The Abdus Salam
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School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

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Scanning Photoemission Microscopy: Applications and Examples

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Scanning Photoemission Microscopy: Applications and Examples

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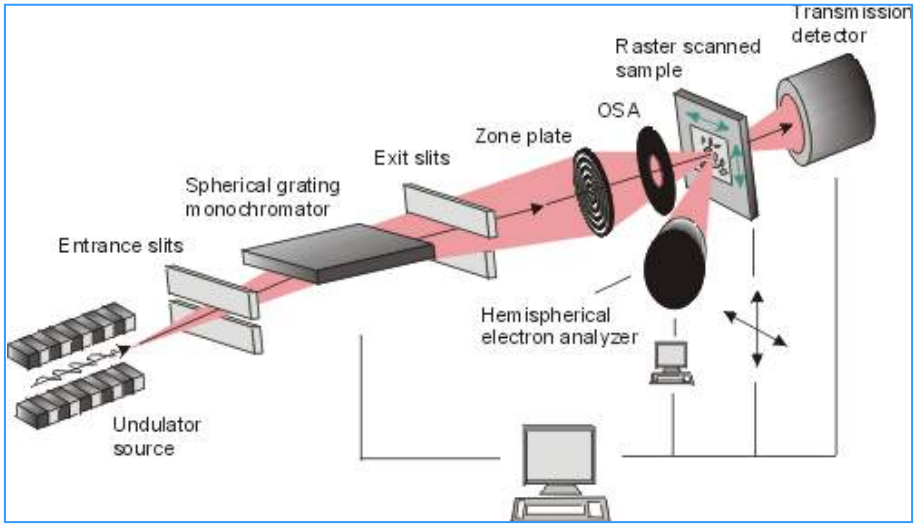
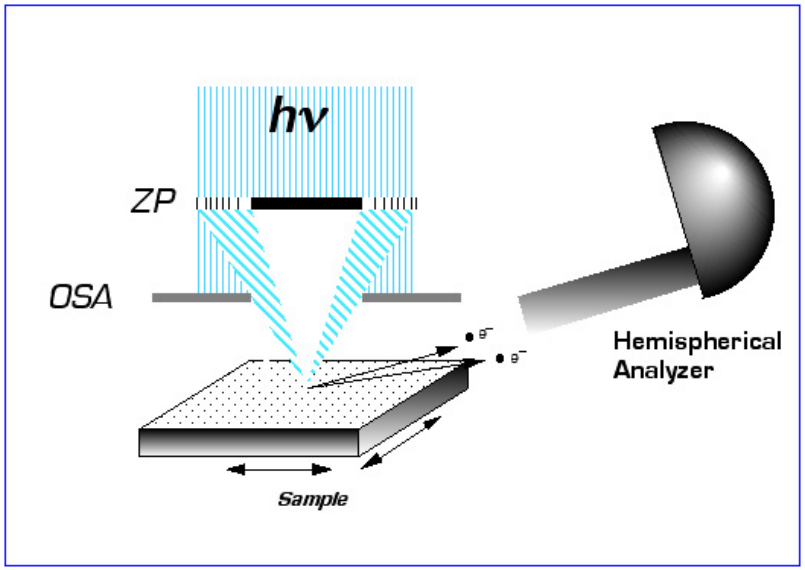
X-ray microscopy: method characteristics

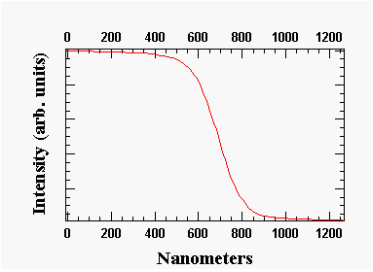
Beamline Layout and SPEM setup





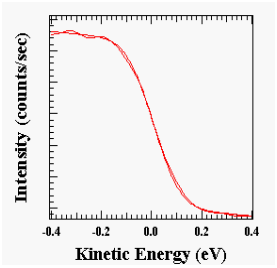
SPEM actual performances

Spatial resolution



- **Best resolution:**
  ~100nm (ZonePlates ltd)
- **Best transmission:**
  8% (ZP ltd.)

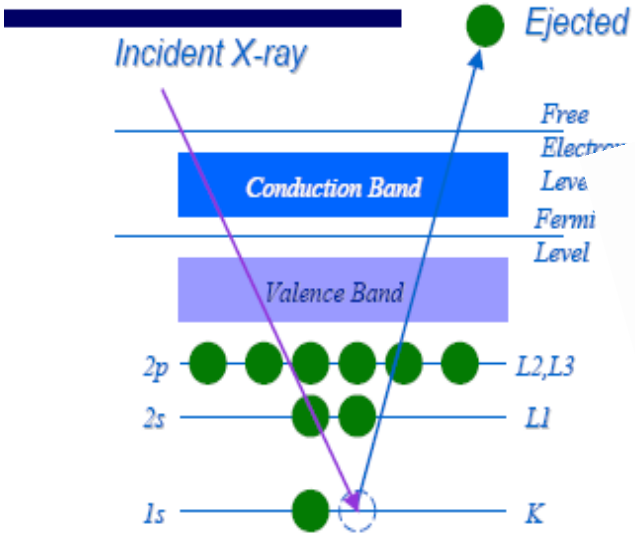
Overall energy resolution

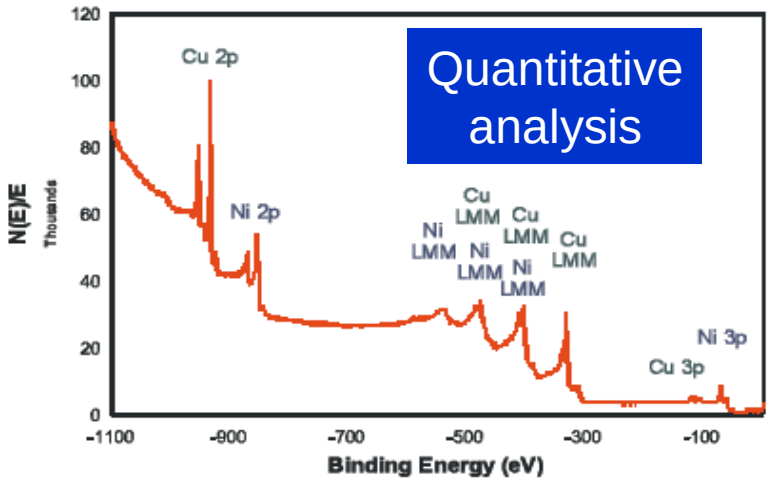


- **Energy resolution: ~180meV**
- **Standard conditions**
- **Room Temperature**
- **Photon Energy: 500 eV**

Photon energy range: 350 eV (min) – 800 eV (actual, undulator transmission)

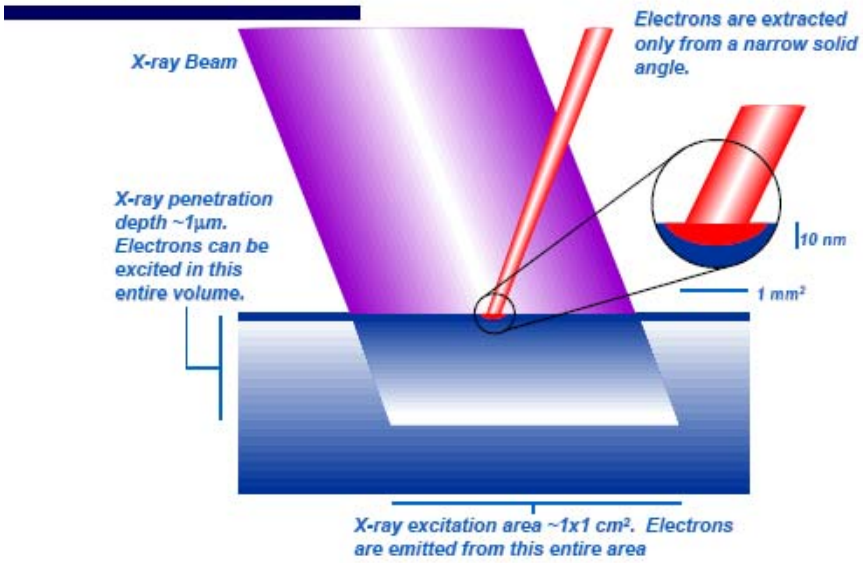
The Photoelectric Process



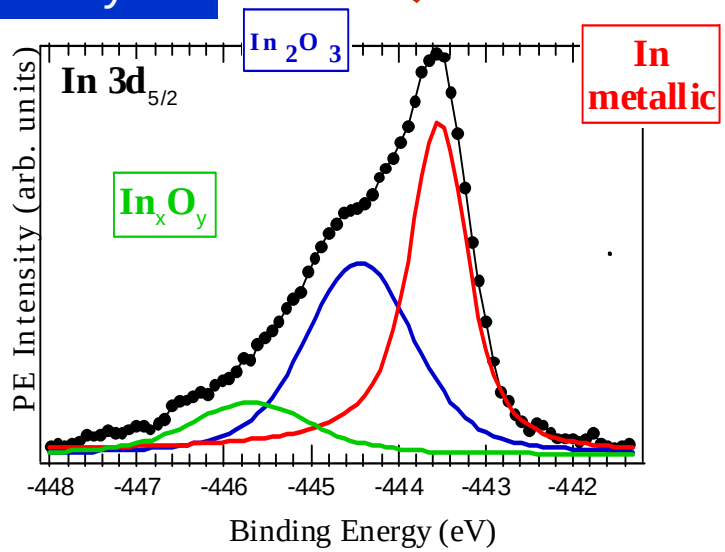


X-ray Photoelectron Spectroscopy

Small Area Detection



Fine Chemical analysis

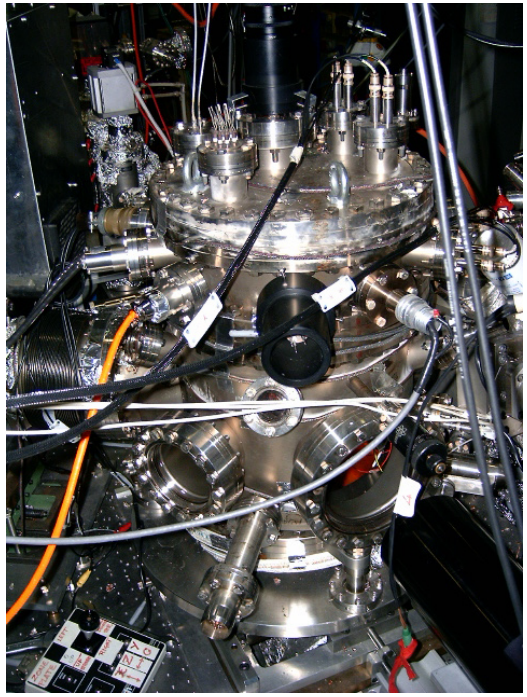


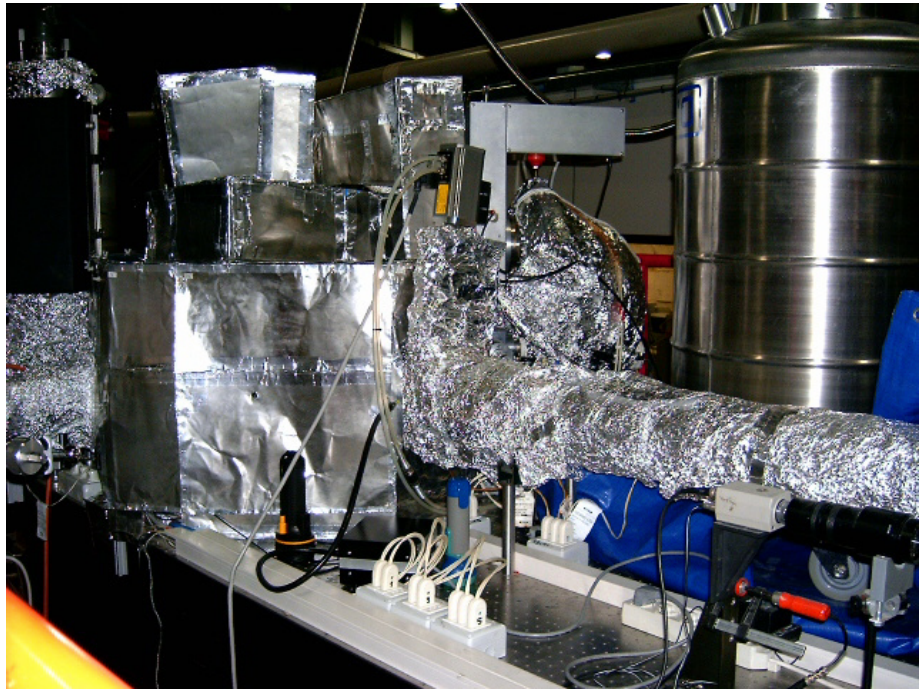
Outline:
Ingredients of a Scanning Photoemission Microscope (SPEM) based on Zone Plates

- Vacuum chambers
- Sample and optics manipulators
- Sample holders
- Electron analyzers
- Electron detectors

Vacuum chambers

- No standard geometry
- Dimensions depends mainly from the size of the manipulators
- Large flanges for the manipulators (>CF200)
- Geometry limits the possibility of in-situ experiments





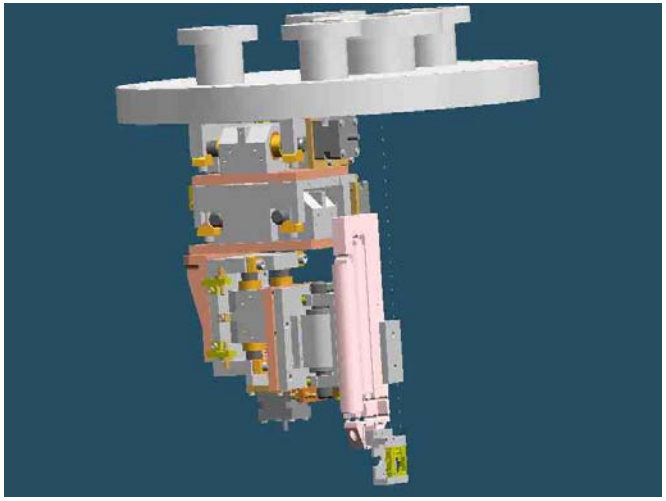
Manipulators

Sample

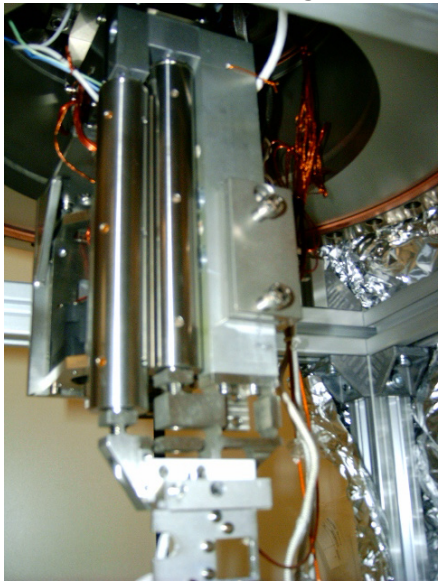
- Large scanning range (>1mm) with large steps (1-100 μm)
- Small scanning range (<3mm) with small steps (10-50 nm)
- The most common choice is to use two kind of motors: stepper (for large scans) and piezo (for small scans)
- Compact design to improve the stability

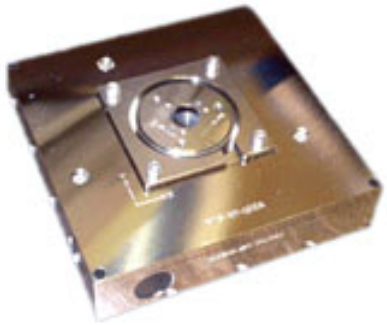
Optics (ZP+OSA)

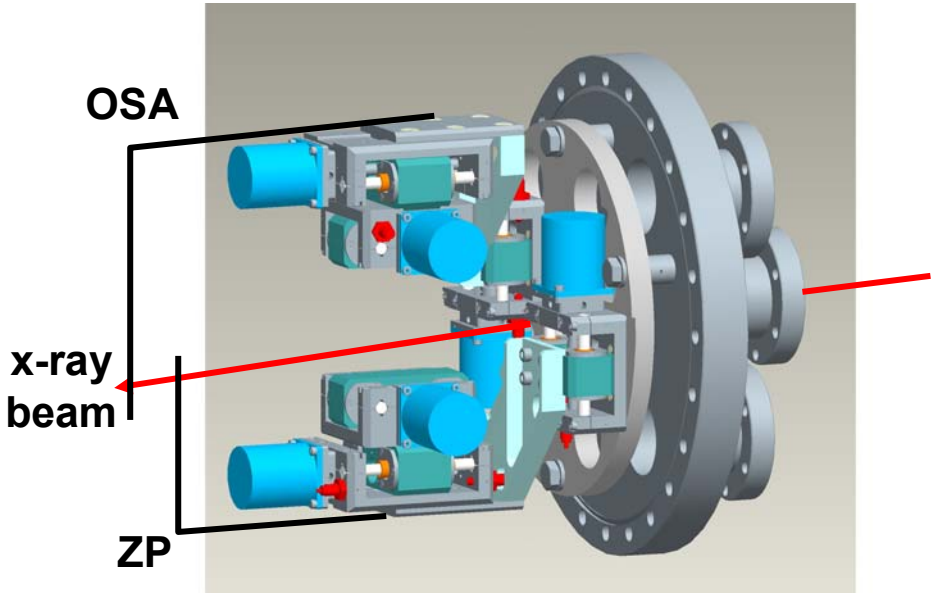
- 6-axis needed: 3 for the ZP and 3 for the OSA
- Typical range: 10 - 15 mm
- Movement resolution of 1-3 μm
- Only one type of motors needed (stepper or inchworm)
- Compact design to improve the stability



