The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2332-20

School on Synchrotron and FEL Based Methods and their Multi-Disciplinary Applications

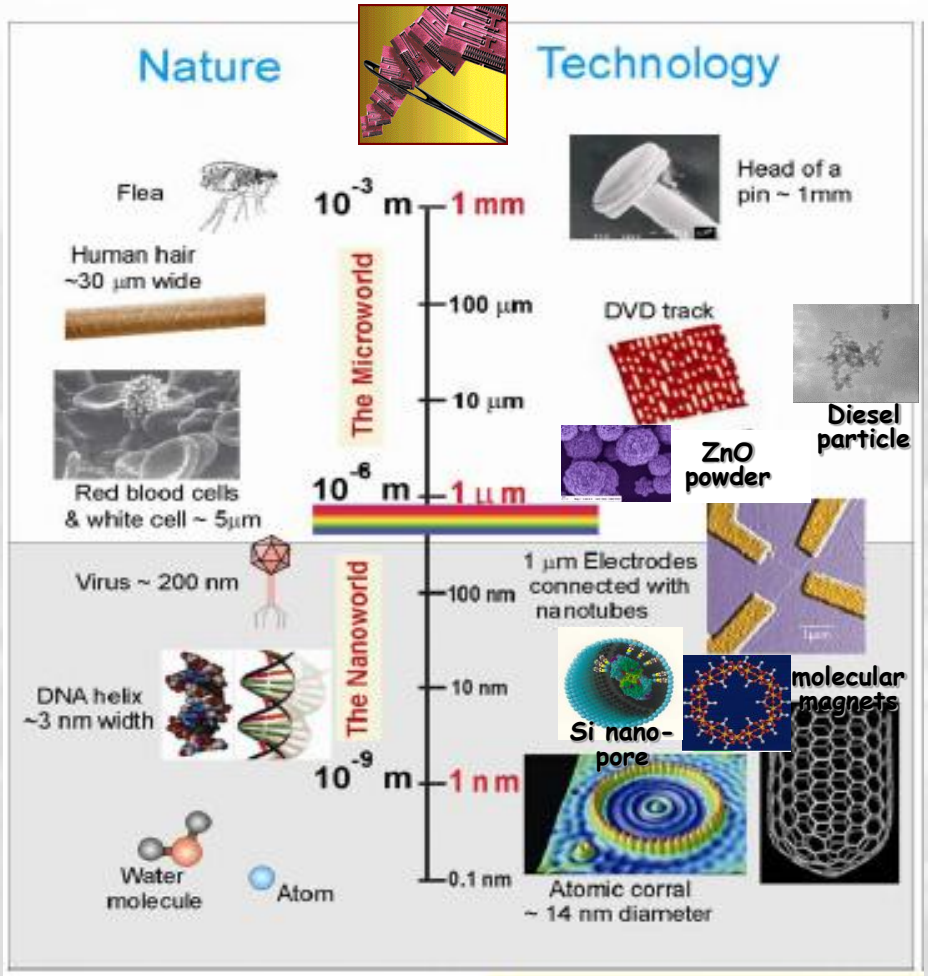
19 - 30 March 2012

Introduction to X-ray microscopy and spectro-microscopy

Kiskinova Maya
Sincrotone, Trieste

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

Introduction to X-ray microscopy and spectro-microscopy



- Materials have properties varying at various depth and length scales.
- Structure and chemical composition usually is different at the surface and in the bulk.
- New properties expected with decreasing the dimensions stepping in nanoworld.

What we NEED:

Spatial resolution & chemical sensitivity, morphology & structure, varying probing depth, temporal resolution..

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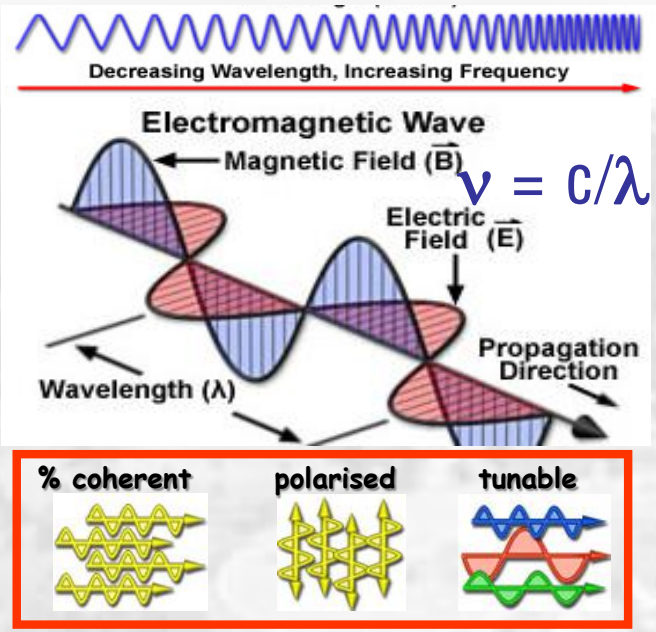
Why using synchrotrons for microscopy?

Only 'LIGHT' with comparable wavelength, λ, can visualize the micro- and nano-structured world



Synchrotron Light

- ❖ High brightness.
- ❖ Tunability
- ❖ Polarization.
- ❖ Time structure.
- ❖ Coherence.

Modern technology

- ✓ X-ray focusing optics.
- ✓ X-ray or electron detectors.

X-Rays compared to charged particles:

- ➢ Higher penetration power: wavelenght controlled.
- ➢ Great variety of spectroscopies-elemental, chemical etc information.
- ➢ Variety of imaging contrasts with diffraction limited resolution.
- ➢ Less sensible to sample environment in photon-out detection mode.

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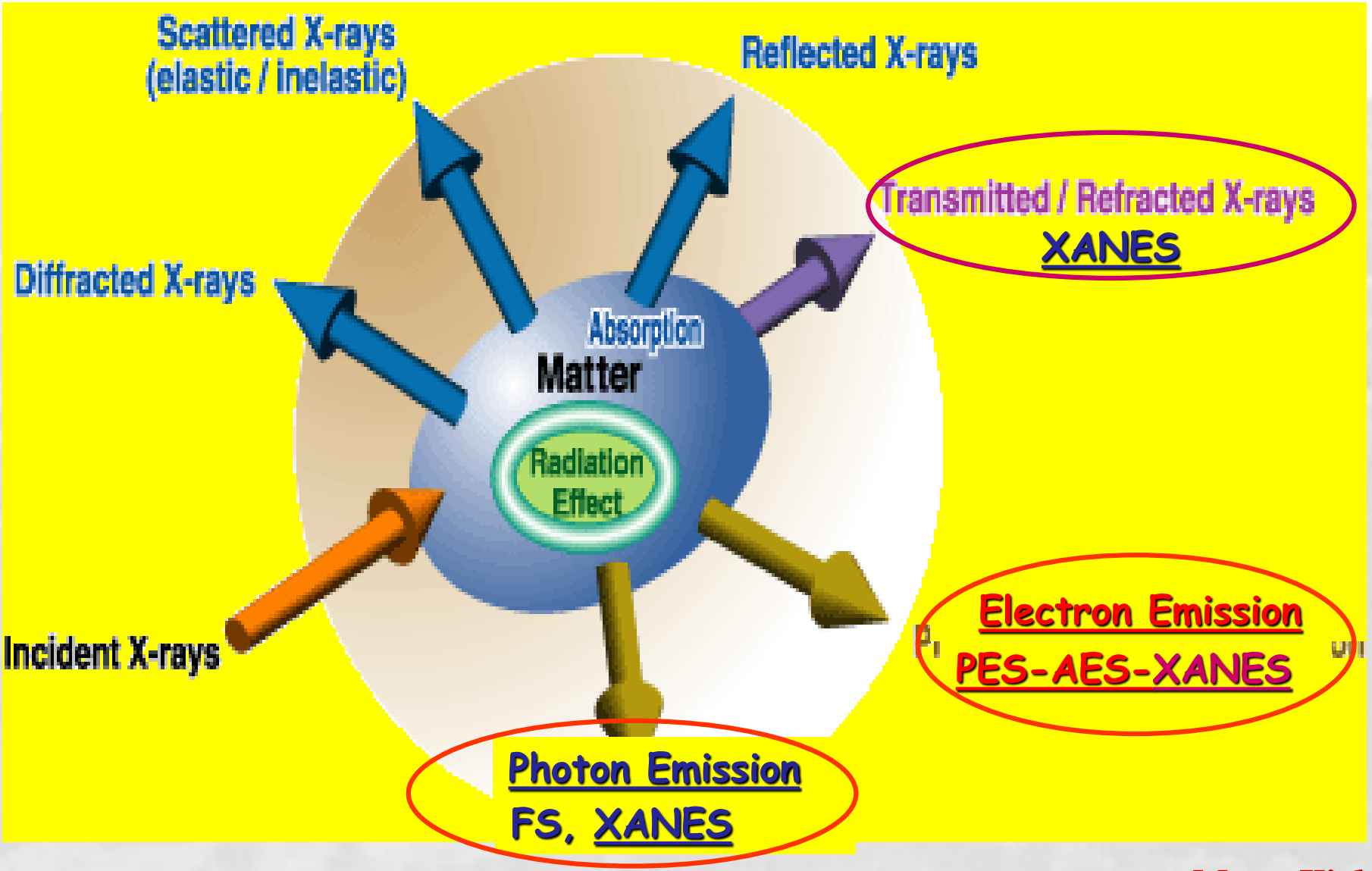
Interactions of x-rays with the matter:

redirection & absorption ⇒ x-ray transmission and x-ray or electron emission



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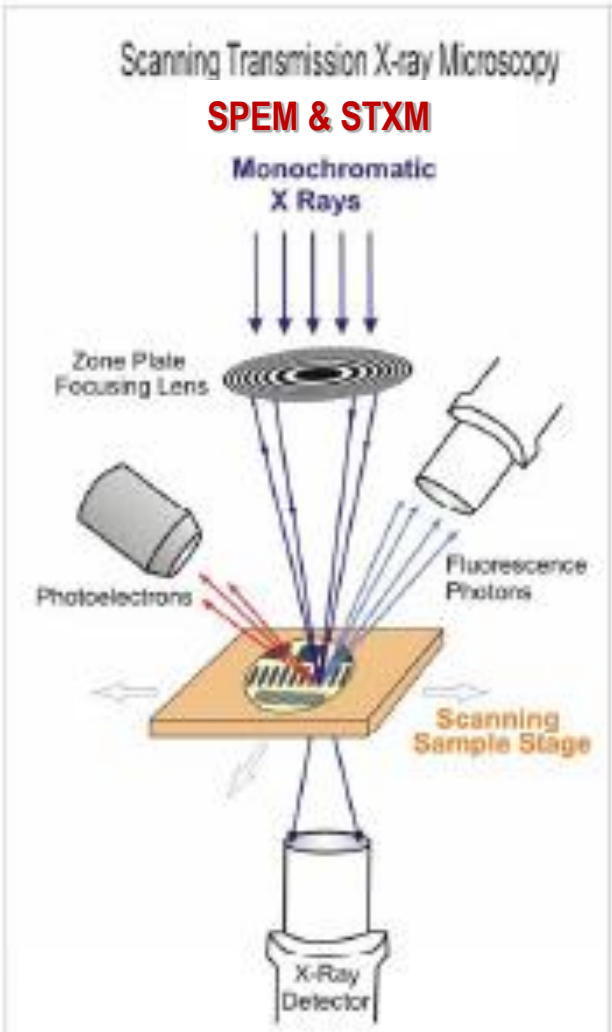
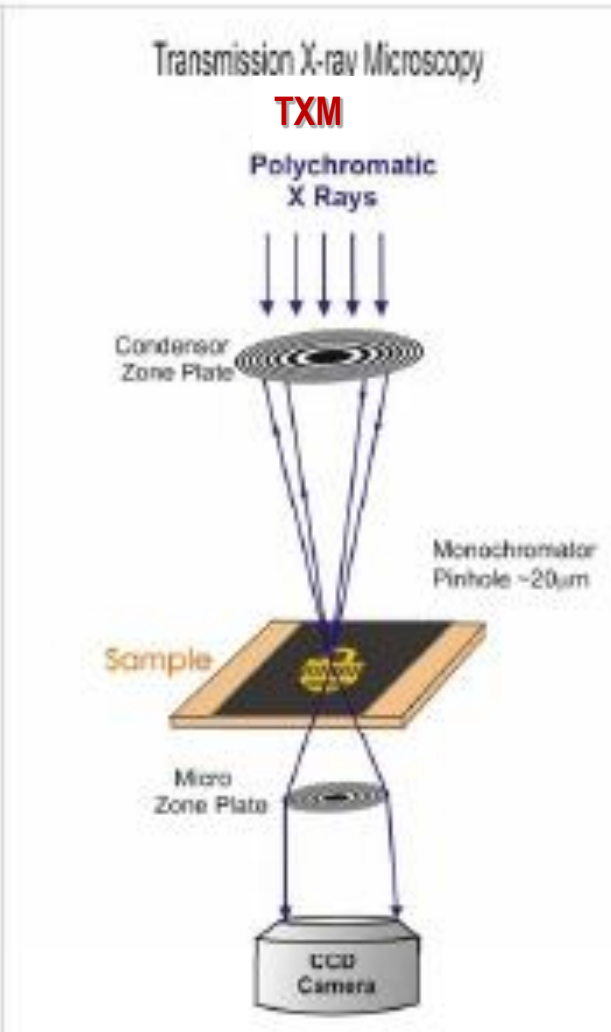
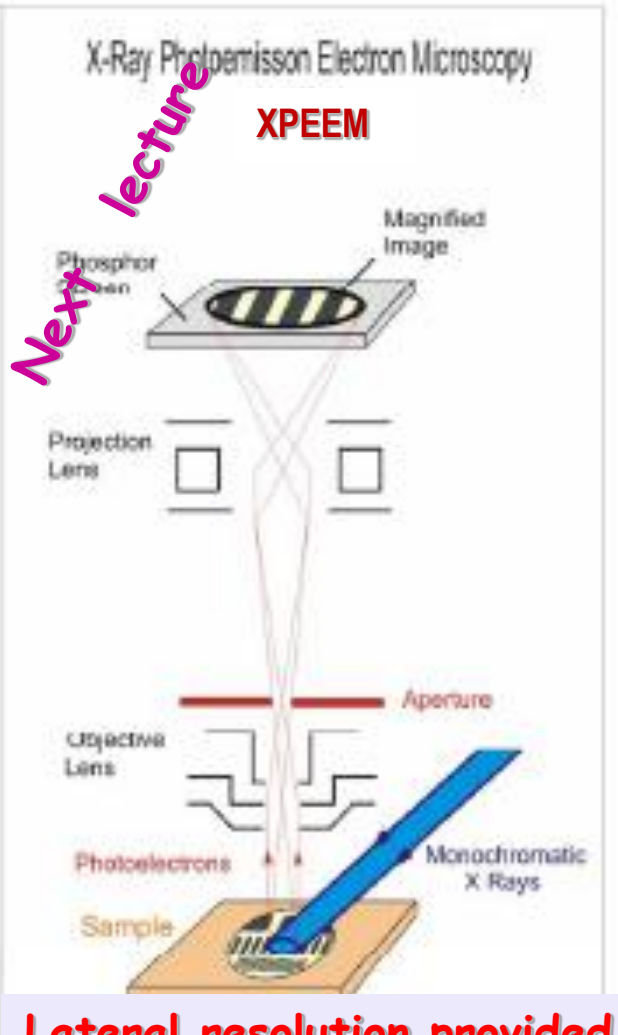
Microscopy Approaches :
X-ray or electron optics; X-ray or electron detection







Lateral resolution provided by photon optics

Lateral resolution provided by electron optics

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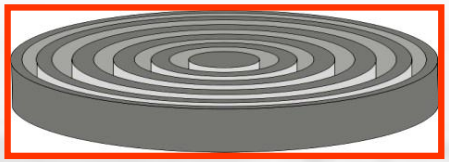
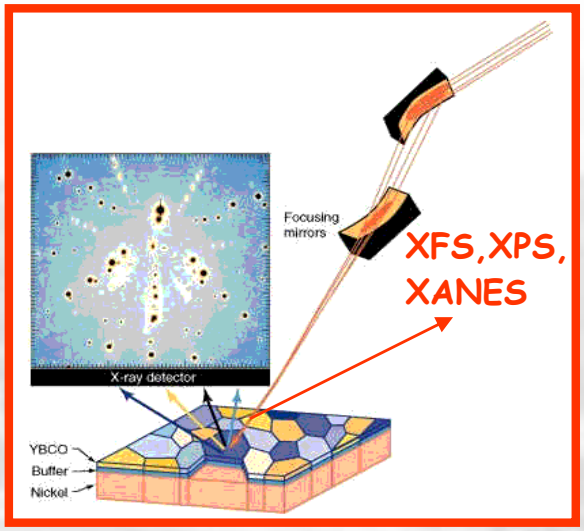
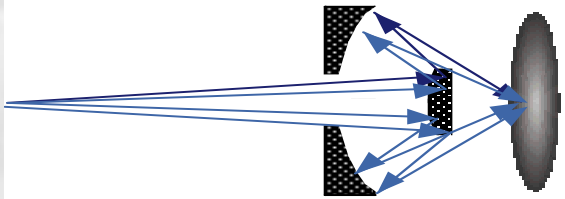
X-ray focusing optics:
zone plates, mirrors, capillaries



Zone Plate optics: from ~ 200 to ~ 10000 eV
Monochromatic:
Resolution achieved 15 nm in transmission

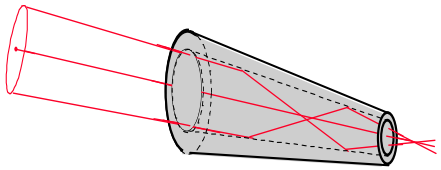


KP-B mirrors each focusing in one direction: soft & hard: ~ 1000 nm
Soft & hard x-rays!
achromatic focal point, easy energy tunability, comfortable working distance
Resolution ≤ 100 nm



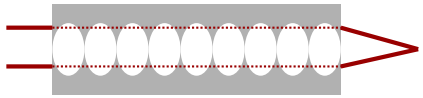
Normal incidence:
spherical mirrors with multilayer interference coating (Schwarzschild Objective)
Monochromatic, good for E < 100eV
Resolution: best ~ 100 nm

Capillary: multiple reflection concentrator



Hard x-rays ~ 8-18 keV
Resolution: > 3000 nm

Refractive lenses



Hard x-rays ~ 4-70 keV
Resolution: > 1000 nm

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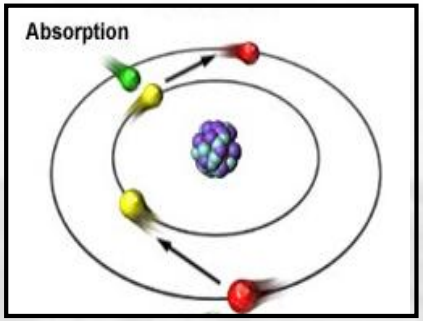
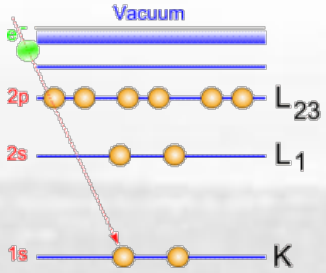
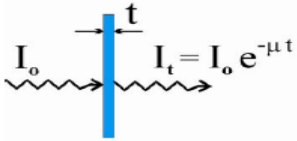
Synchrotrons offer a variety of imaging approaches, based on x-ray absorption, scattering and spectroscopies

