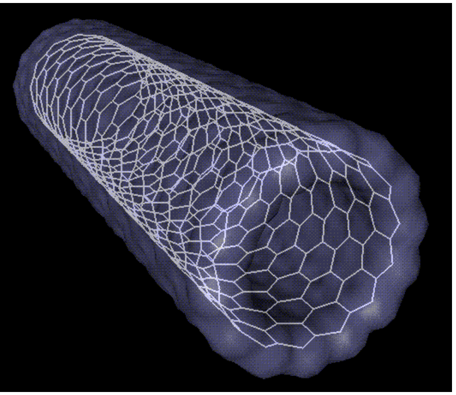
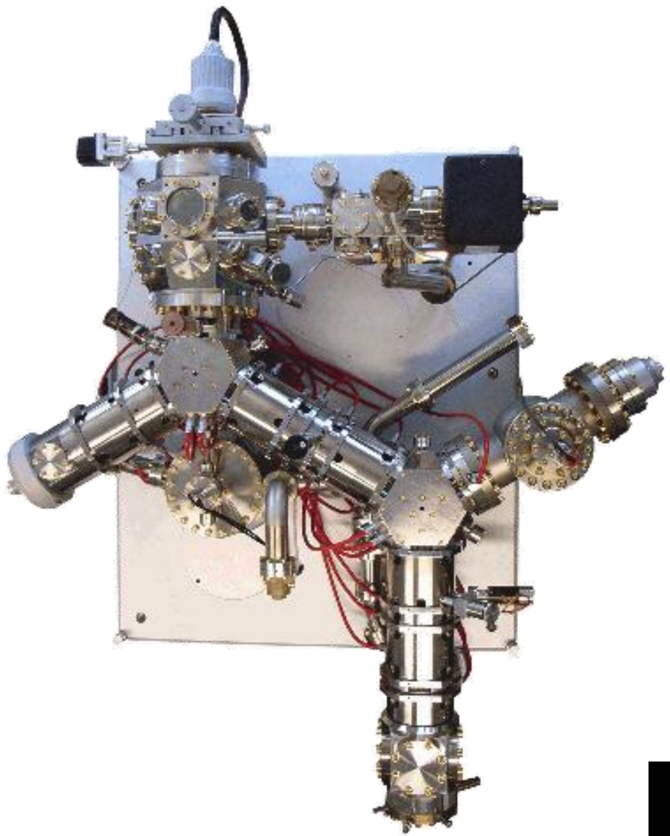
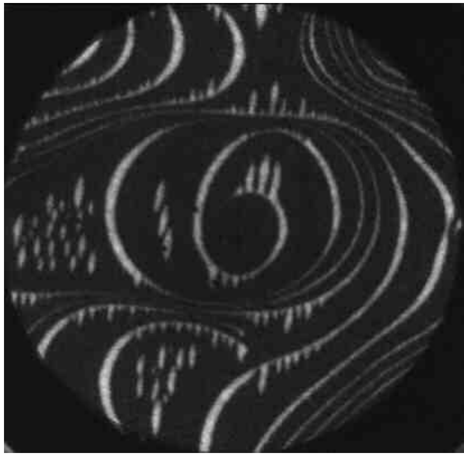
PEEM and Nanoscience

Dr Anton Tadich

Australian Synchrotron







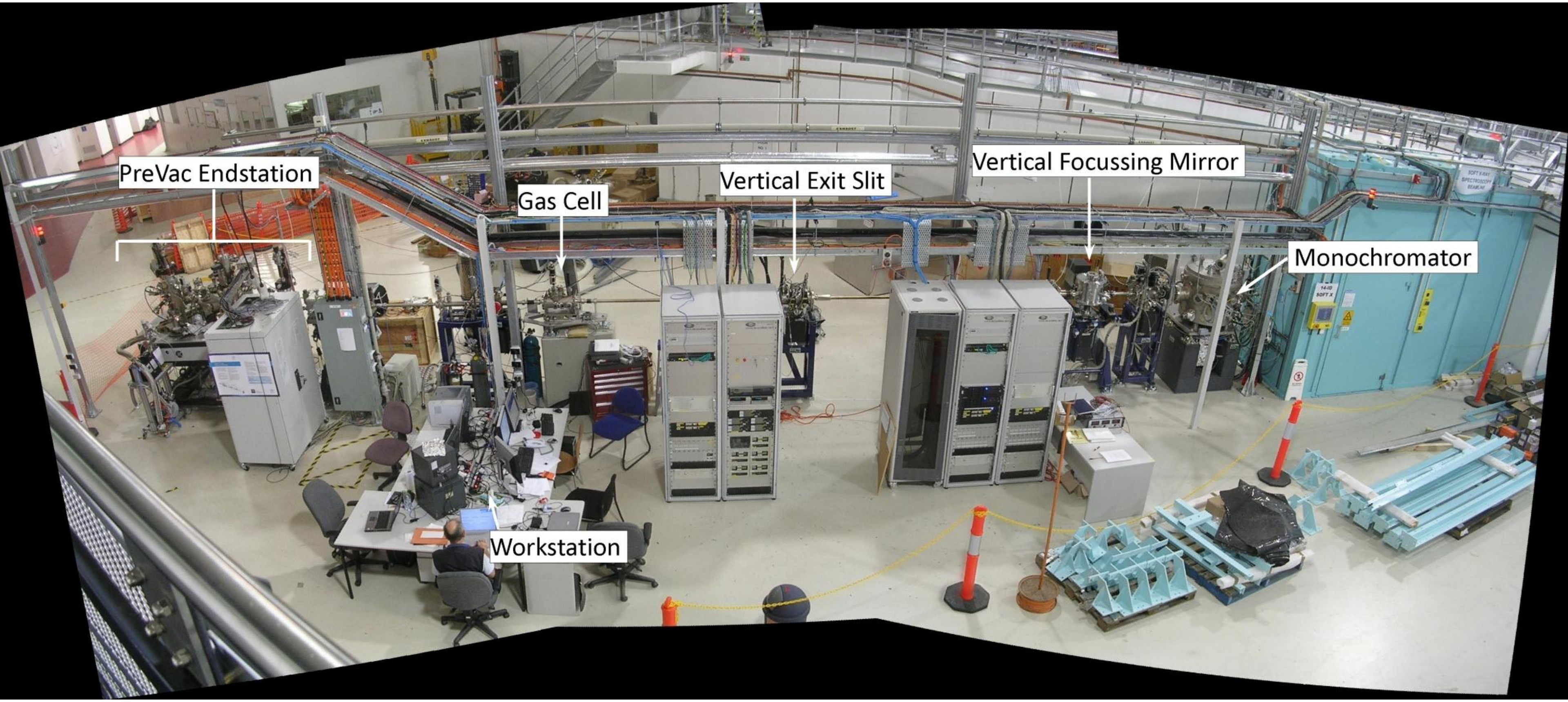
Australian Synchrotron

2nd AOFSRR Summer School

Cheiron School 2008

The Australian Synchrotron

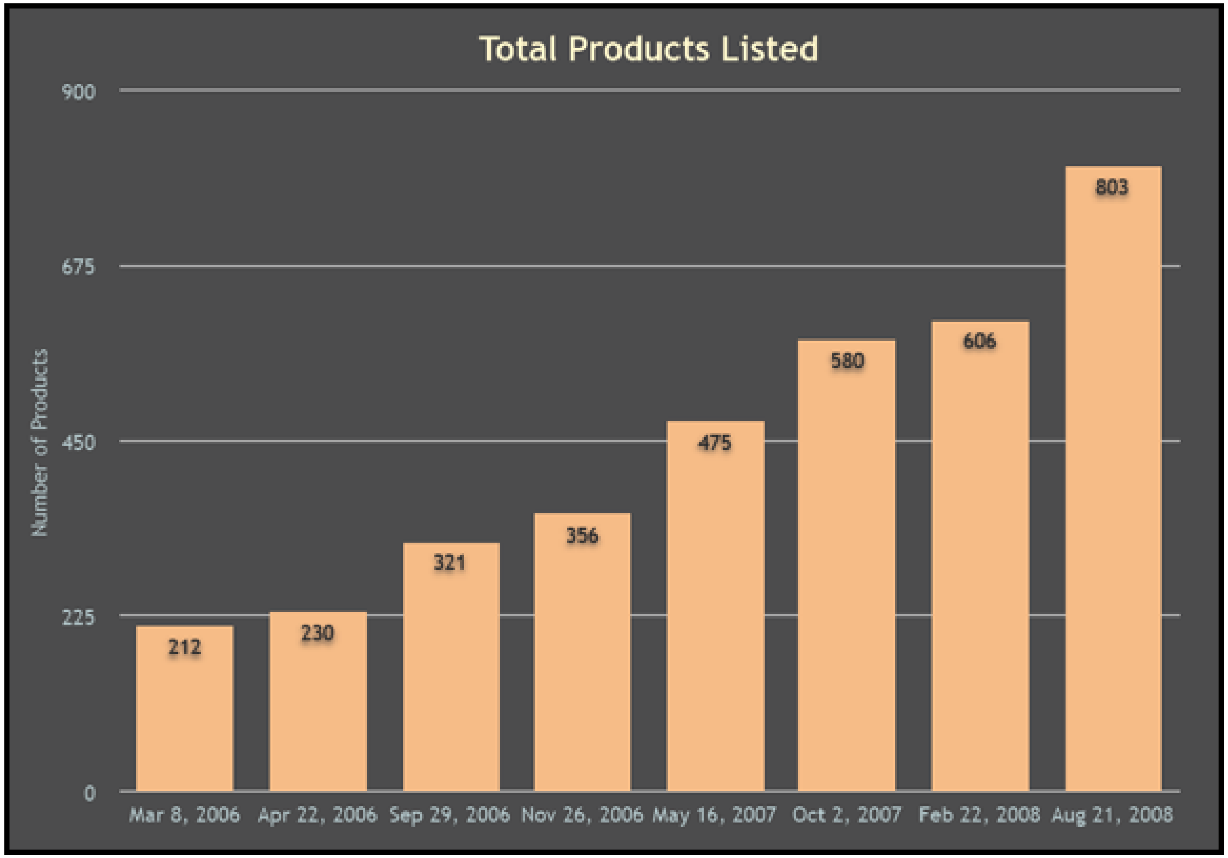
The Soft X-ray beamline



- "APPLE II" undulator: variable polarisation: linear (horizontal to vertical), circular (left and right)
- Photon energy range 90 – 2500eV; $E/\Delta E$ = 5000 to 10000
- Current endstation: NEXAFS (TEY, PEY, TFY), XPS (SPECS Phiobos 150 HSA), cleaving facility, sample heating and cooling, preparation chamber, glovebox…

The Growth of Nanotechnology

- Nanotechnology represents a rapidly expanding sector of materials technology
- There has been a 279% increase in nanotechnology-based products since 2006
- Predicted worldwide turnover of over 1 trillion Euro by 2015.



Source: http://www.nanotechproject.org/inventories/consumer/analysis_draft/

Characterisation at the Nanoscale

- The continual miniaturization of devices and material structures demands novel methods for nanoscale investigations of surfaces, thin films and interfaces

- There are a number of tools which excel in either <u>spatial</u> or <u>chemical</u> investigations

"Real Space" structure (nm and below)

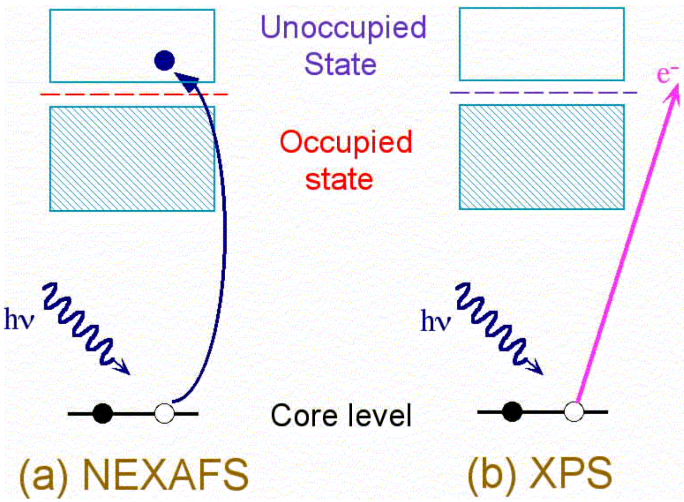
Scanning and Transmission Electron Microscopy (SEM, TEM), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM), … → Morphology, geometric structure, atomic positions and surface reconstructions

"Chemical" information

X-Ray Absorption Spectroscopy (NEXAFS, EXAFS) Photoelectron Spectroscopy (XPS, UPS) Infrared (IR), NMR, … → Elemental information, chemical environment, adsorbate geometry, bonding configuration, oxidation state, magnetic properties etc..

