# Surface studies of crystals

**Bogdan J. Kowalski**

***IF PAN***

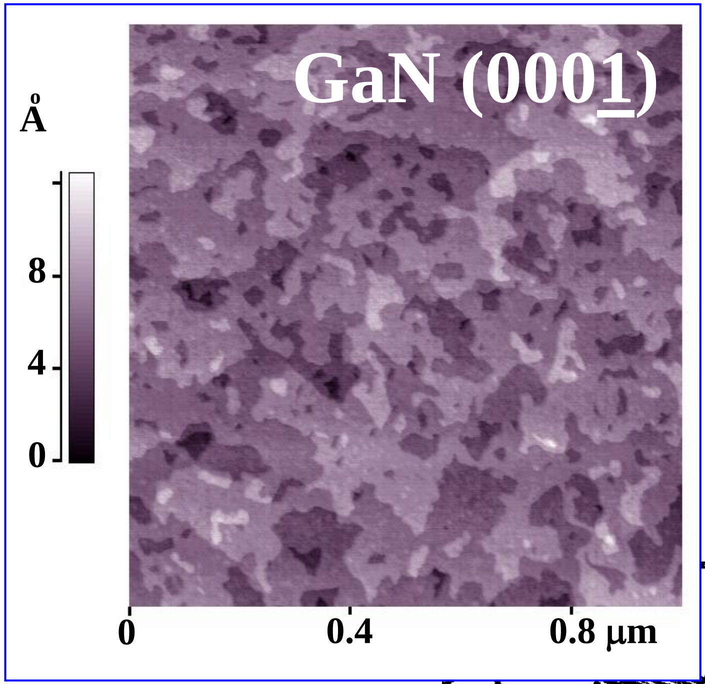
**„God made solids, but surfaces were the work of the Devil”**

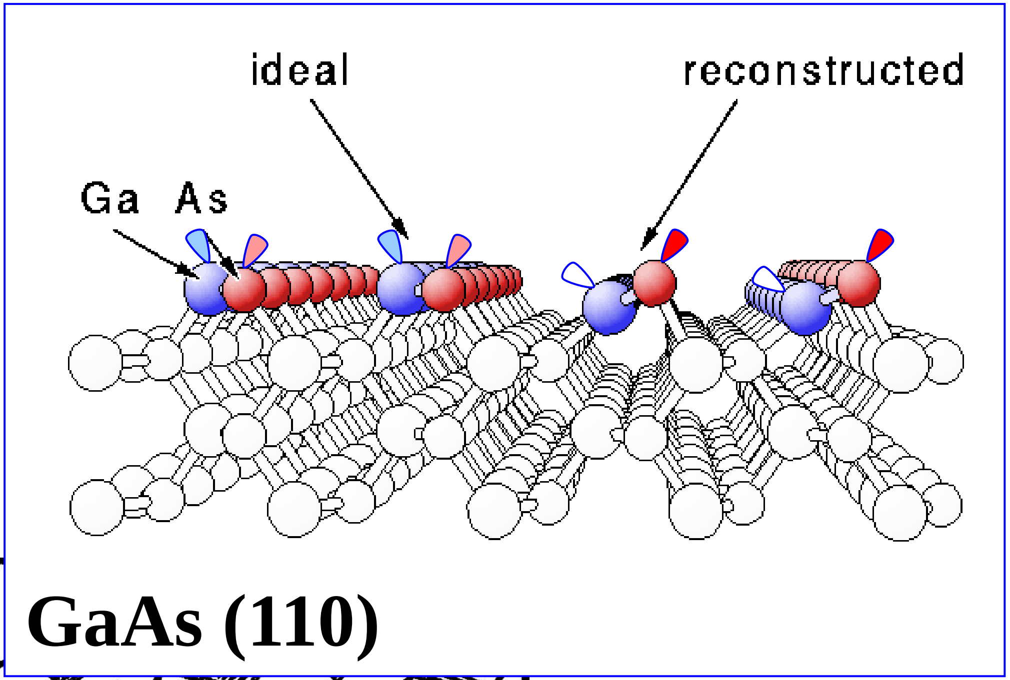
**Wolfgang Pauli**

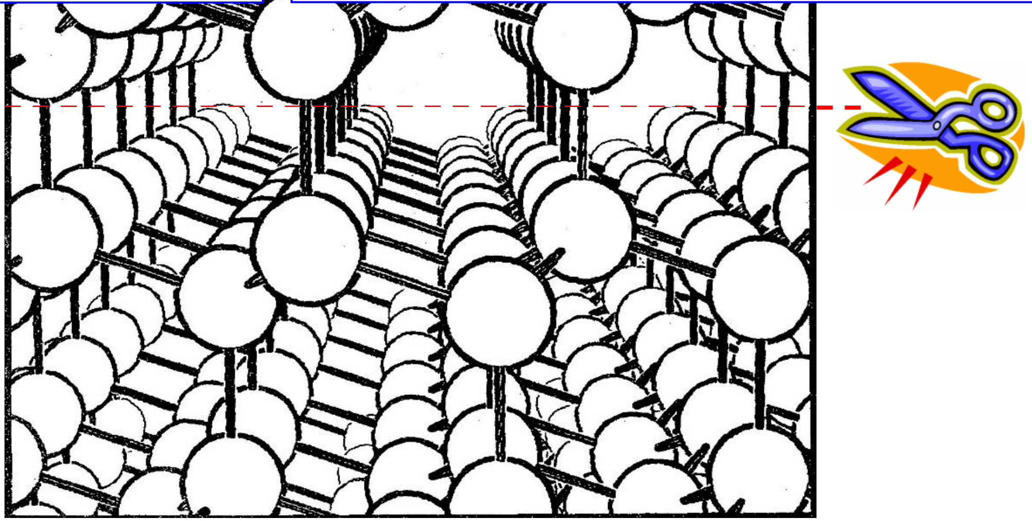
www.weltchronik.de

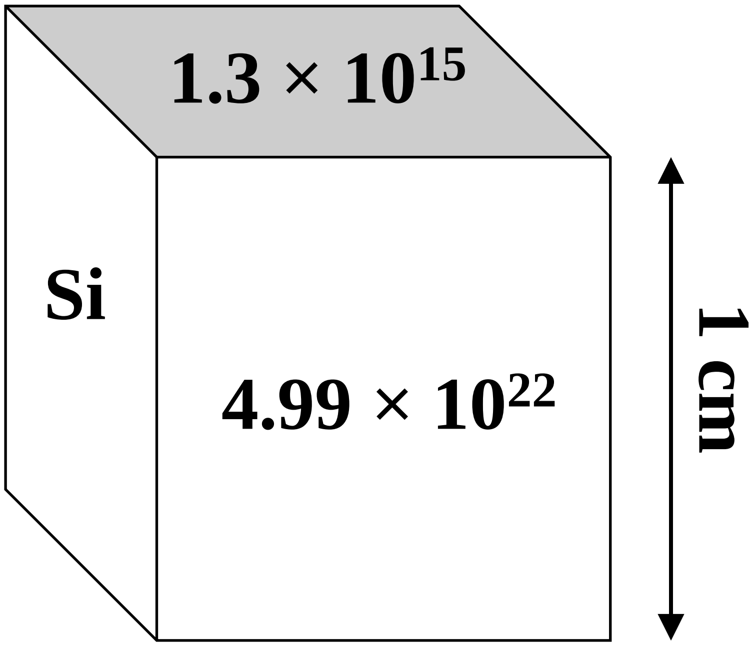
# What does it mean *surface?*

# Surface


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


ideal
reconstructed
Ga
As
GaAs (110)





The density of silicon is 2.33 g/cm$^3$. The mass of a silicon atom is 4.664 × 10$^{-23}$ g. The number of silicon atoms in a cubic centimeter is 4.99 × 10$^{22}$

# Does *the surface* matter?

# A FinFET with one atomic layer channel

Mao-Lin Chen *et al*., Nature Communications 11, 1205 (2020)

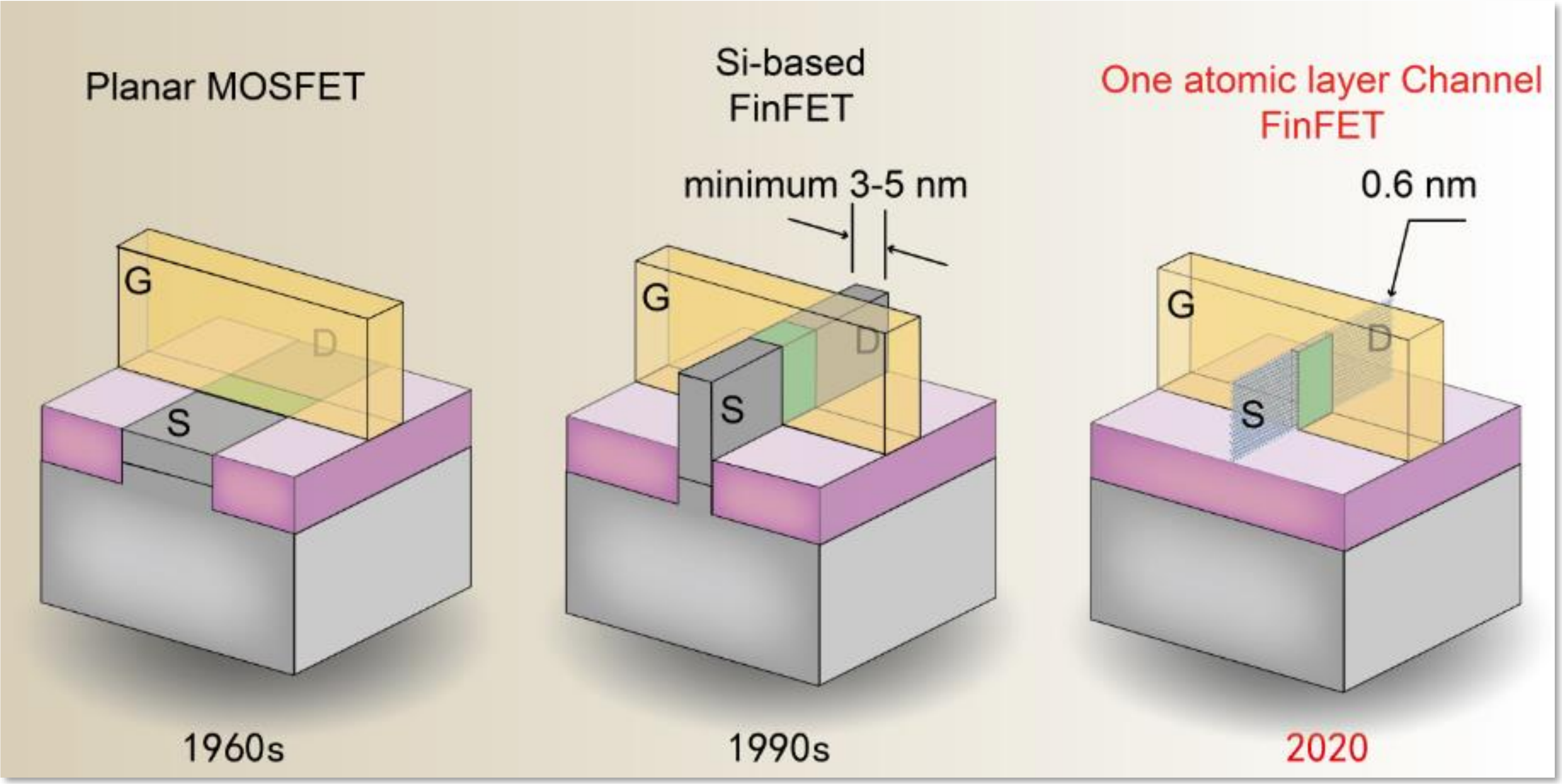
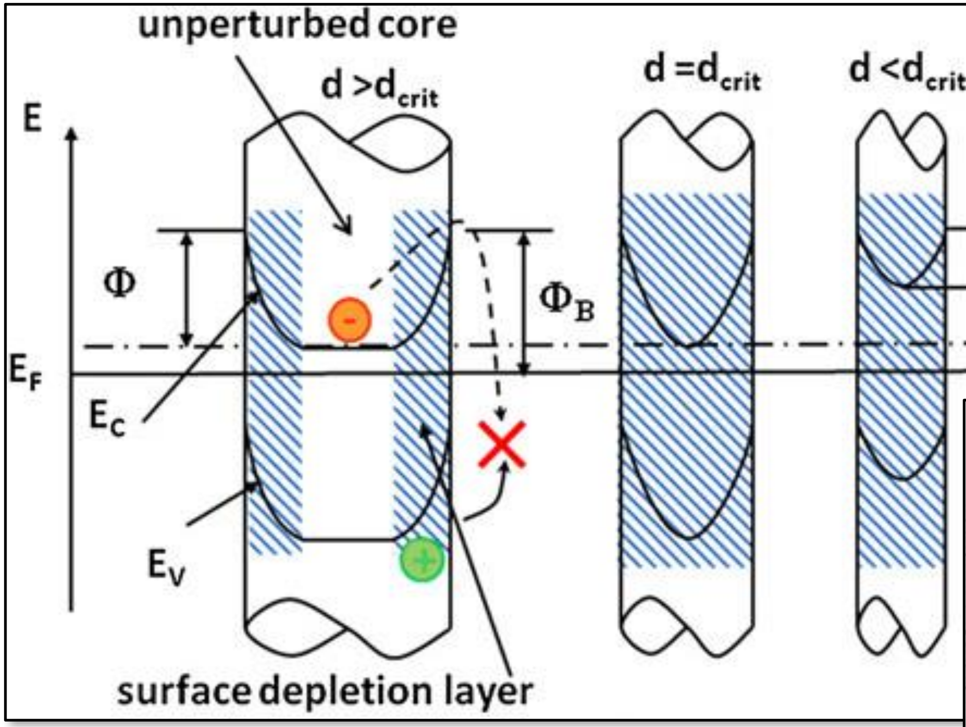


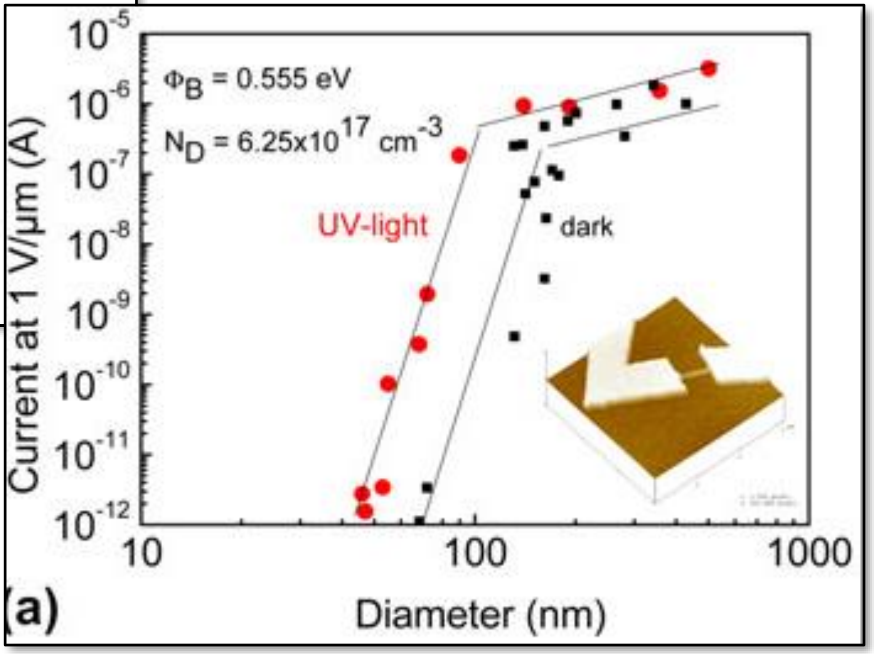
Image by the Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China
https://english.cas.cn/newsroom/research_news/tech/202003/t20200310_230971.shtml

# Surface-induced effects in GaN nanowires

Raffaella Calarco, Toma Stoica, Oliver Brandt, Lutz Geelhaar

J. Mater. Res., 26, 2157 (2011)





**$d_{crit}$ = 80 nm**

for GaN n-type nanowires with $N_D$=6.25x10$^{17}$ cm$^{-3}$

# Outline

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

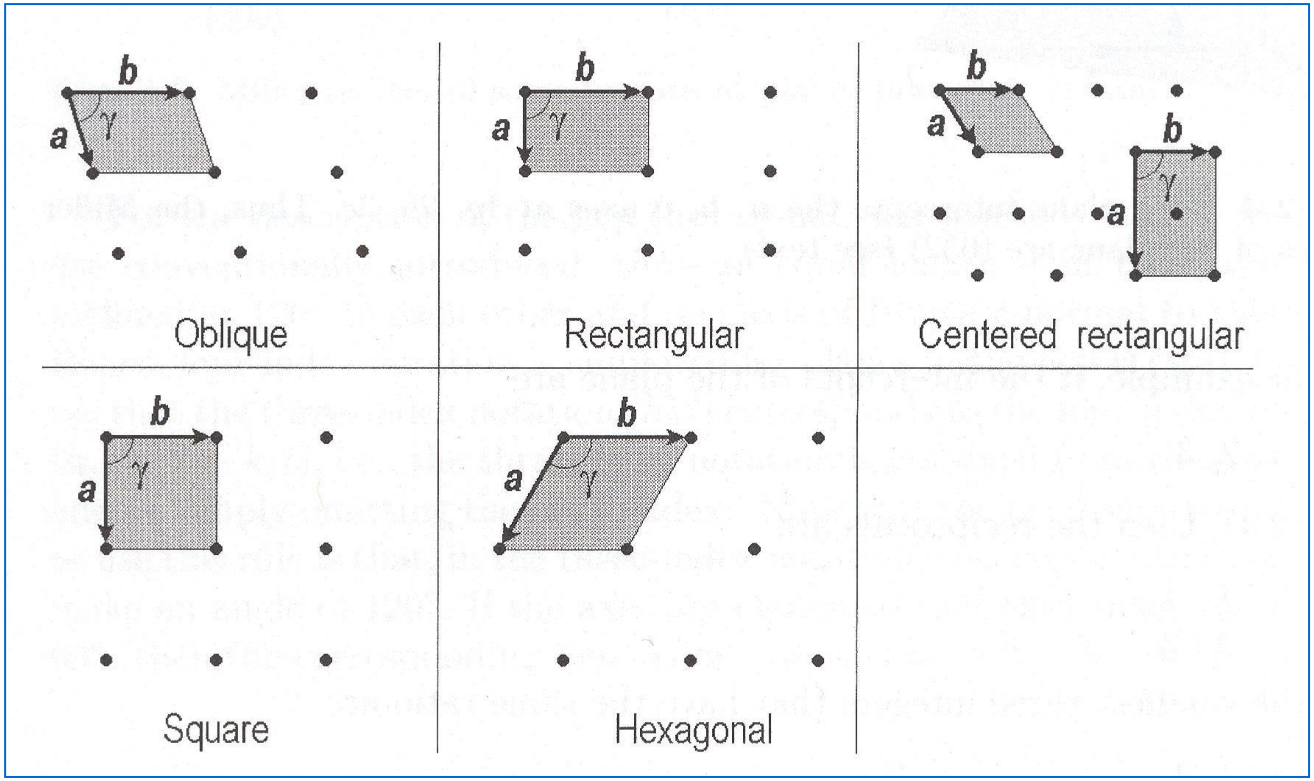
# Surface description: Bravais lattices

## 5 2-dimensional Bravais lattices

## (14 3-dimensional Bravais lattices)

**$|a| \neq |b|$**

**$|a| = |b|$**



**K.Oura et al.**
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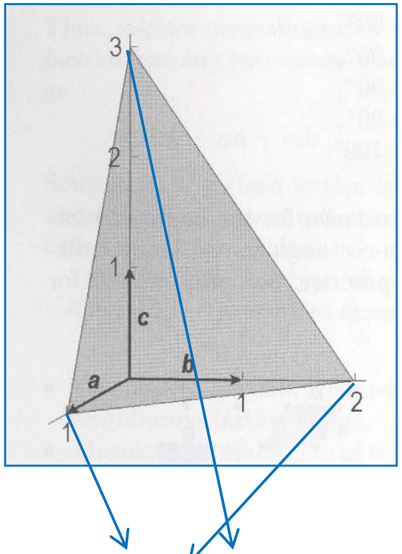
# Surface description: Miller indices

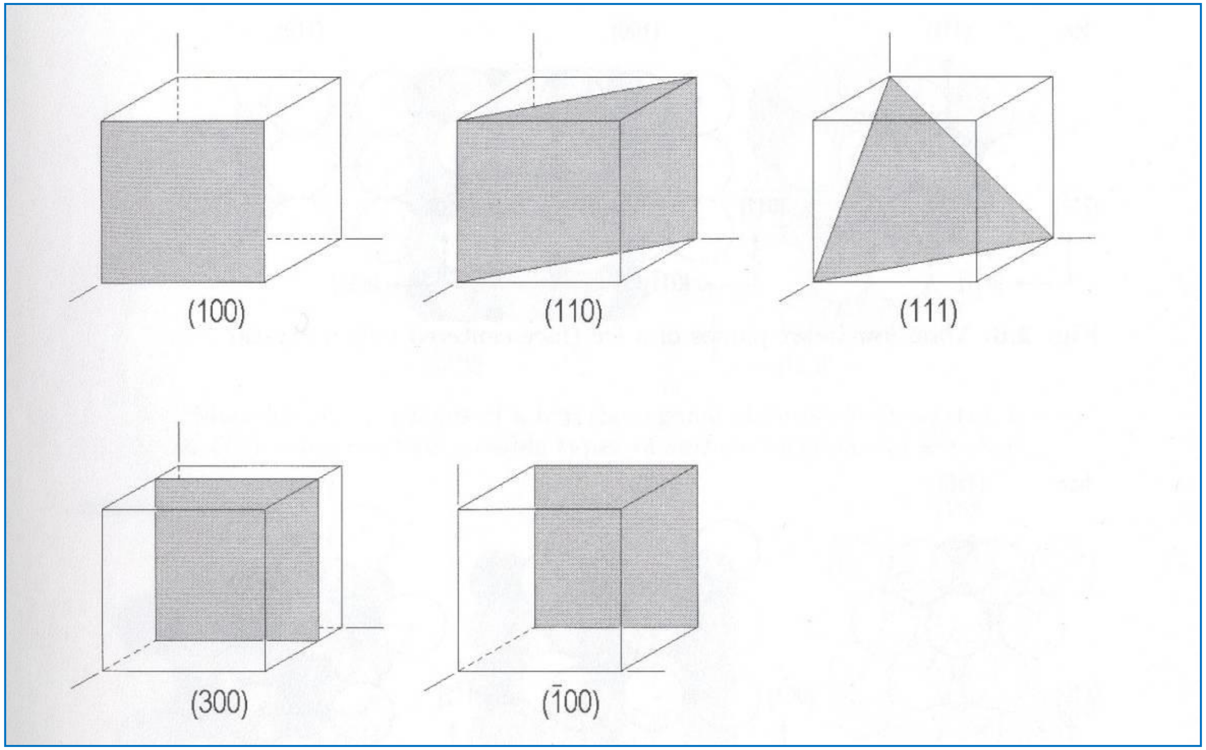


**1, 2, 3**

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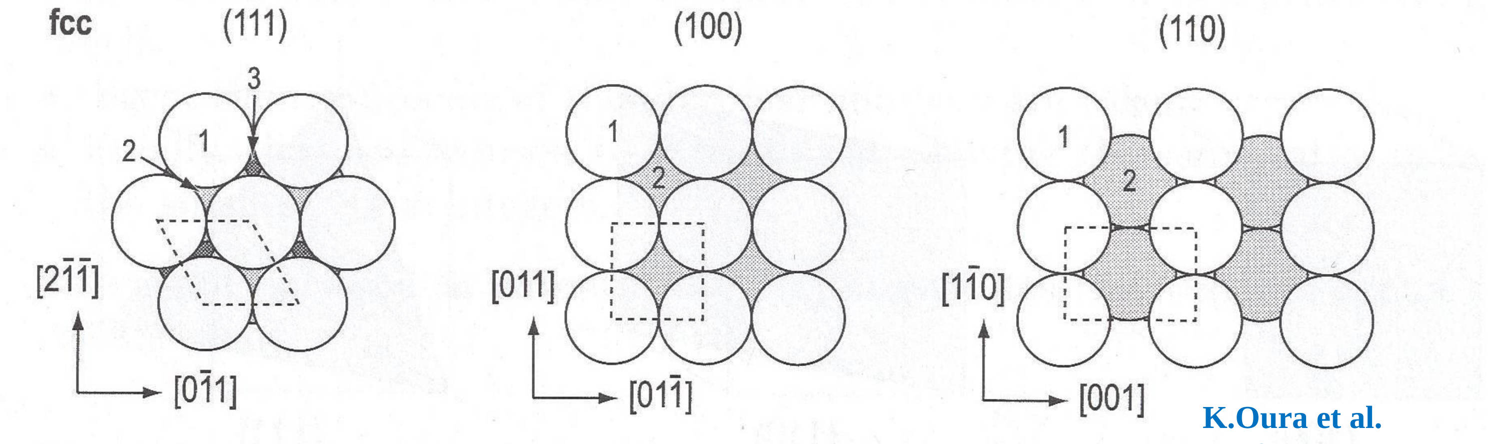
**For a hexagonal structure**
**(h, k, -h-k, l)**

# Atomic structure of surfaces - examples

## Face-centered cubic crystal



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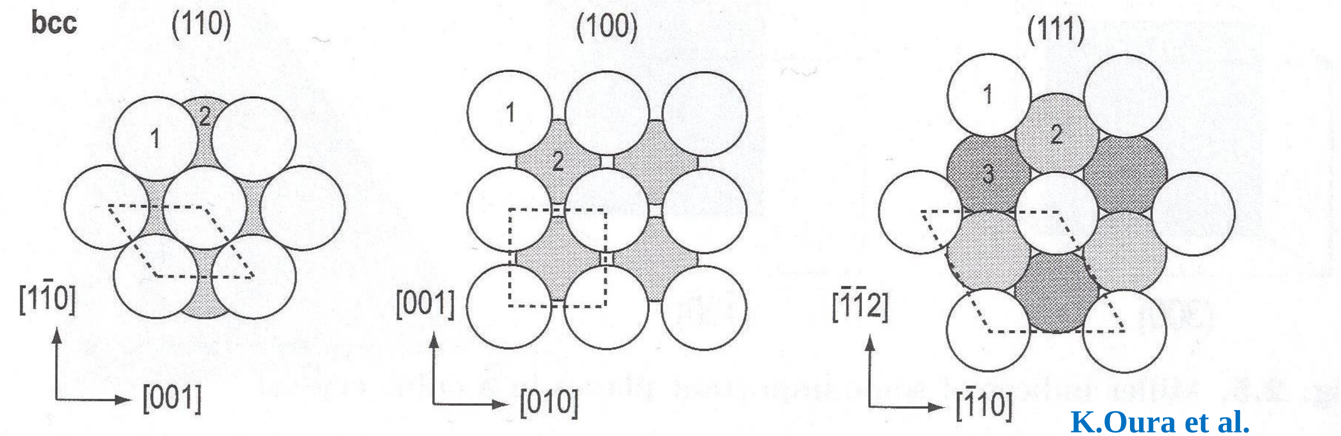
## Body-centered cubic crystal



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# Surface structure description - notations

## Wood's notation

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

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

$$\mathrm{S}(hkl) - \underset{\substack{\downarrow \\ (p\text{ or }c)}}{i}(m \times n)R\phi^\circ - N\ Ad$$

