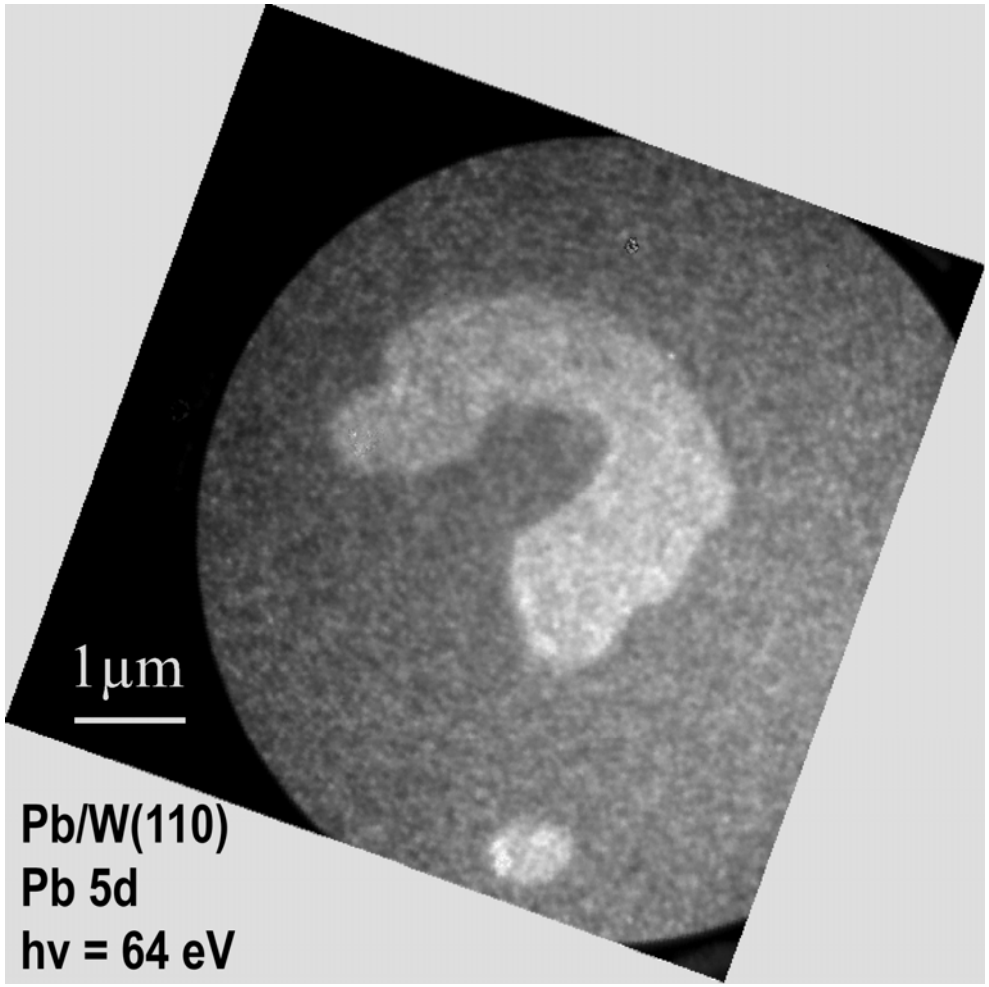
Photoelectron spectroscopy on semiconductor nanostructures

S. Heun

Sincrotrone Trieste

Motivation



Why spectro-microscopy ?

- (semiconductor) nanostructures
  - lithography
  - self-organization
- devices
- laterally inhomogeneous surfaces
- segregation at defects
- alloying (silicide formation)
- 2-compound growth on surfaces
- ...

Outline

Spectromicroscopy at Elettra

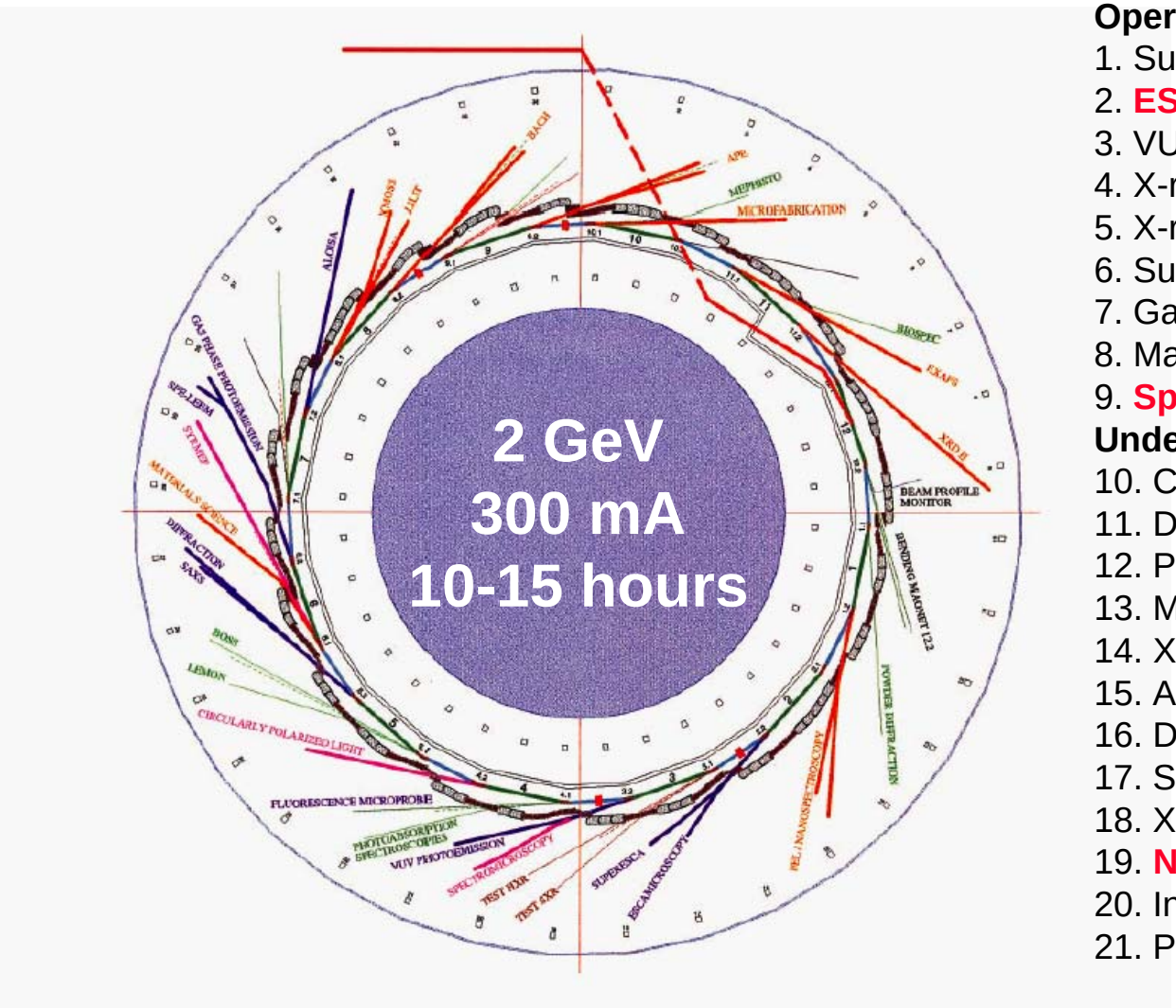
- ESCA - microscopy
  Example: Nanotubes

- SPELEEM
  Example: Nanocrystals

Both experiments in collaboration with Y. Watanabe (NTT Japan).

Location of Elettra

Elettra Beamlines



Operational:

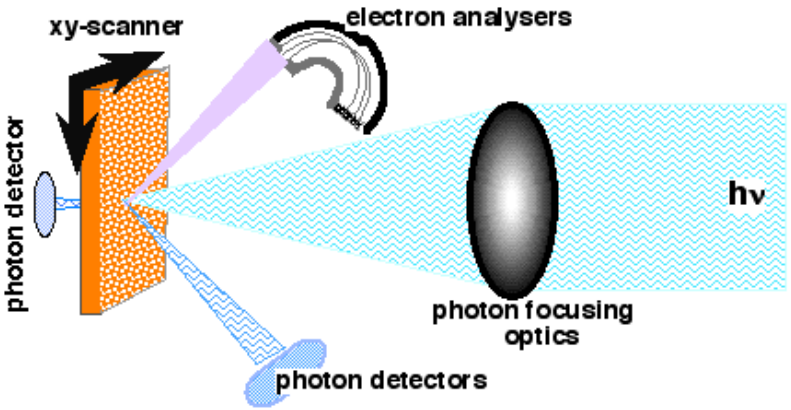
1. Super ESCA
2. **ESCA Microscopy**
3. VUV Photoemission
4. X-ray Diffraction
5. X-ray Small-angle Scattering
6. Surface Diffraction (ALOISA)
7. Gas-Phase Photoemission
8. Mammography (SYRMEP)
9. **Spectromicroscopy**

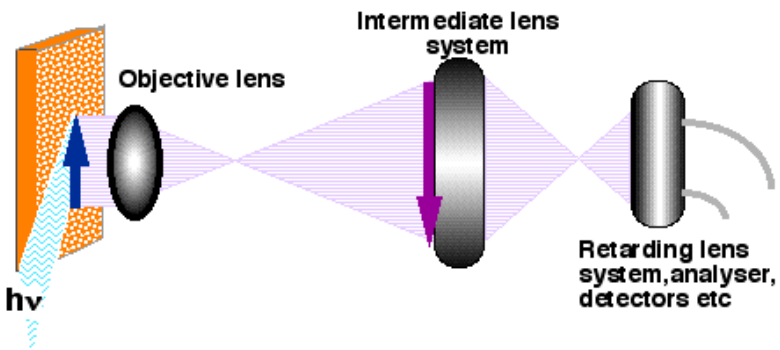
Under commisioning or construction:

10. Circular Polarized Light
11. Deep Lithography (Microfabrication)
12. Proximity Photolithography (LILIT)
13. Materials Science
14. XAFS
15. Advanced Dichroism (BACH)
16. Dichroich Photoemission (APE)
17. Soft X-ray Optical Spectroscopy
18. XRD II
19. **Nanospectroscopy**
20. Inelastic UV Light Scattering
21. Powder Diffraction

ELETTRA Highlights 1999 - 2000.

Approaches to SR-XPS-Microscopy





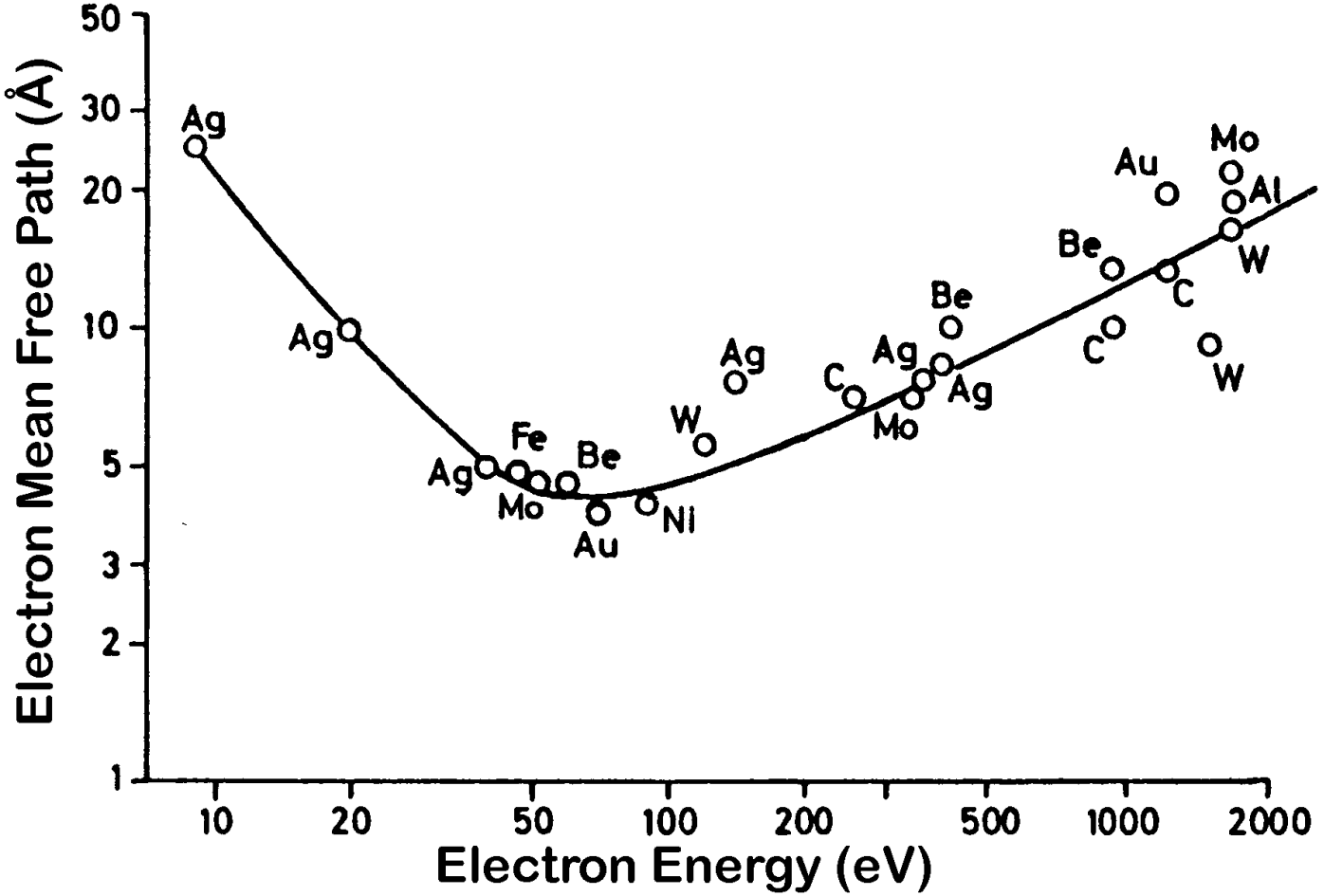
Photon optics is demagnifying the beam:
<u>scanning instrument</u>

