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Scanning Photoemission Microscopy: Applications and Examples

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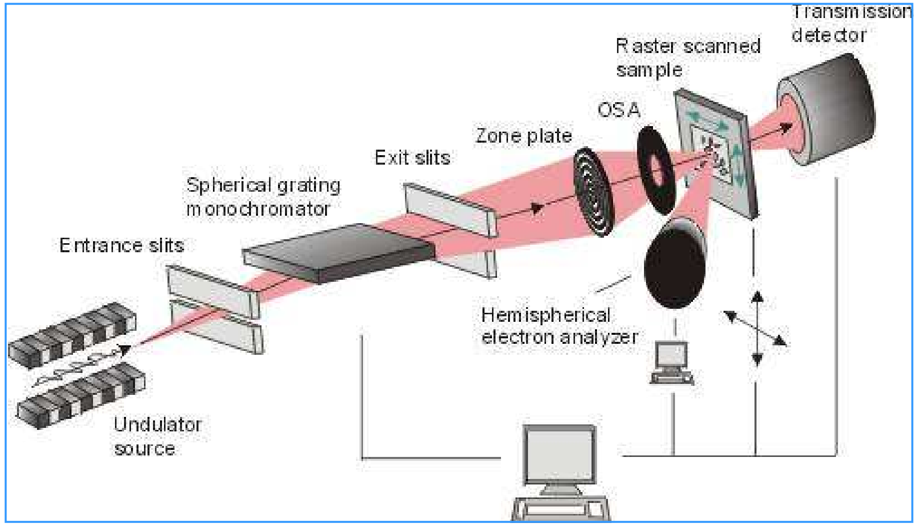
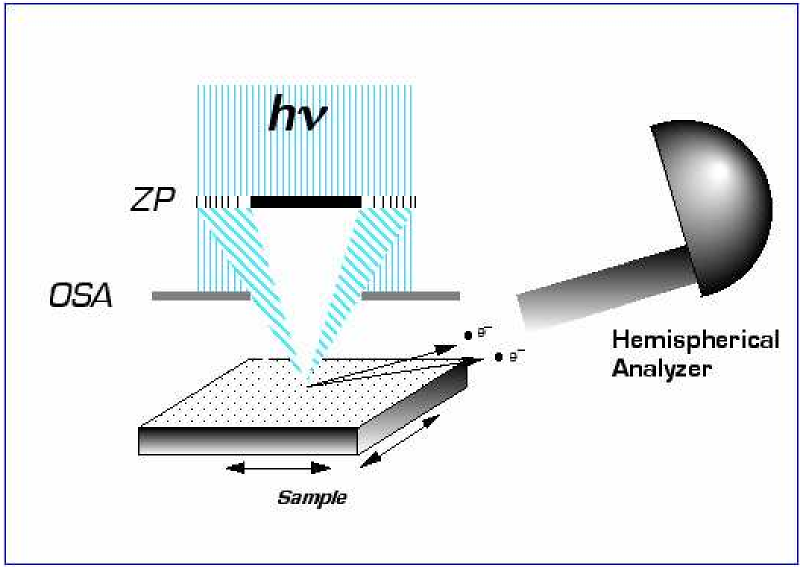
X-ray microscopy: method characteristics

