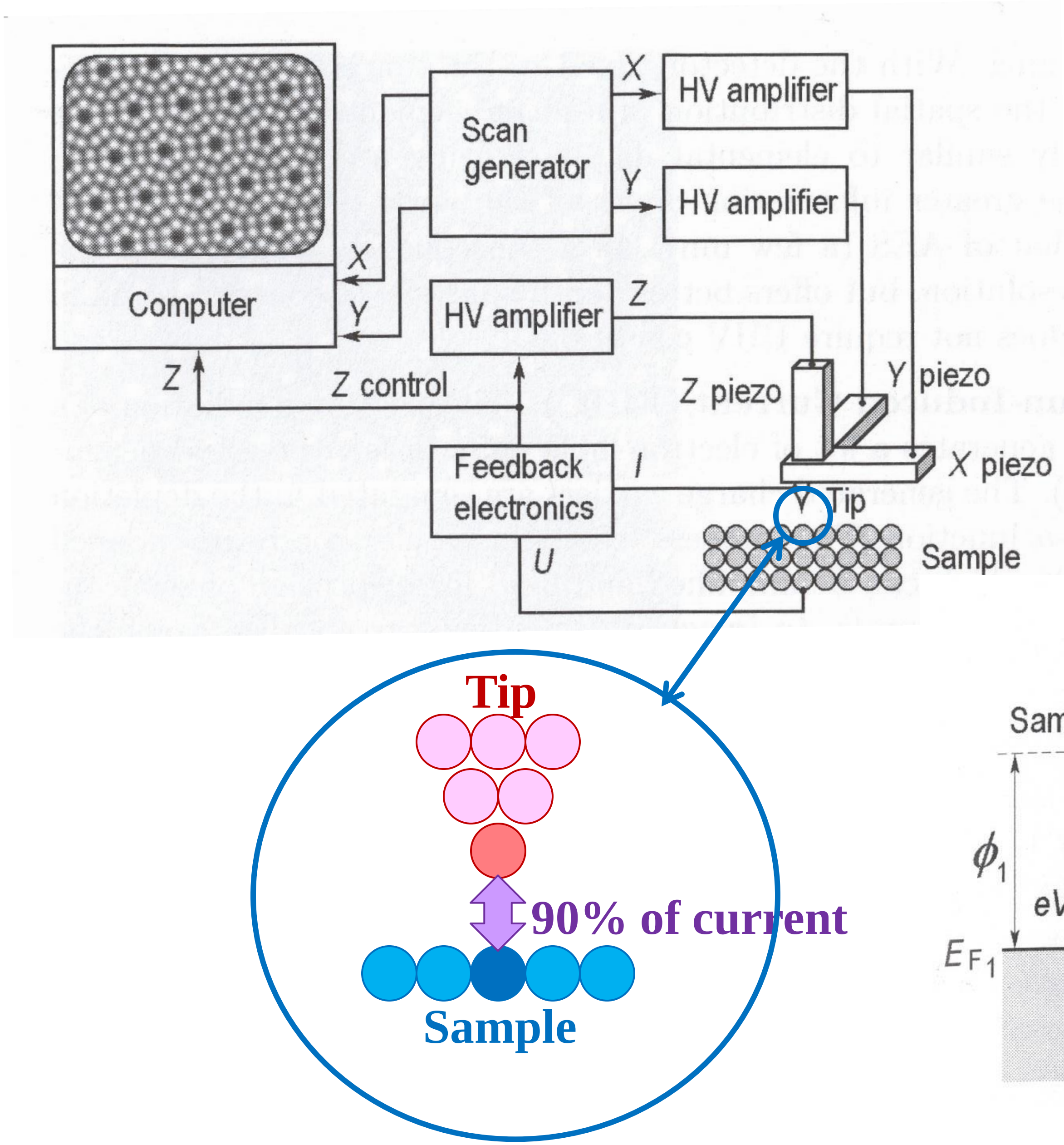


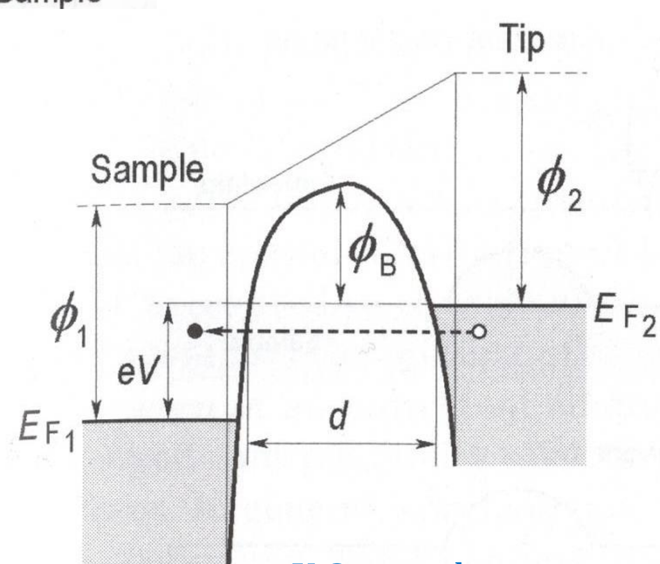
ZnO



ZnTe nanowires

Scanning Tunnelling Microscopy (STM)





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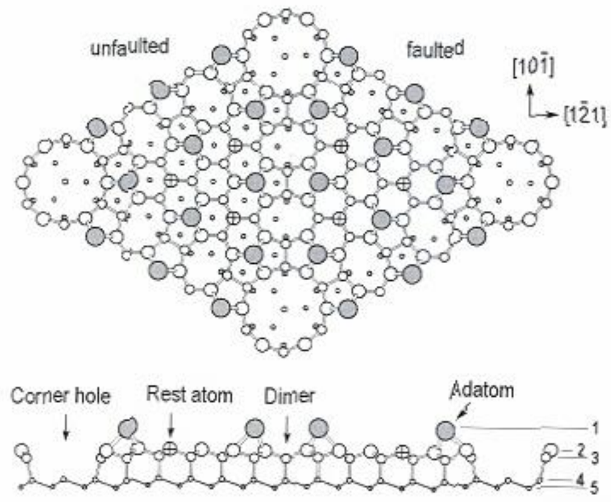
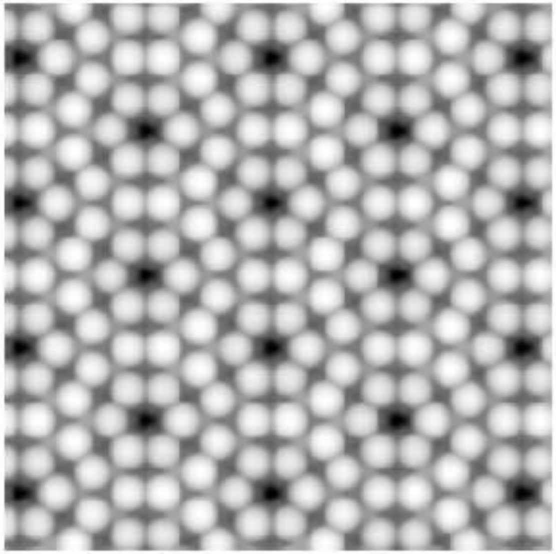
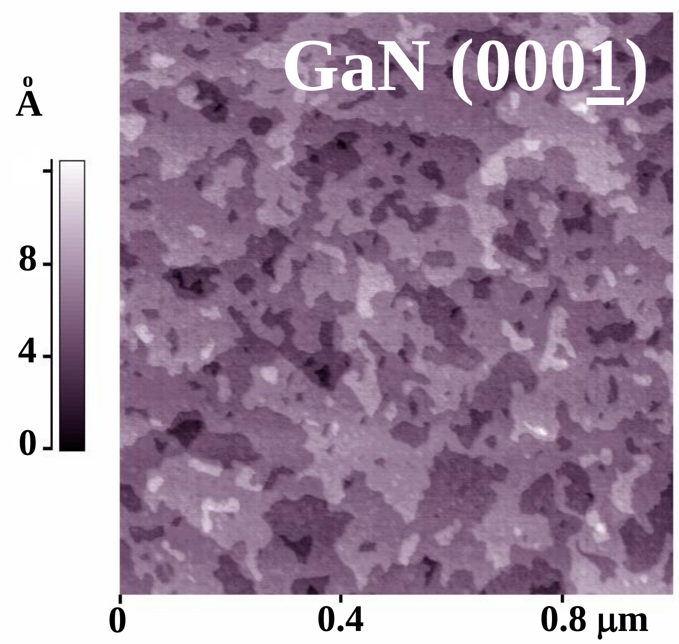
Scanning Tunnelling Microscopy (STM) (cont.)



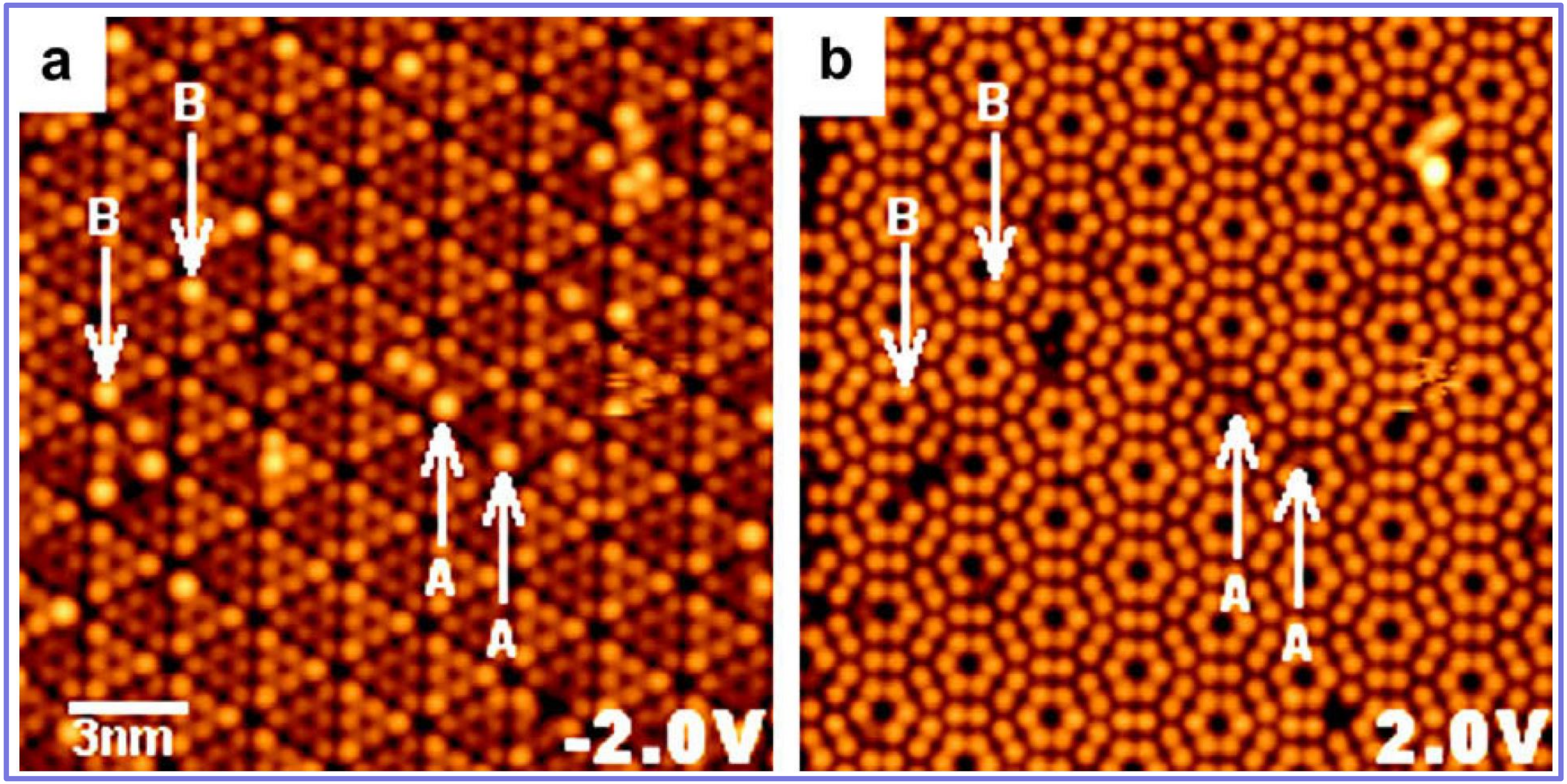
Si(111)- (7x7)





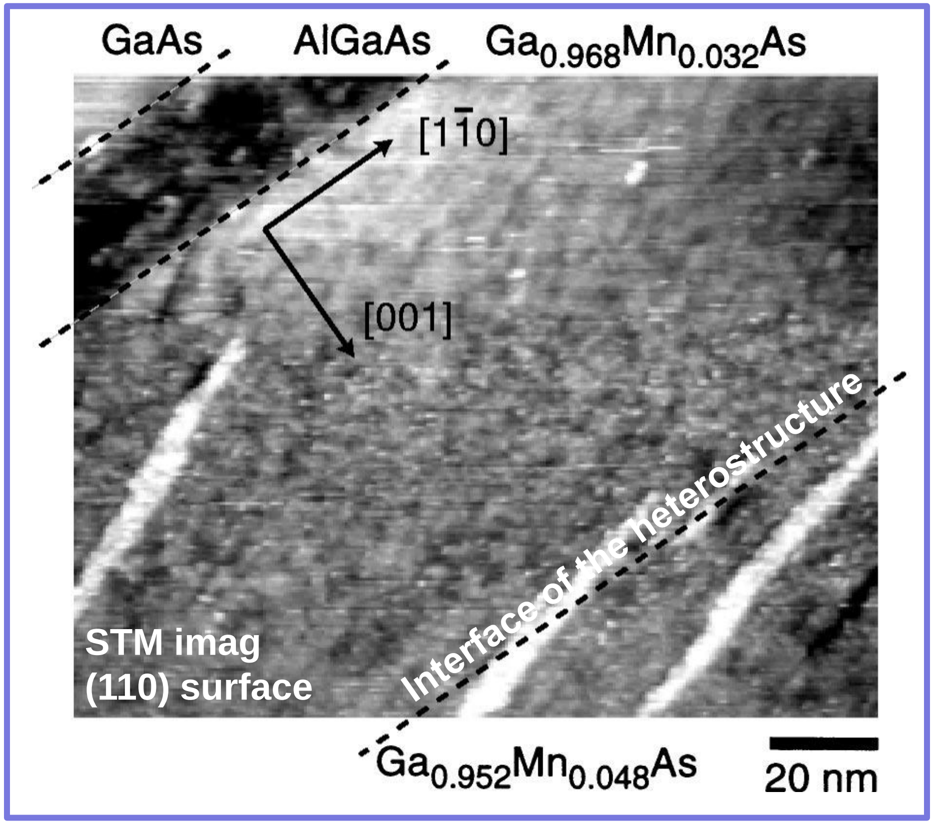
GaN(000<u>1</u>)- (1x1)

Scanning tunnelling microscopy (STM) (cont.)

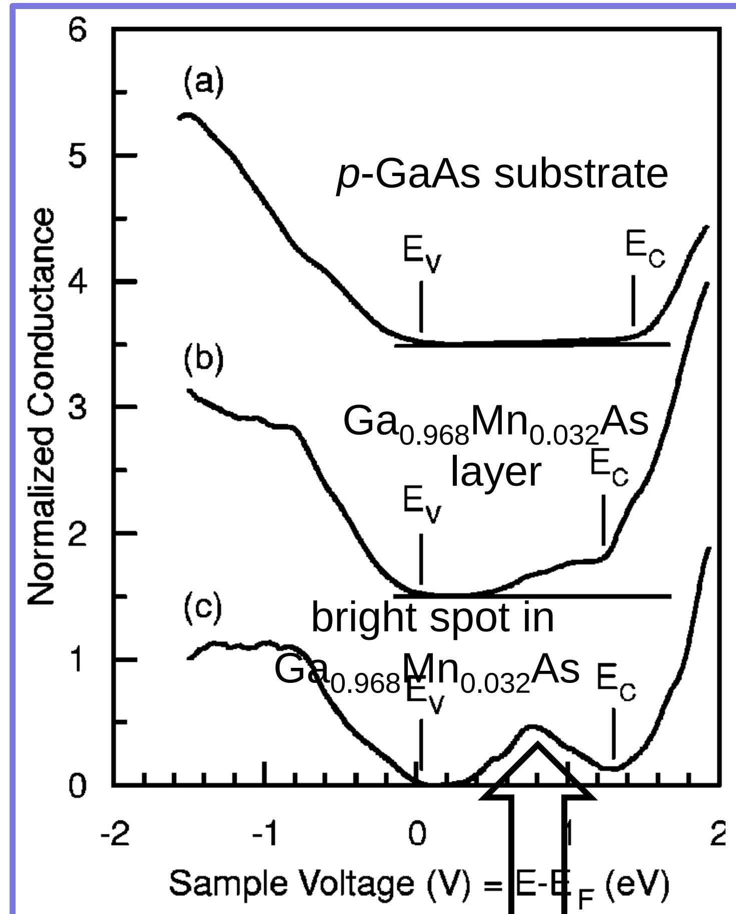


Filled and empty electronic states in STM images of Si(111)-7x7 upon deposition of 0.05 ML of Ta. (P. Shukrynau *et al*. Surface Science **603**, 469 (2009)**)**

Scanning tunnelling spectroscopy (STS)



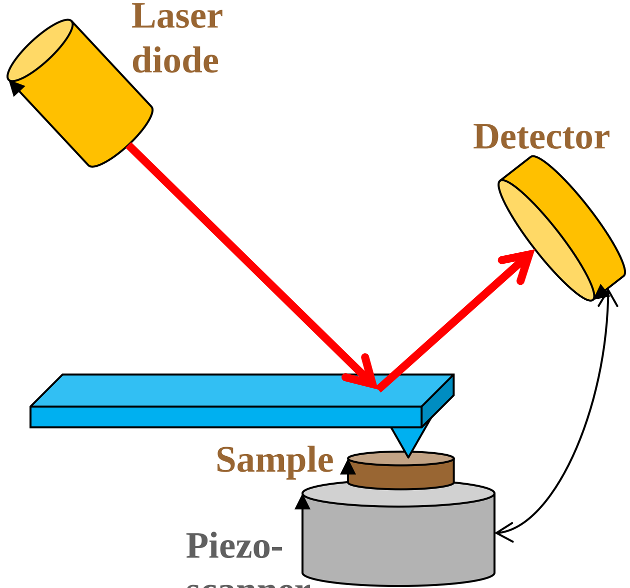
T. Tsuruoka *et al*. Appl. Phys. Lett. **81**, 2800 (2002)