1. Whole power of XPS in a small spot spectroscopy mode.
2. Flexibility for adding different detectors.
3. Limited use for fast dynamic processes.
4. Lower resolution than imaging instruments.

Electron optics to magnify irradiated area:
<u>imaging instrument</u>

1. High lateral resolution (20 nm).
2. Multi-method instrument (XPEEM/PED).
3. Excellent for monitoring dynamic processes.
4. More difficult to operate.
5. Sensitive to rough surfaces.

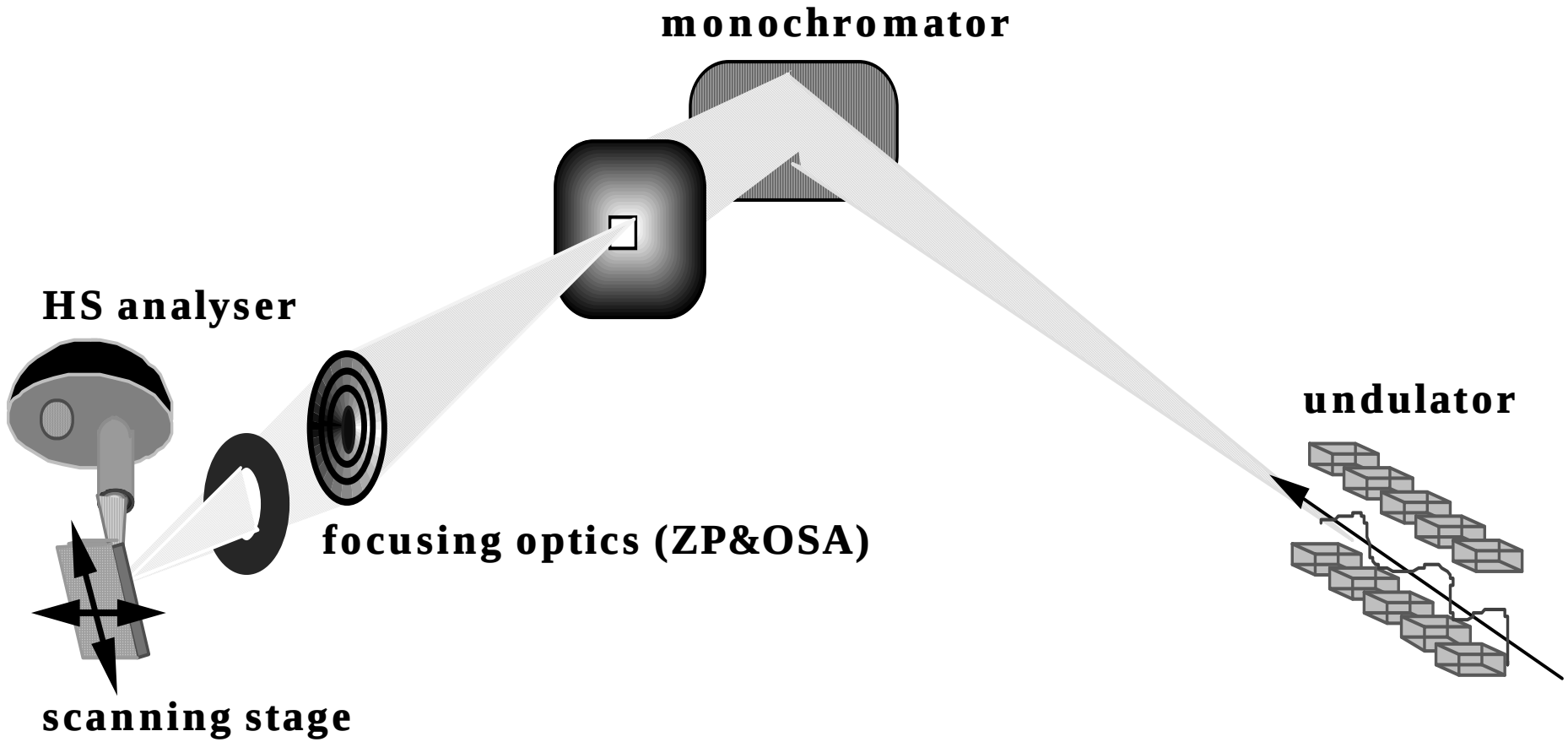
Photoelectron Mean Free Path



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

ESCA Microscopy Beamline

- **Flux density in a 0.01 μm^2 spot ~ 1- 5*10^9 ph/sec.**

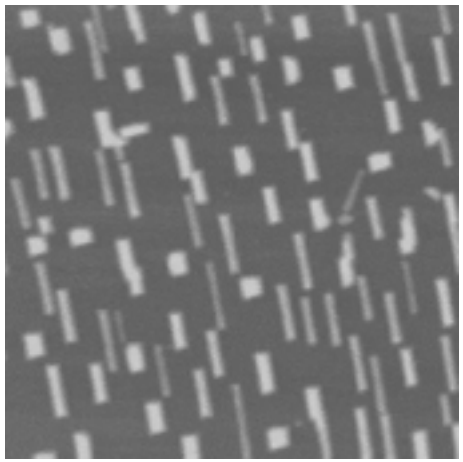


M. Marsi, L. Casalis, L. Gragoratti, S. Günther, A. Kolmakov, J. Kovac, D. Lonza, and M. Kiskinova, J. Electron Spect. **84** (1997) 73.

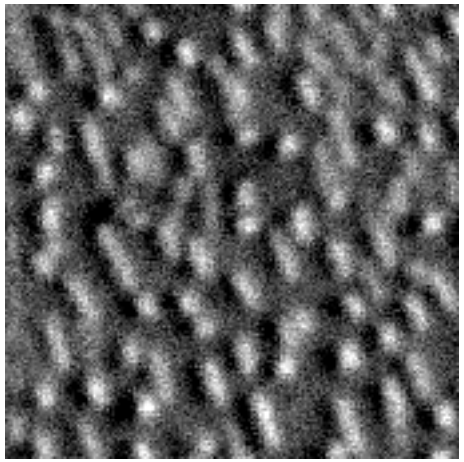
Lateral Resolution

Lateral resolution of SPEM using
60 nm / 200 µm zone plate
fabricated in CXRO-Berkeley (Dr. E. Anderson).

AFM image



Fe 3p image



1 µm

Lateral resolution: 80 nm.

AFM and SPEM images of assembled directionally grown $SmFe_2$ films on a Mo buffer, fabricated by pulsed laser deposition.
(Project of Dr. J. Vogel et al., Louis Neel Lab, Grenoble, Feb. 99)

M. Marsi, L. Casalis, L. Gragoratti, S. Günther, A. Kolmakov, J. Kovac, D. Lonza, and M. Kiskinova, J. Electron Spect. **84** (1997) 73.

Carbon Nanotubes

- highly one-dimensional structure

- specific electronic structure expected at tips, where graphene cylinders are semi-spherically closed

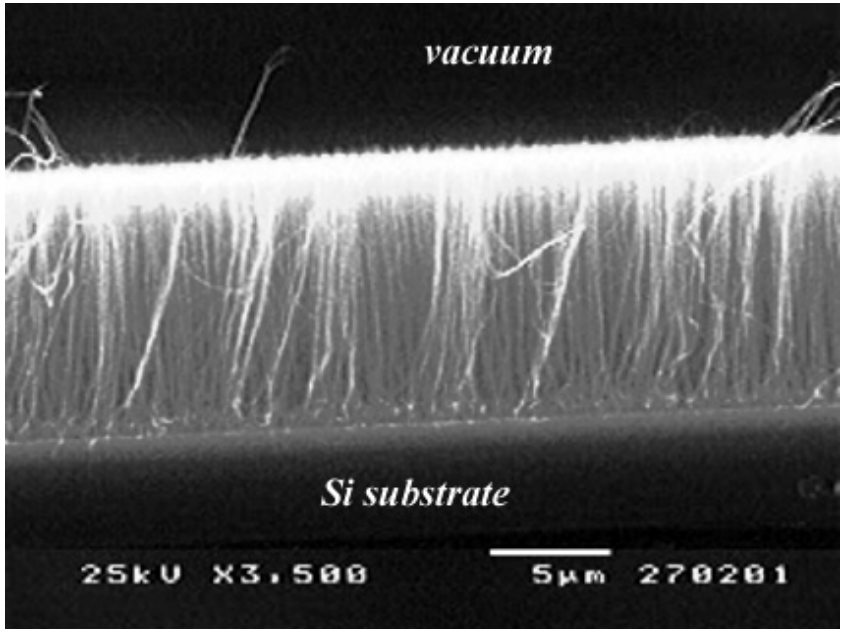
- application as field emitters

<u>Suzuki et al, APL 76 (2000) 4007:</u>
work function changes after Cs-deposition

Choi et al, APL 75 (1999) 3129

Sample preparation

<u>Bower et al, APL 77 (2000) 830:</u>
Multi-walled carbon nanotubes
aligned perpendicular to Si substrate
grown by CVD method
length: 10 µm, diameter: 30 nm

