Soft x-ray microscopy

(Zone-plate based soft-x-ray spectro-microscopy)

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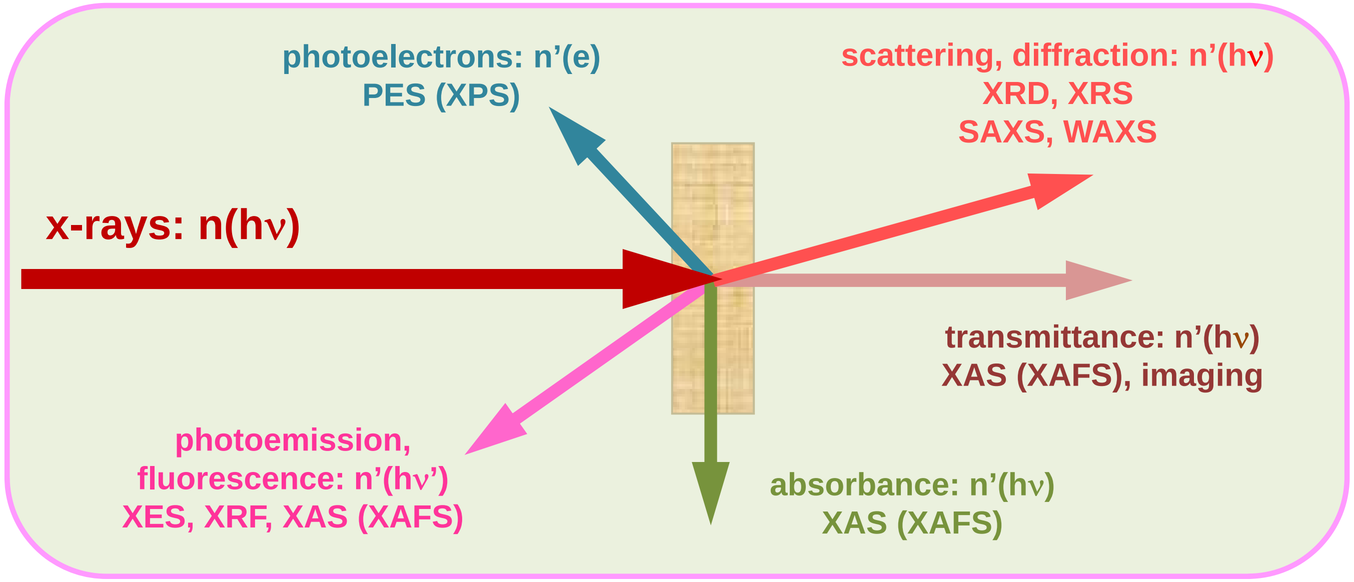
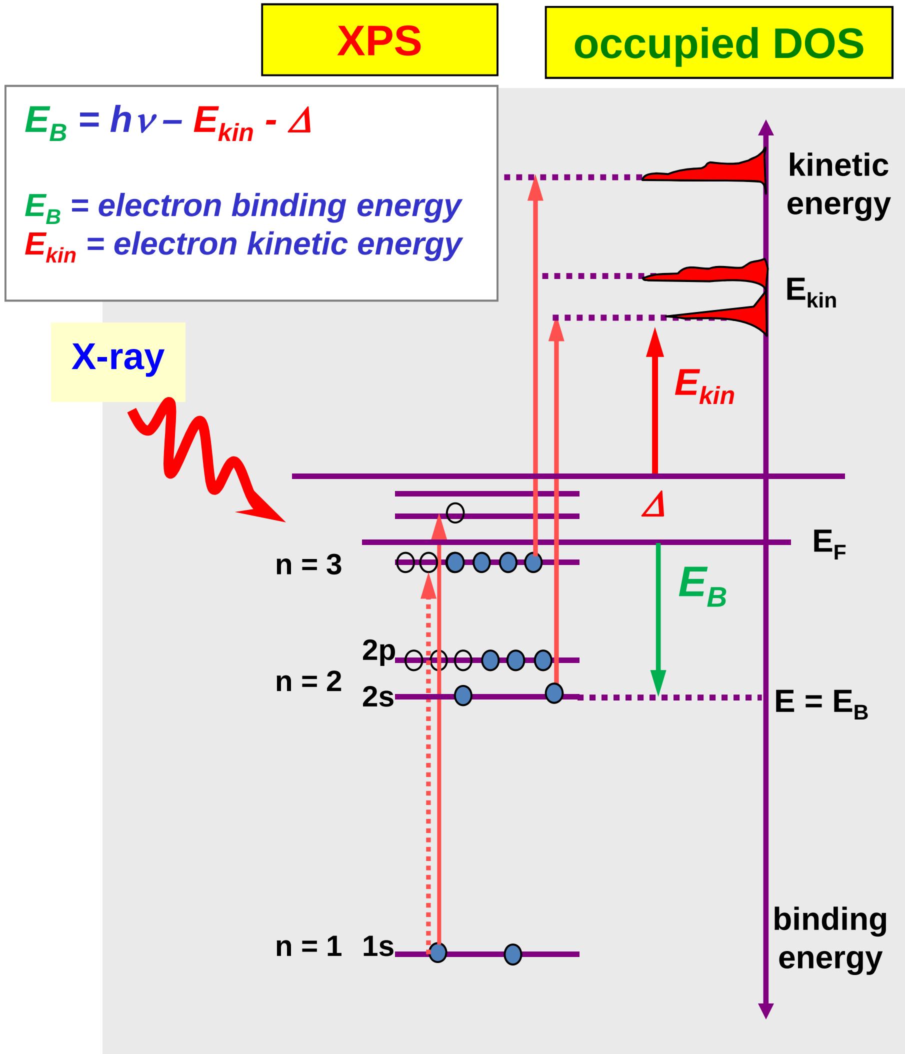
Contents

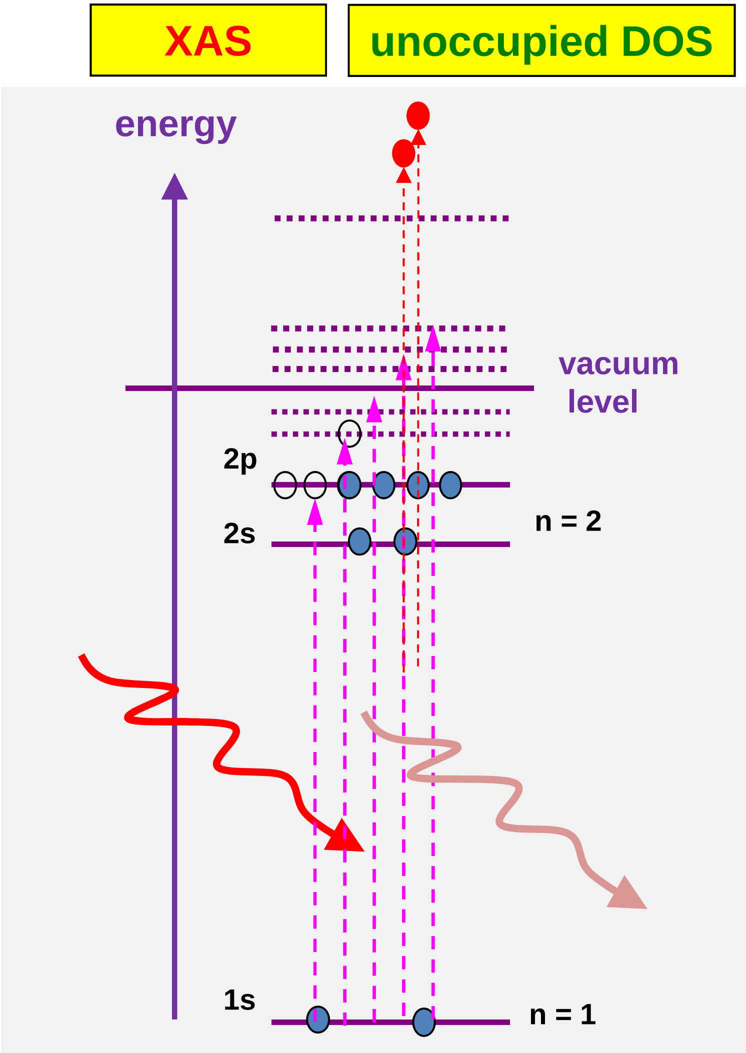
1. Use of x-rays



PES: photoemission/ photoelectron spectroscopy
XPS: X-ray photoemission/ photoelectron spectroscopy
XRD: X-ray diffraction
XRS: X-ray scattering
SAXS: Small angle x-ray scattering
WAXS: Wide angle x-ray scattering
XAS: X-ray absorption
XAFS: X-ray absorption fine structure
XES: X-ray emission spectroscopy
XRF: X-ray fluorescence

1. XPS & XAS for materials science…





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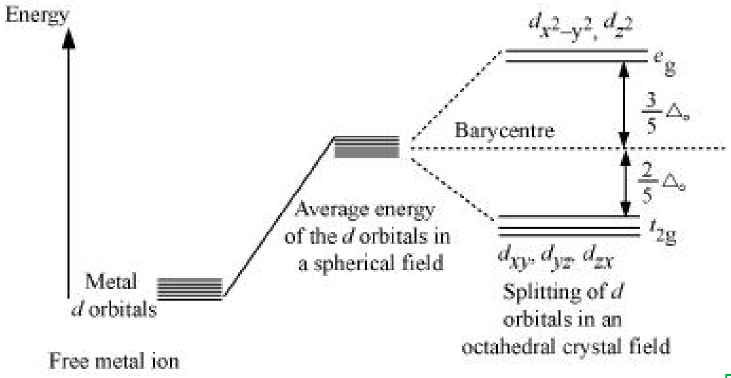
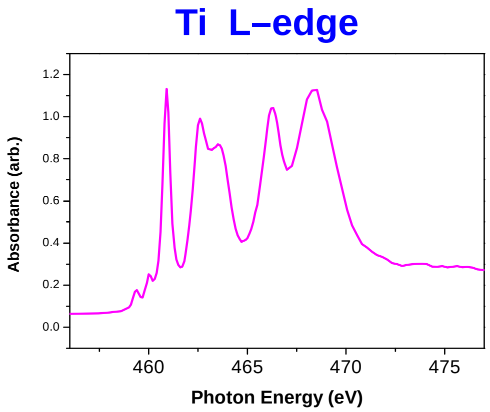
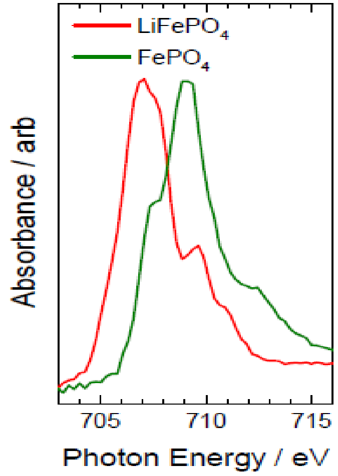
1. Practical use of XPS & XAS spectroscopy…

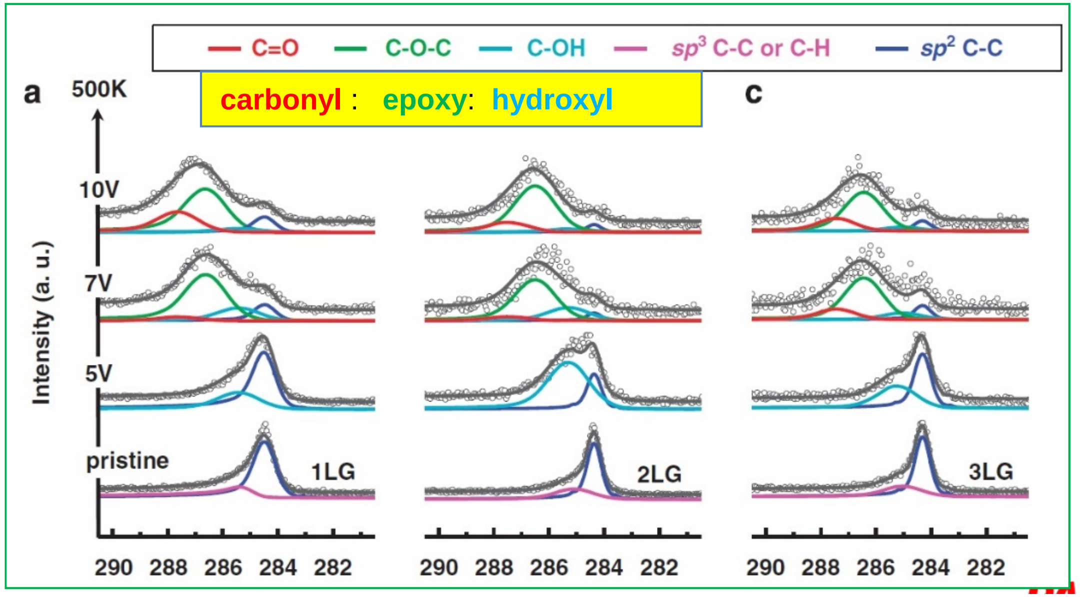
element, crystal structure, chemical states, oxidation state, magnetic moment, electronic structure, …

W. C. Chueh et al, Sandia Report, 2012.









I. –S. Byun et al., NPG Asia Materials (2014) 6, e102

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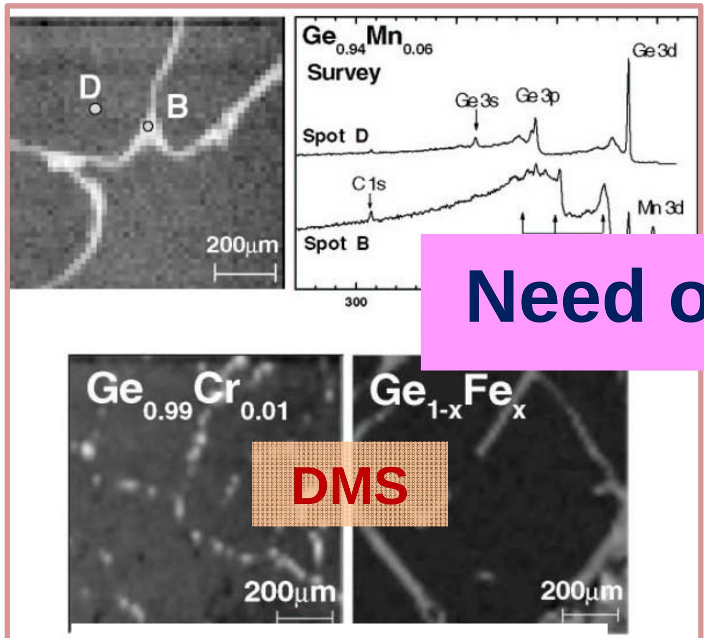
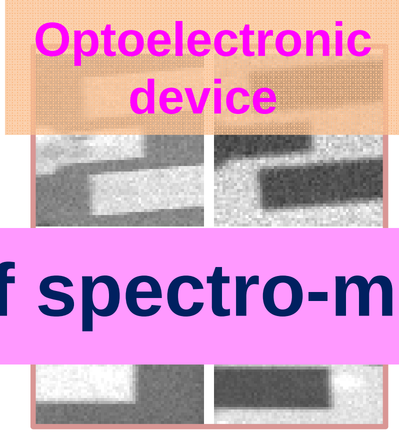
Need of spectro-microscopy

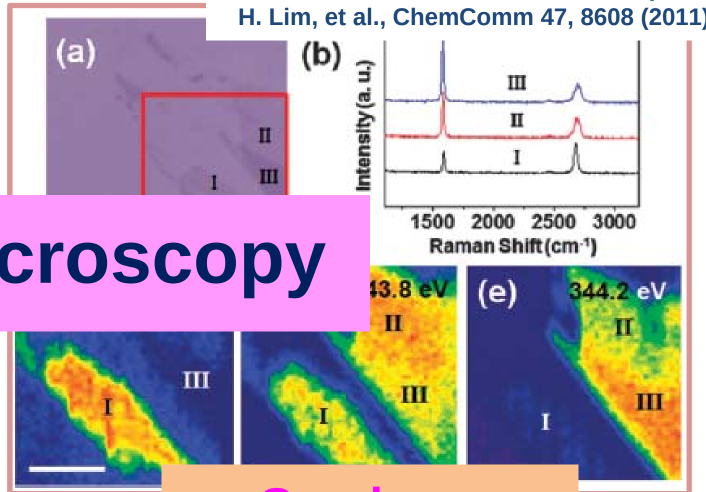


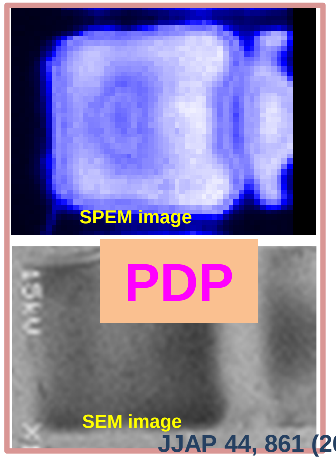
J. S. Kang, et al., Phys. Rev. Lett. (2005)



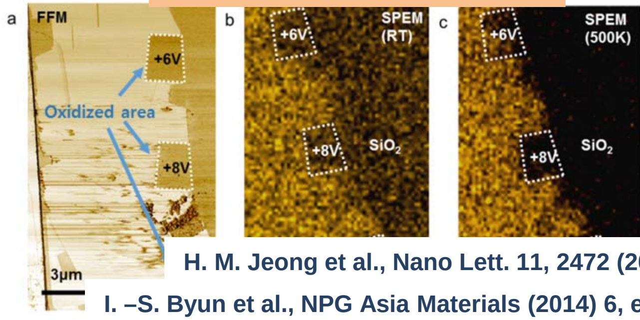
Appl. Phys. A 78, 623 (2004)

K.J. Kim et al., Adv. Mater. 20, 3589 (2008)
H. Lim, et al., ChemComm 47, 8608 (2011)

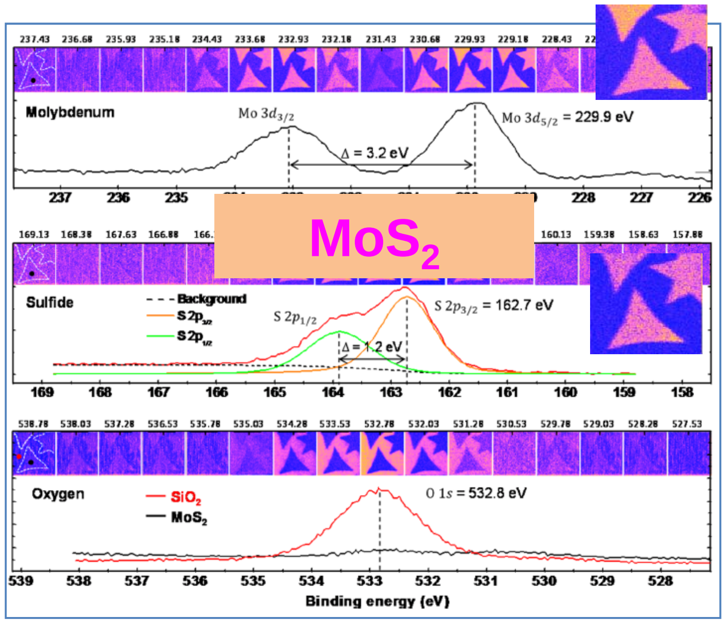




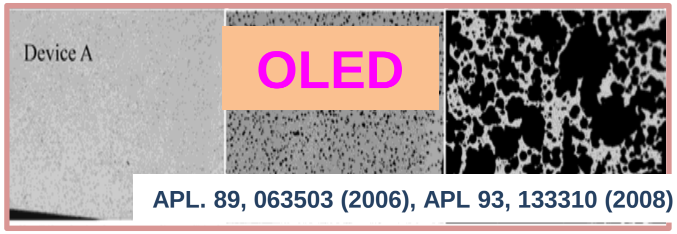
JJAP 44, 861 (2005)



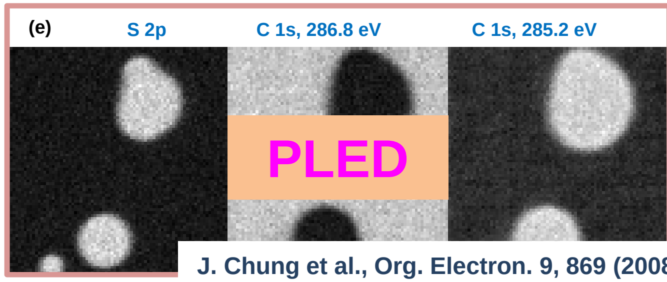
H. M. Jeong et al., Nano Lett. 11, 2472 (2011)
I. –S. Byun et al., NPG Asia Materials (2014) 6, e102



I. Song et al., Angew. Chem. Int. Ed. 53, 1266 (2014)
W. Park et al., ACS Nano 8, 4961 (2014)



APL. 89, 063503 (2006), APL 93, 133310 (2008)



J. Chung et al., Org. Electron. 9, 869 (2008)

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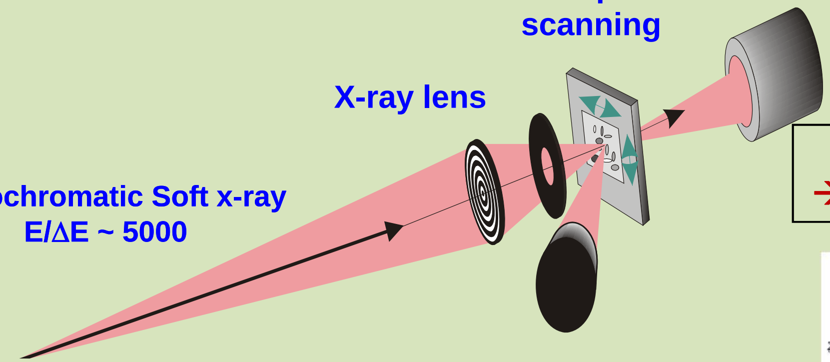
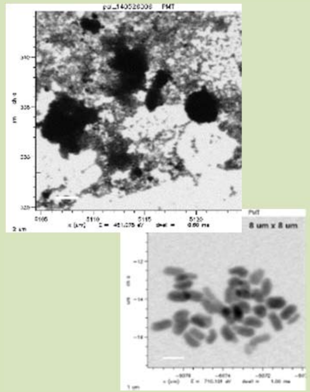
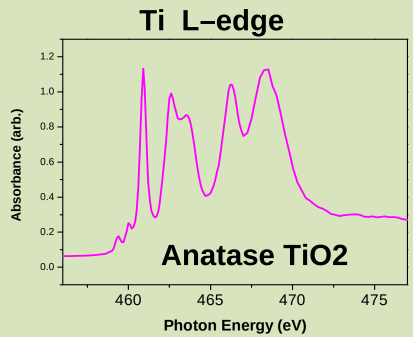
1. Spectromicroscopy schematic