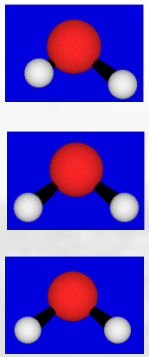


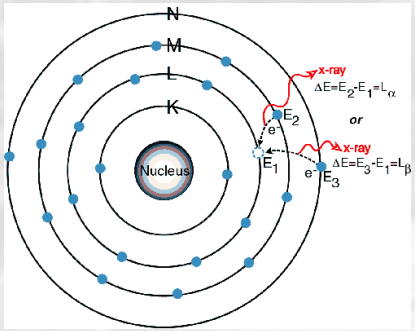
Photon or e⁻ emision

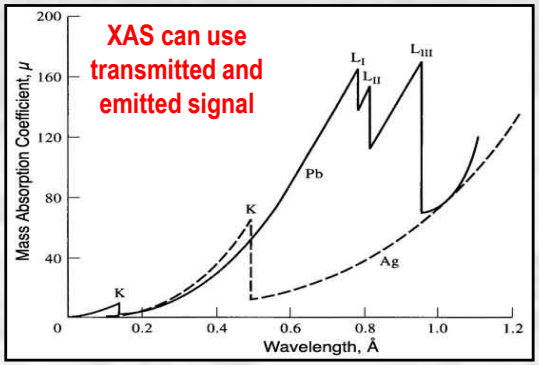


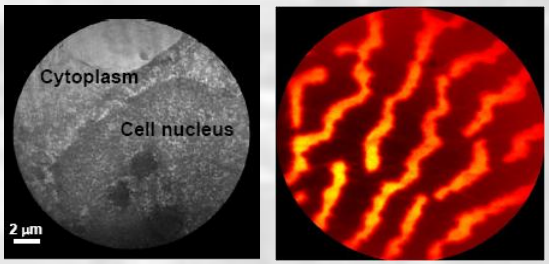
Photon transmission

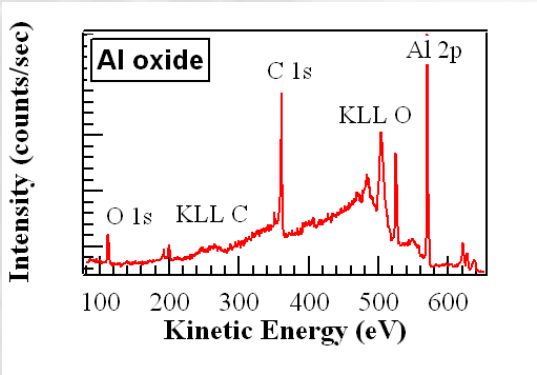


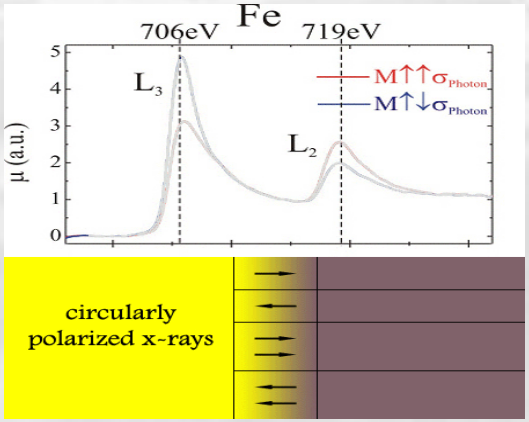












Imaging: morphology (absorption and scattering) or composition (spectroscopy)

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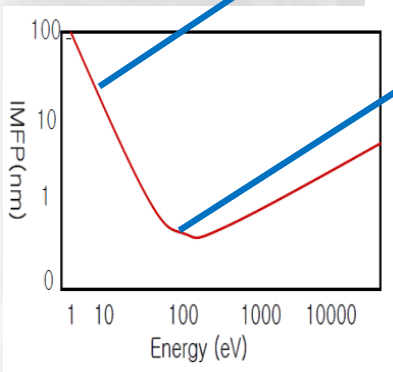
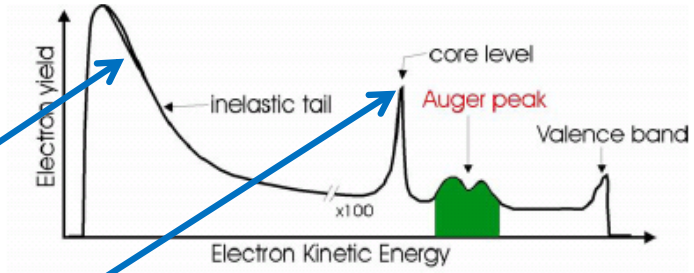
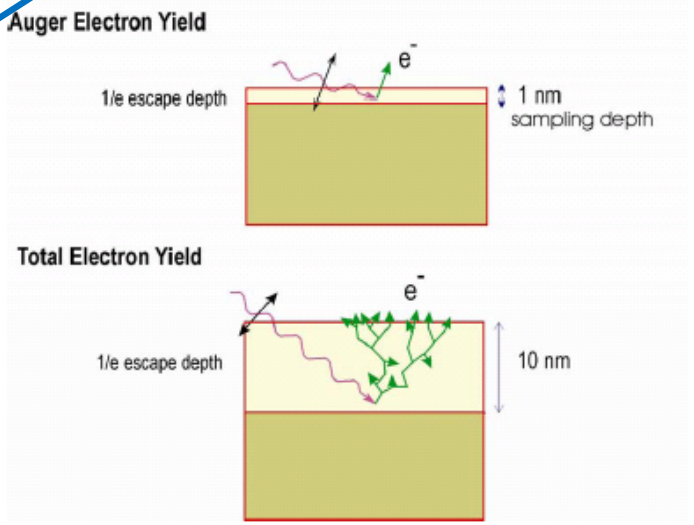
Sampling depths depend on the detected signal
(electrons or photons)



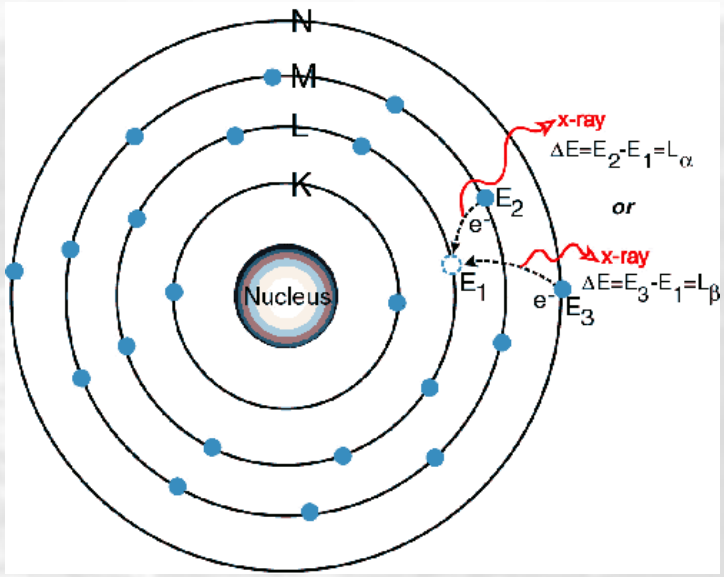
TEY, core, valence and Auger electron emission

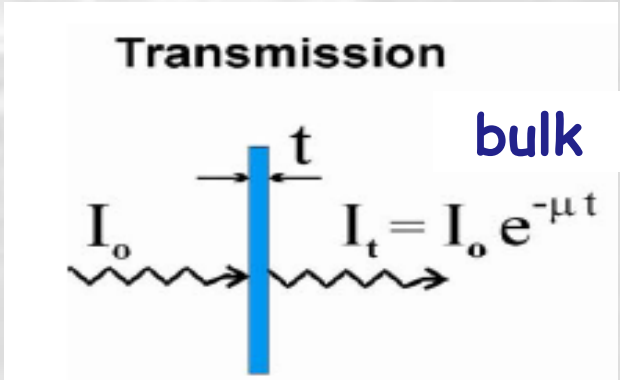




Fluorescence emission:

Probe depth- > 100 nm = f(photon energy, matrix)





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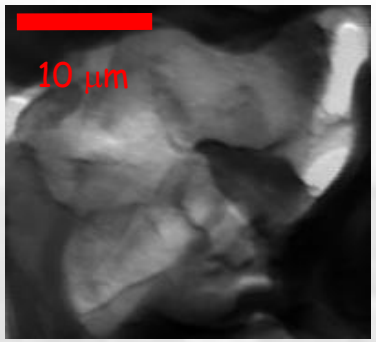
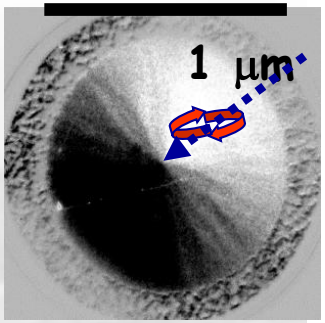
Imaging and μ-spectroscopy

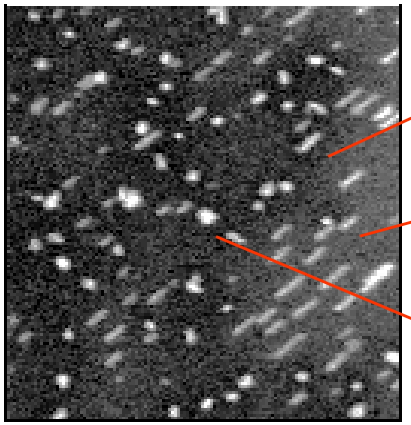
Illy coffee cells

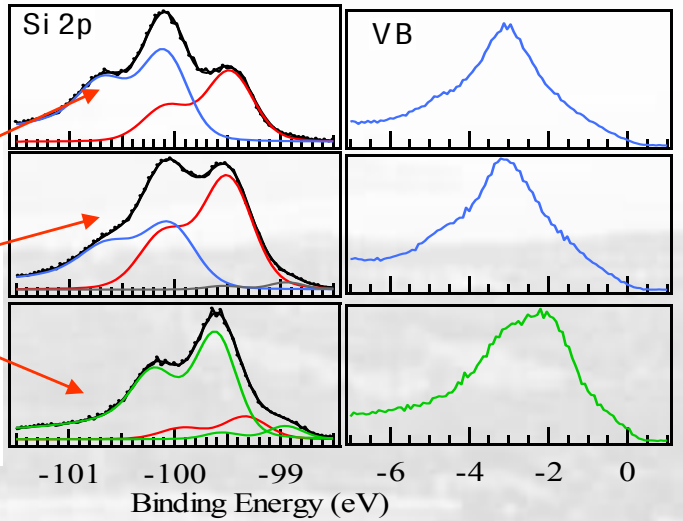


Permaloy NS



Ni/Si-Ni3p map





The image contrast based Emitted electrons (XPS,XANES), Transmitted/emitted photons (XANES,FS) can provide:

- Morphology: density, thickness..
- Element presence and concentration;
- Chemical state;
- Band-bending or charging;
- Magnetic spin or bond orientation.

Microspectroscopy: μ-XPS, μ-XANES, μ-XRF in selected areas from the images: detailed characterization of the chemical and electronic structure of coexisting micro-phases.

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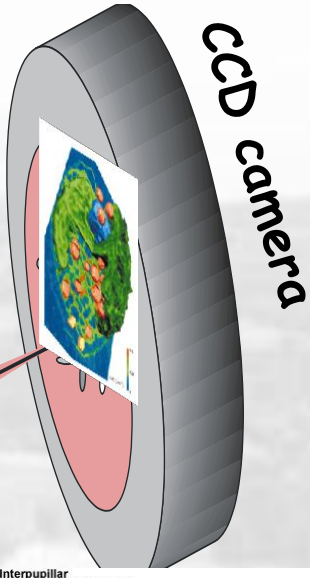
X-ray transmission microscope (TXM-FFIM)

Full-field X-ray imaging or "one shot" X-ray image acquisition can be considered as the optical analog to visible light transmission microscope

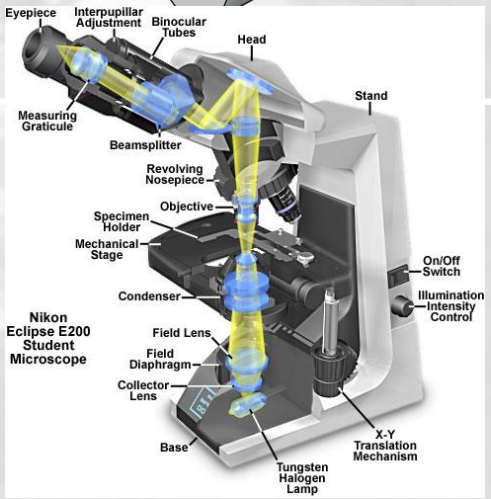
Günther Schmahl, 1st experiment DESY 1976

What we need?
- a suited condenser system
- a specimen stage (automated)
- an eyepiece/camera

Objective ZP to magnify the image onto the detector



Specimen environment to be adapted to application



X-ray light

Condenser illuminating the object field: ZP, capillary

2006 - XTM (7+4): - ALS (2), SSRL (1), APS (2), BESSY II (1), ELETTRA (1), ESRF (1), ASTRID (1), SPRING'8 (1), AURORA (1), DIAMOND (1),SOLEIL (1), ALBA (1), SLS (1). Resolution achieved 15 nm.

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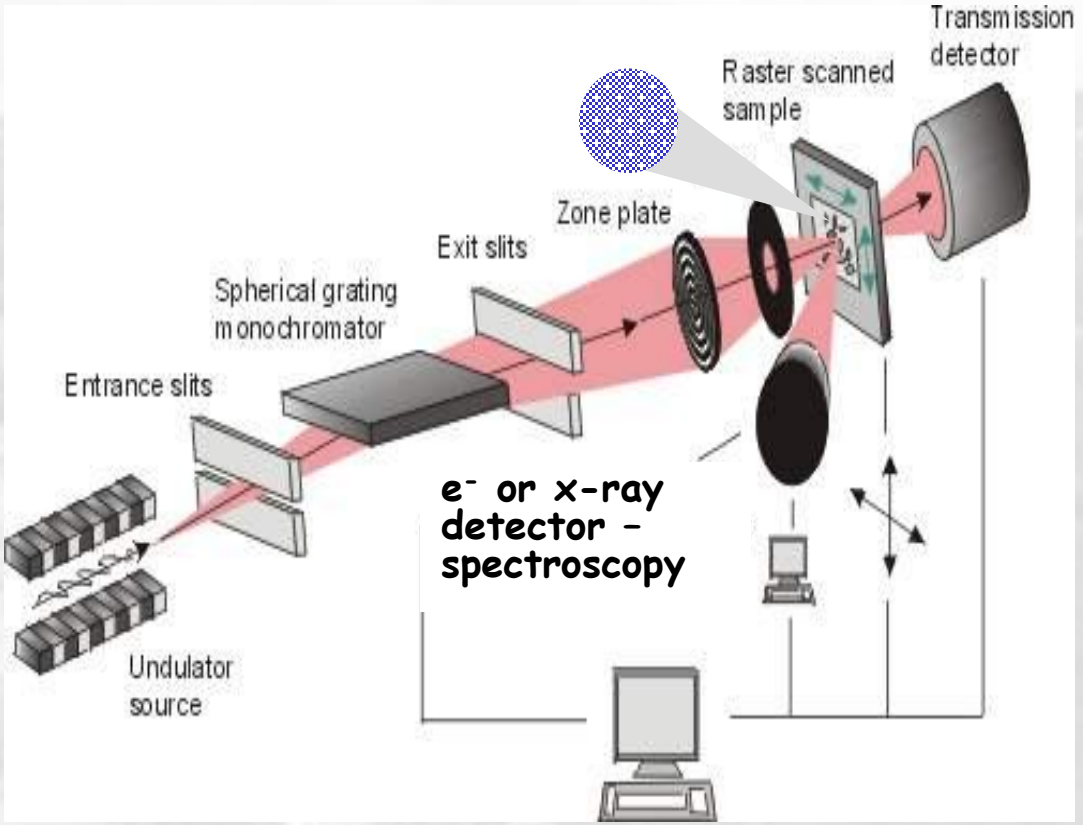
X-ray Scanning microscopy: uses focusing x-ray optics (preferred zone plates)

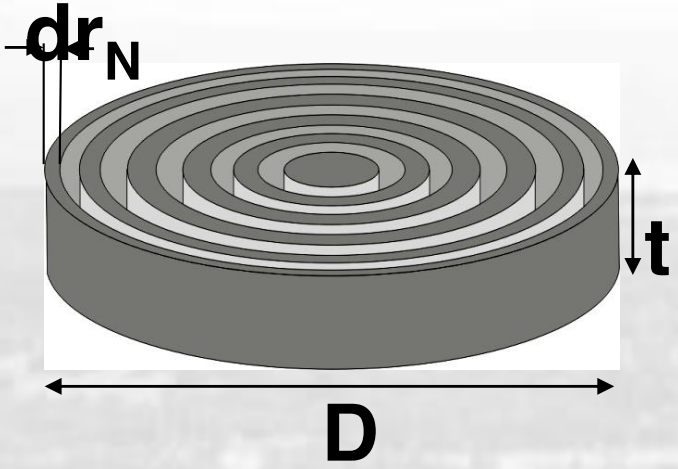
Works in Transmission and Emission + spectroscopy from the spot

Janos Kirz, 1st operating STXM 1983
SPEM 1990

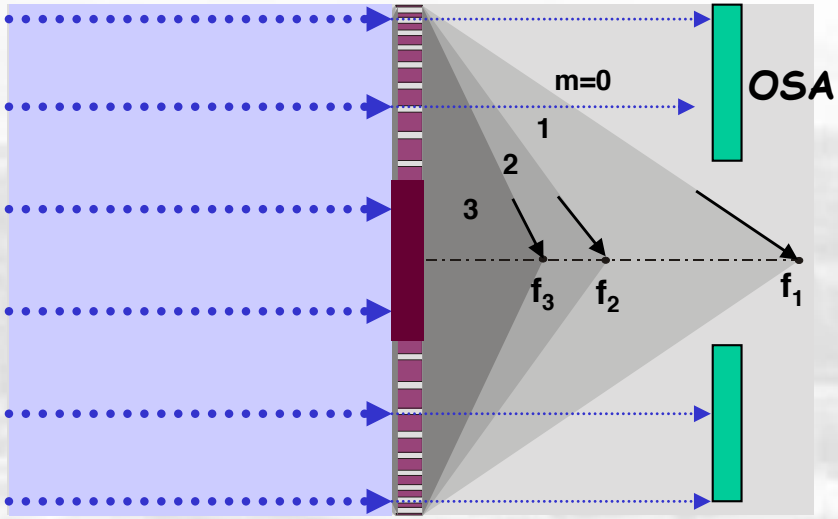


STXM and/or SPEM (17): – ALS (4), SSRL (1), APS (2), BESSY2 (1), ELETTRA (3), ESRF (1), PLS (1), NSLS (1), SLS (2), SPRING'8 (1), SRRC (1), CLS (1), DIAMOND (2), Soleil (1),NSLS-II (2) Resolution achieved 25 nm.

Zone plate: circular diffraction grating of N lines with radially decreasing line width operating in transmission



$$f_m = D.dr/\lambda_m$$



Important parameters:

Finest zone width, dr_N (10-100 nm) determines the Rayleigh resolution (microprobe size) $\delta t = 0.61\ \lambda/(\theta) = 1.22\ \delta r_N$

Diameter, D (50-250 mm) determines the focal distance f_m.

Efficiency % of diffracted x-rays: 10-40% (4-25%)

Monochromaticity required: $\lambda/d\lambda \geq N$ (increases with dr and D).

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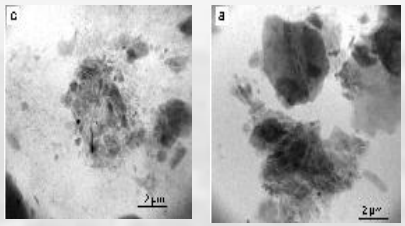
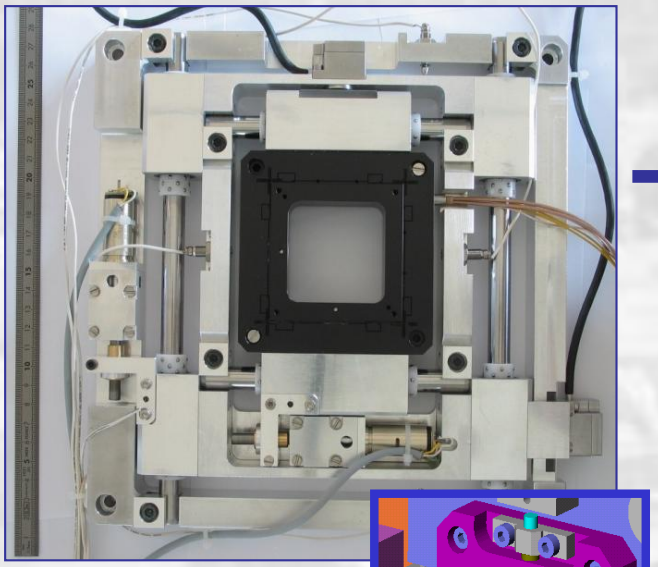
Photon-in/photon-out microscopy
versatile specimen environment – no requirement for UHV!

