Local Anodic Oxidation with AFM: A Nanometer-Scale Spectroscopic Study with Photoemission Microscopy

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A. Locatelli
Sincrotrone Trieste, ELETTRA

Location of TASC and Elettra

TASC-INFM National Laboratory

- **T**ecnologie **A**vanzate e Nano**SC**ienza (Advanced Technology and Nanoscience)
- Director: Giorgio Rossi
- www.tasc.infm.it

- 99 Researchers (13 Professors, 47 Scientists, 28 PhD students, 11 other)
- 17 Technicians, 9 Administrative staff
- Publications: 2003: 105, 2004: 110, 2005: 85

TASC Laboratories

- AD - Analytical Division
- AMD - Advanced Material and Devices group
- HAS - He Atom Scattering
- IPES - Inverse Photoemission laboratory
- MBE - Materials Division
- NED - Nanoscale Electronic Devices
- OxMBE - Oxide MBE
- PLL - PhotoLum Laboratory
- SSR - Surface Structure and Reactivity Group
- TEM - Transmission Electron Microscopy
- XSTM and low-temperature STM of nanostructures

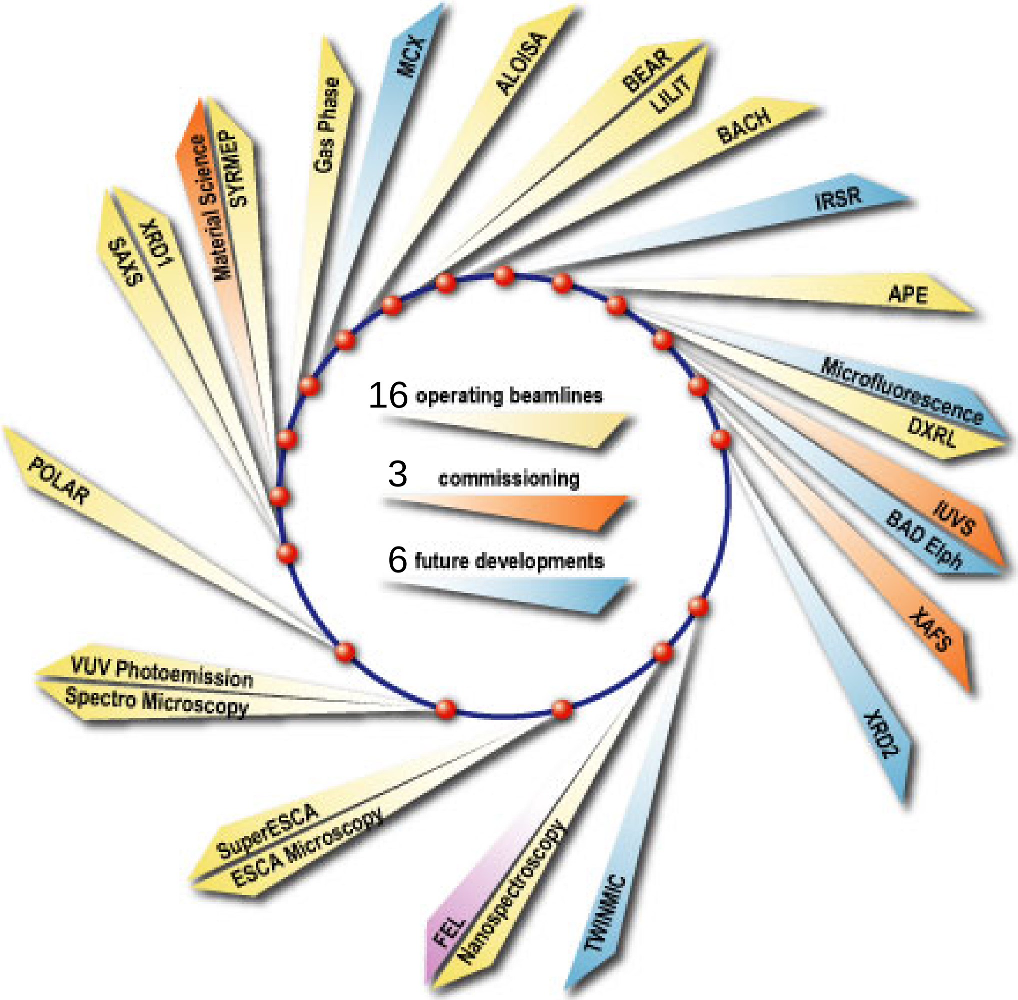
TASC Facilities

- Class 1000 Cleanroom
- Optical Lithography
- Metal deposition
- Dielectric films deposition
- AFM and AFM lithography
- X-Ray Diffraction

TASC Beamlines at Elettra

- ALOISA - Advanced Line for Overlayer, Interface and Surface Analysis
- APE - Advanced Photoemission Experiment
- BACH - Beamline for Advanced diCHroism
- BEAR - Bending magnet for Emission Absorption and Reflectivity
- GAPH - Gas Phase Photoemission
- LILIT - Laboratory for Interdisciplinary Lithography

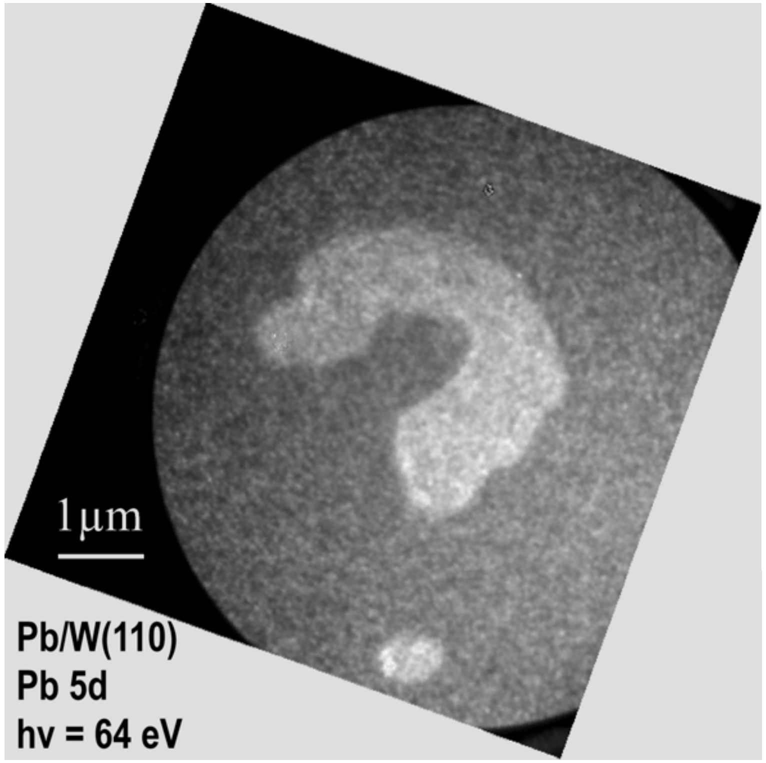
Beamlines at Elettra



TASC BL @ Elettra:
ALOISA
APE
BACH
BEAR
GAPH
LILIT

Spectromicroscopy:
ESCA Microscopy
Nanospectroscopy
Spectromicroscopy
IR Microscopy
Microfluorescence
TwinMic

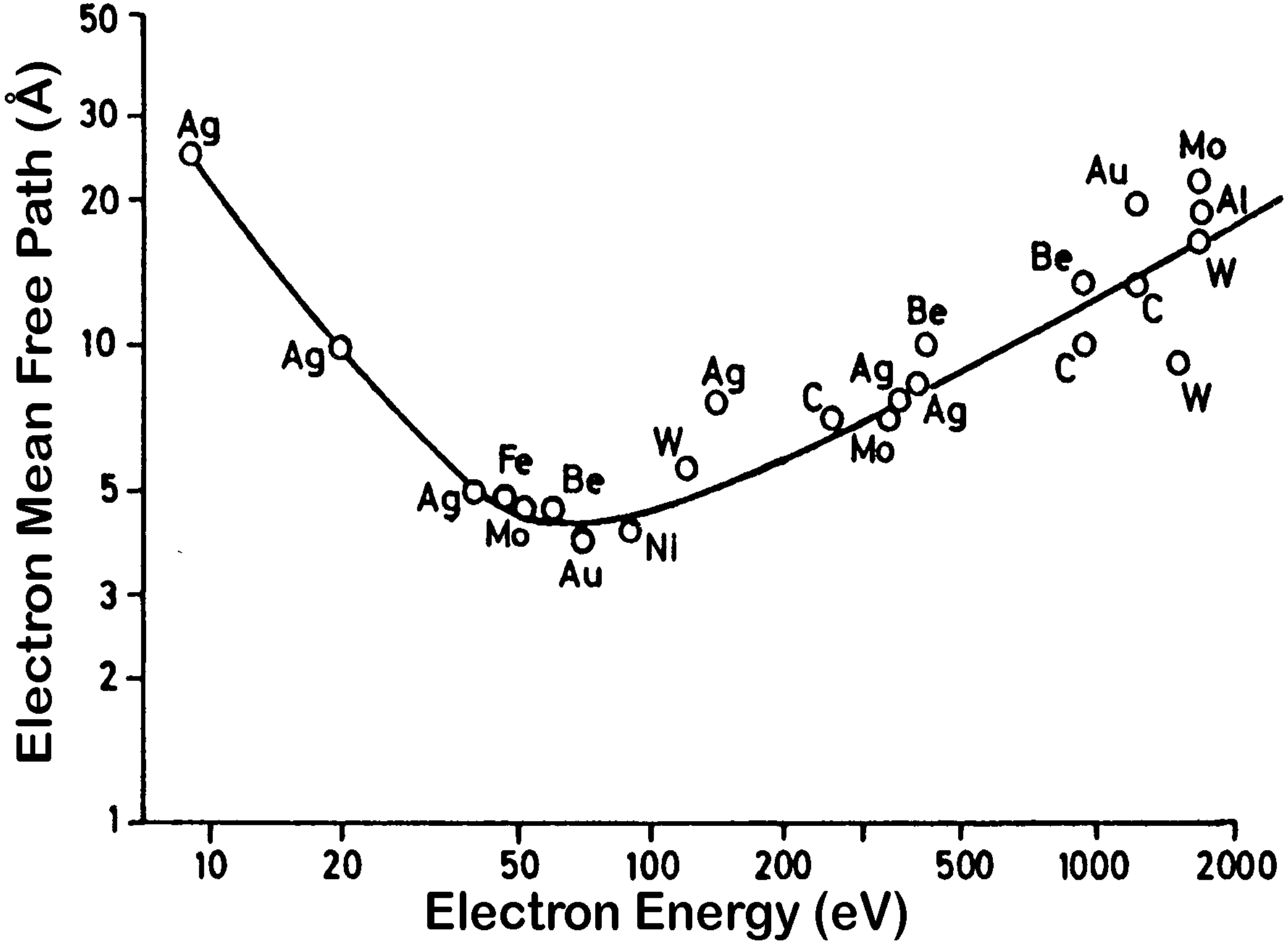
Motivation



Why XPS?

