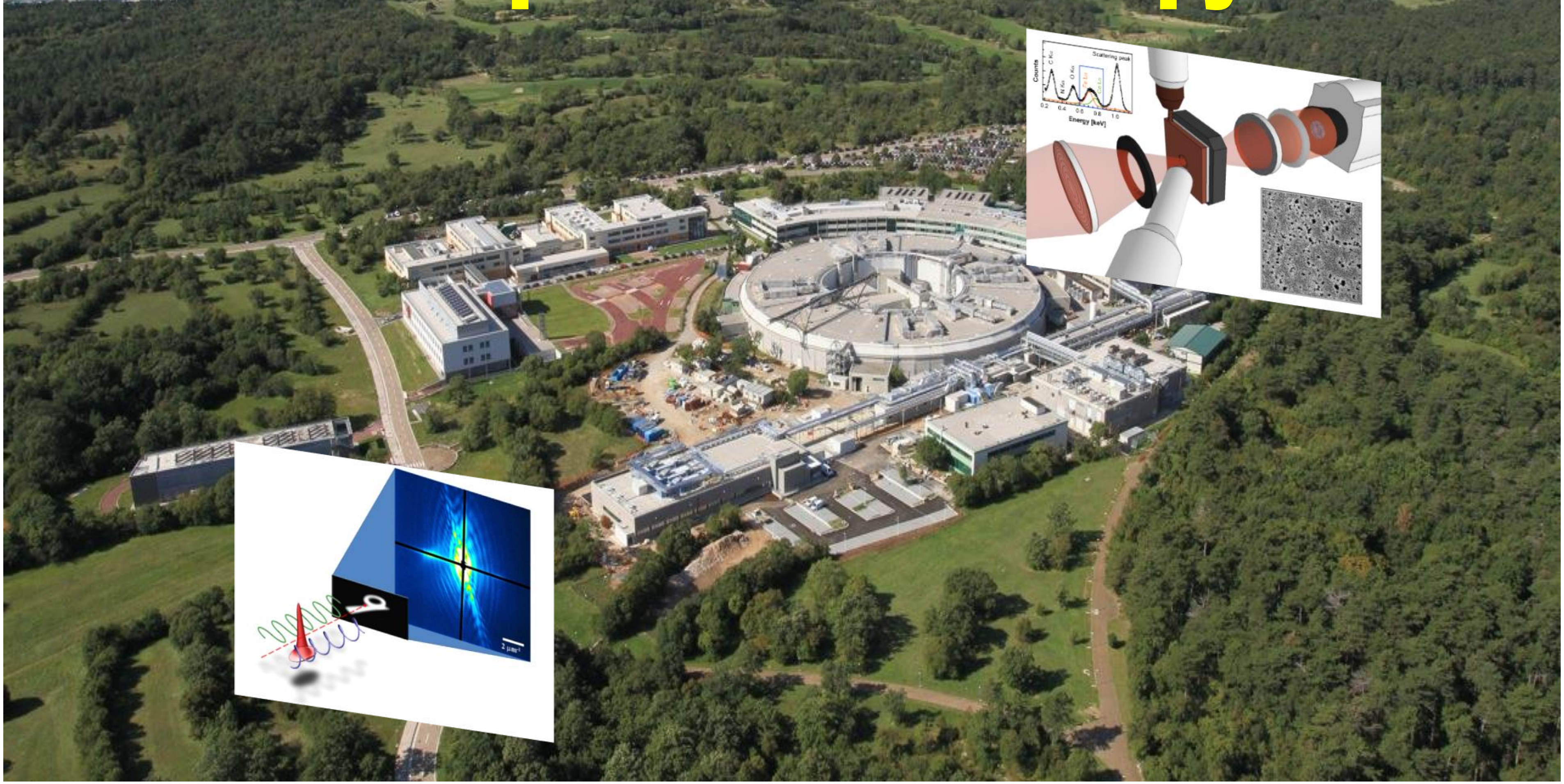
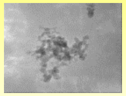
Fundamentals of X-ray microscopy and spectro-microscopy



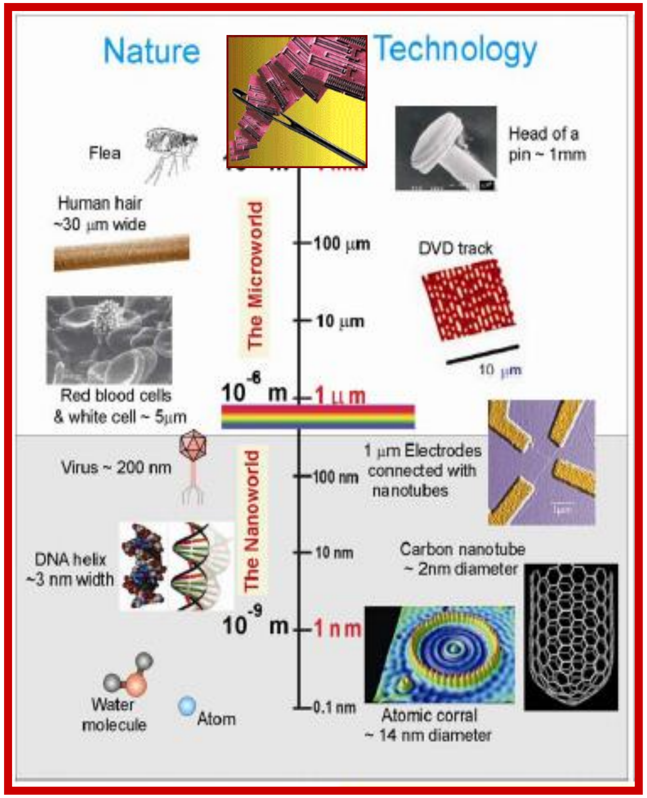
May 8th 2018 ICTP School on Synchrotron and FEL Applications

Maya Kiskinova



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

There's Plenty of Room at the Bottom *Richard P. Feynman* - *1959!!!*



'NANO'
by nature, design or externally- induced changes

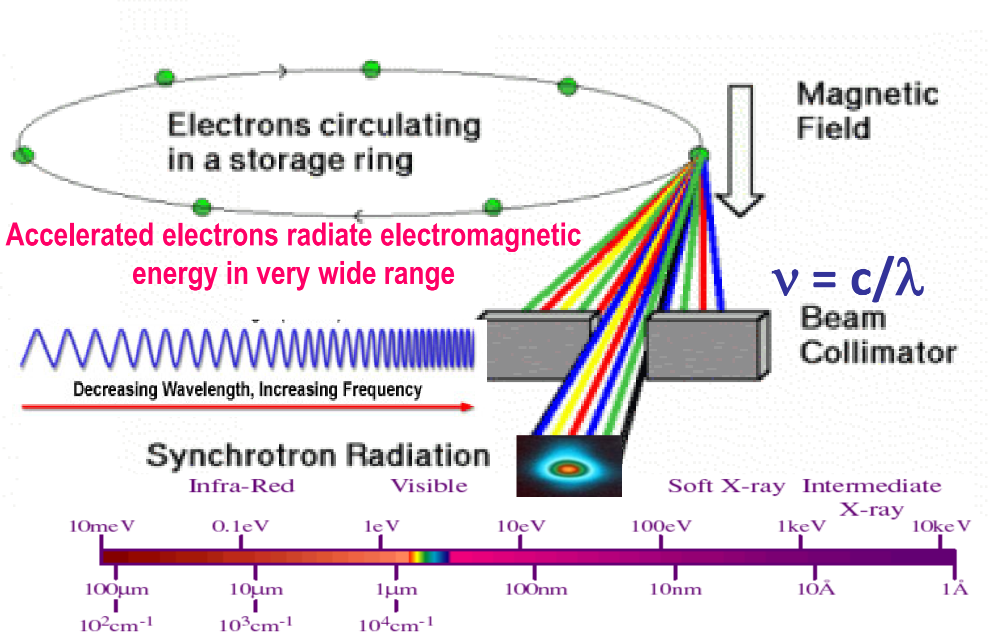
- Materials properties vary at various depth and length scales: atomic, nano or meso dimensions.
- Structure and chemical composition uually is different at the surface and in the bulk.
- New properties expected with decreasing the dimensions stepping into nanoworld.

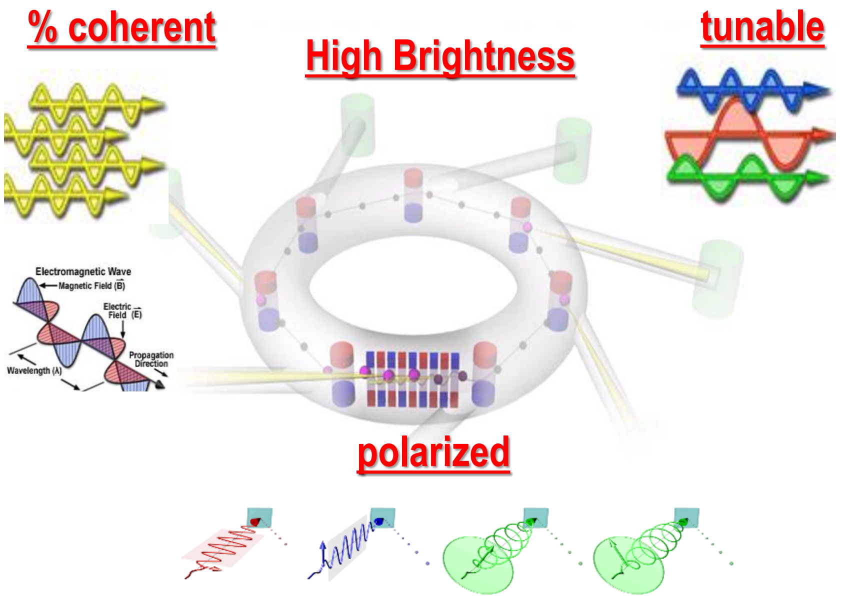
What we NEED:

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.

Why Microscopy needs Synchrotrons

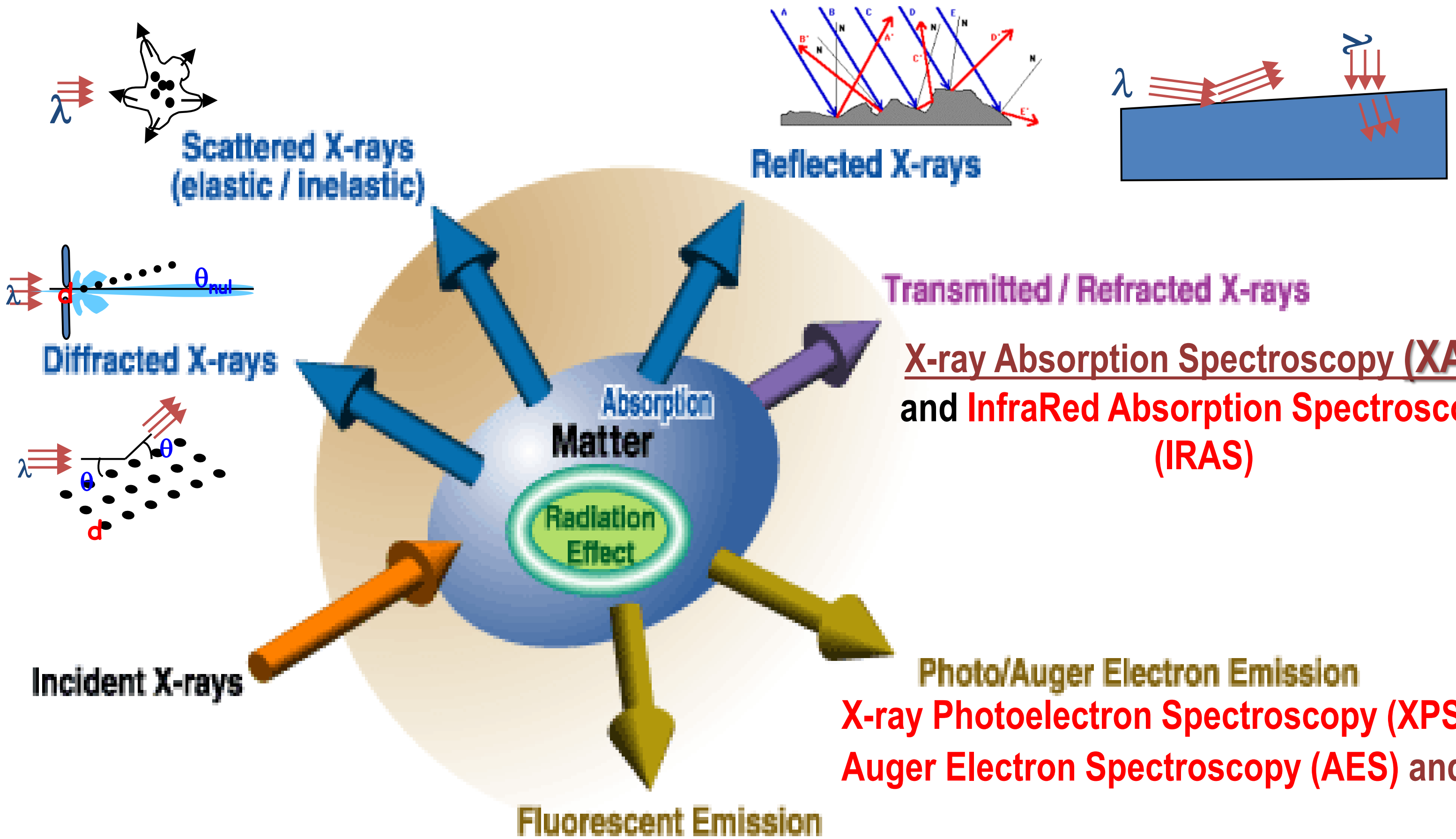




Synchrotron light advantages

- 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 .

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



X-ray Absorption Spectroscopy (XAS) and InfraRed Absorption Spectroscopy (IRAS)

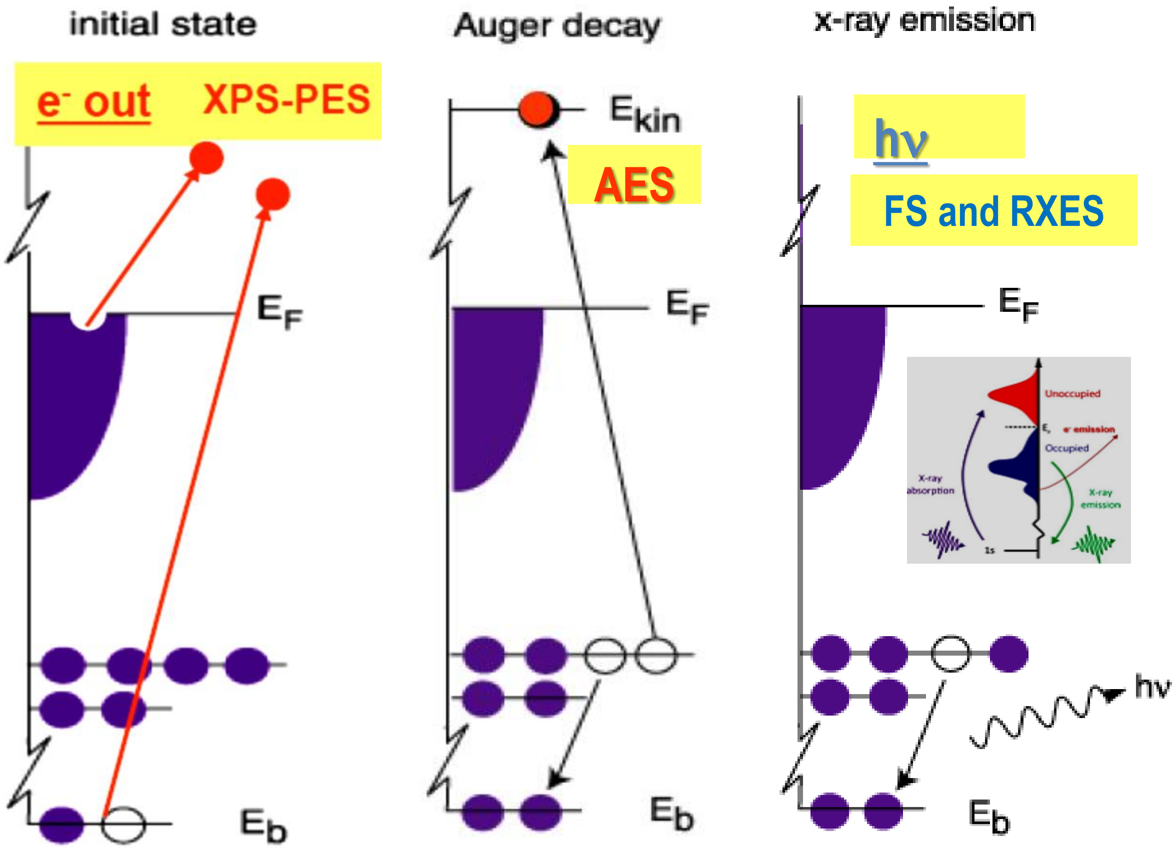
X-ray Photoelectron Spectroscopy (XPS)

Auger Electron Spectroscopy (AES) and XAS

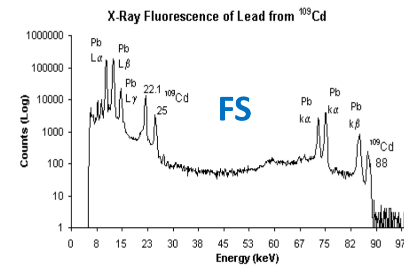
Fluorescence Spectroscopy (FS), RXES and XAS

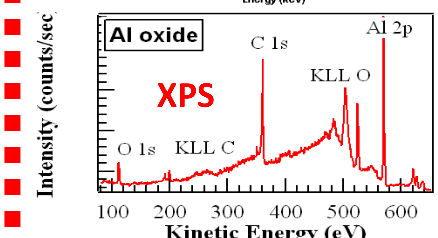
Spectroscopies @ synchrotron light sources: XPS-AES, XES, XAS

Photoelectric effect & de-excitation processes = chemical specific spectroscopies



$E_{h\nu}$ is constant & energy filtering of emitted photons and electrons

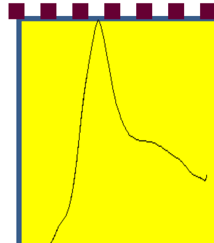




PES=XPS+AES

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

e⁻ and hν detection.