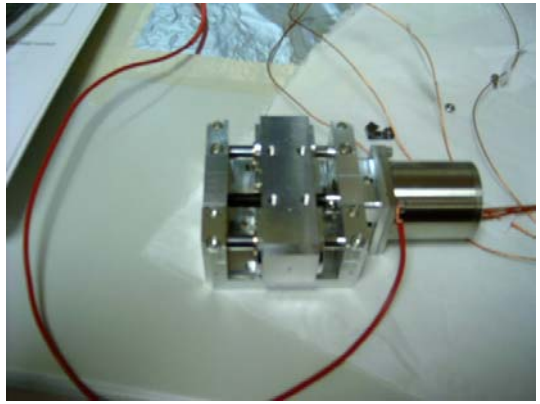
x-y piezo stages





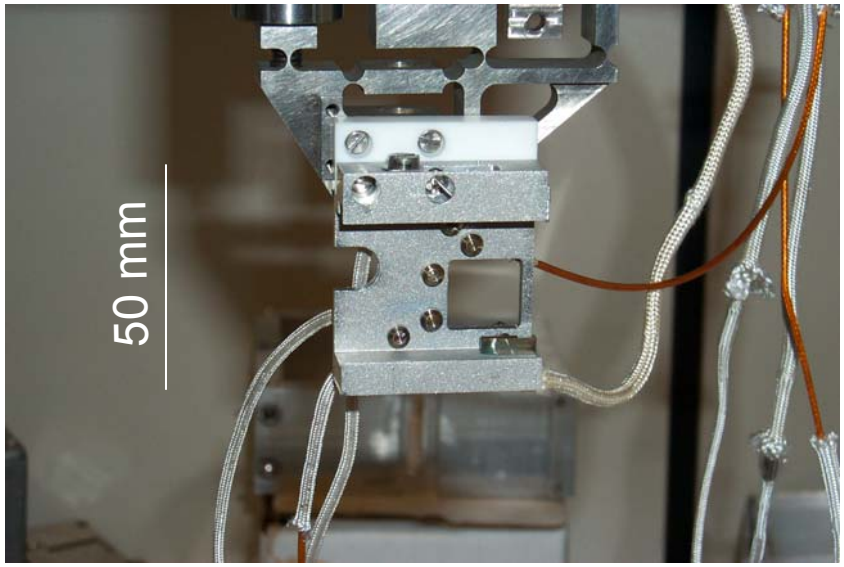


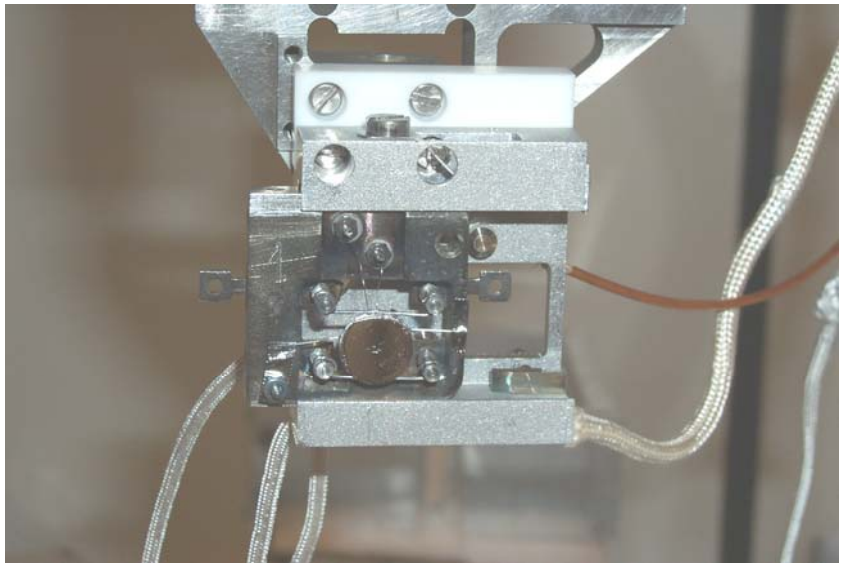
1 axis coarse translation stage



Sample holders

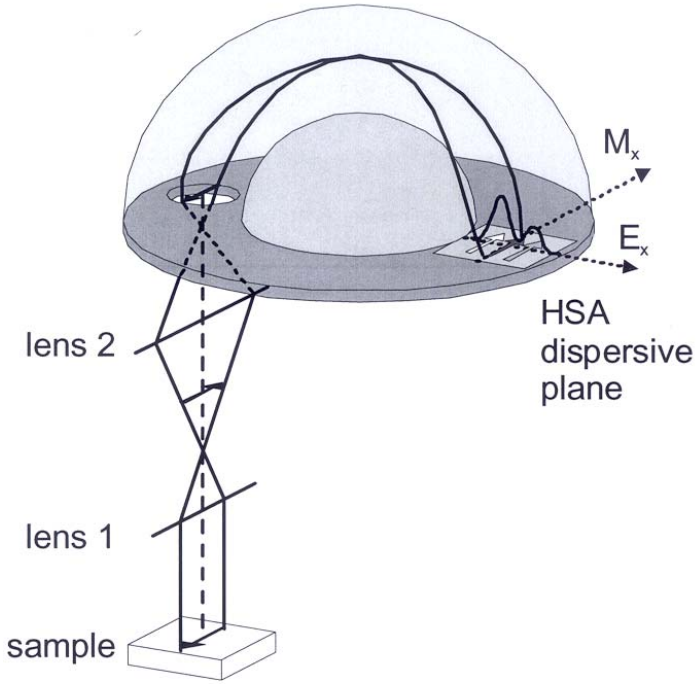
- Cabling used for the contacts (heating, grounding, potentials, etc.) must not interfere with the scanning motion.
- Cooling needs special design
- In most of the cases sample holders are home designed (or modified from standard designs)



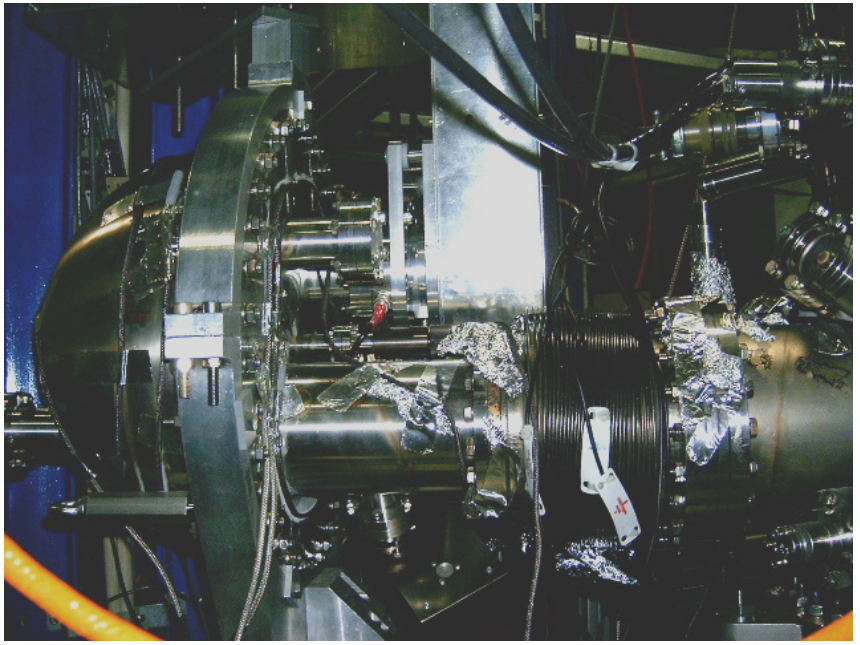


Electron analyzers

- The most used type of electron analyzer is the Hemispherical Electron Analyzer (HEA)
- Due to geometrical constrains the detection in mainly grazing



Electron analyzer of the SPEM



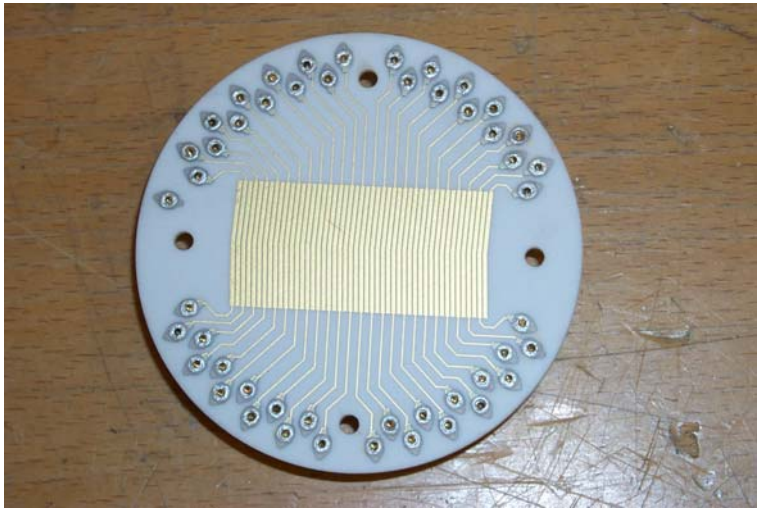
Electron detectors

Single channel

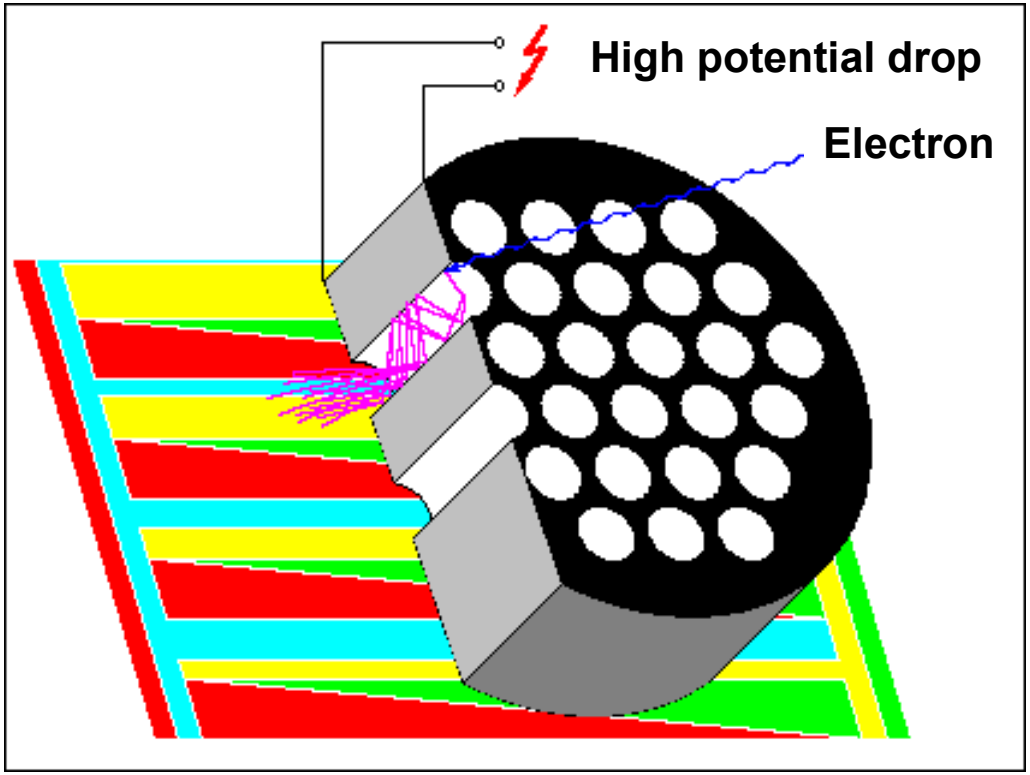
- Single channeltron
- Single Au plated anode
- Not very diffused

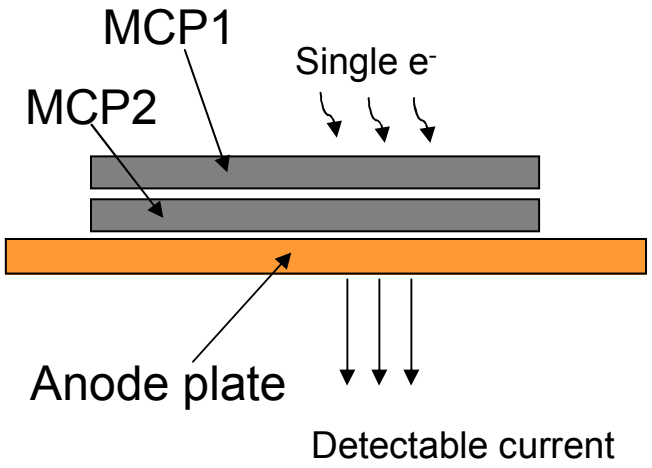
Multi channel

- Array of channeltron (low number of channels)
- Multi Au plated anodes (100 channels)
- 2D-CCD detectors

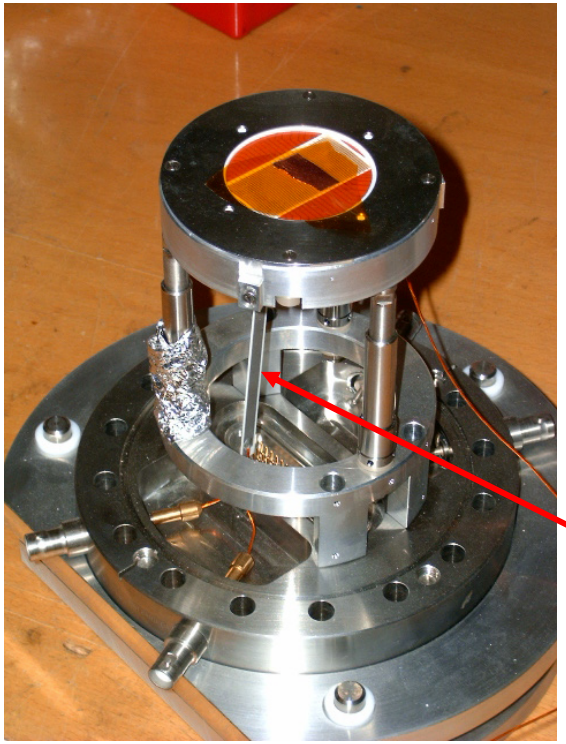


Electron detectors based on micro channel plates

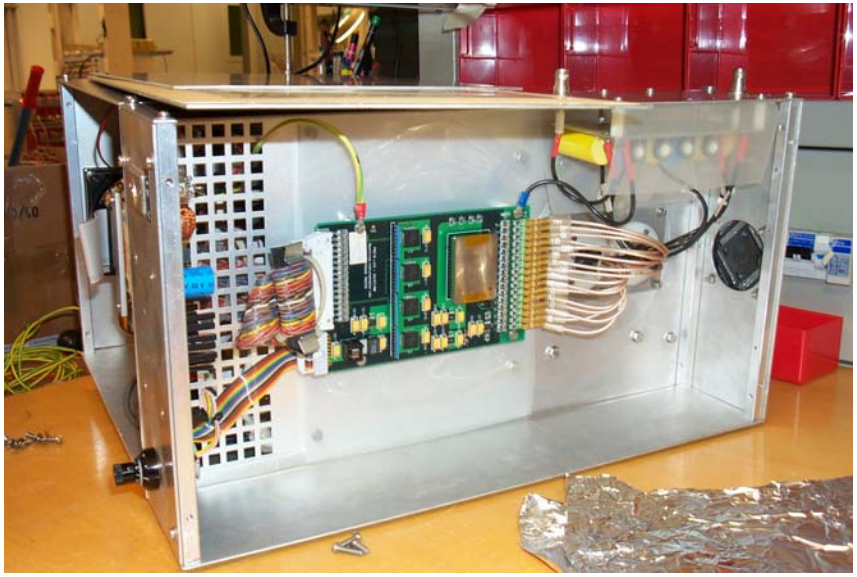


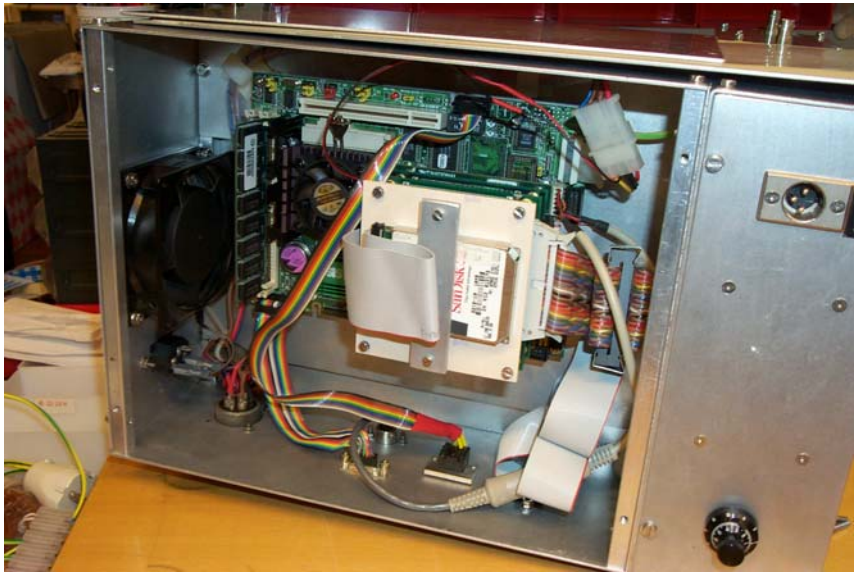


The Microchannel Plate (MCP) consists of millions of very-thin, conductive glass capillaries (4 to 25 micro meters in diameter) fused together and sliced into a thin plate. Each capillary or channel works as an independent secondary-electron multiplier to form a two-dimensional secondary-electron multiplier.



