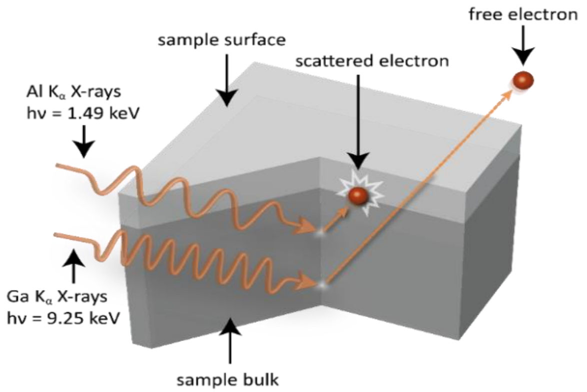


Extending photoelectron spectroscopy into the bulk using Hard X-rays (HAXPES)

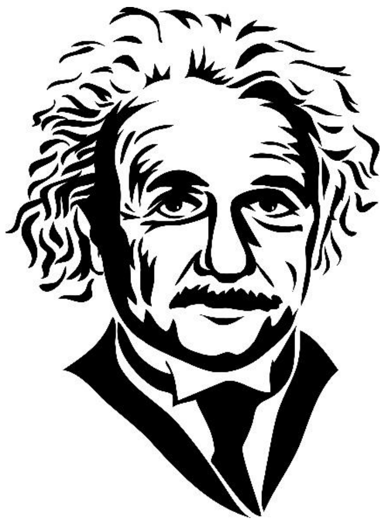
Ben F Spencer

Department of Materials, University of Manchester

Sir Henry Royce Institute for Advanced Materials

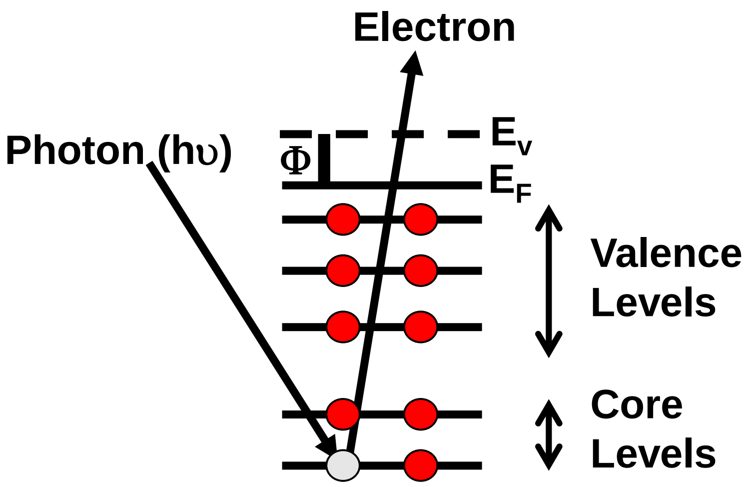
19/02/2020

Photoelectron spectroscopy

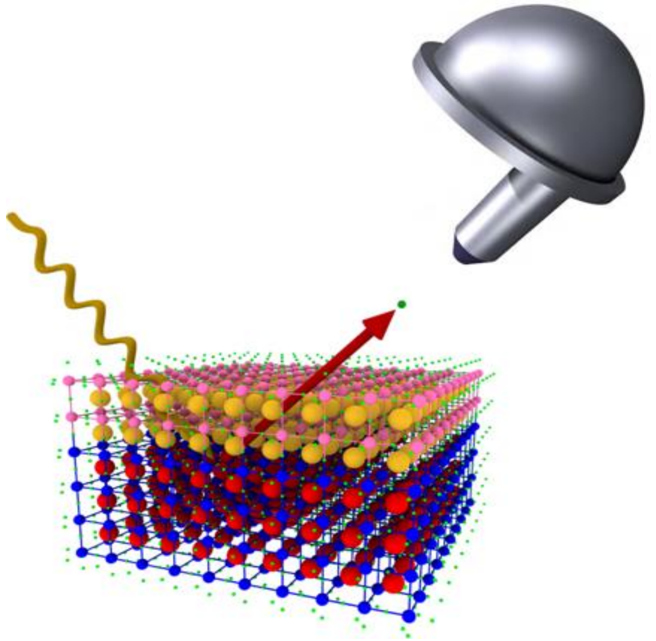


$$E_{KE} = h\upsilon - E_b - \Phi$$

E_{KE} - kinetic energy (measured)
$h\upsilon$ - photon energy (known)
E_b - binding energy of photoelectron
Φ - work function (known)



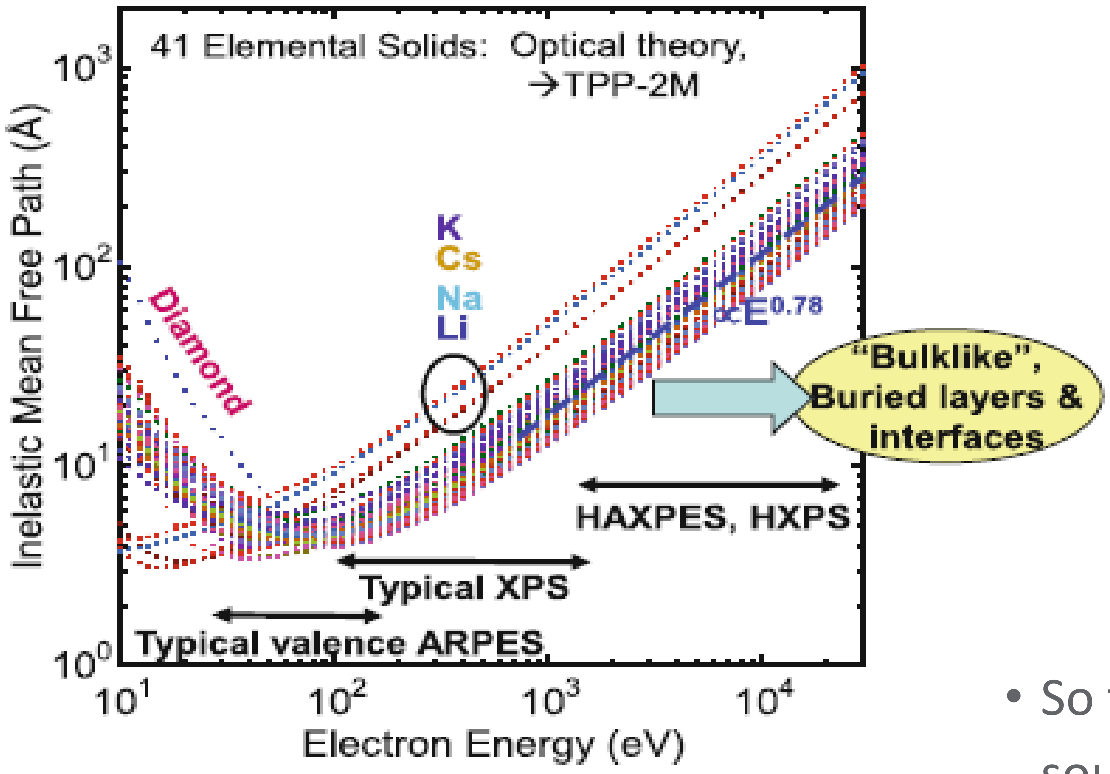
- The basis of chemical analysis using X-ray photoelectron spectroscopy (XPS)
- Used ubiquitously



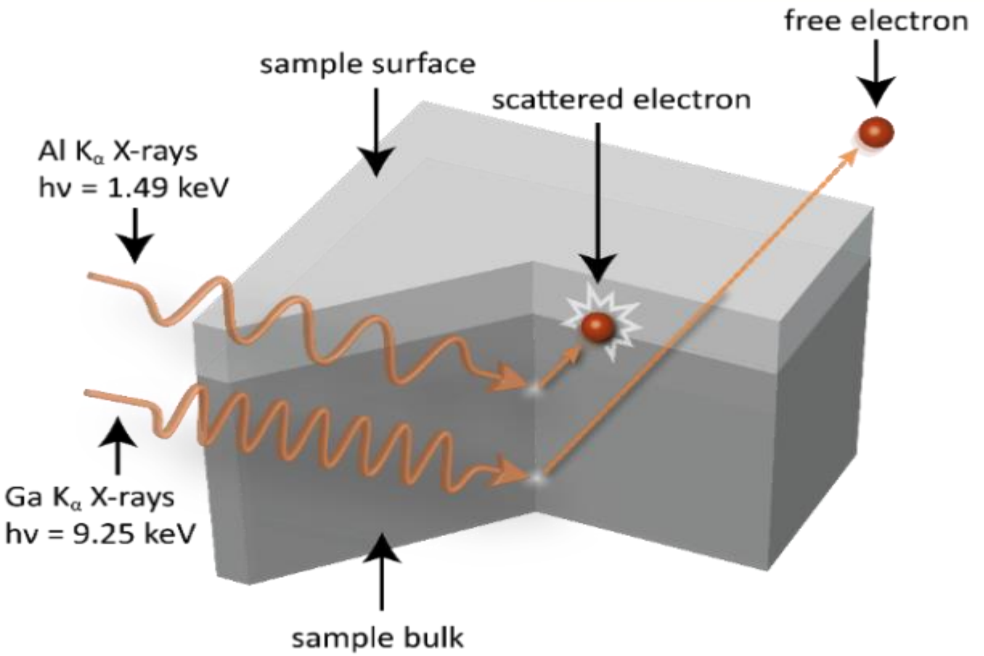
- BUT the electrons can only escape from the top surface layers
- So the sampling depth is only a few nm

http://www.psi.ch/science/syn-highlights

Hard X-ray Photoelectron Spectroscopy (HAXPES)



The Universal Curve of electron pathlength



- So to probe deeper, we just use a harder X-ray source, right?
- Yes, but photoionisation cross sections plummet!
- Need a very high intensity source.

(Hard X-ray Photoelectron Spectroscopy (HAXPES), Ed: Joseph C. Woicik, Springer (2016)) https://www.scientaomicron.com/en/products/haxpes-lab/instrument-concept

HAXPES facilities at world synchrotron sources

Diamond, Oxford- I09

SOLEIL, Paris - GALAXIES

Canadian Light Source – 06B1-1

DESY, Hamburg – P22 (new)

ESRF, Grenoble – EH2 B

BESSY, Berlin – KML1 (new HIKE upgrade)

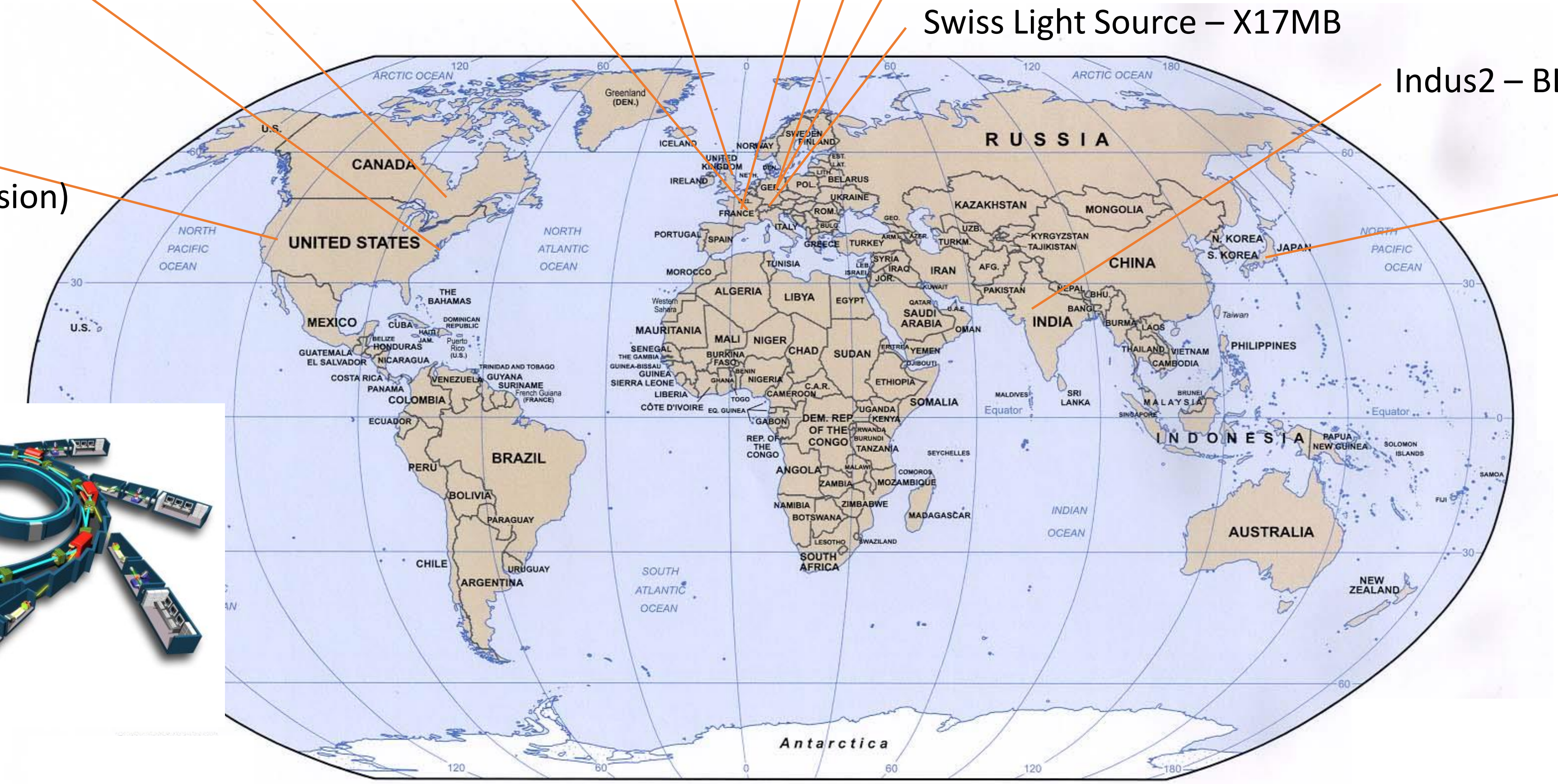
NSLSII, Brookhaven – SST2

Swiss Light Source – X17MB

Indus2 – BL14

ALS - 9.3.1
(under commission)

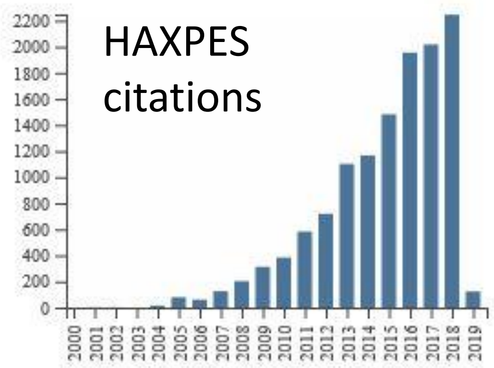
Spring8, Japan -
7 beamlines!

