MANCHESTER 1824
The University of Manchester

Centre for

Quantum Scale Devices

Towards charge and photon imaging of nanostructures using X-UV pumped scanning probes

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Acknowledgments:

• Masashi Ishii developed all of the SPM work, and did experiments in Manchester/SRS during 2004

• Nigel Poolton developed all of the photon detection work

• Nikos Rigopoulos, Brian Towlson, Graeme Davies and Sanadrine Beranardini are post-docs working on project

• Janet Jacobs (Nottingham) grew CNT's

• Peter Parbrook (Sheffield) grew InGaN quantum dots

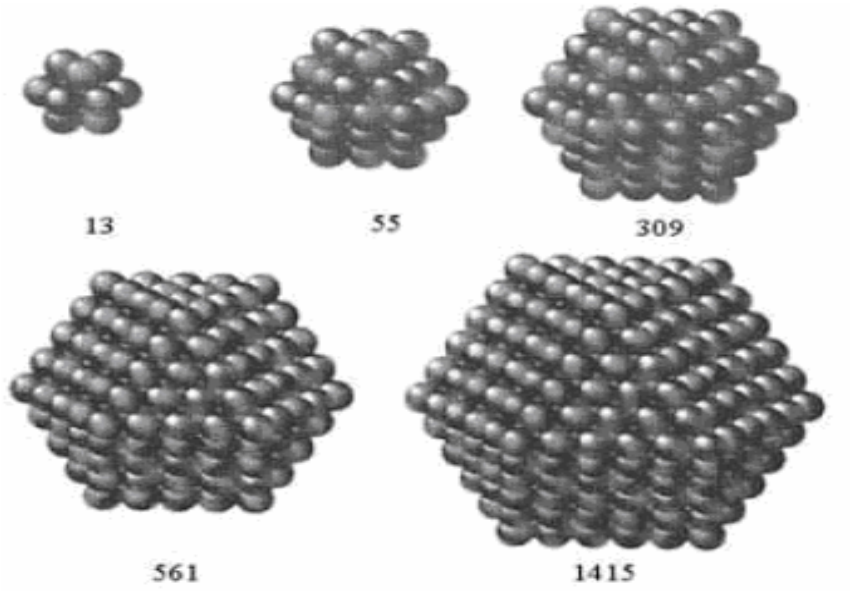
• Paul Christian (Manchester) grew the II-VI nanoparticles

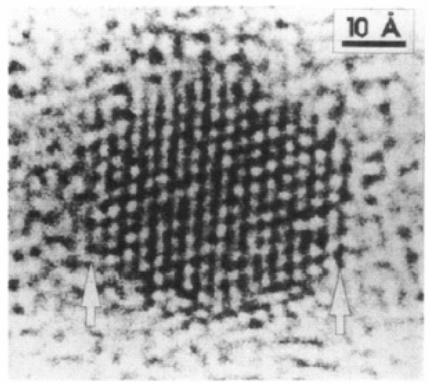
OUTLINE

1. Brief background to the work
2. X-SPM Bound state charge spectroscopy and imaging
3. Photon detection; at the limit of far field …towards SNOM.
4. Where to go with x-tip type work?

1. BACKGROUND

Nano materials are complex. Properties depend on SIZE, SHAPE and CHEMISTRY





- Experimental science is lagging behind the prolific developments in synthesis and fabrication
- SPM is good for size, shape, local electrical spectroscopy and (bit less good) for photon detection…….also images on sub nm scale
- SR is good for local chemical information and structural information at the atomic level.
- There are compelling reasons to try to join these two ……open up SR to make major contribution to nanoscience.

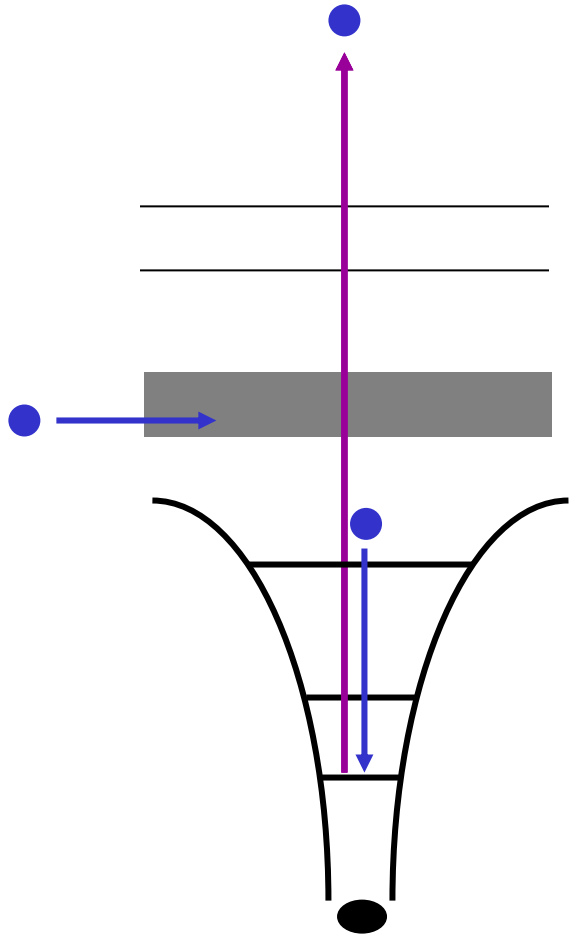
There are many detection modes for SPM

We have so far, concentrated on two for the x-ray excitation work.

Charge

Photons

How do we think about the link?
(meV---100eV-------11000 eV)



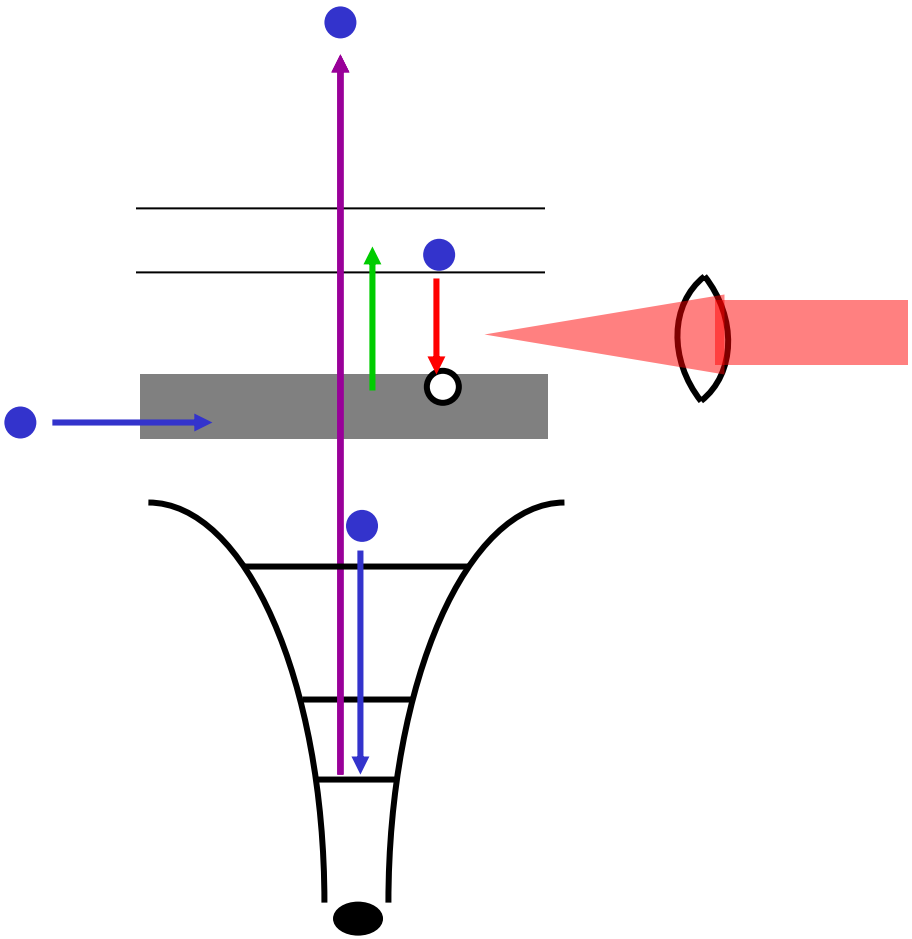
Conventional XAFS

charge balanced fast (fs)

detect by absorption of primary beam or fluorescence

This work:

slightly less conventional XAFS in the detection mode.
First: 0PTICAL

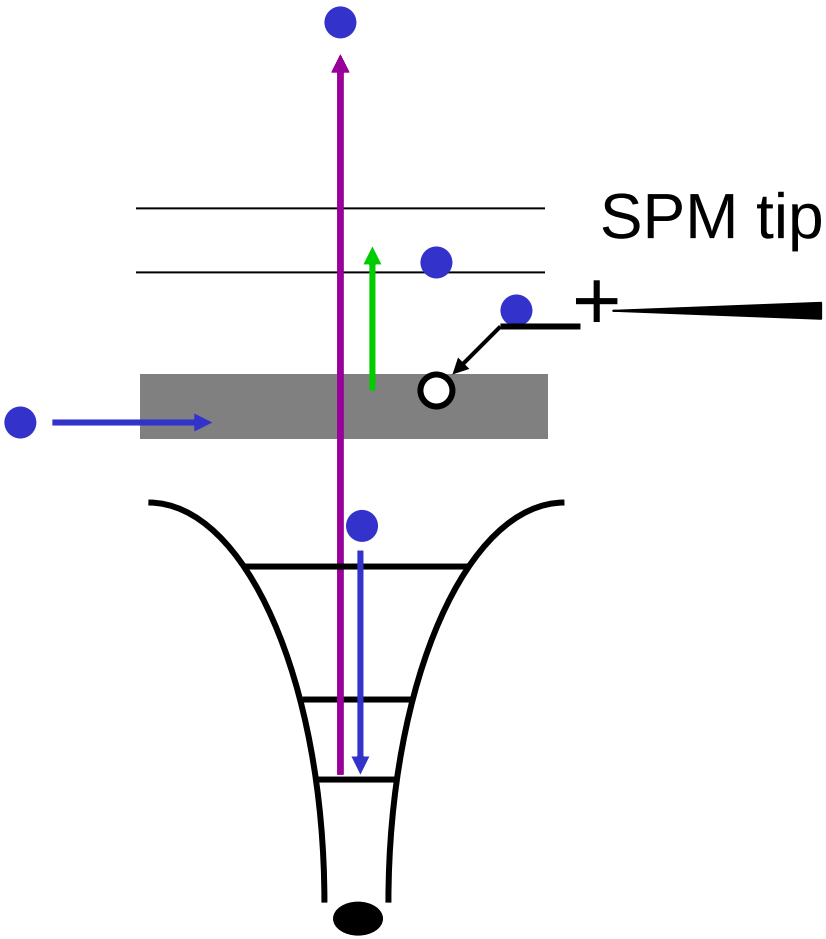


the primary interaction leads to local excitation of the bands (e-h)

The subsequent decay (luminescence) can be detected.