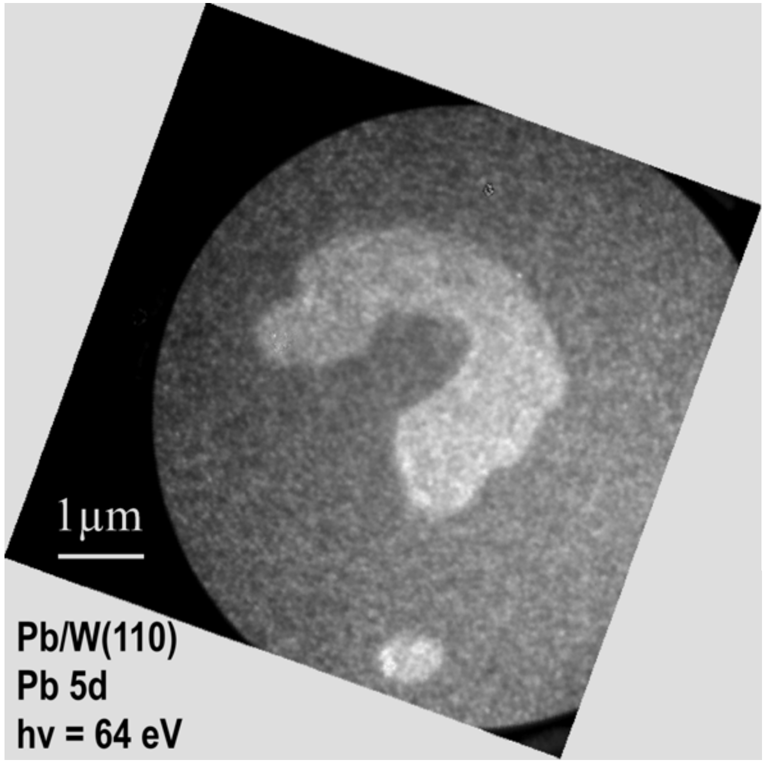
- chemical state information
- surface sensitive
- ease of quantification
- (in general) nondestructive

Photoelectron Mean Free Path



M. P. Seah and W. A. Dench: Surf. Interface Anal. **1** (1979) 2.

Motivation



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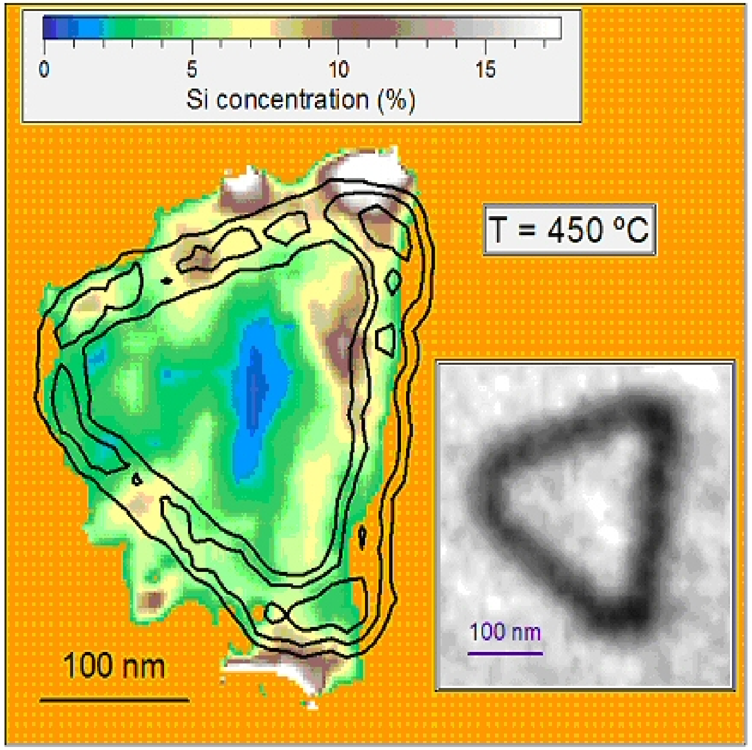

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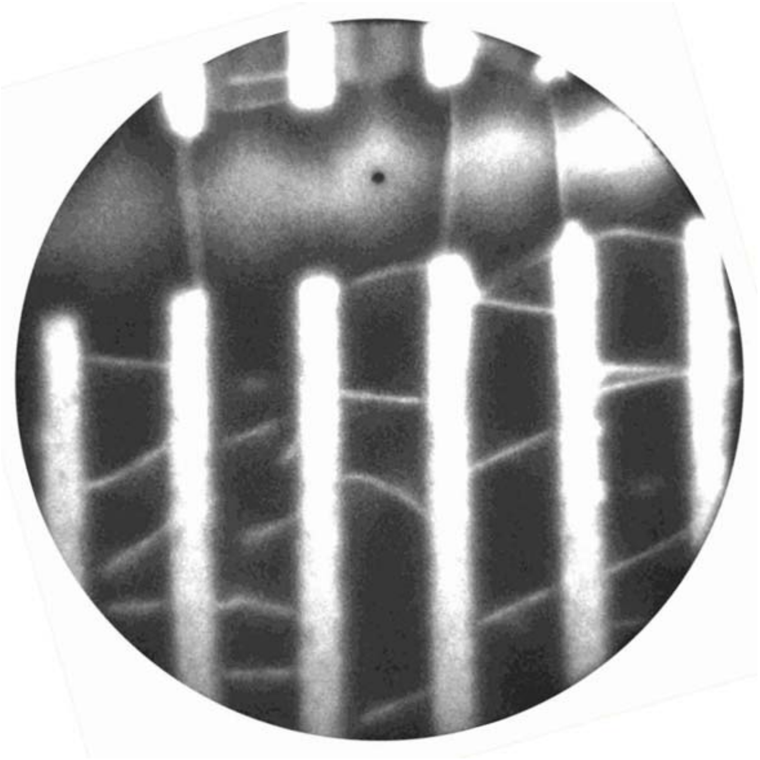
Why spectromicroscopy ?

- semicond. nanostructures: self-organized islands (dots)

F. Ratto et al.: Appl. Phys. Lett. **84** (2004) 4526.

Motivation



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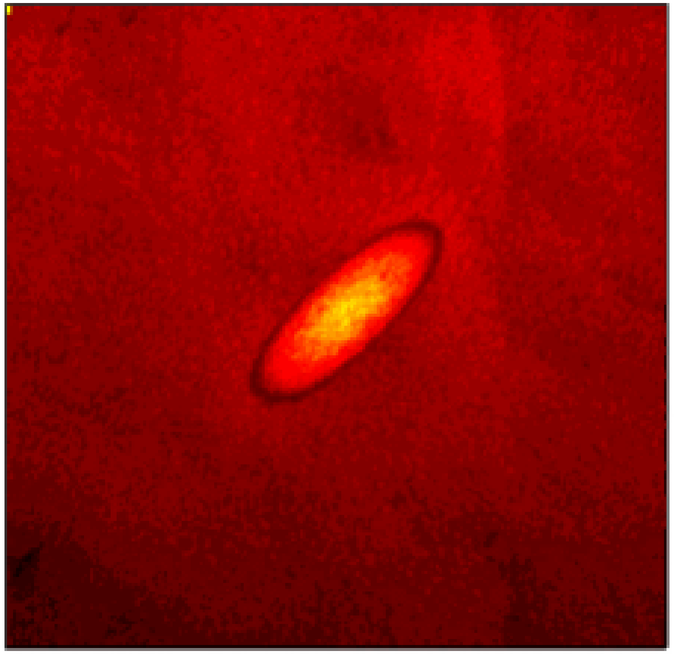
Why spectromicroscopy ?

- semicond. nanostructures: self-organized islands (dots)
- carbon nanotubes

S. Suzuki et al.: Appl. Phys. Lett. **85** (2004) 127.

Motivation



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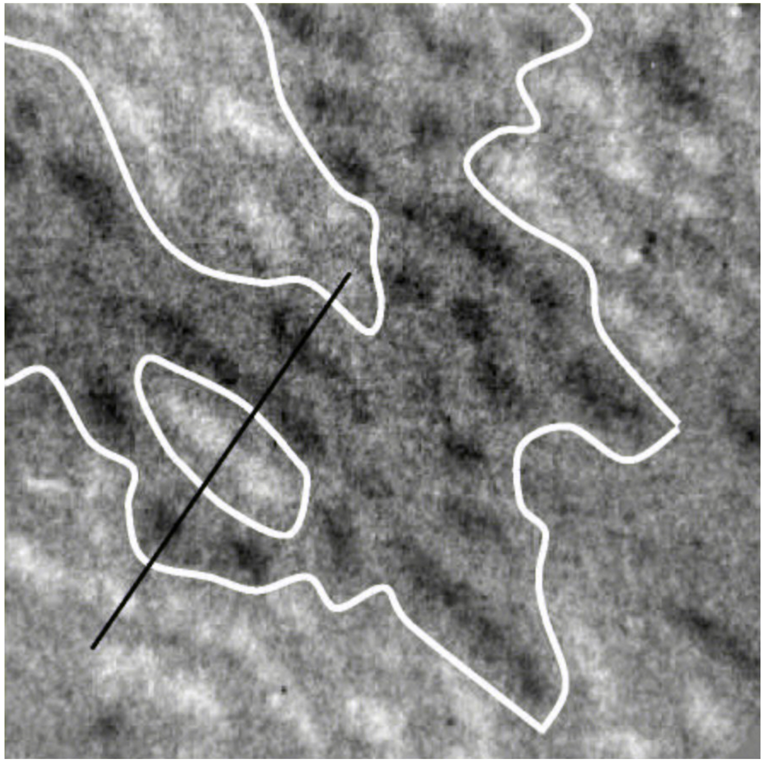
Why spectromicroscopy ?

- semicond. nanostructures: self-organized islands (dots)
- carbon nanotubes
- catalysis, chemical waves

A. Locatelli et al.: J. Am. Chem. Soc. **127** (2005) 2351.

Motivation



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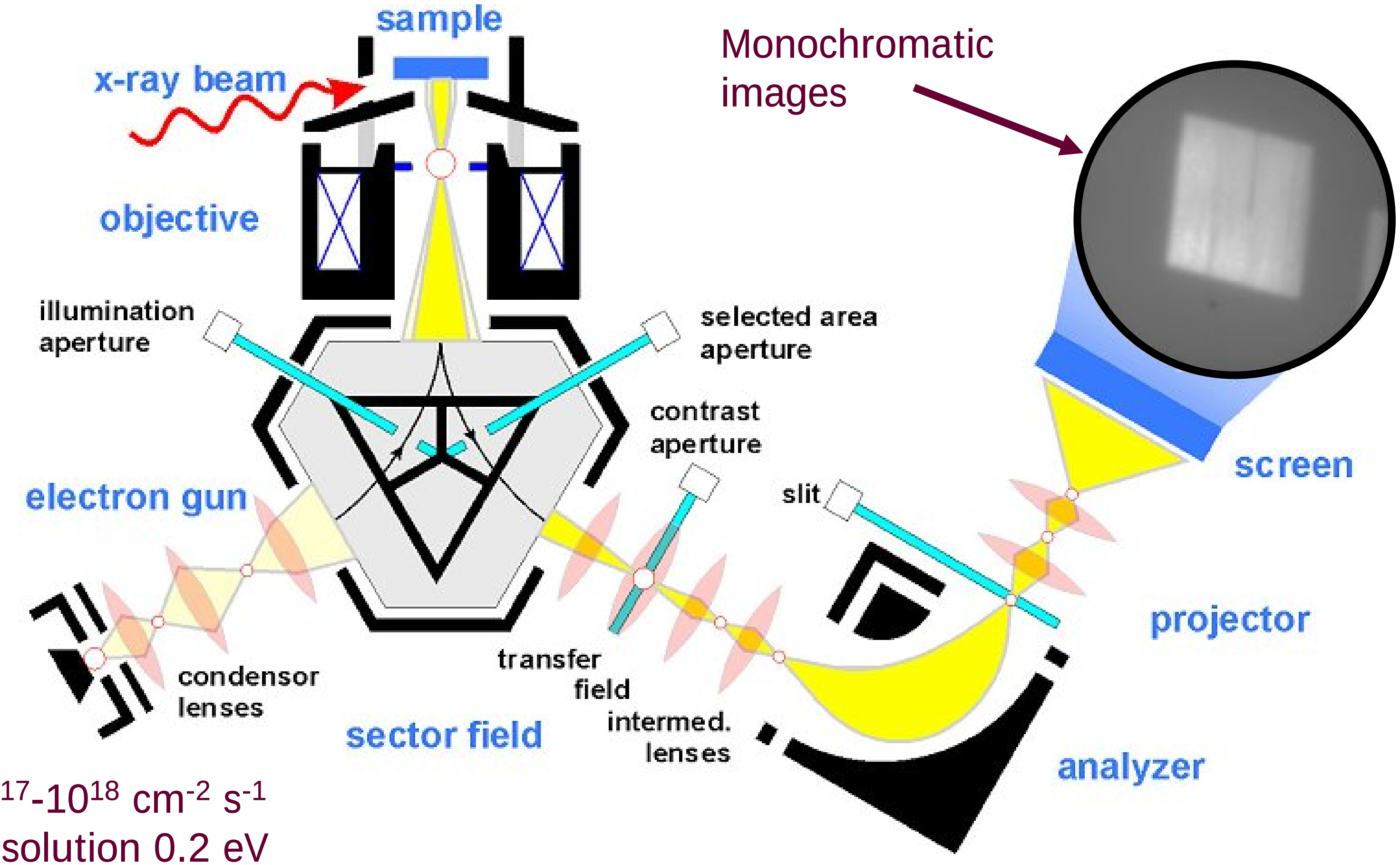
Why spectromicroscopy ?