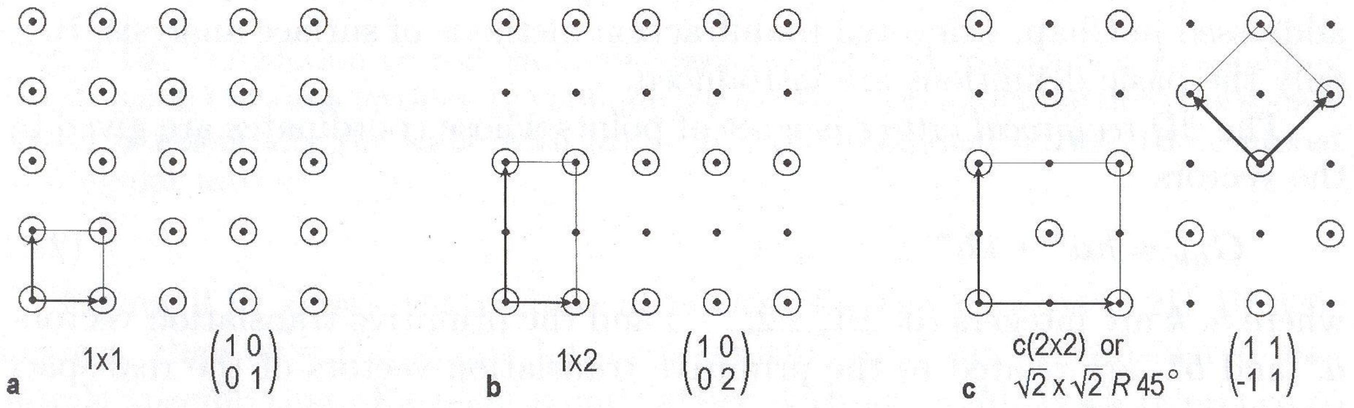
$$\mathrm{Ni}(100) - \left(2\sqrt{2} \times \sqrt{2}\right)R45^\circ - O$$

## 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

K.Oura et al.
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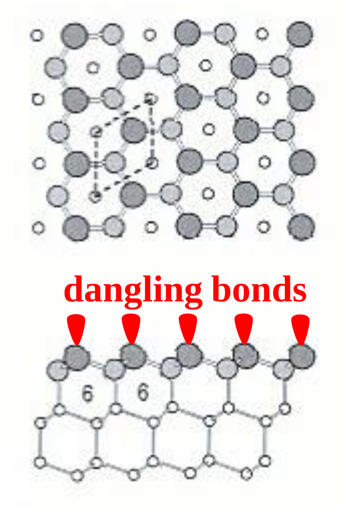
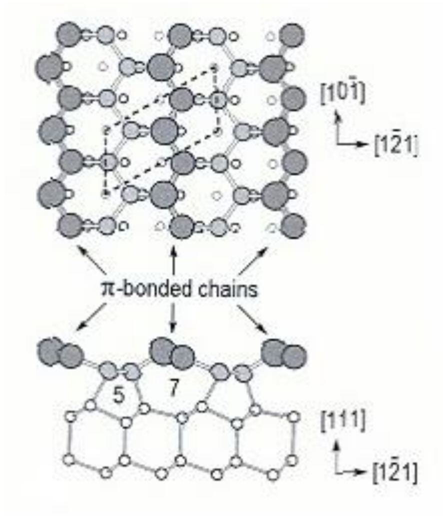


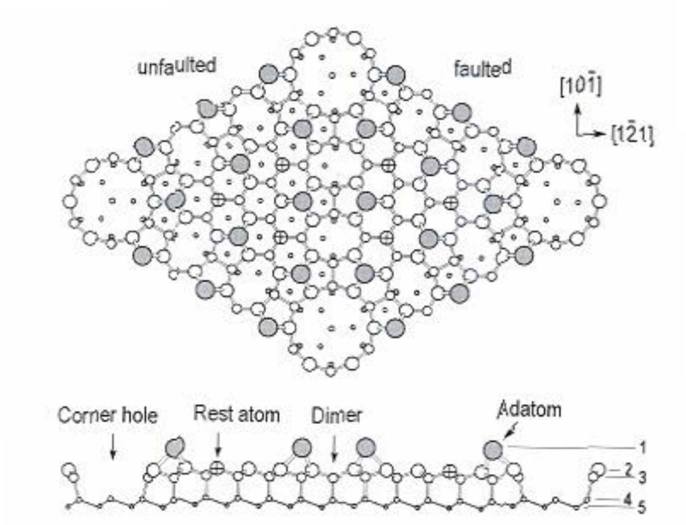
**Si(111)- (1x1)**

**ideal cut**



**Si(111)- (2x1)**

**crystal cleaved along (111)**



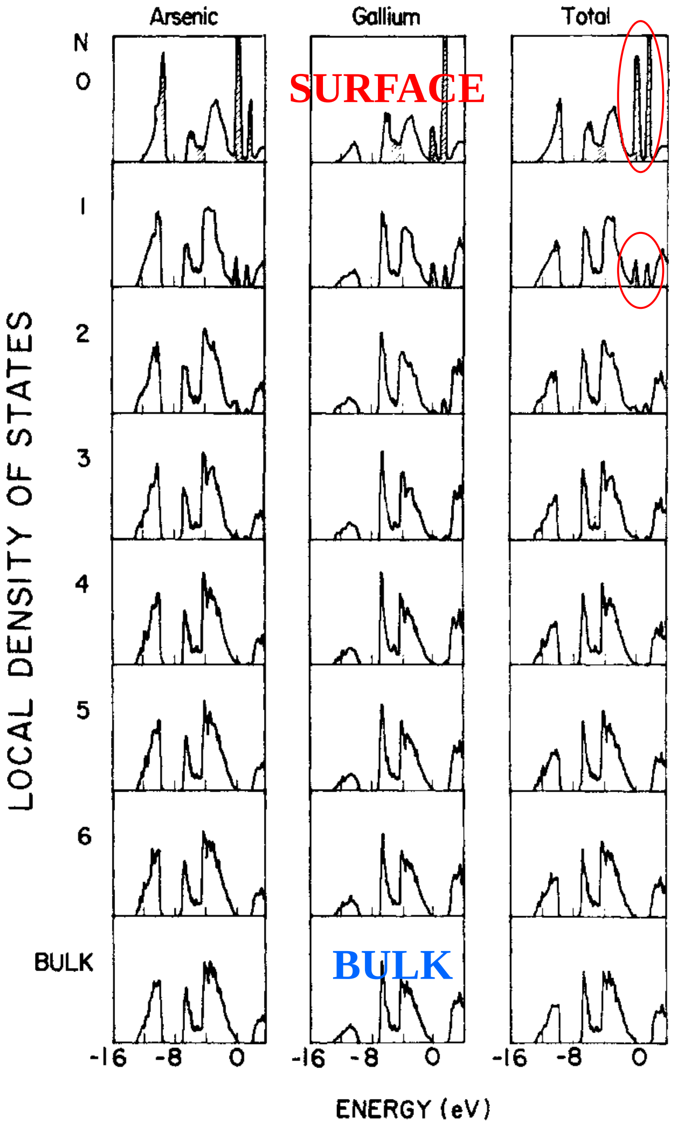
**Si(111)- (7x7)**

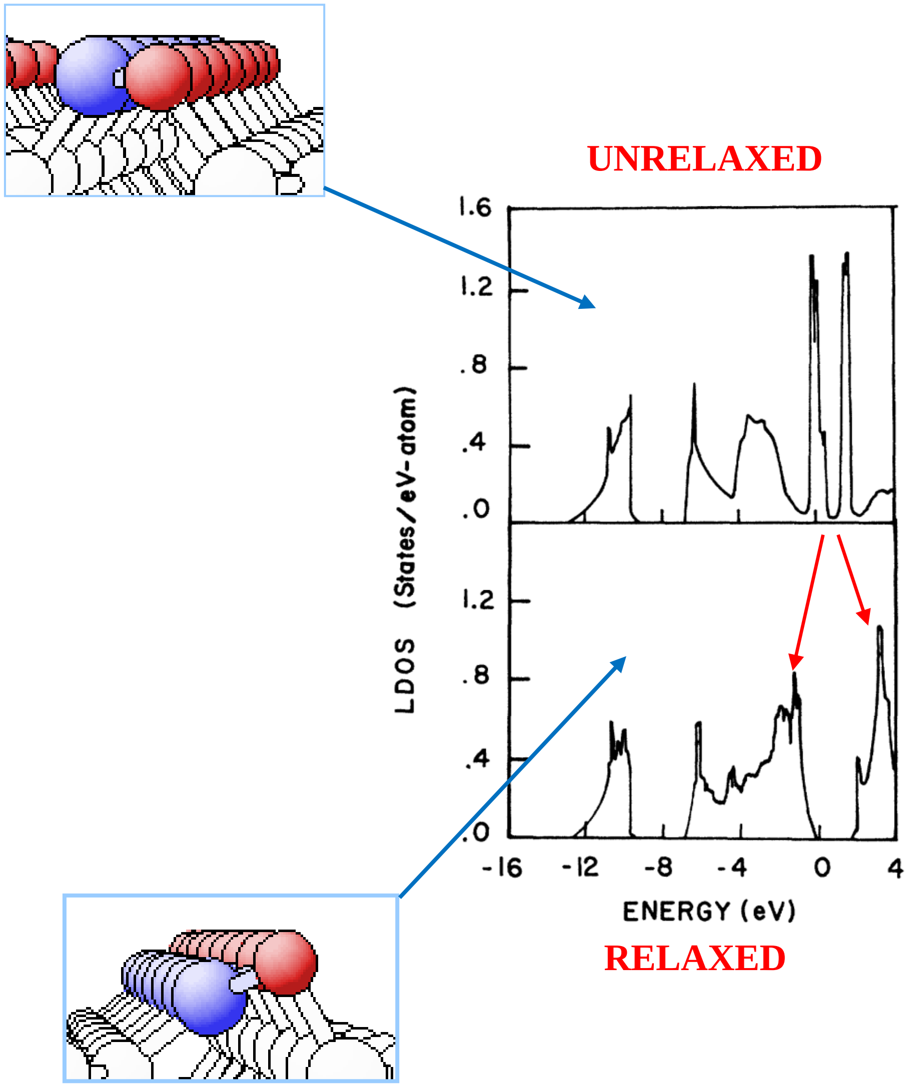
**obtained from 2x1 by annealing at 450$^0$C**

***dimer-adatom-stacking fault (DAS) model***

# Electronic structure of the surface

## unrelaxed GaAs(110)

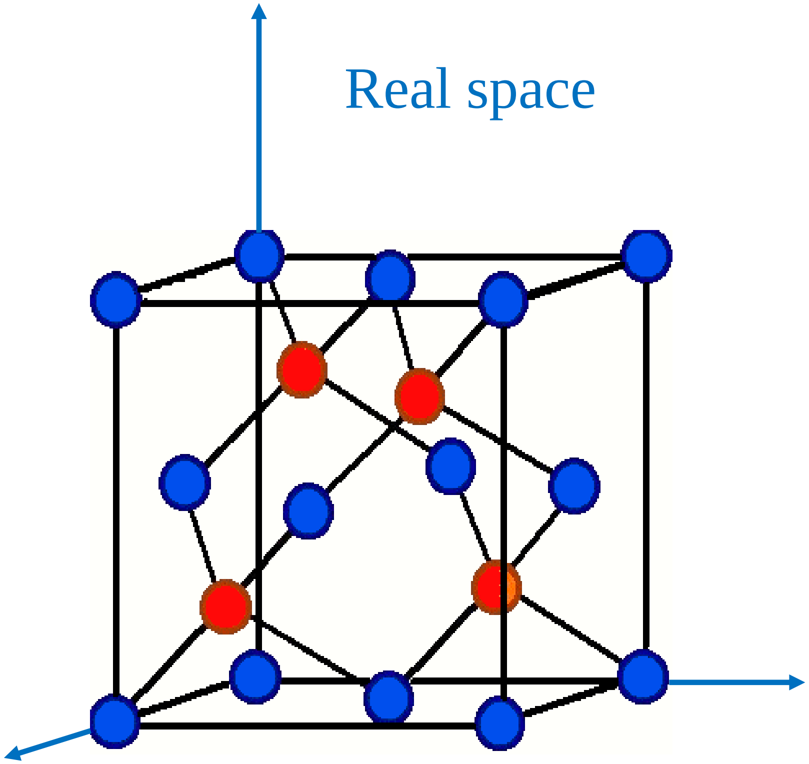




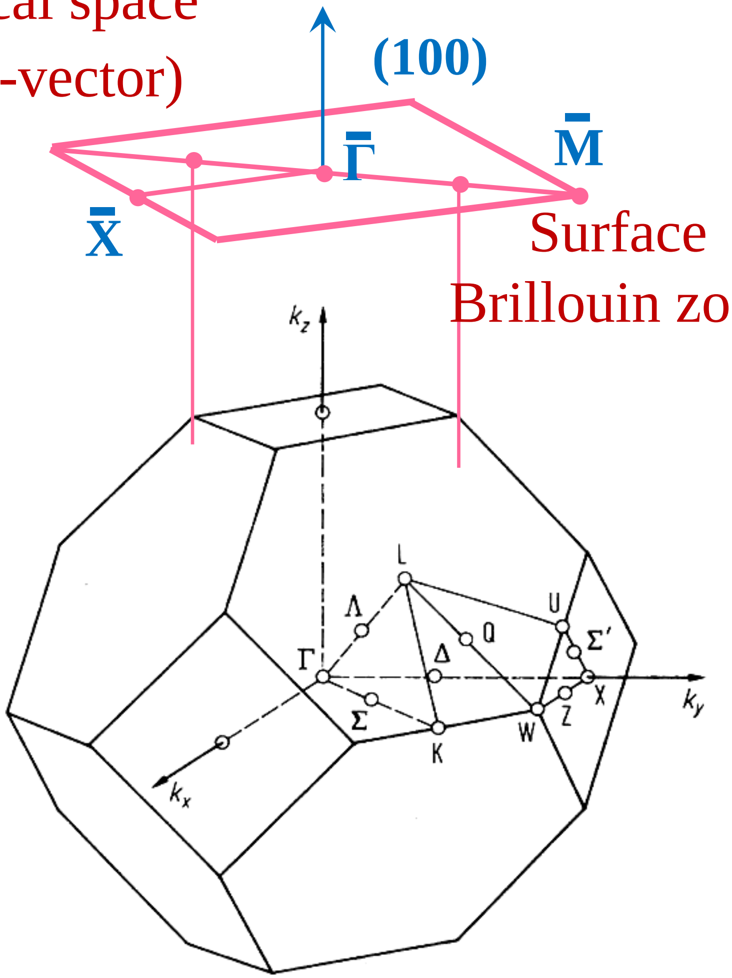
E.J. Mele…, Phys. Rev. B. **17,** 1816 (1978)

# Electronic structure of the surface (cont.)

## Brillouin zones



Real space

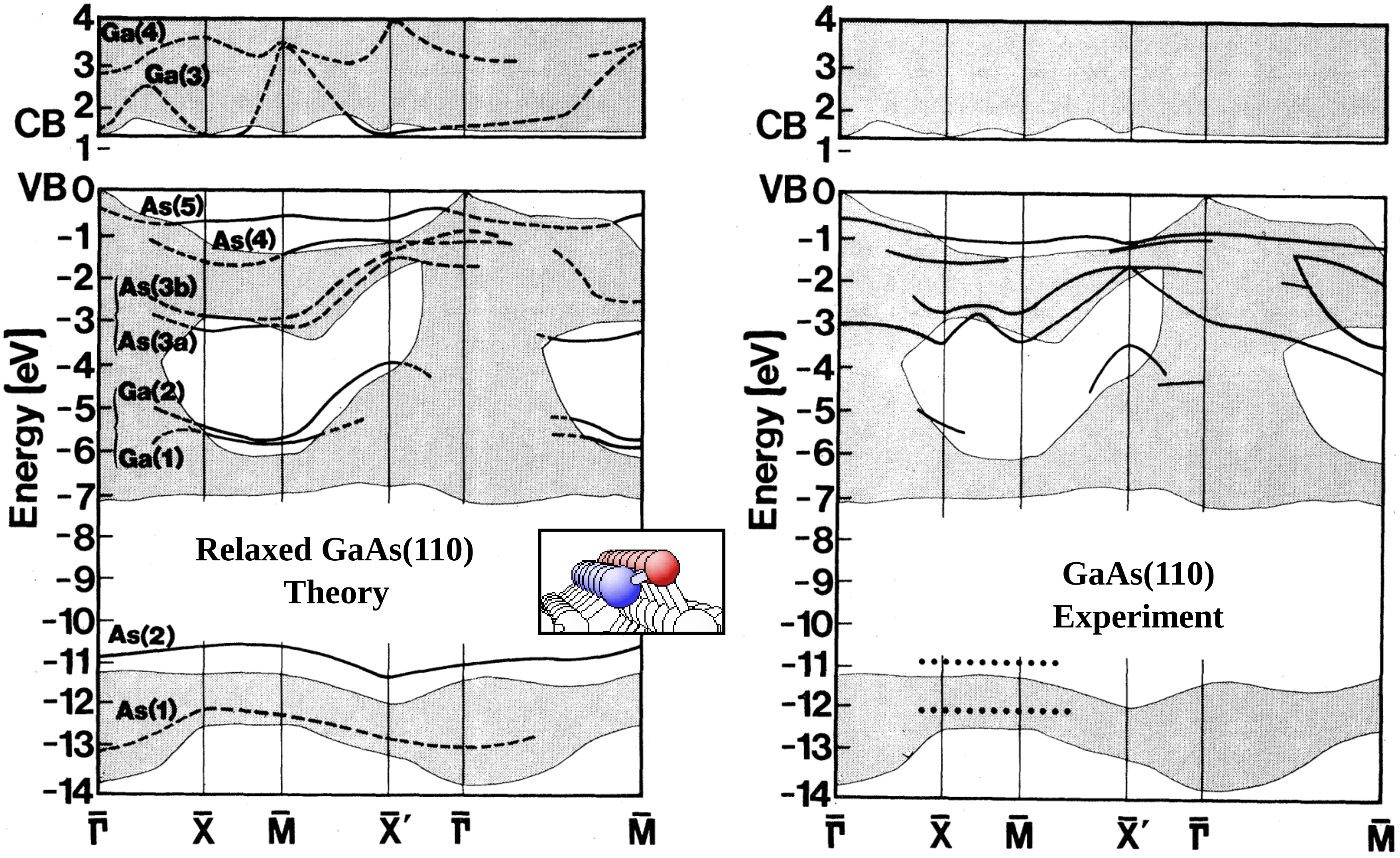


Reciprocal space (k-vector)

Surface Brillouin zone

Bulk Brillouin zone

# Electronic structure of the surface (cont.)

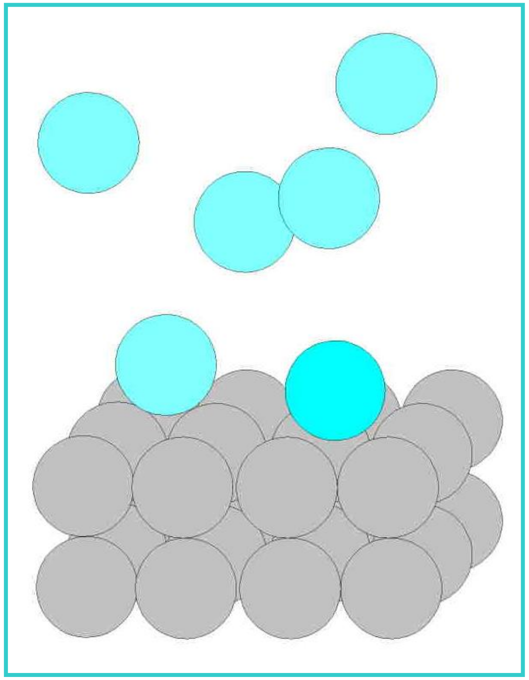


A. Zunger, Phys. Rev. B **22**, 959 (1980)

# 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 | 3x$10^{23}$ | 3 ns |
| $10^{-3}$ | 5 cm | 4x$10^{17}$ | 2 ms |
| $10^{-9}$ | 50 km | 4x$10^{11}$ | 1 hour |

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

**K.Oura et al.**
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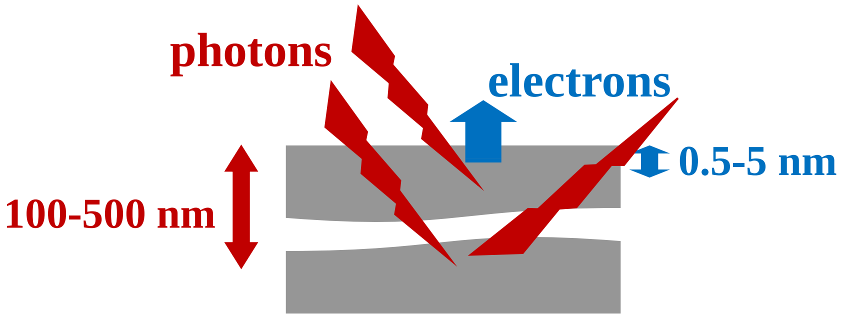
**Pressure of the order of $10^{-10}$ hPa is necessary for studying pristine surfaces!**

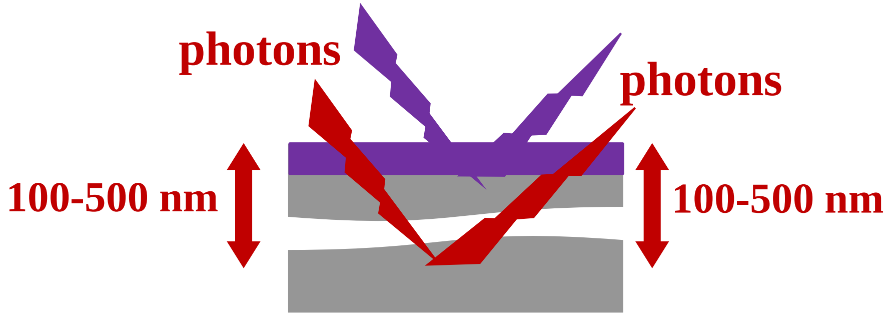
# How to extract the signal coming from the surface?

We have to find a proper „probe”



or

a proper surface-related property



# What can be a surface sensitive „probe”?

- **Electrons**

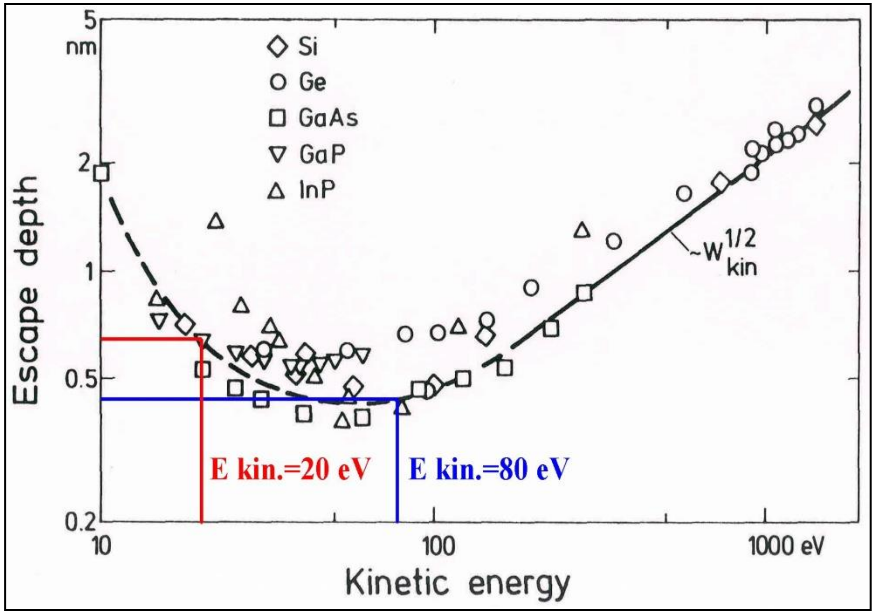
**Short escape depth**

**Available techniques:**

**•Microscopy**

**•Diffraction (LEED, RHEED)**

**•Spectroscopy (photoemission, Auger electron spectroscopy)**



W. Mönch „Semiconductor surfaces and interfaces” 1993

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

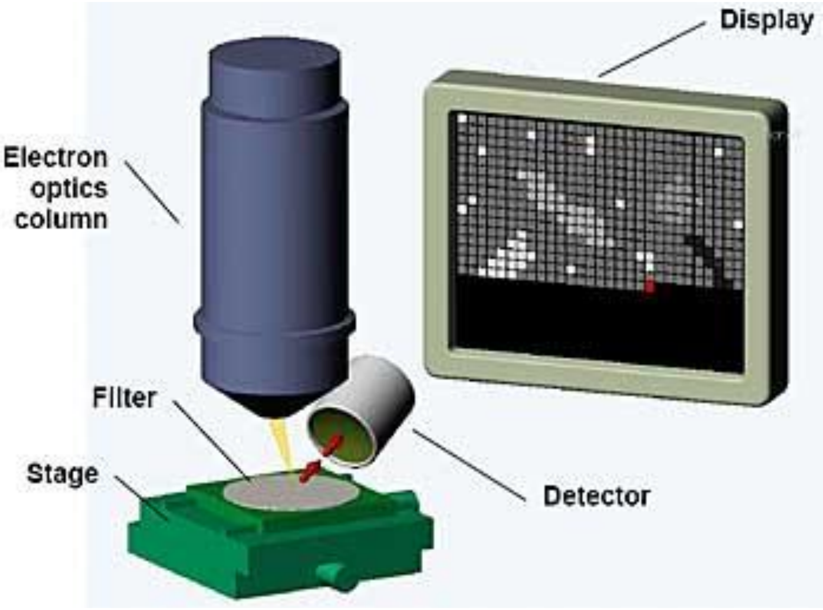
- **Ions**
  - **Scattering (n.p. RBS)**

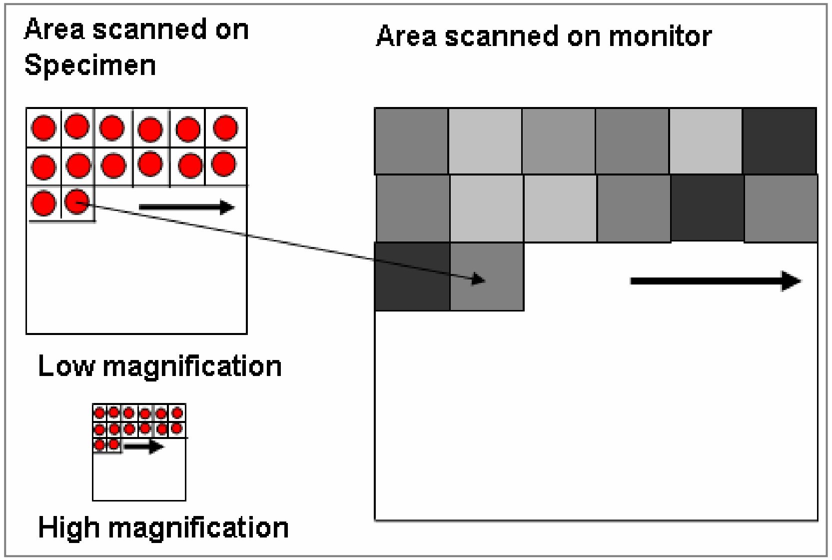
    Increased surface sensitivity for selected crystallographic directions (channelling)
  - **Surface sputtering (SIMS)**
- **Photons**
  - **Surface differential spectroscopy**
  - **X-ray diffraction**

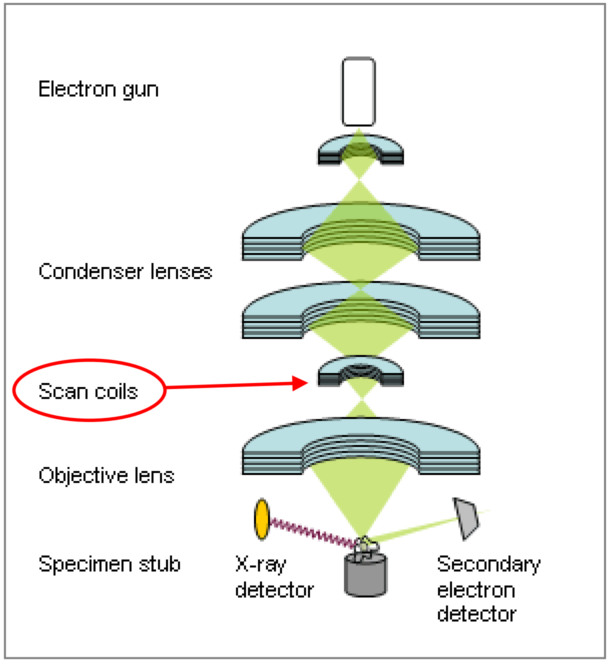
    Increased surface sensitivity for glancing incidence