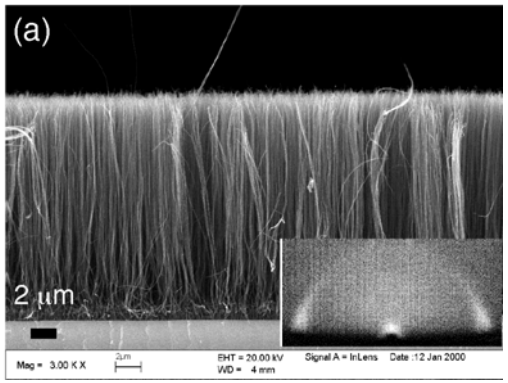


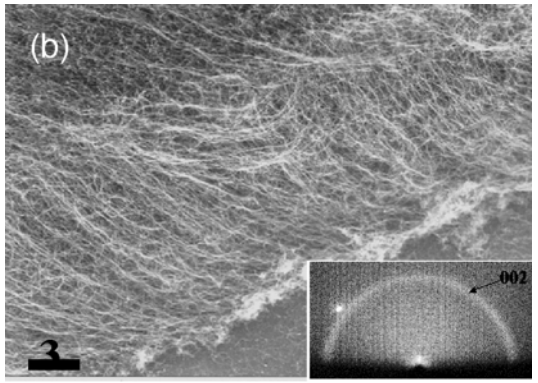
Integral PES

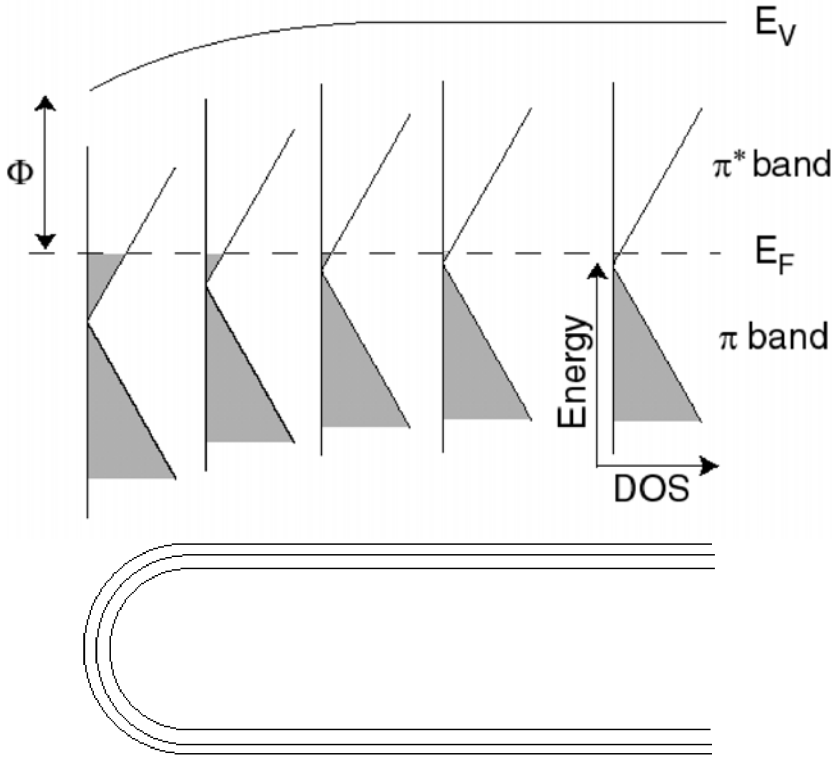
PES: electronic structure
(work function, VB, core levels)

NTT: smaller work function at tip
larger density of states at E_F
slight band bending

Two different kinds of samples:
(a) aligned (b) unaligned





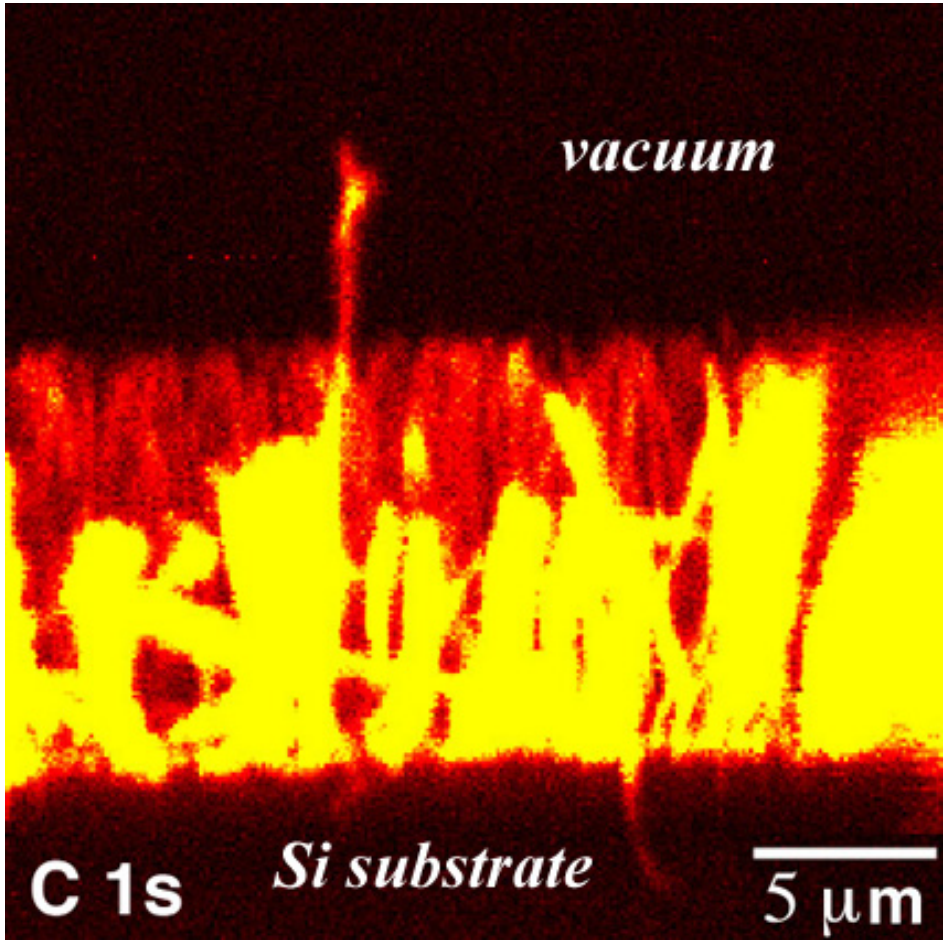


S. Suzuki, Y. Watanabe, T. Kiyokura, K. G. Nath, T. Ogino, S. Heun, W. Zhu, C. Bower, and O. Zhou: PRB, in press.

Results @ ELETTRA

Experiment:
Laterally resolved PES on nanotube side and tip in cross-section (core levels, VB, work function)

Results:
- At tips larger density of states near Fermi-Edge
- Cs concentration along the tube axis

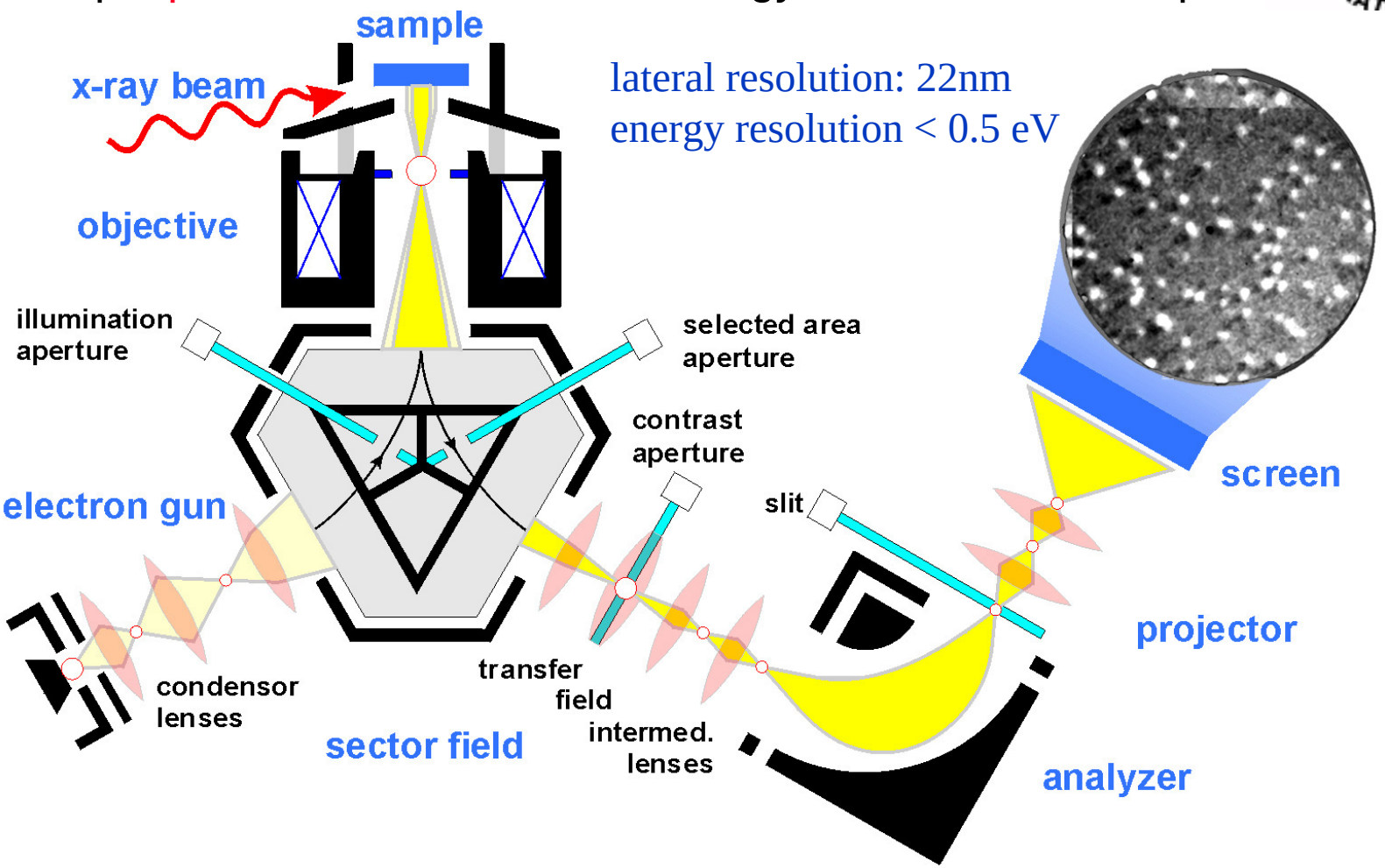


S. Suzuki, Y. Watanabe, S. Heun, L. Gregoratti, A. Barinov, B. Kaulich, C. Bower, O. Zhou, W. Zhu, T. Ogino, M. Kiskinova: unpublished.

The SPELEEM at ELETTRA

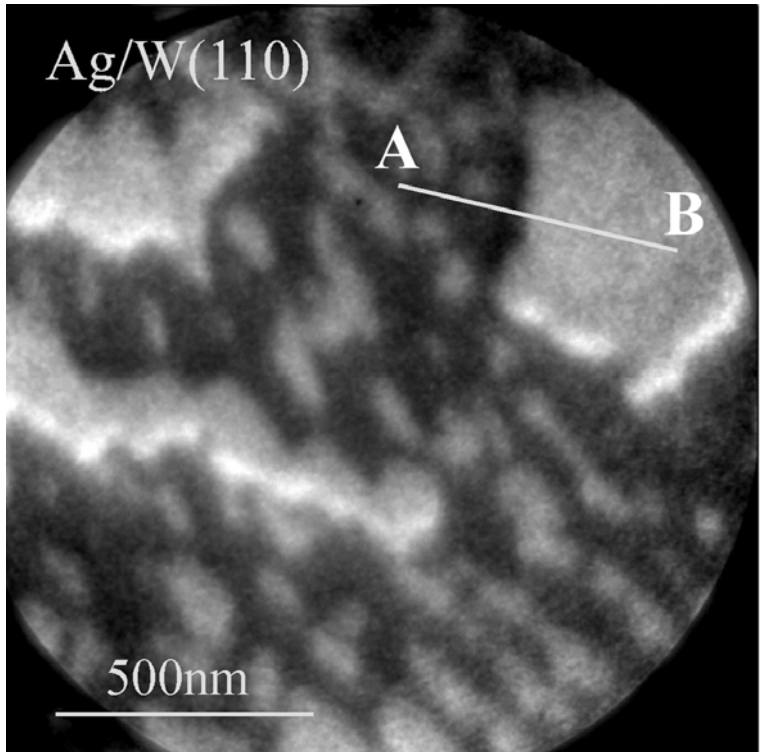
Spectroscopic photoemission and low energy electron microscope

