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Scanning photoemission imaging and spectro-microscopy: a direct approach to spatially resolved XPS

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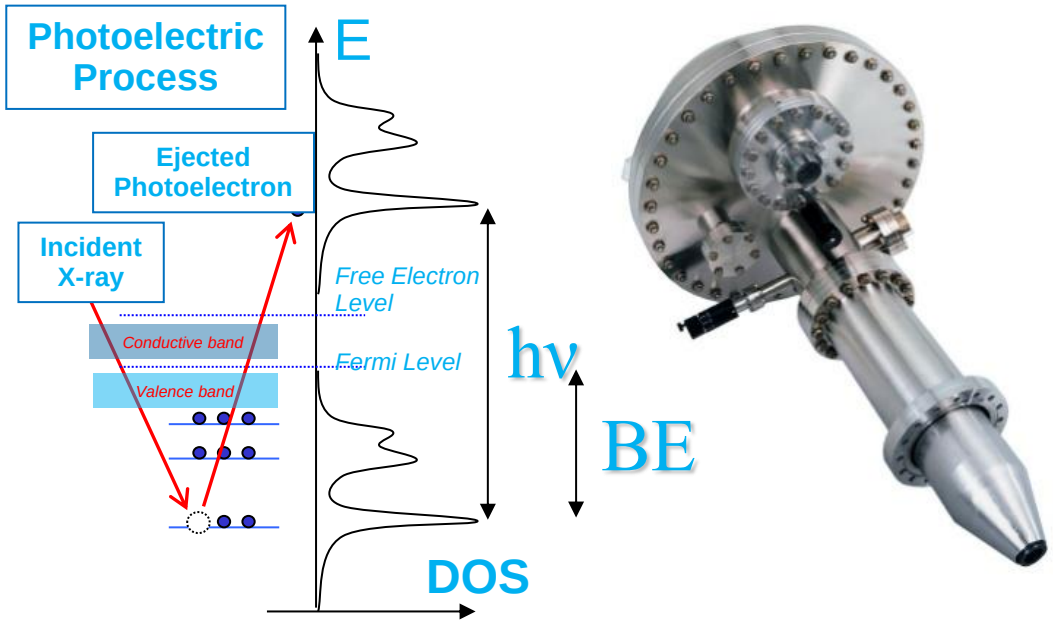
EWinS 2016, 1 – 11 February,
Ajdovščina, Slovenia

Photoelectron Spectroscopy – Material & Pressure Gaps



XPS = X-ray Photoelectron Spectroscopy

ESCA = Electron Spectroscopy for Chemical Analysis

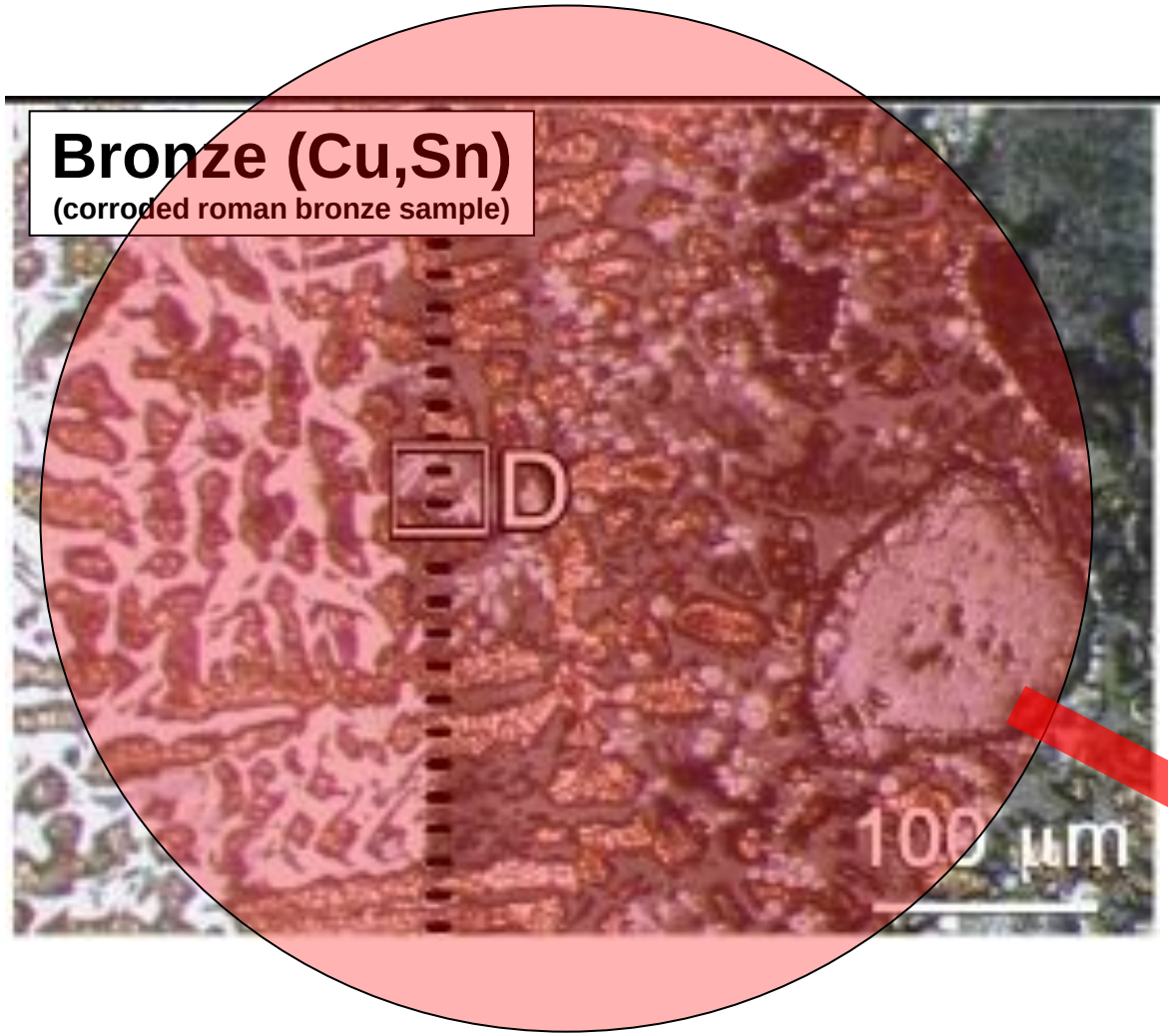
$$BE = h\nu - KE - \Phi_s$$

Spatial Resolution → opportunities for monitoring material changes and mass transport events occurring at submicron length scales
"MATERIAL GAP"

Realistic condition → In-situ at the maximum GAS pressure with operating temperature and byas
"PRESSURE GAP"

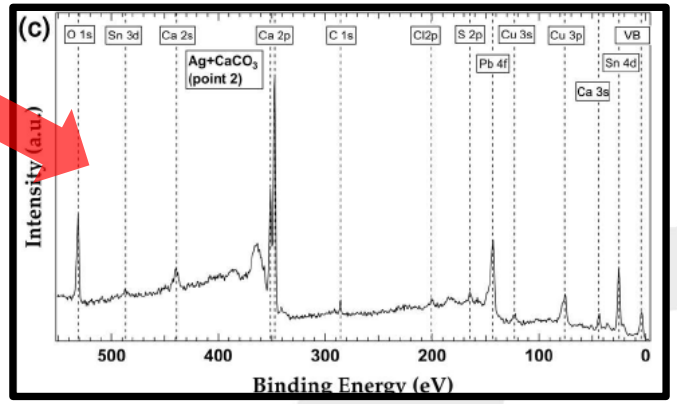
Photoemission spectromicroscopy

Bronze (Cu,Sn)
(corroded roman bronze sample)



XPS informations

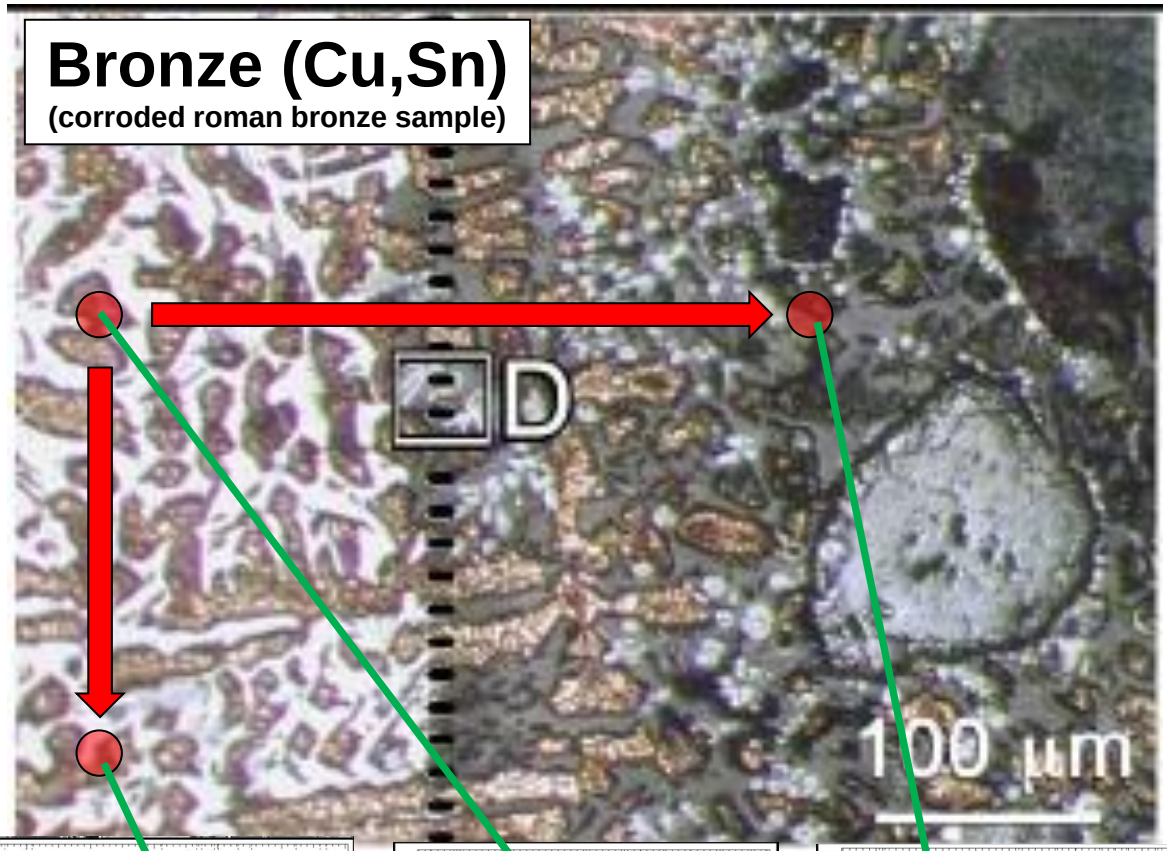
Avarage informations from ALL the illuminated part of the sample

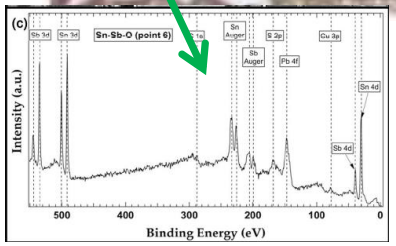


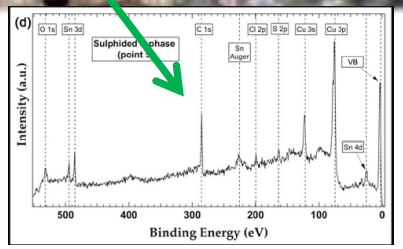
https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

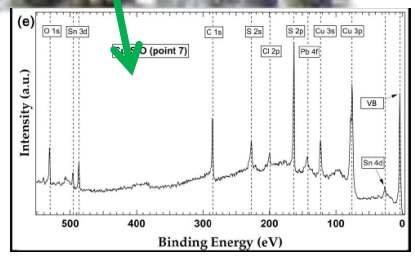
Scanning PhotoElectron Microscopy (SPEM)