Operation in air, vacuum and inert gas atmosphere



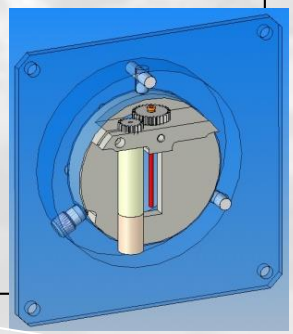
"Wet cell" environment for imaging of liquids (agglomeration, solidification, hydratation)

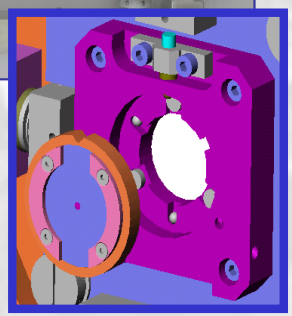
Chemical reaction cell for catalysis experiments under normal conditions



Magnetic cell for dichroism studies

3D imaging environment: Stereo-imaging and tomography: FFI is the better choice





Development of cryo-techniques for for radiation sensitive specimen

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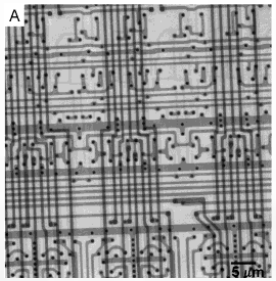
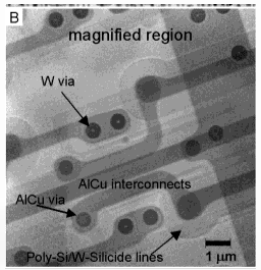
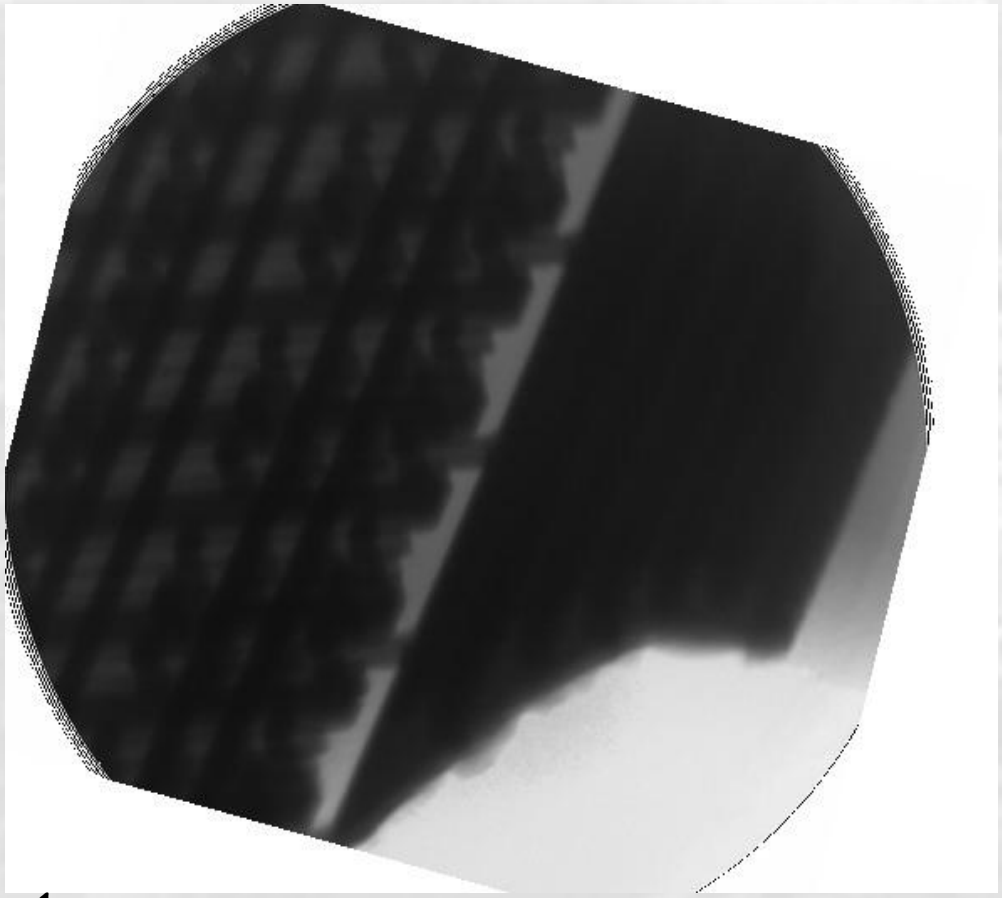
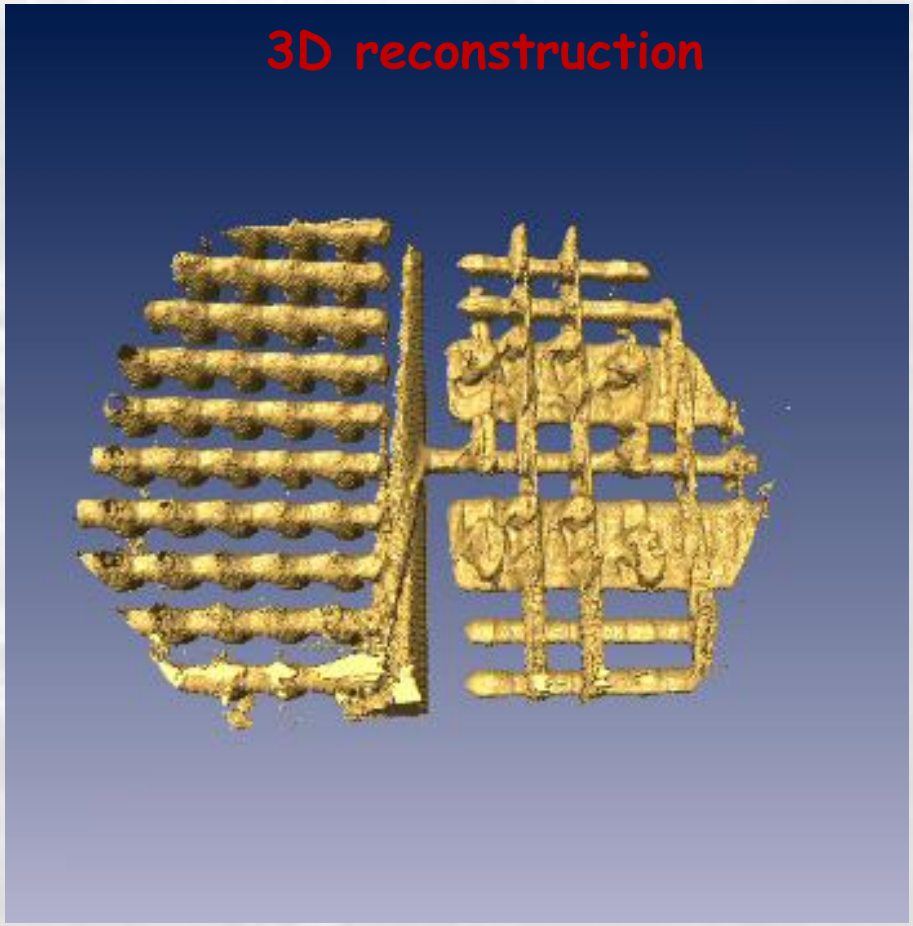
Computed tomography of Cu interconnects with the BESSY TXM





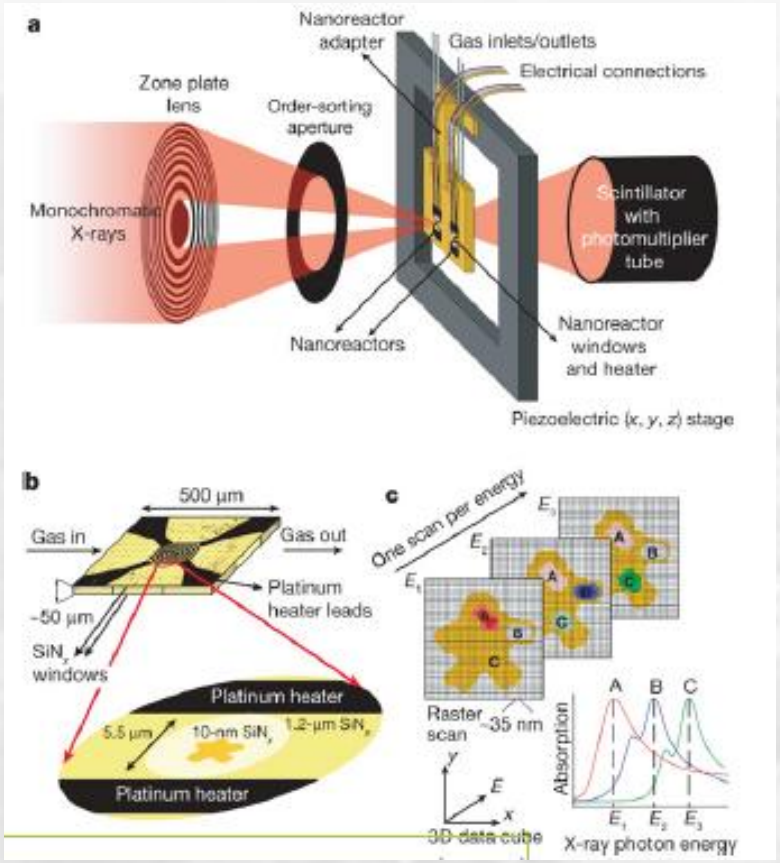
High resolution images of ICs after alignment (50 projections, 140°)

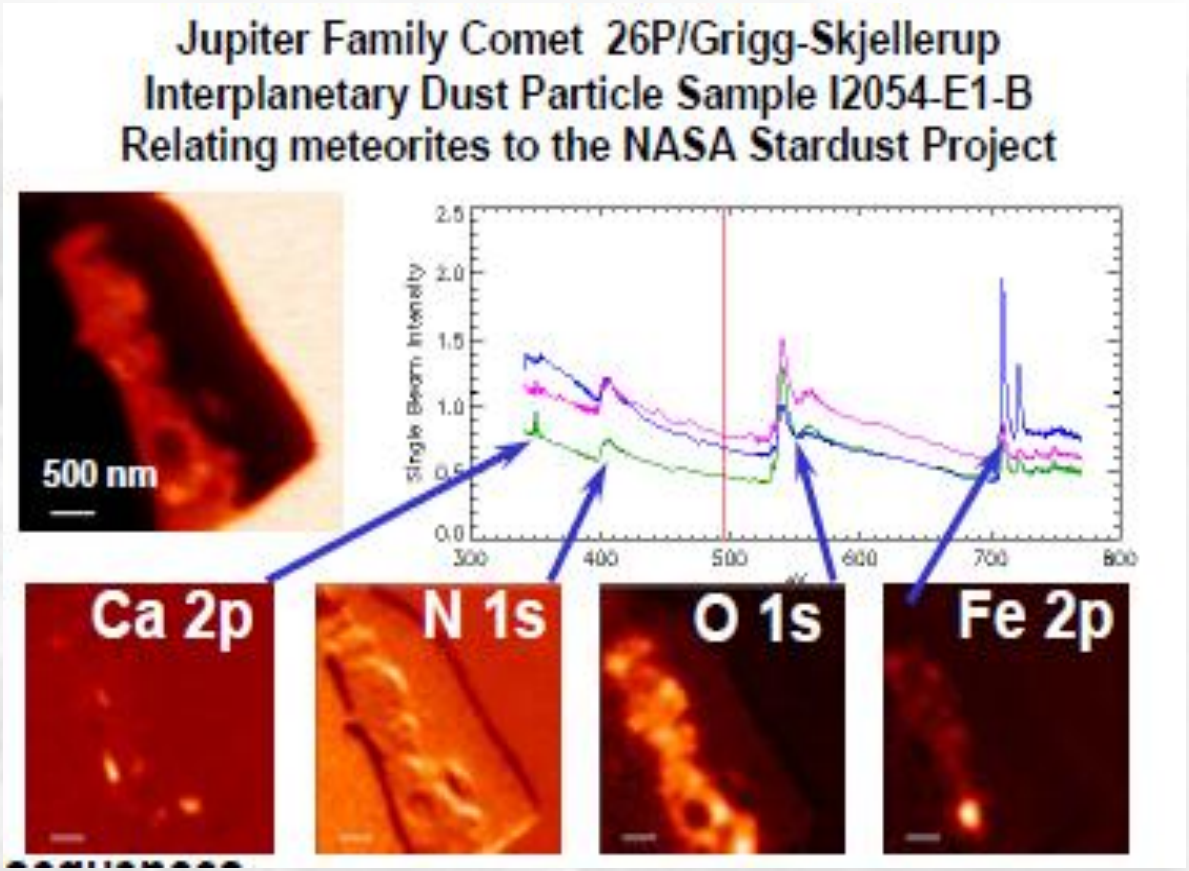




G. Schneider et al., J. Vac. Sci. Technol. B 20, 3089 (2002)

Chemical mapping of interplanetary dust particles with STXM at ALS





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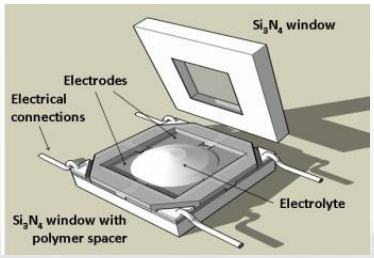
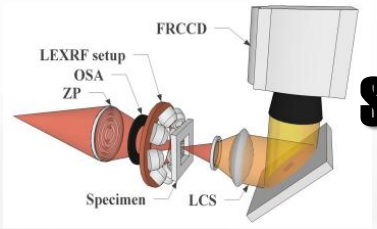
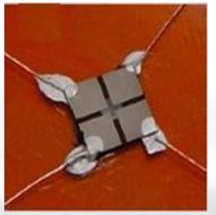
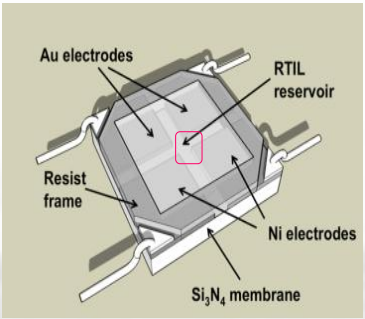
Proton Exchange Membrane Fuel Cell (PEMFC) with in-situ soft X-ray micro-spectroscopy: metal electrode stability





STXM – LEXRF - XANES



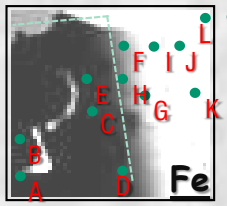


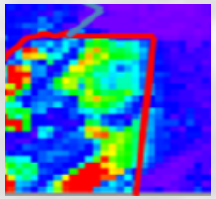
water solution Nafion 0.25 %, isopropyl alcohol 3.75 %

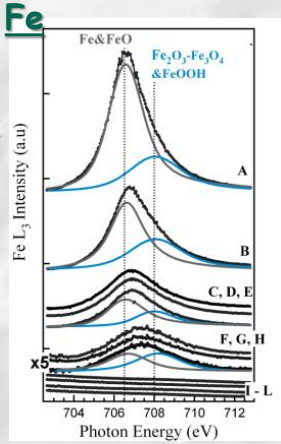
Metallic Plate Corrosion and Uptake of Corrosion Products by Nafion in Polymer Electrolyte Membrane Fuel Cells
B. Bozzini et al, ChemSusChem 3, 1, 2010

Corrosion of Ni in 1-butyl-1-methyl-pyrrolidinium bis (trifluoromethylsulfonyl) amide room-temperature ionic liquid: operated at anodic polarization of 0.5 V vs Au electrode
B. Bozzini et al, ChemPhysPhysChem (in press)

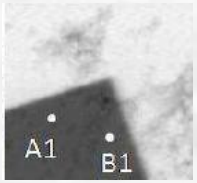
Fe

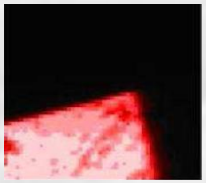


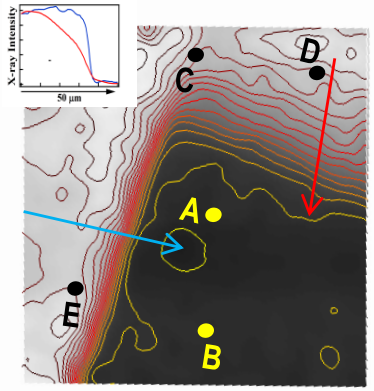


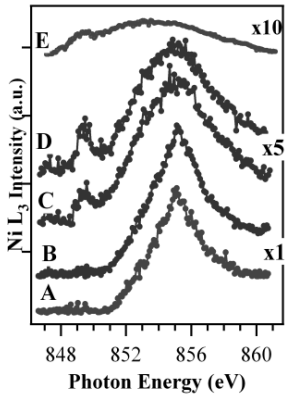


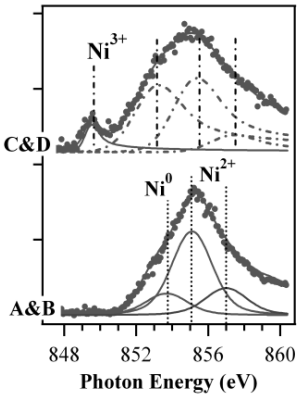
Ni











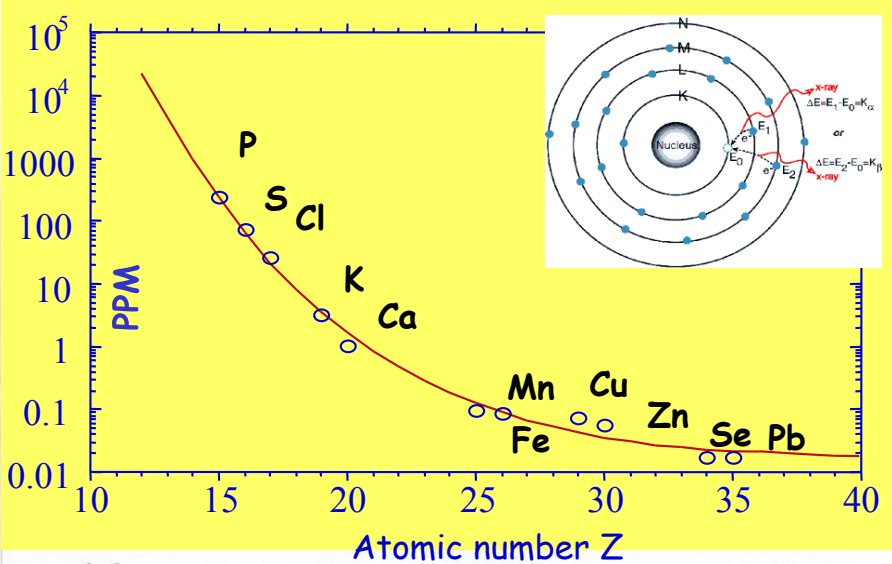
Fe undergoes corrosion and diffuses in the Nafion, whereas the Ni electrode remains apparently intact.

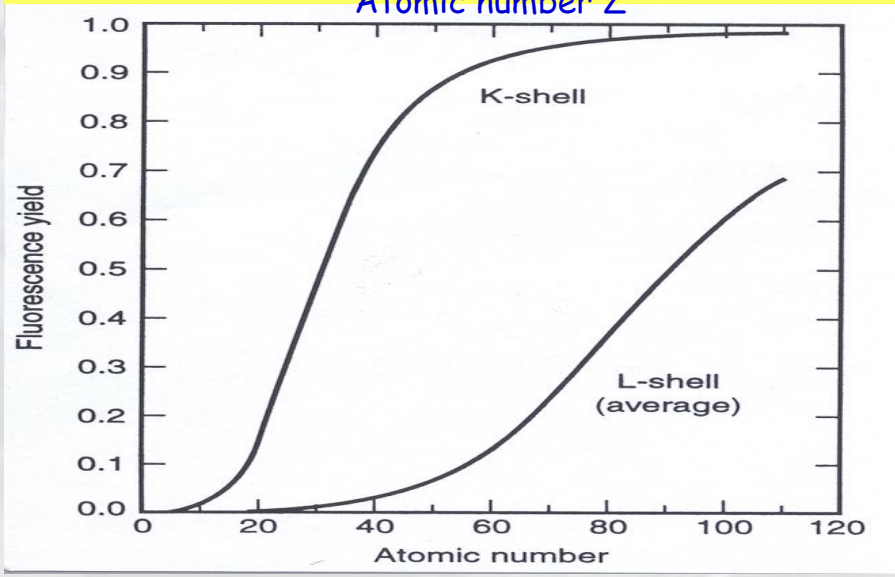
Ni corrosion products tend to interact with the RTIL within the zone close to the electrode, changing the Ni valence state. The localisation of the higher-valence form of oxidised Ni in the high-current density region is coherent with the higher anodic potentials developed there.