Vacuum compatible condensor

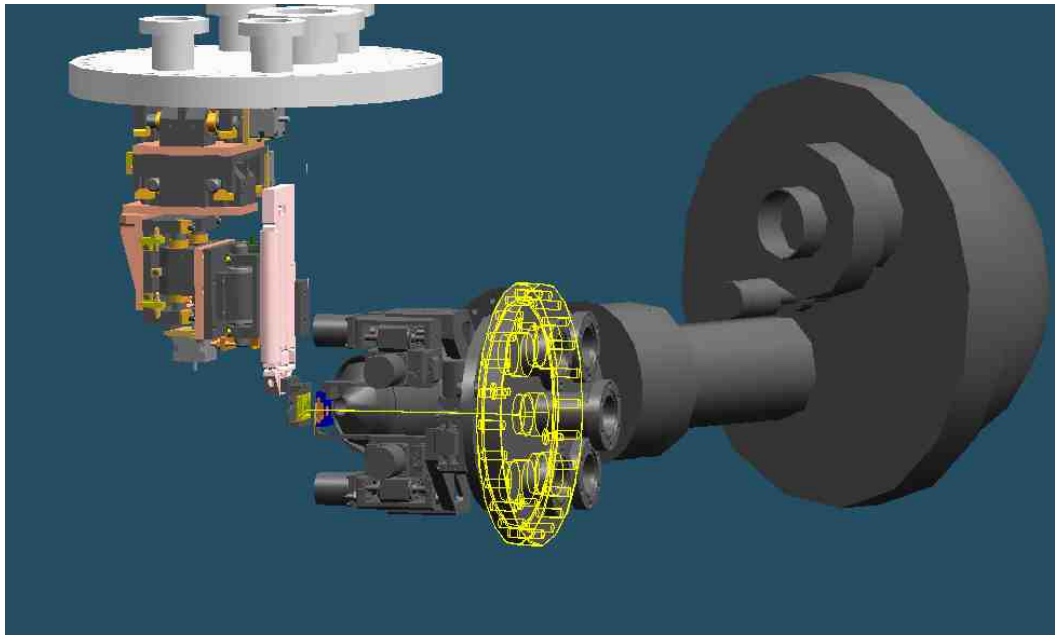


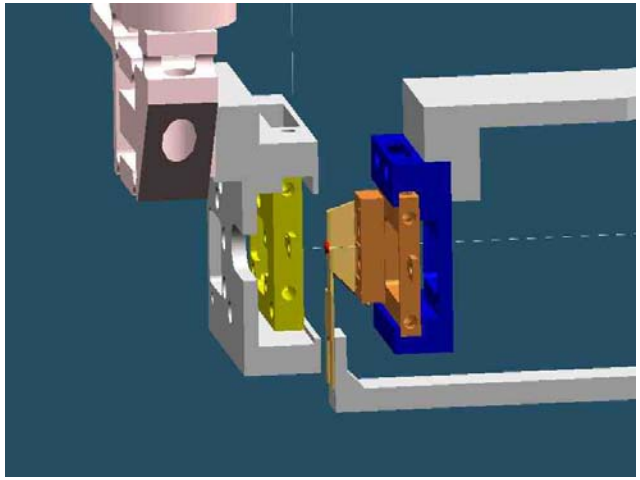


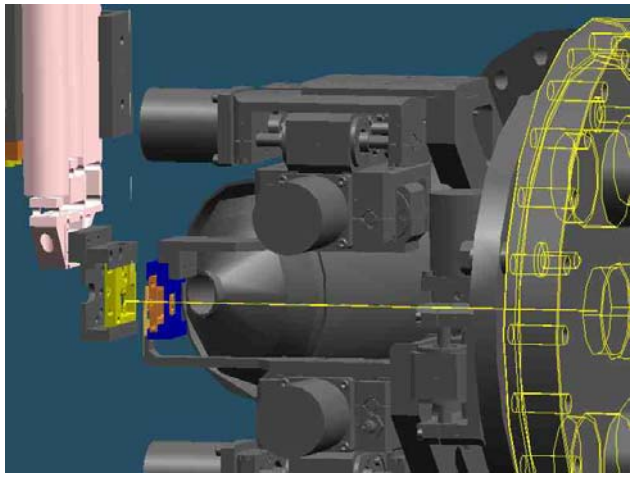
Electron Detector Electronics

- Discriminators
- Preamplifiers
- Counters

Final layout of the experimental chamber

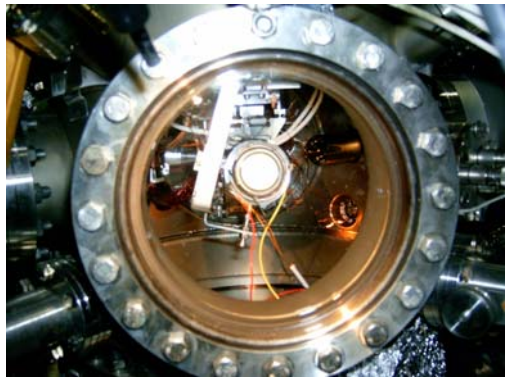


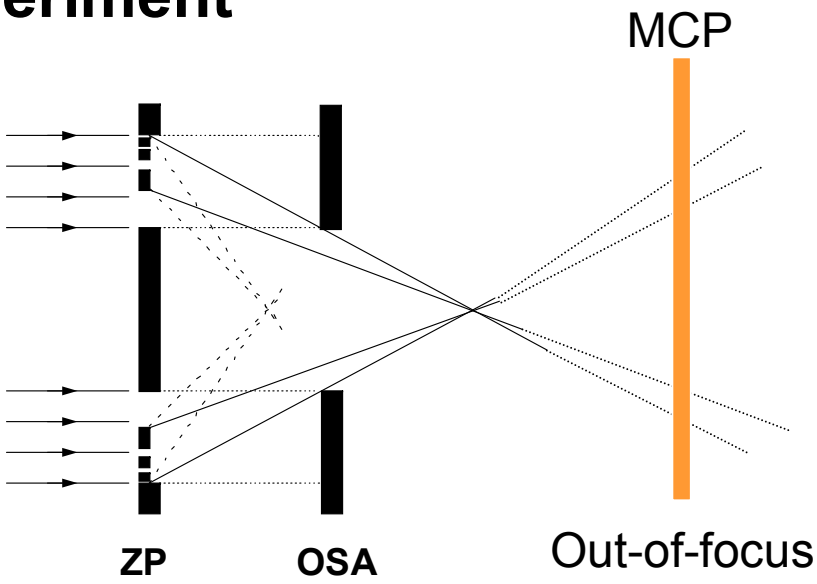




Start-up of an experiment

1. Optics alignment

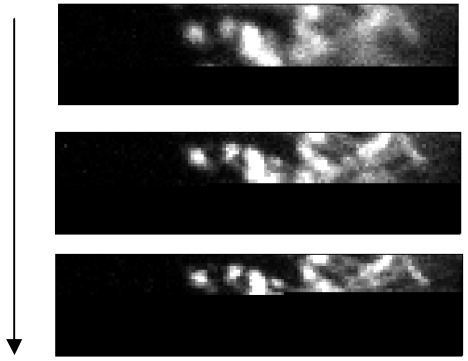


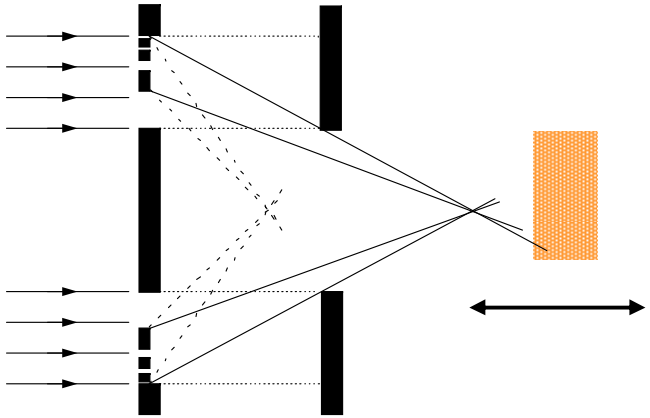


2. Sample on the x-ray focus

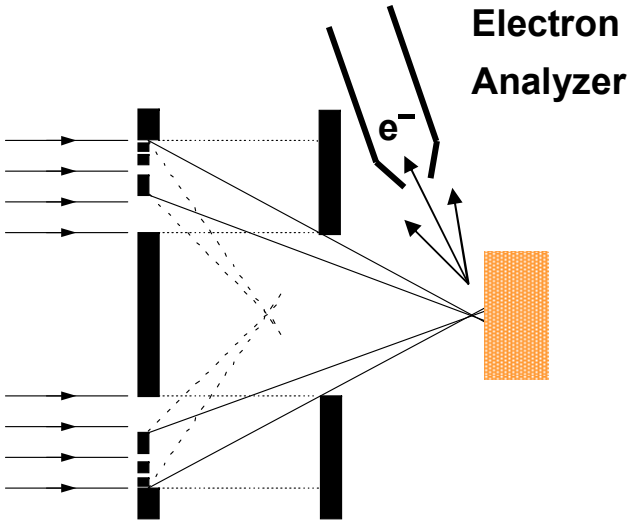
$$DOF = \frac{\delta r}{D} f_m$$

Typical: 5-15μm





3. Analyzer adjustment



4. Data acquisition

- Images: electron analyzer set to a fixed energy and sample rastered
- Photoemission Spectra: sample fixed and energies scanned

Image analysis

- Nature of the contrast in the images
- Getting the chemical information out of the artefacts
- Multichannel detection

- Chemical inhomogeneity

Ni islands on Si

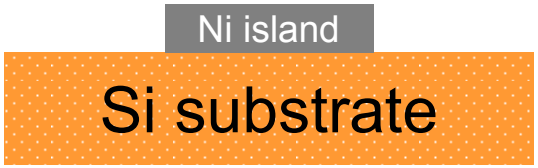


Image on Ni

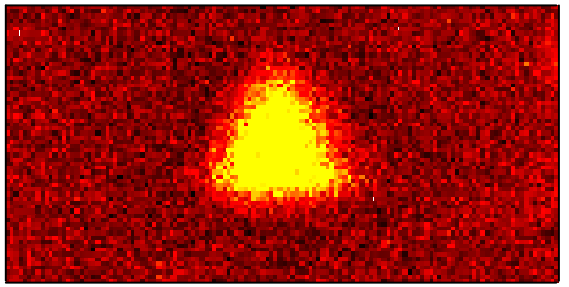
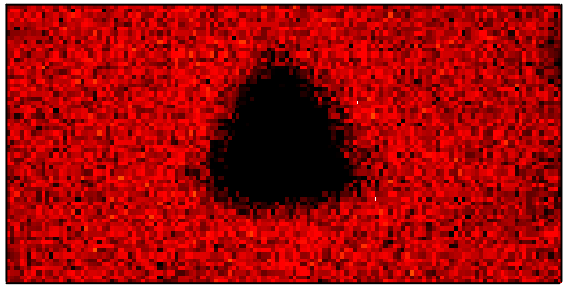


Image on Si



Au patch on Rh(110)

Image on Rh

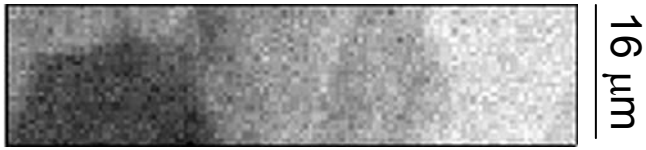
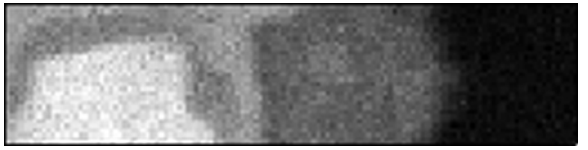


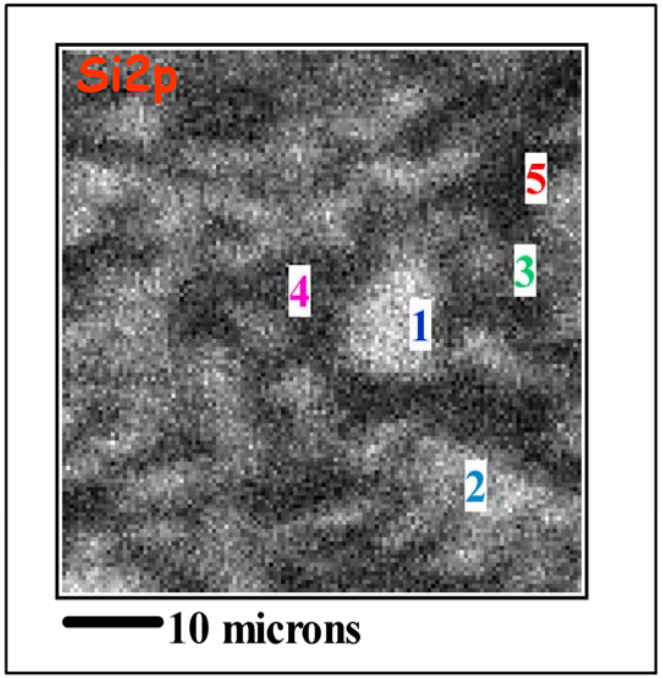
Image on Au

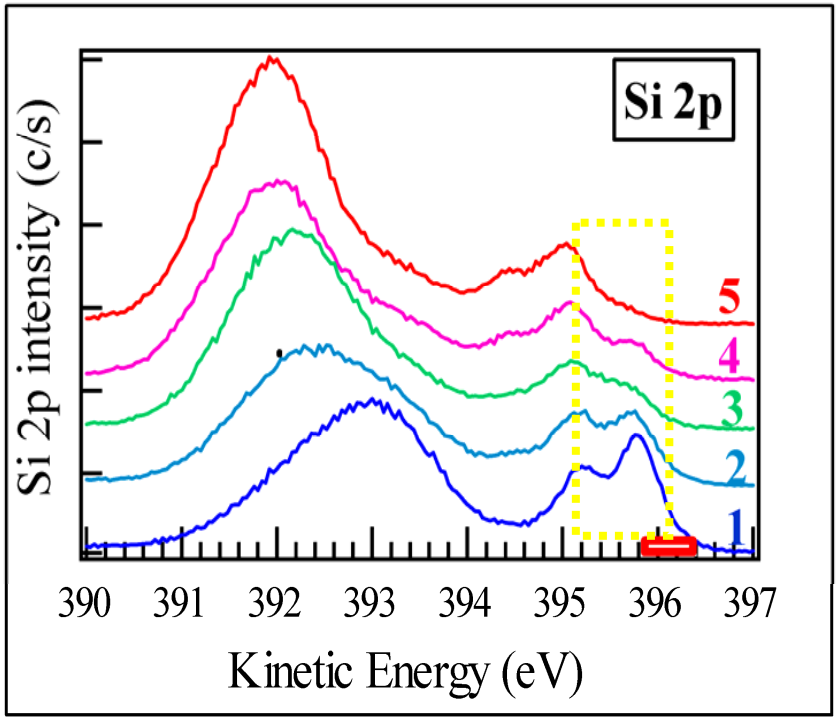


- Topography

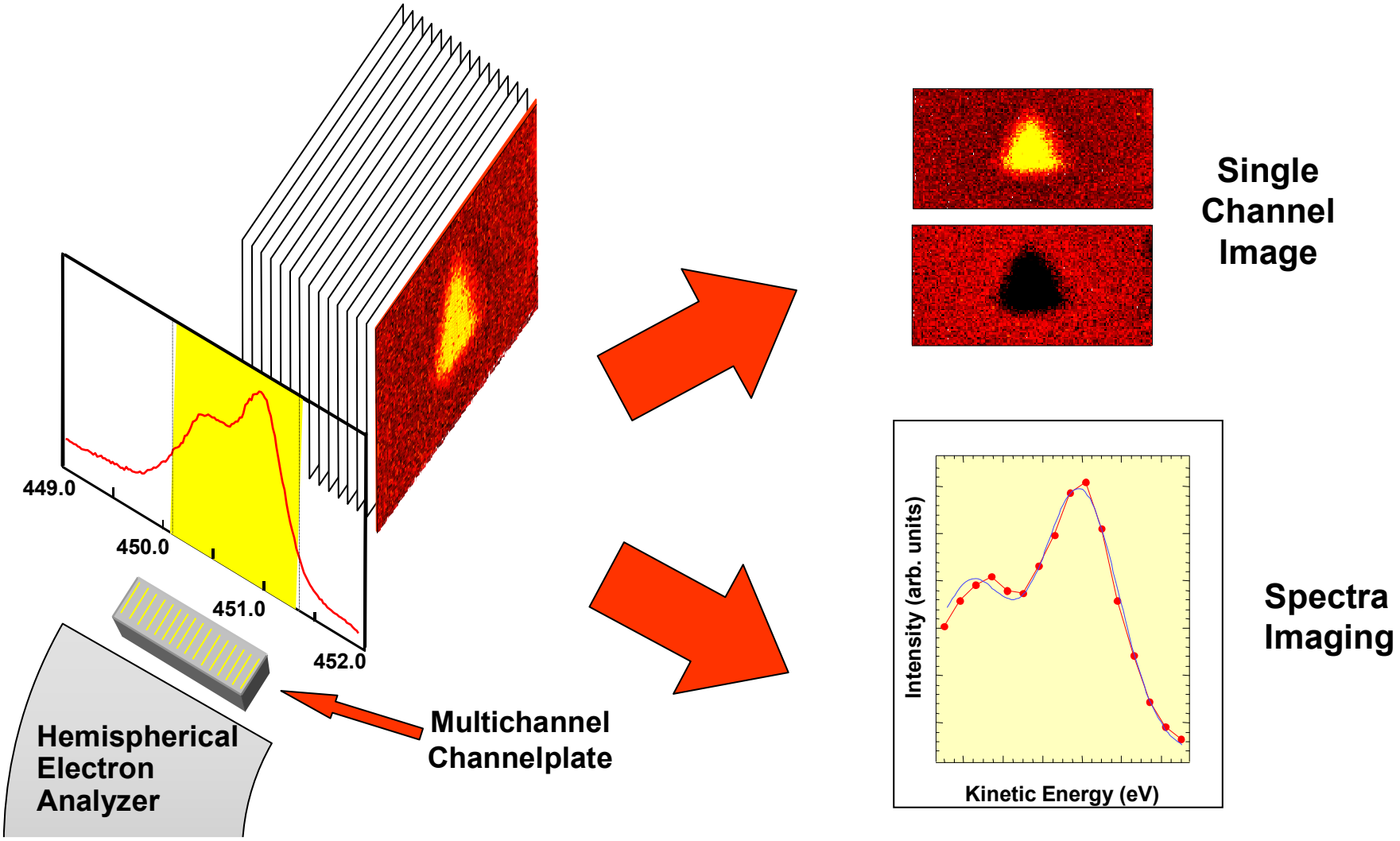
- Other sources of contrast

charging





Multichannel detection



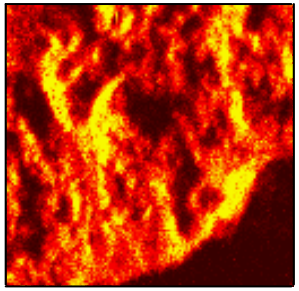
Single Channel Analysis

Carbon nanotubes on SiC

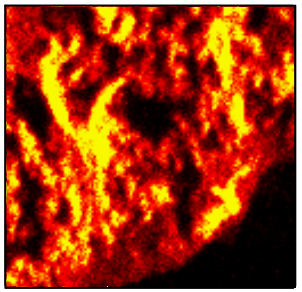
R. Larciprete – Enea - Italy

C 1s map: integration over the window energy

a)