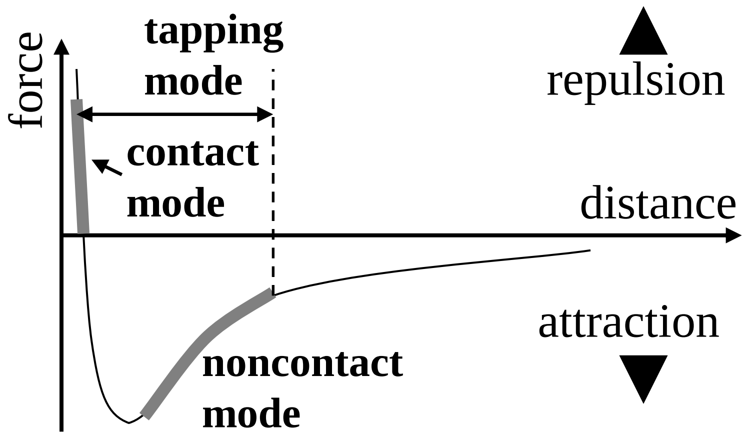


Tunnelling conductance spectra (STS)

tunnelling into the levels of As antisites

Atomic Force Microscopy (AFM)





Forces:

1. Repulsive force, due to the Pauli principle ($z < 0.1$ nm).

2. Force due to the binding between atoms ($z = 0.1$–0.4 nm).

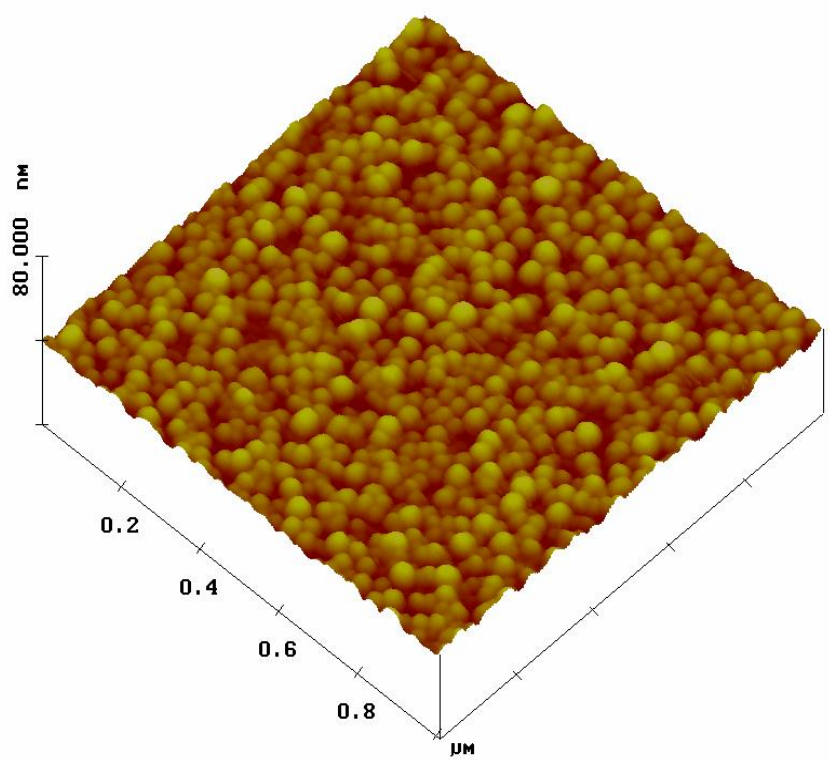
3. Attractive van-der-Waals force (long range, dominating for $z \gg 0.5$ nm).

4. Electrostatic forces (long range, dominating for $z \gg 0.5$ nm).

5. Attractive capillary forces (long range, larger than van-der-Waals force) additionally occur in non-UHV environments.

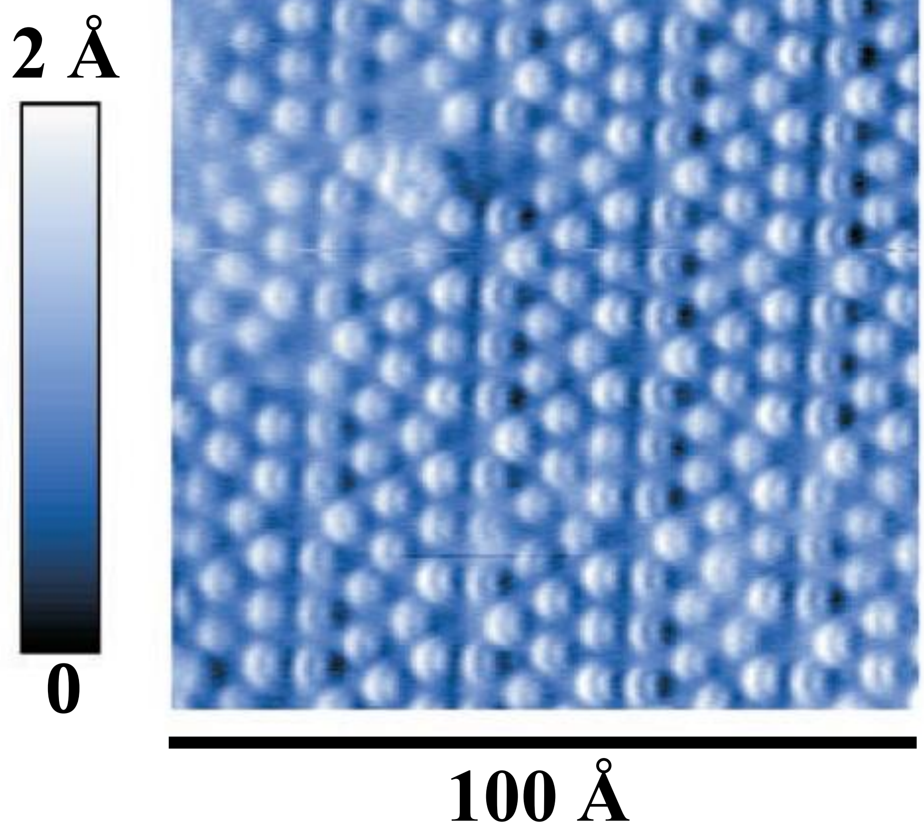
sjhsrc.wikispaces.com

Atomic Force Microscopy (AFM) (cont.)



MnAs dots on GaN(000$\underline{1}$)

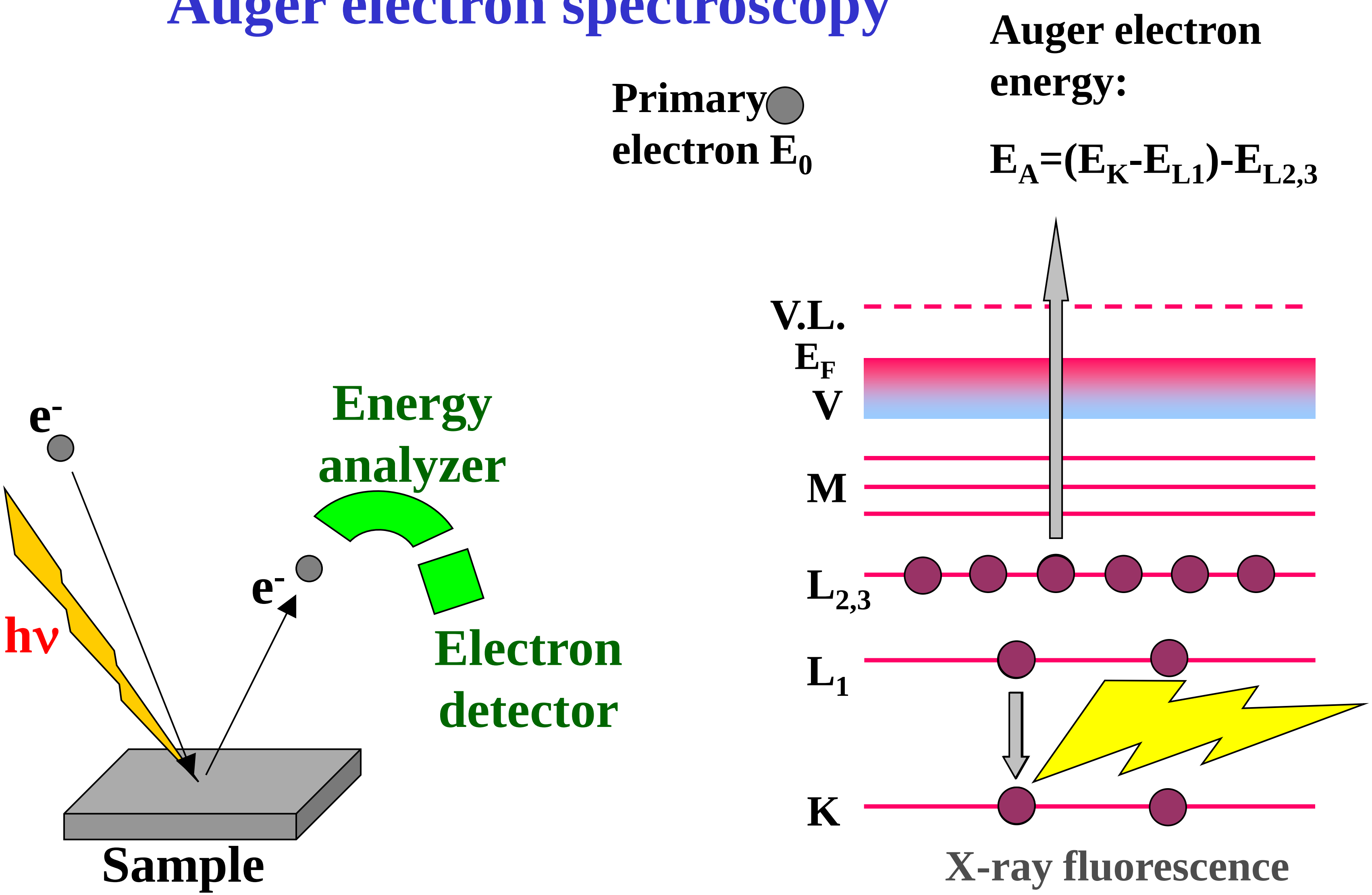
Si(111)-(7x7)

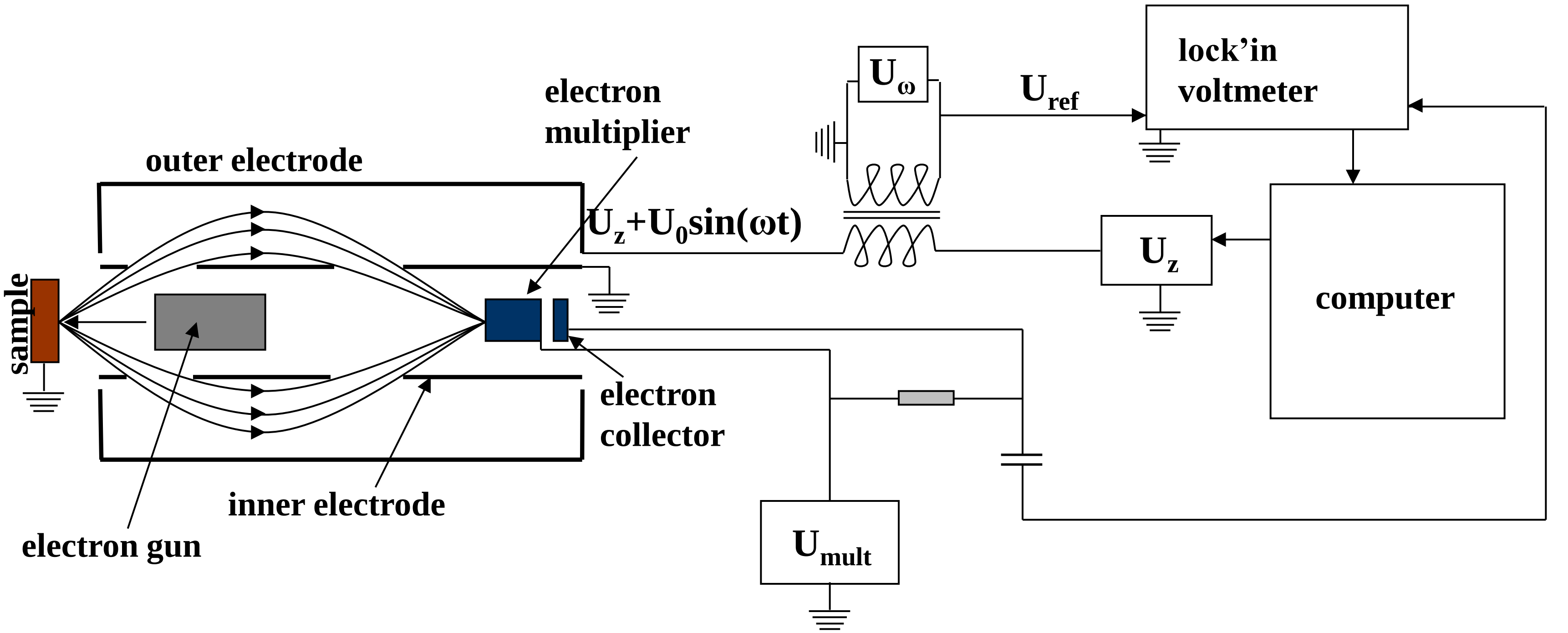


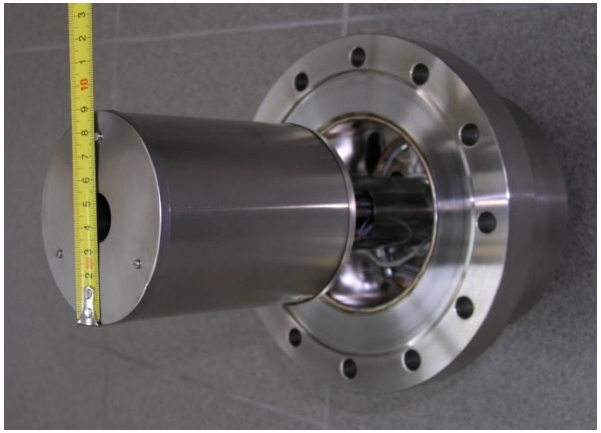
F.J. Giessibl et al., Science **289**, 422 (2000)

Electron spectroscopies

Auger electron spectroscopy







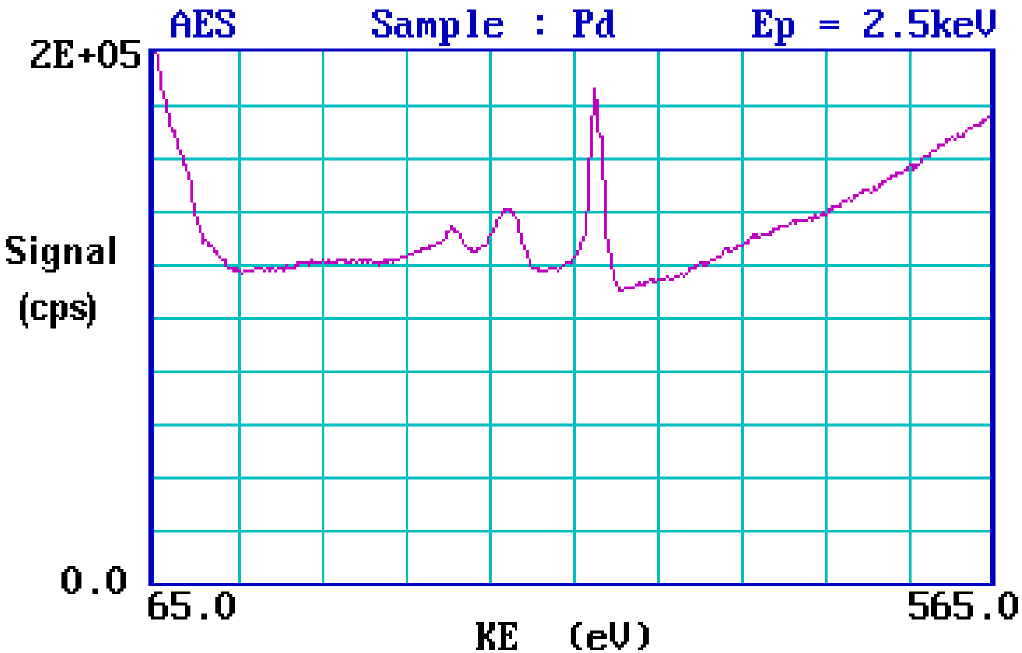
Auger electron spectrometer with a cylindrical mirror analyser

Primary electron energy: up to 3kV

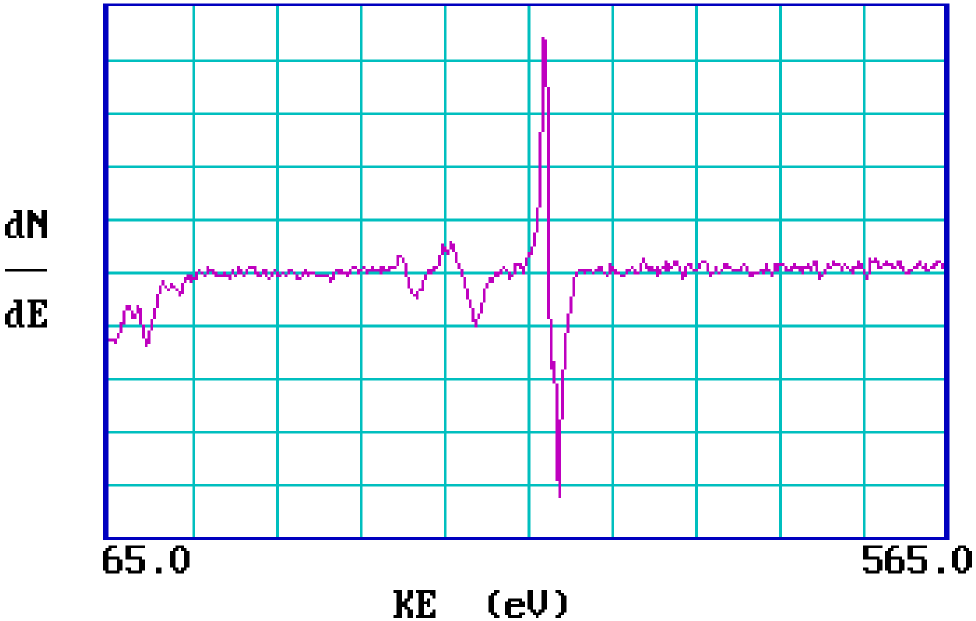
Resolving power: E/ΔE > 145

Modes of AES spectra acquisition:

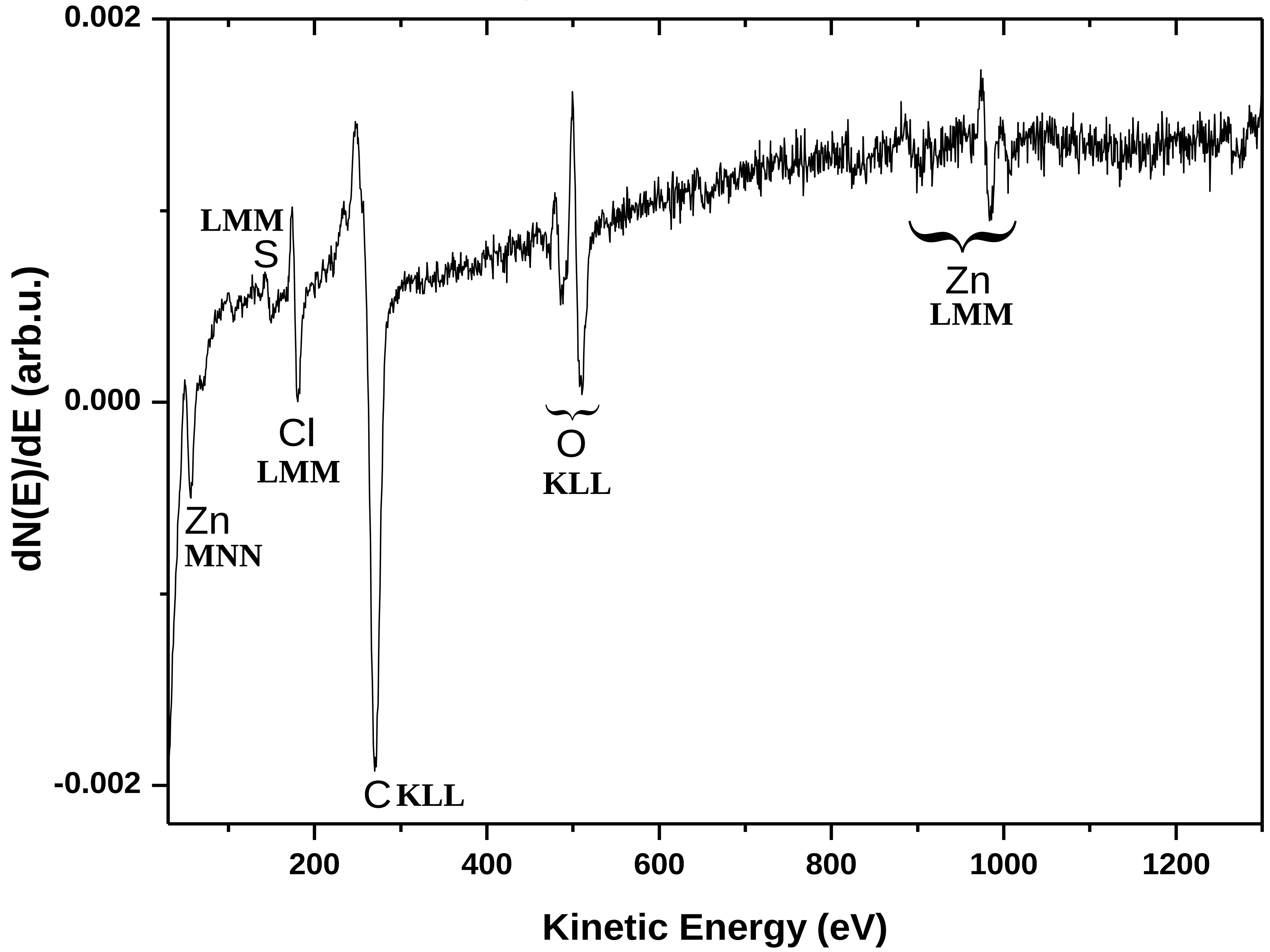
integral



differential

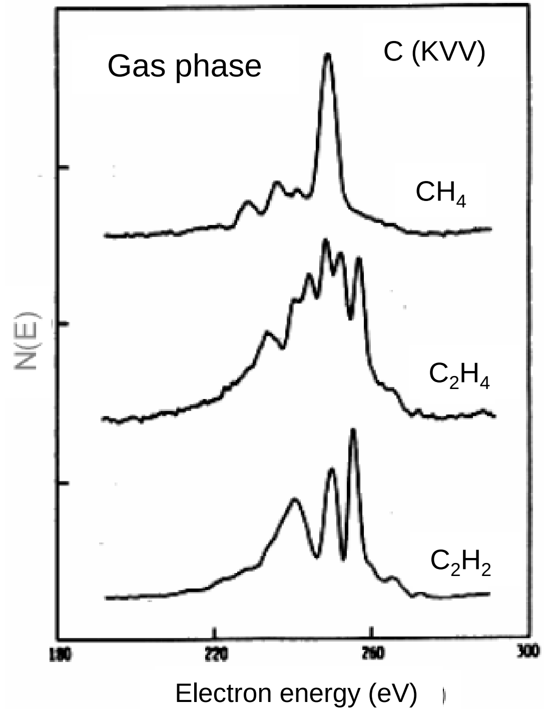


Auger electron spectrum of a ZnO layer grown by ALD

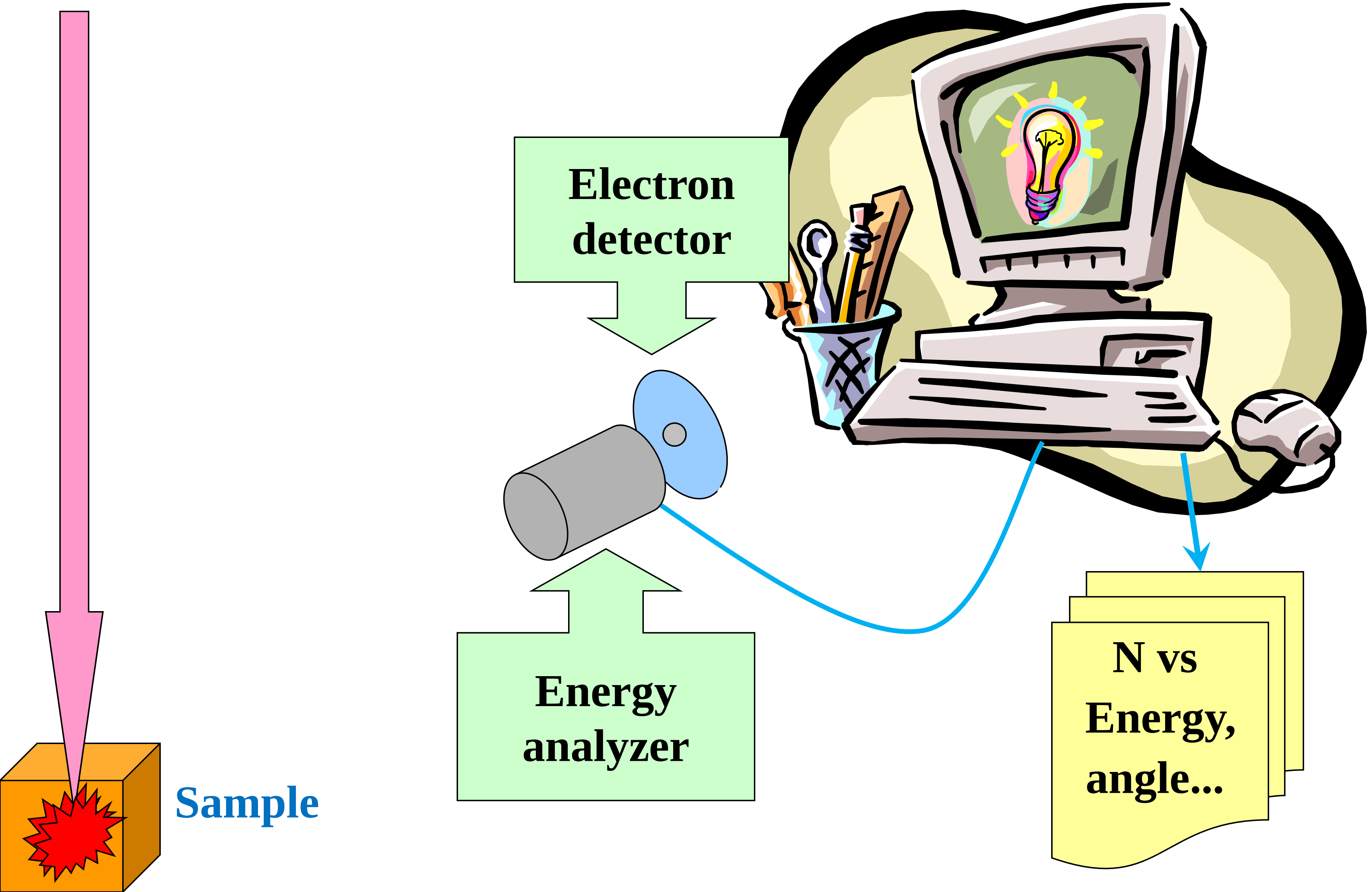


Auger electron spectroscopy:

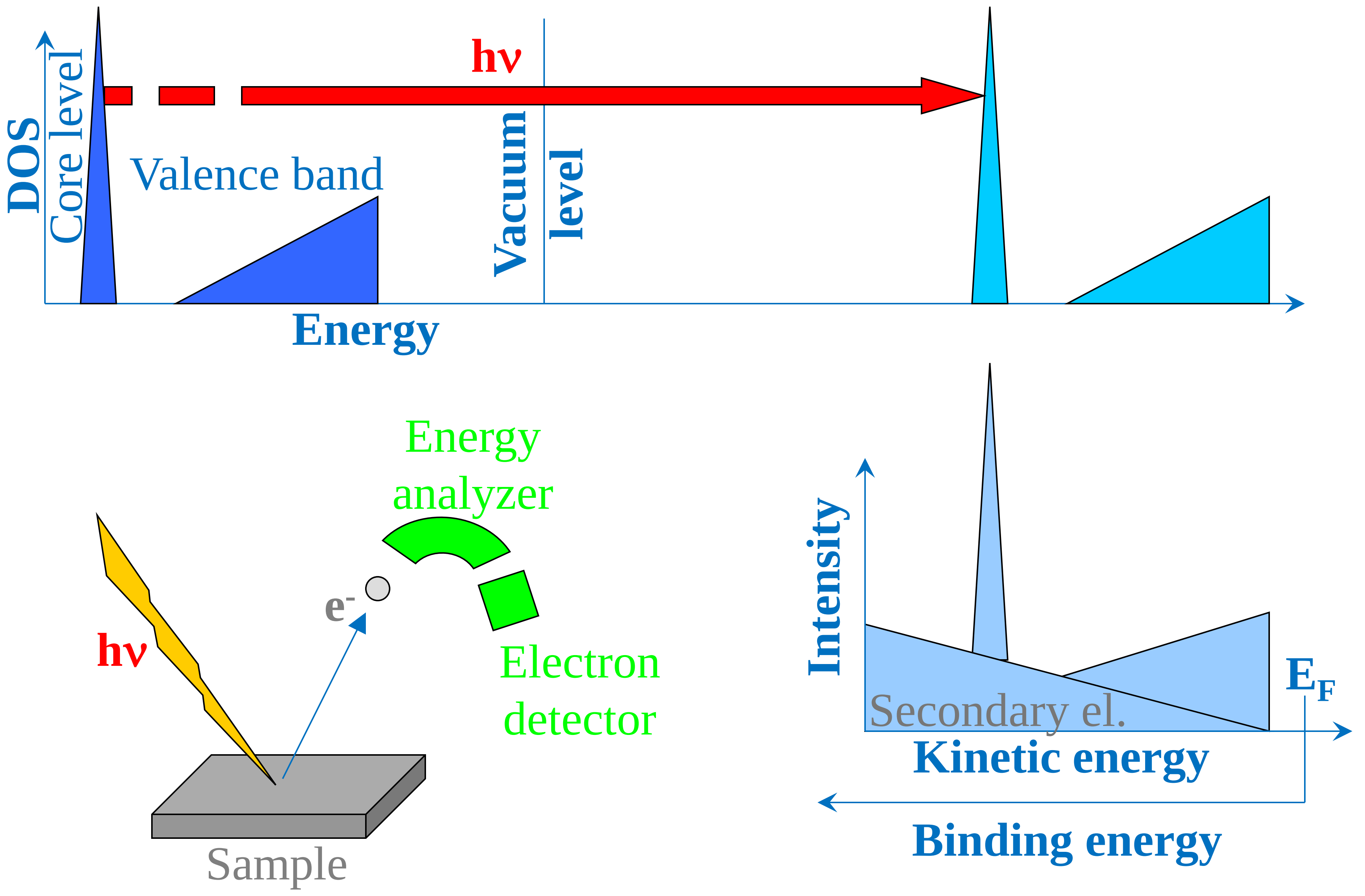
1. Analysis of the sample surface composition - detection of all elements except hydrogen and helium
2. Simple interpretation of spectra - a large database of reference spectra
3. Quantitative analysis possible - especially by comparison with standards
4. Possibility to analyze the 2D or 3D distribution
5. Sometimes spectra are sensitive to chemical bonds



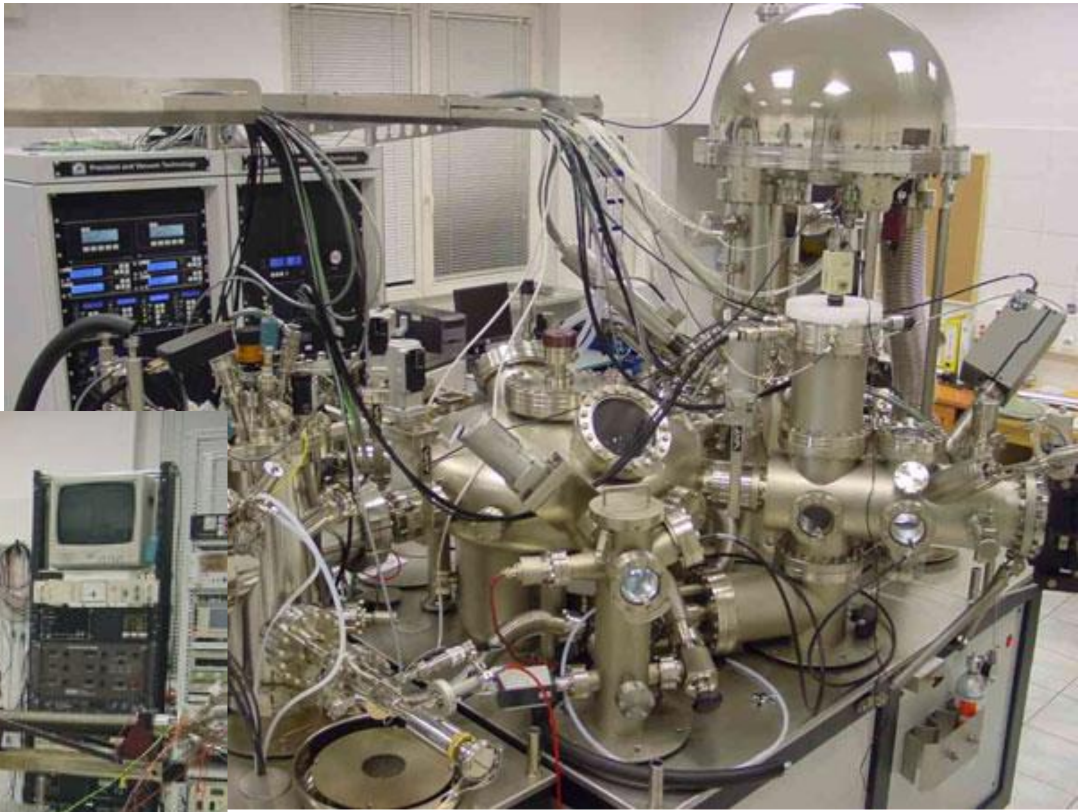
Photoemission spectroscopy



Spektroskopia fotoemisyjna



Photoemission needs Ultra High Vacuum (UHV)!

