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International Atomic Energy Agency

2245-22

Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology in Hydrogen-Based Energy Systems

13 - 18 June 2011

Scanning photoemission microscope: A powerful tool for studies on Fuel cells and catalysis supporting material

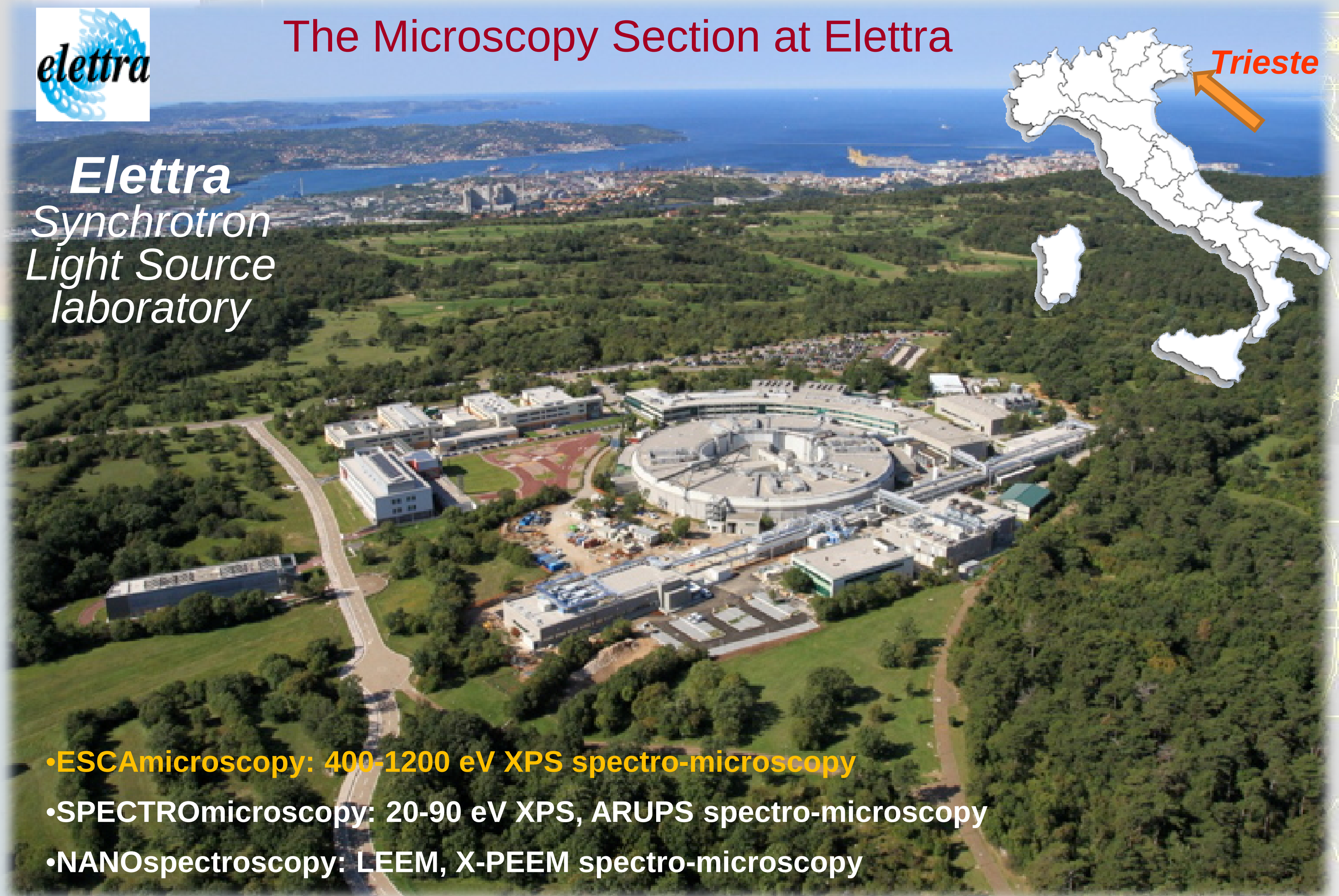
Majid Kazemian Abyaneh
Sincrotrone Trieste SpA
Trieste

Scanning photoemission microscope: A powerful tool for studies on Fuel cells and catalysis supporting material

Majid Kazemian Abyaneh
Sincrotrone Trieste SCpA

The Microscopy Section at Elettra

Elettra
Synchrotron Light Source laboratory



- **ESCAmicroscopy: 400-1200 eV XPS spectro-microscopy**
- **SPECTROmicroscopy: 20-90 eV XPS, ARUPS spectro-microscopy**
- **NANOspectroscopy: LEEM, X-PEEM spectro-microscopy**
- **TwinMic: X-ray transmission and absorption spectro-microscopy**
- **SISSY: infrared spectro-microscopy**

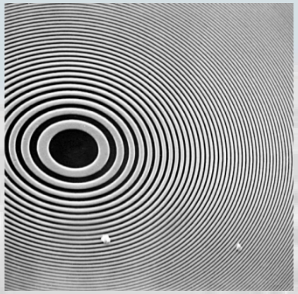
X-ray photoemission microscopy at synchrotrons: methods

Scanning

SPEM

Zone Plates lenses

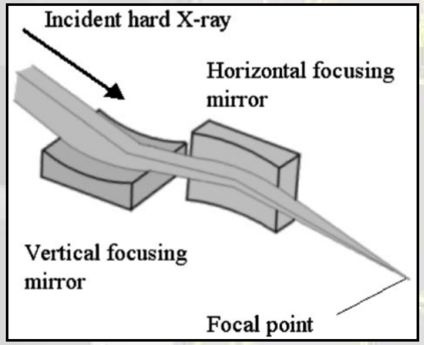
- **Elettra (ESCA B.L.)**
- **ALS**
- **SRRC**
- **PAL**



Focusing mirrors

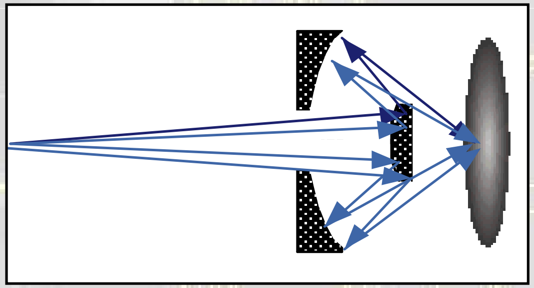
Kirkpatrick-Baez

- **Max-Lab**



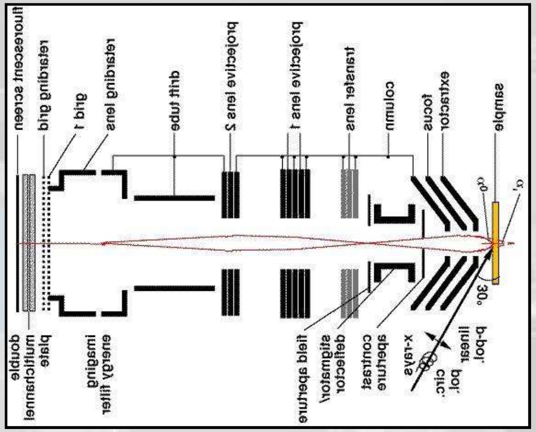
Schwarzschild mirrors

- **Elettra (SpectroMic B.L.)**
- **Madison**



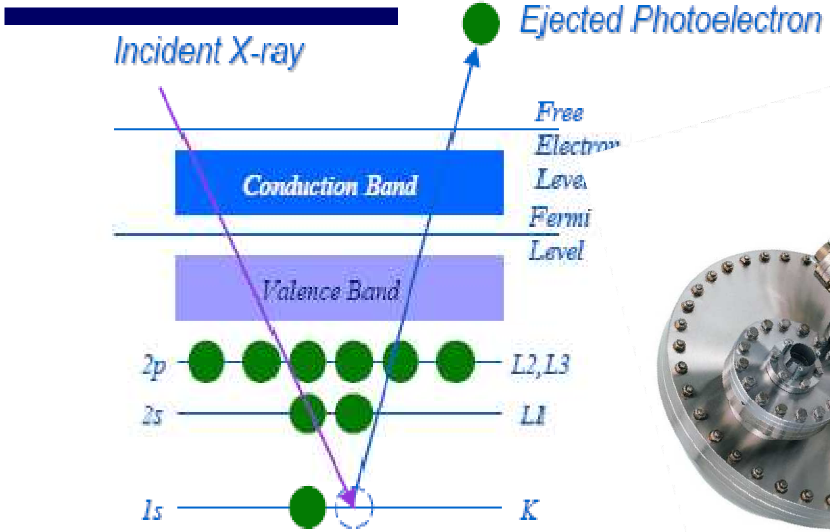
No scanning

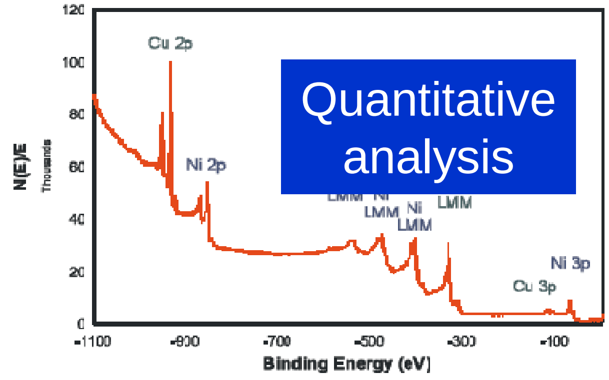
XPEEM (XPEEM, SPELEEM)



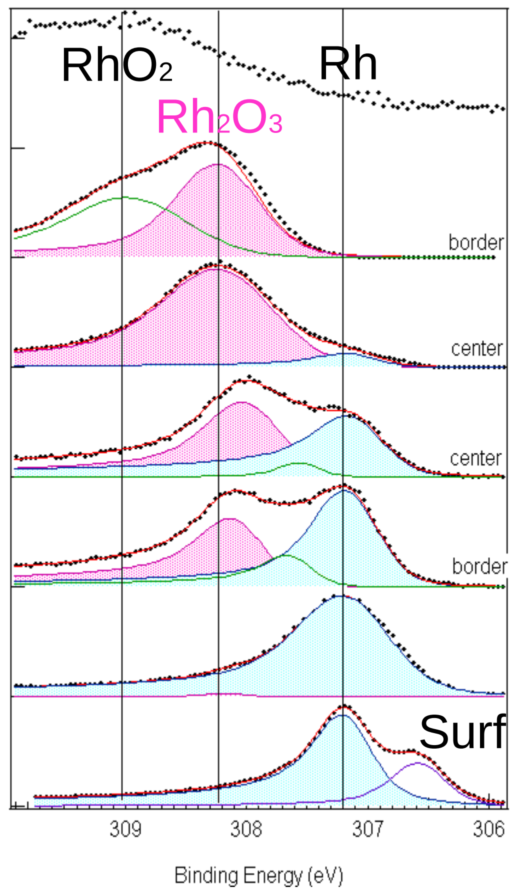
- **Elettra (Nanospectro B.L.)**
- **SLS**
- **MAX-lab**
- **BESSY**
- **Madison**
- **Spring8**

