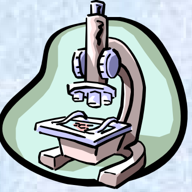


Scanning photoemission microscopy: spatial resolution & chemical sensitivity

Maya Kiskinova, Sincrotrone Trieste

There's Plenty of Room at the Bottom

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

Richard P. Feynman - 1959!!!

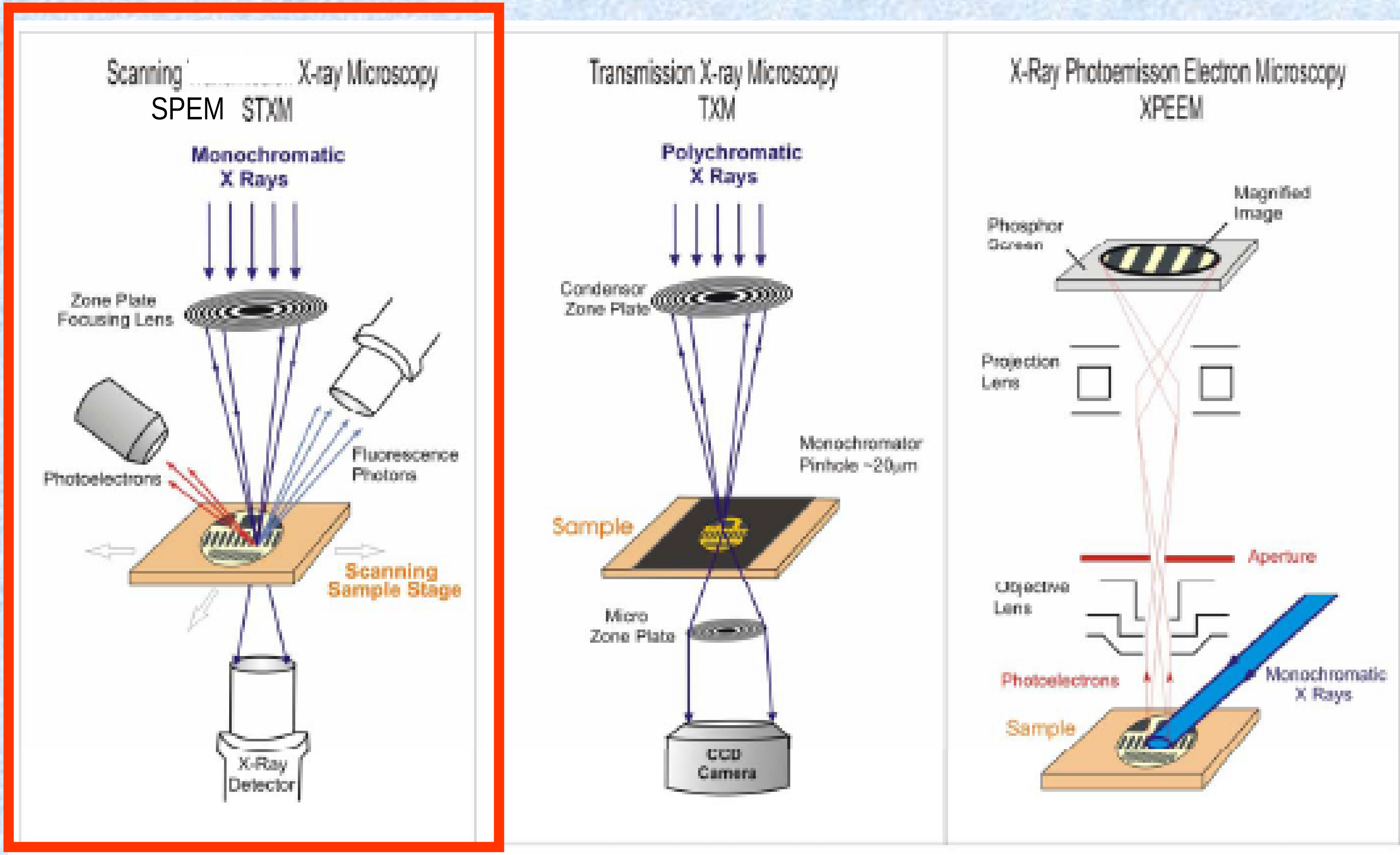
1) STATIC: Heterogeneity by nature (e.g. phase separation), by design (e.g. μ and nanostructures), generated in reactive environment by local radiation or heat.

2) STATIC: Reduced dimensionality and unique properties, e.g. structural and electron confinement effects.

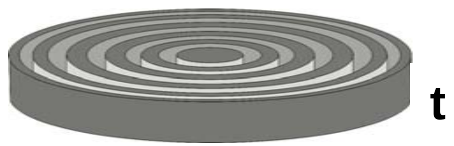
3) MASS TRANSPORT: thermal and electro-migration, reorganizations in reactive environment.

ICTP- Synchrotron Radiation School, May 2006

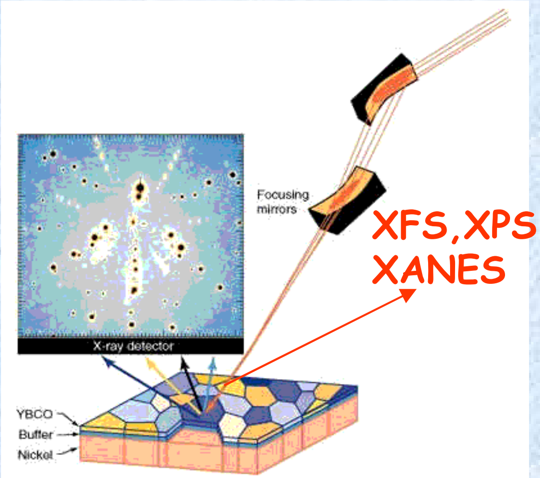
Types of X-ray microscopes using soft x-rays



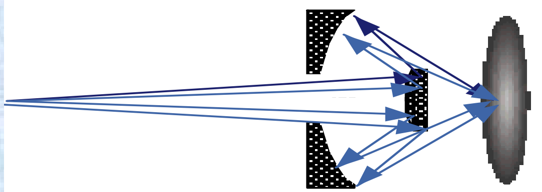
Focusing optics: zone plates, mirrors, capillaries



Zone Plate optics: from ~ 200 to ~ 8000 eV
Resolution: 30 nm in transmission

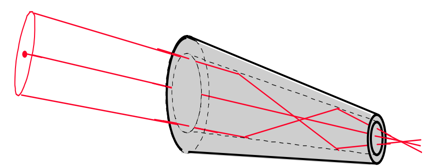


KP-B mirrors each focusing in one direction: soft & hard: ~ 1000 nm
Soft & hard x-rays!
chromatic focal point, easy energy tunability, comfortable working distance
Resolution ~ 1000 nm



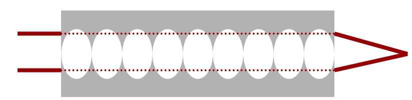
Normal incidence: spherical mirrors with multilayer interference coating (Schwarzschild Objective)
not tunable, E < 100 eV
Resolution: best ~ 100 nm

Capillary: multiple reflection concentrator



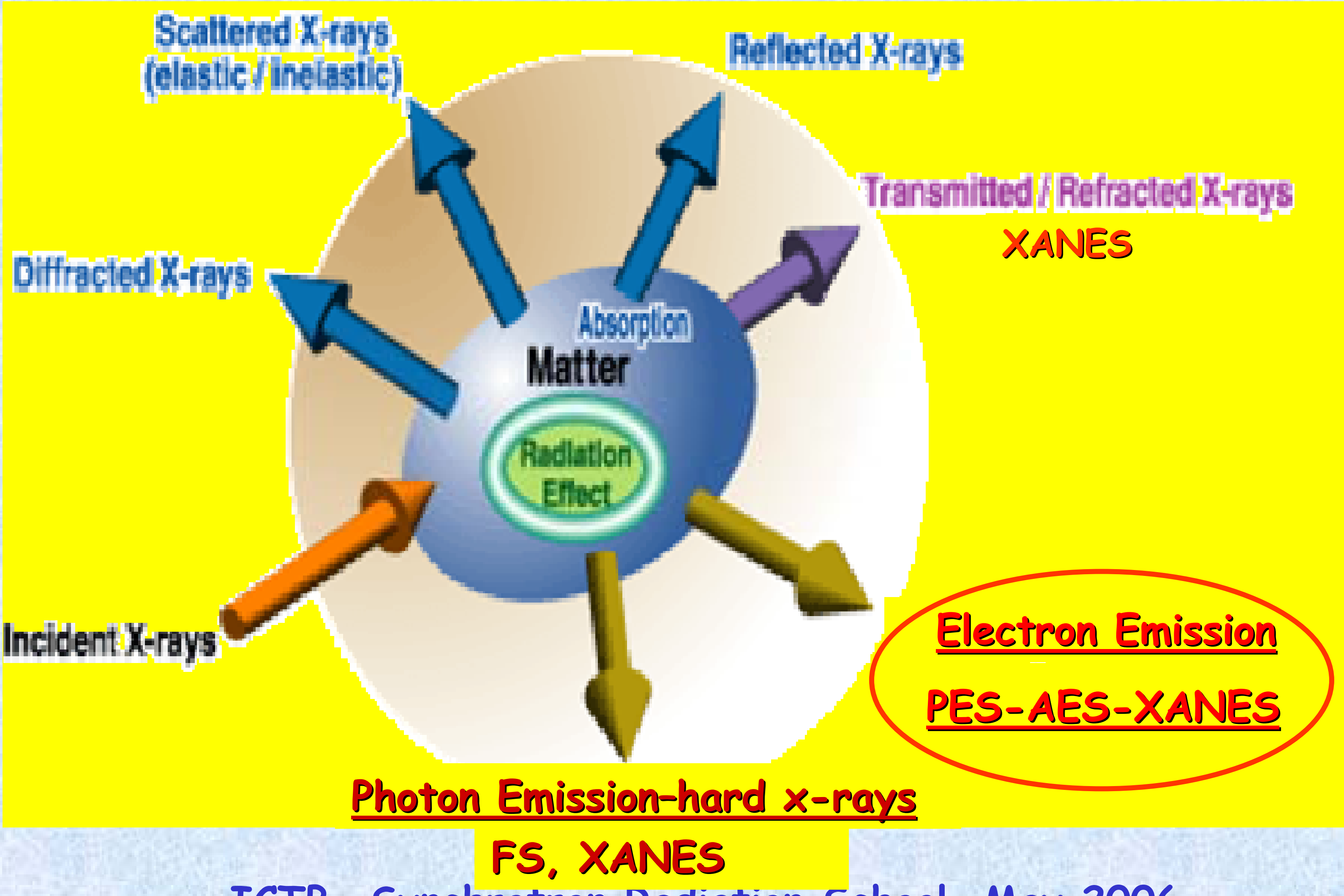
Hard x-rays ~ 8-18 keV
Resolution: > 3000 nm

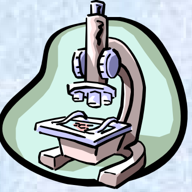
Refractive lenses



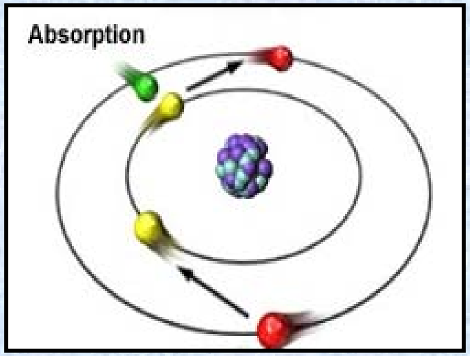
Hard x-rays ~ 4-70 keV
Resolution: > 1000 nm