Avarage informations from ALL the illuminated part of the sample









SMALL X-ray PROBE

Move the X-ray PROBE across the sample

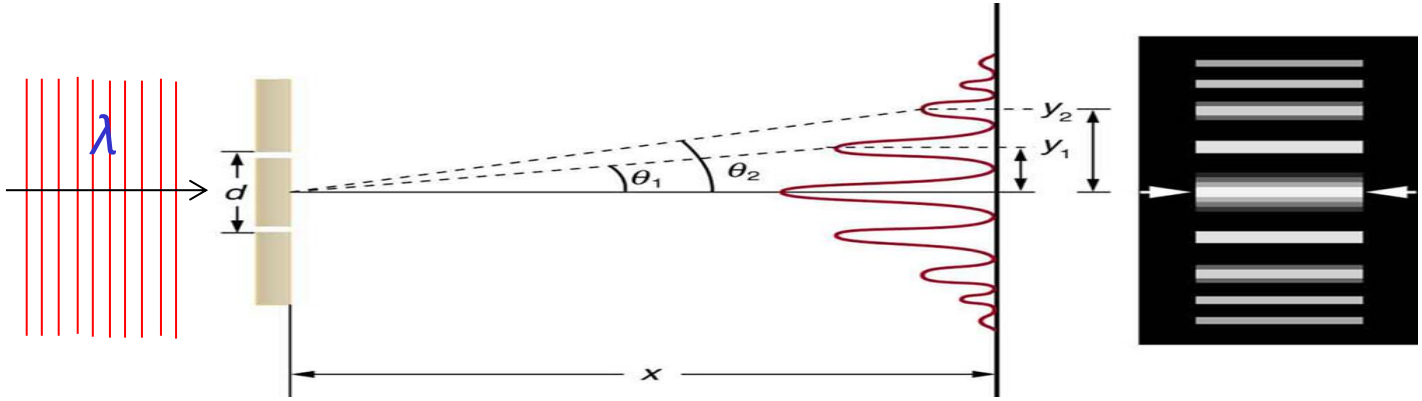
Spatial resolution

Smaller is the probe higher is the spatial resolution

https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

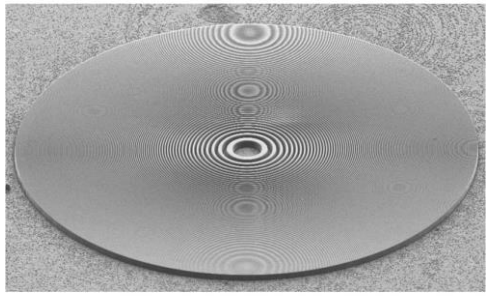
Synchrotron beam focusing

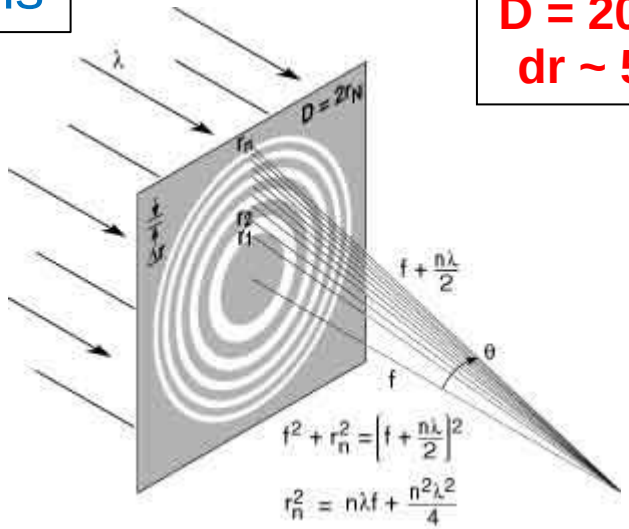
Synchrotron beam → Partially coherent



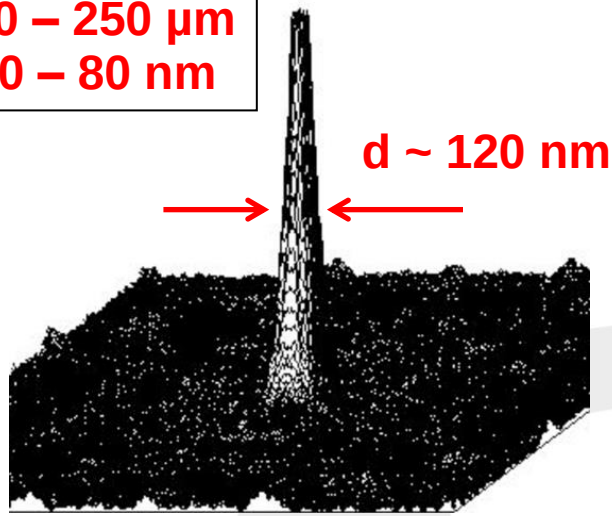
interference pattern

Fresnel zone plate lens



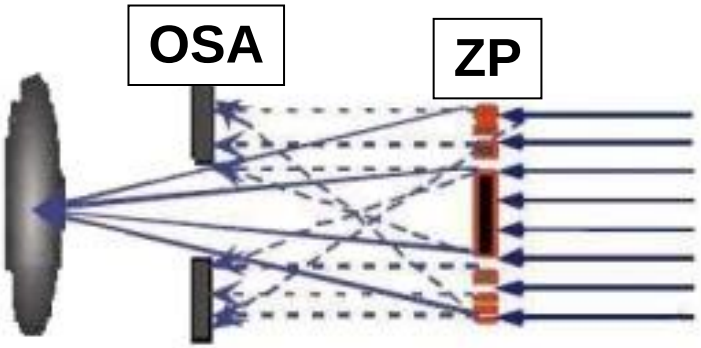


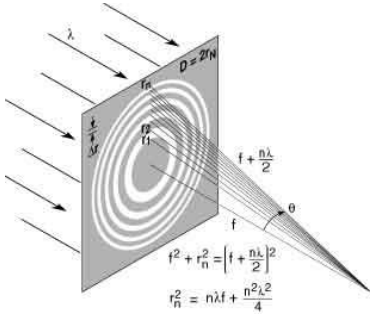
D = 200 – 250 µm
dr ~ 50 – 80 nm

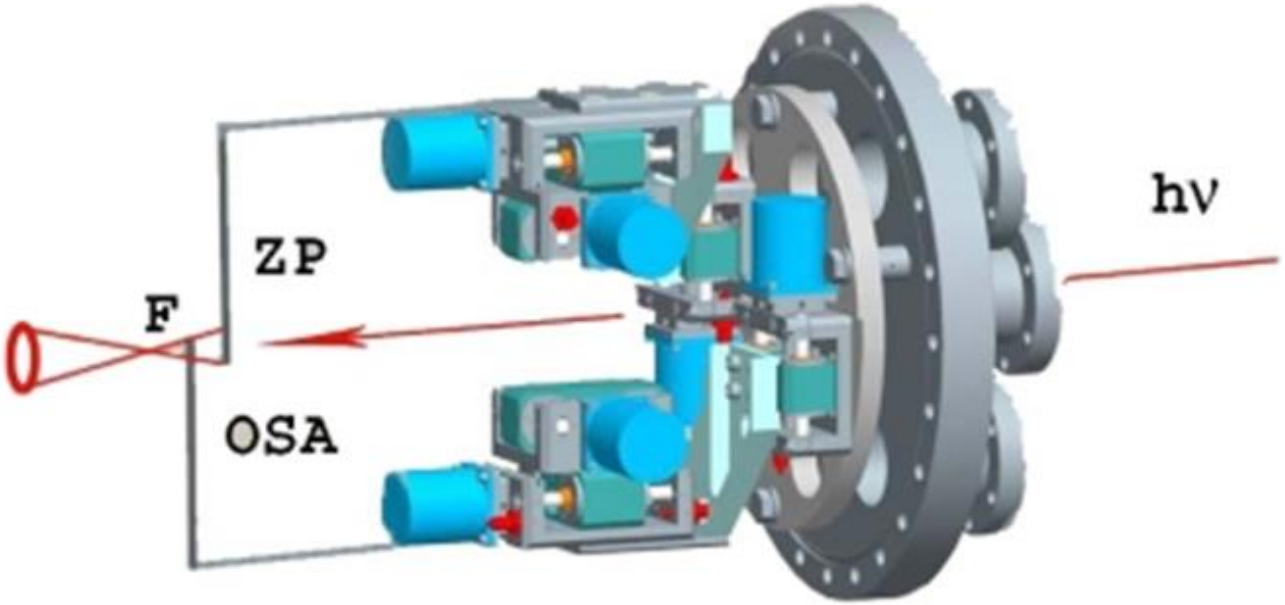


https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

ESCAmicroscopy - SPEM optics







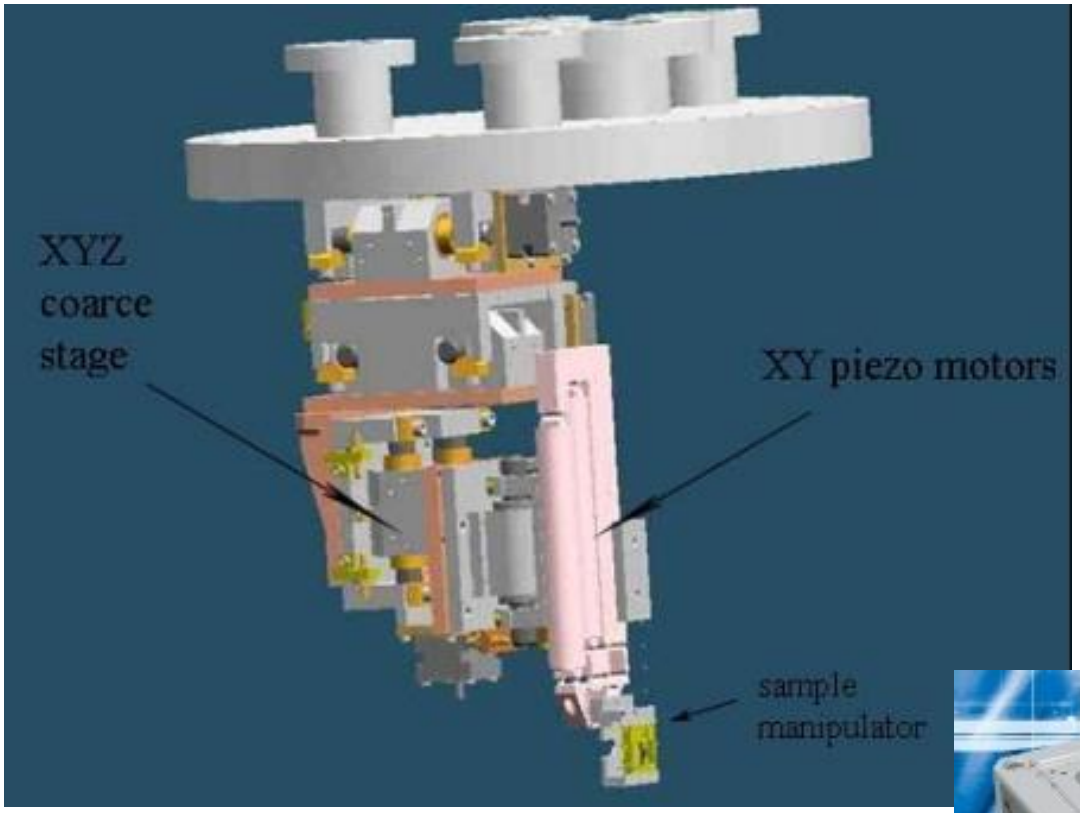
D = 200 – 250 µm
dr ~ 50 – 80 nm

Photon energy range:
350 eV (min) – 1200 eV

f = 5 – 15 mm
d down to 120nm

https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

ESCAmicroscopy – SPEM sample stage

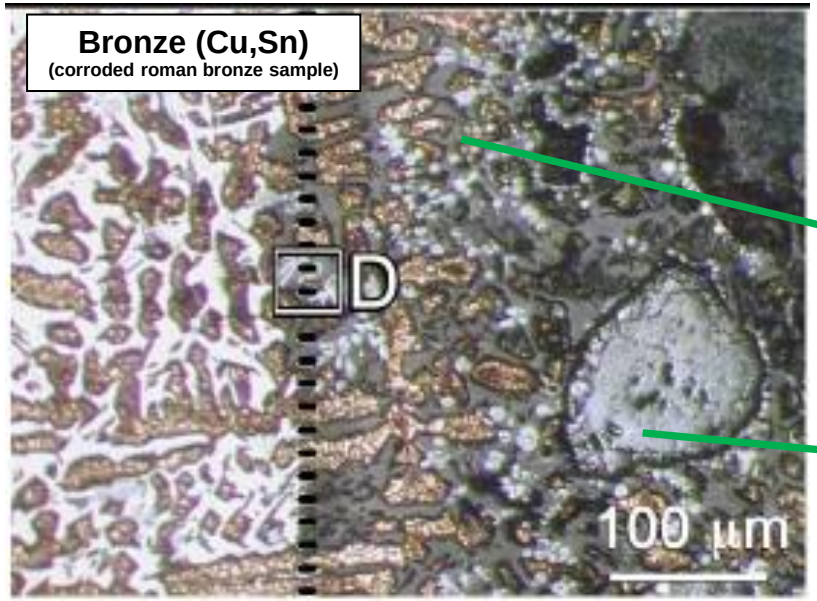


Stepper motor XYZ:
Range = 30mm
Minimum step = 1 µm

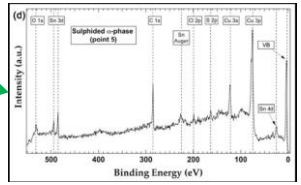
Piezoelectric XY:
Range = 100 µm
Minimum step = 5 nm

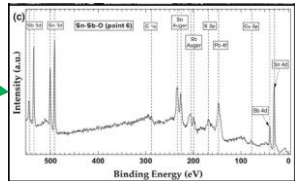
https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

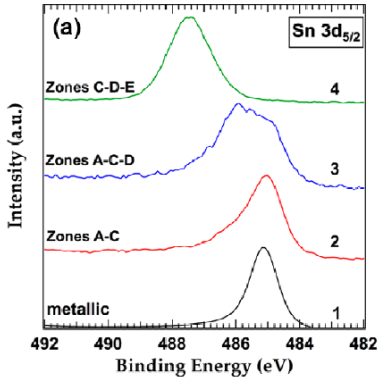
ESCAmicroscopy – Scanning PhotoElectron Microscopy (SPEM)



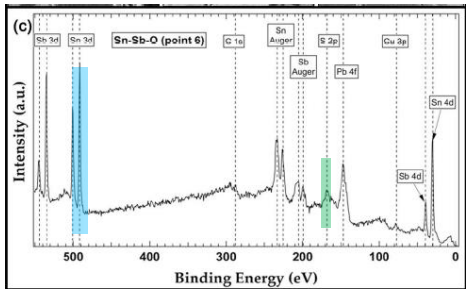
XPS from a sub-micron spot
(spectra mode)

