Zone plate based scanning photoemission imaging and spectromicroscopy at Elettra: recent achievements and future projects in surface and interface studies

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Sincrotrone Trieste SCpA

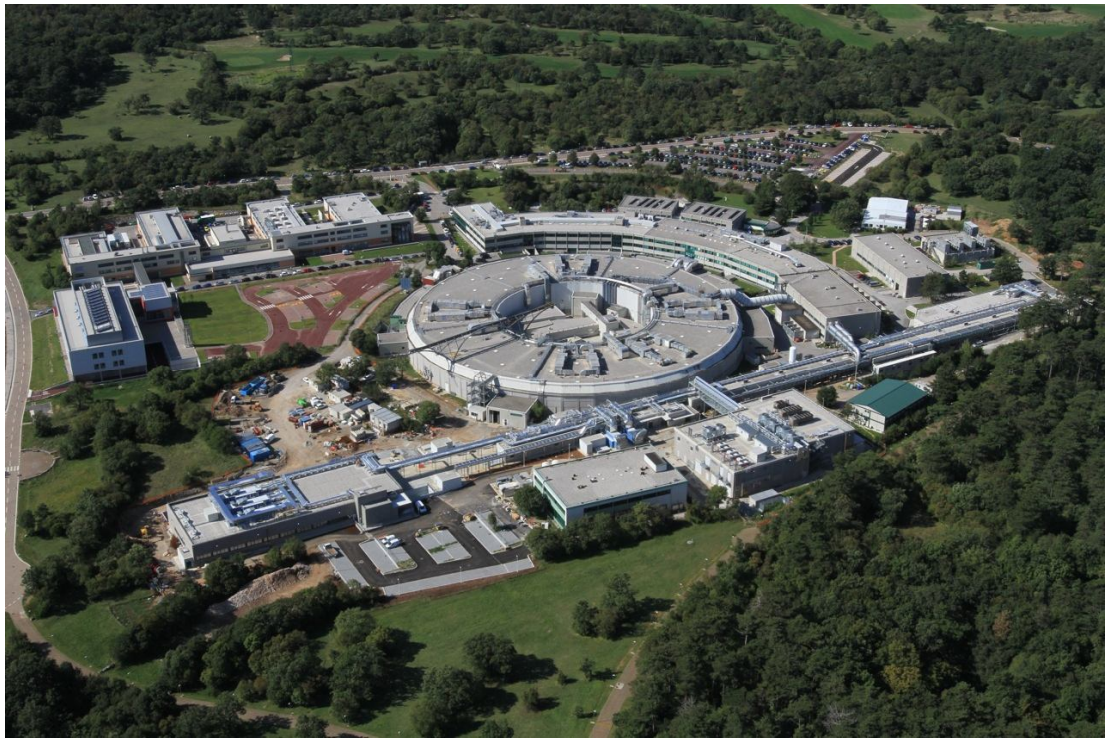
BNL – 23rd May 2011

The SPEM of Elettra: a short history

Designed and developed in 1993-1995

First user: July 1995 Francisco Braz Fernandez (Portugal)

Picture taken on May 14, 1992 by a Soviet spy satellite.



Aerial view of Elettra – November 2010

Experimental chambers major upgrades: 2001-2003

Range of low photon energies: <1-2 keV

Most diffused techniques of investigation used in synchrotron spectromicroscopy experimental facilities

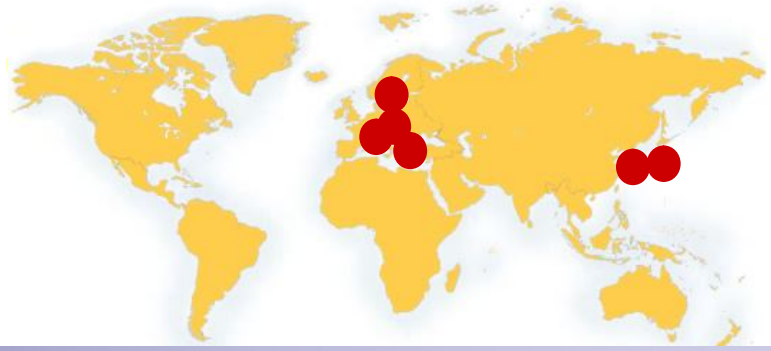
- Fluorescence
- Transmission
- Diffraction
- Tomography

} Better with higher photon energies

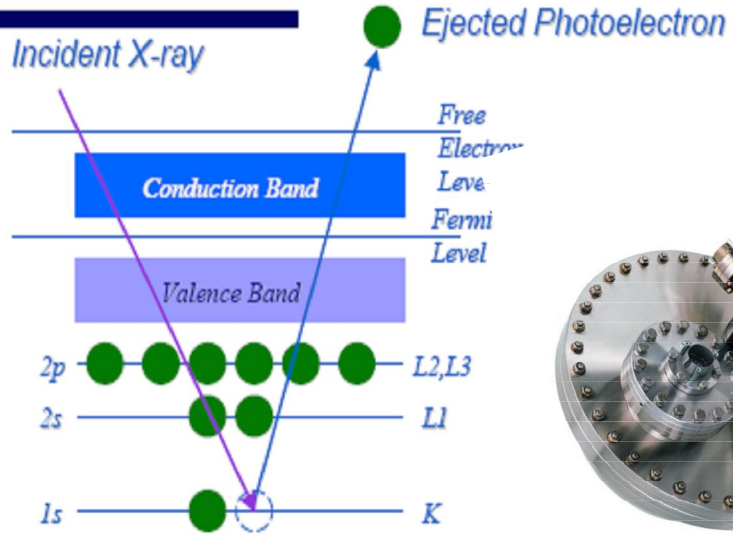
- Photoemission → Ideal at low photon energies

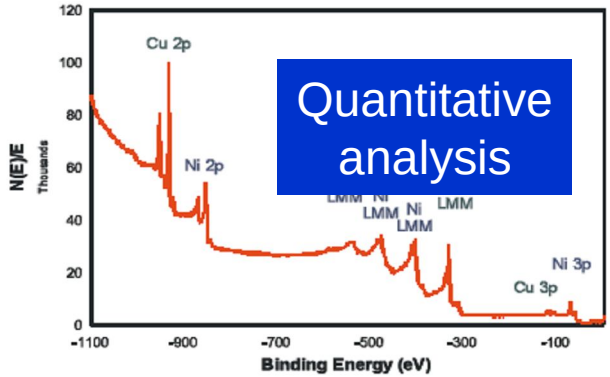
Main Synchrotron Light Sources with photoemission based spectromicrosopy facilities

- Elettra – 2.0/2.4 GeV
- Bessy – 1.7 GeV
- MAX-lab – 1.5 GeV
- NSRRC – 1.5 GeV
- PAL – 2.5 GeV
- SLS – 2.4 GeV
- SOLEIL – 2.75 G NEW
- Spring8 – 8 GeV NEW

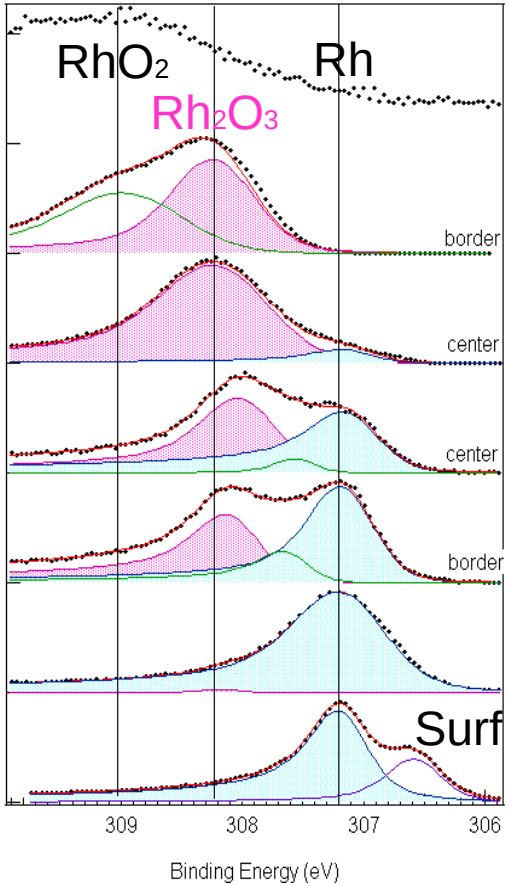


The Photoelectric Process



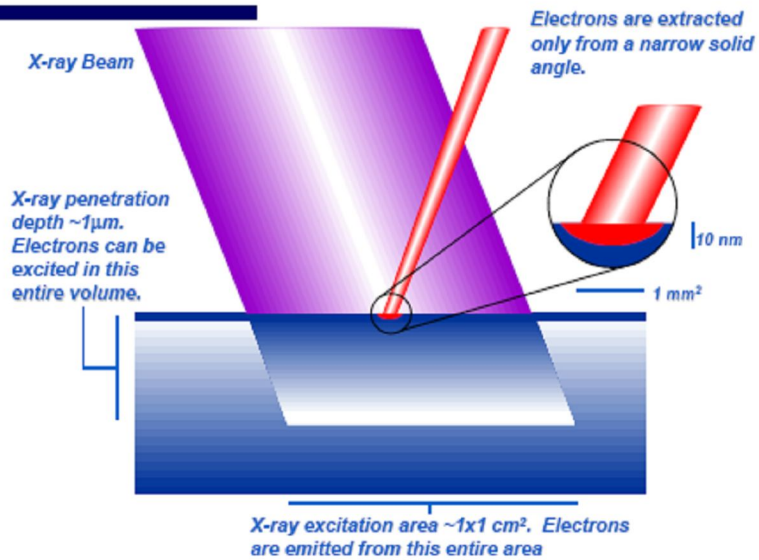


Fine Chemical analysis



X-ray Photoelectron Spectroscopy

Small Area Detection



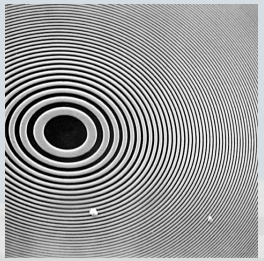
X-ray photoemission microscopy at synchrotrons: methods

Scanning

SPEM

Zone Plates lenses

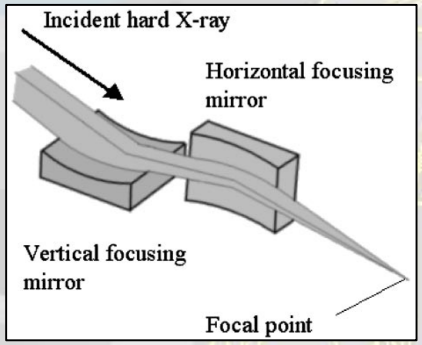
- **Elettra**
- **ALS**
- **SRRC**
- **PAL**