- An understanding of the properties of novel systems benefits greatly from spatially-resolved spectroscopic measurements with "nanometer" resolution

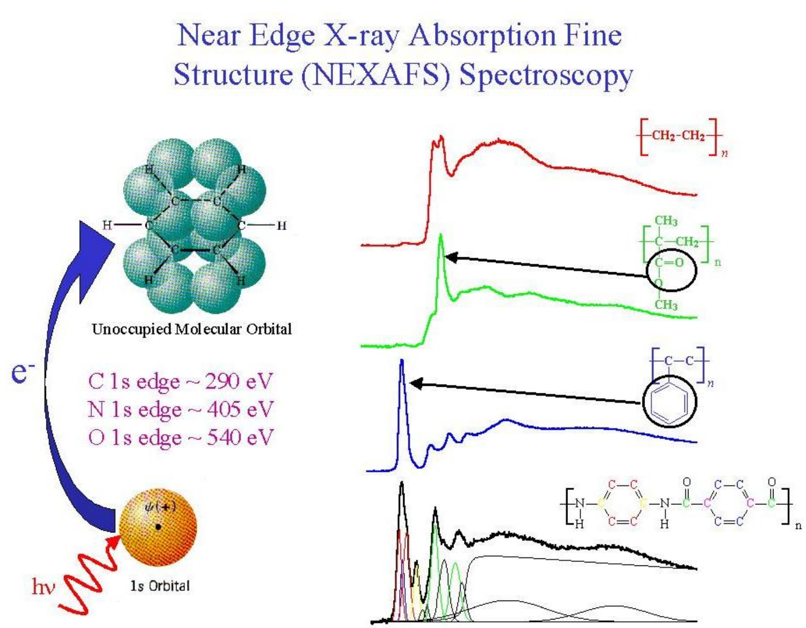
Image courtesy: www.theochem.kth.se



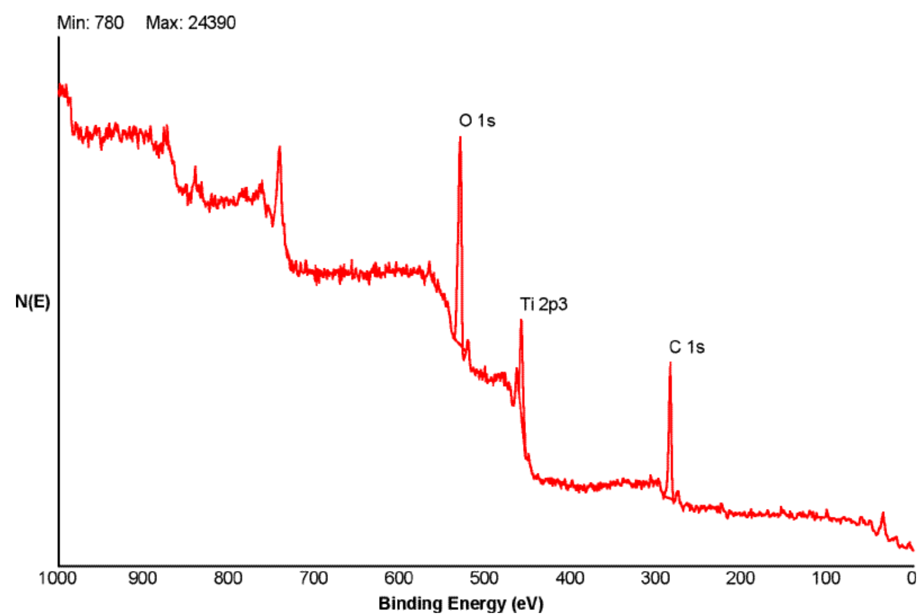
- NEXAFS and XPS are well established techniques for surface chemical characterisation

- Traditional instruments integrate spectral information over the photon-illuminated area

  - How can we extend these methods to spatially discriminate on the nanoscale?



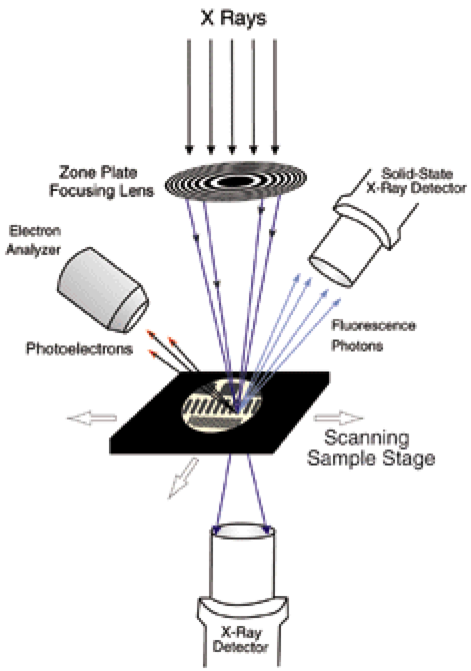
www.physics.ncsu.edu/stxm/NEXAFS.jpg

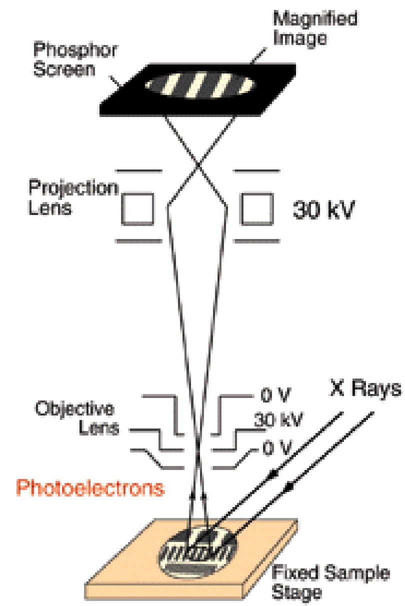


http://www.emal.engin.umich.edu/instruments/resources/XPSsurvey.gif

Soft X-ray Microscopy

- Soft X-ray based spectroscopic microscopy using synchrotron radiation is increasingly the main tool for laterally-resolved spectroscopy on the nanoscale
- One can distinguish methods using *sequential* acquisition (microspectroscopy), and those featuring *parallel* acquisition (spectromicroscopy)





Microspectroscopy

- ➢ Highly focused probe-beam (KB mirror or zone plates)
- ➢ Sequential detection (x-rays, electrons)

Spectromicroscopy

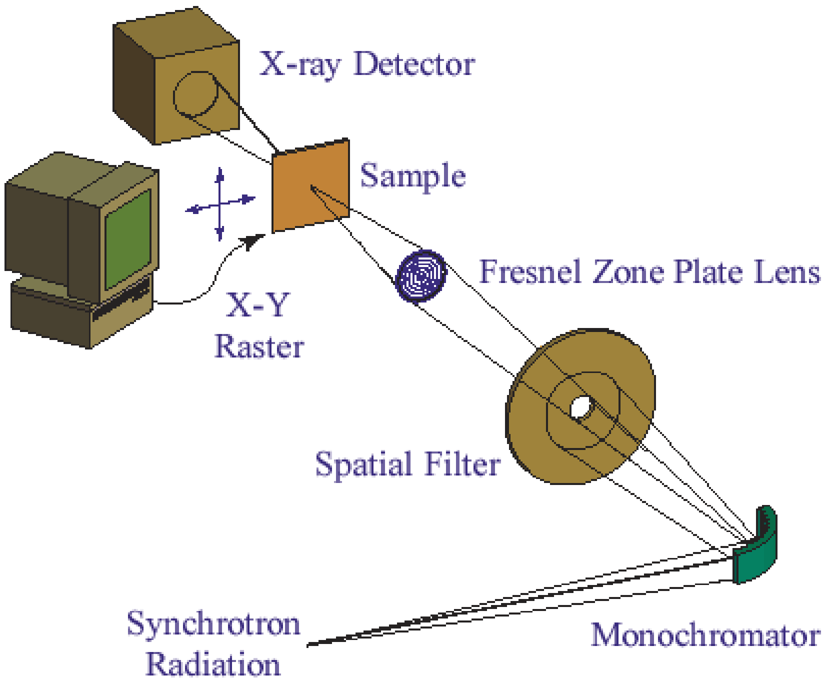
- ➢ "Large" area probe-beam
- ➢ Parallel imaging (electrons)

Images courtesy: www-als.lbl.gov/als/workshops/scidirecthtml/4Magnetic/magnetic.html

Some examples of microspectroscopy

Scanning X-ray Transmission Microscopy (STXM)

- X-rays focused using zone plate optics. Sample is rastered at the focus, and the transmitted intensity measured
- Chemical/elemental information is obtained by determining the X-ray absorption by the sample (NEXAFS)
- Can obtain NEXAFS spectra at fixed position, or single image at fixed energy
- Spatial resolution of 30-50nm. Depth information possible.
- Samples must be partly transparent at the X-ray energies of interest



Experimental geometry of a STXM experiment

Image courtesy: srs.dl.ac.uk/XRS/diamond/SpectroMicroscopy

Scanning Photoemission Microscopy (SPEM)

- A SPEM instrument combines zone plate focussing optics and a conventional electron energy analyzer to perform laterally-resolved photoemission spectroscopy

Schematic of U5-SPEM instrument, NSRRC.

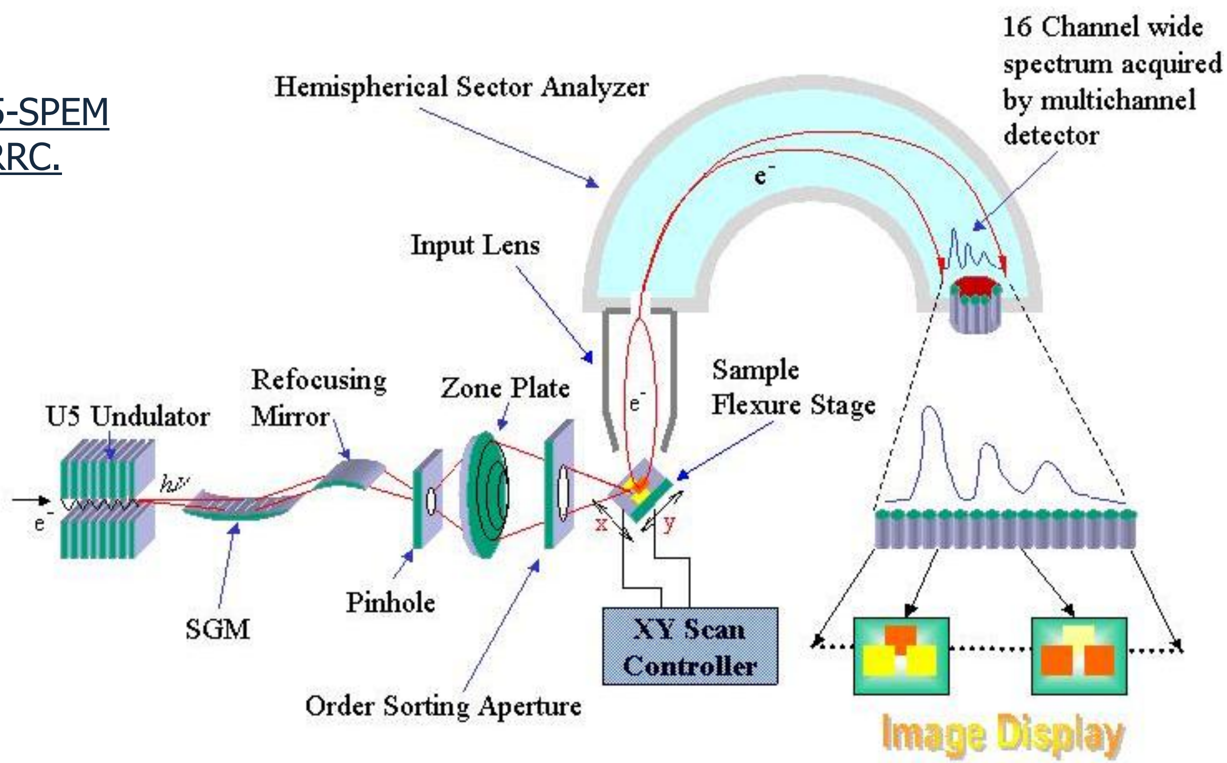


Image courtesy: http://140.110.203.42/spem.htm

- High energy resolution is achieved due to well-established spectrometer design
- Poorer spatial resolution than STXM: combined geometry of illumination and detection yields a resolution of ~ 200nm for modern instruments

Disadvantages of scanned-mode acquisition

- The probe is a *focussed* x-ray beam. The spatial resolution is capped at the diffraction limit of the x-rays
- The focal length of zone plates are a function of x-ray energy: One must displace the sample as the photon energy is changed
- More time consuming than parallel acquisition; time-resolved studies limited

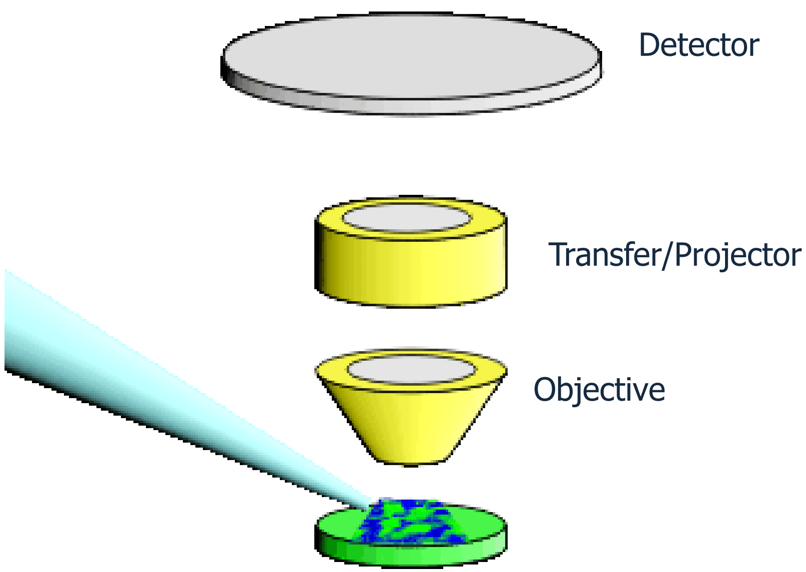
Parallel imaging with photoelectrons: advantages