The Photoelectric Process



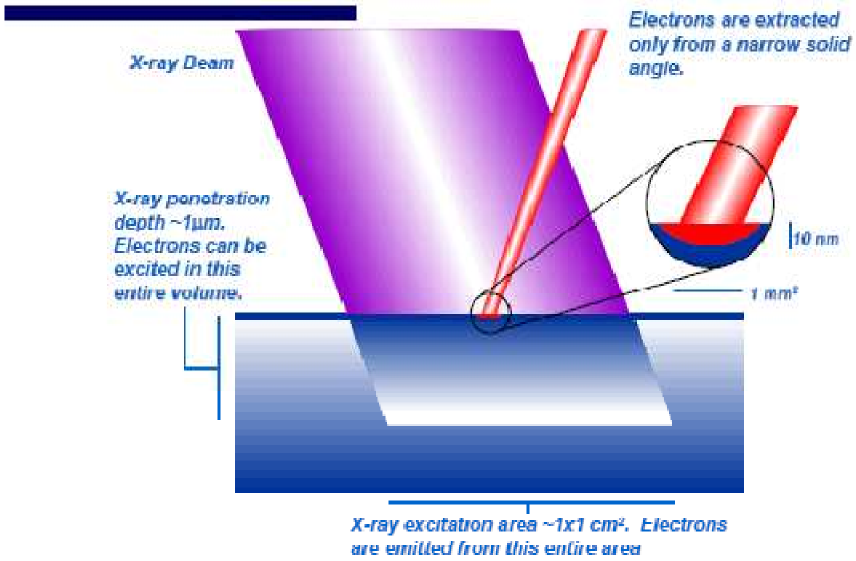


Fine Chemical analysis

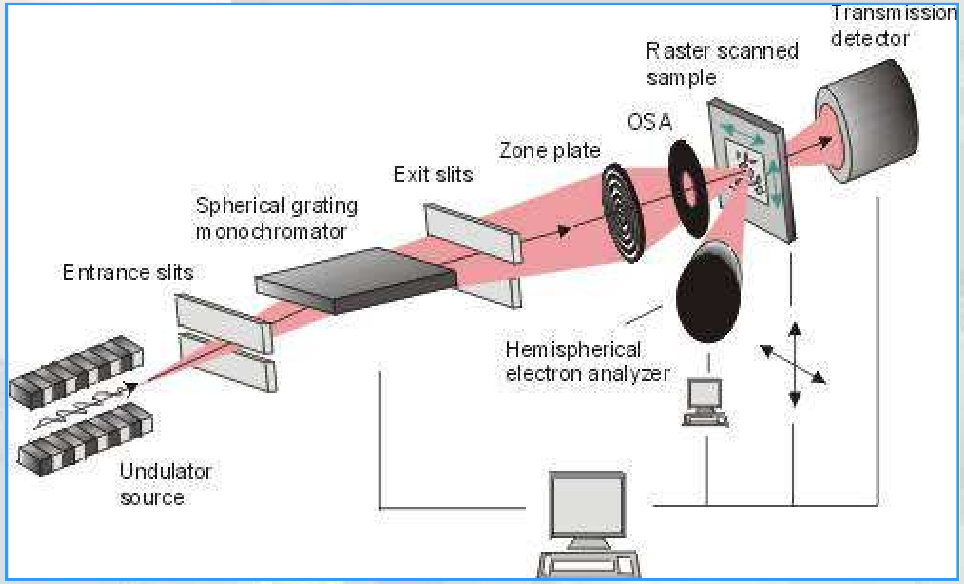


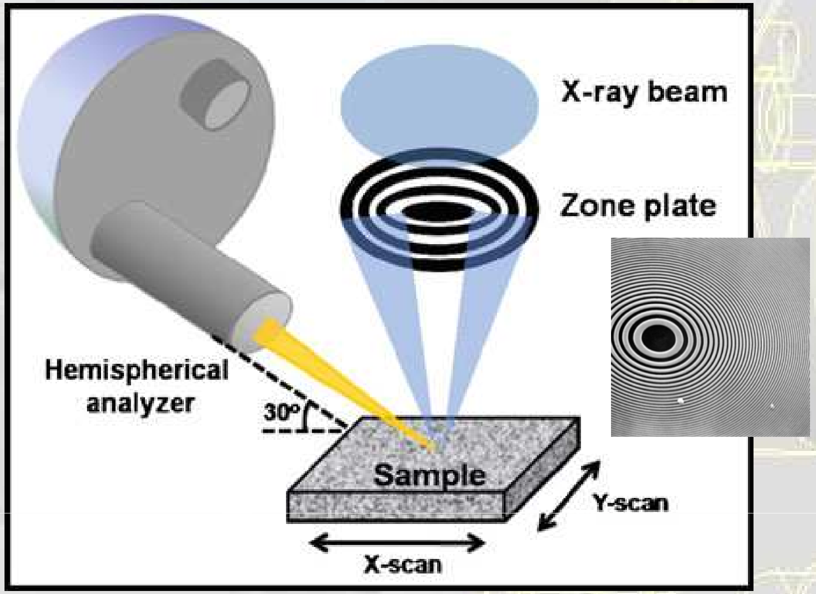
X-ray Photoelectron Spectroscopy

Small Area Detection



SPEM layout and performance



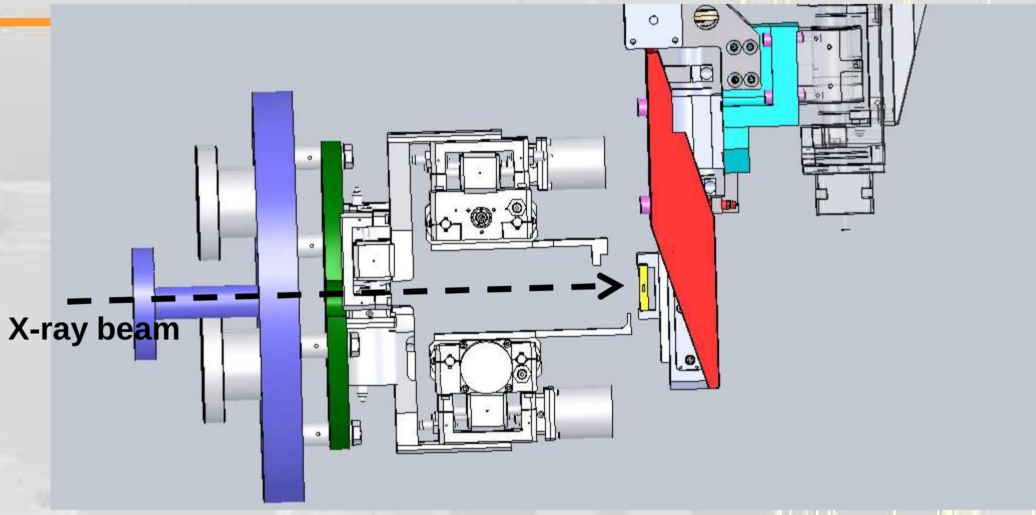


Spatial resolution

- **Imaging: < 50 nm**
- **Microspectroscopy: 120 nm**

Overall energy resolution

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

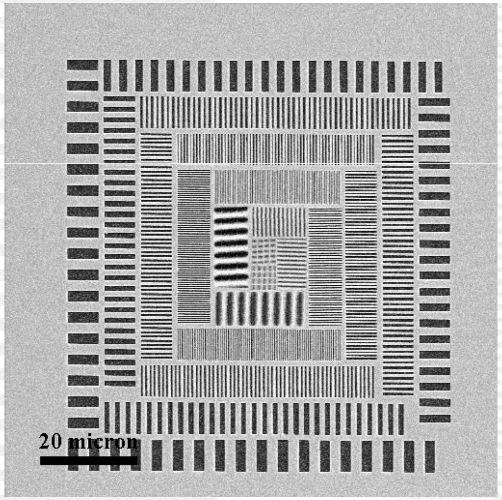


Spatial resolution

Zone plate used: xradia *insight in 3D* Zoneplates.com

Best ZP: D=200 μm, dr=50 nm

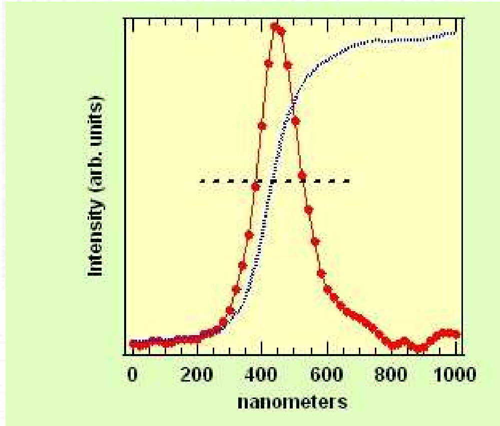
Other sizes: D=250 μm, dr=100nm
D=250 μm, dr=80nm



50 nm test object

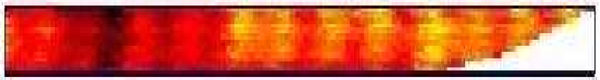
Spectromicroscopy:
real beam size and shape

135 nm

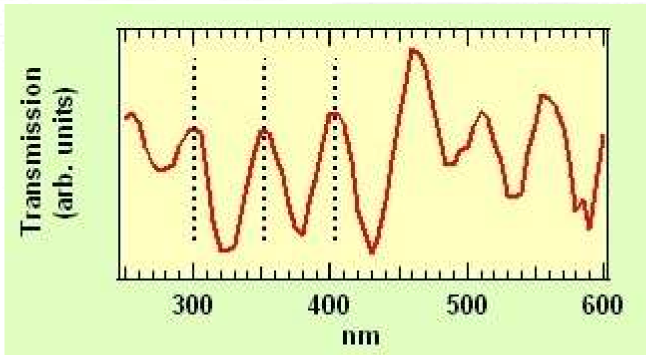


Imaging:
effectice resolution

< 50 nm

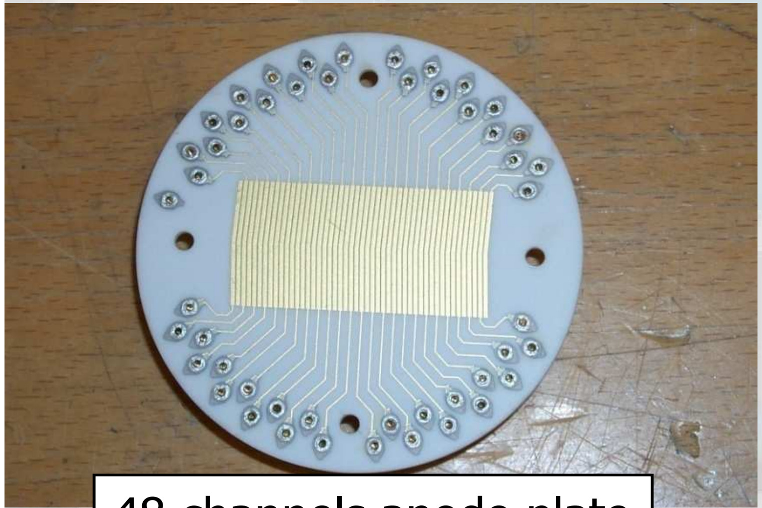


Horizontal scan



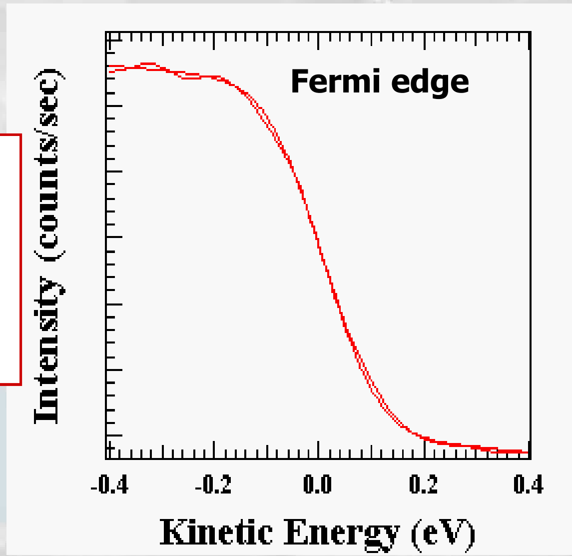
Energy resolution

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

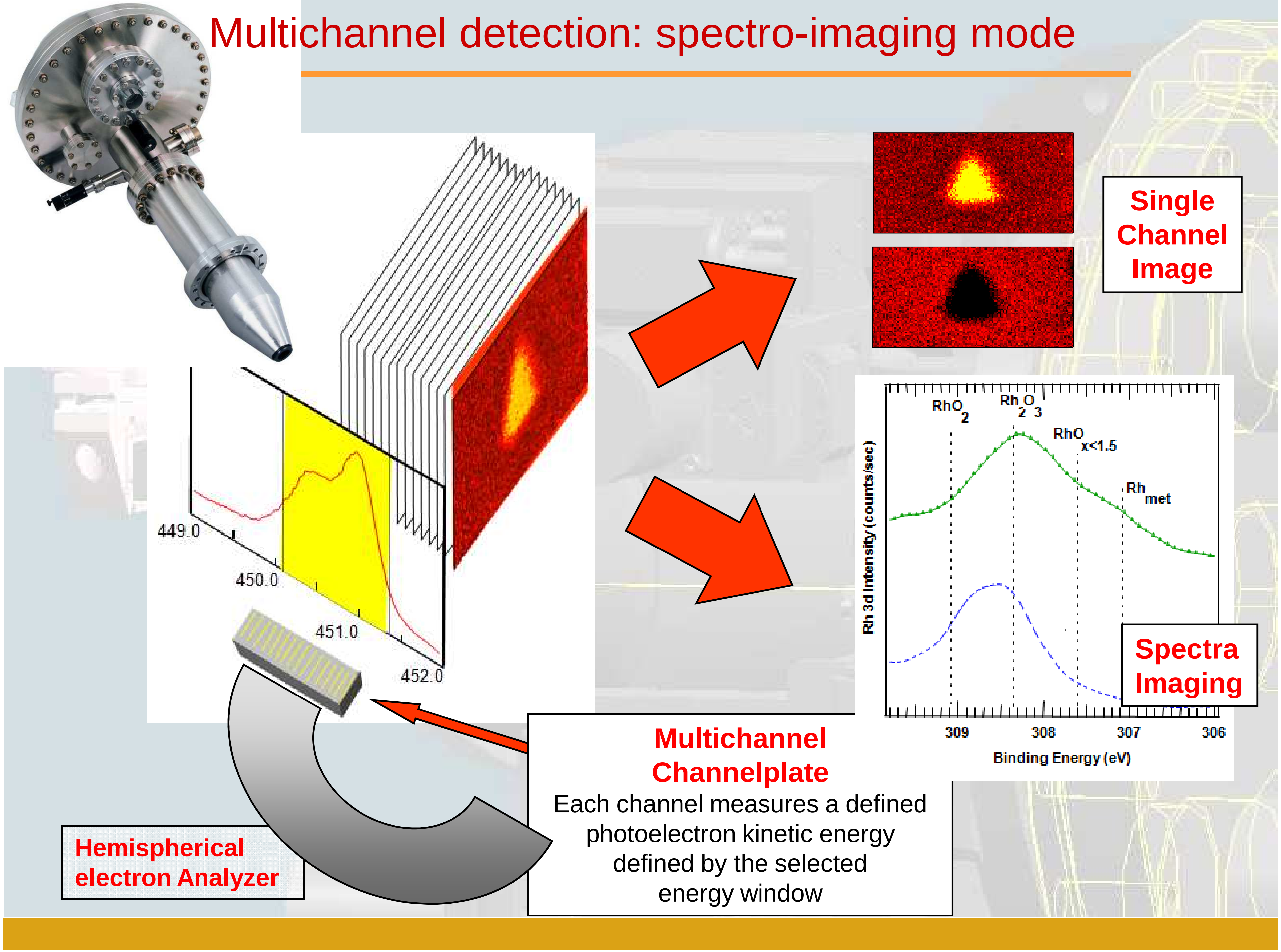


48 channels anode plate

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



Multichannel detection: spectro-imaging mode



SPEM experiments: main topics

Nanostructures/devices characterization

- **MWCNTs mass transport and reactivity**
- **e-noses**
- **Size dependent electronic properties of semiconductors**