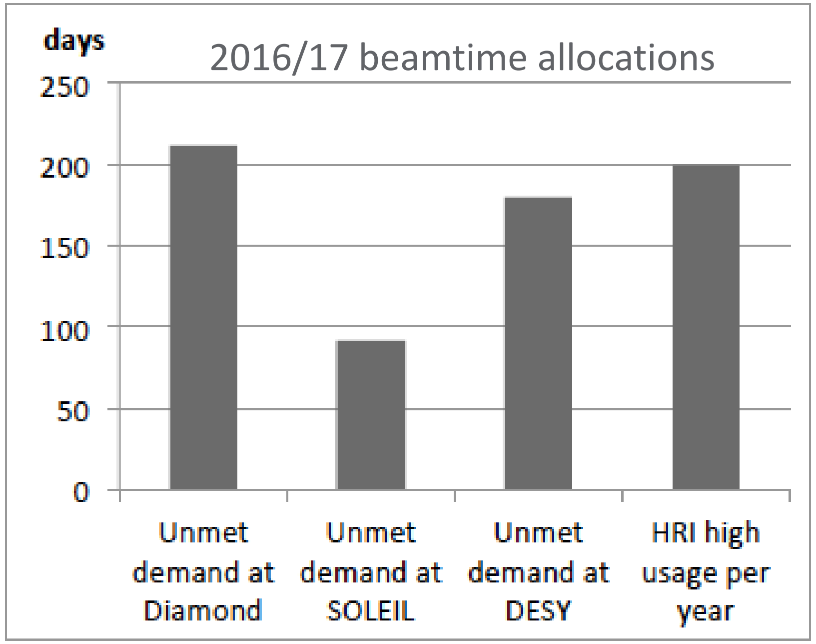


- 3-4 x over-subscribed!

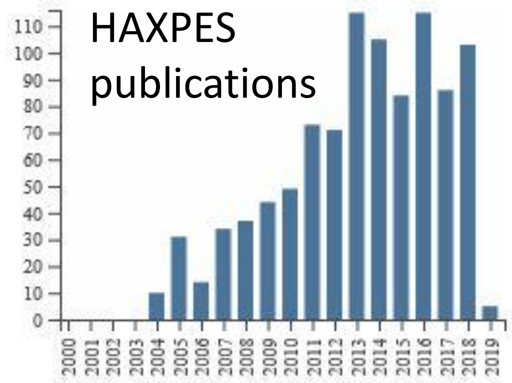
International unmet demand

- The oversubscription of international facilities has led to saturation in the amount of work that can be carried out, but the impact of HAXPES continues to rise.





- Urgent need to develop high intensity lab-based sources



- Underprovision recognised in EPSRC roadmap (2017):
  http://www.epsrc.ac.uk/files/research/roadmap-for-photoelectron-spectroscopy/

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Hard X-ray Photoelectron Spectroscopy (HAXPES) at HRI

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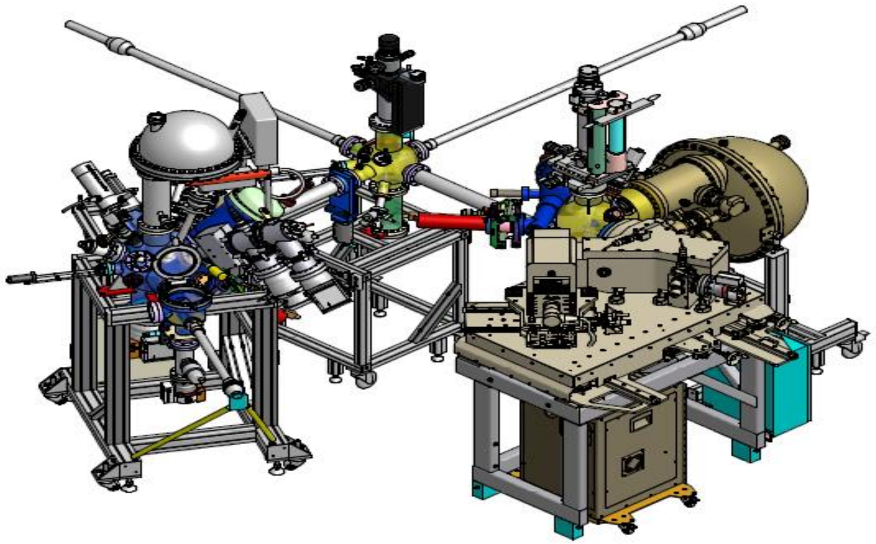
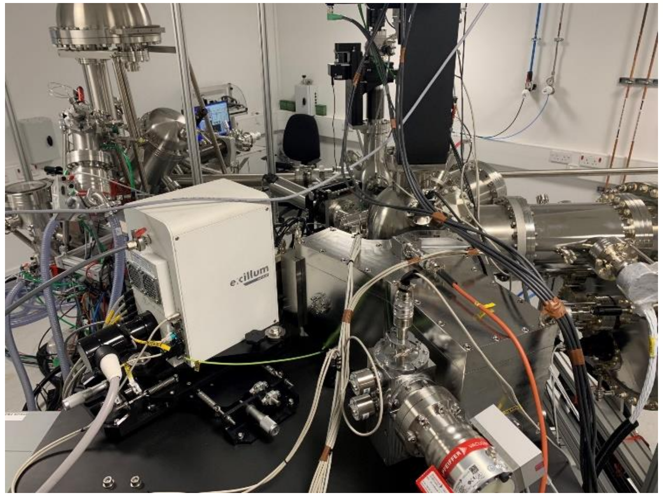
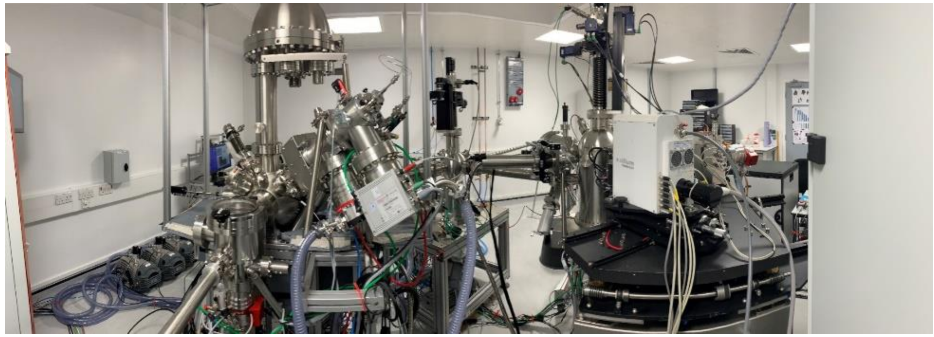
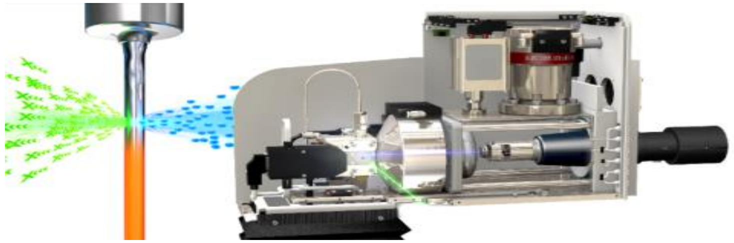
- three orders of magnitude increase in X-ray intensity
- 50 μm spot size
- X-ray photon energy 9.25 keV (Excillum Ga metal jet)
- High throughput, high kinetic energy electron analyser (EW4000)

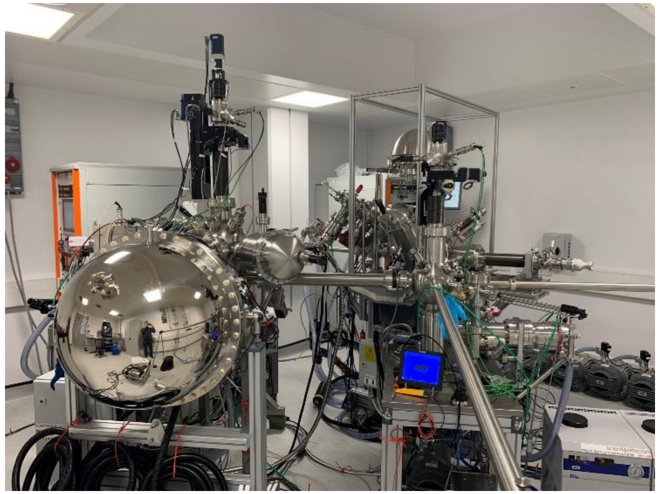








excillum



Regoutz *et al.*, Rev. Sci. Instr. **89** 073105 (2018)

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Combined HAXPES and XPS at HRI

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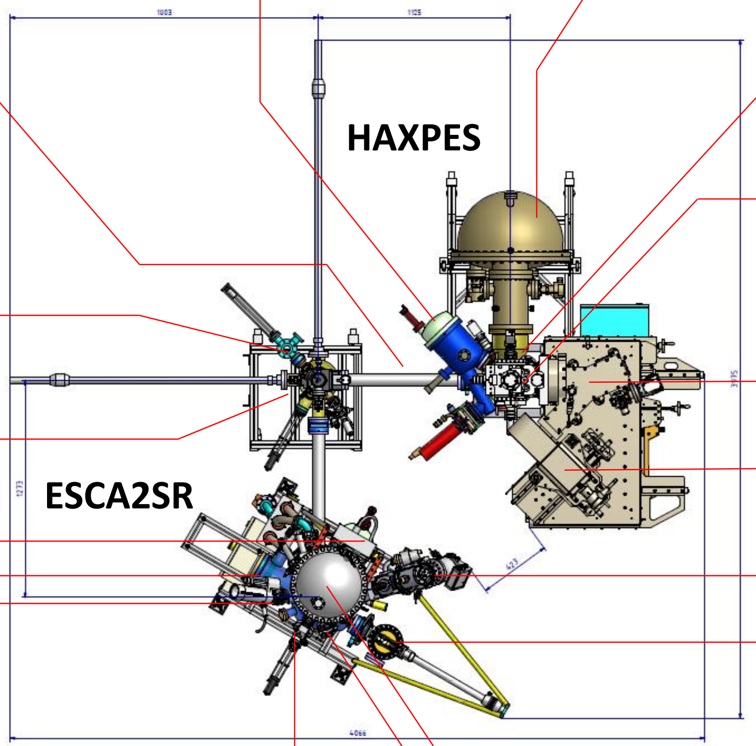

+ a vacuum suitcase for sample loading from external glove box, other UHV systems

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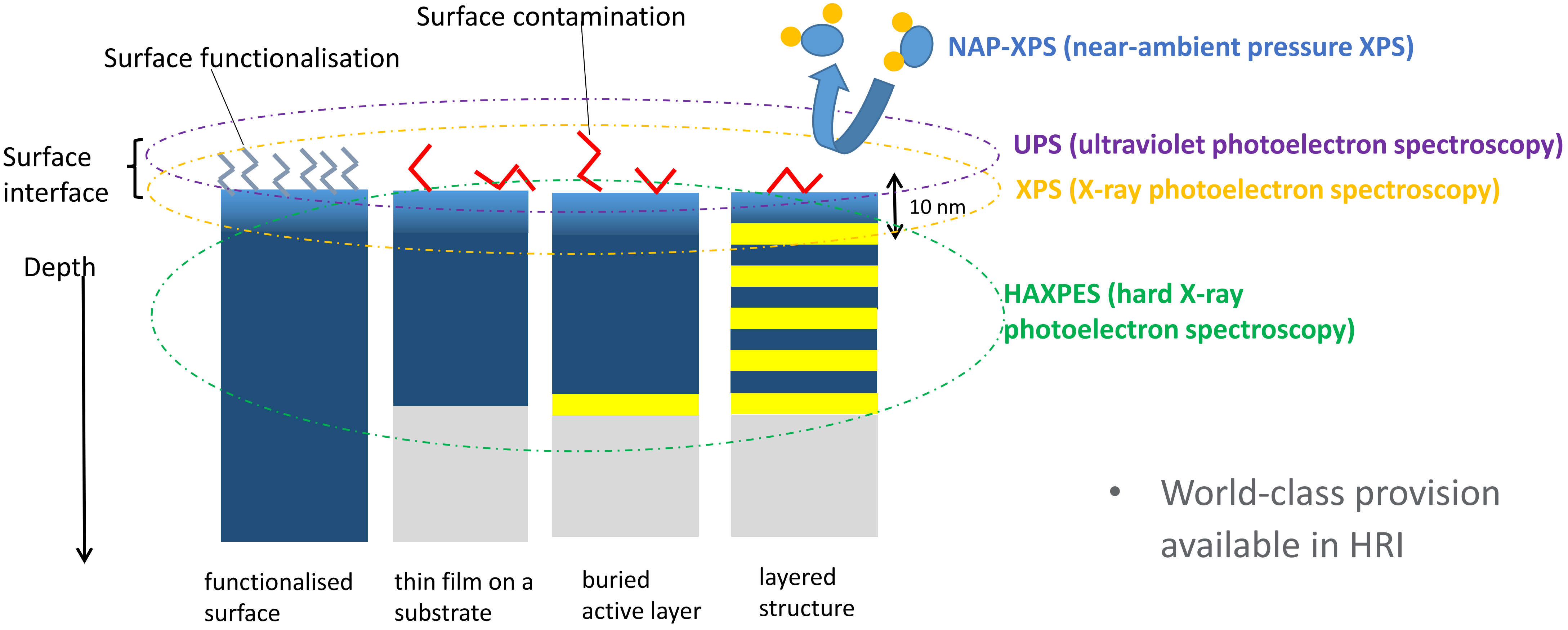
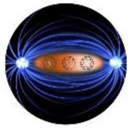
Chemical state profiling from the surface to the bulk