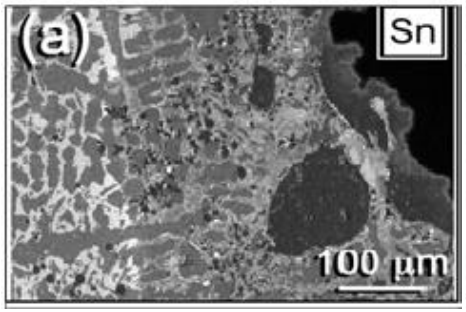


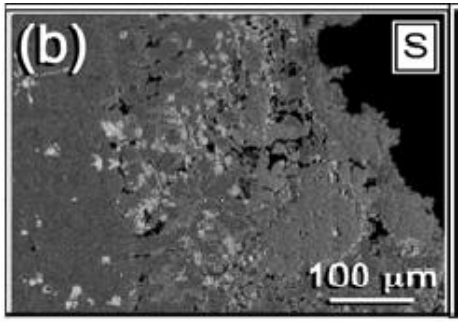


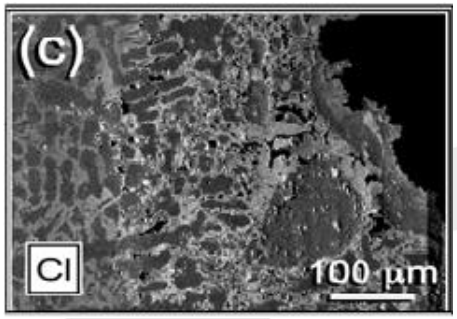


Photoelectron maps
(image mode)





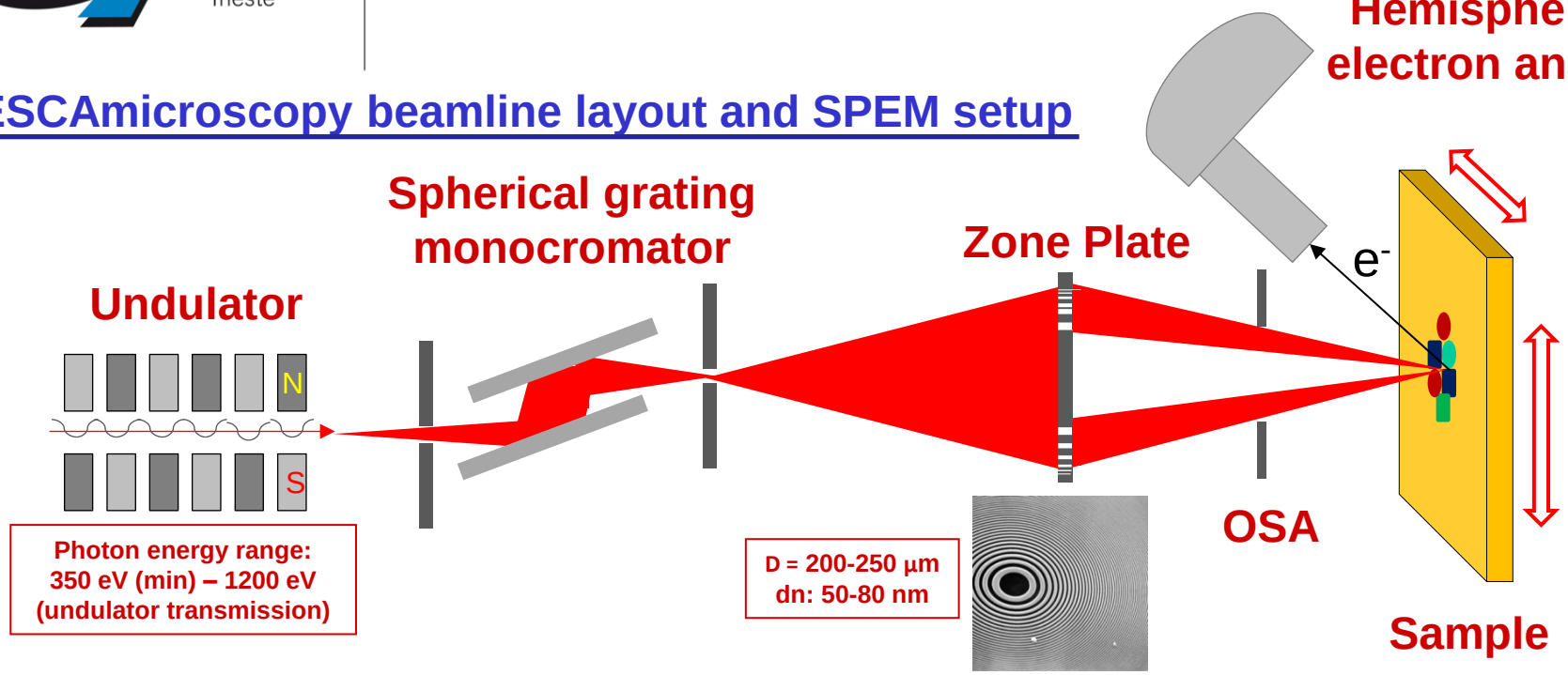




https://www.elettra.eu/elettra-beamlines/escamicroscopy.html

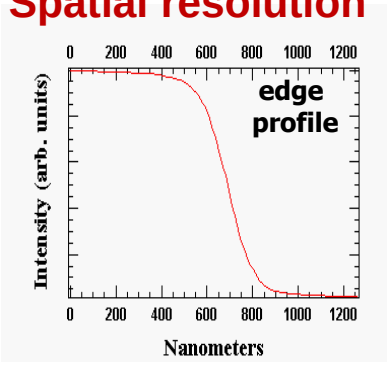
SPEM layout and performance

ESCAmicroscopy beamline layout and SPEM setup



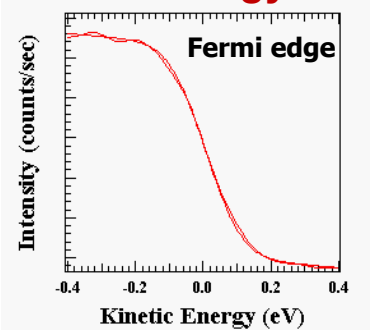
SPEM actual performances

Spatial resolution



- Imaging: < 50 nm
- Microspectroscopy: 120 nm

Overall energy resolution



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

https://www.elettra.trieste.it/elettra-beamlines/escamicroscopy.html

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SPEM experiments: main topics

Nanostructures/devices characterization

- **MCNTs mass transport and reactivity**
- **e-noses**
- **Size dependent electronic properties of semiconductors**
- **Growth mechanism**

Electrochemistry/SOFC

- **Electrochemical stability of materials**
- **Corrosion**
- **Mass Transport**

Nanocomposite materials

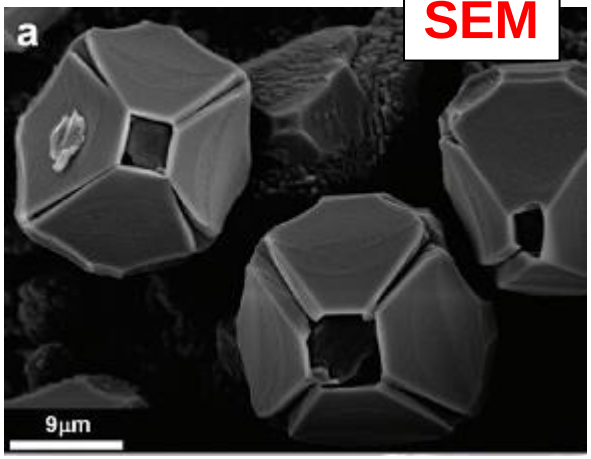
- **Sample preparation**
- **Ageing**

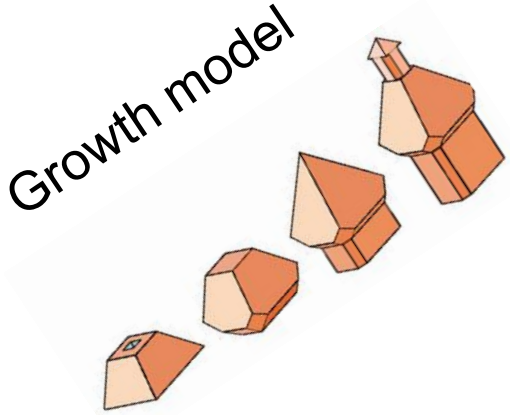
Catalysis

- **'Material' gap: from model single-crystal metal catalysts to supported metal nano-particles.**
- **In situ PLD particle deposition**

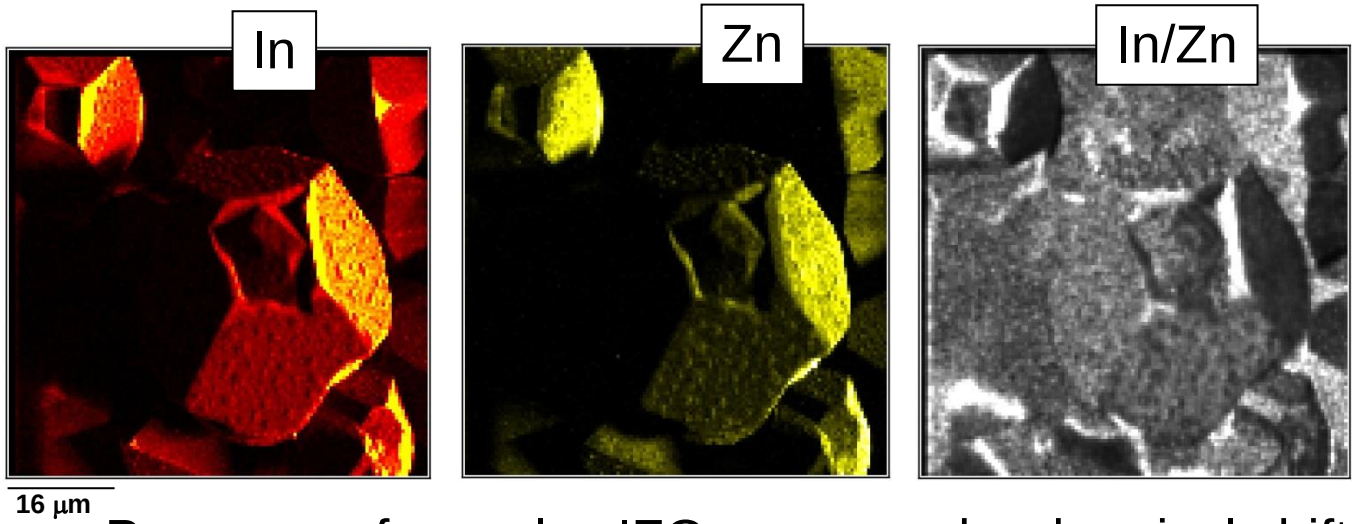
Indium Zinc Oxide Pyramids with Pinholes and Nanopipes (in collaboration with A. Cremades – Uni Complutense Madrid – Spain)

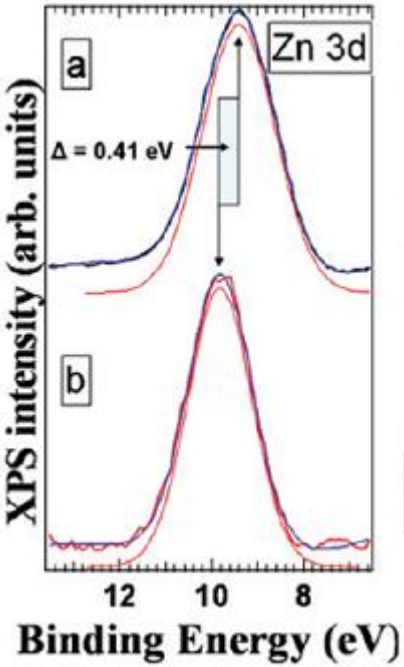
Micropyramids of zinc-doped indium oxide grown by thermal treatments of compacted InN and ZnO powders at temperatures between 700 and 900 C under argon flow.





