Chemical Characterization of Nanostructures by Photoemission X-ray Microscopy

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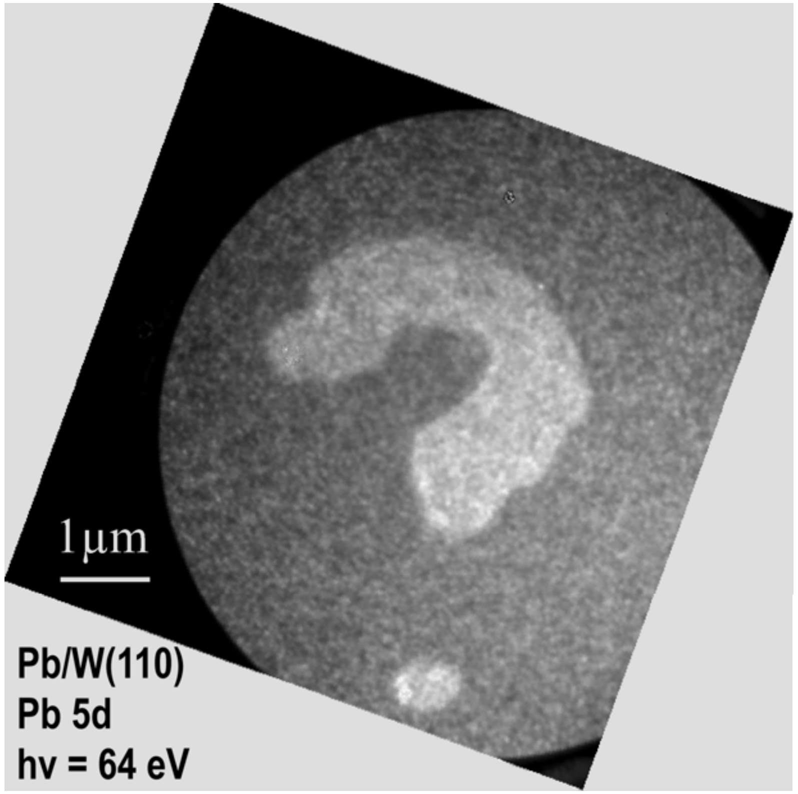
Outline

- A brief introduction to spectromicroscopy
- The SPELEEM at Elettra
    - SPELEEM = spectroscopic photoemission and low energy electron microscope
- Application example:
    - AFM local anodic oxidation
    - Si oxides
    - GaAs oxides

Motivation



Why XPS?

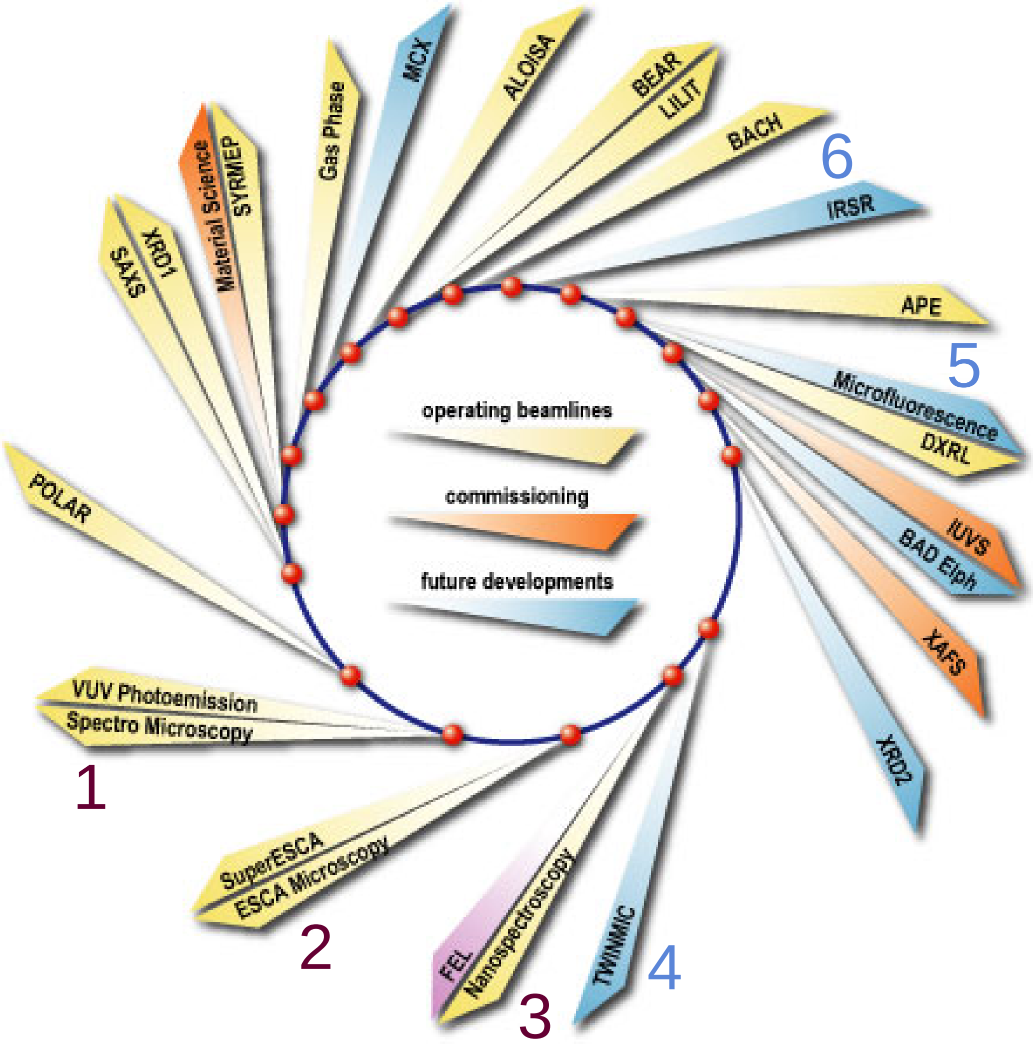
- chemical state information
- surface sensitive
- ease of quantification
- nondestructive

Why spectromicroscopy ?

- (semicond.) nanostructures: self-organization, lithography
- devices
- diffusion, segregation
- alloying (silicide formation)
- catalysis, chemical waves
- surface magnetism (XMCD)

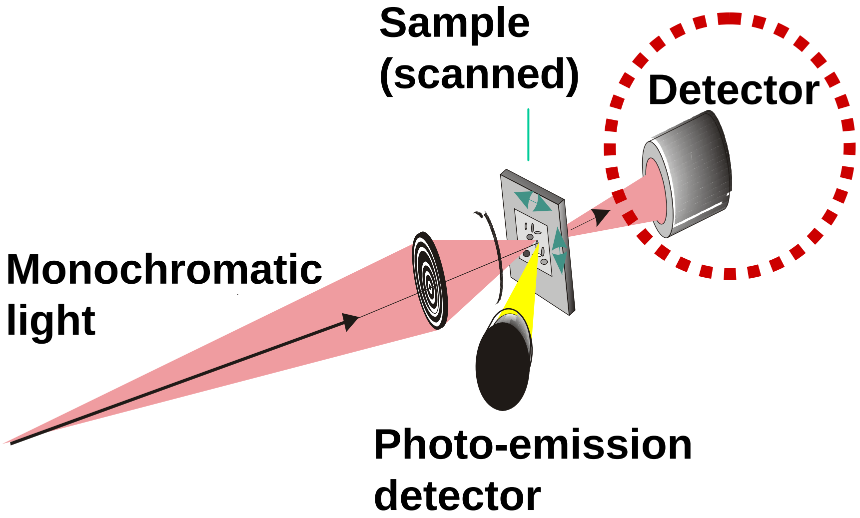
Location of TASC and Elettra

Elettra Beamlines



exit	beamline	source
1.1L	TWINMIC	short id
1.2L	Nanospectroscopy	id
1.2R	FEL (Free-Electron Laser)	-
2.2L	ESCA Microscopy	id
2.2R	SuperESCA	id
3.2L	Spectro Microscopy	id
3.2R	VUV Photoemission	id
4.2	Circularly Polarised Light	id
5.2L	SAXS (Small Angle X-Ray Scattering)	id
5.2R	XRD1 (X-ray Diffraction)	id
6.1L	Material science	bm
6.1R	SYRMEP (SYnchrotron Radiation for MEdical Physics)	bm
6.2R	Gas Phase	id
7.1	MCX (Powder Diffraction Beamline)	bm
7.2	ALOISA (Advanced Line for Overlayer, Interface and Surface Analysis)	id
8.1L	BEAR (Bending magnet for Emission Absorption and Reflectivity)	bm
8.1R	LILIT (Lab of Interdisciplinary LIThography)	bm
8.2	BACH (Beamline for Advanced DiCHroism)	id
9.1	IRSR (Infrared Synchrotron Radiaton Microscopy)	bm
9.2	APE (Advanced Photoelectric-effect Experiments)	id
10.1L	X-ray microfluorescence	bm
10.1R	DXRL (Deep-etch Lithography)	bm
10.2L	IUVS (Inelastic Ultra Violet Scattering)	id
10.2R	BAD Elph	id
11.1	XAFS (X-ray Absorption Fine Structure)	bm
11.2	XRD2 (X-ray Diffraction)	id

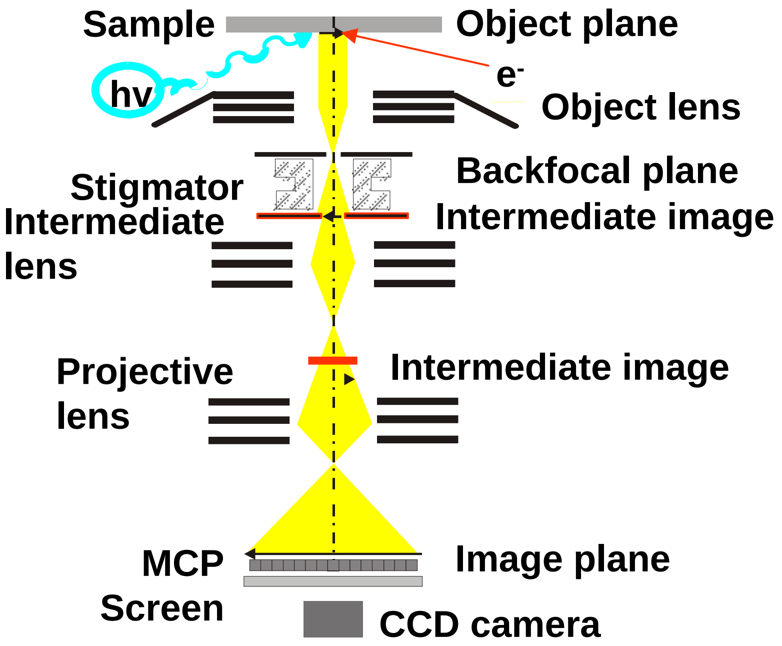
Scanning vs. direct imaging type



Photon optics is demagnifying the beam:

Scanning Instrument

- 🟩 Whole power of XPS in a small spot mode.
- 🟩 Flexibility for adding different detectors.
- 🟩 Rough surfaces can be measured.
- 🟥 Limited use for fast dynamic processes.
- 🟥 Lower lateral resolution than imaging instruments



Electron optics to magnify irradiated area:

Imaging Instrument

- 🟩 High lateral resolution (20 nm).
- 🟩 Multi-method instrument (XPEEM/PED).
- 🟩 Excellent for monitoring dynamic processes.
- 🟥 Poorer spectroscopic ability.
- 🟥 Sensitive to rough surfaces.

