Applications of Spectromicroscopy at ELETTRA

S. Heun

Sincrotrone Trieste

Outline

- Introduction
- Some applications:
  - Electronic Structure at Carbon Nanotube Tips
  - Nanoscopic Pattern Formation
  - Spectroscopy from Individual Nanocrystals
- New Nanospectroscopy Beamline at Elettra

Coworkers

- **NTT Basic Research Labs:** Y. Watanabe, D. Bottomley, S. Suzuki, T. Kiyokura, K. G. Nath, T. Ogino

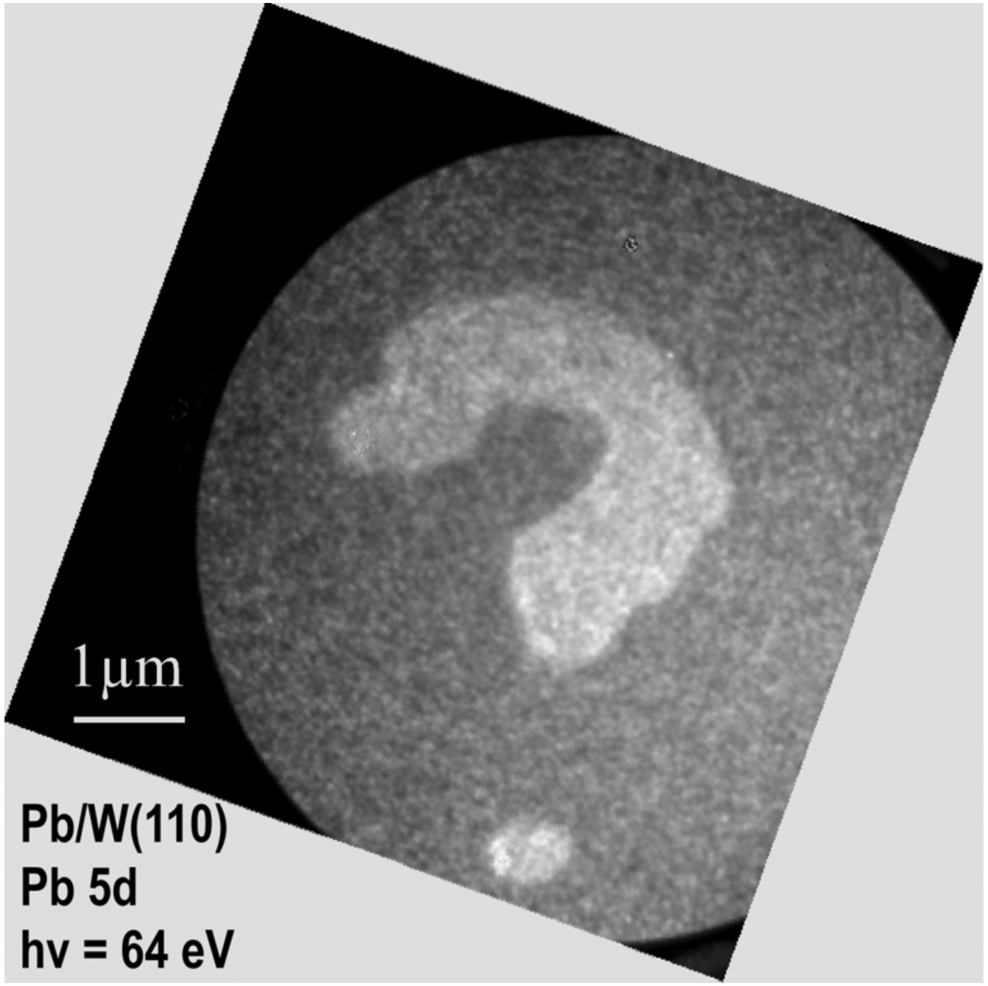
- **Bell Labs:** W. Zhu

- **University of North Carolina:** C. Bower, O. Zhou

- **Universität Hannover:** F.-J. Meyer zu Heringdorf, R. Hild, P. Zahl, M Horn-von Hoegen

- **ELETTRA:** D. Cocco, M. Marsi, M. Kiskinova, K. C. Prince, Th. Schmidt, E. Bauer, B. Ressel, L. Gregoratti, A. Barinov, B. Kaulich, A. Locatelli, M. Pasqualetto

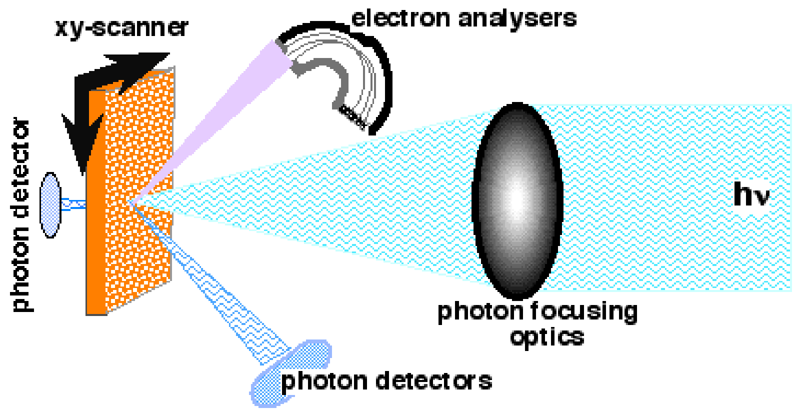
Motivation

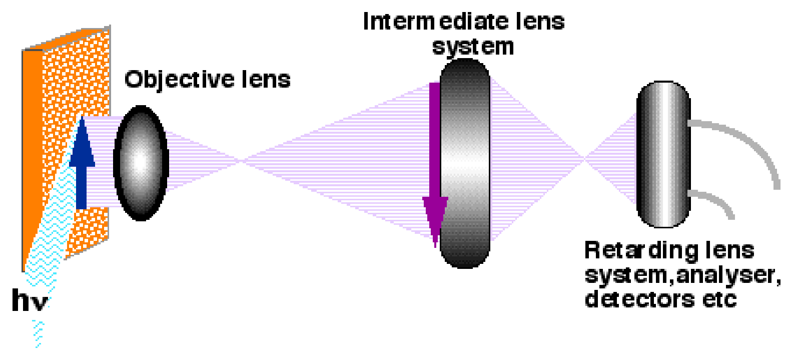


Why spectro-microscopy ?

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

Approaches to SR-XPS-microscopy





Photon optics is demagnifying the beam:
scanning instrument

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:
imaging instrument

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.

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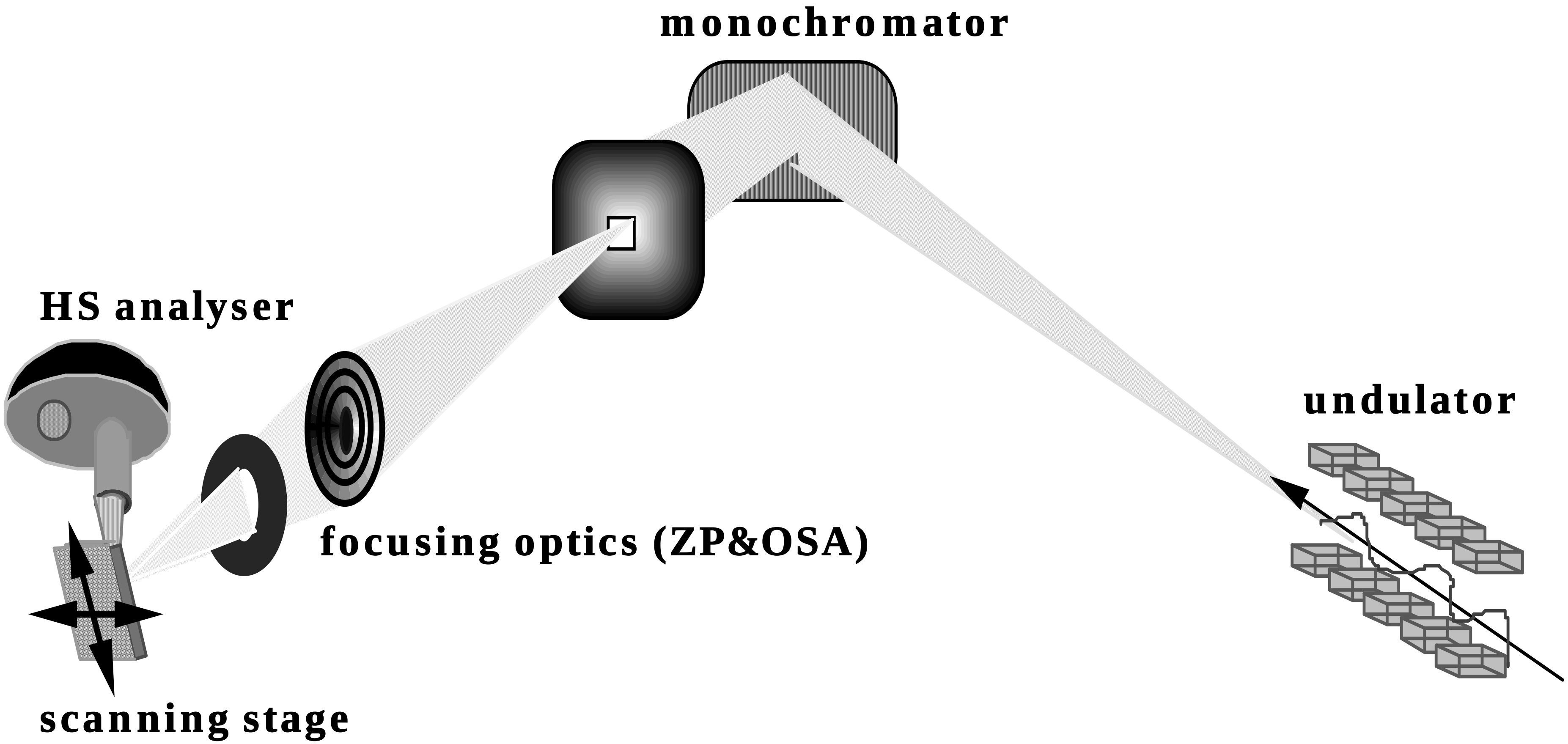
ESCA Microscopy Beamline

- **Flux density in a 0.01 μm² spot ~ 1- 5*10⁹ 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.