This carries EXTRA electronic information

Second: BOUND STATE CHARGE



the primary interaction leads to local excitation of the bands (e-h)

This causes charge transfer at a localised state (defect sate) associated with the parent atom. Not charge balanced.

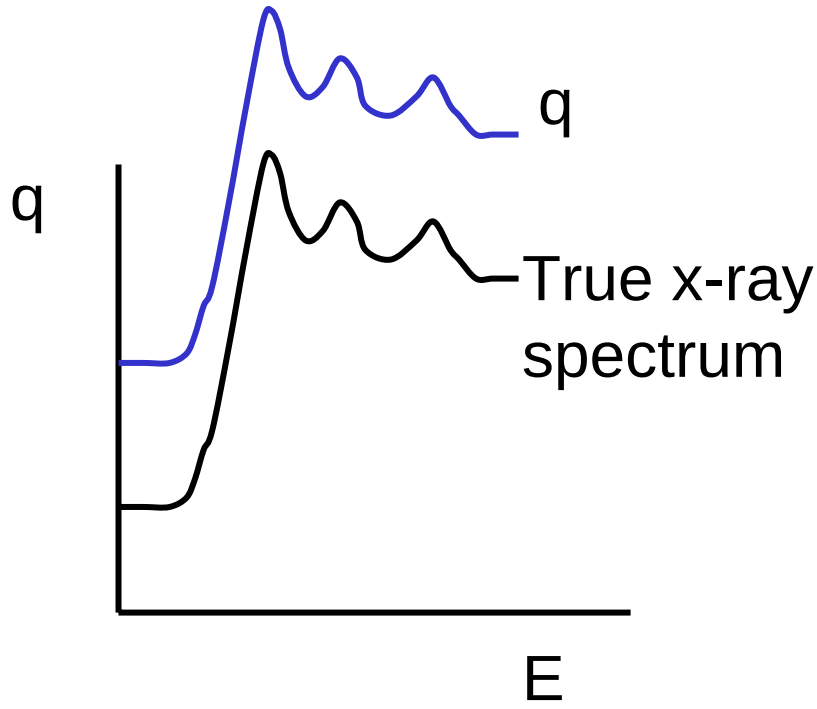
Detect AFM, KFM

Spectroscopy of bound state charge?

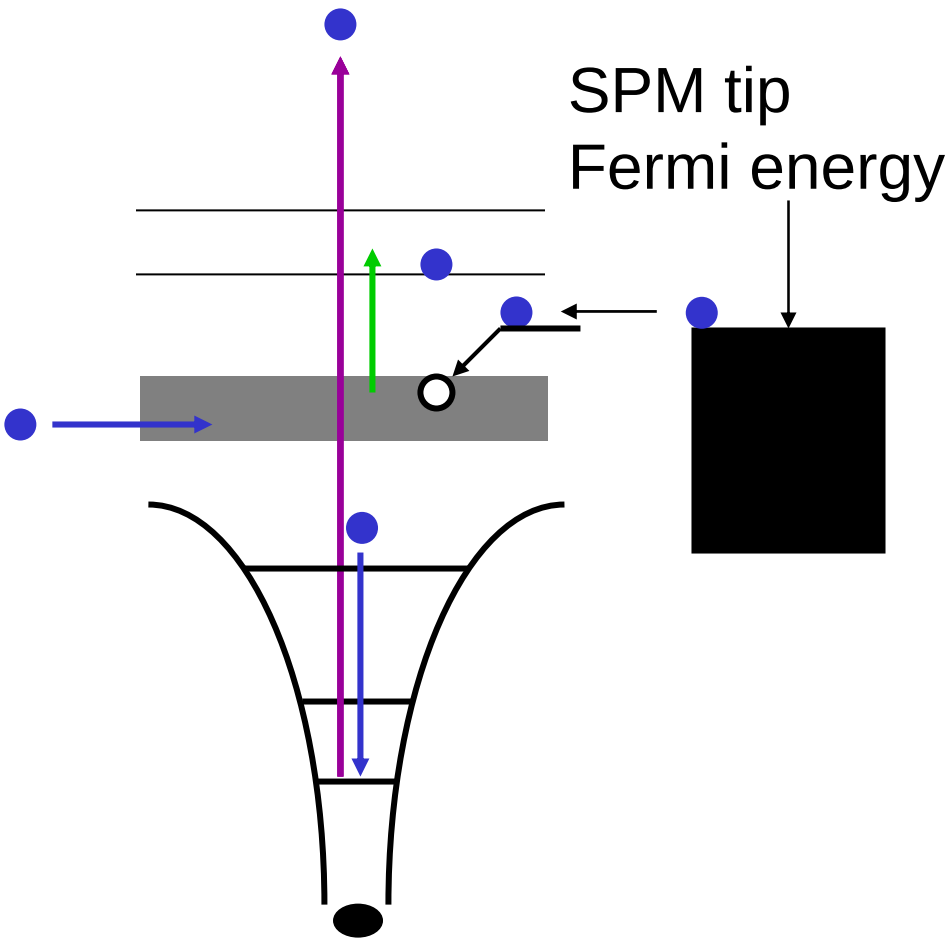
To get a spectrum the charge must increase and decrease as we scan through the core level absorption structure.

Maybe 100 eV photons simply saturate or “lock up” the charge state.

Defect charge would be unaware of the edge structure.



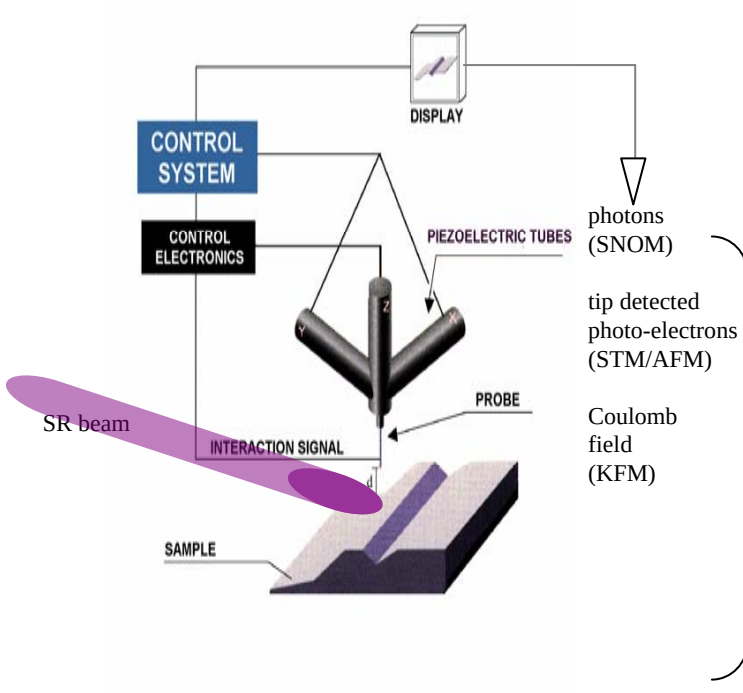
BOUND STATE CHARGE SPECTROSCOPY:



The electron population of the defect state must have (roughly) equal filling and emptying rates. Scanning the edge then perturbs the balance in a linear response mode.

It seems that this can be achieved with a resonance between E_F of tip and the bound state

ULTIMATE AIM

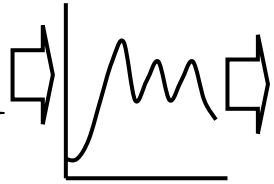


photons (SNOM)

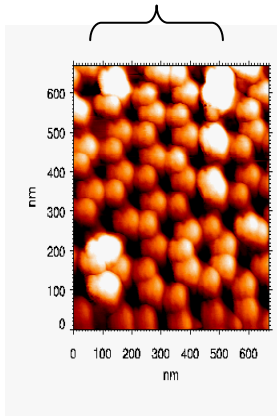
tip detected photo-electrons (STM/AFM)

Coulomb field (KFM)

tip detected EXAFS



nano image of x-ray data

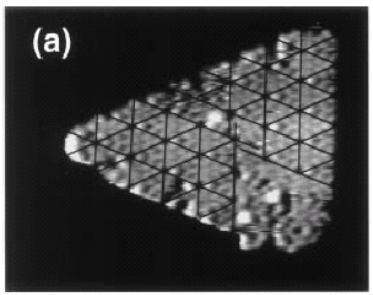


2. CHARGE MEASURENT

- Point defects at the Si-SiO_2 interface
- Charge localisation at distorted single walled carbon nanotubes

The (111) Si-SiO_2 surface; off line data

60^0 Triangular islands driven by 7X7 reconstruction. Monolayer steps. Disorder on and between islands nucleates new island

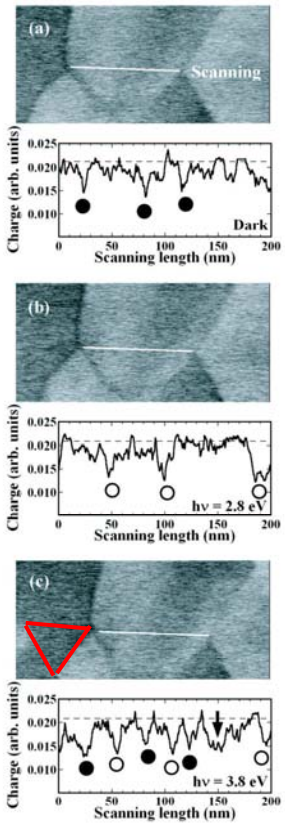


Voigtlander and Weber PRL, **77**, 3861

Toplogy image, charge (KFM) line scan (dark)

Visible laser

UV laser



The afm likes to detect edges orthogonal to scan direction. The charge detection line scan was taken along a line known to be an island edge but *in* the scan direction.