Focusing mirrors

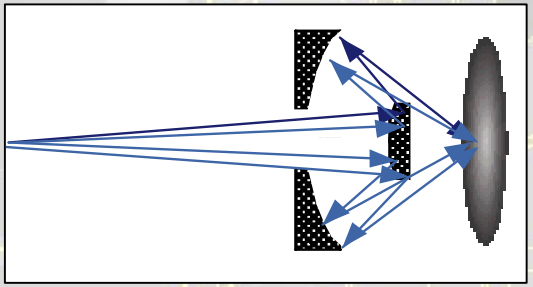
Kirkpatrick-Baez

- **Max-Lab**



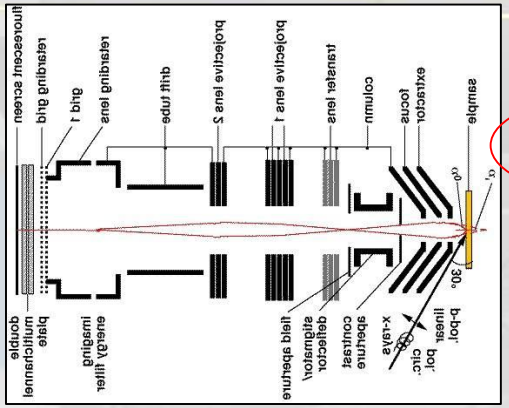
Schwarzschild mirrors

- **Elettra**
- **Madison**



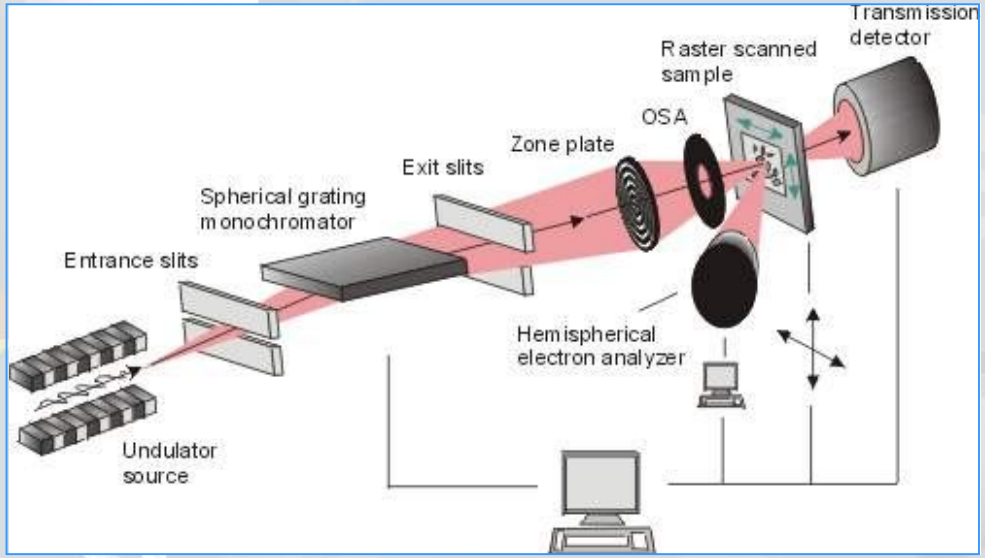
No scanning

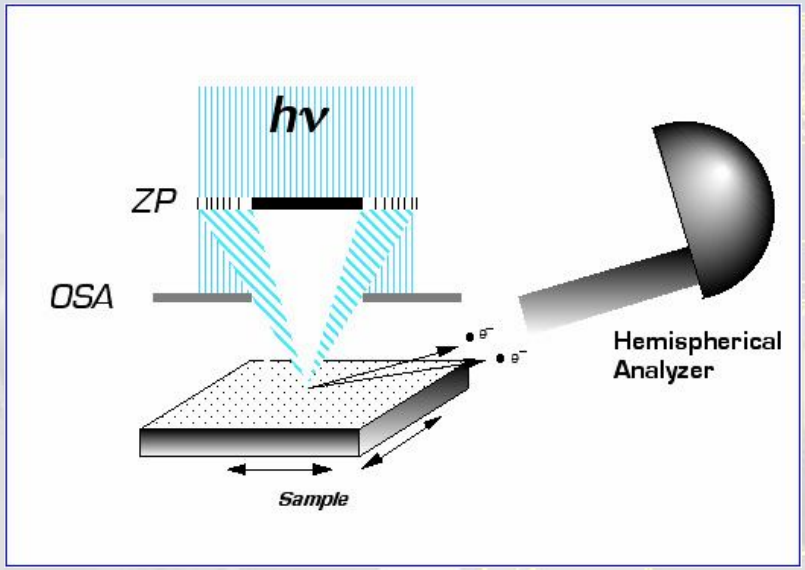
XPEEM
(XPEEM, SPELEEM)

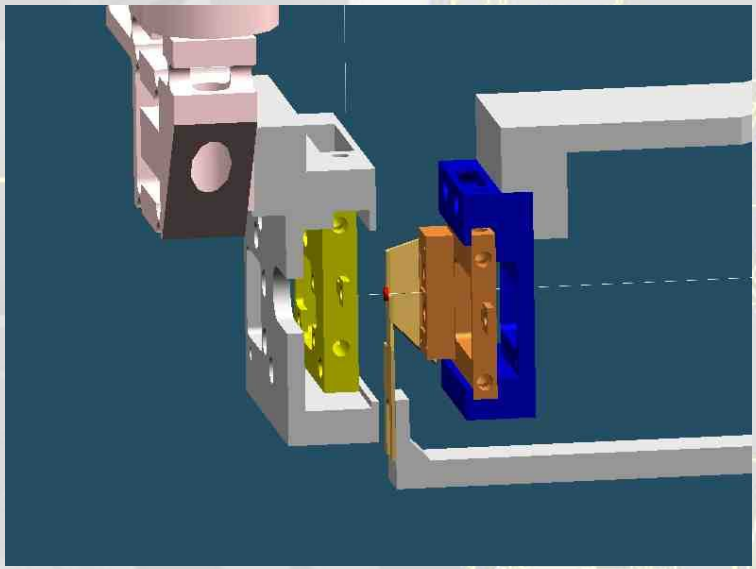


- **Elettra**
- **SLS**
- **MAX-lab**
- **BESSY**
- **Madison**
- **Spring8**

SPEM layout and performance



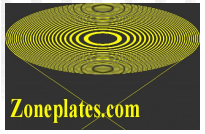




- Linearly Polarised Undulator
- Photon energy range: 350 eV (min) – 750 eV
- SGM monochromator equipped with 2 gratings for low and high photon energy
- Beam source size: 10-70 μm

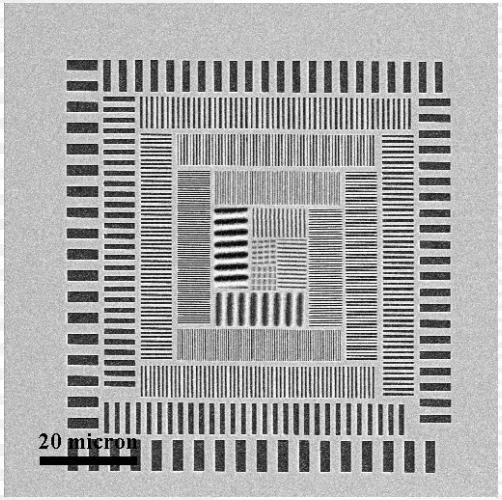
Spatial resolution

Zone plate used: xradia insight in 3D



Best ZP: D=200 μm, dr=50 nm

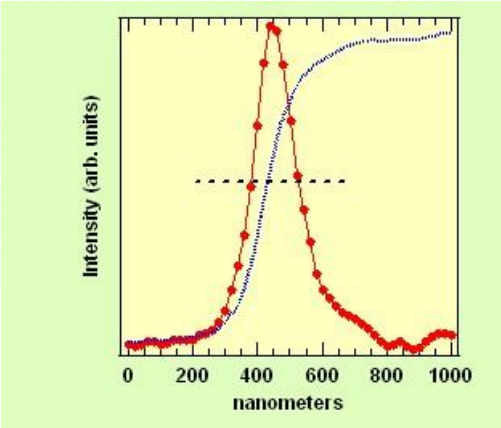
Other sizes: D=250 μm, dr=100nm
D=250 μm, dr=80nm