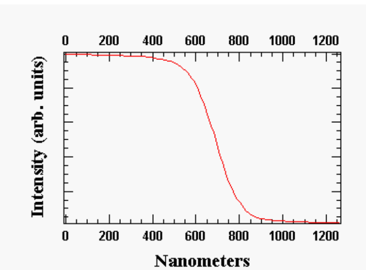
Beamline Layout and SPEM setup





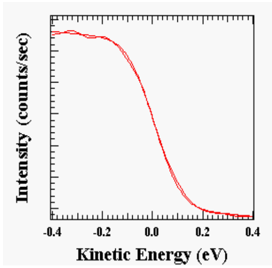
SPEM actual performances

Spatial resolution



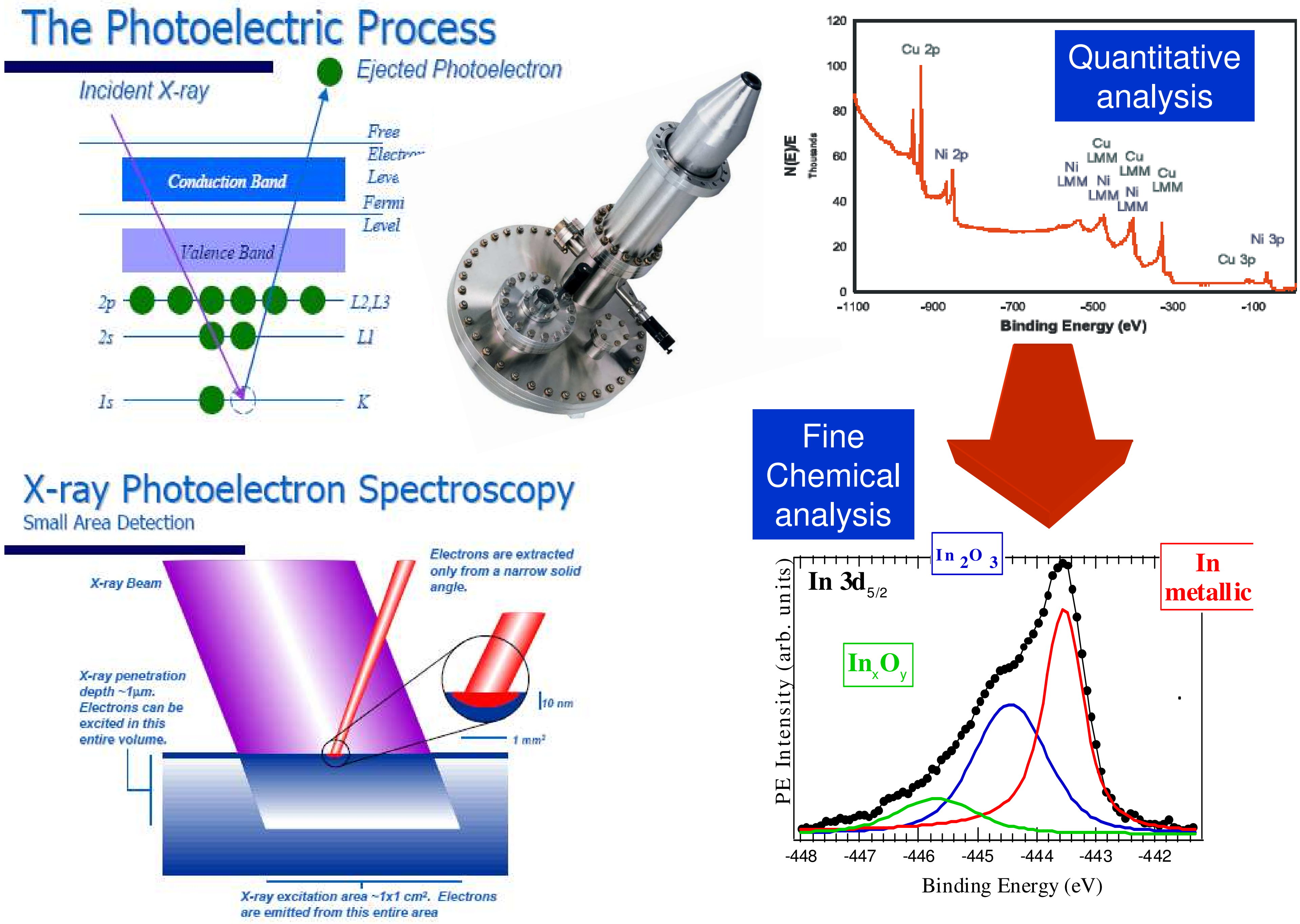
- **Best resolution: ~150nm (ZonePlates ltd)**
- **Best transmission: 8% (ZP ltd.)**

Overall energy resolution



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

Photon energy range: 350 eV (min) – 900 eV (actual, undulator transmission)



The Photoelectric Process
Ejected Photoelectron
Incident X-ray
Free Electron Level
Conduction Band
Fermi Level
Valence Band
2p
L2,L3
2s
L1
1s
K
X-ray Photoelectron Spectroscopy
Small Area Detection
X-ray Beam
Electrons are extracted only from a narrow solid angle.
X-ray penetration depth ~1µm. Electrons can be excited in this entire volume.
10 nm
1 mm²
X-ray excitation area ~1x1 cm². Electrons are emitted from this entire area
Quantitative analysis
Cu 2p
Ni 2p
Cu LMM
Ni LMM
Ni 3p
Cu 3p
N(E)/E
Thousands
120
100
80
60
40
20
0
-1100
-900
-700
-500
-300
-100
Binding Energy (eV)
Fine Chemical analysis
In 3d5/2
In2O3
In metallic
InxOy
PE Intensity (arb. units)
-448
-447
-446
-445
-444
-443
-442
Binding Energy (eV)