Carbon Nanotubes

• highly one-dimensional structure

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

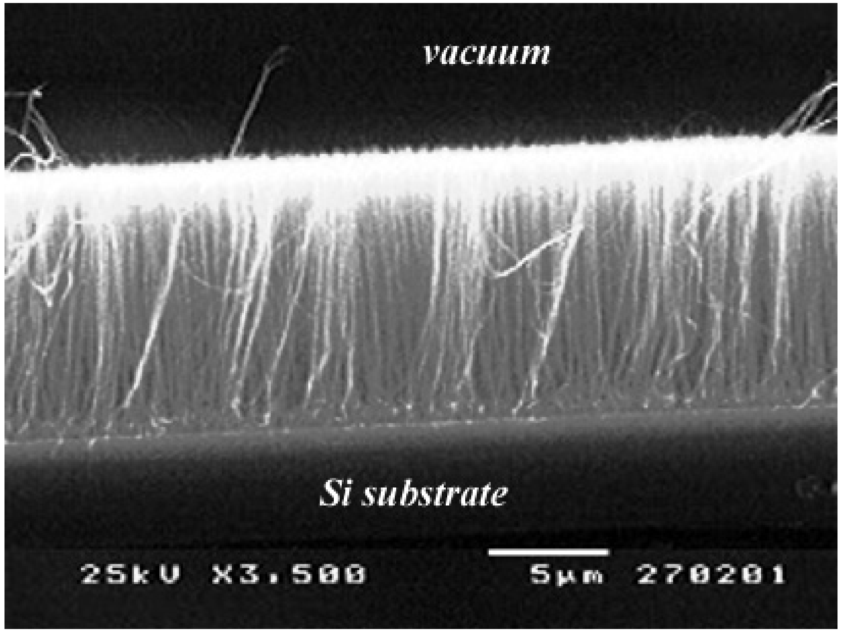
• application as field emitters

<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

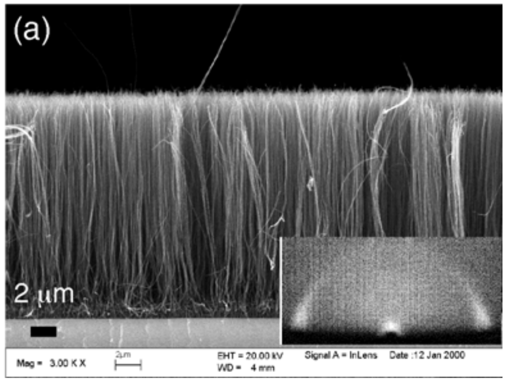


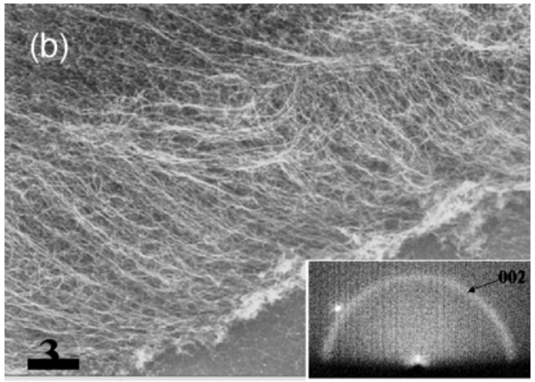
Integral PES

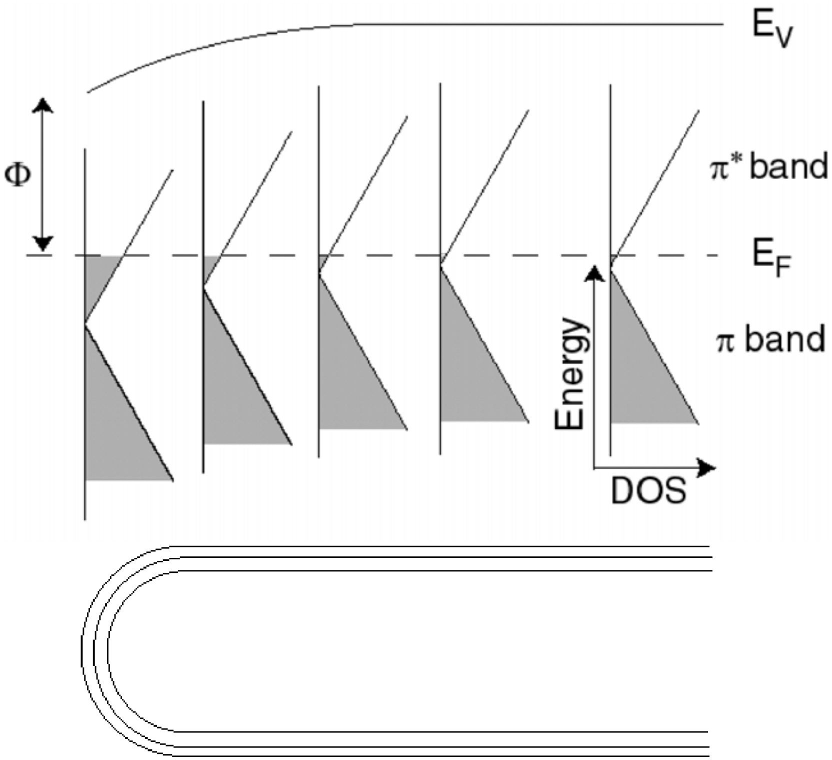
PES: electronic structure
(work function, VB, core levels)

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





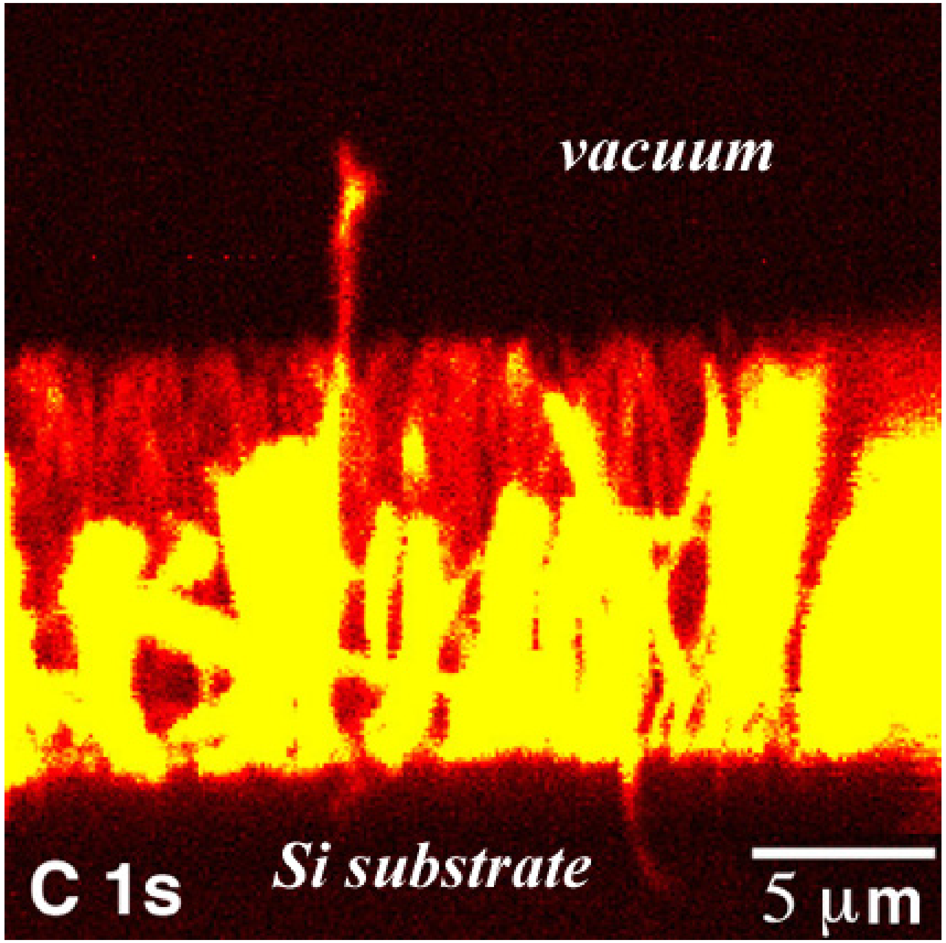


S. Suzuki, Y. Watanabe, T. Kiyokura, K. G. Nath, T. Ogino, S. Heun, W. Zhu, C. Bower, and O. Zhou: PRB **63** (2001) 245418.

Results at 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: Elettra News **40** (2001).

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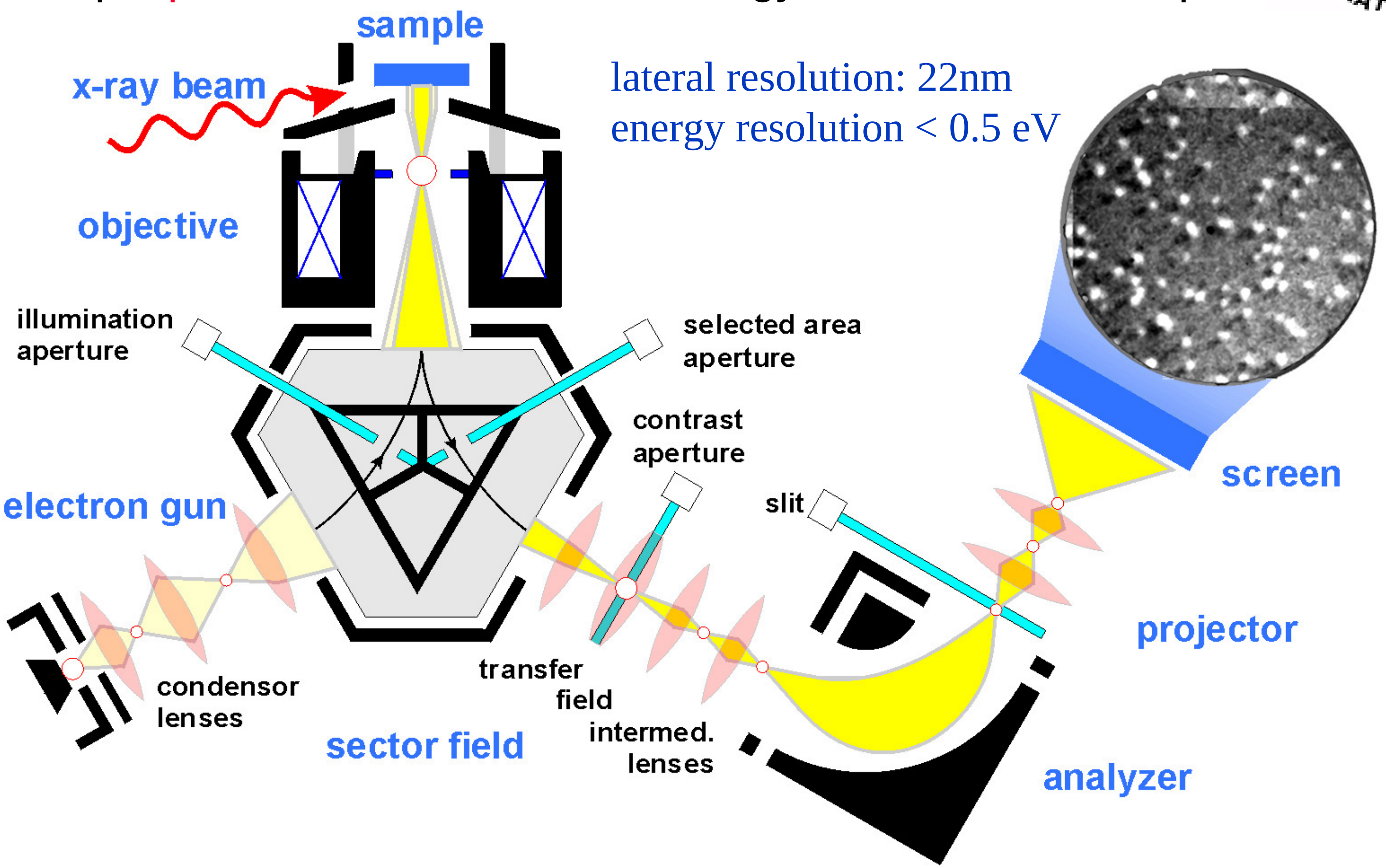
The SPELEEM at ELETTRA

