

Surface studies of crystals

Bogdan J. Kowalski

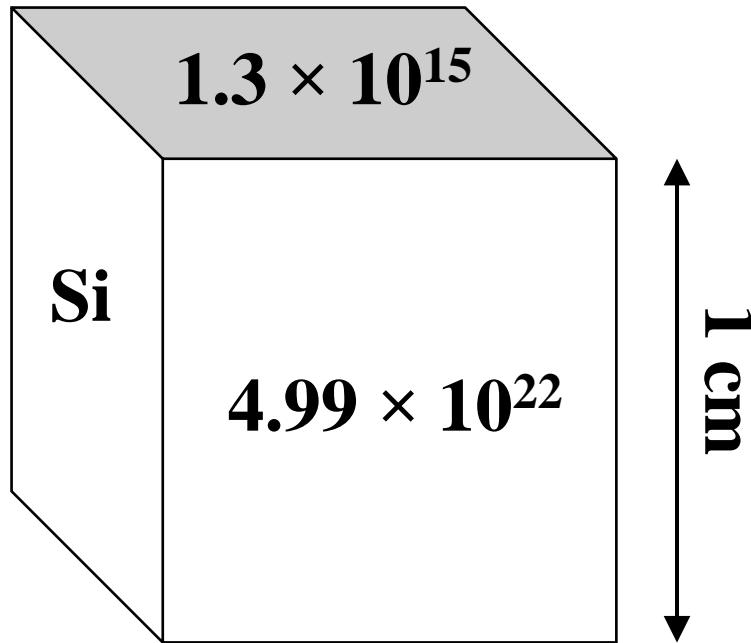
IF PAN

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

Wolfgang Pauli

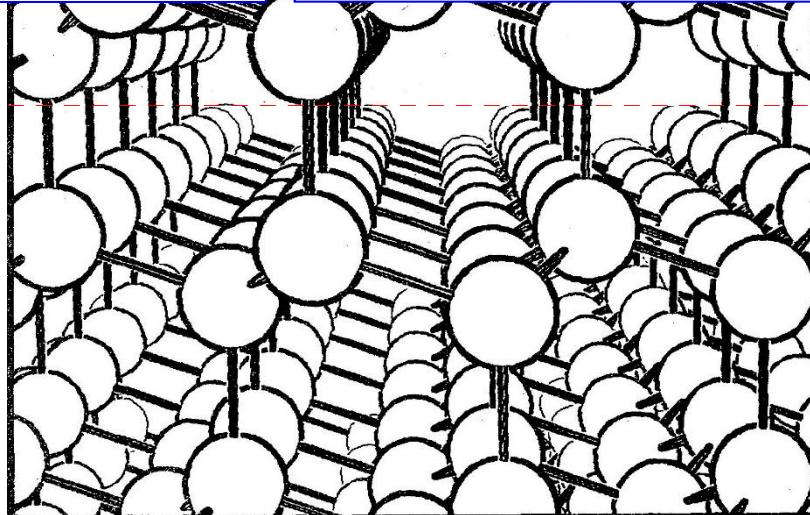
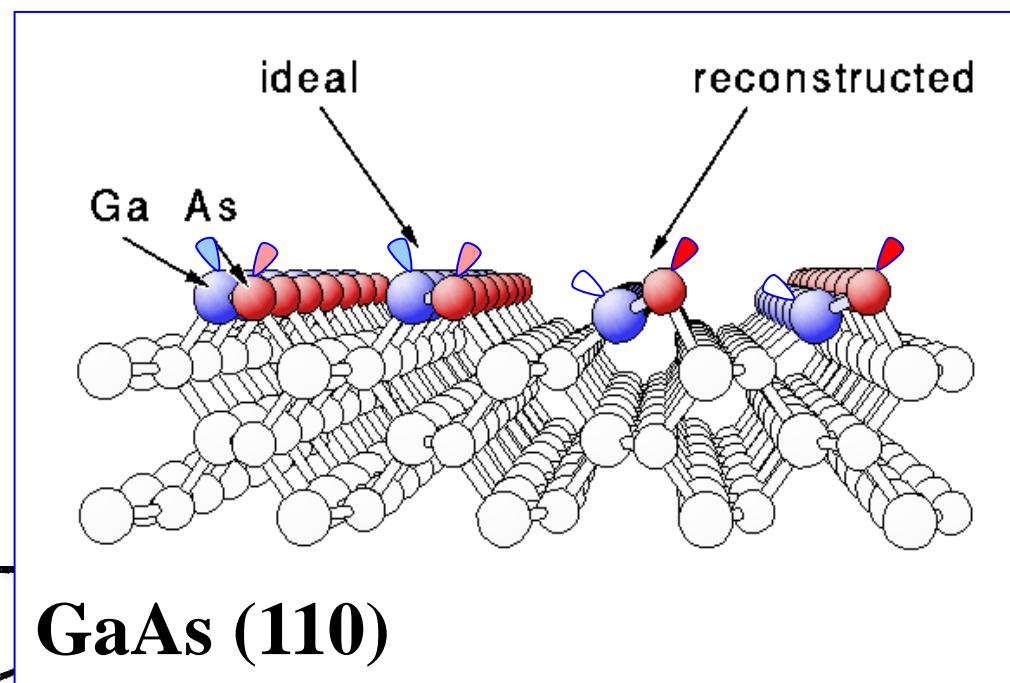
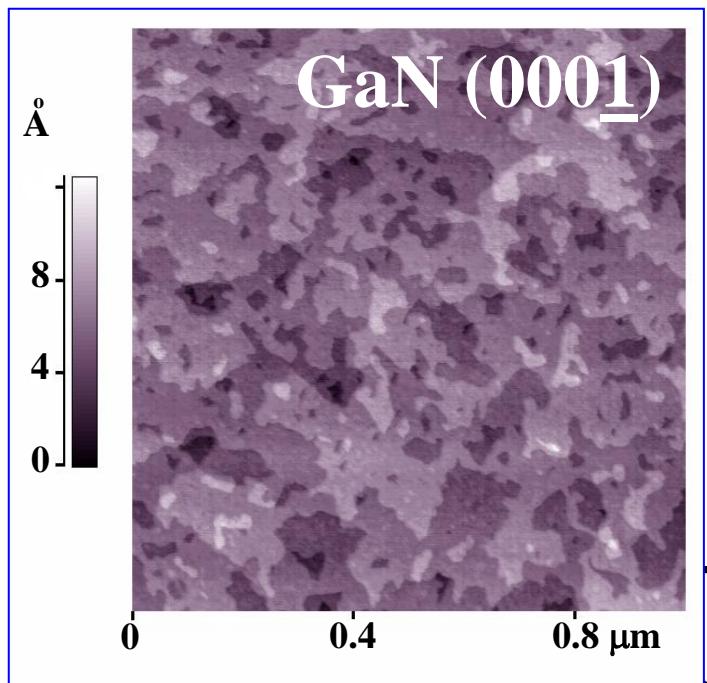


What does it
mean
surface?



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

Surface

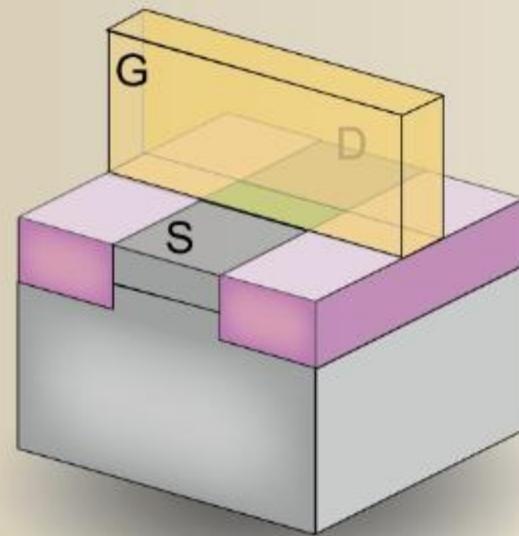


**Does the
surface
matter?**

A FinFET with one atomic layer channel

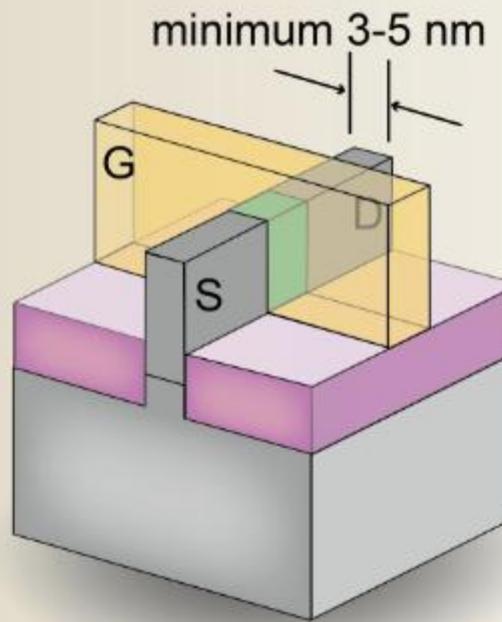
Mao-Lin Chen *et al.*, Nature Communications 11, 1205 (2020)

Planar MOSFET



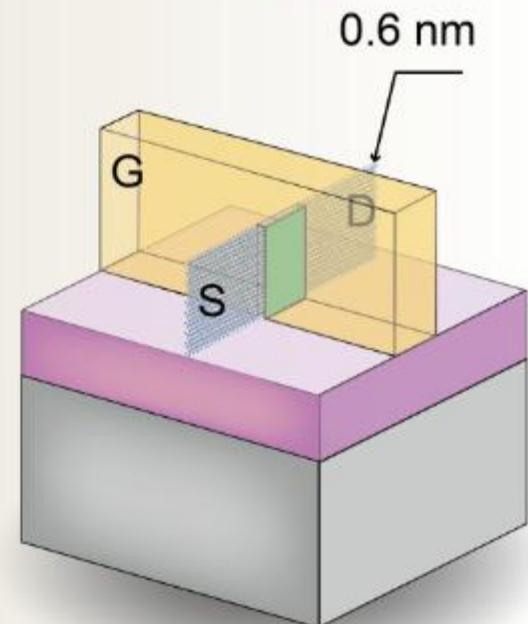
1960s

Si-based
FinFET



1990s

One atomic layer Channel
FinFET



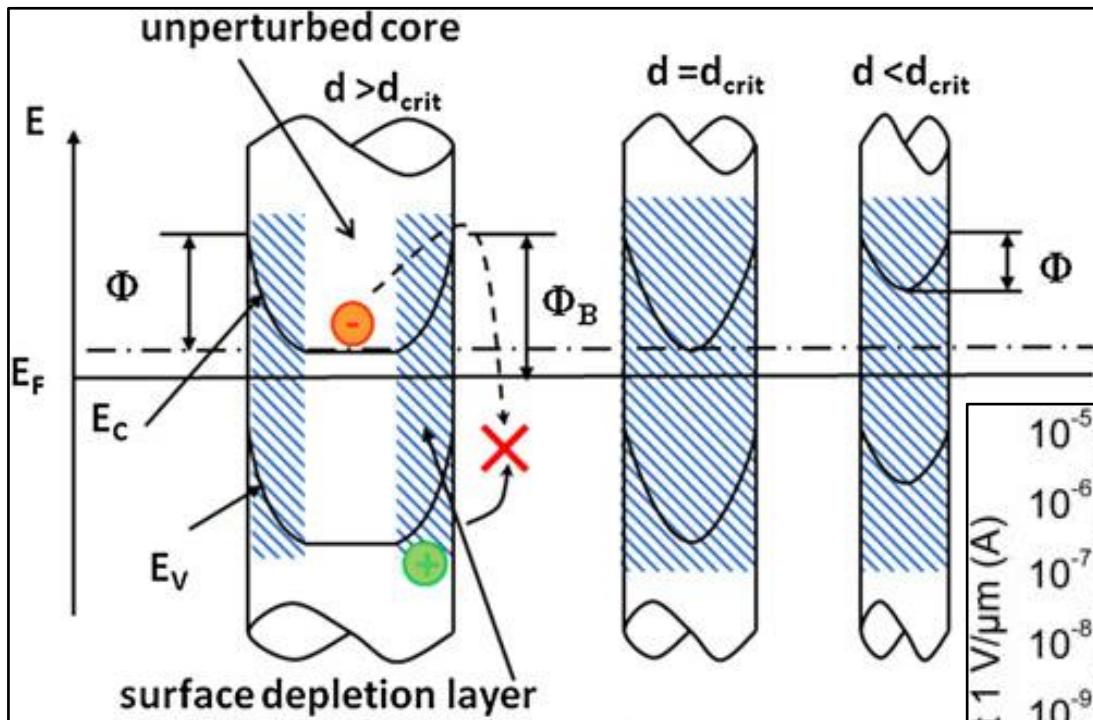
2020

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

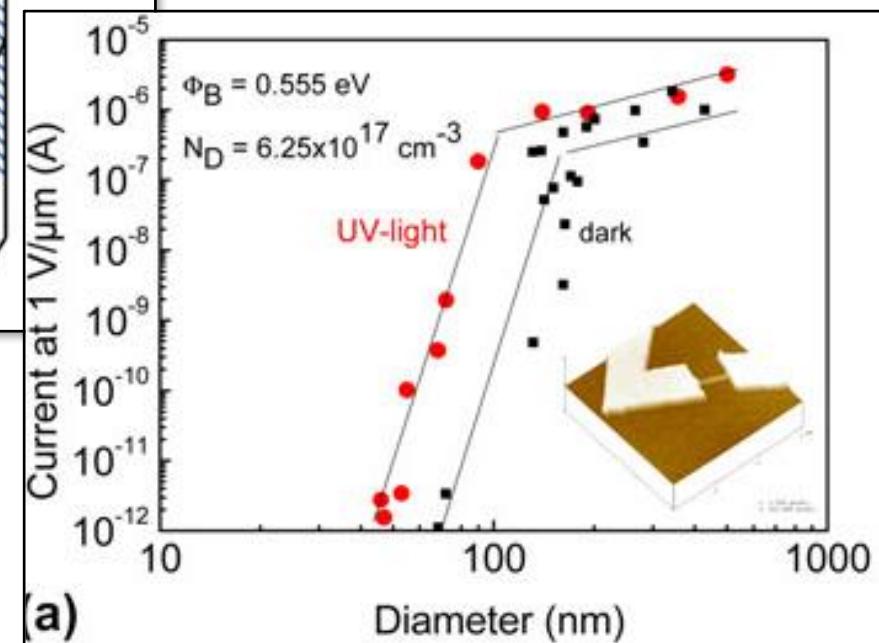
Raffaella Calarco, Toma Stoica, Oliver Brandt, Lutz Geelhaar

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



$$d_{crit} = 80 \text{ nm}$$

for GaN n-type nanowires
with $N_D = 6.25 \times 10^{17} \text{ cm}^{-3}$



Outline

- **Introduction**

- **Methods:**

- Electron microscopy**

- Scanning probe microscopies**

- Electron spectroscopies**

- Diffraction methods**

- Ion techniques**

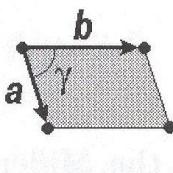
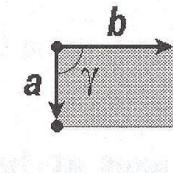
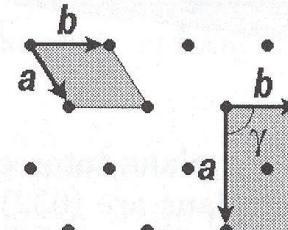
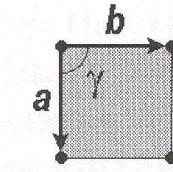
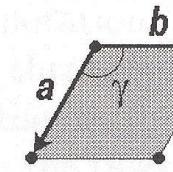
- Surface-sensitive optical techniques**

- **Summary, literature**

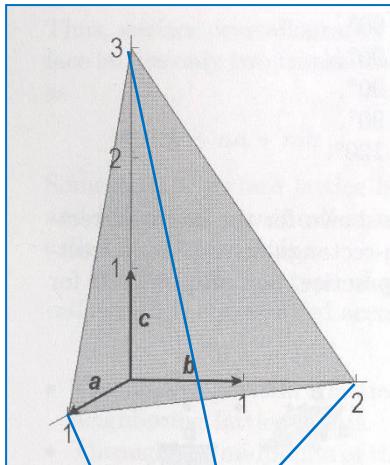
Surface description: Bravais lattices

5 2-dimensional Bravais lattices

(14 3-dimensional Bravais lattices)

$ \mathbf{a} \neq \mathbf{b} $	 <p>Oblique</p>	 <p>Rectangular</p>	 <p>Centered rectangular</p>
$ \mathbf{a} = \mathbf{b} $	 <p>Square</p>	 <p>Hexagonal</p>	

Surface description: Miller indices



1, 1/2, 1/3

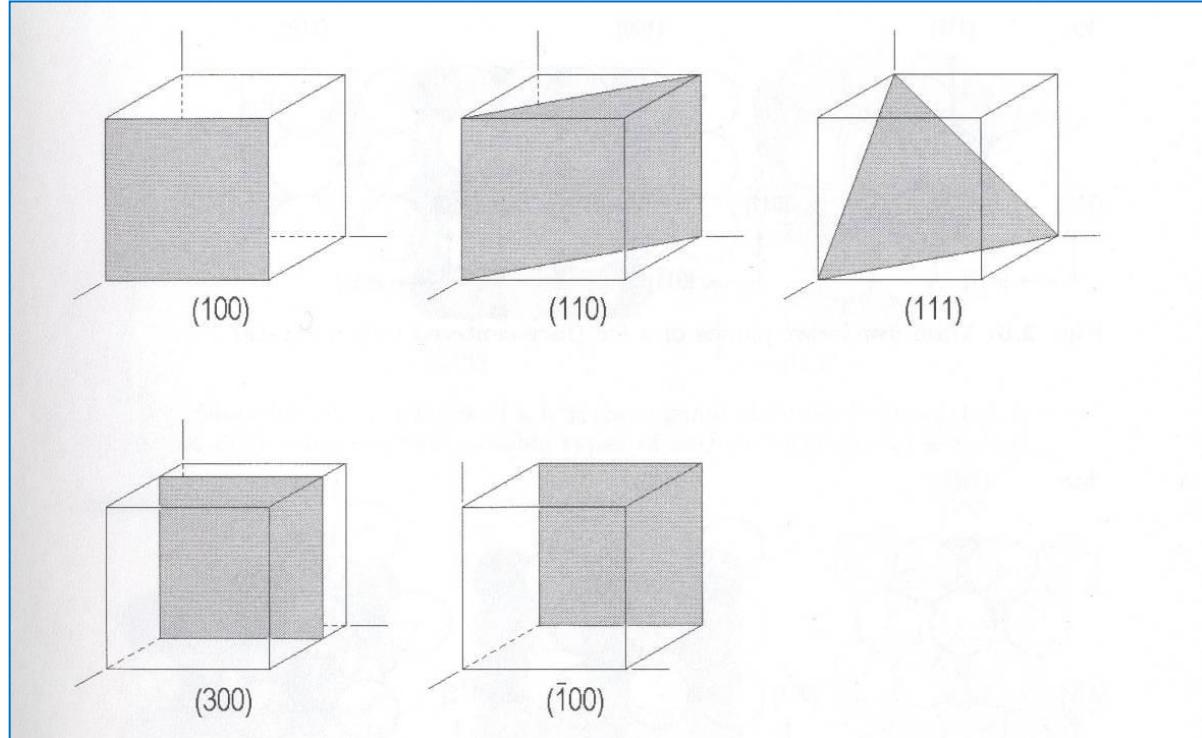


1, 1/2, 1/3



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

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

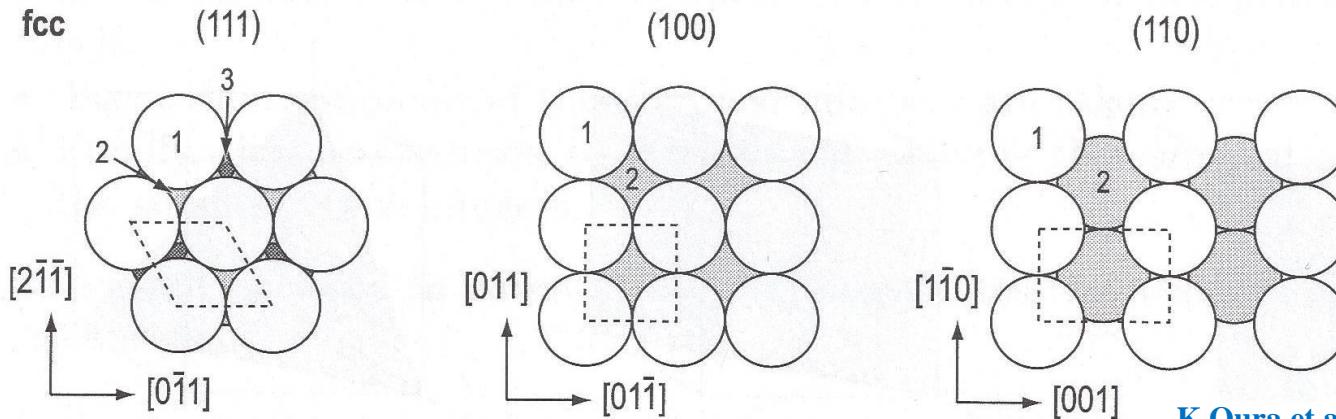


K.Oura et al.
Surface Science. An Introduction

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

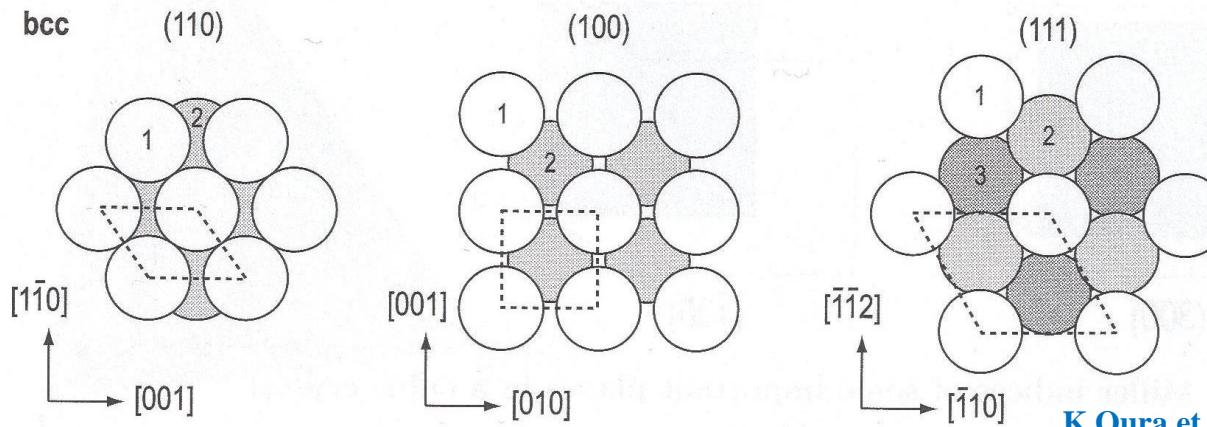
Atomic structure of surfaces - examples

Face-centered cubic crystal



K.Oura et al.
Surface Science. An Introduction

Body-centered cubic crystal



K.Oura et al.
Surface Science. An Introduction

Surface structure description - notations

Wood's notation

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

$$S(hkl) - i(m \times n)R\phi^\circ - N Ad$$

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

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

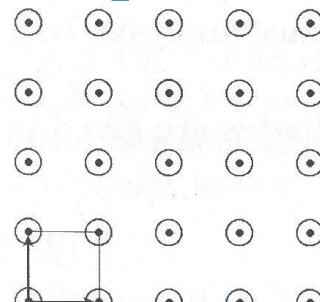
Matrix notation

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

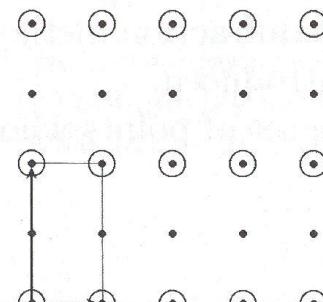
$$G = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$$

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

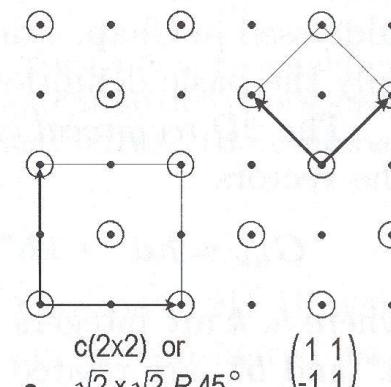
Examples:



$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

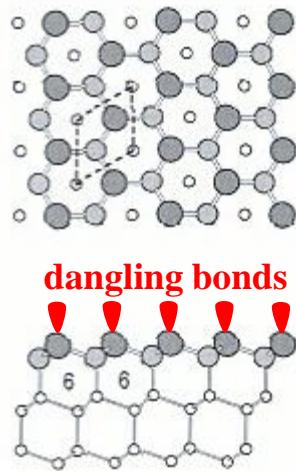


$$\begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$$

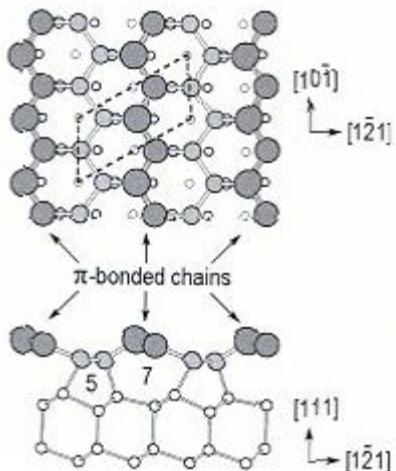


$$\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

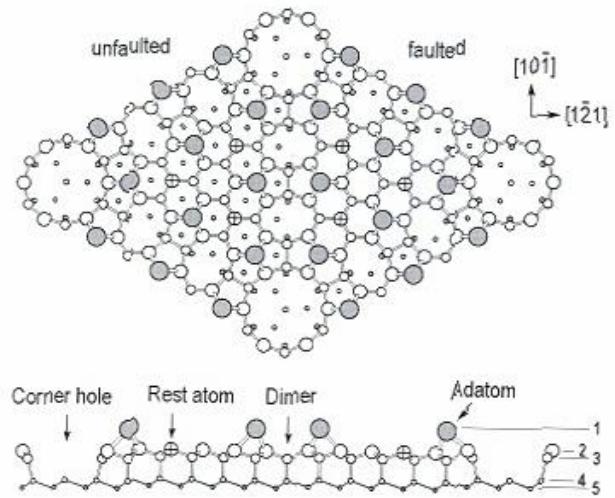
Example: Si (111) surface



Si(111)- (1x1)
ideal cut



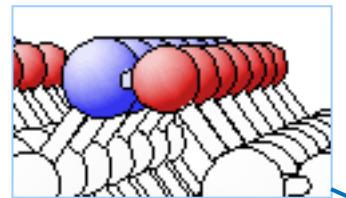
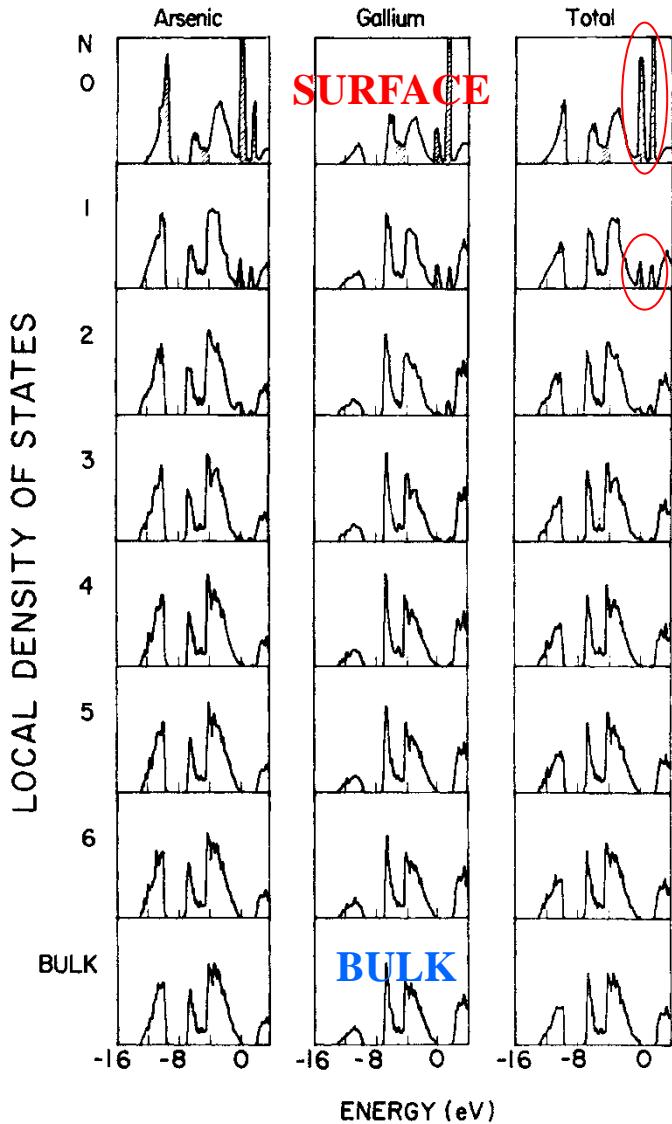
Si(111)- (2x1)
crystal cleaved
along (111)



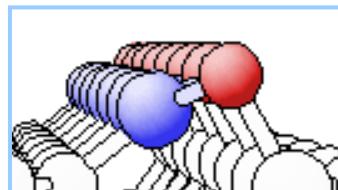
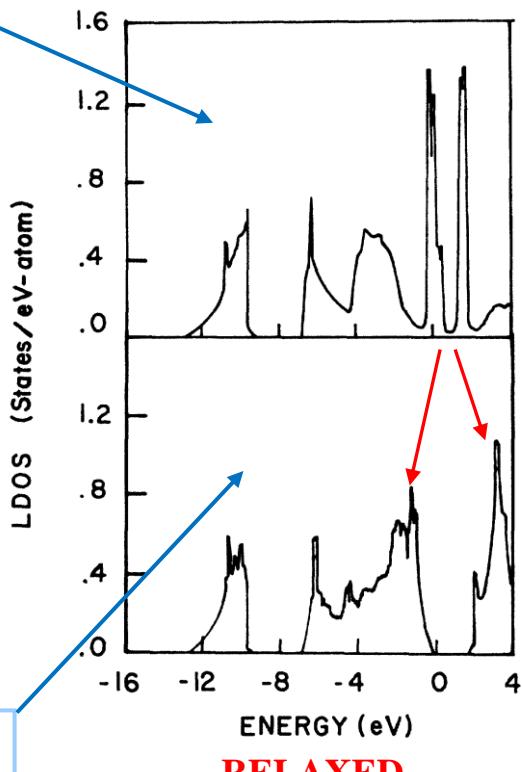
Si(111)- (7x7)
obtained from 2x1 by
annealing at 450°C
*dimer-adatom-stacking fault
(DAS) model*

Electronic structure of the surface

unrelaxed GaAs(110)



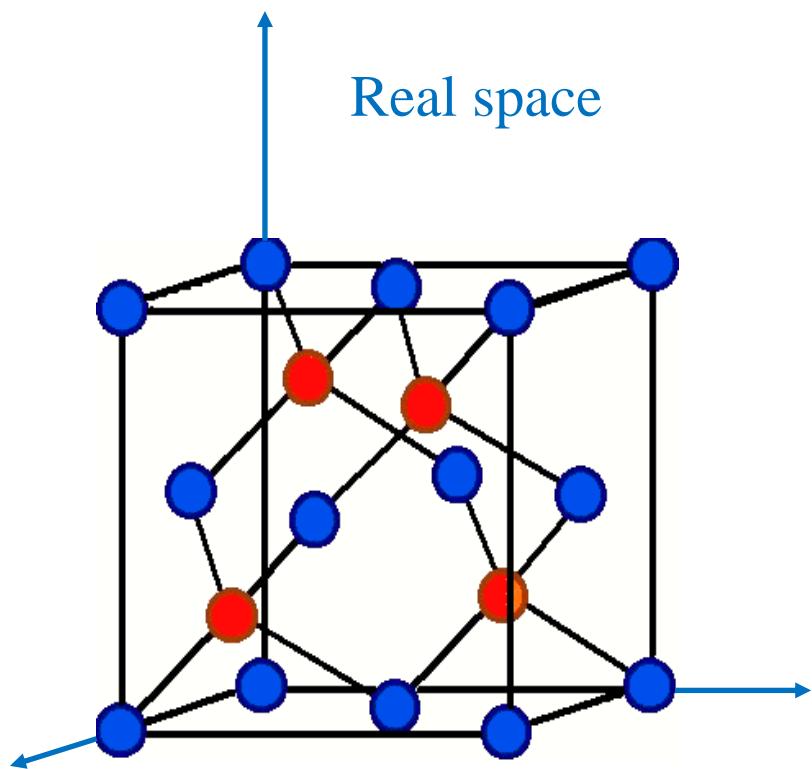
UNRELAXED



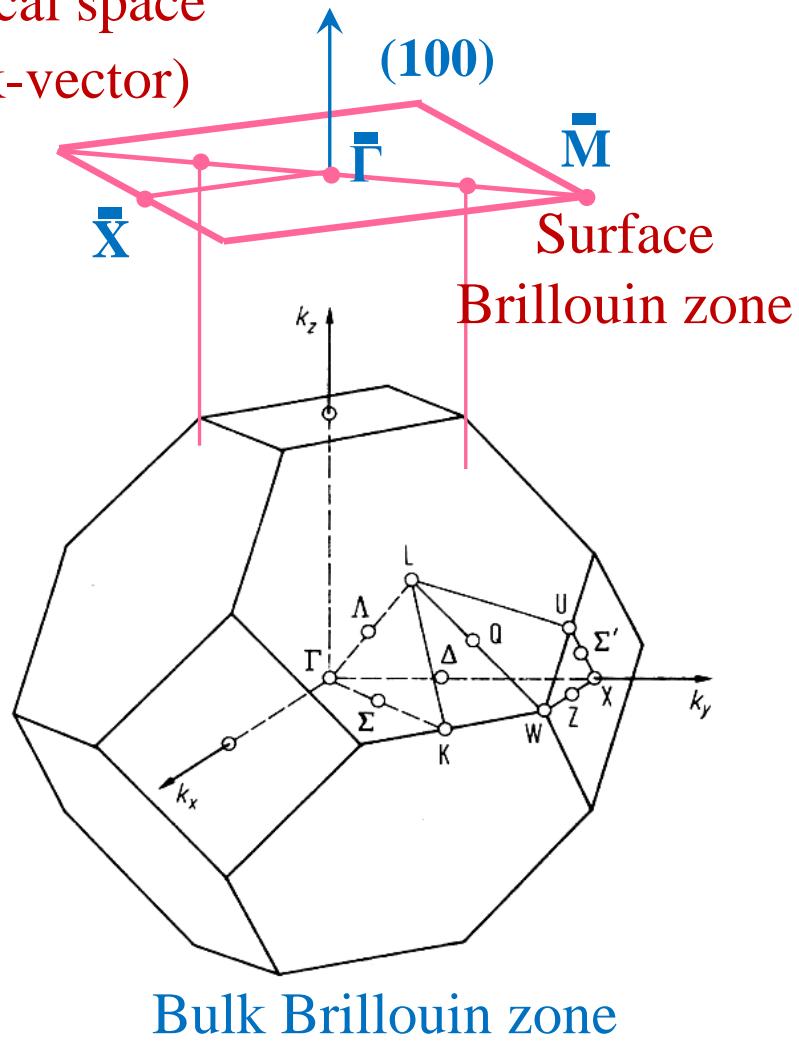
RELAXED

Electronic structure of the surface (cont.)

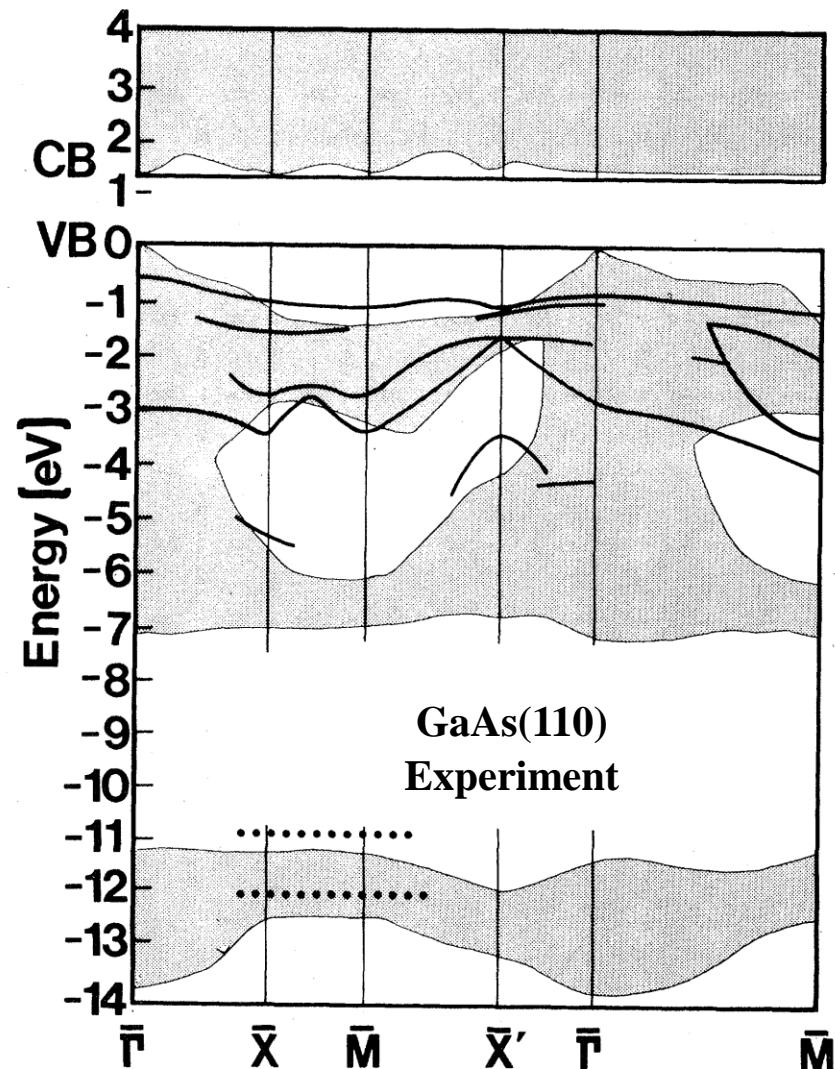
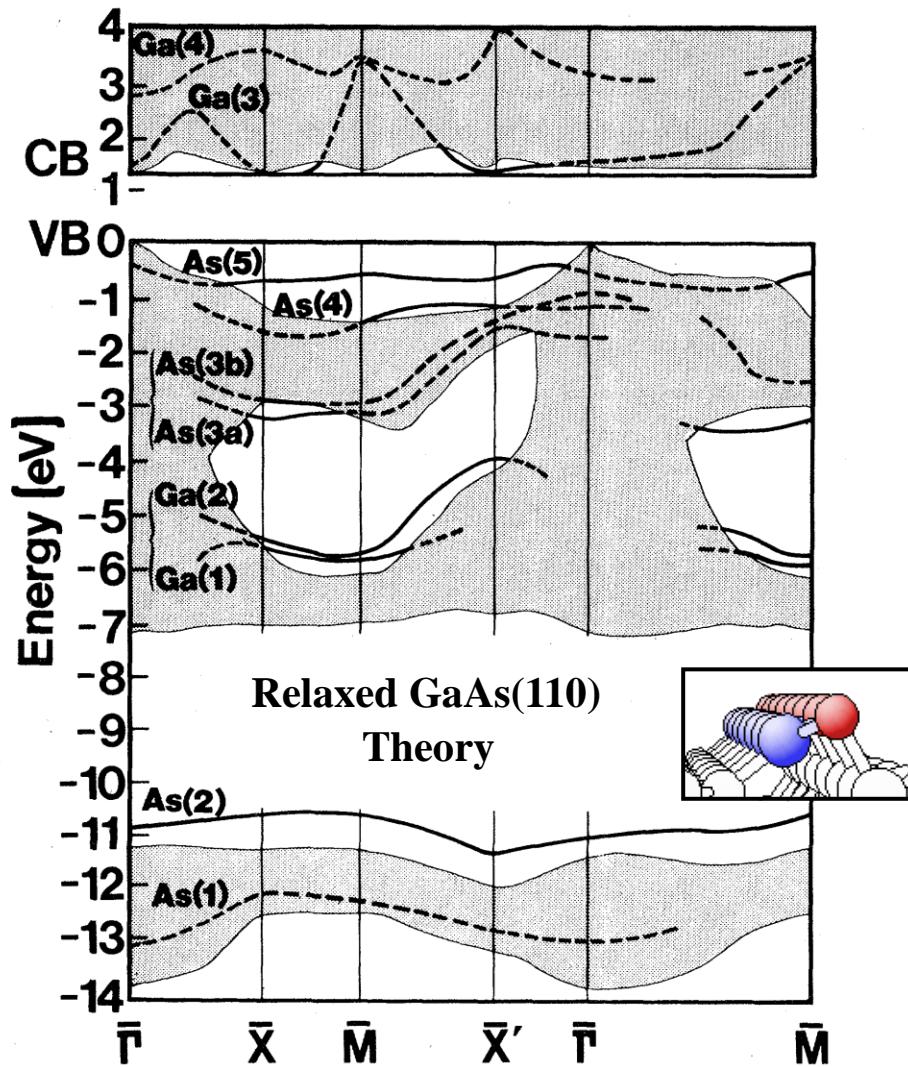
Brillouin zones



Reciprocal space
(k -vector)



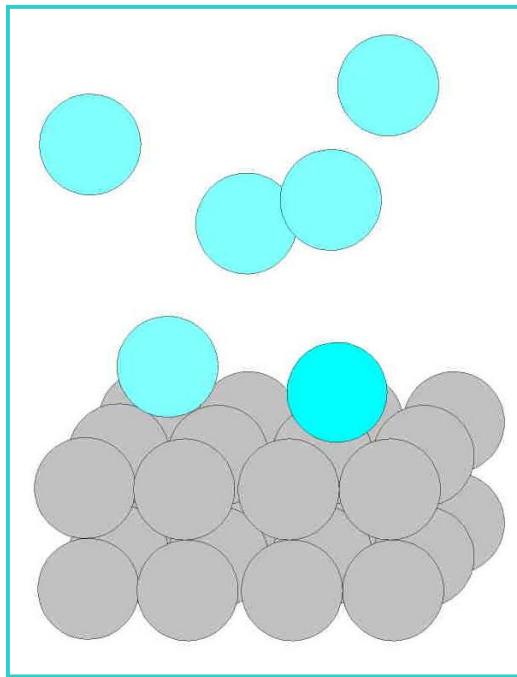
Electronic structure of the surface (cont.)



What do we want to know about surfaces?

- Morphology
- Chemical composition (cleanliness, 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 – 10¹⁵ cm⁻², sticking coefficient = 1

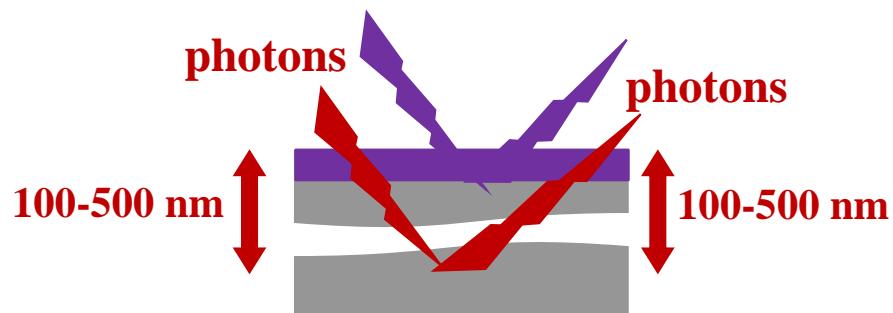
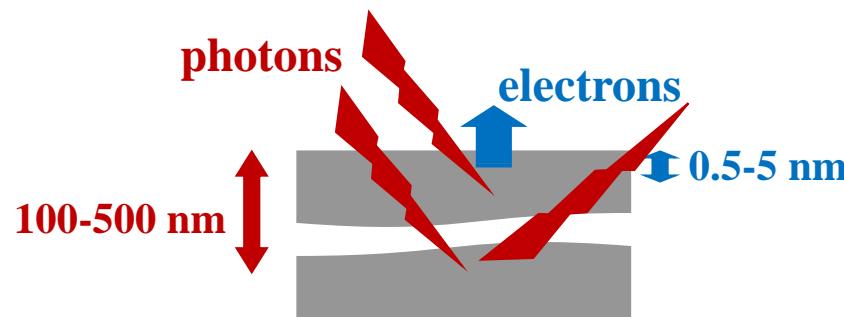
Pressure of the order of 10⁻¹⁰ hPa is necessary for studying pristine surfaces!

How to extract the signal coming from the surface?

We have to find a proper „probe”

or

a proper surface-related property



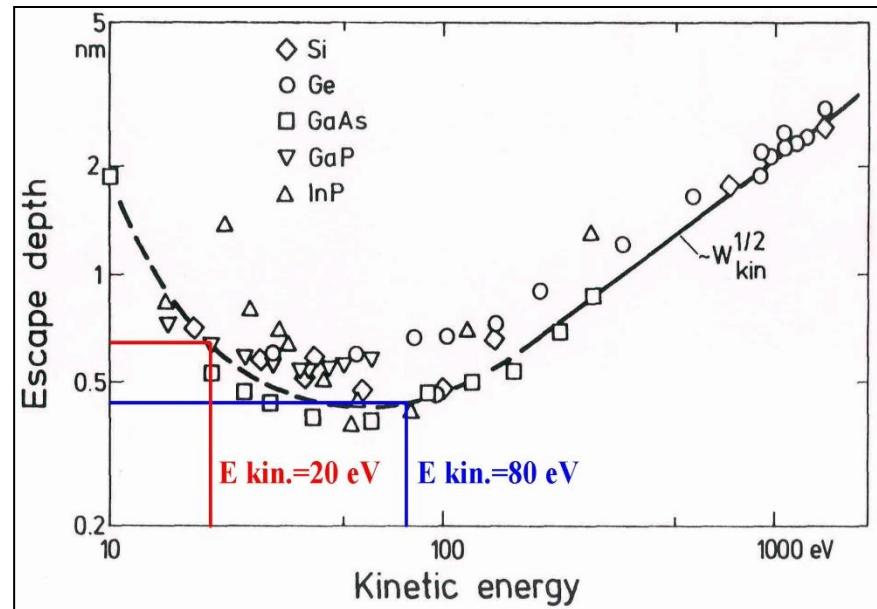
What can be a surface sensitive „probe”?

- 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

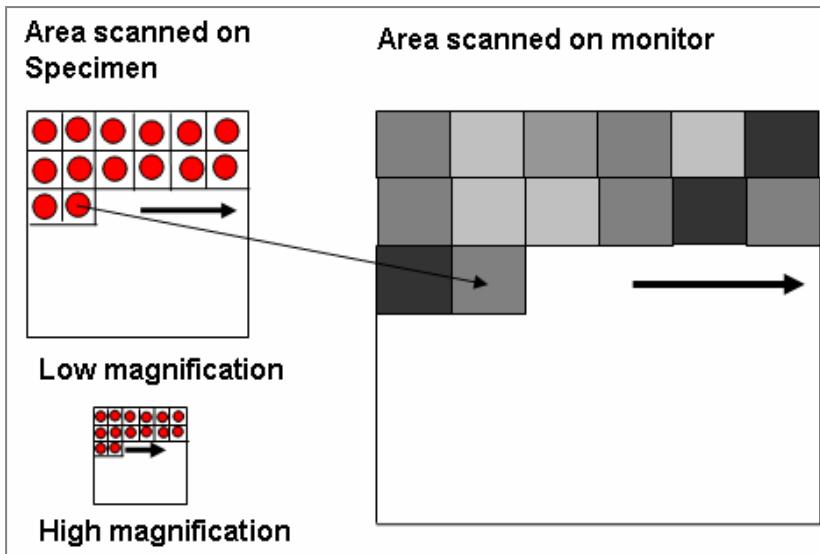
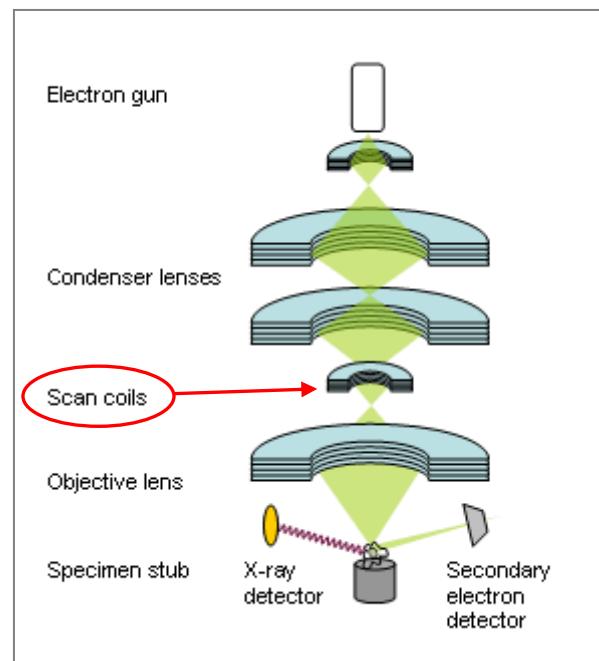
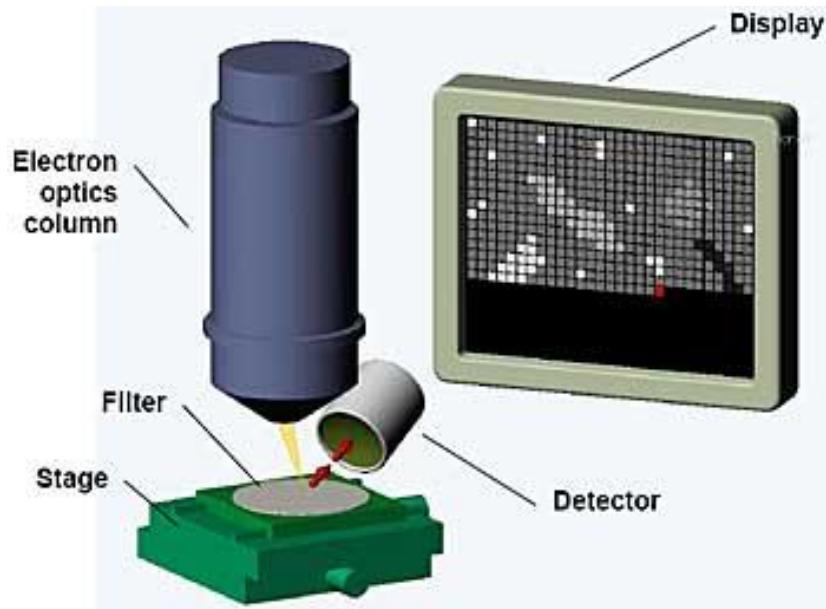
- Surface differential spectroscopy

- X-ray diffraction

Increased surface sensitivity for glancing incidence

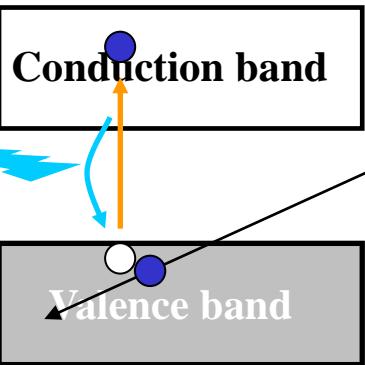
Microscopies

Scanning Electron Microscopy (SEM)



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

CL



Primary electrons

Cathodoluminescence (CL)

X-rays

Back-scattered electrons (BSE)