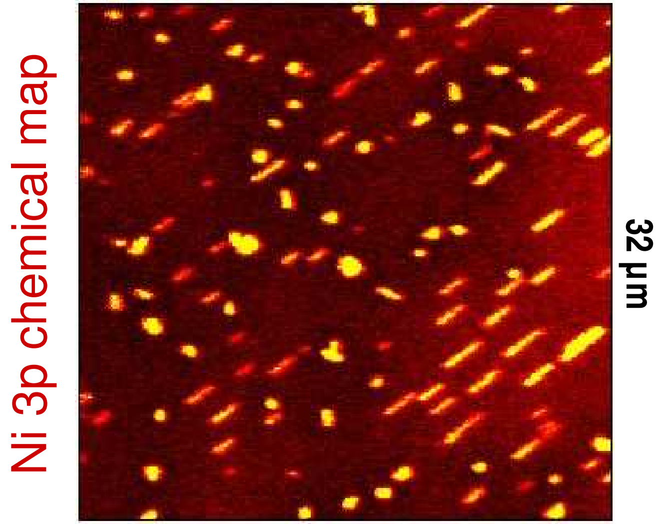
SPEM experiments: main topics

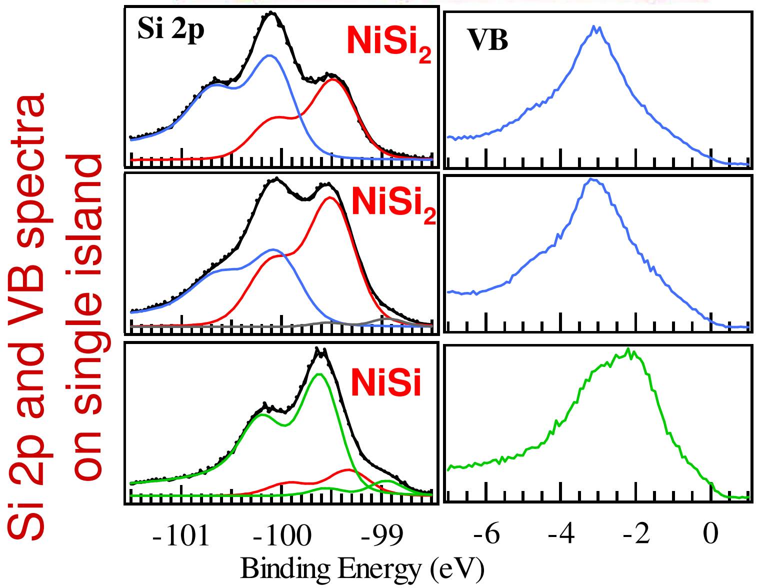
- Bulk-adlayer interfaces: metal/metal metal/semiconductor
  - Silicide formation (Ni, Co, Pd, Pt, Ag, Au)
  - Surface alloying and alloying (Ni/Pd, Au/Rh, Rh/Au)
- Catalysts&catalysis
  - Size gap
  - Model reactions (Rh, Pt, Ru)
- Nano and micro clusters properties
- Material characterization
- Organic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

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

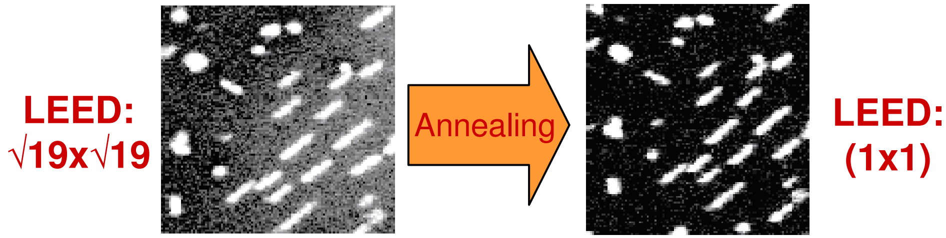
•Deposition of 2ML of Ni on Si(111)-7x7 and thermal activation of the silicide formation