# Microscopies

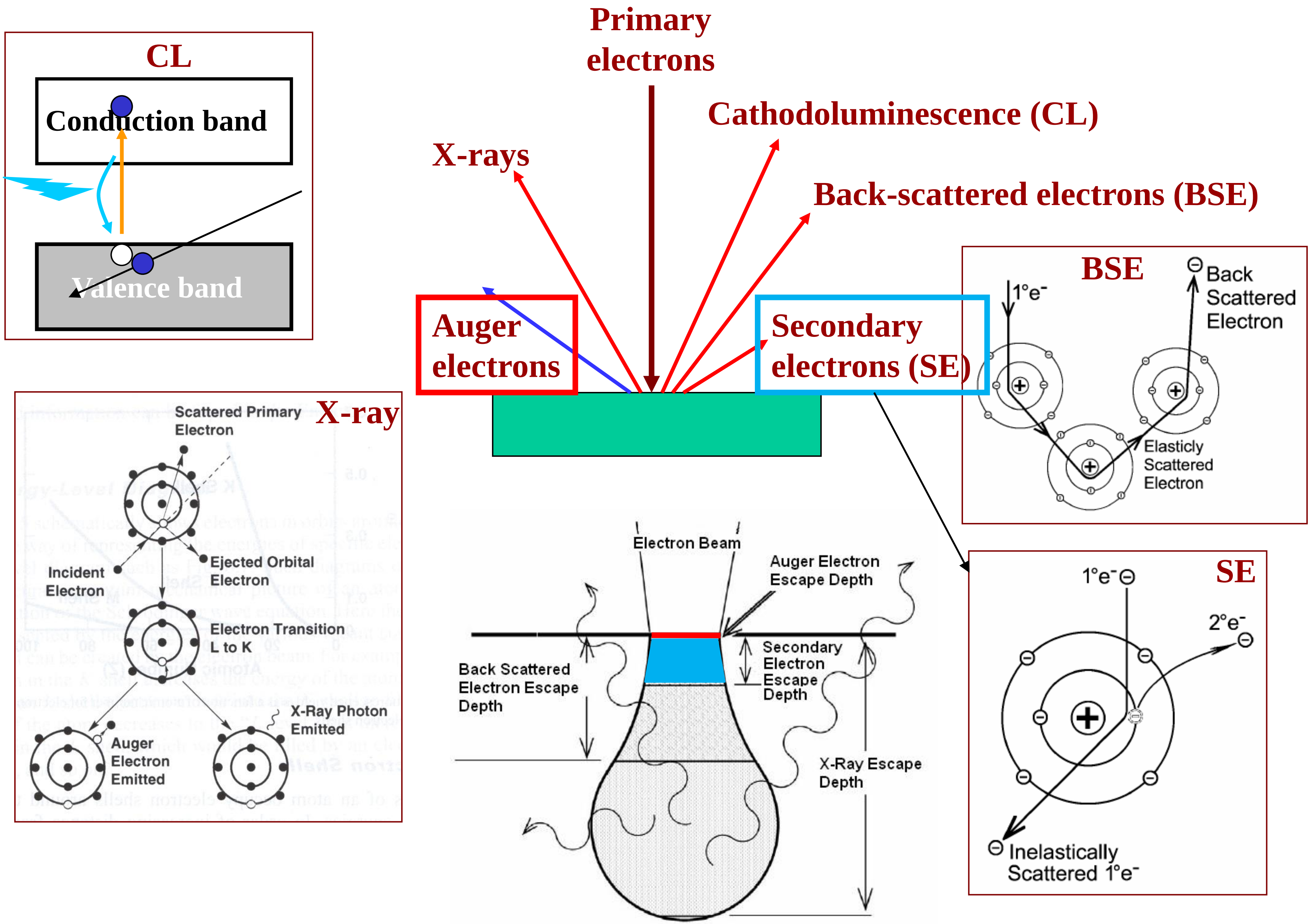
# Scanning Electron Microscopy (SEM)



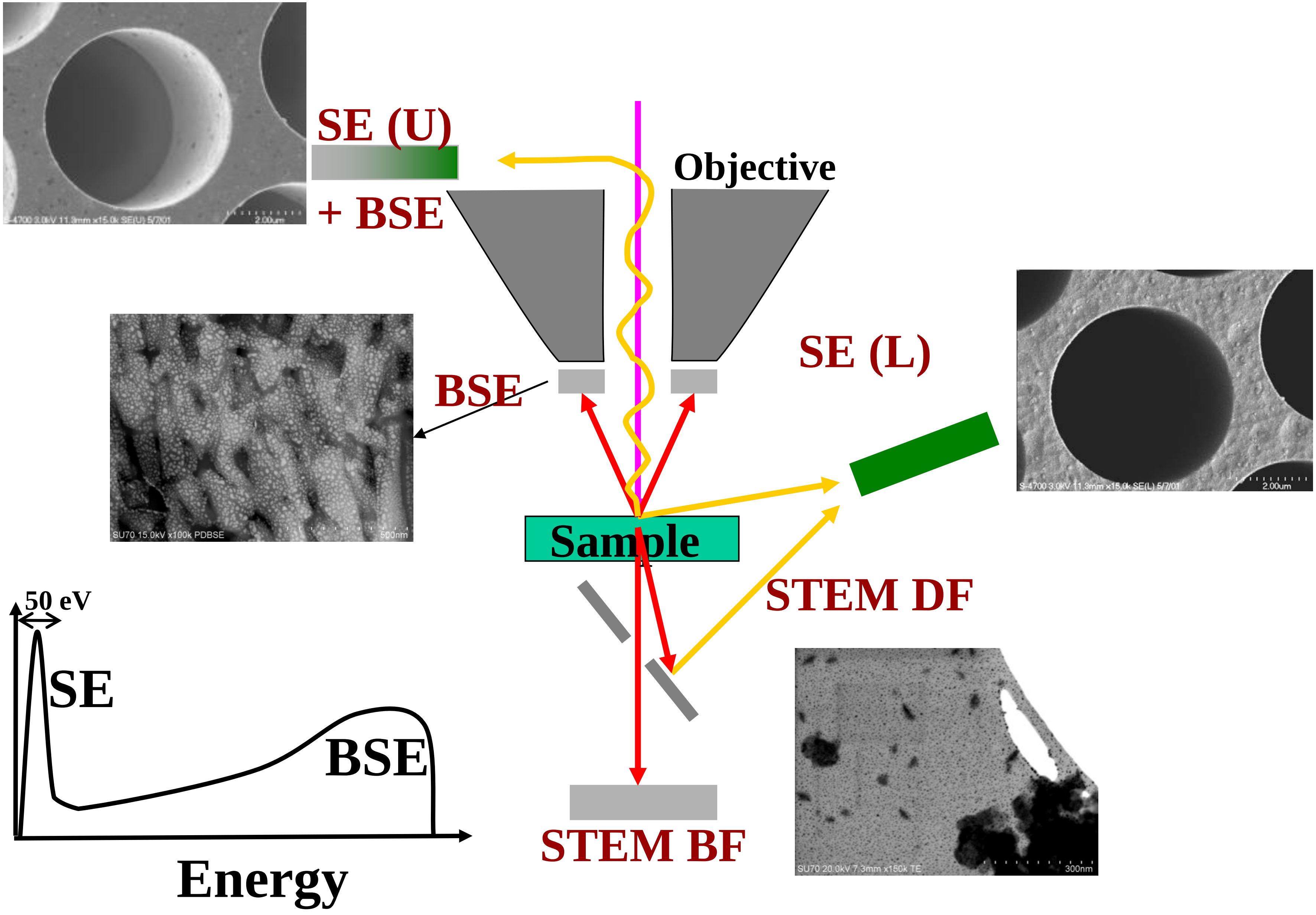


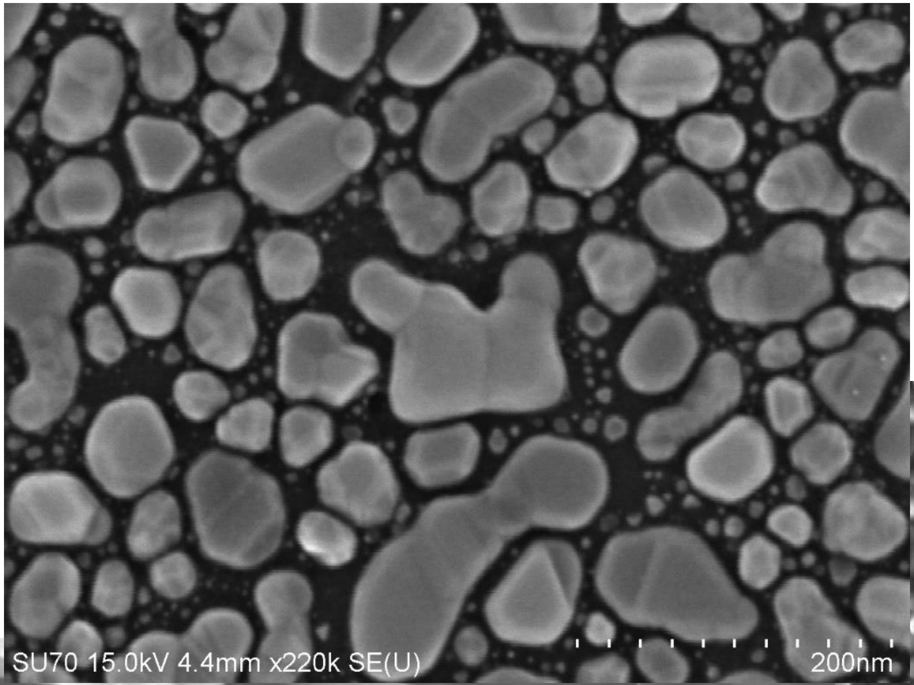


- opaque samples
- R ≈ 1 nm
- $U_{acc} \leq 30$ kV

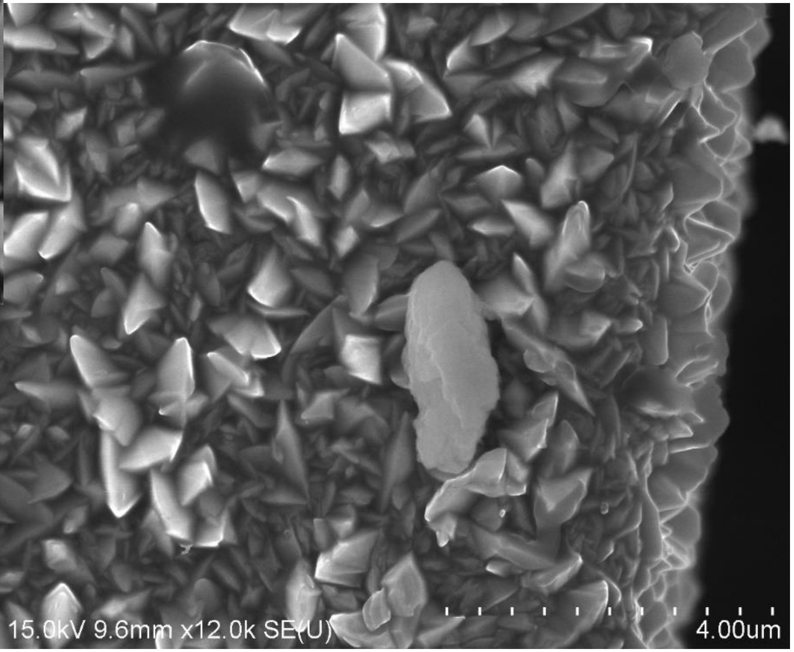

Primary electrons
Cathodoluminescence (CL)
X-rays
Back-scattered electrons (BSE)
Auger electrons
Secondary electrons (SE)
CL
Conduction band
Valence band
X-ray
Scattered Primary Electron
Incident Electron
Ejected Orbital Electron
Electron Transition L to K
Auger Electron Emitted
X-Ray Photon Emitted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

# Electron detection in SEM

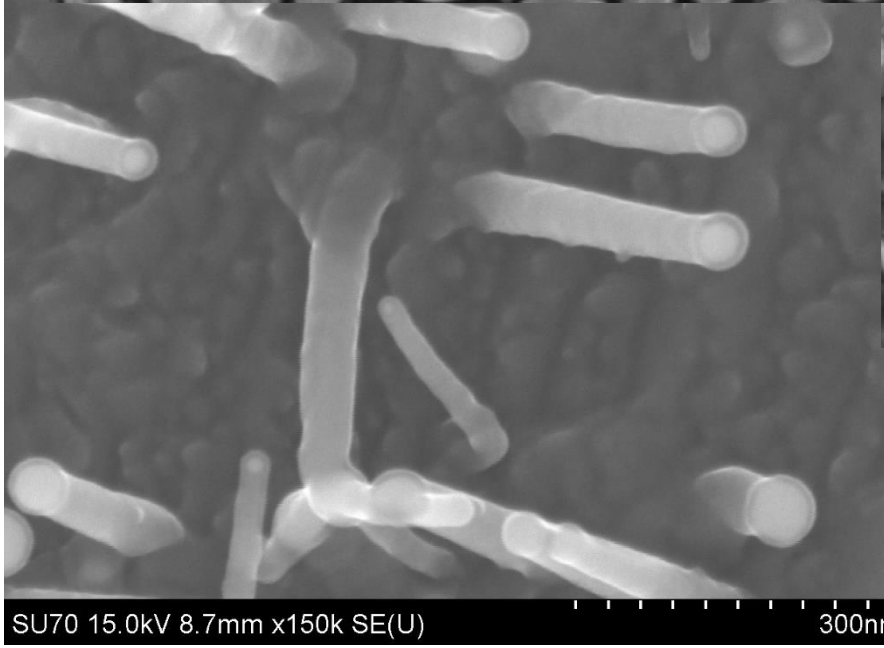




Au islands on C

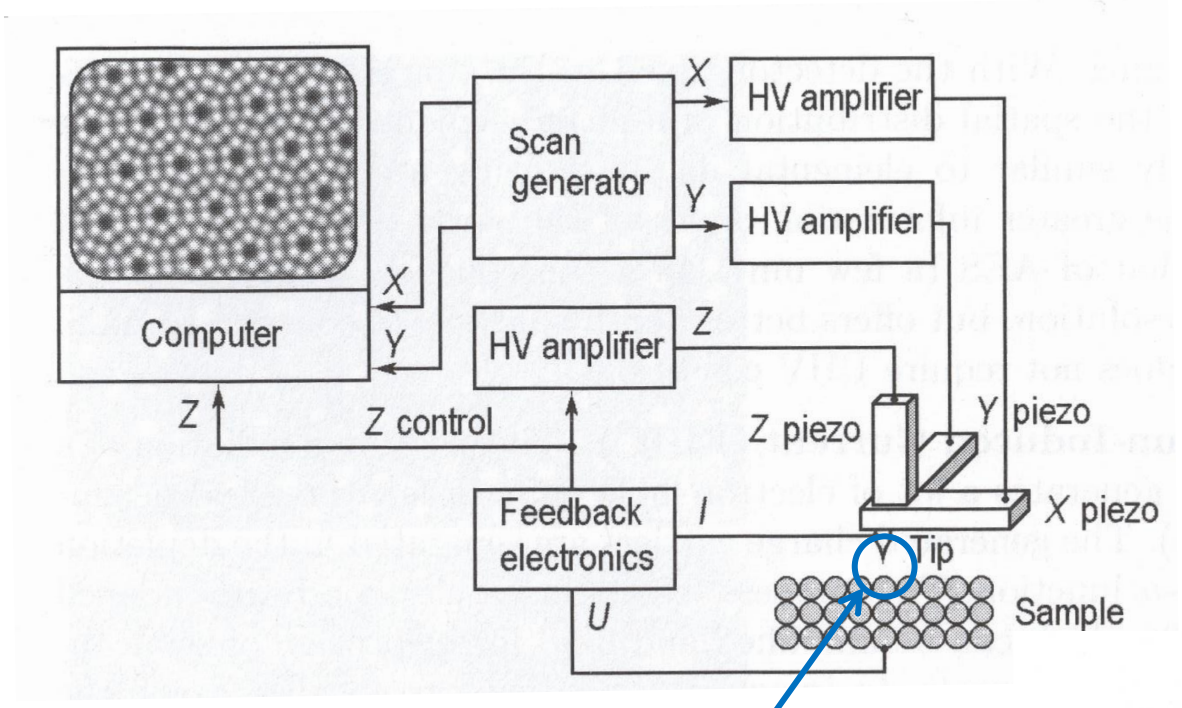


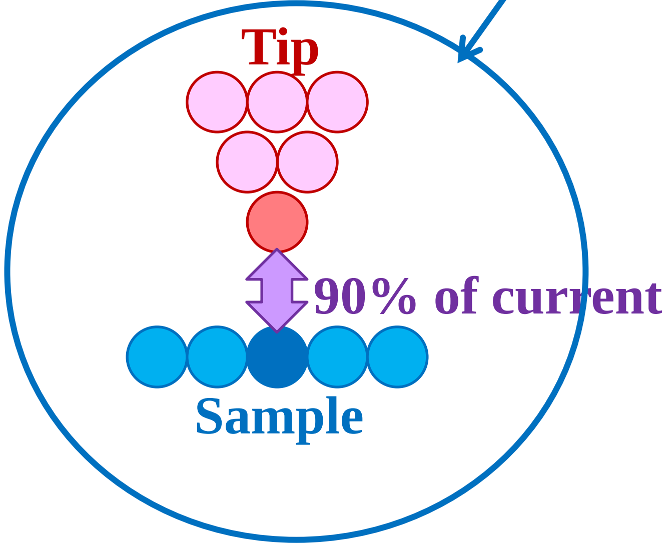
ZnO

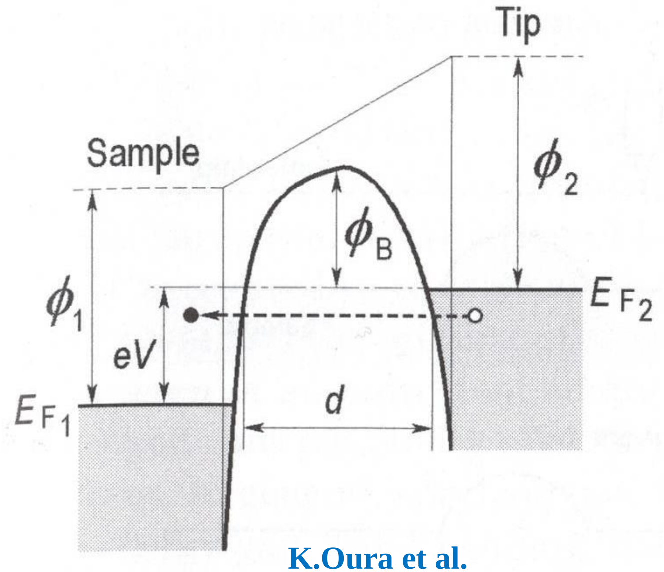


ZnTe nanowires

# Scanning Tunnelling Microscopy (STM)







**K.Oura et al.**
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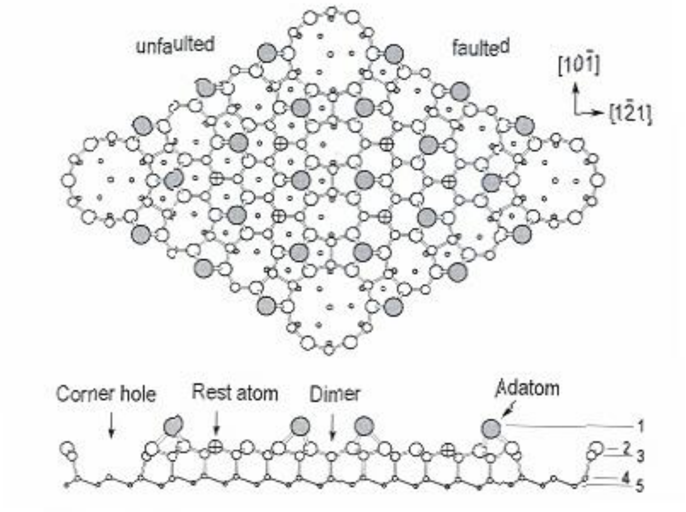
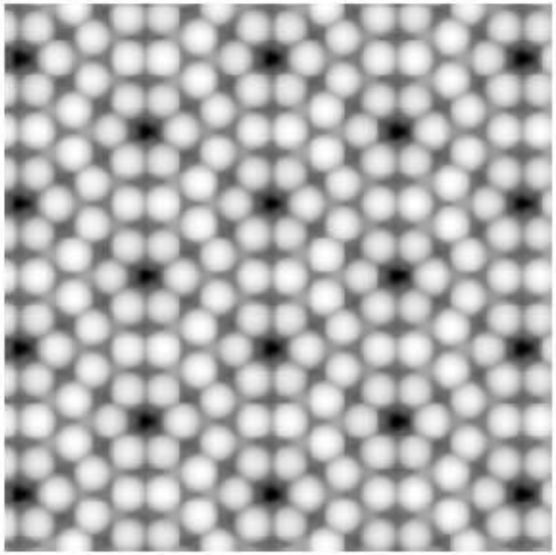
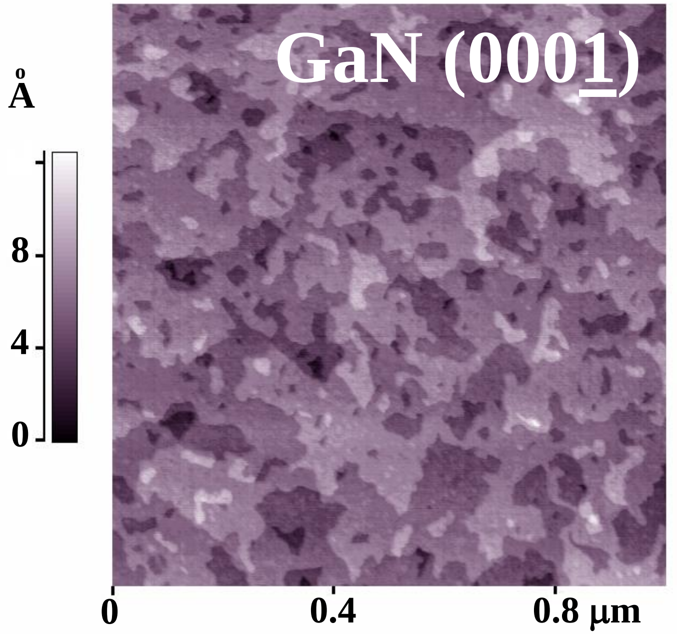
# Scanning Tunnelling Microscopy (STM) (cont.)



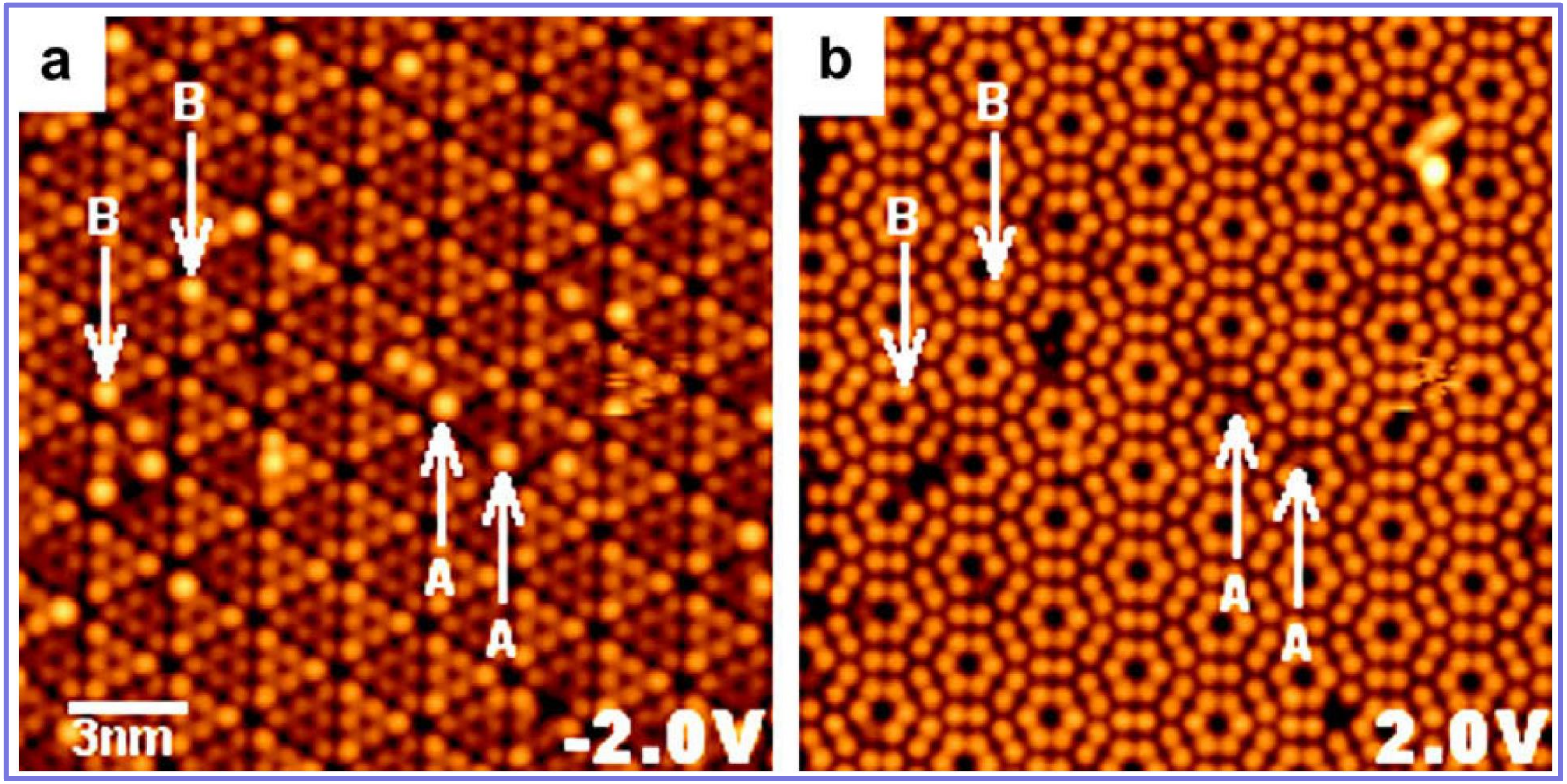
Si(111)- (7x7)





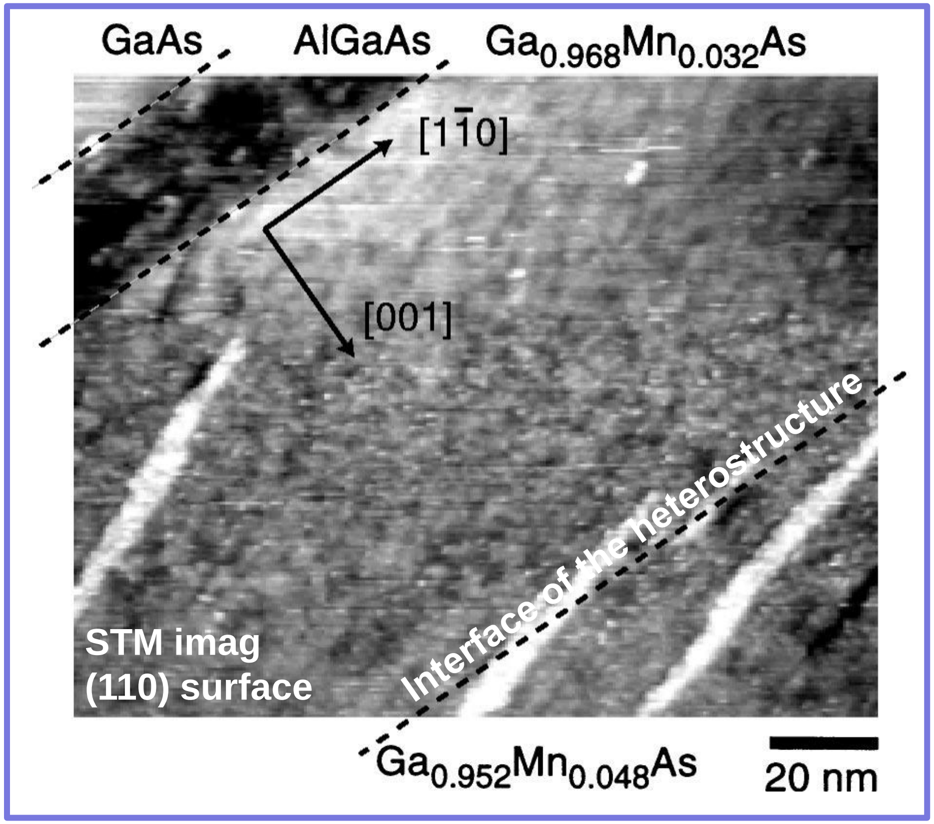
GaN(000$\underline{1}$)- (1x1)