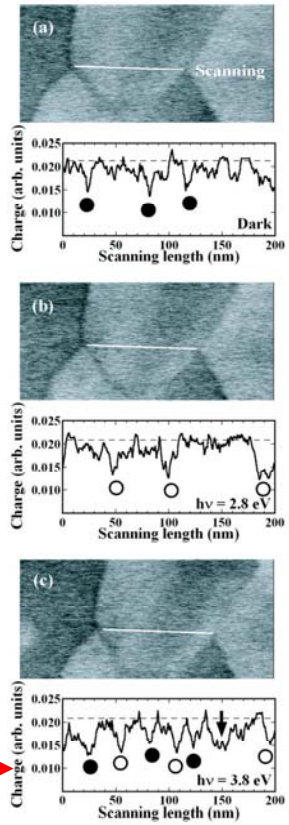
Scan in UHV at 300 K

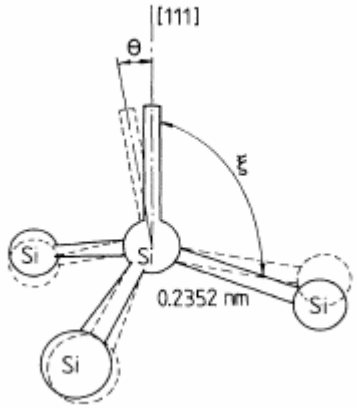
Detect seven isolated point charge events.

Pumping with lasers could change the events detected

UV laser tended to populate all seven…..stochastic influence

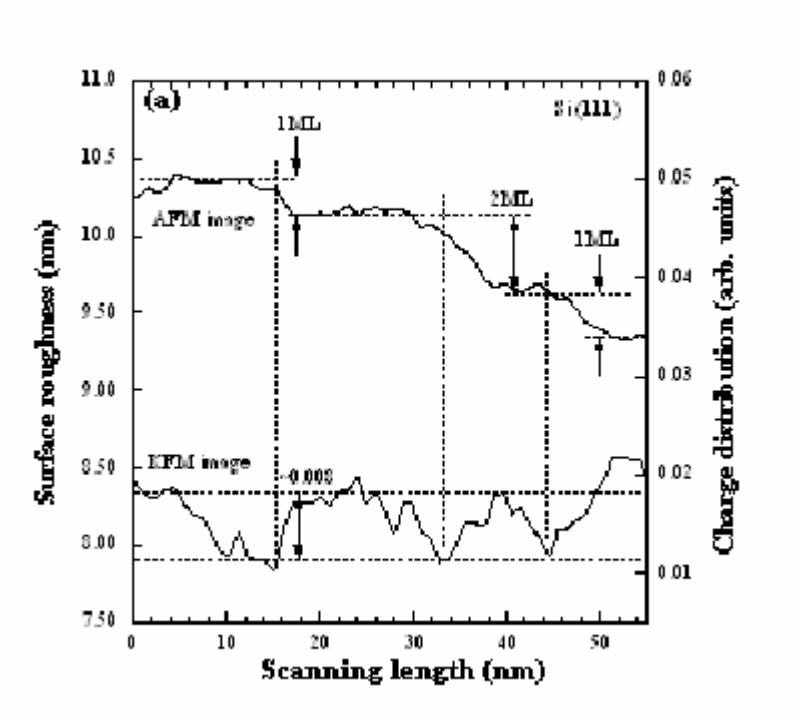
Scan long times and only see same seven sites.





The P_b Centre in Si, from EPR data

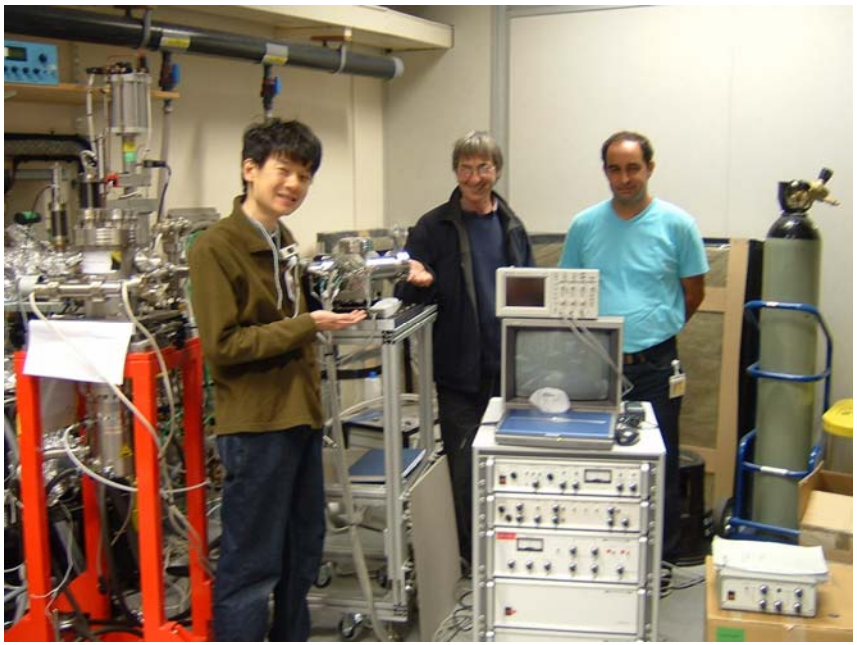
A Stesmans PRB 48 2418 (1993)

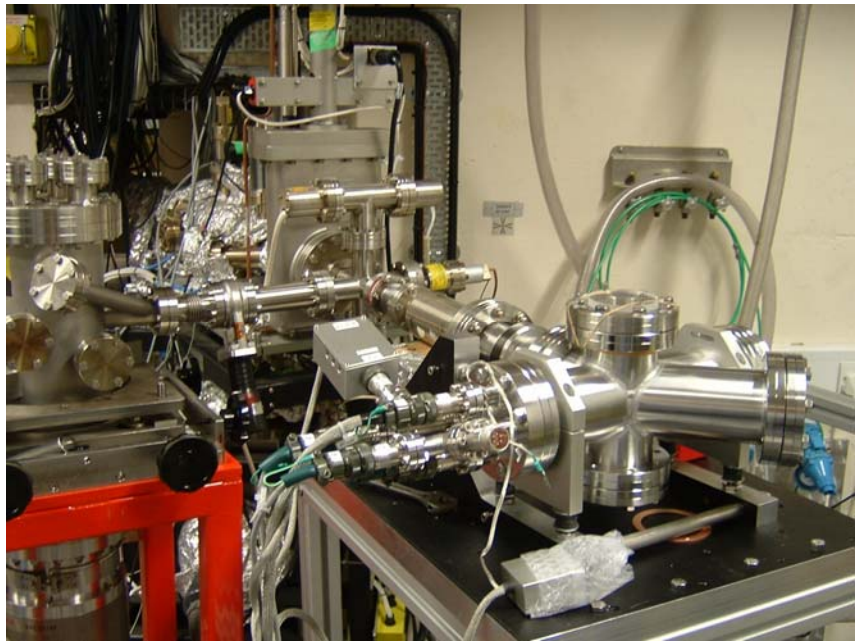


These data suggest that the principle "dangling bond" defect for the Si-SiO_2 interface may be physically located at a step edge where oxidation is energetically more difficult

M Ishii and B Hamilton: APL **85**, (30) (2004)

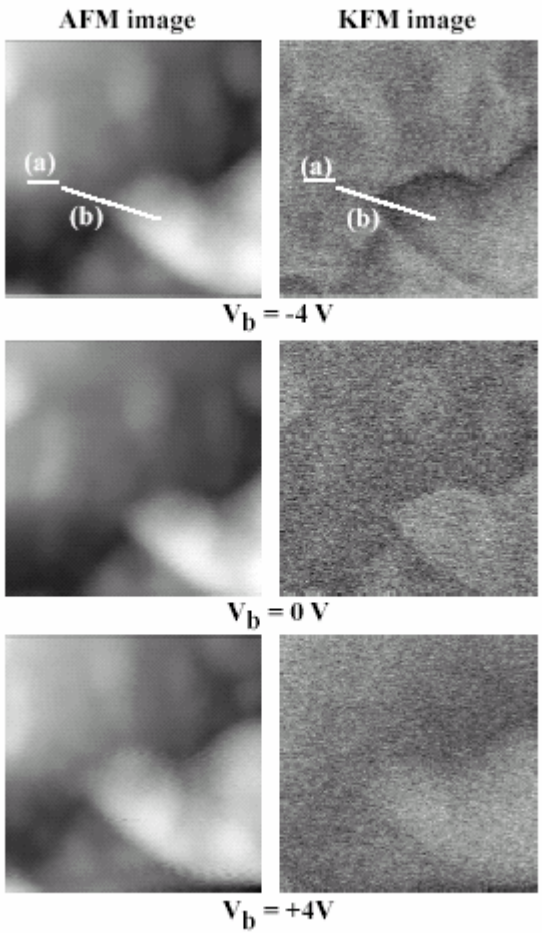
Take AFM to the SRS and try to extend measurements to x-ray excitation

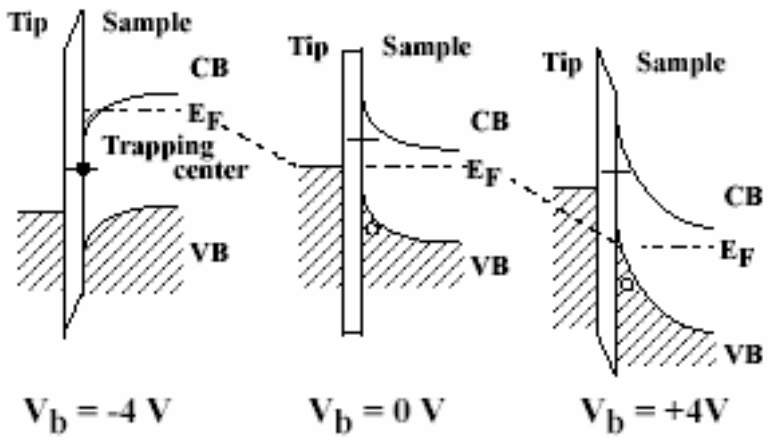




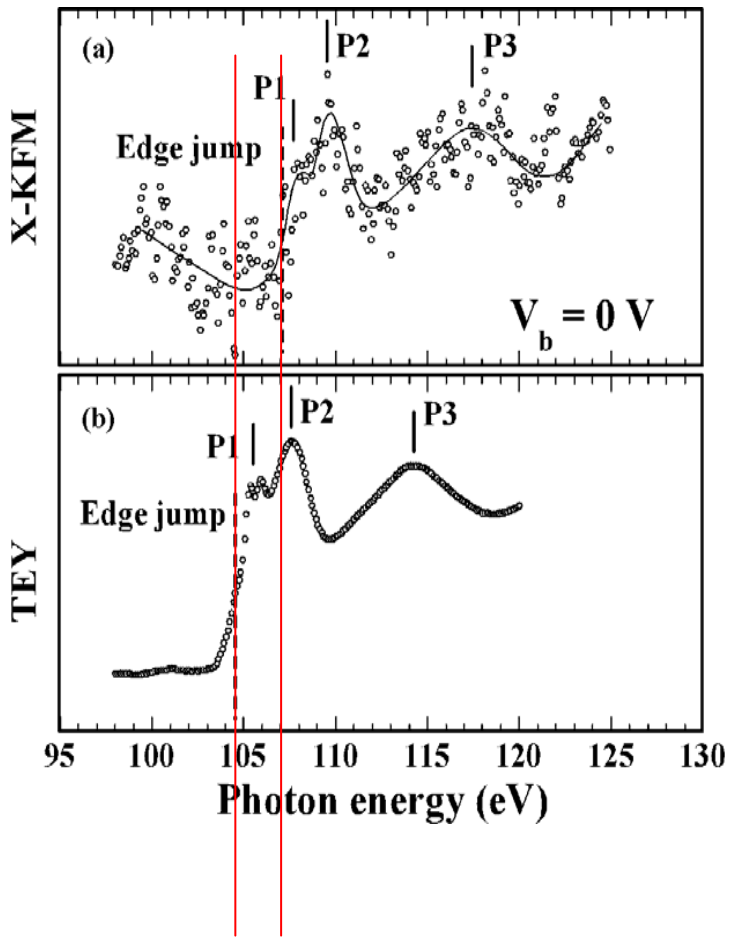
AFM system installed on beamline MPW6.1 at the SRS, Daresbury, for KFM-EXAFS measurements.