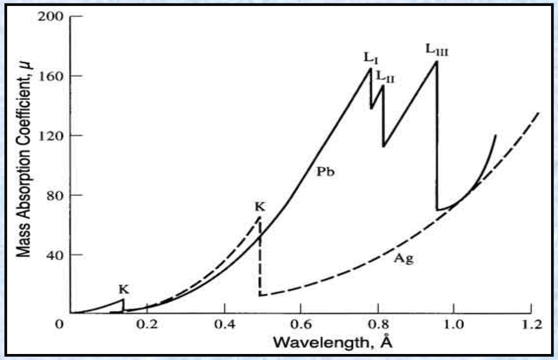
Interactions of x-rays with the matter: redirection & absorption: x-ray transmission and x-ray and electron emission

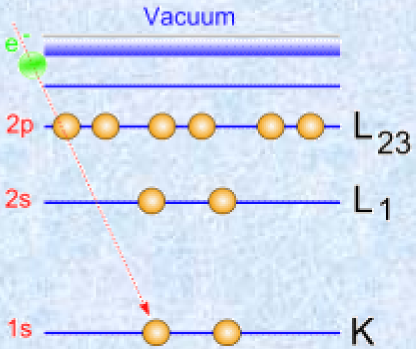


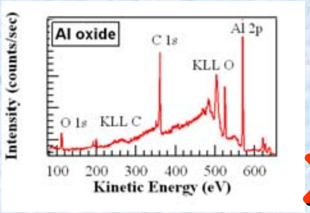


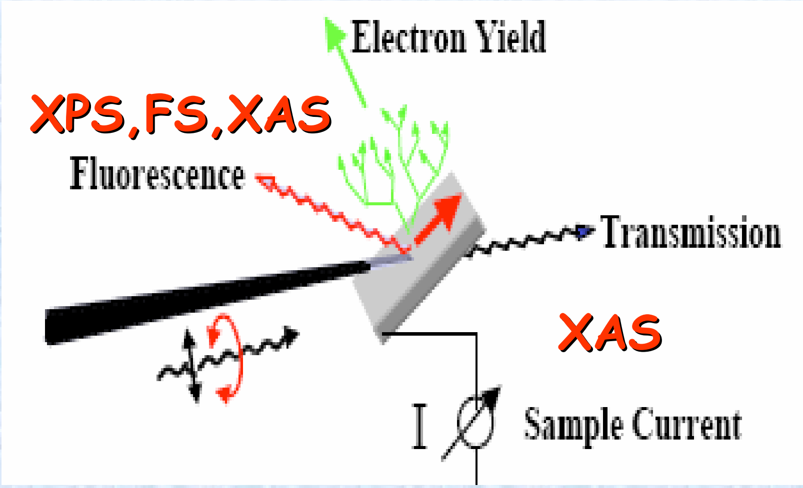
All chemical specific spectroscopies are based on absorption of the photons by the matter and following excitation & de-excitation processes

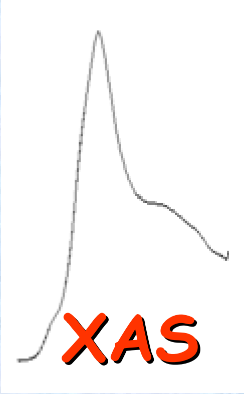






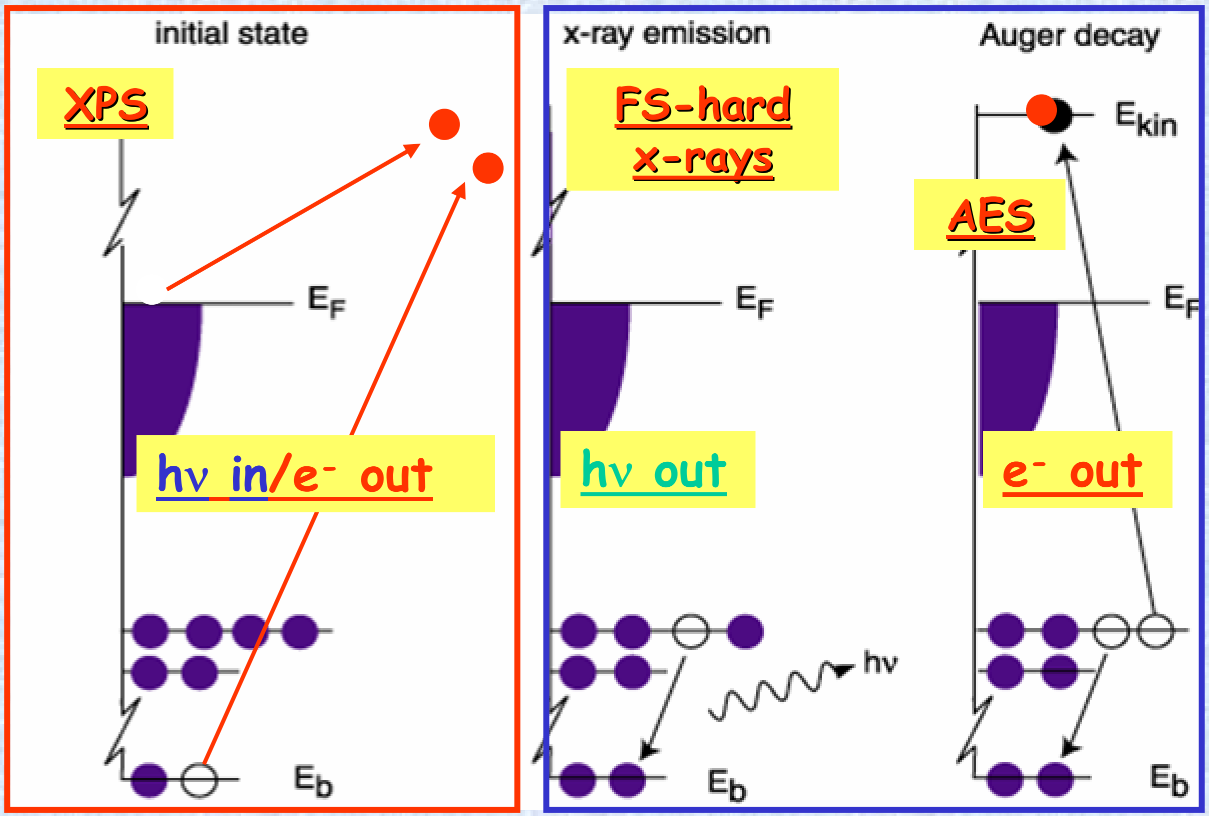


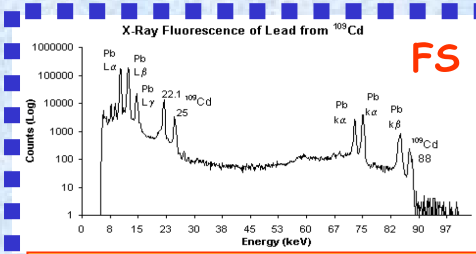




XPS & FS

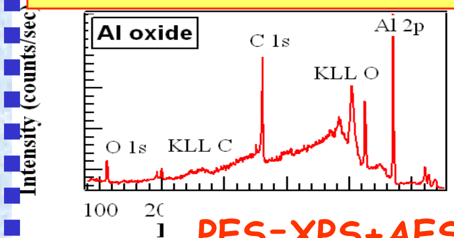
Photoelectric effect & de-excitation processes = chemical specific spectroscopies