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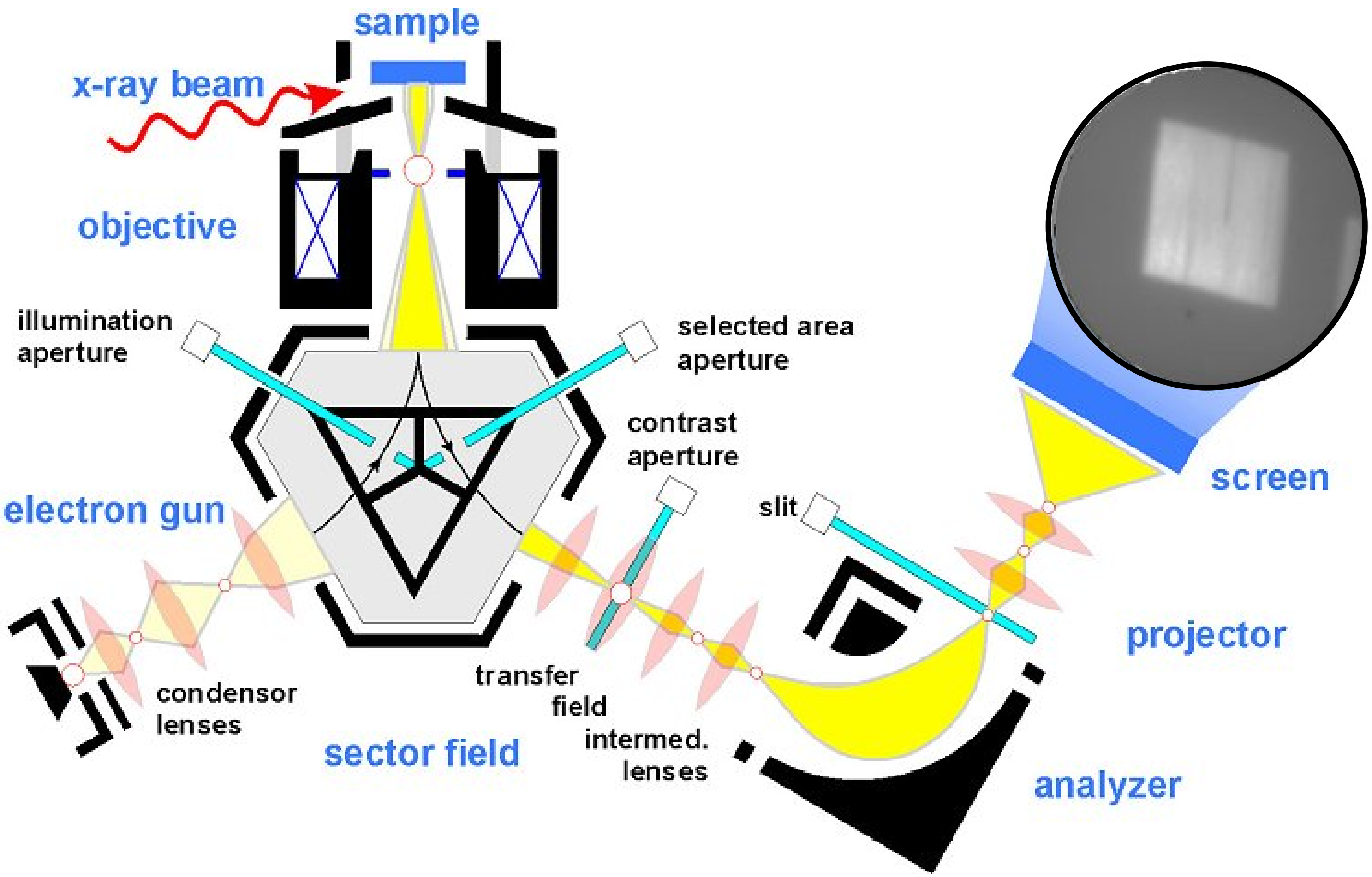
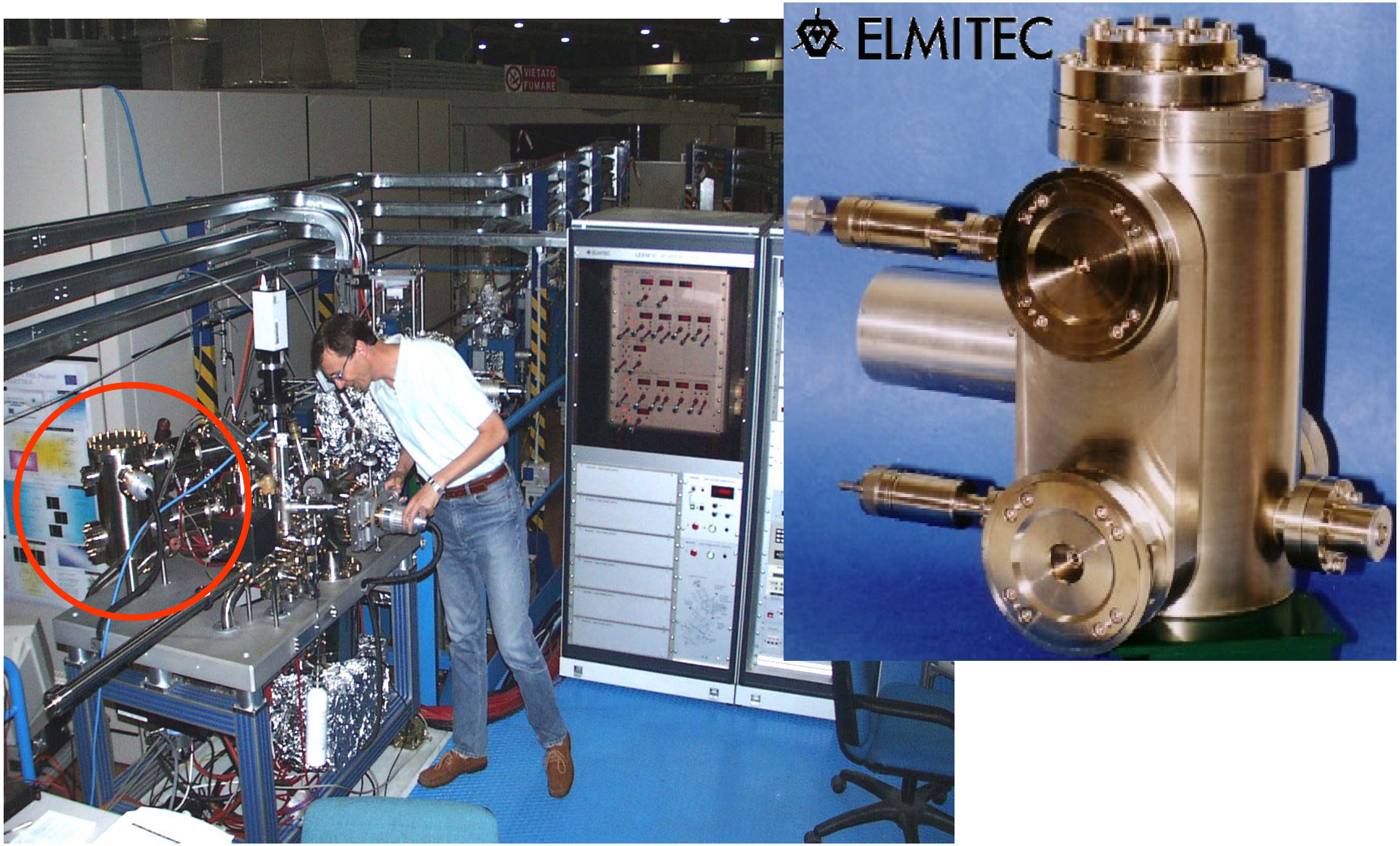
The SPELEEM at Elettra