50 nm test object

Spectromicroscopy:
real beam size and shape

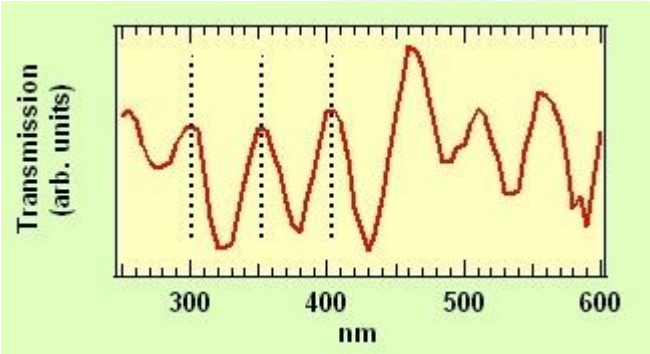
135 nm



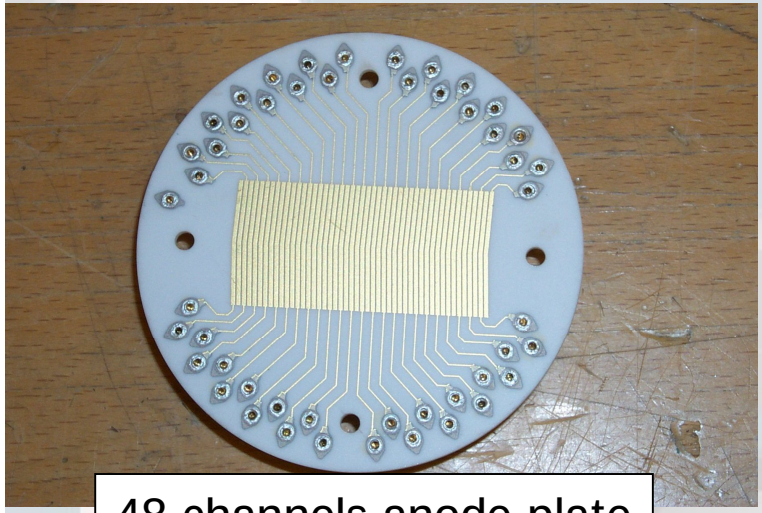
Imaging:
effectice resolution

< 50 nm

Horizontal scan

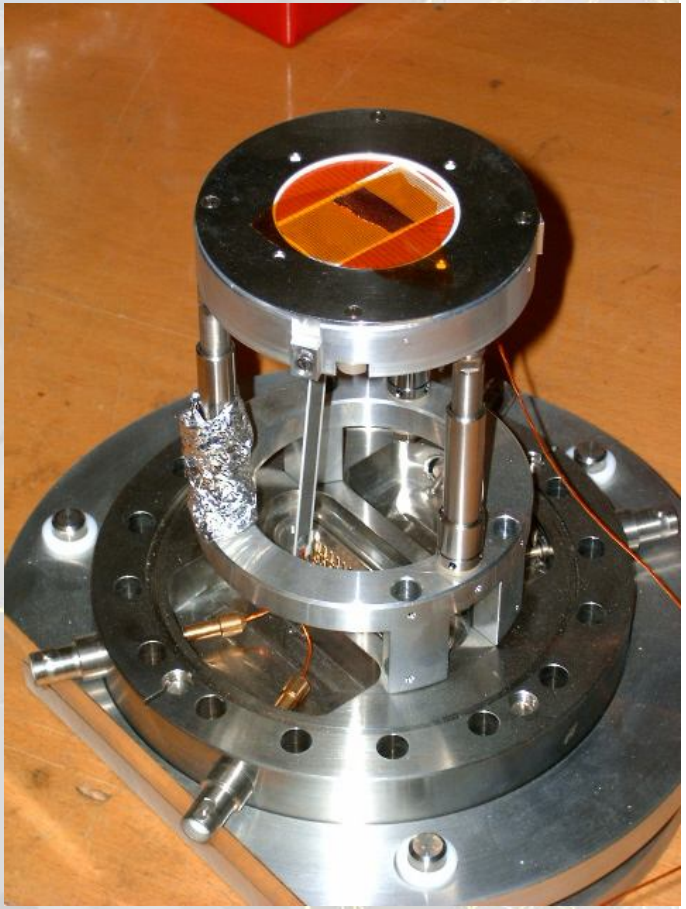


Energy resolution

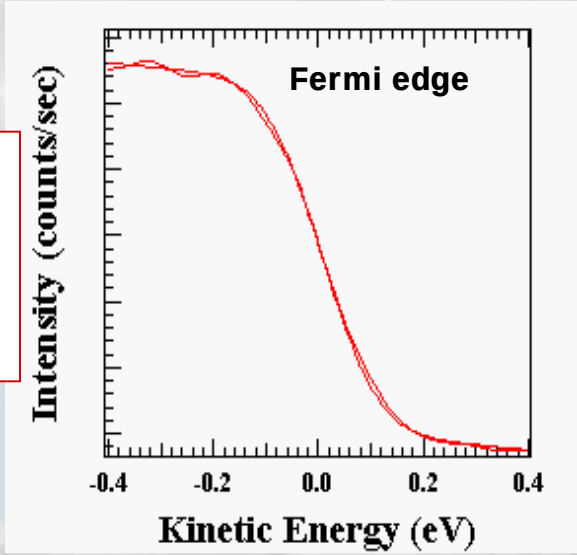


48 channels anode plate

- HEA: SPECS® PHOIBOS 100
- Detector: 48 channels anode designed at Elettra



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



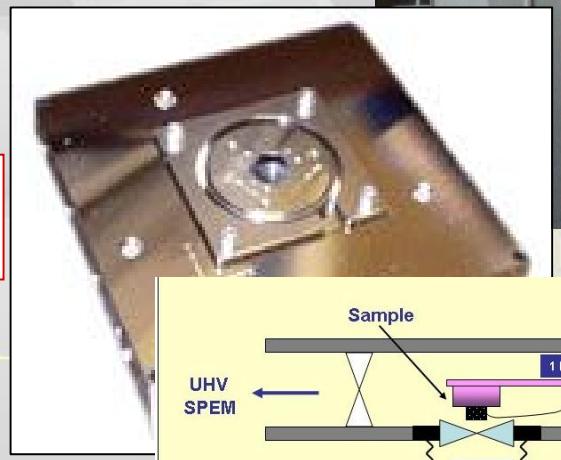
HW improvements

New undulator

- **4.5 m long, 46 mm period**
- **Extended photon range**
- **Higher brilliance**
- **Better coherence**

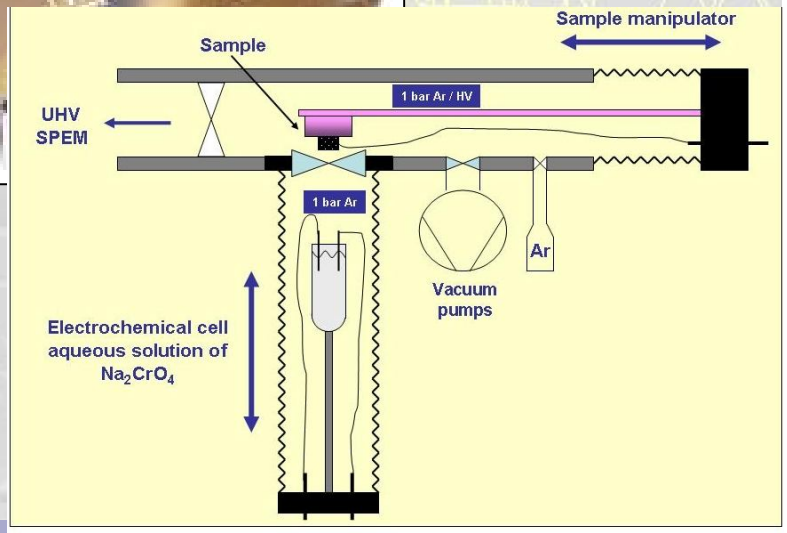
New piezo scanner

- **PI 2 axis 100x100 μm**
- **Low voltage**



Liquid exposure setup

- **Electrochemical reactions**
- **Semicond decapping**



SPEM experiments: main topics

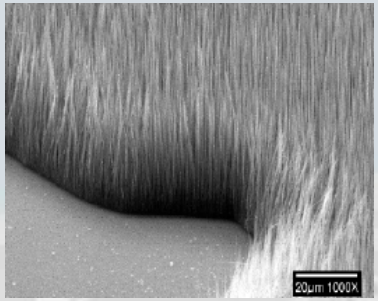
Nanostructures/devices characterization

- **MCNTs mass transport and reactivity**
- **e-noses**
- **Size dependent electronic properties of semiconductors**
- **Chemical imaging of nanostructures: from old configurations to new setups**

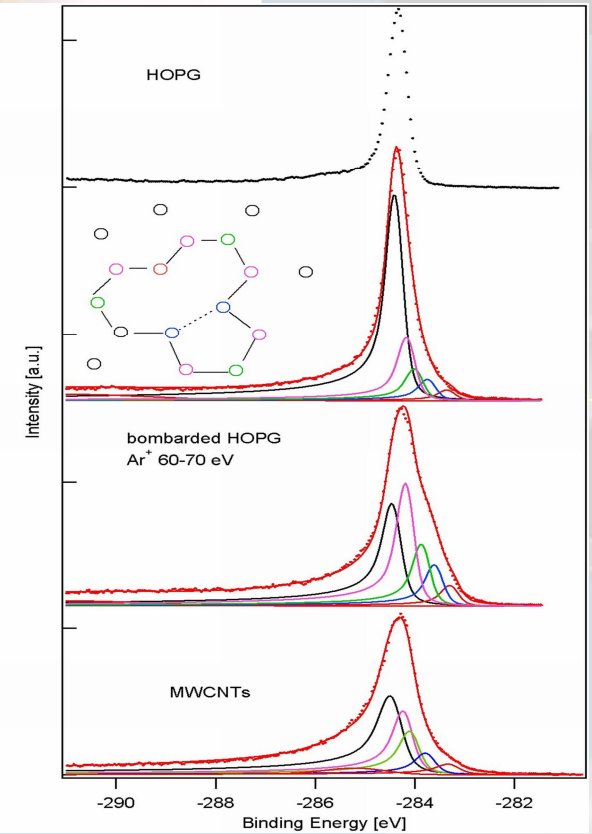
Metal adsorbate on MWCNT array with SPEM

(in collaboration with the *theory@elettra group*)

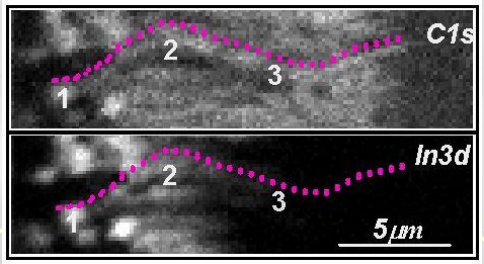
Characterization of MWCNT surface; analysis of C1s photoemission in comparison with clean and defective HOPG surfaces

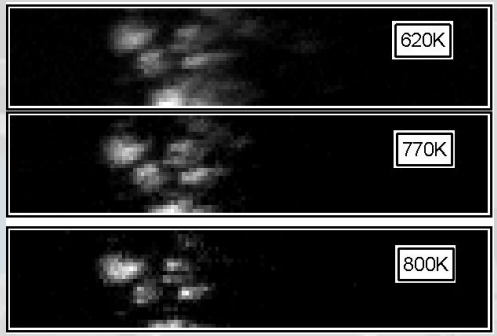


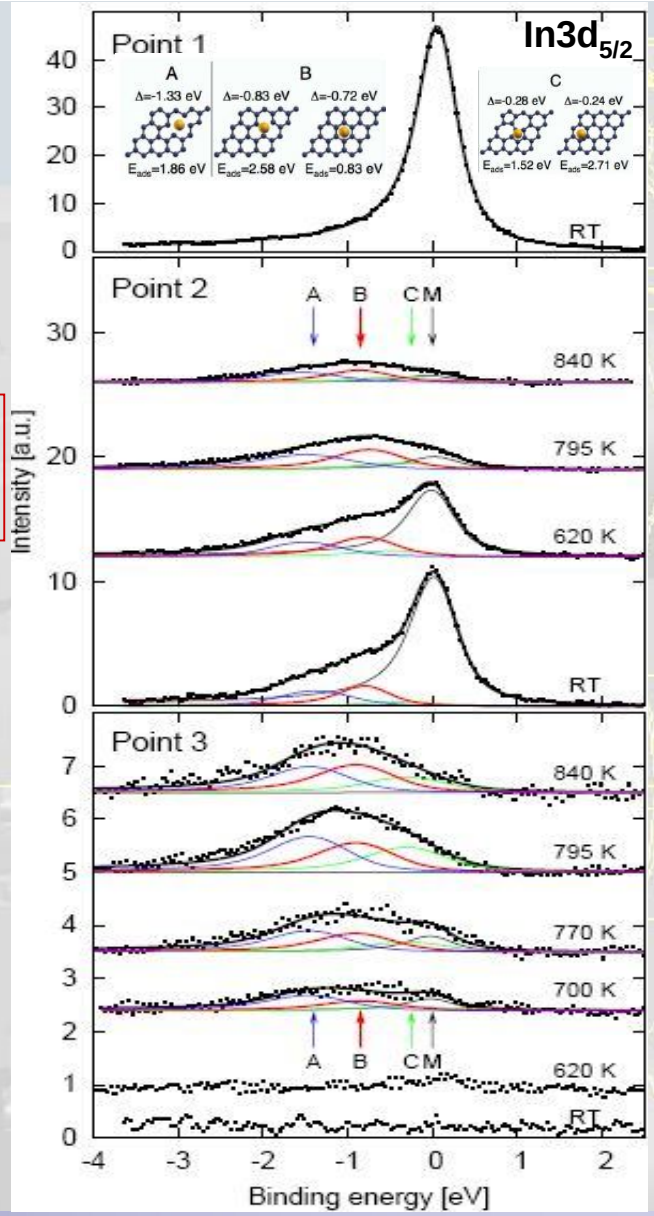
CVD forests from Nanolab Inc.