Electrochemistry/SOFC

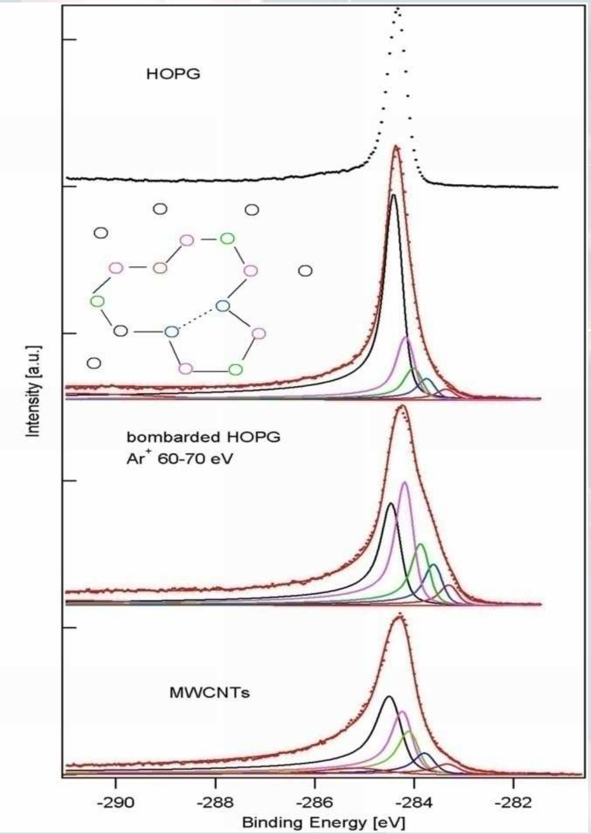
- **Electrochemical stability of materials**
- **Challenging experiments: high temps, biasing, low concentrations**

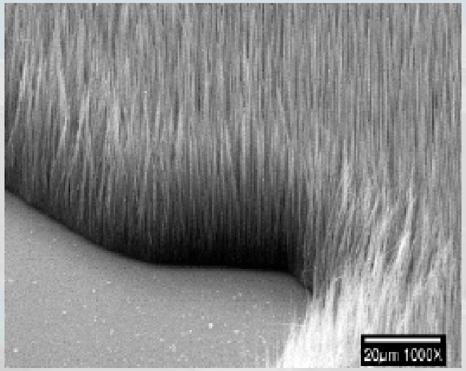
Catalysis

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

Imaging and spectroscopy from metal adsorbate on MWCNT array with SPEM (in collaboration with the *theory@elettra group*)

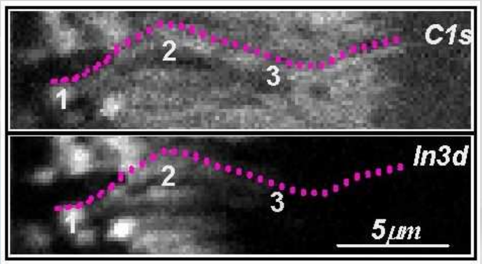
Characterization of MWCNT surface; analysis of C1s photoemission in comparison with clean and defective HOPG surfaces

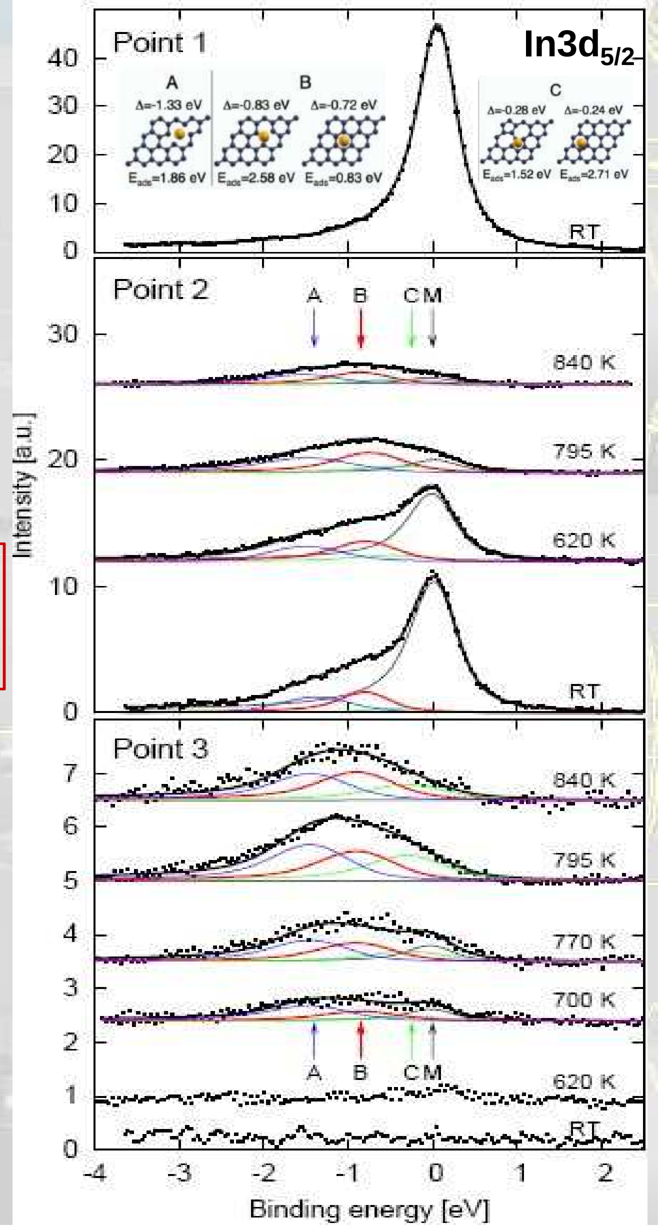




CVD forests from Nanolab Inc.

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

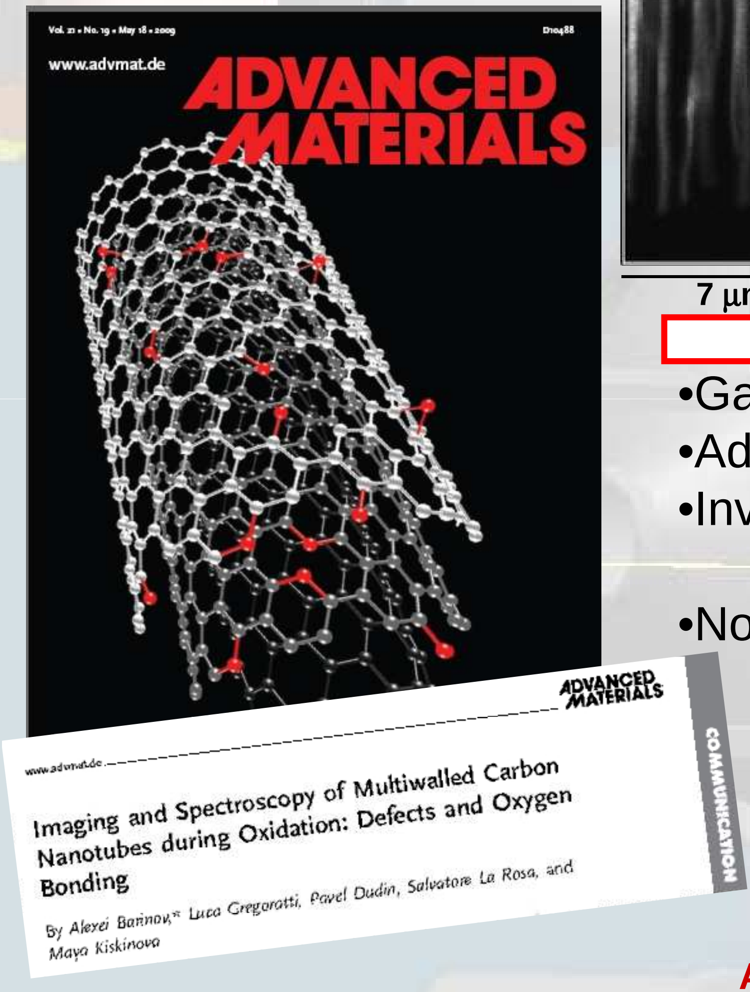




A. Barinov et al. Phys. Rev. Lett. 99, 046803 (2007)

Gas phase oxidation of MCNT

CNT



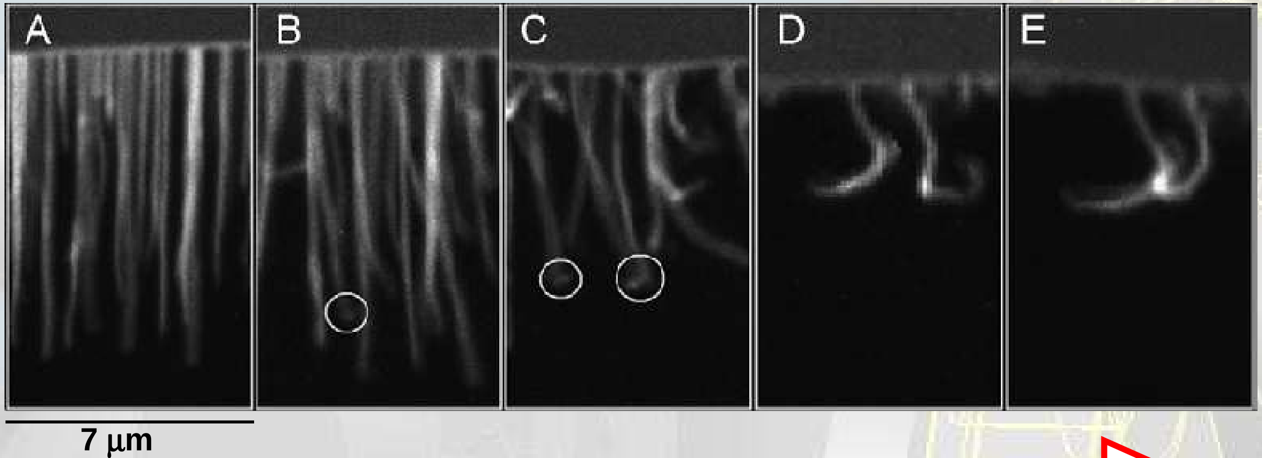
ADVANCED MATERIALS

www.advmat.de

COMMUNICATION

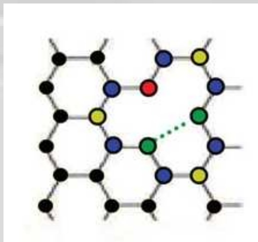
Imaging and Spectroscopy of Multiwalled Carbon Nanotubes during Oxidation: Defects and Oxygen Bonding

By Alexei Barinov,* Luca Gregoratti, Pavel Dudin, Salvatore La Rosa, and Maya Kiskinova

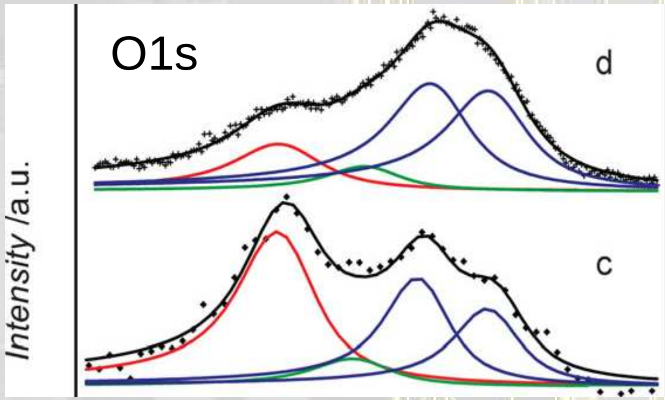


Increasing oxygen dosage

- 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

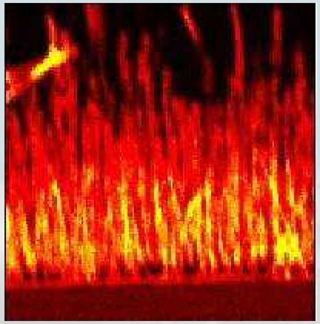


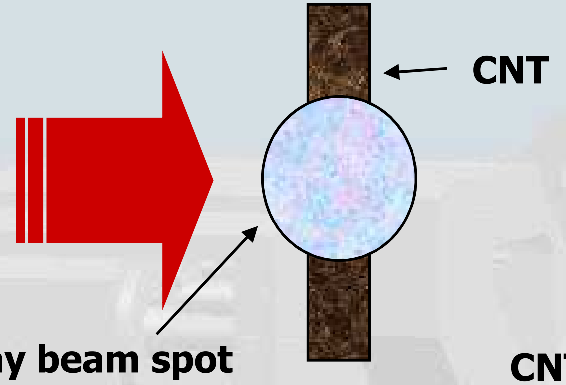
Atomic arrangement

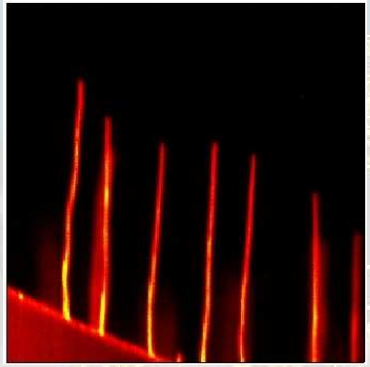


Improving the sample setup for nanostructures

1 From high density to low density MCNT arrays

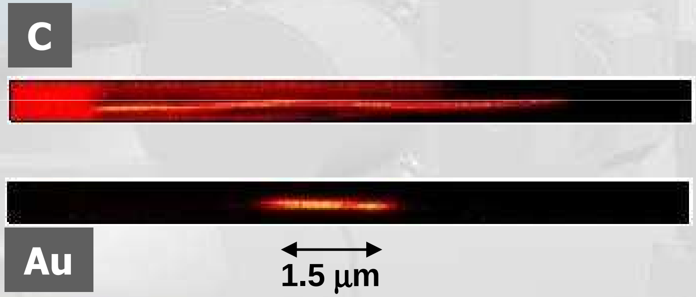


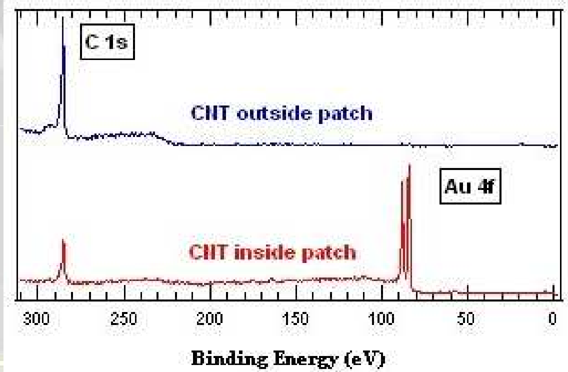




CNT diameter: 60-70 nm

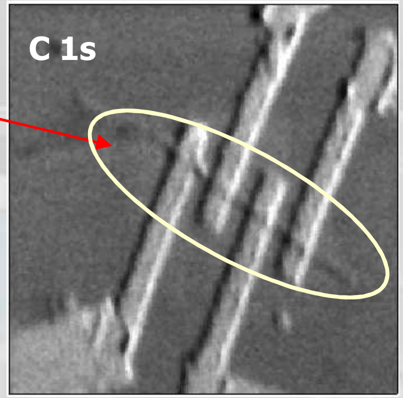
2 Confined patches on single nanostructure