- semicond. nanostructures: self-organized islands (dots)
- carbon nanotubes
- catalysis, chemical waves
- surface magnetism (XMCD)

A. M. Mulders et al.: Phys. Rev. B **71** (2005) 241422.

The SPELEEM at Elettra

Spectroscopic photoemission and low energy electron microscope

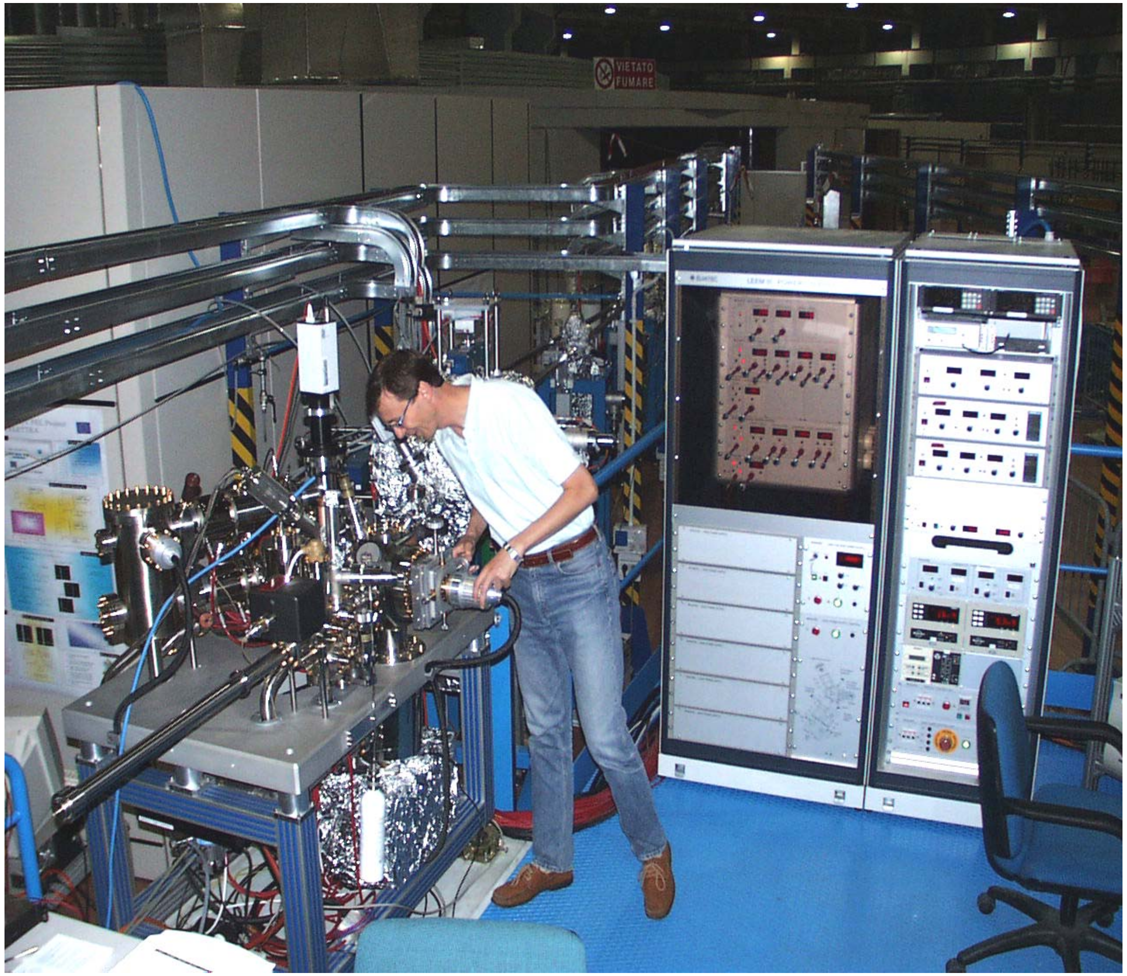


<u>Main features</u>

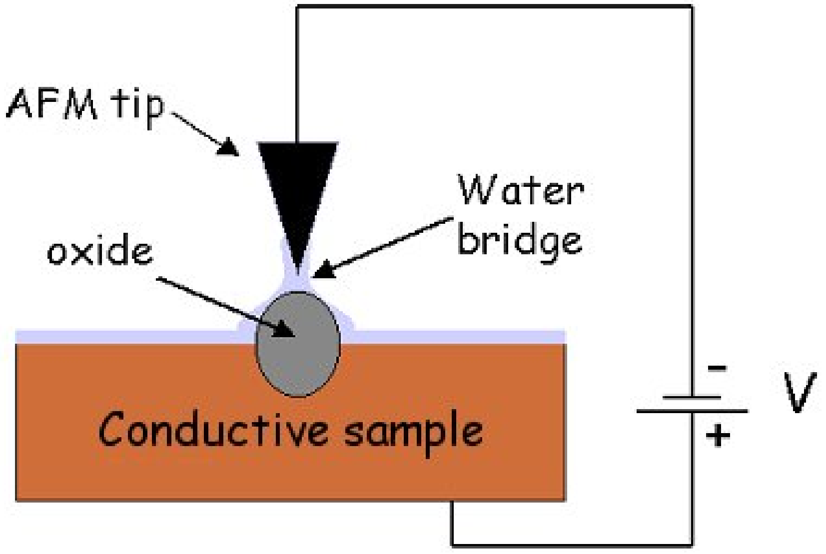
- Photon flux 10^{17}-10^{18} cm^{-2} s^{-1}
- Best Energy resolution 0.2 eV
- Lateral resolution 25 nm

The SPELEEM at ELETTRA

Spectroscopic photoemission and low energy electron microscope



Local Anodic Oxidation (LAO)



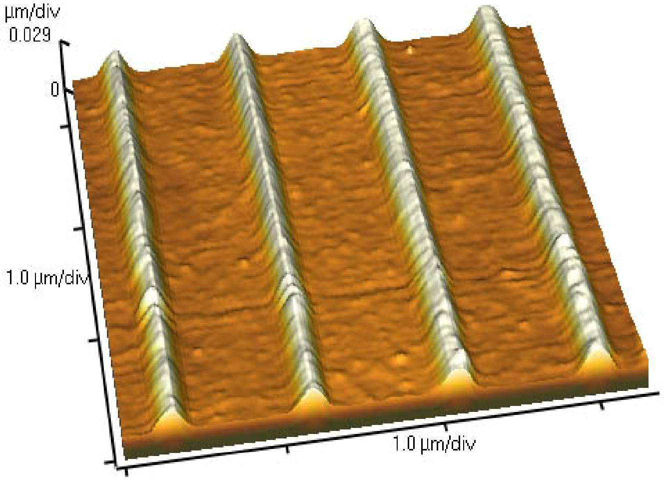
Commonly used model:

- Water electrolysis $H_2O \rightarrow H^+ + OH^-$.
- OH^- groups (or O^-) migrate towards the substrate-oxide interface.
- Oxide penetration induced by the intense local electric field ($>10^7$ V/cm).

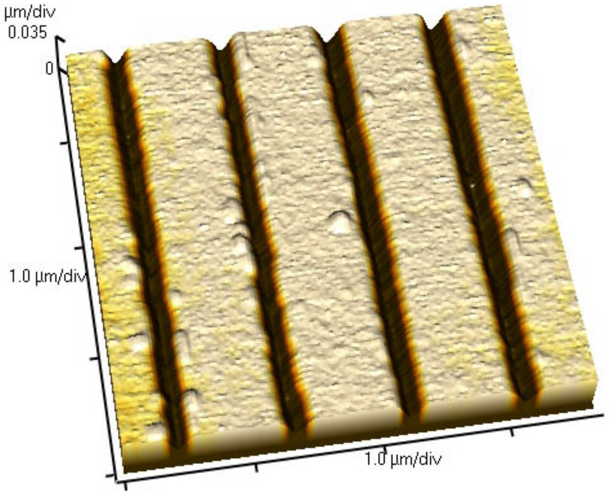
Versatile tool at relatively low cost

High lateral resolution but small area

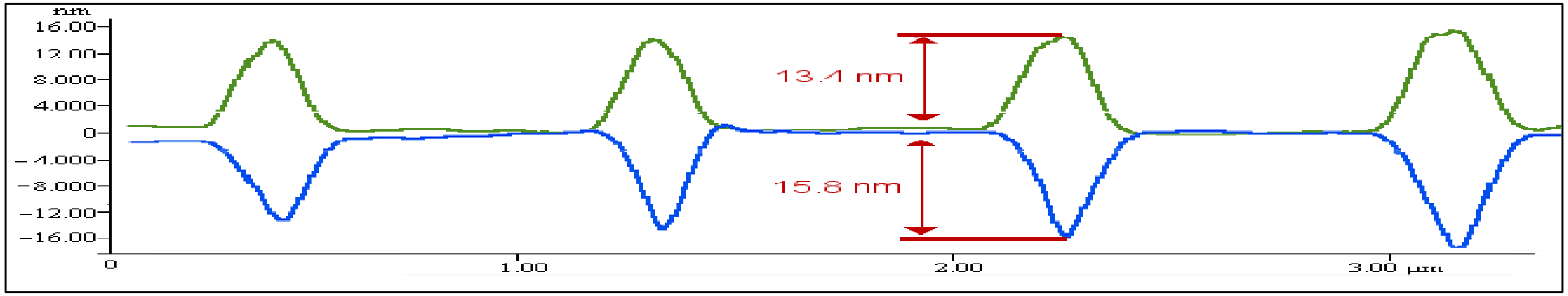
Local Anodic Oxidation (LAO)



After oxidation.



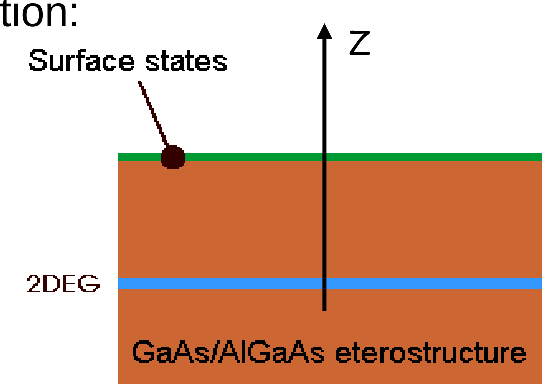
Oxide removal with HF 10%, 30 s.

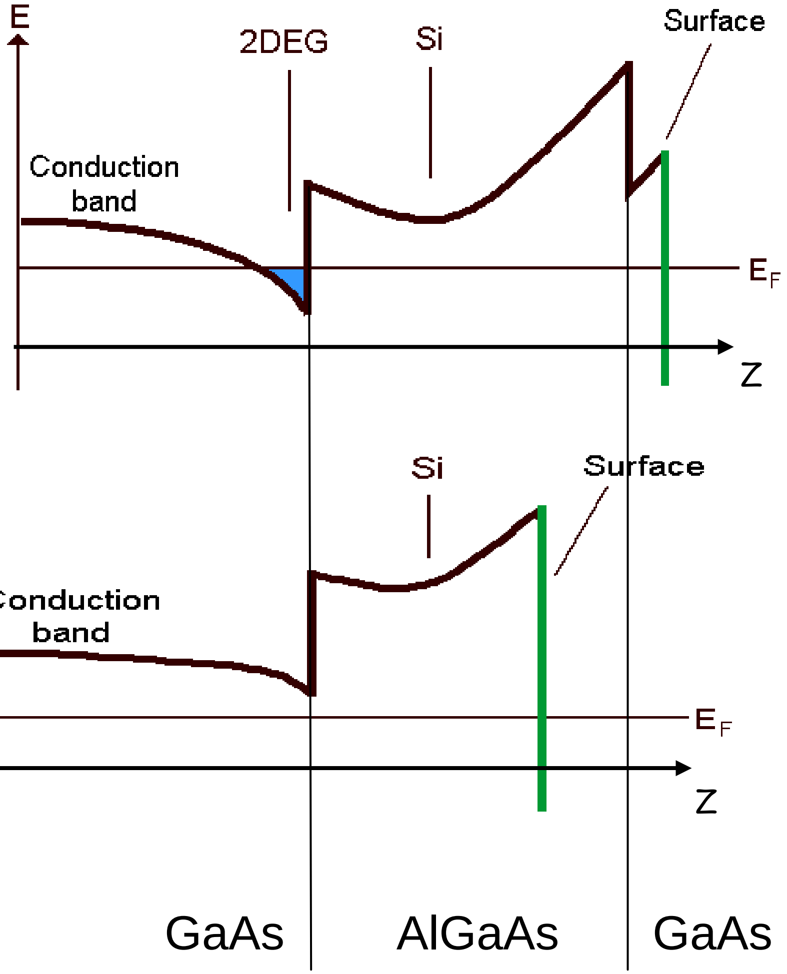


The penetration depth is 1.0-1.5 times the oxide height.