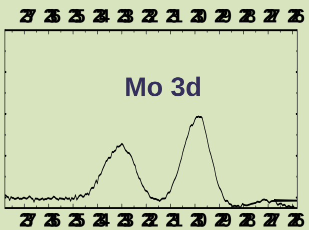


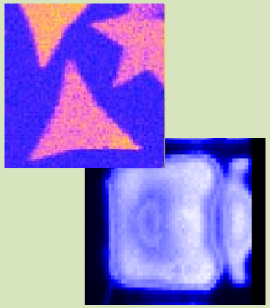
XAS (x-ray absorption spectroscopy)
→ STXM (scanning transmission x-ray microscopy)





XPS (x-ray photoelectron spectroscopy)
→ SPEM (scanning photoelectron microscopy)

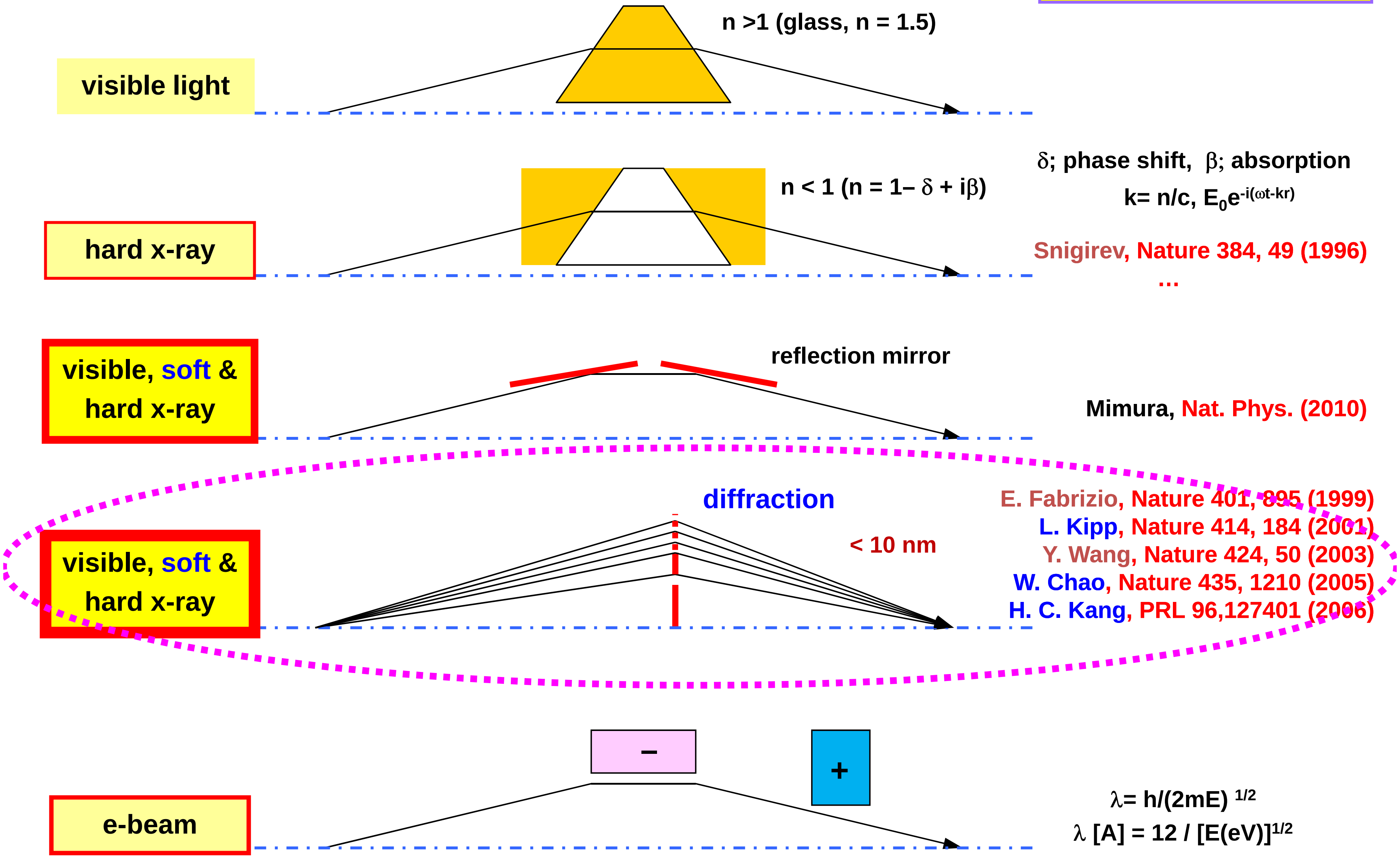




→ **element, crystal structure, chemical states, oxidation state, electronic structure, magnetic moment, …**

1. Lenses for microscopy

Diffraction limit ~ 1.22 λ



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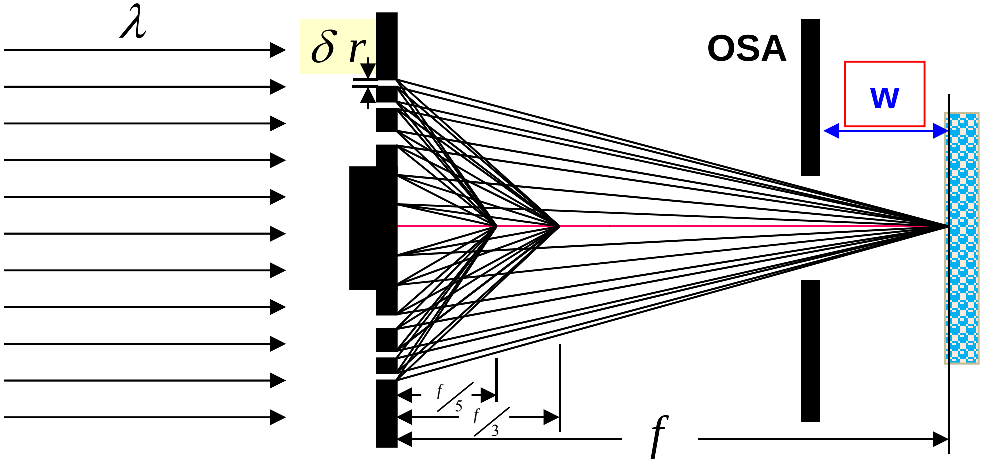
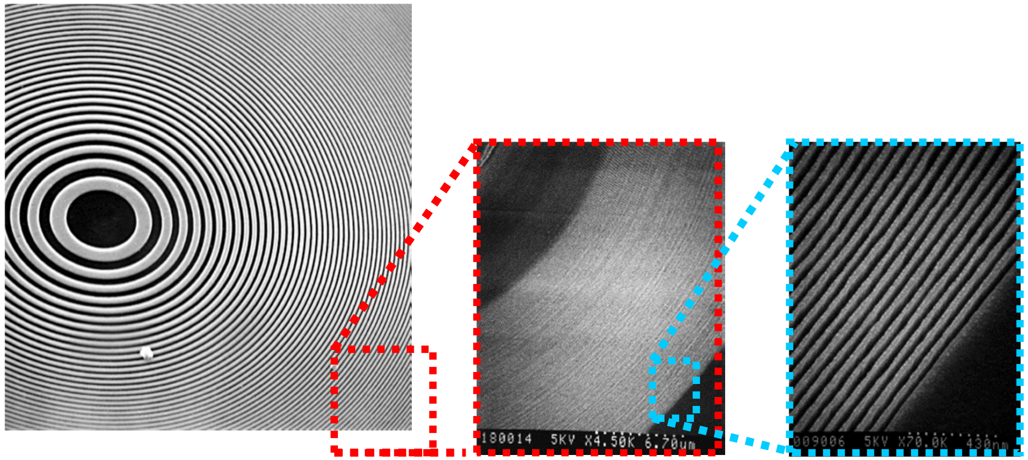
1. zone plate as a focusing lens (< 10 nm)

Focal length: depends on E.
Order sorting aperture (OSA) is needed: short working distance (w).



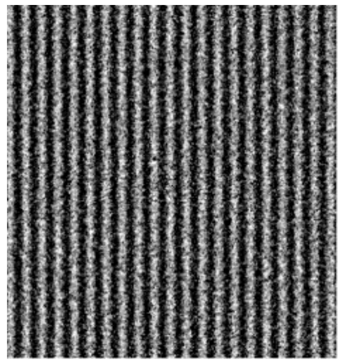
$$f = \frac{4N(\delta r)^2}{\lambda}$$

$$\text{S.R.} = 1.22 \times \delta r$$



Soft x-ray image of
15 nm Cr/Si lines & spaces

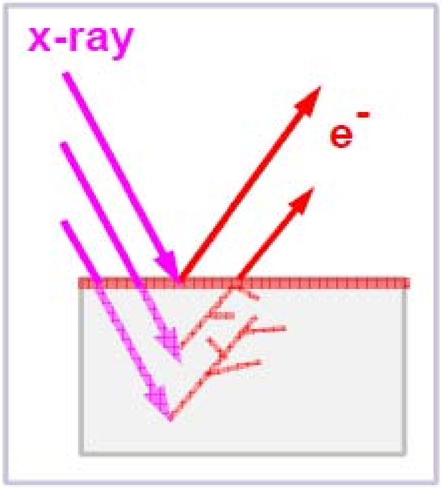
W. Chao, Nature 435, 1210 (2005)



1. Probing depth/ escape depth

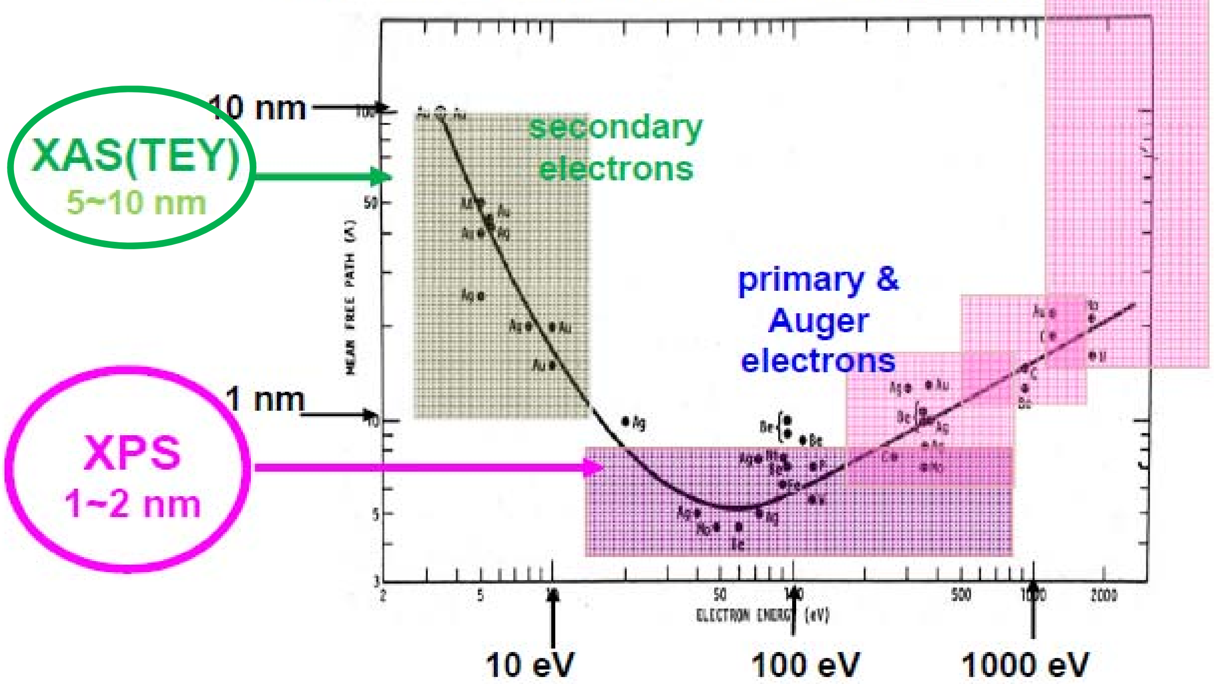
XAS (Tr)
~ 100 um
~ 100 nm

database: www.cxro.lbl.gov



XPS: primary electrons
XAS: secondary (& primary) electrons

B. K.Teo, *EXAFS: Basic Principles and Data Analysis*, Springer, 1986.



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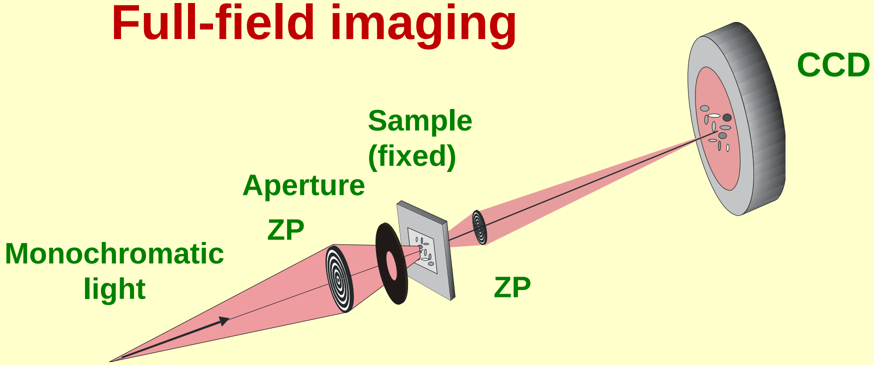
2. Soft X-ray (spectro)-Microscopes

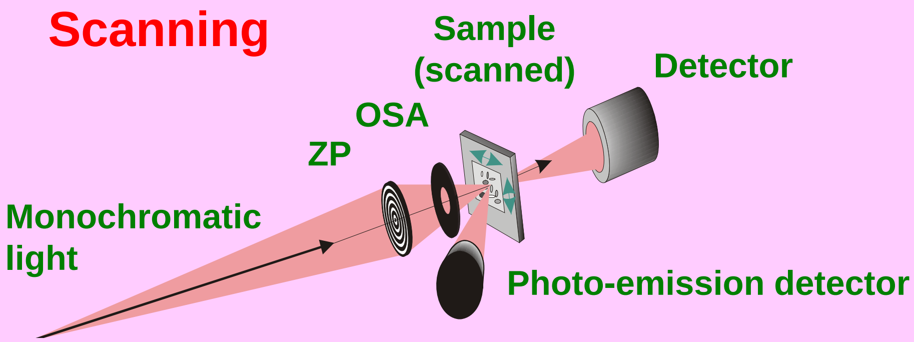
Full-field imaging



XAS → TXM

schematic: www.elettra.trieste.it

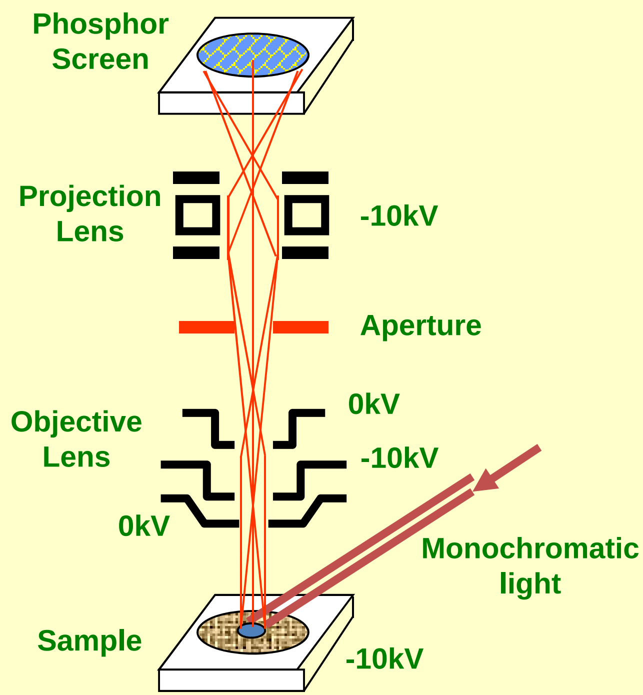
Scanning



XPS → SPEM

XAS → STXM

Full-field imaging w/ electron lens; PEEM



Ptychography

Lensless imaging: CDI

2.1 TXM (transmission x-ray microscopy)

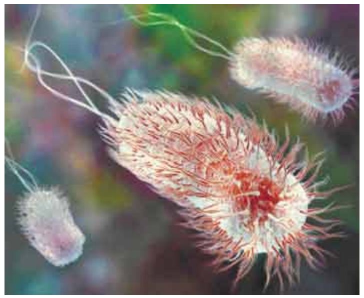
Nondestructive, element specific, …

Spatial resolution: 20 ~ 50 nm.

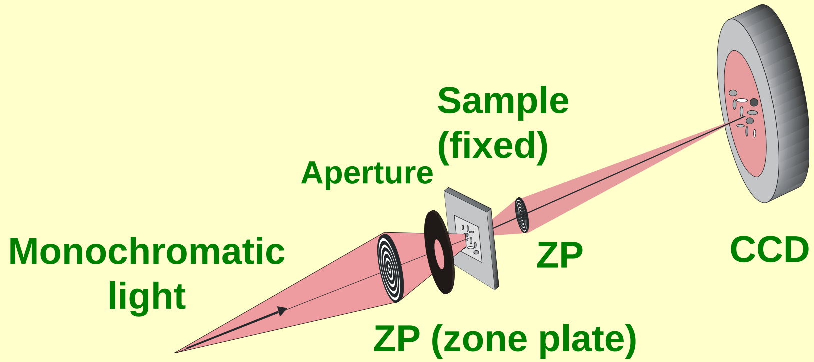
Advantage in bio sample investigation: - no additive for contrast, - internal structure visualization, - 3D CT data acquisition time is shorter than other tools

- easy alignment and operation
- sample can be in atmospheric pressure …

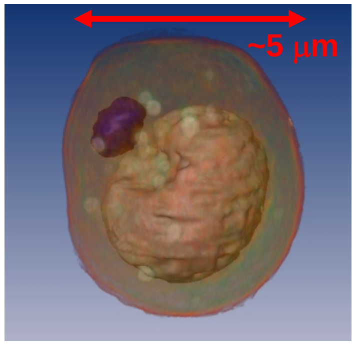
Light microscope

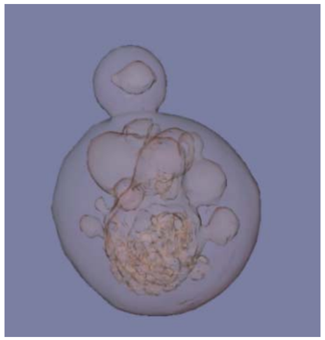


200 ~ 1000 nm



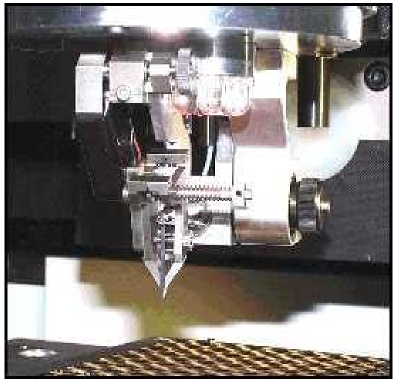
schematic: www.elettra.trieste.it

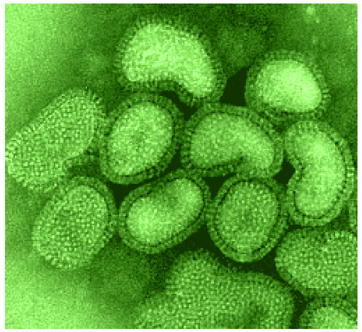




Larabell & Le Gros, Mol. Biol. Cell, 15, 957 (2004)

Electron microscope





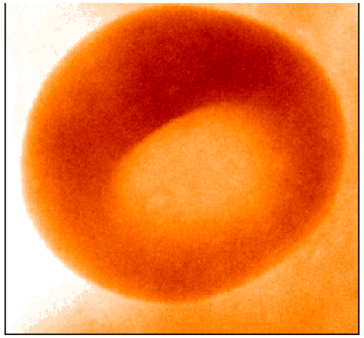
< 1 nm

2.1 TXM application examples:

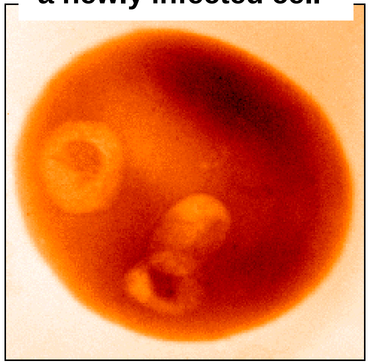
Malaria infected blood cells

Life cycle of malaria in human red blood cells.