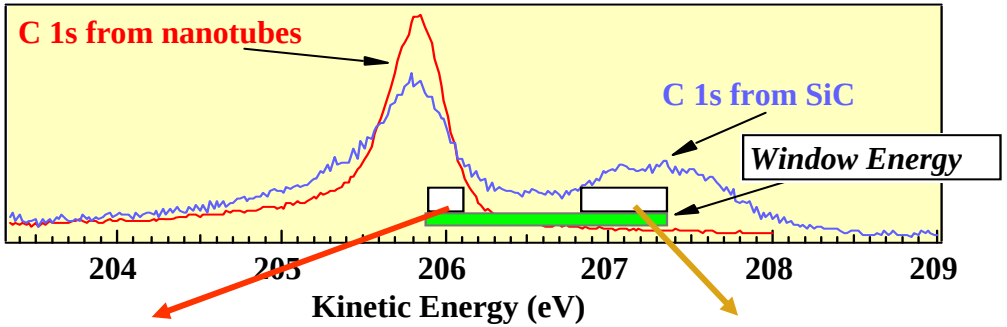


64 μm

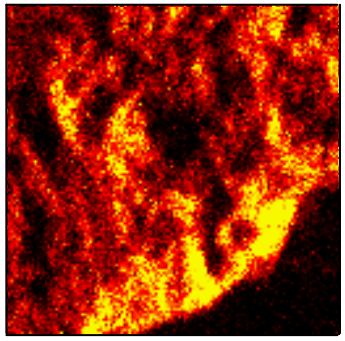


b)

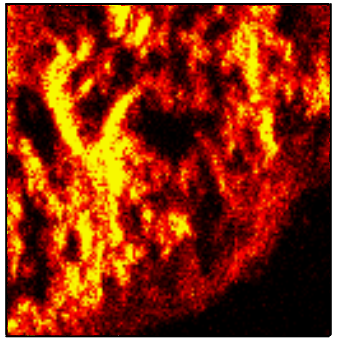
Topography map (C 1s background at 215 eV)



c)

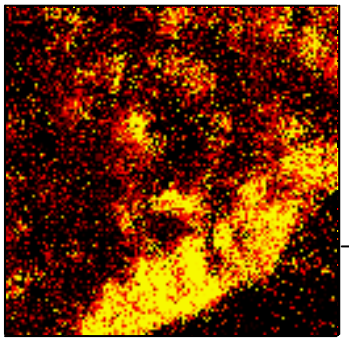


Selected energy maps



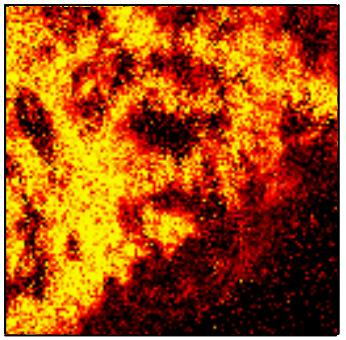
d)

e)



c)/b)

d)/b)



C1 1s Chemical maps

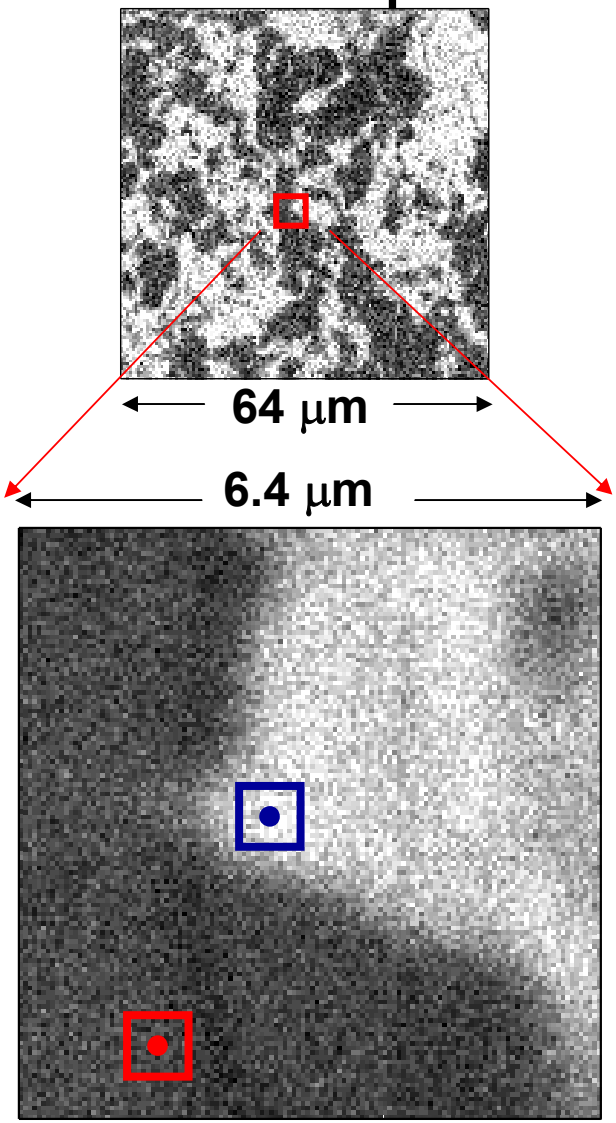
f)

Spectra Imaging

Ru(0001) oxidation

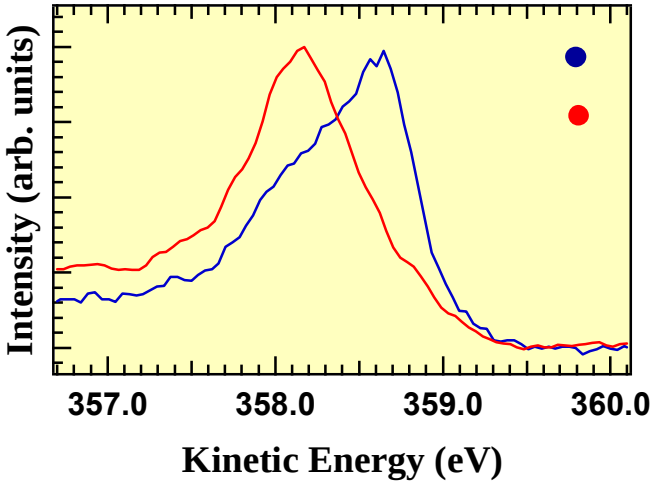
H. Conrad – FHI - Germany

Ru 3d maps

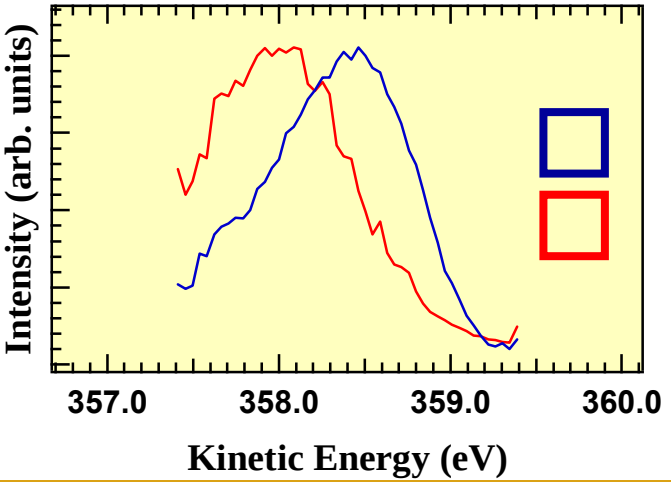


Ru $3d_{5/2}$ spectra

Conventional Scanning Spectroscopy (48 points - 70 sec)



Inherent Dispersion Energy Spectroscopy (48 points - 10 sec)



Getting the chemical information out of the artefacts

Artefacts

1. Topography
2. Beam induced effects:
   - C deposition (residual gases)
   - O_2 reduction
   - Charging
3. Background level

How to remove the topographic contribution

$$I = \frac{I_{peak} - I_{bkg}}{I_{peak} + I_{bkg}}$$

$$I = \frac{I_{peak} - I_{bkg}}{I_{bkg}}$$

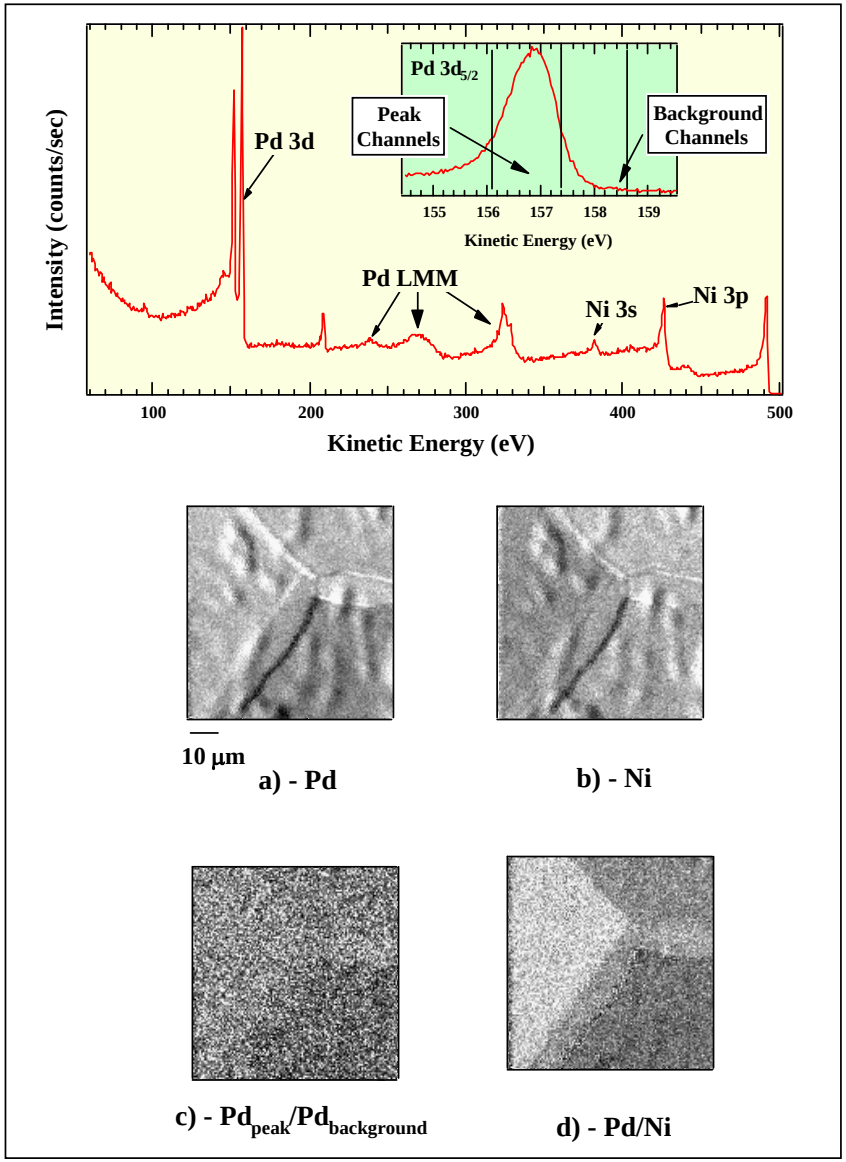
$$I = \frac{I_{peak}}{I_{bkg}}$$

sometimes only:

$$\frac{I_{peak1}}{I_{peak2}}$$

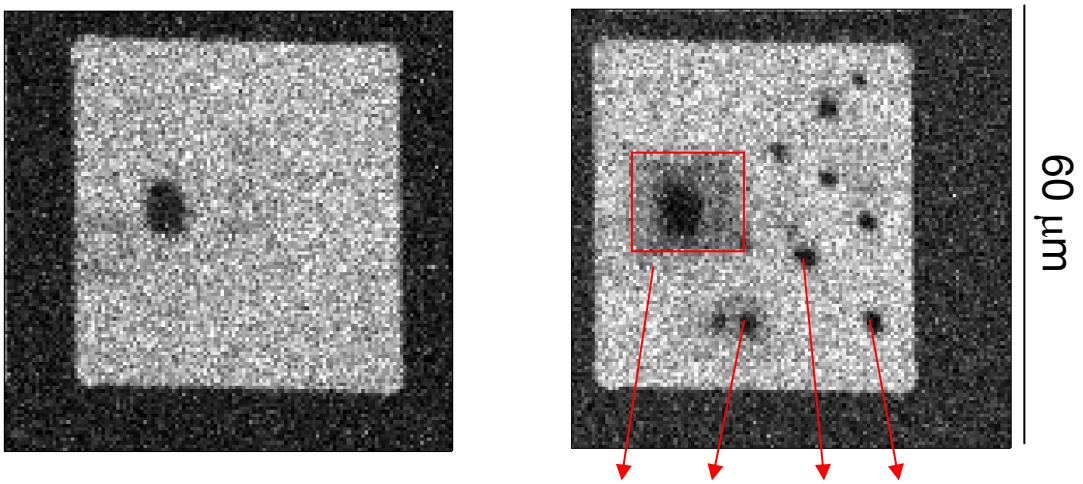
Which I_{bkg} ?

- $I_{bkg\ left}$
- $I_{bkg\ right}$
- $I_{bkg\ (left+right)}$
- *secondaries*



C growth

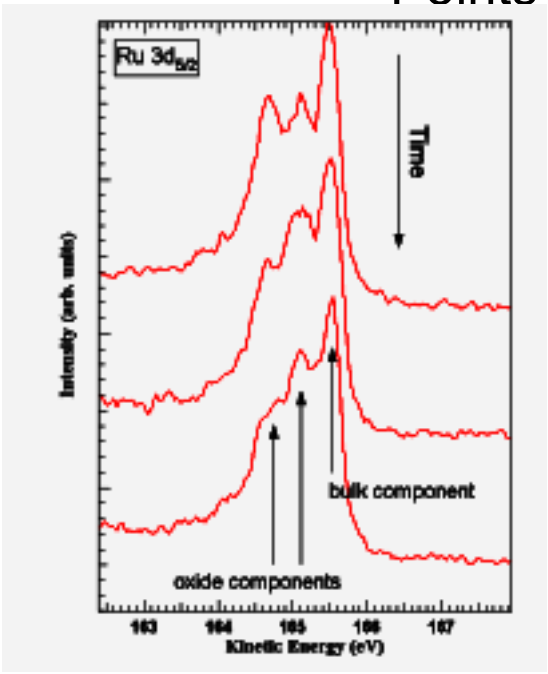
SiO_x sample
Si2p maps



Points irradiated (>10 min)

O_2 reduction

RuO_x sample



Each spectrum every 1 min

References

S. Guenther, B. Kaulich, L. Gregoratti, M. Kiskinova, “Photoelectron Microscopy and Applications in Surface and Material Science”, PROG SURF SCI, 70-, pp. 187-74 (2002).

A.W. Potts, G.R. Morrison, L. Gregoratti, A. Barinov, B. Kaulich, M. Kiskinova, “The exploitation of multichannel detection in scanning photoemission microscopy”, SURF REV LETT, 9-2, pp. 705-8 (2002).

L. Gregoratti, A. Barinov, E. Benfatto, G. Cautero, C. Fava, P. Lacovig, D. Lonza, M. Kiskinova, R. Tommasini, S. Mahl, “48-Channel electron detector for photoemission spectroscopy and microscopy”, REV SCI INSTRUM, 75-1, pp. 68-4 (2004).