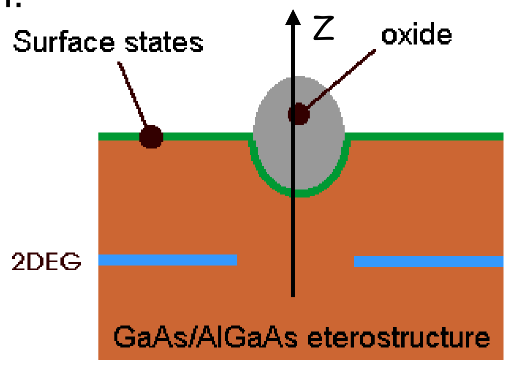
LAO on GaAs/AlGaAs

Before oxidation:

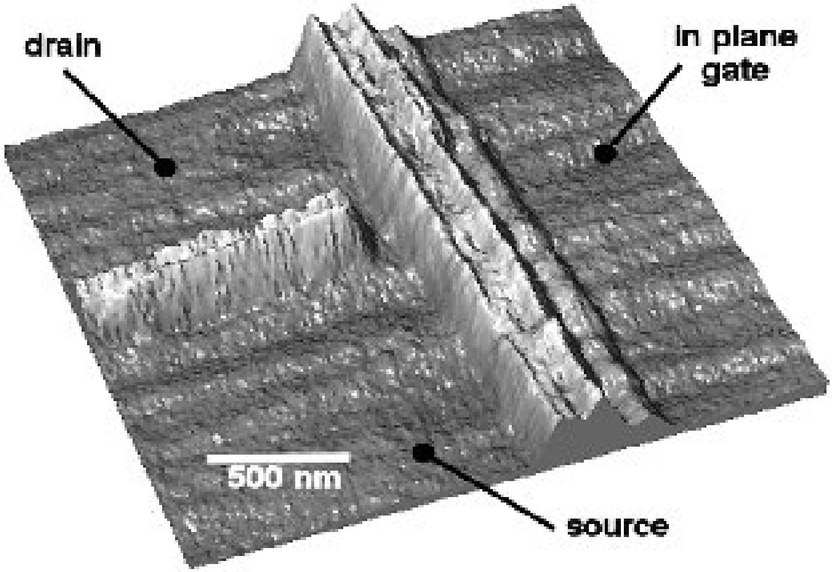


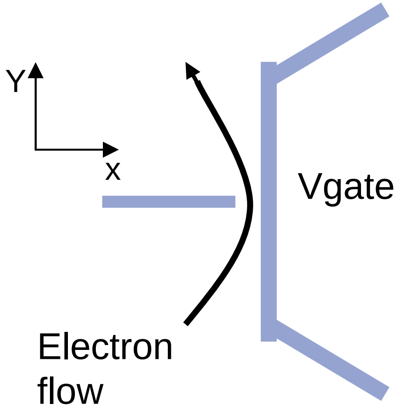


After oxidation:



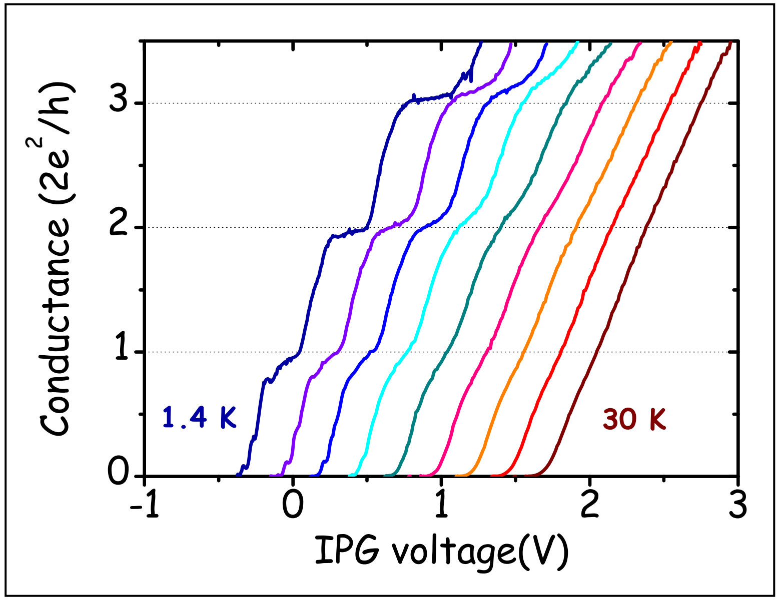
Quantum Point Contact





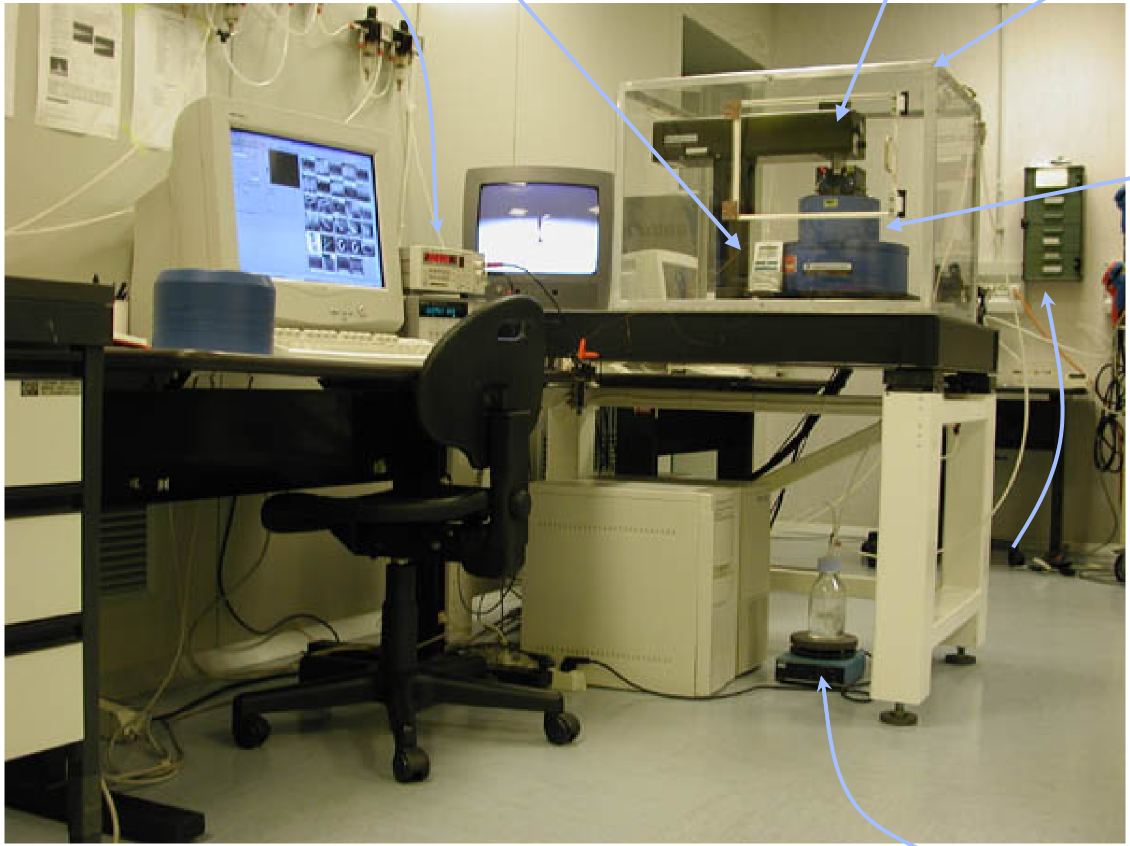
Vgate

Electron
flow



G. Mori et al, J. Vac. Sci. Technol. B **22** (2004) 570.

Setup for Lithography on GaAs



voltage source

Hygrometer

AFM camera

Plexiglass hood

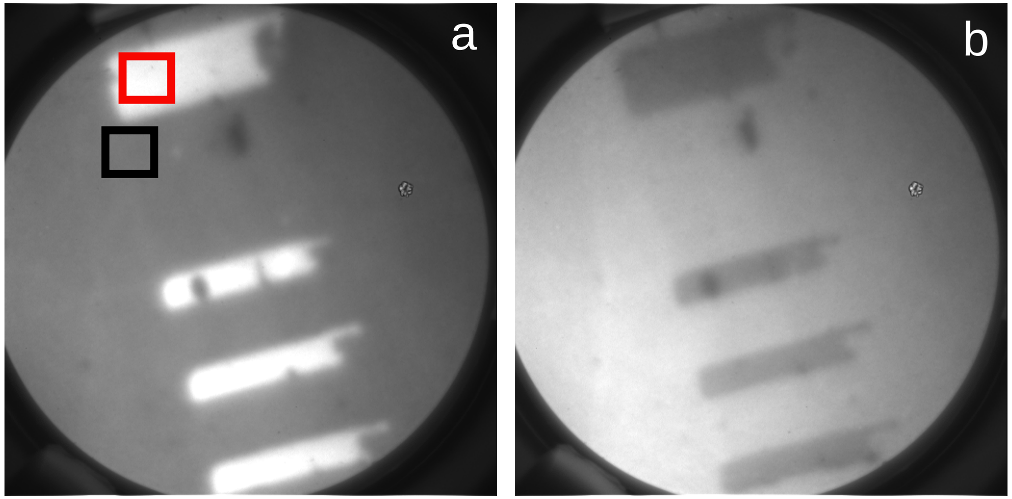
AFM

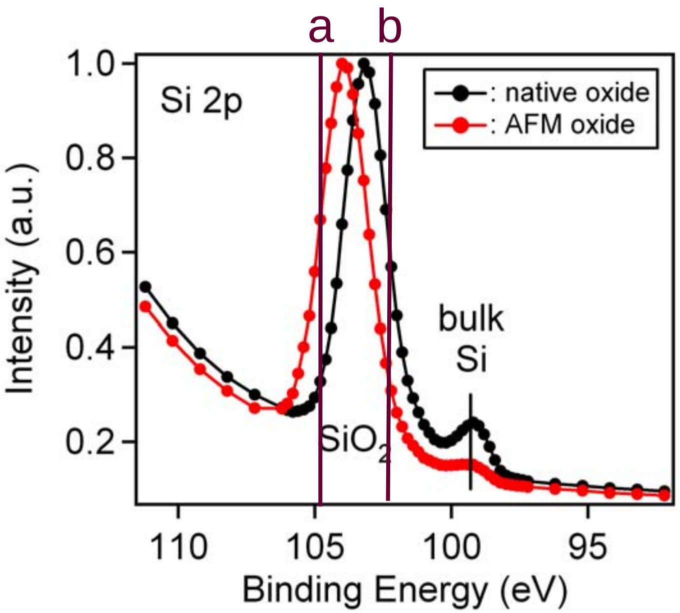
$N_2 + H_2O$

VEECO Autoprobe CP

water bottle

LAO on Silicon



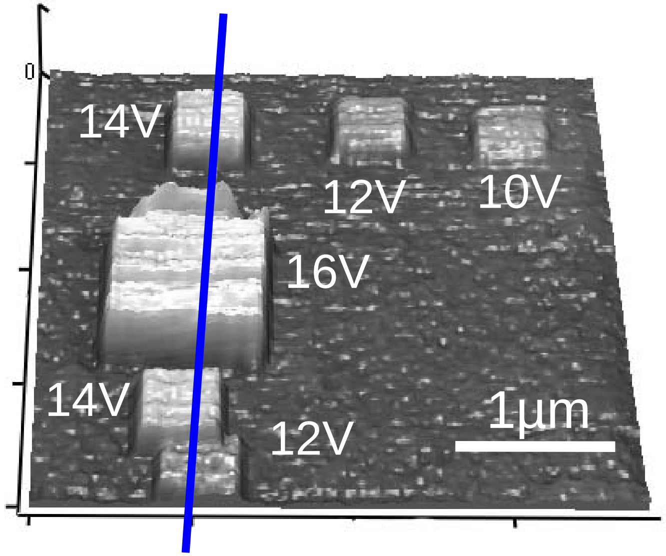


- LAO oxide consists of SiO_2
- Properties similar to those of thermally grown SiO_2