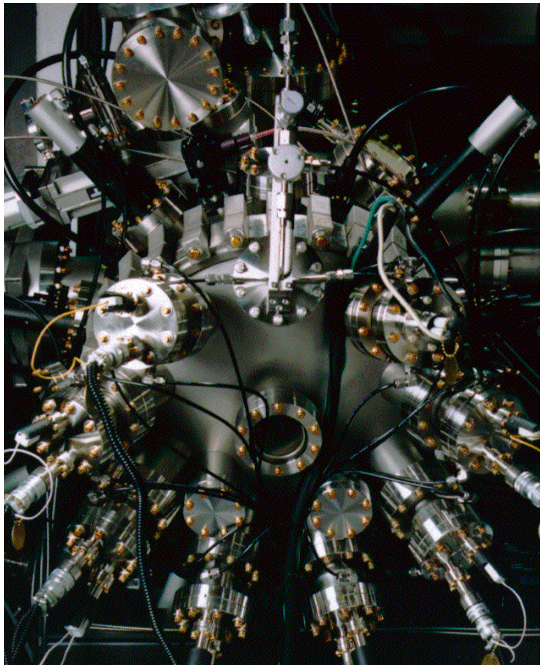


atom.ik-pan.krakow.pl

Surface preparation

www.mshel.com

- **Cleavage**



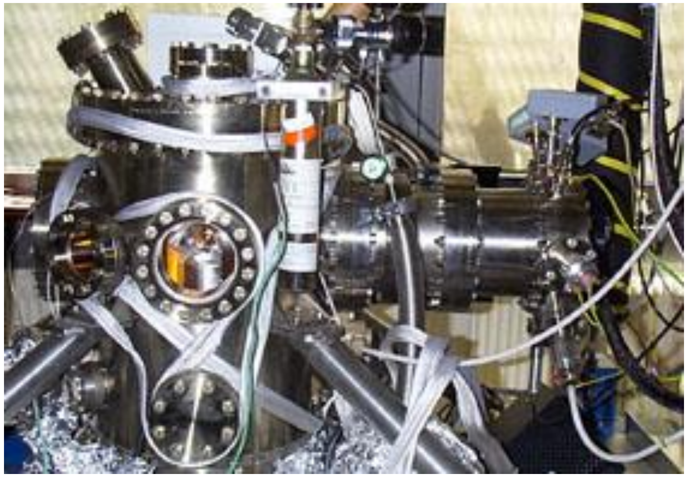
www.ems.psu.edu

- ***In situ* epitaxy**

- ***In situ* cleaning:**

  - ion etching

  - annealing



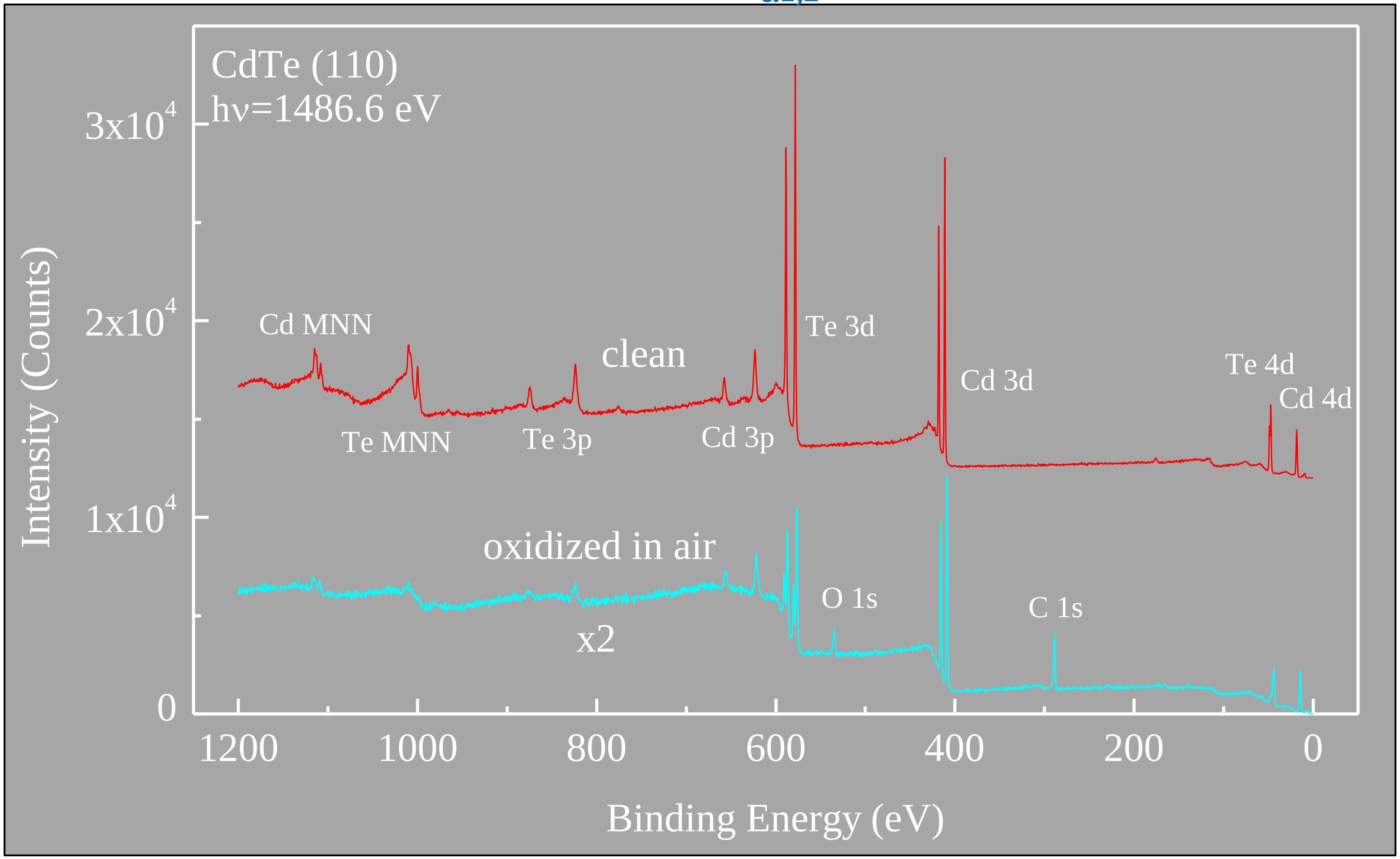
www.exphys.uni-linz.ac.at

X-ray **P**hotoelectron **S**pectroscopy **(XPS)**

or **E**lectron **S**pectroscopy for **C**hemical **A**nalysis **(ESCA)**

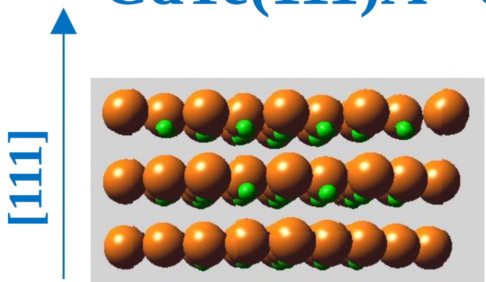
XPS: $h\nu > 1000$ eV; $h\nu = 1000$ eV $\rightarrow$ $\mathbf{k} = 0.506$ Å^{-1}

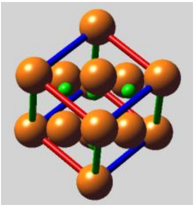
X-ray source: Al $K_{\alpha 1,2}$ - 1486.6 eV

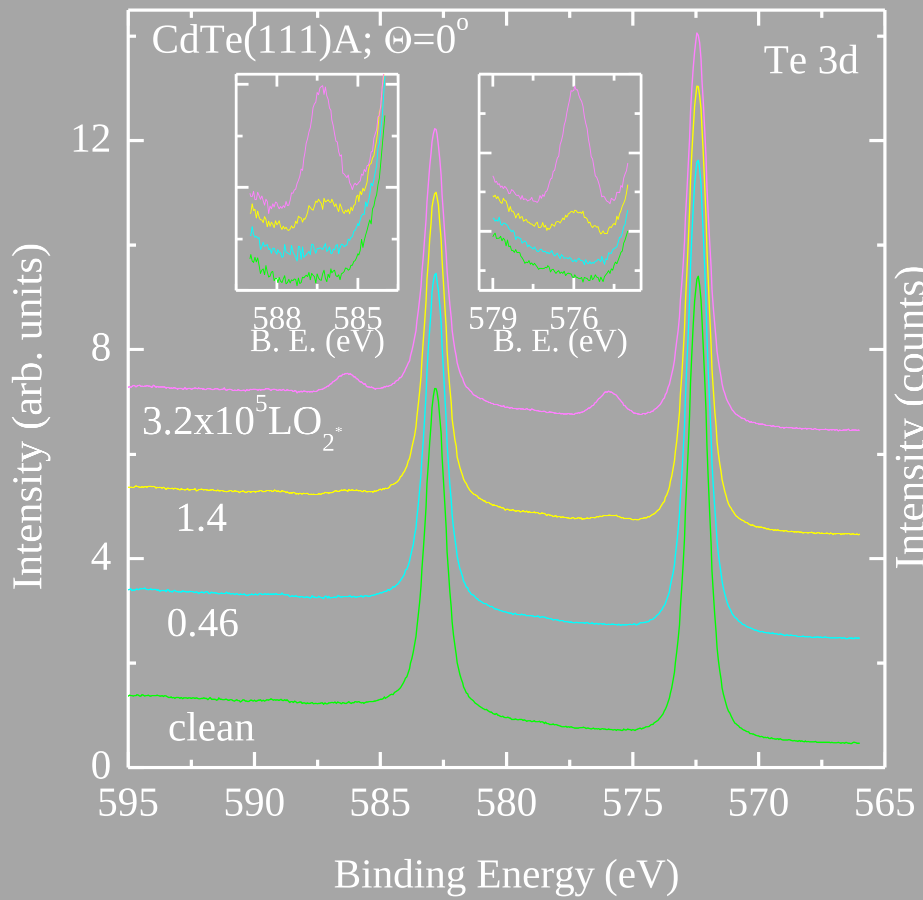


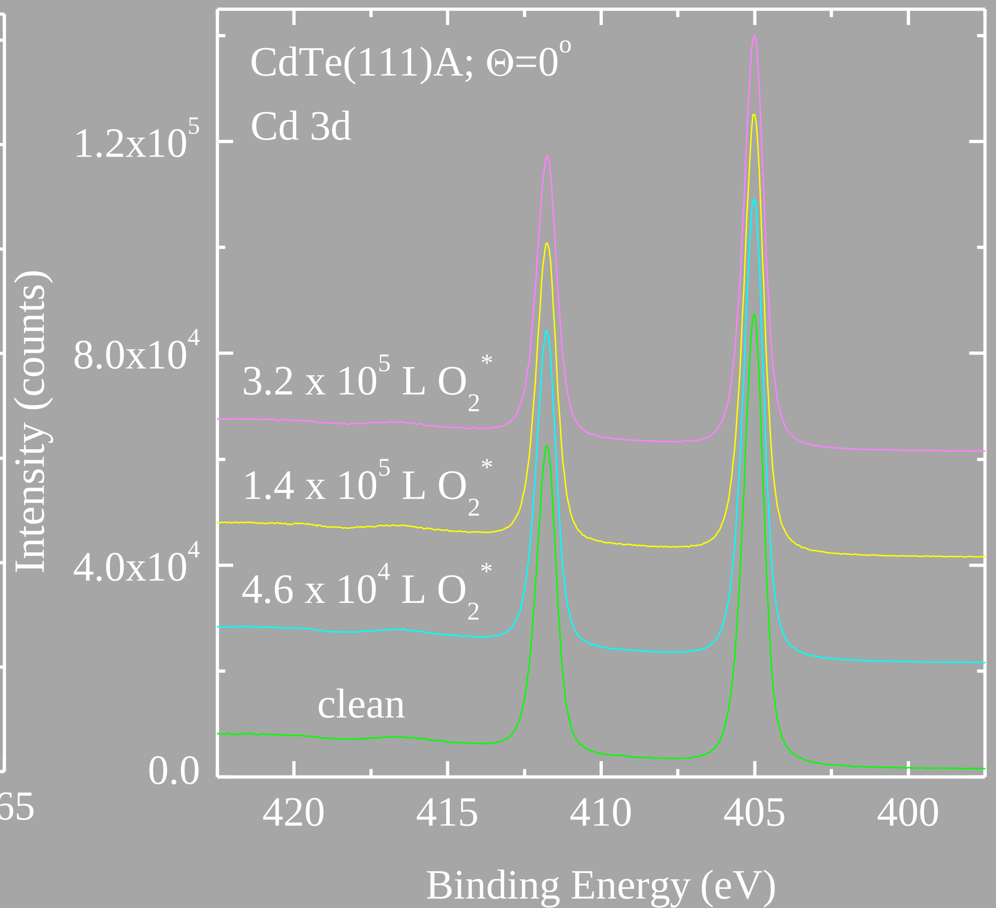
B.J. Kowalski, B.A. Orlowski, J. Ghijsen, Appl. Surf. Sci. **166,** 237 (2000)

CdTe(111)A - oxidation





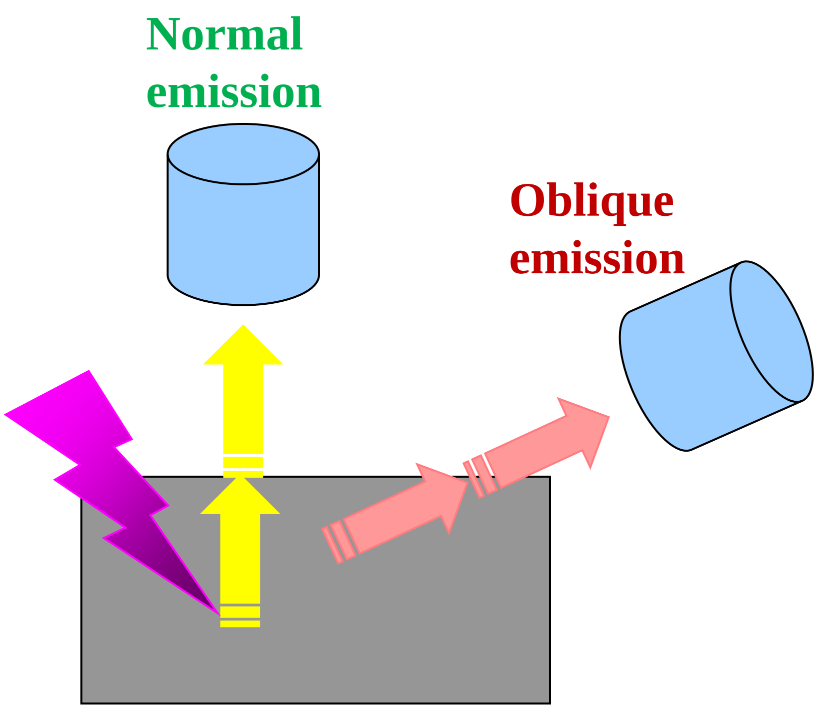




B.J. Kowalski, B.A. Orlowski, J. Ghijsen, Appl. Surf. Sci. **166,** 237 (2000)

Angular XPS

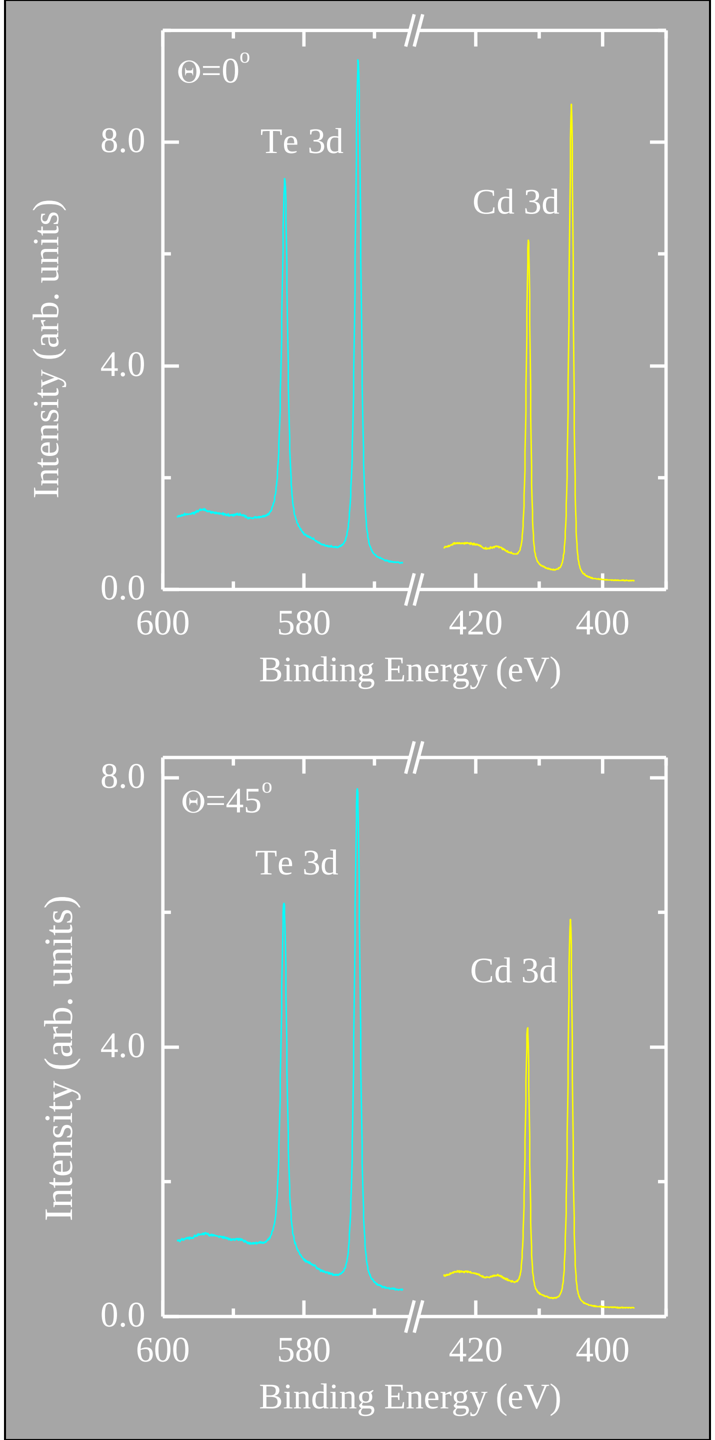
- enhanced surface sensitivity



CdTe(111)A

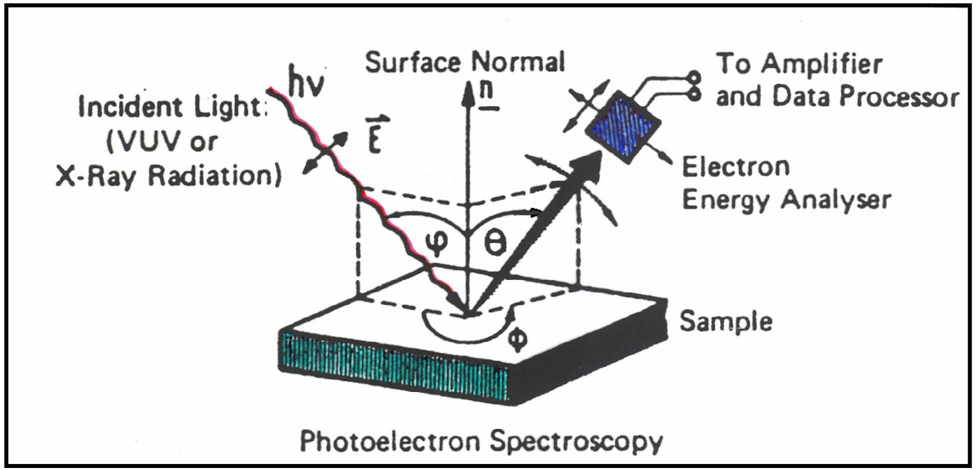
Normal emission

Oblique emission

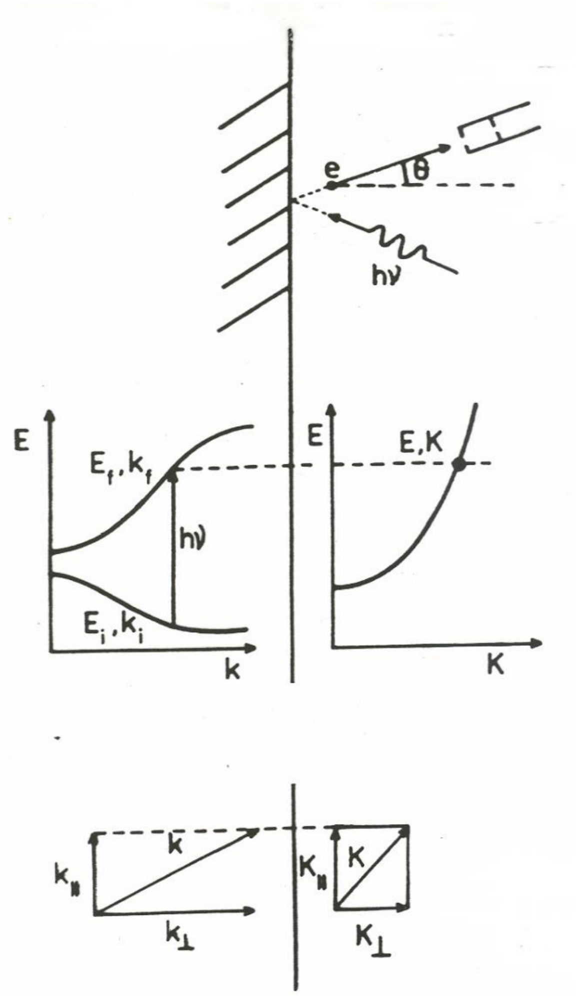


B.J. Kowalski, B.A. Orlowski, J. Ghijsen, Appl. Surf. Sci. **166,** 237 (2000)