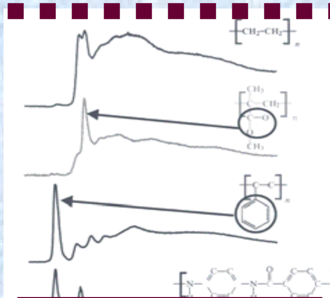
FS

$E_{h\nu}$ = constant & energy filtering



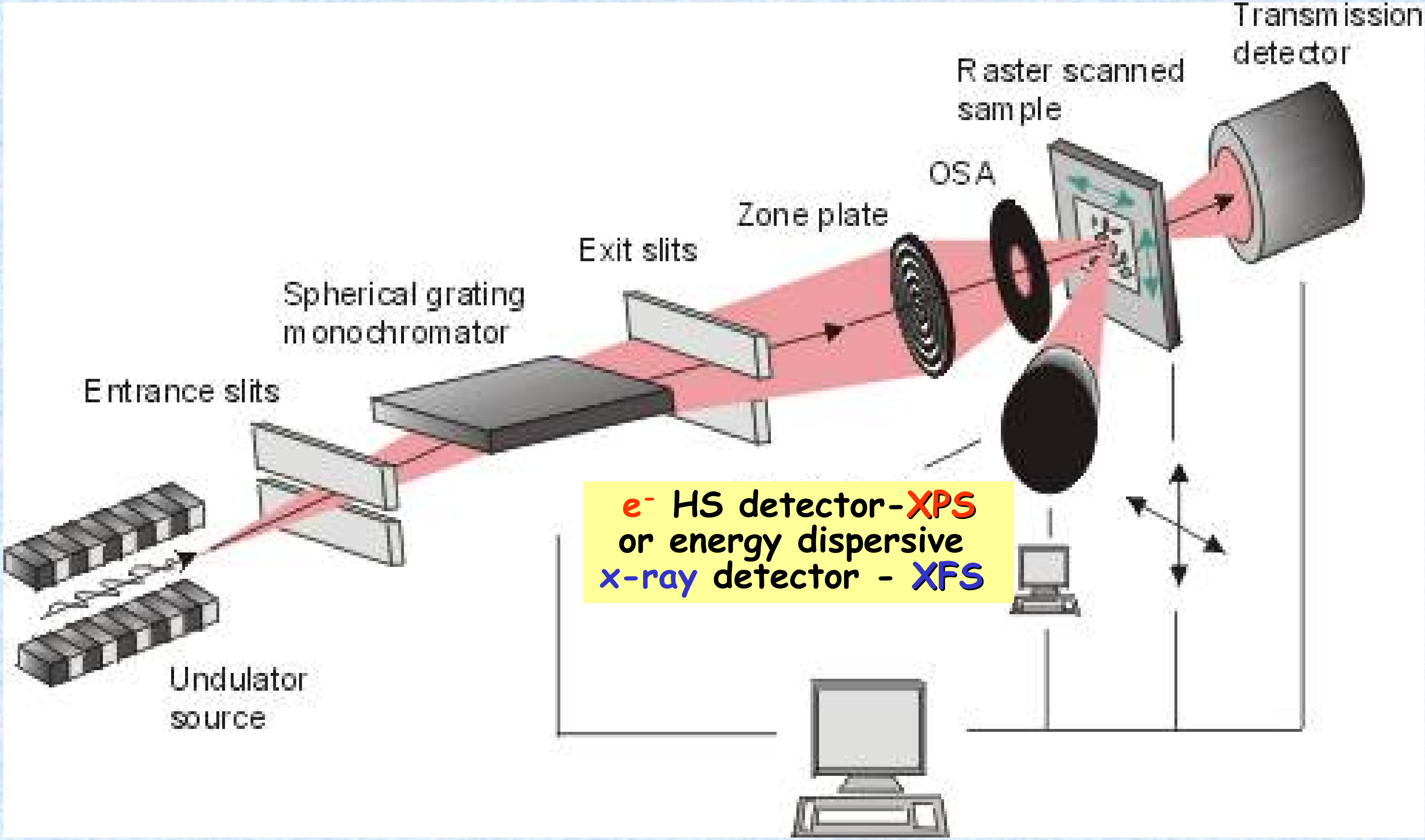
PES=XPS+AES

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

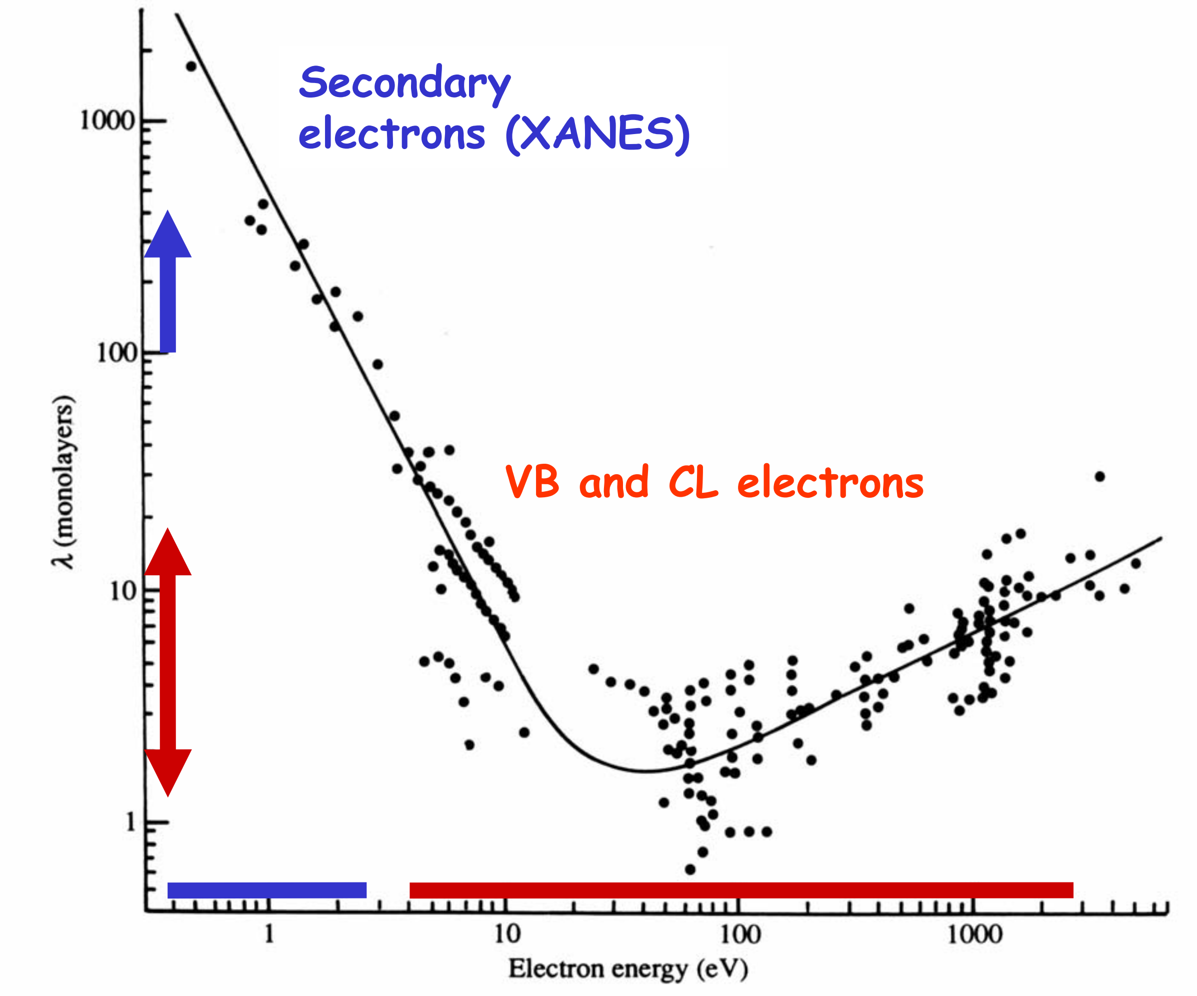


$E_{h\nu}$ scanned

Scanning photoemission microscopy: photoelectron, fluorescence and XAFS

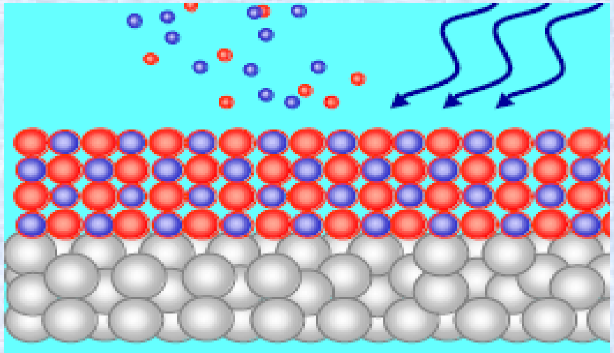


Sampling depth:
determined by the inelastic mean free path ("universal curve")

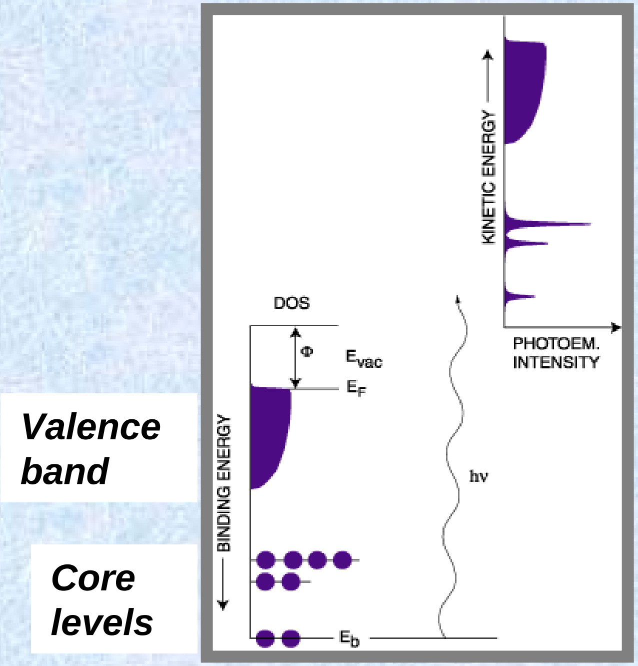


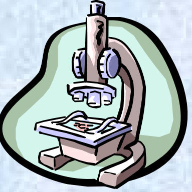
What does photon-induced electron emission provide

- 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).
- Information depth < 10 nm (surface sensitive)

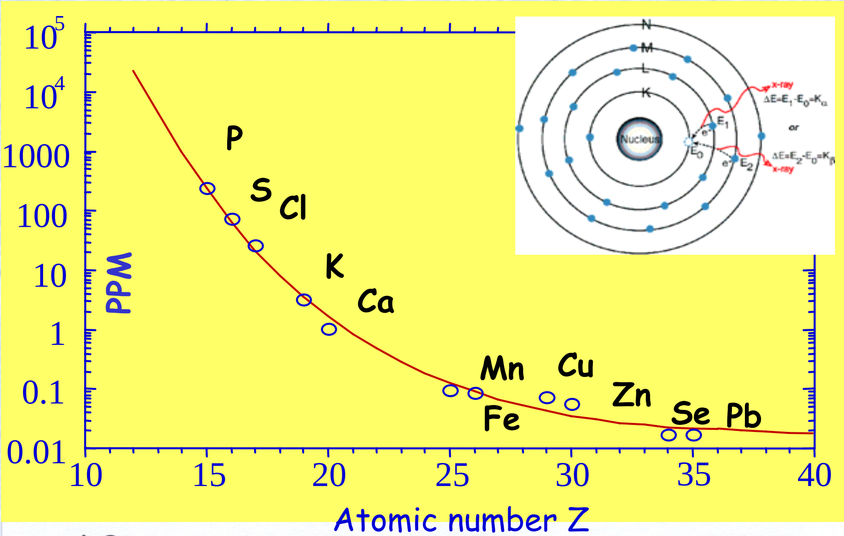


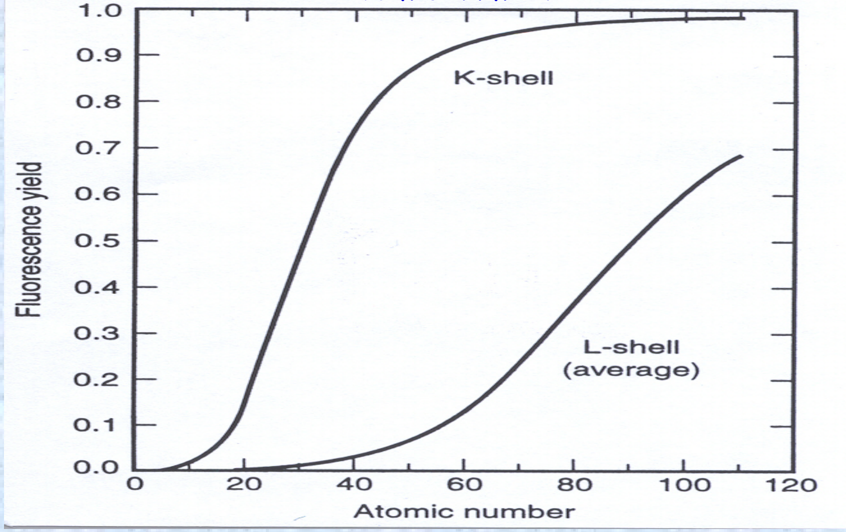
Information depth = d$\sin\theta$
d = Escape depth ~ 3 λ
θ *= Emission angle relative to surface*
λ *= Inelastic Mean Free Path*





Hard X-ray Microscopy: lower spatial resolution but X-ray fluorescence

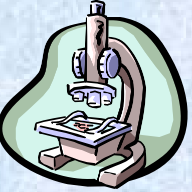




- Penetration depth: > 50μm
- Fluorescence yield.
- All type of samples
- μ-XANES (S, P, K, Ca, Fe..)