$E_{h\nu}$ scanned

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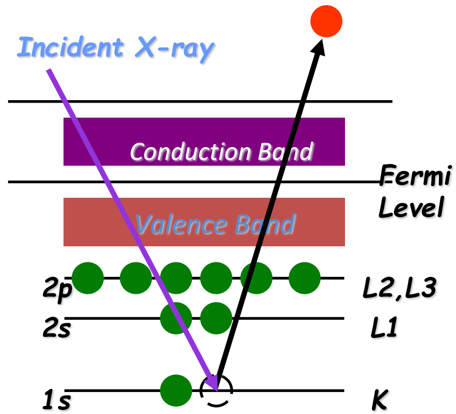
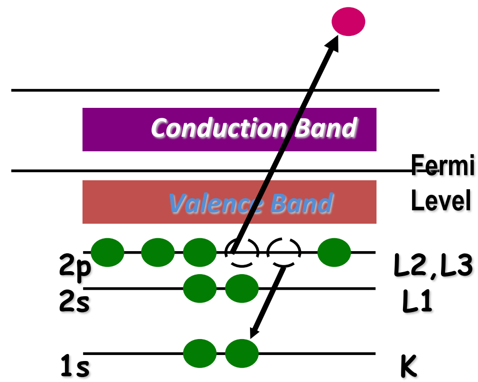
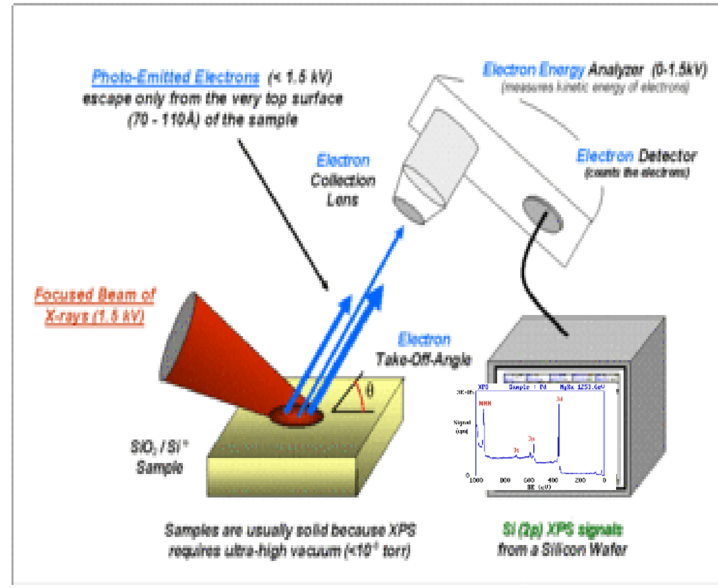
X-ray PhotoElectron Spectroscopy detects the electron emission, known as XPS, PES or ESCA (Electron Spectroscopy for Chemical Analysis).



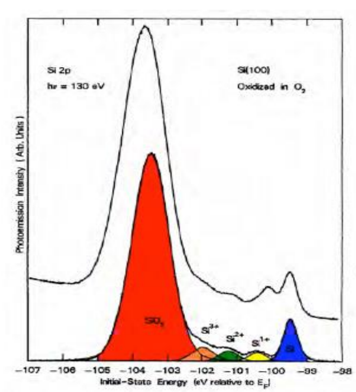
- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy: KE=hv-BE-f

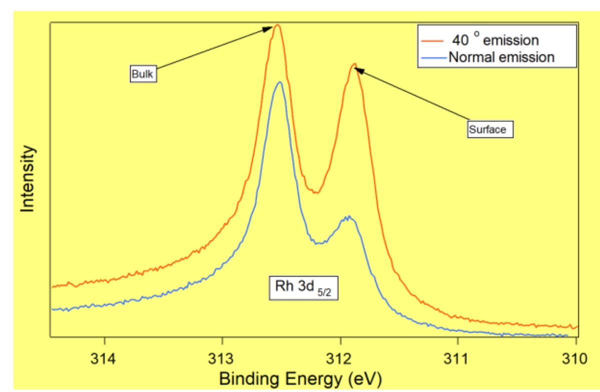


- KLL Auger electron emitted to conserve energy released.
- The KE of the emitted Auger electron is: KE=E(K)-E(L2)-E(L3).



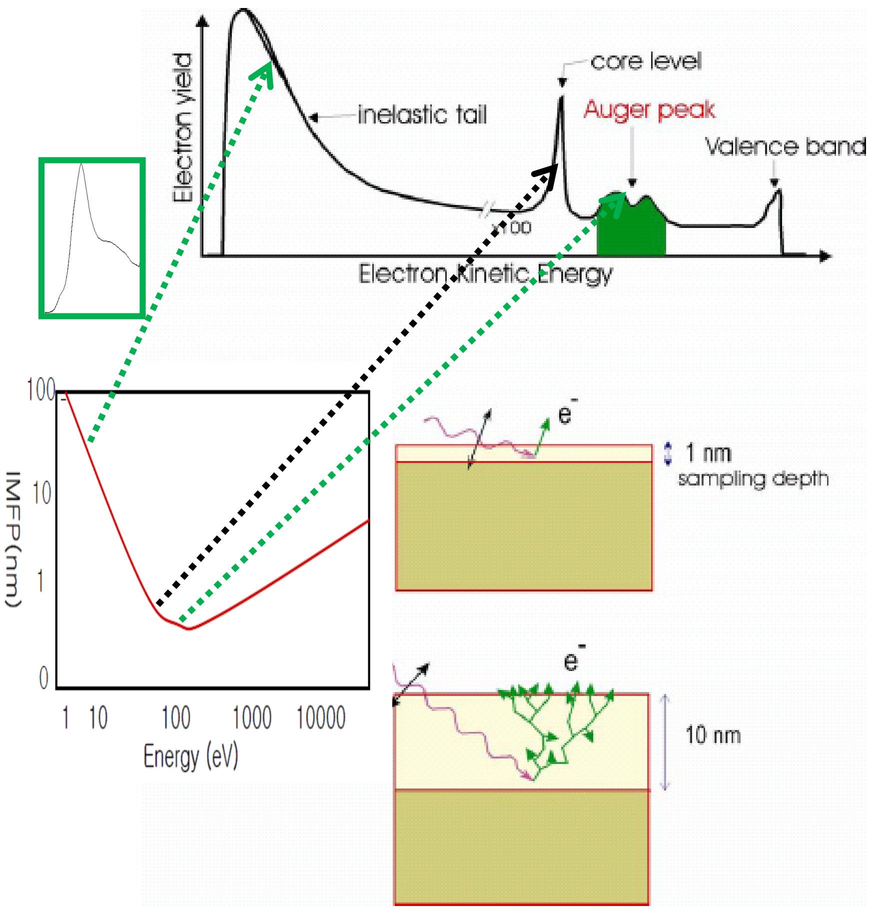
‘Chemical shifts’ due to chemical bond in solid state or different coordination of emitting atom.



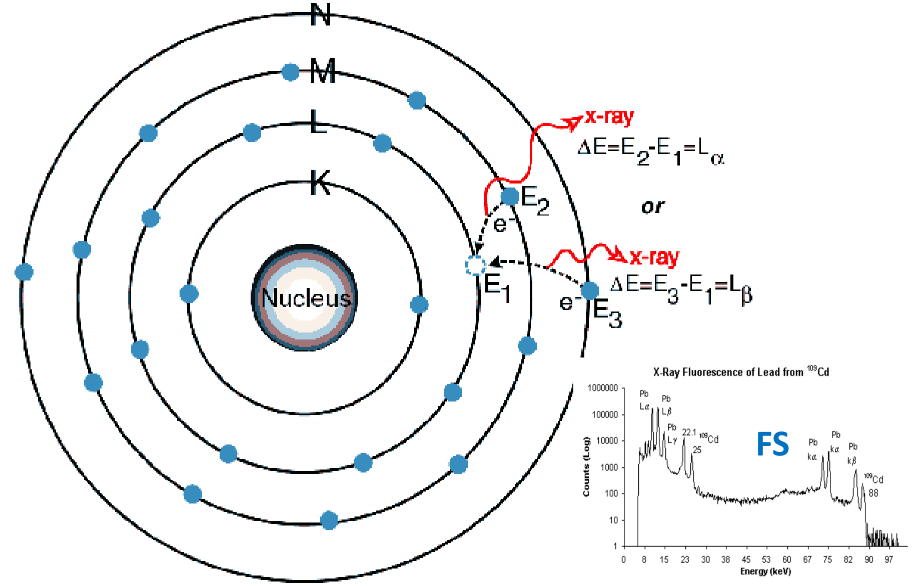


Sampling depths: depend on the detected signal (electrons or photons)

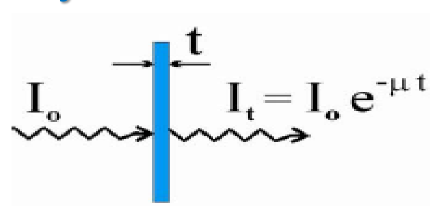
TEY& Auger electron emission (XAS), core&valence PES: Probe depth 1- 10 nm



Fluorescence emission (XAS and FS): Probe depth > 100 nm = f(E$_{ph}$, matrix)



X-ray transmission: 'bulk'

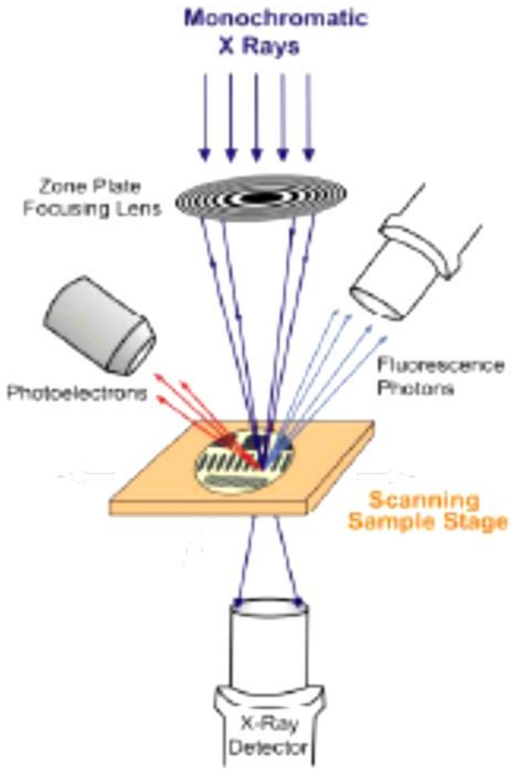


Microscopy Approaches :

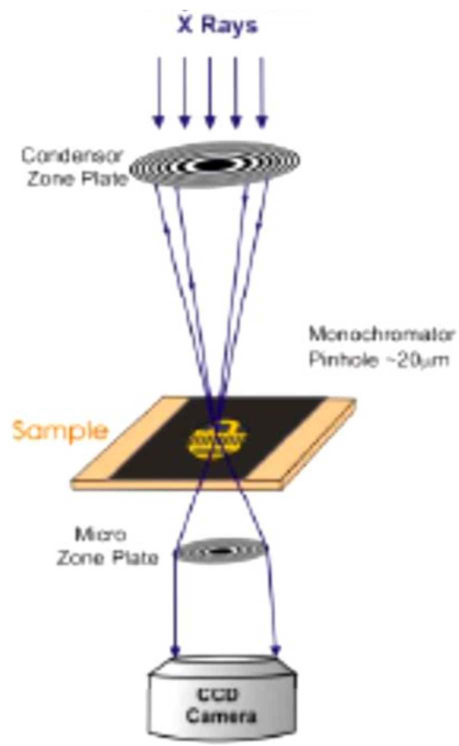
X-ray or electron optics; X-ray or electron detection

XRF, XPS, XAS = elemental and chemical information; X-ray transmission and scattering = morphology; Topology – electron emission

Scanning X-ray Microscopy SXM (SPEM, STXM)

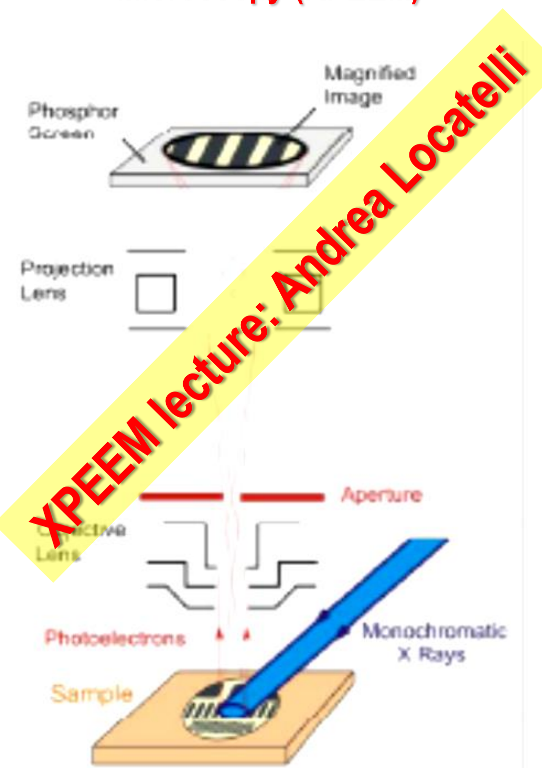


Transmission X-ray Microscopy TXM



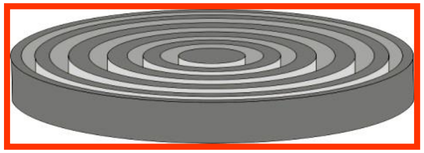
Lateral resolution provided by photon optics

X-ray PhotoElectron Emission Microscopy (XPEEM)



Lateral resolution using electron optics

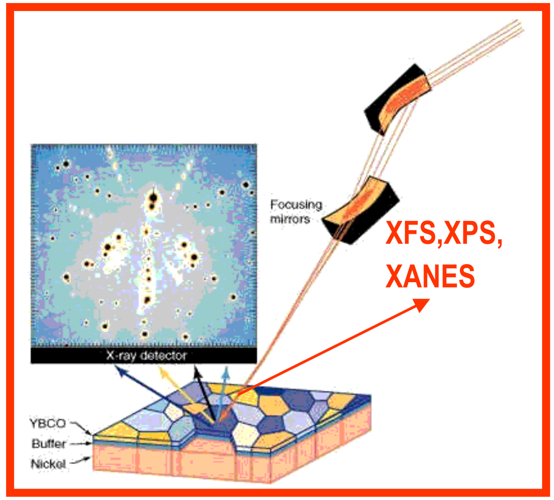
X-ray focusing optics:
zone plates, mirrors, capillaries



Zone Plate optics: from ~ 200 to ~ 10000 eV

Monochromatic:

Resolution achieved 15 nm in transmission

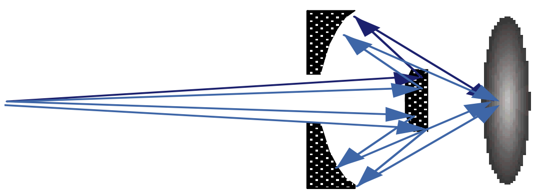


KP-B mirrors each focusing in one direction: soft & hard: ~ 1000 nm

Soft & hard x-rays!

achromatic focal point, easy energy tunability, comfortable working distance

Resolution ≤ 100 nm



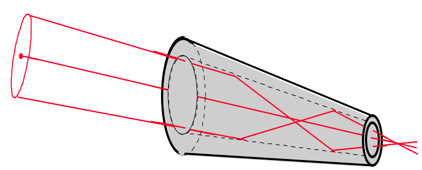
Normal incidence:

spherical mirrors with multilayer interference coating (Schwarzschild Objective)

Monochromatic, good for E < 100eV

Resolution: best ~ 100 nm

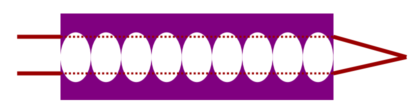
Capillary: multiple reflection concentrator



Hard x-rays ~ 8-18 keV

Resolution: > 3000 nm

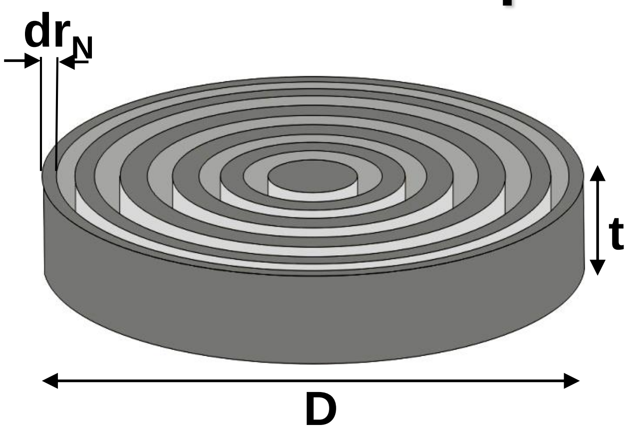
Refractive lenses



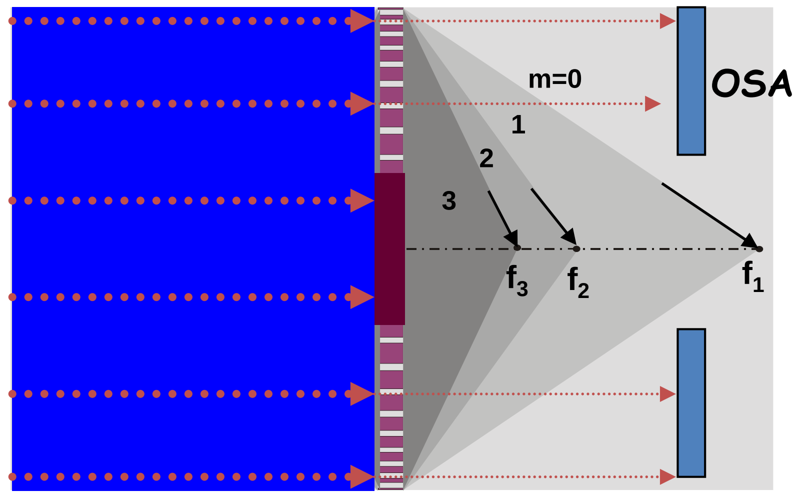
Hard x-rays ~ 4-70 keV

Resolution: > 1000 nm

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) δt=0.61 $\lambda/(\theta)$ =1.22 δr_N

Diameter, D (50-250 μm) determines 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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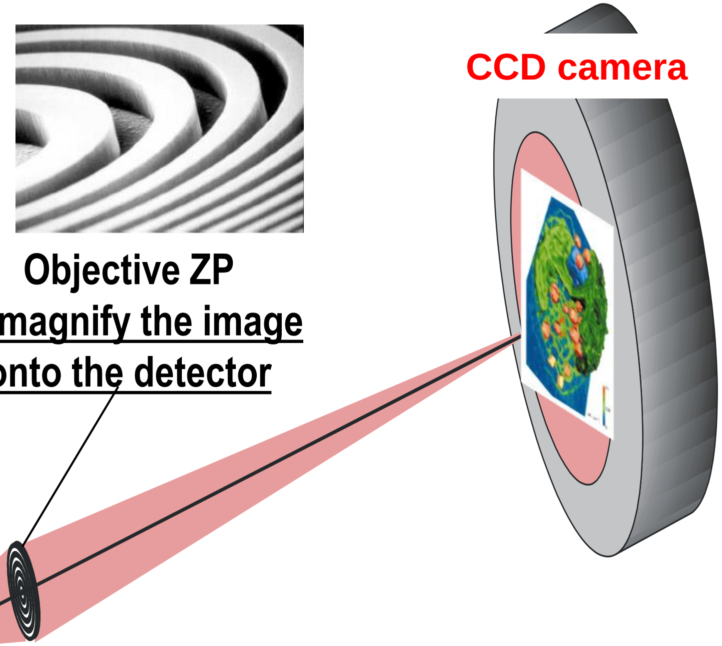
X-ray transmission microscope (TXM-FFIM)

Full-field X-ray imaging or “direct” X-ray image acquisition can be considered as an optical analog to visible light transmission microscope.