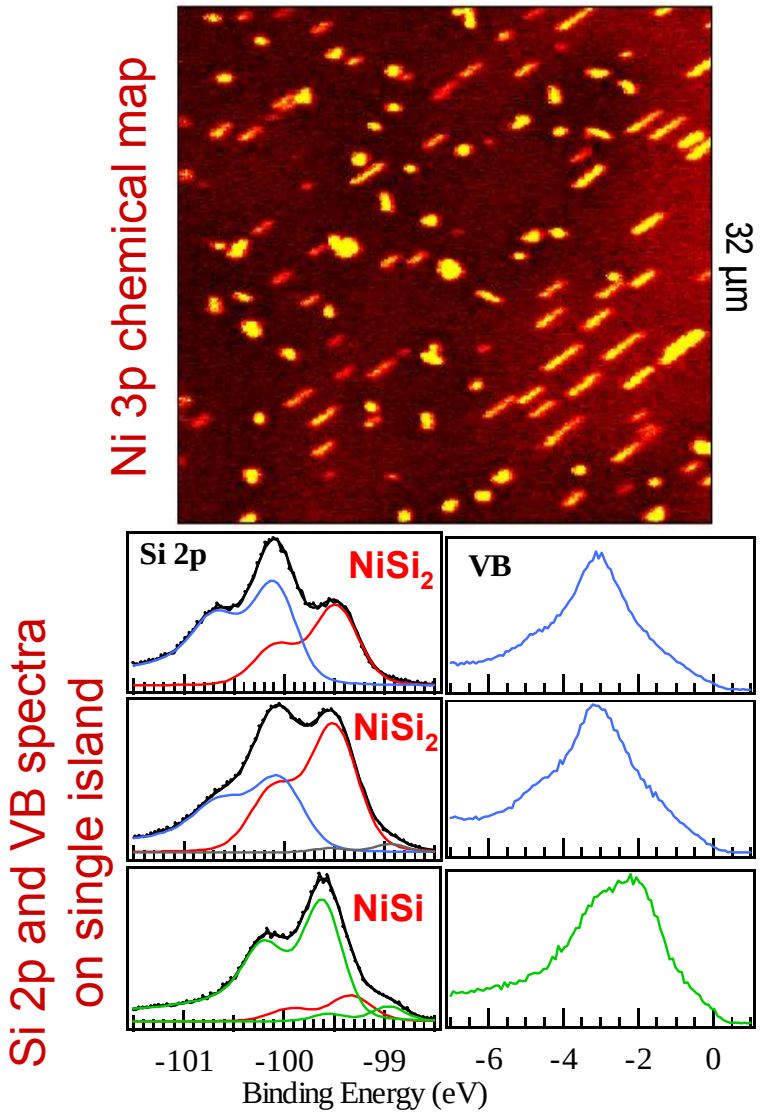
SPEM experiments: main topics

- Bulk-adlayer interfaces: metal/metal metal/semiconductor
  - Silicide formation (Ni, Co, Pd, Pt, Ag, Au)
  - Surface alloying and alloying (Ni/Pd, Au/Rh, Rh/Au)
- Catalysts&catalysis
  - Size gap
  - Model reactions (Rh, Pt, Ru)
- Nano and micro clusters properties
- Material characterization
- Organic and inorganic NT and nanostructures

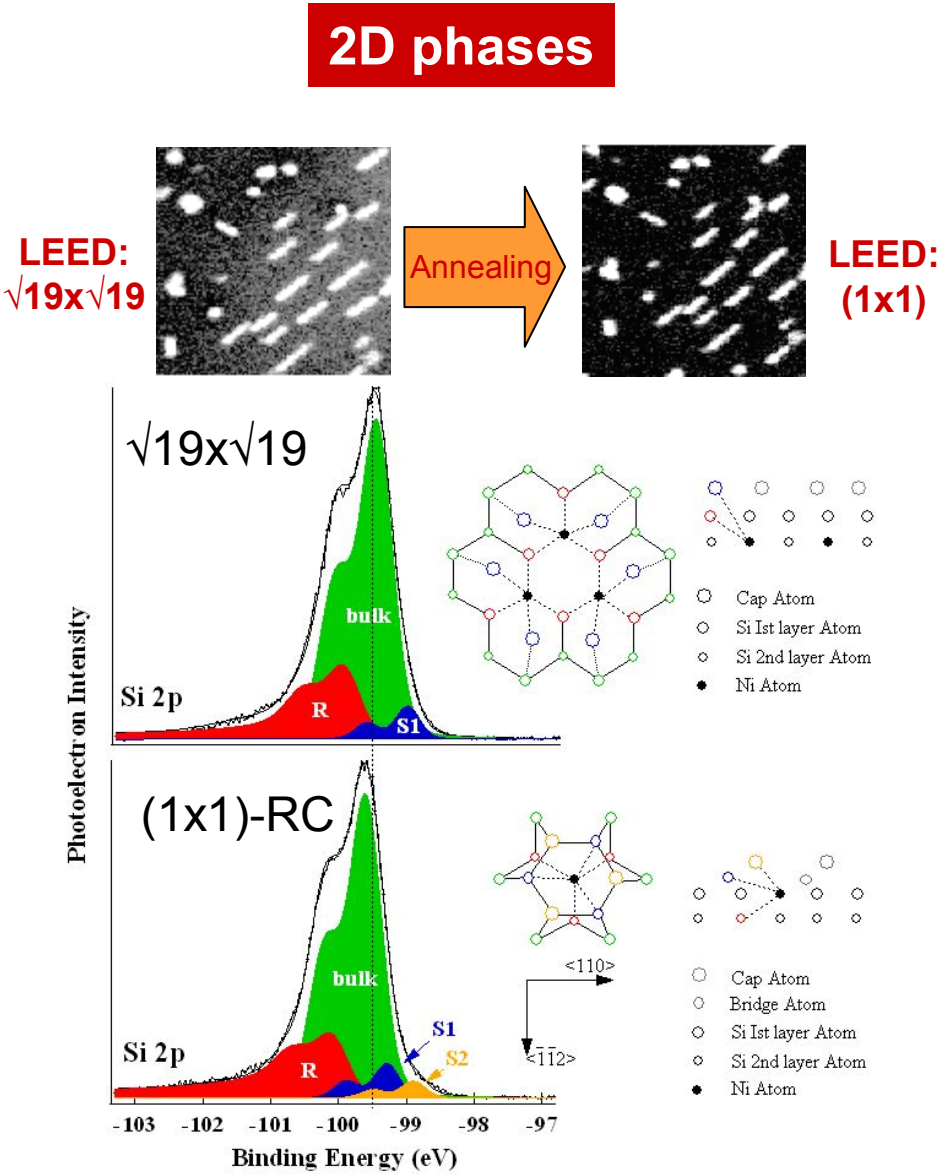
Ni silicides on Si(111): nucleation of 2D and 3D heterogeneous phases

•Deposition of 2ML of Ni on Si(111)-7x7 and thermal activation of the silicide formation

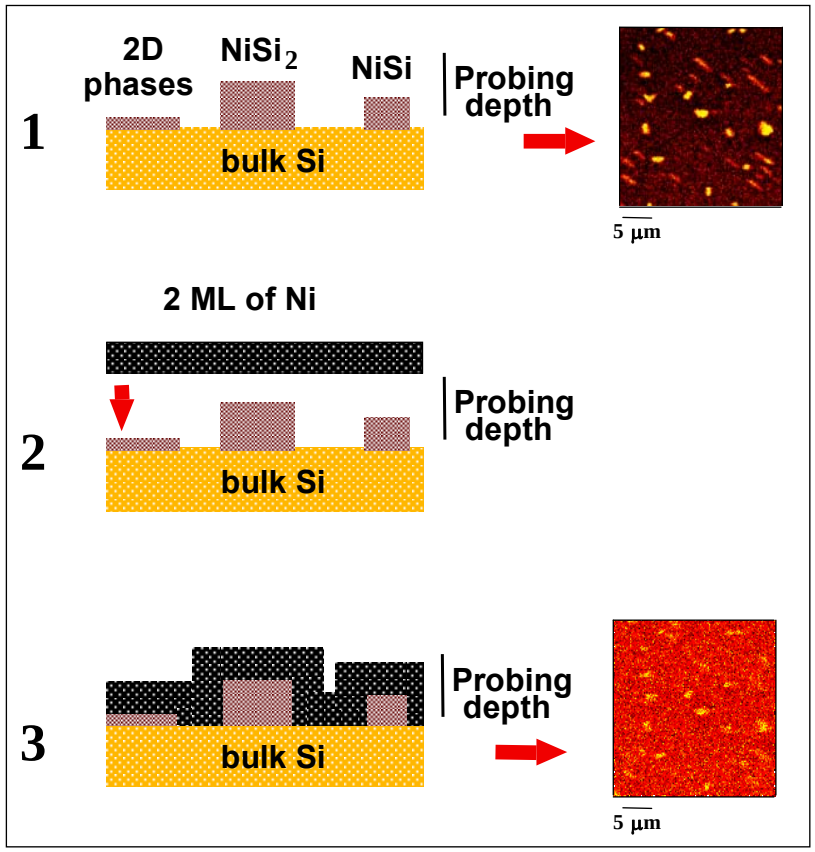
3D phases

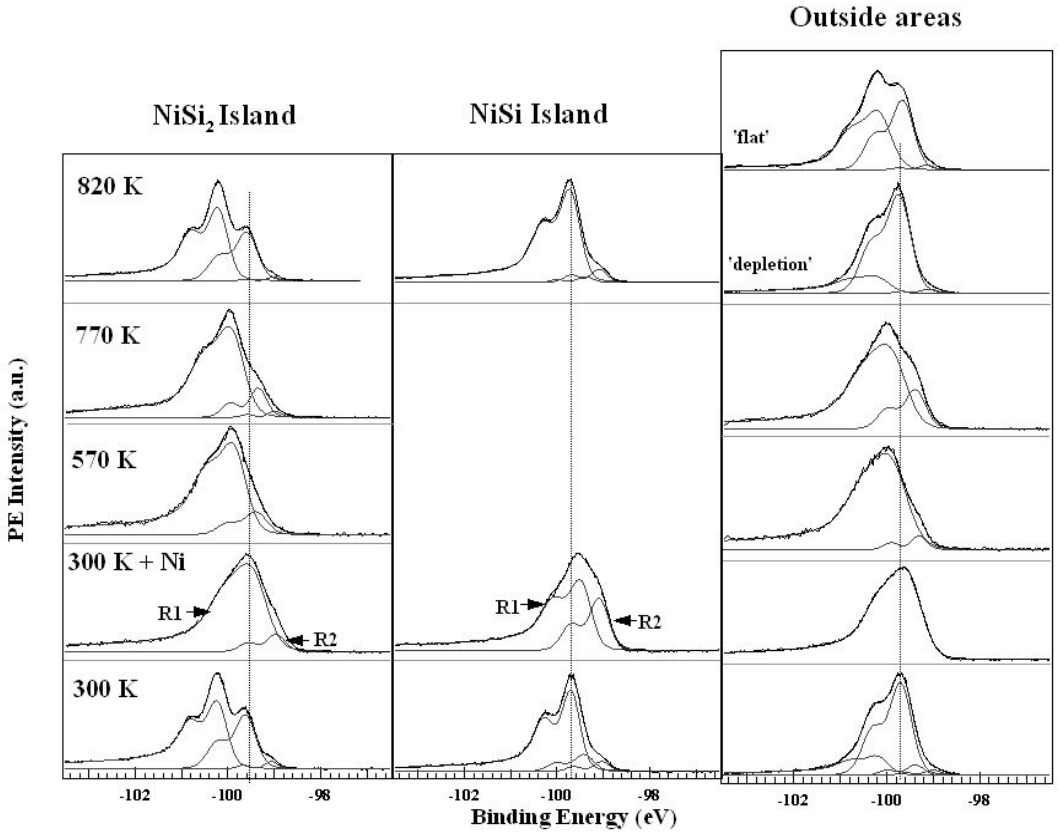


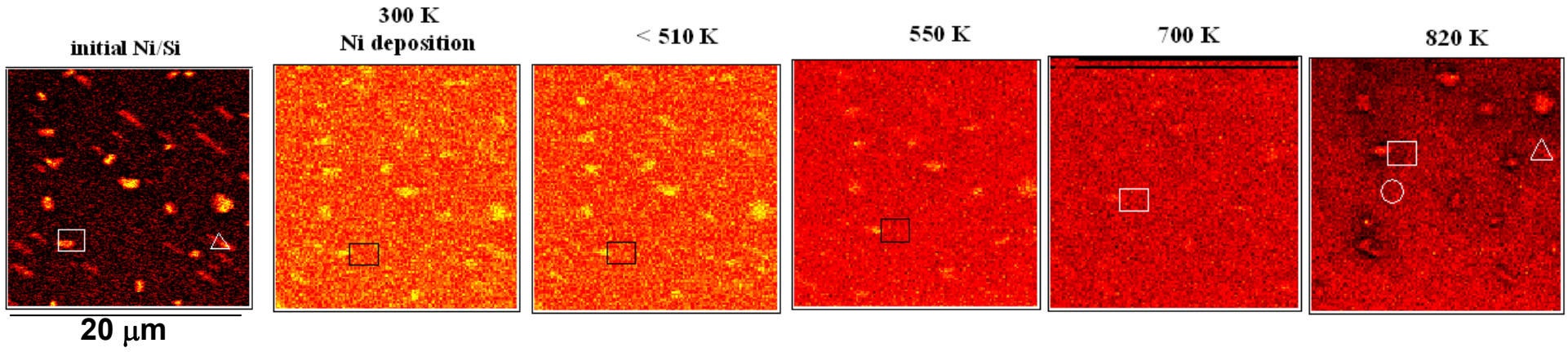
2D phases



Ni silicides on Si(111): intermediate phases

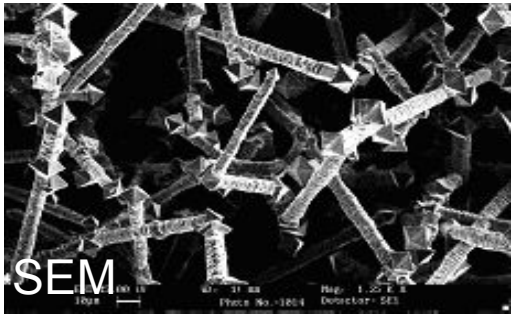




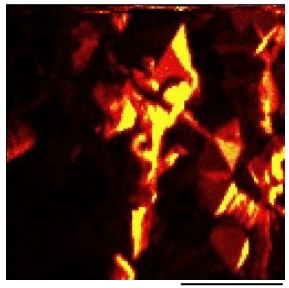


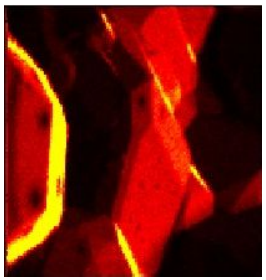
Compositional and electronic study of TCO nano and microtubes by Photoelectron Microscopy (in collaboration with A. Cremades UCM)

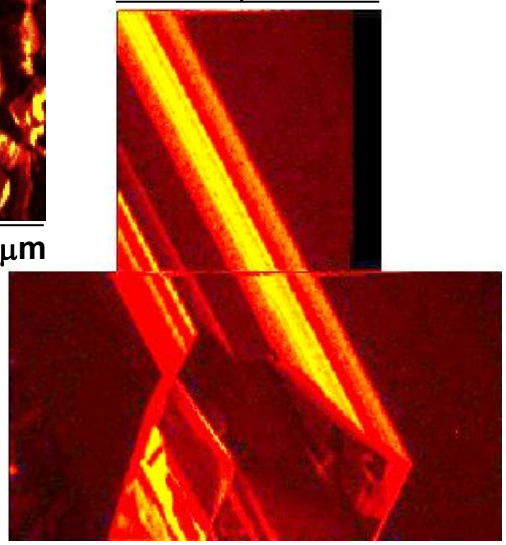
- **Catalyst free growth of TCO structures (Sn_xO_y/In_xO_y/In_xN_y,Ge_xO_y,etc.)**
  D. Alina Magdas et al. APL 88, 113107 (2006)
- **SPEM characterization of morphological complex structures difficult with other PEM**



SPEM images

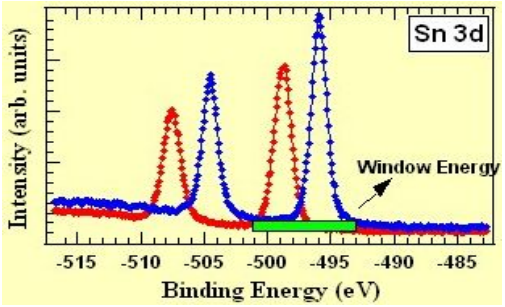


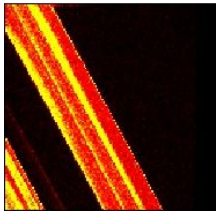




Electronic behaviour of a single structure

- **Charging due to differences in the electronic structure**
- **Mapping of the charging with the multichannel acquisition**

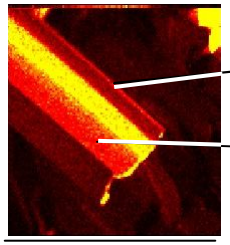


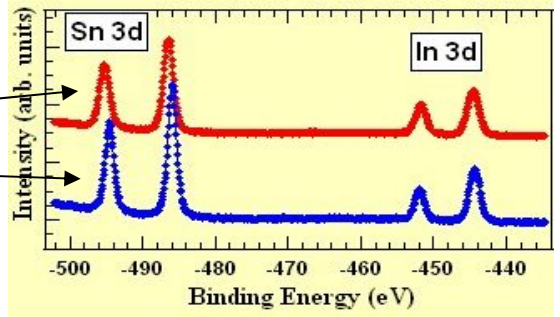


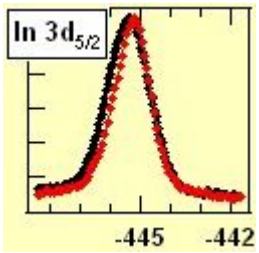
ΔE=3eV

Local chemical composition of the structures

- **Heterogeneous elemental distribution locally defined**
- **Fine chemical analysis**





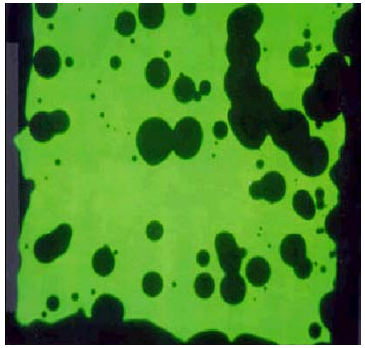


Degradation of light emitting diodes: a SPEM analysis

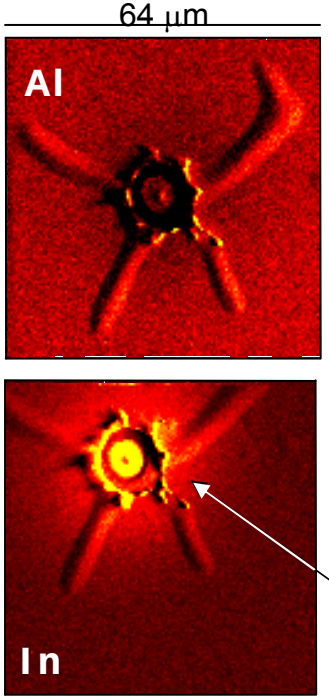
(in collaboration with P. Melpignano CRP, R. Zamboni CNR-ISMN)

OLED Display Screen (from Universal Display Corp)