# Scanning tunnelling microscopy (STM) (cont.)

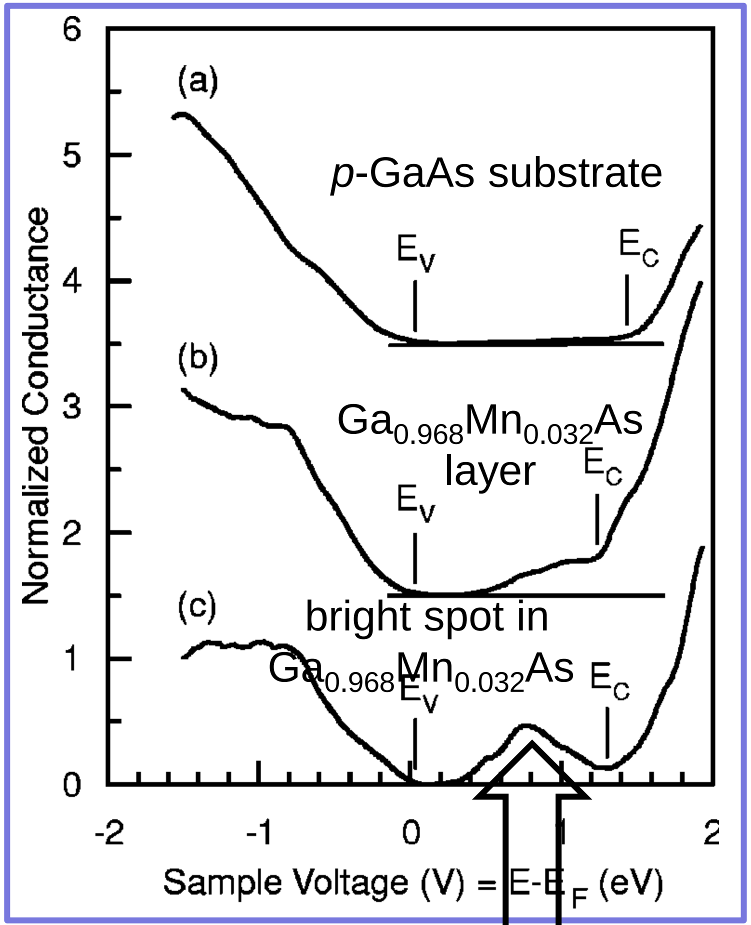


**Filled and empty electronic states in STM images of Si(111)-7x7 upon deposition of 0.05 ML of Ta. (**P. Shukrynau *et al*. Surface Science **603**, 469 (2009)**)**

# Scanning tunnelling spectroscopy (STS)



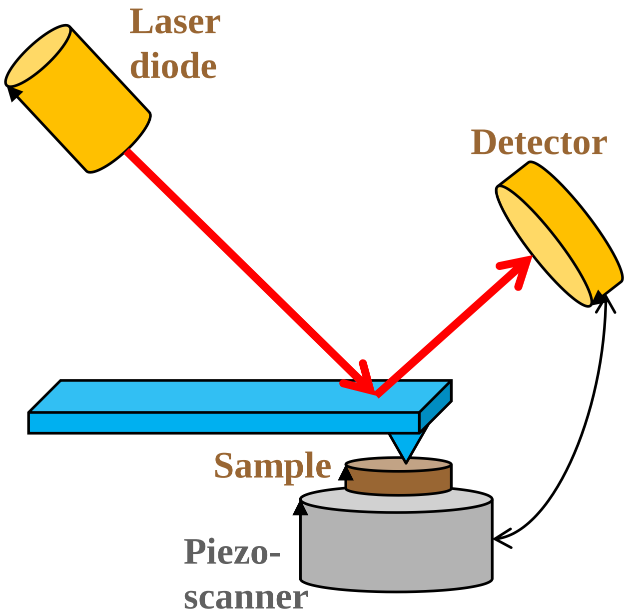
T. Tsuruoka *et al*. Appl. Phys. Lett. **81**, 2800 (2002)

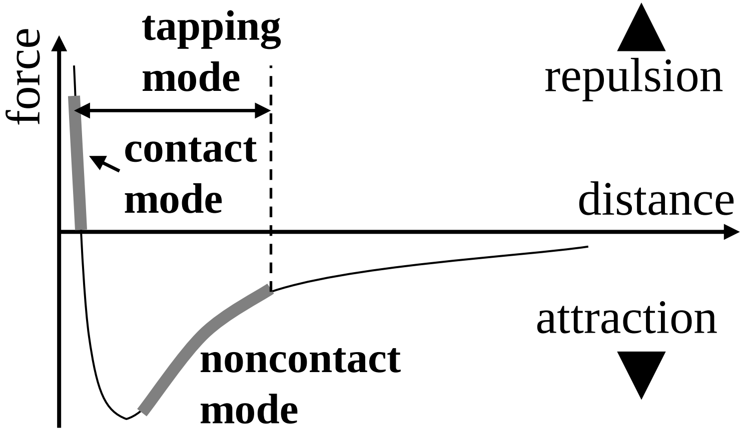


Tunnelling conductance spectra (STS)

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).

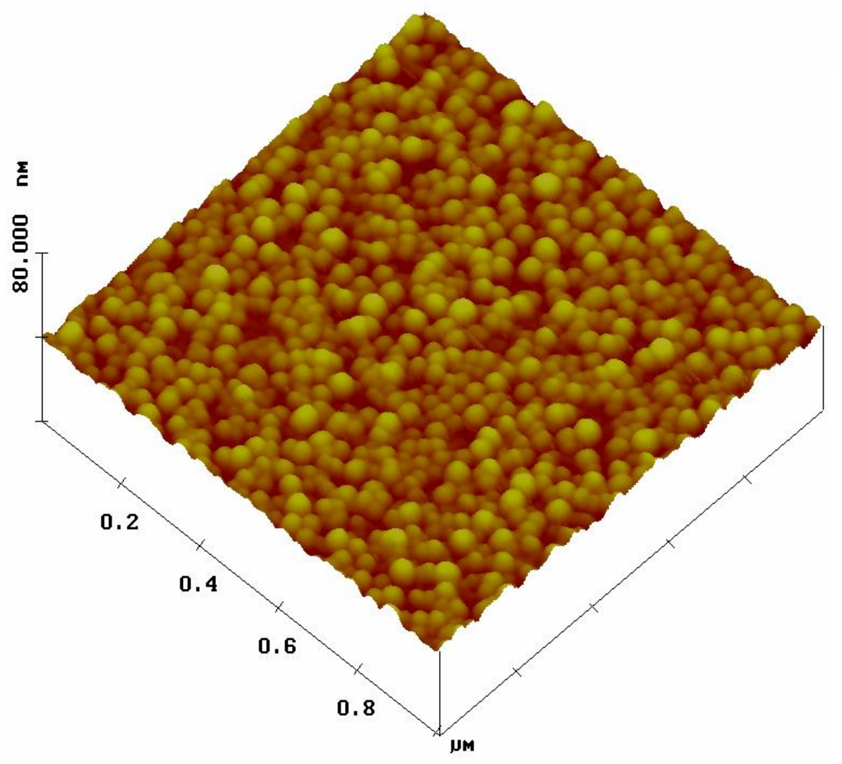
3. Attractive van-der-Waals force (long range, dominating for $z \gg 0.5$ nm).

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.

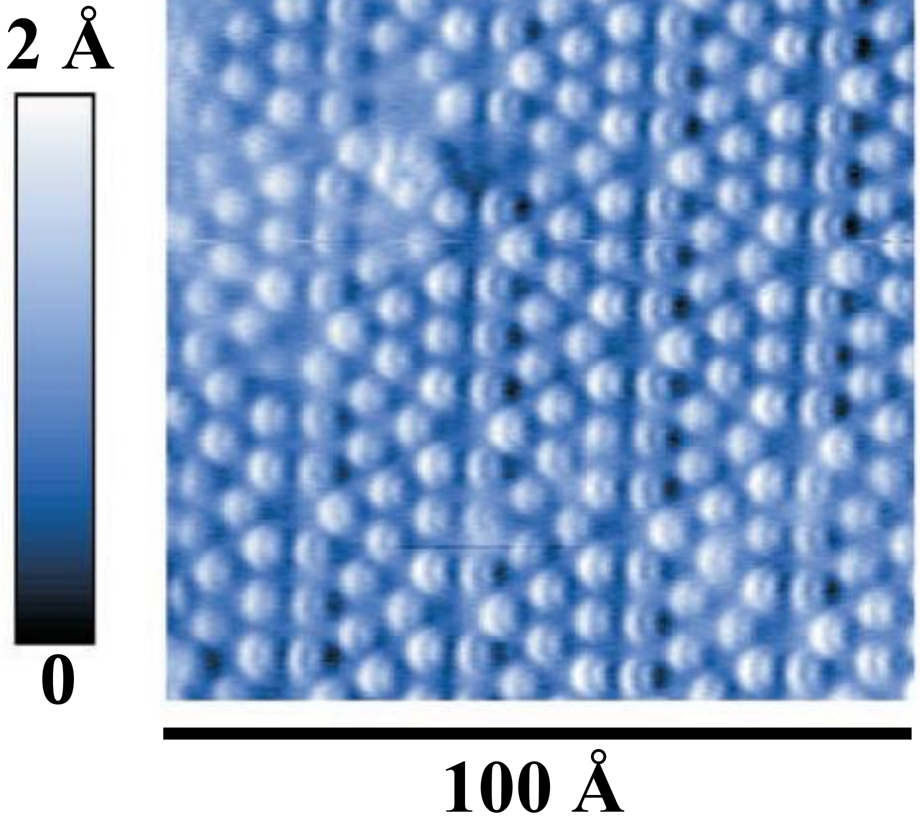
sjhsrc.wikispaces.com

# Atomic Force Microscopy (AFM) (cont.)



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

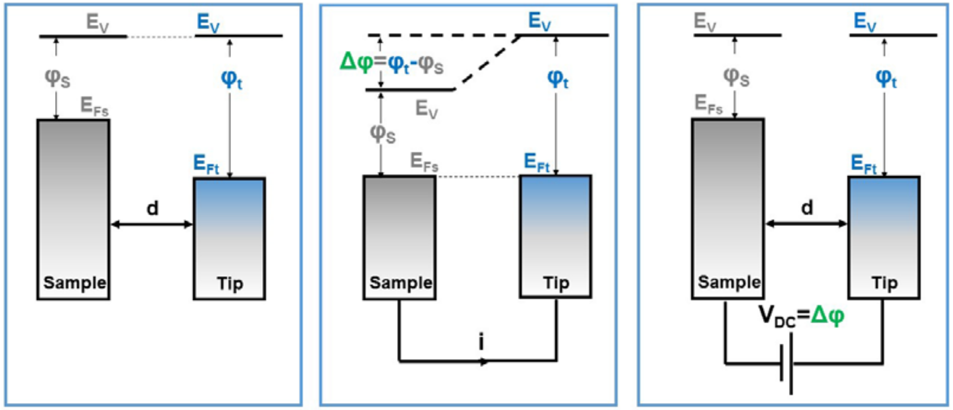
**Si(111)-(7x7)**



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

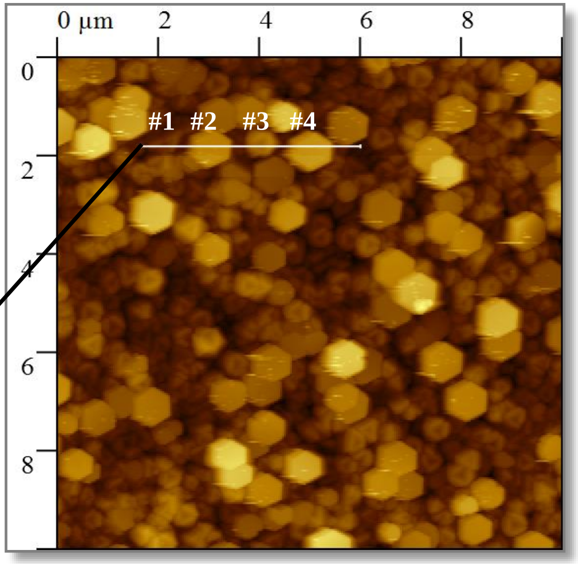
# Kelvin Probe Force Microscopy (KPFM)

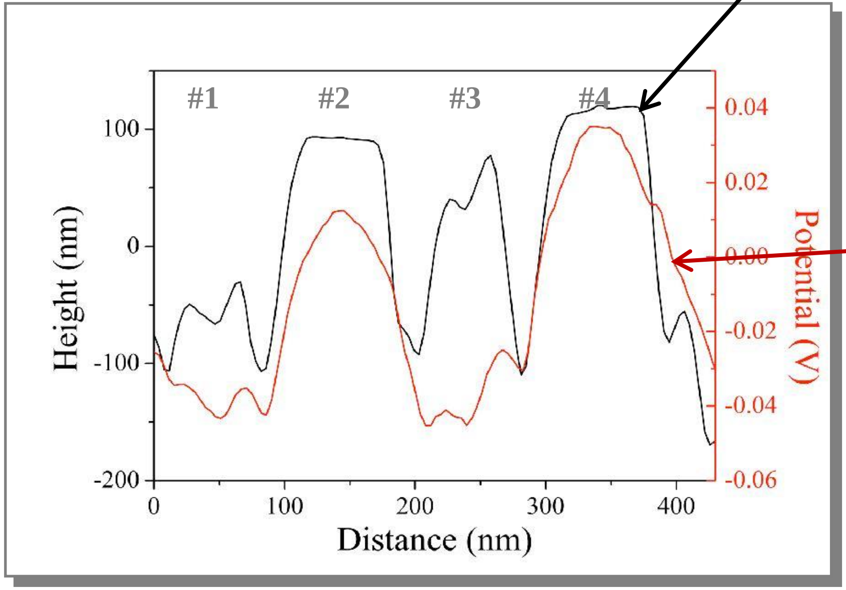
## Principle of Kelvin probe experiment



M.Paul Narchi, PhD Theses, Palaiseau 2016

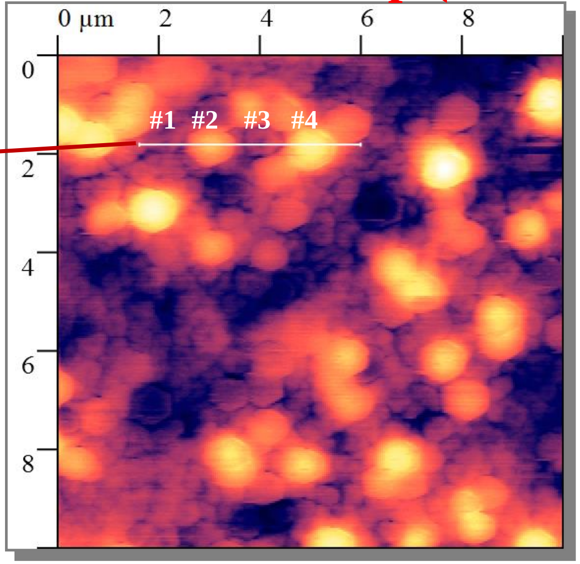
## Topography (AFM)





Rafal Bożek, *Faculty of Physics, University of Warsaw*

## Work function map (KPFM)



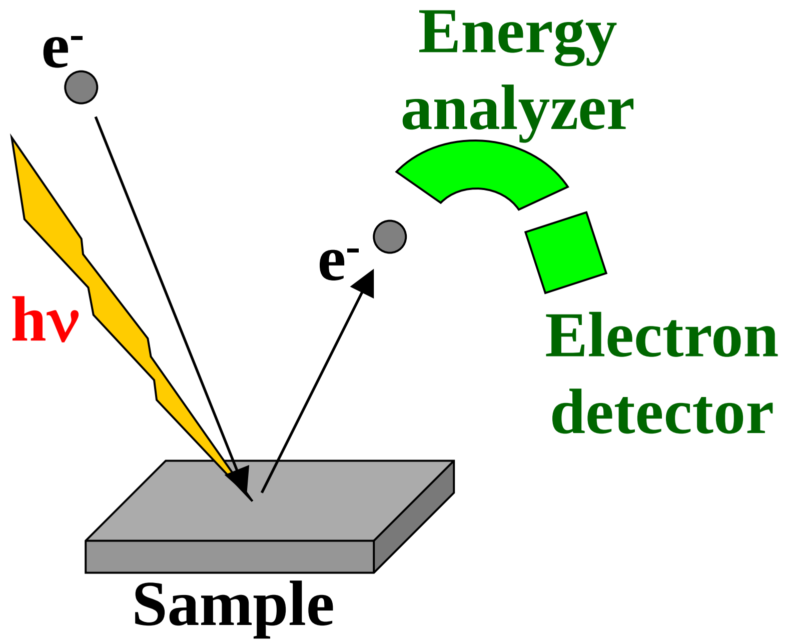
# Electron spectroscopies

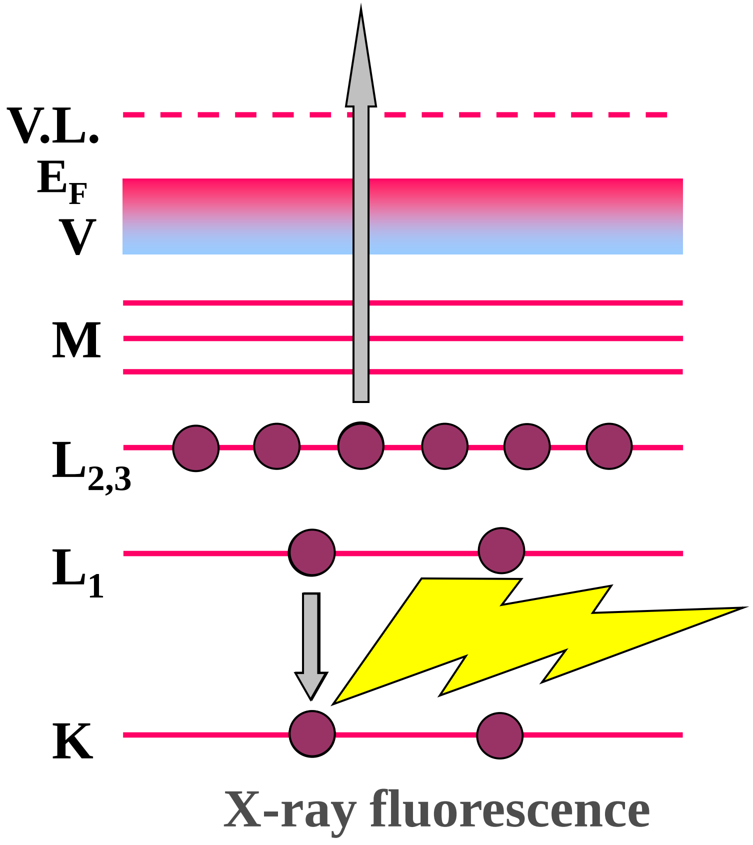
# Auger electron spectroscopy

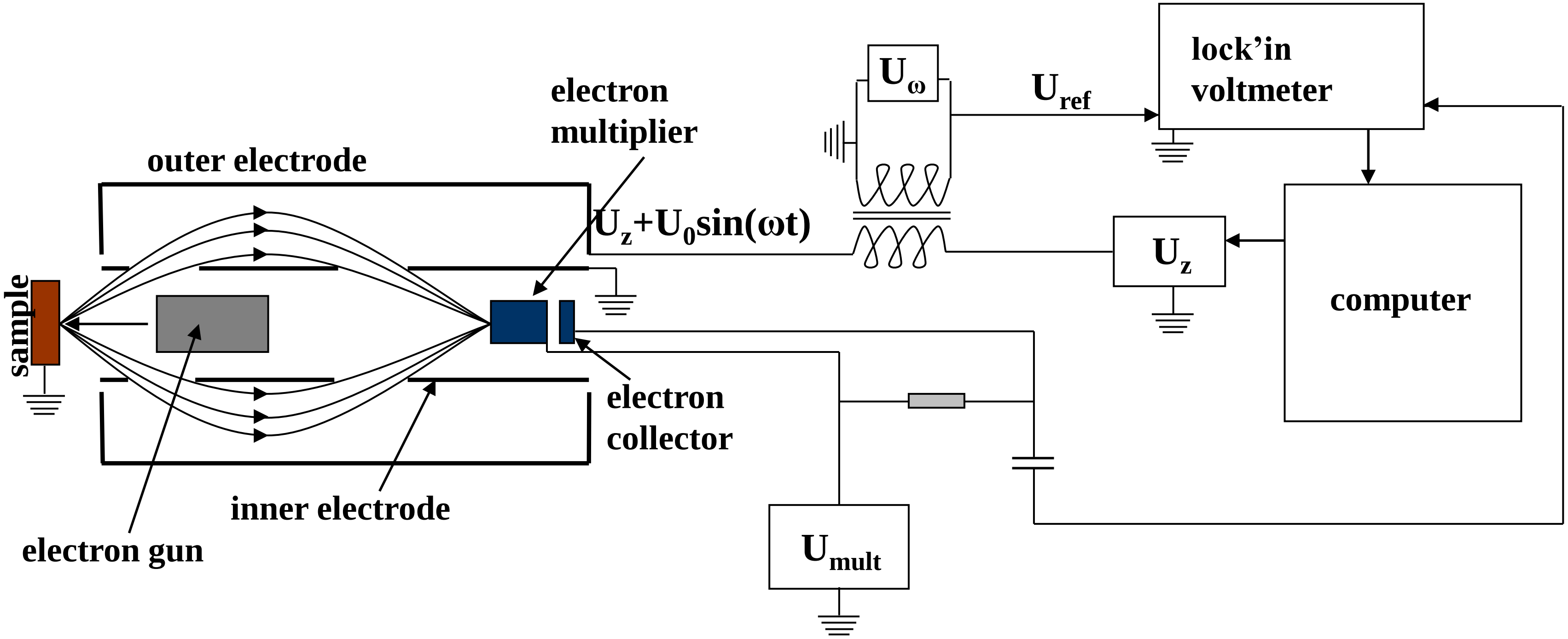
Primary ● electron $E_0$

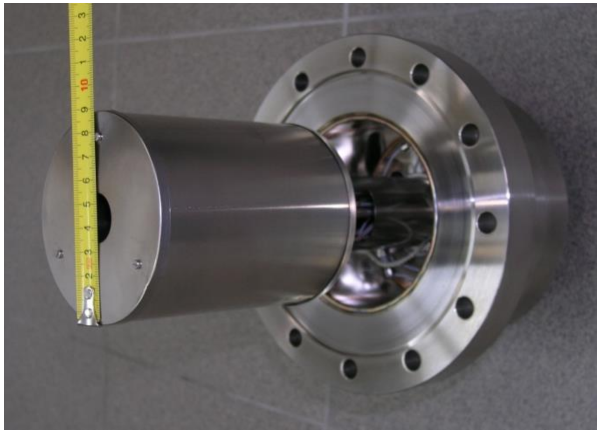
Auger electron energy:

$E_A=(E_K-E_{L1})-E_{L2,3}$









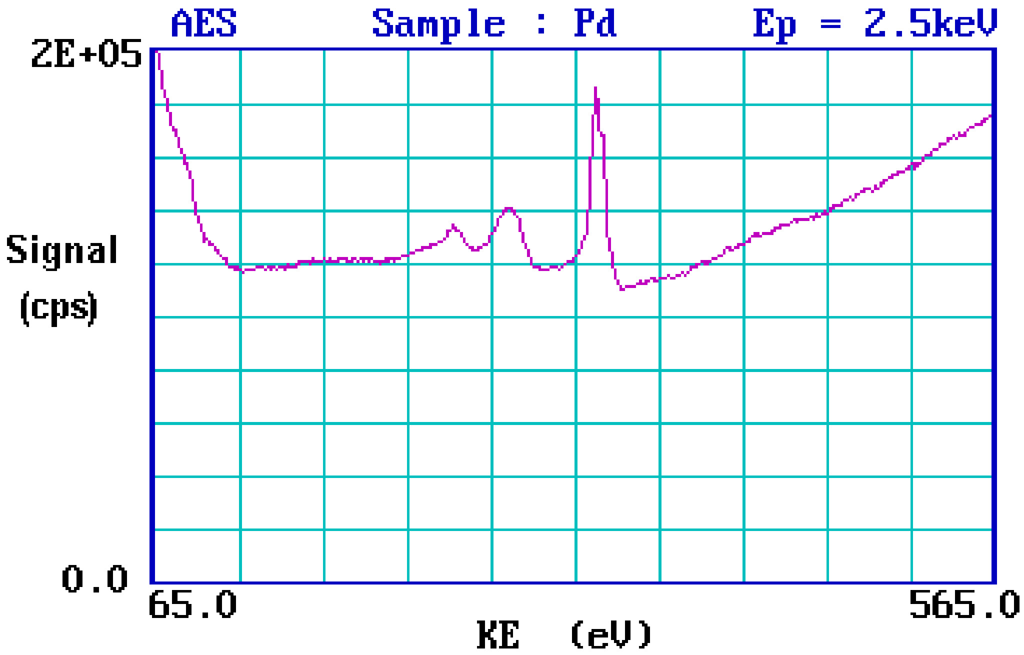
**Auger electron spectrometer with a cylindrical mirror analyser**