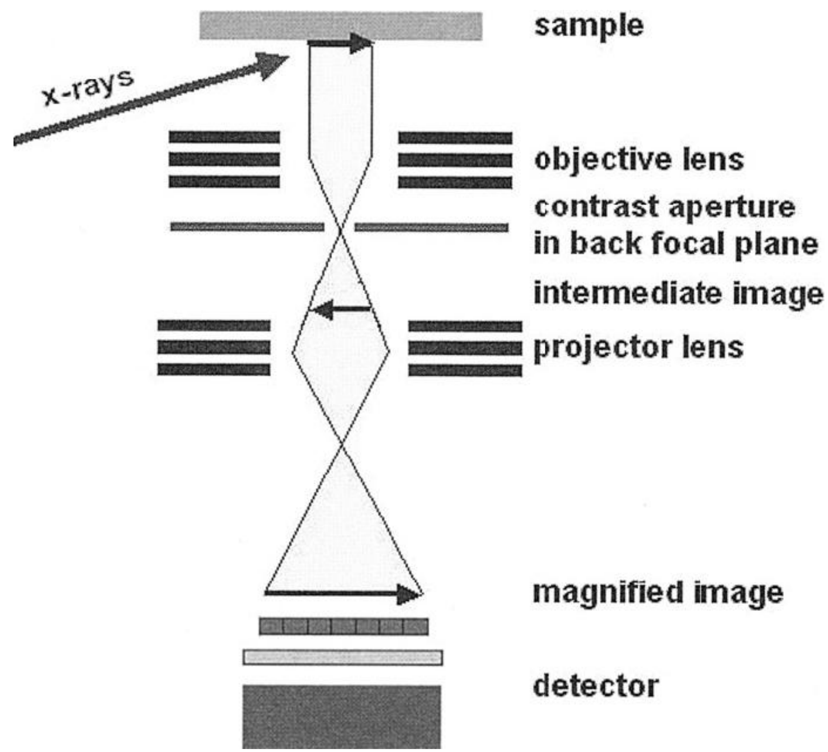
- Spatial resolution is only limited by aberrations in electron-optical imaging system. Can be improved by design
- Rapid measurement: video rate imaging, time resolved studies (e.g. "pump-probe" experiments)

The most popular type of instrument is the **P**hoto **E**mission **E**lectron **M**icroscope **(PEEM)**

Basic Principles of PEEM

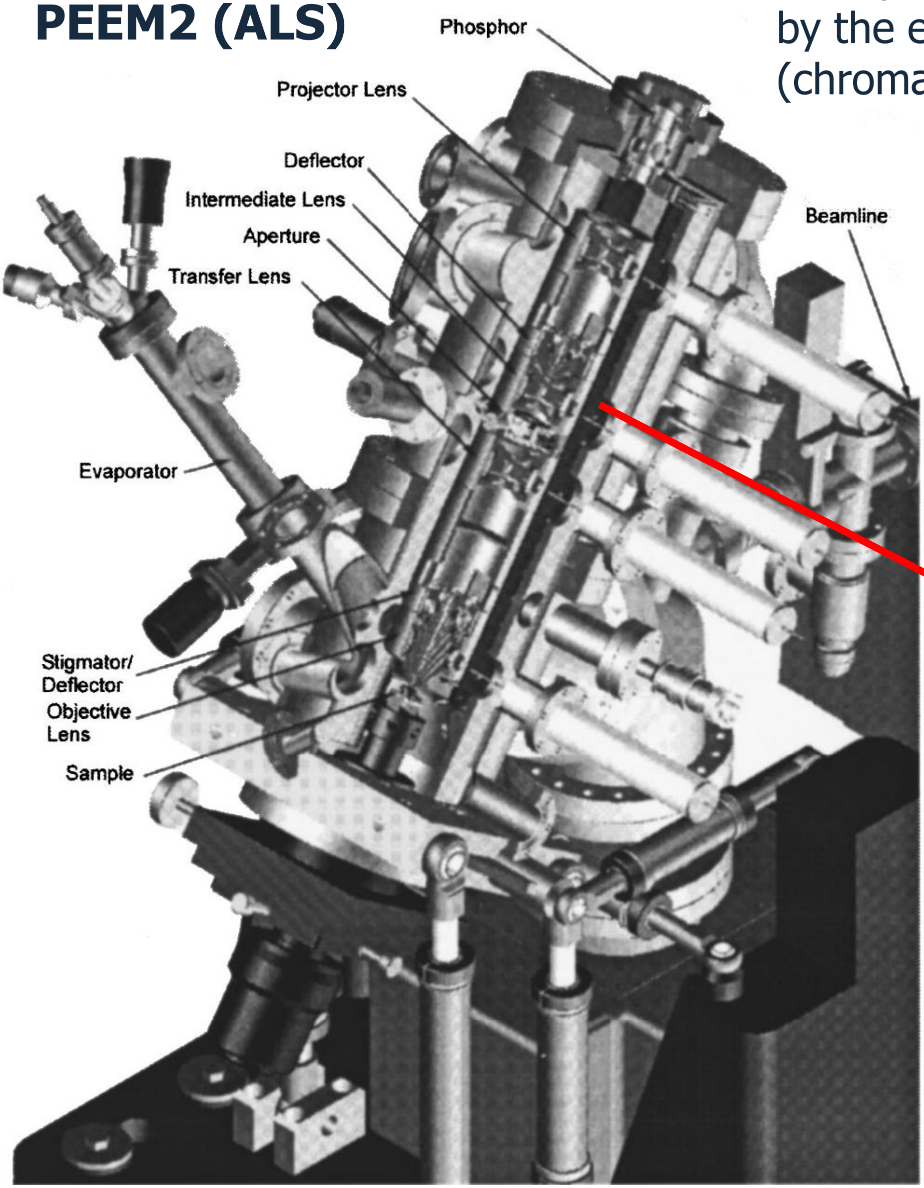
- In PEEM, the sample is homogeneously illuminated with soft X-rays or ultraviolet (UV) radiation with a spot size ~ field of view of the microscope (1 – 100μm)
- An objective lens operating at high potential (10-30kV) is used to extract the emitted electrons, focussing them to an intermediate image at a back focal plane.
- Projector and transfer optics are used to further magnify the intermediate image onto a 2D detector





http://xraysweb.lbl.gov/peem2/webpage/Project/TutorialPEEM.shtml

PEEM2 (ALS)



PEEM2 microscope (ALS); a resolution of 20nm can be reached with X-ray energies

Image courtesy: S Anders *et al*, Rev. Sci. Instr, 70(10) (1999), 3973

- The spatial resolution of a PEEM instrument is degraded by the energy spread of the transmitted electrons (chromatic aberrations)

- PEEMs contain a contrast aperture to restrict the energy & angular spread of electrons, allowing tradeoff between resolution and transmission

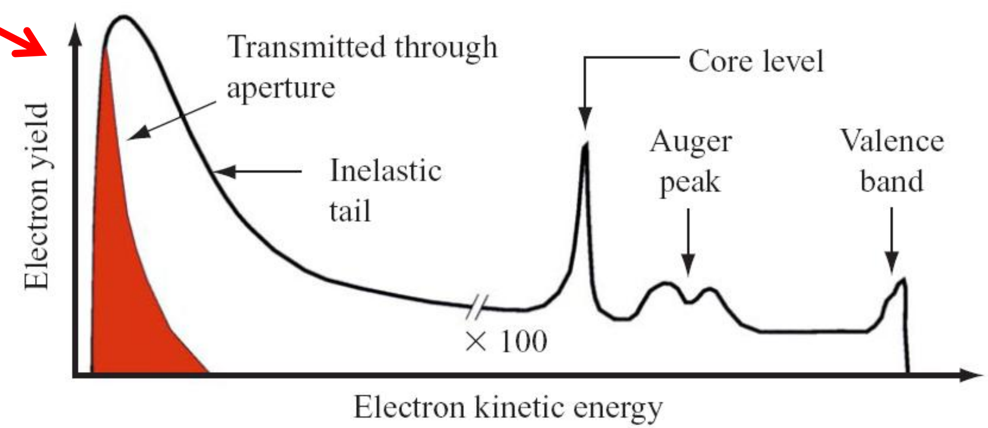
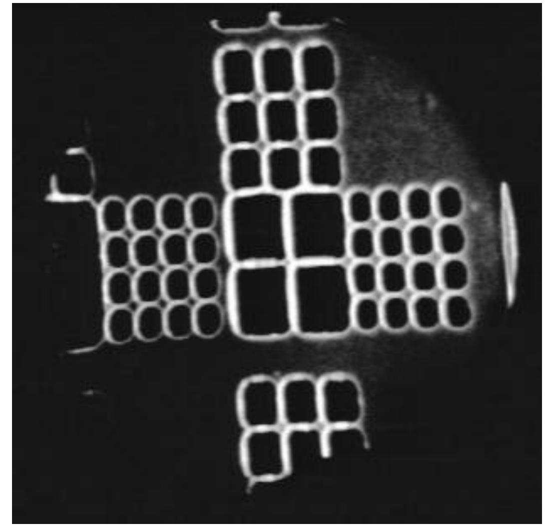


Image courtesy: J Stöhr *et. al*, *IBM J. Res. Develop,* 44(4), (2002), p. 535

- The aperture is typically adjusted enhance the transmission of secondary electrons

Commercial PEEM: Elmitec “PEEM III”



Etching pits in Si(001) wafer

140μm

Cu on Mo (110)

5μm

Specifications

- Field of view: 2 – 150μm; best resolution <15nm
- Sample temperature: RT to 1800K
- Electron energy analyser can be added for spectroscopic imaging

(Images courtesy www.elmitec-gmbh.com)

SPELEEM: Spectroscopic **P**hotoemission and **L**ow **E**nergy **E**lectron **M**icroscope

- This instrument combines the structural sensitivity of Low Energy Electron Microscopy (LEEM, resolution <5nm) with the flexible spectroscopy of *energy-filtered* PEEM.
- Separation between incoming and outgoing electron beams achieved with a magnetic prism
- Electron microscopy, X-ray photoemission microscopy and diffraction (angular) mapping can be performed on the same sampling area => multi-technique approach to studies.

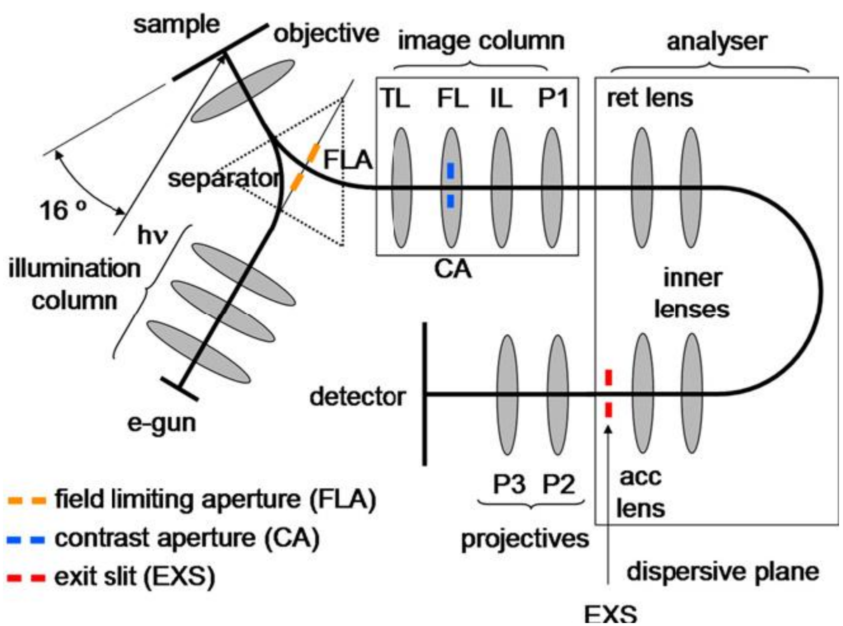
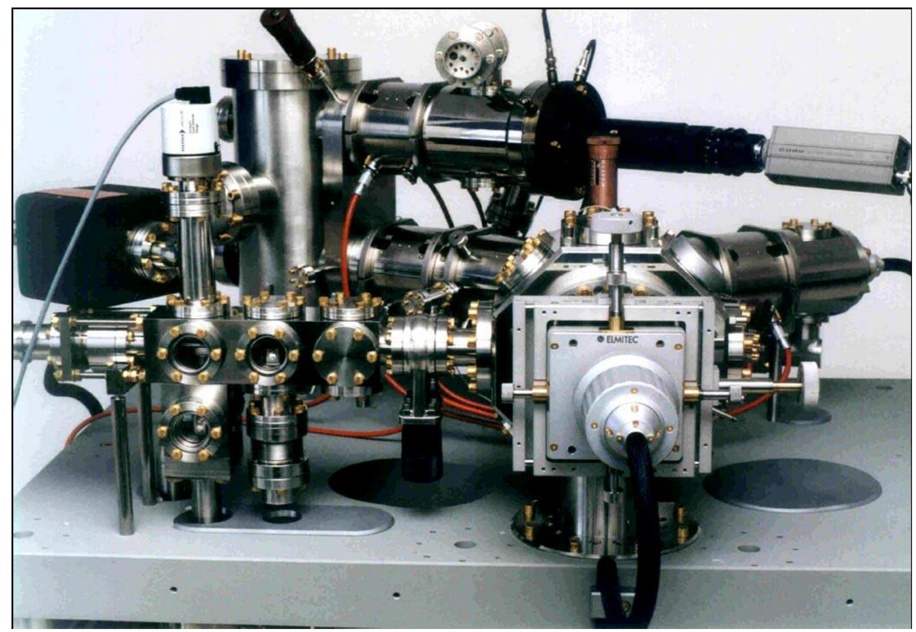