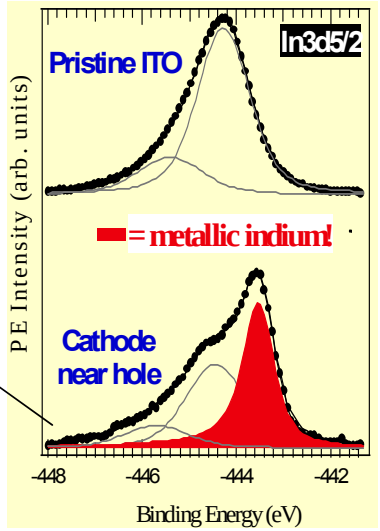
OLED exposed to atmospheric moisture: failure due to light emission

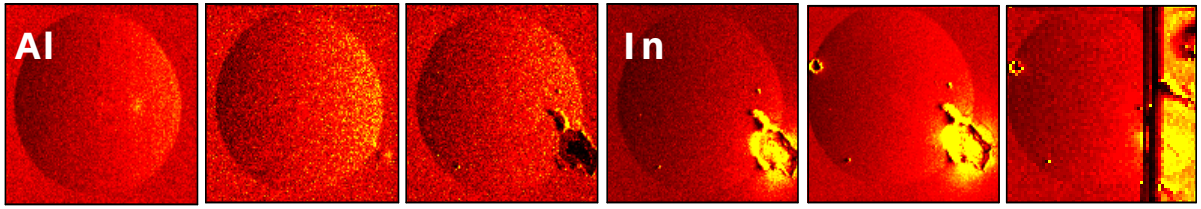


Dark spot in OLED



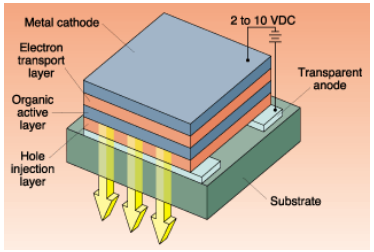
•Decomposition of ITO

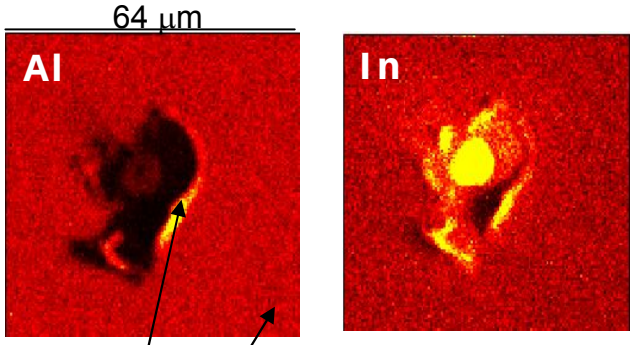


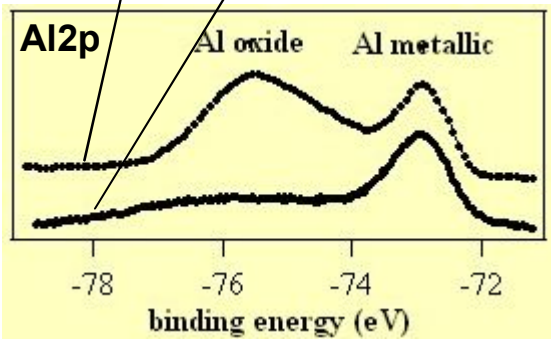


increasing voltage and operating time

"Clean" experiment: OLED growth and operated in the SPEM (UHV ambient) : failure due to light emission



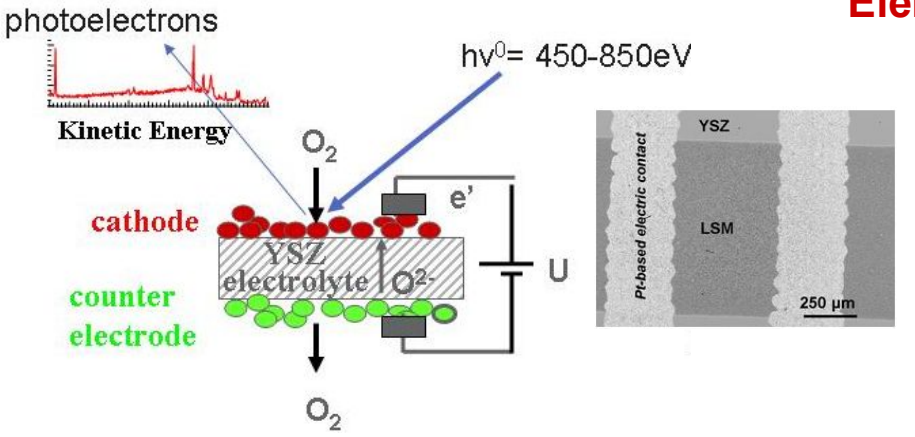




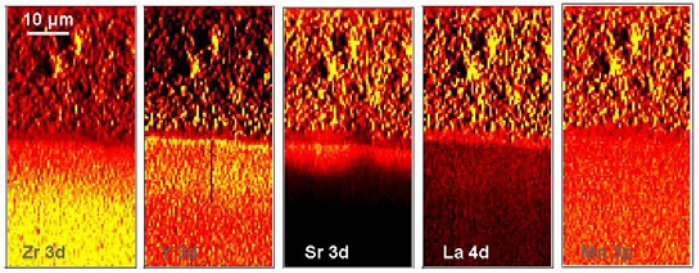
Solid State Ionics Award for the Best Paper in the journal Solid State Ionics in 2008

Operating SOFC: mass transport

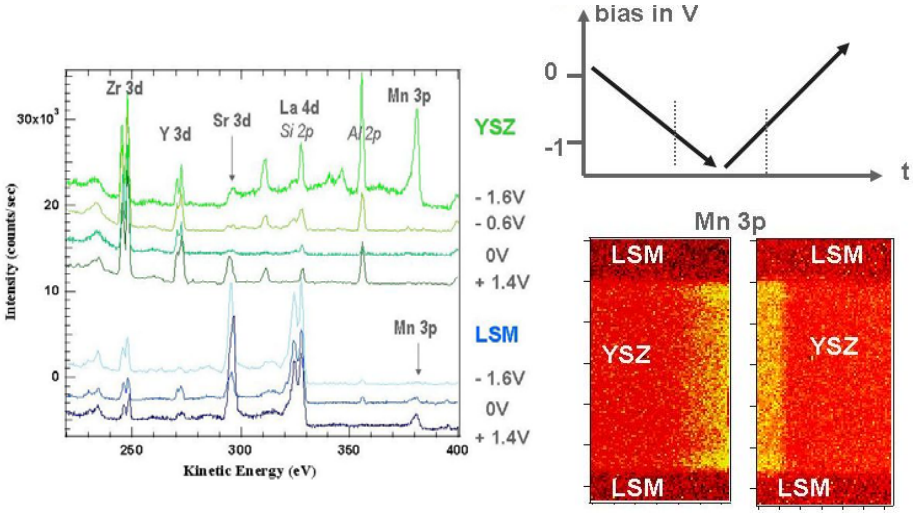
(in collaboration with M. Backhaus- Corning Inc. - USA)



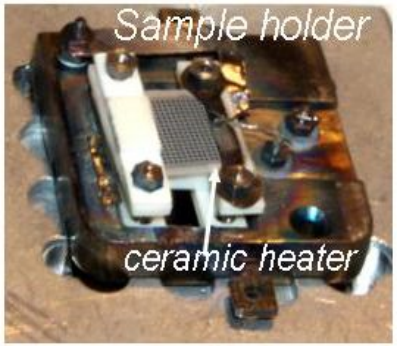
Elemental distribution at electrolyte/LSM interface



Surface composition change with bias



Strongly constraining experimental setup



- Real samples
- High T = 650-700°C
- pO_2=1x10^{-6} mbar
- Applied potentials
  -2V<U<+2V
- Surface sensitive technique
- High lateral resolution

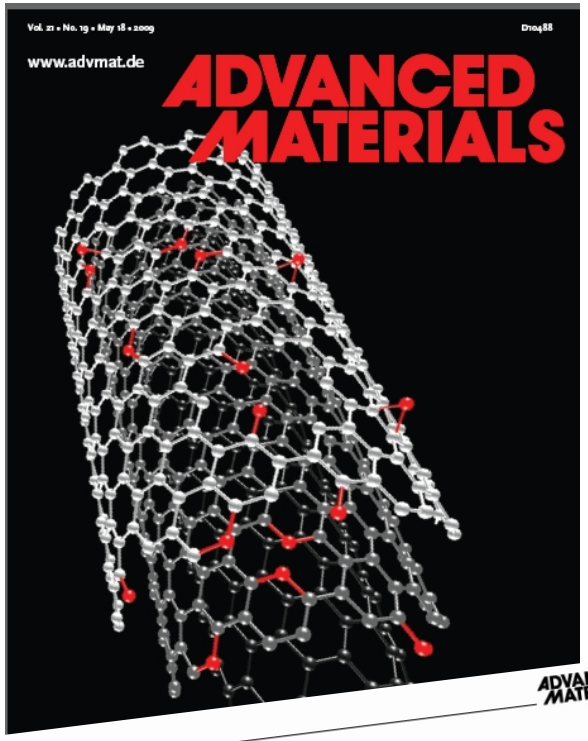
Observation and explanation of electrochemical cathode activation

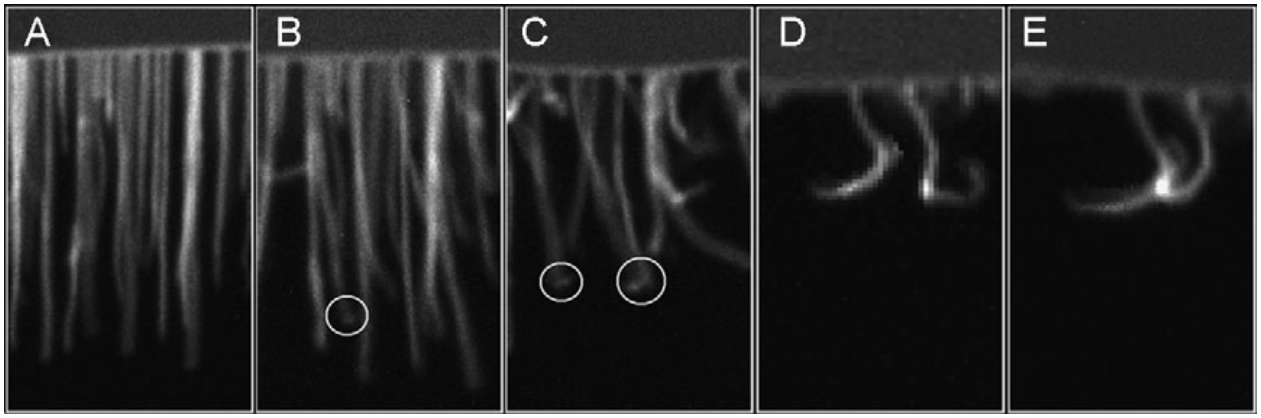
- Strong current increase under negative bias when Mn spreads on electrolyte
- Mn2+ electrolyte surface enrichment→electrolyte surface conductivity → direct oxygen incorporation into electrolyte
- Oxygen incorporation extends under bias from TPB to the entire electrolyte surface

M. Backhaus et al. Solid State Ionics 179 (2008) 891–895 , M. Backhaus et al. Advances in Solid Oxide Fuel Cells III 28 (4), 2007

Gas phase oxidation of MCNT

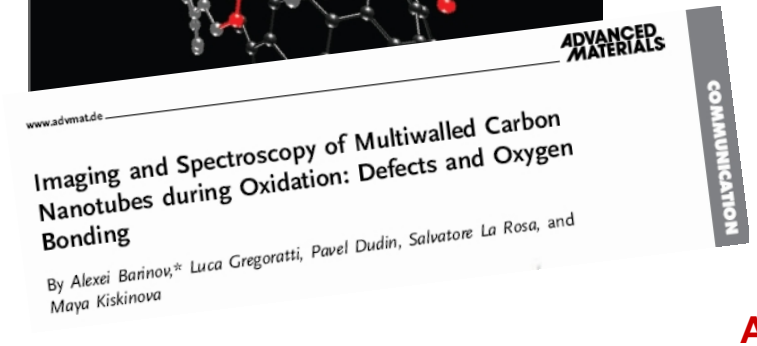
CNT

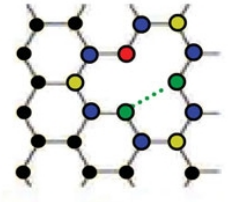




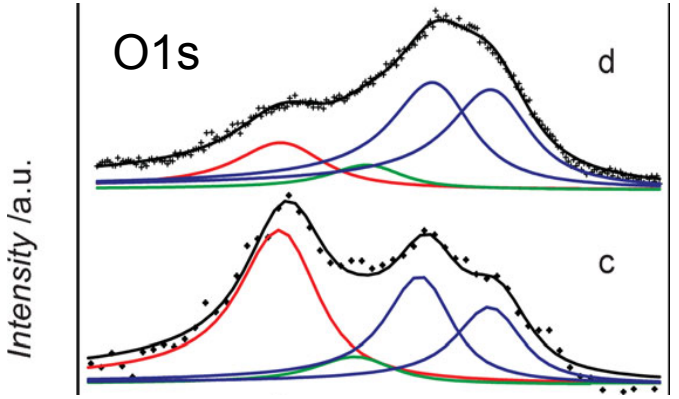
Increasing oxygen dosage

- Gas phase oxidation with atomic oxygen
- Advanced oxidation stages
- Investigation of the formation of oxygenated functional groups and morphological changes
- Non linear consumption of the CNT



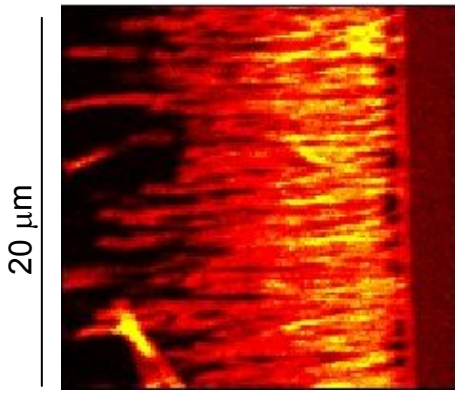


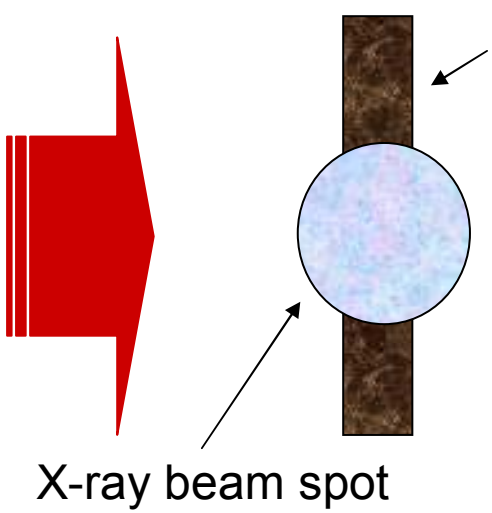
Atomic arrangement



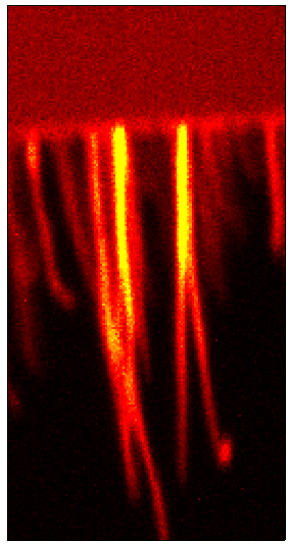
Imaging and spectroscopy from single MWCNT with SPEM

High density





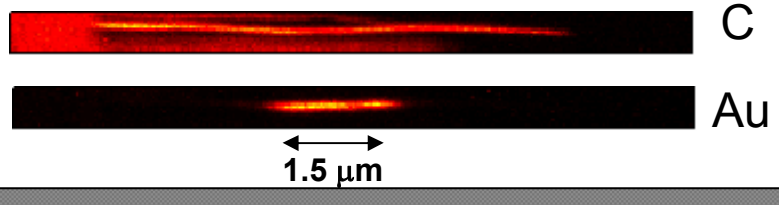
Low density



Nanostructure width lower than 50 nm !

NEW

- Confined patches on a single CNT
- Investigation of mass transport, surface and bulk diffusion, etc.