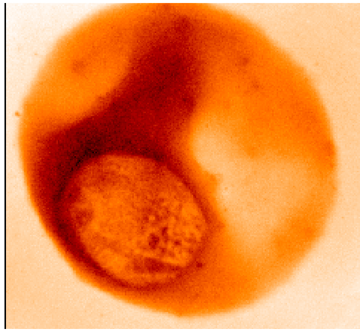
uninfected blood cell



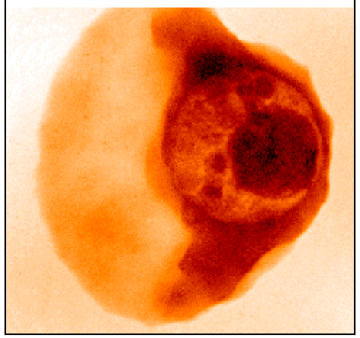
a newly infected cell



a 12- hour old parasite



Leupeptin treated cell

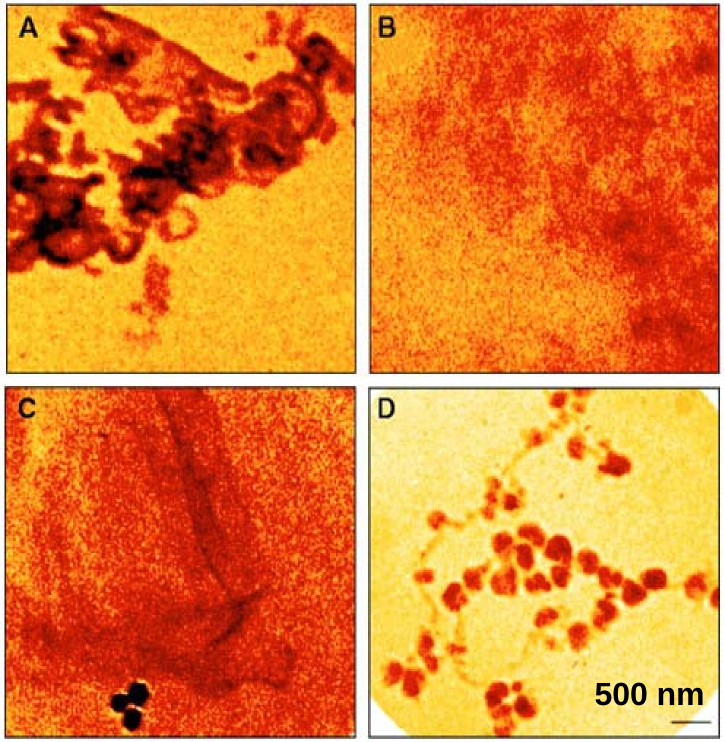


Tubular structure protruding from the parasite into the red blood cell cytosol seen with a young parasite.

Image size = 7 μm x 7 μm

http://www-cxro.lbl.gov

Humic substances: how would they dissolve in the soil?



Effect of solution pH.
- A) Globular and ring-like structures in acidic solution.
- B) Uniform, small aggregates in alkaline solution

Effect of cation presence.
- C) Thread-like structures with divalent cations.
- D) Globular and thread-like structures with trivalent cations.

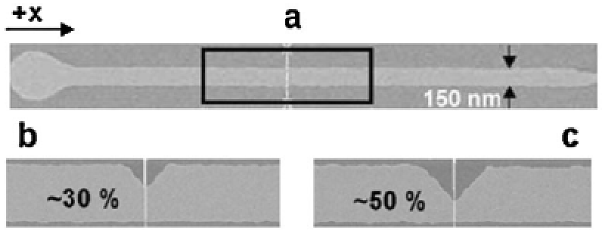
S. Myneni, Science 286, 1335 (1999).

2.1 TXM application examples: 2D-samples

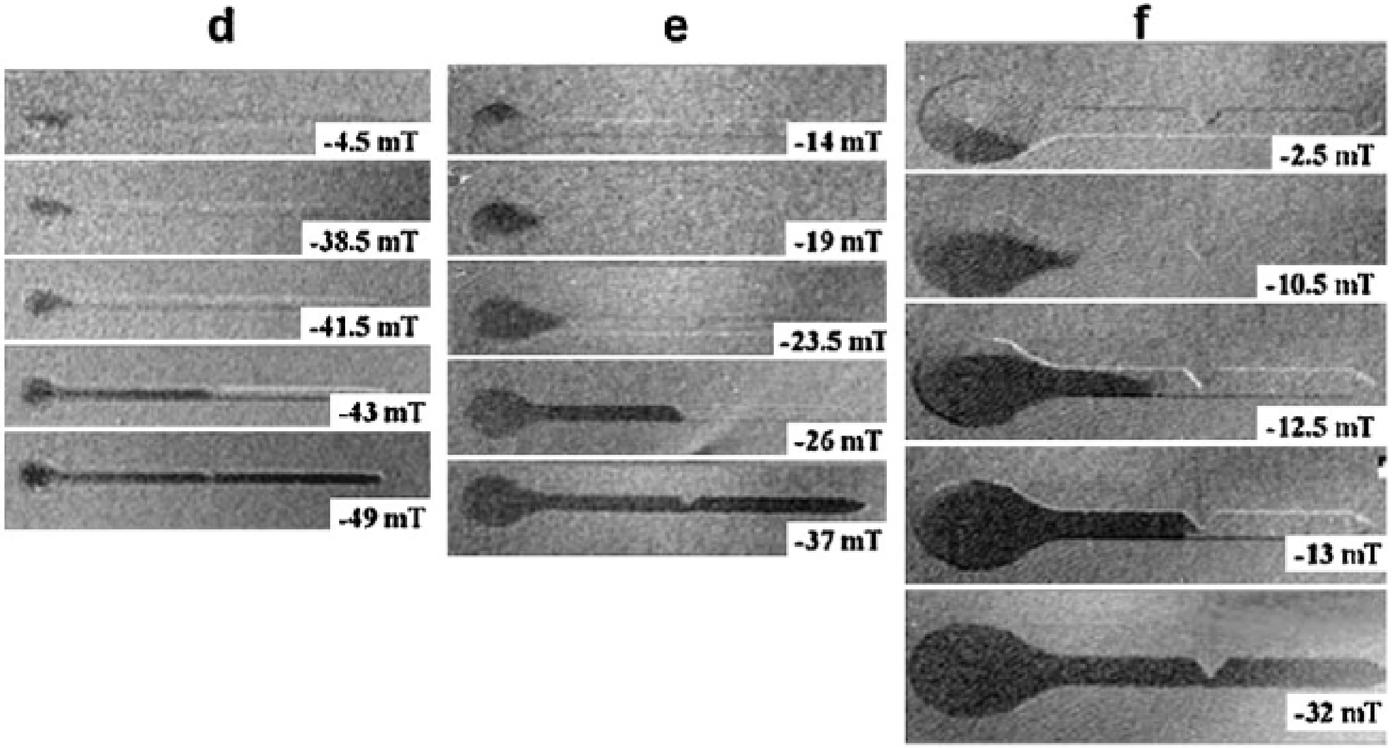
Im et al., Phys. Rev. Lett. 102, 147204 (2009)

Direct observation of stochastic domain-wall depinning in magnetic nanowires

(a) Typical SEM image of a 50 nm thick nanowire with a width of 150 nm together with enlarged notch patterns with notch depths of about 30% (b) and about 50% (c) of the wire width.



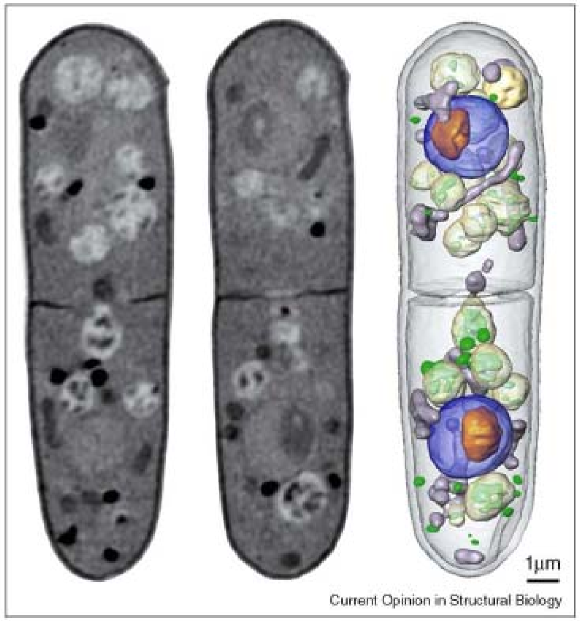
Three representative image sequences of magnetic domain-wall evolution along the hysteresis cycle for wire widths of w ¼ 150 nm (d), 250 nm (e), and 450 nm (f). The magnetic field of the DW evolution pattern is indicated on the lower right.



2.1 TXM application examples: 3D

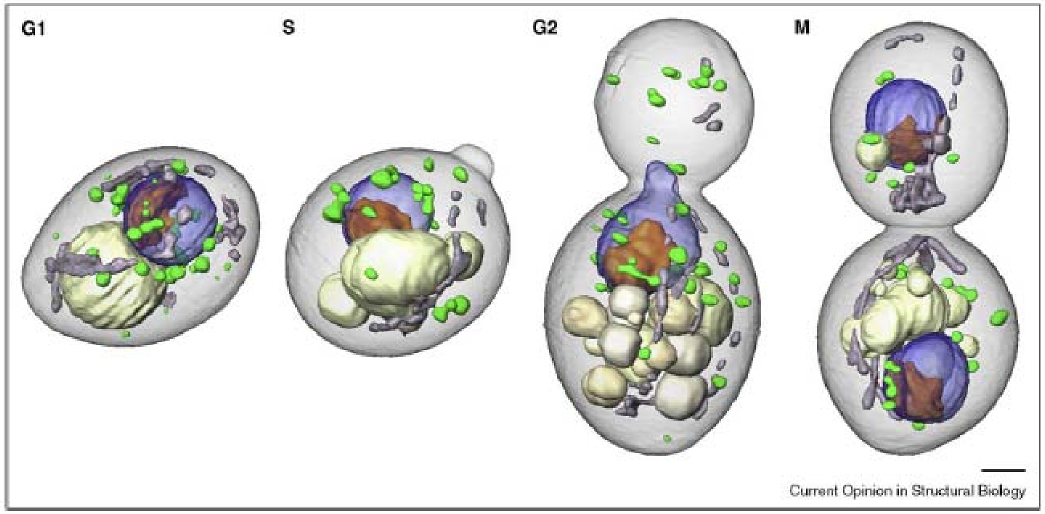
Rapidly frozen fission yeast

Soft X-ray tomography of a rapidly frozen fission yeast, *Schizosaccharomyces pombe*. The data for the complete three-dimensional reconstruction were composed of 90 images, collected through a total of 180° of rotation. Two computer-generated sections through the tomographic reconstruction are shown along with an image showing select organelles that have been segmented and color-coded according to type. Key: nucleus, blue; nucleolus, orange; mitochondria, gray; vacuoles, white; lipid-rich vesicles, green. (X-ray tomographic reconstructions are an update of the work outlined in [27,28••].)



Rapidly frozen Saccharomyces cerevisiae cells

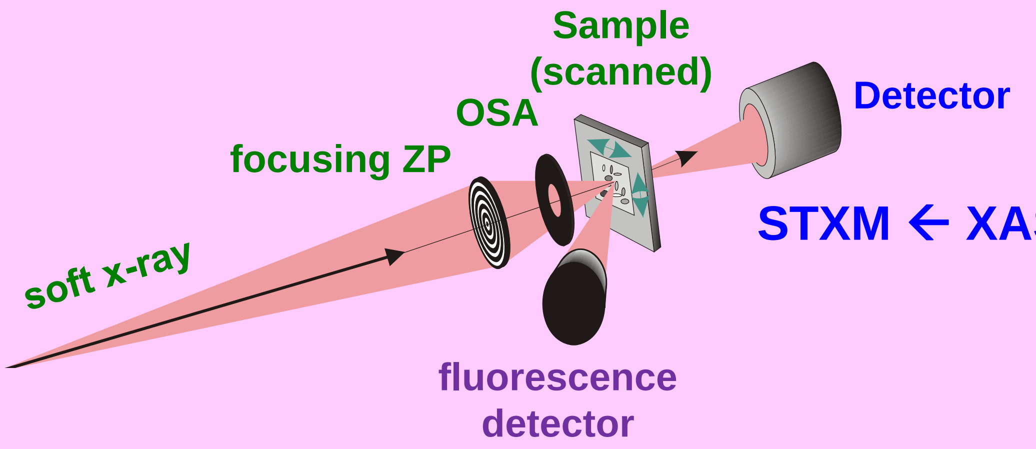
Soft x-ray tomography of rapidly fronzen Saccharomyces cerevisiae cells imaged at each phase of cell cycle – G1, S, M, and G2. Organelles are color-coded as follows: blue, nucleus; orange, nucleolus; gray, mitochondria; ivory, vacuoles; green, lipid bodies. Scale bar, 2um.



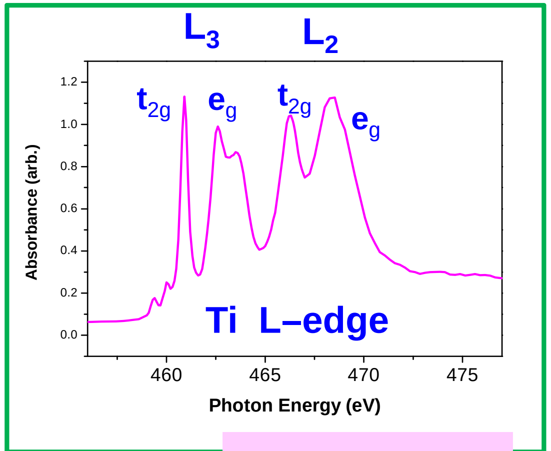
C. A. Larabell and K. A. Nugent, Current Opinion in Structural Biology 2010, 20: 623

2.2 STXM (scanning transmission x-ray microscopy)

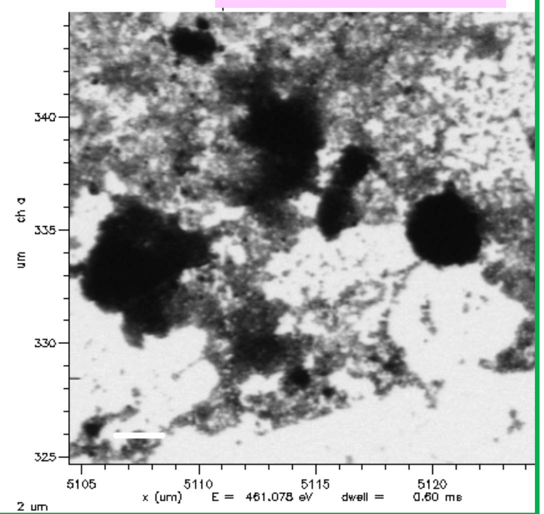
Scanning imaging mode



STXM ← XAS



Anatase TiO_2



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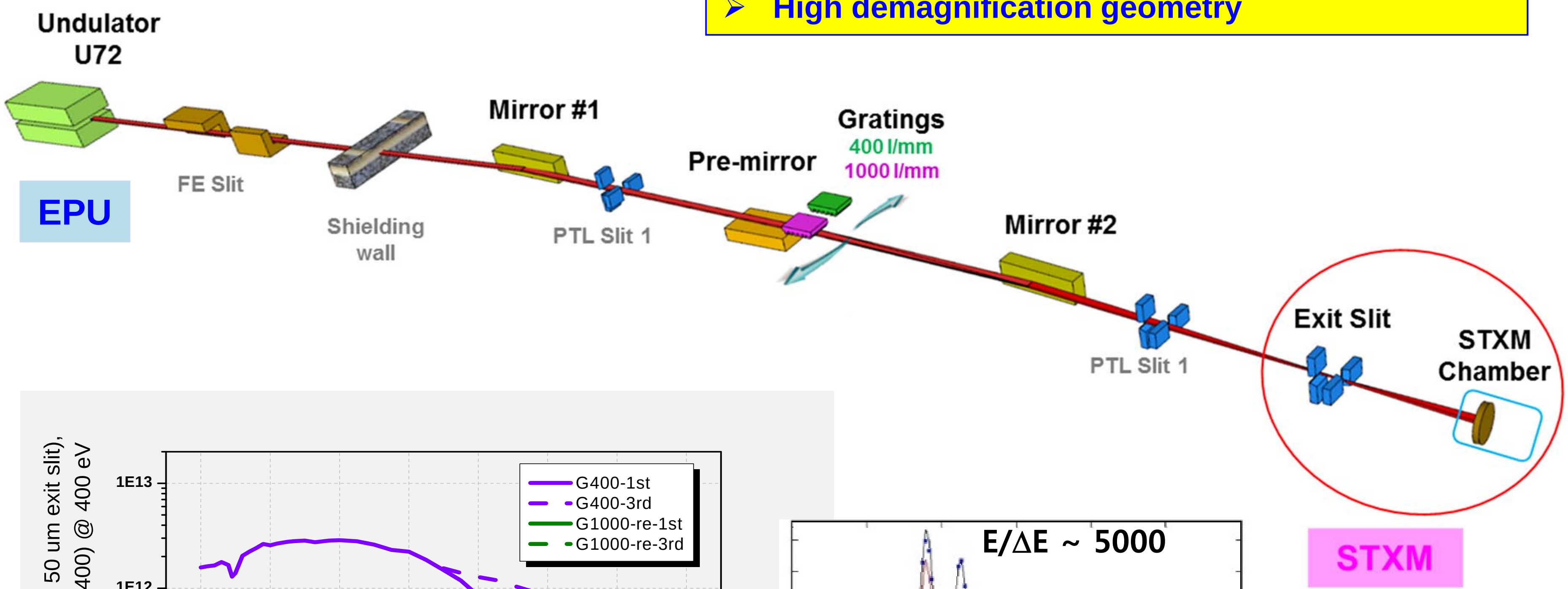
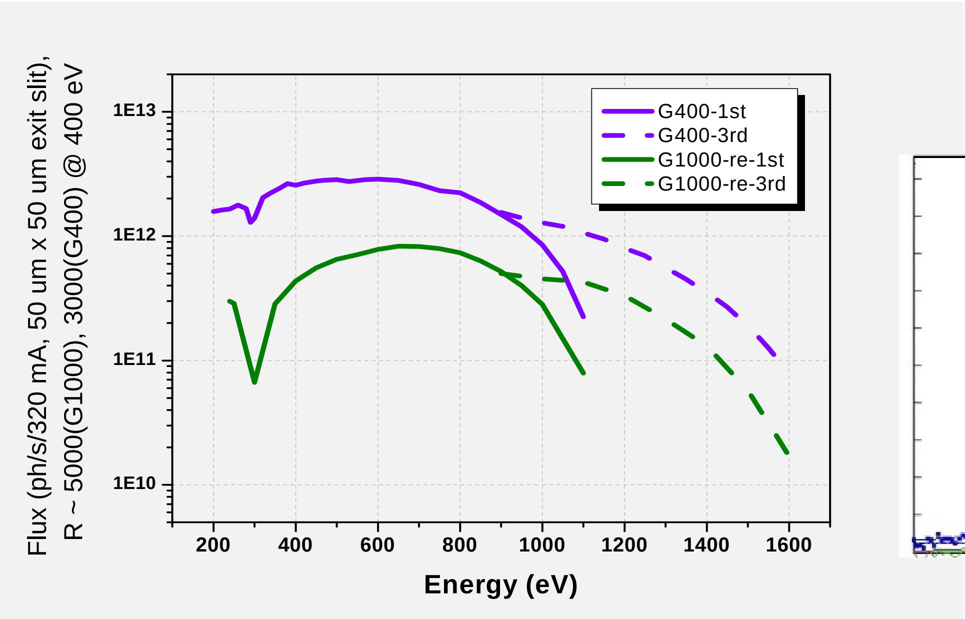
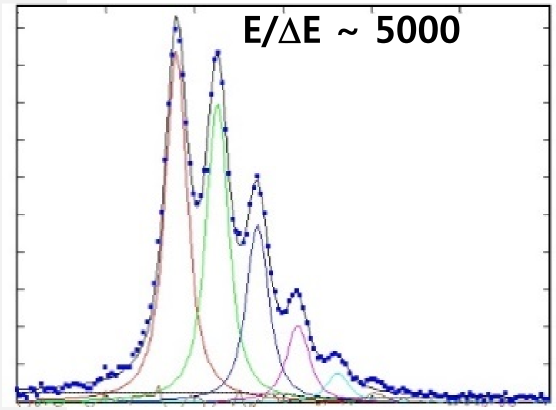
2.2 STXM requirement: beamline specification

- **EPU beamline is better**
- **Enough flux in wide energy range: 100 – 2000 eV**
- **Energy resolving power: E/ΔE > 2,000**
- **Small virtual source size**
- **High demagnification geometry**



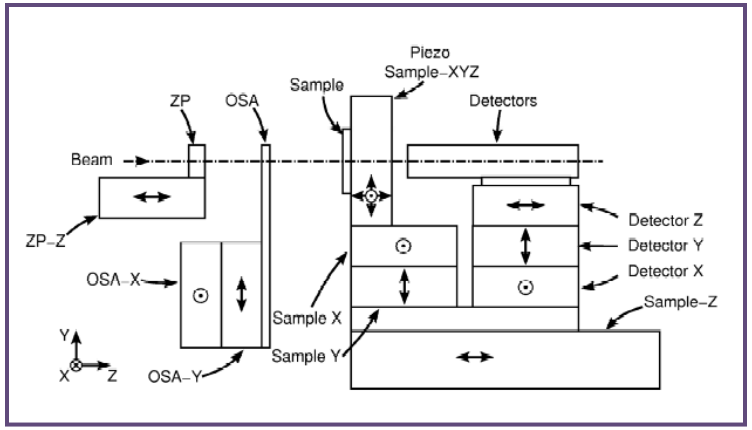


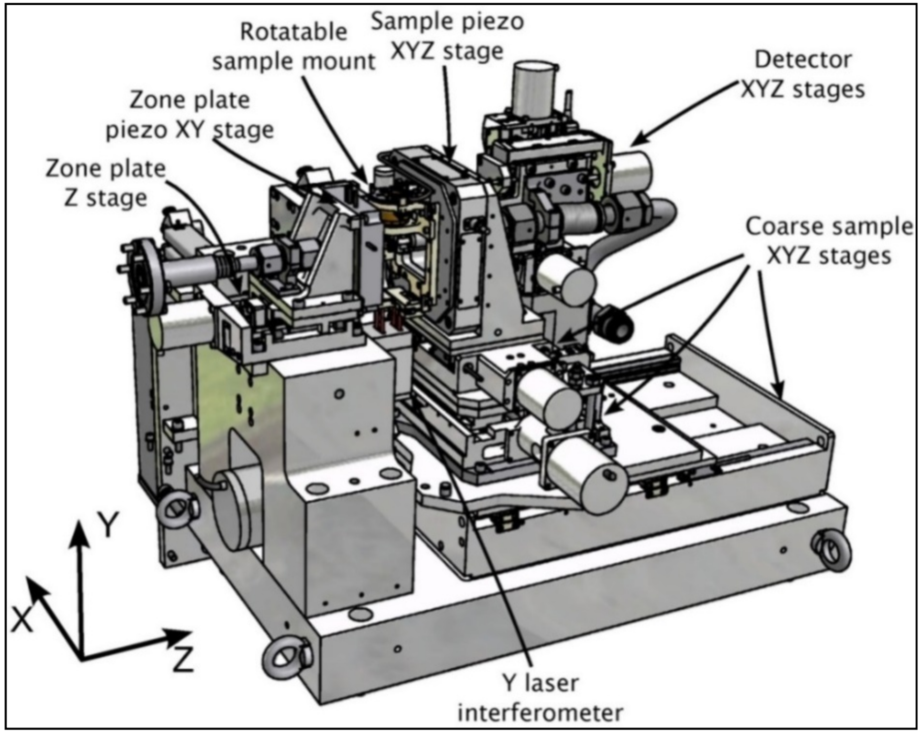


2.2 STXM requirement; apparatus

- Accurate and fast scanning stages
- Accurate and fast position monitoring
- Accurate and fast feedback system (Laser interferometry)
- Fast detector