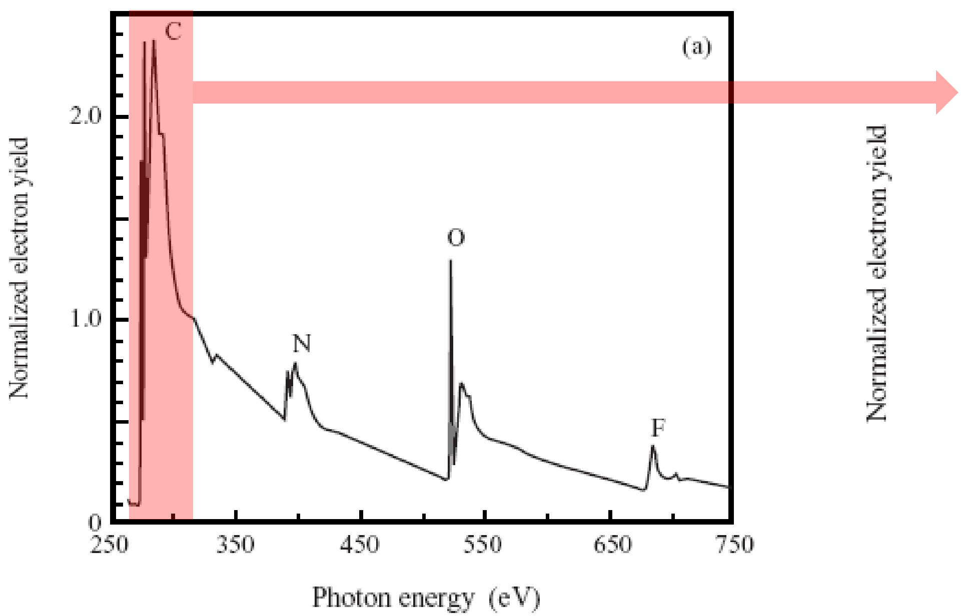
Image courtesy: Locatelli, A *et. al*, J. Phys. Condens. Mater, **20** (2008), 3



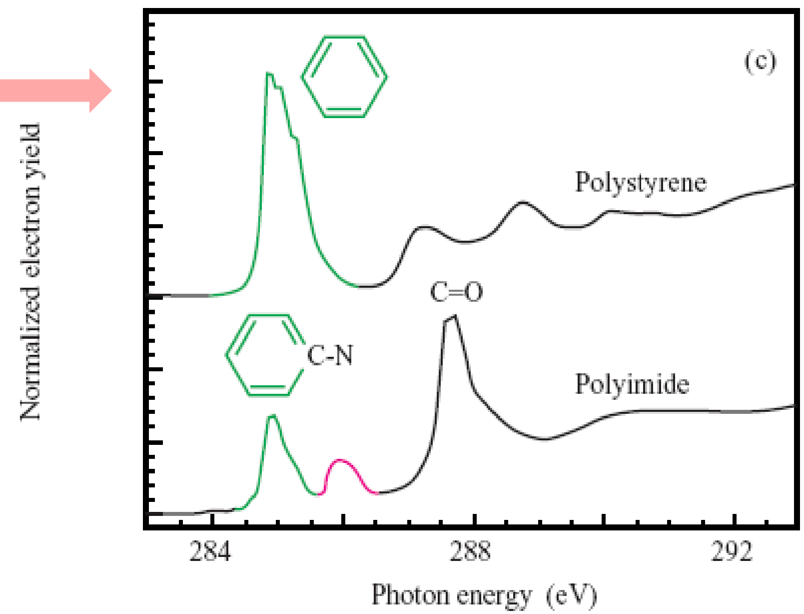
Schematic and photo of SPELEEM

Elemental and Chemical Contrast

- Generation of core holes upon x-ray absorption leads to creation of Auger electrons. Inelastic scattering of the Auger electron contributes to the secondary electron background
- The Auger/secondary electron yield is proportional to the x-ray absorption. At an absorption edge, secondary electron intensity will increase. This is a large, accessible signal for PEEM.
- Regions of the sample containing that element will appear brighter => element selective contrast. Tuning through several photon energies allows for NEXAFS analysis => chemistry



Tuning to the absorption edge of an element will enhance secondary electron yield for element specific imaging

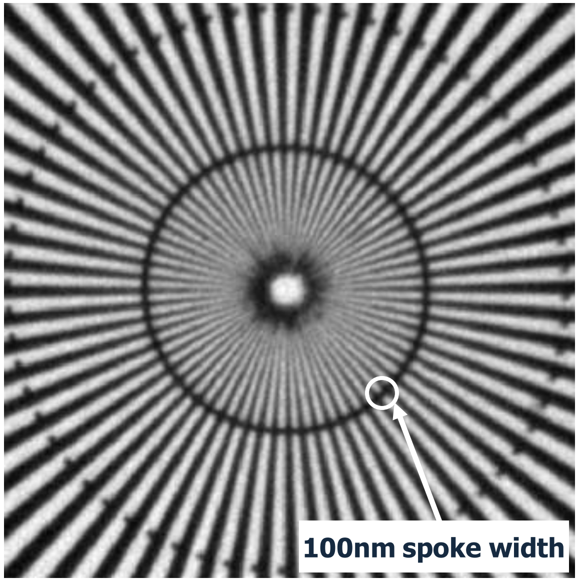


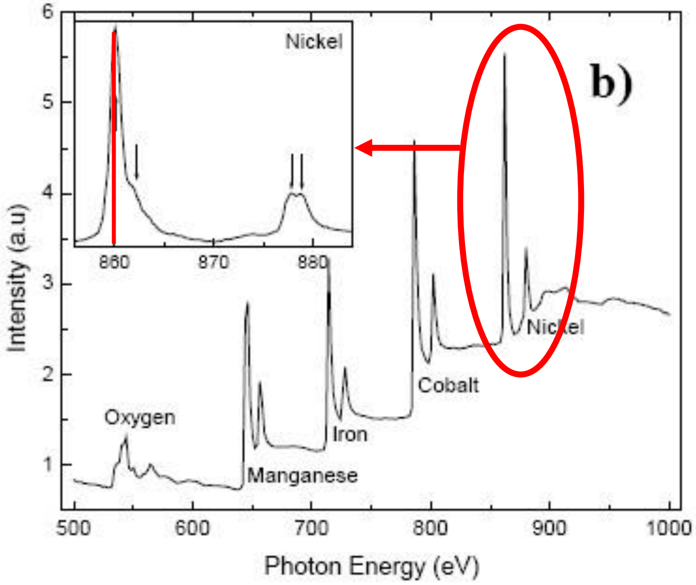
Fine structure in the absorption edge (NEXAFS) can be investigated with PEEM, yielding chemical structure

Images courtesy: J Stöhr *et. al*, *IBM J. Res. Develop,* 44(4), (2002), p. 535

Examples of elemental and chemical imaging

- Nickel+photoresist test pattern for PEEM2 project (ALS).
- With photon energy tuned to Nickel L_3 edge, nickel areas appear bright
- Loss of detail in inner rings at 30nm due to limit of e-beam lithography patterning

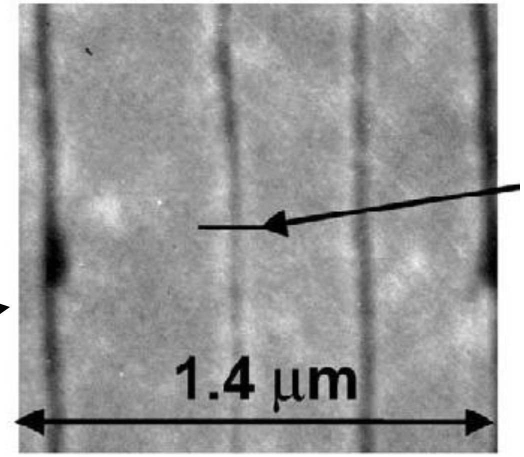


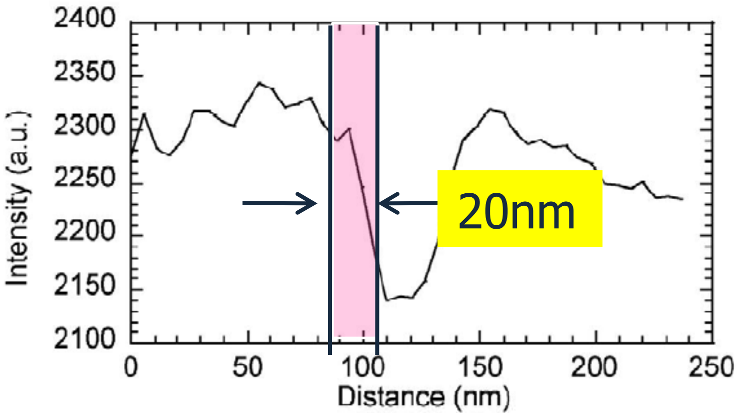


http://xraysweb.lbl.gov/peem2/webpage/Project/TutorialContrast.shtml

- PEEM image of $LaFeO_3$ thin film, generated by tuning photon energy to the La M_5 edge (60s exposure time)

Vertical features are tracks generated by electrical discharge on sample surface



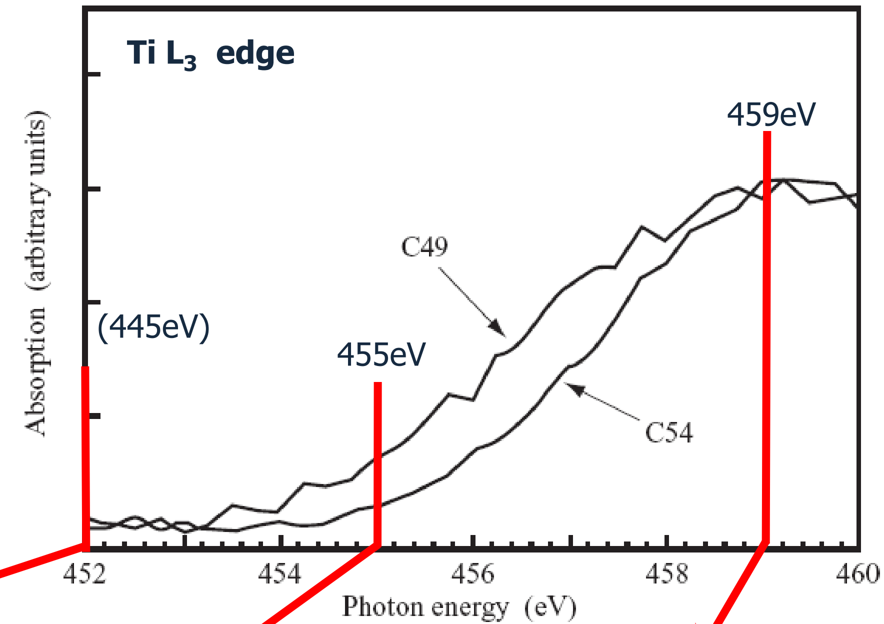


Data taken from: Scholl, A. *Current Opinions in Solid State and Materials Science*, 7 (2003), p59

- $TiSi_2$ exists in 2 structural phases: low conductivity C49, and high conductivity C54. Bonding configuration yields different NEXAFS spectra for the phases (right)

- XPEEM images of a micropatterned $TiSi_2$ sample, taken at 3 photon energies about the Ti L_3 edge

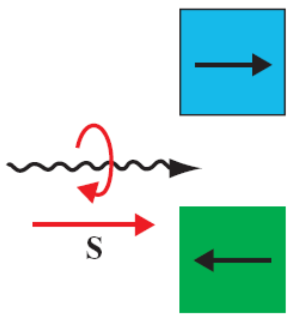
- NEXAFS-XPEEM results yield location of C49 phase relative to C54 phase

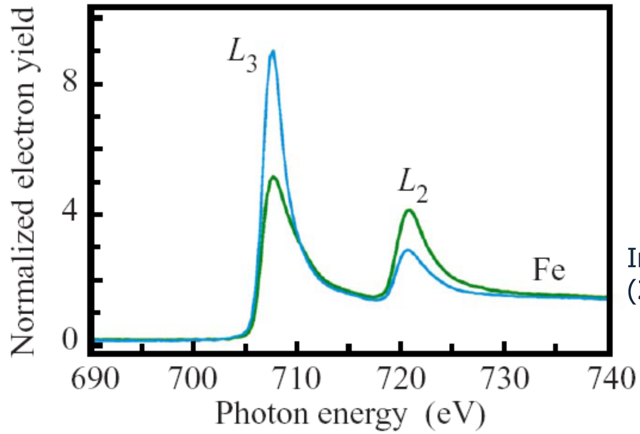


Data reproduced from S Singh *et. al, Appl. Phys. Lett,* 71 (1997), 55

Magnetic Contrast

- PEEM is able to resolve ferromagnetic domains, and determine the size and orientation of magnetization vectors, via X-ray Magnetic Circular Dichroism (XMCD)





XMCD: The absorption of circularly polarised light by ferromagnetic domains depends upon the relative orientation of the domain's magnetic moment and photon helicity vector

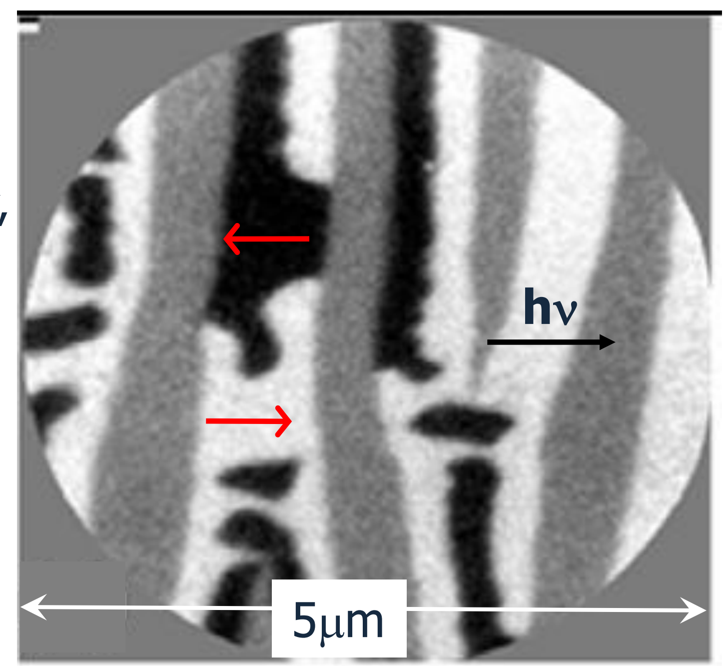
Image courtesy: J Stöhr *et. al*, *IBM J. Res. Develop*, 44(4), (2002), p. 535

- Extra contrast in XMCD-PEEM image can obtained by subtracting two images measured at a fixed photon energy, but with opposing helicity vectors

XMCD difference-image of ferromagnetic MnAs on GaAs.