**Primary electron energy: up to 3kV**

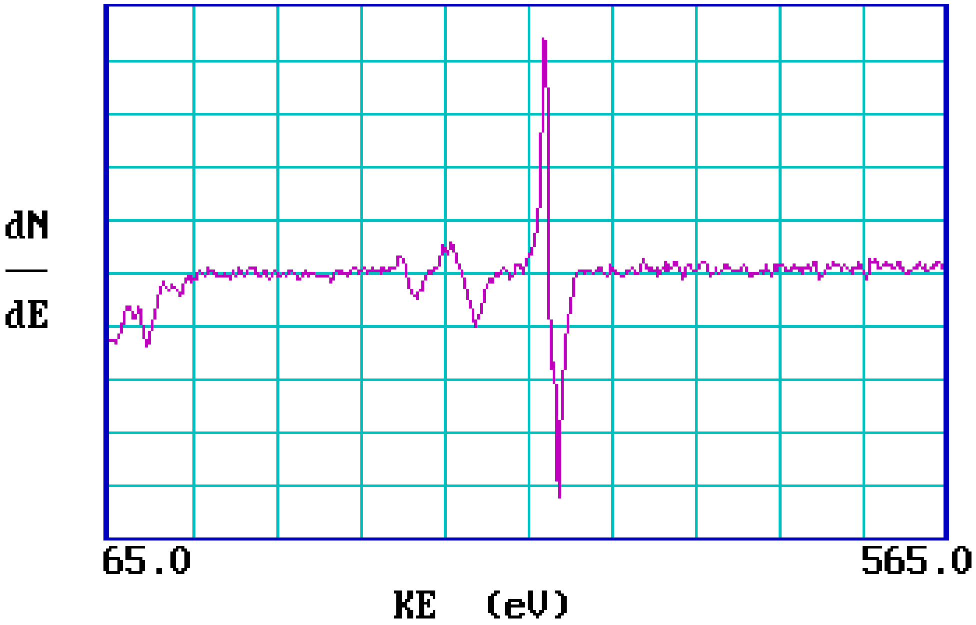
**Resolving power: E/ΔE > 145**

# Modes of AES spectra acquisition:

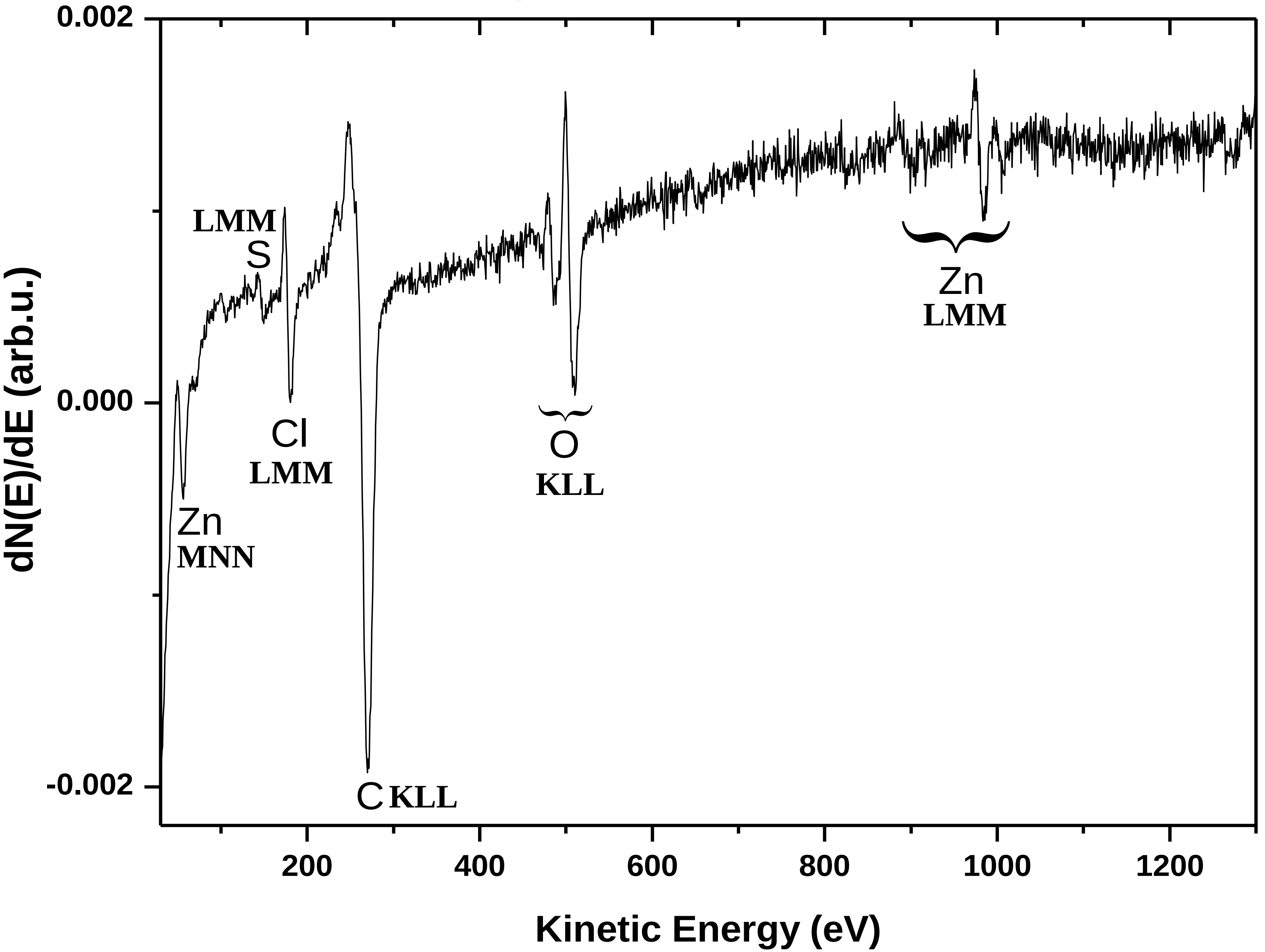
**integral**



**differential**

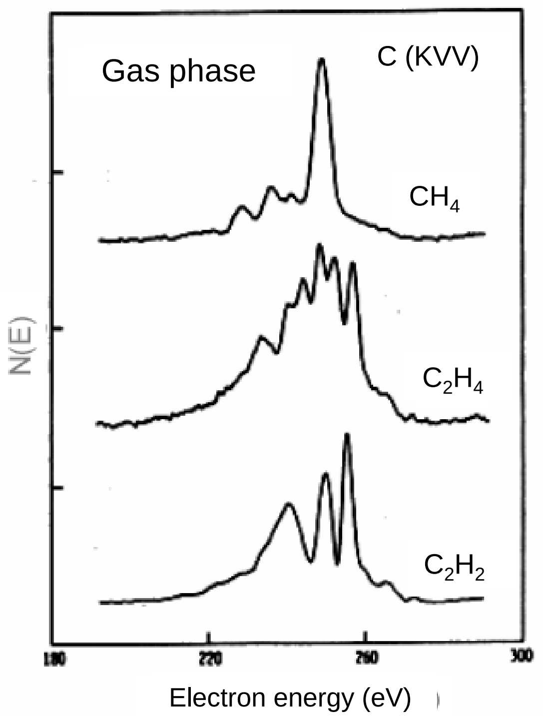


# Auger electron spectrum of a ZnO layer grown by ALD

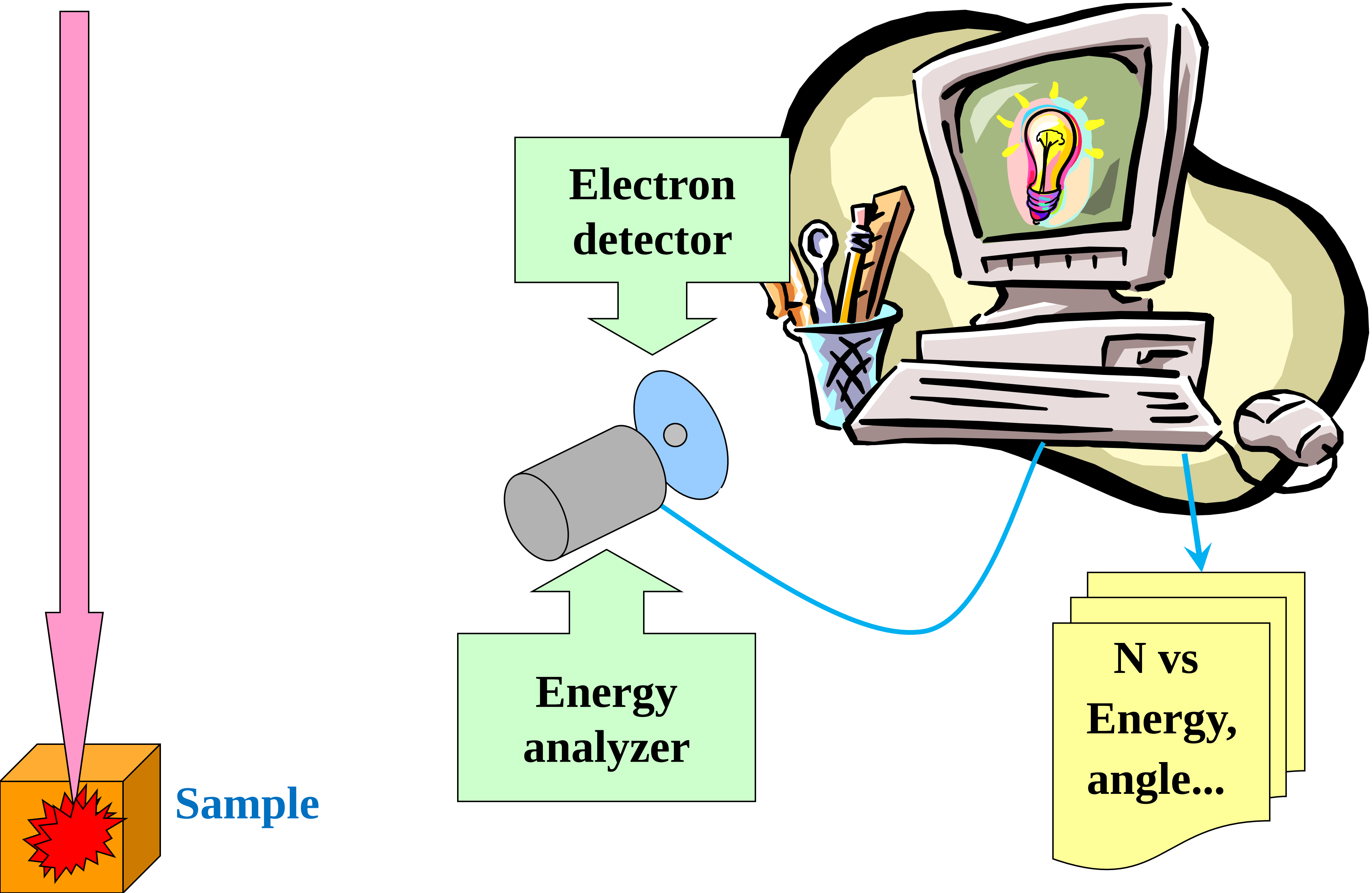


# Auger electron spectroscopy:

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



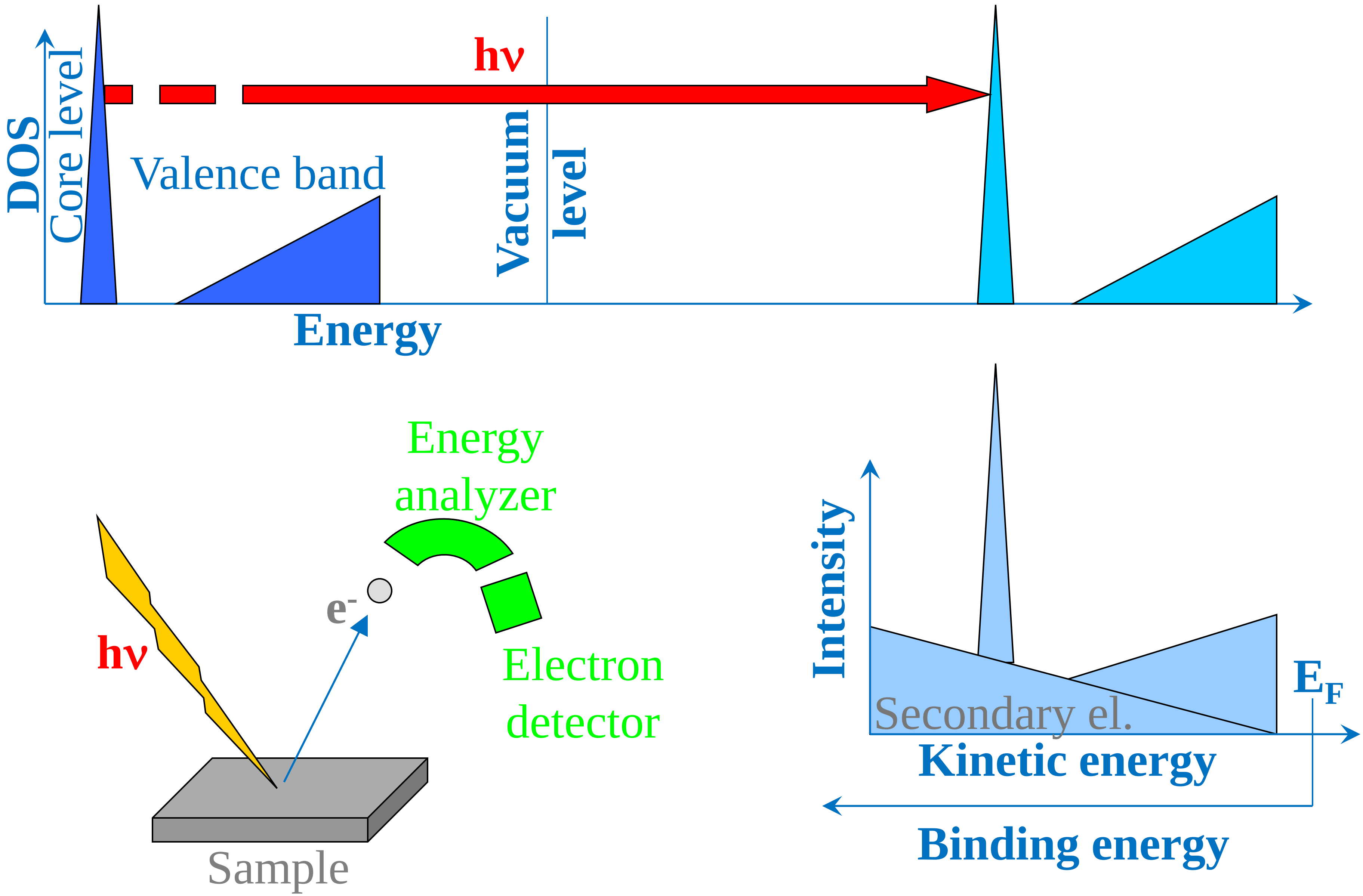
Electron detector

Energy analyzer

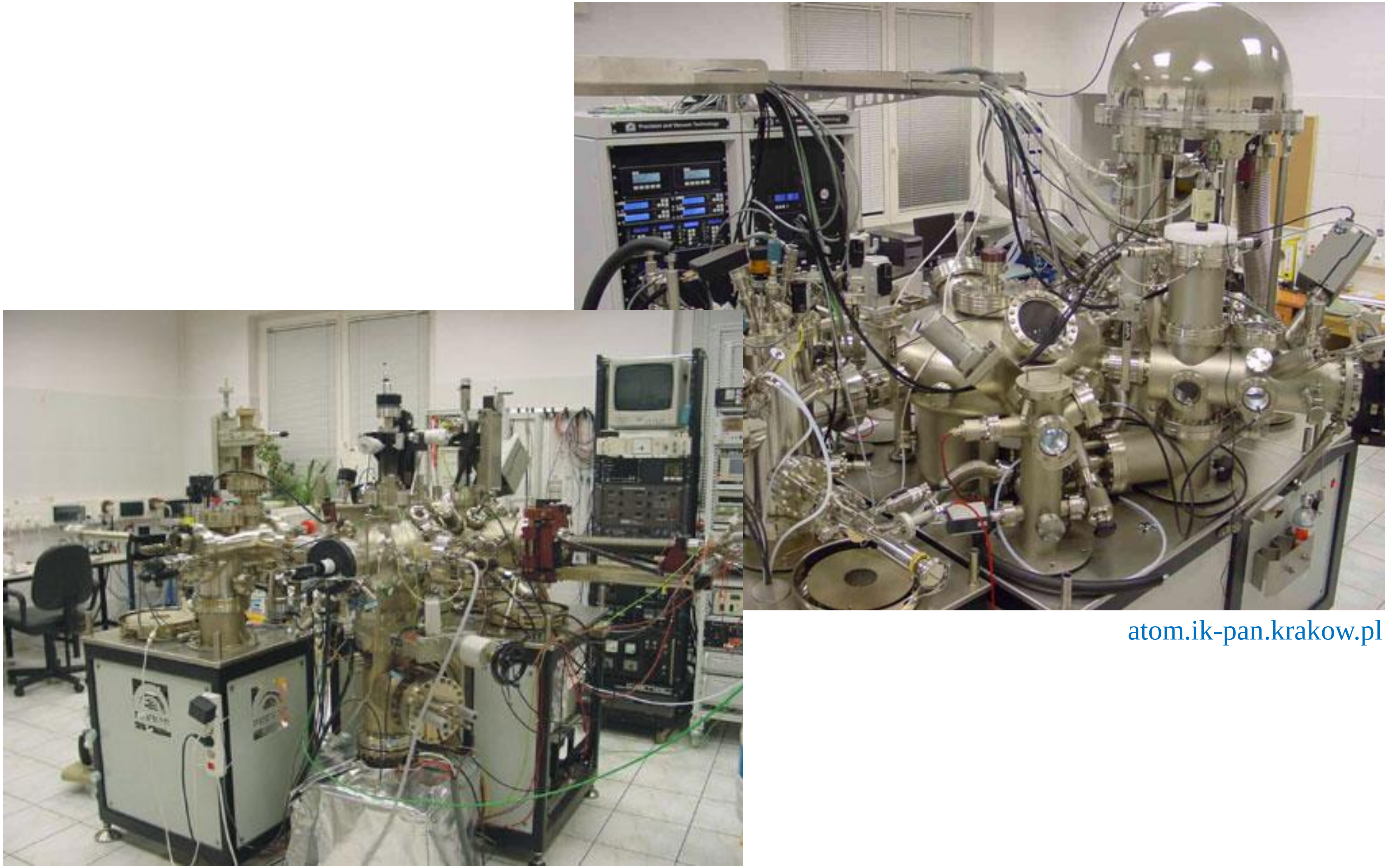
Sample

N vs Energy, angle...

# Spektroskopia fotoemisyjna



# Photoemission needs Ultra High Vacuum (UHV)!



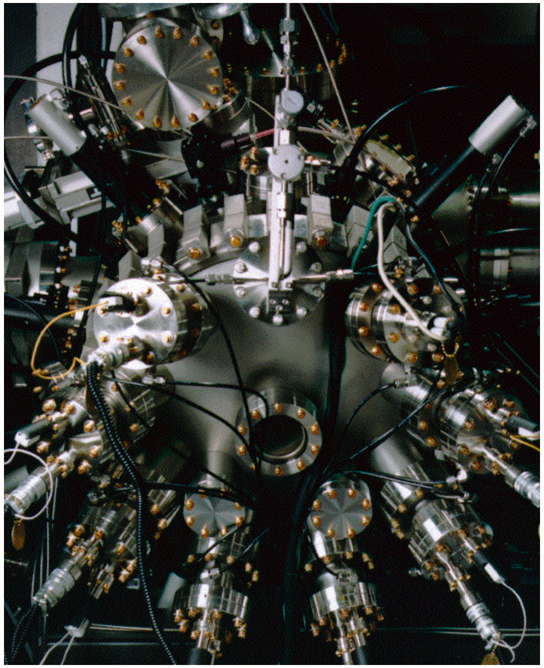
atom.ik-pan.krakow.pl

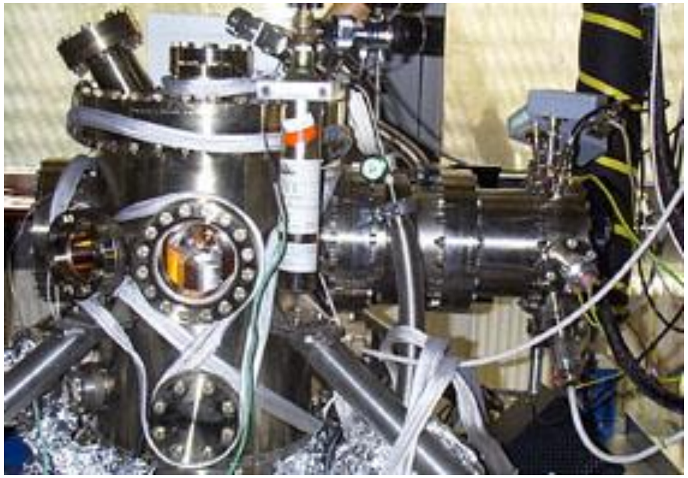
# Surface preparation


www.mshel.com

- **Cleavage**

- ***In situ* epitaxy**


www.ems.psu.edu


www.exphys.uni-linz.ac.at

- ***In situ* cleaning:**

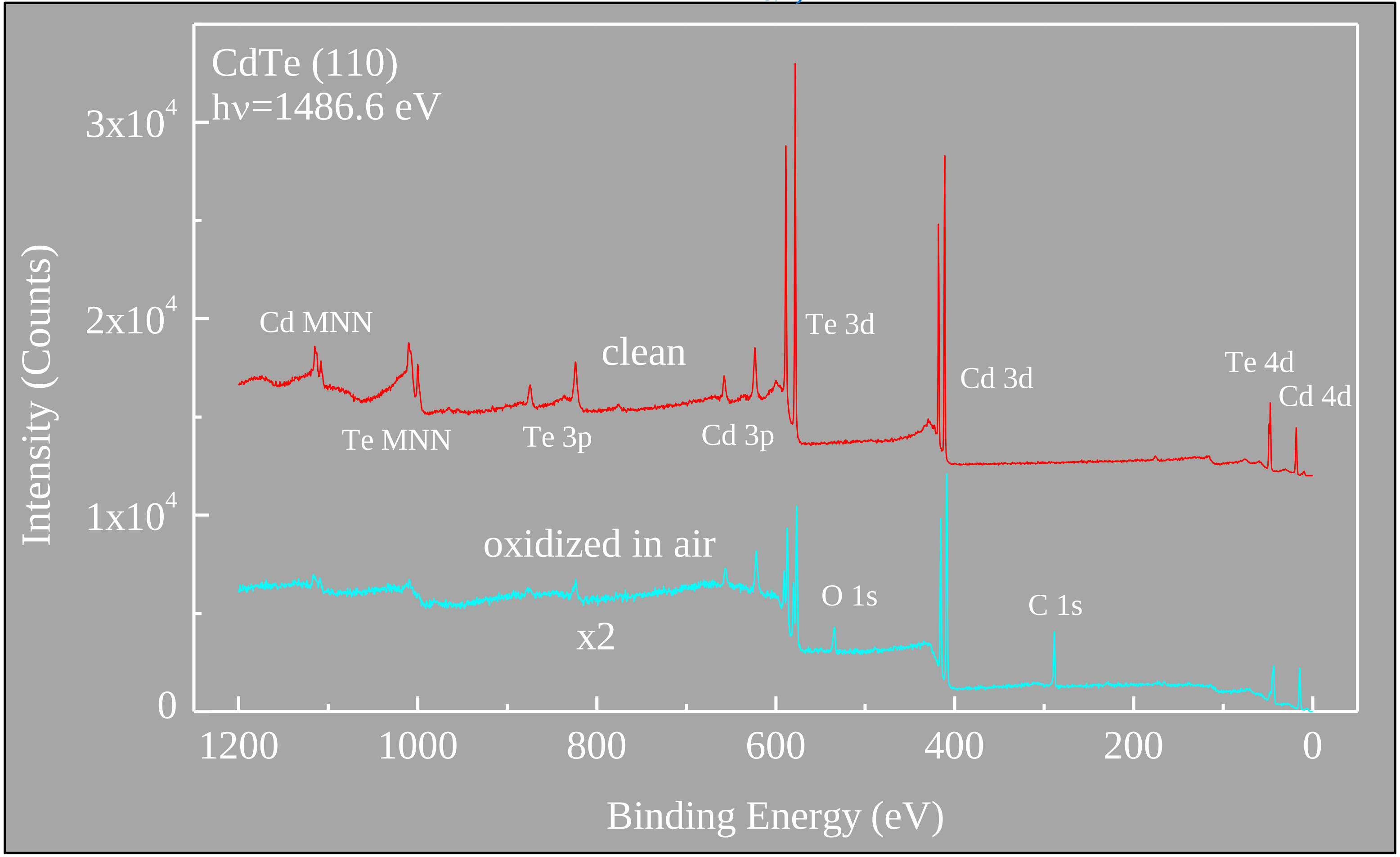
  **- ion etching**

  **- annealing**

# **X**-ray **P**hotoelectron **S**pectroscopy **(XPS)**
## or **E**lectron **S**pectroscopy for **C**hemical **A**nalysis **(ESCA)**

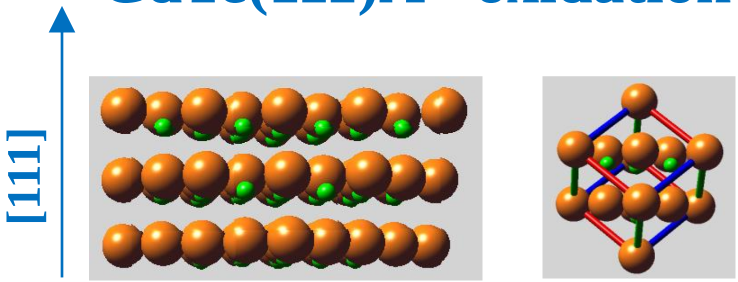
XPS: hν>1000 eV; hν = 1000 eV → **k** = 0.506 Å$^{-1}$

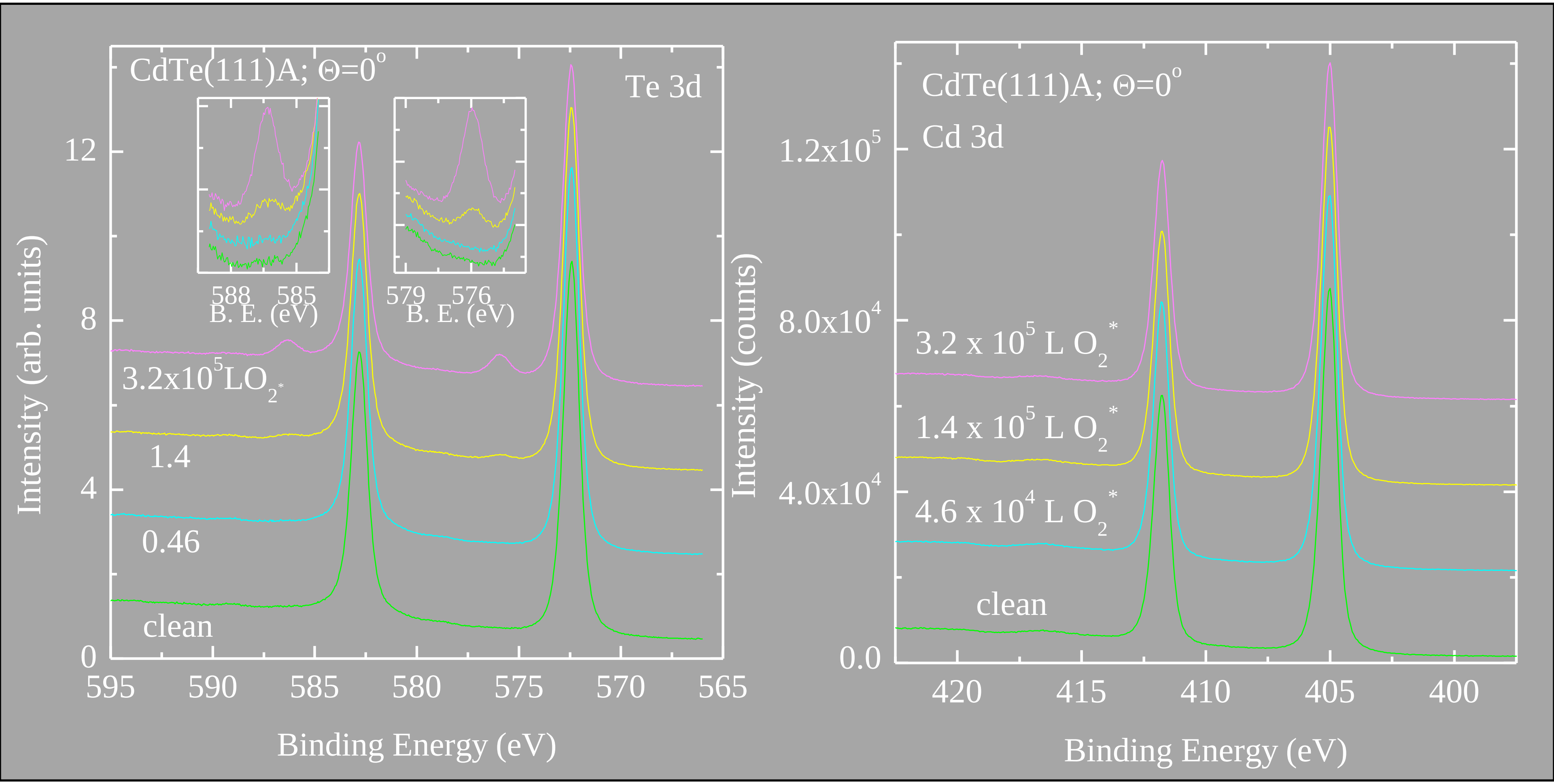
**X-ray source: Al $K_{\alpha 1,2}$ - 1486.6 eV**