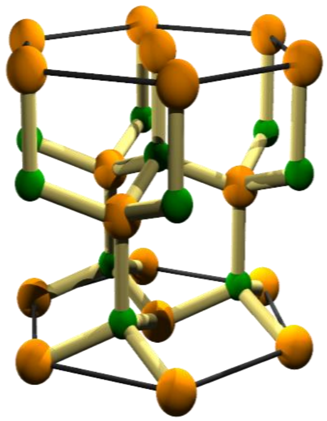
Angle-resolved photoelectron spectroscopy



Crystal Vacuum

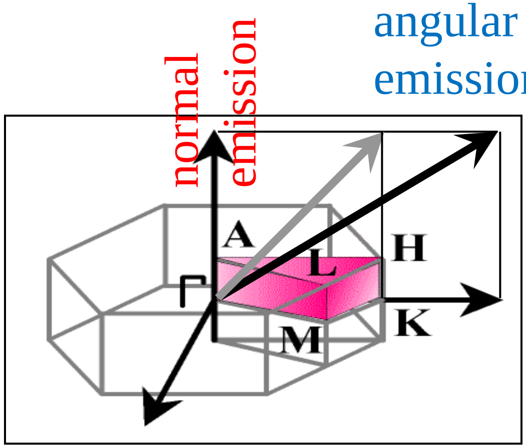


Example:



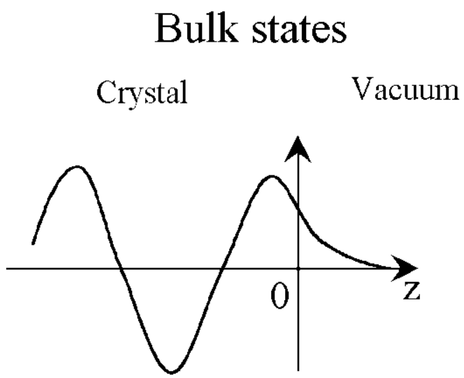
Wurtzite structure

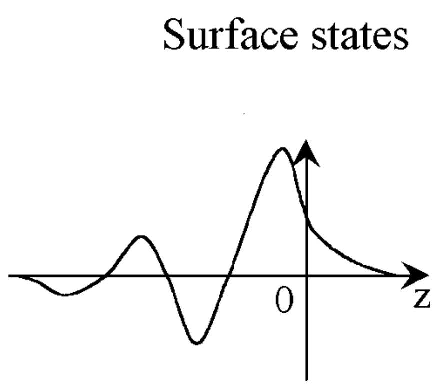
angular emission

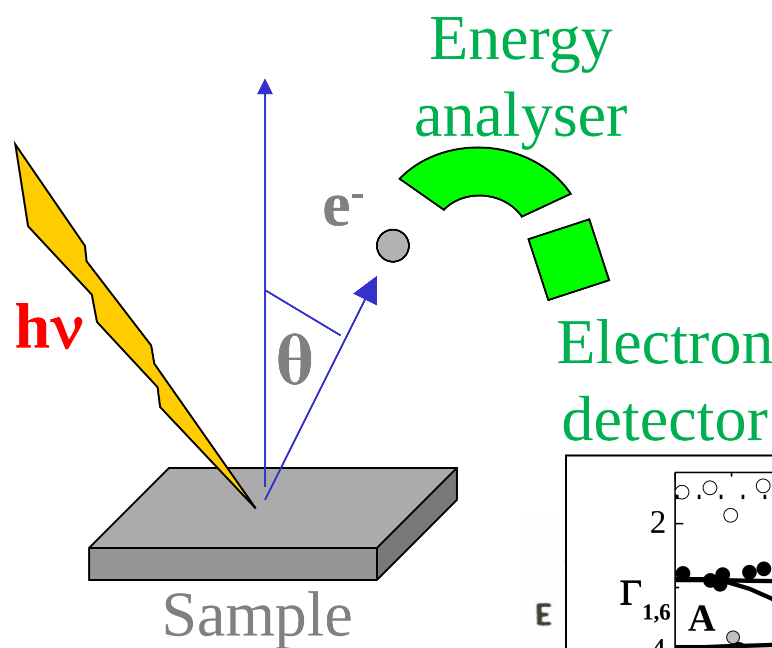


Brillouin zone

Angle-resolved photoelectron spectroscopy of surface and bulk states

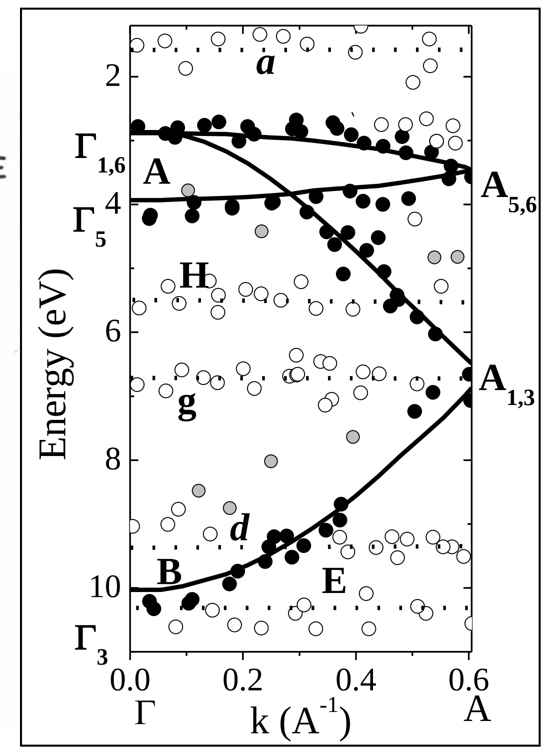


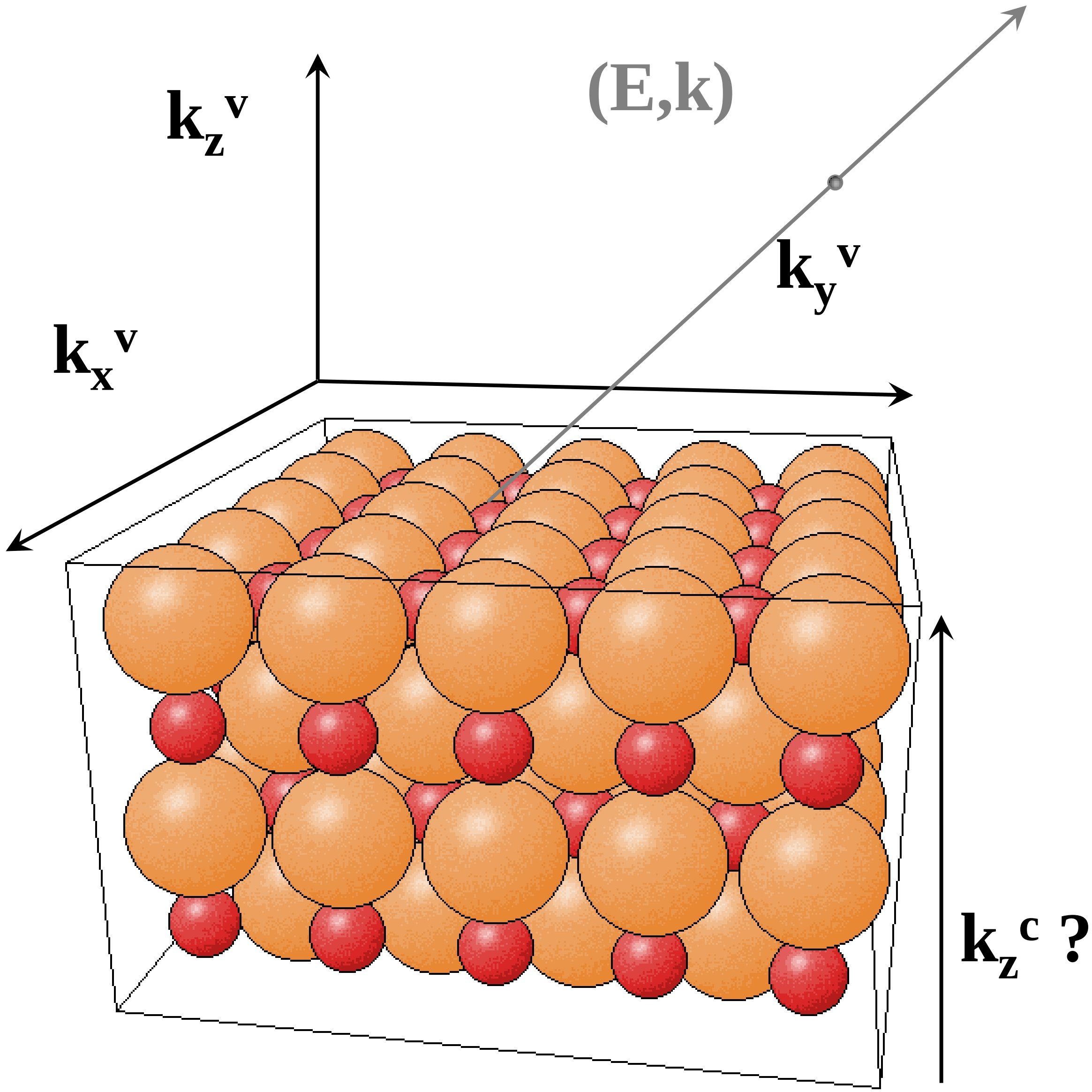




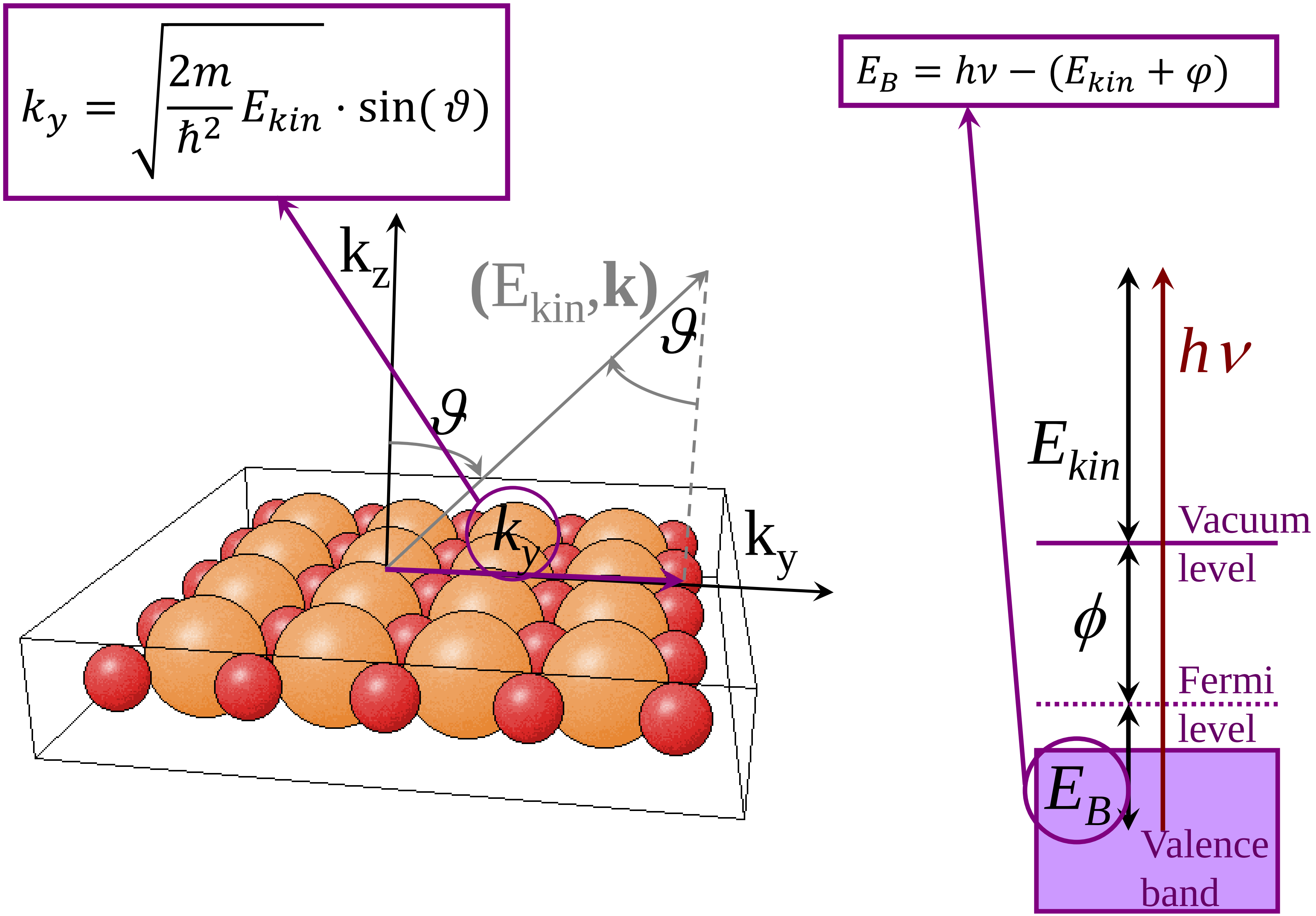
$$k_{i||} = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \cdot \sin(\vartheta)$$

$$k_{i\perp} = \sqrt{\frac{2m}{\hbar^2}(E_{kin} + |E_0|) - G_\perp}$$

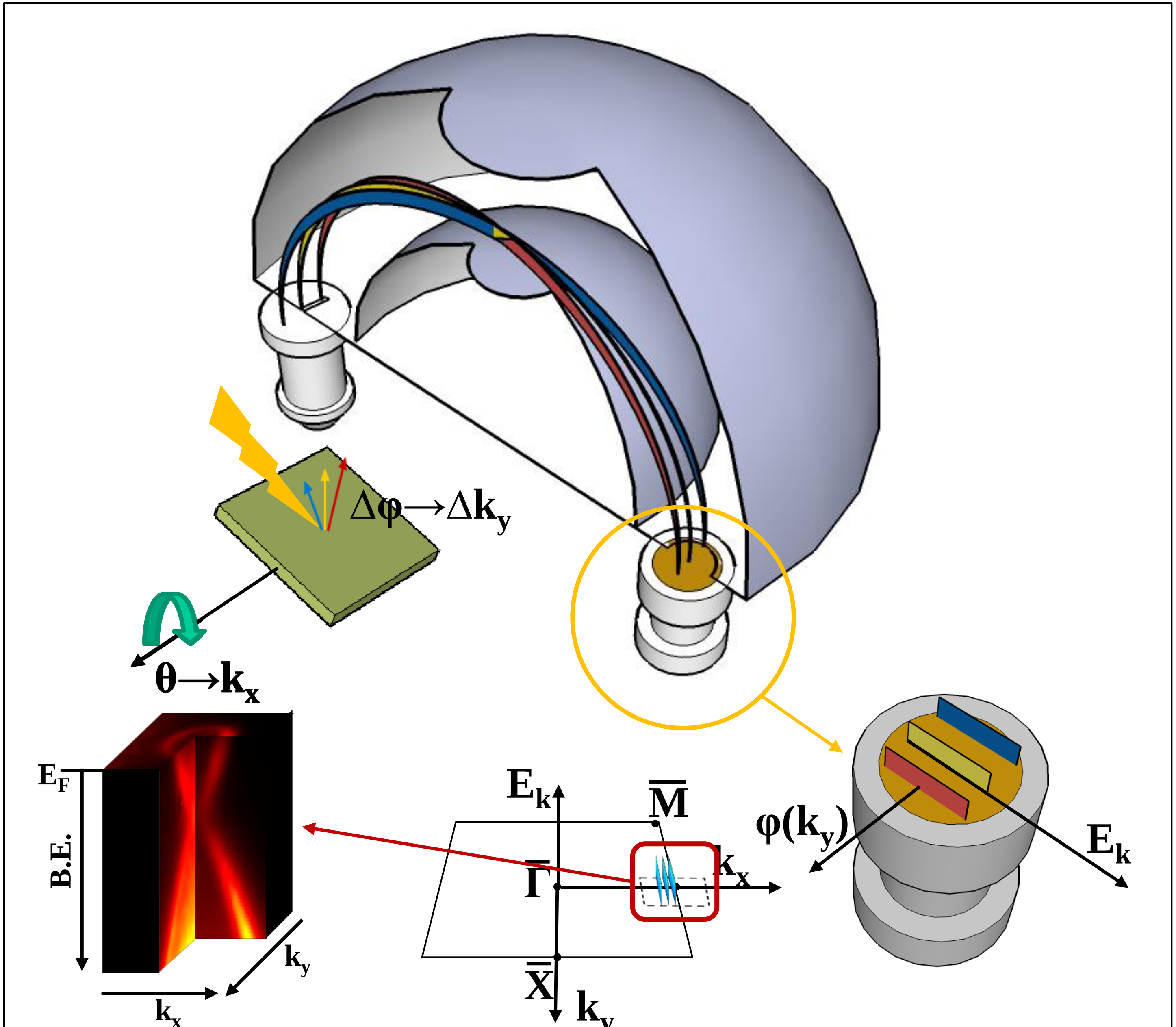




k_z^v
(E,k)
k_y^v
k_x^v
k_z^c ?

