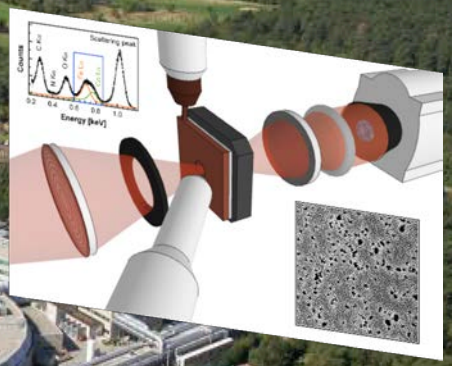
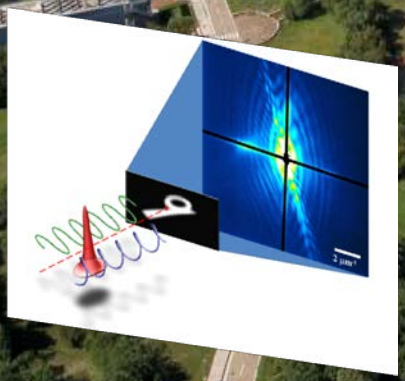
Elettra Sincrotrone Trieste

Elettra and FERMI lightsources

SEARCH
SITEMAP
PHONEBOOK

Introduction to X-ray microscopy and spectroscopy





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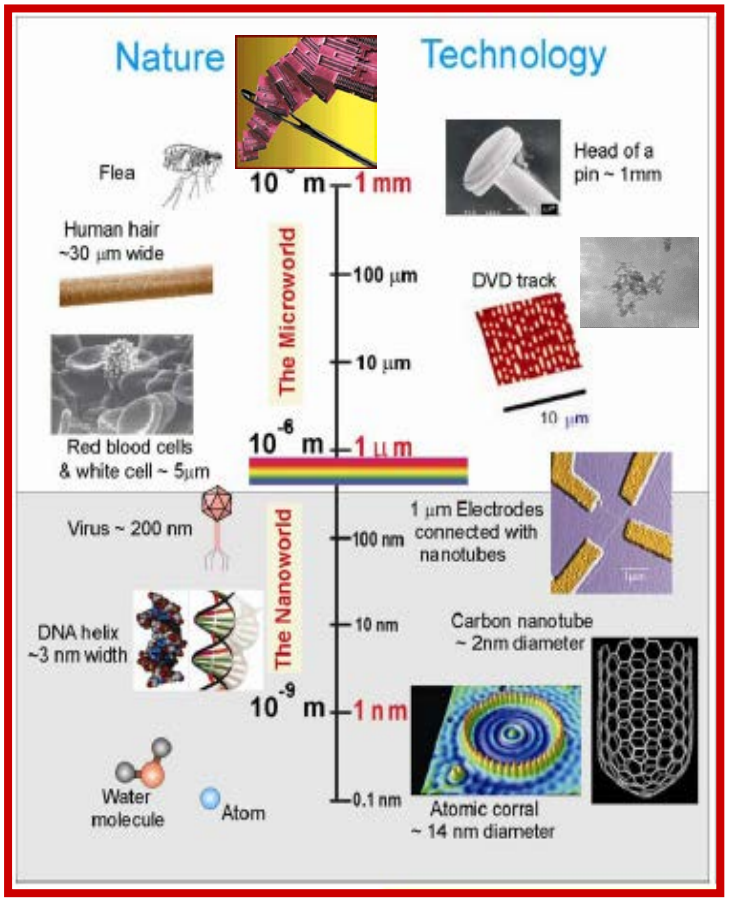

An Invitation to Enter a New Field of Physics & Material Science

Richard P. Feynman - 1959!!!

There's Plenty of Room at the Bottom

'NANO'

by nature, design or externally-induced changes

- Materials have properties varying at various depth and length scales and are usually laterally inhomogeneous at atomic, nano or meso scales.
- Structure and chemical composition usually is different at the surface and in the bulk.
- New properties expected with decreasing the dimensions stepping into nanoworld.

What we NEED:

Chemical sensitivity, spatial resolution & morphology & structure, varying probing depth, temporal resolution when possible.

Majority of these methods are based on interaction of the matter with photon, electron or ion radiation.

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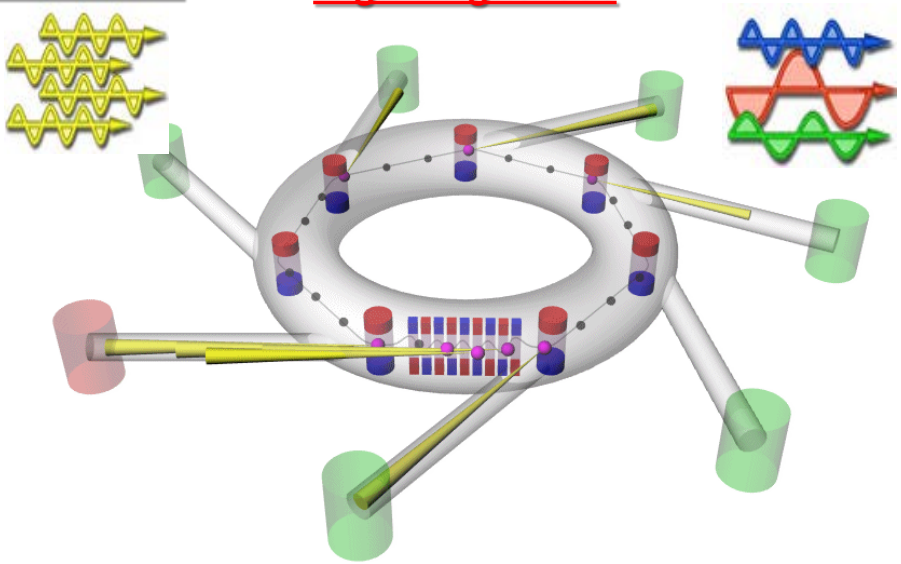
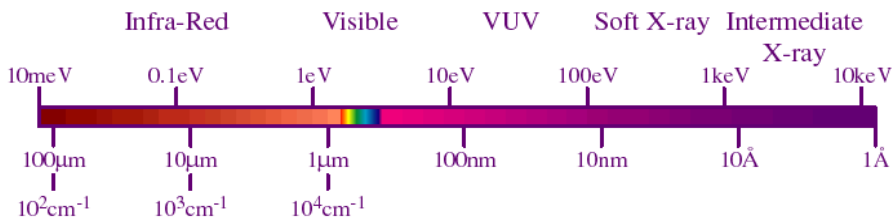
Why Microscopy needs Synchrotrons

% coherent

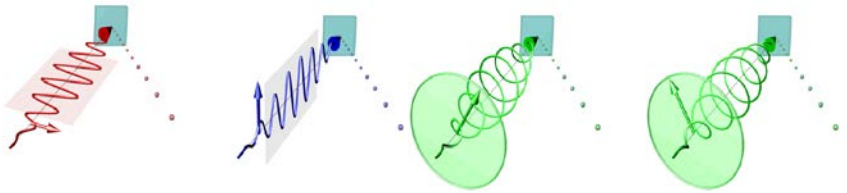
High Brightness

tunable





polarized



Synchrotron light advantages

- Very bright, wave-length tunable (cross sections and atomic edges), multiply polarized (dichroic effects, bonding orientation), partly coherent.
- Great variety of spectroscopies - elemental, chemical, magnetic information
- Variety of imaging contrasts based on photon absorption, scattering or spectroscopic feature.
- Higher penetration power compared to charged particles - less sensible to sample environment .

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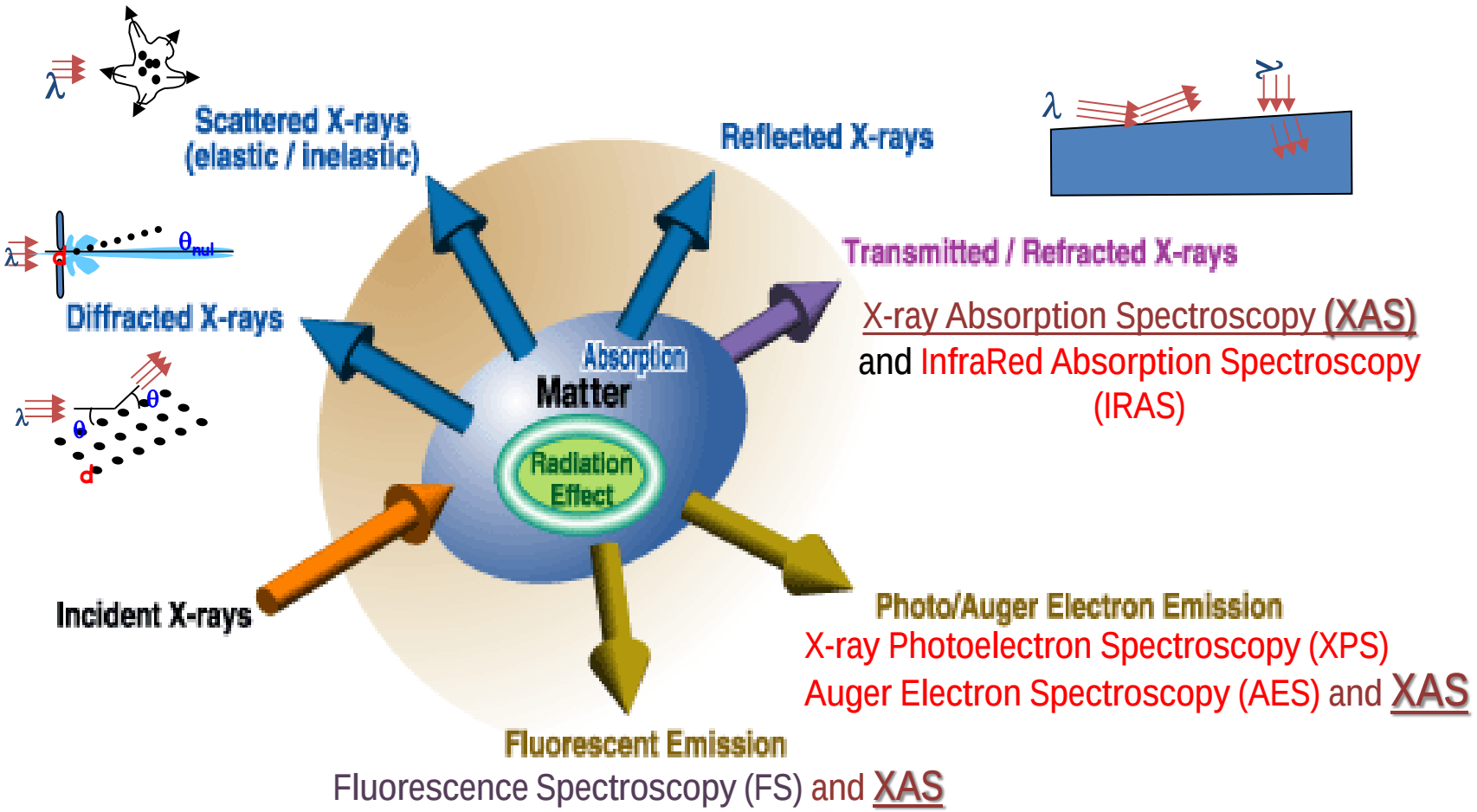
All methods using SR are based on the interaction of photons with the matter and find applications in all domains of science and technology



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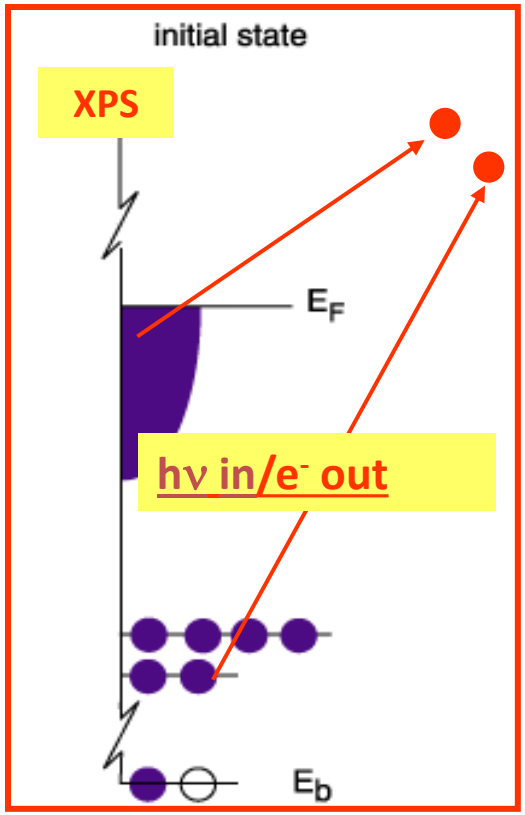
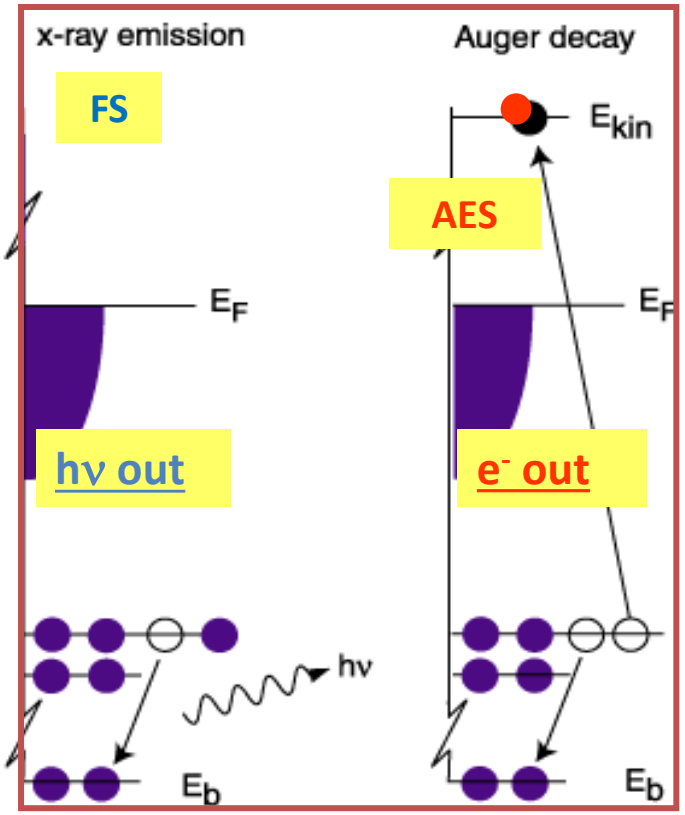
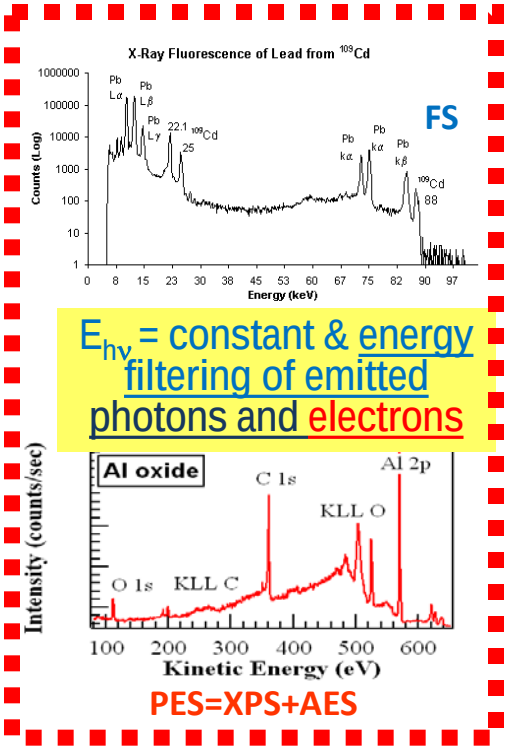
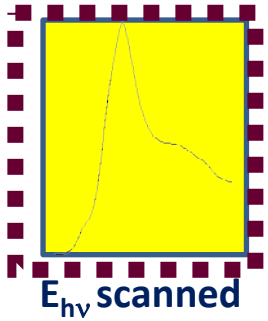
Spectroscopies @ synchrotron light sources: XPS-AES, XRF, XAS, RIXS