Initial Charge imaging





Si L edge charge detected absorption data: step edge on the native oxide.



Locate charge and scan Si L edge get (noisy) spectrum, but we think a single charge involved. The data are a time average of a stochastic process.

Two important new things emerged: (i) bias dependence, and (ii) energy location.

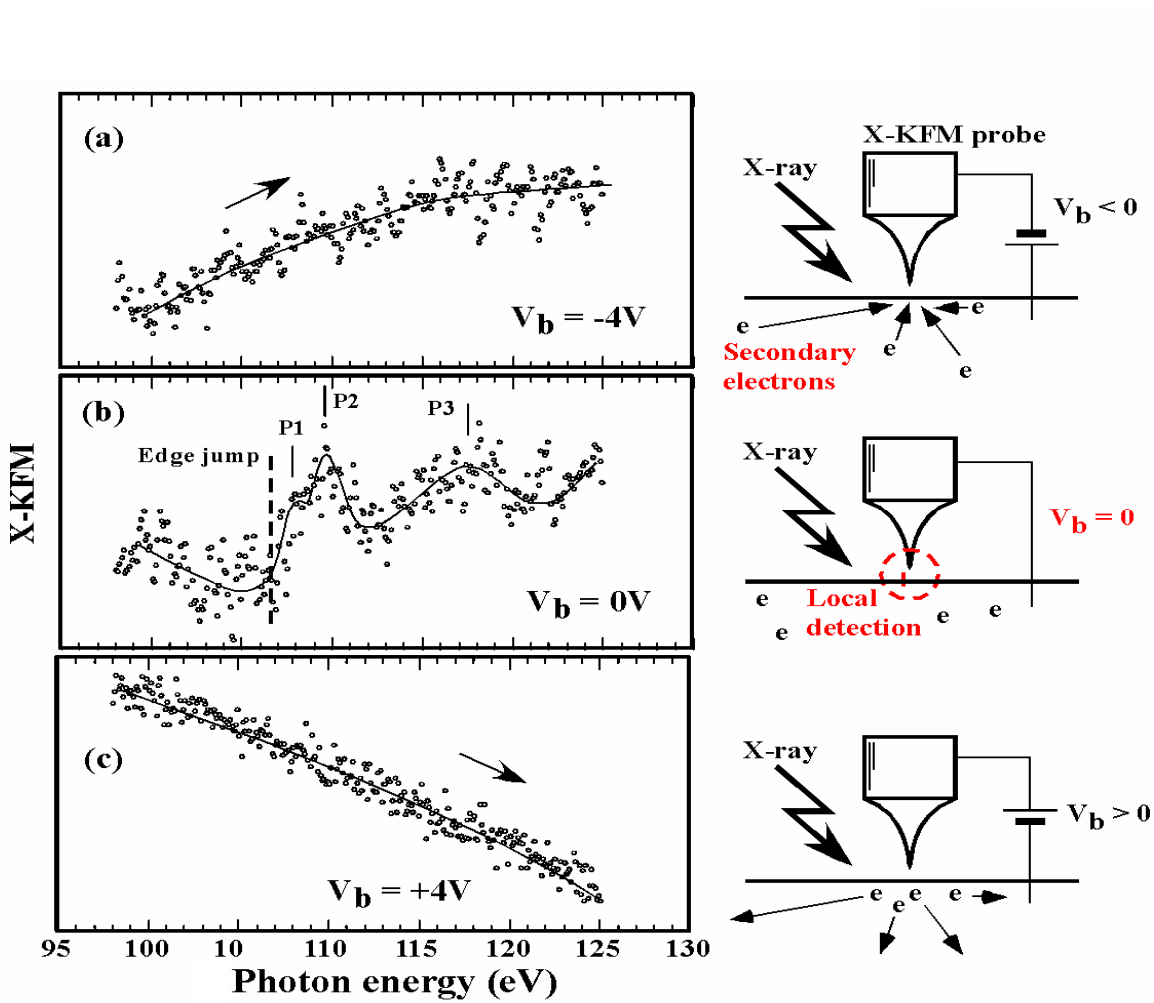
BIAS:

We only get the spectral information for sample bias near to zero.

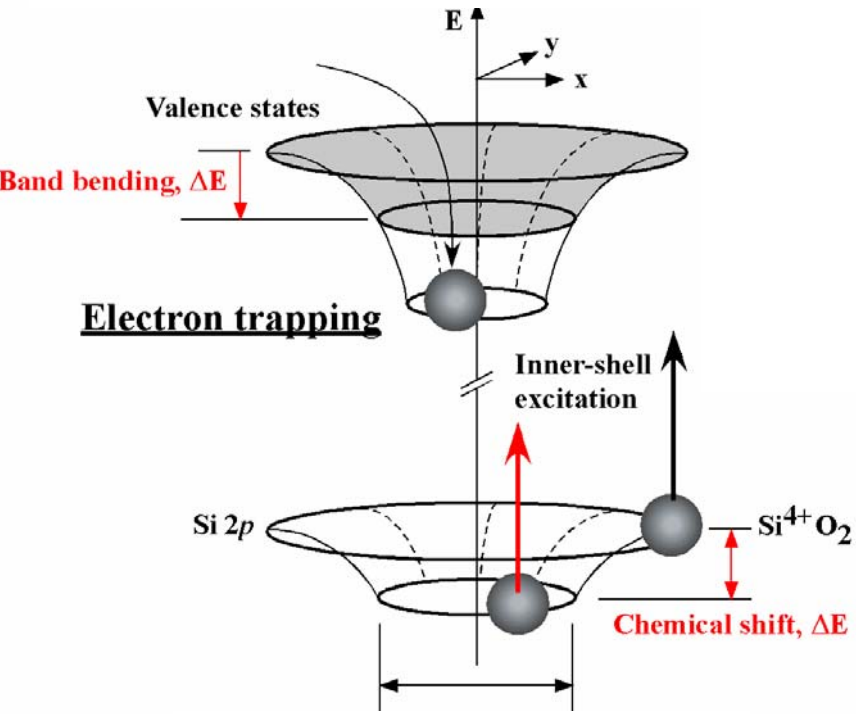
This is probably due to the resonant particle transfer process.

At very low bias the defect ground state is resonant with the tip Fermi energy.

Any other bias switches on sensitivity to secondary electrons



ENERGY



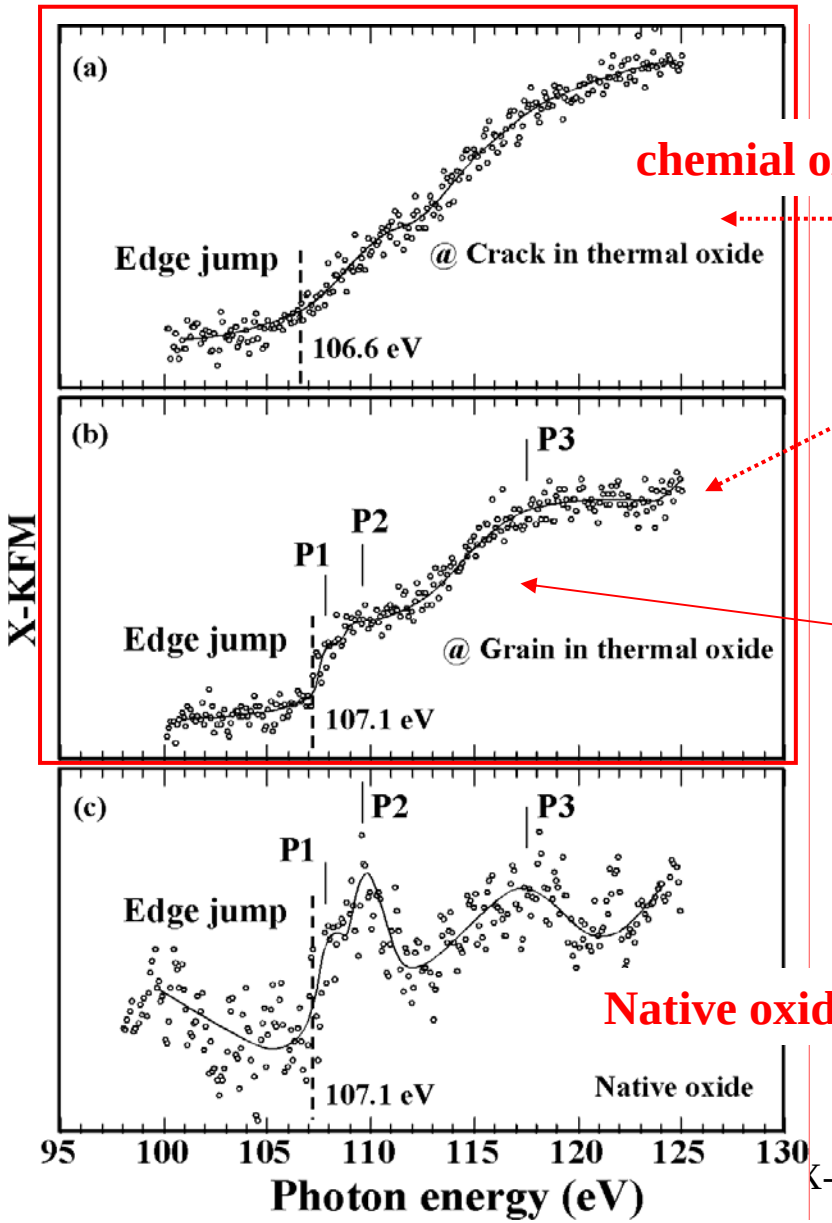
The defect centre has a localising potential, placing the electron in bound state

All photoemission events associated with are shifted by this “band bending” effect

The probe singles out the localised charge effects and should therefore detect this.