$f = D \Delta r / \lambda$
** OSA

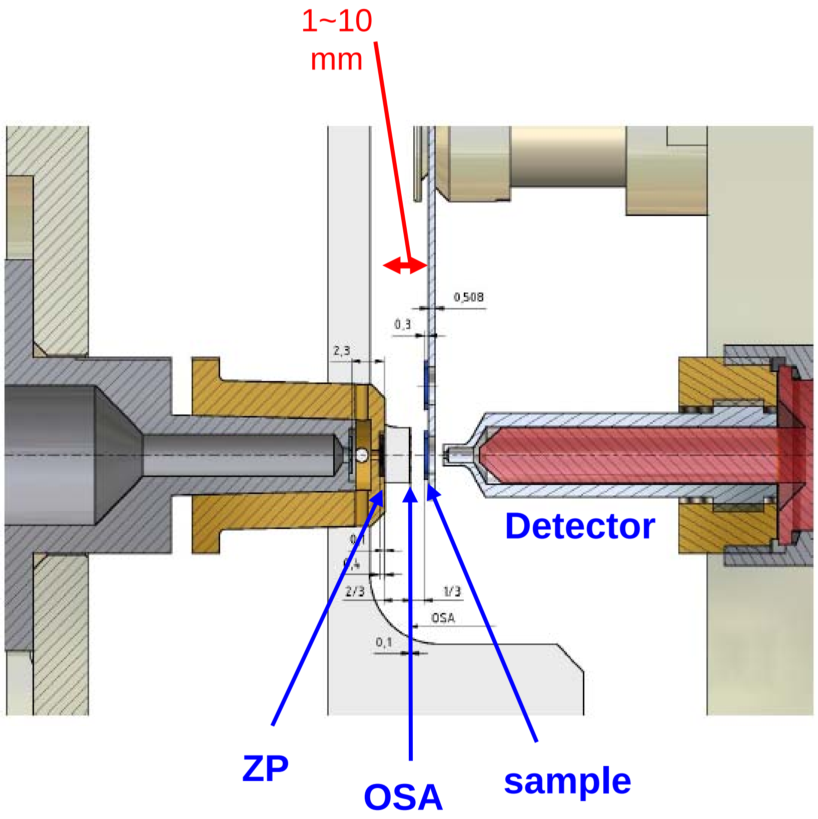


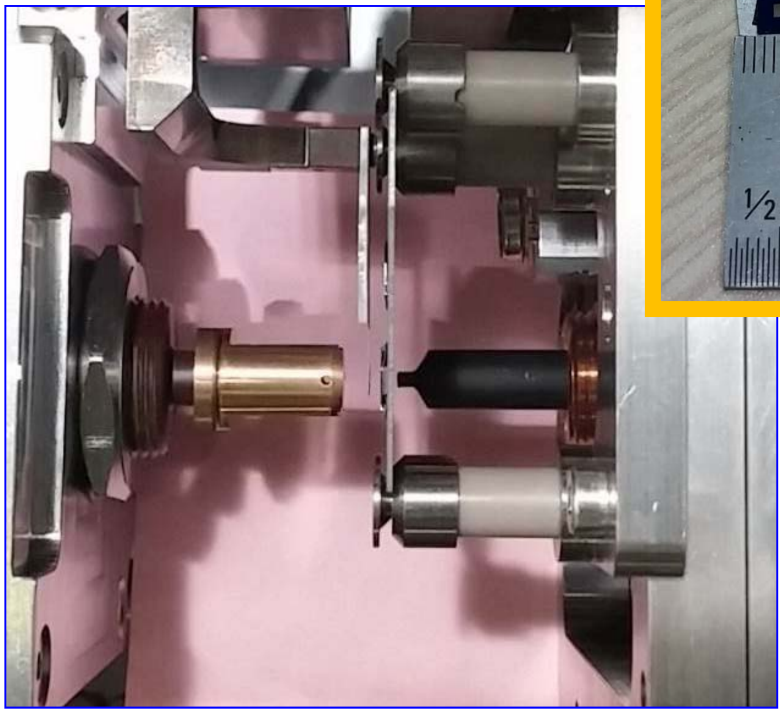


http://www-als.lbl.gov
& Bruker Ltd.

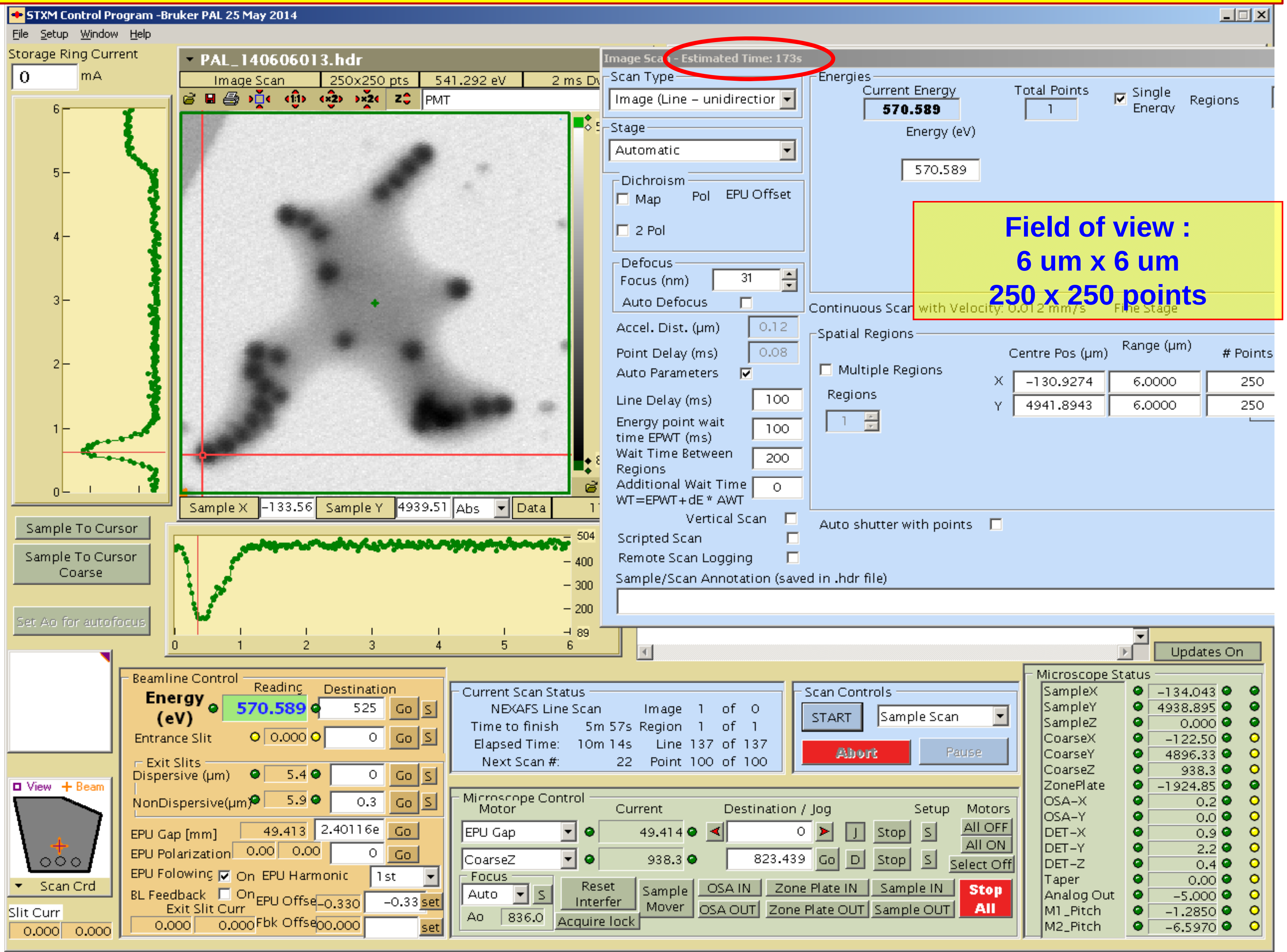
2.2 STXM in real shape

- easier to find ROI within sample
- easier to find the best focus
- easier and faster sample loading
- detector is efficient for fast counting…



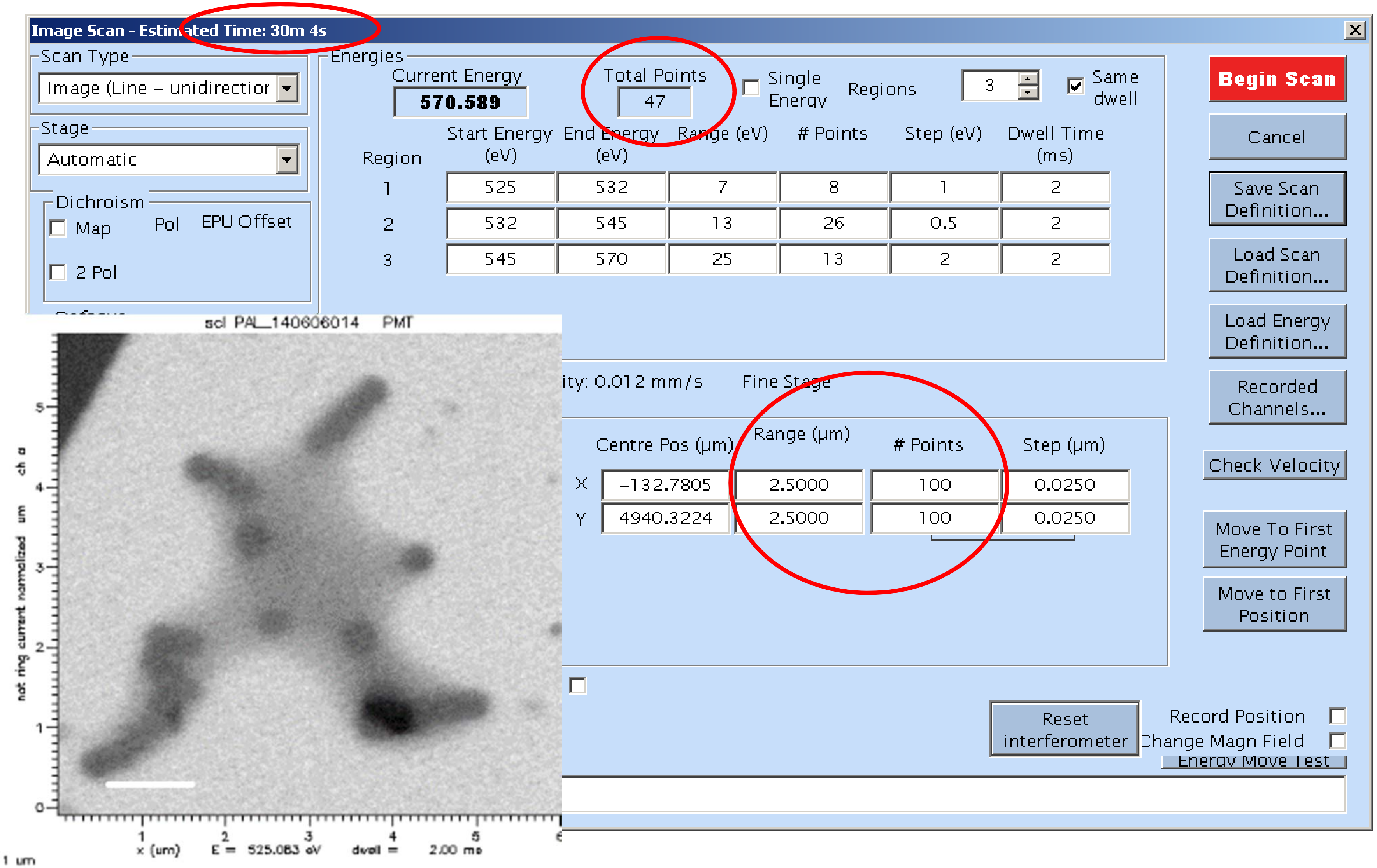


2.2 STXM: single image acquisition



Field of view :
6 um x 6 um
250 x 250 points

2.2 STXM stack images: acquisition of point intensity/ line intensity profile/ 2-D image at different photon energy for taking spectral information…



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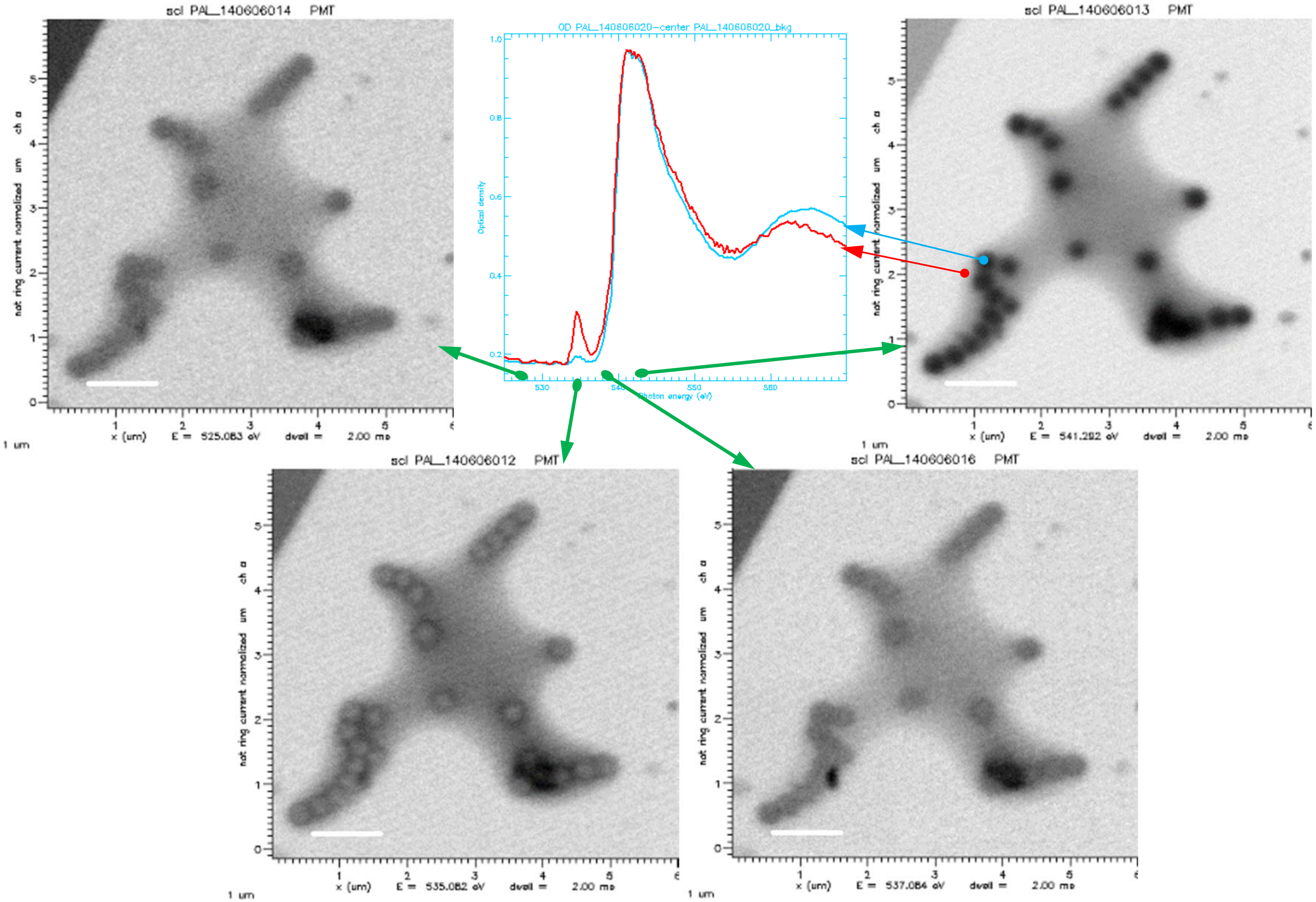
2.2 STXM: images at different photon energies & spectra at any point or region of interest.

300 nm silica images at different photon energies &
O K-edge spectra from edge & center of silica nano particle



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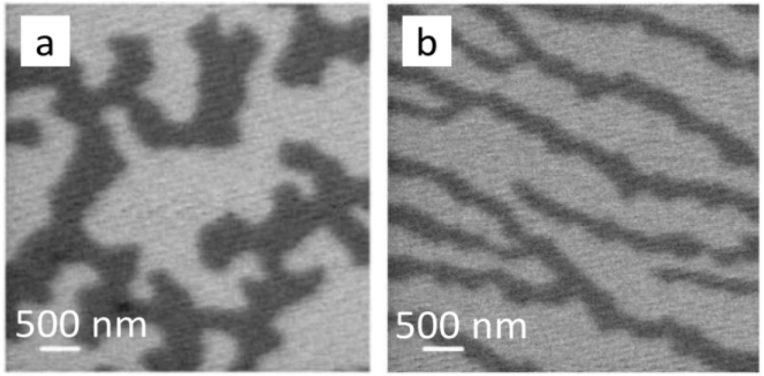
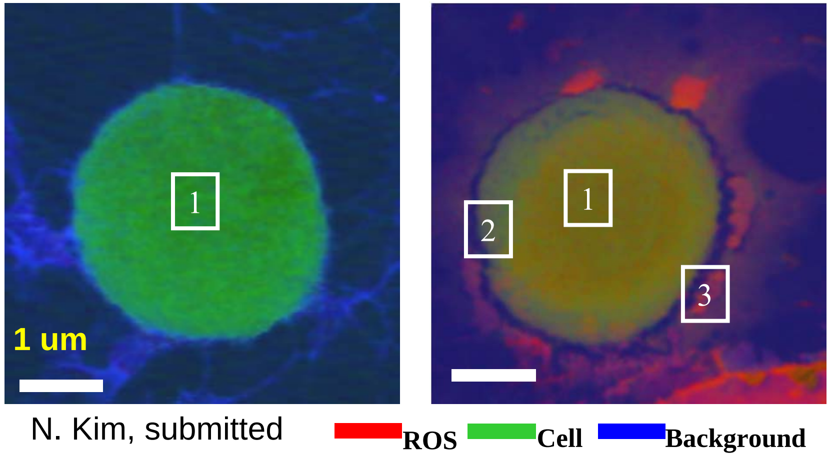
PAL

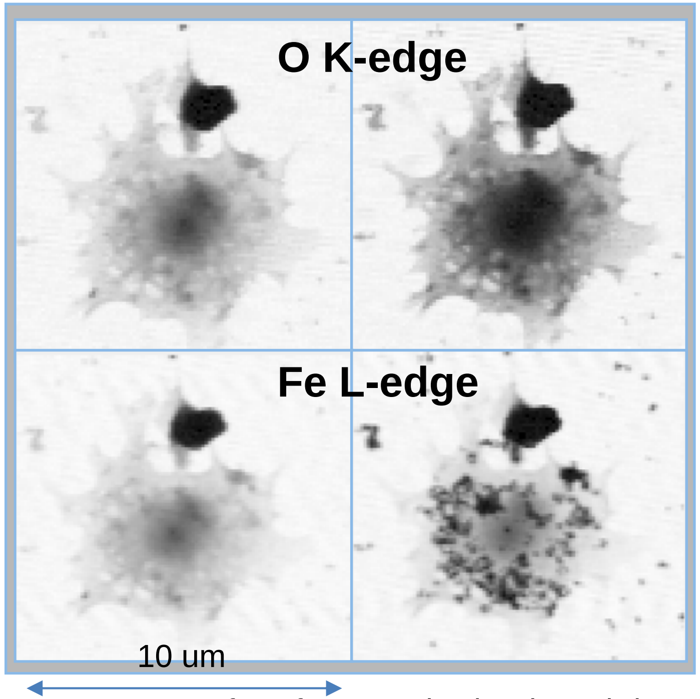
2.2 STXM application examples



Courtesy of Prof. D. H. Kim (Chungbuk Univ.)