lateral resolution: 22nm
energy resolution < 0.5 eV

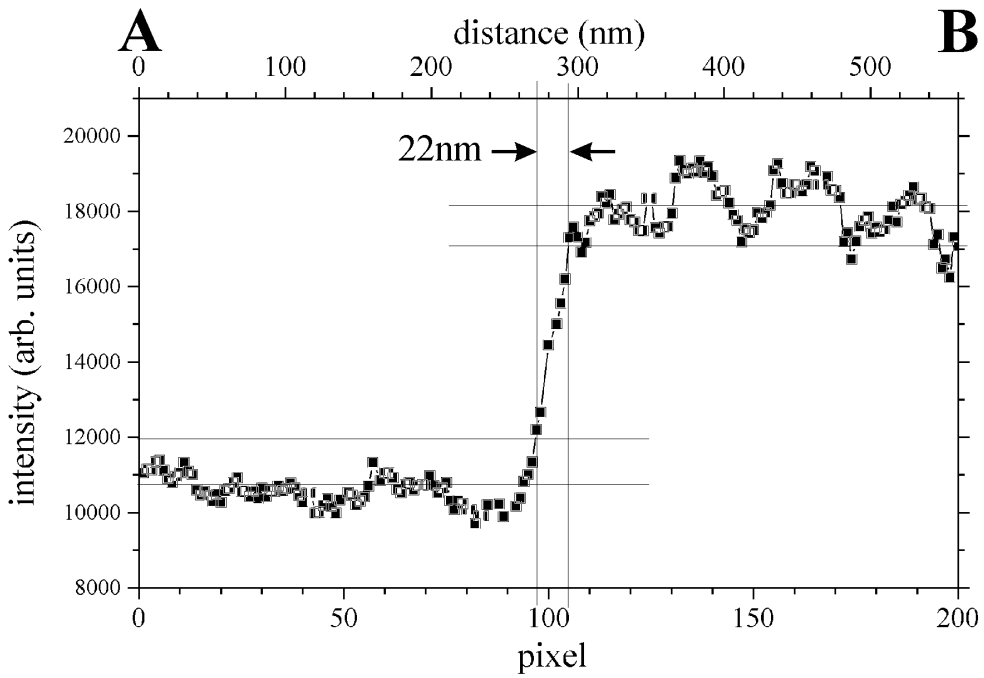


S. Heun, Th. Schmidt, B. Ressel, E. Bauer, and K. C. Prince, Synchrotron Radiation News Vol. 12, No. 5 (1999) 25.

Lateral Resolution of XPEEM

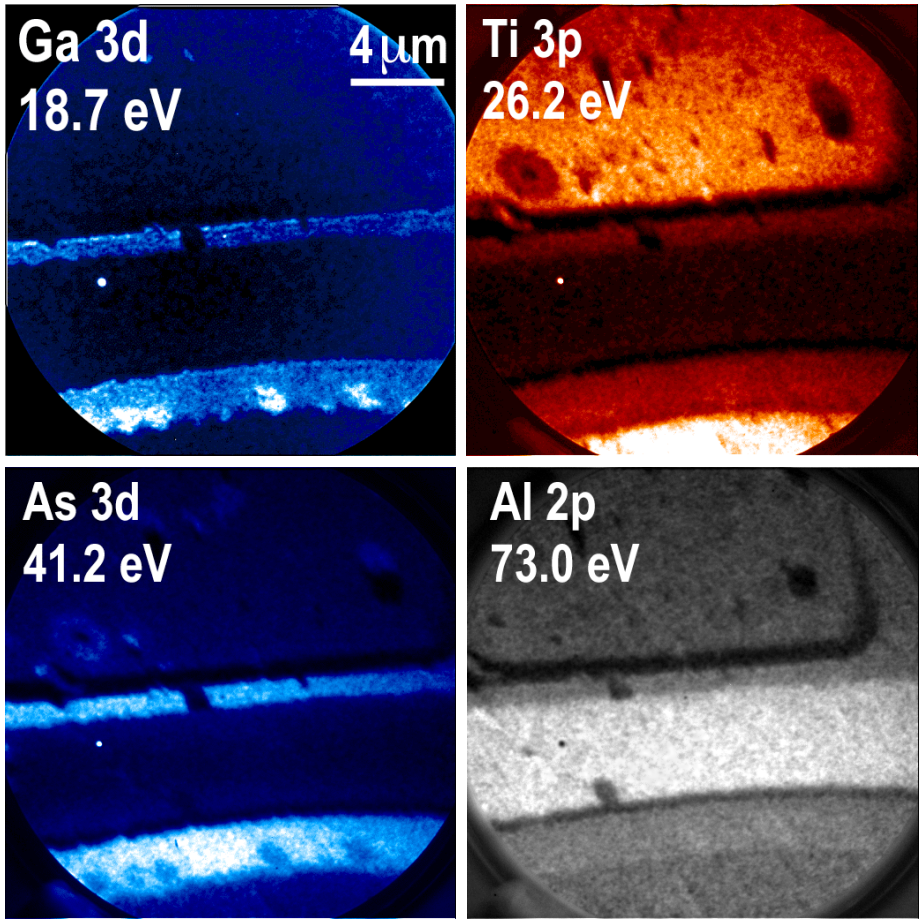


Evaluated spatial resolution in XPEEM mode: **22nm**

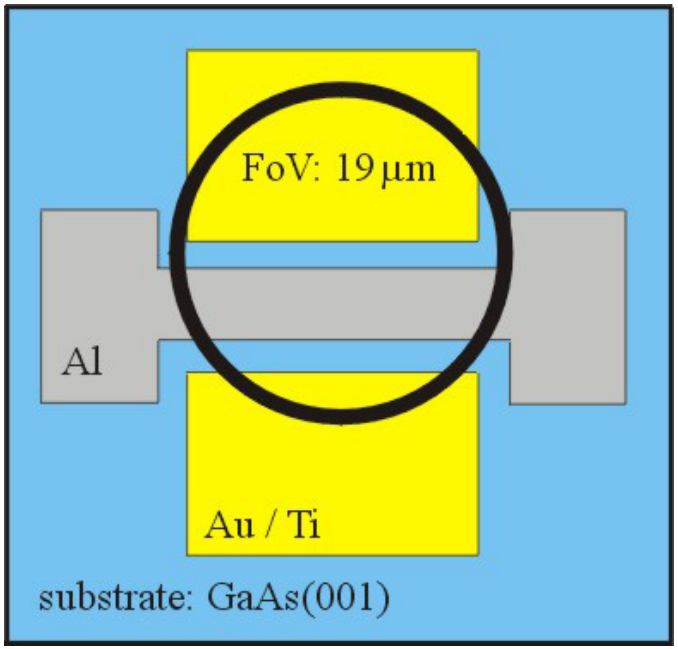


Th. Schmidt, S. Heun, J. Slezak, J. Díaz, K. C. Prince, G. Lilienkamp, E. Bauer: Surf. Rev. Lett. 5 (1998) 1287.

Spectroscopic Microscopy



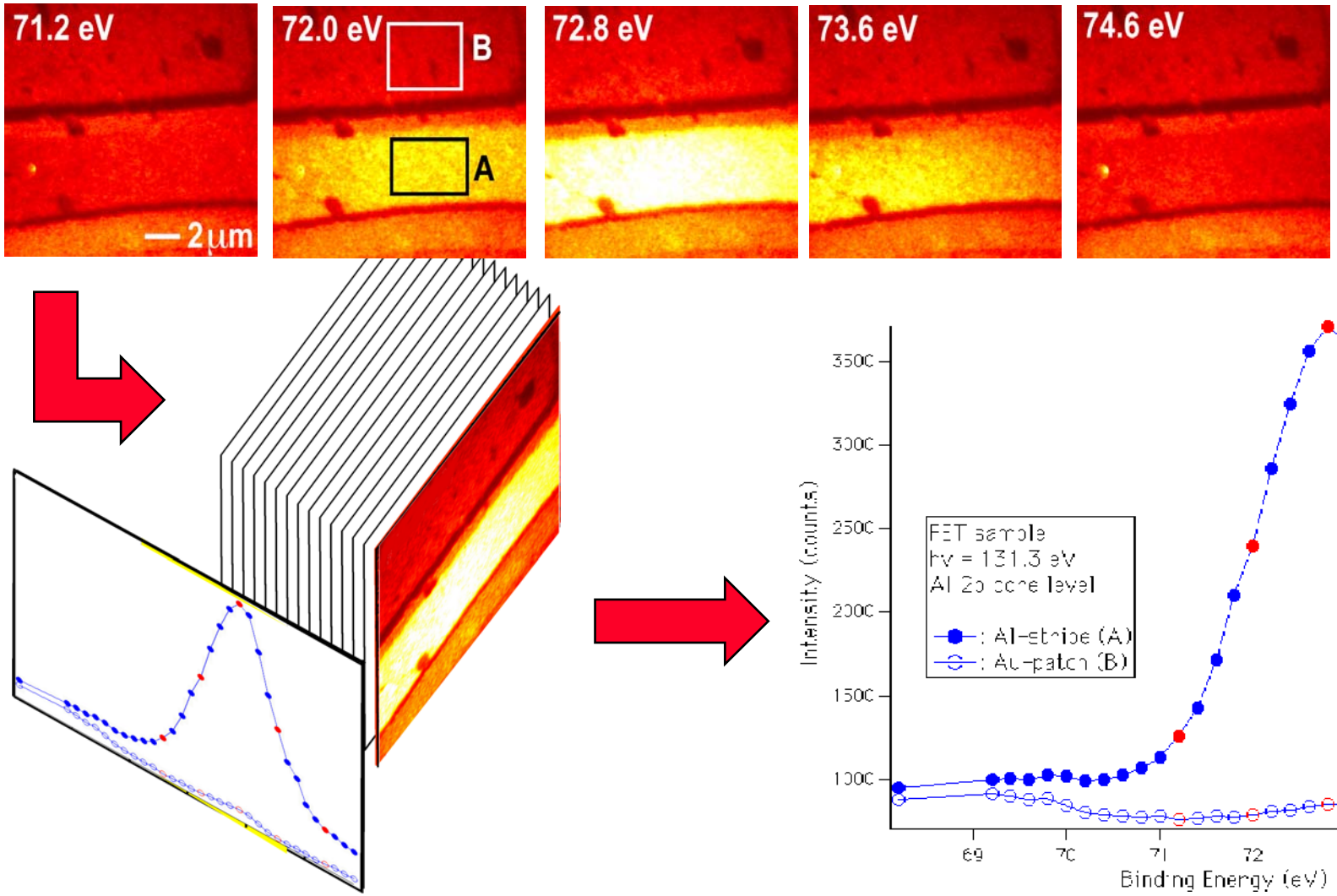
Images from a Field Effect Transistor (FET) at different binding energies.
Photon energy hv = 131.3 eV.



Sample from M. Lazzarino, L. Sorba, and F. Beltram, Laboratorio TASC-INFM, Trieste, Italy

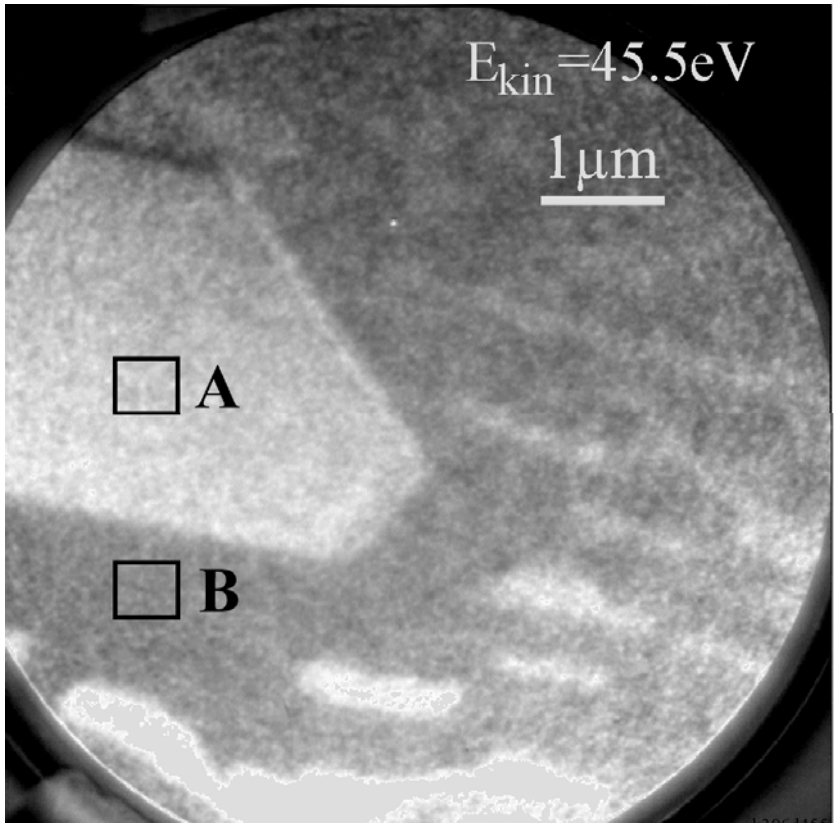
S. Heun, Th. Schmidt, B. Ressel, E. Bauer, and K. C. Prince, Synchrotron Radiation News Vol. 12, No. 5 (1999) 25.