Maya Kiskinova

Hard X-ray SXM:

lower resolution but XRF with depth and ppm sensitivity



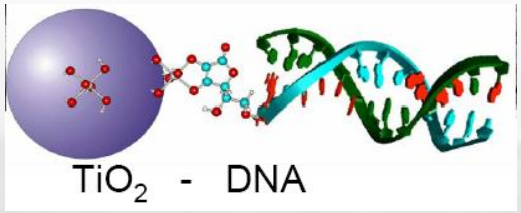


- Element specific (no labelling)
- Co-localisation
- Low detection limit (trace element).
- High signal-to-background ratio (low dose)

- Penetration depth: > 50μm
- All type of samples
- μ-XANES (S, P, K, Ca, Fe..) in total fluorescence yield

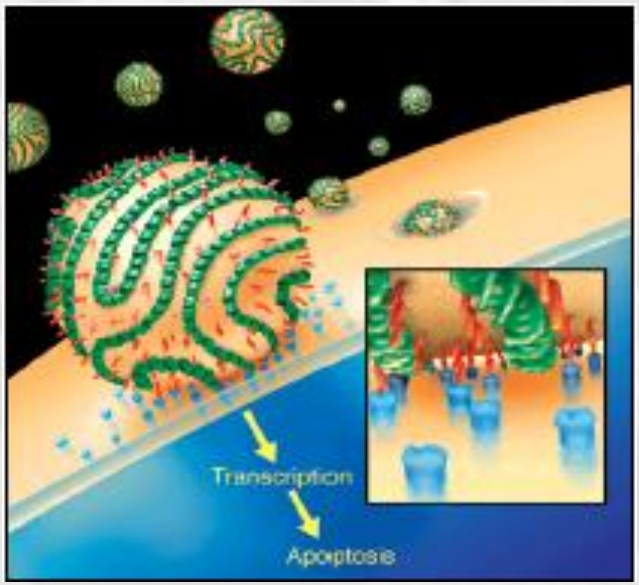
Maya Kiskinova

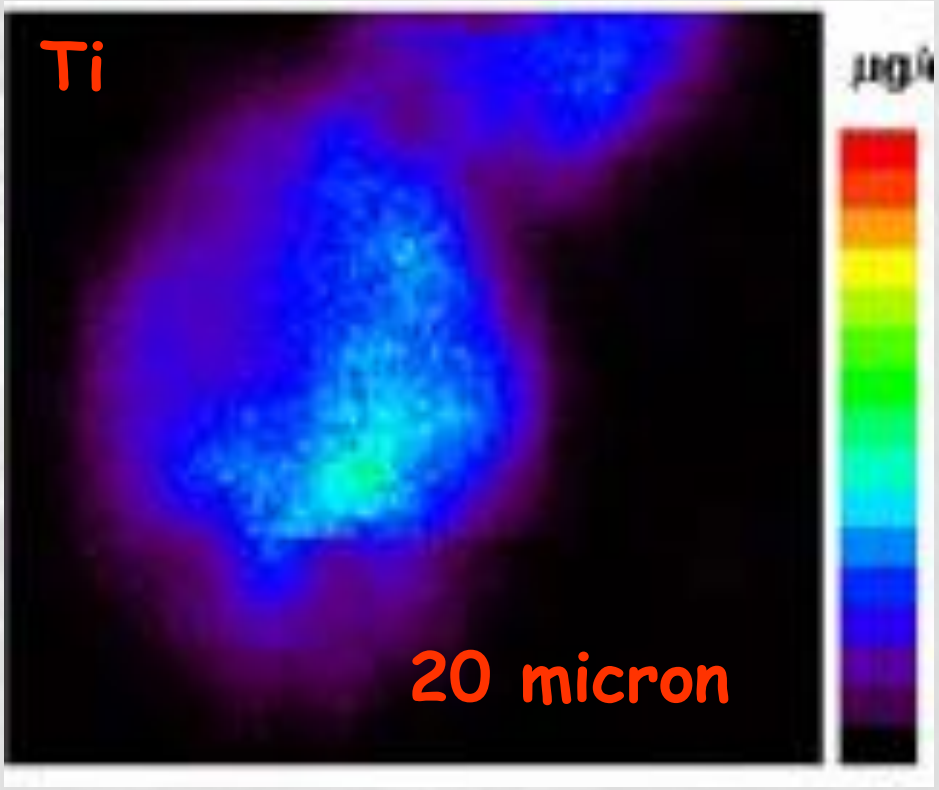
TiO2-DNA nano-composites for in-vivo Gene Surgery: XRF maps



Chemical FS imaging is crucial to quantify the success rate and reveal the location of the single stranded nanoparticle in the cell chromosome

DNA-TiO2 particle crossing cell walls





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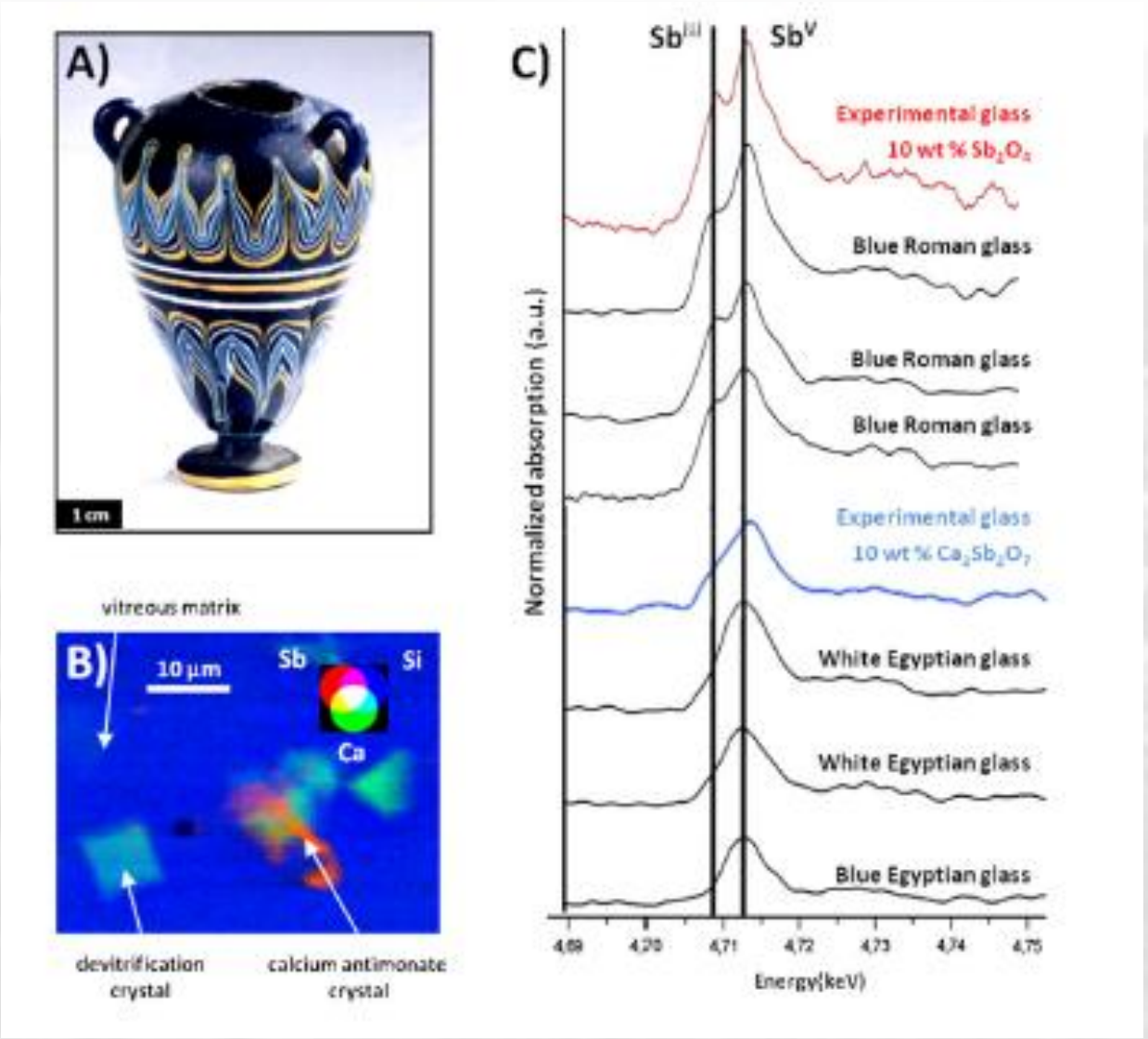
Determination of the Sb oxidation state in ancient glasses, opacified by the presence of Ca antimonate crystals: XANES in Total Fluorescence detection

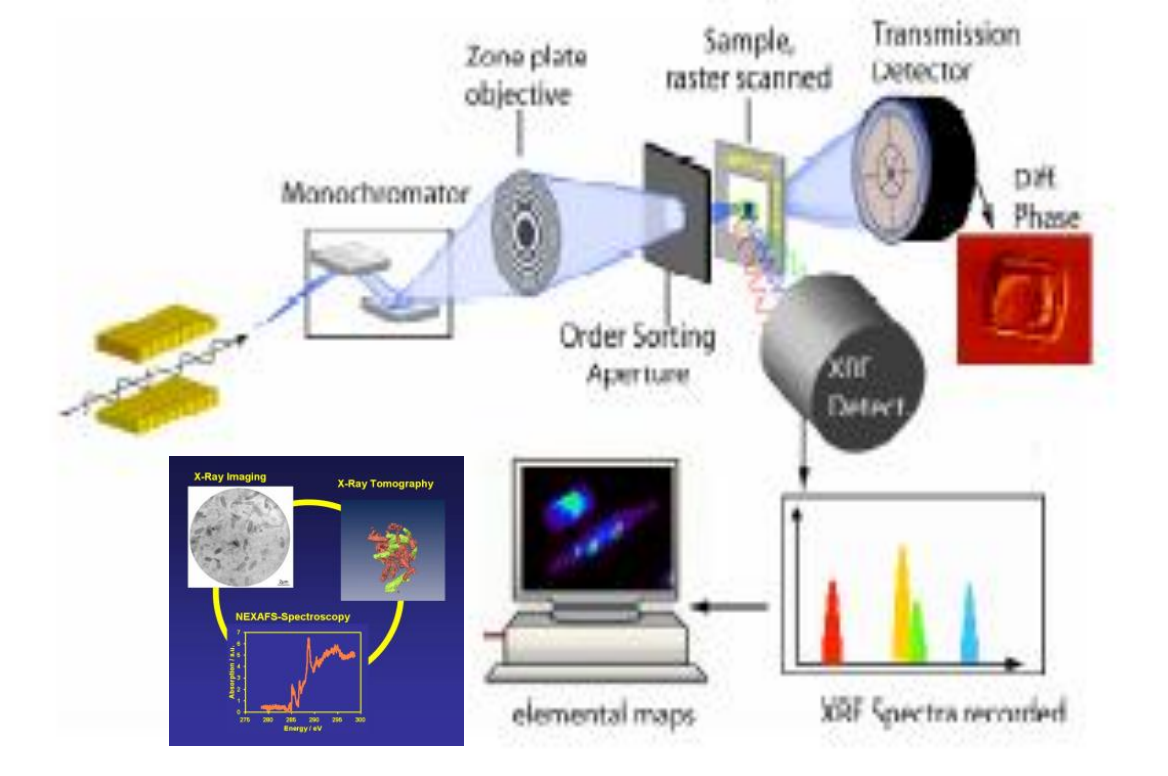


ID21, ESRF

Maya Kiskinova

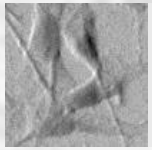
X-ray contrast based on photon detection
Bulk sensitive

COMPLEMENTARY: transmission & XRF + XANES



X-ray Absorption

- Bright-field imaging – morphology
- Chemical and magnetic contrast: XAS and XFS



X-ray Scattering: morphology

- Phase contrast
- Dark-field imaging
- Ptyhography

More details for the FFIM and STXM + XRF techniques and applications in the forthcoming lectures of Alessandra Gianoncelli

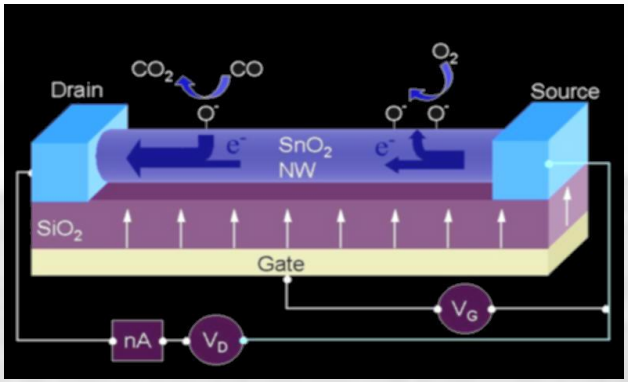
Maya Kiskinova

Low-dimensional materials and their unique properties

There's Plenty of Room at the Bottom

An Invitation to Enter a New Field of Physics & Material Science

Richard P. Feynman - *1959!!!*



Increased surface-to-volume ratio: the surface status controls physical and chemical properties

Surface 'geometric' structure

Surface chemistry

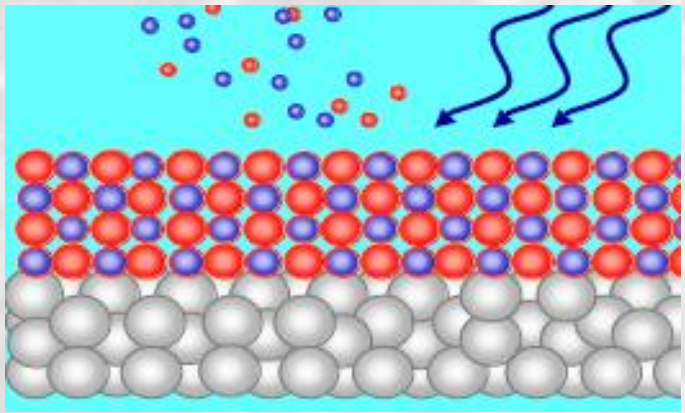
Electronic properties and confinement effects

Spatial resolution with chemical and structural surface sensitivity are needed.

Maya Kiskinova

All information of PES at microscopic scales

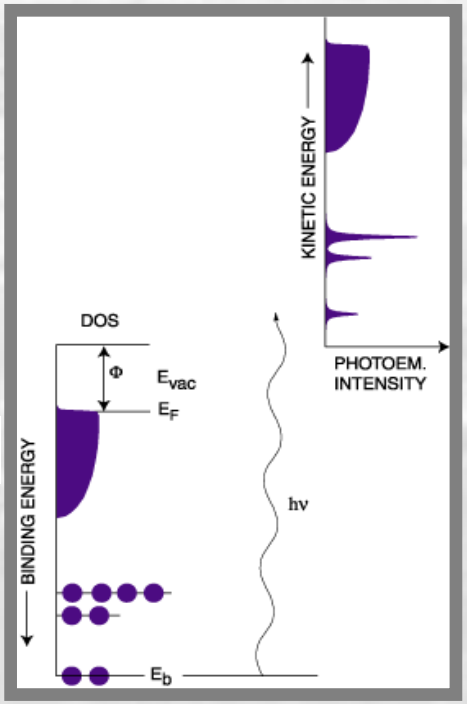
- Qualitative and quantitative elemental information: CL
- Chemical composition and chemical bonding:CL & VB
- Electronic and magnetic structure (VB, ARUPS, PED, XMCD-XMLD with secondary electrons (XANES).
- Information depth < 10 nm (surface sensitive)

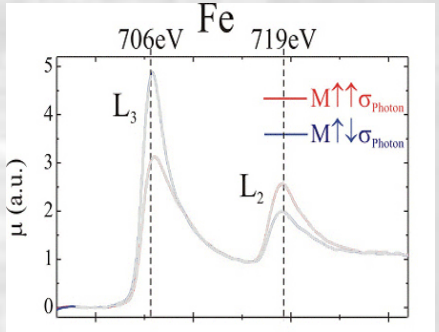


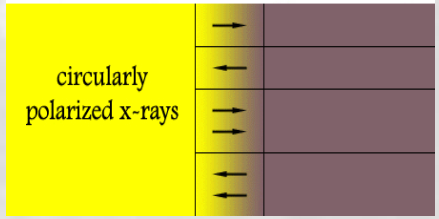
Information depth = dsinθ
d = Escape depth ~ 3 λ
θ = Emission angle relative to surface
λ = Inelastic Mean Free Path

VB

CL







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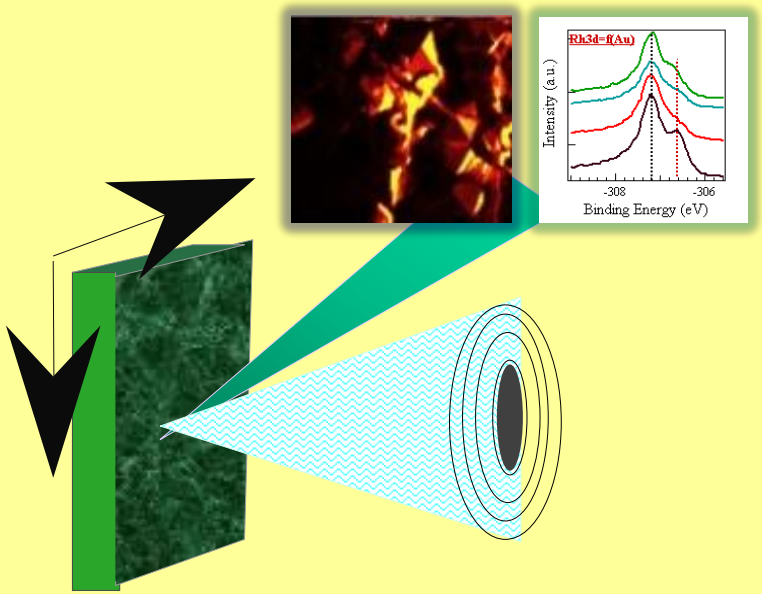
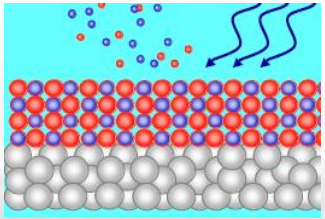
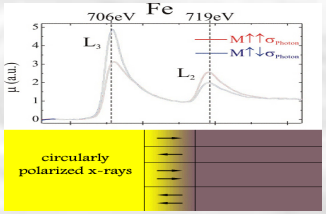
Synchrotron-based photoelectron microscopes: they are complementary

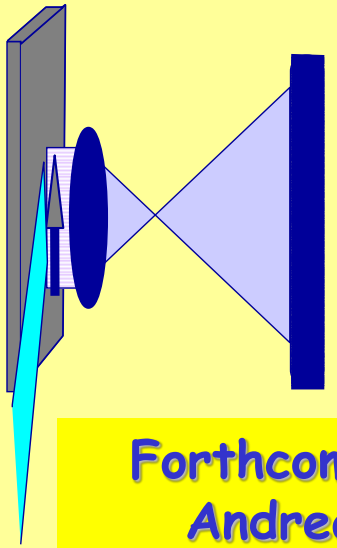
SPEM

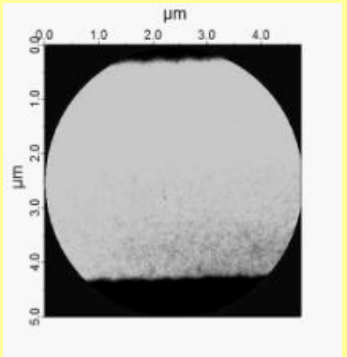






XPEEM-LEEM





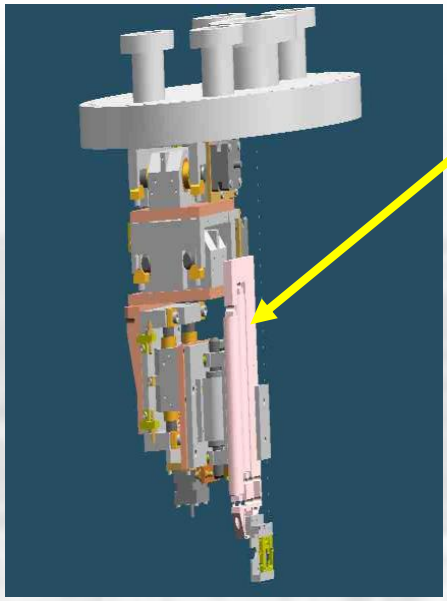
Forthcoming lecture: Andrea Locatelli

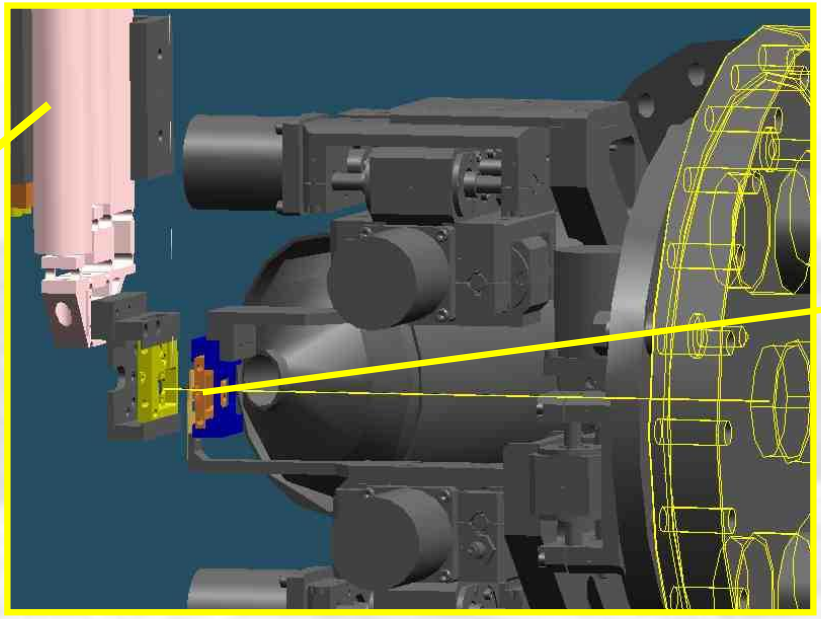
+ Full power of XPS
+ Spectro-imaging.
+ Flexible sample geometry and FOV.
+ Insensitive to sample roughness;
- Fast processes or XANES.
- Lateral resolution (50 nm).