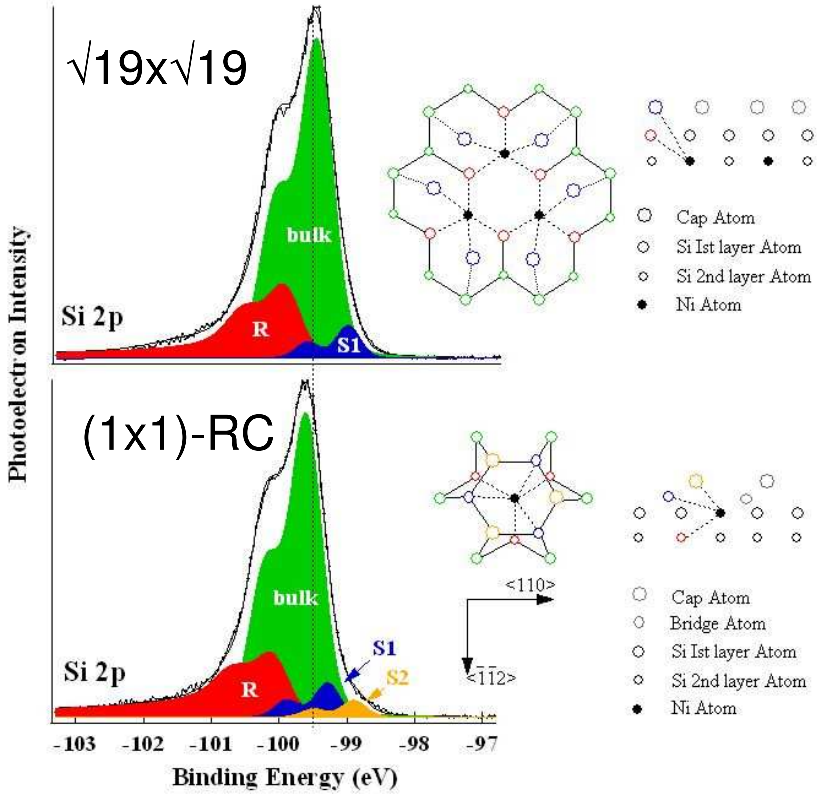
3D phases



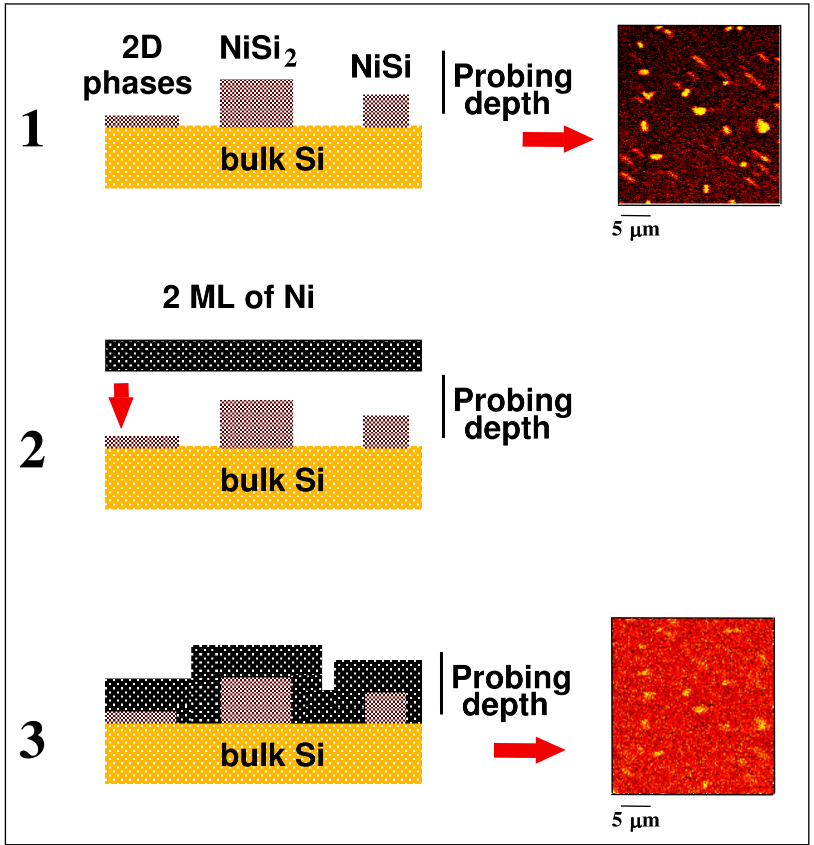


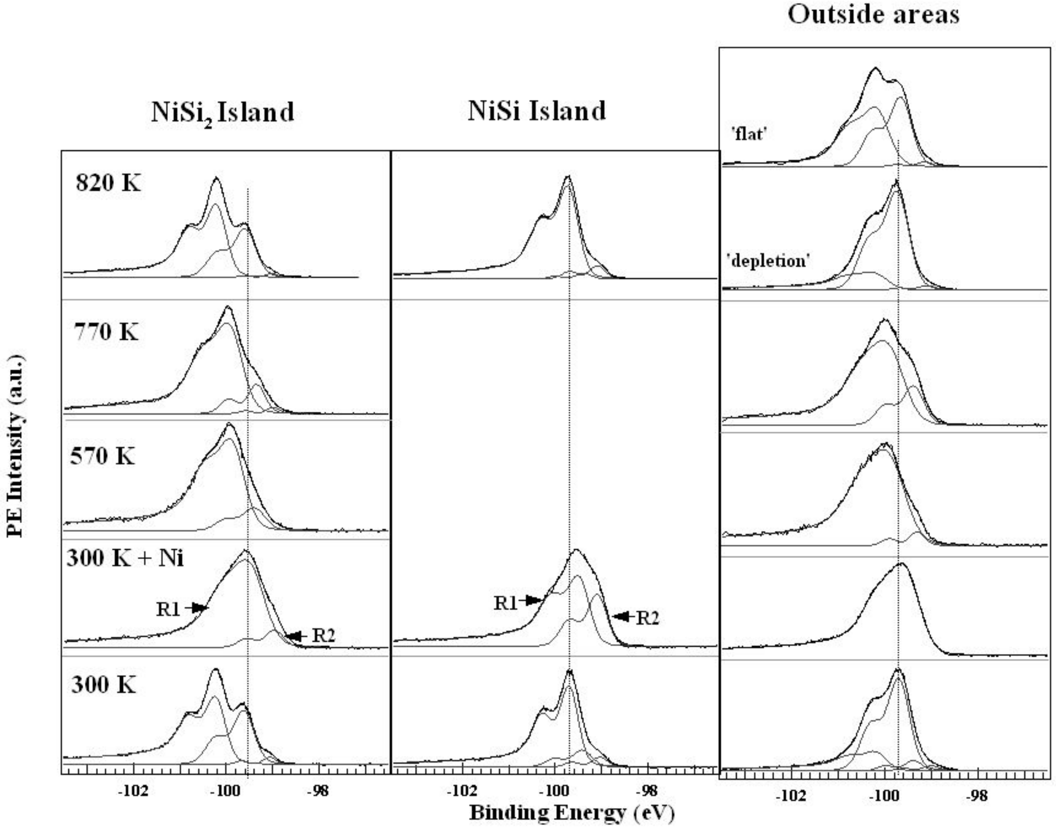
2D phases

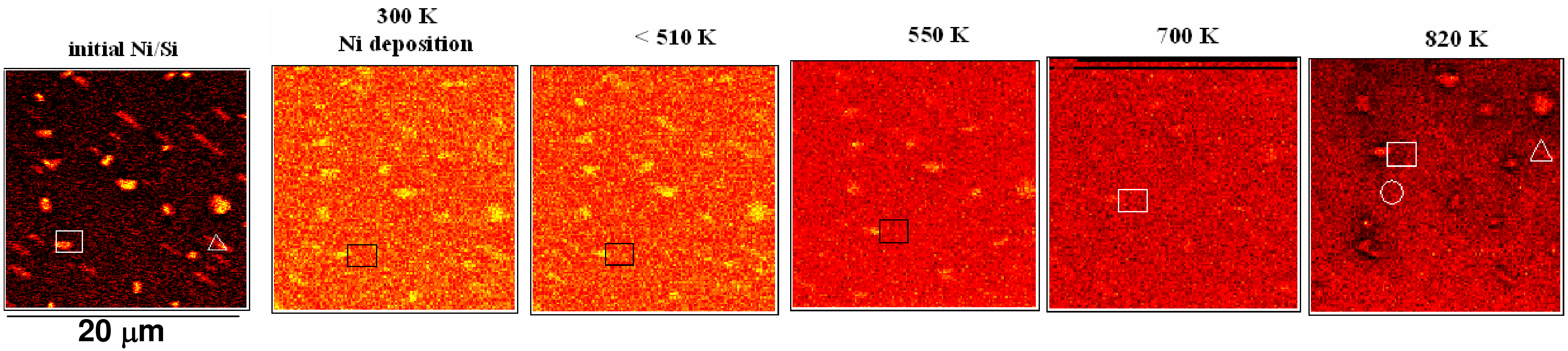




Ni silicides on Si(111): intermediate phases