M. Lazzarino.: Appl. Phys. Lett. **81** (2002) 2842.

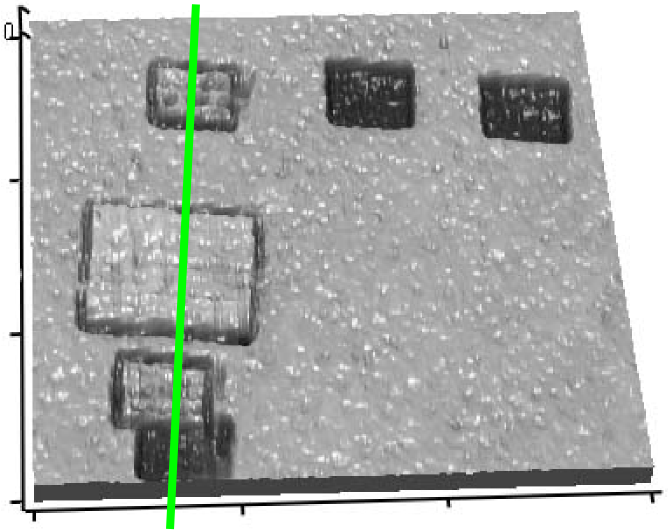
GaAs LAO-Oxide: Desorption

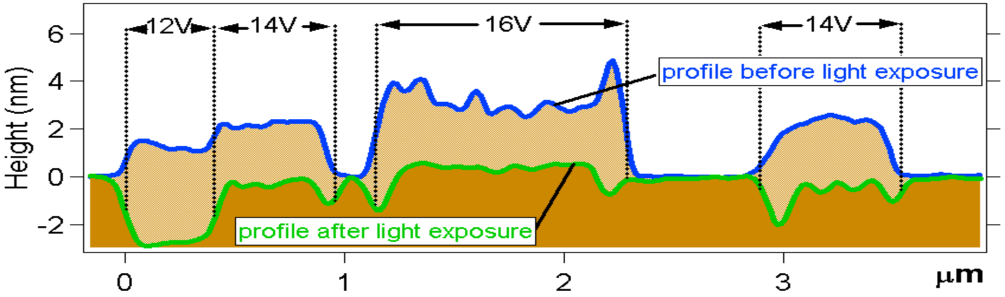
Before exposure to x-rays



hν = 130eV

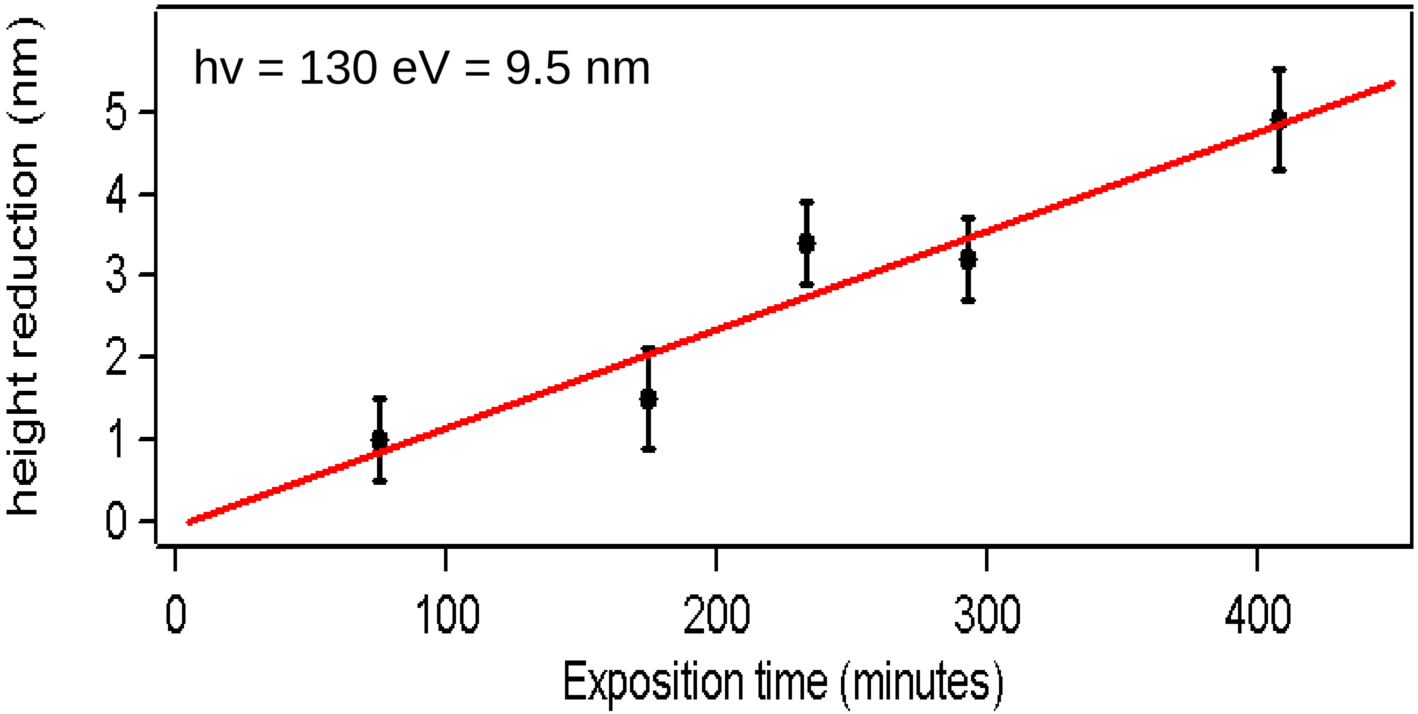
After hours of exposure





D. Ercolani et al.: Adv. Funct. Mater. **15** (2005) 587.

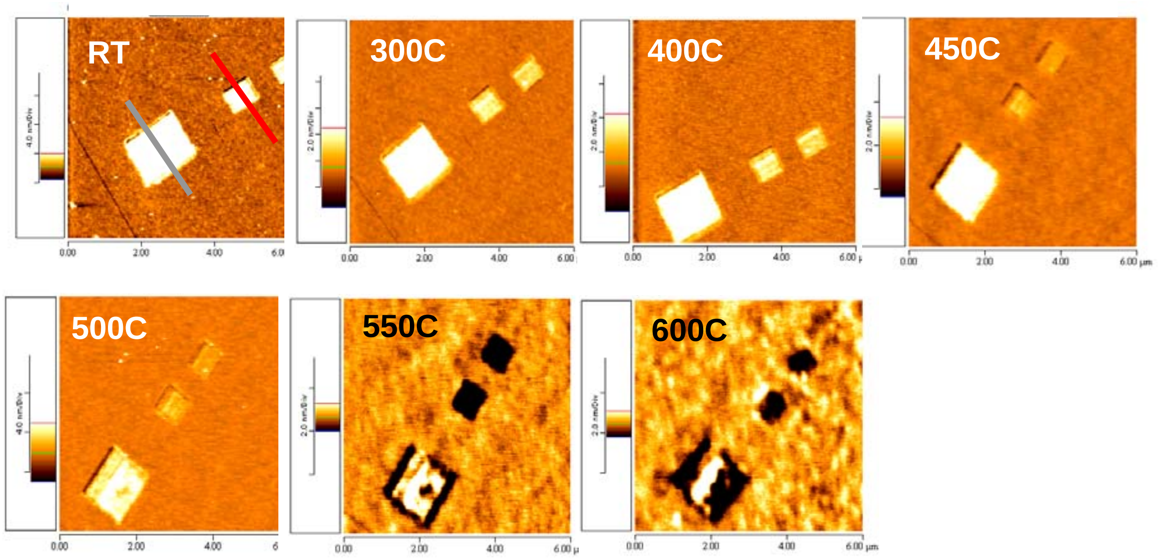
Height reduction vs. exposure time

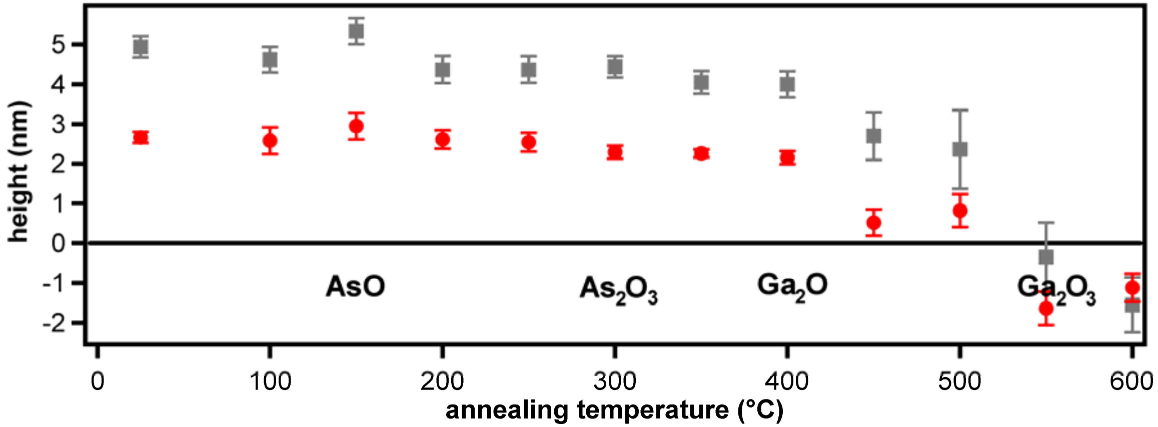


- We observe a linear relation between exposure time and height reduction.
- A dependence on other oxidation parameters (bias, writing speed) could not be detected.

D. Ercolani et al.: Adv. Funct. Mater. **15** (2005) 587.

Thermal stability

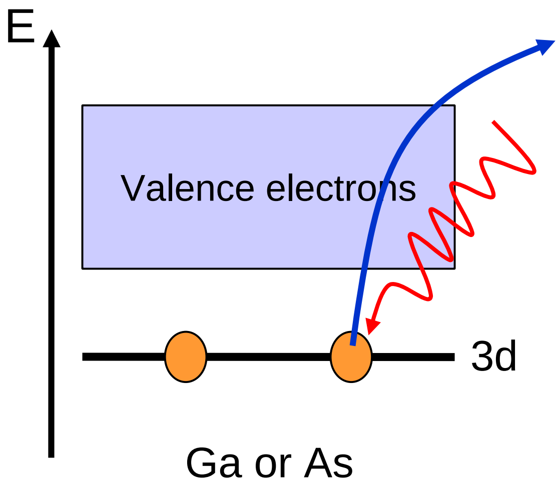




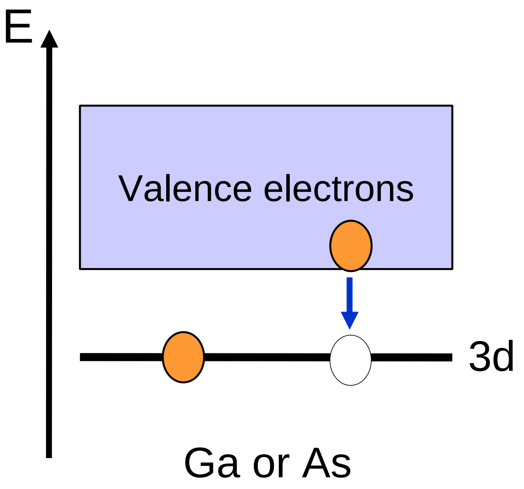
Each annealing step:
10 minutes
in N_2 atmosphere

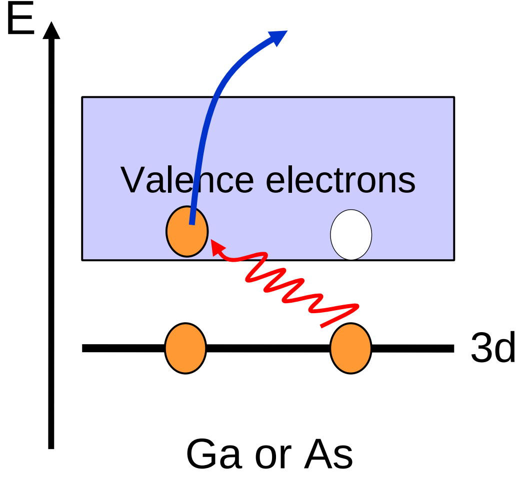
D. Ercolani et al.: Adv. Funct. Mater. **15** (2005) 587.