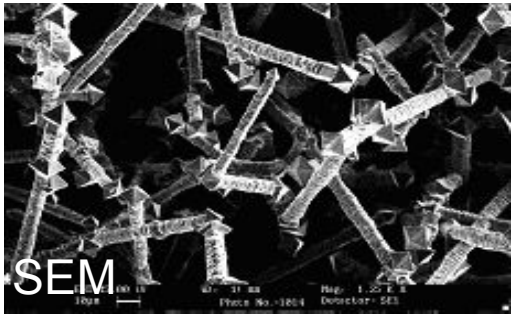
Research Topics

- Ag, Au, Pd adsorbate interaction
- PLD deposition of catalytic nanocluster

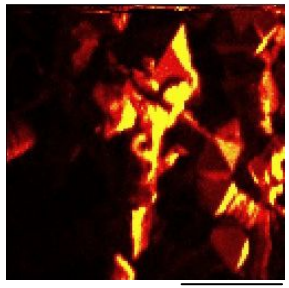
Compositional and electronic study of TCO nano and microtubes

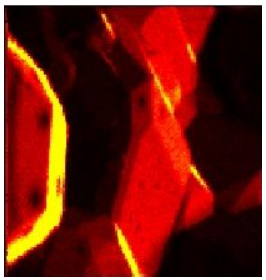
(in collaboration with A. Cremades - UCM - Spain)

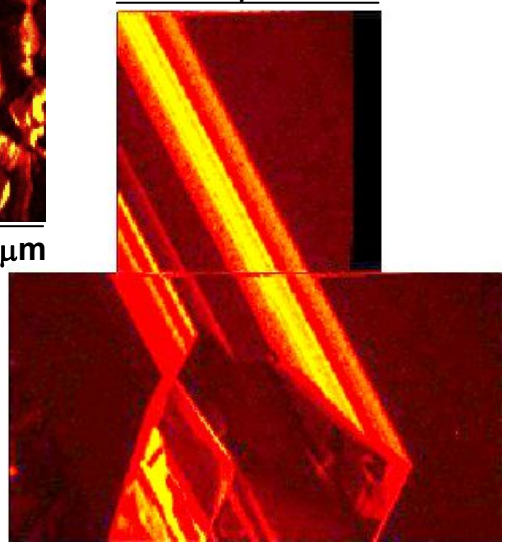
- **Catalyst free growth of TCO structures (Sn_xO_y/In_xO_y/In_xN_y,Ge_xO_y,etc.)**
- **SPEM characterization of morphological complex structures difficult with other PEM**



SPEM images

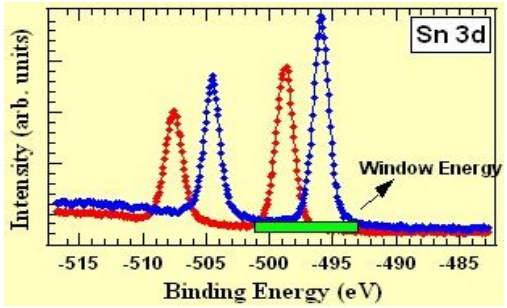


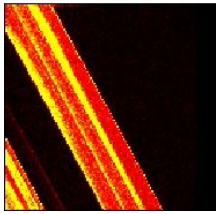




Electronic behaviour of a single structure

- **Charging due to differences in the electronic structure**
- **Mapping of the charging with the multichannel acquisition**

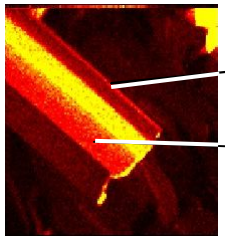


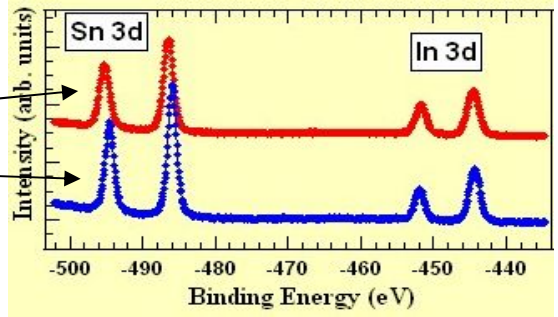


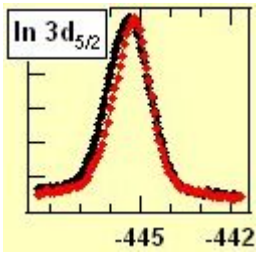
ΔE=3eV

Local chemical composition of the structures

- **Heterogeneous elemental distribution locally defined**
- **Fine chemical analysis**





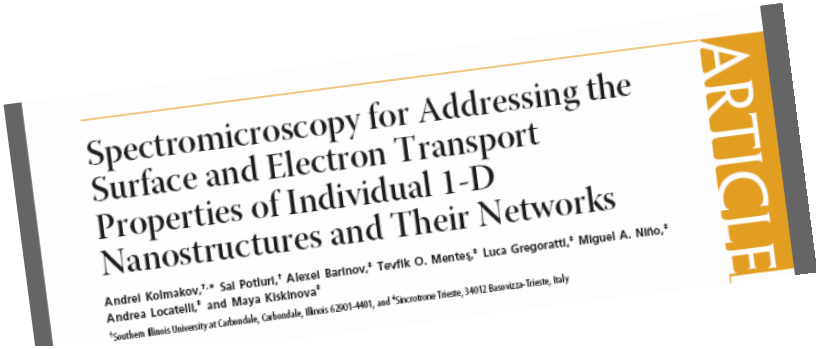


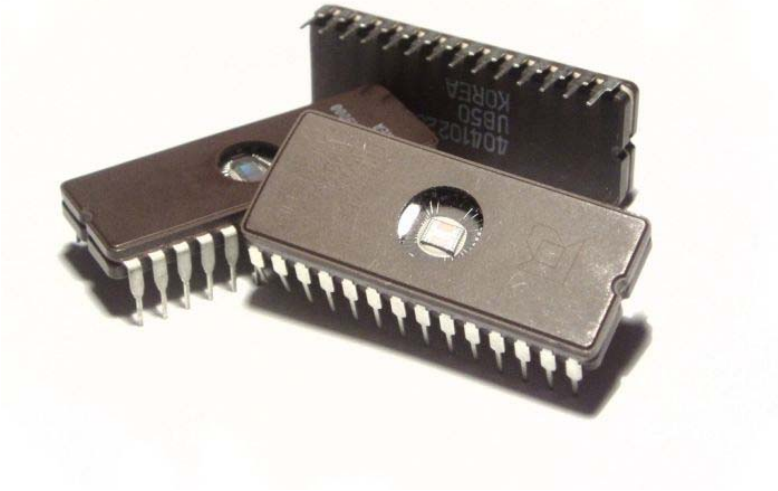
D. A. Magdas et al. Superlat. and Microstr. 45 (2009) 429-434 , D. Maestre et al. Journ. of Appl. Phys. 103, 093531 (2008)

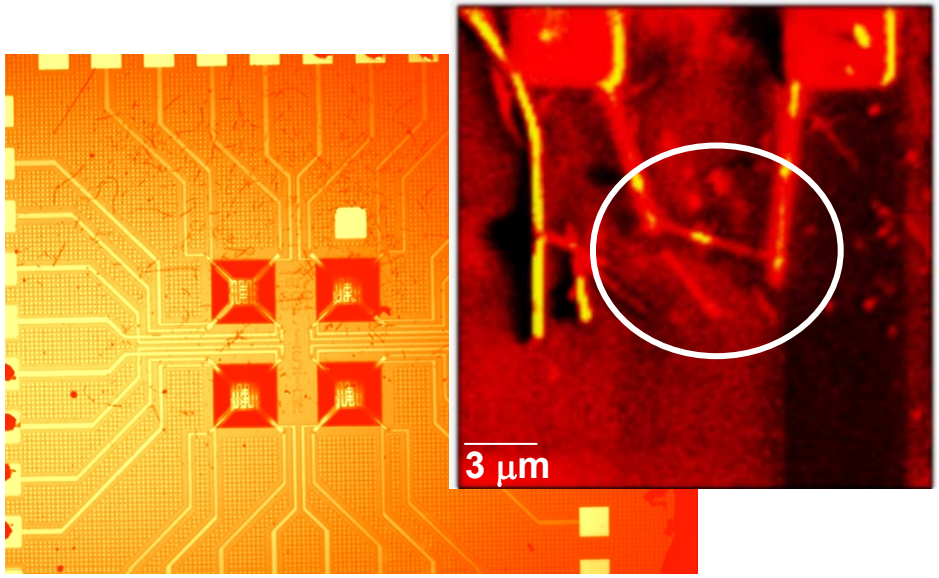
Chemical and electronic characterization of nanosensors

(in collaboration with A. Kolmakov – Souther Illinois Uni. - USA)

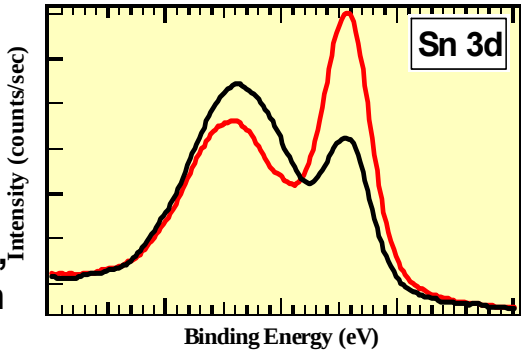
- Chemical & electronic characterization under working conditions
- SnO_2, VO_x, …
- Sensing properties vs oxygen, hydrogen, …

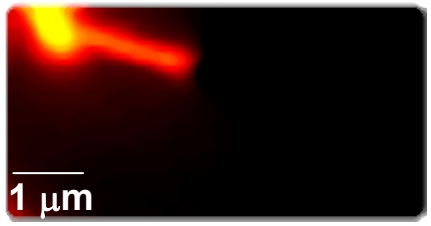


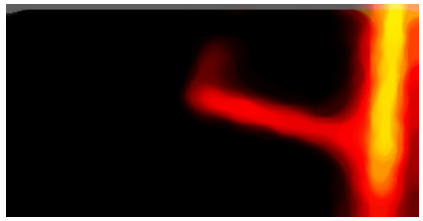




- **Addressing the electron transport in a workin device (temperature, close biasing, etc.)**
- **Surface stoichiometry, coordination, oxidation state, etc.**



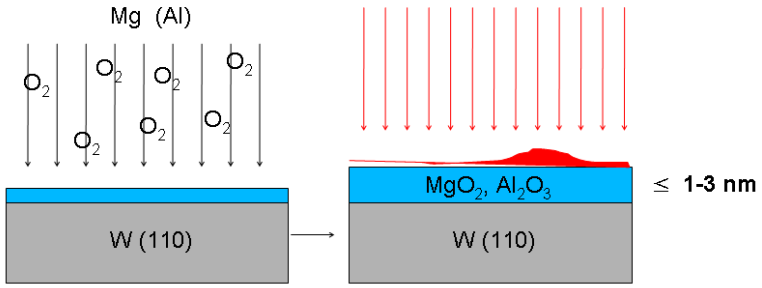




A. Kolmakov et al. ACS 2 (10) 2008, 1993

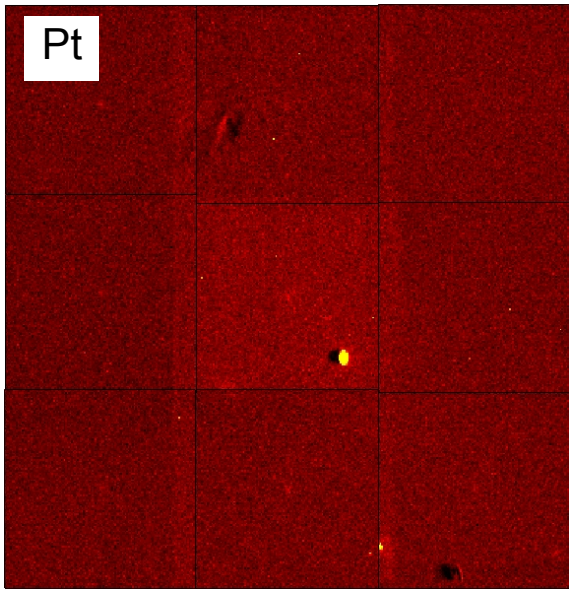
‘Material’ gap: from model crystalline materials to metal nano-particles on metal oxide. In situ PLD particle deposition

PLD from a $Pt_{50}Rh_{50}$ target



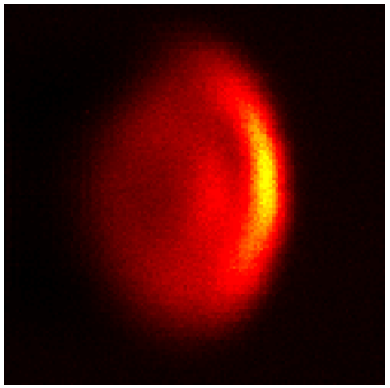
No charging of the substrate because of the low thickness, XPS and SPEM are possible

SPEM



64 μm

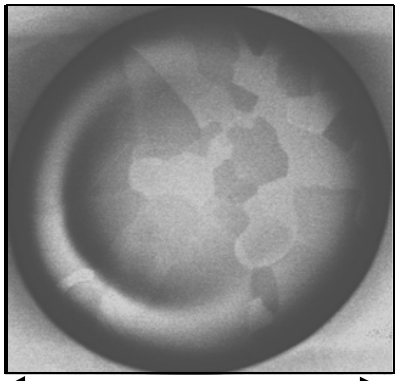
Low density of micron sized particles



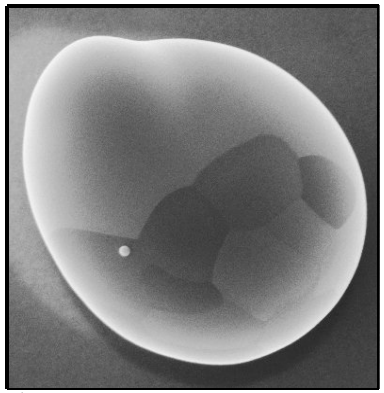
3 μm

Nano-cluster of average size < 10 nm

SEM



1.5 μm

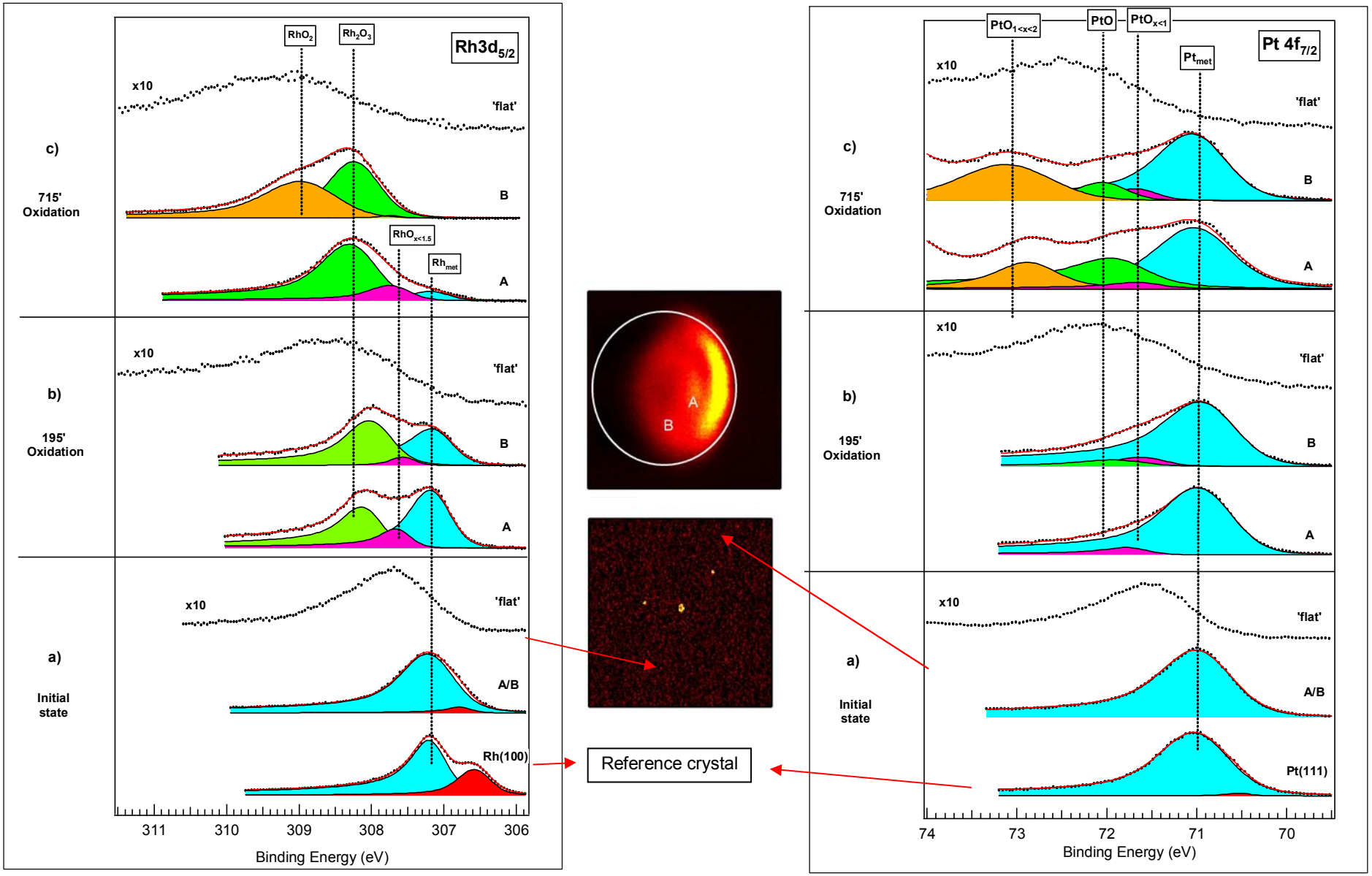


0.7 μm

- Poly-crystalline nature of the particles
- Size effects during chemical reaction
- Proximity effects
- Simple model reaction: O_2 (+H_2)
- Unconventional procedure for particle generation (thermodynamics)

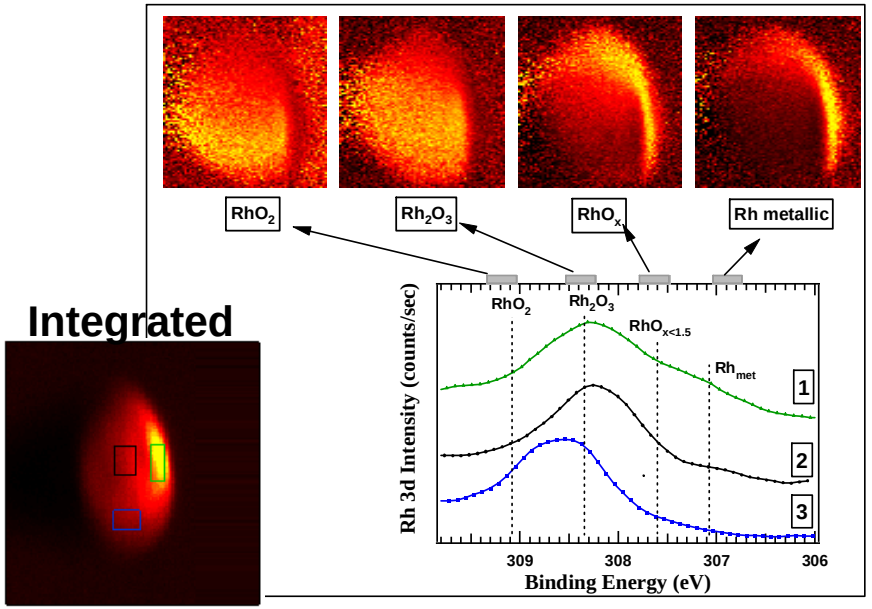
M. Dalmiglio et al. J. Phys. Chem. submitted