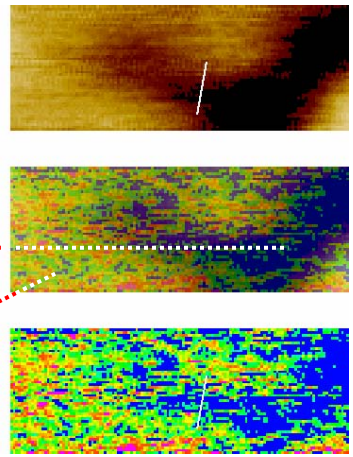
This is the origin of the 2 eV shift observed

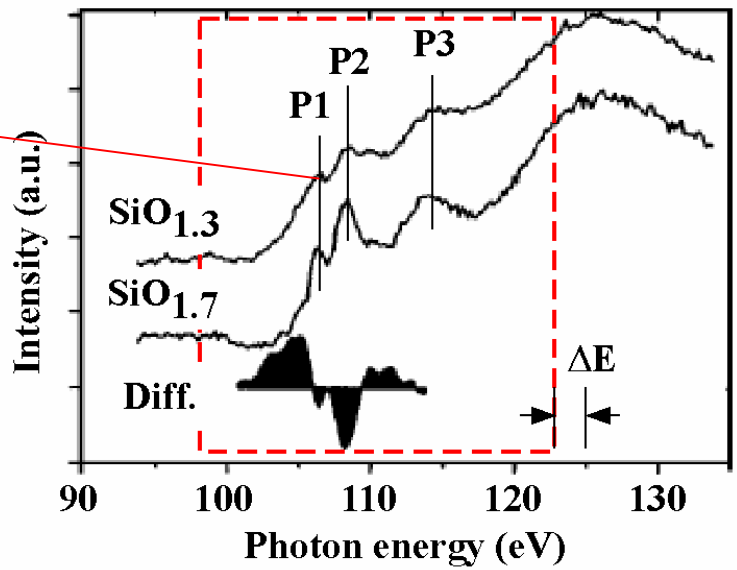
SiO_x spectrum dependent on probe position



chemial oxide

Native oxide

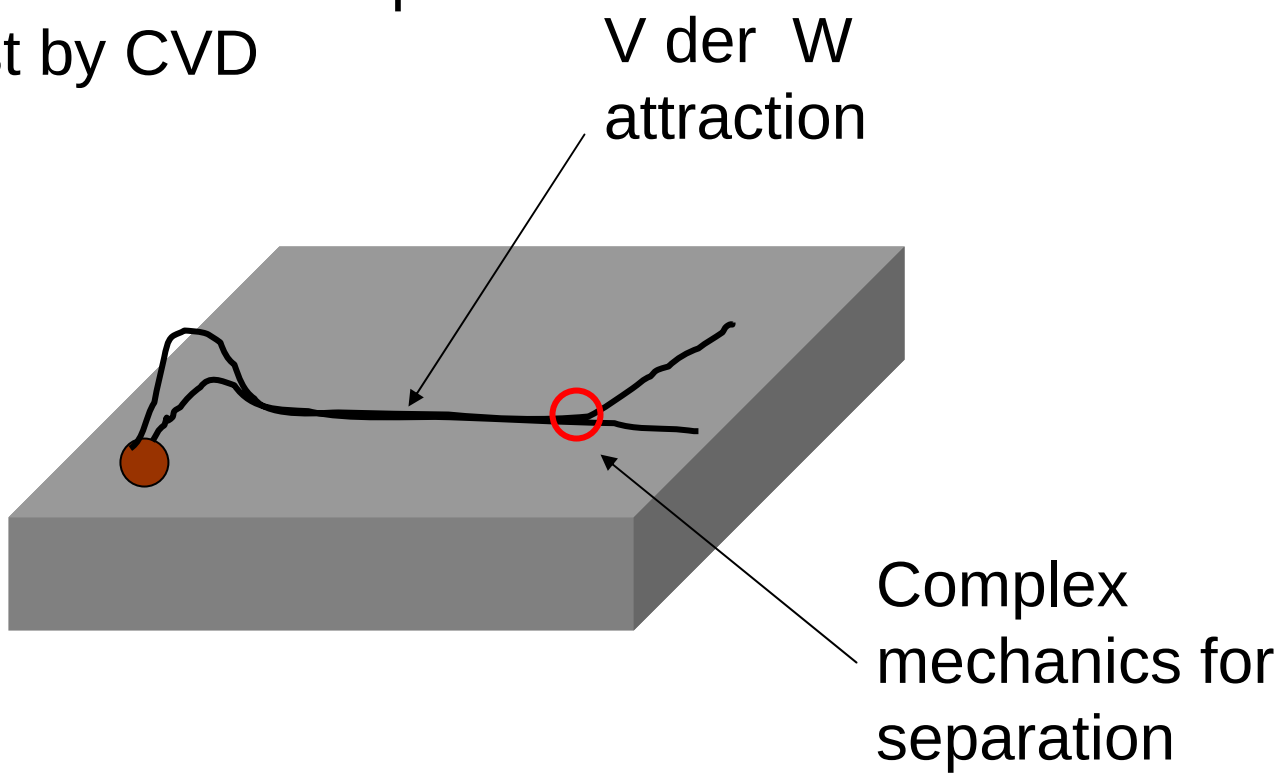




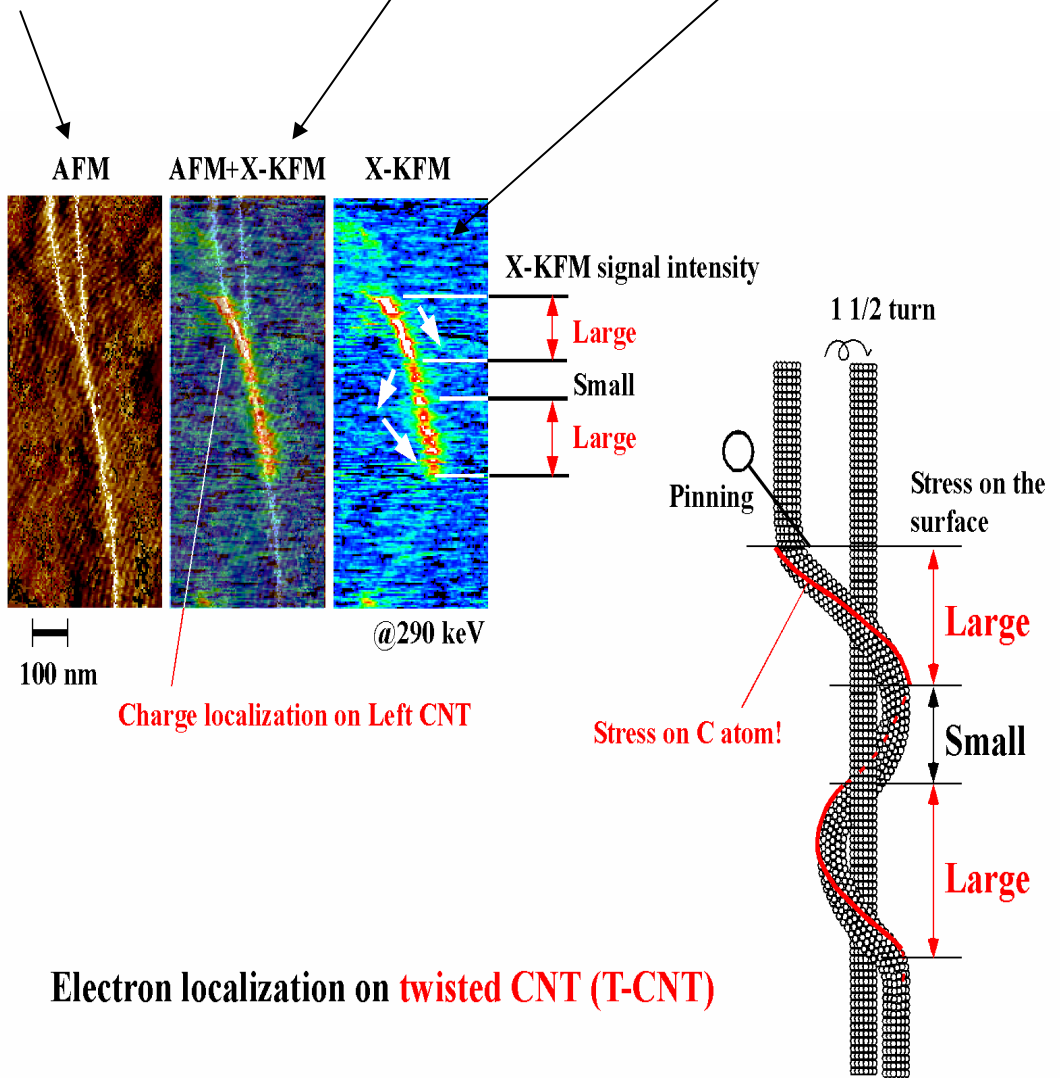
A. Brranco *et al.*, JAP 97, 113714 (2005).