Auger electrons

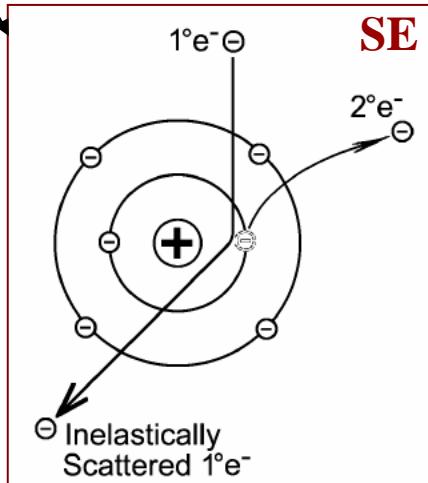
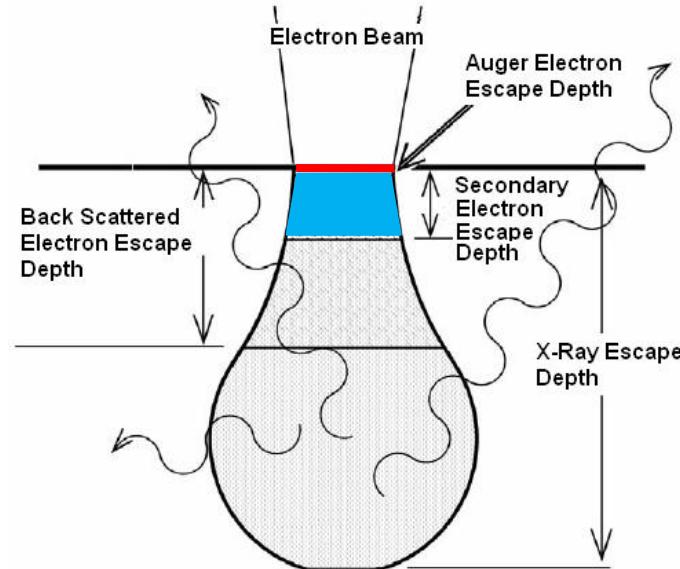
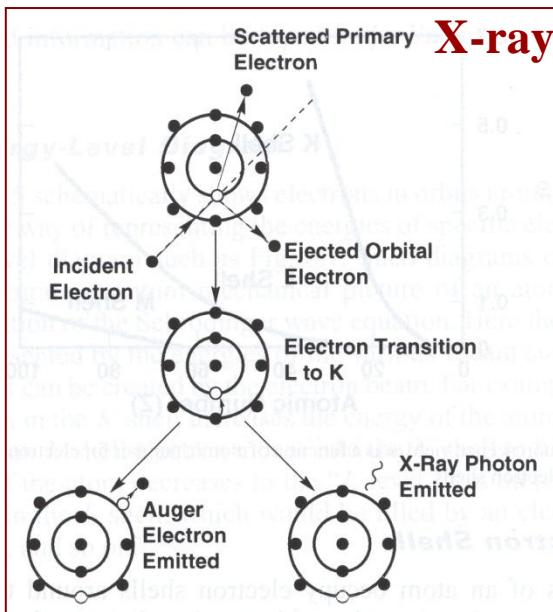
Secondary electrons (SE)

BSE

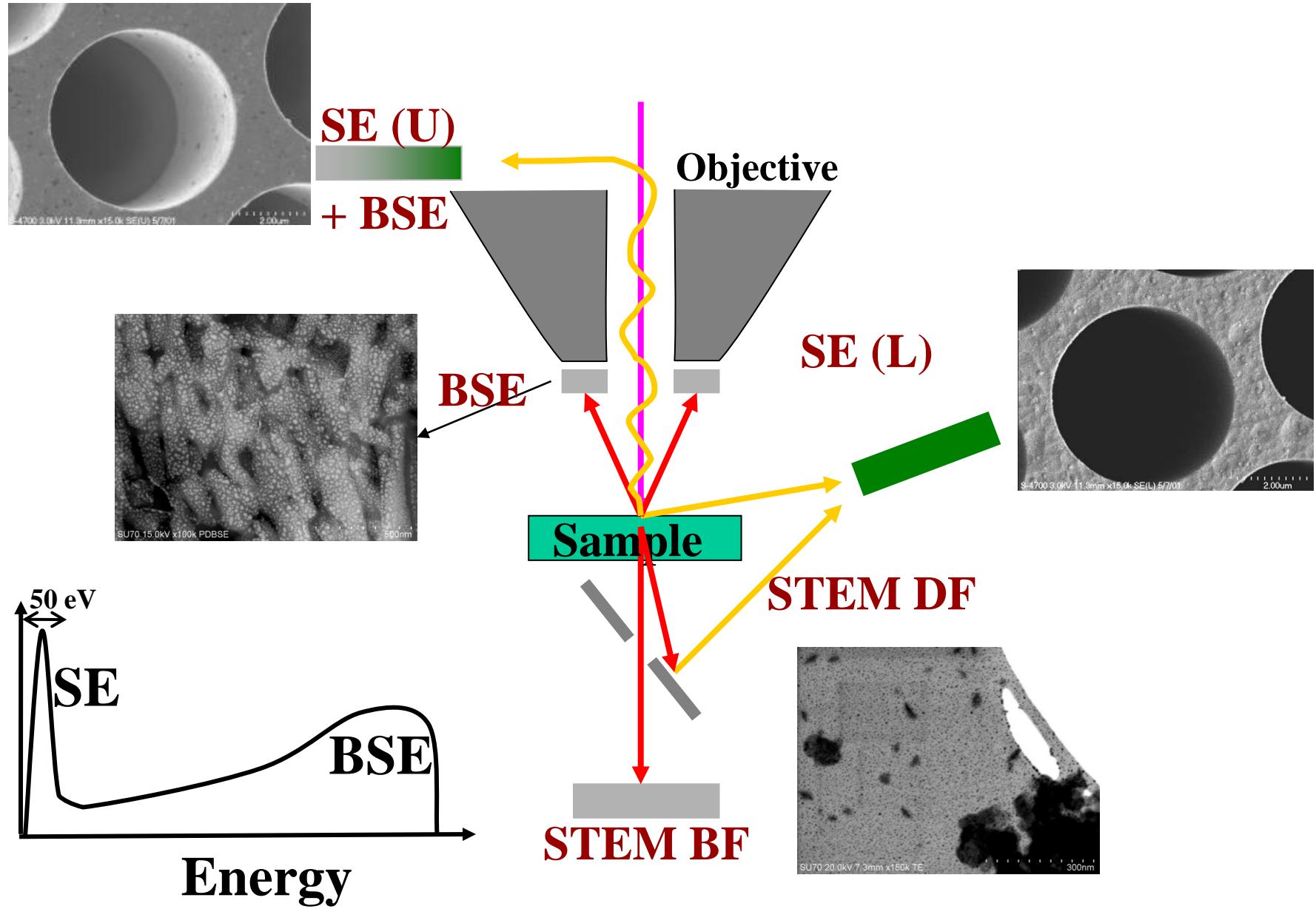
Back Scattered Electron

Elastically Scattered Electron

X-ray



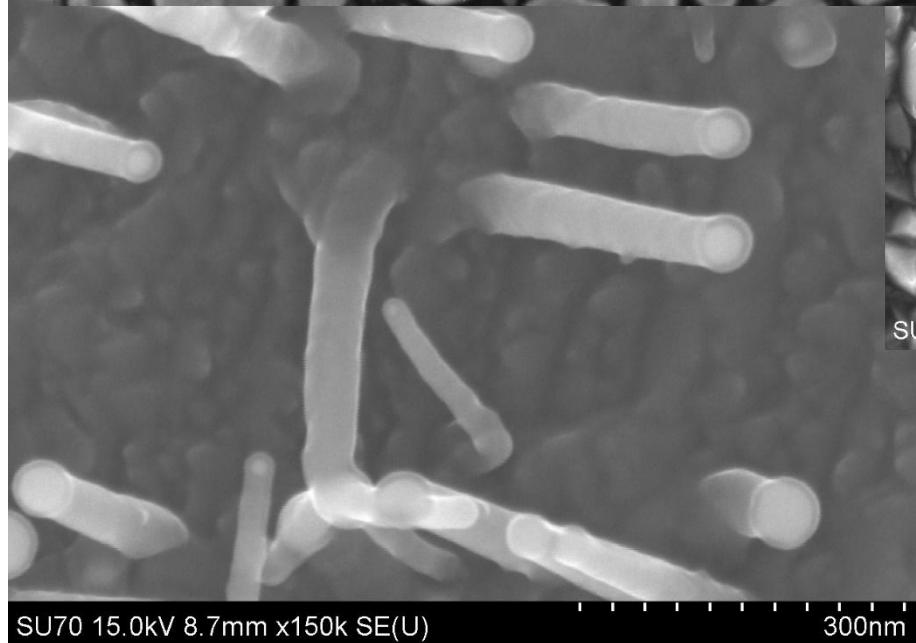
Electron detection in SEM



Au islands on C

SU70 15.0kV 4.4mm x220k SE(U)

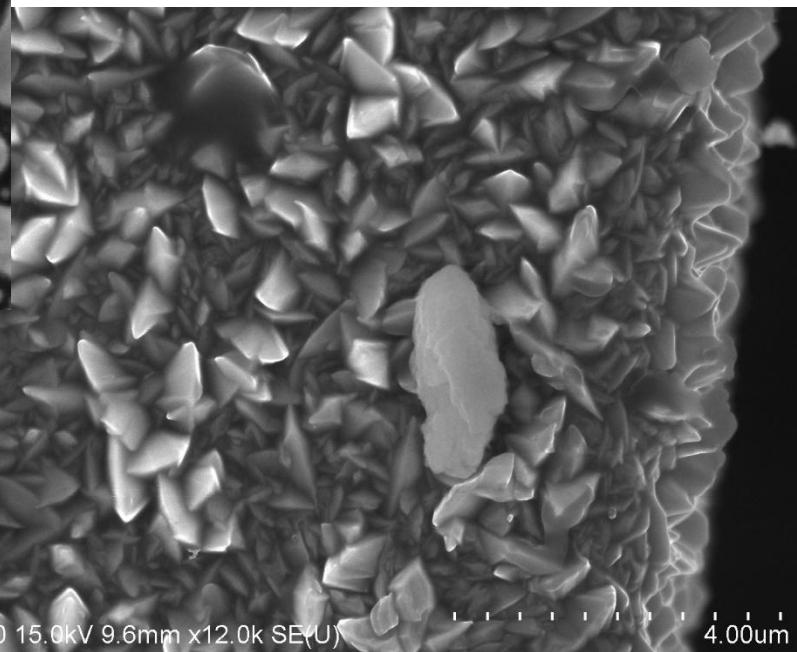
200nm



SU70 15.0kV 8.7mm x150k SE(U)

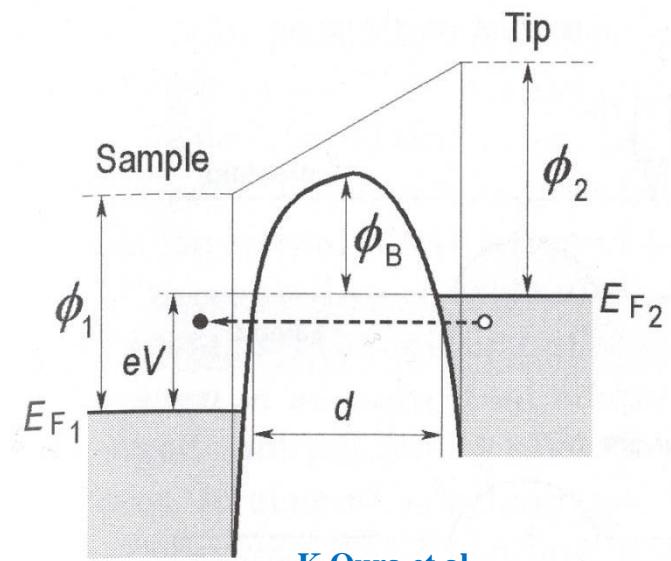
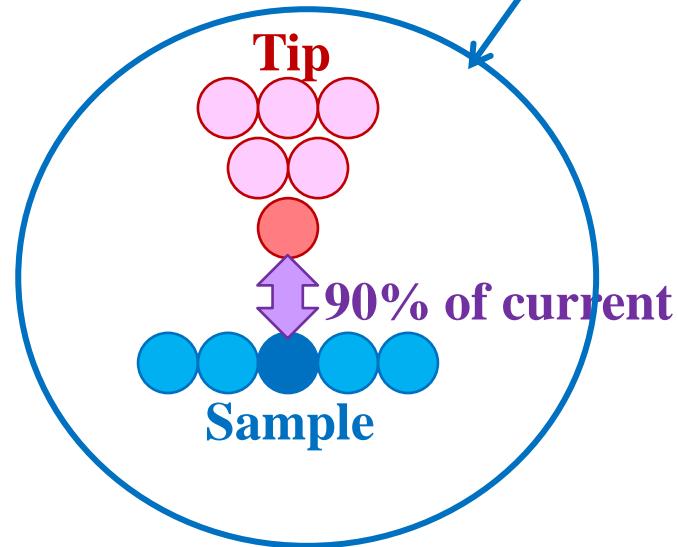
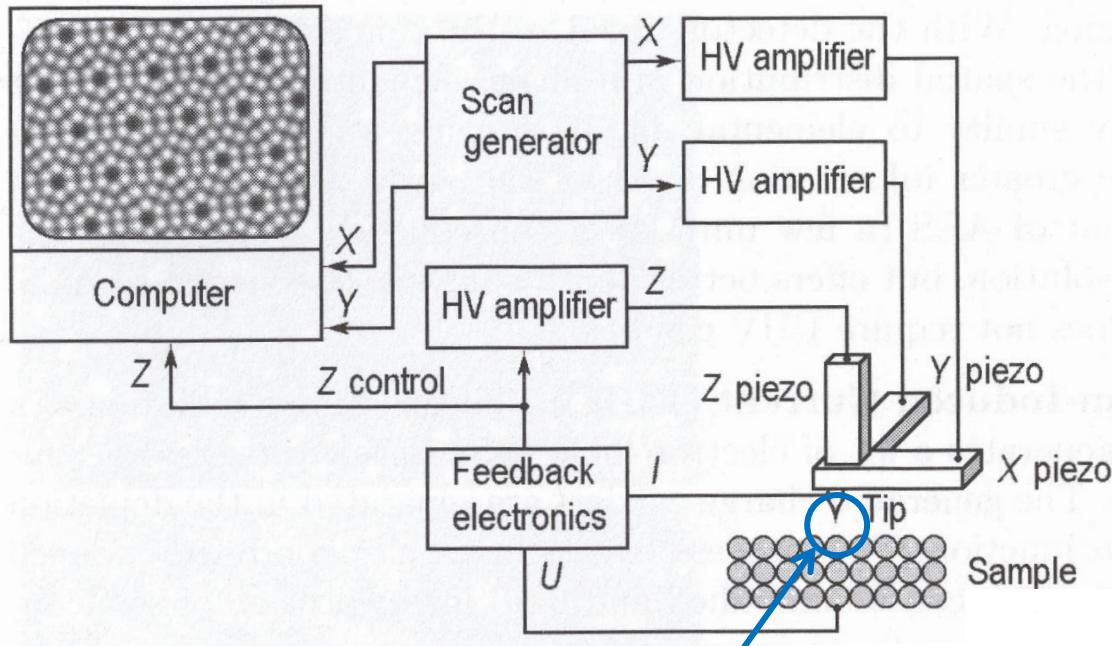
300nm

ZnTe nanowires

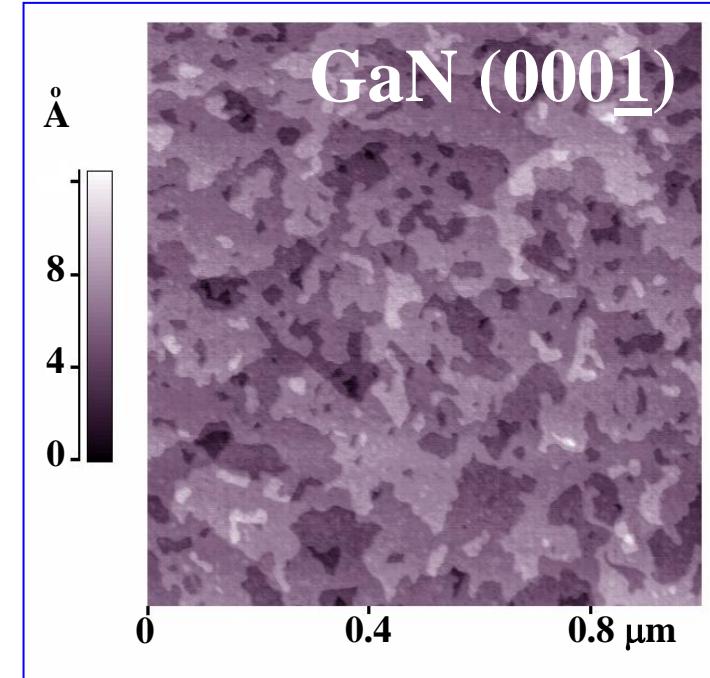
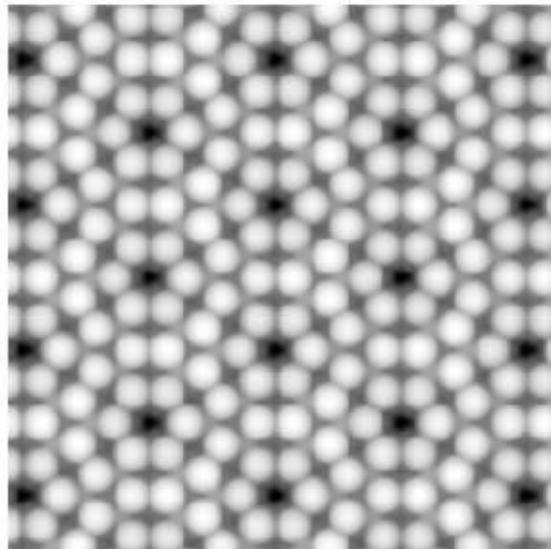
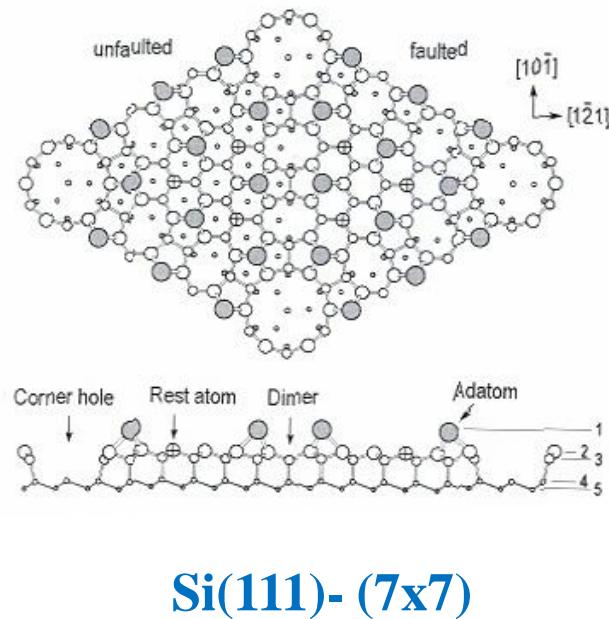


ZnO

Scanning Tunnelling Microscopy (STM)

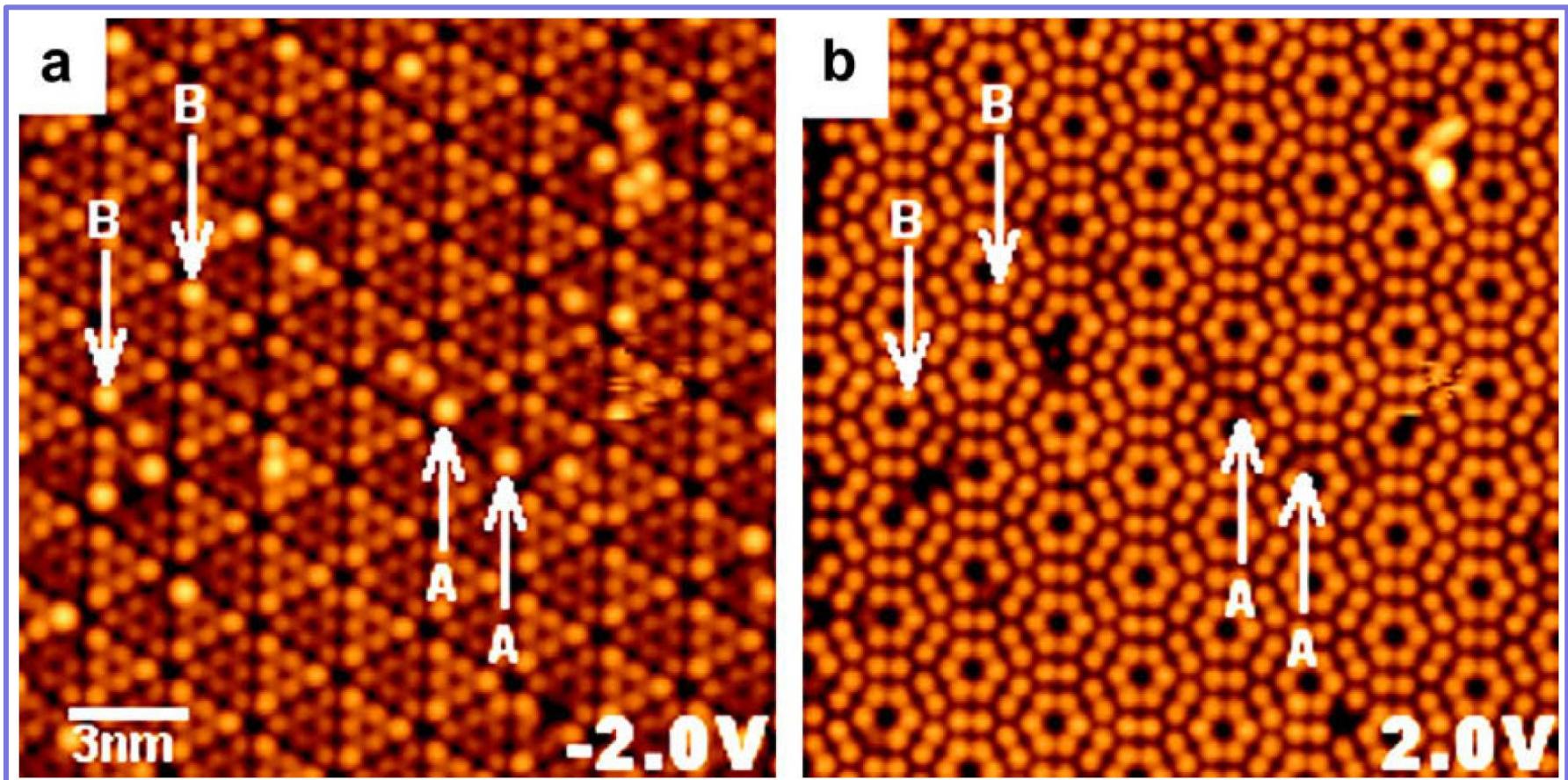


Scanning Tunnelling Microscopy (STM) (cont.)



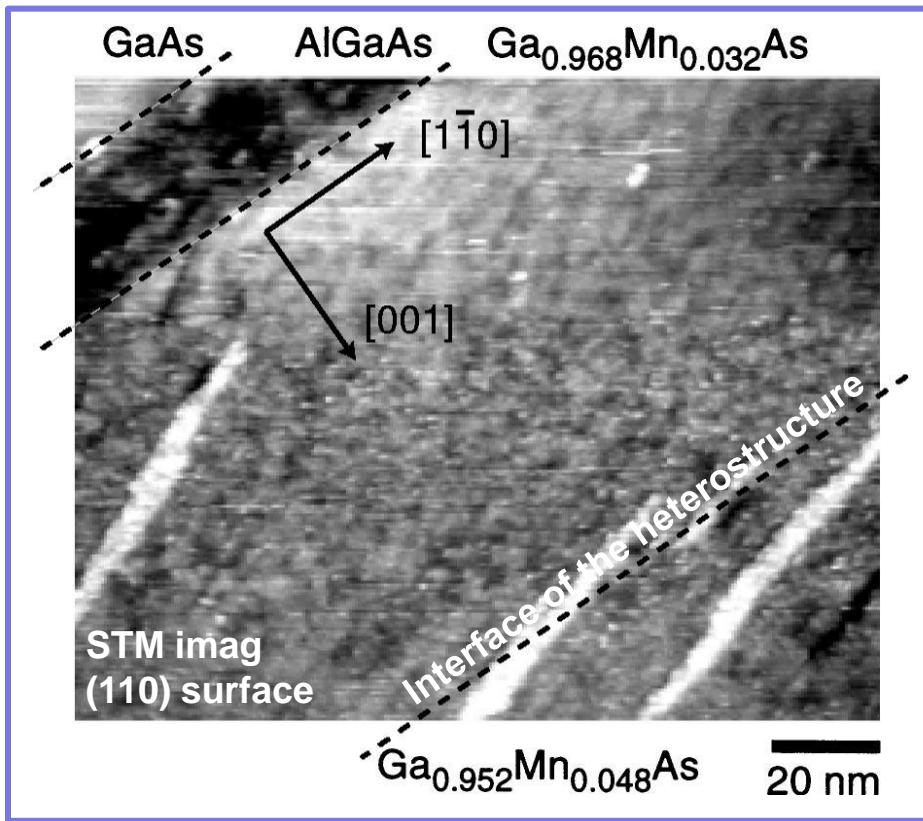
$\text{GaN}(000\bar{1})$ - (1×1)

Scanning tunnelling microscopy (STM) (cont.)