Spectroscopic photoemission and low energy electron microscope

lateral resolution: 22nm
energy resolution < 0.5 eV

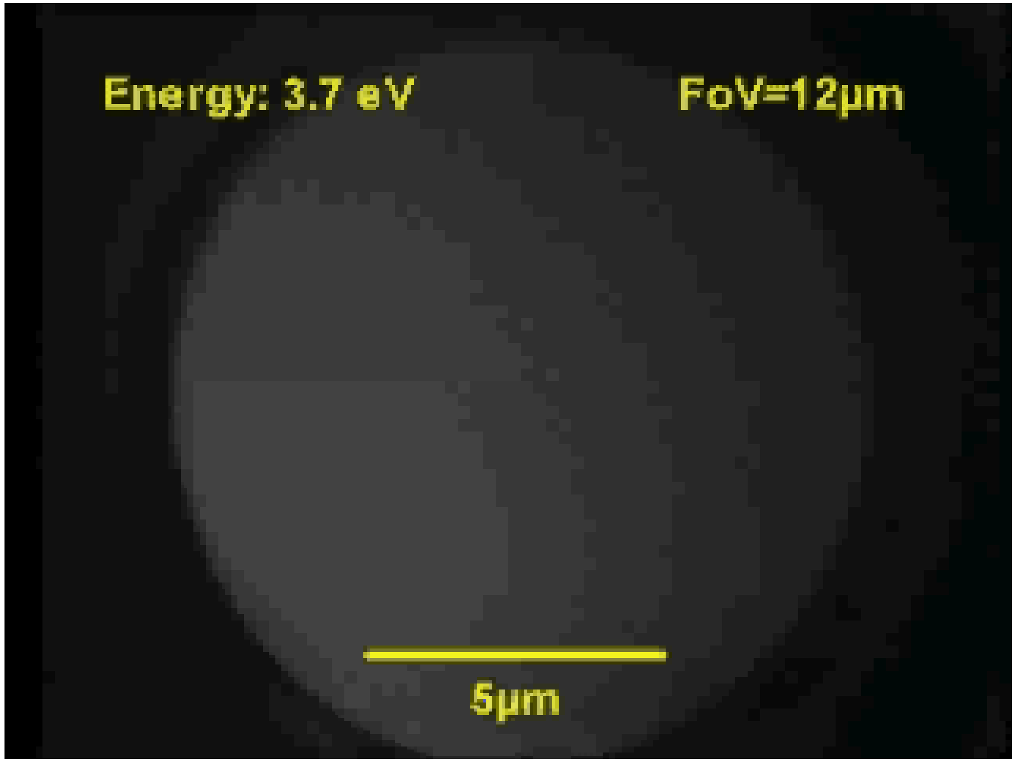


S. Heun, Th. Schmidt, B. Ressel, E. Bauer, and K. C. Prince, Synchrotron Radiation News Vol. 12, No. 5 (1999) 25.

Introduction

- Decreasing structure size in semiconductor technology
- Fabrication of ordered arrays of nanowires (transport properties)
- Use faceted semiconductor surface as template
- Important: understanding of key paramaters such as
  - width, length, height of step bunches
  - staightness and regularity of arrangement of bunches
- Here: Au-induced faceting of 4° vicinal Si(001)

LEEM Movie

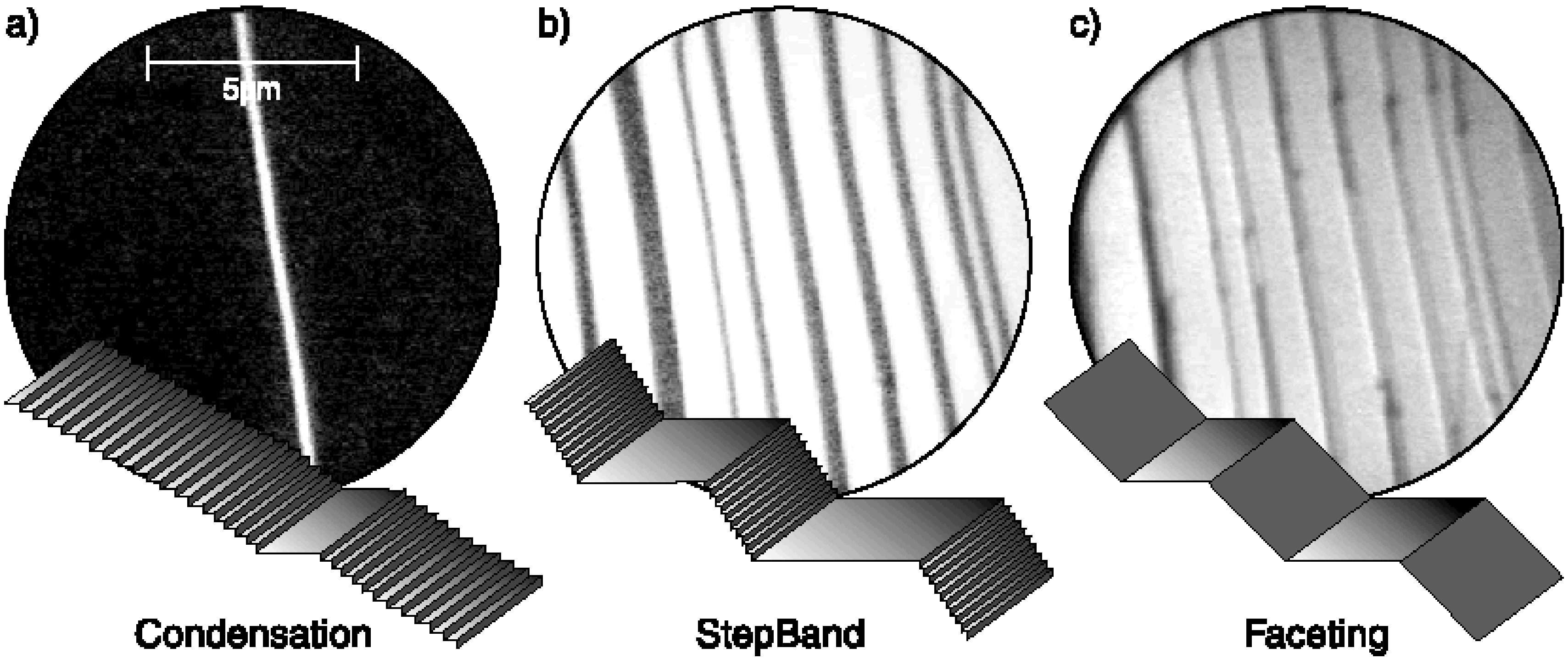


LEEM Movie using bright field imaging condition
http://www.elettra.trieste.it
(FoV: 12 µm)

F.-J. Meyer zu Heringdorf, R. Hild, P. Zahl, Th. Schmidt, S. Heun, B. Ressel, E. Bauer, M. Horn-von Hoegen: Elettra News **36** (1999).

Au induced faceting of vicinal Si(001)

LEEM images during Au deposition at 850°C:



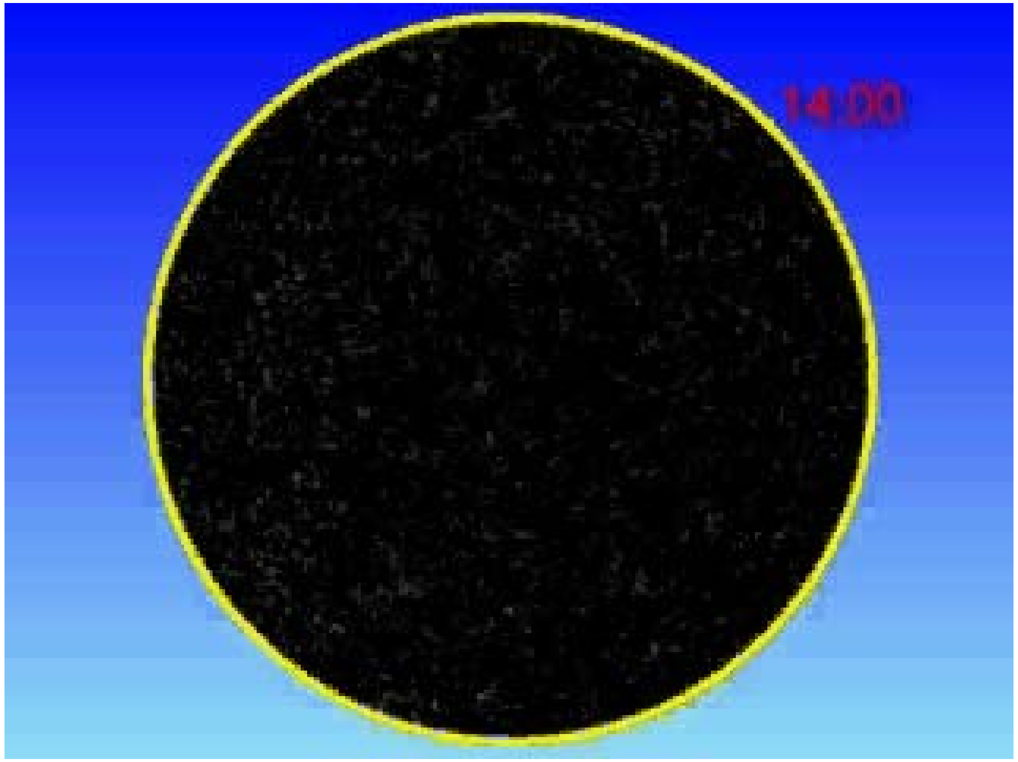
a) 4° vicinal Si(001), at θ_c=1/3 ML: formation of (001) terraces

b) terraces exhibit (5x3.2) reconstruction

c) at α=16°: formation of (119) facets
d = 400nm, L > 100µm

F.-J. Meyer zu Heringdorf, R. Hild, P. Zahl, Th. Schmidt, B. Ressel, S. Heun, E. Bauer, M. Horn von Hoegen: Surf. Sci. **480** (2001) 103.