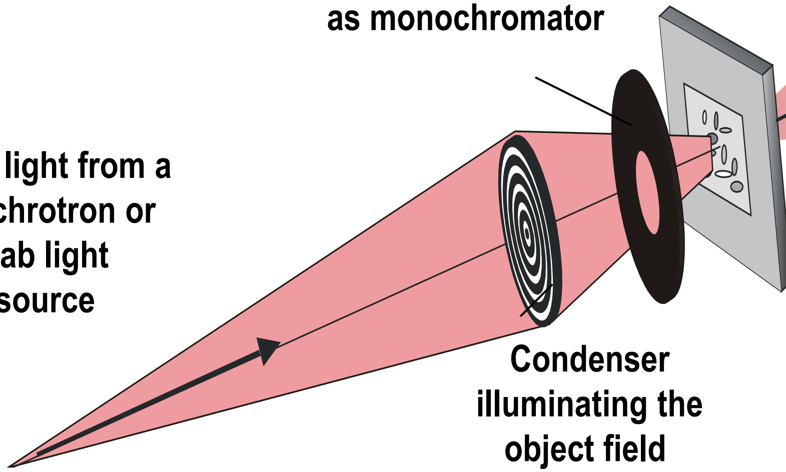
Günther Schmahl, 1st experiment DESY 1976



CCD camera

Objective ZP
to magnify the image onto the detector

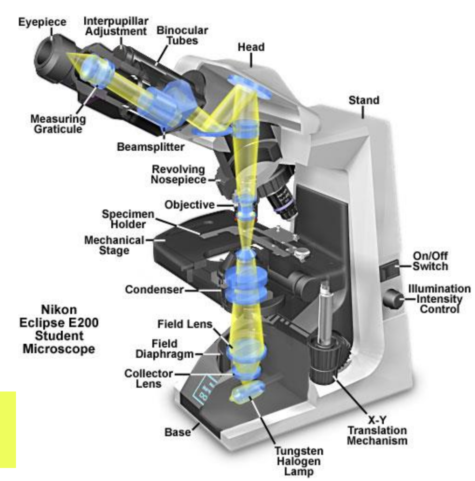
Aperture:
removes (i) unwanted diffraction orders and straylight, and serves (ii) with condenser as monochromator



X-ray light from a Synchrotron or Lab light source

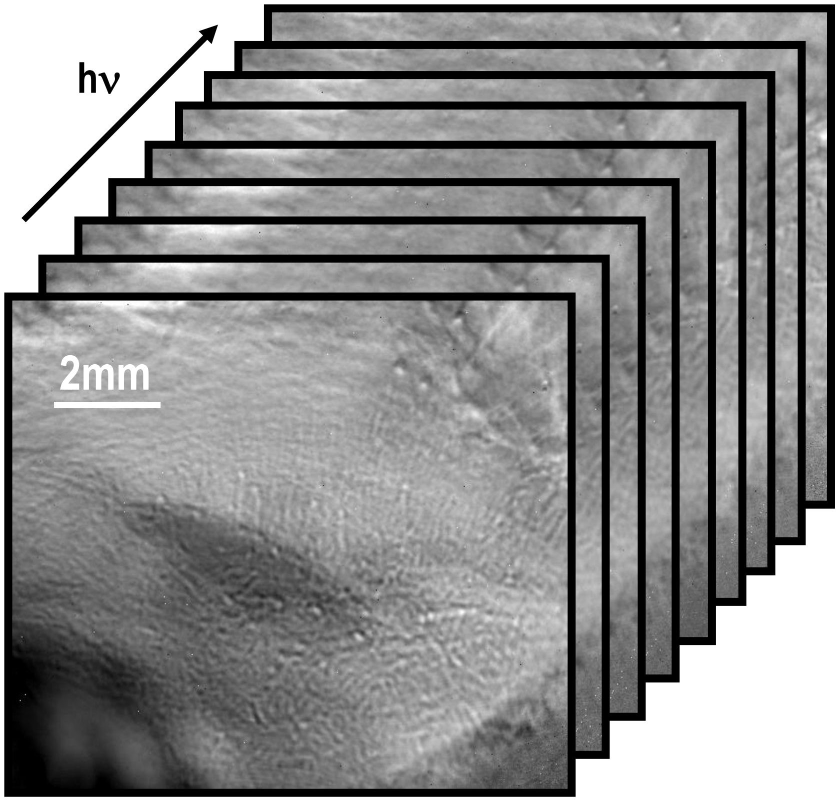
Condenser illuminating the object field

Specimen environment: to be adapted to application



Resolution achieved better than 15 nm.

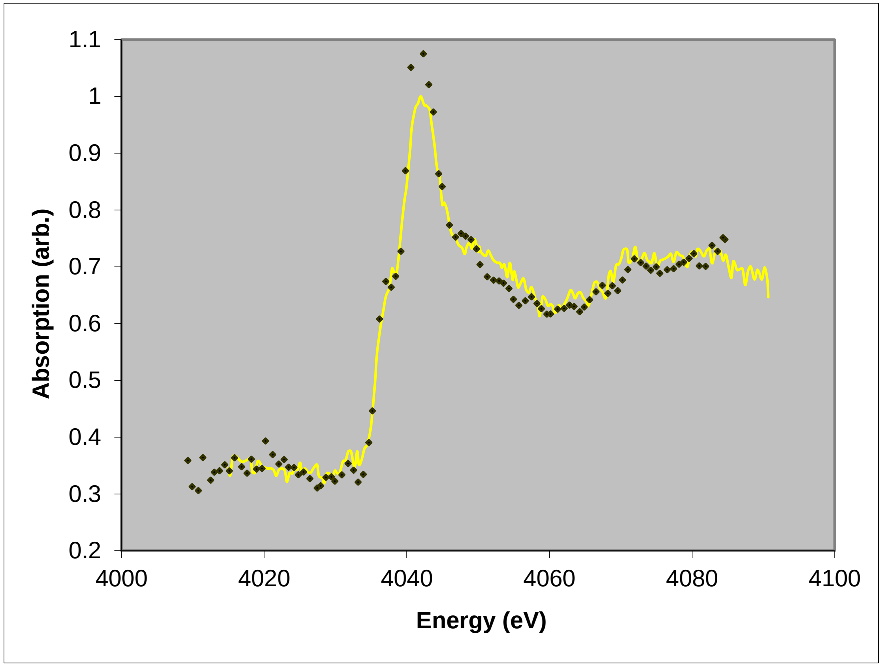
Spectro-microscopy (XANES) with TXM-FFIM:
requires collection of a set of images at different photon energy



Trabecular bone of a mouse femur sample (10μm thick); Image field is 27 x 21 μm^2

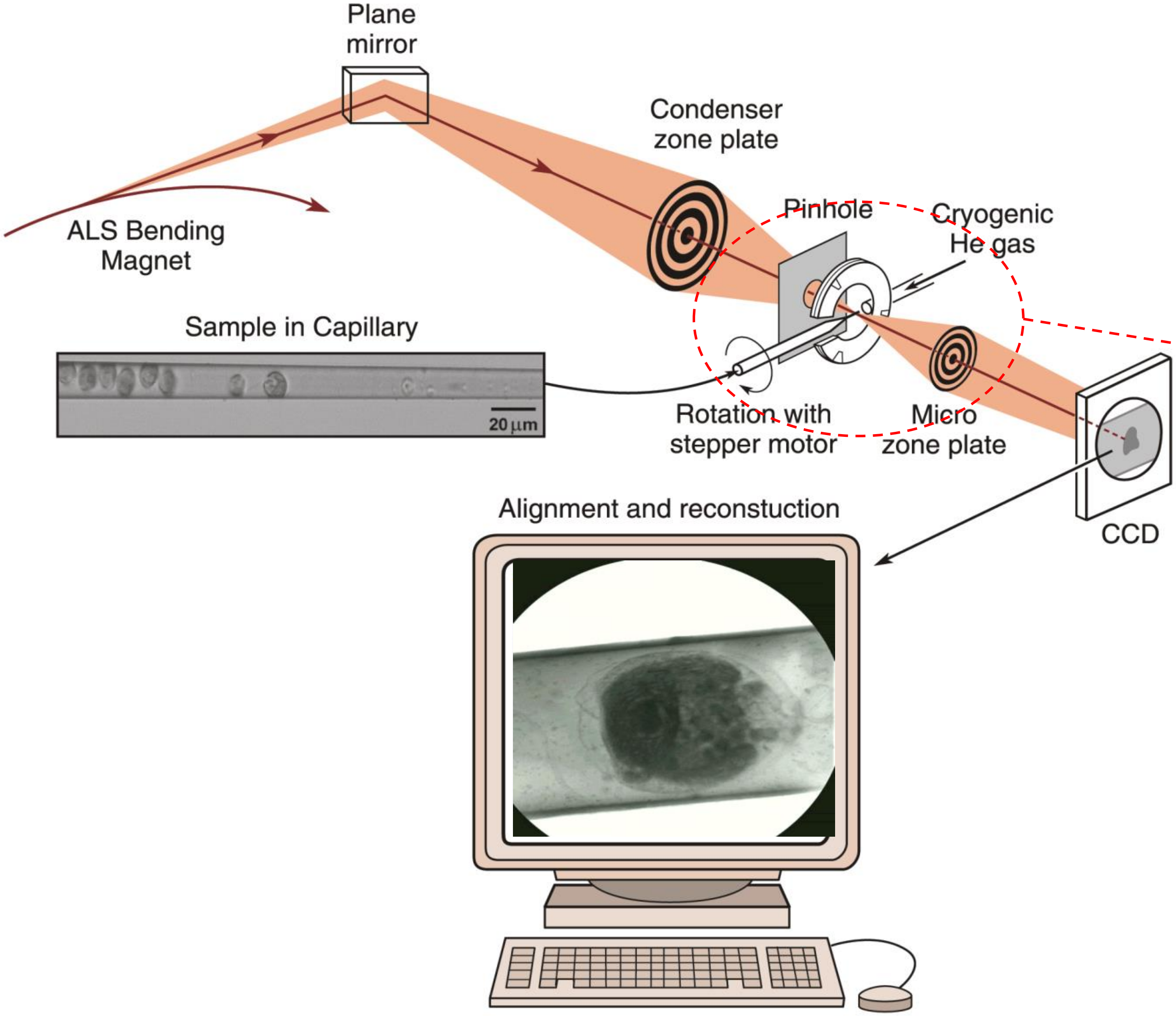
Study dealing with genetic determinism of immobilization induced bone loss with the FFIM at ID21, ESRF, France (Ca XANES)

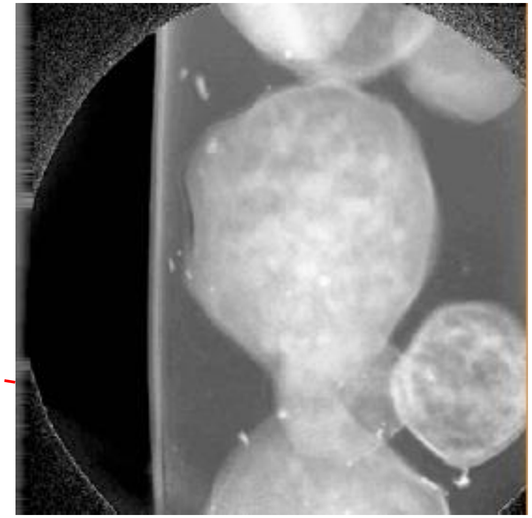
M.Salome et al.

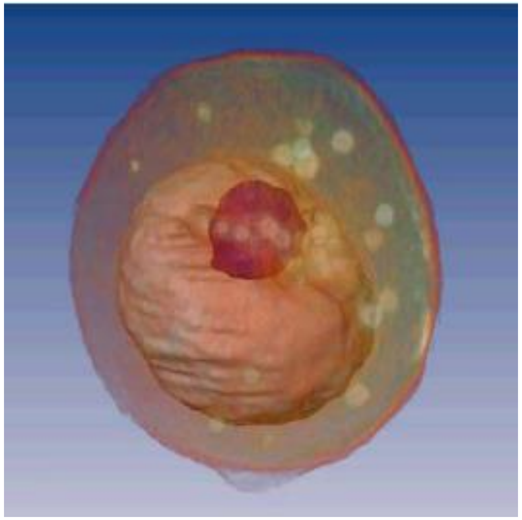


Hydroxy-apatite spectrum recovered from a stack of 200 images

Cryogenic 3D imaging of biological cells



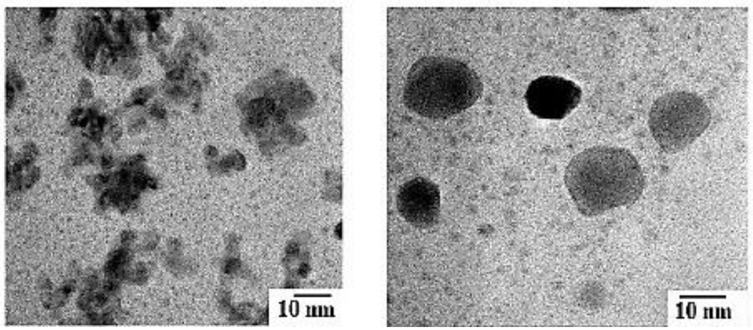


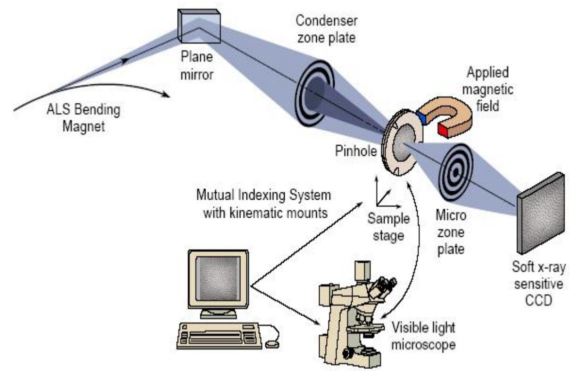


Following dynamic processes during temperature treatment, applying magnetic/electric field or pumping with optical lasers X

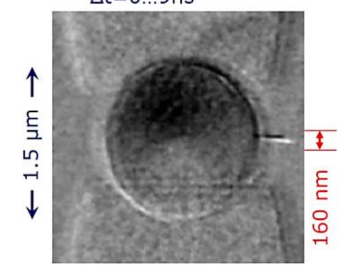
Fe38Rh62 nanoparticles

as-deposited　　after annealing



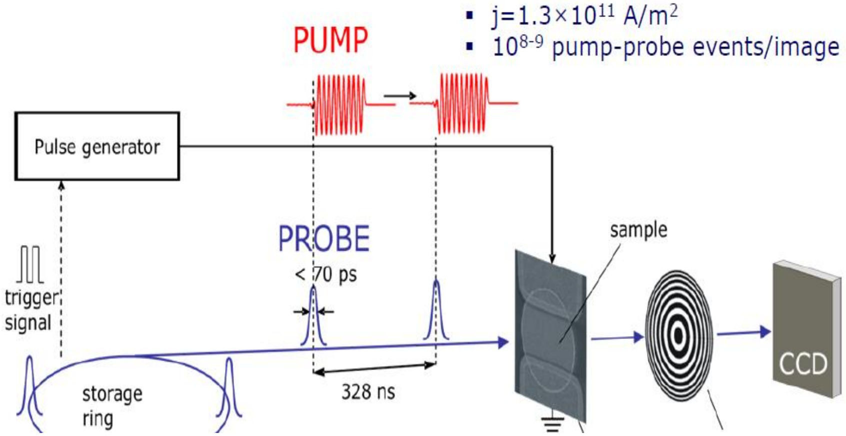


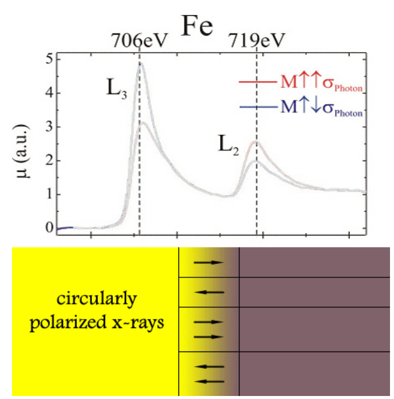
Permalloy ($Fe_{80}Ni_{20}$)
t=40 nm
f=220 MHz
Δt=0…9ns

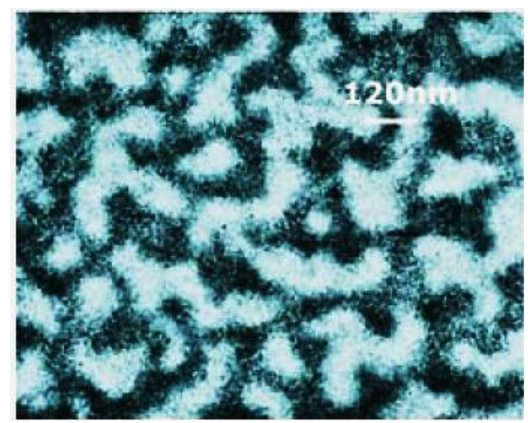


XAS-XMCD X-Ray Magnetic Circular Dichroism

- $j=1.3\times10^{11}$ A/m^2
- $10^{8\text{-}9}$ pump-probe events/image







X-ray Scanning Microscopy: uses focusing x-ray optics (preferred zone plates)
Imaging in Transmission & Emission + Nano-micro spot spectroscopy

Janos Kirz, 1st operating STXM 1983
SPEM 1990, STXM+XRF 1995

Can use all detection modes!
Resolution achieved better than 25 nm in transmission.