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

# CdTe(111)A - oxidation

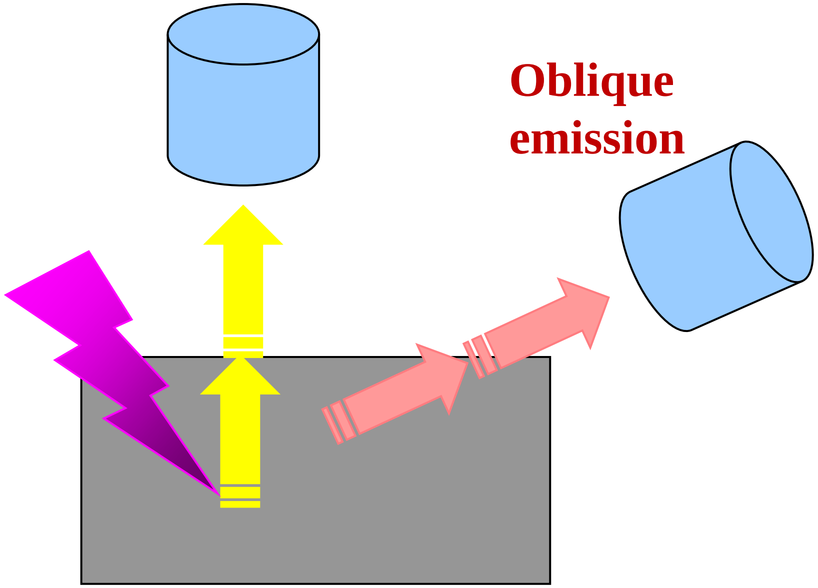




B.J. Kowalski, B.A. Orlowski, J. Ghijsen, Appl. Surf. Sci. **166,** 237 (2000)

# Angular XPS

## - enhanced surface sensitivity



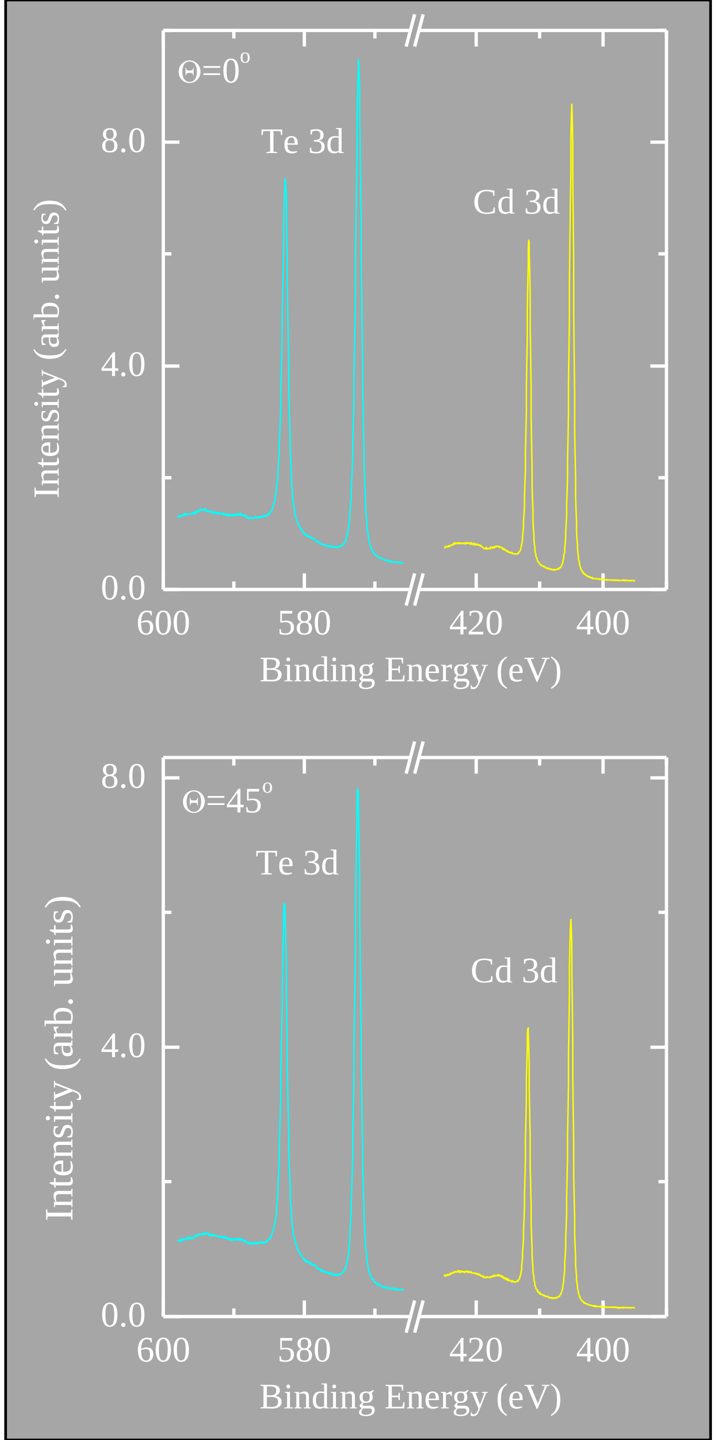
**Normal emission**

**Oblique emission**

**CdTe(111)A**

**Normal emission**

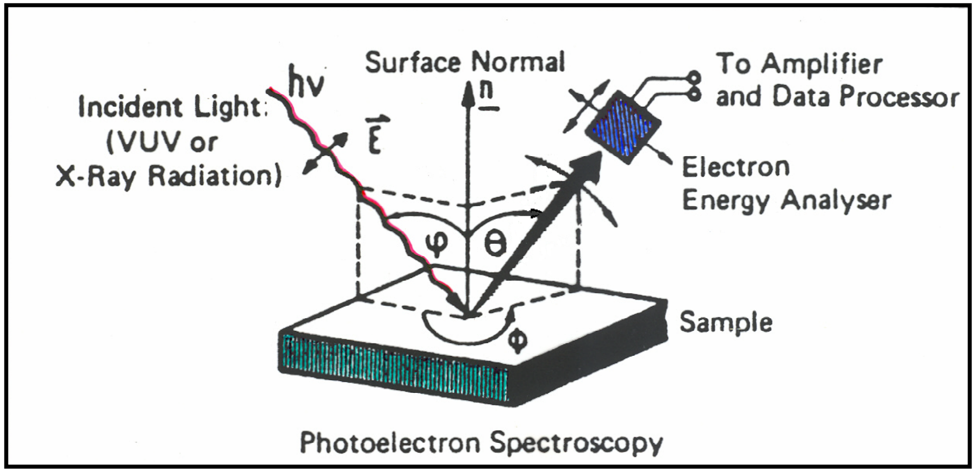
**Oblique emission**



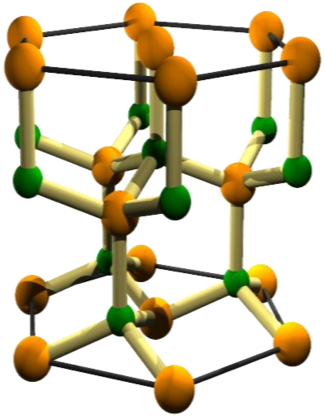
B.J. Kowalski, B.A. Orlowski, J. Ghijsen,

Appl. Surf. Sci. **166,** 237 (2000)

# Angle-resolved photoelectron spectroscopy



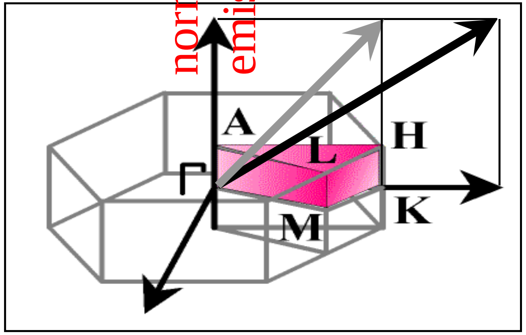
Example:



Wurtzite structure

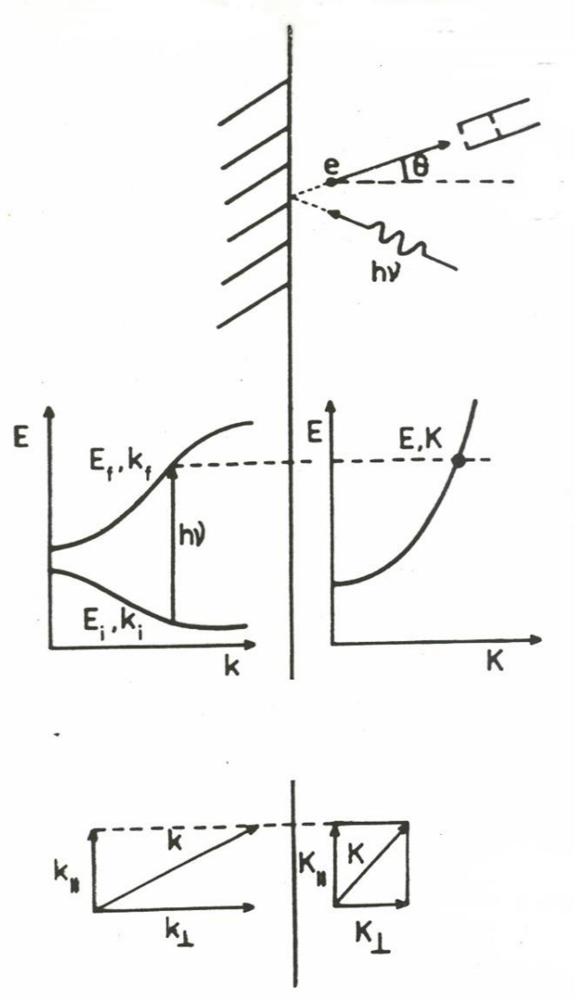
angular
emission

normal
emission



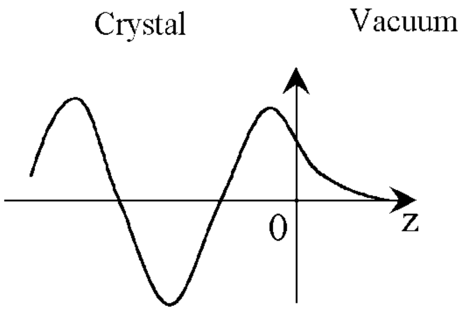
Brillouin zone

**Crystal** **Vacuum**

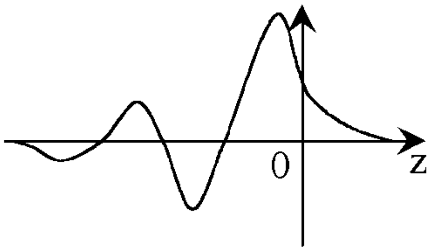


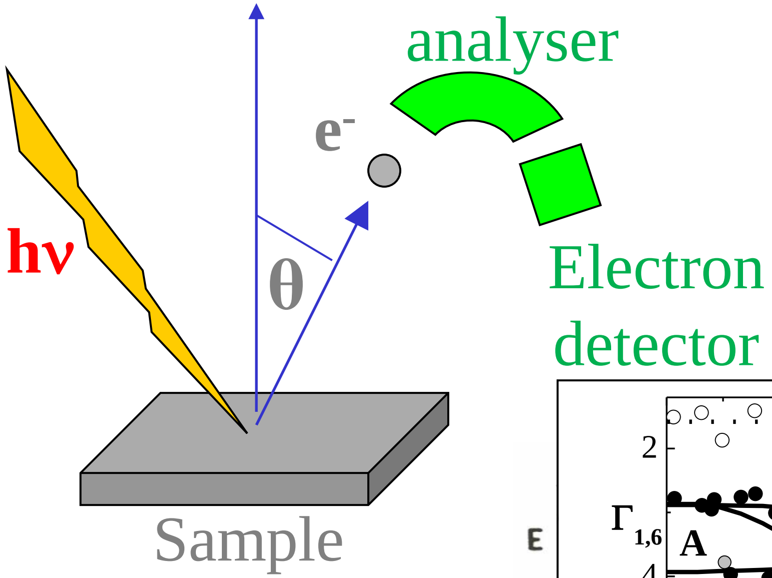
# Angle-resolved photoelectron spectroscopy of surface and bulk states

Bulk states



Surface states





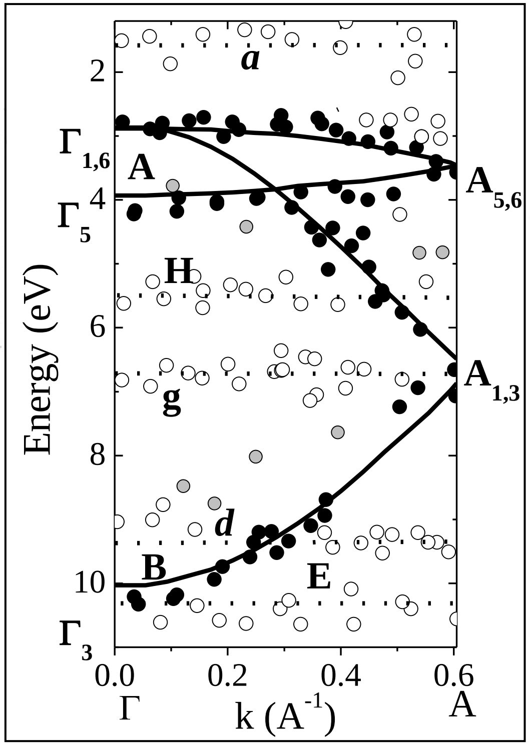
Energy analyser

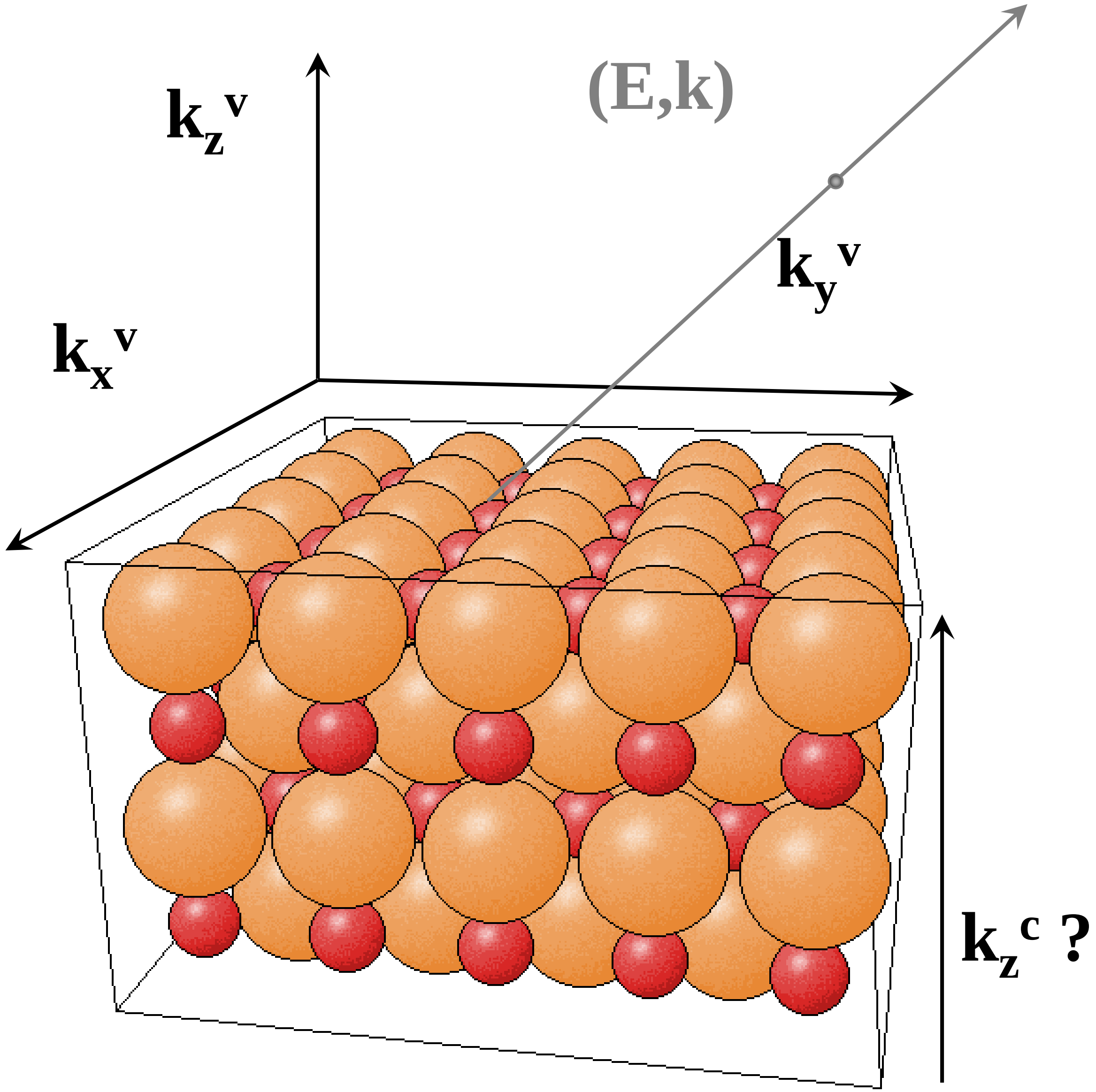
Electron detector

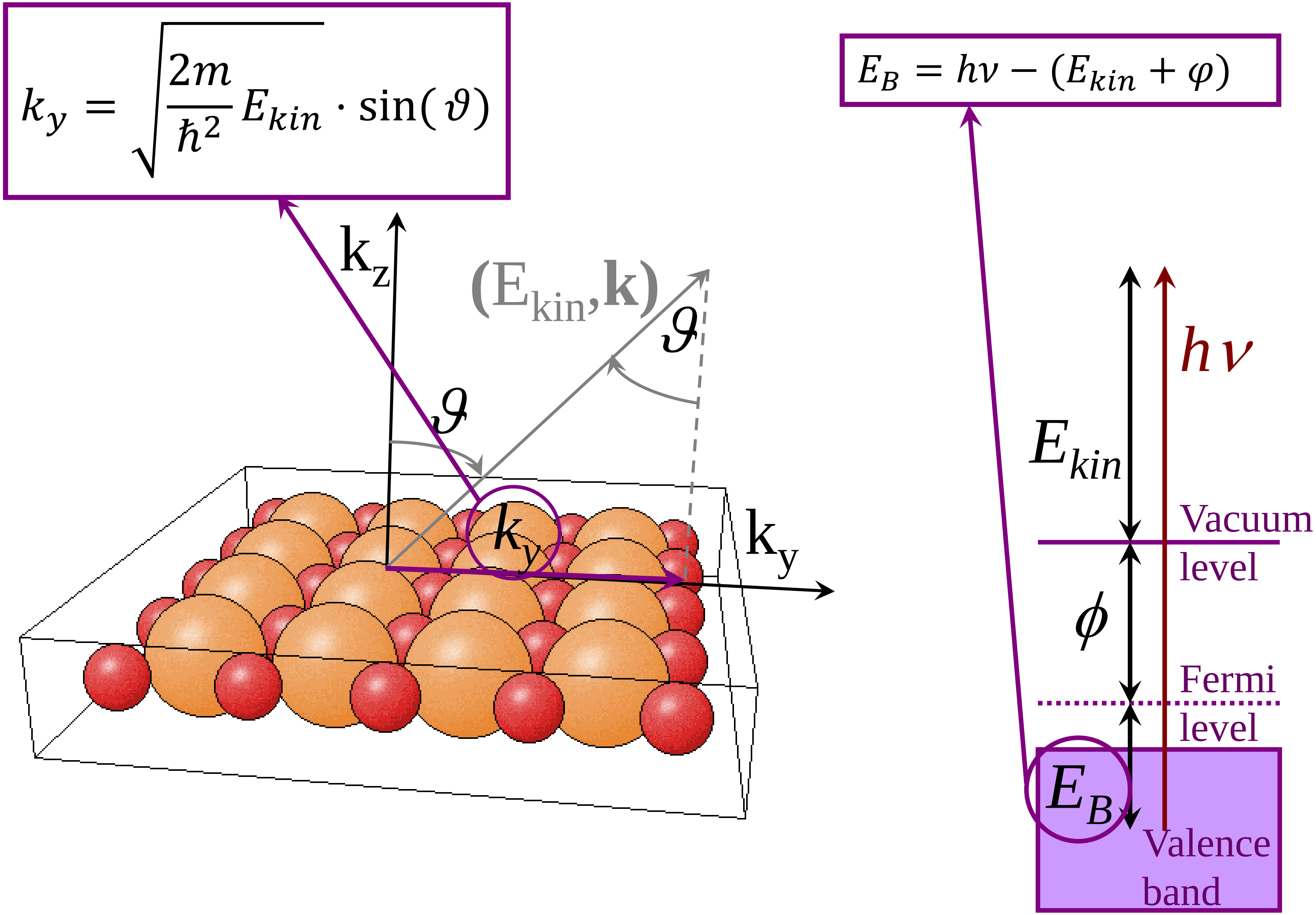
Sample

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

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

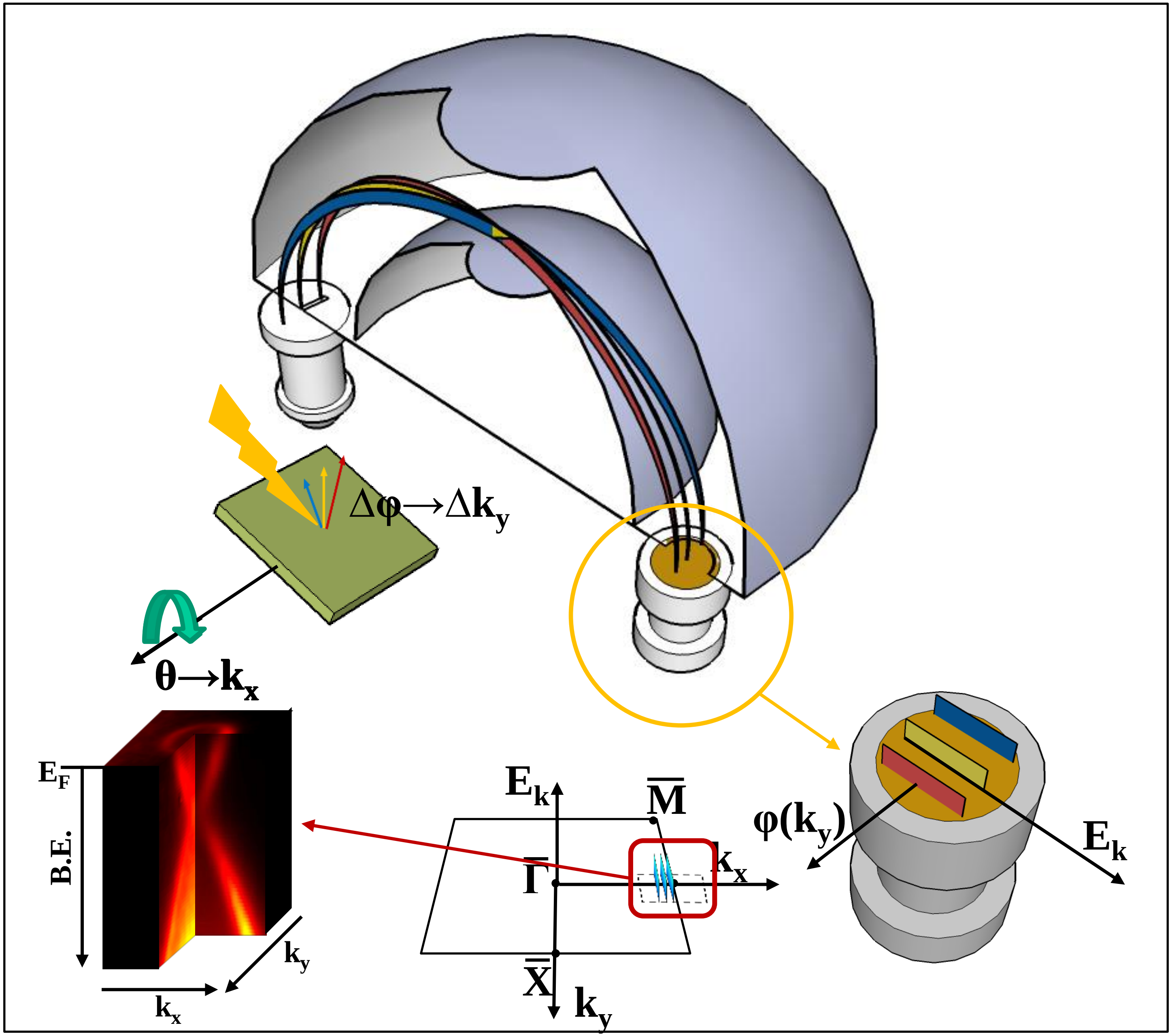



$k_z^v$
(E,k)
$k_y^v$
$k_x^v$
$k_z^c$ ?