XPEEM Movie



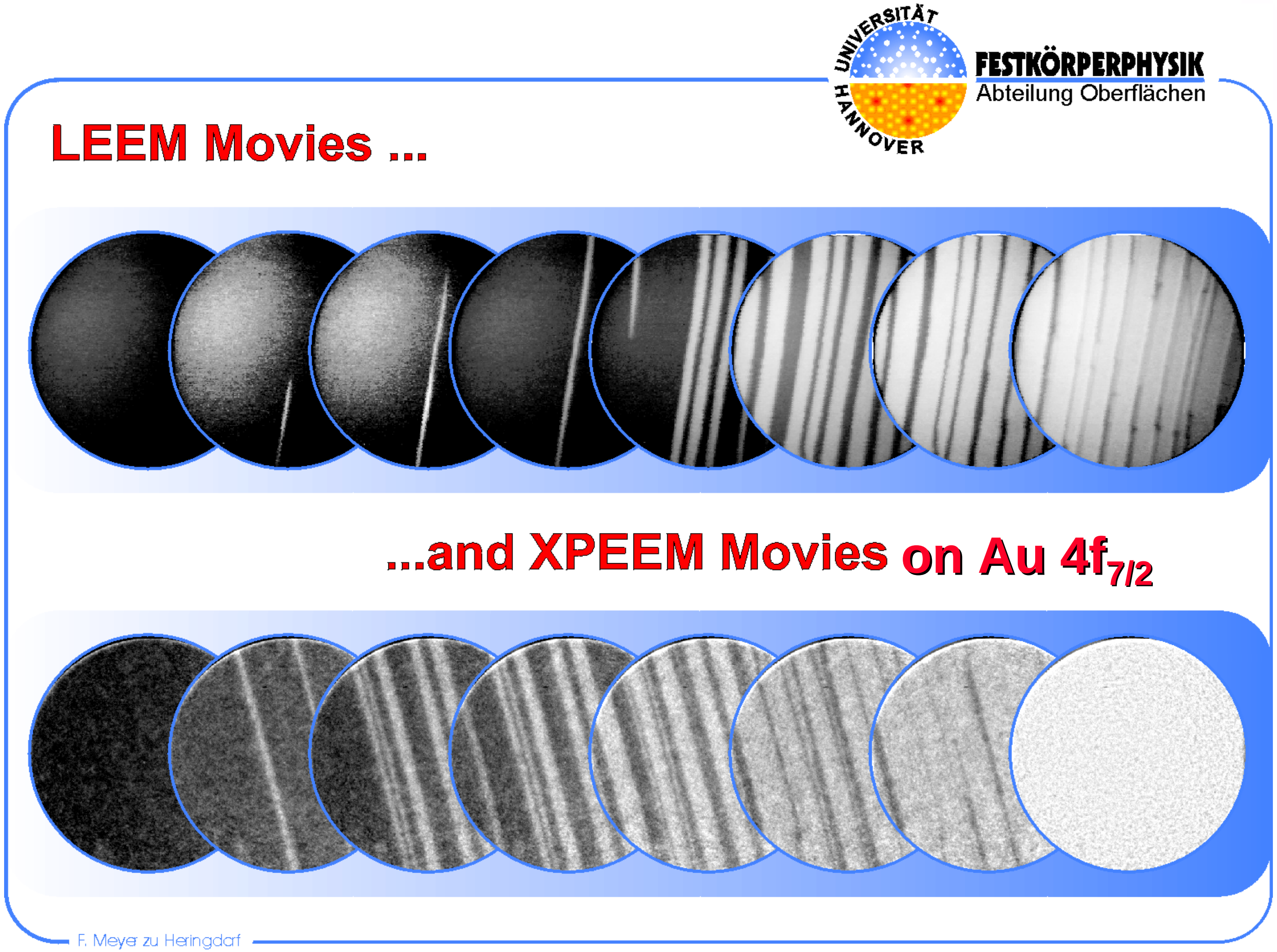
XPEEM Movie on the Au $4f_{7/2}$ core level emission

http://www.elettra.trieste.it

(FoV: 12 µm)

F.-J. Meyer zu Heringdorf, R. Hild, P. Zahl, Th. Schmidt, S. Heun, B. Ressel, E. Bauer, M. Horn-von Hoegen: Elettra News **36** (1999).

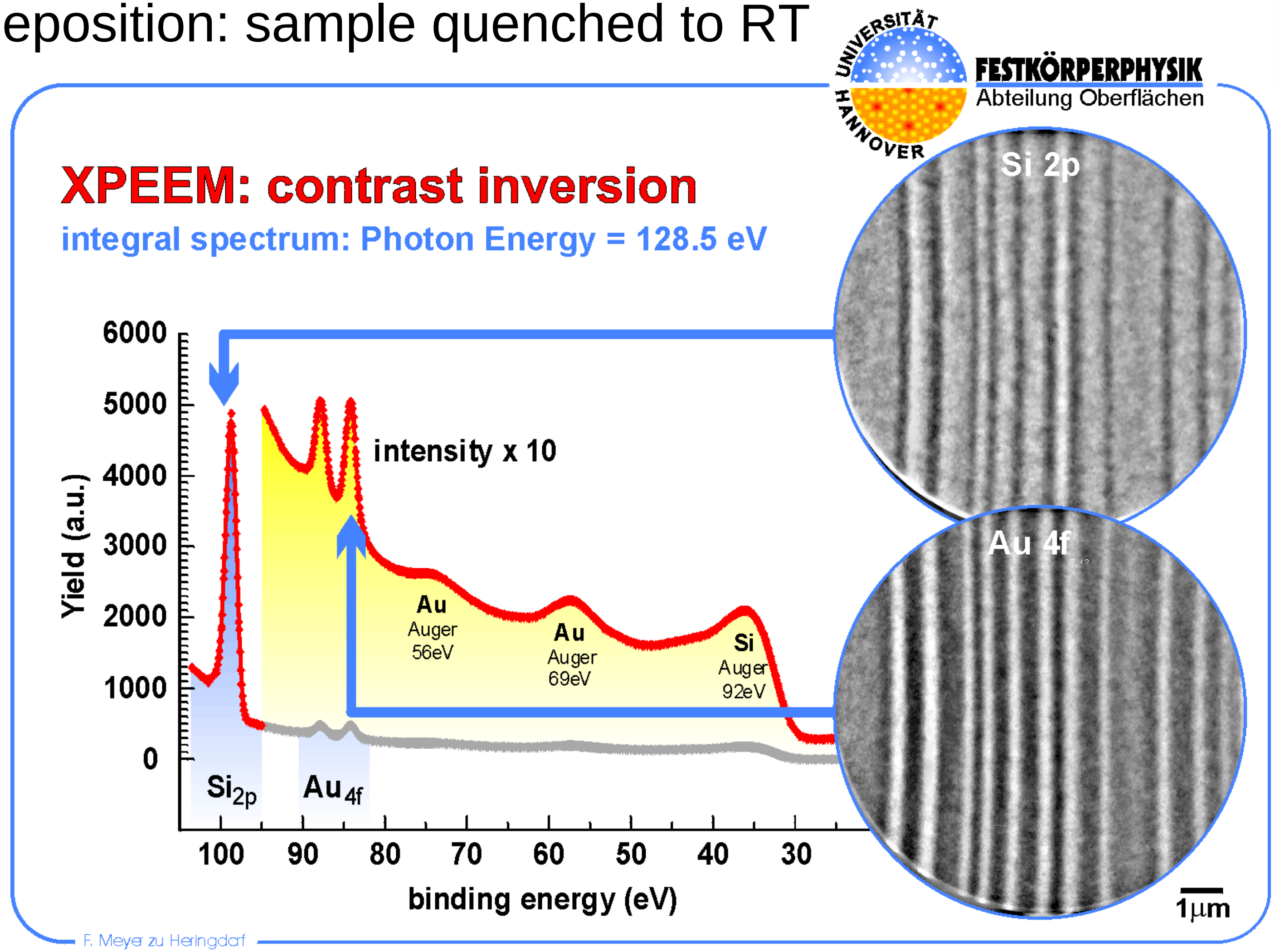
LEEM and XPEEM movies



F.-J. Meyer zu Heringdorf, R. Hild, P. Zahl, Th. Schmidt, S. Heun, B. Ressel, E. Bauer, M. Horn-von Hoegen: Elettra News **36** (1999).

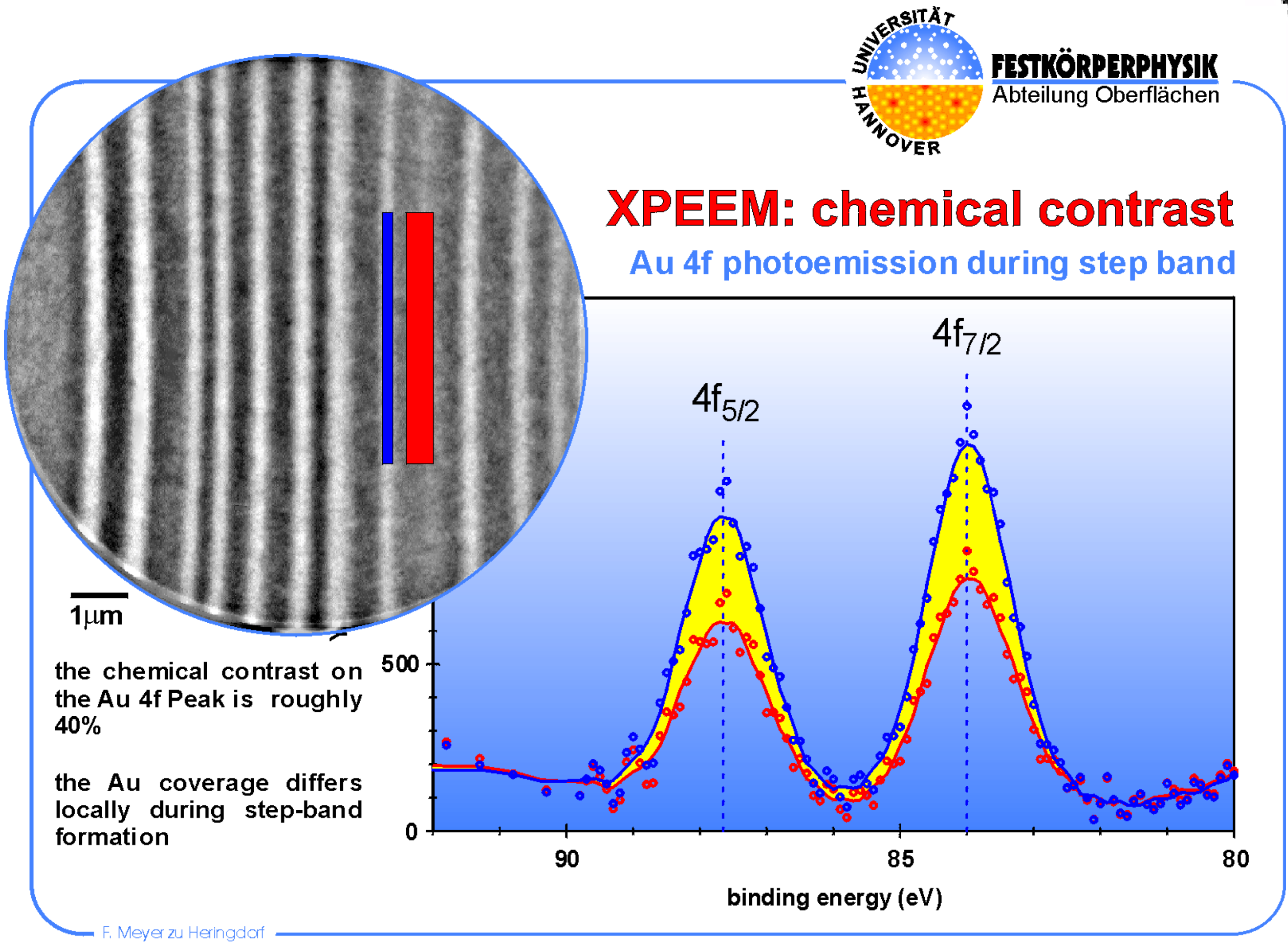
XPEEM images

during deposition: sample quenched to RT



F.-J. Meyer zu Heringdorf, Th. Schmidt, S. Heun, R. Hild, P. Zahl, B. Ressel, E. Bauer, M. Horn-von Hoegen: PRL **86** (2001) 5088.