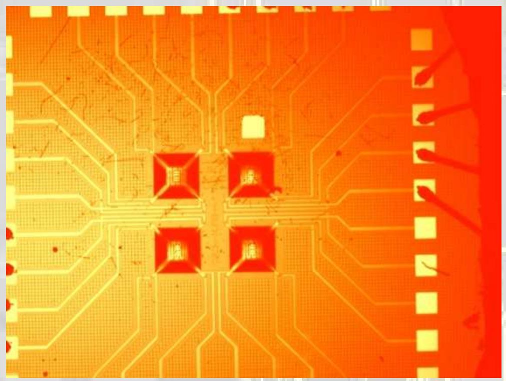




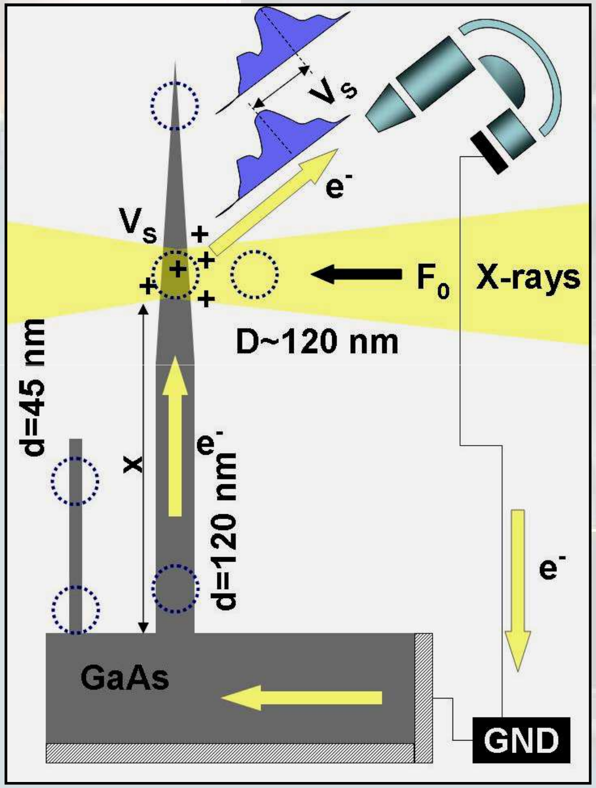
3 Electric transport/ biasing

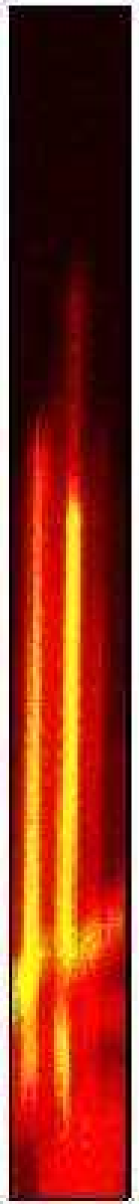
MCNT

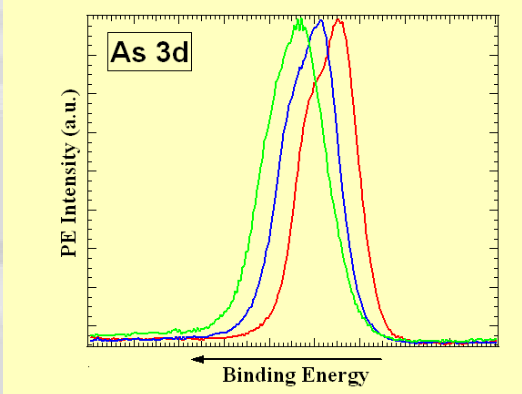




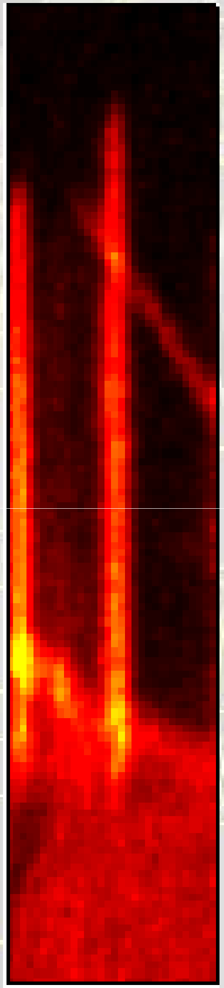
Effects on size and surface chemistry on the conductivity of MBE-grown GaAs nanowires *(in collaboration with S. Rubini – TASC Laboratory - Italy)*







- Increasing surface-to-volume ratio
- Size dependence of the depletion width, band gap widths, recombination barriers, etc.
- i.e. Debye length comparable to the radius of NW



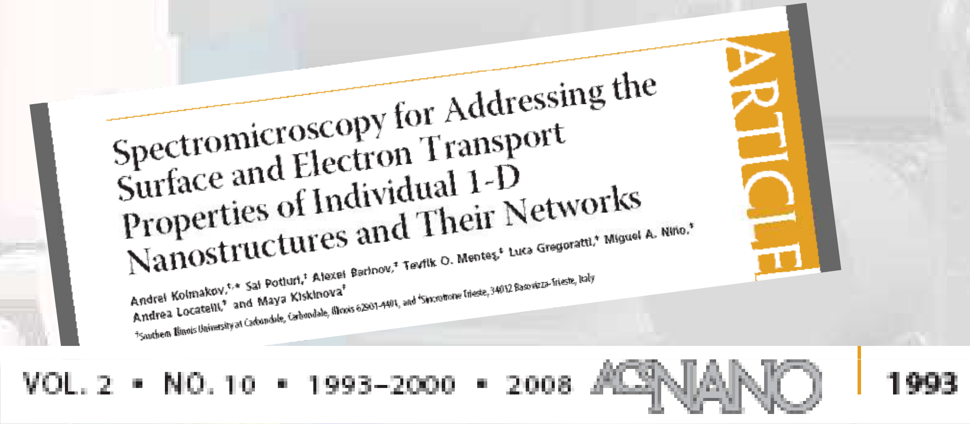
45 nm width GaAs wires!

F. Jabeen et al. in preparation

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, …

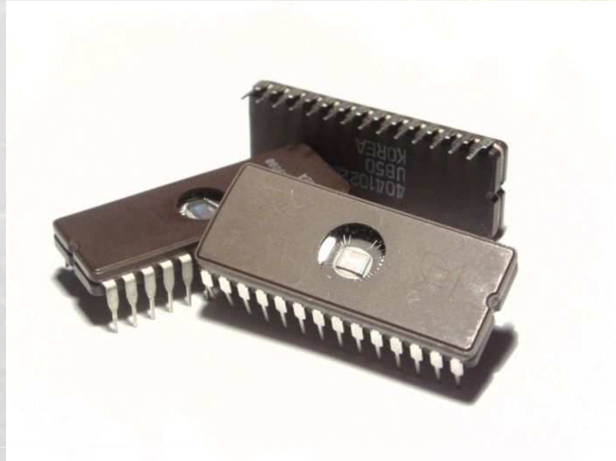

ARTICLE

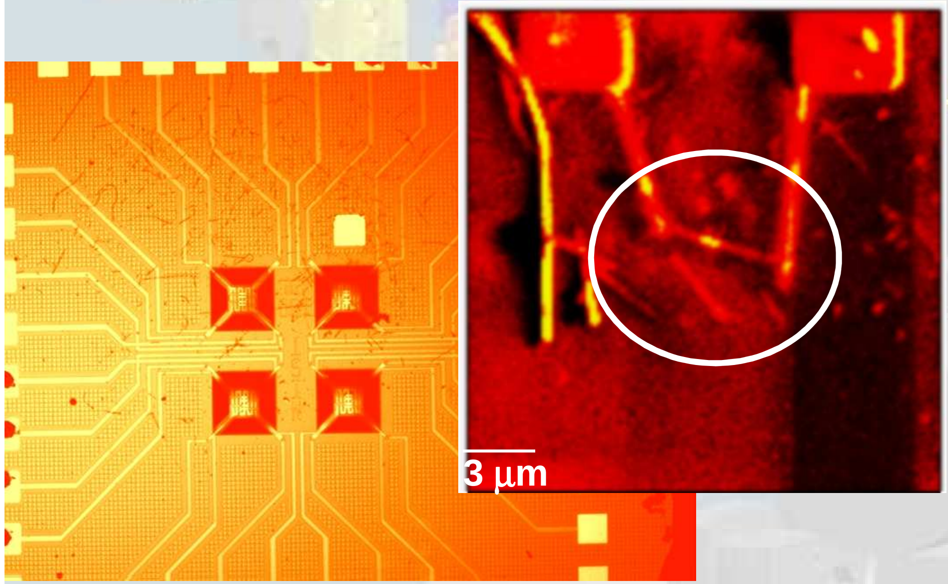
Spectromicroscopy for Addressing the Surface and Electron Transport Properties of Individual 1-D Nanostructures and Their Networks

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

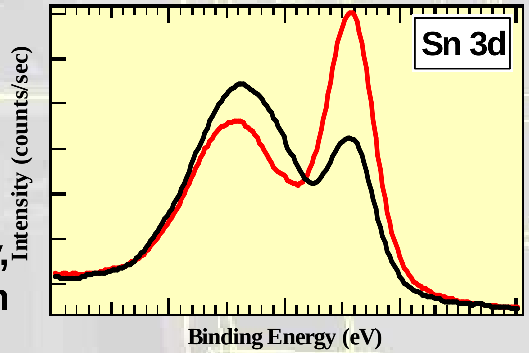
[†]Southern Illinois University at Carbondale, Carbondale, Illinois 62901-4401, and [‡]Sincrotrone Trieste, 34012 Basovizza-Trieste, Italy

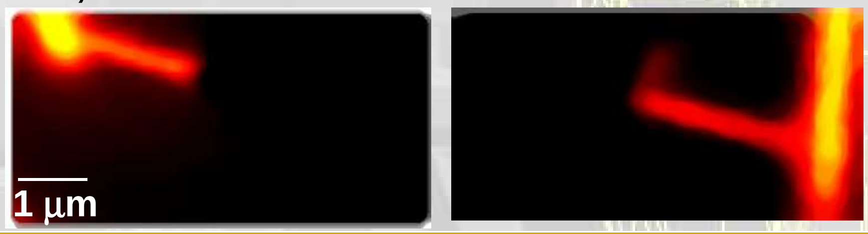
VOL. 2 • NO. 10 • 1993–2000 • 2008 ACSNANO 1993





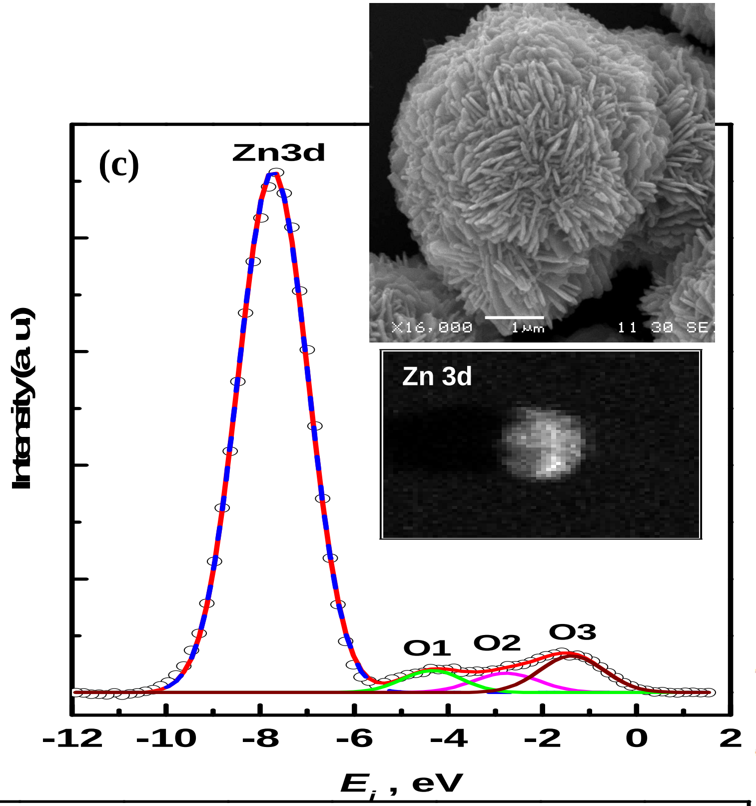
- Addressing the electron transport in a workin device (temperature, close biasing, etc.)
- Surface stoichiometry, coordination, oxidation state, etc.