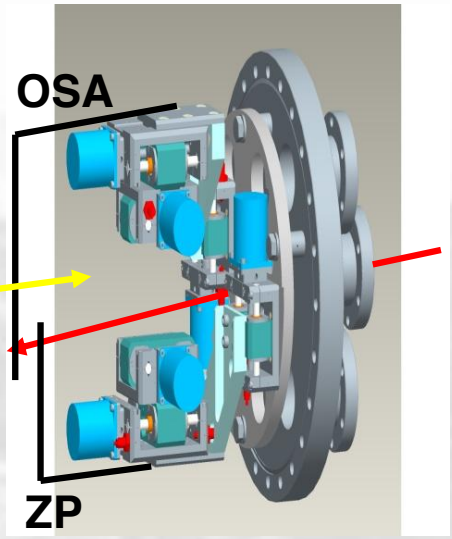
+ Lateral resolution (<5nm imaging)
+ Dynamic studies;
+ XANES, PED&ARUPS.
+ LEEM & m-LEED: structure
- XPS spectral resolution
- sample roughness and size.

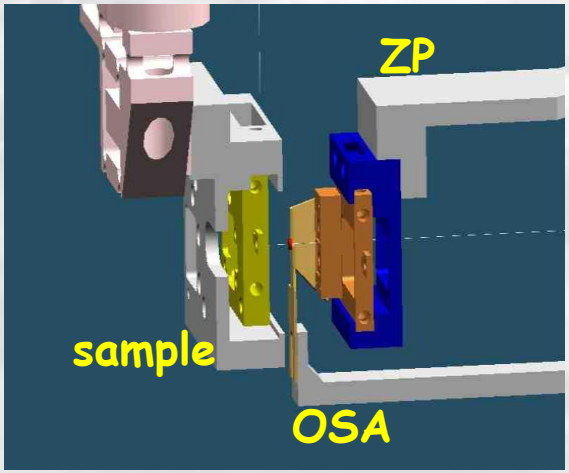
Maya Kiskinova

Layout of SPEM: ZP optics, sample and positioning systems







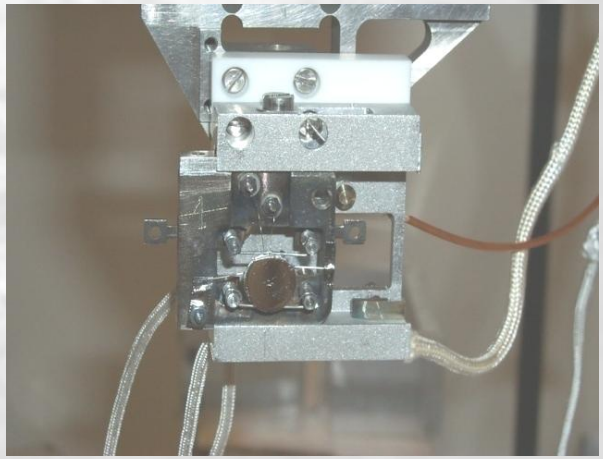


Spatial resolution in emission limited by the sample-to-optics distance !

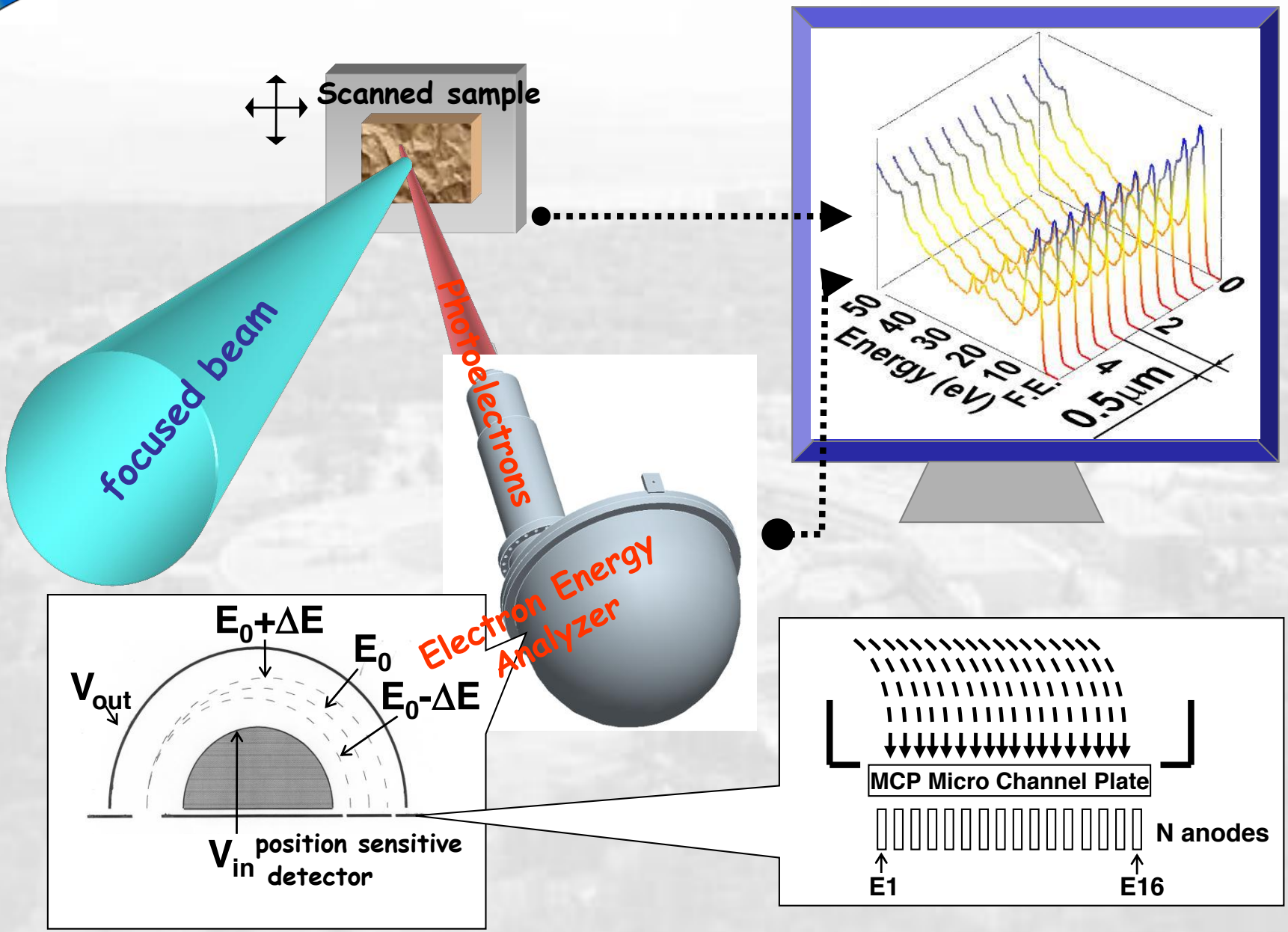
$f_m = D_x dr_x E_{ph} / 1240$

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

Typical: 5-15 μm



SPEMs energy-filtering electron analysers
MCD developed @ ELETTRA



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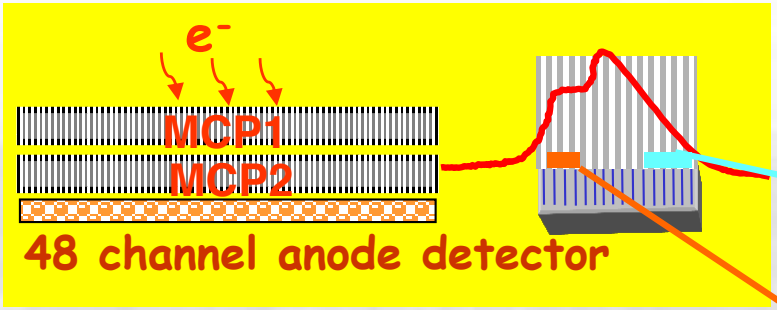
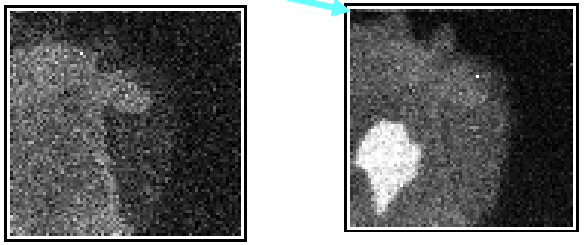
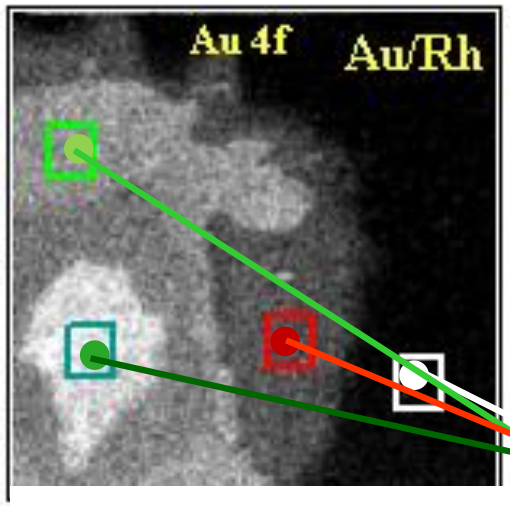
Multichannel detection in SPEM: each pixel = spectrum



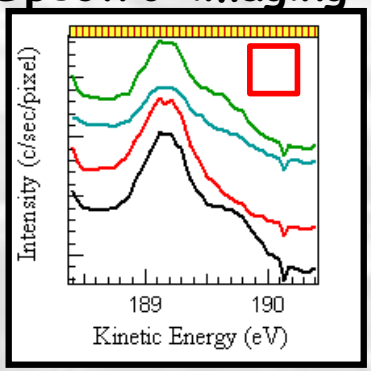
Selected channels: chemical map



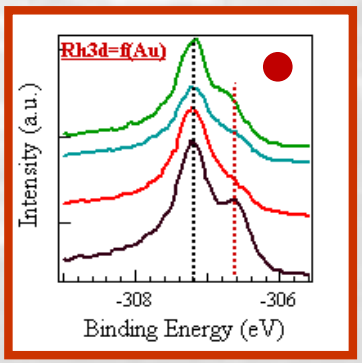


concentration map

Spectro-imaging



spectroscopy



Maya Kiskinova

Catalysis-related research

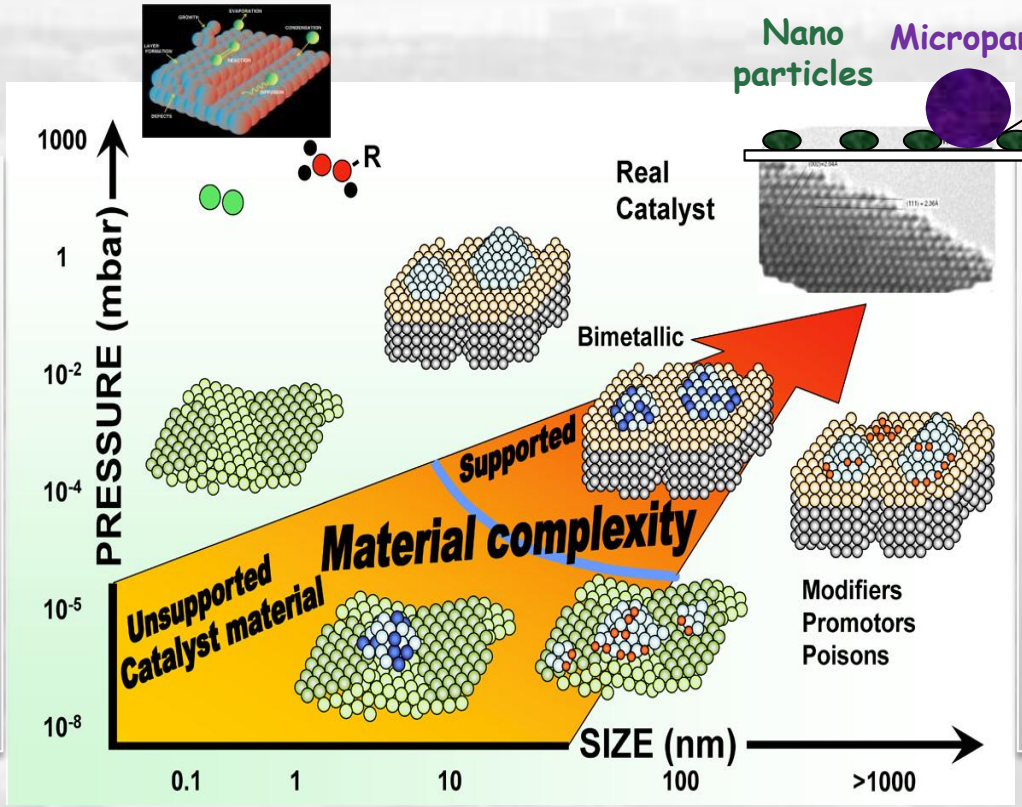
single crystals, supported particles, modifiers and pattern formation

New York Times: June 8, 1923

Catalysis, that strange principle of chemistry which works in ways more mysterious and inexplicable than almost any other of the many curious phenomena of science

Structural effects:

grains, facets, steps, roughness, % unsaturated atoms, induced reconstructions.



Electronic effects:

electron confinement, contact with support, modifiers.

What is the active catalyst state: can we describe it as a single phase??

Dynamic changes under reaction conditions (structural, chemical..)!!

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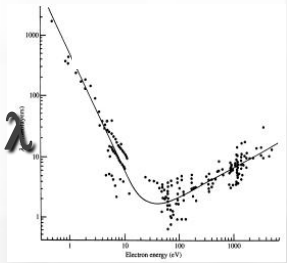
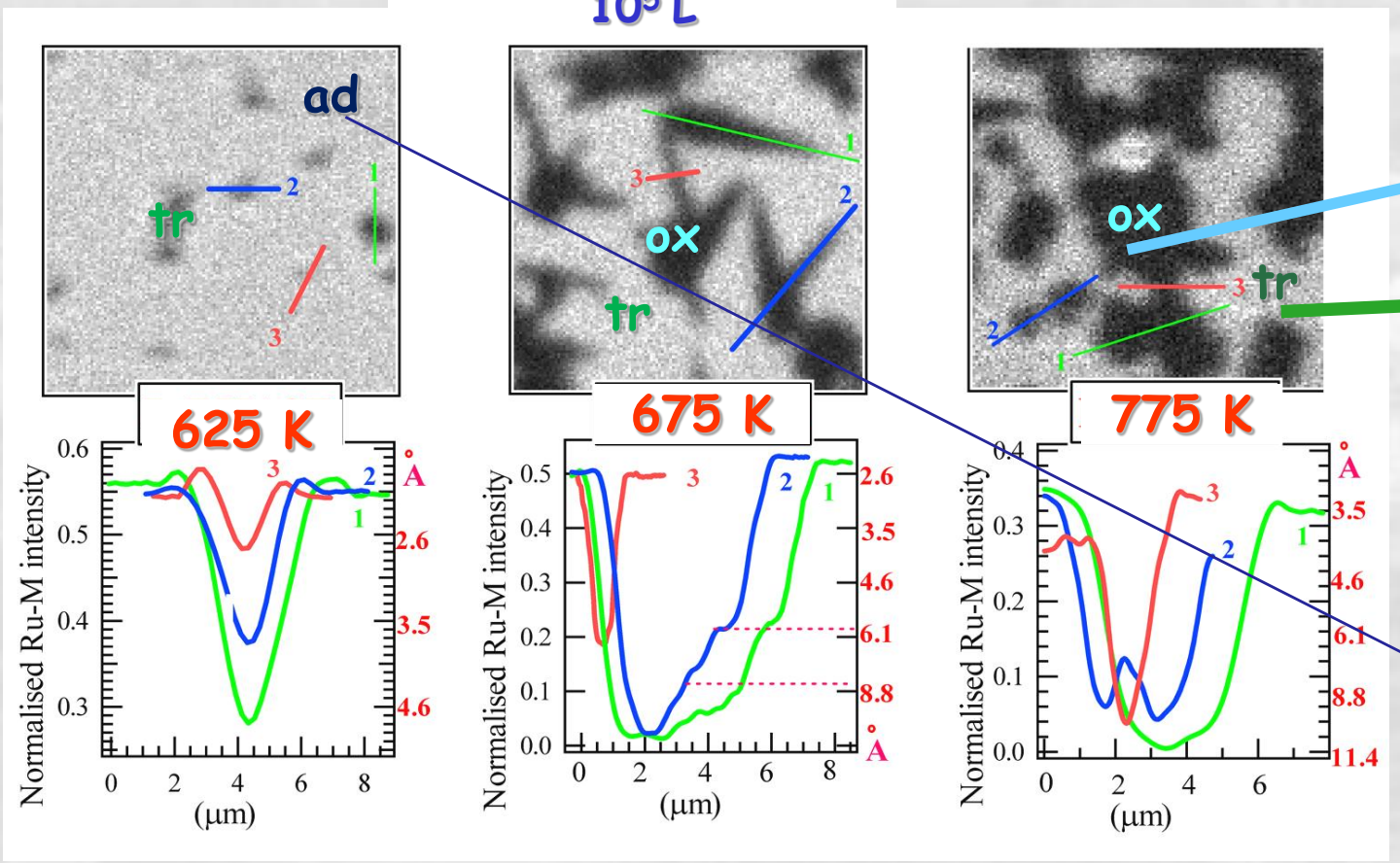
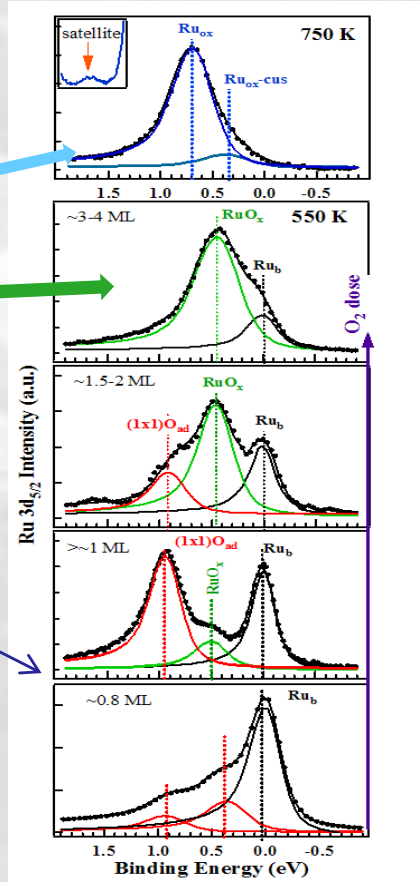
Imaging 'Ru_{met} attenuation' > spatial anisotropy in the oxide film thickness on Ru(0001)



Maps of Ru metallic component: measure of Ru oxide thickness: $I_{Ru(b)} = I_{Ru(0)} . e^{-x(Ru_{ox})/\lambda\cos\theta}$

RuO_2 layer-by layer growth in preferred crystallographic directions above 'critical thickness of 2 layers!