Ferromagnetic/paramagnetic striping observed during growth

Black/white areas are opposing ferromagnetic domains. Grey areas are paramagnetic, and show no change upon altering the helicity.

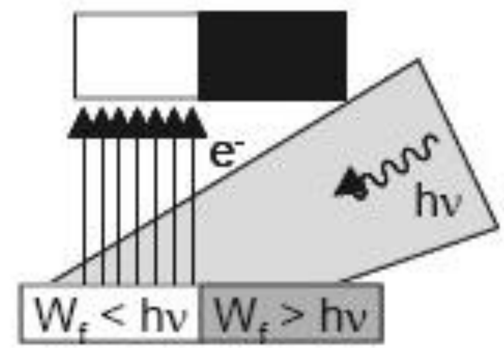


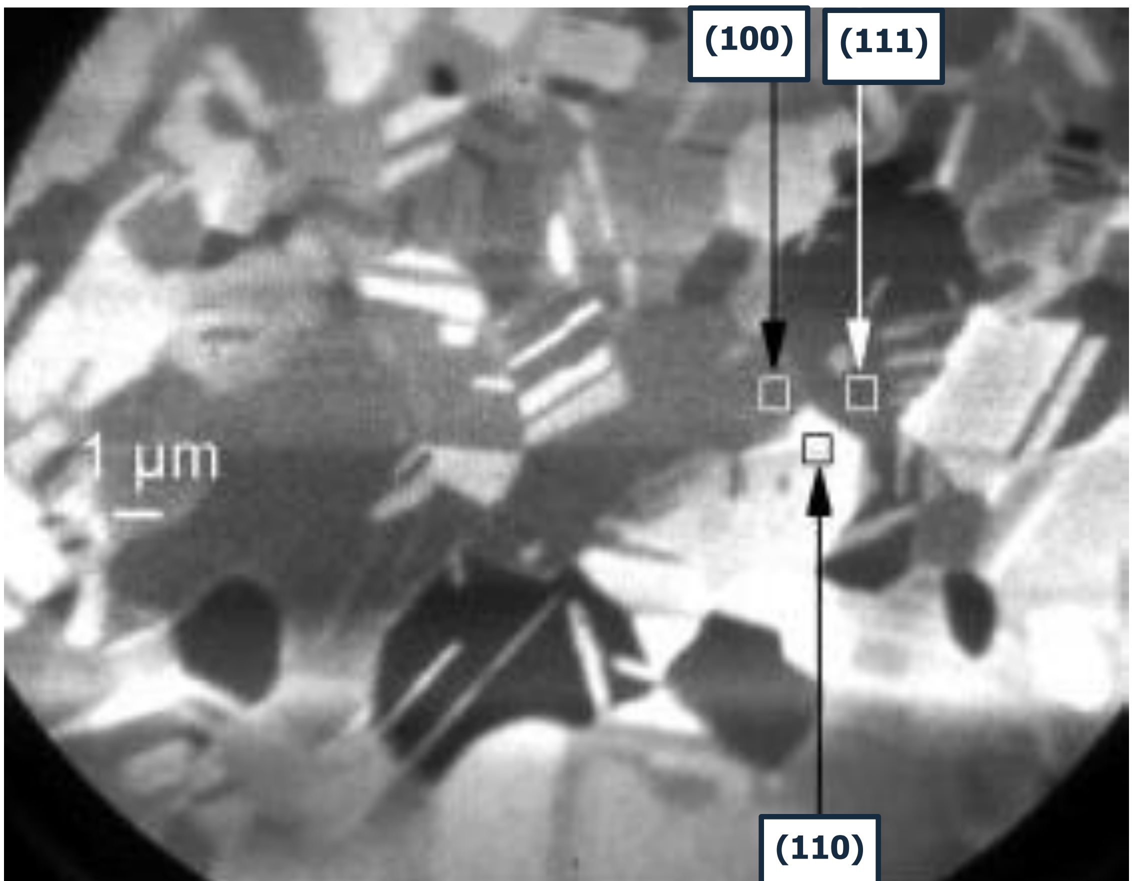
Data taken from: Engel-Herbert *et. al*, *J. Magn Magn. Mater*, **305**, p457

Work Function Contrast

- Usually performed with UV sources, e.g. Hg lamp ($h\nu$ = 4.9eV) => "UV-PEEM"

- Applied to metals, this technique leads to a narrow energy range excited from the Fermi Energy, depending on work function
- Variations in the work function across the sample surface leads to strongly varying electron yield.





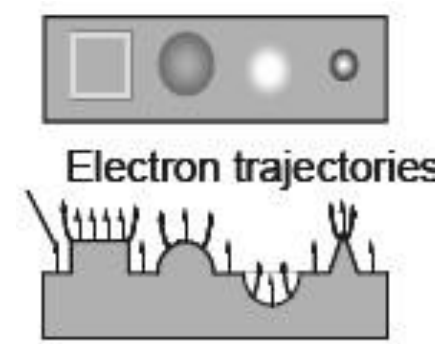
- Due to smaller energy range from sample, UV-PEEM has higher resolution (10nm)

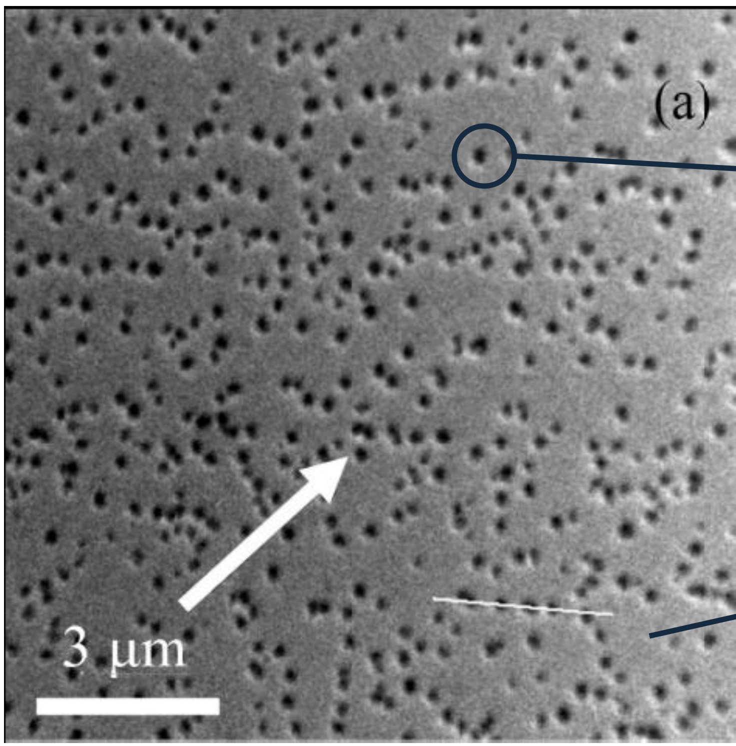
UV-PEEM image of polycrystalline Cu. Individual grains of Cu(100), Cu(110) and Cu(111) can be distinguished due to work function differences between the faces

O Renault *et al*, Surf. Interface. Anal, 38 (2006), 375

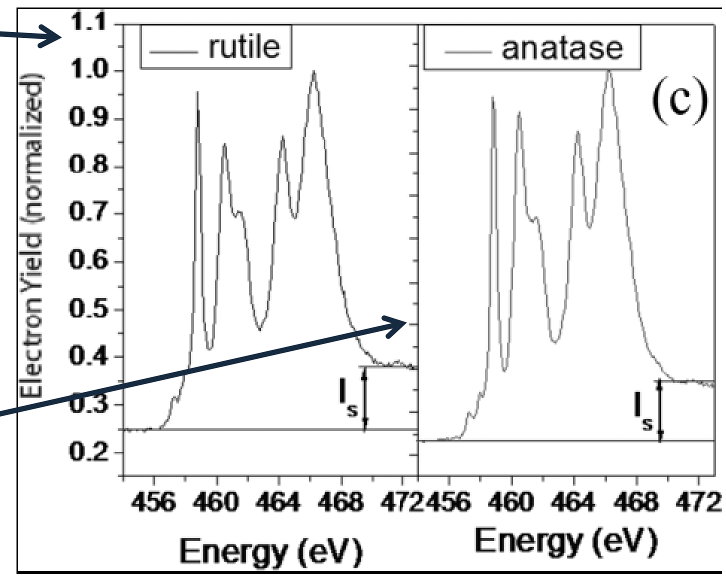
Topological Contrast

- For rough samples, the electric field around topographical features is distorted; localised focusing causes contrast in the final image
- Shadowing effects also provide an additional contrast mechanism





X-ray PEEM (X-PEEM) of TiO (rutile-phase) nanocrystals embedded in a TiO (anatase-phase) film. Contrast is due to nanocrystal topography.



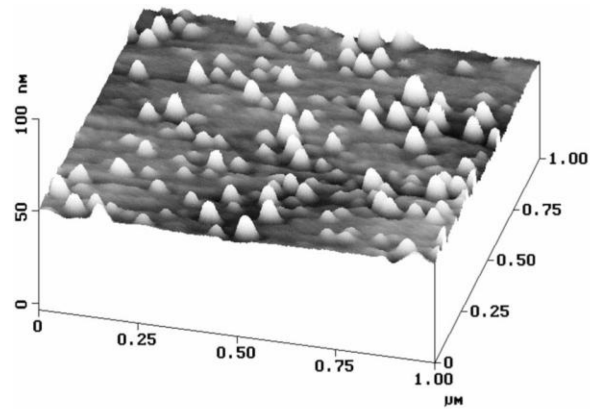
μ-NEXAFS of nanoparticles and substrate indicates contrast is *not* due to X-ray absorption (elemental) differences

Xiong, G *et al*. Advanced Functional Materials, 17, pp 2133-2138, 2007

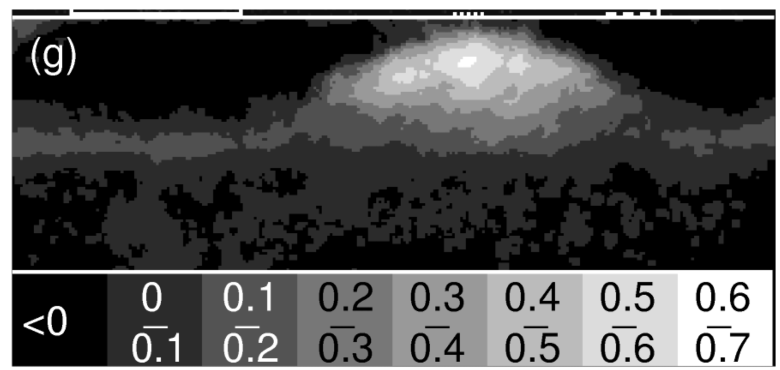
Case Study: Surface Compositional Gradients of InAs/GaAs quantum dots

G Biasiol *et. al*, Appl. Phys. Lett, 87 (2005) p.223106

- Understanding of the quantum-confined energy states in self-assembled $In_xGa_{(1-x)}As/GaAs$ quantum dots (QD) require an accurate knowledge of the QD shape and composition distribution



- Previous work has obtained QD cross sectional composition using Energy Selective Imaging (ESI) in a TEM