Photoelectric effect & de-excitation processes = chemical specific spectroscopies









XAS: based on absorption coefficient $\mu = f(h\nu - E_{core})$ and resonant electronic transitions governed by selection rules

e^- and hν detection

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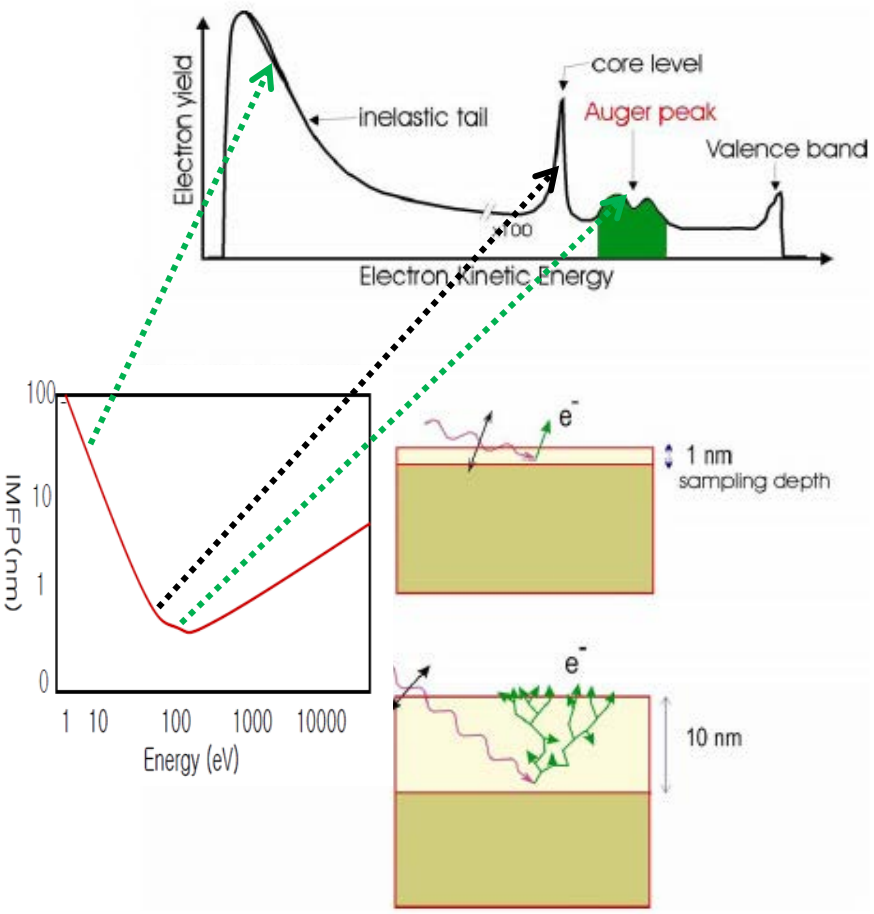
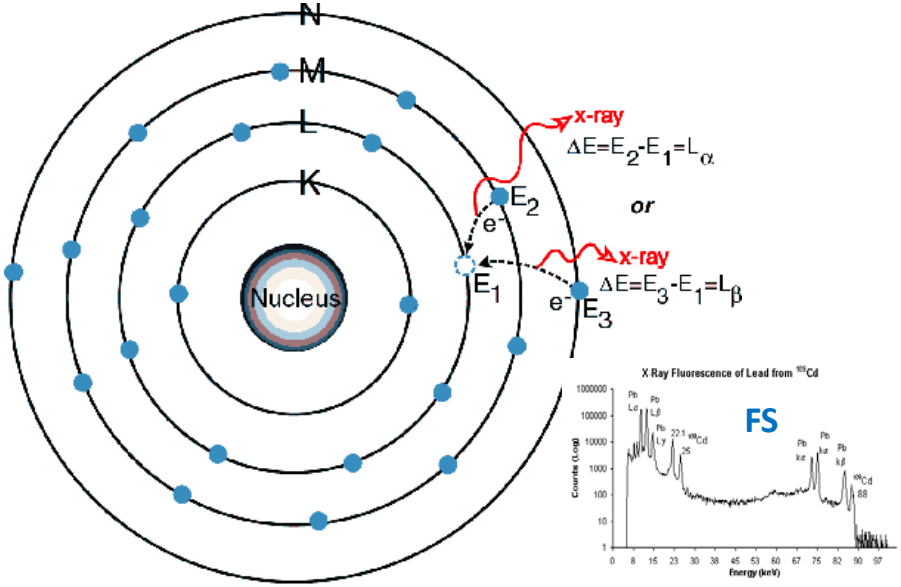
Sampling depths: depend on the detected signal (electrons or photons)

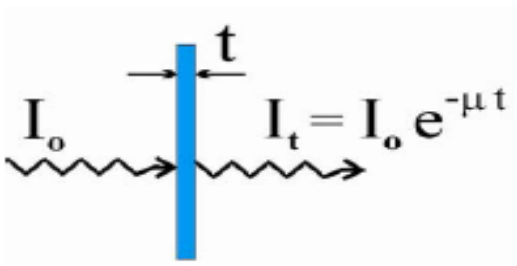
TEY& Auger electron emission (XAS), core&valence PES: Probe depth 1- 10 nm



Fluorescence emission (XAS and FS): Probe depth > 100 nm = f(Eph, matrix)



X-ray transmission: 'bulk'



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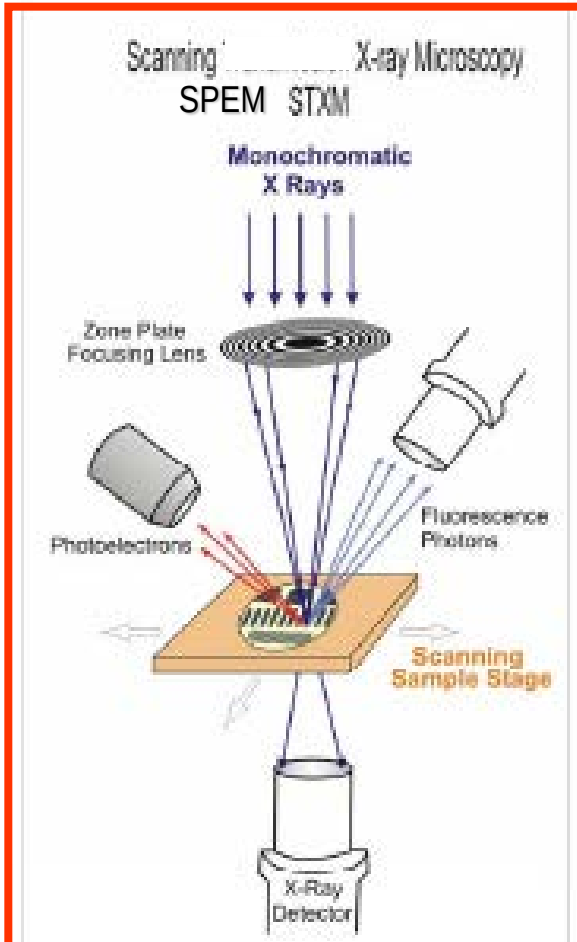
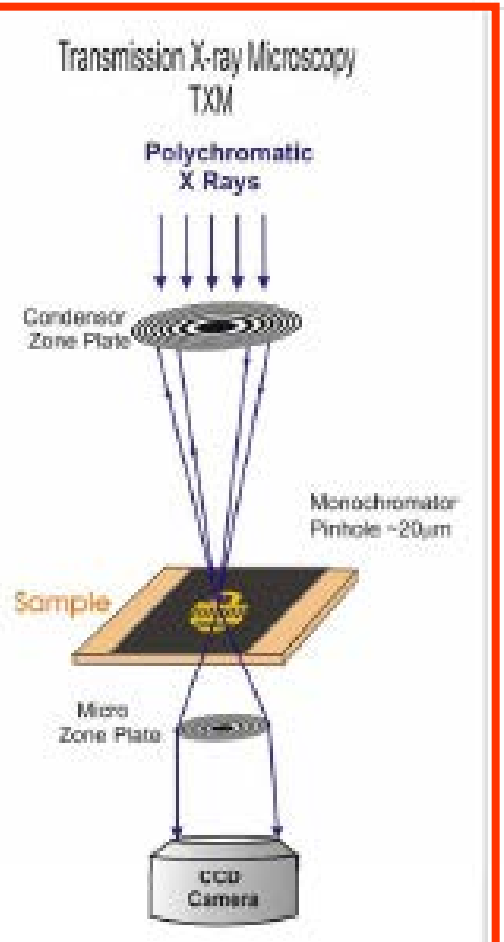
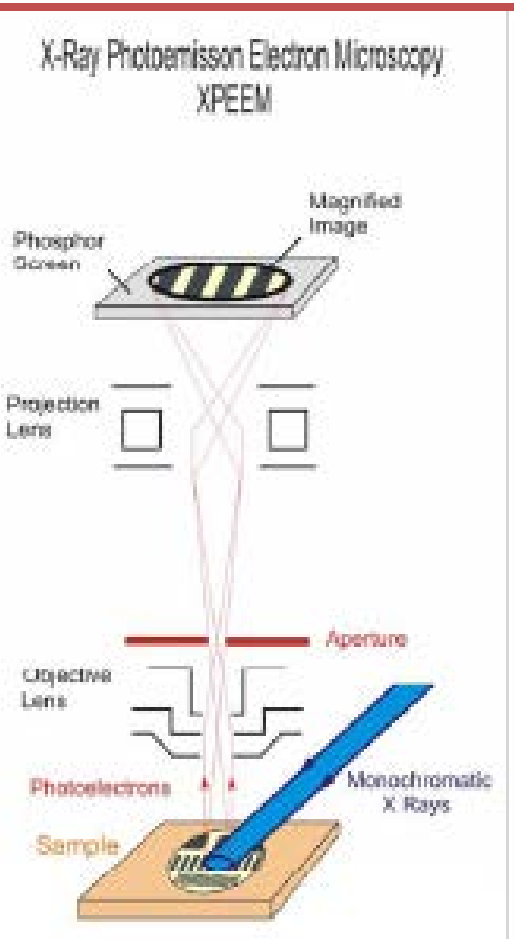
Microscopic Approaches, Adding Spatial Resolution: X-ray or electron optics



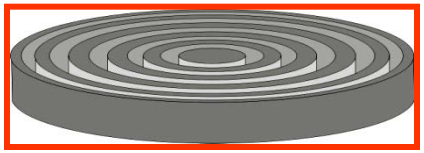


Lateral resolution provided by photon optics



Lateral resolution using electron optics

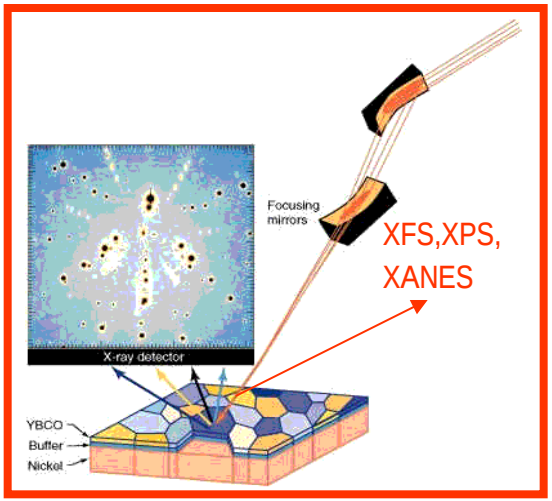
X-ray focusing optics:
zone plates, mirrors, capillaries



Zone Plate optics – circular grating with decreasing width: from ~ 200 to ~ 10000 eV

Monochromatic:

Resolution achieved 15 nm in transmission



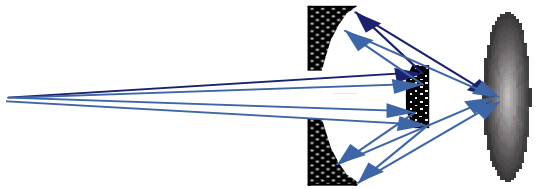
XFS,XPS, XANES

KP-B mirrors each focusing in one direction: soft & hard X-rays: ~ 100 nm

Soft & hard x-rays!

achromatic focal point, easy energy tunability, comfortable working distance

Resolution ≤ 100 nm

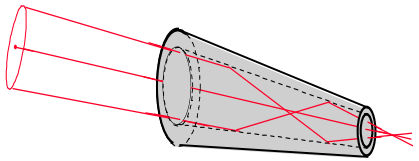


Normal incidence:
spherical mirrors with multilayer interference coating (Schwarzschild Objective)

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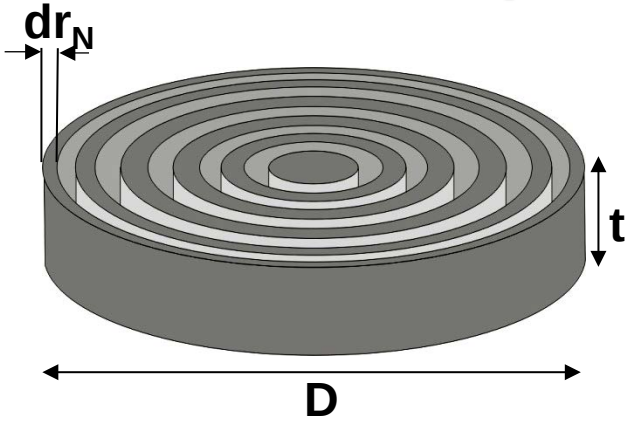
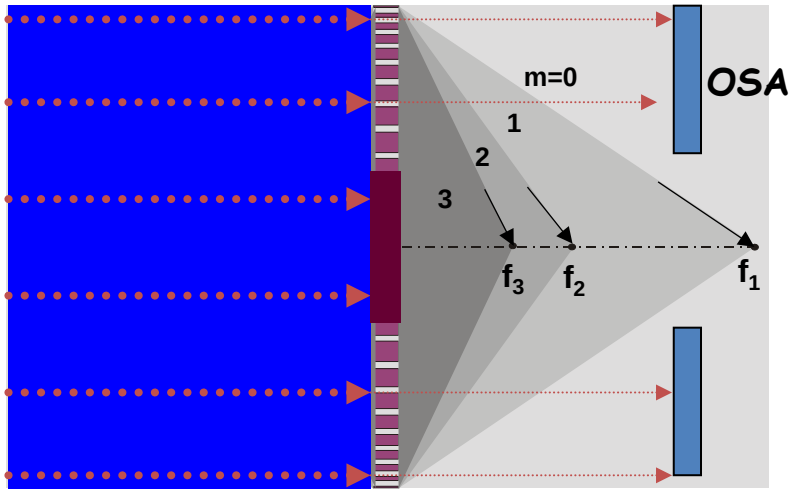
Zone plate: circular diffraction grating of N lines with radially decreasing line width operating in transmission



$$f_m = D.dr_N/\lambda$$



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 μm), dr_N and λ determine the focal distance **f**.