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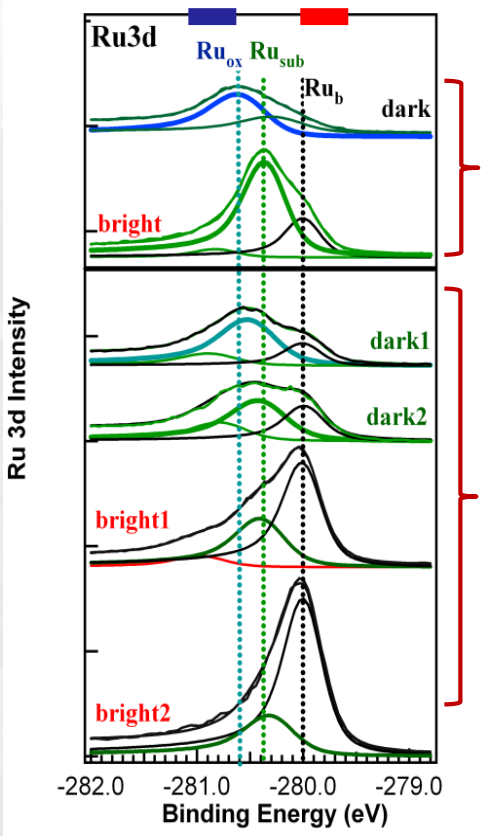
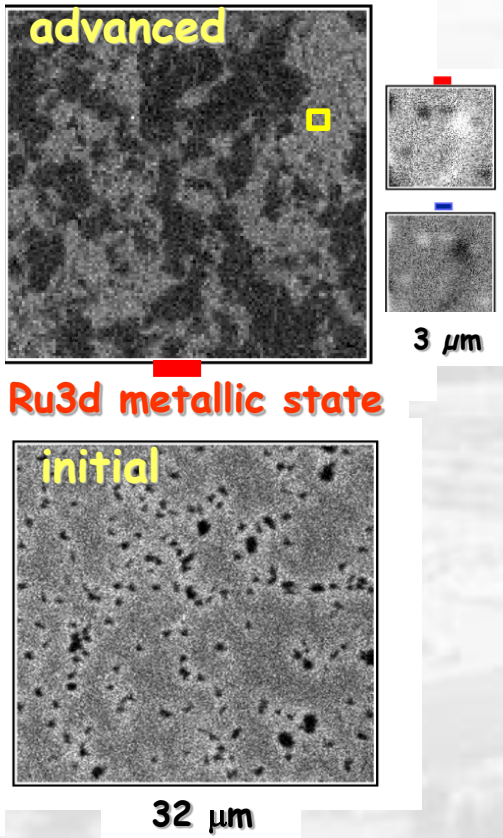
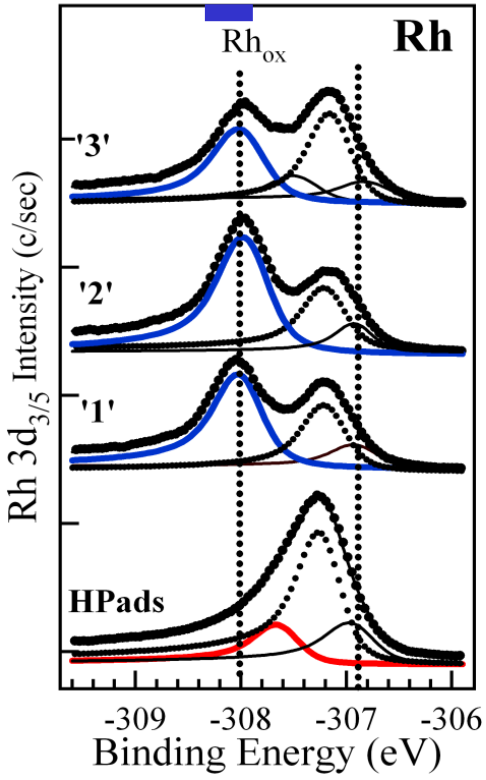
Model Ru(0001) and Rh(110) catalysts

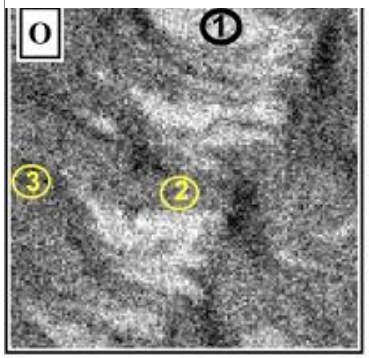
Oxidation states: Ru(Rh)3d maps & Ru(Rh)3d μ-PES







Rh3d oxide state



SPEM=500 STM

14052 *J. Phys. Chem. B* **2005**, *109*, 14052−14058

Identification of Subsurface Oxygen Species Created during Oxidation of Ru(0001)

Raoul Blume,*,† Horst Niehus,† Horst Conrad,‡ Artur Böttcher,# Lucia Aballe,§ Luca Gregoratti,§ Alexei Barinov,§ and Maya Kiskinova*,§

Initial Oxidation of a Rh(110) Surface Using Atomic or Molecular Oxygen and Reduction of the Surface Oxide by Hydrogen *J. Phys. Chem. B* **2005**, *109*, 13649−13655

P. Dudin,† A. Barinov,† L. Gregoratti,† M. Kiskinova,*,† F. Esch,‡ C. Dri,‡,§ C. Africh,‡,§ and G. Comelli‡,§

THE JOURNAL OF CHEMICAL PHYSICS 125, 094701 (2006)

Initial oxidation of the Rh(110) surface: Ordered adsorption and surface oxide structures

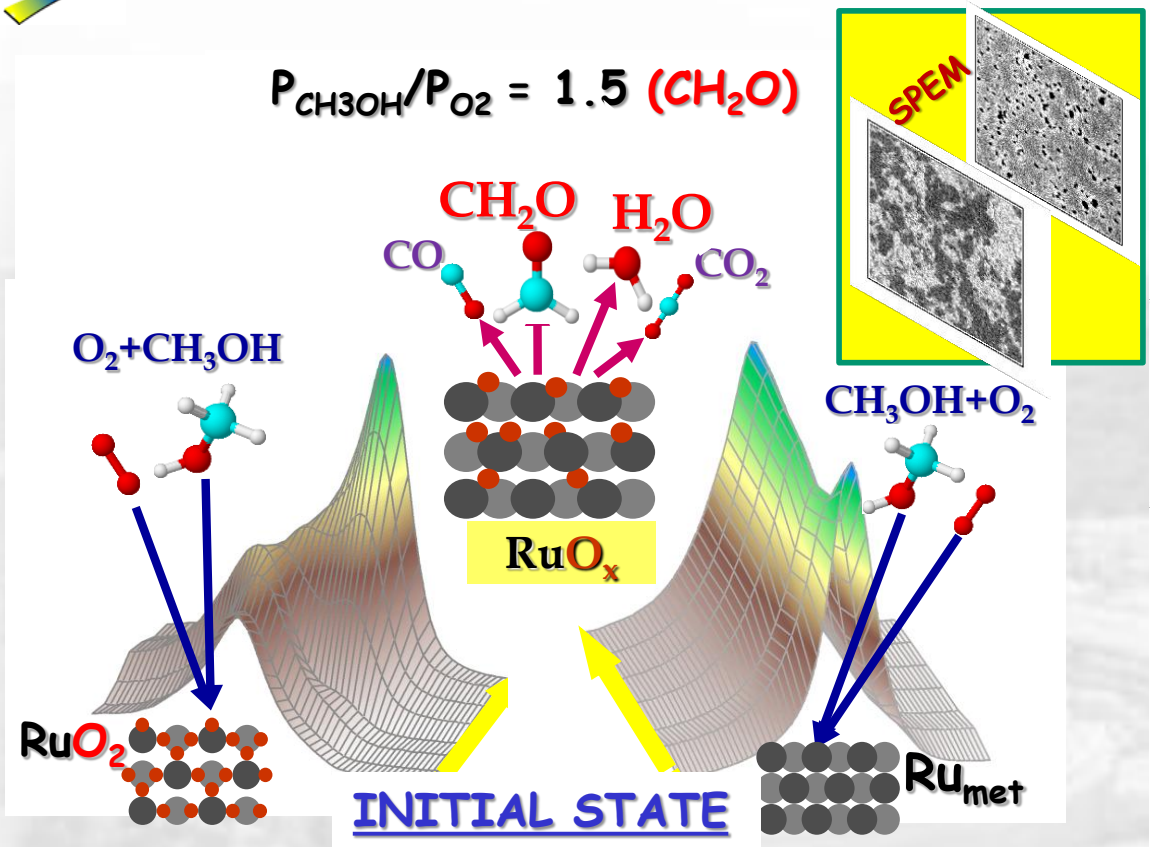
'Transient Surface Oxide' (TSO) ~ 10-12 Å: Ru(Rh) oxides nucleate inside the 'amorphous' TSO

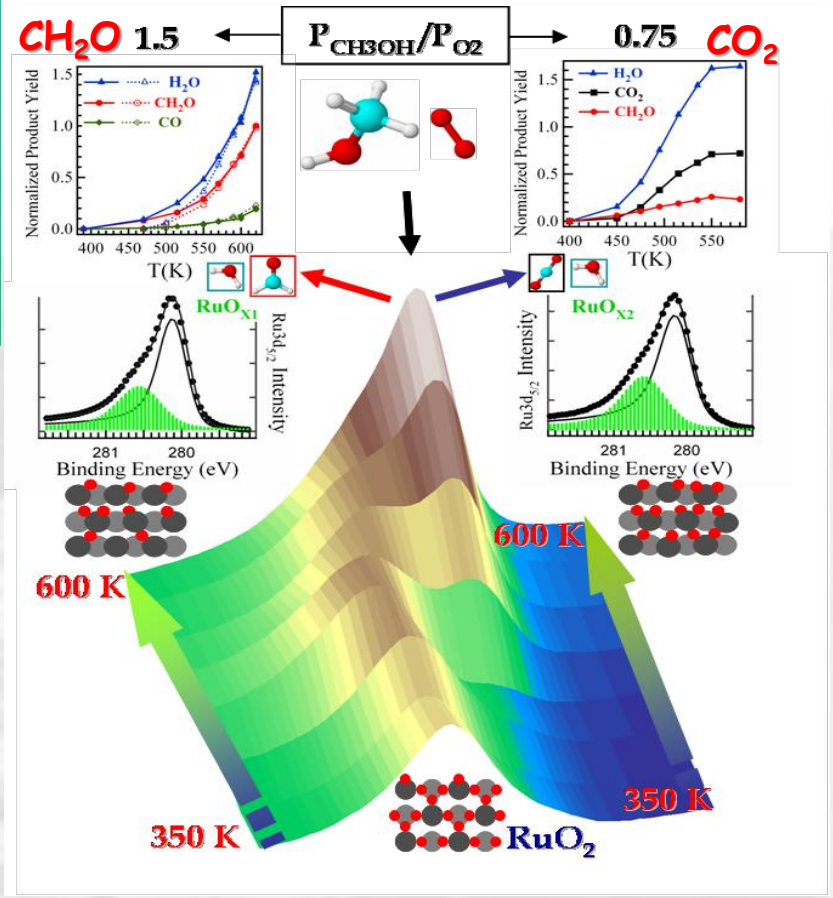
Maya Kiskinova

Active Ru state in CH_3OH oxidation: XP-XPS

FINAL STATE: transient RuO_x, 'x' determines the selectivity

P_{CH3OH}/P_{O2} = 1.5 (CH_2O)





The long-range ordered structures are not necessarily the ones working under conditions of high chemical potential and enabled structural dynamics. 'SPEM prompts complex Ru surface morphology but in-situ AP-SPEM needed to prove it!

R. Blume et al, Cat.Tod. & PCCP (2007); Book Chapter in Nanostructured Catalysis, RCS 2011

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Model catalyst system: Rh micro- and nano-particles or nano-crystalline films

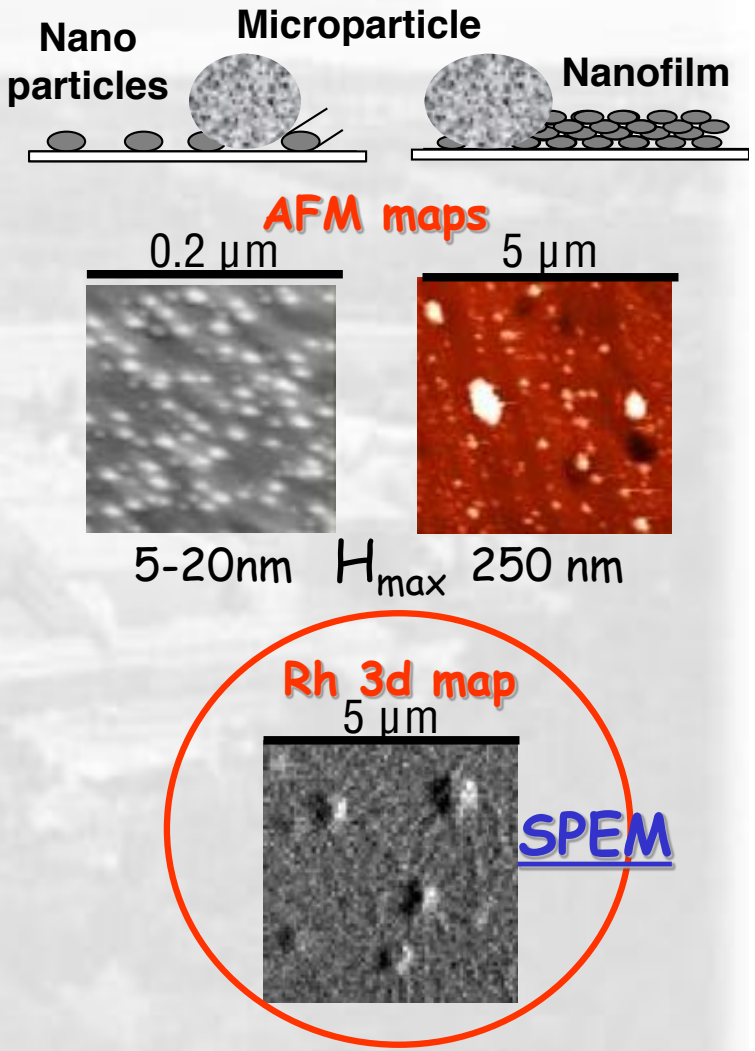
Deposited by PLD on MgO

SPEM

Complex & variable morphology :

1) 'Defined' (crystalline) or 'not-defined' structure;
2) Structural effects: relative concentration of unsaturated atoms is size dependent and affects the reactivity.
3) Relative number of constituent atoms in contact with the support is size dependent.
4) Electron confinement below ~ 5 nm.

Thin films are nano-crystalline



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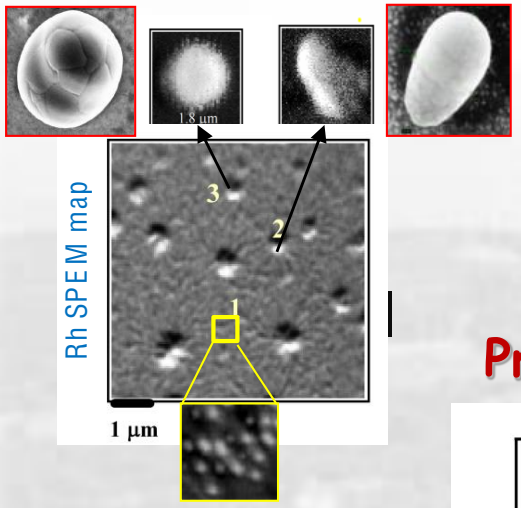
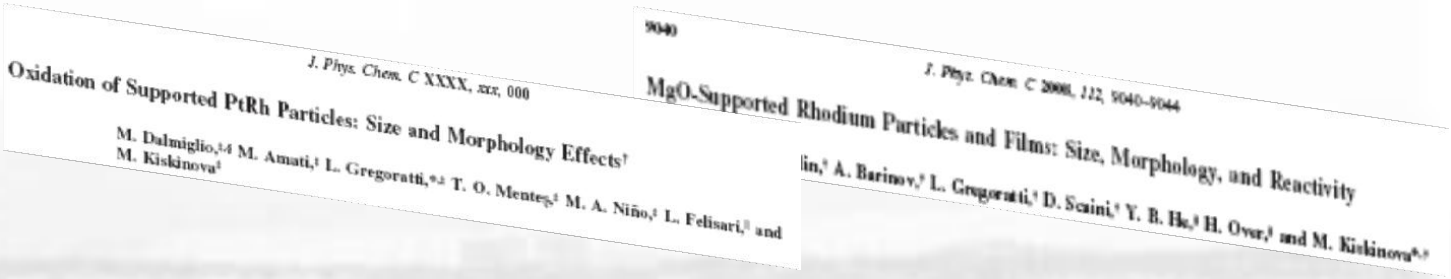
Supported Metal Particles:
reactivity of μm- vs nm- particles




J. Phys. Chem. C XXXX, xxx, 000

Oxidation of Supported PtRh Particles: Size and Morphology Effects†

M. Dalmiglio,‡,§ M. Amati,‖ L. Gregoratti,*,‖ T. O. Menteş,⊥ M. A. Niño,⊥ L. Felisari,‖ and M. Kiskinova*,‡

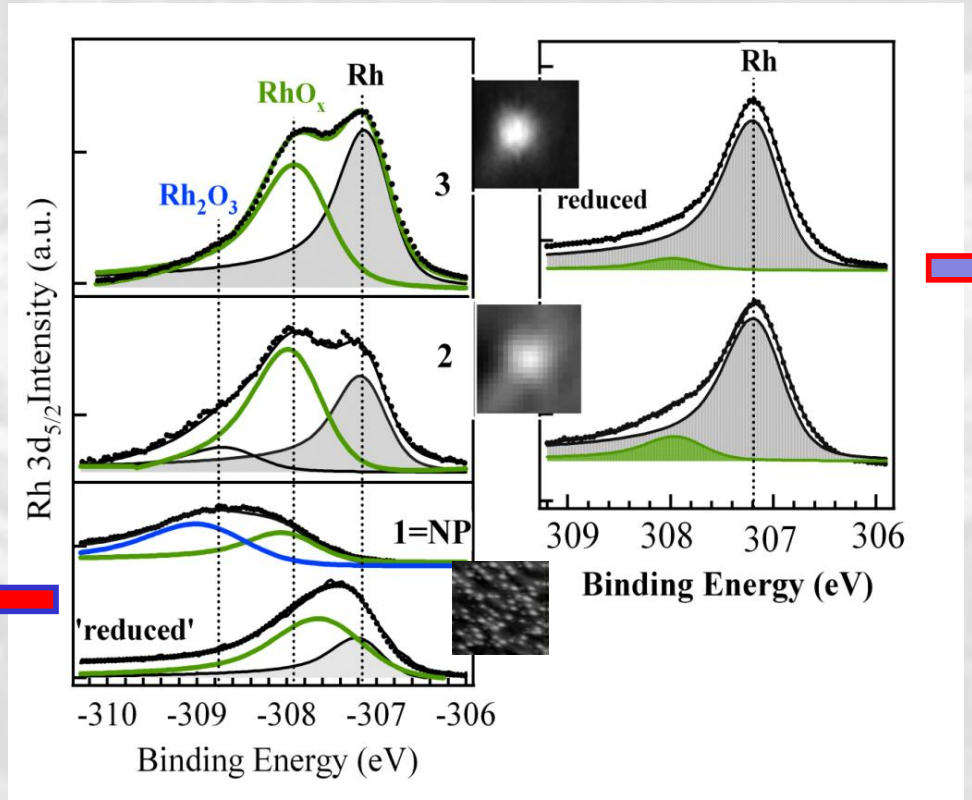
J. Phys. Chem. C 2008, 112, 9040–9044

MgO-Supported Rhodium Particles and Films: Size, Morphology, and Reactivity

A. Barinov,† L. Gregoratti,‡ D. Scaini,† Y. B. He,§ H. Over,§ and M. Kiskinova*,†

μ-Ps (500-3000nm) & NPs (5-20 nm) on MgO support

Probed under identical oxidation and reduction conditions



NPs oxidize faster but complete reduction of 'oxidized' NPs requires ~ 4 times longer exposure to H_2 than MPs

Micro-particles of similar sizes show different reactivity: different morphology - grains, facets, defect concentration ..