SPEM reveals the heterogeneous distribution of In and Zn

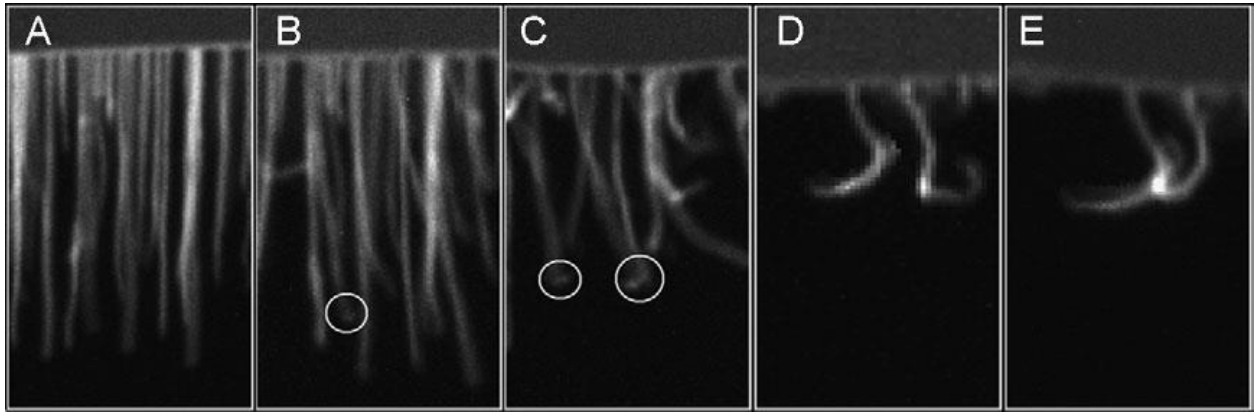




Presence of complex IZO compounds: chemical shifts

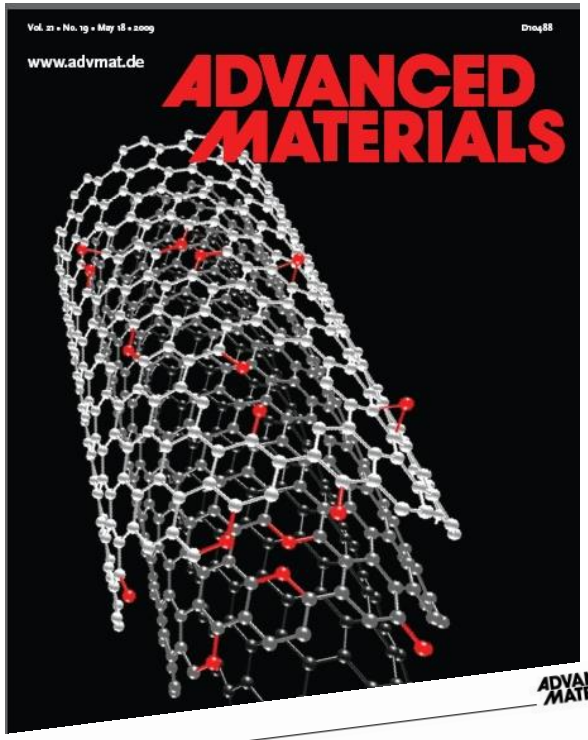
Javier Bartolomé et al., J. Phys. Chem. C, 2011, 115 (16), pp 8354–8360

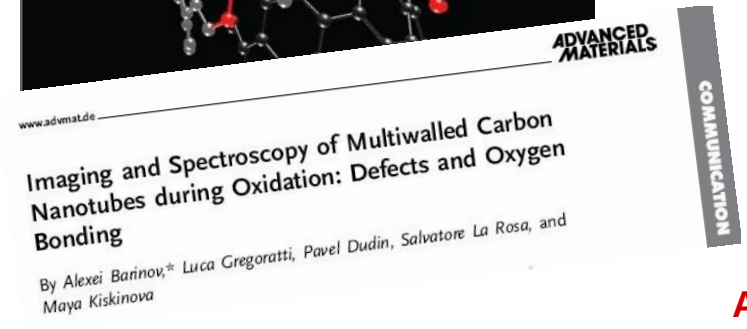
Gas phase oxidation of MCNT

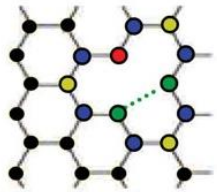


Increasing oxygen dosage

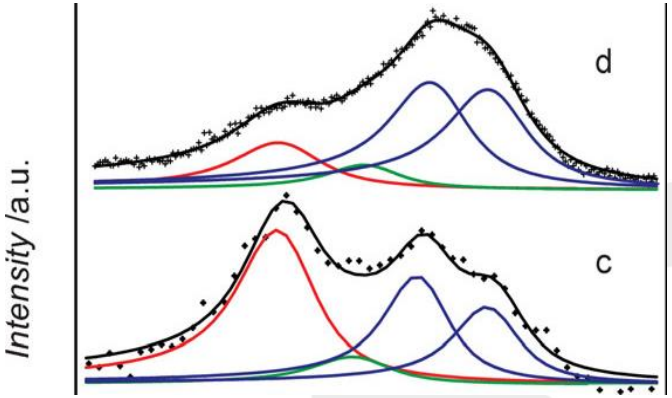
- Gas phase oxidation with atomic oxygen
- Advanced oxidation stages
- Investigation of the formation of oxygenated functional groups and morphological changes
- Non linear consumption of the CNT





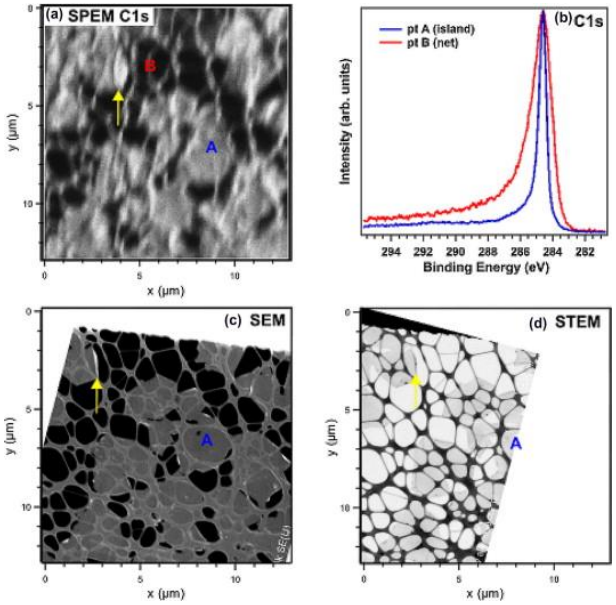


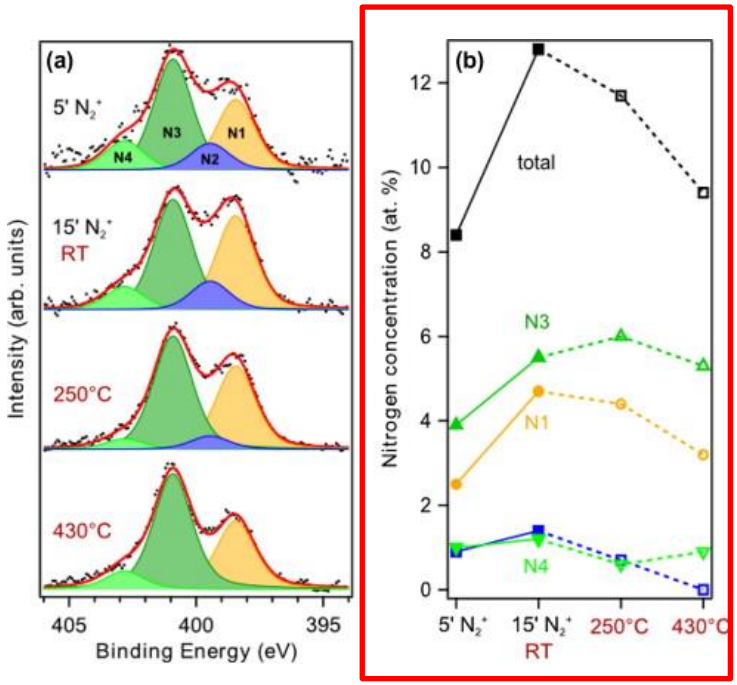
Atomic arrangement

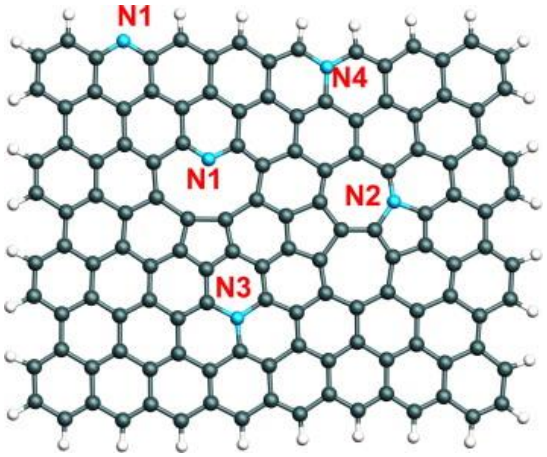


A. Barinov et al. Adv. Mat. 21 (19) 1 (2009)

Doping by nitrogen ion implantation of suspended graphene flakes





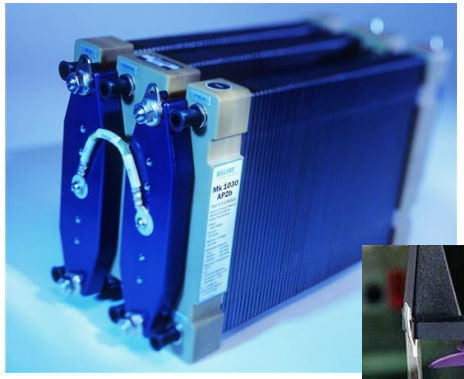


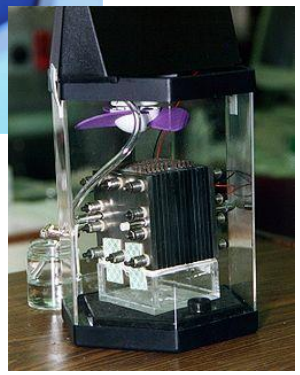
Control of nitrogen component by heating the sample to mid-temperatures (430°C)

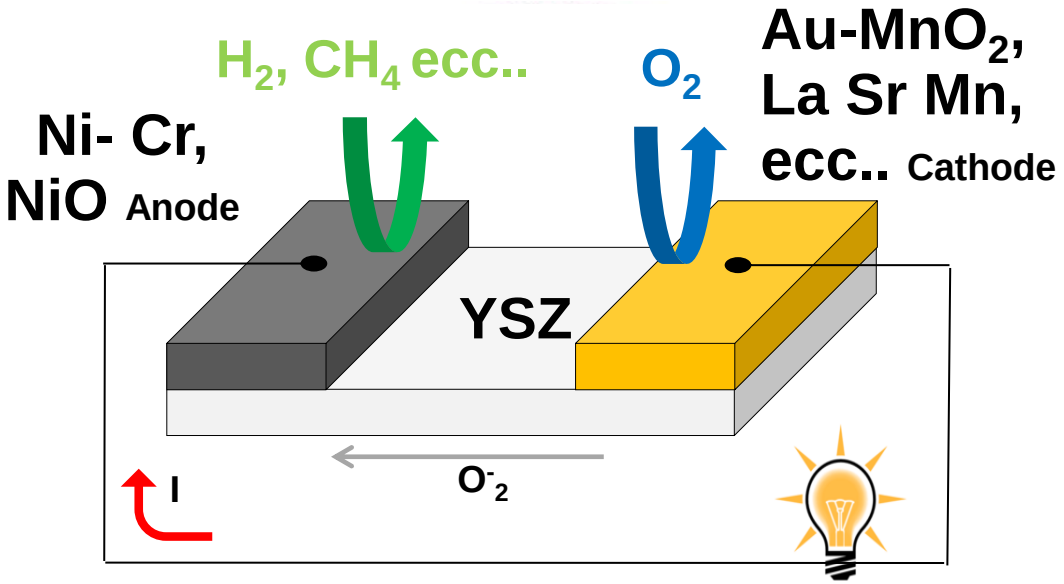
Difference between supported and suspended graphene (role of the substrate)
(Supported: unwanted disorder due to recoil and backscattering)

M. Scardamaglia et al., Carbon 73, 371 (2014)

SOFC operating under working condition







collaborations:

M. Backhaus - Corning Inc. (USA)

B. Luerssen - University of Giessen (Germany)

B. Bozzini - Università del Salento, Lecce (Italy)

Bocchetta et al. ACS Appl. Mater. Interfaces. 6 (2014) 19621–19629

Bozzini et all. Electrochem Comm, Vol. 24, pp.104-107 (2012)

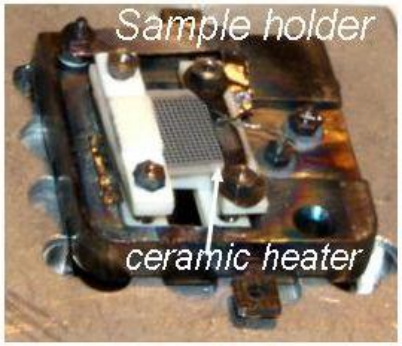
Bozzini et all. ChemSusChem, Vol. 4 - 8, pp. 1099-1103 (2011)

Backhaus et al. Advances in Solid Oxide Fuel Cells III 28 (4), 2007.