SPEM imaging of temperature evolution of In deposits on the surface of MWCNT array





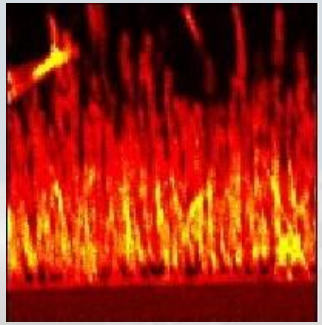


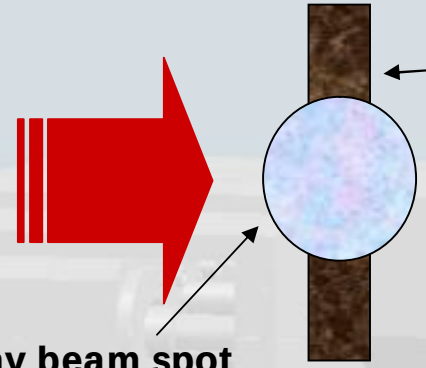
A. Barinov et al. Phys. Rev. Lett. 99, 046803 (2007)

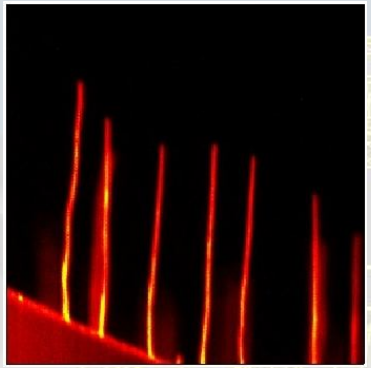
Improving the sample setup for nanostructures

1

From high density to low density MCNT arrays



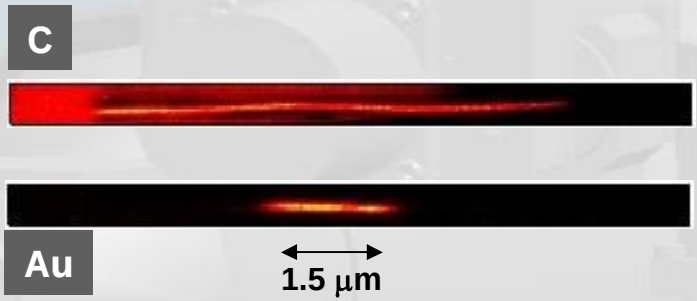


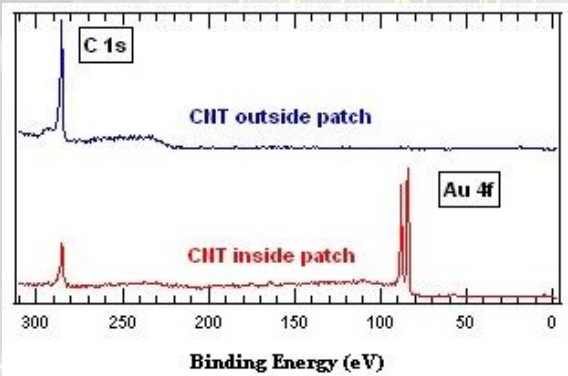


CNT diameter: 60-70 nm

2

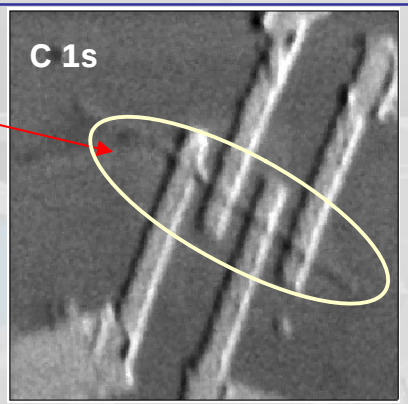
Confined patches on single nanostructure