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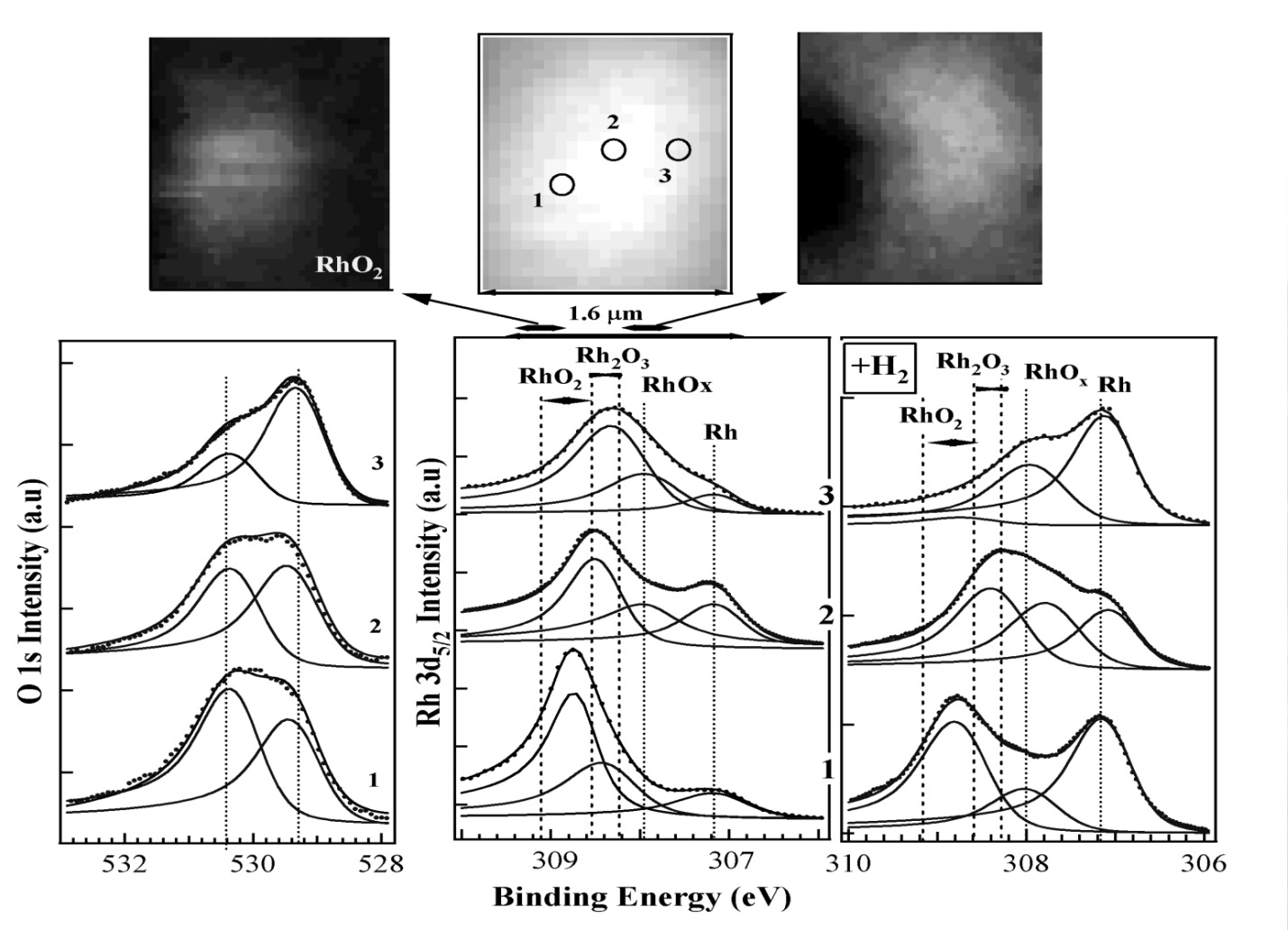
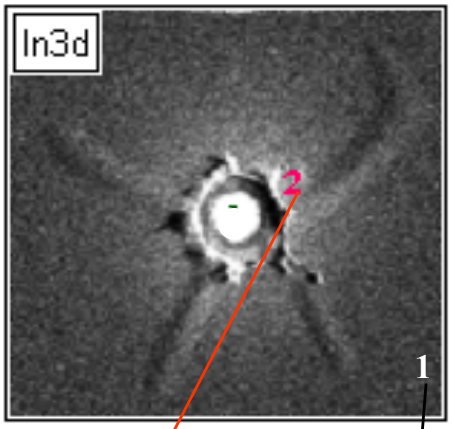
Oxidation states within a single Rh micro-particle

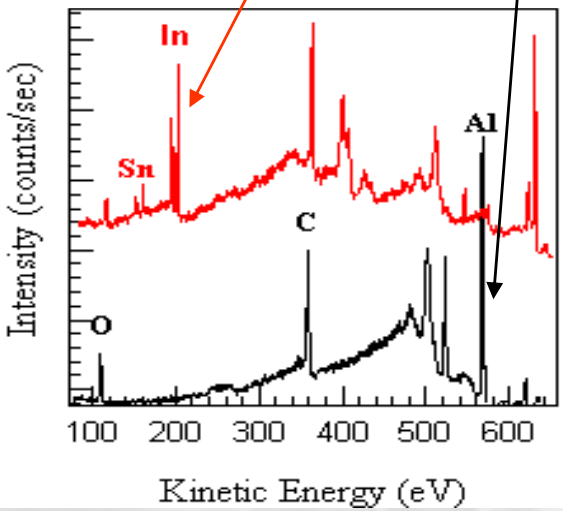


Lateral inhomogeneity in the oxidation state; some 'aggregates' reach oxidation states (RhO_2) not observed with extended Rh samples.

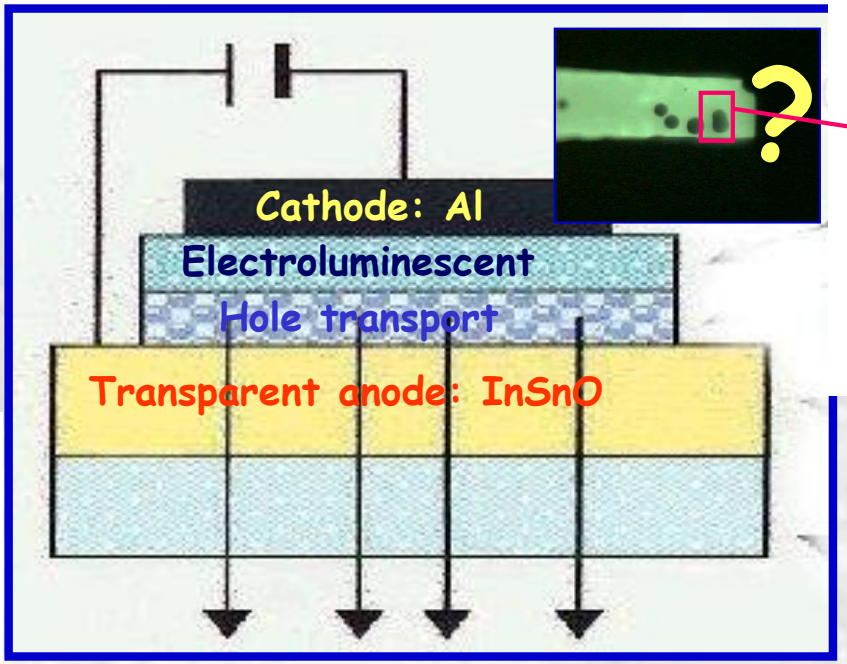
P. Dudin el al, JCP in press

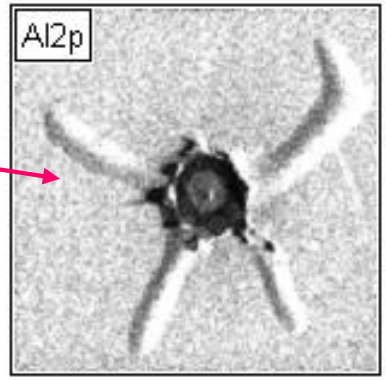
Degradation of organic light emission devices mechanism revealed by SPEM





P. Melpigniano et al, APL 86, 41105





Why do they degrade? What causes the break of the cathode (black spots) ?

Topographic features due to fracture: clearly seen as enhancement and shadowing of the emitted electrons

Chemical imaging & μ-XPS revealed anode material (In and Sn) deposited around the hole created in the Al cathode.

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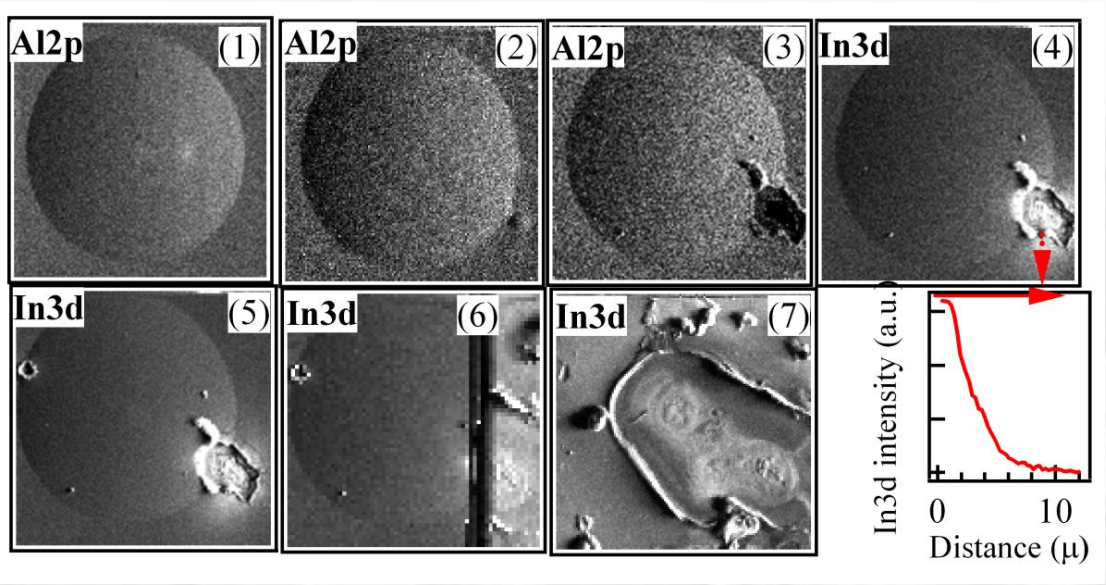
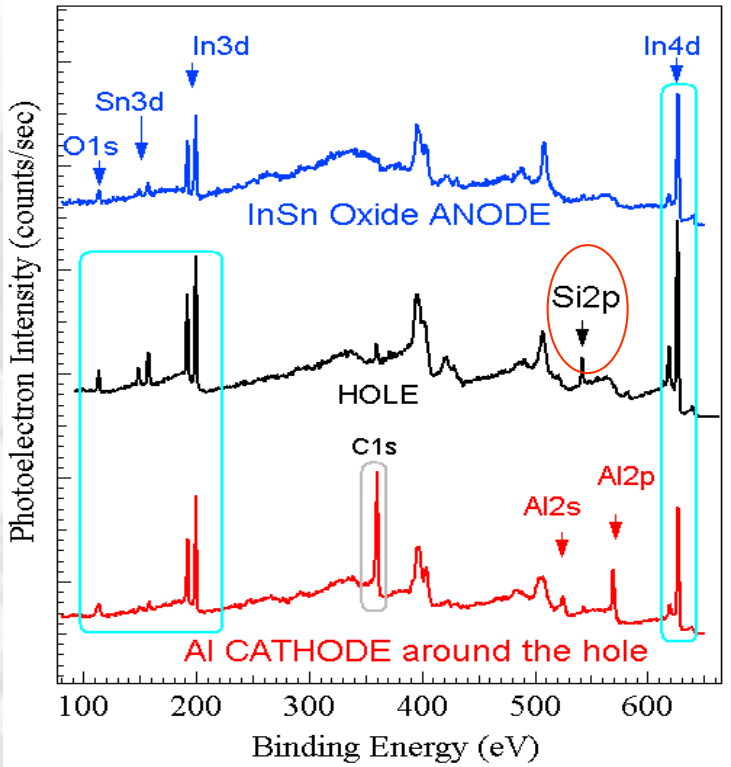
‘In-situ’ imaging of the local deformation and fracturing of the OLED cathode surface during device operation in the SPEM

Operation time at 10-25 V





Lateral inhomogeneity of the surface topography and chemistry of the InSn oxide anode films suggested as the major reasons for the device failures.

P. Melpigniano et al, APL 86, 41105

Local decomposition of InSn oxide and organic layer, caused by spikes is evidenced by the spectra taken inside the hole.

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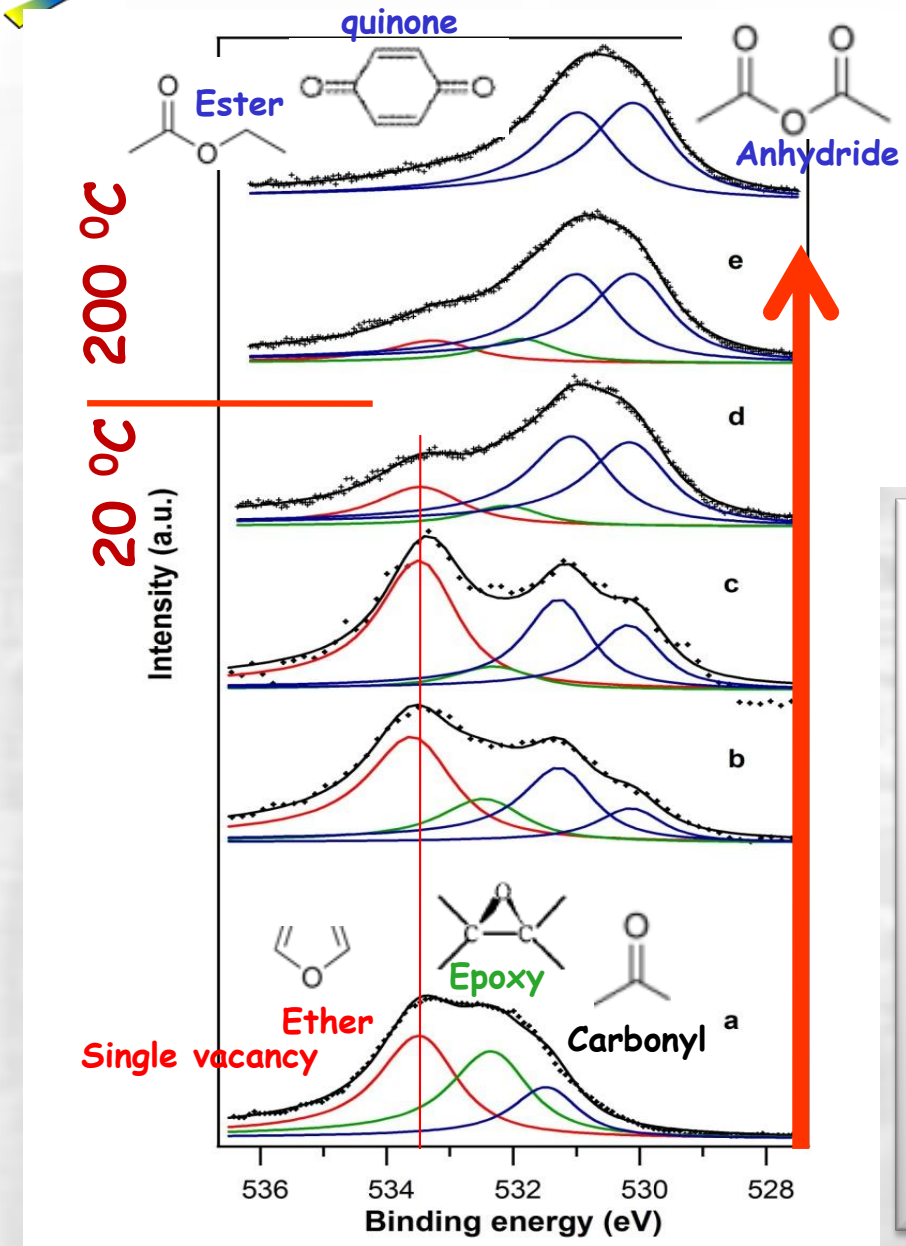
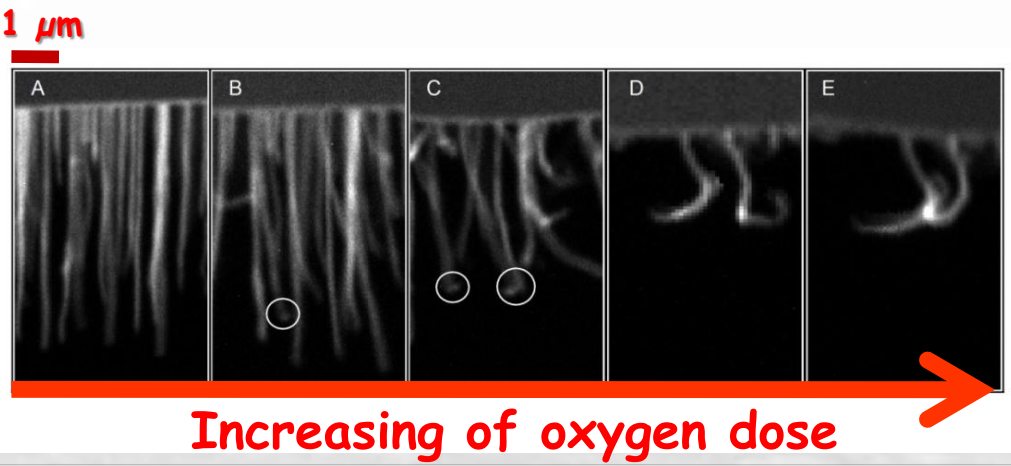
CNTs oxidation: morphology and oxygen bonding configurations





The consumption of the CNTs starts from the tips and correlates with the abundance of particular oxygenated functional groups.

The variations in the defect density and type between individual CNTs account for different consumption rates.

The continuous increase of the number of broken C-C bonds with advancing the gasification leads to non-linear consumption with increasing O dose.