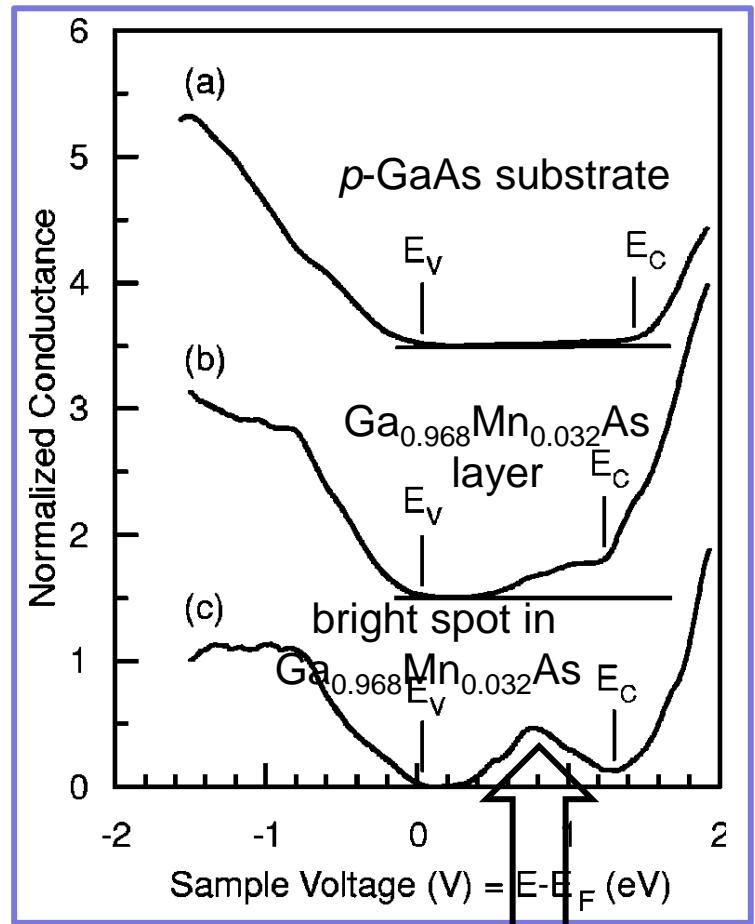


Filled and empty electronic states in STM images of Si(111)-7x7 upon deposition of 0.05 ML of Ta. (P. Shukrynau *et al.* Surface Science 603, 469 (2009))

Scanning tunnelling spectroscopy (STS)



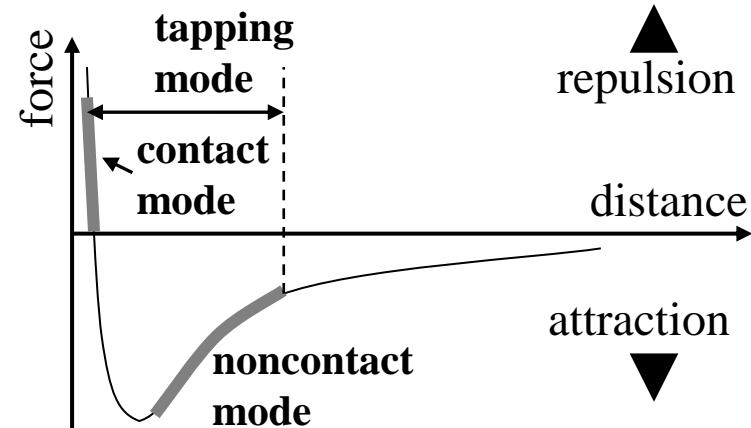
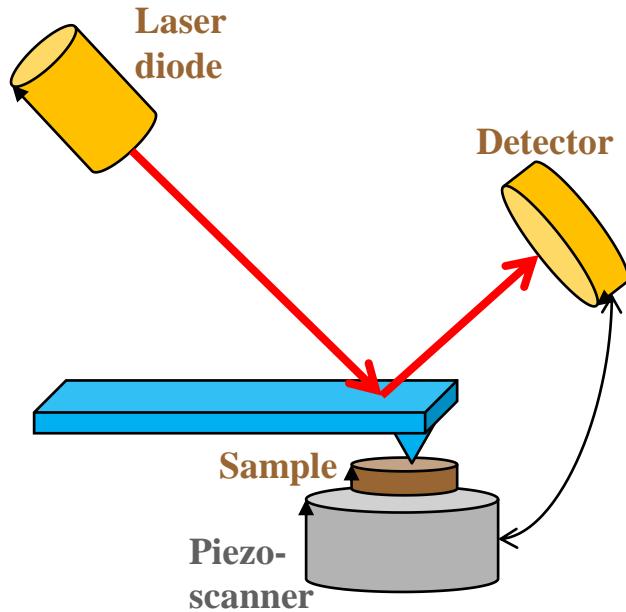
T. Tsuruoka *et al.* Appl. Phys. Lett. **81**, 2800 (2002)



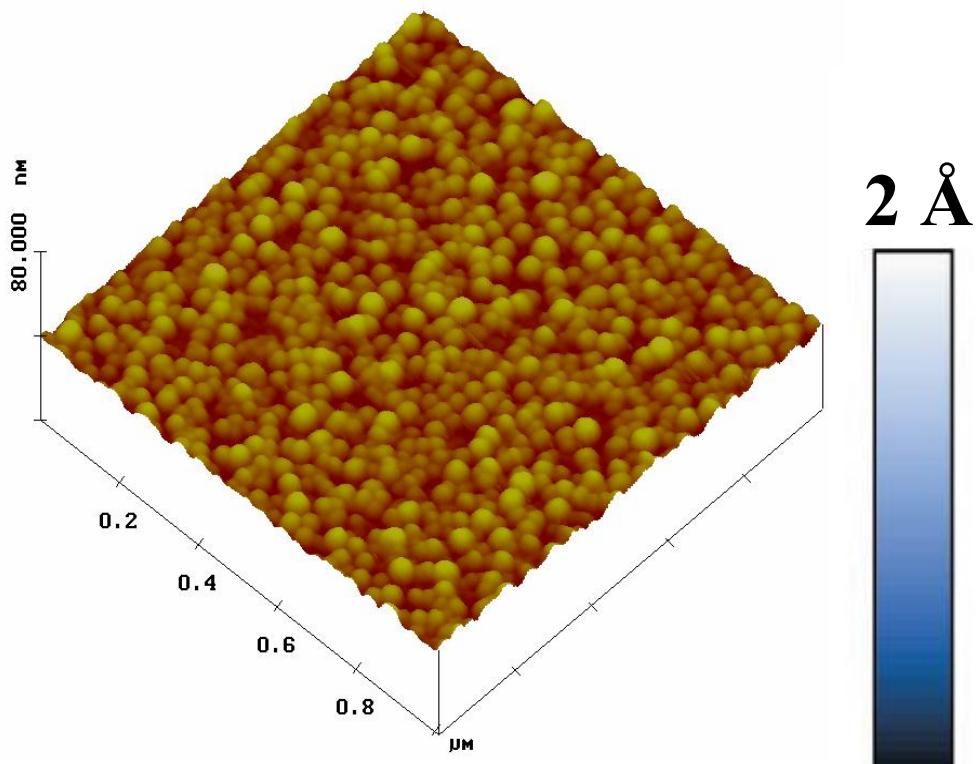
Tunnelling conductance spectra (STS)

tunnelling into
the levels of As
antisites

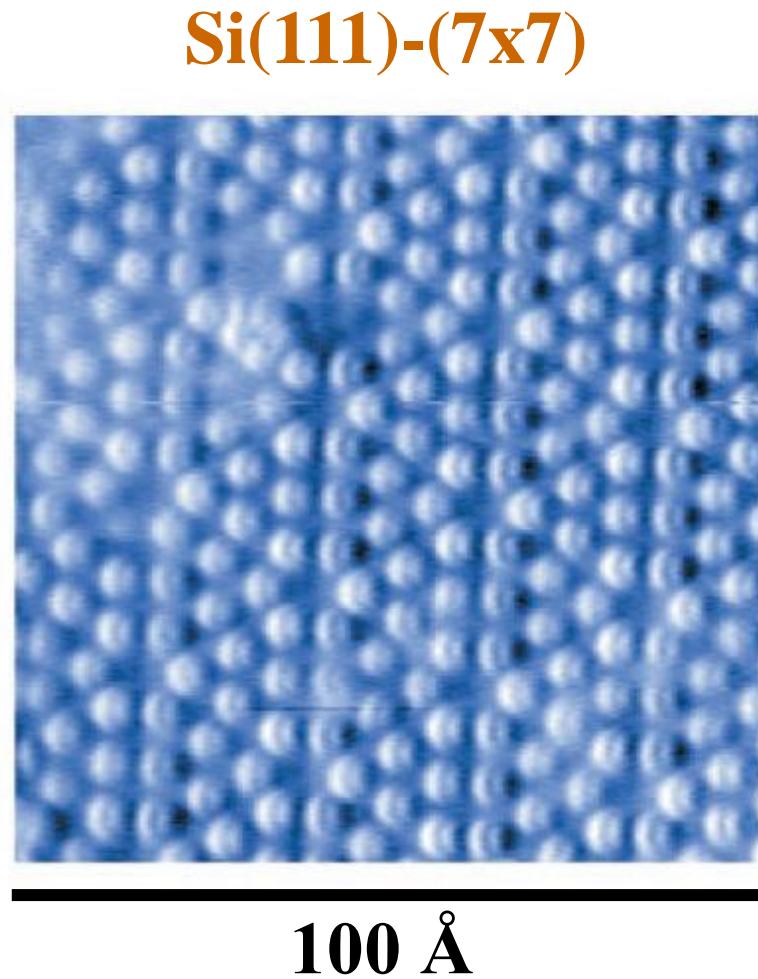
Atomic Force Microscopy (AFM)



Atomic Force Microscopy (AFM) (cont.)



MnAs dots on
GaN(0001)

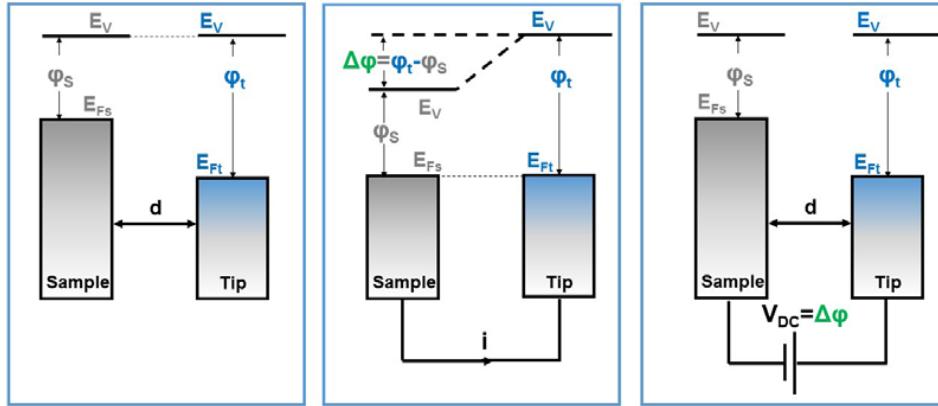


Si(111)-(7x7)

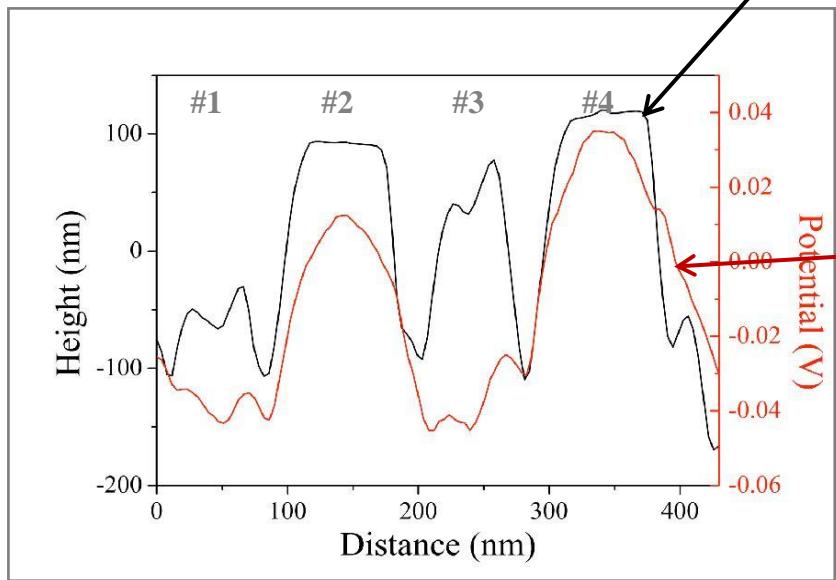
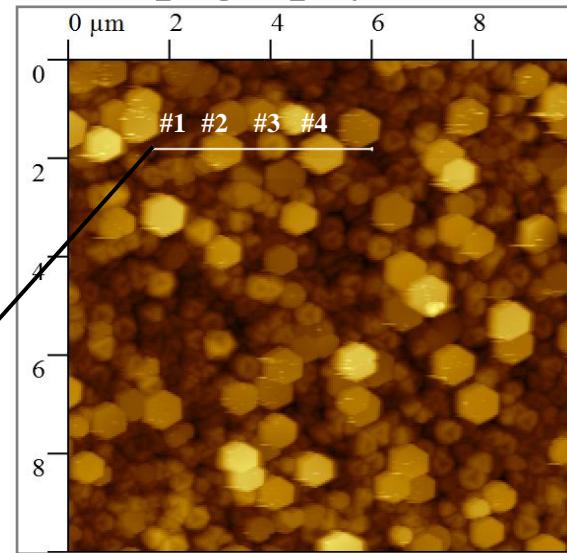
Kelvin Probe Force Microscopy (KPFM)

Topography (AFM)

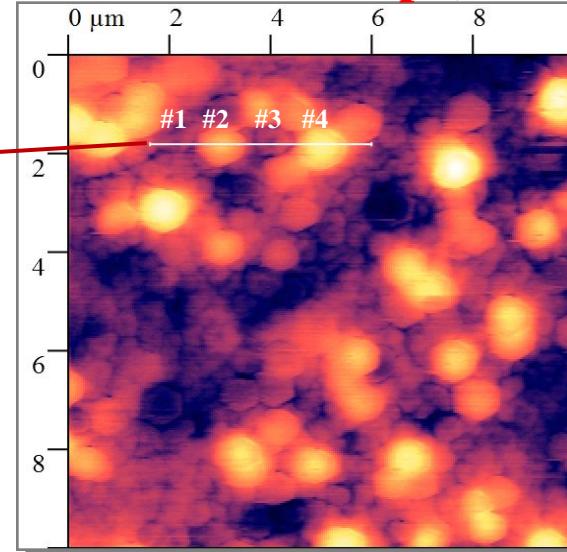
Principle of Kelvin probe experiment



M.Paul Narchi, PhD Theses, Palaiseau 2016



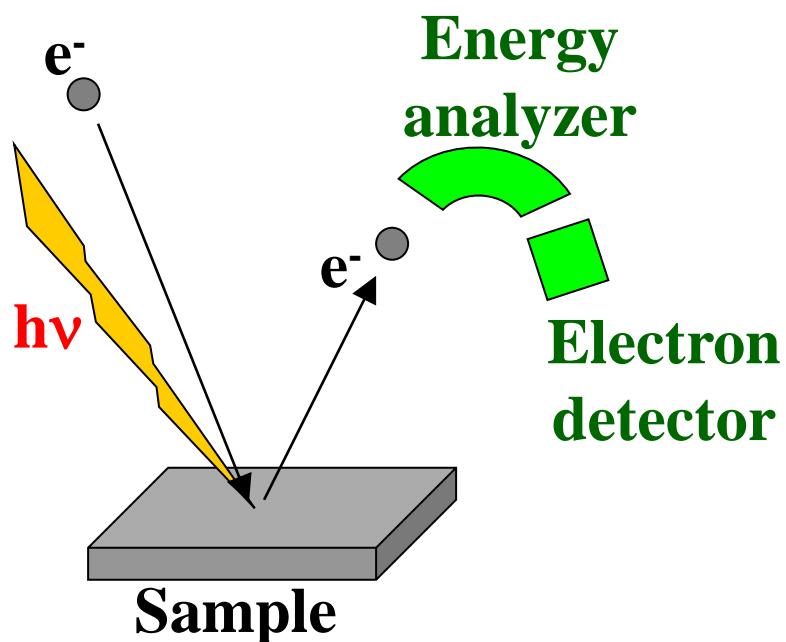
Work function map (KPFM)



Rafal Bożek, Faculty of Physics,
University of Warsaw

Electron spectroscopies

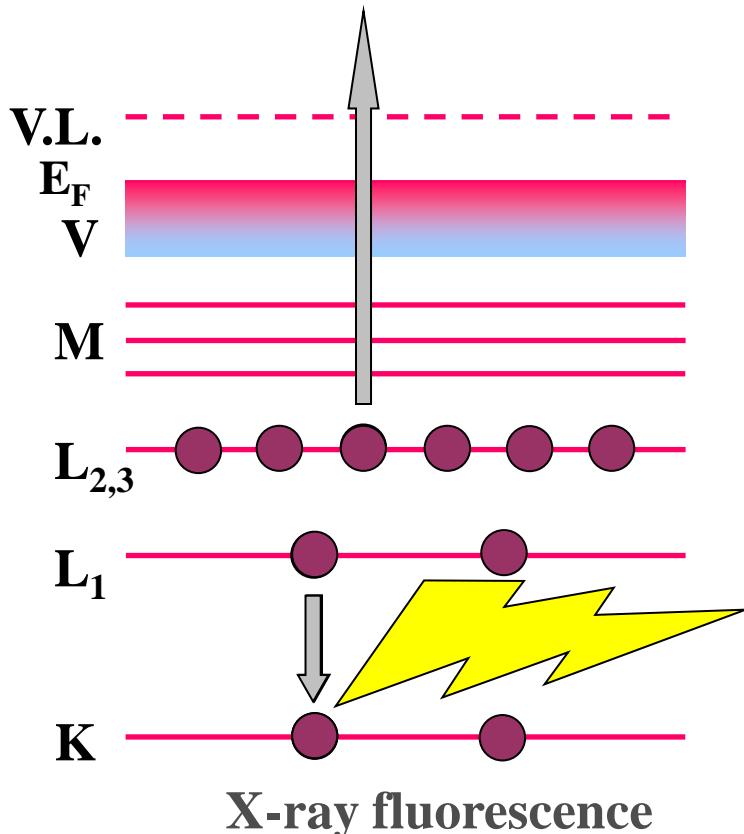
Auger electron spectroscopy

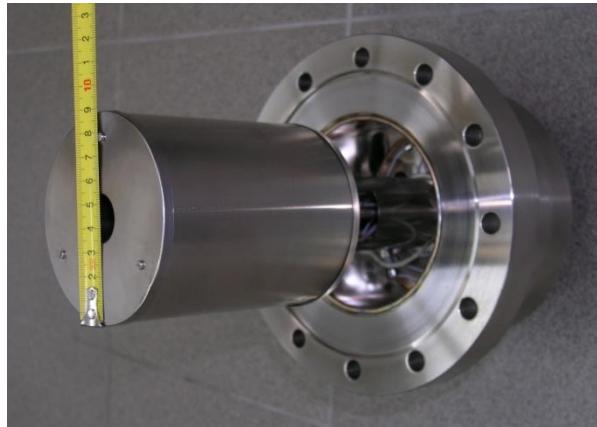
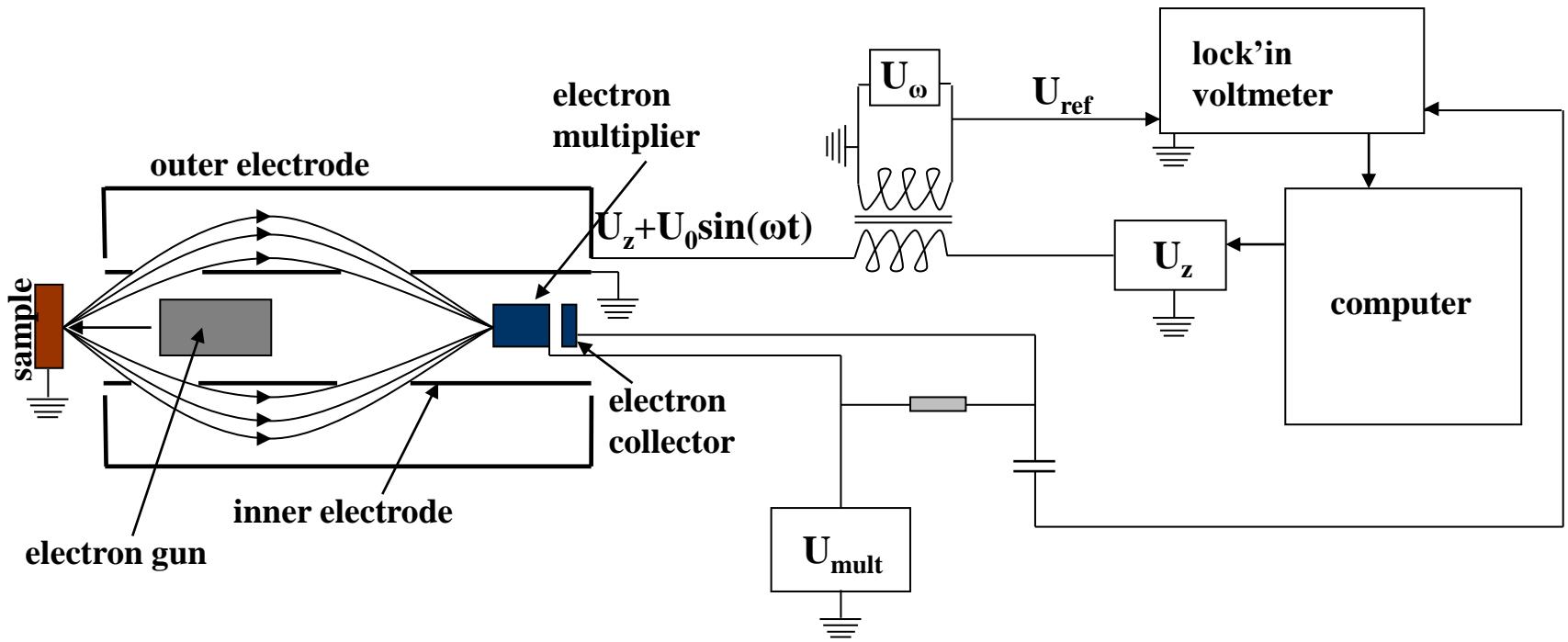


Primary electron E_0

Auger electron energy:

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





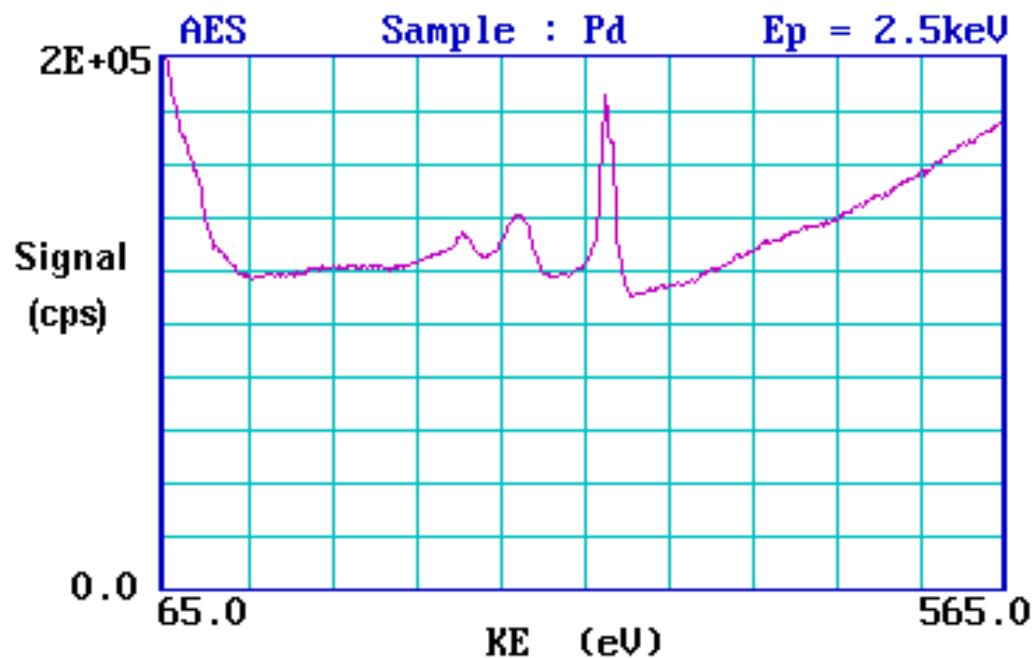
Auger electron spectrometer with a cylindrical mirror analyser

Primary electron energy: up to 3kV

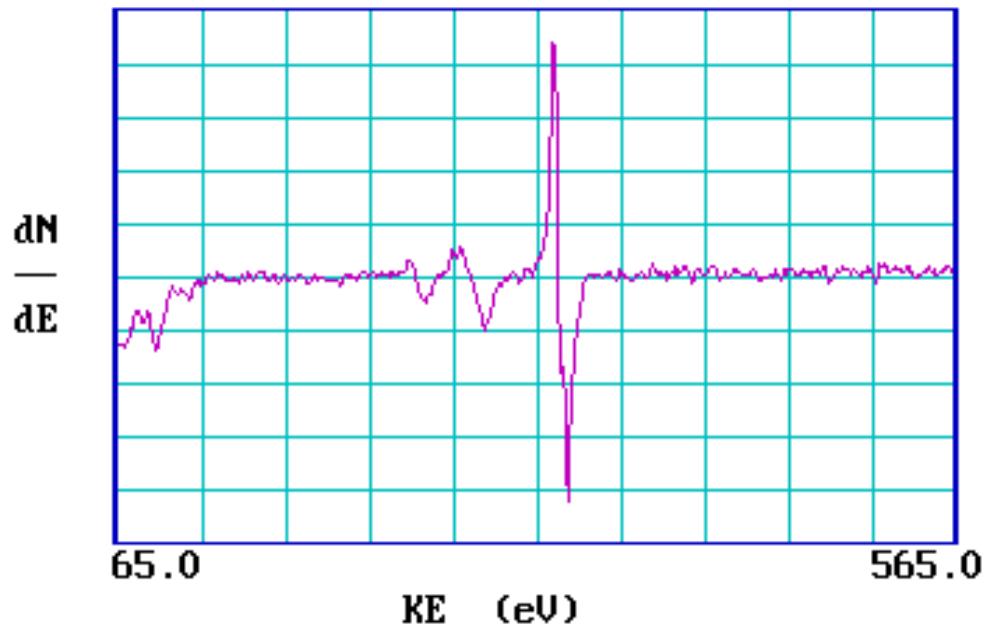
Resolving power: $E/\Delta E > 145$

Modes of AES spectra acquisition:

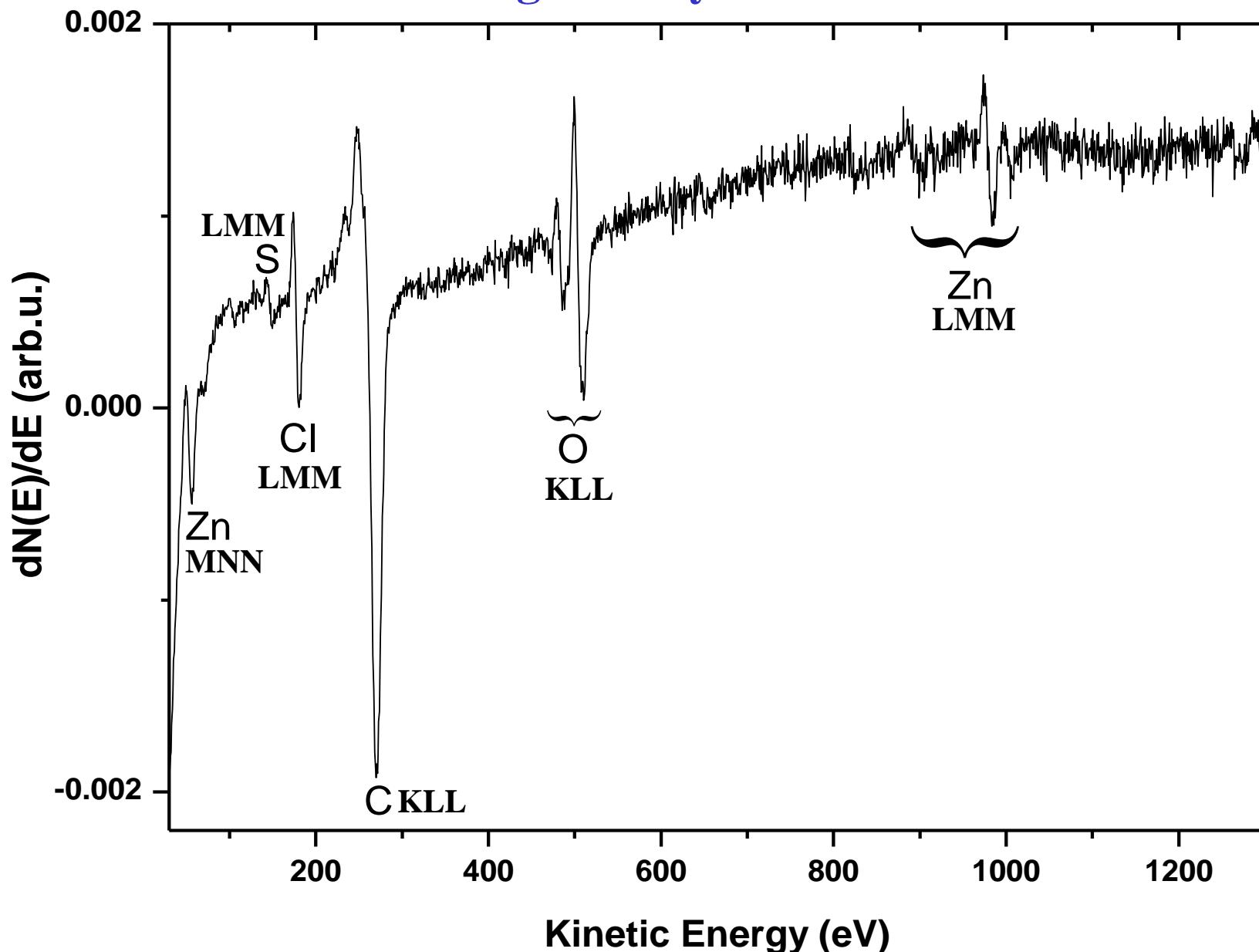
integral



differential

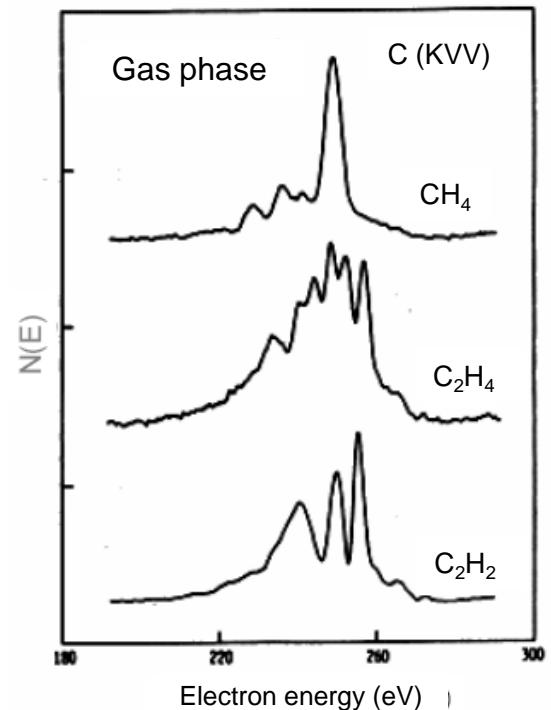


Auger electron spectrum of a ZnO layer grown by ALD

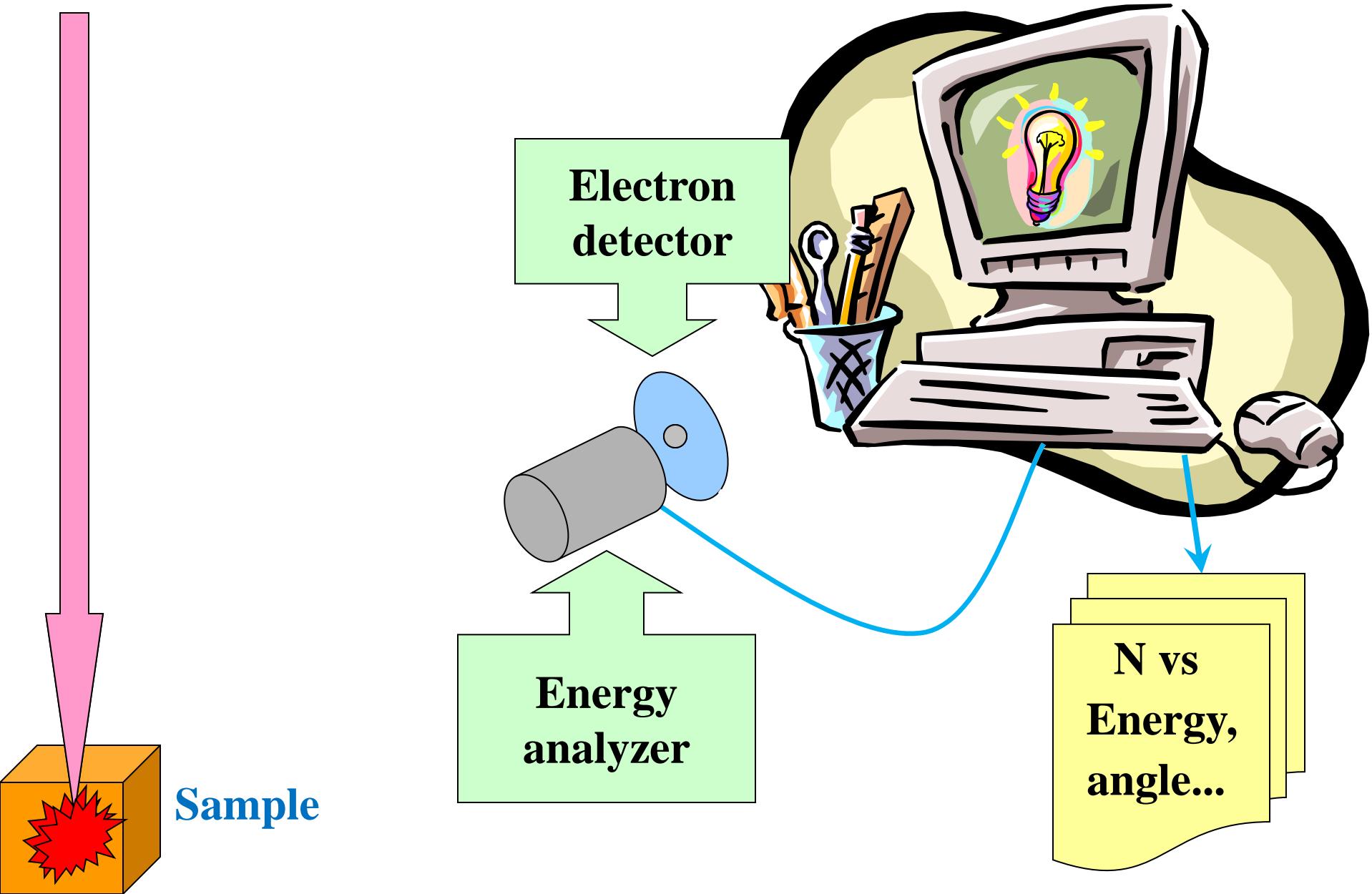


Auger electron spectroscopy:

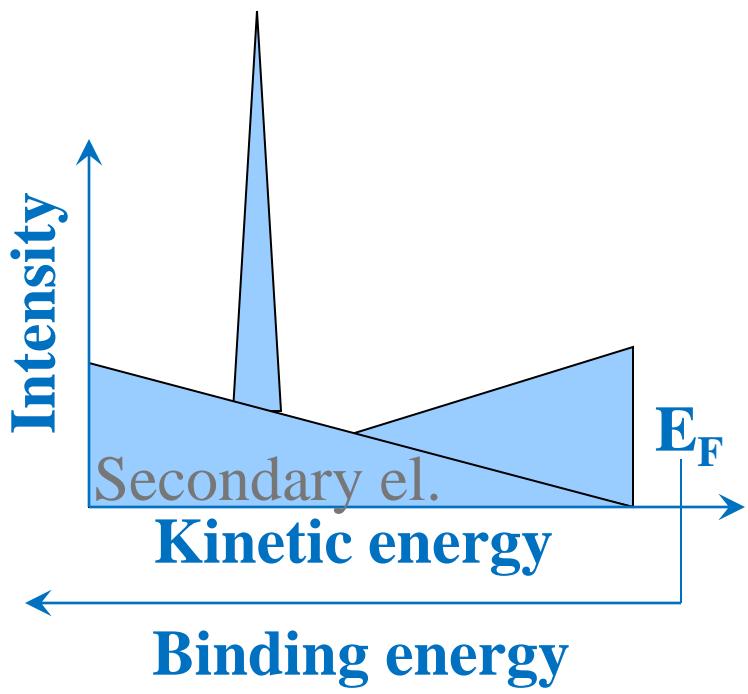
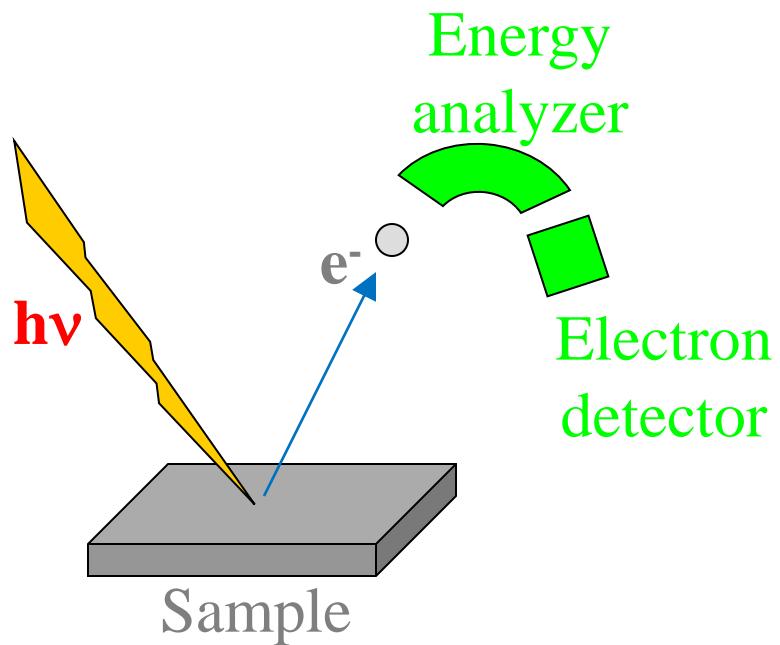
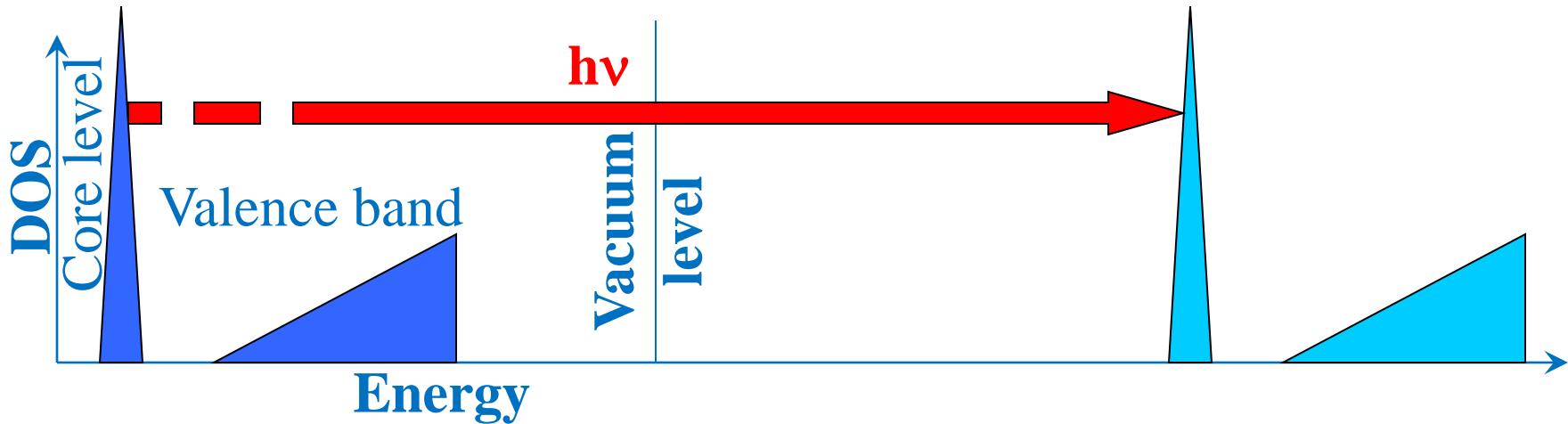
1. Analysis of the sample surface composition - detection of all elements except hydrogen and helium
2. Simple interpretation of spectra - a large database of reference spectra
3. Quantitative analysis possible - especially by comparison with standards
4. Possibility to analyze the 2D or 3D distribution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



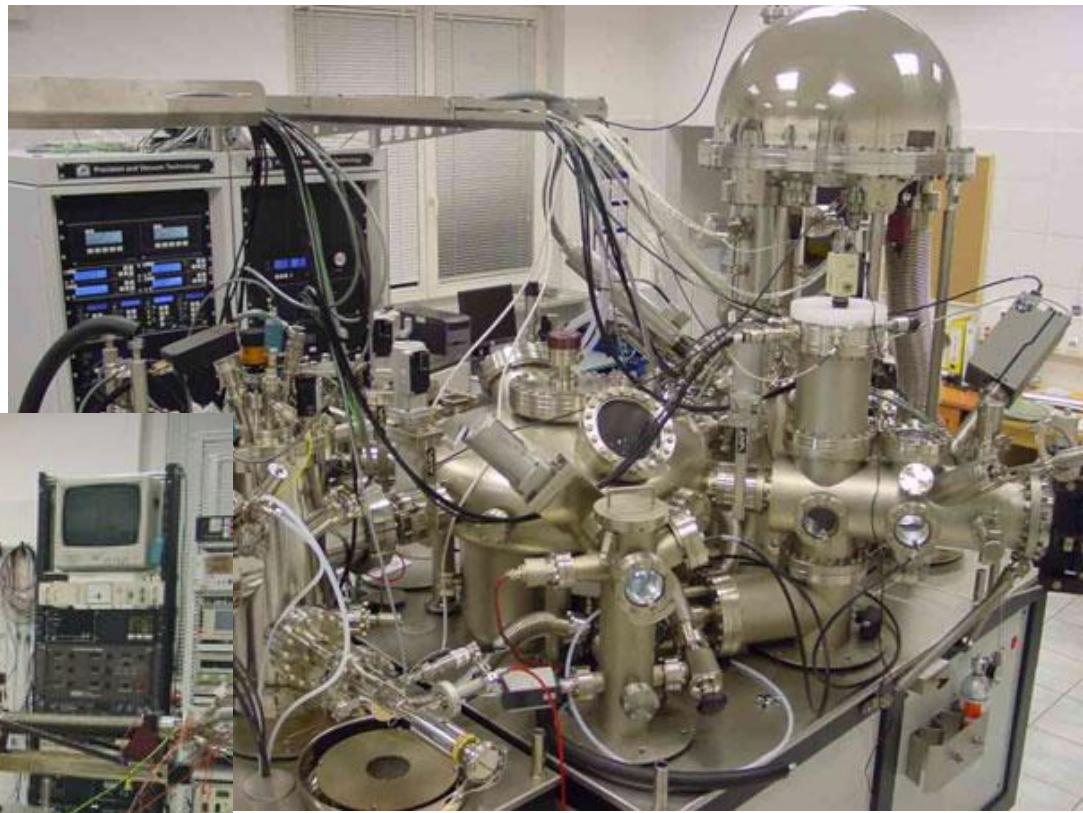
Photoemission spectroscopy



Spektroskopia fotoemisyjna



Photoemission needs Ultra High Vacuum (UHV)!



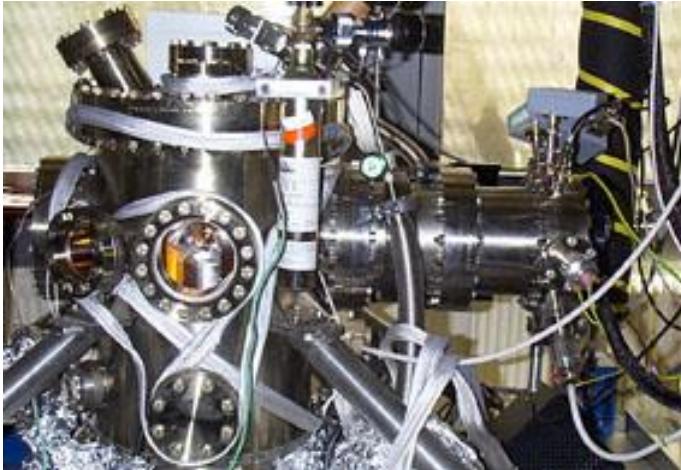
atom.ik-pan.krakow.pl

Surface preparation

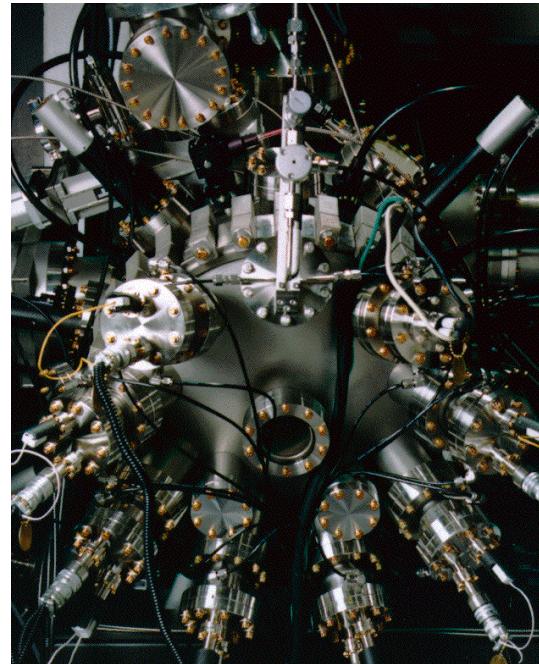
www.mshel.com



□ Cleavage



□ *In situ* epitaxy



www.ems.psu.edu

□ *In situ* cleaning:

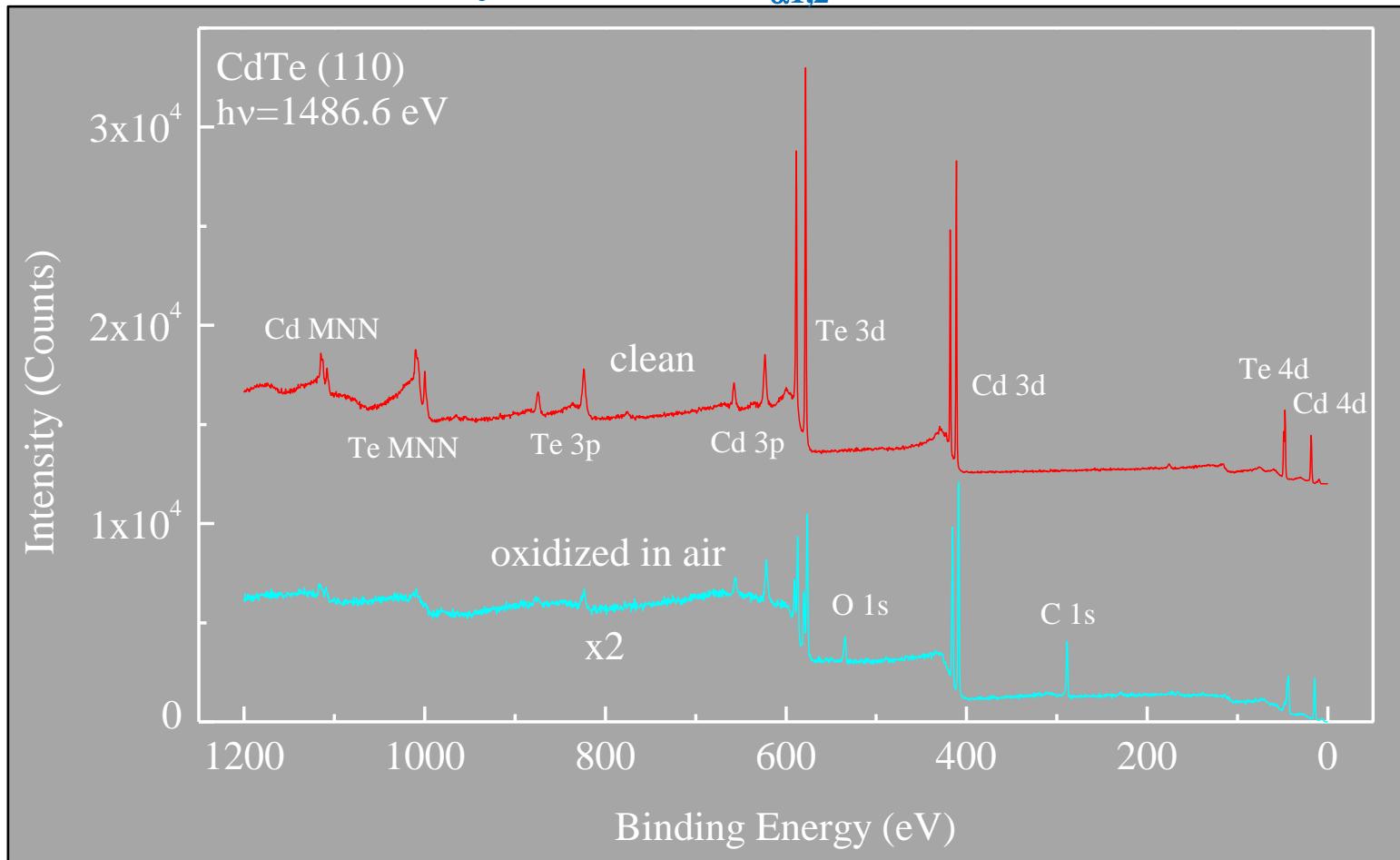
- ion etching
- annealing

www.exphys.uni-linz.ac.at

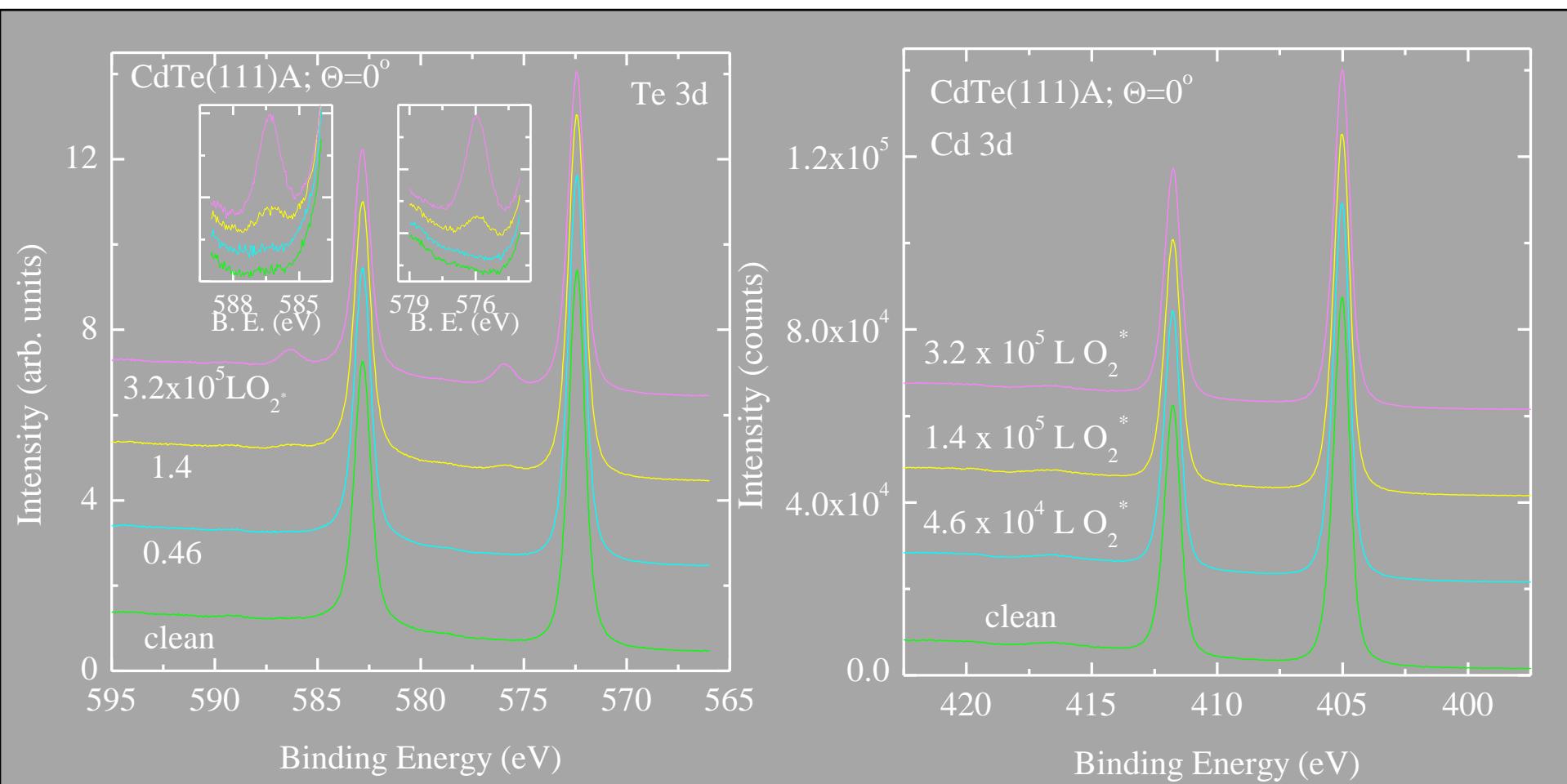
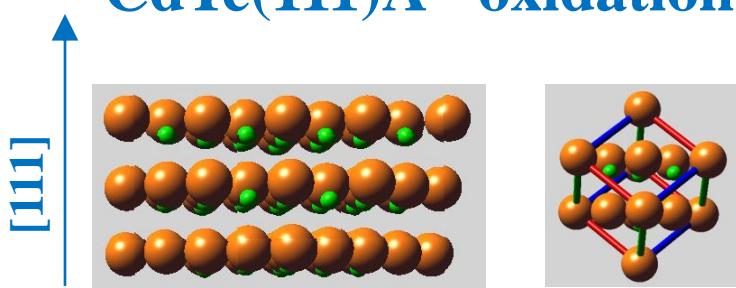
X-ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)