XPEEM



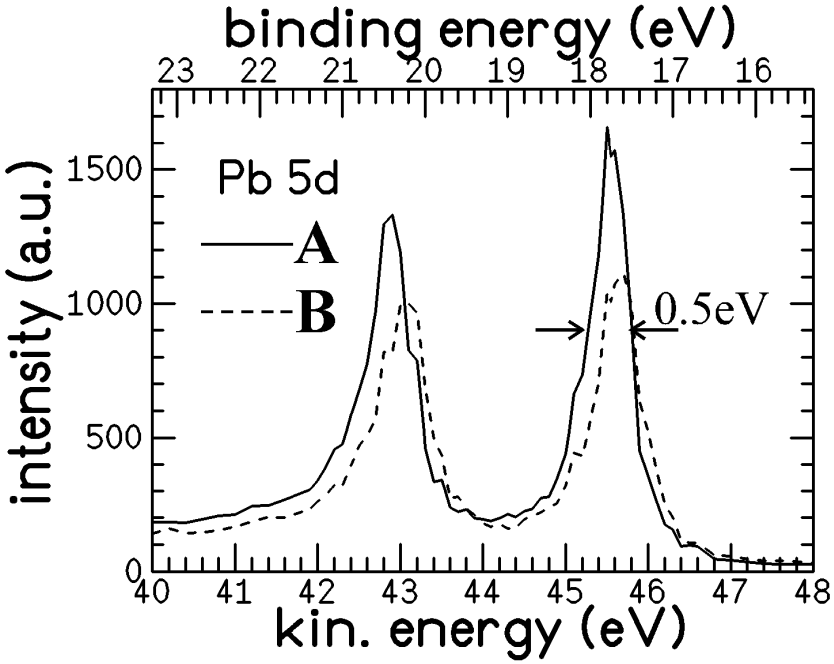
S. Heun, Th. Schmidt, B. Ressel, E. Bauer, and K. C. Prince, Synchrotron Radiation News Vol. 12, No. 5 (1999) 25.

Energy Resolution of XPEEM



Pb/W(110)

Energy resolution better than **0.5 eV**



Th. Schmidt, S. Heun, J. Slezak, J. Díaz, K. C. Prince, G. Lilienkamp, E. Bauer: Surf. Rev. Lett. 5 (1998) 1287.

InAs Nanocrystals on Se / GaAs

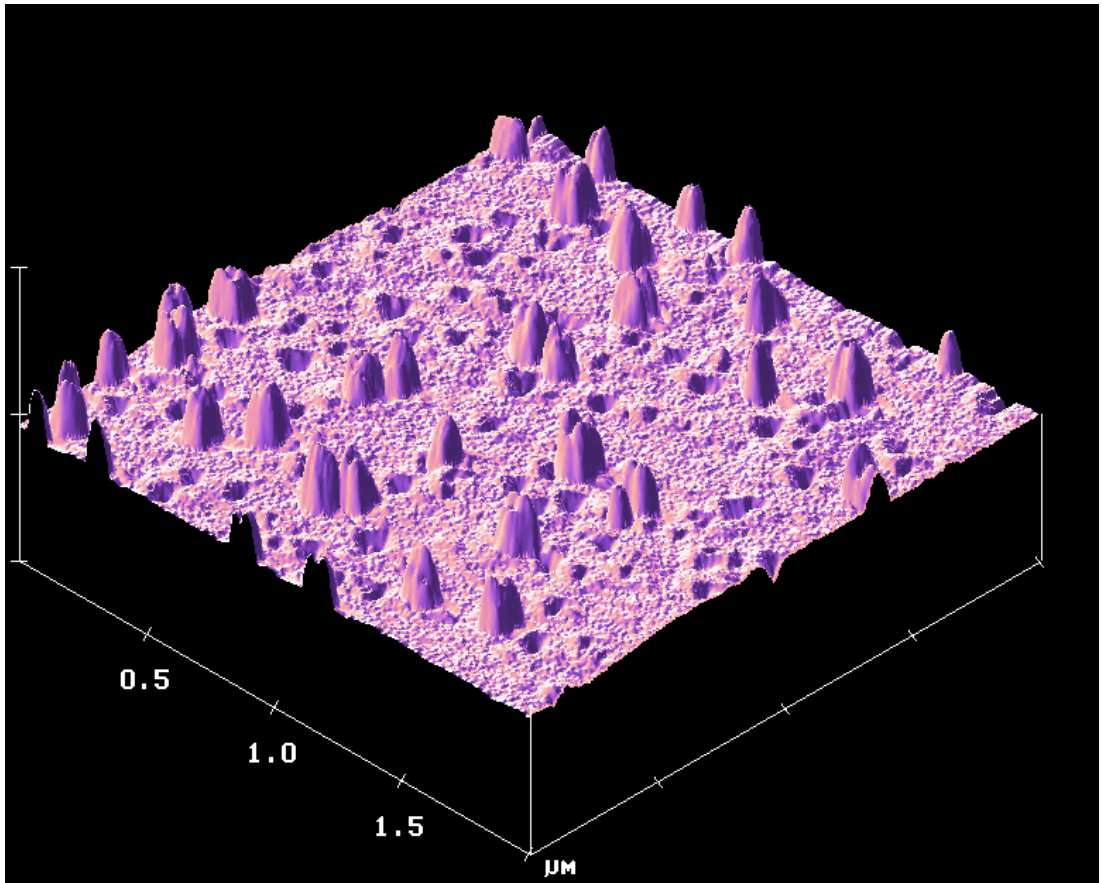
Nanocrystals formed during strained-layer epitaxy
- Quasi zero-dimensional nature (quantum dots)
- Semiconductor lasers and memory applications
- No lithography: cost-effective fabrication of devices

Problems:
- Size fluctuations: need for nano-scale spectroscopy
- Segregation and interdiffusion observed for Ge/Si and for InAs/GaAs

Purpose of this work:
- Determination of the elemental composition of the nanocrystals
- Photoelectron spectroscopy with high lateral resolution
- Electronic structure of a single InAs nanocrystal

S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

AFM



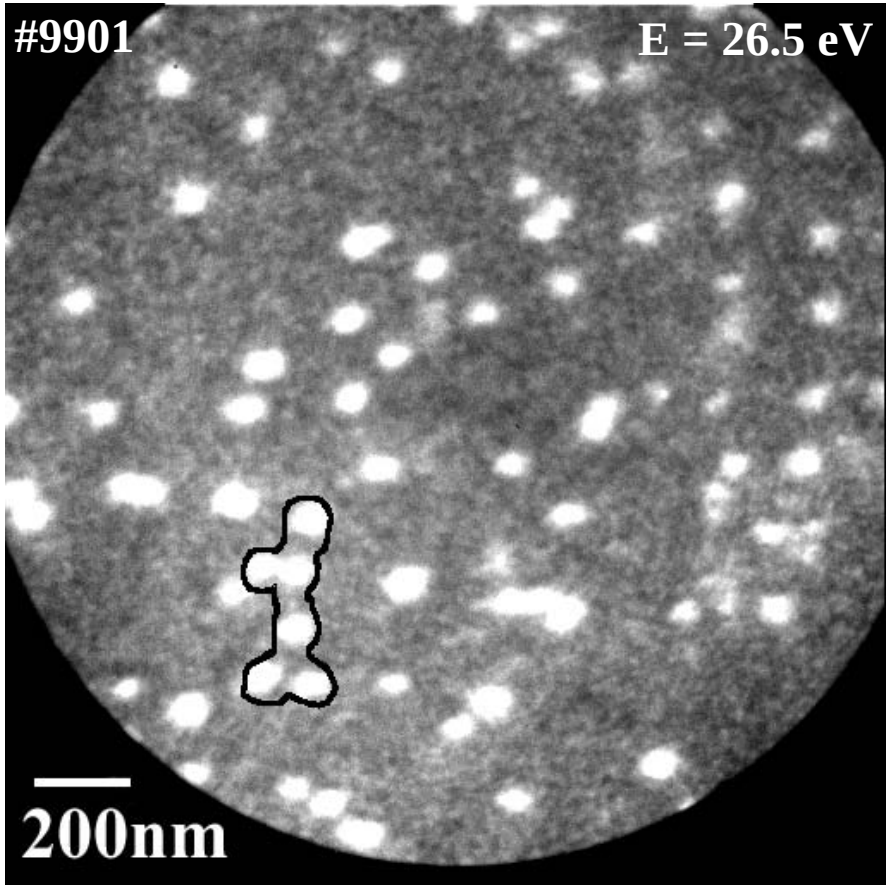
Field of view: 2 µm x 2 µm.

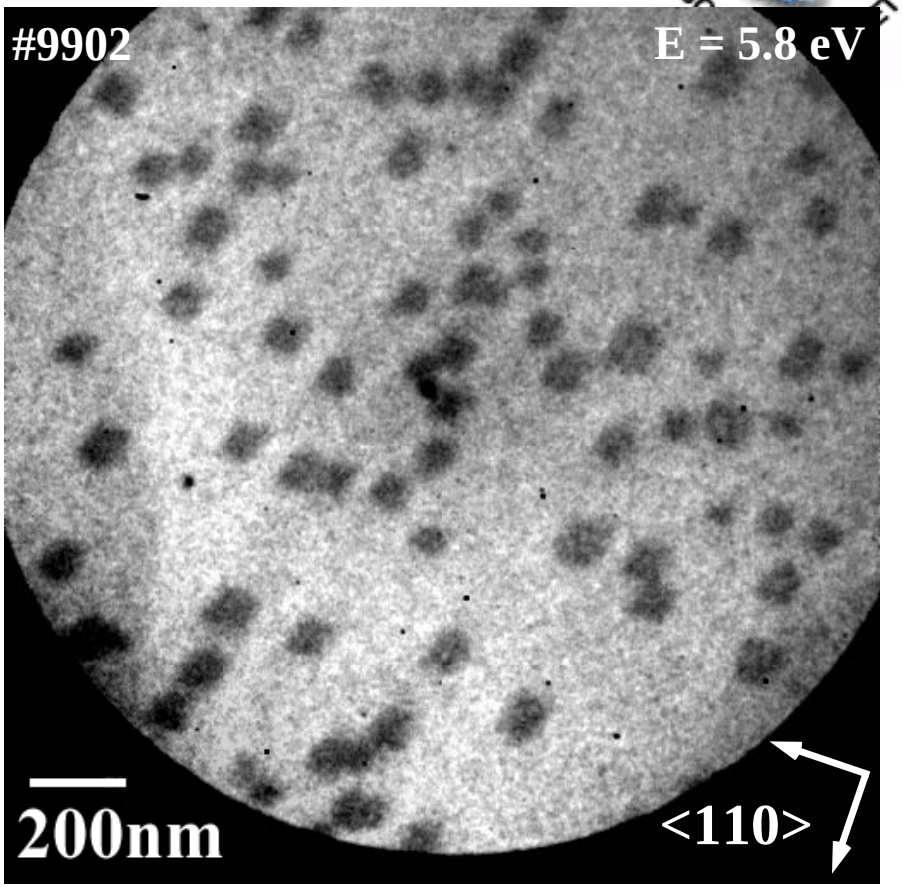
InAs / Se / GaAs
after capping and decapping.