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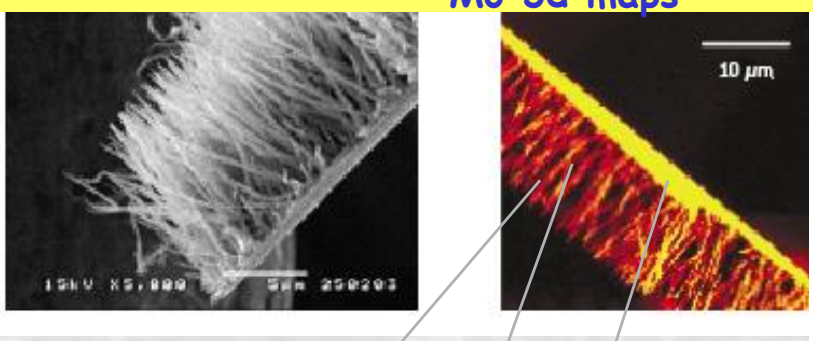
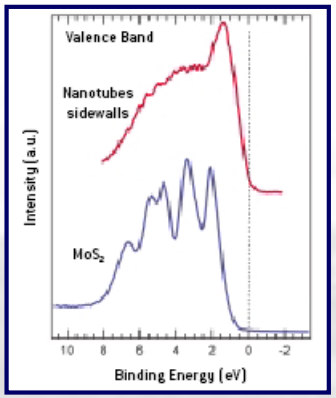
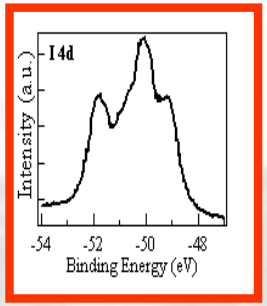
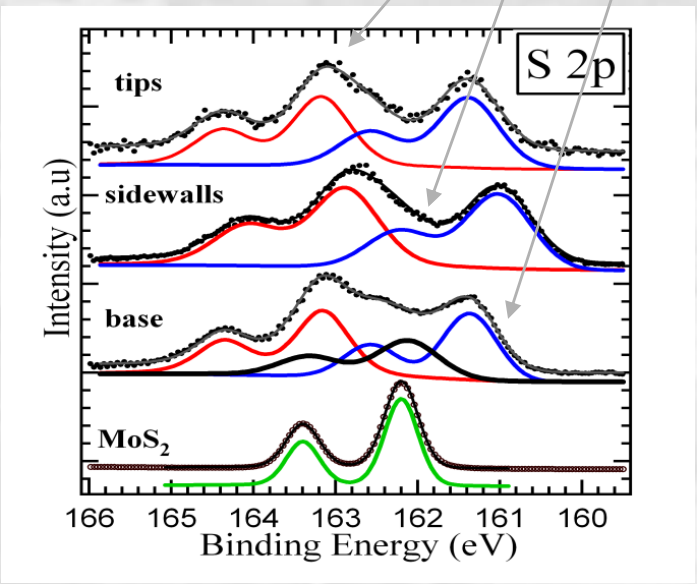
SPEM characterization of MoS_2-nanotubes

Twisted chiral bundles of Mo-S individual cylinders: Mo 3d maps









SPEM revealed I (used as a carrier) in interstitial positions between the tubes bonded to the outer S atoms.

Due to the low dimensionality the S 2p, Mo 3d and VB spectra are position-dependent and reflect electronic properties significantly different those of the MoS_2 crystal.

Maya Kiskinova

Classical X-ray imaging and spectromicroscopy: brief outline

SURFACES & INTERFACES: XPEEM and SPEM	BULK SAMPLES STXM-SPEM-TXM
PHOTON IN/ ELECTRON OUT	PHOTON IN/PHOTON OUT
(probing depth=f(E_{el}) max ~ 20 nm)	(probing depth = f (E_{ph}) > 100 nm)
Spectroscopy (XPS-AES-XANES)	(Spectroscopy – XFS or XANES)
ONLY CONDUCTIVE SAMPLES	
Total e^- yield (sample current)	XANES: Total hν yield, Transmitted x-rays
➢ Chemical surface sensitivity: Quantitative μ-XPS (0.01 ML)	Chemical bulk sensitivity Quantitative μ-XFS
➢ Chemical & electronic (VB) structure	Trace element mapping

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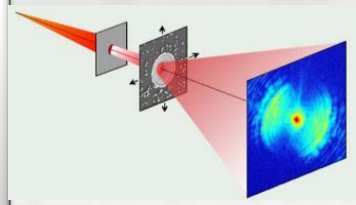
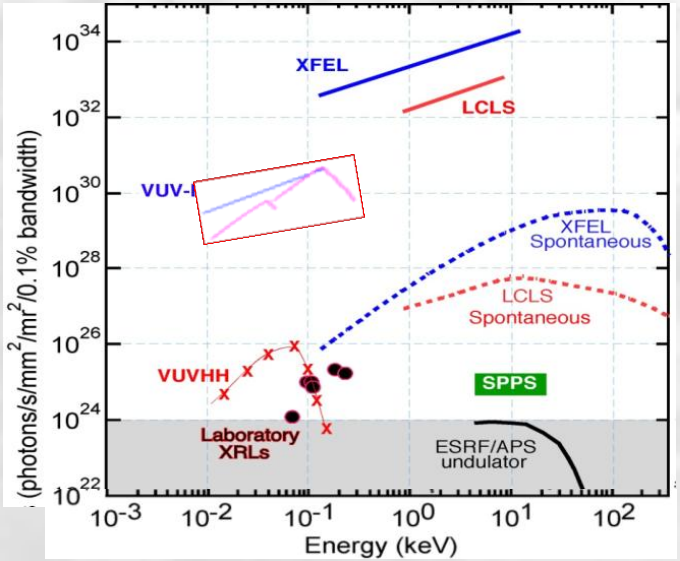
Imaging: spatial and temporal limitations

➢ Classical XRM (scanning & full field): (1) limited in resolution and focal depth by the optical elements; (2) morphology evolution of non-periodic systems > ms; (3) radiation damage: serious issue.

The optics depth and spatial resolution limitations can be overcome by image reconstruction from measured coherent X ray scattering pattern visualizing the electron density of non-crystalline sample.



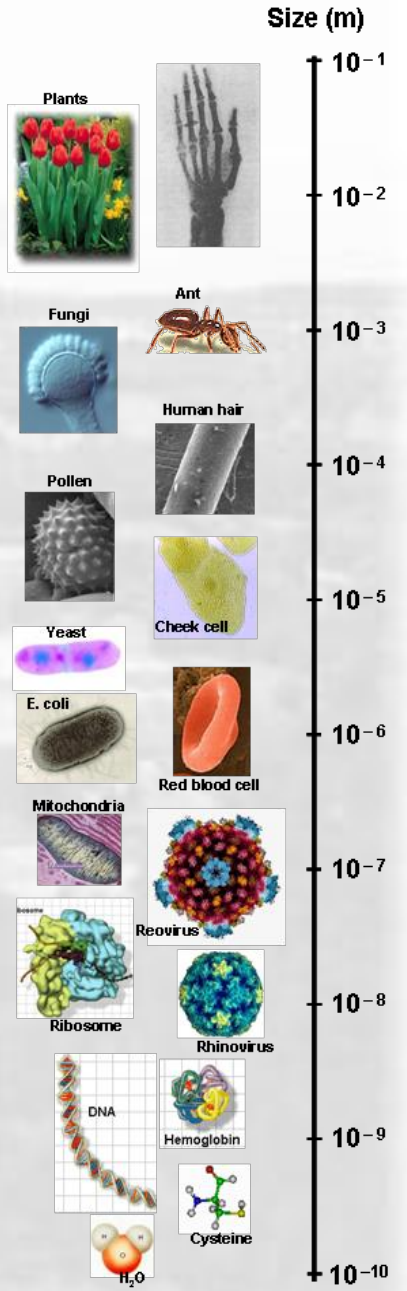


The temporal resolution can go to a few fs range, beating the radiation damage by single-shot imaging..

Lectures Kirz-Chapman

Imaging

Scattering



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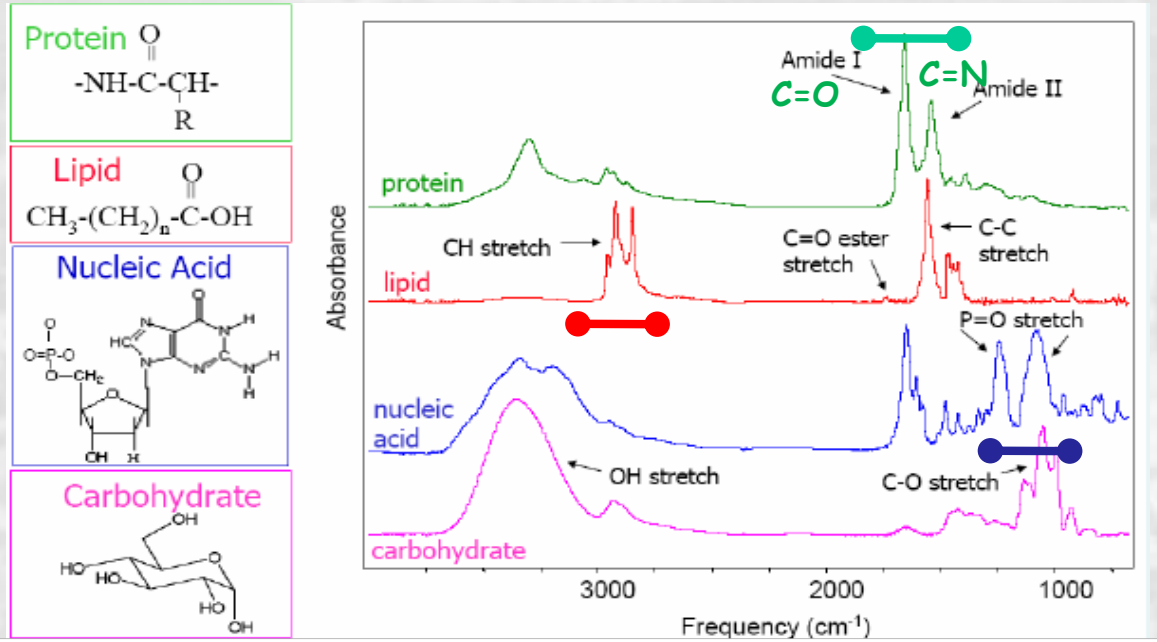
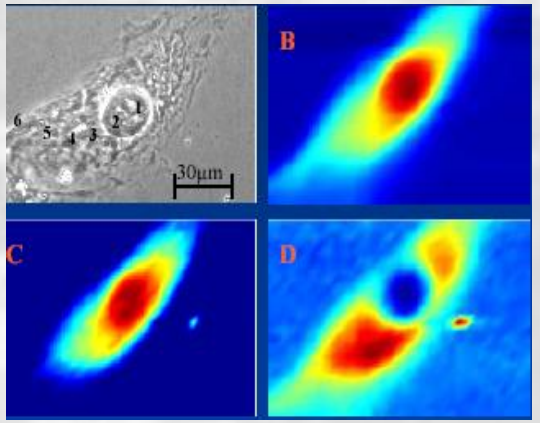
Infrared Specromicroscopy: microprobe – apertures (diffraction limited)

near IR: 0.8-2.5 μm
Phonons,
Molecular Rotations

mid IR: 2.5-50 μm
Molecular Vibrations
Electronic excitations

far IR: 50-1000 μm
Molecular Overtones
Bands combinations,
Excitons



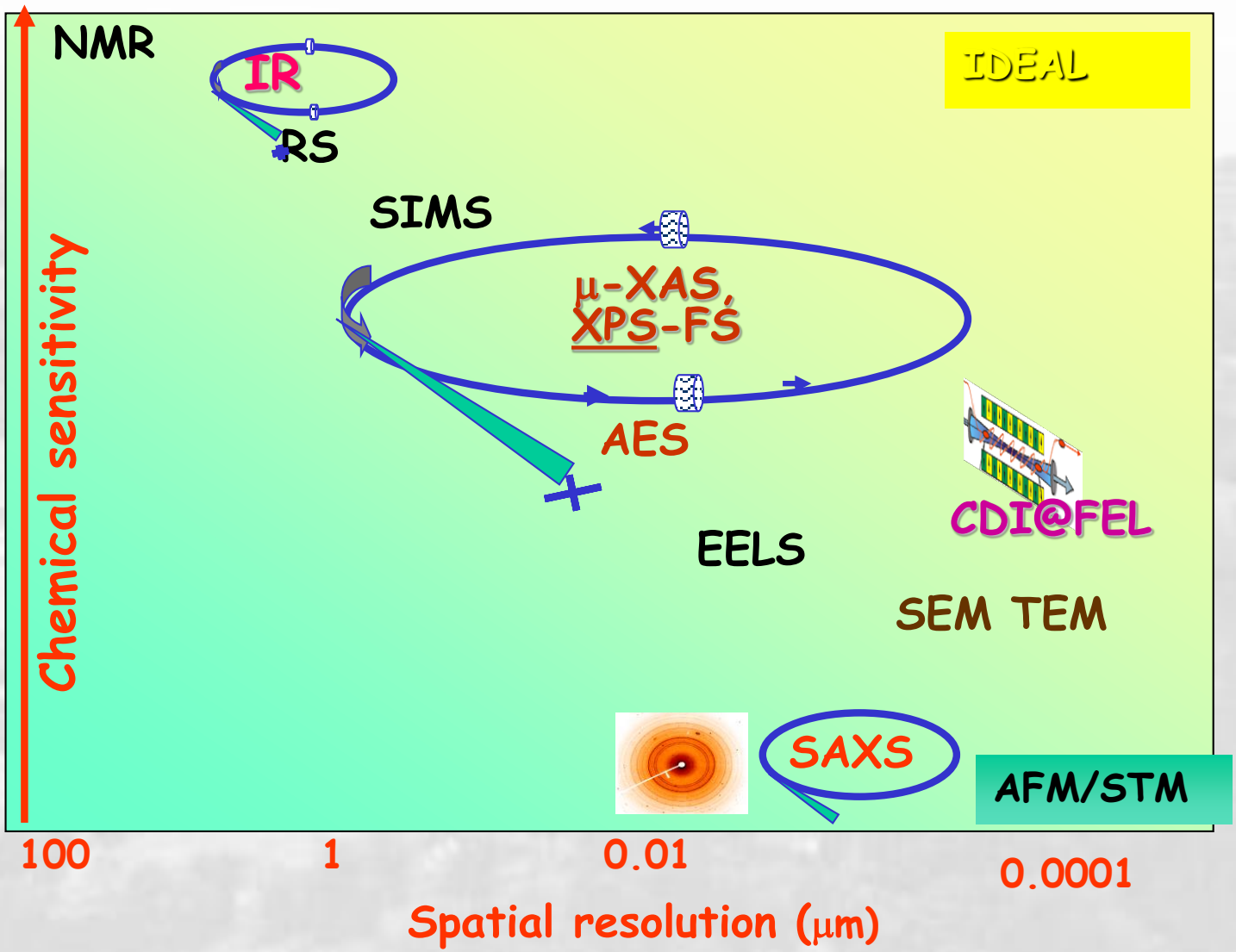


Band components (intensity, position, width and shape) are sensitive to chemical changes and physical properties

More details for the IRMS technique and applications in the forthcoming lecture of Lisa Vaccari

Maya Kiskinova

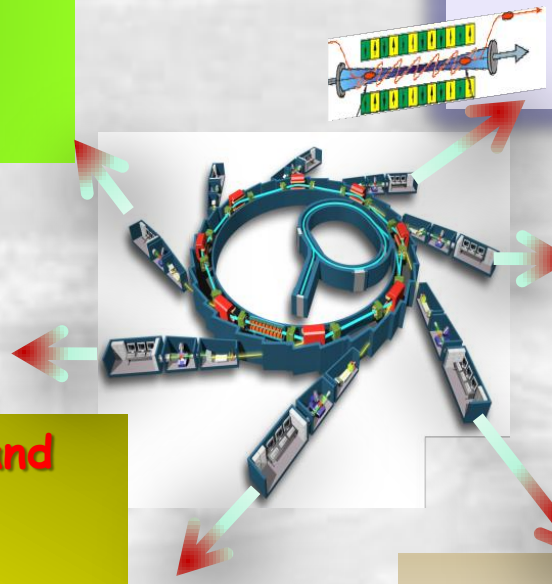
Chemical specificity and resolution using SR



Enjoy the following Lectures

X-ray microscopy: absorption & phase contrast
(lecture Gianoncelli)
- 2D/3D morphology
- High resolution.
- Density mapping.

X-ray (Coherent) Scattering
(lectures Kirz-Chapman)
- Structure: stress/strain/texture 2D/3D mapping.
- Chemistry at resonances



Fluorescence spectromicroscopy
(lecture Gianoncelli)
- Elemental quantification
- Elemental mapping
- Bulk sensitive

Photoelectron imaging and Spectromicroscopy:
(lecture: Locatelli)
- Chemical state
- Chemical and magnetic mapping.
- Surface sensitive.

Infrared Spectromicroscopy
(lecture Vaccari)
- Molecular groups and structure
- High S/N for organic matter
- Functional group imaging.
- Modest resolution but non-destructive radiation.

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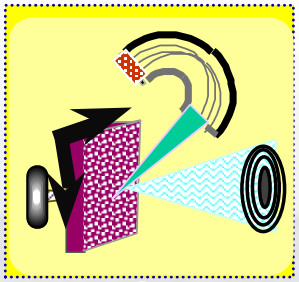
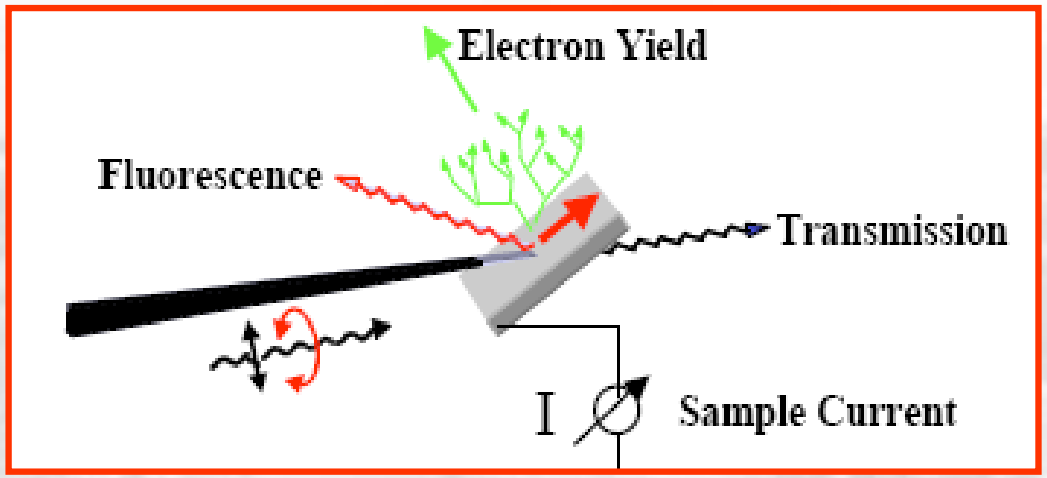
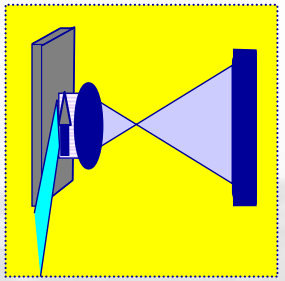
Microscopy @ Elettra Laboratory

hν-in/e⁻-out: PE & XAS

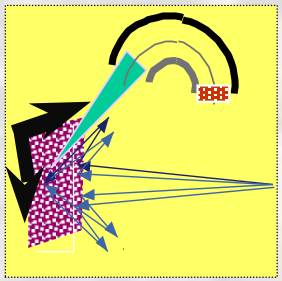


SPEM-ZP:
ESCA microscopy
1995 -



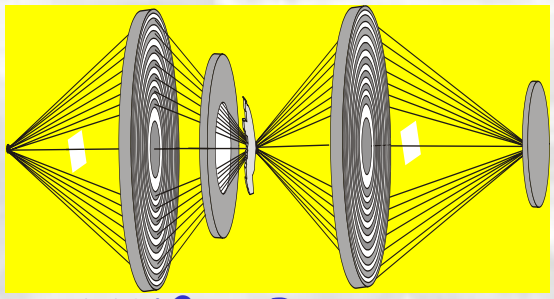


XPEEM:
Nanospectroscopy
2001 -

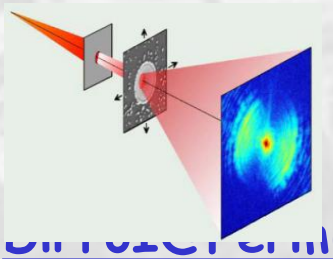


SPEM-SO:
Spectromicroscopy
1998 -
now developed as
μ-ARPES

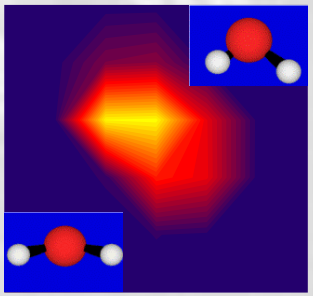
hν-in/hν-out: XAS (FS), CDI & IRAS



TXM²-ZP: TwinMic
2005 -



commissioning



IRAS: SISSI
2005

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