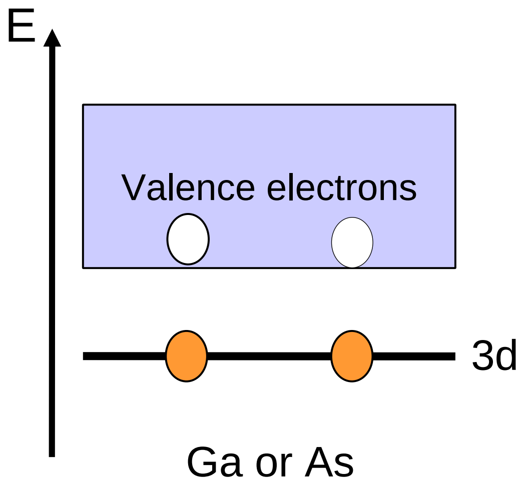
The Knotek-Feibelman mechanism



Initial state





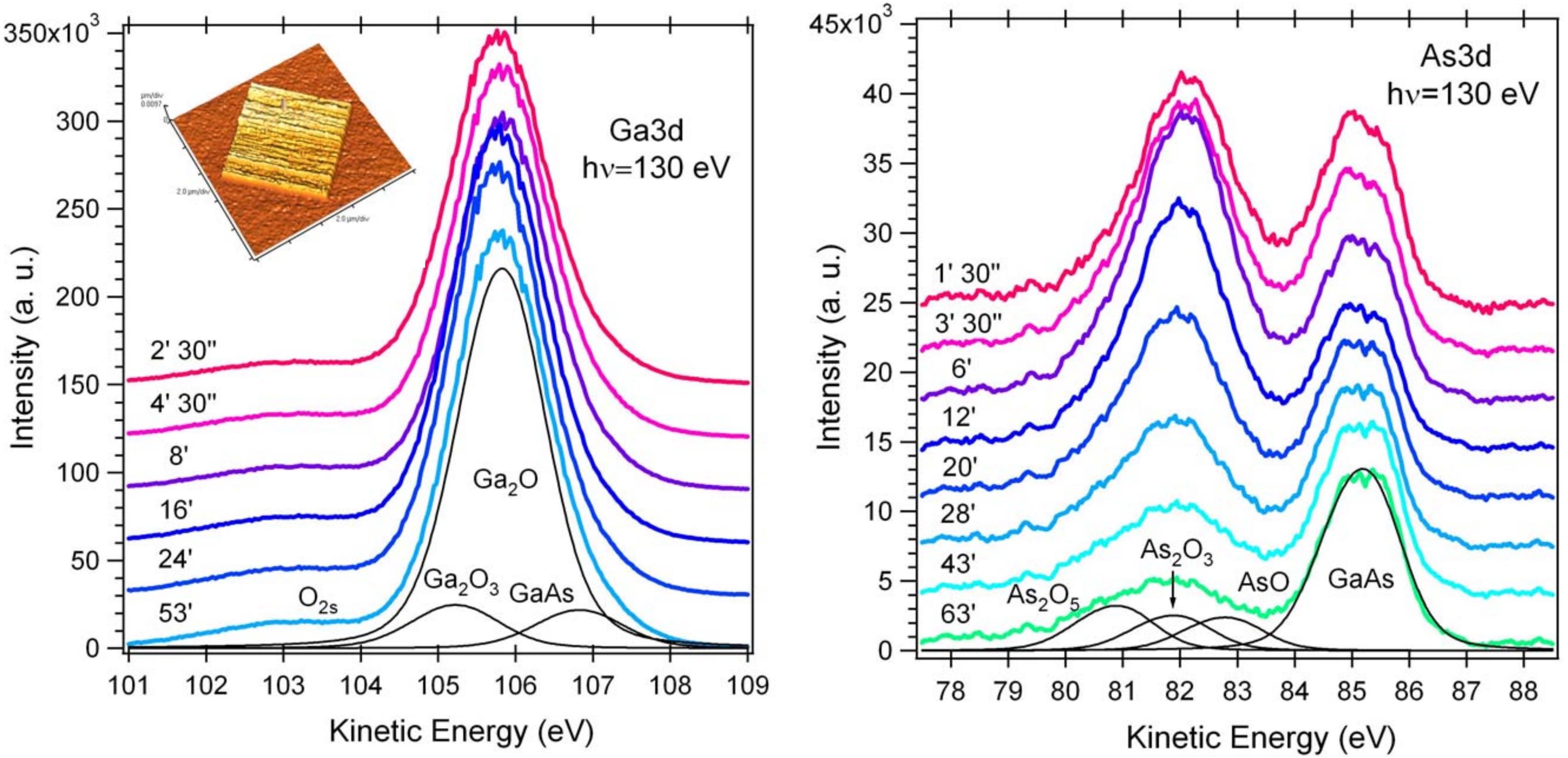


Final state

- This Auger decay leads to a final state with two vacancies in the valence band weakening the bond between Ga or As and O.

D. Ercolani et al.: Adv. Funct. Mater. **15** (2005) 587.

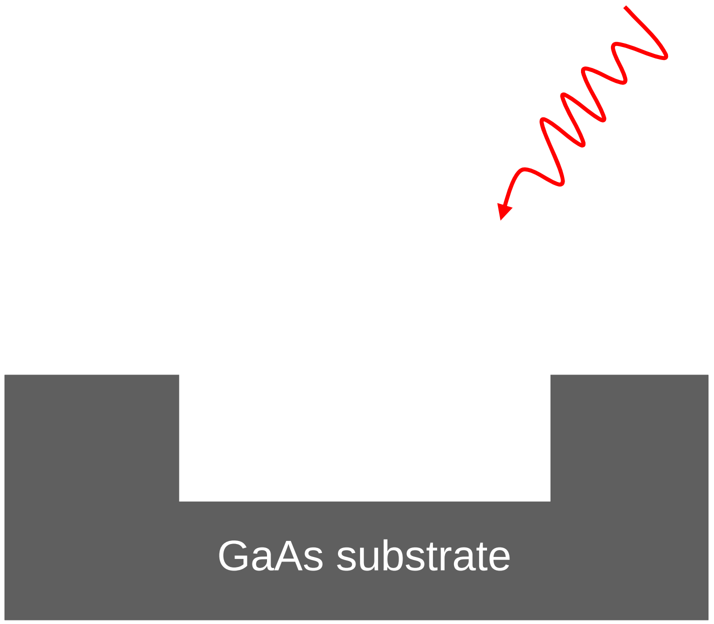
Spectra From GaAs LAO-Oxide



G. Mori et al.: J. Appl. Phys. **97** (2005) 114324.

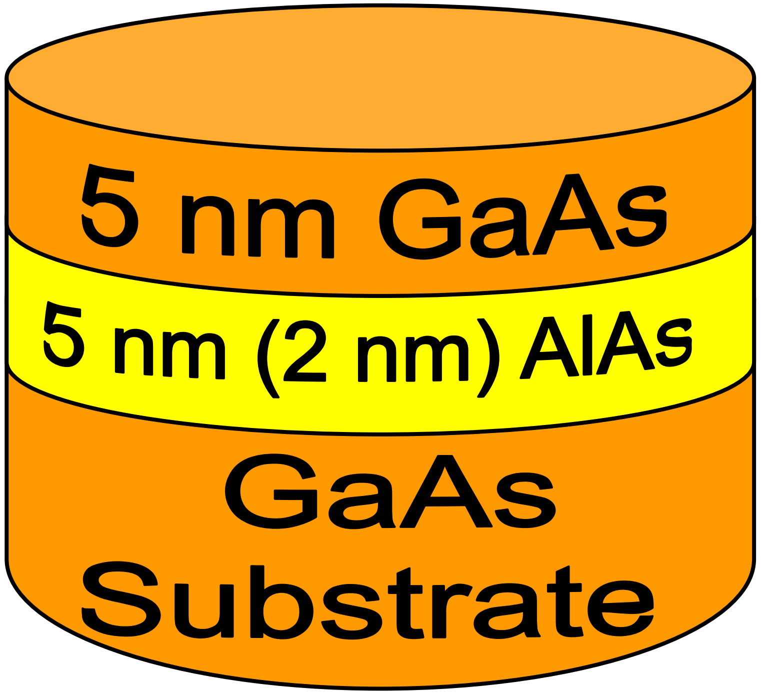
Chemistry of the GaAs LAO-Oxide

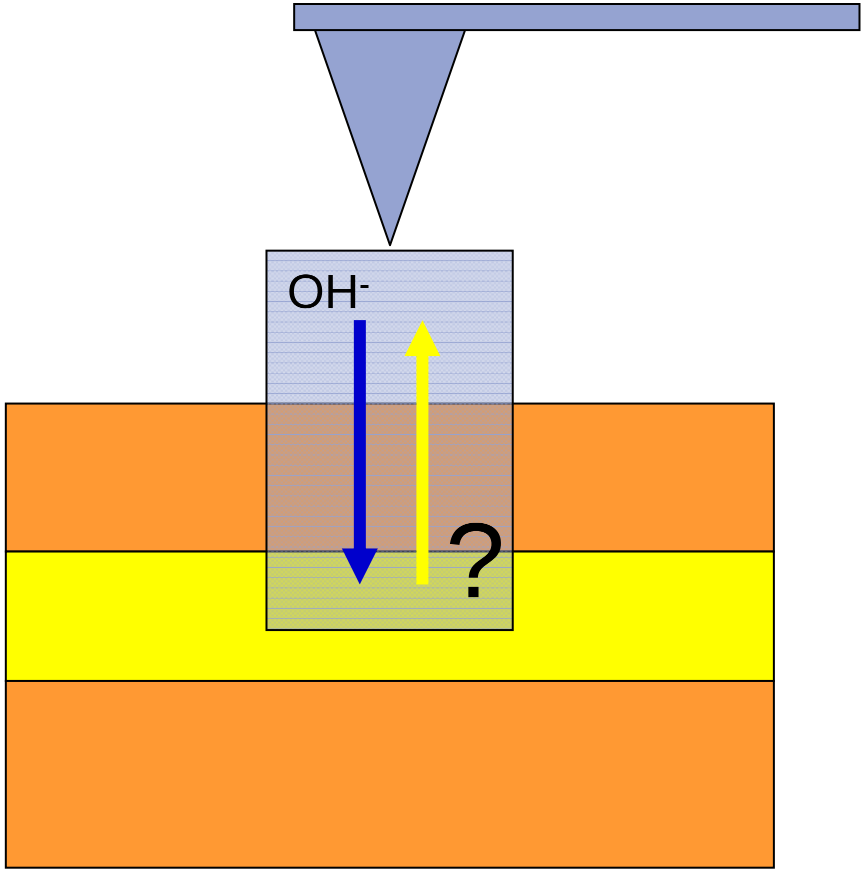
- Photon assisted partial desorption of the AFM-grown oxide was observed.
- The AFM-oxide is mainly composed of Ga_2O, with a small fraction of Ga_2O_3 and As-oxides.
- The shape of the Ga peak does not change with exposure time (early stage of desorption), however, Ga-oxides do desorb.
- All As-oxides desorb completely. No As-oxides detected after some hours of exposure.
- The As-oxides are located only at the surface.
- Evidence for the presence of unoxidized GaAs in the LAO-oxide.
- Chemical composition does not depend on writing bias.



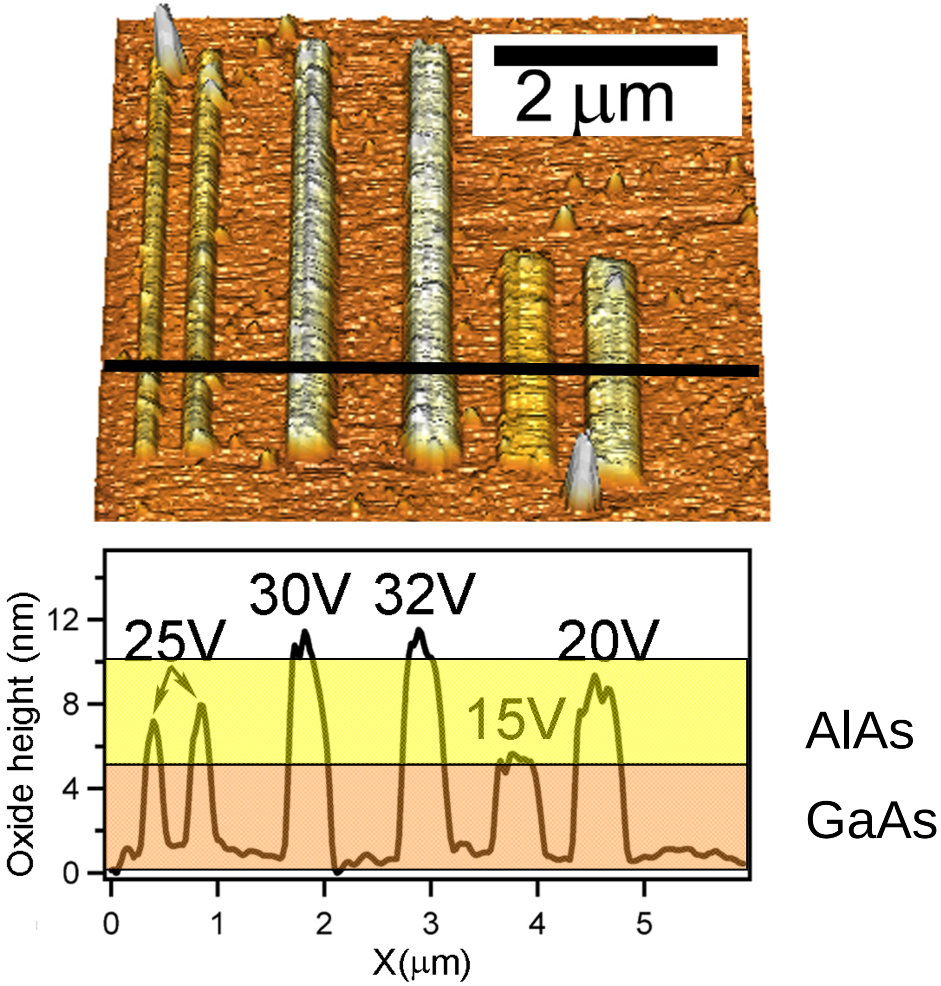
G. Mori et al.: J. Appl. Phys. **97** (2005) 114324.