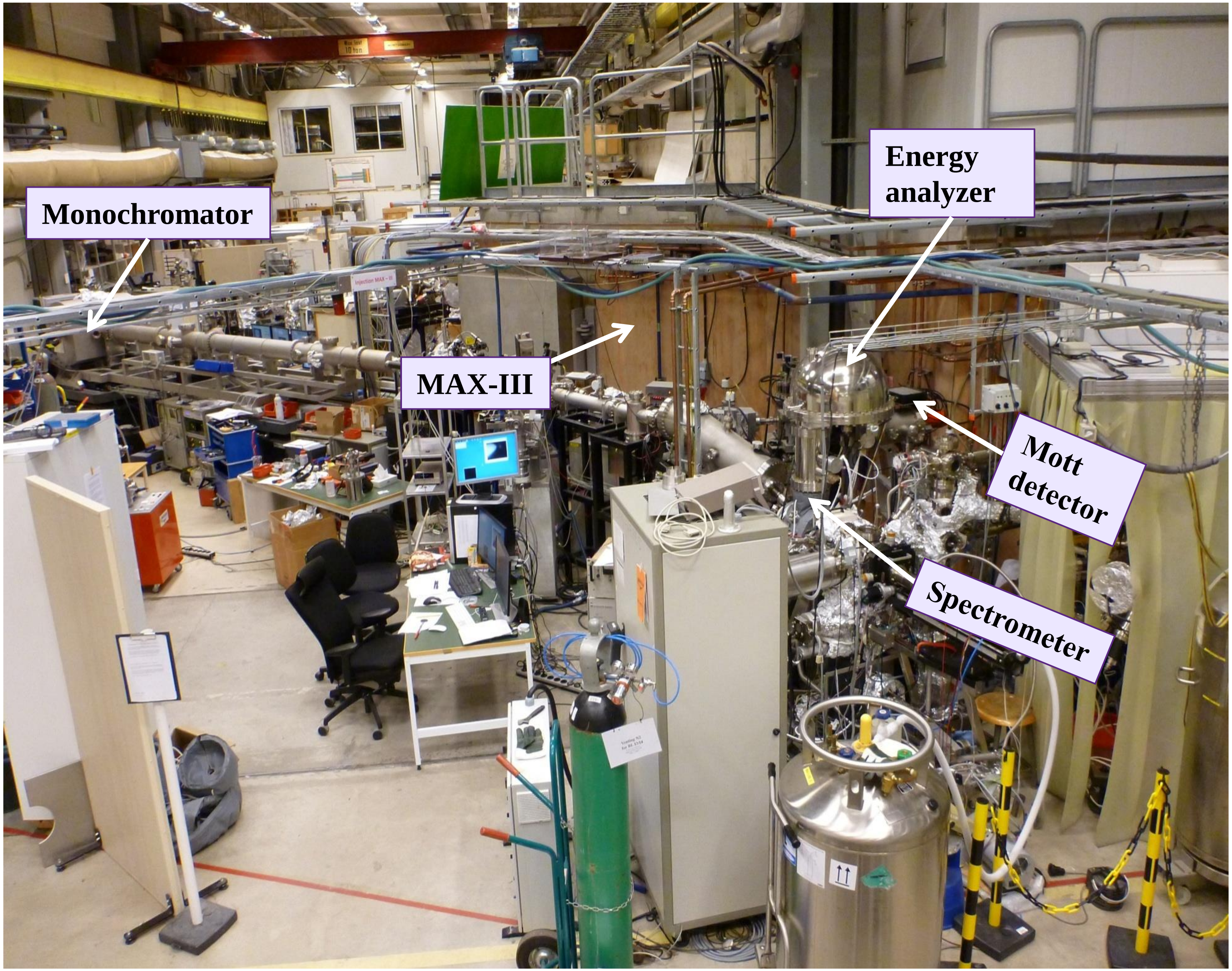


$k_y = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \cdot \sin(\vartheta)$
$E_B = h\nu - (E_{kin} + \varphi)$
k_z
$(E_{kin}, \mathbf{k})$
ϑ
ϑ
k_y
k_y
$h\nu$
E_{kin}
Vacuum level
ϕ
Fermi level
E_B
Valence band



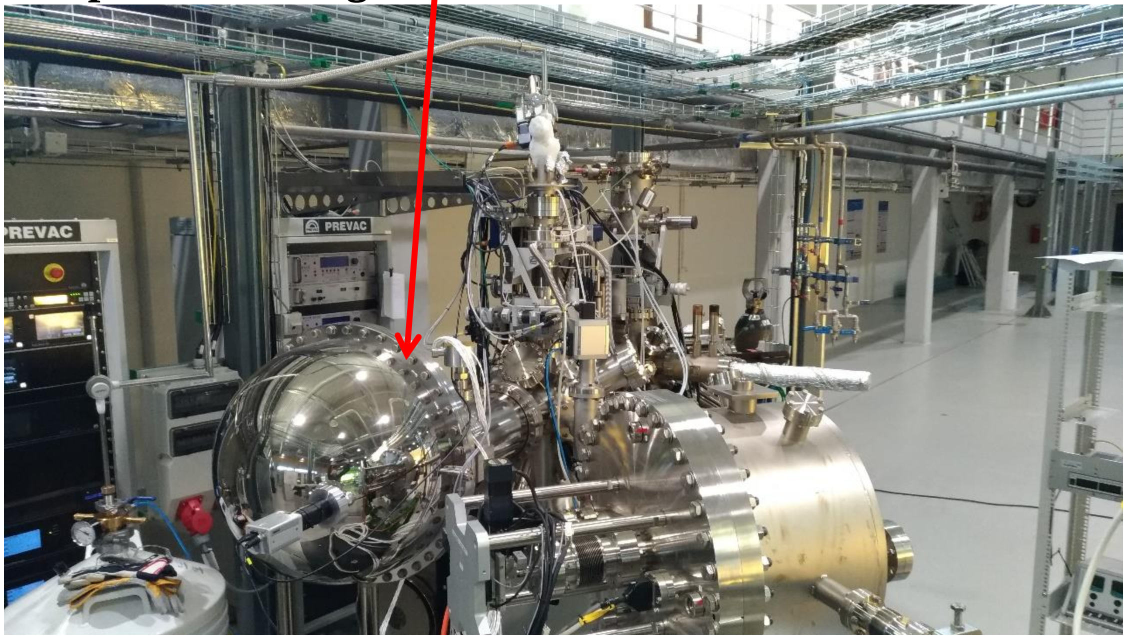
Δφ→Δk_y
θ→k_x
E_F
B.E.
k_x
k_y
E_k
M̄
Γ̄
X̄
k_x
k_y
φ(k_y)
E_k

Beamline I3
MAX-lab, Lund University, Sweden

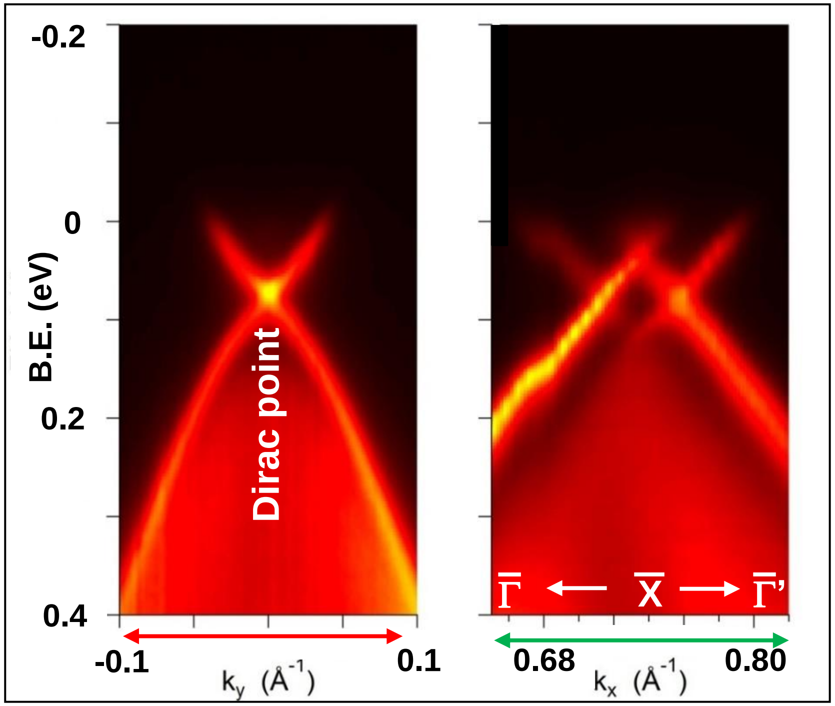


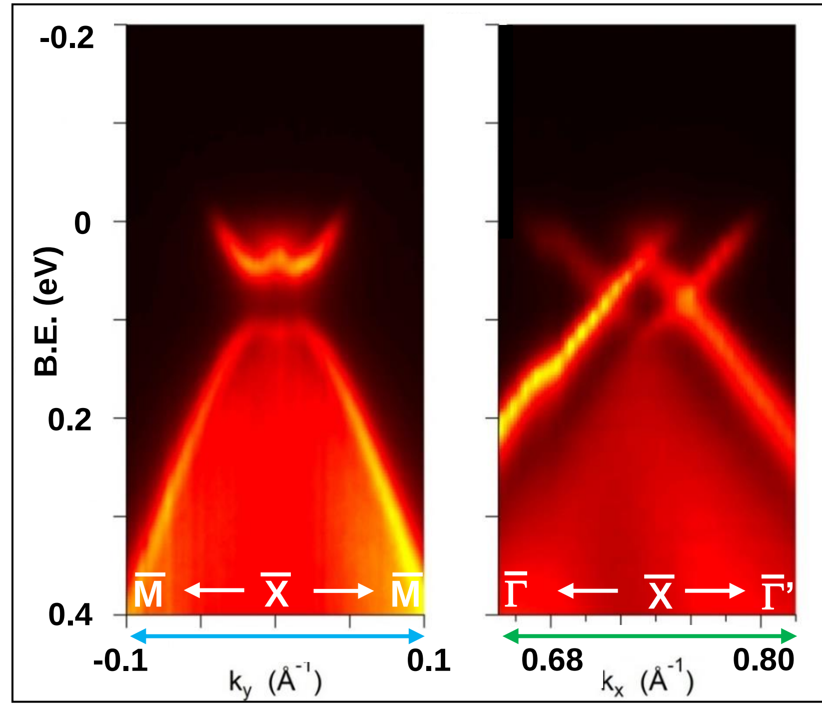
Beamline UARPES
NCSR SOLARIS, Jagiellonian University, Kraków, Poland

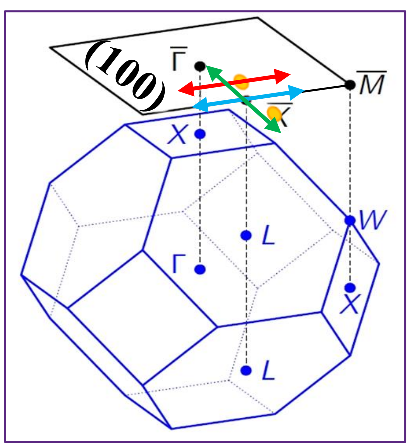
- **Elliptically polarizing quasiperiodic undulator of APPLE II type**
- **Monochromator combining normal (NIM) and grazing incidence (PGM) optics (the photon energy range of 8–100 eV)**
- **SCIENTA OMICRON DA30L photoelectron spectrometer**
- **The energy and angular resolution: 1.8 meV and 0.1°**
- **Temperature range 10 – 500 K**



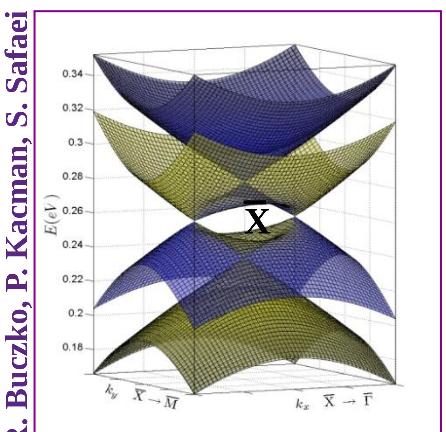
Topological crystalline insulator $Pb_{0.67}Sn_{0.33}Se$, T=87 K, hν=18.5 eV





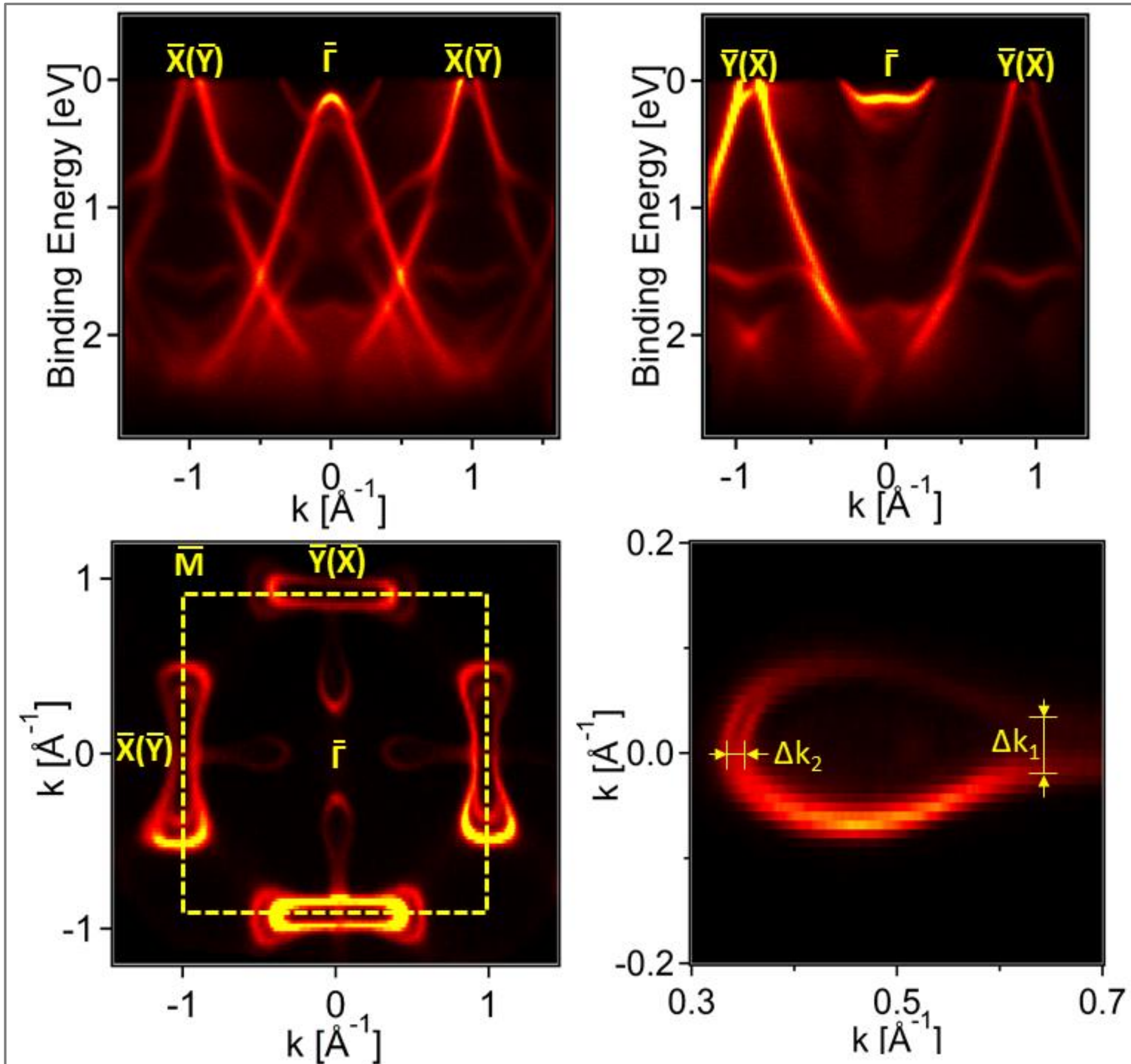


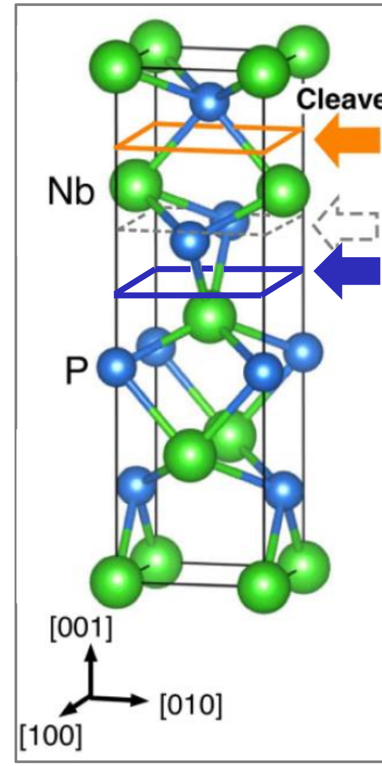
Theory-
R. Buczko, P. Kacman, S. Safaei



P. Dziawa, B. J. Kowalski, K. Dybko, R. Buczko, A. Szczerbakow, M. Szot, E. Łusakowska, T. Balasubramanian, B. M. Wojek, M. H. Berntsen, O. Tjernberg, T. Story, *Nature Materials* **11**, 1023 (2012)

Weyl semimetal NbP





S.Souma et al., Phys.Rev.B (2016)

ARPES data for NbP(001) P-face taken at UARPES (SOLARIS)

Diffraction methods

Surface X-ray diffraction

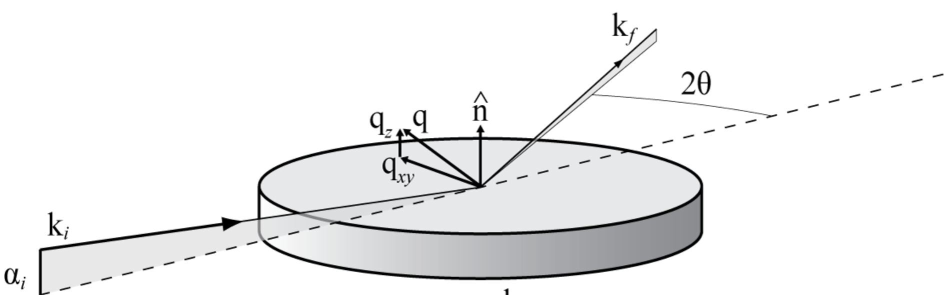
X-ray total-external-reflection–Bragg diffraction: A structural study of the GaAs-Al interface

W. C. Marra, P. Eisenberger, and A. Y. Cho
Bell Laboratories, Murray Hill, New Jersey 07974

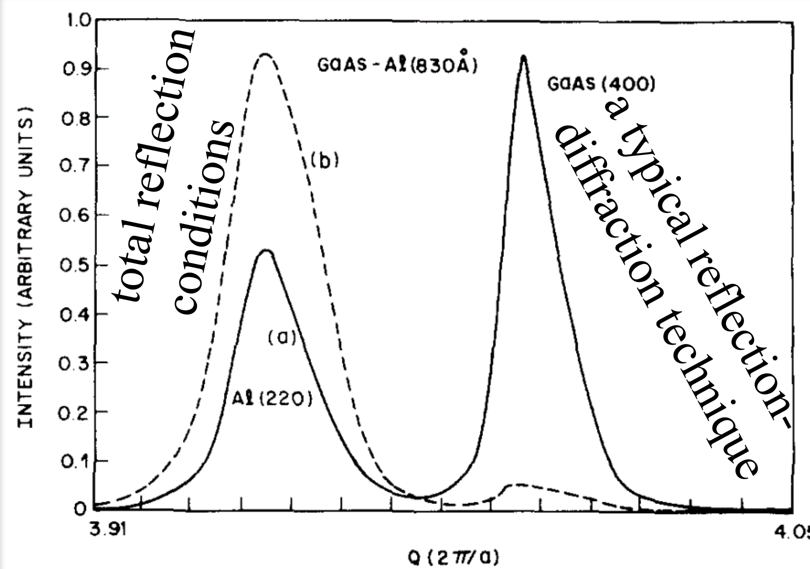
(Received 19 March 1979; accepted for publication 8 June 1979)

A new technique utilizing conventional x-ray diffraction in conjunction with total external reflection has provided a powerful tool for studying ordered interfaces and surface phenomena. It has been used in this work to study the details of the interface region of a molecular beam epitaxially grown Al single crystal on a molecular beam epitaxially grown GaAs single-crystal substrate. A simple model including variations of the lattice parameter and disorder in the interface region is in agreement with these experimental results.