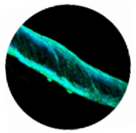


- World-class provision available in HRI

HAXPES in the Royce- supporting themes



- *Atoms to devices*: locate buried interfaces in semiconductor heterostructures



- *Biomedical materials*: measure light elements (C,N) in prototype medical devices without damage

- *Energy storage*: characterise buried interfaces in working batteries, understand the solid-electrolyte interface

- *Materials systems for demanding environments*: understand corrosion scales from surface to bulk

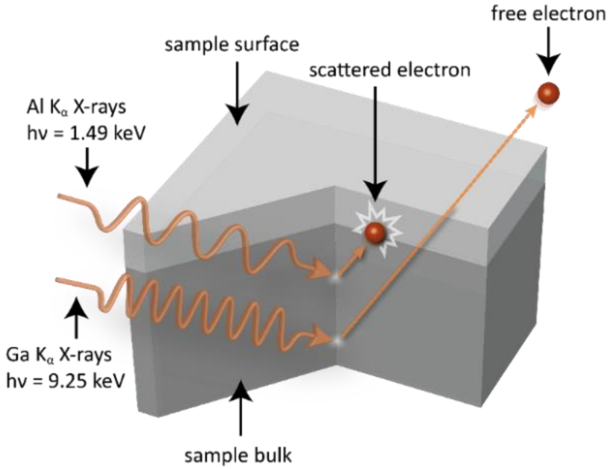
- *Nuclear materials*: safely & non-destructively measure corrosion and contamination; contribute to whole-life management of materials

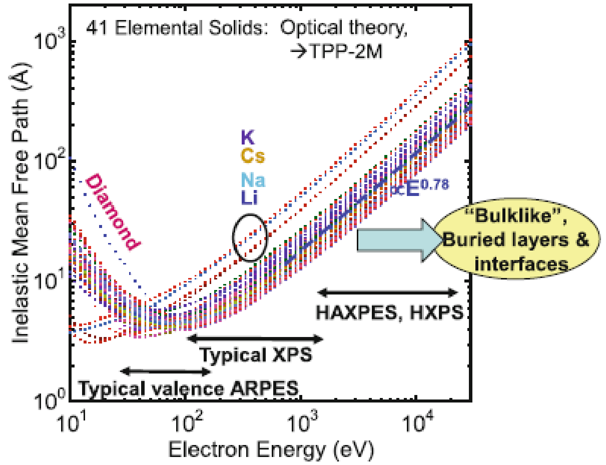
- *2D materials*: obtain layer-by-layer information from van der Waals heterostructures and nm-scale devices

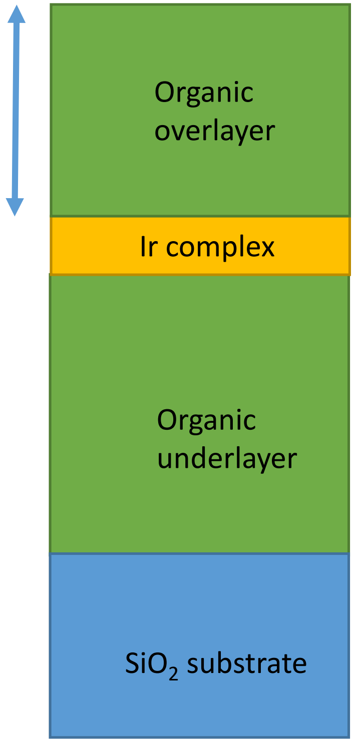
Materials for Energy Efficient ICT: buried interfaces, layered structures, thin coatings, bulk chemical environment

Establishing lab-based HAXPES @ 9.25 keV now requires:

- Sensitivity factors – quantification
- Detection limits
- Analysis protocols
- Use of inelastic background modelling for depth profiling beyond the elastic limit
- Standardisation, incl compare lab system to synchrotron data







Test using a model system -- Ir-complex (green emitter in organic-LED displays) buried under organic

- Prepared at NPL - high quality, with precision layer thicknesses
- Due to be part of an upcoming BIPM (International Bureau of Weights and Measures) study to establish accuracy in the measurement of buried organic layers

A G Shard *et al.*, Analytical Chemistry **84** 7865 (2012)

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NPL

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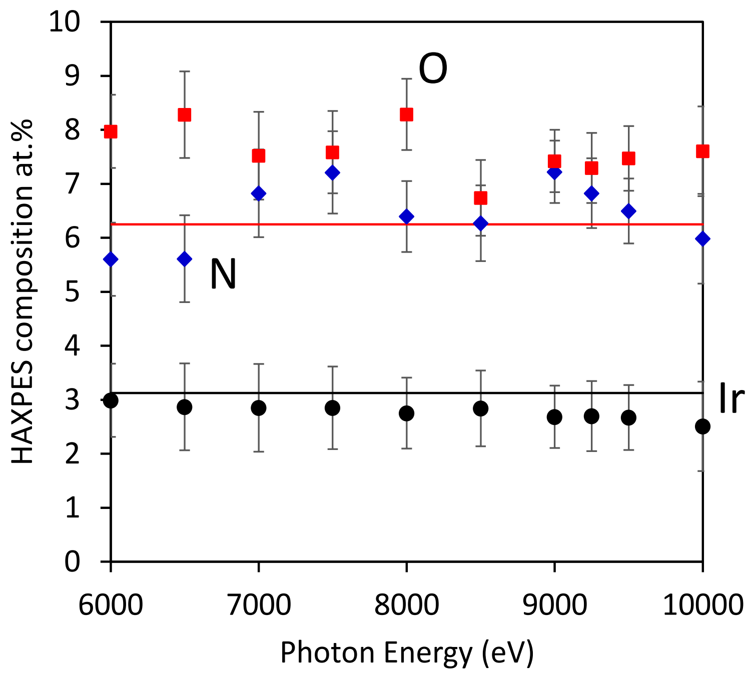
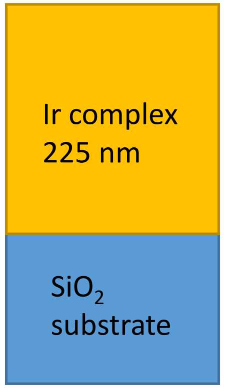
Sensitivity factors

$$X_A = 100\% \times \frac{A_A/I_A}{\sum_i A_i/I_i}$$

$$I \propto J_{h\nu} T_E \lambda \frac{\sigma}{4\pi}(1+\beta)$$

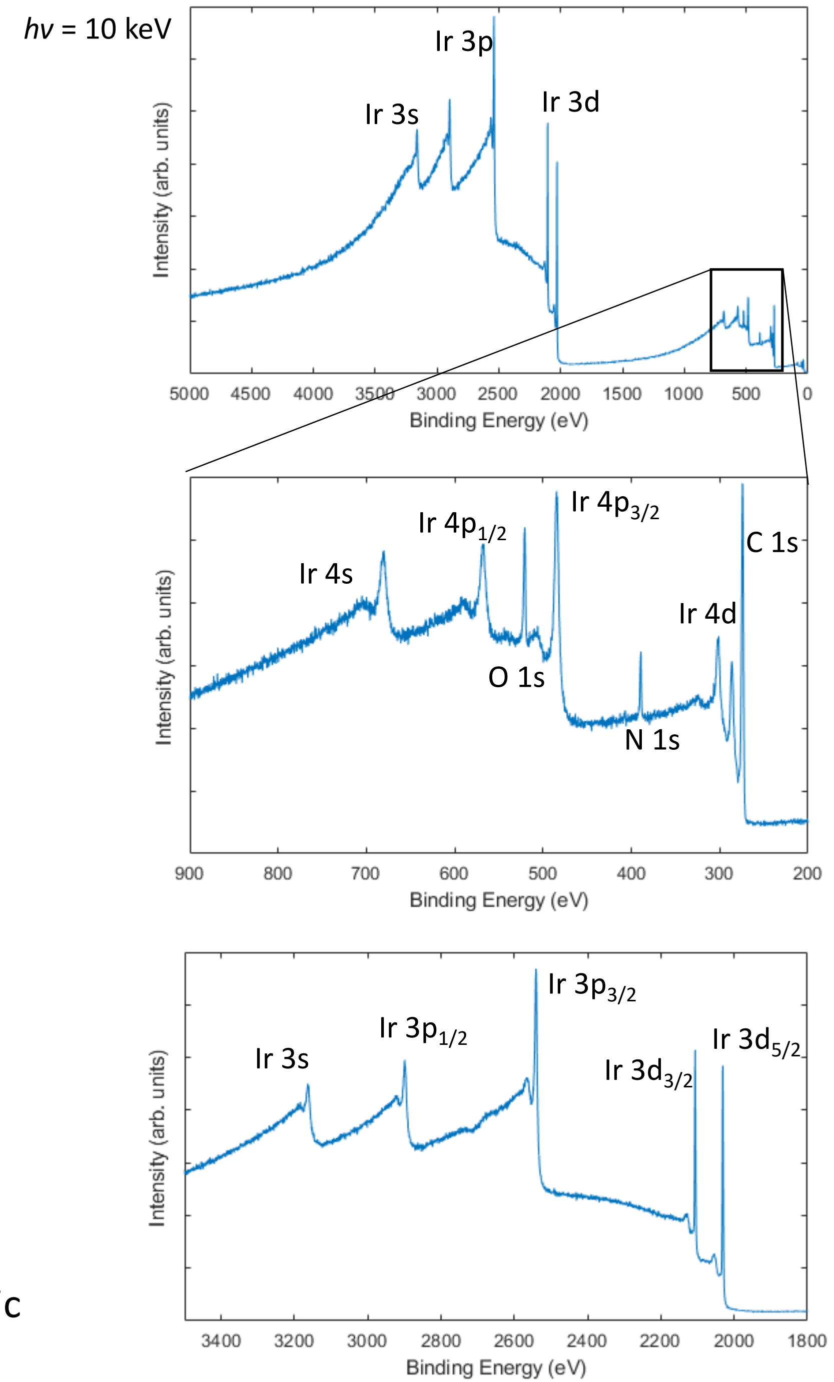
$$I_A = \lambda_A \sigma_A (1+\beta_A)$$





Reference sample – pure Ir complex
$Ir(ppy)_2(acac)$, $C_{27}H_{23}IrN_2O_2$

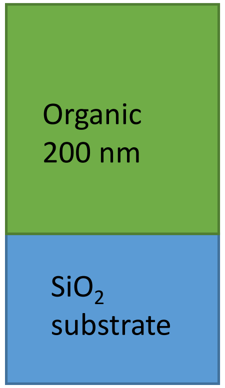
Consistent for hv = 6, 7, 8, 9, 10 keV
Consistent using Ir 3s through 4d.