Typical island size: 50 nm.
Typical island height: 20 nm.
Typical island density: 25 μm^{-2}

Y. Watanabe, S. Heun, Th. Schmidt, and K. C. Prince: Jpn. J. Appl. Phys. **38**, Suppl. 38-1 (1999) 556-559.

LEEM

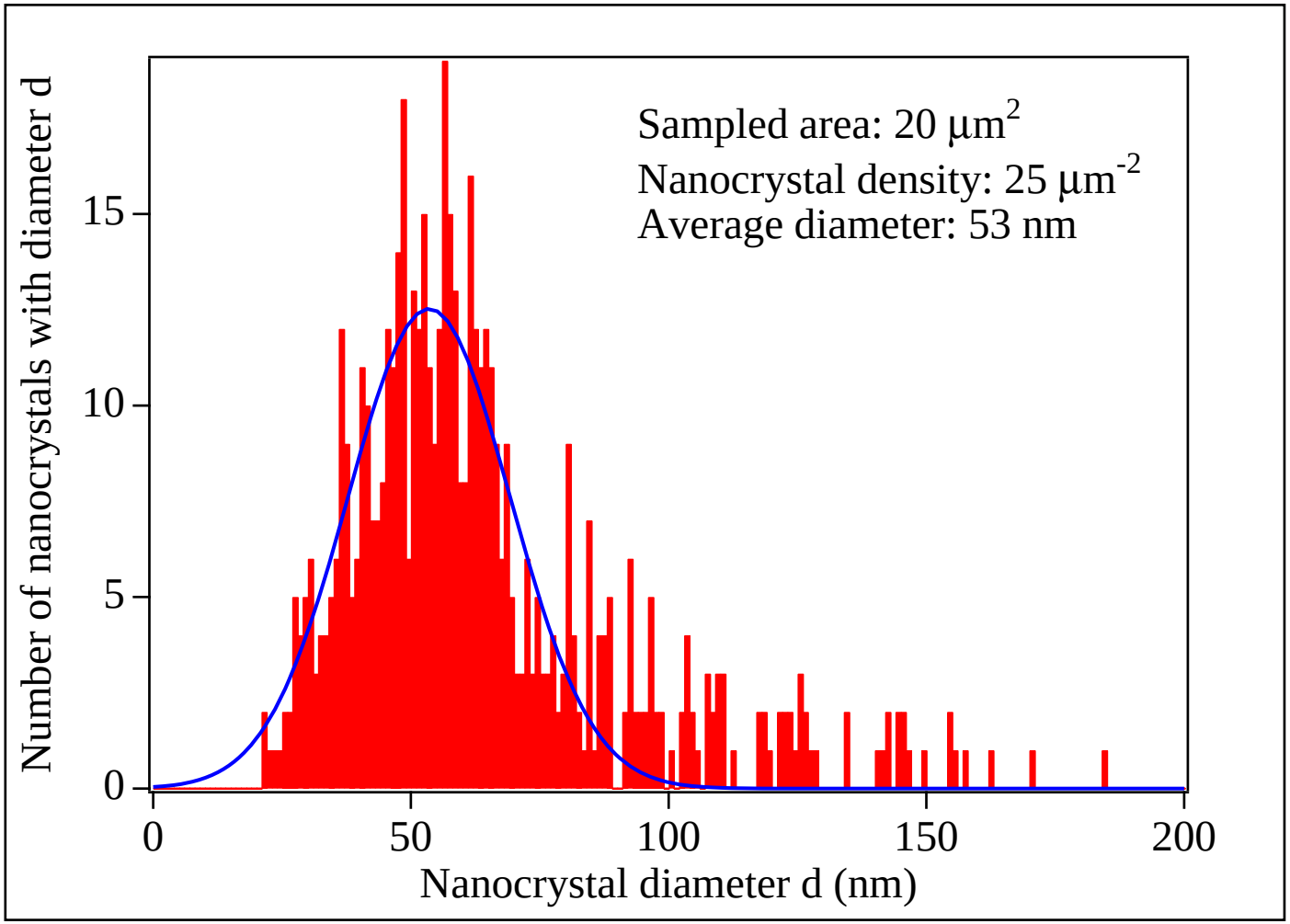




nanocrystals have square base oriented along <110>

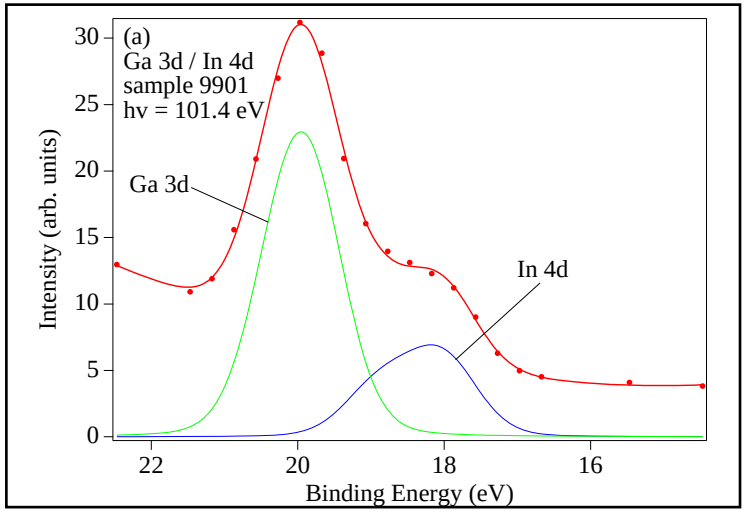
S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

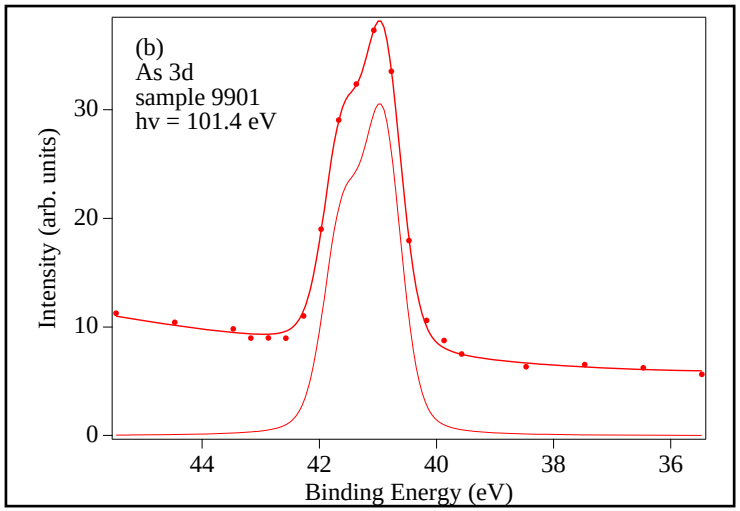
Island Size Distribution

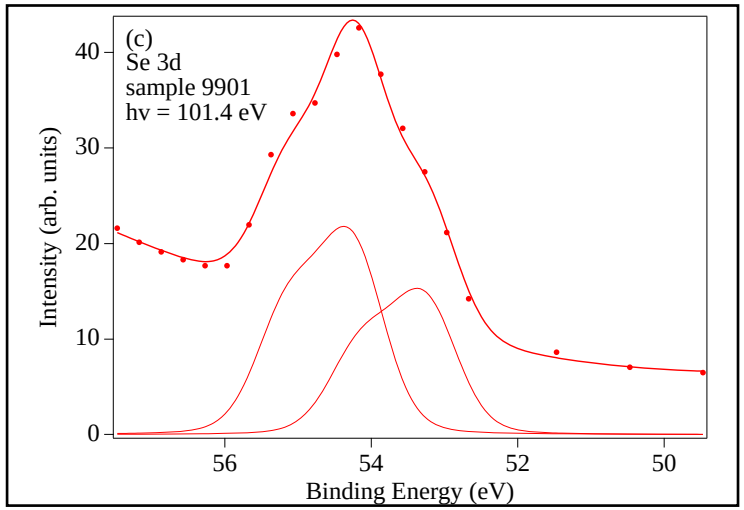


S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

Core Level Spectra





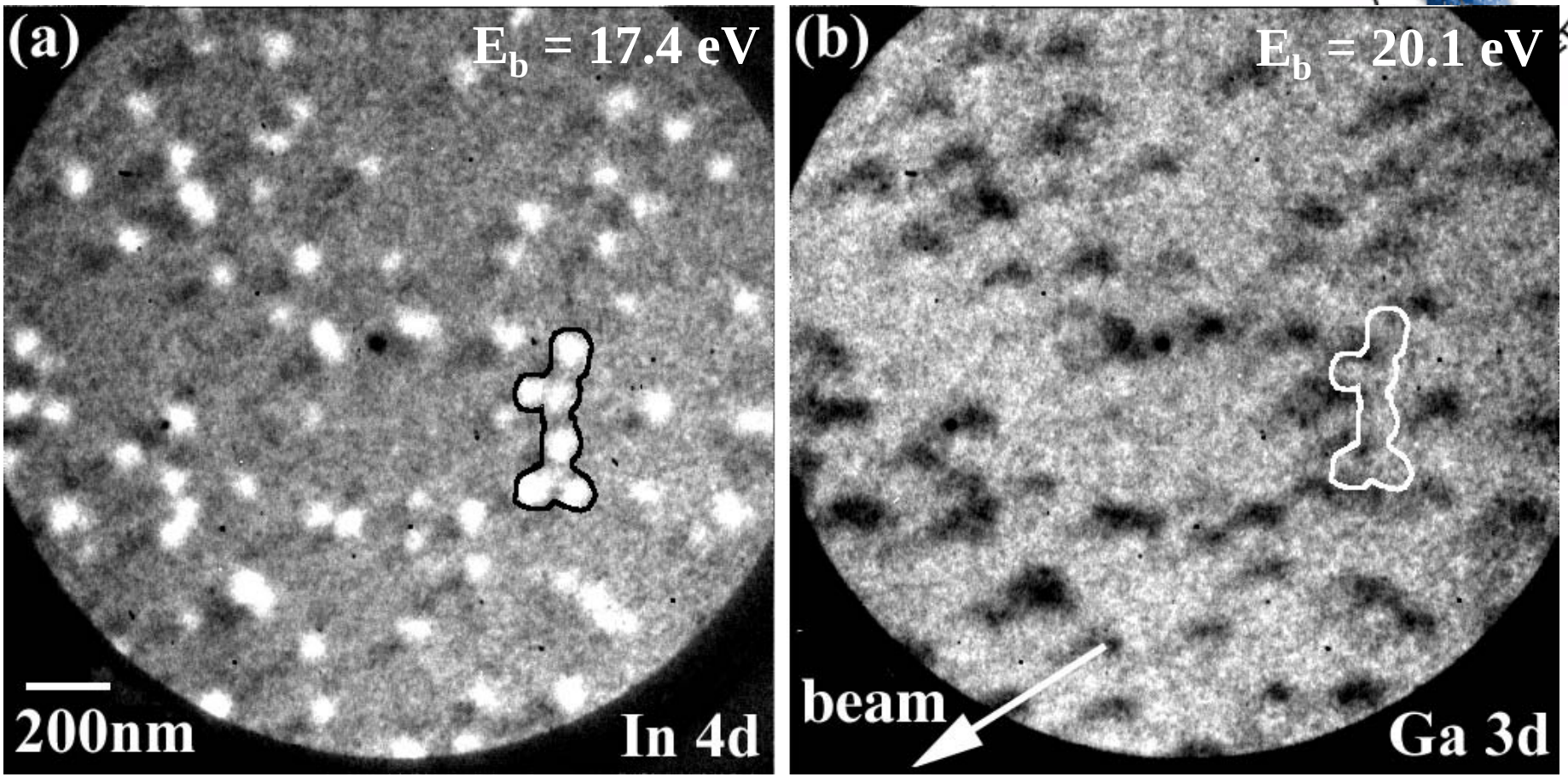


Integral photoemission spectra from a 3 μm^2 area,
obtained by integration of a series of SPELEEM images.