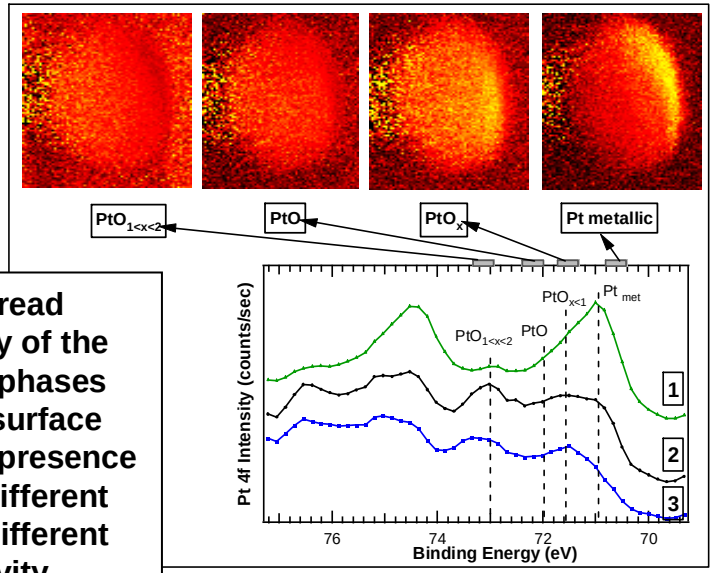
‘Material’ gap: from model crystalline materials to metal nano-particles on metal oxide. In situ PLD particle deposition



Oxide phase distribution on the particles surface

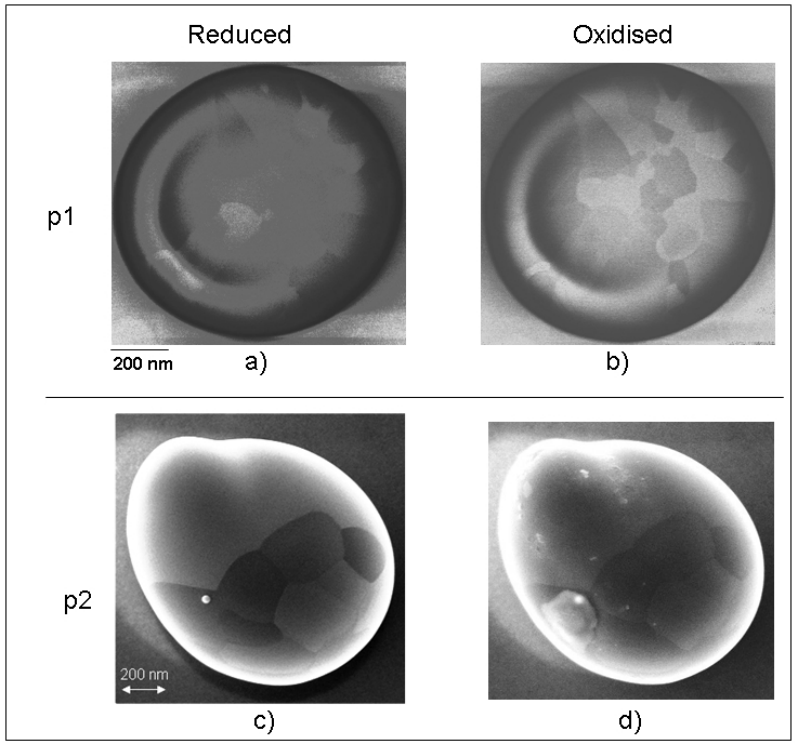
SPEM





The spread anisotropy of the chemical phases over the surface reveals the presence of many different areas of different reactivity

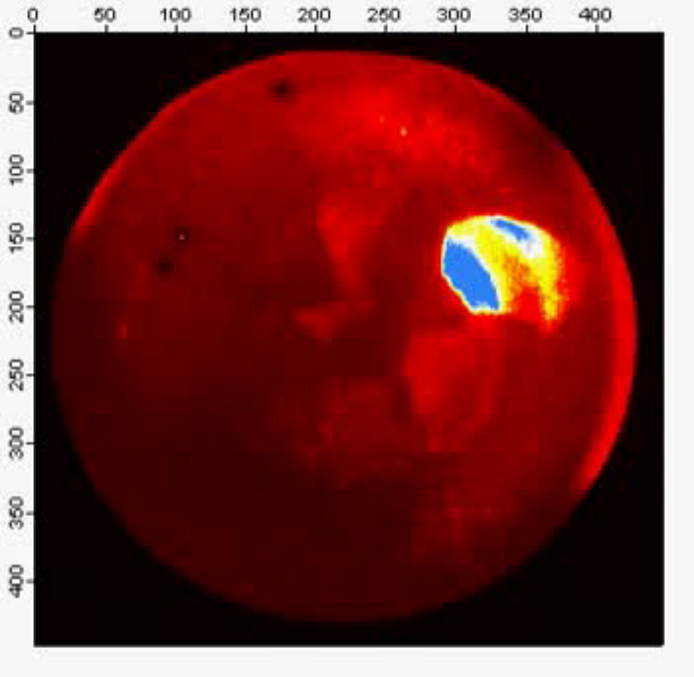
SEM



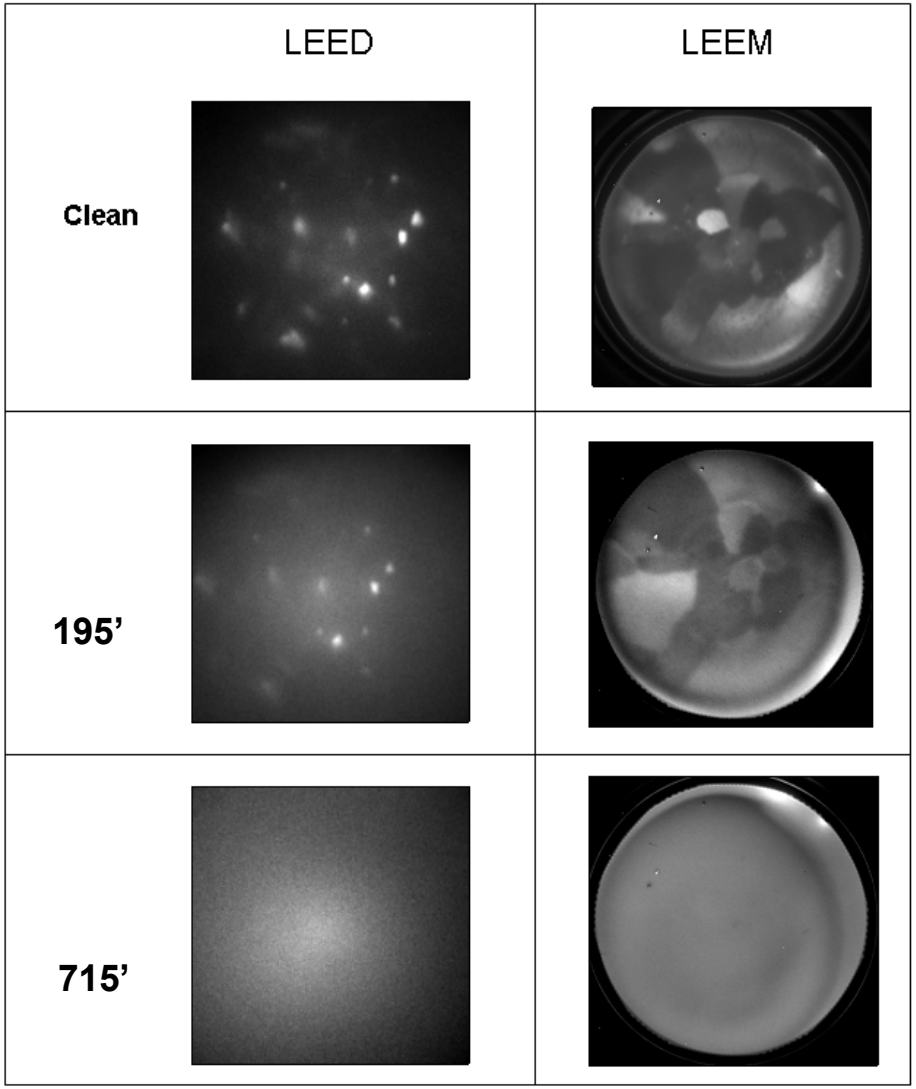
How to correlate chemical reactivity to structural changes?

SEM to LEEM

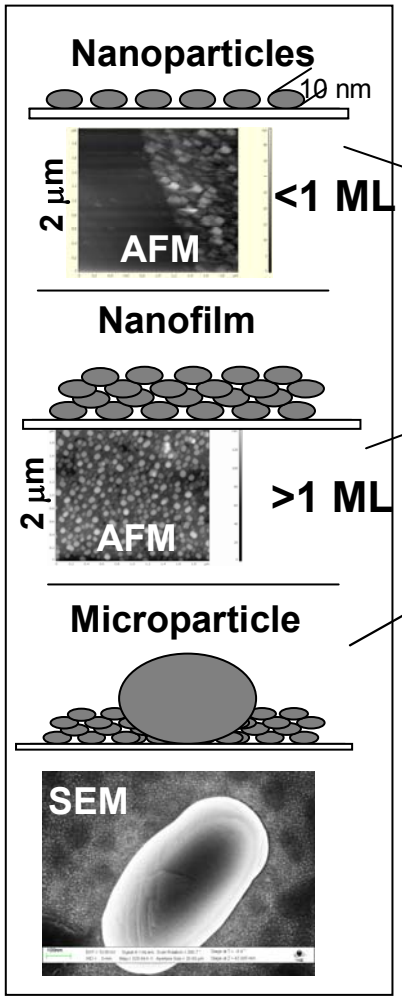
Structural changes of a PtRh particle upon oxidation: LEEM and μ-LEED



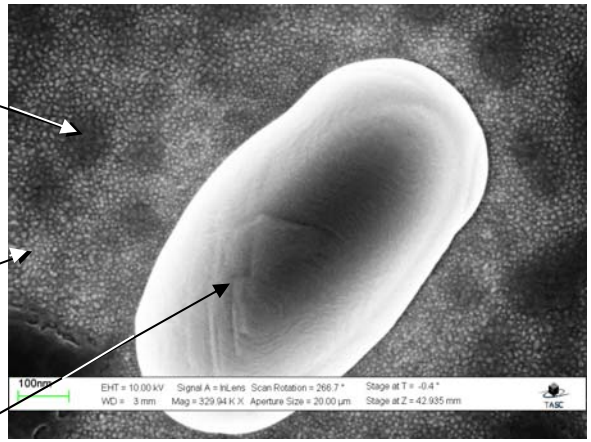
Increasing the oxidation time we have less defined contrast between the facets and at the end we lose all the information on the long range order of the crystal surface



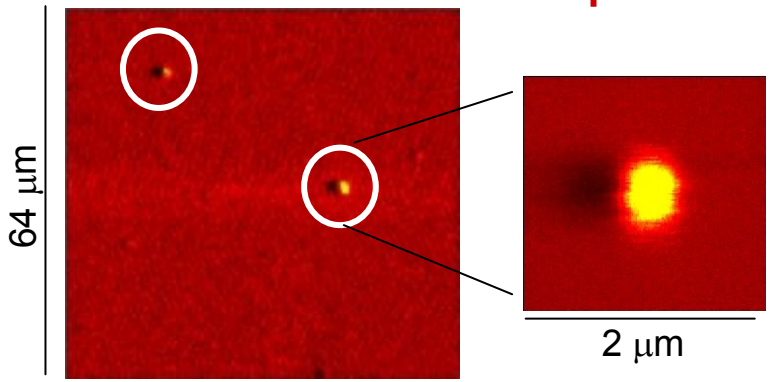
‘Material’ gap: from model crystalline materials to metal nano-particles on metal oxide. In situ PLD particle deposition



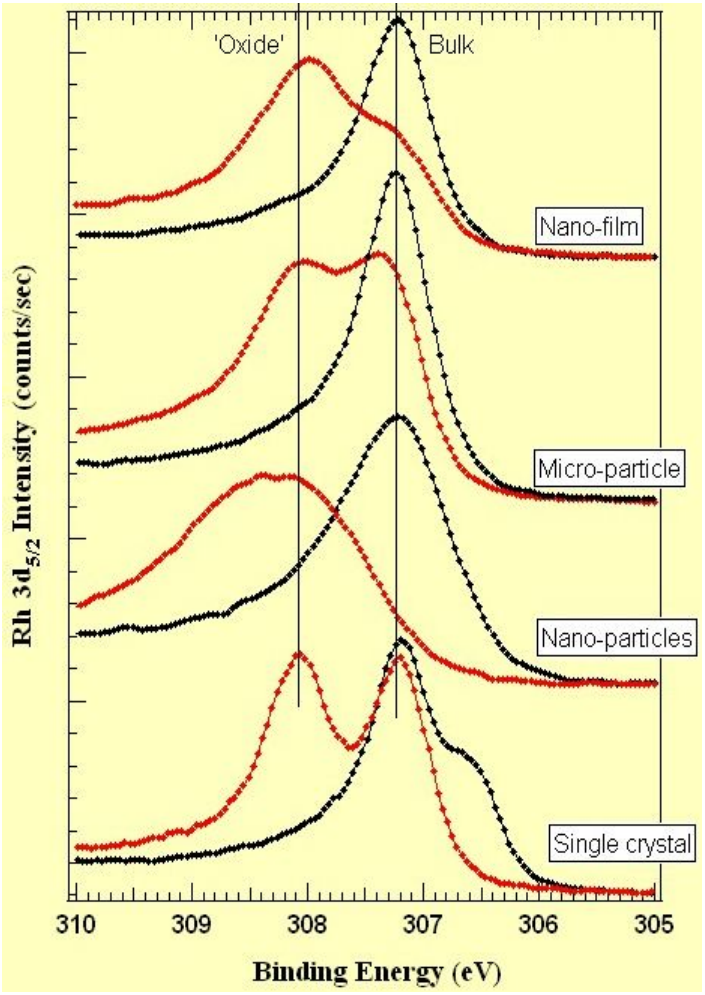
Rh on MgO/W(110) PLD species are highly-defected due to non-thermic evaporation



SPEM Rh3d maps



Oxidation/reduction reactions



- **The nanoparticles/nanofilm possess different oxidation/reduction ability than the microparticle**
- **Reducing rate: Micro-part.> Nano-crystalline film > Nano-particles**
- **Micro-particles of similar sizes show variation in the reactive properties: different structure, local environ.**

Bibliography

- L. Gregoratti, S. Gunther, J. Kovac, L. Casalis, M. Marsi and M. Kiskinova, *'Reinvestigation of the Ni/Si interface: spectromicroscopic evidence for multiple silicide phases*', PRB 57 (1998) pp. R6799-6802.
- L. Gregoratti, S. Gunther, J. Kovac, M. Marsi and M. Kiskinova, *'Spectromicroscopy of silicide phases formed at Ni/Si interfaces'*, Proceedings of the IVC-14 conference – UK 1998, Appl. Surf. Sci. 144-145, (1999) pp. 255-259.
- M. Kiskinova, L. Casalis, L. Gregoratti, S. Gunther, M. Marsi, *'Esca Microscopy on Elettra: chemical characterization of surfaces and interfaces with sub-micron spatial resolution'*, MRS-1998 Spring Meeting Symposium Proceedings, 524 (1998) pp. 203-214.
- L. Gregoratti, S. Gunther, J. Kovac, M. Marsi, R. J. Phaneuf and M. Kiksinova, *"Ni/Si(111) system: Formation and evolution of two- and three-dimensional phases studied by spectromicroscopy'*, Phys. Rev. B 59 (3), pp. 2018-2024, (1999).
- L. Gregoratti, S. Gunther, J. Kovac, M. Marsi, and M. Kiskinova*, 'Intermediate phases and mass transport during interaction of a thin Ni film with a laterally heterogeneous Ni-Si(111) interfaces*', Surf. Sci. (1999) pp. 120-130.
- L. Gregoratti, A. Barinov, L. Casalis and M. Kiskinova, *"Spectromicroscopy of interfacial interactions between between thin Ni films and a Au-Si surface"* Appl. Surf. Sci. 6663 (2000) pp. 1-10.
- Gardonio S, Gregoratti L, Melpignano P, Aballe L, Biondo V, Zamboni R, Murgia M, Caria S, Kiskinova M, '*Degradation of organic light-emitting diodes under different enviroment at high drive conditions*', ORGANIC ELECTRONICS 8(1), pp. 37-43, 2007.
- Caria S, Zamboni R, Murgia M, Melpignano P, Biondo V, Aballe L, Barinov A, Gardonio S, Gregoratti L, Kiskinova M '*Degradation of organic light-emitting diode* ', PROC. SPIE Vol. 6192, 61922D.
- M. Backhaus, K. Adib, T. St. Clair, B. Luerssen, L. Gregoratti, A. Barinov, P. Dudin, 'Photoelectron microscopy study of the surface chemistry of operating LSM-YSZ SOFC cathodes', Advances in Solid Oxide fuel cells III CESP_Vol28_4-2007
- M. Backhaus-Ricoult, K.Adib, T. St.Clair, B. Luerssen, L. Gregoratti, A. Barinov, 'In-situ study of operating SOFC LSM/YSZ cathodes under polarization by photoelectron microscopy', Solid State Ionics, in press
- D. Maestre, A. Cremades, L. Gregoratti and J. Piqueras , 'Growth and Luminescence of N Doped TiO2 Nanowires ', Small DOI: 10.1002/smll.2006.
- D. Maestre, A. Cremades and J. Piqueras, L. Gregoratti, 'Thermal growth and structural and optical characterization of indium tin oxide nanopyramids, nanoislands and tubes ', submitted
- P. Dudin1, A. Barinov1, L. Gregoratti1, D. Sciani1, Y. B. He2, H. Over2 and M. Kiskinova1, 'MgO-supported Rh particles and films: size, morphology and reactivity ', J. of Phys. Chem., in press.