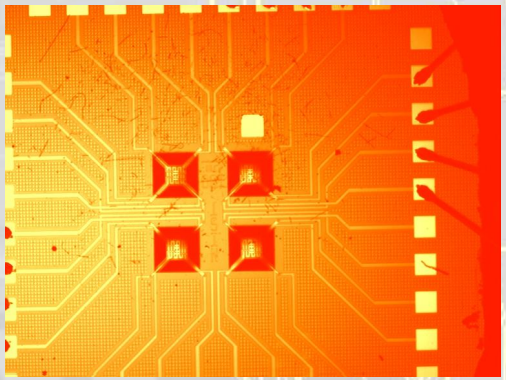




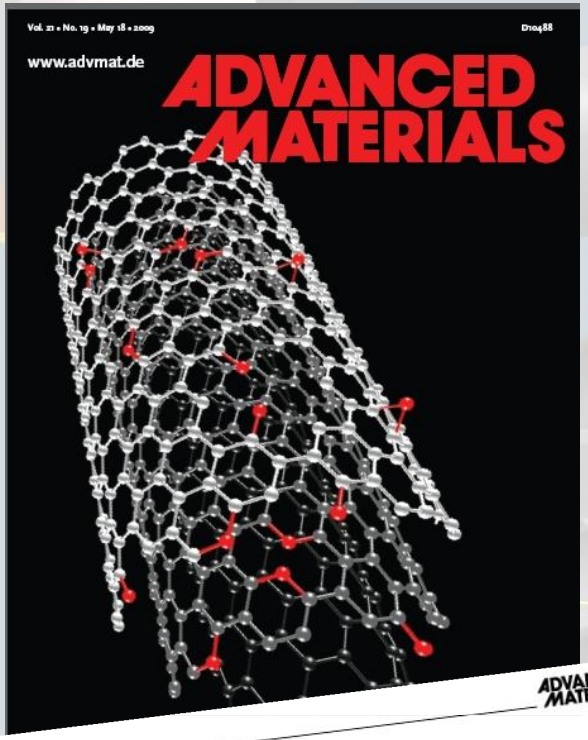
3

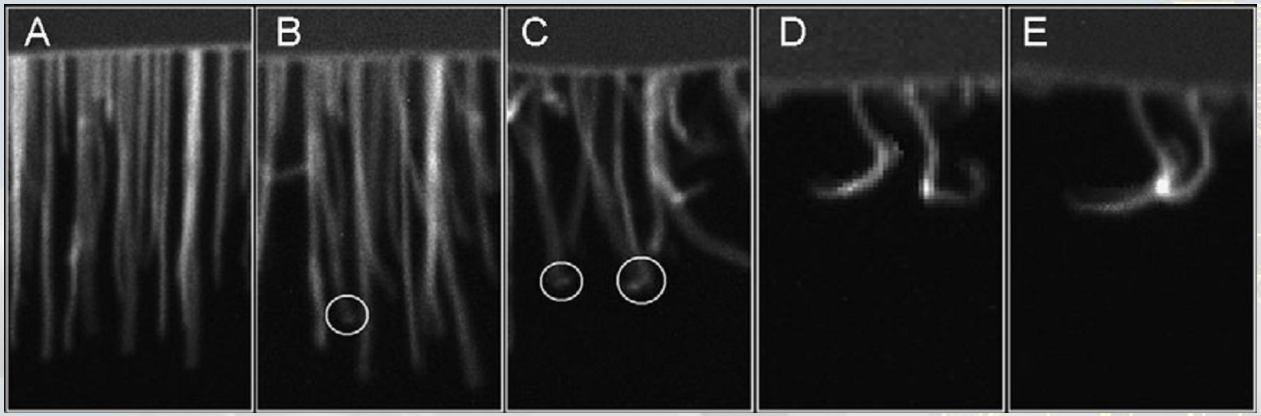
Electric transport/ biasing





Gas phase oxidation of MCNT

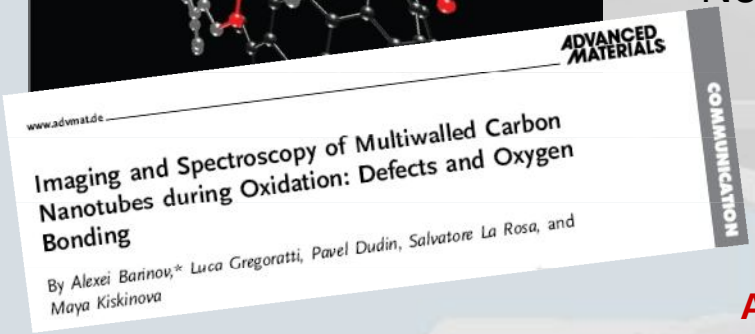


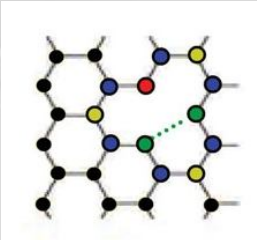


7 μm

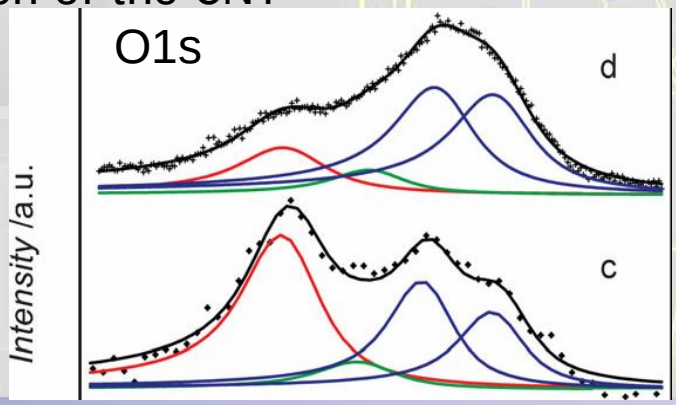
Increasing oxygen dosage

- 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

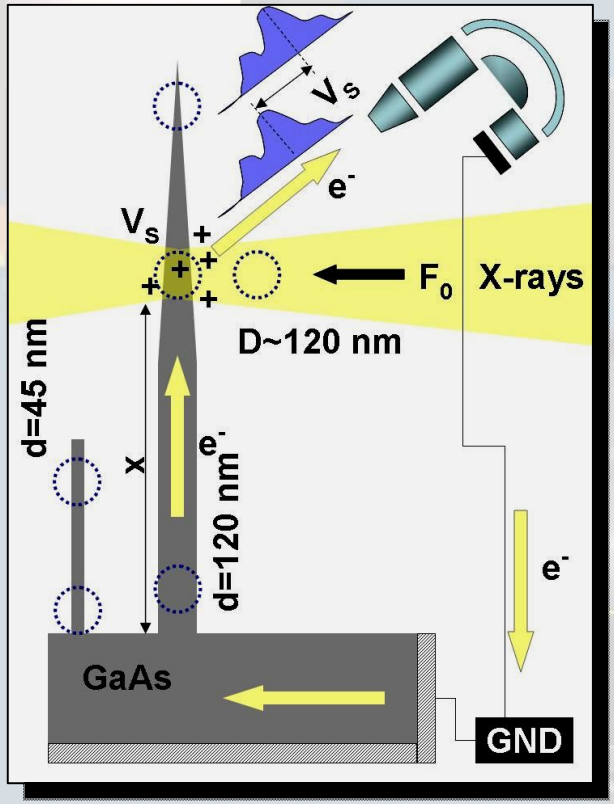


A. Barinov et al. Adv. Mat. 21 (19) 1 (2009)

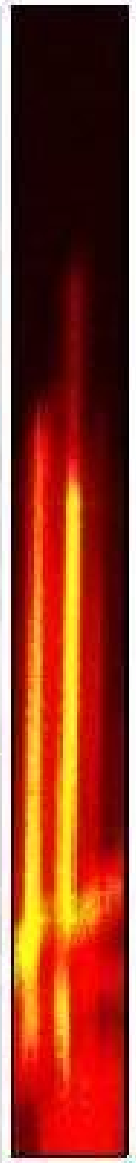
Contactless monitoring of the diameter-dependent conductivity of GaAs nanowires

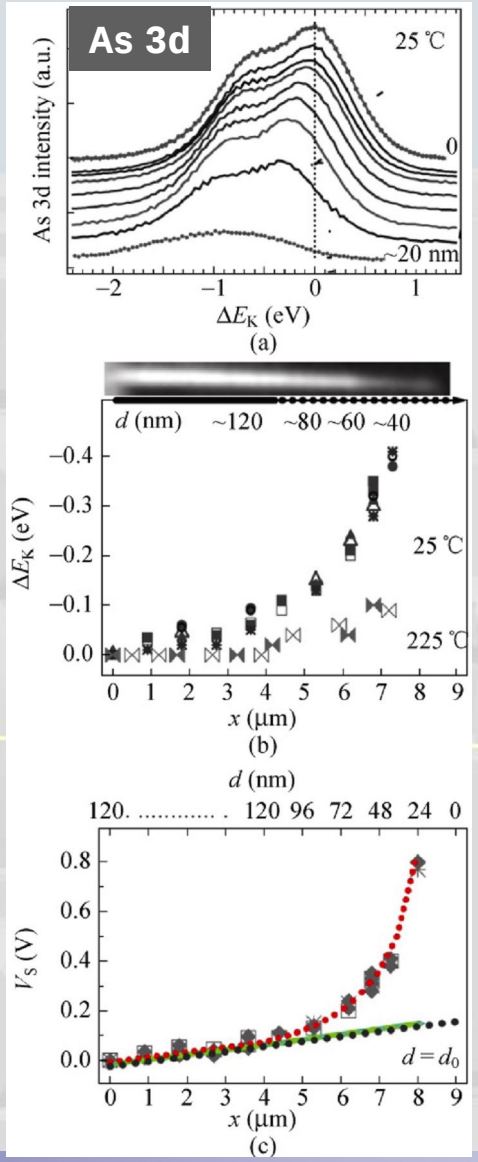
(in collaboration with S. Rubini – CNR-IOM Laboratory - Italy)

D<3nm



D=120nm





Debye lengths~*d*

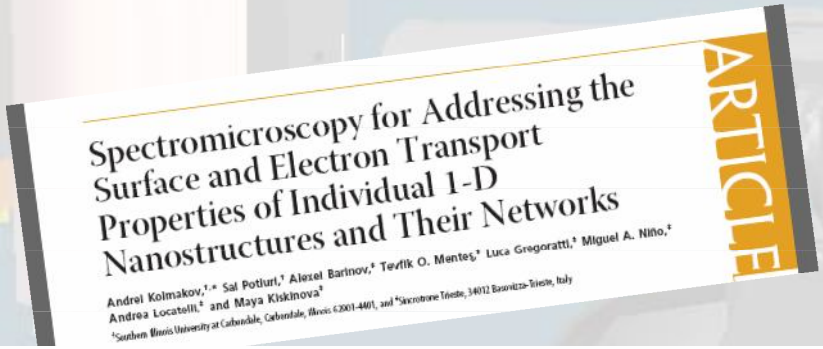
Influence of size (temperature and surface treatment) on the conductance of individual low-doped GaAs NWs can be addressed and quantified by contactless measurements of the photon beam-induced surface potential along a NW axis using photoelectron microspectroscopy

F. Jabeen et al. Nano Res. 2010, 3(9): 676–684

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, …


ARTICLE

Spectromicroscopy for Addressing the Surface and Electron Transport Properties of Individual 1-D Nanostructures and Their Networks

Andrei Kolmakov,[†,*] Sal Potluri,[†] Alexei Barinov,[‡] Tevfik O. Mentes,[‡] Luca Gregoratti,[‡] Miguel A. Niño,[‡] Andrea Locatelli,[‡] and Maya Kiskinova[‡]

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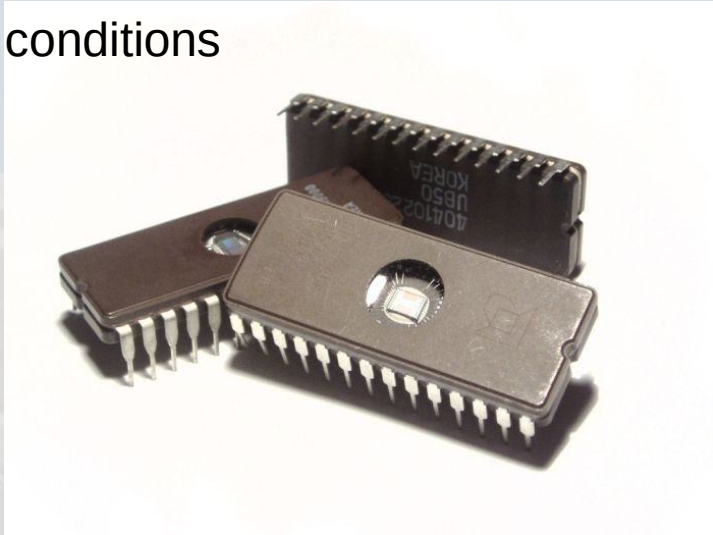
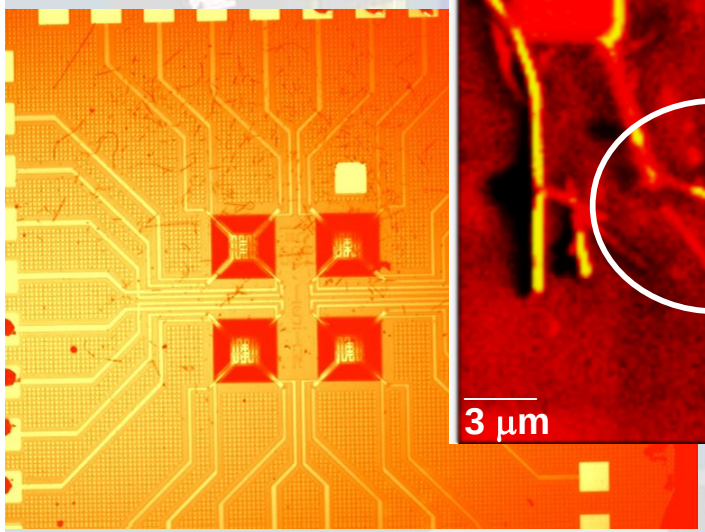
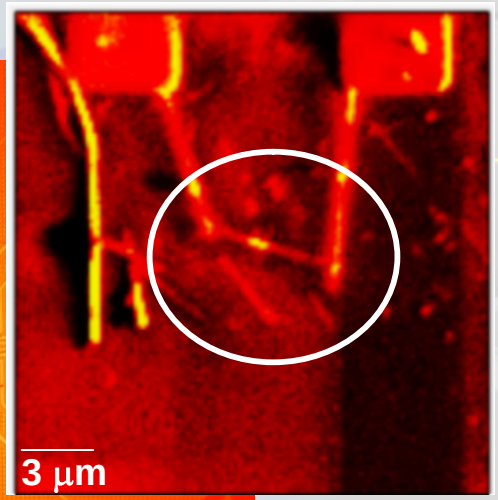
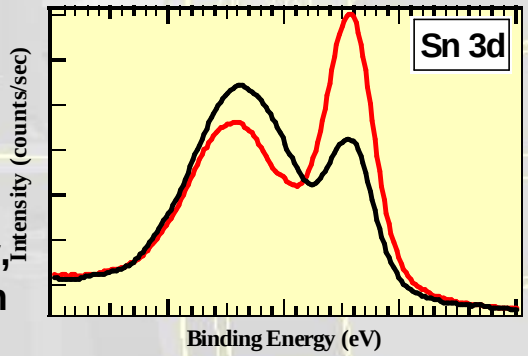
VOL. 2 ▪ NO. 10 ▪ 1993–2000 ▪ 2008 ACSNANO 1993

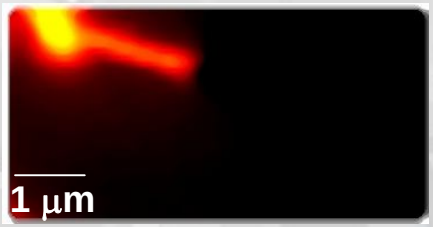


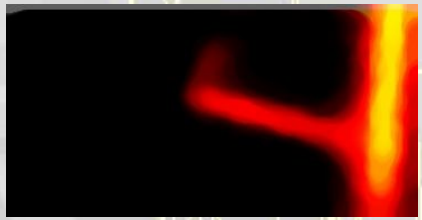




- **Addressing the electron transport in a workin device (temperature, close biasing, etc.)**
- **Surface stoichiometry, coordination, oxidation state, etc.**