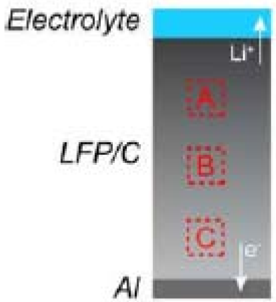


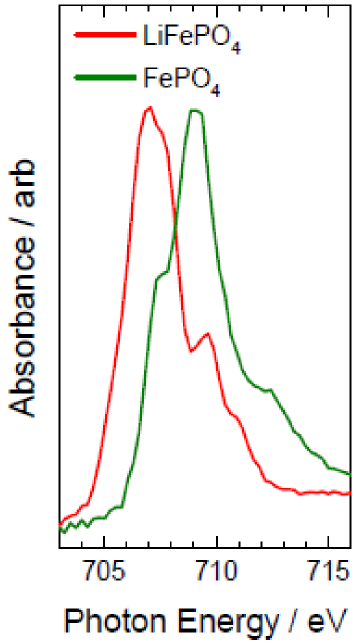
N. Kim, submitted

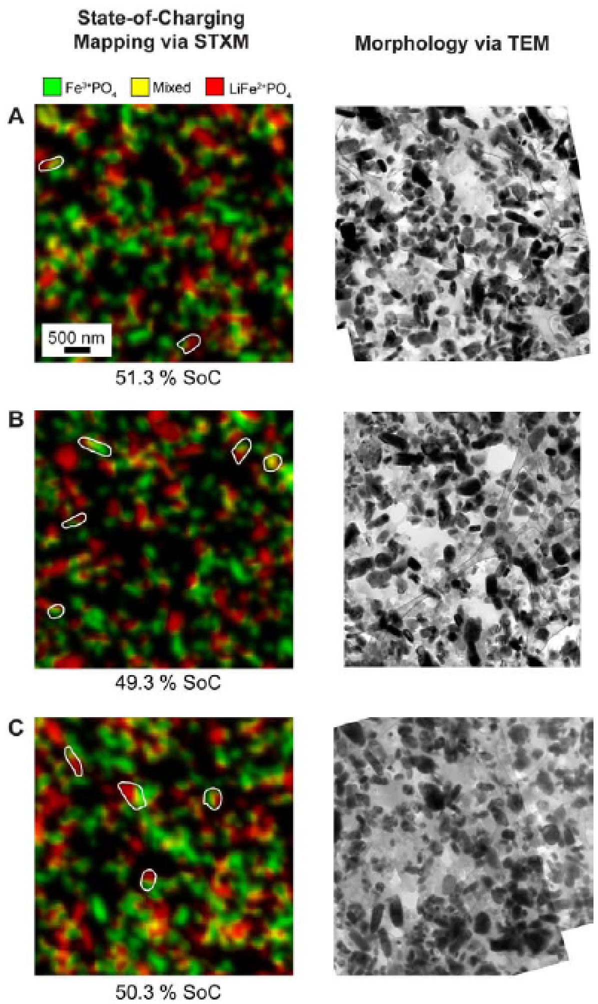


Courtesy of Prof. J. -K. Kim (Cath. Univ.)

2.2 STXM application examples : Quasi in-situ study of phase transformation in Lithium-ion batteries

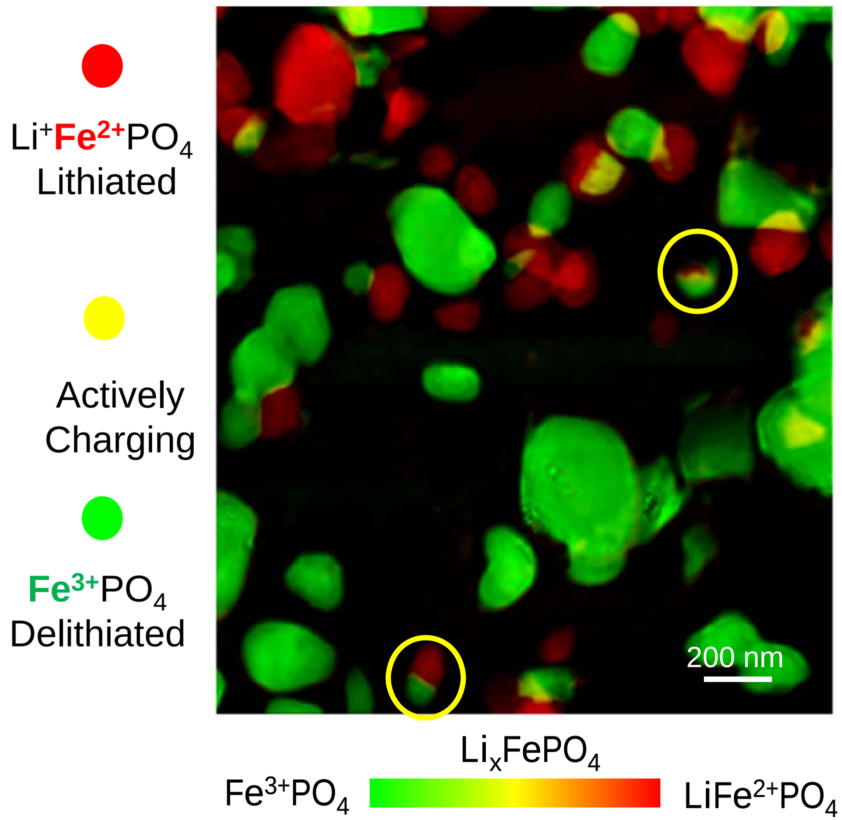






W. C. Chueh et al. , Sandia Report, 2012.

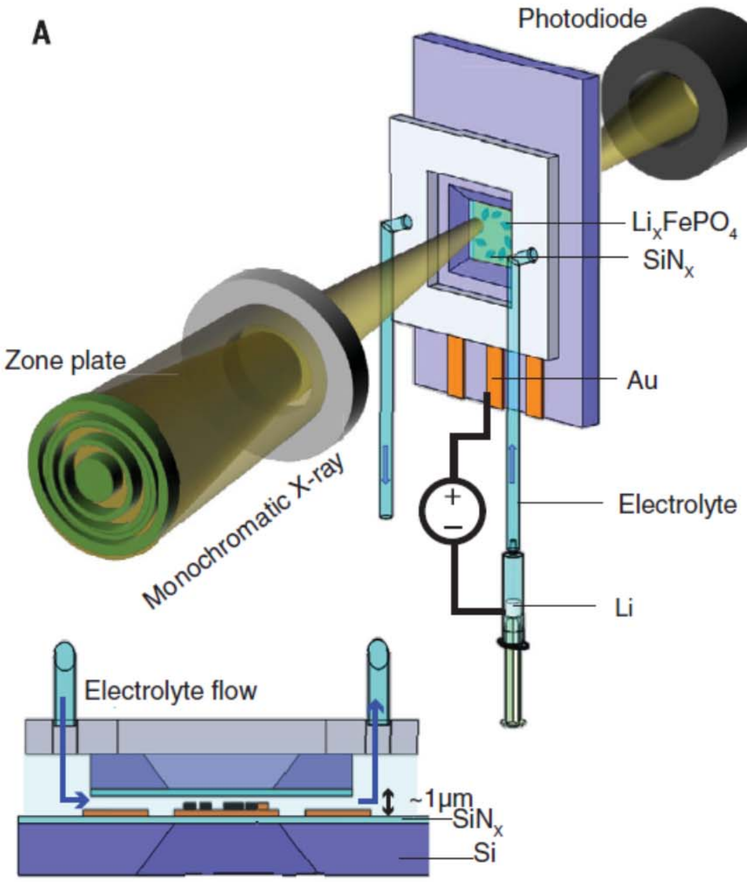
Ex-situ inter-particle heterogeneity

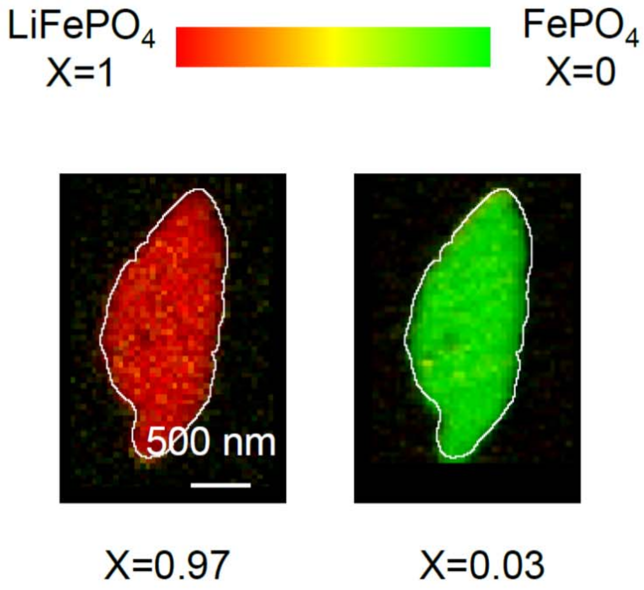


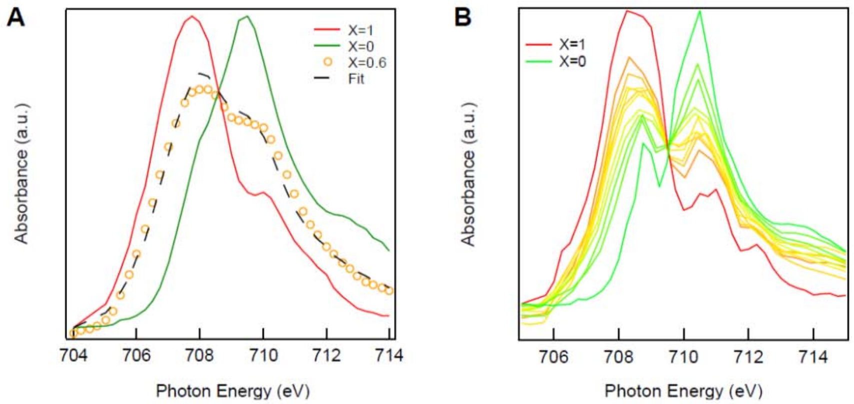
Y. Li#. S. Meyer#, et al. *Adv. Mater.* 27, (2015), 6591

H. J. Shin

2.2 STXM application examples: Operando investigation of lithiation and delithiation process of LixFePO4…

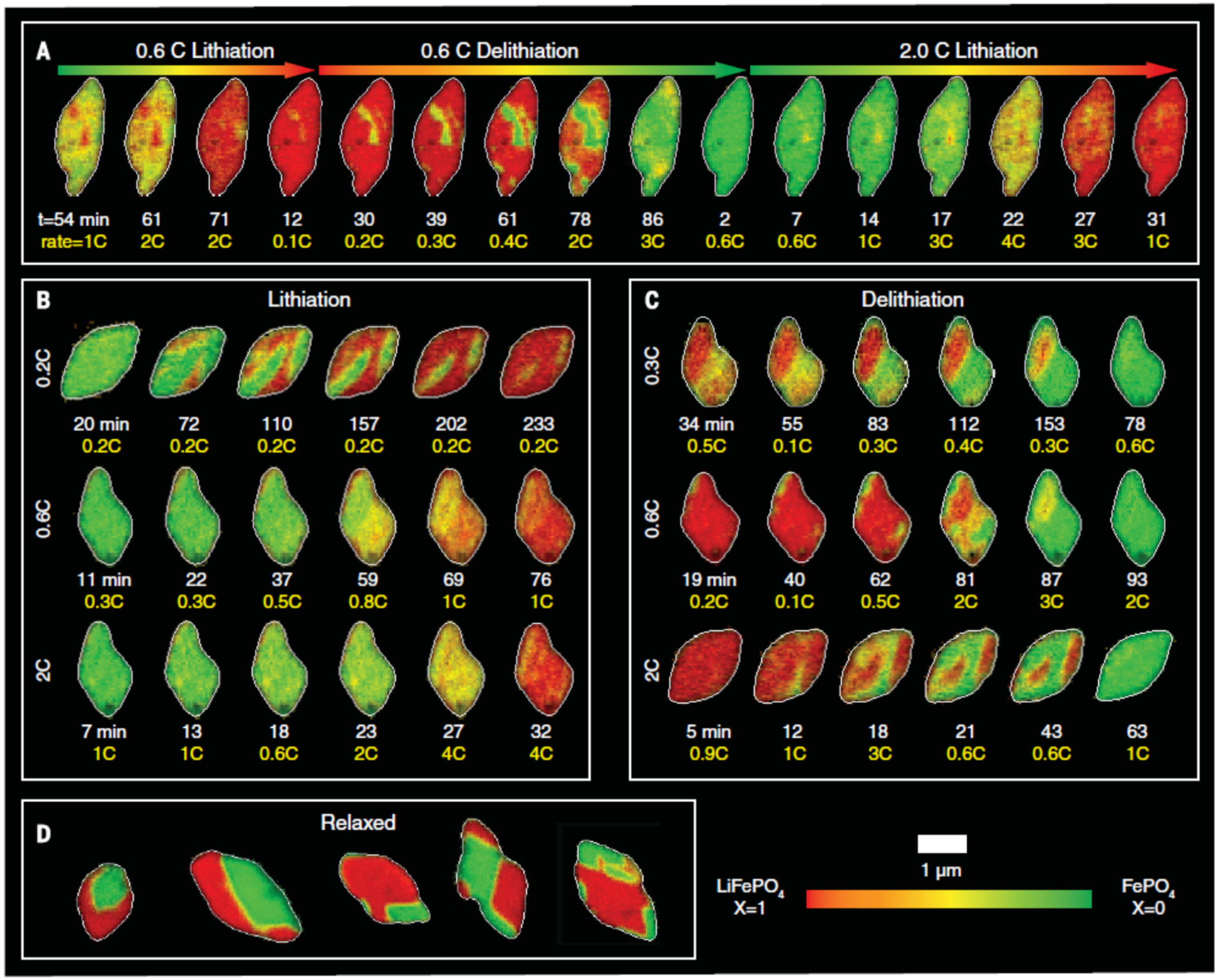






J. Lim et al., Science, 353, 566 (2016)

Rate dependent (de) lithiation heterogeneity (0.6 C, 2C)
Current density (insertion rate) quantification
Exchange current density vs. Li composition
Origin of heterogeneity.



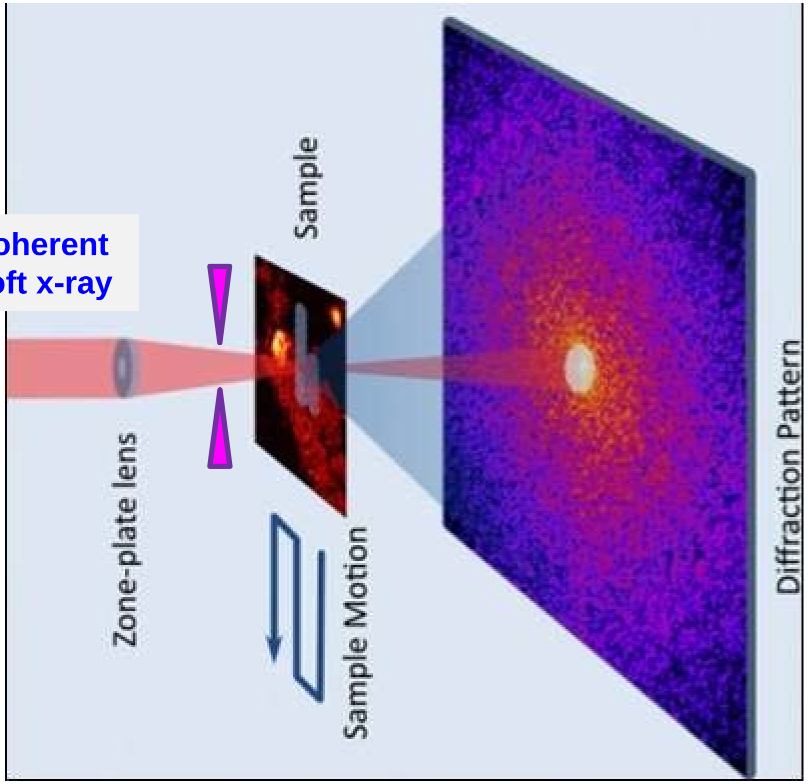
J. Lim et al., Science, 353, 566 (2016)

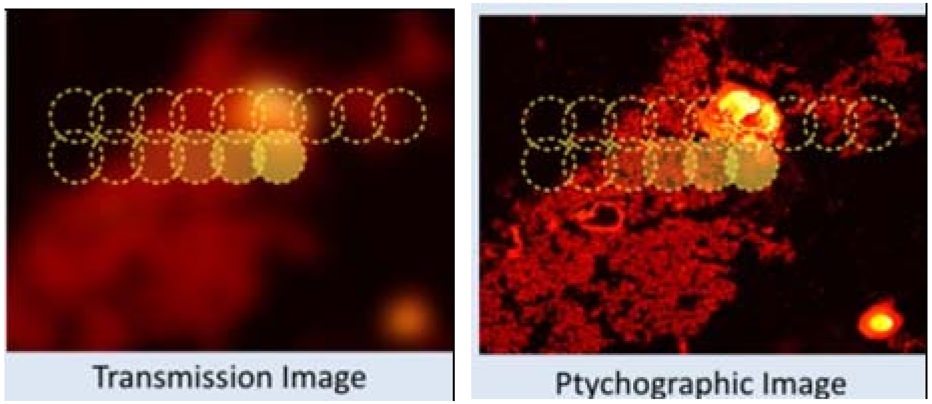
2.2 STXM; ptychography mode to improve space resolution…

D. Shapiro, T. Tyliszczak et al., Nat. Photonics (2014).
Nat. Mater. (2014).
Nano Lett. (2015).

Increase of N.A. :
~ 2-5 nm space resolution is possible …

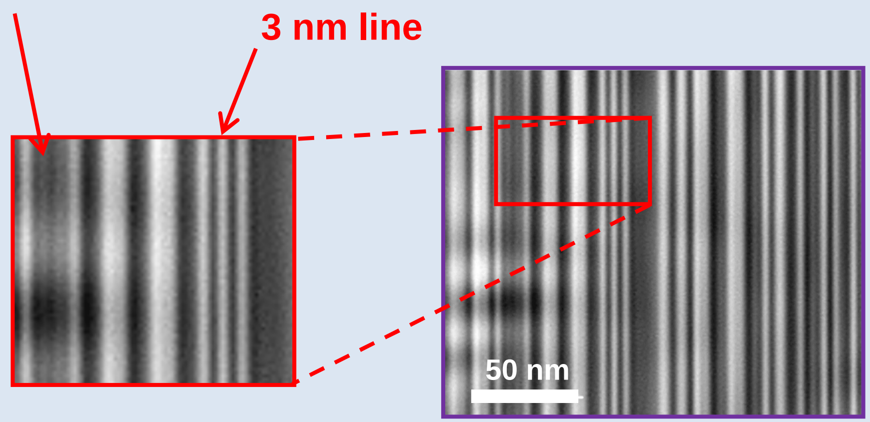
Coherent soft x-ray





ALS, Berkeley

1.5 nm line resolved



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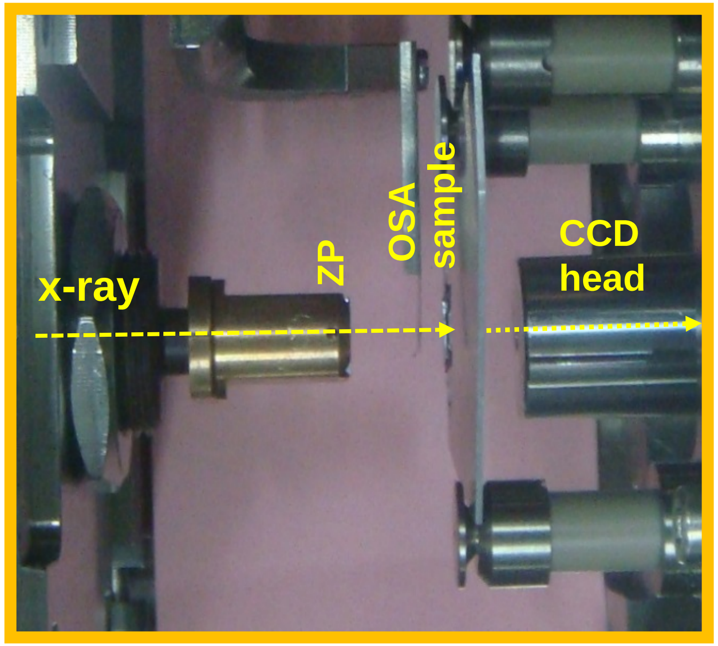
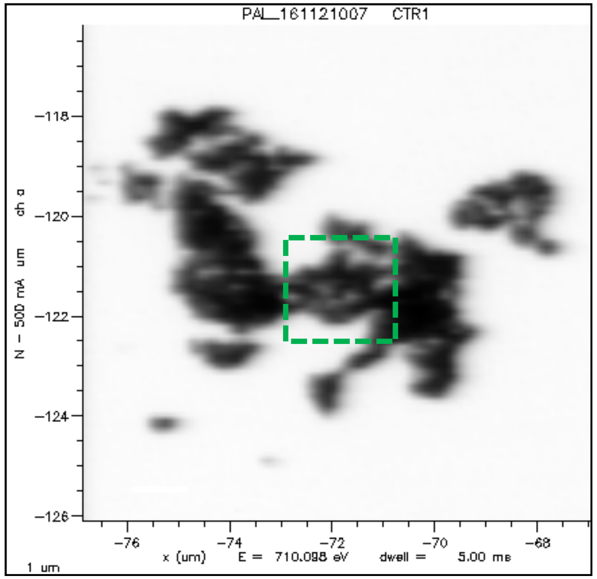
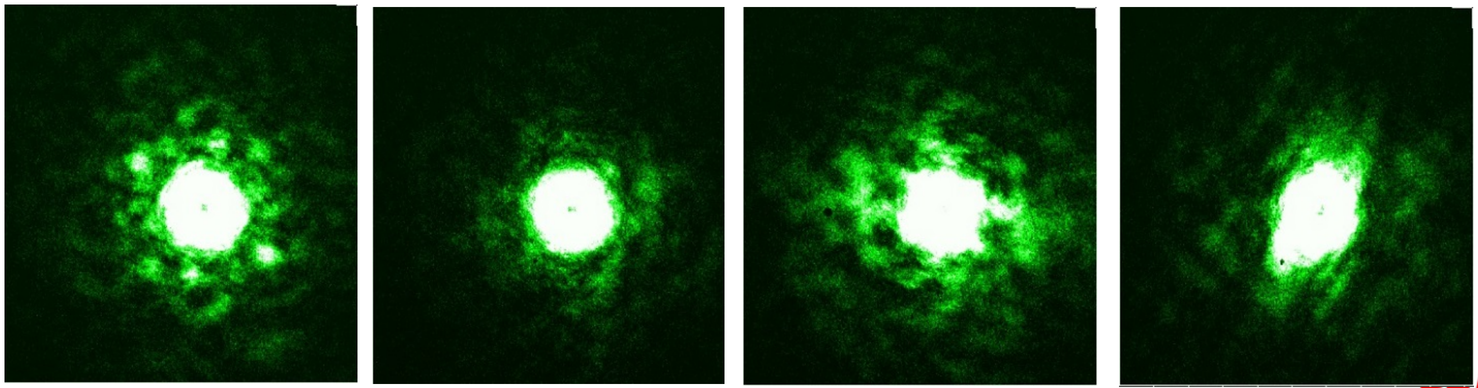
2.2 STXM; ptychography setup in practical example



Sample: FeO_x nanoparticles
Photon energy: 710 eV
1 um x 1 um (20 x 20 points)
Beam size at sample = ~70 nm
Sample to CCD distance = ~80 mm