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

X-ray source: Al K_{α1,2} - 1486.6 eV



CdTe(111)A - oxidation

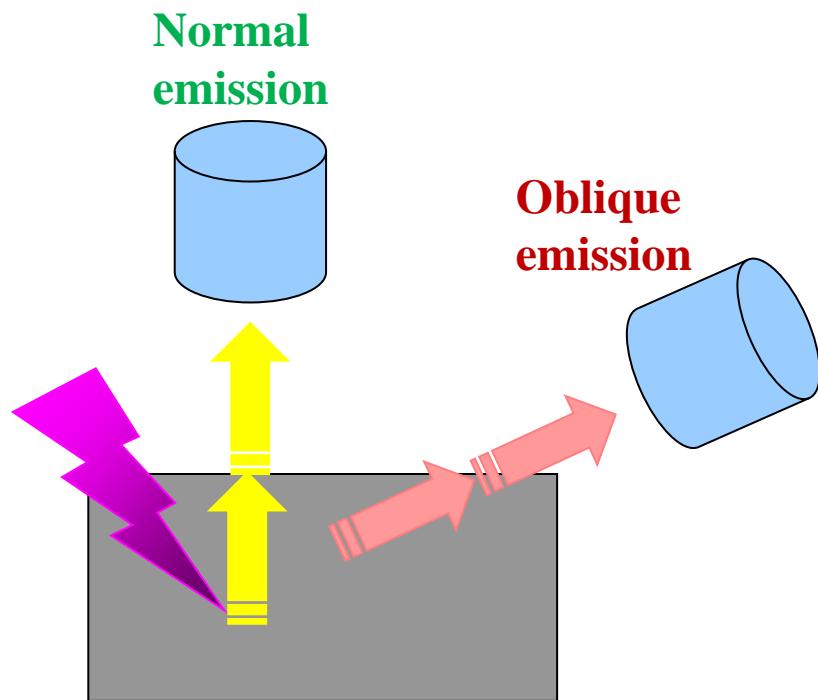


Angular XPS

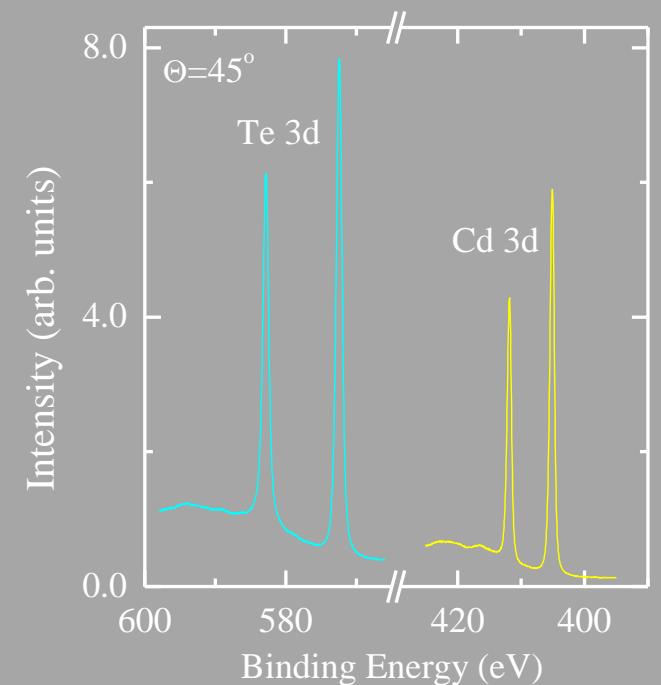
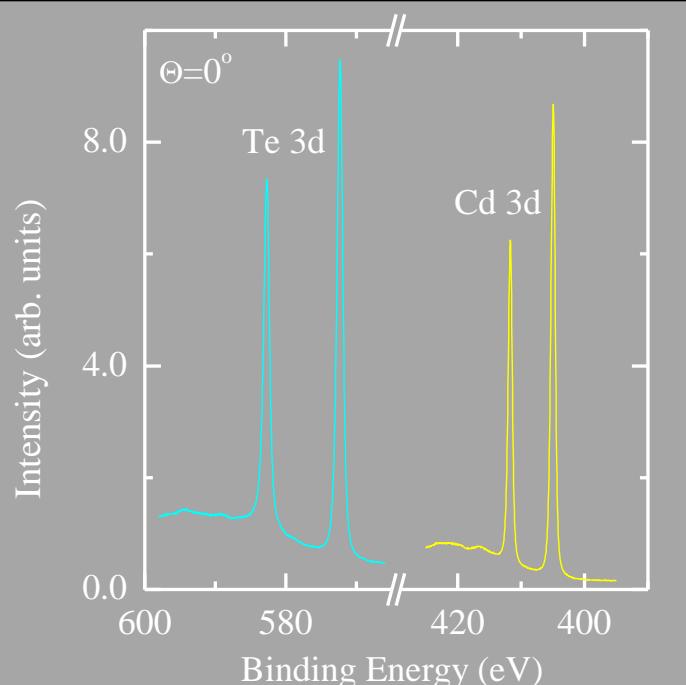
- enhanced surface sensitivity

CdTe(111)A

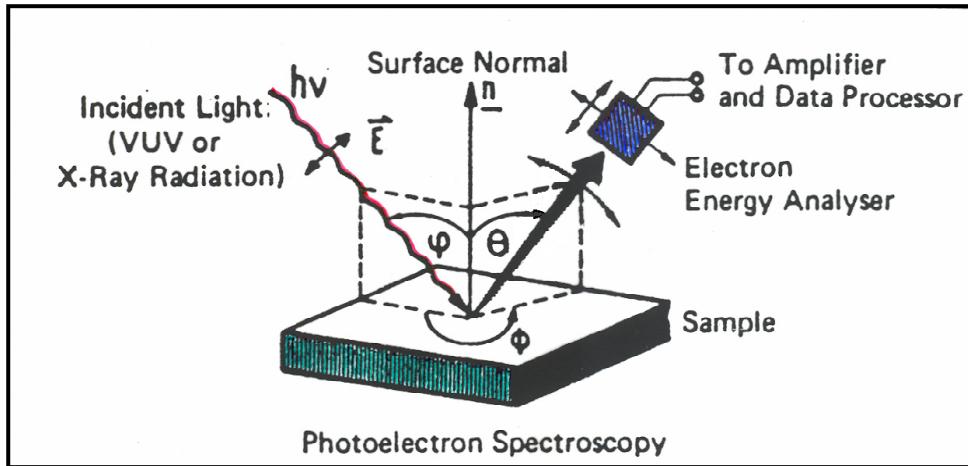
Normal
emission



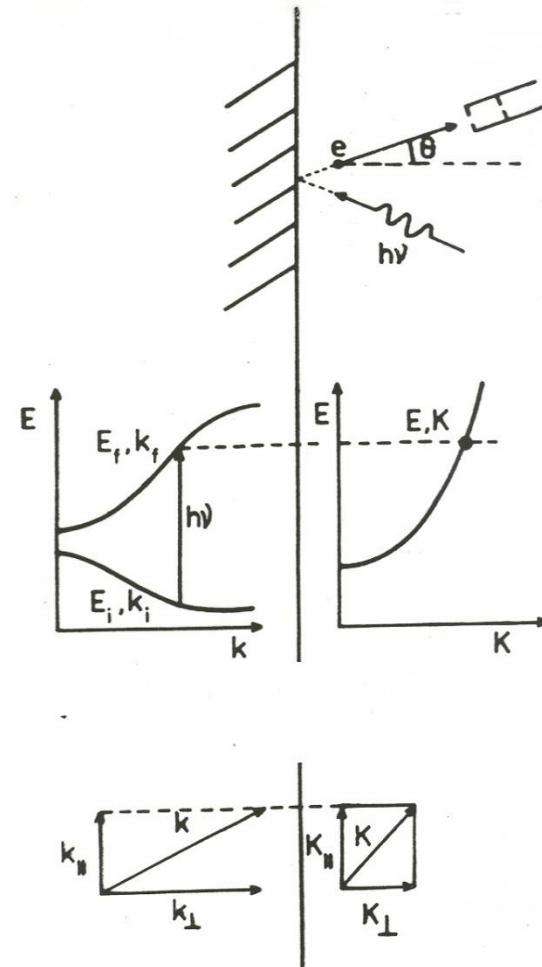
B.J. Kowalski, B.A. Orlowski, J. Ghijsen,
Appl. Surf. Sci. **166**, 237 (2000)



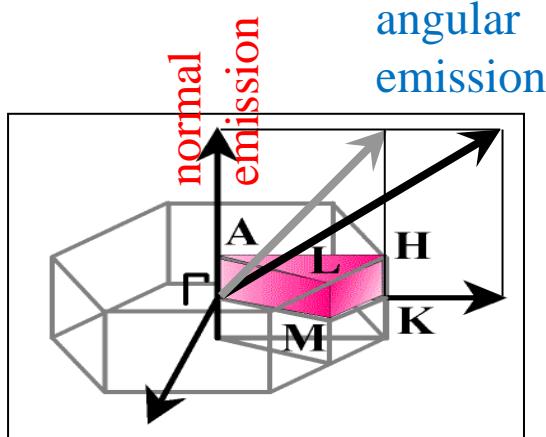
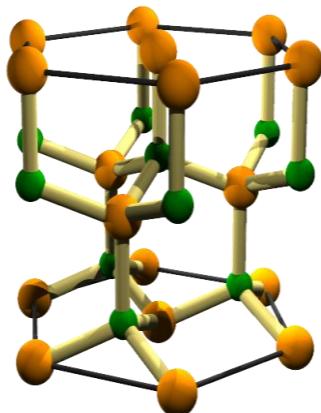
Angle-resolved photoelectron spectroscopy



Crystal Vacuum



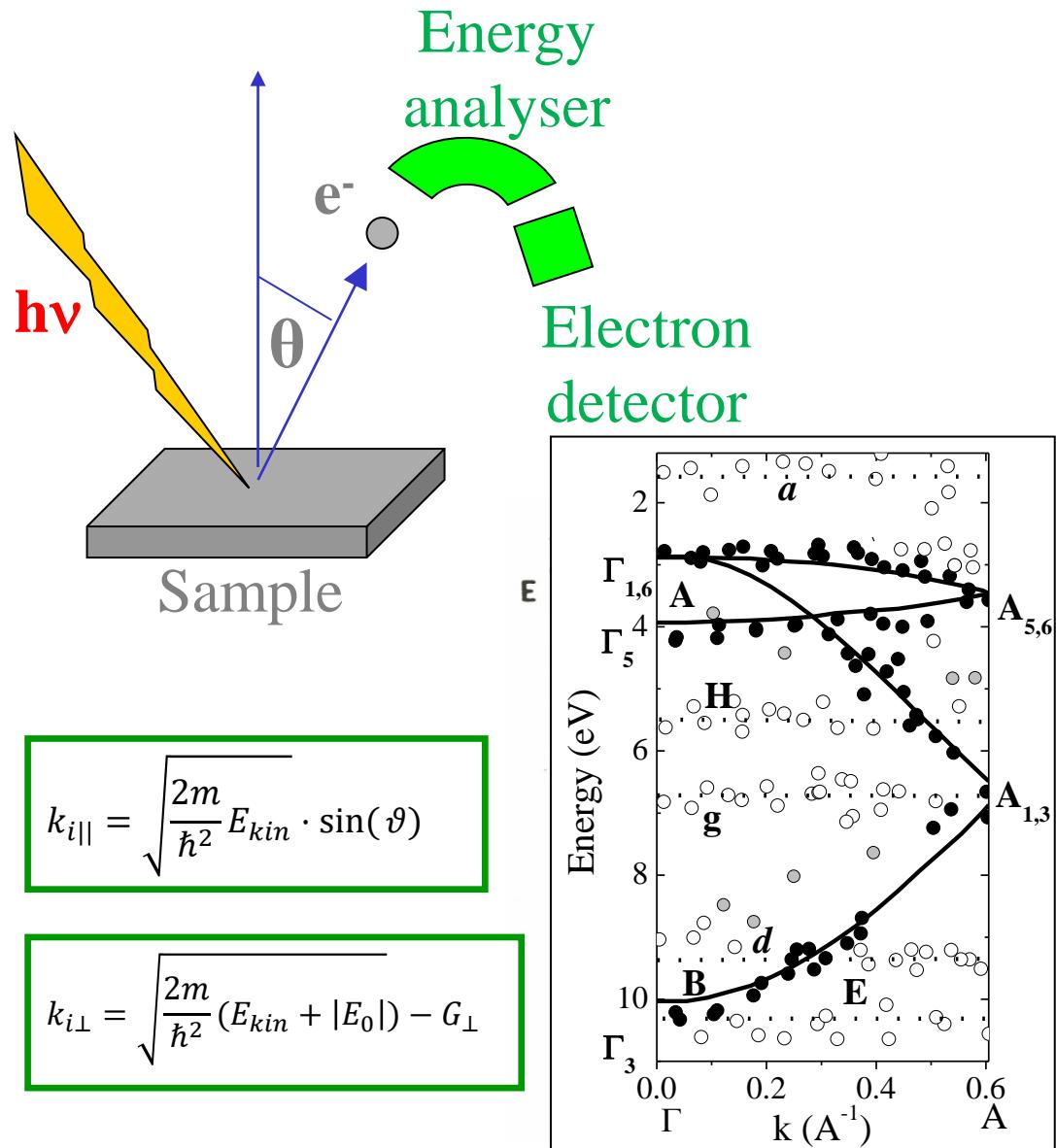
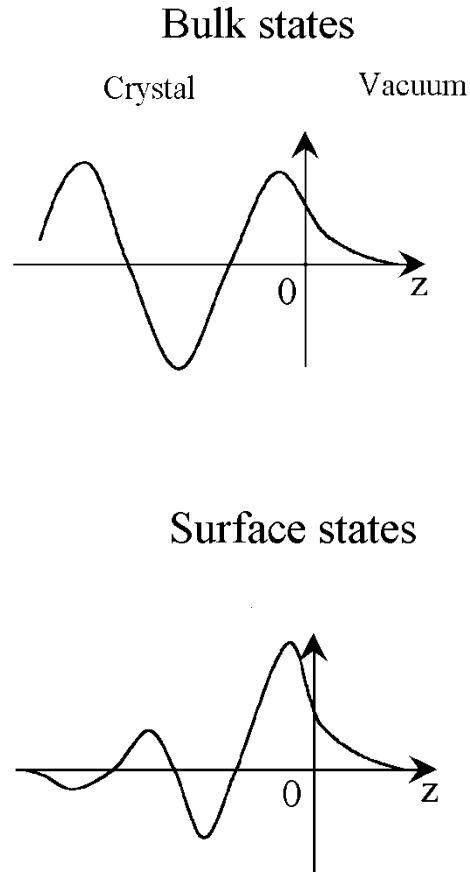
Example:

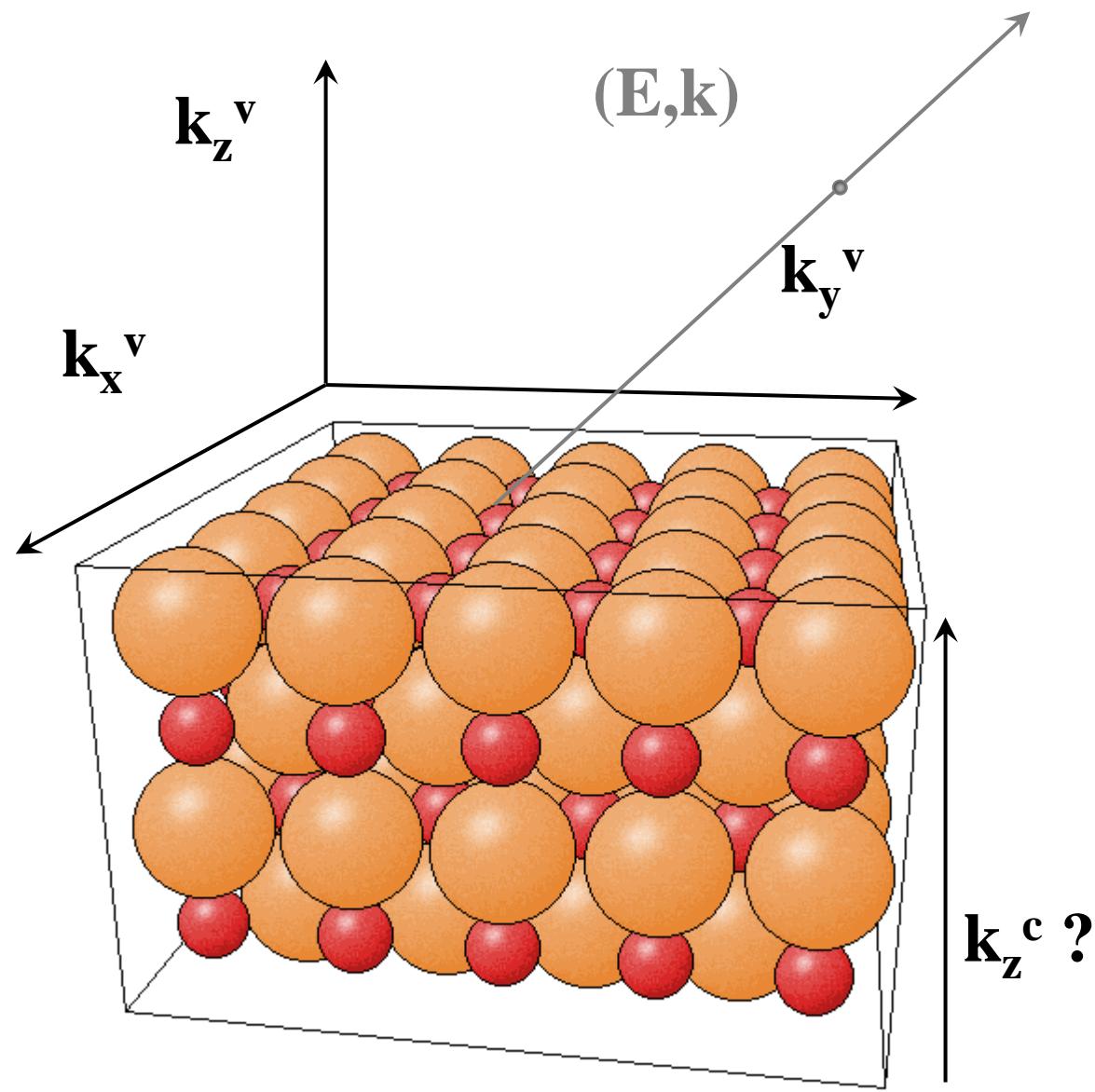


Brillouin zone

Wurtzite structure

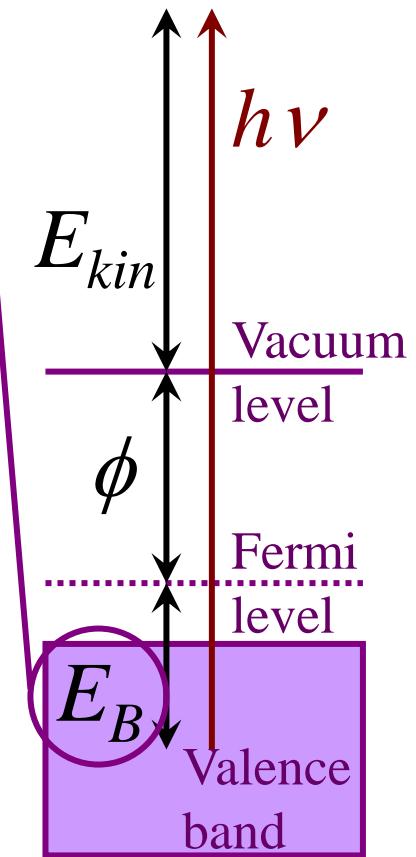
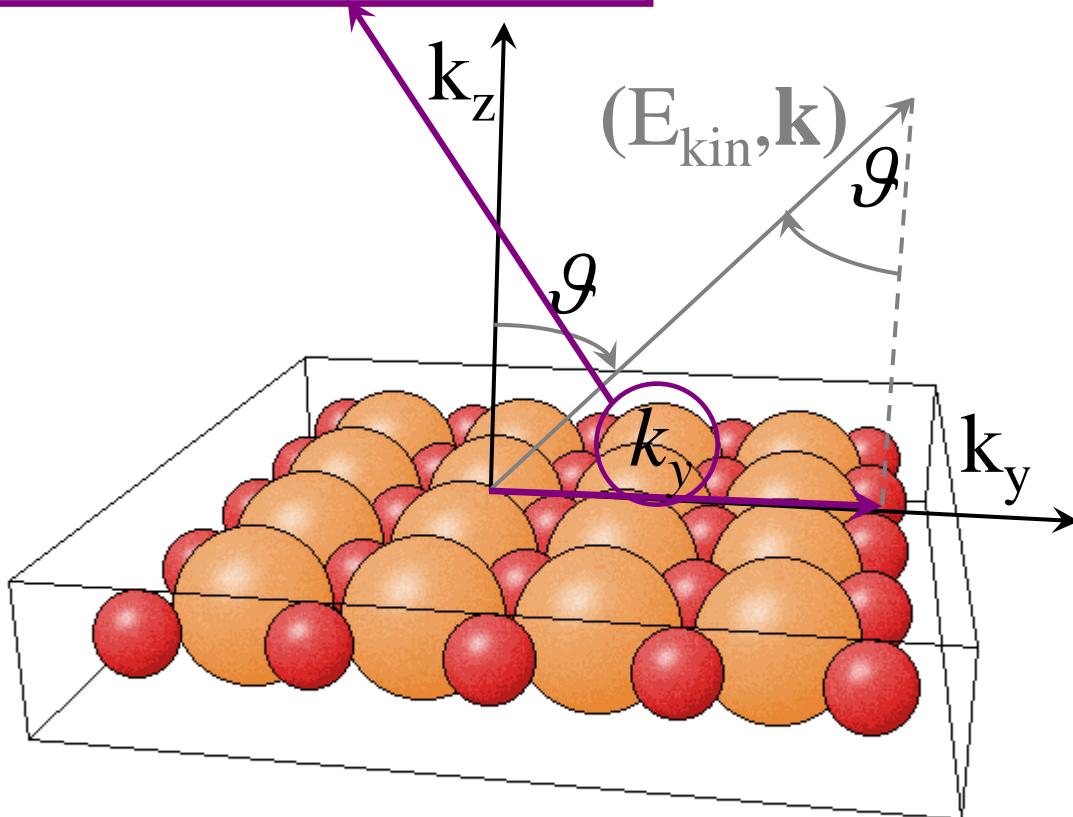
Angle-resolved photoelectron spectroscopy of surface and bulk states