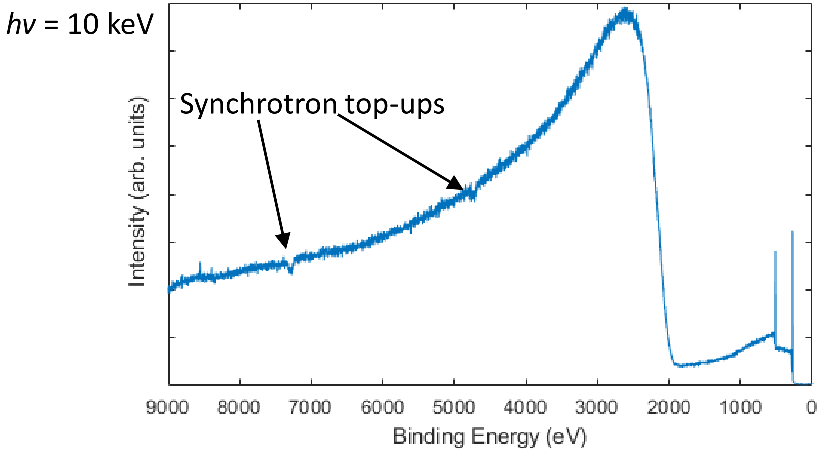


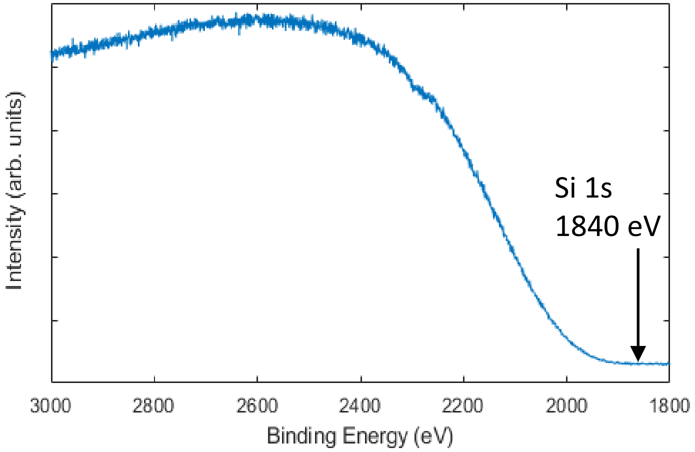
M.B. Trzhaskovskaya, V. G. Yarzhemsky, Atomic Data and Nuclear Data Tables 2018 & 2019

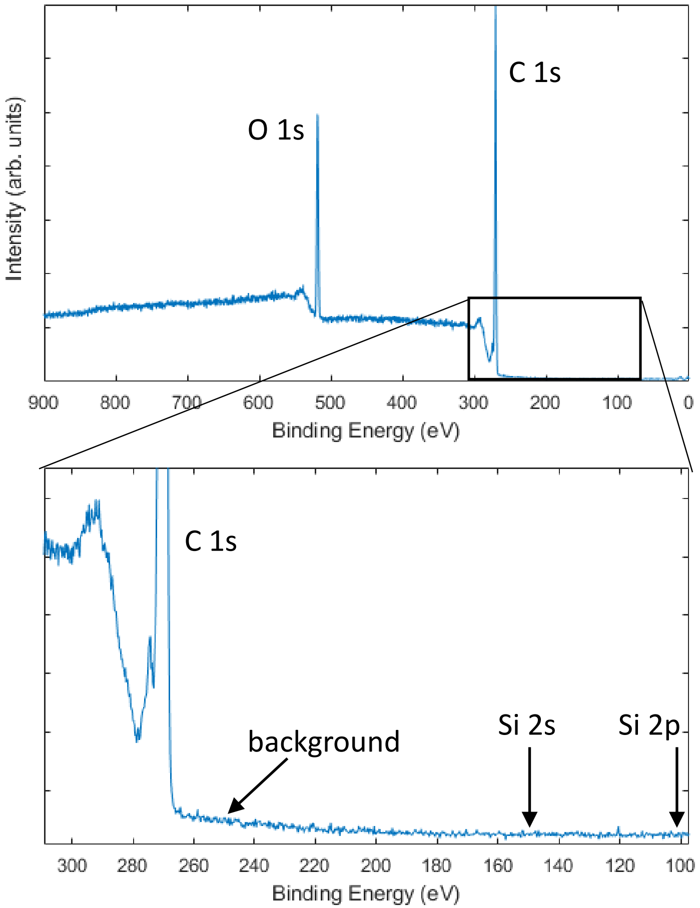
Reference sample – 200 nm organic underlayer on SiO_2
Irganox (1010) $C_{73}H_{108}O_{12}$

	Percentage	
hv	C	O
10000	85.72	14.28
9000	86.05	13.95
8000	85.14	14.86
7000	85.17	14.83
6000	84.90	15.10
Average	85.39	14.61
Expected	85.88	14.12



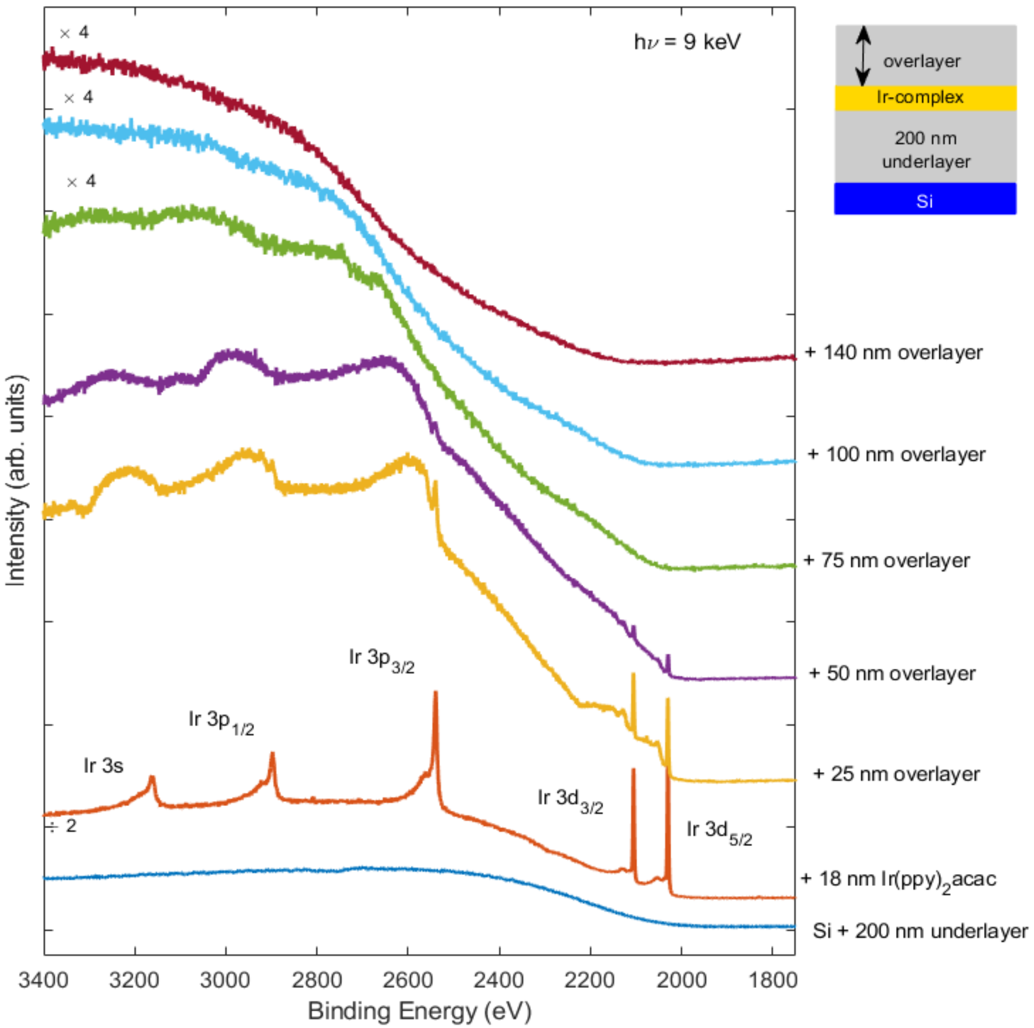






Inelastic background originating from the Si 1s core level already shows the potential for extracting depth information over >> 50 nm

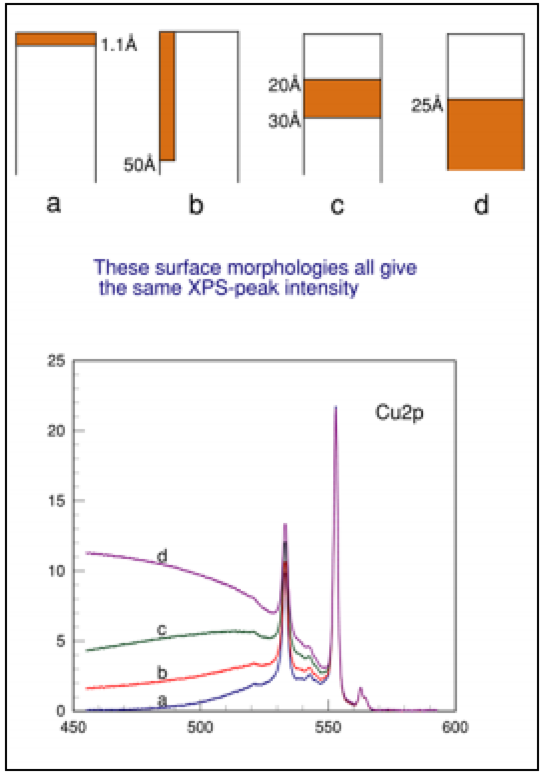
Calculation method can be extended to all elements; requires further testing

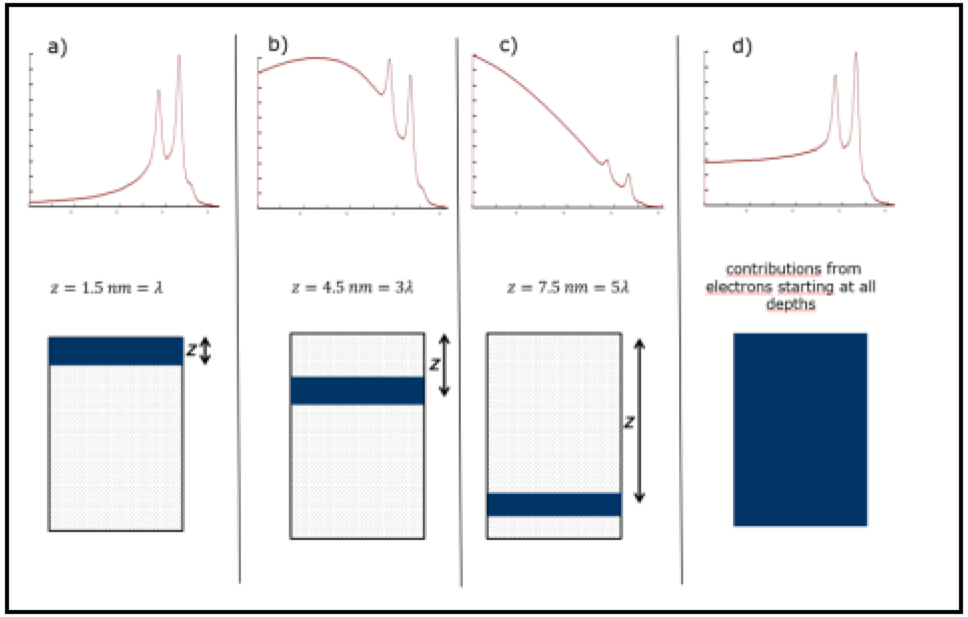


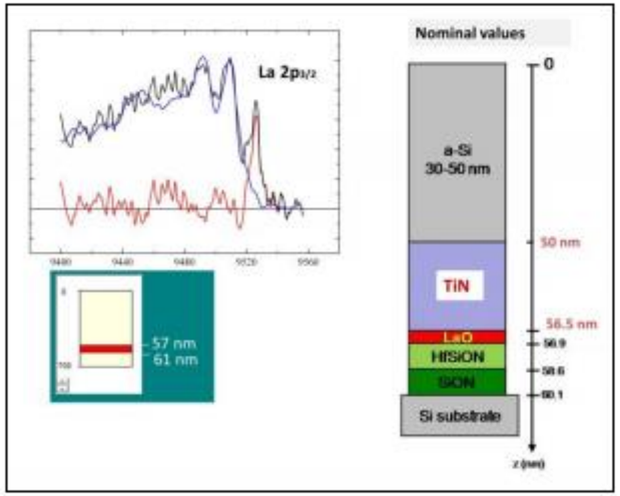
Inelastic background originating from each core level creates a distinctive “signature”