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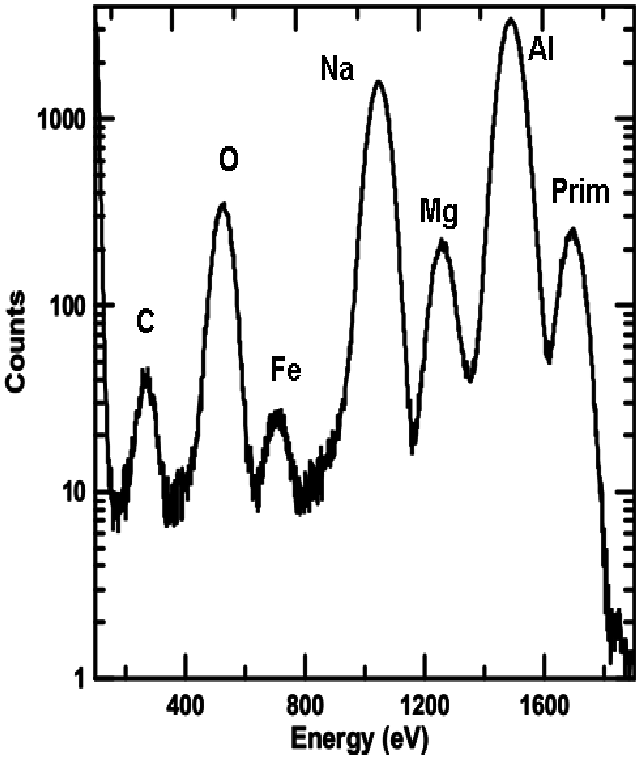
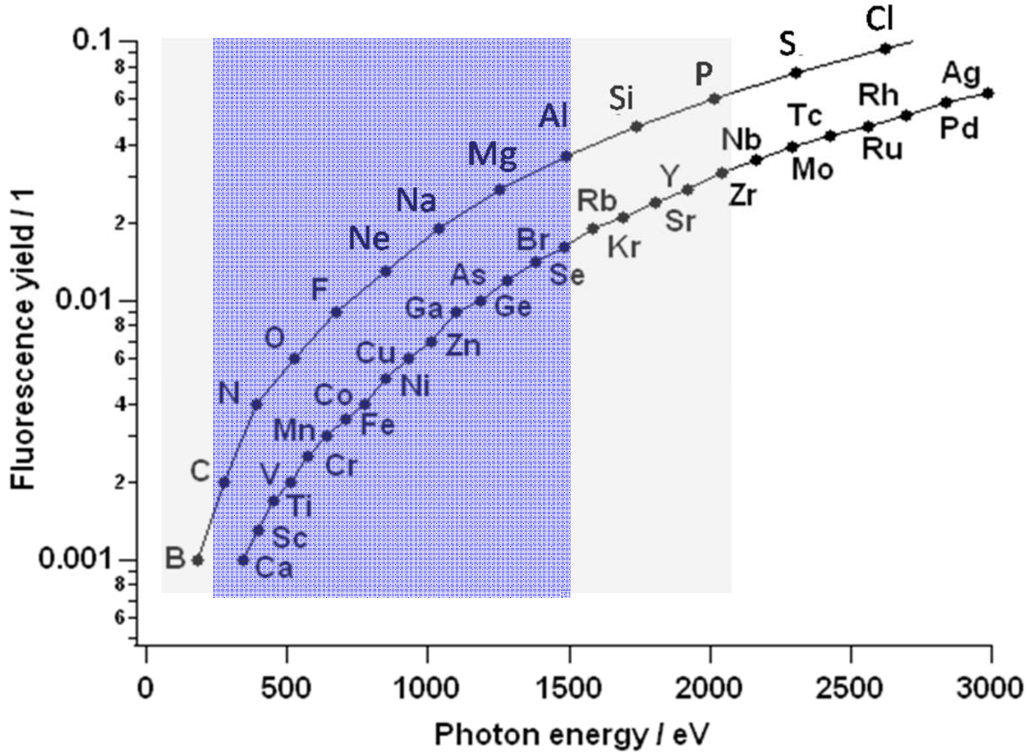
2.2 STXM; fluorescence mode

- **Fluorescence yield is low for soft X-rays..**

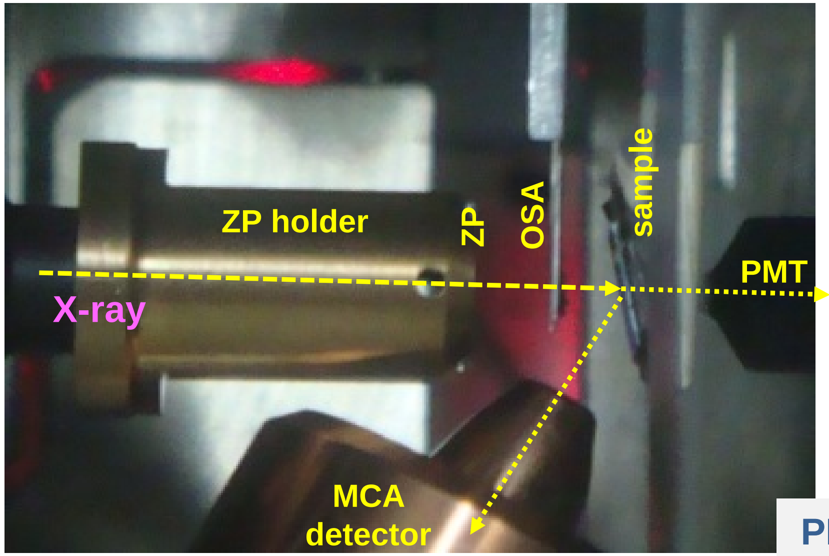
- **Multi element information in a single scan !**
- **Low Z elements !**
- **Can probe thick sample ...**





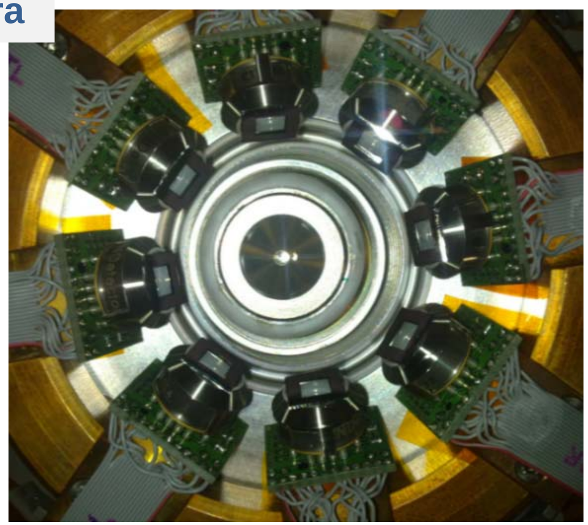
A. Gianoncelli,et al., NIMA 608 (1), 195.

2.2 STXM; fluorescence mode in practical application



PLS, ALS, CLS

Elettra



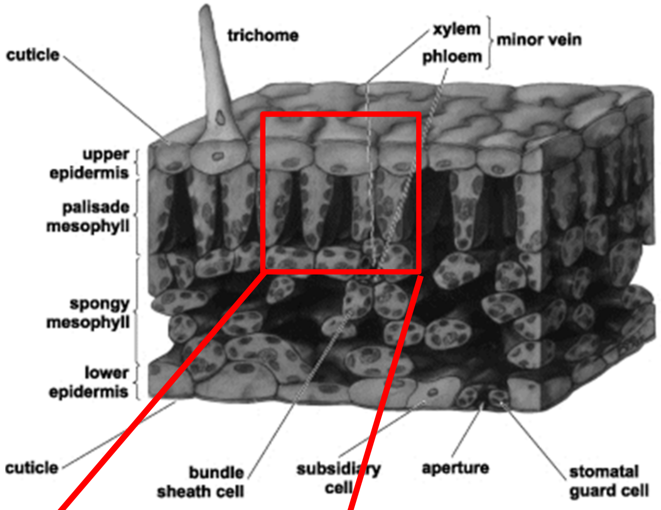
A. Gianoncelli, B. Kaulich, M. Kiskinova, R. Alberti, T. Klatka, A. Longoni, A. de Marco, A. Marcello, Simultaneous Soft X-ray Transmission and Emission Microscopy, Nucl. Instr. and Meth. A 608 (1), 195-198

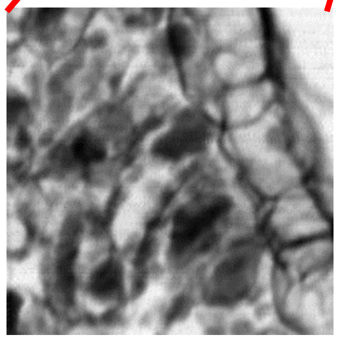
2.2 STXM; fluorescence mode application example

Al in tea leaves

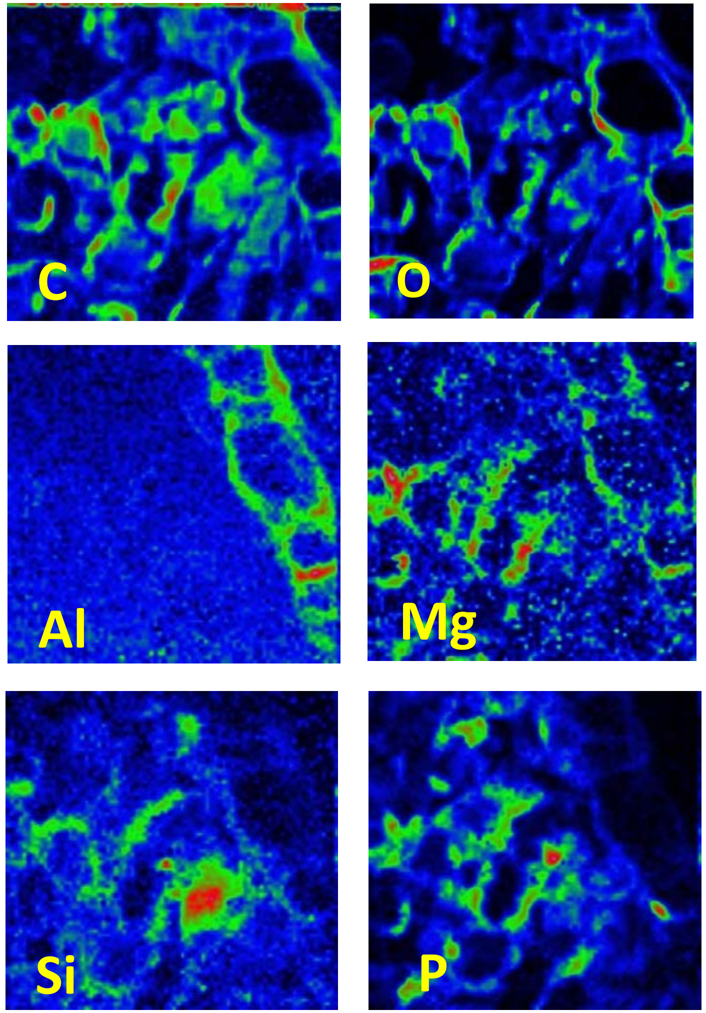
Functionality and toxicity of Al in tea leaves analyzed on sub-cellular level

Cross-section of a leaf





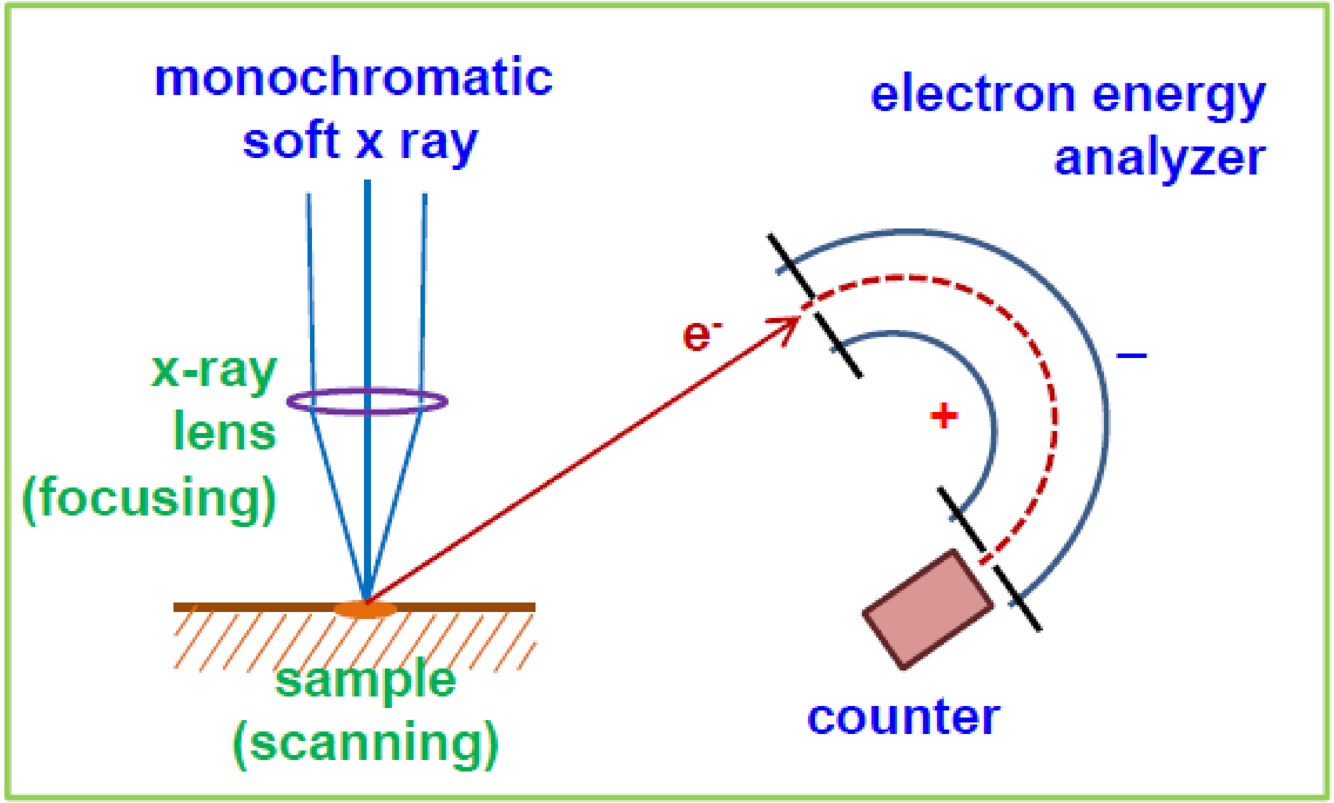
In young tea leaves the preferential accumulation of Al occurs at the end of the transpiration stream, in the epidermal cell walls



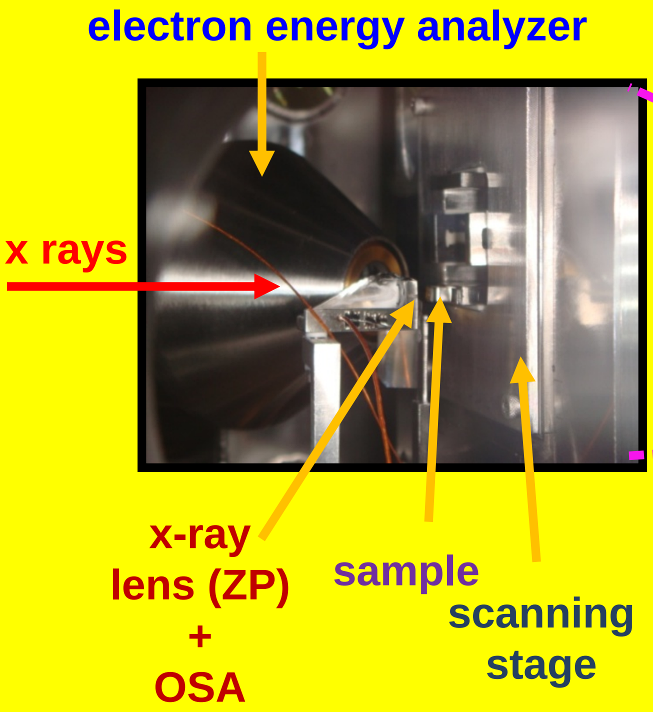
R. Tolra, K. Vogel-Mikus, R. Hajiboland, P. Kump. P. Pongrac, B. Kaulich, A. Gianoncelli, V. Babin, J. Barcelo, M. Regvar, C. Poschenrieder, *Localization of aluminium in tea (Camellia sinensis) leaves using low-energy X-ray fluorescence spectro-microscopy*, J Plant Research 124, 165-172.

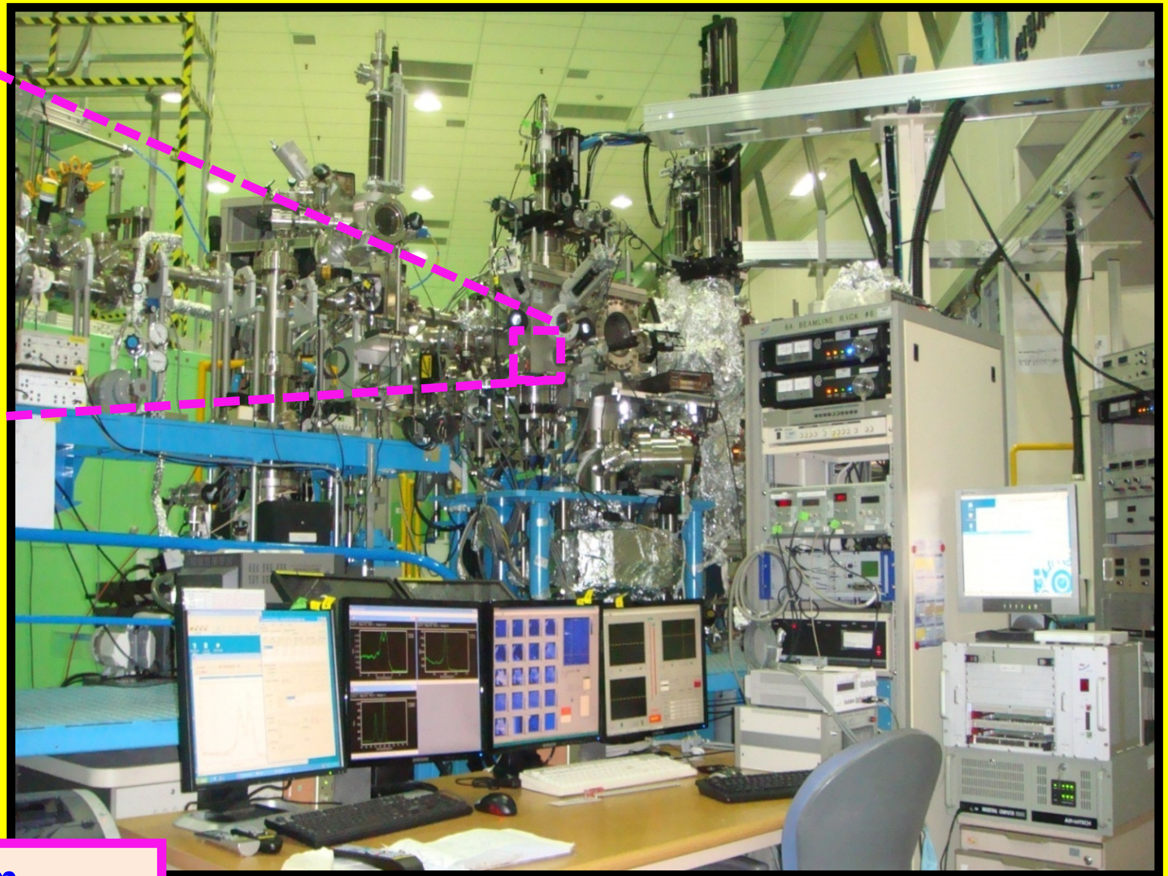
2.3 SPEM (Scanning photoelectron microscopy)

X-ray photoelectron spectroscopy (XPS)
- **is a useful probe to investigate chemical states, electronic structure, ...**
- **is very sensitive to surface.**



2.3 SPEM in real world…



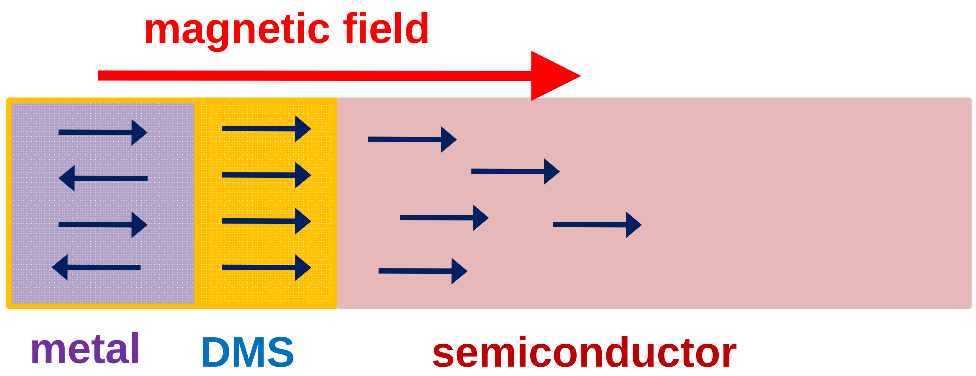


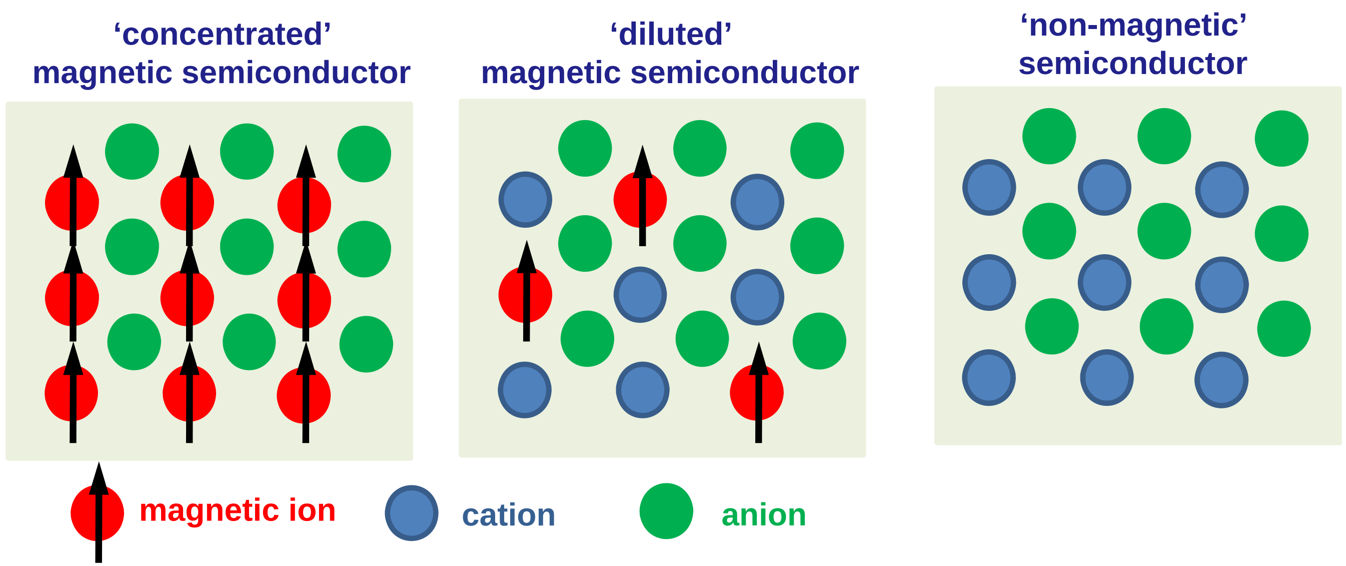
Space resolution: 200 nm ~ 1 um
(nano-ARPES: 50 – 100 nm)
X-ray photon energy: 100 – 1100 eV
Surface sensitive (< 2 nm)
UHV environment, in-situ experiments