The microscopical dynamics of LAO



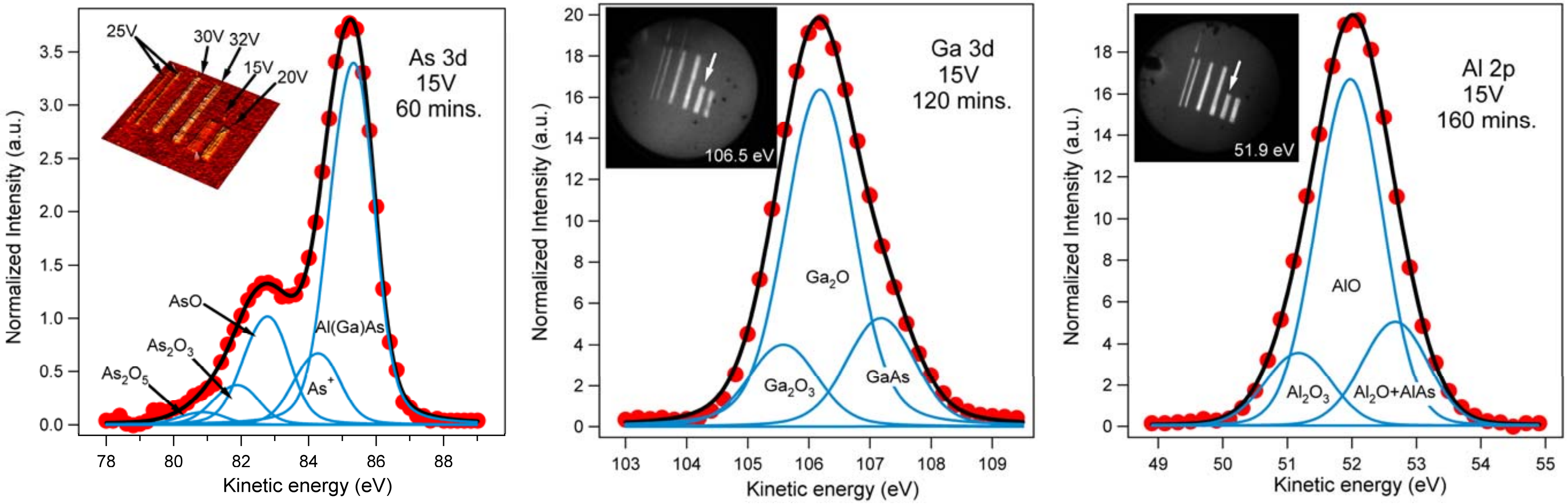


LAO on III-V Heterostructures



G. Mori et al.: submitted to J. Appl. Phys.

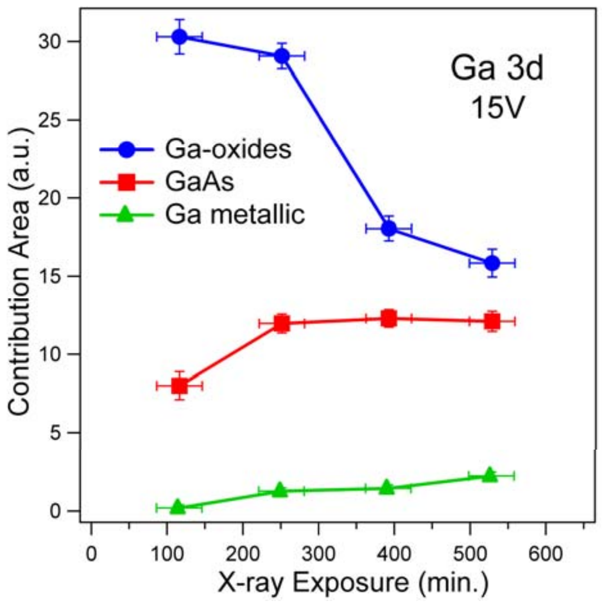
Chemical composition of LAO oxide

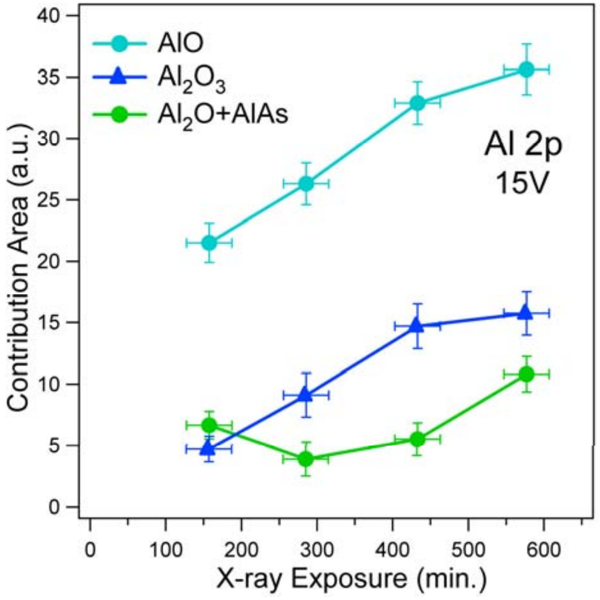


- Aluminium observed at the surface of the LAO oxide
- No Al in the regions not oxidized with LAO
- The other oxide lines do not show remarkable differences between the relative concentration of the components in each core level.

G. Mori et al.: submitted to Nucl. Instr. and Meth. B

The effect of X-ray exposure

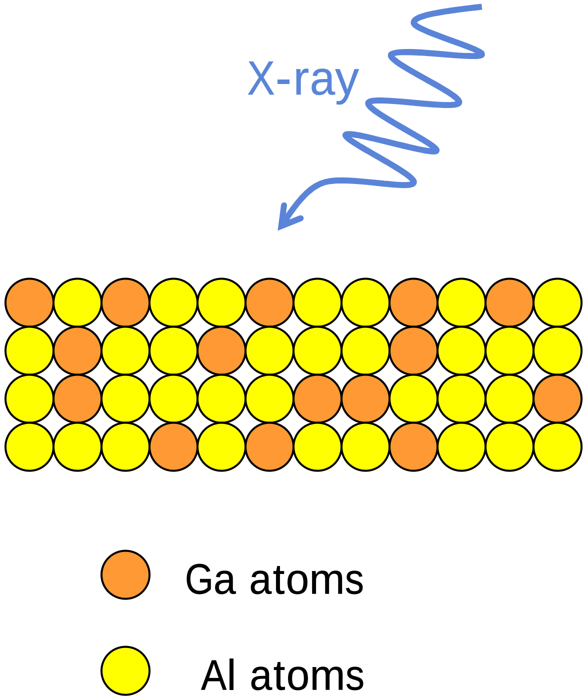




- The X-ray exposure is removing the Ga oxides faster than the Al ones resulting in a surface enrichment with Al.
- The Al oxides are more stable to X-ray exposure than Ga oxides

G. Mori et al.: submitted to Nucl. Instr. and Meth. B

The effect of X-ray exposure



$$N_{Ga}(t) = N_{Ga}^{0} \cdot e^{-\frac{t}{\tau_{Ga}}}$$

N^0_{Ga} is the number Ga atoms at the surface before exposure

τ_{Ga} is the probability that a Ga atom is desorbed and is replaced by an underlying Al atom.

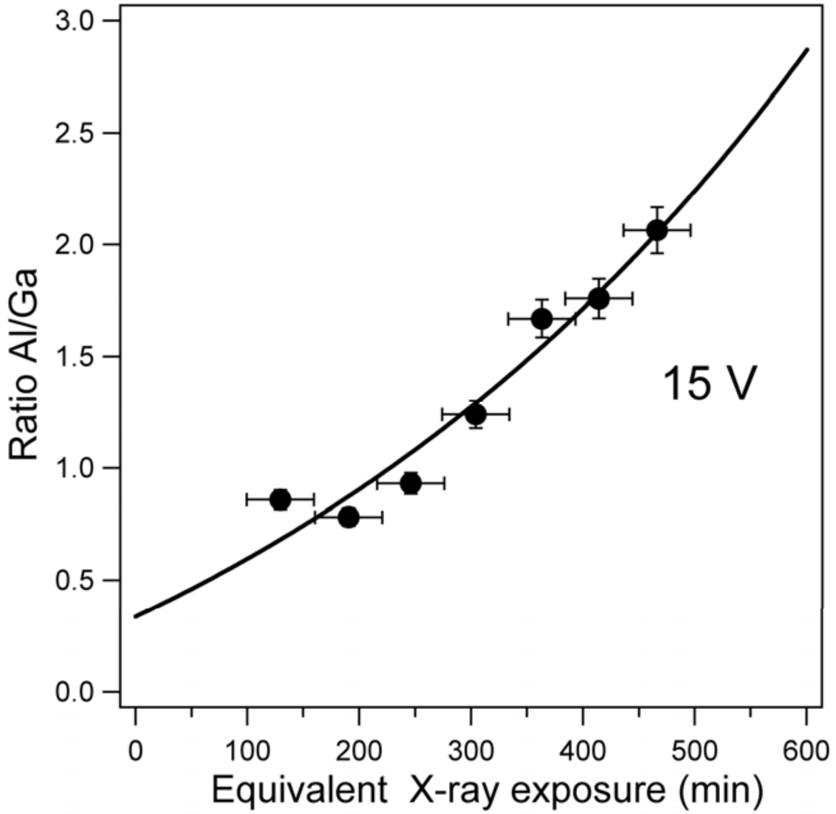
Assuming that the Ga atoms desorbs much faster that the Al ones

$$N_{Al}(t) \cong N_{Al}^{0} + N_{Ga}^{0} \cdot \left(1 - e^{-\frac{t}{\tau_{Ga}}}\right)$$

With this simple model we can calculate R(Al/Ga) for any exposure time.