Backhaus et al. Solid State Ionics 179 (2008) 891–895 , M. Valov et al. *Phys. Chem. Chem. Phys.*, 2011, 13, 3394-3410

Ecc…

Strongly constraining experimental setup



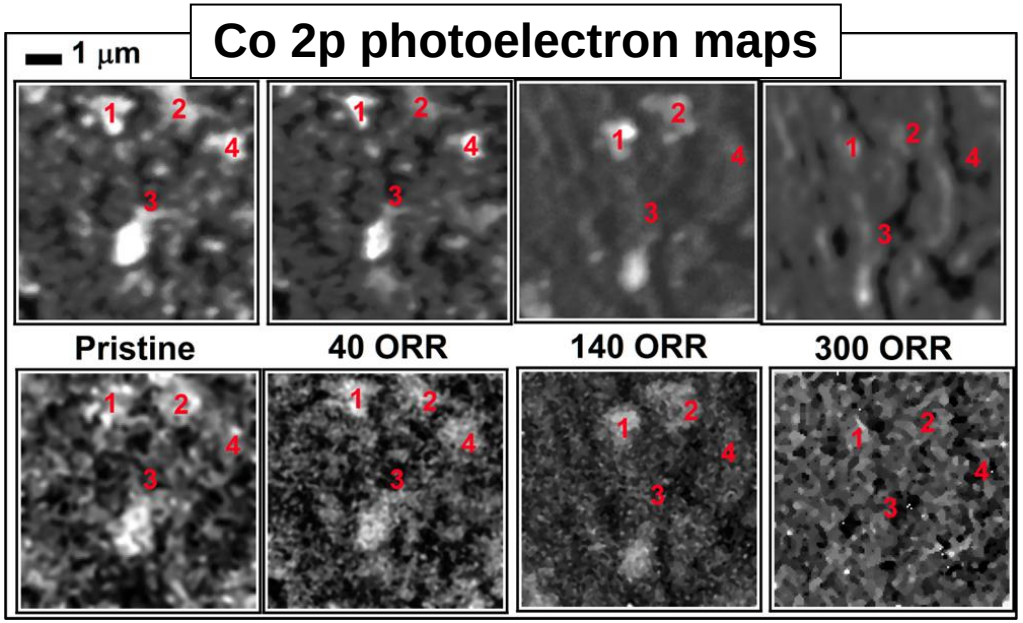
- **Real samples**
- **High T = 650-700°C**
- **P=1x10^{-6} mbar**
- **Applied potentials -2V<U<+2V**
- **Surface sensitive technique**
- **High lateral resolution**

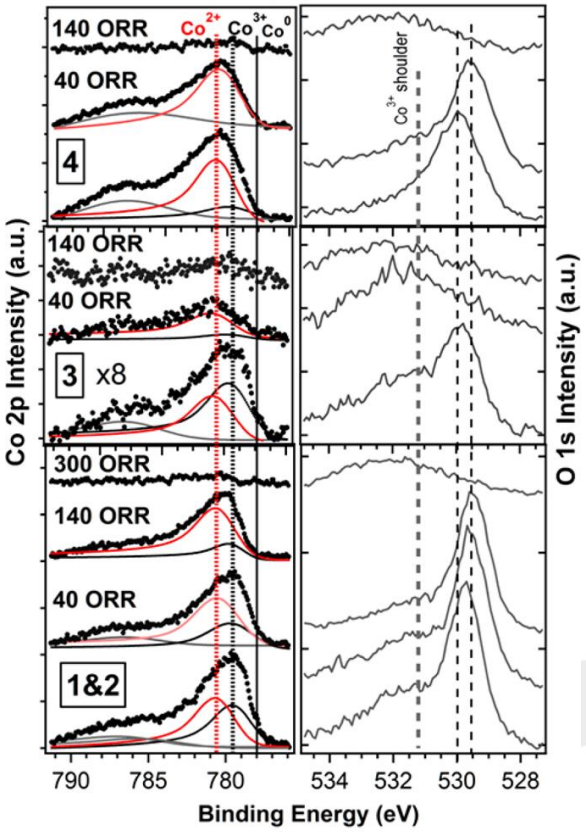
ESCAmicroscopy – electrochemical SPEM characterizzation

Catalyst stability in acidic solution under oxygen reduction

Pyrolized Co/PPy on Graphite

Aging: Voltammetric cycle in O_2-saturated 0.5M H_2SO_4



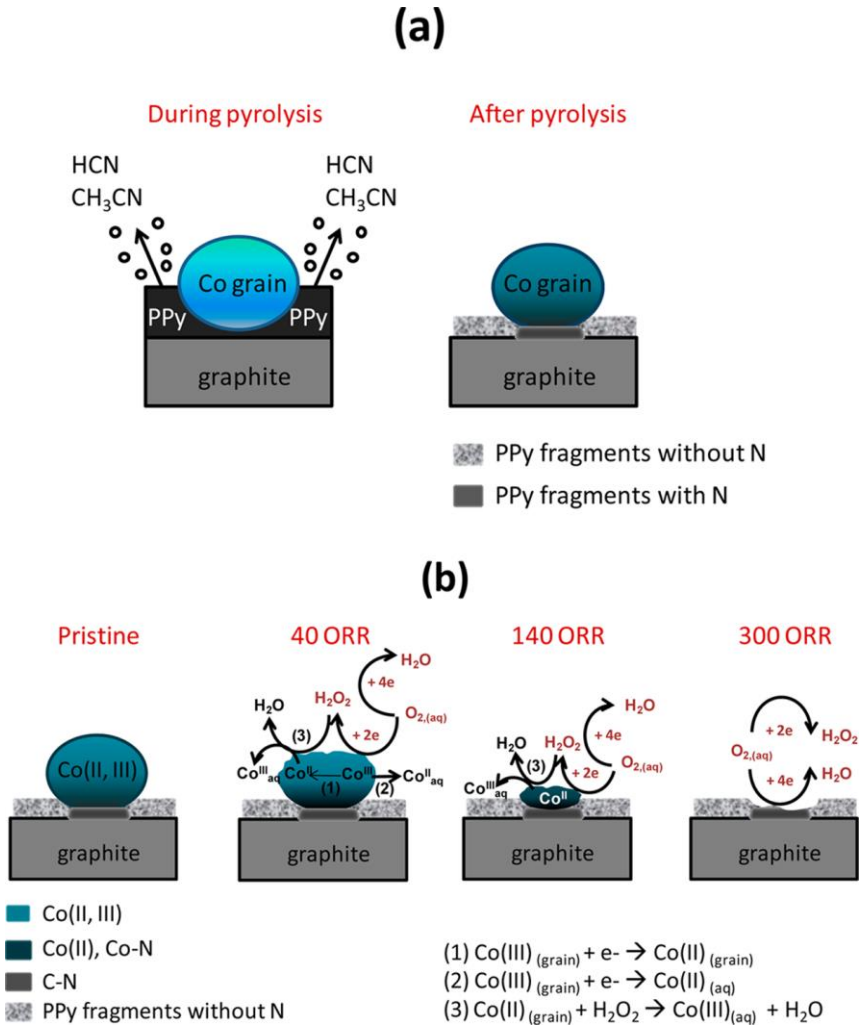


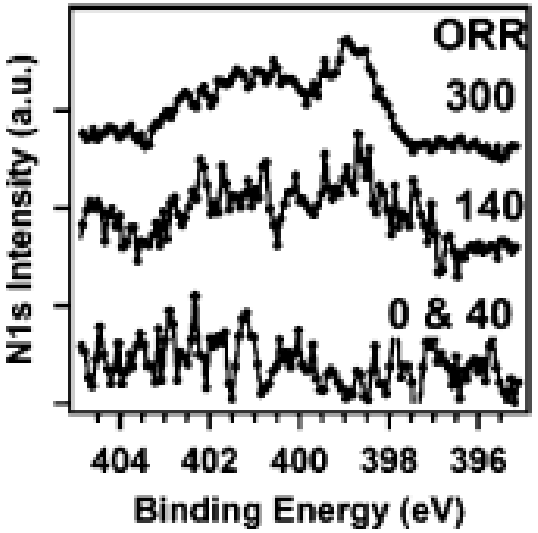
Co gradual loss

reduction of Co(III) to Co(II)

Bocchetta et al. ACS Appl. Mater. Interfaces. 6 (2014) 19621–19629

ESCAmicroscopy – electrochemical SPEM characterizzation

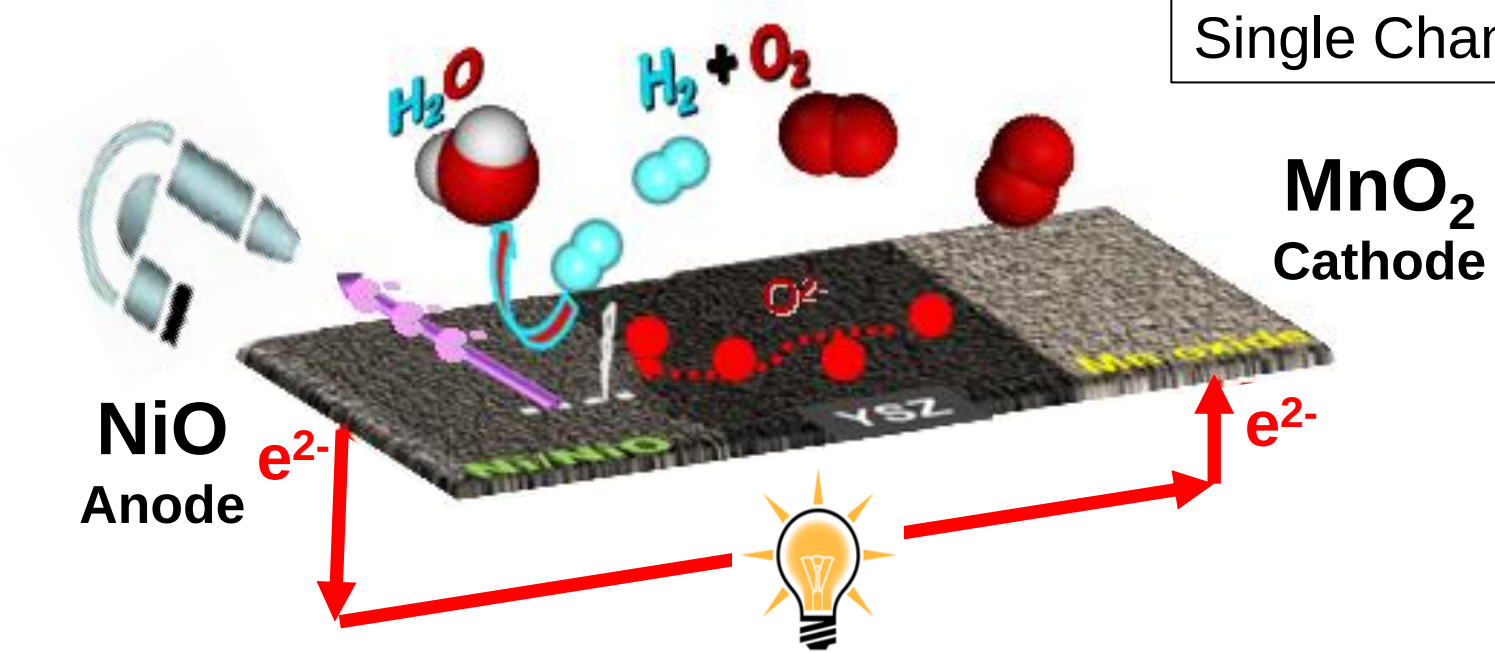




Bocchetta et al. ACS Appl. Mater. Interfaces. 6 (2014) 19621–19629

ESCAmicroscopy – Self Driven Single Chamber SOFC *In operando* condition

NiO/MnO_2
Single Chamber



NiO
Anode

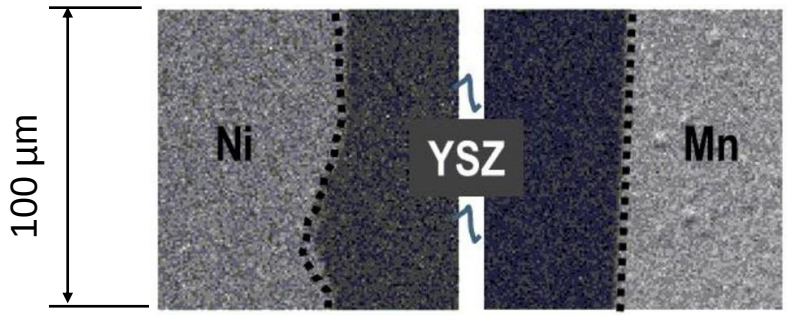
MnO_2
Cathode

$1x10^{-5}$ mbar of O_2 → **P=$1x10^{-5}$ mbar of H_2 + O_2 (1:1)**

200–400 nA

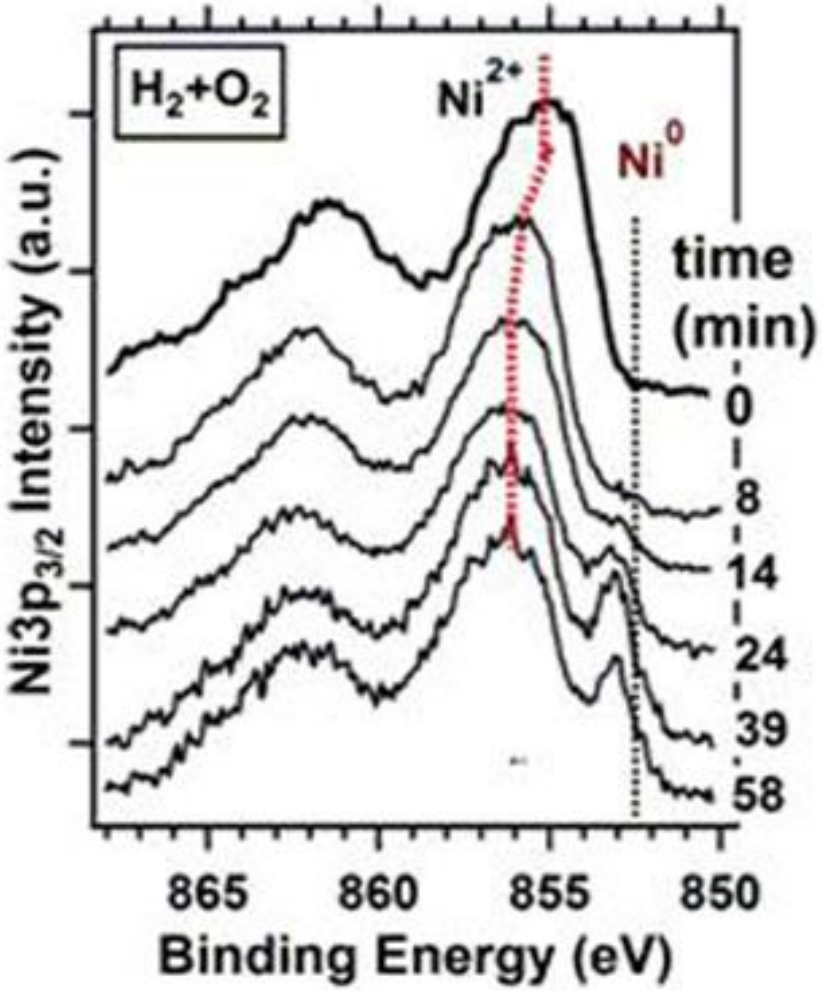
B. Bozzini et al. Scientific Report 3, 2848, 2013