Spectroscopic photoemission and low energy electron microscope

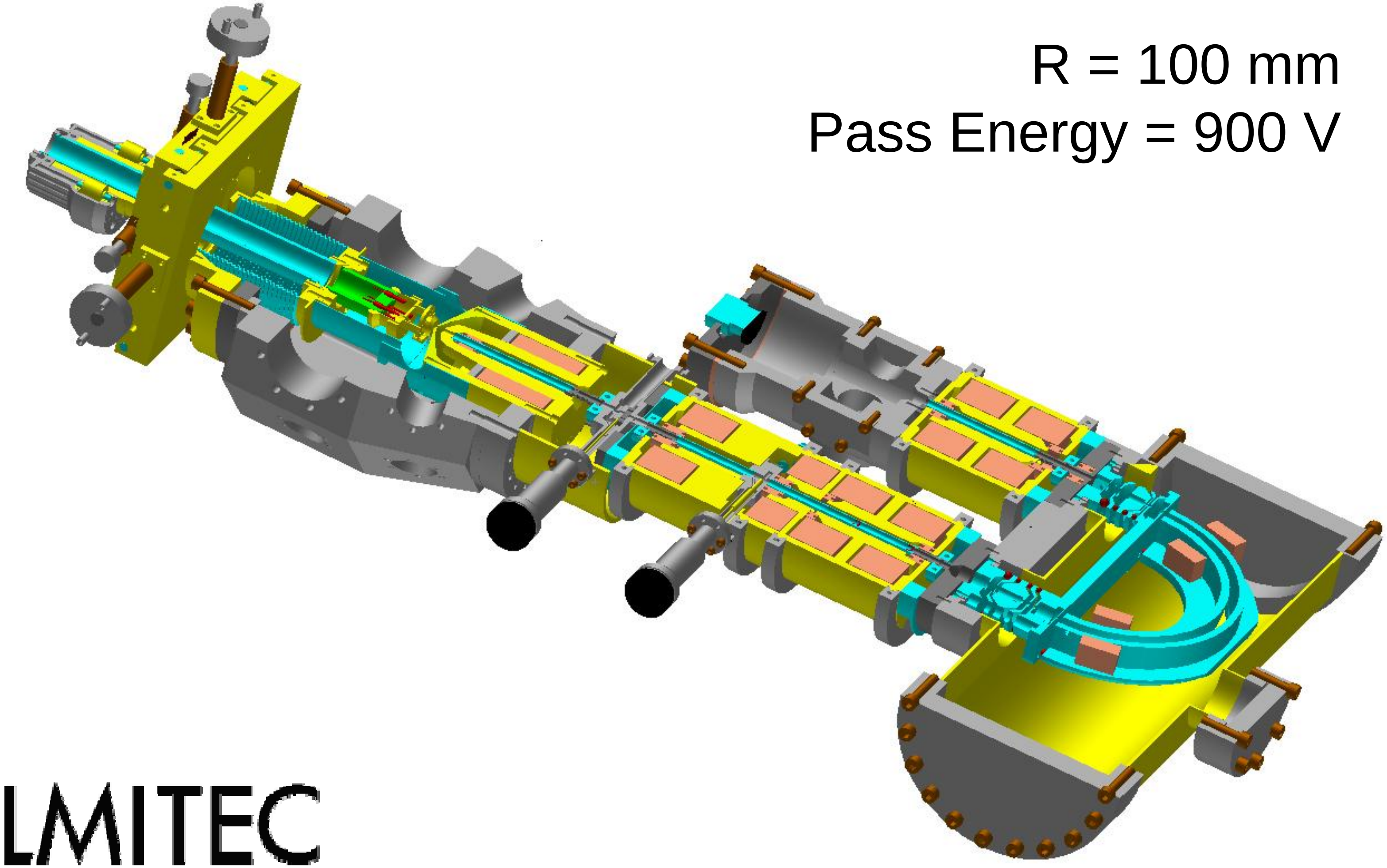


The SPELEEM at ELETTRA



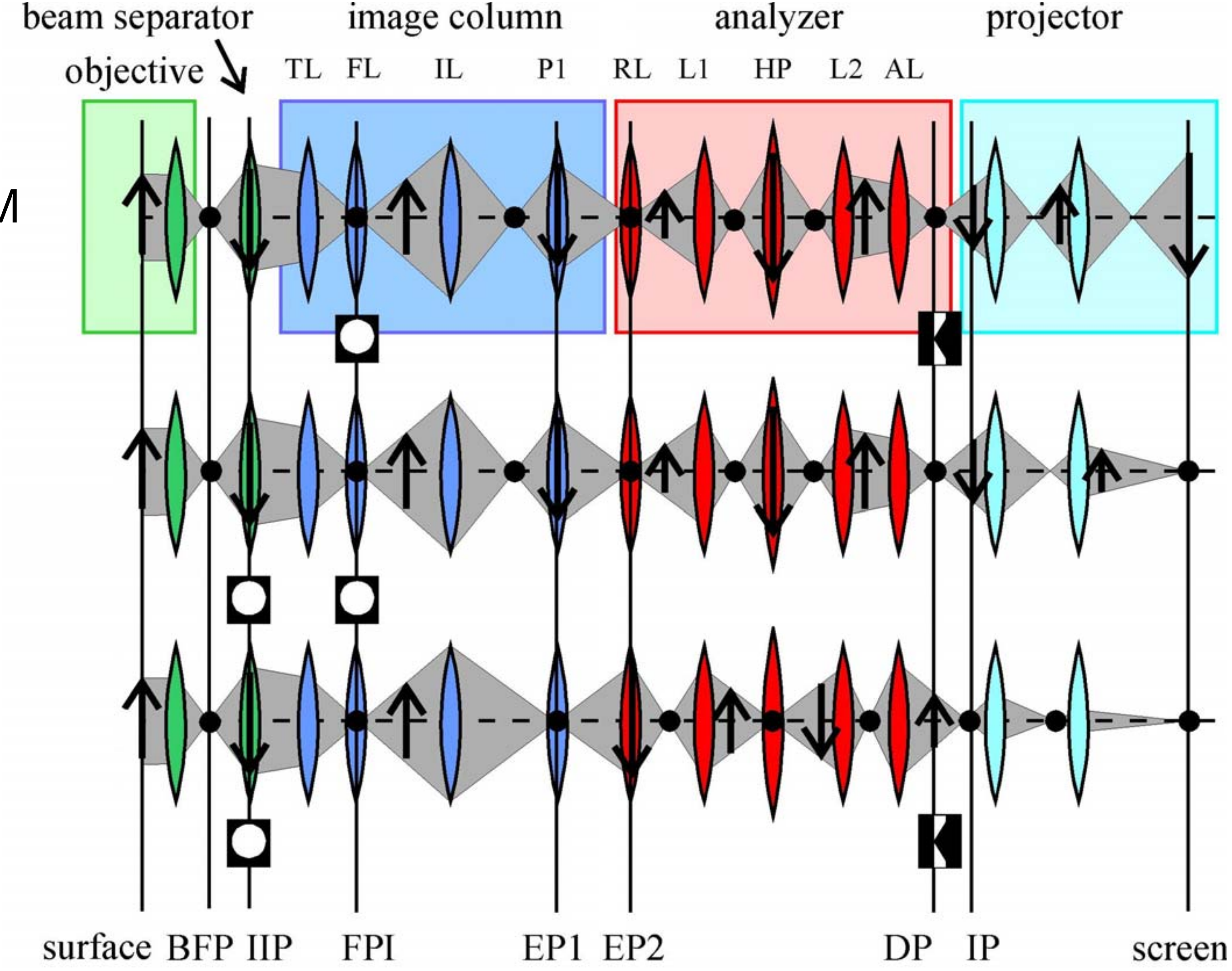
The energy filter

R = 100 mm
Pass Energy = 900 V



ELMITEC

Modes of Operation

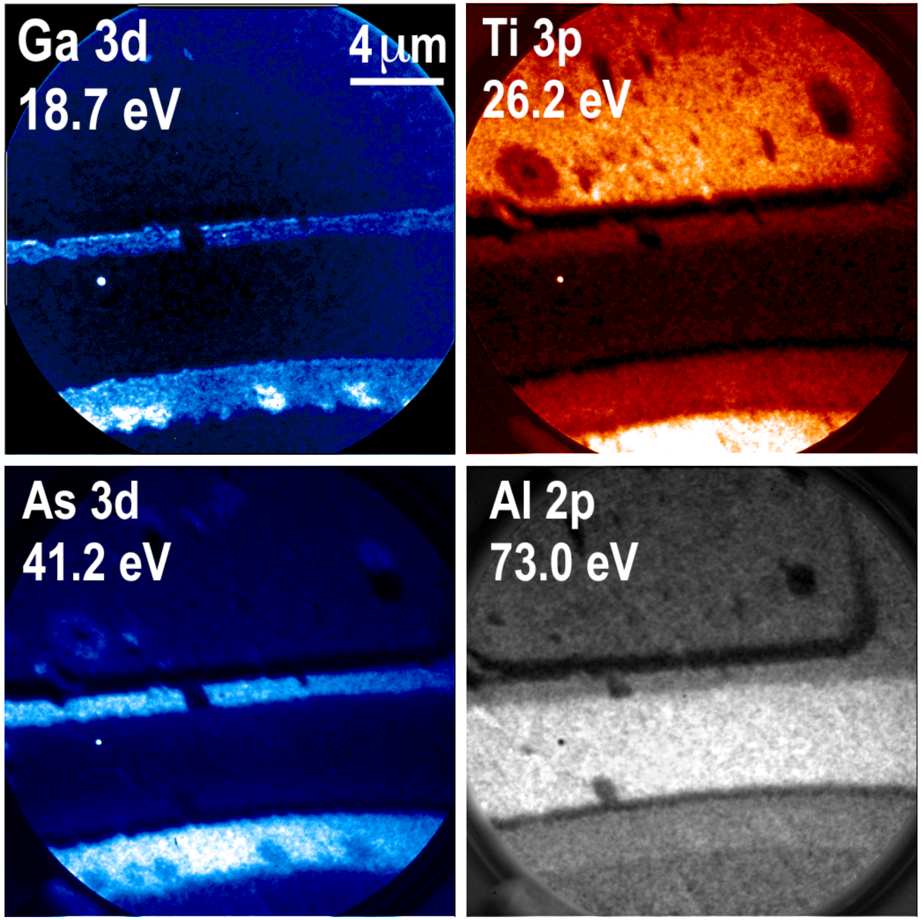


XPEEM
LEEM

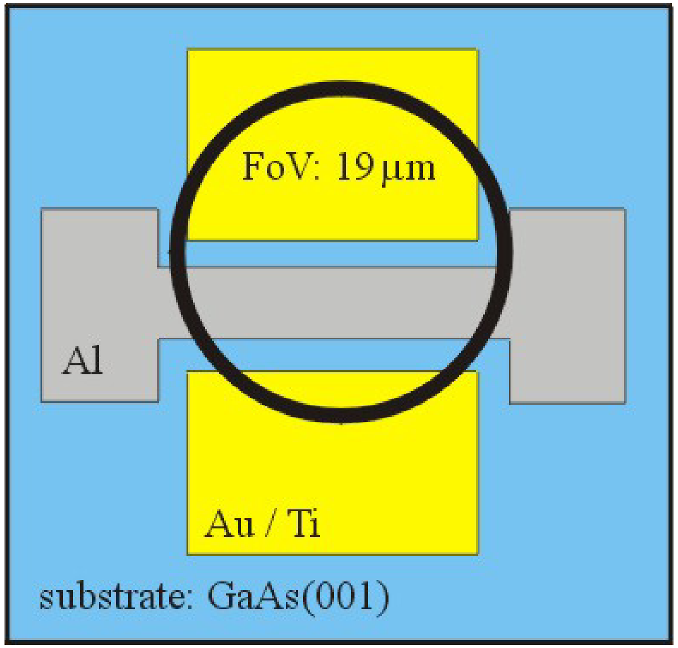
PES
ELS

PED
LEED

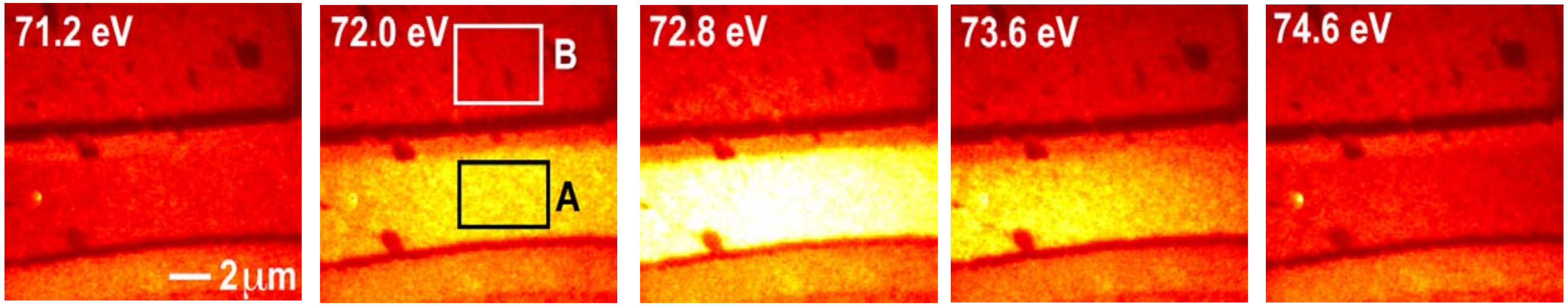
XPEEM: Spectroscopic Microscopy

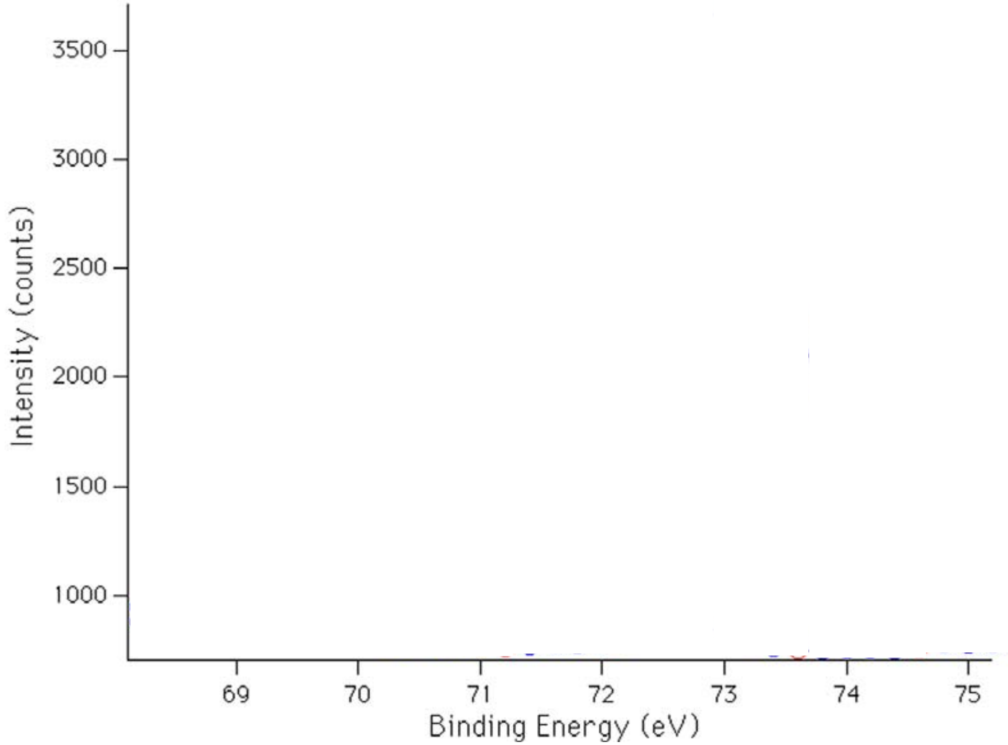


- Images from a Field Effect Transistor (FET) at different binding energies.
- Photon energy 131.3 eV.