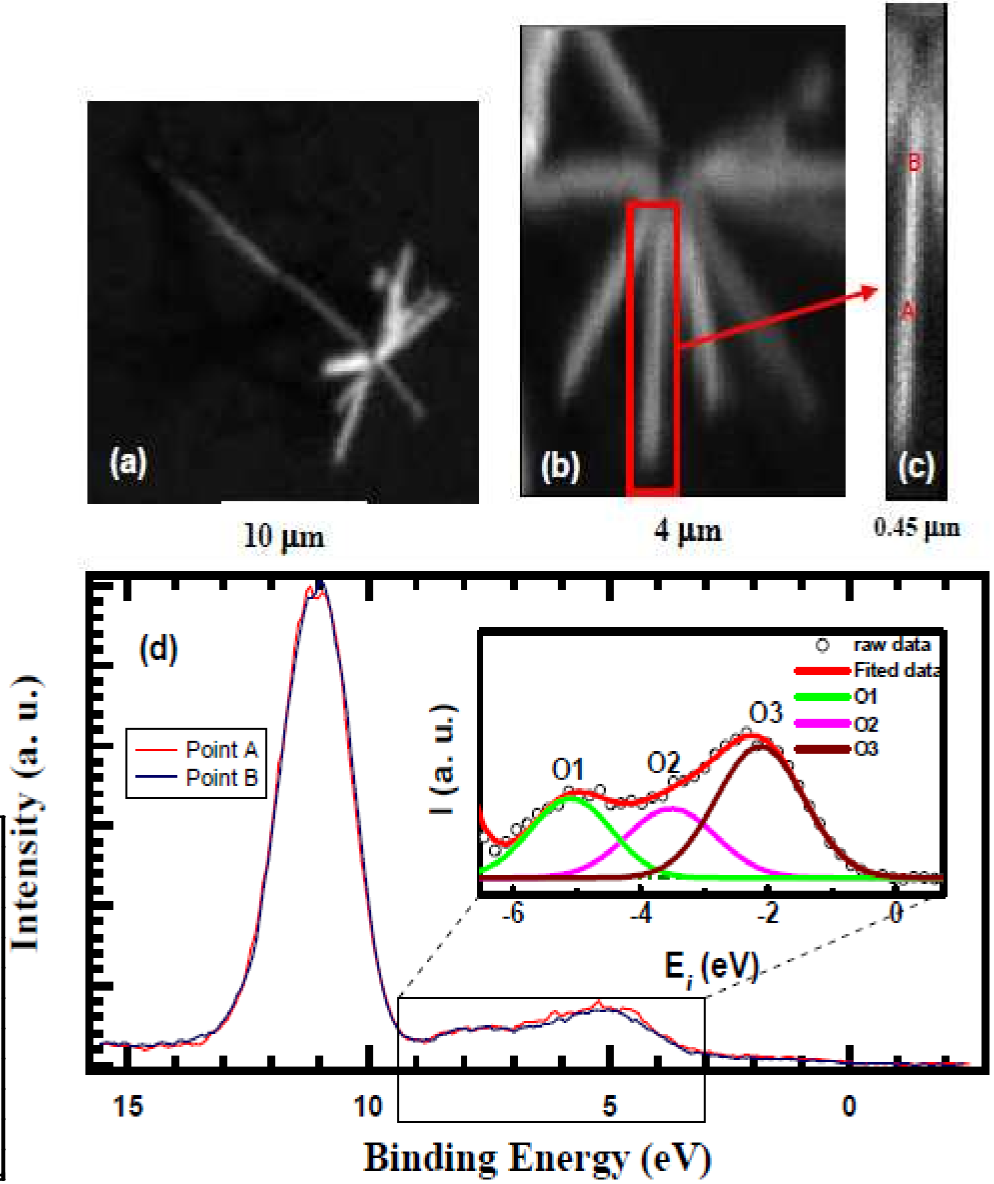


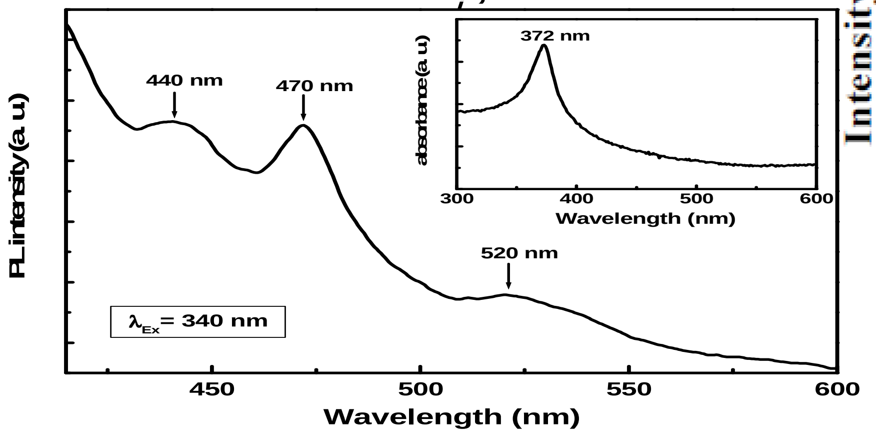


A. Kolmakov et al. ACSNano 2 (2008) 1993

Spectromicroscopy and photoluminescence analysis of ZnO nanostructures





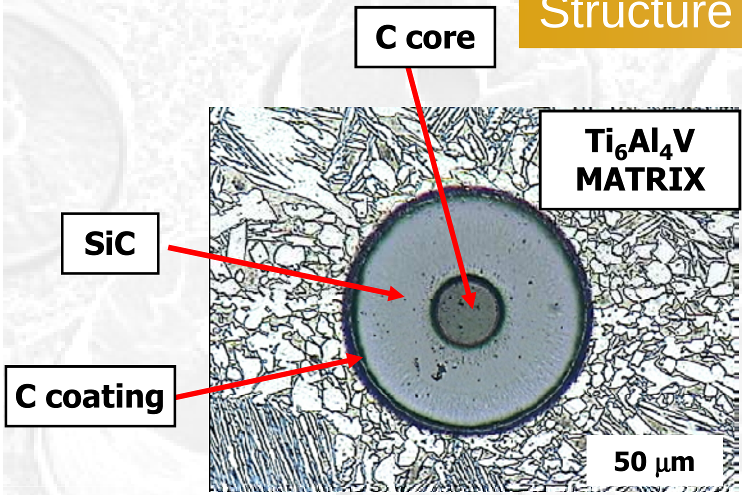


M. Kazemian Abyaneh et al. J Nanopart Res 13(2010)1311

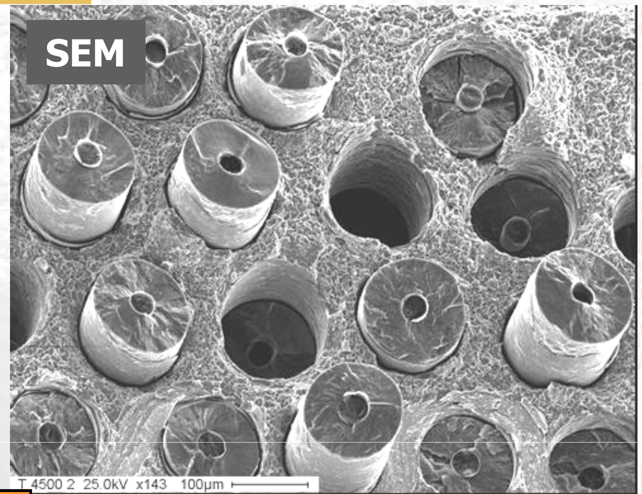
Ti6Al4V-SiC$_f$ composite produced by HIP for aeronautical applications

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

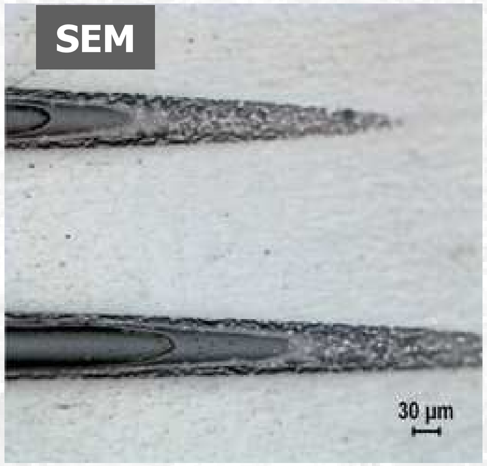
Structure of the composite material

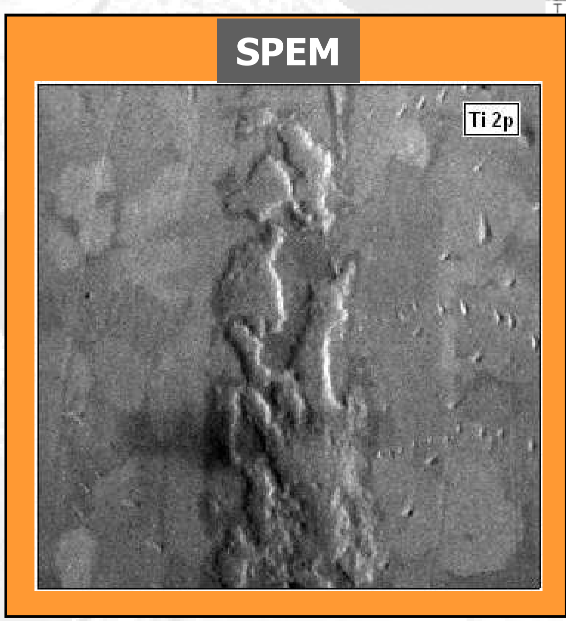


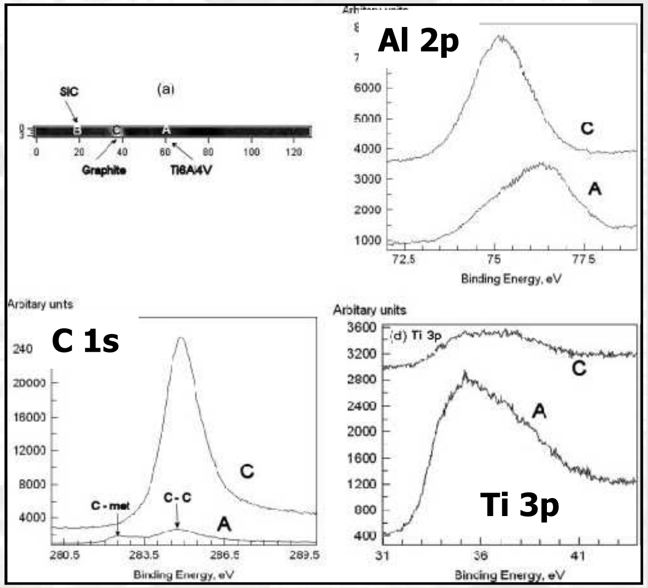
Get access to the interfaces



Sample lapping at grazing angle





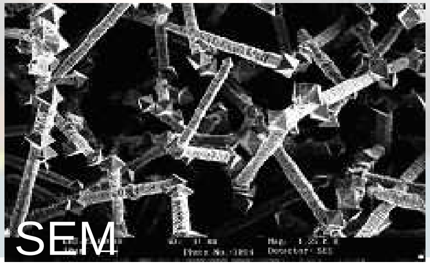


S. Kaciulis et al. *Surf. Interface Anal.* **2010**, *42*, 707–711

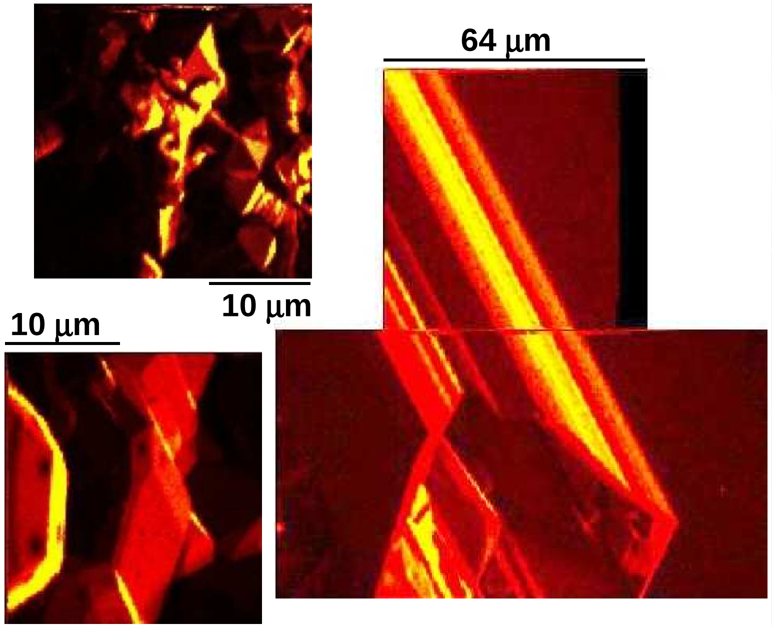
Compositional and electronic study of TCO nano and microtubes