Cross sectional In concentration (x) for $In_xGa_{1-x}As$ QD, obtained by ESI

(Images courtesy: Walther, T. *Phys Rev Lett.* 86(11) (2001), p2381

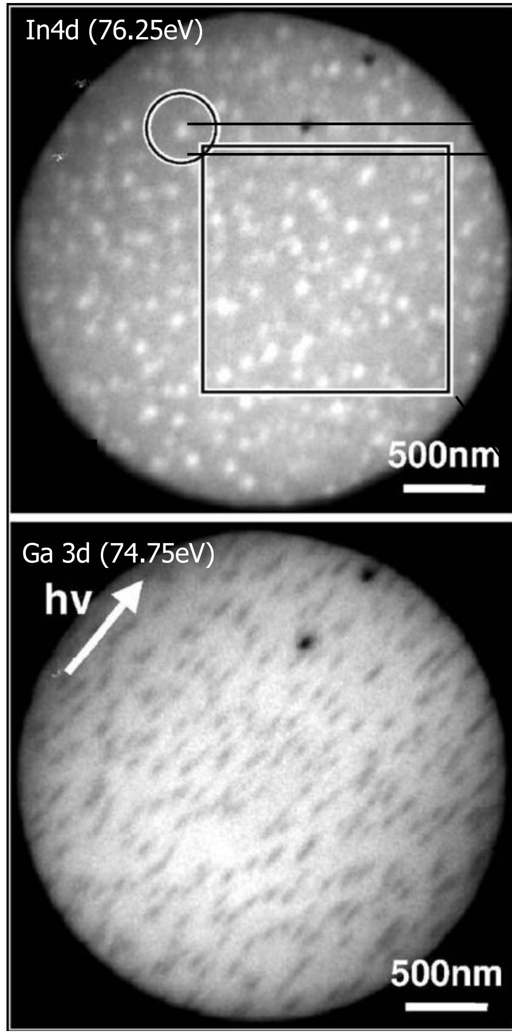
- Measurements on the top down (lateral) distribution and concentration of In were needed

- Energy filtered XPEEM spectra were acquired using SPELEEM at ELETTRA

- Localised photoemission spectra and image maps were obtained to quantitatively determine the lateral In and Ga concentrations

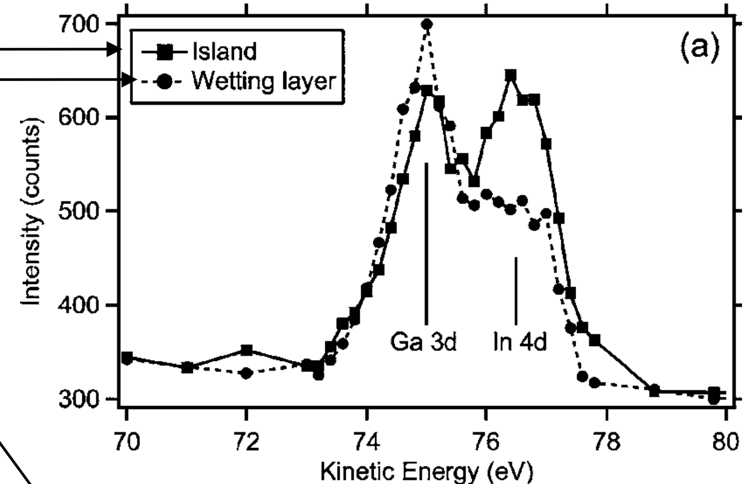
Results

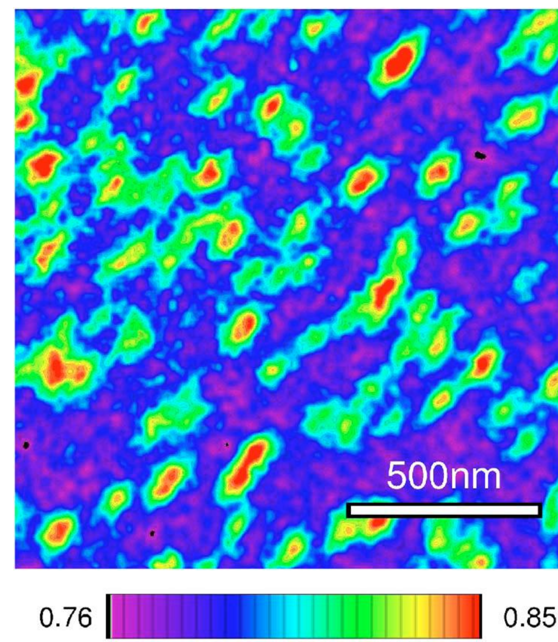
- In 4d PEEM image clearly shows increased concentration of In at location of QDs
- Remnant Ga intensity at QD locations due to alloying from substrate GaAs => QDs are actually $In_xGa_{1-x}As$, as expected
- Quantitative In concentration map indicates higher than expected values at QD centres (x = 0.9)
- Due to surface sensitivity of PEEM, this is most likely due to In segregation to the surface of the QD. This has not been resolved in ESI measurements



X-PEEM images taken at In4d (upper) and Ga3d (lower) core levels, for InAS QDs grown on GaAs(100)

Local Spectra of island and wetting layer, obtained using 25 x 25nm integration area





In concentration (x) map (x =In/In+Ga)

Next Generation PEEM: Pure Aberration Correction

All electron-optical systems exhibit image degradation effects:

Diffraction

- ➢ Can be reduced by using high electron energy and large apertures

Astigmatism

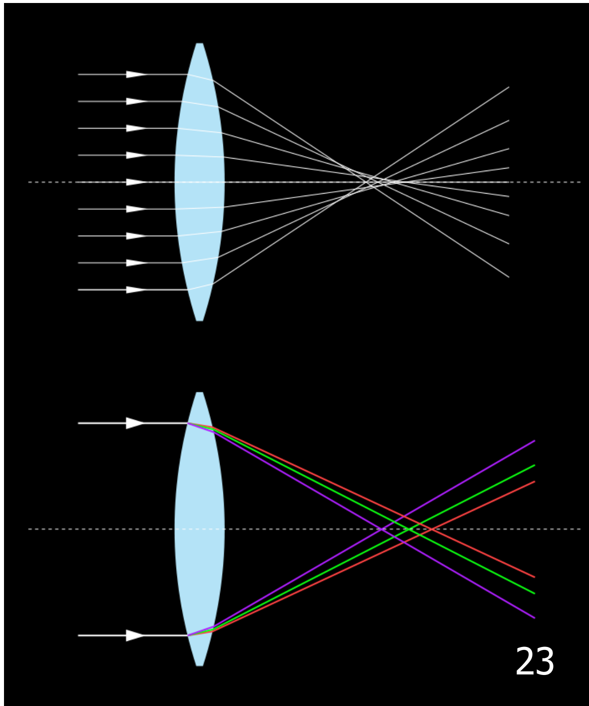
- ➢ Caused by mechanical misalignment and tolerances. In a PEEM, corrected using "stigmator" and "deflector" electrodes.

Spherical aberrations

- ➢ Electrons entering regions of different field curvature will be focussed to different degrees. By limiting the acceptance angle of electrons, thus keeping electrons near-axis, aberrations are reduced.

Chromatic aberrations

- ➢ Caused by the energy spread of electrons. Energy foci are spread along principal axis. Small if the energy range is restricted.



The radius of the disc of confusion from the objective is given by:

$$\boxed{d = \sqrt{d_d^2 + \left({d_s}/{2} \right)^2 + d_c^2}}$$

The contribution of each aberration:

Diffraction

$$\boxed{d_d = \frac{0.61\lambda}{\sin\alpha}}$$

Spherical aberrations

$$\boxed{d_s = C_s \sin^3 \alpha}$$

Chromatic aberrations

$$\boxed{d_c = C_c \frac{\Delta E}{E_o} \sin\alpha}$$

Where:

α = acceptance angle

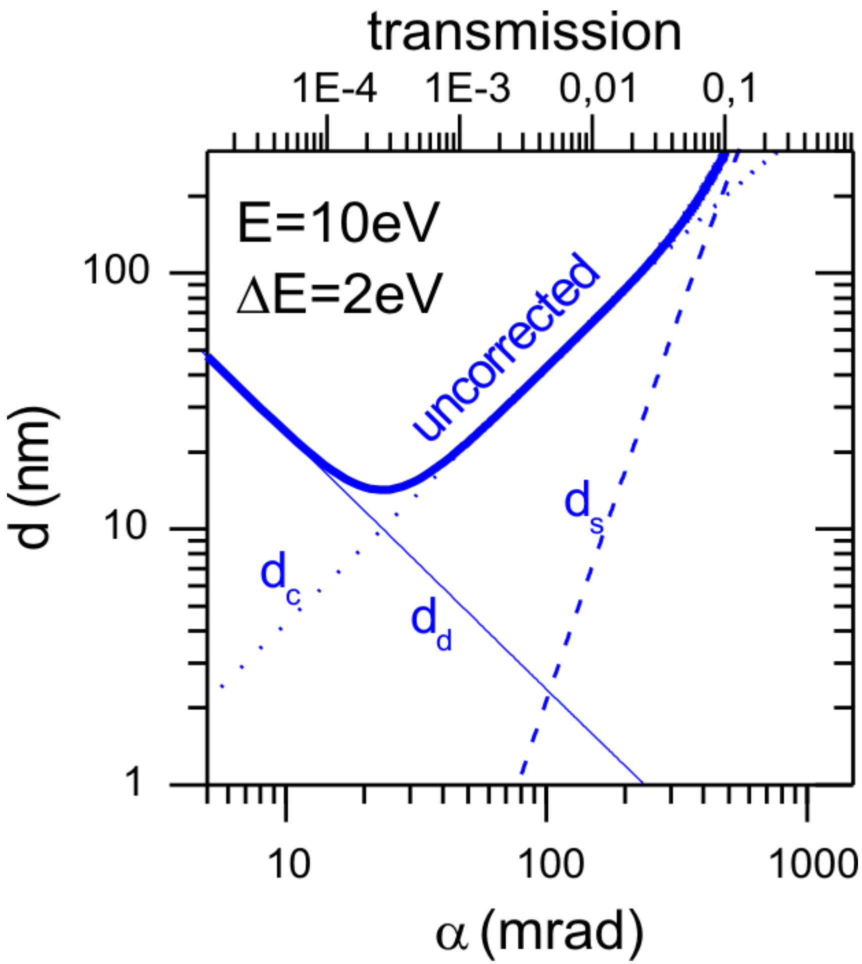
λ = electron wavelength (nm)

E_0 = Start Energy (eV)

ΔE = energy spread (eV)

The resolution limit calculated for a typical objective lens:

- For $\alpha < 20$ mrad, resolution is *diffraction* limited
- For $\alpha \approx$ 20 - 400mrad, resolution is dominated by *chromatic* aberrations
- For $\alpha >$ 400 mrad, resolution is dominated by the *spherical* aberrations
- Clearly, improvement is needed for resolving structures less than 5nm in size!



Notes:

- Rapid increase in *transmission* as a function of α
- One optimal aperture for best resolution

Figure courtesy of: Th. Schmidt *et. al Surface Review and Letters* , 9 (2002), no. 1, 223–232.

- Modern TEM and SEM instruments are now corrected for chromatic and spherical aberrations. Progress in LEEM/PEEM has been slower.

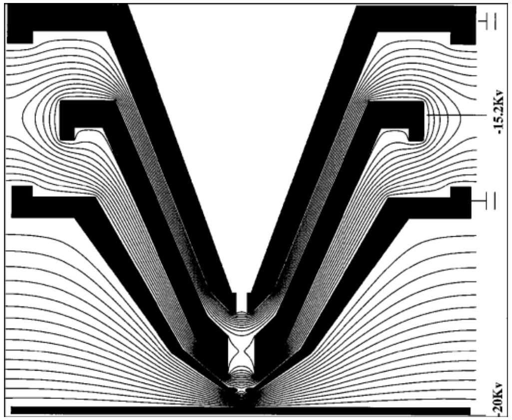


Image: J. Feng, Rev. Sci. Instr, 73, no. 3 (2002), 1514

- Majority of the aberrations are caused by the high electric field and focussing in the objective lens

- Although the contrast aperture in the back focal plane can be adjusted (reduce α) to reduce the chromatic/spherical aberrations, it is at the expense of transmission

- For PEEM2, 20nm resolution occurs at 1% transmission! How can we cope with **radiation sensitive samples**???

- A major effort has been to remove instrinsic aberrations via use of an electron tetrode *mirror*. Goal is to obtain an order of magnitude in resolution for given transmission.