Core levels measured up to 50 nm overlayers

Inelastic background Tougaard analysis



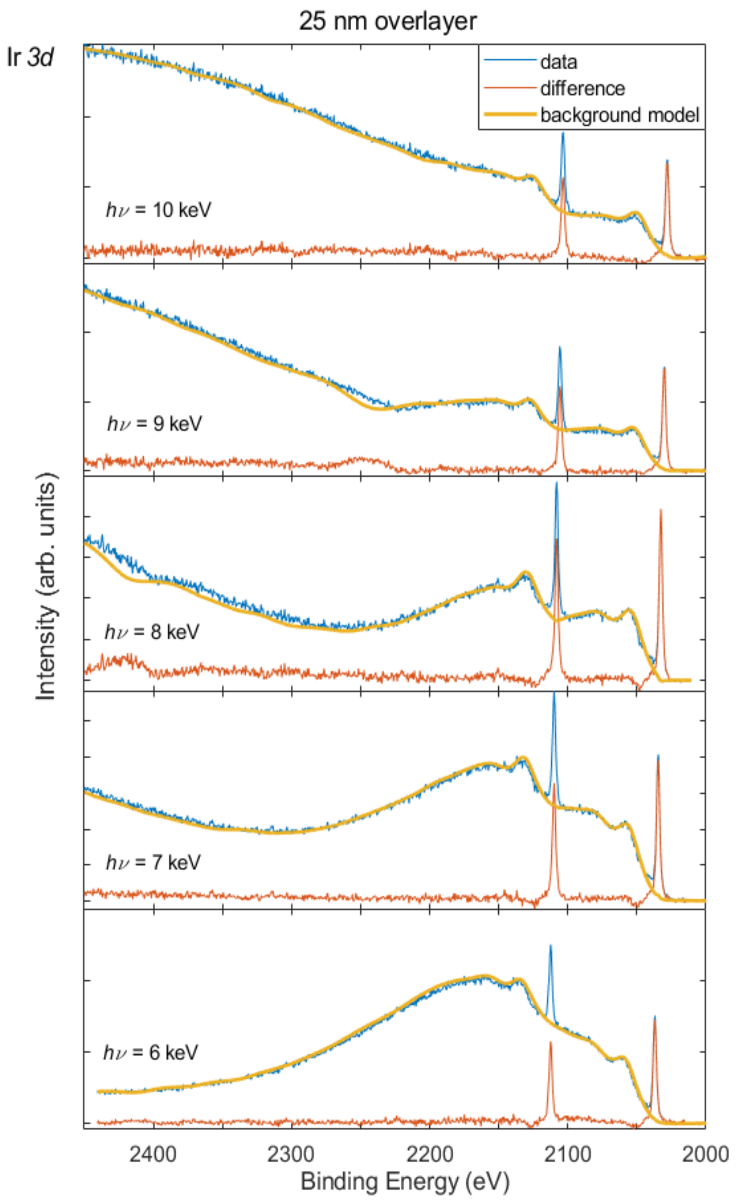


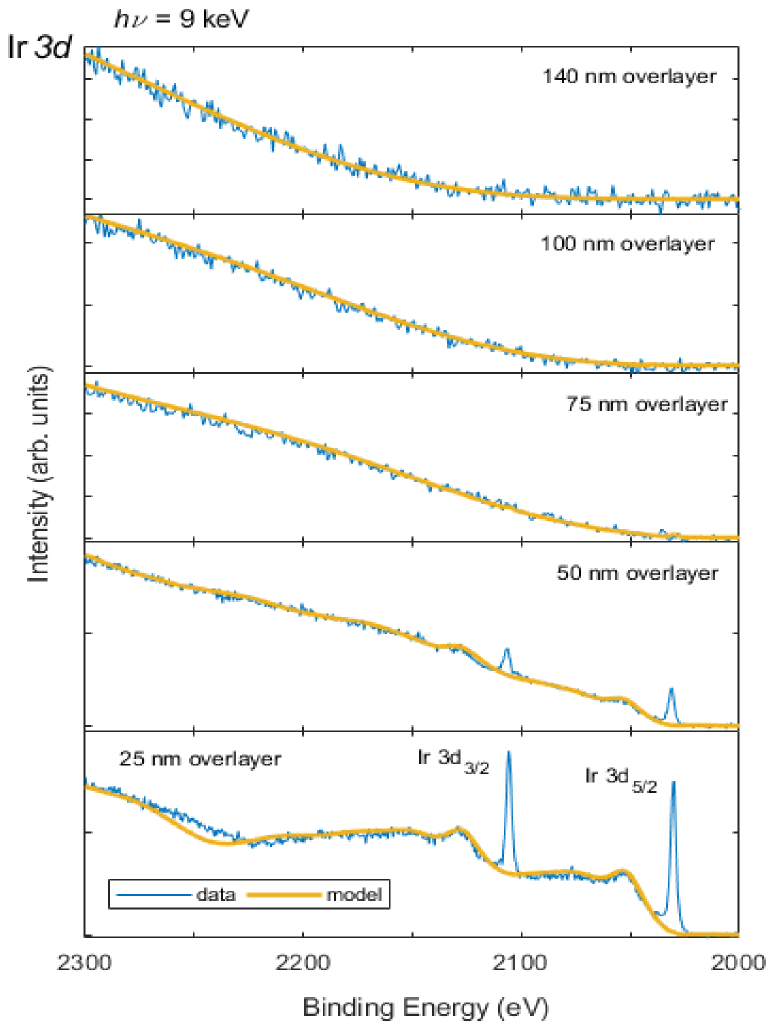


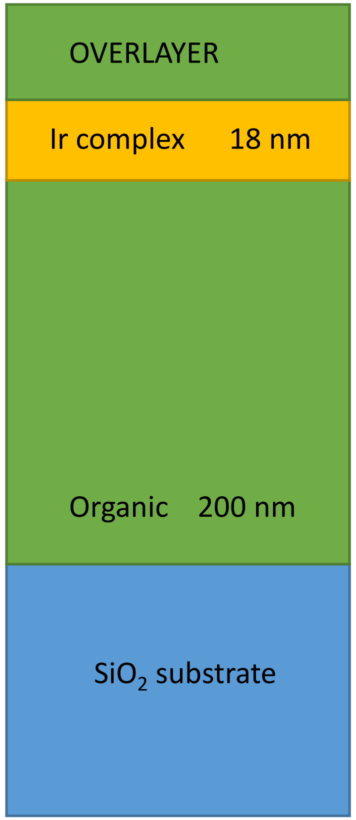
Enabled in QUASES software (www.quases.com)

- IMFP is a critical parameter
- Reference data important for layered structures
- Proposed that this enables information from depths ~ 20 x IMFP for HAXPES (spectra contain wider region of energy loss)

Y.-T. Cui *et al.,* J. Appl. Phys. **121** 225307 (2017)
S. Tougaard, Journal of Surface Analysis **24** 107 (2017)
S. Tougaard, Surf. and Inter. Anal. **11** 453 (1988)





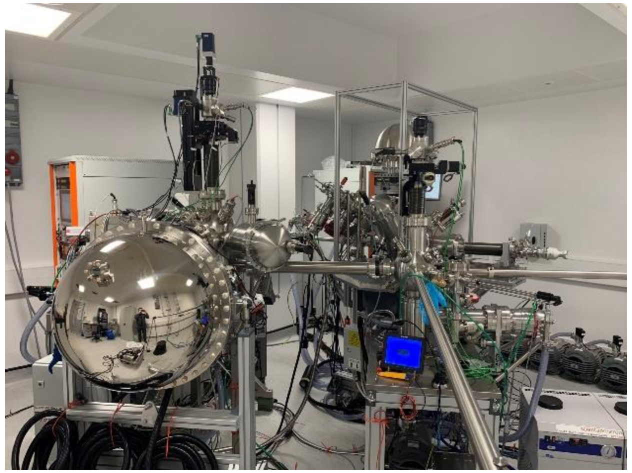


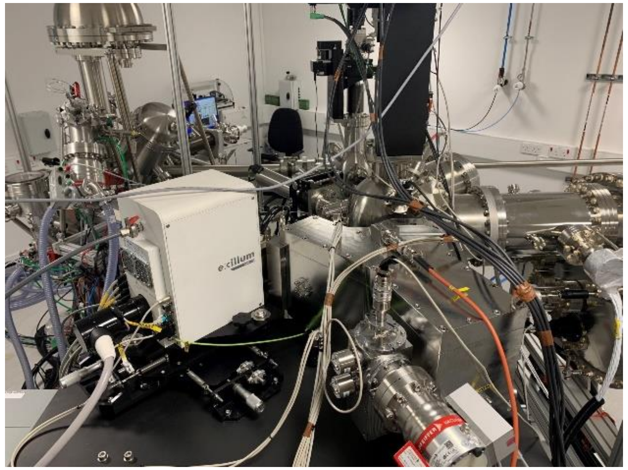
Overlayer thickness modelled with ~ 5% error consistently for data using *hv* = 6-10 keV

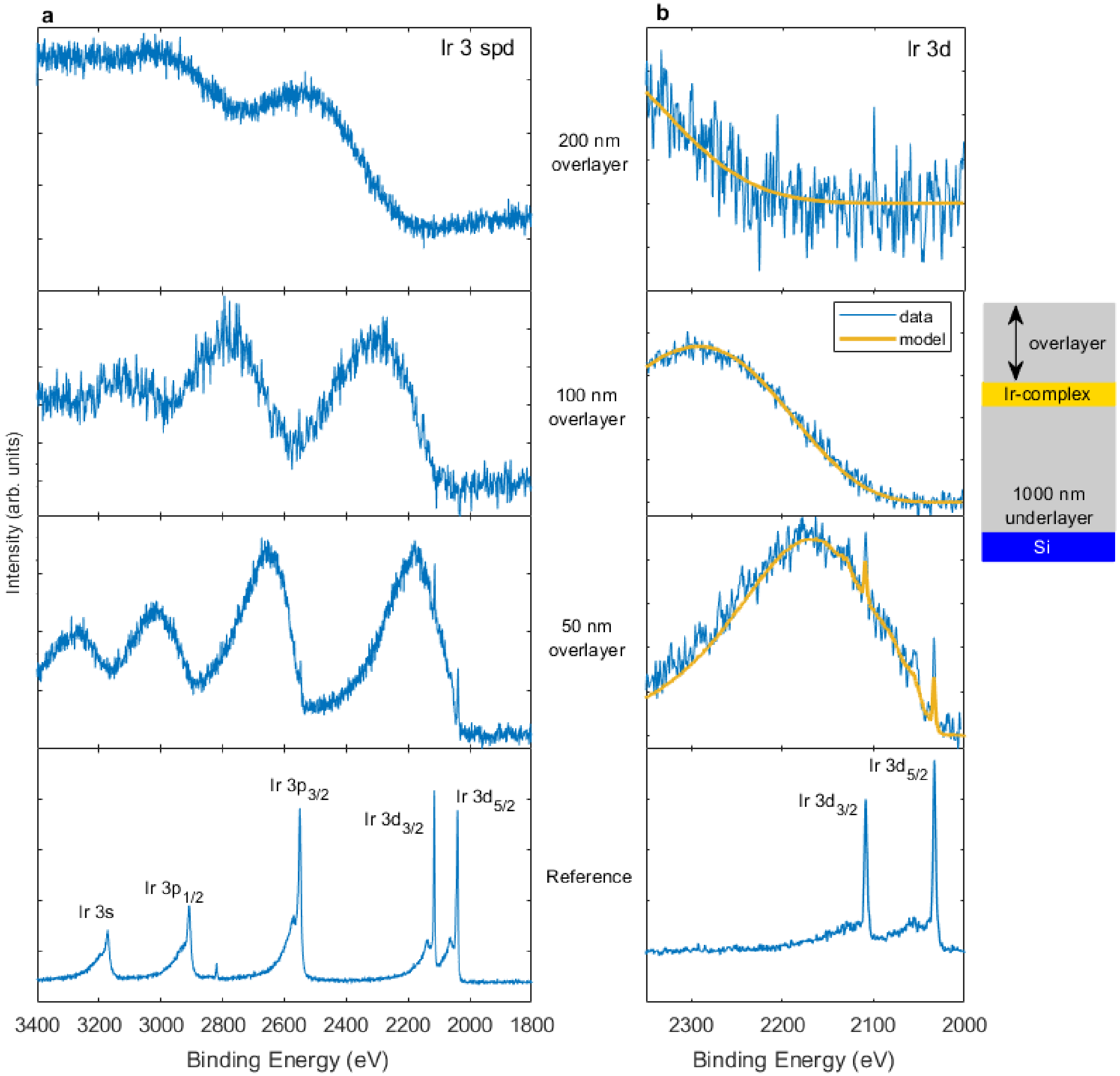
Lab-based HAXPES @ 9.25 keV

So much less flux- but so much more time!

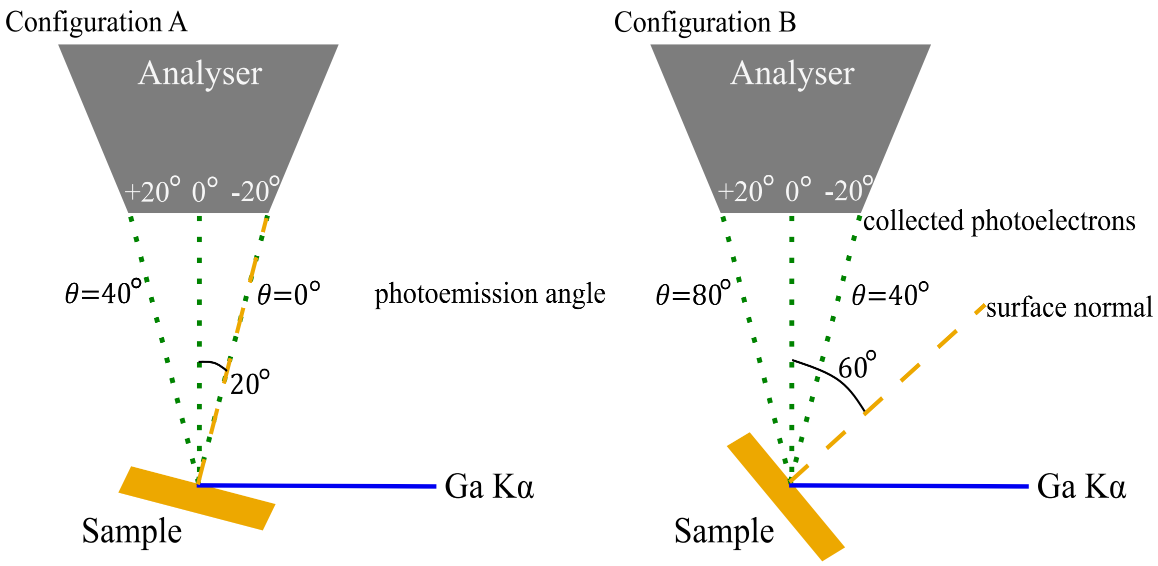
Can measure insulators using a neutraliser