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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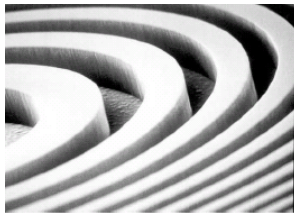
X-ray transmission microscope (TXM-FFIM)

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



Objective ZP
to magnify the image
onto the detector

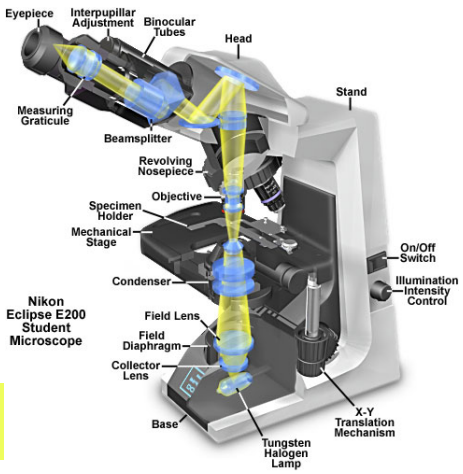
CCD camera

Aperture:
removes (i) unwanted
diffraction orders and straylight,
and serves (ii) with condenser
as monochromator

X-ray light
from a 2nd or 3rd
generation light
source

Condenser
illuminating the
object field

Specimen
environment: to be
adapted to application



Resolution achieved better than 15 nm.

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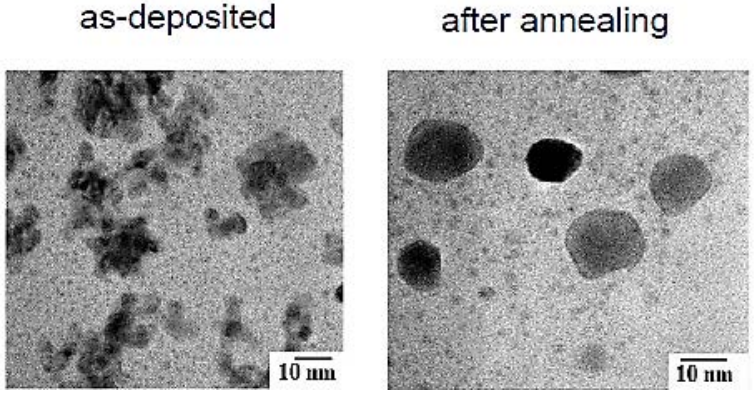
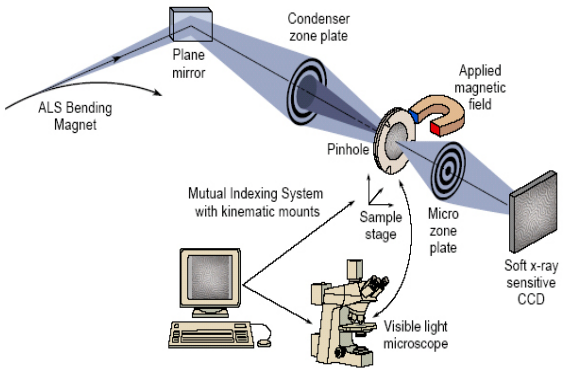
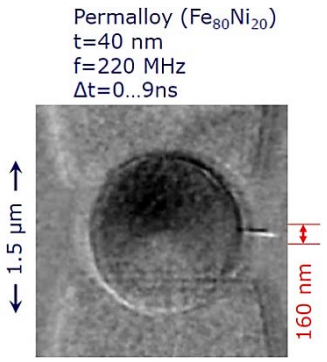
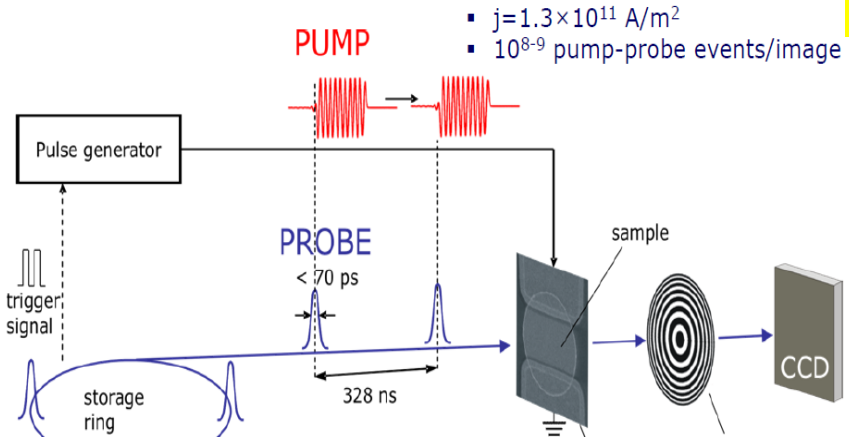
Following dynamic processes during temperature treatment, applying magnetic/electric field or pumping with optical lasers X

Fe38Rh62 nanoparticles

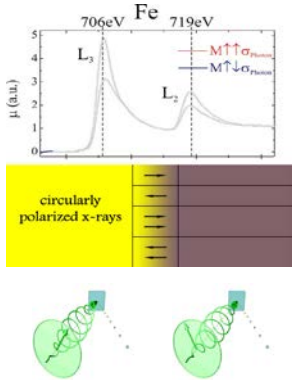


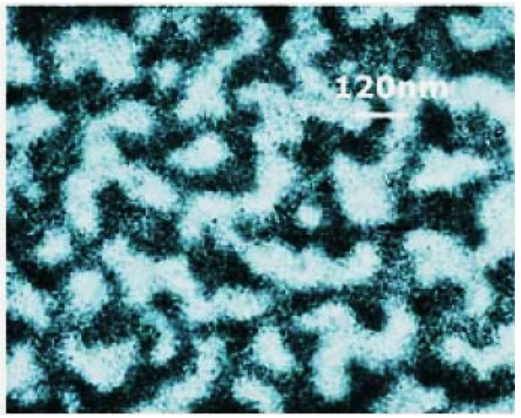






XAS-XMCD X-Ray Magnetic Circular Dichroism





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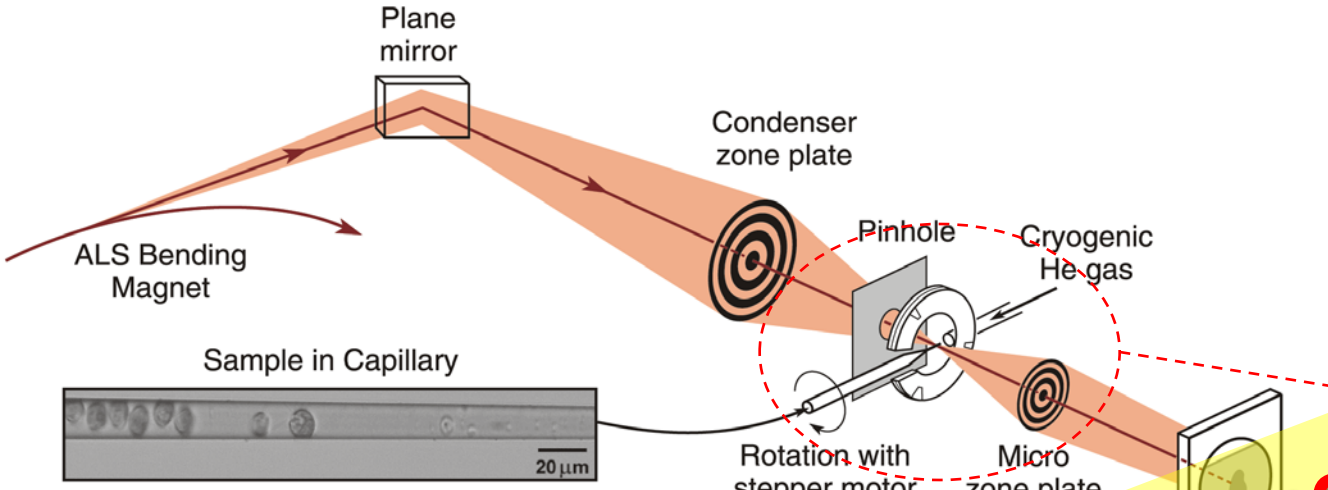
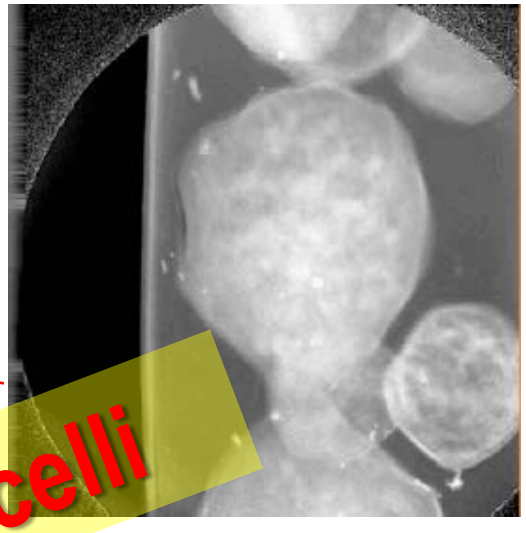
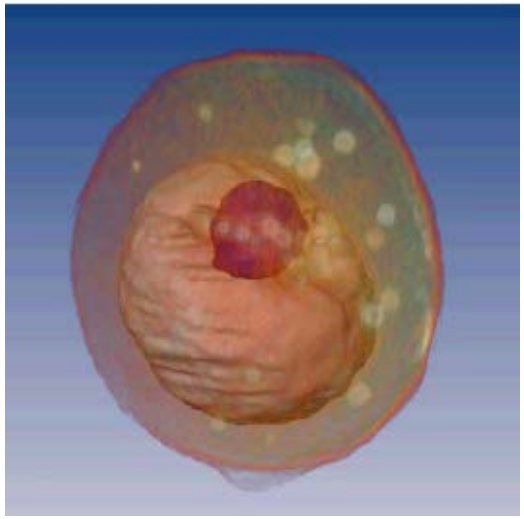
Cryogenic 3D imaging of biological cells







Lecture: Alessandra Gianoncelli

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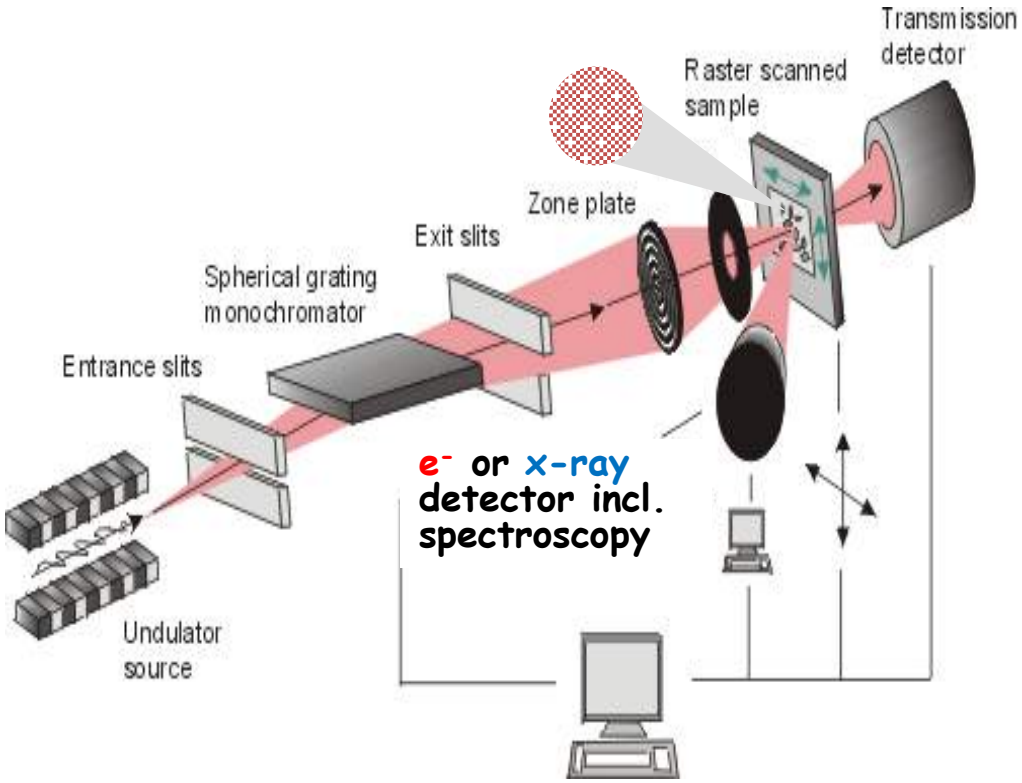
X-ray Scanning microscopy: uses focusing x-ray optics (preferred zone plates)

Works in Transmission and Emission + microspot spectroscopy

Janos Kirz, 1st operating STXM 1983
SPEM 1990



Can use all detection modes!

Resolution achieved 25 nm in transmission.