J. Appl. Phys. 50(11), November 1979



http://en.wikipedia.org



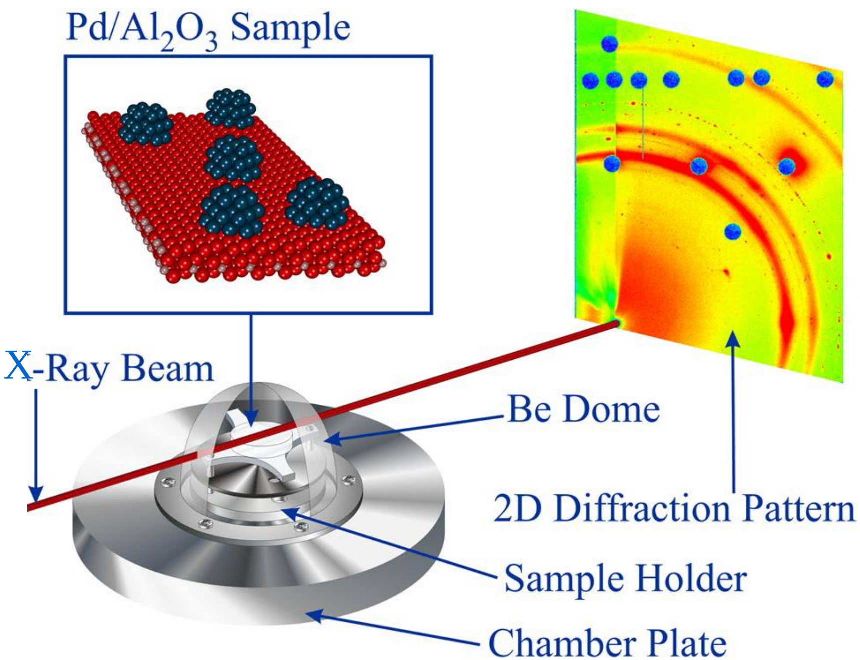
Al(415 ML) on GaAs

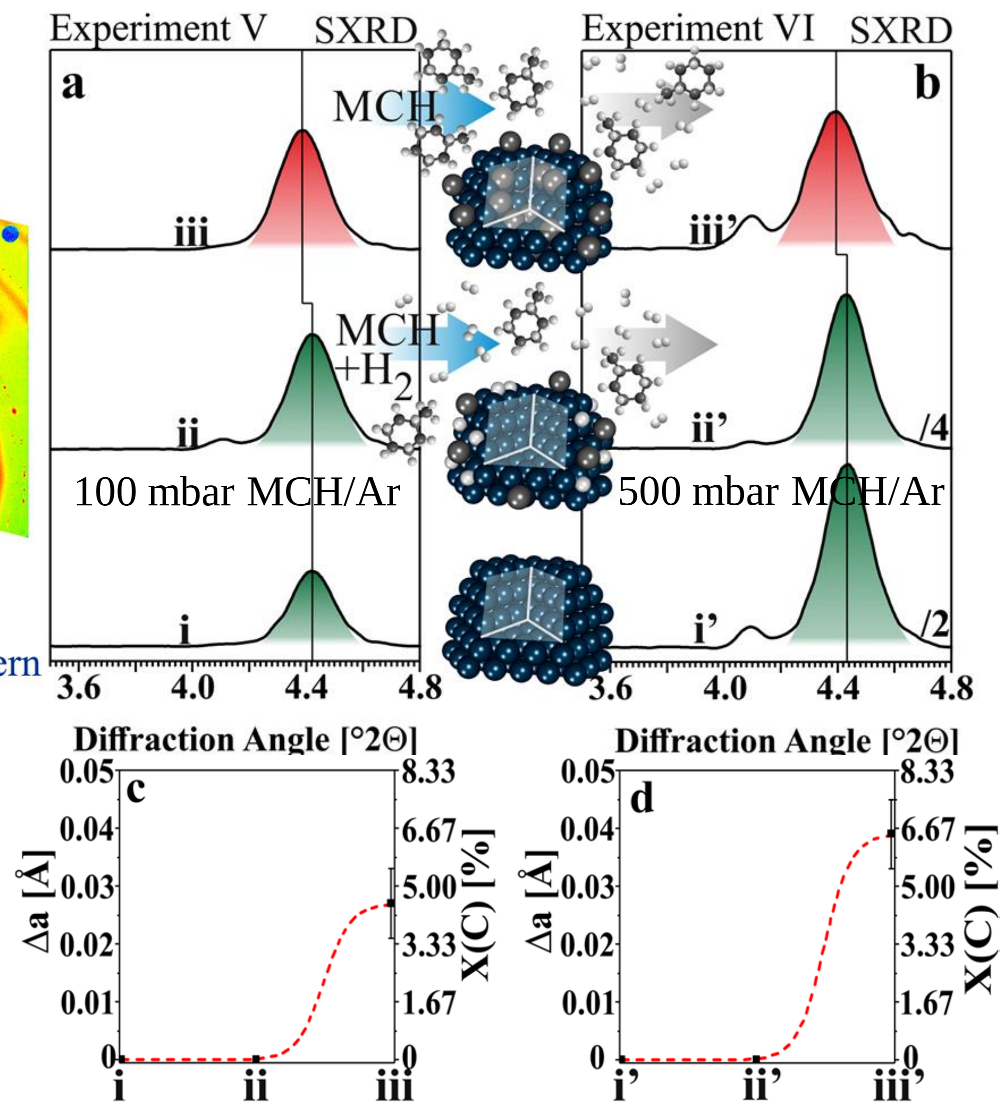
Needs strong X-ray beam – usually from a synchrotron!

Surface X-ray diffraction (cont.)

Dehydrogenation of Liquid Organic Hydrogen Carriers on Supported Pd Model Catalysts: Carbon Incorporation Under Operation Conditions, Ralf Schuster et al., Catalysis Letters **148**, 2901 (2018)

MCH: methylcyclohexane

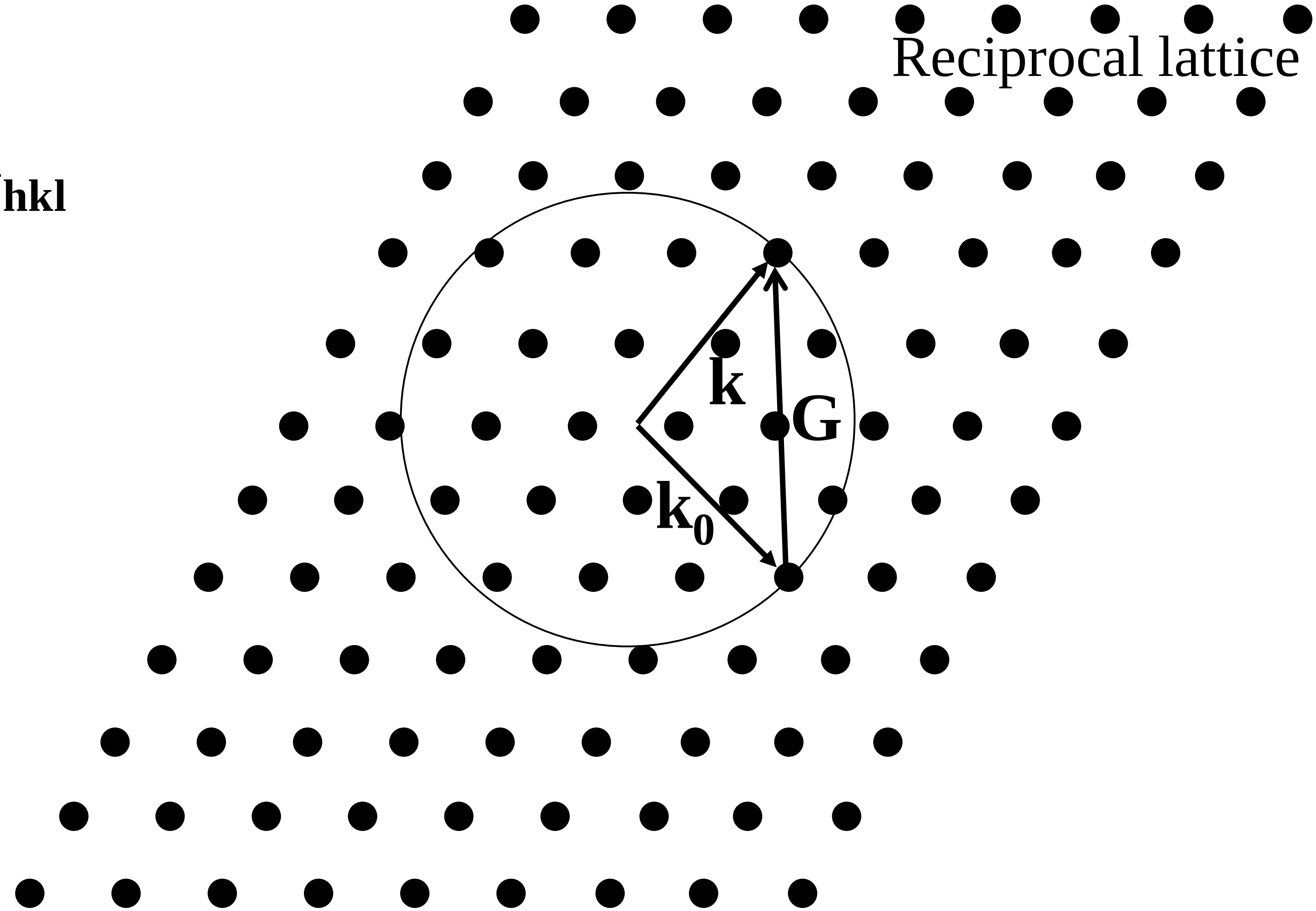




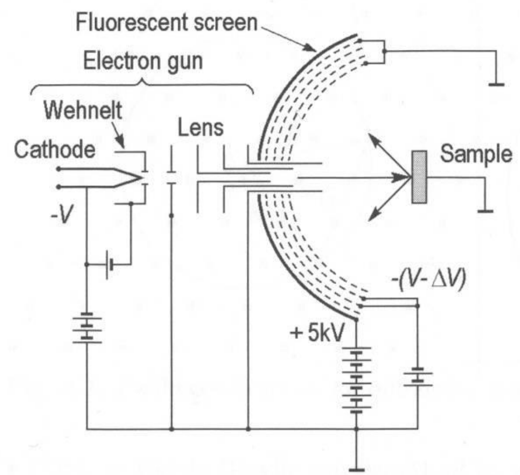
Construction of the Ewald sphere

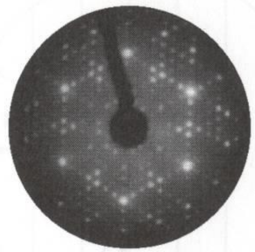
$$\mathbf{k}-\mathbf{k}_0=\mathbf{G}_{hkl}$$

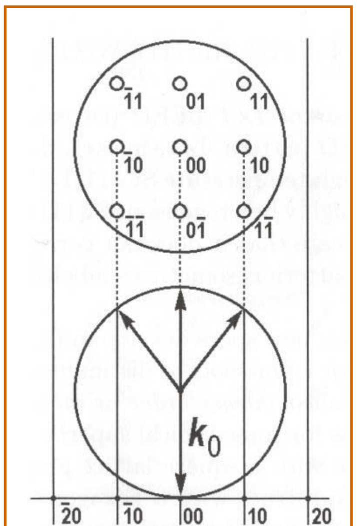
$$|\mathbf{k}|=|\mathbf{k}_0|$$

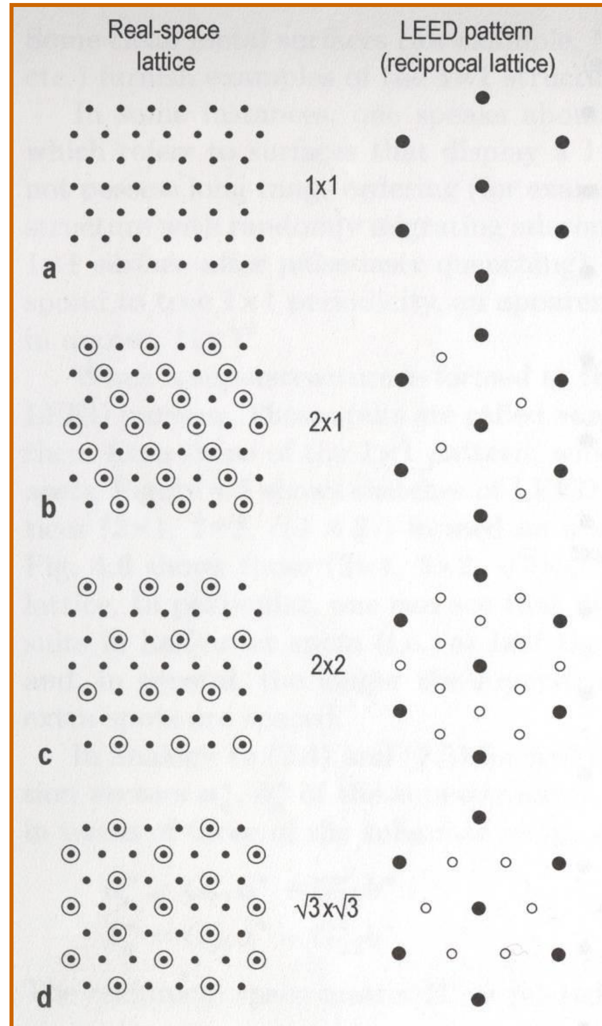


Low-Energy Electron Diffraction (LEED)



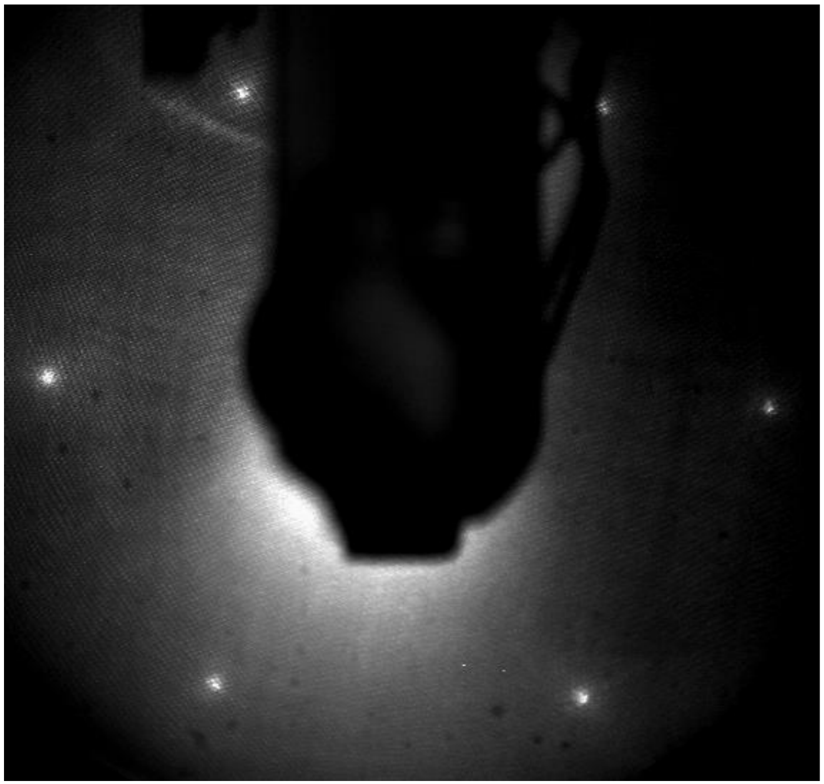




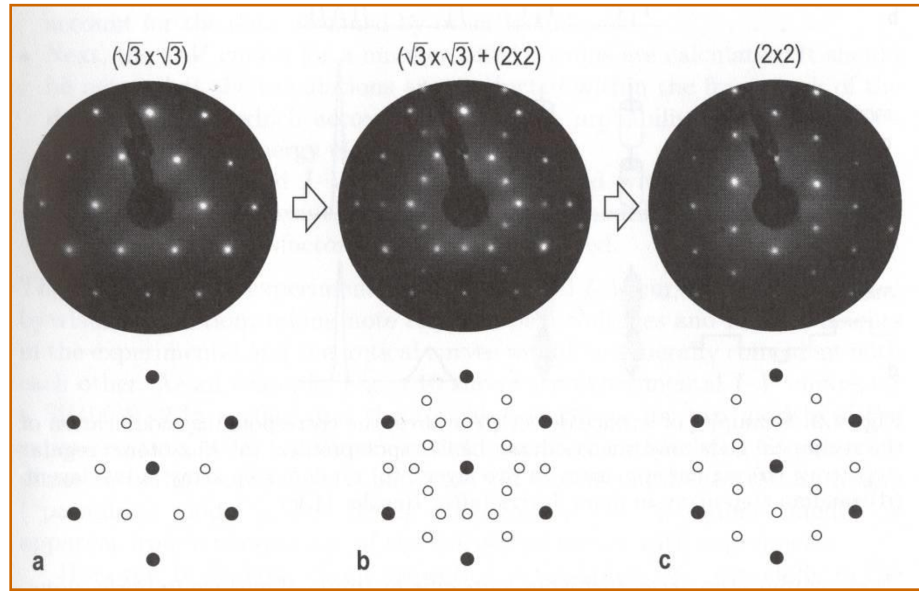


K.Oura et al.
Surface Science. An Introduction

Low-Energy Electron Diffraction (LEED) (cont.)