Charge localisation at distortions in single walled carbon nanotubes

Grown from Fe nanoparticle catalyst by CVD



Topolgy, topolgy + charge, charge



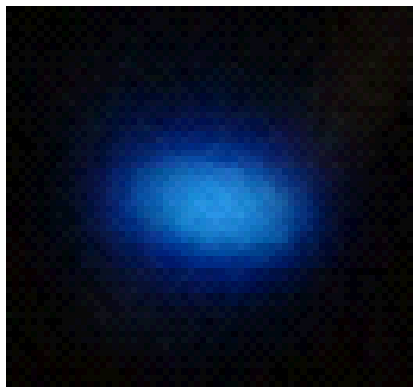
Bending alone will not localise charge but twisting will (we think)

3. PHOTON DETECTION

Quick summary of where we are currently and where we are going

X-ray excited luminescence is identical to laser excited

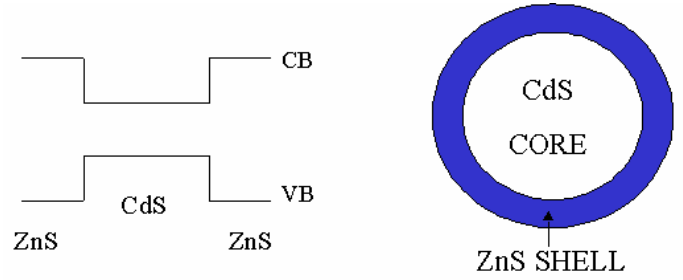
SiO_2:

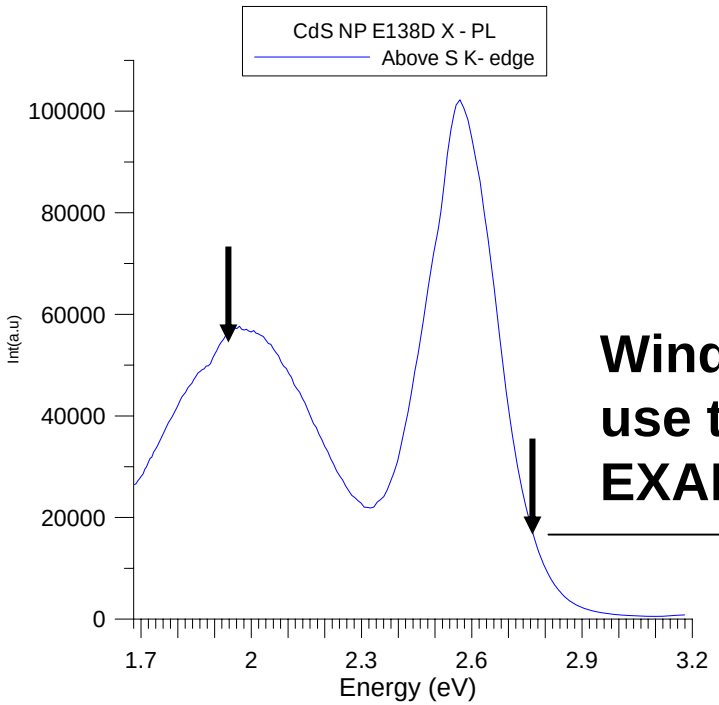


Luminescence

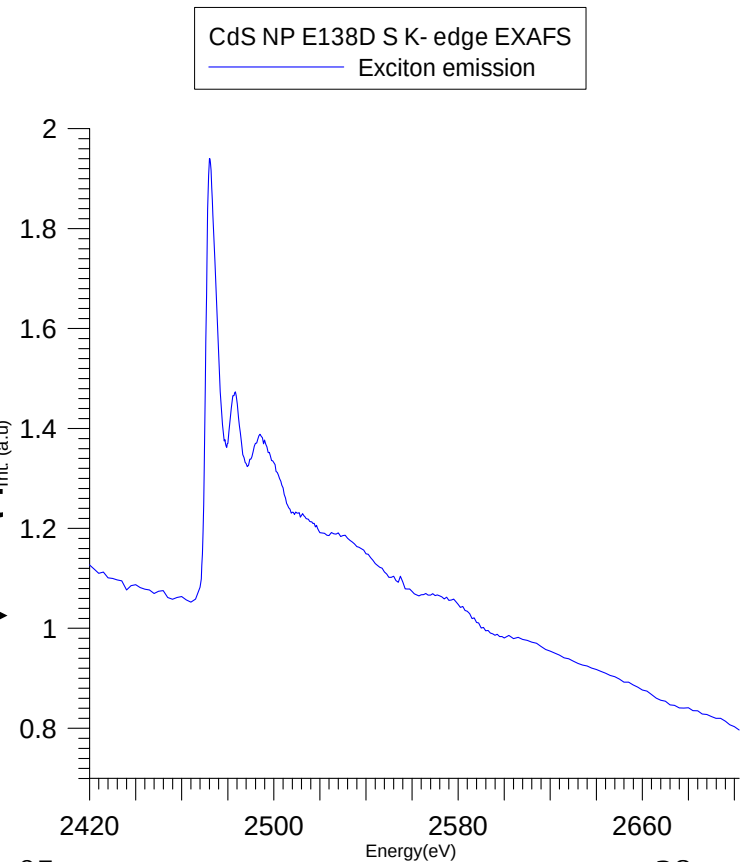
Window and detect absorption

II-VI core shell nanoparticles MPW 6 SRS





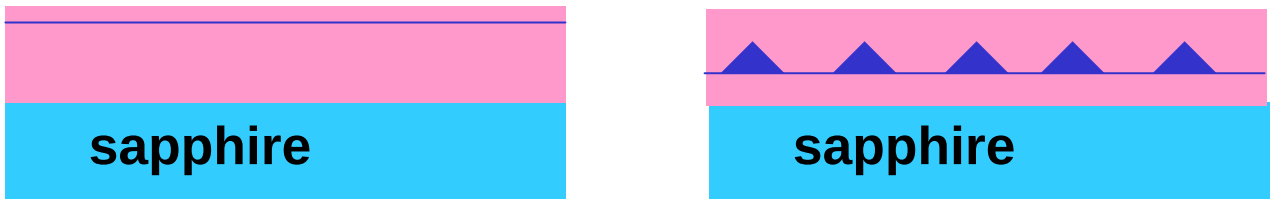
Window and use to detect EXAFS



InGaN Single quantum wells, and single layer quantum dots: (not to scale!)

Excite luminescence Ga K edge; He temp.

Window on a band and measure exafs

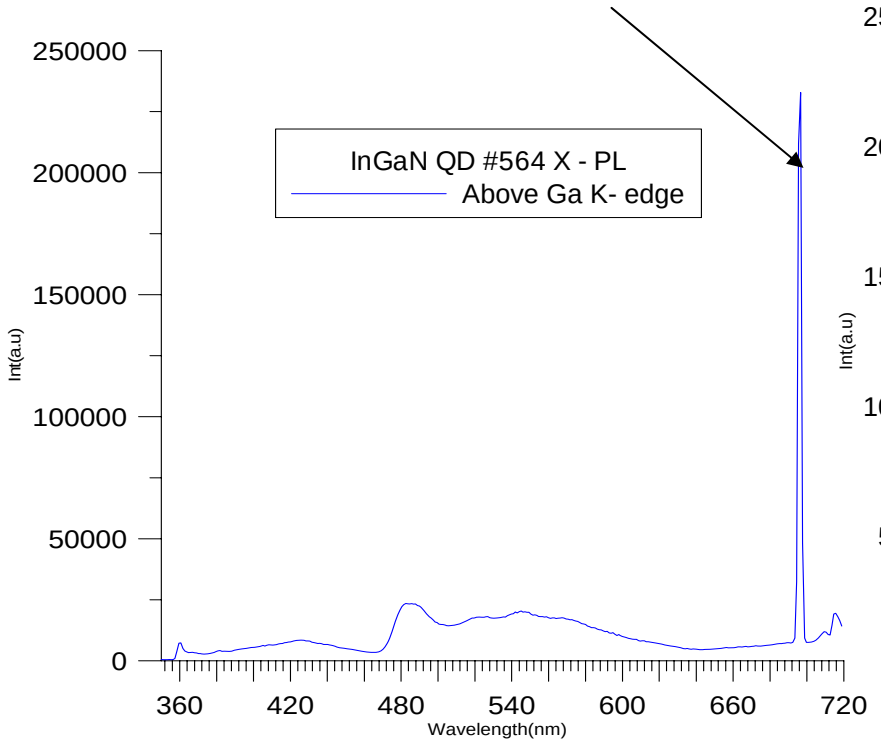


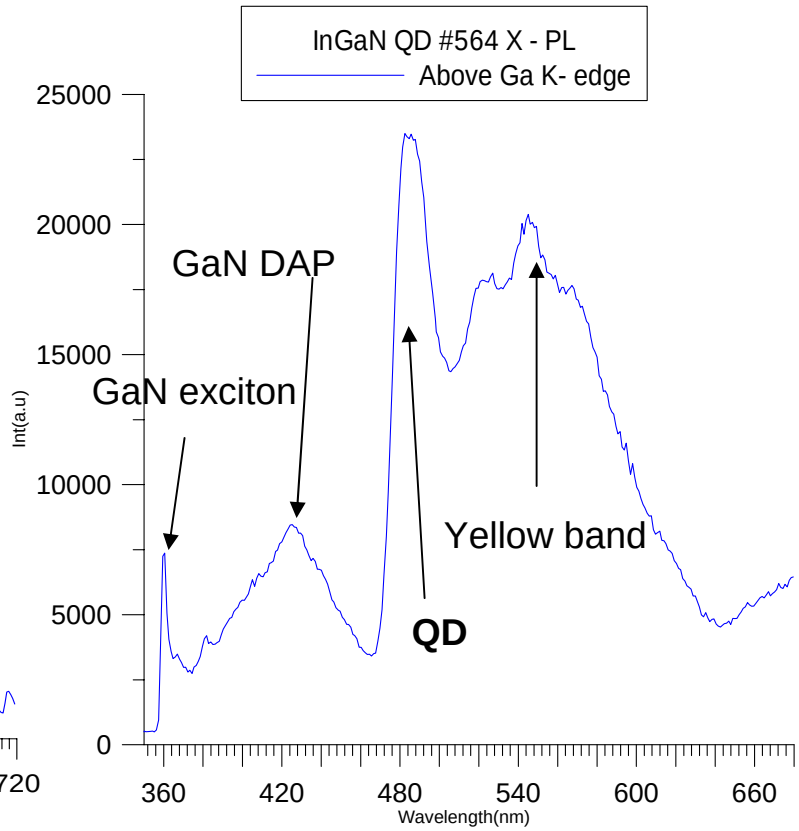
NOTE: these are single 2 and 0D layers, not thick epitaxy. Only one Ga atom in 5000 is in heterostructure

X-luminescence: 10 KV photons excite the whole structure. He temperature.