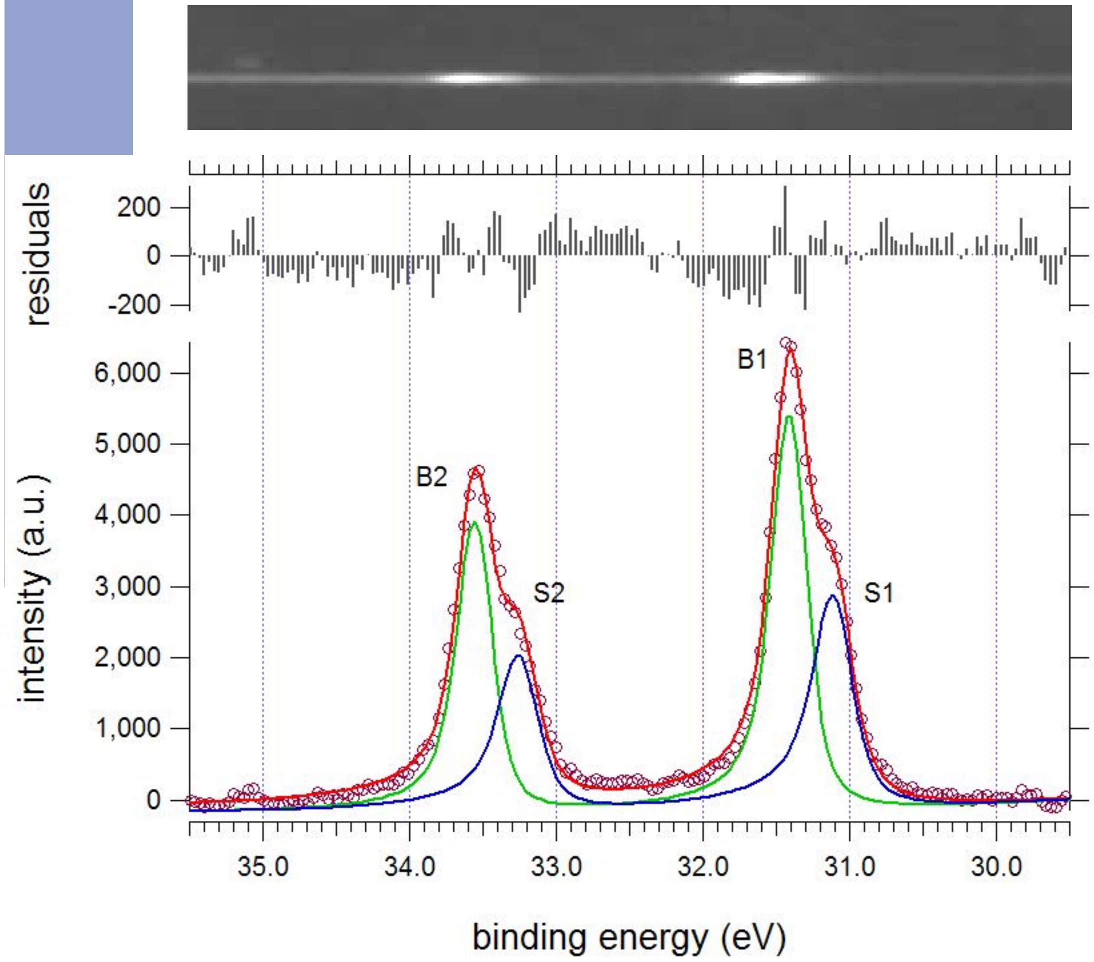
XPEEM: Core Level Spectroscopy

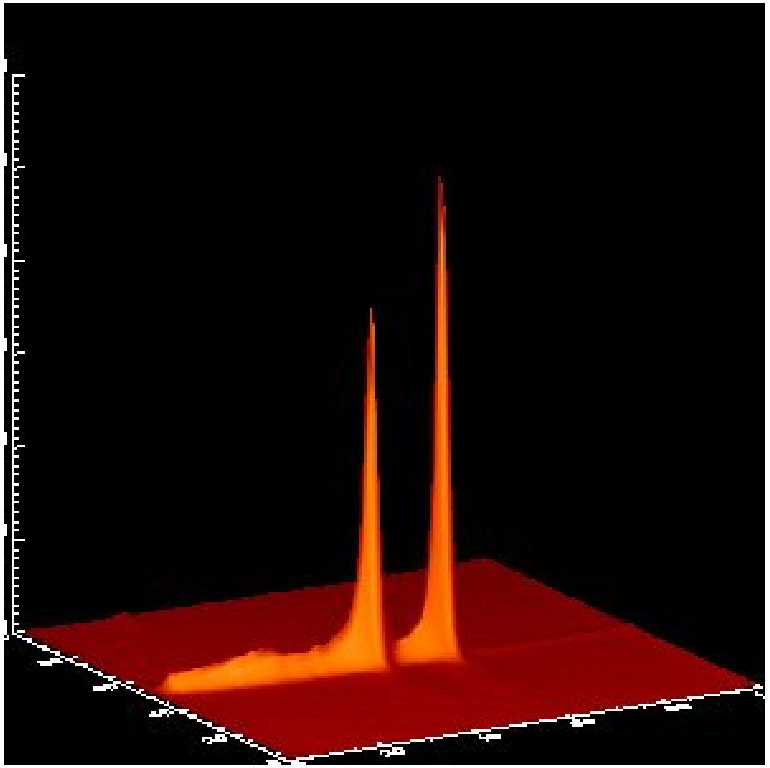




Imaging of Dispersive Plane

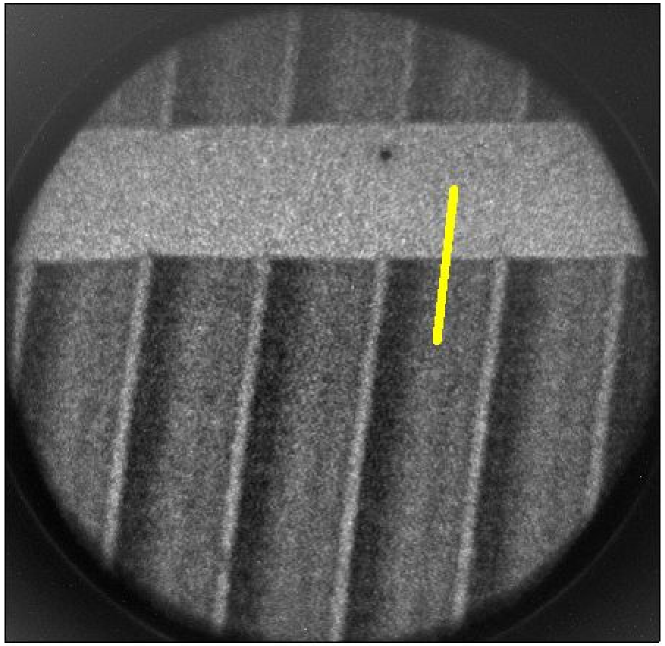
- W{110} clean surface
- W 4f core level

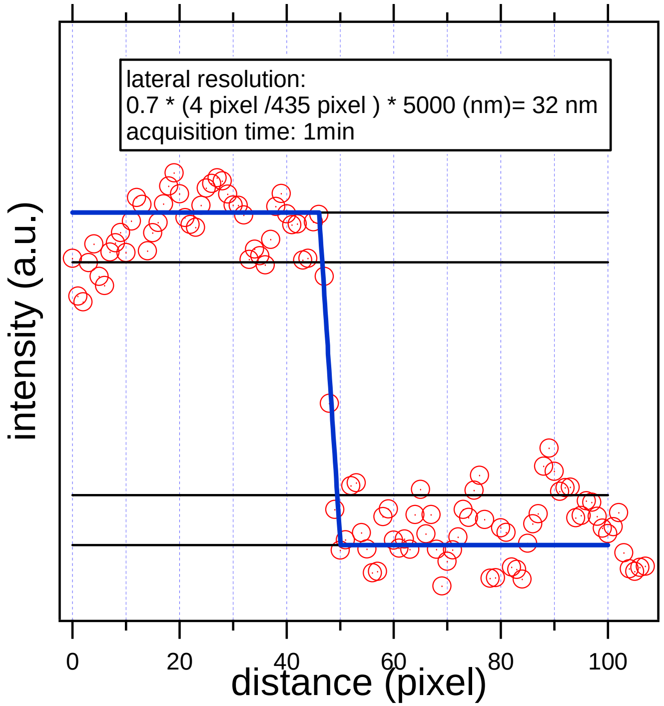




Lateral resolution

- C 1s image (hv= 350 eV, KE = 62 eV)





lateral resolution:
0.7 * (4 pixel /435 pixel) * 5000 (nm)= 32 nm
acquisition time: 1min

- Lateral resolution: 32 nm

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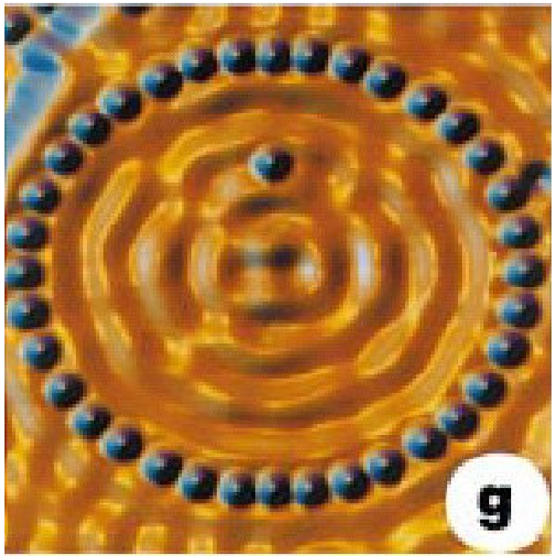
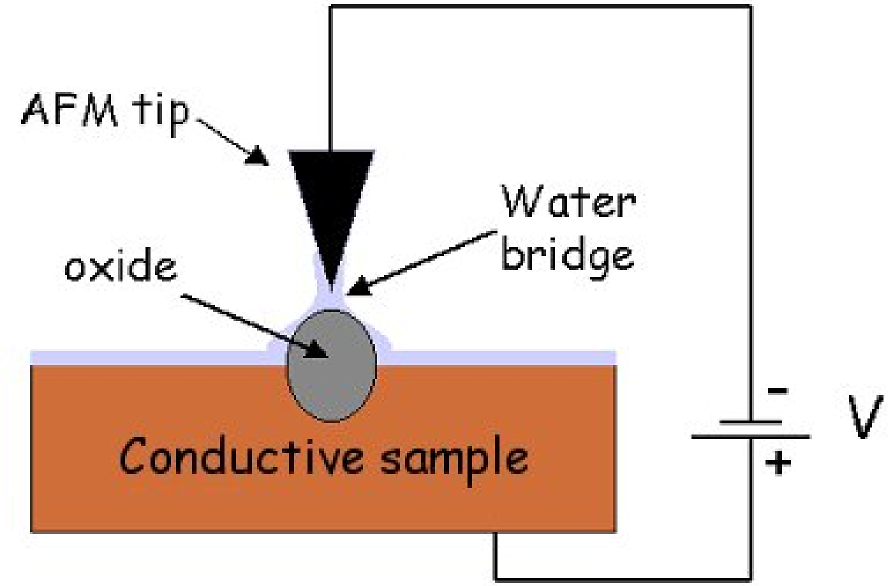
Motivation

- Lithography for fabrication of state-of-the-art semiconductor nanostructures
- Basic research and quantum device applications
- Approaches:
  - Traditional lithography
  - Proximal probes (STM or AFM)



H.C. Manoharan, C.P. Lutz,
D.M. Eigler: Nature **403** (2000) 512

Local Anodic Oxidation (LAO)



- Water electrolysis $H_2O \rightarrow H^+ + OH^-$.
- OH^- groups migrate towards the sample.
- Oxide penetration induced by the intense local electric field.