Good agreement with literature values
↑ samples not changed by capping / decapping

S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

XPEEM



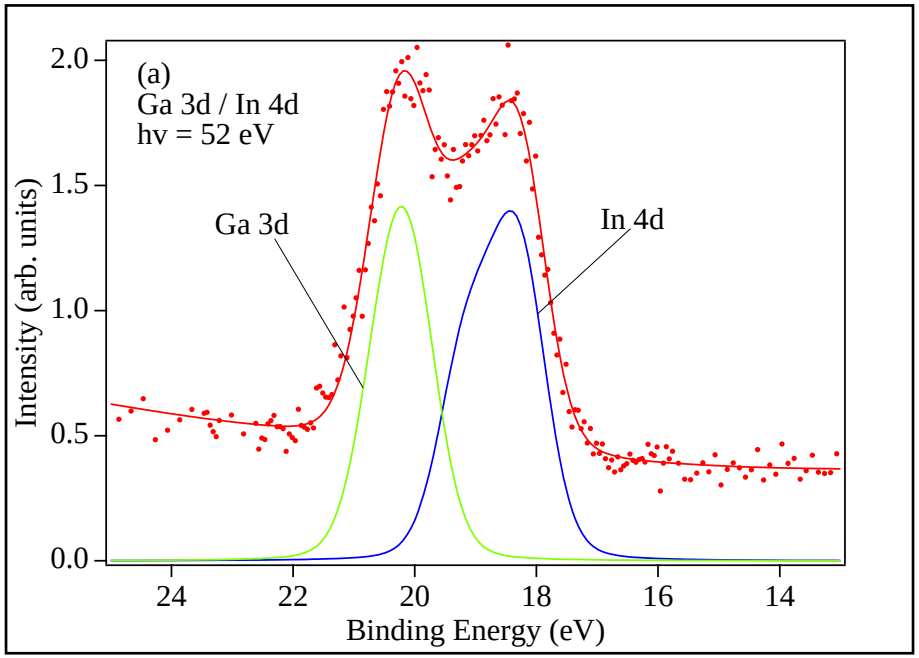
hv = 52 eV, FoV = 2µm

nanocrystal height from their shadow length: 22 nm

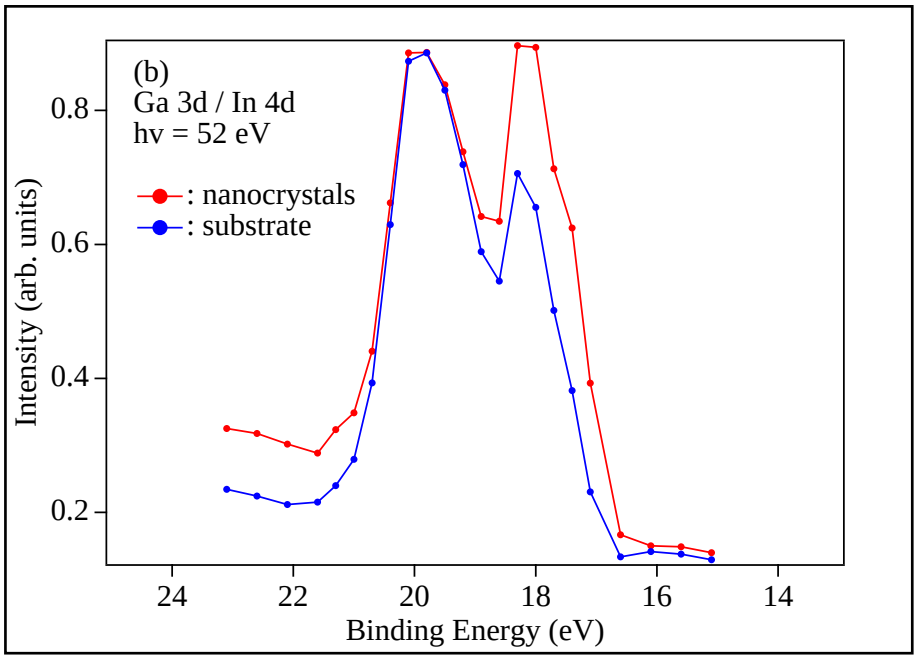
S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

Laterally resolved core level spectroscopy

Integral spectrum



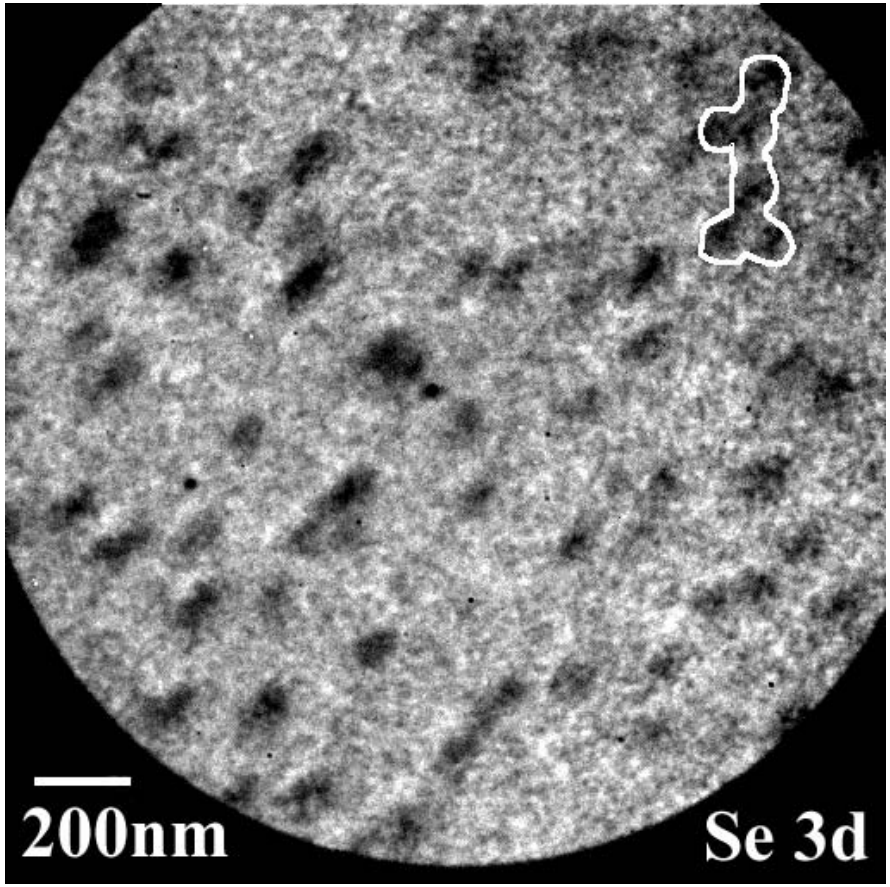
Laterally resolved spectra



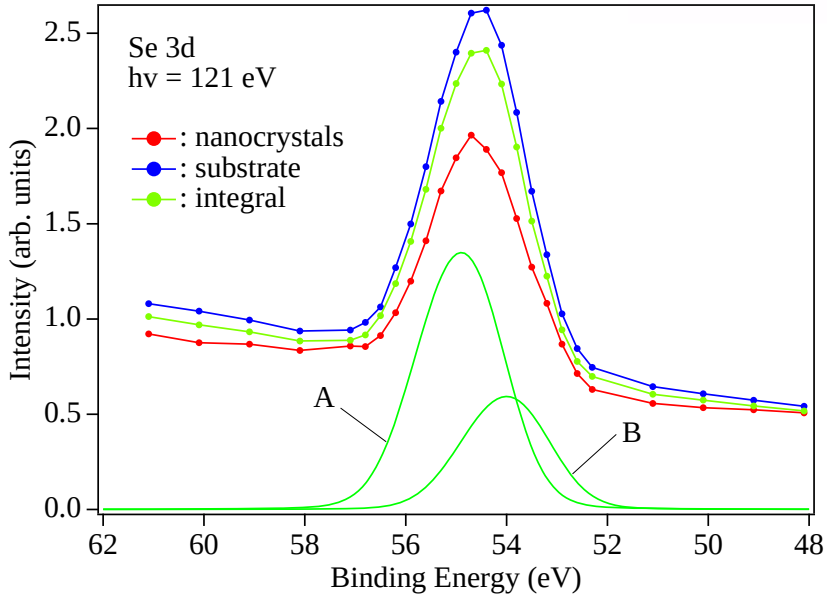
Indium on substrate ↑ SK growth mode
Gallium on nanocrystals

S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

XPEEM



hv = 121 eV, E_b = 54.7 eV, FoV = 2µm

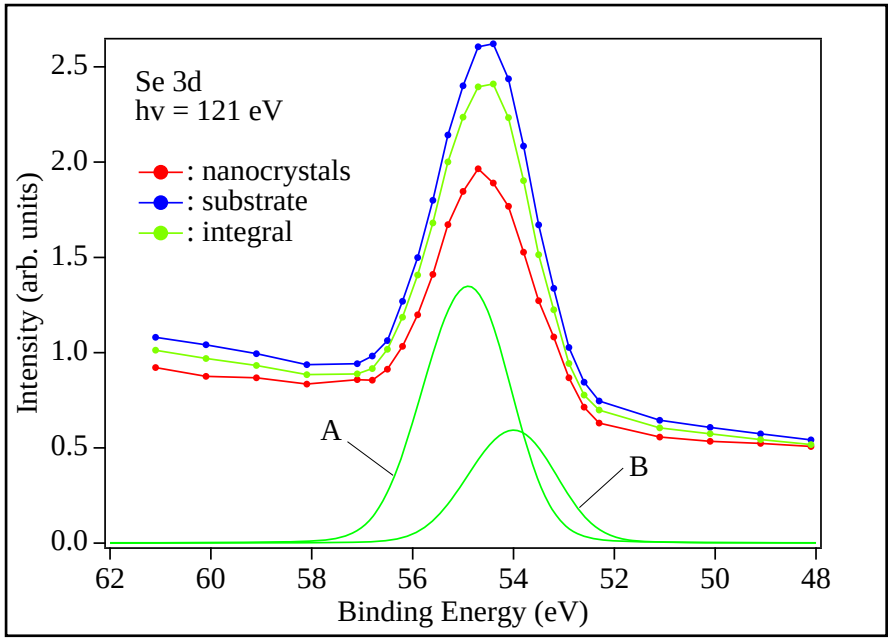


Selenium on the nanocrystals

Valence band and work function data: Further evidence for the presence of Selenium at the surface of the nanocrystals

S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

Se 3d core level spectra



F. Maeda et al.: PRB **48** (1993) 4956.

- Ga_2Se_3: zincblende structure with ordered Ga vacancies.
- A: Se with no Ga vacancy as nearest neighbor
- B: Se with one Ga vacancy as nearest neighbor
- B species closer to the surface than A species
- clean Se/GaAs: A / B = 1.51

Here: intensity ratio A / B = 2.26

↑ less B species after deposition of InAs

↑ some material moved from surface to nanocrystals

From LEEM: volume of nanocrystals: 6 x 10^5 nm^3 per μm^2

2 ML InAs correspond to 6 x 10^5 nm^3 per μm^2

SK growth mode

↑ nanocrystal volume is greater than expected

↑ additional material from another source (Ga_2Se_3)

S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

Discussion

- Reaction between InAs and Ga_2Se_3
- No GaAs reaction (growth at 200°C)

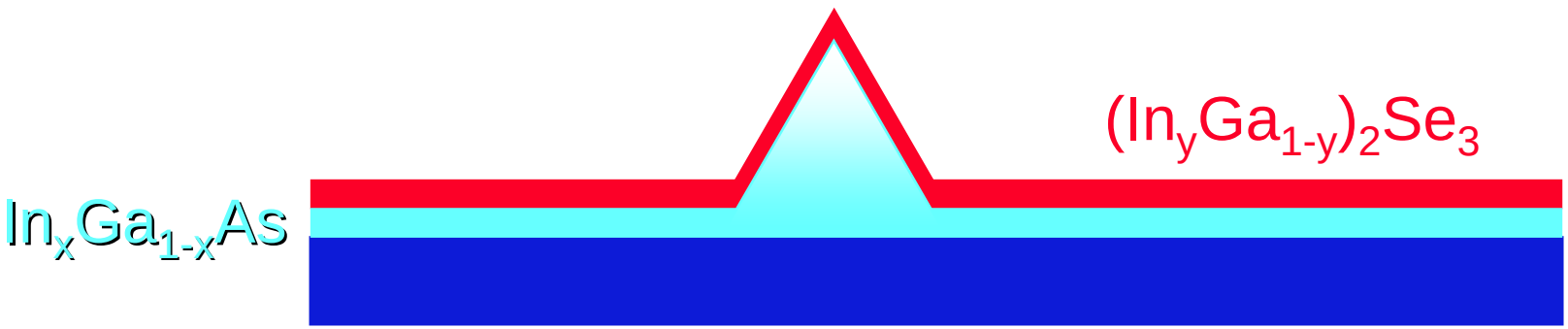
- Formation of a quaternary unlikely (As and Se from different chemical groups)
- Alloying on cation sublattice (strain minimization)
- Phase separation on anion sublattice (like in $InAs_xSb_{1-x}$)

- No bulk inclusions of Ga_2Se_3 in the InAs nanocrystals (10% lattice mismatch)