XPEEM spectrum



F.-J. Meyer zu Heringdorf, Th. Schmidt, S. Heun, R. Hild, P. Zahl, B. Ressel, E. Bauer, M. Horn-von Hoegen: PRL **86** (2001) 5088.

Local Au coverage vs. time

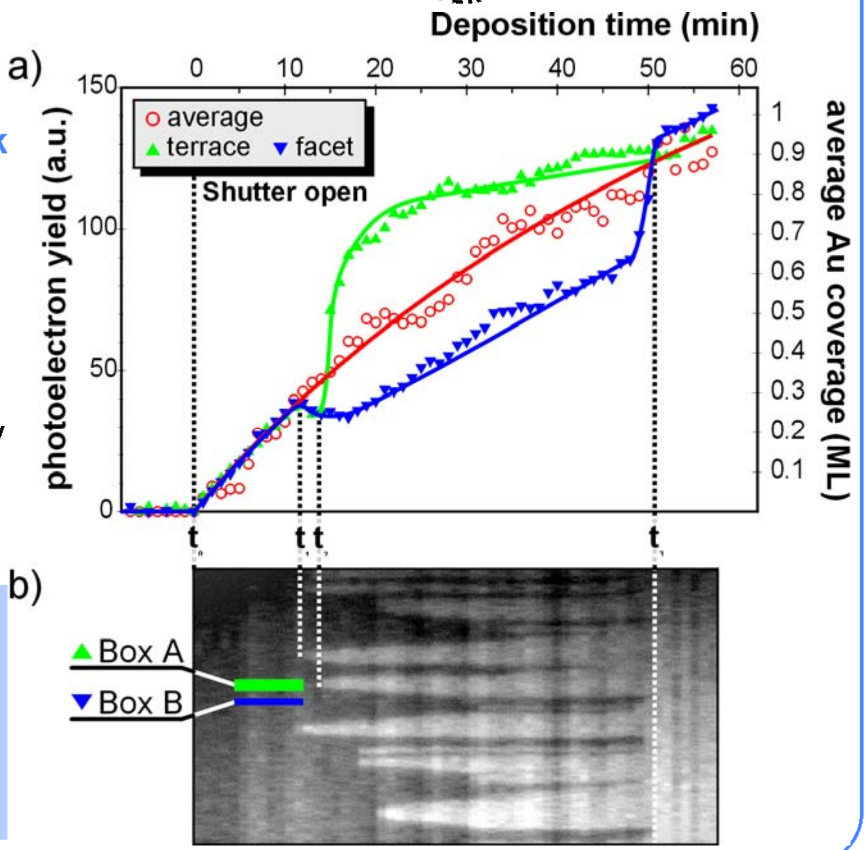
XPEEM during adsorption

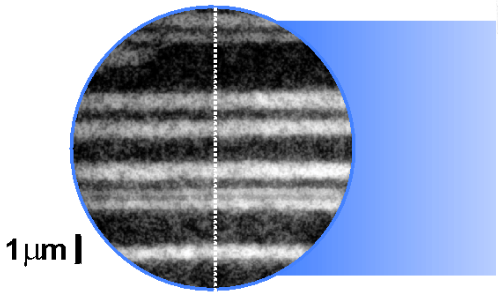
Au $4f_{7/2}$ Photoemission Peak

* monitoring of intensity with time
* constant Au deposition rate

Results:

* spatially integrated intensity increases linearly
=> peak intensity is proportional to the coverage
* local coverage develops differently after nucleation of (100) facets Au atoms are trapped from the neighbourhood.





F. Meyer zu Heringdorf

t_0: shutter open.

t_2: terrace forms, Au coverage in

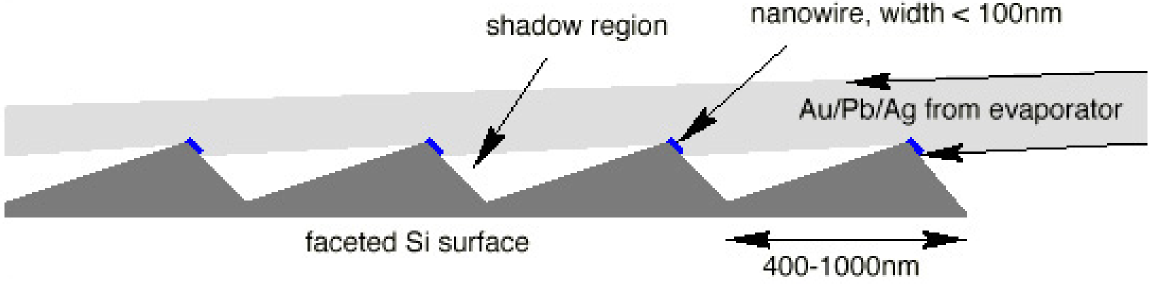
- Box A doubles,
- Box B decreases.

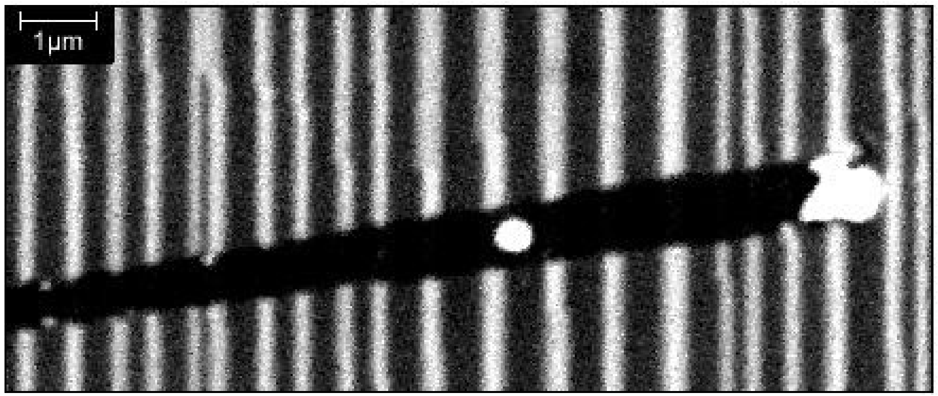
t_1: confirms this model.

F.-J. Meyer zu Heringdorf, Th. Schmidt, S. Heun, R. Hild, P. Zahl, B. Ressel, E. Bauer, M. Horn-von Hoegen: PRL **86** (2001) 5088.

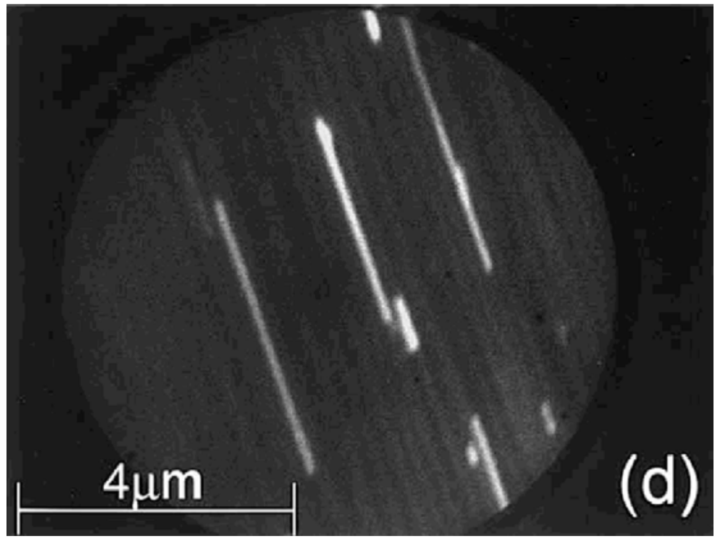
Growth of metallic nanowires

Deposition under glancing angle:





Ex-situ Au deposition, SEM image
(Meyer zu Heringdorf, Ph.D. thesis, 1999)



In-situ Pb deposition,
annealing at 260°C,
LEEM study
(Jalochowski and Bauer,
Surf. Sci. **480** (2001) 109.)

Conclusions

• Local variation of Au coverage has been determined quantitatively and time resolved.

• Phase separation of Au coverage.

• Terraces collect Au atoms from the neighborhood, suppressing the formation of other terraces in a given area.

• Demonstration of metallic nanowire growth on this surface

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InAs Nanocrystals on Se / GaAs