8A1 beamline, PLS

2.3 SPEM application: diluted magnetic semiconductor (DMS)

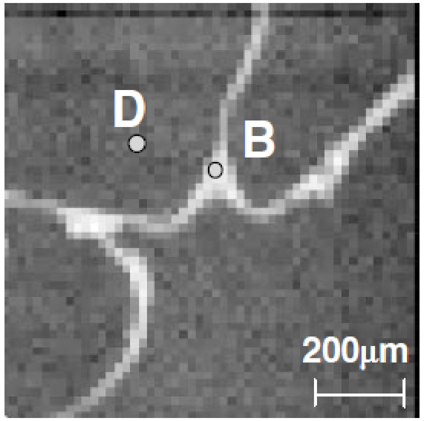
Injection of spin-oriented electrons into semiconductor

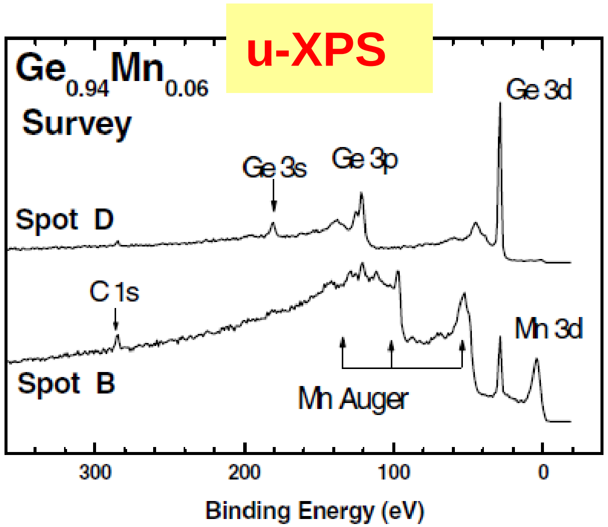




Observation of Mn rich phase in $Ge_{0.94}Mn_{0.06}$ DMS

DMS: Ge(0.94)Mn(0.06)



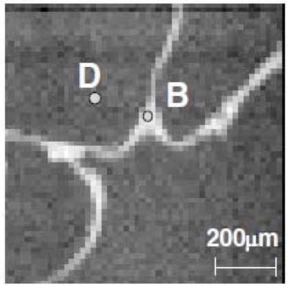


Observation of chemical phase separation into Mn rich and Mn depleted phases.

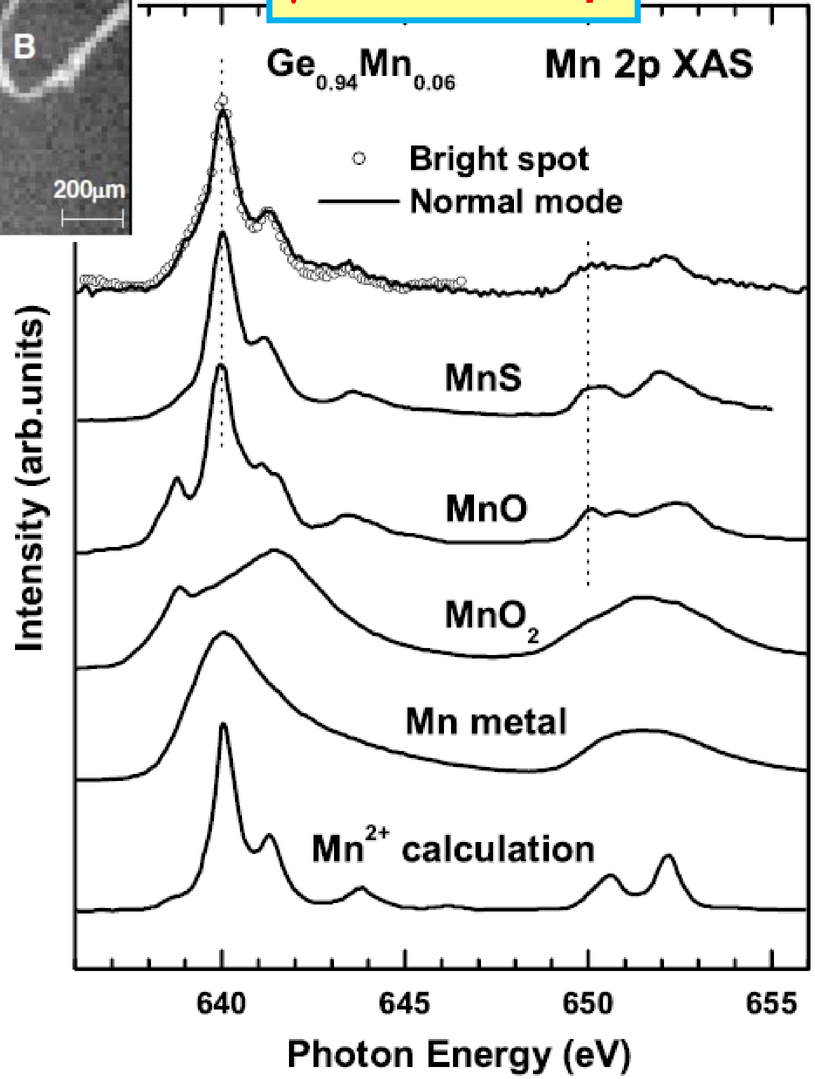
Similar phase separation of Cr and Fe -rich and -depleted phases were observed in the Ge(0.99)Cr(0.01) and Ge(1-x)Fe(x) DMS materials.

J. S. Kang, et al. , Phys. Rev. Lett. 94, 147202 (2005)

Observation of Mn rich phase in $Ge_{0.94}Mn_{0.06}$ DMS



μ-XAS: Mn 2p



u-XAS from the stripe-shaped microstructure.

→ Valence state of Mn ions: Mn^{2+} , not Mn^{4+}, nor Mn^{0+} (metallic cluster).

Theory expects that the Mn-rich stripe-shaped microstructure has divalent and high spin Mn ($3d^5$, total spin S = 5/2).

Mn: $3d^5\,4s^2$

J. S. Kang, et al. , Phys. Rev. Lett. 94, 147202 (2005)

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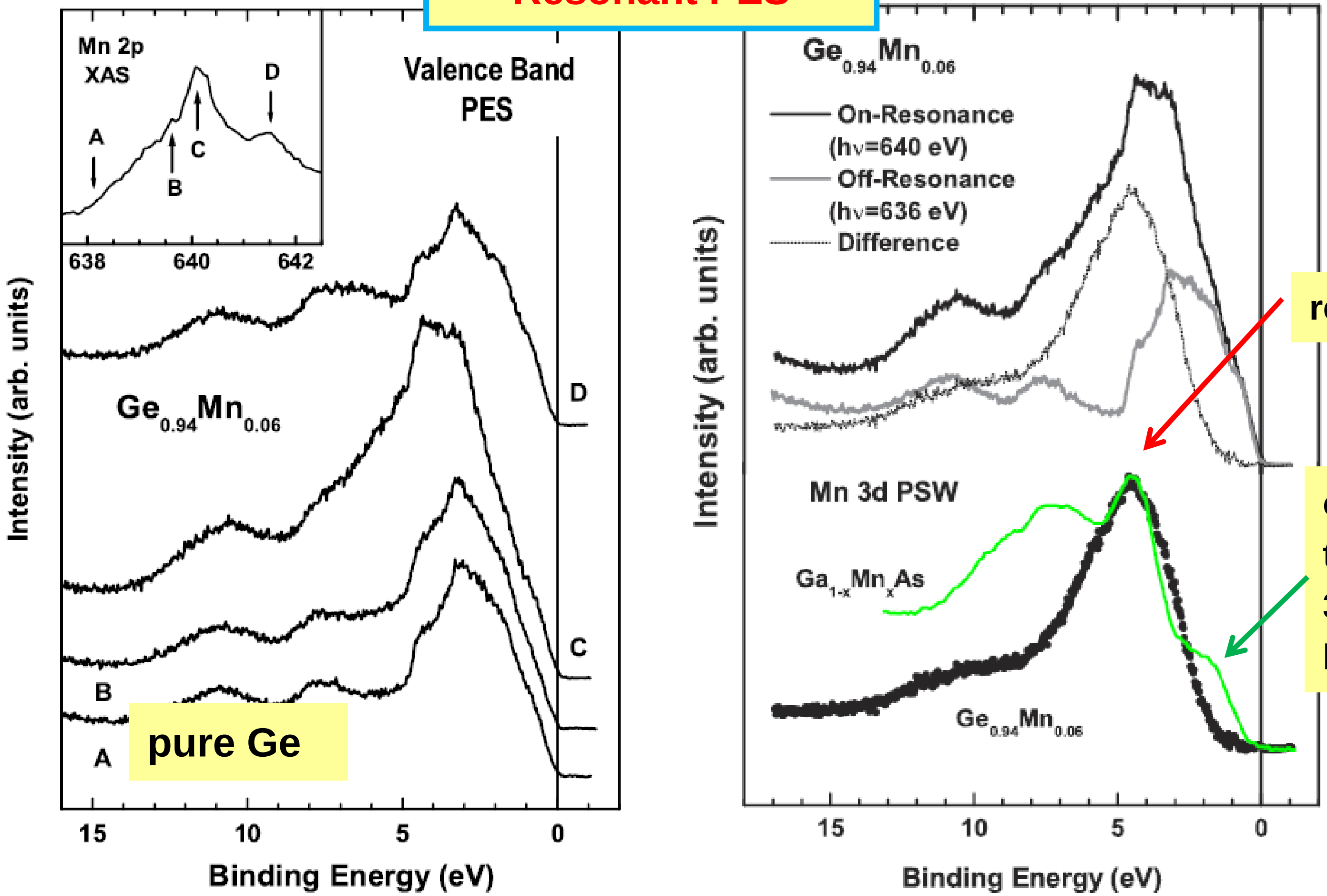
Observation of Mn rich phase in $Ge_{0.94}Mn_{0.06}$ DMS

Resonant PES



resonating Mn 3d

charge transfer through strong Mn 3d ($3d^5$) and As 2p hybridization

Mn 3d are located well below the E_F, and occupy the deep levels.

Confirms the Mn^{2+} valence state. Hybridization with Ge 2p is weaker.

The Mn-rich microstructure may explain the ferromagnetism in the Ge(0.94)Mn(0.06) DMS.

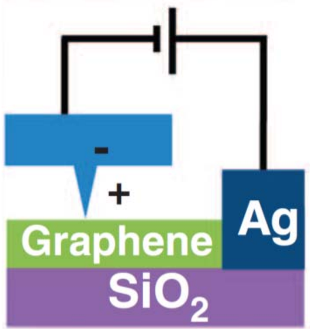
J. S. Kang, et al. , Phys. Rev. Lett. 94, 147202 (2005)

2.3 SPEM application: control of graphene functionalization...

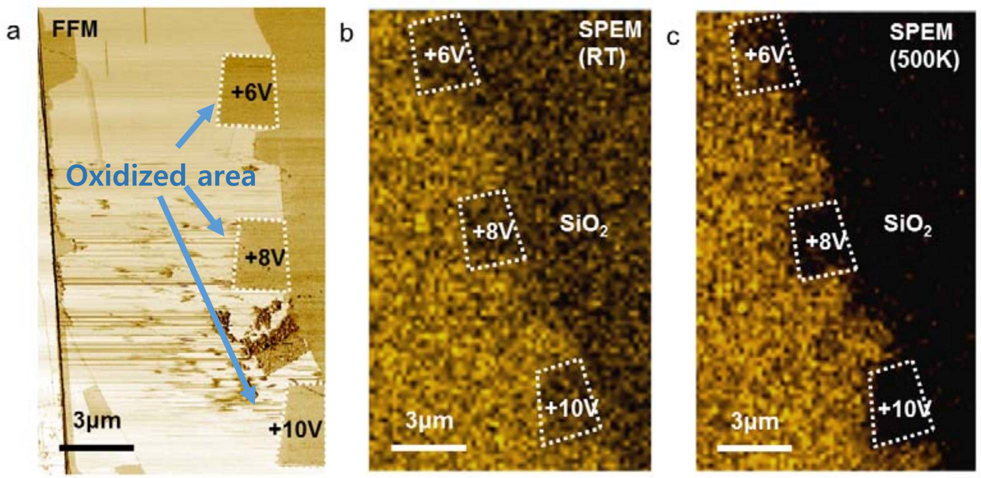
Electrical control of nanoscale functionalization in graphene by the scanning probe technique...

I. –S. Byun et al., NPG Asia Materials (2014) 6, e102

Schematic setup of oxidation lithography using AFM.

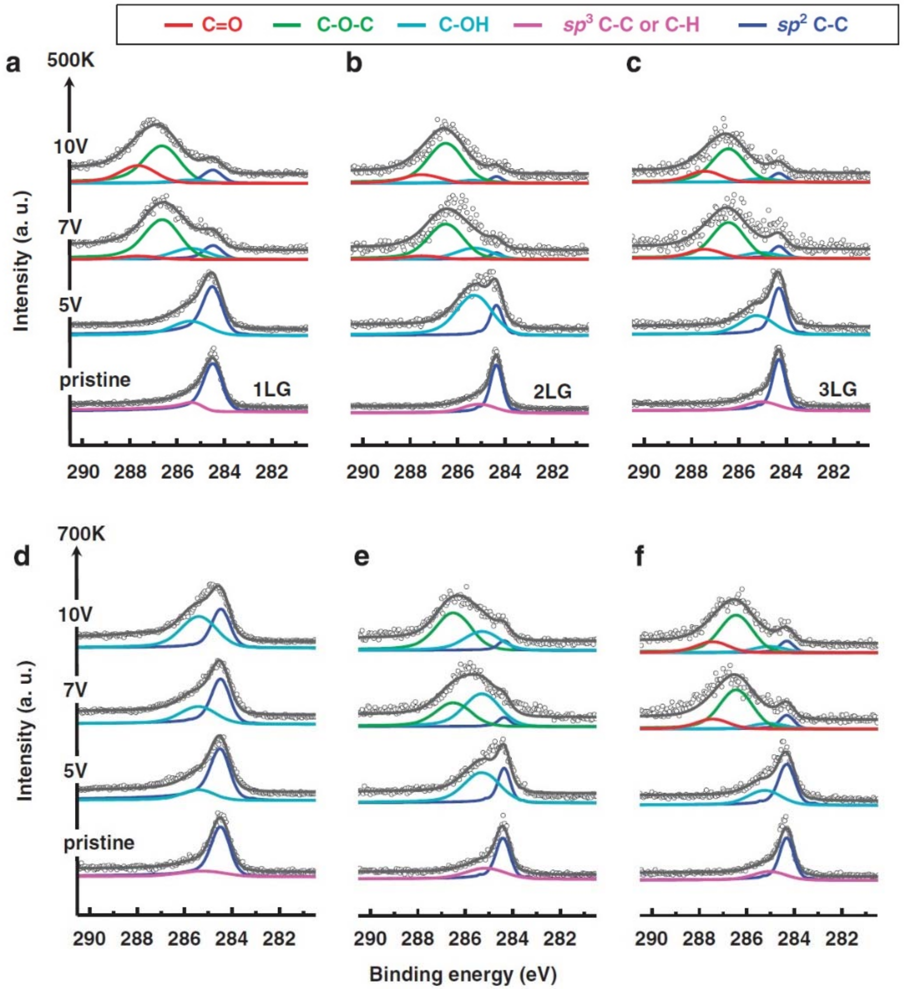


Effect of pre-annealing treatment (carbon contaminants removal)



FFM (a) and C1s@284.5eV SPEM (b and c) images of pristine and oxidized graphene on SiO_2 substrate before (a and b) and after (c) pre-annealing treatment at 500 K.

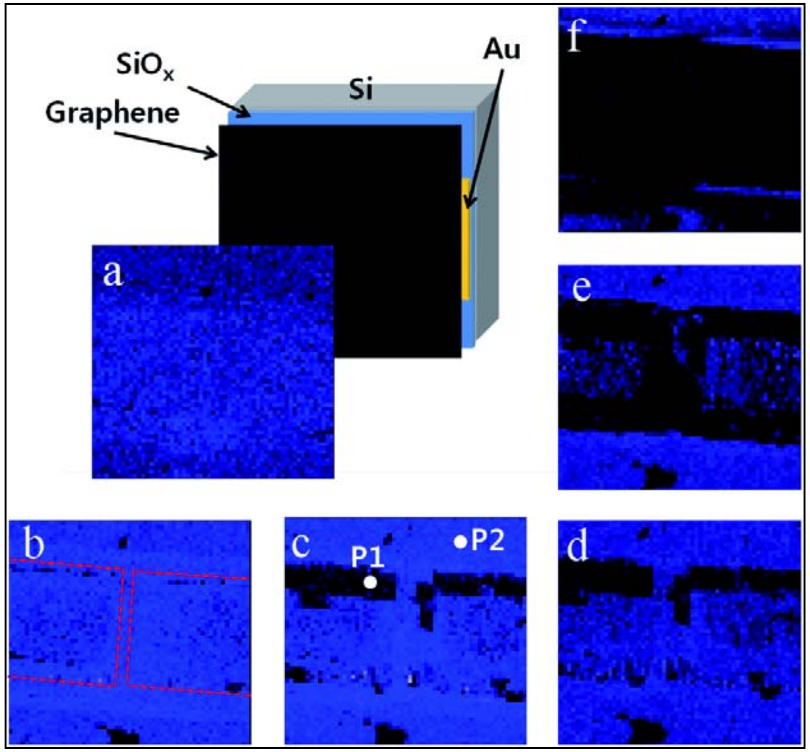
C=O: carbonyl, C-O-C: epoxy, C-OH: hydroxyl,



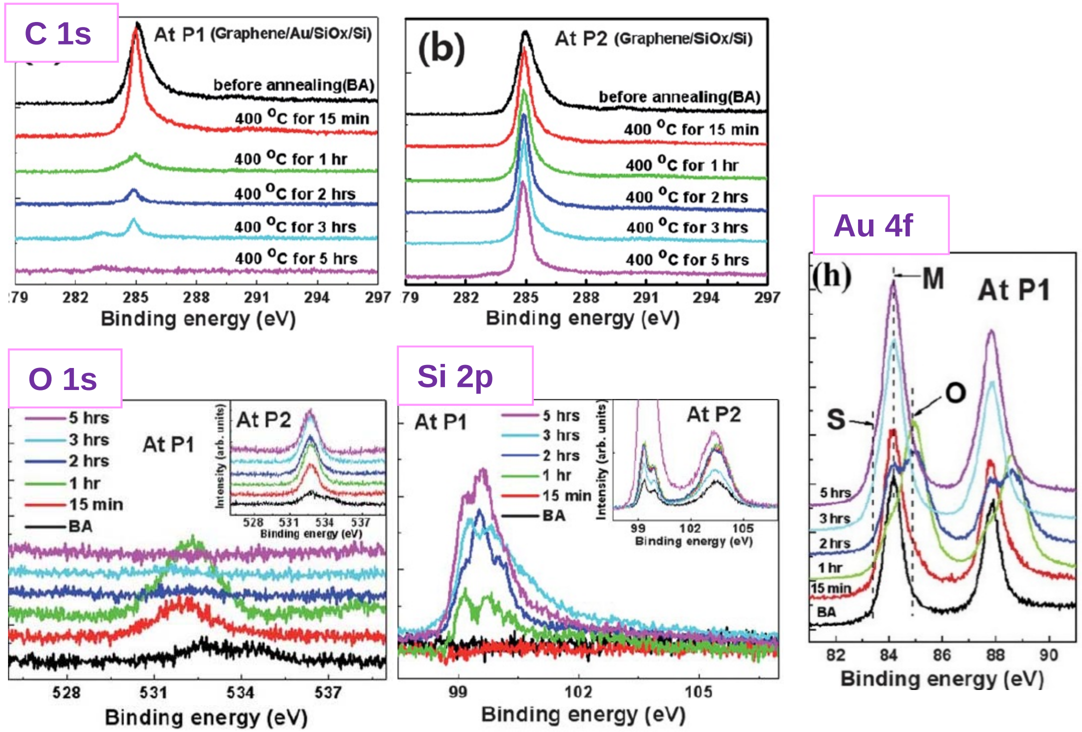
2.3 SPEM application: selective catalytic burning of graphene by SiOx layer depletion...