XRF (Scanning + energy/wavelength dispersive detection)

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



X-ray SPECTRO-microscopy and imaging

soft (< 1500 eV)	*hard (2-20 keV)*
SURFACES & INTERFACES:	**BULK SAMPLES**
PHOTON IN/ELECTRON OUT	PHOTON IN/PHOTON OUT
(probing depth=f(E_{el}) max ~ 20 nm)	(probing depth = f (E_{ph}) > 100 nm)
PE spectroscopy (XPS-AES)	X-ray Fluorescence spectroscopy (XFS)
ONLY CONDUCTIVE SAMPLES	
Chemical surface sensitivity:	Chemical bulk sensitivity
Quantitative μ-XPS (0.01 ML)	Quantitative μ-XFS
chemical & electronic (VB) structure	Trace element mapping
	(ppm 0.01/Pb – 200/S)

Total e^- yield (sample current) — Absorption spectroscopy XANES — Total hν yield

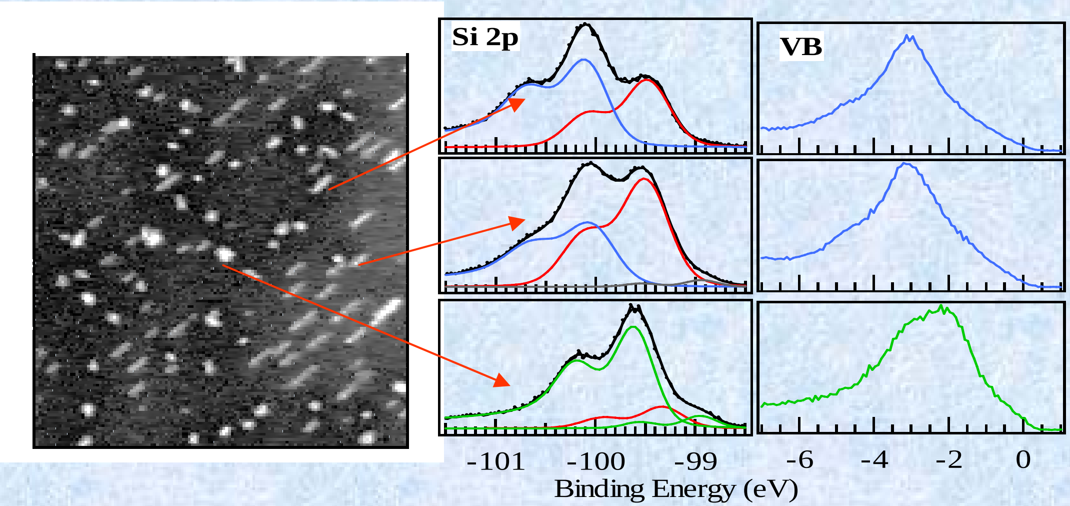
Transmitted x-rays

(ZP) focal length and depth of focus increases with E_{ph}: more space around the sample for detectors!

Chemical Imaging and μ-spectroscopy

2D maps of energy window:

the contrast reflects element concentration (XPS&XFS), different chemical states (XPS& XANES), BB (XPS) shifts etc.

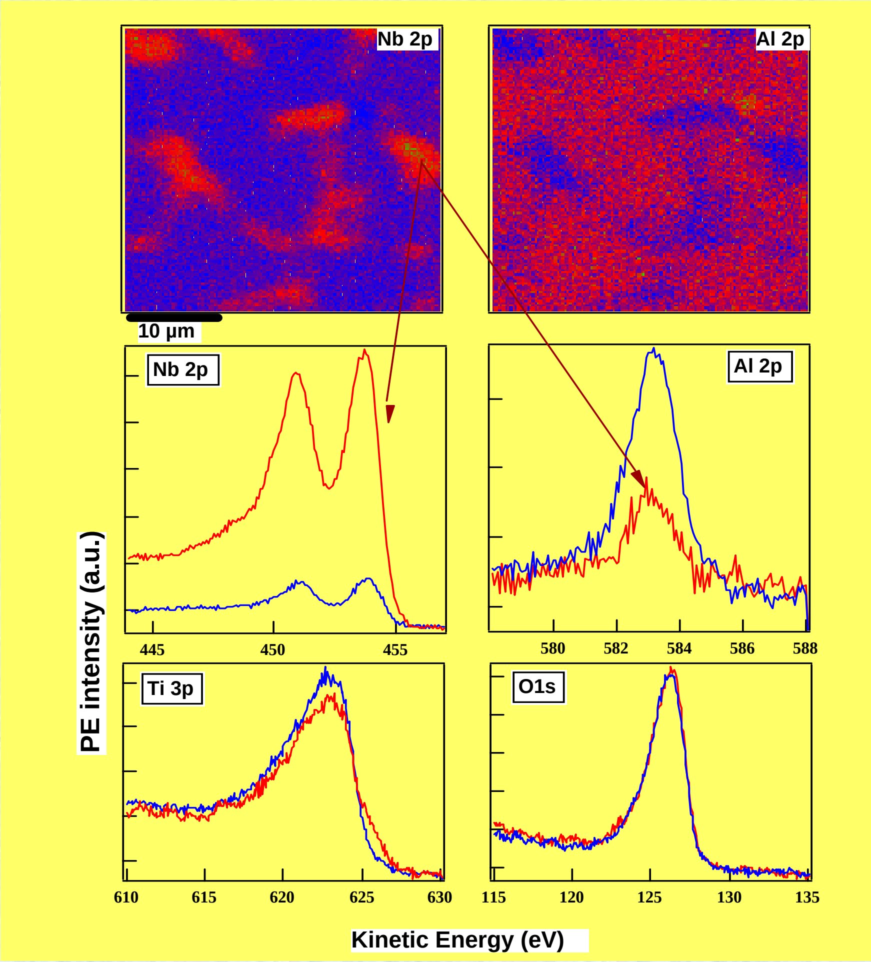


- **Detailed characterization of coexisting micro-phases via microspectroscopy**

  XPS, XFS or XANES from selected spots: fingerprints of local composition, chemical state, electronic properties, BB, charging state, magnetic spin, MOs etc

Maping core level electron emission (CLEE): 'concentration' inhomogeneity of solid materials

SPEM



Ti6Al7Nb (wt%): biocompatible alloy used for implantation in bone surgery: surface composition affect the local reactivity and in turn the degree of acceptance by the human body:

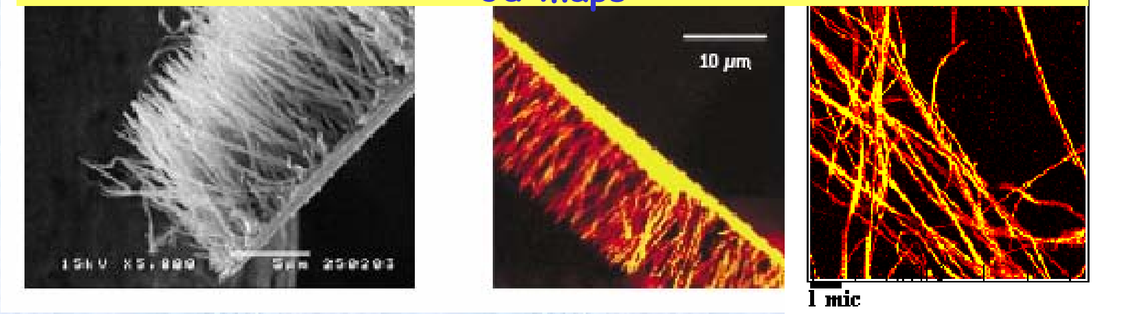
SAM has inferior chemical sensitivity

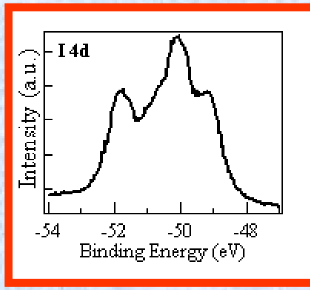
Maping core level electron emission (CLEE):

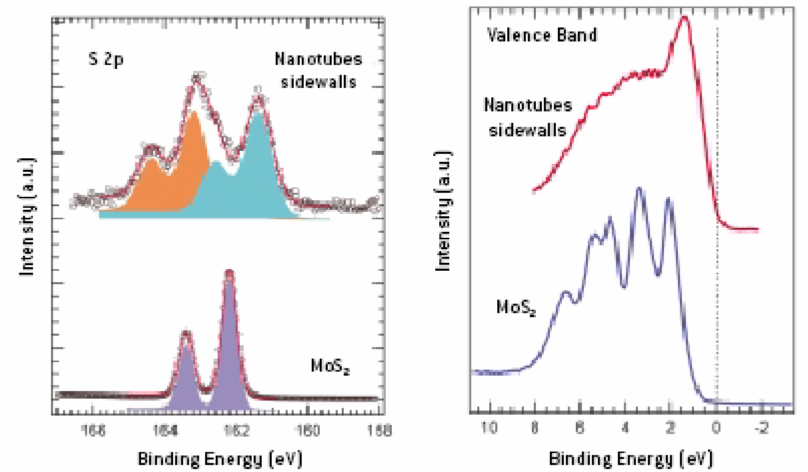
Characterization of nanomaterials MoS_2-nanotubes

ZP-SPEM

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



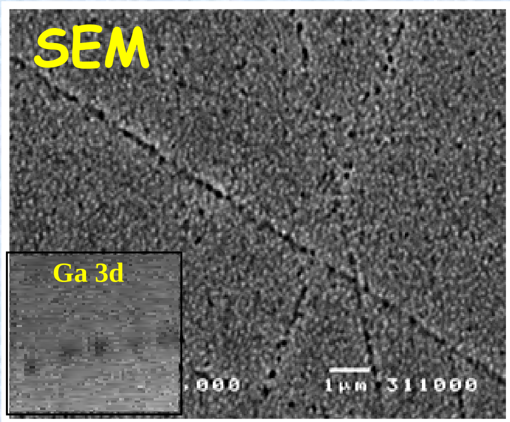




Due to the low dimensionality and/or presence of I the S 2p, Mo 3d and VB spectra, reflecting the electronic properties, differ significantly from those of the MoS_2 crystal. SPEM revealed I (used as a carrier) in interstitial positions between the tubes bonded to outer S atoms.

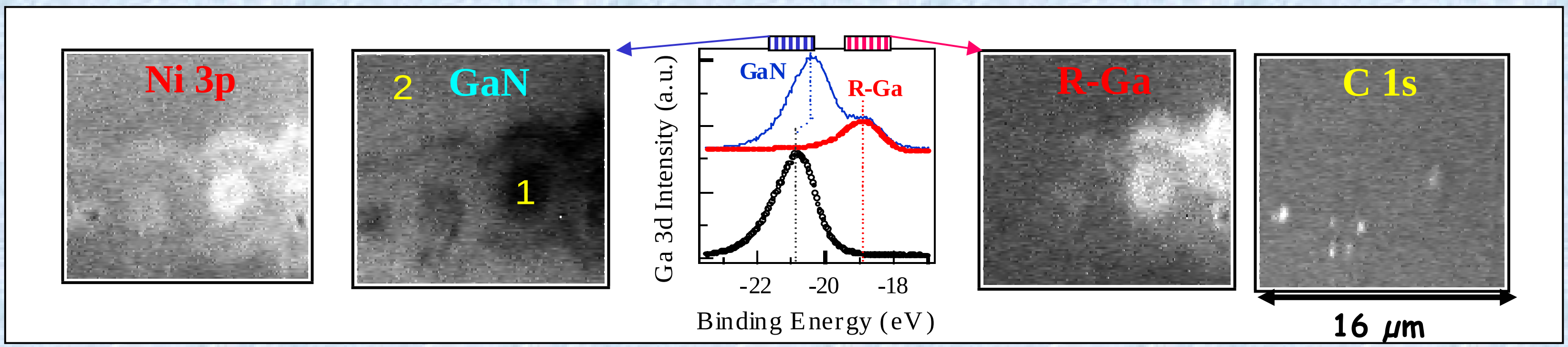
J. Kovac, A. Zalar, M. Remaskar et al, Josef Stefan Inst., Luibljana,& ESCAMicroscopy

Heterogeneity related to defective structure
Me/SC interfaces: Ni/GaN



Interfacial reaction: ⇒ $Ni_xGa_y(N)+N_2$;
- Starts at RT;
- Higher activity at the 'defect areas';
- Heterogeneity 'maximum' at ~300 C;
- Ni penetration into GaN lattice;
- C embedded in the 'holes';

SiC defects propagating into GaN epilayers lead to notorious changes in the film morphology: 'dark holes' in the Ga3d and N1s maps = micropipes?