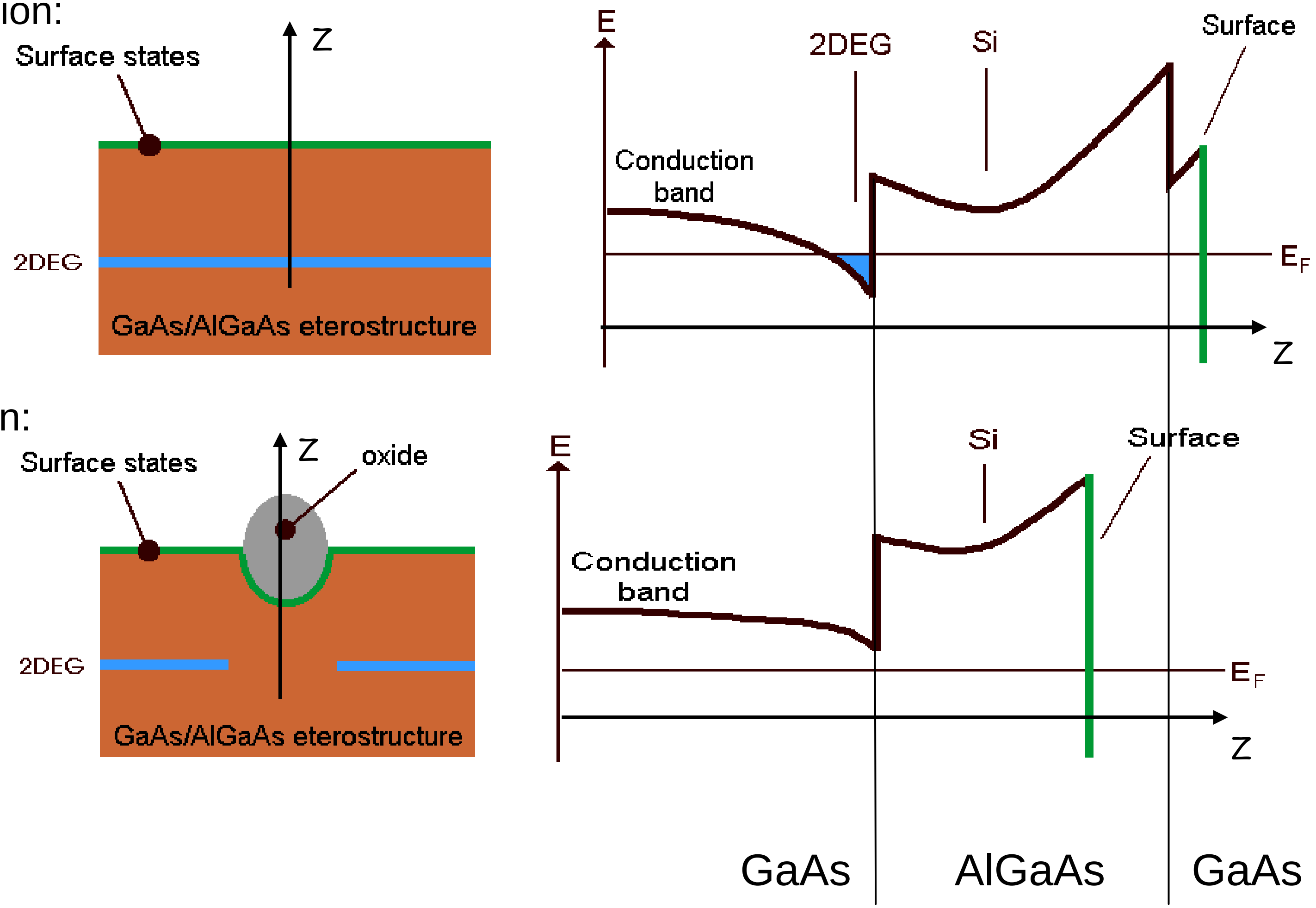
Versatile tool at relatively low cost

High lateral resolution but small area

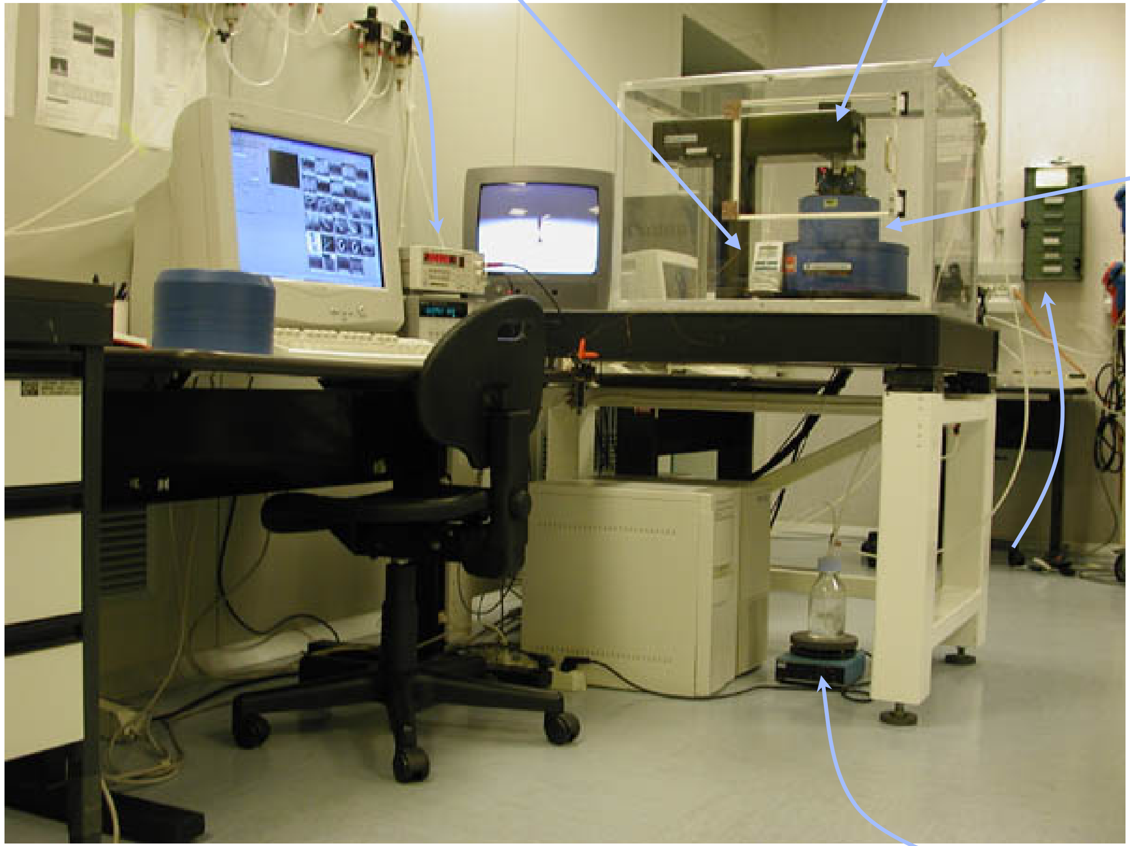
LAO on GaAs/AlGaAs

Before oxidation:

After oxidation:



Setup for Lithography on GaAs



voltage source

Hygrometer

AFM camera

Plexiglass hood

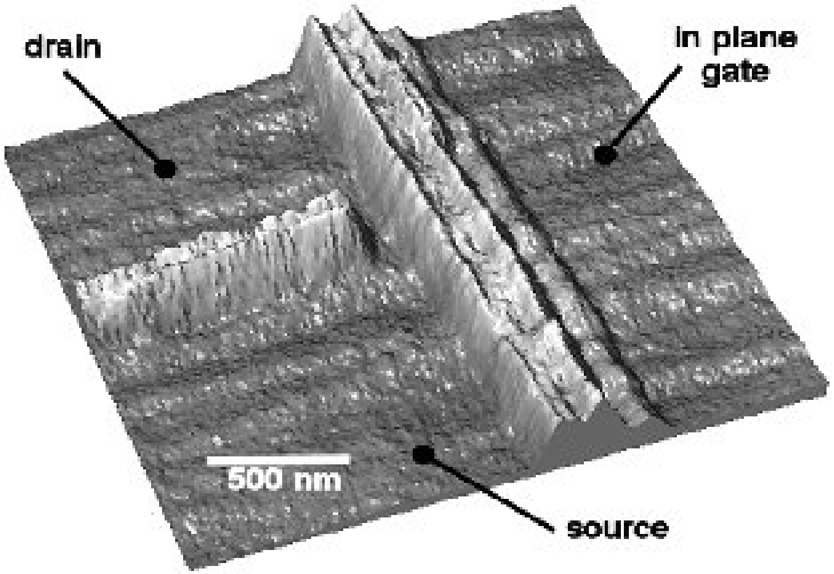
AFM

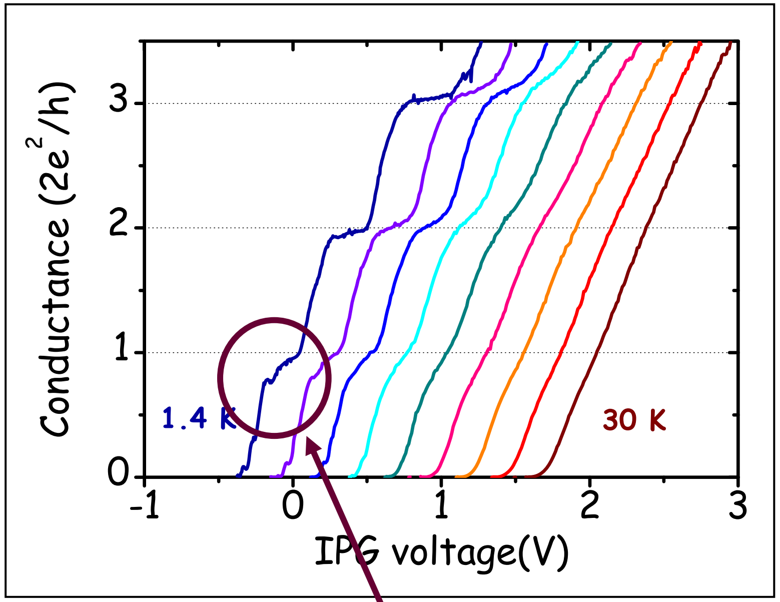
$N_2 + H_2O$

water bottle

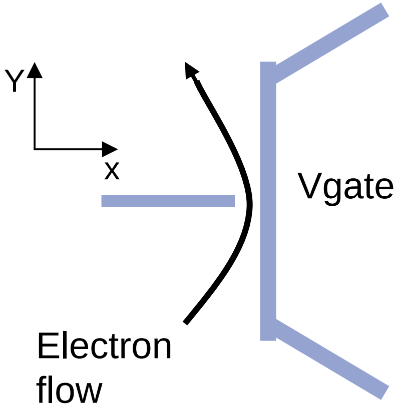
Thermomicroscope Microcope CP-Resource

Quantum Point Contact





Peaked structures present in the low temperature curves



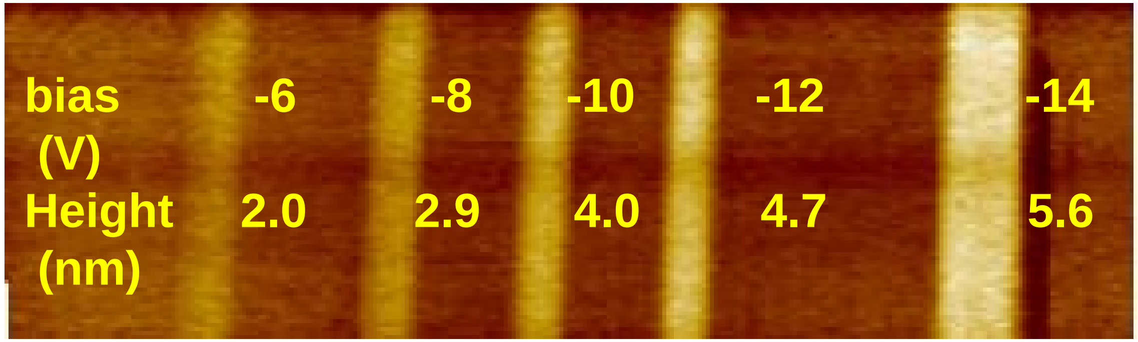
G. Mori et al, JVST B **22** (2004) 570.

Why Spectroscopic Microscopy?

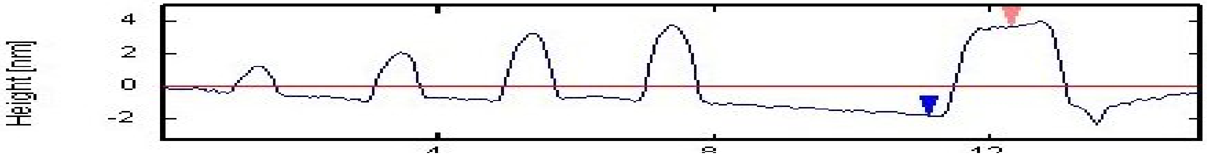
- Lack of information on the oxidation process and on the chemical nature of the grown oxides.
- Information on the uniformity of the grown oxides (electrical and chemical properties).
- Effect of oxidation parameters.

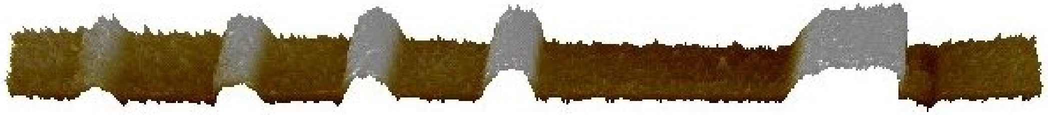
- Lack of reliable microscopic techniques able to perform chemical analysis on such small structures.