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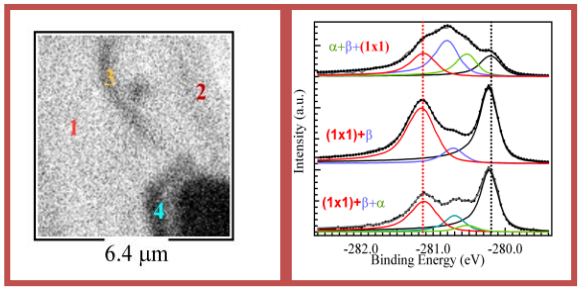
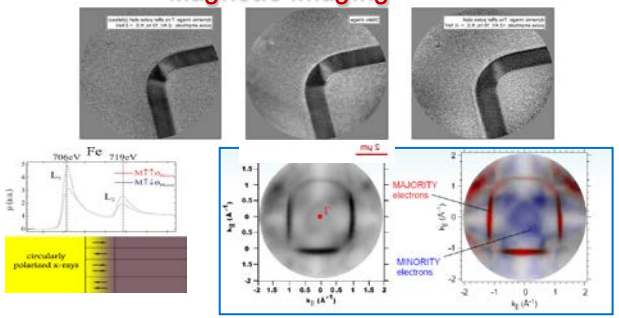
Microscopy Approaches @ ELETTRA storage ring:
X-ray or electron optics; X-ray or electron detection

PES Imaging and microspectroscopy

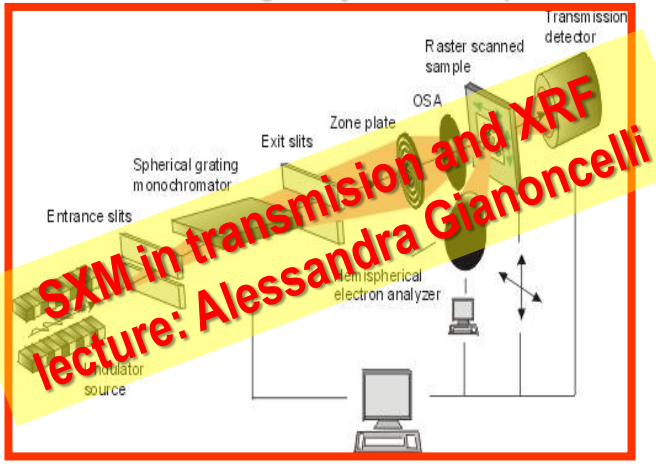


XRF, XPS, XAS = elemental and chemical information
X-ray transmission and scattering (phase contrast) - morphology
Topology – electron emission

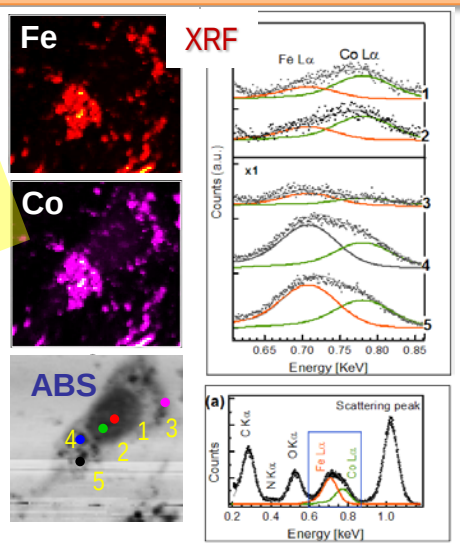
Magnetic imaging



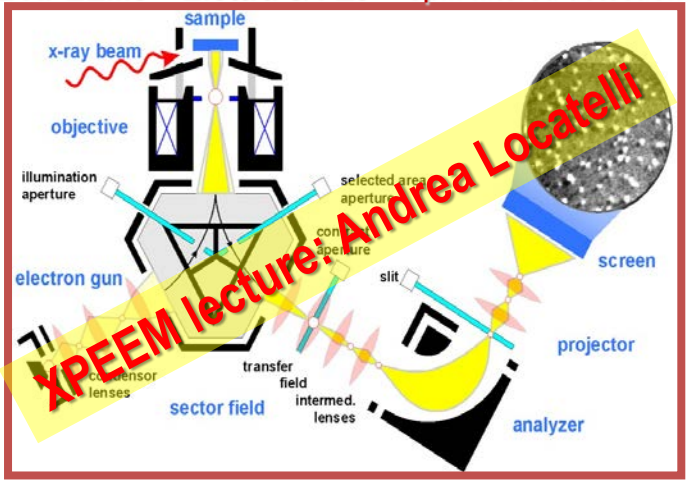
3 Scanning x-ray microscopes



SXM in transmision and XRF
lecture: Alessandra Gianoncelli



2 XPEEMs – Elettra & FZJ + Spin filtered detection



XPEEM lecture: Andrea Locatelli

The image contrast can provide:

- Morphology: density, thickness (transmission)
- Element presence and concentration- e^-, $h\nu$;
- Chemical state, band-bending, charging e^-;
- Magnetic spin or bond orientation – e^-, $h\nu$

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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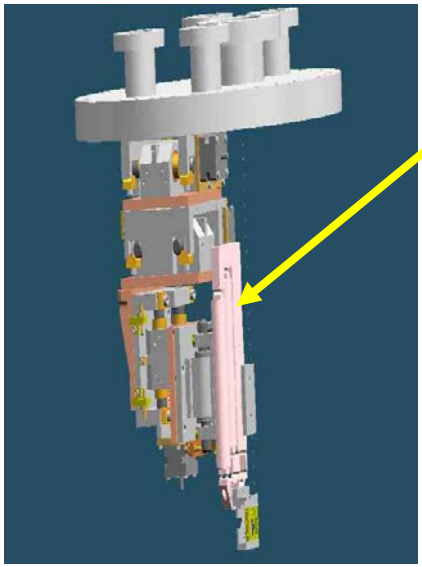
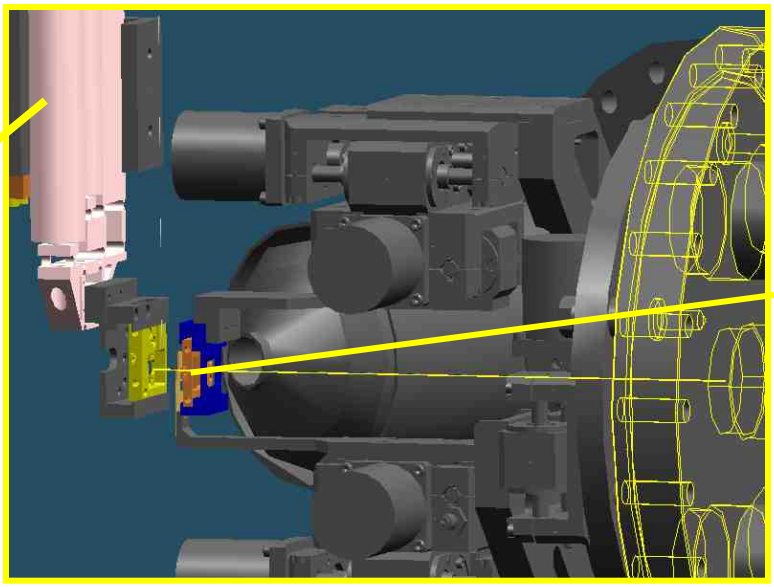
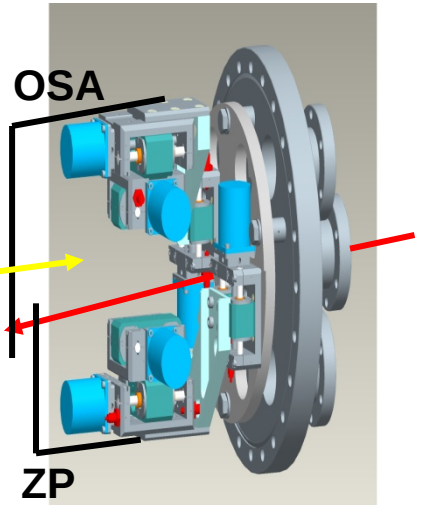
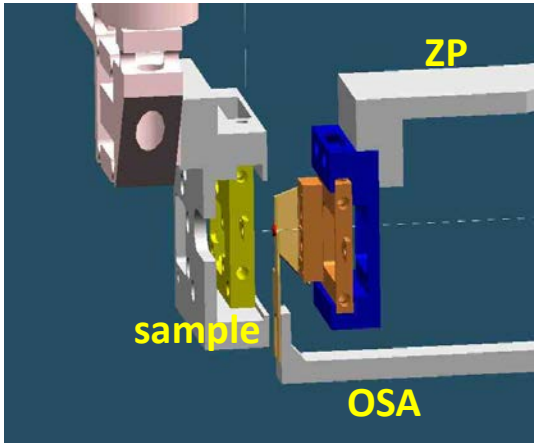
Layout of SPEM: Focusing optics (ZP, SO or K-B), sample and positioning systems









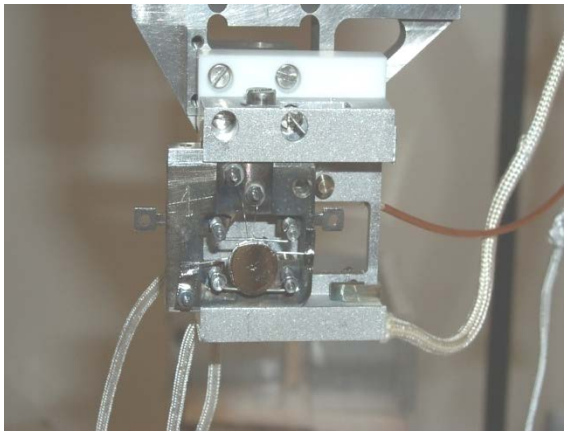
Spatial resolution in electron emission limited by the sample-to-optics distance !

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

~10 mm for soft X rays

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

Typical: 5-15 μm



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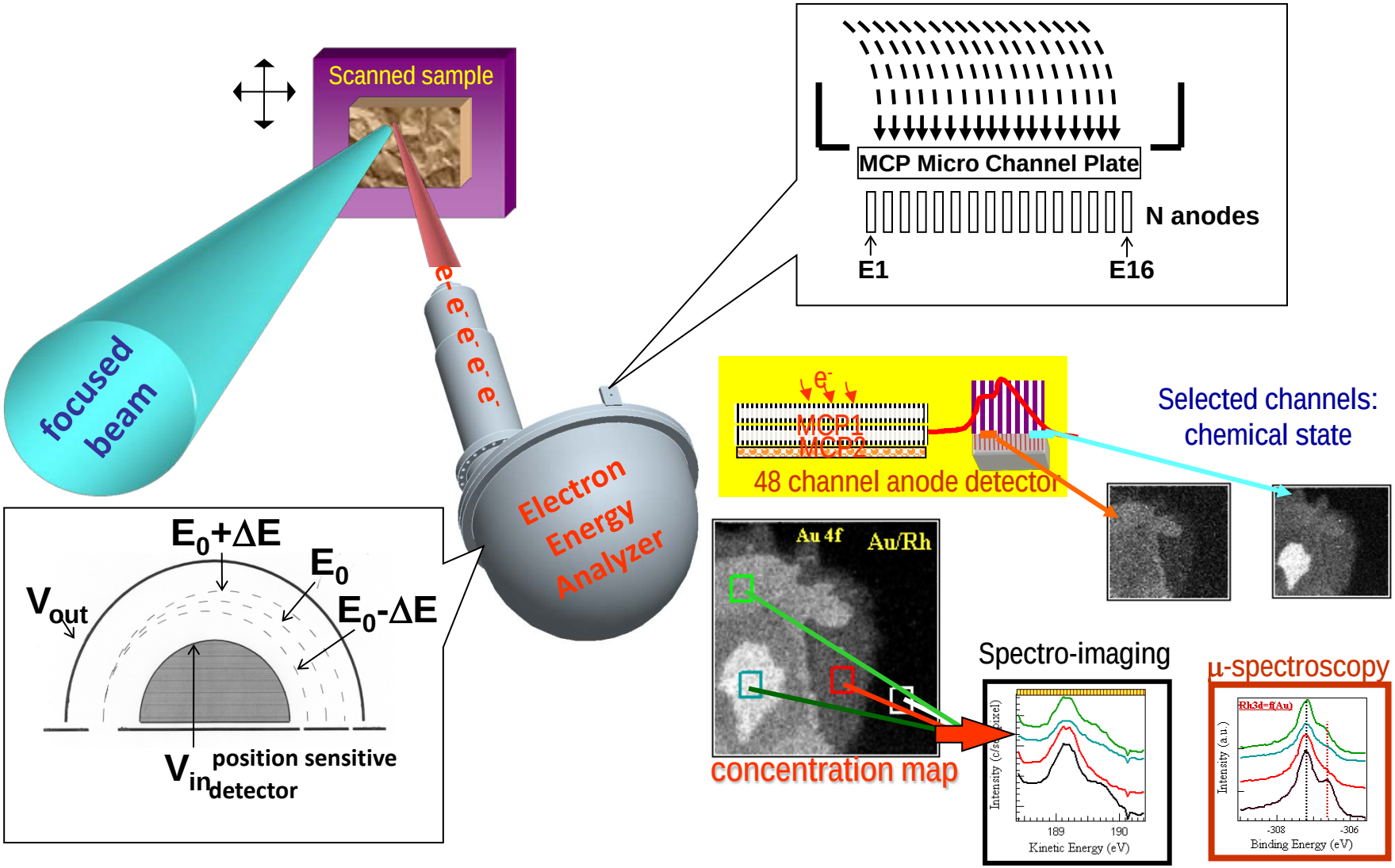
SPEMs energy-filtering electron analyzers
MCD developed @ ELETTRA



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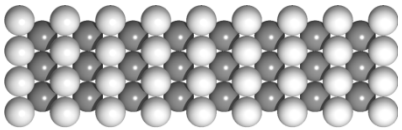
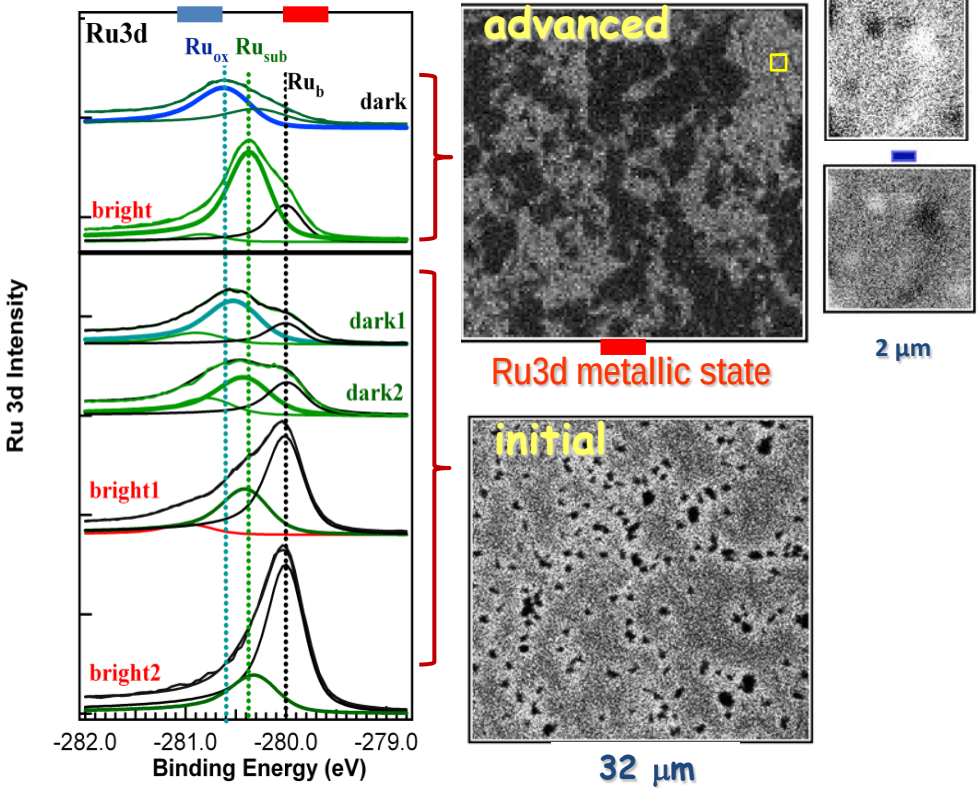
Model catalyst systems studied with SPEM: single crystals and supported metal particles on MgO