ESCAmicroscopy – Self Driven Single Chamber SOFC *In operando* condition



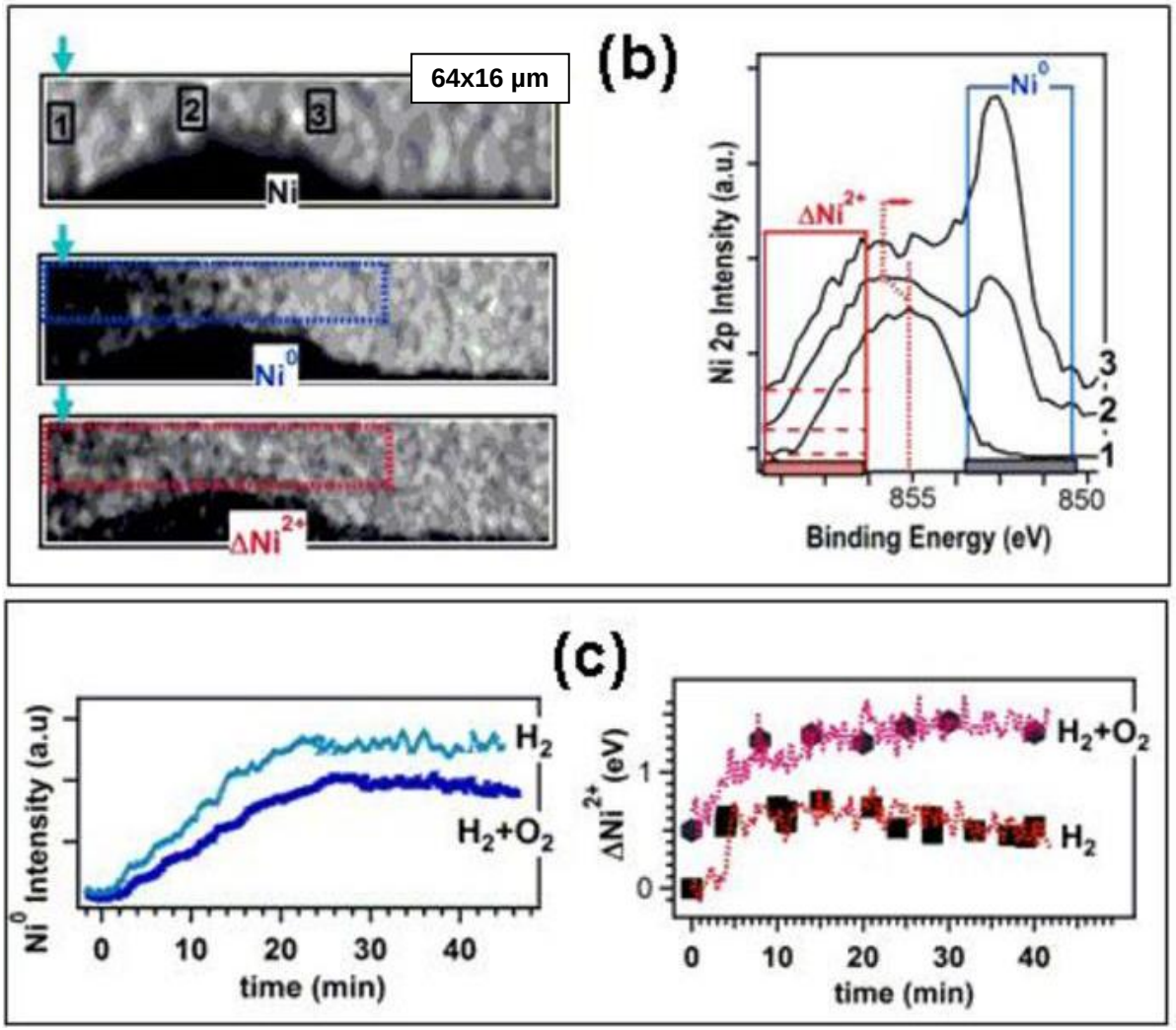
self-driven activity of electrochemical cell starts

Chemical reduction
$Ni^{2+}+H_2 \rightarrow Ni+2H^+$



B. Bozzini et al. Scientific Report 3, 2848, 2013

ESCAmicroscopy – Self Driven Single Chamber SOFC *In operando* condition



Simultaneously mapping the local chemical state and the local electrochemical activities

B. Bozzini et al. Scientific Report 3, 2848, 2013

Near ambient pressure XPS

- short mean free path of electrons in a gas phase
- High voltage components to detect the single electron

State of the art approach:

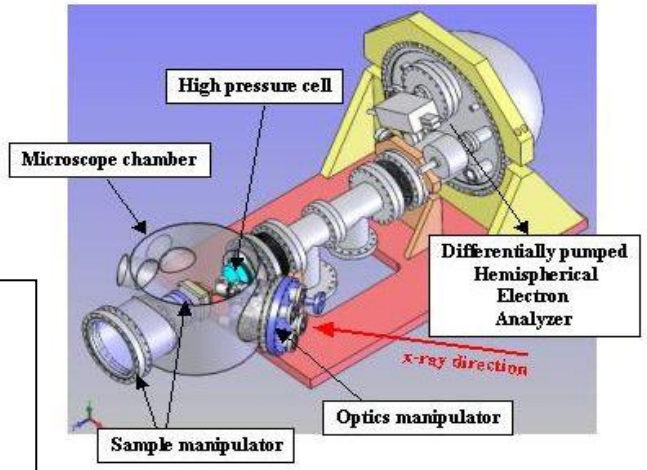
- Electron analyzers coupled with sophisticated differentially pumped lenses

Confine the high pressure at the sample

Ambient pressure SPEM:

- X-ray optics
- Sample Stage
- Differentially pumped analyzer

Challenging technical solutions



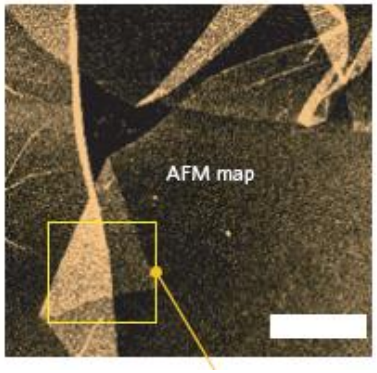
Environmental cell using graphene oxide windows

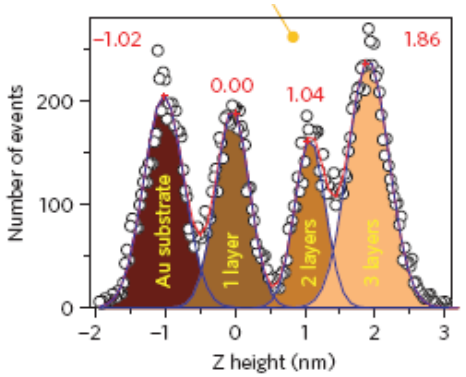
(in collaboration with A. Kolmakov – Souther Illinois Uni. - USA)

nature nanotechnology
ARTICLES
PUBLISHED ONLINE: 28 AUGUST 2011 | DOI: 10.1038/NNANO.2011.130

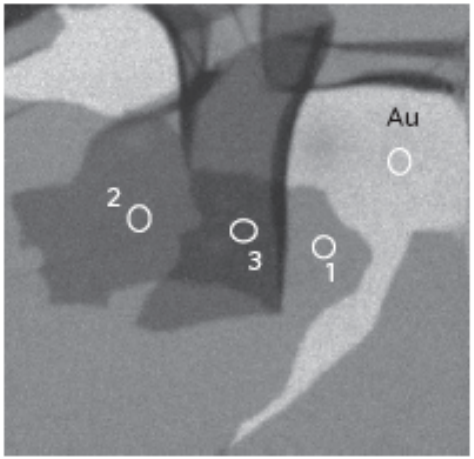
Graphene oxide windows for *in situ* environmental cell photoelectron spectroscopy

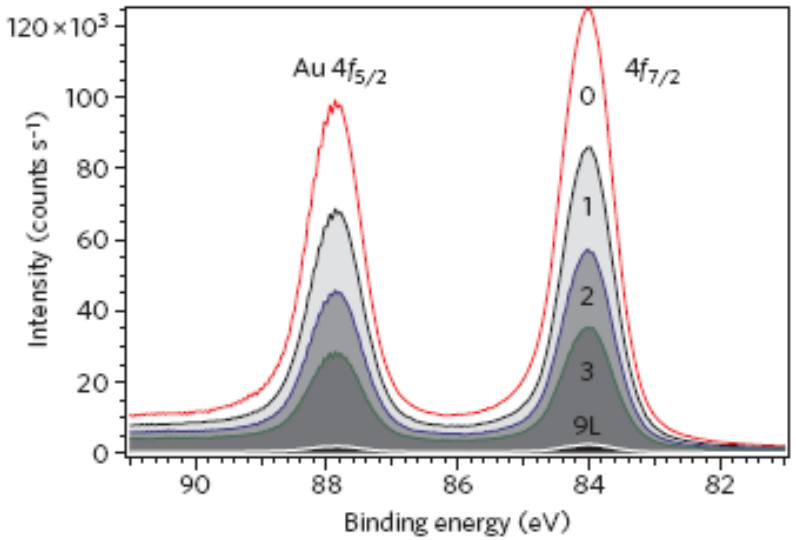
Andrei Kolmakov[1]*, Dmitriy A. Dikin[2], Laura J. Cote[2], Jiaxing Huang[2], Majid Kazemian Abyaneh[3], Matteo Amati[3], Luca Gregoratti[3], Sebastian Günther[4] and Maya Kiskinova[3]

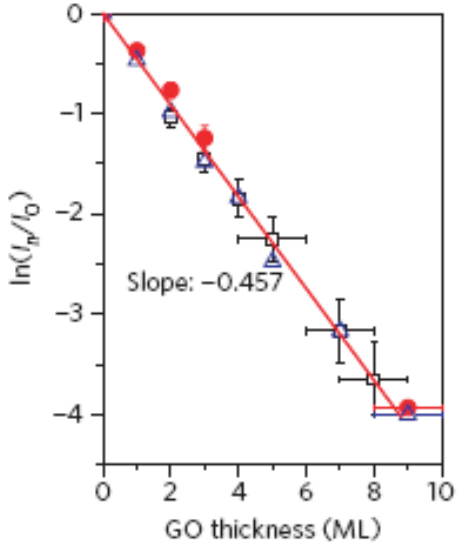




- **low-cost, single-use environmental cells**
- **compatible with XPS and Auger instruments**







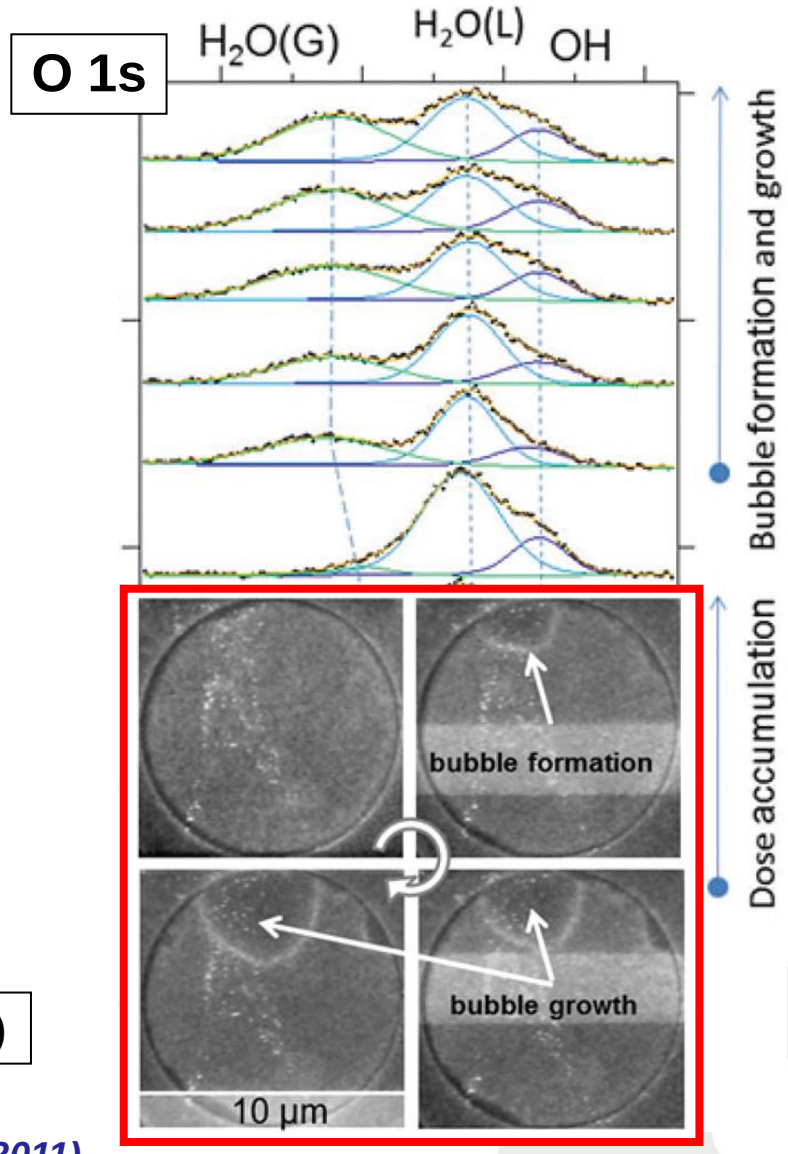
A.Kolmakov et al. Nature Nanotechnology 6, 651–657 (2011)
J.Kraus et al. Nanoscale, 2014, 6, 14394