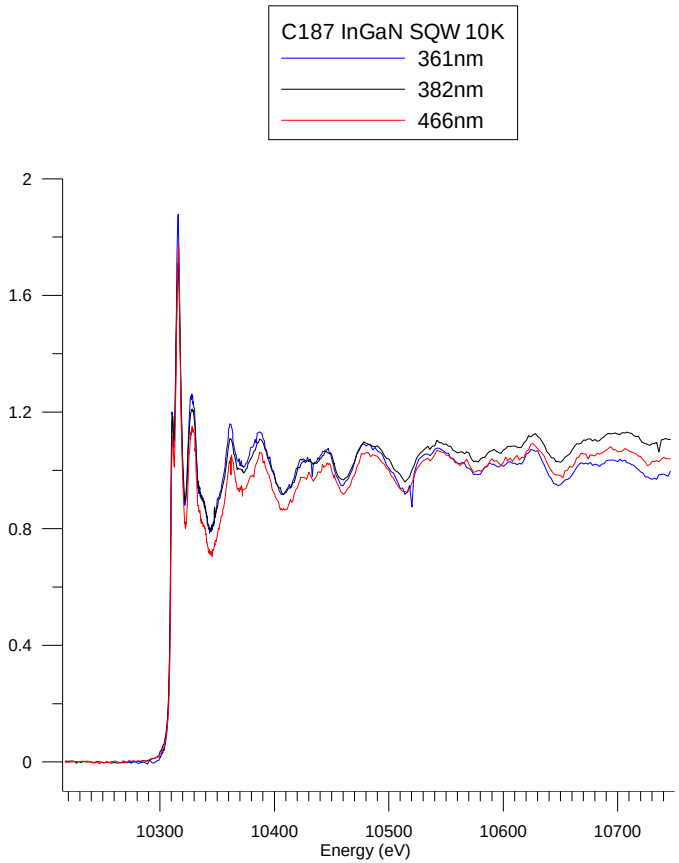
Beamline I811
MaxLab

Cr in sapphire





Window on various bands and use to detect EXAFS



EXAFS fits:

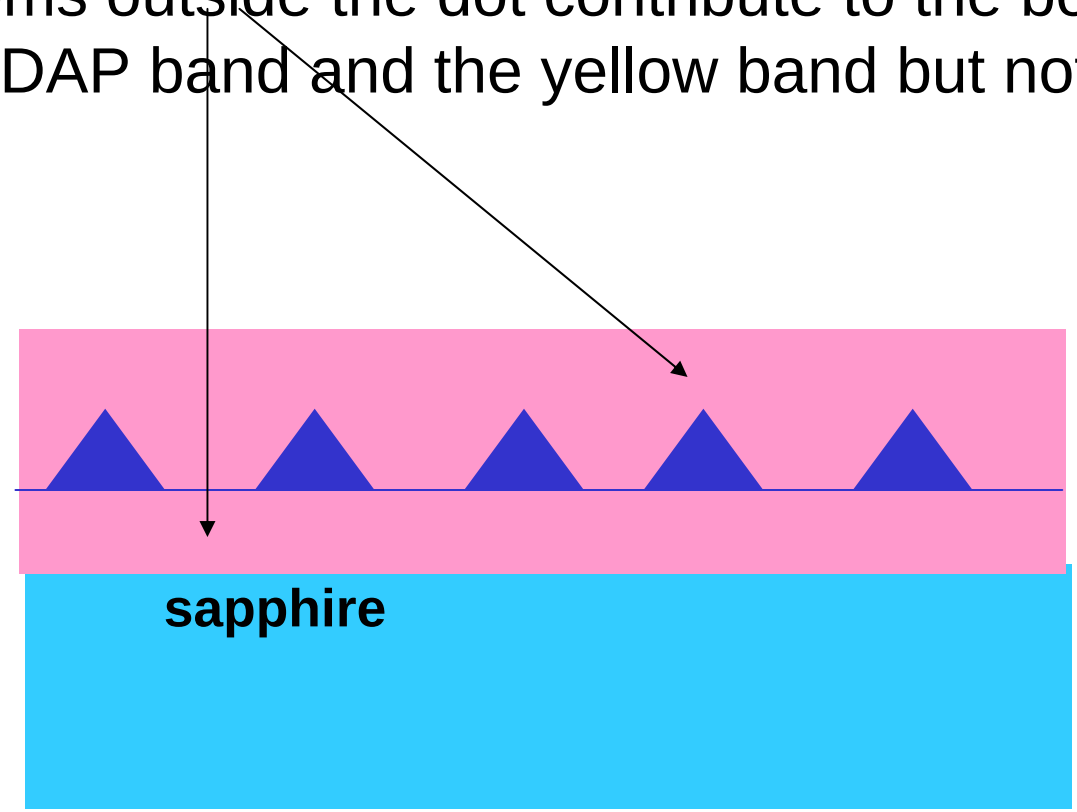
GaN, DAP..perfect GaN

QD…….poor fit to GaN. needs In atoms in second shell to fit and we can use these data to determine if In is clustered.

Why can Ga edge EXAFS detect In on QD luminescence when there is only a tiny fraction of Ga atoms in the dot?

Because the exciton pumped by the x-rays do not form a “gas” they from a “solid”. At He T they trap instantaneously.

So Ga atoms outside the dot contribute to the bound exciton band, the DAP band and the yellow band but not the QD band



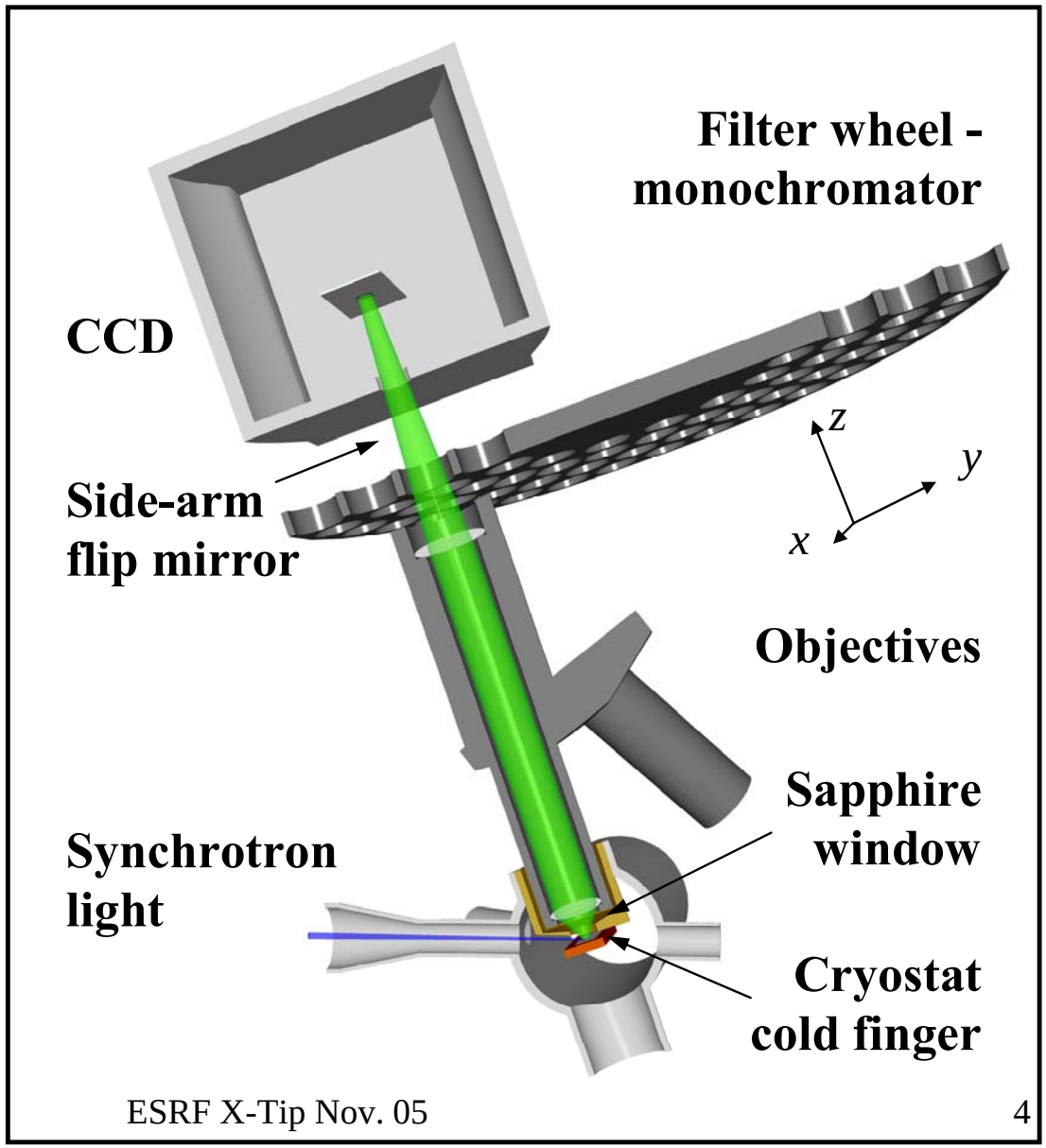
Micro-imaging XAS using optical detection methods

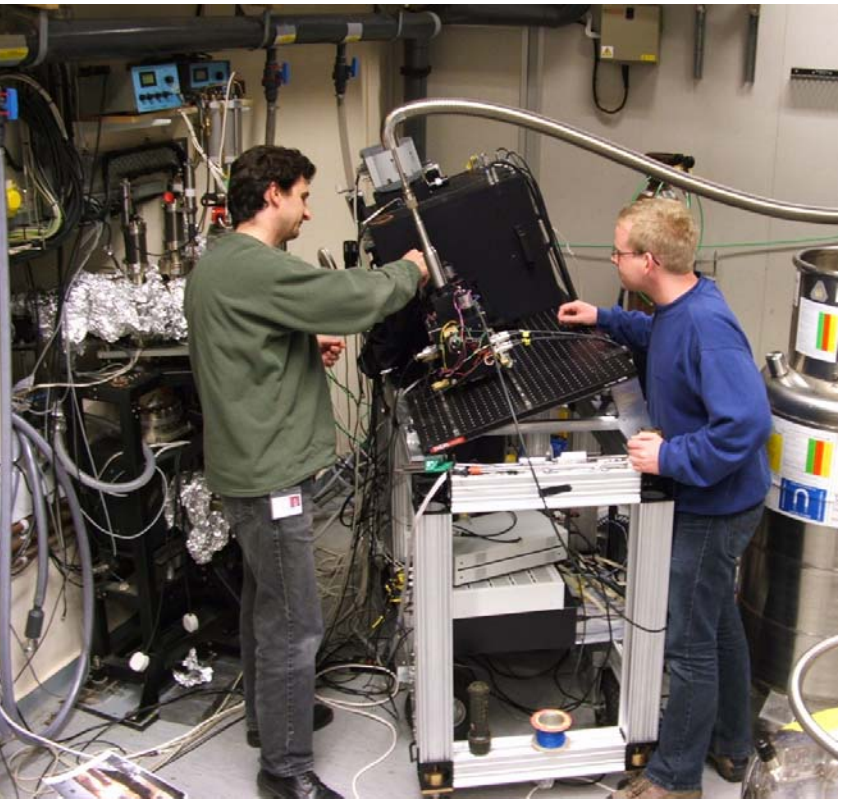
Schematic of CLASSIX1

Chemistry,
Luminescence
And
Structure of
Surface by micro-
Imaging
X-ray absorption

A joint project between CCLRC Daresbury Laboratory and Manchester University.