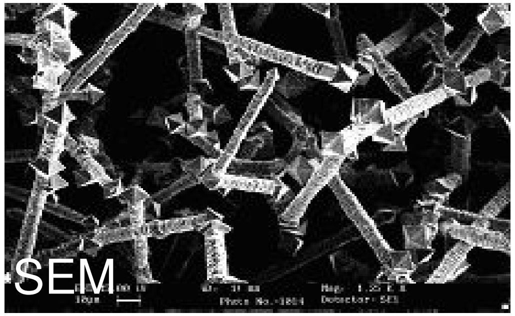




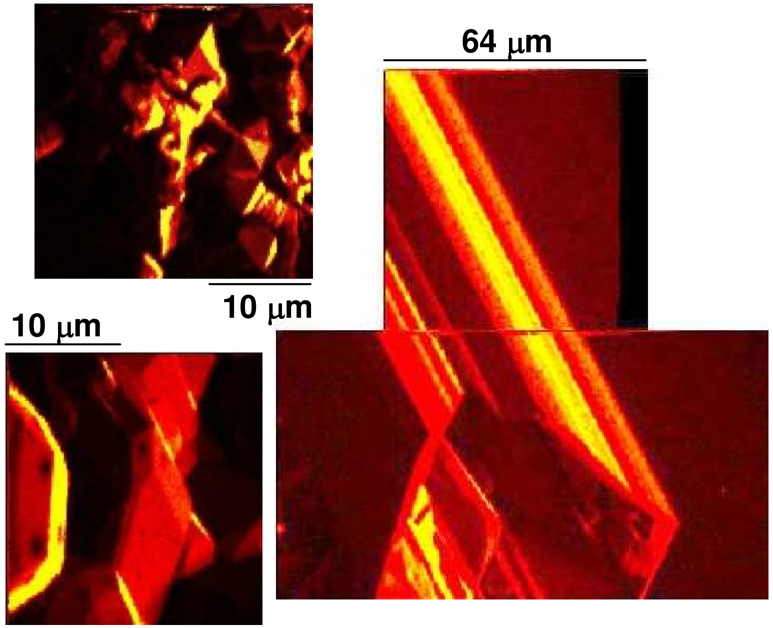
Compositional and electronic study of TCO nano and microtubes by Photoelectron Microscopy (in collaboration with A. Cremades UCM)