Environmental cell using graphene oxide windows

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

kinetic energies > 450–500 eV

- **liquid or gases (bar)**



A.Kolmakov et al. Nature Nanotechnology 6, 651–657 (2011)
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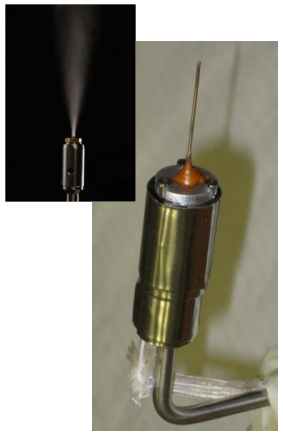
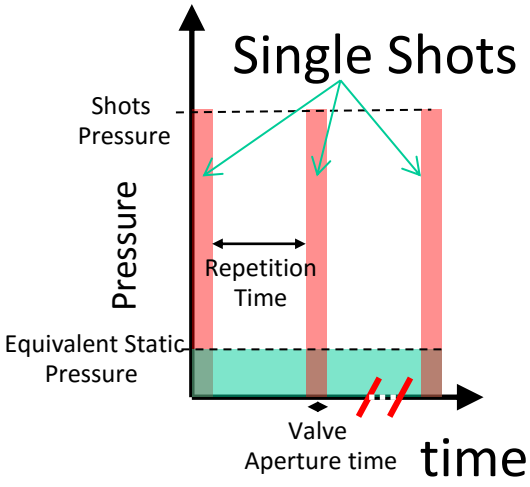
Dynamic high pressure XPS

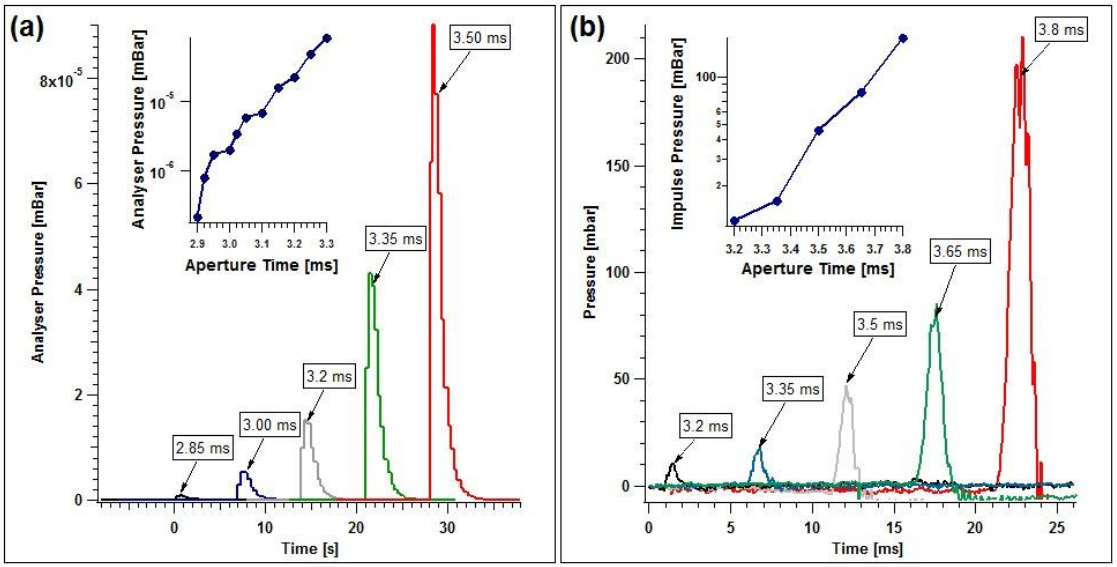


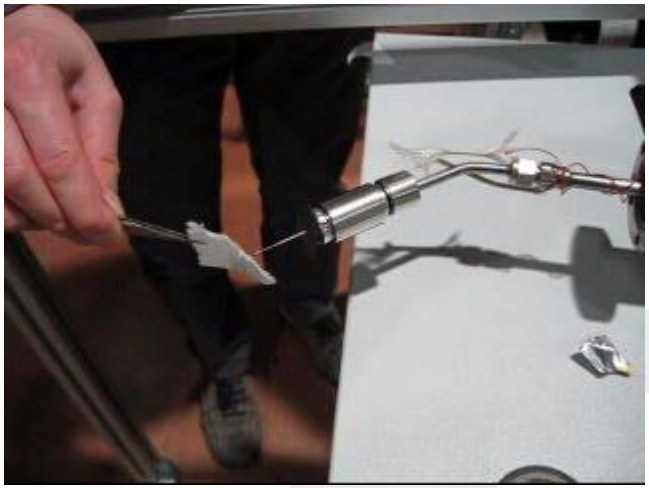
Pulsed supersonic beam

- High freq pulsed dosing valve + nozzle
- UHV compatible system
- Low cost
- Compact design
- Can be used in any SPEM/XPS/Auger system



t_{AP} ~ 3 ms
f_{AP} = 350 mHz
P_{valve} = 3.5 bar





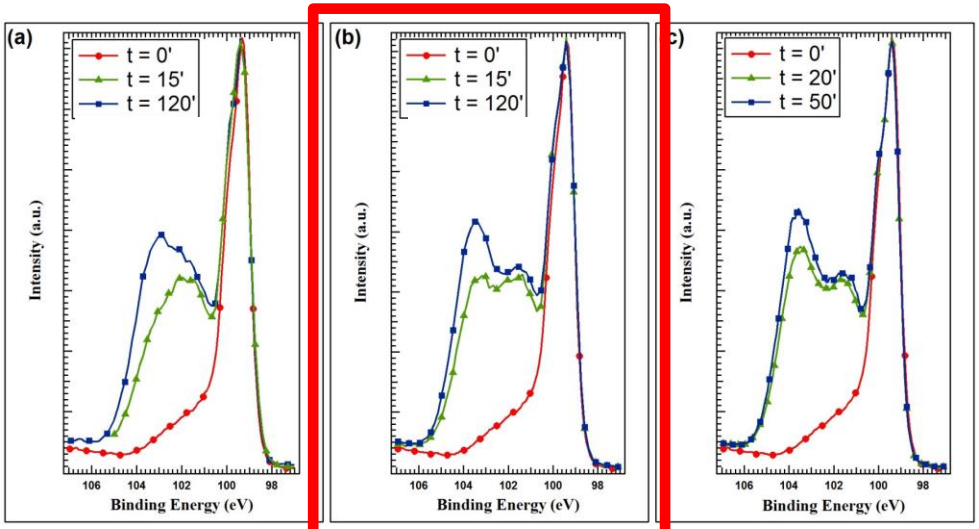
M Amati et al. Journal of Instrumentation, Vol. 8 - 05, pp. T05001 (2013)

Dynamic high pressure XPS

Si oxidation (530°C)
STATIC <-> Dynamic HP comparison

Equivalent Static Pressure
10^{-3} - 10^{-2} mbar

Single Shot MAX pressure
~ 10 mbar

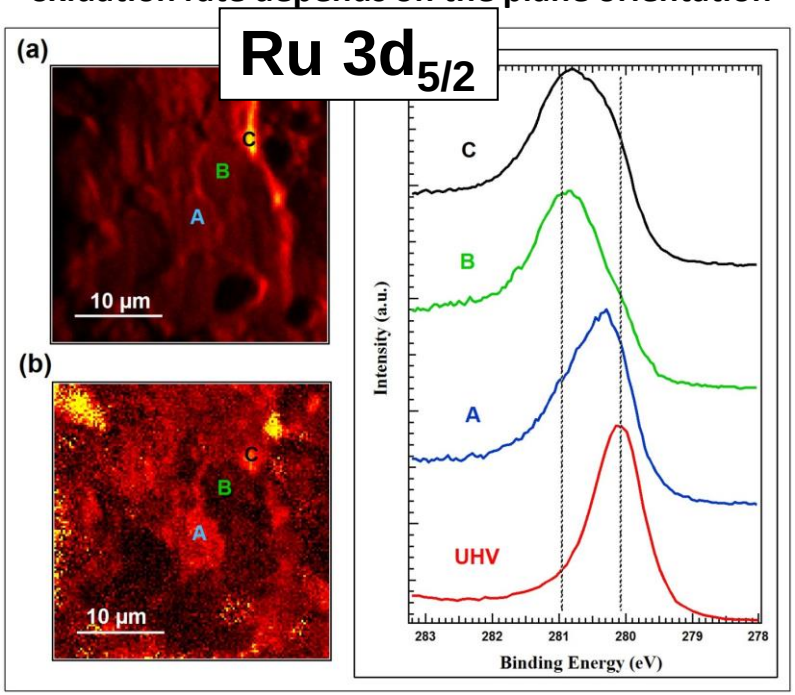


Static Pressure
1 x 10^{-3} mbar

HP
t_{AP} ~ 2.9 ms
f_{AP} = 300 mHz
P_{valve} = 3.5 bar

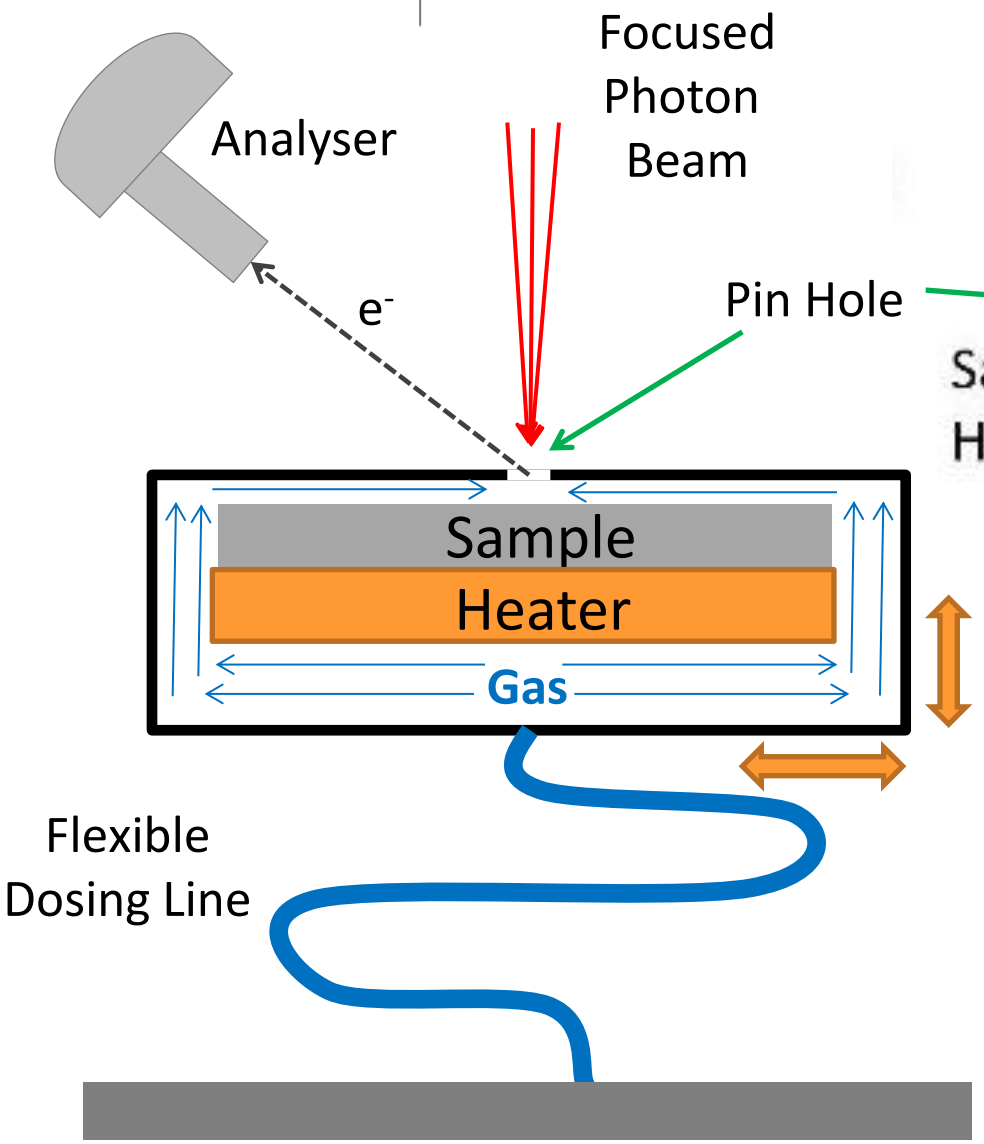
Static Pressure
1 x 10^{-2} mbar

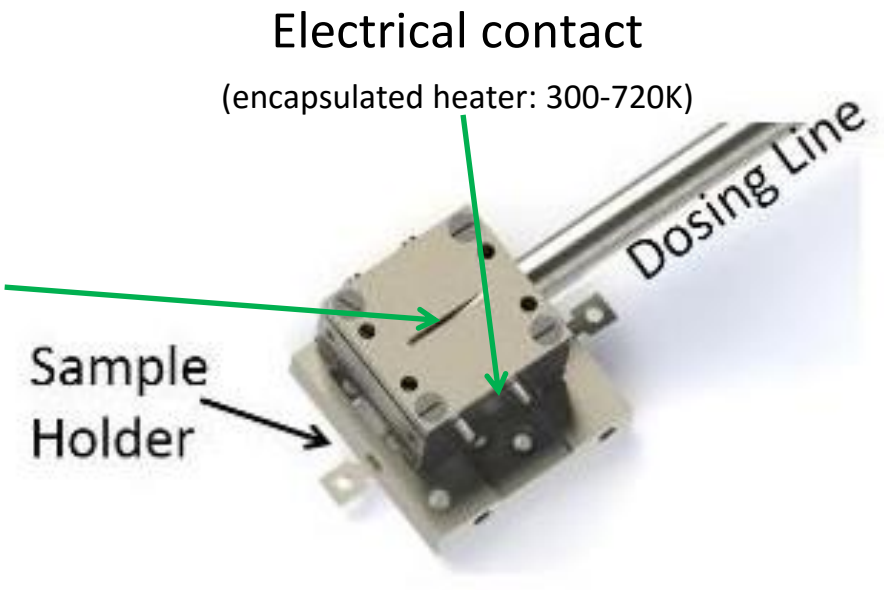
Ru polycrystal oxidation (Dynamic HP 30 min): oxidation rate depends on the plane orientation