G. Mori et al.: submitted to Nucl. Instr. and Meth. B

The effect of X-ray exposure

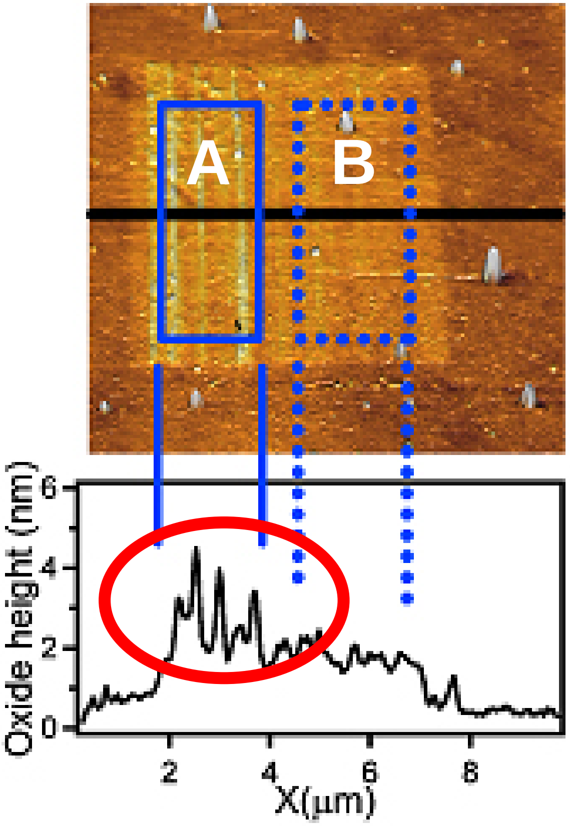


- Initially: R(Al/Ga)=0.34±0.10
- τ_{Ga}= 560 ± 60 min

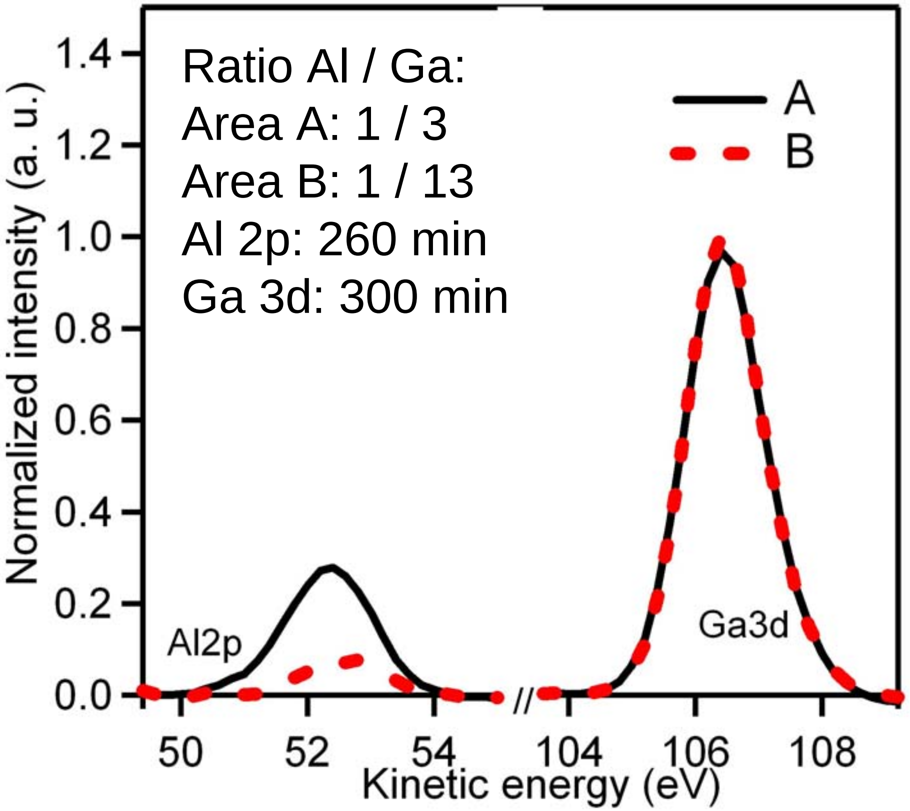
- We are able to quantify the effect of X-ray exposure on the surface chemical composition of the LAO oxide.

G. Mori et al.: submitted to Nucl. Instr. and Meth. B

Shallow Oxidations



Average oxide height:
Area A: 1.9 ± 0.7 nm
Area B: 1.3 ± 0.3 nm

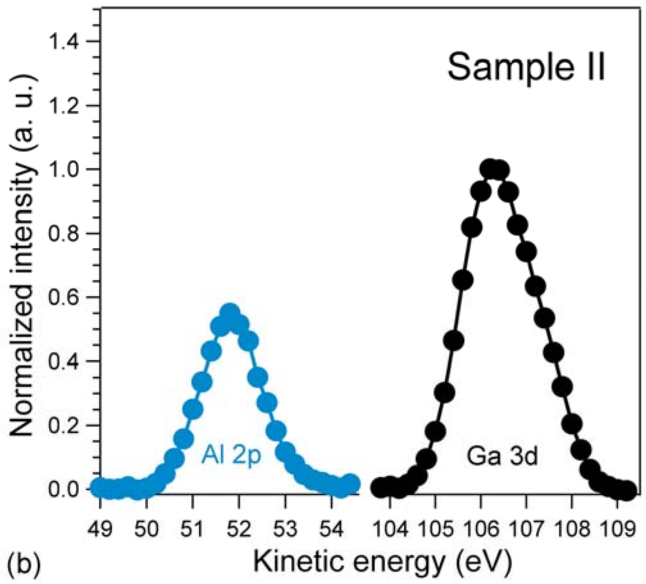


Al content depends strongly on oxide height

G. Mori et al.: submitted to J. Appl. Phys.

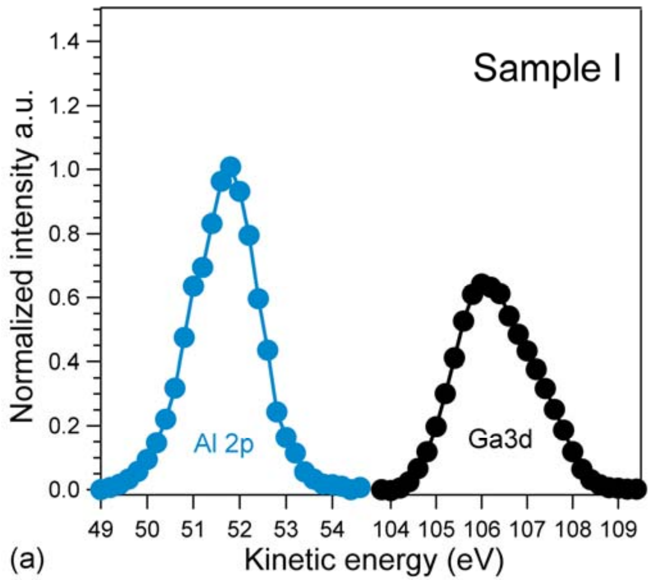
Variation in AlAs layer thickness

- 2 nm AlAs
- Oxide height 9.0 ± 1.0 nm



- **Ratio Al / Ga: 0.5**
- Al 2p: 220 min
- Ga 3d: 300 min

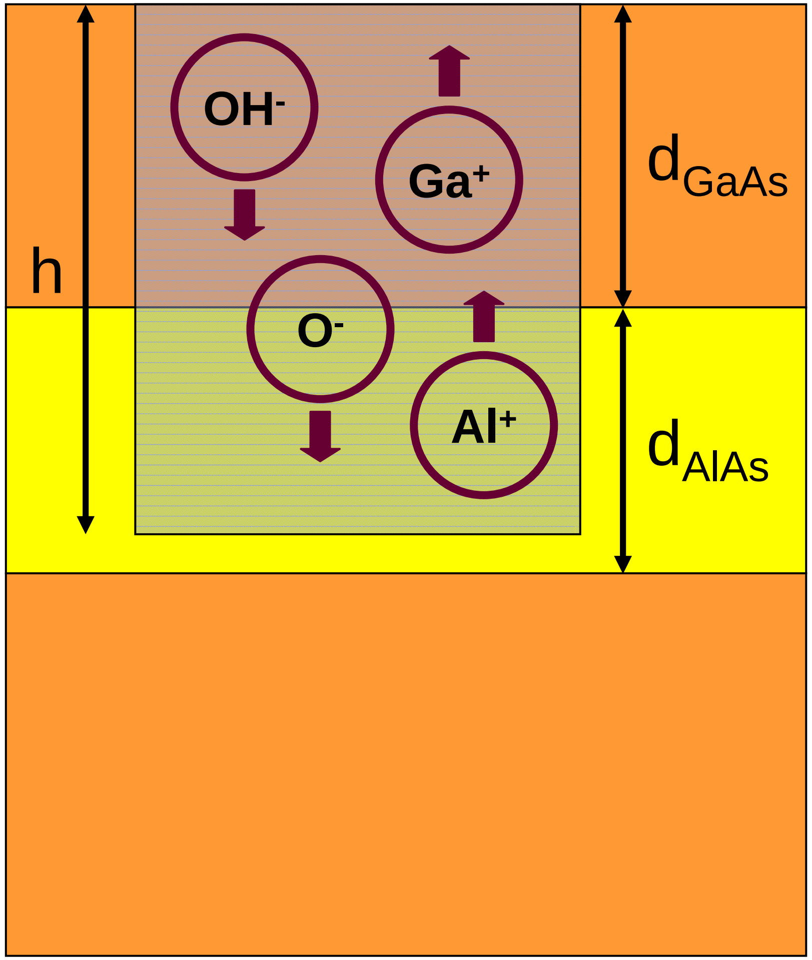
- 5 nm AlAs
- Oxide height 8.9 ± 0.9 nm



- **Ratio Al / Ga: 1.3**
- Al 2p: 260 min
- Ga 3d: 230 min

G. Mori et al.: submitted to J. Appl. Phys.

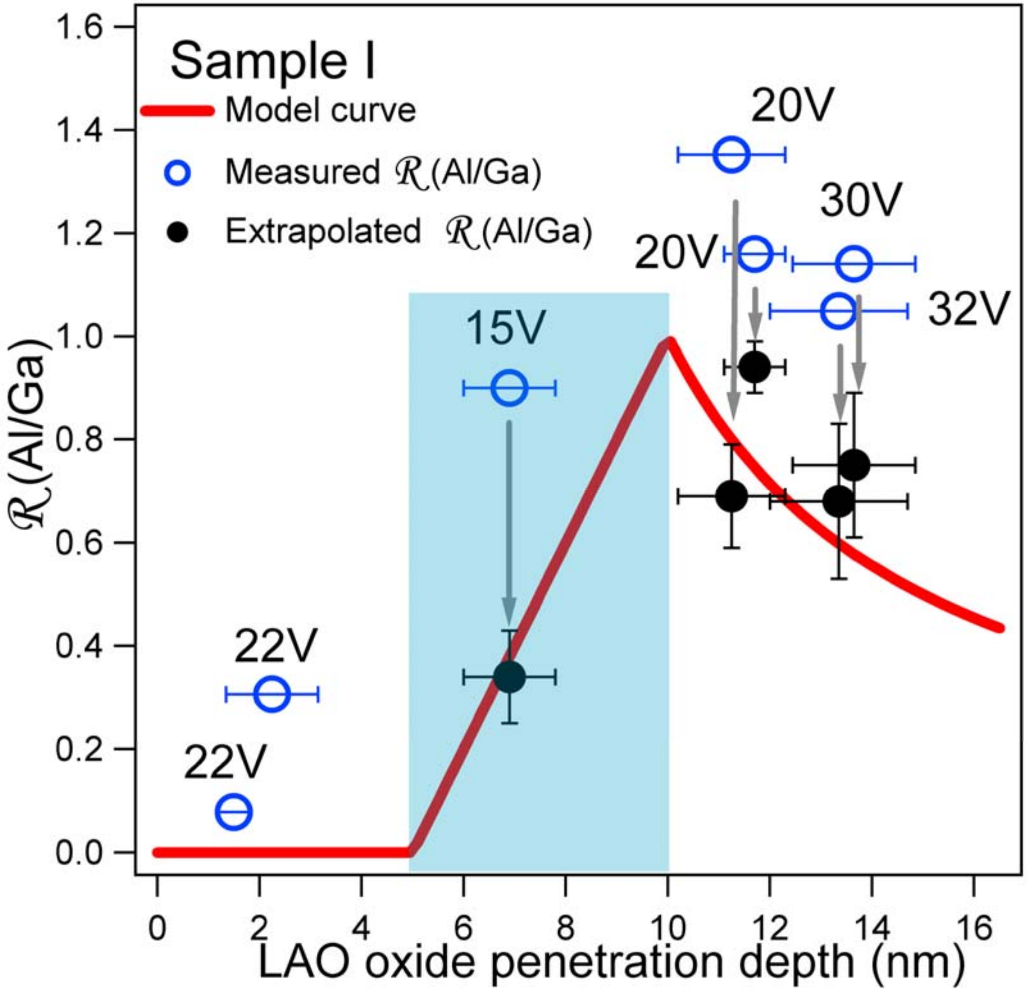
Refined Model



- Diffusion of oxygen-rich ions **plus** substrate ions
- Homogeneous mixing of components
- Ratio Al / Ga:
  - 0 for $h < d_{GaAs}$
  - $(h - d_{GaAs}) / d_{GaAs}$ for $d_{GaAs} < h < d_{GaAs} + d_{AlAs}$
  - $d_{AlAs} / (h - d_{AlAs})$ for $h > d_{GaAs} + d_{AlAs}$

G. Mori et al.: submitted to J. Appl. Phys.

Comparison with Experiment



G. Mori et al.: submitted to J. Appl. Phys.

Summary

- Investigation of chemical properties of LAO nanostructures on epitaxial GaAs/AlAs/GaAs layers.
- Presence of Al-oxides in the surface layers of the LAO nanostructures detected.
- Classical model of LAO process has to be revised.
- More general model is proposed which includes the diffusion of ionized substrate atoms to the surface.
- Good agreement between model and experiment is observed.