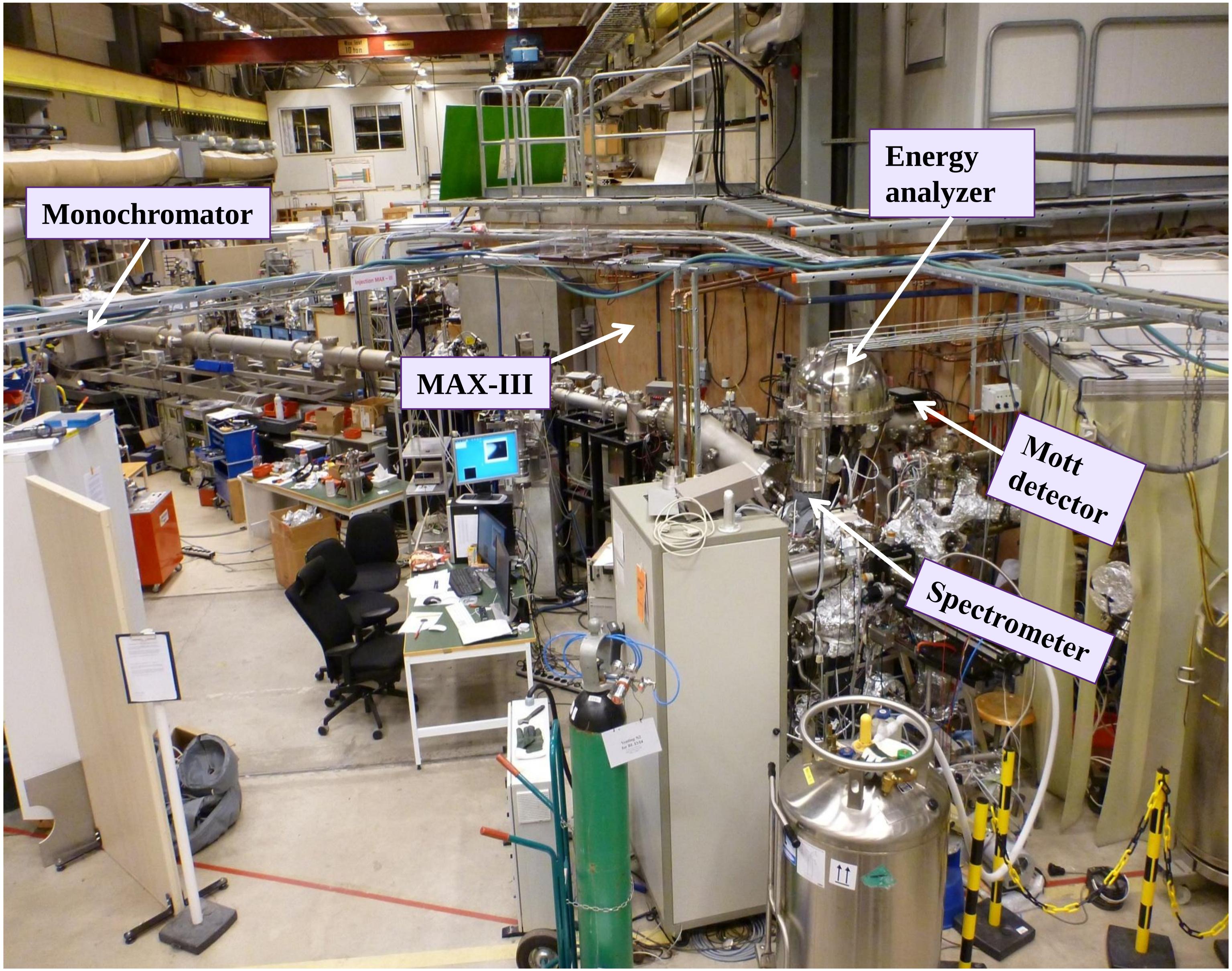


$$k_y = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \cdot \sin(\vartheta)$$

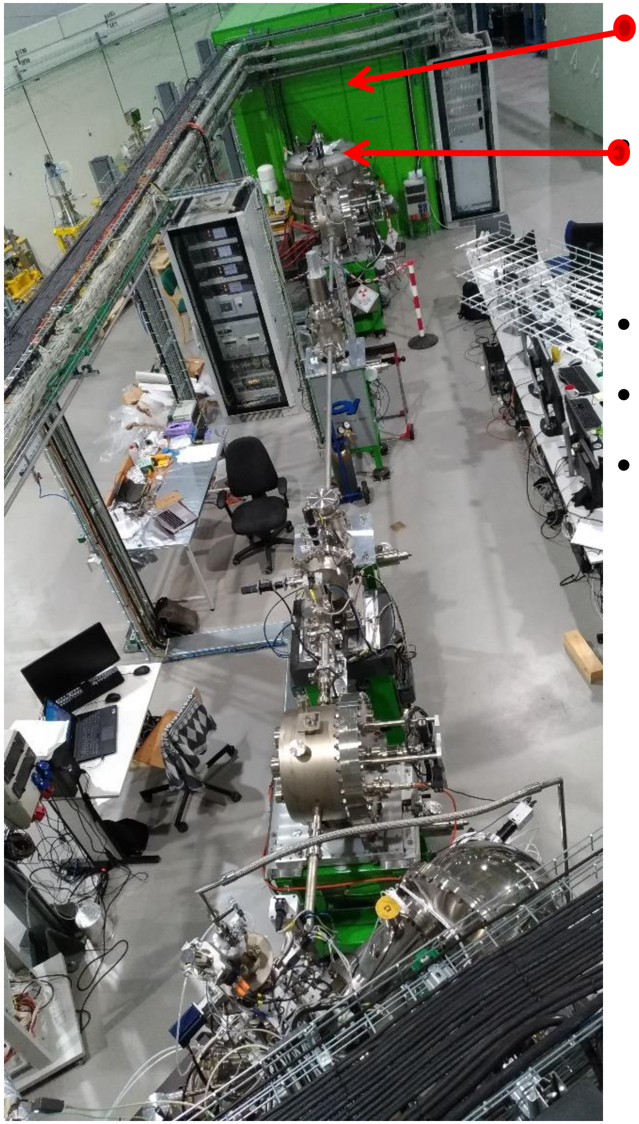
$$E_B = h\nu - (E_{kin} + \varphi)$$


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$_k$

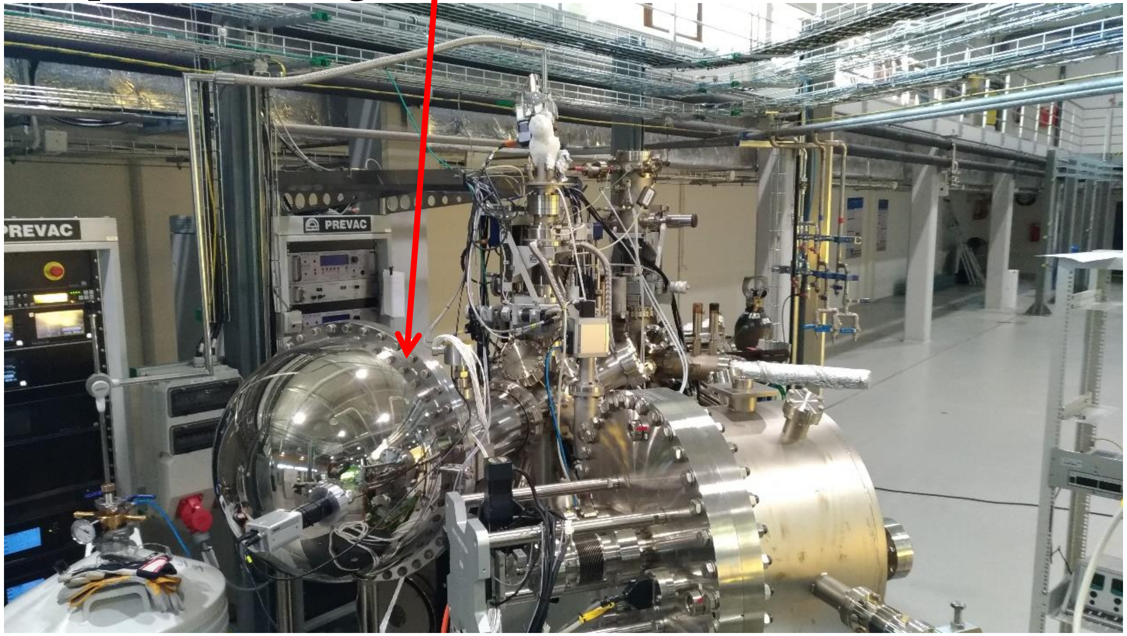
# Beamline I3
# MAX-lab, Lund University, Sweden



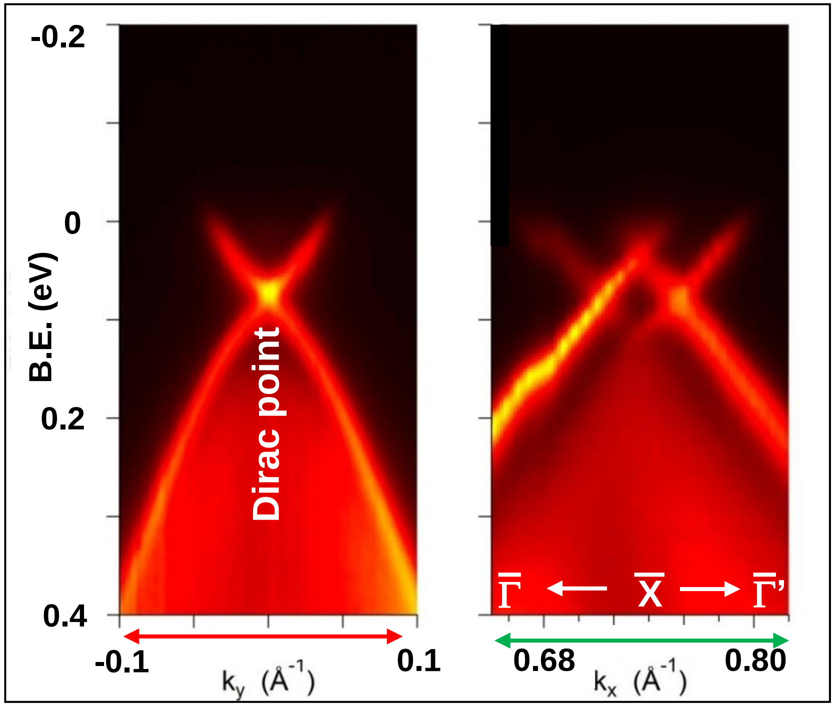
# Beamline URANOS
# NCSR SOLARIS, Jagiellonian University, Kraków, Poland

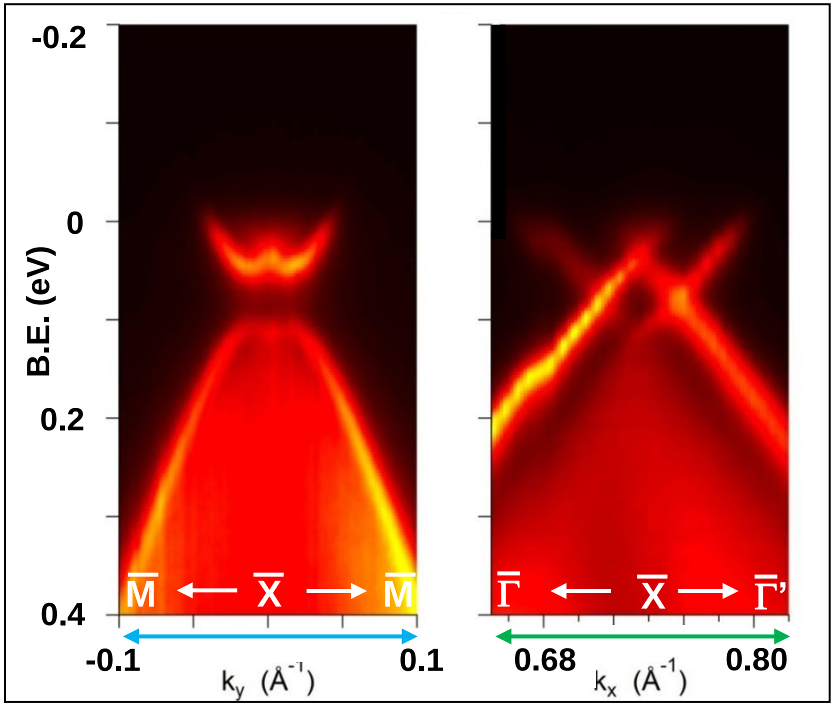


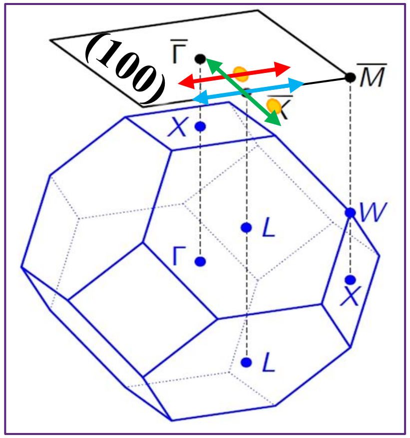
- Elliptically polarizing quasiperiodic undulator of APPLE II type
- Monochromator combining normal (NIM) and grazing incidence (PGM) optics (the photon energy range of 8–100 eV)
- SCIENTA OMICRON DA30L photoelectron spectrometer
- The energy and angular resolution: 1.8 meV and 0.1°
- Temperature range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



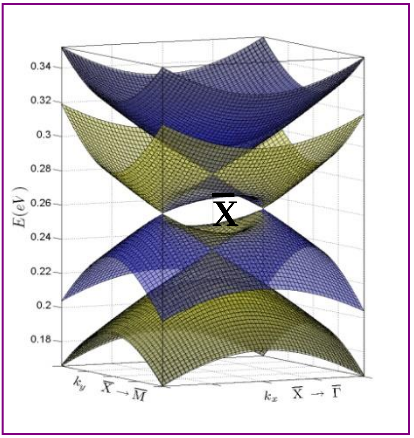
# Topological crystalline insulator $Pb_{0.67}Sn_{0.33}Se$, T=87 K, hν=18.5 eV





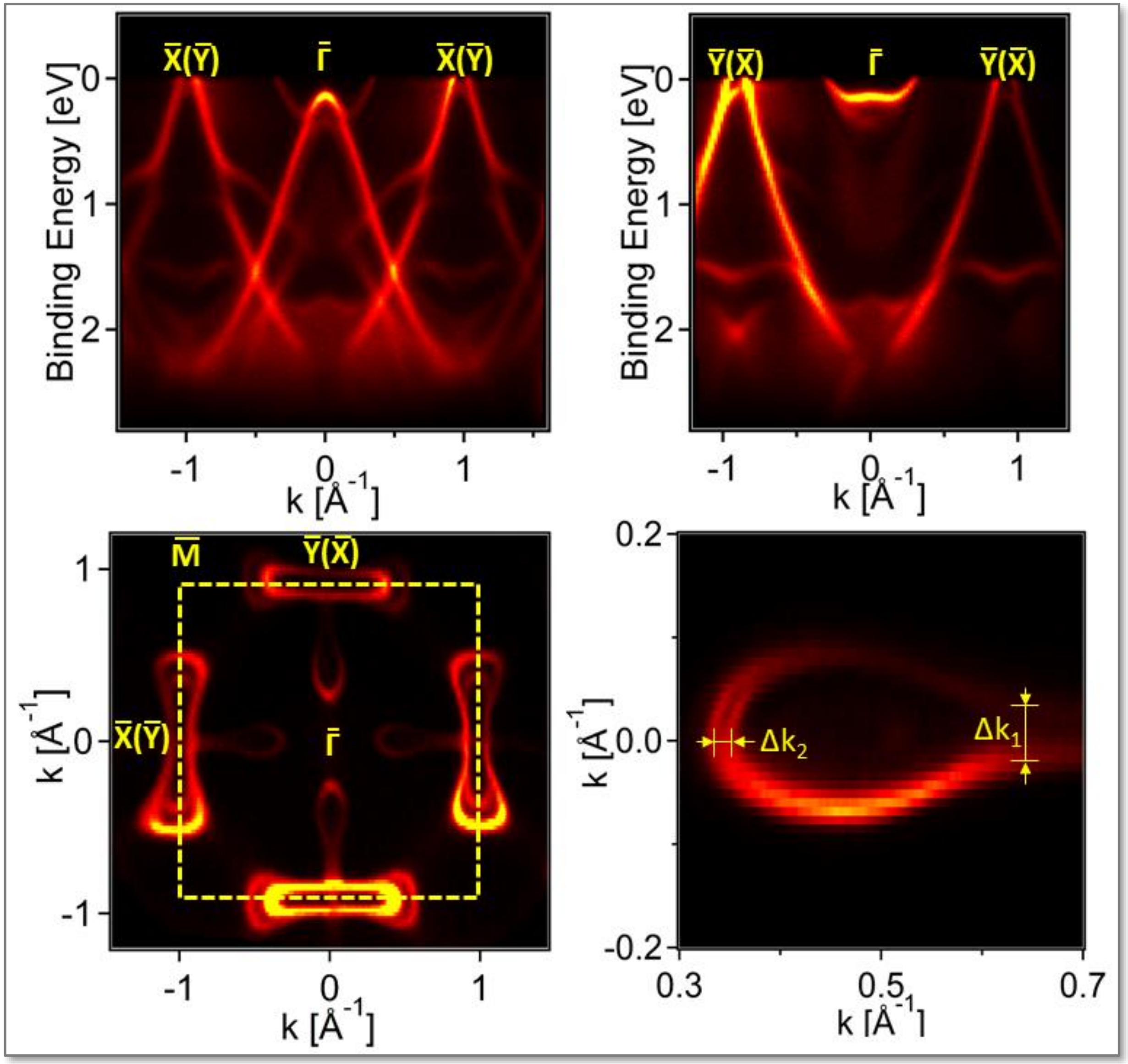


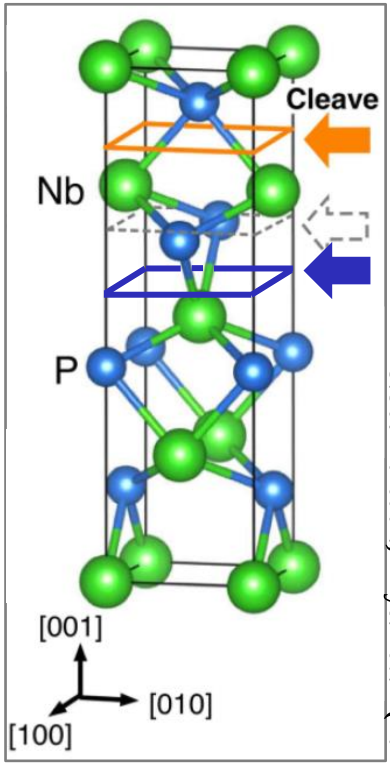
Theory-
R. Buczko, P. Kacman, S. Safaei



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



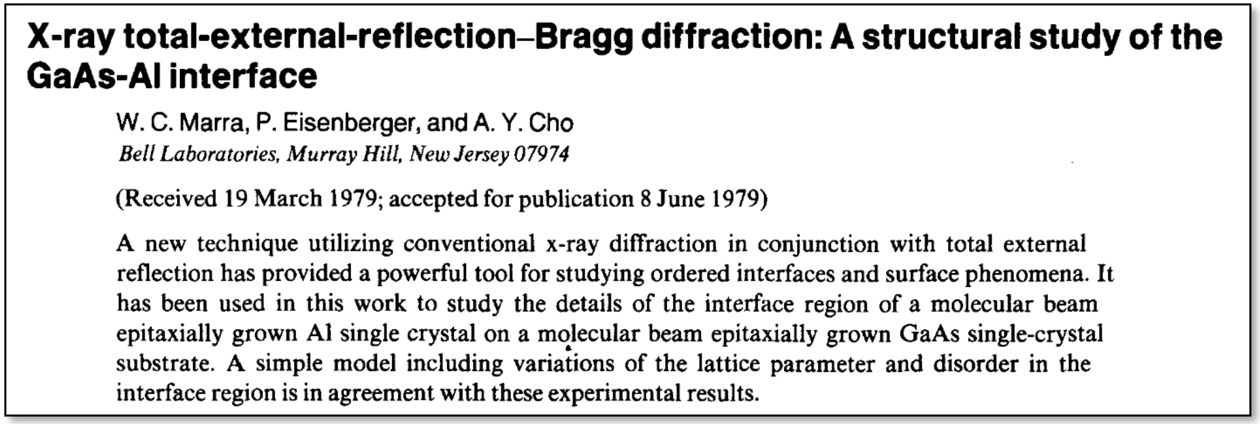


S.Souma et al., Phys.Rev.B (2016)

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

# Diffraction methods

# Surface X-ray diffraction



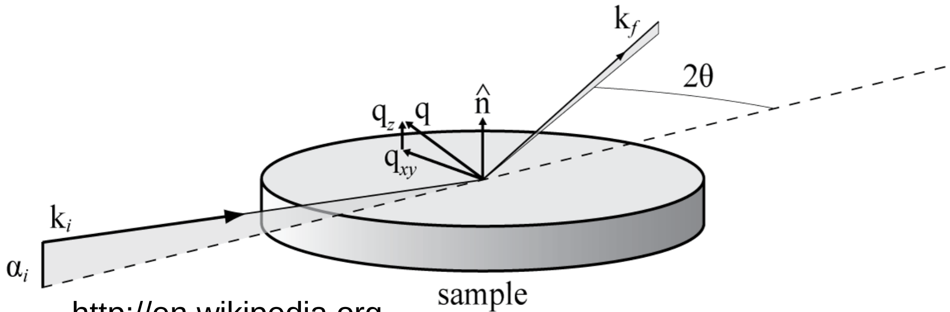
**X-ray total-external-reflection–Bragg diffraction: A structural study of the GaAs-Al interface**

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

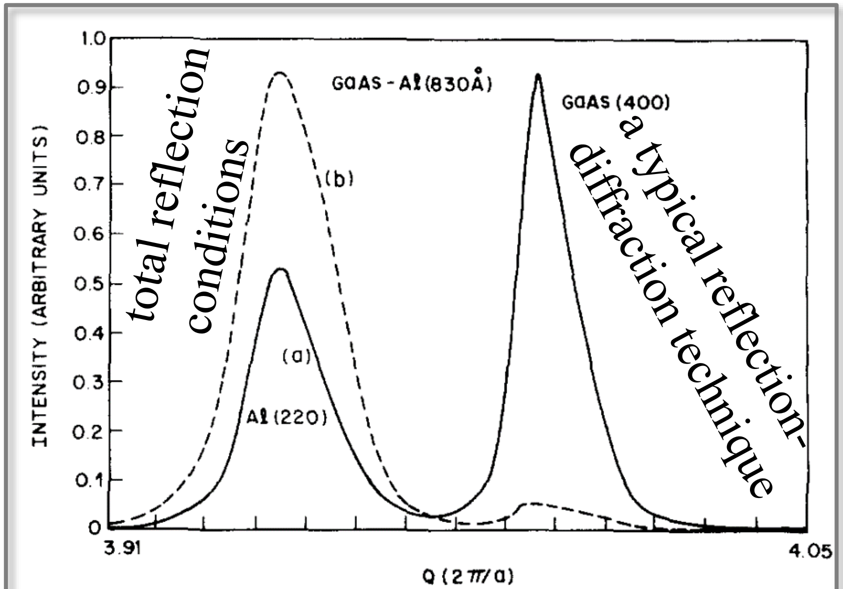
(Received 19 March 1979; accepted for publication 8 June 1979)

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



*total reflection conditions*

*a typical reflection-diffraction technique*

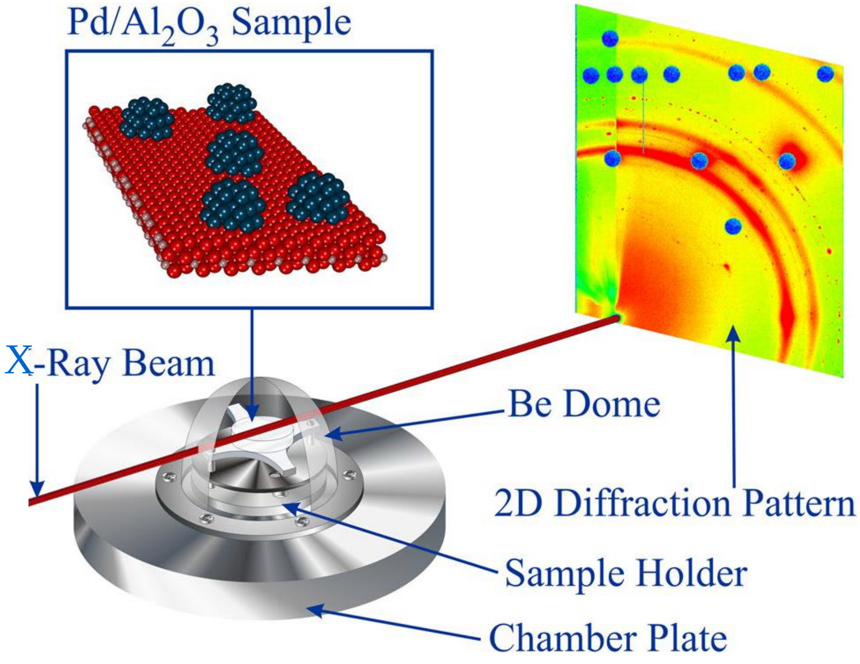
**Al(415 ML) on GaAs**

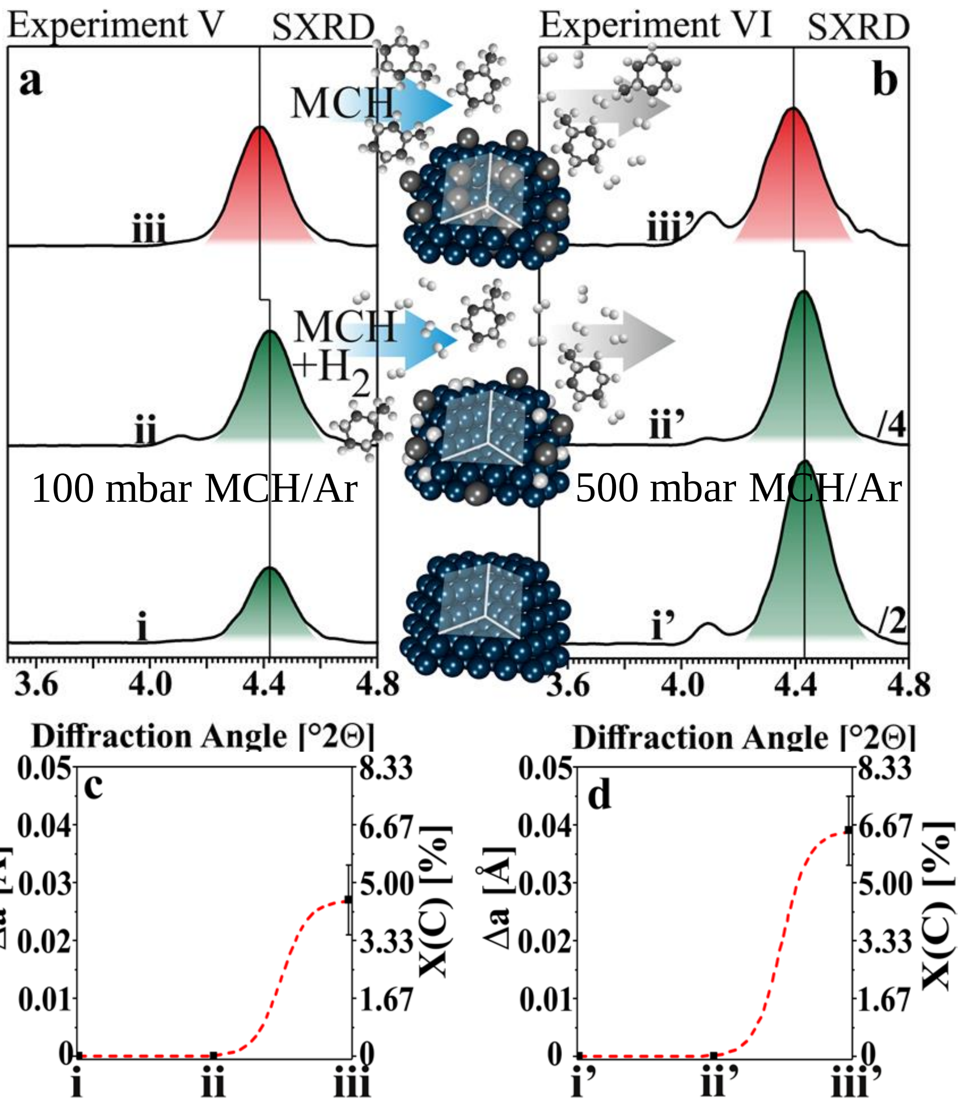
**Needs strong X-ray beam – usually from a synchrotron!**