- **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**

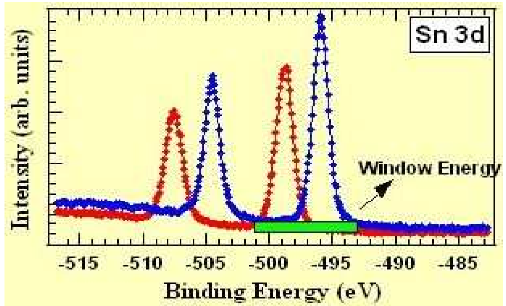


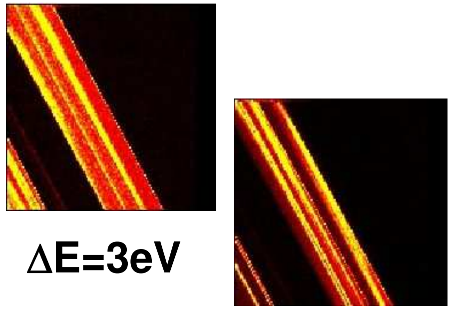
SPEM images



Electronic behaviour of a single structure

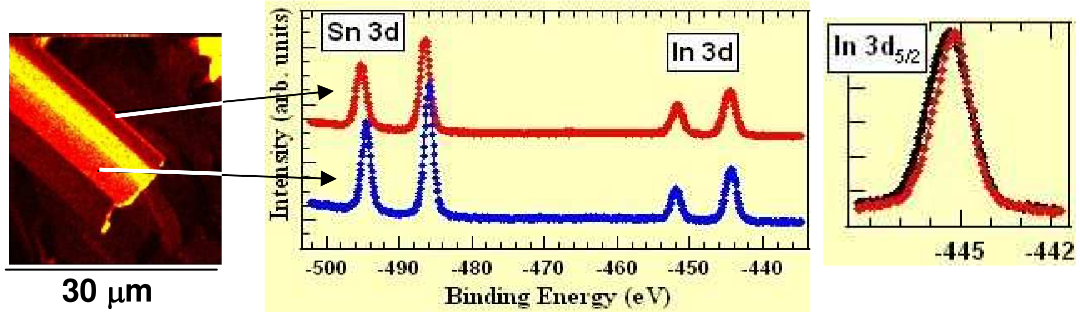
- **Charging due to differences in the electronic structure**
- **Mapping of the charging with the multichannel acquisition**





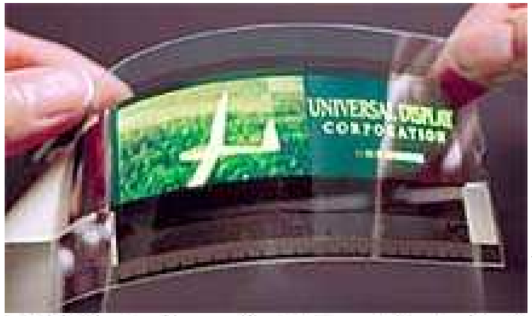
Local chemical composition of the structures

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

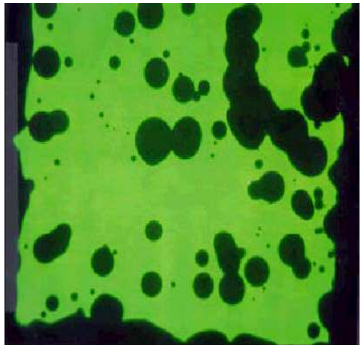


Degradation of light emitting diodes: a SPEM analysis

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

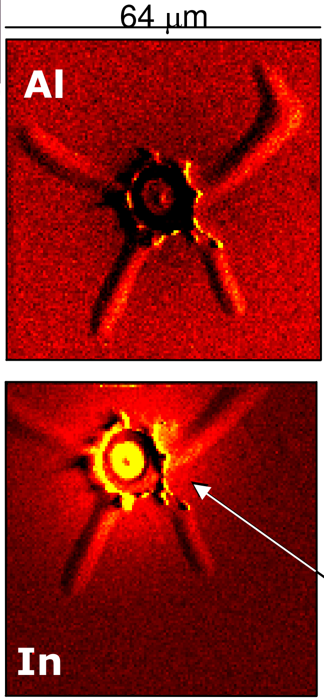


OLED Display Screen (from Universal Display Corp)