(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



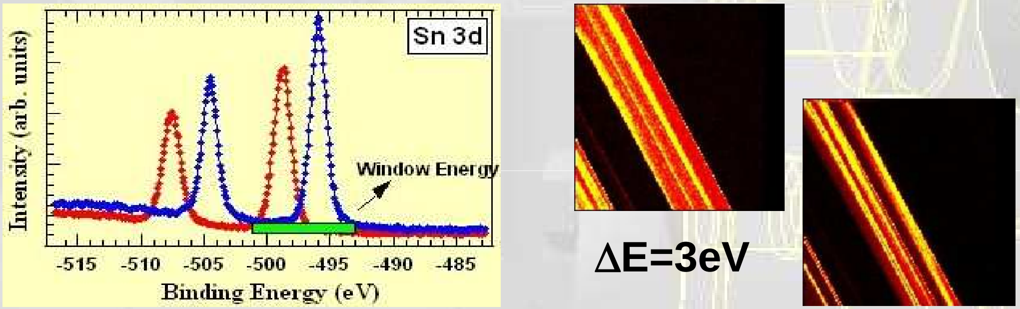
SPEM images



D. A. Magdas et al. Superlat. and Microstr. 45 (2009) 429-434 ,
D. Maestre et al. Journ. of Appl. Phys. 103, 093531 (2008)
D. Maestre et al. J. Phys. Chem. C, 2010, 114 (27), pp 11748–11752

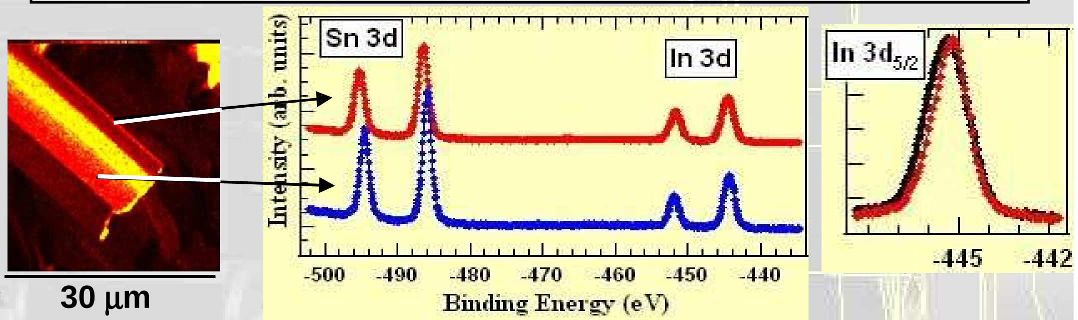
Electronic behaviour of a single structure

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



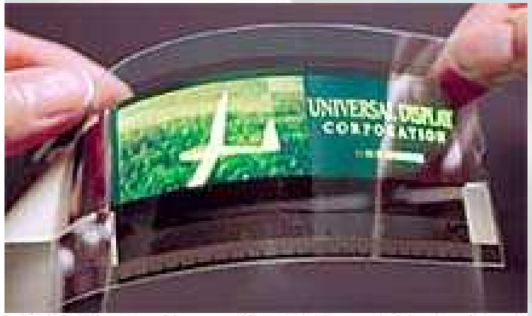
Local chemical composition of the structures

- Heterogeneous elemental distribution locally defined
- Fine chemical analysis

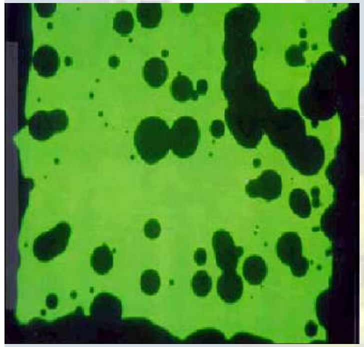


Degradation of light emitting diodes: a SPEM analysis

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



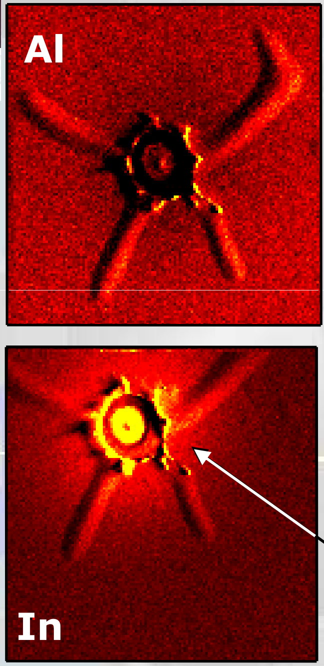
OLED Display Screen (from Universal Display Corp)



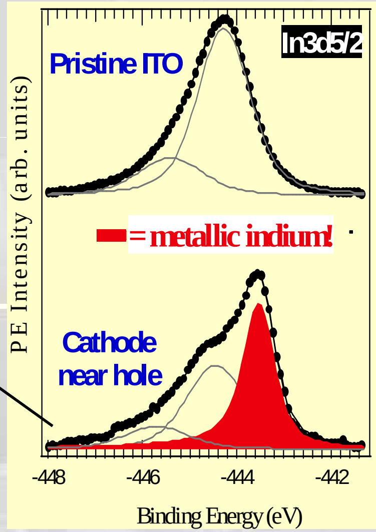
Dark spot in OLED

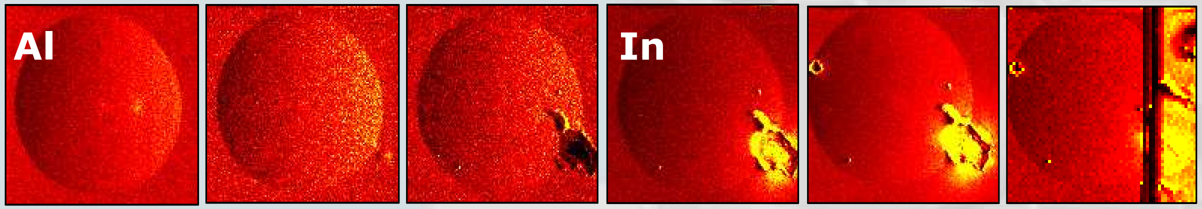
OLED exposed to atmospheric moisture: failure due to light emission

64 µm



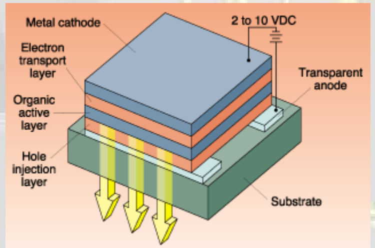
•**Decomposition of ITO**



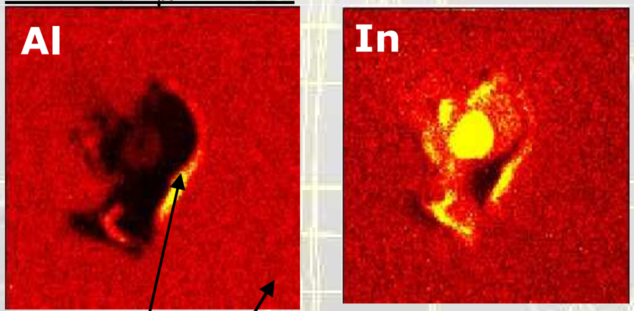


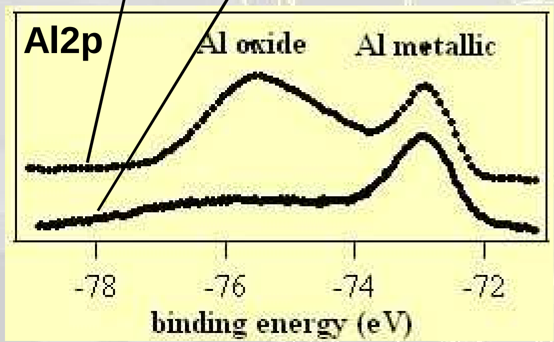
increasing voltage and operating time

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



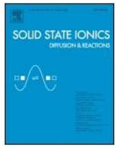
64 µm





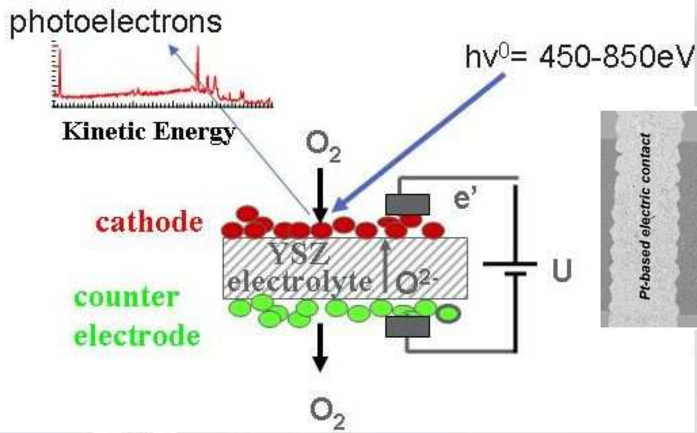
P. Melpignano et al. Appl. Phys. Lett. 86, 041105 (2005), S. Gardonio et al. Org. Electr. 8 (1), 37-43, (2007)

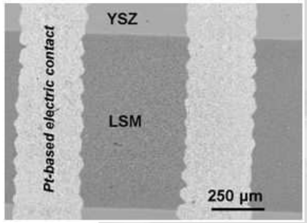
Solid State Ionics Award
for the Best Paper in the journal
Solid State Ionics in 2008



Operating SOFC: mass transport

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

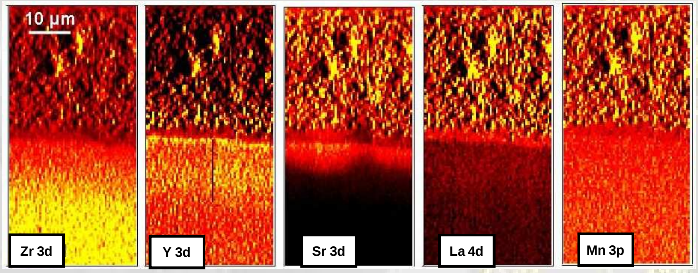




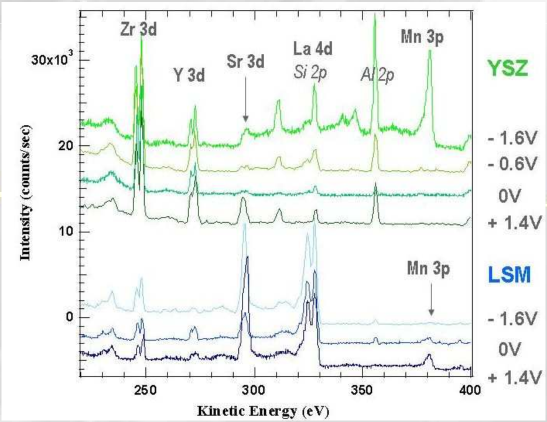
Strongly constraining experimental setup

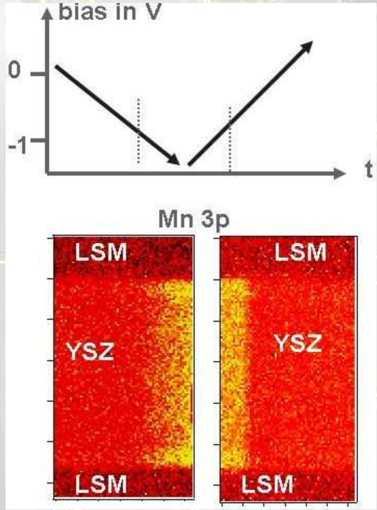
- •Real samples
- •High T = 650-700°C
- •pO_2=1x10^{-6} mbar
- •Applied potentials -2V<U<+2V
- •Surface sensitive technique
- •High lateral resolution

Elemental distribution at electrolyte/LSM interface



Surface composition change with bias





Observation and explanation of electrochemical cathode activation

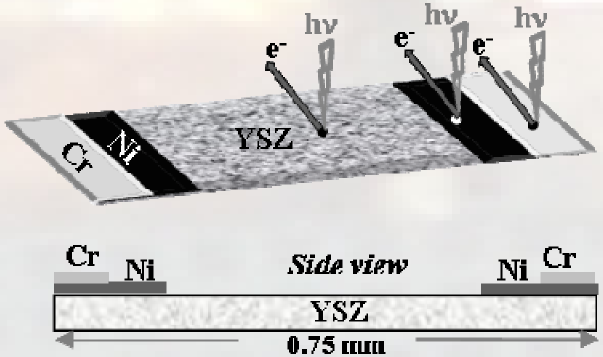
- •Strong current increase under negative bias when Mn spreads on electrolyte
- •Mn2+ electrolyte surface enrichment→electrolyte surface conductivity → direct oxygen incorporation into electrolyte
- •Oxygen incorporation extends under bias from TPB to the entire electrolyte surface

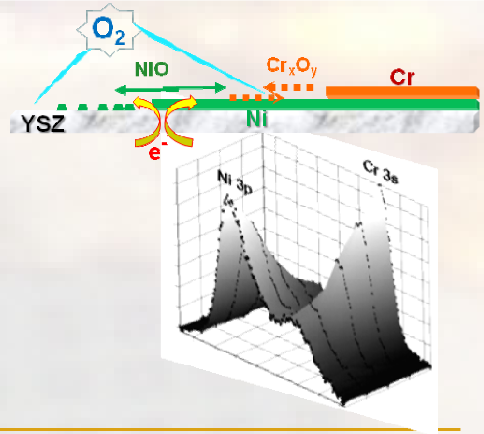
M. Backhaus et al. Solid State Ionics 179 (2008) 891–895 , M. Backhaus et al. Advances in Solid Oxide Fuel Cells III 28 (4), 2007