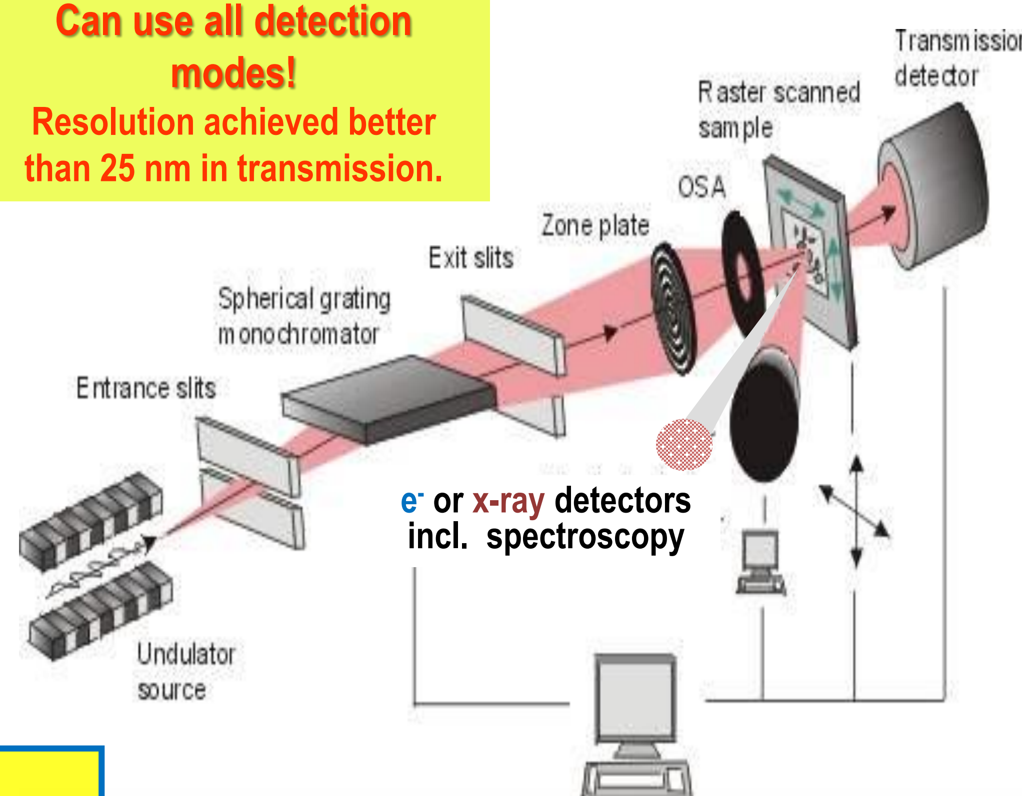


Image contrast
- Density, thickness, morphology (incl. phase contrast and ptychography);
- Element presence and concentration;
- Chemical state, band-bending, charging;
- Magnetic spin or bond orientation.

Microspectroscopy:
μ-XPS, μ-XANES or μ-XES (XRF) from selected spots – detailed chemical and electronic structure of coexisting micro-phases.

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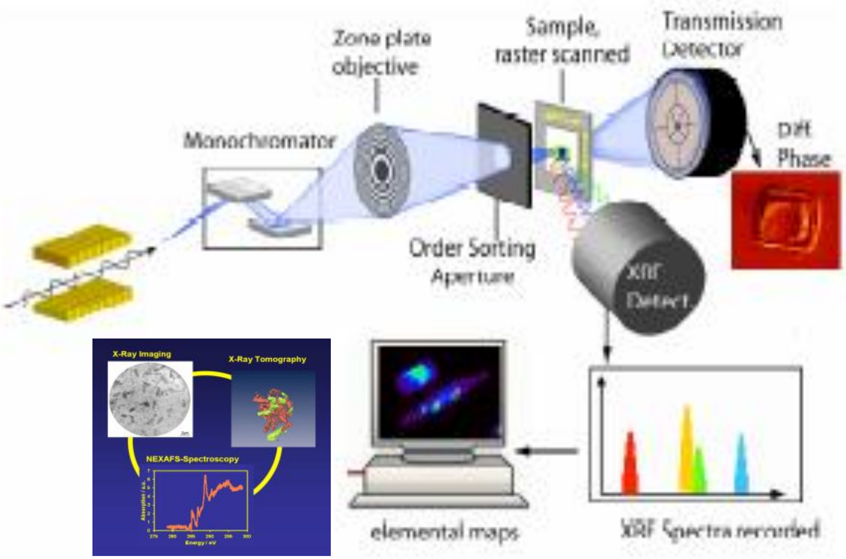
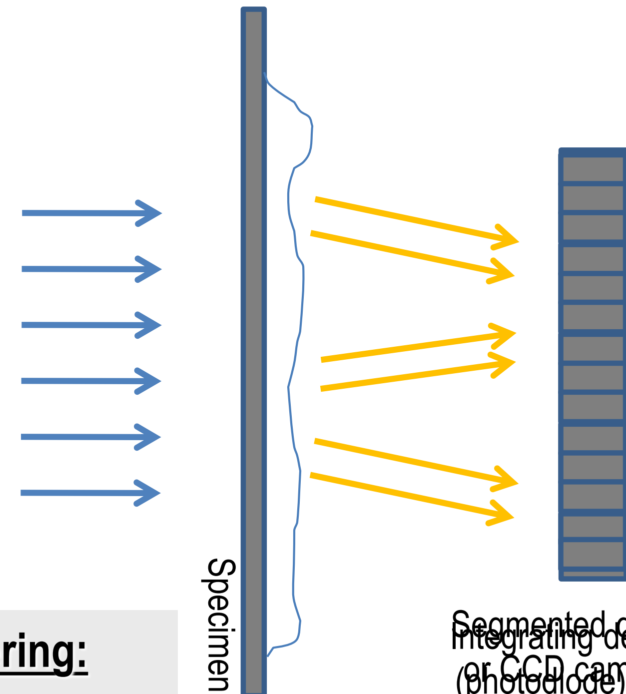
SXM: contrast based on photon detection

Bulk sensitive

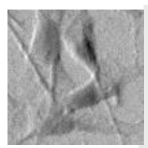
COMPLEMENTARY: transmission & XRF + XANES





X-ray Absorption

- **Density**
- Chemical-magnetic contrast: XAS



X-ray Scattering: morphology

- Phase contrast – phase change encoded by refracrive index, δ.
- Ptychography

The number of photons absorbed within thickness x is given as number *N* of photons penetrating to depth *x*, times the number *n* of absorbers per unit volume and the absorption cross section σ: $dN/dx = -Nn\sigma$ or $N = N_0 \exp(-n\sigma x)$.

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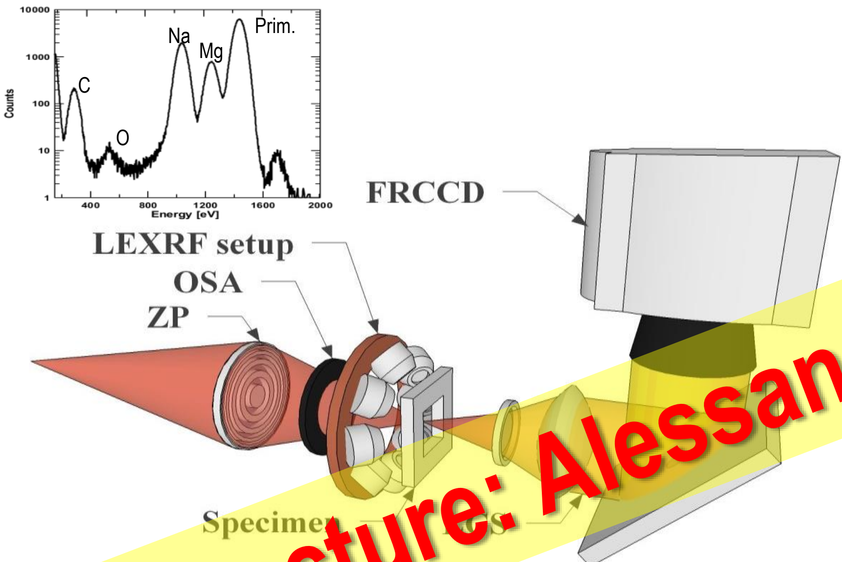
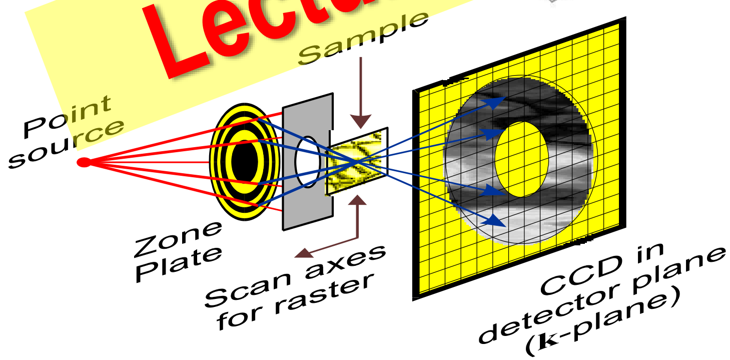
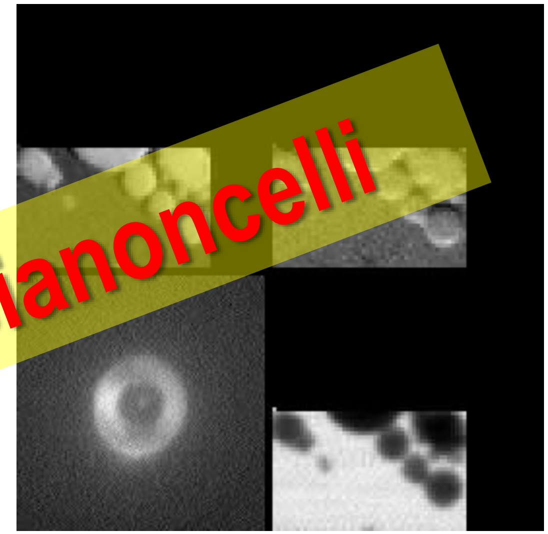
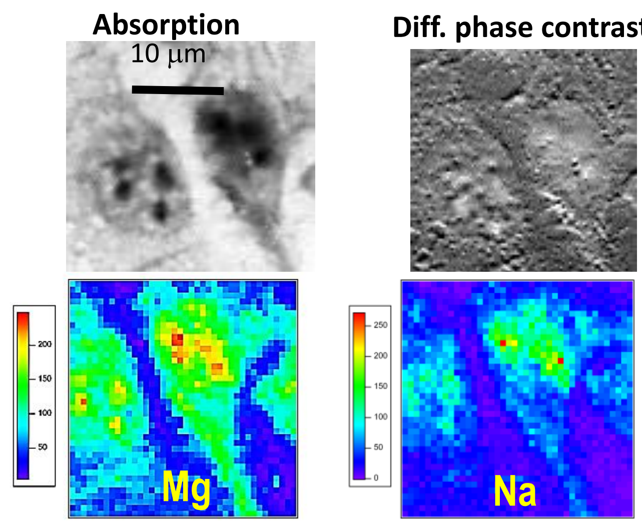
Simultaneous acquisition of absorption and phase-sensitive X-ray transmitted signals & XRF

Lecture: Alessandra Gianoncelli









Epatocytes from human liver

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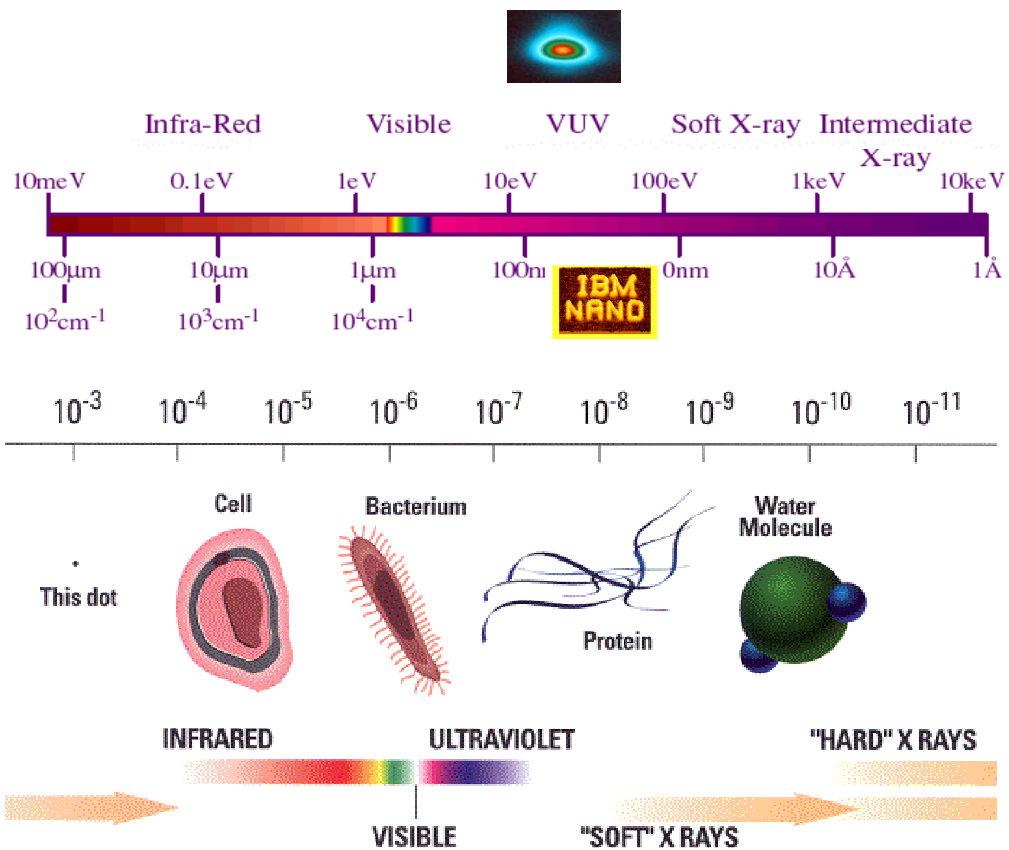
Simultaneous soft X-ray transmission and emission microscopy

A. Gianoncelli [a,*], B. Kaulich [a], R. Alberti [b,c], T. Klatka [b,c], A. Longoni [b,c], A. de Marco [d], A. Marcello [d], M. Kiskinova [a]

Advantages of microscopy using in-out X-rays

Optical resolution scales with the light wavelength



- Orders of magnitude higher penetration power of X-rays compared to charged particles.
- Elemental, chemical and magnetic sensitivity using multiple spectroscopies
- Multiple Imaging contrasts: transmission, emission, scattering.
- Imaging in solid or liquid environment is easier

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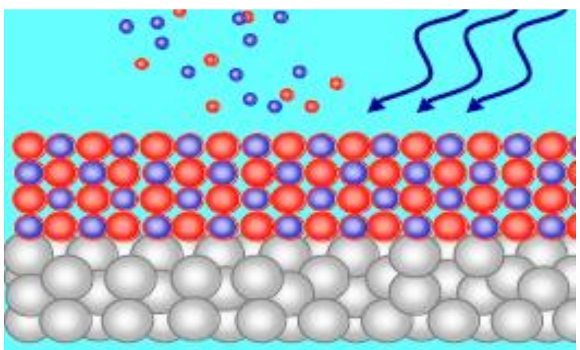
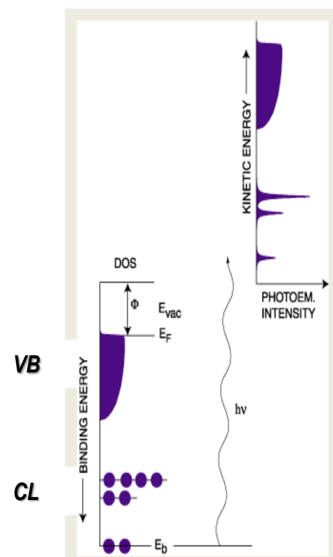
Information from emitted electrons

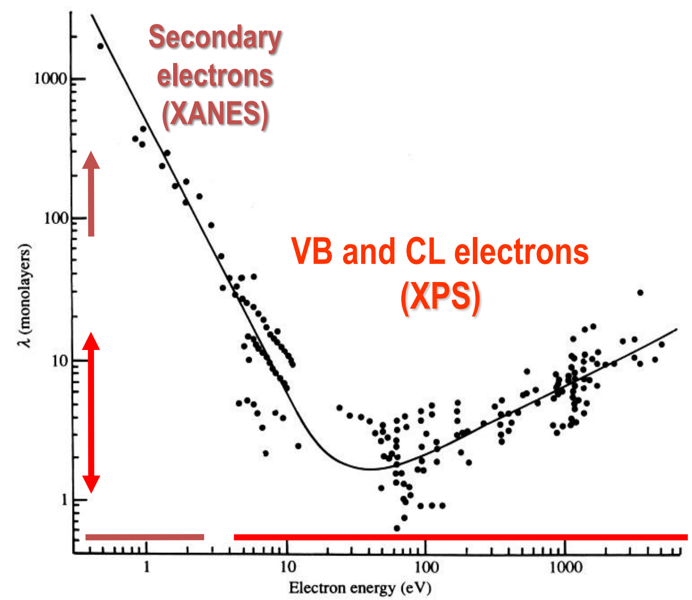
- Qualitative and quantitative elemental information: Core Level spectra.
- Chemical composition and chemical bonding: Core Level shifts.
- Valence band: LOCAL electronic structure (micro-ARPES).
- Sensitivity to local structure (micro-XPD).
- XMCD-XMLD with secondary electrons (XAS).
- Information depth < 10 nm (surface sensitive).