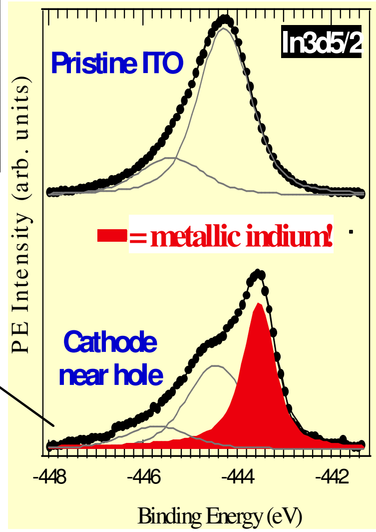


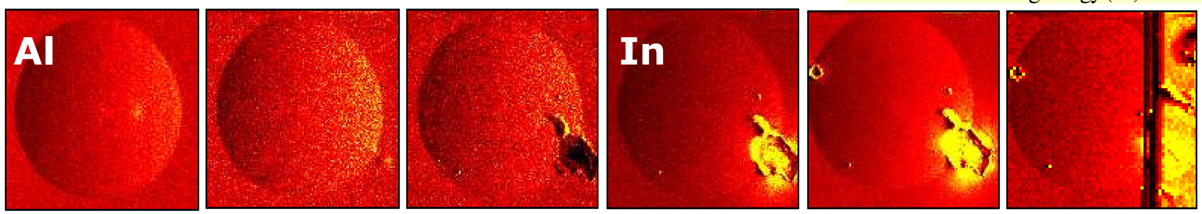
Dark spot in OLED

OLED exposed to atmospheric moisture: failure due to light emission



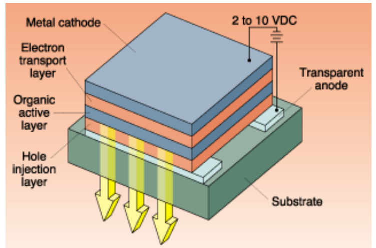
•Decomposition of ITO

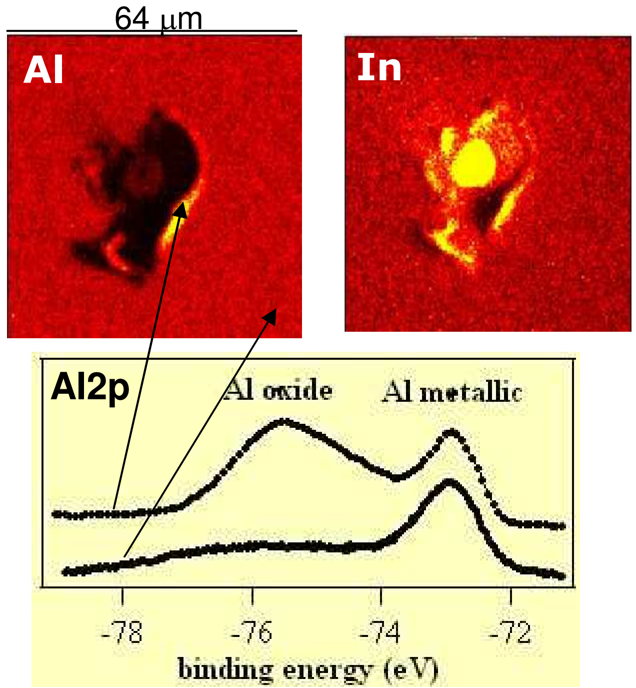




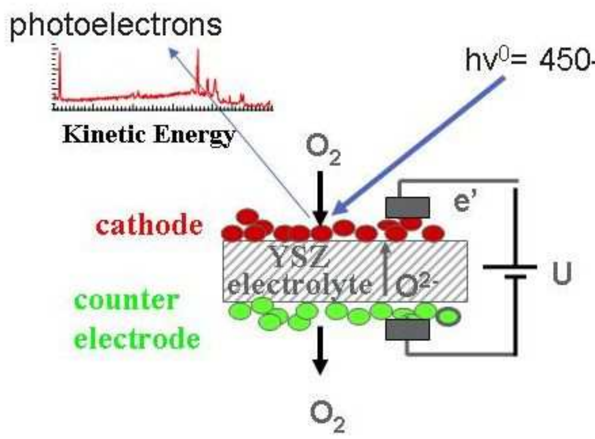
increasing voltage and operating time

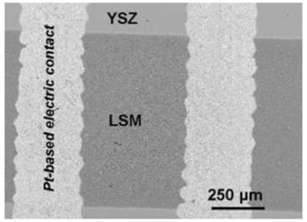
"Clean" experiment: OLED growth and operated in the SPEM (UHV ambient) : failure due to light emission





Photoelectron microscopy study of operating LSM-YSZ cathode surfaces of SOFC *(in collaboration with M. Backhaus Corning Inc.)*

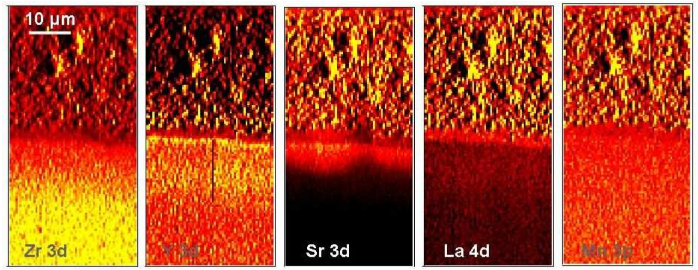




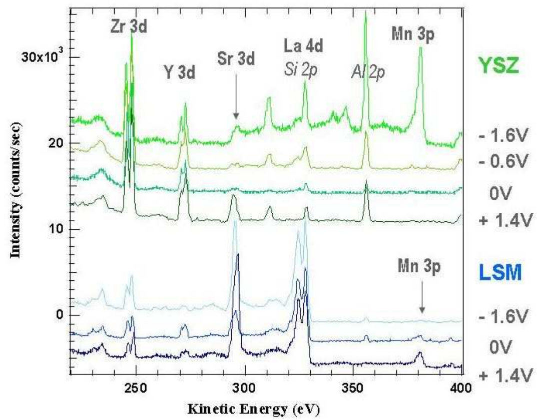
Strongly constraining experimental setup

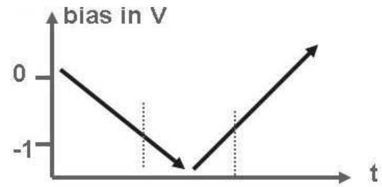
- •Real samples
- •High T = 650-700℃
- •pO_2=1x10^{-6} mbar
- •Applied potentials
  -2V<U<+2V
- •Surface sensitive technique
- •High lateral resolution

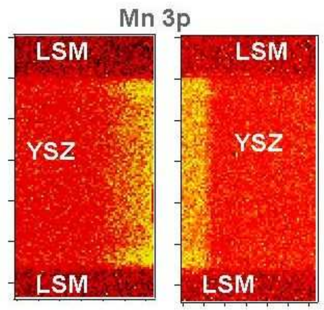
Elemental distribution at electrolyte/LSM interface