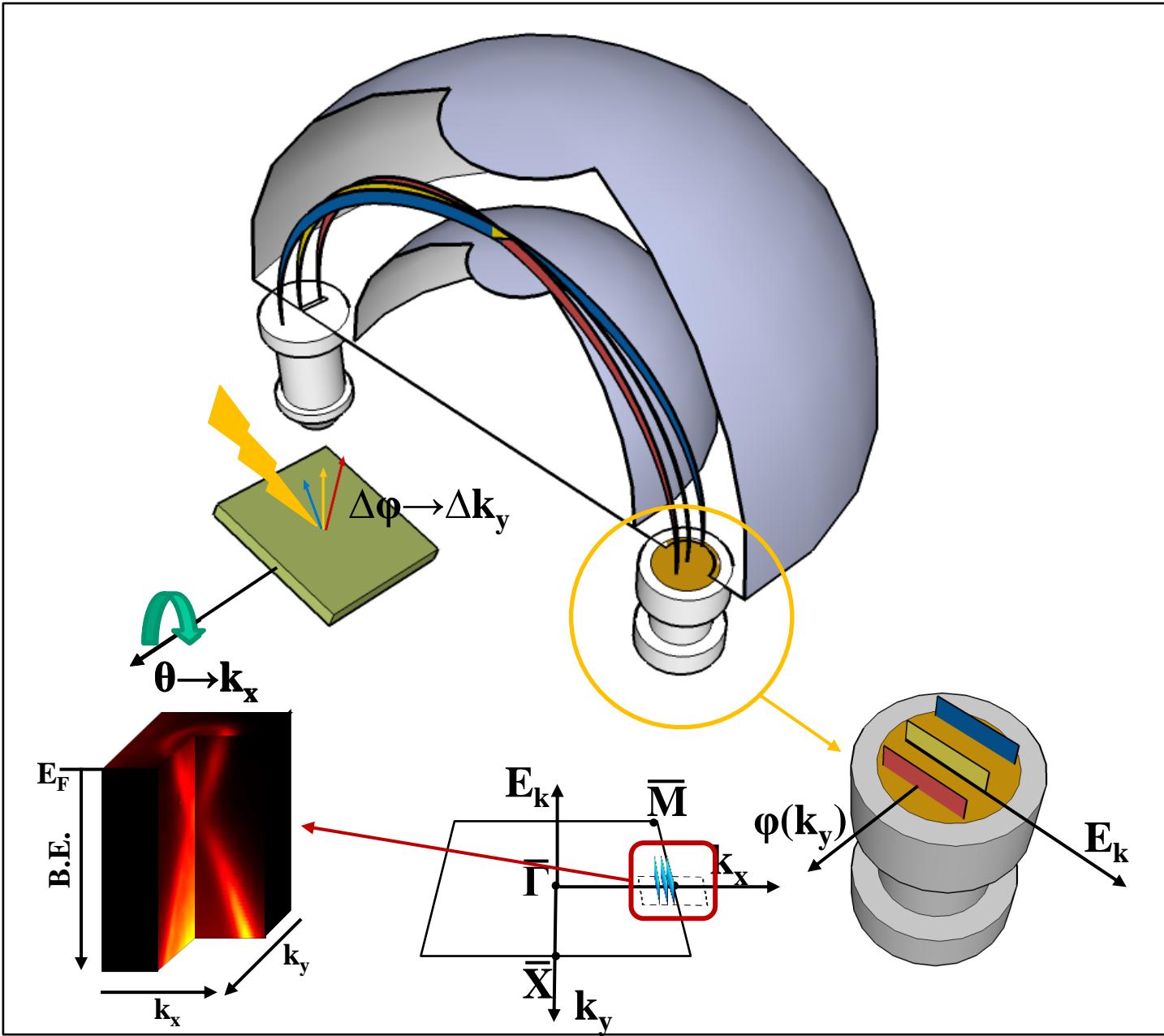




$$k_y = \sqrt{\frac{2m}{\hbar^2} E_{kin} \cdot \sin(\vartheta)}$$

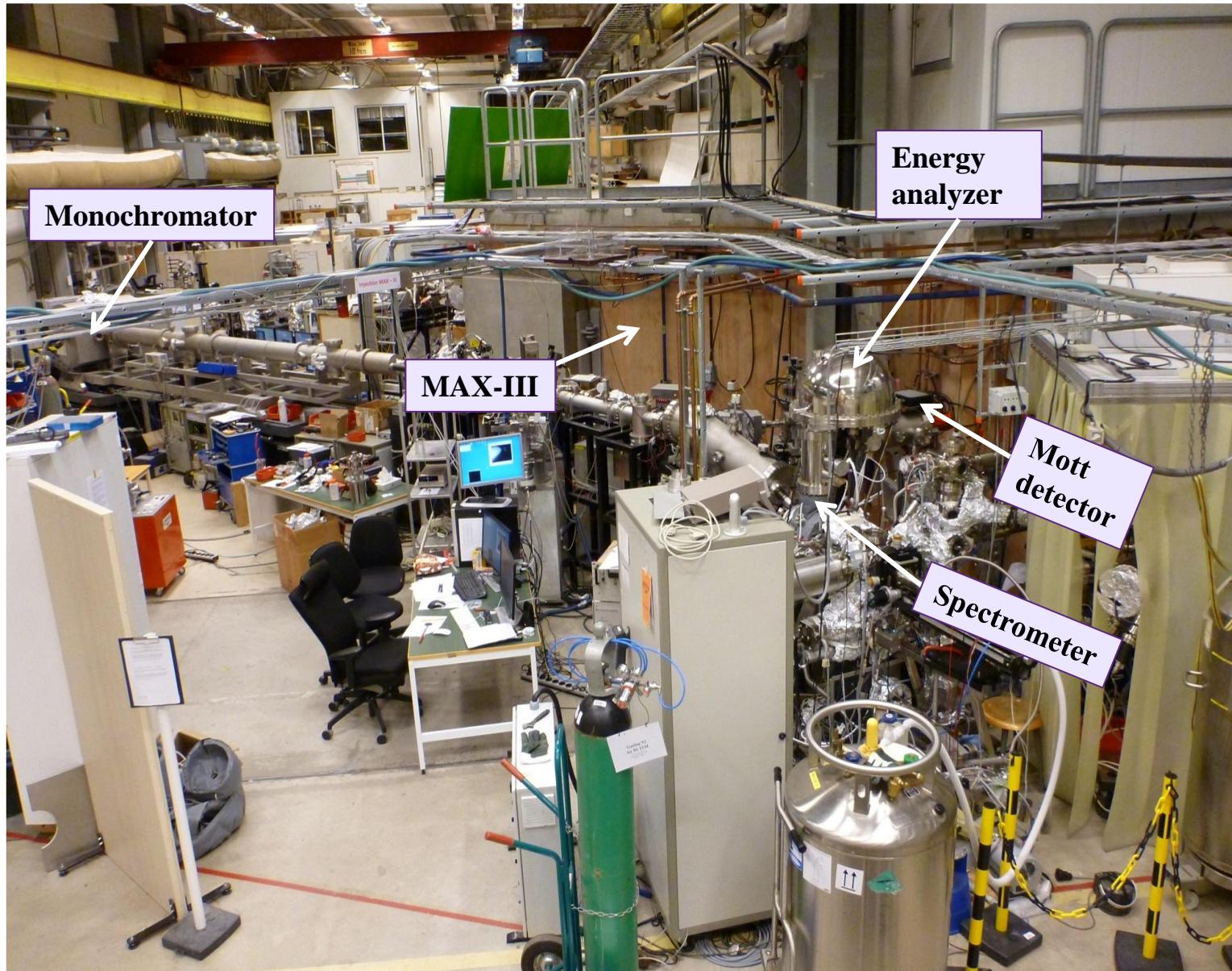
$$E_B = h\nu - (E_{kin} + \phi)$$





Beamline I3

MAX-lab, Lund University, Sweden

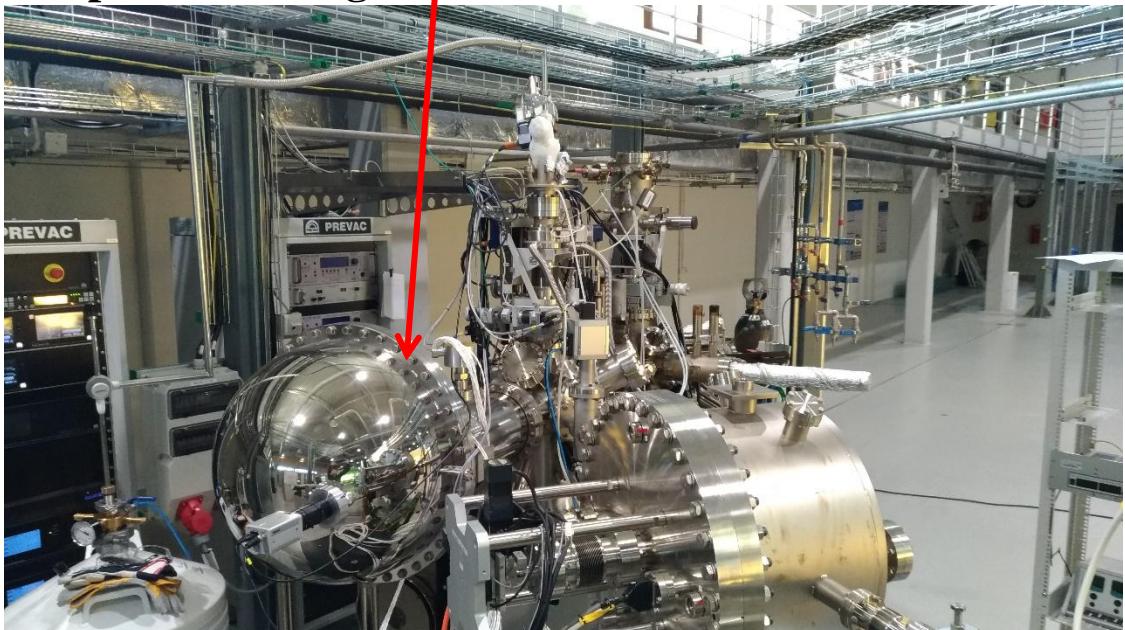


Beamline URANOS

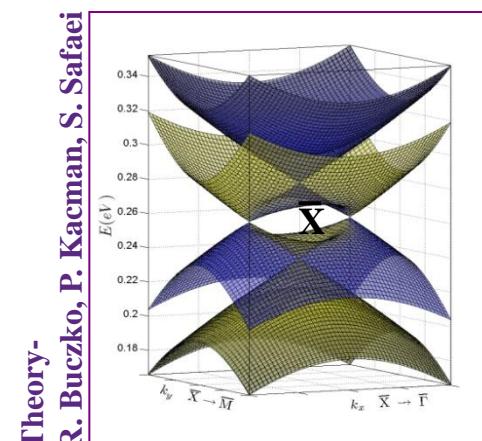
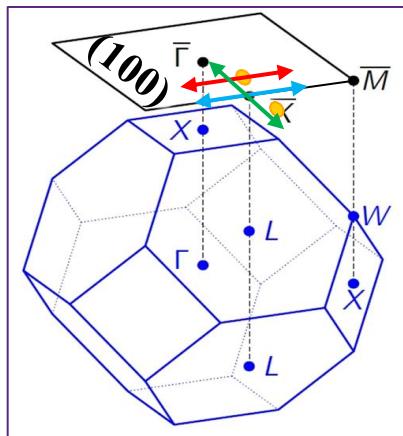
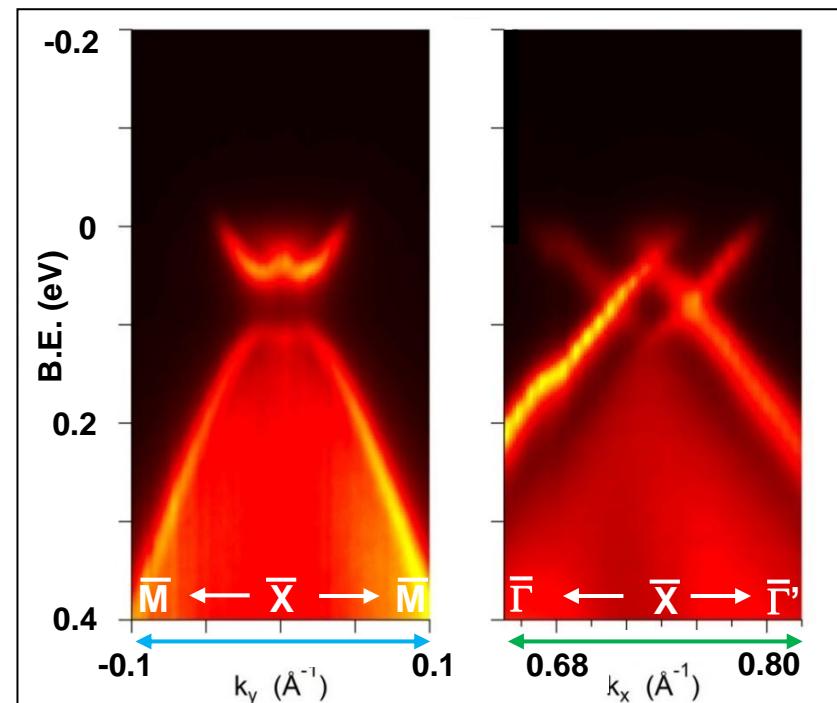
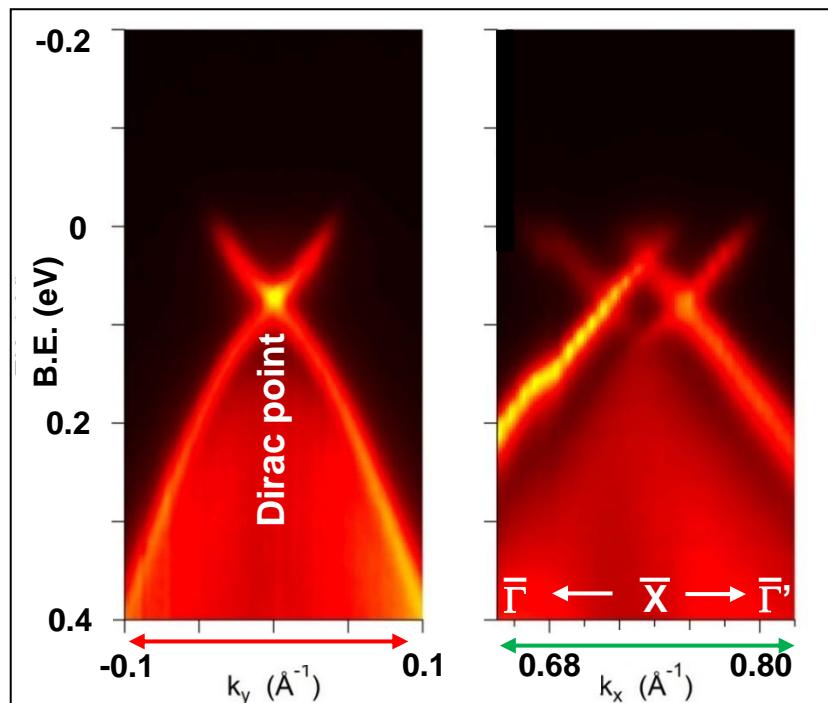
NCSR SOLARIS, Jagiellonian University, Kraków, Poland



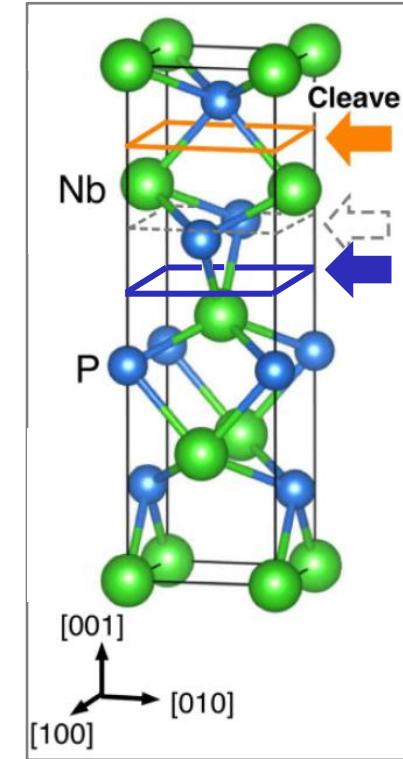
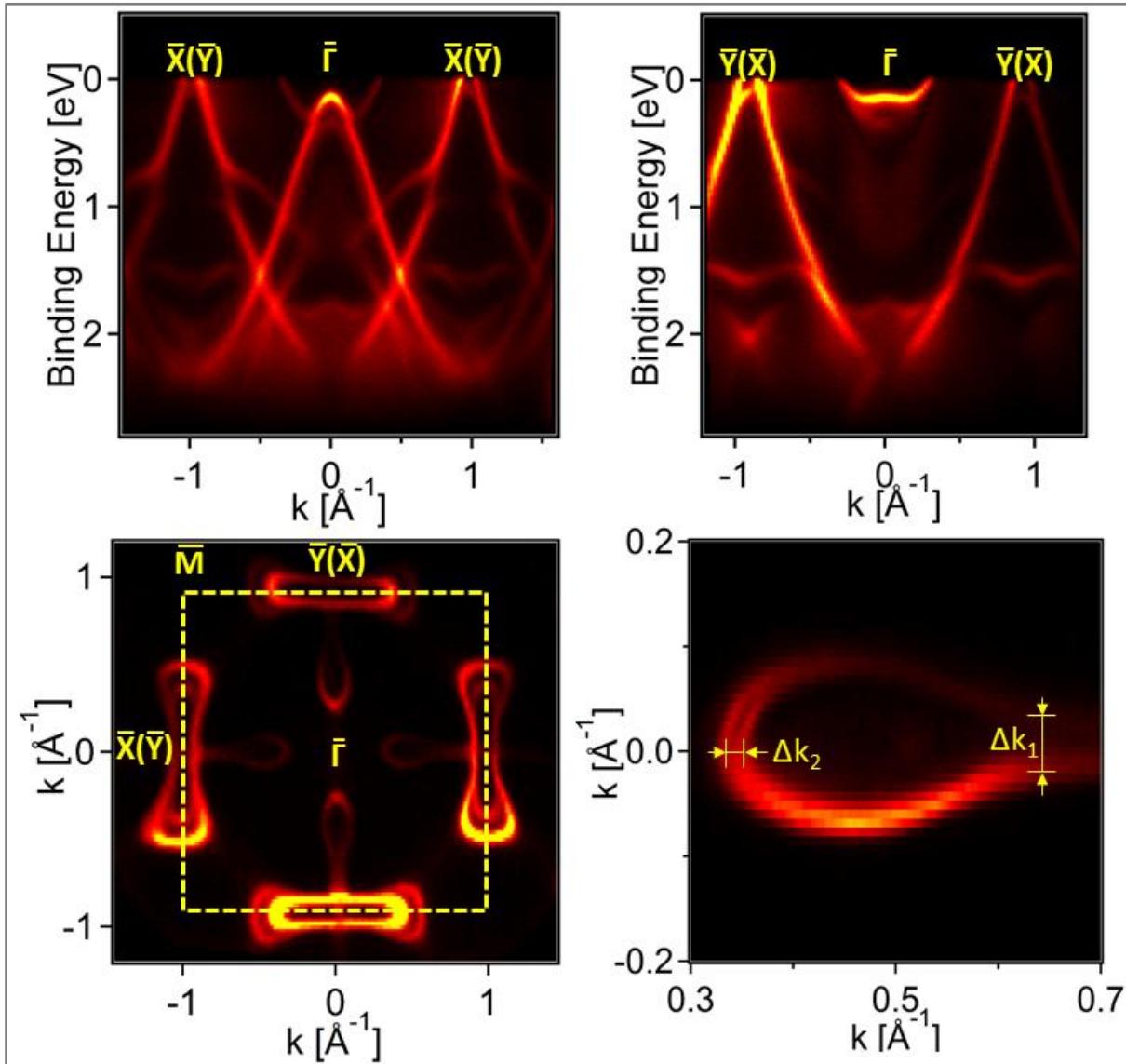
- Elliptically polarizing quasiperiodic undulator of APPLE II type
- Monochromator combining normal (NIM) and grazing incidence (PGM) optics (the photon energy range of 8–100 eV)
- SCIENTA OMICRON DA30L photoelectron spectrometer
- The energy and angular resolution: 1.8 meV and 0.1°
- Temperature range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



Topological crystalline insulator $\text{Pb}_{0.67}\text{Sn}_{0.33}\text{Se}$, $T=87$ K, $h\nu=18.5$ eV



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

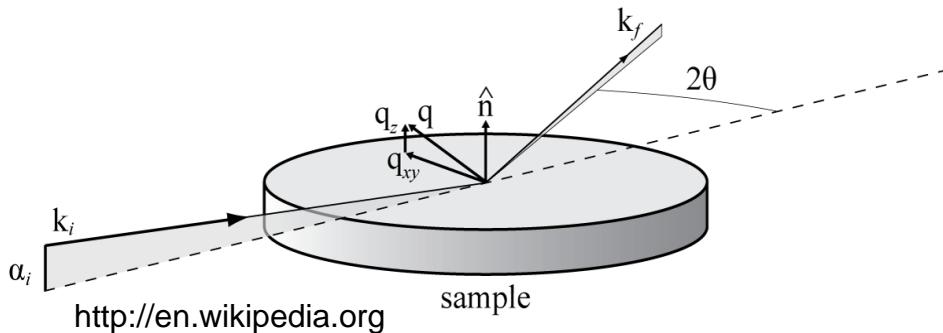
X-ray total-external-reflection–Bragg diffraction: A structural study of the GaAs-Al interface

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

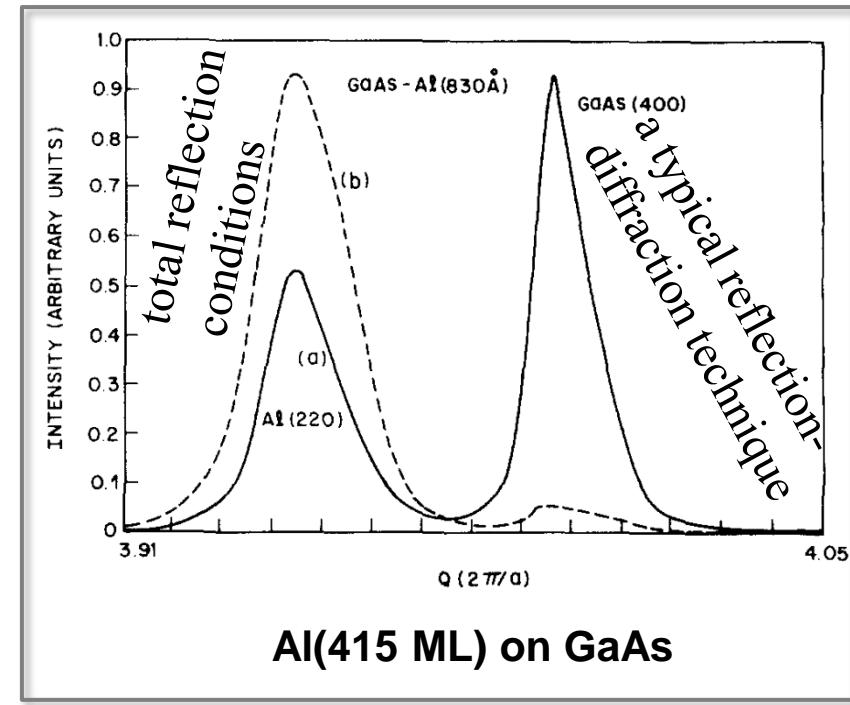
(Received 19 March 1979; accepted for publication 8 June 1979)

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



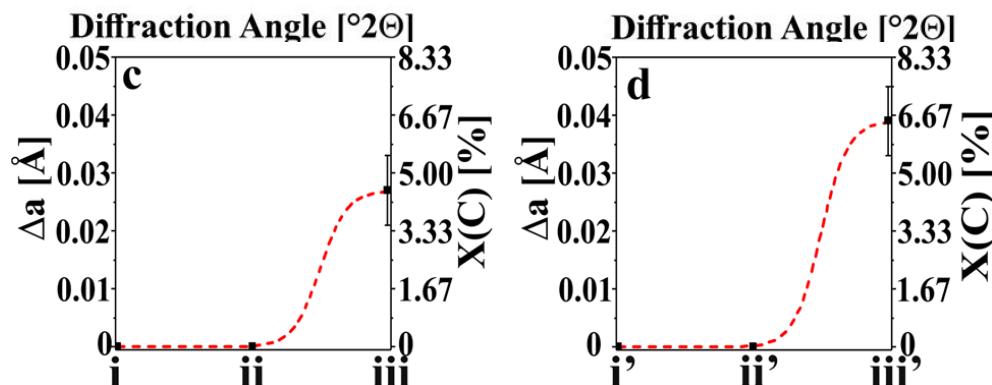
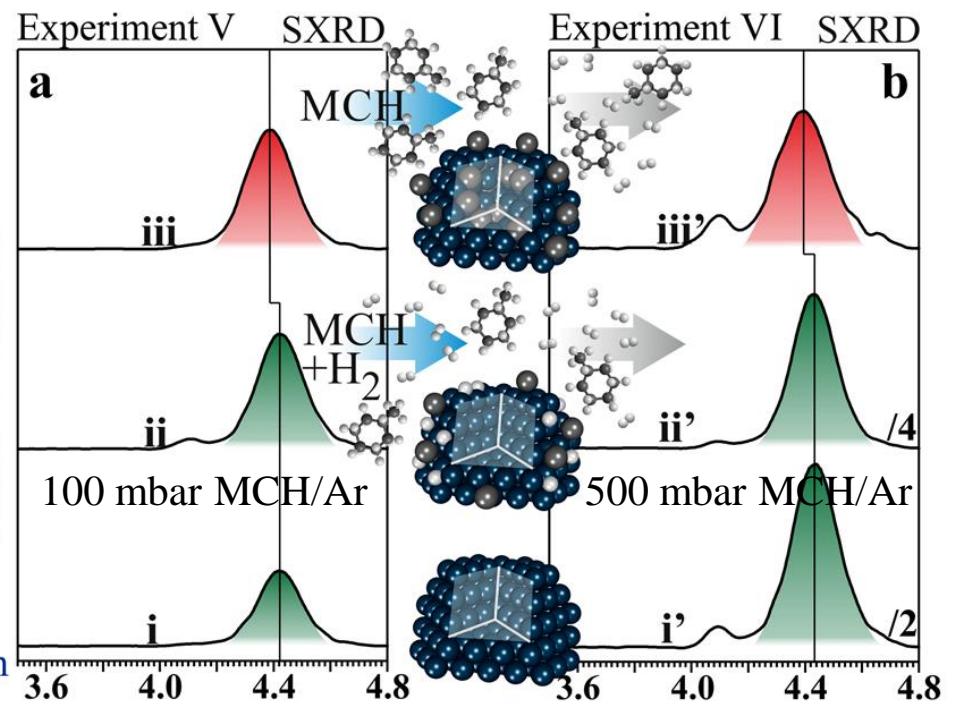
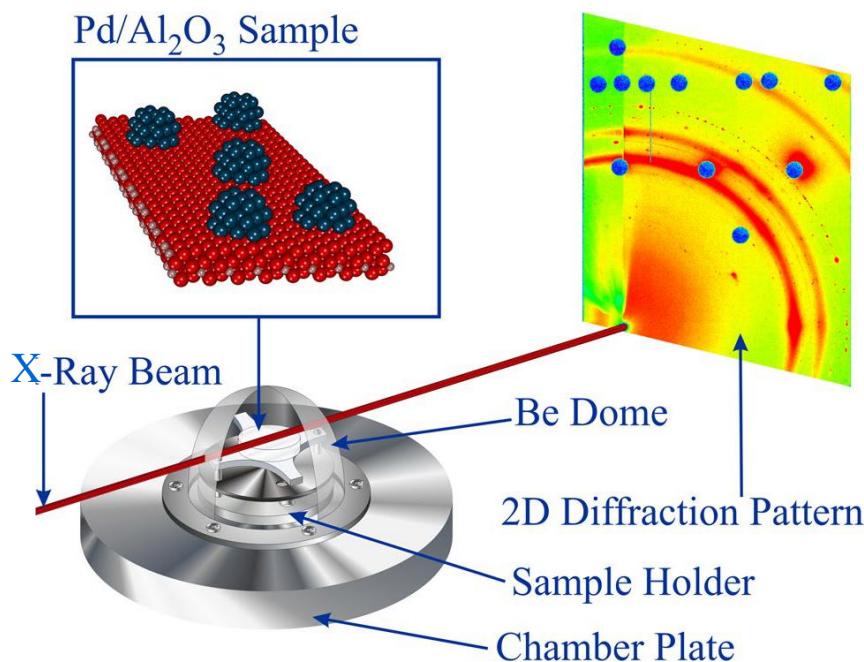
Needs strong X-ray beam –
usually from a synchrotron!