N. Poolton,
B. Hamilton and
B. Towlson.



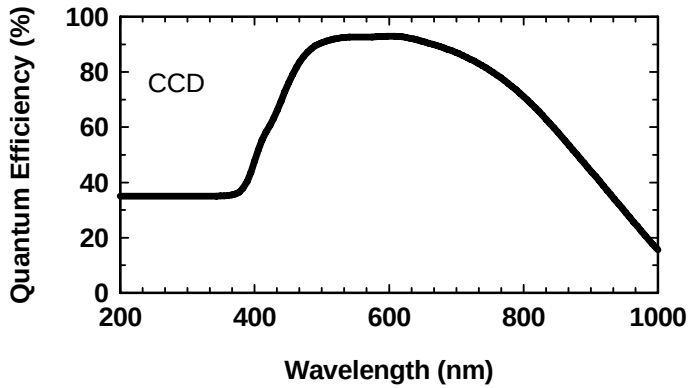


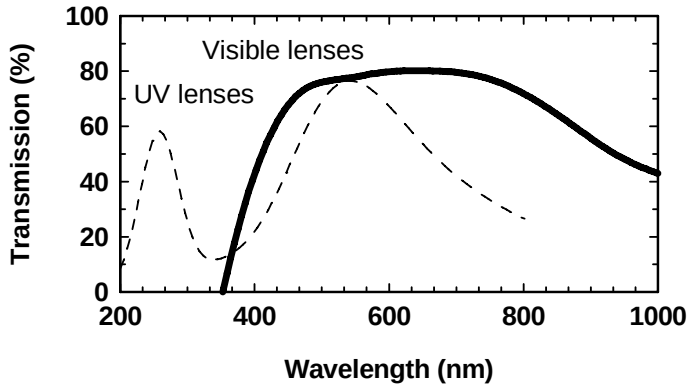
CLASSIX1 on beamline XUV mpw6.1 at SRS Daresbury (40-450eV)

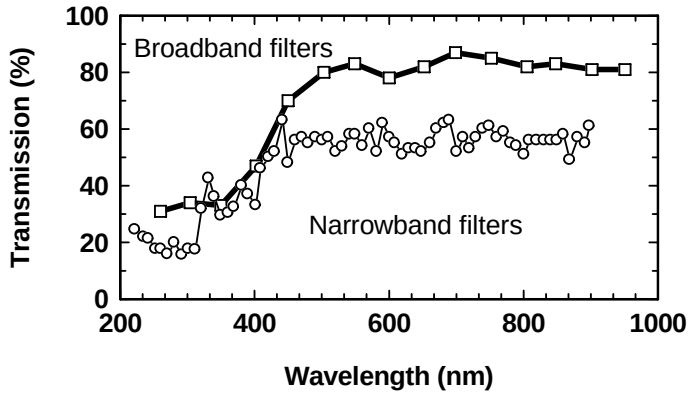
(above: happy users)

(Right: details of the machine, with blackout panels removed).

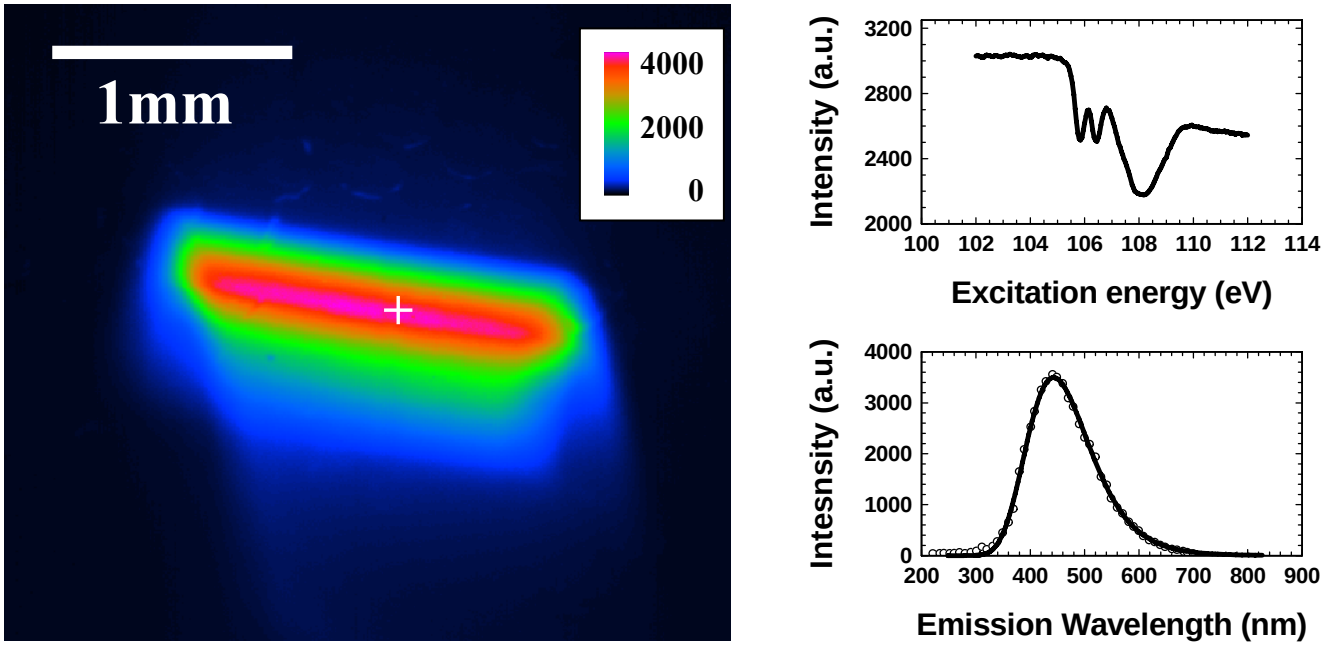
ESRF



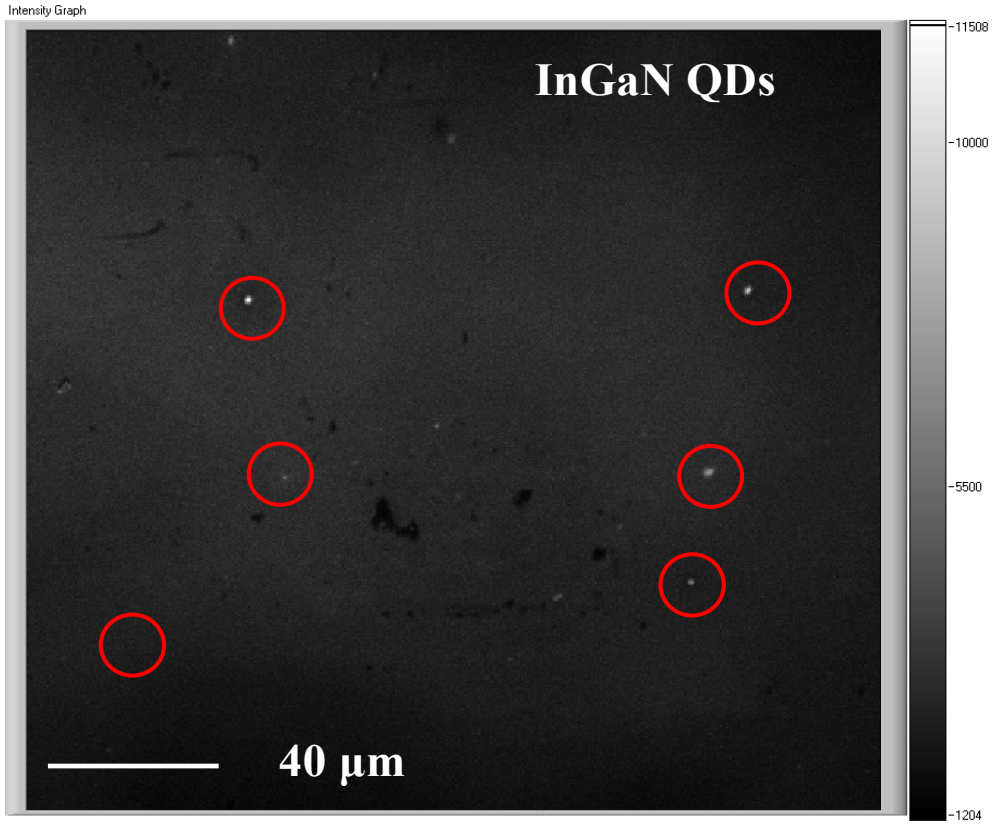




Characteristic of the optical components of CLASSIX1



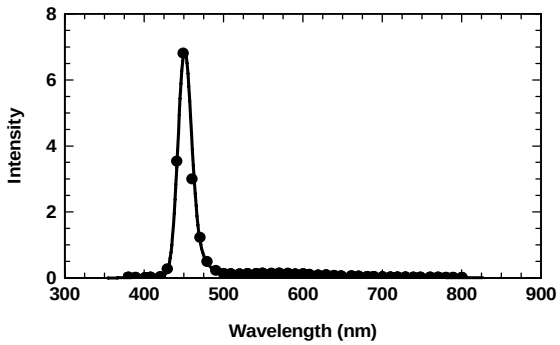
Demonstration of the imaging area. The emission is from a high-purity SiO_2 crystal. The luminescing area reflects the beam footprint. XAS and emission are shown here for the single point "+"

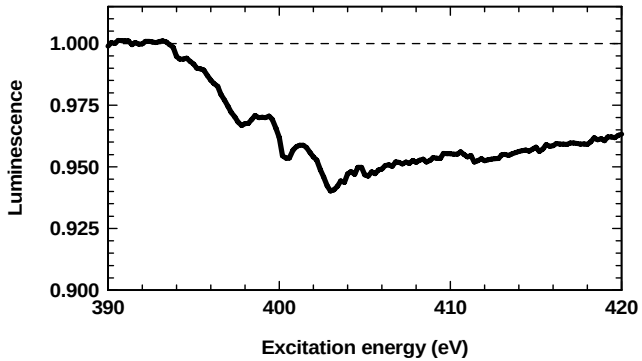


Micro-imaging InGaN quantum dots. Sparse dot sample.

(left) The luminescence image clearly shows clumping of the dots, although there is low-level emission everywhere.

(bottom) The emission and N edge ODXAS from a single bright spot. This is the same as from the weaker background.





5. Where do we go?

- SPM offers truly complementary style of measurement to PEEM
- existence theorem established
- but need activity at SR facilities as well as academic labs.
- need versatility of measurement modes