Surface composition change with bias



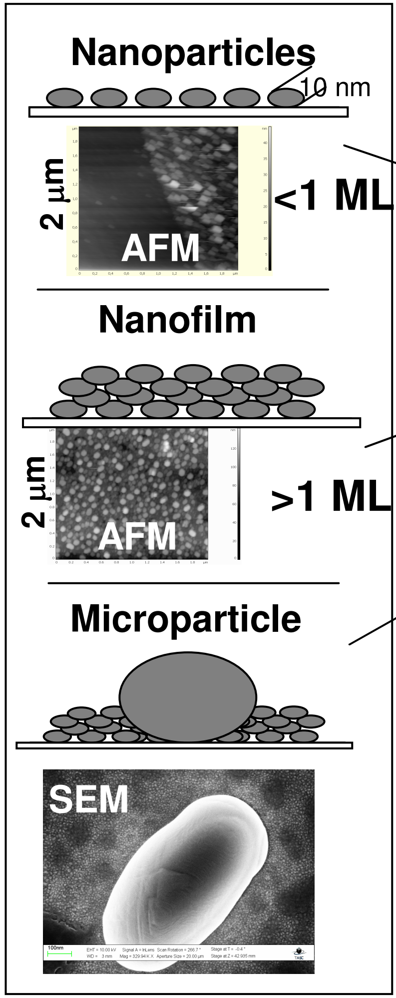




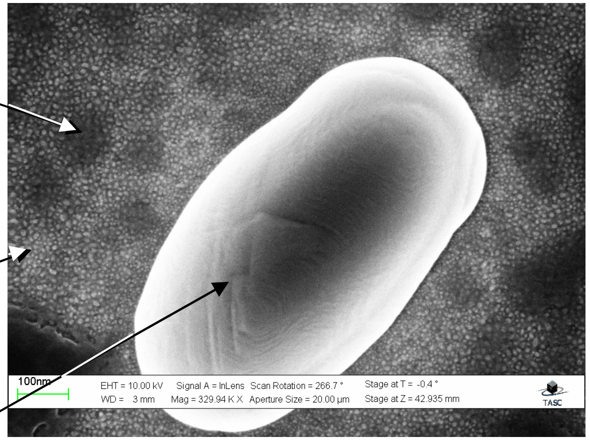
Observation and explanation of electrochemical cathode activation

- •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

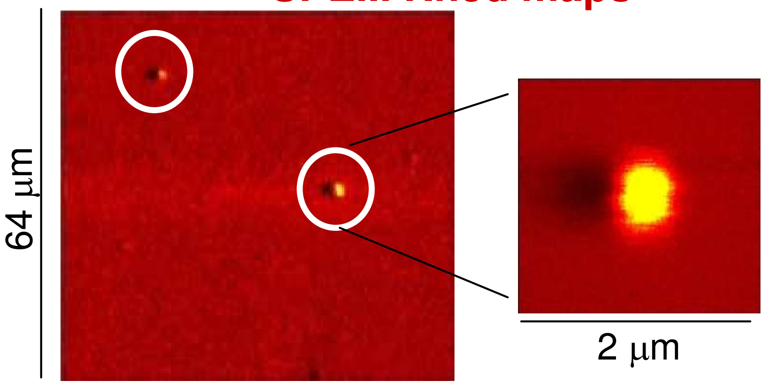
‘Material’ gap: from model crystalline materials to metal nano-particles on metal oxide. In situ PLD particle deposition



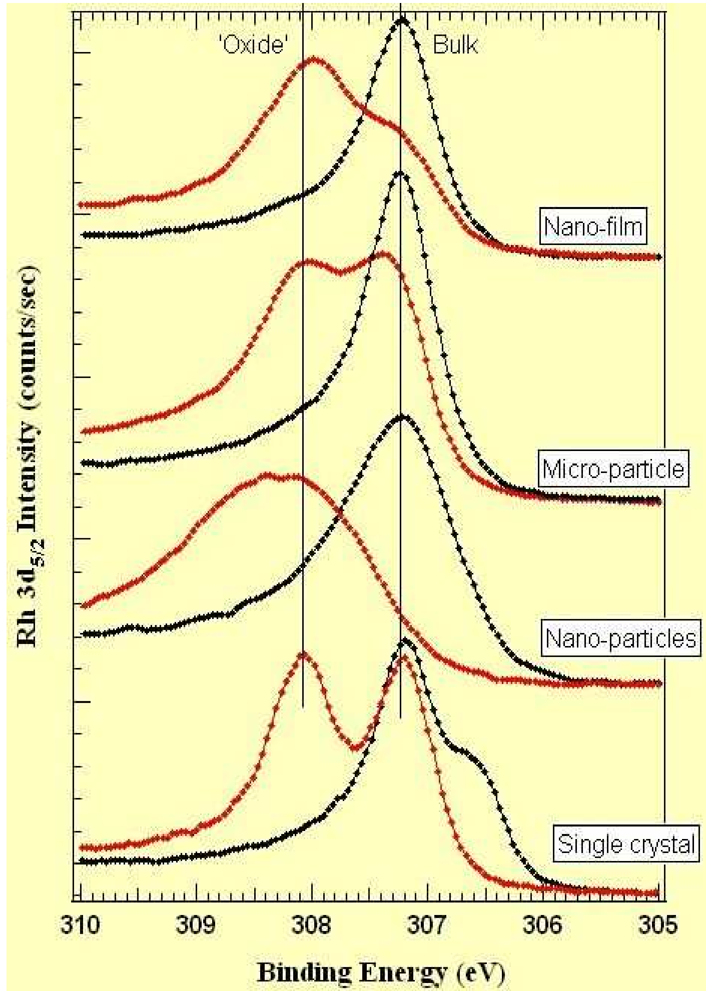
Rh on MgO/W(110) PLD species are highly-defected due to non-thermic evaporation



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.