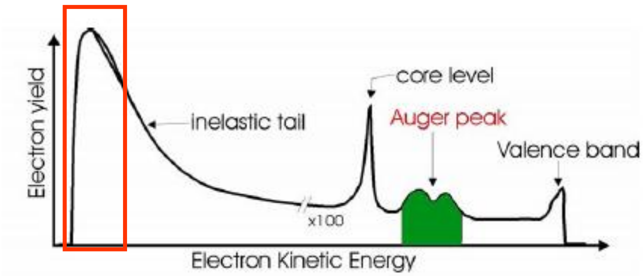
Information depth = d.sinq
d = Electron Escape depth ~ 3-15 atomic layers for PES; XAS upto 100 atomic layers
q = Emission angle relative to surface



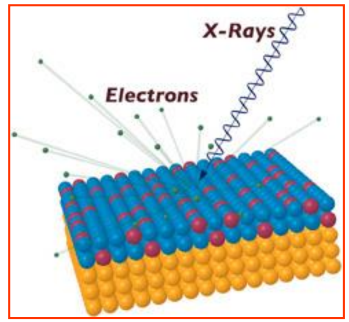
Electron Mean Free Path

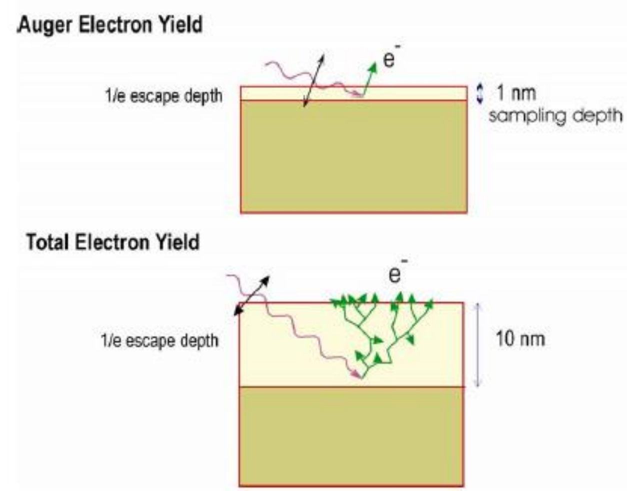


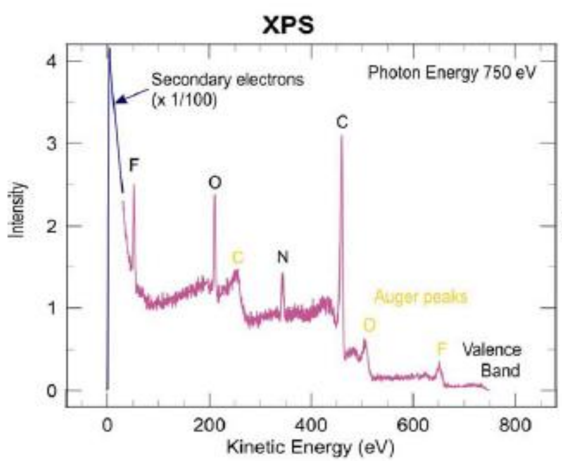
XAS and XPS using electron detection



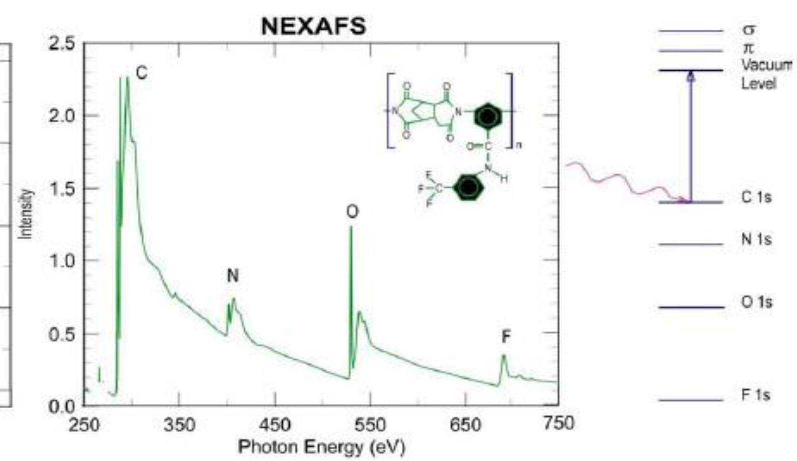
NEXAFS electron KE < 50 eV: the core electron emission is negligibly weak compared to the inellastic secondary electron signal



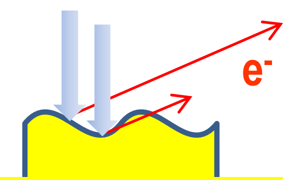




Constant Phonon Energy: 750 eV

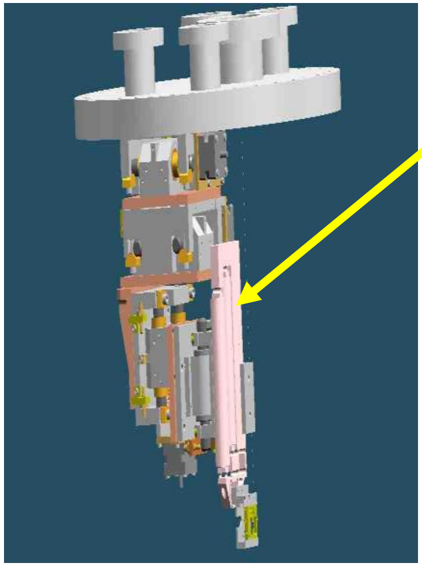


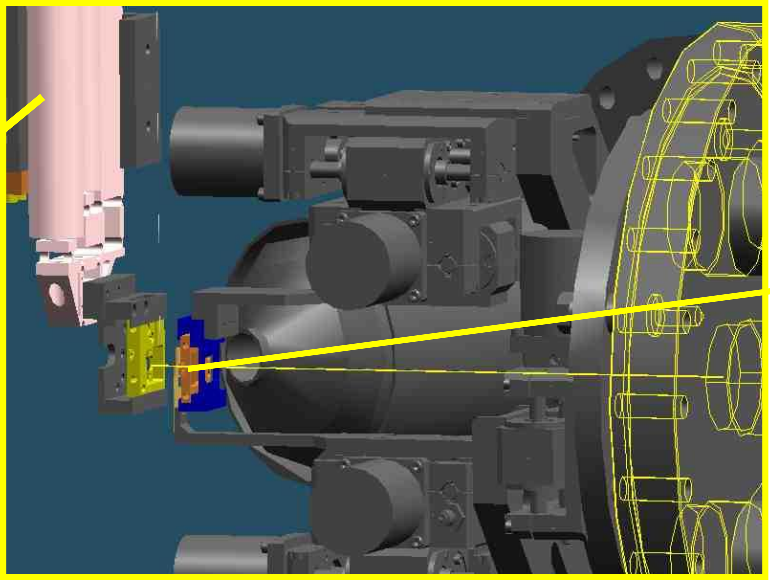
Photon energy scan from 250 to 750 eV

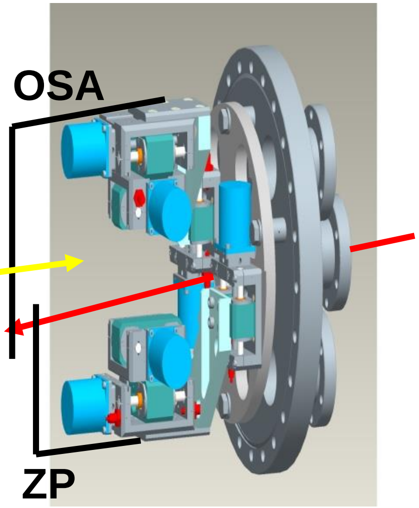


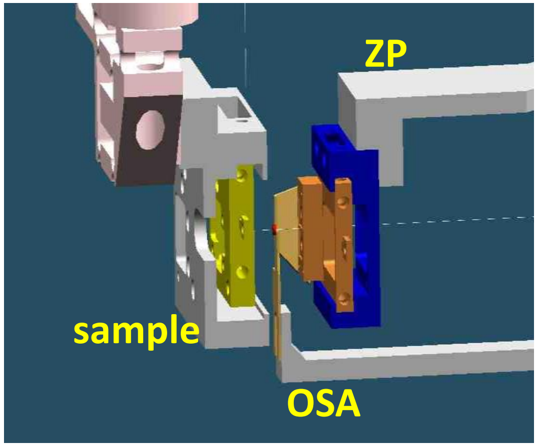
Electron emission shadowing and enhancement: **topography**

Layout of SPEM: ZP optics, sample and positioning systems









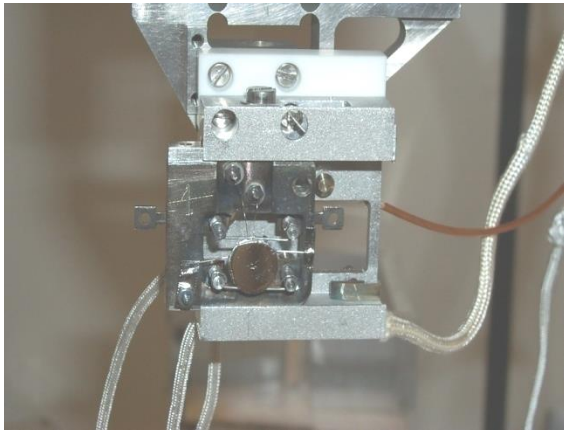
Spatial resolution in emission limited by the sample-to-optics distance !

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

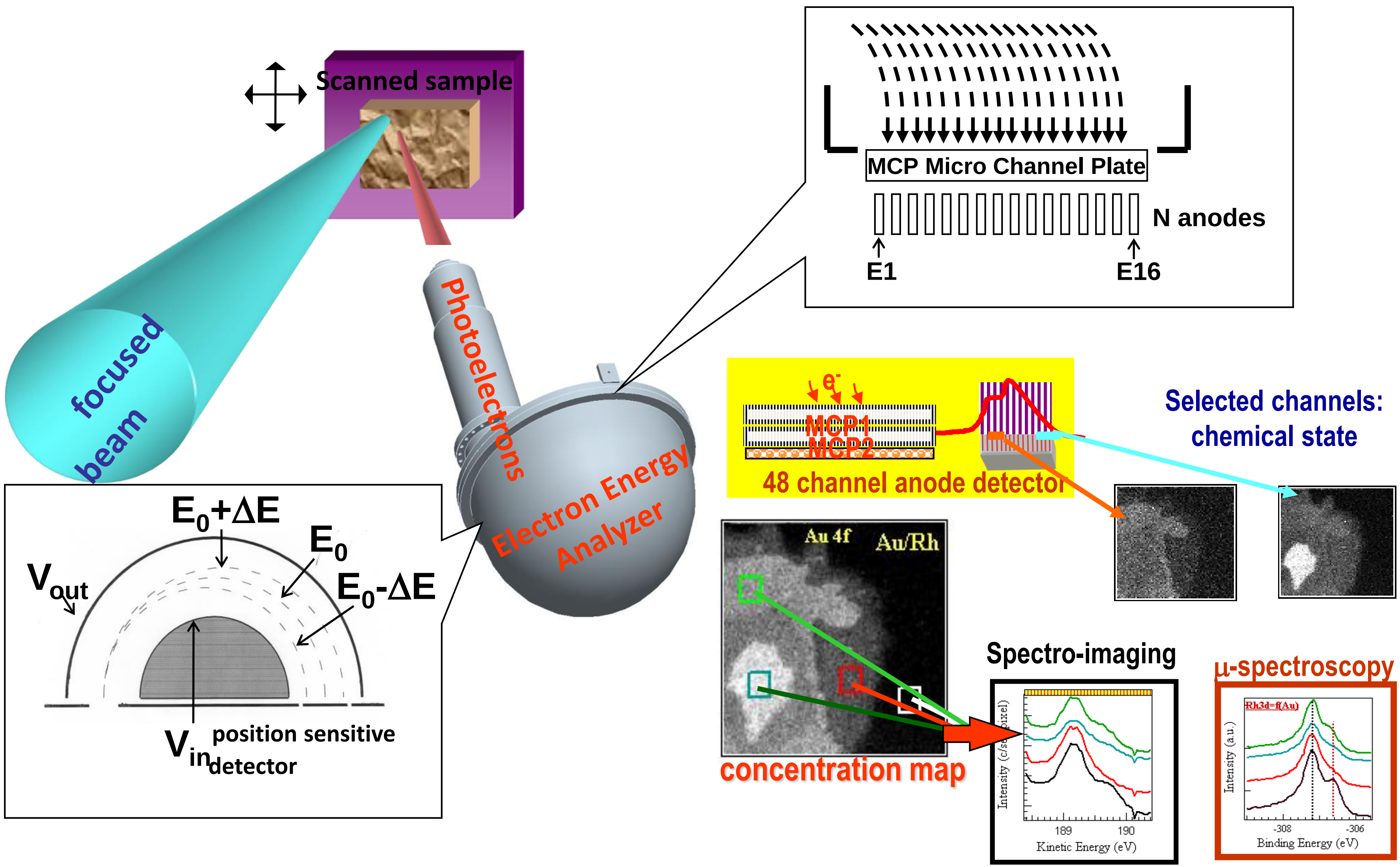
Ranging around 10 mm

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

Typical: 5-15 μm



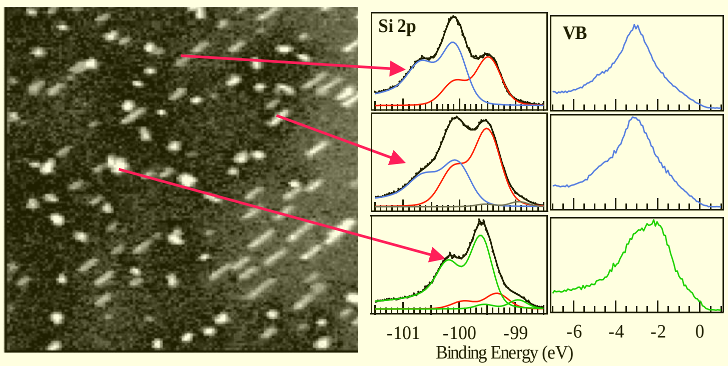
SPEMs energy-filtering electron analysers MCD developed @ ELETTRA

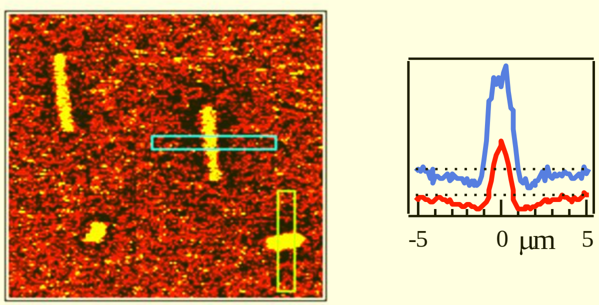


Local chemistry at the metal/ semiconductor interfaces and 'inhomogeneous' oxidation of metals

L. Gregoratti et al, PRB 57 (98) L2134, PRB 59 (99)

Ni/Si interface: mass transport and coexisting 19, NiSi and $NiSi_2$ phases

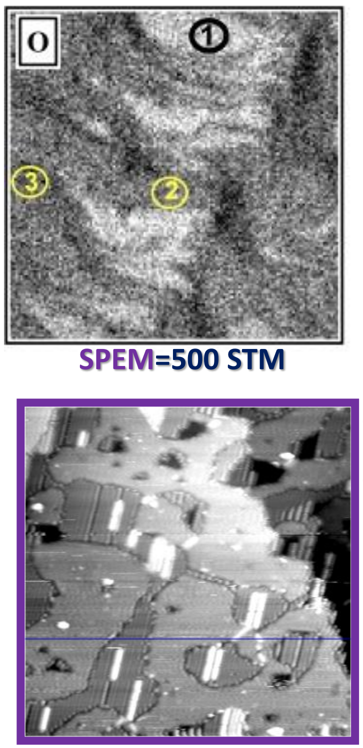


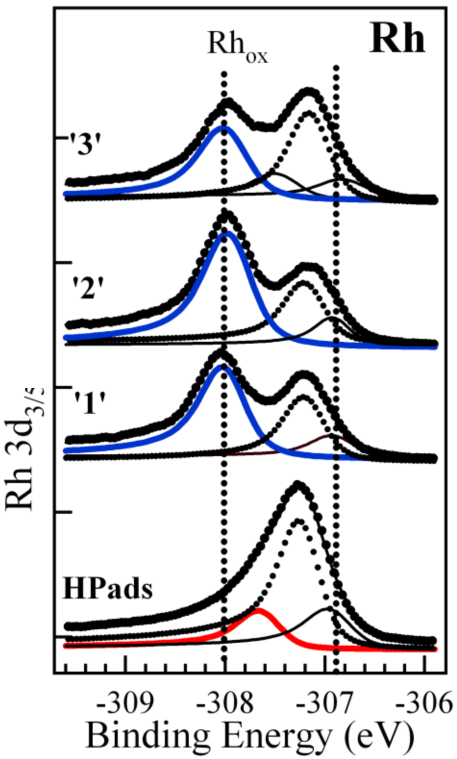


- Identified the presence of a NiSi phase.
- Determined the mobility of Ni in the different phases

P. Dudin et al, J. Chem Phys. 1019 (2005)

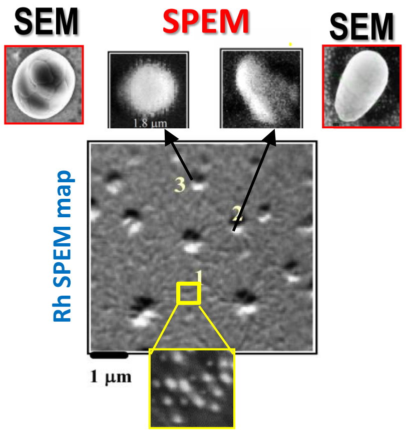
O 2p maps & Rh 3d µ-PES after exposure of Rh(110) to oxygen



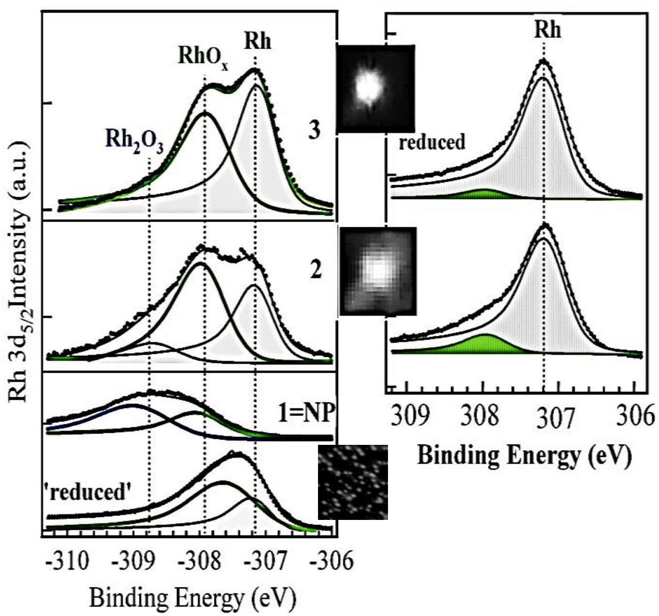


Model catalyst systems studied with SPEM:

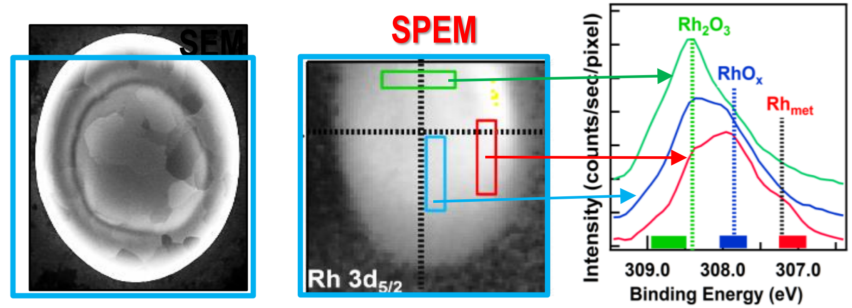
supported Rh metal particles on MgO

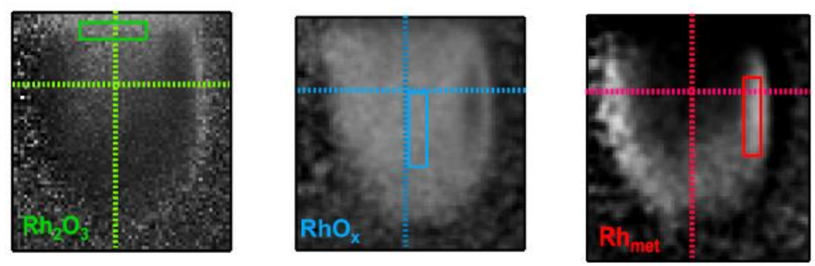


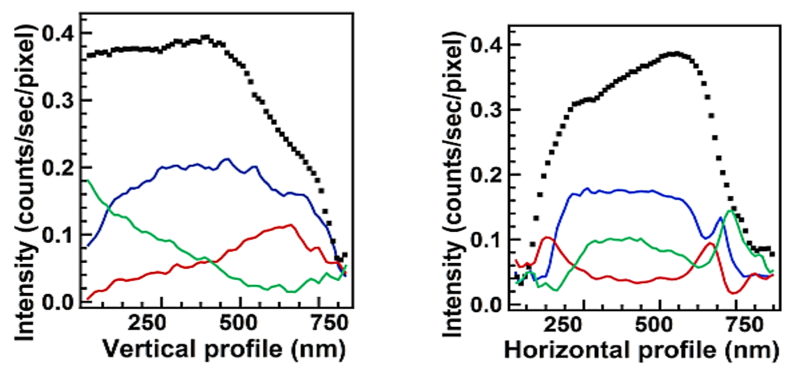
No simple size effect on reactivity in oxidative and reductive ambient