Si Oxide: Sample



bias (V)	-6	-8	-10	-12	-14
Height (nm)	2.0	2.9	4.0	4.7	5.6



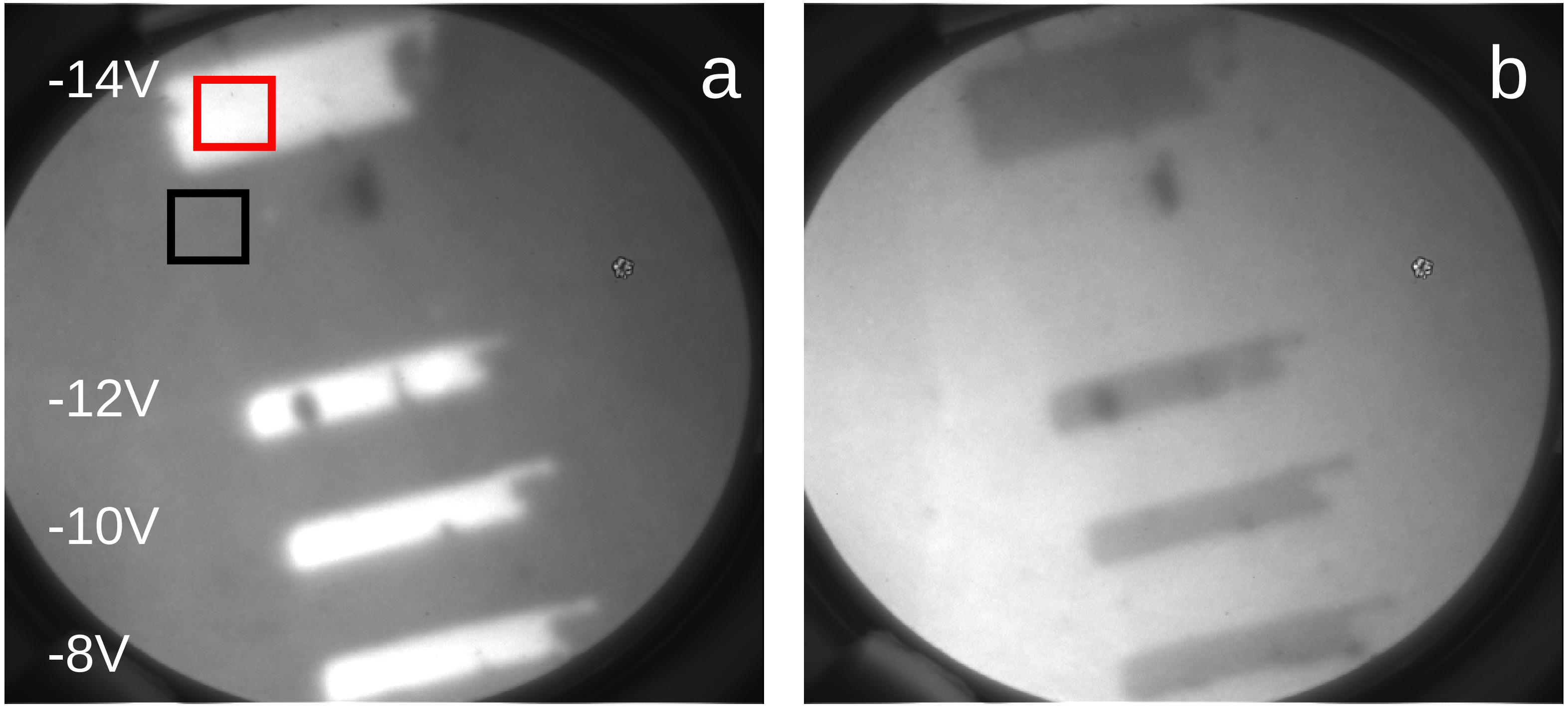


Morphology studied after oxidation by AFM.
Thickness increases with writing voltage!

M. Lazzarino, S. Heun, B. Ressel, K. C. Prince, P. Pingue, and C. Ascoli: Appl. Phys. Lett. **81** (2002) 2842.

Si Oxide: Image Contrast at Si 2p

Field of view 12 µm, hv = 132.5 eV, energy resolution: 1 eV

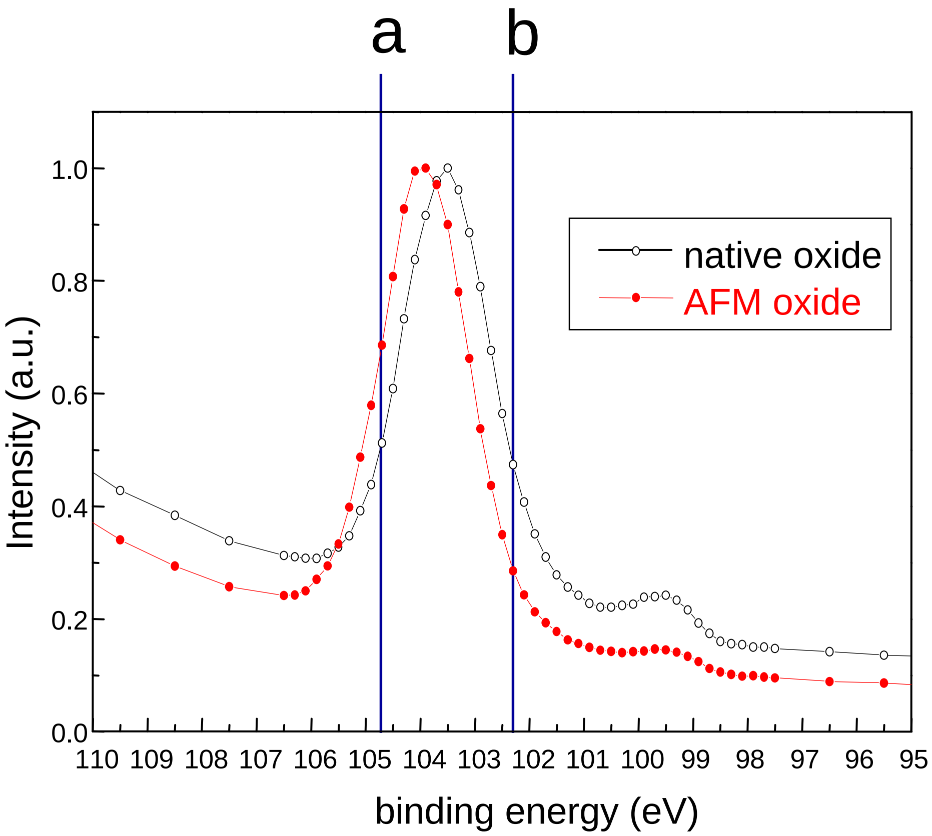


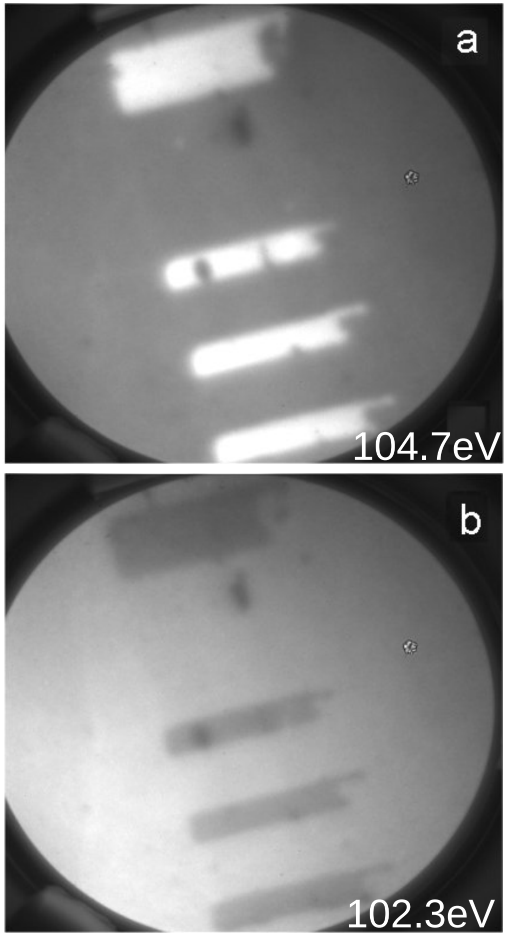
Binding energy 104.7 eV

Binding energy 102.3 eV

M. Lazzarino, S. Heun, B. Ressel, K. C. Prince, P. Pingue, and C. Ascoli: Appl. Phys. Lett. **81** (2002) 2842.

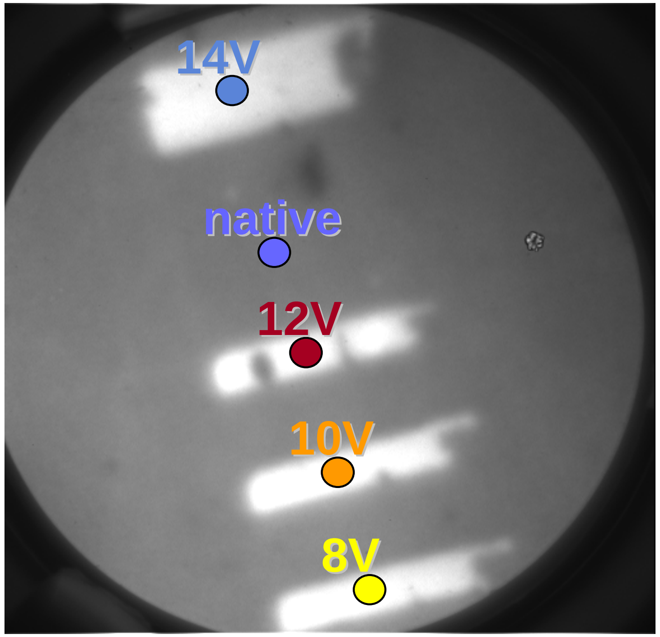
Si Oxide: Spectroscopy at Si 2p

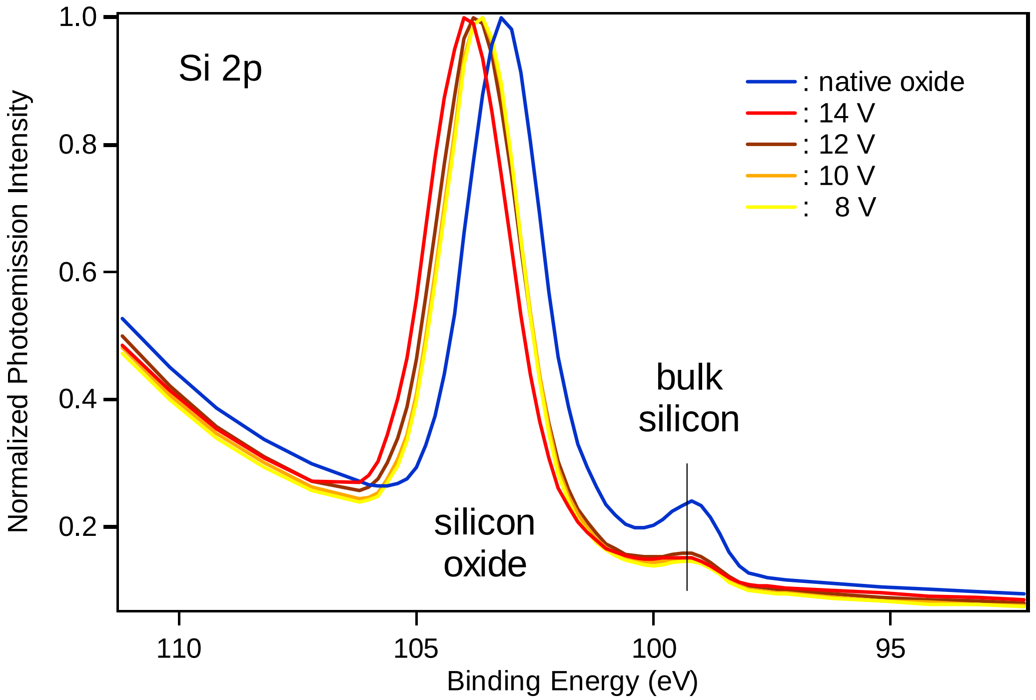




M. Lazzarino, S. Heun, B. Ressel, K. C. Prince, P. Pingue, and C. Ascoli: Appl. Phys. Lett. **81** (2002) 2842.

Si Oxide: Writing Voltage Effect





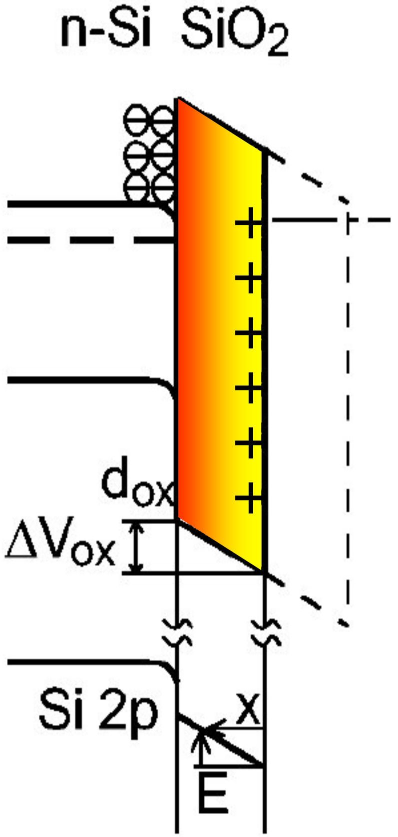
ΔE = 3.97 eV (native)
ΔE = 4.62 eV (U = 14V)
ΔE = 4.46 eV (U = 12V)
ΔE = 4. 41 eV (U = 10V)
ΔE = 4.39 eV (U = 8V)

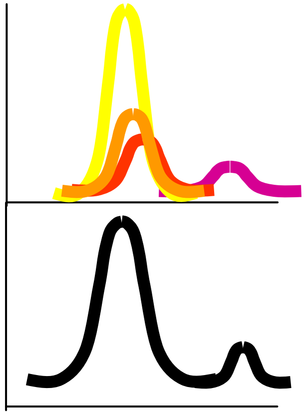
Shift (Si_{bulk} - SiO_x) increases with increasing writing voltage (oxide thickness).