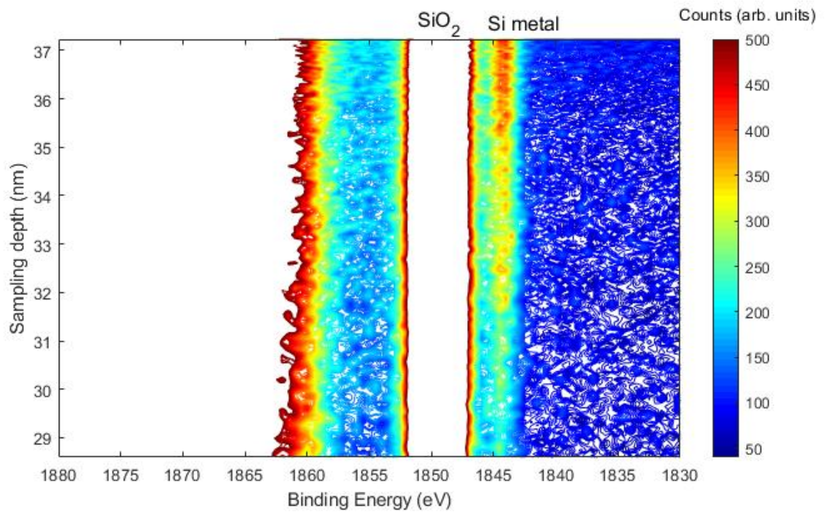


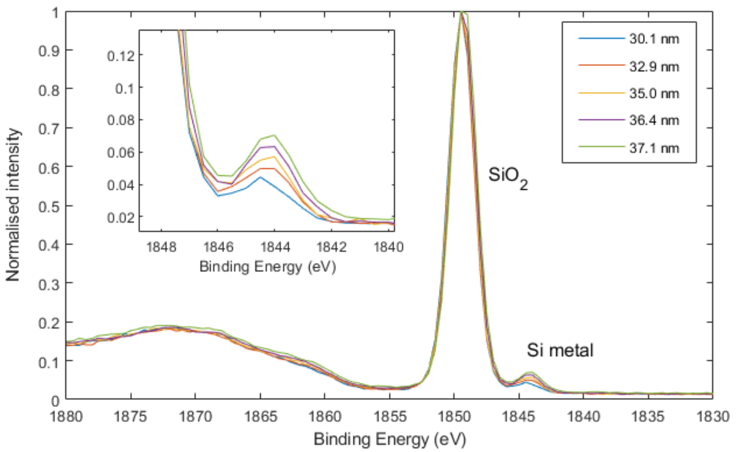


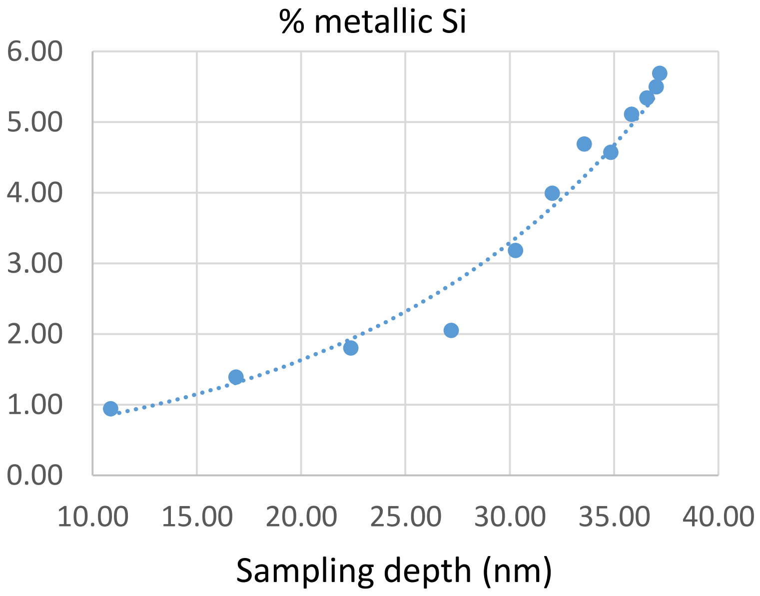
Use analyser in angle-resolved mode for depth profiling



Si 1s – Si substrate with SiO_2 overlayer







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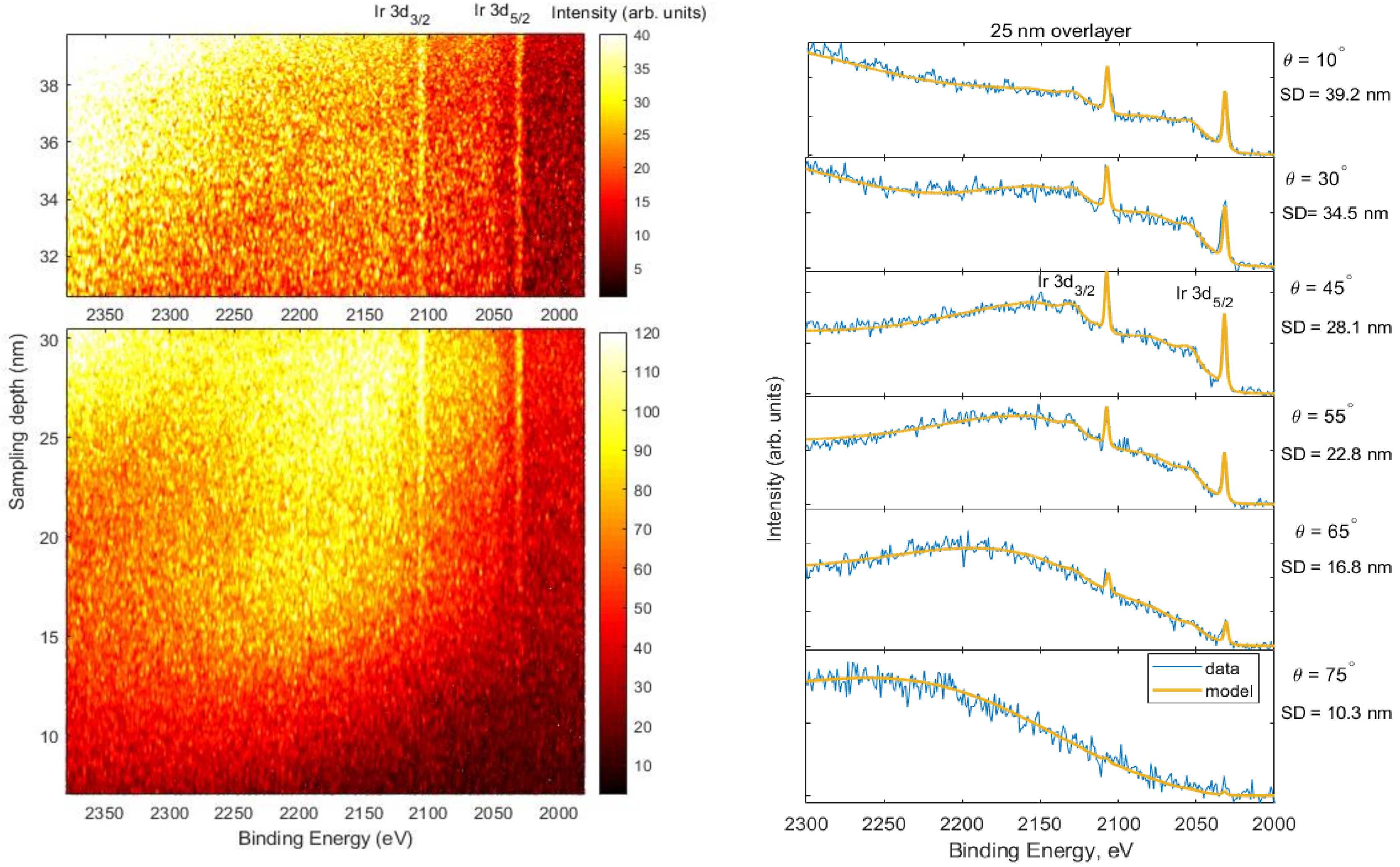
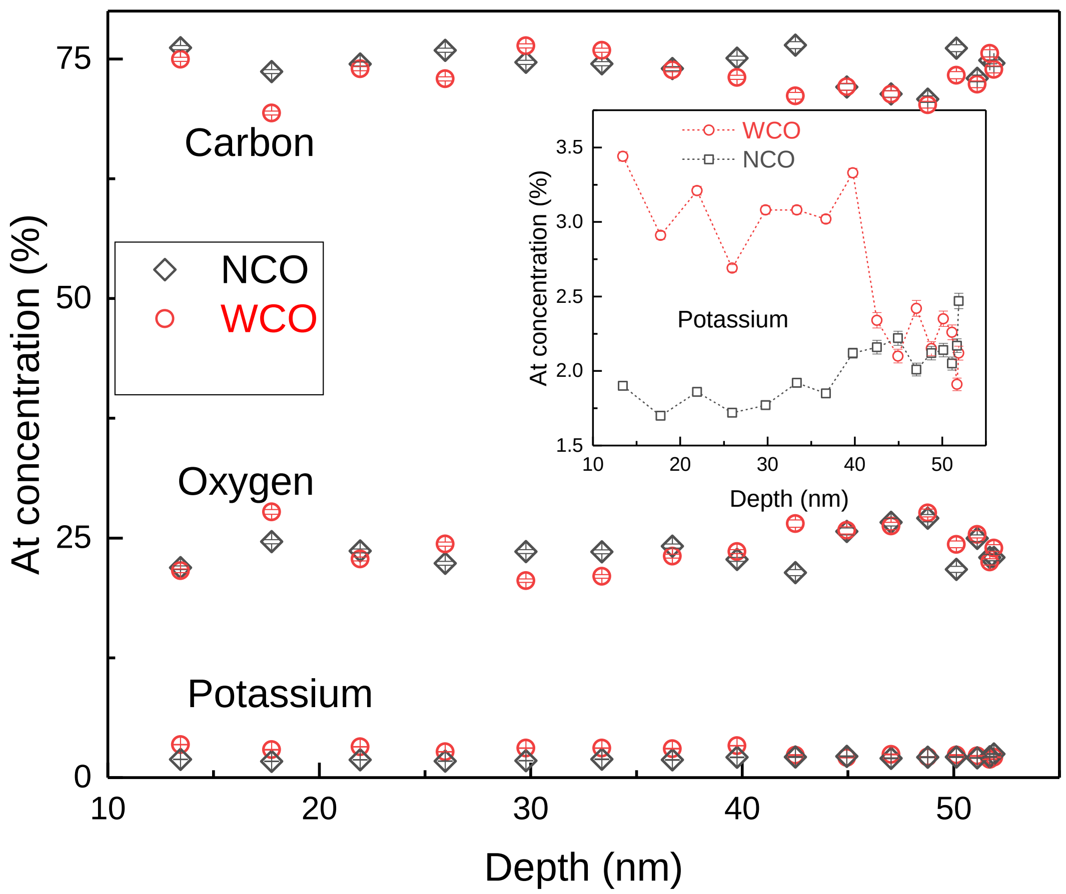
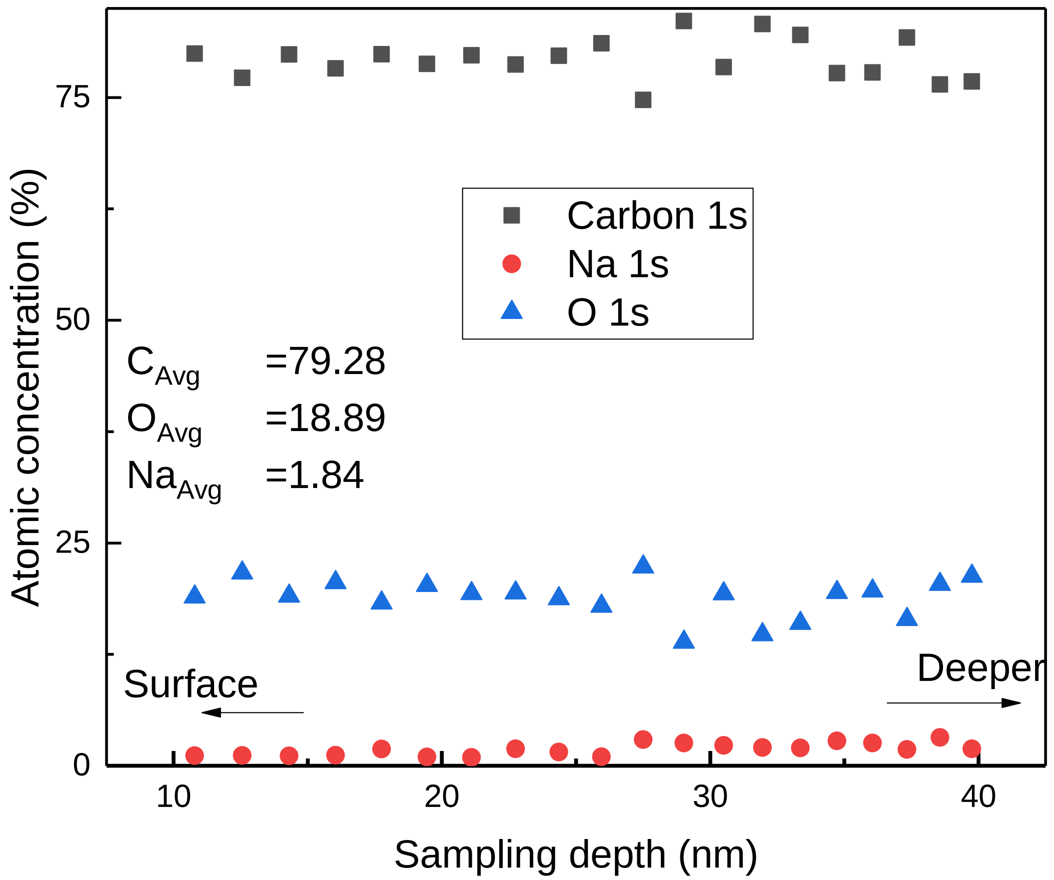