Lateral variation of Rh oxidation state within ~ 1 μm^2 supported Rh particle

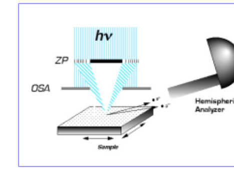




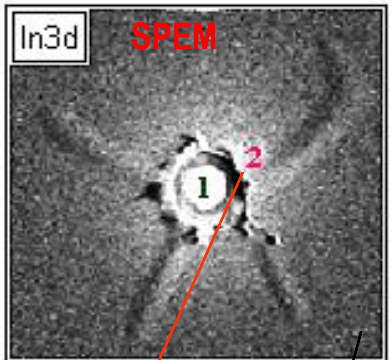


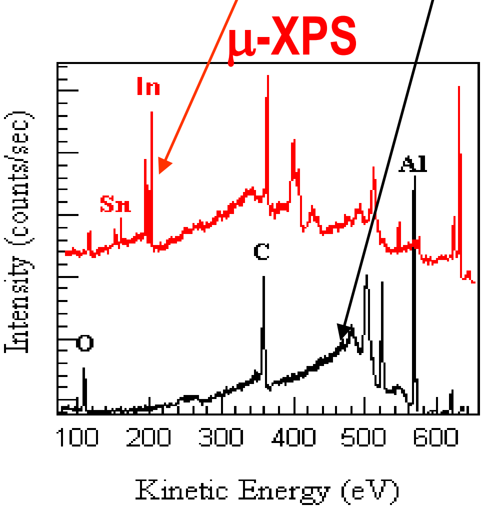
P. Dudin et al, JPC C 1112, 9040;; M. Dalmiglio JCP C, 114 16885; M. Amati et al, Surf. Sci. 652, 2016

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

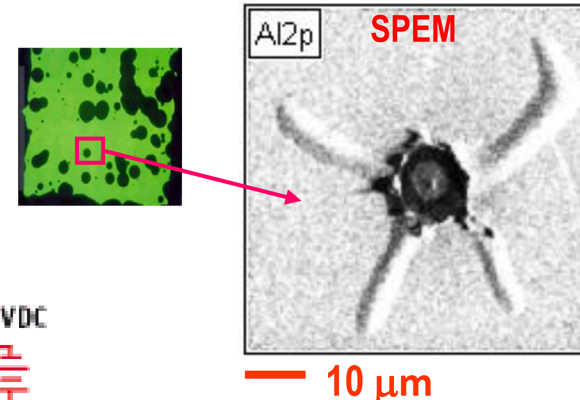


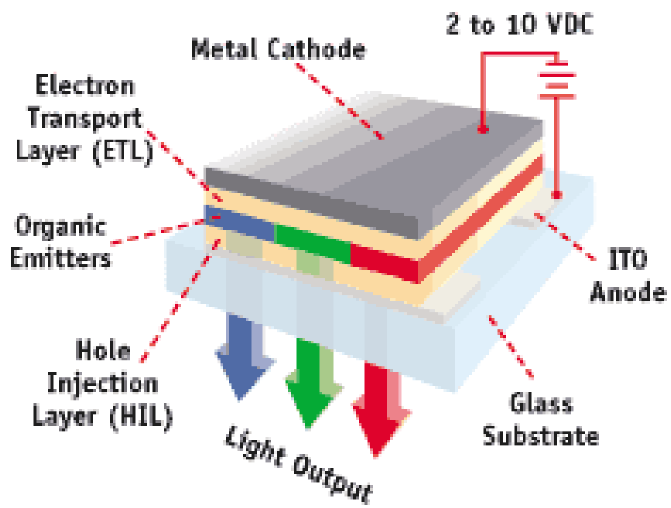
OLED exposed to ambient: moisture? supposed to be the damaging factor





OLED Display Screen (from Universal Display Corp)



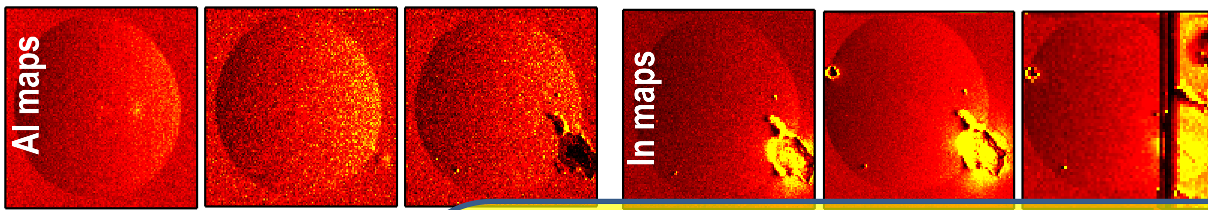


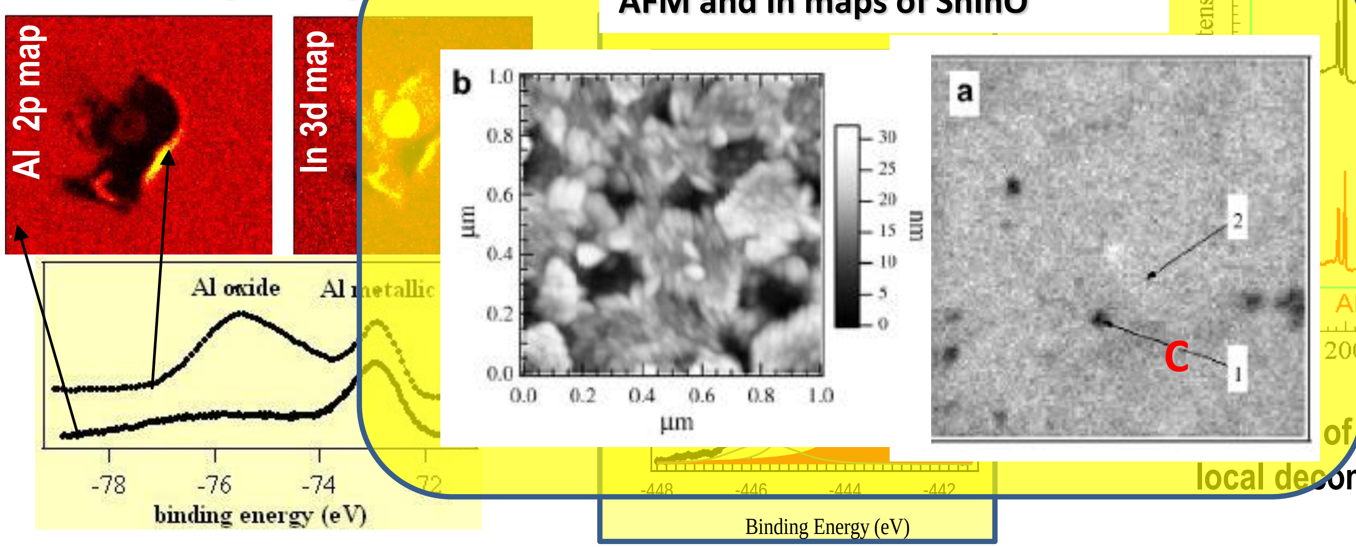
Topographic features due to fracture: clearly seen as enhancement and shadowing of the emitted electrons

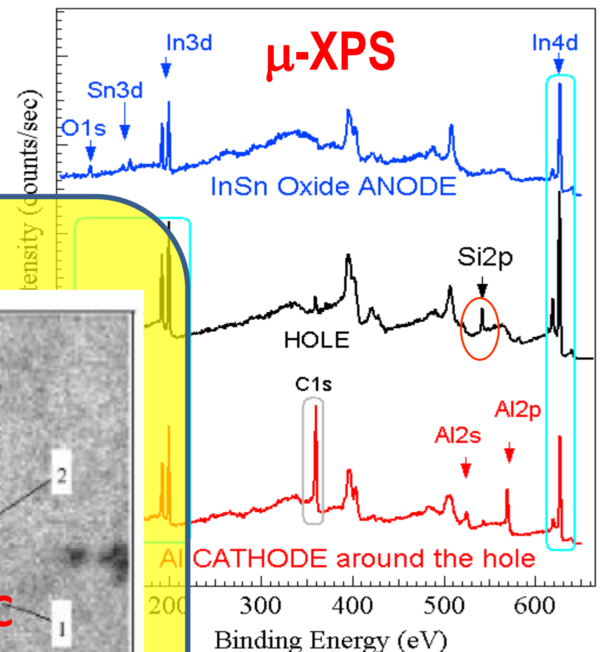
Chemical imaging & μ-XPS revealed anode material (In and Sn) deposited around the hole created in the Al cathode of OLEDs.

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

“Clean” experiment: OLED growth and operated in the SPEM (UHV ambient) : failure due to light emission in absence of humidity!







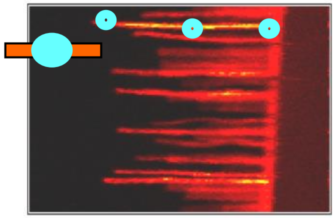
of InSn oxide and organic layer local decomposition, caused by spikes

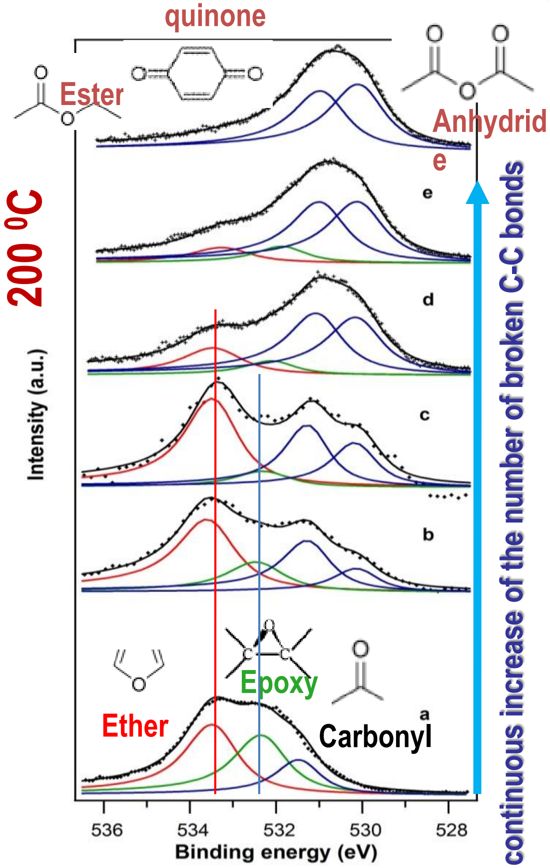
Lateral variations of the surface topography and chemistry of the InSn oxide anode films suggested as the major reasons for the device failures.

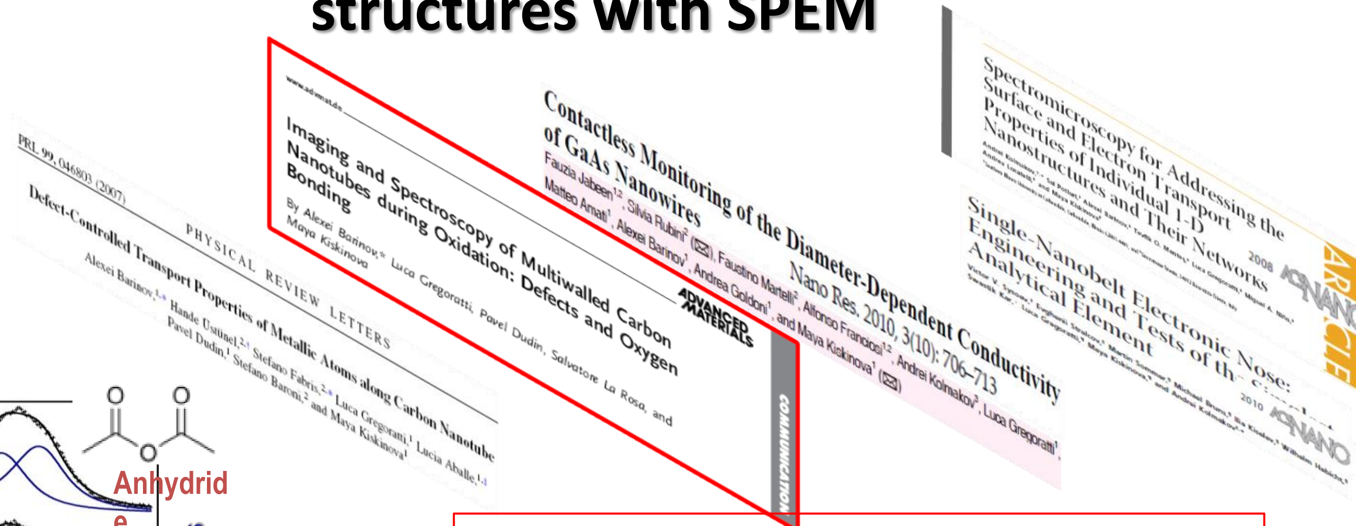
P. Melpigniano et al, APL 86, 41105,
S. Gardonio, Org.Electr. 9, 253

Exploring properties of individual and free-standing nano-structures with SPEM

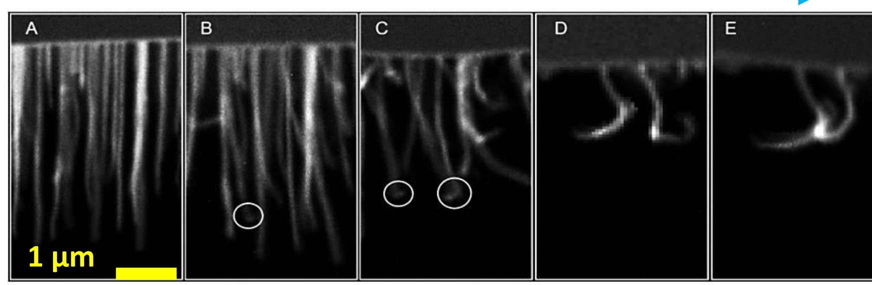
Low density NWs

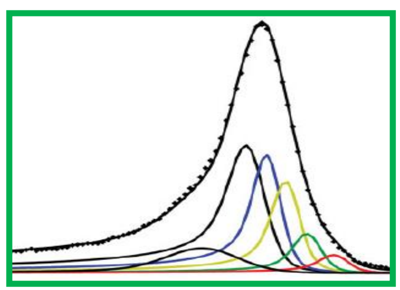




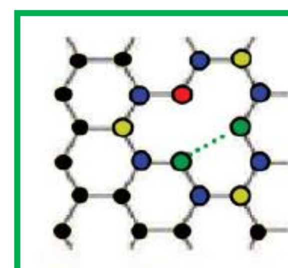


C NTs evolution with increasing of oxygen dose





The density and type of defects the C1s spectra is unique for each CNT and account for different consumption rate

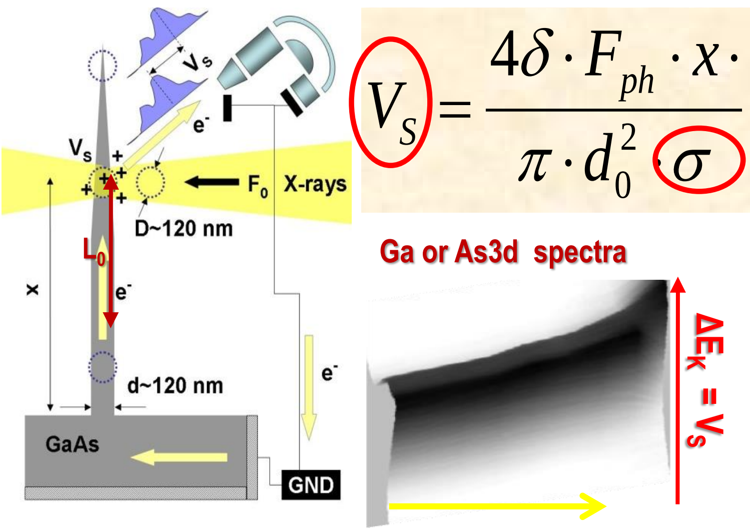


Surface potential V_s & GaAs NWs conductivity, σ : non-ohmic behavior with reducing diameter, environment effects, effect of growth conditions

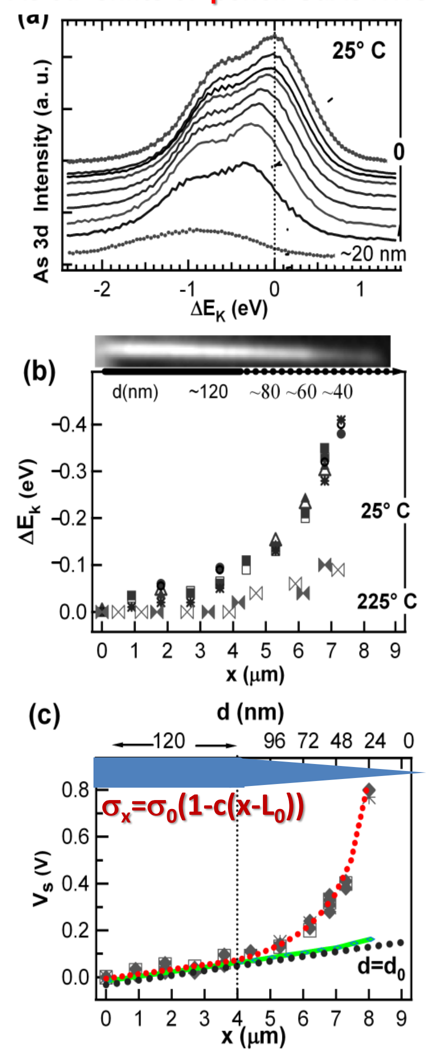
$E_K = E_{Ko} \pm E_{BB} \pm E_{SPV} - V_s$

V_s = f(Ohmic neutr. current)

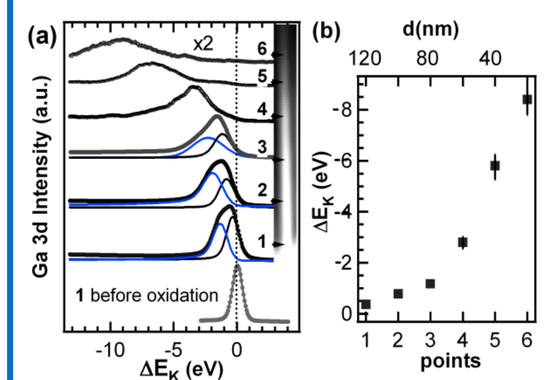
$$V_S = \frac{4\delta \cdot F_{ph} \cdot x \cdot}{\pi \cdot d_0^2 \cdot \sigma}$$



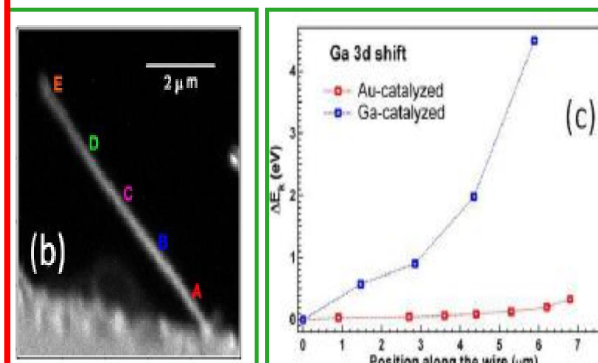
As 3d shifts of pencil GaAs NWs



Ga 3d shifts of oxidized pencil GaAs NWs



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



Metal catalyst > drastic conductivity increase

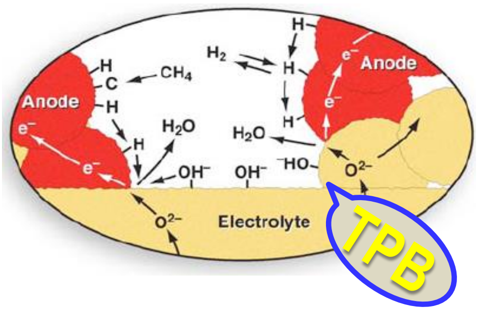
- Conductivity of pencil-like NWs: non-ohmic behavior as a function of d.
- The data fit to linear decrease of σ with decreasing d.