SOFC & electrochemical architectures

B. Bozzini

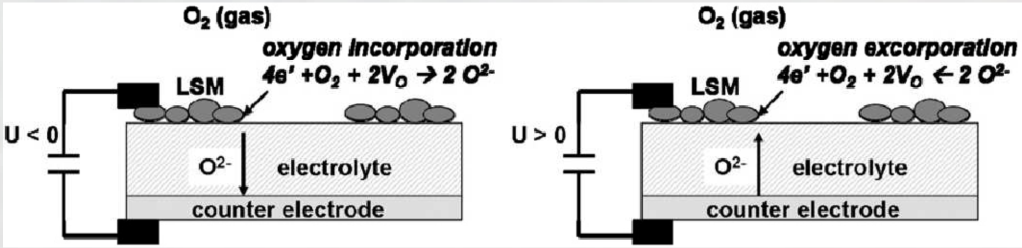
UNIVERSITÀ DEL SALENTO

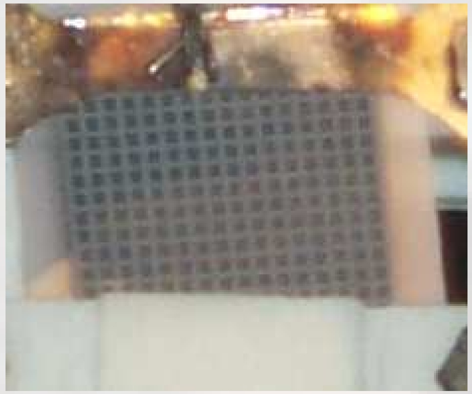




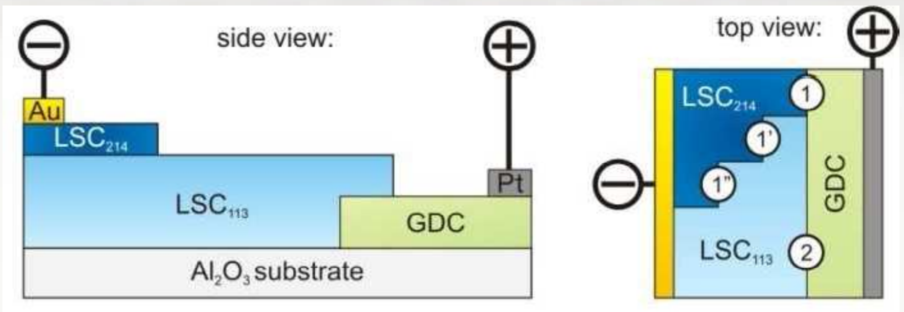
M. Backhaus

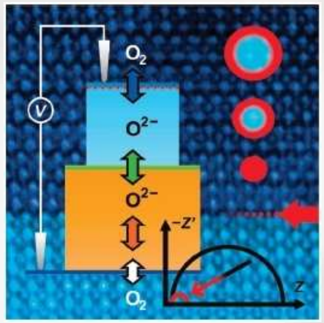
CORNING





E. Mutoro

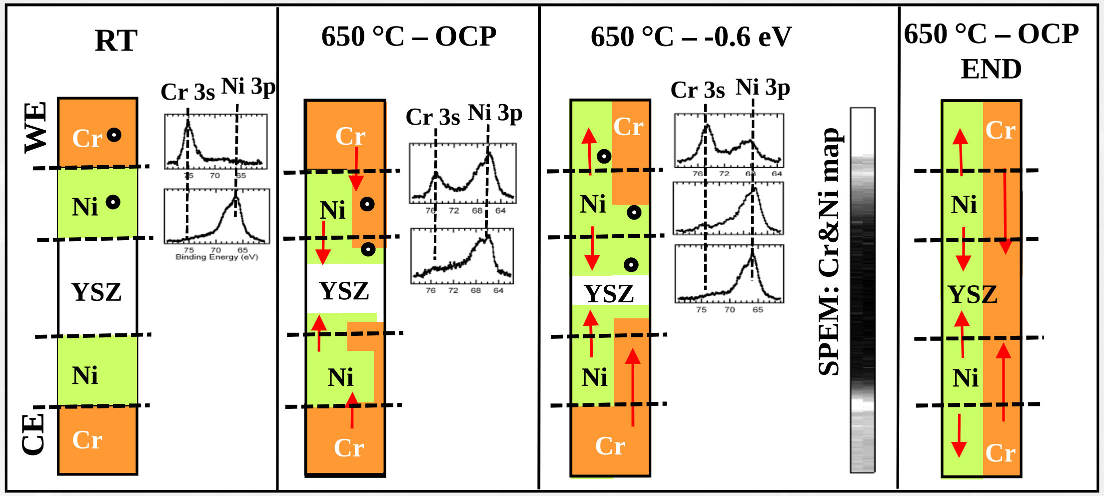




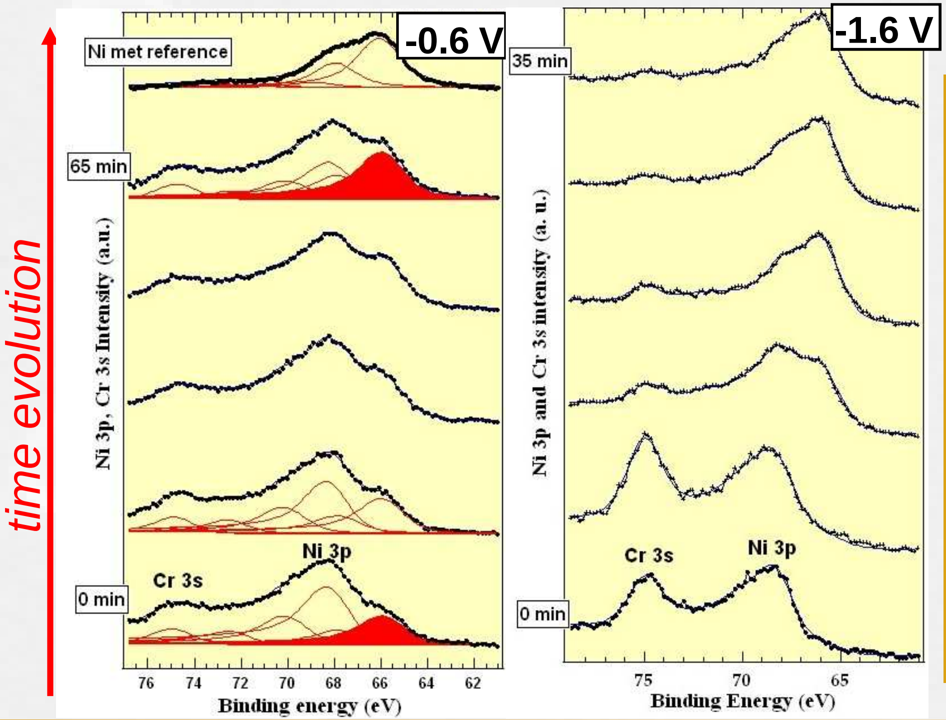
Material stability of SOFC metal interconnects

(in collaboration with B. Bozzini – Uni. Salento – Italy)

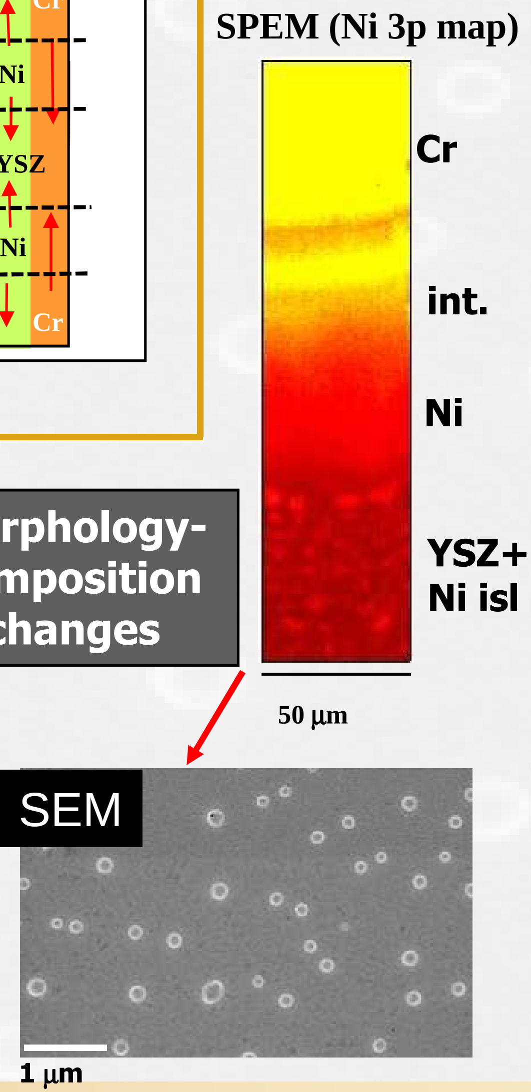
Temperature-induced and potential-induced diffusion of Ni and Cr



Oxidation-reduction processes

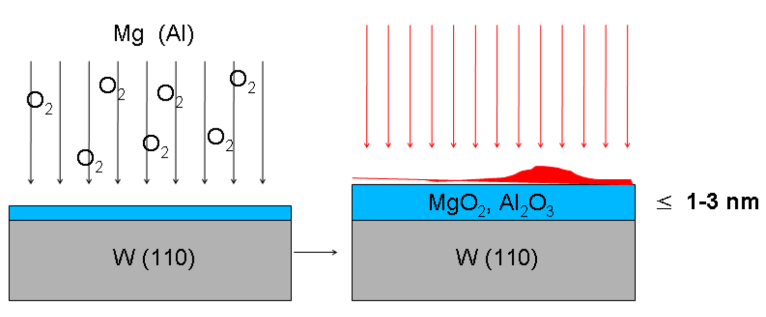


Morphology-composition changes



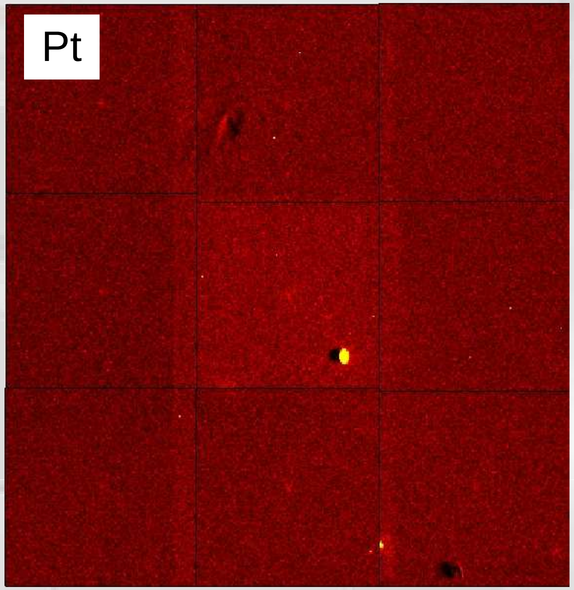
‘Material’ gap: from model crystalline materials to metal nano-particles on metal oxide. In situ PLD particle deposition

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



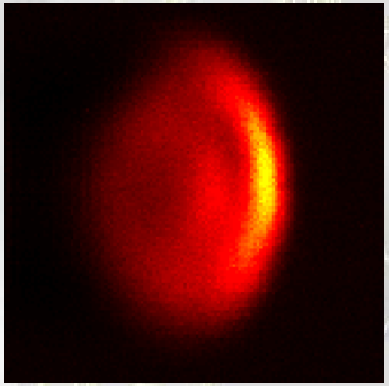
No charging of the substrate because of the low thickness, XPS and SPEM are possible

SPEM



64 µm

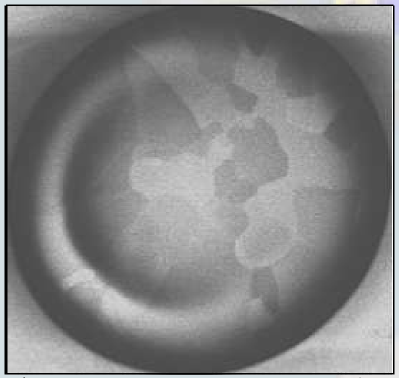
Low density of micron sized particles



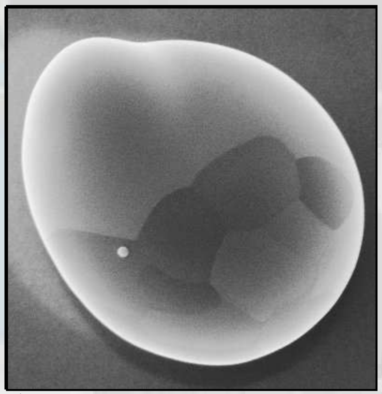
3 µm

Nano-cluster of average size < 10 nm

SEM



1.5 µm

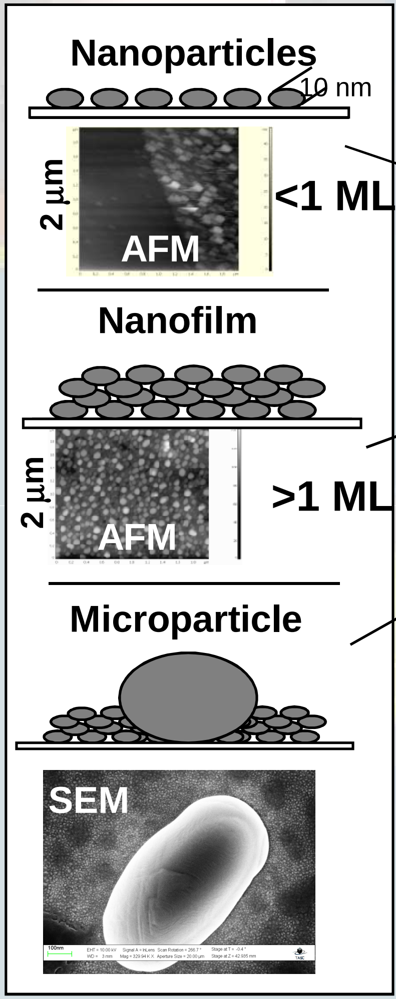


0.7 µm

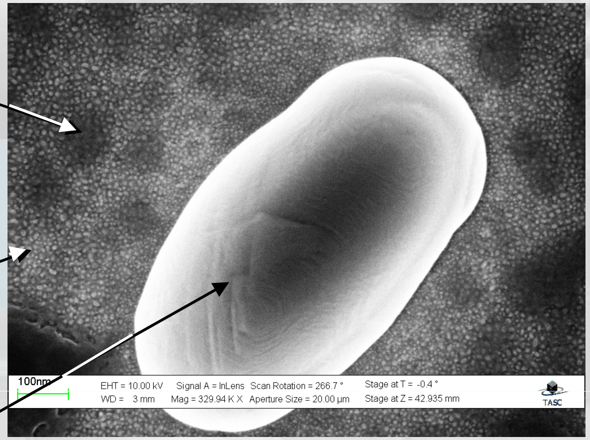
- Poly-crystalline nature of the particles
- Size effects during chemical reaction
- Proximity effects
- Simple model reaction: O_2 (+H_2)
- Unconventional procedure for particle generation (thermodynamics)