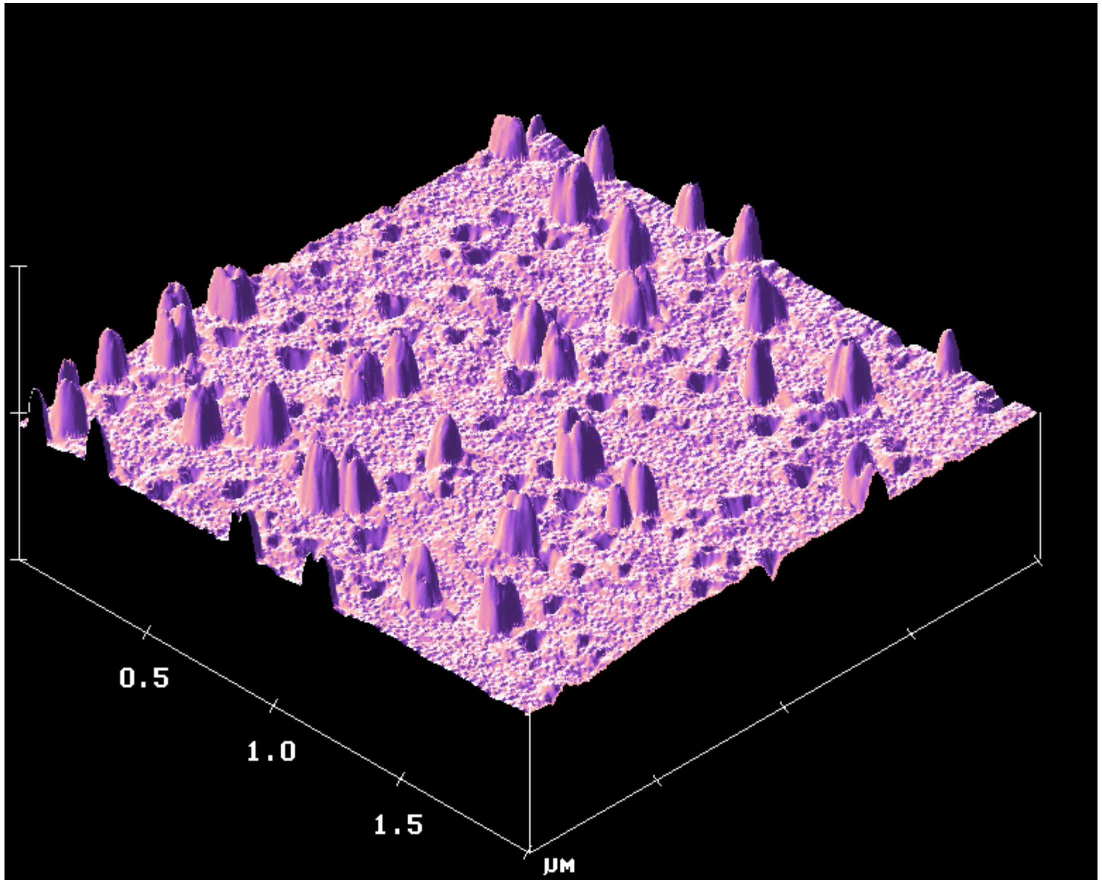
Nanocrystals formed during strained-layer epitaxy
- Quasi zero-dimensional nature (quantum dots)
- Semiconductor lasers and memory applications
- No lithography: cost-effective fabrication of devices

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



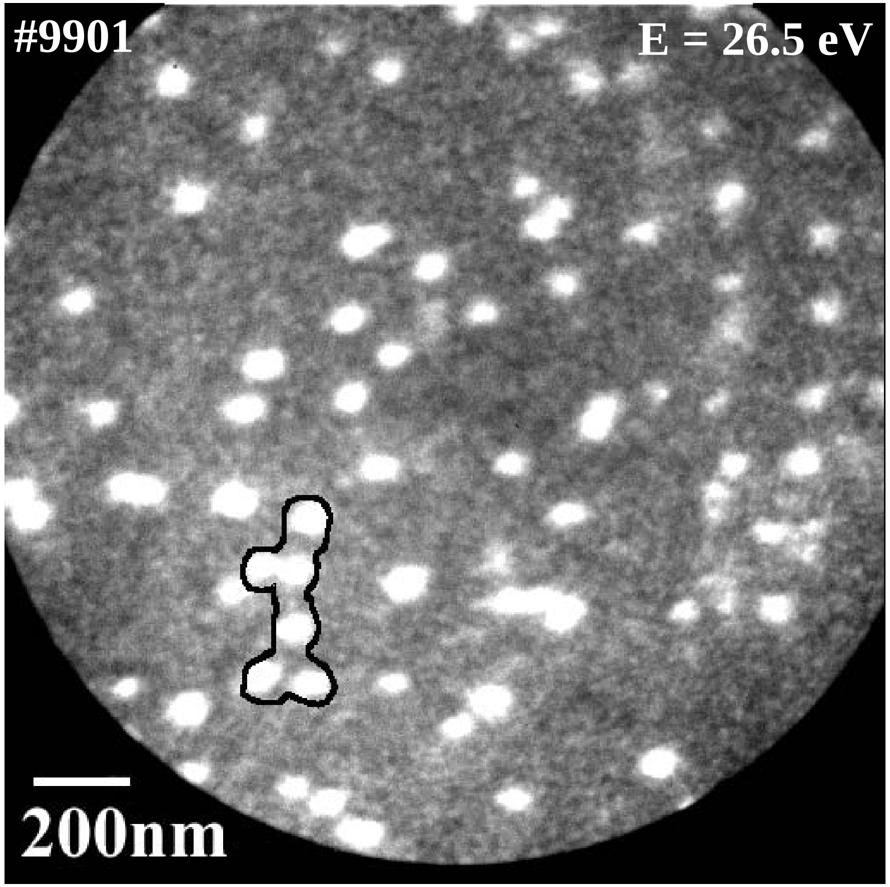
Field of view: 2 µm x 2 µm.

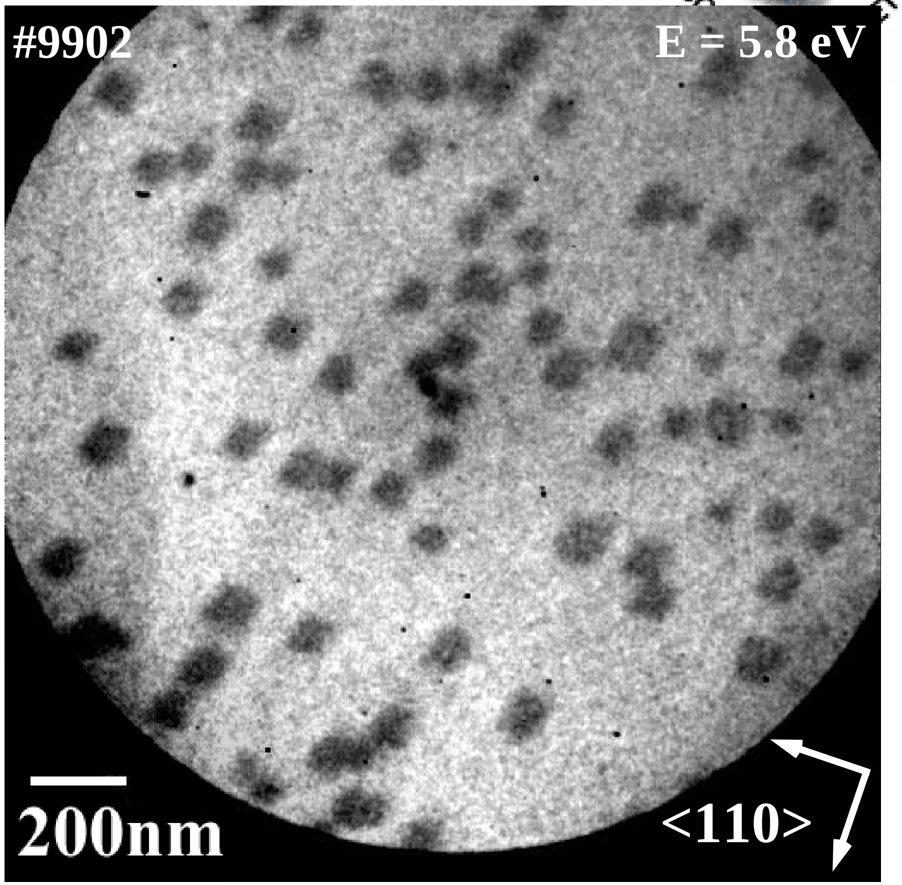
InAs / Se / GaAs
after capping and decapping.