- 2 projects are heading toward completing an aberration corrected PEEM: the "PEEM3" project at the ALS, and the "SMART" project at BESSY2

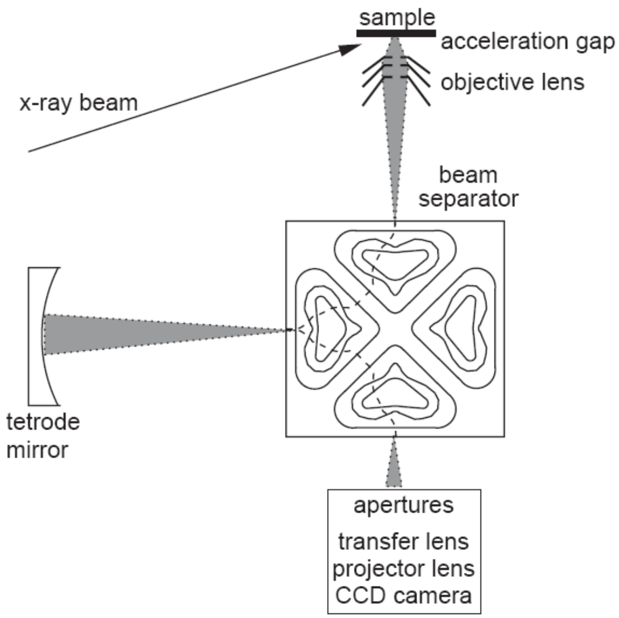
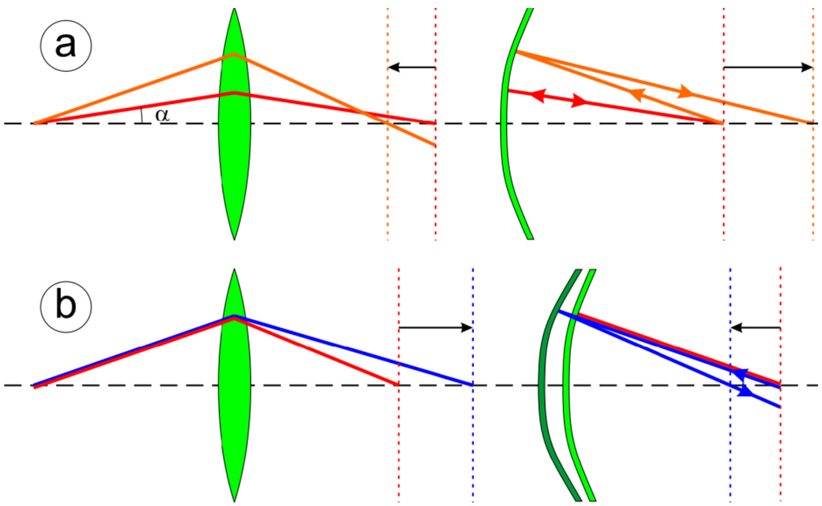


Image: Wu, Y.K, Nucl Instr. Methods. Phys. Res. A, 519 (2004), 230

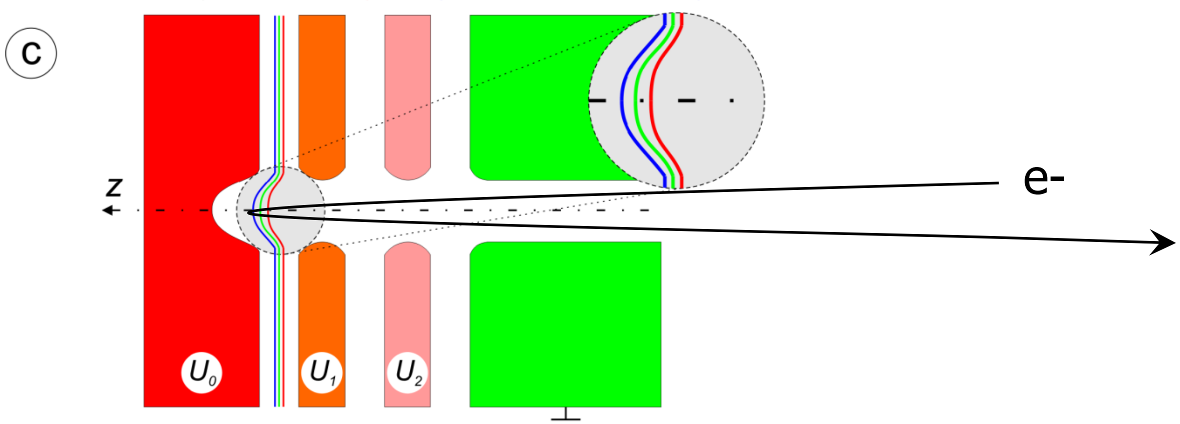
How does an electron mirror correct aberrations?

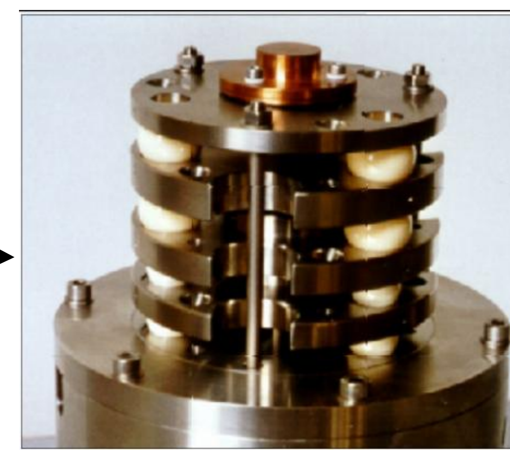
- A tetrode electron mirror is able to induce aberrations of the opposite sign to those created in the objective lens of a PEEM



Spherical aberration correction

Chromatic aberration correction





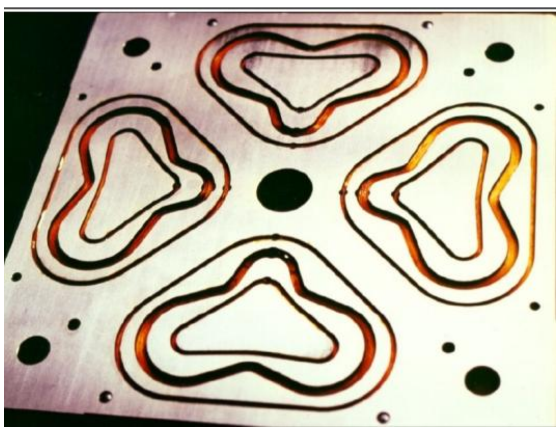
- Adjustment of the 3 potentials allows correction of a range of aberration coefficients (C_s, C_c) corresponding to different imaging conditions (E, ΔE, etc..)

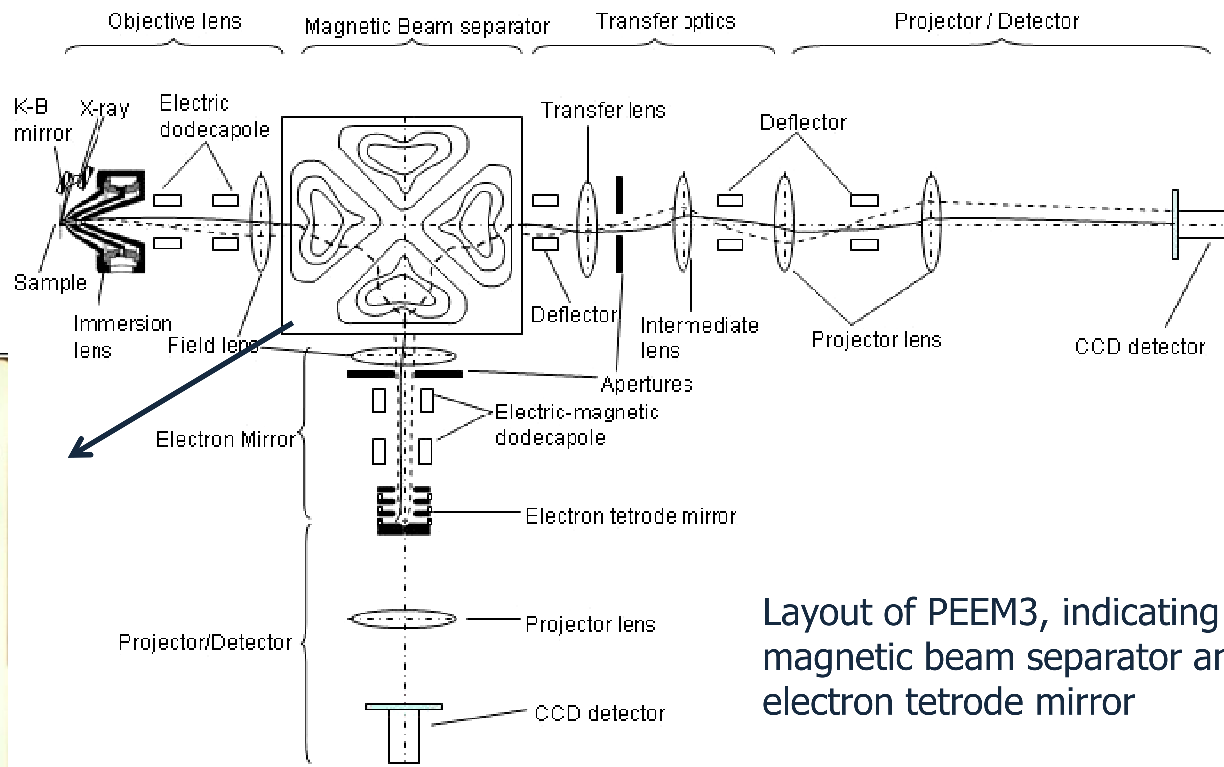
Incorporating the electron mirror: PEEM3

- A *magnetic beam separator* is used to deflect the electrons into the mirror

- The (aberrated) image is formed by the objective lens at the entrance to the beam separator

Design challenge: the separator needs to designed nearly free of aberrations in magnetic field





Layout of PEEM3, indicating magnetic beam separator and electron tetrode mirror

Image courtesy: J Feng *et.al*, *J. Phys. Condens. Mater*, 17, S1339, 2005

- Reflection occurs in the mirror, with the image then diverted to the exit of the beam separator for subsequent imaging by projection optics