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

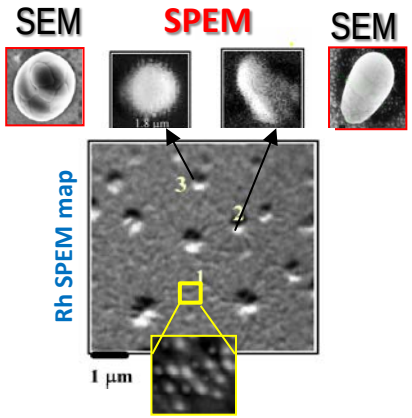
R. Blume et al, JPC B 109, 14058; P. Dudin et al, JPC B 109, 13649; 125, 94701



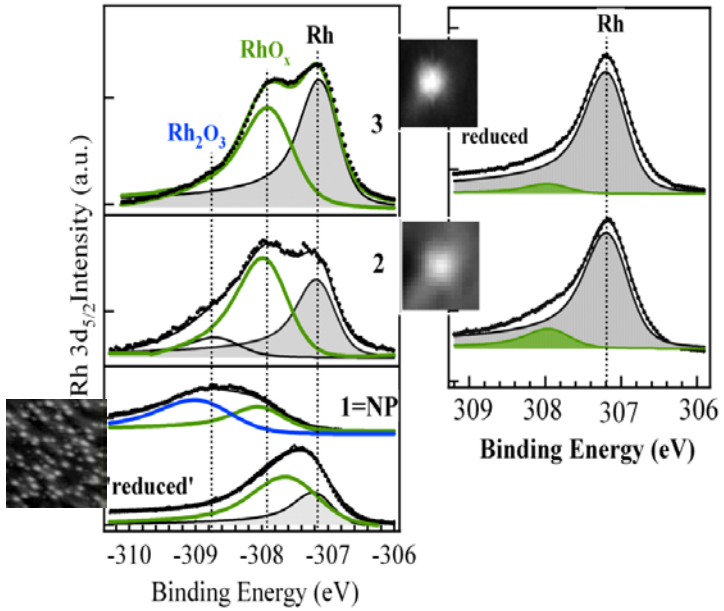
Ru(0001) ≡ Rh(110)



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



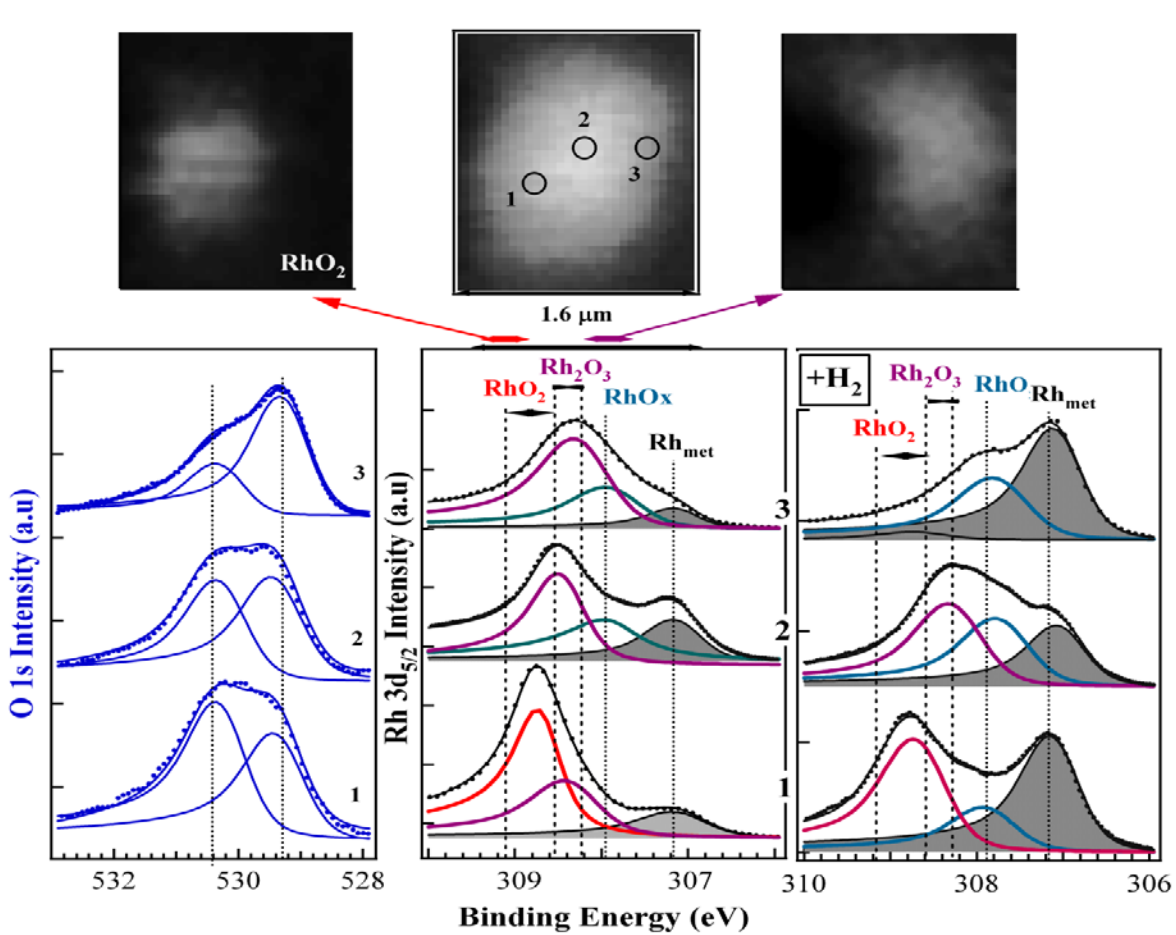
No simple size effect

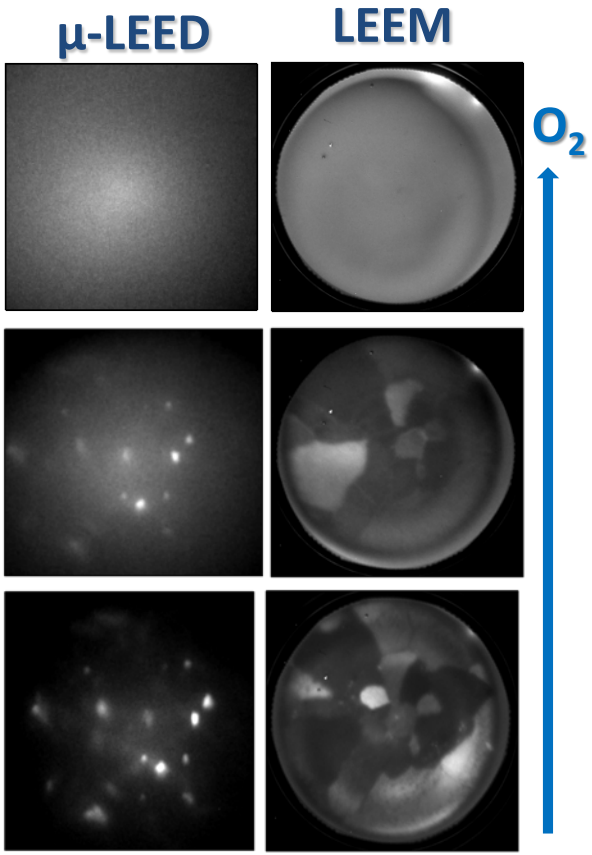


P. Dudin et al, JPC C 1112, 9040;
M. Dalmiglio JCP C, 114 16885

Maya Kiskinova

Correlation of the µm-particle reactivity to its complex surface structure: SPEM - LEEM





- 'Inhomogeneous' reactivity in µ-Ps related to the surface morphology;
- Structural evolution upon oxidation ends with a disordered oxide

M. Dalmiglio, *JPC-C 114,* 2010, 16885.

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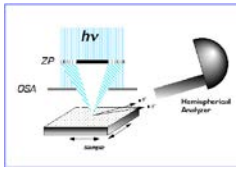
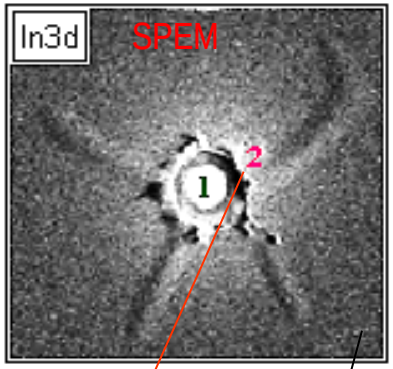
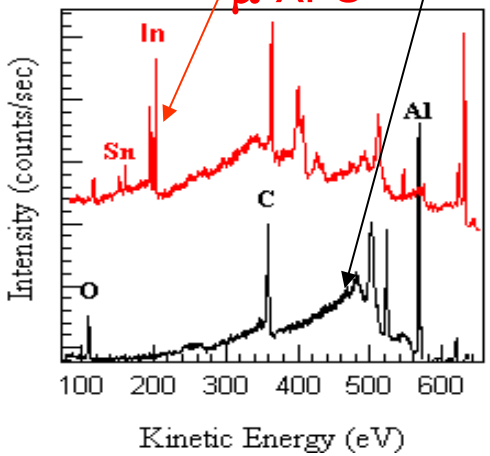
Degradation of organic light emission devices: mechanism revealed by 'in-situ' SPEM



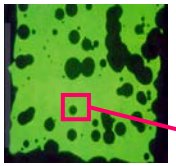
OLED exposed to ambient: **moisture?** supposed to be the damaging factor

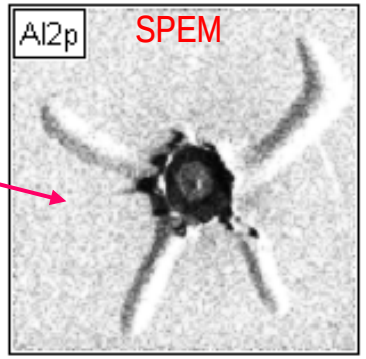


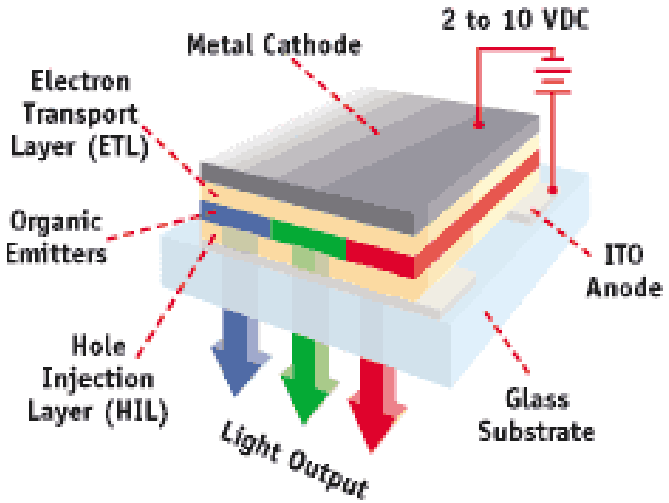
μ-XPS



OLED Display Screen (from Universal Display Corp)







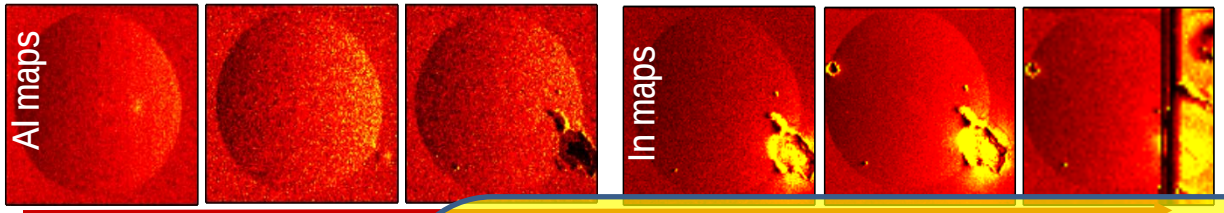
Topographic features due to fracture: clearly seen as enhancement and shadowing of the emitted electrons

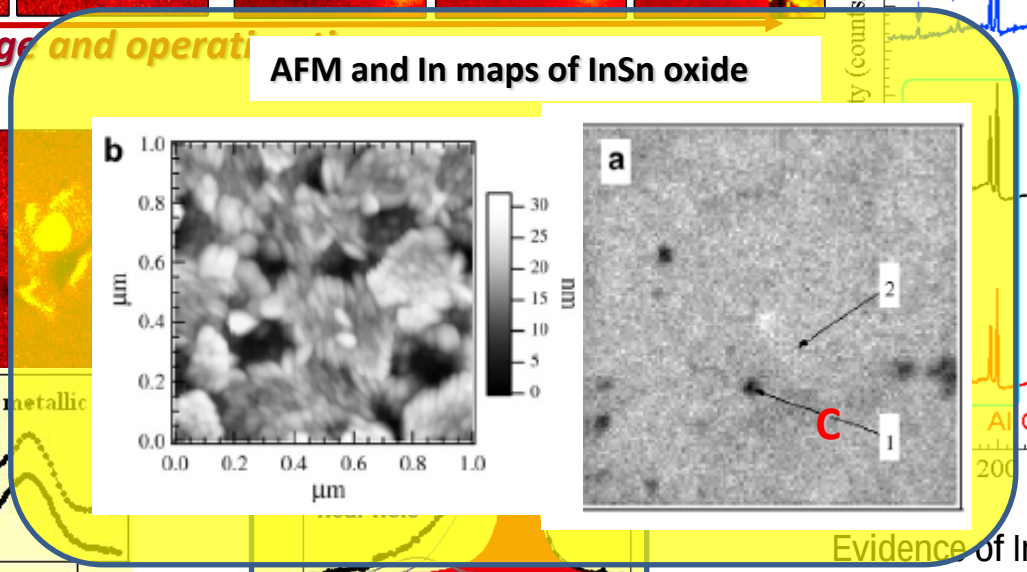
Chemical imaging & μ-XPS revealed anode material (In and Sn) deposited around the hole created in the Al cathode of OLEDs.