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

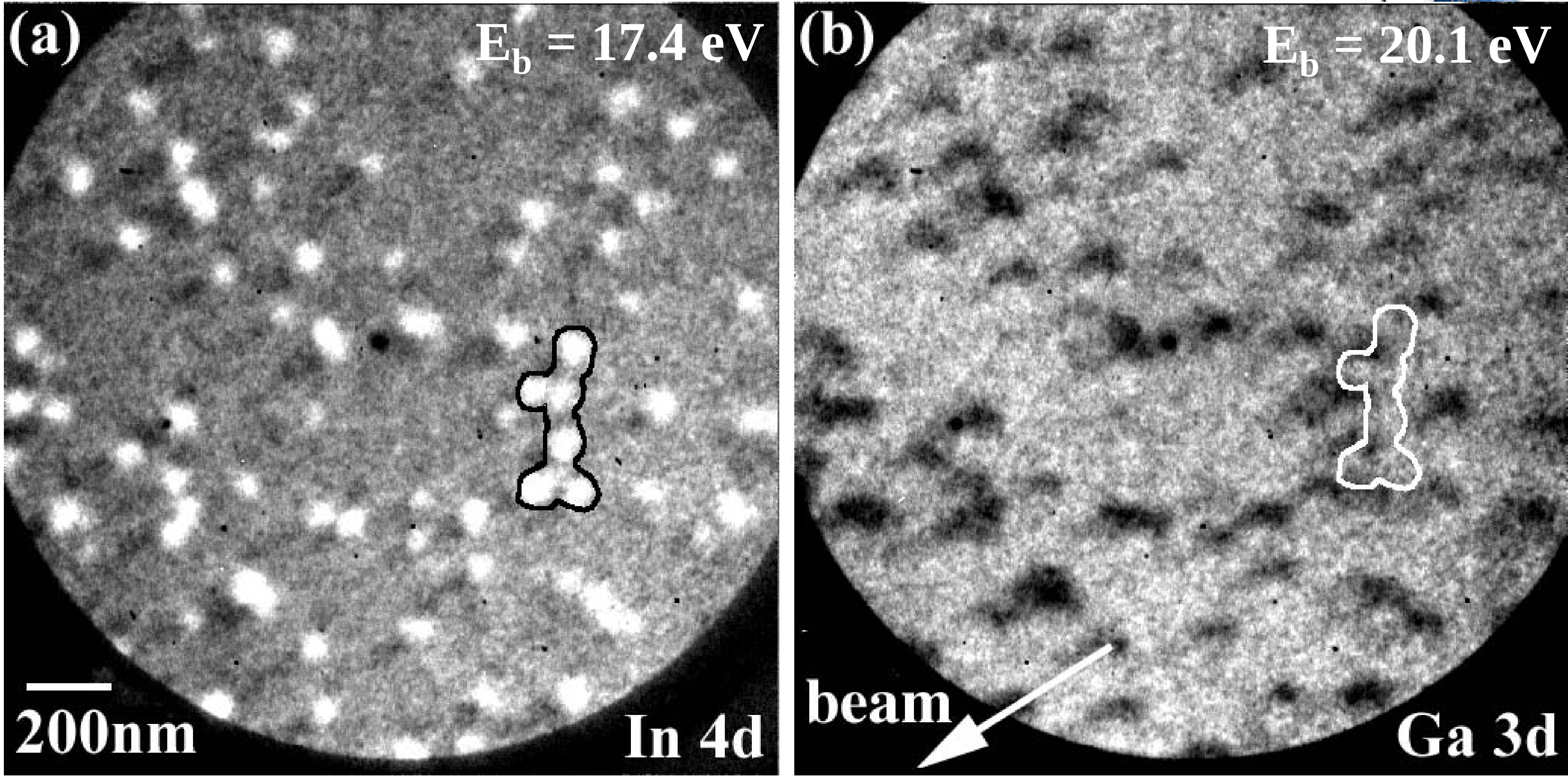




nanocrystals have square base oriented along <110>

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

XPEEM



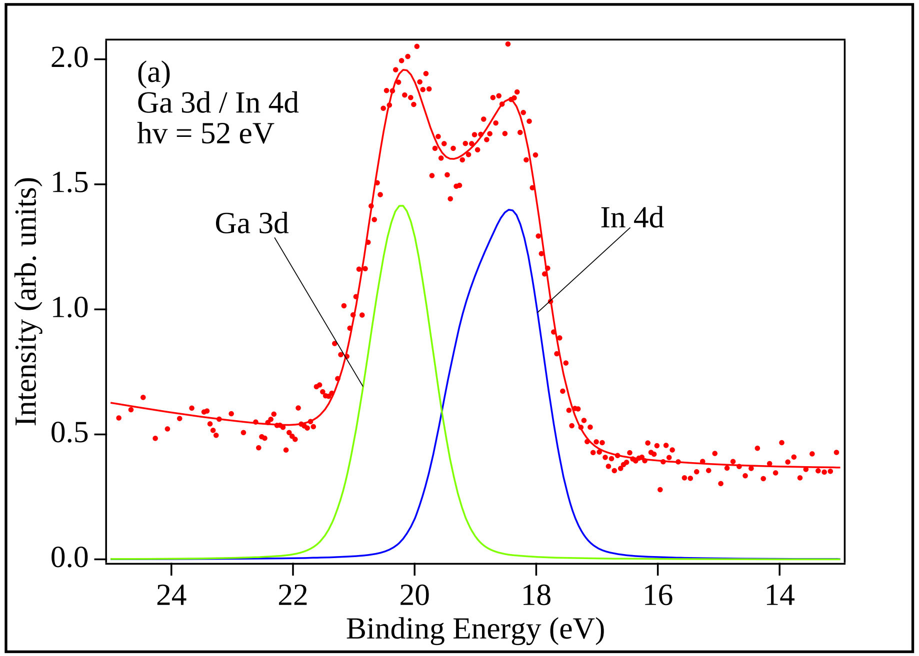
hv = 52 eV, FoV = 2µm

nanocrystal height from their shadow length: 22 nm

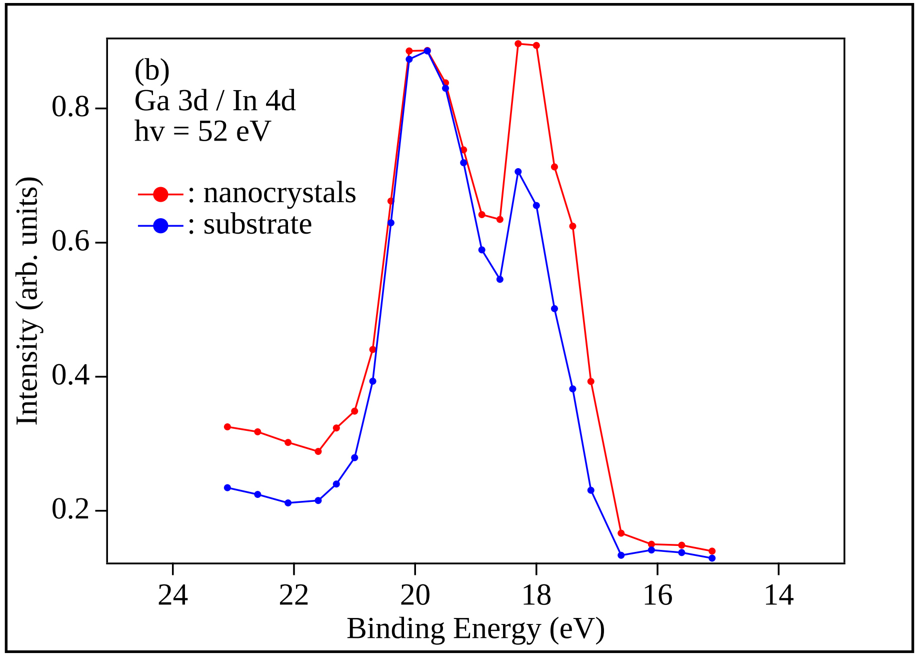
S. Heun, Y. Watanabe, B. Ressel, D. Bottomley, Th. Schmidt, and K. C. Prince, Phys. Rev. B **63** (2001) 125335.

Laterally resolved core level spectroscopy

Integral spectrum



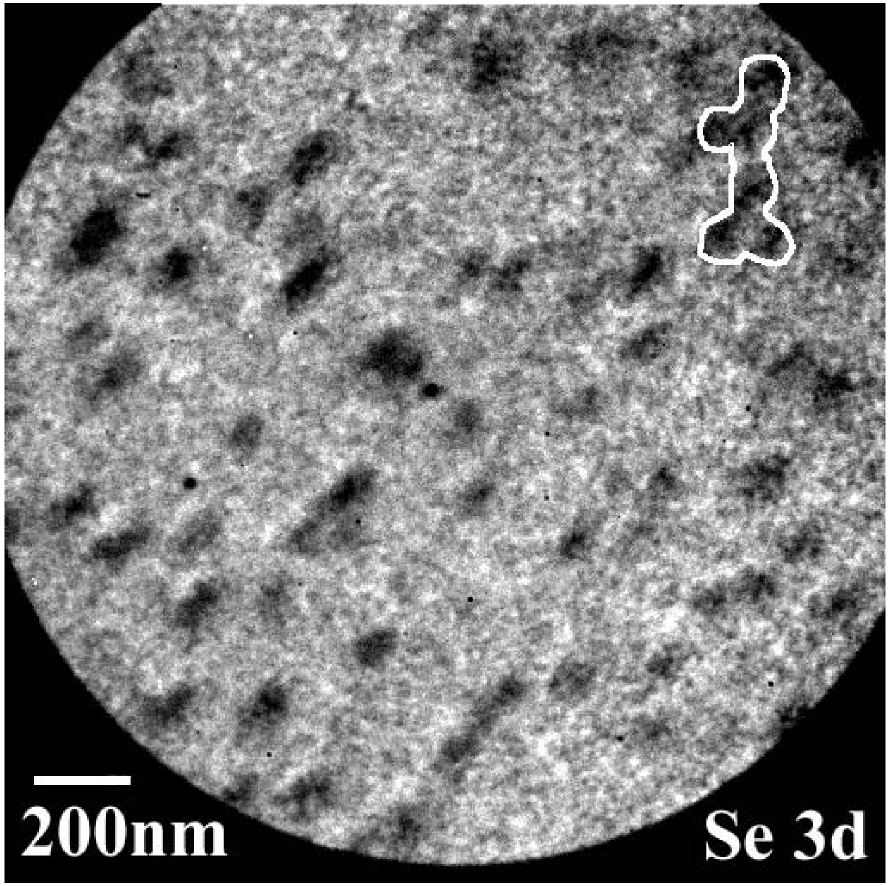
Laterally resolved spectra



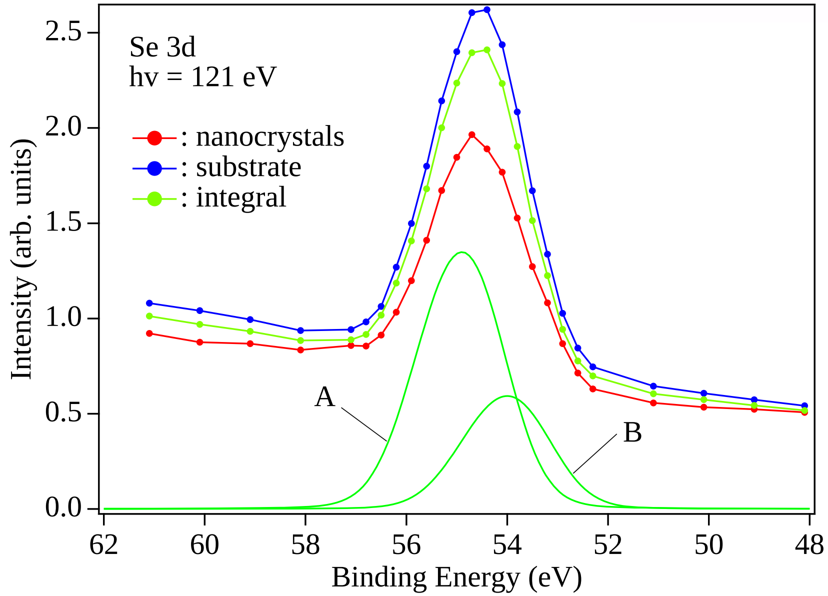
Indium on substrate ↑ SK growth mode
Gallium on nanocrystals

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



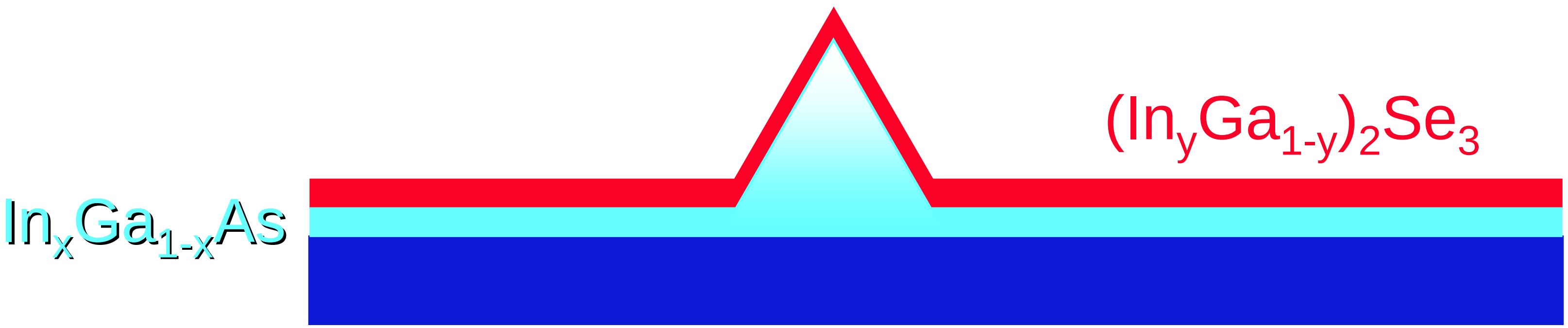
Selenium on the nanocrystals

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.