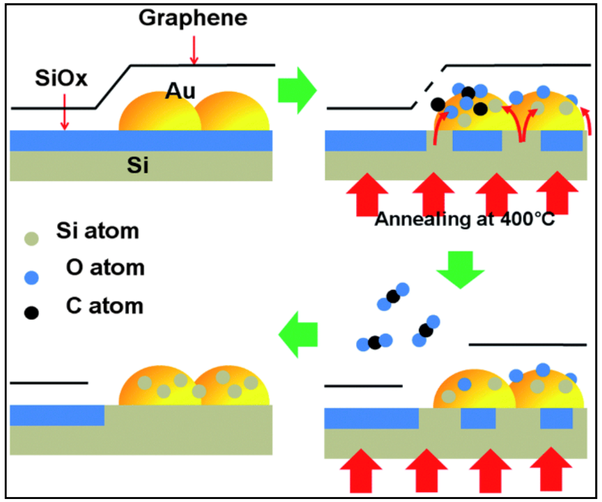
K. –J. Lee et al., Nanoscale 6, 1474-1479 (2014)

C 1s SPEM images (600 um x 600 um)



(a) SPEM image (600 × 600 μm^2), contrasted with the C 1s peak intensities, of the sample before annealing. Annealing time dependence of SPEM images (600 × 600 μm^2), contrasted with C 1s peaks, at 400 ˚C: (b) 15 min, (c) 1 h, (d) 2 h, (e) 3 h, and (f) 5 h. Local points P1 and P2 indicate the graphene/Au/SiO$_x$/Si and graphene/SiO$_x$/Si surfaces, respectively.





Schematic diagram of the catalytic oxidation process

Thermal dissociation of SiO$_x$:
400 C/ 737 °C
Contact resistivity:
26.17 / 1.58 x 10^{-4} Ohm cm^2

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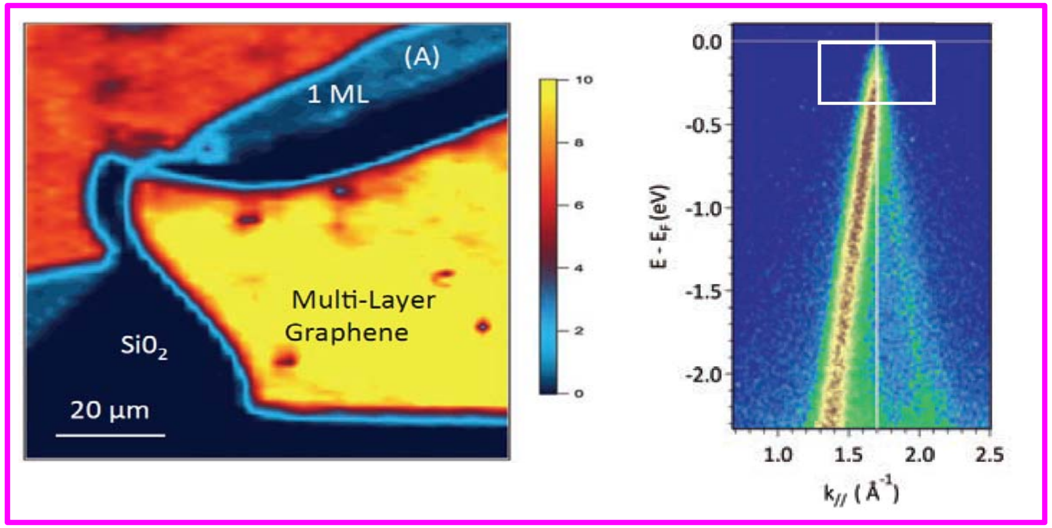
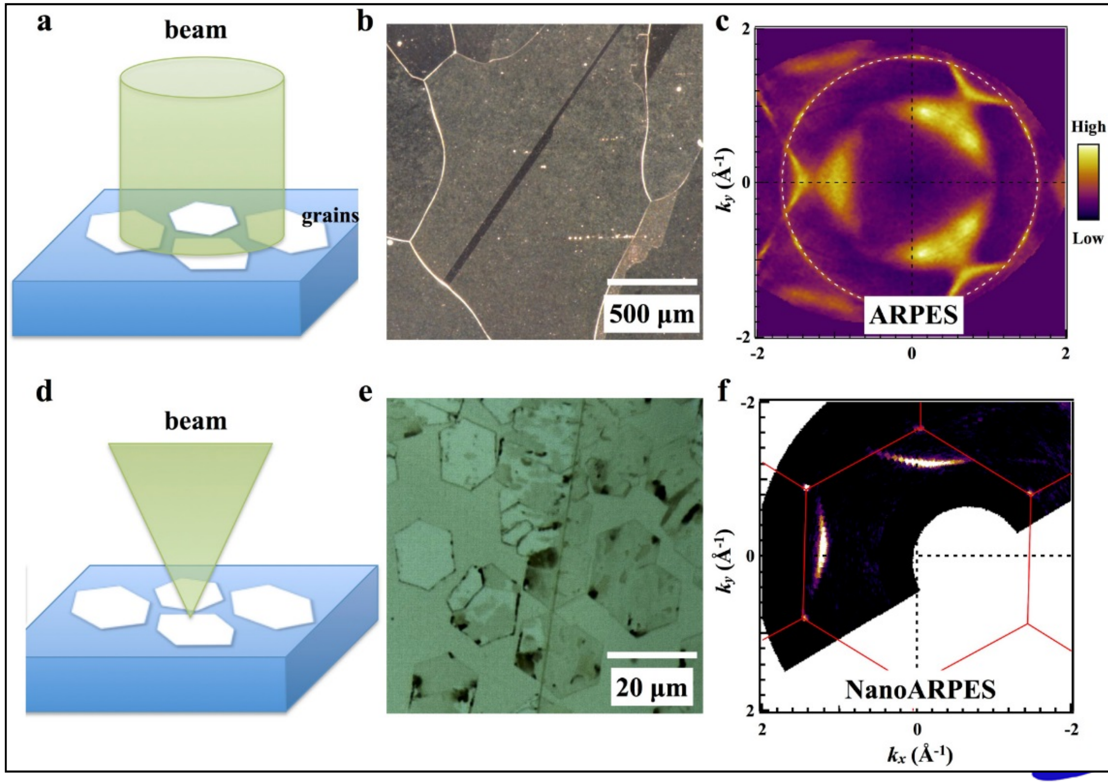
2.3 SPEM application: graphene layers (Nano-ARPES)



SOLEIL



Limitations of traditional ARPES and the necessity of NanoARPES to study the intrinsic electronic structure of CVD graphene/Cu. (a) and (d) Scale difference of beam size and crystalline size in ARPES measurement. (b) and (e) Optical images of polycrystalline CVD graphene/Cu at different scales. (c) ARPES Fermi surface of polycrystalline CVD graphene/Cu as shown in (b) with a beam spot much bigger than the graphene domain size. The white dashed circle indicates the polycrystalline graphene FS. (f) NanoARPES FS from one single CVD graphene grain on Cu foil as shown in (e). Red hexagons indicate the Brillouin zone of graphene.

C. Chen, et all, J. Phys.: Cond. Matt. (2017)

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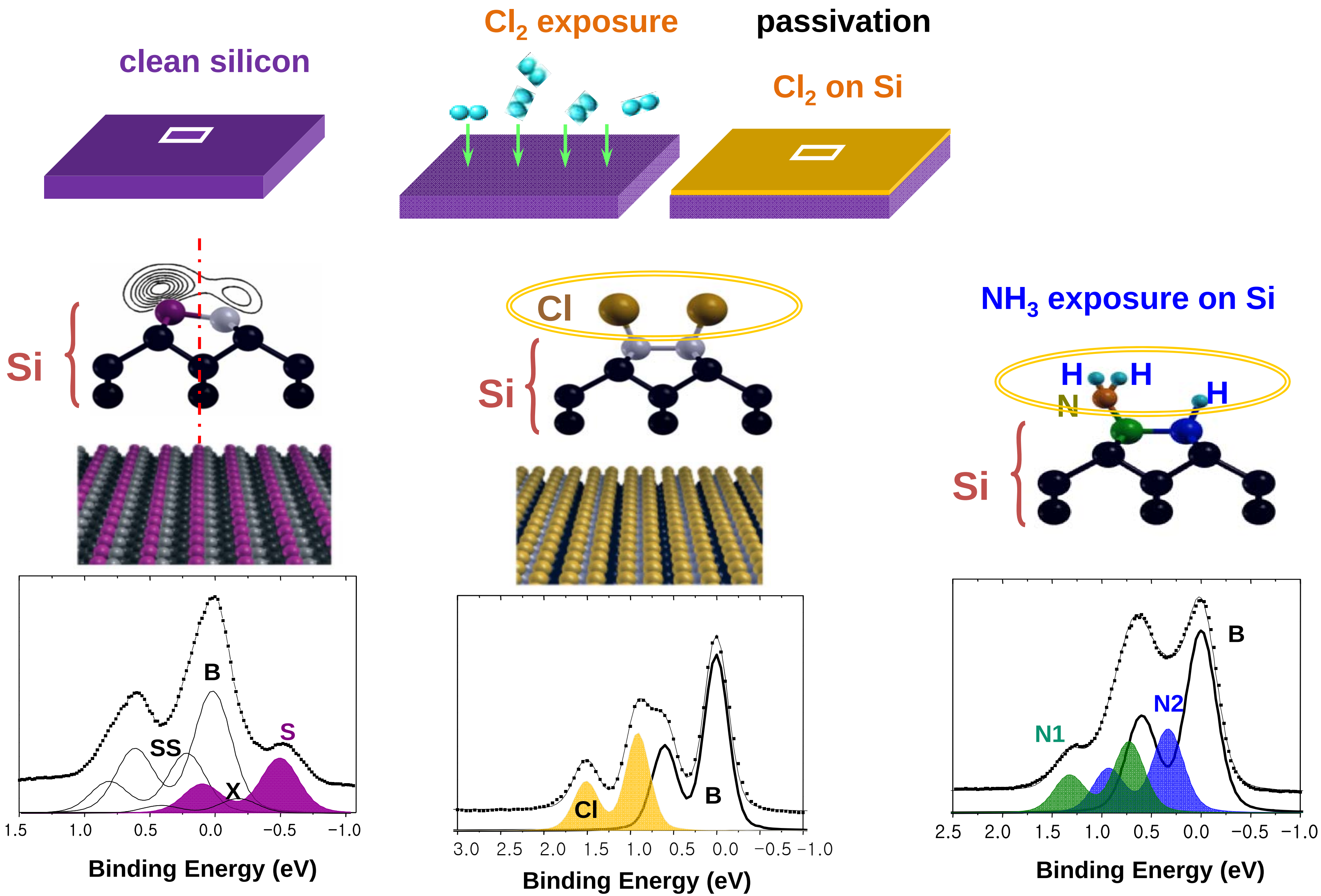
2.3 SPEM application: Atomic/molecular layer patterning



S. W. Moon *et al*., Adv. Mat. 19, 1321 (2007)

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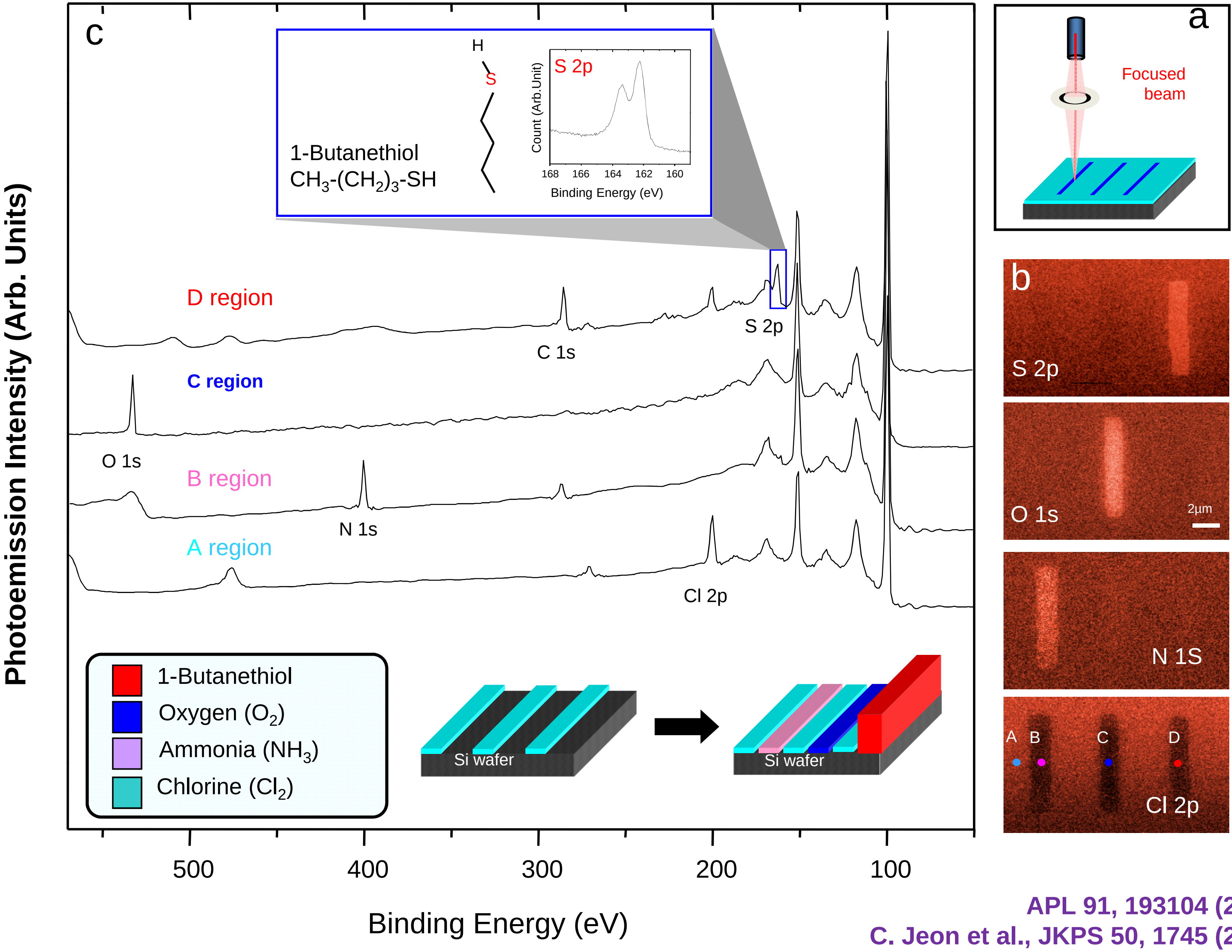
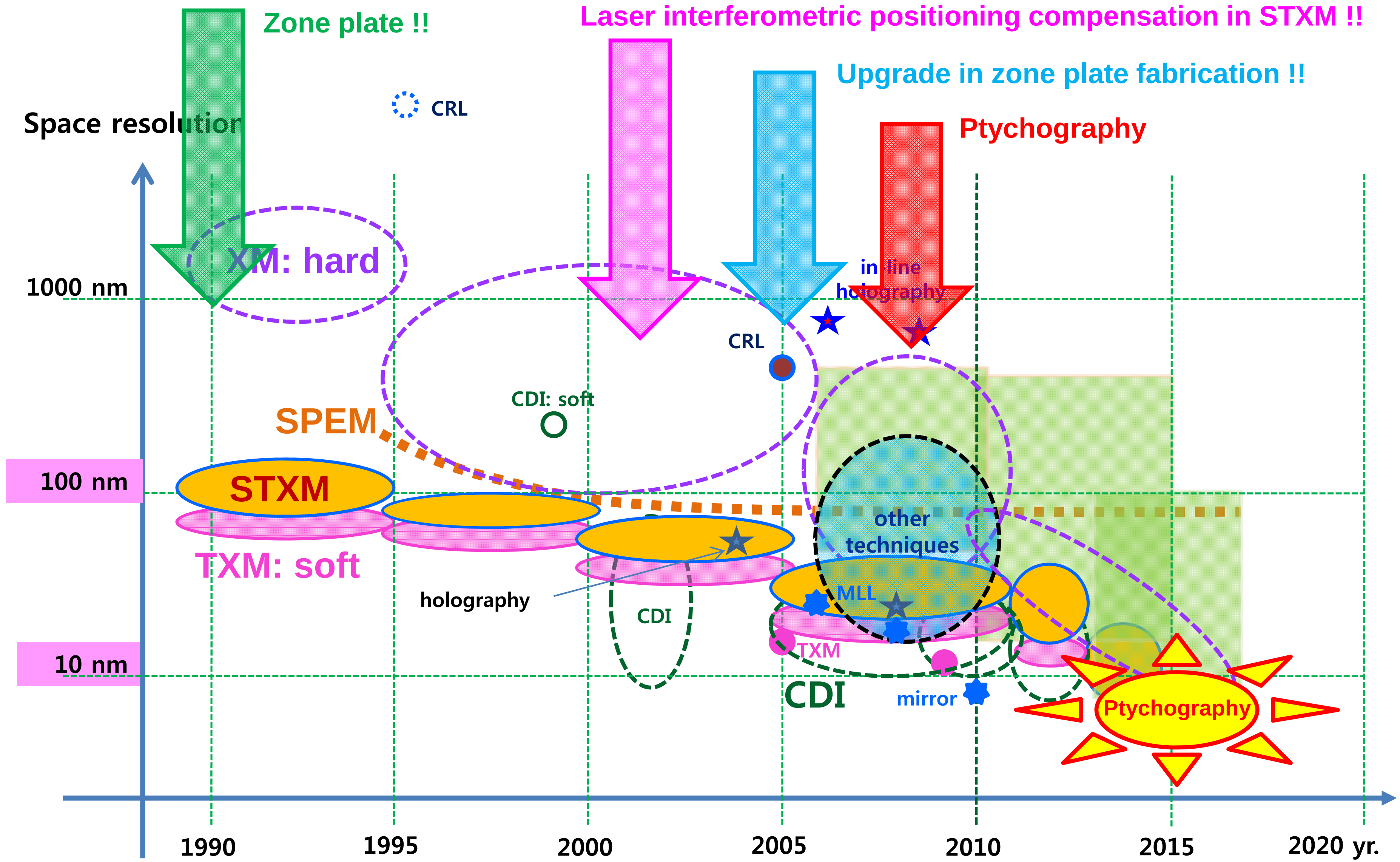
2.3 SPEM application: Atomic/molecular layer patterning



APL 91, 193104 (2007)
C. Jeon et al., JKPS 50, 1745 (2007)
S. W. Moon *et al*., Adv. Mat. 19, 1321 (2007)

3. Discussion: Evolution of space resolution of x-ray nanoscopy ..



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3. Discussion: application fields …

- **Nano particles: catalytic reaction, …**
- **Nano bio materials: nano ptl's influence on cell, …**
- **Bio, medical application**
- **Environmental materials**
- **Polymers**
- **Thin film devices (in-situ degradation)**
- **Secondary ion battery materials**
- **Magnetic materials**
- **Geo- and extraterrestrial- materials**
- **…**

- **in-situ experiments (annealing, biasing, magnetic field application, time resolved experiment, …) are feasible**
- **samples in solution environment**
- **soft materials (less radiation damage due to higher efficiency in contrast)**
- **polarization sensitive materials**
- **from high vacuum to atmospheric pressure environment**
- **…**

3. Discussion: soft x-ray microscopes…

(last changed: 31-Jan-2012)

Originally published in Handbook of Nanoscopy, Vol 2 (2012)

Courtesy of Prof. A. Hitchcock

Type	Facility	name	City	Country	Source	E-range (eV)	Status
TXM	Alba	Mistral	Barcelona	Spain	BM	270-2600	construction
TXM	ALS	XM1	Berkeley	USA	BM	250-900	operating
TXM	ALS	XM2 (NCXT)	Berkeley	USA	BM	250-6000	operating
TXM	Astrid	XRM	Aarhus	Denmark	BM	500	operating
TXM	Bessy	U41-TXM	Berlin	Germany	Und-L	250 - 600	operating
TXM	Diamond	B24 cryo-TXM	Harwell	UK	BM	250-2500	construction
TXM	NSRL	TXM	Hefei	China	BM	500	operating
TXM	Ritsumeikan	BL12	Kyoto	Japan	BM	500	operating
STXM	ALS	5.3.2.2	Berkeley	USA	BM	250-750	operating
STXM	ALS	5.3.2.1	Berkeley	USA	BM	250-2500	commissioning
STXM	ALS	11.0.2	Berkeley	USA	EPU	100-2000	operating
STXM	Bessy	old-STXM	Berlin	Germany	BM	250-600	decommissioned
STXM	Bessy	MAXYMUS	Berlin	Germany	EPU	250 – 1500	operating
STXM	CLS	10ID1	Saskatoon	Canada	EPU	130-2500	operating
STXM	Diamond	I08	Harwell	UK	EPU	250-2500	construction
(S)TXM	Elettra	Twin-mic	Trieste	Italy	Und-L	250 - 2000	operating
STXM	UVSOR	BL4U	Okazaki	Japan	Und-L	50-800	construction
STXM	NSLS	X1A (2)	Upton	USA	Und-L	250-1000	decommissioned
STXM	PLS	nanoscopy	Pohang	Korea	EPU	100 - 2000	construction
STXM	SLS	PolLux	Villigen	Switzerland	BM	250-750	operating
STXM	SLS	NanoXAS	Villigen	Switzerland	BM	250-750	commissioning
STXM	Soleil	Hermes	Saint-Aubin	France	EPU	250 – 1500	construction
STXM	SSRF	SXS	Shanghai	China	EPU	200 - 2000	operating
STXM	SSRL	13-1	Stanford	USA	EPU	250 – 1000	operating
SPEM	ALS	BL 7.0	Berkeley	USA	Und-L	90-1300	decommissioned
SPEM	ALS	Maestro	Berkeley	USA	EPU	90-1300	commissioning
SPEM	Elettra	BL 2.2 L	Trieste	Italy	Und-L	200-1400	operating
SPEM	Elettra	BL 3.2 L	Trieste	Italy	Und-L	27, 95	construction
SPEM	MAX-lab	BL 31	Lund	Sweden	Und-L	15-150	operating
SPEM	NSRRC	BL09A1	Hinschu	Taiwan	Und	60-1500	operating
SPEM	PAL	8A1	Pohang	Korea	Und	20 - 2000	operating
SPEM	Soleil	Antares	Saint-Aubin	France	EPU	50 - 1500	commissioning