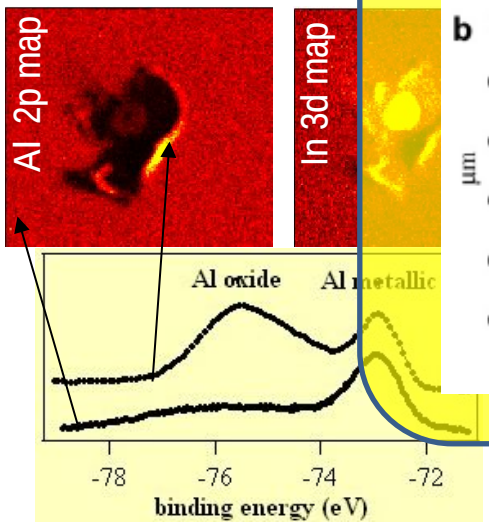
Maya Kiskinova

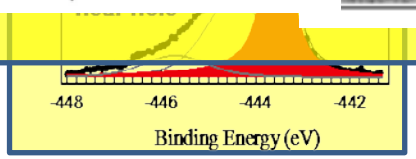
‘In-situ’ imaging of the local deformation and fracturing of the OLED cathode surface

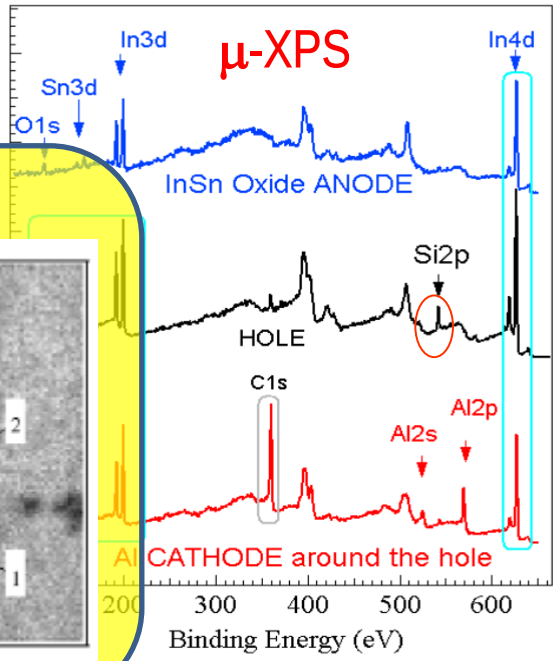
“Clean” failure experiment: OLED growth and operated in the SPEM (UHV ambient)











Evidence of InSn oxide and organic layer local decomposition, caused by spikes

Lateral variations 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,
S. Gardonio, Org.Electr. 9, 253

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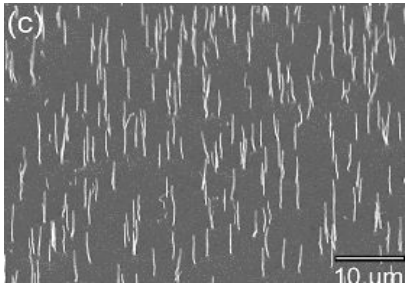
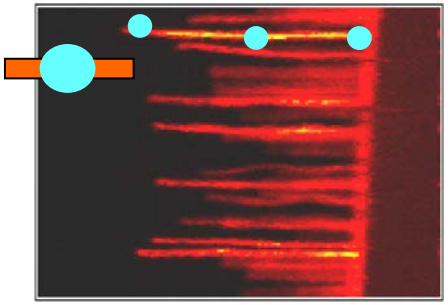
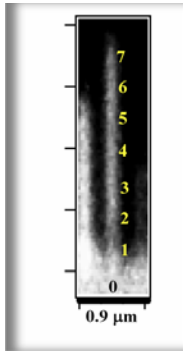
Exploring the properties of individual and free-standing nano-structures

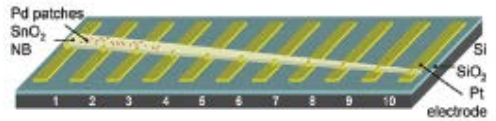
Low density NWs

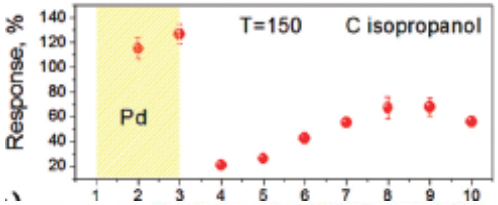


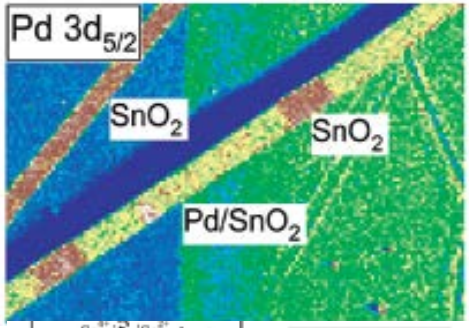


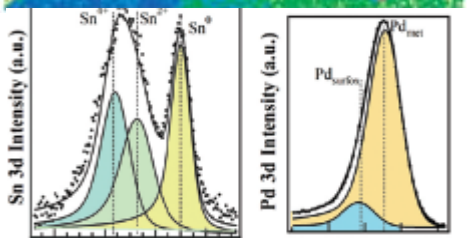


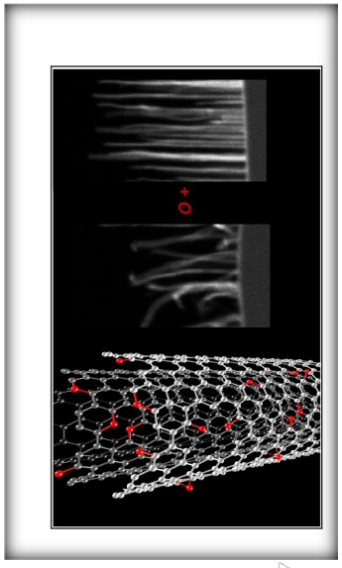
NB electronic nose

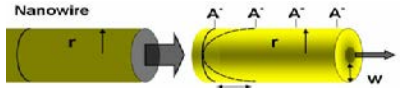


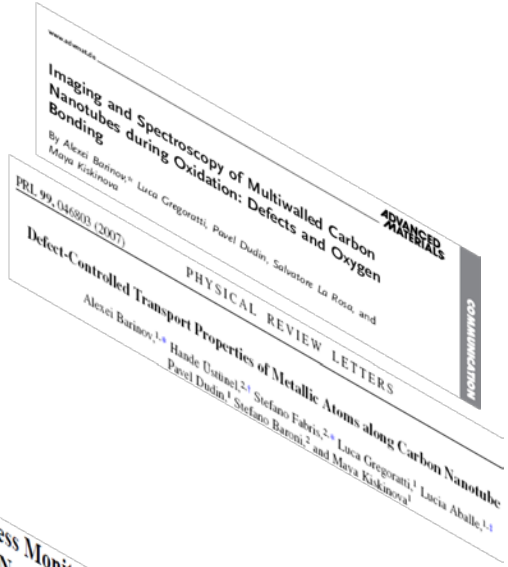


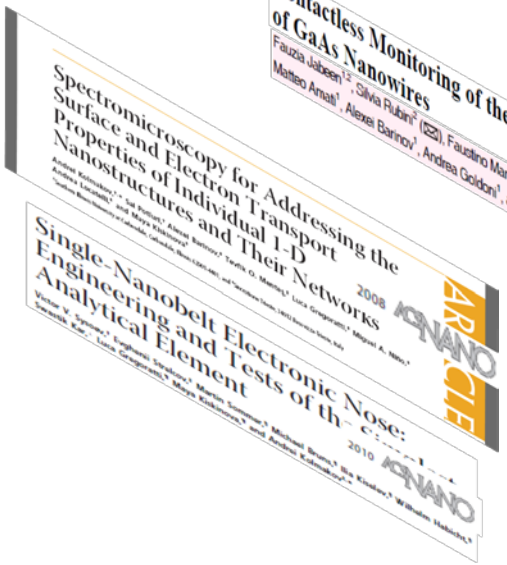








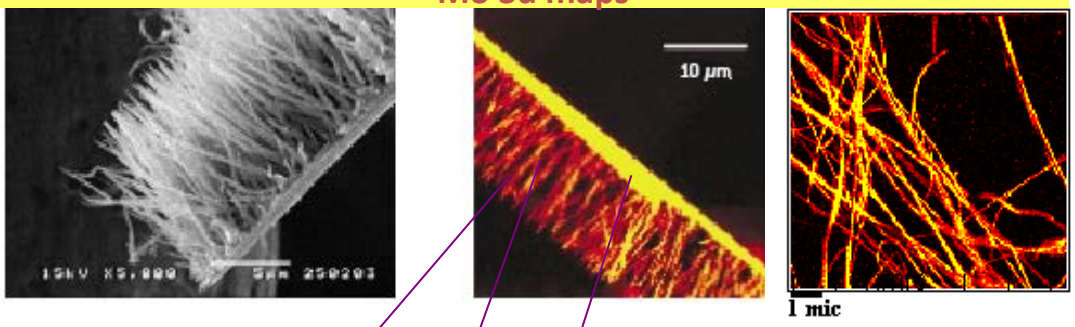


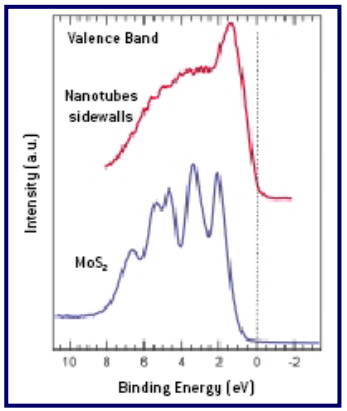


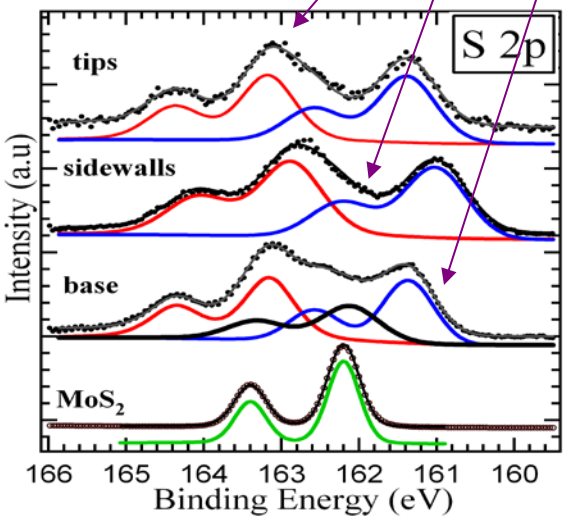
Maya Kiskinova

SPEM characterization of MoS_2-nanotubes

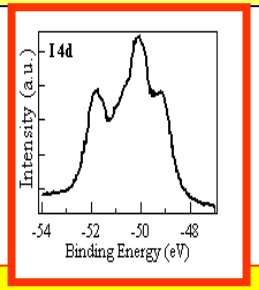
Twisted chiral bundles of Mo-S individual cylinders: Mo 3d maps







? It that due to the low dimensionality the S 2p, Mo 3d and VB spectra are position-dependent?
This should indicate electronic properties significantly different those of the MoS_2 crystal.



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

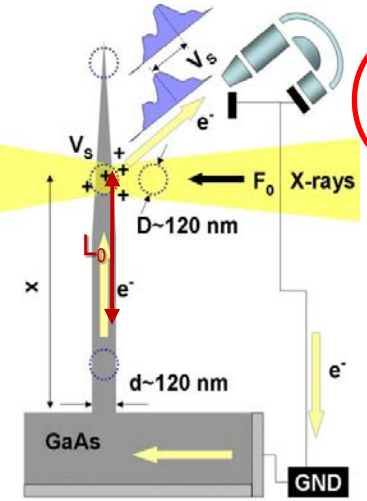
Maya Kiskinova

GaAs NWs conductivity measured with SPEM:

non-ohmic behavior with reducing diameter, environment effects, effect of growth conditions

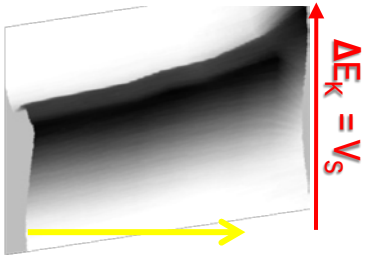
$$E_K = E_{Ko} \pm E_{BB} \pm E_{SPV} - V_s$$

$$V_s = f(\text{Ohmic neutr. current})$$



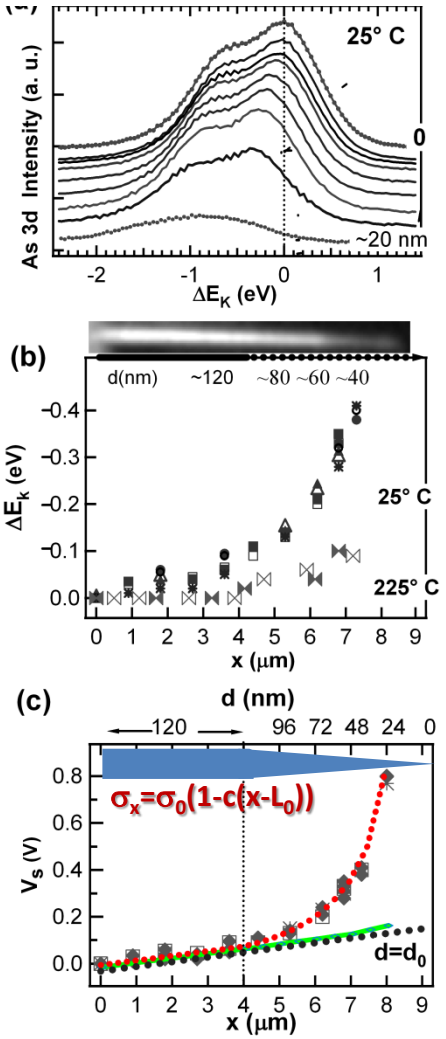
$$V_S = \frac{4\delta \cdot F_{ph} \cdot x \cdot}{\pi \cdot d_0^2 \cdot \sigma}$$

Ga or As3d spectra

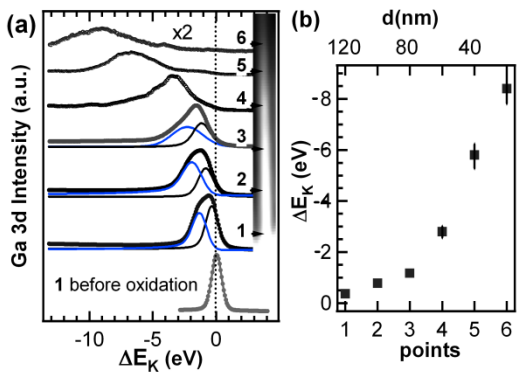


- Conductivity of pencil-like NWs: non-ohmic behavior as a function of d.
- The data fit to linear decrease of σ with decreasing d > confirms size effects

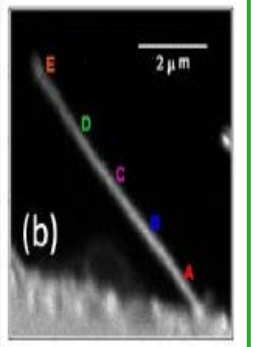
As 3d shifts of pencil GaAs NWs

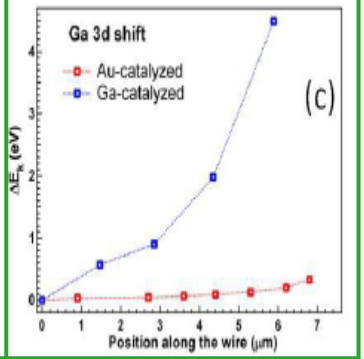


Ga 3d shifts of oxidized pencil GaAs NWs



Oxidation: drastic reduction in the carrier density : transport properties = f(ambient)





Metal catalyst > drastic conductivity increase

F. Jabeen, Nano Res. 2010, 3(10): 706–713

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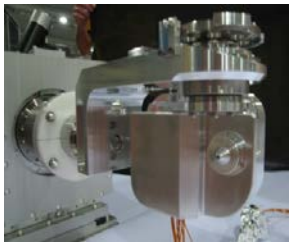
SPEM - μ-ARUPS