M. Dalmiglio et al. J. Phys. Chem. C, 114(2010) 16885

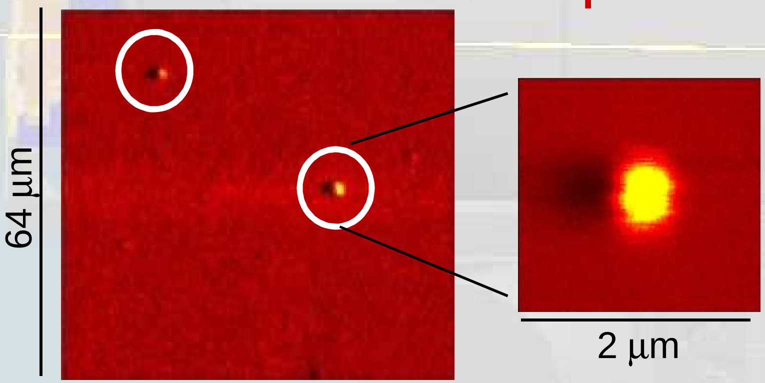
‘Material’ gap: from model crystalline materials to metal nano-particles on metal oxide. In situ PLD particle deposition



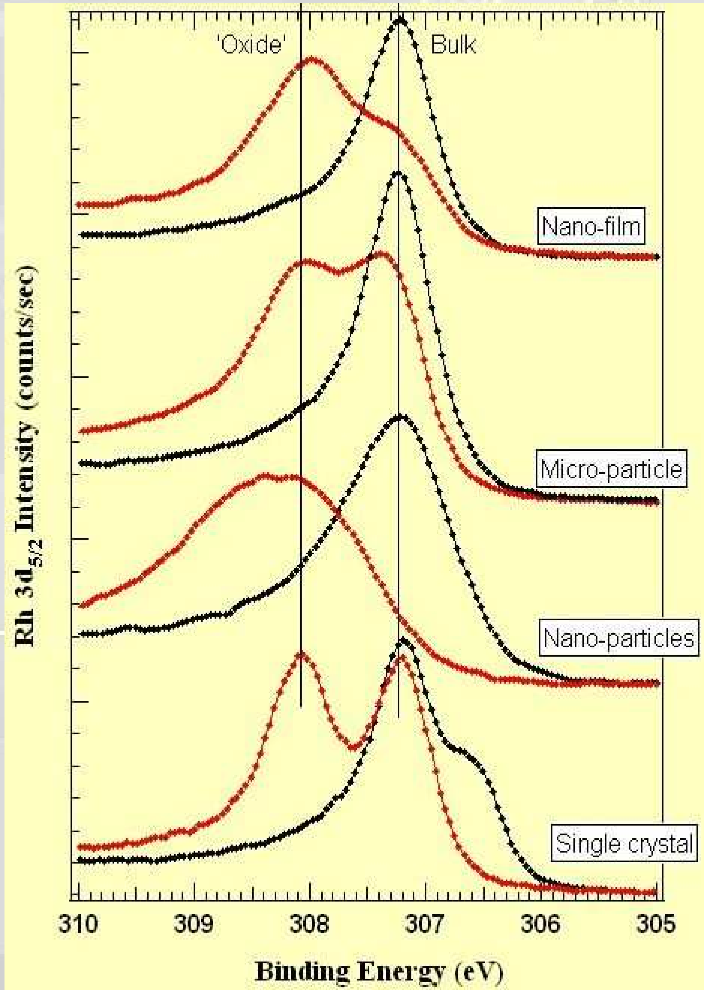
Rh on MgO/W(110) PLD species are highly-defected due to non-thermic evaporation



SPEM Rh3d maps



Oxidation/reduction reactions



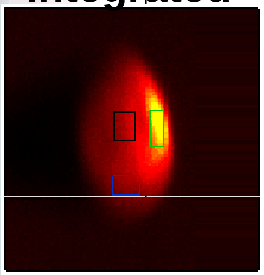
- **The nanoparticles/nanofilm possess different oxidation/reduction ability than the microparticle**
- **Reducing rate: Micro-part.> Nano-crystalline film > Nano-particles**
- **Micro-particles of similar sizes show variation in the reactive properties: different structure, local environ.**

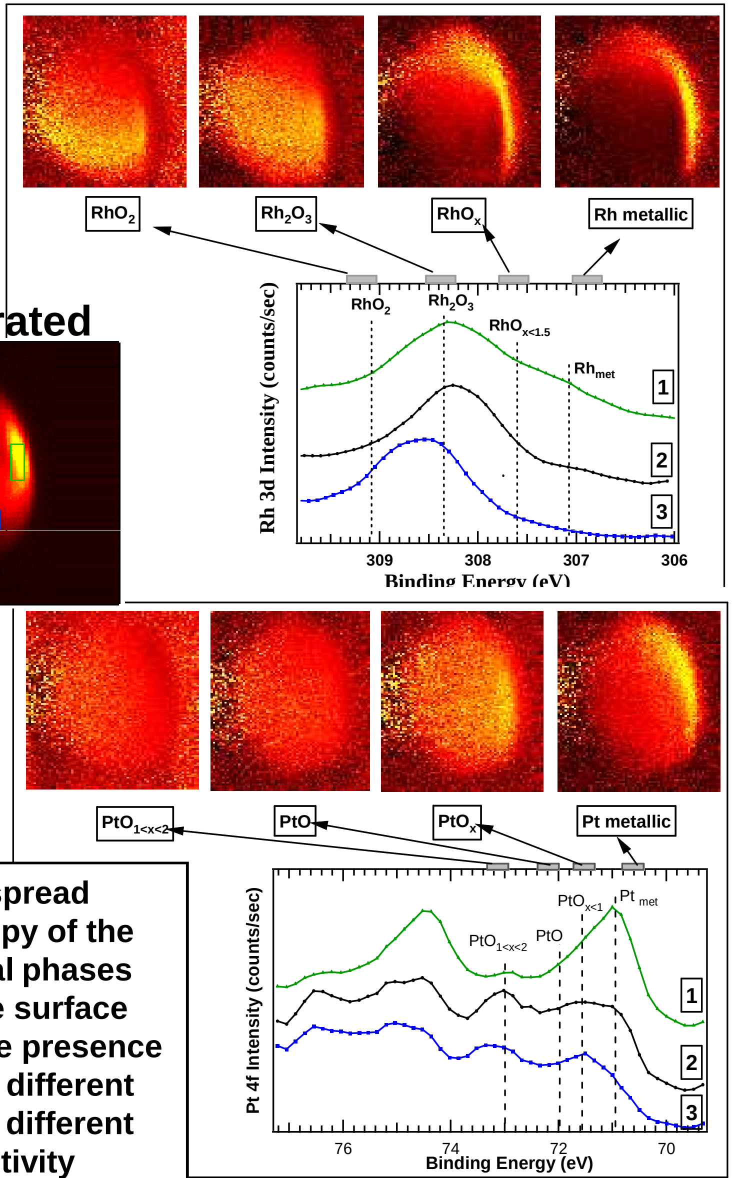
P. Dudin et al. J. Phys. Chem. C 2008, 112, 9040–9044

Oxide phase distribution on the particles surface

SPEM

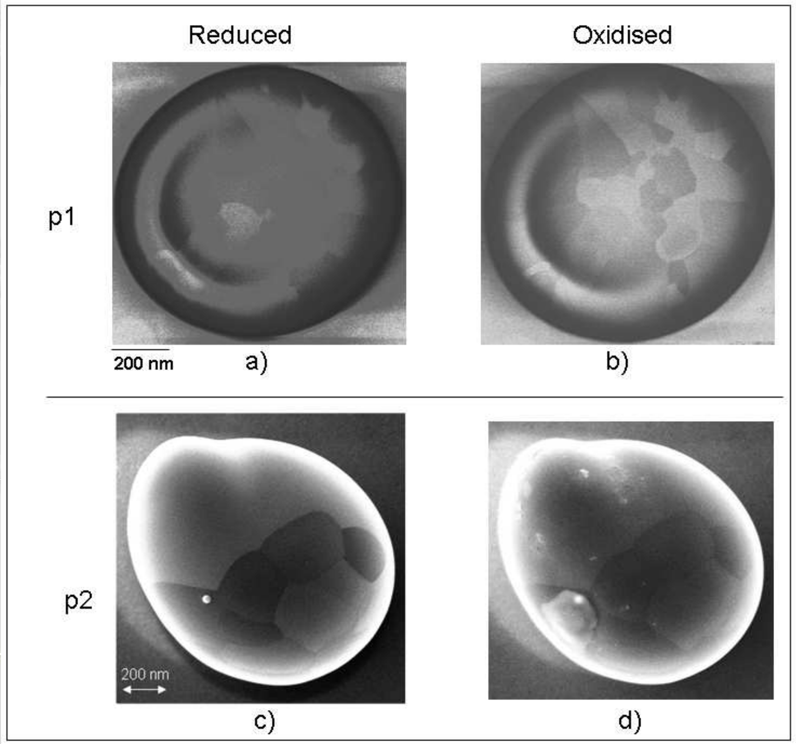
Integrated





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

M. Dalmiglio et al. J. Phys. Chem. C http://dx.doi.org/10.1021/jp910370r

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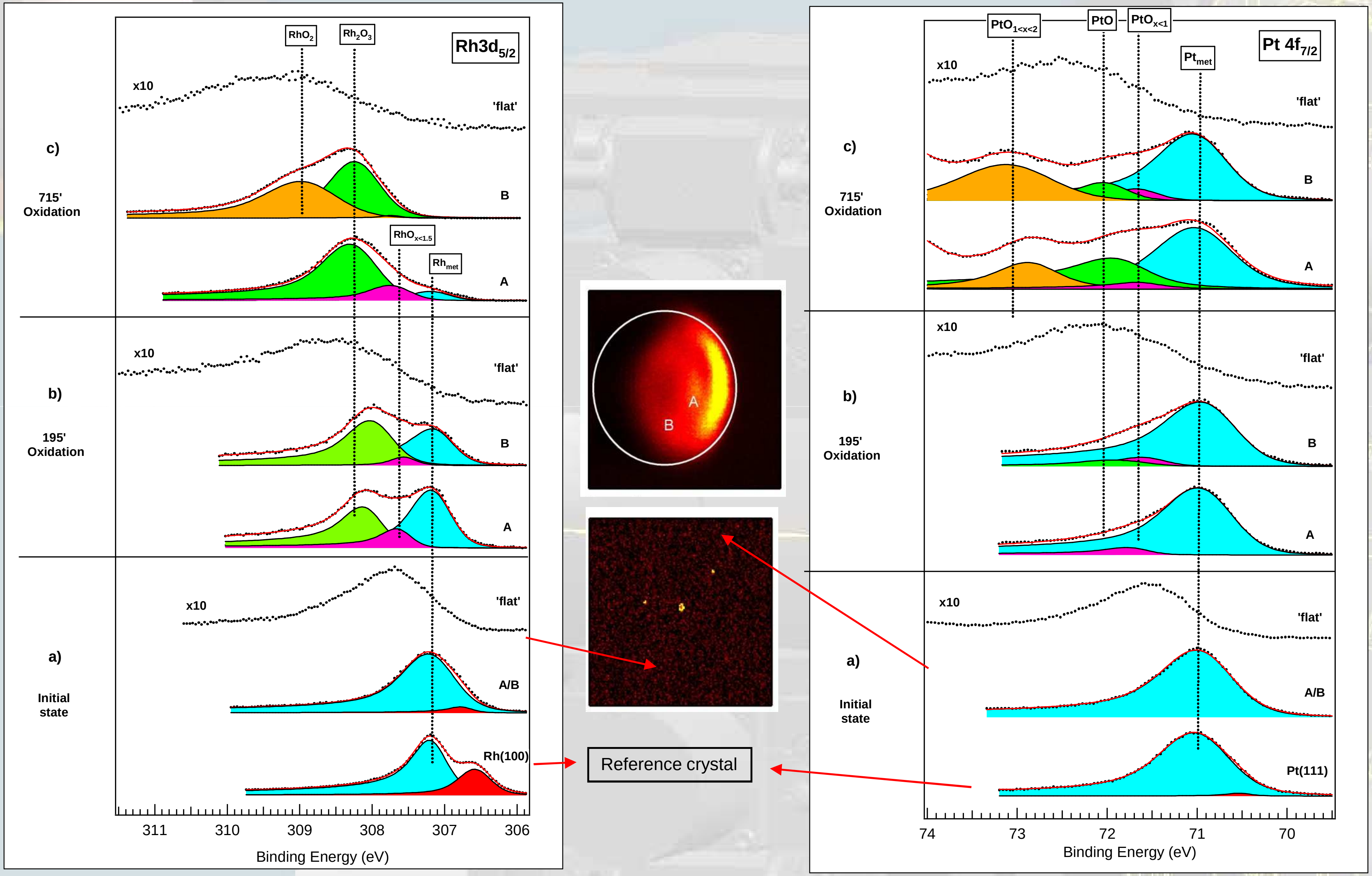

M. Dalmiglio et al. J. Phys. Chem. C, 114(2010) 16885

Thank You

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