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)

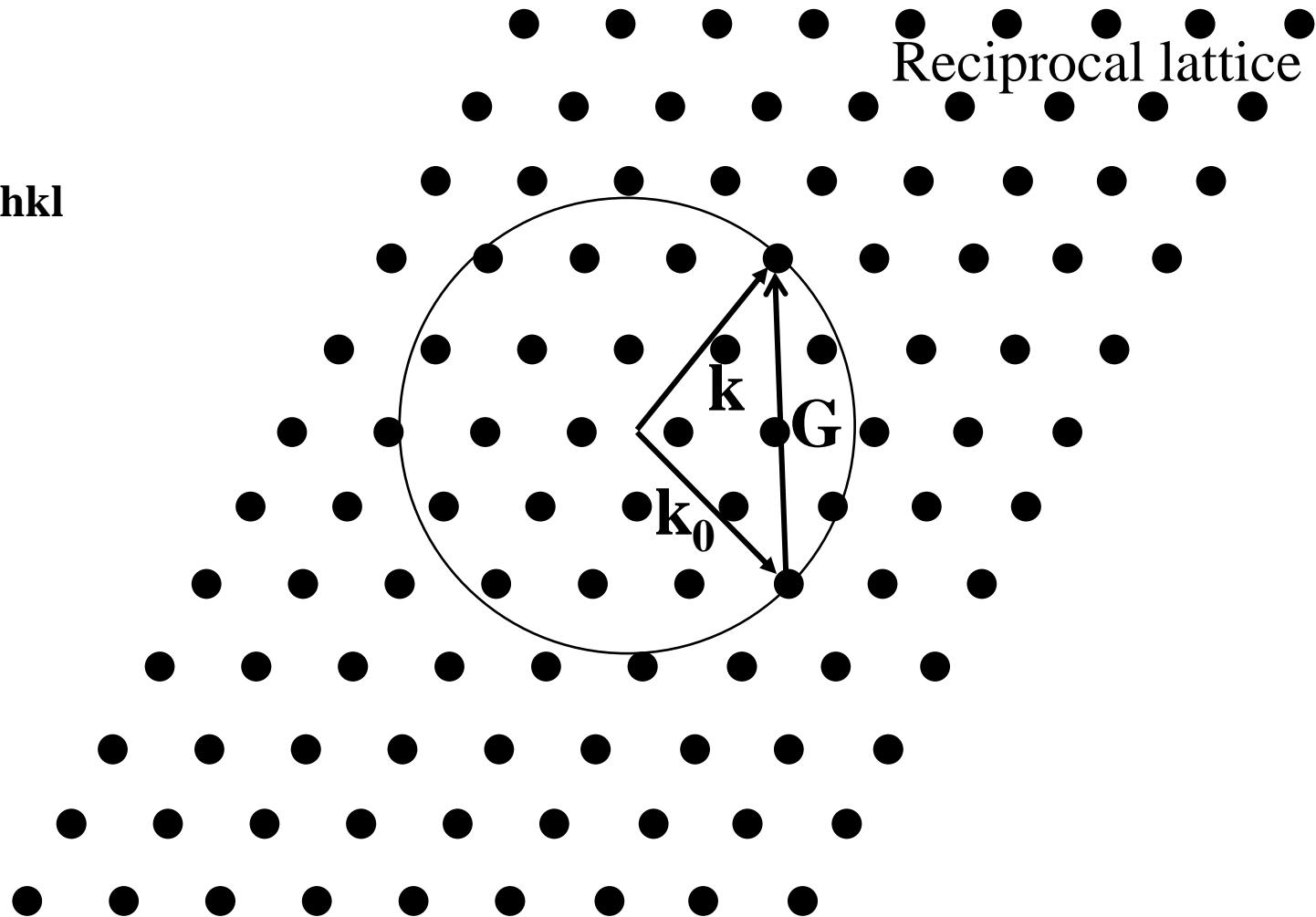
MCH: methylcyclohexane



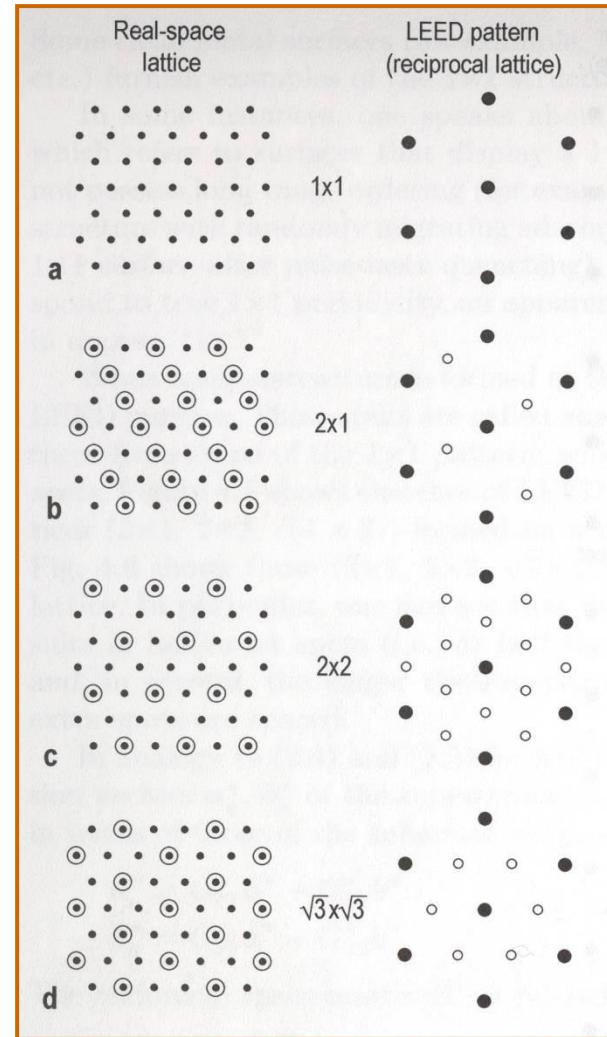
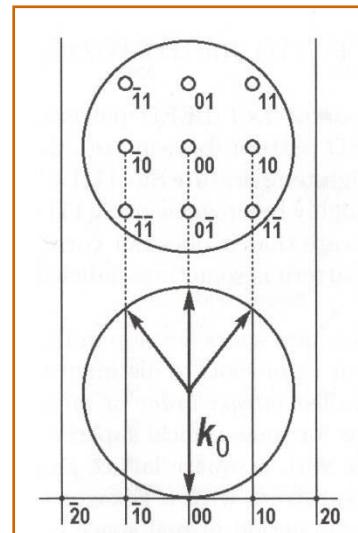
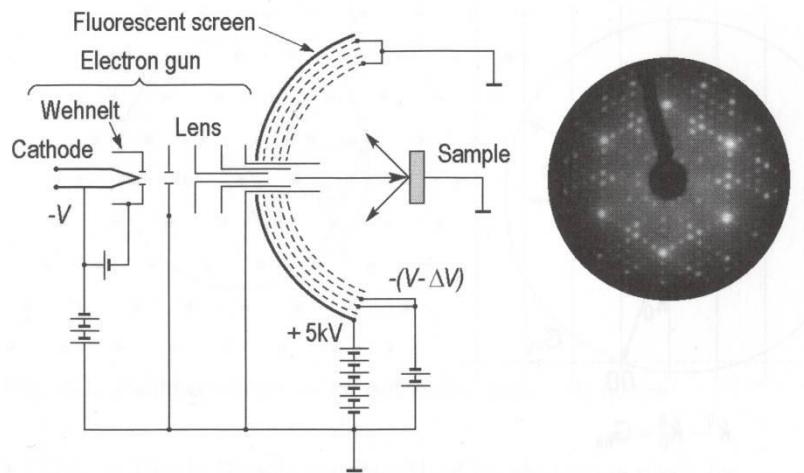
Construction of the Ewald sphere

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

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

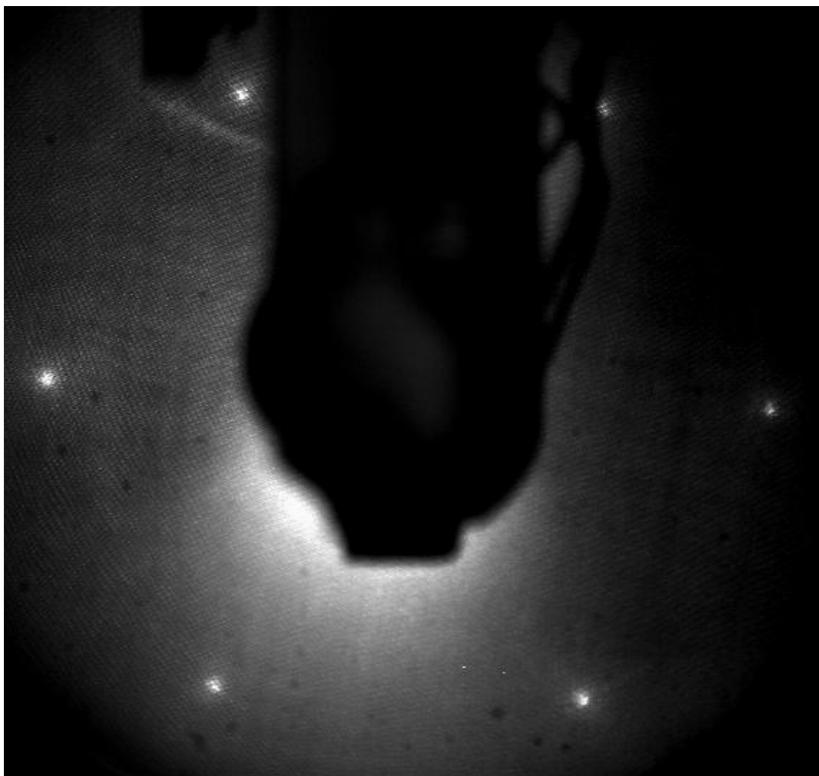


Low-Energy Electron Diffraction (LEED)

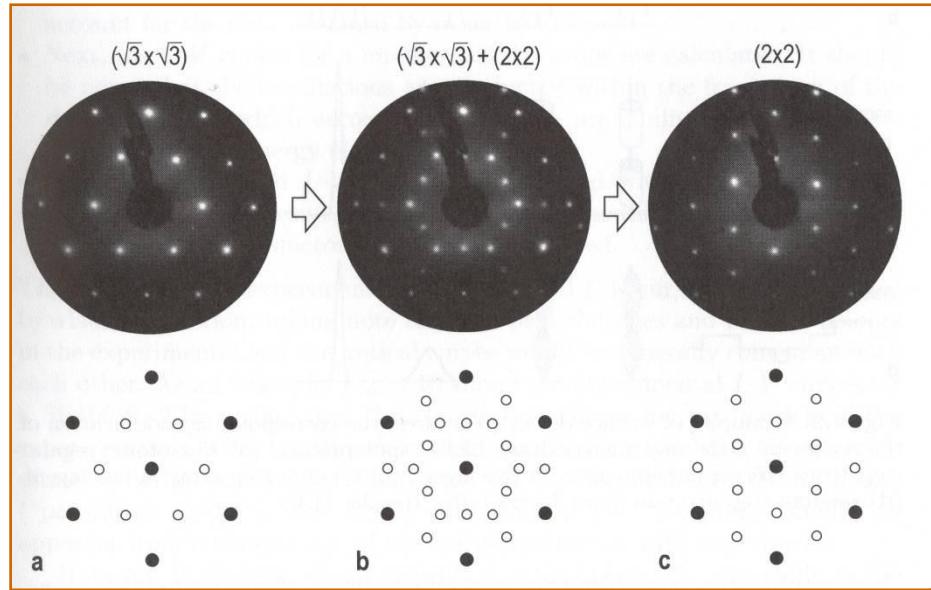


K.Oura et al.
Surface Science. An Introduction

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

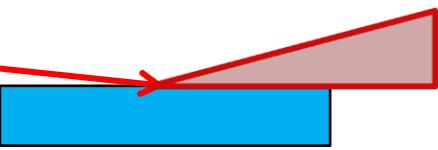
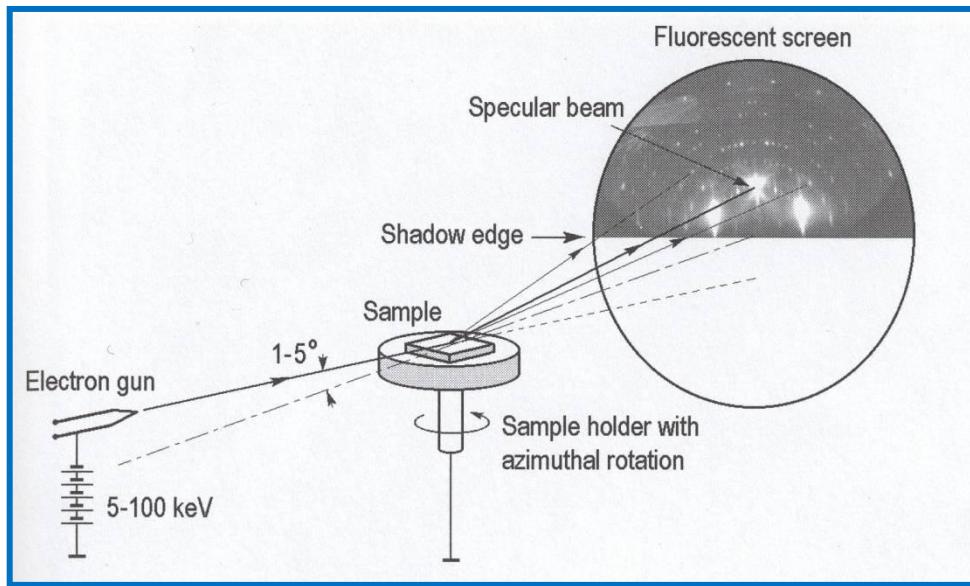


GaN(0001) (1x1)

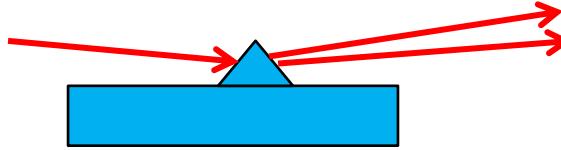


In deposition on
Si(111) $\sqrt{3} \times \sqrt{3}$ -R30°

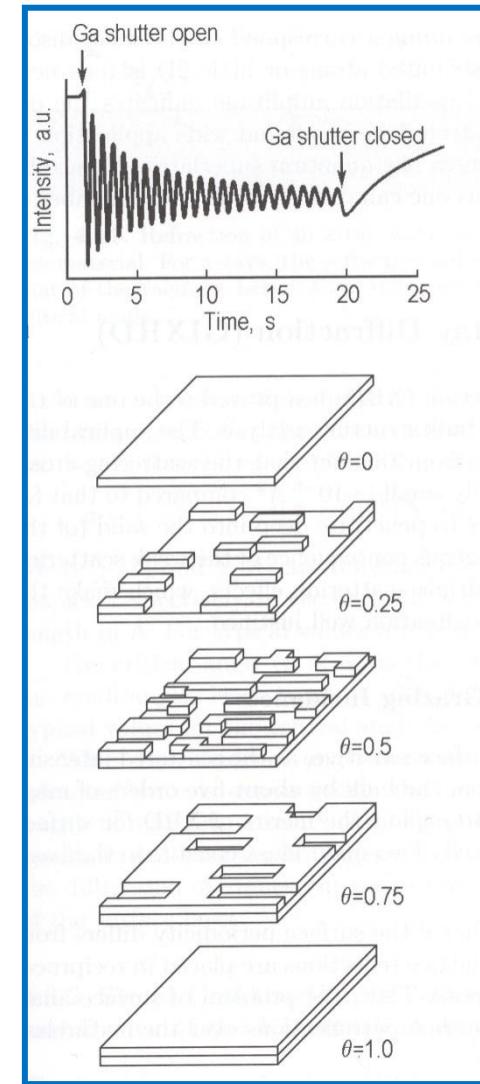
Reflection High-Energy Electron Diffraction (RHEED)



2D structure
Streaks in the
image



3D structure
Dots in the image



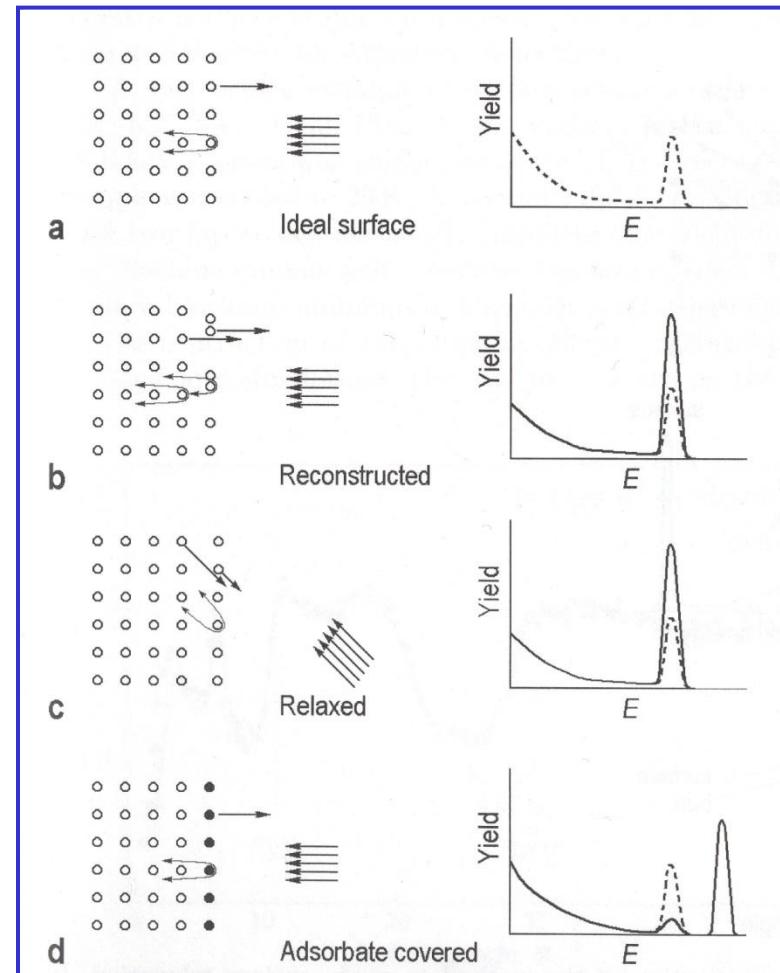
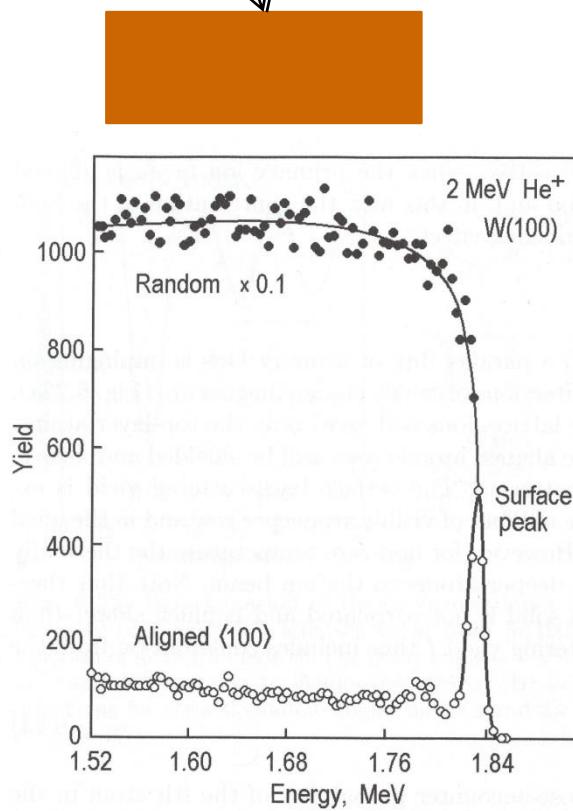
K.Oura et al.
Surface Science. An Introduction

Ion scattering methods

Rutherford Backscattering Spectrometry (RBS)

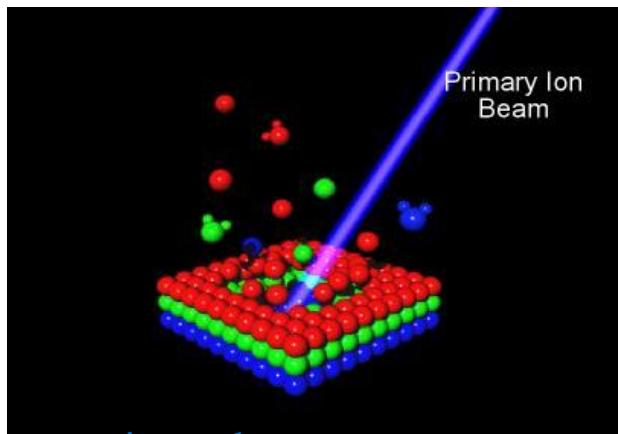
e.g. ${}^4\text{He}$
2 MeV

detector



Secondary Ion Mass Spectrometry (SIMS)

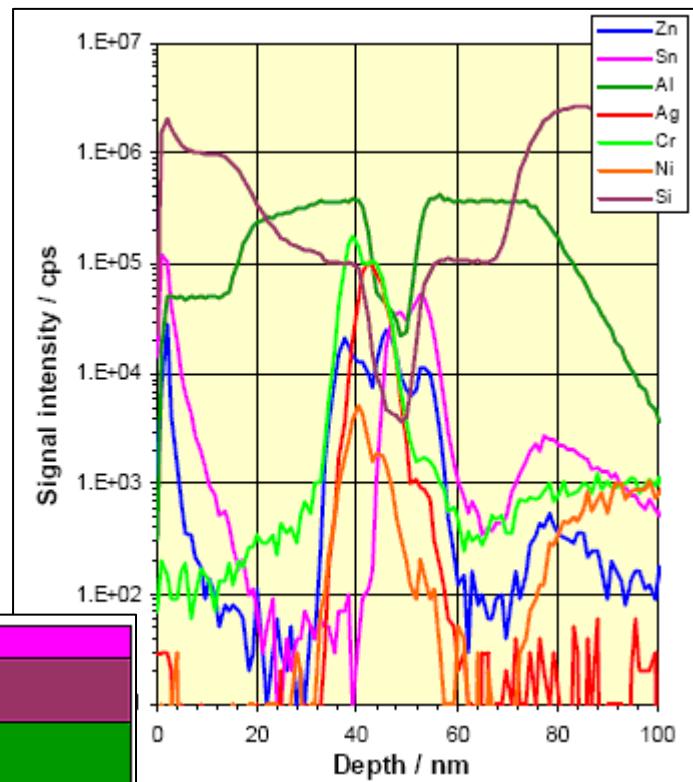
e.g. Cs^+ lub Ar^+
1-30 keV



www.ainse.edu.au



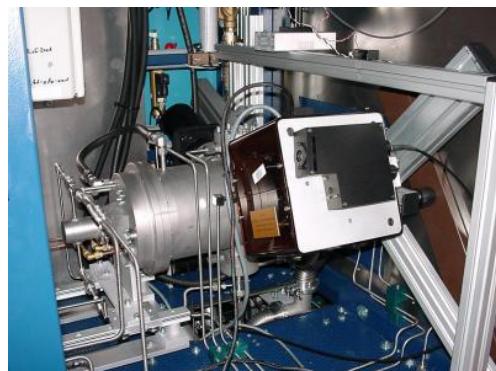
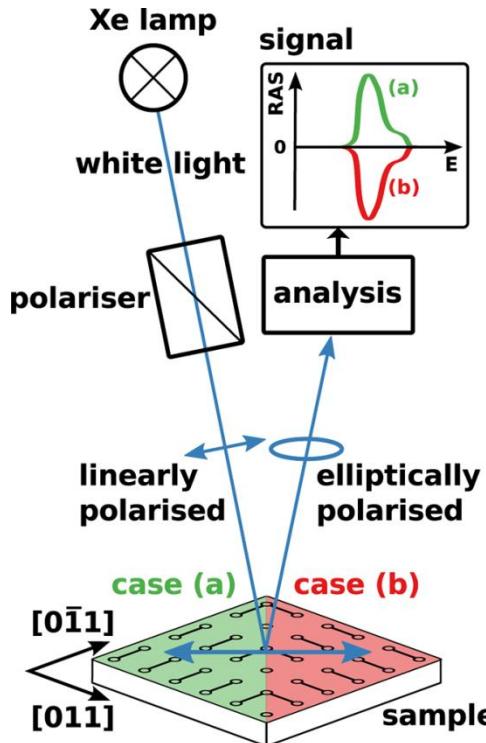
Zinc Tin Oxide
Silicon Nitride
Aluminium Nitride
Zinc Aluminium Oxide
Nickel Chrome Oxide (NiCrO_x)
Silver (10 nm)
Zinc Oxide
Zinc Tin Oxide
Aluminium Nitride
Glass Substrate



www.azom.com

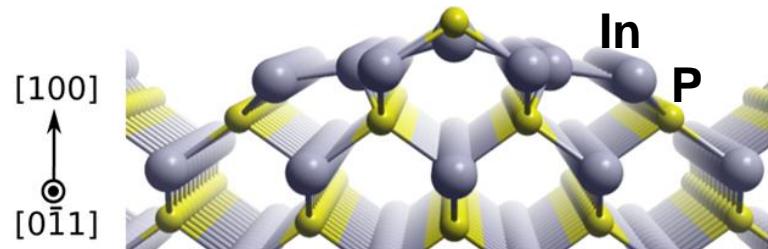
Optical methods

Reflection Anisotropy Spectroscopy (RAS)

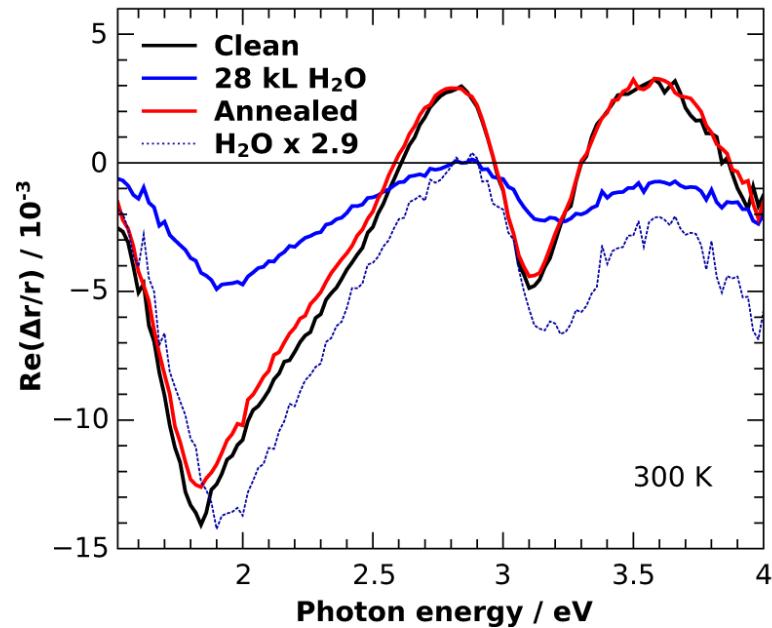


An MOCVD reactor with the RAS system
Institute of Semiconductor and Solid State
Physics, University of Linz, Austria

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



In-rich
(2x4) reconstructed
InP(100) surface



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