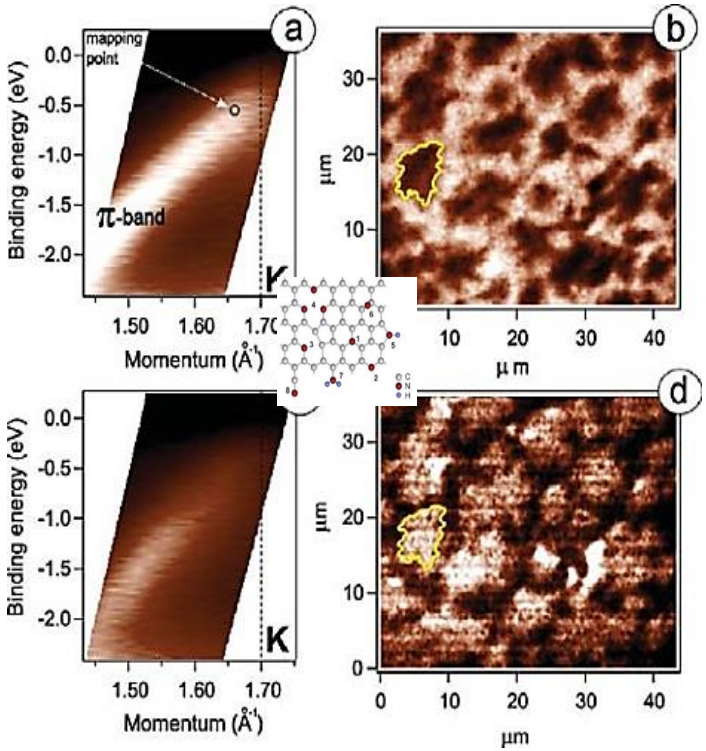


NANO LETTERS

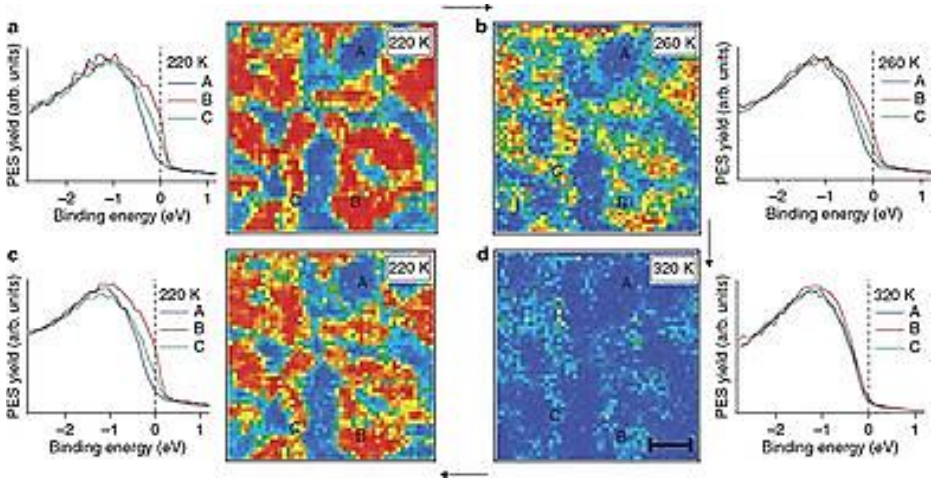
Nitrogen-Doped Graphene: Efficient Growth, Structure, and Electronic Properties

D. Usachov,*,† O. Vilkov,† A. Grüneis,*,§ D. Haberer,‡ A. Fedorov,† V. K. Adamchuk,† A. B. Preobrajenski,∥ P. Dudin,⊥ A. Barinov,⊥ M. Oehzelt,¶ C. Laubschat,# and D. V. Vyalikh

μ-ARPES of quasi-free standing N-doped graphene: EVIDENCE OF COEXISTENCE OF AT LEAST TWO DOMAINS ROTATED BY 30 deg: found T-dependence and extinctions of the B-domains.



Metal-insulator transition in Cr-doped V_2O_3 with decreasing T, microscopic domains become metallic and coexist with an insulating background.



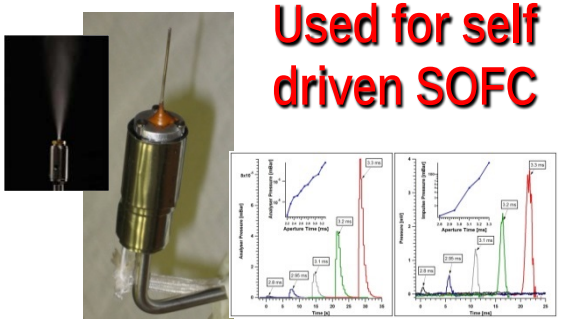
S. Lupi *et al.*, Nature Comm. 1, 105 (2010)

Maya Kiskinova

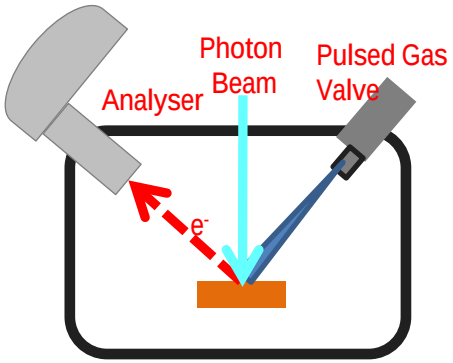
Onogoing μ-PES developments

THE CHALLENGE:

In-situ measurements of nano-structured matter under realistic ambient conditions needs to overcome the UHV limitations



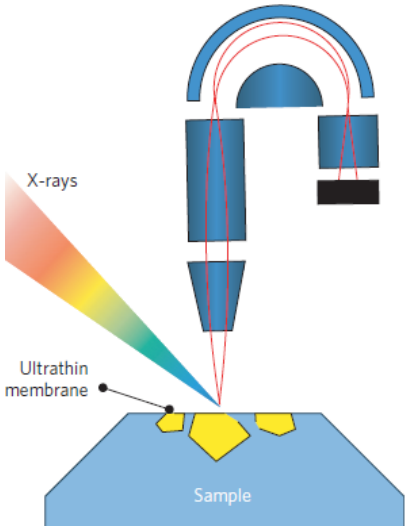
Used for self driven SOFC



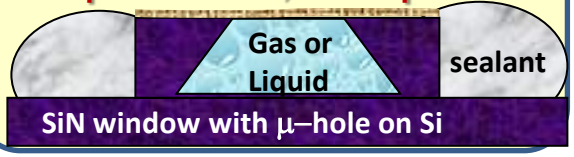
Pulsed supersonic beam: Dynamic local pressure of 10^{-2} mbar using high freq pulsed dosing valve + nozzle

M.Amati et al, J. Instr.8, 2013, T05001

J. Kraus et al, Nanoscale 2014, DOI: 10.1039/c4nr03561e



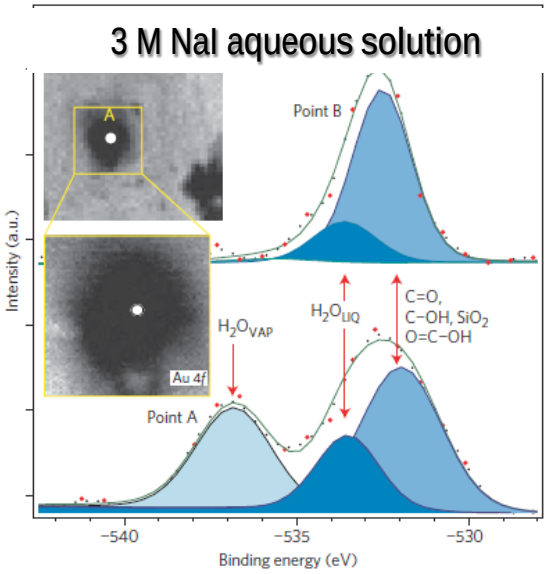
G-GO windows: robust, impermeable, transparent



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]



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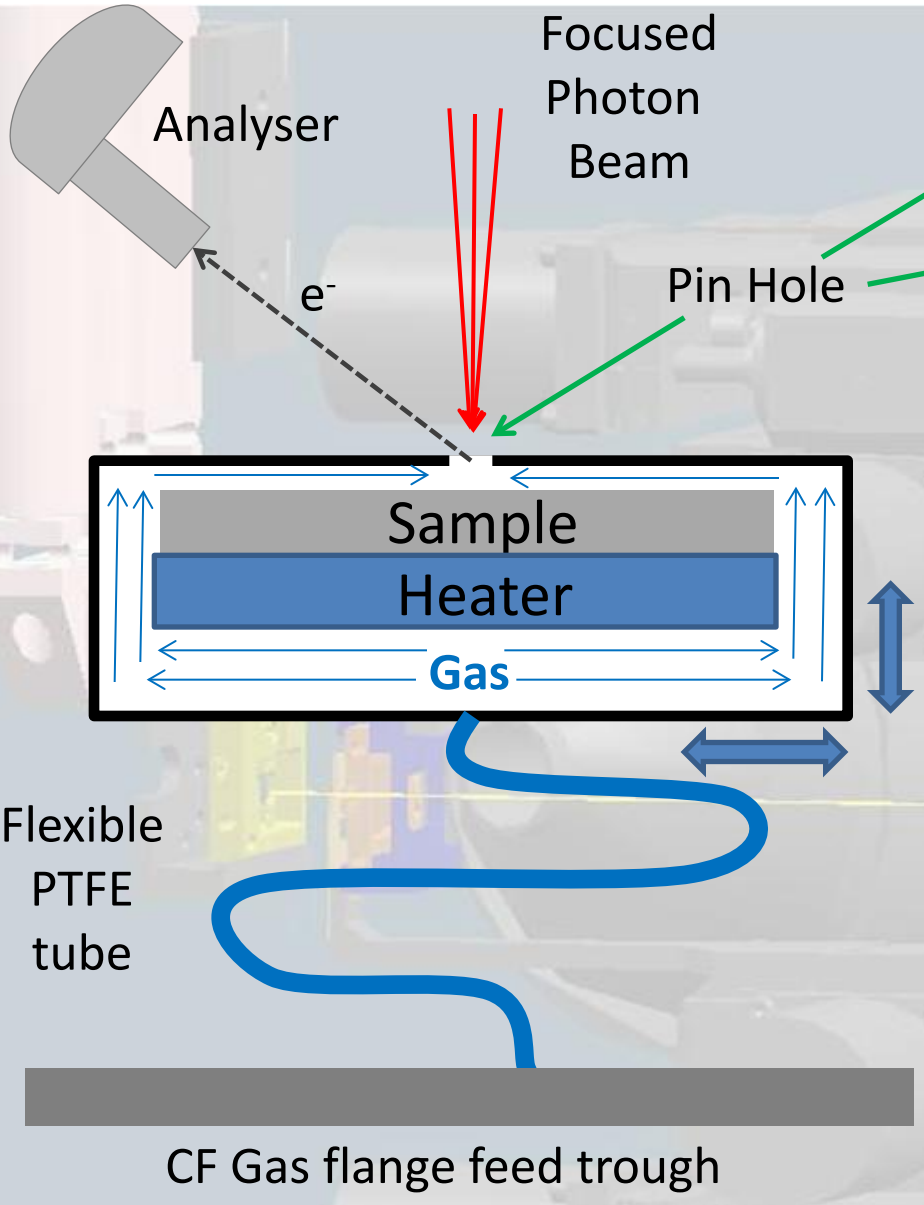
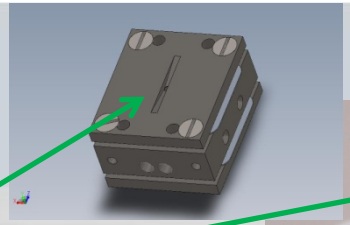
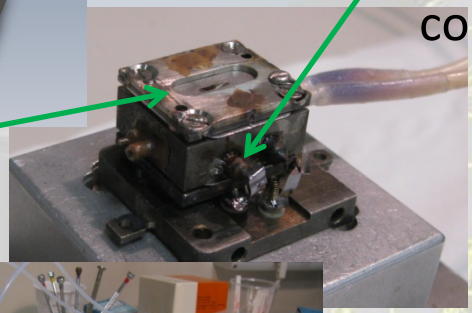
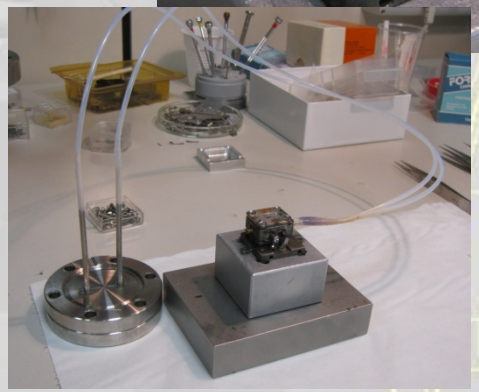
Static high pressure XPS









$\Phi_{\text{pin hole}} = 200\ \mu m$

$P_{cell} \sim 1\ mbar$

$P_{SPEM} \sim 10^{-5}\ mbar$

M. Amati et al. In preparation

Classical X-ray imaging and spectromicroscopy: brief outline

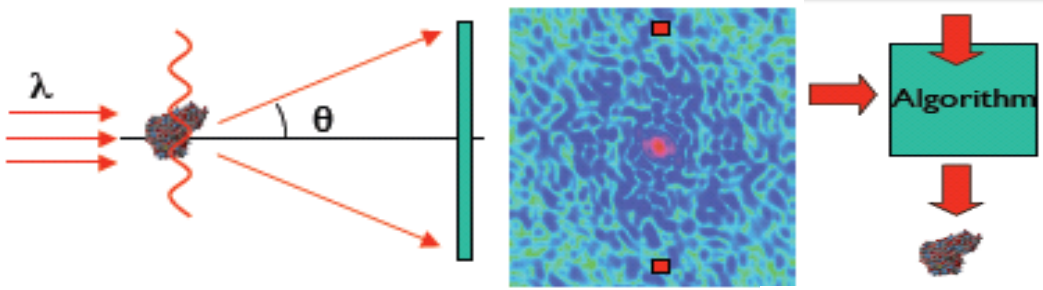
SURFACES & INTERFACES: XPEEM and SPEM		BULK Information STXM/SPEM & TXM
PHOTON-IN/ ELECTRON-OUT		PHOTON-IN/PHOTON-OUT
(probing depth=f(E_{el}) max ~ 20 nm)		(probing depth = f (E_{ph}) > 100 nm)
Spectroscopy (XPS-AES-XANES)		(Spectroscopy – XFS or XANES)
ONLY CONDUCTIVE SAMPLES		
Total e^- yield (sample 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

Maya Kiskinova

Imaging: spatial and temporal limitations

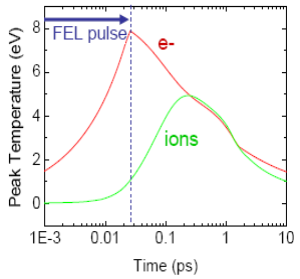
- **Classical XRM (scanning & full field):** acquire information in real space
- BUT: (1) limited in resolution and focal depth by the optical elements; (2) dynamics of non-periodic systems > ns; (3) radiation damage: serious issue.