M Amati et al. Journal of Instrumentation, Vol. 8 - 05, pp. T05001 (2013)
Doh et al. ChemElectroChem Vol. 1 - 1, pp. 180-186 (2014)

High pressure cell





$\Phi_{pin\ hole}$ = 200 µm

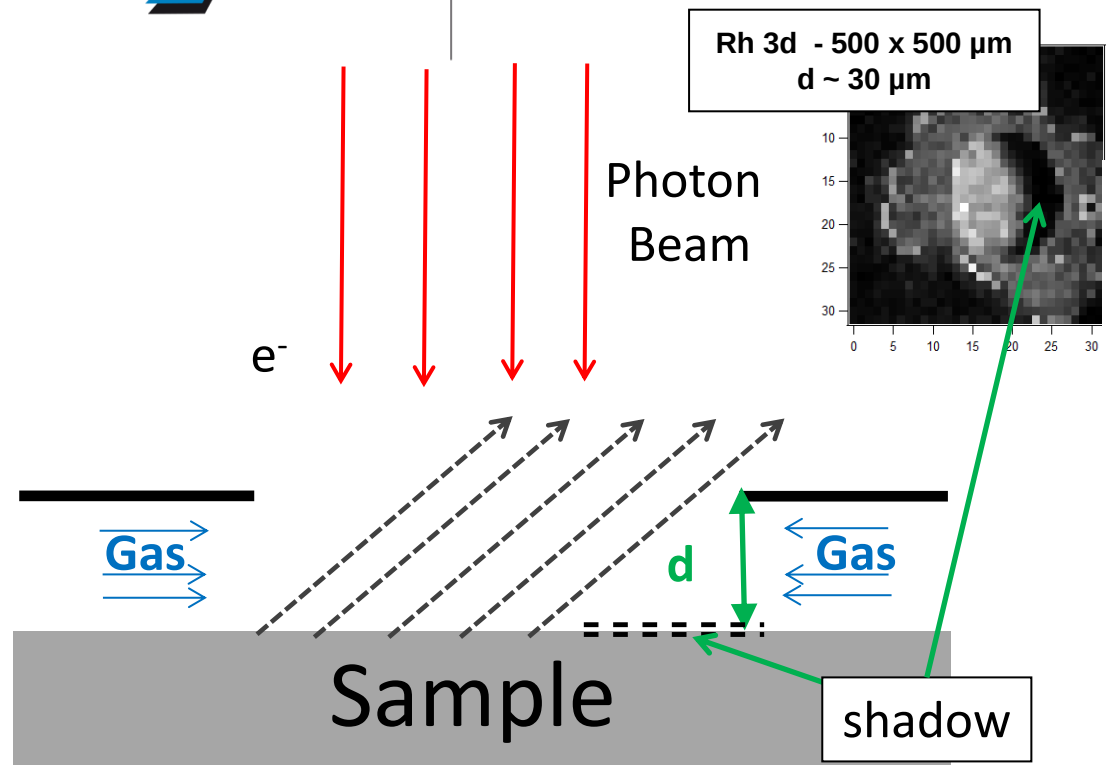
P_{cell} ~ 1 mbar

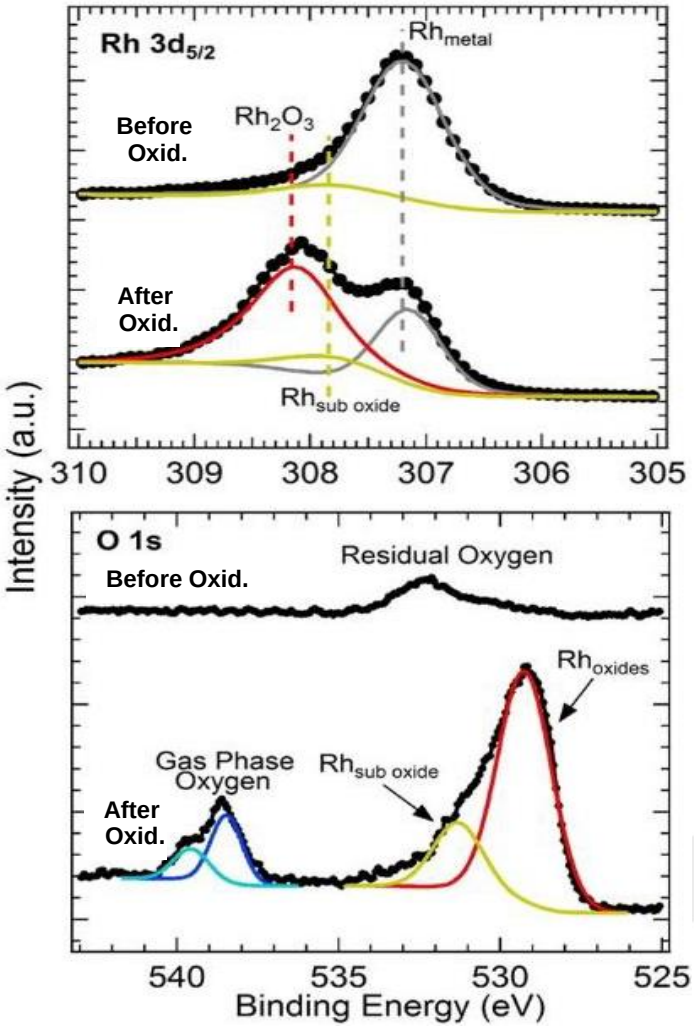
P_{SPEM} ~ 10^{-5} mbar

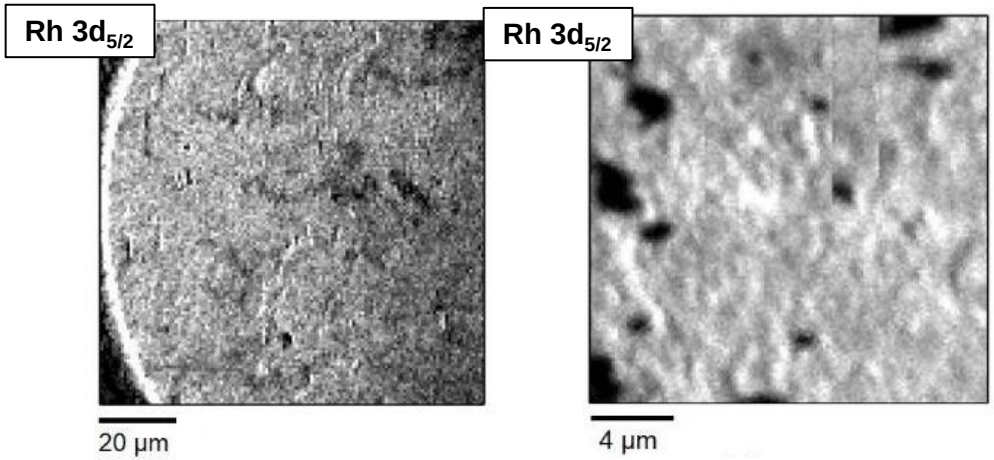
Elettra Sincrotrone Trieste

High pressure cell

Rh sample
1 mbar O_2 @ 670K
(cleaned in 1 mbar H2 @ 570K)



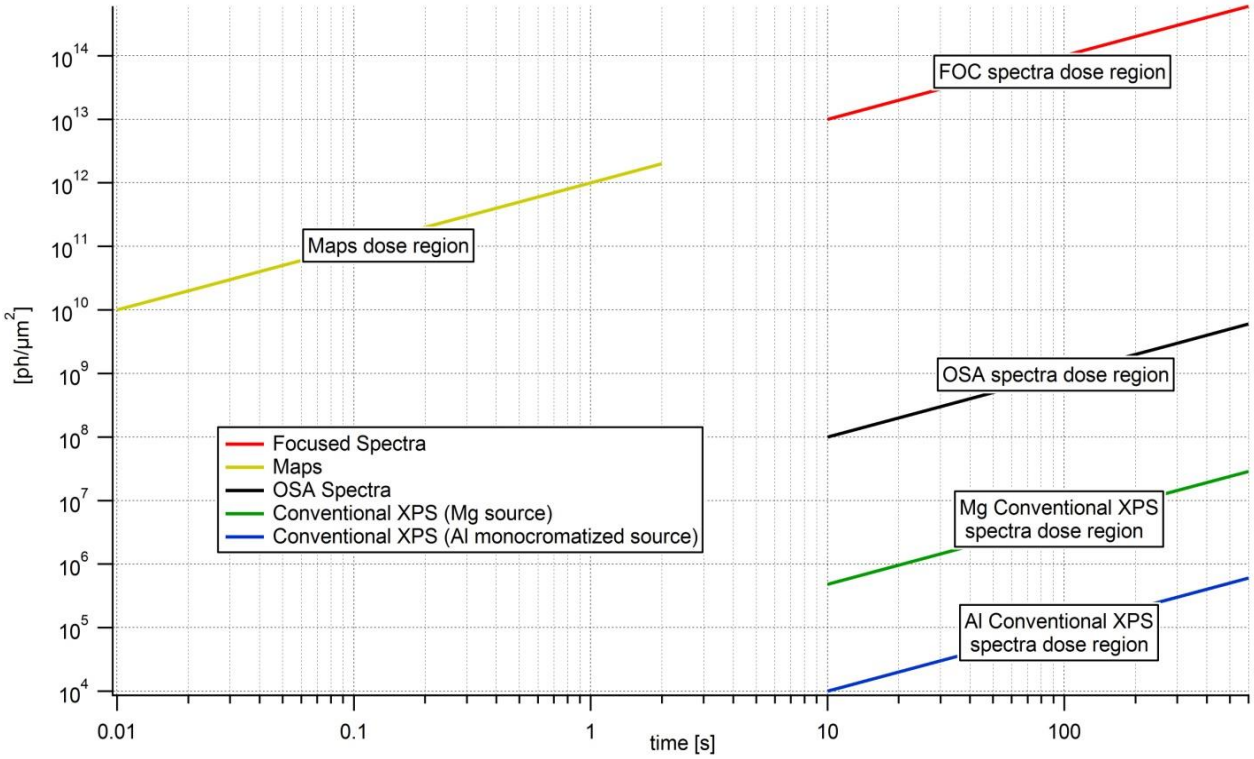


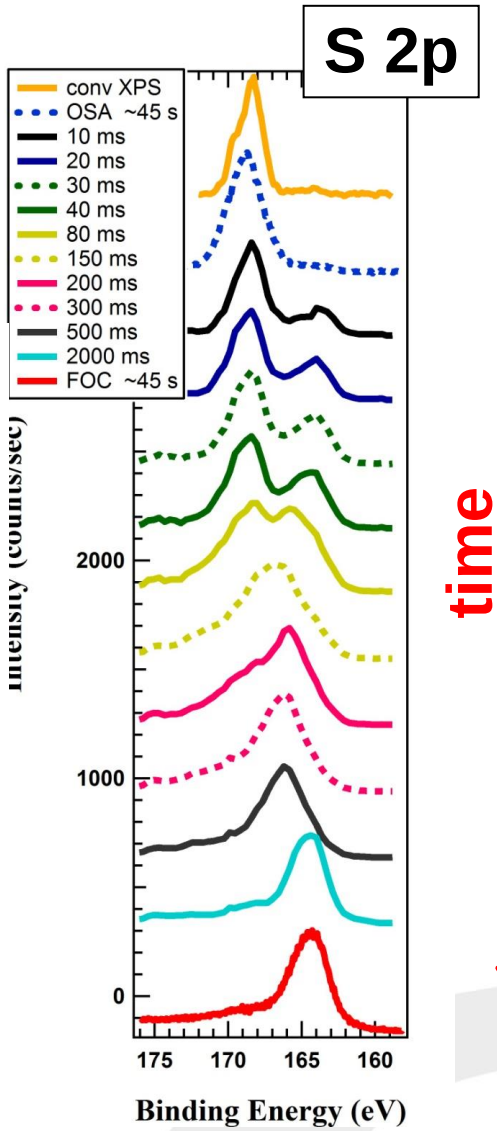


Radiation Damage

PEDOT – PSS film

- **Conventional XPS and OSA spectra are similar**
- **Even the faster map show damage**





Elettra
Sincrotrone
Trieste

Thank you!

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