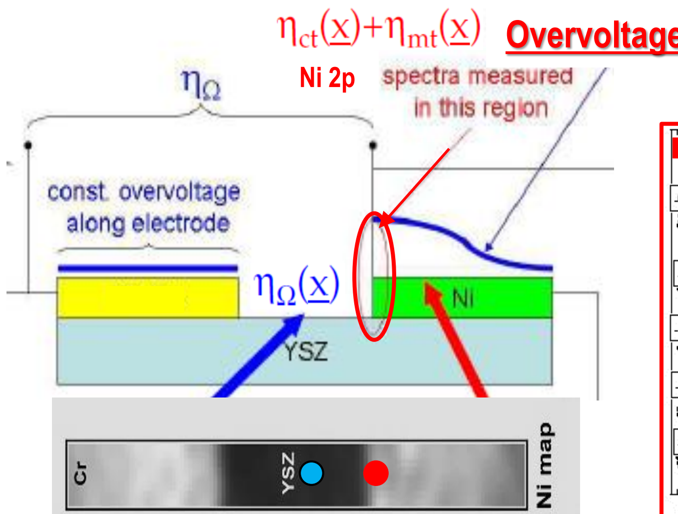
  confirms size effects

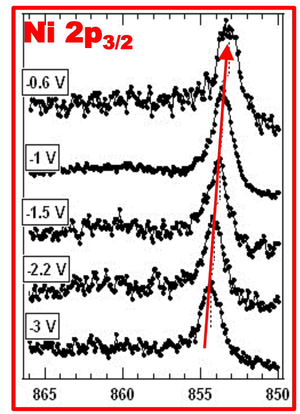
F. Jabeen, Nano Res. 2010, 3, 706

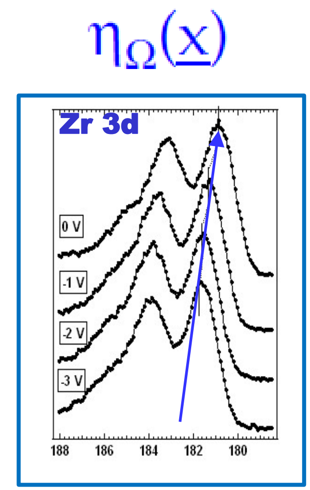
SOFCs under operating conditions with SPEM:
local chemical state and overpotential

O_2 reduction at the cathode, diffusion of the O- through a electrolyte, and oxidation of the fuel by at the anode.

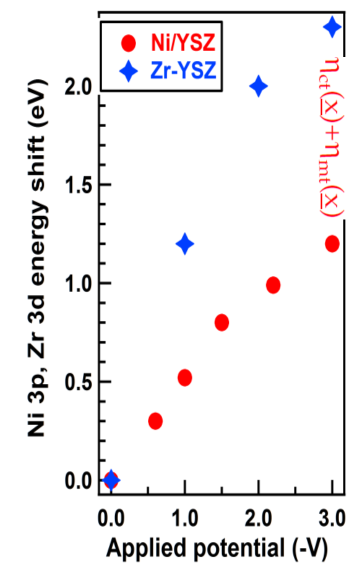






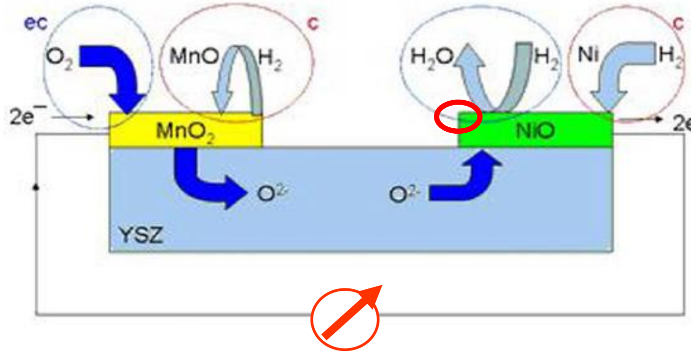


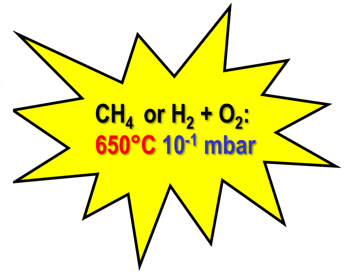
- Activation over-potentials represent chemical energy needed to overcome charge transfer barrier.
- The potential contributions: ohmic η_Ω (x), charge transfer,η_{ch} (x), and mass-transport of electroactive species,η_{mt}(x), :depend on the location within the cell.
- The highest contributions of charge-transfer and species transport are at the electrode–electrolyte interface where the electrochemical reactions occur.
- Overvoltage contribution can be measured from CL shifts,

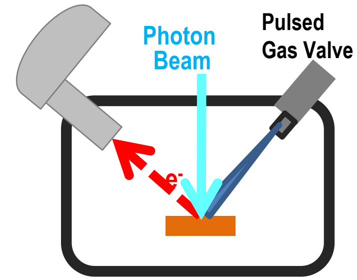


JPCC 116 (2012) 23188, JPS 196(2011), Electrochem. Comm. 24 (2012), Chemistry A E. J. 18 (2012), Sci.Rep.3 (2013). JPC 231(2013) 6.

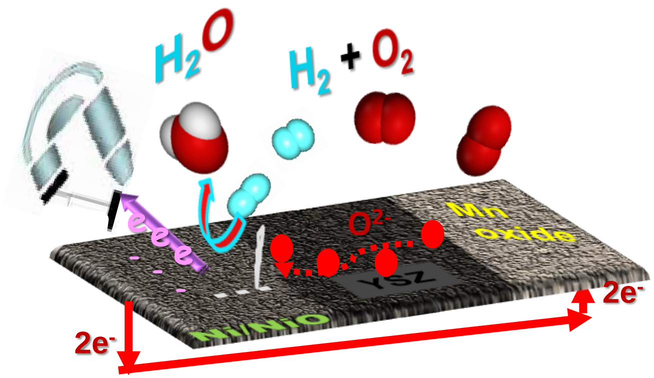
Self-driven single Mn oxide/Ni cell:



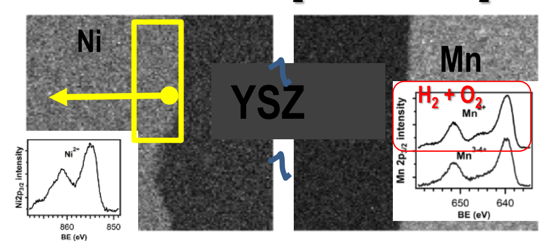




Local pressure upto 10^{-1} mbar with high frequency pulsed valve + nozzle.

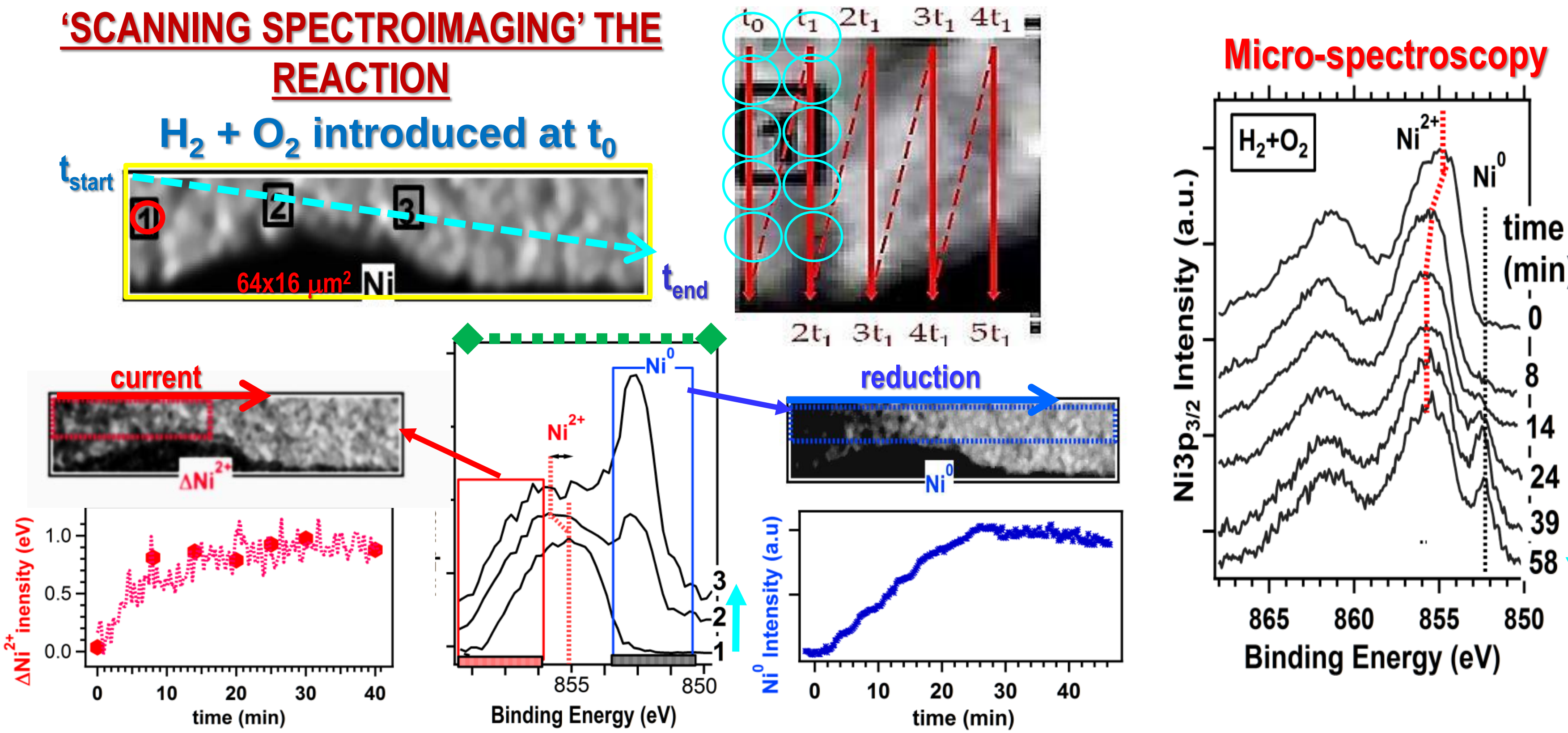


Initial states in O_2: NiO & MnO_2



The spectral transients, recorded under operating conditions resulting in generation of electric current, encodes both: (1) time-dependent electrochemical kinetics (current flow) through rigid spectral energy shifts and the electrodes oxidation states resulting from the electrochemical and chemical processes through CL chem. shifts .

Single Mn/Ni cell: simultaneous monitoring reduction and current during reaction



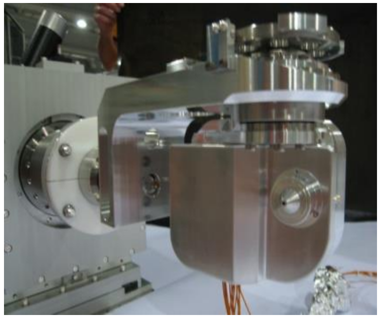
Steady state overpotential ~ 0.8 eV ~ 10 min: in concert with thermodynamic predictions for the potential generated by the electrochemical reaction:

$$\Delta G(10^{-5}\ \text{mbar}) = -322\ \text{kJ/mol} \Rightarrow E = 0.83\ \text{V}$$

Steady state chemical state ~ 30 min: anodic oxidation and chemical reduction concur.

Scientific Reports, DOI: 10.1038/srep02848

μ-ARPES SPEM @ Elettra



NANO LETTERS

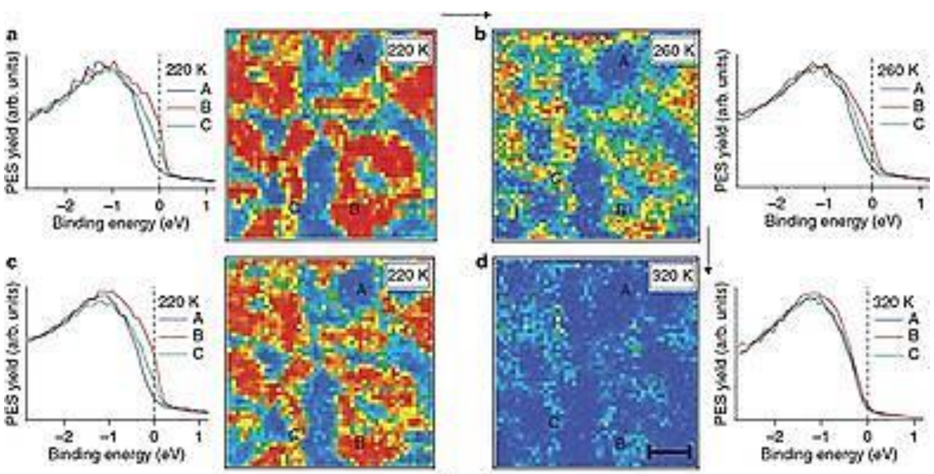
D. Usachov *et al*

The real space structure of graphene domains, visualized with PE microscopy at different PE azimuthal angles, corresponding to the highest intensity of the π-band in the mapping point.

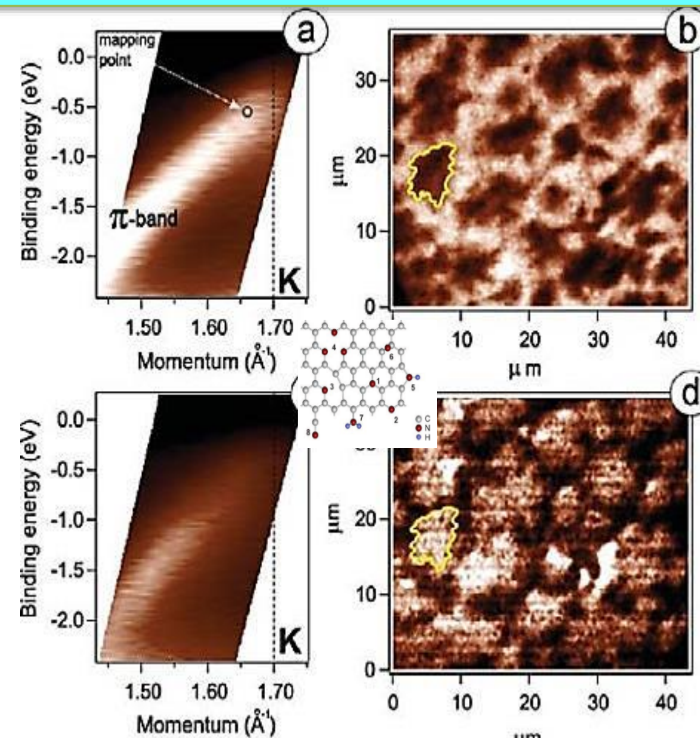
Domain formation during Metal-Insulator Transitions

Spatial distribution of the photoelectron intensity for the d band reveal the evolution during the metal-insulator transition in Cr-doped V_2O_3 with decreasing T, microscopic domains become metallic and coexist with an insulating background.

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.



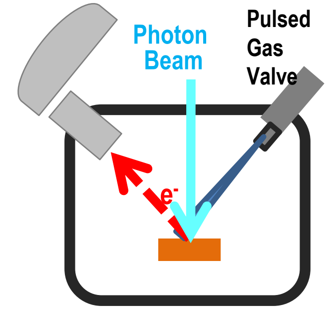
S. Lupi *et al.*, Nature Comm. 1, 105 (2010)



Maya Kiskinova

Outlook and Challenges

For μ-PES: In-situ measurements of nano-structures under realistic ambient conditions: options to overcome the UHV limitations.



Local pressure upto 10^{-1} mbar with high frequency pulsed valve + nozzle
M.Amati et al, J. Instr.8, 2013, T05001.