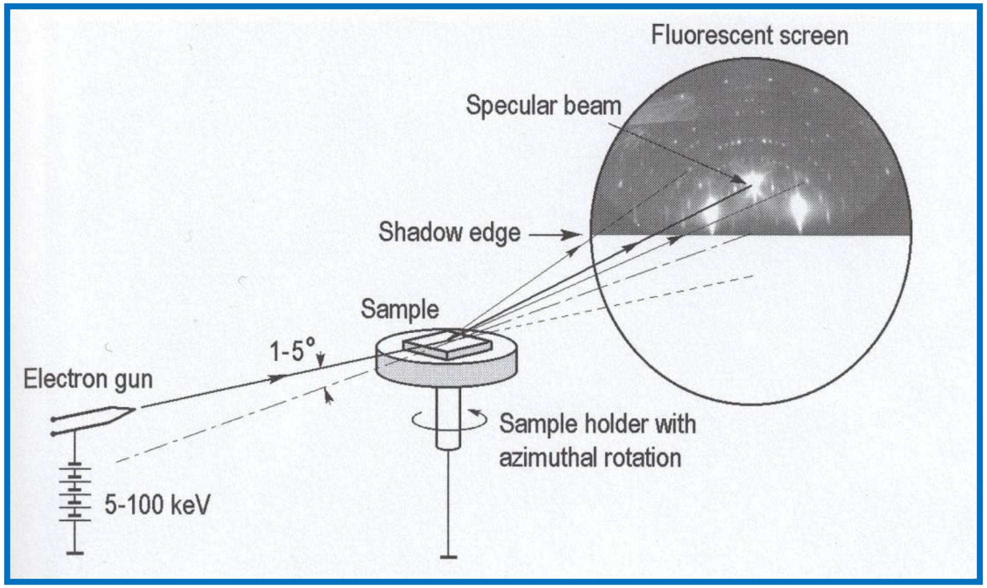


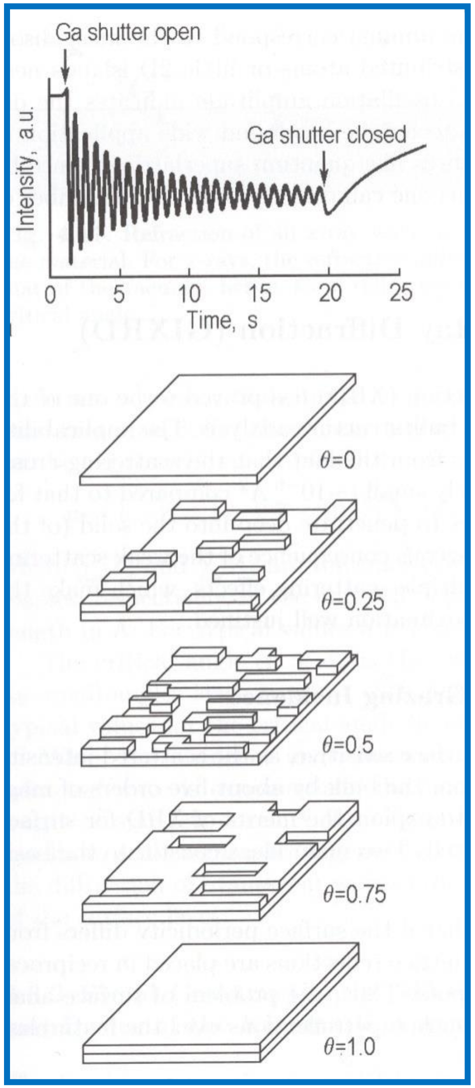
GaN(000$\underline{1}$) (1x1)



In deposition on Si(111)√3x √ 3-R30^0

Reflection High-Energy Electron Diffraction (RHEED)





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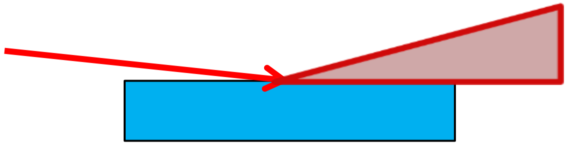
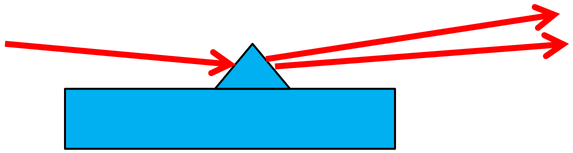


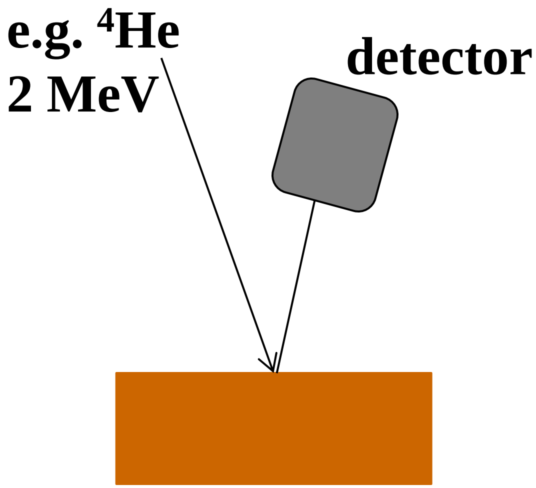
2D structure
Streaks in the image

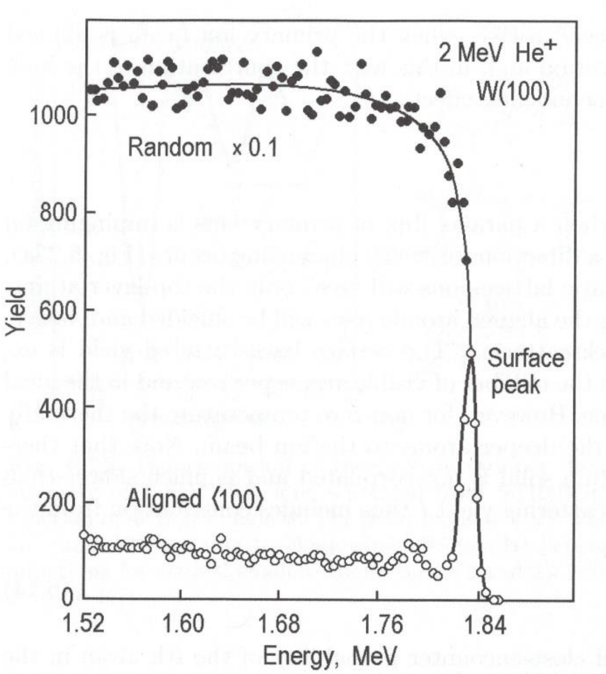


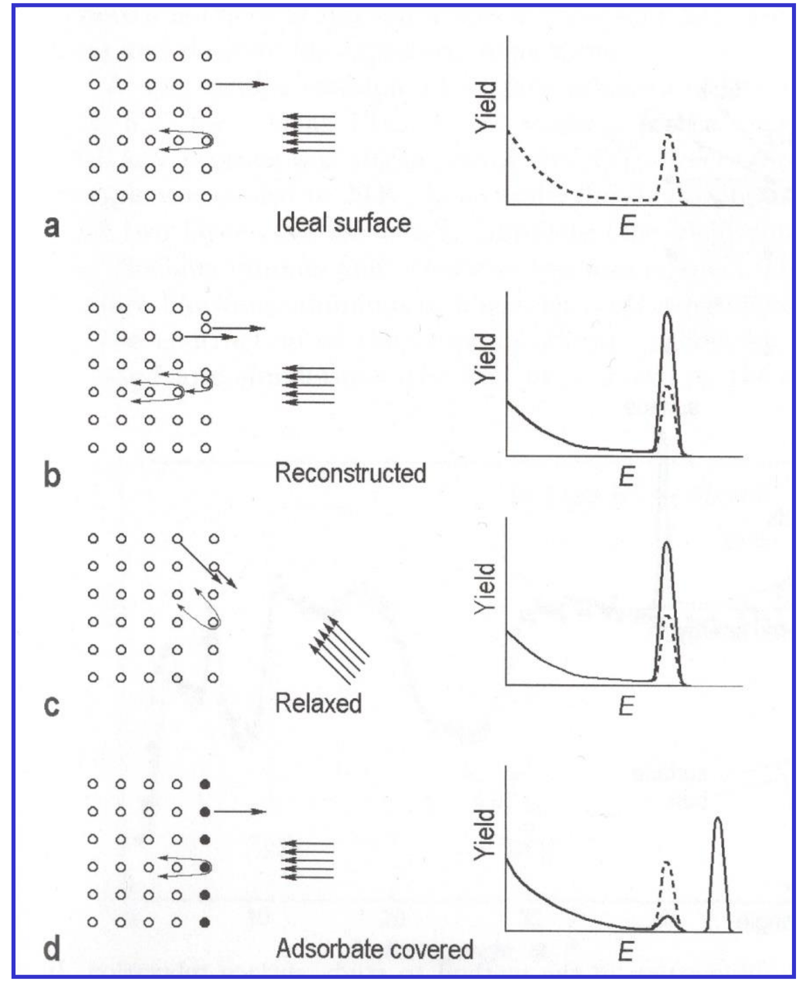
3D structure
Dots in the image

Ion scattering methods

Rutherford Backscattering Spectrometry (RBS)







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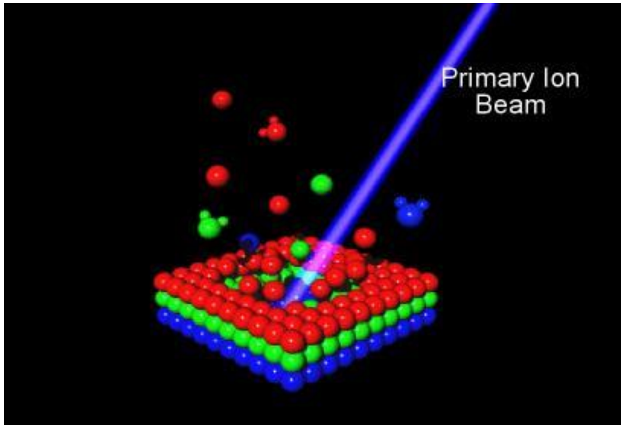
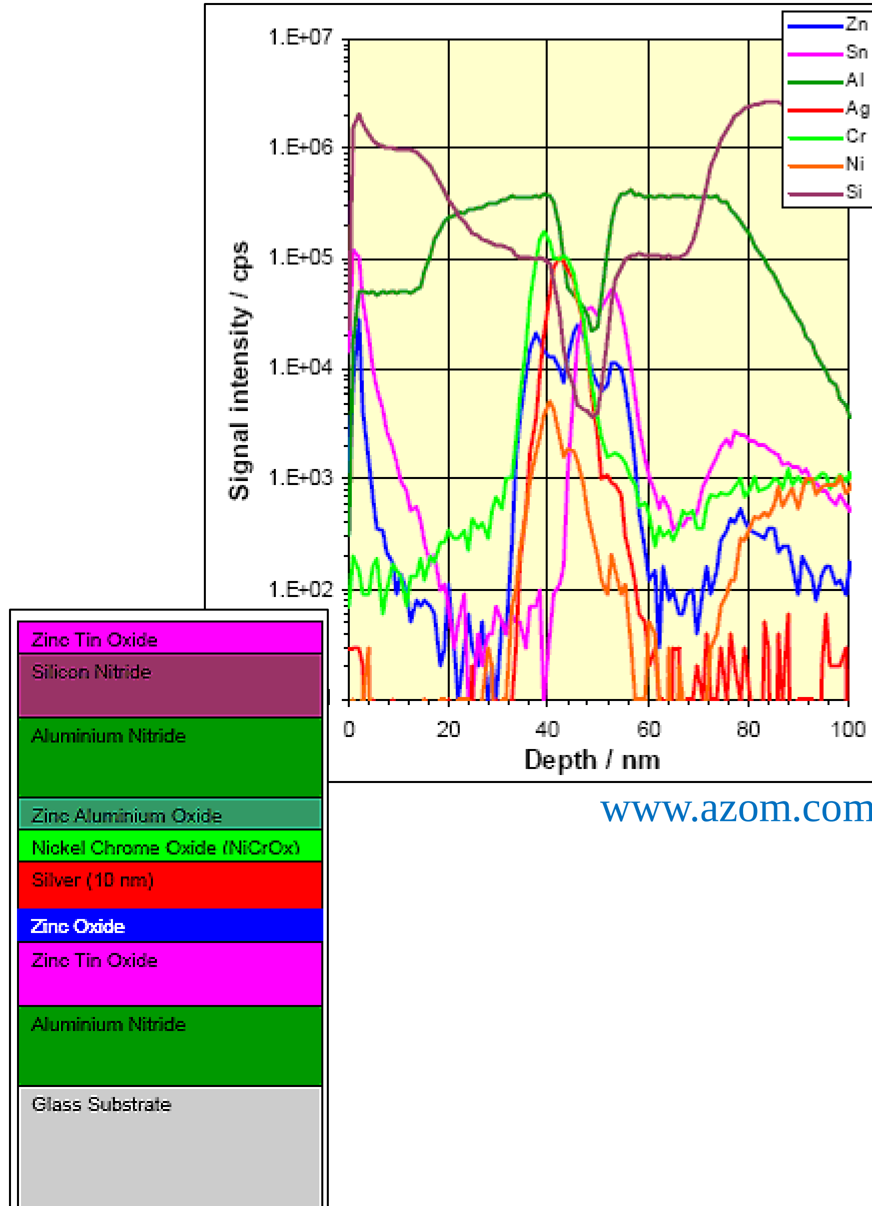
Secondary Ion Mass Spectrometry (SIMS)

e.g. Cs^+ lub Ar^+
1-30 keV



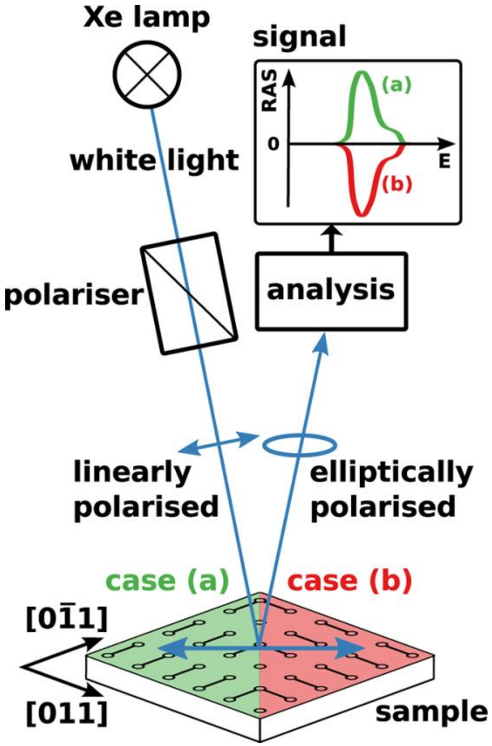
www.ainse.edu.au



www.azom.com

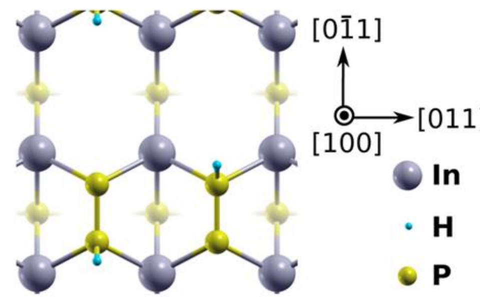
Optical methods

Reflection Anisotropy Spectroscopy (RAS)

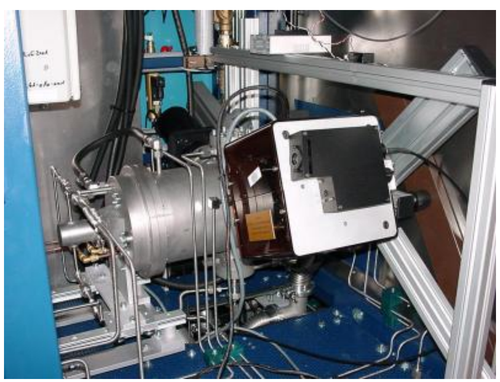


$$\frac{\Delta r}{r} = 2\,\frac{r_{[0\bar{1}1]} - r_{[011]}}{r_{[0\bar{1}1]} + r_{[011]}}$$

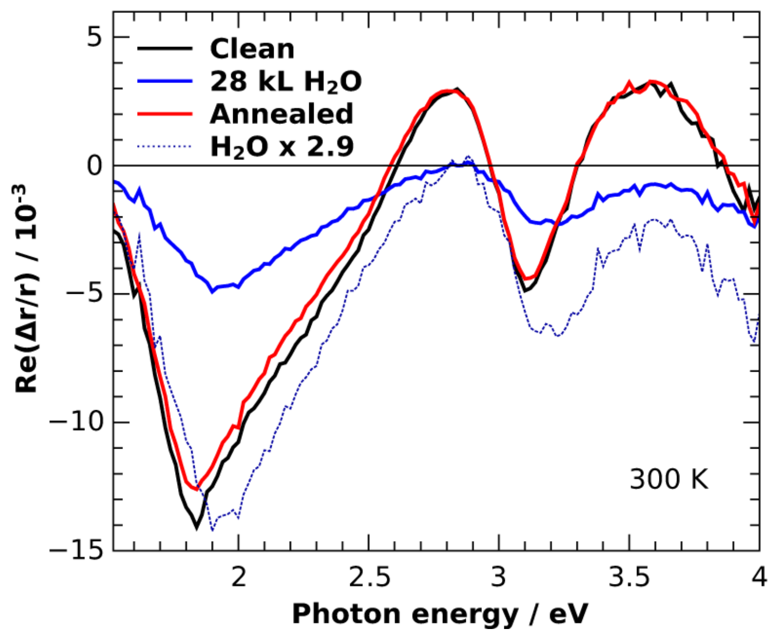
P-rich



Reconstructed InP(100) surface



An MOCVD reactor with the RAS system
Institute of Semiconductor and Solid State Physics, University of Linz, Austria



Summary

We can test various surface properties using:

Electron microscopy (SEM)

Scanning probe microscopies (STM, AFM)

Electron spectroscopies (XPS, ARPES, AES)

Diffraction methods (X-ray, LEED, RHEED)

Ion techniques (RBS, SIMS)

Surface-sensitive optical techniques (RAS)

and many others...

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H. Lüth
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