# 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**

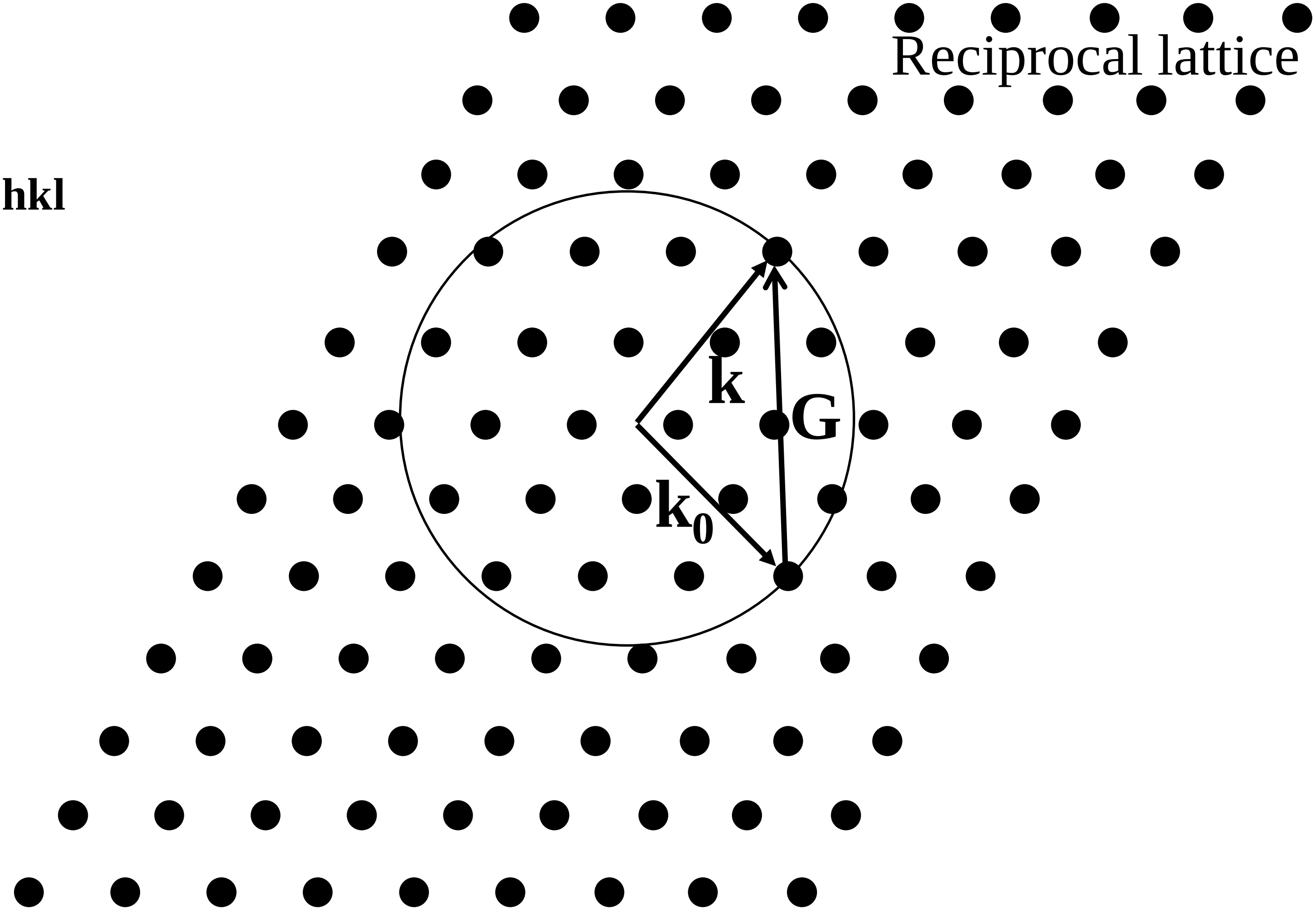




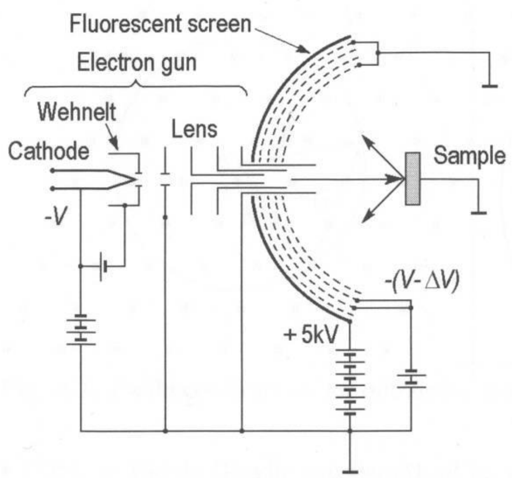
# Construction of the Ewald sphere

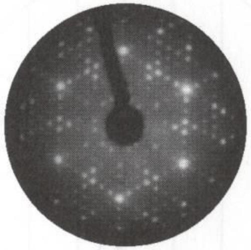
$\mathbf{k}-\mathbf{k}_0=\mathbf{G}_{hkl}$

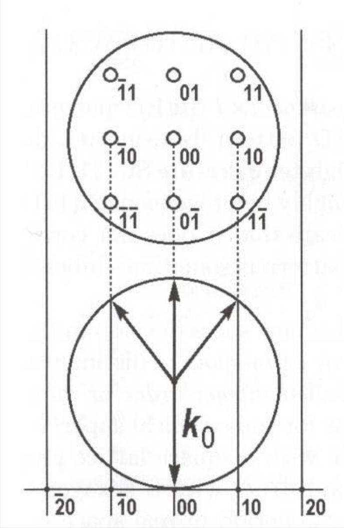
$|\mathbf{k}|=|\mathbf{k}_0|$

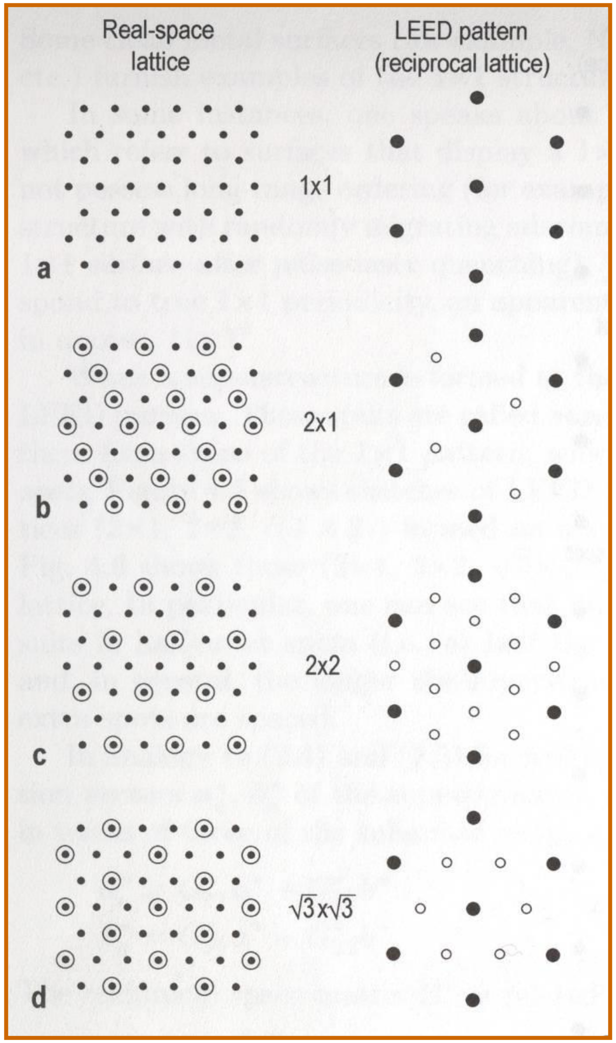


# Low-Energy Electron Diffraction (LEED)



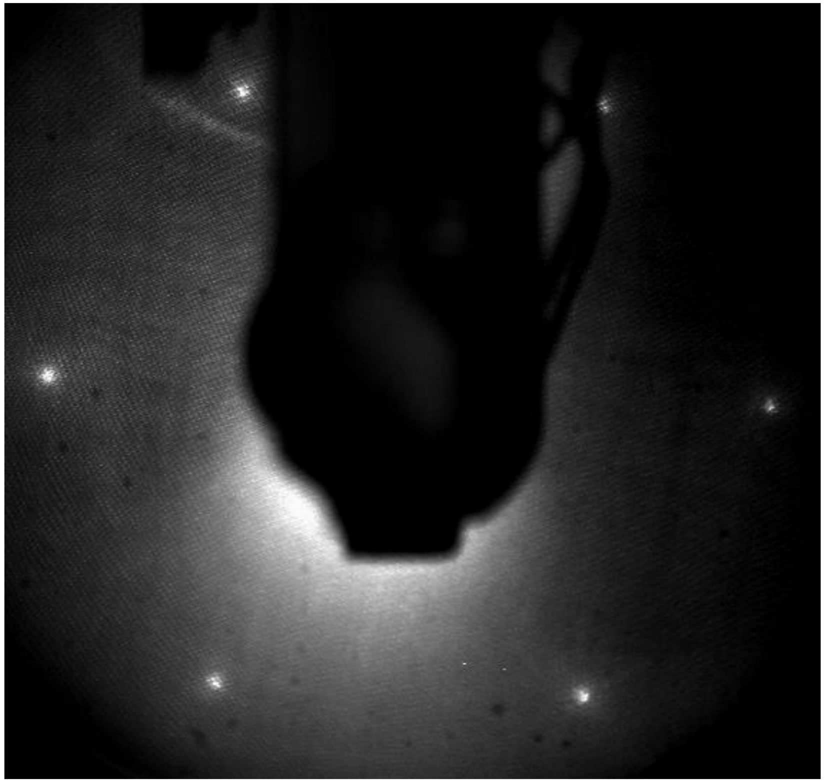




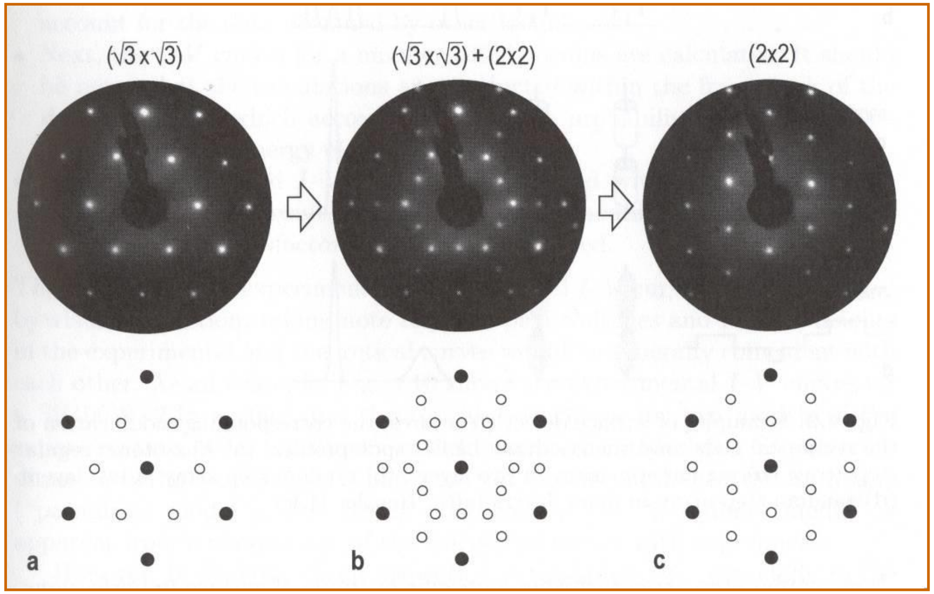


K.Oura et al.
*Surface Science. An Introduction*

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

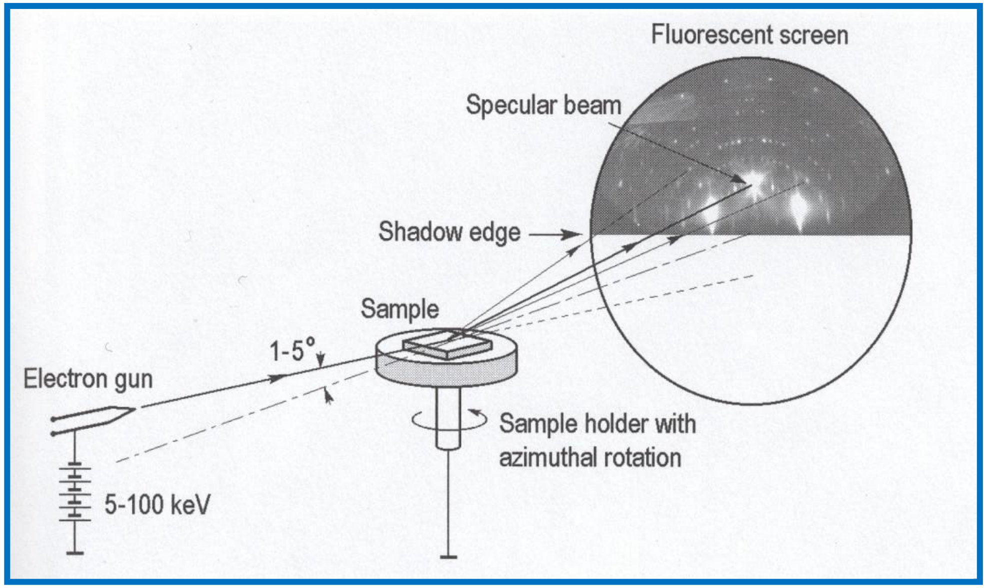


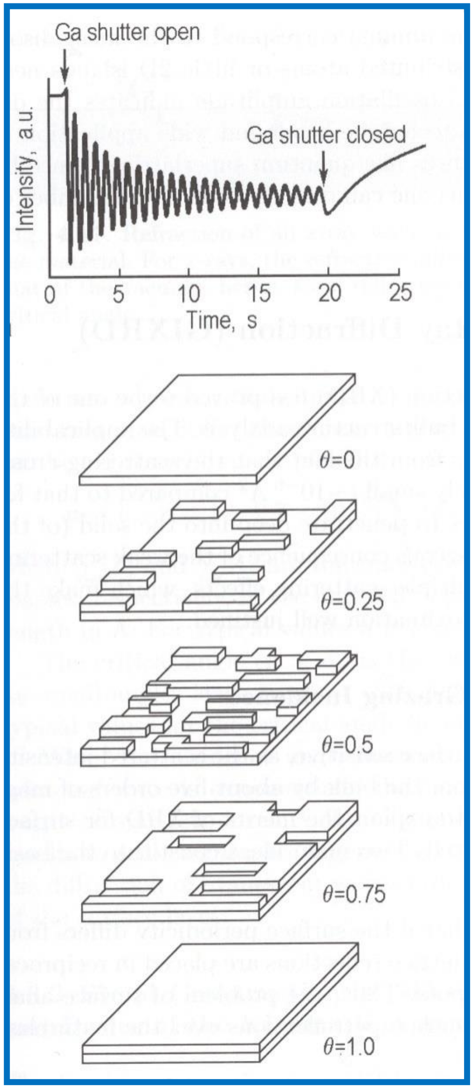
**GaN(000$\underline{1}$) (1x1)**



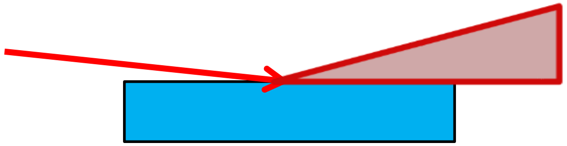
**In deposition on Si(111)√3x √ 3-R30$^0$**

# Reflection High-Energy Electron Diffraction (RHEED)

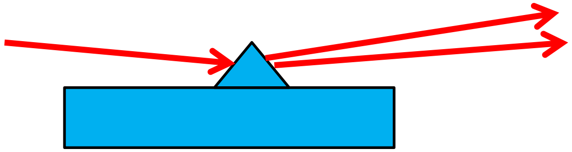




**K.Oura et al.**
***Surface Science. An Introduction***



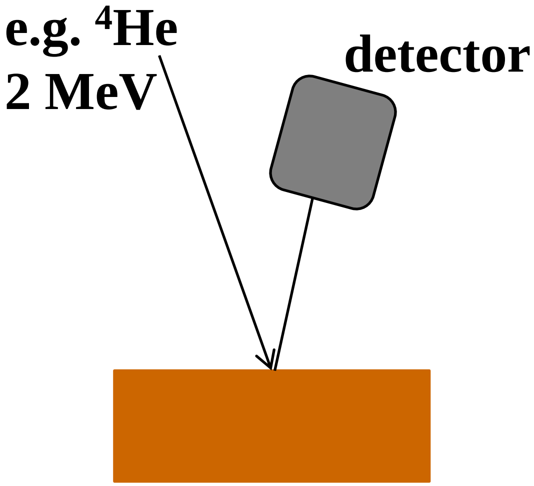
**2D structure**
**Streaks in the image**



**3D structure**
**Dots in the image**

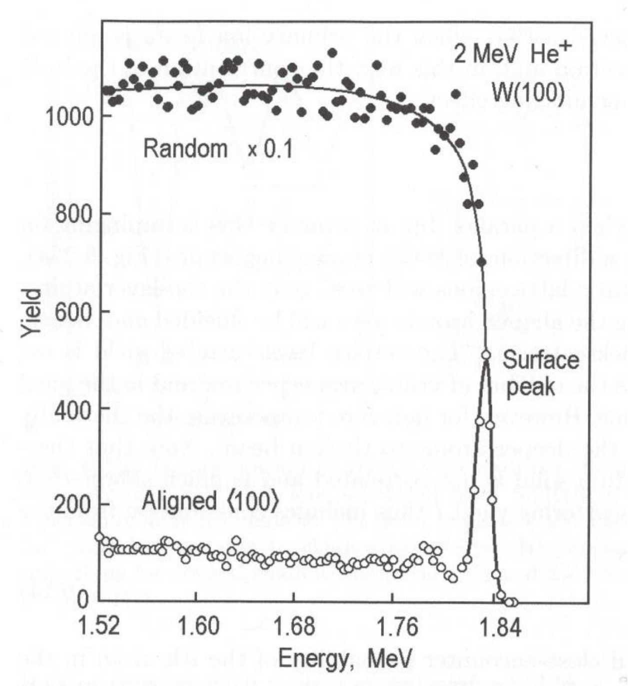
# Ion scattering methods

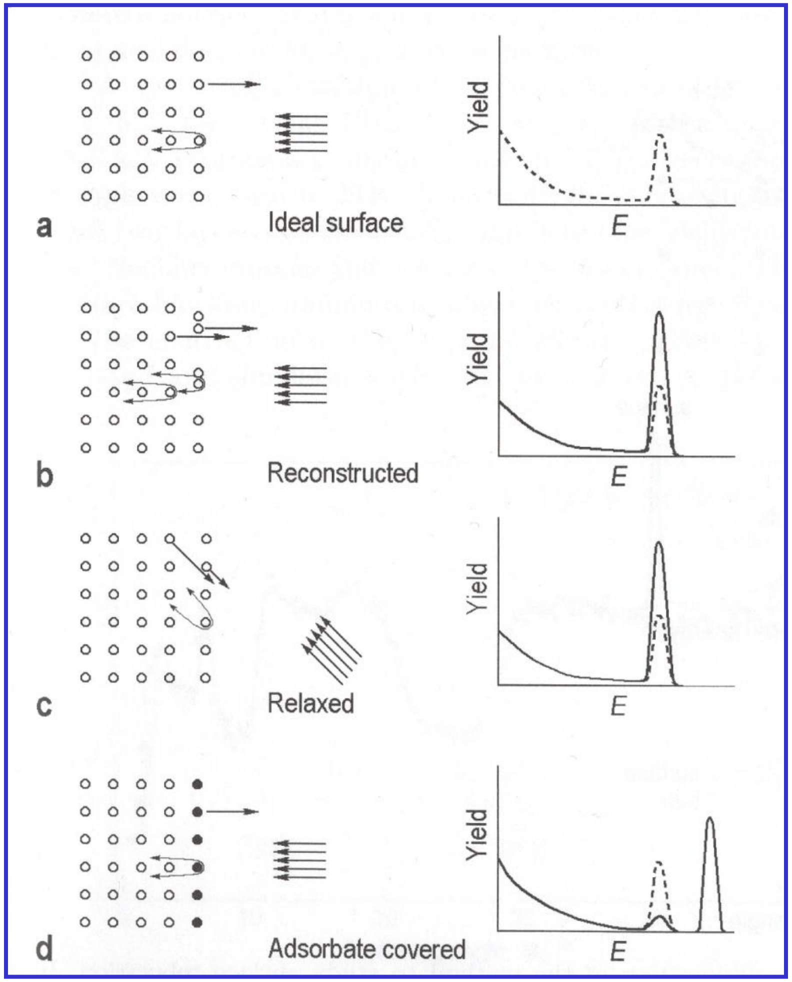
# Rutherford Backscattering Spectrometry (RBS)



**e.g. $^4$He 2 MeV**

**detector**

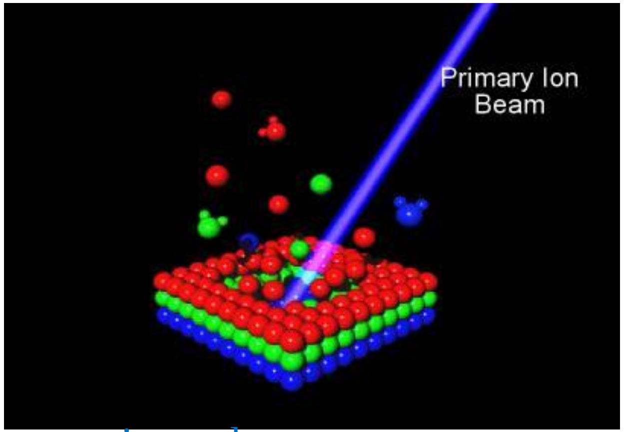




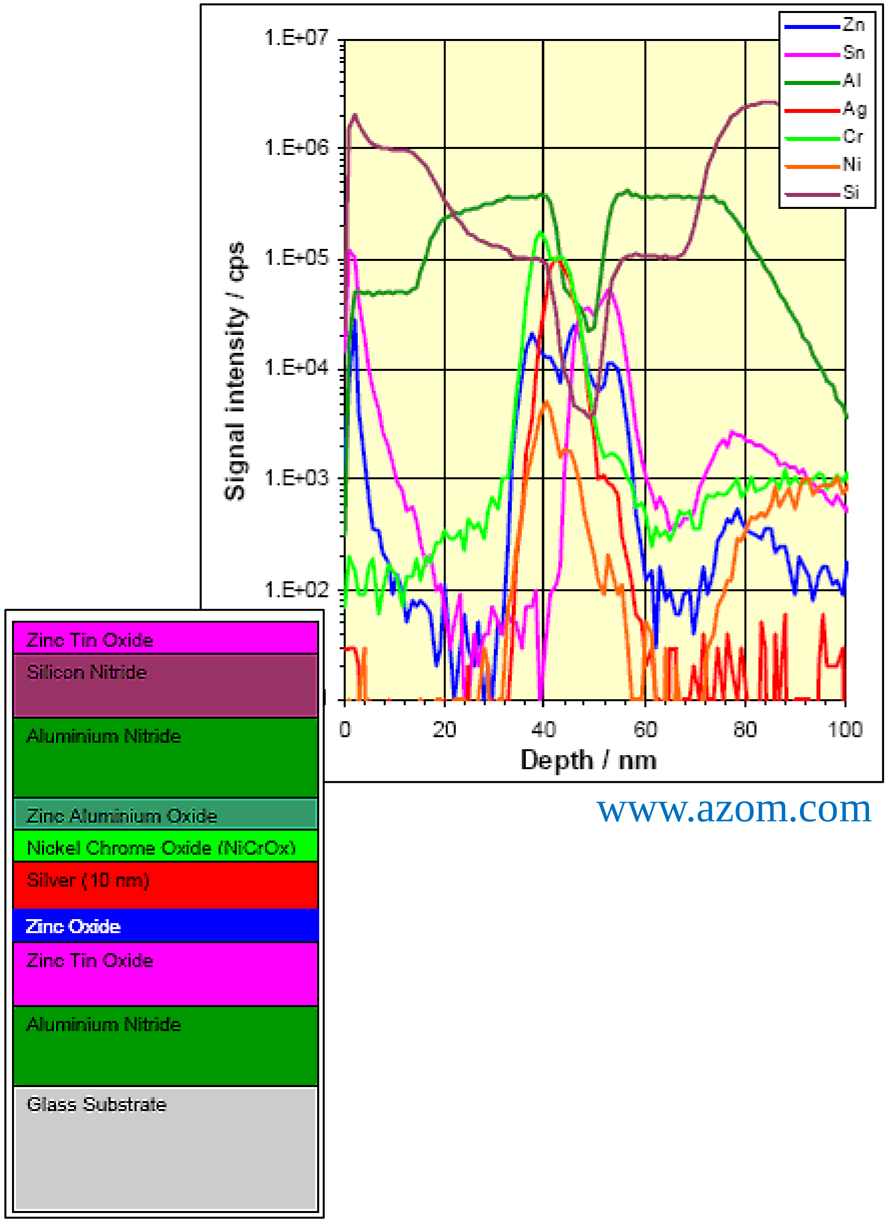
**K.Oura et al.**
***Surface Science. An Introduction***

# Secondary Ion Mass Spectrometry (SIMS)

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



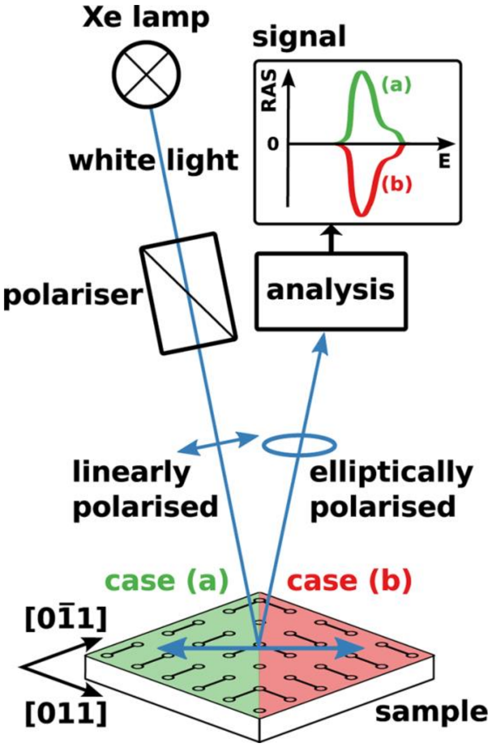
www.ainse.edu.au



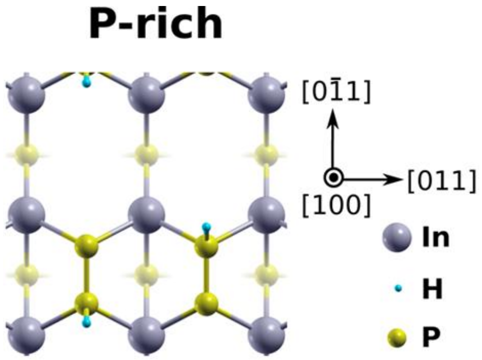
www.azom.com

# Optical methods

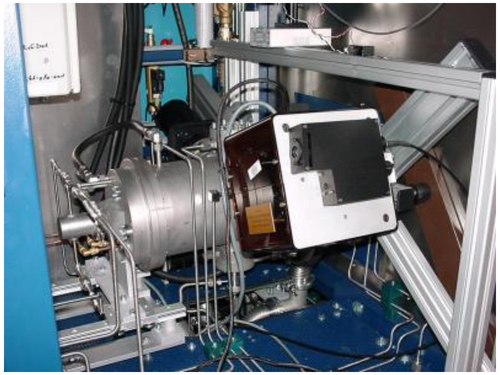
# Reflection Anisotropy Spectroscopy (RAS)



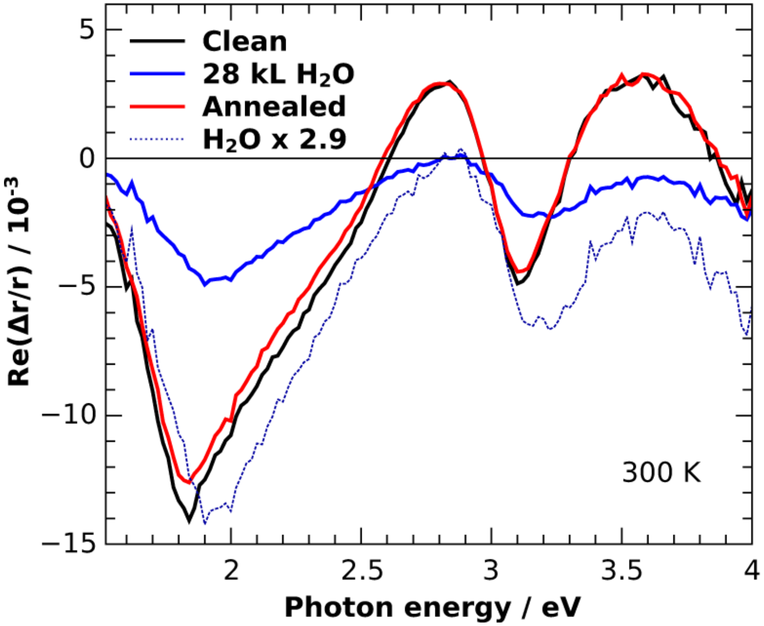
$$\frac{\Delta r}{r} = 2\,\frac{r_{[0\bar{1}1]} - r_{[011]}}{r_{[0\bar{1}1]} + r_{[011]}}$$



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...**

# Literature:

**T. Fauster, L. Hammer, K. Heinz, A. Schneider**
***Surface Physics. Fundamentals and methods***
**De Gruyter 2020**

**K. Oura, V.G. Lifshits, A.A. Saranin, A.V. Zotov, M. Katayama**
***Surface Science. An Introduction***
**Springer 2003**

**D.P. Woodruff, T.A. Delchar**
***Modern Techniques of Surface Science***
**Cambridge University Press 1988**

**H. Lüth**
***Surfaces and Interfaces of Solid Materials***
**Springer 1995**