In submission to Applied Surface Science

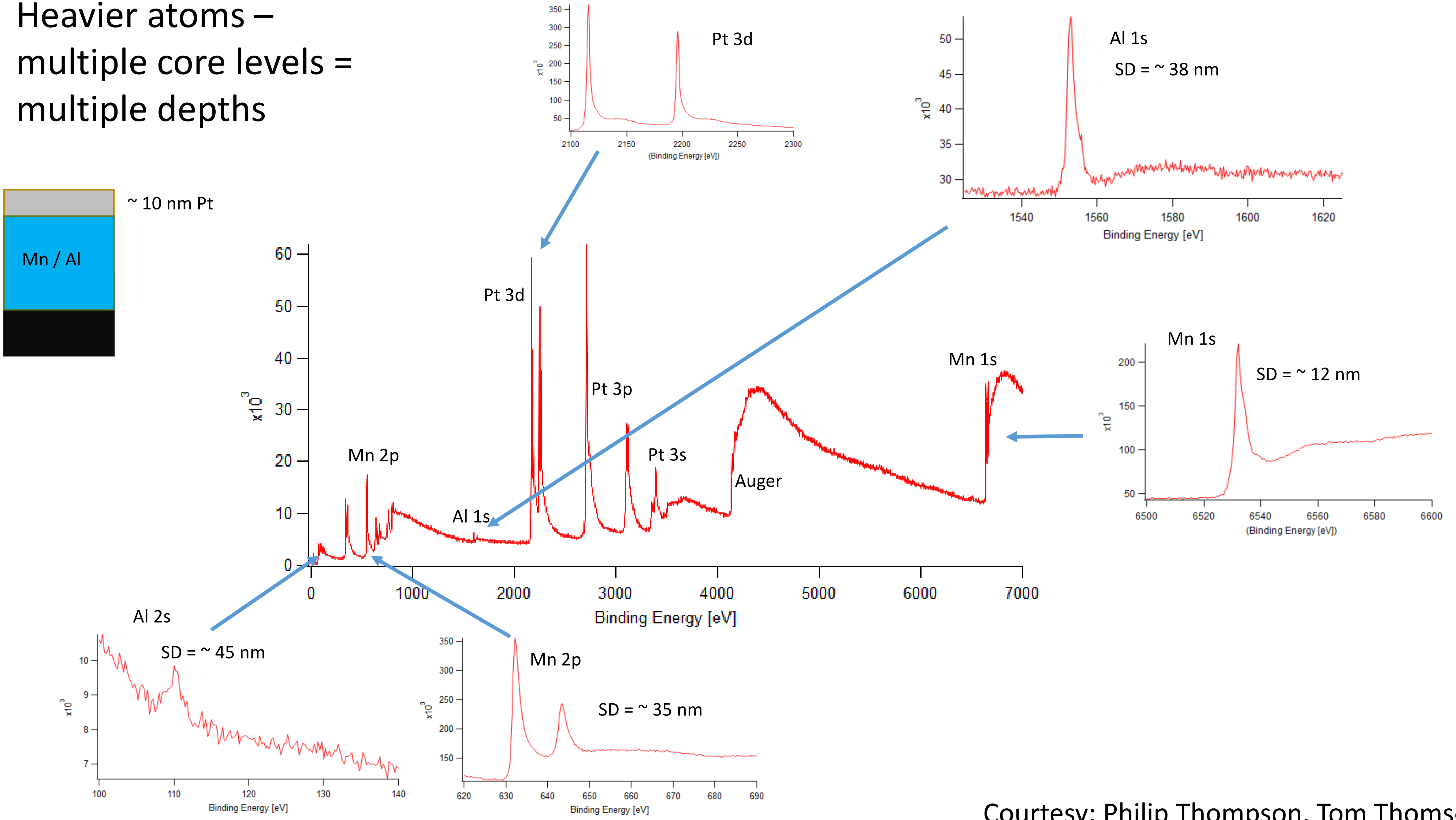
Trapping of ions in graphene oxide films





Courtesy: Prem Pillai, Rahul Nair

Heavier atoms – multiple core levels = multiple depths



Courtesy: Philip Thompson, Tom Thomson

What Lies Beneath? In situ and operando characterisation of battery materials

- Develop new in situ and operando platforms that will enable characterisation of buried interfaces in working batteries
- **PI:** Prof Robert Weatherup (Oxford)
- **Co-Is:** Dr Alex Walton (Manchester), Prof Rob Dryfe (Manchester), Dr Nicholas Lockyer (Manchester), Prof Wendy Flavell (Manchester), Prof Martin Castell (Oxford), Dr Tien-Lin Lee (Diamond)







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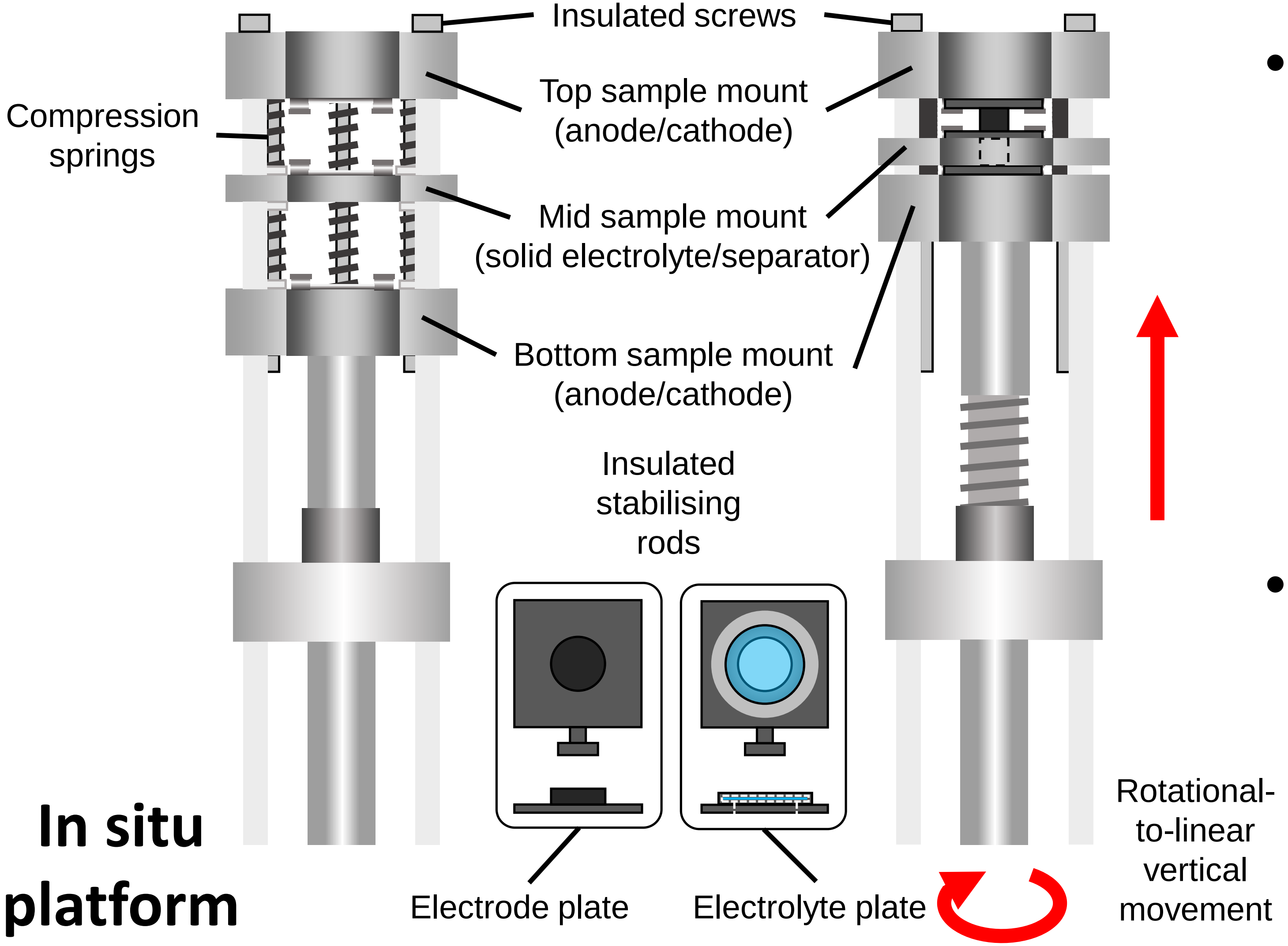
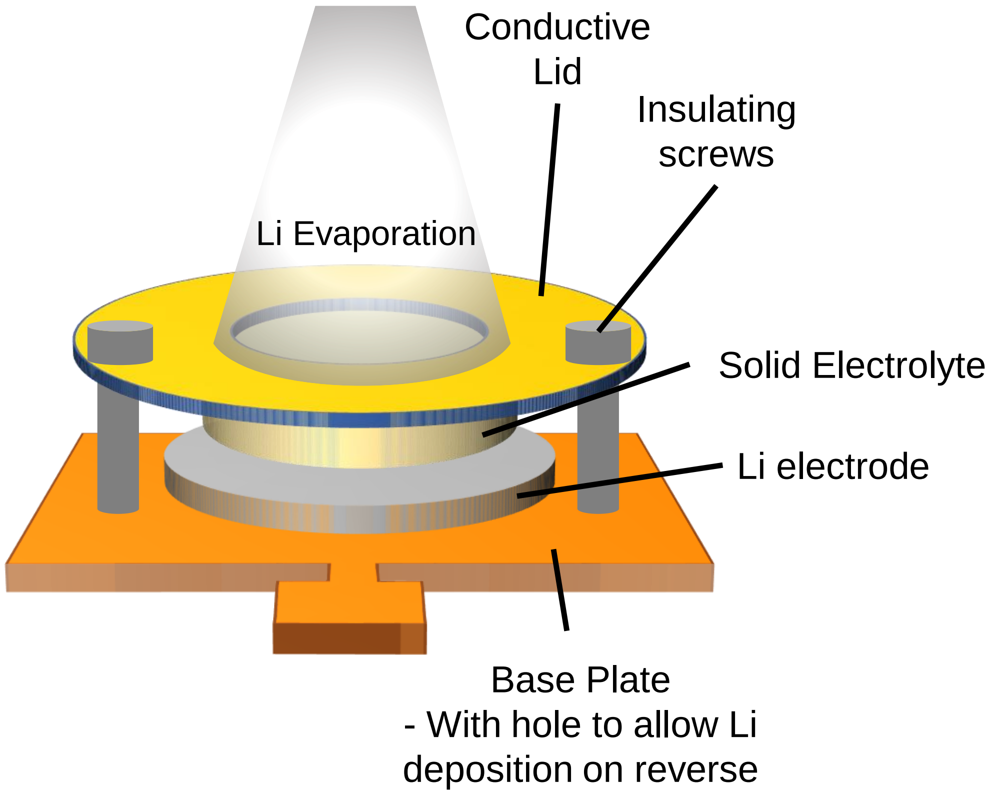
What Lies Beneath? In situ and operando characterisation of battery materials



- **In situ platform:** aiming to assemble/disassemble/reassemble battery components (anode, cathode and solid electrolyte/separator) at various states of charge under high vacuum conditions
- Can then transport components to characterisation equipment (HAXPES, NEXAFS, SIMS, SEM)

What Lies Beneath? In situ and operando characterisation of battery materials

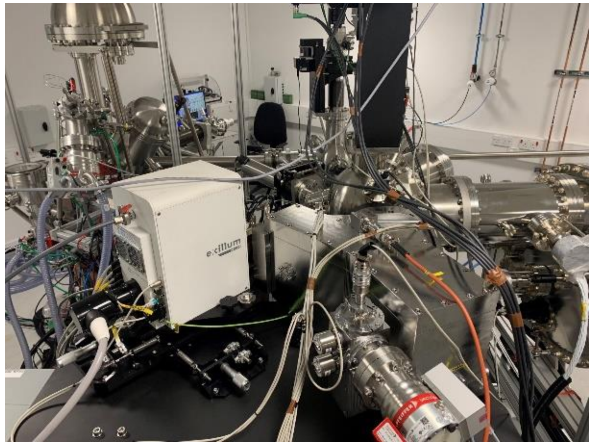
- **Operando platform:** aiming to directly measure battery interfaces during cycling
- Deposition of Li metal onto solid electrolyte to make symmetric cell (Li/solid electrolyte/Li)
- Cycle under high vacuum conditions and measure interface simultaneously

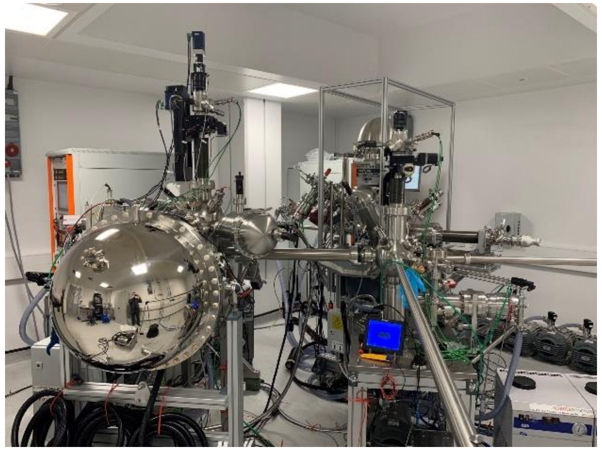


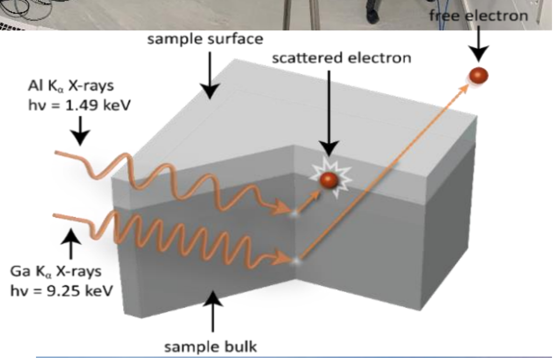
Operando platform

HAXPES benefits
“XPS on steroids”