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:.

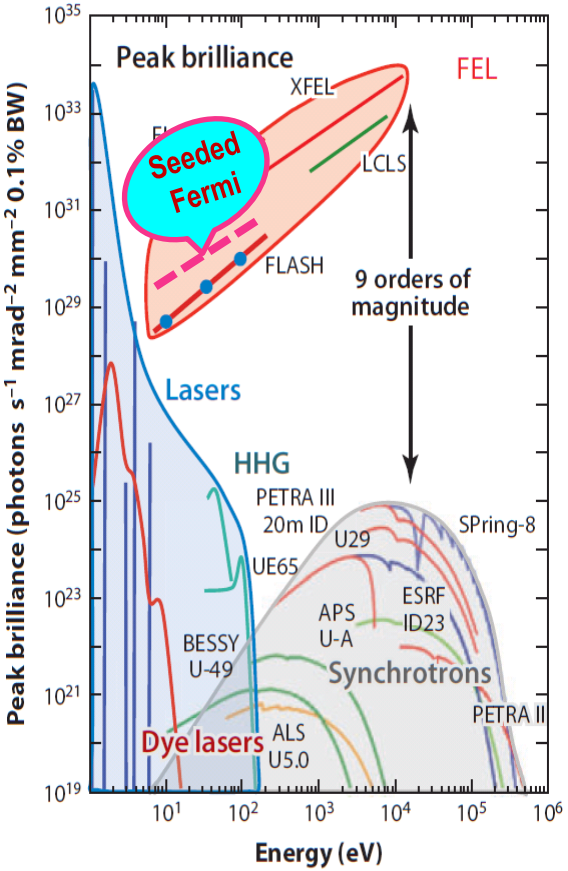


CDI acquire data in reciprocal space:
Resolution: $\delta = \lambda / \sin\theta$

computationally demanding phase retrieval



Ultra-short (fs) and ultra-bright FEL pulses allow imaging with single pulse before the radiation damage manifests itself !



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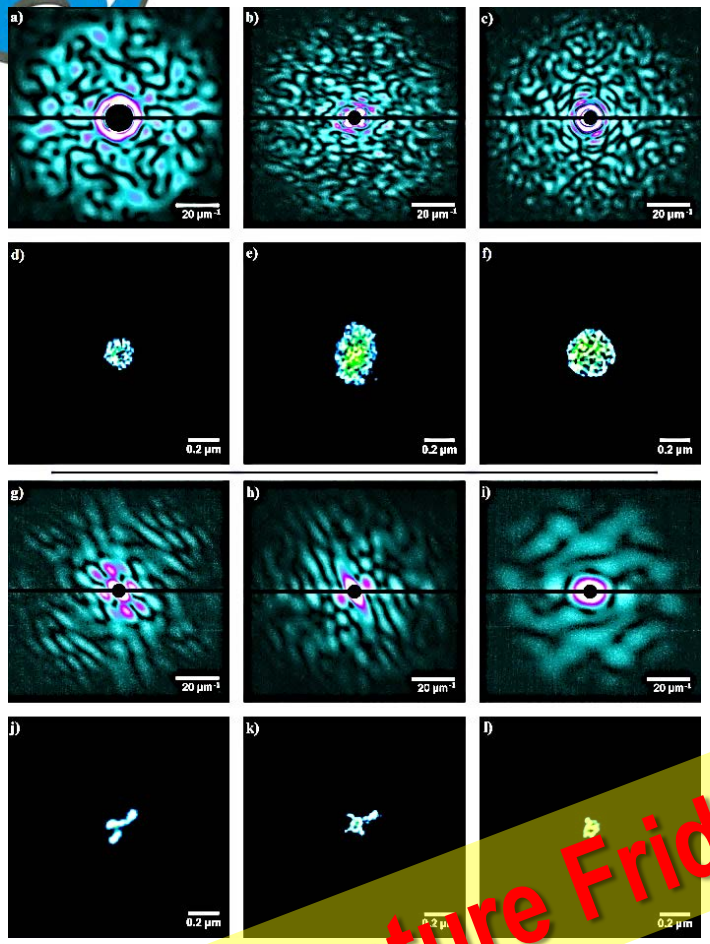
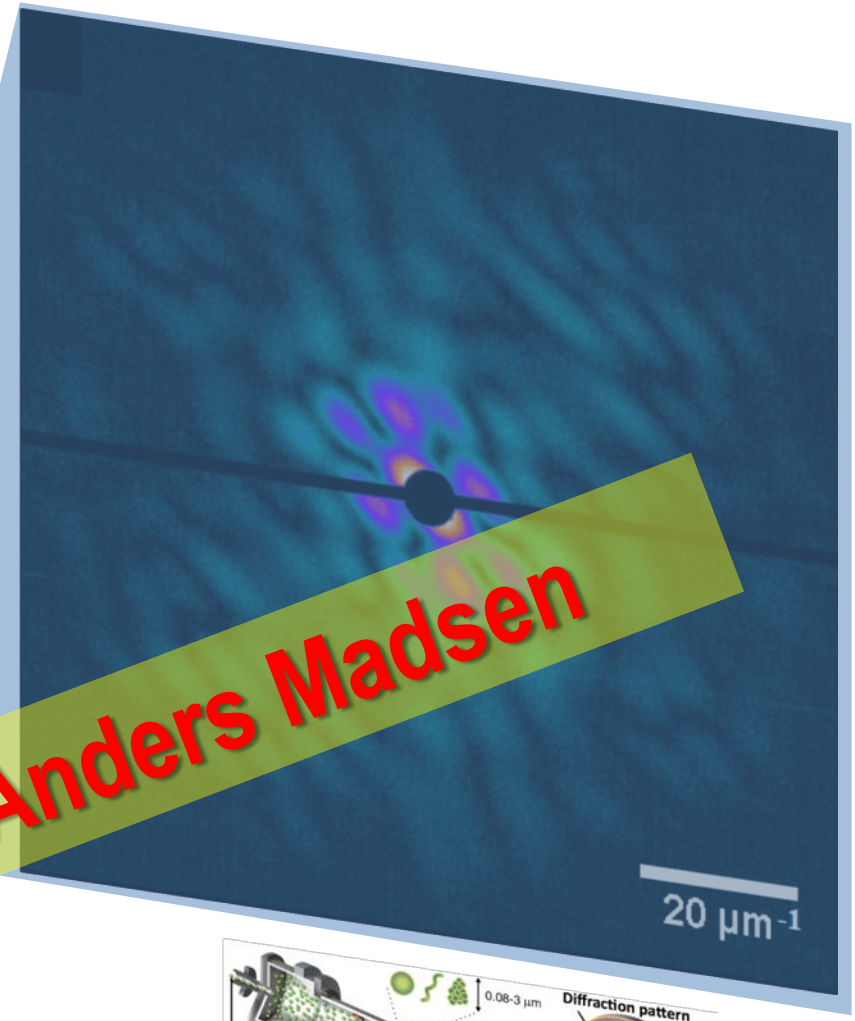
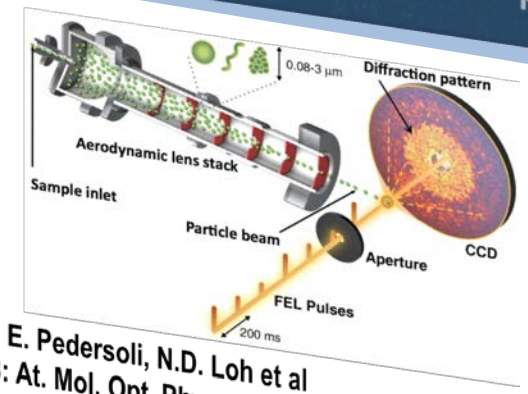




Lecture Friday: Anders Madsen

Appealing to explore the new collective properties resulting from the secondary structures of the assembled NP



E. Pedersoli, N.D. Loh et al
J. Phys. B: At. Mol. Opt. Phys,. 46 (2013) 164033

Duane Loh: XRM2014 - 11:40 Thursday room 203

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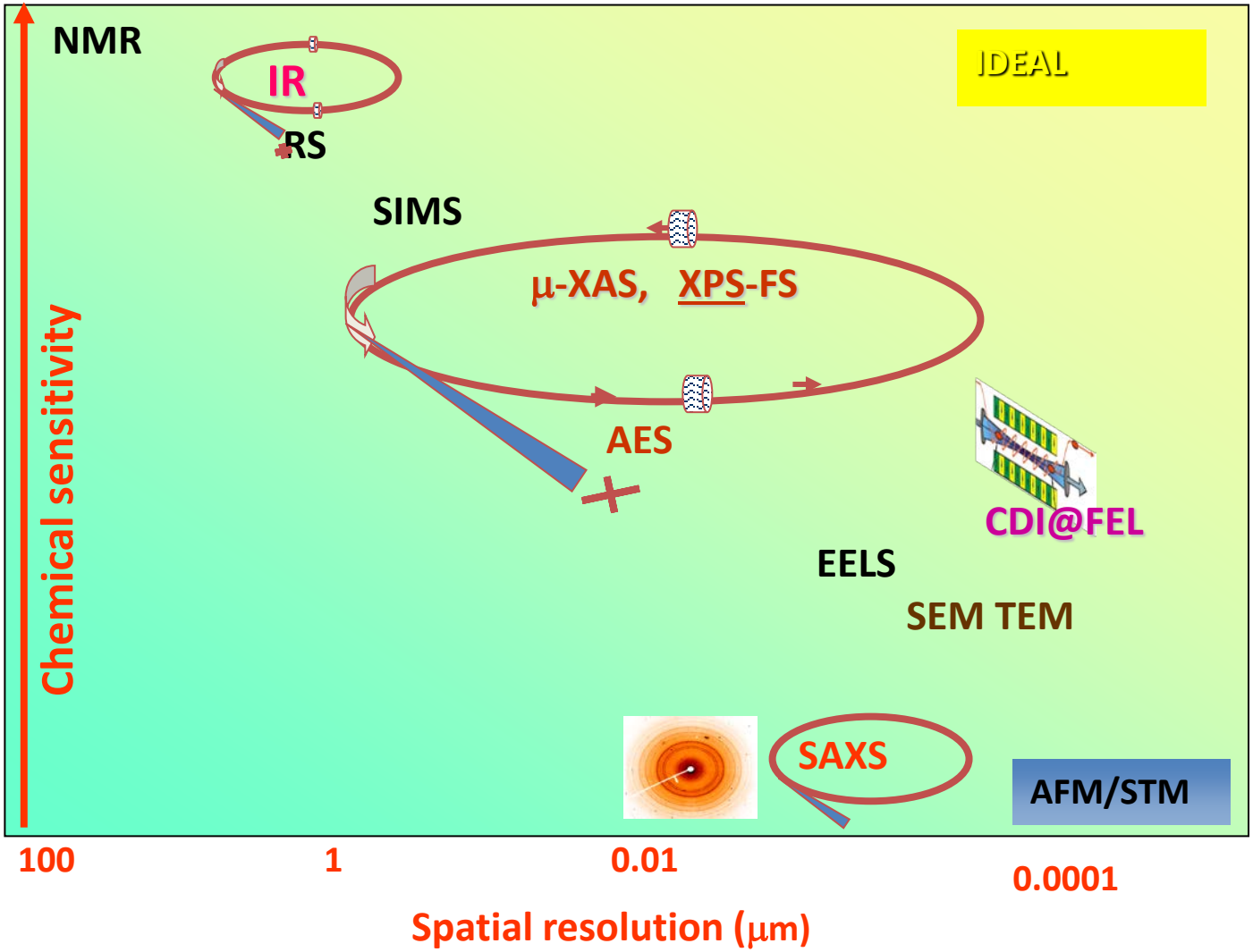
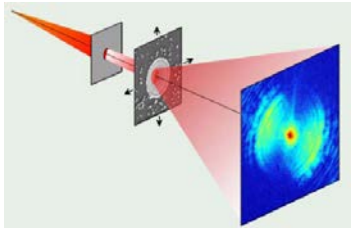
Chemical specificity and resolution using SR

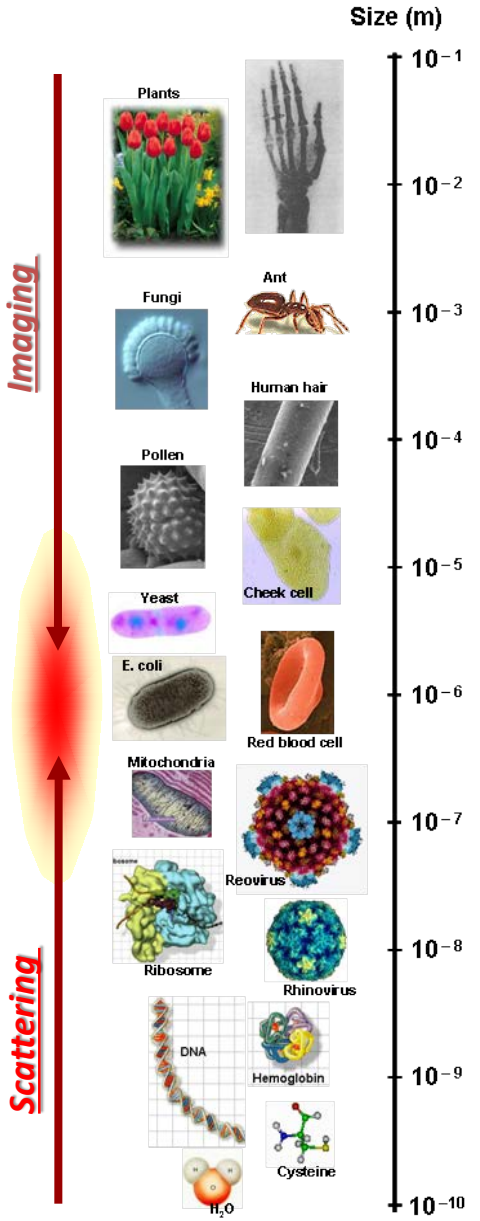


Imaging-resolution-penetration-time

- Scanning microscopes monitoring electrons - limited to surfaces.
- Transmission electron microscopes can resolve even atoms but are limited in penetration (samples thinner than ~ 30 nm).
- X-ray crystallography reveals the globally averaged 3D atomic structures based on the diffraction phenomenon, but requires crystals.
- Classical x-ray microscopy – limited in resolution and focal depth by the optical elements. Temporal resolution - **≥ ns**

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





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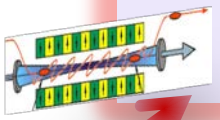
Enjoy the following Lectures

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

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



Hard X-ray Imaging and tomography
(Lecture Tromba)

SXM – XRF and XAS
(Lecture: Gianoncelli)
- Elemental quantification
- Elemental mapping
- Bulk sensitive

Photoelectron imaging and Spectromicroscopy with XPEEM :
(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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