M. Lazzarino, S. Heun, B. Ressel, K. C. Prince, P. Pingue, and C. Ascoli: Appl. Phys. Lett. **81** (2002) 2842.

Si Oxide: Charging Effects

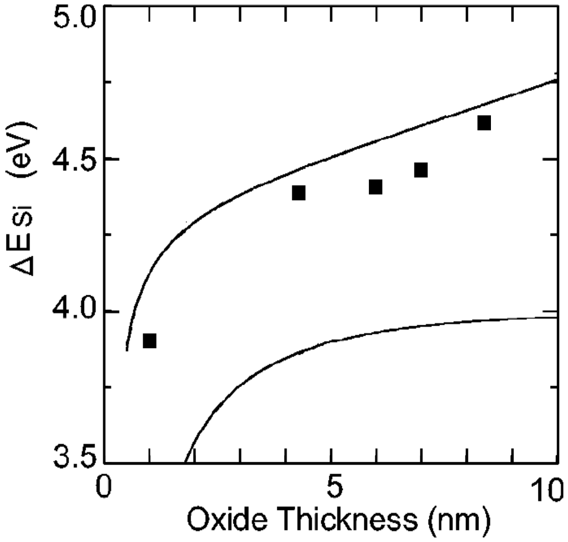
H. Kobayashi, T. Kubota, H. Kawa, Y. Nakato, and M. Nishiyama: Appl. Phys. Lett. **73** (1998) 933.



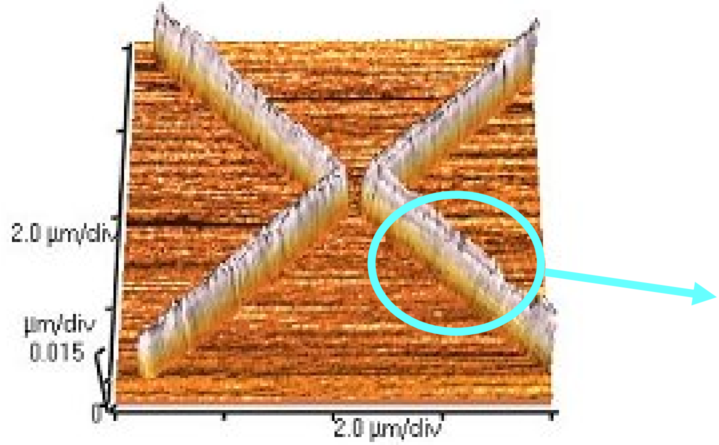


Intensity decreases due to escape depth effect
Charged (yellow) layer contribution is more important

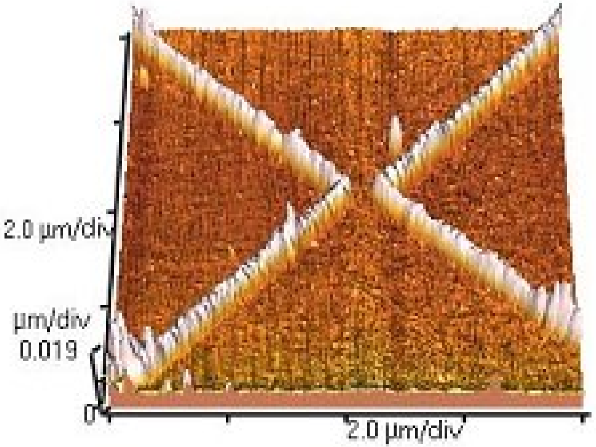
Squared points: our data
Line: Kobayashi model



GaAs Oxide: Photon Exposure



AFM before: height 18nm

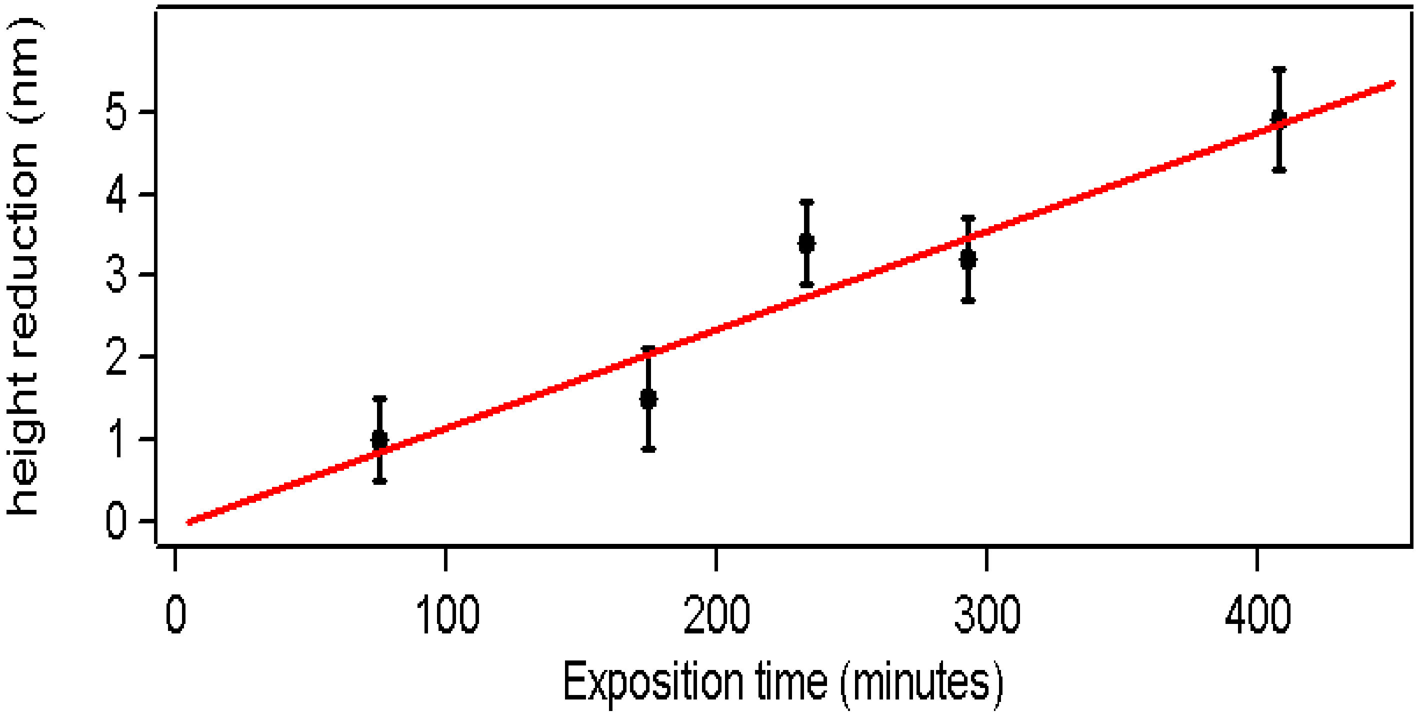


AFM after: height 13nm

Images taken with secondary electrons

- Photon energy: 125 eV
- Kinetic energy: 4 eV
- Field of view: 10 µm
- One image every 2 sec

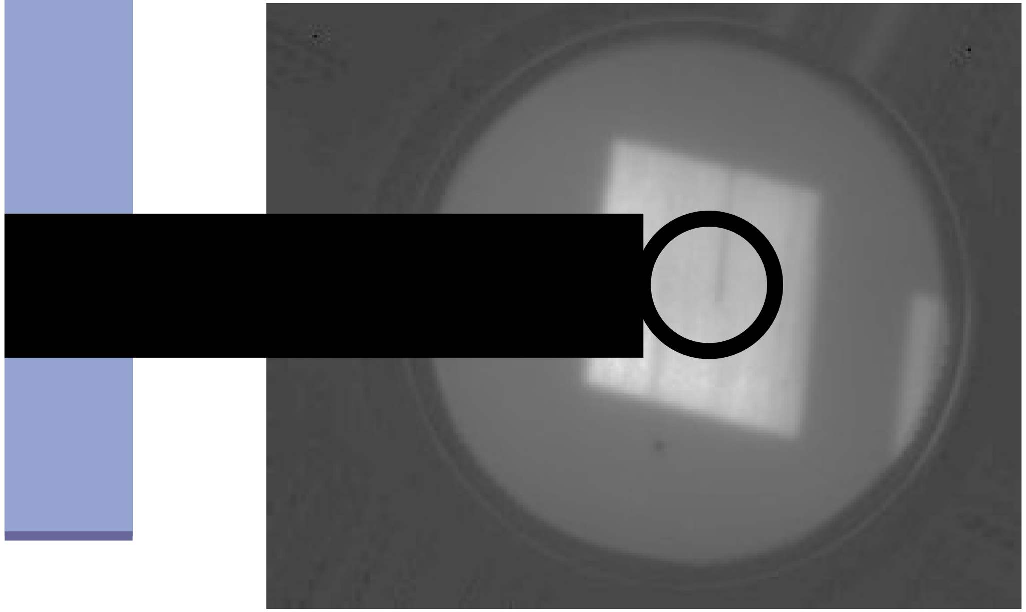
Height reduction vs. exposure time



- We observed a linear relation between exposure time and height reduction.
- A dependence on other oxidation parameters (bias, speed) could not be detected.

Spectra From AFM GaAs Oxide

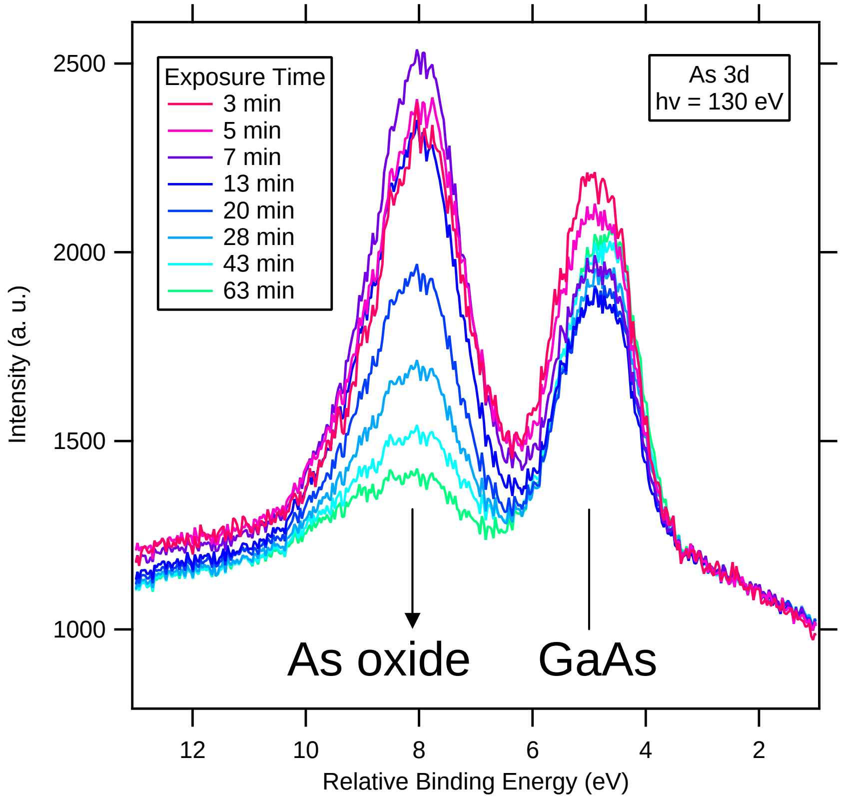
Time resolved spectroscopy with SPELEEM using Dispersive Plane (hv = 130 eV)