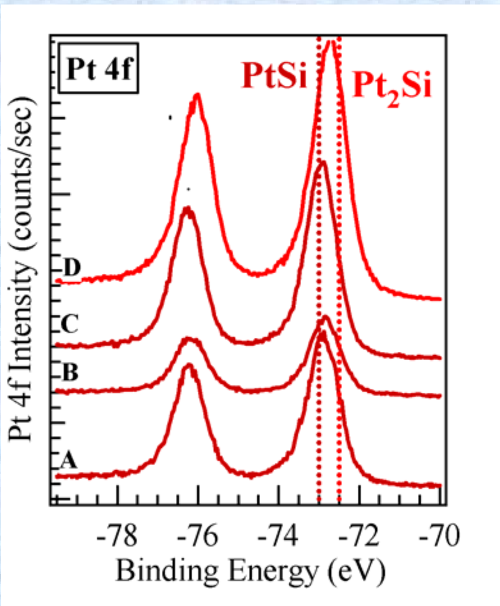
A.Barinov et al. APL 79, 2752.

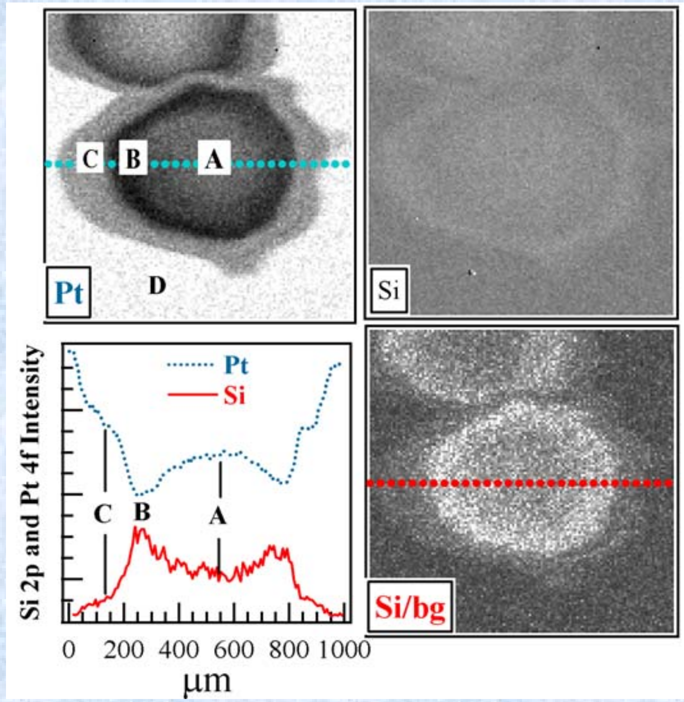
Maping core level electron emission (CLEE):

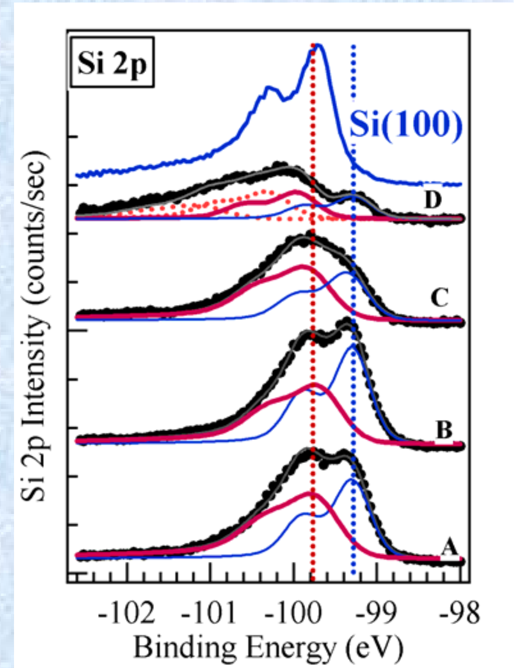
Laser-induced reactions used for “writing” silicide interconnects

ZP-SPEM

Lateral distribution of Pt-silicide phases: Pt4f and Si2p maps





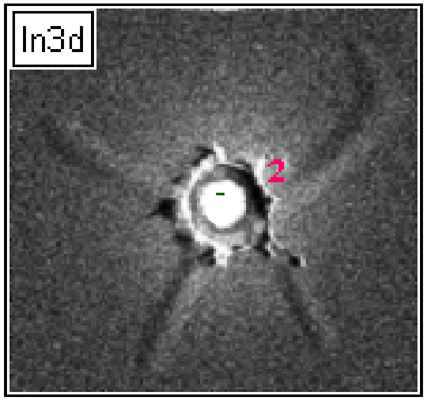


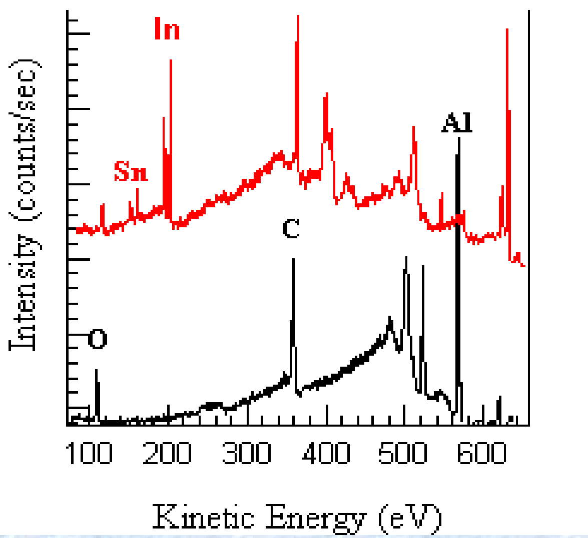
The reaction rate in molten state (A) is faster and causes depletion of Pt from the surrounding region (B). Beyond (B) the magnitude of Pt – Si intermixing and the PtSi film thickness is exclusively controlled by the temperature. A. Nelson et al, APL 81, 11246

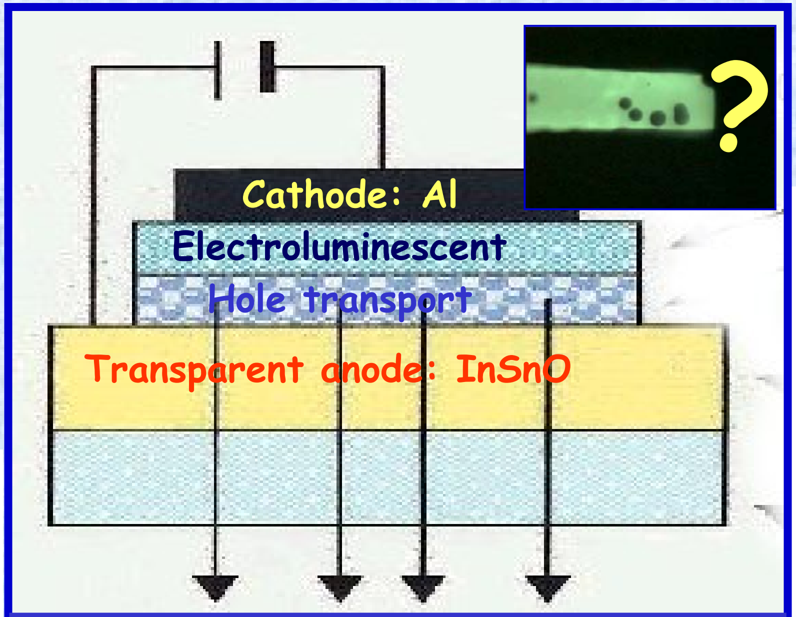
Maping core level electron emission (CLEE):

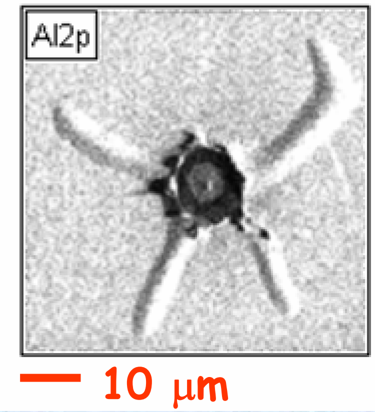
Degradation of organic light emission devices

ZP-SPEM









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

With SPEM we found anode material (In and Sn) deposited around the hole created in the Al cathode.

P. Melpigniano et al, APL 86, 41105

Imaging 'signal attenuation': spatial anisotropy in the oxide film thickness on Ru(0001)

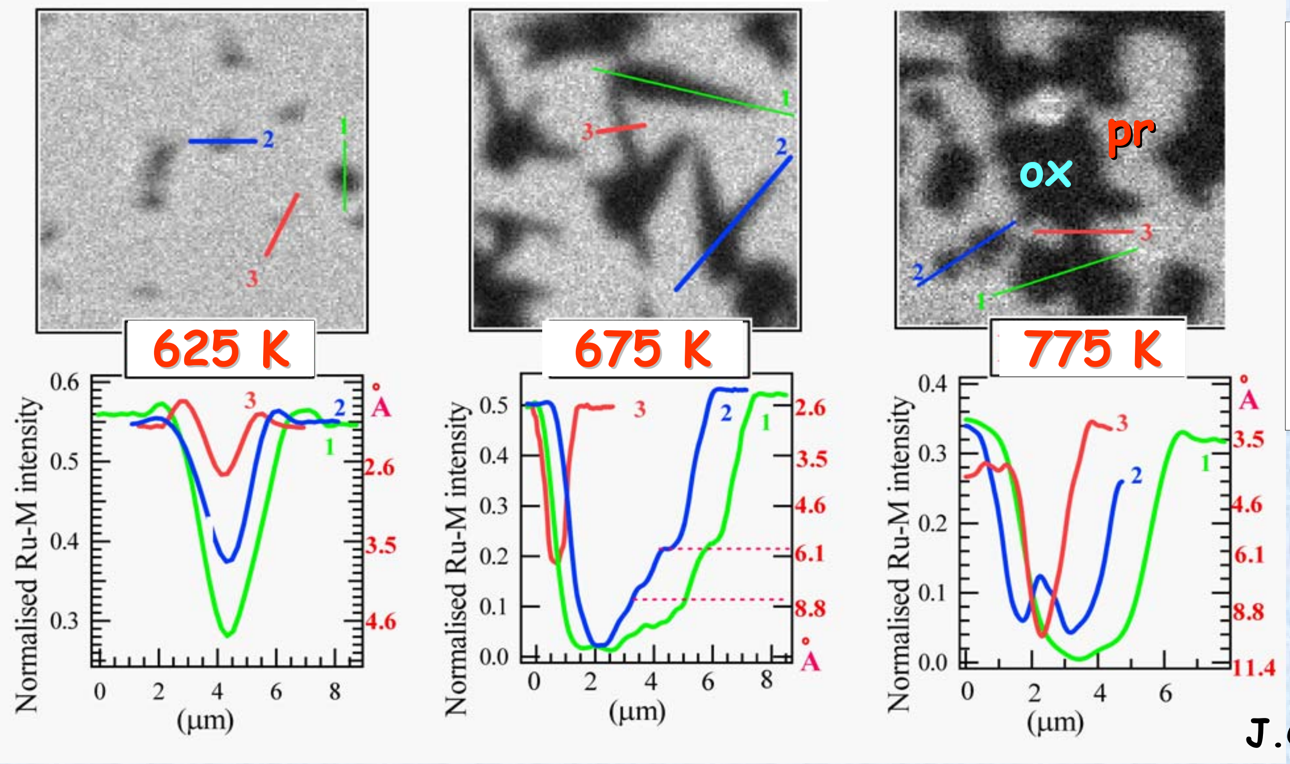
ZP-SPEM

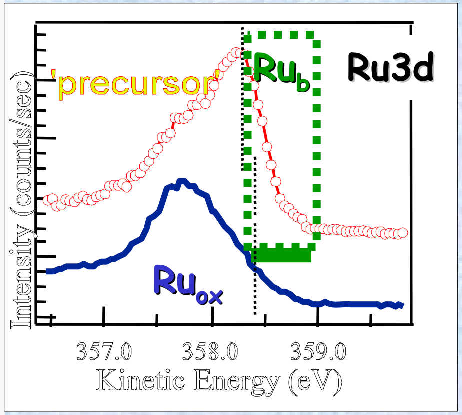
Maps of Ru bulk component: measure of the Ruox thickness:

$$I_{Ru(b)} = I_{Ru(0)} \cdot e^{-x(Ruox)/\lambda\cos\theta}$$

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

10^5 L



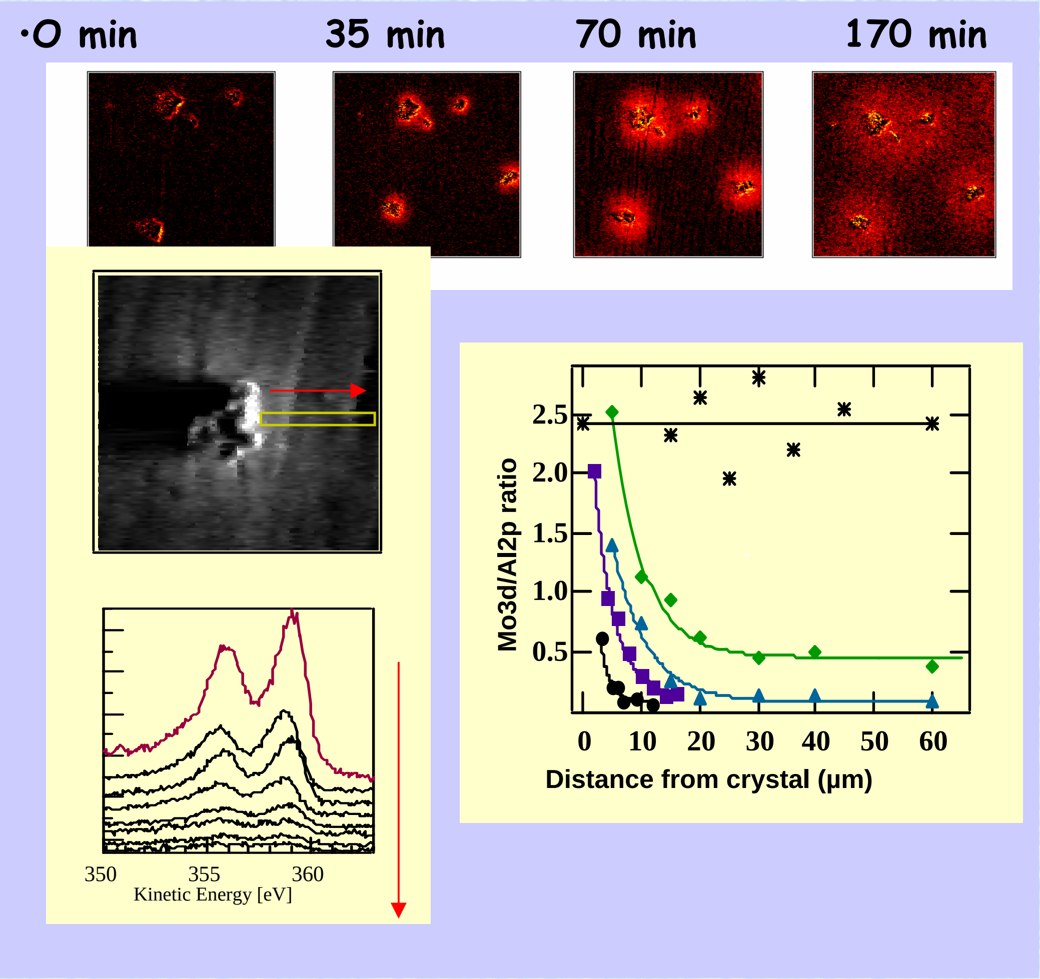


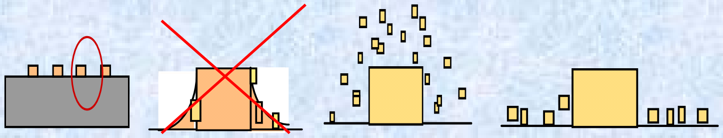
A. Bottcher et al, J.Chem.Phys. 117, 8104.

Maping core level electron emission (CLEE):

Spreading of MoO_3 on Al_2O_3 at 630 K

ZP-SPEM



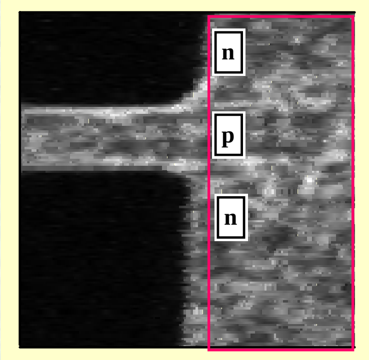


- Ruled out the 'unrolling' carpet mechanism: coverage of the spread phase remains below 1 ML.
- Determined the diffusion constant at 630 K: <u>0.47 μm/min.</u>

S. Günther, J. Chem. Phys. 112 (2000) 5440.

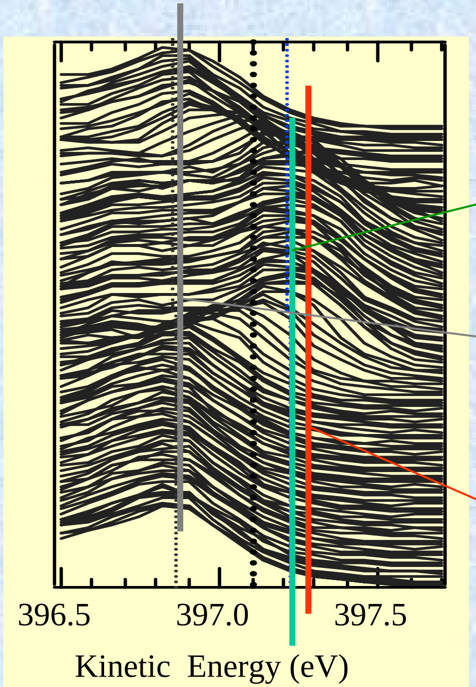
Imaging of band-bending: Si 2p shifts across p-n junctions indicate anomalous spatial variations in the doping profile across a pn-junction Si device:

ZP-SPEM

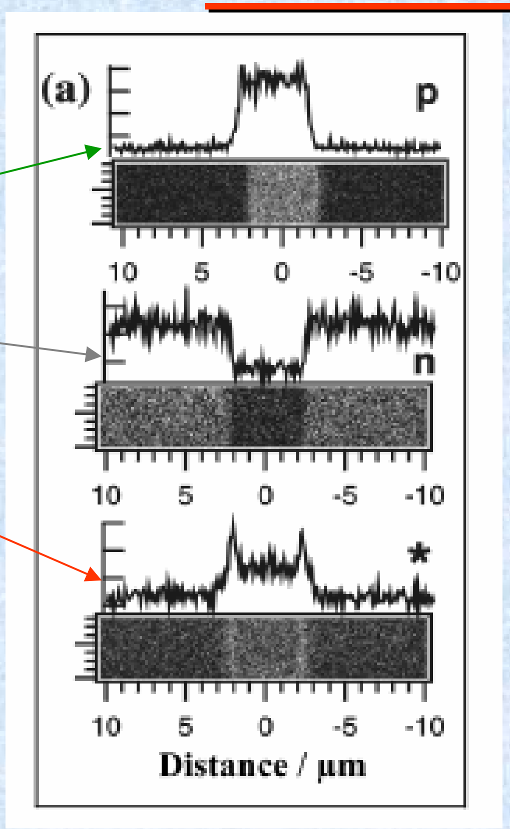


12. 8 μm

Si 2p image :
p-stripe
N=10^{18}/cm^3
(ion implanted B into n-doped Si(100) N=10^{14} /cm^3)

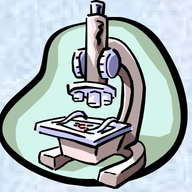


Reconstructed Si 2p spectra corresponding to the p, n and p edge



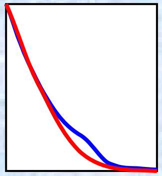
enhanced dopant concentration at the p-edge

R. Phaneuf, JAP88 (2000) 863

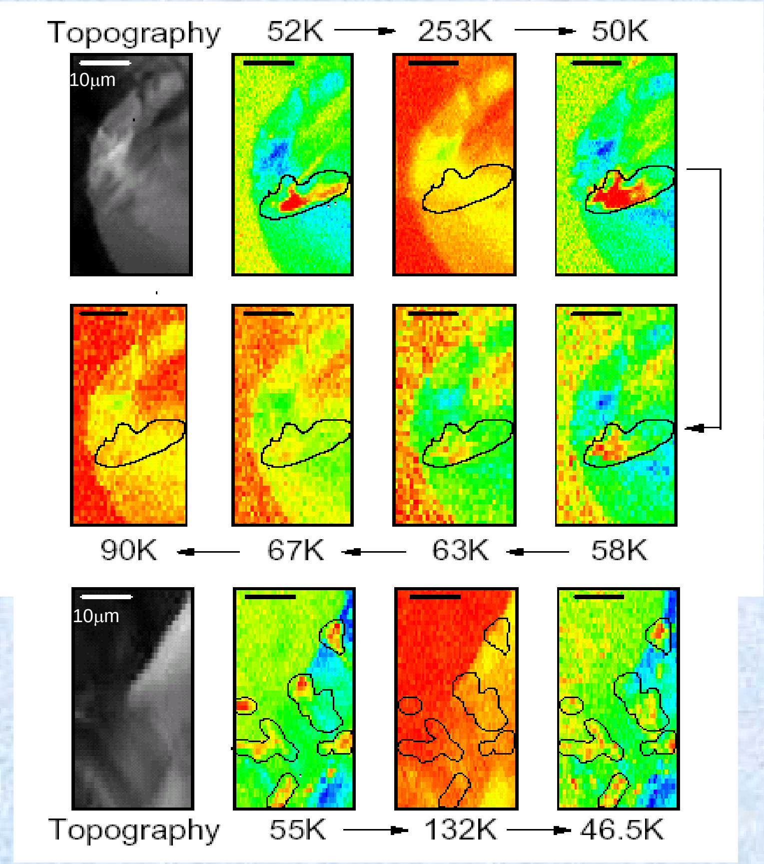


Imaging Fermi edge and the valence band:

metal-insulator transitions in colossal magneto-resistive (CMR) oxides

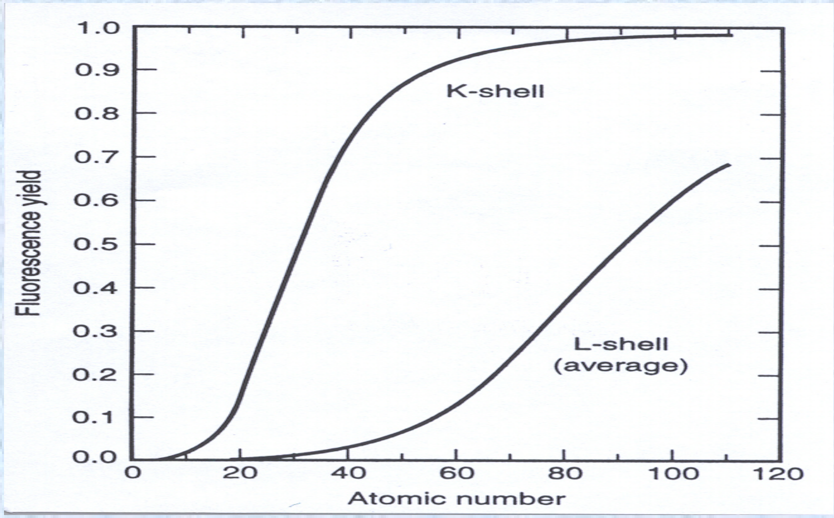


SO-SPEM

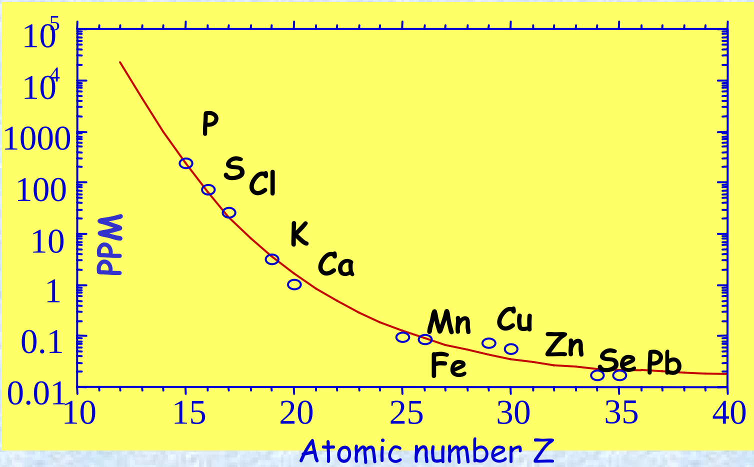


'Electronic phase separation': SPEM spatially resolved images (20x50 μm^2) of the valence band provided the first evidence of memory effects (not related to topography) in the electronic domains during T-induced phase transition from antiferromagnetic, charge-ordered insulating phase to ferromagnetic metallic phase of $La_{1/4}Pr_{3/8}Ca_{3/8}MnO_{3}$:
Insulating patches are reappearing inside the metallic phase: most likely long-range strain effects.
D. D. Sarma et al, PRL 93, 097202

Hard X-ray Microscopy: lower spatial resolution but X-ray fluorescence

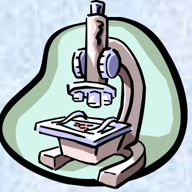


- Penetration depth: > 50μm
- Fluorescence yield.
- *All type of samples*
- μ-XANES (S, P, K, Ca, Fe..)

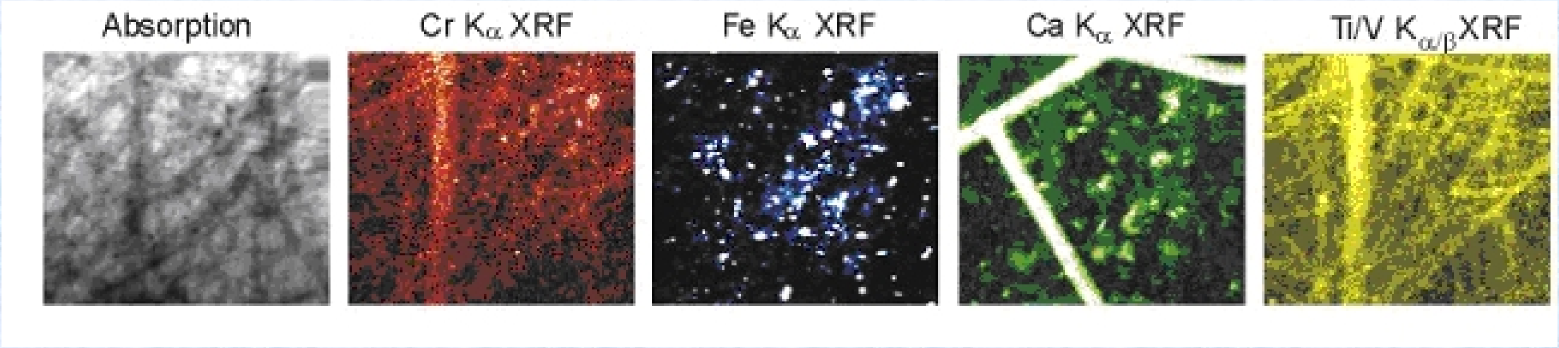


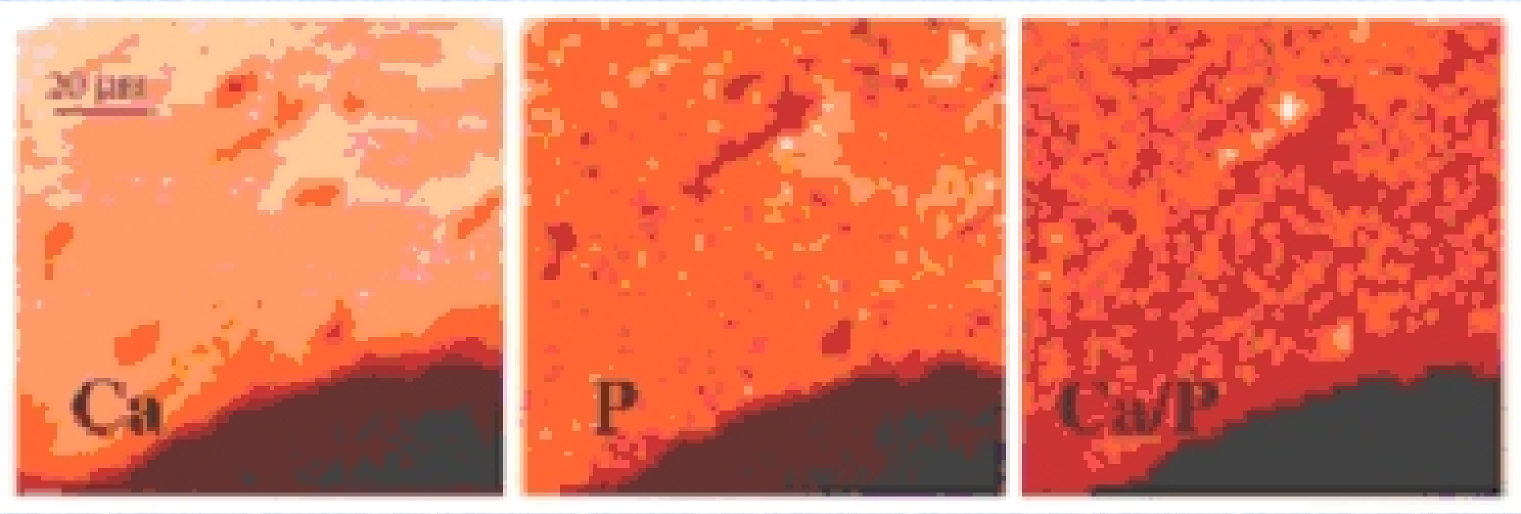
XRF (Scanning + energy/wavelength dispersive detection)

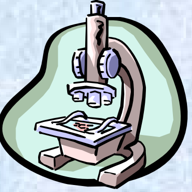
- Element specific (no labelling)
- Low detection limit (trace element).
- High signal-to-background ratio (low dose)



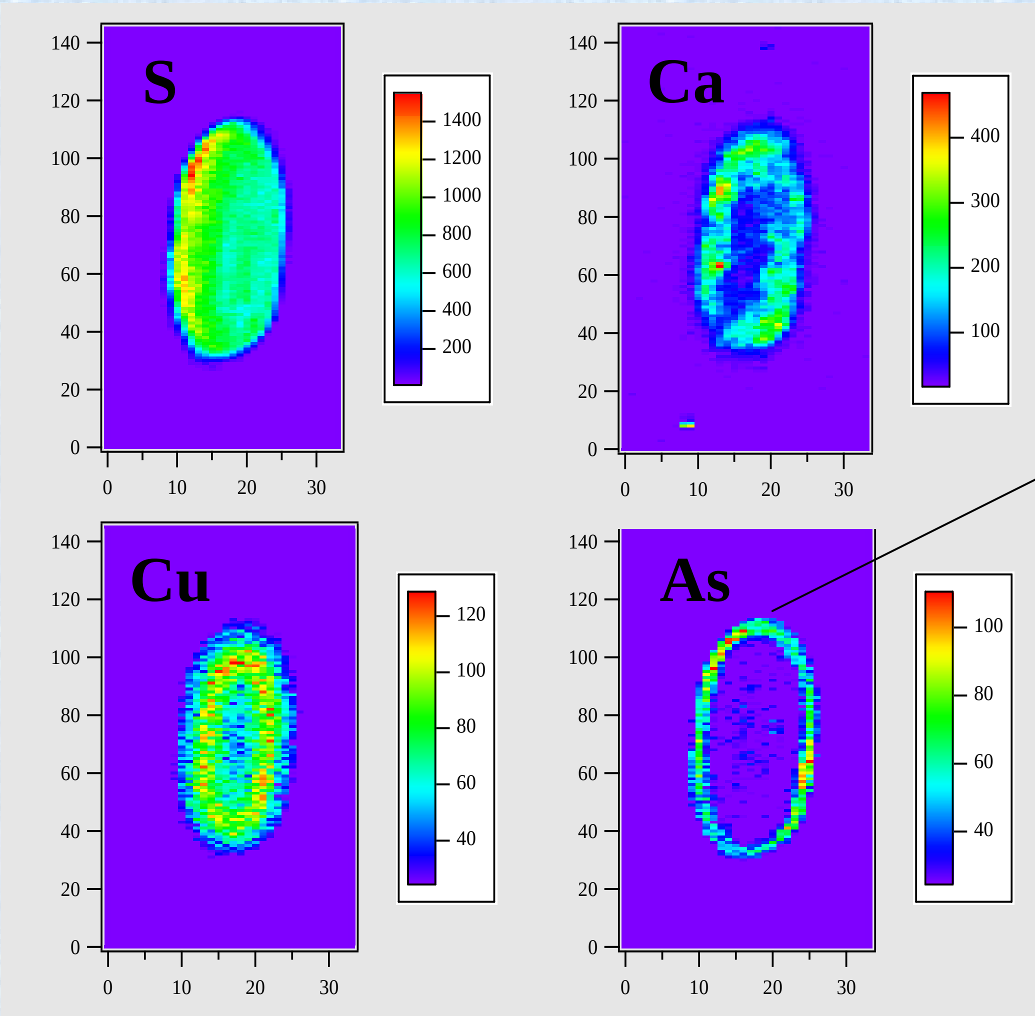
XFS imaging of environmental samples (polluted area near metallurgic plant) and human bones (osteoporosis)