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

SPEM experiments: main topics

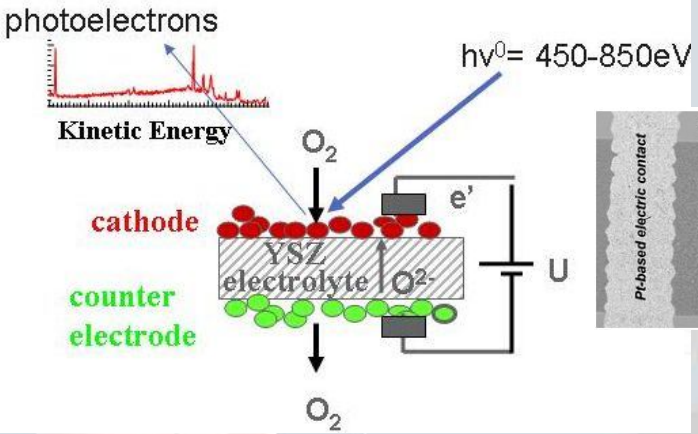
Electrochemistry/SOFC

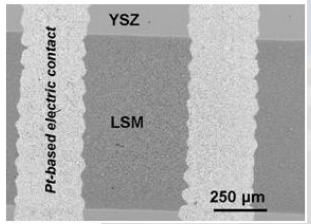
- **Electrochemical stability of materials**
- **Challenging experiments: high temps, biasing, low concentrations**

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

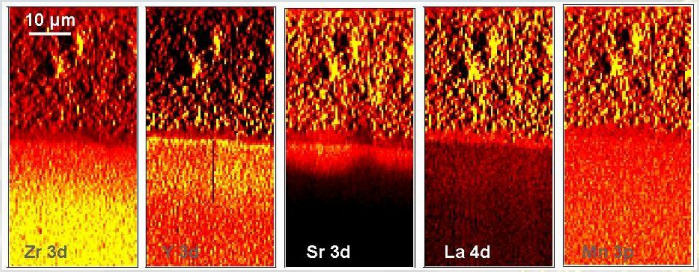
Operating SOFC: mass transport

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

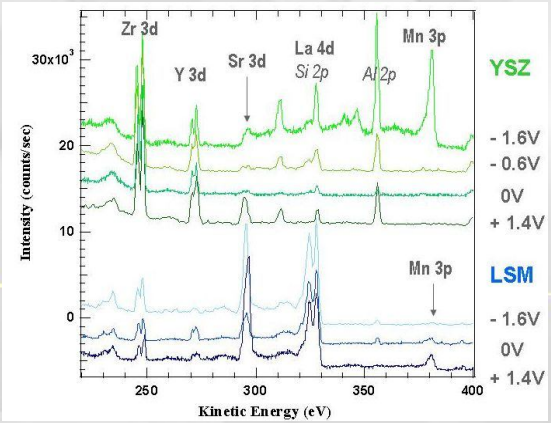


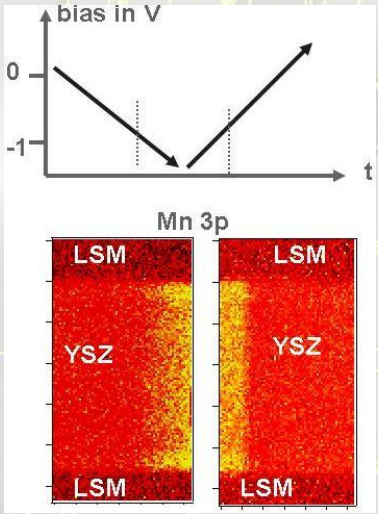


Elemental distribution at electrolyte/LSM interface

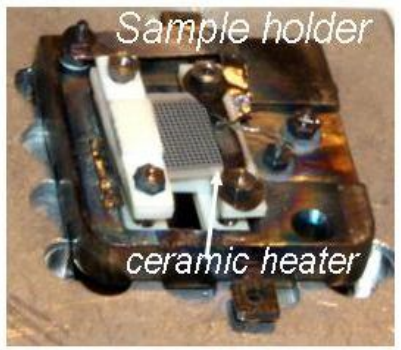


Surface composition change with bias





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

SPEM experiments: main topics

[redacted]

Nanocomposite materials

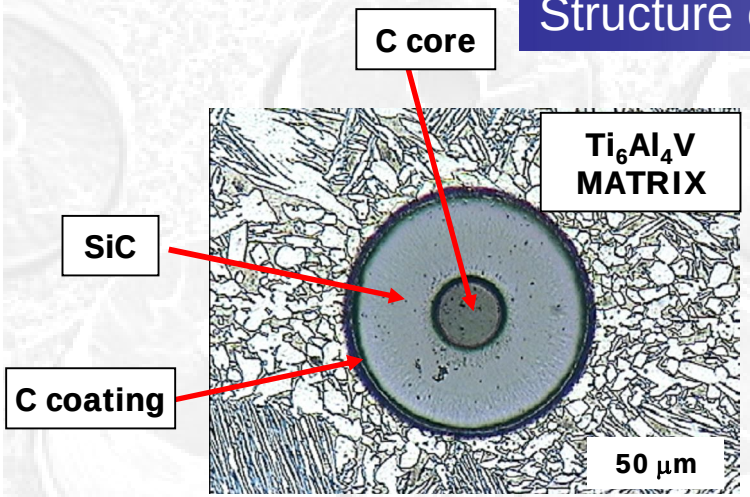
- **Sample preparation**

[redacted]

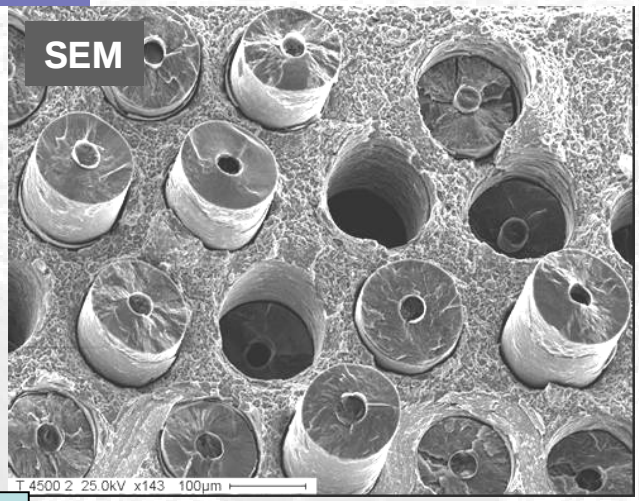
Ti6Al4V-SiC_f composite produced by HIP for aeronautical applications

(in collaboration with S. Kaciulis – ISMN-CNR, Rome, Italy)

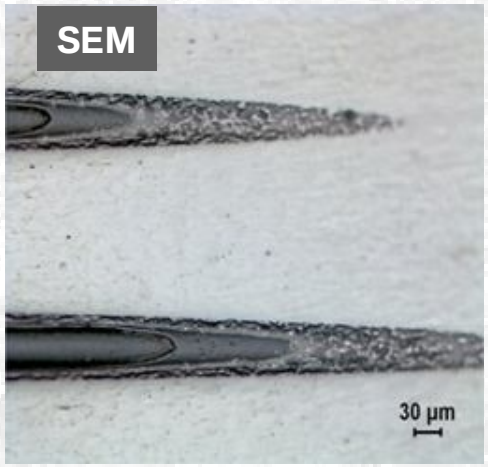
Structure of the composite material

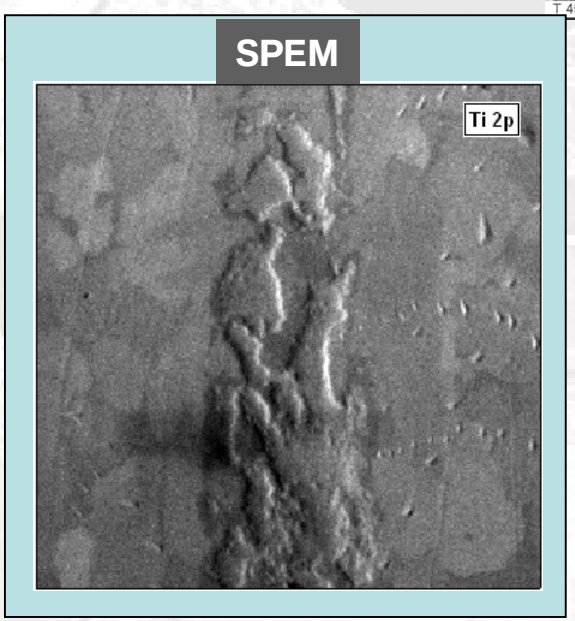


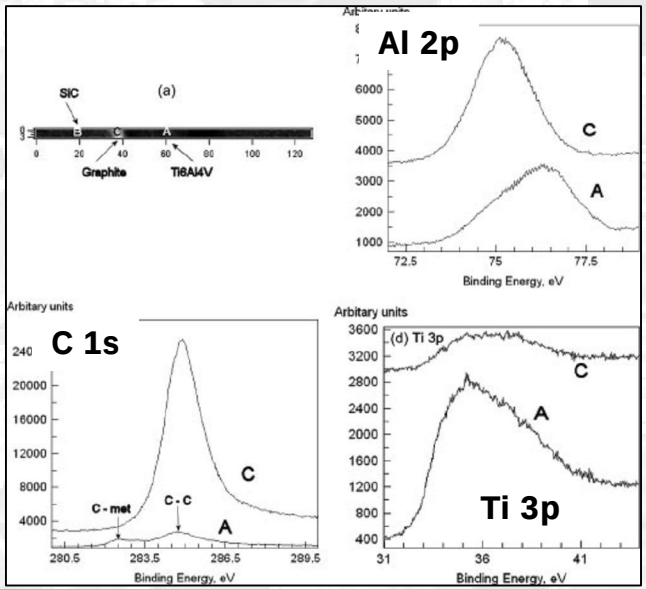
Get access to the interfaces



Sample lapping at grazing angle







S. Kaciulis et al. *Surf. Interface Anal.* **2010**, *42*, 707–711

SPEM experiments: main topics

[redacted]

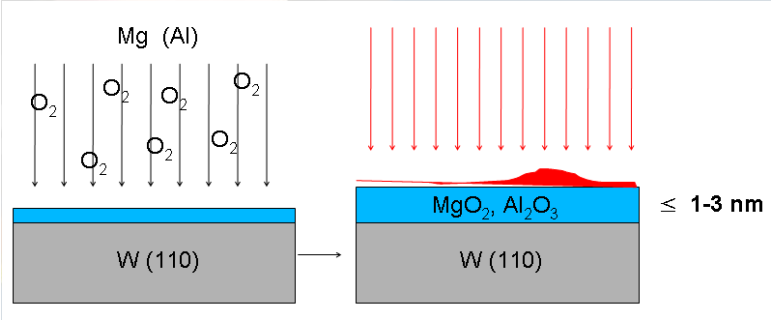
Catalysis

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

[redacted]