Simulations of resolution gain using the tetrode mirror

SMART project

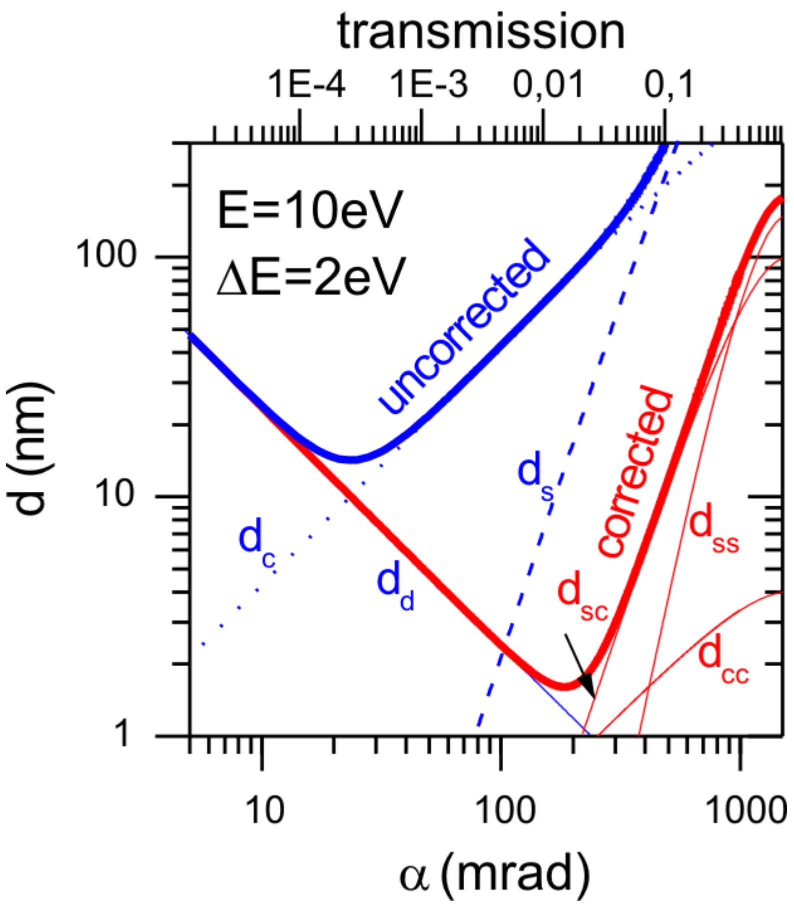


Image courtesy: Schmidt, Th *et.al.*, Surf. Rev. Lett, 9(1) (2004) 223

PEEM3

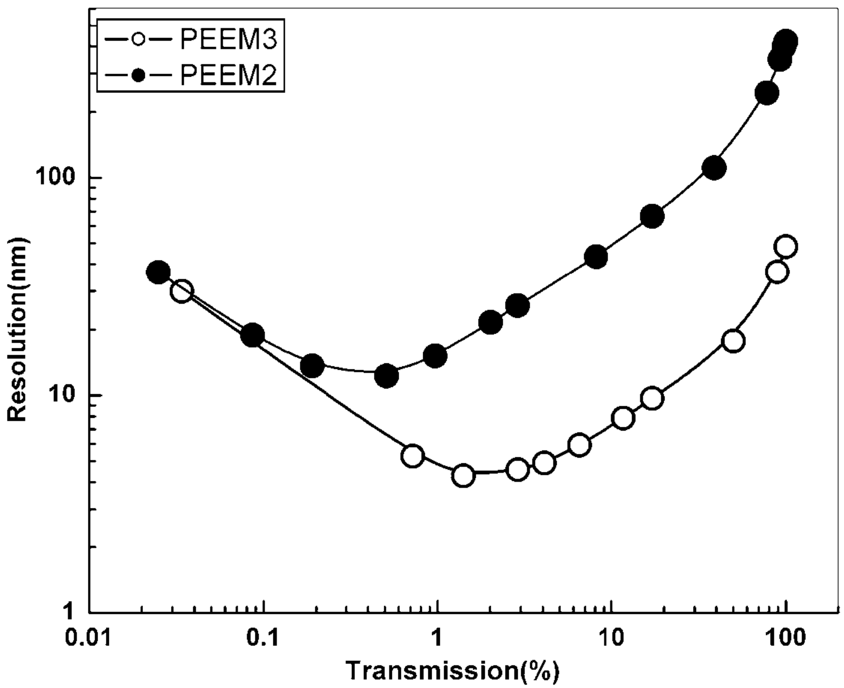
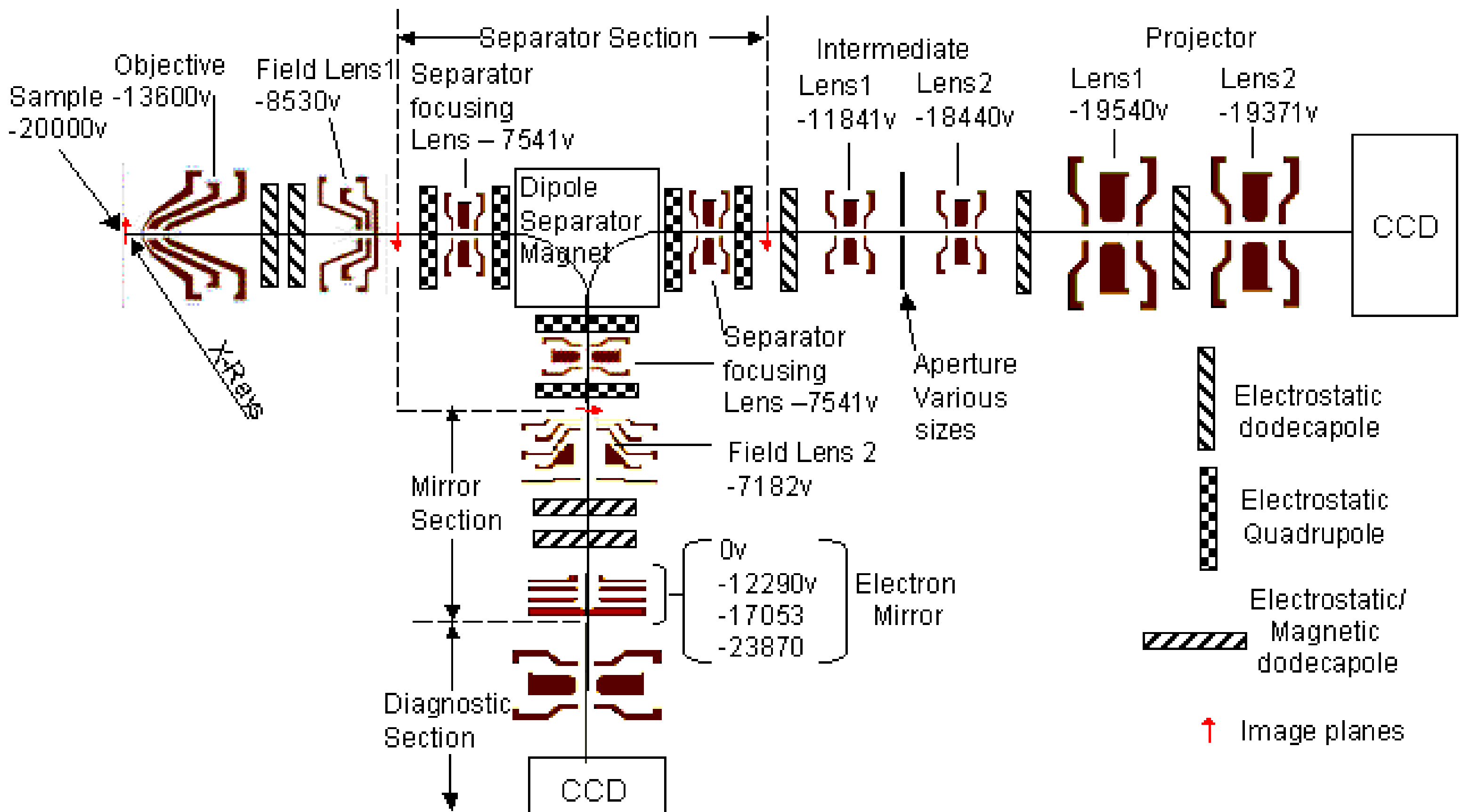


Image courtesy: J. Feng *et. al*, J. Phys. Condes. Matter, 17 (2005) S1339

Design vision of PEEM3 at the ALS

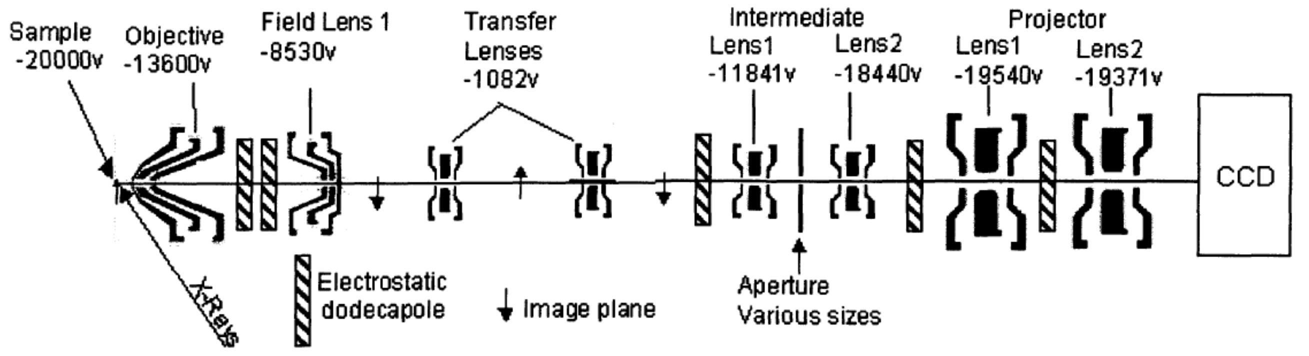


Resolution Goals (XPEEM)

- 50nm resolution at a transmission of 100%
- 4nm resolution at a transmission of 1-2%

Progress on PEEM3

An intermediate version of the instrument is being commissioned while the separator and corrector are completed offline



Electron optics

Mu-metal shielding: 3 layers!

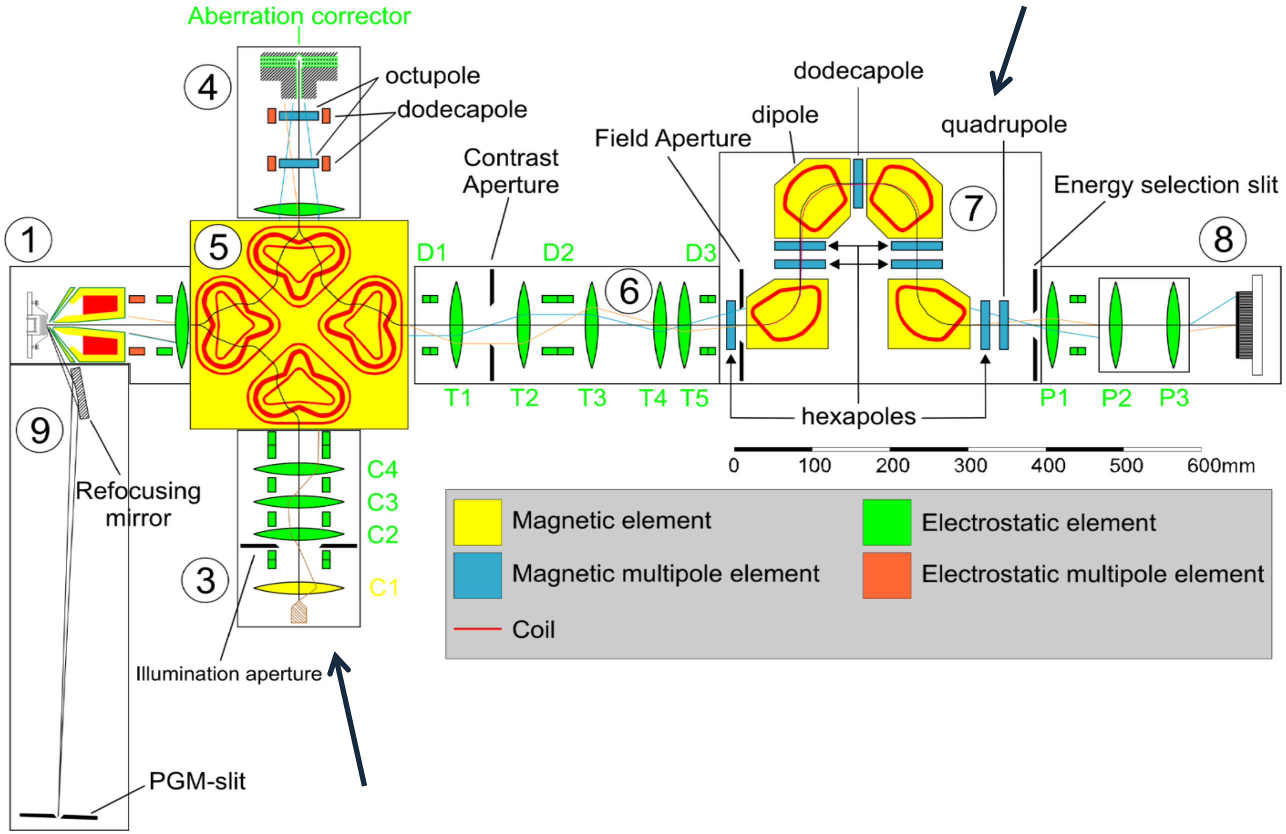
Space for corrector

Sample Manipulator

Images courtesy: MacDowell A.A *e al*, Synchrotron Radiation Instrumentation: 9th International Conference (2007), 1341

SMART (Spectro Microscope For All Relevant Techniques): BESSY2

Ω–filter: energy filtering, dispersive energy plane imaging



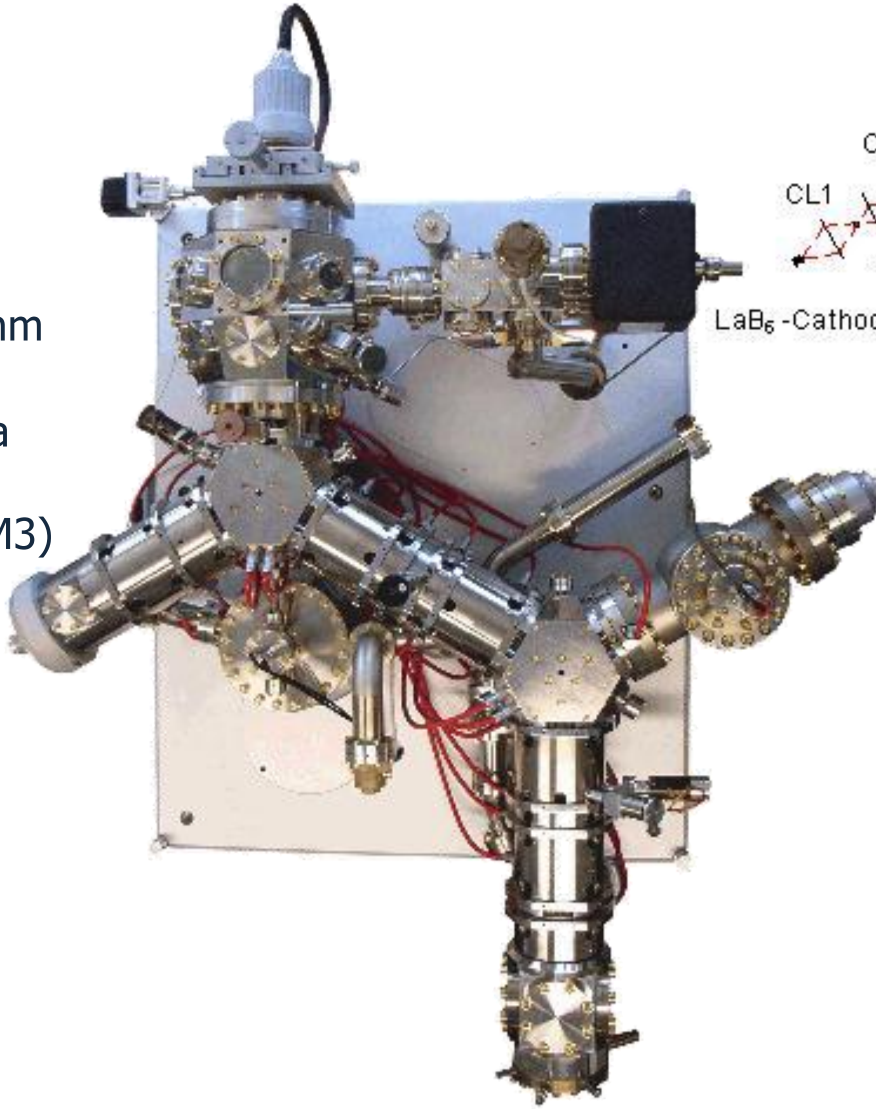
LEEM optics

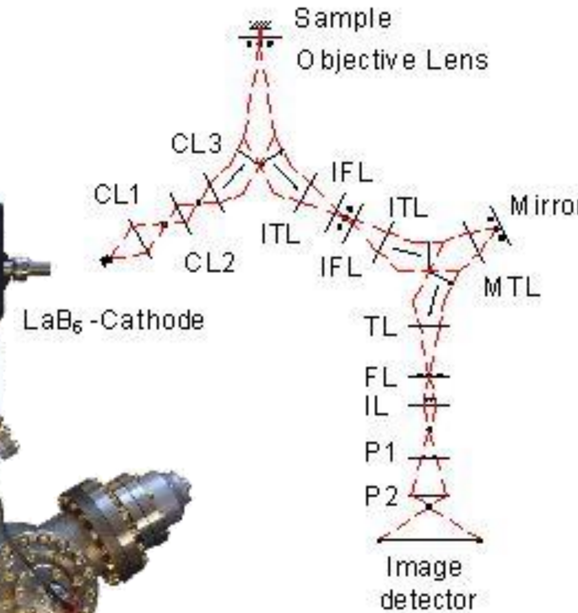
- The SMART allows for interchange of energy filtered diffraction or real image planes, permitting angular distribution measurements e.g. for ***k***-space mapping, PED, Fermi Surface

Elmitec are prototyping an aberration corrected LEEM/PEEM: The "AC LEEM/PEEM"

Specifications

- Imaging modes: PEEM, LEEM, LEED, MEM….
- Calculated best resolution <3nm
- Up to 8 times the intensity at a given resolution compared to previous "PEEMIII" (NOT PEEM3)





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Aberration Correction PEEM3/SMART

Thank You!