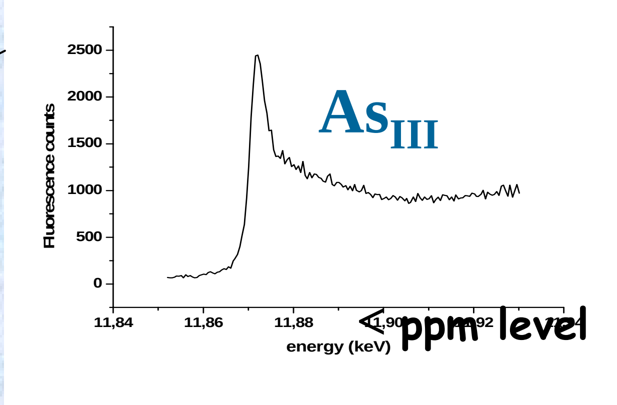




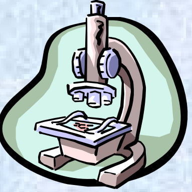
Metabolism of a new As-based drug: μ-XF imaging and spectroscopy on patient's hair



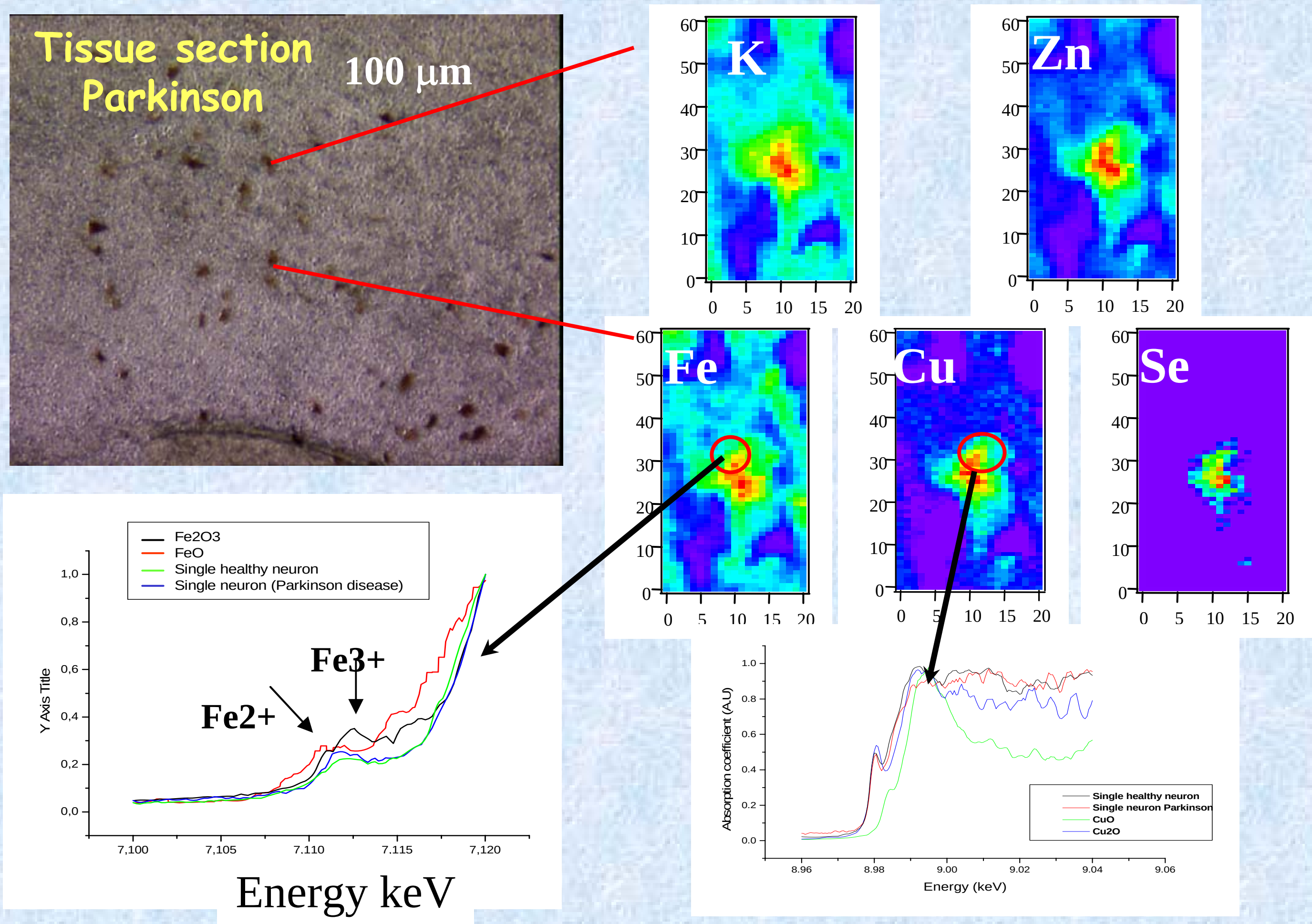
- Hair section from patient with acute leukemia treated with pharmacological doses of arsenic trioxide (>1 mmol/l)



I. Nicolas, Faculté de Pharmacie, Paris V
S. Benazeth, LURE

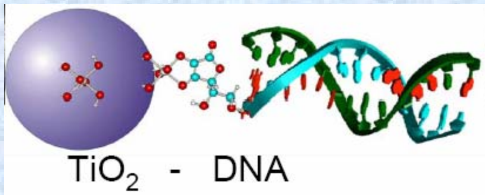


μ-XANES of single neuron: role of metals in processes leading to degeneration and atrophy of nerve cells in Parkinson's disease (PD) & Amyotrophic Lateral Sclerosis (ALS)



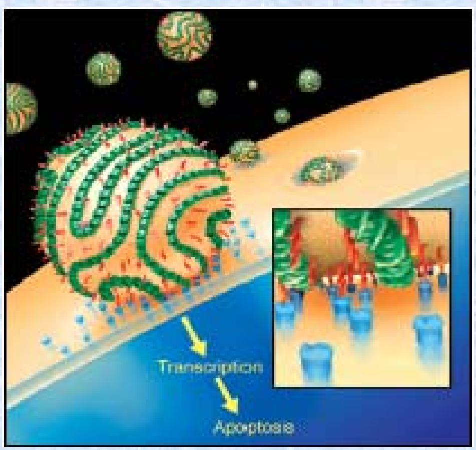
Courtesy J. Susini, ESRF

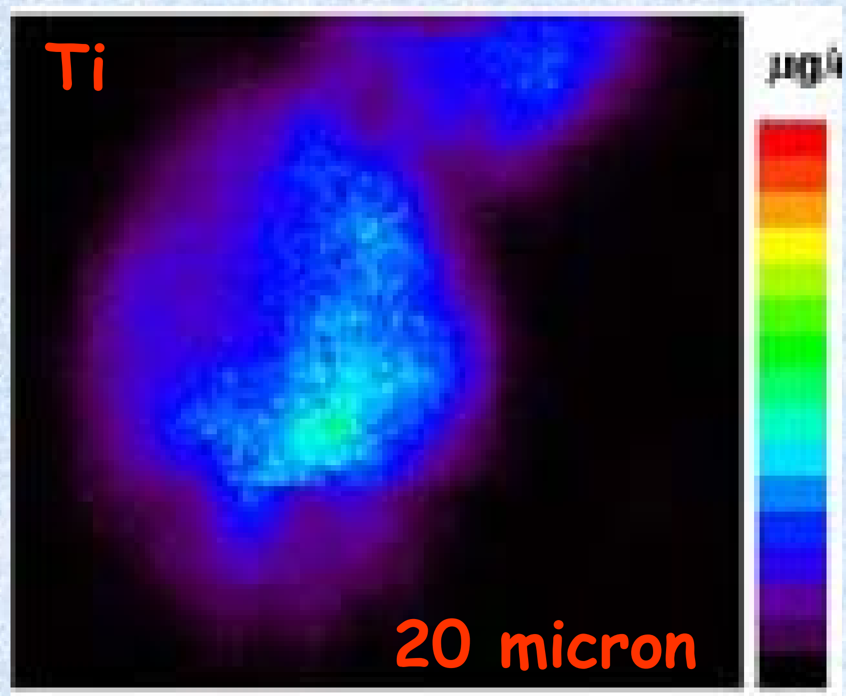
TiO2-DNA nano-composites for in-vivo Gene Surgery: XRF maps

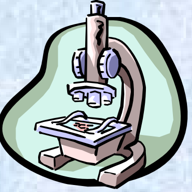


Chemical FS imaging is crucial to quantify the success rate and reveal the location of the single stranded nanoparticle in the cell chromosome

DNA-TiO2 particle crossing cell walls

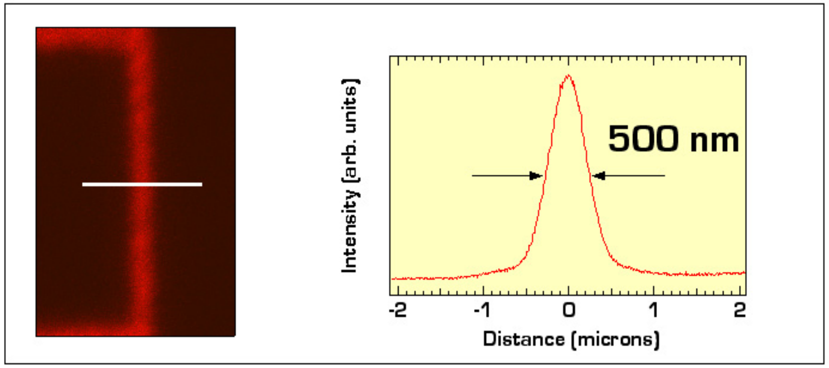






New perspectives for more efficient utilisation of the synchrotron facilities: direct writing of photoluminescent structures with focused beam

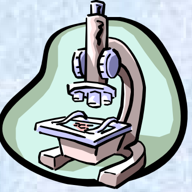
Main advantages of using x-rays for maskless writing: (i) smaller lateral spreading of the x-ray beam and (ii) weaker charging effects



Stable Color Centers with fabricated in thin LiF films using SPEM at ELETTRA

Applications: efficient point light sources in near-field optical microscopy and optical memories, novel miniaturised coherent light sources, such as active waveguides and microcavities for optolectronics

R. Larciprete et al, Appl.Phys.Lett. 80 (2002) 3862



Multiple applications by choosing the best spectroscopic μ- approach

Different domains of material science:

(Surf-XPS & Surf&Bulk – XANES, bulk – FS&XANES)

- Composition, electronic and magnetic properties at micro and nano-scales complex materials, micro- and nano - structures, superconductors, polymers, astrophysics, tribology and corrosion phenomena etc. XPS, XFS & XANES
- Mass transport due to reactions, bulk and surface electromigration: XPS & XFS.
- Environmental and Earth Sciences XFS & XANES
- Bio-science and medicine XFS & XANES

samples “natural” environment: liquid or air, cryo-techniques, high pressure