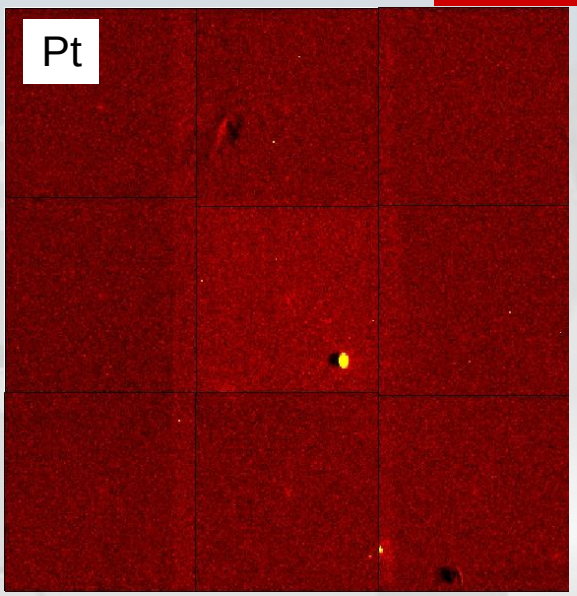
Oxidation of PtRh particles produced by in situ PLD

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



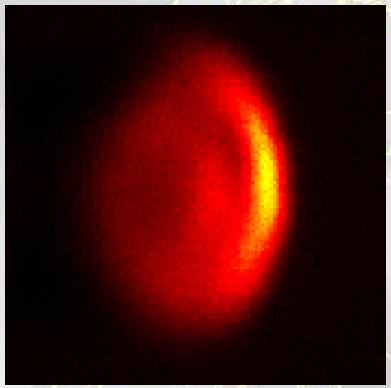
No charging of the substrate because of the low thickness, XPS and SPEM are possible

SPEM



64 μm

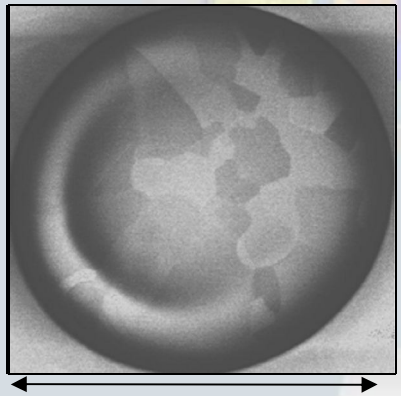
Low density of micron sized particles



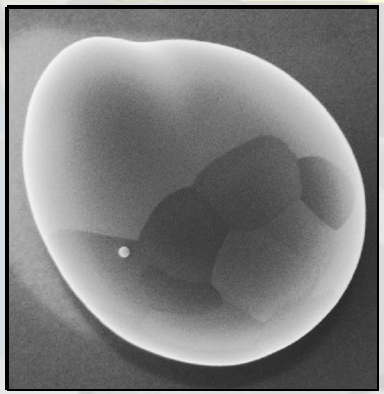
3 μm

Nano-cluster of average size < 10 nm

SEM



1.5 μm

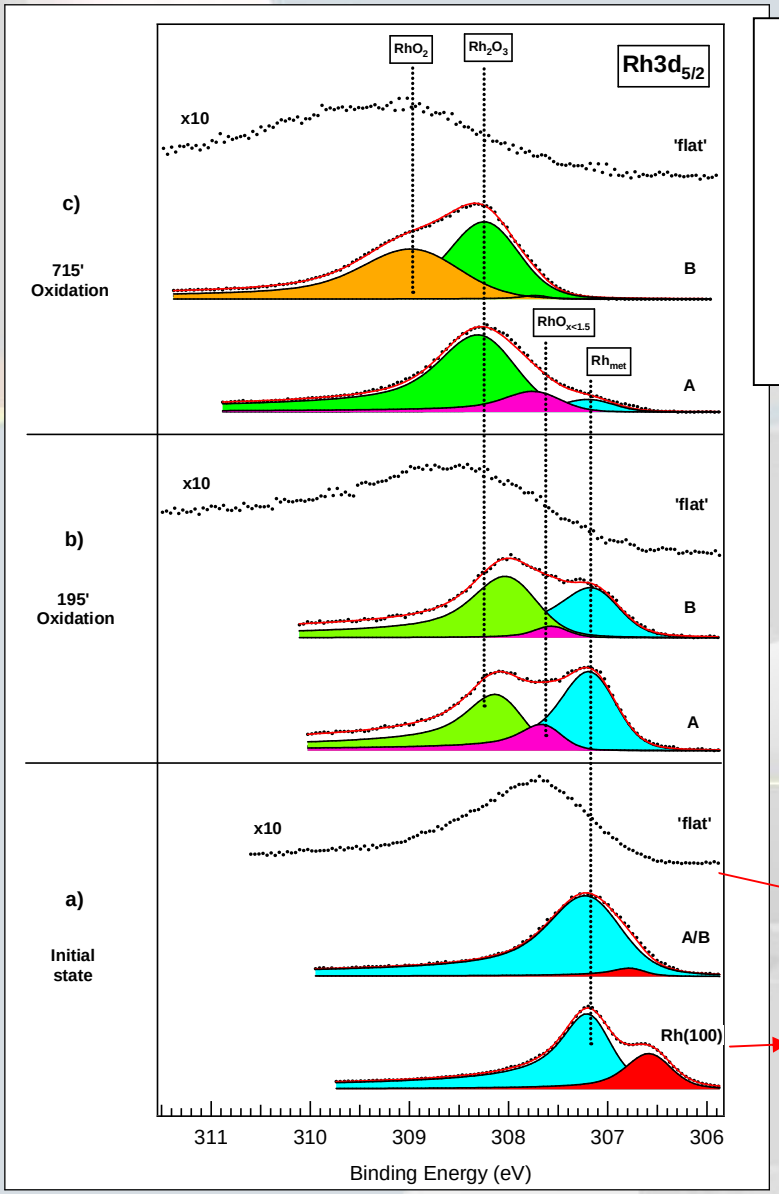


0.7 μm

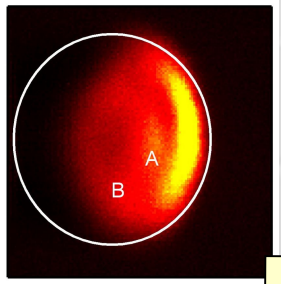
- Poly-crystalline nature of the particles
- Size effects during chemical reaction
- Proximity effects
- Simple model reaction: O_2 ($+H_2$)
- Unconventional procedure for particle generation (thermodynamics)

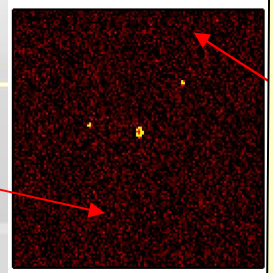
M. Dalmiglio et al. J. Phys. Chem. C – available on web

Oxidation of PtRh particles produced by in situ PLD

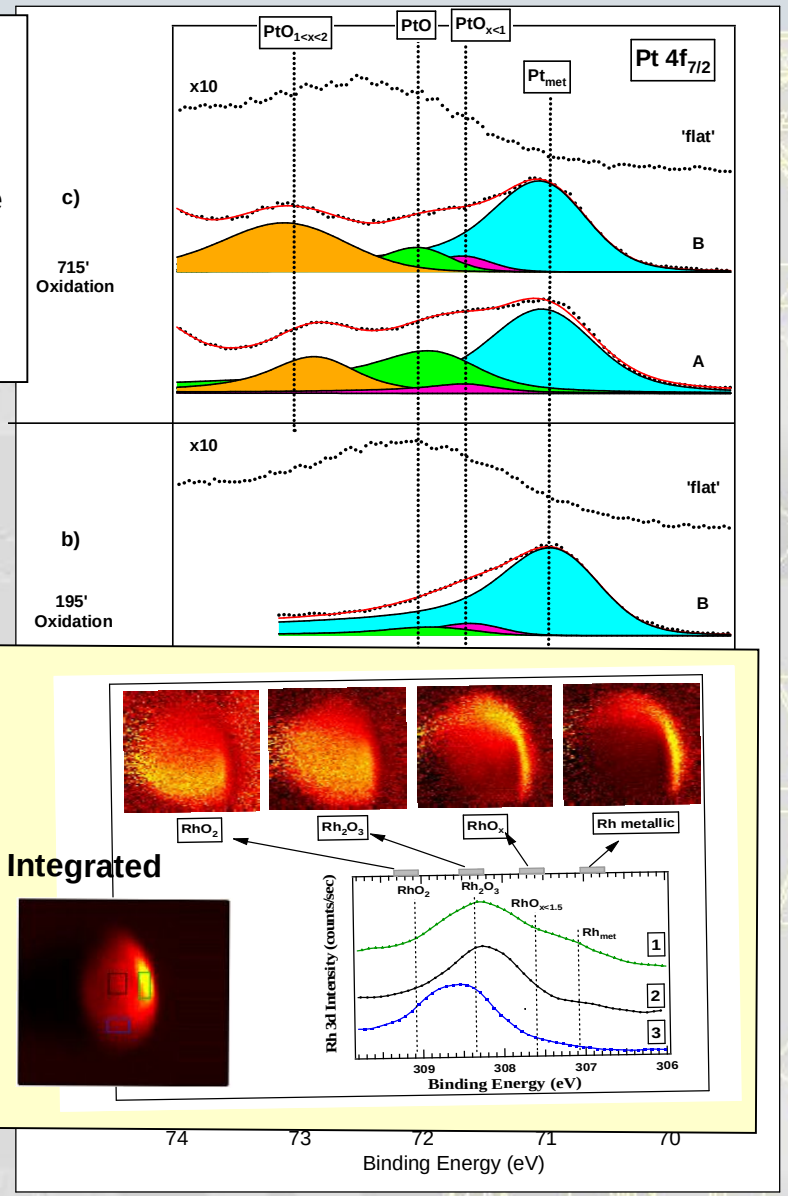


The spread anisotropy of the chemical phases over the surface reveals the presence of many different areas of different reactivity