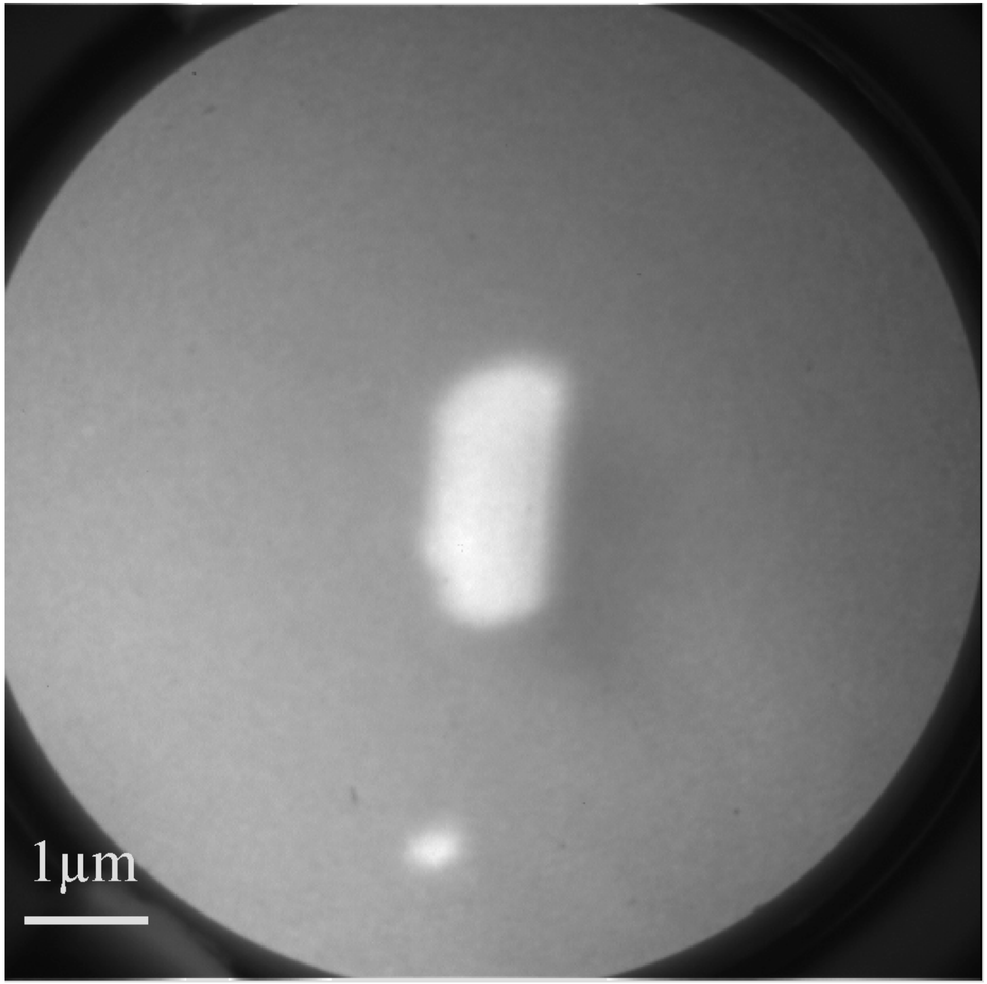
Conclusions

- 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.

Summary



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

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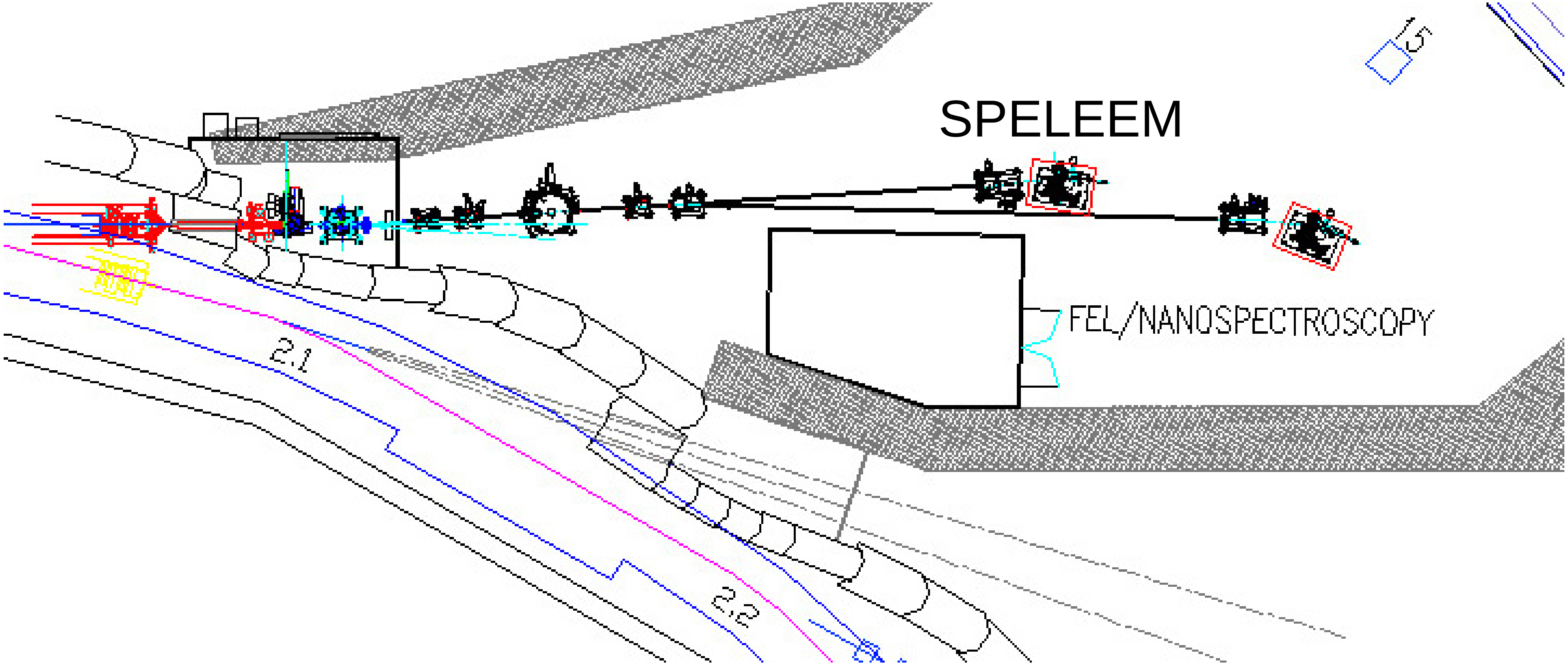
Nanospectroscopy beamline

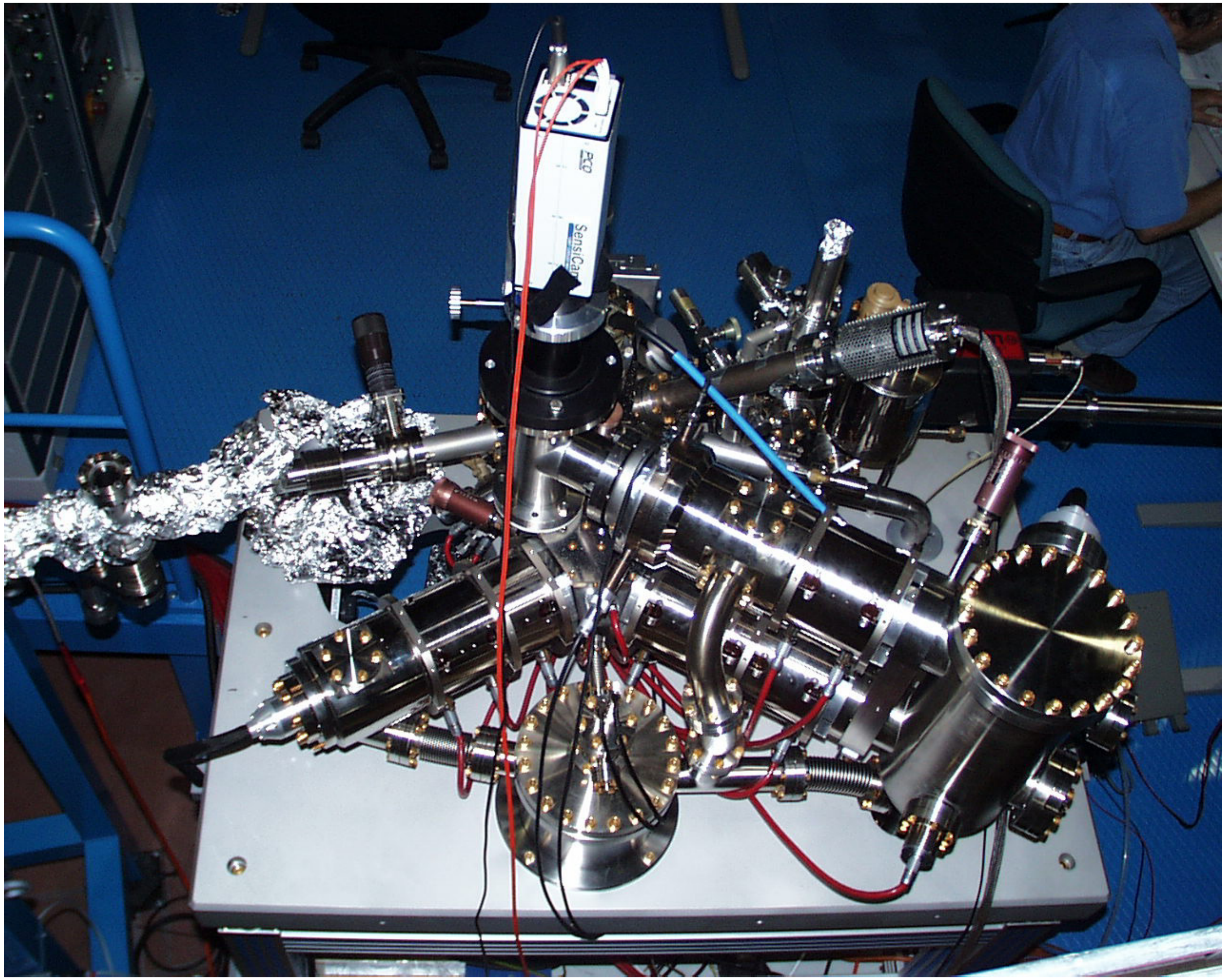
Now under commissioning !



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

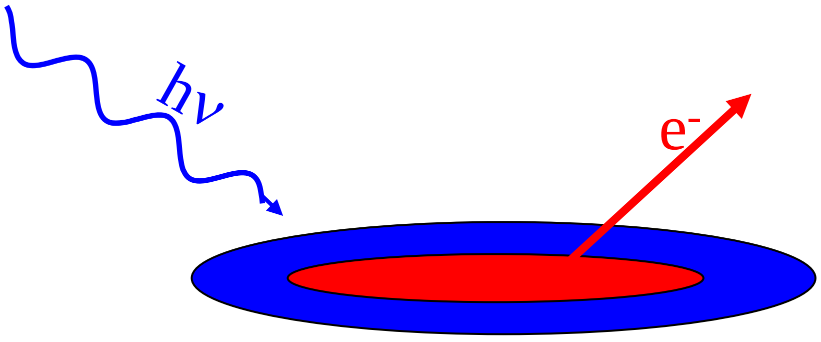
The Nanospectroscopy Beamline

The SPELEEM at ELETTRA



Nanospectroscopy beamline characteristics

Source:	Apple II type undulator, 10 cm periods elliptical and linear polarization 240 µm x 40 µm source dimension
Monochromator:	20 - 1000 eV (2 VLS plane gratings) E/ΔE > 4000
Spot:	High photon flux density (10^{12}-10^{14} ph/sec) Spot as small as possible (10 μm^2) 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.