G-windows robust, impermeable and electron transparent

nature nanotechnology Vol. 6, 2011, 651 ARTICLES

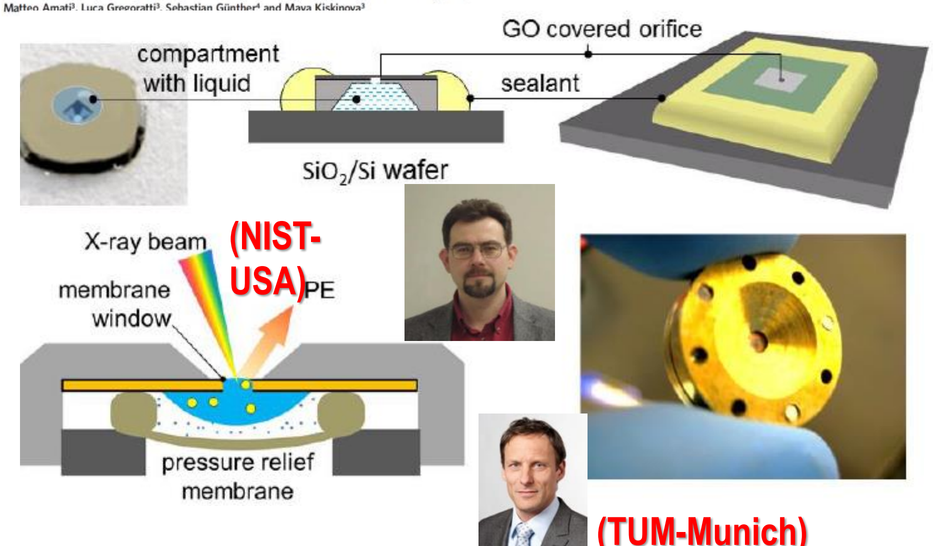
Graphene oxide windows for *in situ* environmental cell photoelectron spectroscopy

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]

Nanoscale 2014, DOI: 10.1039/c4nr03561e

Photoelectron spectroscopy of wet and gaseous samples through graphene membranes†

Jürgen Kraus,[a] Robert Reichelt,[a] Sebastian Günther,[a] Luca Gregoratti,[b] Matteo Amati,[b] Maya Kiskinova,[b] Alexander Yulaev,[c,e] Ivan Vlassiouk[d] and Andrei Kolmakov[*e]

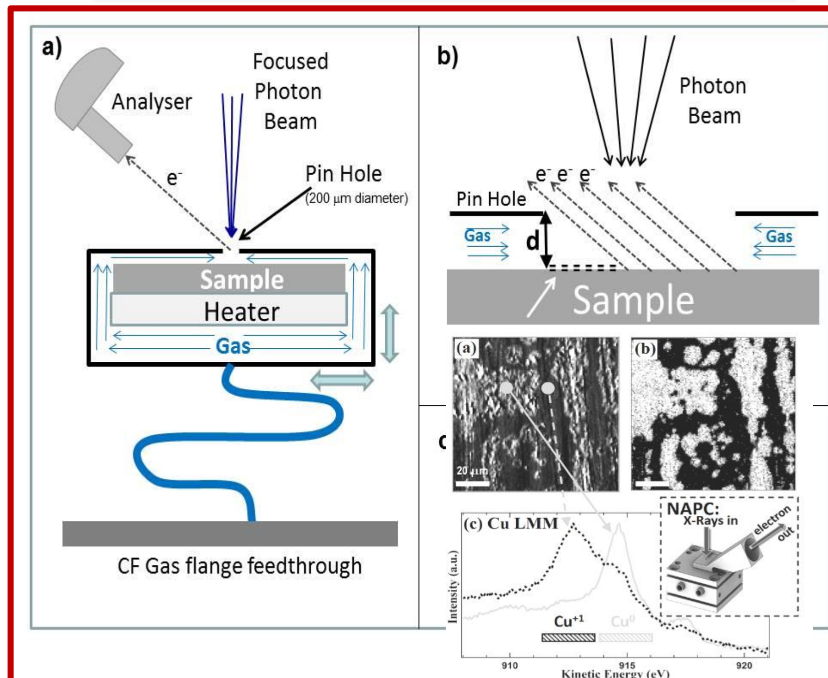


Top Catal (2016) 59:448–468

Recent Approaches for Bridging the Pressure Gap in Photoelectron Microspectroscopy

Andrei Kolmakov[1] · Luca Gregoratti[2] · Maya Kiskinova[2] · Sebastian Günther[3]

SPEM set-up with reaction cell



Maya Kiskinova

Classical X-ray imaging and spectromicroscopy: brief outline

SURFACES & INTERFACES:
XPEEM and SPEM

PHOTON-IN/ ELECTRON-OUT
(probing depth=f(E_{el}) max ~ 20 nm)

Spectroscopy (XPS-AES-XANES)
ONLY CONDUCTIVE SAMPLES

BULK Information
STXM/SPEM & TXM

PHOTON-IN/PHOTON-OUT
(probing depth = f (E_{ph}) > 100 nm)

(Spectroscopy – XFS or XANES)

XANES

Total e^- yield
(sample current)

Total hν yield,
Transmitted x-rays

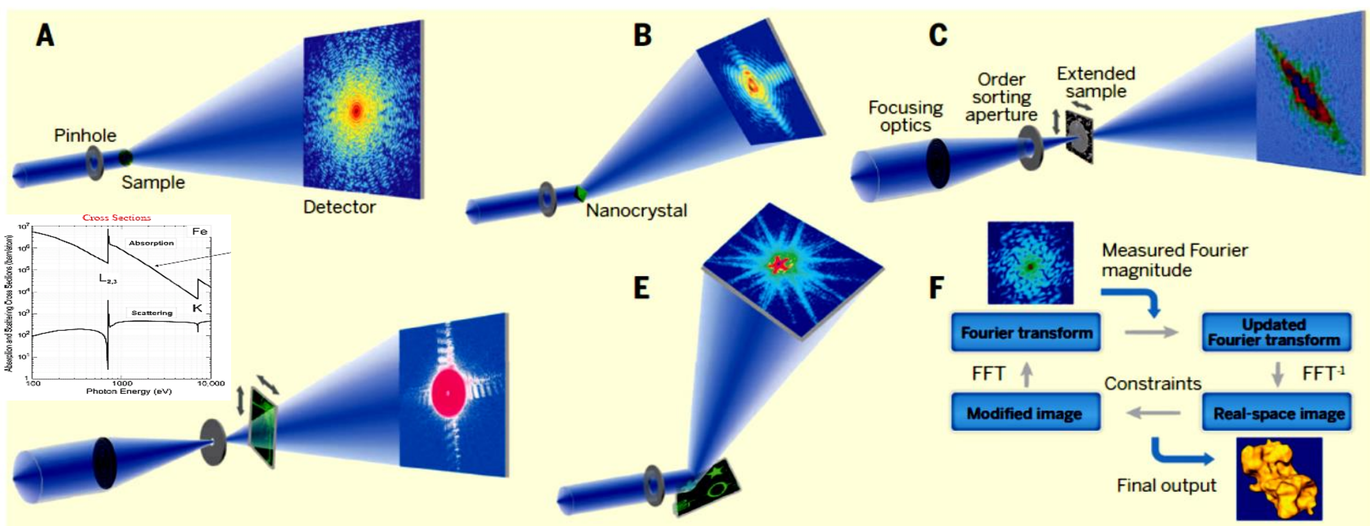
- **Chemical surface sensitivity:**
  Quantitative μ-XPS (0.01 ML)
- **Chemical & electronic (VB) structure**

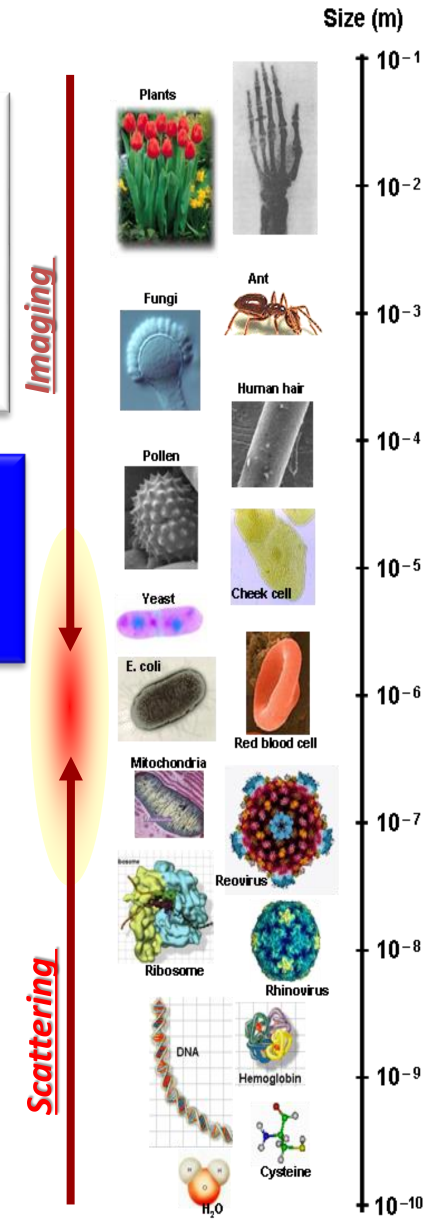
Chemical bulk sensitivity
Quantitative μ-XFS
Trace element mapping

Imaging-resolution-time

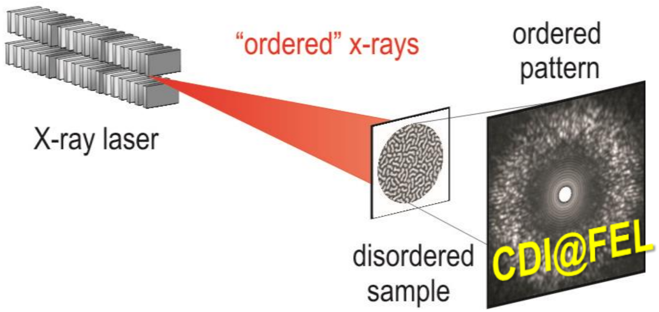
- All ‘classical x-ray microscopy’– limited in resolution focal depth by the optical elements. Time resolution - ≥ 0.1 ns.
- Transmission electron microscopes can resolve even atoms but are limited in penetration (samples thinner than ~ 30 nm).

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. Tuning to the atomic edges adds speciation.

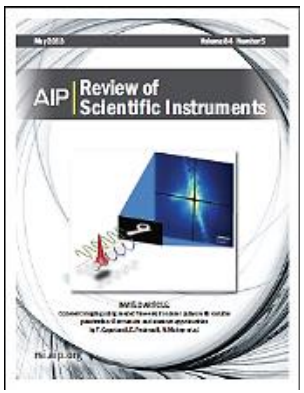


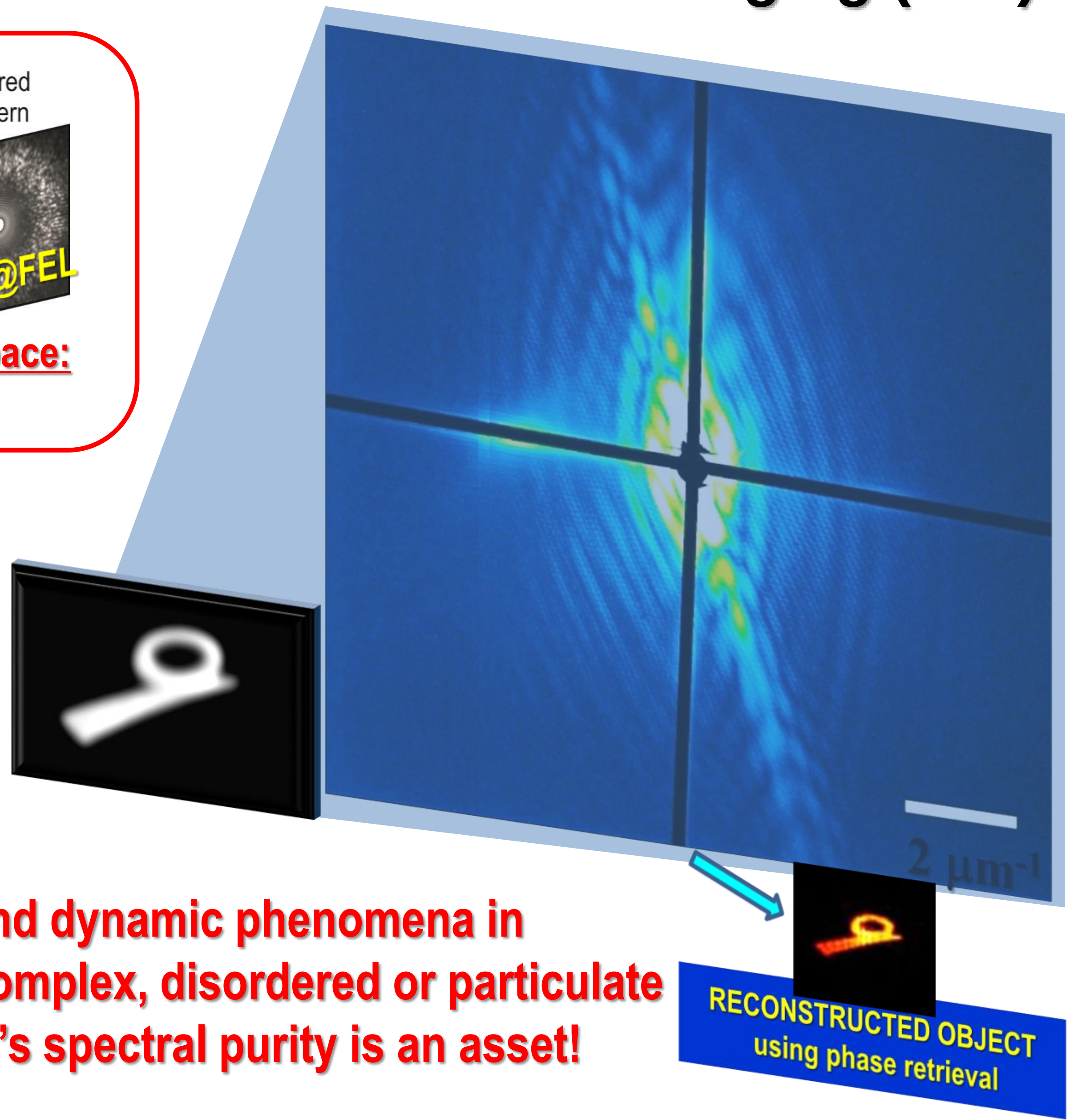


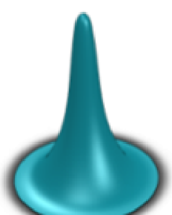
Single shot Coherent Diffraction Imaging (CDI)



Acquire data in **reciprocal space:**
Resolution: $\delta = \lambda / \sin\theta$

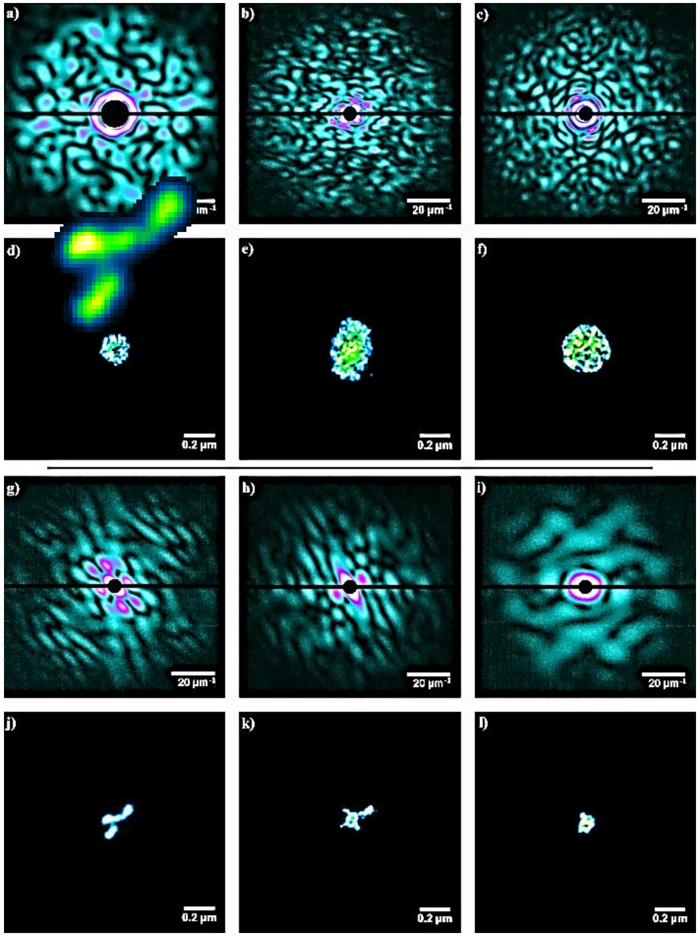




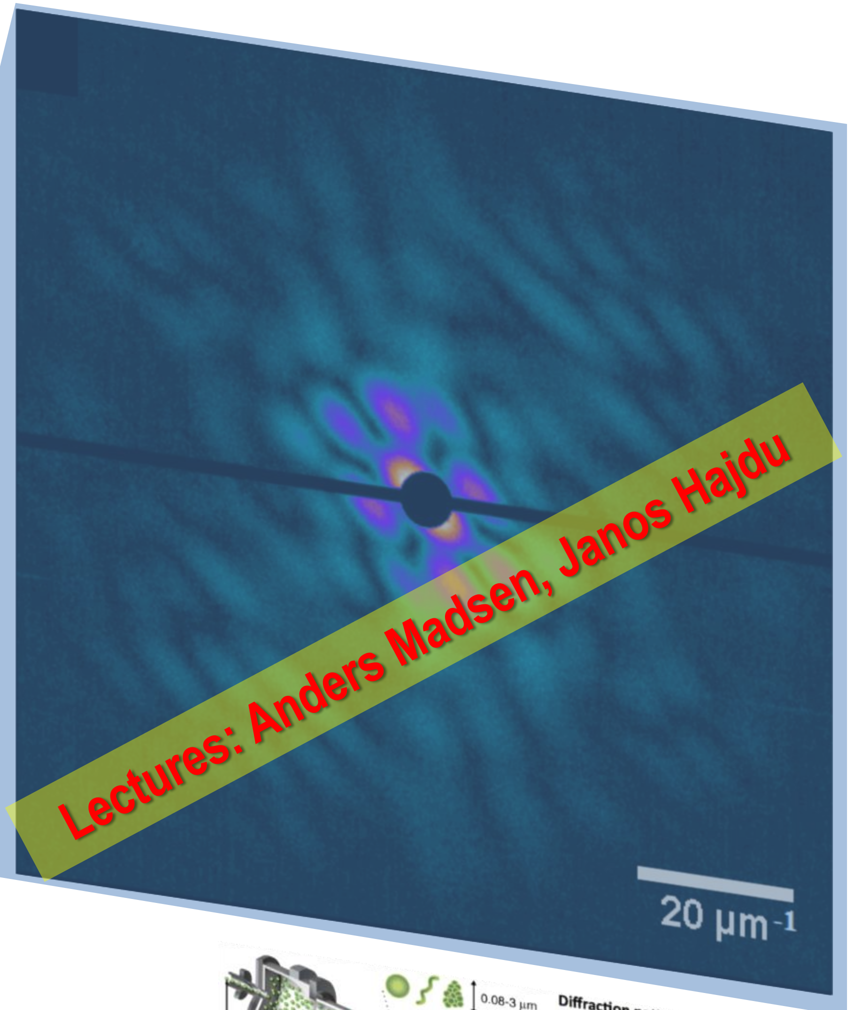


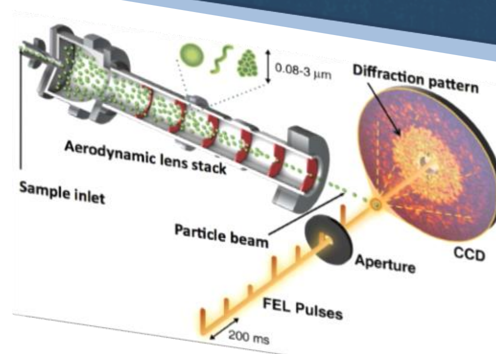
Structure and dynamic phenomena in morphologically complex, disordered or particulate matter – Fermi's spectral purity is an asset!

Maya Kiskinova



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



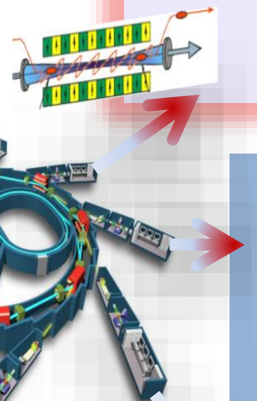


E. Pedersoli et al,
J. Phys. B: At. Mol. Opt. Phys. 46 (2013) 164033

Enjoy the following Lectures

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

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



Hard X-ray Imaging and tomography
(Lecture Giuliana Tromba)

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

Photoelectron imaging and Spectromicroscopy with XPEEM :
(Lecture: Andrea Locatelli)
- Chemical state
- Chemical and magnetic mapping.
- Surface sensitive.

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