S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

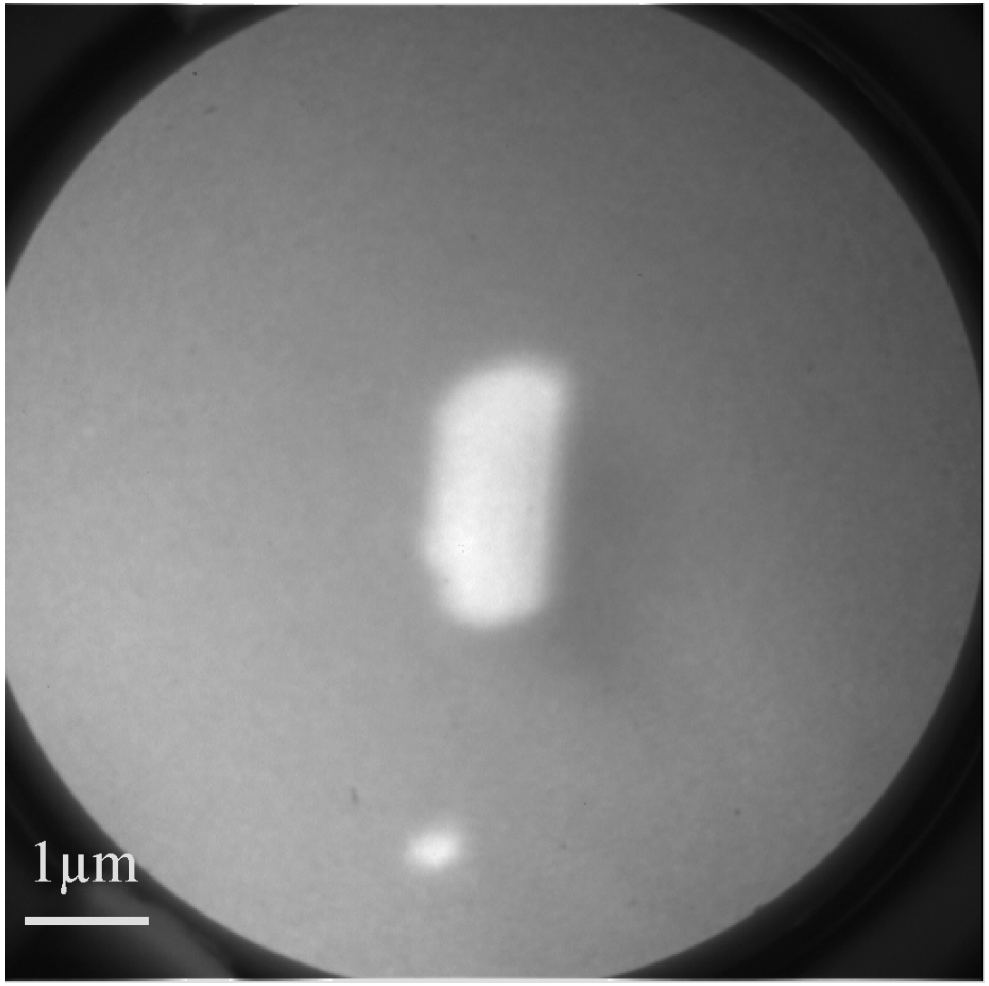
Summary

- During heteroepitaxy, the InAs reacts with the Ga_2Se_3.
- Phase separation on anion sublattice, alloying on cation sublattice.
- A wetting layer of $In_xGa_{1-x}As$ is formed covered by $(In_yGa_{1-y})_2Se_3$.
- $(In_yGa_{1-y})_2Se_3$ covered nanocrystals are formed on this surface.



S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

Conclusions



ESCA microscope:

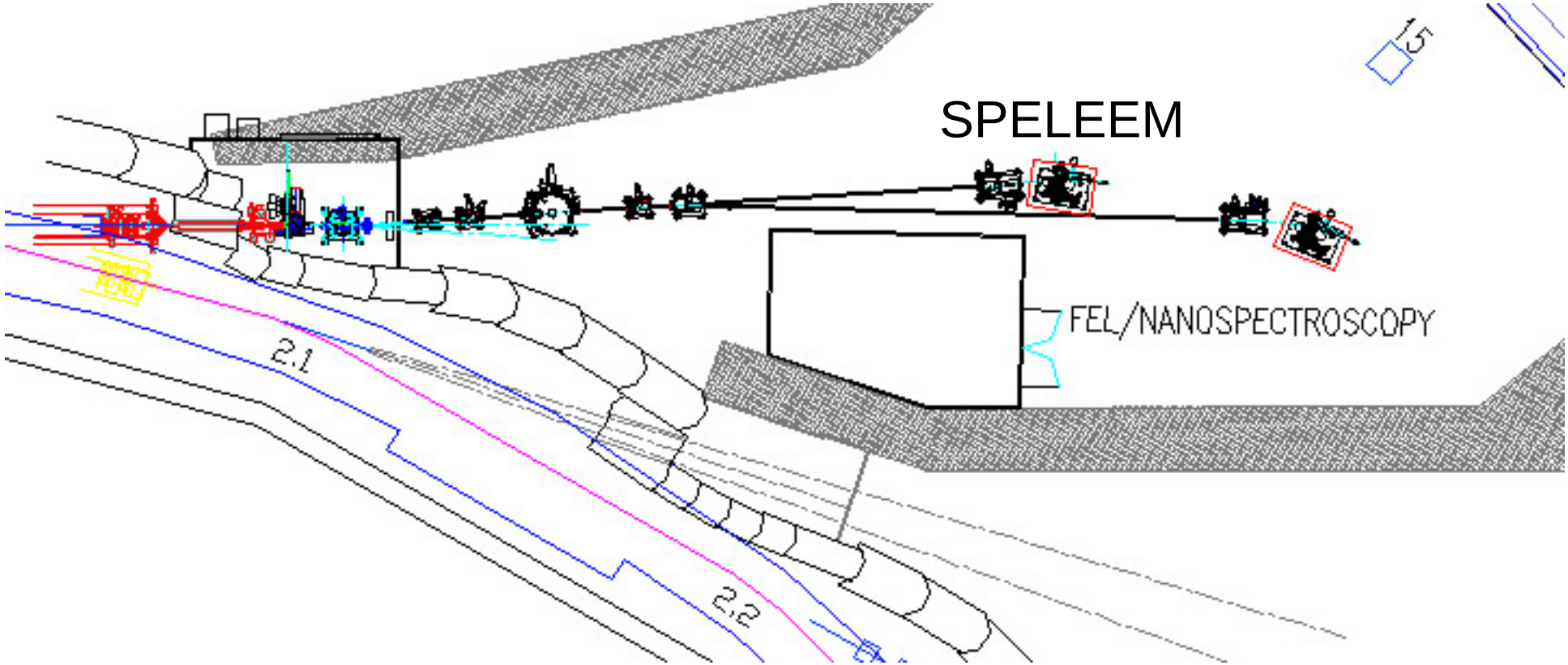
- Easy to use
- Cross section possible
- 100 nm lateral resolution
- 300 meV energy resolution

SPELEEM:

- Multi-method instrument
- structural information
- chemical information
- 20 nm lateral resolution
- 500 meV energy resolution

Nanospectroscopy beamline

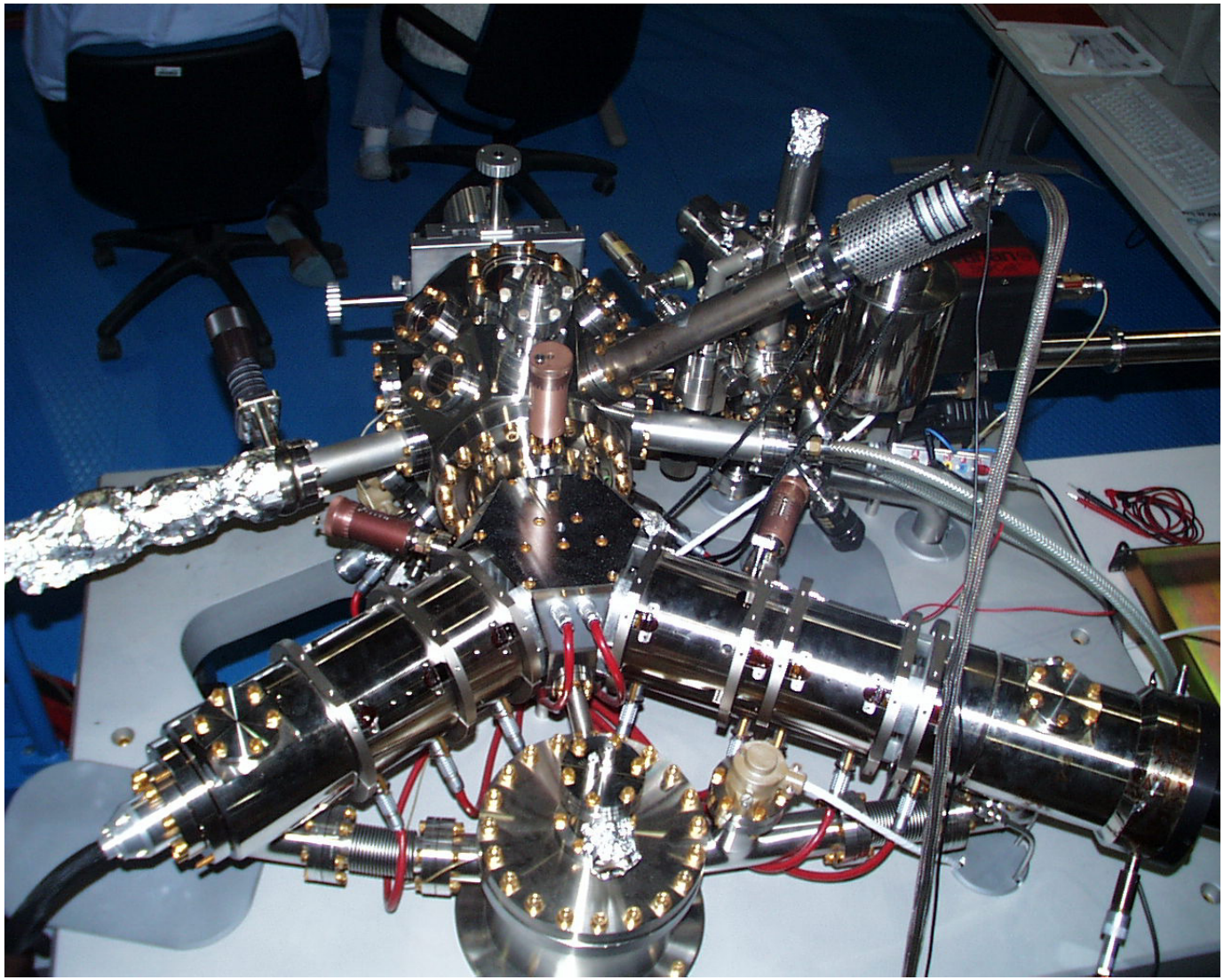
Now under commissioning !



D. Cocco, M. Marsi, M. Kiskinova, K. C. Prince, T. Schmidt, S. Heun, and E. Bauer: Proc. SPIE **3767** (1999) 271.

The Nanospectroscopy Beamline

The SPELEEM at ELETTRA



Nanospectroscopy beamline characteristics

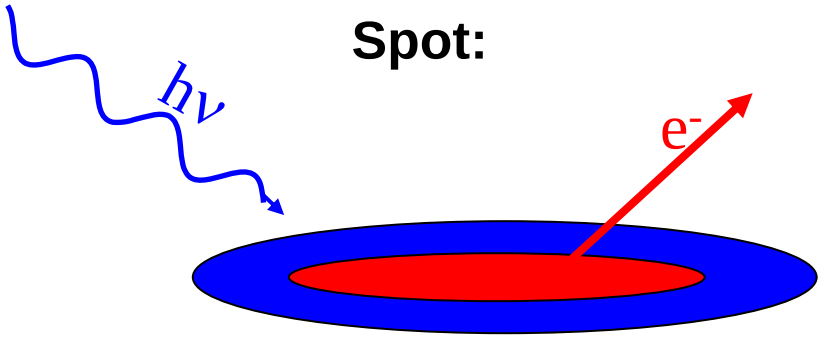
Source:

Sasaki type undulator, 10 cm periods
elliptical and linear polarization
20 - 1000 eV @ 2 GeV (5 eV @ 1 GeV)
240 µm x 40 µm source dimension

Monochromator:

20 - 1000 eV (2 VLS plane gratings)
< 20 eV + 0. order (spherical grating)
$E/\Delta E > 4000$

Spot:



High photon flux density (10^{14} ph/sec/µm^2)
Spot as small as possible (2 µm x 2 µm)
Constant divergence
Variable photon density
Uniform photon distribution

D. Cocco, M. Marsi, M. Kiskinova, K. C. Prince, T. Schmidt, S. Heun, and E. Bauer: Proc. SPIE **3767** (1999) 271.