1. Deeper core levels for larger atoms (Si+) – high sensitivity factors (sometimes >100 x sensitivity of C)
2. Deeper core levels – multiple depths using different KE electrons
3. Extension of sampling depth up to ~ 50 nm using core levels, potentially hundreds of nm using inelastic background
4. Angle-resolved mode for non-destructive depth profiling from the surface into the bulk (XPS can then be used as a surface reference measurement)
5. Expect a rise in application of HAXPES now viable measurements enabled in the lab (not just triage experiments ahead of SR time, lab environment allows fast design/implementation of sample preparation/ in situ/ operando schemes)







HarwellXPS

EPSRC National XPS Research Facility

www.harwellxps.uk

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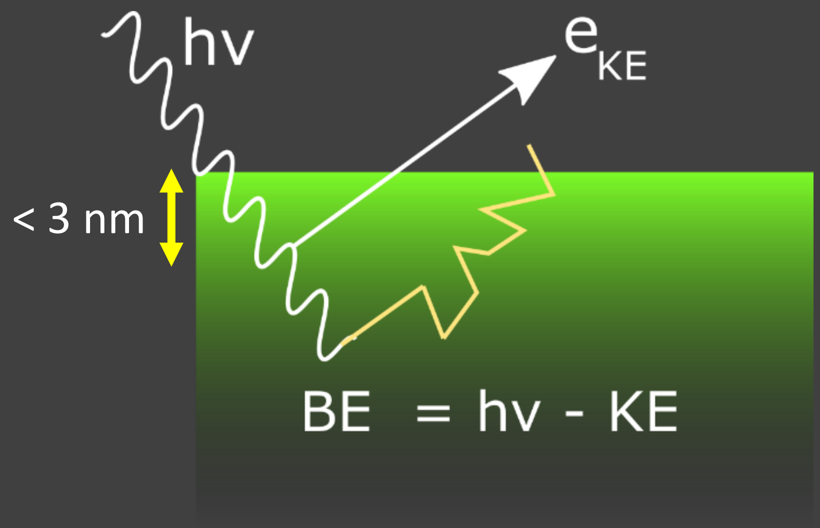
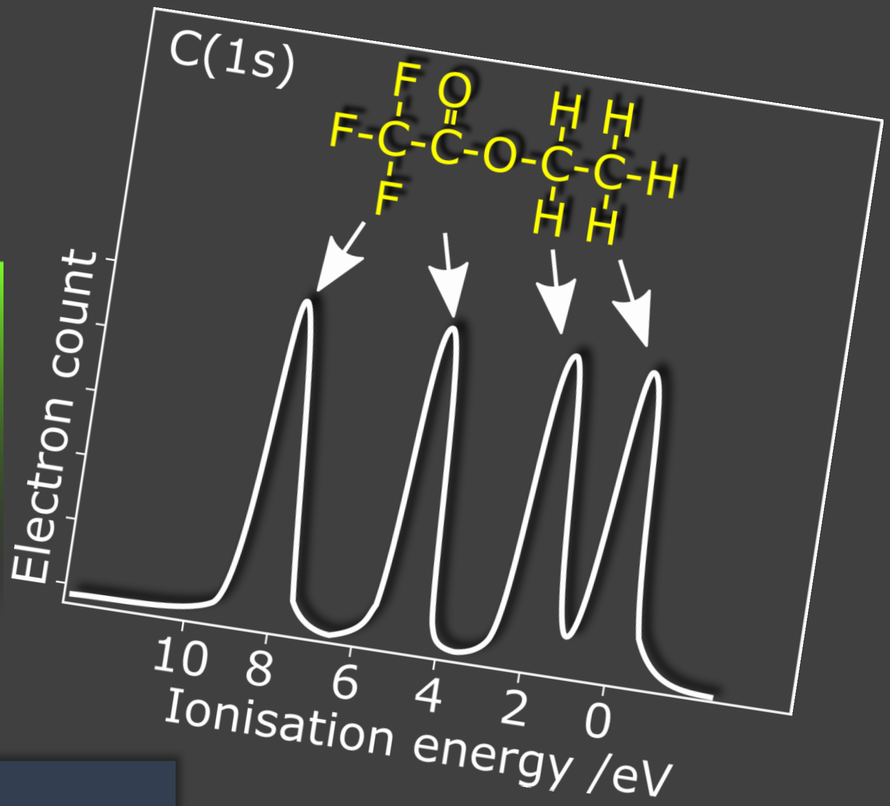
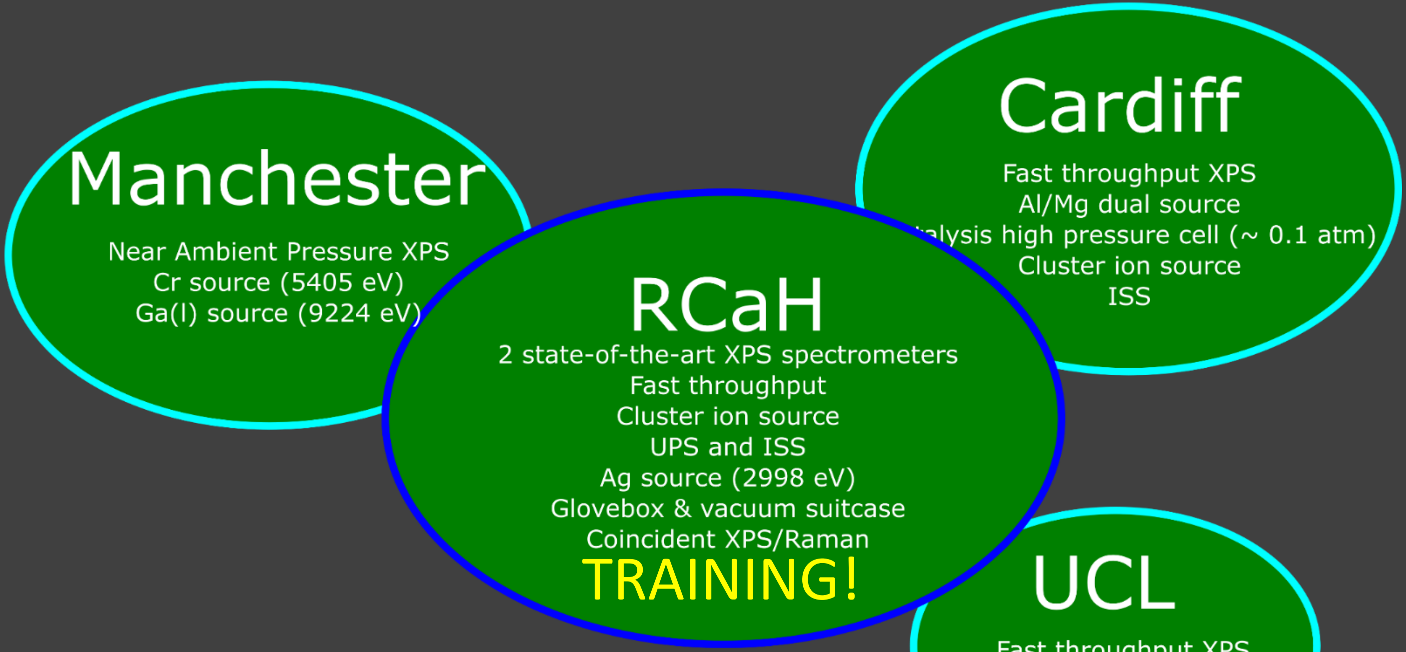
X-Ray Photoelectron Spectroscopy





X-Ray Photoelectron Spectroscopy
- Surface sensitive
- Elemental and chemical sensitivity
- Quantitative

HarwellXPS
hub & spoke structure



Management Team

Director:	Prof Philip R. Davies (Cardiff)
Co-Director:	Prof Robert G. Palgrave (UCL)
Technical Manager:	Dr David J. Morgan (Cardiff)
NAPXPS Director:	Prof Wendy Flavell (Manchester)

RCaH Hub

Research Officers: Dr Mark Isaacs & Dr Shaoliang Guan

Manchester Hub

Research Officers: Dr Alex Walton & Dr Ben Spencer

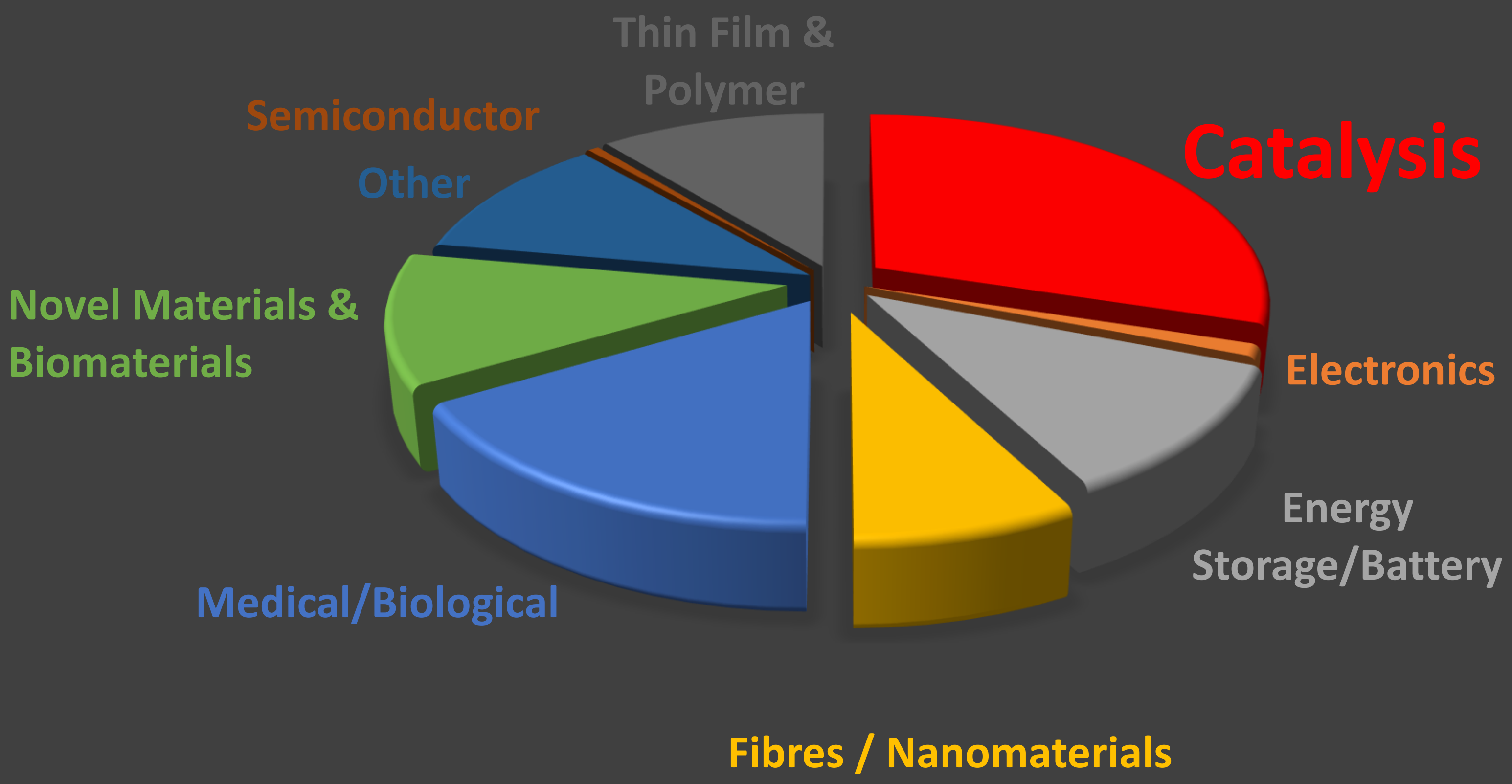
Training

XPS analysis looks easy, *its not!*

Avoid mistakes, get trained by the experts

Training days	Date	Where
Harwell XPS Training Day 1 (Beginners)	15/11/2019	Harwell
TWO Day Training (Beginners & Intermediate)	*14th & 15th April 2020*	*SCI offices London*
THREE Day Training (Intermediate & Advanced)	*Sept 2020*	*Cardiff*
Annual conference	10/6/2019	Harwell
Faraday Discussion Meeting	April 2022	London

Samples by research area



67.5 % of samples analysed within 1 day
93.8 % of samples analysed within 1 week

www.uksaf.net

New technologies and advancements in Surface Analysis

Summer meeting 8-9 July 2020
Henry Royce Institute Hub, Manchester

Tues 7th July	– QUASES workshop with Sven Tougaard
Weds 8th July	– Conference dinner
Thursday 9th July	– Tour of the facilities
Friday 10th July	– CASAXPS training with Neil Fairley

For more info please contact me at
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Henry Royce Institute

Elizabeth Gardner
Helen Ryder
Julia Lawson
Cath Davies
Dan Lake

SDU University of Southern Denmark

Sven Tougaard

scientaomicron

Susanna Eriksson
Ad Ettema
Shoresh Soltani
Manfred Maschek
Tomas Weill

diamond

Tien-Lin Lee
Pardeep Kumar Thakur

… and thank you for your attention!

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