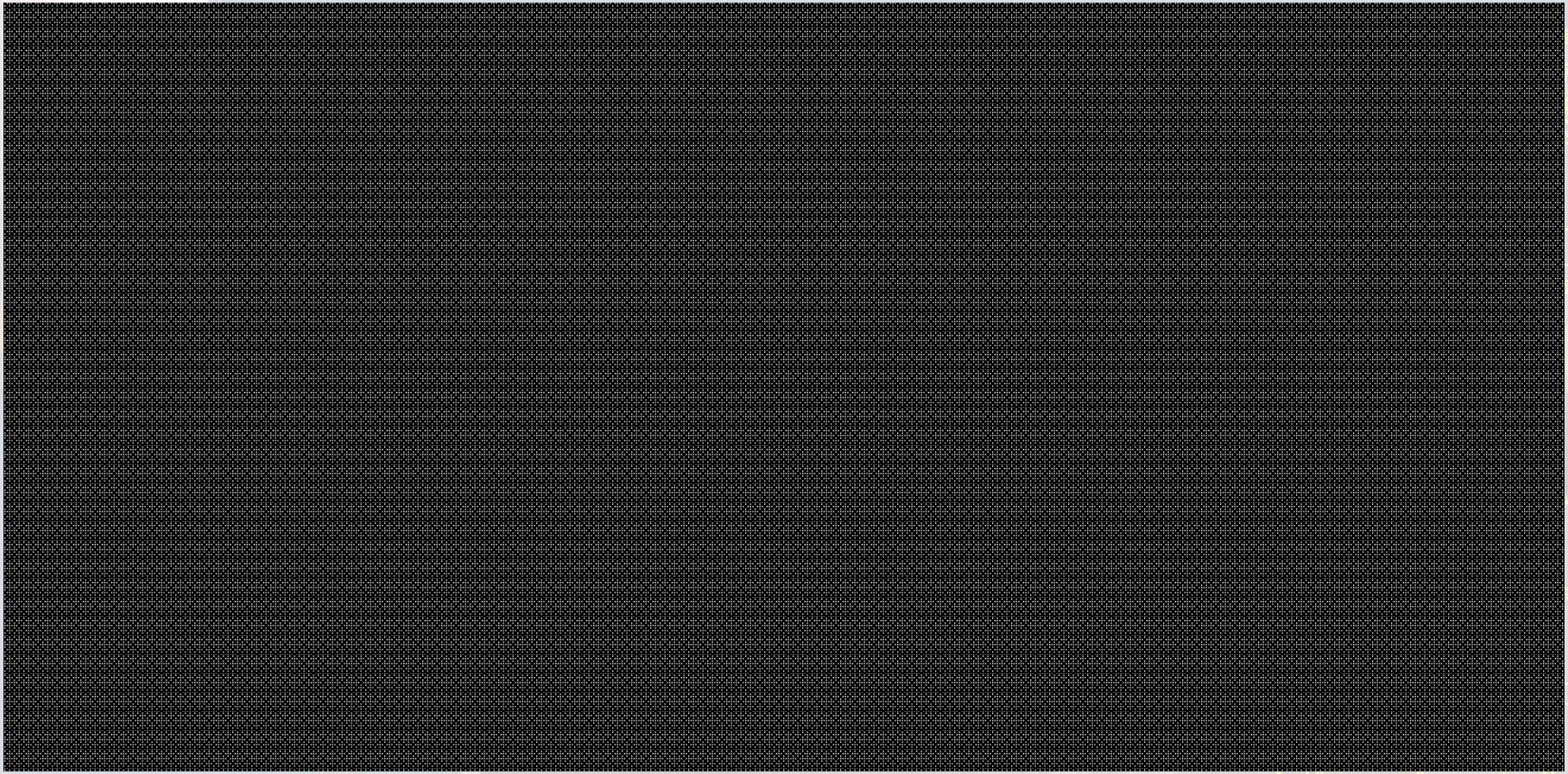




Reference crystal



SPEM experiments: main topics

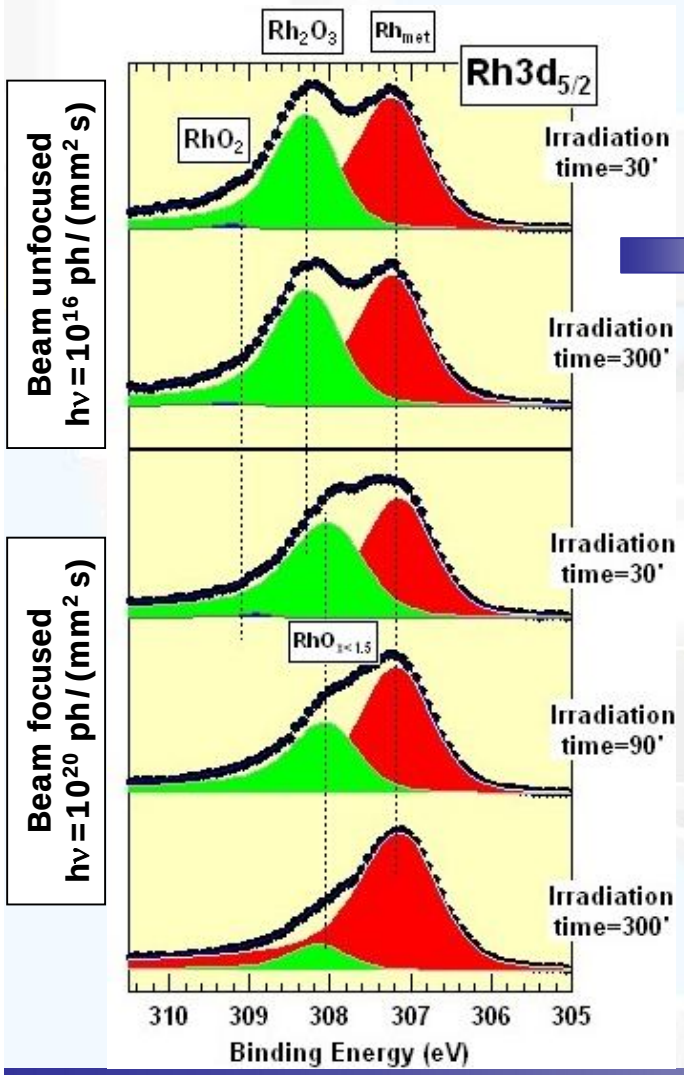


X-ray damage

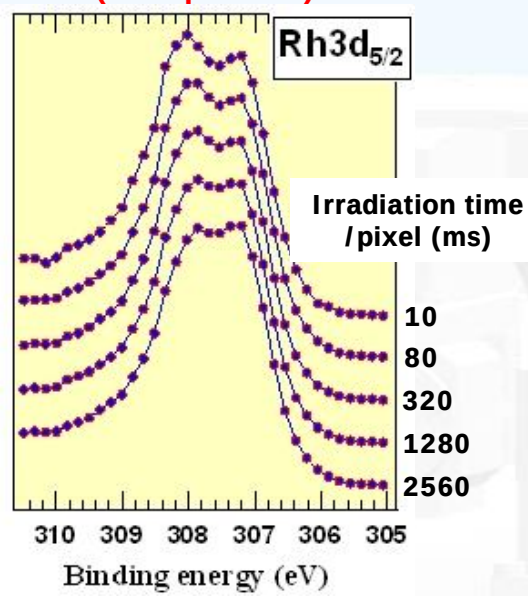
- **Characterization of ablated materials (in-situ, ex-situ, FEL optics, …)**
- **Which scanning photoemission spectromicroscopy on organic materials?**

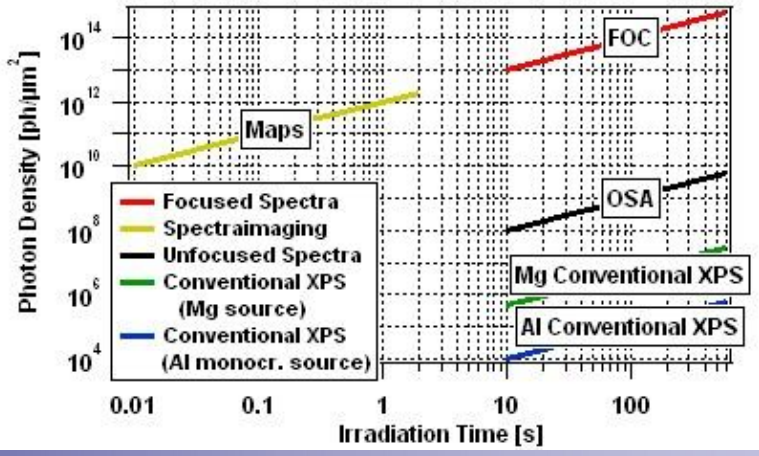
Beam-induced effects in soft X-ray photoelectron emission microscopy experiments

Inorganic samples



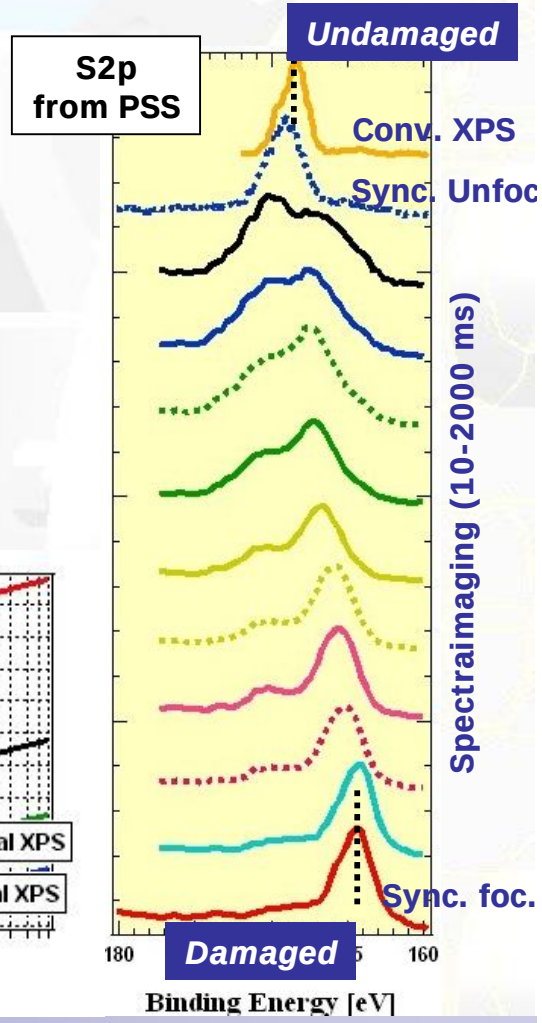
Spectraimaging (snapshot)





Organic samples

Is is possible to use the SPEM?



In preparation

Conclusions

2011-12

- Test the microscope with the new upgrades (Elettra ring allignment, undulator, piezo scanner)
- Improve the lateral and energy resolutions
- Develop a technical upgrade to approach the “pressure gap” problem

Web link:
www.elettra.trieste.it
Profile on linkedin:
www.linkedin.com/companies/sincrotrone-trieste-s.c.p.a
YouTube Channel:
www.youtube.com/Sincrotronetrieste