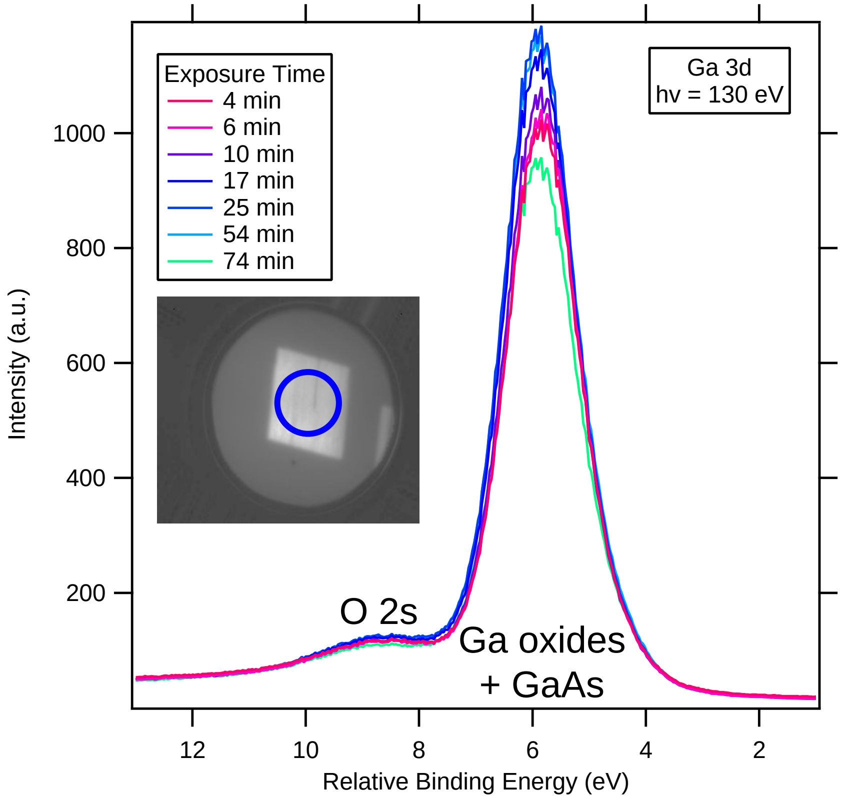


- Sample S03B
- Hole (3,2)
- Writing voltage 15 V
- Structure height 3 nm
- Image taken with secondary electrons:
  - Photon energy: 130 eV
  - Kinetic energy: 0.3 eV
  - Field of view: 10 µm

Spectra From AFM GaAs Oxide

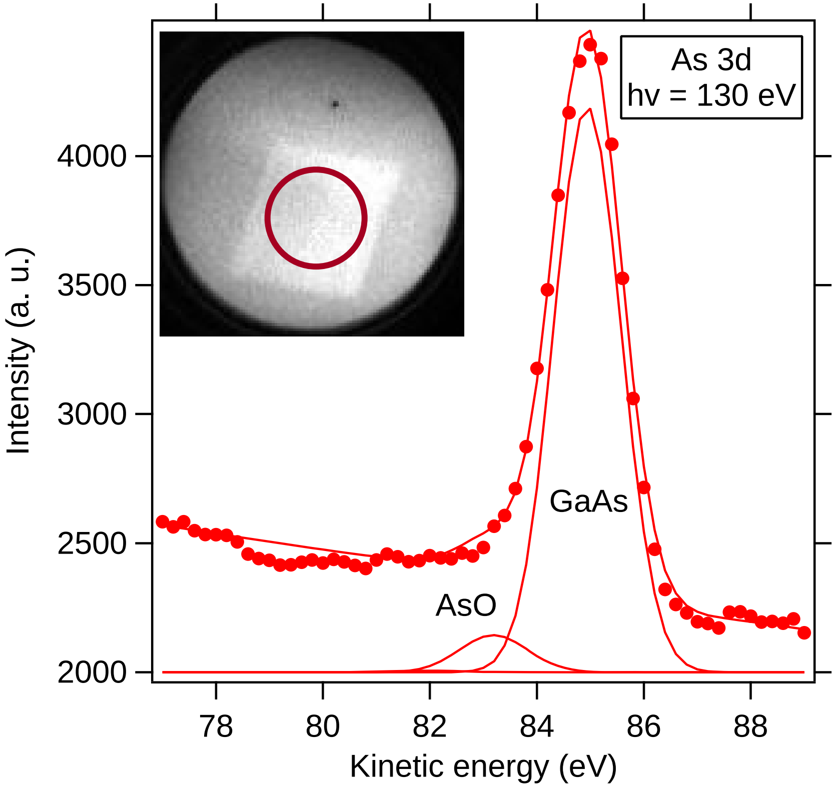
Time resolved spectroscopy with SPELEEM using Dispersive Plane (hv = 130 eV)

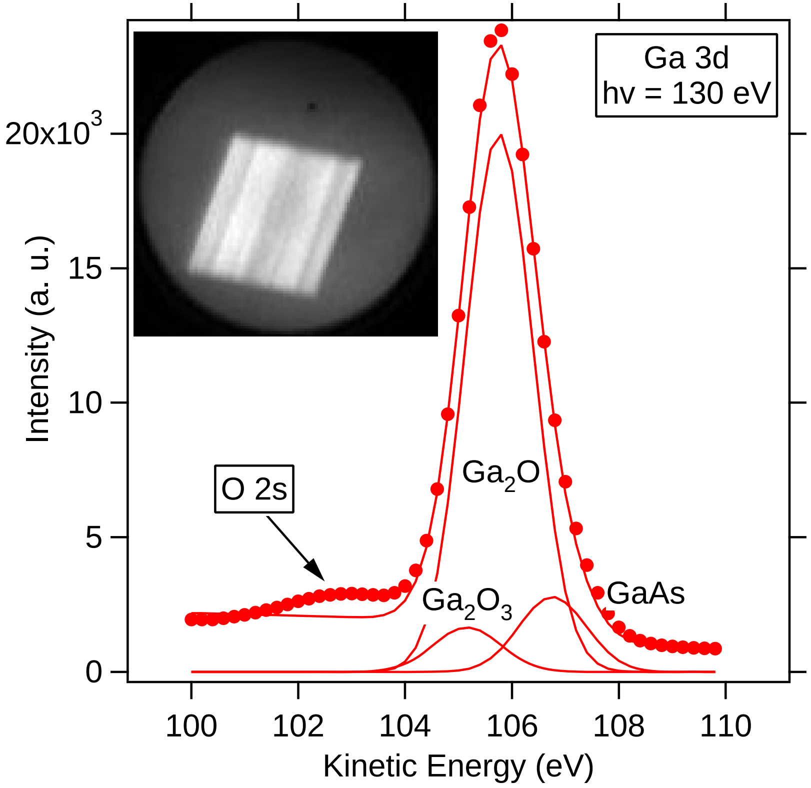




- The As-oxide signal goes to zero with time.
- The Ga-oxide signal remains unchanged (early stage of exposure).

Spectra From AFM GaAs Oxide



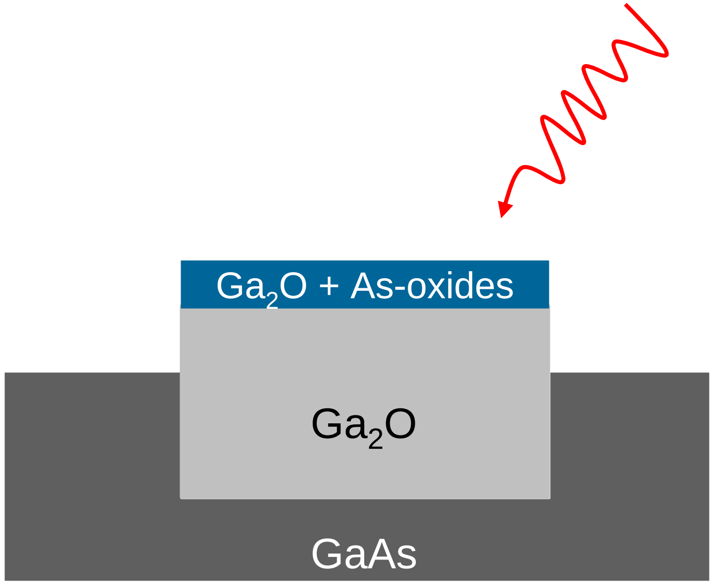


- The AFM-oxide is mainly composed of Ga_2O.
- After about 1 hour of exposure, only traces of As-oxides observed in the As 3d.

A possible model for the desorption

Our Observations:

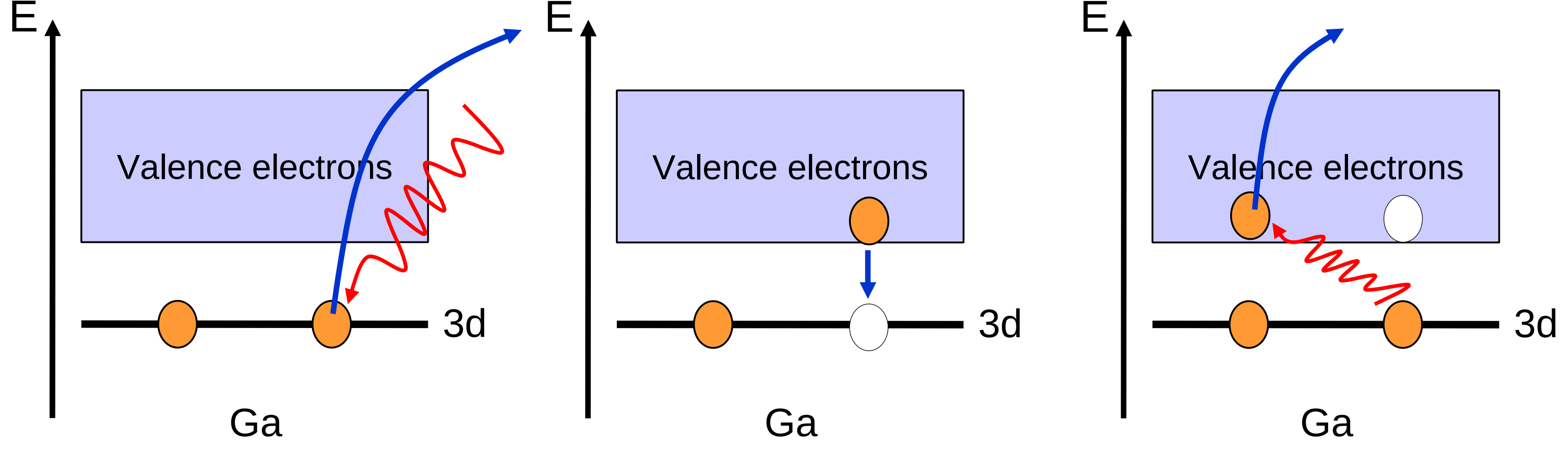
- The AFM-grown oxide exposed to 130 eV photons desorbs linearly with the exposure time.
- The AFM-oxide is mainly composed of Ga_2O with traces of As-oxide.
- The shape of the Ga peak does not change with exposure time (early stage of desorption).
- The As-oxides desorb completely after tens of minutes of exposure.



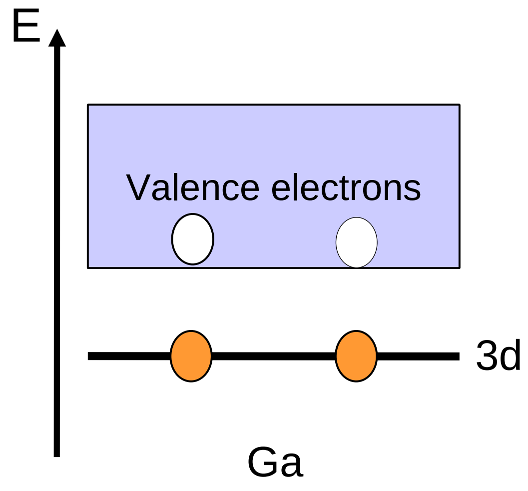
The physics underlying the desorption

- Does the desorpion depend on the total amount of energy delivered to the system?
  - No! We delivered the same amount of energy with electrons and conventional XPS but no desorption took place.
- Does the photon beam heat up the system enough to locally deoxidize the sample?
  - No! The oxides are stable up to 400ºC. The calculated local heating is less than 10ºC.
- The desorption depends on photon flux and energy!

The Knotek-Feibelman mechanism



Initial state



Final state

- The valence electrons are mainly localized at O atoms.
- This Auger decay leads to a final state with two vacancies in valence band weakening the bond between Ga and O.

Summary

- Si oxide:
  - The AFM induced oxidation produces chemically uniform, stoichiometric SiO_2 with dielectric properties comparable to those of thermal SiO_2.
- GaAs oxide:
  - The AFM-oxide is mainly composed of Ga_2O with traces of As-oxide.
  - Photon assisted partial desorption of the AFM-grown oxide was observed.
  - All As oxides and the oxygen-rich Ga oxides are desorbed.
  - We proposed a simple model for the dynamics of the desorption.

Acknowledgements

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- P. Pingue (NEST-INFM and Scuola Normale Superiore, I-56012 Pisa, Italy)